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.

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 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 $pH_{insitu}$ 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 $pH_{insitu}$ trends, and then check ocean acidification effect (DIC (AirCO2)) for the populations of $pH_{25}$ 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.

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

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## Abstract

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

43 rate of ocean acidification can be identified from changes in pH and other variables in the open ocean
44 (Gonzalez-Davila et al. 2007; Dore et al. 2009; Bates 2007; Bates et al. 2014; Midorikawa et al. 2010;
45 Olafsson et al. 2009; Wakita et al. 2017). Analysis of pH data measured in situ at the European Station
46 in the Canary Islands (ESTOC) in the North Atlantic from 1995 to 2003 and normalized to 25 deg. C
47 showed that $pH_{25}$ decreased at a rate of 0.0017 ± 0.0005 $yr^{-1}$ (Gonzalez-Davila et al. 2007). Similarly,
48 analysis of the Hawaii Ocean Time-series (HOT) (Dore et al. 2009) and the Bermuda Atlantic Time
49 Series (BATS) (Bates 2007) showed that pH at ambient (in-situ) sea surface temperature ($pH_{insitu}$)
50 decreased by 0.0019±0.0002 and 0.0017±0.0001 $yr^{-1}$ from 1988 to 2007 and from 1983 to 2005,
51 respectively. Analysis of data collected along the hydrographic observation line at 137°E in the western
52 North Pacific by the Japanese Meteorological Agency (JMA) showed that $pH_{25}$ decreased by
53 0.0013±0.0005 $yr^{-1}$ in summer and 0.0018±0.0002 $yr^{-1}$ in winter from 1983 to 2007 (Midorikawa et
54 al. 2010). The winter $pH_{insitu}$ in surface water in the Nordic Seas decreased at a rate of 0.0024±0.0002
55 $yr^{-1}$ from 1985 to 2008 (Olafsson et al. 2009). This rate was somewhat more rapid than the average
56 annual rates calculated for the other subtropical time-series stations in the Atlantic Ocean, BATS, and
57 ESTOC, and was attributed to the air–sea $CO_2$ flux and buffering capacity (higher Revell factor)
58 (Olafsson et al. 2009), which were higher and lower than those in subtropical regions, respectively.
59 Wakita et al. (2017) estimated that the annual and winter $pH_{insitu}$ at station K2 in the subarctic western
60 North Pacific decreased at rates of 0.0025 and 0.0008 $yr^{-1}$, respectively, from 1999 to 2015. The lower
61 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

protocols.

Monitoring operations are occupied at 1481 sites along the Japan coast shown in Figure 1a. Most stations locate coastal area while <10 % of the station locates estuary. In each monitoring sites, basic surveys were held 4 to 40 times a year dependent to the site. Information on the sampling frequency at the monitoring sites is presented in Table 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 the bottom depth was more than this) four 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.

Measurements of pH for each water sample were made following the Japanese Industrial Standard protocol JIS Z 8802 (2011), which is equivalent to ISO10523 (https://www.iso.org/standard/51994.html). Namely, pH was measured by glass electrode calibrated by NBS standard buffers. Basically, pH measurement was carried out just after the water sampling at in-situ water temperature. Permitted repeatability in each measurement was ±0.07. NIES gathered all pH data measured at each site and calculated annual minimum and maximum pH, providing them through their website.

The published WPCL pH dataset only contains these annual minimum and maximum pH data in each year, reported on the NBS pH scale ($pH_{insitu}$) and rounded to one decimal place. Water temperature data are also available for each sampling event (http://www.nies.go.jp/igreen/md_down.html).

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 ($H_2O \leftrightarrow H^+ + OH^-$); the pH values were lowest in summer and highest in winter, in both the open ocean (e.g. Bates et al. 2014) and coastal sea waters (e.g., Frankignoulle and Bouquegneau 1990; Byrne et al. 2013; Hagens et al. 2015; Challener at al. 2016). We therefore assumed that the minimum and maximum pH data coincided with the highest and lowest temperatures, respectively (Fig. 2), and we used these data to calculate $pH_{25}$ in Section 4.2. NIES do not discriminate surface (0.5m – 2m) and subsurface (10 m) data when they calculate annual maximum and minimum pH, so it is speculated that annual maximum pH substantially represents winter pH of surface waters, while annual minimum pH represents summer pH of subsurface waters.

The monitoring operations were carried out by licensed operators as outlined in the annual plan of the Regional Development Bureau of each prefecture. These specific licensed operators were retained for the duration of the measurement period, which means that the same laboratories were always in charge of collecting the data. This approach helps to prevent systematic errors that might arise both between measurement facilities and over time, and ensures the datasets are accurate.

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

We selected all the data for fixed sites in coastal sea waters that had continuous time-series from 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 ($\sigma_\beta$)
272 is estimated by the following equation (e.g., Luenberger 1969):

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

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 $\sigma_\beta$ 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 ($\sigma_\beta$) 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.

For our null hypothesis, we assumed that the population of the trends with an average of −0.0014 $yr^{-1}$ (−0.0024 $yr^{-1}$) and a standard deviation of 0.0033 $yr^{-1}$ (0.0042 $yr^{-1}$) was sampled from a population with an average trend of 0.0000 $yr^{-1}$ and a standard deviation of 0.0020 $yr^{-1}$. When the sample size was 289, the *t*-values and the degrees of freedom were 8.7 (6.2) and 412.2 (474.4), respectively. Since the *p* value was less than 0.001, the null hypothesis was rejected. Welch's t test confirmed that the average trends for both the minimum and maximum $pH_{insitu}$ data were negative.

We also applied a paired t-test for the two trends calculated from the averaged minimum and maximum $pH_{insitu}$ data, to verify whether two trends are significantly different. The population mean and the sample size were 0.0 and 289, respectively. Since the *t*-value was calculated to be 4.64 (the degrees of freedom = 288), the null hypothesis was rejected. The paired t-test suggested that the two trends calculated from the averaged minimum and maximum $pH_{insitu}$ data are significantly different.

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

To facilitate our discussion of the factors that influenced the $pH_{insitu}$ trends, we used the conceptual models of acidification and basification in coastal sea waters of Sunda and Cai (2012) and Duarte et al. (2013), as follows:

$$PH_{insitu} = \text{Function (D (T), DIC (Air } CO_2\text{, B (T, N)), Alk(S))} \quad (2)$$

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

To evaluate the direct thermal effects related to process D (T) in equation 2, we estimated the pH values normalized to 25 deg. C ($pH_{25}$), assuming that the minimum (maximum) $pH_{insitu}$ and highest (lowest) temperature and other parameters were measured at the same time. By assuming the other parameters that affected the pH calculation in the CO2sys (Lewis and Wallace 1998, csys.m), such as salinity, DIC, and alkalinity, did not change (these parameters are not measured as part of the WPCL program), we used the method of Lui and Chen (2017) to calculate the $pH_{25}$, as follows:

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

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

The distributions of the trends in $pH_{25}$ after applying equation 3 are shown in Fig. 10. The minimum and maximum $pH_{25}$ data were normally distributed, meaning that the distributions of the $pH_{insitu}$ trends were maintained after applying equation 3 (Fig. 7e, f). The averages (± standard deviations) of the minimum and maximum $pH_{25}$ trends were −0.0010±0.0032 and −0.0014±0.0041 $yr^{-1}$, respectively. The averaged trends are consistent with those reported by Midorikawa et al. (2010), who calculated that $pH_{25}$ decreased at rates of -0.0013±0.0005 $yr^{-1}$ and -0.0018±0.0002 $yr^{-1}$ in summer and winter from 1983 to 2007 along the 137°E line of longitude in the north Pacific. The asymmetry of the $pH_{25}$ trends between minimum and maximum estimates would be related to the seasonal variations of $pCO_2$ and the associated asymmetric response of air-sea $CO_2$ flux (Landschutzer et al. 2018; Fassbender et al. 2018).

