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Seasonality of CO_2 in coastal oceans altered by increasing anthropogenic nutrient delivery from large rivers: evidence from the Changjiang–East China Sea system

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Abstract. Model studies suggested that human-induced increase in nutrient load may have stimulated primary production and thus enhanced the CO_2 uptake capacity in the coastal ocean. In this study, we investigated the seasonal variations of the surface water's partial pressure of CO_2 ($p\mathrm{CO}_2^{\mathrm{sw}}$) in the highly human-impacted Changjiang–East China Sea system between 2008 and 2011. The seasonality of $p\mathrm{CO}_2^{\mathrm{sw}}$ has large spatial variations, with the largest extreme of 170 ± 75 µatm on the inner shelf near the Changjiang Estuary (from 271 ± 55 µatm in summer to 441 ± 51 µatm in autumn) and the weakest extreme of 53 ± 20 µatm on the outer shelf (from 328 ± 9 µatm in winter to 381 ± 18 µatm in summer). During the summer period, stronger stratification and biological production driven by the eutrophic Changjiang plume results in a very low dissolved inorganic carbon (DIC) in surface waters and a very high DIC in bottom waters of the inner shelf, with the latter returning high DIC to the surface water during the mixed period. Interestingly, a comparison with historical data shows that the average $p\mathrm{CO}_2^{\mathrm{sw}}$ on the inner shelf near the Changjiang Estuary has decreased notably during summer, but has increased during autumn and winter from the 1990s to the 2000s. We suggest that this decadal change is associated with recently increased eutrophication. This would increase both the photosynthetic removal of DIC in surface waters and the respiratory release of DIC in bottom waters during summertime, thereby returning more DIC to the surface during the subsequent mixing seasons and/or episodic extreme weather events (e.g., typhoons). Our finding demonstrates that increasing anthropogenic nutrient delivery from a large river may enhance the sequestration capacity of CO_2 in summer but may reduce it in autumn and winter. Consequently, the coastal ocean may not necessarily take up more atmospheric CO_2 in response to increasing eutrophication, and the net effect largely depends on the relative timescale of air–sea gas exchange and offshore transport of the shelf water. Finally, the case we report for the Changjiang system may have general ramifications for other eutrophic coastal oceans.

1 Introduction

Human activities such as fertilizer usage, fossil fuel combustion, and coastal urbanization have greatly accelerated the flows of nutrients to coastal oceans by rivers, groundwater, and the atmosphere over the past century (Howarth et al., 1995; Boyer and Howarth, 2008). Such anthropogenic enhancement of nutrient inputs (eutrophication) is generally believed to be the primary cause driving the explosive expansion of hypoxic zones in the global coastal oceans since the 1980s (Diaz and Rosenberg, 2008; Paerl and Piehler, 2008). Although the ecological impacts of eutrophication and hypoxia (e.g., changes in the phytoplankton community, harmful algal blooms, decreases in biodiversity, declines in fishery production, etc.) are becoming increasingly well documented (Cloern, 2001; Diaz and Rosenberg, 2008; Zhang et al., 2010), perturbations to the capacity of coastal waters to take up atmospheric CO_2 remain an under-examined consequence of the increased nutrient load (Doney, 2010; Howarth et al., 2011).

Some recent model studies, on both regional and global scales, demonstrated that human-induced changes in nutrient delivery (both in quantity and quality) may play a pivotal role on the long-term evolution of the air–sea CO_2 flux in the coastal zone. For instance, Andersson and Mackenzie (2004) suggested that the global coastal oceans have probably acted as a source of atmospheric CO_2 throughout most of the past 300 yr, but they have recently switched, or will switch soon, to a sink of CO_2, because of rising atmospheric CO_2 and increasing nutrient loads (also see Cai, 2011). More recently, Gypense et al. (2009) suggested that the eutrophic Belgian coastal zone might have shifted from a source to a sink of atmospheric CO_2 due to increased N and P loads during the 1970s and 1980s but switched back to a CO_2 source in the late 1990s, responding to the decreased P loads resulting from nutrient reduction policies. The modeling result of Borges and Gypens (2010) also indicates that carbon chemistry in the coastal zone may respond more strongly to eutrophication than to ocean acidification. Although these model studies give a general overview of how the human-induced increased nutrient load may have stimulated primary production and thus may have enhanced the CO_2 uptake capacity in the coastal ocean, their results have never been verified by any field data, mainly because of the lack of CO_2 measurements before the severely eutrophic era.

The East China Sea (ECS), located off the southeast coast of China, is one of the largest marginal seas in the northwestern Pacific. The Changjiang (Yangtze River), the largest river in Asia and the fourth largest in the world, empties into the northwestern part of the ECS with an enormous water discharge of $9 \times 10^{11}\,\mathrm{m^3\,yr^{-1}}$ (Dai and Trenberth, 2002). Due to industrial development and increased agricultural production associated with the rapid growth of the Chinese population and economy over the past 20 yr, the export of dissolved inorganic N from the Changjiang increased threefold between 1970 and 2003 (Yan et al., 2010). This is ten times faster than the increase of total global river export over the period 1970–2000 (35 %; Seitzinger et al., 2010). Consequently, the ECS may represent one of the areas most impacted by worsening eutrophication over recent decades, and therefore it can provide a unique opportunity for examining the potential influence of eutrophication on the CO_2 uptake capacity with field data. Recently, Chou et al. (2011) found that the wintertime partial pressure of surface water CO_2 ($p\mathrm{CO_2}$) on the inner shelf near the Changjiang Estuary has increased remarkably between the 1990s and the 2000s. The authors postulated that this increase may reflect the fact that eutrophication might have caused a greater CO_2 accumulation in bottom water during the summer over recent decades, which can supply more CO_2 to the surface when stratification breaks down in winter.

In this study, we first report newly measured seasonal underway $p\mathrm{CO_2}$ data from summer, autumn, and winter over the ECS shelf. We then investigate the processes controlling the spatial variation of $p\mathrm{CO_2}$ seasonality. Last, we compare the present $p\mathrm{CO_2}$ seasonality with that in the early 1990s, and find that $p\mathrm{CO_2}$ in the late 2000s was markedly lower than that in the early 1990s during the summer, but it was apparently higher during the autumn and winter. We suggest that the increased eutrophication over the past few decades could account for the observed decadal change in the seasonal variation of $p\mathrm{CO_2}$ on the inner shelf near the Changjiang Estuary.

