Interannual variations of net community production and air-sea CO₂ flux from winter to spring in the western subarctic North Pacific

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ABSTRACT

The role of spring biological production for the air-sea CO₂ flux was quantified in the Western Subarctic Gyre (48°N, 165°E), where the vertical profile of temperature revealed the existence of a temperature minimum (T_{\min}) layer in the North Pacific. The vertical profiles of temperature, salinity, dissolved oxygen, nutrients and dissolved inorganic carbon, DIC, in the upper water column were significantly variable year by year in spring, 1996-2000. Correspondingly, surface seawater at this site in spring was supersaturated with CO₂ in 1997, 1999 and 2000, but was undersaturated in 1996 and 1998. The concentrations of DIC and nutrients in the winter mixed layer were estimated from those in the T_{min} layer in spring with a correction for particle decomposition based on the apparent oxygen utilization. The net community production (NCP) and air-sea CO₂ flux from winter to spring were calculated from the vertically integrated deficits of DIC and nutrients in the upper water column between the two seasons. The calculation of the carbon budget indicated large interannual variations of NCP (0-13 mmol $m^{-2} d^{-1}$) and CO₂ efflux (4–16 mmol $m^{-2} d^{-1}$) for this period. The CO₂ efflux was generally low in the year when NCP was high. The close coupling between biological production and CO₂ efflux suggested the important role of the changes in the mixed-layer depth, as a key process controlling both processes, especially of the timing, so that a decrease in the mixed-layer depth could result in the activation of biological production. The early biological consumption of the surface DIC concentration could shorten the period for acting as a source for atmospheric CO_2 and depress the CO_2 efflux in the Western Subarctic Gyre from winter to spring in 1996 and 1998. On the contrary, in 1997, persistently deep vertical mixing until late spring could suppress the biological activity and give rise to long-lasting CO₂ efflux.

1. Introduction

Recent studies have revealed that the North Pacific is a sink for atmospheric carbon dioxide as a whole region (e.g. Takahashi et al., 2002). By contrast, it has been reported that the Western Subarctic Gyre (WSG), located off southeast of Kamchatka, could persistently be acting as a source from winter through early summer and on an annual scale from the observations (Nojiri et al., 1999; Midorikawa et al., 2002) and from model calculations (Sasai et al., 2000). Midorikawa et al. (2002) reported that a large CO_2 efflux from the WSG during the period from winter (March) through June 1997 was inferred from the decrease in dissolved inorganic carbon, DIC, in the upper water column above the layer of temperature minimum

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 T_{min} . Murphy et al. (1998) indicated the occurrence of large spatial and interannual variability of the partial pressure of CO₂, pCO₂^{sea}, in the subarctic North Pacific for the period of August–September. The contribution of the air–sea CO₂ flux in this region to the atmospheric CO₂ concentration over the long period is still not understood sufficiently because of the paucity of data.

It has been indicated that large seasonal amplitudes in pCO_2^{sea} and surface DIC concentrations in the western subarctic North Pacific could be attributed to high winter pCO_2^{sea} due to the vertical mixing with DICrich deep waters and intense summer photosynthetic utilization of DIC, compared with those in the eastern subarctic region (Takahashi et al., 1991; 1993). The interannual variability of winter pCO_2^{sea} in the WSG has not been documented yet. With regard to biological effects, it has been suggested that the photosynthetic utilization of DIC in surface waters produces a large drawdown of pCO_2^{sea} (Takahashi et al., 1991) and year-to-year variations of net carbon utilization (i.e. net community production, NCP; Minas et al., 1986) could greatly contribute to those of pCO_2^{sea} in the subarctic North Pacific (Murphy et al., 1998). However, the controlling factors of biological productivity in the WSG, showing a large seasonal and spatial variations, are not well known because of very few observations of the biological and geochemical characteristics of this region, compared with the eastern subarctic region (Harrison et al., 1999). Climatologically, shallowing of the mixed-layer depth from winter to spring explains the general basin-scale features of the spring bloom of phytoplankton in the western North Pacific (Obata et al., 1996). The regional difference in primary production and biomass in the entire North Pacific could be caused mainly by a combination of the surface vertical mixing and Ekman upwelling in winter (Kawamiya, 1997). Sugimoto and Tadokoro (1997; 1998) have reported the interdecadal-scale variations in chlorophyll-a concentration and plankton biomass associated with the changes in the physical environments in the North Pacific. They indicated that the high phytoplankton spring bloom in the cold Oyashio water could be resulted from the early start of density stratification due to the decrease in surface salinity.

In the present study, the interannual variabilities of NCP and CO₂ flux for winter to spring were investigated based on the observations of the concentrations of DIC and nutrients above the T_{min} layer in the WSG in spring, 1996–2000. The controlling factors for the variations of CO₂ flux during this period in the western subarctic North Pacific are quantitatively discussed.