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 $0.021\pm0.040$ and $0.047\pm0.036$ 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

393 ### 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

et al. 2014). The rates at which marine organisms photosynthesize and respire in ocean waters decrease and increase, respectively, in water polluted with heavy metals and oils (process DIC in equation 2) because of biotoxicity and eutrophication, thereby resulting in acidification (Hing et al. 2011; Huang et al. 2011; Gilde and Pinckney 2012).

## 5. Conclusions

We estimated the long-term trends in $pH_{insitu}$ in Japanese coastal sea waters and examined how the trends varied regionally. The long-term $pH_{insitu}$ data show highly variable trends, although ocean acidification has generally intensified in Japanese coastal sea waters. We found that the annual $pH_{insitu}$ minimum (in summer) and $pH_{insitu}$ maximum (in winter) decreased at overall rates of −0.0014 and −0.0024 $yr^{-1}$, respectively, in Japanese coastal sea waters. The averages of the minimum and maximum $pH_{25}$ trends were −0.0010 and −0.0014 $yr^{-1}$, respectively. The differences between the $pH_{insitu}$ and the corresponding $pH_{25}$ trends in summer (-0.0004 $yr^{-1}$) and winter (−0.0010 $yr^{-1}$) can be partly explained by the thermal effects. The negative shifts of the $pH_{25}$ trend distributions suggest a signal of ocean acidification in Japanese coastal sea water.

There were striking spatial variations in the $pH_{insitu}$ trends. Correlations among the $pH_{insitu}$ time series at different sites revealed that the high variability in the $pH_{insitu}$ trends was not caused by analytical errors in the data but reflected the large spatial variability in the physical and chemical characteristics of coastal environments, such as water temperature, nutrient loadings, and autotropic/heterotrophic

conditions. While there was a general tendency towards coastal acidification, there were positive trends in $pH_{insitu}$ at 25%–30% of the monitoring sites, indicating basification, which suggests that the coastal environment might not be completely devastated by acidification. If we can manage the coastal environment effectively (e.g., control nutrient loadings and autotropic/heterotrophic conditions), we might be able to limit, or even reverse, acidification in coastal areas.

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615

## Figure captions

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 ($\boldsymbol{r}$ = 0.12, degrees of freedom = 283).

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673

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676

677 Fig. 14 Correlation between trends in total nitrogen (TN) and trends in (a) minimum and (b) maximum
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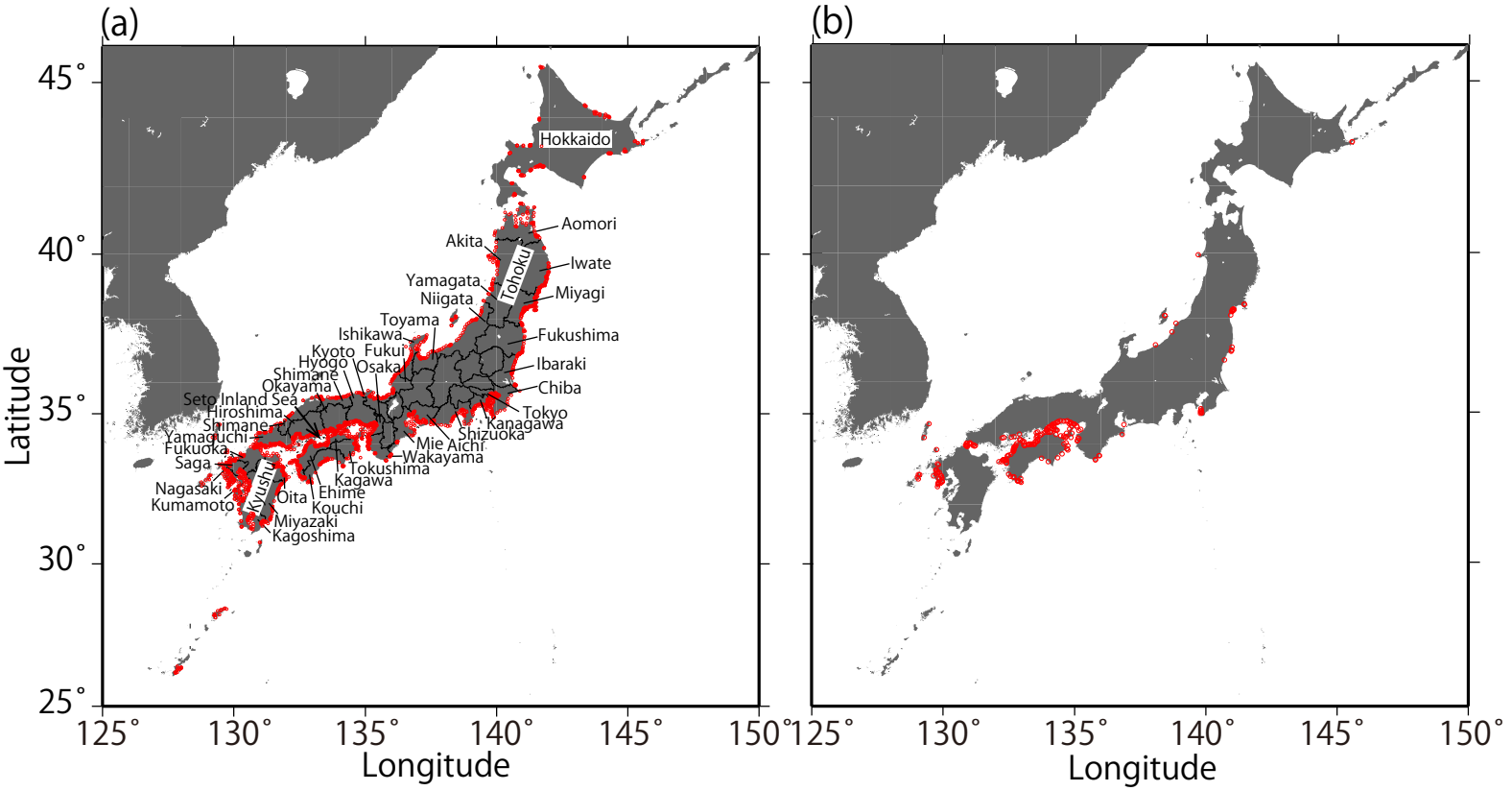