2 Materials and methods

Three cruises making direct underway measurements of $p\mathrm{CO_2}$ in surface water concurrently with hydrographic surveys were conducted on the ECS shelf in summer (1–11 July 2011), autumn (22 October–3 November 2011), and winter (2–11 January 2008), aboard the R/V *Ocean Researcher I*. The winter data have been reported previously in Chou et al. (2011). During the cruises in summer and autumn, surface temperature and salinity were recorded continuously using a SBE21 SEACAT thermosalinograph system (Sea-Bird Electronics Inc.). The underway $p\mathrm{CO_2}$ measurements were made with a continuous flow equilibration system (see Jiang et al., 2008 for a detailed description of the system). The equilibrator used in this system has a head-space volume of about 1 L and is equipped with a specially designed water-drain system, which prevents direct contact of the gas in the head space with the outside air, and it keeps the pressure inside and outside the equilibrator balanced. The equilibrated headspace gas was dried by passage through an electric Peltier cooler and then a drying tube filled with $Mg(ClO_4)_2$. The CO_2 mole fraction ($x\mathrm{CO_2}$) of the dried air was detected using a non-dispersive, infrared spectrometer (LI-COR 7000), which was calibrated every 4 h against a CO_2-free reference gas (N_2) and three gas standards (the $x\mathrm{CO_2}$ of the three standards was 298.85, 399.73, and 492.13 ppm) provided by the US National Oceanic and Atmospheric Administration (NOAA). The measured $x\mathrm{CO_2}$ data were converted into surface water $p\mathrm{CO_2}$ by correcting to 100 % humidity and to in situ water temperature after Pierrot et al. (2009) and Jiang et al.(2008).

At each hydrographic station, depth profiles of temperature and salinity were recorded using a Seabird SBE9/11-plus conductivity-temperature-depth (CTD) system. Dissolved oxygen (DO) was determined by calibrated DO sensor (SBE43, Sea-Bird Electronics, Inc.; Chou et al., 2009a). Apparent oxygen utilization (AOU = saturated DO – measured DO) was calculated using Benson and Krause's formula (1984). Discrete water samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) analysis were drawn from

Go-Flo bottles into 350 mL pre-cleaned borosilicate bottles. These samples were subsequently poisoned with 200 µL of $HgCl_2$-saturated solution to halt biological activity, sealed, and returned to the laboratory. DIC samples were analyzed using a DIC analyzer (AS-C3, Apollo SciTech Inc., Georgia, USA) with a precision of 0.2 % (Cai and Wang, 1998). Seawater samples of 0.75 mL were acidified by addition of 0.5 mL 10 % H_3PO_4. The extracted CO_2 gas was subsequently measured using a non-dispersive infrared CO_2 detector (Li-COR, LI-7000). TA was measured by Gran titration of a 20 mL seawater sample with 0.1 N HCl in an open-cell setting (Cai et al., 2010). Each sample was titrated at least twice with a precision of 0.1 %. Certified reference material provided by A. G. Dickson (Scripps Institution of Oceanography) was used throughout this study for calibration and accuracy assessments for both DIC and TA measurements. $p\mathrm{CO}_2$ at discrete depths of water column was calculated from DIC and TA using the CO2SYS program (Lewis and Wallace, 1998), in which the dissociation constants for carbonic acid of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and for $KHSO_4^-$ of Dickson (1990) were used. Errors in the computed $p\mathrm{CO}_2$ were estimated to be ± 5 µatm deriving from the uncertainties in the measurements of DIC and TA.

3 Results and discussion

3.1 Seasonal variations of surface water temperature, salinity and $p\mathrm{CO}_2$ on the ECS shelf

The distributions of surface water temperature (SST) and salinity (SSS) for summer, autumn, and winter cruises on the ECS shelf are shown in Fig. 1. In summer, SST was high and varied within a relatively narrow range between 21.9 and 28.8 °C (Fig. 1a), while SSS was low and showed a relatively wide range between 18.5 and 34.1 (Fig. 1b). The lowest SST and SSS water was confined mainly to the northwestern part of the study area. In autumn, SST and SSS ranged from 20.6 to 27.7 °C and 29.5 to 34.6, respectively (Fig. 1c, d). These values are between those for summer and winter, and show an eastwardly increasing pattern from the coast of mainland China to the shelf break. In contrast to the situation in summer, SST was low and varied within a relatively wide range between 12.2 and 24.4 °C, whereas SSS was high and showed a relatively narrow range between 30.6 and 34.6 in winter (Fig. 1e, f). The distribution pattern of SST and SSS in winter is generally similar to that in autumn, increasing in an eastwardly direction.

In general, the observed seasonal distributions of SST and SSS corresponded well to the seasonal circulation pattern in the ECS (Lee and Chao, 2003), and they were consistent with those reported in the previous studies (Chen et al., 2006; Park and Chu, 2006). During the wet season (May to October), when the Changjiang is in flood, the mixing of freshwater and shelf seawater forms the Changjiang diluted water (CDW), which is characterized by low salinity and high nutrient content (Gong et al., 1996). Under the influence of the southwest monsoon, the CDW disperses eastwards over the broad ECS shelf (Beardsley et al., 1985), as indicated by the low SSS waters in the northwestern part of the study area in summer (Fig. 1b). During the dry season (November to April), when the Changjiang discharge is low, the prevailing northeast monsoon confines the CDW to the western side of the ECS shelf. The CDW moves southward to the Taiwan Strait, forming a narrow band along the coast of China, as identified by the low SSS waters in the western part of the study area in autumn and winter (Fig. 1d, f; Gong et al., 2003). Off the shelf break, the Kuroshio is the western boundary current of the North Pacific Ocean, and it is characterized by high temperature and salinity and oligotrophic conditions (Gong et al., 1999). It flows northeastward along the shelf break all year round, as traced by the high SST and SSS waters in the southeastern part of the study area in all three seasons.

