Long-term trends in pH in Japanese coastal seawater

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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 seawater 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 seawater. Using water quality data collected at 289 monitoring sites as part of the Water Pollution Control Program, we evaluated the long-term trends ~~in~~ the pH_{insitu} in Japanese coastal seawater at ambient temperature from 1978 to 2009. We found that the annual maximum pH_{insitu}, which generally represents the pH of surface waters in winter, had decreased at 75% of the sites, but had increased at the remaining sites. The temporal trend in the annual minimum pH_{insitu}, which generally represents the pH of subsurface water in summer, also showed a similar distribution, although it was relatively difficult to interpret the trends of annual minimum pH_{insitu} because the sampling depths differed ~~from station to station~~. The annual maximum pH_{insitu} decreased at an average rate of −0.0024 yr^{-1}, with relatively large deviations from the average value. Detailed analysis suggested that the decrease in pH was caused partly by warming of winter surface waters in Japanese coastal seawater. The pH normalized to 25°C, however, showed decreasing trends, suggesting that dissolved inorganic carbon from anthropogenic sources was increasing in Japanese coastal seawater.

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

1. Introduction

43 The effect of ocean acidification on several marine organisms, including calcifiers, is widely
44 acknowledged and is the topic of various marine research projects worldwide. Chemical variables
45 related to carbonate cycles are monitored in several ongoing ocean projects to determine whether the
46 rate of ocean acidification can be identified from changes in pH and other variables in the open ocean
47 (Gonzalez-Davila et al. 2007; Dore et al. 2009; Bates 2007; Bates et al. 2014; Midorikawa et al. 2010;
48 Olafsson et al. 2009; Wakita et al. 2017). Analysis of pH data measured in situ at the European Station
49 in the Canary Islands (ESTOC) in the North Atlantic from 1995 to 2003 and normalized to 25 °C
50 showed that the pH_{25} decreased at a rate of 0.0017±0.0005 yr^{-1} (Gonzalez-Davila et al. 2007). Similarly,
51 analysis of the Hawaii Ocean Time series (HOT) (Dore et al. 2009) and the Bermuda Atlantic Time
52 Series (BATS) (Bates 2007) showed that the pH at ambient (in situ) sea surface temperature (pH_{insitu})
53 decreased by 0.0019±0.0002 and 0.0017±0.0001 yr^{-1} from 1988 to 2007 and from 1983 to 2005,
54 respectively. Analysis of data collected along the hydrographic observation line at 137°E in the western
55 North Pacific by the Japanese Meteorological Agency (JMA) showed that the pH_{25} decreased by
56 0.0013±0.0005 yr^{-1} in summer and 0.0018±0.0002 yr^{-1} in winter from 1983 to 2007 (Midorikawa et
57 al. 2010). The winter pH_{insitu} in surface water in the Nordic Seas decreased at a rate of 0.0024±0.0002
58 yr^{-1} from 1985 to 2008 (Olafsson et al. 2009). This rate was somewhat more rapid than the average
59 annual rates calculated for the other subtropical time series in the Atlantic Ocean, BATS, and ESTOC,
60 and was attributed to the air–sea CO_2 flux and buffering capacity (higher Revell factor) (Olafsson et
61 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) that resulted from climate-related variations in ocean currents.

These long-term time series from various sites in the open ocean indicate consistent changes in surface ocean carbon chemistry, which mainly reflect the uptake of anthropogenic CO_2, with consequences for ocean acidity. Coastal seawater, however, differ from the open ocean as they are subjected to multiple influences, such as hydrological processes, land use in watersheds, nutrient inputs (Duarte et al. 2013), changes in the structure of ecosystems caused by eutrophication (Borges and Gypens 2010; Cai et al. 2011), marine pollution (Zeng et al. 2015), and variations in salinity (Sunda and Cai 2012).

Duarte et al. (2013) hypothesized that anthropogenic pressures would cause the pH_{insitu} of coastal seawater to decrease (acidification) or increase (basification), depending on the balance between the atmospheric CO_2 inputs and watershed exports of alkaline compounds, organic matter, and nutrients. For example, in Chesapeake Bay, the pH_{insitu} has shown temporal variations over the last 60 years, presumably because of the combined influence of increases and decreases in pH_{insitu} in the mesohaline and polyhaline regions of the main part of the bay, respectively (Waldbusser et al., 2011; Duarte et al., 2013).

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

81 acidification, meaning that the outcomes for coastal ecosystems in different regions will vary. At
82 present we have limited information about long-term changes in pH in coastal seawater, mainly
83 because of the difficulty involved in collecting continuous long-term data from coastal seawater around
84 an entire country at a spatial resolution that sufficiently covers the high regional variability in coastal
85 pH.

86 The Water Pollution Control Law (WPCL) was established in 1970 to deal with the serious
87 pollution of the Japanese aquatic environment in the 1950s and 1960s. Several environmental variables,
88 including pH_{insitu}, have been continuously measured in coastal waters since 1978, using consistent
89 methods enacted in the monitoring program under the leadership of the government, to help protect
90 coastal water and groundwater from pollution and retain the integrity of water environments. The errors
91 in pH measurements collected in this program were assessed as outlined in the JIS Z8802 (JIS;
92 Japanese Industrial Standard) standard protocol (2011) that corresponds to the ISO 10523 (ISO;
93 International Organization for Standardization) standard protocol. Compared with the specialized
94 oceanographic protocols described in the United States Department of Energy (DOE) Handbook
95 (1994), it is not difficult to achieve the JIS protocol. The JIS and DOE standard protocols allow
96 measurement errors of less than ±0.07 and ±0.003, respectively, for the glass electrode method, and
97 the DOE protocol demands a precision of ±0.001 for the spectrophotometric method. Measurements
98 are generally made with the higher-quality spectrophotometric method during major oceanographic
99 studies (e.g. Midorikawa et al. 2010).

100 Regardless of any shortcomings, the WPCL coastal monitoring program in Japan includes more
101 than 2000 monitoring sites that cover most parts of the coastline (Fig. 1), so the dataset provides the
102 opportunity to estimate the overall trend in pH in Japanese coastal areas and the regional variability in
103 the trends from data of known precision. Suitable analytical methods could make up for these
104 shortcomings of the WPCL dataset. In this study, we focused on the general characteristics of the
105 overall pH trends at the all monitoring sites rather than examining the trend in pH at each site in detail,
106 after carefully considering the accuracy of the dataset.

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

112

113 2. Materials and Methods

114 2.1 Water Pollution Control Law (WPCL) monitoring data

115 Data for several environmental variables, including pH_{insitu}, and the associated metadata, are
116 available on the website of the National Institute for Environmental Studies (NIES)
117 (www.nies.go.jp/igreen; http://www.nies.go.jp/igreen/md_down.html). We downloaded pH_{insitu} data
118 from 1978 to 2009 for the trend analysis. We also downloaded temperature (T) and total nitrogen (TN)

119 data that were measured at the same sites as the pH_{insitu} data for the same time period (data for T and
120 TN were available from 1981 to 1995), to check the quality of the pH_{insitu} data (Section 2.2), and to
121 discuss which coastal processes influenced the pH_{insitu} (Section 4.2).

122 The data were collected by the Regional Development Bureau of the Ministry of Land,
123 Infrastructure, Transport and Tourism, and the Ministry of the Environment under the WPCL
124 monitoring program. Monitoring protocols (sampling frequencies, locations, and methods) are outlined
125 in the program guidelines (NIES 2018; Ministry of Environment (MOE) 2018) written in Japanese,
126 and we have provided a summary of these protocols in this manuscript.

127 Monitoring is carried out at 1481 sites along the Japanese coasts, as shown in Figure 1a. While
128 most sites are in coastal sea areas, up to 10% are in estuaries. At each monitoring site, basic surveys
129 were carried out between 4 and 40 times a year, depending on the site. Information on the sampling
130 frequency at the monitoring sites is presented in Table 1. During basic surveys, water samples were
131 collected from 0.5 and 2.0 m below the surface at all sites; at sites where the bottom depths were
132 greater than 10 m, a further sample was collected from a depth of 10 m at about 13−15% of the sites.
133 Water samples were collected four times a day to cover diurnal variation. At sites where the variation
134 in the daily pH was large, samples were also collected over a period of one day at 2-hourly intervals
135 (ca. 13 times a day) at least twice a year to check the adequacy of the basic water sampling protocol.

136 The pH for each water sample was measured in accordance with the Japanese Industrial Standard
137 protocol JIS Z 8802 (2011), which is equivalent to ISO10523

138 (https://www.iso.org/standard/51994.html). The pH was measured by glass electrode calibrated by
139 NBS standard buffers. The electrode and pH meter had to produce measurements that were repeatable
140 to ±0.05. The pH was measured immediately after the water samples were collected, at the ambient
141 water temperature. The repeatability permitted in each measurement was ±0.07. The pH data were
142 ~~collated~~ by the environmental bureau of each prefectural government, which reported only annual
143 minimum and maximum pH values at each station to the MOE, because the original purpose of the
144 WPCL program was to monitor whether the annual variations in water properties (in this case pH)
145 were within ranges set by the national environmental quality standard. The published WPCL pH
146 dataset therefore contains only these annual minimum and maximum pH data in each year, reported
147 on the NBS pH scale (pH_{insitu}) and rounded to one decimal place. Water temperature data are also
148 available for each sampling event (http://www.nies.go.jp/igreen/md_down.html). Previous studies
149 have reported negative correlations between seasonal variations in pH and water temperature, mainly
150 because of changes in the dissociation equilibrium constant ($H_2O \leftrightarrow H^+ + OH^-$); the pH values were
151 lowest in summer and highest in winter, in both the open ocean (e.g. Bates et al. 2014) and coastal
152 seawater (e.g., Frankignoulle and Bouquegneau 1990; Byrne et al. 2013; Hagens et al. 2015; Challener
153 at al. 2016). We therefore assumed that the minimum and maximum pH data coincided with the highest
154 and lowest temperatures, respectively (Fig. 2), and we used these data to calculate the pH_{25} (Section
155 4.2).
156 The monitoring operations were carried out by licensed operators as outlined in the annual plan of

157 the Regional Development Bureau of each prefecture. These specific licensed operators were retained
158 for the duration of the measurement period, which means that the same laboratories were always in
159 charge of collecting the data. This approach helps to prevent systematic errors that might arise both
160 between measurement facilities and over time, and ensures the datasets are accurate.
161
162 2.2 Quality control procedures and assessing the consistency of the WPCL monitoring data
163 We selected all the data for fixed sites in coastal seawater that had continuous time series from
164 1978 to 2009. There were 2463 regular and non-regular monitoring sites in 1978 and 2127 sites in
165 2009. While there were very few sites in some prefectures in Hokkaido and Tohoku, the monitoring
166 sites covered almost all the coastline in Japan (Fig. 1).
167 As explained in more detail later in this section, we applied a three-step quality control procedure.
168 We excluded 1) discontinuous time sequences, 2) time sequences that had extreme outliers in each year,
169 and 3) time sequences that included significant random errors, and which were only weakly correlated
170 with time sequences at adjacent sites.
171 When we excluded the sites that had discontinuous pH_{insitu} time sequences from 1978 to 2009, 1481
172 sites remained (Fig. 1). We then excluded time sequences with outliers, defined as sites with data points
173 that were more than three standard deviations from the average of minimum and maximum pH_{insitu}
174 values for each year. After this step, 1127 sites remained (not shown). We calculated the trends in the
175 unbroken continuous time sequences of the minimum and maximum pH_{insitu} data at each site with

176 linear regression (Fig. 3), and the slopes of the linear regression were taken as the minimum and
177 maximum pH_{insitu} trends (e.g. Fig. 3). The linear regression trends might have been influenced by
178 random errors or variations at different temporal scales in the data for each site. To eliminate the
179 influence of these errors and variations as far as possible, we removed the data that had significant
180 random errors, defined as the time sequences for which the standard deviations of pH_{insitu} exceeded the
181 average standard deviation of the pH_{insitu} time sequences at the 1127 sites. After this step, 302 sites
182 remained (see Fig. 1b for site locations).

