https://doi.org/10.5194/egusphere-2024-1836
Preprint. Discussion started: 25 June 2024

Long-term variations of pH in coastal waters along the Korean Peninsula

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Abstract. The decreasing seawater pH trend associated with rising atmospheric CO_2 levels adversely affects marine organisms and ecosystems, posing significant concerns for coastal fisheries and economies. Despite this, long-term pH variation in coastal waters remains poorly understood. This study investigates pH variability in the coastal waters of Korea over 11 years (2010-2020) and identifies the principal drivers of pH fluctuations. Unlike the persistent pH decline observed in open oceans and other coastal systems, Korean coastal waters showed no significant pH variation, suggesting local biogeochemical processes may exert a greater influence than atmospheric CO_2. Analysis of environmental data (temperature, salinity, chlorophyll a, and dissolved oxygen (DO)) revealed a strong correlation between pH and DO. However, instances of pH changes exceeding those predicted by DO depletion indicate additional biogeochemical factors at play. As global seawater warms, reduced dissolved gases, including oxygen, are expected to cause further pH decline in coastal waters. This trend could critically impact Korean coastal waters, which support extensive aquaculture operations integral to the local and national economy. Therefore, high-frequency monitoring is essential to extend current time series and predict future water quality.

1 Introduction

The alarming increase in atmospheric carbon dioxide (CO_2) poses a significant concern for the climate crisis. Since the industrial revolution, atmospheric CO_2 concentration has nearly doubled, reaching 420 ppm at Mauna Loa, Hawaii (https://gml.noaa.gov). The ocean and terrestrial biosphere absorb approximately 50% of the increased atmospheric CO_2

(Friedlingstein et al., 2022), leading to negative impacts on marine organisms. As of now, the ocean has absorbed about 26% of the total anthropogenic CO_2 released between 1850 and 2020 (IPCC, 2022), with an estimated cumulative uptake of 170 ± 35 GtC, over two-thirds of which occurred post-1960. The oceanic CO_2 sink has increased from 1.1 ± 0.4 GtC yr^{-1} in the 1960s to 2.8 ± 0.4 GtC yr^{-1} during 2011-2020 (IPCC, 2022).

Air-sea gas exchange is the primary pathway for oceanic CO_2 uptake, though riverine input can be significant in coastal where river-dominated areas (Cai, 2011). Once CO_2 dissolves in seawater, it undergoes a series of chemical reactions: CO_2 reacts with water to form carbonic acid (H_2CO_3), which dissociates into hydrogen and bicarbonate (HCO_3^-) ions, of which the bicarbonate ion further dissociates to carbonate ion (CO_3^{2-}) by releasing additional hydrogen ion. This process increases the concentrations of hydrogen ions, thereby lowering seawater pH and causing ocean acidification (OA). In fact, the increase in atmospheric CO_2 has already led to a pH decrease, as evidenced by long-term datasets such as the Hawaii Ocean Tower (HOT) Time-series, the Bermuda Atlantic Time-Series (BATS), and the European Station for Time Series in the Atlantic Ocean, which have recorded a pH decline of approximately 0.02 units per decade since the 1980s (Solomon et al., 2007). Additionally, surface water pH in the open ocean has dropped by 0.1-0.2 units since preindustrial times due to anthropogenic CO_2 (Pelejero et al., 2005), with projections indicating a further decline of 0.3-0.4 units by the end of the 21st century. This would correspond to an approximate 150% increase in H^+ concentration and a 50% decrease in CO_3^{2-} concentration (Orr et al., 2005).

Ocean acidification (OA) reduces carbonate ion concentrations in seawater by increasing $[H^+]$ ions, posing a significant threat to calcareous marine organisms. The reduction in calcium carbonate ($CaCO_3$) saturation in surface waters, linked to OA, is well-documented through models, field surveys, and long-term monitoring studies (Caldeira and Wickett, 2003; Feely et al., 2004 and 2008; Orr et al., 2005; Solomon et al., 2007). For example, a long-term monitoring at the HOT station reveals that surface pCO_2 increases correlate with atmospheric CO_2, driving increases in dissolved inorganic carbon (DIC) and decreases in $CaCO_3$ saturation (Chen et al., 2023; Takahashi et al., 2009; Doney, 2008; Doney et al., 2007). Lower carbonate ion concentrations result in $CaCO_3$ undersaturation, adversely affecting shell-forming marine organisms such as plankton, mollusks, echinoderms, and corals (Doney et al., 2007; Smith and Buddemeier, 1992; Kleypas and Yates, 2009; Feely et al., 2016; Orr et al., 2005; Kroeker et al., 2013; Nilsson et al., 2012). This undersaturation can decrease growth, locomotion, reproductive capacity, and homeostasis in these organisms if they cannot control calcification conditions (Hendriks et al., 2015). Consequently, OA critically impacts marine ecosystem structure and function, affecting trophic levels.

In addition to atmospheric CO_2 introduction, environmental changes can exacerbate the OA. For instance, in the Louisiana Shelf of the northern Gulf of Mexico, where severe bottom water hypoxia has occurred annually since the mid-1980s, Cai et al. (2011) found a pH decrease of 0.01 over the 1980-2010 period. They attributed this decrease to anthropogenic CO_2 inputs and CO_2 release during hypoxia. Similarly, in the East China Sea, Cai et al. (2011) observed pH decreases linked to coastal eutrophication and low-oxygen-related CO_2 inputs. Globally, hypoxic regions are expanding in size and duration (Breitburg et al., 2018), suggesting future intensification of coastal pH decline.

Ocean CO_2 uptake and the resultant OA are, however, not uniform globally. For example, the Mediterranean Sea, with its unique biogeochemical and hydrodynamic characteristics—such as high alkalinity water and active thermohaline circulation—exhibits a larger absorption of atmospheric CO_2, leading to a pH decrease of 0.0044 units per year (Hassoun et al., 2015; Palmieri et al., 2015; Flecha et al., 2015 and 2019). In contrast, in the northern Pacific Ocean, surface pH has decreased by 0.0012 ± 0.0003 units per year from 1965 to 2010, a rate about four times lower than that observed in the Mediterranean Sea (Watanabe et al., 2018). This discrepancy in pH decrease rates is likely associated with varying biogeochemical properties, such as nutrient levels and freshwater inputs affecting alkalinity (Flecha et al., 2015).

While long-term pH monitoring is well-established in open ocean systems, coastal zones have notably fewer studies. Unlike the open ocean, where pH consistently decreases due to anthropogenic CO_2, coastal pH trends can differ significantly due to their complex physical and biogeochemical dynamics, including nutrient and organic matter inputs from river runoff and groundwater discharge, oceanic forces (waves, tides, currents), seasonal variations, and human activities (Crossland et al., 2005, Flecha et al., 2012). Consequently, coastal pH varies widely and shows different long-term trends (Borges and Gypensb, 2010; Carstensen and Duarte, 2019; Bates et al., 2014). For example, Carstensen and Duarte (2019) reported a broad range of pH trends (-0.023 to 0.023 units yr^{-1}), predominantly associated with terrestrial inputs. Observations from Dutch coastal zones revealed pH change rates exceeding those expected from CO_2 uptake alone, indicating significant influences from other biogeochemical processes, possibly related to nutrient loading changes (Provoost et al., 2010). Nevertheless, because of many biogeochemical processes, coastal pH variations are not well studied. In particular, the long-term trend of pH in Korean coastal waters has not been reported, despite the presence of semi-closed bays, rivers, and fish farms that could impact pH changes alongside climate change. Southern Korea features ria coasts with numerous semi-enclosed bays and fish farms. The west coast has high tidal prisms, extensive land reclamation, and large coastal cities. In contrast, the east coast has a narrow continental shelf, a simple coastline with no bays or fish farms, and is less populated, making it relatively pristine. Therefore, Korean coast is a great testbed to investigate how different biogeochemical settings affecting pH over a long-time scale. We investigated in-situ trends of pH, temperature, salinity, dissolved oxygen (DO), and chlorophyll *a* (chl *a*) in surface and bottom coastal seawaters of Korea, as part of ongoing monitoring programs since 2010. Using data from 2010 to 2020, we address seasonal and spatial pH variations and identify predominant factors influencing these changes. Our results would provide a quantitative reference for future studies on coastal carbon dynamics and the impacts of anthropogenic climate forces and environmental changes.

