Thank you for your comments. We have replied your comments as follows. We show your comments and our replies in black and blue texts, respectively.

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 pHmin 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 pH_{insitu}, 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 (pH_{insitu}) 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 CO_2. 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 pCO_2 and the asymmetric response of air-sea CO_2 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 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 "$H_2O \leftrightarrow H^+ + OH^-$" 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 ($H_2O \leftrightarrow H^+ + OH^-$)."

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 pH_{insitu} 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±0.0033 and -0.0024±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 pH$_{insitu}$ 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 significance for ΔpH not zero, indicating that the trends with *ΔpH ≒0* 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 *Δ*pH≒0, which must actually exist.
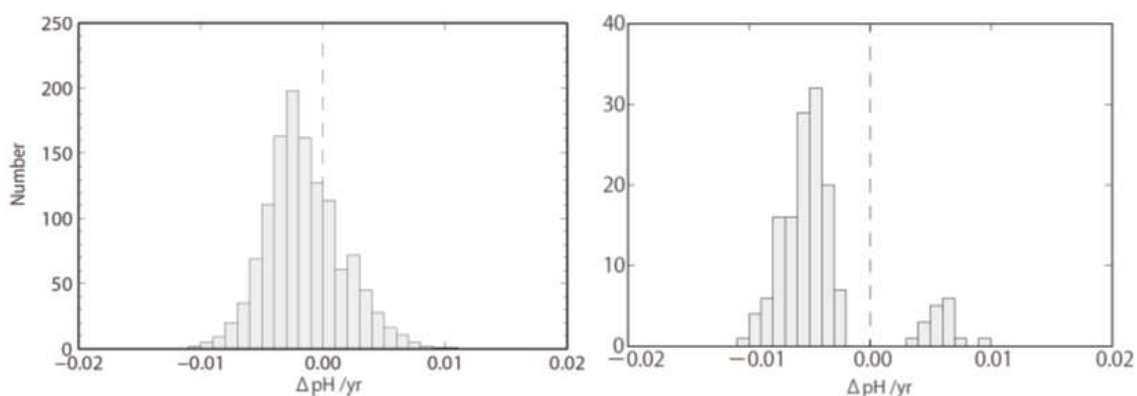
Figure R1. Examples of histograms of pH trends both with and without statistical significance for ΔpH not zero (left) and only with significance (right).

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 pH_{insitu}", 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 pH_{insitu} 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 pH_{insitu} 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 pH_{insitu} 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 pH_{insitu} 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.

1 # Long-term trends in pH in Japanese coastal sea waters

3 Miho Ishizu[1], Yasumasa Miyazawa[1], Tomohiko Tsunoda[2], Tsuneo Ono[3]

5 [1]E-mail: mishizu@jamstec.go.jp

6 [1]E-mail: miyazawa@jamstec.go.jp

7 Japan Agency for Marine-Earth Science and Technology, Environmental Variability Prediction and

8 Application Research Group, Yokohama Institute for Earth Sciences, 3173-25 Showa-machi,

9 Kanagawa-ku, Yokohama 236-0001, Japan

10 Tel: +81-45-778-5875

11 Fax: +81-45-778-5497

13 [2]E-mail: t-tsunoda@spf.or.jp

14 The Ocean Policy Research Institute of the Sasakawa Peace Foundation, 1-15-16, Toranomon Minato-

15 ku, Tokyo 105-8524, Japan

17 [3]E-mail: tono @affrc.go.jp

18 Japan Fisheries Research Education Agency, 15F Queen's Tower B, 2-3-3 Minato Mirai, Nishi-ku,
19 Yokohama, Kanagawa 220-6115, Japan

21 ## Abstract

22 In recent decades, acidification of the open ocean has shown consistent increases. However,

23 analysis of long-term data in coastal sea waters shows that the pH is highly variable because of coastal

processes and anthropogenic carbon inputs. It is therefore important to understand how anthropogenic carbon inputs and other natural or anthropogenic factors influence the temporal trends in pH in coastal sea waters. Using water quality data collected at 289 monitoring sites as part of the Water Pollution Control Program, we determined the long-term trends of pH_{insitu} in Japanese coastal sea waters at ambient temperature from 1978 to 2009. We found that pH_{insitu} decreased (i.e., acidification) at between 70% and 75% of the sites and increased (i.e., basification) at between 25% and 30% of the sites. The rate of decrease varied seasonally and was, on average, -0.0014 yr^{-1} in summer and -0.0024 yr^{-1} in winter, but with relatively large deviations from these average values. The seasonal variation in the average pH_{insitu} trends reflects variability in warming trends. The trend distributions of pH normalized at 25 deg. C also showed negative shifts, suggesting indication of ocean acidification that has occurred in Japanese coastal sea waters.

Keywords: pH, CO_2, Global warming, Ocean acidification, Coastal acidification/basification, Data analysis

1. Introduction

The effect of ocean acidification on several marine organisms, including calcifiers, is widely acknowledged and is the topic of various marine research projects worldwide. Chemical variables related to carbonate cycles are monitored in several ongoing ocean projects to determine whether the

rate of ocean acidification can be identified from changes in pH and other variables in the open ocean (Gonzalez-Davila et al. 2007; Dore et al. 2009; Bates 2007; Bates et al. 2014; Midorikawa et al. 2010; Olafsson et al. 2009; Wakita et al. 2017). Analysis of pH data measured in situ at the European Station in the Canary Islands (ESTOC) in the North Atlantic from 1995 to 2003 and normalized to 25 deg. C showed that pH_{25} decreased at a rate of 0.0017 ± 0.0005 yr^{-1} (Gonzalez-Davila et al. 2007). 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 (pH_{insitu}) decreased by 0.0019 ± 0.0002 and 0.0017 ± 0.0001 yr^{-1} from 1988 to 2007 and from 1983 to 2005, respectively. Analysis of data collected along the hydrographic observation line at 137°E in the western North Pacific by the Japanese Meteorological Agency (JMA) showed that pH_{25} decreased by 0.0013 ± 0.0005 yr^{-1} in summer and 0.0018 ± 0.0002 yr^{-1} in winter from 1983 to 2007 (Midorikawa et al. 2010). The winter pH_{insitu} in surface water in the Nordic Seas decreased at a rate of 0.0024 ± 0.0002 yr^{-1} from 1985 to 2008 (Olafsson et al. 2009). This rate was somewhat more rapid than the average annual rates calculated for the other subtropical time-series stations in the Atlantic Ocean, BATS, and ESTOC, and was attributed to the air–sea CO_2 flux and buffering capacity (higher Revell factor) (Olafsson et al. 2009), which were higher and lower than those in subtropical regions, respectively. Wakita et al. (2017) estimated that the annual and winter pH_{insitu} at station K2 in the subarctic western North Pacific decreased at rates of 0.0025 and 0.0008 yr^{-1}, respectively, from 1999 to 2015. The lower rate in winter was explained by increases in dissolved inorganic carbon (DIC) and total alkalinity (Alk)

62 that resulted from climate-related variations in ocean currents.

63 These long-term time-series from various sites in the open ocean indicate consistent changes in

64 surface ocean carbon chemistry, which mainly reflect the uptake of anthropogenic CO_2, with

65 consequences for ocean acidity. Coastal sea waters, however, differ from the open ocean as they are

66 subjected to multiple influences, such as hydrological processes, land use in watersheds, nutrient inputs

67 (Duarte et al. 2013), changes in the structure of ecosystems caused by eutrophication (Borges and

68 Gypens 2010; Cai et al. 2011), marine pollution (Zeng et al. 2015), and variations in salinity (Sunda

69 and Cai 2012).

70 Duarte et al. (2013) hypothesized that anthropogenic pressures would cause the pH_{insitu} of coastal

71 sea waters to decrease (acidification) or increase (basification), depending on the balance between the

72 atmospheric CO_2 inputs and watershed exports of alkaline compounds, organic matter, and nutrients.

73 For example, in Chesapeake Bay, trends in pH_{insitu} have shown temporal variations over the last 60

74 years, presumably because of the combined influence of increases and decreases in pH_{insitu} in the

75 mesohaline and polyhaline regions of the mainstem of the bay, respectively (Waldbusser et al. 2011;

76 Duarte et al. 2013).

77 These processes that occur only in coastal regions might cause increases or decreases in the rate of

78 acidification, meaning that the outcomes for coastal ecosystems in different regions will vary. At

79 present we have limited information about long-term changes in pH in coastal sea waters, mainly

80 because of the difficulty involved in collecting continuous long-term data from coastal sea waters

around an entire country at a spatial resolution that is sufficient to cover the high regional variability in coastal pH.

The Water Pollution Control Law (WPCL) was established in 1970 to deal with the serious pollution of the Japanese aquatic environment in the 1950s and 1960s. Several environmental variables, including pH_{insitu}, have been continuously measured in coastal waters since 1978, using consistent methods enacted in the monitoring program under the government leadership, to help protect coastal water and groundwater from pollution and retain the integrity of water environments. The errors in pH measurements collected in this program were assessed as outlined in the JIS Z8802 (JIS; Japanese Industrial Standard) standard protocol (2011) that corresponds to the ISO 10523 (ISO; International Organization for Standardization) standard protocol. Compared with the specialized oceanographic protocols described in the United States Department of Energy (DOE) Handbook (1994), it is not difficult to achieve the JIS protocol. The JIS and DOE standard protocols allow measurement errors of less than ±0.07 and ±0.003, respectively, for the glass electrode method, and the DOE protocol demands a precision of ±0.001 for the spectrophotometric method. Measurements are generally made with the higher-quality spectrophotometric method during major oceanographic studies (e.g. Midorikawa et al. 2010). The coastal monitoring program in Japan comprises more than 2000 monitoring sites that cover most parts of the coastline (Fig. 1), so the dataset provides the opportunity to estimate the overall trend in pH in Japanese coastal areas and the regional variability in the trends from data with a known precision.

In the present study, we examined the pH_{insitu} trends in surface coastal sea waters from data measured as part of WPCL monitoring programs. We then examined the trends at specific locations. The remainder of this manuscript is organized as follows: the data and methods are described in Section 2, and trends in pH_{insitu} are presented in Section 3, the results are discussed in Section 4 and the concluding remarks are provided in Section 5.

2. Materials and Methods

2.1 Water Pollution Control Law (WPCL) monitoring data

Data for several environmental variables, including pH_{insitu}, and the associated metadata, are available on the website of the National Institute for Environmental Studies (www.nies.go.jp/igreen; http://www.nies.go.jp/igreen/md_down.html). We downloaded data for pH_{insitu} from 1978 to 2009 for the trend analysis. We also downloaded temperature (T) and total nitrogen (TN) data that were measured at the same sites as the pH_{insitu} data for the same time period (data for T and TN from 1981 to 1995 were available), to check the quality of the pH_{insitu} data (Section 2.2), and to discuss coastal processes that influenced the pH_{insitu} (Section 4.2).

The data were collected by the Regional Development Bureau of the Ministry of Land, Infrastructure, Transport and Tourism, and the Ministry of the Environment under the WPCL monitoring program. Monitoring protocols (sampling frequencies, locations, and methods) are outlined in the program guidelines (NIES 2018; MOE 2018) written in Japanese, and here we summarize these

119   protocols.

120   Monitoring operations are occupied at 1481 sites along the Japan coast shown in Figure 1a. Most

121   stations locate coastal area while <10 % of the station locates estuary. In each monitoring sites, basic

122   surveys were held 4 to 40 times a year dependent to the site. Information on the sampling frequency at

123   the monitoring sites is presented in Table 1. At each basic survey, water samples were collected at

124   several depths (0.5 and 2.0 m below the surface for all sites, and 10 m where the bottom depth was

125   more than this) four times a day to cover diurnal variation. At sites where large variation is found in

126   the daily pH data, additional one day water sampling at 2-hourly intervals (ca. 13 times a day) was

127   made at least twice a year to check the adequacy of basic water sampling protocol.

128   Measurements of pH for each water sample were made following the Japanese Industrial

129   Standard   protocol   JIS   Z   8802   (2011),   which   is   equivalent   to   ISO10523

130   (https://www.iso.org/standard/51994.html). Namely, pH was measured by glass electrode calibrated

131   by NBS standard buffers. Basically, pH measurement was carried out just after the water sampling at

132   in-situ water temperature. Permitted repeatability in each measurement was ±0.07. NIES gathered all

133   pH data measured at each site and calculated annual minimum and maximum pH, providing them

134   through their website.

135   The published WPCL pH dataset only contains these annual minimum and maximum pH data in

136   each year, reported on the NBS pH scale (pH_{insitu}) and rounded to one decimal place. Water temperature

137   data   are   also   available   for   each   sampling   event   (http://www.nies.go.jp/igreen/md_down.html).

138 Previous studies have reported negative correlations between seasonal variations in pH and water

139 temperature, mainly because of changes in the dissociation constant in dissociation equilibrium

140 ($H_2O \leftrightarrow H^+ + OH^-$); the pH values were lowest in summer and highest in winter, in both the open

141 ocean (e.g. Bates et al. 2014) and coastal sea waters (e.g., Frankignoulle and Bouquegneau 1990; Byrne

142 et al. 2013; Hagens et al. 2015; Challener at al. 2016). We therefore assumed that the minimum and

143 maximum pH data coincided with the highest and lowest temperatures, respectively (Fig. 2), and we

144 used these data to calculate pH_{25} in Section 4.2. NIES do not discriminate surface (0.5m – 2m) and

145 subsurface (10 m) data when they calculate annual maximum and minimum pH, so it is speculated that

146 annual maximum pH substantially represents winter pH of surface waters, while annual minimum pH

147 represents summer pH of subsurface waters.

148   The monitoring operations were carried out by licensed operators as outlined in the annual plan of

149 the Regional Development Bureau of each prefecture. These specific licensed operators were retained

150 for the duration of the measurement period, which means that the same laboratories were always in

151 charge of collecting the data. This approach helps to prevent systematic errors that might arise both

152 between measurement facilities and over time, and ensures the datasets are accurate.

