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Revisiting the Seasonal Variations of Sea-Air CO_2 Fluxes in the Northern East China Sea

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ABSTRACT

Temperature, salinity, chlorophyll *a* (Chl-*a*), nitrate, and sea-air differences of CO_2 partial pressure (ΔpCO_2) were extensively investigated in the northern East China Sea (ECS) during seven research cruises from 2003 to 2009. The ΔpCO_2 showed large intraseasonal variation in the spring and summer. In spring, the areal mean ΔpCO_2 in May 2004 was almost half of that in April 2008, probably associated with differences in sea surface temperature (SST). In summer, the areal mean ΔpCO_2 in August 2003 was also twice as large as that in July 2006. In addition, ΔpCO_2 exhibited large seasonal variation with positive values in autumn and negative values in other seasons. The positive ΔpCO_2 in autumn was ascribed to vertical mixing with CO_2-enriched subsurface waters and relatively high SST in this season. The annually integrated sea-air CO_2 flux in the northern ECS was -2.2 ± 2.1 mol m^{-2} yr^{-1}, indicating CO_2 absorption from atmosphere to the sea, which was more than two times lower than the previous estimate (Shim et al. 2007) reported for the same region. This large difference was presumably responsible for the underestimation of winter CO_2 influx by Shim et al. (2007) and the large interannual variation of CO_2 flux. The CO_2 influx in the ECS was twice that estimated for continental shelves worldwide, suggesting that the ECS acts as a strong sink of atmospheric CO_2 compared to other continental shelves.

Key words: Surface pCO_2, SST, SSS, Sea-air CO_2 flux, Seasonal variation, East China Sea

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1. INTRODUCTION

Although continental margins cover only about 7% of the world's ocean surface area, they play a major role in oceanic carbon cycling, receiving larger nutrient supplies from riverine input and sustaining higher biological production because of coastal upwelling (Chen and Borges 2009). The complex and dynamic nature of the continental margin produces highly variable sea-air CO_2 fluxes. Recently, Chen and Borges (2009) synthesized worldwide measurements of the partial pressure of CO_2 (pCO_2) at the continental shelves and suggested that the temperate and high-latitude shelves are undersaturated with respect to atmospheric CO_2 in all seasons, while low-latitude shelves are oversaturated. On the basis of pCO_2 data obtained at 60 continental shelves around the world, they also concluded that continental shelves indeed act as a sink for atmospheric CO_2. However, large ranges of error are involved in estimating the role of coastal carbon uptake in the global carbon cycle due to the complexity of coastal ecosystems and hydrodynamics (Zhai et al. 2005; Shim et al. 2007; Chen and Borges 2009; Zhai and Dai 2009). Therefore, spatially and temporally high-resolution pCO_2 measurements are needed to obtain precise estimates of sea-air CO_2 fluxes at the continental margin.

The East China Sea (ECS) is the third largest marginal sea in the world and includes a large area of shallow continental shelf with enormous freshwater inputs from the Changjiang. The ECS is one of the most productive marginal seas in the world due to the large nutrient supply from the Changjiang and upwelling (Wong et al. 2000; Gong et al. 2003). Measurements of the surface pCO_2 and other carbon parameters have been carried out in the ECS since the late

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1990s (Tsunogai et al. 1997, 1999; Peng et al. 1999; Wang et al. 2000; Shim et al. 2007; Chou et al. 2009; Zhai and Dai 2009). Tsunogai et al. (1999) measured the surface CO_2 fugacity in the central ECS over five cruises in various seasons and suggested that the ECS absorbed atmospheric CO_2 at a rate of 2.9 mol m^{-2} yr^{-1}. Shim et al. (2007) observed the surface pCO_2 in the northern ECS during four cruises in three seasons and estimated sea-air CO_2 flux to be -0.87 mol m^{-2} yr^{-1} based on Wanninkhof's (1992) equation; this estimate was more than three times lower than the estimate provided by Tsunogai et al. (1999). In addition, Zhai and Dai (2009) examined surface pCO_2 and dissolved oxygen in the outer Changjiang Estuary during seven field surveys and estimated the integrated sea-air CO_2 flux to be -1.9 mol m^{-2} yr^{-1}, with CO_2 influx more than double the estimate of Shim et al. (2007). The results of previous studies suggest that sea-air CO_2 fluxes are fairly variable in the different regimes of the ECS. Because the ECS is hydraulically dynamic and complex due to influences of the Kuroshio Current and large river discharge from the Changjiang, high-resolution temporal and spatial measurements are essential to obtain unbiased estimates of sea-air CO_2 fluxes in the ECS.

We measured pCO_2 during seven research cruises in the northern ECS in various seasons from 2003 to 2009; Shim et al. (2007) estimated the sea-air CO_2 fluxes in the northern ECS based on the pCO_2 data obtained from 2003 to 2005. The additional pCO_2 data from 2006 to 2009 may provide a better estimate of sea-air CO_2 fluxes than the previous estimate of Shim et al. (2007). The goals of this study were to monitor sea-air differences of CO_2 partial pressure (ΔpCO_2), elucidate intra- and interseasonal variations of ΔpCO_2, and provide an unbiased estimate of sea-air CO_2 fluxes in the northern ECS.

2. MATERIALS AND METHODS

2.1 Analytical methods

Measurements for this study were performed during seven cruises of the R/V *Eardo* in the spring (29 April - 8 May 2004, 14 - 24 April 2008), summer (26 August - 3 September 2003, 19 - 25 July 2006), autumn (3 - 8 October 2004, 1 - 8 November 2005), and winter (16 - 22 February 2009). Shim et al. (2007) used the data obtained from 2003 to 2005 for the estimate of the sea-air CO_2 fluxes in the northern ECS. The study area was the northern ECS surrounding Cheju Island (31°30'N - 34°0'N, 124°0'E - 127°30'E) and was divided into eastern and western parts on the basis of the thermohaline front located around 125 - 126.5°E (Fig. 1), which formed between the Tsushima Warm Current water and coastal water (Hickox et al. 2000). The eastern part of the study area with properties of the Tsushima Warm Current had warmer temperatures and higher salinities than the western part.

