

Response to Review #1

We would like to thank Reviewer #1 for their thorough and insightful comments, which have significantly helped improve the clarity and accuracy of our manuscript. Below, we provide detailed responses to each of the points raised:

General comments:

This manuscript investigates trends in pH over an 11-year period (2010-2020) in Korean coastal waters and claims to identify the principal drivers. The authors conclude that local biogeochemical processes are more important than ocean acidification driven by increasing atmospheric CO₂, confirming what has been reported in several studies already – some of those referenced in the manuscript. Thus, I do not find any novel contributions in the manuscript, except that it presents data from a less well-studied area.

- ⇒ Many studies, including those cited in our manuscript, have been conducted in a limited number of offshore sites, often at considerable distances from the shore. In contrast, our study focuses on regions in close to the shoreline, primarily within 5 km, where the majority of sea-based economic activities occur. Consequently, our study provides a critical baseline for pH and other parameters, as these nearshore coastal waters have not been previously investigated.

The authors never try to further investigate which biogeochemical processes are most important. They conclude that “biogeochemical factors such as nutrient levels, biological production, oxygen conditions, and contaminant inputs likely play significant roles”, although the causal linkages are not explained.

- ⇒ We conducted a principal component analysis (PCA), though the results are not presented here. However, the Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy was less than 0.5 for all datasets, indicating that PCA was not appropriate for this analysis. Consequently, we investigated the linear relationships between pH and each ancillary parameter, providing a brief explanation of the results. Contrary to findings in other regions, such as those reviewed by Zang et al. (2011), we did not observe any statistically significant

relationships among these variables. Additionally, we estimated pH based on oxygen consumption and the associated introduction of CO₂, comparing these estimates with observed pH values. The strong correlation found between estimated and observed pH suggests that oxygen conditions and the associated CO₂ levels play a critical role in regulating pH in Korean coastal waters. Further statistical analyses, including cluster analysis, will be incorporated in the revised version of the manuscript

In fact, I am not convinced about the contaminant inputs, which is only supported by stating that “greater contaminant inputs in Niigata, a megacity on the Japanese coast, may contribute to the observed differences” in primary production between the Korean and Japanese side of the East Japan Sea. This assertion is completely unsupported and most likely wrong, as the authors have not considered other explanations such as effects of upwelling.

⇒ The contaminant inputs in this context include nutrients and the conventional pollutants. In particular, coastal regions near megacities, where both the number and concentration of contaminants can be substantial. It is well-documented that such contaminants contribute to eutrophication, thereby enhancing primary production. The referenced study (i.e., Ishizu et al. 2019) suggests a potential increase in primary production as a result of these contaminant inputs and thus pH variation.

Not being an expert in the study area, I do think that the strong north-going current could drive upwelling along the Korean coast by Ekman transport. Dominant wind patterns could also drive upwelling along the Korean coast. Why haven't the authors investigated the hydrography of the area in more detail before making such assertion?

⇒ Upwelling occurs along the eastern coast of Korea, but it is confined to relatively small areas (e.g., off Pohang). Moreover, our sampling sites were located very close to the shore, where the influence of upwelled water is likely minimal compared to local physical processes.

Going back to the aim of identifying the drivers of pH trends, I do not think the authors have managed to do so. One of the final comments is that “our understanding of pH variability and ocean acidification in the carbonate system will remain incomplete until

we fully characterize the CO₂ systems in Korean coastal oceans". This conclusion is somewhat disappointing, since the processes of the carbonate system are well described and it should be possible to tease out the importance of different processes by solving the equations in CO₂SYS or similar program. The authors should be able to conduct a more thorough and detailed analysis of their data.

⇒ We estimated pH using the CO₂SYS program, incorporating salinity, nutrients (dissolved silicate), AOU-derived CO₂, and total alkalinity (Lines 241-244). A strong correlation was observed between the estimated and measured pH values, indicating that dissolved oxygen conditions and associated CO₂ inputs significantly influence on the pH variation in coastal waters. However, it is important to note that the alkalinity values used in the CO₂SYS calculations were not determined in this study but were obtained from previous research. This prior research primarily focused on the carbonate system in relatively open ocean waters, rather than in the shallow nearshore waters along the Korean peninsula. Therefore, we emphasize that to fully understand pH variations, the CO₂ system in coastal waters needs to be more precisely constrained.

This brings me to my next general comment about the separation of data into three regions. If local conditions, particularly inputs of nutrients and organic matter from land, are more important then why pool sites together that have very different connectivity to land into three study regions? It would be more meaningful to separate the sites into different coastal types such as river-dominated estuaries, estuaries, lagoons, embayments, coast, etc. and perhaps use stratification patterns as another descriptor for separating sites into more similar groups. Given that the coastal systems included within each group are so diverse, averaging across these are likely to produce 'no information'.