2 Methods and Materials

2.1. Data collection

The data set used in this study was derived from a monitoring program conducted by the Korea Marine Environment Management Corporation (KOEM) since 2010, aimed at assessing water quality along the entire Korean coast (Fig. 1). This program includes 356 sites where water quality parameters are measured in both surface and bottom waters four times a year (February, May, August, and November). Detailed information on the program can be found in KOEM (https://www.meis.go.kr). For this study, we examined data collected from 2010 to 2020, comprising 30,000 measurements for each parameter. We created two average data sets: one for each coastal region (south, west, and east) and one for the entire Korean coast.

In this investigation, we analyzed a comprehensive 11-year dataset to assess long-term variations in seawater pH alongside temperature, salinity, DO, and chl *a* levels along the Korean coast. All sampling locations were situated within 6 km from the shoreline, predominantly in shallow waters with depths of < 10 m, except for a few sites along the eastern coast. These sites are influenced by factors such as riverine inputs, land use patterns, and climatic conditions, all of which are susceptible to the impacts of global warming and climate change.

2.2 Site Description

Korea's geography is characterized by a highly mountainous east coast and plateau-like south and west coasts, leading to less steep continental slopes in the south and west. Major river systems are developed in the west and south, but not in the east. The west coast, facing the Yellow Sea, features a typical drowned valley shoreline with shallow waters, a maximum depth of about 40 m, and extensive muddy tidal flats accounting for 3% of the world's tidal flats. This area experiences high turbidity, macrotidal conditions (tidal amplitudes up to 5 m), and significant land reclamation for agriculture, industry, and residential use, which has altered currents, sediment transport, and biogeochemical properties (Williams et al., 2014, 2015). The west coast is influenced by the Korean Coastal Current from the Kuroshio warm current in summer and the Yellow Sea Cold Current in winter (Hwang et al., 2014). Three major rivers (Han, Geum, and Yeongsan) and numerous streams drain into this region.

The southern coast features ria estuaries with moderate relief and V-shaped valleys. It has many islands and semi-enclosed bays, resulting in slow currents and a semi-diurnal tidal range of 1-3 m, supporting extensive fish farming (Williams et al., 2013). Major rivers like Nakdong and Seomjin, along with numerous tributaries, provide freshwater into the coast. Recent dam constructions in the Nakdong River system have significantly reduced freshwater and nutrient inputs (Williams et al., 2013). The southern seas are influenced by the Tsushima Current, a branch of the Kuroshio Current, bringing high-temperature, high-salinity waters, with occasional inputs from the Changjiang diluted water during summer (Lie and Cho, 1994) (Fig. 1).

The eastern coastline of Korea is relatively simple and monotonous compared to the southern and western coasts. Due to its mountainous terrain, the eastern coast features a very narrow continental shelf with a steep slope. There are no major rivers along this coast, so most materials, including nutrients and organic matter, are transported via the Tsushima Current, which flows through the southern coast of Korea (Jang et al., 2013).

2.3. Water collection and measurement

To examine the temporal and spatial distribution of marine environmental parameters (temperature, salinity, pH, dissolved oxygen, and chl *a*), seawater samples were collected using 5-L Niskin bottles attached on a rosette sampler equipped on a research vessel of the KOEM. Seawater temperature and salinity were measured using a CTD profiler (Seabird 19plus, Sea-Bird electronics Inc., USA). For pH measurements, a portable sensor (Orion Star A329, Thermo Scientific, USA) with an accuracy of ±0.002 pH unit was used. All pH measurements were performed onboard soon after water collection to minimize temperature changes. Briefly, water samples were collected from both surface and bottom depths using Niskin samplers, and upon retrieval, water samples were transferred into glass containers (a beaker) using a silicone tube. Immediately after transfer, the pH sensor was immersed in the water sample, and pH readings were recorded once the values stabilized, typically within a few tens of seconds. Calibration of the pH sensor was conducted daily prior to sample measurements using three standard buffer solutions (pH 4, 7, and 10), in accordance with the manufacturer's guidelines. The DO in seawater was measured using the Winkler-Sodium Azide titration method. For the chl *a* analysis, seawater samples (1 L) were collected at the surface and bottom layers and filtered onboard using 0.45 μm pore-sized membrane filters (47 mm diameter), which were then stored at -20 °C until analysis. In the laboratory, the chl *a* extraction from the filters was conducted, and fluorescence was measured using a fluorometer (Turner Designs, 10-AU model, San Jose, CA, USA).

3 Result and Discussion

3.1. Long-term trend of pH

The foremost concern within coastal aquatic ecosystems amidst global warming pertains to the OA, given its profound impact on biota (Raven et al., 2020; Hinga, 2002). Consequently, the issue of OA assumes particular significance along the Korean coastline, which hosts a considerable number of fish and seaweed farms. The variations in average pH levels across the entire Korean coastal waters are depicted in Figures 2-5 (Supplementary Figure 1-6 provides a comprehensive dataset). Monthly averages, in February, May, August, and November of each year, exhibited a pH range of 7.96 to 8.30 (mean, 8.13; n=88). Notably, bottom waters exhibited slightly lower pH levels compared to surface waters, likely attributable to organic matter decomposition releasing CO_2 into both the sediment and water column. Over the 11-year timeframe, monthly averaged pH levels displayed a discernible increasing trend in both surface and bottom depths, with slopes of 0.00009 yr^{-1} (± 0.00001).

However, this regression trend appeared statistically insignificant, with an F value of 0.0003, suggesting that Korean coastal waters do not exhibit a pH decrease, at least over a decadal scale. This observed long-term pH trend somewhat contrasts with prior studies, which have reported decreasing pH trends in both coastal and open ocean systems. For example, pH declines have been documented in other coastal regions worldwide, such as the Mediterranean Sea (Flech et al., 2015), Dutch coasts (Provoost et al., 2010; Hofmann et al., 2011), the Washington coast, USA (Lowe et al., 2019), and various other areas (refer to review articles by Duarte et al., 2013; Carstensen and Duarte, 2019; Wootton et al., 2008). These studies have reported substantial ranges of decreasing rates, ranging from -0.045 to -0.0044 yr^{-1}. Carstensen and Duarte (2019) further observed that in certain sites (21 out of 83), pH declined even more rapidly than the rate of decrease observed in the open ocean (i.e., -0.0018 yr^{-1}), originated from both atmospheric CO_2 forcing and variations of local salinity and primary production.

