Journal of Oceanography, Vol. 57, pp. 177 to 188, 2001

Excess CO_2 and pH_{excess} in the Intermediate Water Layer of the Northwestern Pacific

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(Received 28 April 2000; in revised form 23 October 2000; accepted 23 October 2000)

Excess CO_2 and pH_{excess} showing an increase in dissolved inorganic carbon and a decrease in pH from the beginning of the industrial epoch (middle of the 19th century) until the present time have been calculated in the intermediate water layer of the northwestern Pacific and the Okhotsk Sea. It is concluded that: (1) The Kuril Basin (Okhotsk Sea) and the Bussol' Strait areas are characterized by the greatest concentrations of excess CO_2 at isopycnal surfaces due to the processes of formation and transformation of intermediate water mass. (2) The largest difference in excess CO_2 concentration between the Okhotsk Sea and the western subarctic Pacific (about 8 μmol/kg) is found at the $\sigma_\theta = 27.0$. (3) The difference in excess CO_2 between the western subarctic Pacific and subtropical regions is significant only in the upper part of the intermediate water layer ($\sigma_\theta = 26.7$–27.0). (4) About 10% of the excess CO_2 accumulation in the subtropical north Pacific is determined by water exchange with the subarctic Pacific and the Okhotsk Sea.

Keywords:
· Carbon cycle,
· antropogenic CO_2,
· North Pacific.

1. Introduction

The increase of CO_2 in the atmosphere leads to an increase in total dissolved inorganic carbon (TCO_2) concentrations (Brewer, 1978; Winn *et al*., 1998) and to a decrease in pH in seawater. Excess CO_2 and pH_{excess} are defined as the increase in TCO_2 and the decrease in pH from the beginning of the industrial epoch (middle of the 19th century) until the present time. These changes in dissolved inorganic carbon and pH take place in the surface seawater layer where the ocean interacts with the atmosphere. The penetration of the excess CO_2 signal into deep water is determined by advection and turbulent diffusion. In this way, excess CO_2 and pH_{excess} can be used as tracers for the study of transport processes in the ocean. The northwestern Pacific is considered a region of intermediate water ($\sigma_\theta = 26.7$–27.6) formation and transformation (Reid, 1965; Talley *et al*., 1995). From this point of view, the most interesting areas to study are the Kuril Straits area (mainly the Bussol' Strait) where an exchange of water between the Okhotsk Sea and the western subarctic Pacific occurs, and the region between the Oyashio front and the Kuroshio Extension (Kuroshio-Oyashio Interfrontal Zone (Yasuda *et al*., 1996)) where the formation of the main salinity minimum in the intermediate water layer takes place.

All current estimates of excess CO_2 concentrations in the ocean, based on the original method proposed by Brewer (1978), and Chen and Pytkowicz (1979) or with some modification (Gruber *et al*., 1996), have used the TCO_2 and total alkalinity (TA) data. Taking into account the linear relationship between pH_{25} (pH at 25°C), TA and TCO_2 in the intermediate water layer of the northwestern Pacific, we intent to propose an equation for the determination of the excess CO_2 and pH_{excess} from TCO_2-pH data.

The distribution of excess CO_2 concentrations in the northwestern Pacific at transects along 165°E and 175°E and its changes from 1973 (GEOSECS) to 1993–1994 were analyzed by Chen (1993), Tsunogai *et al*. (1993) and Watanabe *et al*. (1996). We will indicate the main features of excess CO_2 and pH_{excess} distributions in different parts of the northwestern Pacific, including the Okhotsk Sea and the Bering Sea.

The presented distributions of excess CO_2 and pH_{excess} can be used to calibrate carbon-ocean circulation models and to quantify the shift in the form and migration of chemical elements in seawater due to pH changes.

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2. Data and Methods

In our calculation, data from the following three main sources were used:

1) Potential temperature, salinity, dissolved oxygen, pH, total alkalinity and total inorganic carbon data collected at 23 deep stations in the northwestern Pacific (including 6 stations in the southwestern Bering Sea and 2 stations in the Bussol' Strait) during the joint Canada-Russia expeditions in April–July 1991 and August 1992 aboard the R/V "Akademik Vinogradov" (hereafter AV-91 and AV-92). Locations of the stations of AV-92 cruise in the subarctic Pacific and southwestern Bering Sea coincide with those of AV-91 cruise.

2) Potential temperature, salinity, dissolved oxygen and carbonate parameters (pH and total alkalinity) data collected at 26 stations in the Kuril Basin (Okhotsk Sea) and the Kuril Straits area (Fig. 1) aboard the R/V "Akademik Lavrentiev" in April–May 1995 (AL-95).

3) Potential temperature, salinity, dissolved oxygen, pH, total alkalinity and total inorganic carbon data collected at 14 deep stations in the Oyashio-Kuroshio interfrontal zone during a cruise of the R/V "Mirai" (Japan Marine Science and Technology Center) in November–December 1998 (MR98-K01) (Fig. 1).

