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## Ocean acidification off the south coast of Japan: A result from time series observations of CO<sub>2</sub> parameters from 1994 to 2008

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[1] Ocean acidification resulting from increases in present and future atmospheric CO<sub>2</sub> levels could seriously affect diverse coastal and oceanic ecosystems. In this work, we determine that a significant trend in ocean acidification is superposed on the large seasonal and interannual variabilities of acidity in surface waters off the south coast of Honshu, Japan, based on our repeated observations of partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ), total inorganic carbon (TCO<sub>2</sub>), and pH. Multiple regression analysis of TCO<sub>2</sub> as a function of temperature, salinity, and timing of observations shows that TCO<sub>2</sub> increased at a rate of  $+1.23 \pm 0.40 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  for the period 1994–2008, while no long-term change has been determined for total alkalinity calculated from TCO<sub>2</sub> and  $p\text{CO}_2$  in seawater. These results indicate that pH and the aragonite saturation state ( $\Omega_{\text{arag}}$ ) are decreasing at a rate of  $-0.020 \pm 0.007 \text{ decade}^{-1}$  and  $-0.12 \pm 0.05 \text{ decade}^{-1}$ , respectively. If future atmospheric CO<sub>2</sub> levels keep increasing as predicted by the Intergovernmental Panel on Climate Change emission scenario A1FI, which postulates intensive fossil fuel use associated with very rapid economic growth, a further reduction of  $-0.8$  to  $-1.0$  in  $\Omega_{\text{arag}}$  is likely in the next 50 years. Such a rapid reduction of  $\Omega_{\text{arag}}$  could have negative impacts on a variety of calcareous organisms.

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### 1. Introduction

[2] Long-term increases of CO<sub>2</sub> levels in seawater and the atmosphere have been observed in various oceanic zones such as subtropical North Pacific and North Atlantic [e.g., Inoue *et al.*, 1995; Midorikawa *et al.*, 2005; Takahashi *et al.*, 2006; Bates, 2007; Dore *et al.*, 2009], the equatorial Pacific [e.g., Feely *et al.*, 2006; Ishii *et al.*, 2009], subarctic North Pacific and North Atlantic [e.g., Schuster *et al.*, 2009; Metzl *et al.*, 2010; Wakita *et al.*, 2010; Wong *et al.*, 2010] and the Southern Ocean [Inoue and Ishii, 2005; Takahashi *et al.*, 2009; Metzl, 2009]. Although it is important to understand the changes in ocean circulation, biogeochemical processes and their roles in changing oceanic CO<sub>2</sub> levels, the long-term CO<sub>2</sub> increase in the ocean is predominantly attributable

to the absorption of CO<sub>2</sub> that is rapidly increasing in the atmosphere, primarily as a result of human activities such as fossil fuel combustion and land-use changes.

[3] The absorption of CO<sub>2</sub> by the ocean is chemically equivalent to the addition of carbonic acid to seawater. It is evident that the addition of carbonic acid raises the hydrogen ion concentration ( $[\text{H}^+]$ ) and lowers carbonate ion concentration ( $[\text{CO}_3^{2-}]$ ), thus lowering the degree of calcium carbonate (CaCO<sub>3</sub>) saturation of seawater. These changes in carbonate chemistry, commonly referred to as ocean acidification, may seriously affect marine organisms and ecosystems throughout the oceans [Doney *et al.*, 2009]. It is presumed that the ocean acidification has been in progress not only in open oceans where long-term increases in CO<sub>2</sub> have been observed but also in coastal zones through the air-sea CO<sub>2</sub> exchange and mixing with waters from offshore open zones. In addition to habitat loss, water pollution, eutrophication, and overexploitation, ocean acidification may be another human-induced threat to coastal marine ecosystems and sustainable fisheries. However, little is known about the progress of acidification in coastal oceans at present [Santana-Casiano *et al.*, 2007; Feely *et al.*, 2008].

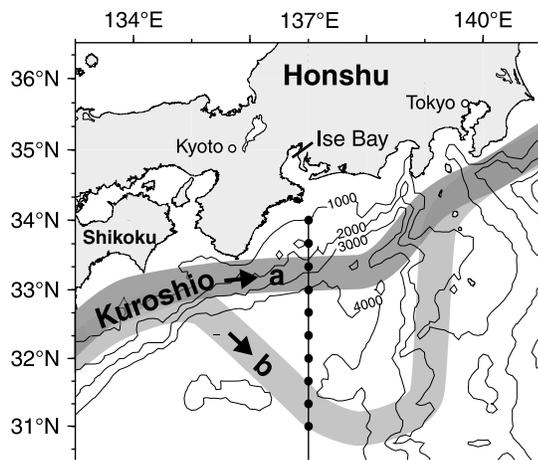
[4] In this study, we focus on the coastal ocean between the south coast of Honshu, Japan, and the Kuroshio (Figure 1), and investigate the trend of ocean acidification on the basis

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**Figure 1.** Repeat stations along 137°E in the vicinity of the Kuroshio off the south coast of Honshu, Japan. Also shown are the approximate positions of the nearshore nonlarge meander path (point a) and offshore large meander path of the Kuroshio (point b).

of the time series data of seawater  $\text{CO}_2$  parameters from samples collected near the surface. In contrast to the oligotrophic open subtropical zone south of the Kuroshio, the studied region in the northern side of Kuroshio is characterized by higher primary productivity ( $>200 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) [Yokouchi *et al.*, 2006] with high biomass of diatom ( $80\text{--}270 \text{ mg m}^{-2}$  in euphotic layer) in spring phytoplankton bloom [Sugisaki *et al.*, 2010]. This is also an important spawning region for many species of pelagic fish such as sardine and mackerel. Owing to the close proximity to densely populated regions in Japan, the fish catch and the crop of aquaculture in this zone amounted to 470,000 tons in 2009 (see [http://www.maff.go.jp/j/tokei/kouhyou/kaimen\\_gyosei/index.html](http://www.maff.go.jp/j/tokei/kouhyou/kaimen_gyosei/index.html)). In regard to calcareous organisms, the crop of aquaculture on the coast included 5000 tons of oysters and 2 tons of pearls. This region is also known as a habitat of a coccolithophore *Gephyrocapsa oceanica*. Its massive bloom sometimes develops extensively in late spring [e.g., Kai *et al.*, 1999]. The south coast of Honshu is also the northern limit of tropical reef corals' habitat in the North Pacific [Yamano *et al.*, 2011].