2. Methods

2.1. Sampling

Observations of pCO_2 , DIC, temperature, salinity, dissolved oxygen and nutrients in surface waters were carried out on board the R/V *Ryofu Maru* of Japan Meteorological Agency (JMA) at 48°N, 165°E in the WSG in May 1996, June 1997, June 1998, May 1999 and May 2000. In June 1997, only the surface properties and hydrographic profiles of temperature, salinity and dissolved oxygen were observed, but vertical profiles of DIC and nutrients were not at 48°N, 165°E. Because the hydrographic profiles at 49.4°N, 165°E. Because the hydrographic profiles at 49.4°N, 165°E, as reported by Midorikawa et al. (2002), the vertical profiles of DIC and nutrients observed at 49.4°N, 165°E in 1997 files of DIC and nutrients observed at 49.4°N, 165°E in 1997 and compared with those in other years.

Surface water was pumped continuously from the ship's seachest at ~ 4 m depth by an underway pumping system for the pCO_2^{sea} measurements. At depth, seawater was collected with 12-L PVC Niskin bottles mounted on a Conductivity Temperature Depth (CTD)/rosette sampler.

2.2. Measurements

The underway pCO_2^{sea} measurements were made using an equilibrator of the shower-head type and a nondispersive infrared (NDIR) gas analyzer (model 4.1, Binos), based on the WMO 1995 mole fraction scale, as described earlier (Midorikawa et al., 2002). The conversion of mole fraction to the equilibrator pCO_2^{sea} was based on the equation of Weiss and Price (1980). Values of pCO_2^{sea} were corrected to those at in-situ temperature using the relationship given by Takahashi et al. (1993). The precision of pCO_2^{sea} measurements was 2 μ atm. For the pCO₂^{air} measurements, a sample of air was pumped continuously from the bow of the ship and introduced into the NDIR analyzer after drying. The precision of pCO_2^{air} measurements was better than $0.2 \,\mu$ atm. The DIC concentrations were measured with the coulometric technique using an automated CO2 extraction unit and a coulometer (model 5012, UIC Inc., USA) with the precision of 2–3 μ mol kg⁻¹, according to the procedure of Ishii et al. (1998), except for 1996. 0.2 mL of saturated HgCl2 was added to subsamples (300 mL) for DIC measurements as a preservative immediately after sampling. The DIC concentration was quantified based on Certified Reference Material provided by Dr. A. G. Dickson of the Scripps Institution of Oceanography. In 1996, the DIC concentrations were measured with the spectroscopic technique using NDIR gas analyzer (model TOC 5000, Shimadz, Kyoto, Japan) after the CO₂ extraction by the addition of 25% phosphoric acid. The uncertainty was less than 8 μ mol kg⁻¹.

Nitrate (NO_3^-) , phosphate (PO_4^{3-}) and silicate (SiO_4^{4-}) were measured by standard colorimetric methods using an auto-analyzer (Auto Analyzer II, Bran Luebbe). The dissolved oxygen measurements were made with a standard automated Winkler technique with photometric end-point detection (ART-3, Hirama Laboratories). In order to establish the compatibility of five sets of measurements in 1996-2000, the cruise-to-cruise systematic differences in concentrations of nutrients and dissolved oxygen were corrected on the basis of the measured values for deep waters from 400 to 1000 m (seven layers) in 1998 (middle year). The magnitudes of the corrections as a percentage of the ambient value ranged from 0-2.4%, 0-1.8%, 0-1.0% and 0-0.3% for nitrate, phosphate, silicate and dissolved oxygen, respectively. The corrections made for the measured values in the T_{\min} layer were -0.57-0.06, -0.027-0.034, -0.44-0.14 and $-0.11-0.98 \ \mu \text{mol kg}^{-1}$ for nitrate, phosphate, silicate and dissolved oxygen, respectively. The precision, including corrections between cruises, was 0.2, 0.02, 0.4 and 0.7 μ mol kg⁻¹ for nitrate, phosphate, silicate and dissolved oxygen, respectively.

The total alkalinity (TA) was calculated from the observed values of pCO_2^{sea} , concentrations of DIC, phosphate and silicate, temperature, salinity and the set of dissociation constants and calculation routines described in DOE (1994). The uncertainty of total

alkalinity was 4–5 μ mol kg⁻¹ from 1997–2000 and 10 μ mol kg⁻¹ in 1996. The apparent oxygen utilization (AOU) was calculated by subtracting the observed concentration of dissolved oxygen from the saturated one calculated from equation of Weiss (1981) and the in-situ temperature and salinity. The uncertainty of AOU is equivalent to that (0.7 μ mol kg⁻¹) of dissolved oxygen.