On these cruises, pH was measured potentiometrically in a closed cell at 25°C with some modifications to the electrodes and buffer solutions applied. On the expeditions AV-91, AV-92 and AL-95 a glass pH and calomel reference electrodes made by the Hungarian company "Radelkis" were used. To calibrate the electrodes, a phosphate buffer (NBS scale) and a TRIS buffer in seawater (Sea Water Scale) were used. The repeatability of the pH measurements was ±0.003 pH unit (1σ). On the cruise MR98-K01, a glass pH and silver/silver chloride reference electrode from the "Radiometer" company was used. Two different sets of solutions were used for the calibration of electrodes: 1) NBS buffer (phosphate) and 2) TRIS and AMP in seawater, prepared according to the recommendation by Dickson and Goyet (1994). The repeatability of the pH measurements, calculated from 66 duplicate measurements, was ±0.004 pH unit (1σ).

To obtain excess CO_2 and pH_{excess} signals, the difference in concentration of the carbonate parameters in the intermediate water of the northwestern Pacific was calculated relative to the deep water layer. The results of the calculation do not depend on the pH scale prescribed. The pH values measured on different cruises were not adjusted to one scale.

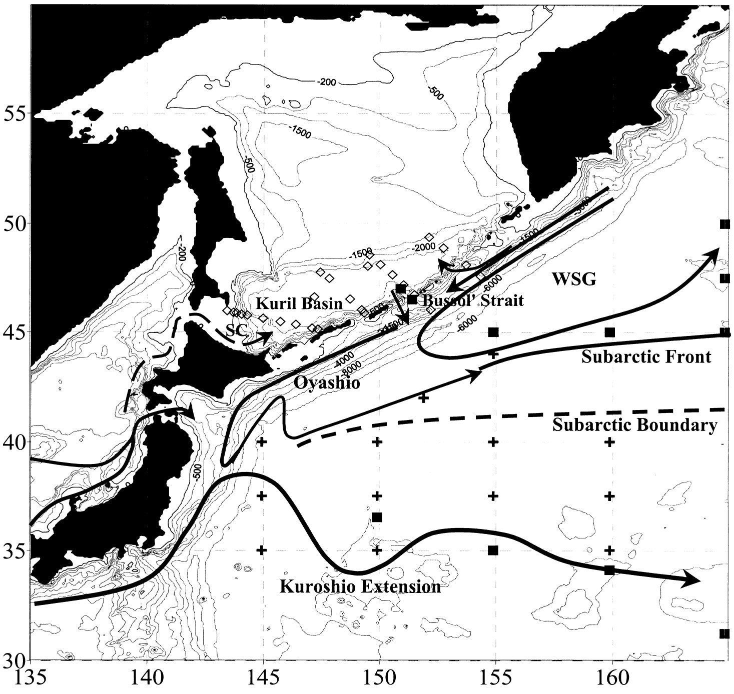

Fig. 1. Schematic representation of the current and frontal systems in the northwestern Pacific (reproduced from Yasuda *et al.*, 1996) and station locations for the "Mirai-98" (MR98-K01: November–December 1998) (+), "Akademik Lavrentiev-95" (AL95: April–May 1995) (◇) and "Akademik Vinogradov-91, 92" (AV-91: April–July 1991, AV-92: August 1992) (■) cruises. Location of a few stations of "Akademik Vinogradov-91, 92" cruises (in the southwestern Bering Sea and along 45°N from 165°E to 175°W) are not shown.

On the expeditions AV-91, AV-92 and AL-95 total alkalinity was analyzed by the method of Bruevich (Rogachev *et al.*, 1996). The repeatability (1σ) of the total alkalinity measurements on these cruises was ±4 μmol/kg (AV-91, AV-92) and ±2 μmol/kg (AL-95). On the cruise MR98-K01, total alkalinity was determined by potentiometric titration in an open cell (Dickson, unpublished).

On the expeditions AV-91, AV-92 and MR98-K01, total dissolved inorganic carbon was measured on a coulometric system (Johnson and Sieburth, 1987). The repeatibility (1σ) of TCO_2 measurements was ±2 μmol/kg (AV-91, AV-92) and ±3 μmol/kg (MR98-K01). On the cruise AL-95, total dissolved inorganic carbon was computed from pH and TA data using the dissociation constants recommended by Millero (1995).

3. Theory

3.1 The relation between TCO_2, TA and pH

The concentration of TCO_2 and pH in seawater below the euphotic layer can be expressed as the pre-industrial, preformed value (TCO_2^0, pH^0) together with the change in concentration due to organic matter oxidation (ΔTCO_2(org.ox.), ΔpH(org.ox.)), carbonate dissolution (ΔTCO_2(carb.dis.), ΔpH(carb.dis.)) and the increasing CO_2 content of the atmosphere ($CO_{2\text{excess}}$, pH_{excess}):

$$TCO_2 = TCO_2^0 + \Delta TCO_2(\text{org.ox.}) + \Delta TCO_2(\text{carb.dis.}) + CO_{2\text{excess}} \tag{1}$$

$$pH = pH^0 + \Delta pH(\text{org.ox.}) + \Delta pH(\text{carb.dis.}) + pH_{\text{excess}}. \tag{2}$$