Continuous measurements of pCO_2, temperature, and salinity were made for surface water which was pumped on board from 5 m below the sea surface during the survey. The pCO_2 of surface water and bow air was measured every minute and every hour, respectively, using a flowing pCO_2 system and a showerhead equilibrator. The pCO_2 measurements were described in detail by Shim et al. (2007). Vertical profiles of temperature and salinity were measured with a SeaBird conductivity-temperature-depth sensor (CTD; SBE 9/11 plus, SeaBird Inc., Bellevue, WA, USA). Seawater samples were collected for nitrate and chlorophyll *a* (Chl-*a*) analyses using a Rosette sampler with 10-L Niskin bottles mounted on the CTD assembly at seven water depths (0, 10, 20, 30, 50, 75, and 100 m). Bottom samples were col-

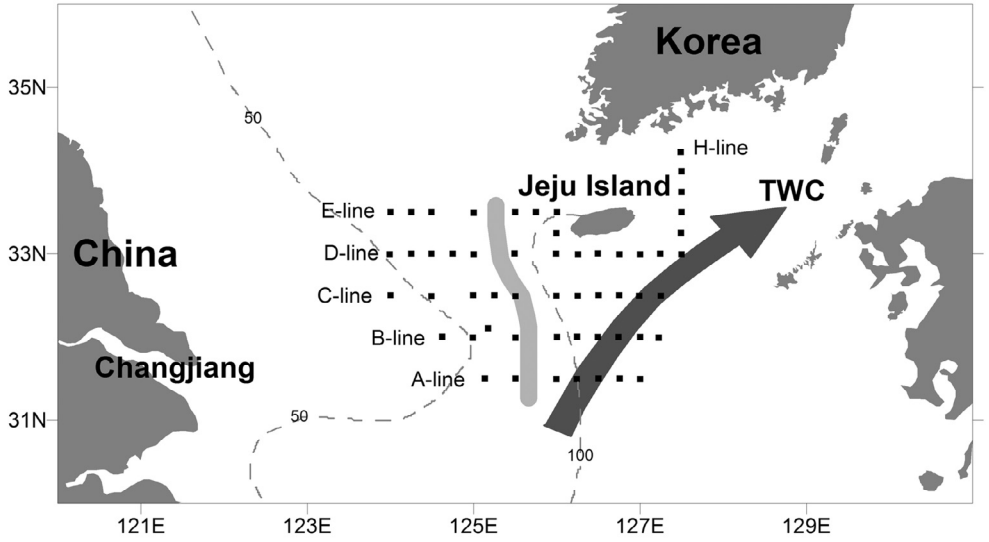

Fig. 1. Study area and locations of sampling stations in the northern East China Sea. The thick gray line indicates a thermohaline front. TWC: Tsushima Warm Current.

lected at 5 m above the bottom for stations with water depth of less than 100 m. Water samples for nitrate analysis were filtered through GF/F filter paper (25 mm, Whatman, Middlesex, UK), placed in acid-cleaned polyethylene bottles, and poisoned with $HgCl_2$, which did not have any effect on the determination of nitrate concentration (Kattner 1999). Nitrate concentrations were measured using a flow injection autoanalyzer (model QuikChem AE, Lachat, Loveland, CO, USA) and standard colorimetric procedures (Strickland and Parsons 1972) and calibrated using brine standard solutions (CSK Standard Solutions, Wako Pure Chemical Industries, Osaka, Japan). Duplicate analyses suggested that the precision of the nitrate measurements was 3%. Water samples for Chl-*a* analysis were filtered through GF/F filter paper (47 mm, Whatman); the filters were then immediately frozen with liquid nitrogen. The Chl-*a* concentration in the extracted filtrate mixed with 90% acetone for 24 h was determined using a Turner-designed fluorometer (10-006R, Turner BioSystems, Sunnyvale, CA, USA).

2.2 Calculation of Sea-Air CO_2 Flux

The CO_2 exchange fluxes across the sea-air interface were calculated based on the equation $F = k \times s \times \Delta pCO_2$, where k is the gas transfer velocity (cm h^{-1}), s is the solubility of CO_2 gas in seawater (mol kg^{-1} atm^{-1}) (Weiss 1974), and ΔpCO_2 is the sea-air differences of CO_2 partial pressure. The parameterization implies that fluxes at the sea-air interface into the surface water (sinks) are negative and fluxes within the atmosphere (sources) are positive. We used the formula for k from Wanninkhof [1992, $k = 0.31u^2(Sc/660)^{-1/2}$] to allow for comparison of our results with those of most other studies. Wind speed is the main force driving gas exchange at the sea-air interface. This study used the daily averaged QuikSCAT wind speed data for the cruise dates obtained from the Physical Oceanography Distributed Active Archive Center of the Jet Propulsion Laboratory, National Aeronautics and Space Administration of the United States (PO.DAAC, JPL, NASA: http://podaac.jpl.nasa.gov).

3. RESULTS

3.1 Spring Observations

Spring observations were conducted in May 2004 and April 2008. In May 2004, sea surface temperatures (SSTs) ranged from 13.6 to 23.4°C, with an increasing gradient from west to east across the study area; these temperatures were slightly higher than those in April 2008, which ranged from 11.1 to 18.1°C (Fig. 2). Sea surface salinities (SSSs) also showed an increasing gradient from west to east and did not exhibit a considerable difference between May 2005 and April 2008. In spring, the thermohaline front was located around 126°E. Average atmospheric pCO_2 was 378.0 ± 6.3 and 382.5 ± 3.3 μatm in May 2004 and April 2008, respectively (Table 1). In May 2004, the sea-air ΔpCO_2 had negative values in most parts of the study area, with a minimum of -126 μatm, and positive values west of 125°E, with a maximum of 54 μatm (Fig. 2). In April 2008, however, the values for ΔpCO_2 were negative across the entire study area, with a range of approximately -152 to -13 μatm. The highest negative ΔpCO_2 was observed at the frontal area located at 126°E. The areal mean ΔpCO_2 was -48 ± 41 μatm in May 2004 and -87 ± 20 μatm in April 2008 (Table 2). In spring, high surface Chl-*a* concentrations were observed in the western part of the study area, with maximum values of 3.7 and 8.1 mg m^{-3} in May 2004 and April 2008, respectively (Fig. 2). Noh et al. (2005) reported that spring bloom started in April in the northern ECS. Surface nitrate concentrations were highest in the westernmost part of the study area, and decreased gradually eastward; concentrations in the eastern part of the study area were lower than 1.0 μmol L^{-1} (Fig. 2). Kim et al. (2009) suggested that the high surface nitrate concentrations in the northern ECS during spring resulted from vertical mixing, which brought large supplies of nitrate from deep water.