[5] Trend in  $p\text{CO}_2\text{sw}$  in the northern side of Kuroshio is also quite different from that in the south. Shipboard underway measurements of partial pressure of  $\text{CO}_2$  in surface seawater ( $p\text{CO}_2\text{sw}$ ) and in the overlying atmosphere ( $p\text{CO}_2\text{air}$ ) have been made every winter (January–February) since 1983 from 3°N through 34°N along 137°E [Inoue *et al.*, 1995; Midorikawa *et al.*, 2005]. In the southern side of Kuroshio, the mean rate of  $p\text{CO}_2\text{sw}$  increase for each 1° in latitude between 22°N and 30°N ranged from  $+1.48 \pm 0.10$  to  $+1.70 \pm 0.12 \mu\text{atm yr}^{-1}$  for 1983–2007. These rates were not significantly different from the rate of increase in  $p\text{CO}_2\text{air}$  ( $+1.63 \pm 0.04$  to  $+1.70 \pm 0.03 \mu\text{atm yr}^{-1}$ ) [Midorikawa *et al.*, 2010]. These findings strongly suggest that the surface waters in the open subtropical zone are being acidified as a result of net transfer of anthropogenic  $\text{CO}_2$  into the ocean. The rate of pH decrease has been calculated to be  $-0.019 \pm 0.001$  to  $-0.021 \pm 0.002 \text{ decade}^{-1}$ . In the northern side of Kuroshio at around 34°N above conti-

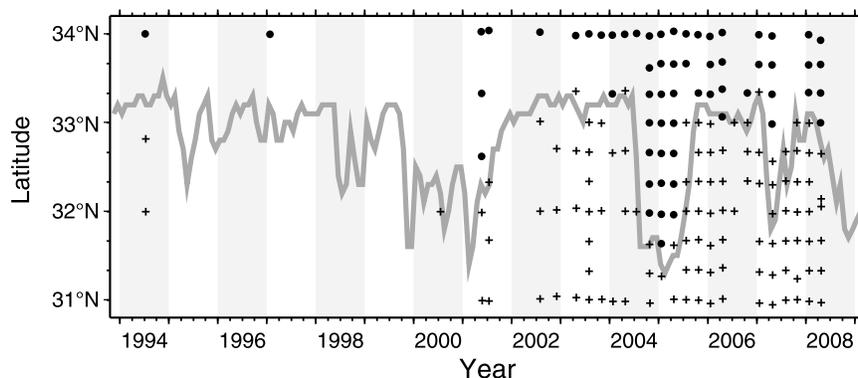
mental slope  $\sim 25 \text{ km}$  off the coast, the long-term increase in  $p\text{CO}_2\text{sw}$  has also been observed in winter ( $+1.78 \pm 0.50 \mu\text{atm yr}^{-1}$ ). However, the interannual variability in  $p\text{CO}_2\text{sw}$  ( $\pm 14.6 \mu\text{atm}$ ) was about three times as large as that in the southern side ( $\pm 3.4$  to  $\pm 5.4 \mu\text{atm}$ ). Owing to this large interannual variability, the uncertainty (standard error) in the rate of  $p\text{CO}_2\text{sw}$  increase ( $\pm 0.50 \mu\text{atm yr}^{-1}$ ) is three to four times as large as that in the south. Sea surface temperature (SST) at 34°N also showed larger interannual variability ( $16.7 \pm 1.4 (1\sigma) \text{ }^\circ\text{C}$ ) than those in the south (e.g.,  $20.0 \pm 0.5 \text{ }^\circ\text{C}$  at 30°N). When thermodynamic effects of SST change,  $+4.0\% \text{ }^\circ\text{C}^{-1}$ , and salinity change,  $+4.4\%$  per salinity unit, were corrected, the rate of long-term increase in  $p\text{CO}_2\text{sw}$  was even more uncertain ( $+1.5 \pm 1.0 \mu\text{atm yr}^{-1}$ ) and statistically not significant ( $\alpha = 0.05$ ). For these reasons, the rate of pH decrease in the coastal ocean north of the Kuroshio at 34°N has not been evaluated from the time series data of  $p\text{CO}_2\text{sw}$  in winter.

[6] In this study, we investigate the seasonal and interannual variability in total dissolved inorganic carbon ( $\text{TCO}_2$ ) and total alkalinity (TA) together with those in SST and salinity that control the variability in  $p\text{CO}_2\text{sw}$  and pH for the coastal ocean north of the Kuroshio. The long-term trends of  $\text{TCO}_2$  and TA in surface water are determined by multiple regression analyses for the data that have been acquired since 1994. The rate of changes in pH and the saturation states of aragonite and calcite are determined from these results for changes in carbonate chemistry, and their future projections are discussed.

## 2. Materials and Methods

[7] Oceanic and atmospheric  $\text{CO}_2$  observations have been repeated together with the hydrographic/hydrochemical observations in the western North Pacific along 137°E onboard the Japan Meteorological Agency's research vessels *Ryofu Maru* and *Keifu Maru*. The frequency of observations has changed from annually each winter in the 1980s, to biannually each winter and summer in the 1990s and early 2000s although  $\text{TCO}_2$  measurements were made at irregular intervals (Figure 2), to each season since 2003.

[8] Underway measurements of  $p\text{CO}_2\text{sw}$  and  $p\text{CO}_2\text{air}$  have been made since 1983 using an automated  $\text{CO}_2$  analyzer equipped with a nondispersive infrared (NDIR) gas analyzer, a showerhead equilibrator and four  $\text{CO}_2$  standards in air. Details of the method have been described by Inoue [2000] and Midorikawa *et al.* [2006]. Seawater was pumped up continuously from the bottom of the ship ( $\sim 5 \text{ m}$  below sea level) and introduced into the equilibrator for  $p\text{CO}_2\text{sw}$  measurements. We think that the error in  $p\text{CO}_2\text{sw}$  data is  $\pm 2 \mu\text{atm}$ . This is primarily ascribed to the uncertainty ( $\pm 0.1 \text{ }^\circ\text{C}$ ) in measuring the temperature change of water in the inner piping from the water intake to the equilibrator and its thermodynamic effect on  $p\text{CO}_2\text{sw}$  (about  $+4.0\% \text{ }^\circ\text{C}^{-1}$ ). The data of  $p\text{CO}_2$  obtained by JMA are available from the World Data Centre for Greenhouse Gases (WDCGG; <http://gaw.kishou.go.jp/wdcgg/>). They have also been stored in LDEO Database V2009 [Takahashi *et al.*, 2010] ([http://cdiac.ornl.gov/oceans/LDEO\\_Underway\\_Database/](http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/)) and Surface Ocean Carbon Atlas (SOCAT) Database (<http://cdiac.ornl.gov/oceans/SOCAT/>).



**Figure 2.** Time series of the southernmost latitude of the Kuroshio axis at 136°–140°E ([http://www.data.kishou.go.jp/shindan/b\\_2/kuroshio\\_stream/kuroshio\\_stream.html](http://www.data.kishou.go.jp/shindan/b_2/kuroshio_stream/kuroshio_stream.html)) and time-latitude distributions of total dissolved inorganic carbon ( $\text{TCO}_2$ ) data along 137°E in the north (circles) and the south (crosses) of the Kuroshio.