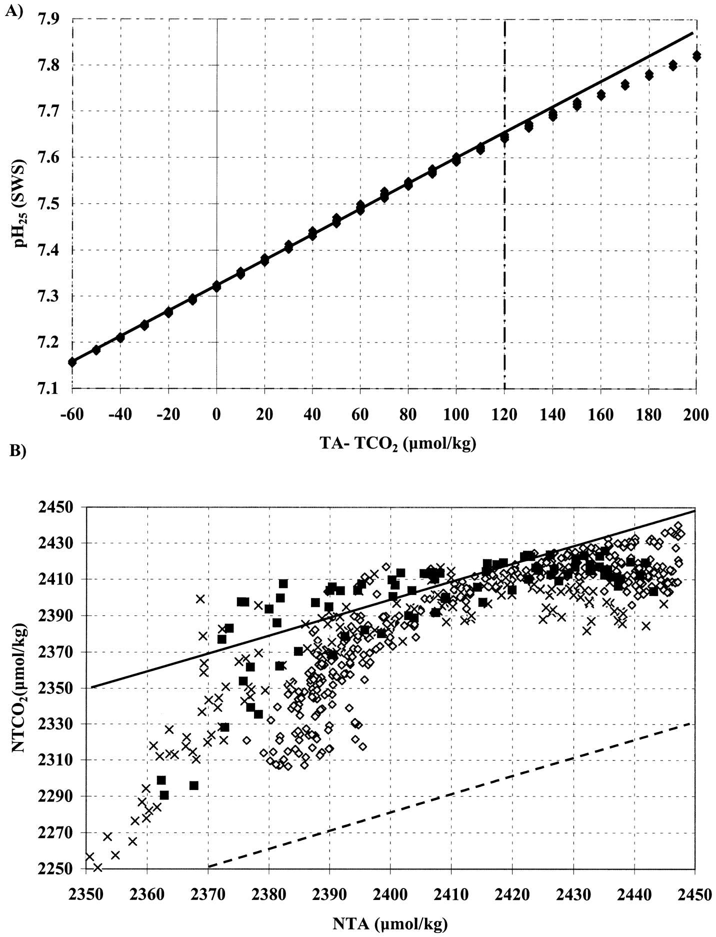

Fig. 2. (A) The calculated values of pH_{25} (Sea Water Scale) versus the difference between total alkalinity and total dissolved inorganic carbon ($TA - TCO_2$). pH_{25} was computed in the 33.3–34.6 pss of salinity, 2350–2450 μmol/kg of total alkalinity and 2250–2450 μmol/kg of total CO_2 range; (B) The salinity normalized total alkalinity versus salinity normalized total dissolved inorganic carbon in the intermediate water layer (σ_θ = 26.7–27.6) of the Okhotsk Sea (◇), the subarctic western Pacific (■) and K/O interfrontal zone (×). The solid and dotted lines show where $NTCO_2$ = NTA and $NTCO_2$ = NTA – 120 μmol/kg, respectively.

Total alkalinity changes due to carbonate dissolution (ΔTA(carb.dis.)) and organic matter oxidation (ΔTA(org.ox.)) (Brewer *et al.*, 1975):

$$TA = TA^0 + \Delta TA(org.ox.) + \Delta TA(carb.dis.) \qquad (3)$$

where TA^0 is the preformed total alkalinity.

Of these three carbonate parameters (TA, TCO_2 and pH) only two are independent (Park, 1969). To order to express the relationship between total alkalinity, total dissolved inorganic carbon and pH_{25} (pH at 25°C) in the intermediate water layer of the study region, we introduce the coefficients k_1 and k_2, corresponding the change in pH_{25} with TCO_2 at a constant TA

$$k_1 = \Delta pH_{25}/\Delta TCO_2|_{TA=const} \qquad (4)$$

and the change in pH_{25} with TA at a constant TCO_2

$$k_2 = \Delta pH_{25} / \Delta TA|_{TCO_2=const}. \qquad (5)$$

Using k_1 and k_2, the change in pH of seawater can be related to the change in the concentration of TCO_2 and TA:

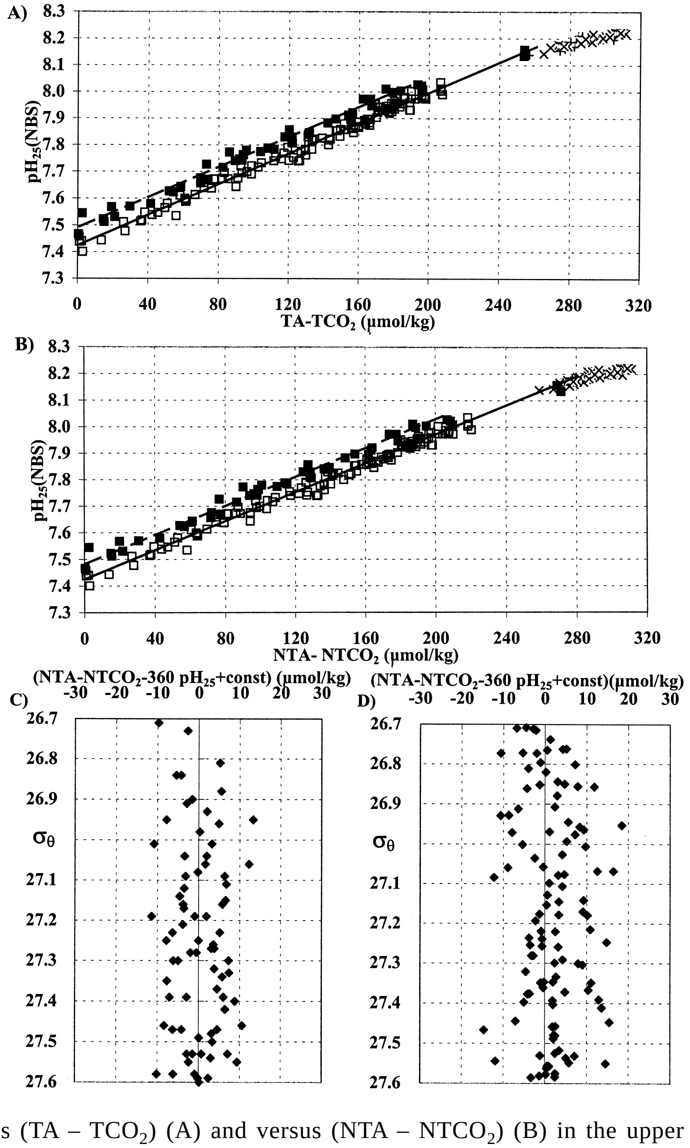

Fig. 3. Measured pH_{25} versus (TA – TCO_2) (A) and versus (NTA – $NTCO_2$) (B) in the upper water layer (0–200 m) of the northwestern Pacific ((■) - subarctic region and subarctic frontal zone (AV-92 cruise), (×) - subtropical area, (□) - subarctic region and subarctic frontal zone (AV-91cruise)); distribution of the (NTA – $NTCO_2$ – $360pH_{25}$ + const) residual on isopycnals in the western subarctic Pacific (AV-91, 92 cruises) (C) and K/O interfrontal zone (MR98-K01) (D).

$$\Delta pH(org.ox.) = k_1 \cdot \Delta TCO_2(org.ox.) + k_2 \cdot \Delta TA(org.ox.) \quad (6)$$

$$\Delta pH(carb.dis.) = k_1 \cdot \Delta TCO_2(carb.dis.) + k_2 \cdot \Delta TA(carb.dis.) \quad (7)$$

$$pH_{excess} = k_1 \cdot CO_{2excess}. \quad (8)$$

In general, k_1 and k_2 can be expressed as functions of the dissociation constants of carbonic acid, boric acid and the concentrations of TA and TCO_2 (Park, 1969). Figure 2(A) shows pH_{25} versus the difference between total alkalinity and total dissolved inorganic carbon (TA – TCO_2). pH_{25} was computed from TA and TCO_2 in the 33.3–34.6 pss salinity, 2350–2450 μmol/kg TA and 2250–2450 μmol/kg TCO_2 ranges using dissociation constants recommended by Millero (1995). The results of the calculation indicate that the relationship between (TA – TCO_2) and pH_{25} can be approximated by a linear regression with a slope equal to 360 μmol/kg/pH unit if the difference between TA and TCO_2 is less than 120 μmol/kg. In the intermediate water (σ_θ = 26.7–27.6) of the Okhotsk Sea, the western subarctic Pacific and K/O interfrontal zone, the difference between TA and TCO_2 does not exceed 120 μmol/kg (Fig. 2(B)) and thus for these regions we can assume that

$$TA = TCO_2 + 360 \cdot pH_{25} + const. \quad (9)$$

Using (9), we obtain from (4) and (5) that

$$k_1 = -k_2 = -1/360. \quad (10)$$

In order to assure the result of our calculation, we examine the relationship between the measured values of pH_{25}, TA and TCO_2 in the study area. In the upper 200 meters of the northwestern Pacific, a significant deviation from the linear relationship between pH_{25} and (TA – TCO_2) (Fig. 3(A)) is observed only in the waters of the subtropical region which are characterized by high values of (TA – TCO_2) (>240 μmol/kg). The inconsistency between AV-91 and AV-92 carbonate data sets (Fig. 3) is caused by the systematically higher AV-91 alkalinity data than these of AV-92 by 20 μmol/kg. The use of TA and TCO_2 normalized to a salinity of 35 pss (NTA and $NTCO_2$) leads to a linear correlation between total alkalinity, total dissolved inorganic carbon and pH_{25} in the wider TA – TCO_2 range (Fig. 3(B)). In the intermediate water layer of the western subarctic Pacific and K/O zone, the residual (NTA – $NTCO_2$ – $360 \cdot pH_{25}$ + const) does not show any trend with depth (potential density) (Figs. 3(C) and (D)).

3.2 *The equation for the calculation of excess CO_2 and pH_{excess}*

Combining equations (1) and (3) and taking into account that

$$\Delta TCO_2(carb.dis.) = 0.5 \cdot \Delta TA(carb.dis.),$$

we introduce an equation for the determination of excess CO_2 concentrations in seawater from total alkalinity and total dissolved inorganic carbon data (Chen and Pytkowicz, 1979):

$$CO_{2excess} = NTCO_2 - TCO_2^0 - (\Delta TCO_2(org.ox.) - 0.5 \cdot \Delta TA(org.ox.)) - 0.5 \cdot (NTA - TA^0). \quad (11)$$

In the calculation of excess CO_2 concentrations in the north Pacific (Chen, 1982, 1993; Tsunogai *et al.*, 1993; Watanabe *et al.*, 1996), it was assumed that:

$$\Delta TCO_2(org.ox.) - 0.5 \cdot \Delta TA(org.ox.) = 0.78 \cdot AOU,$$

$$TA^0 = a_1 - 3.0 \cdot \theta$$

and

$$TCO_2^0 = a_2 - 11.5 \cdot \theta$$

where AOU is Apparent Oxygen Utilization (the difference between the equilibrium and measured concentration of dissolved oxygen), a_1 and a_2 are constants, θ is potential temperature.

