

Interactive comment on “Long-term trends in pH in Japanese coastal waters” by Miho Ishizu et al.

Anonymous Referee #2

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This study determined the long-term trends (from 1978 to 2009) of pH in Japanese coastal waters. They found that both positive and negative pH trends distributed along Japanese coasts. Majority sites have decreasing trends, which is consistent with open ocean. The authors then discussed the impact of warming on the spatial distribution of pH trend and speculated the potential impacts from other processes. Overall, this study presented a very good dataset, but I have less confidence in the methodology in order to derive a robust story.

1. After finishing this MS, I am still not sure what kind of data this study used. First, this study did not show any information about salinity, so, the dataset was from freshwater, brackish water or sea water? Can you give more information about the pH measurement? Was pH measured under in-situ temperature, or the samples were taken back to lab and measured at 25°C? Where did pH minimum or maximum come from? It seems like the min or max values were from entire water column in each site based

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on Lines 137-138 “NIES gathered all pH data measured at each site and calculated annual minimum and maximum pH”. However, the respiration was more powerful in decreasing pH comparing to anthropogenic CO₂ intrusion (Cai et al, 2011), so, the pH_{min} generally came from bottom water, while the maximum came from surface water (without considering other local processes). In other words, pH_{max} and pH_{min} totally represented the values from different water depth, so, all trend interpretation should be related to the water sources.

2. I am not sure how pH_{min} or pH_{max} could be representative of the average pH situation in specific year. This min or max values have a good chance to be affected by extreme events, for example, phytoplankton blooms or heavy flooding events. I am not sure whether the trends or pH_{min} or pH_{max} can represent the overall pH change rates in that sites. However, it did represent the variation of pH in each year. Did the authors find the difference between pH_{max} and pH_{min} change (increase or decrease) over time? This examination can also help derive useful information about CO₂ chemistry data change over time, because extreme values matter. Here are a few references the authors may need.

Fassbender, A. J., K. B. Rodgers, H. I. Palevsky, and C. L. Sabine (2018), Seasonal Asymmetry in the Evolution of Surface Ocean pCO₂ and pH Thermodynamic Drivers and the Influence on Sea-Air CO₂ Flux, *Global Biogeochemical Cycles*, 32(10), 1476-1497.

Landschützer, P., N. Gruber, D. C. E. Bakker, I. Stemmler, and K. D. Six (2018), Strengthening seasonal marine CO₂ variations due to increasing atmospheric CO₂, *Nature Climate Change*.

3. The authors did a lot of work in quality control by step 1, 2, 3. In my opinion, step 1 is strict enough. Removing the outlier points instead of entire time sequence can keep all 1481 sites. I do not agree with “step 3” to get rid of “random errors”. The authors removed the time sequences whose pH_{insitu} stdev > the average stdev of 1127 sites.

C2

With this process, you actually removed all the sites that have a high stdev, which may have nothing to do with random errors. For the sites with a strong biological activity, or a site that is easy affected by the river discharge, they all have large stdev. However, this is their feature, but not caused by “error”. With this operation (step 3, and extra step from Line 197-198), you have already excluded all the sites that were affected by B(T,N) and Alk (S). Thus, only the sites with mild hydrological or biological variation, and strong thermal impact were left. I fail to see why this process was included in this manuscript.

4. I have difficulty in understanding why the authors compared pHmin with Tmax or pHmax with Tmin across the maintext. Line 142 “the pH values were lowest in summer and highest in winter”. My concern is the pH value was also impacted by biological activities (photosynthesis and respiration). Thus, high temperature in summer cannot guarantee low surface pH, when the photosynthesis was very strong. Please check through the maintext.

5. Based on the 289 sites, the authors derived two sets of pH trends: -0.0014 ± 0.0033 and $-0.0024 \pm 0.0042 \text{ yr}^{-1}$ for pHmin and pHmax, respectively. Are these two trends significant different? A paired t-test is needed here.

6. Fig. 7 included all the trends across the 289 sites, both significant and insignificant. Can you only include the significant trends? What is the average value of significant trends? Based on the discussion in section 4.1, the threshold of significant pH trend (caused by measurement precision only) is $\pm 0.002 \text{ yr}^{-1}$. Other variation of pH (i.e. caused by local processes), should also impact the detection of significant trends. This can be further examined by previous comment (#5).

7. The discussion between pH change and heterotrophic or autotrophic is very weak. In addition, I still think the 289 sites have already excluded the stations that have strong biological activities.

8. Do the salinity or water discharge change support the conclusion in Line 431?

C3

There is also some unclear description in maintext, figure caption, and legend.

1. It should be 289 sites (under current version) in the abstract, but not 1481.

2. How did you get the mean value in Line 165? Average of pHmin and pHmax?

3. Lines 206-211, what is the “standard deviations of pHinsitu trends”? The legend and caption of figure 6 is very confusion. A comment here (in my opinion), this MS studied the trend instead of absolute value. So, the site crosscheck may have very minor impact on the final results.

4. Lines 232 to 235, the reference here reported pH25, so this comparison should be moved to later section.

5. Lines 319-321, I have difficulty in understanding “both DIC (B (T, N)) and Alk (S) are difficult to have general trends that covered all monitoring sites, because factors that control these variables have no mutual trends all over the Japan coast”.

6. Lines 331- 324, why did “same trend of B (T, N) leads opposite trends of DIC (B (T, N) between autotrophic and heterotrophic ocean”? How do you define the “autotrophic and heterotrophic” here? 7. Line 365, a typo? from 8.2565 to 8.2560?

8. Line 384-396, how would the previous studies relate to your results? Some more in-depth discussion is needed here.

9. Fig. 3. Red and blue colors indicated the annual MAXIMUM and MINIMUM pHinsitu data.

10. Fig. 9, there is no “black and red shading” as said in captain.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-150/bg-2019-150-RC2-supplement.pdf>

C4