[9] Since 1994,  $\text{TCO}_2$  has been measured using a  $\text{CO}_2$  extraction–coulometry method [Ishii *et al.*, 1998], and since 2003, pH has been measured using an indicator dye–spectrophotometry method in total hydrogen ion concentration scale ( $\approx -\log_{10}\{([\text{H}^+]_{\text{F}} + [\text{HSO}_4^-])/\mu\text{mol kg}^{-1}\}$ ) at 25°C ( $\text{pH}_{\text{T}25}$ ) [Saito *et al.*, 2008]. Samples for  $\text{TCO}_2$  and  $\text{pH}_{\text{T}25}$  analyses were taken from the water that was continuously pumped up for  $p\text{CO}_{2\text{sw}}$  measurement or water taken at 5 m below sea surface with Niskin bottles on CTD/carousel multi sampler. They have been sampled in 250  $\text{cm}^3$  borosilicate glass bottles with ground glass stoppers lubricated with Apiezon L grease. For the majority of cruises, samples were poisoned with mercury(II) chloride and analyzed in the laboratory on land after the cruise. During some cruises, samples were measured onboard immediately after collection. In July 1994, samples for  $\text{TCO}_2$  have also been collected at depths from the surface to near bottom at some stations around the Kuroshio as a part of World Ocean Circulation Experiment Hydrographic Program P09 one-time cruise, and they were analyzed immediately after sampling on board. To establish the identical concentration scale among cruises, we used numbers of batches of Certified Reference Material (CRM) for  $\text{TCO}_2$  and TA analyses provided by Dickson [1991] and Dickson *et al.* [2003] (<http://andrew.ucsd.edu/co2qc/index.html>) for quality control. Certified values of  $\text{TCO}_2$  and TA were used to calculate the reference value of  $\text{pH}_{\text{T}25}$  for quality control of  $\text{pH}_{\text{T}25}$  measurements. We used dissociation constants for carbonic acid given by Lueker *et al.* [2000] as recommended by Dickson *et al.* [2007] in all calculations of carbonate chemistry in seawater. We also prepared a lot of batches of reference seawater in a similar method to that of Dickson [1991] from the oligotrophic surface waters in western North Pacific, and calibrated its  $\text{TCO}_2$  and  $\text{pH}_{\text{T}25}$  with the CRM. Before and after each run of analyses (usually 20 to 30 samples in each run), either CRM or reference seawater was also analyzed. The precision of analysis is smaller than  $\pm 2 \mu\text{mol kg}^{-1}$  for  $\text{TCO}_2$  and smaller than  $\pm 0.002$  for  $\text{pH}_{\text{T}25}$ .

[10] The value of TA was calculated from  $p\text{CO}_{2\text{sw}}$ ,  $\text{TCO}_2$ , SST and salinity for 1994–2008. Its repeatability is estimated to be  $\pm 3 \mu\text{mol kg}^{-1}$  from the precisions of  $p\text{CO}_{2\text{sw}}$  and  $\text{TCO}_2$  measurements. For 2003–2008, the value of TA was also calculated from  $\text{pH}_{\text{T}25}$ ,  $\text{TCO}_2$  and

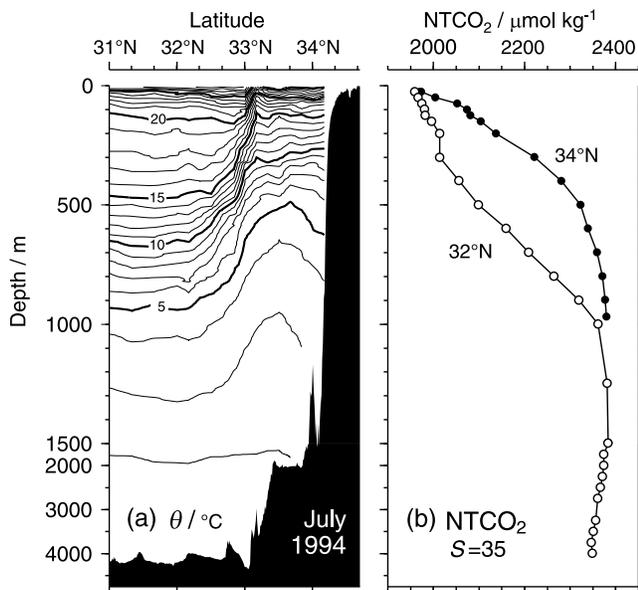
salinity at 25°C. The differences in TA values calculated from these pairs of  $\text{CO}_2$  parameters were  $2.4 \pm 3.0 \mu\text{mol kg}^{-1}$  (mean  $\pm 1s$ ;  $n = 62$ ) for samples collected from 32°N to 34°N. Midorikawa *et al.* [2010] also showed that  $\text{pH}_{\text{T}25}$  measured with spectrophotometry and that calculated from  $p\text{CO}_2$ ,  $\text{TCO}_2$ , SST and salinity also agreed well. Their difference averaged  $0.0026 \pm 0.0050$  (mean  $\pm 1s$ ) in winters of 2003–2008, supporting the internal consistency of  $\text{CO}_2$  parameters when the dissociation constants given by Lueker *et al.* [2000] was used for calculations. We also calculated pH at SST from  $\text{pH}_{\text{T}25}$ ,  $\text{TCO}_2$ , SST and salinity, and the saturation state ( $\Omega$ ) for both naturally occurring crystal forms of calcium carbonate, aragonite and calcite, using their apparent solubility products  $K'_{\text{sp}}$  [Mucci, 1983]:

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K'_{\text{sp}}. \quad (1)$$

### 3. Oceanographic Setting

[11] The Kuroshio is the western boundary current in the subtropical zone of the western North Pacific. At around 137°E, it usually flows due eastward at around 33°10'N above the continental rise (nearshore nonlarge meander path) (Figures 1 and 2). However, it sometimes takes offshore large meander paths [Kawabe, 1985]. One of the remarkable meanders has occurred in August 2004 and continued until July 2005 for 1 year. In this period, the strongest part of the Kuroshio, the Kuroshio axis, that is conventionally defined as the latitude where the 15°C isotherm intersects the 200 m isodepth [Kawai, 1969], has been steadily located south of 32°N and moved even further south to 31°20'N in February 2005 (Figure 2) (<http://www.data.kishou.go.jp/kaiyou/db/kaikyoseries/junkro.html>). Consequently, the locations of sampling stations at 31°40'N through 33°20'N moved back and forth between the southern and the northern sides of the Kuroshio depending on its path for 1994–2008. In contrast, the stations at 33°40'N and 34°00'N that are located nearshore above the continental slope have always been on the northern side of the Kuroshio.

[12] The Kuroshio is a geostrophic current, and the depths of isotherms and contour lines of other physical and chemical parameters change largely across the Kuroshio



**Figure 3.** (a) Vertical section of potential temperature between 31°N and 34°N and (b) vertical profiles of salinity-normalized TCO<sub>2</sub> ( $S = 35$ ) at 32°N and 34°N along 137°E in July 1994 during the World Ocean Circulation Experiment P09 cruise. Data are available from the Climate Variability and Predictability program and the Carbon Hydrographic Data Office (<http://cchdo.ucsd.edu/pacific.html>).

(Figure 3a) [Kaneko *et al.*, 1998]. For example, in July 1994 when the Kuroshio took a nearshore nonlarge meander path, the 15°C isotherm lay at the depth of ~450 m in the southern offshore side, but it lay at ~120 m in the northern nearshore side. The mixed layer in winter can reach 150 m below surface (Figure 4) in the north while it can reach 200 m in the south. Accordingly, mean SST in midwinter (early March) is significantly lower in the north than in the south ( $+14.9 \pm 1.3^\circ\text{C}$  and  $+19.1 \pm 0.5^\circ\text{C}$  in  $1^\circ \times 1^\circ$  pixel centered at 137.5°E, 34.5°N and 137.5°E, 30.5°N for 1994–2008, respectively).

