

Insights from a changing ocean:
Evolving biogeochemistry and its impacts on marine ecosystems and climate

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Abstract

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Marine biogeochemistry integrates chemical, biological, geological, and physical processes that are fundamental to Earth's climate and ecosystems. As elements cycle through the ocean, atmosphere, and biosphere, they leave behind biogeochemical fingerprints that serve as proxies to track environmental change. Over the industrial era, anthropogenic CO₂ emissions and other human activities have caused the oceans to change rapidly, perturbing this biogeochemical landscape. Characterizing biogeochemical shifts is critical to advance our understanding of climate-driven impacts, assess marine ecosystem health, and evaluate climate solutions.

Recent advancements in biogeochemical tools and technologies have deepened our insights into oceanic change. The development of high-precision paleoproxies has extended records of ocean conditions into the pre-industrial era, while the Argo float array has enabled four-dimensional monitoring of biogeochemistry globally. High-resolution numerical modeling has also improved our ability to capture complex interactions at fine spatial and temporal scales, offering a holistic framework to understand anthropogenic impacts from past to future. Together, these technologies provide a comprehensive toolkit to characterize shifts in ocean biogeochemistry in unprecedented detail and advance our understanding of global environmental change.

This thesis weaves together applications of novel biogeochemical tools to examine the drivers, impacts, and mitigation strategies of a rapidly changing ocean. Each chapter leverages diverse datasets and multiple tools to provide new insights on ocean change based on marine biogeochemistry. In Chapter 2, I combine boron-isotope measurements from cold-water corals with a biogeochemical model to reconstruct and investigate subsurface acidification trends over the industrial era in the California Current System. In Chapter 3, I combine Argo-based biogeochemical data products, archival tagging records, and machine learning methods to develop a four-dimensional species distribution model for an economically important fishery species, revealing biogeochemical constraints on its migration. In Chapter 4, I employ a high-resolution biogeochemical model of the Salish Sea to evaluate the detectability of ocean alkalinity enhancement, a marine carbon dioxide removal strategy for climate mitigation. These studies provide new frameworks and tools to investigate, monitor, and respond to a changing ocean.

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I wanted to do something fun with my acknowledgments for each of you, so I had this idea to dig through the archives and find the acknowledgements from YOUR dissertations. It felt like a fitting, full-circle moment and unsurprisingly, I found some gems. For each of you, I chose a phrase or two that stood out, either because it was insightful, poetic, reflective of my own experience in grad school, or just made me laugh.

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science – as integrative, intentional, and deeply connected to the world. You also mentioned a postdoc superpower (“*who knew postdocs could fly*”) that I look forward to unlocking someday.

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Chapter 1: Introduction

The ocean plays a critical role in the physical, chemical, and biological processes that are fundamental to the Earth system. Central to this function is the ocean's modulation of key biogeochemical dynamics and cycles, including those of carbon, oxygen, and nutrients. These components are essential for regulating Earth's climate, sustaining marine ecosystems, and mediating interactions between the ocean, atmosphere, and biosphere.

The cycling of these components is driven primarily by two independent but complementary processes: the biological pump and the solubility pump. In the sunlit surface ocean, phytoplankton take up nitrate, phosphate, and CO_2 to fuel photosynthesis and produce organic matter. These primary producers supply half of the world's oxygen and form the basis of marine food webs. As organic matter sinks from the surface into the ocean interior, it is remineralized through microbial decomposition, which converts organic nitrogen, phosphorous, and carbon back into inorganic forms. Regenerated nutrients are returned to the surface ocean via upwelling, mixing, and advection, further sustaining primary production. A small fraction of the sinking organic matter escapes remineralization and is sequestered in the deep ocean on centennial to millennial timescales (Le Moigne, 2019; Siegel et al. 2014). This export and long-term storage of carbon from the surface to the deep ocean constitutes the biological pump.

Complementary to this mechanism, the solubility pump is governed by physical and chemical processes that control the exchange of carbon between the atmosphere and ocean. At the air-sea interface, CO_2 is absorbed into the surface ocean in efforts to reach equilibrium with the atmosphere, in accordance with Henry's Law. Once dissolved, aqueous CO_2 undergoes a series of chemical reactions that convert it into more stable forms of inorganic carbon, including bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). In fact, CO_2 constitutes only 1% of dissolved inorganic carbon in seawater; roughly 90% exists as bicarbonate ions and the remaining 9% as

carbonate ions. These chemical transformations comprise the ocean carbonate system, which expands the carbon storage capacity of the ocean to more than 50 times that of the atmosphere (Sabine and Feely 2007). Carbon absorbed at the surface is subsequently transported to the deep ocean via mixing and large-scale thermohaline circulation. The biological and solubility pumps together position the ocean as a dynamic reservoir of carbon and nutrients, a central regulator of global climate, and a critical component of Earth's biogeochemical balance.

Anthropogenic climate change has fundamentally reshaped the ocean's role in the global carbon cycle. Since the onset of the Industrial Revolution, atmospheric CO₂ has increased by 140 μatm , an unprecedented rise in both magnitude and rate over the previous 800,000 years (Lüthi et al. 2008). This increase exceeds the ~ 100 μatm variability in CO₂ associated with glacial-interglacial oscillations over the same time period (Petit et al. 1999). Since the late 19th century, the ocean has absorbed approximately one-third of anthropogenic CO₂ emissions (Friedlingstein et al. 2020), substantially slowing the progression of climate change. However, this mitigation service has come at a cost. As anthropogenic CO₂ dissolves into seawater, it forms a weak acid that shifts carbonate chemistry from carbonate toward bicarbonate and aqueous CO₂, increasing surface ocean acidity 30% (Sabine and Feely 2007). This phenomenon, known as ocean acidification, poses threats to calcifying organisms such as corals, pteropods, and shellfish by reducing the availability of carbonate ions needed to build their shells and skeletons (Kroeker et al. 2013; Doney et al. 2009). It also affects the larvae of many non-calcifying species including fish and echinoderms by disrupting development, altering sensory and behavioral functions, and increasing mortality (Dupont, Ortega-Martínez, and Thorndyke 2010; Munday et al. 2009).

Beyond acidification, climate change has disrupted Earth's radiative balance and caused extensive warming driven by greenhouse gas emissions. The oceans have absorbed over 90% of

this excess heat, resulting in substantial and accelerating increases in ocean temperatures (Legg 2021). Warming impacts the density structure of water masses and can alter global circulation, with cascading effects on nutrient transport and the productivity of marine ecosystems (e.g., Bopp et al. 2013). It also decreases the solubility of oxygen, causing hypoxic conditions that constrain suitable habitat for marine organisms (Keeling, Körtzinger, and Gruber 2010). Anthropogenic emissions have driven profound changes in ocean biogeochemistry over the industrial era, with implications for climate, marine ecosystems, and the services the ocean provides to society.

Anthropogenic perturbations to ocean chemistry and ecosystems have left behind biogeochemical fingerprints that can serve as proxies to track environmental change. These fingerprints offer critical insight into the ocean's response to climate stressors and strategies to mitigate future impacts and protect marine ecosystems. Traditional observation methods such as ship-based sampling, moorings, and underway sensors have long provided valuable but limited snapshots of the biogeochemical landscape. This sparsity in observations in both space and time has made it challenging to detect and attribute anthropogenic changes against natural variability. Recent advancements in biogeochemical tools and technologies have enabled a new era of ocean observation. Autonomous platforms and the expansion of the Argo float array has dramatically improved the spatiotemporal resolution of environmental data, enriching our knowledge of fundamental biogeochemical processes and their variability across timescales. Characterization of the interior ocean has also opened pathways to link patterns of subsurface biogeochemistry with habitat suitability for key marine species. This growing wealth of biogeochemical data is increasingly being integrated into high-resolution models that provide a more holistic view on the complex interaction between natural and anthropogenic forces that drive change.

This dissertation weaves together applications of novel biogeochemical tools to monitor, better understand, and respond to a time of significant ocean change. These technologies support deeper investigation into the mechanisms driving biogeochemical shifts, the complex interactions that shape marine habitat, and the evaluation of potential climate solutions. Each chapter leverages diverse datasets and multiple tools to provide new insights on ocean change through the lens of marine biogeochemistry. Specifically, this work focuses on ocean acidification, fisheries habitat, and marine carbon dioxide removal (mCDR). Collectively, these studies advance our capacity to track ocean acidification, improve habitat predictions, and assess the effectiveness of emerging mCDR approaches, laying the foundation for more informed management and mitigation in a rapidly changing ocean.

In Chapter 2, I investigate the drivers and magnitude of biogeochemical change associated with the ocean's uptake of anthropogenic carbon, or ocean acidification. While most open-ocean surface waters equilibrate with atmospheric CO₂ on the order of months to years, acidification in coastal regions can be complex due to the combined influence of anthropogenic and natural sources of acidity. The California Current System (CCS), for instance, naturally experiences acidified conditions relative to the open surface ocean driven by coastal upwelling, which transports low-pH, high-*p*CO₂ waters from depth to the surface. Acidification may have profound impacts on this biologically productive and economically important region, but predicting its progression is uniquely challenging because the anthropogenic contribution is intertwined with other natural sources. Disentangling long-term acidification trends over the industrial era from shorter timescales of variability requires observational records that extend beyond the limited range of instrumental measurements. To address this gap, I reconstruct carbonate chemistry in the CCS using a boron isotope pH proxy preserved in cold-water corals to quantify and explain the

magnitude of acidification over the industrial era (1890 to 2020). This study represents the application of the most precise boron isotope proxy in cold-water corals to date, which was established through culture experiments in the same species of corals. I further integrate these geochemical records with output from a biogeochemical Regional Ocean Modeling System (ROMS) simulation of the CCS to attribute observed changes to oceanographic processes and predict future conditions. This work provides insights into the progression and dynamics of acidification in high-carbon upwelling regimes that support marine ecosystems of economic, cultural, and biological importance. A manuscript based on this chapter has been accepted at *Nature Communications* under the title “A Century of Change in the California Current: Upwelling System Amplifies Acidification”.

In Chapter 3, I explore a novel approach to integrate four-dimensional (4D) biogeochemical data into species distribution models (SDMs) to improve habitat predictions in diverse marine environments. SDMs have emerged as essential tools for identifying habitat hotspots, informing conservation strategies, and guiding dynamic ocean management to reduce bycatch. The diverse applications of SDMs are grounded in an understanding of the physical, chemical, and biological conditions that foster suitable marine habitat. However, many SDMs fail to capture biogeochemical dynamics that vary with depth, despite their critical role in constraining the extent of suitable habitat. The Biogeochemical Argo (BGC-Argo) float array has transformed our ability to observe the ocean’s 4D biogeochemical landscape, offering a new platform to investigate linkages between species distributions and environmental conditions. In this chapter, I leverage archival tagging datasets, mapped ocean biogeochemistry data products informed by BGC-Argo, and machine learning methods to evaluate how depth-resolved biogeochemical information influences the extensive migrations of North Pacific albacore tuna (*Thunnus*

alalunga). The resulting SDMs incorporate multiple 4D biogeochemical predictors that capture both environmental deterrents (e.g., oxygen limitation) and environmental attractants (e.g., chlorophyll and particulate organic carbon) to predict habitat suitability across space, time, and depth. This work advances the field of marine species distribution modeling by demonstrating the value of new depth-resolved, biogeochemical tools to improve habitat predictions for the first time. A manuscript based on this chapter is currently under review at *Proceedings of the National Academy of Sciences* under the title “Leveraging 4-Dimensionally Mapped Ocean Biogeochemistry to Inform Species Distribution Modeling”.

In Chapter 4, I evaluate a proposed marine carbon dioxide removal (mCDR) strategy designed to counteract the climate and biogeochemical perturbations caused by anthropogenic emissions. Ocean alkalinity enhancement (OAE) involves the addition of alkalinity to seawater, which locally and temporarily mitigates ocean acidification while expanding the ocean’s capacity to uptake atmospheric CO₂ (NASEM 2021; Mongin et al. 2021). Central to mCDR is the challenge of detectability, or the ability to distinguish OAE-induced changes from natural variability and other sources of uncertainty. Robust and scalable monitoring strategies will be critical to ensure transparency, safety, and scientific credibility of future mCDR interventions. In this study, I apply a detectability framework to evaluate the effectiveness of various observing strategies to detect OAE signals in the dynamic coastal environment of the Salish Sea. I use a high-resolution biogeochemical model to provide a controlled counterfactual environment and compare three monitoring approaches that differ in measurement quality, frequency, and duration. The detectability framework presented here provides a practical tool for designing site-specific, scientifically rigorous monitoring systems that will be essential for effective and credible carbon removal pathways. A manuscript based on this chapter is soon to be submitted at *AGU Earth’s*

Future under the title “Improving the Detection of Marine Carbon Dioxide Removal with Empirically-Derived Counterfactuals”.

This dissertation demonstrates how new biogeochemical tools can offer novel insights into a changing ocean. In Chapter 5, I synthesize the implications of the approaches used in Chapters 2, 3, and 4, and highlight how these technologies advance our understanding of ocean biogeochemical change.

Chapter 2: A Century of Change in the California Current: Upwelling System Amplifies Acidification

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2.0 Abstract

Over the past century, oceanic uptake of anthropogenic CO₂ has caused seawater to become more acidified. The California Current System (CCS), which naturally experiences more acidified conditions compared to the open ocean because of upwelling, serves as an indicator of ecosystem response to acidification. However, predicting the pace of acidification in the CCS is complicated because the anthropogenic contribution is intertwined with other natural sources of acidification and variability. A central and contested question is whether acidification in the CCS will follow the pace of increasing atmospheric CO₂, or if dynamical climate effects and other biogeochemical processes will act to either amplify or attenuate acidification. Here we apply the boron isotope pH proxy to cold-water orange cup corals to establish a historic level of acidification in the CCS, a productive upwelling system, and the Salish Sea, an associated marginal sea. Through a combination of complementary modeling and geochemical approaches, we show that the CCS and Salish Sea have experienced amplified acidification over the industrial era driven by equilibration of atmospheric CO₂ and a thermodynamic buffering effect in the carbonate system that intensifies biogeochemical changes in high-carbon regimes. From this foundation, we analyze projections for future acidification in the CCS under continued elevated CO₂ emissions. The projected change in *p*CO₂ over the 21st century will continue to outpace atmospheric CO₂, posing challenges to marine

ecosystems of biological, cultural, and economic importance. Acidification of this magnitude is predicted to have profound impacts on the CCS in the coming century.

2.1 Introduction

Since the beginning of the Industrial Revolution, the oceans have absorbed approximately a third of anthropogenic CO₂ emissions, corresponding to an acidity increase of 25% and a 0.1 decline in pH in the open surface ocean (Raven et al. 2005; Sabine and Feely 2007). While most open ocean surface waters equilibrate with atmospheric CO₂, the magnitude of acidification in coastal regions can be complex due to the combination of both anthropogenic and natural sources of acidity, particularly at depth. For example, in the California Current System (CCS), the eastern boundary current off the west coast of North America (Figure 1a), intense, episodic coastal upwelling of low-pH, high-*p*CO₂ waters is driven by alongshore winds and associated Ekman transport (Hickey 1979; 1989). As a result, the CCS and adjacent waterways, such as the Salish Sea in the Pacific Northwest, represent a leading edge of ocean acidification (OA) impacts while also providing a window into future ocean conditions and processes. Understanding the impact of ocean acidification in this upwelling system is particularly critical, as the associated delivery of nutrients from the deep ocean fuels one of the most biologically productive and economically vital ecosystems in the world (Carr and Kearns 2003). Even though organisms in the CCS have historically been exposed to acidified and variable conditions, a synthesis of several studies suggests that many regional species are sensitive to OA (Sunday et al. 2022). Despite its importance and potential vulnerability, the trajectory of future acidification in this upwelling system remains unclear due to the interplay of processes that impact regional biogeochemistry.

A central question is whether acidification in the productive CCS will follow the pace of increasing atmospheric CO₂, or if dynamical climate effects or other processes will act to either

amplify or attenuate acidification. Processes that can modulate acidification in the CCS include changes in upwelling dynamics, shifts in the source of upwelled water, and changes in the amount of exported material from the surface ocean that is remineralized along upwelled isopycnals (Figure 1b). Recent research has also brought attention to thermodynamic buffering effects that amplify the impact of this remineralization on seawater pH and $p\text{CO}_2$ when water masses accumulate anthropogenic carbon (Figure 1c). This thermodynamic effect highlights the vulnerability to acidification in carbon-rich waters due to low buffering capacity.

Unfortunately, current studies using coupled ocean-atmosphere models and wind stress analyses differ on the predicted sign and magnitude of changes to the mean state and variability of the CCS in the past and future (Bakun 1990; Brady 2019; Chavez 2017; Gruber et al. 2012; Hauri et al. 2009; Howard, Frenzel, et al. 2020; Quilfen et al. 2021; Rykaczewski et al. 2015; Samantha A. Siedlecki et al. 2020; Sydeman et al. 2014; Turi et al. 2016; Wang et al. 2015). Furthermore, while the effects of thermodynamic buffering have long been acknowledged and attempts have been made to calculate the impact of changing oceanic carbon buffering capacity (Revelle, R., and H. E. Suess 1957; Broecker et al. 1979; Takahashi, T., W. S. Broecker, S. R. Werner, and A. E. Bainbridge 1980), their implications have only recently been applied to evaluate spatial patterns and rates of OA (Arroyo et al. 2022; Carter et al. 2019; Fassbender, Sabine, and Palevsky 2017; Feely et al. 2018). Given the wide range of results in the literature, the role of climate effects and their interplay with biogeochemistry in a changing CCS remains uncertain. Testing these predictions and resolving long-term trends from natural decadal variability requires observational data that extends beyond the limited range of instrumental records to span longer timescales.

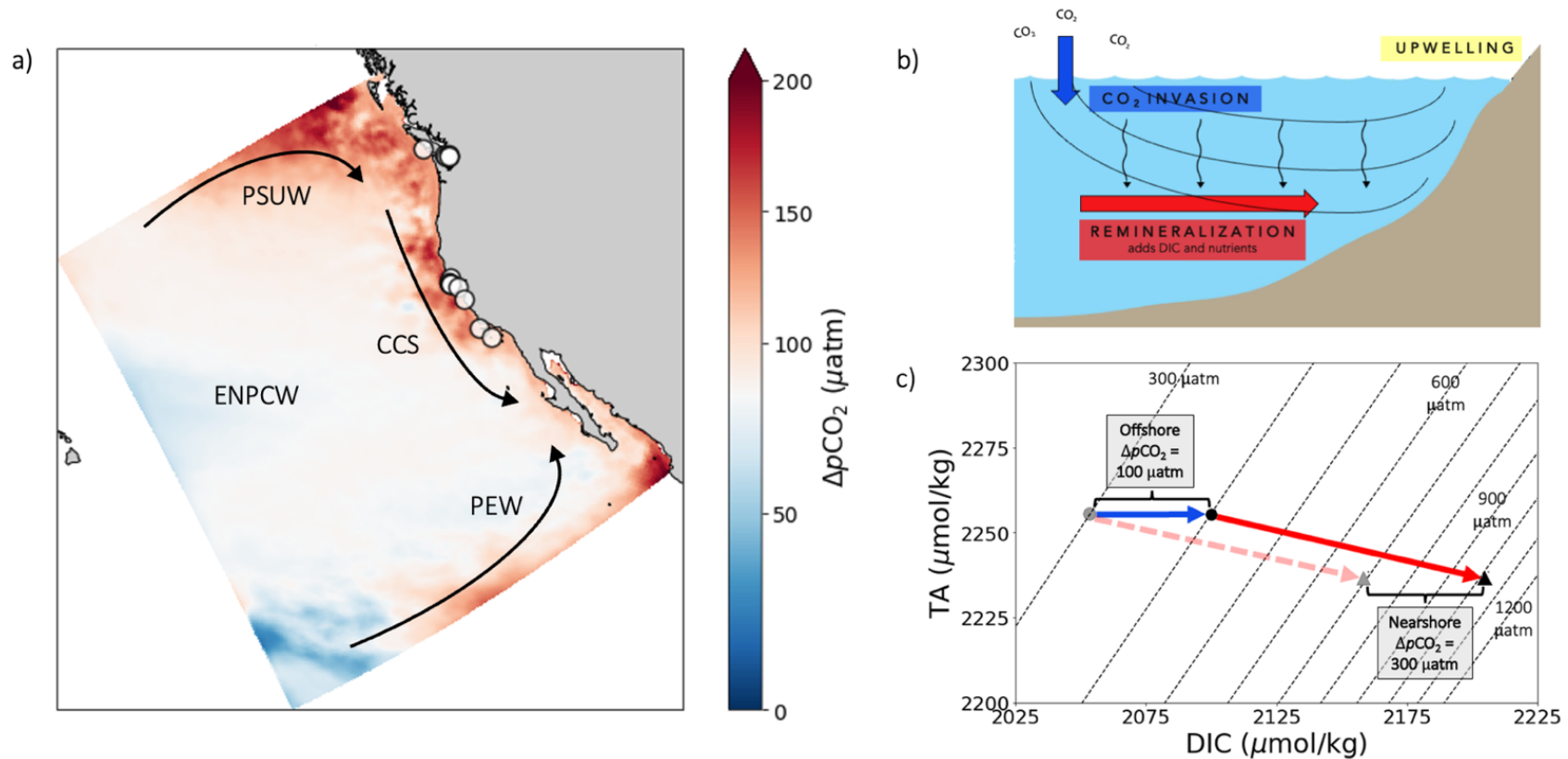


Figure 1| Processes influencing carbonate chemistry in the CCS over the 20th century. a) Climatological mean map of $p\text{CO}_2$ anomaly at 75 meters depth over the ROMS domain. 20th century change ($\Delta p\text{CO}_2$) was evaluated by calculating the difference between a 7-year average in the historic (1897–1904) and modern (2000–2007) model simulations. The color bar is centered at 80 μatm to represent the atmospheric change in CO_2 over the modeled time period (1900–2000). Red areas in coastal upwelling regions as well as the northern and southern boundaries indicate an amplified increase in seawater $p\text{CO}_2$ relative to the atmosphere. The Pacific Subarctic Upper Water (PSUW), Eastern North Pacific Central Water (ENPCW), and Pacific Equatorial Water (PEW) mix to form the California Current System (CCS), which flows along the US West Coast. Outlined circles represent the historic coral locations. b) A generalized cartoon section of the California Current upwelling region with a depiction of relevant processes that influence biogeochemistry. Isopycnals outcrop in open ocean locations and exchange with atmospheric CO_2 (blue arrow). These outcrops are far from shore, but the figure has been condensed for graphical representation. During transport along an isopycnal from the open ocean, the water mass accumulates additional carbon via remineralization (red arrow) of organic matter exported from the surface ocean (black wavy lines). In the CCS, alongshore winds and associated Ekman transport induce upwelling of deep, carbon-rich waters. c) The processes presented in panel b impact carbonate chemistry in the CCS, depicted by the same color arrows. In the historic era, open ocean outcrops equilibrated with atmospheric CO_2 (gray circle), and DIC increased from the open ocean to the CCS due to remineralization (red dashed arrow). In the modern ocean, the offshore outcrop accumulates more carbon (black circle) due to equilibration of anthropogenic CO_2 (blue arrow). Even if the magnitude of remineralization remains the same between the historic and modern ocean, and $p\text{CO}_2$ of the outcrop region exactly follows atmospheric changes, the CCS will experience amplified $\Delta p\text{CO}_2$ relative to the atmosphere and open ocean region. This is because increased initial DIC in the modern outcrop region results in lower buffering capacity (Jiang et al. 2019) such that the impact of subsequent remineralization on $p\text{CO}_2$ is amplified. This thermodynamic buffering effect can be seen as tighter contours between lines of constant $p\text{CO}_2$ as DIC increases.

To address this knowledge gap, we reconstruct carbonate chemistry along the US West Coast and Salish Sea over the industrial era (1890 to 2020) through measurements of boron isotopes ($\delta^{11}\text{B}$) in the preserved aragonite (CaCO_3) skeletons of *Balanophyllia elegans*, a common cold-water coral (Methods). To quantify the magnitude of acidification over the past century, we compare historic museum specimens that grew during the Industrial Revolution (1890s) with modern (2020) corals collected from the same locations (Methods, Figure S1). To attribute the geochemical signals to oceanographic processes and predict future conditions, we contextualize the coral record with a biogeochemical regional ocean modeling system (ROMS) that simulates the CCS and an additional box model to represent the Salish Sea. We compare the geochemical and modeled acidification signals to a ‘baseline’ level of acidification, which we define as the magnitude of acidification associated with the uptake of atmospheric CO_2 over the industrial era, to assess whether coastal processes attenuate or amplify acidification from CO_2 invasion. We analyze acidification in terms of $p\text{CO}_2$ as opposed to pH, allowing us to directly compare magnitudes of acidification independent of background carbonate chemistry. Our study builds on the foundational work of Feely et al. 2016 and Fassbender et al. 2017 that described key processes and extends this analysis through time, permitting us to disentangle process-specific signals obscured in short-term records and resolve their impact on carbonate chemistry controls in the CCS over the 20th century.

2.2 Results and Discussion

2.2.1 A Century of Acidification in the Salish Sea

Focusing first on the primary geochemical record in the Salish Sea, we find that the mean $\delta^{11}\text{B}$ of modern corals is significantly lower than the mean of historic samples from the same locations ($p = <0.001$; Methods, Figure 2). We translate the measured decrease in coral $\delta^{11}\text{B}$ into

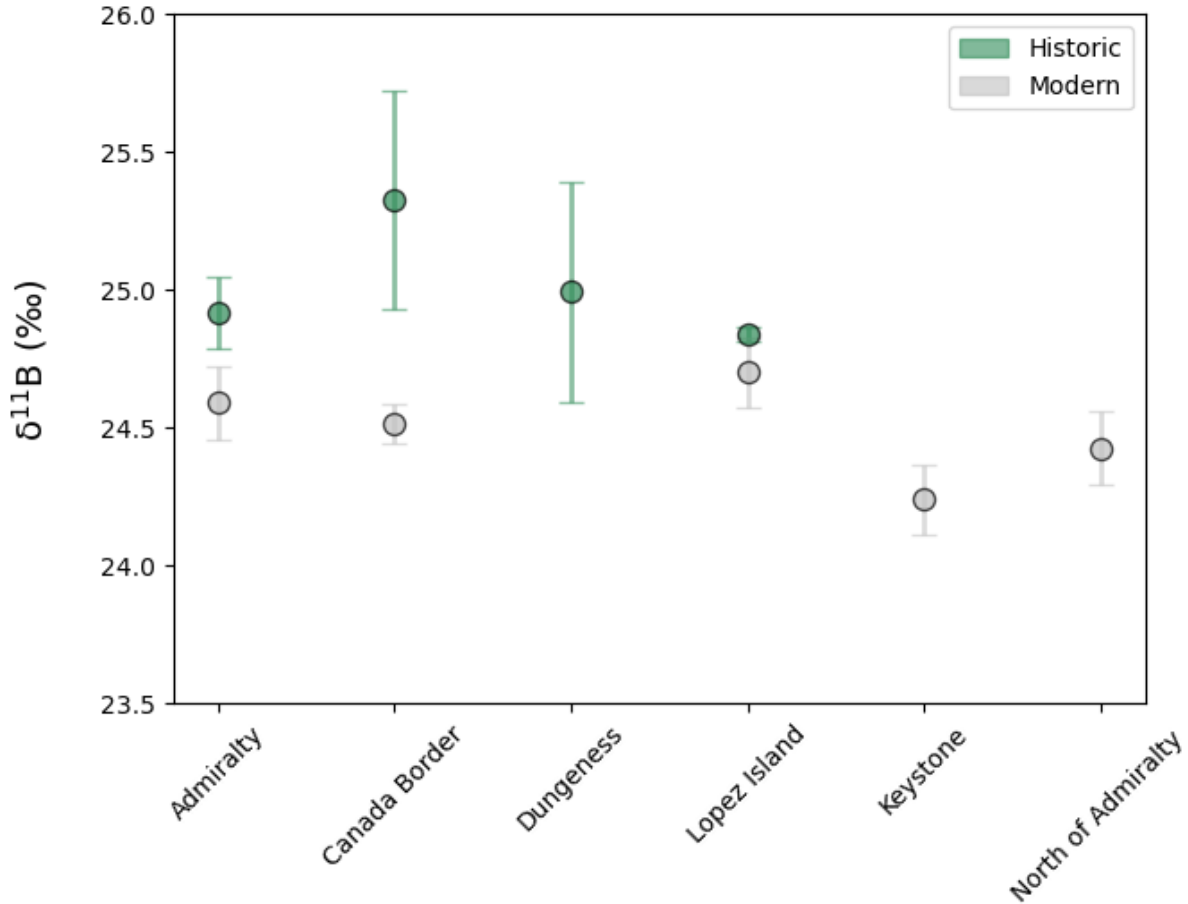


Figure 2| Location-averaged coral skeletal $\delta^{11}\text{B}$ measurements from the Salish Sea. Historic (green) skeletal $\delta^{11}\text{B}$ data from the Salish Sea are significantly higher than modern (gray) samples from the same locations. Sample sizes: Salish Sea historic, $n = 13$; Salish Sea modern, $n = 52$. Error bars represent the standard error of the mean for each location. For sites where only one coral was sampled, the population standard deviation was applied. This value was calculated as the average of the sample standard deviation across all locations with 8 or more corals. Sample locations are shown in Figure S1, and individual coral data points are detailed in Figure S2.

implied changes in carbonate chemistry over the last 130 years using a high-precision $\delta^{11}\text{B}$ calibration from lab-cultured corals of the same species (Gagnon et al. 2021) (Methods). Because our culture calibration and analogous research in tropical corals (Comeau et al. 2017) show that coral $\delta^{11}\text{B}$ is sensitive to both pH and dissolved inorganic carbon (DIC), we represent the way that $\delta^{11}\text{B}$ constrains seawater carbonate chemistry as a line in pH (total scale) vs. DIC space (Figure S4, Methods Equations 1 and 2). The pH-DIC lines described by our coral data in Figure S4 are nearly parallel with the contour lines corresponding to specific seawater $p\text{CO}_2$ values, which

means we can make robust estimates of changes in $p\text{CO}_2$ over the past century (hereafter denoted Δ : $\Delta X = X_{\text{modern}} - X_{\text{historic}}$) in the Salish Sea regardless of process causing the shift in ocean chemistry or changes in DIC (Methods). The coral record indicates that $p\text{CO}_2$ increased by $172 \pm 41 \mu\text{atm}$ between the 1890s and 2020, exceeding the rise in atmospheric CO_2 of 120 ppm over the same time period (1900–2020). The implied pH change over the industrial era is -0.095 (standard error of the difference between means $\sigma_{M_{\text{Historic}}-M_{\text{Modern}}} = 0.025$). Importantly, had acidification in the Salish Sea followed the pace of atmospheric CO_2 (our baseline case), ΔpH would be only -0.06 (Methods). The $p\text{CO}_2$ and pH signals from the coral records indicate that the Salish Sea experienced amplified acidification over the 20th century. Even though the Salish Sea has naturally low pH and high $p\text{CO}_2$ and is a net source of CO_2 to the atmosphere, our coral records imply that these highly acidified waters not only became even more acidified over the last 130 years, but exceeded the magnitude of acidification implied by atmospheric CO_2 .

To further interpret our record in terms of absolute pH, we align the modern corals with nearby modern observational data, which are offset by -0.1 (Methods). We attribute this difference to culture conditions described in Gagnon et al. 2021 to establish the $\delta^{11}\text{B}$ calibration, which do not exactly match the natural wild coral setting (Supplementary Methods 1.3). This does not affect the interpretation of data from the Salish Sea where we have historic-modern pairs, but applying this same offset to all coral samples anchors the historical West Coast coral data where modern corals have not been collected so they can be compared to modeled historic values and other proxies.

While different oceanographic processes influence the Salish Sea and CCS, the Salish Sea represents an extension of the CCS given that Salish Sea deep waters are sourced from upwelled water masses of the northern CCS. Therefore, our coral record serves as an indirect indicator of

general shifts in seawater chemistry of the CCS. As an additional, independent test for amplified acidification across the CCS and in the Salish Sea, we complement our coral data with an evaluation of processes that influence estuarine acidification (Supplementary Discussion 1.1) and a modeling approach. Using an eddy-resolving physical-biogeochemical ROMS that extends along the CCS, we conducted two hindcast simulations spanning 1891–1904 and 1994–2007, hereafter referred to as historic and modern simulations, respectively (Methods). These ROMS model datasets were compared to corals from the West Coast (discussed below) and were also used to set the composition of upwelled water entering a box model of the Salish Sea, which is not resolved in the ROMS model (Supplementary Discussion 1.2). To account for the temporal offset between the modern model (1994–2007) and modern corals (2020), during which additional atmospheric carbon accumulation occurred, we augment modeled $p\text{CO}_2$ from 2007 to 2020 to match the collection date of the modern corals (Supplementary Discussion 1.2). The Salish Sea box model approach predicts that seawater $p\text{CO}_2$ increased by $185 \pm 15 \mu\text{atm}$ between the 1890s and 2020, agreeing with the magnitude of $\Delta p\text{CO}_2$ reconstructed using corals. Both the box model and our Salish Sea corals reveal a larger $\Delta p\text{CO}_2$ than that implied by atmospheric $\Delta p\text{CO}_2$ and support amplified acidification in this region.

2.2.2 Amplified Acidification in the California Current System

We then expanded our analysis of historic acidification to the broader CCS using the same hindcast ROMS simulations. While the complex physics captured by the model results in spatial heterogeneity, as in the real ocean, robust patterns in the depth structure of acidification are evident (Methods, Figure S7). The well-ventilated upper 25 meters of the nearshore CCS (<100 km) show 20th century changes in the carbonate system that closely track the atmospheric increase in CO_2 . Below this surface mixed layer, $p\text{CO}_2$ changes outpace the atmosphere, indicative of amplified acidification. Averaging the CCS across 50–200 meters depth, the ocean has outpaced the

atmospheric $p\text{CO}_2$ rise by 50%. The magnitude of $\Delta p\text{CO}_2$ increases with depth below 25 meters, reaching a maximum at 100–125 meters (Figure S8).

To assess the accuracy of the historic model, we introduce a new record of $p\text{CO}_2$ based on skeletal $\delta^{11}\text{B}$ of *B. elegans* along the US West Coast (Methods, Figure S4). Our coral record presents general patterns and trends of acidification that are reproduced in the model (Figure 3). The corals collected in the upper 25 meters suggest that $p\text{CO}_2$ has followed the atmospheric rise in CO_2 since the 1890s, aligning with modeled predictions in the upper ocean. Below 50 meters, every coral record suggests that the magnitude of 20th century acidification has matched or exceeded the rise in atmospheric CO_2 . The corals demonstrate that the CCS has indeed experienced amplified acidification over the industrial era, and even capture the trend of stronger amplification of acidification with depth.

In addition to these overall trends, it is worth noting specific differences between coral records and model simulations. For instance, the corals at several locations collected between 100–125 meters outpace modeled $\Delta p\text{CO}_2$, suggesting even more amplified acidification. Our coral data from the Santa Barbara Basin (SBB) deviate most from the model and indicate an even lower historic $p\text{CO}_2$ than that represented in the model, and thus a larger relative increase in $p\text{CO}_2$ (Figure 3; $n=5$). Notably, one of the only previously published records of SBB carbonate chemistry over the industrial era also indicates lower historic $p\text{CO}_2$, like our historic corals (Osborne et al. 2020) (Supplementary Discussion 1.4). Although our data from this region are too sparse to be conclusive, it is possible that regional processes that amplify acidification in the SBB even more than the rest of the CCS are not captured in the model and warrant further investigation.

Overall, the coral record reproduces broad patterns of acidification in the biogeochemical model, and they collectively suggest that the CCS has experienced amplified acidification over the

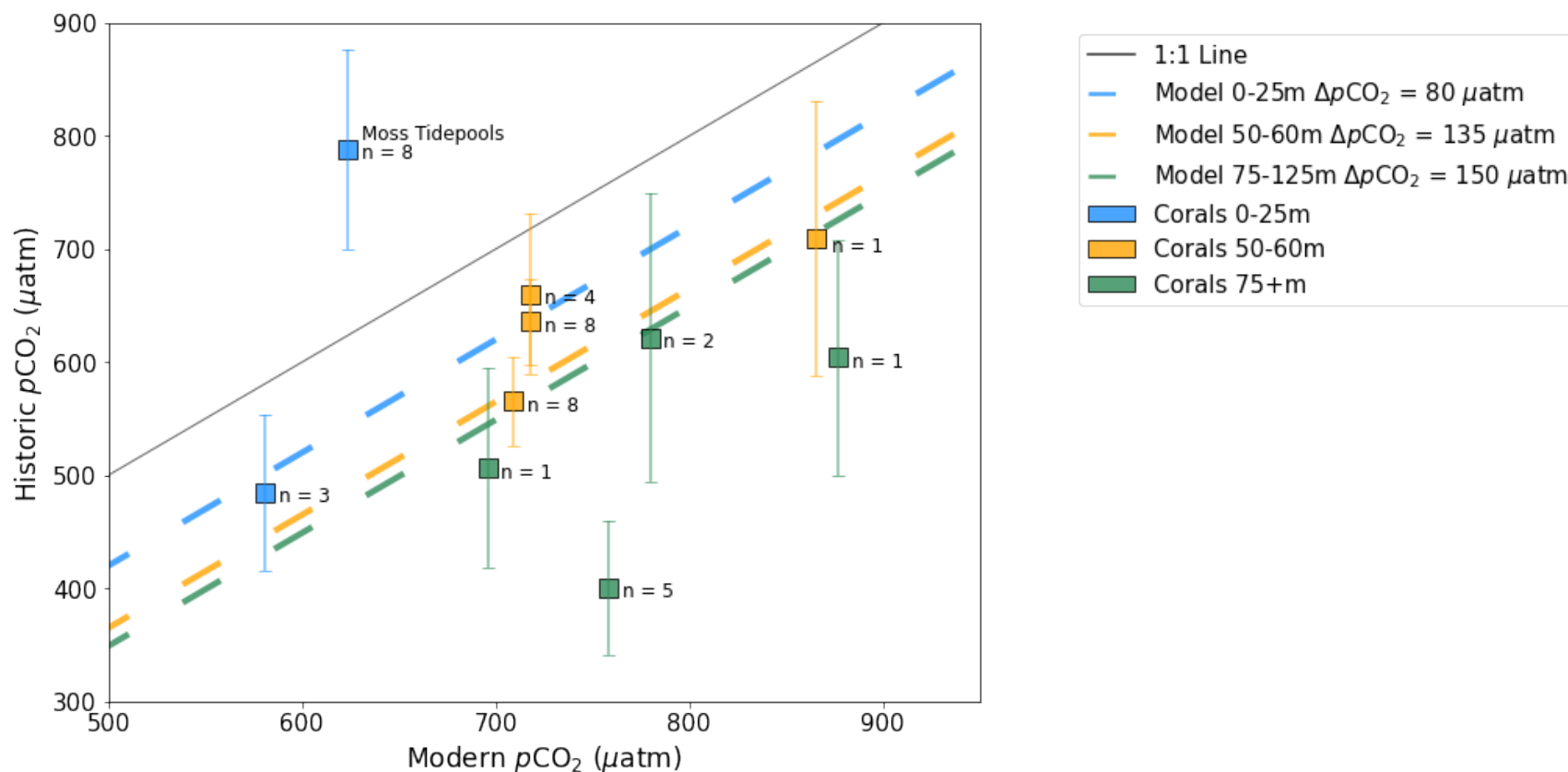


Figure 3| Geochemical and model records of 20th century acidification in the California Current. Comparison between modeled historic $p\text{CO}_2$ and measured historic coral $p\text{CO}_2$ in the CCS as a function of modern modeled $p\text{CO}_2$. *Lines:* The solid 1:1 line indicates no acidification over the past century (historic $p\text{CO}_2$ = modern $p\text{CO}_2$). The magnitude of boreal summertime acidification over the 20th century ($\Delta p\text{CO}_2$) produced in the model is dependent on depth, represented by the blue, orange, and green dashed lines to reflect different depth bins, which is consistent with marine biogeochemical processes. Acidification in the upper 25 meters (blue line) has largely followed the trend of atmospheric CO_2 ($\Delta p\text{CO}_2 = 80 \mu\text{atm}$) over the 20th century (1900–2000). Modeled $\Delta p\text{CO}_2$ below 50 meters outpaces the rise in atmospheric CO_2 and suggests that the California Current has experienced amplified acidification. As depth increases in the CCS, the model implies that the strength of amplified acidification also increases. *Coral data:* Squares represent the average coral data from individual locations and align with general patterns of modeled acidification (Methods, Supplementary Data). The depths of coral collection are color coded to match the depth of modeled data. Vertical error bars represent standard errors of the mean. Error bars for locations with only one coral represent the population standard deviation, inferred by locations with 8+ samples (Methods). n = number of corals sampled at each location. The width of the rectangles represents the average modern model standard error of the mean across locations ($x = 6 \mu\text{atm}$). Only one coral location implies a lower modern $p\text{CO}_2$ than historic $p\text{CO}_2$ (USNM 78638); these corals were collected from a tidepool near Moss Beach, California where the high variability associated with the intertidal zone likely influenced the $\delta^{11}\text{B}$ skeletal signatures.

20th century. To probe potential drivers of this acidification, we test for shifts in upwelling and biological activity over the past century using the ROMS simulations (Methods). A climatology of modeled upwelling velocity suggests that upwelling has weakened slightly during the summer months and its onset has shifted earlier in the year over the 20th century. Comparing 7-year averages of upwelling velocity between the historic and modern eras, the decline in the CCS is statistically significant but only represents a 2% change in strength and is unlikely to have driven the observed amplification of acidification (Methods). Changes in the biological pump could also affect the integrated impact of remineralization on DIC. We quantified this change in integrated remineralization using apparent oxygen utilization. Over the 20th century, changes in remineralization can account for 15% of modeled Δ DIC in the CCS on average but cannot explain the driving force of amplified acidification (Figure S9).

Much of the amplified increase in $p\text{CO}_2$ that we observe in the CCS can be explained by thermodynamic buffering effects. The isopycnals corresponding to upwelled water masses outcrop at open ocean locations, distant from the CCS. Here, we assume that water masses interact with the overlying atmosphere such that initial preformed $p\text{CO}_2$ follows increasing atmospheric $p\text{CO}_2$. After subduction, remineralization increases DIC, $p\text{CO}_2$, and acidification as the water circulates along an isopycnal and is eventually upwelled in the CCS. Increasing initial preformed DIC in response to rising atmospheric $p\text{CO}_2$ has an outsized effect on $p\text{CO}_2$ and pH in upwelled water due to a reduction in buffering capacity, even if remineralization and circulation rates remain the same (Figure 1c). This amplification highlights the need to assess rates of acidification with careful consideration of the mean state of the carbonate system, especially in extreme domains in carbonate chemistry space, such as high-carbon upwelling systems. While local physical and biogeochemical factors in other upwelling systems may exert additional influences, the chemical

principles underlying the amplification are inherent to all upwelling regimes, underscoring the global implications of this chemical non-linearity.

Averaging across the CCS, estimates of ΔDIC derived from equilibration of atmospheric CO_2 at outcropping regions and accompanying thermodynamic buffering effects (Methods Equation 4) can explain the modeled ΔDIC to within $\pm 15\%$ relative error (Methods, Figure S10). This analysis shows that atmospheric CO_2 and thermodynamic buffering effects drive the magnitude of acidification in large areas of economic and ecological value. The remaining residual leaves room for second order effects such as shifts in upwelling strength and remineralization rates, as described above. Notably, this analysis also underscores the importance of water mass age when attributing biogeochemical change to anthropogenic carbon (Methods). Given the rapid increase in atmospheric CO_2 over the past 50 years, considering water mass age in upwelling regions markedly changes the accumulation of anthropogenic carbon, as deeper, older water was in contact with its contemporary atmosphere less recently (Murray et al. 2015). Acidification in the CCS lags the imprint of modern atmospheric CO_2 due to water mass age, suggesting that acidification will continue to amplify and worsen in the coming decades.

2.3 Conclusions

Our historic coral data build confidence in the patterns and magnitude of acidification produced by our model, including amplified acidification. From this foundation, we analyze projections for future acidification in the CCS under representative concentration pathway 8.5 (RCP 8.5). Although RCP 8.5 represents a high-forcing scenario, there is value in bracketing the upper end of potential future states (Christensen, Gillingham, and Nordhaus 2018). These analyses build on a multi-resolution model study that assessed the value of resolving coastal processes in predicting future change (Samantha A. Siedlecki et al. 2020). Amplified acidification is projected to continue

in the subsurface CCS throughout the 21st century (Figure 4d and 4e). Ominously, $\Delta p\text{CO}_2$ in the CCS is estimated to continue to outpace the atmospheric rise in CO_2 in the coming century by 20% between 50–75 meters and 60% between 100–150 meters. pH is expected to decline by -0.30 below 50 meters, equivalent to the predicted change for the global surface ocean (Lee et al. 2021). While comparable in magnitude to ΔpH , the increase in hydrogen ion concentration $[\text{H}^+]$ in deeper waters is nearly double that at the surface because of the logarithmic nature of the pH scale (Fassbender, Orr, and Dickson 2021). The CCS is projected to experience low aragonite saturation states ($\Omega < 1$) and absolute pH levels as low as 7.5 at 75 meters due to the already highly acidified conditions of the CCS. Local marine organisms of economic, cultural, and biological importance are predicted to experience significant physiological challenges in response to the increasingly acidified conditions (Sunday et al. 2022). For instance, Dungeness crab, the largest US West Coast fishery by revenue, are expected to experience reduced growth and survival in early life stages as acidification progresses (Sunday et al. 2022; Alin et al. 2023). While the surface ocean across the model domain largely followed atmospheric CO_2 over the 20th century, surface $\Delta p\text{CO}_2$ lags the atmospheric increase in the 21st century, indicative of the surface ocean's limit in mitigating the accumulation of atmospheric CO_2 as its buffer capacity declines (Figure 4e). Acidification of this magnitude is predicted to have profound impacts on ecosystems of the CCS in the 21st century.

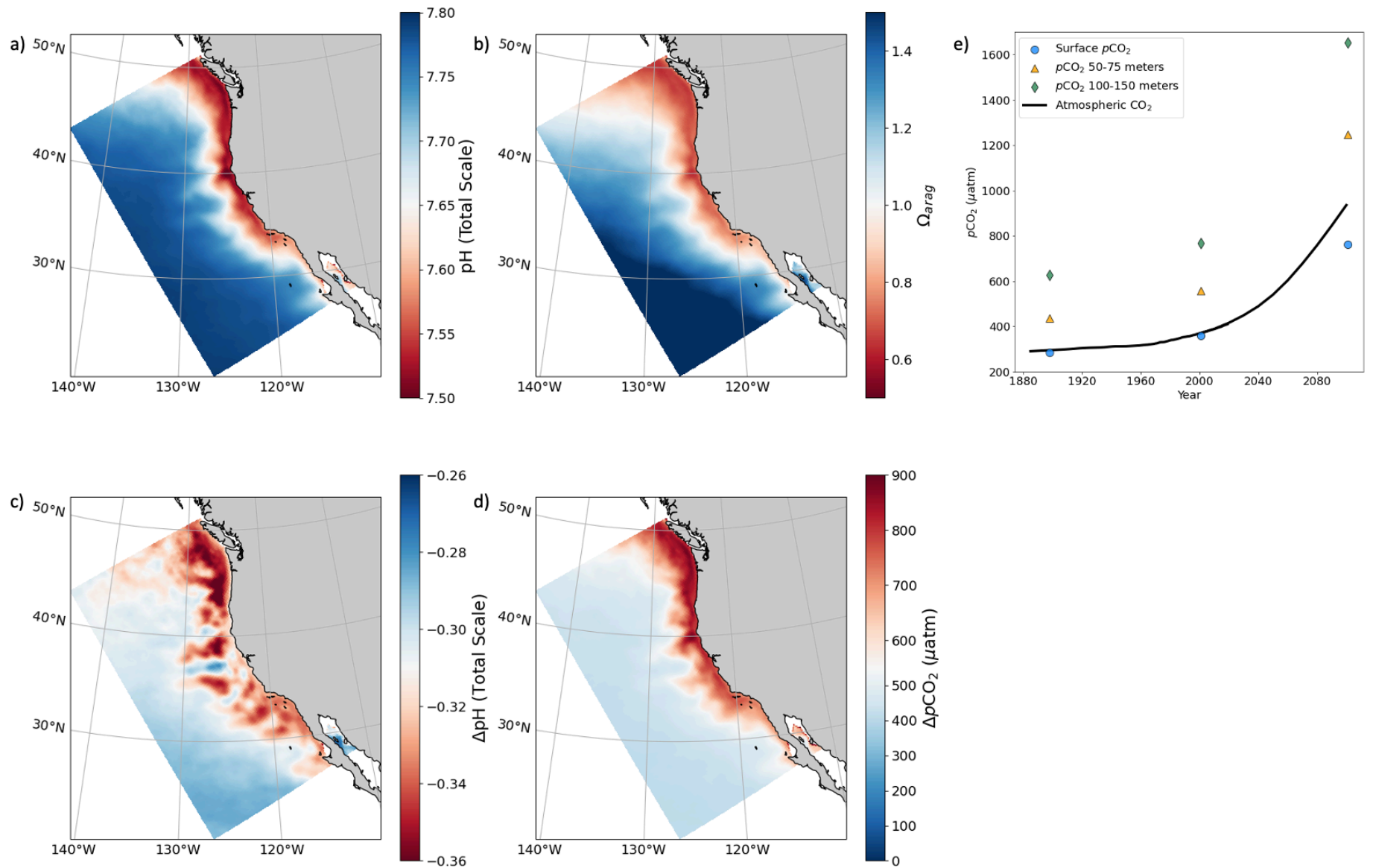


Figure 4| Future acidification in the CCS following RCP 8.5 emissions scenario. 7-year averages at 75 meters for 2097–2104 of **a)** pH (total scale) and **b)** aragonite saturation state (Ω). 21st century changes in **c)** pH and **d)** pCO_2 . The color bar in d) is centered at 550 μatm to reflect the expected rise in atmospheric CO_2 following RCP 8.5 over the 21st century; red colors indicate amplified acidification. **e)** 7-year modeled averages of the CCS seawater pCO_2 at the surface (blue), 50–75 meters (orange), and 100–150 meters (green) in the historic (1897–1904), modern (2000–2007), and future (2097–2104) simulations. Black line represents atmospheric CO_2 following RCP 8.5. The subsurface CCS is expected to experience amplified acidification relative to the atmospheric rise in CO_2 .