153

154 2.2 Quality control procedures and assessing the consistency of the WPCL monitoring data

155   We selected all the data for fixed sites in coastal sea waters that had continuous time-series from

156 1978 to 2009. There were 2463 regular and non-regular monitoring sites in 1978 and 2127 sites in

157 2009. While there were few sites in some prefectures in Hokkaido and Tohoku, the monitoring sites

158 covered almost all the coastline in Japan (Fig. 1).

159 As explained in more detail later in this section, we applied a three-step quality control procedure.

160 We excluded 1) discontinuous time sequences, 2) time sequences that had extreme outliers in each year,

161 and 3) time sequences that included significant random errors and which were only weakly correlated

162 with time sequences at adjacent sites.

163 When we excluded the sites that had discontinuous time sequences of pH_{insitu} from 1978 to 2009,

164 1481 sites remained (Fig. 1). We then excluded time sequences with outliers, defined as sites with data

165 points that were more than three standard deviations from the average of minimum and maximum

166 pH_{insitu} for each year. After this step, 1127 sites remained (not shown). We calculated the trends in the

167 unbroken continuous time sequences of the minimum and maximum pH_{insitu} data at each site with

168 linear regression (Fig. 3), and the slopes of the linear regression were taken as the minimum and

169 maximum pH_{insitu} trends (e.g. Fig. 3). The linear regression trends might have been influenced by

170 random errors or variations at different temporal scales in the data for each site. To eliminate the

171 influence of these errors and variations as far as possible, we removed the data that had significant

172 random errors, defined as the time sequences for which the standard deviations of pH_{insitu} exceeded the

173 average standard deviation of the pH_{insitu} time sequences at the 1127 sites. After this step, 302 sites

174 remained (see Fig. 1b for site locations).

175 For the 302 sites, we calculated the correlations of water temperature (Fig. 4a−b) and pH_{insitu} (Fig.

176 4c−d) at adjacent monitoring sites in the same prefecture (Fig. 4). At most of the stations, the

177 correlations between the temperatures at the site pairs were relatively strong, which indicates that the

178 temperature followed similar patterns over time at adjacent sites (Fig. 4a−b). The correlations tended

179 to be strong when the sites were close together, but gradually weakened with increasing distance

180 between sites. The patterns in the pH_{insitu} and temperature correlations were similar (Fig. 4), which

181 indicates that the pH_{insitu} and temperature data at adjacent monitoring sites varied in the same way. In

182 other words, the relative ratios of the measurement errors in pH_{insitu} and the natural spatio-temporal

183 variations at these monitoring sites were similar to those for temperature. The absolute values of the

184 pH_{insitu} correlation coefficients were slightly lower than those for temperature for each corresponding

185 pair of sites (Figs. 4 and 5), and might reflect the fact that pH_{insitu}, but not the water temperature, is

186 subjected to strong forcing by coastal biological processes, which causes short-term variations in

187 pH_{insitu}. The correlations between the minimum pH_{insitu} data (Fig. 4c) were weaker than those for the

188 maximum pH_{insitu} data (Fig. 4d) because the degree of biological forcing varied by season and was

189 stronger in summer when pH_{insitu} was at a minimum and weaker in the winter when pH_{insitu} was at a

190 maximum. Despite the influence of biological processes on pH_{insitu}, the correlation coefficients

191 remained high and were significant (r=0.367, p<0.05) at most of the monitoring sites, especially at

192 sites that were less than 5 km apart within the same prefecture; at such sites, pH_{insitu} followed similar

193 patterns. In the final step of the quality check procedure (step 3), we removed all the time sequences

194 with weak and insignificant correlations for temperature and pH_{insitu} (Figs. 4 and 5). After this final

195   step, 289 sites remained.

196   As shown in Table 2, the correlations between temperature and pH_{insitu} at sites that were within 15

197   km of each other strengthened after steps 2 and 3, which suggests that the reliability of the dataset

198   improved at each step of the quality control. The mutual correlations among the pH_{insitu} and temperature

199   measurements at adjacent sites (Table 2), and the correlations between pH_{insitu} trends and TN ones

200   (Table 3) show that the quality control procedures were effective.

201   The monitoring in each prefecture is carried out by different licensed operators, decided by the

202   Regional Development Bureau in each prefecture. Inter-calibration essays have not been conducted

203   between different licensed operators. Even though all the operators follow the same JIS protocol,

204   manual monitoring can introduce systematic errors into the data. Some adjacent monitoring sites are

205   close to each other but are managed by different operators, such as sites close to the boundaries between

206   Osaka and Hyogo (Fig. 6a), Hyogo and Okayama (Fig. 6b), Kagawa and Okayama (not shown), and

207   Kagawa and Ehime (not shown). The pH_{insitu} time sequences for these site pairs were generally similar,

208   even though there were some deviations when compared with the time sequences for adjacent sites

209   within the same prefecture, monitored by the same operator (lines of the same color in Fig. 6). The

210   standard deviations of the pH_{insitu} trends between these site pairs close to the boundaries of Osaka and

211   Hyogo, Hyogo and Okayama, Kagawa and Okayama, and Kagawa and Ehime were 0.0014, 0.0012,

212   0.0026, and 0.0017 yr^{-1}, respectively, and were smaller than the acceptable measurement errors of the

213   JIS standard protocols. We can therefore say that the measurements from the different operators in

214   different prefectures were consistent.

215

216   3. Results

217   3.1 Variations in pH_{insitu} highlighted by regression analysis

218   The histograms of the calculated pH_{insitu} trends (yr^{-1}), for the minimum and maximum pH_{insitu} after

219   each quality control step, are shown in Fig. 7. The histogram in Fig. 7a–b shows data of the 1481 sites

220   (discontinuous sites excluded). The data for 1127 sites (i.e., data without outliers from step 2) are

221   shown in Fig. 7c–d, and the data for 289 sites (from step 3) are shown in Fig. 7e–f (Section 2.2). The

222   number of sites decreased at each step of the quality control, but the shapes of the histograms were

223   generally similar for both the minimum and maximum pH trends. The total trends showed overall

224   normal distributions with a negative shift for all the processing level.

225   We detected both positive (basification) and negative (acidification) trends, which contrasts with

226   the findings of other researchers who reported only negative trends (ocean acidification) in the open

227   ocean (Bates et al. 2014; Midorikawa et al. 2010; Olafsson et al. 2009; Wakita et al. 2017). The average

228   (± standard deviation) trends for the minimum and maximum pH_{insitu} data were -0.0002 ± 0.0061 and

229   -0.0023 ± 0.0043 yr^{-1} for the 1481 sites (Fig. 7a−b), and -0.0005 ± 0.0042 and -0.0023 ± 0.0036 yr^{-1} for

230   the 1127 sites (Fig. 7c−d), respectively. The average trends for the minimum and maximum pH_{insitu}

231   data for the 289 sites that remained after step 3 were -0.0014 ± 0.0033 and -0.0024 ± 0.0042 yr^{-1},

232   respectively (Fig. 7e−f).

233   The negative trends were relatively weak for the minimum pH_{insitu} data and relatively strong for

234 the maximum pH_{insitu} data, but there was an overall tendency towards acidification. At the 289 sites,

235 there were 204 negative and 86 positive trends for the minimum pH_{insitu} data and 217 and 72 negative

236 and positive trends for the maximum pH_{insitu} data. This shows that for the minimum data, there were

237 acidification and basification trends at 70% and 30% of the monitoring sites, respectively, with values

238 of 75% and 25% for the maximum data, respectively.

239

240 ## 3.2 Local patterns in acidification and basification

241   We examined the pH_{insitu} trends for the 289 sites for local patterns in acidification and basification

242 (Section 2.2), and found that the trends seemed to be randomly distributed. For example, the values

243 were different at sites that were less than 50 km apart (Fig. 8). There are many monitoring sites in the

244 Seto Inland Sea and in Western Kyushu. The trends for the minimum and maximum pH_{insitu} showed

245 both acidification and basification in the Seto Inland Sea (Fig. 8a−b, 8c−d). In the western part of

246 Kyushu, acidification dominated (Fig. 8a−b, 8c−d) and there were few clusters of basification in

247 pH_{insitu} for both the minimum and maximum pH_{insitu} data (Fig. 8b, d). Figure 8a (b) and Figure 8c (d)

248 are similar, which suggests that, at most of the sites where we detected acidification and basification,

249 the trend directions were consistent for the minimum and maximum pH_{insitu} (Fig. 8a−b, 8c−d).

250   By examining the average minimum and maximum pH_{insitu} trends in each prefecture (Fig. 9a−b, d−e,

251 g−h, j−k), we found that, while the average values were slightly different, the trends in the averaged

252   values and the patterns in acidification and basification for both the minimum and maximum pH$_{insitu}$

253   were the same from north to south and from west to east. We also found acidification trends in most of

254   the prefectures with at least 17 sampling sites, namely Miyagi, Wakayama, Hyogo, Okayama,

255   Yamaguchi, Tokushima, Kagawa, Ehime, and Nagasaki (Figs. 1a and 9c, f, i, l). The average estimates

256   for the maximum pH$_{insitu}$ were larger than those for the minimum pH$_{insitu}$ in these prefectures.

257   We found more acidification trends for the minimum pH$_{insitu}$ in the southwestern prefectures of

258   Yamaguchi, Kagawa, Ehime, Hyogo, and Nagasaki than in the northeastern prefecture of Miyagi (Fig.

259   9a, d, g, i) (see Fig. 1 for locations). The maximum and minimum pH$_{insitu}$ trends indicated basification

260   in Wakayama and Okayama prefectures (Fig. 9c). The trends in Osaka, Hyogo, Okayama, Hiroshima,

261   Yamaguchi, Kagawa, and Ehime prefectures (Fig. 1a) were different from each other, even though they

262   were all located in the same part of the Seto Inland Sea (Fig. 9d−e). The trends in Hiroshima and

263   Okayama, within the Seto Inland Sea, were weaker than those in Hyogo, Yamaguchi, Kagawa, and

264   Ehime, which were outside the sea (Fig. 9d−e). The pH$_{insitu}$ trend values indicated relatively strong

265   acidification at −0.0025 yr^{-1} in Niigata in the Japan Sea (Fig. 9j−l) but there were fewer than the

266   threshold of 17 monitoring sites in the prefectures.

267

268   4. Discussion

269   4.1 Statistical evaluation of our estimated overall trends

270   The JIS Z8802 (2011) allows a measurement error of ±0.07 and this treatment further enhanced the

271   uncertainty of the published data to ±0.1. The uncertainty of the slope of the linear regression line (σ_β)

272   is estimated by the following equation (e.g., Luenberger 1969):

273         $\sigma_\beta = \{\sigma^2{}_y / \Sigma(x_i - [x])^2\}^{1/2}$ (1)

274   where $\sigma^2{}_y$ is the theoretical variance in a pH value caused by the measurement error (in this case, 0.1^2

275   = 0.01); and x_i and $[x]$ represent the year and the year averaged for all data at a station, respectively.

276   In the WPCL dataset, there are generally 32 data points for each station (for every year from 1978 to

277   2009), spaced at consistent intervals. In this case, $\Sigma(x_i - [x])^2$ becomes 2728 and σ_β becomes 0.0020

278   yr^{-1}, which is the threshold of significance for the pH trend. This means that our estimated trends

279   included standard deviations that were less than 0.0020 yr^{-1}, and, if there were no trends, a histogram

280   of pH trends should have a normal distribution with an average and standard deviation (σ_β) of 0.0000

281   and 0.0020 yr^{-1}, respectively (Fig. 7). The average trend in the maximum pH_{insitu}, however, shifted

282   from zero in a negative direction at a rate of more than 0.0020 yr^{-1} for all three scenarios (Fig. 7b, d,

283   f). This result implies that averaged over the whole country, the Japanese coast was acidified in winter

284   to a degree that could be detected from the historical WPCL pH data, even with an uncertainty of ±0.1.

285   The observed standard deviation for the maximum pH_{insitu} was also larger than the expected value of

286   0.0020 yr^{-1} because of local variations in the pH trends. The average shift in the minimum pH_{insitu} data

287   was smaller than 0.0020 yr^{-1}, but all three scenarios showed negative shifts in the average minimum

288   pH_{insitu} value (Fig. 7a, c, e).

289   We used Welch's t test to assess the direction of the average minimum and maximum pH_{insitu} trends.

290   For our null hypothesis, we assumed that the population of the trends with an average of -0.0014 yr^{-1}

291   (-0.0024 yr^{-1}) and a standard deviation of 0.0033 yr^{-1} (0.0042 yr^{-1}) was sampled from a population

292   with an average trend of 0.0000 yr^{-1} and a standard deviation of 0.0020 yr^{-1}. When the sample size

293   was 289, the t-values and the degrees of freedom were 8.7 (6.2) and 412.2 (474.4), respectively. Since

294   the p value was less than 0.001, the null hypothesis was rejected. Welch's t test confirmed that the

295   average trends for both the minimum and maximum pH_{insitu} data were negative.

296   We also applied a paired t-test for the two trends calculated from the averaged minimum and

297   maximum pH_{insitu} data, to verify whether two trends are significantly different. The population mean

298   and the sample size were 0.0 and 289, respectively. Since the t-value was calculated to be 4.64 (the

299   degrees of freedom = 288), the null hypothesis was rejected. The paired t-test suggested that the two

300   trends calculated from the averaged minimum and maximum pH_{insitu} data are significantly different.

301

302 ## 4.2 Possible influences on the pH_{insitu} trends in coastal sea waters

303   To facilitate our discussion of the factors that influenced the pH_{insitu} trends, we used the conceptual

304   models of acidification and basification in coastal sea waters of Sunda and Cai (2012) and Duarte et

305   al. (2013), as follows:

306   PH_{insitu} = Function (D (T), DIC (Air CO_2, B (T, N)), Alk(S))   (2)

307   The pH_{insitu} varies with the ambient temperature (T) on seasonal, inter-annual, and decadal time scales

308   mainly because of changes in the water dissociation constant in dissociation equilibrium (D;

309     $H_2O \leftrightarrow H^+ + OH^-$). Changes in dissolved inorganic carbon (DIC), alkalinity (Alk), and salinity (S)

310   also affect the pH_{insitu} trends. The solubility pump, which is controlled mainly by the atmospheric CO_2

311   concentration (Air CO_2; $CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$), affects DIC, and ocean acidification occurs

312   when the Air CO_2 increases. Dissolved organic carbon can also be affected by biological processes (B)

313   that depend on the ambient temperature (T) and the nutrient loading (N). There are contrasting

314   relationships between DIC and N in heterotrophic and autotrophic oceans. In the waters where primary

315   productivity is predominantly to organic decomposition (i.e., autotrophic water), N increase will

316   enhance primary production and hence decrease DIC, causing basification. In the adjoining waters of

317   this autotrophic water mass (for example, subsurface waters), however, N increase will arise increase

318   of POC (Particle Organic Carbon) transport from the autotrophic water mass, and this leads increase

319   of POC-decomposed DIC (i.e., hetelotrophic water) and cause acidification (e.g., Sunda and Cai 2012;

320   Duarte et al. 2013). Alkalinity (Alk) generally varies with salinity (S) in coastal oceans and might also

321   affect the pH_{insitu} trend.