[13] The vertical profiles of TCO<sub>2</sub> as well as other chemical components also differ largely between the southern and the northern sides. In the north, the vertical gradient of TCO<sub>2</sub> in the top 500 m is much steeper than in the south (Figure 3b). In July 1994, NTCO<sub>2</sub> at the depth of 100 m, which is thought to be near the bottom of the mixed layer in the preceding winter, was  $2074 \mu\text{mol kg}^{-1}$ . It was more than  $100 \mu\text{mol kg}^{-1}$  higher than in the surface ( $1970 \mu\text{mol kg}^{-1}$ ) and suggests the importance of vertical mixing in raising the NTCO<sub>2</sub> in surface water in winter.

[14] Direction of coastal current changes with time ([http://www.data.kishou.go.jp/kaiyou/db/kobe/jun/current\\_k.html](http://www.data.kishou.go.jp/kaiyou/db/kobe/jun/current_k.html)). When Kuroshio takes offshore large meander path, a westward current prevails at around 34°N due to the cyclonic eddy formed in the interior of the meander path [e.g., Rikiishi, 1974; Kamachi *et al.*, 2004], and this region becomes rather warmer [Sugimoto and Yoshida, 2005] (Figure 4). It has also been recognized that the oceanic water in the off of south coast intrudes into the adjacent coastal basins such as Ise Bay by tidal current [Kasai *et al.*, 2004]. Intrusion of the

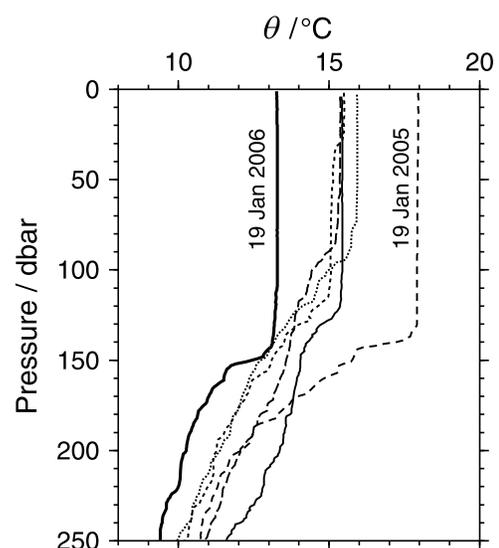
oceanic water greatly affects physical, chemical and biological properties in the coastal basins.

## 4. Results

### 4.1. Seasonal and Interannual Variations

[15] The coastal ocean south of Honshu is a strong sink for atmospheric CO<sub>2</sub>, as is the same latitudinal zone in the open western North Pacific around the Kuroshio Extension [Takahashi *et al.*, 2009]. In spring,  $p\text{CO}_{2\text{sw}}$  usually shows the lowest values that are about  $80 \mu\text{atm}$  lower than  $p\text{CO}_{2\text{air}}$  (Figure 5a). In summer,  $p\text{CO}_{2\text{sw}}$  tends to show the highest values that are comparable to  $p\text{CO}_{2\text{air}}$ . Also note that, in fall and winter,  $p\text{CO}_{2\text{sw}}$  shows large interannual variability. For example,  $p\text{CO}_{2\text{sw}}$  at 34°N was  $314 \mu\text{atm}$  in January 2005 and  $362 \mu\text{atm}$  in January 2006.

[16] These large seasonal and interannual variations in  $p\text{CO}_{2\text{sw}}$  are attributable to large variations in SST ( $+13.7$  to  $+27.6^\circ\text{C}$ ) and salinity-normalized TCO<sub>2</sub> (NTCO<sub>2</sub>) ( $1969$  to  $2088 \mu\text{mol kg}^{-1}$  at  $S = 35$ ; Figures 5b and 5f). In general, NTCO<sub>2</sub> increases as SST decreases, but their relationship varies among SST domains (Figure 6). In warm seasons ( $+23^\circ\text{C} < \text{SST}$ ) when  $p\text{CO}_{2\text{sw}}$  varies widely ( $315$  to  $384 \mu\text{atm}$ ), variations in NTCO<sub>2</sub> are relatively small ( $1969$  to  $1991 \mu\text{mol kg}^{-1}$ ), and the thermodynamic effects of temperature changes (about  $+4.0\% \text{ } ^\circ\text{C}^{-1}$ ) mainly control the variation of  $p\text{CO}_{2\text{sw}}$ . In the SST range from  $16.5^\circ\text{C}$  to  $21.5^\circ\text{C}$ , when  $p\text{CO}_{2\text{sw}}$  is the lowest ( $275$  to  $322 \mu\text{atm}$ ), the change in NTCO<sub>2</sub> is large ( $1981$  to  $2029 \mu\text{mol kg}^{-1}$ ) and its effect on  $p\text{CO}_{2\text{sw}}$  compensates for the thermodynamic effect of temperature change. Consequently,  $p\text{CO}_{2\text{sw}}$  is apparently insensitive to changes in SST. In the coldest time (SST  $< +16^\circ\text{C}$ ), the effect of the change in NTCO<sub>2</sub> ( $2042$  to  $2088 \mu\text{mol kg}^{-1}$ ) becomes dominant, and  $p\text{CO}_{2\text{sw}}$  increases as SST decreases. The marked increase in NTCO<sub>2</sub> causes the increase in  $p\text{CO}_{2\text{sw}}$  in winter (Figure 5a), and the large interannual variability of  $p\text{CO}_{2\text{sw}}$  in winter is mainly ascribed to the large interannual



**Figure 4.** Vertical profiles of temperature at 137°E, 34°N observed in each January of 2003–2008.

variability of  $\text{NTCO}_2$  that is closely related to the variability of SST.

[17] The  $\text{pH}_{\text{T}25}$  is lower (7.90 to 7.94) in winter and higher (8.08 to 8.16) in summer (Figure 5c). This seasonality is opposite that of  $\text{NTCO}_2$ . In contrast, salinity-normalized total alkalinity (NTA) calculated from  $p\text{CO}_{2\text{sw}}$  and  $\text{TCO}_2$ , or  $\text{TCO}_2$  and  $\text{pH}_{\text{T}25}$ , together with temperature and salinity shows very small variation (Figure 5d). The mean value of NTA calculated from  $p\text{CO}_{2\text{sw}}$  and  $\text{TCO}_2$  is  $2305.1 \pm 5.0 \mu\text{mol kg}^{-1}$  ( $n = 52$ ), which is significantly higher than in the south of Kuroshio ( $2295.1 \pm 5.2 \mu\text{mol kg}^{-1}$ ;  $n = 159$ ) calculated in the same method [Midorikawa *et al.*, 2010]. These results indicate that changes in  $\text{pH}_{\text{T}25}$  are tightly coupled to changes in  $\text{NTCO}_2$ . The controlling factors of seasonal  $\text{NTCO}_2$  variation are yet to be quantified, but are

possibly ascribed to the vertical mixing in fall and winter, net biological  $\text{CO}_2$  uptake in winter and summer, and net air-sea  $\text{CO}_2$  exchange as in the south of the Kuroshio [Ishii *et al.*, 2001].