In regions geographically proximate to Korea, coastal waters from Japan and China have also shown a decline in pH levels. For instance, Ishida et al. (2021) conducted a 30-year monitoring study from 1980 to 2010 at two coastal sites in Japan, revealing decreasing pH trends ranging from - 0.0032 to -0.0068 yr^{-1}, with greater declines observed on the Pacific side compared to the East Sea (or Sea of Japan) side. The observed regional differences may be attributed to local biophysical and chemical factors, with the Pacific side influenced by meandering Kuroshio Currents and coastal eutrophication, exacerbating pH decrease (Ishida et al., 2021). Recently, Ishize et al. (2019) reported long-term pH trends from over 280 sites in Japanese coastal waters, spanning a 30-year monitoring period. They observed that in the majority of areas (>75%), the annual maximum pH exhibited a decrease of -0.0024 yr^{-1}. Moreover, Cai et al. (2011) found that regions such as the East China Sea and the Louisiana Shelf, characterized by seasonal bottom water hypoxia, experienced more severe pH declines than those attributed solely to atmospheric CO_2. All of these previous studies suggest that, for coastal waters, pH variation could be predominantly governed by local biogeochemical properties and thus appear differently among places.

Conversely, some sites have exhibited an increase in pH. Notably, the remaining 25% of sites in Ishize's study showed an upward trend, although no geographic patterns were evident among these sites. Additionally, Carstensen and Duarte (2019) documented a wide range of pH trends, with slopes ranging from -0.023 to 0.023 yr^{-1}. Their analysis revealed that, though the majority (46 out of 83 sites) of coastal areas were experiencing pH declines, the remaining 37 sites displayed either increasing trends or negligible changes, mirroring observations in our study. Hence, despite the overarching influence of global atmospheric CO_2 forcing, regional variations in pH fluctuations can be substantial. Therefore, the lack of substantial changes in pH along the Korean coasts is not unique and reflects the complexities of pH dynamics in coastal waters, where local biogeochemical properties differ from those in the open ocean as well as among different regions.

3.2. Local pH variations

While overall pH variations along the entire Korean coast were not statistically significant, localized pH changes in specific coastal regions exhibited nuanced seasonal and vertical dynamics. Generally, pH levels were higher along the southern and eastern coasts (~8.15) compared to the western coast (~8.10). Seasonally, peaks and troughs in pH were observed in

February and August, respectively, along the southern and western coasts, whereas the seasonality in the east coast did not display consistent patterns compared to the other regions (Figs. 3-5). Furthermore, surface-bottom pH disparities were absent along the western coast, whereas notable differences were observed between surface and bottom waters, particularly in May and August, along the east and south coasts (Figs. 3-5).

The spatial variations in pH were likely influenced by physiographic features. Specifically, the western coast of Korea is characterized by shallowness and a significantly high tidal prism (up to 5 m). Given that our sampling sites predominantly had depths of <10 m along the western coast, the substantial tidal prism and semi-diurnal tidal cycle promote homogeneous vertical mixing. Conversely, the eastern coasts feature a narrow continental shelf, with water depths exceeding 100 m just a few kilometers offshore. Unlike the western coast, the tidal prism along the eastern coast is approximately 1 m, coupled with seasonal variations in coastal currents (Chang et al., 2000), contributing to persistent stratification, evident in nearly all water quality parameters (Fig. 5), except in February.

In terms of these physiographic characteristics, the southern coast likely occupies an intermediate position between the other two regions, with a tidal prism of 3 m and average water depths of a few tens of meters. However, the southern coast is characterized by numerous semi-enclosed bays with limited water exchanges and frequent occurrences of bottom water hypoxia (Lee et al., 2018; Lee et al., 2021; Huang and An, 2022), resulting in more pronounced vertical gradients in water quality parameters, including pH, during summer compared to winter (Fig. 3).

3.3 Factors influencing pH variations

The pH variations within coastal systems are influenced by a multitude of physical, biogeochemical, and ecological processes, including temperature, salinity, DO, and biological production/respiration, which impact gas solubilities, alkalinity, and CO_2 dynamics within the water column (Doney, 2008; Dore et al., 2009; Duarte et al., 2013). Additionally, fluctuations in currents can influence pH values by affecting open ocean endmember conditions (Ishida et al., 2021). Water temperature plays a crucial role in pH regulation by modulating gas solubility; colder water can dissolve more gas than warmer water, potentially resulting in increased acidity. Consequently, long-term pH trends may exhibit a negative correlation with temperature, particularly in the open ocean where pH regulation factors are limited. However, within coastal environments, the influence of water temperature on pH variations is less pronounced compared to other factors such as dissolved oxygen and primary production. In our study, we did not observe a significant correlation between pH and temperature in either surface or bottom waters (Supplementary Figs 7-10). Despite a clear increasing trend in water temperature, with a rate of 0.0009 yr^{-1} observed across all regions of the Korean coast (Fig. 2 and supplementary Fig. 11), the weak correlation between pH and temperature suggests that temperature is not the primary driver of pH variation in this system.

Salinity serves as an indicator of freshwater input, which typically has lower alkalinity, a key factor influencing pH dynamics (Saraswat et al., 2015; Carstensen and Duarte, 2019). And, a positive correlation between pH and salinity is often observed in regions with low salinity (<20), where buffering capacity is minimal (Carstensen and Duarte, 2019). However, most of our study sites exhibited salinity levels greater than 23, indicating sufficient alkalinity to buffer pH changes.

Nevertheless, we did not observe a strong agreement between pH and salinity in our study (Supplementary Figs 7-10), implying that salinity (or freshwater input) may not be the primary driver of pH changes in Korean coastal waters.

Primary production, indicated by chl *a* levels, can directly influence pH by consuming CO_2 through photosynthesis, particularly in surface waters (Soetaert et al., 2007), and thus, increased pH can be observed during day time when photosynthetic activity (Cummings et al., 2019; Wootton et al., 2008; Ono et al., 2023). However, the variations in chl *a* over the 11-year period in this study were considerably different from pH variations, suggesting that chl *a* may not be the primary driver of pH variation. However, it is important to note that the observed relationship between chl *a* and pH has primarily been documented in controlled settings (e.g., closed chamber experiments; Cummings et al., 2019) or over short time scales (e.g., daily observations; Wootton et al., 2008; Ono et al., 2023). This relationship is less evident in natural environments, potentially due to the time lag or varying response times of biological productivity (chl *a*) to environmental changes (e.g., pH) (Supplementary Figs 7-10). Despite the apparent decoupling between pH and chl *a* in our study, it's important to recognize that pH can still be greatly impacted by primary production processes (Duarte et al., 2013; Ono et al., 2023).

Reducing DO concentration generally reflect the biological respiration in the water column and sediments, releasing CO_2 and subsequently impacting pH (Cai et al., 2011; Lowe et al., 2019). Moreover, increased water temperature can also lead to the degassing of DO from the water. Previous studies, such as that by Cai et al. (2011), have observed severe pH drops under conditions of low DO (<64 μM) in the Louisiana Shelf, where pH levels fell below 7.8. However, the monthly average DO concentrations along each side of the Korean coasts never dropped below 128 μM. Consequently, our observed pH levels were not as low as those observed in the Louisiana Shelf, but were still notably lower, approximately ~7.93, compared to normal conditions (~8.20). To better understand DO consumption and pH changes, we calculated the apparent oxygen utilization (AOU) by subtracting the measured concentration from the temperature-salinity derived saturation concentration. Thus, positive values indicate DO consumption (or depletion). In surface waters across all regions and seasons, DO consumption did not occur (Figs. 2-5). However, in bottom waters, pH exhibited a strong negative correlation with DO depletion (Fig. 6), suggesting that CO_2 introduction into the water column indeed led to pH decrease. For instance, along the south coast, DO consumption reached up to 52.2 μM (~23.6%), which, equates to 40.1 μM of CO_2 when converted using the Redfield ratio (106/138 for CO_2/O_2, Cai et al., 2011). This CO_2 introduction could lead to a pH drop of approximately 0.08 pH units under specific conditions of 1986 μmol/kg, 2228 μmol/kg, 1 μM, and 15 μM of dissolved inorganic carbon, total alkalinity (Hwang and Lee, 2022), total dissolved phosphate, total dissolved silicate concentrations, respectively. Moreover, pH induced by released CO_2 resulting from DO consumption was within the range the observed pH variation (i.e., 0.54; differences between 8.40 (maximum) and 7.86 (minimum)) (Fig. 7). Furthermore, while other parameters must be considered for accurate pH estimation, pH estimated from CO_2 introduction (derived from DO consumption) exhibited a strong correlation with measured pH (Fig. 7). This suggests that pH in Korean coastal waters is primarily controlled by oxygen conditions and associated CO_2 dynamics, similar to the observations in Louisiana Shelf and East China seas where severe hypoxia occurs annually (Cai et al., 2011).