183 For the 302 sites, we evaluated whether the water temperature (Fig. 4a−b) and pH_{insitu} (Fig. 4c−d)
184 were correlated at adjacent monitoring sites in the same prefecture (Fig. 4). At most of the stations, the
185 correlations between the temperatures at the site pairs were relatively strong, which indicates that the
186 temperature followed similar patterns over time at adjacent sites (Fig. 4a−b). The correlations tended
187 to be strong when the sites were close together, but gradually weakened with increasing distance
188 between sites. The pH_{insitu} correlations followed a similar pattern (Fig. 4), which indicates that the
189 pH_{insitu} and temperature data at adjacent monitoring sites varied in the same way. In other words, the
190 relative ratios of the measurement errors in pH_{insitu} and the natural spatio-temporal variations at these
191 monitoring sites were similar to those for temperature. The absolute values of the correlation
192 coefficients for the pH_{insitu} were slightly lower than those for temperature for each corresponding pair
193 of sites (Figs. 4 and 5), and might reflect the fact that pH_{insitu}, but not the water temperature, is subjected
194 to strong forcing by coastal biological processes, which causes the pH_{insitu} to vary on the short-term.

195 The correlations between the minimum pH_{insitu} data (Fig. 4c) were weaker than those for the maximum
196 pH_{insitu} data (Fig. 4d) because the degree of biological forcing varied by season and was stronger in
197 summer when the pH_{insitu} was at a minimum and weaker in the winter when the pH_{insitu} was at a
198 maximum. Despite the influence of biological processes on the pH_{insitu}, the correlation coefficients
199 remained high and were significant (r=0.367, p<0.05) at most of the monitoring sites, especially at
200 sites that were less than 5 km apart within the same prefecture, where the pH_{insitu} followed similar
201 patterns. In the final step of the quality check procedure (step 3), we removed all the time sequences
202 with weak and insignificant correlations for temperature and pH_{insitu} (Figs. 4 and 5). After this final
203 step, 289 sites remained.

204 As shown in Table 2, the correlations between temperature and pH_{insitu} at sites within 15 km of
205 each other strengthened after steps 2 and 3, which suggests that the reliability of the dataset improved
206 at each step of the quality control. Also, the negative correlations between trends in pH_{insitu} and TN
207 were enhanced after the quality control procedures (Table 3), as discussed in Section 4.3.2.

208 The monitoring in each prefecture is carried out by different licensed operators, decided by the
209 Regional Development Bureau in each prefecture. Inter-calibration measurements have not been
210 conducted between different licensed operators. Even though all the operators follow the same JIS
211 protocol, manual monitoring can introduce systematic errors into the data. Some adjacent monitoring
212 sites are close to each other but are managed by different operators, such as sites close to the boundaries
213 between Osaka and Hyogo (Fig. 6a), Hyogo and Okayama (Fig. 6b), Kagawa and Okayama (not

214 shown), and Kagawa and Ehime (not shown). The pH_{insitu} time sequences for these site pairs were
215 generally similar, even though there were some deviations when compared with the time sequences
216 for adjacent sites within the same prefecture, monitored by the same operator (lines of the same color
217 in Fig. 6). The standard deviations of the pH_{insitu} trends between these site pairs close to the boundaries
218 of Osaka and Hyogo, Hyogo and Okayama, Kagawa and Okayama, and Kagawa and Ehime were
219 0.0014, 0.0012, 0.0026, and 0.0017 yr^{-1}, respectively, and were smaller than the acceptable
220 measurement errors of the JIS standard protocols. We can therefore ~~say~~ that the measurements from
221 the different operators in different prefectures were consistent.
222
223 # 3. Results
224 ## 3.1 Variations in pH_{insitu} highlighted by regression analysis
225 The histograms of the calculated pH_{insitu} trends (yr^{-1}), for the minimum and maximum pH_{insitu} after
226 each quality control step, are shown in Fig. 7. The histogram in Fig. 7a–b shows the data for the 1481
227 sites (discontinuous sites excluded). The data for the 1127 sites from step 2 (i.e., data without outliers)
228 are shown in Fig. 7c–d, and the data for the 289 sites from step 3 are shown in Fig. 7e–f (Section 2.2).
229 The number of sites decreased at each step of the quality control, but the shapes of the histograms were
230 generally similar for both the minimum and maximum pH trends. The total trends showed overall
231 normal distributions with a negative shift at all levels of quality control.
232 We detected both positive (basification) and negative (acidification) trends, which contrasts with

233 the findings of other researchers who reported only negative trends (ocean acidification) in the open
234 ocean (Bates et al. 2014; Midorikawa et al. 2010; Olafsson et al. 2009; Wakita et al. 2017). The average
235 (±standard deviation) trends for the minimum and maximum pH_{insitu} data were −0.0002±0.0061 and
236 −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
237 the 1127 sites (Fig. 7c–d), respectively. The average trends for the minimum and maximum pH_{insitu}
238 data for the 289 sites that remained after step 3 were −0.0014±0.0033 and −0.0024±0.0042 yr^{-1},
239 respectively (Fig. 7e–f).

240 The negative trends were relatively weak for the minimum pH_{insitu} data and relatively strong for
241 the maximum pH_{insitu} data, but there was an overall tendency towards acidification. At the 289 sites,
242 there were 204 negative and 86 positive trends for the minimum pH_{insitu} data and 217 and 72 negative
243 ~~and positive~~ trends for the maximum pH_{insitu} data. This shows that, for the minimum pH_{insitu} data, there
244 were acidification and basification trends at 70% and 30% of the monitoring sites, respectively, and at
245 75% and 25% for the maximum pH_{insitu} data, respectively.

246

247 ## 3.2 Local patterns in acidification and basification

248 We examined the pH_{insitu} trends for the 289 sites for local patterns in acidification and basification
249 (Section 2.2) and found that the trends seemed to be randomly distributed. For example, the values
250 were different at sites that were less than 50 km apart (Fig. 8). There are many monitoring sites in the
251 Seto Inland Sea and in Western Kyushu. The trends for the minimum and maximum pH_{insitu} showed

252 both acidification and basification in the Seto Inland Sea (Fig. 8a−b, 8c−d). In the western part of
253 Kyushu, acidification dominated (Fig. 8a−b, 8c−d) with only basification in pH_{insitu} at a few sites for
254 both the minimum and maximum pH_{insitu} data (Fig. 8b, d). Figure 8a (b) and Figure 8c (d) are similar,
255 which suggests that, at most of the sites where we detected acidification and basification, the trend
256 directions were consistent for the minimum and maximum pH_{insitu} (Fig. 8a−b, 8c−d).

257 By examining the average minimum and maximum pH_{insitu} trends in each prefecture (Fig. 9a−b, d−e,
258 g−h, j−k), we found that, while the average values were slightly different, the trends in the averaged
259 values and the patterns in acidification and basification for both the minimum and maximum pH_{insitu}
260 were the same from north to south and from west to east. We also found acidification trends in most of
261 the prefectures with at least 17 sampling sites, namely Miyagi, Wakayama, Hyogo, Okayama,
262 Yamaguchi, Tokushima, Kagawa, Ehime, and Nagasaki (Figs. 1a and 9c, f, i, l). The average estimates
263 for the maximum pH_{insitu} were larger than those for the minimum pH_{insitu} in these prefectures.

264 We found more acidification trends for the minimum pH_{insitu} in the southwestern prefectures of
265 Yamaguchi, Kagawa, Ehime, Hyogo, and Nagasaki than in the northeastern prefecture of Miyagi (Fig.
266 9a, d, g, i) (see Fig. 1 for locations). The maximum and minimum pH_{insitu} trends indicated basification
267 in Wakayama and Okayama prefectures (Fig. 9c). The trends in Osaka, Hyogo, Okayama, Hiroshima,
268 Yamaguchi, Kagawa, and Ehime prefectures (Fig. 1a) were different, even though they were all located
269 in the same part of the Seto Inland Sea (Fig. 9d−e). The trends in Hiroshima and Okayama, within the
270 Seto Inland Sea, were weaker than those in Hyogo, Yamaguchi, Kagawa, and Ehime, which were

271 outside the sea (Fig. 9d−e). The pH_{insitu} trend values indicated relatively strong acidification at a rate
272 of −0.0025 yr^{-1} in Niigata in the Japan Sea (Fig. 9j−l) but there were fewer than the threshold of 17
273 monitoring sites in the prefectures.
274
275 # 4. Discussion
276 ## 4.1 Statistical evaluation of our estimated overall trends
277 The JIS Z8802 (2011) allows a measurement error of ±0.07 and this treatment further enhanced the
278 uncertainty of the published data to ±0.1. The uncertainty of the slope of the linear regression line (σ_β)
279 is estimated with the following equation (e.g., Luenberger 1969):
280 $$\sigma_\beta = \{\sigma^2_y / \Sigma(x_i\text{-}[x])^2\}^{1/2} \quad (1)$$
281 where σ^2_y is the theoretical variance in a pH value caused by the measurement error (in this case, 0.1^2
282 = 0.01); and x_i and [x] represent the year and the year averaged for all data at a station, respectively.
283 In the WPCL dataset, there are generally 32 data points for each station (for every year from 1978 to
284 2009), spaced at consistent intervals. In this case, $\Sigma(x_i - [x])^2$ becomes 2728 and σ_β becomes 0.0020
285 yr^{-1}, which is the threshold of significance for the pH trend. This means that our estimated trends
286 included standard deviations that were less than 0.0020 yr^{-1}, and, if there were no trends, a histogram
287 of the pH trends should be normally distributed with an average and standard deviation (σ_β) of 0.0000
288 and 0.0020 yr^{-1}, respectively (Fig. 7). The average trend in the maximum pH_{insitu}, however, shifted
289 from zero in a negative direction at a rate of more than 0.0020 yr^{-1} for all three scenarios (Fig. 7b, d,

290 f). This result implies that, averaged over the whole country, the Japanese coast was acidified in winter
291 to a degree that could be detected from the historical WPCL pH data, even with an uncertainty of ±0.1.
292 The observed standard deviation for the maximum pH_{insitu} was also larger than the expected value of
293 0.0020 yr^{-1} because of local variations in the pH trends. The average shift in the minimum pH_{insitu} data
294 was smaller than 0.0020 yr^{-1}, but all three scenarios showed negative shifts in the average minimum
295 pH_{insitu} value (Fig. 7a, c, e).