Using the above equations for ($\Delta TCO_2(org.ox.)$ – $0.5 \cdot \Delta TA(org.ox.)$), TA^0 and TCO_2^0, Eq. (11) can be written as

$$CO_{2excess} = NTCO_2 - 0.5 \cdot NTA - 0.78 \cdot AOU + 10\theta + a_3 \quad (12)$$

where a_3 is a constant.

We have indicated that TA can be expressed in terms of pH and TCO_2 (Eq. (9)) in the intermediate water of the northwestern Pacific. Thus, the equation for the determination of excess CO_2 concentration in seawater from pH and TCO_2 data is

$$CO_{2excess} = 0.5 \cdot NTCO_2 - 180 \cdot pH_{25} - 0.78 \cdot AOU + 10 \cdot \theta + a_4 \quad (13a)$$

where a_4 is a constant.

Combining equations (8) and (10), we obtain

$$pH_{excess} = -(1/360) \cdot CO_{2excess}. \quad (13b)$$

Since there is no deep water formation in the north Pacific, penetration of gases of anthropogenic origin like freons and excess CO_2 is limited by the lower boundary of the intermediate water layer (σ_θ = 27.5–27.6) (Chen, 1993; Watanabe *et al*., 1994; Warner *et al*., 1996). The constant a_4 in Eq. (13a) can be determined by assuming that the concentration of excess CO_2 and pH_{excess} in the deep water layer ($\sigma_\theta \geq 27.6$) of the northwestern Pacific are equal to zero.

Then, the equation for the calculation of excess CO_2 and pH_{excess} at an isopycnal surface (x) in the intermediate water layer of the northwestern Pacific, is

$$\begin{aligned} CO_{2excess}(x) &= -360 \cdot pH_{excess} \\ &= 0.5 \cdot (NTCO_2(x) - NTCO_2(27.6)) \\ &\quad - 180 \cdot (pH_{25}(x) - pH_{25}(27.6)) \\ &\quad + 0.78 \cdot (AOU(27.6) - AOU(x)) \\ &\quad + 10 \cdot (\theta(x) - \theta(27.6)), \end{aligned} \tag{14}$$

where $NTCO_2(27.6)$, $pH_{25}(27.6)$, AOU(27.6) and $\theta(27.6)$ are the total dissolved inorganic carbon normalized to salinity 35 pss, pH_{25}, Apparent Oxygen Utilization and potential temperature at the σ_θ = 27.6, respectively. By calculating the excess CO_2 in the intermediate water relative to a deep water layer in Eq. (14) we eliminate the systematic errors in the pH, TCO_2 and DO.

In Appendix, we present the uncertainty in the excess CO_2 calculation from TCO_2-pH_{25}-O_2 data (Eq. (13a)) and from TCO_2-TA-O_2 data (Eq. (12)).

4. Results and Discussion

The distribution of excess CO_2 and pH_{excess}, calculated using Eq. (14), at isopycnal surfaces in the Okhotsk Sea (Kuril Basin area), the western subarctic Pacific and subtropical regions and K/O interfrontal zone are presented in Fig. 4. Because pH_{excess} is calculated by multiplying excess CO_2 by a constant (Eq. (13b)) the distribu-

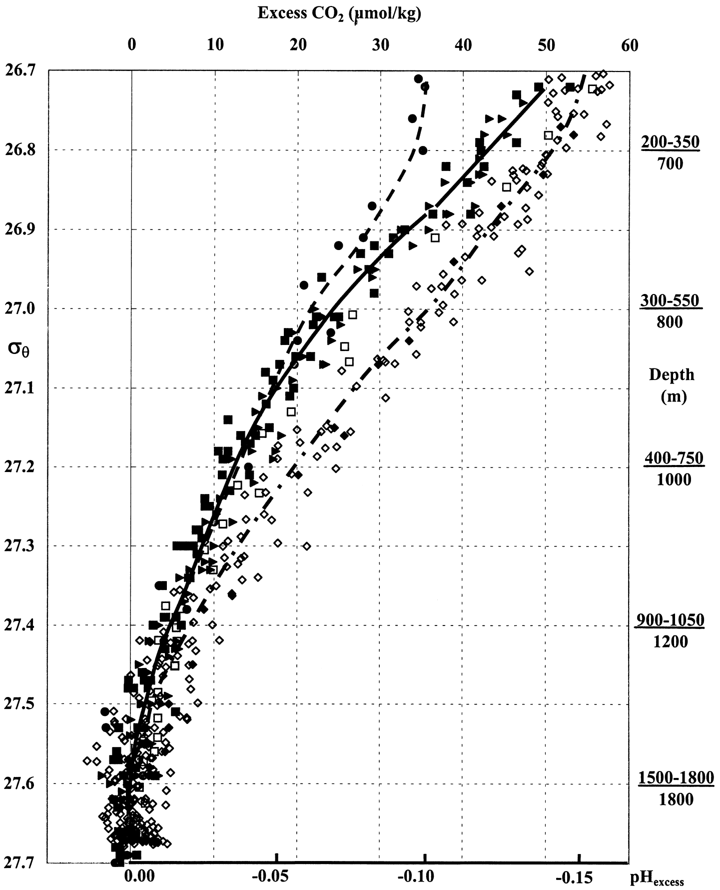

Fig. 4A. Excess CO_2 and pH_{excess} versus potential density in the Bussol Strait (◆), the Bering Sea and WSG region (■), zone of Subarctic Front (▶) and subtropical area of the northwestern Pacific (●) (AV-91, 92); the Okhotsk Sea (Kuril Basin area) (◇) and WSG (□) (AL-95). ((200–350)/700) is the average depth of the isopycnal surfaces at the stations in the western subarctic Pacific—the Okhotsk Sea (numerator) over those in the subtropical northwestern Pacific (denominator). The dashed, solid and dashed-dotted lines represent the fit curves for the stations located, respectively, in the subtropical and the subarctic western Pacific (data of AV-91 and AV-92) and the Kuril Basin of the Okhotsk Sea (data of AL-95).

tion of $\mathrm{pH_{excess}}$ in the intermediate water layer of the northwestern Pacific is exactly the same as that of excess CO_2 discussed below.