⇒ Thank you for the suggestion. The revised version of the manuscript will include pooled data categorized by different coastal types. However, the primary objective of this study is to establish a baseline for pH in each region, which has not been thoroughly studied, and to investigate how pH has varied over the past 11 years at different sites. Our focus is on discussing pH variation at a regional scale and then integrating the data to represent the broader Korean coast. We believe that averaging across regions does provide valuable information, as this approach has been commonly used in earlier monitoring studies.

Following that, it appears that there is a lack of consistency in the sampling among cruises. Fig. 1 shows 356 sites that have been monitored, but looking at the figures in the SI it does not appear that all these sites have been monitored in each cruise. This would imply ~120 observations for each time point in each region. The consistency of monitoring is not described in the M&M, and in case that all stations are not monitored at each monitoring time point, averaging across different sites for each time point creates a bias in the time series. The authors need to address this issue more clearly.

⇒ Supplementary Figures 1-6 illustrate the surface and bottom depths across the southern, western, and eastern coastal regions, respectively, while Figure 1 provides an overview of all the sample collection sites. For reference, the map can be accessed at <https://www.meis.go.kr/map/oemsBaseMap.do>.

In fact, there is no description of how data were processed, i.e. how were trends assessed (with or without seasonal adjustment), how was the pH in Fig. 7 estimated and what were the assumptions, the calculation of AOU, etc.? How were surface and bottom waters distinguished and was the water column always stratified? Data processing methods seem to be introduced along the way in the results and discussion section without clear explanation as why they were chosen and what was the hypothesis. This needs to be better structured.

⇒ We plan to restructure the Methods and Materials section in the revised version of the manuscript. However, the supplementary figures displayed all the raw data, and the averaged and moving average (with seasonal adjustment) were shown in figures in the main text. Also, the estimation of pH and AOU is already described in Lines 241-244. In this monitoring study, samples were collected only from the surface and near the bottom (~1 m above the seabed). Additionally, since no vertical profiles were obtained, stratification is inferred solely from the differences between the surface and bottom layers.

Moreover, I am surprised to see that there is no apparent connection between low DO and low pH in Figure S2, S4 and S6. There is an intricate relationship between DO and pH, since oxygen consumption (mainly) produces CO₂. Many months have low DO without pH dropping at the same time. This is indeed surprising and makes me think that there could be issues with measuring pH (calibration?). Normally, low DO (<2-3 mg

L-1) should be accompanied by pH less than ~7.5, but this does not seem to be the case. I recommend the authors to plot measurements of DO versus pH and check for consistency in the relationships across time and region. Similarly high pH (>8.5) without extremely high chl_a are also unusual, confirming my assertion that something could be wrong with the data.

- ⇒ The pH sensor was calibrated daily before sample measurements using three standard buffer solutions (pH 4, 7, and 10), following the manufacturer's guidelines. Dissolved oxygen (DO) concentrations do not always accurately reflect the degree of oxygen consumption or CO₂ production. Therefore, we used DO depletion (%) as a more appropriate measure instead of DO concentration. Graphs of DO concentrations and pH will be included in the supplementary materials.
- ⇒ In relatively stratified deep systems, low DO levels, indicative of oxygen consumption, typically correlate linearly with a decrease in pH. However, in shallow coastal waters where wind, currents, and tidal forces are active, CO₂ may escape from the water column before it can fully dissolve. As a result, not all oxygen consumption leads to a pH drop. Consequently, in many water bodies, pH does not always correlate with DO consumption (e.g., Li et al., 2024). Additionally, high DO levels do not necessarily indicate high primary production (e.g., chlorophyll a concentration) but can result from episodic wind events (e.g., Pidgeon and Winant, 2005) or production by macroalgae (e.g., Kelp, Frieder et al., 2012). Thus, pH does not always strongly correlate with chlorophyll a.

Finally, the language is not always clear and it is difficult to see whether it is due to language difficulties or lack of understanding of the biogeochemistry. I found statements that were wrong, unclear and misleading, but the cause of this is not clear to me.

- ⇒ We apologize for any difficulties in reading this manuscript. However, the language has been reviewed by a professional manuscript-language service (e.g., Elsevier English Language Service) and a commercially available scientific manuscript review system.

Specific comments:

67: High alkalinity would actually buffer against acidification, so this can hardly be an explanation to higher trends in the Mediterranean Sea!

⇒ We will clarify this sentence. However, we did not imply that high alkalinity decreases pH. The sentence aims to describe the unique biogeochemical and hydrodynamic characteristics of some places in the Mediterranean Sea.

86: Pristine implies a state before human disturbance. I doubt that the east coast is entirely undisturbed, so better to say "relatively undisturbed".