2.4 Methods

2.4.1 Sample Measurements: Sample Collection

Historic samples of *Balanophyllia elegans* (*B. elegans*) were collected live by the R/V *Albatross* between 1888 and 1894, and by Ernest Harrison Quayle in 1932. All historic samples were archived in the Smithsonian National Museum of Natural History (Figure S1, Supplementary Data). Samples were dried upon collection and archived dry following Smithsonian preservation guidelines. In the Salish Sea, a total of $n = 13$ historic corals were collected from five sites. A total of $n = 41$ historic corals were collected along the outer US West Coast from 10 sites that span from Vancouver Island, British Columbia, to the Channel Islands, California. These corals were collected in the 1890s from sites that would coincidentally become the major federal marine sanctuaries of the US West Coast.

Modern corals ($n = 42$) were collected from the same locations as the historic corals in the Salish Sea aboard the University of Washington R/V *Rachel Carson* in Fall 2020 (Figure S1, Supplementary Data). These were collected in 2020, so reflect conditions from approximately 2010 to 2020.

While the collection dates of most coral locations are known and all corals were living, the age of each coral is unknown. The age of the historic coral at the time of collection is unlikely to affect the study outcome, as pH values were assumed to be relatively stable. Additionally, all of the historic corals in the CCS were collected within 1.5 years of each other (September 1888 to March 1890). The age of the modern corals is also unlikely to impact the modern pH values, as they represent conditions over a narrow time window (5-10 years). Any uncertainty in the exact age, and therefore presumed pace of acidification over this period, is within the measurement error of the corals.

2.4.2 Sample Measurements: Boron Isotope Analysis

Skeletal sections of ~5 mg CaCO₃ were sampled along the primary growth axis from each coral using a Dremel tool approximately ~0.5-1 cm deep. Sampling is large compared to skeletal microstructures like centers of calcification, which we think means that the impacts of these features are largely averaged and homogenized across the bulk sample. This is supported by the systematic trends and tight precision of even smaller samples from Gagnon et al. 2021. Additionally, the Gagnon et al. 2021 calibration suggests that intraspecies variability is small compared to environmental effects. The collected material from each coral represents an average over the entire growth period of the coral. It has been estimated that the average life span for *B. elegans* in the California Current is 6.5 to 11 years (Fadlallah 1983). This time window is sufficiently narrow that any secular change in pH due to acidification within this period is within the measurement error of the corals. By sampling along the whole primary growth axis, we assume that different coral skeletal components are evenly represented in each sample.

The skeletal subsamples were then analyzed for their boron isotope composition ($\delta^{11}\text{B}$) in the St Andrews Isotope Geochemistry laboratories (STAiG) of the University of St Andrews, UK. Samples were first rinsed with ultra-pure water (Milli-Q, 18.2 Ω) and subsequently oxidized to remove any organic fractions using 1% H₂O₂ buffered with 0.1 M NH₄OH at 80°C following routine sample preparation protocols for boron isotope analyses (e.g. Rae, 2018). All samples were of the same weight (~5 mg) and treated identically during cleaning to minimize the risk of preferential dissolution of specific coral skeletal components biasing results. Clean samples were dissolved in distilled 0.5 M HNO₃ with the aid of ultrasonication. A small aliquot of the dissolved sample (<10% volume) was measured on an Agilent 8900 Triple Quadrupole ICP-MS to determine the boron content in sample along with major, minor and trace element composition. The rest of the dissolved sample was separated from the carbonate matrix on an Amberlite IRA 743 boron-

specific anionic exchange resin (Kiss 1988; Foster 2008), following the batch protocol of Trudgill et al. 2024. Purified boron solutions were spiked with HF to aid boron wash out and measured in a 0.5 M HNO₃ + 0.3 M HF matrix (Misra et al. 2014; Zeebe and Rae 2020) on a Thermo Scientific Neptune Plus MC-ICP-MS equipped with a HF-resistant sample introduction kit and 10¹³ Ω resistors (see (Crumpton-Banks et al. 2022) for further details). Instrumental mass bias was corrected by standard sample-bracketing with a 15 ppb NIST SRM 951 solution. Total procedural blanks contained <20 pg B ($n = 4$), and hence were negligible against the typical sample size of ~20 ng B (< 0.1%). Full procedural uncertainty was assessed using repeat measurement of NIST RM 8301 (Coral) consistency standard run during this analytical campaign, yielding an average value of 24.28 ± 0.12 ‰ (2 SD, $n = 8$) that is consistent with long term lab reproducibility and interlaboratory reference values (J. A. Stewart et al. 2021) (24.17‰). Skeletal data are summarized in Supplementary Data.

2.4.3 Data Processing: The Boron Isotope-pH Proxy

Paleoproxies provide an invaluable tool to reconstruct historic ocean conditions and contextualize current climate change. Stable boron isotope ratios ($\delta^{11}\text{B}$) are recorded in the skeletons of marine calcifiers such as corals, which function as time capsules of past carbonate system chemistry (Rae et al. 2018). We utilized this method to reconstruct the historic state of the CCS through measurements of *Balanophyllia elegans*, a common cold-water orange cup coral that spans a wide geographic range from Southern Alaska to Baja California.

To test the null hypothesis that $\delta^{11}\text{B}$ of borate ion has not changed over the past century in the Salish Sea, we conduct a two-sample t-test to determine any difference between historic and modern $\delta^{11}\text{B}$. Averaging data across sample locations in the Salish Sea (Supplementary Methods 1.1), there is a significantly higher $\delta^{11}\text{B}$ in the historic corals ($M = 24.94$, $SE = 0.10$) compared to $\delta^{11}\text{B}$ measurements from modern corals ($M = 24.52$; $SE = 0.06$); $t(63) = 3.53$, $p = <0.001$.

Assuming that the physiology of coral calcification and total seawater $\delta^{11}\text{B}$ have not changed over the past century, we can reject the null hypothesis and conclude that $\delta^{11}\text{B}$ of borate ion incorporated in the coral skeletons has declined as a result of declining seawater chemistry (Figure S2).

2.4.4 Data Processing: Coral-Based Estimates of $p\text{CO}_2$ in the Salish Sea

We then translate the coral data into constraints on past seawater carbonate chemistry to add meaning to this measured $\Delta(\delta^{11}\text{B})$ (Δ = modern – historic). In a previous study, the same species of corals (*B. elegans*) was cultured under controlled conditions to produce a calibration curve that links skeletal $\delta^{11}\text{B}$ and seawater pH, the predominant metric to assess ocean acidification (Gagnon et al. 2021) (Equation 2). The same culture study also uncovered a subtle but significant relationship between skeletal $\delta^{11}\text{B}$ and dissolved inorganic carbon (DIC), even at constant pH (Gagnon et al. 2021) (Equation 1). A similar relationship between $\delta^{11}\text{B}$, pH, and DIC is apparent in culture studies of tropical corals (Comeau et al. 2017).

Equation 1:

$$\delta^{11}\text{B}_{\text{correction}} = \left(\text{DIC} - 2.5 \text{ mmol/kg} \right) \times 1.08$$

Equation 2:

$$\text{pH}_{\text{TOTAL}} = \frac{\delta^{11}\text{B}_{\text{measured}} + 1.08 \times \text{DIC} + 7.2}{4.33}$$

Albeit minor relative to the skeletal $\delta^{11}\text{B}$ -pH relationship, the impact of DIC on skeletal $\delta^{11}\text{B}$ is nonetheless considered in our interpretation of the coral data (Equation 2). Because two environmental parameters exert control on $\delta^{11}\text{B}$, we explore the coral record in pH vs DIC space as shown in Figure S4. Historic and modern skeletal $\delta^{11}\text{B}$ measurement averages are indicated by lines in this space. Fortuitously, we find that $\delta^{11}\text{B}$ provides a tight constraint on $p\text{CO}_2$ regardless of changes in DIC, as can be seen on these plots. Over a large range of DIC values, lines of constant

$\delta^{11}\text{B}$ are nearly parallel with the contour lines corresponding to specific seawater $p\text{CO}_2$ values (Figure S4). While individual contours are parallel between $p\text{CO}_2$ and $\delta^{11}\text{B}$ over a wide range of DIC values, the spacing between contours does change subtly with absolute DIC. However, the effect of DIC falls within the measurement error and was not found to have a meaningful effect. Once a rough DIC is established for the modern ocean at coral collection locations from observational (bottle) data, the $\Delta p\text{CO}_2$ between historic and modern eras is simply the distance in space between the modern and historic constant $\delta^{11}\text{B}$ lines. Note that DIC does not need to be known well, as it is just used to generally indicate the region of carbonate system space for making the plots used here.

We use climatological means of bottle data from the Washington Ocean Acidification Center cruises to obtain modern values of mean DIC, pH at the sites of coral collection (Alin et al. 2021) (Supplementary Methods 1.2). Most of our Salish Sea coral samples were collected near Admiralty Inlet, a narrow channel at the eastern terminus of the Strait of Juan de Fuca through which most of the seawater that fills Puget Sound flows. Tidal mixing over a shallow glacial sill leads to similar seawater properties through much of the water column at Admiralty Inlet, meaning the properties are generally homogenous with depth. Climatologies of modern carbonate chemistry parameters for Admiralty Inlet at the coral collection depth of 70 meters were generated from several years of bottle data. There is a seasonal pattern of low TA and DIC during the winter months followed by high TA and DIC during the fall (Supplementary Methods 1.2; Figure S13). We conducted a sensitivity analysis using both annual and summertime (JJA) averages for modern DIC and found only a minor difference in our reconstructed $\Delta p\text{CO}_2$ results for the Salish Sea. This is in part because summer and annual climatological means of pH averages are approximately equivalent in the Salish Sea. Armed with this constraint on typical DIC, we can make robust

estimates of $\Delta p\text{CO}_2$ in the Salish Sea regardless of the process that drives the 20th century change ($\Delta p\text{CO}_2 = 172 \mu\text{atm}$; standard error of the difference between means $\sigma_{M_{\text{Modern}}-M_{\text{Historic}}} = 41 \mu\text{atm}$).

We assessed the temperature effect on the k value by conducting a sensitivity analysis on our $p\text{CO}_2$ calculations. Temperature values were based on summertime averages from bottle data collected at the Washington Ocean Acidification Center (WOAC) station 21 (Table S1), located near a majority of coral sampling sites. Under the assumption that temperature remained constant over the past century, we calculated $\Delta p\text{CO}_2 = 172 \mu\text{atm}$. However, if we assume that historical temperatures were 1°C cooler, then $\Delta p\text{CO}_2$ increases slightly to 176 μatm . This small temperature effect is well within the uncertainty range of the coral records ($\pm 41 \mu\text{atm}$). Furthermore, if temperatures have indeed warmed over the past century, our acidification estimates would be even larger and more extreme. We adopt a conservative approach and assume a constant temperature over the past century, and thus report $\Delta p\text{CO}_2 = 172 \mu\text{atm}$ in the Salish Sea.

2.4.5 Coral-Based Estimates of pH in the Salish Sea

The modern observational data provides additional information that we can use to better calibrate our proxy and to estimate ΔpH for the Salish Sea. Comparing modern observational DIC and pH data (red circle, Figure S4, Supplementary Methods 1.2) to modern $\delta^{11}\text{B}$ (grey line, Figure S4), we found that a pH offset of -0.10 was necessary to align the two datasets. We attribute this difference to culture conditions not exactly matching the natural wild coral setting. To calibrate the coral data, we apply this pH offset of -0.10 to all our coral data, including our historic and modern records from the Salish Sea and historic records from the US West Coast. This offset does not impact the interpretation of data from the Salish Sea where we have historic-modern pairs but applying this same offset to all coral samples anchors the historical West Coast coral data so they

can be accurately compared to modeled historic values and other proxies. We also find that the summer and annual climatological pH averages are approximately equivalent in the Salish Sea, so applying an offset informed by the observational summertime average instead of choosing the annual average has little impact. Nonetheless, we operationally had to make a choice between summertime or annual averages. We used summertime for our offset correction because there is evidence that skeletal growth of *B. elegans* and other closely related cold-water coral species is biased towards summer (Fadlallah 1983; Jantzen et al. 2013; Beck 2018) (Supplementary Methods 1.3).

Unlike $\Delta p\text{CO}_2$, accurately reconstructing ΔpH requires knowledge about the process driving this shift in pH. Different biogeochemical processes lead to different paths in pH-DIC space between the $\delta^{11}\text{B}$ curves representing modern and historic coral data. This choice of path will result in slightly different implied ΔpH values (but does not significantly impact $\Delta p\text{CO}_2$). For example, if most of the Salish Sea seawater changes captured by $\delta^{11}\text{B}$ were driven by accumulation of anthropogenic CO_2 , then the implied pH would be slightly smaller than if seawater chemistry changes were primarily driven by shifts in ecosystem calcification and CaCO_3 dissolution (see colored paths in Figure S4). We assume that CO_2 invasion is the main driver of the 20th century change (as explained in Supplementary Discussion 1.1), which constrains the historic estimate of DIC and allows us to calculate an absolute estimate of historic pH. This biogeochemically reasonable assumption also leads to a smaller, more conservative ΔpH estimate than other processes like shifts in calcification and CaCO_3 dissolution. Note again that the sensitivity of ΔpH to the choice of processes is small compared to other sources of uncertainty. The intersections of the CO_2 invasion line and historic and modern coral records in Figure S4 imply $\Delta\text{pH} = -0.095$ (standard error of the difference between means $\sigma_{M_{\text{Modern}}-M_{\text{Historic}}} = 0.025$) and $\Delta\text{DIC} = 28$

$\mu\text{mol/kg}$. This estimate of ΔDIC is comparable to estimates of industrial era ΔDIC in the Salish Sea from a high-resolution biophysical modeling study (Jarníková et al. 2022).

Despite the coral-based ΔpH and ΔpH of the open surface ocean over the past century being comparable in magnitude (~ -0.1), the ΔpH reported in the Salish Sea subsurface still supports amplified acidification due to the logarithmic nature of the pH scale (Fassbender, Orr, and Dickson 2021). The mean chemical state of the open ocean surface is vastly different than that at depth in the Salish Sea; therefore, the *same* amount of atmospheric CO_2 change will lead to *different* changes in pH dependent on the background carbonate chemistry of the system. The Salish Sea has a higher DIC:TA value than the open ocean surface and thus a lower buffering capacity. To understand the effect of this background state on subsequent changes in carbonate chemistry, we can calculate the predicted ΔpH in our ‘baseline’ scenario, defined as the magnitude of acidification associated with the uptake of atmospheric CO_2 over the industrial era ($\Delta\text{CO}_{2\text{ atm}} = 120$ ppm between 1900 and 2020). (Feely et al. 2010) Table 1 provides historic and modern estimates for DIC, TA, and pH at depth at Admiralty Inlet, where the majority of our corals were collected. From these variables we can calculate historic $p\text{CO}_2$, and estimate modern pH assuming modern $p\text{CO}_2 = \text{historic } p\text{CO}_2 + 120 \mu\text{atm}$ (the change in atmospheric CO_2 over the 20th century). The predicted ΔpH for this baseline scenario is -0.06, far smaller than the -0.095 change suggested by the coral record. Furthermore, the absolute change in $[\text{H}^+]$ is 1.5 times larger in the Salish Sea (associated with the baseline scenario yielding a -0.06 pH decline) versus that in the open ocean (associated with -0.1 pH decline) given the logarithmic nature of the pH scale. For these reasons, the ΔpH in the Salish Sea is in fact amplified when compared to the magnitude of acidification that follows the pace of atmospheric change.

2.4.6 Data Processing: Coral-Based Estimates of Acidification in the CCS

West Coast $\delta^{11}\text{B}$ data are interpreted in a similar way as our Salish Sea corals, including the application of a -0.10 pH offset. While the summer and annual pH averages are approximately equivalent in the Salish Sea, locations along the West Coast have different climatologies. The West Coast locations experience low pH earlier in the season compared to the Salish Sea (Figure S3). As a result, the annual and summer pH averages along the West Coast are different whereas they are approximately equivalent in the Salish Sea. Given that different choices lead to smaller or larger offsets between the West Coast model and coral data, different assumptions can affect the extent of overlap between the coral data and the model. However, all but one combination of these various assumptions are consistent with amplified acidification. Furthermore, the one outlier scenario results in historic $p\text{CO}_2$ values that are unrealistically high, so we feel confident in excluding this interpretation from our analysis.

For the reasons described previously, the $p\text{CO}_2$ of historic corals in the CCS are well constrained by historic $\delta^{11}\text{B}$ measurements. These reconstructed $p\text{CO}_2$ values are independent of our model and can be compared to modern data, modeled or observational, as well as other proxies. The results of our study are primarily based on these independent $p\text{CO}_2$ reconstructions.

It is also convenient to estimate past pH from historic $\delta^{11}\text{B}$ measurements, even if this requires some other constraint on past DIC. We use an average DIC extracted from the ROMS model by calculating a 7-year summertime average of historic DIC in the nearshore CCS over 0–125 meters depth (last 7 years of the historic run). The average DIC value is substituted into Equation 1, the $\delta^{11}\text{B}$ -DIC correction equation described above. The $\delta^{11}\text{B}$ correction values and location-averaged $\delta^{11}\text{B}$ measurements were then substituted into Equation 2 to obtain DIC-corrected pH values at each coral location.

Standard errors of the mean were calculated for pH and $p\text{CO}_2$ at every location. For locations with only one coral, the standard error of the mean is equal to the population standard deviation, inferred by calculating the average standard deviation at locations with 8+ samples. The $p\text{CO}_2$ data and standard error of the mean values described here represent the y-axis values in Figure 3. The coral-based calculations of historic pH and $p\text{CO}_2$ can be found in Table S3.

2.4.7 Data Processing: Physical-Biogeochemical ROMS of the CCS

A regional eddy-resolving physical-biogeochemical Regional Ocean Modeling System (ROMS) was used to assess the change in carbonate chemistry along the US West Coast over the 20th century. Two hindcast simulations were analyzed spanning 1994–2007 in the modern era and 14 years representing end of 19th century conditions as in the historic era. The horizontal grid is 322 x 450 cells with a resolution of $dx = 12$ km, $dy = 12$ km, $dt = 32$ minutes, and $dz = 42$ terrain-following sigma layers with decreasing layer thickness towards the surface. For the purposes of our analyses, the model results are interpolated to 25-meter depth increments and saved as monthly averages. While the modern model has been evaluated against observational data and faithfully reproduces the modern CCS mean state (Figure S6), no long-term dataset exists across the CCS of carbonate chemistry parameters in the early 1900s to assess the accuracy of the historical run. Additional details on the model configuration and reproducibility can be found in (Renault et al. 2020) and (Deutsch et al. 2021). The input for the historical run is based on the input for the hindcast run, with long-term trends of temperature and DIC between the two periods removed. The interannual variability of the surface forcing is the same in both runs. Long term trends in radiation and relative humidity were removed for the historical run.

The model domain was divided into nearshore (<100 km) and offshore (>200 km) regions during analysis to capture variability in biogeochemical patterns between the coastal CCS and open ocean. All averages of modeled parameters represent 7-year summertime or annual averages

in the historic (last 7 years of the historic run) and modern (December 2000–November 2007) simulations. Only the final seven years of the simulations were included in the calculations to remove model biases due to spin-up and deviations from the mean state, such as the 1997–1998 El Niño.

To compare West Coast coral and model data, the coral data are compared to a modeled summer average, since the corals grow with a seasonal bias in the summer (Supplementary Methods 1.3).

2.4.8 Data Processing: Model Estimates of Acidification in the CCS

Model predictions for 20th century changes in pH, DIC, and $p\text{CO}_2$ are assessed along the US West Coast (Figure S7). We primarily analyze acidification in terms of $p\text{CO}_2$ as opposed to pH, allowing us to directly compare magnitudes of acidification independent of background carbonate chemistry. Model estimates of $\Delta p\text{CO}_2$ are also obtained from several depth regimes in the nearshore CCS to align with the coral depths of collection. Above 25 meters depth, $\Delta p\text{CO}_2$ from 1890–2005 slightly lags the atmospheric rise in CO_2 ($\Delta p\text{CO}_2 = 75 \mu\text{atm}$; $\Delta p\text{CO}_{2 \text{ atm}} = 80 \mu\text{atm}$). At 50–60 meters, $\Delta p\text{CO}_2$ in the nearshore CCS is $120 \mu\text{atm}$; at 75–125 meters depth, $\Delta p\text{CO}_2$ in the nearshore CCS is $140 \mu\text{atm}$. Summertime averages of $\Delta p\text{CO}_2$ are also evaluated to compare the coral records, which grow with a seasonal bias (Supplementary Methods 1.3). In the upper 25 meters of the water column, $\Delta p\text{CO}_2$ from 1890–2005 in the summer months follows the atmospheric rise in CO_2 ($\Delta p\text{CO}_2 = 80 \mu\text{atm}$). At 50–60 meters depth during the summer, $\Delta p\text{CO}_2$ in the nearshore CCS is $135 \mu\text{atm}$. At 75–125 meters depth, $\Delta p\text{CO}_2$ in the nearshore CCS is $150 \mu\text{atm}$. The above summertime $\Delta p\text{CO}_2$ values at 0–25 meters, 50–60 meters, and 75–125 meters are reproduced in Figure 3 to represent average model predictions of acidification in the nearshore CCS.

Since no historic-modern pairs exist along the outer West Coast, modeled historic $p\text{CO}_2$ and measured historic coral $p\text{CO}_2$ are both compared to modern modeled $p\text{CO}_2$. Both historic and modern model $p\text{CO}_2$ averages are calculated over a 7-year period at every coral location from December 1897–November 1904 and December 2000–November 2007, respectively. Since the corals are presumed to grow with a seasonal bias during the summer due to optimized feeding and nutrient supply (Supplementary Methods 1.3), the modern model averages include data only from summer. In all but one location, the season of environmental conditions that aligns with optimal growth corresponds with June, July, and August. Our northernmost location (USNM 92621), however, shows a different climatology where optimized nutrient conditions are delayed. This is likely due to the cumulative seasonal respiration, which contributes to acidified and hypoxic conditions in the northern CCS through the upwelling season where there is longer retention (Feely et al. 2018; Alin et al. 2023; S. A. Siedlecki et al. 2015). For this location, we select a 3-month window including July, August, and September. The $p\text{CO}_2$ averages are calculated over a 3-cell x 3-cell area (36 km x 36 km) centered on the grid cell nearest the coral location.

The model output is interpolated to 25-meter depth intervals. Even though most collection depths are within 5 meters of a 25-meter increment, USNM 92626, USNM 36416, and USNM 92625 are located halfway between depth bins (Supplementary Data). In these cases, the model is linearly interpolated between the two adjacent depth bins to account for $p\text{CO}_2$ gradients with depth. The historic, coral-based $p\text{CO}_2$ data are plotted against this modern, model-based $p\text{CO}_2$ data in Figure 3 to compare model and geochemical estimates of 20th century acidification.

2.4.9 Data Interpretation: Quantifying Acidification in the CCS Attributed to Changes in Upwelling and Remineralization

To probe the dominant driver of 20th century acidification, we test for shifts in upwelling and biological activity over the past century using our model. Upwelling strength was evaluated

by comparing 7-year averages of upwelling velocity in the nearshore CCS (<100 km) at every depth bin in the historic and modern model simulations. A paired *t*-test reveals a statistically significant decline in upwelling velocity of 2% in the upper 200 meters.

To capture the integrated impact of shifting upwelling patterns and remineralization rates on carbonate chemistry, we calculate the change in apparent oxygen utilization (AOU) over the 20th century.

To determine changes in remineralization, we calculate DIC attributed to respiration inferred by AOU and the stoichiometric Hedges ratio in both the historic and modern model simulations (Hedges et al. 2002). For AOU calculations, preformed O₂ values are calculated at every grid cell in the nearshore CCS for both the historic and modern eras, informed by 7-year averages of temperature and salinity for the given grid cell (Garcia and Gordon 1992). Model O₂ is subtracted from preformed O₂ to give O₂ remineralization, the oxygen consumed during the transformation of organic matter to inorganic carbon. To obtain DIC produced via remineralization, the AOU was multiplied by the Hedges stoichiometric relationship C/O₂ = 106/152.5. DIC production attributed to respiration was compared in the historic and modern eras ($\Delta\text{DIC}_{\text{remineralization}} = \text{DIC}_{\text{remineralization, modern}} - \text{DIC}_{\text{remineralization, historic}}$) to determine 20th century changes in remineralization. Figure S9 shows the fraction of ΔDIC that can be explained by 20th century changes in remineralization ($\Delta\text{DIC}_{\text{remineralization}}/\Delta\text{DIC}$), which is small relative to other sources of change. Thus, neither shifts in upwelling strength nor changes in remineralization can explain the dominant driver of 20th century acidification in the CCS.

2.4.10 Data Interpretation: Quantifying Acidification in the CCS Attributed to Anthropogenic Carbon

Anthropogenic carbon is transported to the CCS along isopycnals that initially outcrop in the open ocean. These water masses subduct at the outcrop regions where the water is in exchange

with CO₂ in the overlying atmosphere. To estimate the change in carbonate chemistry attributed to anthropogenic carbon that enters the ocean at outcrop regions, we calculate the $\Delta\text{DIC}_{\text{preformed}}$ expected from just an increase in atmospheric $p\text{CO}_2$:

Equation 3:

$$\Delta\text{DIC}_{\text{preformed}} = \text{DIC}_{\text{preformed, modern}} - \text{DIC}_{\text{preformed, historic}}$$

We assume for this simplified test that the increase in atmospheric $p\text{CO}_2$ between historic and modern eras translates into an equal change in sea surface $p\text{CO}_2$. This assumption does not necessarily imply equilibration, but it does make the simplifying assumption of a constant air-sea offset for the outcrop of a particular isopycnal with time. At each grid cell in the CCS, surface, preformed DIC at the outcropping region was calculated using 1) atmospheric CO₂ and 2) a 7-year average of the grid cell TA. Note that the difference in preformed DIC between historic and modern is only weakly sensitive to the alkalinity of the preformed water, because contours of constant $p\text{CO}_2$ are roughly parallel over the relevant range of carbonate system parameters. Thus, our results are robust to even large uncertainties in mean alkalinity or alkalinity changes.

Water mass age affects our calculations of preformed DIC because this age determines the date when the water mass was most recently in exchange with the atmospheric CO₂, which has changed rapidly in the modern era. We assume a typical age structure for the CCS where deeper water masses are older. Our analysis was conducted assuming ages of 0, 13, and 25 years at 0–50 meters, 75–125 meters, and 150–200 meters, respectively, to reflect varying time since last ventilation. In the modern model (2000–2007), these ages correspond with atmospheric CO₂ concentrations of 376, 360, and 339 μatm for ~2005, 1995, and 1980, respectively (Switzerland Institute for Atmospheric and Climate Science, Annual CO₂ Data). Given the rapid rise of atmospheric CO₂ since the 1970s, accounting for water mass age is an important consideration when analyzing acidification patterns in the CCS. In the historic model (end of 19th century),

atmospheric CO₂ was relatively constant over the prior 25 years, so water mass age makes little difference in terms of anthropogenic carbon accumulation (CO_{2 atm} = 296 μatm).

The difference between modern and historic preformed DIC values represents the estimated ΔDIC attributed to anthropogenic carbon (ΔDIC_{preformed}, Equation 3). The ratio of estimated, preformed ΔDIC to modeled ΔDIC is calculated at every grid cell to determine how much modeled 20th century changes can be explained by uptake of anthropogenic CO₂. Figure S10 shows the percent that uptake of anthropogenic CO₂ can explain modeled ΔDIC at 0–50 meters, 75–125 meters, and 150–200 meters depth, assuming structured water mass age. Estimates of preformed ΔDIC derived from equilibration of atmospheric CO₂ at outcropping regions and accompanying thermodynamic buffering effects can explain modeled ΔDIC within 15% relative error. The remaining residual leaves room for second order effects such as changes in upwelling strength and biological activity, independently estimated based on AOU calculations and model-based upwelling parameters, described above.

Modeled and estimated acidification attributed to anthropogenic carbon were also compared in terms of *p*CO₂ and pH. Estimates of modern DIC assuming atmospheric CO₂ invasion and thermodynamic buffering effects are obtained by adding the preformed ΔDIC from Equation 3 to a 7-year modeled average of historic DIC at each grid cell (Equation 4). The 7-year average of modeled modern TA and the estimate of modern DIC from Equation 4 inform estimates of *p*CO₂ and pH.

Equation 4:

$$\text{DIC}_{\text{estimate, modern}} = \text{DIC}_{\text{model, historic}} + \Delta\text{DIC}_{\text{preformed}}$$

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Chapter 3: Leveraging 4-Dimensionally Mapped Ocean Biogeochemistry to Inform Species Distribution Modeling

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3.0 Abstract

Understanding the drivers of animal migratory patterns in a four-dimensional (4D) ocean is essential for developing reliable species distribution models (SDMs) that support ecosystem-based management. Despite recent advances in biologging and monitoring technologies, many SDMs overlook dynamic, subsurface biogeochemical conditions that impose critical constraints on suitable habitat. The Biogeochemical Argo (BGC-Argo) float array has revolutionized our view of the 4D biogeochemical landscape, providing new perspectives on the linkages between species distributions and environmental conditions. To assess the utility of depth-resolved, biogeochemical information in SDMs, we leverage archival tagging datasets, mapped ocean biogeochemistry data products, and machine learning methods to examine the extensive migrations of North Pacific albacore tuna (*Thunnus alalunga*), a commercially important fishery species. Our SDM predicts habitat suitability with high skill across space and time using multiple 4D biogeochemical predictor variables that capture both environmental deterrents (e.g. oxygen limitation) and attractants (e.g. chlorophyll, particulate organic carbon). These conditions strongly impact albacore vertical distributions, influencing both seasonal shifts and large-scale migration patterns. While temperature is a key determinant of habitat suitability, our findings demonstrate

that biogeochemical variables substantially expand or contract habitat beyond what is thermally suitable. In this study, biogeochemical predictors contract suitable habitat by more than 60% in winter and expand it by 25% in summer, emphasizing the influence of subsurface biogeochemistry in modulating habitat availability. This scalable framework can be applied to other taxa and regions, offering new avenues to improve bycatch avoidance, catch per unit effort estimates, and predictions of climate-driven habitat shifts.

3.1 Introduction

3.1.1 Background and Motivation

Effective ecosystem-based management requires accurate predictions of species distributions to guide decision-making that balances ecological conservation with economic interests. Species distribution models (SDMs) have emerged as essential tools for supporting these objectives (Robinson et al. 2017) by identifying habitat hotspots, informing conservation strategies, and guiding dynamic ocean management to reduce bycatch (Hazen et al. 2018). SDMs can also be leveraged to incorporate species-environment relationships into broader ecosystem models, revealing trophic dynamics and community-level processes that support holistic ecosystem management. As climate change progresses, SDMs are increasingly utilized to project range shifts or redistributions of ecologically and commercially important species (Gormley et al. 2015; Sinclair, White, and Newell 2010).

The diverse applications of SDMs are grounded in an understanding of the physical, chemical, and biological characteristics that foster suitable marine habitat (Elith and Leathwick 2009; Melo-Merino, Reyes-Bonilla, and Lira-Noriega 2020). Historically, marine SDMs have relied primarily on surface-oriented variables such as sea surface temperature (SST) and chlorophyll-*a* concentration (Chl), and relatively static variables such as bathymetry to

characterize potential habitat (Robinson et al. 2017; Pickens et al. 2021). While these data are readily available and globally comprehensive, they fail to capture depth-dependent biogeochemical controls that impose critical constraints on suitable habitat. Low oxygen levels can cause hypoxia and high carbon dioxide partial pressure ($p\text{CO}_2$) can lead to hypercapnia, both of which affect metabolic rates and stress tolerance (Breitburg 2002; Heuer and Grosell 2014; Pollock, Clarke, and Dubé 2007). Nutrient availability shapes prey abundance and trophic dynamics, mediating feeding behavior and community interactions. Given that these biogeochemical characteristics are fundamental to species survival and depth-dependent, incorporating this vertical information in SDMs provides a basis for more reliable, mechanistic relationships between species and their environment (Elith and Leathwick 2009; Mac Nally 2000).

Recent work has explored using ocean circulation model output to incorporate subsurface conditions into two-dimensional SDMs (Becker et al. 2016; Brodie et al. 2018; Scales et al. 2017), but model biases and a lack of in situ data for validation can limit the reliability of these approaches. Advancements in observational technologies have greatly increased the availability of accurate data that reflect real-world conditions and spatio-temporal variability. The global Biogeochemical Argo (BGC-Argo) float array has already revolutionized our view of the subsurface ocean and enabled the oceanographic community to study chemical, biological, and physical processes from a new perspective (Claustre, Johnson, and Takeshita 2020; Johnson and Claustre 2016). These floats provide direct, in situ measurements of key biogeochemical variables, including pH, oxygen, nitrate, chlorophyll-*a* fluorescence as a proxy for Chl concentration (Roesler et al. 2017), and particulate backscattering coefficient as a proxy for particulate organic carbon (POC) (Cetinić et al. 2012; Stramski et al. 1999). The extensive spatial and temporal observing coverage achieved by these floats has also facilitated the development of four-

dimensional (4D; temporal plus three spatial dimensions) gridded data products that capture both the mean state and variability of ocean conditions (e.g., Sharp et al. 2022). Mapped ocean biogeochemistry data products mark a groundbreaking shift in our ability to investigate fundamental processes that influence species distributions, such as biological productivity, deoxygenation, ocean acidification, and marine ecosystem health, over a wider range of temporal and spatial scales than previously possible.

The integration of 4D biogeochemical information with species observations offers a new approach to study species distributions and improve SDMs. In this study, we evaluate the utility of depth-resolved data products informed by BGC-Argo to characterize the environmental conditions experienced by a highly migratory albacore tuna species. Our overarching goal is to investigate whether interior ocean biogeochemical information can improve SDM performance and provide a more mechanistic understanding of species–environment relationships.

3.1.2 Case Study: Juvenile Albacore Tuna

We use juvenile North Pacific albacore tuna (*Thunnus alalunga*) as a case study organism given their migratory nature and economic value as a U.S. fishery (\$36 million in 2022), consistently ranking among the top ten Pacific Coast commercial fisheries over the past decade (NOAA Fisheries Office of Science and Technology, n.d.). North Pacific albacore can be classified into three migratory sub-groups: long-migratory, short-migratory, and resident fish (Figure S1, (Muhling et al. 2022)). In the eastern North Pacific, long-migratory albacore undertake extensive seasonal migrations between coastal ecosystems in the California Current, where they reside during summer and fall, and the subtropical North Pacific, where they reside during winter and spring (Figure S2, (Childers, Snyder, and Kohin 2011)). Short-migratory albacore follow a similar seasonal pattern but do not travel west of 150°W, while resident fish remain off the coasts of Southern California and Baja California year-round.

In addition to their expansive horizontal range, albacore exhibit energetic diving behavior, frequently descending below 200 meters depth during the day (Childers, Snyder, and Kohin 2011). Cumulative daily vertical travel for juvenile albacore ranges from about 8 km in the California Current to nearly 12 km in the subtropical North Pacific (Arostegui et al. 2023), reflecting regional differences in behavior and habitat use. Foraging strategies vary across biogeographic regimes, with diving patterns and diet composition shifting between epipelagic forage fish in the California Current (Glaser, Waechter, and Bransome 2015; Nickels et al. 2023) and mesopelagic prey in the offshore North Pacific (Iglesias et al. 2023; Watanabe et al. 2004), aligning with deeper diving behavior. This dietary transition also corresponds with environmental differences between regions, as subtropical waters tend to be warmer at depth and allow greater light penetration compared to the California Current. Together, these extensive horizontal and vertical movements expose albacore to a wide range of oceanographic conditions and distinct biogeochemical regimes throughout their migration.

Several studies have attempted to link albacore migration patterns to the ambient oceanographic conditions. Early research demonstrated that SST strongly influences juvenile horizontal movements, contracting suitable habitat seasonally along latitudinal gradients (Clemens 1961; Michael and Lynn 1977). Advancements in remote sensing capabilities facilitated analyses of albacore catch data in relation to surface Chl concentrations (Laurs, Fiedler, and Montgomery 1984; Polovina et al. 2001) and distributions of key forage species and prey (Muhling et al. 2019). More recently, researchers have incorporated modeled biogeochemical properties into SDMs in two spatial dimensions (latitude and longitude; (B. A. Muhling et al. 2022; Frawley et al., n.d.). However, despite advances in biologging and biogeochemical data integration, knowledge gaps persist regarding albacore migratory patterns in the context of a 4D ocean.

This study evaluates how the inclusion of biogeochemical information in SDMs can improve predictions of seasonal albacore habitat utilization in both two and three spatial dimensions. To investigate this, we leverage archival tagging datasets, mapped ocean biogeochemistry data products, and machine learning methods to examine the extensive migratory behaviors of albacore tuna. Our SDMs are trained on a balanced dataset of presences (Table S1) and pseudo-absences and a subset of environmental predictors including temperature, oxygen, and proxies for optimal foraging conditions (Chl and POC; Materials and Methods). We assume that high levels of Chl and POC, as indicators of primary productivity, are linked to forage species and thereby suggest the presence of productive albacore feeding grounds (e.g., (Nagatomo et al. 2023)).

We constructed SDMs that predict the probability of occurrence, as a proxy for habitat suitability, in both two-dimensional (2D) and three-dimensional (3D) space (Table S2). First, we constructed and compared two 2D SDMs, each estimating albacore occurrence probabilities across seasons (2004–2013), latitude, and longitude to capture horizontal habitat utilization. One SDM was trained on surface biogeochemical data from satellites, while the other was trained on gridded, depth-integrated (0–200 meters) biogeochemical data derived from BGC-Argo floats. Hereafter, these are referred to as the satellite-based 2D SDM and the float-based 2D SDM, respectively. By comparing their performance, we assessed the potential benefits of depth-integrated information on predictions of albacore habitat utilization. We also developed 3D SDMs for each season (2004–2013) that resolved habitat suitability across latitude, longitude, and depth. To investigate how environmental conditions drive subsurface habitat suitability, we compared a 3D SDM trained on both biogeochemical and temperature variables (hereafter, BGC + temp 3D SDM) with a temperature-only model (hereafter, temp 3D SDM).

Model performance was assessed using multiple validation methods and evaluation metrics including the validation accuracy, Area Under the Receiver Operating Characteristic Curve (AUC-ROC), and F-1 score (Materials and Methods). For each metric, values closer to 1 indicate stronger predictive skill. We calculated the metrics reported in the main text using a five-fold leave-fish-out cross-validation, in which the fish presences and pseudo-absences were divided into five groups (Materials and Methods). In this cross-validation, we trained the model on four groups, evaluated performance on the excluded group, and repeated the process until each group had been left out once. This process reduced the chance that the error metrics were biased by our choice of training and validation data. Global evaluation metrics, which provide an overall assessment of model performance across all cross-validation iterations, were then calculated as the mean and standard deviation of the performance metrics across the five splits. To further test the robustness of the model on unseen data, we did additional cross-validation assessments where the training and validation data splits were either done randomly, by season, or by geographic region (Materials and Methods).

3.2 Results

3.2.1 Impact of Depth-Integrated Information on 2D Habitat Utilization

The 2D SDMs based on either depth-integrated profiling float observations or surface satellite observations similarly and effectively captured broad-scale albacore habitat utilization and migratory patterns (Figures S3 and S4), aligning with archival tagging observations (Figure S2). Modeled occurrence predictions reflect seasonal shifts in biomass distribution, with albacore occupying the California Current during summer and fall, then migrating to the subtropical North Pacific in winter and spring. Both models also indicate higher probabilities of occurrence along coastal upwelling regions and transition zones, consistent with earlier findings on albacore

movement ecology (Childers, Snyder, and Kohin 2011; Michael and Lynn 1977). Each 2D SDM demonstrated strong predictive skill, as indicated by global evaluation metrics (Materials and Methods), which summarize overall classification performance across all data. The float-based 2D SDM appeared to outperform the satellite-based model in validation accuracy (0.83 ± 0.02 vs. 0.81 ± 0.02), F1 score (0.84 ± 0.02 vs. 0.82 ± 0.02), and AUC-ROC (0.89 ± 0.01 vs. 0.87 ± 0.01); however, these differences were not statistically significant (Table S3).

Despite similar global evaluation metrics, the float-based and satellite-based 2D SDMs produced distinct habitat utilization patterns across seasons and regions (Figures 1, S2 and S3). For instance, in the subtropical North Pacific between 160°W and 125°W (boxed region; Figure 1a), the float-based 2D model estimated higher occurrence probabilities (higher likelihood of a presence; darker green in Figure 1) than the satellite-based model during spring. A regional analysis revealed that the float-based model improved presence prediction accuracy by 25% in this area, whereas the satellite-based model failed to classify presences in almost 40% of cases. Across the broader study domain, the float-based 2D model improved presence classification accuracy by 6% in spring. In summer and winter, the satellite-based 2D SDM improved regional presence classification accuracy in a region centered around 30°N , 130°W (boxed regions in Figures S5b, S5d), with gains of 6% and 15%, respectively. However, these improvements occurred in areas with relatively few presence observations, and the float-based model maintained higher overall presence accuracy globally in all seasons.

The float-based 2D model also produced more accurate pseudo-absence predictions (lower likelihood of a presence; darker brown in Figure 1) across multiple regions and seasons. This model consistently generated lower probabilities of occurrence in the subtropical eastern North Pacific ($140\text{--}110^{\circ}\text{W}$, $\sim 20\text{--}40^{\circ}\text{N}$, polygon region boxed in Figure 1b-d), improving absence

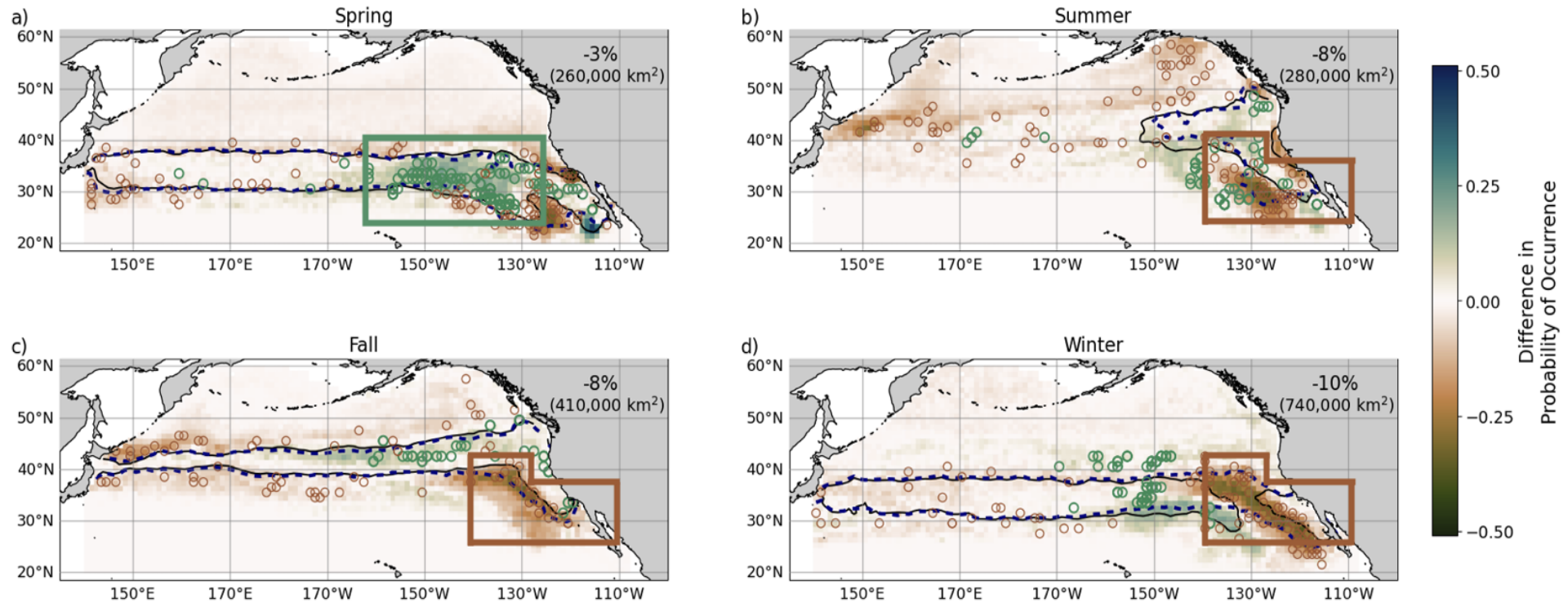


Figure 1 | (a–d) Seasonal maps show differences in probabilities of occurrence predicted by the float-based and satellite-based 2D SDMs (Figures S3 minus S4). The models were applied to all predictor variables from 2004 to 2013 and model predictions were averaged seasonally over the 10-year period. Green (brown) coloring indicates higher (lower) probabilities predicted by the float-based model. Circles mark locations where only the float-based model correctly classified a presence (green) or a pseudo-absence (brown). Areas where the map and circles colors coincide highlight locations where only the float-based model captured key environmental information that influenced fish movements. This effect was particularly pronounced in specific regions and seasons (colored boxes). The circles in each panel represent 8%, 6%, 4%, and 6% of total observations in spring, summer, fall, and winter, respectively. The solid and dashed lines represent contours of 0.5 probability predictions for the float-based and satellite-based 2D SDMs, respectively (Figures S3 and S4). Values in the top right of each panel represent the difference in predicted suitable habitat area in percentages and absolute values, calculated relative to the satellite-based model. The satellite-based model predicts suitable habitat areas of 8.3, 3.4, 5.0, and 7.1 million km² in spring, summer, fall, and winter, respectively.

classifications by 6–14% relative to the satellite-based approach across all seasons. In the summer and fall, when albacore tend to reside near the coastal California Current, the float-based model improved absence predictions in this region by 14% and 10% in those respective seasons.

3.2.2 Correspondence between Surface and Depth-integrated Predictor Variables Over Time

The 2D habitat utilization findings suggest that subsurface information is particularly valuable in environmental contexts where surface data may not fully capture important habitat characteristics at depth. To investigate this finding further, we calculated correlations between the surface and depth-integrated seasonal means of Chl and POC data products over a 10-year period (Materials and Methods, Figures S6 and S7). This approach allowed us to identify areas where patterns of surface and depth-integrated indicators of biological activity diverge, perhaps due to stratification, the presence of a deep chlorophyll maximum, or other water column processes.

We first examined areas where the float-based model achieved higher accuracy in presence predictions. In the subtropical North Pacific (160–125°W, 25–40°N), the float-based model demonstrated a 25% improvement in presence prediction accuracy during spring (boxed region in Figures 1a and 2a). Here, the median spring season correlation coefficient for POC data products was 0.73 (Figure S6a), whereas Chl data products showed a weak, negative correlation of –0.23 (Figures 2b and S6a). While POC maintained weak to moderately strong positive surface-to-subsurface correlations within this region across all seasons, Chl exhibited greater spatial and temporal variability, with correlations ranging from slightly positive to negative (Figure S6).

To further consider how disagreements between the surface and depth-integrated predictor variable information align with fish distributions, we evaluated diving behavior across the study domain in spring at locations where only one of the two models correctly identified a presence (float-based SDM: Figure 1; satellite-based SDM: Figure S5). Our results indicated that dives were

significantly deeper at locations where only the float-based model correctly classified presences, with an interquartile range of 70–138 meters compared to 35–101 meters for the satellite-based model (Figure 2c). Moreover, the float-based model alone correctly identified nearly three times as many presences as the satellite-based model alone (circles, Figure 2a), underscoring its predictive advantage in this environment.

We next examined regions where the float-based model achieved higher accuracy in pseudo-absence predictions. In the subtropical eastern North Pacific, the float-based model outperformed the satellite-based model in classifying pseudo-absences during summer and fall. The median POC correlation in the boxed polygon region in Figures 1b and 1c was 0.55 in summer and 0.44 in fall, whereas Chl correlations were lower, at 0.07 in summer and -0.43 in fall (Figures S6 and S7). These relatively weak correlations suggest that surface and subsurface properties diverge in this region. Further examination revealed that surface and depth-integrated Chl correlations were stronger in nearshore upwelling regions and weaker or slightly negative beyond the upwelling front. Our results indicate that the float-based model most clearly outperformed the satellite-based model just offshore of the upwelling front in summer and fall, where surface and subsurface Chl concentrations are decoupled (Figure S6 and Figure 1b, 1c).