4.1 The distribution of excess CO_2 on isopycnal surfaces in the northwestern Pacific

At the σ_θ = 27.6–27.7 (1900–3000 m depth) in the Okhotsk Sea and at the σ_θ = 27.6–27.8 (1600–4000 m depth) in the western subarctic Pacific and K/O zone, the concentration of excess CO_2 calculated by Eq. (14) was 0.5 ± 0.9 μmol/kg and 0.3 ± 0.6 μmol/kg, respectively. This supports our assumption that the deep water in the northwestern Pacific has not been affected by the excess CO_2 input.

The Okhotsk Sea (Kuril Basin region) is characterized by high excess CO_2 on isopycnal surfaces in the intermediate water layer (Fig. 4A). At the σ_θ = 26.7, there was no difference in excess CO_2 between the western subarctic Pacific and the Okhotsk Sea. The concentration of excess CO_2 was 50–55 μmol/kg. The difference in the excess CO_2 between these regions becomes significant with increasing potential density in the intermediate water layer. The difference goes through a maximum at the σ_θ = 27.0 (about 8 μmol/kg) (Fig. 4A). The distribution of excess CO_2 at the isopycnal surfaces in the zone of Subarctic Front, the southwestern Bering Sea and the Western Subarctic Gyre (WSG) was quite uniform (Fig. 4A, data of AV-91 and AV-92 cruises). Thus, the concentration of excess CO_2 was 23 ± 2 μmol/kg at the σ_θ = 27.0. In the upper part of the intermediate layer (σ_θ = 26.7–27.0) of the subtropical region, the concentration of excess CO_2 on isopycnal surfaces was less than in the subarctic. In the lower part of the intermediate water layer, the difference in excess CO_2 concentrations between the subarctic and subtropical regions was negligible.

The intermediate water in the Kuroshio-Oyashio interfrontal zone is formed by mixing of Oyashio and Kuroshio Extension water components. The highest values of excess CO_2 on isopycnals in this area were found at Stn. 1 (42°N, 152°E), KNOT (44°N, 155°E) and Stn. 8 (40°N, 145°E), located in the zone of Oyashio Current influence (Fig. 4B). As the amount of water from the

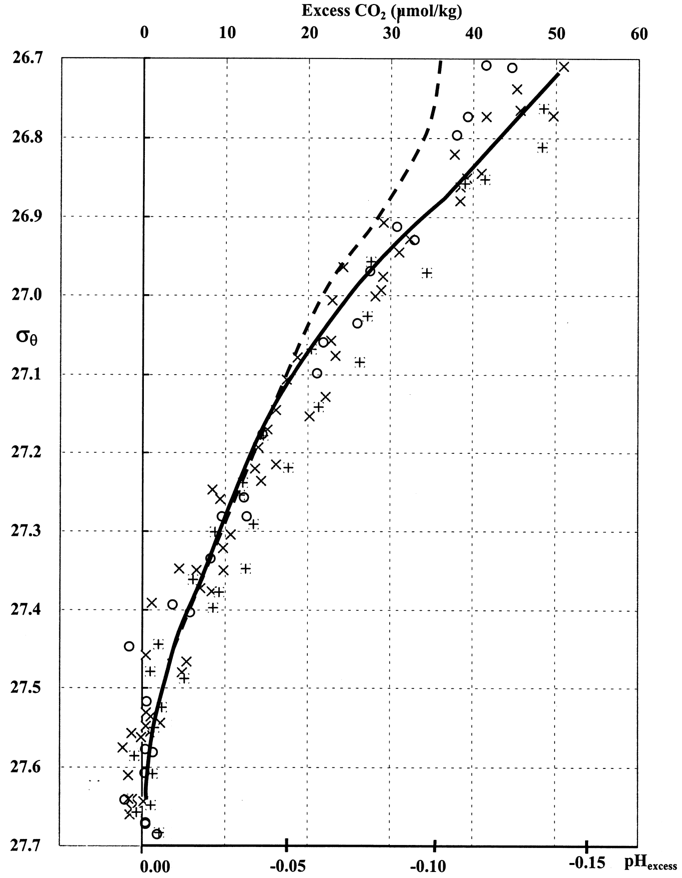

Fig. 4B. Excess CO_2 and $\mathrm{pH_{excess}}$ versus potential density in the K/O interfrontal zone. (+) Stns. 1 (42°N, 152°E), KNOT (44°N, 155°E) and 8 (40°N, 145°E); (×) Stns. 9, 12–15, 18 and 19 (37.5°N, 145–160°E; 40°N, 150–160°E); (○) Stns. 10, 11, 16 and 17 (35°N, 145–160°E) (MR98-K01). The dashed and solid lines are fit curves shown in Fig. 4A.