322   The DIC process (Air CO_2) of ocean acidification in equation 2 generally occurred at all monitoring

323   sites when the Air CO_2 concentrations were horizontally uniform, resulting in overall negative trends

324   in minimum and maximum pH_{insitu}. D (T) also has an overall trend of warming in Japan coastal area,

325   and hence made some affections to the observed pH_{insitu} trend. Both the DIC (Air CO_2) and D (T) could

326   be associated with the global processes: ocean acidification and global warming, which were triggered

327   by the increase of CO_2 concentration in the global atmosphere. We will discuss about these global

effects focusing on the averages of the whole pH trends in Section 4.2.1.

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 (e.g., salinity of coastal water and terrestrial nutrient loading) have no common trends all over the Japan coast in this dataset. The WPCL data should contain stations of both autotrophic and heterotrophic oceans (Smith and Hollibaugh 1992), and this condition further obscure influence of DIC (B (T, N)) to overall pH_{insitu} trend, as the same trend of B (T, N) leads opposite trends of DIC (B (T, N) in autotrophic and heterotrophic ocean (Duarte et al. 2013). Wide-varying nature of DIC (B (T, N)), and Alk (S) depending on the region might have caused the regional differences of pH_{insitu} trends among stations, contributing relatively large standard deviations of both the minimum and maximum pH_{insitu} trends (Fig. 7). We will discuss about these local effects associated with the regional differences in Section 4.2.2.

4.2.1 Global effects on pH_{insitu} trends

Our analysis was based on the pH_{insitu} data, so the difference between the trends might reflect long-term changes in water temperature that affected the dissociation constant (process D (T) in equation 2) or changes in the coastal carbon cycle (including absorption of anthropogenic carbon by the solubility pump, represented by DIC in equation 2) (process DIC (Air CO_2) in equation 2). A part of D (T) and DIC (Air CO_2) effects driven by ocean acidification and global warming could affect the all monitoring sites, and result in the trend distributions with negative shifts.

347  To evaluate the direct thermal effects related to process D (T) in equation 2, we estimated the pH

348  values normalized to 25 deg. C (pH$_{25}$), assuming that the minimum (maximum) pH$_{insitu}$ and highest

349  (lowest) temperature and other parameters were measured at the same time. By assuming the other

350  parameters that affected the pH calculation in the CO2sys (Lewis and Wallace 1998, csys.m), such as

351  salinity, DIC, and alkalinity, did not change (these parameters are not measured as part of the WPCL

352  program), we used the method of Lui and Chen (2017) to calculate the pH$_{25}$, as follows:

353  $$pH_{25} = -pH_{insitu} + a_1(T - 25 \text{ deg. C}), \qquad (3)$$

354  where a_1 is set to −0.015 and T is the observed temperature.

355  The distributions of the trends in pH$_{25}$ after applying equation 3 are shown in Fig. 10. The minimum

356  and maximum pH$_{25}$ data were normally distributed, meaning that the distributions of the pH$_{insitu}$ trends

357  were maintained after applying equation 3 (Fig. 7e, f). The averages (± standard deviations) of the

358  minimum and maximum pH$_{25}$ trends were −0.0010±0.0032 and −0.0014±0.0041 yr^{-1}, respectively.

359  The averaged trends are consistent with those reported by Midorikawa et al. (2010), who calculated

360  that pH$_{25}$ decreased at rates of -0.0013±0.0005 yr^{-1} and -0.0018±0.0002 yr^{-1} in summer and winter

361  from 1983 to 2007 along the 137°E line of longitude in the north Pacific. The asymmetry of the pH$_{25}$

362  trends between minimum and maximum estimates would be related to the seasonal variations of pCO$_2$

363  and the associated asymmetric response of air-sea CO$_2$ flux (Landschutzer et al. 2018; Fassbender et

364  al. 2018).

365  We also used Welch's t test to assess the direction of the averages of minimum and maximum pH$_{25}$

366 trends, as same as applying it to the pH_{insitu} trends. The p value was calculated to be less than 0.001 in

367 this case, so the null hypothesis was again rejected. Welch's t test confirmed that the average trends

368 for both the minimum and maximum pH_{25} data were negative as well, suggesting that the DIC

369 $(AirCO_2)$ effect (i.e. ocean acidification) caused negative shifts of the pH trend distribution after

370 normalizing at 25 deg. C.

371   The pH_{25} and pH_{insitu} trends from north to south and from west to east were similar among the

372 prefectures (Fig. 11), except in Miyagi and Tokushima. The trends in the minimum pH_{insitu} and summer

373 pH_{25} were quite similar, but the minimum and maximum pH_{insitu} trends tended to be more negative (by

374 about -0.0010 yr^{-1}) than the corresponding pH_{25} trends, especially in Wakayama, Hiroshioma, Kagawa,

375 and Ehime, which met the threshold number of sampling sites.

376   The average highest temperatures observed at the minimum pH_{insitu} were close to 25 deg. C in the

377 regions south of Chiba prefecture (Figs. 1 and 12a−d), so the normalization at 25 deg. C did not much

378 affect the evaluation of the minimum pH_{25} in the southern prefectures. In contrast, the maximum

379 pH_{insitu} values were observed at temperatures that were more than 10 deg. lower than 25 deg. C, so the

380 normalization worked well on the winter data. We estimated the temperature trends from the highest

381 and lowest temperatures at the 289 sites that remained after quality control step 3. The trends in the

382 highest and lowest temperatures generally indicated warming, with an average and standard deviation

383 of 0.021 ± 0.040 and 0.047 ± 0.036 deg. yr^{-1}, respectively (Fig. 13). Estimations from the CO2sys

384 indicate that these warming trends influenced the pH values and were related to the changes of -0.0004

385   and -0.0010 yr^{-1} in the pH trends in summer and winter, respectively (Fig. 7e−f and 10a−b).

386   We estimated that the pH$_{insitu}$ would change from 8.0150 to 8.0147 in summer and from 8.2568 to

387   8.2560 in winter, for temperature changes from 25.00 deg. to 25.02 deg., and from 10.00 deg. to 10.04

388   deg., respectively, for a salinity of 34, DIC of 1900 millimol m^{-3}, and alkalinity of 2200 millimol m^{-3}.

389   The differences between the pH$_{insitu}$ and the corresponding pH$_{25}$ trends in summer (-0.0004 yr^{-1}) and

390   winter (-0.0010 yr^{-1}) can be partly explained by the difference between the decrease in the pH trends

391   in summer (-0.0003 yr^{-1}) and winter (-0.0005 yr^{-1}) (Fig. 7e−f) arising from the thermal effects.

392

4.2.2 Local effects on pH$_{insitu}$ trends

394   We found regional differences in pH$_{insitu}$ values itself (e.g. Fig. 6) and pH$_{insitu}$ trends (Figs. 8−9).

395   The negative pH$_{insitu}$ trends (acidification) were more significant in southwestern Japan than in

396   northeastern Japan, especially for the minimum pH$_{insitu}$ data (Fig. 9 and Section 3.2). The JMA (2008,

397   2018) reported that over the past 100 years, the increase in water temperature in western Japan was

398   ~1.30 deg. C greater than that in northeastern Japan.

399   We used CO2sys (Lewis and Wallace 1998) to predict how pH$_{insitu}$ would change under a

400   temperature difference of 0.01 deg. C yr^{-1} between the northeastern and southwestern areas, and found

401   that pH decreased by 0.0002 (0.0002) yr^{-1} when the temperature changed from 10.00 deg. C to 10.01

402   deg. C (25.0 deg. to 25.01 deg. C), assuming a salinity of 34, DIC of 1900 millimol/m^3, and alkalinity

403   of 2200 millimol/m^3. The contrasting trends in the northeast and southwest can be also partly explained

404   by the difference in warming trends (process D (T) in equation 2).

405   The summer pH_{insitu} is affected by ocean uptake of CO_2 (process DIC; Bates et al. 2012; Bates 2014)

406   through long-term changes in biological activity (Cai et al. 2011; Sunda and Cai 2012; Duarte et al.

407   2013; Yamamoto-Kawai et al. 2015) as well as the effect of changes in the dissociation constant. The

408   responses of pH_{insitu} to changes in marine productivity are, however, complicated.

409   Previous studies have reported that nutrient loadings in Japan have decreased over recent decades

410   (e.g., Yamamoto-Kawai et al. 2015; Kamohara et al. 2018; Nakai et al. 2018), with variable effects on

411   summer pH_{insitu} in coastal sea waters. TN was monitored for a shorter period than pH_{insitu} (1995 to

412   2009). We assumed that the TN was mainly dissolved inorganic nitrogen, and determined the

413   correlations between TN and the minimum and maximum pH_{insitu} data (Fig. 14). There were significant

414   negative correlations between TN and minimum (−0.30) and maximum (−0.29) pH_{insitu}. These

415   correlations apparently imply that the conditions in most of the monitoring areas of the WPCL

416   programs were heterotrophic. This results also implies that recent decrease of TN loadings had partly

417   offset anthropogenic CO_2-induced pH decrease in coastal sea waters. However, we should also be

418   careful about the possibility that this may be a result of simultaneous progress of independent two

419   things (i.e., anthropogenic carbon uptake of ocean and decrease of TN loadings in Japan).

420   Nakai et al. (2018) reported that nutrient loadings have decreased in the most parts of the Seto Inland

421   Sea from 1981 to 2010, but several areas remain eutrophic. Because of geographical variations in

422   nutrient loadings and the uneven distribution of autotrophic and heterotrophic water areas, there are

423   significant spatial variations in pH trends in the Seto Inland Sea (Fig. 8). The pH trends in coastal areas

424   of western Kyushu, where the anthropogenic nutrient loadings are relatively low, therefore reflect the

425   decreases in nutrient discharges, resulting in variations between regions (e.g., Nakai et al. 2018;

426   Yamamoto and Hanazato 2015; Tsuchiya et al., 2018). Several cities in this area have introduced

427   advanced sewage treatment to prevent eutrophication in coastal sea waters (Nakai et al. 2018;

428   Yamamoto and Hanazato 2015).

429   Regional variations in coastal alkalinity along with salinity might be related to changes in land use

430   and might affect the trends (process Alk(S) in equation 2). Taguchi et al. (2009) measured alkalinity in

431   the surface waters of Ise, Tokyo, and Osaka bays between 2007 and 2009, and reported that total

432   alkalinity was highly correlated with salinity in each bay. For a temperature, salinity, dissolved carbon,

433   and alkalinity of 25.00 deg. C, 35, 1900 millimol m^{-3}, and 2300 millimol m^{-3}, respectively, pH_{insitu} (=

434   pH_{25}) was estimated at 8.1416 using the CO2sys (Lewis and Wallace 1998). By changing the salinity

435   and alkalinity to 34 and 2200 millimol m^{-3}, respectively, pH_{insitu} (= pH_{25}) decreased by 0.0081 to

436   8.0150. This shows that pH could deviate significantly from average trends if the inputs of alkaline

437   compounds are changed; consequently, some of our pH trends could have been affected by changing

438   discharge from different land-use types.

439   Regional differences in pH_{insitu} trends in coastal sea waters might be caused by ocean pollution. The

440   speciation and bioavailability of heavy metals change in acidic waters, causing an increase in the

441   biotoxicity of the metals (Zeng et al. 2015; Lacoue-Labarthe et al. 2009; Pascal et al. 2010; Cambell

442   et al. 2014). The rates at which marine organisms photosynthesize and respire in ocean waters decrease

443   and increase, respectively, in water polluted with heavy metals and oils (process DIC in equation 2)

444   because of biotoxicity and eutrophication, thereby resulting in acidification (Hing et al. 2011; Huang

445   et al. 2011; Gilde and Pinckney 2012).

446

5. Conclusions

448   We estimated the long-term trends in pH_{insitu} in Japanese coastal sea waters and examined how the

449   trends varied regionally. The long-term pH_{insitu} data show highly variable trends, although ocean

450   acidification has generally intensified in Japanese coastal sea waters. We found that the annual pH_{insitu}

451   minimum (in summer) and pH_{insitu} maximum (in winter) decreased at overall rates of -0.0014 and

452   -0.0024 yr^{-1}, respectively, in Japanese coastal sea waters. The averages of the minimum and maximum

453   pH_{25} trends were -0.0010 and -0.0014 yr^{-1}, respectively. The differences between the pH_{insitu} and the

454   corresponding pH_{25} trends in summer (-0.0004 yr^{-1}) and winter (-0.0010 yr^{-1}) can be partly explained

455   by the thermal effects. The negative shifts of the pH_{25} trend distributions suggest a signal of ocean

456   acidification in Japanese coastal sea water.

457   There were striking spatial variations in the pH_{insitu} trends. Correlations among the pH_{insitu} time series

458   at different sites revealed that the high variability in the pH_{insitu} trends was not caused by analytical

459   errors in the data but reflected the large spatial variability in the physical and chemical characteristics

460   of coastal environments, such as water temperature, nutrient loadings, and autotropic/heterotrophic

461 conditions. While there was a general tendency towards coastal acidification, there were positive trends

462 in pH_{insitu} at 25%–30% of the monitoring sites, indicating basification, which suggests that the coastal

463 environment might not be completely devastated by acidification. If we can manage the coastal

464 environment effectively (e.g., control nutrient loadings and autotropic/heterotrophic conditions), we

465 might be able to limit, or even reverse, acidification in coastal areas.