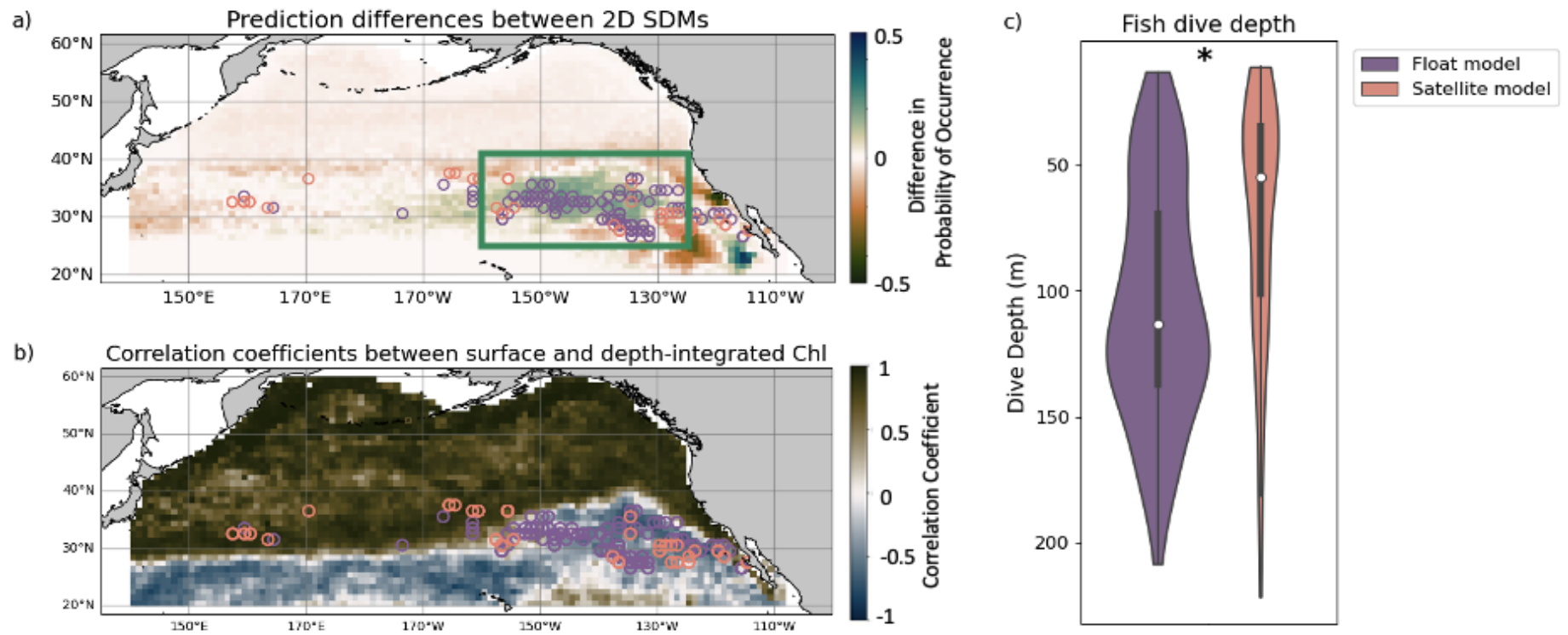


Figure 2 | a) Map of the difference in occurrence probabilities predicted by the float-based and satellite-based 2D SDMs in spring (reproduced from Figure 1a). Purple circles ($n = 172$) represent locations where *only* the float-based model correctly classified a fish presence, aligning with regions where the float-based model predicted higher probabilities of occurrence (green). Pink circles ($n = 60$) represent locations where *only* the satellite-based model correctly classified a fish presence. b) Map showing the correlation coefficients between spring-season means of surface satellite Chl and depth-integrated Chl (from CMEMS data product, (European Union-Copernicus Marine Service 2019) over a 10-year study period (2004–2013) in each 1° grid cell (Materials and Methods). Circles correspond to those in Figure 2a, aligning with regions of weak or strongly negative surface–depth-integrated Chl correlations. c) A violin plot comparing fish diving behavior at locations where only one model correctly identified a presence in spring across the study domain. Kernel density estimates are scaled according to the number of classified samples in each group. The black bars within each violin plot represent mini box plots showing the median (white dot), interquartile range (IQR, thick black line), and full range of data (thin black line). Dives were significantly deeper (asterisk) according to a Mann-Whitney U test ($p < 0.05$) where only the float-based model correctly classified a presence (IQR: 70–138 meters) compared to the satellite-based model (IQR: 35–101 meters).

3.2.3 Impact of Depth-Resolved Information on 3D Habitat Utilization

The 2D habitat utilization analyses underscored the importance of subsurface information in accurately predicting albacore movements, particularly in certain regions and seasons. While depth-integrated biogeochemical data improved species distribution model performance, the occurrence probabilities remain inherently limited to two dimensions. To investigate how environmental conditions drive subsurface habitat suitability, we compared a three-dimensional SDM trained on both biogeochemical and temperature variables (BGC + temp 3D SDM) with a temperature-only model (temp 3D SDM; Table S2). We evaluated model performance by examining the predictions against dive depth records of individual fish, as well as domain-wide spatial patterns of predicted occurrence to isolate the influence of biogeochemical conditions on vertical habitat utilization.

The 3D BGC + temp model accurately captured where the fish resided in the water column, as represented by the mean and 90th percentile dive depth time series (e.g., Figure 3a). The model predicted high occurrence probabilities only in the upper water column during summer and fall (California Current), but also deeper in the water column during winter and spring (subtropical North Pacific), aligning with observations in the fish tagging data. This pattern was observed for all of the long-migratory fish that traverse these distinct biogeographic regimes.

To isolate the role of biogeochemical predictors in controlling vertical habitat utilization, we compared predictions from the 3D BGC + temp model to those from the temp 3D SDM along the same fish track (Figures 3c and 3d). The two models produced distinct habitat utilization patterns with depth across seasons and biogeographic regimes. While the temp 3D SDM predicted higher probabilities of occurrence along the mean dive depth time series in summer when fish occupied the California Current region, it failed to identify suitable habitat along the 90th

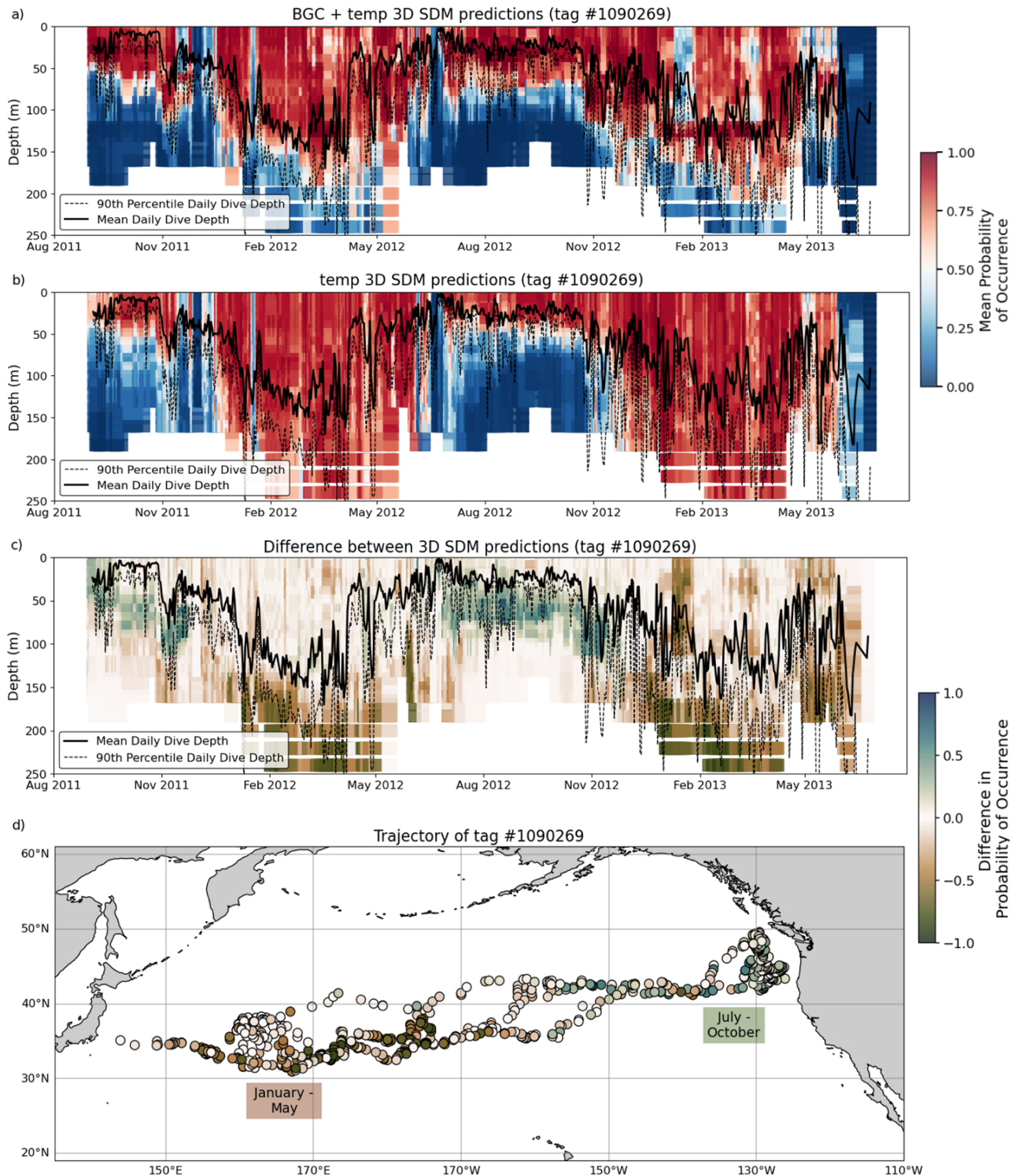


Figure 3| a–c) Daily mean (solid black line) and daily 90th percentile (dashed black line) fish diving depths for a single long-migratory fish (tag #1090269). Modeled probabilities of occurrence throughout the water column along the fish track are shown for (a) the BGC + temp 3D SDM and (b) the temp 3D SDM. c) Difference between the probabilities of occurrence shown in (a) and (b); brown indicates areas where biogeochemical information decreases the likelihood of occurrence (contracting suitable habitat), and green indicates areas where it increases the likelihood of occurrence (expanding suitable habitat). d) Daily locations of the fish (circles), colored by the difference in occurrence probability along the 90th percentile dive depth in panel c.

percentile dive time series (Figure 3a). In contrast, the BGC + temp 3D SDM captured deeper habitat utilization and more accurately predicted higher probabilities of occurrences at depth in summer (Figure 3b), improving presence predictions along the 90th percentile dive trajectory by over 20% compared to the temp 3D SDM in summer (Figure S8). We expanded this analysis to all long-migratory fish tracks and found a 15% improvement in presence accuracy along all 90th percentile dive time series (Figure S8). Conversely, the BGC + temp 3D SDM predicted lower probabilities at depth in winter (Figure 3c), suggesting a seasonal, biogeochemically-driven expansion and contraction of subsurface habitat suitability. This pattern was consistently observed across all long-migratory fish tracks, emphasizing the robust influence of biogeochemical variables on albacore distribution across space and time.

The BGC + temp 3D SDM demonstrated high skill over space and time, with a validation accuracy of 0.86 ± 0.02 , F1-score of 0.86 ± 0.03 , and an AUC-ROC of 0.94 ± 0.01 (Materials and Methods, Table S3). The model captured the same large-scale migration pattern identified by the float-based 2D SDM: many albacore migrate westward to the subtropical North Pacific during winter and return to the California Current in summer (Figure 4). The 3D BGC + temp SDM also accurately captured deeper diving behavior in subtropical waters during winter and spring, compared to shallower dives in the California Current during summer and fall.

The BGC + temp 3D SDM not only reflected observed large-scale migration patterns and seasonal shifts in vertical habitat utilization, but also demonstrated superior predictive skill compared to the temp 3D SDM. Across all global evaluation metrics, the BGC + temp 3D SDM outperformed the temp 3D SDM, achieving higher validation accuracy, F1-score, and AUC-ROC (temp 3D SDM: validation accuracy: 0.82 ± 0.01 , F1-score: 0.82 ± 0.01 , AUC-ROC: 0.89 ± 0.01 ; Table S3). The observed increases in validation accuracy and AUC-ROC were statistically

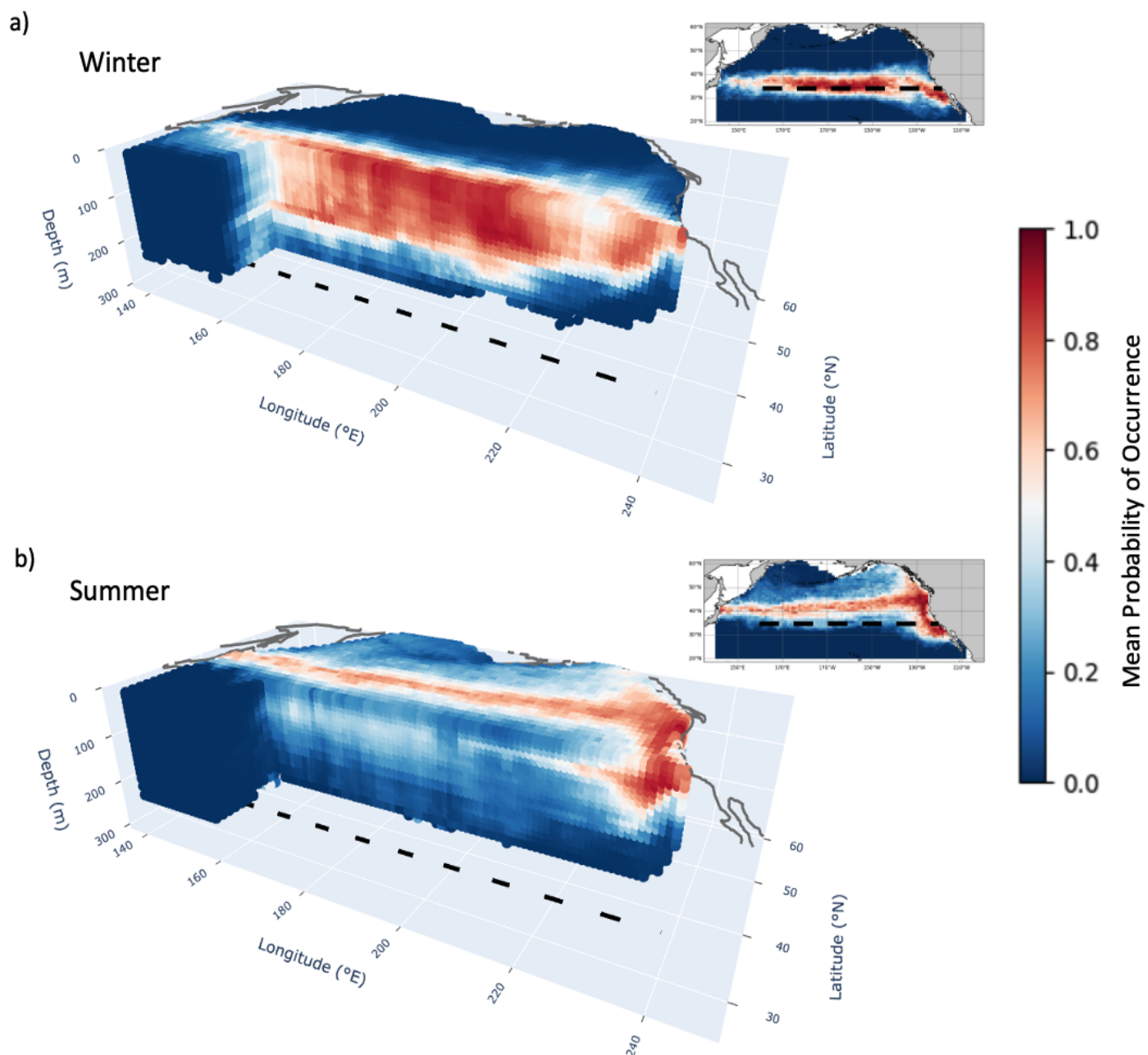


Figure 4 | Two- and three-dimensional representations of modeled probabilities of occurrence predicted by the BGC + temp 3D SDM in (a) winter and (b) summer. 2D maps show occurrence probabilities at the surface; the dashed line at 35°N marks the location of a vertical slice in the 3D representations to expose predictions in the interior ocean.

significant, indicating that the inclusion of biogeochemical information meaningfully enhanced habitat suitability predictions. Comparing performance in each season for presence versus pseudo-absence classifications, the addition of biogeochemical predictors improved presence classifications by 13% in summer and 8% in fall, while improving pseudo-absence predictions by 18% in winter and 12% in spring. Biogeochemical variables proved particularly valuable in specific seasons, demonstrating the dynamic role of environmental factors in shaping albacore distribution.

3.2.4 Disentangling the Influence of Individual Biogeochemical Variables

Our primary analyses examined the combined impact of three biogeochemical variables—Chl, POC, and oxygen—on suitable habitat predictions. To isolate the role of each variable on albacore habitat utilization, we evaluated each variable’s feature importance and assessed their relative contribution to the performance of the BGC + temp 3D SDM (Figure S11). Unsurprisingly, SST emerged as the most influential predictor overall, reflecting the well-known temperature constraints on albacore movement and physiology (Frawley et al., n.d.; Snyder 2016). Biogeochemical variables collectively accounted for over 40% of the feature importance, though their relative impact varied by season and peaked in summer and fall. Based on these results, we conducted a targeted case study in summer and fall, when albacore typically reside in the California Current, to determine how individual biogeochemical variables affect fish behavior and habitat suitability.

In summer, biogeochemical variables comprised 56% of the feature importance, with Chl and POC each contributing ~20%. These predictors ranked as the second and third most important environmental variables, surpassing depth-resolved temperature, which may reflect subsurface productivity in the region and associated foraging opportunities. In fall, biogeochemical variables also contributed substantially to model performance, comprising 45% of the overall feature

importance. However, the importance of Chl and POC declined to less than 10% each in fall, while that of oxygen increased to over 25%, ranking it as the second most important predictor behind SST.

Model predictions with and without oxygen as a predictor variable revealed that the inclusion of oxygen reduced suitable habitat by 10–15% between August and October. Tunas may be sensitive to oxygen < approximately 160 $\mu\text{mol/kg}$ (Brill 1994), so seasonal changes in occurrences are likely related to changes in the vertical oxygen gradient in the California Current. To mechanistically understand this habitat contraction, we explored seasonal oxygen data in the California Current. In the upper 150 meters, oxygen levels reach their annual minimum in fall, likely due to the cumulative seasonal respiration and circulation patterns (Siedlecki et al. 2015; Feely et al. 2018; Alin et al. 2023)

. In some regions of the California Current, the depth of the albacore's oxygen threshold shoals to 70 meters, well within the range of diving behavior.

3.3 Discussion

3.3.1 2D Habitat Utilization

Our results from the horizontal habitat utilization analyses demonstrated the importance of subsurface biogeochemical information in improving albacore habitat suitability predictions. While both the float-based and satellite-based 2D SDMs captured large-scale migratory patterns, the float-based model exhibited higher accuracy in specific regions and seasons, suggesting that surface information may not always represent the environmental constraints influencing albacore distributions. Here, we examined the mechanistic drivers behind the improved predictive performance for both presence and pseudo-absence classifications in the regions identified in the Results.

One of the most notable improvements in the float-based model's presence predictions occurred in the North Pacific subtropical gyre during spring, where classification accuracy was 25% higher than that of the satellite-based model. This region exhibits weak and negative correlations between surface and depth-integrated Chl in spring (Figure 2b); the anti-correlations in Figure 2b suggest regions where lower (higher) surface Chl is associated with higher (lower) Chl at depth. The spatial overlap between presences identified by only the float-based model and anti-correlations between surface and depth-integrated Chl suggests that habitat suitability here may be explained by depth-integrated productivity rather than surface conditions.

The North Pacific subtropical gyre is characterized by a nearly permanent deep chlorophyll maximum (DCM) that displays seasonal and interannual variability (Mignot et al. 2014; Letelier et al. 2004). Its depth is primarily governed by light availability; the DCM shoals in winter as light intensity reaching the surface ocean declines and deepens in summer when light penetration increases (Mignot et al. 2014; Letelier et al. 2004; Cornec et al. 2021). However, DCMs are not often visible to satellites occurring below or at the basis of the mixed-layer (Joint and Groom 2000; Platt and Sathyendranath 1999). In fact, prior studies have shown that subsurface blooms were not captured by satellites in the subtropical North Pacific (Wilson et al. 2013; Villareal et al. 2011), reinforcing the limitations of surface-only data in describing biologically relevant habitats.

The observed decoupling between surface and subsurface Chl is pronounced in spring when albacore are present in the region. This coincides with the onset of a seasonal increase in depth-integrated Chl as greater light availability supports the proliferation of phytoplankton at depth (Mignot et al. 2014). In this region, subsurface Chl has been positively associated with communities of small mesopelagic fishes, which provide prey for higher trophic levels and predatory fish (Nagatomo et al. 2023). At the same time, surface Chl typically declines from winter

to spring due to reduced photoacclimation in the upper layer under increasing light, further contributing to the negative correlation between surface and subsurface Chl (Mignot et al. 2014). As a result, seasonal shifts in the DCM can produce marked differences between surface and subsurface biogeochemical conditions, likely influencing albacore movements and foraging behavior (Arostegui et al. 2023). The float-based SDM's superior presence predictions in the subtropical North Pacific suggest that subsurface conditions serve as important habitat cues for albacore and surface conditions fail to reflect the extent of available foraging resources.

The importance of subsurface productivity in shaping habitat utilization was further corroborated by albacore diving behavior. Albacore dove significantly deeper in locations where only the 2D float-based model correctly identified presences. Median dive depths in this region were nearly twice as deep as those where only the satellite-based model correctly predicted presences, suggesting that albacore were targeting subsurface productivity layers. We extended this analysis to the entire study domain across all seasons and found that dives remained significantly deeper in areas where only the float-based model successfully identified presences (Figure S8). These findings highlight the role that subsurface conditions play in dictating albacore habitat use, particularly in environments where surface data fail to capture critical habitat controls. Incorporating depth-integrated information into the 2D SDM improves the representation of ecological constraints and migratory behaviors of this highly mobile species.

Our results also demonstrated that the float-based model improved pseudo-absence predictions in the far eastern subtropical North Pacific during summer and fall (polygon region boxed in Figure 1b-c). The most notable improvements were observed offshore of the upwelling front, where surface and subsurface Chl concentrations decoupled (Figure S6b-c). This pattern suggests that surface Chl alone is insufficient to characterize habitat suitability in these dynamic

transitional zones. To mechanistically explain the float-based model improvements in this region, we examine the physical and biological characteristics of upwelling ecosystems.

In coastal regions, wind-driven upwelling transports nutrient-rich deep water into the euphotic zone, often leading to elevated surface Chl concentrations. However, offshore of the upwelling front, surface and depth-integrated properties can diverge because the front delineates distinct water masses. These frontal zones create sharp biogeochemical gradients that influence nutrient availability, prey distribution, and habitat conditions, making them ecologically important features in marine ecosystems (Barth et al. 2007; Jamil, Kavanaugh, and Spitz 2023; Sato et al. 2018; Taylor et al. 2012). Although surface Chl concentrations are typically low beyond the frontal system, these transitional zones often support enhanced biological activity through strong physical dynamics that aggregate prey (Franks 1992), attracting albacore to these optimal foraging grounds (Nieto et al. 2017). This aligns with studies on the trophic ecology of albacore, which have a varied diet but tend to target epipelagic fishes and cephalopods, species that are often found in these frontal upwelling features (Romanov et al. 2020). Since the position of these fronts shift seasonally and inter-annually with oceanographic dynamics, wind patterns, and upwelling intensity, the strength of surface–subsurface relationships in these regions can vary substantially. The float-based model’s improved pseudo-absence predictions beyond the frontal zone indicate that albacore distributions likely track shifts in the location of productive feeding grounds, and surface Chl alone is an unreliable indicator of habitat suitability in these dynamic environments.

Depth-integrated information provides a more accurate representation of the variable ecological drivers shaping albacore distributions, particularly in frontal zones and open ocean regions containing DCMs where productivity signals are depth-dependent. By incorporating depth-integrated biogeochemical data, the float-based model more accurately captured spatial and

temporal shifts in suitable habitat, leading to improved predictions in both subtropical gyre and coastal environments. These findings reinforce the importance of subsurface characteristics in structuring albacore habitat and emphasize the value of depth-integrated biogeochemical data in SDMs.

3.3.2 3D Habitat Utilization

Our novel approach included multiple biogeochemical predictors that captured not only environmental deterrents, such as oxygen limitation, but also environmental attractants, such as Chl and POC abundance. These conditions play a critical role in shaping albacore vertical distributions, influencing both seasonal shifts and large-scale migration patterns. While temperature has long been recognized as a key determinant of habitat suitability, our findings demonstrate that biogeochemical variables can expand or contract habitat availability beyond what is thermally suitable. By examining individual fish tracks, we gained valuable insights into the mechanisms driving albacore movements in the subsurface ocean (e.g., Figure 3a and 3b). Notably, the inclusion of biogeochemical variables resulted in distinct patterns of habitat use that are linked to different biogeographic regimes (Figure 3c and 3d). Biogeochemical predictors contracted habitat availability at depth in the subtropical North Pacific during winter and spring relative to thermally suitable habitat. This finding implies that albacore avoided deeper dives due to suboptimal biogeochemical conditions, despite habitable temperatures within the species' tolerance range. Conversely, in the California Current during summer and fall, these biogeochemical predictors expanded habitat availability at depth relative to thermally suitable habitat, likely reflecting improved foraging opportunities even though the temperature landscape appeared less favorable. The 90th percentile dive depth time series (Figure 3c) confirms utilization of this deeper habitat, which was identified as suitable only when biogeochemical predictors were included (Figure 8). Therefore, the productivity-linked variables appeared to influence albacore

diving depth and reinforced the importance of subsurface productivity in defining suitable habitat. These results highlight how biogeochemical variables mediate access to deeper habitats in ways that temperature alone cannot explain.

Beyond individual tracks, broader comparisons between the BGC + temp and temp 3D SDMs revealed statistically significant improvements in habitat suitability predictions, with the inclusion of biogeochemical variables contributing to higher accuracy across seasons and regions (Figure 4). Improvements were particularly pronounced in winter and summer, when biogeochemical factors constrained or expanded available habitat, respectively. Biogeochemical predictors contracted suitable habitat by more than 60% in winter and expanded it by 25% in summer (Figure S10e and S10f). These substantial changes underscore the importance of biogeochemical predictors in capturing environmental constraints that underlie albacore distribution and migratory behavior in different biogeographic regimes.

While our 3D analyses primarily focused on the collective influence of biogeochemical predictors, it is important to note that our approach can also differentiate the effects of individual variables. For instance, a case study in the California Current showed that low oxygen levels acted as a deterrent in the fall and reduced suitable habitat by 10-15%. This capability allows us to disentangle the relative contributions of individual biogeochemical variables, reveal the mechanisms that shape species movements, and provide insights into the complex interplay of multiple biogeochemical conditions.

The addition of a vertical dimension in SDMs captures habitat constraints often missed by surface-only approaches. Subsurface productivity gradients, oceanographic fronts, and oxygen minima play pivotal roles in habitat suitability, particularly for species that move across a wide range of biogeographic regimes in both horizontal and vertical space (e.g., Braun et al. 2022;

Carlisle et al. 2017; Vedor et al. 2021). 4D observational data products from sources like BGC-Argo are invaluable because they are grounded in in situ measurements that reflect actual conditions experienced by marine species. Moreover, these observational data products enable researchers to capture transient events, such as episodic upwelling, phytoplankton blooms, or hypoxic intrusions, each of which can affect marine species. Incorporating subsurface, BGC-Argo based information ultimately facilitates a more nuanced understanding of species–environment relationships and advances observational, data-driven approaches to species distribution modeling.

Subsurface habitat utilization patterns often vary across life stages, and understanding these vertical differences is critical for effective management. Different life stages of albacore occupy distinct depth ranges, with adult albacore deeper in the water column than juveniles. In addition, both adults and juveniles likely adjust their depth depending on ocean conditions, which has implications for their overlap with fishing gears deployed at different depths (Frawley et al., n.d.). Accurately resolving 3D habitat for species such as albacore thus has direct implications for fisheries stock assessment and management, where gear selectivity impacts indices of catch per unit effort that inform abundance trends (Punt et al. 2014). A more complete understanding of 3D habitat use among protected species can also assist with bycatch reduction efforts (Swimmer et al. 2017).

Significant efforts are also underway to advance ecosystem-based management in the United States and elsewhere (Link and Marshak 2019; Bastardie et al. 2021), including initiatives such as the NOAA Changing Ecosystems and Fisheries Initiative (CEFI). Our findings demonstrate the value of observation-based, mechanistic SDMs in capturing complex environmental relationships that influence marine species distributions, and may inform ecosystem approaches to management. These SDMs may also improve dynamical ecosystem models, which

are necessary to scale empirical relationships across broader temporal and spatial domains. Integrating mechanistic insights from SDMs into long-term planning frameworks could enhance our ability to predict habitat shifts under climate change and inform adaptive management strategies. As ocean conditions continue to change, 3D SDMs will become increasingly important for assessing the impact of expanding low-oxygen zones, shifts in productivity, increasing frequency of marine heatwaves (MHWs), and coastal eutrophication that may alter habitats of commercially and biologically valuable species. Recent studies have shown how coastal eutrophication is exacerbating the fall shoaling of hypoxic conditions in the Southern California Bight (Frieder et al. 2024), which could impact species like albacore in terms of habitat loss and prey availability. Incorporating such dynamics into SDMs could provide valuable predictions for fisheries management and aid in identifying areas where species might migrate under changing conditions (Smith et al. 2023).

While our current analysis focuses primarily on modeling species distributions, future work could integrate metabolic indices, such as the ratio of oxygen supply to demand, to link ecophysiological traits to species distributions and further validate the mechanistic processes underlying observed patterns. These indices could provide valuable insights into how albacore tuna and other high-metabolism predators are affected by oxygen availability in relation to their depth-specific habitat preferences (Deutsch et al. 2015; Deutsch, Penn, and Seibel 2020; Howard, Penn, et al. 2020). Such data would enhance our understanding of habitat suitability by incorporating metabolic constraints, especially as climate change alters oxygen availability and thermal landscapes regionally and temporally.

In parallel, it is important to contextualize climate stressors within the baseline of seasonal variability. While climate change is poised to introduce both acute and chronic stresses, these

should be considered within the broader seasonal range of conditions that marine species already experience. Seasonal temperature changes, for instance, naturally drive recurring habitat compression across a large geographic and thermal range (e.g., Clemens 1961; Zainuddin et al. 2006). Understanding how transient anomalies, such as MHWs, compare to these established seasonal cycles can clarify whether they impose temperature extremes beyond species' resilience or, alternatively, create new habitat opportunities. The impact of a MHW could expand or contract suitable habitat depending on its timing, location, and origin in the surface or subsurface ocean. Given that typical SST anomalies associated with MHW range from under 1°C to 4°C globally (Jacox et al. 2020), MHW-induced warming will remain smaller than the amplitude of natural seasonal temperature ranges encountered by albacore. While beyond the scope of this study, future work could explore how SDMs perform under anomalous climate conditions, such as the 2014 Pacific Blob (Bond et al. 2015; Welch et al. 2023), by comparing 2D and 3D models against fishery catch data. Quantifying these relationships across depth and biogeographic regions could refine our understanding of how short-term extreme events interact with long-term environmental change to influence species distributions.

3.4 Conclusions

This study demonstrates the role of subsurface biogeochemical information in refining habitat predictions for a highly migratory species in both 2D and 3D frameworks. We showed that float-based depth-integrated data improved 2D habitat utilization predictions, especially in specific regions and seasons where surface and subsurface conditions diverged. Subsurface information improved our understanding of species migrations within their desired habitat zones by providing a refined view of regions with high primary productivity and biomass. We extended our approach by developing a 3D SDM that revealed how depth-resolved temperature, Chl, POC, and oxygen

drive albacore migratory behavior and vertical habitat use. Further analyses showed that biogeochemical variables exert distinct controls on habitat suitability depending on the season and biogeographic regime. Biogeochemical predictors substantially influenced habitat availability beyond thermal suitability, contracting it by more than 60% in winter and expanding it by 25% in summer. Collectively, these results emphasize that incorporating subsurface biogeochemical information can significantly improve the accuracy of SDMs of a highly migratory pelagic species.

While this study focused on juvenile albacore tuna, the depth-resolved, biogeochemically informed modeling framework described here can be broadly applied to other marine species (and across various life stages) that have robust presence data across diverse biogeographic regimes. Future research could incorporate additional variables (e.g., $p\text{CO}_2$, pH), or explore alternative modeling approaches as high-resolution, open-access data products become increasingly available. The expanding global BGC-Argo float array facilitates scaling this framework to broader regions, providing opportunities to investigate multi-species interactions, extreme events, climate-driven range shifts, and ecosystem-level processes. Integrating these SDMs into broader ecosystem models could also advance predictions of habitat competition among species and comprehensive ecosystem-based management strategies. As marine ecosystems continue to change, depth-resolved SDMs grounded in real-world conditions will remain a powerful tool to understand the complex interplay among physical and biogeochemical processes, ultimately guiding more sustainable ocean resource stewardship.

3.5 Methods

3.5.1 Study Site

The study domain spans the North Pacific Ocean, from 20°N to 60°N and 140°E to 108°W, encompassing the locations of tagged albacore tuna and the diverse biogeographic regimes they encounter during migration.

3.5.2 Fisheries Data

The albacore Archival Tagging Program is described in detail in Childers et al. (2011), Snyder et al. (2017) and Muhling et al. (2022), with a brief summary provided here. The program is supported by the NOAA Southwest Fisheries Science Center and the American Fishermen's Research Foundation (now the Albacore Research Foundation). Between 2003 and 2011, three types of archival tags (Lotek LTD2310, Lotek LAT2810, and Wildlife Computers MK9) were implanted in 1,086 albacore tuna. Nineteen recovered tags with sufficiently long deployment histories were analyzed as a part of this study, and data were limited to 2004–2013 to align with environmental data availability (Table S1). Tagging data provided high-resolution records of diving depth, ambient temperature, and body temperature, collected at 1-minute intervals. Daily locations (Figure S2) were estimated using light from the tag sensors, and refined using SST and water depth (Muhling et al. 2022).

3.5.2 Environmental Variables

Environmental predictors used to fit the species distribution models include temperature, oxygen, and proxies for optimal foraging conditions including chlorophyll-*a* (Chl) and particulate organic carbon (POC). Chl and POC serve as indirect indicators of trophic dynamics, with elevated concentrations often signifying regions of high primary productivity or prey abundance. A limited set of variables was selected to isolate the predictive power of biogeochemical variables and to minimize multicollinearity.

While surface values of several of these variables have previously been identified as important predictors of marine predator migratory movements (Brodie et al. 2018; Muhling et al. 2019), this study extends their application to depth and includes additional biogeochemical predictors. The depth-resolved data products leveraged in this work are derived from Argo float profiles, which are spatiotemporally mapped to produce gridded parameter fields. Oxygen data were sourced from the machine learning-based Gridded Ocean Biogeochemistry from Artificial Intelligence-O₂ (GOBAI-O₂, Sharp et al. 2022) data product. We used Chl and POC data products from the Copernicus Marine Environmental Monitoring Service (European Union-Copernicus Marine Service 2019). These data products were generated using the Satellite Ocean-Color and Argo (SOCA) method, which integrates satellite ocean-color data with Argo profiles to infer vertical distributions of a given variable (Sauzède et al. 2016). Temperature data, both at the surface (SST) and at depth, were obtained from the Roemmich and Gilson (2009) data product, which is derived primarily from Argo float observations. Both the satellite- and float-based 2D SDMs used SST data from this data product to ensure consistency and allow model differences to be attributed to the biogeochemical data rather differences between satellite- and float-based SST. All data products are depth-resolved, time-resolved at monthly intervals, and spatially gridded at 1° resolution. The 2D and 3D SDMs were trained on different combinations of these predictor variables (Table S2).

To assess the value of subsurface biogeochemical variables in SDMs, we compared their performance against SDMs trained on satellite data. Surface satellite values of Chl and POC were obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) onboard NASA's Aqua satellite. Data was downloaded from the NASA Ocean Biology Processing Group and

averaged at monthly intervals and 1° spatial resolution (NASA Ocean Biology Processing Group 2017; 2022).

3.5.3 Chlorophyll Fluorescence Slope Correction

Recent research has brought attention to biases in chlorophyll-*a* estimates derived from fluorescence measurements (Roesler et al. 2017), like those made on profiling floats (Long et al. 2024). A bias correction, defined as the ratio between the fluorescence measurement and the true chlorophyll-*a* concentration, is typically applied to reduce error in Chl estimates. Currently, a uniform correction factor of 2 is applied to all profiling float fluorescence measurements (Schmechtig et al. 2014), which is then used to inform the CMEMS Chl data product (European Union-Copernicus Marine Service 2019). However, the value of the correction factor has been shown to vary regionally and seasonally, ranging from less than 1 to greater than 10 (Long et al. 2024).

To account for these biases, we corrected surface, float-derived chlorophyll-*a* concentrations to match the satellite-based estimates in time and space at monthly and 1° resolution, ensuring consistency between the two datasets. The time- and space-resolved correction was then applied throughout the water column as a set ratio to the float-derived estimates. Standardizing surface chlorophyll-*a* concentrations across data sources allowed us to isolate the influence of subsurface biogeochemical information in SDMs. This approach ensures that differences between satellite-based and depth-integrated, float-based SDMs are driven by subsurface information, rather than artifacts introduced in the conversion of fluorescence to Chl.

3.5.4 Species Distribution Model Development

Species distribution models (SDMs) for juvenile albacore tuna were developed using a machine learning algorithm called XGBoost, a decision tree-based ensemble learning method (Chen and Guestrin 2016). XGBoost is well-suited for species distribution modeling because it

can capture complex, non-linear relationships among environmental variables with low computational time and high accuracy. We used XGBoost to construct SDMs that predict the probability of occurrence in both 2D and 3D space (Table S2). The 2D SDMs estimate occurrence probabilities relative to time, latitude, and longitude. To assess the value of subsurface information in predicting albacore habitat, we compared two 2D SDMs: one using surface biogeochemical data from satellites (satellite-based 2D SDM) and the other using depth-integrated biogeochemical data from in situ floats (float-based 2D SDM).

We then developed two 3D SDMs to predict suitable habitat from 0–200 meters, providing insights into albacore environmental associations throughout the water column. One model was trained on depth-resolved temperature, Chl, POC, and oxygen, and SST, and is referred to as the BGC + temp 3D SDM. To isolate the effect of biogeochemical conditions on albacore movements in the interior ocean, we compared this model to a temperature-only model trained solely on SST and depth-resolved temperature (hereafter, temp 3D SDM; Table S2).

All SDMs were trained on a balanced dataset of presences and pseudo-absences. Tagged fish locations were averaged daily to the nearest spatial 1° degree. Pseudo-absence locations were generated by randomly sampling the background domain to match the timestamps of the presences dataset (consistent with the approach of Hazen et al. 2021, (Hazen et al. 2021)). To improve ecological realism, pseudo-absences were constrained to locations within the SST range of the archival tag data. The 3D SDMs used the same presences and pseudo-absences locations as the 2D models, and incorporated dive depth information. Mean daily dive depths were calculated for the tagged fish, and pseudo-absence depths were randomly sampled from the distribution of observed dive depths, truncated at the 95th percentile.

To generate spatial predictions of habitat suitability, each SDM was trained on the full presences and pseudo-absences dataset and then applied to environmental predictor variables spanning 2004–2013. Resulting model predictions were averaged by season across the 10-year study period to produce seasonally averaged habitat probability maps in both 2D and 3D (ie Figure 4, Figures S3 and S4). In addition to these domain-wide analyses, we examined the model predictions against dive depth records of individual fish to understand the role of biogeochemical conditions on vertical habitat utilization.

3.5.5 Species Distribution Model Performance and Assessment

The SDMs were optimized using a 5-fold leave-fish-out (LFO) cross-validation for model and hyperparameter tuning. Each LFO split contained ~20% of the fisheries data and a distribution of migratory pattern types reflective of the entire dataset. Individual fish were considered independent samples, and each tag was generally assigned to a single split to preserve sample independence (Table S1). However, to achieve five evenly distributed splits that each contain ~20% of the data and reflect the same distribution of migratory sub-groups, two fish tracks had to be divided among multiple splits. We selected tags 394 and 396 and split their records with respect to time to balance the seasonal distribution of data across the cross-validation splits. The five-fold LFO cross-validation approach ensured that model performance was not only evaluated on a single split but rather assessed for its consistency and robustness across multiple data splits. This cross-validation approach gave us confidence that the SDMs were providing robust fits to the training data without overfitting.

Model performance reported in the main text was evaluated across the full study domain using this five-fold LFO cross-validation, with values for validation accuracy, F1-score, and Area Under the Receiver Operating Characteristic Curve (AUC-ROC) representing the mean $\pm$ standard deviation across all splits. This LFO approach was also used to evaluate the ability of the 3D SDMs

to capture albacore diving behavior. For each fish, observed dive depths were compared to the model's predicted probabilities of occurrence along its track. Each model was trained with the LFO data split that excluded that fish's tag from model training (Table S1).

The validation accuracy measures the proportion of correctly classified instances in the validation set (accuracy = correct predictions / total predictions). The F-1 score combines the precision and recall scores of a model, assessing the model's ability to correctly classify occurrences while minimizing false positives and false negatives. The AUC-ROC quantifies the model's ability to discriminate between presences and pseudo-absences across all numerical classification thresholds. Validation accuracy and F-1 score range from 0 to 1, with higher values indicating better performance. AUC-ROC ranges from 0.5 to 1 with a value of 0.5 indicating the same performance as random guessing and a value of 1 indicating perfect performance.

Additional cross-validation splits were then used to assess model robustness in terms of predicting on unseen input data and to check for any biases by region or season (Stock 2022). These included splitting the training and validation data randomly (with respect to the daily archival tag measurements), by season, and by geographic region. The seasonal cross-validation included four splits with nearly even percentages of the full dataset (Winter: 28%, Spring: 30%, Summer: 21%, Fall: 21%), and the geographic cross-validation divided the North Pacific into nine regional splits (~20° longitude x 25° latitude boxes). For each cross-validation split, model performance was evaluated using validation accuracy, AUC-ROC, and F-1 score (Table S4 and S5).

In addition to global evaluation metrics, we assessed the role of each predictor variable on habitat utilization in the BGC + temp 3D SDM using feature importance (Figure S10). Feature importance from XGBoost quantifies the relative contribution of each predictor variable to the

model's predictions, based on how frequently and effectively a feature is used to split data across decision trees.

3.5.6 Correlation Coefficients between Surface and Depth-Integrated Data Products

To evaluate the influence of predictor variables on the 2D SDM performance, we seasonally averaged Chl and POC data from each year and calculated the correlation coefficient between the surface (satellite-based) and depth-integrated (float-based) values over the 10-year study period (2004–2013) for each 1° grid cell (Figures S6 and S7). This analysis identified regions where subsurface conditions deviate from surface patterns. Strong positive correlations suggest that surface conditions provide a strong proxy for depth-integrated biological activity, which may occur in well-mixed regions. Conversely, weak correlations indicate that surface data may fail to accurately represent water column productivity, highlighting areas where subsurface measurements could improve habitat prediction from SDMs.

3.6 Acknowledgements

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Chapter 4: Improving the Detection of Marine Carbon Dioxide Removal with Empirically-Derived Counterfactuals

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4.0 Abstract

Ocean alkalinity enhancement (OAE) is a marine carbon dioxide removal (mCDR) method with the potential to expand the oceanic carbon sink and temporarily and locally mitigate ocean acidification. Central to mCDR is the challenge of detectability, or the ability to distinguish induced changes from natural variability and other sources of uncertainty. In this study, we present a detectability framework to evaluate the effectiveness of different observing strategies in detecting mCDR signals in a dynamic coastal environment. We leverage high-resolution biogeochemical model simulations of an OAE intervention in the Salish Sea to provide a controlled counterfactual environment, and compare monitoring approaches that vary in measurement quality, frequency, duration, and analysis. Detection potential depended on the strategy and interaction of signal magnitude, background variability, and observing platform design. A minimal observation strategy, consisting of a single measurement before and after the intervention, yielded no detectable area as the OAE signals never exceeded the noise from unconstrained variability. A long-term averaging strategy with measurements every three hours over one year reliably detected OAE signals, but its high resource demands may limit scalability. Predictive algorithms that estimate carbonate chemistry from routinely measured physical and biogeochemical properties offered a scalable alternative that substantially expanded the spatial footprint of detection. OAE-

induced changes in dissolved inorganic carbon, a critical metric for quantifying net carbon removal, remained undetectable under all strategies. The detectability framework presented here provides a practical tool for designing scientifically rigorous, site-specific monitoring systems that will be essential for effective carbon removal pathways.

4.1 Introduction

Achieving net zero emissions and limiting global warming to the targets set by the Paris Agreement requires active removal of carbon dioxide (CO₂) from the atmosphere (IPCC 2022; UNFCCC 2015). This urgent need has accelerated the exploration and development of carbon dioxide removal technologies across terrestrial, atmospheric, and oceanic domains. Among these, marine carbon dioxide removal (mCDR) is particularly promising because the ocean serves as a vast geochemical carbon reservoir and has already absorbed approximately 30% of anthropogenic CO₂ emissions (Friedlingstein et al. 2020). However, the oceanic uptake of carbon has come at a cost, driving ocean acidification with a global surface ocean pH decline surpassing ~0.12 by 2010 (Jiang et al. 2023).

Ocean alkalinity enhancement (OAE), a proposed mCDR method, has the potential to expand the oceanic carbon sink while temporarily and locally counteracting the harmful effects of ocean acidification (National Academies of Sciences 2021; Mongin et al. 2021). OAE introduces particulate or dissolved alkalinity to seawater, which stimulates the storage of CO₂ into other stable forms of dissolved inorganic carbon (DIC). Specifically, the increase in total alkalinity (TA) results in an immediate rise in pH and induces a chemical shift from aqueous CO₂ to bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions (Schulz, Bach, and Dickson 2023). The consequent change in the air-sea CO₂ gradient can promote atmospheric CO₂ drawdown or reduce oceanic CO₂ outgassing over the course of months to years (Jones et al. 2014; Oschlies et al. 2023).

Several critical research areas must be addressed to ensure safe, transparent, and effective deployment of OAE technologies. Carbon credits depend on accurate quantification of net carbon removal, including associated uncertainties in the magnitude and duration of carbon sequestration. These measurements are fundamental for informing additionality and durability, two central components of monitoring, reporting, and verification (MRV) for mCDR (Ho et al. 2023). Beyond carbon accounting, monitoring local changes in carbonate chemistry is necessary to quantify acidification mitigation, ensure permit compliance, and maintain perturbations within acceptable thresholds. OAE site selection must consider regional carbon removal efficiency and ecological risks to ensure interventions are effective, quantifiable, and environmentally responsible.

Central to all of these research areas is the challenge of detectability—the ability to distinguish OAE-induced changes from natural variability and other sources of uncertainty. Critically, OAE signals are not directly measurable; they are defined by the difference between observed conditions and those that would have existed without intervention. Observational platforms near the intervention site may be capable of capturing the addition of alkalinity and measuring near-field perturbations to carbonate chemistry, such as $p\text{CO}_2$ and pH. However, the dynamic nature of oceanic systems and the timescales of air-sea CO_2 equilibration cause OAE signals to dilute rapidly, often falling below the detection limits of sensing technologies and becoming indistinguishable from background variations (Cyronak, Albright, and Bach 2023; Ho et al. 2023). Moreover, most gas exchange is expected to occur after substantial dilution far from the intervention site (Khangaonkar et al. 2024; Wang et al. 2023), further complicating efforts to detect and attribute changes to OAE.

Given these challenges, numerical simulations will serve as essential tools to isolate OAE signals from background variability and other uncertainties. Simulations also provide a controlled,

counterfactual environment where the simulated OAE signal is exactly known. They therefore offer an idealized environment in which to test detection strategies, which are fundamental to addressing the critical research areas outlined above and ensuring the safe, transparent, and effective deployment of OAE (Fennel et al. 2023).

In this study, we present a framework to assess the detectability of OAE interventions using a high-resolution biogeochemical model of the Salish Sea estuary as a case study. We simulate a full-scale OAE deployment in Sequim Bay, a coastal embayment within the Salish Sea, at two locations: a tidally-energetic nearshore site where field trials are being planned (Savoie et al., in review) and a mid-bay site (Figure 1, inset). The experimental simulations are compared to a baseline or counterfactual scenario where the only difference between scenarios is the addition of alkalinity. The alkalinity addition changes seawater carbonate chemistry and air-sea CO₂ exchange but does not otherwise affect the physics or other biogeochemical processes represented in the model. This simulation therefore allows for direct attribution of modeled changes to the OAE intervention.

This study aims to evaluate the detectability of OAE signals in Sequim Bay using a range of measurement strategies tested under realistic conditions of natural variability. Specifically, we explore how monitoring strategies, signal characteristics, site selection, and environmental variability influence the ability to detect OAE-induced changes. Our approach builds on the detectability framework proposed by Carter et al. (2019), which evaluates climate signal detection against background variability and measurement uncertainties. We adapt this framework for OAE, testing a range of measurement strategies defined by measurement quality, frequency, duration, and analysis. This approach provides a robust method to quantify detection limits and optimize detectability for OAE that can be applied to other interventions and oceanographic contexts. A

model environment is not required to employ the approach if the user has other means of estimating some of the variability, signal, and uncertainty terms in the framework (e.g., from an ongoing time series).

4.2 Methods

4.2.1 Domain Characterization

The Salish Sea is a marginal sea of the North Pacific that spans the coastal waterways of southern British Columbia, Canada and northwestern Washington, US (Figure 1). Forming a transition zone between the open ocean and coast, the Salish Sea is one of the largest estuaries in the US where complex climate, oceanic, riverine, and land-based processes converge (Stewart 2017). Amplified acidification in the region is threatening economically and culturally important marine organisms (Sunday et al. 2022), driven by a reduction in buffering capacity that amplifies biogeochemical change in high-carbon regimes (Arroyo et al. 2022; Santana and Shull 2023; Feely et al. 2018; Stoll et al. *accepted*). Given the biological importance and chemical mean state of the Salish Sea, the region is a promising candidate for both effective OAE and meaningful mitigation of ocean acidification.

4.2.2 Model Description and Simulation Design

To simulate the complex coastal environment of the Salish Sea, this study utilized the *Salish Sea Model* (Khangaonkar et al. 2018; 2021), developed using a finite volume coastal ocean (hydrodynamic) model (FVCOM, (Chen, Liu, and Beardsley 2003) externally coupled with a biogeochemical model, FVCOM-ICM (Kim and Khangaonkar 2012). The model was refined at the intervention sites to resolve mixing-zone processes (25–100 meters) and local-scale dynamics across Sequim Bay (~13 km²), capturing a full range of spatial scales relevant to OAE detection. A comprehensive description of the model setup, configuration, and simulated OAE intervention is provided in the companion paper, Khangaonkar et al. 2024.

In brief, the model simulates TA and DIC throughout the water column and accounts for key biogeochemical processes that modulate their concentrations. TA is influenced by primary production, remineralization, denitrification, and sediment fluxes, while DIC is affected by the same processes in addition to nitrification and air-sea gas exchange. The model calculates the partial pressure of carbon dioxide ($p\text{CO}_2$) and pH using CO2SYS (Lewis, Wallace, and Allison 1998) formulations embedded in FVCOM-ICM, based on TA and DIC concentrations.