296 We used Welch's t test to assess the direction of the average minimum and maximum pH_{insitu} trends.
297 For our null hypothesis, we assumed that the population of the trends with an average of −0.0014 yr^{-1}
298 (−0.0024 yr^{-1}) and a standard deviation of 0.0033 yr^{-1} (0.0042 yr^{-1}) was sampled from a population of
299 the minimum (maximum) pH_{insitu} trends with an average trend of 0.0000 yr^{-1} and a standard deviation
300 of 0.0020 yr^{-1}. When the sample size was 289, the *t*-values and the degrees of freedom were 8.7 (6.2)
301 and 412.2 (474.4), respectively. Since the *p* value was less than 0.001, the null hypothesis was rejected.
302 Welch's t test confirmed that the average trends for both the minimum and maximum pH_{insitu} data were
303 negative.

304 We also applied a paired t test to determine whether the two trends calculated from the averaged
305 minimum and maximum pH_{insitu} data were significantly different. The population mean and the sample
306 size were 0.0 and 289, respectively. The *t* value of 4.64 (with 288 degrees of freedom) shows that the
307 null hypothesis was rejected, with the paired t test thus indicating that the two trends calculated from
308 the averaged minimum and maximum pH_{insitu} data were significantly different.

309

310 ## 4.2 Effects of sampling depth

311 The WPCL dataset did not discriminate between surface (0.5–2 m) and subsurface (10 m) data when
312 calculating the annual maximum and minimum pH_{insitu}, although monitoring depths were fixed
313 throughout the monitoring period at all the sites. We estimated the percentage possibility that samples
314 were collected at 10 m depth for the quality-controlled datasets with 1481, 1127, and 289 sites,
315 assuming that pH values were measured at the same depth as temperature, and found that samples
316 might have been collected at a depth of 10 m at 13%, 13%, and 15% of the 1481, 1127, and 289 sites,
317 respectively.

318 Usually the pH is lower in subsurface water than in surface water, as primary production decreases
319 and increases the DIC concentrations in surface and subsurface water, respectively, because of
320 decomposition when Particulate Organic Carbon (POC) is produced by primary producers. We
321 therefore speculate that the annual maximum pH includes very little data from a depth of 10 m, and so
322 this value does represent the winter pH of surface waters. In contrast, the annual minimum pH was
323 somewhat difficult to interpret, as it may have contained data from 10 m at some monitoring sites but
324 only surface data at other sites shallower than 10 m.

325 Results of statistical analysis (Section 4.1) confirm that the trends in minimum and maximum pH_{insitu}
326 data tended to be negative in the seawater around Japan. The negative tendency of the annual maximum
327 pH_{insitu} trends may imply a trend of overall acidification in winter in surface waters around the Japanese

328 coasts, but the pattern in the annual minimum pH_{insitu} trends was difficult to interpret. Nevertheless,
329 the annual minimum pH_{insitu} trends were, as for the annual maximum pH_{insitu}, also negative (Section
330 3.1) and the trends in the annual minimum pH_{insitu} and in the annual maximum pH_{insitu} showed similar
331 patterns locally (Section 3.2), which indicate that long-term variations in the annual minimum and
332 maximum pH_{insitu} were controlled by the same forcing, so that the pH_{insitu} trends changed in the same
333 direction at both surface and subsurface. Global phenomena such as increases in atmospheric CO_2 and
334 warming of surface water temperatures may cause these forcings.
335
336 ## 4.3 Possible influences on the pH_{insitu} trends in coastal seawater
337 To facilitate our discussion of the factors that influenced the pH_{insitu} trends further, we used the
338 conceptual models of acidification and basification in coastal seawater of Sunda and Cai (2012) and
339 Duarte et al. (2013), as follows:
340 PH_{insitu} = Function (D (T), DIC (Air CO_2, B (T, N)), Alk(S)) (2)
341 The pH_{insitu} varies with the ambient temperature (T) on seasonal, inter-annual, and decadal time scales
342 mainly because of changes in the water dissociation constant in equilibrium (D; $H_2O \leftrightarrow H^+ + OH^-$).
343 Changes in dissolved inorganic carbon (DIC), alkalinity (Alk), and salinity (S) also affect the pH_{insitu}
344 trends. The solubility pump, which is controlled mainly by the atmospheric CO_2 concentration (Air
345 CO_2; $CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$), affects DIC, and ocean acidification occurs when the Air CO_2
346 increases. Dissolved organic carbon can also be affected by biological processes (B) that depend on

347 the ambient temperature (T) and the nutrient loading (N). There are contrasting relationships between
348 DIC and N in heterotrophic and autotrophic oceans. In the waters where organic decomposition is
349 dominated by primary productivity (i.e., autotrophic water), increases in N will enhance primary
350 production and cause DIC to decrease, raising pH. When N increases in the waters adjoining this
351 autotrophic water mass (for example, subsurface waters), POC transport from the autotrophic water
352 mass will also increase, and DIC will increase as POC decomposes (i.e., heterotrophic water), causing
353 acidification (e.g., Sunda and Cai 2012; Duarte et al., 2013). Alkalinity (Alk) generally varies with
354 salinity (S) in coastal oceans and may also affect the pH_{insitu} trend.

355 The DIC process (Air CO_2) of ocean acidification shown in equation 2 generally occurred at all
356 monitoring sites when the Air CO_2 concentrations were horizontally uniform, resulting in overall
357 negative trends in minimum and maximum pH_{insitu}. There was also an overall warming trend in D (T)
358 in Japanese coastal areas, which may have affected the observed pH_{insitu} trend. Both the DIC (Air CO_2)
359 and D (T) may be associated with global processes of warming and ocean acidification, which were
360 triggered by the increases in CO_2 concentrations in the global atmosphere.

361 It is difficult to observe general trends in both DIC (B (T, N)) and Alk (S) at all monitoring sites,
362 because there were no common trends in the factors that control these variables (e.g., salinity of coastal
363 water and terrestrial nutrient loadings) around the Japanese coast in this dataset. The WPCL data
364 should contain stations with both autotrophic and heterotrophic properties (Smith and Hollibaugh,
365 1992), which further obscures the influence of DIC (B (T, N)) on the overall pH_{insitu} trend, as the same

366 trend in B (T, N) leads to opposite trends in DIC (B (T, N) in autotrophic and heterotrophic ocean
367 waters (Duarte et al., 2013). The wide variations in DIC (B (T, N)) and Alk (S) between regions might
368 have caused the regional differences in pH_{insitu} trends among stations, contributing to relatively large
369 standard deviations in both the minimum and maximum pH_{insitu} trends (Fig. 7).

370 ~~We discuss t~~he effects of global processes on the overall average pH trends are discussed in Section
371 4.3.1. The relationships between local effects and regional differences are discussed in Section 4.3.2.

372

373 ## 4.3.1 Global effects on pH_{insitu} trends

374 Our analysis was based on pH_{insitu} data, so differences observed in trends may reflect long-term
375 changes in water temperature that affected the dissociation constant (process D (T) in equation 2) or
376 changes in the coastal carbon cycle, including absorption of anthropogenic carbon by the solubility
377 pump (process DIC (Air CO_2) in equation 2). Some of the effects of D (T) and DIC (Air CO_2) driven
378 by global warming and ocean acidification may have affected all monitoring sites, and may have
379 contributed to the negative shifts in trend distributions.

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

385 we used the method of Lui and Chen (2017) to calculate the pH_{25}, as follows:

386 $$pH_{25} = -pH_{insitu} + a_1(T - 25\ °C), \quad (3)$$

387 where a_1 was set to −0.015 and T was the observed temperature.

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

398 We used Welch's t test to assess the direction of the averages of minimum and maximum pH_{25}
399 trends. The p value was less than 0.001, so the null hypothesis was rejected again. The results of the t
400 test confirm that the average trends for both the minimum and maximum pH_{25} data were also negative,
401 suggesting that the DIC ($AirCO_2$) effect (i.e., ocean acidification) caused the negative shifts in the
402 distribution of the trend for the pH normalized to 25°C.

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

prefectures (Fig. 11), except in Miyagi and Tokushima. The trends in the minimum pH_{insitu} and summer pH_{25} were quite similar, but the minimum and maximum pH_{insitu} trends tended to be more negative (by about −0.0010 yr^{-1}) than the corresponding pH_{25} trends, especially in Wakayama, Hiroshioma, Kagawa, and Ehime, which met the threshold number of sampling sites.

The average highest temperatures observed at the minimum pH_{insitu} were close to 25 °C in the regions south of Chiba prefecture (Figs. 1 and 12a−d), so the normalization at 25 °C did not have much effect on the minimum pH_{25} in the southern prefectures. In contrast, the maximum pH_{insitu} values were observed at temperatures that were more than 10 °C lower than 25 °C, so the normalization worked well on the winter data. We estimated the temperature trends from the highest and lowest temperatures at the 289 sites that remained after quality control step 3. The trends in the highest and lowest temperatures generally indicated warming, with an average and standard deviation of 0.021±0.040 and 0.047±0.036 ~~deg~~ yr^{-1}, respectively (Fig. 13). Estimations from the CO2sys indicate that these warming trends influenced the pH values and were related to the changes of −0.0004 and −0.0010 yr^{-1} in the pH trends in summer and winter, respectively (Fig. 7e−f and 10a−b).

We estimated that the pH_{insitu} would change from 8.0150 to 8.0147 in summer and from 8.2568 to 8.2560 in winter, for temperature changes from 25.00 to 25.02 °C, and from 10.00 ° to 10.04 °C, respectively, for a salinity of 34, DIC of 1900 millimol m^{-3}, and alkalinity of 2200 millimol m^{-3}. 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 difference between the decrease in the pH trends in

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

424

425 ### 4.3.2 Local effects on pH_{insitu} trends

426 We found regional differences in the pH_{insitu} values (e.g. Fig. 6) and pH_{insitu} trends (Figs. 8−9). The
427 negative pH_{insitu} trends (acidification) were more significant in southwestern Japan than in northeastern
428 Japan, especially for the minimum pH_{insitu} data (Fig. 9 and Section 3.2). The JMA (2008, 2018)
429 reported that over the past 100 years, the increase in water temperature in western Japan was ~1.30 °C
430 greater than that in northeastern Japan.

431 We used CO2sys (Lewis and Wallace 1998) to predict how pH_{insitu} would change under a
432 temperature difference of 0.01 °C yr^{-1} between the northeastern and southwestern areas, and found
433 that pH decreased by 0.0002 (0.0002) yr^{-1} when the temperature changed from 10.00 to 10.01 °C (25.0
434 to 25.01 °C), assuming a salinity of 34, DIC of 1900 millimol/m^3, and alkalinity of 2200 millimol/m^3.
435 The contrasting trends in the northeast and southwest can be also partly explained by the difference in
436 warming trends (process D (T) in equation 2).

437 The summer pH_{insitu} is affected by ocean uptake of CO_2 (process DIC; Bates et al., 2012; Bates
438 2014) through long-term changes in biological activity (Cai et al., 2011; Sunda and Cai 2012; Duarte
439 et al., 2013; Yamamoto-Kawai et al., 2015) as well as the effect of changes in the dissociation constant.
440 The responses of pH_{insitu} to changes in marine productivity are, however, complicated.