The distributions of surface water $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{\mathrm{sw}}$) also showed a significant seasonal variation (the left panels in Fig. 2). In summer, $p\mathrm{CO}_2^{\mathrm{sw}}$ ranged from 100 to 451 µatm. Major CO_2 sink areas (where $p\mathrm{CO}_2^{\mathrm{sw}} <$ atmospheric $p\mathrm{CO}_2 = 378$ µatm) were largely confined to the inner shelf within the low salinity CDW, while CO_2 source areas ($p\mathrm{CO}_2^{\mathrm{sw}} > 378$ µatm) were generally found along the coast of mainland China beyond the influence of CDW. The middle and outer shelf areas were relatively closer to equilibrium with respect to the atmospheric value than the inner shelf area. Our previous summer survey (Chou et al., 2009b) has shown that the CO_2 sink in the CDW area was caused by high biological production fueled by enormous nutrient discharge from the Changjiang (0.75–8.65, 0.001–0.041 and 0.34–9.19 kmol s^{-1} in summer for nitrate, phosphate and silicate, respectively; Zhang et al., 2007), and that the CO_2 source in the nearshore area was associated with the seasonal coastal upwelling induced by the southwesterly summer monsoon. In autumn, $p\mathrm{CO}_2^{\mathrm{sw}}$ varied from 335 to 557 µatm. In stark contrast to the distribution pattern in summer, the highest autumn $p\mathrm{CO}_2^{\mathrm{sw}}$ values were observed on the inner shelf near the Changjiang Estuary, where $p\mathrm{CO}_2^{\mathrm{sw}}$ had the lowest values in summer. Furthermore, $p\mathrm{CO}_2^{\mathrm{sw}}$ values along the coast of mainland China were apparently supersaturated with respect to atmospheric CO_2, indicating that the entire inner shelf acted as a CO_2 source in autumn. Similar to the situation in summer, the remaining shelf areas (middle and outer shelf) were nearly in equilibrium with the atmosphere. Finally, in winter, $p\mathrm{CO}_2^{\mathrm{sw}}$ varied within a relatively narrow range, from 306 to 390 µatm, most of which is undersaturated with respect to atmospheric $p\mathrm{CO}_2$, indicating that the overall ECS shelf acted as a CO_2 sink during the winter.

In summary, the seasonality of $p\mathrm{CO}_2^{\mathrm{sw}}$ on the ECS shelf demonstrates strong spatial variation. The largest seasonal fluctuation of $p\mathrm{CO}_2^{\mathrm{sw}}$ was found on the inner shelf near

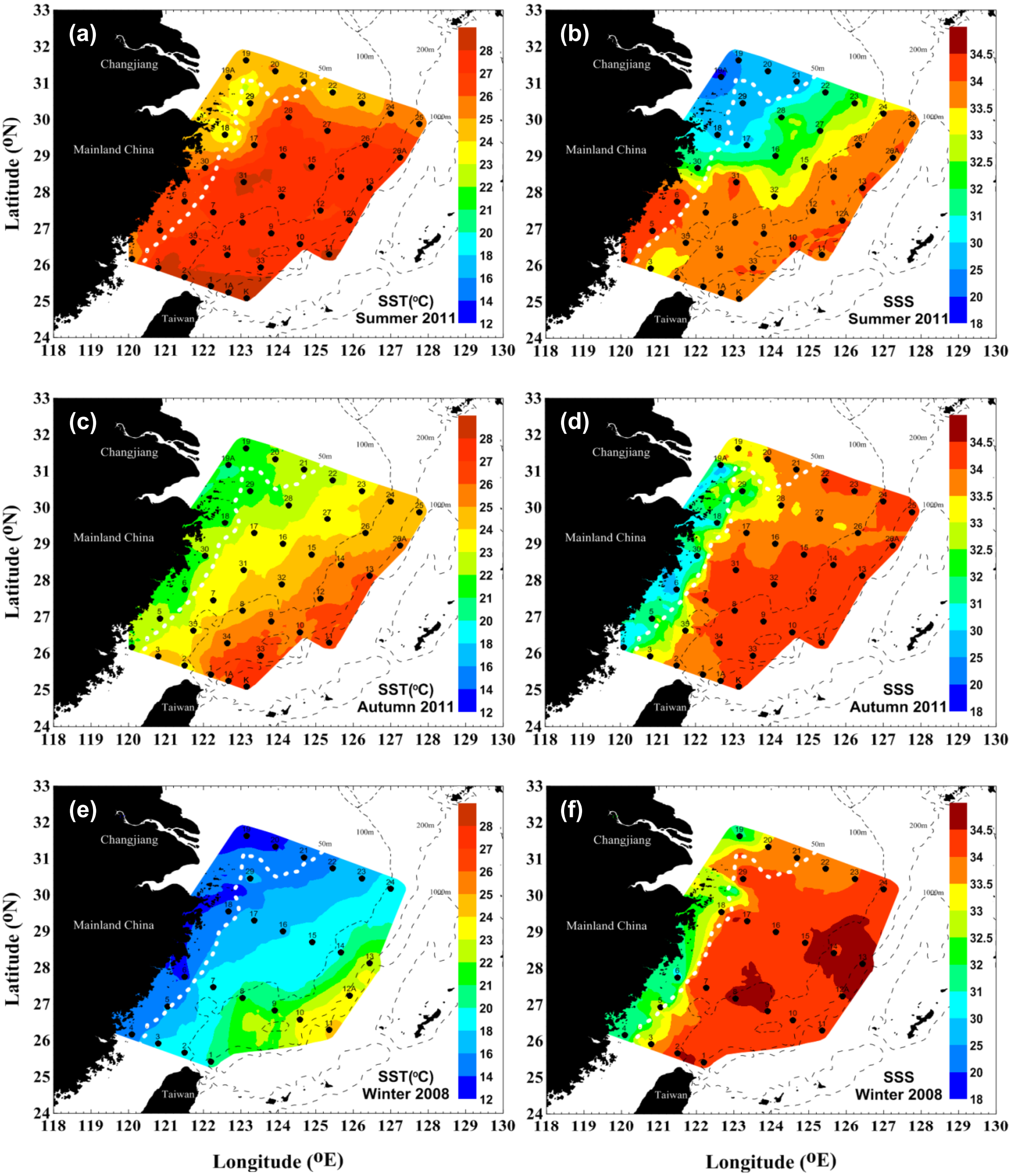

Fig. 1. Spatial distributions of **(a)** SST in summer 2011, **(b)** SSS in summer 2011, **(c)** SST in autumn 2011, **(d)** SSS in autumn 2011, **(e)** SST in winter 2008 and **(f)** SSS in winter 2008 on the East China Sea shelf. SST: sea surface temperature. SSS: sea surface salinity. The bold dotted line indicates the 50 m isobath.