2.3. Time-series data of 10-d mean sea surface temperature

The sea surface temperature (SST) was taken from compiled temperature data (JMA, 1996–2000) from ships in the western North Pacific. The computation procedure of the grid position values was described elsewhere (JMA, 1991). Time series of 10-d mean SST, calculated as an average in a box of $48 \pm 1^{\circ}$ N, $165 \pm 1^{\circ}$ E, are shown in Fig. 1.

In the present study, winter was defined as the time when SST was the lowest in the year and, consequently, the mixed-layer depth was the deepest, i.e. winter was early March to early April in the study region in the years of 1996–2000. The latest 10 d when there occurred SST within 1σ of the lowest SST were referred as mid-winter. At this time, any carbon deficit was reset and began to be accumulated in the mixed layer due to the following CO₂ flux and biological consumption.

2.4. Calculations

A description of the calculation procedure was reported in detail previously by Midorikawa et al. (2002)



Fig. 1. Temporal variations of 10-d mean SST at 48°N, 165°E, taken from compiled temperature data from ships (JMA, 1996–2000). Broken line shows the temperature observed in the spring T_{min} layer. Solid square shows mid-winter for each year. In 1997, SST from mid-winter to the spring observation time at 49.4°N, 164°E (solid circle), where the vertical observation was performed (see text in section 2.1), is also shown. It resembles closely to that at 48°N, 165°E.

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but mentioned briefly. Temperature in the T_{\min} layer at 48°N, 165°E in spring (May or June) was close to winter SST (March or April) in respective years, as shown in Fig. 1. The findings of minor seasonal changes in temperature in the T_{\min} layer were evidence for the occurrence of minimal vertical mixing. The concentrations of DIC and nutrients in the T_{\min} layer could be altered by the decomposition of sinking particles originating from primary production in the upper water column, but not by the vertical mixing across the T_{\min} layer, from winter to spring. The concentrations of DIC and nutrients in the subsurface T_{\min} layer were used as a proxy for these properties in the preceding winter mixed layer after a correction was made based on the AOU value, to account for the regeneration from sinking biogenic particles. The calculations of the winter concentrations were made on the assumption that dissolved oxygen was homogeneously saturated (i.e. AOU = 0) throughout the mixed layer in winter. A correction for regeneration was made by using the average regeneration ratio of C/N/Si/P/O₂ = $(130 \pm 22)/(19 \pm$ $3)/(18 \pm 6)/1/(-182 \pm 19)$ observed in the depth range 50-100 m from June to September in 1997 (Midorikawa et al., 2002). Vertically integrated seasonal deficits of DIC and nutrients from winter to spring were calculated on the basis of their winter concentrations. Seasonal NCP was estimated from the deficit of nitrate and the C/N ratio of 7.8 for biological consumption observed in the western subarctic region. The net air-sea CO2 flux was evaluated by balancing the DIC deficit and NCP. The NCP and CO₂ flux were represented as the deficiency rate averaged for the time period from winter to the spring observation time in respective years.

3. Results

3.1. Surface properties

Table 1 shows surface properties observed at 48°N, 165°E in spring 1996–2000. The SST in 1999 and 2000 was lower than that in 1996–1998. The pCO_2^{sea} was relatively low in 1996 and 1998, and the difference in pCO_2 between air and sea, ΔpCO_2 , was negative in the two years, indicating that this region was acting as a sink for atmospheric CO₂ in these years. Correspondingly, the concentrations of nutrients and DIC were also low in these years. On the other hand, in 1997, 1999 and 2000, this region was a source and, especially, ΔpCO_2 was markedly high (+50 μ atm) in 1999. In 1999, the concentrations of nutrients and DIC and salinity were much higher than those in other years.

3.2. Vertical distributions

Figure 2 illustrates the results of vertical observations in the upper water column at 48°N, 165°E in spring 1996–2000. The dichothermal structure was observed in all years. The depth and temperature of the T_{min} layer were different in these five years. The halocline occurred just below the T_{min} layer, except for 1999. The depth of halocline was shallow in 1997 and 2000, and the deepest in 1999. Above the halocline, there occurred small changes in salinity, whereas temperature showed a step wise increase from the T_{min} layer to the surface, indicating the remnant of the intervallic development of the stratification. The distributions of potential density, σ_{θ} , corresponded to those of temperature above the T_{min} layer. Temperature

					C	oncentrati	on (μ mol k	$(g^{-1})^a$		
Year	Date	<i>T</i> (°C)	S	$\sigma_{ heta}$	NO ₃	PO ₄	SiO ₄	DIC	pCO_2^{sea} (μ atm)	$\Delta p CO_2$ ($\mu a tm$)
1996	May 19	4.17	33.01	26.19	20.2	1.41	19.4	2080	344	-21
1997	June 06	4.33	32.91	26.09	22.3	1.76	40.5	2092	380	+14
	June 05 ^b	4.53	32.94	26.09	21.7	1.72	40.1	2090	382	+16
1998	June 17	4.49	32.97	26.12	21.0	1.65	36.9	2080	355	-11
1999	May 16	2.32	33.08	26.41	25.8	1.95	45.9	2118	423	+50
2000	May 09	2.27	32.99	26.34	22.0	1.73	37.8	2102	394	+20

Table 1. Concentrations of nutrients and DIC and pCO₂ observed in the surface water at 48°N, 165°E in spring

^aValues normalized to S = 33.