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

(e.g., Yamamoto-Kawai et al. 2015; Kamohara et al. 2018; Nakai et al. 2018), with variable effects on summer pH_{insitu} in coastal seawater. TN was monitored for a shorter period than pH_{insitu} (1995 to 2009). We assumed that the TN was mainly dissolved inorganic nitrogen and determined the correlations between TN and the minimum and maximum pH_{insitu} trends (Fig. 14). There were significant negative correlations between TN and the minimum (−0.30) and maximum (−0.29) pH_{insitu}. These correlations imply that the conditions in most of the monitoring areas of the WPCL programs were heterotrophic. The results also imply that recent decreases in TN loadings partly offset anthropogenic CO_2-induced decreases in pH in coastal seawater. However, we should also be careful when interpreting these results, as this may be a result of simultaneous progress in independent two phenomena (i.e., anthropogenic carbon uptake from the ocean and decreases in TN loadings in Japan).

Nakai et al. (2018) reported that nutrient loadings decreased in the most parts of the Seto Inland Sea from 1981 to 2010, but that several areas remained eutrophic. Because of geographical variations in nutrient loadings and the uneven distribution of autotrophic and heterotrophic water areas, there are significant spatial variations in pH trends in the Seto Inland Sea (Fig. 8). The pH trends in coastal areas of western Kyushu, where the anthropogenic nutrient loadings are relatively low, therefore reflect the decreases in nutrient discharges, resulting in variations between regions (e.g., Nakai et al. 2018; Yamamoto and Hanazato 2015; Tsuchiya et al., 2018). Several cities in this area have introduced advanced sewage treatment to prevent eutrophication in coastal seawater (Nakai et al. 2018; Yamamoto and Hanazato 2015).

Regional variations in coastal alkalinity along with salinity might be related to changes in land use and might affect the trends (process Alk(S) in equation 2). Taguchi et al. (2009) measured alkalinity in the surface waters of Ise, Tokyo, and Osaka bays between 2007 and 2009, and reported that total alkalinity was highly correlated with salinity in each bay. For a temperature, salinity, dissolved carbon, and alkalinity of 25.00 °C, 35, 1900 millimol m^{-3}, and 2300 millimol m^{-3}, respectively, pH_{insitu} (= pH_{25}) was estimated at 8.1416 using the CO2sys (Lewis and Wallace 1998). By changing the salinity and alkalinity to 34 and 2200 millimol m^{-3}, respectively, pH_{insitu} (= pH_{25}) decreased by 0.0081 to 8.0150. This shows that the pH could deviate significantly from average trends if the inputs of alkaline compounds are changed; consequently, some of our pH trends could have been affected by changing discharge from different land-use types.

Regional differences in pH_{insitu} trends in coastal seawater might be caused by ocean pollution. The speciation and bioavailability of heavy metals change in acidic waters, causing an increase in the 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 seawater 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 seawater. We found that the annual maximum pH_{insitu} at each station, which generally represents the pH of surface waters in winter, had decreased at 75% of the sites and had increased at the remaining 25% of sites. The temporal trend in the annual minimum pH_{insitu}, which generally represents the summer pH in subsurface water at each site, was also similar, but it was relatively difficult to interpret the trends of annual minimum pH_{insitu} because the sampling depths differed ~~from~~ station ~~to station~~. The average rate of decrease in the annual maximum pH_{insitu} was -0.0024 yr^{-1}, with relatively large deviations from the average value. Detailed analysis suggests that the decrease in the pH was partly caused by warming of Japanese surface coastal seawater in winter. However, the distributions of the trend in pH normalized to 25°C also showed negative shifts, suggesting that anthropogenic DIC was also increasing in Japanese coastal seawater.

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

499 suggests that the coastal environment might not be completely devastated by acidification. If we can
500 manage the coastal environment effectively (e.g., control nutrient loadings and
501 autotropic/heterotrophic conditions), we might be able to limit, or even reverse, acidification in coastal
502 areas.

503

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512

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652

653 Figure captions

654

655 Fig. 1 Coastal maps and monitoring sites in Japan. Red points in (a) indicate the fixed sites (n = 1481)
656 monitored by the Regional Development Bureau of the Ministry of Land, Infrastructure, Transport,
657 and Tourism, and the Ministry of the Environment (Japan) under the WCPL monitoring program. (b)
658 Monitoring sites that met the strictest criterion (n = 302).

659

660 Fig. 2 Distributions of the monthly number of data points (N) for (a) maximum and (b) minimum
661 temperatures collected in each prefecture from the 302 most reliable monitoring sites.

662

663 Fig. 3 Examples of (a) acidification (Kahoku Coast in Ishikawa) and (b) basification (Funakoshi Bay
664 in Iwate) trends at monitoring sites. Blue and red colors indicate the annual minimum and maximum
665 pH_{insitu} data and their trends, respectively.

666

667 Fig. 4 Correlations of water temperature and pH_{insitu} at adjacent monitoring sites in the same prefecture.
668 Thin lines denote significant correlations ($\boldsymbol{r}$ = 0.12, degrees of freedom = 283).

669

670 Fig. 5 Scatter plots of correlation coefficients for water temperature and pH_{insitu} at adjacent monitoring
671 sites in the same prefecture. Fig. 5a shows the highest temperature and the minimum pH_{insitu} and Fig.

672 5b shows the lowest temperature and maximum pH_{insitu}, respectively.

673

674 Fig. 6 Examples of time-series for annual minimum and maximum pH_{insitu} data at adjacent monitoring
675 sites close to the boundaries between (a) Osaka and Hyogo and (b) Kagawa and Ehime. Lines of the
676 same color indicate data collected at the same site. Thin and bold lines indicate the annual minimum
677 and maximum pH_{insitu} data, respectively, at each monitoring site. Site locations are included to the
678 right of each panel, with the text color corresponding to the colors in each panel.

679

680 Fig. 7 Histogram of pH trends, represented by ΔpH_{insitu}, showing the slopes of the linear regression
681 lines for the annual minimum (left) and maximum (right) pH_{insitu} data at each monitoring site. The
682 histograms in (a, b), (c, d), and (e, f) show three scenarios: (a, b) all 1481 available sites with
683 continuous records before quality control, (c, d) 1127 sites without outliers, and (e, f) 289 sites that
684 meet the strictest criterion.

685

686 Fig. 8 Distributions of long-term trends in pH_{insitu} (ΔpH_{insitu}/yr) in Japanese coastal seawater. The colors
687 indicate the ranges of acidification (a, c) and basification (b, d). (a, b) and (c, d) are linked to the data
688 used in Figs. 7e and 7f, respectively.

689

690 Fig. 9 (a−b, d−e, g−h, j−k) Average minimum and maximum pH_{insitu} trends (ΔpH_{insitu}/yr) in each

691 prefecture. These figures show each side of the Pacific (a−b), the Seto Inland Sea (d−e), the East
692 China Sea (g−h), and the Japan Sea (j−k). The prefecture names are arranged vertically from eastern
693 (northern) to western (southern) areas. Black shading indicate one standard deviation from the
694 average. (c, f, i, l) Number of monitoring sites in each prefecture and the thin dashed line is the
695 threshold value of 17 (i.e., the average number of monitoring sites in all prefectures). The prefectures
696 that meet the threshold are indicated in purple. The figure is based on the results shown in Figs. 7 (e,
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698
699 Fig. 10 Same as Fig. 7, but showing the pH_{25} trends at 289 sites (selected by quality control step 3).
700 The value of pH_{25} was estimated using the method of Lui and Chen (2017).
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703 maximum pH_{25} trends (ΔpH_{25}/yr) for each prefecture. Red lines and points indicate the average
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705
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707 for each prefecture. The blue and red lines and shading indicate the average and one standard
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709 purple, as in Figs. 9 (c-l) and 11 (c-l).

710

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712 by quality control step 3).

713

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

717

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

719

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

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

729 procedure. Degrees of freedom in step 1 and 2 are same values, because TN data are not necessarily
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731 and 2 were therefore the same number. Significant levels of 5% and degrees of freedom are also
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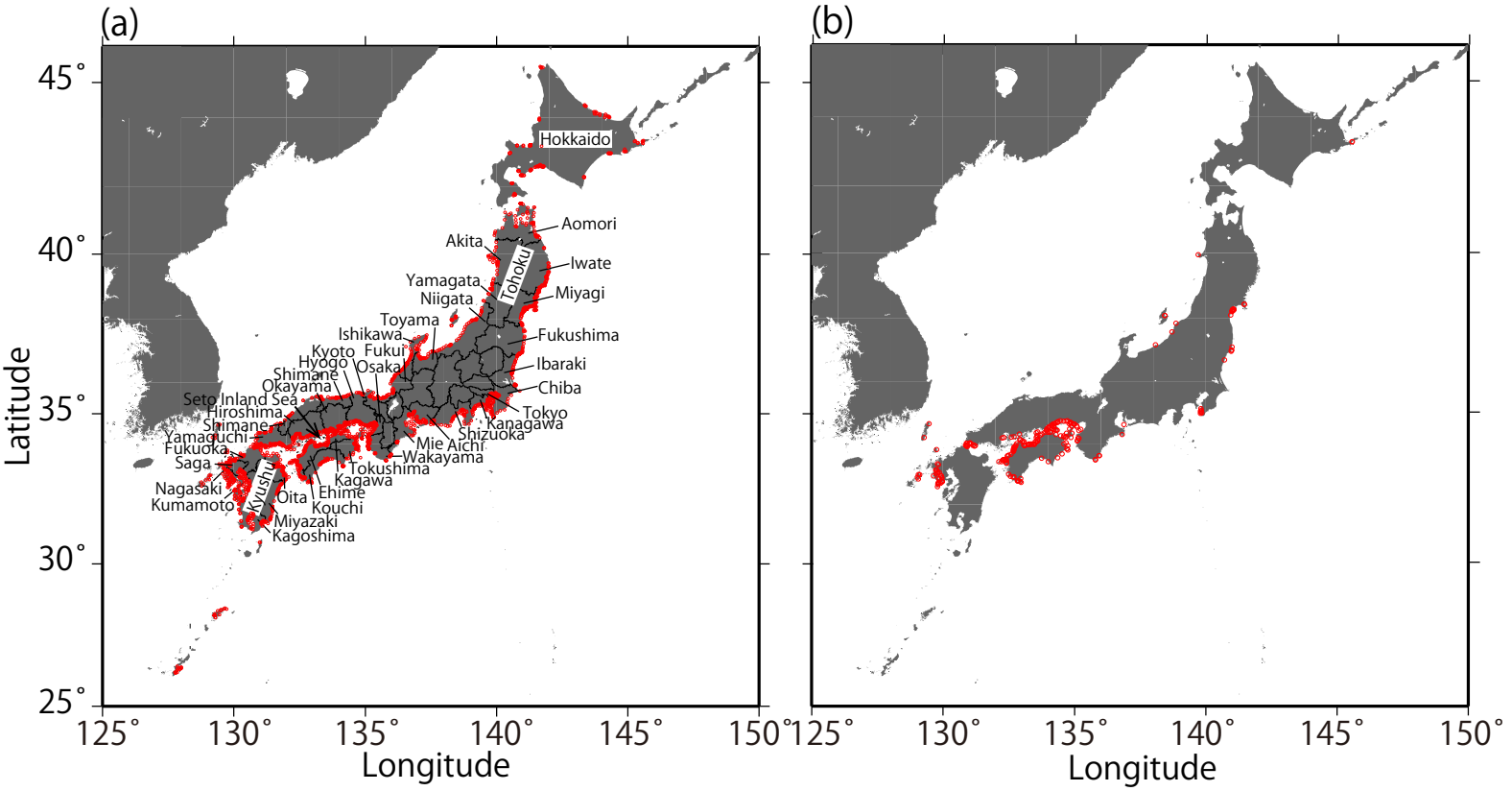


Fig. 1 Coastal maps and monitoring sites in Japan. Red points in (a) indicate the fixed sites (n = 1481) monitored by the Regional Development Bureau of the Ministry of Land, Infrastructure, Transport, and Tourism, and the Ministry of the Environment (Japan) under the WCPL monitoring program. (b) Monitoring sites that met the strictest criterion (n = 302).