466

467 Acknowledgments

468   We thank the scientists, captain, officers, and personnel of the National Institute for Environmental

469 Studies, Regional Development Bureau of the Ministry of Land, Infrastructure, Transport and Tourism,

470 who contributed to this study. We acknowledge financial support from the Sasakawa Peace Foundation

471 of the Ocean Policy Research Institute. We also appreciate discussions with members of the

472 Environmental Variability Prediction and Application Research Group of the Japanese Agency for

473 Marine-Earth Science and Technology. Suggestions by two reviewers helped us to improve an earlier

474 version of the manuscript.

475

476 References

477 Bates, N. R.: Interannual variability of the ocean CO_2 sink in the subtropical gyre of the North Atlantic

478   Ocean over the last 2 decades, J. Geophys. Res. 112, C09013, doi:10.1029/2006JC003759, 2007.

479 Bates, N. R.: Multi-decadal uptake of carbon dioxide into subtropical mode waters of the North

480   Atlantic Ocean. Biogeosciences 9:2, 649−2, 659, http://dx.doi.org/10.5194/bg-9-2649-2012, 2012.

481 Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., Gonzalez-Davila, M., Lorenzoni, L.,

482   Muller-Karger, F., Olafsson, J., and Santana-Casiano, J. M.: A time-series view of changing surface

483   ocean chemistry due to ocean uptake of anthropogenic CO_2 and ocean acidification, Oceanography,

484   27 (1):126−141, http://dx.doi.org/10.5670/oceanog.2014.16, 2014.

485   Bednarsek, N., Tarling, G. A., Bekker, D. C. E., Fielding, S., Jones, E. M., Venables, H. J., Ward, P.,

486   Kuzirian, A., Leze, B., Feely, R. A., and Murphy, E. J.: Extensive dissolution of live pteropods in

487   the Southern Ocean, Nature Geoscience Letter, 5, 881−885, doi: 10.1038/NGEO1635, 2012.

488   Bednarsek, N., Feely, R. A., Reum, J. C. P., Peterson, B., Menkel, J., Alin, S. R., and Hales, B.:

489   *Limacina helicina* shell dissolution as an indicator of declining habitat suitability due to ocean

490   acidification in the California Current Ecosystem, Proc. R. Soc. B, 281 20140123, doi:

491   10.1098/rspb.2014.0123, 2014.

492   Borges, A. V. and Gypen, N.: Carbonate chemistry in the coastal zone responds more strongly to

493   eutrophication than to ocean acidification, Limnology and Oceanography 55: 346−353, 2010.

494   Montagna, R.: Description and quantification of pteropod shell dissolution: a sensitive bioindicator of

495   ocean acidification, Global Change Biology, 18, 2378−2388, doi: 10.1111/j.1365−2486.2012.02668,

496   2012.

497   Byrne, M., Lamare, M., Winter, D., Dworjanyn, S. A., and Uthicke, S.: The stunting effect of a high

498   CO_2 ocean on calcification and development in the urchin larvae, a synthesis from the tropics to the

499   poles, Philosophical Transactions of the Royal Society B, 368, 20120439. Doi:

500   10.1098/rstb.2012.0439, 2013.

501 Cai ,W., Hu, X., Huang, W., Murell, M. C., Lehrter, J. C., Lohrenz, S. E., Chou, W., Zhai, W.,

502   Hollibaugh, J. T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M., and Gong, G.: Acidification

503   of subsurface coastal waters enhanced by eutrophication, Nature Geoscience, 4, 766−700, 2011.

504 Campbell, A. L., Mangan, S., Ellis, R. P., and Lewis, C.: Ocean acidification increases copper toxicity

505   to the early life history stages of the polychaete arenicola marina in artificial seawater, Environ. Sci.

506   Technol. 48, 9745−9753, 2014.

507 Challener, R. C., Robbins, L. L., and McClintock, J. B.: Variability of the carbonate chemistry in a

508   shallow, seagrass-dominated ecosystem: imprications for ocean acidification experiments, Marine

509   and Freshwater Research, 67, 163−172. Doi:10.1071/MF14219, 2016.

510 DOE (United States Department of Energy): Handbook of methods for the analysis of the various

511   parameters of the carbon dioxide system in sea water; ver. 2, edited by A. G. Dickson and C. Goyet,

512   ORNL/CDIAC-74, 1994.

513 Dore, J. E., Lukus, R., Sadler, D. W., Church, M. J. and Karl. D. M.: Physical and biogeochemical

514   modulation of ocean acidification in the central North Pacific, Proc. Natl. Acad. Sci. 106, 12 235−12

515   240, 2009.

516 Doney, S.C., Fabry, V. J., Freely, A., and Kleypas, J. A.: Ocean acidification: The other CO_2 program,

517   Annu. Rev. Mar. Sci, 1, 169−192, 2009.

518 Duarte, C. M., Hendriks, I. E., Moore, T. S., Olsen, Y. S., Steckbauer, A., Ramajo, L., Carstensen, J.,

519 Trotter, J. A., and McCullouch, M.: Is ocean acidification an open ocean syndrome? Understanding

520 anthropogenic impacts in seawater pH, Estuaries and Coasts 36, 221−236.doi:10.1007/s12237-013-

521 9594-3, 2013.

522 Fassbender J. A., Rodgers B. K., Palevsky I. H., and Sabine L. C.: Seasonal asymmetry in the evolution

523 of surface ocean pCO_2 and pH thermodynamic drivers and the influence on sea-air CO_2 flux, Global

524 Biogeochemical Cycles, 32, 11476−1497, 2018.

525 Frankignoulle, M., and Bouquegneau, J. M.: Daily and yearly variations of total inorganic carbon in a

526 productive coastal area, Estuarine, Coastal and Shelf Science 30, 79−89, 1990.

527 Gattuso, J. P., and Hansson, L.: Ocean acidification, Oxford Univ. Press, Oxford, 2011.

528 Glide, K., and Pinckney, J. L.: Sublethal effects of crude oil on the community structure of estuarine

529 phytokton, Estuar. Coasts 35, 853−861, 2012.

530 Gonzalez-Davila, M., Santana-Casiano, J. M., and Gonzalez-Davila, E. F.: Interannual variability of

531 the upper ocean carbon cycle in the northeast Atlantic Ocean, Geophys. Res. Lett. 34, L07608,

532 doi:10.1029/2006GL028145, 2007.

533 Hagens, M., Slomp, C. P., Meysman, F. J. R., Seitaj, D., Harlay, J., Borges, A. V., and Middelburg, J.

534 J.: Biogeochemical processes and buffering capacity concurrently affect acidification in a seasonally

535 hypoxic coastal marine basin, Biogeoscience 12, 1561−1583. Doi:10.5194/bg-12-1561-2015, 2015.

536 Hing, L. S., Ford, T., Finch, P., Crane, M., and Morritt, D.: Laboratory stimulation of oil-spill effects

537   on marine phytoplankton, Aquat. Toxicol 103, 32−37, 2011.

538 Huang, Y. J., Jiang, Z. G., Zeng, J. N., Chen, Q. Z., Zhao, Y. Q., Liao, Y. B., Shou, L., and Xu, X. Q.:

539   The chronic effects of oil pollution on marine phytoplankton in a subtropical bay, China. Environ.

540   Monit. Assess. 176, 517−530, 2011.

541 Intergovernmental Panel on Climate Change (IPCC): Climate Change 2013: The Physical Science

542   Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental

543   Panel on Climate Change, ed. Stocker, T. F., Qin, D., Plattner, Gian-Kasper., Tignor, M. M. B., Allen,

544   S. K., Boschung, J., Nauels, A., Zia Y., Bex, V., Midgley, P. M., 1−1535 pp. Cambridge,

545   UK: Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

546 Japanese Industrial Standard Z8802 : http://kikakurui.com/z8/Z8802-2011-01.html (in Japanese), 2011.

547 Japanese   Meteorological   Agency   :

548   http://dl.ndl.go.jp/view/download/digidepo_3011050_po_synthesis.pdf?itemId=info%3Andljp%2F

549   pid%2F3011050&contentNo=1&alternativeNo=&__lang=en, 2008.

550 Japanese   Meteorological   Agency   :

551   https://www.data.jma.go.jp/kaiyou/data/shindan/a_1/japan_warm/japan_warm.html (in Japanese),

552   2018.

553 Kamohara, S., Takasu, Y., Yuguchi, M., Mima, N., and Yoshunari, A.: Nutrient decrease in Mikawa

554   Bay, Bulletin of Aichi Fisheries Research Institute 23, 30−32. (in Japanese), 2018.

555 Keeling, C. D., and Whorf, T. P.: Atmospheric CO_2 concentration–Manoa Loa Observatory, Hawaii,

556   1958-1997 (revised August 1998), ORNL NDP−001, Oak Ridge Nathl. Lab. Oak Ridge, TN, 1998.

557 Lacou-Labarthe, T., Martin, S., Oberhansli, F., Teyssie, J. L., Jeffree, R., Gattuso, J. P., and

558   Bustamante, P.: Effects of increased pCO_2 and temperature on tracer element (Ag, Cd and Zn)

559   bioaccumulation in the eggs of the common cuttlefish, Sepia officinalis. Biogeosciences 6,

560   2561−2573, 2009.

561 Landschutzer P, Gruber N, Bakker C. E. D., Stemmler I, Six D. K.: Strengthening seasonal marine

562   CO_2 variations due to increasing atmospheric CO_2. Nature Climate Change, 8, 146−150, 2018.

563 Lemasson, A. J., Fletcher, S., Hall-Spence, J. M., and Knights, A. M.: Linking the biological impacts

564 of ocean acidification on oysters to changes in ecosystem services: A review, Journal of Experimental

565   Marine Biology and Ecology, 492, 49−62, 2017.

566 Lewis, E., and Wallace, D. W. R.: Program Developed for CO2 System Calculations. ORNL/CDIAC-

567   105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department

568   of Energy, Oak Ridge, Tennessee, 1998.

569 Luenberger, D. G.: Optimization by vector space methods, pp. 1-326, John Wiley & Sons, Inc., New

570   York, N.Y, 1969.

571 Lui, H., and Chen, A. C.: Reconciliation of pH_{25} and pH_{insitu} acidification rates of the surface oceans:

572   A simple conversion using only in situ temperature, Limnology and Oceanography: methods, 15,

573   328−355, doi:1002/lom3.10170, 2017.

574 Midorikawa, T., Ishii, M., Sailto, S., Sasano, D., Kosugi, N., Motoi, T., Kamiya, H., Nakadate, A.,

575   Nemoto, K., and Inoue, H.: Decreasing pH trend estimated from 25-yr time series of carbonate

576   parameters in the western North Pacific, Tellus, 62B, 649−659, doi:

577   10.111/j.1600−0889.2010.00474.x, 2010.

578 Ministry of the Environment: http://www.env.go.jp/hourei/05/000140.html (in Japanese), 2018.

579 Nakai, S., Soga, Y., Sekito, S., Umehara, S., Okuda, T., Ohno, M., Nishijima, W., and Asaoka, S.:

580   Historical changes in primary production in the Seto Inland Sea, Japan, after implementing

581   regulations to control the pollutant loads, Water Policy wp2018093. Doi:10.2166/wp.2018.093, 2018.

582 National Institute for Environmental Studies :

583   https://www.nies.go.jp/igreen/explain/water/content_w.html (in Japanese), 2018.

584 Olafsson, J., Olafsdottir, S. R., Benoit-Cattin, A., Danielsen, M., Arnarson, T. S., and Takahashi, T.:

585   Rate of Iceland Sea acidification from time series measurements, Biogeosciences 6:2, 661−2, 668,

586   http://dx.doi.org/10.5194/bg−6−2661−2009, 2009.

587 Pascal, P. Y., Fleeger, J. W., Galvez, F., and Carman, K. R.: The toxicological interaction between ocean

588   acidity and metals in coastal meiobenthic copepods, Mar. Pollut. Bull, 60, 2201−2208, 2010.

589 Sarmiento, J. L., and Gruber, N.: Ocean Biogeochemical dynamics, pp. 1-503, Princeton Univ. Press,

590   Princeton, New Jersey; Oxfordshire, United Kingdom, 2006.

591 Smith, S.V., and Hollibaugh, J. T.: Coastal metabolism and the oceanic carbon balance. Review of

592   Geophysics, 31, 75-89, 1993.

593   Sunda, W. G., and Cai, W. J.: Eutrophication induced CO_2-acidification of subsurface coastal waters:

594   interactive effects of temperature, salinity, and atmospheric pCO_2, Environ. Sci. Technol. 46,

595   10651−10659, 2012.

596   Taguchi, F., Fujiwara, T., Yamada, Y., Fujita, K., and Sugiyama, M.: Alkalinity in coastal seas around

597   Japan, Bulletin on coastal oceanography, Vol.47, No.1, 71−75, 2009.

598   Yamamoto-Kawai, M., Kawamura, N., Ono, T., Kosugi, N., Kubo, A., Ishii, M., and Kanda, J.: Calcium

599   carbonate saturation and ocean acidification in Tokyo Bay, Japan, J. Oceanogr. 71:427−439, doi

600   10.1007/s10872-015-0302-8, 2015.

601   Tsuchiya, K., Ehara, M., Yasunaga, Y., Nakagawa, Y., Hirahara, M., Kishi, M., Mizubayashi, K.,

602   Kuwahara, V. S., and Toda, T.: Seasonal and Spatial Variation of Nutrients in the Coastal Waters

603   of the Northern G*oto Islands, Japan, Bulletin on coastal oceanography, 55, 125-138. (in*

604   *Japanese)*, 2018.

605   Yamamoto, T., and Hanazato, T.: Eutrophication problems of oceans and lakes, -fishes cannot live in

606   clean water, pp. 1−208, ChijinShokan Co. Ltd, ISBN978-4-8052-0885-4, (in Japanese), 2015.

