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

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Thank you for your comments. There were a lot of comments you gave us. For convenience, we have added the supplement file including our responses and our manuscript revised for your comments. We have replied your comments as follows, but please see our supplement files as well.

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 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, pHmax and pHmin totally represented the values from different water depth, so, all trend interpretation should be related to the water sources.

We have modified the relevant descriptions to include more detailed information about the measurements by the WPCL program.

>The dataset was from freshwater, brackish water or sea water?

Over 90 % of the data comes from coastal sea water, while less than 10 % comes from estuary. We carefully extracted the measurements in sea water from the whole data archive. To clear this matter, we have changed the term “coastal waters” to “coastal sea waters” in the present manuscript. Readers also can get the information of latitude and longitude, measured pH data, in the supplement data.

>Was pH measured under in-situ temperature, or the samples were taken back to lab and measured at 25_C?

The pH was measured under in-situ temperature. We have analyzed pHinsitu, which means pH at ambient sea surface temperature. We have added the word, “in-situ” to clarify this point in the revised version, as follows:

“Similarly, analysis of the Hawaii Ocean Time-series (HOT) (Dore et al. 2009) and the Bermuda Atlantic Time Series (BATS) (Bates 2007) showed that pH at ambient (in-situ) sea surface temperature (pHinsitu) decreased by 0.0019±0.0002 and 0.0017±0.0001 yr−1 from 1988 to 2007 and from 1983 to 2005, respectively.”

>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 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 pHmin generally came from bottom water, while the maximum came from surface water (without considering other local processes). In orther words, pHmax and pHmin totally represented the values from different water depth, so, all trend interpretation should be related to the water sources.

As we mentioned in Section 2.1, “at each basic survey, water samples were collected at several depths (0.5 and 2.0 m) below the surface for all sites, and 10 m where bottom depth was more than this) for times a day to cover diurnal variation. At sites where large variation is found in the daily pH data, additional one day water sampling at 2-hourly intervals (ca. 13 times a day) was made at least twice a year to check the adequacy of basic water sampling protocol.” The measurement depths depend on the area and rely on the licensed operators. NIES does not discriminate surface and 10m data, so we speculate that pH maximum substantially represents winter pH of surface waters, while pH minimum represents summer pH of 10m waters. As you noticed, this means that pH maximum may have been affected mainly by historical change of marine production rather than anthropogenic CO2. We assessed this possibility in line 414-419 in revised manuscript. Anyway, we can state that the measurement depth at each site did not change case by case. It was routinized.

We speculate that some monitoring sites should be forced by biological activity, but some not. The situations depend on time and place. To remove extreme data that would be affected by significant biological activity, we adopted the strict quality control procedures and then used the time-series of pH that passed the strict criteria in the analysis. We consider that the remaining moderated max-min variations in the data after QCs were mainly caused by the seasonal variations of the thermal effect (D(T)).

2) I am not sure how pHmin or pHmax 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 pHmin or pHmax 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 pHmax and pHmin change (increase of 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.

Thank you for your suggestions. But we have avoided analyzing the difference between pHmax and pHmin because differencing two variables could lead to enhancement of data errors. As for the references mentioned above, those references could be useful to mention seasonal variability of pCO2 and the asymmetric response of air-sea CO2 flux. We have added relevant new descriptions in Section 4.2.1.

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

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removed the time sequences whose pHinsitu stdev> the average stdev of 1127 sites. 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.

We keep this form by using the quality control (QC) steps 1, 2 and 3, because if the data include a lot of processes resulting in the large variability deviating from the average pH, the discussion would be more complicated. So it would be better to keep this form and to use the data only with moderated variations.

We partly agree with your comment: "you have already excluded all the sites that were affected by B(T, N) and Alk (S)". But even after applying the all QC steps, the trend distributions involve some variability around the averages (Figs.7e and 7f). We thus discuss possible variations which might be caused by area-dependent B(T, N) and Alk (S) effects. Since there is no available data of ALK(S) for checking our data, we do not much discuss the influence of Alk (S) (Section 4.2). As for the discussion of B(T, N), we suggest coastal acidification/basification mechanisms by comparing the pH trends and TN ones (Section 4.2.2 and Fig. 14).

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".

To make readers more clearly understand this thermal effect, we have added a term " " in this part as follows. "Previous studies have reported negative correlations between seasonal variations in pH and water temperature, mainly because of changes in the dissociation constant in dissociation equilibrium ( ).”