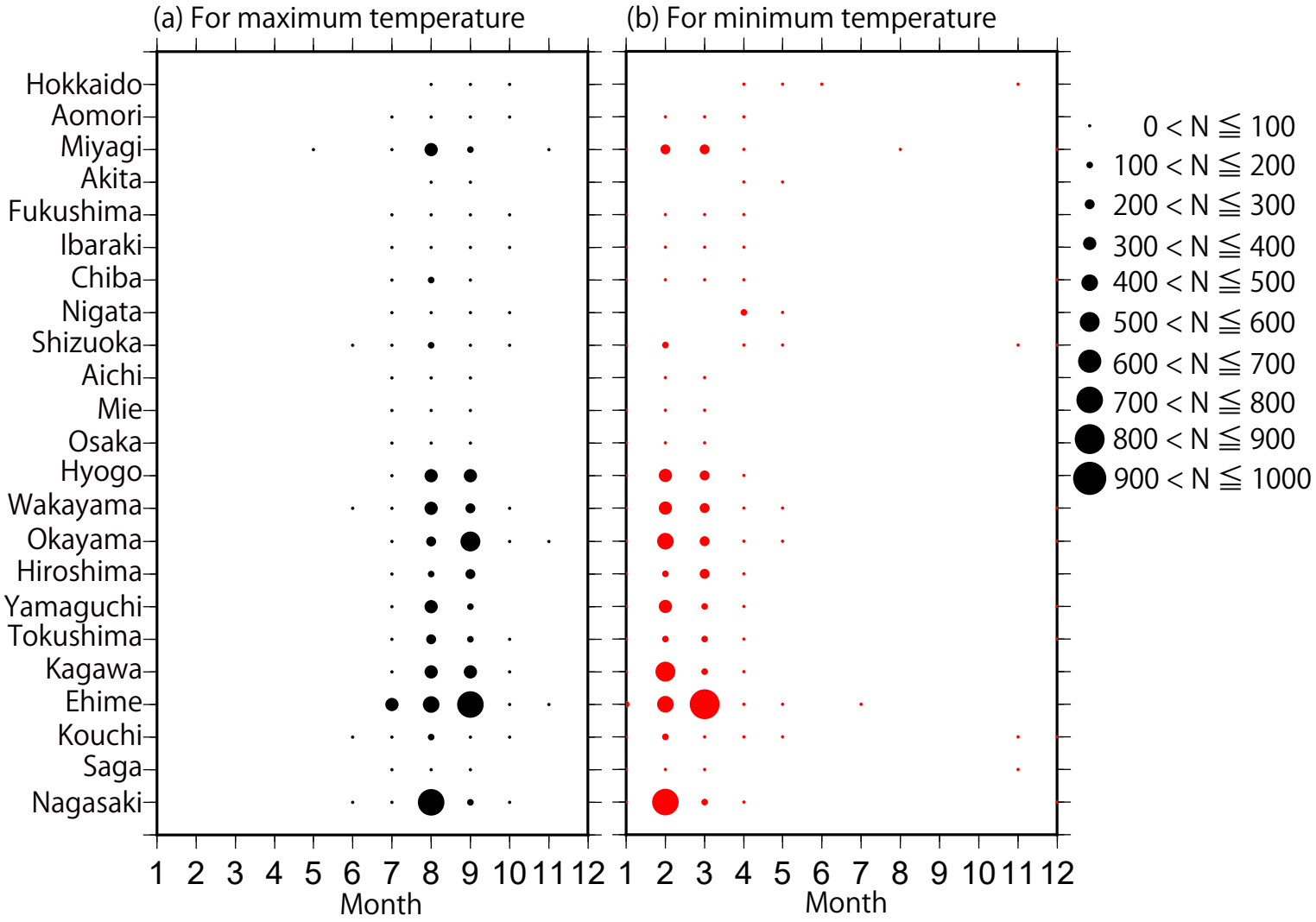


Fig. 2 Distributions of the monthly number of data points (N) for (a) maximum and (b) minimum temperatures collected in each prefecture from the 302 most reliable monitoring sites.

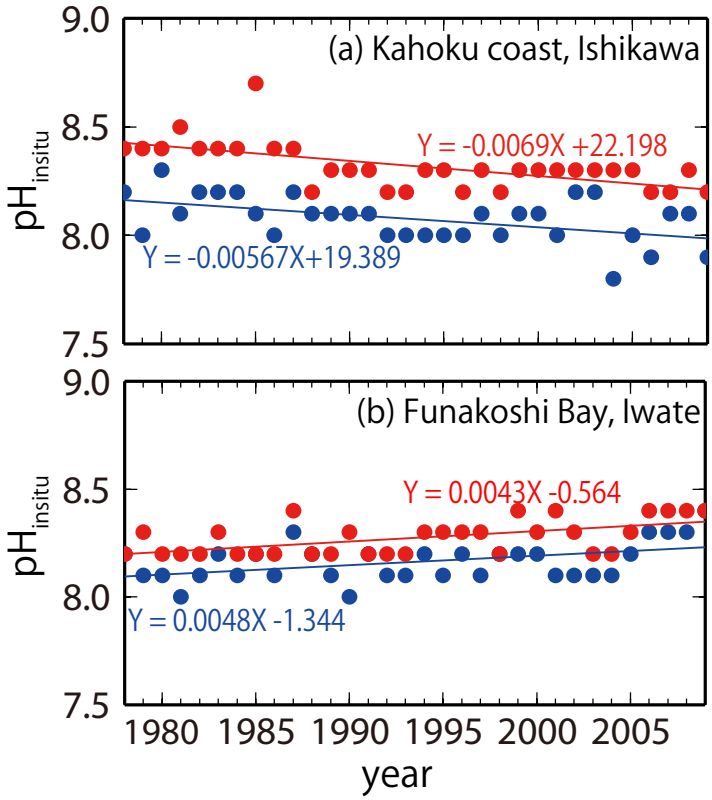


Fig. 3 Examples of (a) acidification (Kahoku Coast in Ishikawa) and (b) basification (Funakoshi Bay in Iwate) trends at monitoring sites. Blue and red colors indicate the annual minimum and maximum pH_{insitu} data and their trends, respectively.

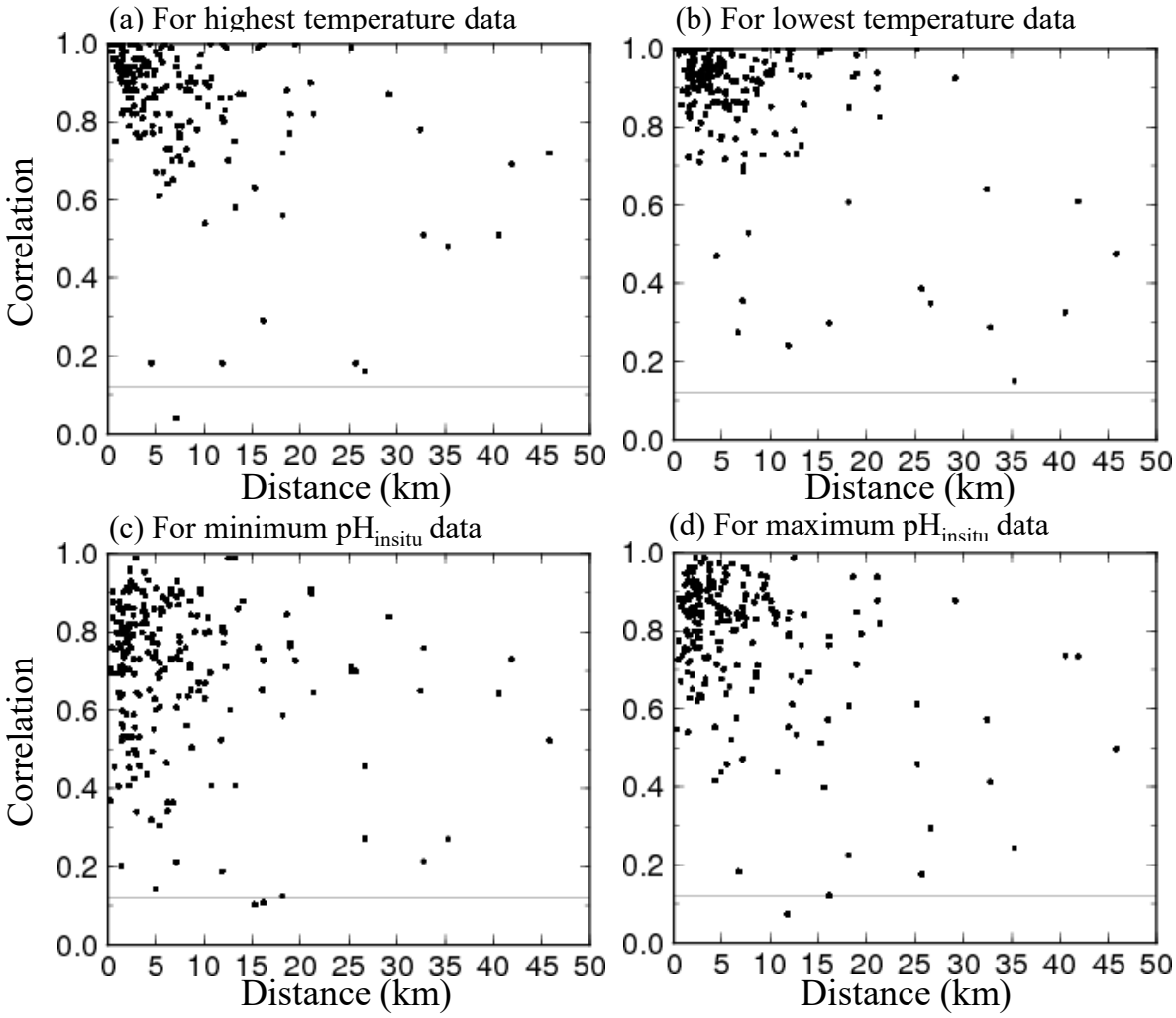


Fig. 4 Correlations of water temperature and pH$_{insitu}$ at adjacent monitoring sites in the same prefecture. Thin lines denote significant correlations ($\boldsymbol{r}$ = 0.12, degrees of freedom = 283).