All simulations were conducted at hourly temporal resolution under Year 2014 baseline conditions established through prior validation (Khangaonkar et al. 2021). The baseline scenario simulation was continued for an additional year with conditions identical to 2014. The concentration of alkalinity for the OAE intervention was informed by the Ebb Carbon bipolar electro dialysis system (Ringham et al. 2024; M. D. Eisaman et al. 2012; 2018; de Lannoy et al. 2018; M. Eisaman et al. 2023; M. D. Eisaman 2024) and adheres to water quality discharge standards for this site, requiring pH below 9 (Savoie et al. *in review*). The simulated OAE deployments represent a hypothetical full-scale operation, with a TA concentration of 2997 mmol/m³ and a discharge rate of 40 million gallons per day, on the order of an industrial wastewater discharge. Two experimental simulations were conducted at two intervention sites: a mid-bay site and a field-trial site near the entrance of Sequim Bay that corresponds to a wastewater outfall for the Pacific Northwest National Laboratory Sequim facility (Figure 1, inset). The field trial site has strong and variable tidally-driven currents while the mid-bay site was chosen as a comparatively quiescent counterpoint. The simulated interventions were handled as additional input of alkalinity, represented as a TA flux in mmol/sec without any corresponding fluxes of

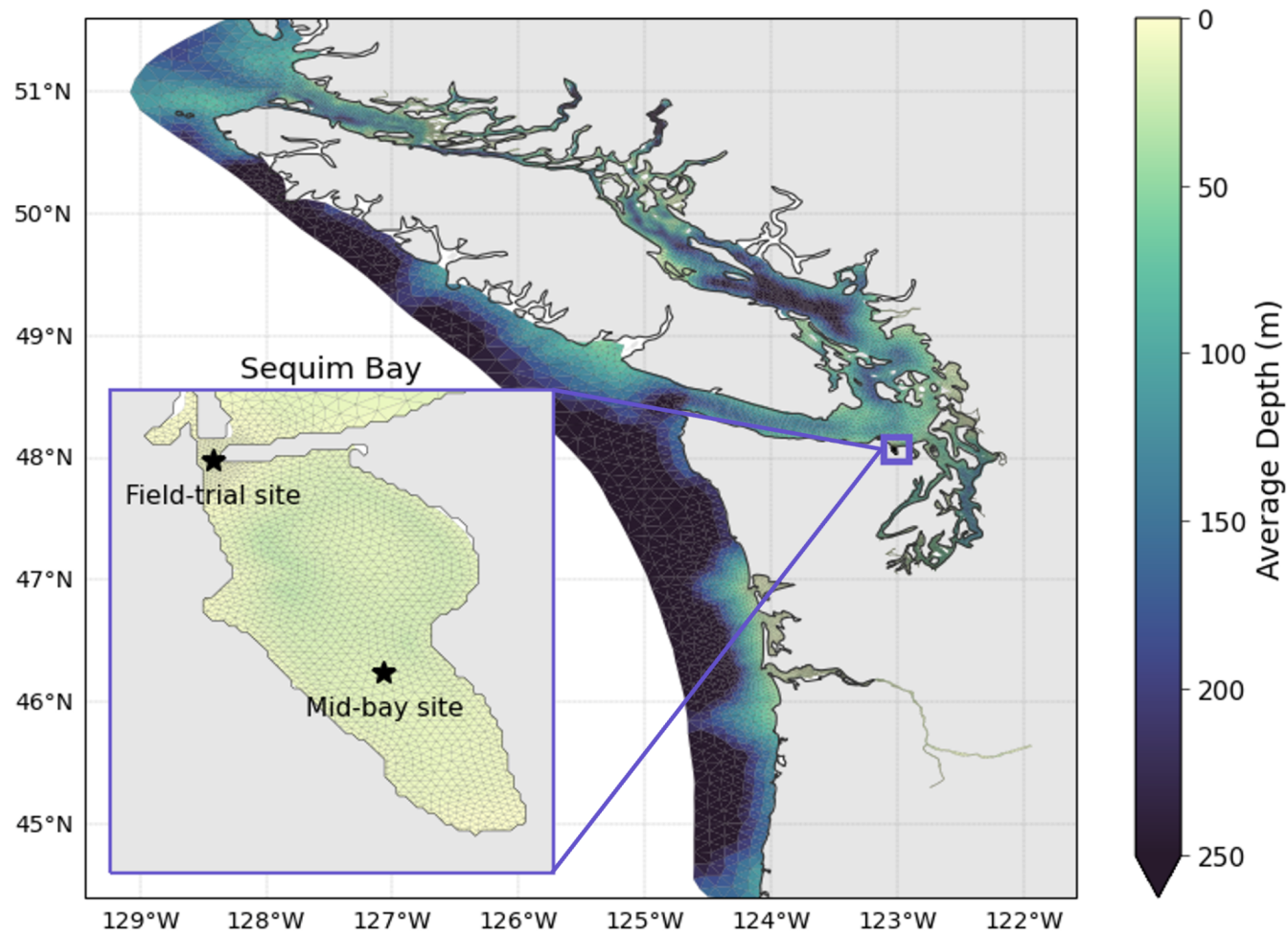


Figure 1| Regional domain of the *Salish Sea Model* and locations of OAE deployment in Sequim Bay (inset). Colors indicate average water column depth (meters) and triangles represent the unstructured FVCOM mesh grid for the regional simulations. Black stars denote the field-trial site at the tidally-energetic northern entrance of Sequim Bay and the mid-bay site, located in the quiescent bay interior.

freshwater, salinity, or nutrients. These scenarios were compared to a baseline scenario without any such TA additions. Circulation is computed before simulating biogeochemical cycling, and there are no modeled feedbacks that allow the TA additions to change the physical state or circulation between the control and experiment simulations.

4.2.3 OAE Detection Framework

The detectability framework used in this study was adapted from Carter et al. (2019), who developed a method to determine whether ocean acidification signals could be detected amid natural variability. This approach involved the evaluation of multiple observing strategies by varying measurement accuracy, frequency, and duration to determine their effectiveness in detecting signals. The framework is grounded in the principle that a signal of interest (S) must be at least twice the magnitude of the noise (N) to permit confident detection (Equation 1, Keller, Joos, and Raible 2014).

$$S \geq 2N \quad (1)$$

For our study, the signal, S , is exactly known and is defined as the difference in a parameter (e.g. TA, DIC, $p\text{CO}_2$) between experimental (OAE) and baseline scenarios (Figure 2). In typical practice, however, the S must be defined using an imperfect counterfactual. The noise, N , then encompasses any process or property that obscures the S by creating changes in the apparent S that are unrelated to the intervention. Depending on the counterfactual used, these can include natural variability (Frölicher et al. 2009), measurement uncertainty, and counterfactual assumption uncertainty. The N is calculated as the square root of the sum of squares of all of its possible components:

$$N = \sqrt{U_M^2 + U_A^2 + V_D^2 + V_{SS}^2 + V_S^2 + V_I^2} \quad (2)$$

where U_M = measurement uncertainty, U_A = assumption uncertainty, V_D = daily variability, V_{SS} = sub-seasonal variability, V_S = seasonal variability, and V_I = interannual variability. Daily, sub-seasonal, and seasonal variability were calculated at each model node to capture natural variability across multiple timescales, though these terms could alternatively be estimated from observational time series by users of this framework who lack highly resolved model output. V_D was calculated as the standard deviation of hourly deviations from daily means; V_{SS} was calculated as the standard deviation of daily deviations from monthly means; V_S was calculated as the standard deviation of monthly deviations from the annual mean. Interannual variability (V_I) was excluded because the experimental model simulations were limited to a single year, making this source of variability non-representative, and we later consider how the exclusion of this term affects interpretation of our results. Measurement uncertainty (U_M) reflects errors associated with sensor accuracy, precision, or calibration, whereas assumption uncertainty (U_A) quantifies the new uncertainty introduced when efforts are made to reduce the N or eliminate the various terms that comprise N in Equation 2.

An example of U_A comes from the practice of averaging frequent measurements made over a period of time to reduce the contributions to N from daily, sub-seasonal, and seasonal variability. An example might be if continuous measurements were averaged over one year before and after a mCDR intervention, and the differences between the two annually-averaged values were examined. Before computing the uncertainty on the difference, we first compute the uncertainty on each mean value. When this is done in our framework, the variability terms are removed from Equation (2) and replaced by a U_A term representing the uncertainty of the mean value attributable to the removed variability. If natural variability led to uncorrelated noise in a measured quantity that was independent between subsequent observations, then the uncertainty on the mean values

would be equal to the combined effects of the removed variability divided by the square root of the number of observations averaged. However, the impacts of natural variability are often correlated on shorter timescales (e.g., seasonality generates evolving “red” noise curves in measurements rather than “white” noise), so the true number of degrees of freedom is less than the number of averaged measurements. Recognizing this, (Carter et al. 2019) conservatively argued that averaging a varying signal instead reduces natural variations for a timescale by the square root of the number of the corresponding timescales spanned by the observations. However, this implies that the impacts of natural variations on the measurement are perfectly correlated over the period of the natural variability and uncorrelated on longer timescales. We can avoid this untested simplifying assumption by directly computing the *effective* number of independent observations from the temporal decorrelation timescale (τ , (North, Wang, and Genton 2011) and the length of the time series (dt). The τ associated with each mode of variability is defined as the lag at which the autocorrelation falls to $1/e$, providing a measure of that mode’s persistence in the environment. Specifically, we estimate τ_D from the autocorrelation of hourly anomalies about the daily mean, τ_{SS} from the autocorrelation of daily anomalies about the monthly mean, and τ_S from the autocorrelation of monthly anomalies about the annual mean. These τ values (with units of years) are then used to compute the number of independent realizations of each mode of variability as the dt divided by the τ (North, Wang, and Genton 2011), with a minimum of one because the first measurement is always independent. For the average of a long time series of measurements, this would imply that:

$$U_A = \sqrt{\left(\frac{V_D^2}{1 + dt / (\tau_D/(365 \times 24))}\right) + \left(\frac{V_{SS}^2}{1 + dt / (\tau_{SS}/(12 \times 30))}\right) + \left(\frac{V_S^2}{1 + dt / (\tau_S/12)}\right)} \quad (3)$$

Once the uncertainties are known for the “before” and “after” mean values, the uncertainty on the signal, or their difference, may be computed by adding the uncertainties in quadrature (i.e., as the root sum of their squares).

Carter et al. (2019) considered long climate time series, and another modification needs to be made to the framework to adapt it for the short timescale records that may be common when monitoring local impacts of OAE and other mCDR interventions. This modification comes from a recognition that correlated red noise variability emerges over time, or that the influences of a seasonal cycle tend to emerge over months rather than hours. We again use the τ timescales to determine whether a time series is sufficiently long for the influences of each timescale to be felt, and replace each variability term (V_D , V_{SS} , V_S) with:

$$V = \min\left(V, V \times \frac{dt + gap}{\tau}\right) \quad (4)$$

where dt is the total monitoring duration in years and τ is the decorrelation timescale of that variability mode in years. This ‘minimum’ function allows for short-term monitoring durations to discount variability modes whose timescales exceed the monitoring duration. A gap in monitoring before and after the OAE deployment, if there is one, is also allowed for here, since variability can decorrelate between periods of continuous measurements.

The framework enables the assessment of different observing strategies in terms of the maximum allowable measurement uncertainty (U_M , expressed as the standard deviation of the long term measurement error) that permits signal detection. Rearranging Equation 2 and solving for U_M establishes an upper limit on U_M given the contributions of other noise components. In other words, it provides a benchmark to evaluate whether an observing strategy meets the requirements to

permit detection. With this definition, it is not uncommon that the U_M is an imaginary number, which implies that the signal is undetectable irrespective of the uncertainty of the measurements.

As with natural variability, it may be possible to reduce the impact of U_M by averaging repeated observations. It is usually unrealistic to assume that measurement errors are entirely correlated or uncorrelated over time, so a similar set of considerations and equations may be applied to the U_M term, as was applied to the V terms in Equations 3 and 4. However, measurement errors vary significantly between measurement approaches in their—often unknown—decorrelation timescales, so we do not attempt these calculations in this study. Instead, the U_M that we compute and discuss is that which remains after any reduction through averaging repeated measurements or a consideration of the timescales over which certain errors appear (e.g., a sensor drift over years may not meaningfully contribute to a week-long record).

Different observing or detection strategies may target or resolve specific modes of noise depending on the balance between measurement quality, frequency, duration, and analysis. One strategy may prioritize frequent but moderately-accurate measurements, another may benefit from less frequent but highly-accurate measurements, and still another may show that an expected signal would be undetectable regardless of monitoring strategies. The optimal strategy depends on the system's characteristics and the detection objectives, balancing measurement quality, frequency, and duration against coverage and cost.

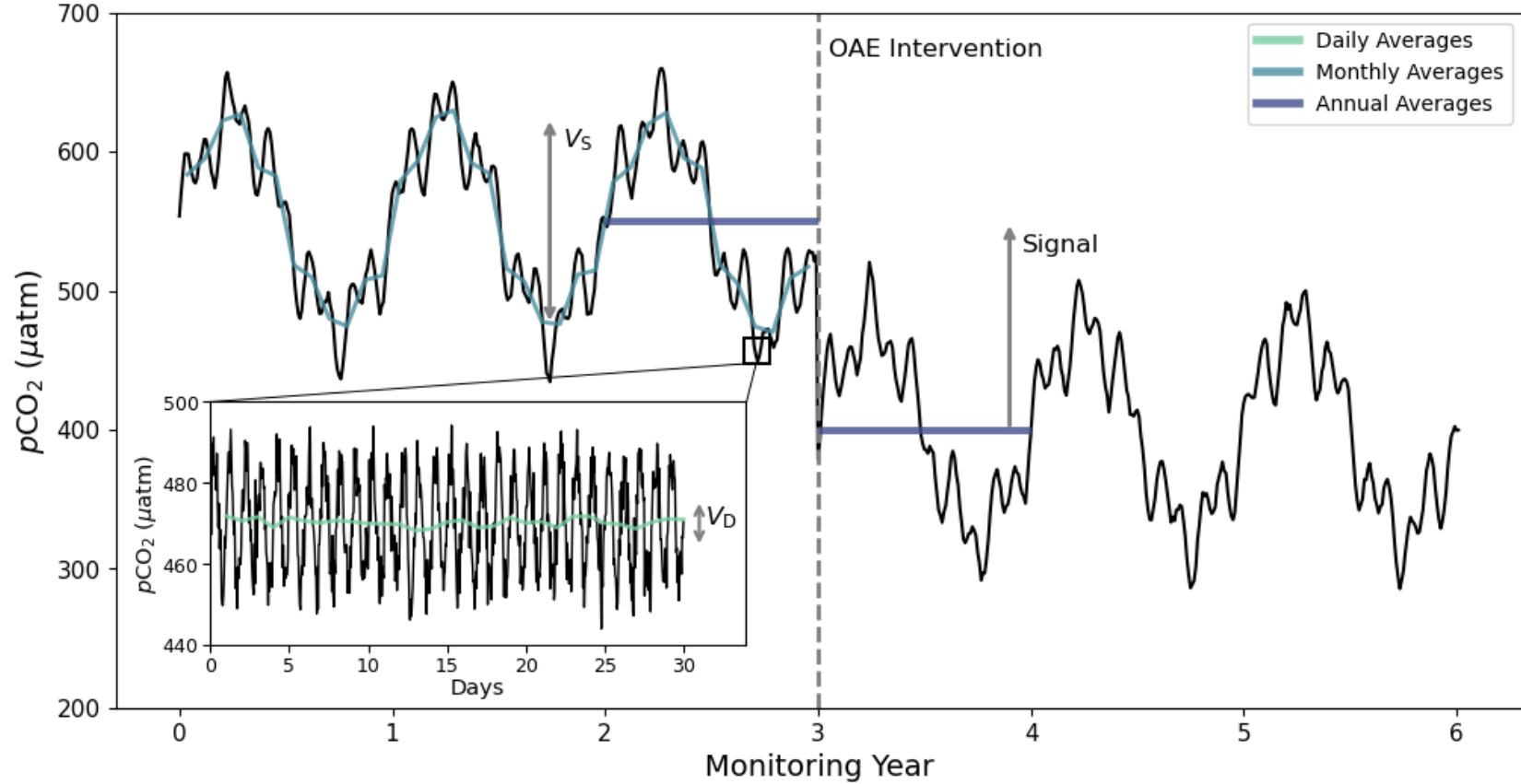


Figure 2| Example $p\text{CO}_2$ time series illustrating modes of natural variability and the OAE-induced signal. The synthetic $p\text{CO}_2$ record spans six monitoring years, with the OAE intervention occurring at year three (vertical dashed line). Overlaid colored lines represent averaged values at daily (green), monthly (blue), and annual (purple) scales. The horizontal purple bars, or one-year pre-and post-intervention mean $p\text{CO}_2$ values, are used to measure the signal, S (single-sided arrow). Modes of natural variability, denoted by V_D and V_S for daily and seasonal variability (double-sided arrows), produce large fluctuations and contribute to the noise (N), which masks detection of the OAE signal both before and after deployment. The inset zooms in on a one-month, detrended time series prior to the intervention, revealing high-frequency diel variability.

4.2.4 Observing Strategies to Reduce Noise and Uncertainties

This study tested three distinct observing strategies to assess their ability to detect OAE-induced signals against the background of natural variability, reflecting a single-measurement strategy, a long-term averaging strategy, and an approach relying on empirical prediction algorithms to eliminate the impacts of natural variations on the N . These strategies reflect real-world monitoring approaches but were applied to model output in this study to allow for consistent, controlled comparison across strategies. They spanned a spectrum from minimal observational knowledge to highly-resolved monitoring, each with different assumptions about data availability (Table 1).

1. The *single-measurement* strategy represents a minimal observational approach, where signal detection relies on a single measurement taken at a location of interest both before and after the intervention. This strategy effectively compares two mean values pre- and post-intervention, where no prior observational knowledge of background variability is available. The apparent S is then the difference between these measurements, and the N reflects all factors that would challenge the interpretation that the S is attributable to the TA addition. The N for measurements before and after the intervention are assumed to be the same, so the uncertainty on their difference is greater than either individual uncertainty by a multiple of the square root of two (Table 1). The dt for this scenario is 0 years, and, as a worst case scenario, we also assume that enough time elapsed between the measurements for all time scales of variability to become uncorrelated (i.e., the *gap* term exceeds all τ timescales). At each grid cell, the signal needed to exceed the magnitude of natural variability and other uncertainties by at least a factor of two (Equation 1) to permit detection with that single measurement pair before and after the intervention. This

approach represents the lowest resolution strategy with the highest uncertainty because it lacks any temporal context to distinguish the OAE-induced signal from natural fluctuations.

2. The *long-term averaging* strategy represents a long-term, high-frequency monitoring approach. Conceptually, it is based on a mooring system that measures carbonate chemistry parameters (e.g., $p\text{CO}_2$) every three hours over a one-year period both before and during an intervention, consistent with autonomous sensor systems (Sutton et al. 2014). These measurements were derived from model output and provided continuous, high-frequency data that resolved natural variability across multiple temporal scales. In this approach, the counterfactual is defined at the same location where subsequent monitoring of the signal occurs. For this scenario, we replaced V_D , V_{SS} , and V_S in Equation 2 with U_A following Equation 3. As before, we included a coefficient of two in the noise equation to account for uncertainties and assumptions in both the pre- and post-intervention periods (N equation in Table 1). While this strategy was primarily assessed under a one-year monitoring duration, we also evaluated this strategy over a range of durations from one day to 10 years. To ensure that low-frequency variability modes did not inflate U_A when dt was short, we applied the minimum correction function (Equation 4) to U_A (Equation 3) with an assumed *gap* of 0 years. In each case, it was assumed that the monitoring that preceded the intervention extended for a dt equaling that of the monitoring that continued during the intervention.
3. The *predictive algorithm monitoring* strategy applies a data-driven approach where carbonate chemistry parameters are estimated using multiple linear regression models. For this strategy, a predictive algorithm was developed that relates measurements of key

parameters taken before the intervention to other variables that strongly correlate with those parameters, but that are unaffected by the intervention. Then, the algorithm can be used with measurements of the correlating variables after the intervention to obtain a time-varying counterfactual accounting for the correlated natural variability. The algorithms were derived from a set of physical and biogeochemical variables (e.g., temperature (T), salinity (S), oxygen (O), nitrate (N), and phosphate (P)). Tested combinations of predictor variables included TS , TSO , TSN , TSP , $TSO\!N$, and $TSO\!N\!P$ for all three target carbonate chemistry parameters (TA, DIC, and $p\text{CO}_2$). The algorithm was trained on model output from the first year of the baseline scenario at the model node corresponding to each intervention site, with predictor data sampled at varying temporal resolutions (hourly, daily, and weekly). There were therefore 36 total algorithms considered, though we limit our discussion to a subset of these possibilities. Once trained, the algorithms were tested against hourly model output from a second, independent year of the baseline scenario across Sequim Bay to generate continuous, spatially-resolved carbonate chemistry estimates. By applying the algorithm to a second, independent year, we ensure it must predict new natural patterns rather than simply reproducing those seen during training. While predictions were made across the full domain, the algorithm's counterfactual was trained using data only from the intervention site, regardless of where subsequent monitoring occurred. This contrasts with the long-term averaging strategy, where the counterfactual was defined at the same location as the post-intervention monitoring. This scenario saw the removal of all timescales of natural variations from Equation 2 and their replacement with a U_A reflecting the uncertainty of the algorithm predictions in terms of the root mean square error (RMSE, N equation in Table 1). In Supplementary Text S1, we

review how these algorithms were formulated and evaluated for our modeled Sequim Bay test environment, how the impacts of measurement uncertainty on the algorithm training data were assessed, and how their U_A terms were assigned for each grid cell in the model domain.

The performance of the three observing strategies outlined in Methods 2.4 was evaluated using the adapted detectability framework for three carbonate chemistry parameters including TA, DIC, and $p\text{CO}_2$. For each parameter and observing strategy, we quantified the maximum allowable measurement uncertainty (U_M) that would permit confident detection (rearranging Equation 2). Noise (N) was calculated using Equation 2 and represents the remaining modes of variability or uncertainty that the signal must exceed (by a factor of two) to permit detection. We also assessed the spatial extent of detectability, or the total area where the maximum allowable uncertainty exceeded the commonly reported measurement uncertainty. We define this detection threshold as $2 \mu\text{atm}$ for $p\text{CO}_2$ and 2 mmol/m^3 for TA and DIC. This area was averaged over a one-year intervention period, providing a measure of the persistent spatial footprint of detectability under each observing strategy.

Table 1| Characteristics of measurement type, quality, frequency, and duration for the three monitoring strategies assessed in this study. The final column presents each strategy’s noise (N) equation, representing unresolved modes of variability or uncertainty.

Observing Strategy	Measurement Type	Quality	Frequency	Duration	Modes of Variability Unresolved (Noise Equation)
Single-measurement Strategy	Carbonate chemistry parameter	High	Low (1 time)	Low (1 time)	$N = \sqrt{2 \times (V_D^2 + V_{SS}^2 + V_S^2 + U_M^2)}$
Long-term Averaging Strategy	Carbonate chemistry parameter	High	High (every 3 hours)	Medium (1 year)	$N = \sqrt{2 \times (U_M^2 + U_A^2)}$
Predictive Algorithm Monitoring Strategy	Combination of temperature, salinity, oxygen, and/or nutrients + carbonate chemistry parameter	High	Medium – High (hourly, daily, weekly)	Medium (1 year)	$N = \sqrt{U_M^2 + RMSE^2}$

4.3 Results

4.3.1 Characterization of OAE Signal and Noise in Sequim Bay

Perturbations in carbonate chemistry variables attributed to the OAE deployment exhibited spatial heterogeneity across Sequim Bay (Figure 3, Figure S1). The largest TA and $p\text{CO}_2$ signals were concentrated near the intervention sites and gradually dissipated with distance from the deployment. These signals reached magnitudes of approximately 200 mmol/m³ for TA and $-150 \mu\text{atm}$ for $p\text{CO}_2$ at both the field-trial and mid-bay locations. In general, the spatial extent of large signals was greater at the mid-bay site compared to the field-trial site. The DIC signals were substantially smaller (Figure S1c–d), ranging from 0 to 12 mmol/m³, and lacked pronounced hot-spots near the intervention sites. This is because the air-sea CO_2 equilibration is slow compared to the residence time of seawater in Sequim Bay, and water is diluted through mixing and advected from the bay before it accumulates all of the expected additional DIC (Khangaonkar et al., 2024).

Averaged regionally, the magnitude of simulated natural variations (Figures 4, S2) were larger on longer timescales for all carbonate chemistry variables. The areas of highest natural variability were located at the southern end of the bay and near the region of tidal flushing at the northern bay entrance. Consequently, the region surrounding the field-trial site experienced greater natural variability compared to the mid-bay site.

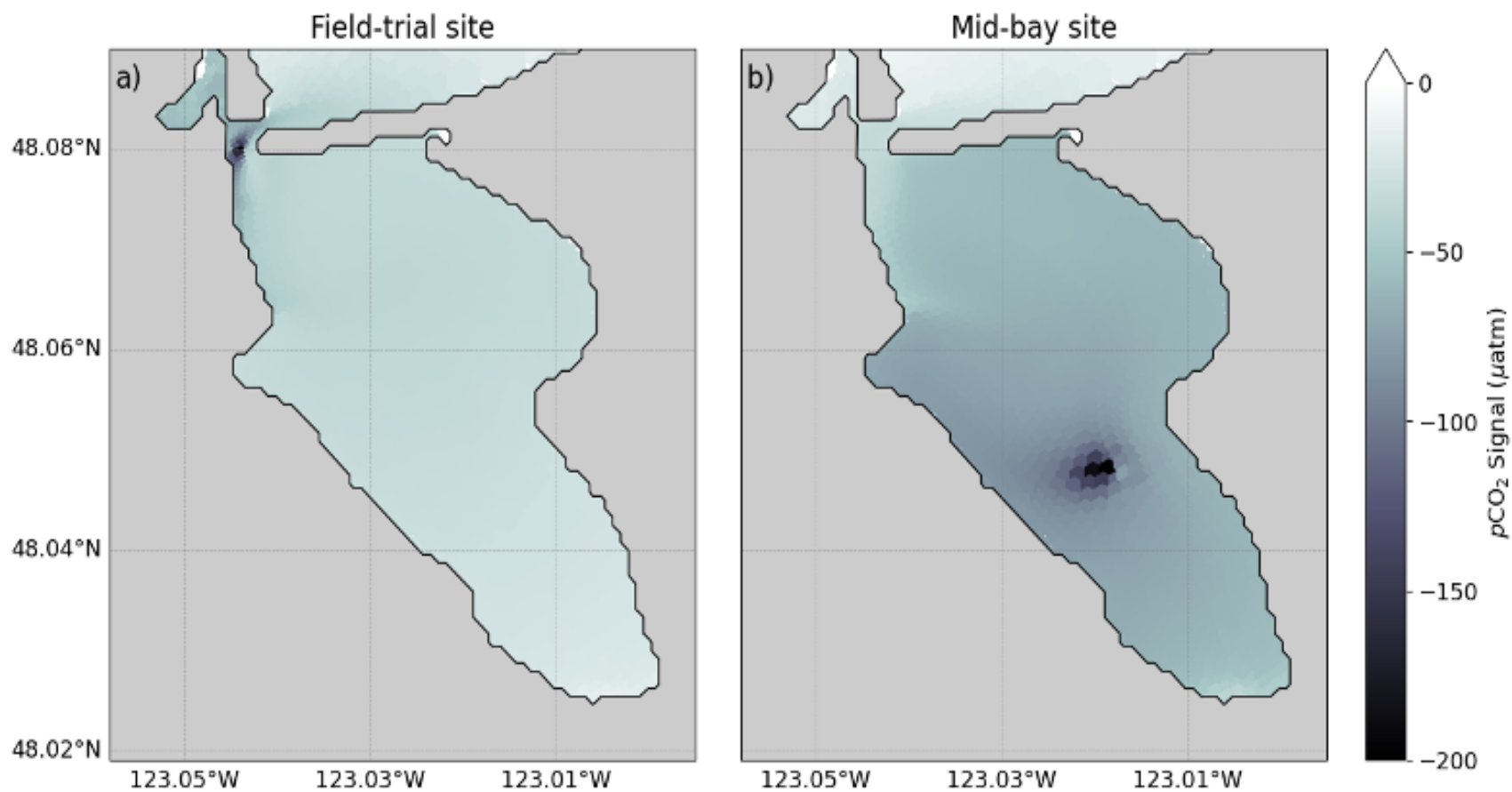


Figure 3| Maps of the annual mean OAE-induced $p\text{CO}_2$ signals at the a) field-trial site and b) mid-bay site. The signal (S) is defined as the difference between the annual average of hourly modeled values in the experimental scenario and the baseline scenario ($S = \text{experimental} - \text{baseline}$).

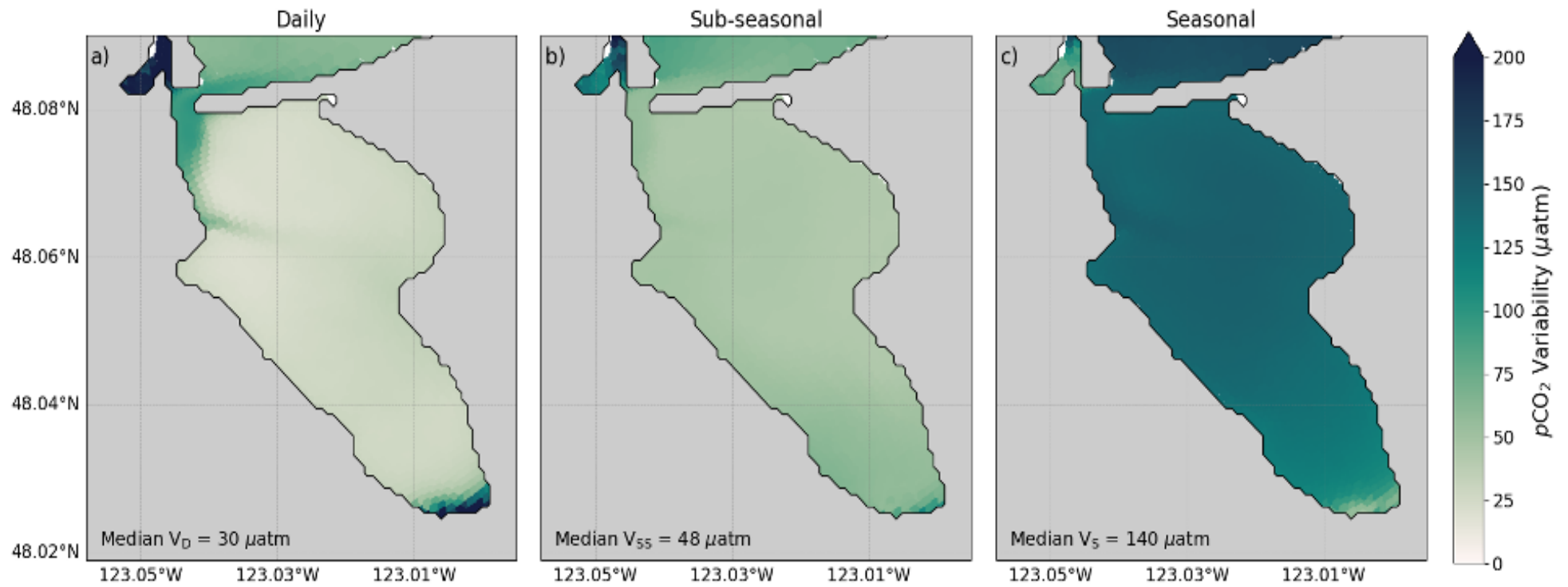


Figure 4| Maps of a) daily, b) sub-seasonal, and c) seasonal $p\text{CO}_2$ variability across Sequim Bay.

4.3.2 Assessing Noise Reduction Across Observing Strategies

The effectiveness of each observing strategy in reducing the combined noise, N , was evaluated using the equations in Table 1. The single-measurement strategy was unable to average out any modes of natural variability or uncertainty, leaving all components of N unresolved (Equation 2, with U_A equal to 0 and multiplied by $\sqrt{2}$ to capture uncertainties both before and after the intervention). As a result, the magnitude of the residual noise was high because it reflected the complete variability and uncertainty of the system. Averaged across Sequim Bay, this strategy produced the highest overall N compared to the other two strategies for all carbonate chemistry variables (Figures 5a, S5a, and S6a). The unresolved N exhibited spatial heterogeneity, with the largest values located at the southern end of Sequim Bay and the bay entrance. These regions were also characterized by relatively high natural variability (Figures 4, S2). The long-term averaging strategy, however, substantially reduced the residual noise across all carbonate chemistry variables, and managed to reduce residual noise in highly variable regions such as the northern bay entrance and southern region (Figures 5b, S5b, S6b).

To calculate unresolved noise for the predictive algorithms, we first selected model configurations based on their performance in a random five-fold cross-validation conducted at each intervention site (Supplementary Text S1). The resulting RMSE values are summarized in heat map tables (Figures 6, S3 and S4) and illustrate the influence of predictor combinations and sampling frequency on residual noise. Based on these results, we focused on a subset of algorithms for spatial analysis to quantify prediction error and evaluate detectability across Sequim Bay. For each carbonate chemistry variable, we chose three representative predictor configurations: TS alone, TS plus the best-performing single additional predictor, and the full $TSO\!NP$ predictor combination. Oxygen was the optimal additional predictor for DIC and TA and nitrate was best

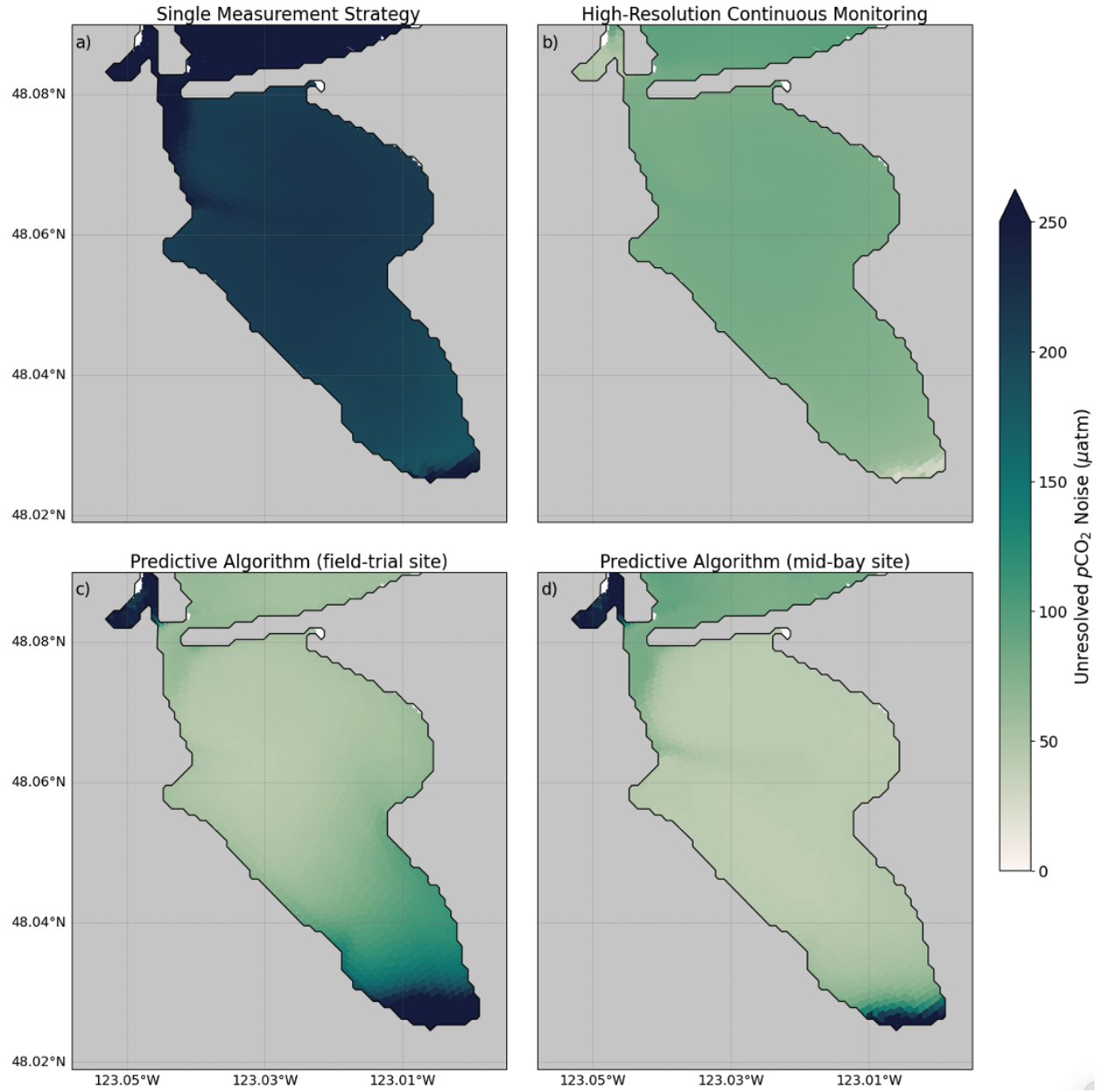


Figure 5| Maps of the unresolved $p\text{CO}_2$ noise under three observing strategies: a) the single-measurement strategy, b) the long-term averaging strategy, and c–d) the predictive algorithm monitoring strategy. The predictive algorithms were trained on daily TSN data from the field-trial site (c) and mid-bay site (d), and then applied to the entire bay. The noise (N) equations for each strategy are derived from Equation 2 but differ in modes of variability and uncertainty they resolve. The specific formulations used to generate these maps are given in Table 1.

to estimate $p\text{CO}_2$ at each grid cell. The RMSE was calculated at each grid cell by comparing predicted and true model output. These values were used as the model node-specific assumption uncertainty (U_A in Equation 2) so that the unresolved noise associated with each algorithm reflected the prediction error.

The effectiveness of the predictive algorithms in reducing unresolved noise varied by the intervention site and the target carbonate chemistry variable. For $p\text{CO}_2$, the predictive algorithms meaningfully outperformed the long-term averaging approach in noise reduction (Figure 5). At both the field-trial (Figure 5c) and mid-bay (Figure 5d) sites, the algorithms minimized noise more effectively than the long-term averaging strategy (Figure 5b). Compared to the single-measurement strategy, the predictive algorithms reduced unresolved noise by approximately a factor of four, indicating a substantial improvement in detection potential.

The difference in performance between the predictive algorithms and long-term averaging strategy was less pronounced for TA and DIC (Figures S5, S6). Both approaches achieved similar TA noise reduction at the mid-bay site, but the long-term averaging strategy reduced noise to a greater extent near the field-trial site. The predictive algorithms reduced noise more broadly across the interior of Sequim Bay for DIC, while the long-term averaging strategy was more effective at reducing noise in highly variable regions, particularly in the northern inlet and southern bay. For comparisons in such regions it should be noted that the algorithm counterfactual is defined using measurements of other locations, whereas the long-term averaging counterfactual is instead derived using local measurements within the highly variable regions. We did not attempt to derive algorithms for each grid cell for more direct comparisons.

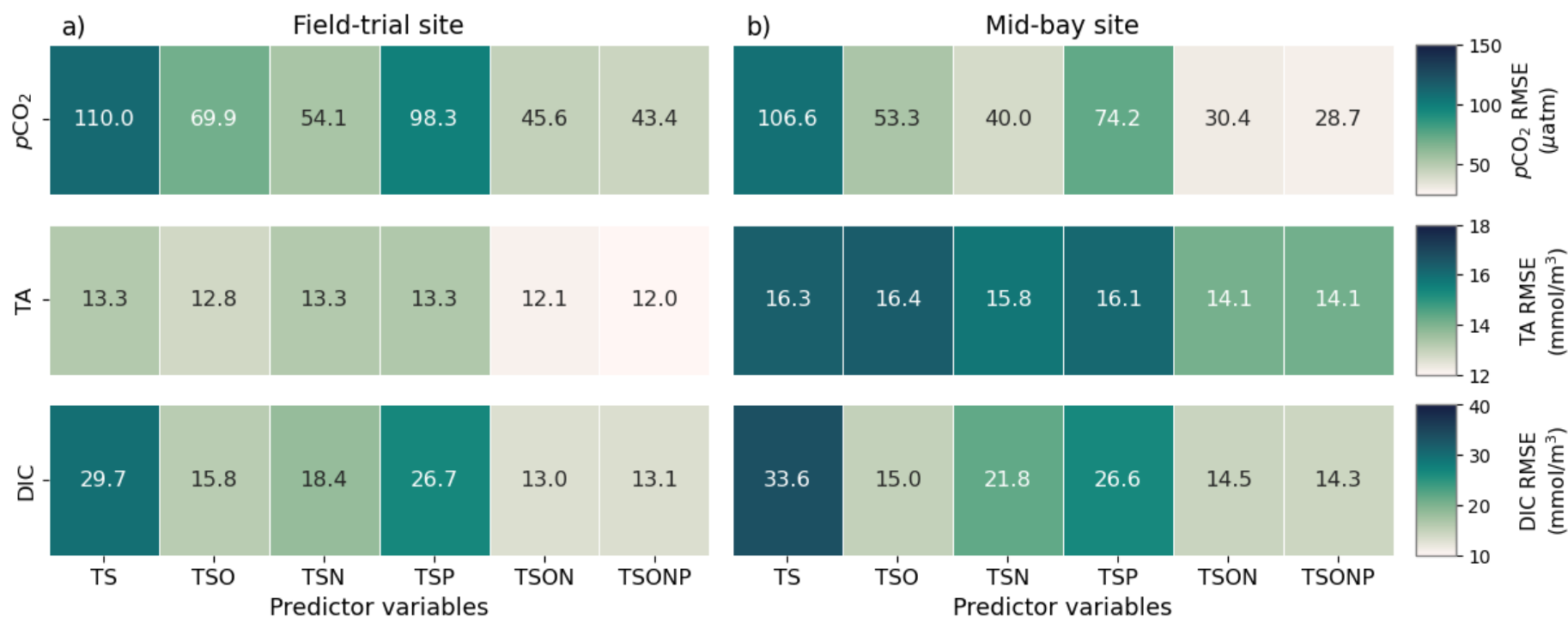


Figure 6 | Cross-validation RMSE for predictive algorithms at the field-trial (a) and mid-bay (b) sites. Each panel shows a heat-map table of mean RMSE values from five-fold cross-validation, calculated for three target carbonate chemistry variables ($p\text{CO}_2$, TA, and DIC) across different predictor combinations (*TS*, *TSO*, *TSN*, *TSP*, *TSON*, and *TSONP*). The predictive algorithms represented here were constructed using daily sampling frequency for the predictor variables. Results for hourly and weekly sampling frequencies are shown in Figure S3 and the standard deviation of the five-fold cross-validations are provided in Figure S4.

4.3.3 Evaluating Spatial Extent of Detectable OAE Signals Across Observing Strategies

To assess the spatial extent of detectability, we calculated the maximum allowable measurement uncertainty (U_M) that would permit confident detection based on the local signal and noise terms (rearranging Equation 2). This calculation was applied at each grid cell, which generated spatially explicit maps of detectability for each carbonate chemistry variable and observing strategy.

The single-measurement strategy failed to detect any perturbations in carbonate chemistry attributed to the OAE intervention across Sequim Bay (Figure S7). This outcome was consistent for all three carbonate chemistry variables at both the field-trial and mid-bay deployment sites. Implementation of the long-term averaging strategy, which emphasized frequent and high-quality measurements over one year, substantially expanded the spatial footprint of detectable area for TA and $p\text{CO}_2$ (Figure 7). Under a one-year deployment of high-resolution monitoring both before and after the intervention, the detectable area at the mid-bay site was 7.5 km² for TA and 0.03 km² for $p\text{CO}_2$, whereas at the field-trial site it was 0.7 km² for TA and 0.01 km² for $p\text{CO}_2$. The mid-bay deployment consistently produced larger detectable areas (Figure 7d–f) than the field-trial deployment (Figure 7a–c), reflecting the broader signal extent (Figures 3, S1) and lower background variability (Figures 4, S2). The detectable area at the mid-bay site was approximately three times greater for $p\text{CO}_2$ and ten times greater for TA relative to that at the field-trial site. Notably, perturbations in DIC remained undetectable under a one-year implementation of the long-term averaging strategy, despite the intensity of sampling effort (Figure 7c, f).

The extent of detectable area under the predictive algorithm monitoring strategy depended on the sampling frequency and choice of predictor variables in algorithm construction. Every tested configuration produced some detectable area for TA and $p\text{CO}_2$, demonstrating a clear improvement over the single-measurement strategy (Figure 8). Detection of $p\text{CO}_2$ perturbations

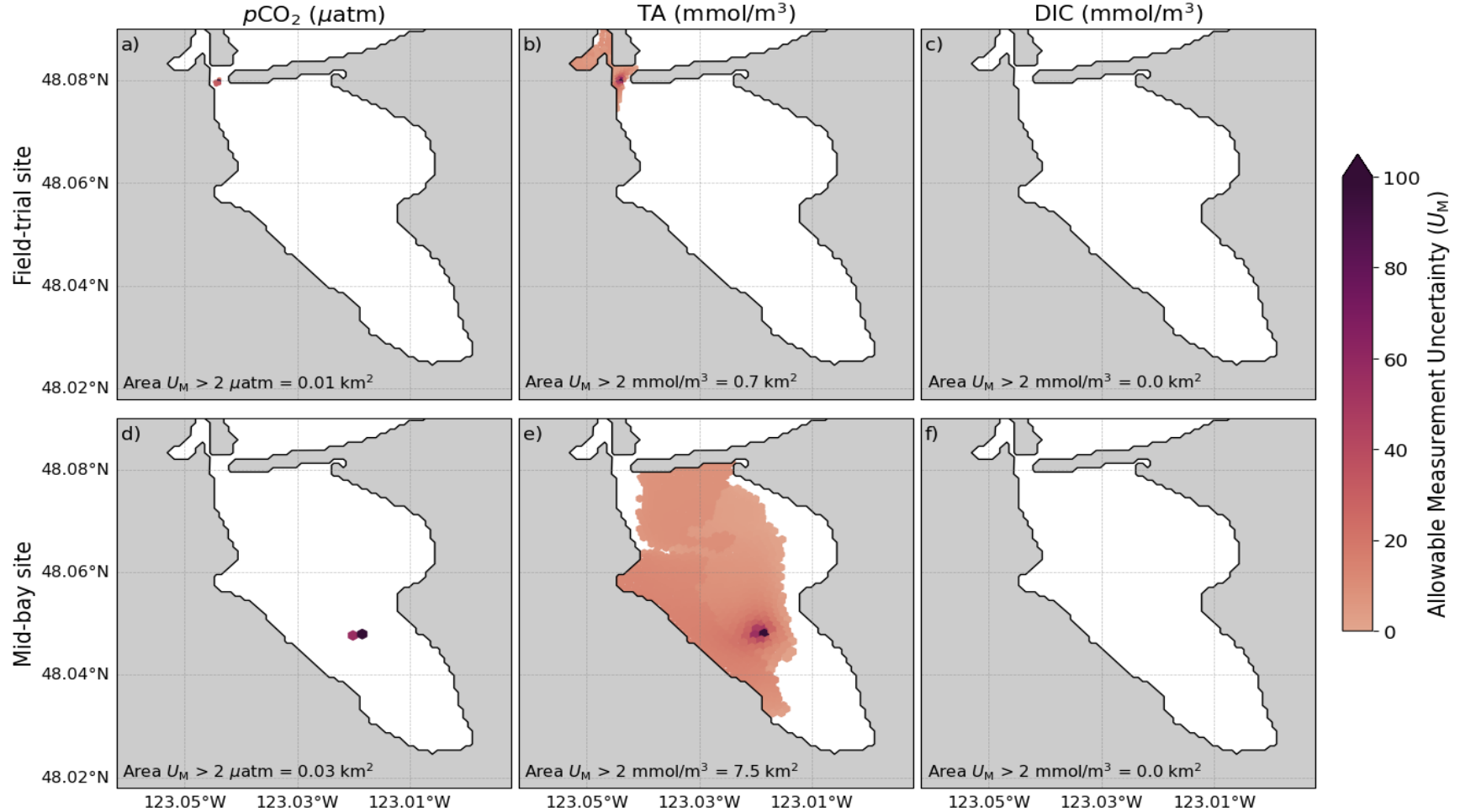


Figure 7| Detectable area of OAE-induced perturbations under one year of the long-term averaging strategy for $p\text{CO}_2$, TA, and DIC at two intervention sites. Detectable area is substantially smaller at the field-trial site (a–c) than at the mid-bay site (d–f) for $p\text{CO}_2$ and TA. Color shading indicates the allowable measurement uncertainty (U_M) that permits detection of the OAE signal (μatm for $p\text{CO}_2$; mmol/m^3 for TA and DIC). White regions fall below the detection threshold. The annotated text in each panel reports the total area (km^2) for which U_M exceeds a predefined threshold ($\geq 2 \mu\text{atm}$ for $p\text{CO}_2$; $\geq 2 \text{ mmol/m}^3$ for TA and DIC), consistent with expected field measurement uncertainty. Notably, no area is detectable for DIC at either site under this one-year monitoring framework.

was strongly influenced by sampling frequency and predictor variables, in agreement with patterns observed during algorithm validation (Supplementary Text S1). At the field-trial site, adding predictors to the *TS* model expanded detectable area by a factor of 10 with *TSN* and 25 with *TSO_{NP}*. At the mid-bay site, these expansions rose even more dramatically to factors of 80 with *TSN* and 400 with *TSO_{NP}* (Figure 8). Sampling frequency also affected detectability of $p\text{CO}_2$, albeit to a lesser extent than the choice of predictor variables. Increasing sampling frequency from weekly to hourly expanded the detectable area for $p\text{CO}_2$ by ~40% at the field-trial site and 25–50% at the mid-bay site (Figure 8), depending on predictor configuration. By comparison, detection of OAE-induced changes in TA were only marginally affected by sampling frequency and predictor variables, influencing detectable area by ~10% at the mid-bay site and 10–20% at the field-trial site. As observed with the long-term averaging approach, the mid-bay deployment produced larger detectable areas than the field-trial site for both TA and $p\text{CO}_2$, reflecting stronger signals and reduced background variability. No combination of predictor variables, intervention site, or sampling frequency reduced N sufficiently to permit detection of DIC due to low *S*.

