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Interactive
comment

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.

In this study, the authors estimated the long-term trends of pH in Japanese coastal waters from 1978 to 2009. In 70 to 75 % of the monitored sites, they found acidification trends while they obtained basification trends in 25 to 30 % of the sites. The authors tried to interpret the spatio-temporal patterns in pH based on the in situ pH, temperature and total nitrogen data. The paper's idea is very important taking into consideration the increasing need of a continuous OA monitoring, particularly in coastal areas where OA effects on marine ecosystems could be exacerbated due to local pressures. However,

I do have some major concerns about the pH data and the methodology used to get it:

1) Are the authors calibrating the glass electrode with TRIS solutions for seawater measurements? I'm not against NBS standard buffers for experimental essays or to check the in situ variations of pH in coastal stations to assess the pollution there or whatsoever, but pH potentiometric measurements with NBS calibrations are strictly not recommended for seawater monitoring, particularly for long term surveys (climatic survey) where the pH uncertainty should be around 0.003 pH unit. Moreover, this technique's results are not comparable with the ones adopted for seawater elsewhere and mentioned in the entire text (i.e. Bates et al., 2014, etc.). Please check the following useful links for the recommended strategies to better study the OA in open and coastal areas for long or short periods: - http://goa-on.org/documents/general/GOA-ON_Implementation_Strategy.pdf - http://goa-on.org/resources/sdg_14.3.1_indicator.php

Thank you for your information of the links to the monitoring strategies recently recommended by GOA-ON for studying the ocean acidification. We understand that the NBS standard buffers are not appropriate for long-term monitoring focusing on climatic survey as we described in the introduction (Chapter 1). However, widespread use of seawater-scale pH buffers started in 1994 (Dickson and Goyet, 1994). This means that we MUST use NBS-scaled pH data if we want to analyze interannual variation of pH with time scale longer than 25 years.

The WPCL program fully realizes uncertainty of their seawater pH data, and this is because they set their permissible range of pH data as 0.1 pH. This precision is, of course, far insufficient to assess a temporal trend of a single station. We, therefore, focus on statistical characteristics of all derived trends instead of assessing each single trend. We demonstrate in section 4.1 that even if each trend at each site involves non-negligible measurement error, evaluation of whole statistical characteristics of the population (group) is feasible. To clarify the punch-line of our study, we have added new descriptions, especially in Section 4.2.

In summary, we propose here one practicable way to extract some meaningful information from past NBS-scale pH datasets. We believe this approach more useful than just revoking all past NBS-scale pH data.

2) The authors did not explain why they calculated trends for minimum and maximum pH values? Why didn't you calculate the trends based on the annual average pH instead of doing it for the minimum and maximum values separately?

As described in Section 2.1, the WPCL pH dataset contains only the annual minimum and maximum pH data without any information of the detailed measurement time. We assume that basically the annual minimum and maximum represents summer pH of 10m water and winter pH of surface water, respectively. As these two valuables represent pH trends at different water depths, we did not calculate average of these values. Moreover, the situation would be different at each site in summer and winter; therefore we calculated trends for minimum and maximum pH values separately. For example, in summer, biological activity would be more active but in winter, winter mixing would be more active. Such situation should be totally different from each other. Our analysis results of thermal effects on the trends are consistent with our assumption that annual minimum and maximum pH were measured in summer and winter, respectively.

3) The authors are relying on this methodology: ISO10523 (https://www.iso.org/standard/51994.html) mentioned in P7, L135. This method is adopted mainly for freshwater measurements. Could you please provide more information about the JIS Z8802 standard protocol (2011). It is apparently accredited in JIS list (file:///C:/Users/user/Downloads/jis-japanese-industrial-standards.pdf; p397) but I couldn't find its details.

ISO10523 is the methodology mainly adopted for freshwater measurements, but as we mentioned in the reply 1), this method had been adopted also for seawater measurement until 1994. JIS Z8802 is Japanese standard protocol that is formally compatible with ISO 10523. WPCL adopted this methodology for seawater pH measurement as it

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has launched in 1970, and they had not changed the methodology to maintain continuity in the measurements. We are now proposing to Japan Ministry of Environment to add pH measurements with present standard methods (ca. Dickson, Sabine and Christian 2007) in some coastal stations, but so far, only available dataset is the presented ISO10523-based dataset.

4) Any inter-calibration essays have been conducted to compare the pH results between the licensed operators/ labs?

We have found no information about inter-calibration essays between the licensed operators/labs in the WPCL program. We suppose that inter-calibration essays have not been conducted. To check the data quality by ourselves, we compared the pH trends measured by different licensed operators (see Section 2.2 and Fig. 6) and processed the data selection by the multi-step quality checking procedure.