607   Yara, Y., Vogi ,M., Fujii, M., Yamano, H., Hauri, C., Steinacher, M., Gruber, N. and Yamano, Y. : Ocean

608   acidification limits temperature-induced poleward expansion of coral habitats around Japan,

609   Biogeosciences, 9, 4955−4968, doi : 10.5194/bg-9-4955-2012, 2012.

610   Zeng, X., Chen, X., and Zhuang, J.: The positive relationship between ocean acidification and pollution,

611   Mar. Poll. Bull, 91, 14−21, 2015.

612   Wakita, M., Nagano, A., Fujiki, T., and Watanabe, S.: Slow acidification of the winter mixed layer in

613   the subarctic western North Pacific, J. Geophys. Res. Oceans, 122, 6923−6935,

614   doi:10.1002/2017JC013002, 2017.

615

616   Figure captions

617

618   Fig. 1 Coastal maps and monitoring sites in Japan. Red points in (a) indicate the fixed sites (n = 1481)

619   monitored by the Regional Development Bureau of the Ministry of Land, Infrastructure, Transport,

620   and Tourism, and the Ministry of the Environment (Japan) under the WCPL monitoring program. (b)

621   Monitoring sites that met the strictest criterion (n = 302).

622

623   Fig. 2 Distributions of the monthly number of data points (N) for (a) maximum and (b) minimum

624   temperatures collected in each prefecture from the 302 most reliable monitoring sites.

625

626   Fig. 3 Examples of (a) acidification (Kahoku Coast in Ishikawa) and (b) basification (Funakoshi Bay

627   in Iwate) trends at monitoring sites. Blue and red colors indicate the annual minimum and maximum

628   pH_{insitu} data and their trends, respectively.

629

630   Fig. 4 Correlations of water temperature and pH_{insitu} at adjacent monitoring sites in the same prefecture.

631   Thin lines denote significant correlations (r = 0.12, degrees of freedom = 283).

632

633   Fig. 5 Scatter plots of correlation coefficients for water temperature and pH_{insitu} at adjacent monitoring

634   sites in the same prefecture. Fig. 5a is for the highest temperature and the minimum pH_{insitu} data and

635   Fig. 5b for the lowest temperature and maximum pH$_{insitu}$ data, respectively.

636

637   Fig. 6 Examples of time-series for annual minimum and maximum pH$_{insitu}$ data at adjacent monitoring

638   sites close to the boundaries between (a) Osaka and Hyogo and (b) Kagawa and Ehime. Lines of the

639   same color indicate data collected at the same site. Thin and bold lines indicate the annual minimum

640   and maximum pH$_{insitu}$ data, respectively, at each monitoring sites. Site locations are included to the

641   right of each panel, with the text color corresponding to the colors in each panel.

642

643   Fig. 7 Histogram of pH trends, represented by ΔpH$_{insitu}$, showing the slopes of the linear regression

644   lines for the annual minimum (left) and maximum (right) pH$_{insitu}$ data at each monitoring site. The

645   histograms in (a, b), (c, d), and (e, f) show three scenarios: (a, b) all 1481 available sites with

646   continuous records before quality control, (c, d) 1127 sites without outliers, and (e, f) 289 sites that

647   meet the strictest criterion.

648

649   Fig. 8 Distributions of long-term trends in pH$_{insitu}$ (ΔpH$_{insitu}$/yr) in Japanese coastal sea waters. The

650   colors indicate the ranges of acidification (a, c) and basification (b, d). (a, b) and (c, d) are linked to

651   the data used in Figs. 7e and 7f, respectively.

652

653   Fig. 9 (a−b, d−e, g−h, j−k) Average minimum and maximum pH$_{insitu}$ trends (ΔpH$_{insitu}$/yr) in each

654   prefecture. These figures show each side of the Pacific (a−b), the Seto Inland Sea (d−e), the East

655   China Sea (g−h), and the Japan Sea (j−k). The prefecture names are arranged vertically from eastern

656   (northern) to western (southern) areas. Black shading indicate one standard deviation from the

657   average. (c, f, i, l) Number of monitoring sites in each prefecture and the thin dashed line is the

658   threshold value of 17 (i.e., the average number of monitoring sites in all prefectures). The prefectures

659   that meet the threshold are indicated in purple. The figure is based on the results shown in Figs. 7 (e,

660   f) and 8.

661

662 Fig. 10 Same as Fig. 7, but showing the pH_{25} trends at 289 sites (selected by quality control step 3).

663   The value of pH_{25} was estimated using the method of Lui and Chen (2017).

664

665 Fig. 11 (a−b, d−e, g−h, j−k) Same as Fig. 9, but showing the average estimated minimum and

666   maximum pH_{25} trends (ΔpH_{25}/yr) for each prefecture. Red lines and points indicate the average

667   minimum and maximum pH_{insitu} trends shown in Fig. 9.

668

669 Fig. 12 Average highest and lowest temperatures observed for the minimum and maximum pH_{insitu} data

670   for each prefecture. The blue and red lines and shading indicate the average and one standard

671   deviation from the average, respectively. The prefectures that met the threshold of 17 are shown in

672   purple, as in Figs. 9 (c-l) and 11 (c-l).

673

Fig. 13 Same as Fig. 7, but showing the highest and lowest temperature trends at 289 sites (selected by quality control step 3).

Fig. 14 Correlation between trends in total nitrogen (TN) and trends in (a) minimum and (b) maximum pH_{insitu}. The correlation coefficients are -0.30 and -0.29 for the minimum and maximum pH_{insitu}, respectively (significance level of 0.05, r = 0.128; degrees of freedom = 236).

Table 1 Number of samples (N) collected at each of the 1481 monitoring sites each year.

Table 2 Average mutual correlation coefficients among water temperature and pH_{insitu} measurements at adjacent monitoring sites in the same prefecture. The averages were calculated from the data for the highest and lowest temperature, and minimum and maximum pH_{insitu} within 15 km for the three criteria. We refined the sites using three quality control steps, yielding 1481 (step 1), 1127 (step 2), and 302 (step 3) sites. Two right columns represent a significant level of 5% and a degree of freedom for the correlation coefficients of each quality check procedure.

Table 3 Average correlation coefficients between minimum and maximum pH_{insitu} trends and total inorganic nitrogen (TN) ones, respectively. We evaluated this for the data after each quality check

692   procedure. Degrees of freedom in step 1 and 2 are same values, because TN data are not necessarily

693   measured at the whole of pH_{insitu} monitoring sites. The sampling number of monitoring sites at step 1

694   and 2 were therefore the same number. Significant levels of 5% and degrees of freedom are also

695   represented.