[18] In contrast to the seasonal variation of  $\text{pH}_{\text{T}}$  measured at  $25^\circ\text{C}$ ,  $\text{pH}$  at in situ temperatures ( $\text{pH}_{\text{TSSST}}$ ) tends to be higher (8.14–8.18) in winter and spring, and lower ( $\sim 8.06$ ) in summer (Figure 5c). As for  $p\text{CO}_{2\text{sw}}$ , such a seasonal variation in  $\text{pH}_{\text{TSSST}}$  is attributable to variations in SST and  $\text{NTCO}_2$ . In warm seasons, the increase in SST has a large thermodynamic effect on carbonate chemistry and elevates the concentration of hydrogen ion in seawater.

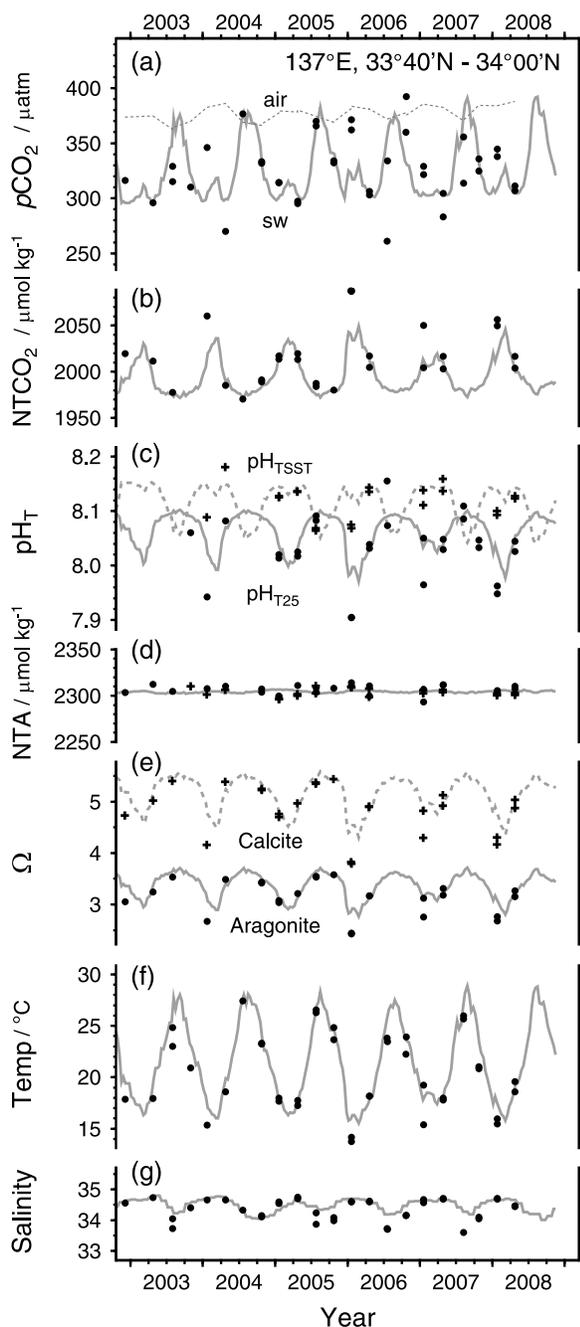
[19] The seasonality of  $\Omega$  is similar to that of  $\text{pH}_{\text{T}25}$  rather than of  $\text{pH}_{\text{TSSST}}$  (Figure 5e). In summer, saturation state of aragonite ( $\Omega_{\text{arag}}$ ) reaches its maximum value of about 3.8, but it decreases in winter to less than 3.0. Note that  $\Omega_{\text{arag}}$  dropped to 2.45 in January 2006 when conditions of low SST ( $13.7^\circ\text{C}$ ), high  $\text{NTCO}_2$  ( $2088 \mu\text{mol kg}^{-1}$ ), and low  $\text{pH}_{\text{T}25}$  (7.905) were observed at the sampling site of  $34^\circ\text{N}$ .

## 4.2. Multiple Regression Analysis for Long-Term Trends

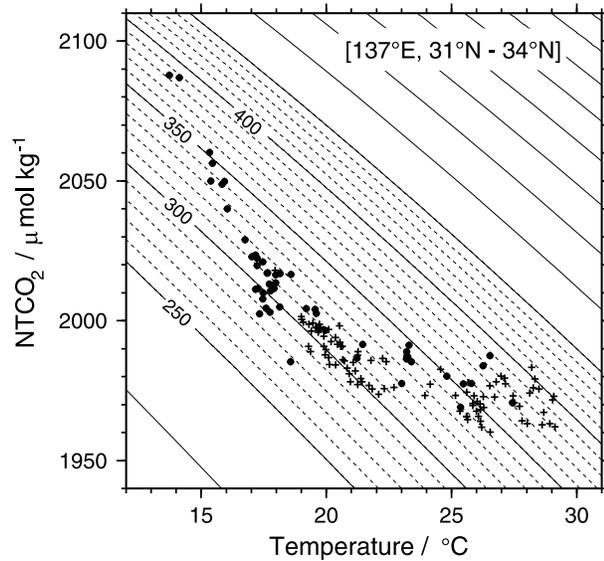
[20] In this study, we applied multiple regression analysis to  $\text{NTCO}_2$  data from measurements and NTA data calculated from  $p\text{CO}_{2\text{sw}}$  and  $\text{TCO}_2$  in surface water. The observed  $\text{NTCO}_2$  was fitted as an empirical function of timing of observation (yr) and physical parameters such as temperature (SST) and salinity (SSS):

$$\begin{aligned} \text{NTCO}_2 / \mu\text{mol kg}^{-1} &= \text{TCO}_2 \cdot S^{-1} \cdot 35 / \mu\text{mol kg}^{-1} \\ &= f(\text{yr}, \text{SST}, \text{SSS}) = c_0 + c_1 \cdot \text{yr} + c_2 \cdot \text{SST} \\ &\quad + c_3 \cdot \text{SST}^2 + c_4 \cdot \text{SST}^3 + c_5 \cdot \text{SSS} + \varepsilon, \end{aligned} \quad (2)$$

where  $\text{yr} = \text{year} - 2000$ ,  $\text{SST} = \text{temperature}/^\circ\text{C} - 20.0$ , and  $\text{SSS} = \text{salinity} - 35.0$ . The terms  $c_0$ ,  $c_1$ ,  $c_2$ ,  $c_3$ ,  $c_4$ , and  $c_5$  are coefficients of multiple regression, and  $\varepsilon$  represents the residual of the fitting. The polynomial of temperature (SST)