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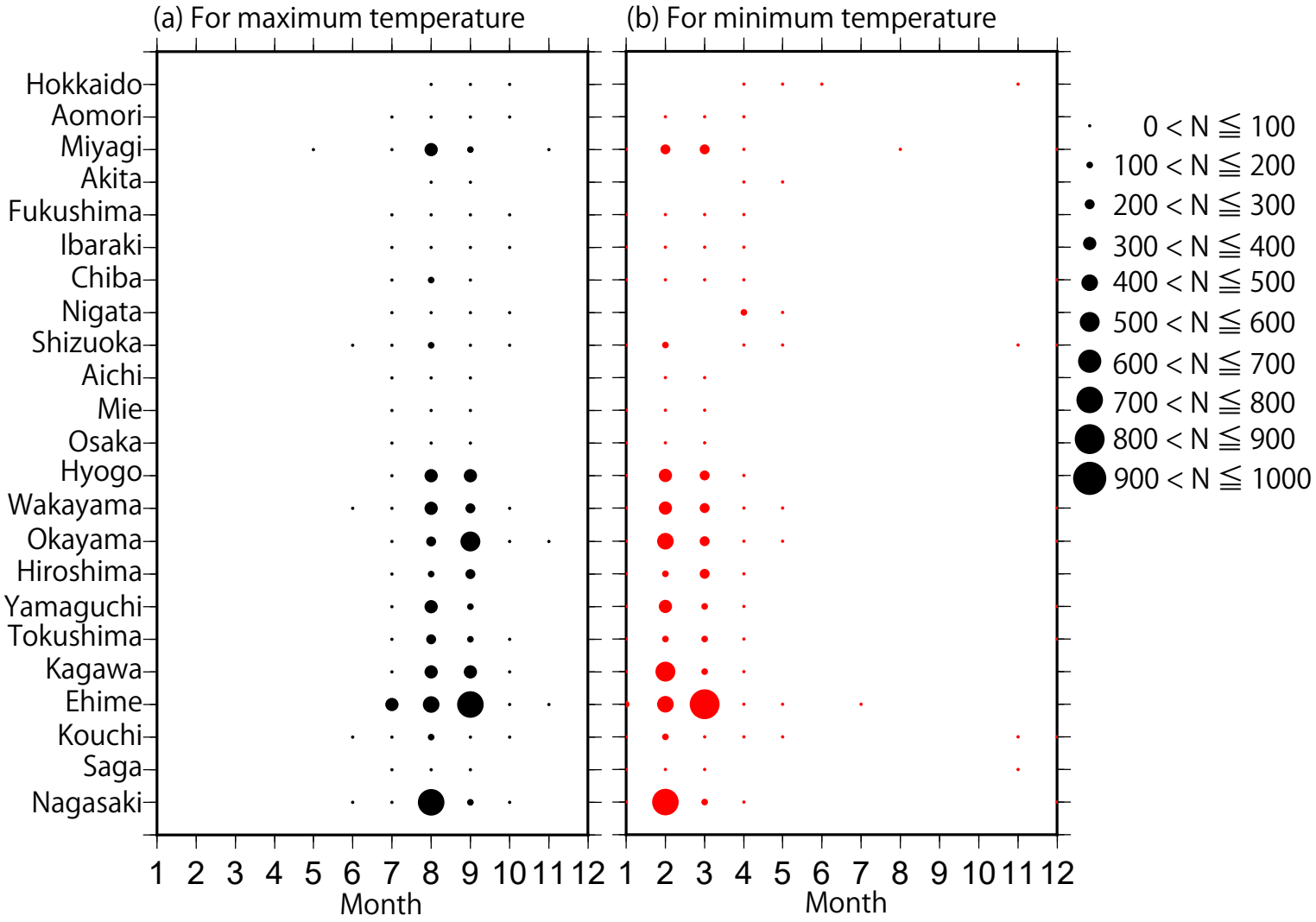


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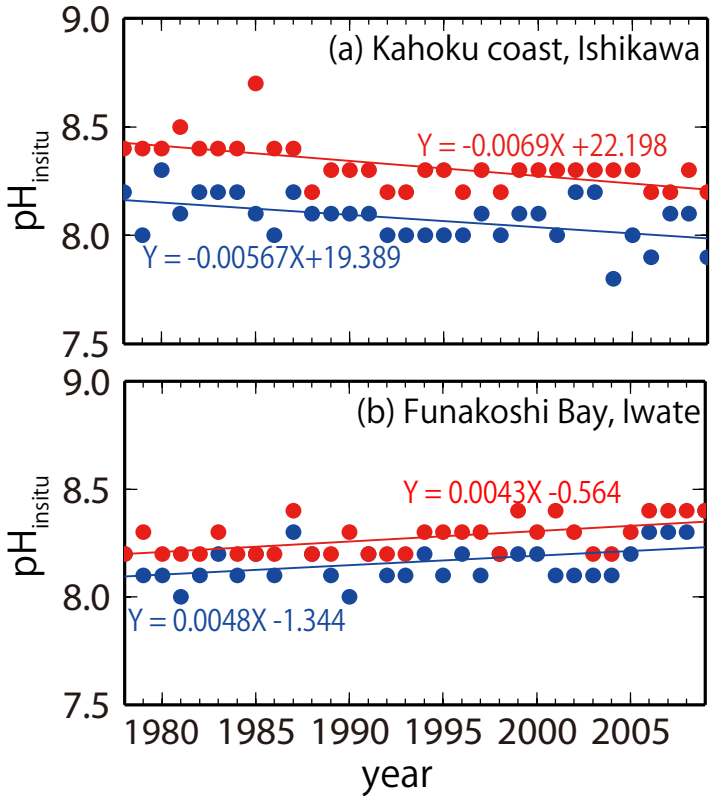