the Changjiang Estuary, which is under the influence of the Changjiang discharge: $p\mathrm{CO}_2^{\mathrm{sw}}$ was strongly undersaturated with respect to the atmosphere (i.e., it was a CO_2 sink) in summer, but it was highly supersaturated (i.e., it was a CO_2 source) in autumn, and it was approximately in equilibrium with the atmosphere in winter. In contrast, $p\mathrm{CO}_2^{\mathrm{sw}}$ in the outer shelf area, which is occupied by the Kuroshio, exhibits a very weak seasonality: $p\mathrm{CO}_2^{\mathrm{sw}}$ was nearly in equilibrium with the atmosphere in both summer and autumn, and slightly undersaturated in winter.

3.2 Factors controlling $p\mathrm{CO}_2^{\mathrm{sw}}$ seasonality on the inner and outer shelves of the ECS

To examine the potential cause(s) resulting in the distinctly different seasonality of $p\mathrm{CO}_2^{\mathrm{sw}}$ between the inner and outer

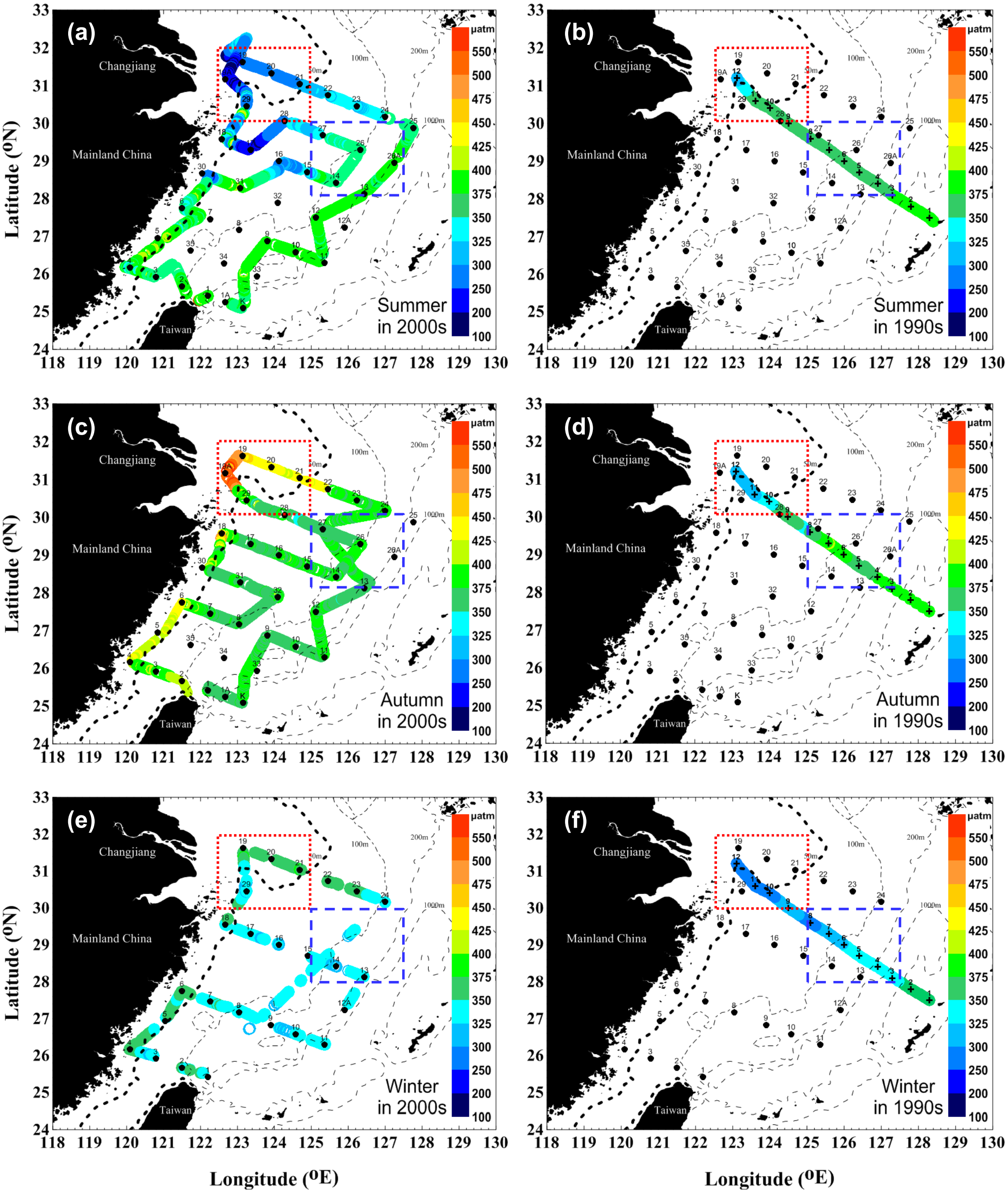

Fig. 2. Spatial distributions of surface water $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{\mathrm{sw}}$) in summer, autumn and winter on the entire East China Sea shelf in the 2000s (the left panel), and along the PN line in the 1990s (the right panel). The latter was reproduced by digitizing Fig. 2 of Tsunogai et al. (1999). The summer, autumn and winter $p\mathrm{CO}_2^{\mathrm{sw}}$ data in the 2000s and the 1990s were collected in July 2011, late October to early November 2011, January 2008, August 1994, October 1993 and February 1993, respectively. The dotted rectangular area indicates the inner shelf region (30–32° N, 122.5–125° E) that is susceptible to the influence of the Changjiang discharge, whereas the dashed rectangular area indicates the outer shelf region (28–30° N, 125–127.5° E) that is generally away from the influence of the Changjiang discharge. The bold dotted line indicates the 50 m isobath.