**Figure 5.** Time series of seawater  $\text{CO}_2$  and hydrographic parameters in surface water of the coastal ocean south of Honshu, Japan (a composite of data at  $137^\circ\text{E}$ ,  $33^\circ40'\text{N}$ – $34^\circ\text{N}$ ), for December 2002–April 2008. (a) Partial pressure of  $\text{CO}_2$  in seawater ( $p\text{CO}_{2\text{sw}}$ , circles) and in the atmosphere (dashed shaded line); (b) salinity-normalized total inorganic carbon at  $S = 35$  ( $\text{NTCO}_2$ ); (c)  $\text{pH}$  in total hydrogen ion concentration scale measured at  $25^\circ\text{C}$  ( $\text{pH}_{\text{T}25}$ , circles) and that calculated at SST from  $\text{NTCO}_2$ ,  $\text{pH}_{\text{T}25}$ , sea surface temperature (SST), and sea surface salinity (SSS) ( $\text{pH}_{\text{TSSST}}$ ; crosses); (d) salinity-normalized total alkalinity at  $S = 35$  (NTA) calculated from  $p\text{CO}_{2\text{sw}}$ ,  $\text{NTCO}_2$ , SST, and SSS (circles) and NTA calculated from  $\text{NTCO}_2$ ,  $\text{pH}_{\text{T}25}$ , SST, and SSS (crosses); (e) saturation state of aragonite ( $\Omega_{\text{arag}}$ , circles) and calcite ( $\Omega_{\text{calc}}$ , crosses); (f) SST; and (g) SSS. Also shown with solid shaded lines in Figures 5f and 5g is 10 day  $1^\circ \times 1^\circ$  mean SST (<http://goos.kishou.go.jp/rtrdb/jma-pro.html>) and monthly  $1^\circ \times 1^\circ$  mean SSS provided by data assimilation [Usui *et al.*, 2006], respectively. Solid shaded lines in Figures 5a–5e and dashed shaded lines in Figures 5c and 5e are the simulated time series data from  $1^\circ \times 1^\circ$  mean SST, SSS, and equations (3) and (5).



**Figure 6.** Temperature versus salinity-normalized total inorganic carbon at  $S = 35$  ( $\text{NTCO}_2$ ) in surface water at  $137^\circ\text{E}$ ,  $31^\circ\text{--}34^\circ\text{N}$  for December 2002–April 2008 in the north (circles) and south (crosses) of the Kuroshio axis. Contour lines show the  $p\text{CO}_{2\text{sw}}$  field calculated at a salinity of 34.5 (the average salinity for this region) and a salinity-normalized total alkalinity at  $S = 35$  (NTA) of  $2301 \mu\text{mol kg}^{-1}$  (the average NTA for this region).

in equation (2) exhibits the strong correlation between  $\text{NTCO}_2$  and temperature in the seasonal, interannual, and spatial variations (Figure 6), and it is assumed that these regression coefficients did not change over the period of time series observations (1994–2008).

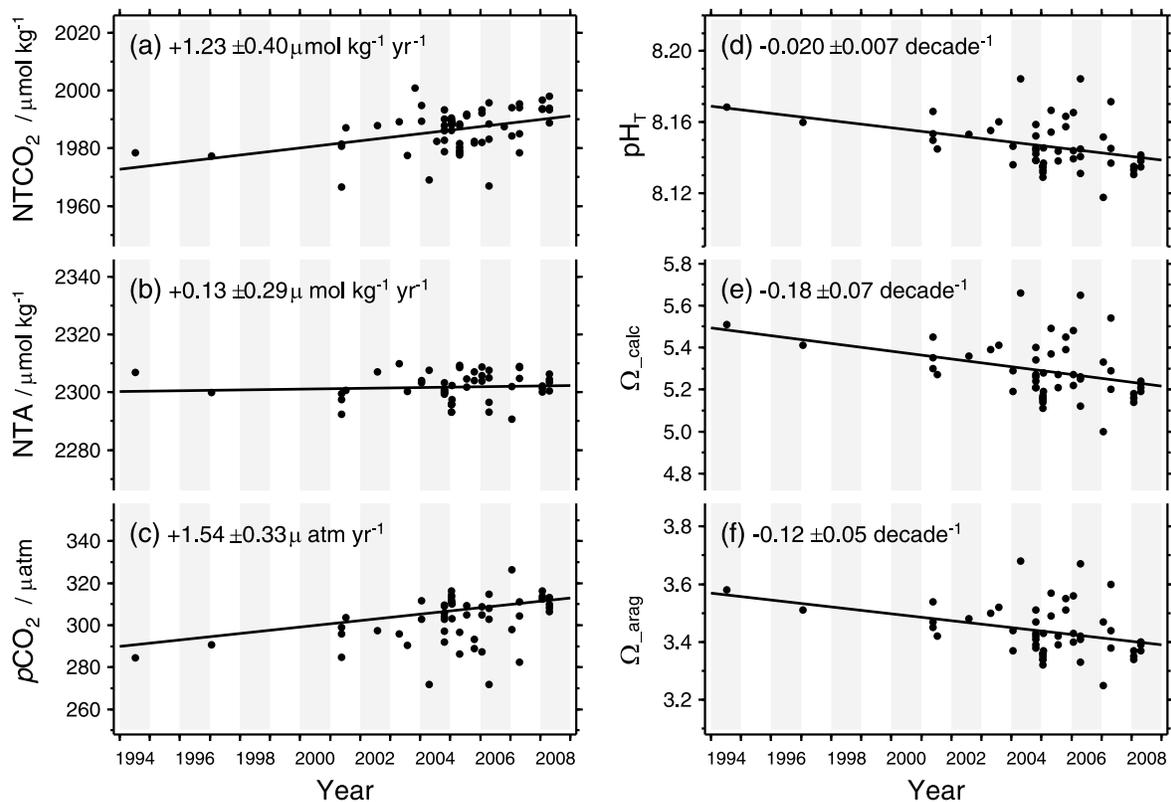
[21] For the coastal ocean between the south coast of Honshu and the Kuroshio in all seasons from July 1994 through April 2008, near-surface  $\text{NTCO}_2$  was expressed as

$$\begin{aligned} \text{NTCO}_2 / \mu\text{mol kg}^{-1} = & 1980.1(\pm 4.0) + 1.23(\pm 0.40) \cdot \text{yr} \\ & - 6.61(\pm 0.69) \cdot \text{SST} + 1.05(\pm 0.08) \cdot \text{SST}^2 \\ & - 0.072(\pm 0.019) \cdot \text{SST}^3 - 13.0(\pm 5.6) \\ & \cdot \text{SSS} + \varepsilon. \end{aligned} \quad (3)$$

The standard errors are shown in parentheses, and the root mean square of  $\varepsilon$  was  $6.6 \mu\text{mol kg}^{-1}$  ( $n = 61$ ). The time series of seasonally detrended  $\text{NTCO}_2$  at SST of  $20^\circ\text{C}$  and salinity of 35, i.e.,

$$\begin{aligned} \text{Seasonally detrended } \text{NTCO}_2 = & c_0 + c_1 \cdot \text{yr} + \varepsilon \\ = & 1980.1 + 1.23 \cdot \text{yr} + \varepsilon, \end{aligned} \quad (4)$$

is shown in Figure 7. Spatial and interannual variations of  $\text{NTCO}_2$  that accompany changes in SST and salinity in the same relationship as seasonal variation are also detrended with this process. The rate of linear increase in  $\text{NTCO}_2$ , i.e., the regression coefficient  $c_0$  is  $+1.23 \pm 0.40 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  ( $n = 61$ ), and the 95% confidence interval is from  $+0.43$  to



**Figure 7.** Seasonally detrended time series of (a) salinity-normalized total inorganic carbon at  $S = 35$  ( $\text{NTCO}_2$ ), (b) salinity-normalized total alkalinity at  $S = 35$  (NTA), (c) partial pressure of  $\text{CO}_2$  in seawater ( $p\text{CO}_{2\text{sw}}$ ), (d) pH in total hydrogen ion concentration scale ( $\text{pH}_T$ ), and (e) saturation state of calcite ( $\Omega_{\text{calc}}$ ) and (f) that of aragonite ( $\Omega_{\text{arag}}$ ) in surface water north of the Kuroshio axis at  $137^\circ\text{E}$ .