We next compared the performance of the predictive algorithms and the one-year long-term averaging strategy to evaluate their effectiveness in detecting OAE-induced signals. For TA, the predictive algorithms achieved a detectable area that was comparable to that of long-term averaging at the mid-bay site. At the field-trial site, coverage from predictive algorithms was only one-tenth that of long-term averaging. For $p\text{CO}_2$, however, the *TSN* and *TSO_{NP}* predictive algorithms outperformed the one-year long-term averaging strategy at both sites and produced larger spatial footprints of detection. In particular, the top-performing hourly *TSO_{NP}* algorithm expanded the detectable area of $p\text{CO}_2$ by a factor of nearly 300 at the mid-bay site and 5 at the

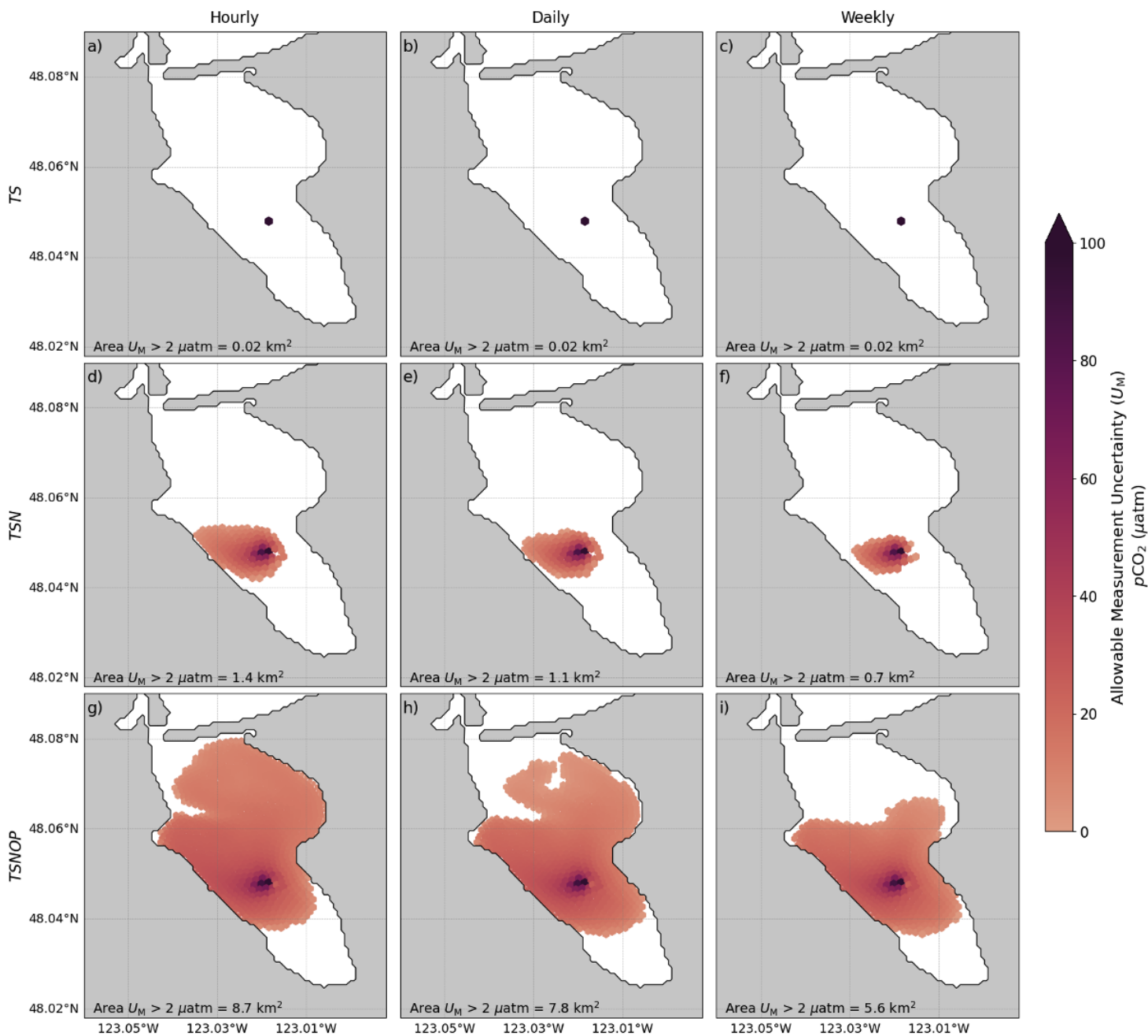


Figure 8| Detectable area of OAE-induced changes in $p\text{CO}_2$ using predictive algorithms across sampling frequencies and sets of predictor variables at the mid-bay site. Rows correspond to predictor combinations (TS , TSN , and $TSNOP$) and columns correspond to sampling frequency of the data used to train the algorithms (hourly, daily, and weekly). Color shading represents the maximum allowable measurement uncertainty (U_M in μatm) at each grid cell that permits detection of the OAE signal. White areas fall below the detection threshold. The annotated text in each panel reports the total area (km^2) for which $U_M \geq 2 \mu\text{atm}$. Adding a biogeochemical predictor to the base TS model markedly expands the spatial footprint of detection. These results demonstrate that both predictor selection and sampling frequency strongly influence the extent over which OAE-induced $p\text{CO}_2$ changes can be detected.

field-trial site relative to the long-term averaging approach. This dramatic increase demonstrates the potential of predictive algorithms to enable the detection of OAE-induced perturbations.

While the evaluation of these three strategies focused primarily on a one-year timescale, detectability of OAE signals depends critically on the duration of observations relative to the timescales of background variability. To explore this relationship, we assessed how detectable area evolves under the long-term averaging strategy as monitoring duration increases from one day to 10 years for TA and $p\text{CO}_2$ at both intervention sites (Figure 9). Although even shorter durations (on the order of a few hours) may precede the emergence of all variability modes, the OAE signal likely has not dispersed sufficiently across the bay to be detectable. At a duration of one day, detectable area was comparable to that achieved after a decade of monitoring for $p\text{CO}_2$ and 30-60% of that for TA at both sites, since sub-seasonal and seasonal variability had not yet emerged. As the monitoring duration approached the sub-seasonal decorrelation timescale ($\tau_{ss} \sim 4$ days, Figure S8), the detectable area declined sharply because sampling intervals coincided with the dominant mode of variability. By several weeks to one month, intermediate-frequency variability effectively masked the OAE signal, reducing detectable area to near zero for $p\text{CO}_2$ and TA at both sites. Extending monitoring beyond seasonal cycles ($\tau_s \sim 2$ months, Figure S8) allowed sampling to integrate over multiple and longer variability cycles. After one year of the long-term averaging monitoring approach, the detectable area for TA reached $\sim 50\%$ of that achieved after 10 years at the mid-bay site but only $\sim 5\%$ at the field-trial site. Detectable area for $p\text{CO}_2$ remained near zero at both sites. At a decadal scale, averaging over multiple interannual cycles substantially increased detectability.

An important caveat of these results is that we do not explicitly include the unknown influence of interannual variations (V_I), which would likely decrease detectability over long (multi-

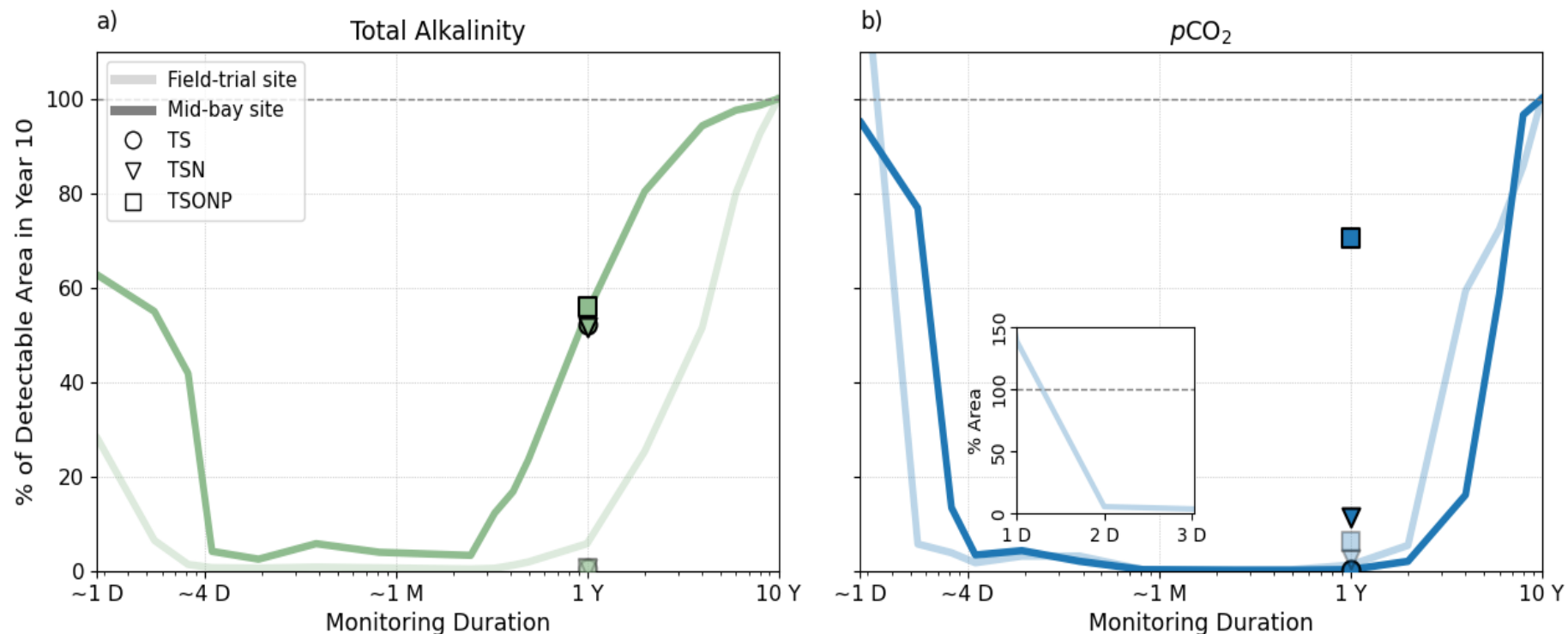


Figure 9| Detectable area as a function of monitoring duration for the long-term averaging strategy, shown for TA (left) and $p\text{CO}_2$ (right). The vertical axis represents the percentage of detectable area that is achieved after 10 years of the long-term averaging approach. Monitoring duration is assessed over a range of timescales from one day to 10 years, with notable timescales marked on the x-axis. In each panel, light colors denote the field-trial site and dark colors denote the mid-bay site. Solid lines show how detectable area varies when the long-term averaging strategy is deployed over progressively longer durations. Markers indicate detectable area achieved using three predictive algorithms constructed from one year of daily predictor data (circle: *TS*, triangle: *TSN*, and square: *TSONP*). After 10 years of employing the long-term averaging monitoring approach, the absolute detectable areas are as follows: TA: 11.9 km² at the field-trial site and 13.8 km² at the mid-bay site; $p\text{CO}_2$: 0.8 km² at the field-trial site and 12.3 km² at the mid-bay site. For reference, the total area of Sequim Bay is approximately 13 km².

year) timescales but have minimal influence on shorter timescales. Across all durations, the mid-bay site consistently yielded a larger detectable area due to lower background noise and a stronger signal (TA: 11.9 km² at the field-trial site and 13.8 km² at the mid-bay site; *p*CO₂: 0.8 km² at the field-trial site and 12.3 km² at the mid-bay site).

4.4 Discussion

Detection of OAE-induced signals is dependent on multiple interacting factors including the magnitude of the signal, the structure of background natural variability, and the design of the observing strategy. In Sequim Bay, these factors combined in complex ways across both deployment sites, producing a wide range of detection outcomes from no detectable signal to detection across almost the entire bay.

4.4.1 Spatial Heterogeneity of Signal-to-Noise Dynamics in Sequim Bay

Sequim Bay experiences highly dynamic carbonate chemistry, influenced by the interaction of land, oceanic, and riverine processes. These include pelagic and sedimentary biological activity, freshwater inflow, air-sea gas exchange, calcification, nitrification, and mixing of upwelled bottom-water from the California Current (Alin et al. 2024; Pelletier et al. 2018). These processes affect individual carbonate system parameters in different ways, driving variability through distinct mechanisms and timescales. For example, air-sea gas exchange strongly influences *p*CO₂ and DIC but has no direct impact on TA. This exchange exhibits strong seasonality in the Salish Sea, with outgassing prevailing from October to March and ingassing from April to September (Khangaonkar et al. 2024)

Spatial heterogeneity further modulated detection potential within the bay. Background variability was elevated at the southern end of Sequim Bay due to freshwater inputs from precipitation and snowmelt. At the narrow northern entrance, strong tidal mixing introduced

variability by flushing waters from the Strait of Juan de Fuca. Across all temporal modes examined, variability was consistently higher at the bay entrance than in the more quiescent interior (Figures 4, S2).

The magnitude and spatial extent of perturbations associated with the OAE intervention also differed by site and carbonate chemistry parameter. Deployment at the mid-bay site generated stronger and more spatially extensive signals than that at the tidally energetic field-trial site, where rapid dilution reduced the signal footprint. Among the carbonate variables, TA and $p\text{CO}_2$ exhibited clear local maxima near the intervention sites, reflecting their immediate chemical response to added alkalinity. In contrast, DIC showed no such localized enhancement due to its delayed response governed by air-sea CO_2 re-equilibration, which occurs over months to years (Jones et al. 2014; Oschlies et al. 2023). As a result, DIC perturbations were more diffuse and often transported beyond the bounds of Sequim Bay before a strong signal could accumulate.

These characteristics underscore the critical role of site selection in implementing detectable OAE interventions. Local hydrodynamics and biogeochemical processes not only modulate the magnitude and structure of background variability, which define the baseline against which OAE signals must be distinguished, they also determine how OAE-induced signals disperse and evolve in the environment. Together, these dynamics establish the feasibility and limits of detection. Evaluating how different observing strategies interact with this spatial and temporal landscape offers a powerful framework to design monitoring approaches that effectively isolate OAE-induced signals from background conditions.

At the same time, detectability should not be the sole consideration when selecting deployment sites. While environments with low natural variability may facilitate detection, high variability regions may present lower ecological risks, as biota are often more acclimated to change

and potentially less sensitive to perturbations. Moreover, given that DIC was undetectable under the realistic monitoring strategies presented in this study, models may remain essential for MRV, regardless of the observational approach. From this perspective, a deployment site where the signal is undetectable might be desirable since the environment would be minimally altered. Conversely, applications that aim to deliberately modify local conditions, for instance, to enhance water quality for aquaculture, then stronger and more detectable signals may be advantageous. This trade-off between detectability and environmental impact warrants careful consideration in future site selection for OAE deployments.

4.4.2 Evaluating Performance Across Observing Strategies for OAE Detection

This analysis enabled a direct comparison of the capabilities of three observing strategies to optimize detectability of OAE-induced signals. By systematically testing a range of monitoring strategies that varied in measurement quality, frequency, duration, and analysis, we identified tradeoffs in their ability to resolve perturbations in carbonate chemistry attributed to an OAE intervention.

The contrasting results from the single-measurement and long-term averaging strategies underscore the importance of context for baseline biogeochemical variations to assess OAE detectability. The single-measurement strategy, which lacked any prior knowledge of natural variability, left all modes of environmental variability unconstrained. The magnitude of the signal never surpassed this high-noise threshold, and consequently yielded no detectable area for any of the carbonate chemistry variables. The long-term averaging strategy, conceptualized as a mooring system that collects high-quality measurements at frequent intervals for a one-year duration both before and after the intervention, resulted in more comprehensive detection. This intensive sampling effort dramatically reduced residual N and improved the isolation and detection of TA and $p\text{CO}_2$ changes attributed to the OAE intervention. Despite its effectiveness in expanding the

spatial footprint of detection, the logistical and financial demands of implementing this strategy at scale are substantial.

The predictive algorithm monitoring strategy offered a promising approach by leveraging routinely measured physical and biogeochemical variables to estimate carbonate chemistry. This strategy reduces the need for intensive direct measurements across the entire spatial domain and supports monitoring tailored to local system dynamics. Our results demonstrated how both predictor variable selection and sampling frequency influence model performance and how these frameworks can be optimized for OAE detectability. The top-performing predictive algorithms resulted in minor improvements for TA detection at the mid-bay site but substantially expanded the spatial footprint of $p\text{CO}_2$ detection. Specifically, the top-performing algorithms expanded detectable area for $p\text{CO}_2$ by factors of 300 at the mid-bay site and 5 at the field-trial site relative to the long-term averaging strategy. These results indicate that predictive algorithms are particularly valuable for parameters that exhibit high natural variability, such as $p\text{CO}_2$.

The TA algorithms showed only marginal sensitivity to sampling frequency and predictor variable selection at both sites, resulting in just 10–20% variation in detectable area. The limited improvement in the U_A when increasing the temporal resolution of the training data indicates that predictive algorithms remain viable even when long, high-frequency records are impractical prior to an OAE intervention. This marks a clear advantage over the long-term averaging strategy, which requires extensive spatial and temporal data coverage before deployment. In contrast, choices of sampling frequency and predictor variables had a far greater influence on the detectable area of $p\text{CO}_2$. Adding a single biogeochemical predictor to the base *TS* model expanded the detectable footprint by a factor of 80 at the mid-bay site and 10 at the field-trial site. The full suite of predictors (*TSO NP*) further increased those areas by factors of 25 and 400, respectively. These improvements

underscore the value of incorporating tracers that capture dominant biogeochemical processes linked to carbonate system variability. Even modest expansions in observational capacity, such as measuring dissolved oxygen or one macronutrient at the intervention site, can substantially constrain uncertainty in derived carbonate parameters and enhance detectability. Although increasing sampling frequency from weekly to hourly resulted in ~40% and 25–50% expansions in detectable area for $p\text{CO}_2$ at the field-trial and mid-bay sites, respectively, these improvements were minor relative to the effect of additional predictors. These results illustrate a spectrum of potential trade-offs, for instance, between higher-frequency sampling, longer records, or broader sets of predictor variables. The predictive algorithm monitoring strategy provides a flexible framework to test this matrix of choices and optimize detectability of OAE.

An interesting observation comes from the similarity of unresolved noise produced by the algorithms derived from data at the two different release sites (Figure 5c and 5d). This implies that measurements from one site could inform a viable algorithm applied to the other, even if the intervention itself has minimal influence beyond its immediate surrounding area. This suggests that simultaneous measurements in a nearby, unaffected “control” environment could serve as an empirical algorithm-based counterfactual for an intervention, potentially even after deployment has begun. However, the areas of high unresolved noise in Figure 5 imply that not all nearby areas are suitable for this approach. The similarities between Figures 5c and 5d also imply that the large differences in detectable area between sites were driven primarily by discrepancies in signal strength and background natural variability, rather than differences in algorithm performance.

Collectively, these findings emphasize the importance of carefully selecting both predictor variables and sampling resolution when designing predictive monitoring strategies for OAE. Across both intervention sites for $p\text{CO}_2$ and TA, the predictive algorithms outperformed the one-

year long-term averaging strategy in all cases except for TA at the field-trial site. The predictive algorithm approach provides a comprehensive characterization of system dynamics and achieves comparable or substantially improved detection performance at a fraction of the logistical and financial cost. This strategy presents a practical and scalable alternative for OAE monitoring, particularly in settings where long-term sensor deployments are infeasible.

While these strategies were primarily assessed under the assumption of a one-year monitoring duration, the selected monitoring duration and approach should align with the specific objectives of OAE monitoring. The duration analysis of the long-term averaging monitoring strategy illustrates two effective regimes to achieve a large detectable area: short-duration monitoring, where sampling outpaces natural fluctuations, and long-duration monitoring, where integration over many variability cycles constrains background noise. At intermediate timescales, however, the detectable area of OAE-induced changes sharply declines. In this “MRV valley of death”, detectability essentially vanished from approximately four days to several months for TA and extended up to a year for $p\text{CO}_2$ in this case study. The timing of this detectability dead zone will vary by parameter, site, signal strength, and natural variability. In our analysis, detection under the long-term averaging monitoring strategy required monitoring durations that were either shorter than the shortest dominant mode of variability or noise, or long enough to capture multiple variability cycles. This pattern highlights the complex relationship between monitoring duration and OAE detectability and emphasizes that monitoring duration should be informed by intended objectives. Predictive algorithms may be able to circumvent some of these intermediate-term blind spots by leveraging multiple tracers and flexible sampling.

These results also underscore the importance of selecting appropriate carbonate chemistry parameters based on the specific objectives of OAE monitoring. For example, $p\text{CO}_2$ may serve as

a practical proxy to demonstrate mitigation of ocean acidification. Alternatively, TA may help to track ecological impacts, especially if alkaline feedstocks introduce trace metals of concern upon dissolution. Unfortunately, DIC proved much more challenging to detect. Under all three sampling strategies, DIC signals associated with the OAE intervention remained below detection thresholds in Sequim Bay. It was not until 10 years of continuous, long-term averaging monitoring that a small area (0.2 km²) became detectable in the northern inlet under deployment at the field-trial site. This outcome carries significant implications for quantifying mCDR for carbon crediting purposes, where DIC is a critical indicator of net carbon uptake. While predictive algorithms may offer a path forward in improving detectability, these results suggest they may be insufficient to resolve the challenge of DIC detection in coastal systems characterized by high variability and rapid signal dilution. Additional observational strategies, modeling tools, or crediting frameworks may be needed to credibly evaluate carbon removal in such environments.

4.4.3 Utility and Limitations of Predictive Framework and Future Work

Designing an effective observing strategy to detect OAE-induced signals requires consideration of a matrix of interacting factors. The magnitude and persistence of the signal, structure of natural variability, local hydrodynamics, and tradeoffs between measurement frequency, quality, and duration are critical considerations to optimize detection in a given deployment system. In dynamic environments with high background variability, sustained high-frequency sampling or algorithm-based approaches may be optimal to isolate the signal. In more stable regions characterized by lower natural variability, infrequent sampling may suffice. The selection of an appropriate observational platform should be tailored to cost considerations, sensor availability, personnel with relevant expertise, synergies with other observing efforts, and local system characteristics (Table 2). Ultimately, balancing spatial coverage, temporal resolution, and sensor quality is essential to meet the specific objectives of MRV for OAE deployments. The

Table 2| Characteristics of measurement considerations for different observational platforms. The final column represents the modes of variability that are (un)resolved, which informs the implementation of Equations 2–4 to ultimately determine the spatial footprint of detection that can be achieved.

Observing Strategy	Measurement Type	Quality	Frequency	Duration	Modes of Variability Resolved (Unresolved)
Autonomous mooring	$p\text{CO}_2$, pH, temperature, salinity	High	High (every 3 hours)	Medium–High (1–10+ years)	V_D, V_{SS}, V_S (U_A)
Monthly time series	$p\text{CO}_2$, pH, temperature, salinity	High	Medium (monthly)	High (?)	V_{SS}, V_S (V_D, U_A)
BGC-Argo floats	Temperature, salinity, pH, oxygen	High	Medium (every 5 to 10 days)	High (10+ years)	V_{SS}, V_S (V_D, U_A)
Ship	$p\text{CO}_2$, TA, DIC, temperature, salinity, oxygen, nutrients	High	Low (seasonal to annual+)	Low (cruise lasting ~days)	(V_D, V_{SS}, V_S, U_A)

framework that we present allows a quantitative approach to these considerations, and users can, for example, rearrange equations to calculate the minimum measurement precision required for their purposes, or the minimum scale of the intervention that would be needed to create a detectable signal.

While this study presented a robust framework to evaluate the performance of different observing strategies, several limitations and caveats should be noted. Our analysis was based on a single year of high-resolution model output, which limited our ability to quantify interannual variability. Although we excluded this source of noise from our calculations, interannual variability may be an important source of noise in long-term monitoring, especially in regions influenced by severe climate change, climate oscillations, or other episodic events. Consequently, the interpretation of long-term detectability (i.e., the detectable area achieved with a 10-year monitoring duration in Figure 9) should be viewed with caution. In addition, the results presented here were based on synthetic model data. While Monte Carlo simulations with regards to the predictive algorithm strategy showed that realistic levels of measurement uncertainty had little effect on algorithm performance, field deployments may introduce additional challenges such as sensor drift and biofouling that could degrade measurement confidence over time. We contend this framework could be extended to examine how correlations in measurement errors would challenge signal detection, but we do not explicitly perform these calculations herein. Moreover, it is likely that there are processes acting in the real ocean that are not fully resolved in the model.

Despite these limitations, the detectability framework presented here is broadly applicable to other systems and can inform site-specific monitoring strategies for future OAE interventions. Expanding this approach to regions governed by different dominant processes could help to explore the range of optimal OAE monitoring designs. Future work could also incorporate machine

learning methods to improve predictive skill or reduce the required observational input for algorithm construction. Additionally, extending this framework to evaluate subsurface detectability would support a more comprehensive understanding of the vertical transport and fate of added alkalinity, as well as ecosystem perturbations. Together, these efforts can help to advance the science, optimization, and implementation of OAE and other mCDR monitoring strategies.

4.5 Conclusions

As an increasing number of mCDR technologies move toward field deployment, robust and scalable monitoring strategies will be essential to ensure transparency, safety, and scientific credibility. In this study, we developed and applied a detectability framework to evaluate the effectiveness of different observing strategies to detect OAE signals in the dynamic coastal environment of Sequim Bay. We leveraged a high-resolution biogeochemical model to compare three monitoring approaches that varied in measurement quality, frequency, duration, and analysis. Detection potential was strongly modulated by the interaction of OAE-induced signal strength, background natural variability, and the design of the observing platform.

Our results reinforce the importance of resolving natural variability to distinguish OAE-induced signals from background conditions. The single-measurement strategy yielded no detectable area even with our comparatively large simulated intervention, as the signal never exceeded the high level of noise associated with unresolved modes of natural variability for any of the measurable parameters. The long-term averaging strategy effectively detected OAE-induced changes in TA and $p\text{CO}_2$, but the resource demands of such deployments may limit scalability. The predictive algorithm monitoring strategy offered a cost-effective, scalable alternative, substantially reducing residual noise and expanding the spatial footprint of detectable area. The predictive algorithms were particularly effective at capturing the highly variable dynamics of

$p\text{CO}_2$, with the top-performing algorithms increasing detectable area by up to 300 times compared to the long-term averaging strategy. Notably, however, OAE-induced increases in DIC, a critical metric to quantify net carbon removal, remained undetectable for nearly all cases considered due to rapid signal dilution and long timescales of air-sea CO_2 equilibration.

These findings highlight the need for site-specific monitoring designs that align with local biogeochemical and physical dynamics. The optimal configuration will differ across sites and depend on the primary monitoring goals. Each carbonate chemistry variable provides a distinct perspective on the intervention, whether related to ecological impacts, ocean acidification mitigation, or net carbon uptake. Accordingly, observing strategies should be tailored not only to site characteristics, but also to the parameter most relevant to a given monitoring objective.

More broadly, our results point to a growing challenge for mCDR, where carbon accounting frameworks must reconcile the larger signals required for detection and credible verification with moderation and permitting constraints intended to prevent large-scale local impacts. In dynamic coastal systems, detection of DIC may be infeasible using current methods, calling for integrated approaches that combine modeling, monitoring, or revised verification frameworks. The detectability framework presented here offers a practical tool to support the design of scientifically rigorous and site-specific monitoring systems. As interest in OAE and other mCDR approaches grows, such tools will be essential to build carbon removal pathways that are both technically effective and verifiable.

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Chapter 5: Dissertation Summary

This dissertation integrates novel biogeochemical tools and approaches to advance our understanding of a rapidly changing ocean. Across three studies, I explored critical areas where ocean biogeochemistry intersects with climate change and marine ecosystems from the perspectives of ocean acidification, habitat suitability, and marine carbon dioxide removal (mCDR). This dissertation highlights how new observational and analytical tools enable new insights into ocean change.

In Chapter 2, I reconstructed ocean acidification over the industrial era in the California Current System using a high-precision boron isotope ($\delta^{11}\text{B}$) pH proxy preserved in cold-water corals. This work represents the application of the most precise $\delta^{11}\text{B}$ proxy in cold-water corals to date, enabled by species-specific calibration. By pairing these proxy records with output from a regional biogeochemical model, I quantified the magnitude of acidification over the industrial era and identified the biogeochemical drivers underlying the observed changes. This work extends the observational record of acidification beyond the instrumental era in the California Current and reveals how anthropogenic CO_2 interacts with natural carbon pools in upwelling systems. These records show that the CCS has experienced amplified acidification over the industrial era, significantly exceeding the rise in atmospheric CO_2 . This amplification is primarily driven by a thermodynamic response in the carbonate system that amplifies anthropogenic change in high-carbon regimes. Model projections indicate this trend will continue, with acidification outpacing atmospheric CO_2 through 2100. The study demonstrates the power of combining paleo-proxy reconstructions with numerical models to quantify long-term anthropogenic signals in complex, upwelling environments.

Chapter 3 builds on the growing availability of autonomous biogeochemical observations by incorporating four-dimensional (4D) data products into species distribution models (SDMs). Using depth-resolved BGC-Argo data products and machine learning methods, I modeled the habitat of North Pacific albacore tuna, a highly migratory species. The resulting SDMs incorporated both deterrents (e.g., low oxygen) and attractants (e.g., chlorophyll, particulate organic carbon) to predict habitat suitability across space, time, and depth. The inclusion of 4D biogeochemical predictors significantly improved model performance and revealed strong seasonal shifts in habitat extent. This work advances the field of marine species distribution modeling by demonstrating the value of new depth-resolved, biogeochemical tools to improve habitat predictions for the first time. The framework presented can be applied across diverse contexts in the marine environment, from enhancing bycatch avoidance and catch per unit effort estimates, to informing climate-driven habitat shifts and ecosystem-based fisheries management.

In Chapter 4, I evaluated the detectability of ocean alkalinity enhancement (OAE), a proposed mCDR strategy, in a dynamic coastal environment of the Salish Sea. Using a high-resolution biogeochemical model, I applied a detectability framework to assess the effectiveness of three monitoring approaches that varied in measurement quality, frequency, and duration. Detection potential was strongly influenced by the interaction of signal strength, background variability, and observational design. The predictive algorithm monitoring strategy offered a promising approach by leveraging routinely measured physical and biogeochemical variables to estimate carbonate chemistry. This strategy reduces the need for intensive direct measurements across the entire spatial domain and supports monitoring tailored to local system dynamics. These results indicate that predictive algorithms are particularly valuable for parameters that exhibit high natural variability, such as $p\text{CO}_2$. The detectability framework presented here provides a practical

tool for designing site-specific monitoring strategies aligned with regional dynamics and natural variability. As mCDR strategies progress from theory to field trials and full-scale deployment, such tools will be essential to build carbon removal pathways that are both technically effective and verifiable.

These three studies illustrate the utility of novel biogeochemical tools to monitor, investigate, and respond to ocean change. While each chapter focuses on a distinct aspect, they are unified by a shared goal: to improve the resolution, relevance, and applicability of biogeochemical information to better understand a changing ocean. This dissertation contributes to the growing body of work that emphasizes the value of expanding spatial and temporal observations, interdisciplinary methods, and high-resolution models to advance ocean science.

Looking forward, these approaches have the potential to inform policy, conservation, and climate mitigation strategies. As climate change progresses, the need for timely, accurate, and reliable information about the ocean's biogeochemical state will become increasingly important. Continued innovation in how we observe, interpret, and apply biogeochemical data will be essential for supporting resilient marine ecosystems and effective climate action in the decades ahead.

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Appendix A: Supplementary Materials for Chapter 2

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Supplementary Methods

1. Coral Calibration and Data Preparation

Historic samples of *Balanophyllia elegans* (*B. elegans*) were collected by the R/V *Albatross* between 1888 and 1894, and by Ernest Harrison Quayle in 1932 (Figure S1). All historic samples were archived in the Smithsonian National Museum of Natural History. In the Salish Sea, modern corals were collected from nearby locations in 2020 (Figure S1). The raw and location-averaged skeletal $\delta^{11}\text{B}$ data can be found in Figure S2. Skeletal $\delta^{11}\text{B}$ data can also be found in Supplementary Data.

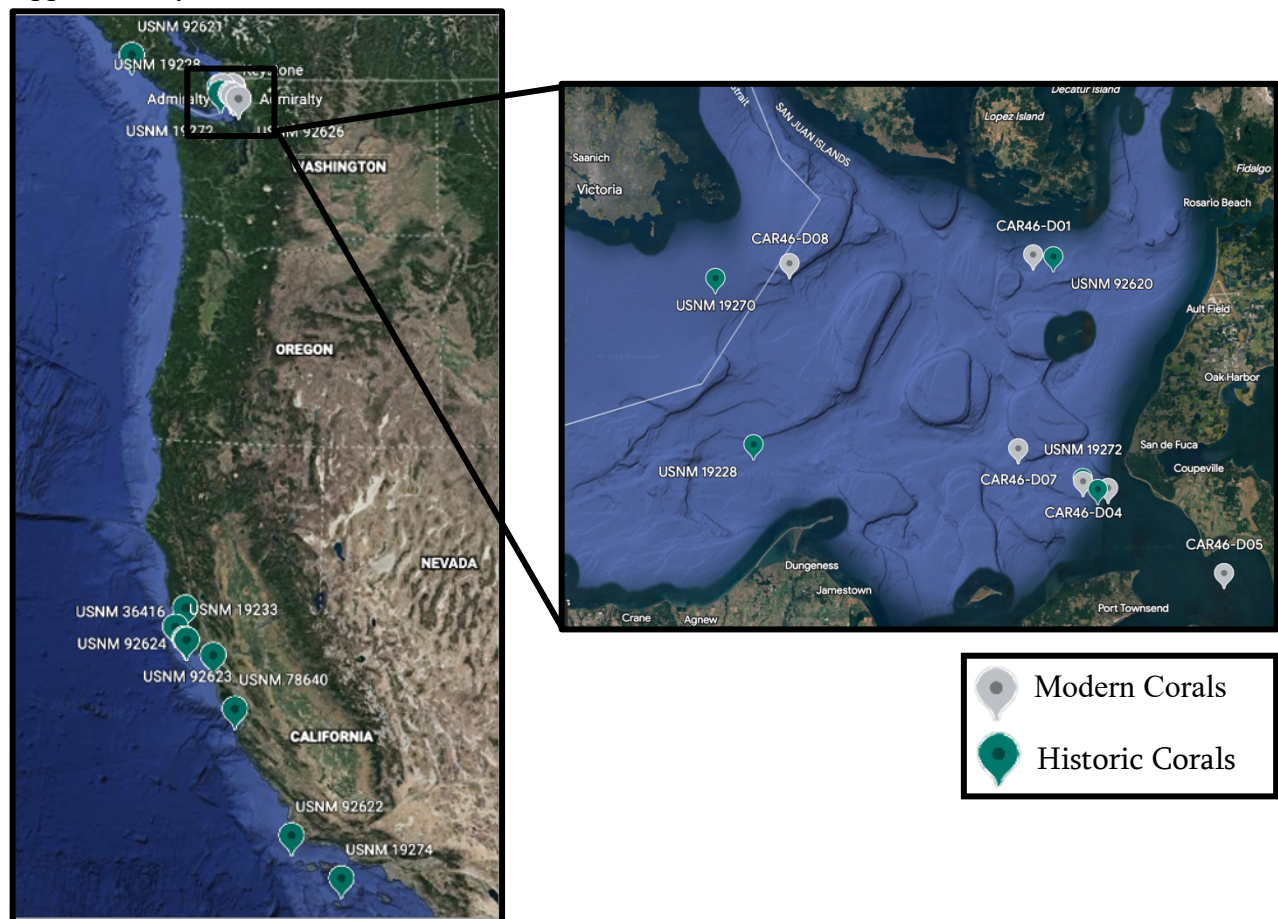


Figure S1 | Map of historic and modern coral locations along the US West Coast (left) and the Salish Sea (right). Historic corals were collected between 1888 and 1894 with the exception of USNM 78638 and 78640 (1930s) and archived in the Smithsonian National Museum of Natural History (green). Modern corals were collected from nearby locations in the Salish Sea aboard the University of Washington R/V *Rachel Carson* in 2020 (gray). Location ID's specified in Supplementary Data.

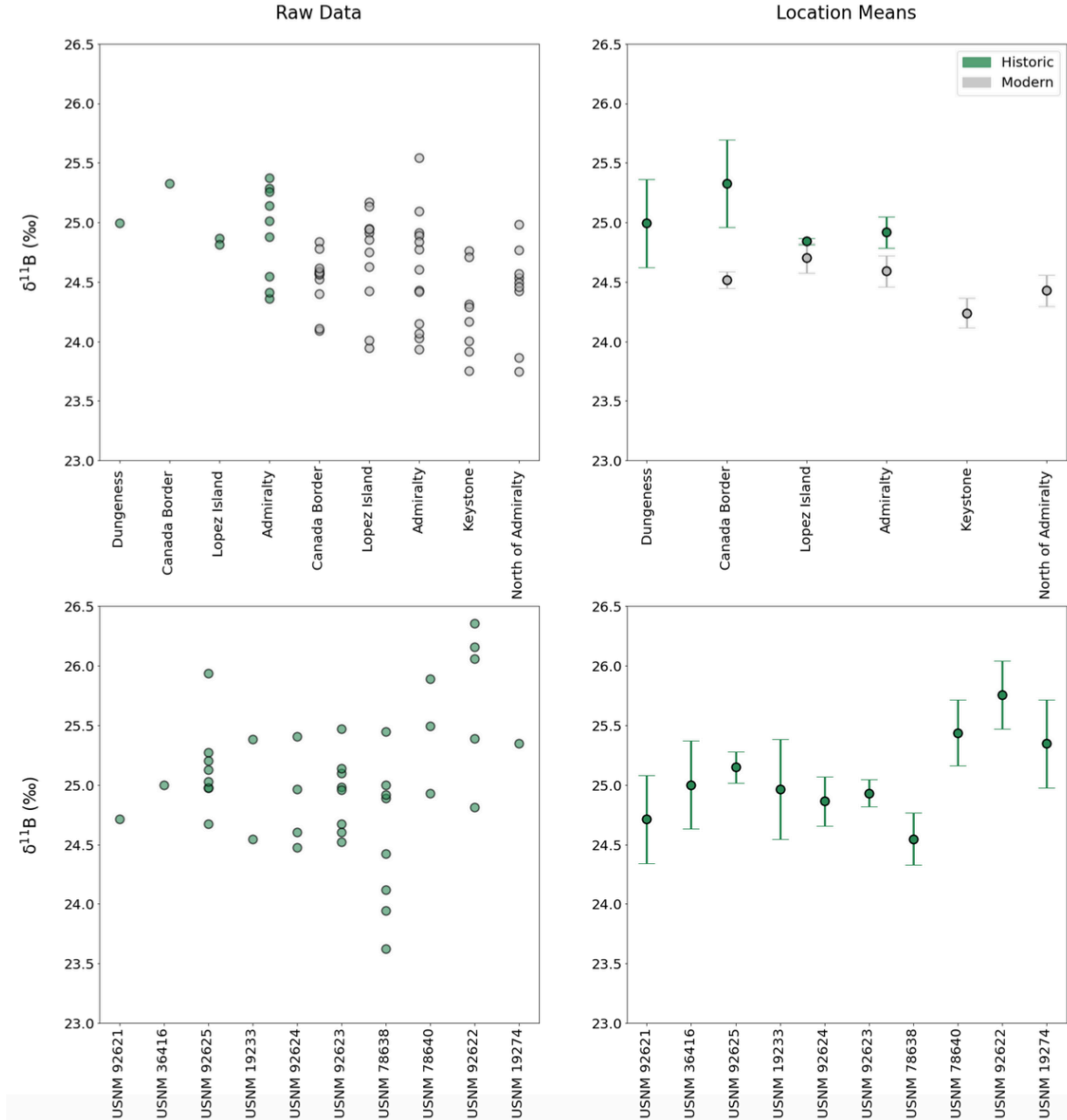


Figure S2 | Skeletal $\delta^{11}\text{B}$ data from the Salish Sea (top row) and the US West Coast (bottom row). *Left column*: Raw skeletal $\delta^{11}\text{B}$ at individual locations. Each point represents a sample from a single coral. Historic measurements are shown in green and modern measurements shown in gray. Historic Salish Sea $n = 13$; modern Salish Sea $n = 52$; historic West Coast $n = 41$. *Right column*: Location-averaged $\delta^{11}\text{B}$ data. Error bars represent the standard error of the mean at each location. If only one coral was sampled, the population standard deviation was used. The population standard deviation was calculated by averaging the sample standard deviation at every location where 8 or more corals were collected. USNM 78638 was excluded from this calculation due to the high variability associated with tide pools.

Prior to interpreting the signals implied by the coral records, several steps are taken to prepare the data for analysis. First, we consider whether the coral data in the Salish Sea are representative of the whole basin or are location specific (Supplementary Methods 1.1). Modern coral data in the Salish Sea are then compared with modern bottle data to determine if corals in the wild match culture-based calibrations and assess the need for an observation-coral offset (Supplementary Methods 1.2). Application of the observation-coral offset and assumptions regarding the coral metadata are described in Supplementary Methods 1.3 and 1.4, respectively.

1.1 Averaging coral data across locations in the Salish Sea

Historic and modern coral data from the Salish Sea span multiple locations and depths (Supplementary Data, Figure S1). Given the spatial distribution, we consider whether the data are representative of the whole Salish Sea or are location specific. To evaluate the similarities and differences among locations, carbonate chemistry is analyzed from the Live Ocean model (<https://faculty.washington.edu/pmacc/LO/LiveOcean.html>), a product from the University of Washington Coastal Modeling Group led by Dr. Parker MacCready that simulates seawater properties in the Salish Sea. Parameters including DIC, TA, salinity, and temperature are analyzed over three years (2018–2020) and analysis of variance (ANOVA) tests are performed to assess the difference in means at each location. A Tukey Honestly Significant Difference test is then used to determine which locations are statistically different from each other. Across parameters, the locations near Admiralty Inlet are statistically indistinguishable, excluding the modern coral location near Keystone Jetty, which does not correspond to a historic coral location anyway. Admiralty Inlet locations are statistically different from those in the Strait of Juan de Fuca, as makes sense due to path of circulation.

We average the historic and modern coral data together due to the clustering of coral collection locations near Admiralty Inlet, meant to represent a central location in the Salish Sea. A statistical test of modern coral data also revealed no significant difference between corals collected near Admiralty Inlet from those in the Strait of Juan de Fuca. The extra detail gained from analyses separated by location does not add new insights to 20th century acidification in the Salish Sea. Including historic and modern coral data outside of Admiralty Inlet in the analysis does not change the ultimate conclusions regarding 20th century acidification.

1.2 Seasonal cycles of carbonate chemistry in the Salish Sea to inform observation-coral offset

Upon averaging the coral data across locations in the Salish Sea, the modern coral data are compared to modern observational data to determine if modern coral data in the wild match culture-based calibrations. To align the coral and observational records, we establish the observation-coral offset with data from Admiralty Inlet due to the abundance of both modern coral data and bottle data. Observational data (pH, DIC, TA, temperature and salinity) were collected from Admiralty Inlet (Washington Ocean Acidification Center (WOAC) cruise station 21), sampled on cruises between 2008 and 2018. While this dataset provides a glimpse into annual averages of carbonate chemistry parameters, it is necessary to fit polynomial curves to the data to estimate average conditions across seasons due to the sparsity of samples. The parameter averages obtained from these climatological curves produce the values to which we compare the coral data and calculate the observation-coral offset.

Seasonal cycles for DIC, TA, temperature, and salinity are estimated from WOAC station 21 bottle data below 50 meters depth, the same depth of coral collection at Admiralty Inlet (Supplementary Data). Upon capturing an annual snapshot of parameters at >50 meters depth at Admiralty Inlet, third order polynomials are fitted to the DIC, TA, and salinity data. A polynomial

fit is chosen to capture the non-periodic nature of the seasonal cycles. Annual and summer (June-August) averages of each parameter are calculated from the seasonal fitted curves (Table S1). The shapes of the seasonal cycles are confirmed by modeled three-year time series from the LiveOcean model at the same location and depth. While the tails of the polynomial fits include extreme values in some cases, they do not appreciably impact the summer or annual averages. To confirm, we also calculated a summer average informed by WOAC station 21 bottle data at >50 meters depth from July only (Table S1). The July data average aligns with parameter estimates obtained from the summertime seasonal fitted curves. The average pH values obtained from the Admiralty Inlet seasonal cycles form the foundation on which we base the observation-coral pH offset.

Table S1 | The top two rows represent annual and summer averages of pH, TA ($\mu\text{mol/kg}$), DIC ($\mu\text{mol/kg}$), temperature ($^{\circ}\text{C}$), and salinity (PSU) at >50 meters depth at Admiralty Inlet in the Salish Sea. Values represent the annual and summertime means of the seasonal cycle fits estimated from WOAC bottle data. The bottom row represents summer averages of pH, TA, DIC, temperature, and salinity at >50 meters depth informed by WOAC bottle data from July only.

	DIC ($\mu\text{mol/kg}$)	pH (total)	TA ($\mu\text{mol/kg}$)	Temp ($^{\circ}\text{C}$)	Sal (PSU)
Seasonal Fitted Curve (Annual Average)	2116	7.73	2165	8.82	31.9
Seasonal Fitted Curve (Summer Average)	2120	7.75	2177	8.84	32.1
July Data Only (Summer Average)	2106	7.75	2165	9.6	31.8

1.3 Applying the observation-coral pH offset and summertime growth of *Balanophyllia elegans*

As described in Supplementary Methods 1.2, the observation-coral pH offset is determined by comparing the annual and summertime averages of bottle data to modern coral data at Admiralty Inlet in the Salish Sea. The averages obtained from observational data are described in Supplementary Methods 1.2 and can be found in Table S1. The average coral-based pH is

determined from the skeletal $\delta^{11}\text{B}$ -seawater pH relationship determined from a controlled laboratory experiment (Gagnon et al. 2021). The summertime average of DIC from observational data (Supplementary Methods 1.2) is used to obtain a $\delta^{11}\text{B}$ DIC-correction value (Methods, Equation 1). The $\delta^{11}\text{B}$ DIC-correction is then substituted into the *B. elegans* calibration equation to calculate a coral-based pH estimate of 7.85 (SE = 0.013) (Methods, Equation 2). pH offsets of -0.127 (annual offset) and -0.101 (summertime offset) are attained by calculating the difference between the coral-based pH estimate and the observational pH data (Table S2).

Table S2| Annual and summer pH offsets between observational data and coral data (observational average – coral average). Annual observational pH average is from a fitted seasonal cycle curve informed by WOAC station 21 bottle data at >50 meters to match the coral depth of collection. Summer observational pH average is obtained from WOAC station 21 bottle data at >50 meters from July only. The coral-based pH average is calculated from modern data at locations near Admiralty Inlet.

Summer pH Offset	Annual pH Offset
-0.101	-0.127

We believe the laboratory-derived $\delta^{11}\text{B}$ -pH calibration requires an offset when applied to wild corals due to seasonal growth biases not replicated in the lab experiments. Several studies suggest that some coral species exhibit growth biases in the summer and do not capture an annual, mean state of surrounding seawater. For instance, Fadlallah 1983 discovered that food availability, as a result of upwelling, could promote growth and larval settlement of *B. elegans*. Jantzen et al. 2013 also found that *Desmophyllum dianthus*, another species of cold-water coral, exhibit higher growth rates in the summer compared to the winter. Beck 2018 confirmed these seasonal growth patterns in *D. dianthus* and determined that the high summer growth rates are likely due to seasonal differences in food availability during peak upwelling of nutrient-rich waters. In addition, the

reproduction cycle of *D. diantus* typically occurs in August and may also explain the reduced growth rates in winter due to the redirection of energy towards reproduction.

In the Salish Sea, the observation-coral pH offset assuming annual versus summer averages is within 0.03 pH units and has little influence on conclusions about 20th century acidification (Table S2). The similarity between the summer and annual offsets is demonstrated in the pH climatology, where the summer data span the inflection point and are similar in magnitude to the annual average (Figure S3). To calibrate the coral records in the wild, we apply the summer pH offset = -0.101 to all pH data produced by the coral record.

While the summer and annual pH averages are approximately equivalent in the Salish Sea, locations along the West Coast have different climatologies. Figure S3 shows pH climatologies from the Salish Sea and every coral location in the CCS. The pH seasonal cycle from the Salish Sea is informed by WOAC bottle data, whereas the pH climatologies along the West Coast represent 7-year Regional Ocean Modeling System (ROMS) output averages from December 2000–November 2007. The West Coast locations experience low-pH values earlier in the season compared to the Salish Sea. As a result, the annual and summer averages along the West Coast differ whereas they are approximately equivalent in the Salish Sea. To align the historic West Coast coral record, we assume that the corals also capture a summer average of surrounding seawater conditions.

Alignment of the modern observational record and modern coral record allows us to obtain absolute values of pH. While much can be gleaned from the relative pH difference produced by historic and modern coral pairs in the Salish Sea, determining a pH offset applicable to all wild corals allows us to anchor the West Coast $\delta^{11}\text{B}$ data, where repeat occupations to collect corals in the modern era have not been achieved.