Fig. 1 Coastal maps and monitoring sites in Japan. Red points in (a) indicate the fixed sites (n = 1481) monitored by the Regional Development Bureau of the Ministry of Land, Infrastructure, Transport, and Tourism, and the Ministry of the Environment (Japan) under the WCPL monitoring program. (b) Monitoring sites that met the strictest criterion (n = 302).
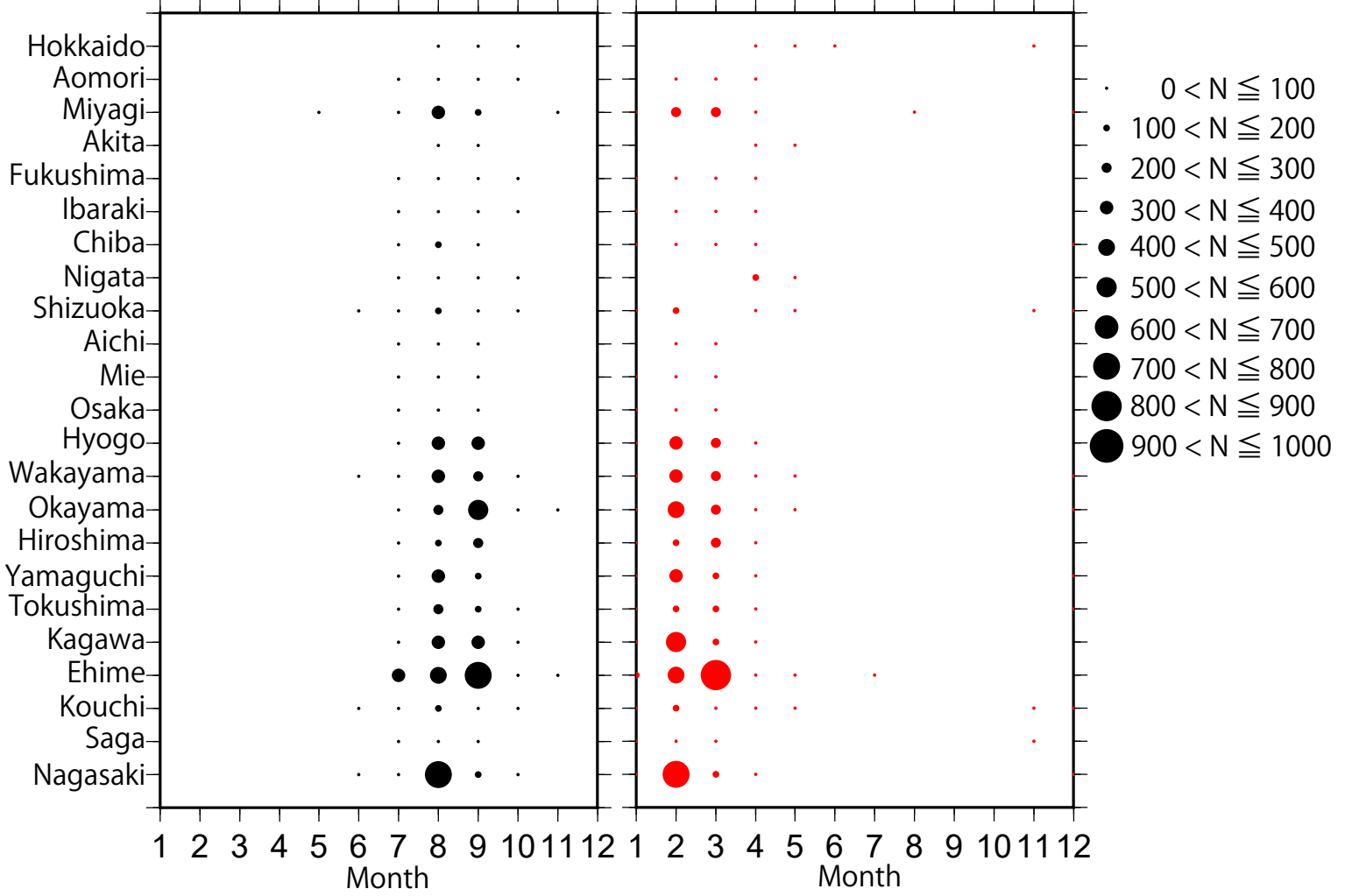
Fig. 2 Distributions of the monthly number of data points (N) for (a) maximum and (b) minimum temperatures collected in each prefecture from the 302 most reliable monitoring sites.
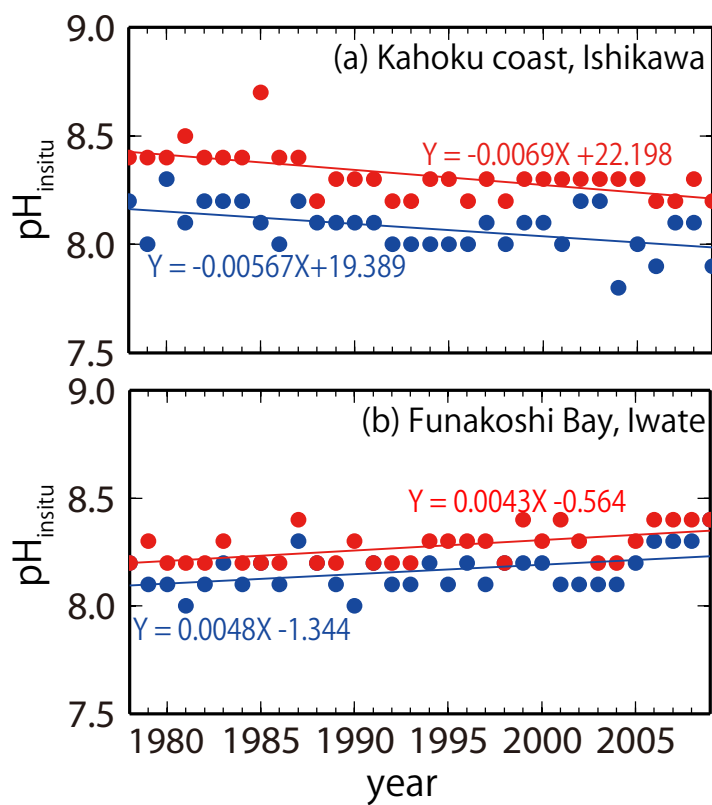
Fig. 3 Examples of (a) acidification (Kahoku Coast in Ishikawa) and (b) basification (Funakoshi Bay in Iwate) trends at monitoring sites. Blue and red colors indicate the annual minimum and maximum pH$_{insitu}$ data and their trends, respectively.
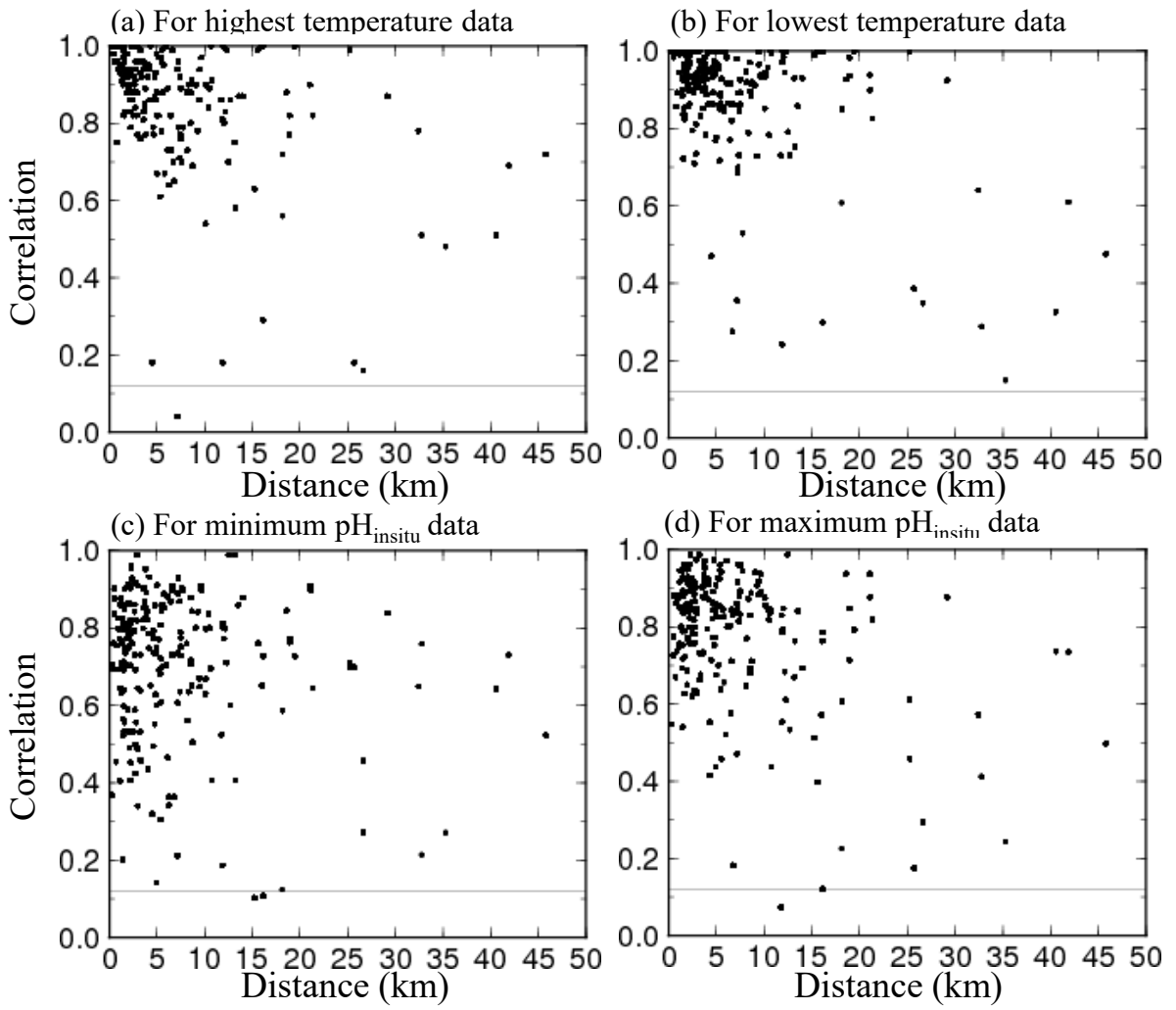
Fig. 4 Correlations of water temperature and pH$_{insitu}$ at adjacent monitoring sites in the same prefecture. Thin lines denote significant correlations (r = 0.12, degrees of freedom = 283).
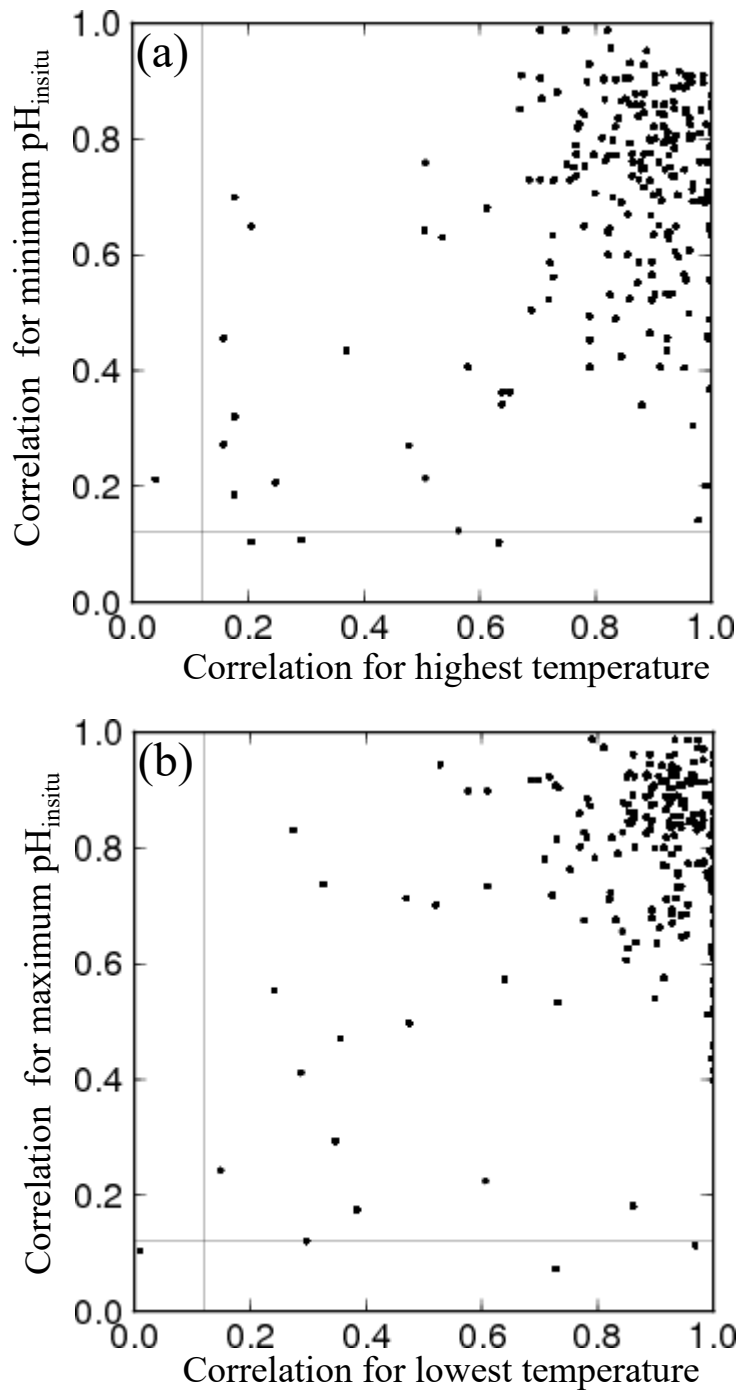
Fig. 5 Scatter plots of correlation coefficients for water temperature and pH$_{insitu}$ at adjacent monitoring sites in the same prefecture. Fig. 5a is for the highest temperature and the minimum pH$_{inisitu}$ data and Fig. 5b for the lowest temperature and the maximum pH$_{insitu}$ data, respectively.
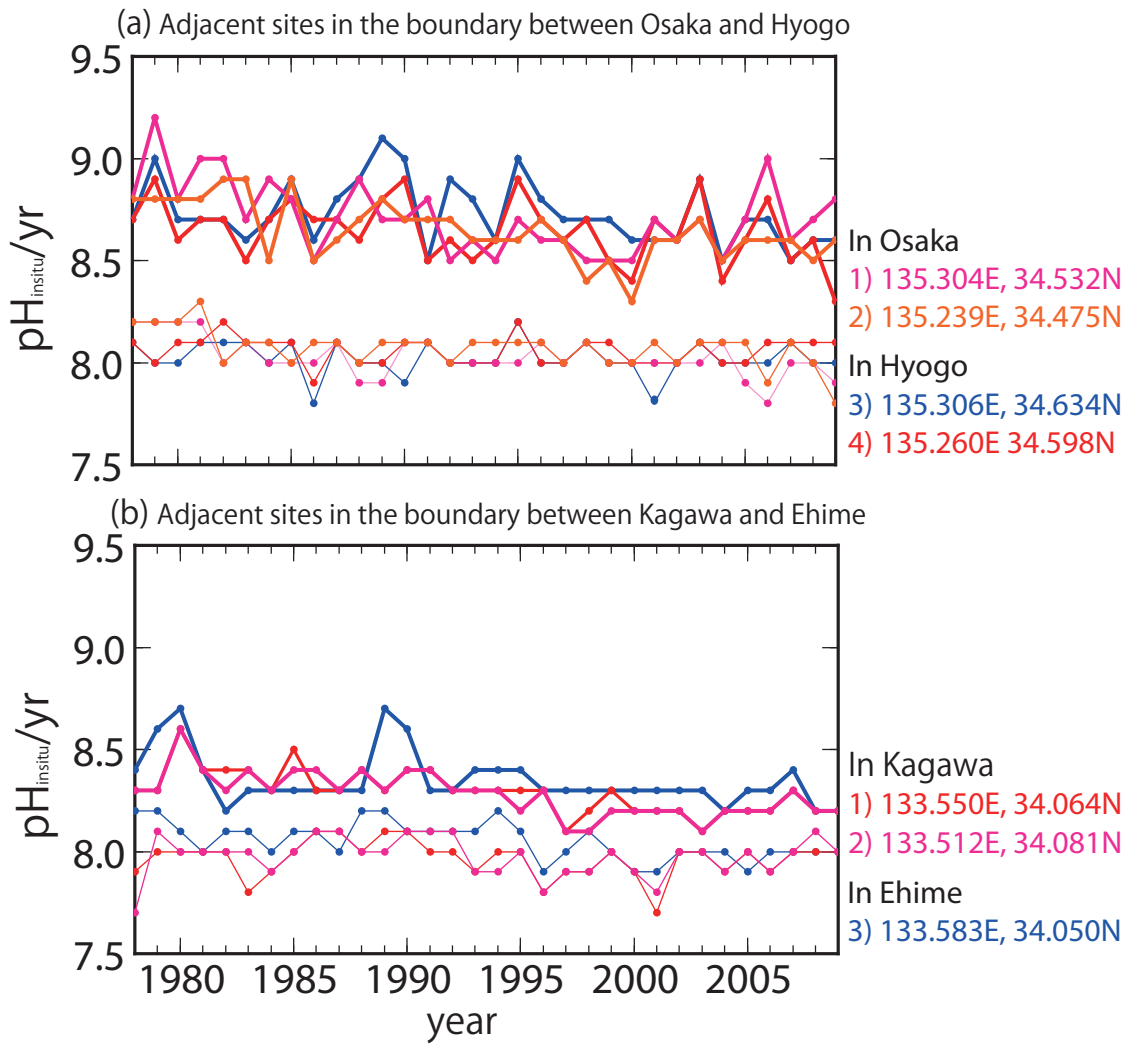
Fig. 6 Examples of time-series for annual minimum and maximum pH_{insitu} data at adjacent monitoring sites close to the boundaries between (a) Osaka and Hyogo and (b) Kagawa and Ehime. Lines of the same color indicate data collected at the same site. Thin and bold lines indicate the annual minimum and maximum pH_{insitu} data, respectively, at each monitoring stations. Site locations are included to the right of each panel, with the text color corresponding to the colors in each panel.
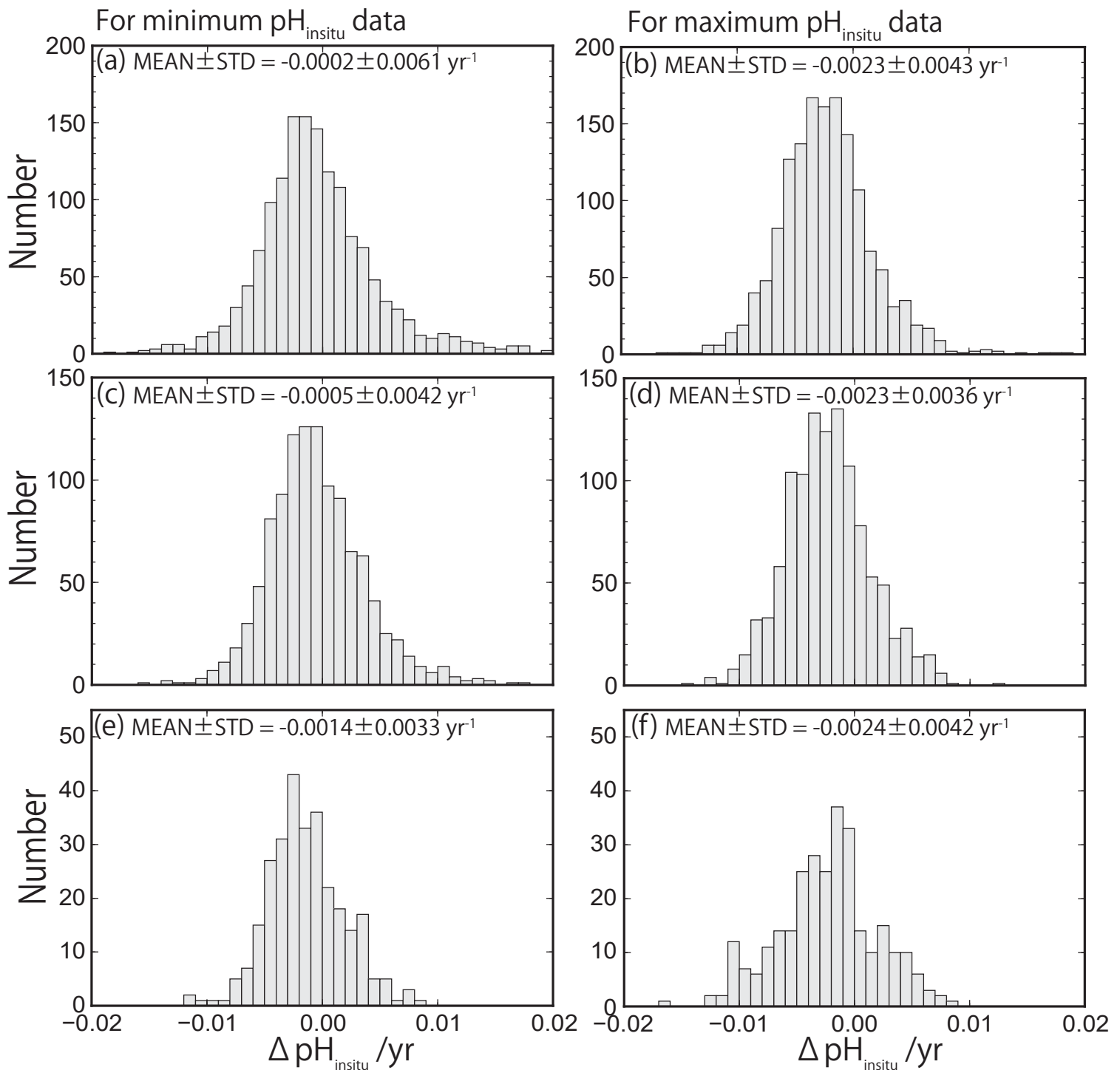
Fig. 7 Histogram of pH trends, represented by ΔpH_{insitu}, showing the slopes of the linear regression lines for the annual minimum (left) and maximum (right) pH_{insitu} data at each monitoring site. The histograms in (a, b), (c, d), and (e, f) show three scenarios: (a, b) all 1481 available sites with continuous records before quality control, (c, d) 1127 sites without outliers, and (e, f) 289 sites that meet the strictest criterion.