^bValues at 49.4°N, 164°E (see text in section 2.1).

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Fig. 2. Vertical profiles of temperature (a), salinity (b), σ_{θ} (c), AOU (d), phosphate (e), nitrate (f), silicate (g) and DIC (h) at 48°N, 165°E in spring, 1996–2000. Concentrations of nutrients and DIC were normalized to S = 33.

was especially low in 1999 and 2000, and salinity, AOU and concentrations of DIC and nutrients were the highest in 1999. The distributions of AOU and concentrations of DIC and nutrients showed a slight increase from the surface to the top of the halocline and steep gradient in the halocline. There occurred a high correspondence between the vertical profiles of concentrations of DIC, nutrients and AOU in respective years.

3.3. Estimation of the winter concentrations

The values of respective properties in the T_{\min} layer are shown in Table 2. The nutrient concentrations in this layer were the highest in 1996 or 1999, and the DIC concentration was the highest in 1997 and the lowest in 1998. The AOU value was the highest in 1996 and low in 1998 and 1999. The differences in these concentrations cannot be directly related to those in the depth, temperature, salinity and σ_{θ} of the T_{\min} layer.

Table 2 also lists the winter concentrations of nutrients and DIC estimated from those in the T_{min} layer by using the above-mentioned method based on the assumption of winter AOU of zero. The winter concentrations were the highest in 1999 and the lowest in 1998. The winter pCO_2^{sea} calculated from the winter DIC concentration by the method of DOE (1994) was in the ranges 383–433 μ atm and the highest in 1997.

3.4. Estimation of seasonal NCP and air-sea CO₂ flux

Figure 3 shows the interannual variations of the seasonal NCP and CO₂ flux estimated for the period from winter to spring. These values varied largely in respective years: NCP, 0–13 mmol m⁻² d⁻¹; CO₂ flux, 4–16 mmol m⁻² d⁻¹. The seasonal CO₂ fluxes were positive in all years, indicating that this region was a source for atmospheric CO₂ in this season. Although this region had changed to being a sink in the spring of 1996 and 1998, the efflux from winter to early spring was considered to exceed the influx after the decrease in pCO_2^{sea} due to biological consumption in the two years. It was found that the CO₂ efflux was generally low in the year when NCP was high. By contrast, there occurred a large CO₂ efflux from winter to spring in 1997 when NCP was relatively low.

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4. Discussion

4.1. Estimation of winter concentrations, NCP and air–sea CO₂ flux

In 1998, because the concentrations of nutrients and DIC in the T_{min} layer (110 m) were not investigated, the estimation of winter concentrations was based on the values in the sampling layer (100 m) nearest to the T_{min} layer. Midorikawa et al. (2002) reported that the estimation based on the values in the layer above T_{min} could lead to the underestimate of the winter DIC concentration by the decrease in the DIC concentration in this layer due to CO₂ efflux from winter to the time, when the mixed-layer depth decreased to less than the sampling depth. The winter DIC concentration, pCO_2^{sea} and resulting CO₂ efflux in 1998 could possibly be underestimated, whereas the winter nutrient concentrations and NCP estimated would be realistic.

The nutrient concentrations were measured in surface waters above 76 m ($T = 2.75 \pm 0.01^{\circ}$ C) at 48°N, 165°E in mid-February, 1998, as follows: 22.4 \pm 0.2 μ mol kg⁻¹ for nitrate, 1.74 \pm 0.02 μ mol kg⁻¹ for phosphate and 38.0 \pm 0.7 μ mol kg⁻¹ for silicate (National Research Institute of Far Seas Fisheries, 1998) after the correction for the cruise-to-cruise systematic differences on the basis of the measured values for deep waters from 400 to 1000 m. The observation time occured just before mid-winter because 10-d mean SST was the lowest $(2.52 \pm 0.08 \text{ °C})$ in mid-March in 1998. The nutrient concentrations in midwinter could possibly be higher than their measured values. Our estimated values for winter nutrient concentrations in 1998 (Table 2) were consistent with their winter values.