3.4. Insight of pH variation in Korean coasts

The 11-year pH monitoring dataset provides an invaluable resource for examining pH conditions in coastal waters with respect to rising atmospheric CO_2 levels. Notably, atmospheric CO_2 concentrations along the Korean coast have significantly increased, possibly at one of the highest rates globally (Fig. 8). Between 2010 and 2020, atmospheric CO_2 concentrations rose from 395 to 424 ppm, at a rate of 2.64 ppm per year on Anmyeon Island, Korea, which is greater than the rate of 2.27 ppm per year at Mauna Loa, Hawaii (https://gml.noaa.gov). Despite this rise, coastal pH variations may not be heavily influenced by atmospheric CO_2 alone due to additional factors such as temperature, salinity, dissolved oxygen, primary production, hydrological processes, land use, nutrient inputs, pollution, and river water inputs. Conversely, open ocean pH levels are likely more affected by atmospheric CO_2 increases.

The East (Japan) Sea (EJS) offers a prime opportunity to compare pH variations between coastal and open ocean environments. As a deep marginal sea with depths exceeding 3,000 meters, the EJS serves as a net sink for atmospheric CO_2, absorbing about 1% of anthropogenic CO_2 emissions (Kim et al., 2022; Kim et al., 2023). Long-term pH monitoring in the central EJS from 1965 to 2015 revealed a decreasing trend at a rate of -0.0016 yr^{-1} (Chen et al., 2017). Similar trends were observed in the North Atlantic (1995-2003) and at the BATS (1983-2005) with pH decreases of -0.0017 ± 0.0005 yr^{-1} and -0.0017 ± 0.0001 yr^{-1}, respectively (Gonzalez-Davila et al., 2007; Bates, 2007). In the Pacific Ocean, surface waters showed a pH decrease of -0.0019 ± 0.0002 yr^{-1} based on in situ measurements from the HOT from 1988 to 2007 (Dore et al., 2009). These findings indicate that the pH decrease in the central EJS mirrors trends in other open ocean regions, suggesting that the EJS exhibits characteristics typical of the open ocean regarding the carbonate system. The observed pH decline is likely due to the gradual increase in atmospheric CO_2 over time.

Coastal regions within the EJS display distinct pH variations relative to the open ocean and the other coastal sides of EJS. The eastern coast of Korea (this study), west of the EJS, do not show a significant pH decrease. In contrast, the Japanese coast of the EJS, southeast of the EJS, exhibits a pronounced pH decline, with rates surpassing those in the central EJS. Studies by Ishizu et al. (2019) and Ishida et al. (2021) reported acidification rates of -0.0025 and -0.003 yr^{-1}, respectively, based on pH measurements from 1978 to 2009 at Niigata and over 30 years at Kashiwazaki Bay. Although comprehensive datasets to identify the exact causes of these spatial variations are lacking, local biogeochemical factors such as nutrient levels, biological production, oxygen conditions, and contaminant inputs likely play significant roles. For instance, primary production is notably higher on the Korean coast compared to the Japanese coast (Joo et al., 2015). Additionally, greater contaminant inputs in Niigata, a megacity on the Japanese coast, may contribute to the observed differences. Nonetheless, the rate of pH decline in Japanese coastal waters is faster than in the central EJS (-0.0016 yr^{-1}) and Korean coastal waters. The reasons for this accelerated acidification in Japanese coastal waters remain unclear (Ishida et al., 2021). Potential factors include pollution by heavy metals, reduced primary production due to bio-toxicity, and variations in DO conditions. Overall, the observed pH variations indicate strong spatial heterogeneity governed by local complexed biogeochemical conditions in coastal waters, contrasting with the more uniform pH trends in open ocean systems.

Global ocean warming is expected to exacerbate pH decline through increased degassing. Along the Korean peninsula, seawater temperatures have shown a rising trend in both surface and bottom waters over the past decades. This warming could accelerate pH decline on the Korean coasts, potentially outweighing local heterogeneity. The pH decline in Korean coastal waters is particularly concerning due to its impact on diverse aquacultures, including shellfish, fish, and seaweeds, which have species-specific tolerance ranges. Ocean acidification could thus have serious economic implications for the local and national economy.

4 Conclusion

The impacts of ocean acidification are influenced by interacting stressors such as temperature and oxygen levels, with pH variations potentially altering tolerance to these stressors and significantly affecting organismal function. Our dataset allows us to explore pH variability in shallow coastal waters and its relation to open ocean variations. Despite the general trend of pH decrease in both open and coastal oceans due to rising atmospheric CO_2, our data indicates that pH decline in Korean coastal waters is not straightforward. This spatial variability in pH is strongly correlated with local biogeochemical characteristics in coastal waters, suggesting that increasing surface water CO_2 levels are not the primary drivers of pH variations in Korean coastal waters. Instead, pH variations are closely linked to dissolved oxygen levels. This connection implies that global warming, which releases dissolved gases including dissolved oxygen, could lead to a pH decline in Korean coastal waters. Such a decrease in pH could have significant implications, since Korean coasts support numerous fish and seaweed farms sensitive to water chemical properties. Overall, our understanding of pH variability and ocean acidification in the carbonate system will remain incomplete until we fully characterize the CO_2 systems in Korean coastal oceans. Therefore, future studies and monitoring efforts are crucial for predicting the impact of ocean acidification on marine ecosystems and the bio-economy along Korean coastal waters.

Data Availability: The datasets analyzed in this study can be found in the national ma-rine environmental measuring network program. The data are available at www.meis.go.kr.

Author Contributions: YWL, MOP, and SGK contributed to the data acquisition and sample collection. DJJ processed the data. YWL, MOP, SGK, THK, YHO, SHL, and DJJ interpreted the biogeochemical data. DJJ wrote the first draft of the manuscript. All authors contributed equally to the review and editing of this manuscript and approved the submitted version.

Competing Interests: The authors declare that they have no conflict of interest.

Supplementary Materials: The Supplementary Material for this article can be found online at:.

Acknowledgement

The authors are grateful to crew members of R/V from KOEM for their assistance. Constructive comments from three anonymous reviewers greatly improved this manuscript. This research was supported by Global-Learning & Academic research institution for Master's·PhD students, and Postdocs (G-LAMP) Program of the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education (No. RS-2023-00301938) and by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-202215000003).

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Figure Captions:

Fig. 1. Sample collection sites along the Korean peninsula. Base map has been downloaded from https://server.arcgisonline.com.

Fig. 2. Variations of monthly averages and centered moving averages (4) of (a) temperature, (b) salinity, (c) pH, (d) DO depletion, and (e) chlorophyll a concentration for the entire seas along the Korean coasts during the 2010-2020 period.

Fig. 3. Variations of monthly averages and centered moving averages (4) of (a) temperature, (b) salinity, (c) pH, (d) DO depletion, and (e) chlorophyll a concentration for the south coasts of Korea during the 2010-2020 period.