shelf areas, the depth profiles of temperature, salinity, AOU, DIC, and $p\mathrm{CO}_2$ at stations 19, 20 and 21 on the inner shelf near the Changjiang Estuary with the strongest $p\mathrm{CO}_2^{\mathrm{sw}}$ seasonality (Fig. 3) are compared with those at stations 13 and 14 on the outer shelf with modest $p\mathrm{CO}_2^{\mathrm{sw}}$ seasonality (Fig. 4). As shown in Fig. 3, a thin layer of low salinity water on top of the water column was observed at the inner shelf stations during summertime when the Changjiang

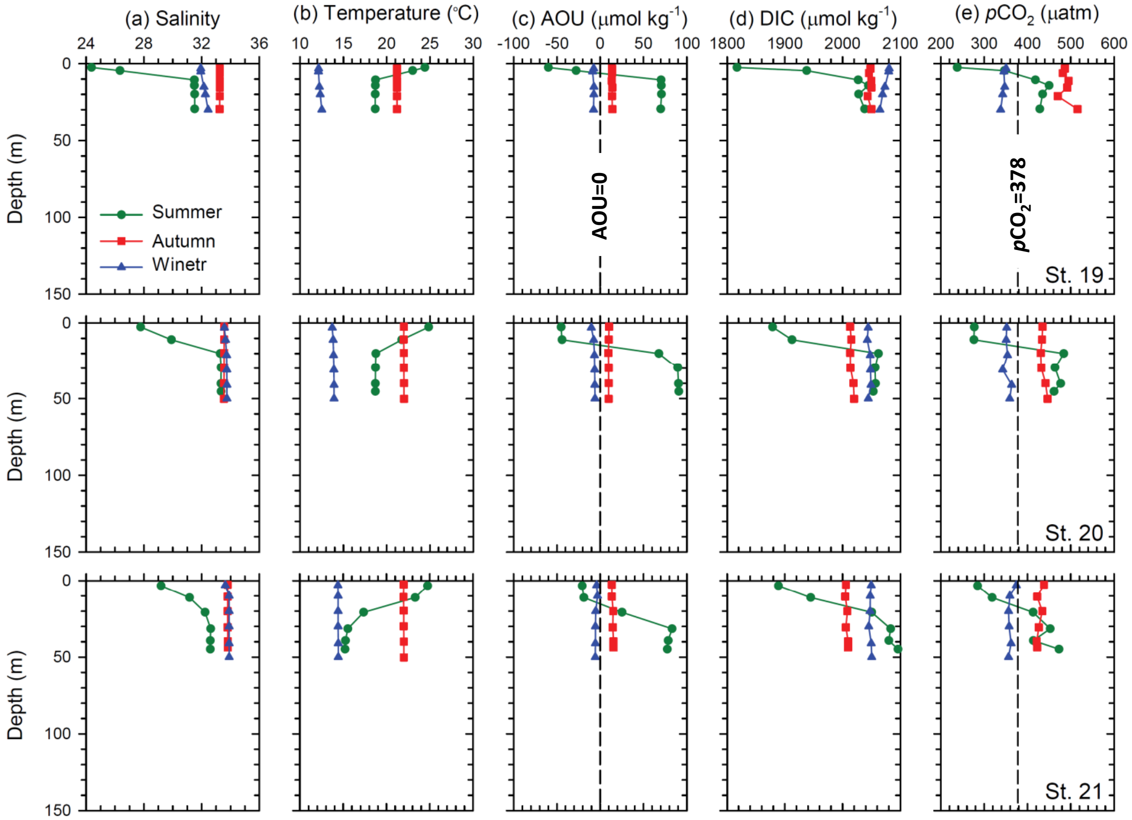

Fig. 3. Depth distributions of **(a)** salinity, **(b)** temperature, **(c)** AOU, **(d)** DIC and **(e)** $p\mathrm{CO}_2$ in summer, autumn, and winter at the stations with the largest seasonal variation of $p\mathrm{CO}_2^{\mathrm{sw}}$ (stations 19, 20, and 21 in the inner shelf near the Changjiang Estuary).

reaches its highest discharge (Fig. 3a). Additionally, temperature also sharply decreased with depth in the surface low-salinity layer (Fig. 3b). A combination of steep haline and thermal gradients would enhance the water column stratification and stabilize the water masses near the bottom (Chen et al., 2007). This feature favors forming a strong vertical gradient of AOU, DIC, and $p\mathrm{CO}_2$, because bottom waters are isolated from exchanging O_2 and CO_2 with surface waters. Furthermore, a phytoplankton bloom is generally found in the surface low-salinity layer on the inner shelf in summer, which is induced by allochthonous nutrients from the Changjiang discharge (Gong et al., 2011). This is evidenced by the extremely negative AOU values in our study (Fig. 3c). High biological production also consumed a large amount of DIC and reduced $p\mathrm{CO}_2$, thus resulting in low DIC and $p\mathrm{CO}_2$ values in the surface layer (Fig. 3d, e). On the other hand, the elevated biological production in the surface layer would supply more organic matter to the bottom water. Tremendous amounts of O_2 and CO_2 were therefore consumed and released (at station 19, for example, AOU and DIC increased from -60 and 1817 μmol kg^{-1} at the surface to 70 and 2027 μmol kg^{-1} at 10 m depth, respectively), during the decomposition process, thus causing the high values of AOU, DIC and $p\mathrm{CO}_2$ in the bottom water. As a whole, because of the combined effect of strong stratification and elevated biological production, the stations in the inner shelf near the Changjiang Estuary were characterized by an extremely steep vertical gradient in AOU, DIC, and $p\mathrm{CO}_2$ during the summertime: that is, negative AOU, low DIC, and undersaturated $p\mathrm{CO}_2$ were found in the surface water, but positive AOU, high DIC, and supersaturated $p\mathrm{CO}_2$ were in the bottom water.