3.2 Summer Observations

Summer data were obtained from two expeditions conducted in August 2003 and July 2006. In August 2003, SSTs showed a high, narrow range between 25.4 and 29.5°C, without a distinct spatial pattern, and were somewhat higher than SSTs in July 2006, which ranged from 22.5 - 27.2°C and had a decreasing gradient from west to east (Fig. 2). Low SSSs (< 29.0) were observed in the western part of the study area during the two summer expeditions (Fig. 2), suggesting large summer inputs of freshwater from the Changjiang. The thermohaline front was located around 126.5°E in August 2003 and 126°E in July 2006. Average atmospheric pCO_2 was 368.8 ± 3.5 and 368.0 ± 6.6 μatm in August 2003 and July 2006, respectively (Table 1). In August 2003, the sea-air ΔpCO_2 showed positive values in the eastern part with a maximum of 67 μatm and negative values in the western part with a minimum of -142 μatm (Fig. 2). In July 2006, the sea-air ΔpCO_2 values were negative across the entire study area with a minimum of -198 μatm, except for the frontal area where pCO_2 was slightly oversaturated. The CO_2 sink in the eastern part was not as strong as that in the western part. The areal mean ΔpCO_2 was -41 ± 47 μatm in August 2003 and -85 ± 59 μatm in July 2006 (Table 2), rather similar to values for spring. Surface Chl-*a* concentrations were much lower in summer than in spring (Fig. 2); in August 2003, surface Chl-*a* concentrations ranged from 0.2 to 1.3 mg m^{-3}, lower than the range of 0.4 - 2.9 mg m^{-3} for July 2006. As in spring, summer surface Chl-*a* concentrations were somewhat higher in the western part than in the eastern part of the study area. In summer, high surface nitrate concentrations were confined to a small region of the

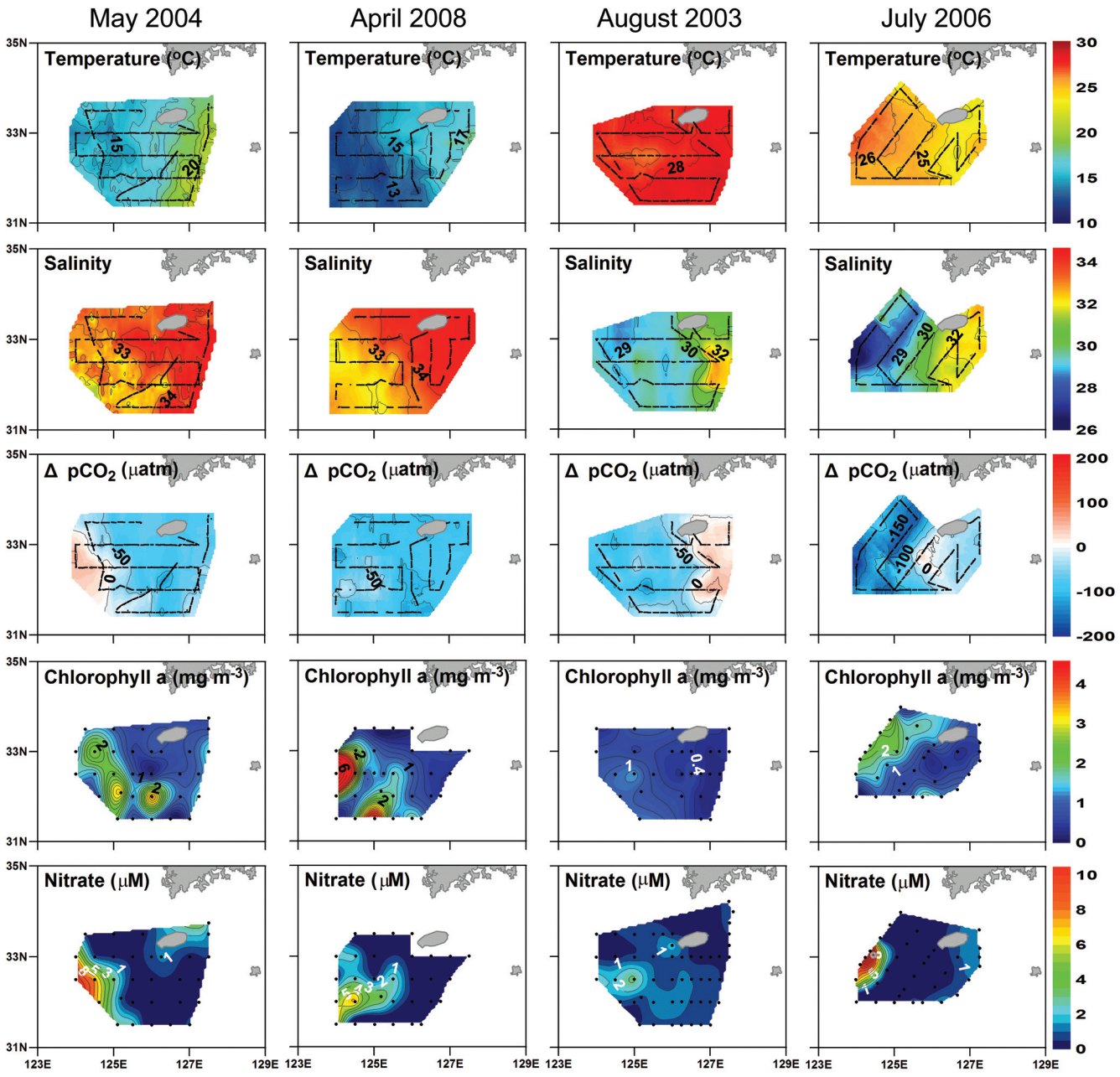

Fig. 2. Surface distributions of temperature, salinity, sea-air differences of CO_2 partial pressure (ΔpCO_2), chlorophyll *a*, and nitrate in the northern East China Sea in spring and summer. Data obtained in August 2003 and May 2004 are from Shim et al. (2007).