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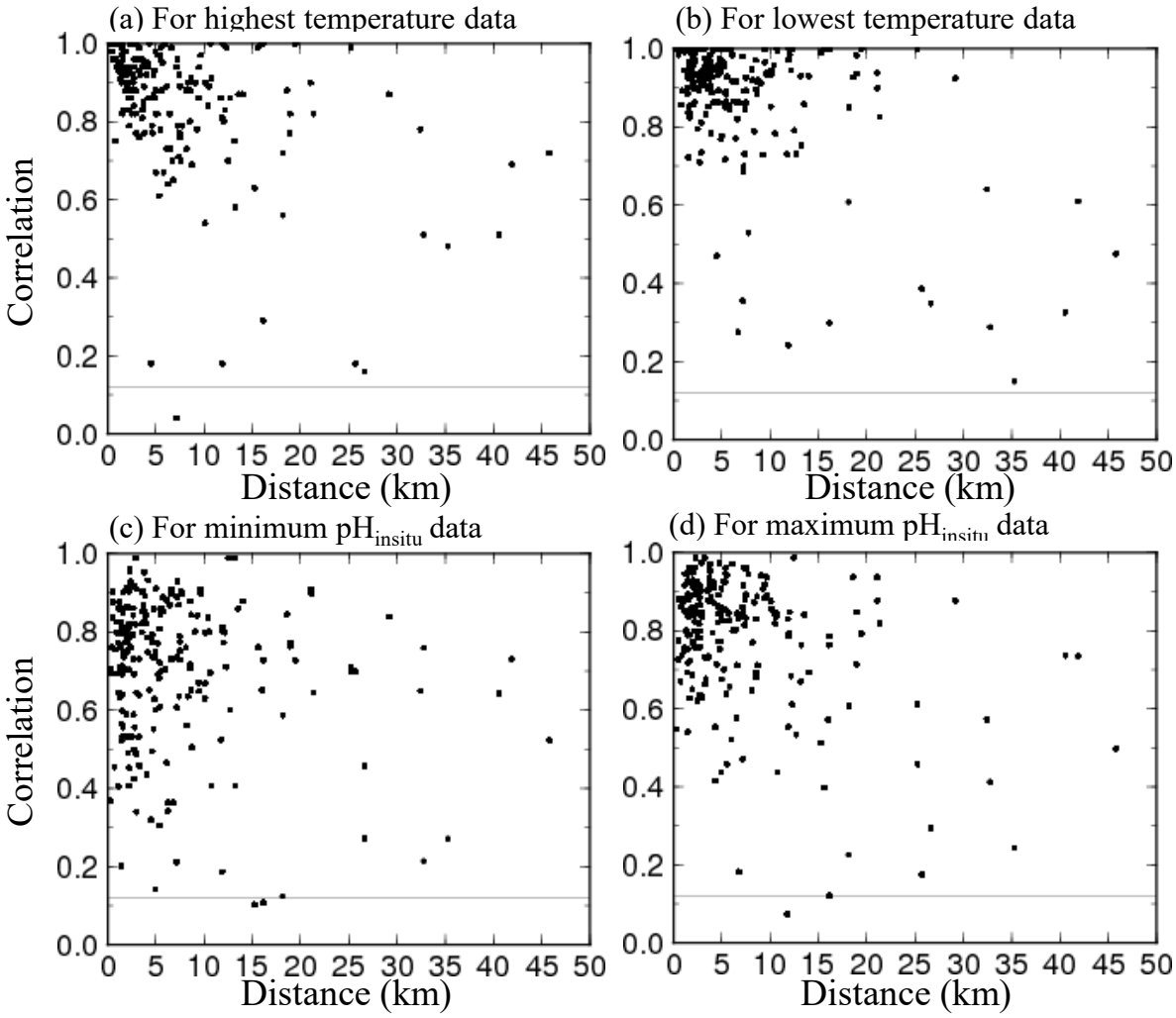


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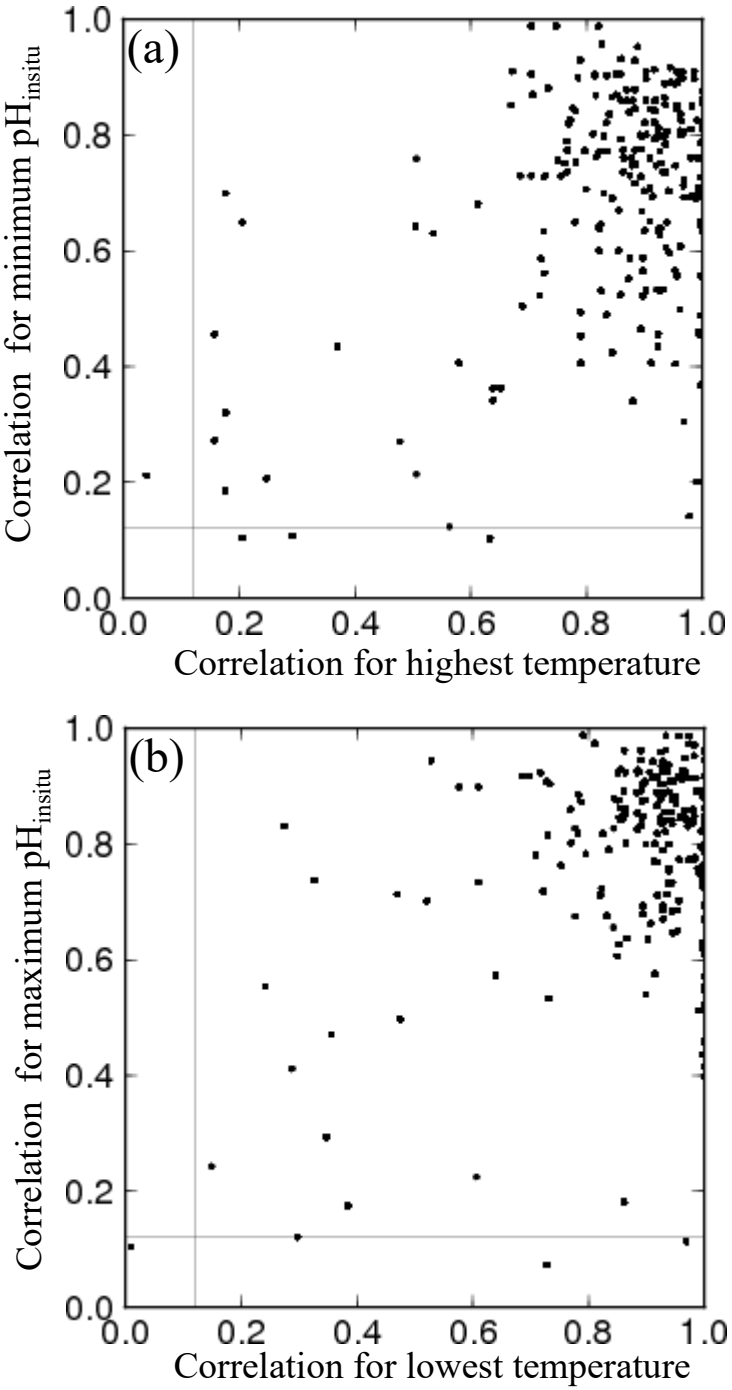