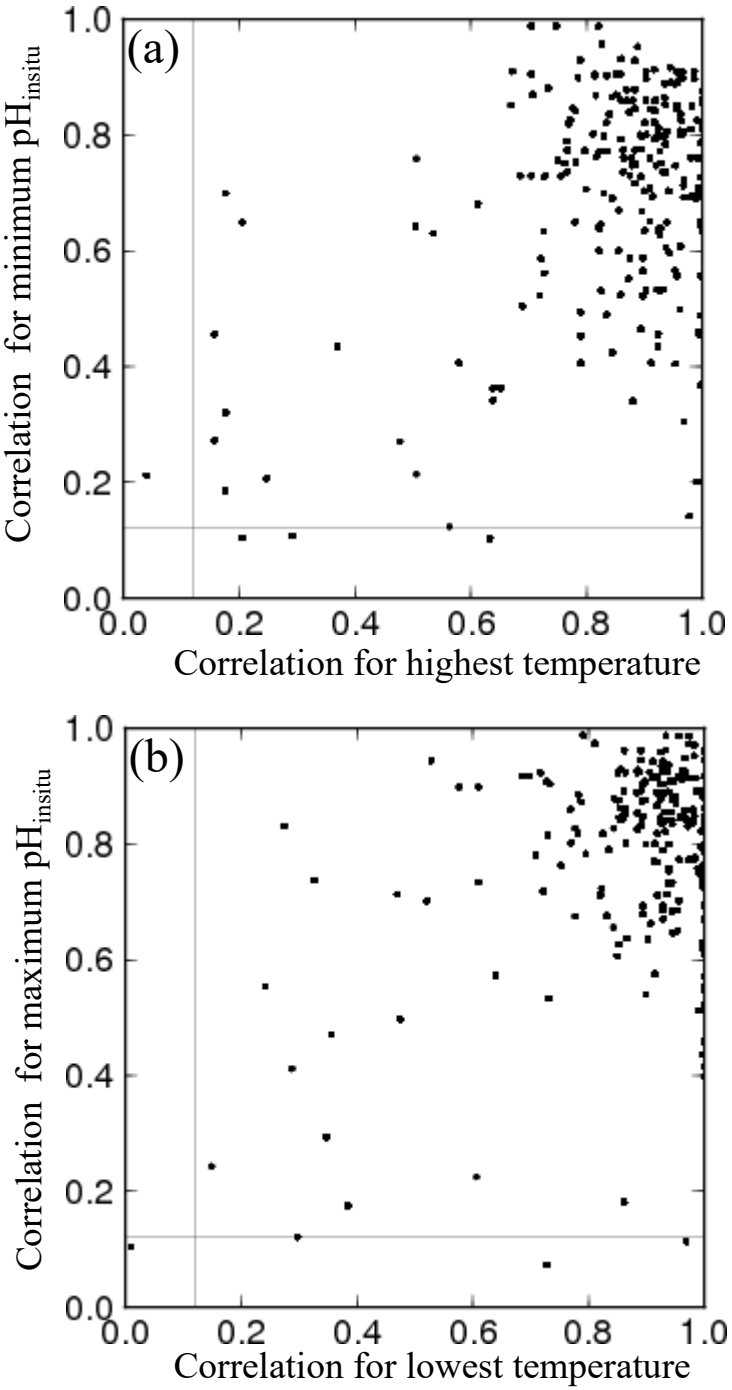


Fig. 5 Scatter plots of correlation coefficients for water temperature and pH_{insitu} at adjacent monitoring sites in the same prefecture. Fig. 5a is for the highest temperature and the minimum $pH_{inisitu}$ data and Fig. 5b for the lowest temperature and the maximum pH_{insitu} data, respectively.

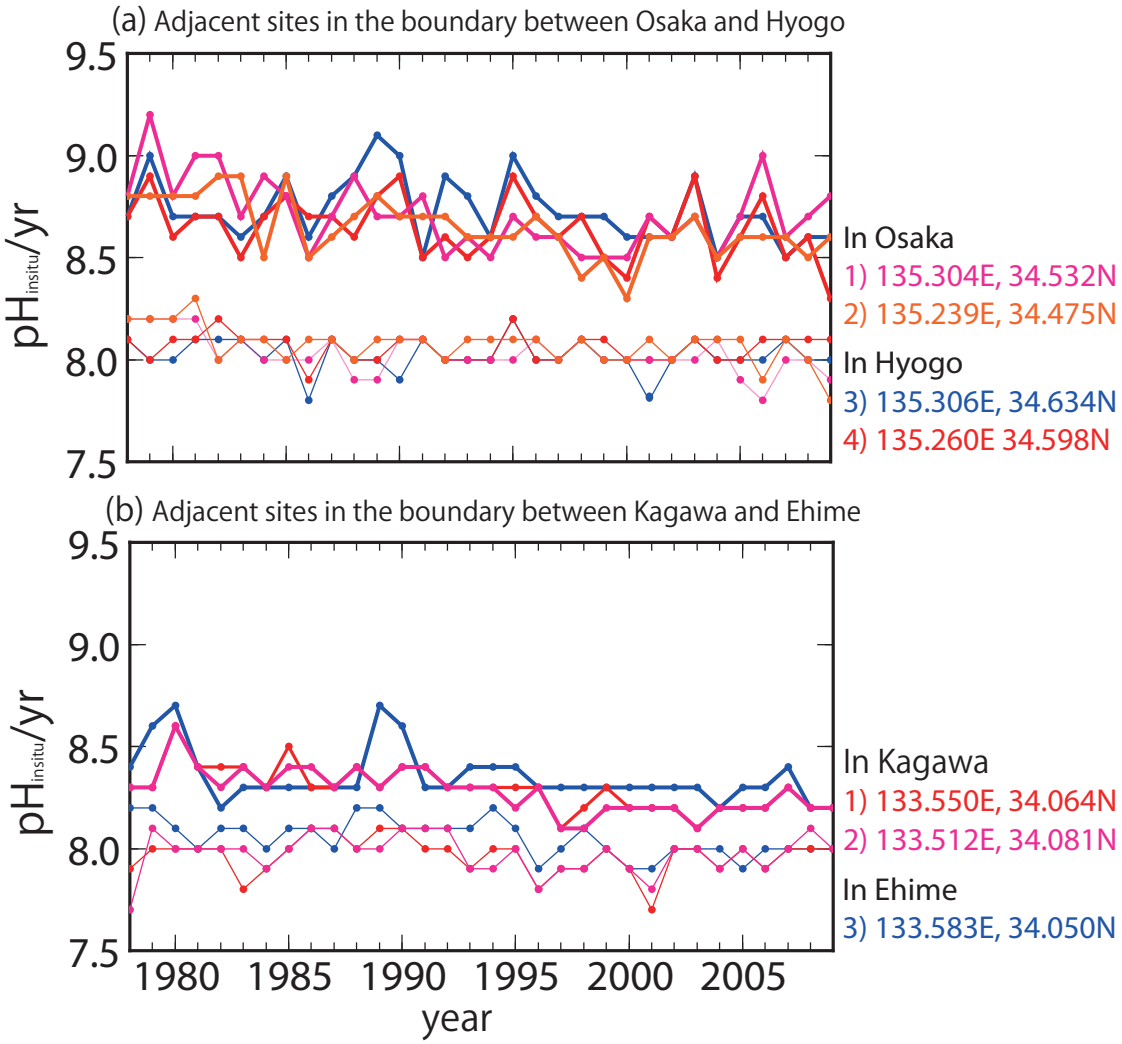
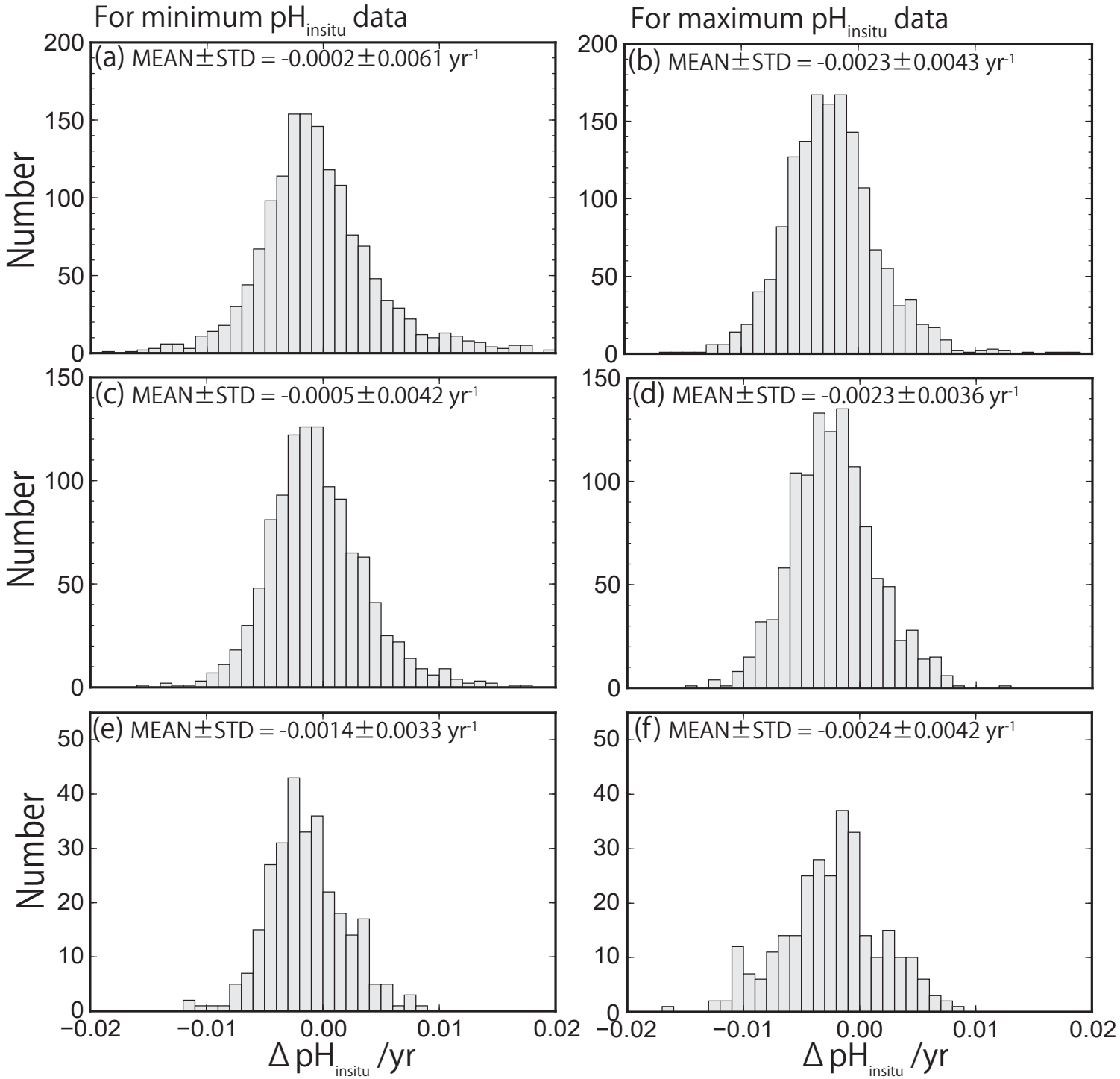


Fig. 6 Examples of time-series for annual minimum and maximum pH_{insitu} data at adjacent monitoring sites close to the boundaries between (a) Osaka and Hyogo and (b) Kagawa and Ehime. Lines of the same color indicate data collected at the same site. Thin and bold lines indicate the annual minimum and 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.