Table 1. Average atmospheric pCO_2 for the seven surveys.

Periods	Atmospheric pCO_2		Periods	Atmospheric pCO_2	
	Fugacity (μatm)	Mole fraction (ppm, in dry air)		Fugacity (μatm)	Mole fraction (ppm, in dry air)
August 2003	368.8 ± 3.5	386.6 ± 4.3	July 2006	368.0 ± 6.6	381.6 ± 7.2
May 2004	378.0 ± 6.3	386.8 ± 6.0	April 2008	382.5 ± 3.3	390.4 ± 3.4
October 2004	365.4 ± 3.0	377.0 ± 3.3	February 2009	384.7 ± 3.1	392.4 ± 2.9
November 2005	376.8 ± 3.8	388.3 ± 4.2			

Table 2. Areal mean sea-air differences of CO_2 partial pressure (ΔpCO_2), mean wind speed, and mean sea-air CO_2 flux in the northern East China Sea over the four seasons.

Season	Observation time	ΔpCO_2 [a] (μatm)	Wind speed [b] (m sec^{-1})	CO_2 flux [c] (mmol m^{-2} day^{-1})	
				Survey average	Seasonal average
Spring	May 2004	-48 ± 41	6.5 ± 3.5	-5.1 ± 4.3	-6.8 ± 4.3
	April 2008	-87 ± 20	6.2 ± 2.7	-8.4 ± 1.9	
Summer	August 2003	-41 ± 47	7.4 ± 2.5	-6.0 ± 6.8	-6.6 ± 8.5
	July 2006	-85 ± 59	5.8 ± 1.8	-7.2 ± 5.1	
Autumn	October 2004	7.9 ± 40	9.1 ± 2.1	1.6 ± 8.2	0.81 ± 7.3
	November 2005	0.1 ± 34	6.4 ± 2.5	0.02 ± 3.5	
Winter	February 2009	-50 ± 17	10 ± 3.5	-12 ± 4.1	-12 ± 4.1

a Mean ΔpCO_2 along cruise tracks expressed as mean ± S.D.

b Mean wind speed of study area (31.5 - 34°N, 124 - 127.5°E) from QuickSCAT satellite data during each observation period expressed as mean ± S.D.

c Mean sea-air CO_2 fluxes based on the transfer coefficient by Wanninkhof (1992) expressed as mean ± S.D. A positive value represents CO_2 emission from the sea to the atmosphere and a negative value refers to CO_2 absorption from atmosphere to the sea.

western part, with all other areas showing very low nitrate concentrations of less than 1.0 μmol L^{-1} (Fig. 2). Kim et al. (2009) suggested that the inflow of the Changjiang plume in summer caused the high surface nitrate concentrations in the northern ECS.

3.3 Autumn Observations

Autumn observations were carried out in October 2004 and November 2005. In October 2004, SSTs varied from 22.2 to 25.7°C, with an increasing gradient from west to east. In November 2005, the range was somewhat lower at 18.7 - 24.5°C (Fig. 3). In the eastern part of the study area, SSSs were relatively high at around 34 and generally similar for the two observations. However, in the western part, SSSs were somewhat lower in November 2005 than in October 2004 (Fig. 3). The thermohaline front was located around 126.5°E in October 2004 and 125°E in November 2005. Average atmospheric pCO_2 was 365.4 ± 3.0 and 376.8 ± 3.8 μatm in October 2004 and November 2005, respectively (Table 1). In October 2004, sea-air ΔpCO_2 was positive in the western part with a maximum of 202 μatm, but negative in the eastern part with a minimum of -40 μatm (Fig. 3). Maximum ΔpCO_2 was observed in the westernmost part and gradually decreased eastward. In November 2005, ΔpCO_2 also showed positive values in the western part with a maximum of 118 μatm and negative values in the eastern part with a minimum of -58 μatm. In autumn, the western part acted as a source of CO_2, and the eastern part as a sink. The areal mean ΔpCO_2 values were 7.9 ± 40 and 0.1 ± 34 μatm in October 2004 and November 2005, respectively (Table 2), implying that the study area was a source of CO_2 in autumn, unlike in other seasons. In autumn, high surface Chl-*a* concentrations were observed in the western part, with maximum values of 2.2 and 4.1 mg m^{-3} in October 2004 and November 2005, respectively (Fig. 3), which were somewhat lower than maximum values in spring. High surface nitrate concentrations were also found in the western part, with maximum values of 4.2 and 12.4 μmol L^{-1} in October 2004 and November 2005, respectively (Fig. 3), which were rather similar to those in spring. In the eastern part, however, surface nitrate concentrations were lower than 1.0 μmol L^{-1}, as in spring.

3.4 Winter Observation

The winter data were based on a single expedition carried out in February 2009. SSTs ranged from 9.6 to 17.1°C with an increasing gradient from west to east across the study area (Fig. 3). SSSs also showed an increasing gradient from west to east, with a range of 32.1 to 34.5 (Fig. 3). In winter, the thermohaline front was located around 126°E. Average atmospheric pCO_2 was 384.7 ± 3.1 μatm in February 2009 (Table 1). The sea-air ΔpCO_2 values were negative across the entire study area, with a minimum of -77 μatm. The areal mean ΔpCO_2 was -50 ± 17 μatm (Table 2), implying that the study area was a CO_2 sink in winter. The CO_2 sink in the western part was not as strong as that in the eastern part. Surface Chl-*a* concentrations were very low, less than 0.6 mg m^{-3}, across the entire study area (Fig. 3). High surface nitrate concentrations were found in the westernmost part, with a maximum value of 13.8 μmol L^{-1}, and decreased gradually eastward (Fig. 3).

4. DISCUSSION

Surface pCO_2 is controlled by several factors, such as temperature, salinity, biological activity, sea-air exchange,

and vertical/lateral advection (Miller et al. 2002; Murata and Takizawa 2003; Schiettecatte et al. 2007; Shim et al. 2007, Zhang et al. 2010). In the northern East China Sea, Shim et al. (2007) suggested that the seasonal variations of surface pCO_2 were primarily ascribed to temperature in the eastern part and vertical mixing in the western part. Figure 4 shows new ΔpCO_2 dataset reported in this study and the old dataset in Shim et al. (2007).