Contrasting the strong stratification in summer, the vertical distributions of all parameters were homogeneous in autumn, indicating that the entire water column was well mixed during this period owing to the seasonal cooling and the intensified monsoonal winds. The enhanced vertical mixing could readily return the summer accumulation of respired CO_2 in the bottom water to the surface. Consequently, $p\mathrm{CO}_2^{\mathrm{sw}}$ on the inner shelf near the Changjiang Estuary changed from being strongly undersaturated in summer to being highly supersaturated in autumn with respect to the atmosphere (Fig. 3e). In winter, the water column remained well mixed. Because of the continuous cooling and CO_2 degassing from autumn to winter, $p\mathrm{CO}_2^{\mathrm{sw}}$ declined to become slightly undersaturated with respect to the atmosphere in winter. The above-described seasonal variation of $p\mathrm{CO}_2^{\mathrm{sw}}$ is generally consistent with the previously reported annual cycle of $p\mathrm{CO}_2^{\mathrm{sw}}$ in

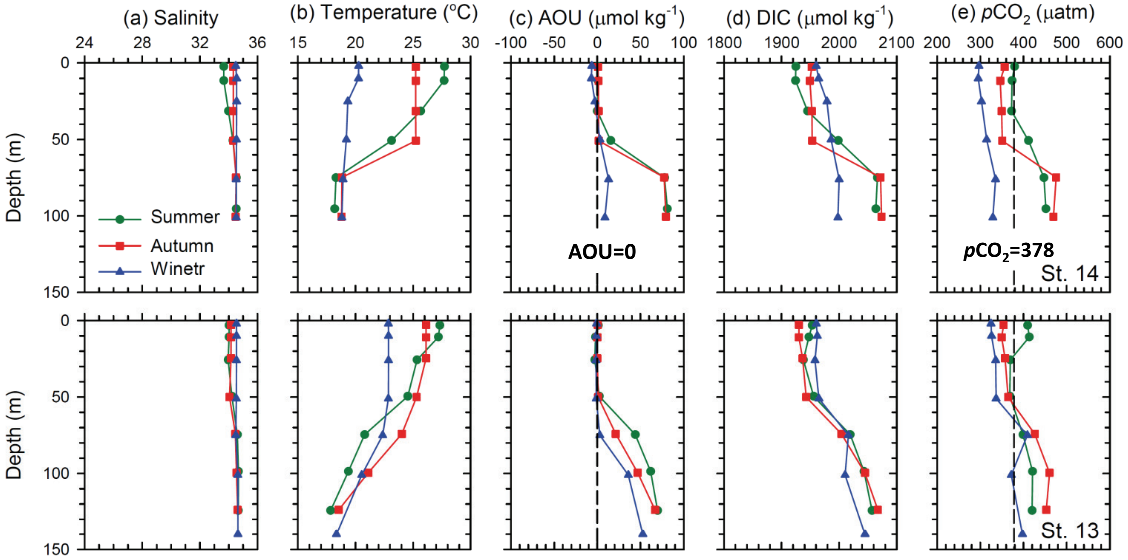

Fig. 4. Depth distributions of **(a)** salinity, **(b)** temperature, **(c)** AOU, **(d)** DIC, and **(e)** pCO_2 in summer, autumn, and winter at the stations with modest seasonal variations of pCO_2^{sw} (stations 13 and 14 in the outer shelf).

the outer Changjiang Estuary during April 2005 to April 2008 (Zhai and Dai, 2009), and in the northwestern ECS shelf during August 2003 to November 2005 (Shim et al., 2007). Furthermore, Wang et al. (2012) recently showed that the annual cycle of hypoxia off the Changjiang Estuary in 2006–2007 began to develop in late spring and early summer, reached its maximum in August, weakened in autumn, and disappeared in winter. Such development occurs essentially in tandem with the observed seasonal cycle of pCO_2^{sw} described in the present study. Therefore, the observed seasonal variation of pCO_2^{sw} in this study is likely a recurring phenomenon in the inner shelf area that is impacted by the CDW in recent years.

In contrast to the stations on the inner shelf near the Changjiang Estuary, high salinity surface water was found at the outer shelf stations in summer (Fig. 4a), suggesting that these stations were generally out of the influence of the nutrient-laden fresh water from the Changjiang. As a result of lower riverine input of nutrients, the summer phytoplankton bloom did not occur at the outer shelf stations, as evidenced by the nearly null values of AOU in the surface layer (Fig. 4c). Moreover, the lack of a surface halocline would weaken the stratification of water column. Both the weaker stratification and lower biological production would hinder formation of steep vertical gradients for the chemical parameters. Accordingly, AOU, DIC, and pCO_2 all exhibited much less pronounced vertical gradients at the outer shelf stations than at the inner shelf stations influenced by the Changjiang discharge, particularly in the top 50 m of the water column. Likewise, the surface mixed layer deepened significantly to a depth of about 50 m at the outer shelf stations in autumn (Fig. 4b), indicating the enhancement of vertical mixing. Nonetheless, unlike the large pCO_2^{sw} augmentation observed in the inner shelf area in autumn (the middle left panel in Fig. 1), pCO_2^{sw} in the outer shelf area did not show a remarkable change in response to the enhancement of vertical mixing. This discrepancy could partially reflect the fact that the vertical gradients of AOU, DIC, and pCO_2 at the outer shelf stations were much smaller than that at the inner shelf stations near the Changjiang Estuary in the previous season, when the water column was strongly stratified. This suggests that less CO_2 could be transported from the bottom water to the surface water when stratification in the upper 50 m depths collapsed in autumn, thus causing the smaller seasonal fluctuation of pCO_2^{sw} between summer and autumn in the outer shelf area compared with the inner shelf area. Similar to the situation in the inner shelf area, the following seasonal cooling would further draw pCO_2^{sw} down to be undersaturated with respect to the atmosphere in the outer shelf area in winter.