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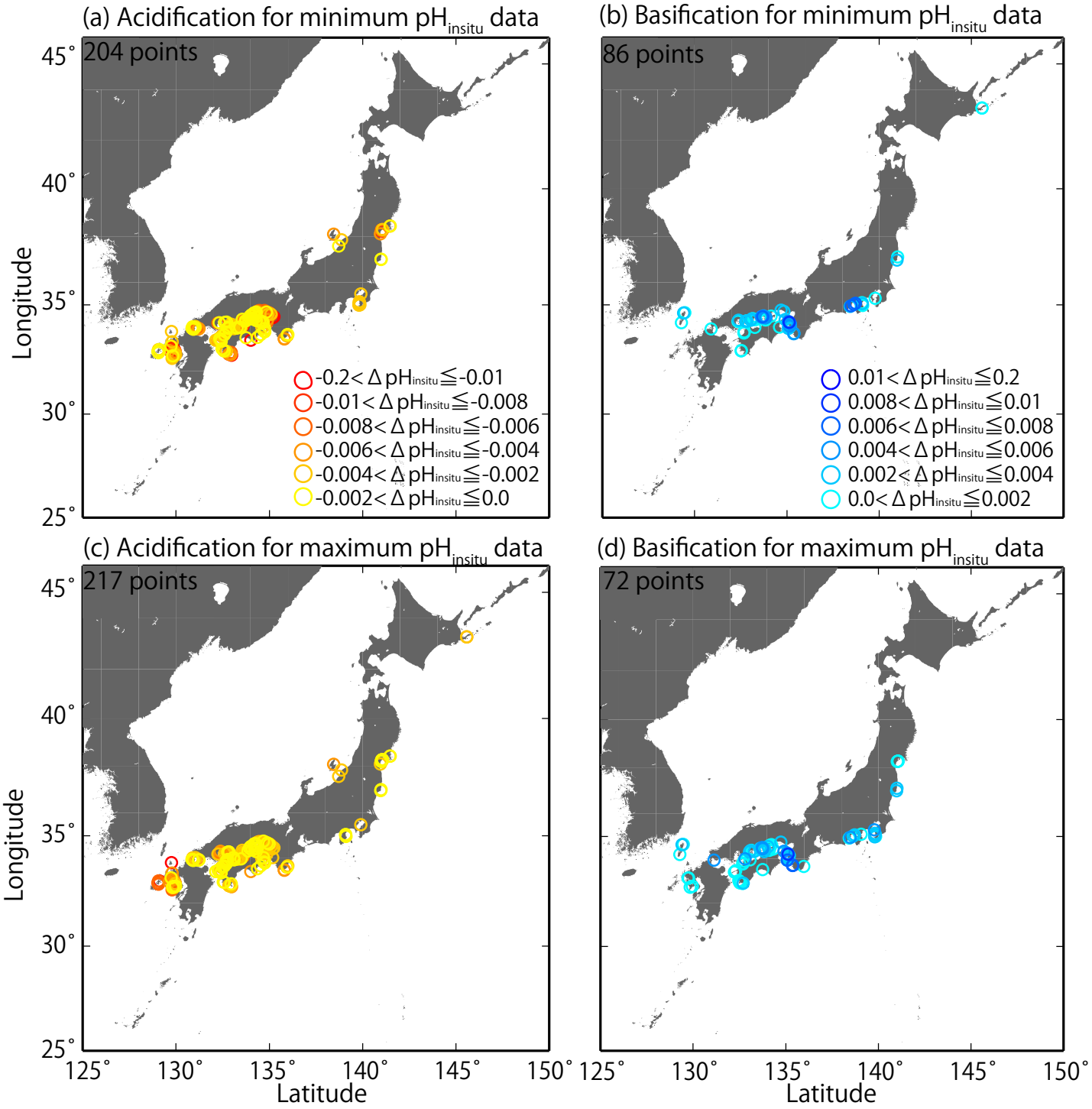
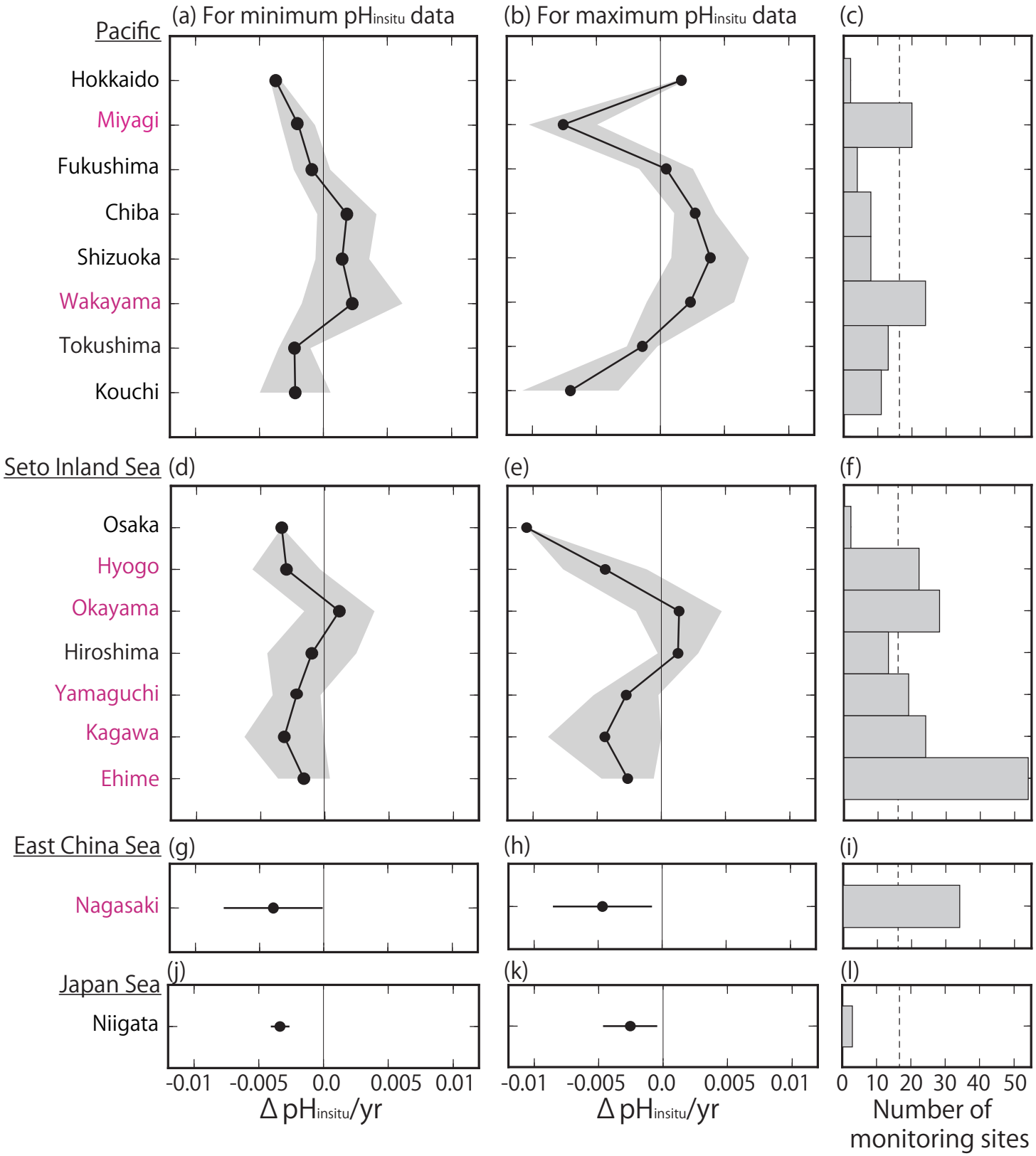


Fig. 8 Distributions of long-term trends in pH$_{insitu}$ (ΔpH$_{insitu}$/yr) in Japanese coastal sea waters. The colors indicate the ranges of acidification (a, c) and basification (b, d). (a, b) and (c, d) are linked to the data used in Figs. 7e and 7f, respectively.



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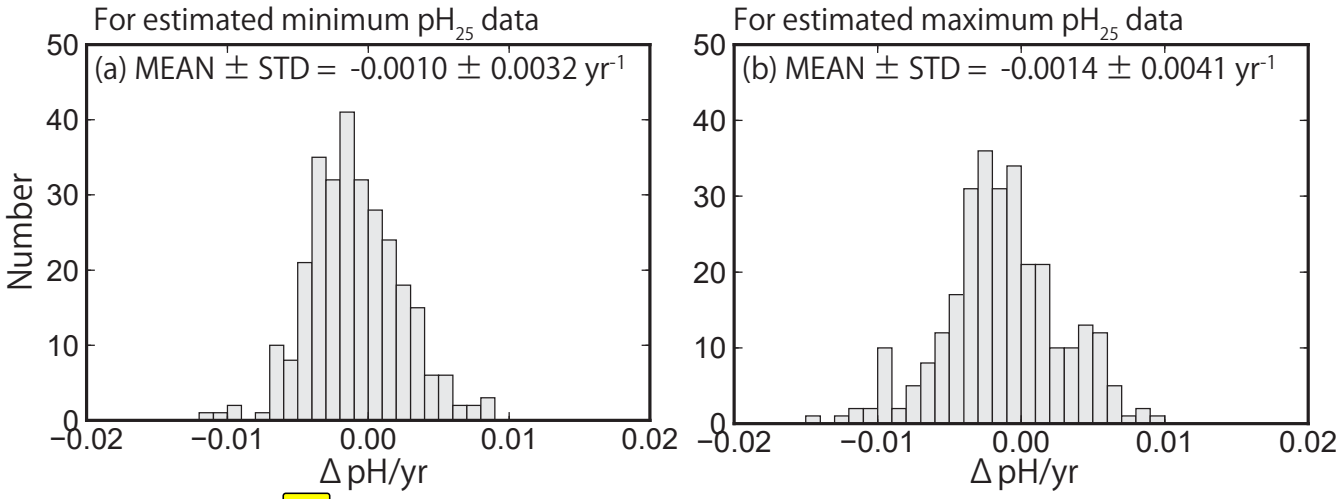
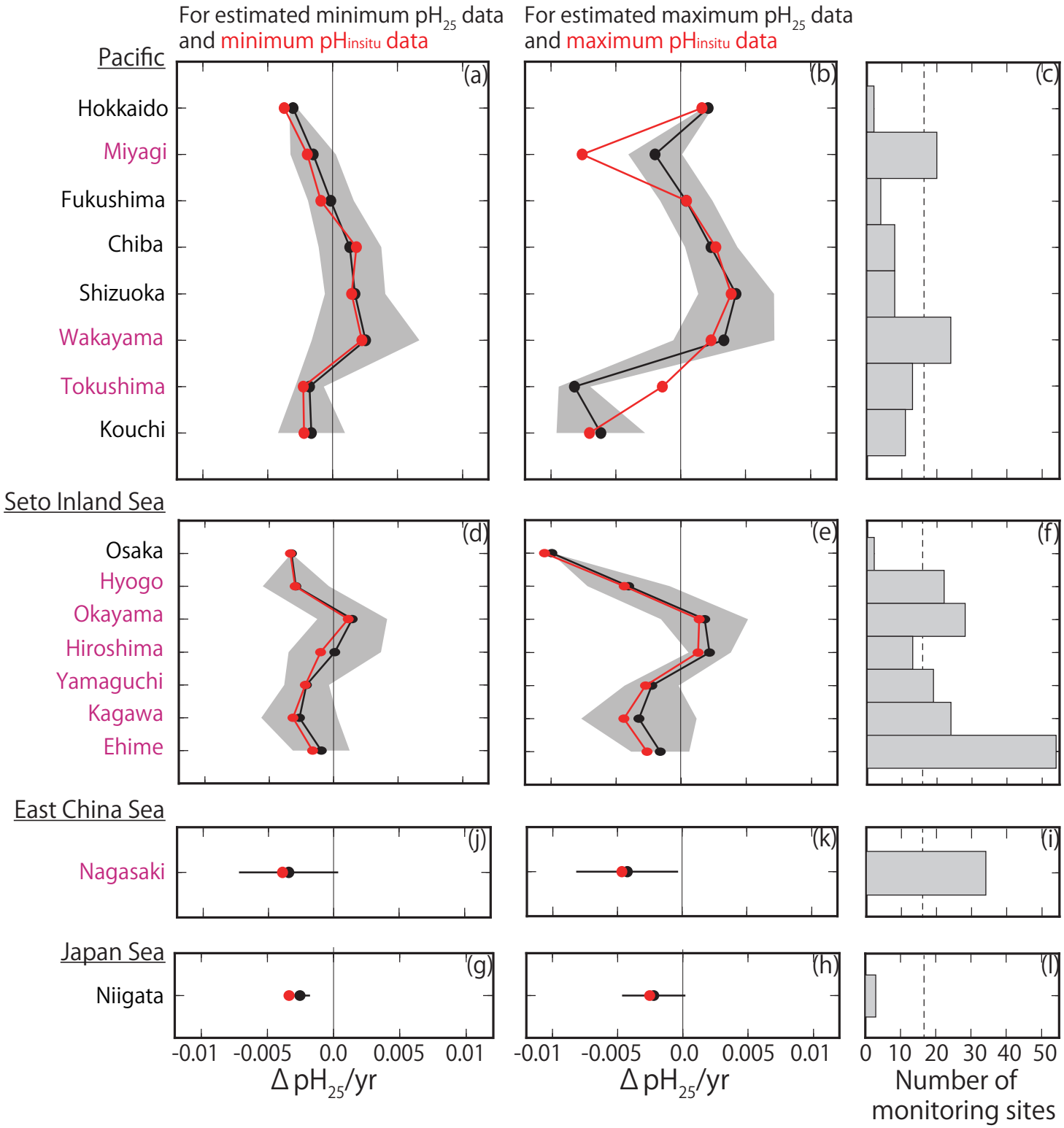