4.2. Interannual variations of concentrations in the winter mixed layer

It appears hat the relationship between the depth of steep gradient and the winter mixed-layer concentration would be complicated; the winter concentrations were the highest in 1999 (Table 2) when the halocline was the deepest (Fig. 2b) but not so low in 1997 and 2000 when the halocline was shallow. The winter surface concentrations of nutrients and DIC are formed by the mixing of the upper water column above the depth of the deepest vertical mixing in mid-winter. For its interannual variations in the WSG, the following three controlling factors have to be considered: (1) Deeper

Depth T Concentration (μ mol kg ⁻¹) ^a Year (m) (°C) S σ_{θ} (μ mol kg ⁻¹) NO ₃ PO ₄ SiO ₄ SiO ₄ DIC 1996 105 2.16 33.06 26.40 28.2 26.5 2.02 45.4 2134 23.6 1.87 42.6 2114 1997 101 2.22 33.01 26.53 19.0 25.3 1.95 43.9 2136 23.3 1.85 42.0 2122 1998* 110 2.49 33.06 26.47 17.6 24.9 1.95 43.9 2136 23.9 1.96 45.9 2102 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2107 22.9 1.80 39.7 2103 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2103 2104 2125 23.0 1.81 41.1 2113					Observati	on in the T _{min} laye	sr in sprir	ß				Est	imation fo	r the winter	mixed layer	
Year (m) (°C) <i>S</i> σ_{θ} (μ mol kg ⁻¹) NO ₃ PO ₄ SiO ₄ DIC NO ₃ PO ₄ SiO ₄ DIC NO ₃ PO ₄ SiO ₄ DIC DIC (m) (°C) <i>S</i> σ_{θ} (μ mol kg ⁻¹) NO ₃ PO ₄ SiO ₄ SiO ₄ DIC NO ₃ PO ₄ SiO ₄ DIC 1996 105 2.16 33.06 26.40 28.2 26.5 2.02 45.4 2134 23.6 1.87 42.6 2114 1998 110 2.49 33.08 26.40 6.0 23.5 1.83 40.3 2107 22.9 1.80 39.7 2103 1999 79 1.37 33.12 26.51 5.9 ⁴ 24.9 1.91 42.8 2126 25.9 1.96 45.9 2122 2000 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to <i>S</i> = 33.		Denth	Т			AOL	Conc	centration	(µmol kg	-1)a	Conc	entration	(µmol kg	(^{−1})a,b	nCO ^{sea c}	AnCO ^d
19961052.1633.0626.4028.226.52.0245.4213423.61.8742.6211419971012.2233.0126.3619.025.31.9543.9213623.31.8542.0212219981102.4933.0826.406.023.51.8340.3210722.91.8039.721031999791.3733.1226.515.9 ^f 26.52.0046.5212625.91.9645.9212220001001.3033.0626.4717.624.91.9142.8212523.01.8141.12113*Values normalized to $S = 33$.*Uncertainties for the estimation of winter concentrations are 0.8, 0.05, 1.3 and 10 μ mol kg ⁻¹ in 1996, and 0.3-0.4, 0.02-0.03, 0.4-0.7 and 3-4 μ r	Year	(u)	(°C)	S	$\sigma_{ heta}$	$(\mu \text{mol kg}^{-1})$	NO_3	PO_4	SiO_4	DIC	NO_3	PO_4	SiO_4	DIC	(μatm)	(μatm)
1997 101 2.22 33.01 26.36 19.0 25.3 1.95 43.9 2136 23.3 1.85 42.0 2122 1998 ^e 110 2.49 33.08 26.40 6.0 23.5 1.83 40.3 2107 22.9 1.80 39.7 2103 1999 79 1.37 33.12 26.51 5.9 ^f 26.5 2.00 46.5 2126 25.9 1.96 45.9 2122 2000 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. Uncertainties for the estimation of winter concentrations are 0.8, 0.05, 1.3 and 10 μ mol kg ⁻¹ in 1996, and 0.3–0.4, 0.02–0.03, 0.4–0.7 and 3–4 μ r intract noosnbate. silicate and DIC, respectively.	966	105	2.16	33.06	26.40	28.2	26.5	2.02	45.4	2134	23.6	1.87	42.6	2114	404	39
1998 ^e 110 2.49 33.08 26.40 6.0 23.5 1.83 40.3 2107 22.9 1.80 39.7 2103 1999 79 1.37 33.12 26.51 5.9 ^f 26.5 2.00 46.5 2126 25.9 1.96 45.9 2122 2000 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 210 26.5 1.91 42.8 2125 23.0 0.4.0.7 3.4 μ Uncertainties for th	1997	101	2.22	33.01	26.36	19.0	25.3	1.95	43.9	2136	23.3	1.85	42.0	2122	433	67
1999 79 1.37 33.12 26.51 5.9^{f} 26.5 2.00 46.5 2126 25.9 1.96 45.9 2122 2000 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 Values normalized to $S = 33$. 210.5 20.4 , $0.02-0.03$, $0.4-0.7$ and $3-4$ μ I 20.6 , 1.3 and $10 \ \mu$ mol kg ⁻¹ in 1996, and $0.3-0.4$, $0.02-0.03$, $0.4-0.7$ and $3-4 \ \mu$ I	1998^{e}	110	2.49	33.08	26.40	6.0	23.5	1.83	40.3	2107	22.9	1.80	39.7	2103	383	15
2000 100 1.30 33.06 26.47 17.6 24.9 1.91 42.8 2125 23.0 1.81 41.1 2113 ^a Values normalized to $S = 33$. ^b Uncertainties for the estimation of winter concentrations are 0.8, 0.05, 1.3 and 10 μ mol kg ⁻¹ in 1996, and 0.3–0.4, 0.02–0.03, 0.4–0.7 and 3–4 μ r nitrate. phosphate. silicate and DIC. respectively.	1999	79	1.37	33.12	26.51	5.9^{f}	26.5	2.00	46.5	2126	25.9	1.96	45.9	2122	414	42
⁴ Values normalized to $S = 33$. ⁹ Uncertainties for the estimation of winter concentrations are 0.8, 0.05, 1.3 and 10 μ mol kg ⁻¹ in 1996, and 0.3–0.4, 0.02–0.03, 0.4–0.7 and 3–4 μ r nitrate. phosphate. silicate and DIC, respectively.	2000	100	1.30	33.06	26.47	17.6	24.9	1.91	42.8	2125	23.0	1.81	41.1	2113	410	37
Consistent from temperature and calling the currine T . Javar actimated winter DIC concentration and alkalingty observed due to concentration UC	^a Values n ^b Uncertai nitrate, ph	ormalize nties for osphate,	d to $S = 3$ the estima silicate ar	33. Ition of wi nd DIC, re	nter conce spectively.	ntrations are $0.8, 0$.05, 1.3 a	nd 10 μπ	ool kg ⁻¹ ir	1 1996, and	0.3–0.4, 0	.02–0.03	, 0.4–0.7 a	and $3-4 \mu$ mc	ol kg ⁻¹ in othe	r years for