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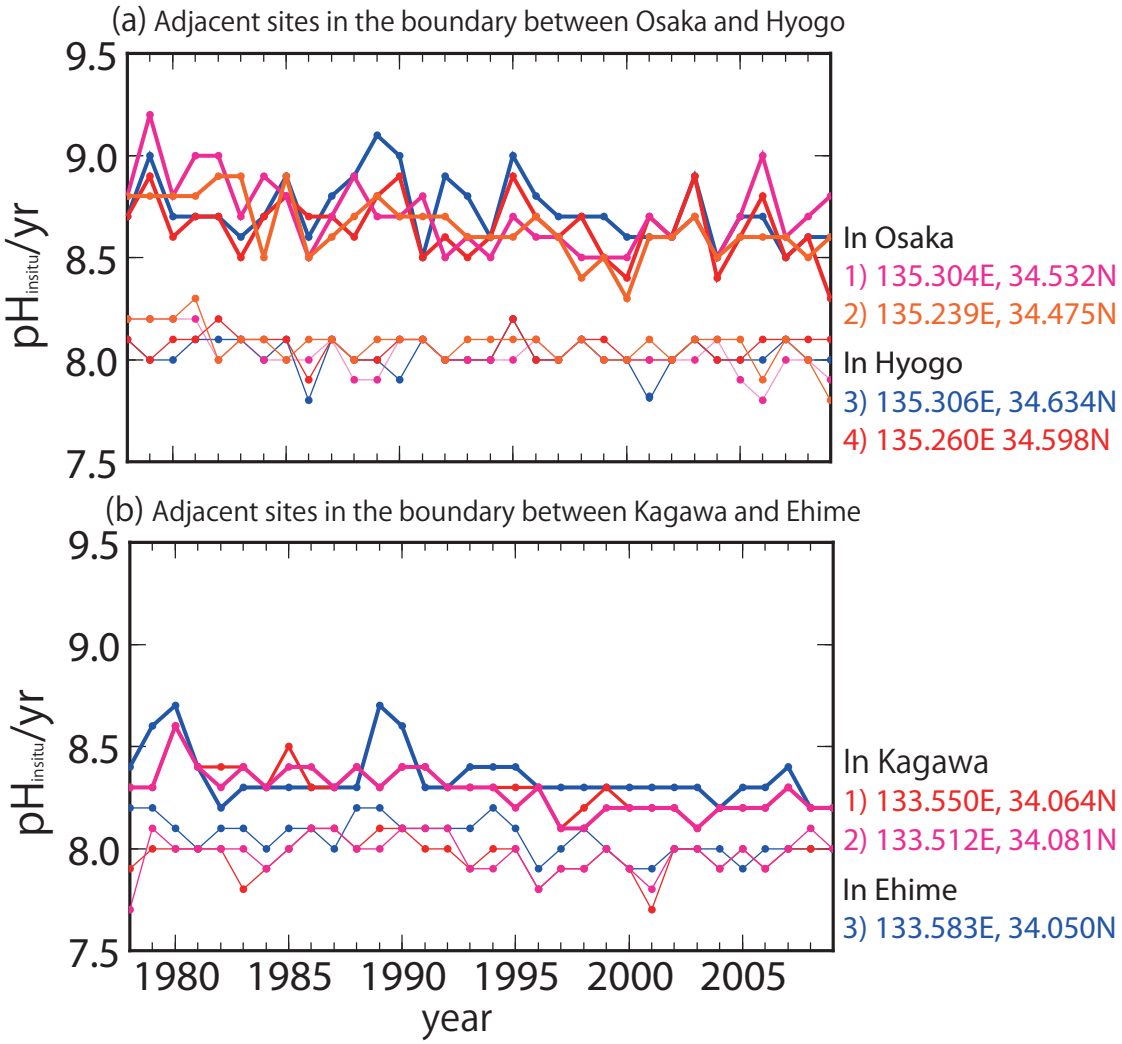


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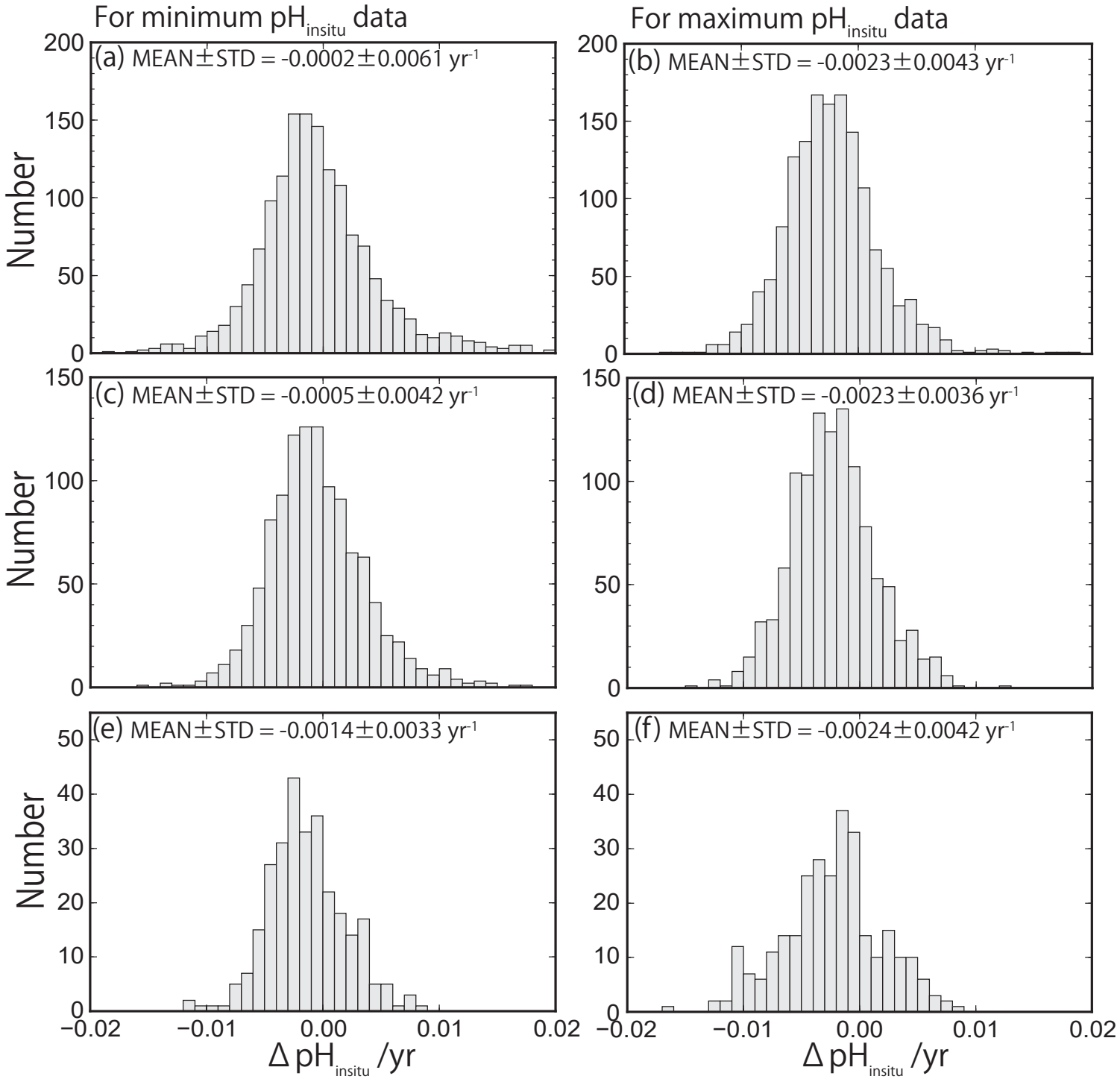