5) 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.

The QC steps effectively work to exclude pHmax and pHmin data caused by the extreme biological effects. Max-min pH variations in the remaining data after QCs are considered to be caused by mainly the seasonal thermal effect as explained above. In the revised manuscript, we have improved the descriptions to clarify our viewpoint about the possible influences on the pHinsitu trends in coastal sea waters (Section 4.2, 4.2.1, 4.2.2).

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

Yes, the two trend averages are significantly different from each other. That suggests the seasonal difference in the thermal effects on pHinsitu trends (Section 4.2.1). We have added this information in the revised manuscript.

7) 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 _0.002 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).

If we select the significant trends alone, the trends with larger magnitudes remain. A left panel of Fig. R1 shows a histogram of some pH trends including both statistically significant and insignificant values, representing a shape like the normally distribution with a negative shift. A right panel shows a histogram of selected trends with statistical

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significance for ΔpH not zero, indicating that the trends with ΔpHâĽŠ0 disappear in this case and the relatively large negative pH trends tend to remain in the distribution. These figures illustrate dominant existence of the negative trends, but this procedure results in deleting the trends of monitoring sites with ΔpHâĽŠ0, which must actually exist.

(Please see our supplement file. We couldn't paste Fig. R1 here.) Figure R1. Examples of histograms of pH trends both with and without statistical significance for ΔpH not zero (left) and only with significance (right).

8) 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.

We suggest possible heterotrophic/ autotrophic pH responses to eutrophication/ oligotrophication inferred by relations between the pH and TN trends shown in Fig.14. The negative correlation evaluated from Fig.14 further suggests dominance of the heterotrophic sites. Since we consider that this result alone is not sufficient for rigid confirmation of our consideration, we modified abstract and relevant descriptions. However, we still note that variability remaining in the pH trends after the QC steps suggests coastal acidification/basification processes, which could be affected by the heterotrophic/ autotrophic conditions of each site.

9) Do the salinity or water discharge change support the conclusion in Line 431?

Salinity data and/or information of water discharges suitable for cross-comparison with the pH data used in this study are not available. It is difficult to directly answer this question.

Replies for your comments in the manuscripts: >There is also some unclear description in maintext, figure caption, and legend. 1.

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

Following your comment, we have changed the part from “1481 monitoring sites” to “289 monitoring sites”.

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

For clarification, we have improved this part with the words “average of minimum and maximum pHinsitu”, as follows, in the present manuscript (Section 2.1). “We then excluded time sequences with outliers, defined as sites with data points that were more than three standard deviations from the average of minimum and maximum pHinsitu for each year.”

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.

We have modified legend and captions of Fig. 6. At first, we have used the thin and bold lines to discern minimum and maximum pHinsitu data at each monitoring station in this figure. We have added the relevant description to the caption.

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

We moved this part to the later section (Section 4.2.1).

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”.

The overall pHinsitu trends shown in Fig.7 were governed by the thermal effect, D(T), and ocean acidification, DIC(Air CO2), because the all monitoring sites are equally affected by these global factors. In contrast, DIC (B(T, N)) and Alk (S) were significantly affected by local situations, depending on regions. The variability among the pHinsitu trends, which are characterized by standard deviations of the trends populations, were caused by such local factors. To emphasize this viewpoint, we have modified abstract and all relevant descriptions.

6. Lines 321- 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?

We consider that the heterotrophic conditions are defined as the increasing (decreasing) response of DIC to eutrophication (oligotrophication), and vice versa for the autotrophic condition. For example, the sites shown in the second quadrant of Fig.14 means negative pH trends (increasing DIC) involve positive TN trends (eutrophication) at those sites. But we realize that this consideration is based on some assumptions that not well confirmed by only the available data from the WPCL data archive. We modified abstract and conclusion for clarification. .

6. Line365, a typo? from 8.2565 to 8.2560?

Yes, this is a typo. We have corrected as 8.2565 to 8.2560. Thank you for your careful notice.

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

Here we discuss possible regional differences in the pH trends caused by the localized biological factors. We have simplified the descriptions to emphasize this point.

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

That is correct. We have modified it.

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

We have deleted it. Thank you for your indication. We have again carefully checked the all captions to remove such incorrect descriptions.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2019-150/bg-2019-150-AC2-supplement.pdf

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-150, 2019.