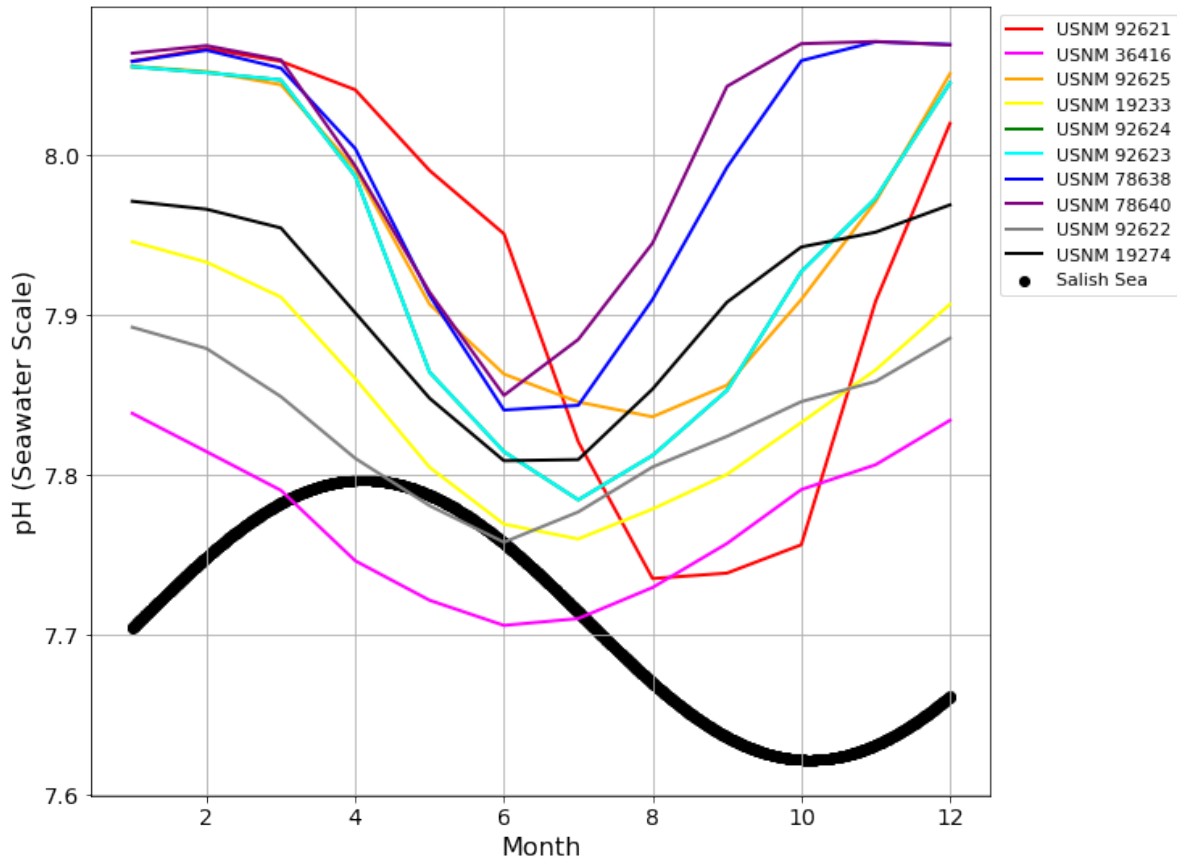


Figure S3| pH climatologies from the West Coast and Salish Sea coral locations. The Salish Sea seasonal cycle is constructed from WOAC bottle data and a curve fitting method at Admiralty Inlet (Supplementary Methods 1.2). West Coast pH climatologies are calculated from a 7-year modeled average in a Regional Ocean Modeling System (ROMS, Methods) from November 2000–December 2007. While Admiralty Inlet experiences lowest pH in the fall, the West Coast experiences lowest pH in the summer, generally from June to August. The delay in acidified conditions in the northern CCS is also apparent in the lagged pH decline at our northernmost West Coast location, near the mouth of the Salish Sea (USNM 92621). This is likely due to the accumulation of respiration and acidified conditions through the upwelling season at these locations where there is longer retention. While the annual pH average at Admiralty Inlet is approximately equal to the summer pH average, the annual and summer pH averages along the West Coast diverge. Since the corals are presumed to grow preferentially in the summer during the upwelling season, the observation-coral pH offset is established from observational summer averages (Table S1). Therefore, the historic West Coast coral data are compared to modeled summer averages.

1.4 Inferring unknown information about West Coast coral locations

Of the ten coral locations along the outer West Coast, eight of the sites were collected by the R/V *Albatross I*. Existing records from the expedition contain pertinent information including

latitude, longitude, and depth of collection (Supplementary Data). The two remaining coral sites, USNM 78638 and USNM 78640, were collected by Ernest Harrison Quayle (1891–1956). While the general locations of the sites were recorded, information including depth, latitude, and longitude are unknown. Only USNM 78640 has a year of collection in 1932.

Due to the lack of information, several inferences are made. First, it is presumed that USNM 78638 was also sampled around 1932. After embarking on the Whitney South Sea Expedition until 1922, Quayle returned to the US with a keen interest in coral reefs. Quayle moved to California in 1931 at the peak of his coral research and published an article on fossil corals in the Transactions of the San Diego Society of Natural History in 1932 (https://data.library.amnh.org/archives-authorities/id/amnhp_1002468). Therefore, we assume that USNM 78638, located near San Francisco, California, was also collected in the early 1930s. Second, the depths of collection for both USNM 78638 and USNM 78640 are presumed to be ~25 meters. USNM 78638 was reportedly collected at a beach and a vessel was not likely used. Third, latitudes and longitudes for both locations were chosen close to the coast given the probable shore-based collection method. Lastly, although the corals were collected in the 1930s, we still compared the coral data to the 1891–1904 ROMS output since the vast majority of anthropogenic CO₂ was emitted later in the 20th century.

The corals at site USNM 78638 were collected from a tidepool near Moss Beach, California—a highly variable environment. This was the only location where modern $p\text{CO}_2$ appeared lower than historic $p\text{CO}_2$, likely due to the extreme variability of the intertidal zone that influenced the $\delta^{11}\text{B}$ skeletal signatures. Given this high natural variability, long-term signals can be obscured by environmental noise. Consequently, these data were not heavily weighted in our

analysis or conclusions. Had they been central to our study, additional efforts to constrain collection dates and reduce uncertainty would have been undertaken.

Supplementary Discussion

1. Coral Record Interpretation and Comparison to Model and Other Proxy Estimates

The coral records in both the Salish Sea and the outer West Coast suggest that the CCS has experienced amplified acidification over the 20th century, exceeding the rise in atmospheric CO₂. We contextualize the coral records with several independent sources to determine the main driver of the acidification signal.

In the Salish Sea, our historic-modern coral pairs imply that pH decreased -0.095 units (standard error of the difference between means $\sigma_{M_1-M_2} = 0.025$) and $p\text{CO}_2$ increased 172 ± 41 μatm over the industrial era. In Supplementary Discussion 1.1, we invoke process-based arguments to assess the likelihood of various mechanisms to explain the coral data. We also compare the coral record with a box model of the Salish Sea, for which a ROMS model sets the composition of upwelled water entering the box model, to consider the impact of estuarine processes on the 20th century signal (Supplementary Discussion 1.2).

Along the outer West Coast, we directly compare coral estimates with ROMS, which resolves the coastal CCS. Historic model summertime averages of $p\text{CO}_2$ are compared to historic coral $p\text{CO}_2$ at every location. The corals demonstrate that the CCS has experienced amplified acidification over the industrial era, and even capture the trend of more severe amplified acidification with depth. In Supplementary Discussion 1.3, we describe the alignment between the coral- and model-based estimates of 20th century acidification. While the corals generally reproduce modeled predictions, the Santa Barbara Basin locations diverge most from the model and correspond to a much lower historic $p\text{CO}_2$ than that presented in the model. Supplementary

Discussion 1.4 describes a previously published proxy record of carbonate chemistry in the Santa Barbara Basin that also indicates a larger magnitude of 20th century acidification.

1.1 Process-based arguments to assess 20th century acidification in the Salish Sea

As described in Supplementary Notes 1.2, several processes influence carbonate chemistry in the Salish Sea. Figure S4 captures the implied changes in carbonate chemistry over the 20th century produced by the coral data assuming the dominant mechanism is 1) calcification/dissolution, 2) mixing source waters, 3) shifts in biological activity, and 4) CO₂ invasion. Below, we discuss the likelihood of each process serving as the driver of 20th century acidification.

Shift in calcium carbonate formation and dissolution rates

The formation of calcium carbonate describes the process by which marine organisms build their shells from calcium ion and carbonate ions in seawater. Calcium carbonate formation implies consumption of 2 $\mu\text{mol/kg}$ TA for every 1 $\mu\text{mol/kg}$ DIC, resulting in increased $p\text{CO}_2$ and acidity. The coral records support a decrease in pH, which indicates that calcium carbonate formation would have had to increase to explain the observed pH change. However, evidence suggests that calcification actually declines in response to corrosive conditions ($\Omega_{\text{aragonite}} < 1$) that accompany pH levels < 7.75 in the CCS (Feely et al. 2016; Kroeker et al. 2013). Assuming the physiology of calcification has not changed, it is unlikely that shifts in calcification explain the 20th century change in pH implied by the coral records given these two effects oppose one other.

Shift in source water mixing

We also consider whether the coral-based ΔpH can be attributed to a shift in the mixing ratio between oceanic and riverine sources. As discussed in Supplementary Notes 1.2, variation in

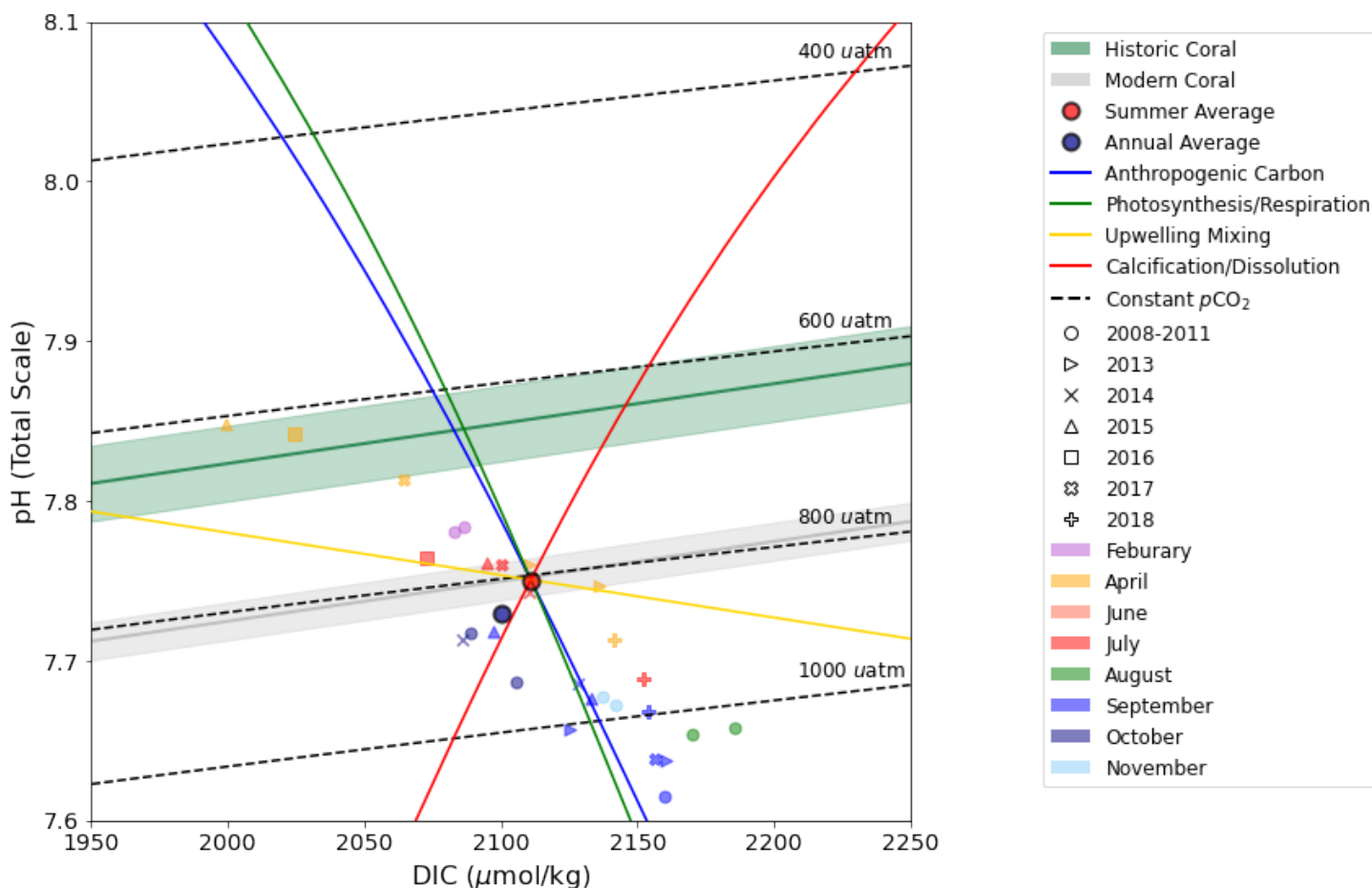


Figure S4 | 20th century changes in $p\text{CO}_2$ ($\Delta p\text{CO}_2$) and pH (ΔpH) in the Salish Sea. Historic (green) and modern (gray) coral records averaged across locations in the Salish Sea (Equations 1 and 2). Changes in seawater chemistry over the past century are bounded by these two lines. Error bands represent standard errors of the mean. Black dashed contours represent lines of constant $p\text{CO}_2$. Note that contours of $p\text{CO}_2$ and the coral-derived bounds on $p\text{CO}_2$ are roughly parallel, so the coral data act to constrain $p\text{CO}_2$ tightly without additional information. The coral record indicates that $p\text{CO}_2$ increased by 172 μatm between the 1890s and 2020 ($\pm 41 \mu\text{atm}$ standard error of the difference between means $\sigma_{M_1-M_2}$). Colored markers represent observational data from 70 meters depth at the Washington Ocean Acidification Center (WOAC) station 21 (Alin et al. 2021). The seasonality in observational data is primarily driven by mixing and freshwater inputs. Summer average (JJA) seawater properties from WOAC station 21 are represented by the red dot: pH = 7.75, DIC = 2106 $\mu\text{mol/kg}$, TA = 2165 $\mu\text{mol/kg}$ (Table S1). To align the modern coral record with the observational data summer average, a pH offset of -0.10 has been applied to both the historic and modern coral records. Colored lines represent the ways that key biogeochemical processes affect pH and DIC: Seawater CO_2 invasion (blue), primary production and respiration (green), upwelling and mixing source waters (yellow), and calcium carbonate formation and dissolution (red) (Supplementary Discussion 1.1). Assuming anthropogenic carbon is the main driver of the 20th century change, we calculate changes in pH and DIC from the intersections of the seawater CO_2 invasion line and historic and modern coral records. The coral data estimate $\Delta\text{pH} = -0.095$ (± 0.025 standard error of the difference between means $\sigma_{M_{\text{Modern}}-M_{\text{Historic}}}$) and $\Delta\text{DIC} = 28 \mu\text{mol/kg}$ for the bottom waters of the Salish Sea.

Salish Sea carbonate chemistry is strongly influenced by water mass mixing. This foundational understanding of seasonal variability today provides an important constraint to assess the likelihood of seasonal patterns as the dominant driver of 20th century change. As seen in Figure S4, seasonal variability in the modern, observational pH data is on the order of ΔpH predicted by the corals; therefore, we explore the possibility of an amplified season to explain 20th century acidification.

In general, observational pH data from the spring and summer months overlap with values implied by the historic coral record (Figure S4). If a shift in mixing (ie more freshwater influx in the historic era) were the main driver of 20th century acidification, then the mean state of the Salish Sea in the early 1900s would resemble modern-day spring and summer carbonate chemistry. As salinity in the Salish Sea is lower in the spring and summer, and salinity serves as a conservative parameter to trace water mass mixing, our shift in mixing hypothesis implies that river flow must have been larger in the early 20th century relative to today. Performing a two end-member mixing system of equations, the observational data suggests that river discharge must have declined by ~20% over the past century to explain the coral-based ΔpH . A best-fit linear regression was applied to Skagit River discharge data from 1940–2020 (USGS Skagit River gauge 1200500). The first three years of the 80-year time series were excluded from the linear regression due to an anomalously severe drought and several consecutive low-precipitation years that biased the slope (Washington State Governor’s Report). This analysis suggests that discharge has declined by only ~5% over the past 130 years, extrapolated back in time to 1890.

This extrapolation likely underestimates changes in river discharge, as the river gauge was put in place after major dam construction on the Skagit River in the early 20th century. This same analysis was applied to another USGS River Gauge (12194000) that extends further back in time

to 1925, however this analysis reveals that river discharge declined by ~6%. Thus, while dam construction likely influenced carbonate chemistry in the Admiralty Inlet area, the coral data suggests an unusually large shift in river discharge would have had to occur over the past 130 years to explain the ΔpH implied by the corals. While dam construction and river discharge likely influenced carbonate chemistry to some extent in the Salish Sea, they are not sufficient to explain the 20th century change in pH.

Shift in primary production and biological activity

The biological activity and CO_2 invasion process lines do not diverge substantially, indicating that the effects of these processes on ΔpH , ΔDIC , and $\Delta p\text{CO}_2$ are approximately equal. Only exceptional shifts in biological activity and a historic ocean with more respiration could have produced the magnitude of change observed in pH, $p\text{CO}_2$, and DIC produced by the corals. However, stable isotope analyses of marine-derived organic matter in the Salish Sea over the past century reveal no significant trend in biological activity (Johannessen, Macdonald, and Strivens 2021). Therefore, anthropogenic carbon is the driving force of 20th century acidification in the Salish Sea.

1.2 Comparison between Salish Sea box model and coral-based $\Delta p\text{CO}_2$

The process-based arguments described in Supplementary Discussion 1.1 provide useful constraints to evaluate the main driver of 20th century acidification. In addition to these lines of evidence, we compare the coral-based estimate of acidification to a simple steady-state box model representing the Salish Sea. Since our ROMS of the CCS does not resolve the Salish Sea, ROMS sets the composition of upwelled waters that enter the box model. The box model predicts both historic and modern DIC in the Salish Sea assuming only two processes, estuarine circulation of

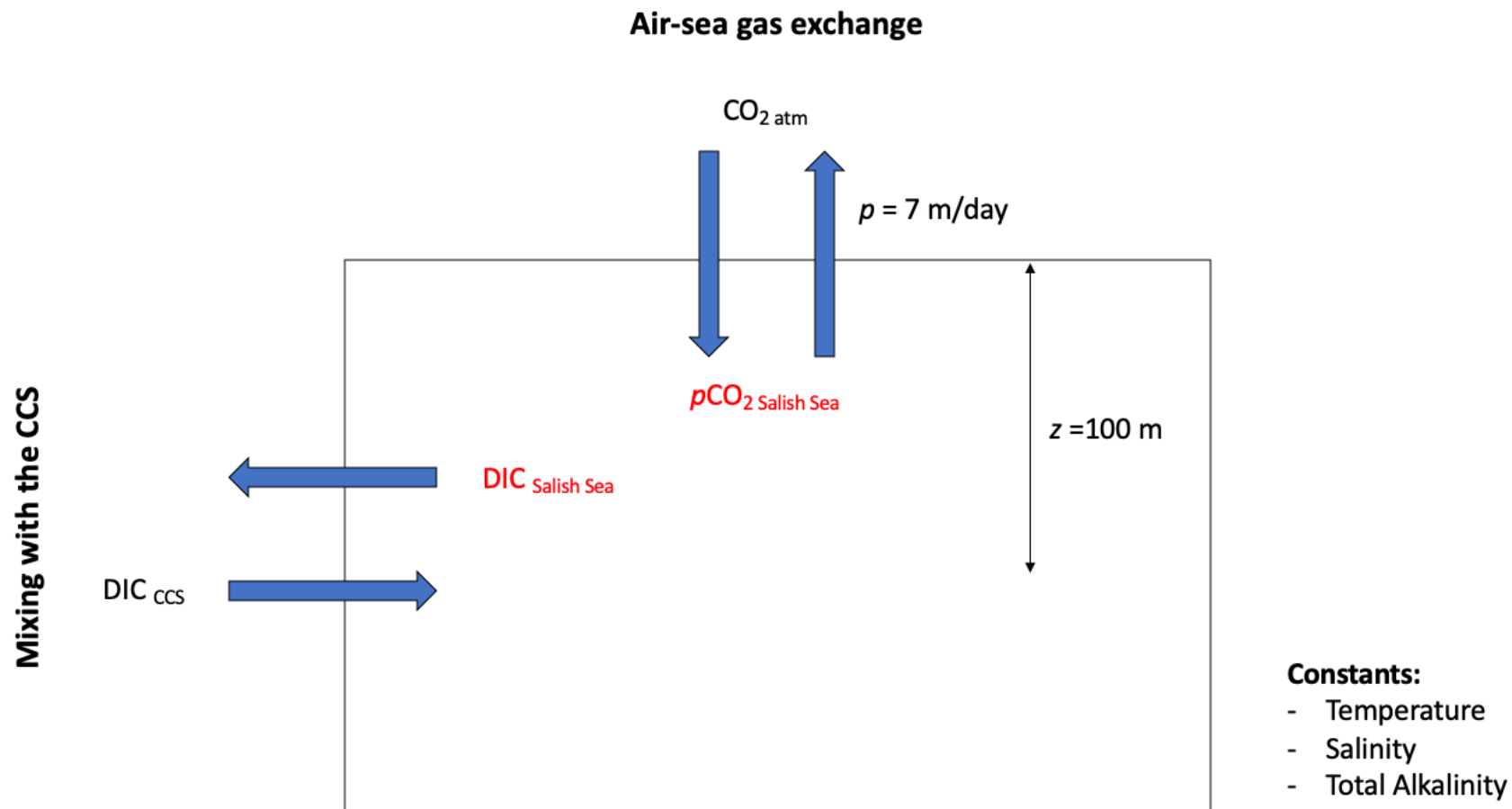


Figure S5| Schematic of the simple steady-state box model to calculate $\Delta p\text{CO}_2$ in the Salish Sea. We assume that carbonate chemistry in the Salish Sea is influenced by two processes including 1) exchange with upwelled waters from the CCS and 2) air-sea gas exchange. This simple box model is solved in both the historic and modern eras to produce an estimate of $\Delta p\text{CO}_2$. This estimate is then compared to the coral-based estimate of $\Delta p\text{CO}_2$ in the Salish Sea.

upwelled waters from the CCS and air-sea gas exchange. A schematic of the box model can be found in Figure S5.

As demonstrated in Supplement Equation (1), the steady-state simple box model is a function of:

Supplementary Equation (1):

$$\frac{dDIC}{dt} = \frac{1}{\tau}(DIC_{CCS} - DIC_{Salish\ Sea}) + \frac{p}{z}(K_0 \times pCO_{2\ atm} - pCO_{2\ Salish\ Sea})$$

DIC of the inflowing, upwelled waters that enter the Salish Sea (DIC_{CCS}), DIC of the Salish Sea or outflowing water ($DIC_{Salish\ Sea}$), gas transfer velocity that governs air-sea gas exchange (p), the mixed layer depth (z), atmospheric CO_2 ($pCO_{2\ atm}$), Henry's Law equilibrium constant (K_0), the dissolved concentration of CO_2 in the Salish Sea ($pCO_{2\ Salish\ Sea}$), and residence time in the Salish Sea (τ). Temperature, salinity, and total alkalinity are assumed to be constant in the outflowing and inflowing water masses and in both the historic and modern eras. Since $pCO_{2\ Salish\ Sea}$ is a function of $DIC_{Salish\ Sea}$ and total alkalinity, Supplementary Equation (1) can be solved for $DIC_{Salish\ Sea}$ alone under a steady-state scenario.

DIC_{CCS} :

Modeled DIC of the upwelled waters that enter the Salish Sea is obtained from ROMS for a 36 km x 36 km area at 150–200 meters depth at the mouth of the Strait of Juan de Fuca by calculating a 7-year summertime (JJA) average in both the historic and modern eras. While the historic timestamps of the coral and model records are offset by ~10 years, we assume the slow progression of CO_2 accumulation in the preindustrial era nullifies the need for a correction. To account for the modern temporal offset (corals collected 2020; model output ~2005), during which rapid carbon accumulation occurred, we advance the modeled DIC_{CCS} from 2005 to 2020 to match the collection date of the modern corals and assume that this advance follows the known rise in atmospheric

CO₂. Given that the water entering the Salish Sea from the CCS is 25 years old (Murray et al. 2015), the water mass represented in the modern model simulation was last in contact with the atmosphere in 1980. To augment modeled DIC from 2005 to 2020, we assume the waters entering the Salish Sea in 2020 were last in contact with the atmosphere in 1995 (CO_{2 atm} 1995 = 360 μatm; ΔCO_{2 atm} 1980–1995 = 21 μatm). We quantify the impact of this anthropogenic carbon on DIC as described in Methods, Equations 3 and 4.

CO_{2 atm}:

Atmospheric CO₂ was 295 and 415 μatm in the historic (1900) and modern (2020) time periods, respectively.

Temperature, salinity, and total alkalinity:

To isolate the impact of anthropogenic carbon on carbonate chemistry, temperature, salinity, and total alkalinity are assumed to be constant between the historic and modern time periods. It is also assumed that these parameters are equivalent in the inflowing and outflowing water masses. These values are informed by July averages of observational bottle data at Admiralty Inlet from the Washington Ocean Acidification Center (Table S1).

p:

The piston velocity, or the gas transfer velocity, is related to wind speed and describes the rate at which air-sea gas exchange occurs. Wind speed in the Strait of Juan de Fuca averages ~11–13 miles per hour, which corresponds to a gas transfer velocity of ~7 m/day (Donelan and Soloviev 2016).

z:

The mixed layer depth is assumed to be 100 meters. This value is informed by salinity and temperature profiles from WOAC observational bottle data in the Salish Sea and CTD casts from NANOOS (Northwest Association of Networked Ocean Observing Systems) near Admiralty Inlet.

τ :

The residence time of the Salish Sea is equivalent to the exchange flow rate divided by the box model volume. The volume of our box model, defined by the region between the mouth of the Strait of Juan de Fuca to Admiralty Inlet (where a majority of our corals are located), is 150,000 km x 25 km x 150 m. The exchange flow rate at the mouth of the Strait of Juan de Fuca is estimated to be 140,000 m³/s (MacCready et al. 2021) whereas the exchange flow rate at Admiralty Inlet is estimated to be 10,000–20,000 m³/s (Sutherland et al. 2011). An exchange flow rate representative of our simple box model is calculated by weighting the mouth exchange flow and Admiralty Inlet exchange flow by 2/3 and 1/3, respectively. This yields a weighted residence time of ~65 days. To account for uncertainties in the calculation of this residence time, we perform a sensitivity analysis at 45, 65, and 85 days.

Results:

We calculate $\Delta p\text{CO}_2$ in the Salish Sea from $\text{DIC}_{\text{Salish Sea}}$, TA, temperature, and salinity using an independent carbonate chemistry solver in Python. We calculate the $\Delta p\text{CO}_2$ at $\tau = 65$ days and the standard error of the mean of the sensitivity analyses to yield $\Delta p\text{CO}_2 = 185 \pm 15 \mu\text{atm}$. This aligns with the coral-based estimate of $\Delta p\text{CO}_2$ in the Salish Sea, suggesting that anthropogenic carbon and thermodynamic chemical equilibrium effects, modulated by estuarine circulation and air-sea gas exchange in the estuary, can explain the 20th century signal.

1.3 Comparison between West Coast model and coral records of acidification

Along the West Coast of the US, we directly compare coral estimates with ROMS output, which resolves the coastal CCS. The ROMS resolves carbonate chemistry parameters (Figure S6) and the magnitude of acidification over the 20th century (Methods, Figure S7) at varying depths (Methods, Figure S8).

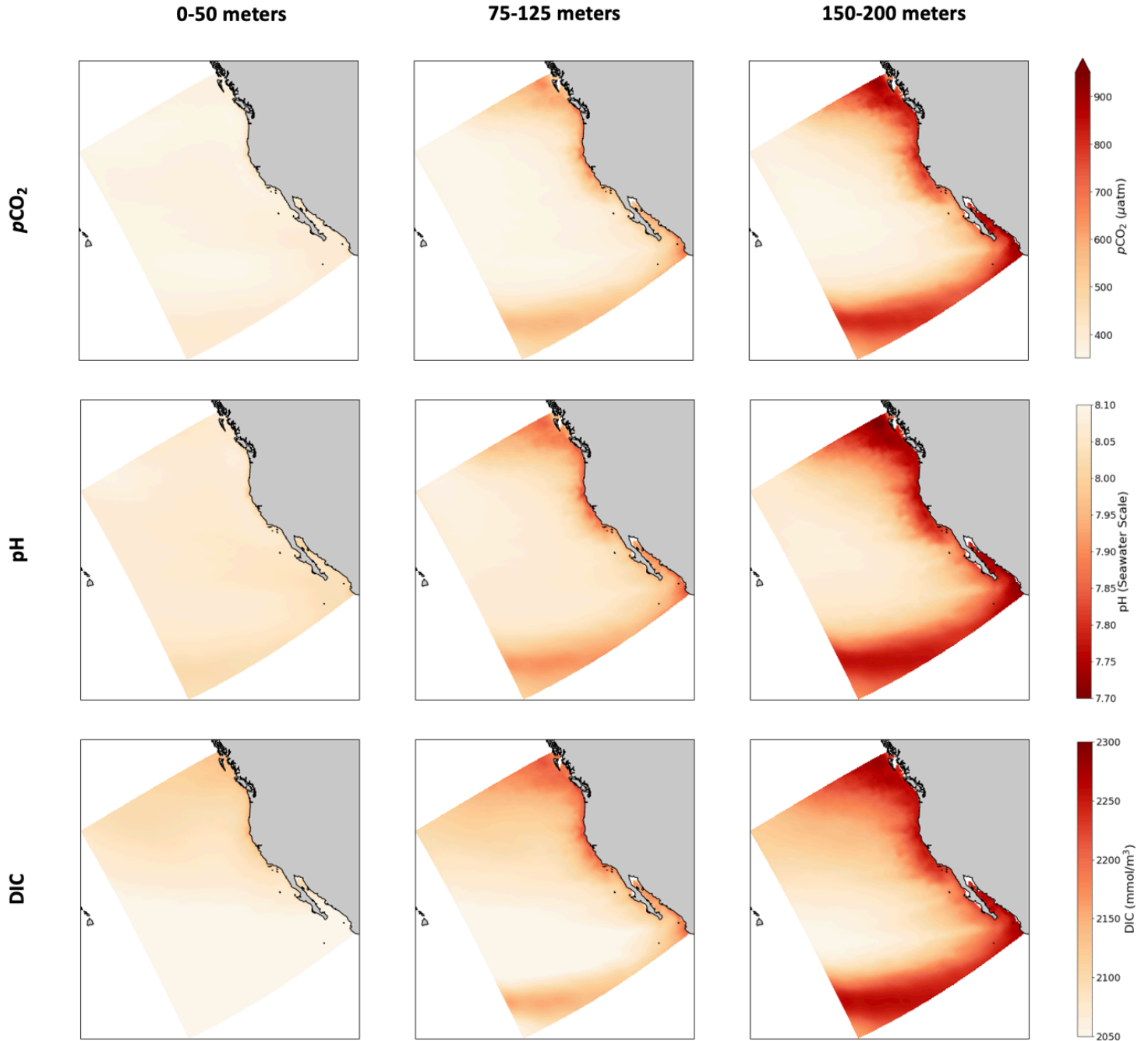


Figure S6] Climatological annual mean maps of pH, $p\text{CO}_2$, and DIC produced by ROMS. Maps represent 7-year averages (December 2000 – November 2007) at an averaged depth intervals of 0–50 meters, 75–125 meters, and 150–200 meters. Below 50 meters, a band of high- $p\text{CO}_2$, low-pH, and high-DIC waters is apparent in the nearshore region. At depth, this pattern of acidification expands in both magnitude and extent into the offshore region. These high $p\text{CO}_2$ conditions are expected in this region due to the tilting upward of isopycnals with high amounts of accumulated remineralization products during upwelling.

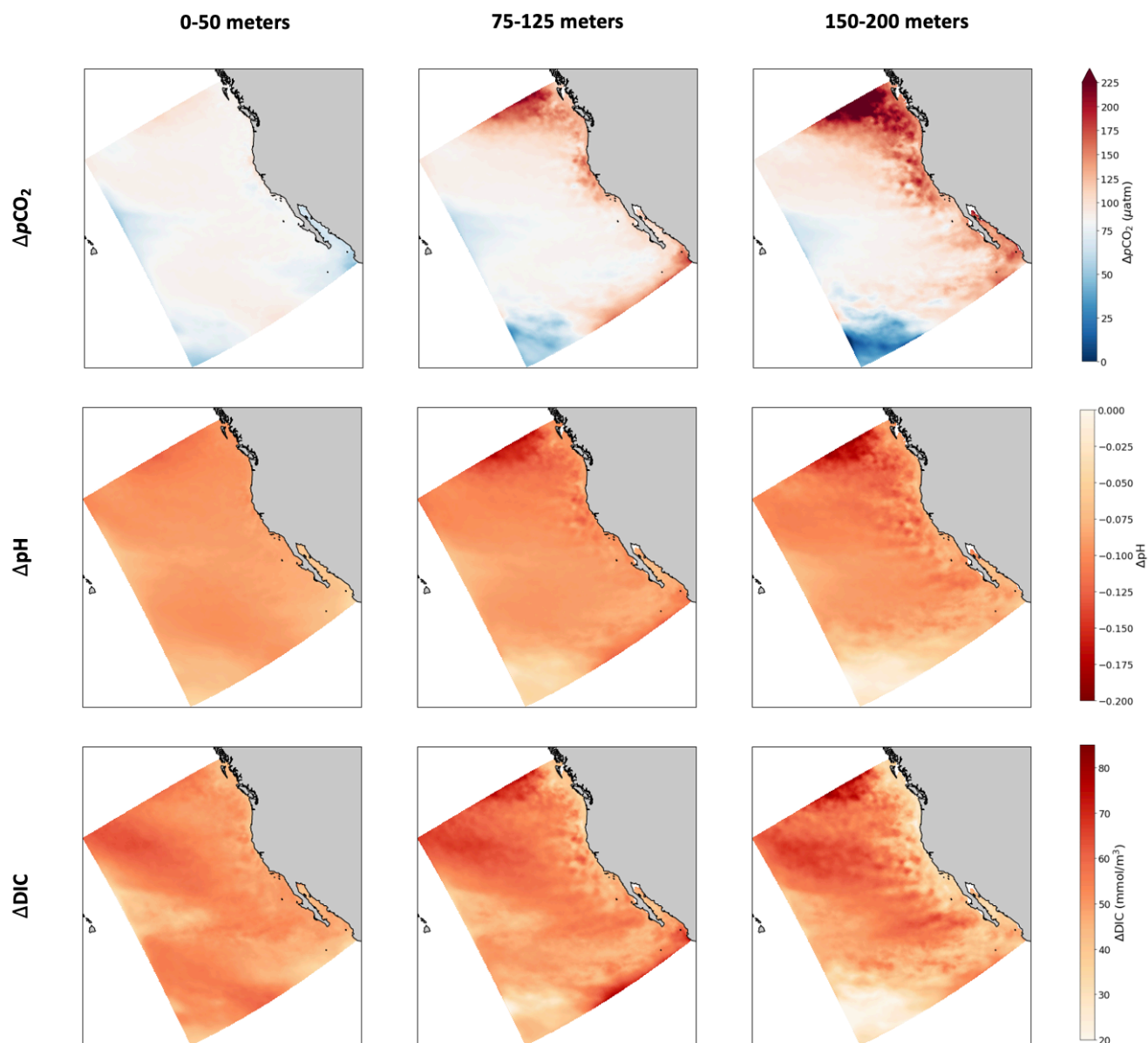


Figure S7 | Climatological mean maps of 20th century changes in $p\text{CO}_2$, pH, and DIC produced by ROMS at 0–50 meters, 75–125 meters, and 150–200 meters. Changes over the past century were evaluated by calculating the difference between a 7-year average in the historic (1897–1904) and modern (2000–2007) model realizations. Below 50 meters depth, we observe amplified acidification in the CCS ($p\text{CO}_2$ color bar is centered at atmospheric change in CO_2 between 1900 and 2000 = 80 μatm). Increasing initial DIC in the outcrop region in response to rising atmospheric CO_2 results in lower buffering capacity, such that the impact of subsequent remineralization on $p\text{CO}_2$ and pH is amplified. We observe relatively muted ΔDIC in the CCS with depth due to older water mass age that has not acquired the recent anthropogenic carbon fingerprint during rapid CO_2 emissions (Feely et al. 2016). Despite the reduction in ΔDIC at depth in the CCS, we still observe changes in $p\text{CO}_2$ that exceed the increase in atmospheric CO_2 due to lower buffering capacity and thermodynamic amplification of $p\text{CO}_2$ and pH. The southern Gulf of Alaska has experienced the most extreme amplified acidification captured in the model domain over the 20th century.

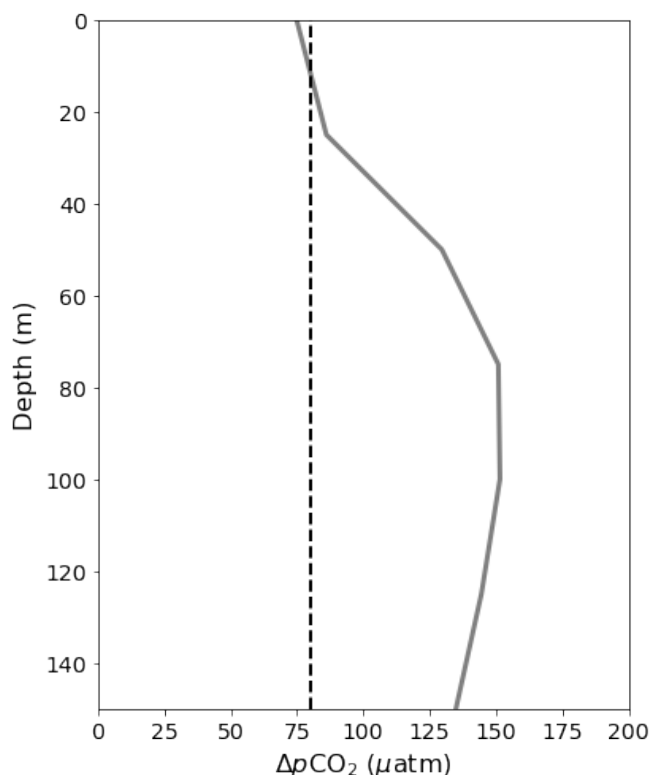


Figure S8 | Profile of modeled summertime (JJA) $\Delta p\text{CO}_2$ in the nearshore CCS (gray). Historic and modern $p\text{CO}_2$ are calculated from 7-year averages between November 1897–November 1904 and December 2000–November 2007, respectively. The black dashed line represents the increase in atmospheric CO_2 over the 20th century ($\Delta p\text{CO}_{2\text{ atm}} = 80 \mu\text{atm}$). Data to the right of this dashed line indicates amplified increases in $p\text{CO}_2$ with respect to the atmosphere. Below 25 meters depth, the CCS has experienced amplified acidification that increases with depth.

To quantify the magnitude of acidification that can be attributed to changes in upwelling and biological activity, we calculate the fraction of modeled ΔDIC that can be explained by 20th century changes in remineralization (Methods, Figure S9). We then calculate the percent that uptake of anthropogenic CO_2 can explain modeled ΔDIC at 0–50 meters, 75–125 meters, and 150–200 meters depth, assuming structured water mass age (Methods, Figure S10).

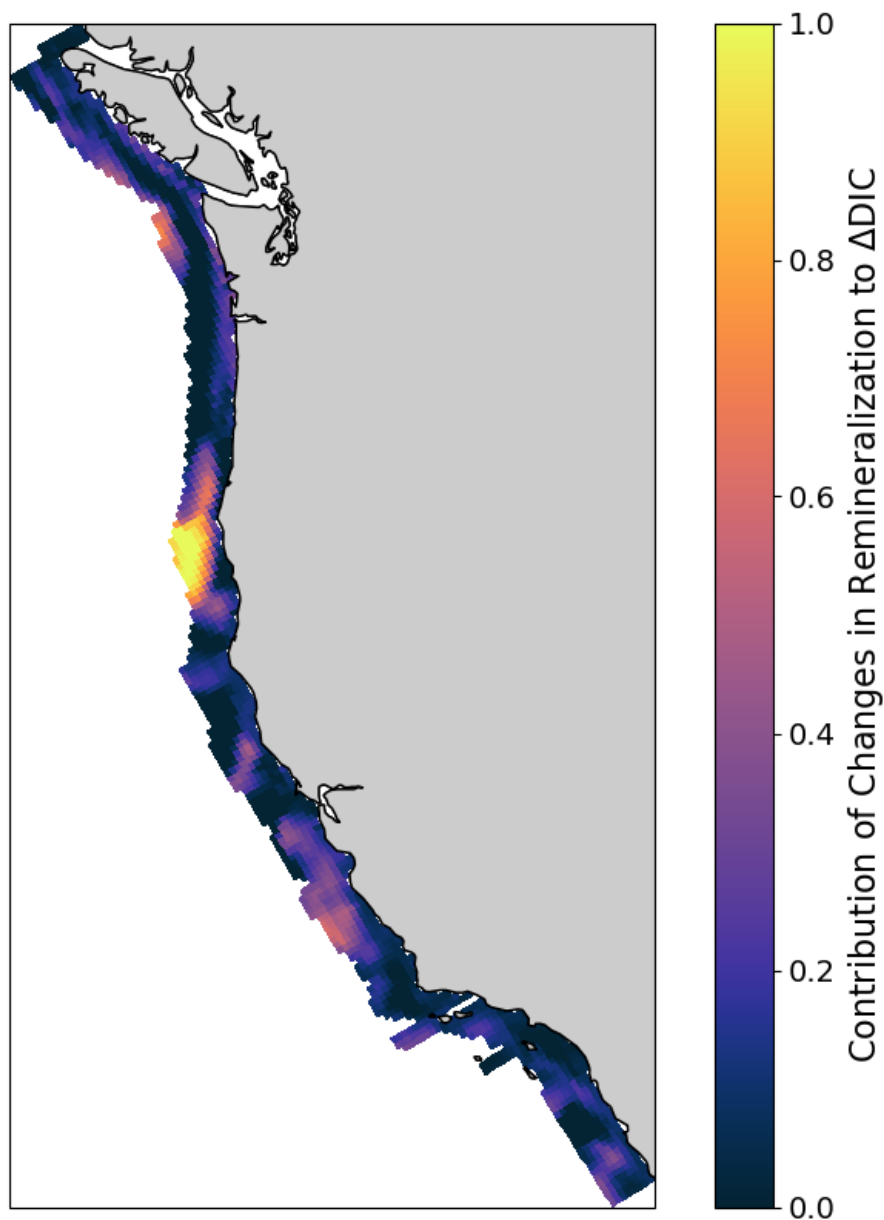


Figure S9 | The ratio of ΔDIC attributed to changes in remineralization to modeled ΔDIC at 0–200 meters depth in the nearshore region that overlaps with the coral locations. Changes in remineralization over the past century are calculated using apparent oxygen utilization and the Redfield ratio determined by Hedges et al. 2002 (Methods). 20th century changes in remineralization can account for 15% of modeled ΔDIC at 0–200 meters depth but this process is insufficient to explain most of the observed acidification over the past century.

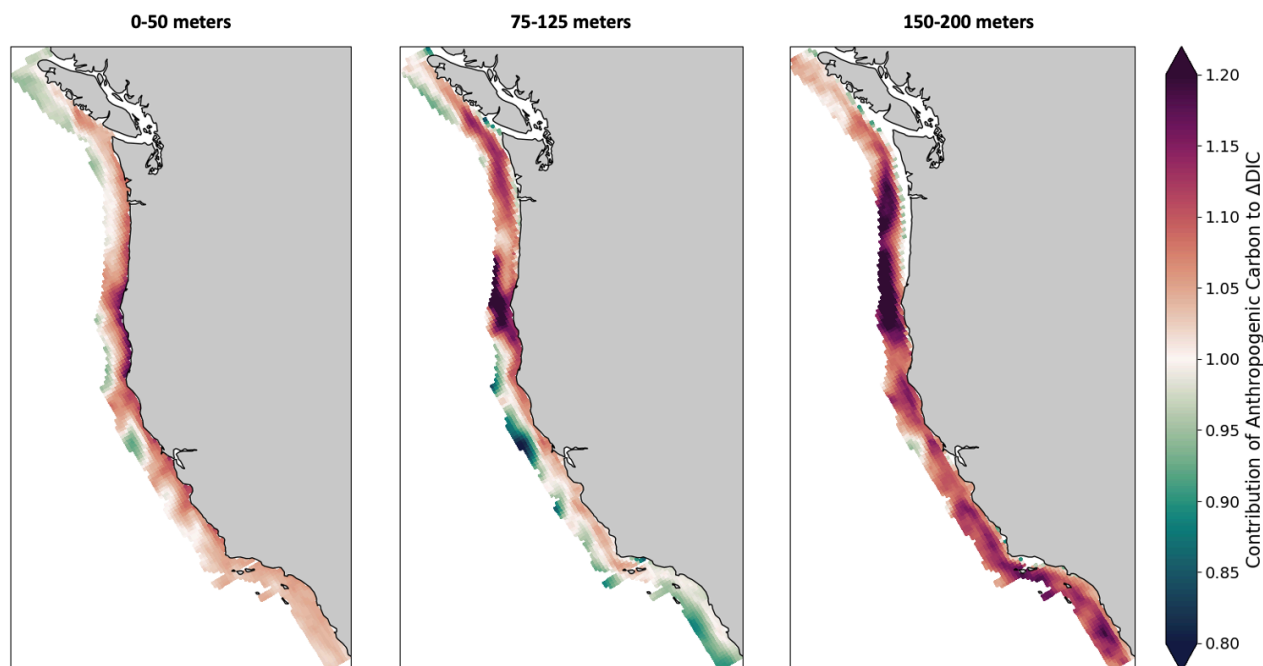


Figure S10 | The ratio of $\Delta\text{DIC}_{\text{preformed}}$ attributed to equilibration of atmospheric CO_2 (Methods, Equation 3) to modeled ΔDIC at 0–50 meters, 75–125 meters, and 150–200 meters depth ($\Delta\text{DIC}_{\text{preformed}}/\Delta\text{DIC}_{\text{modeled}}$, Methods). Each depth bin assumes a different water mass age due to time since last ventilation and contact with the atmosphere (0–50 meters, 75–125 meters, and 150–200 meters depth correspond with 0 years, 13 years, and 25 years old, respectively). Values near 1 indicate that estimated $\Delta\text{DIC}_{\text{preformed}}$ can fully explain modeled ΔDIC . Averaged over the CCS, estimates of ΔDIC derived from equilibration of atmospheric CO_2 at outcropping regions and accompanying buffering effects can explain the modeled ΔDIC within 15% relative error. Remaining minor residuals, identified by the regions shaded white and black, suggest that CO_2 invasion alone cannot entirely explain modeled biogeochemical changes over the 20th century, leaving room for second order effects such as shifts in upwelling and biological activity (Figure S9).

Historic model summertime averages of $p\text{CO}_2$ are also compared to historic coral $p\text{CO}_2$ at every location (Figure S11, Table S3). Details about the model- and coral-based estimates of $p\text{CO}_2$ can be found in Methods. Our coral record reproduces broad patterns and trends of acidification presented in the model (Figure 2).

While the corals reproduce general patterns of acidification in the model, several locations diverge from historic modeled estimates of $p\text{CO}_2$. For instance, while the coral data collected in the Greater Farallones at 50–60 meters depth (USNM 92623 and 92624) are within error of model

predictions at these depths, they align better with modeled $p\text{CO}_2$ in the upper 25 meters (Figure 2). This difference may result from the inability of the model to resolve key bathymetric features at this site; some evidence suggests that there is a small seamount in this location, however the model resolution is not high enough to capture this variability. In addition, corals at site USNM 78638 were collected from a tidepool where the high variability associated with the intertidal zone likely influenced the $\delta^{11}\text{B}$ skeletal signatures. Lastly, our coral data from the Santa Barbara Basin (USNM 92622) deviate most from the model and correspond to a much lower historic $p\text{CO}_2$ than that presented in the model. This divergence has been found in another proxy record from the Santa Barbara Basin (Osborne et al. 2020) (Supplementary Discussion 1.4). Although our data from this region are too sparse to be conclusive, the model may fail to capture important regional processes that amplify acidification in the Santa Barbara Basin even more than the rest of the CCS.

Table S3 | Historic West Coast coral $p\text{CO}_2$ and pH values (total scale) informed by skeletal $\delta^{11}\text{B}$. Average pH values at each location are calculated from the $\delta^{11}\text{B}$ -pH relationship (Methods, Equation 2) and modeled historic DIC (Methods, Equation 1). The -0.10-offset determined in the Salish Sea is applied to the average pH data (Methods). The average DIC represents modeled, historic summertime DIC in the nearshore CCS at 0–125 meters depth between 1897 and 1904.

CatalogID	Average DIC CCS (mmol/m^3)	Average pH (Offset Applied)	Average $p\text{CO}_2$ (μatm)
USNM 92621	2145	7.79	715
USNM 36416	2145	7.86	608
USNM 92625	2145	7.89	570
USNM 19233	2145	7.85	626
USNM 92624	2145	7.83	664
USNM 92623	2145	7.84	640
USNM 78638	2145	7.75	794
USNM 78640	2145	7.96	488
USNM 92622	2145	8.03	403
USNM 19274	2145	7.94	510

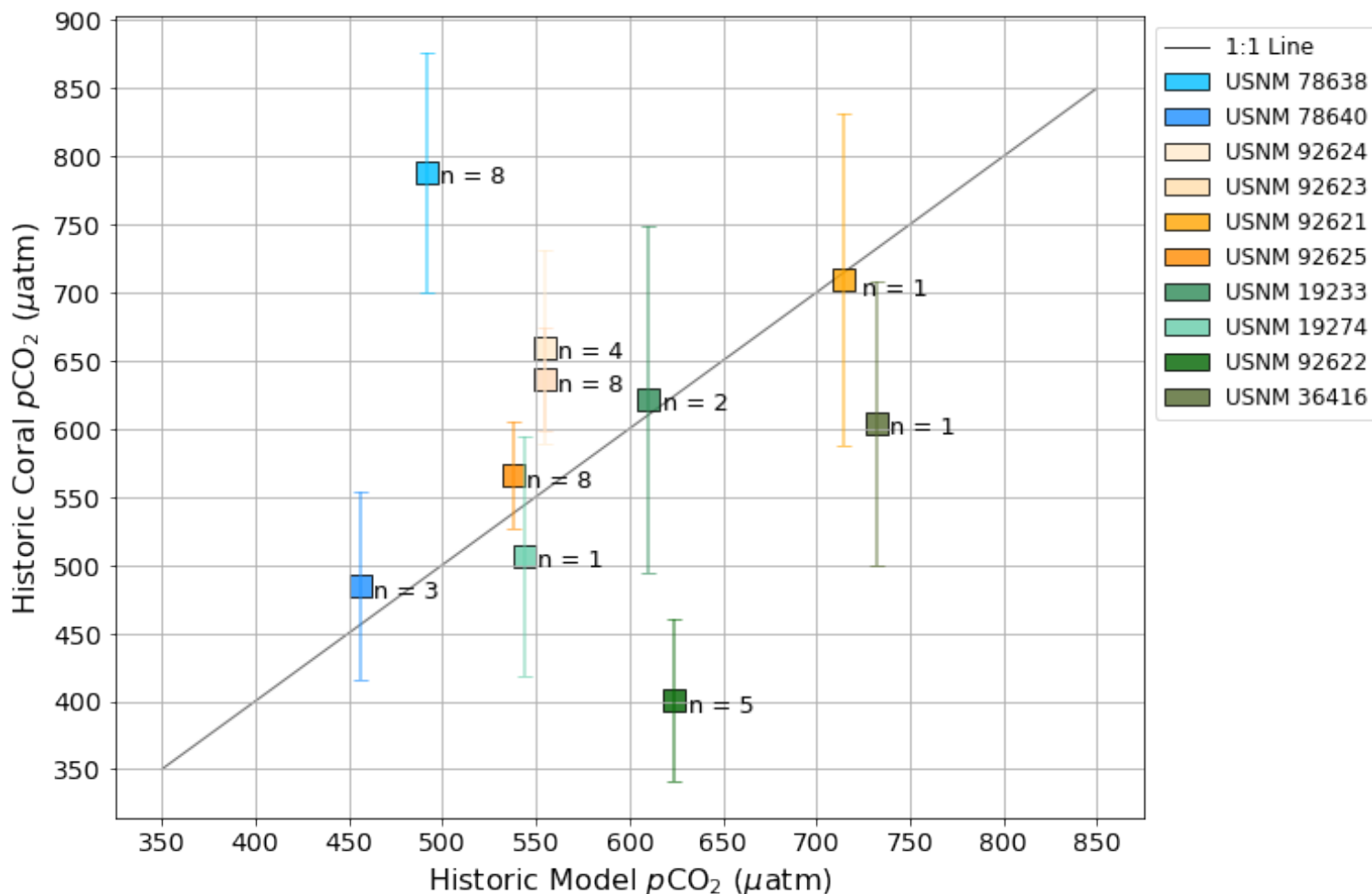


Figure S11 | Comparison between historic model and coral $p\text{CO}_2$ along the West Coast. *Coral data*: $p\text{CO}_2$ is calculated from the $\delta^{11}\text{B}$ -pH relationship at each location (Methods, Supplementary Data). Vertical error bars represent standard errors of the mean. Error bars for locations with only one coral represent the population standard deviation, inferred by locations with 8+ samples. n = number of corals sampled at each location. *Model data*: Modeled $p\text{CO}_2$ represents a 7-year historic summer average aligning with the peak upwelling season (Supplementary Methods 1.3) over a 36 km x 36 km area centered at the coral location from the nearest depth bin of sample collection (Methods).