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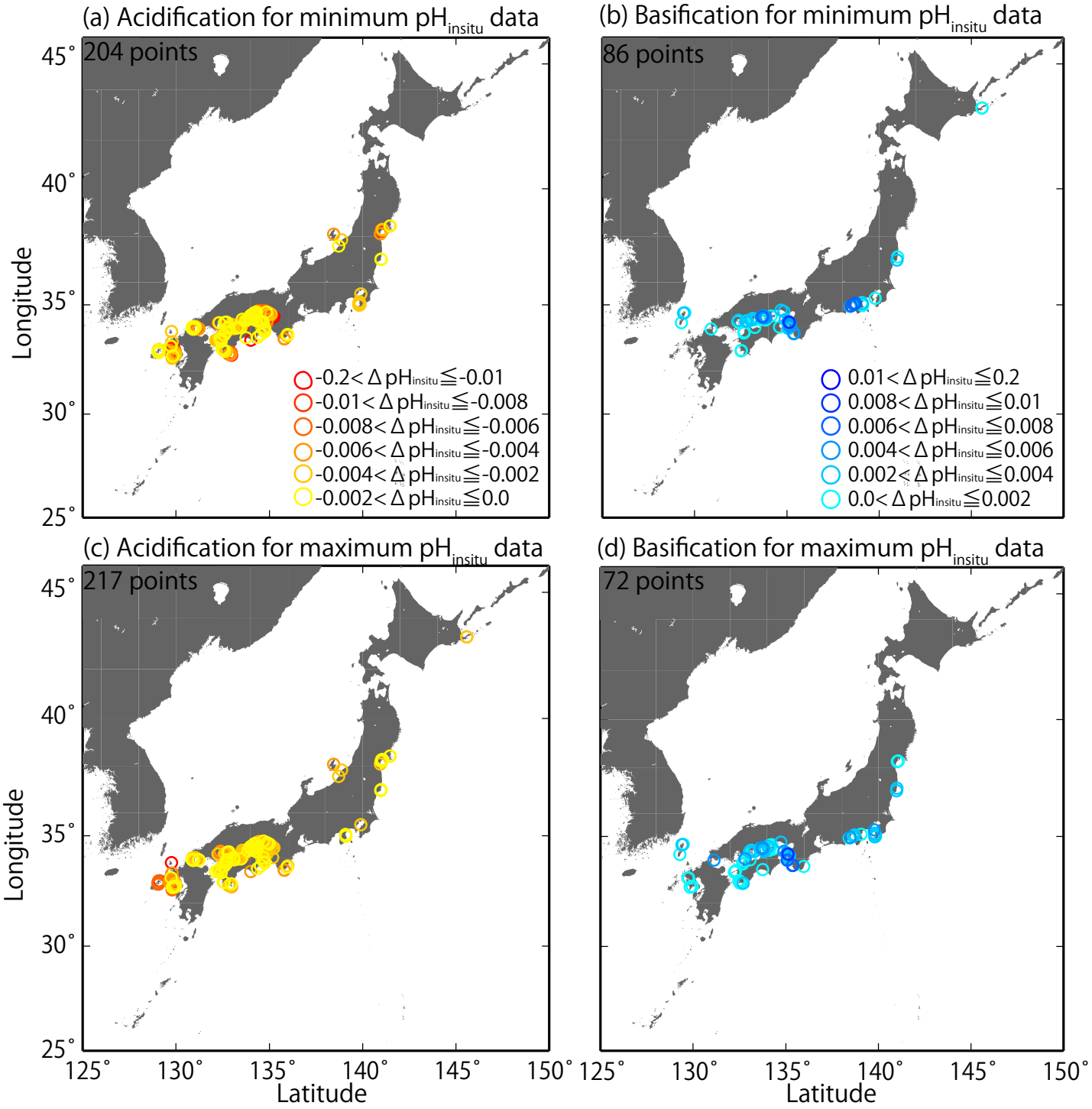


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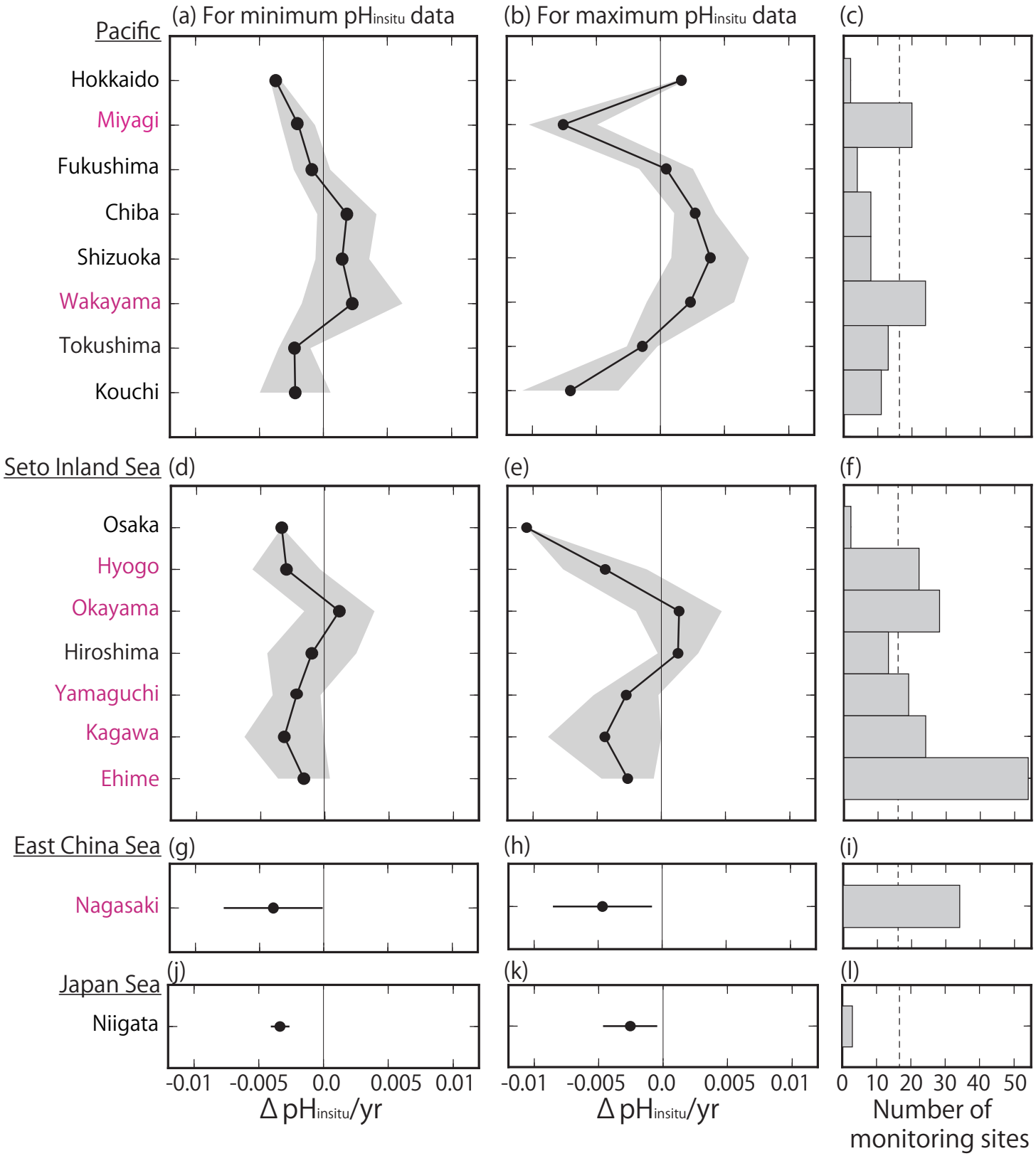