Fig. 4. Variations of monthly averages and centered moving averages (4) of (a) temperature, (b) salinity, (c) pH, (d) DO depletion, and (e) chlorophyll a concentration for the west coasts of Korea during the 2010-2020 period.

Fig. 5. Variations of monthly averages and centered moving averages (4) of (a) temperature, (b) salinity, (c) pH, (d) DO depletion, and (e) chlorophyll a concentration for the east coasts of Korea during the 2010-2020 period.

Fig. 6. Relationships between pH and dissolved oxygen (DO) depletion for (a) the entire Korean, (b) the south, (c) the west, and (d) the east coasts. The DO depletion was calculated by subtracting the measured concentration from the temperature-salinity derived saturation. Thus, a positive value of DO depletion indicates oxygen consumption.

Fig. 7. Distribution of pH-measured and estimated. The pH estimation was calculated at conditions of 35, 25 °C, 1 µmol/kg, 15 µmol/kg, 2228 µmol/kg, and 1986 µmol/kg (initial) of salinity, temperature, phosphate, silicate, total alkalinity, and total CO_2 concentrations, respectively. With exception of CO_2 concentrations, other parameters were not changed for the estimation. The CO_2 concentrations were changed based on DO consumption and Redfield ratio (106/138 for CO_2/O_2).

Fig. 8. Variations of (a) atmospheric CO_2 (ppm) at Anmyeon island and (b) seawater pH along the entire Korean coast.

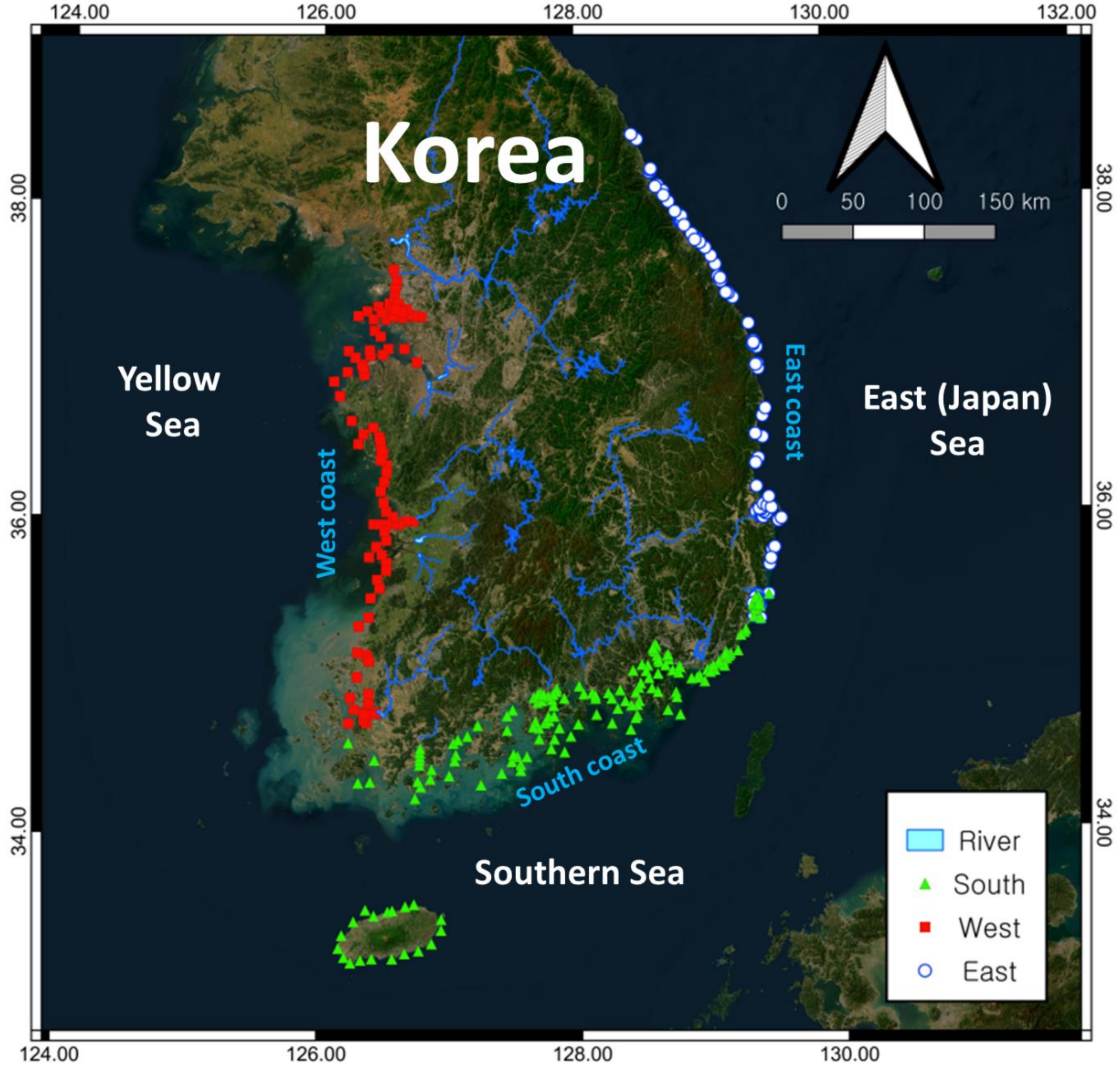

Figure 1.

485

490

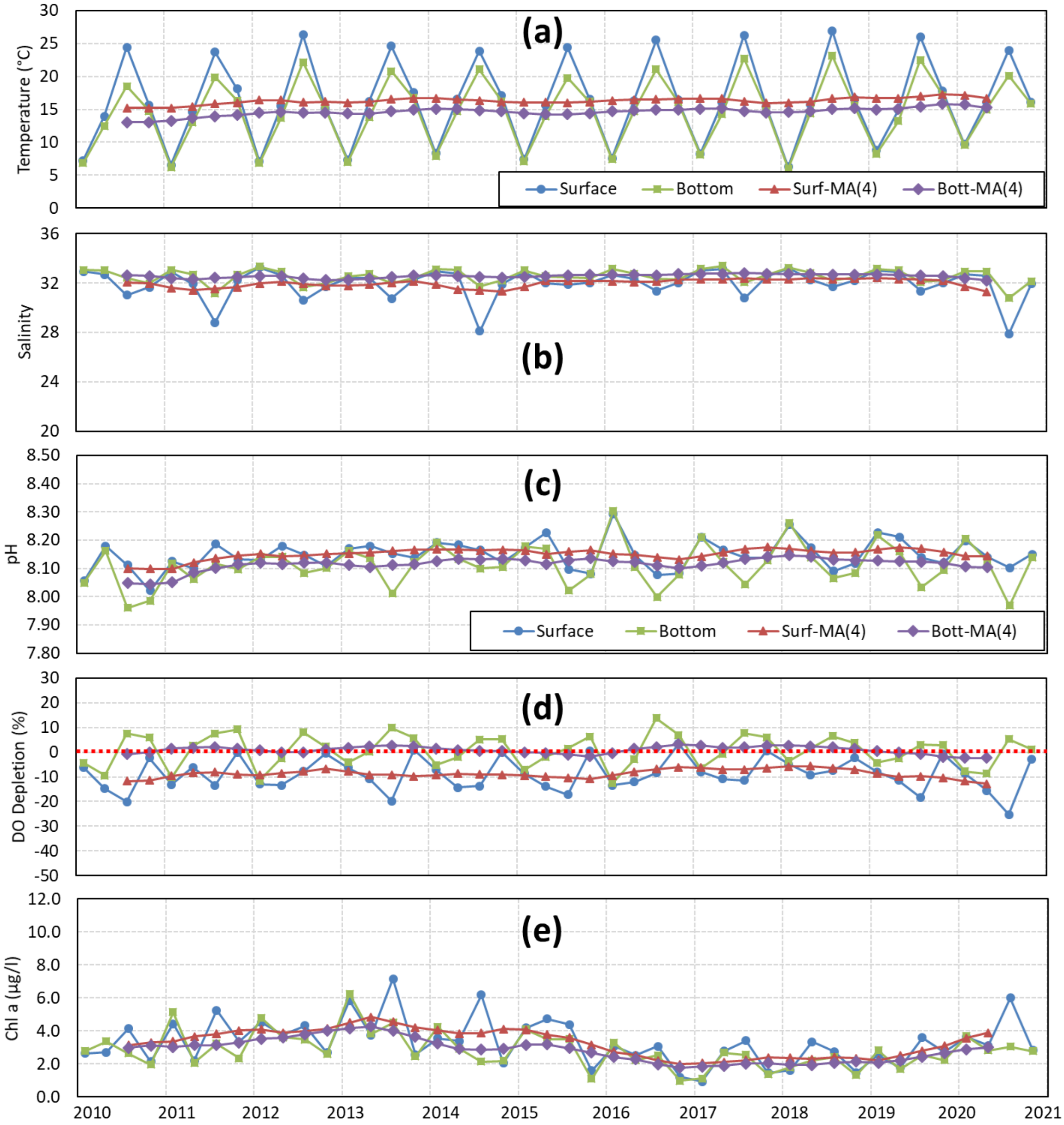
(a)
Temperature (°C)
30
25
20
15
10
5
0
Surface
Bottom
Surf-MA(4)
Bott-MA(4)
(b)
Salinity
36
32
28
24
20
(c)
pH
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
Surface
Bottom
Surf-MA(4)
Bott-MA(4)
(d)
DO Depletion (%)
30
20
10
0
-10
-20
-30
-40
-50
(e)
Chl a (µg/l)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