Fig. 10 Same as Fig. 7, but showing the pH_{25} trends at 289 sites (selected by quality control step 3). The value of pH_{25} was estimated using the method of Lui and Chen (2017).



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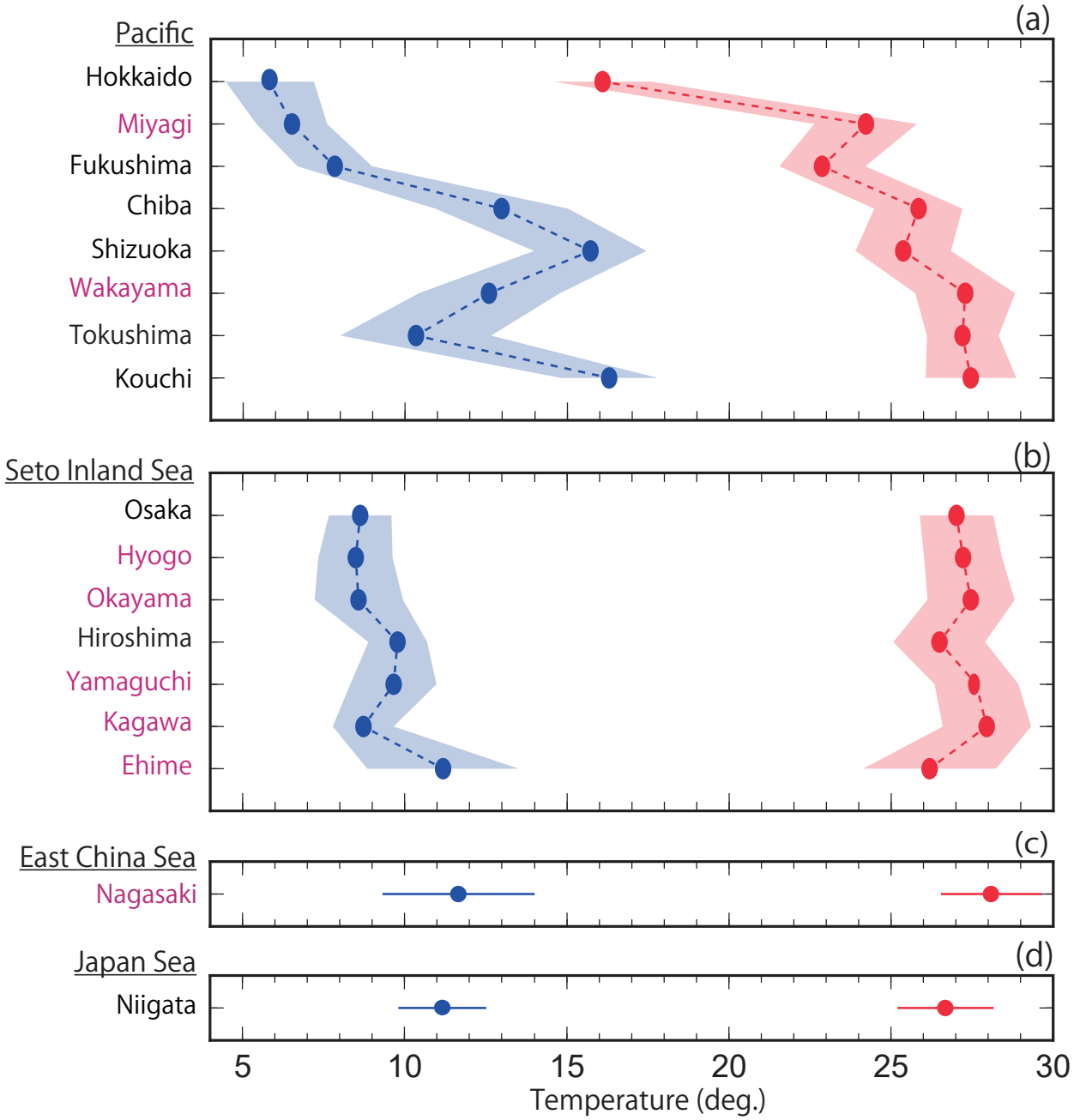

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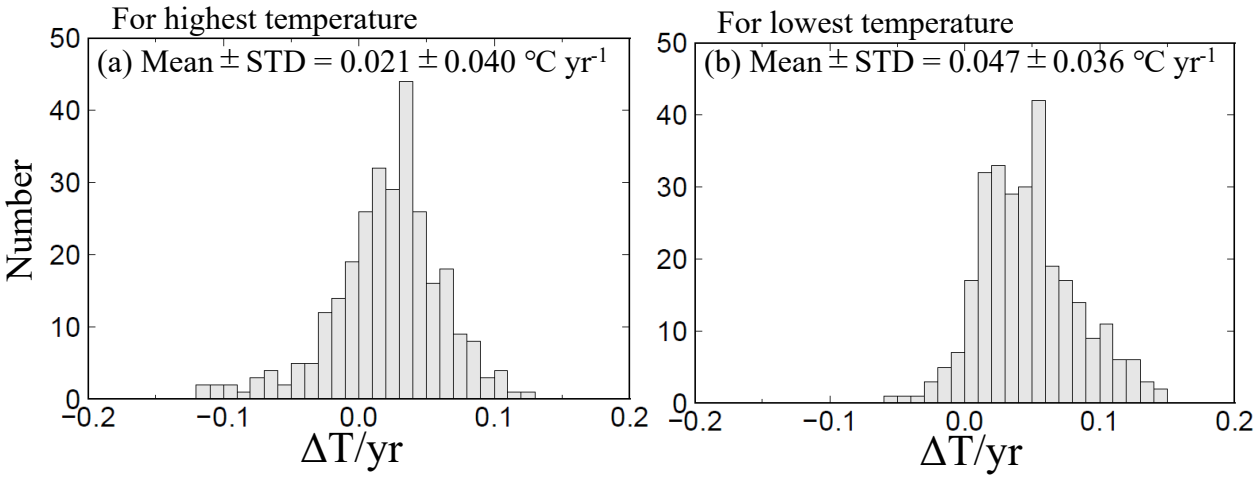

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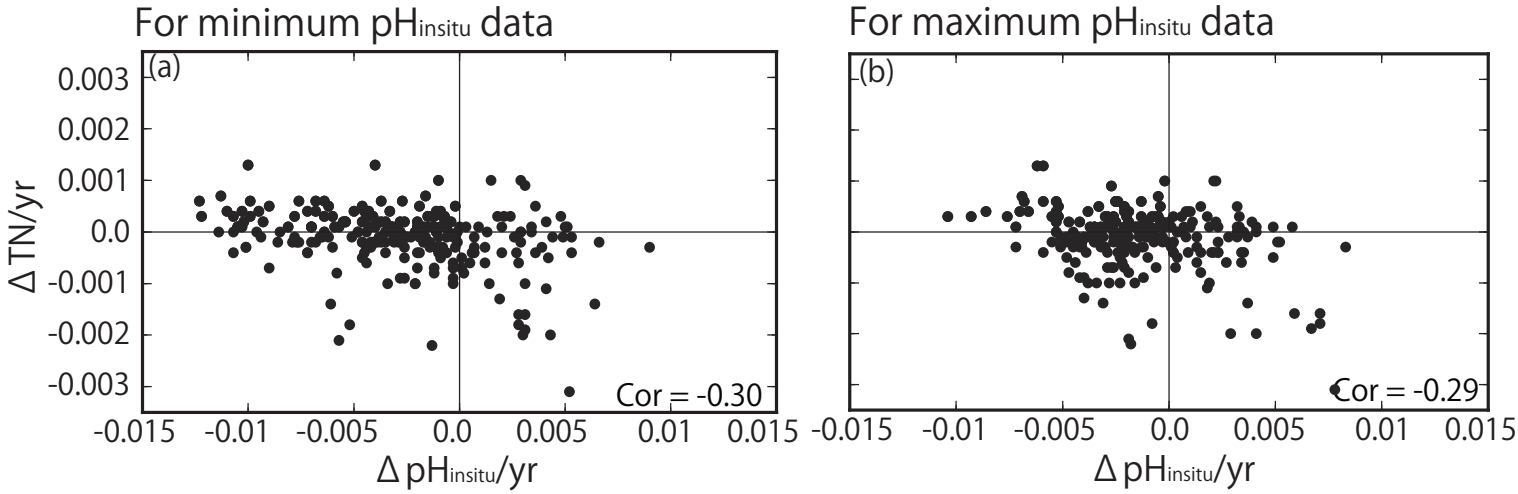

Fig. 14 Correlation between trends in total nitrogen (TN) and trends in (a) minimum and (b) maximum pH_{insitu}. The correlation coefficients are −0.30 and −0.29 for the minimum and maximum pH_{insitu}, respectively (significance level of 0.05, r = 0.128; degrees of freedom = 236).

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

Year	0≦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