+2.02  $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$ . The result indicates that  $\text{NTCO}_2$  is increasing significantly in this region (Figure 7a). Note that there are some outlying data in spring. These outliers are indicative of the decoupling of  $\text{NTCO}_2$  and temperature in spring when  $\text{TCO}_2$  is decreasing due to spring biological production [Yokouchi *et al.*, 2006] while surface water is warming. However, when all spring data are excluded, the multiple regressions still indicate a significant increase in  $\text{NTCO}_2$  at a rate of  $+0.92 \pm 0.34 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  ( $n = 37$ ). It is also noteworthy that the relationship between SST and  $\text{NTCO}_2$  within and south of the Kuroshio overlaps those in the north (Figure 6). The multiple regressions for all  $\text{NTCO}_2$  data in the north of  $32^\circ\text{N}$  regardless of the Kuroshio path gave the rate of increase of  $+0.85 \pm 0.23 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  ( $n = 122$ ) and the 95% confidence interval from  $+0.39$  to  $+1.32 \text{ mol kg}^{-1} \text{ yr}^{-1}$ . This suggests that the rate of increase is not very sensitive to the choice of data near the Kuroshio axis.

[22] The observed near-surface NTA was also fitted as an empirical function of timing of observation (yr) and physical parameters:

$$\begin{aligned} \text{NTA}/\mu\text{mol kg}^{-1} &= \text{TA} \cdot S^{-1} \cdot 35/\mu\text{mol kg}^{-1} \\ &= c'_0 + c'_1 \cdot \text{yr} + c'_2 \cdot \text{SST} + c'_3 \cdot \text{SSS} + \varepsilon' \\ &= 2301.1(\pm 2.8) + 0.13(\pm 0.29) \cdot \text{yr} \\ &\quad - 0.43(\pm 0.17) \cdot \text{SST} - 6.1(\pm 2.7) \cdot \text{SSS} + \varepsilon'. \end{aligned} \quad (5)$$

The root mean square of  $\varepsilon'$  was  $4.9 \mu\text{mol kg}^{-1}$  ( $n = 52$ ). For NTA, however, the linear rate of increase of  $+0.13 \pm 0.29 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  (Figure 7b) determined is not significant. Therefore, there is no evidence that NTA is increasing or decreasing in this zone. The time series of seasonally detrended NTA at SST of  $20^\circ\text{C}$  and salinity of 35, i.e.,

$$\begin{aligned} \text{Seasonally detrended NTA} &= c'_0 + c'_1 \cdot \text{yr} + \varepsilon' \\ &= 2301.1 + 0.13 \cdot \text{yr} + \varepsilon', \end{aligned} \quad (6)$$

is shown in Figure 7. Anthropogenic airborne acid deposition and other acid pollutants potentially have a substantial impact on carbonate chemistry in seawater by reducing NTA [Doney *et al.*, 2007]. However, it is unlikely that they have a significant long-term impact in the coastal ocean we studied.

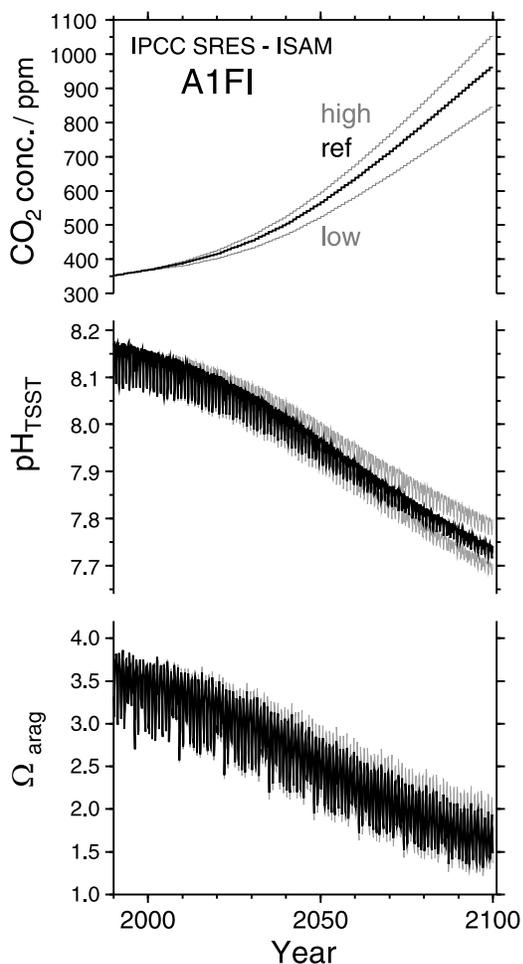
## 5. Discussion

[23] We calculated the rate of increase of  $p\text{CO}_{2\text{sw}}$  in the coastal ocean north of Kuroshio from the detrended  $\text{NTCO}_2$  and NTA that is represented by (4) and (6) at SST of  $20^\circ\text{C}$  and salinity of 35, respectively. Seasonally and interannually detrended  $p\text{CO}_{2\text{sw}}$  thus calculated was increasing at a rate of  $+1.54 \pm 0.33 \mu\text{atm yr}^{-1}$  for 1994–2008 (Figure 7c). This rate agrees well with that of atmospheric  $p\text{CO}_2$  increase ( $+1.99 \pm 0.02 \mu\text{atm yr}^{-1}$ ) measured onboard for the same period. The rate of  $\text{pH}_T$  change was also calculated in the same manner. It was  $-0.020 \pm 0.007 \text{ decade}^{-1}$  (Figure 7d) and is in good agreement with rates that have been determined in the central North Pacific near Hawaii ( $-0.019 \pm 0.002 \text{ decade}^{-1}$ ) [Dore *et al.*, 2009] and the subtropical western North Pacific along  $137^\circ\text{E}$  in winter ( $-0.015 \pm$

$0.002 \text{ decade}^{-1}$  to  $-0.021 \pm 0.002 \text{ decade}^{-1}$ ) [Midorikawa *et al.*, 2010]. The concentration of carbonate ion in seawater is computed to be decreasing by  $-3.2 \pm 0.7\% \text{ decade}^{-1}$ . This decrease corresponds to the lowering of  $\Omega_{\text{calc}}$  and  $\Omega_{\text{arag}}$  at a rate of  $-0.18 \pm 0.07 \text{ decade}^{-1}$  and  $-0.12 \pm 0.05 \text{ decade}^{-1}$ , respectively (Figures 7e and 7f). The record of direct measurements of  $\text{pH}_{T25}$  by spectrophotometry since 2003 (Figure 5c) is not long enough to determine any trends in acidification, but these long-term changes in measured and calculated seawater  $\text{CO}_2$  parameters demonstrate that the coastal ocean off Honshu, Japan, as well as subtropical zone south of the Kuroshio is being threatened by ocean acidification.