In order to further understand controlling mechanisms on the seasonal variability of pCO_2^{sw}, we examine the effect of temperature on pCO_2^{sw} for the inner and outer shelf areas in Fig. 5a and b, respectively (see Fig. 2 for the definitions of the inner and outer shelf areas). Thermodynamically, pCO_2 increases with increasing temperature at a rate about 4 % $^{\circ}C^{-1}$ (Takahashi et al., 1993). Nonetheless, pCO_2^{sw} increased significantly in the inner shelf area from summer to autumn though SST decreased greatly during this period, suggesting that the effect of vertical mixing surpassed the effect of temperature on regulating seasonal pCO_2^{sw} variation when the water column turned from strong stratification in summer to well mixed in autumn. In the outer shelf area, a slightly less but clear SST decrease was observed, but pCO_2^{sw} did not show a significant change (Fig. 5b), implying that the effects of vertical mixing and temperature decrease had comparable importance and compensated each other. As discussed earlier, this discrepancy could be partially attributed to the difference in the vertical gradient of CO_2 between the inner and outer shelf areas during the stratification period. From autumn to winter, $p\mathrm{CO}_2^{\mathrm{sw}}$ decreased with decreasing SST in both the inner and outer shelf areas, suggesting that the cooling effect is the predominant factor in controlling seasonal fluctuation of $p\mathrm{CO}_2^{\mathrm{sw}}$ during the cooling period in both areas. During the warming period (i.e., from winter to summer), $p\mathrm{CO}_2^{\mathrm{sw}}$ decreased in the inner shelf area but increased in the outer shelf area with the SST increase. The divergent relationships of $p\mathrm{CO}_2^{\mathrm{sw}}$ vs. SST suggest that in this period the effect of biological production overwhelmed temperature effect in the inner shelf area; meanwhile temperature was the dominant factor in regulating seasonal $p\mathrm{CO}_2^{\mathrm{sw}}$ oscillation in the outer shelf area. Such contrasting behaviors may result mainly from the fact that the summer phytoplankton bloom only occurs on the inner shelf, which receives an enormous nutrient discharge from the Changjiang, but biological production is very low all year round on the outer shelf, which is generally occupied by the nutrient depleted Kuroshio waters (Gong et al., 2003).

In summary, our results suggest that the extent of stratification and biological production in summer, which would largely control the steepness of the vertical gradient of CO_2 during the stratification period, may play a pivotal role in determining the subsequent seasonal variation of $p\mathrm{CO}_2^{\mathrm{sw}}$ when stratification breaks.

3.3 Eutrophication induced changes between the 1990s and the 2000s

With the intention of examining the potential impact of eutrophication on the seasonal variation of CO_2 uptake in the ECS shelf, the present $p\mathrm{CO}_2^{\mathrm{sw}}$ measurements (referred to as $p\mathrm{CO}_2^{\mathrm{sw}}$ 2000s hereafter) are compared with the historical $p\mathrm{CO}_2^{\mathrm{sw}}$ data set along the PN line (the right panels in Fig. 2; referred to as $p\mathrm{CO}_2^{\mathrm{sw}}$1990s hereafter), which is the earliest $p\mathrm{CO}_2^{\mathrm{sw}}$ survey in the ECS conducted by Tsunogai et al. (1999) nearly 20 yr ago. To facilitate our comparison, the PN line and the present study area were arbitrarily divided into the inner and outer shelf areas (rectangular areas in Fig. 2). The former region corresponds to the typical Changjiang plume or CDW area (also the typical phytoplankton bloom area) in summer (Gao and Song, 2005), and it is thus considered a region that would be affected by eutrophication of the Changjiang over recent decades. The latter region is generally out of the influence of the Changjiang discharge, and thus it represents a region away from the impact of eutrophication.

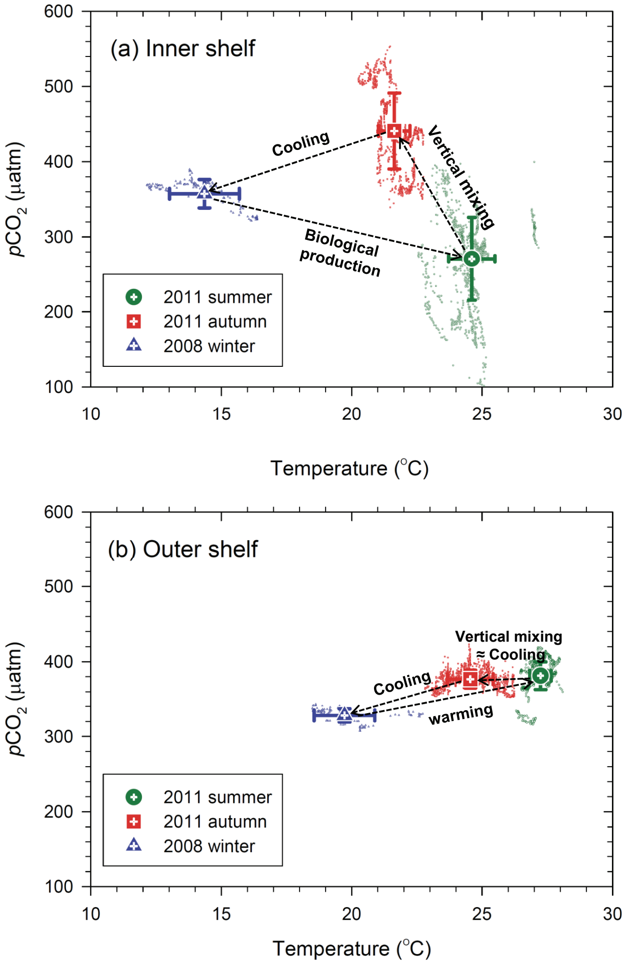

Fig. 5. Plots of $p\mathrm{CO}_2^{\mathrm{sw}}$ vs. temperature for summer 2011, autumn 2011, and winter 2008 data in **(a)** the inner shelf area and **(b)** the outer shelf area. The definitions of the inner and outer shelf areas are the same as in Fig. 2.

As shown in Fig. 2 and summarized in the upper panel in Fig. 6, $p\mathrm{CO}_2^{\mathrm{sw}}$ 2000s shows great seasonal variation and is apparently lower in summer but higher in autumn and winter than $p\mathrm{CO}_2^{\mathrm{sw}}$ 1990s in the defined inner shelf area. In contrast, no discernible difference between $p\mathrm{CO}_2^{\mathrm{sw}}$ 2000s and $p\mathrm{CO}_2^{\mathrm{sw}}$ 1990s was found in the defined outer shelf region in any season (Fig. 2, the lower panel in Fig. 6). We suggest that the discrepancy in the observed decadal change of seasonal $p\mathrm{CO}_2^{\mathrm{sw}}$ variations between the inner and the outer shelf regions reflects the differential impact of the increased eutrophication on the two regions. As depicted in the middle panel in Fig. 6, the increased eutrophication would enhance biological production in summer, and thus cause a lower surface water $p\mathrm{CO}_2^{\mathrm{sw}}$ in the 2000s than in the 1990s, meaning that the capacity of CO_2 sequestration was enhanced in summer. On the other hand, the increasing eutrophication would simultaneously form a steeper vertical gradient of CO_2 in summer in the 2000s compared with the 1990s, as more CO_2 is removed