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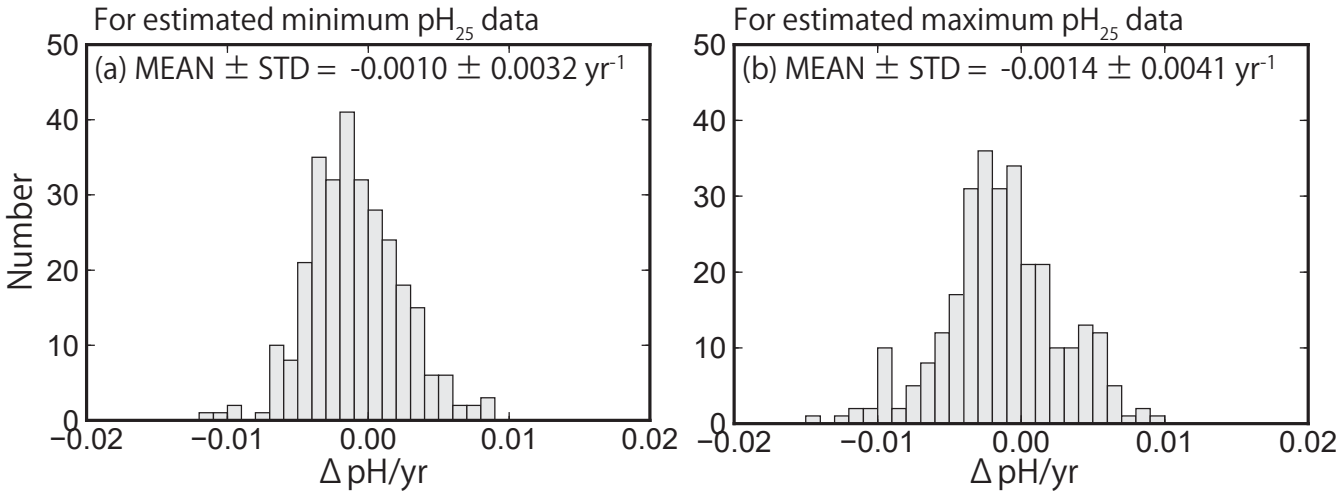


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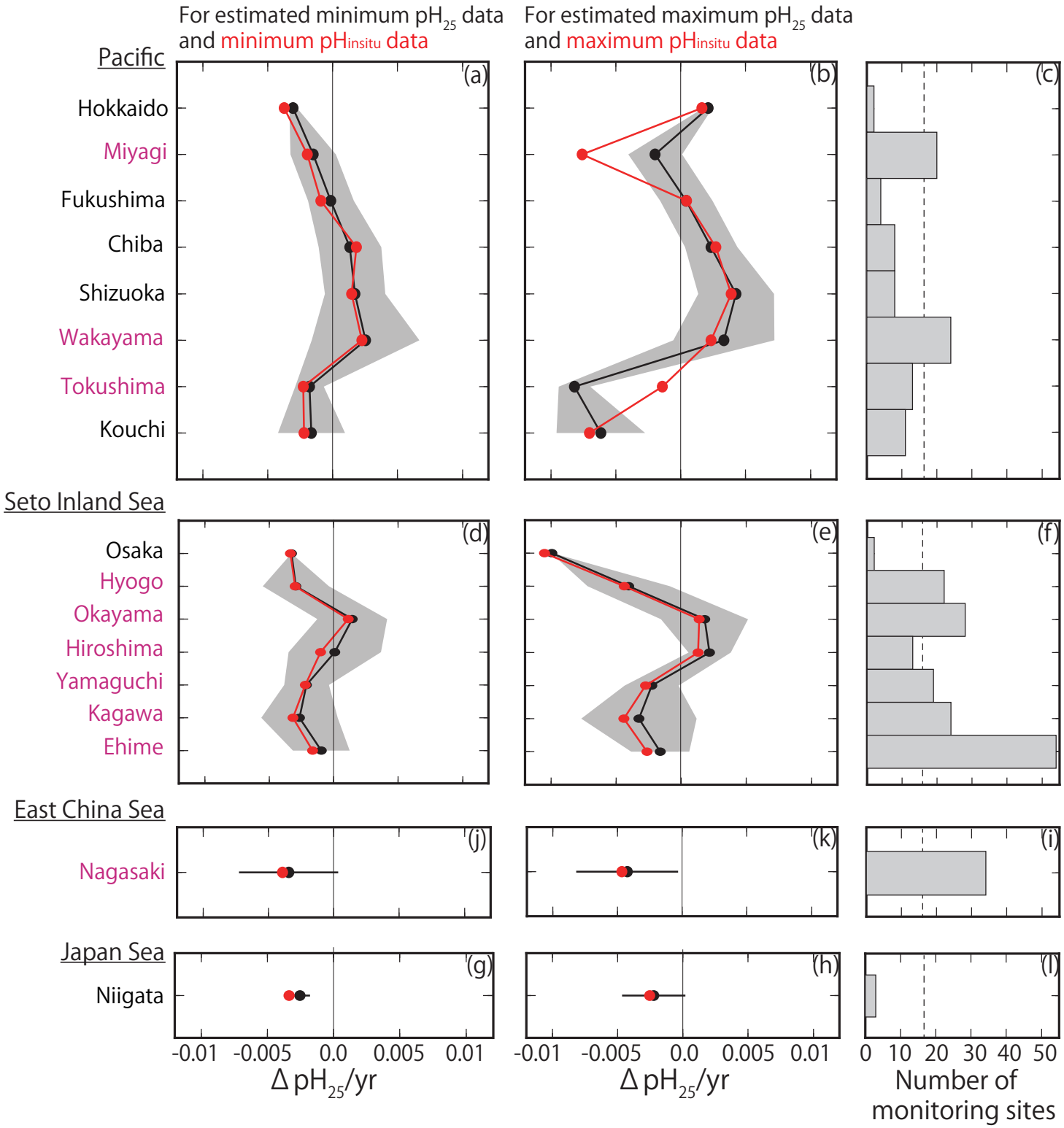