1.4 Reconstruction of fossil foraminifera pH and $p\text{CO}_2$ based on *Globigerina bulloides* shell weights

We investigate other published proxy records of acidification in the CCS to assess the robustness of our conclusions drawn from the model and coral records. Osborne et al. 2020 used the weight and size of fossil foraminifera tests as a proxy for carbonate ion $[\text{CO}_3^{2-}]$ from 1897 to 2002 in the Santa Barbara Basin. To directly compare to our coral data, we recast the foraminifera carbonate ion record into pH and $p\text{CO}_2$ space. The master variables selected to constrain the carbonate system were 1) $[\text{CO}_3^{2-}]$ determined from area-normalized shell weights (ANSW) of *Globigerina bulloides*, as described in Osborne et al. 2020 (Figure S12a); and 2) TA inferred from an empirical salinity-TA relationship based on Scripps Pier data spanning 1916-present, as described in Osborne et al. 2020 (Figure S12b). Historical temperature and salinity data published in Osborne et al. 2020 serve as additional constraints on the pH and $p\text{CO}_2$ calculations. From these data we calculated pH and $p\text{CO}_2$.

The fossil foraminifera record from the SBB produces acidification signals that outpace modeled signals, suggesting even more amplified acidification. Interestingly, our coral data from the Channel Islands near the SBB (Figure S1) also indicate low historic $p\text{CO}_2$ that diverge from modeled estimates of 20th century acidification. Although our data from this region are too sparse to be conclusive, regional processes that may not be resolved in ROMS appear to influence acidification in the SBB even more than the broader and warrant further investigation.

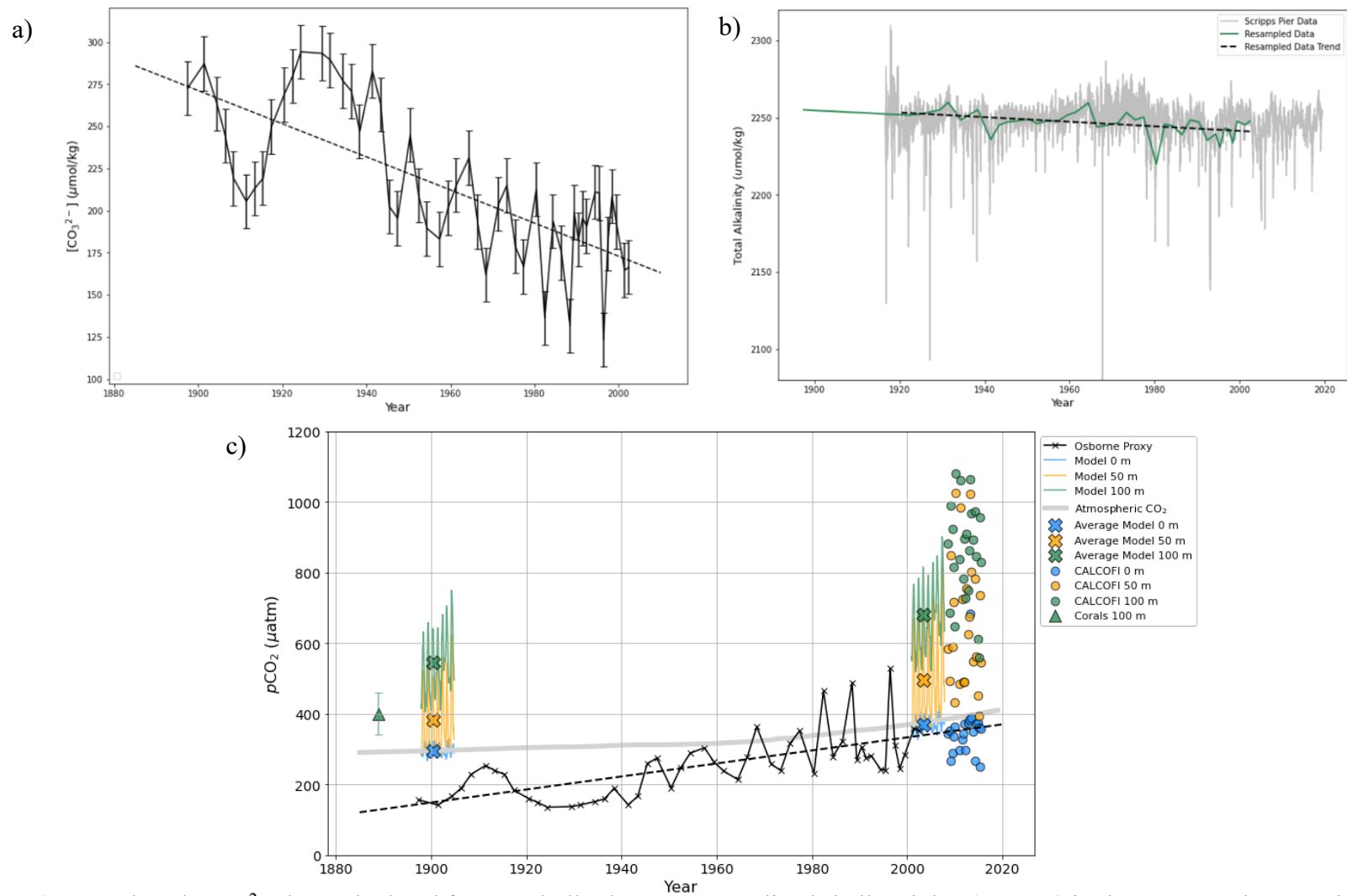


Figure S12 a) Reproduced $[\text{CO}_3^{2-}]$ data calculated from *G. bulloides* area-normalized shell weights (ANSW) in the Santa Barbara Basin from Osborne et al. 2020. Error bars represent the standard error of the $[\text{CO}_3^{2-}]$ mean based on the ANSW-carbonate ion relationship ($\pm 15.63 \mu\text{mol/kg}$). b) Derived alkalinity from Scripps Pier salinity data (gray) using an empirical salinity-TA relationship (Osborne et al. 2020). The green line represents re-sampled TA data to temporally align with the $[\text{CO}_3^{2-}]$ record. A best fit line (dashed black) was applied to the re-sampled TA data to extend the record back in time to overlap with the $[\text{CO}_3^{2-}]$ record, as described in Osborne et al. 2020. The above $[\text{CO}_3^{2-}]$ and TA data represent the master input variables we utilized to calculate pH and $p\text{CO}_2$ from the fossil foraminifera proxy record. c) $p\text{CO}_2$ time series in the SBB from model simulations, observational data, foraminifera proxy record, and coral proxy records. Model data are represented by colored time series and average values (x's) in the historic and modern simulations at 0, 50, and 100 meters depth. Observational data from the California Cooperative Oceanic Fisheries Investigations (CalCOFI) are represented by the circle markers at 0, 50, and 100 meters depth. $p\text{CO}_2$ data informed by the Osborne foraminifera (which typically live in the upper 25 meters of the water column) record is shown by the solid black line and dashed linear trend line). Our coral data from the SBB are represented by the green triangle (collected near 100 meters depth). Atmospheric CO_2 is shown by the gray line. Both the coral record and foraminifera records imply stronger acidification than that implied by the model at their respective depths, suggesting that important second-order effects in the SBB may further amplify acidification.

2. Large-Scale Climate Factors and the Imprint on our Coral Record

2.1 Impact of the Pacific Decadal Oscillation and climate variability on 20th century acidification

While our coral records suggest that anthropogenic sources act as the dominant driver of 20th century acidification in the CCS, natural large-scale climate patterns also play a role in determining carbonate chemistry. The Pacific Decadal Oscillation (PDO), for instance, oscillates on low-frequency decadal to sub-decadal timescales and influences the strength of coastal upwelling. During positive phases of the PDO, the Aleutian Low pressure cell migrates south resulting in weaker winds and a decrease in upwelling strength (Mantua and Hare 2002). Conversely, negative phases of the PDO result in a strengthening of coastal upwelling. Due to this natural oscillation of upwelling strength on decadal timescales, this signal may be imprinted on the 20th century changes implied by the coral records.

To determine the impact of the PDO on the coral record, we examine the PDO index during the dates of collection for the historic corals, modern corals, and modern model. Monthly PDO indices are based on NOAA's ERSST reconstruction of SSTs and obtained from the National Centers for Environmental Information database. Table S4 shows 7–8 year averages of the PDO index during each time period. Since the historic model was forced with climate anomalies from the modern model, the PDO index is equivalent in both hindcast simulations and does not influence the modeled 20th century signal.

To remove the potential influence of the PDO on the 20th century carbonate chemistry signal, it would be ideal to compare records from the historic and modern time periods with similar PDO indices. Along the US West Coast, the average PDO index of the historic corals is within error of that of the modern and historic model (Table S4); therefore, the magnitude of change implied by the outer West Coast coral record should be independent of the PDO.

In the Salish Sea, the modern corals were collected during a weak negative phase of the PDO whereas the historic corals were collected during a more extreme negative phase (Table S4). While the misalignment of PDO phases across time periods may influence the 20th century signal, this shift in phases actually enhances our conclusions drawn from the data. More negative PDO phases correlate with a strengthening of coastal upwelling; this implies that the historic corals experienced relatively *stronger* upwelling conditions as a result of the PDO compared to the modern corals. This suggests that the historic baseline of acidification may have been relatively high due to the more extreme negative PDO phase. As a result, we might expect this misalignment of PDO indices across eras to reduce the magnitude of $\Delta p\text{CO}_2$ or ΔpH implied by the coral record. Instead, we still see a signal that suggests amplified acidification occurred in the Salish Sea between the 1890s and 2020.

Table S4 | Average PDO Index for time periods overlapping with historic coral, modern coral, and modern model records. The time period lengths were inferred by dates of collection and an average coral lifespan of ~8 years. Average PDO indices are inferred from monthly indices from NOAA's ERSST reconstruction of SSTs in the National Centers for Environmental Information database.

Data Source	Time Period	Average PDO Index	Standard Error of Mean
Historic Corals - West Coast	January 1883 - December 1890	-0.30	0.12
Historic Corals - Salish Sea	January 1887 - December 1894	-0.80	0.13
Modern Corals - Salish Sea	November 2012 - October 2020	-0.14	0.09
Modern Model	December 2000 - November 2007	-0.38	0.09

Supplementary Notes

1. Background Information on Study Area

1.1 The California Current upwelling system

The California Current System (CCS), the eastern boundary current off the west coast of North America, spans from British Columbia to Baja California and flows over the continental shelf with a width of 50–100 km (Hickey 1979). Eastern boundary current systems experience low pH and high partial pressure of CO₂ ($p\text{CO}_2$) because of upwelling and ocean circulation (Chan et al. 2017; Reum et al. 2016). As a result, eastern boundary current systems naturally contain some of the most acidified waters in the ocean.

It is hypothesized that climate change will cause a strengthening of alongshore winds due to sharper land-sea temperature gradients, consequently increasing the frequency and intensity of upwelling events in eastern boundary current systems and leading to higher overall acidification levels (Bakun 1990). While successive analyses indicate that upwelling will intensify in the poleward regions of eastern boundary currents (Rykaczewski et al. 2015), others have found muted responses in the CCS compared to other eastern boundary currents (Wang et al. 2015; Howard, Frenzel, et al. 2020) and suggest that the anthropogenic impact on upwelling strength in the CCS will not exceed natural variability until the end of the 21st century (Brady 2019). Still others have analyzed historical wind data and model re-analyses over the past two to six decades and found a strengthening of upwelling-favorable winds (Sydeman et al. 2014; Turi et al. 2016; Quilfen et al. 2021). The wide spread of results in the literature underscores the unknown role dynamic climate effects will play in a changing CCS. Due to the complexity of processes that impact biogeochemistry in the CCS and Salish Sea, a central question is whether acidification in vital and productive eastern boundary current systems such as the CCS will follow the pace of increasing

atmospheric CO₂, or if dynamical climate effects or other processes will act to either amplify or attenuate acidification.

1.2 Characterizing the carbonate chemistry in the Salish Sea

The CCS has a strong influence on coastal ecosystems along the US West Coast and connected water bodies (Hickey 1979; 1989). For instance, the Salish Sea is a marginal sea of the North Pacific that encompasses the coastal waterways of southern British Columbia, Canada and northwestern Washington, US, including Puget Sound. Forming a transition zone between the open ocean and coast, the Salish Sea is one of the largest estuaries in the US of economic and cultural importance, and represents a living lab where complex climate, oceanic, riverine, and land-based processes converge (Stewart 2017). Due to the mixing of upwelled source waters, the carbonate chemistry of the Salish Sea also serves as a useful indicator of upwelling dynamics in the broader CCS (Feely et al. 2010).

In addition to the influence of the CCS, seasonal variability in the Salish Sea impacts carbonate chemistry and provides an important constraint on the main driver of 20th century acidification. Seasonal variability of the carbonate system is influenced by biological activity, influx of freshwater, and mixing of upwelled bottom-water from the CCS (Alin et al. 2023; 2024). Given that attribution of individual effects is difficult, questions remain regarding the dominant force responsible for seasonal variation. We set out to determine whether 1) biological processes or 2) mixing of upwelled and riverine source waters primarily controls interannual variability in the carbonate system. Our analyses focus on characterizing seasonal variation at depth due to the benthic nature of the corals. We find that seasonal shifts in the mixing ratio between upwelled CCS

water and Salish Sea water, which is also influenced by rivers, dominates the variability in carbonate system parameters in the modern system.

Influence of rivers on Salish Sea carbonate chemistry

Admiralty Inlet, situated at the interface between the Strait of Juan de Fuca and Puget Sound, serves as a useful case study due to the breadth of Washington Ocean Acidification Center (WOAC) bottle data and historic and modern coral data. Admiralty Inlet represents a tidally well-mixed area that experiences saltwater influence from the CCS and, like the rest of the Salish Sea, freshwater influence from rivers. The Skagit River represents the largest freshwater input to Puget Sound (Babson and MacCready 2006; Cokelet, Stewart, and Ebbesmeyer 1989) and feeds into Skagit Bay with an average flow rate of $\sim 17,000 \text{ ft}^3/\text{sec}$ (USGS Skagit River gauge 12200500). Skagit River discharge varies seasonally and peaks in the early summer and winter months, coinciding with rapid snowpack melt and maximum precipitation, respectively (USGS Skagit River gauge 12200500).

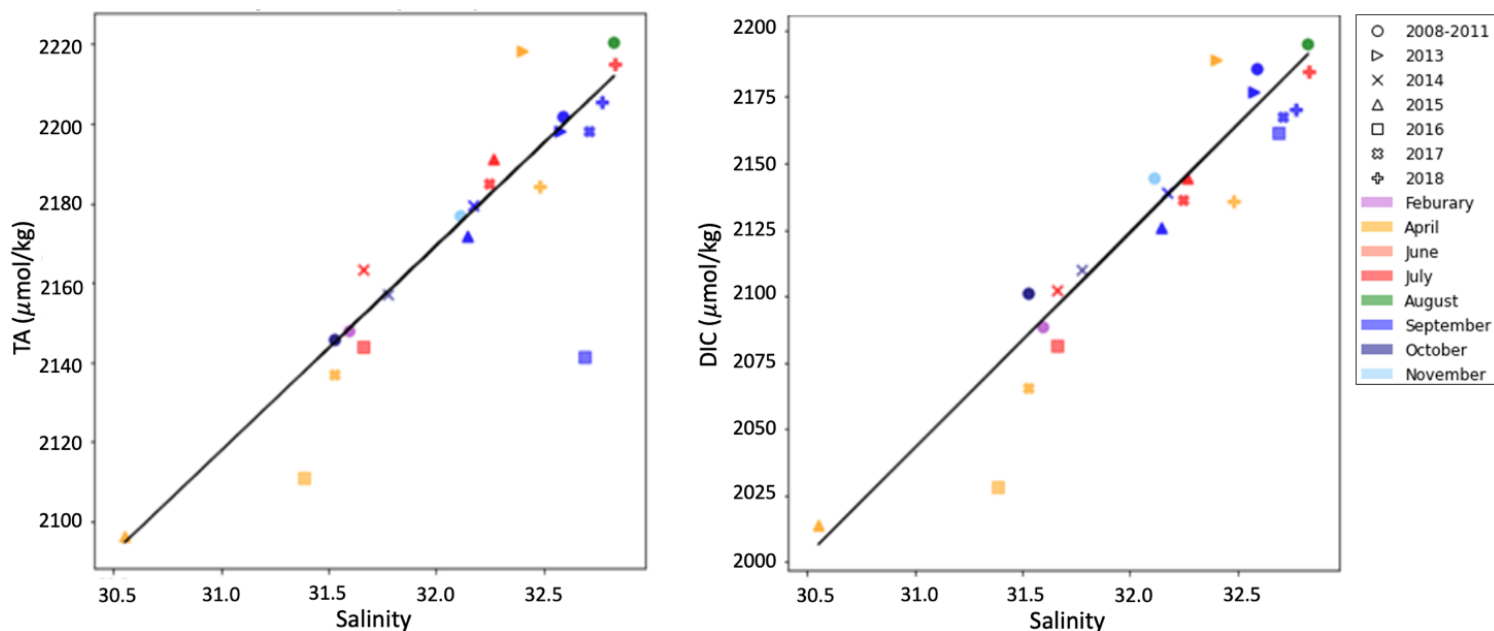


Figure S13| Relationships between a) total alkalinity (TA) and salinity and b) DIC and salinity from WOAC Station 21 near Admiralty Inlet at 70 meters that align with the coral depth of collection. Unsurprisingly, both TA and DIC correlate strongly with salinity. In general, salinity is lower in the late spring and early summer months (April–June) compared with the fall (September–November).

Determining the dominant control on seasonal variability

Biological and mixing processes are tested as the dominant control on seasonal variability of carbonate chemistry in the Salish Sea. To investigate each mechanism, we invoke process-based equations to draw biological activity and mixing lines onto a total alkalinity (TA) vs DIC plot (Figure S14). The mixing line is based on a two end-member mixing scenario between Salish Sea waters and summer upwelled waters from the CCS. Average properties for the Salish Sea were obtained from WOAC bottle data at Admiralty Inlet (Supplementary Methods 1.2) and average properties of upwelled water were obtained from a Regional Ocean Modeling System (ROMS) that resolves the CCS at 150–200 meters depth at the mouth of the Strait of Juan de Fuca. The properties of the upwelled waters from the model align with published properties of the core CCS off the Washington coast (Murray et al. 2015; Pierce et al. 2012). The process line that represents primary production and remineralization (biological activity) was generated from the DIC:TA values implied by Redfield stoichiometry. Pelletier et al. 2018 found tight coupling between biogeochemical changes induced by the phytoplankton growing season in Puget Sound.

Figure S14a shows that the slope of the observational data aligns more closely with the slope of the mixing line compared to the biological activity line. Furthermore, normalizing the TA and DIC for salinity causes the data to collapse and a majority of the seasonal variability is removed (Figure S14b). Although biological arguments may be invoked to explain a portion of the observational data, salinity-based processes are the dominant mechanism responsible for the observed seasonality in carbonate chemistry. This foundational understanding of carbonate chemistry variability provides important context to consider shifts in source water mixing as the

driving force of 20th century acidification in the Salish Sea, described in Supplementary Discussion

1.

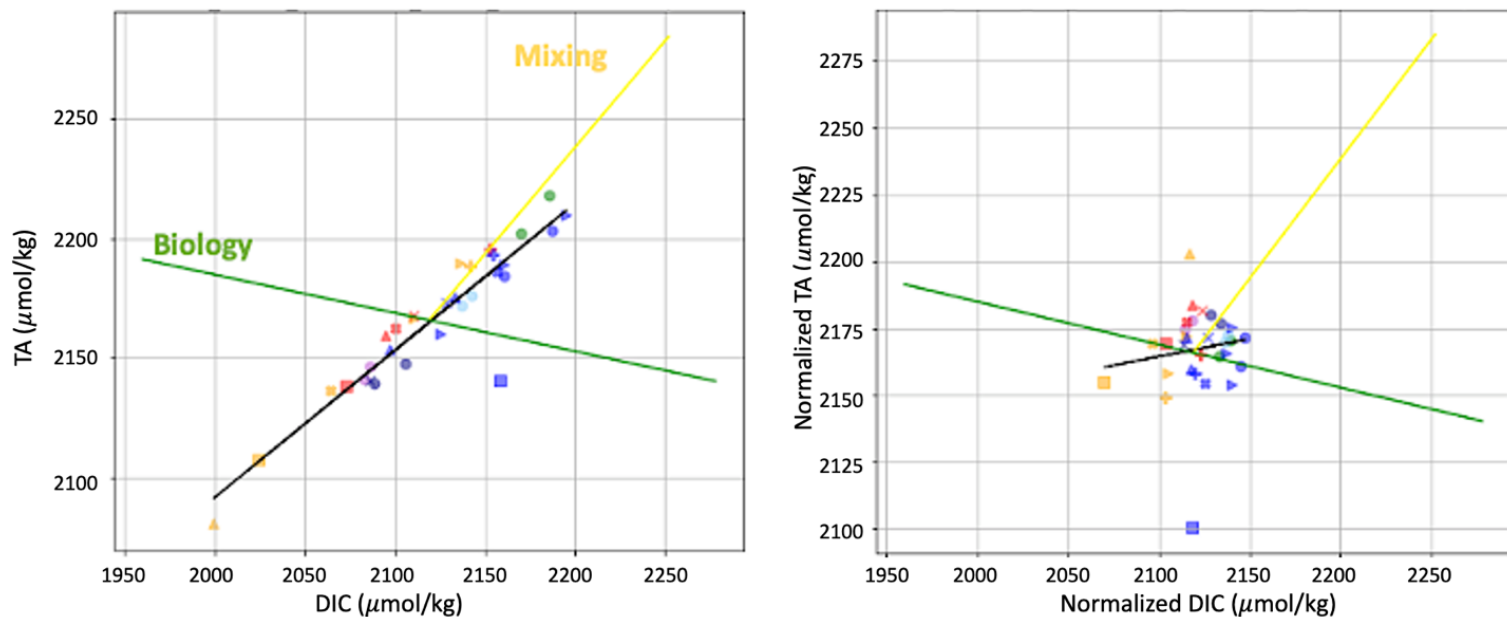


Figure S14 TA vs DIC plots of observational data from WOAC station 21 at 70 meters depth provide information about drivers of seasonal variability in carbonate chemistry. Process lines depicting primary production (green) and mixing (yellow) are produced alongside a best fit line (black) of the observational data. a) The mixing line follows the observational data more closely than the biological process line, suggesting that mixing plays a larger role in controlling seasonal variability in the Salish Sea. b) Upon normalizing the TA and DIC data for salinity, the trend in the observational data disappears. This suggests that the driver of seasonal variability in the Salish Sea is salinity-based, further indicating mixing processes.

Appendix B: Supplementary Materials for Chapter 3

Supplementary Figure List

- Figure S1| Maps of tagged fish tracks and migratory sub-group classifications
- Figure S2| Seasonal map plots of daily tagged fish presences
- Figure S3| Seasonal map plots of float-based 2D SDM predictions
- Figure S4| Seasonal map plots of satellite-based 2D SDM predictions
- Figure S5| Seasonal map plots of differences between float-based and satellite-based 2D SDM predictions
- Figure S6| Surface-to-subsurface correlation coefficient maps of Chl
- Figure S7| Surface-to-subsurface correlation coefficient maps of POC
- Figure S8| Histograms of modeled probabilities of occurrence at the 90th percentile dive depths
- Figure S9| Dive depths by season for select points of interest
- Figure S10| Comparison between BGC + temp 3D SDM and temp 3D SDM in winter and summer
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Supplementary Table List

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- Table S2| Summary of SDMs and predictor variables used to develop SDMs for juvenile albacore tuna
- Table S3| Summary of global evaluation metrics for 2D and 3D SDM model performance
- Table S4| Summary of CV method comparison for the 2D float-based SDM
- Table S5| Summary of CV method comparison for the BGC + temp 3D SDM

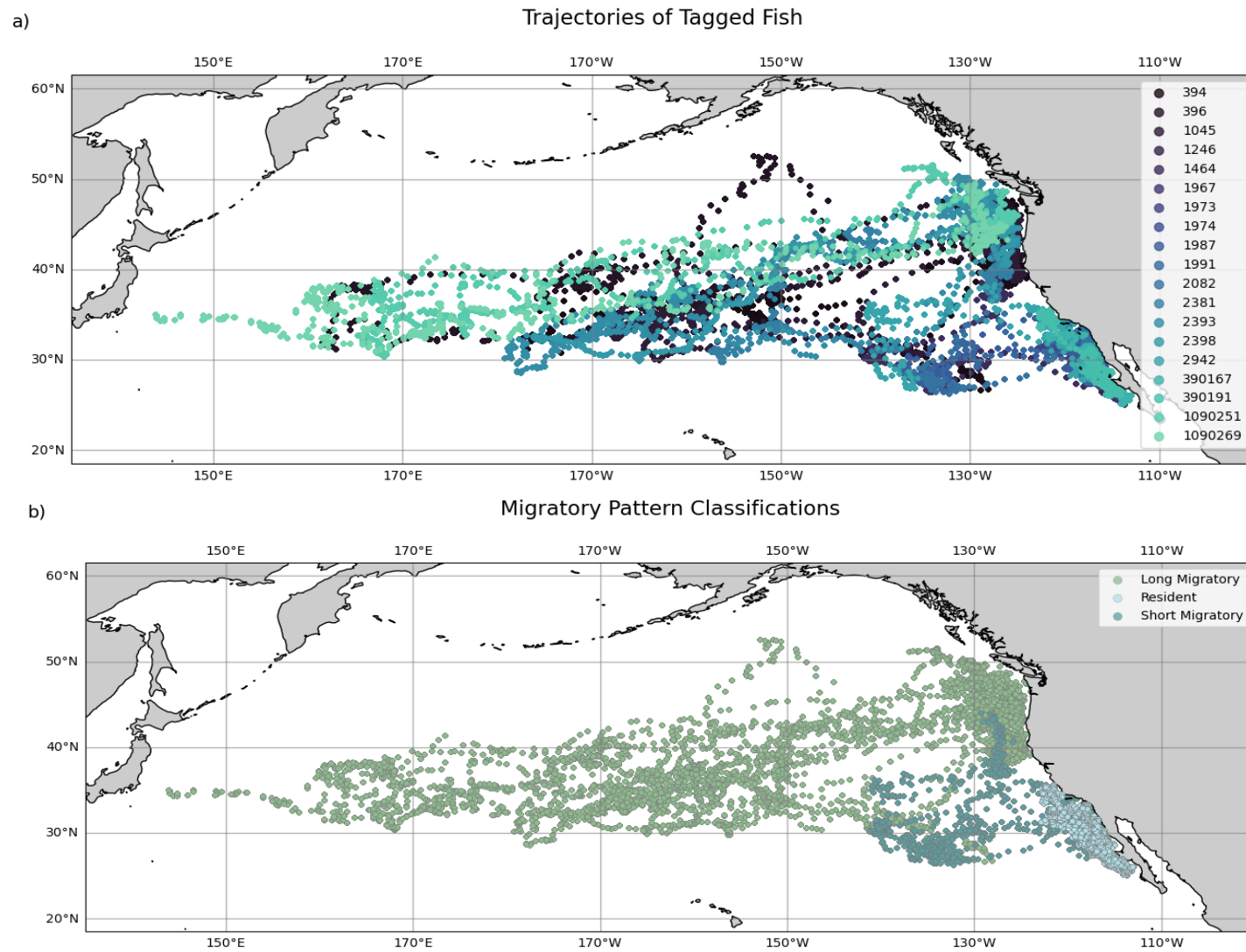


Figure S1 | a) Daily locations of each tagged albacore tuna included in the species distribution modeling study. b) Migratory sub-group classifications for the tagged albacore tuna: long-migratory (green), short-migratory (dark blue), and resident (light blue) fish. Definitions from Muhling et al. 2022.

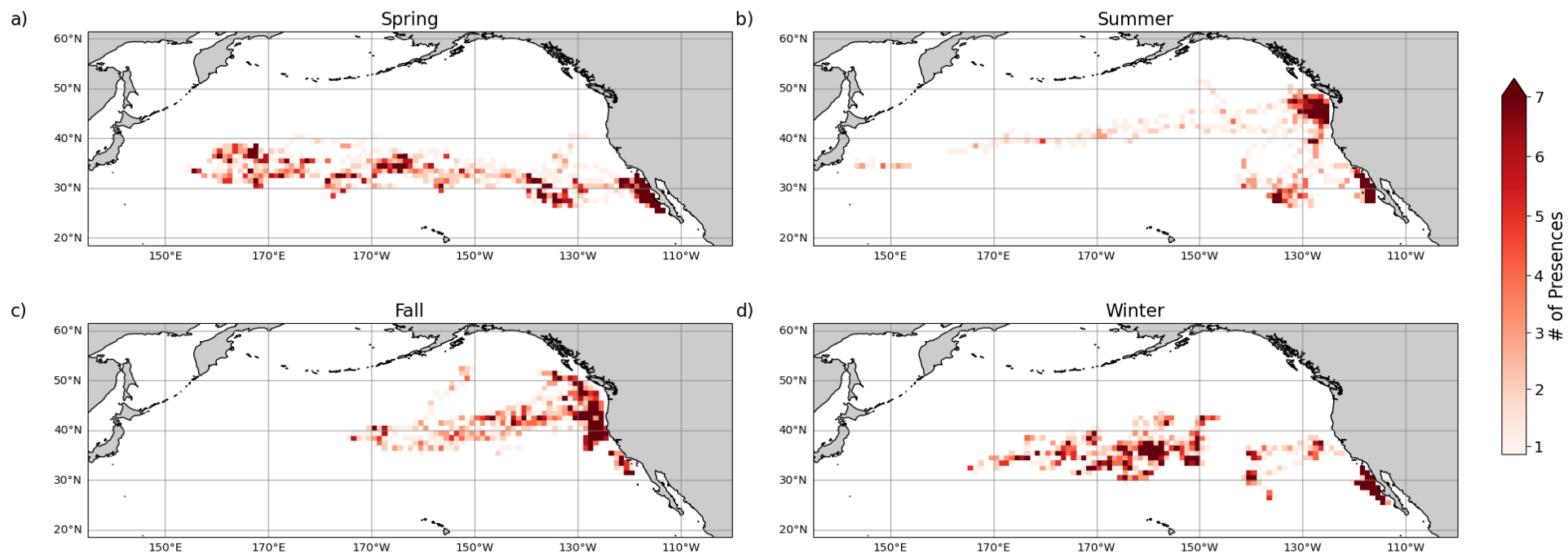


Figure S2| Daily locations of all tagged albacore tuna across seasons (spring: MAM, summer: JJA, fall: SON, winter:DJF). Darker red colors indicate a higher number of presences—either a single fish spent several days in that grid cell, multiple fish were located in that grid cell, or a combination of both factors.

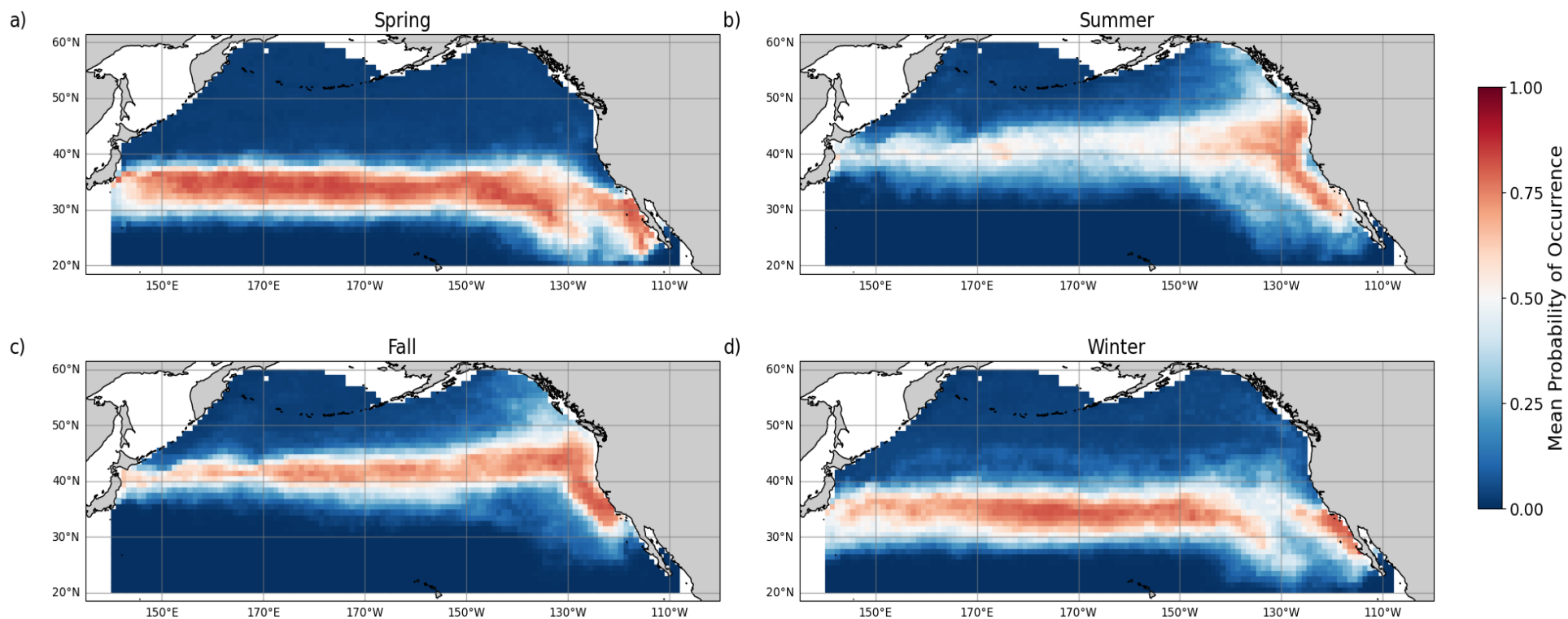


Figure S3| Seasonal maps of modeled probabilities of occurrence predicted by the float-based 2D SDM. The float-based model was trained on three environmental predictors including SST, depth-integrated Chl, and depth-integrated POC. The biological parameters are derived from BGC-Argo-informed data products.

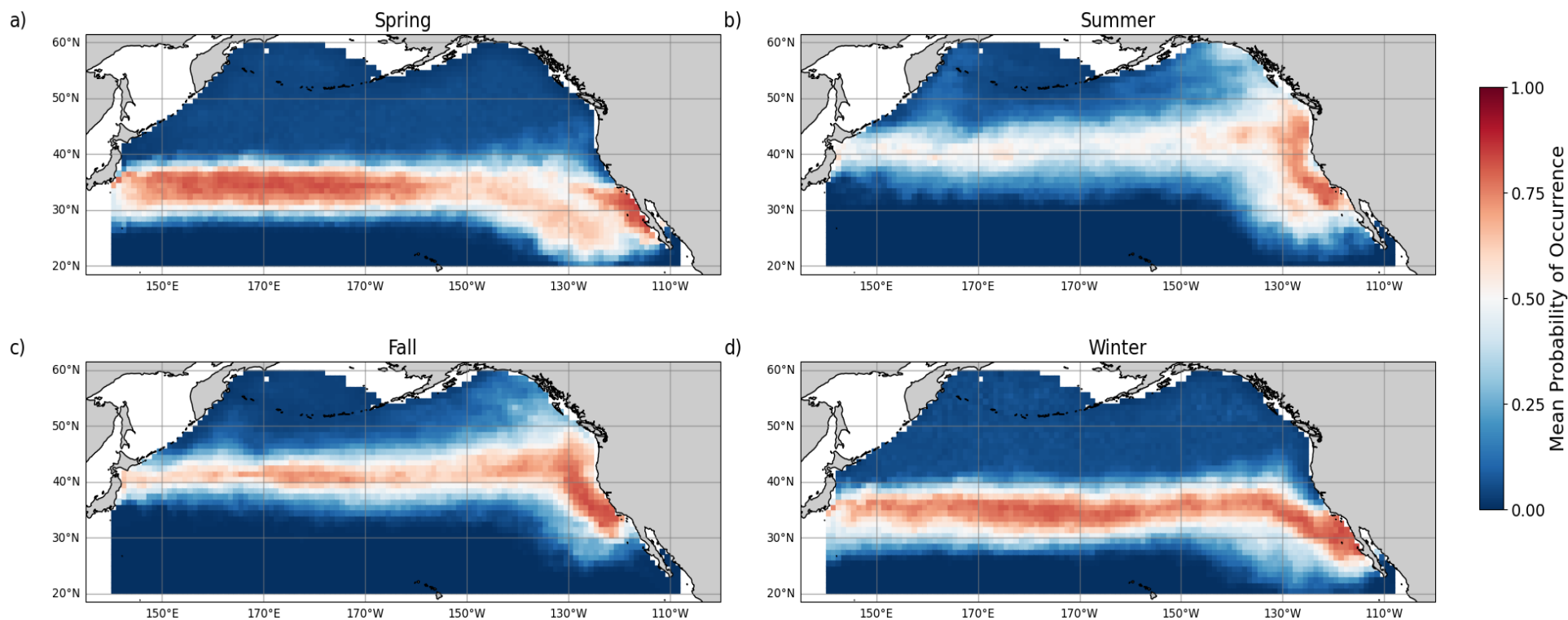


Figure S4| Seasonal maps of modeled probabilities of occurrence predicted by the satellite-based 2D SDM. The satellite-based model was trained on three environmental predictors including SST, satellite surface Chl, and satellite surface POC.

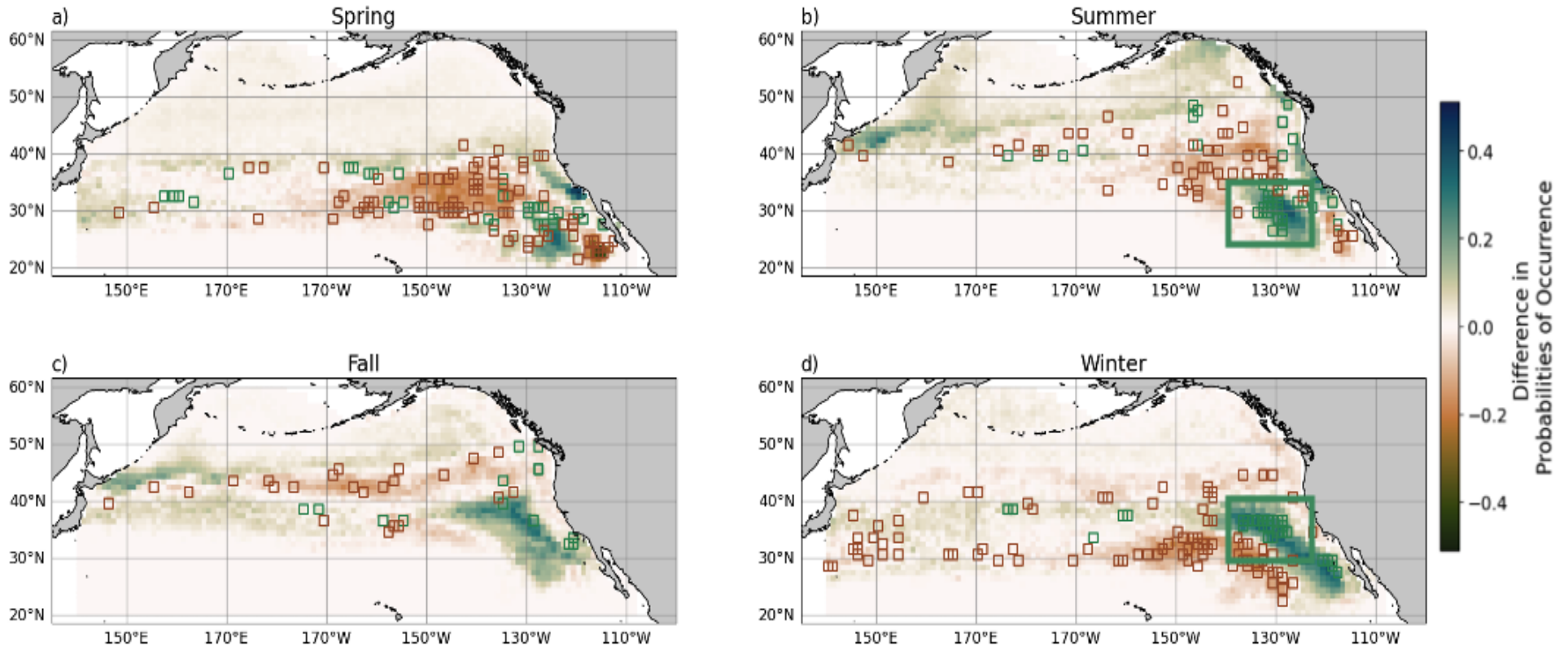


Figure S5 Seasonal maps show differences in probabilities of occurrence predicted by the float-based and satellite-based 2D SDMs (Figures S4 minus S3). The models were applied to all predictor variables from 2004 to 2013 and model predictions were averaged seasonally over the 10-year period. Green (brown) coloring indicates higher (lower) probabilities predicted by the satellite-based model. Small squares mark locations where only the satellite-based model correctly classified a presence (green) or a pseudo-absence (brown). The number of small squares in each panel represent 4%, 5%, 2%, and 4% of total observations in spring, summer, fall, and winter, respectively. Locations where only the satellite-based model captured a presence, thereby indicating that surface data alone was a more powerful predictor of fish presence, are shown by the larger green boxes in summer and winter.

Correlation coefficients between surface satellite and depth-integrated Chl

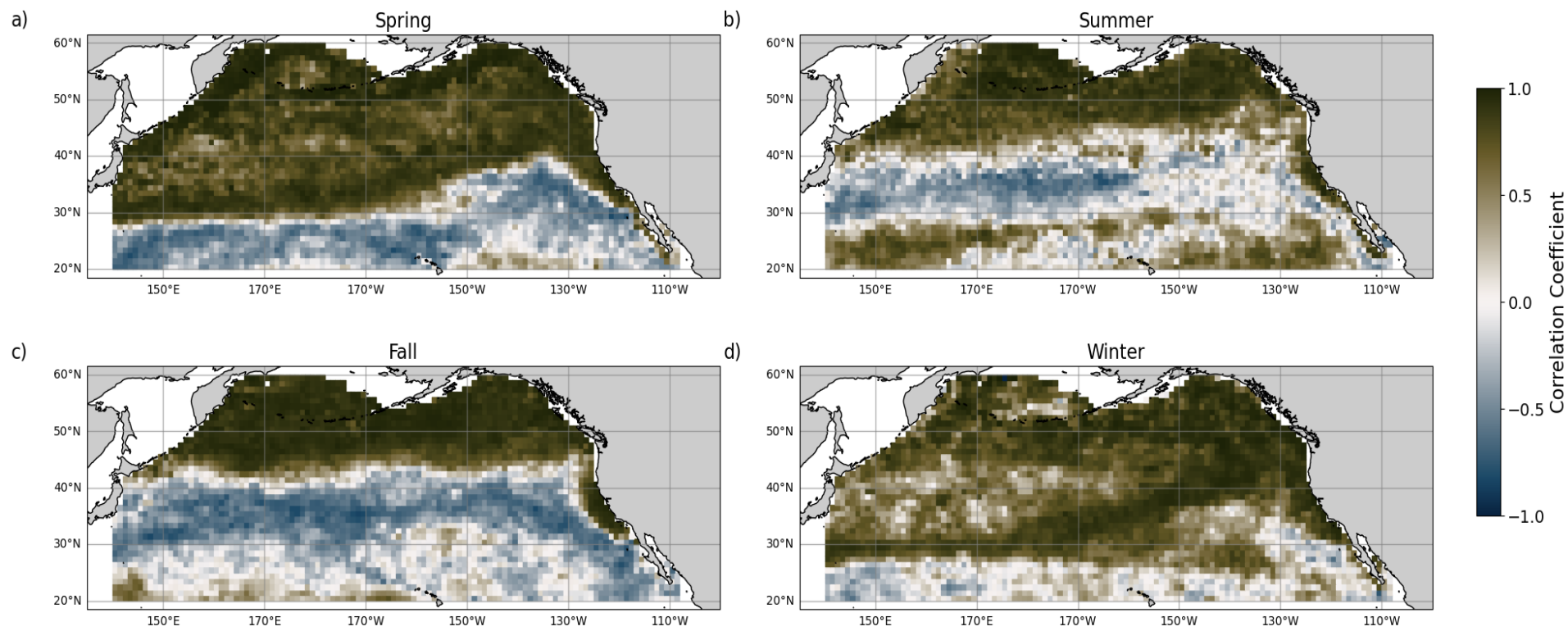


Figure S6 Map showing the correlation coefficients between seasonal means of surface satellite Chl and depth-integrated Chl (from CMEMS data product (E.U. Copernicus Marine Service Information (CMEMS), 2023), over the 10-year study period (2004–2013) in each 1° grid cell (Materials and Methods).

Correlation coefficients between surface satellite and depth-integrated POC

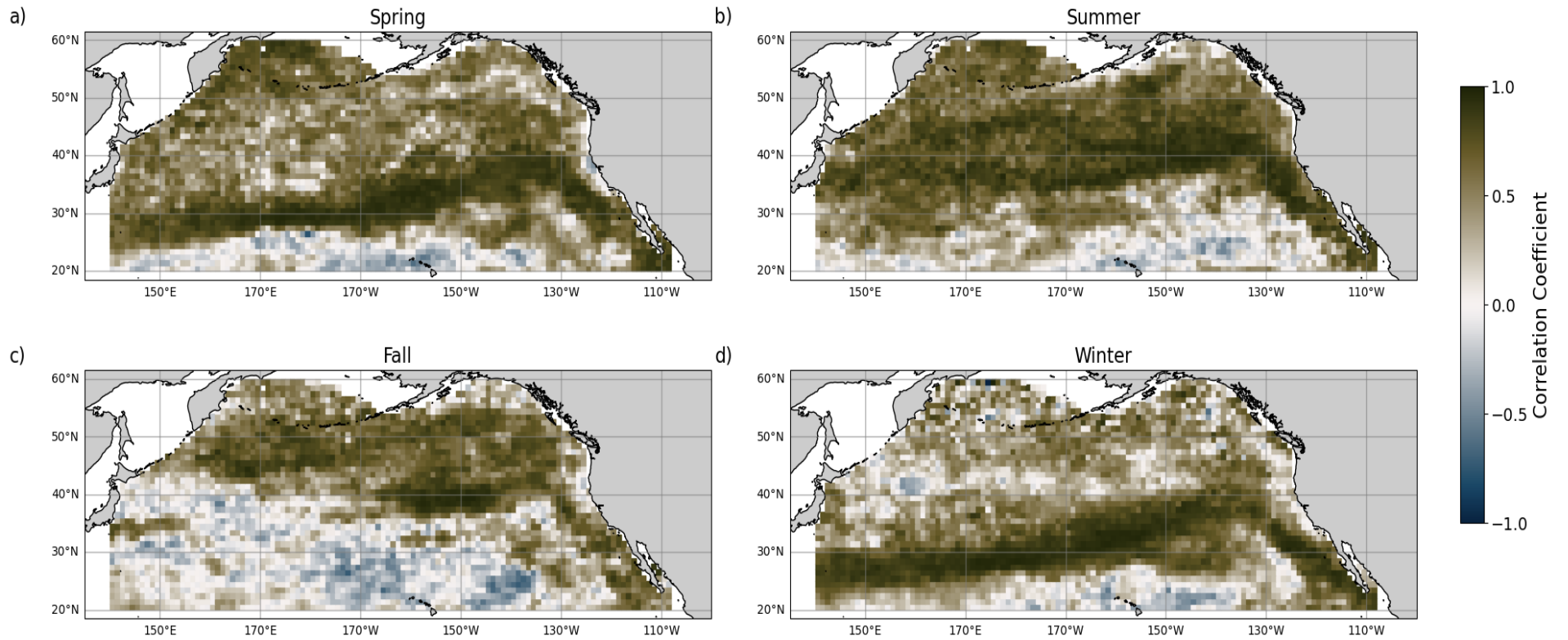


Figure S7| Map showing the correlation coefficients between seasonal means of surface satellite POC and depth-integrated POC (from CMEMS data product, E.U. Copernicus Marine Service Information (CMEMS), 2023) over the 10-year study period (2004–2013) in each 1° grid cell (Materials and Methods).