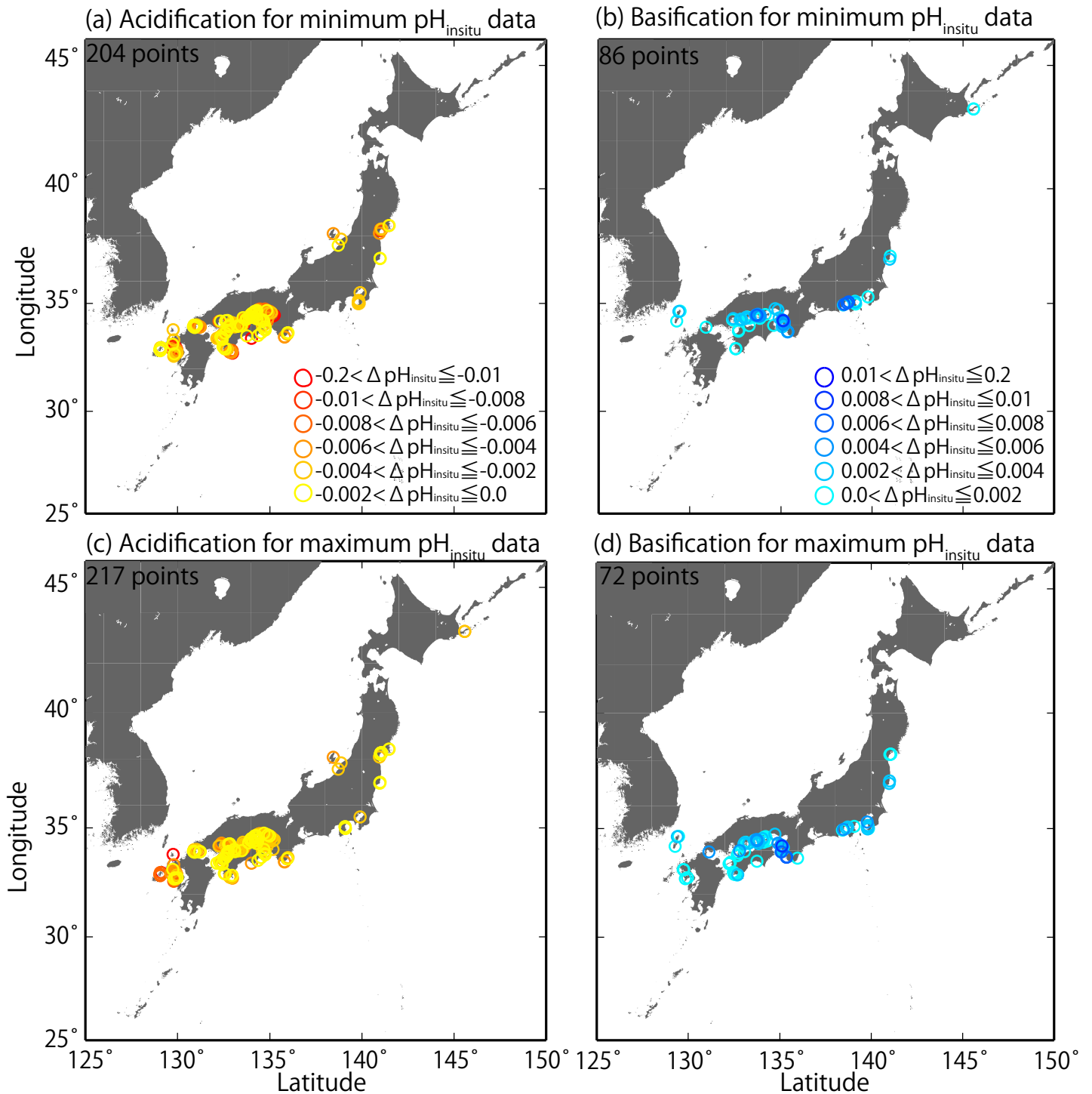
Fig. 8 Distributions of long-term trends in pH_{insitu} (ΔpH_{insitu}/yr) in Japanese coastal sea waters. The colors indicate the ranges of acidification (a, c) and basification (b, d). (a, b) and (c, d) are linked to the data used in Figs. 7e and 7f, respectively.
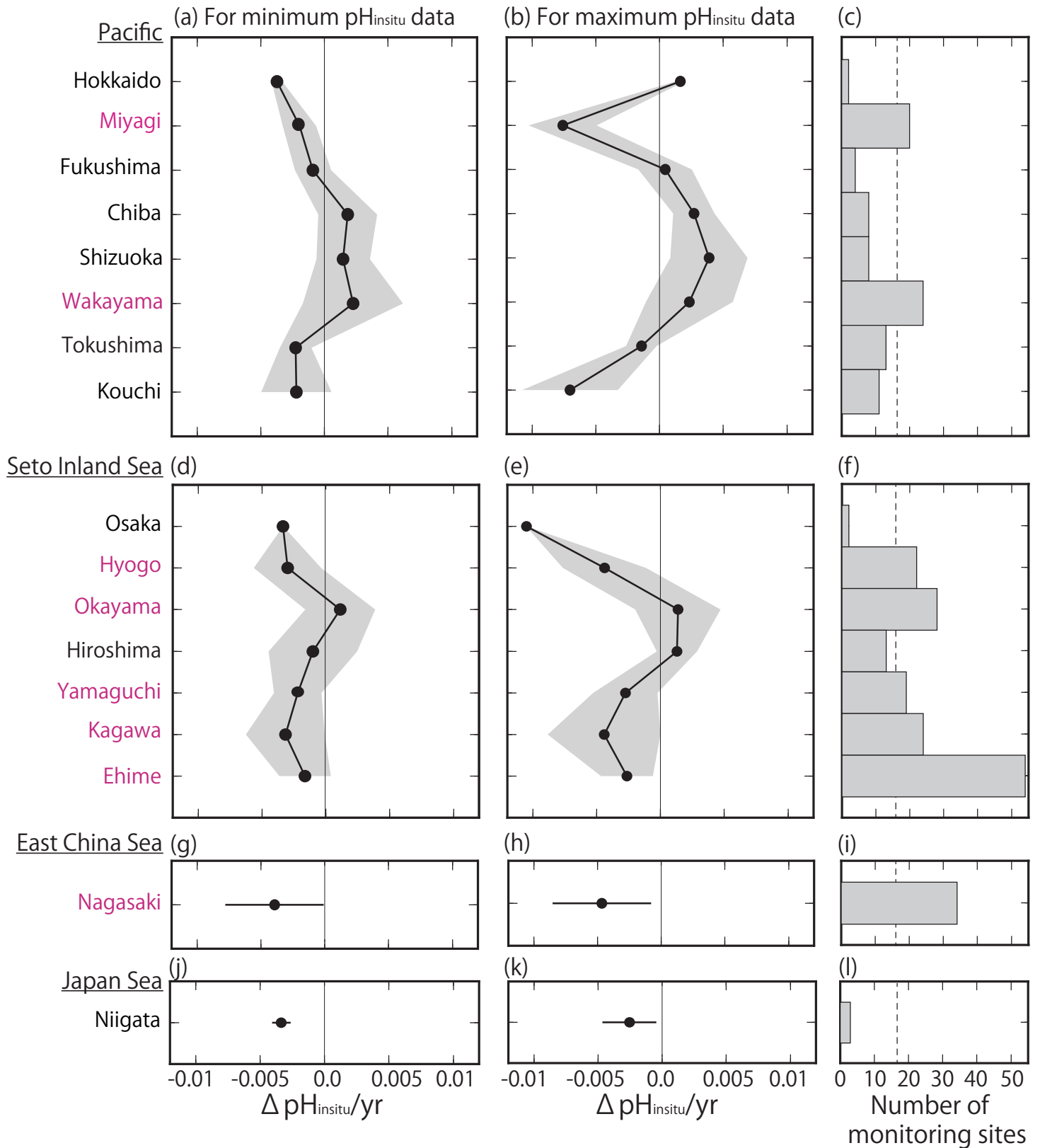
Fig. 9 (a−b, d−e, g−h, j−k) Average minimum and maximum pH$_{insitu}$ trends (ΔpH$_{insitu}$/yr) in each prefecture. These figures show each side of the Pacific (a−b), the Seto Inland Sea (d−e), the East China Sea (g−h), and the Japan Sea (j−k). The prefecture names are arranged vertically from eastern (northern) to western (southern) areas. Black shading indicate one standard deviation from the average. (c, f, i, l) Number of monitoring sites in each prefecture and the thin dashed line is the threshold value of 17 (i.e., the average number of monitoring sites in all prefectures). The prefectures that meet the threshold are indicated in purple. The figure is based on the results shown in Figs. 7 (e, f) and 8.
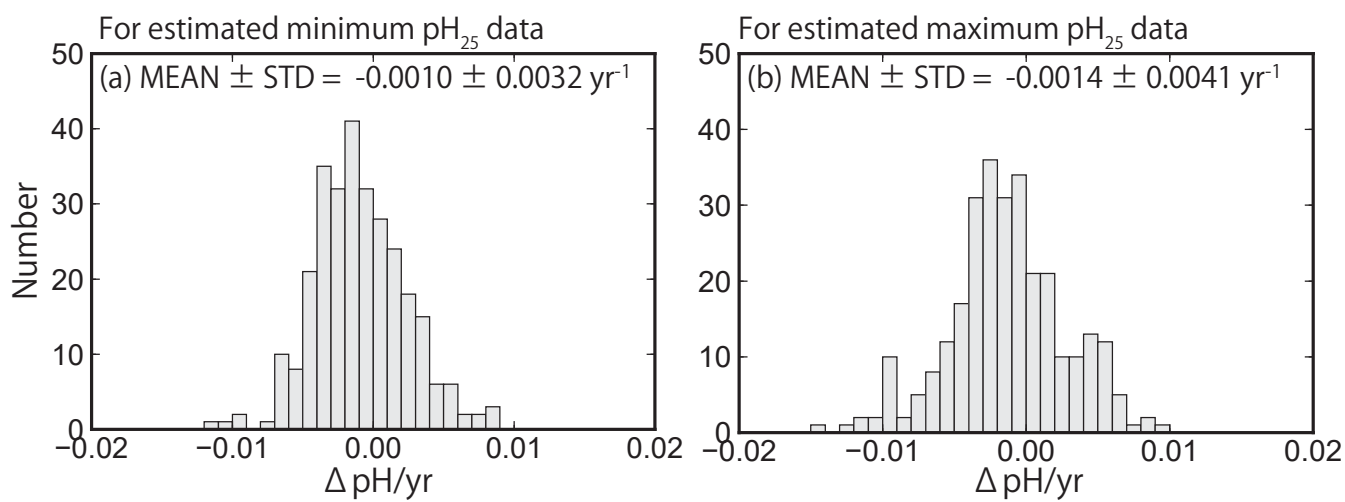
Fig. 10 Same as Fig. 7, but showing the pH$_{25}$ trends at 289 sites (selected by quality control step 3). The value of pH$_{25}$ was estimated using the method of Lui and Chen (2017).
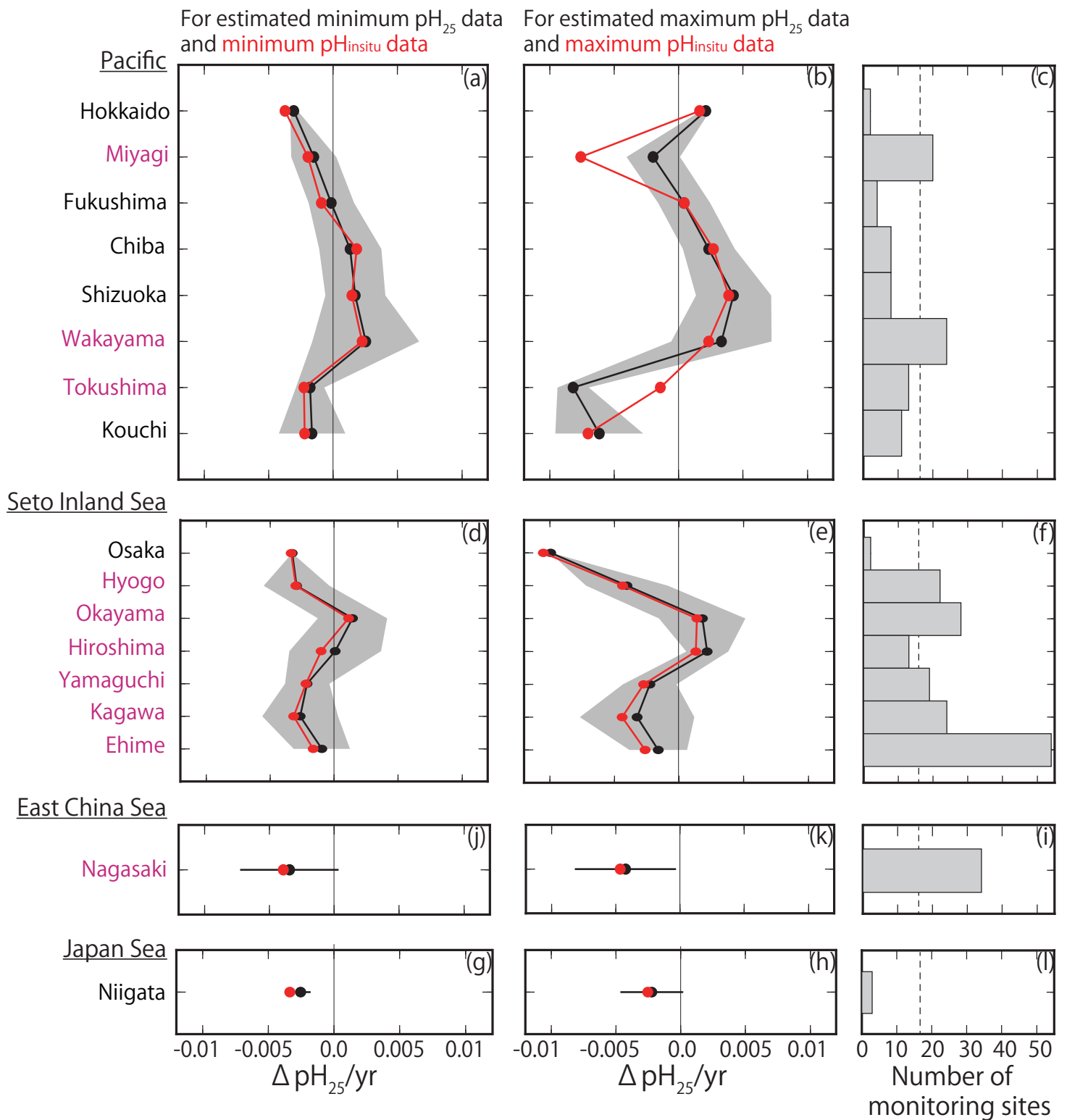
Fig. 11 (a−b, d−e, g−h, j−k) Same as Fig. 9, but showing the average estimated minimum and maximum pH$_{25}$ trends (ΔpH$_{25}$/yr) for each prefecture. Red lines and points indicate the average minimum and maximum pH$_{insitu}$ trends shown in Fig. 9.
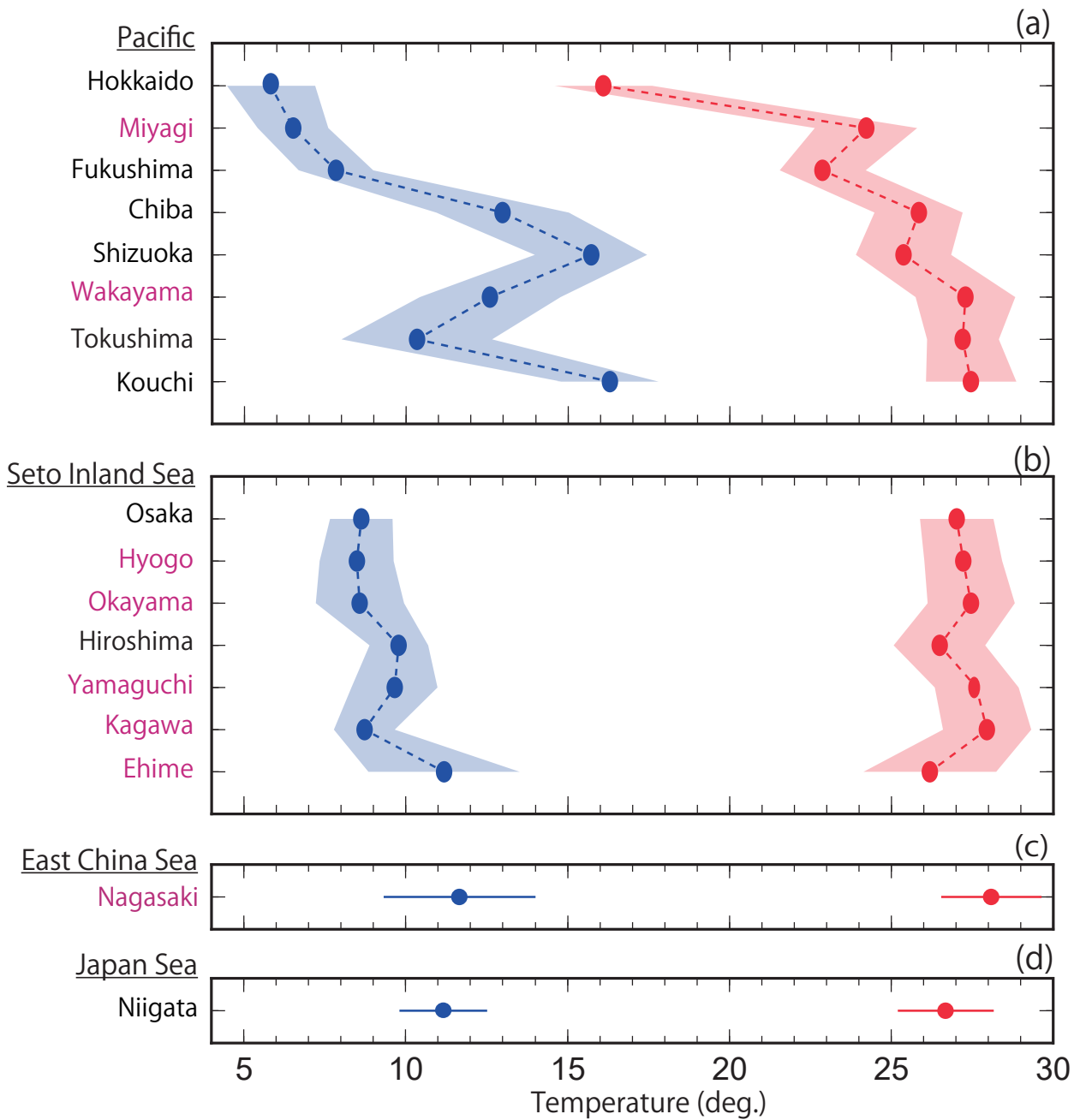
Fig. 12 Average highest and lowest temperatures observed for the minimum and maximum pH$_{insitu}$ data for each prefecture. The blue and red lines and shading indicate the average and one standard deviation from the average, respectively. The prefectures that met the threshold of 17 are shown in purple, as in Figs. 9 (c-l) and 11 (c-l).
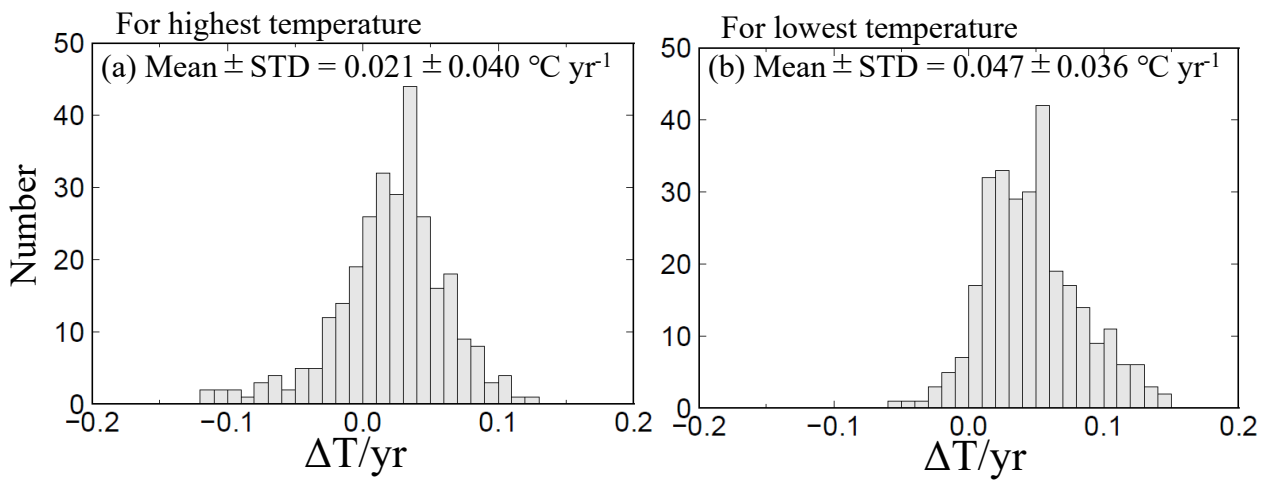
Fig. 13 Same as Fig. 7, but showing the highest and lowest temperature trends at 289 sites (selected by quality control step 3).
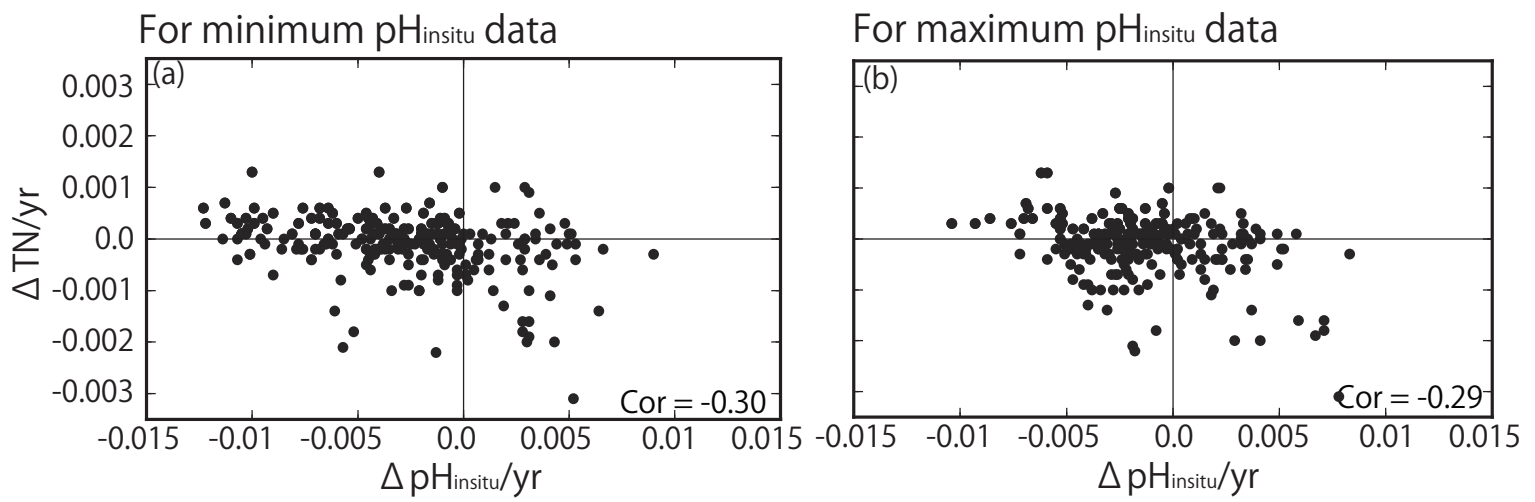
Fig. 14 Correlation between trends in total nitrogen (TN) and trends in (a) minimum and (b) maximum pH$_{insitu}$. The correlation coefficients are −0.30 and −0.29 for the minimum and maximum pH$_{insitu}$, respectively (significance level of 0.05, r = 0.128; degrees of freedom = 236).