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^dCalculated by using the monthly mean pCO_{2}^{alr} at 50 °N in the coldest month, each year, which was taken from the analysis by JMA based on the atmospheric observations of NOAA and JMA. Uncertainties are the same as those for pCO_2^{sea} .

^eSampling of water from the T_{min} layer (110 m) was not performed in 1998. The calculation was based on the values in the sampling layer (100 m) nearest to the T_{min} layer. Therefore, the winter DIC concentration and $\rho CO_{2^{sa}}^{sa}$ in this year could be conservative as reported by Midorikawa et al. (2002). Temperature, salinity and σ_{θ} in the T_{min} layer. were taken from the CTD measurement.

^fThe winter concentration of dissolved oxygen was assumed to be the same as the average value $(326.9 \pm 0.4 \ \mu \text{mol kg}^{-1})$ at the depths between 0–49 m in May, because the concentrations of nutrients estimated based on AOU = 0 in winter were lower than those (Table 1) observed in the surface water in May although the nutrient concentrations in the surface water should be the highest in winter. The AOU value is the difference in the concentration of dissolved oxygen between surface waters and the T_{min} layer $(321.0 \ \mu \text{mol} \text{ kg}^{-1})$. The estimated winter concentrations agreed with the surface concentrations (Table 1) observed above 49 m in May within respective measurement precisions except for DIC; their differences were 0.1, 0.01, 0.0 and 4 μ mol kg⁻¹ for nitrate, phosphate, silicate and DIC, respectively.



Fig. 3. Interannual variations of seasonal NCP (open square) and air–sea CO_2 flux (solid circle) at 48°N, 165°E estimated for the period from winter to spring, 1996–2000. The error bars represent the uncertainties of the estimate resulting from the calculations and the precision of the measurements.

vertical mixing and/or enhanced Ekman upwelling in mid-winter could result in the larger entrainment of deep water, leading to higher winter concentrations. (2) Higher biological consumption during preceding summer to autumn could result in lower winter concentrations. (3) The air–sea CO_2 flux, i.e. influx in autumn and efflux from early winter to mid-winter, could affect on the winter concentrations of DIC but not nutrients.