Fig 2.

495

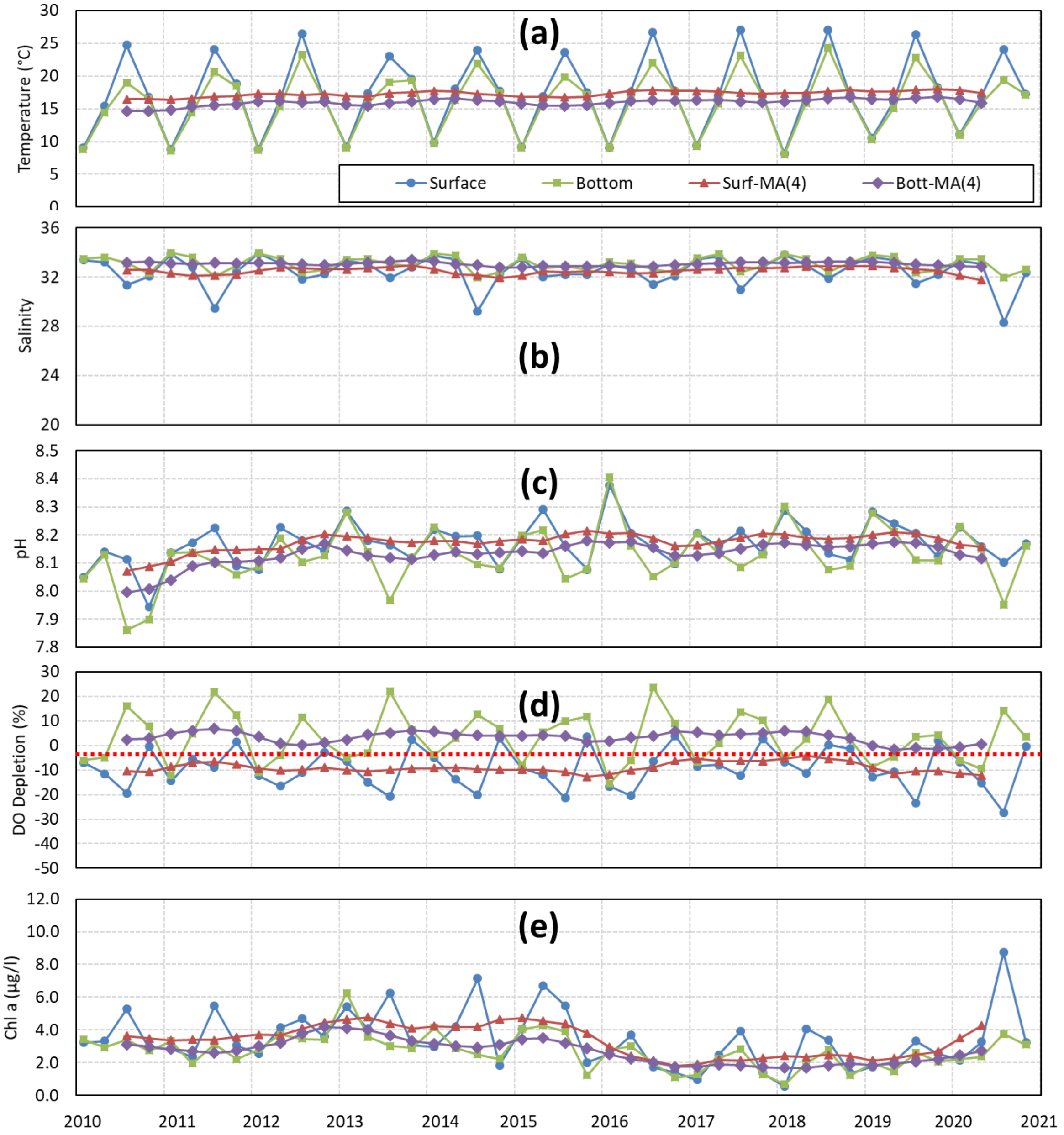
(a)
Temperature (°C)
30
25
20
15
10
5
0
Surface
Bottom
Surf-MA(4)
Bott-MA(4)
(b)
Salinity
36
32
28
24
20
(c)
pH
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
(d)
DO Depletion (%)
30
20
10
0
-10
-20
-30
-40
-50
(e)
Chl a (µg/l)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

Fig. 3

https://doi.org/10.5194/egusphere-2024-1836
Preprint. Discussion started: 25 June 2024