Table 1 Number of samples (N) collected at each of the 1481 monitoring sites each year.

Year	$0 \leqq N < 4$	$4 \leqq N < 8$	$8 \leqq N < 12$	$12 \leqq N < 16$	$16 \leqq N < 20$	$20 \leqq N < 24$	$24 \leqq N < 28$	$28 \leqq N < 32$	$32 \leqq N < 40$
1978	43	391	83	303	87	15	176	9	4
1979	31	372	73	328	101	19	150	11	7
1980	32	363	88	324	101	15	192	12	5
1981	24	347	72	361	99	13	199	11	3
1982	25	350	74	364	93	9	206	11	4
1983	32	355	75	356	91	11	222	12	0
1984	28	362	74	355	96	10	211	11	3
1985	24	354	86	377	96	9	192	11	8
1986	25	361	81	334	98	8	235	11	9
1987	26	357	78	341	98	4	239	11	1
1988	25	366	74	356	82	6	236	11	2
1989	26	365	83	344	84	5	238	17	3
1990	24	377	76	347	83	1	238	14	5
1991	24	367	80	355	93	5	226	13	5
1992	24	367	79	352	95	1	230	16	0
1993	17	374	76	357	94	8	225	14	0
1994	17	376	85	347	102	24	208	14	3
1995	29	376	109	311	104	3	227	12	0
1996	19	419	80	307	104	4	226	14	1
1997	20	396	82	315	115	5	225	13	0
1998	16	389	103	325	99	0	225	12	0
1999	17	396	68	381	67	2	224	12	7
2000	17	389	82	376	72	1	231	6	2
2001	17	392	90	382	50	8	220	6	1
2002	17	368	102	392	49	1	229	7	0
2003	17	365	93	402	51	1	233	6	1
2004	17	370	84	400	50	1	240	5	2
2005	16	354	152	356	46	9	228	3	0
2006	16	370	134	345	50	0	244	5	3
2007	17	399	128	353	62	0	202	5	3
2008	17	402	128	350	64	0	211	5	1
2009	17	403	143	340	58	0	217	5	8

Table 2 Average mutual correlation coefficients among water temperature and pH_{insitu} measurements at adjacent monitoring sites in the same prefecture. The averages were calculated from the data for the highest and lowest temperature, and minimum and maximum pH_{insitu} within 15 km for the three criteria. We refined the sites using three quality control steps, yielding 1481 (step 1), 1127 (step 2), and 302 (step 3) sites. Two right columns represent a significant level of 5% and a degree of freedom for the correlation coefficients of each quality check procedure.

Quality check procedue	highest temperature data	lowest temperature data	minimum pH_{insitu} data	maximum pH_{insitu} data	Significance level of 5%	Degree of freedom
1	0.79	0.78	0.51	0.64	0.10	386
2	0.80	0.79	0.54	0.69	0.15	170
3	0.85	0.87	0.62	0.72	0.25	59

Table 3 Average correlation coefficients between minimum and maximum pH_{insitu} trends and total inorganic nitrogen (TN) ones, respectively. We evaluated this for the data after each quality check procedure. Degrees of freedom in step 1 and 2 are same values, because TN data are not necessarily measured at the whole of pH_{insitu} monitoring sites. The sampling number of monitoring sites at step 1 and 2 were therefore the same number. Significant levels of 5% and degrees of freedom are also represented.

Quality check procedue	Correlation between minimum Δ pHinsitu and ΔTN	Correlation between maximum Δ pHinsitu and ΔTN	Significant level of 5%	Degree of freedom
1	-0.02	-0.29	0.08	622
2	-0.02	-0.29	0.08	622
3	-0.33	-0.35	0.14	215