Both vertical mixing and Ekman upwelling in factor (1) above could cause the nutrient supply from the lower layer to surface waters, but a combination of these two processes could not always result in deep vertical mixing because the uplift of deep water of high salinity and density by upwelling could suppress the deepening of vertical mixing. Furthermore, low salinity in the autumn mixed layer (Midorikawa et al., 2002) could also reduce the wintertime mixed-layer depth by lowering σ_{θ} in this layer. Focusing on density in order to examine the factors causing the interannual variations of respective winter surface properties, then, the interannual ranking of the winter concentrations of nutrients did not coincide with that of σ_{θ} in the T_{\min} layer, suggesting combined contribution of factors of not only (1) but also (2). This hypothesis could be supported by the high correlation (r = 0.979) between the winter concentrations of nitrate and phosphate in five years with the N/P ratio of 18.7 \pm 2.3, which was close to the Redfield ratio (16; Redfield et al., 1963) as well as the regeneration ratio (19 ± 3) just below summer mixed-layer depth from June to September in 1997, compared with those (\sim 14) in deeper water. The difference in the ranking of winter concentrations between nutrients and DIC suggested the difference in the controlling factor between nutrients and DIC, i.e. the significant contribution of above-mentioned CO₂ flux [factor (3)] to the DIC concentration; a larger CO₂ efflux to atmosphere could decrease the DIC concentration to a larger extent in the year when the DIC concentration was higher before mid-winter. Correspondingly, the correlation between nitrate and DIC was not good and indicated the reduced variations of DIC concentrations, compared with those of nitrate (r = 0.606; C/N = 3.9 ± 2.9).

4.3. Controlling factors of seasonal NCP and air-sea CO₂ flux

The interannual variations of the seasonal NCP and CO_2 flux estimated for the period from winter to spring (Fig. 3) suggested the close coupling between two processes. Temperature in spring upper layer (Fig. 2a) was similarly high in 1997 and 1998 when NCP was significantly different, and was low in 1996 when NCP was the highest. In time series of 10-d mean SST, there occurred the period (early and mid-April) when SST in 1997 was higher than that in 1996 and 1998 (Fig. 4). In 2000, despite low SST in both winter and spring observation time, NCP was high, but not in 1999. It appears that absolute value of temperature itself could not be a trigger or determine the threshold of the initiation of active biological production.

Midorikawa et al. (2002) reported that biological consumption of DIC could be activated by the decrease in the mixed-layer depth above the euphotic layer in the WSG. As the first approximation, the changes in the mixed-layer depth in the WSG from winter to spring were considered to be determined primarily by temperature for the following reasons: above the T_{\min} layer, salinity was approximately constant and the vertical changes in σ_{θ} were dependent predominantly on those in temperature in respective years (Fig. 2). Then, it was assumed that when the mixed-layer depth shoaled above the euphotic layer, i.e. SST rose above temperature at the euphotic-layer depth in spring, sudden significant biological production occurred. Time series of 10-d mean SST at 48°N, 165°E from mid-winter to the spring observation time in 1996–2000 (Fig. 4) were extracted from those in Fig. 1.

With regard to the euphotic-layer depth in this region, Hashimoto and Shiomoto (1999; 2000) have reported that it has little seasonal change and is averaged to be 44 ± 6 m between April and August. It appears that their reported value of 44 m for the euphotic-layer



Fig. 4. Temporal variations of 10-d mean SST at 48° N, 165° E from mid-winter to the spring observation time in 1996–2000. SST in 1997 is one at 49.4° N, 164° E (see caption to Fig. 1). Solid bar shows the time when the mixed-layer depth would firstly shoal above the euphotic-layer depth each year.

depth can be regarded as a typical value under the conditions of inactive biological production or before the onset time of active biological production. The euphotic-layer depth, calculated by tripling the observed Secchi disc depth, according to Parsons et al. (1984), was 48 m in June 1997 and 45 m in June 1998, which agreed with that calculated by Hashimoto and Shiomoto (1999; 2000). The euphotic-layer depth in May 1996, when this region was under the conditions like bloom, was 24 m and shallower than a typical value. Although the transparency was not observed in 1999 and 2000 because the observations were conducted in night, the calculated euphotic-layer depth was 57 m at 49°N, 165°E in 1999 and 42 m at 47°N, 165°E in 2000. Here, the onset time of active biological production was assumed to be the time when SST rose above temperature at a depth of 44 m in vertical profile observed in spring.

The onset time of active biological production estimated for respective years was marked by solid bars in Fig. 4. It is suggested that significant biological production occurred early in 1996 (late April) and 1998 (early May) when the CO₂ efflux was low, whereas late in 1997 (late May) when the CO₂ efflux was high. The magnitude of the CO₂ efflux could be determined by not only the Δp CO₂ values but also the length of the period from mid-winter through the onset time of active biological production, which could be controlled by the behavior of the mixed-layer depth, namely the condition of the variations of SST during this period. On the basis of time series of SST, in 1996, the variations of the mixed-layer depth would be small and maintained to be at a depth just below the euphoticlayer depth. These stable conditions could give rise to the early onset of biological production. In 1998, it was possible that the stratification developed in early May for a short time and the mixed-layer depth shoaled above the euphotic-layer depth, inducing active biological production. In 1996 and 1998, early biological DIC consumption could reduce pCO_2^{sea} , depress the CO₂ efflux from the WSG after that and, consequently, shorten the period for acting as a source for atmospheric CO₂. In 2000, although Δp CO₂ was positive at the spring observation time, the decrease in pCO_2^{sea} was considered to result from significant biological DIC consumption, which could occur in mid-April when the mixed-layer depth could shoal due to a temporary SST rise. On the contrary, in 1997, the mixedlayer depth varied largely and was mostly deep and so unstable that biological production could not be activated, leading to long-lasting CO2 efflux. The physical oceanic conditions could control the biological activity, which could govern the oceanic sink/source conditions for atmospheric CO₂ in this region.