[24] Superposed on the long-term trends, cold events in winter further enhance the increase of  $\text{NTCO}_2$  and decrease of saturation states of aragonite and calcite. On 19 January 2006, for example, low SST of  $+13.7^\circ\text{C}$  was recorded when sample of  $\text{TCO}_2$  was taken at  $34^\circ\text{N}$  (Figure 5f). It was  $2.1^\circ\text{C}$  lower than the mean of  $+15.8 \pm 1.2$  (1 $\sigma$ )  $^\circ\text{C}$  at this site in mid January for 1994–2008, and even  $1.2^\circ\text{C}$  lower than that in early March ( $+14.9 \pm 1.3^\circ\text{C}$ ) when mean SST is usually the lowest in a year. At this time,  $\text{NTCO}_2$  ( $2088 \mu\text{mol kg}^{-1}$ ) was the highest and  $\text{pH}_{T25}$  (7.905) and  $\Omega_{\text{arag}}$  (2.45) were the lowest in 2002–2008 (Figures 5b, 5c, and 5e). Temperature in the mixed layer was even lower ( $+13.3^\circ\text{C}$ ) when CTD observation was made at this station. The thickness of mixed layer (150 m) was the deepest and temperature at the depth of 160 m below the mixed layer was the coldest ( $11.5^\circ\text{C}$ ) due to the uplifting of isotherms (Figure 4). From these observations, it is thought that the stronger turbulent mixing by cold wind together with the enhanced upwelling that was related to the ocean dynamics enhanced the entrainment of subsurface  $\text{CO}_2$ -rich water, and thus raised  $\text{NTCO}_2$  and lowered pH and saturation states of carbonates in surface water. On the other hand, in January 2005 when the Kuroshio took a large meander path, mixed layer temperature was  $+18.0^\circ\text{C}$  at  $34^\circ\text{N}$  (Figures 4 and 5f). It was  $+2.2^\circ\text{C}$  higher than the mean in mid-January for 1994–2008. At this time,  $\text{NTCO}_2$  ( $2013 \mu\text{mol kg}^{-1}$ ) was lower and  $\text{pH}_{T25}$  (8.021) and  $\Omega_{\text{arag}}$  (3.08) were higher than in other winter seasons (Figures 5b, 5c, and 5e). It is known that SST in the coastal ocean tends to become higher when the Kuroshio take a large meander path [Sugimoto and Yoshida, 2005]. Changes in ocean dynamics associated with the Kuroshio large meander also affect carbonate chemistry and raise the carbonate saturation state in surface layer at  $34^\circ\text{N}$ .

[25] The difference between  $p\text{CO}_{2\text{sw}}$  and  $p\text{CO}_{2\text{air}}$  ( $\Delta p\text{CO}_2$ ) has not changed significantly for the last 25 years in the northern subtropical zone along  $137^\circ\text{E}$  [Midorikawa *et al.*, 2010]. Assuming that  $p\text{CO}_{2\text{sw}}$  will increase in the same rate as  $p\text{CO}_{2\text{air}}$  while NTA will keep the contemporary value, and that seasonal and interannual variations of temperature and salinity from 1994 through 2008 will repeat, we calculated the future trend of acidification.  $\Omega_{\text{arag}}$  in the coastal ocean south of Honshu will decline from about 2.8 at present to 2.0 when the level of atmospheric  $\text{CO}_2$  reaches 535 ppm in a normal winter (SST =  $15^\circ\text{C}$ ). In a colder winter, such as in January 2006, or at colder sites within this zone where SST is lower than  $14^\circ\text{C}$ ,  $\Omega_{\text{arag}}$  will decline to 2.0 when the level of atmospheric  $\text{CO}_2$  is no more than 500 ppm. To date, annual  $\text{CO}_2$  emissions resulting from combustion of fossil fuels are increasing along a curve



**Figure 8.** Trends forecasted for the end of this century according to the emission scenario A1FI from the Intergovernmental Panel on Climate Change (see [http://www.grida.no/publications/other/ipcc\\_sr/](http://www.grida.no/publications/other/ipcc_sr/)) and seawater  $\text{CO}_2$  parameters in the coastal ocean off the south coast of Honshu, Japan, as determined in this work: atmospheric  $\text{CO}_2$  concentration,  $\text{pH}_T$  at in situ temperatures, and  $\Omega_{\text{arag}}$ .

similar to the A1FI scenario (with intensive fossil fuel use associated with very rapid economic growth) in the Intergovernmental Panel on Climate Change's Special Report on Emissions Scenarios [Le Quéré et al., 2009]. Under this scenario,  $\Omega_{\text{arag}}$  could decline rapidly over the next 50 years by 0.8 to 1.0, depending on the atmospheric  $\text{CO}_2$  concentration increase that is realized (Figure 8).  $\Omega_{\text{arag}}$  could decline to 2.0 by the year 2040 under colder winter conditions, and by the year 2055 under normal winter conditions.

[26] Biological responses to ocean acidification are as yet largely unknown [Doney et al., 2009]. It has been suggested that acidification enhances the production of sea grasses [Palacios and Zimmerman, 2007], diatoms [Riebesell et al., 2007], and nitrogen-fixing cyanobacteria *Trichodesmium* [Barcelos e Ramos et al., 2007] that is encountered in high abundance in surface waters of the Kuroshio and its adjacent regions [Capone, 1997]. In contrast, laboratory experiments have shown that, for a variety of calcareous organisms, the rate of calcification decreases as the  $\text{CO}_2$  level increases and  $\Omega$  decreases. These organisms include corals [e.g.,

*Kleypas and Yates, 2009*], the Pacific oyster *Crassostrea gigas* [Gazeau et al., 2007], and *Gephyrocapsa oceanica* [Riebesell et al., 2000] that are also seen in the region we studied and/or in the adjacent coastal basins. These experimental results suggest that the rapid decline in  $\Omega_{\text{calc}}$  and  $\Omega_{\text{arag}}$  as well as the increase in  $\text{CO}_2$  predicted for the next 50 years would have a large impacts on calcareous organisms and ecosystems in the coastal ocean off of Honshu, even though  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$  values are higher than those in the polar regions where  $\Omega_{\text{arag}}$  is closer to 1.0 [Orr et al., 2005]. Our conclusions on the acidification in the north of the Kuroshio also suggest its impacts on the biogeochemistry and ecosystem in the coastal basins adjacent to this region through the water exchange by tidal mixing. The progress of ocean acidification and its impacts on ecosystems and biogeochemical processes, and their possible feedback mechanisms to acidification, need to be understood by long-term monitoring in coastal zones as well as in open oceans.

[27] **Acknowledgments.** The authors are grateful to the captains and crew of the R/V *Ryofu Maru* and R/V *Keifu Maru* and the staff of the Global Environment and Marine Department, Japan Meteorological Agency, for their efforts in maintaining long-term atmospheric and oceanographic monitoring in the western Pacific. We also thank the two anonymous reviewers for their constructive comments. This research was supported by the Meteorological Research Institute's priority research fund for ocean carbon cycle changes and by the Ministry of the Environment's Global Environment Research Fund D-0803.

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