⇒ The term "pristine" has been revised. However, "pristine" is commonly used in the literature to describe relatively "clean" conditions, and numerous articles have employed this term.

145: The authors claim that OA is the foremost concern for coastal ecosystems. This claim is unsupported and in my view not correct. Eutrophication, food-web alteration from overfishing, physical disturbance from bottom trawling are pressures that are prominent in the coastal zone and have larger impact on organisms and habitats. This sentence should be deleted.

⇒ Thanks for your opinion. In the context of global warming (associated with CO₂) and its impact on water quality and biological productivity (particularly primary production), ocean acidification represents a significant threat to coastal ecosystems. Given the rapid decline in pH levels in many areas, ocean acidification is of particular concern for these ecosystems.

150: Differences between surface and bottom water pH is driven by production in the surface increasing pH and respiration in the bottom decreasing pH. This is not very clearly expressed here and it needs to be.

⇒ We will clarify this by rearranging the information. At the surface, primary production releases oxygen, while oxygen consumption occurs in the bottom water. These oxygen conditions are directly linked to CO₂ dynamics, leading to pH variations. The detailed explanation of this process can be found in the section "3.3 Factors Influencing pH Variations."

152: Was the trend exactly the same for surface and bottom? That seems odd.

- ⇒ The moving average (with 4 cycles and seasonal adjustment) revealed a discernible increasing trend in both surface and bottom depths (Figure 2). The slopes of the surface and bottom datasets differed only at the 6th decimal place, which has been rounded, making them appear identical.

153: $F=0.0003$ and not significant, but the slope was 0.0009 ± 0.0001 which with an ordinary t-test gives a highly significant slope. This does not match and needs to be checked.

- ⇒ Thank you for highlighting this issue. We provided incorrect numbers, and they should be 0.000029 yr^{-1} (± 0.000007) and 0.000035 yr^{-1} (± 0.000009) for the surface and bottom, respectively. However, these corrections do not affect our overall conclusion. Nonetheless, we misinterpreted the statistic. The F-value in ANOVA regression assesses the overall significance of the regression model, calculated as the ratio of the variation between sample means to the variation within the samples. An F-value of 0.0003, which is lower than the significance level $\alpha = 0.01$, indicates statistical significance for the regression model. However, the R-square value for the linear regression was 0.29 ($n=40$) for both surface and bottom depths, indicating that the trend is not statistically significant or meaningful. Additionally, as you pointed out, a change of 0.00003 per year may not be substantial.

166-167: Coastal eutrophication stimulates production in the surface layer causing pH to rise and respiration in the bottom layer causing pH to decrease. The sentence does not articulate this very well and it is misleading or actually wrong.

- ⇒ We will clarify it. The Pacific side is influenced by the Kuroshio Current, whereas the East Sea side is affected by coastal eutrophication. These factors contribute to the exacerbation of pH differences between the two regions (see, Ishizu et al., 2019).

180: Can this be elaborated more specifically? What biogeochemical properties are driving pH dynamics?

- ⇒ We will clarify and elaborate it. The biogeochemical properties that differ between open and coastal oceans include biological productivity, chemical inputs from rivers and sediments, and wind stress, among other factors. These variations all

contribute to differences in pH between open and coastal oceans.

198: Elaborate how this will influence pH?

⇒ We will clarify it. However, the relationship between low O₂ (hypoxia), CO₂, and pH is well-established and was also discussed in the Introduction.

207: "long-term pH trends may exhibit a negative correlation with temperature". The authors refer to CO₂ solubility, but warmer water can contain less CO₂ in equilibrium! This should cause a positive correlation. However, there is another factor that the authors have overlooked, the issue of shifting equilibrium constants in the carbonate system. As the water warms, the carbonate system shifts towards more dissolution, producing more H⁺ ions and thereby lowering pH. This might be more relevant than the equilibrium with the atmosphere due to the slower kinetics of the gas exchange.

⇒ Thank you for your suggestions. We will expand on this topic. Thermodynamically, an increase in temperature leads to an increase in the dissociation constant, which in turn results in a decrease in pH. While temperature can influence gas solubility and degassing, potentially creating a positive correlation between pH and temperature, its more substantial impact occurs through various biogeochemical processes. Elevated temperatures can enhance water column stratification and contribute to bottom water hypoxia, leading to CO₂ accumulation and redox reactions that lower pH. Additionally, higher temperatures can reduce primary production by impairing algal metabolic activity, resulting in decreased CO₂ consumption in the water column. Overall, these factors suggest that temperature has a negative impact on pH.

242-246: This should be described under the Materials and methods section. The calculations are also based on the assumption that DO consumption results from respiration and nitrification?

⇒ It will move to Materials and methods section. The AOU calculation accounts respiration, since Redfield ratio accounts oxygen consumption through organic matter diagenesis.