Kuroshio Extension increased (Stns. 10, 11, 16 and 17, along 35°N), the excess CO_2 content on isopycnal surfaces decreased.

The increase in excess CO_2 in the upper intermediate water layer of the Kuroshio Extension zone (Fig. 4B) between AV-91 (dashed line) and MR98-K01 (not filled circles) cruises (4–6 μmol/kg at the $\sigma_\theta = 26.7$–26.8) could be due to increase of pCO_2 in the atmosphere. The increase rate of the excess CO_2 in the surface seawater layer of the north Pacific from 1991 to 1997 was about 0.7 μmol/kg/yr (Winn *et al.*, 1998). Thus the difference in the excess CO_2 between MR98-K01 and AV-91 cruises looks reasonable. The mixing of WSG waters with Okhotsk Sea waters should result in the excess CO_2 difference between the zone of Oyashio Current (Stns. 1, 8 and KNOT, MR98-K01) and WSG (solid line, AV-91, AV-92) at the $\sigma_\theta = 26.9$–27.2 (Fig. 4B).

4.2 *The relation between the water structure, salinity and distribution of excess* CO_2

The difference in excess CO_2 concentrations in the upper part of the intermediate water layer of the northwestern Pacific and Okhotsk Sea (Fig. 5(C)) can be explained by the depth of the isopycnal surfaces and the vertical water structure. In the western subarctic Pacific such as the Okhotsk Sea, the upper boundary of the intermediate water layer is located close to the sea surface (100–200 m depth). In the wintertime, surface densities in the open north Pacific do not exceed $\sigma_\theta = 26.65$ (Reid, 1965; Levitus, 1982) and hence the direct ventilation of

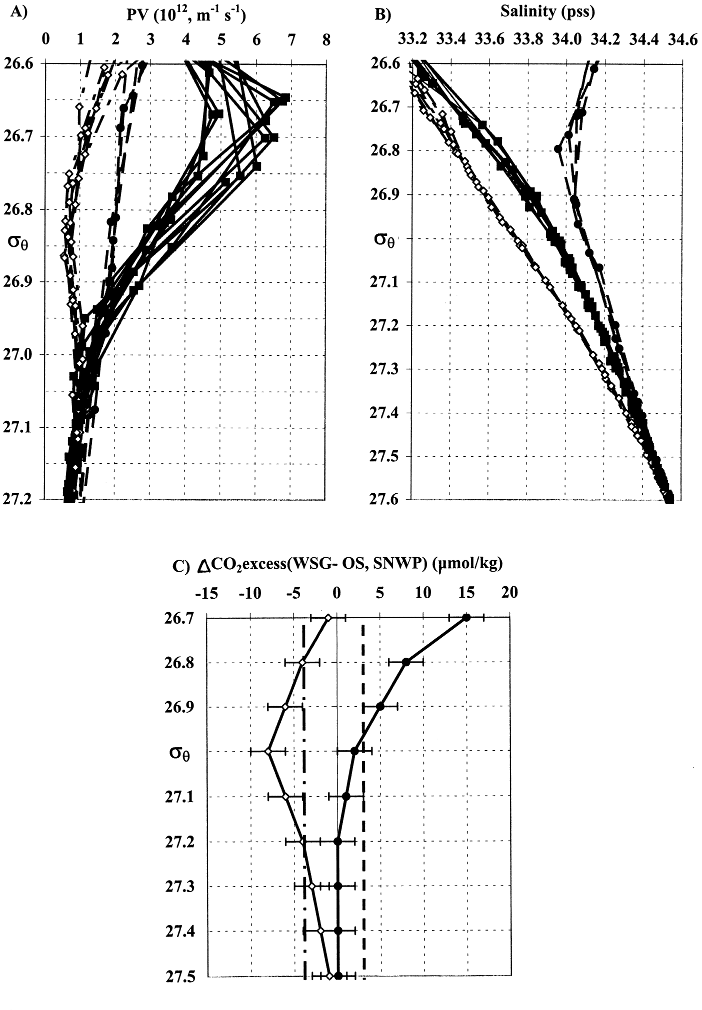

Fig. 5. Potential vorticity ($\rho^{-1}\cdot f\cdot d\rho/dz$, where ρ is density, z is depth, and f is Coriolis parameter) (A) and salinity (B) versus potential density in the Okhotsk Sea (◇), the western subarctic Pacific (■) and subtropical (●) regions; (C) the difference in the excess CO_2, with the standard deviations represented by error bars, between the Okhotsk Sea (OS) (◇), the subtropical northwestern Pacific (SNWP) (●) and WSG versus potential density; the dashed-dotted and dashed lines show the difference in excess CO_2, averaged in the 26.7–27.5 σ_θ range, respectively, between the Okhotsk Sea and WSG, and between subtropical and WSG regions.

the western subarctic Pacific is limited by this isopycnal surface. The water structure of the subarctic Pacific is characterized by a strong pycnocline (high potential vorticity (PV)) closely located to the upper boundary of the intermediate water layer (σ_θ = 26.65–26.75, 100–150 m depth) (Fig. 5(A)). The pycnocline can be considered a barrier, preventing the penetration of excess CO_2 from the surface to the intermediate water layer. In the Okhotsk Sea, the bottom Dense Shelf Water which is formed in coastal polynyas as a result of cooling and brine rejection under ice directly ventilates the surface layer and the upper part of the Okhotsk Sea Intermediate Water with σ_θ = 26.7–27.05. Excepting this phenomena, the cold and high salinity water entering into the Okhotsk Sea from the Sea of Japan in the winter till spring period has a σ_θ = 26.75–27.25 (Talley and Nagata, 1995). In the upper water layer of the Kuril Basin region vertical stratification is low and the vertical distribution of PV is quite uniform with a small minimum centered at the σ_θ = 26.7 and a maximum at the σ_θ = 27.0 (Fig. 5(A)).