5) How did you correlate the pH trends to biological processes? Did you check the correlation between pH and biological parameters measured in parallel at the monitored sites?

Since the pH data under the WPCL program were measured for monitoring the pollution control, the proper biological parameters were basically not included in the targets of the monitoring. Only the Total Nitrogen (TN) data are available from the data archive for a period from 1981 to 1995. We thus use them for the relevant discussion in section 4.2.2.

As mentioned by other reviewer, pH minimum substantially represents summer pH of subsurface (10m) water, so this trend shows negative correlation with that of TN. This relationship had partly offset anthropogenic-CO_2 induced pH decrease, because TN loadings to Japan coastal waters had significantly decreased in recent years.

6) How the dominance of heterotrophs or autotrophs might affect the pH in coastal waters? How did you related these to your data? Based on what have you suggested

that these waters are oligotrophic? Many statements through the text are so weak and need to be better justified.

To consider possible causes leading to contrast in acidification and basification trends among the sites, we assume that the eutrophication enhances acidification (basification) in the heterotrophic (autotrophic) sites (Duarte et al. 2013). We show that the assumption is partly confirmed by checking the negative correlation between pH and TN trends (Table 3). Figure 14 also indicates that some of the sites involve combination of negative (positive) pH and positive (negative) TN trends, suggesting the heterotrophic condition at the sites. The autotrophic condition is suggested by the sites shown in the second and fourths quadrants (Fig.14). We have modified the relevant descriptions to more elucidate this point.

Figures: The style of many figures is very confusing, also their captions! For Fig. 6 for example, the same-color lines indicate the pH values taken for the same place and the same operator, but one for the annual maximum and another one for the annual minimum pH? This was understood from the Fig. 6 caption, but not from the text. Please rephrase.

We have added some explanations about the annual and minimum pHinsitu data in caption of Fig. 6. The captions of other figures were also reconsidered. Thank you for your indication.

Tables: Table 2: How significant were these correlations? Why you didn't present this table the way you did in Table 3?

We have added information about the significance in Table 2.

Replies for the specific comments in your attached document.

L81-L85: Too much info. about only one region "Chesapeake Bay, US".

This part has been removed in the present version.

L310-L312: This sentence is very confusing!

We have revised this part in the present manuscript as follows.

"In the waters where primary productivity is predominantly to organic decomposition (i.e., autotrophic water), N increase will enhance primary production and hence decrease DIC, causing basification. In the adjoining waters of this autotrophic watermass, however, N increase will arise increase of POC transport from the autotrophic watermass, and this leads increase of POC-decomposed DIC (i.e., hetelotrophic water) and cause acidification (e.g., Sunda and Cai 2012; Duarte et al. 2013)."

L314-L317: These statements need to be related to your data.

This part is surely related to the analyses focusing on the distributions of the whole pH trends. We modified it to more emphasize our viewpoint.

L332-L335: In the rest of this section, you have assessed the thermal effect on pH trends by normalizing the pHinsitu to pH25. How did you test the second assumption related to the coastal carbon cycle?

We have modified the relevant description to clarify the logical structure. We first examine the thermal effect (D (T)) targeting the whole populations of pHinsitu trends, and then check ocean acidification effect (DIC (AirCO2)) for the populations of pH25 trends after normalization. Variability inside of the trend populations comes from the regional differences in the trends, which would be affected by other factors.

L356: The captions in your figures need to be clearer, so each color should be better assigned to a specific parameter. Also, please replace "deg" for Temperature by "°C".

The captions in the all figures were reconsidered, being improved. We have replaced "deg. C" for "°C" in the present manuscript.

L380-L381: Mixing the values/trends of both minimum pHinsitu and maximum pHinsitu is very confusing through the entire text. This needs to be improved.

We have unified to use the 'trends' in the present manuscript.

L407-409 how the dominance of heterotrophs or autotrophs might affect the pH in coastal waters? How did you relate these to your data? Based on what have you suggested that these waters are oligotrophic? These statements are so weak and need to be better justified.

We simply speculate possible existence of the heterotrophic and autotrophic sites according to Figure 14. Also see our reply comment to item 6).

L414 : This is weird. Do you mean oligotrophic and eutrophic waters?

We mean heterotrophic and autotrophic conditions for categorization of each site. A heterotrophic site shows a negative (positive) pH trend by responding to an eutrophication (oligotrophication) trend, and vice versa for an autotrophic site.

L451: I think you mean the trophic state index of the waters.

Yes, our categorization of heterotrophic/autotrophic sites is based on basically same terminology.

Please also note the supplement to this comment: ://www https.biogeosciences-discuss.net/bg-2019-150/bg-2019-150-RC1-supplement.pdf

Thank you for careful checking of our manuscript. It was very helpful for improving the description.

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

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2019-150/bg-2019-150-AC1-supplement.pdf

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