4.1 Interannual Variation of Sea-Air ΔpCO_2

Sea-air ΔpCO_2 showed a slight difference between the two spring observations; ΔpCO_2 values were negative across the entire study area in April 2008, but positive values were found in the western part in May 2004 (Fig. 2). Shim et al. (2007) suggested that high surface pCO_2 in the northern ECS during spring resulted from vertical mixing with CO_2-enriched subsurface waters. Thus, the positive ΔpCO_2 in May 2004 was attributed to vertical mixing. In April 2008, the western part showed high surface Chl-*a* concentrations (up to 8.1 mg m^{-3}), which reinforced CO_2 uptake by photosynthesis. This strong biological activity probably offset the increase in surface pCO_2 from vertical mixing and led to the negative ΔpCO_2 in this region. SSTs in the western part were approximately 2.0°C lower in April 2008 than in May 2004, which also decreased the surface pCO_2 and led

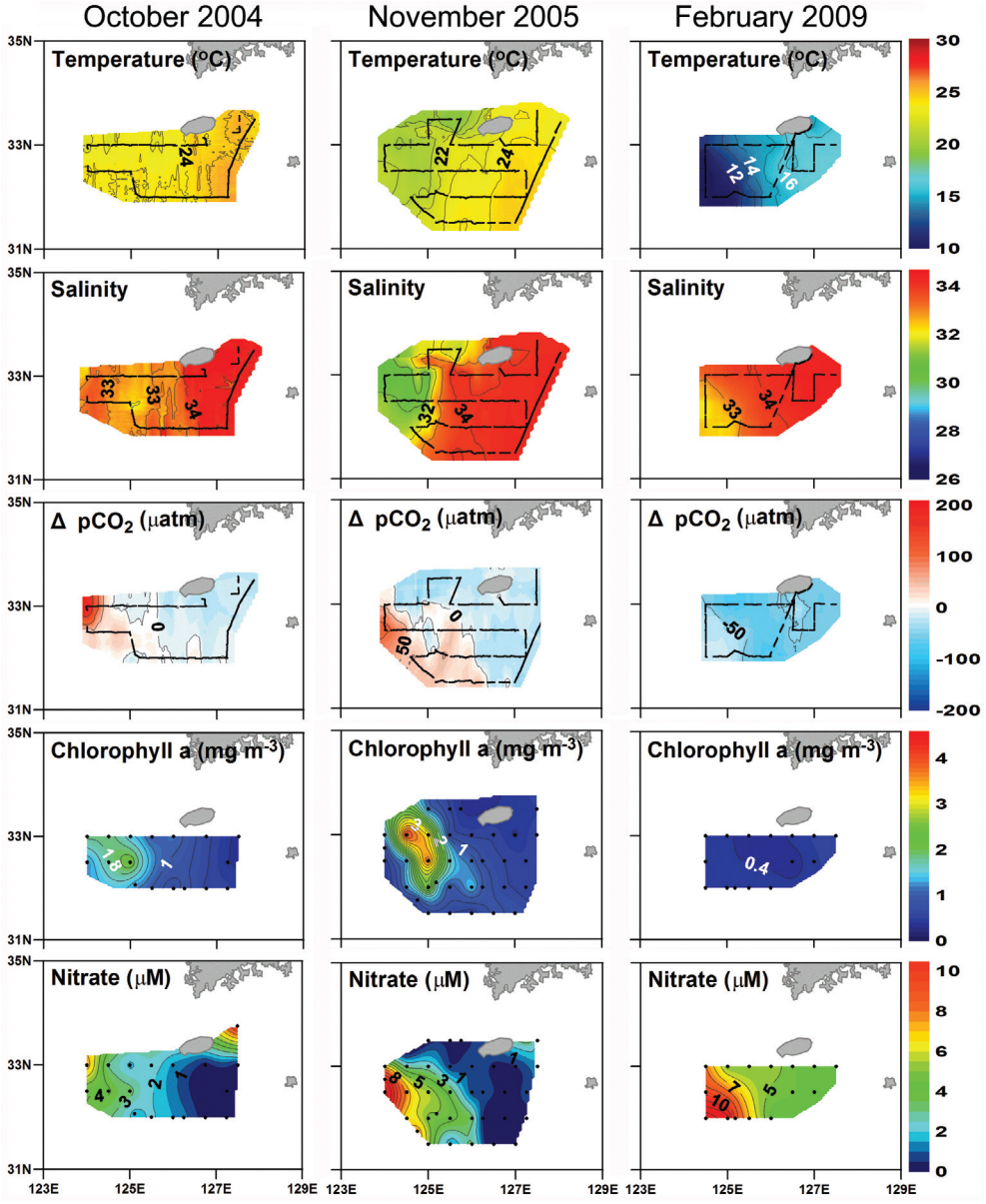

Fig. 3. Surface distributions of temperature, salinity, sea-air differences of CO_2 partial pressure (ΔpCO_2), chlorophyll *a*, and nitrate in the northern East China Sea in autumn and winter. Data obtained in October 2004 and November 2005 are from Shim et al. (2007)

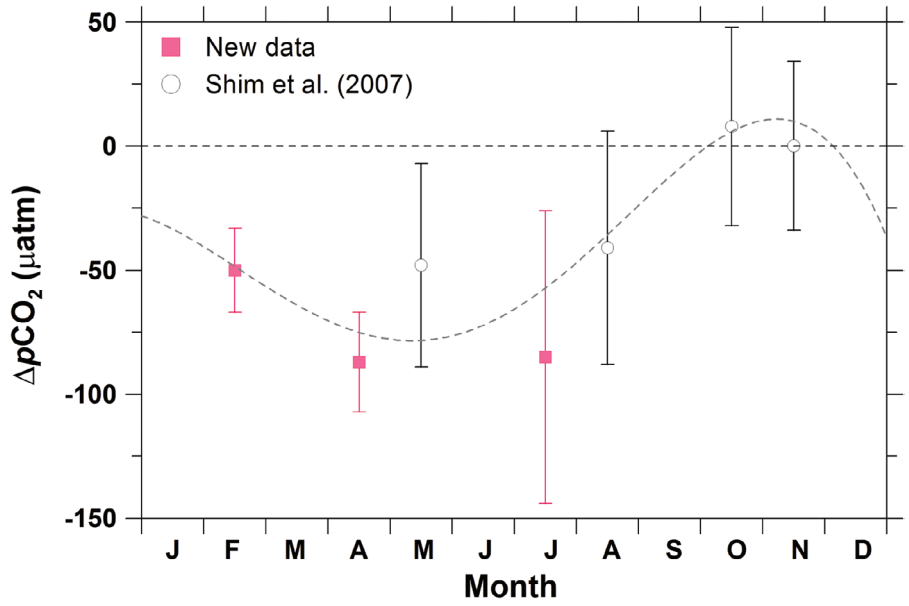

Fig. 4. A comparison between new ΔpCO_2 dataset reported in this study and the old dataset in Shim et al. (2007).