248: "pH in Korean coastal waters is primarily controlled by oxygen conditions". This is not correct. Both DO and pH result from an imbalance between respiration and

production.

- ⇒ We will restate and clarify this point. Apparently, only AOU showed a correlation with pH, despite some offset between estimated and measured pH values. This indicates that oxygen conditions and associated CO₂ dynamics play a crucial role in pH dynamics.

254: Why would atmospheric CO₂ have increased more along the Korean coast? This does not make sense. The atmospheric concentration is relatively constant across the northern hemisphere as well as the southern hemisphere.

- ⇒ East Asia has shown that the atmospheric CO₂ has been increased more rapidly than other continents (see, Yeh et al., 2023).

256: Is this because different periods are compared? The authors cannot compare trends based on different periods.

- ⇒ We are looking the yearly increasing rates, not single month (see, <https://gml.noaa.gov> and https://www.index.go.kr/unity/potal/main/EachDtIPageDetail.do?idx_cd=1399, for Hawaii and Anmyendo, respectively).

295: Same comment as for L. 248.

- ⇒ See above

Technical comments:

37-38: "though land-based input can be significant in river-dominated estuaries".

- ⇒ Corrected

42-43: "Hawaii Ocean Time-series (HOT)"

- ⇒ Corrected.

43-44: "European Station for Time-series in the Ocean of the Canary Islands (ESTOC)"

- ⇒ Corrected.

52: delete "a" before "long-term"

⇒ Corrected.

53: "surface water pCO₂"

⇒ Corrected.

56: replace "plankton" with "coccolithophores" to be more specific.

⇒ Plankton includes also pteropods and various other organisms. Therefore, the term "plankton" is more appropriate in this context.

59: emphasize "affecting many trophic levels" – not all.

⇒ Corrected.

63: insert "atmospheric" at beginning of line.

⇒ Corrected.

70: "decreased only by"

⇒ Corrected.

74: "due to increasing atmospheric CO₂"

⇒ Corrected.

81: "possibly related to decreasing nutrient input (Provoost et al., 2010)"

⇒ Corrected.

91-92: "impacts of atmospheric CO₂, warming and changing environmental conditions"

⇒ Corrected.

95: Should be "Korean Marine Environment Management Corporation (KOEM)"?

⇒ "Korea" is correct.

96: replace "assessing" with "monitoring"

⇒ Corrected.

102: delete "a comprehensive 11-year dataset to assess" – it is repetitive

⇒ Corrected.

104: delete "of" before "< 10 m"

⇒ Corrected.

104: Should be "The sites", not "These sites"

⇒ Corrected.

110: "Large river systems are found in the west and south"

⇒ Corrected.

115: "Korean Coastal Current receiving inputs from the Kuroshio warm current"

⇒ Corrected.

119: replace "provide" with "deliver"

⇒ Corrected.

L131: "KOEM research vessel" and "were measured with a CTD"

⇒ Corrected.

141-142: "the chl a was extracted from the filters and measured with a fluorometer"

⇒ Corrected.

146: start with "OA is of particular concern along the"

⇒ Corrected.

149: "Monthly averages for February, May, "

⇒ Corrected.

154: "at least over the study period. The observed pH trend"

⇒ Corrected.

161: "driven by rising atmospheric CO₂ and variations in local salinity and primary production"

⇒ Corrected.

172: delete last part of sentence. Does not convey anything.

⇒ Corrected.

178: "regional trends in pH fluctuations can differ substantially from OA."

⇒ We think the current version stated more clearly.

211: A temperature increase of 0.0009 yr⁻¹ is nothing. This cannot be a clear increasing trend, i.e. significant?

⇒ Corrected.

214: Freshwater in Korea might have a lower alkalinity in freshwater input than the ocean end-member due to the geology, but this is not the case everywhere. Watersheds with limestone typically have higher alkalinity than the ocean end-member.

⇒ Elaborated. The bedrock of watersheds in Korea is not limestone.

218: This lack of relationship is most likely due to comparing averages, which removes most of the variability between pH and salinity. Try look at the raw data!

⇒ Row data values are provided in the supplementary information. These values did not show any significant correlations.

221: Replace "increased" with "elevated".

⇒ Corrected.

230: "Reduced DO concentration primarily results from biological respiration"

⇒ Corrected.

232: DO can degas from the surface water, if and only if DO is supersaturated.

⇒ This sentence indicates that DO solubility decreases under warming conditions. Additionally, when DO is supersaturated, it can diffuse into the atmosphere.

238: "net DO consumption"

⇒ Corrected.

240: Actually, the correct term to use for this measure is Apparent Oxygen Utilisation (AOU). Please use this consistently.

⇒ Corrected.

245: "range of the observed"

⇒ Corrected.