The spring surface concentrations of nutrients and AOU were low in 1998 and very low in 1996, whereas, the surface concentrations of DIC were in the same level in these two years. The differences in the vertical profile between nutrients and DIC near the surface in 1996 could be attributed to the CO_2 influx after

biological consumption. It is suggested that biological consumption would be activated early and before the observation time there was enough time to absorb atmospheric CO₂, corresponding to the negative ΔpCO_2 values. These observation results could give an evidence for supporting the above-mentioned scenario of the onset time as a key process.

4.4. Implication of variability of CO₂ flux in the WSG

The time period of the CO₂ efflux could be dependent significantly on the onset time of active biological production. It is likely that this region could change to be a sink due to intense biological consumption during a short period after its onset time because of the negative $\Delta p CO_2$ values at the spring observation time in 1996 and 1998. In these years, the time period of the CO₂ efflux was assumed to be the period (50 d, respectively) from mid-winter through the onset time of active biological production. In 1997, 1999 and 2000, because spring $\Delta p CO_2$ was positive and CO_2 efflux had continued up to the spring observation time, its time period was assumed to be the period (90, 40 and 40 d, respectively) from mid-winter through the observation time. The flux values re-calculated based on the assignment of its time period were 12, 16, 7, 10 and 6 mmol $m^{-2} d^{-1}$ in 1996–2000, respectively. The values in 1996 and 1998 would be conservative estimates because the influx after the onset time was also included in these fluxes. These flux values after removing the biological effects were considered to be determined by the values of $\Delta p CO_2$ and wind speed. High CO₂ efflux in 1997 could be attributed to high $\Delta p CO_2$, whereas, in 1999, although NCP was practically zero and $\Delta p CO_2$ was high in both winter and May, the CO₂ efflux was not so high. It is suggested that the CO₂ efflux could be depressed not by biological consumption but by relatively low wind speed in 1999; the wind speed averaged for the period from winter to the onset time of active biological production in this year was by 23% lower than that in 1997, based on the wind data of JMA global atmospheric analysis. On the other hand, in 1998, higher wind speed (12%) could contribute to the CO₂ efflux of 7 mmol $m^{-2} d^{-1}$, considering low $\Delta p CO_2$ even in winter.

These daily efflux values are large, compared with those reported in the following other regions in the North Pacific: -3 to 2 mmol m⁻² d⁻¹ in the eastern subarctic region throughout a year (Wong and Chan, 1991); -1 to 4 mmol m⁻² d⁻¹ in the central subarctic region in August–September (Murphy et al., 1998);

-16 to 4 mmol m⁻² d⁻¹ in the western subtropical region throughout a year (Inoue et al., 1995). The amplitude of its variations are as large as those (2–14 mmol m⁻² d⁻¹ for the period of El Niño–La Niña events; Inoue and Sugimura (1992) in the central equatorial Pacific associated with the ENSO events.

The interannual variations of the CO_2 efflux in the WSG from winter to spring could be controlled basically by those of the seasonal changes in the mixed-layer depth. Several studies have reported the decreases in the mixed-layer depth in recent decades in the wide area of the subarctic North Pacific (e.g. Freeland et al., 1997; Ono et al., 2001). Kawasaki et al. (1999) have reported the decreasing trend of surface salinity in the WSG in 1990s. If the mixed layer would shoal also in the WSG in future, the CO_2 efflux in this region would decrease and the role of this region in the air–sea CO_2 exchange might be changed to be a sink, depending on the extent of warming in surface waters.

Time series data of SST in the North Pacific compiled by JMA showed the decadal variations of SST in March, the coldest month, in the region of 46–50°N, 160-170°E in response to the climatic regime shift (Trenberth and Hurrell 1994); the average SST values were 2.04 \pm 0.49 °C in 1971–1976, 1.59 \pm 0.22 $^\circ C$ in 1977–1989 and 2.54 \pm 0.24 $^\circ C$ in 1990–1995 (Sugimoto, JMA, personal communication). It is suggested that the CO₂ efflux in this region from winter to spring could be enhanced by a deepening of the mixed layer in 1976-1989 and be depressed by a shoaling of the mixed layer in 1990-1995. However, the longterm trend of SST was unclear during this period. The quantification of the variations of the CO₂ efflux in the WSG due to the global warming will be future studies. The continuation of the monitoring of CO₂ flux is required to understand the characteristics of the response of the WSG to the climate-related changes in the oceanographic processes.

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