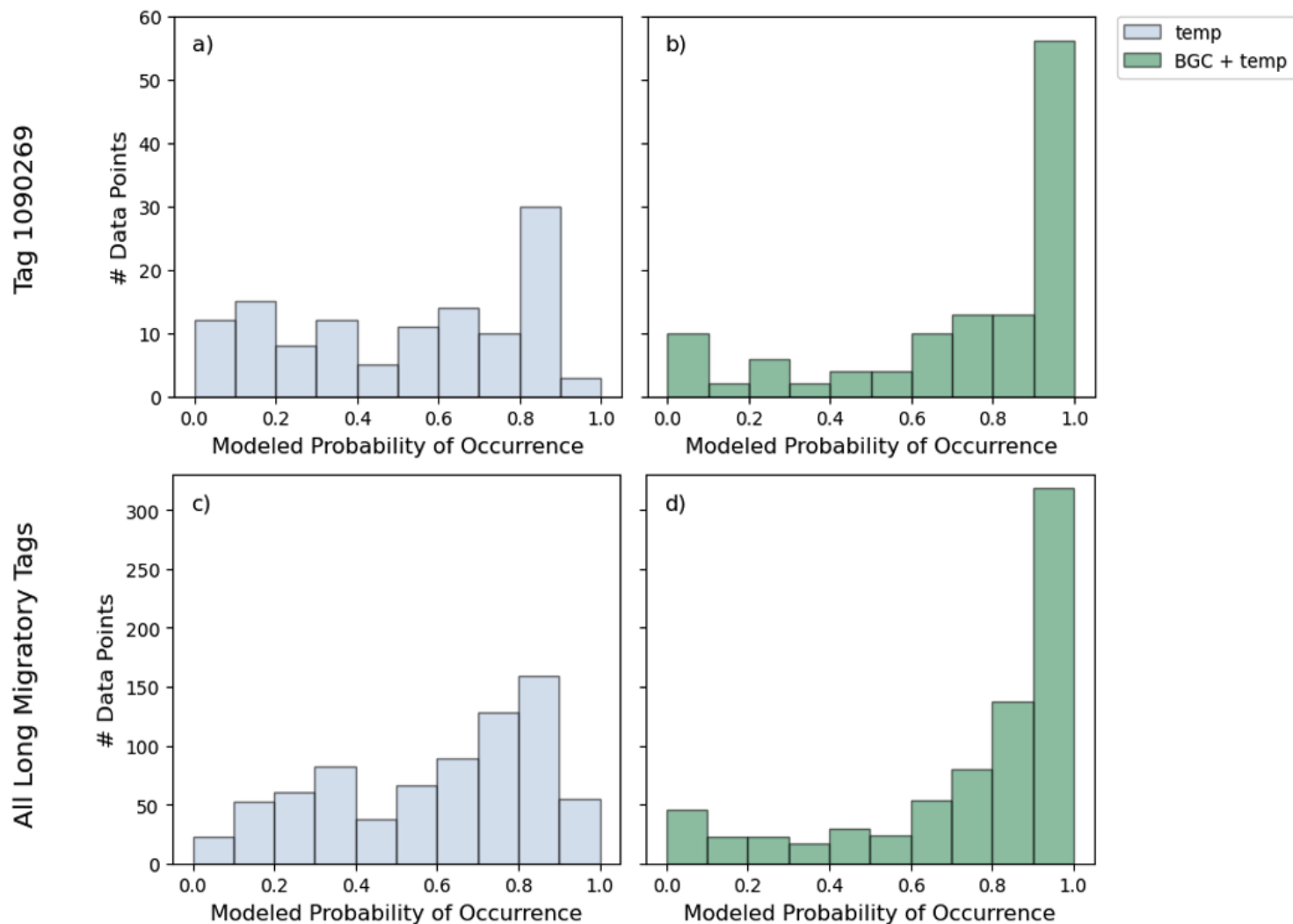


Figure S8| Histograms of modeled probabilities of occurrence at the 90th percentile dive depths predicted along the trajectory of the fish with tag #1090269 (a, b) and all long migratory tags (c, d) in July, August, and September. Results from the temp 3D SDM are shown in light blue (a, c) and results from the BGC + temp 3D SDM are shown in green (b, d). The inclusion of biogeochemical variables in the BGC + temp 3D SDM improved presence classification accuracy (predictions > 0.5) by over 20% for tag #1090269 and over 15% across all long migratory fish, compared to the temp 3D SDM.

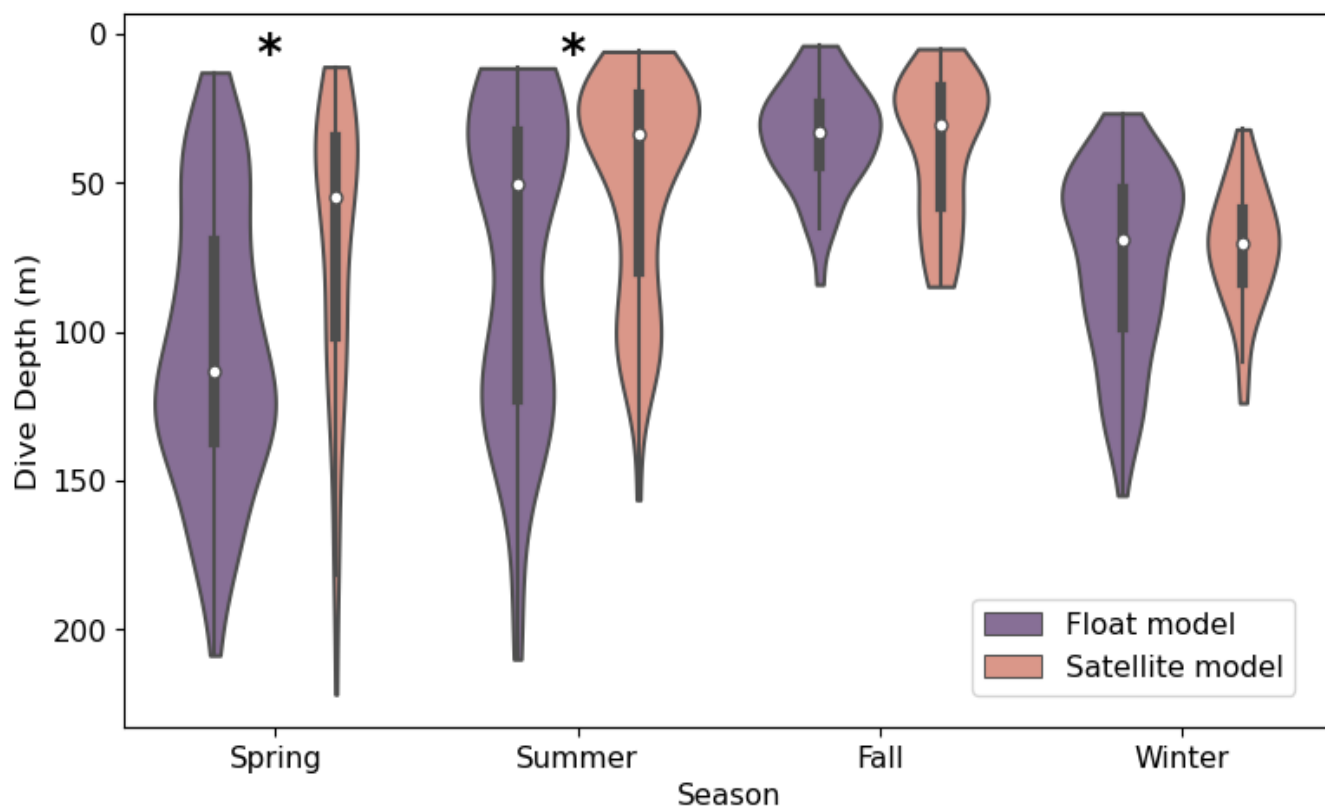


Figure S9 Violin plots comparing seasonal fish diving behavior at locations where only one of the 2D SDMs correctly identified a presence. Purple (pink) represents daily mean dive depths of presences correctly classified by *only* the float-based (satellite-based) 2D SDM. Kernel density estimates are scaled according to the number of correctly classified samples in each group. The black bars within each violin plot represent mini box plots showing the median (white dot), interquartile range (thick black line), and full range of data (thin black line). Dives were significantly deeper (asterisk) according to a Mann-Whitney U test ($p < 0.05$) where only the float-based model correctly classified a presence in both spring and summer.

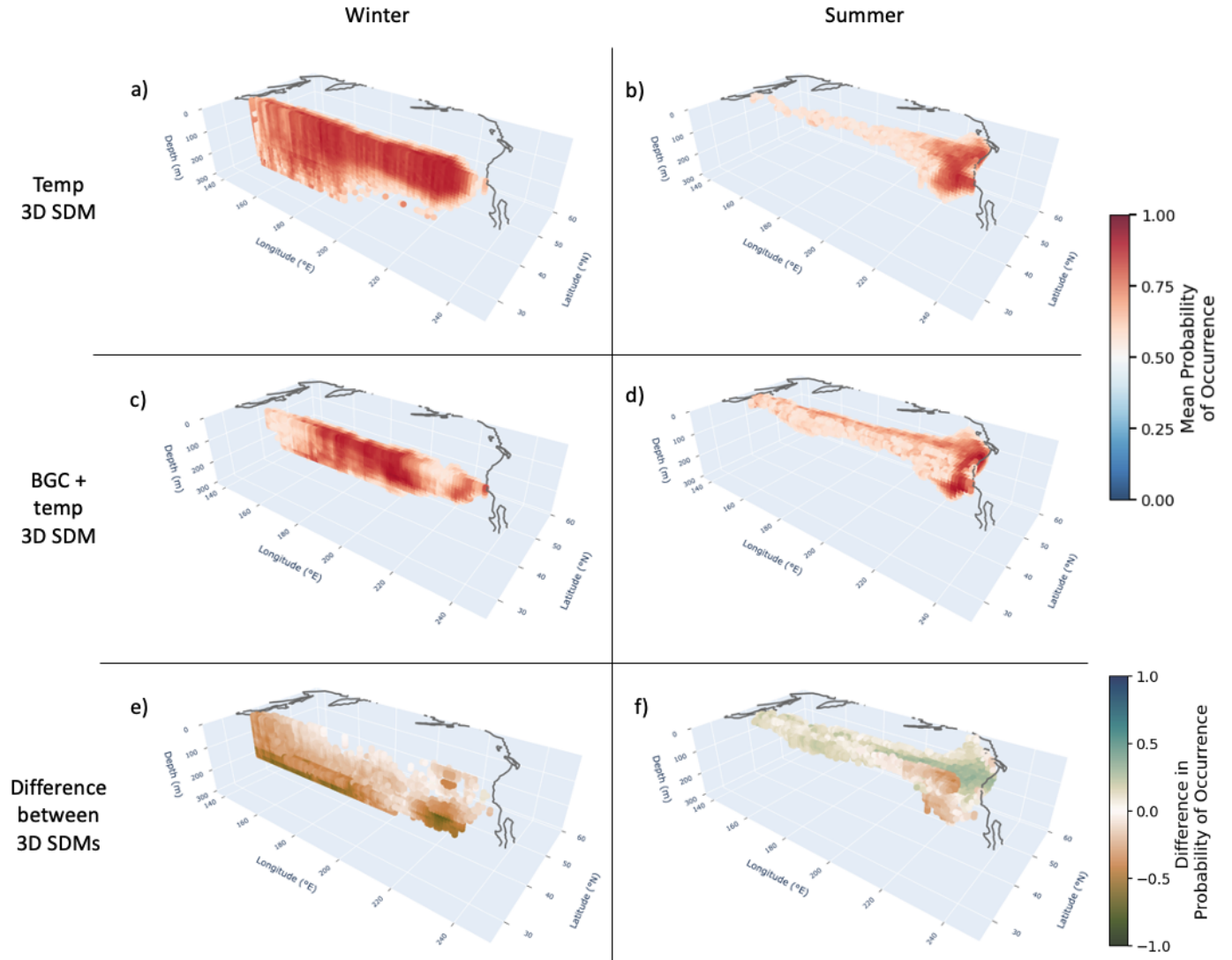


Figure S10 | Modeled probabilities of occurrence for (a, b) the temp 3D SDM and (c, d) BGC + temp 3D SDM in (a, c) winter and (b, d) summer. 3D predictions are shown only for presences (probability > 0.5) along a vertical slice at 35°N to expose probabilities in the interior ocean. e, f) Difference in predicted probabilities between the two 3D SDMs in panels a–d. Only locations where the predicted presence or absence changed as a result of adding biogeochemical predictors are shown in (e) and (f). Brown (green) indicates areas where biogeochemical information decreases (increases) the likelihood of occurrence, contracting (expanding) suitable habitat. The inclusion of biogeochemical predictors (Chl, POC, and oxygen) contracts the suitable habitat volume by over 60% in winter and expands this volume by 25% in summer compared to the temp-only 3D SDM. A majority of this habitat contraction and expansion occurs with respect to the depth dimension.

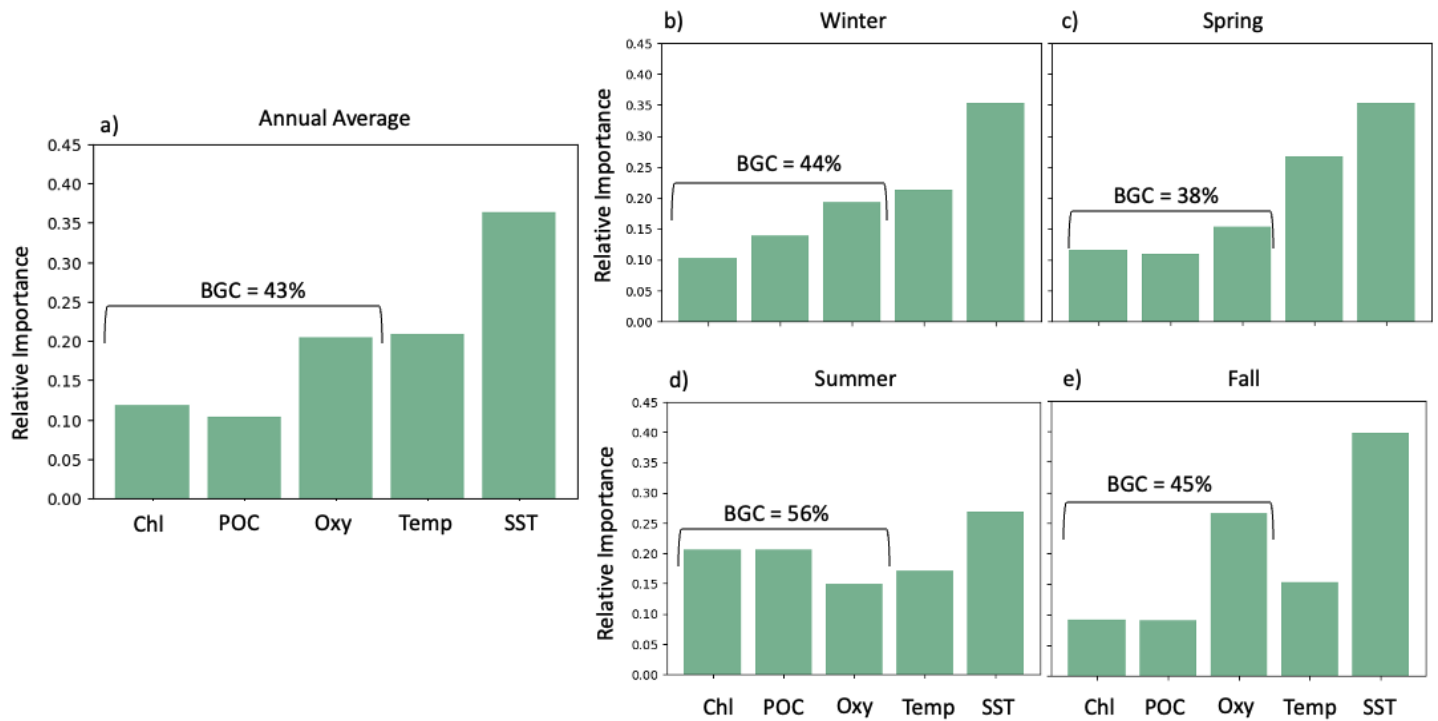


Figure S11 | Feature importance distribution for the BGC + temp 3D SDM for each variable across (a) all seasons, and (b–e) individual seasons. Note that the sum of the feature importance values for each plot is 1. The brackets in each plot represent the collective contribution of the three biogeochemical (BGC) variables (Chl, POC, and oxygen) to feature importance. SST is the most predictive variable in all seasons, reflecting the strong thermal constraint on fish physiology and suitable habitat.

Table S1| Metadata on the 19 archival tagged fish, tracking dates, migratory pattern classifications, and 5-fold leave-fish-out (LFO) split assignments.

Fish Tag	Dates	Number of Months	Migratory Pattern	Leave-Fish-Out (LFO) Split
1045	9/2006 – 3/2008	19	Long migratory	LFO_4
1090251	9/2011 – 5/2013	21	Long migratory	LFO_3
1090269	9/2011 – 4/2013	20	Long migratory	LFO_2
1246	1/2004 – 7/2004	8	Resident	LFO_1
1464	9/2006 – 4/2007	8	Short migratory	LFO_3
1967	1/2004 – 7/2004	7	Resident	LFO_4
1973	1/2004 – 7/2004	7	Resident	LFO_5
1974	1/2004 – 7/2004	7	Resident	LFO_3
1987	1/2004 – 7/2004	7	Short migratory	LFO_4
1991	1/2004 – 7/2004	7	Short migratory	LFO_2
2082	1/2004 – 7/2004	7	Short migratory	LFO_5
2381	7/2004 – 4/2005	10	Long migratory	LFO_5
2393	7/2004 – 5/2006	23	Long migratory	LFO_1
2398	7/2004 – 9/2005	15	Long migratory	LFO_5

2942	9/2004 – 6/2005	10	Short migratory	LFO_2
390167	1/2004 – 7/2004	7	Resident	LFO_2
390191	1/2004 – 7/2004	7	Resident	LFO_2
394	9/2011 – 8/2012	12	Long migratory	LFO_3 and LFO_5
396	9/2011 – 1/2013	17	Long migratory	LFO_1 and LFO_2

Table S2| Summary of model names and predictor variables used to develop two-dimensional (2D) and three-dimensional (3D) SDMs for juvenile albacore tuna.

Model Type	Model Name	Predictor Variables
2D SDM	Float-based 2D SDM	SST, depth-integrated Chl, depth-integrated POC
2D SDM	Satellite-based 2D SDM	SST, satellite Chl, satellite POC
3D SDM	BGC + temp 3D SDM	SST and depth-resolved temperature, oxygen, Chl, and POC
3D SDM	Temp 3D SDM	SST and depth-resolved temperature

Table S3| Summary of global evaluation metrics for the 2D and 3D SDMs using the 5-fold LFO cross-validation design. The predictor variables used to train each model can be found in Table S2.

Model Name	Validation Accuracy	F-1 Score	AUC-ROC
Float-based 2D SDM	0.83 (± 0.02)	0.84 (± 0.02)	0.89 (± 0.01)
Satellite-based 2D SDM	0.81 (± 0.02)	0.82 (± 0.02)	0.87 (± 0.01)
BGC + temp 3D SDM	0.86 (± 0.02)	0.86 (± 0.03)	0.94 (± 0.01)
Temp 3D SDM	0.82 (± 0.01)	0.82 (± 0.01)	0.89 (± 0.01)

Table S4| Summary of global evaluation metrics using several cross-validation designs (Materials and Methods) for the 2D float-based SDM. LFO: 5-fold split based on fish tracks (Table S1). Season: 4-fold split based on seasons. Region: 9-fold splits based on dividing the study domain into nine $\sim 20^\circ$ longitude x 25° latitude boxes. Random: 5-fold random (relative to each daily fish location) splits.

Cross-Validation Design	Validation Accuracy	F-1 Score	AUC-ROC
Leave-Fish-Out (LFO)	0.83 (± 0.02)	0.84 (± 0.02)	0.89 (± 0.01)
Season	0.78 (± 0.08)	0.77 (± 0.10)	0.84 (± 0.07)
Region	0.75 (± 0.11)	0.59 (± 0.32)	0.79 (± 0.12)
Random	0.85 (± 0.01)	0.86 (± 0.01)	0.91 (± 0.004)

Table S5 Summary of global evaluation metrics using several cross-validation designs (Materials and Methods) for the BGC + temp 3D SDM. LFO: 5-fold split based on fish tracks (Table S1). LFO: 5-fold split based on fish tracks (Table S1). Season: 4-fold split based on seasons. Region: 9-fold splits based on dividing the study domain into nine $\sim 20^\circ$ longitude x 25° latitude boxes. Random: 5-fold random (relative to each daily fish location) splits.

Cross-Validation Design	Validation Accuracy	F-1 Score	AUC-ROC
Leave-Fish-Out (LFO)	0.86 (± 0.02)	0.86 (± 0.03)	0.94 (± 0.01)
Season	0.81 (± 0.03)	0.80 (± 0.04)	0.90 (± 0.02)
Region	0.77 (± 0.07)	0.59 (± 0.30)	0.85 (± 0.09)
Random	0.89 (± 0.01)	0.89 (± 0.01)	0.85 (± 0.004)

Appendix C: Supplementary Materials for Chapter 4

Supplementary Text S1

To evaluate algorithm performance at the intervention site, we performed five-fold cross-validation using randomly partitioned subsets of the predictor time series at the prescribed sampling frequency. While this was not necessary to assess performance since the final evaluation was conducted on an independent test year, cross-validation results were used to guide algorithm selection that could be applied across Sequim Bay to baseline year two. We calculated the root mean square error (RMSE) for each predictor combination and sampling frequency to guide algorithm selection (Figures S3 and S4).

For TA, the predictive algorithm based on *TS* provided reasonable estimates at both the field-trial and mid-bay sites (Figure S3c–d). Expanding the predictor set to include all variables (*TSONP*) led to modest improvements in algorithm performance and reduced RMSE by ~10%, consistent with findings from similar algorithm development efforts for the open ocean (Carter et al. 2017). Increasing sampling frequency did not have a clear impact across all parameters and intervention sites. While increasing frequency helped to improve algorithm performance at the field-trial site, it worsened algorithm performance at the mid-bay site.

For $p\text{CO}_2$, predictor variables had a much stronger effect on performance than sampling frequency (Figure S3a–b). The inclusion of one additional predictor beyond *TS*, especially nitrate, reduced RMSE by ~50% at both sites. While adding predictor variables consistently improved algorithm skill, increasing sampling frequency did not always yield better results. In all configurations at the field-trial site and half of those at the mid-bay site, higher sampling frequency actually increased RMSE, indicating that frequent measurements did not consistently improve predictive skill.

Similar to $p\text{CO}_2$, the inclusion of one additional predictor beyond TS reduced RMSE by more than 50% for DIC as well (Figure S3e–f). Oxygen was the most skillful additional predictor and reduced RMSE to the greatest extent at both the field-trial and mid-bay sites. As observed for $p\text{CO}_2$, predictor choice generally had a larger impact on algorithm performance than sampling frequency. In almost all configurations at the field-trial site and half of those at the mid-bay site, higher sampling frequency modestly decreased RMSE.

To evaluate the sensitivity of these results to observational uncertainty, we performed a Monte Carlo simulation by introducing random error to the target carbonate chemistry variables (normal distribution with a standard deviation of 2 mmol/m³ or atm), consistent with expected field measurement uncertainty. This allowed us to evaluate the effect of observation uncertainty on predicted carbonate chemistry parameters. The resulting RMSE values were within the error bounds of the five-fold cross validation, indicating that the added measurement noise did not significantly impact algorithm performance.

The impact of sampling frequency was more apparent in the precision of algorithm estimates (Figure S4). Decreasing sampling from hourly to weekly frequency increased the standard deviation of RMSE across train-test splits for all three carbonate chemistry variables, indicating reduced reliability of predictions. In general, increasing sampling frequency reduced RMSE variability more consistently than expanding the set of predictor variables.

After selecting several top-performing configurations, the trained algorithm was applied to hourly model output from year two of the baseline scenario across Sequim Bay to estimate carbonate chemistry variables at each grid cell. We then calculated RMSE at each grid cell by comparing predicted and true model output. These values were used as the model node-specific assumption uncertainty (U_A in Equation 2).

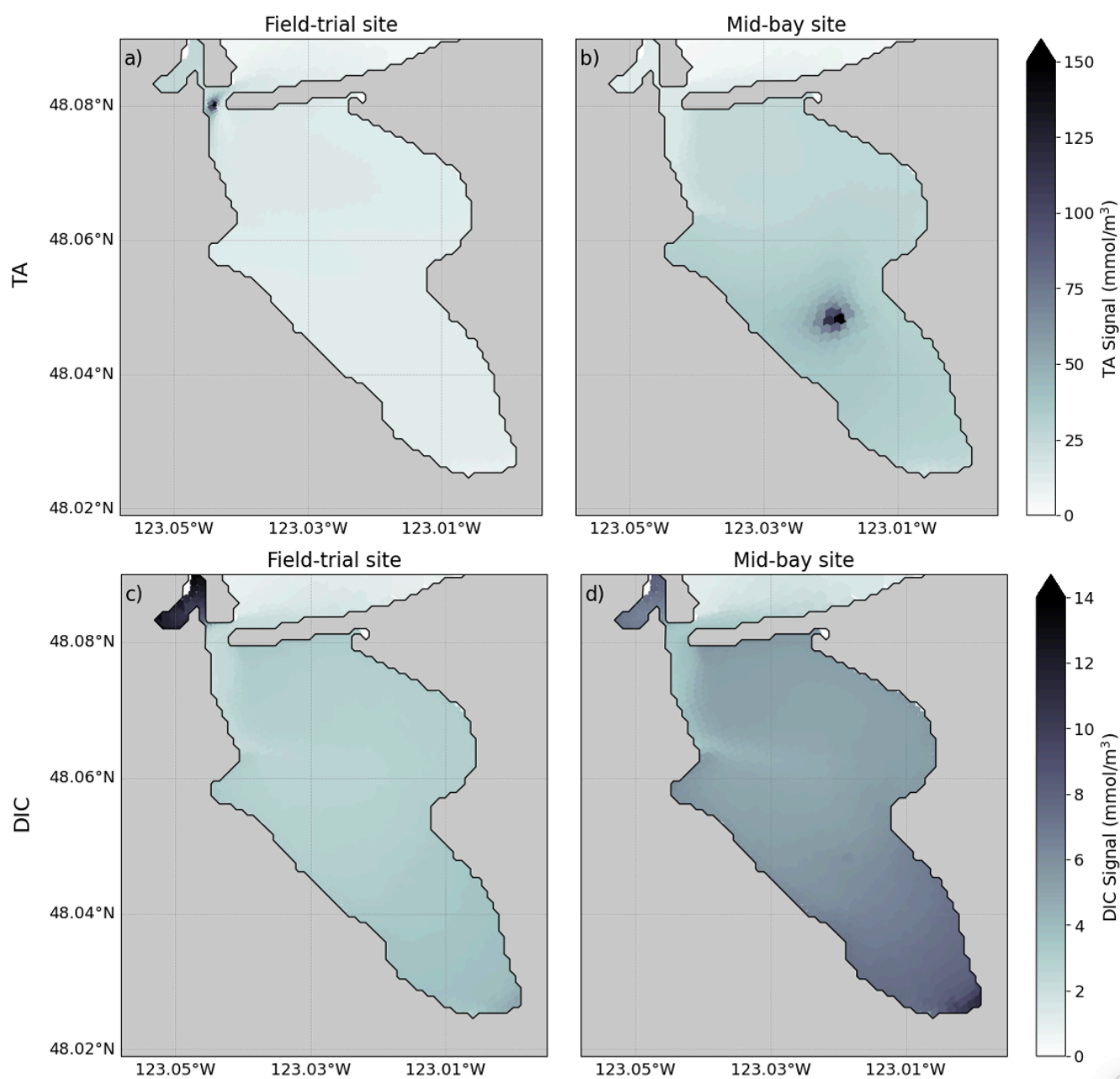


Figure S1 | Maps of the annual mean OAE-induced TA (a, b) and DIC (c, d) signals at the field-trial (a, c) and mid-bay (b, d) sites. The signal (S) is defined as the difference between the annual average of hourly modeled values in the experimental scenario and the baseline scenario ($S = \text{experimental} - \text{baseline}$).

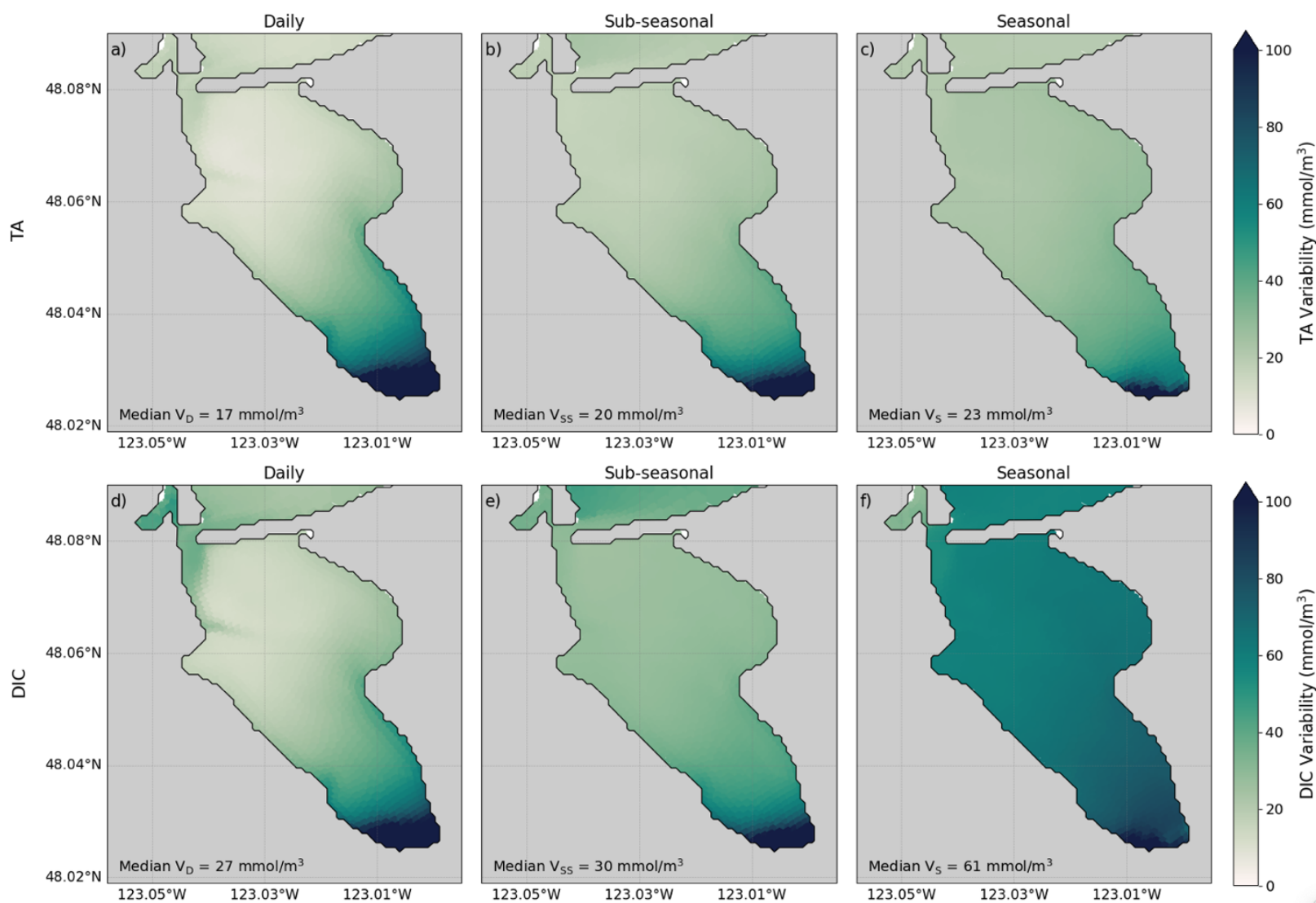


Figure S2 | Maps of daily (a, d), sub-seasonal (b, e), and seasonal (c, f) variability of TA (a–c) and DIC (d–f) across Sequim Bay.



Figure S3| Mean RMSE from five-fold cross-validation of predictive algorithms at the field-trial (a, c, e) and mid-bay (b, d, f) sites. Each panel shows a heat-map table of mean RMSE values from five-fold cross validations, calculated at three sampling frequencies (hourly, daily, weekly) for three carbonate chemistry variables: $p\text{CO}_2$ (a–b), TA (c–d), and DIC (e–f). The columns correspond to different combinations of predictor variables (TS , TSO , TSN , TSP , $TSON$, and $TSONP$). Lower RMSE values denote better algorithm performance.



Figure S4| Standard deviation (SD) of RMSE from five-fold cross-validation of predictive algorithms at the field-trial (a, c, e) and mid-bay (b, d, f) sites. Each panel presents a heat-map table of the standard deviation of RMSE values from five-fold cross validations, calculated at three sampling frequencies (hourly, daily, weekly) for three carbonate chemistry variables: $p\text{CO}_2$ (a–b), TA (c–d), and DIC (e–f). The columns correspond to different combinations of predictor variables (*TS*, *TSO*, *TSN*, *TSP*, *TSON*, and *TSONP*). Lower standard deviations indicate more precise algorithm performance.

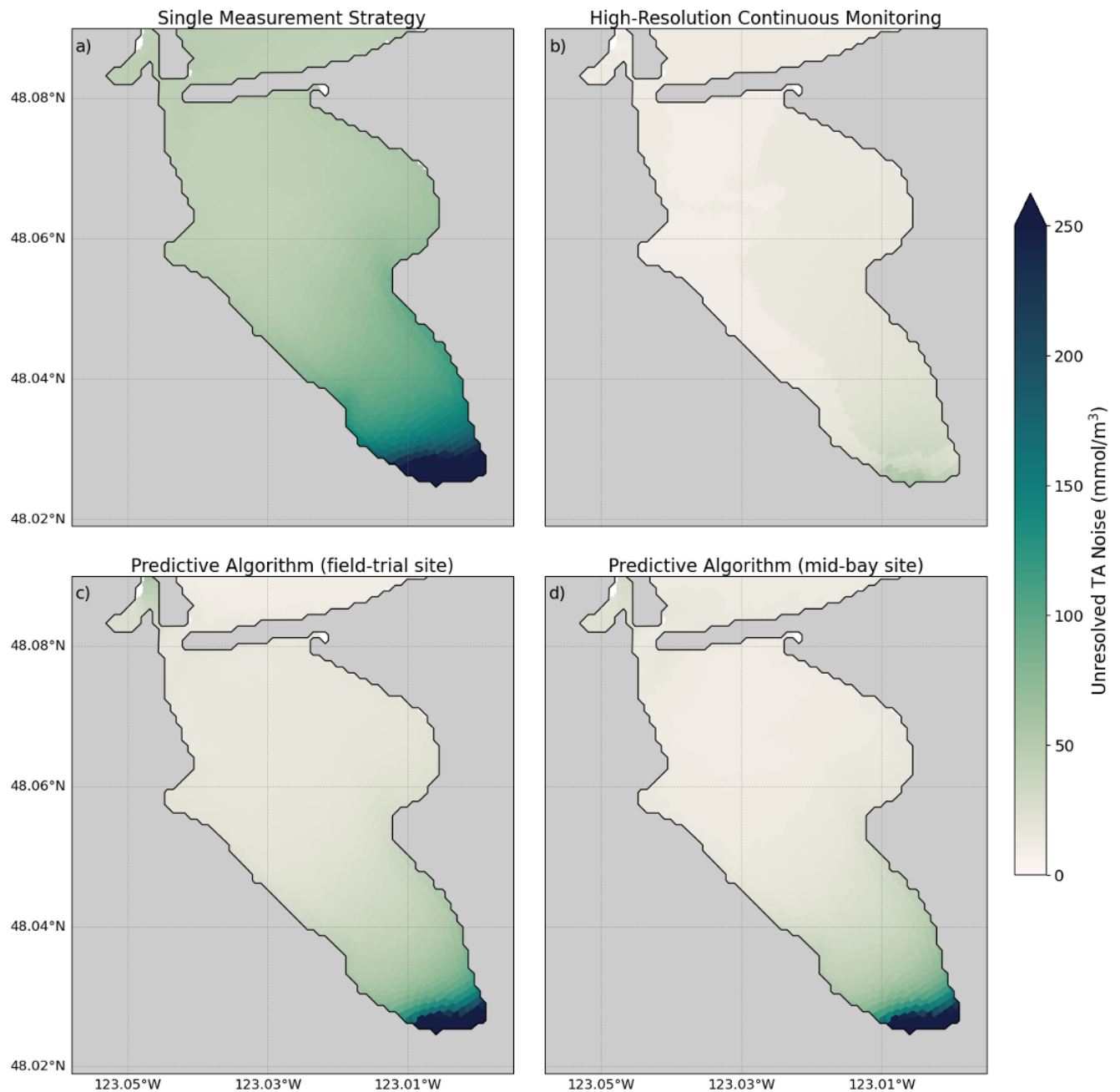


Figure S5| Maps of the unresolved TA noise under three observing strategies: a) the single-measurement strategy, b) the long-term averaging strategy, and c–d) the predictive algorithm monitoring strategy. The predictive algorithms were trained on daily *TSN* data from the field-trial site (c) and mid-bay site (d) and applied to the entire bay. The noise (N) equations for each strategy are derived from Equation 2 but differ in modes of variability and uncertainty they resolve. The specific formulations used to generate these maps are given in Table 1.

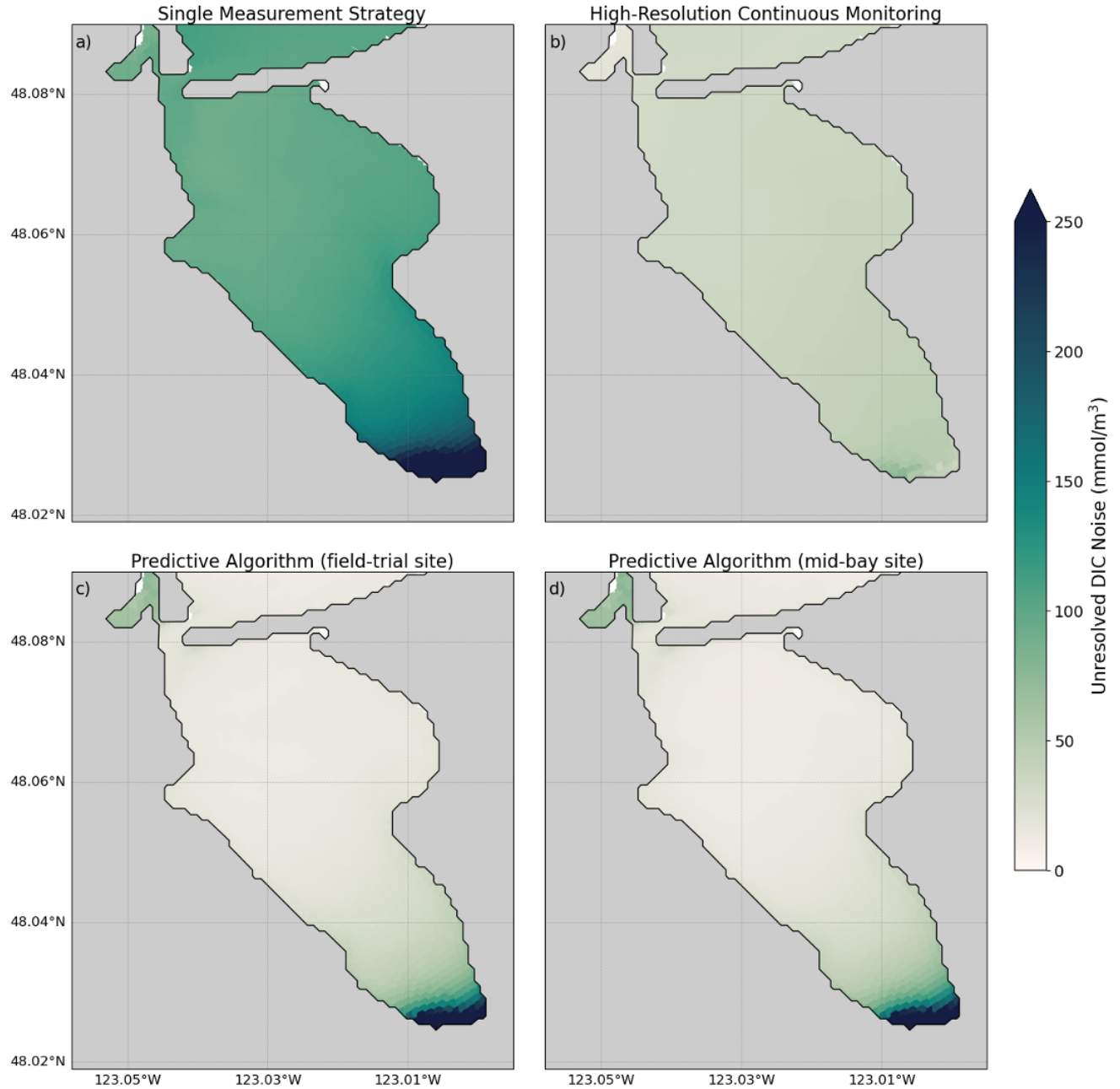


Figure S6 Maps of the unresolved DIC noise under three observing strategies: a) the single-measurement strategy, b) the long-term averaging strategy, and c–d) the predictive algorithm monitoring strategy. The predictive algorithms were trained on daily *TSN* data from the field-trial site (c) and mid-bay site (d) and applied to the entire bay. The noise (N) equations for each strategy are derived from Equation 2 but differ in modes of variability and uncertainty they resolve. The specific formulations used to generate these maps are given in Table 1.

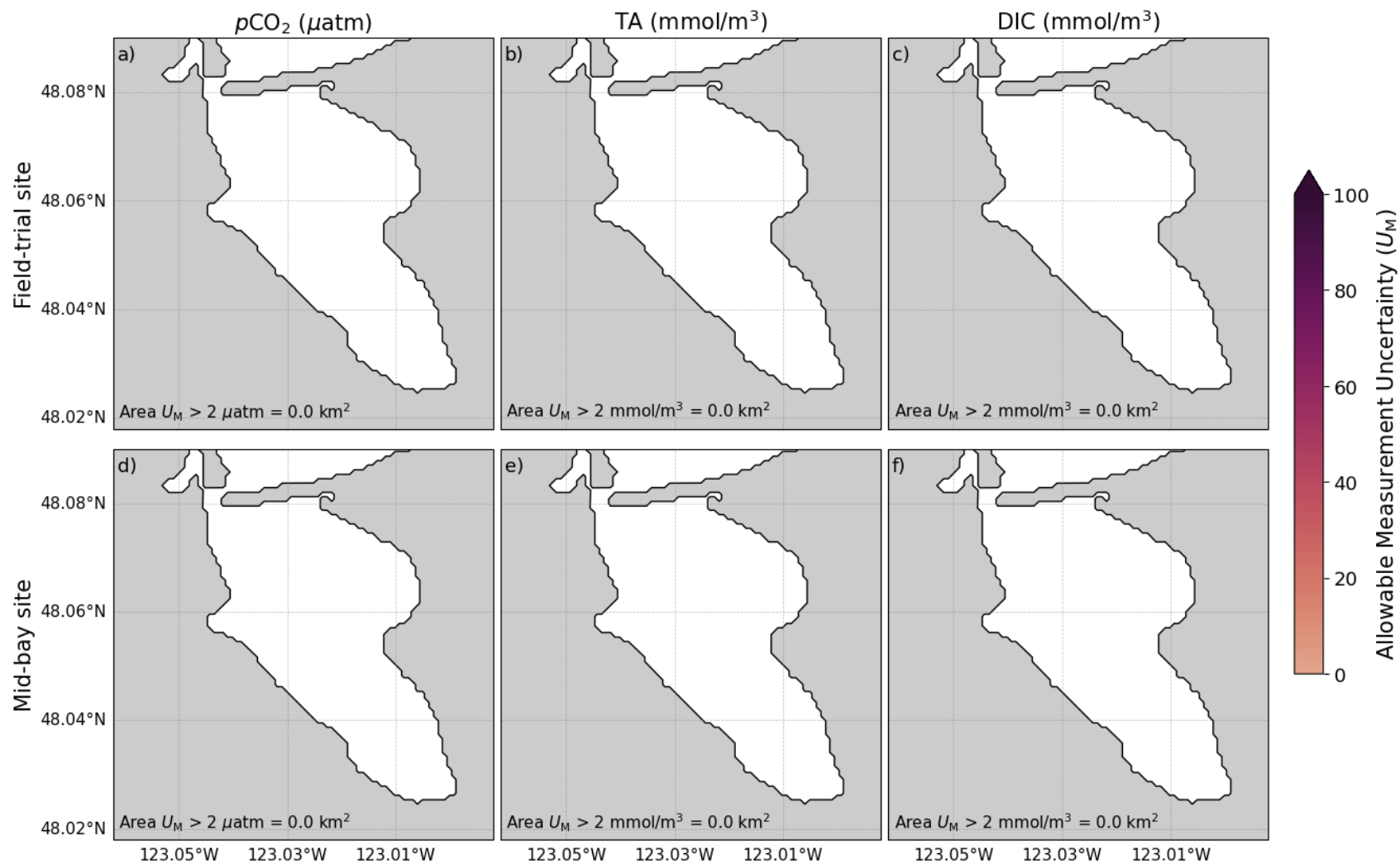


Figure S7] Detectable area of OAE-induced perturbations under the single-measurement strategy for $p\text{CO}_2$, TA, and DIC at two intervention sites. White regions fall below the detection threshold or allowable measurement uncertainty (U_M) that permits detection of the OAE signal. No area is detectable for any of the carbonate chemistry variables at the field-trial site (a–c) nor the mid-bay site (d–f) under this monitoring framework.

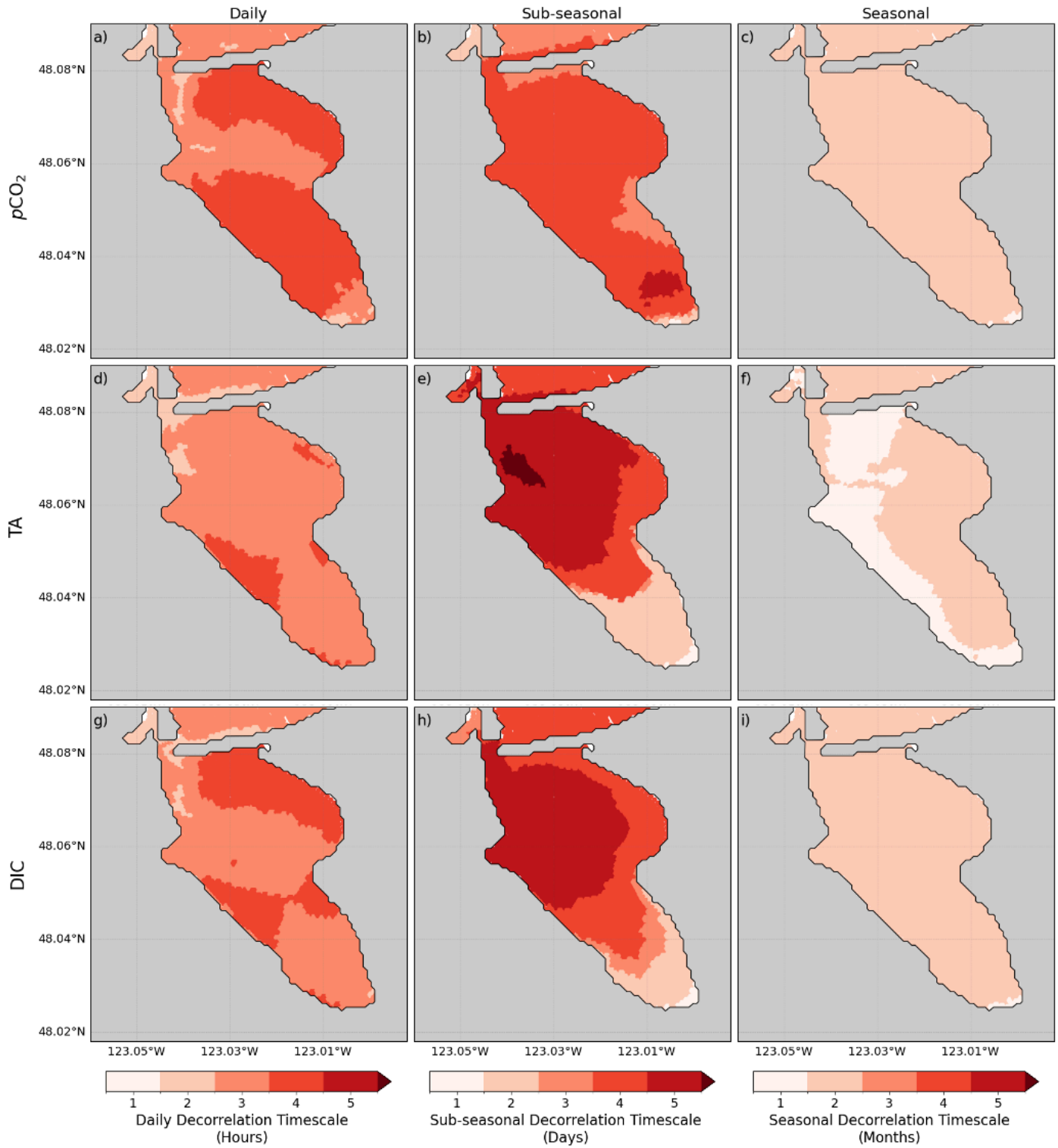


Figure S8 Maps of decorrelation timescales (τ) for $p\text{CO}_2$, TA, and DIC at daily (τ_D), sub-seasonal (τ_{SS}), and seasonal (τ_S) frequencies. Rows represent a carbonate chemistry parameter— $p\text{CO}_2$ (a–c), TA (d–f), and DIC (g–i). Columns correspond to the decorrelation timescales at daily (a, d, g), sub-seasonal (b, e, i), and seasonal (c, f, j) frequencies. Each cell's color indicates the decorrelation timescale (in

hours for daily, days for sub-seasonal, and months for seasonal modes) computed from one year of hourly model output. Light shades indicate shorter decorrelation timescales or faster loss of correlation, whereas darker shades indicate longer decorrelation timescales or slower loss of correlation. Regions with the longest decorrelation timescales represent areas where natural variability persists most strongly at each frequency.