to negative ΔpCO_2 in this region. The areal mean ΔpCO_2 in May 2004 was almost half of that in April 2008, probably because of the differences in SST. The areal mean SST was higher by about 3.0°C in May 2004 than in April 2008 which would increase pCO_2 by 48 μatm in the study area considering the coefficient of 4.23% $°C^{-1}$ (Takahashi et al. 1993) which is rather similar to the difference (39 μatm) in the areal mean ΔpCO_2 between May 2004 and April 2008.

The two summer observations of sea-air ΔpCO_2 also differed. In July 2006, ΔpCO_2 was negative across the entire study area except for the frontal area, but in August 2003 positive values were found in the eastern part (Fig. 2). In summer, the strong CO_2 sink in the western part was ascribed to low SSS in the region, as supported by previous observations of lower pCO_2 in less saline surface waters in the ECS during summer (Tsunogai et al. 1999; Wang et al. 2000; Shim et al. 2007; Chou et al. 2009; Zhai and Dai 2009). In the study area, the less saline surface waters in summer originated mainly from the Changjiang plume (Kim et al. 2009). The positive ΔpCO_2 in August 2003 may have been associated with high SSTs in the eastern part which increased the surface pCO_2 and led to oversaturation with respect to atmospheric CO_2. In July 2006, the negative ΔpCO_2 in the eastern part was probably due to lower SSTs, which were approximately 4°C lower than in August 2003. The areal mean ΔpCO_2 was lower by 44 μatm in July 2006 than in August 2003, probably as a result from differences in SSTs. The areal mean SST was 2.9°C higher in August 2003 than in July 2006, which would increase pCO_2 by 46 μatm in the study area considering the coefficient of 4.23% $°C^{-1}$ (Takahashi et al. 1993). Chou et al. (2009) reported that surface pCO_2 could be significantly influenced by large scale vertical mixing induced by typhoons in the East China Sea during summer. A typhoon had not passed over the study area at least 10 days before two summer expeditions, and thereby, the interannual variation of the sea-air ΔpCO_2 in summer was not associated with severe episodic weather events.

The two autumn observations, while only a month apart, showed a slight difference in the sea-air ΔpCO_2 (Fig. 3). The areal mean ΔpCO_2 differed by only 7.8 μatm between the two autumn observations (Table 2). SST and SSS displayed some differences, especially in the western part of the study area. The areal mean SST and SSS were 2.3°C and 0.5 higher in October 2004 than in November 2005, respectively. Surface Chl-*a* and nitrate concentrations were higher in November 2005 than in October 2004. Lower SSTs and SSSs and higher surface Chl-*a* concentrations in November 2005 might have decreased the surface pCO_2 and led to a lower ΔpCO_2. However, higher surface nitrate concentrations may indicate more active vertical mixing with CO_2-enriched subsurface waters, which would increase the surface pCO_2 and offset the pCO_2 decrease by the lower SSTs and SSSs and higher surface Chl-*a* concentrations. Kim et al. (2009) suggested that the high surface nitrate concentrations in the northern ECS during autumn resulted from vertical mixing with nutrient-enriched subsurface waters.

4.2 Seasonal Variation of Sea-Air ΔpCO_2

The sea-air ΔpCO_2 displayed unique seasonal variation in the northern ECS. In spring and autumn, ΔpCO_2 was positive in the western part and negative in the eastern part, whereas the opposite trend was found in summer. In

spring and autumn, the water column was less stratified and thus vertical mixing was active, especially in the western part where water depths were less than 50 m (Figs. 5 and 6). In spring and autumn, therefore, the positive ΔpCO_2 in the western part resulted from active vertical mixing with the CO_2-enriched bottom waters. Shim et al. (2007) also attributed the high surface pCO_2 in the western part during spring and autumn to vertical mixing with CO_2-rich water masses. Tsunogai et al. (1999) found high surface pCO_2 levels, above atmospheric CO_2 levels, in the western ECS in November 1995 and suggested that this was caused by turbulent mixing of the surface water with CO_2-rich subsurface water. In the eastern part where water depths were relatively deep (~100 m), vertical mixing in spring and autumn was limited to the upper 50 m, where CO_2 was not fully enriched (Peng et al. 1999). Therefore, the surface pCO_2 in the eastern part was not sufficiently increased by vertical mixing, and negative ΔpCO_2 was observed in spring and autumn.

In summer, the water column was strongly stratified (Fig. 5) and therefore, surface pCO_2 was not affected by vertical mixing. The surface pCO_2 in the ECS during summer was primarily determined by SST and SSS (Tsunogai et al. 1999; Wang et al. 2000; Shim et al. 2007; Chou et al. 2009). In summer, both SST and SSS were much higher in the eastern part than in the western part, which led to positive ΔpCO_2 in the eastern part and negative ΔpCO_2 in the western part. The relatively high surface Chl-*a* concentrations in the western part may have been responsible for the negative ΔpCO_2 in this region. Tsunogai et al. (1999) also found that the Kuroshio water was oversaturated with respect to atmospheric CO_2, but the region off the Changjiang was undersaturated.

In winter, the water column in the study area was completely mixed from the surface to the bottom (Fig. 6). Although there was active vertical mixing, values of ΔpCO_2 were negative across the entire study area, presumably due to low SSTs and sea-air CO_2 exchange. In the two autumn observations, ΔpCO_2 values were positive in the western part, indicating CO_2 degassing to the atmosphere in this region. Continuous CO_2 degassing from October to January may have reduced surface pCO_2 to the atmospheric CO_2 level. In the northern ECS, wind speeds were highest in winter (Table 2), which accelerated the CO_2 degassing in this season. In addition, SSTs were about 10°C lower in winter than in autumn, which may have brought surface pCO_2 below the atmospheric CO_2 level. Zhai and Dai (2009) also reported that surface pCO_2 was lower than the atmospheric pCO_2 level in the outer Changjiang Estuary in winter.