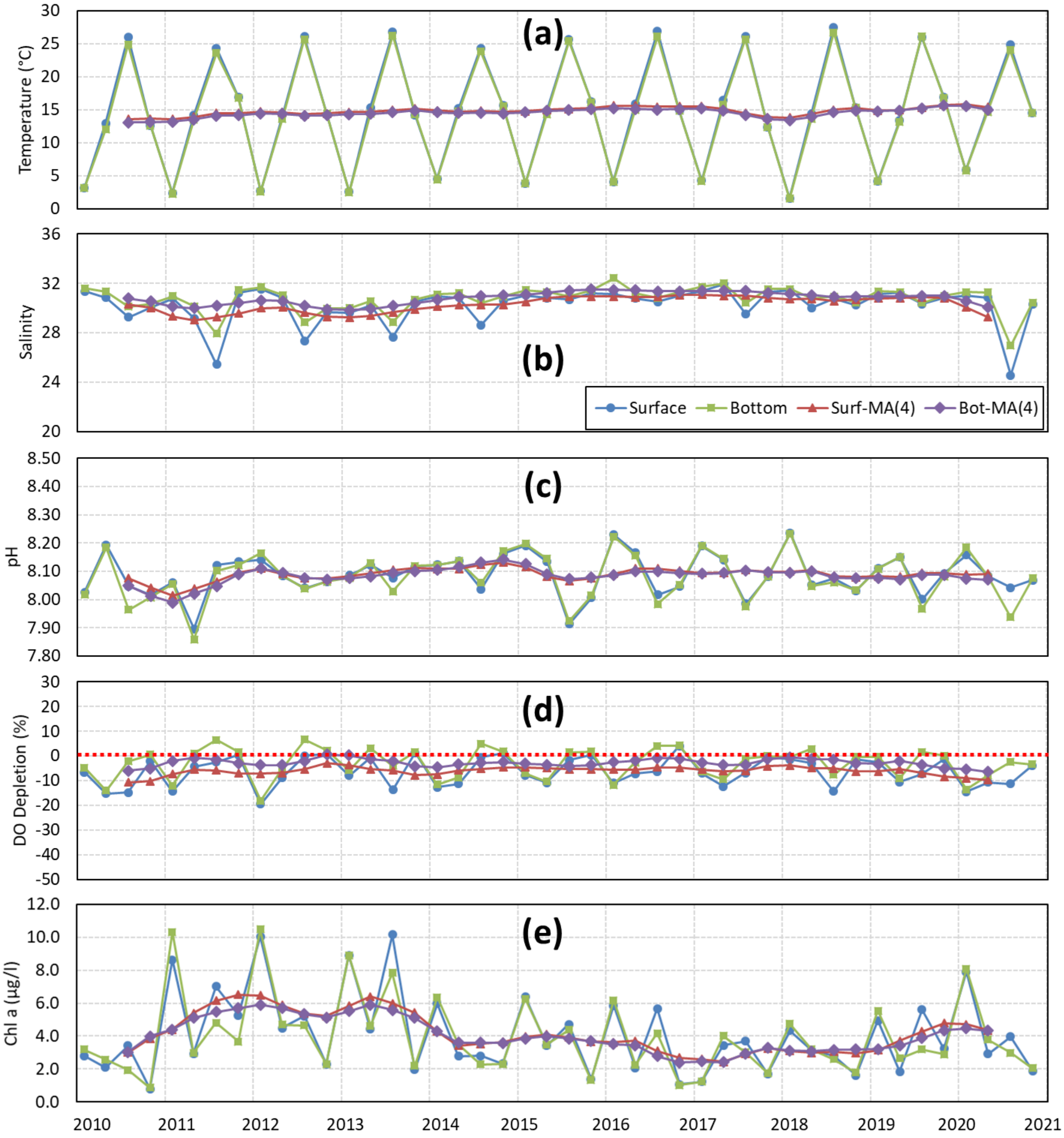

Fig 4.

510

515

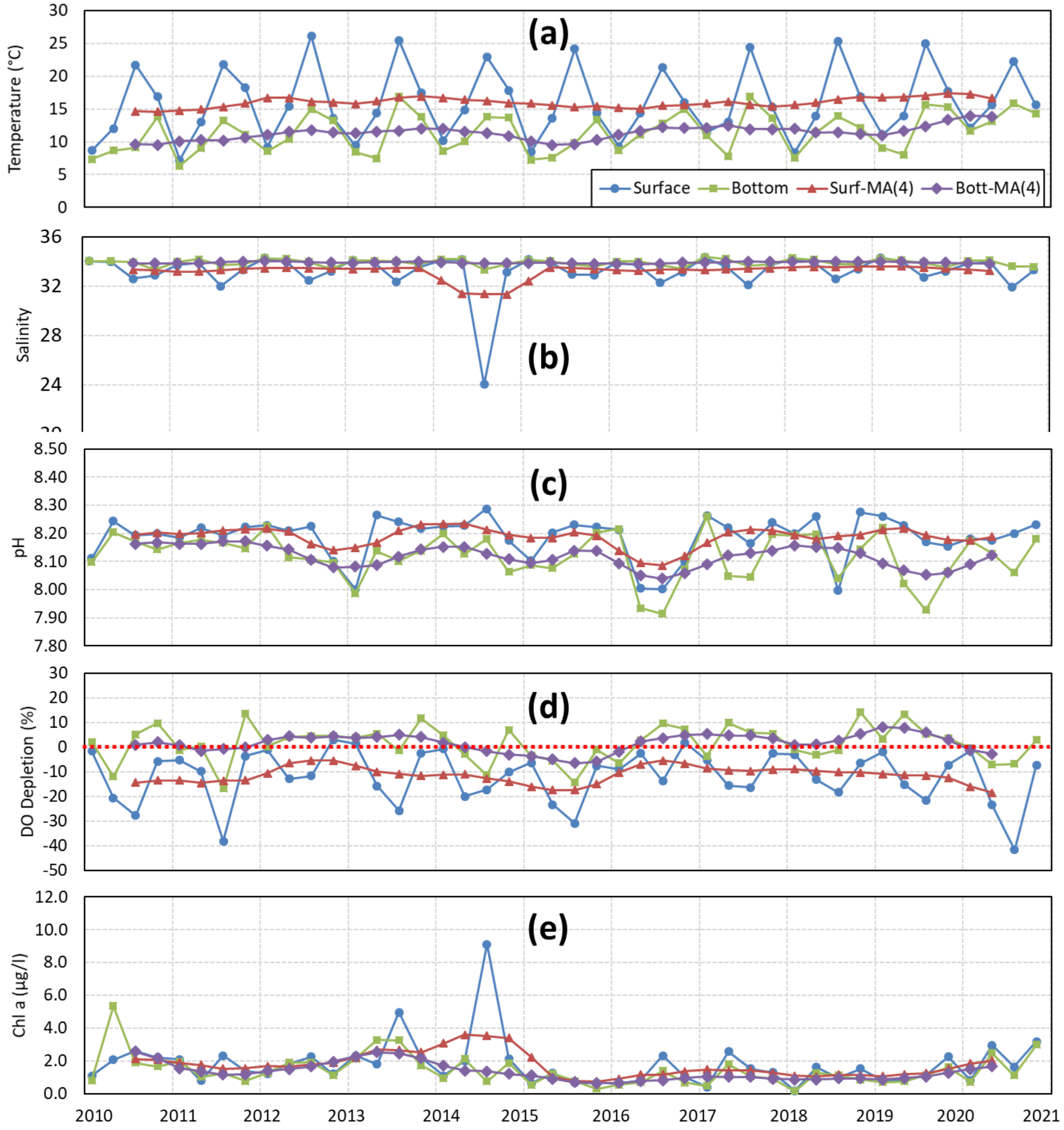
(a)
Temperature (°C)
30
25
20
15
10
5
0
Surface
Bottom
Surf-MA(4)
Bott-MA(4)
(b)
Salinity
36
32
28
24
20
(c)
pH
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
(d)
DO Depletion (%)
30
20
10
0
-10
-20
-30
-40
-50
(e)
Chl a (µg/l)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

Fig 5.