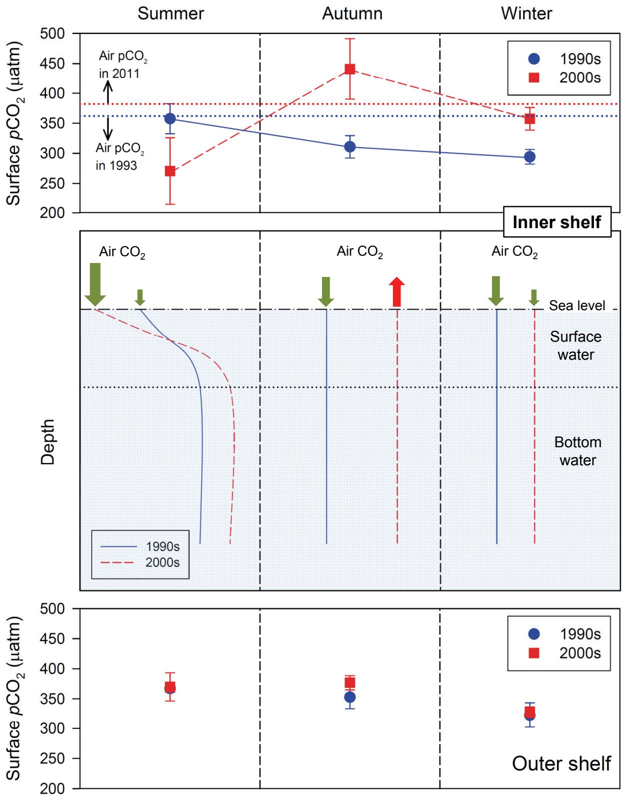

Fig. 6. A conceptual diagram showing the decadal change of seasonal variations of pCO_2 and their vertical distributions between the 1990s and the 2000s related to the worsening eutrophication on the inner shelf near the Changjiang Estuary. The dotted line in the middle panel indicates the depth of pycnocline (P_D), defined as the depth with the steepest vertical gradient in density, based on which the water column was divided into the surface (above the P_D) and the bottom (below the P_D) layers.

in the surface water by enhanced biological production and more CO_2 is released and accumulated in the bottom water through respiration. The subsequent breakdown of stratification in autumn and winter would therefore supply more CO_2 from the bottom water, causing pCO_2^{sw} 2000s to be higher than pCO_2^{sw} 1990s, meaning that the capacity of CO_2 sequestration has declined in autumn and winter. In autumn, the inner shelf near the Changjiang Estuary could even have turned from a CO_2 sink in the 1990s to a CO_2 source in the 2000s. However, it must be pointed out that pCO_2^{sw} in autumn may be more sensitive to the timing of observation, because autumn is the transitional period when the water column changes from strongly stratified to well-mixed. For example, while the water column was completely mixed in the inner shelf during our 2000s survey (in late October to early November), it was still partially stratified during the 1990s survey (in early October; see Fig. 5 in Tsunogai et al., 1999). Thus, the pCO_2^{sw} in the 1990s after the complete water column overturn might have been somewhat higher than what was observed in October, and the exact value after seasonal mixing is subject to question. Nonetheless, our conclusion regarding the nature of the very different seasonal patterns in the variation of inner shelf pCO_2^{sw} between the two decades is solid.

Using Chl *a* concentration as an indicator to evaluate the response of biological production to eutrophication, Wang (2006) found that the surface Chl *a* concentration in the Changjiang plume (or CDW) in summer increased by a factor of four from 1984 to 2002. In addition, Ning et al. (2011) reported that the DO concentration in the bottom water of the Changjiang plume area in summer has gradually decreased, and the hypoxic bottom water near the Changjiang Estuary has progressively expanded eastward over recent decades, implying an increasing bottom accumulation of respired CO_2. These reports are generally consistent with the observed decadal change of seasonal pCO_2^{sw} variation on the inner shelf near the Changjiang Estuary, in which pCO_2^{sw} decreased in summer but increased in autumn and winter from the 1990s to the 2000s.

4 Summary and concluding remarks

In this study, we found that the distinct seasonality of pCO_2^{sw} between the inner shelf near the Changjiang Estuary and the outer shelf of the ECS may be associated with the steepness of the vertical gradient of CO_2 during the stratified period, which is largely determined by the extent of water impacted by the Changjiang discharge. The increasing eutrophication may have enhanced the vertical gradient of CO_2 by taking up CO_2 (photosynthesis) in surface waters and releasing CO_2 (respiration) in deep waters, providing a mechanism for releasing CO_2 to the atmosphere when the bottom water overturns in late autumn, and thereby altering the seasonal variation pattern of pCO_2^{sw} in the inner shelf near the Changjiang Estuary over recent decades. It is noteworthy that in addition to the seasonal overturn of water column, strong vertical mixing induced by episodic severe weather events, such as typhoons, may be another mechanism returning respired CO_2 to the atmosphere (Hung et al., 2010; Hung and Gong, 2011). This process is worth further study, since the strength and frequency of severe weather events are expected to increase with global warming.

Although increased eutrophication/respiration could well explain the observed decadal change in the seasonal variation of pCO_2^{sw}, other processes such as alteration of circulation and/or the Changjiang discharge may also change the seasonal variation of pCO_2^{sw}. Therefore, more long-term studies are needed to unveil the fundamental relationship between changes in oceanic CO_2 uptake and increased eutrophication and hypoxia in the ECS, and in other eutrophication-impacted coastal seas as well. Furthermore, it is not possible at this time to conclude unequivocally whether or not the annual CO_2 sink in the inner shelf near the Changjiang

Estuary has increased or decreased in response to worsening eutrophication/hypoxia over recent decades, because the net CO_2 balance is closely dependent on the relative timescale of air–sea gas exchange and offshore transport of the shelf water (Thomas et al., 2004). Unfortunately, this is not well constrained by the data available. Nevertheless, our finding suggests that CO_2 dynamics in both the surface and bottom waters need to be taken into account together for modeling and observational studies ascribing the change of oceanic CO_2 uptake to eutrophication.

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