The areal mean sea-air ΔpCO_2 showed large seasonal variation, with maxima in autumn and minima in spring (Table 2). The mean ΔpCO_2 in summer was rather similar to that in spring, which was somewhat lower than that in winter. The mean ΔpCO_2 was positive only in autumn and negative in the other seasons. In autumn, temperature gradients disappeared in the upper 40 m, but still had high values, with a range of 21 - 25°C in this layer (Fig. 6). Thus, stratification was weakened in the surface layer and eventually vertical mixing actively occurred, especially in the western part where water depths were shallower than 50 m. Vertical mixing brought CO_2-enriched bottom waters to the

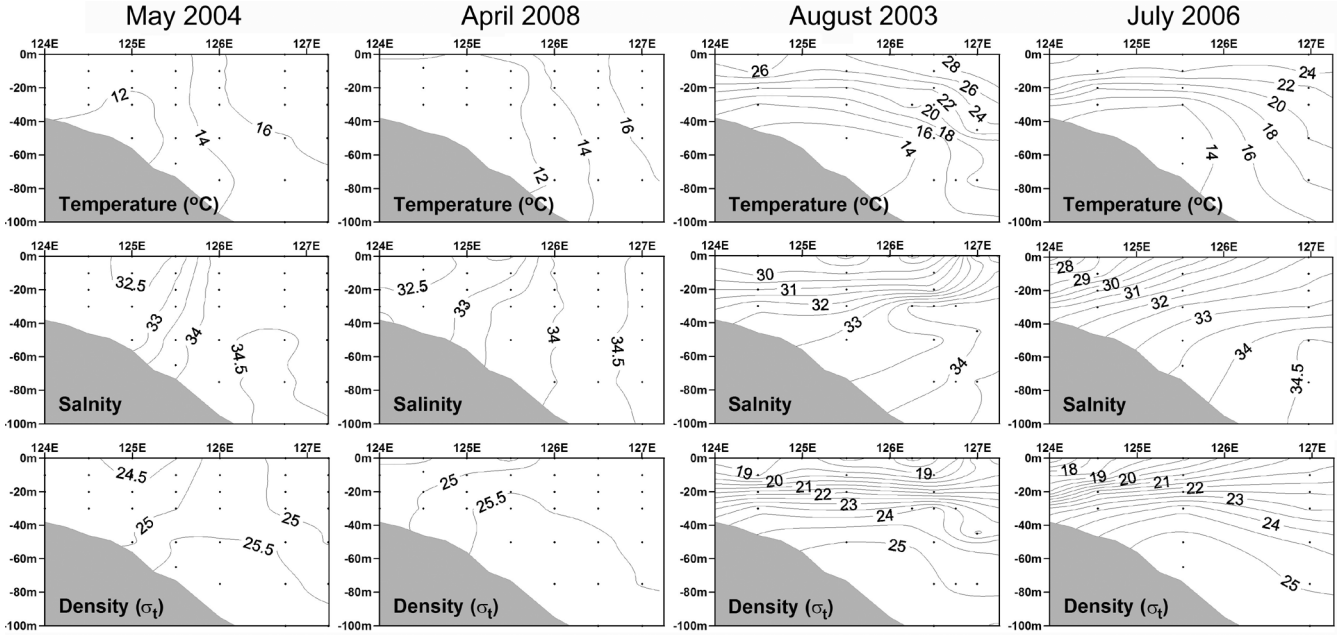

Fig. 5. Vertical distributions of temperature, salinity, and density in the northern East China Sea in spring and summer. Data obtained in August 2003 and May 2004 are from Shim et al. (2007).

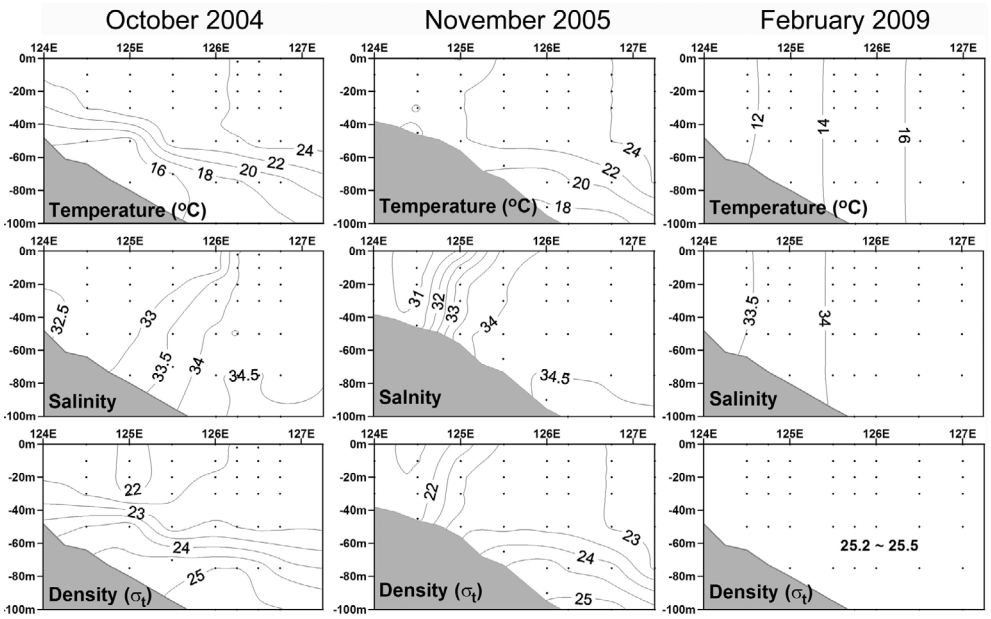

Fig. 6. Vertical distributions of temperature, salinity, and density in the northern East China Sea in autumn and winter. Data obtained in October 2004 and November 2005 are from Shim et al. (2007).

surface and resulted in the positive ΔpCO_2 in autumn. In addition, high SSTs (21 - 25°C) also contributed to maintaining the positive ΔpCO_2. Zhai and Dai (2009) also reported that autumn was the only season when the outer Changjiang Estuary degassed CO_2 to the atmosphere. They suggested that hypoxic and CO_2-rich bottom waters mixed with surface waters in late autumn, and thus degassed CO_2 to the atmosphere.