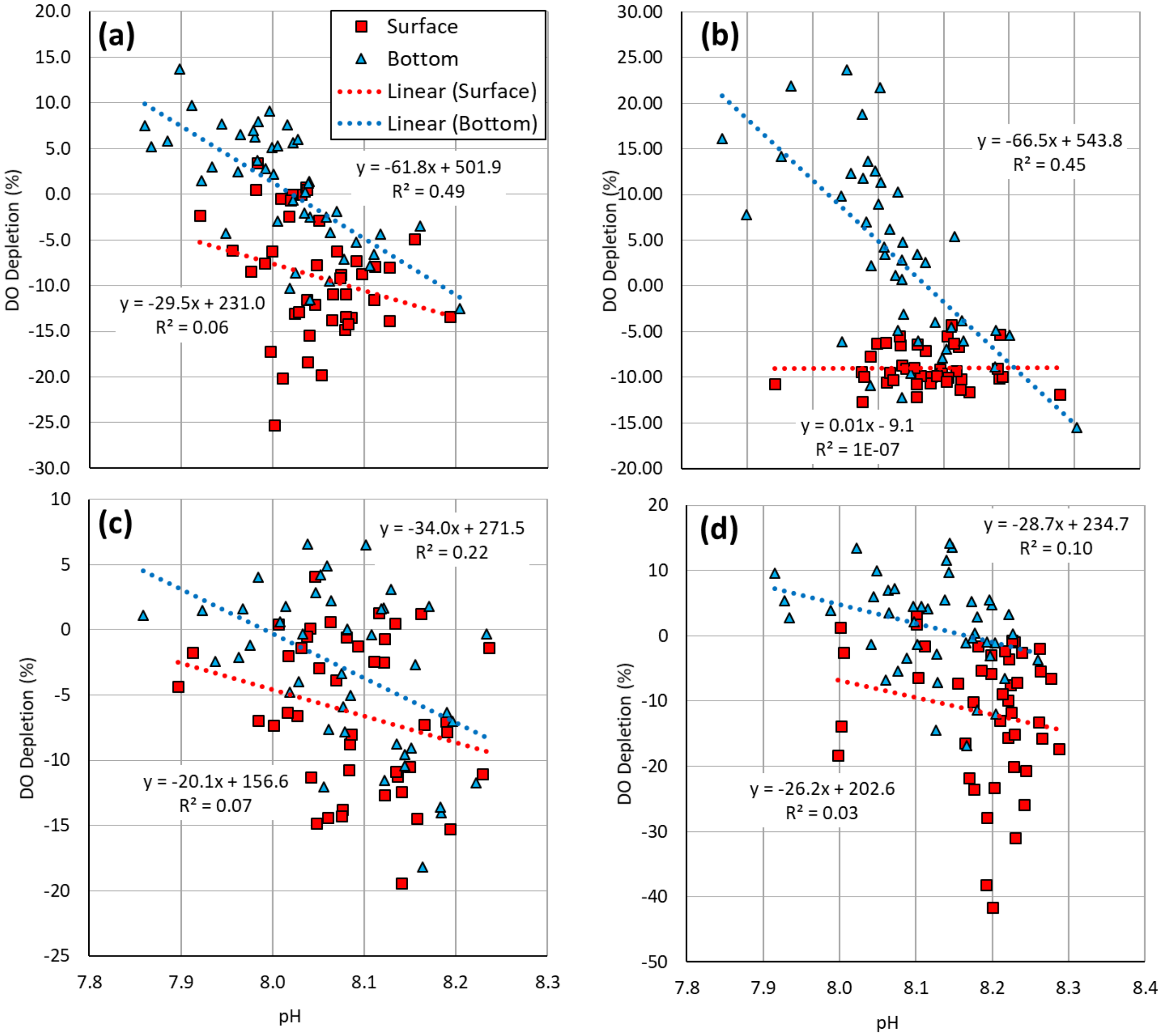
(a)
■ Surface
▲ Bottom
Linear (Surface)
Linear (Bottom)
y = -61.8x + 501.9
R² = 0.49
y = -29.5x + 231.0
R² = 0.06
20.0
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
-25.0
-30.0
DO Depletion (%)
(b)
y = -66.5x + 543.8
R² = 0.45
y = 0.01x - 9.1
R² = 1E-07
30.00
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
-20.00
DO Depletion (%)
(c)
y = -34.0x + 271.5
R² = 0.22
y = -20.1x + 156.6
R² = 0.07
10
5
0
-5
-10
-15
-20
-25
DO Depletion (%)
7.8
7.9
8.0
8.1
8.2
8.3
pH
(d)
y = -28.7x + 234.7
R² = 0.10
y = -26.2x + 202.6
R² = 0.03
20
10
0
-10
-20
-30
-40
-50
DO Depletion (%)
7.8
7.9
8.0
8.1
8.2
8.3
8.4
pH

Figure 6.

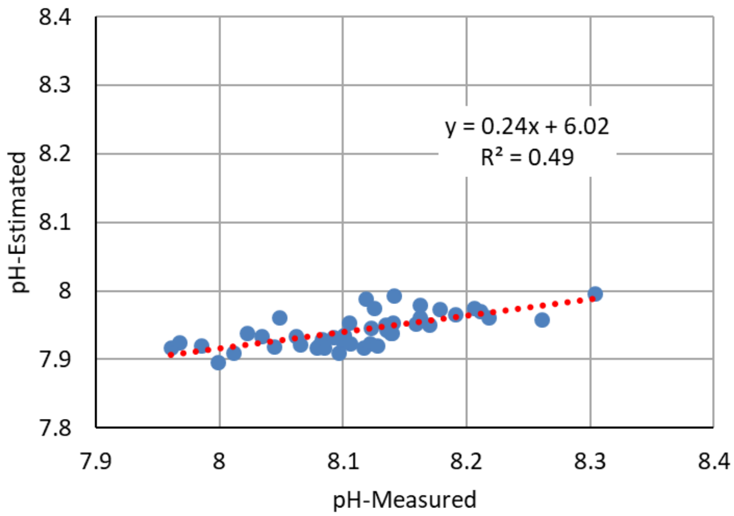
8.4
8.3
8.2
8.1
8
7.9
7.8
pH-Estimated
7.9
8
8.1
8.2
8.3
8.4
pH-Measured
y = 0.24x + 6.02
R² = 0.49

Figure 7.

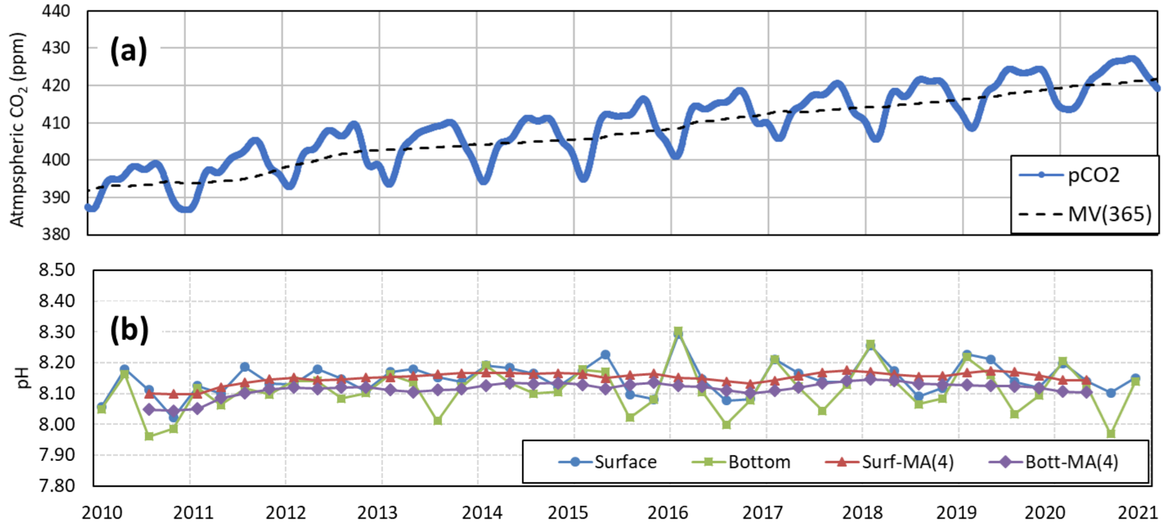
(a)
Atmpspheric CO2 (ppm)
440
430
420
410
400
390
380
pCO2
MV(365)
(b)
pH
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
Surface
Bottom
Surf-MA(4)
Bott-MA(4)
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

Figure. 8.

545