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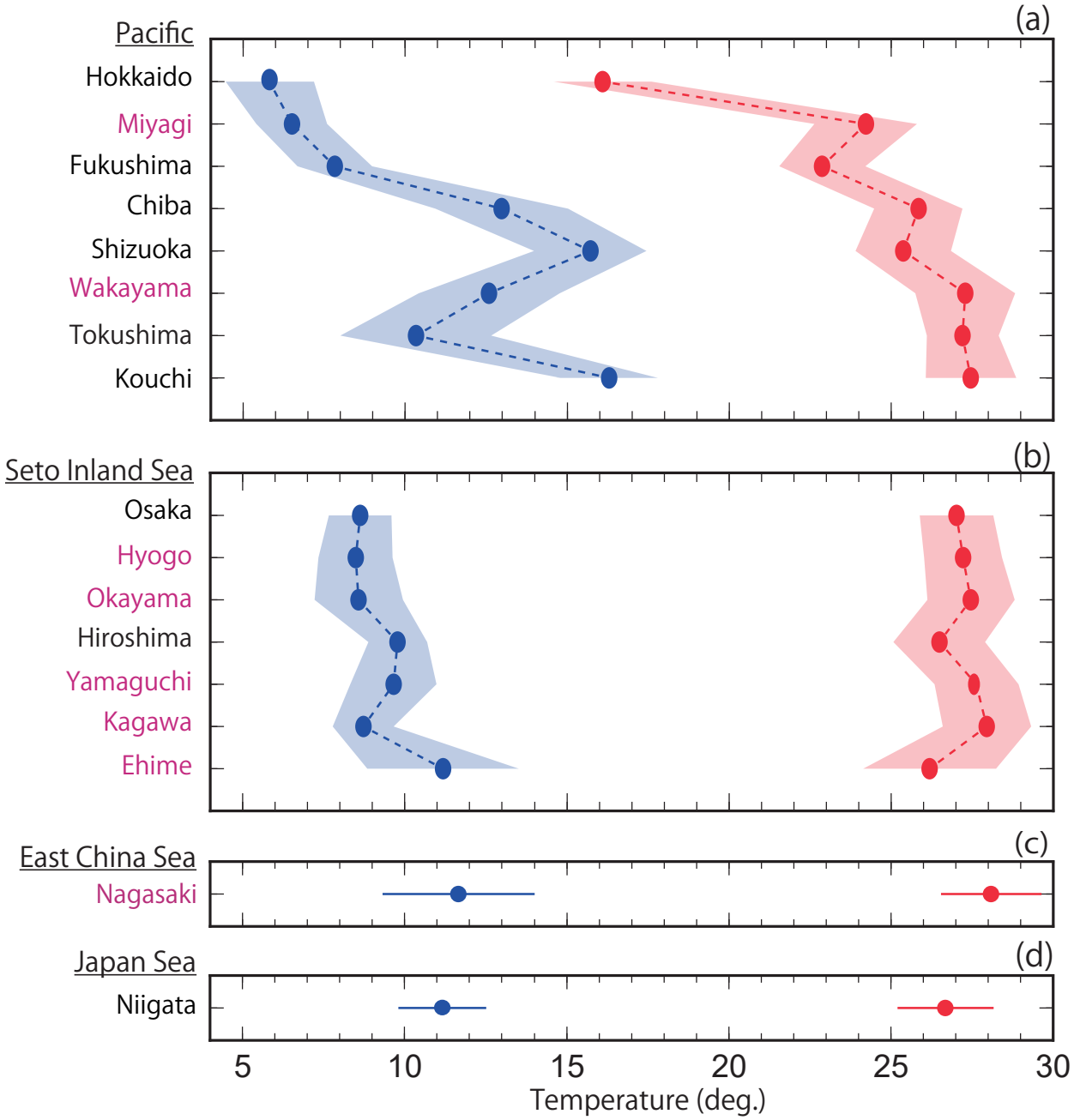


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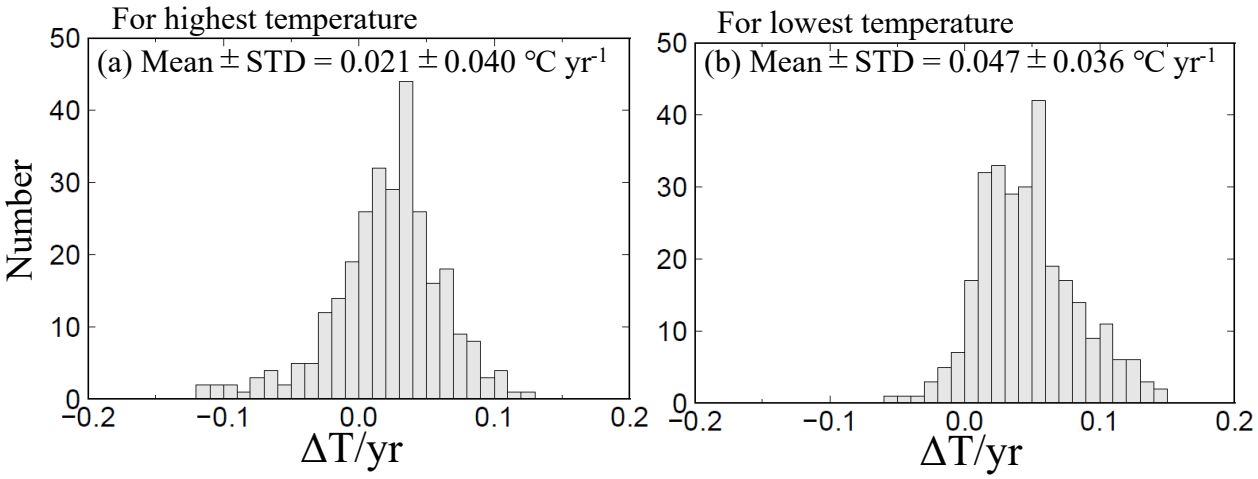


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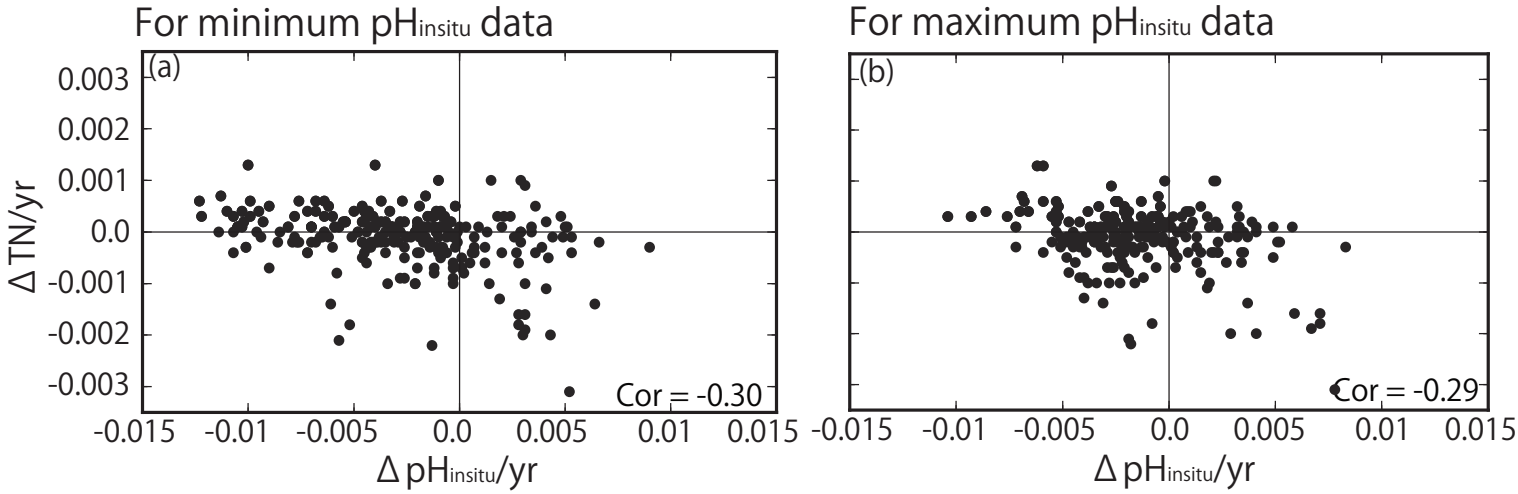


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Table 1 Number of samples (N) collected at each of the 1481 monitoring sites each year.

| Year | 0≦N＜4 | 4≦N＜8 | 8≦N＜12 | 12≦N＜16 | 16≦N＜20 | 20≦N＜24 | 24≦N＜28 | 28≦N＜32 | 32≦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 |