4.3 Sea-Air CO_2 Fluxes

Table 2 displays the areal mean sea-air ΔpCO_2, monthly averaged wind speeds, and the calculated sea-air CO_2 fluxes for the seven expeditions. The calculated CO_2 flux results indicate that the northern ECS was a sink of atmospheric CO_2 in spring, summer, and winter, but a small source of CO_2 to the atmosphere in autumn.

Spring CO_2 influxes (negative sign) were 5.1 ± 4.3 and 8.4 ± 1.9 mmol m^{-2} day^{-1} in May 2004 and April 2008, respectively (Table 2). The higher CO_2 influx in April 2008 was presumably associated with the lower SSTs and higher biological activity compared with those of May 2004. The average CO_2 influx in spring was 6.8 ± 4.3 mmol m^{-2} day^{-1}, which was somewhat lower than that (8.8 ± 5.8 mmol m^{-2} day^{-1}) calculated for the outer Changjiang Estuary during spring (Zhai and Dai 2009), but higher than that (5.8 ± 7.7 mmol m^{-2} day^{-1}) estimated for the ECS during spring (Peng et al. 1999).

In summer, the two estimates of sea-air CO_2 flux did not differ much, despite the large difference in ΔpCO_2 (Table 2). The average CO_2 influx in summer was 6.6 ± 8.5 mmol m^{-2} day^{-1}, rather similar to that in spring. The summer CO_2 influx was somewhat higher than that (4.9 ± 4.0 mmol m^{-2} day^{-1}) for the outer Changjiang Estuary during summer (Zhai and Dai 2009) and similar to that (6.3 ± 3.7 mmol m^{-2} day^{-1}) estimated for the ECS during summer, excluding the coastal upwelling area that was the most important CO_2 source in the ECS (Chou et al. 2009).

In autumn, the northern ECS emitted CO_2 to the atmosphere at a rate of 0.81 ± 7.3 mmol m^{-2} day^{-1} (Table 2). Tsunogai et al. (1997) reported that the East China Sea was undersaturated with respect to atmospheric CO_2 in autumn, and thus absorbed CO_2 from the atmosphere. However, Tsunogai et al. (1999) found high surface pCO_2, above the atmospheric CO_2 level, along the continental shelf zone of the ECS in November 1995. Zhai and Dai (2009) also reported that CO_2 was emitted at a rate of 2.9 ± 2.5 mmol m^{-2} day^{-1}, more than three times our estimate, in the outer Changjiang Estuary during autumn.

The largest CO_2 influx (12 ± 4.1 mmol m^{-2} day^{-1}) occurred in winter (Table 2). This high CO_2 influx can be attributed primarily to high wind speeds in winter, because the winter ΔpCO_2 in water was lower than those in spring and summer. Shim et al. (2007) assumed that the winter CO_2 flux in the northern ECS was an intermediate value (-2.3 mmol m^{-2} day^{-1}) between spring and autumn; their estimate was about five times lower than our estimate. Zhai and Dai (2009) reported that the sea-air CO_2 flux was -10 ± 2.3 mmol m^{-2} day^{-1} in the outer Changjiang Estuary over the winter, which was rather lower than our estimate. Chou

et al. (2011) also reported that the average sea-air CO_2 flux was -14 ± 5.3 mmol m^{-2} day^{-1} in the East China Sea during winter, which was rather higher than our estimate.

The annually integrated sea-air CO_2 flux in the northern ECS was -2.2 ± 2.1 mol m^{-2} yr^{-1} (Table 2), more than two times a previous estimate (-0.87 mol m^{-2} yr^{-1}) for the northern ECS (Shim et al. 2007). This large difference was presumably responsible for the underestimation of winter CO_2 influx by Shim et al. (2007) and the large intraseasonal variation of CO_2 flux. High-resolution temporal observations are the only way to overcome misleading results caused by large intraseasonal variations. Our estimate was rather similar to previous estimates for the ECS (2.0 - 3.0 mol m^{-2} yr^{-1}) (Tsunogai et al. 1997, 1999; Chen and Wang 1999; Wang et al. 2000). Zhai and Dai (2009) estimated an annually integrated CO_2 flux in the outer Changjiang Estuary to be 1.9 mol m^{-2} yr^{-1} based on seven field surveys, but this estimate was confined to the western part of the ECS where Kuroshio water was not observed. The annually integrated CO_2 flux for worldwide continental shelves was -1.1 mol m^{-2} yr^{-1} on average (Chen and Borges 2009), which was lower than the CO_2 influx estimated for the ECS. Therefore, the ECS acts as a strong sink for atmospheric CO_2 in comparison to other continental shelves.

5. CONCLUSIONS

Based on observations from seven research cruises with high temporal and spatial resolution, we showed that the northern ECS acts as an important sink for atmospheric CO_2. The sea-air CO_2 flux displayed large intraseasonal variation, especially in spring when phytoplankton blooms occasionally occurred. Furthermore, CO_2 flux exhibited large interseasonal variation, with CO_2 being emitted to the atmosphere in autumn and absorbed from the atmosphere in other seasons. The CO_2 degassing in autumn was attributable to vertical mixing with CO_2-enriched subsurface waters and relatively high SSTs in this season. In winter, CO_2 influx from the atmosphere was the highest among the four seasons owing to strong winds. The northern ECS adsorbed atmospheric CO_2 at an annual rate of 2.2 ± 2.1 mol m^{-2}, which was more than double a previous estimate (-0.87 mol m^{-2} yr^{-1}) for the northern ECS (Shim et al. 2007). This large difference perhaps resulted from underestimation of winter CO_2 influx by Shim et al. (2007) and the large interannual variation of CO_2 flux. This study corroborated the suggestion by Chen and Borges (2009) that high-resolution coverage, both temporal and spatial, could provide robust and unbiased estimates of sea-air CO_2 fluxes at continental shelves.

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