In the subtropical region, the main limiting factors for the penetration of excess CO_2 from the surface to the intermediate water layer are the deep location of the upper boundary of the intermediate layer (at a depth of about 600–650 m) and the presence of a strong pycnocline in the upper water layer. Direct ventilation in this area only occurs above the σ_θ = 25.5 (Reid, 1965; Levitus, 1982).

The source of low salinity water for the intermediate layer is surface water in the subarctic region (Fig. 5(B)). In the subtropical area, the excess of evaporation over precipitation leads to an increase of salinity at the surface. The isopycnal mixing between Kuroshio and Oyashio source waters has been considered as the main mechanism that produces the salinity minimum in the intermediate water layer of the subtropical region (Yasuda *et al.*, 1996).

For the period between 1991–1992 (cruise of AV-91, AV-92) and 1998 (cruise of MR98-K01) the concentration of excess CO_2 in the seawater should have increased as a result of the pCO_2 increase in the atmosphere. With this in mind, we consider the relation between the distribution of excess CO_2 and salinity at the σ_θ = 26.8 (26.77–26.83), σ_θ = 27.0 (26.97–27.03) and at the σ_θ = 27.2 (27.17–27.23) in the northwestern Pacific (Fig. 6). Figure 6 indicates that there is a tendency towards decreasing excess CO_2 with increasing salinity below the σ_θ = 26.8, which represents the average potential density of the core of the main salinity minimum in the North Pacific. Deviation from the linear relationship between excess CO_2 and salinity in the 34.00–34.15 pss salinity range at the σ_θ = 27.1 (Fig. 6(B)) might be the result of diapycnal mixing of the intermediate water with surface waters of subtropical and tropical regions, which are more saline and have higher concentrations of excess CO_2.

4.3 Exchange of excess CO_2 between the Okhotsk Sea, the western subarctic Pacific and subtropical regions

The distribution of salinity, nutrients (nitrate and silicate) and dissolved oxygen at the isopycnal surfaces in the northwestern Pacific has manifested that water mixing between the subarctic Pacific water, the Okhotsk Sea water and the Kuroshio Extension water in the intermediate water layer of the Kuroshio-Oyashio interfrontal zone is mainly isopycnal (Andreev *et al.*, 2000). Salinity-DIC and salinity-pH diagrams (Fig. 7) also indicate the isopycnal character of water mixing between the Okhotsk Sea, the Western Subarctic Gyre and the Kuroshio Extension Current in the intermediate layer of the northwestern Pacific. The Okhotsk Sea water with

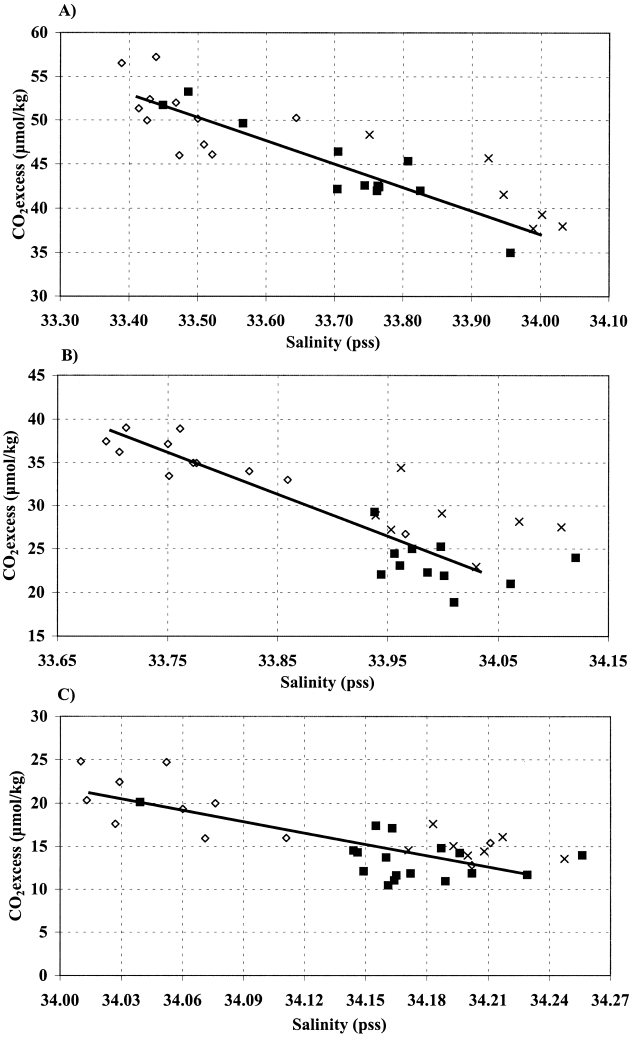

Fig. 6. Excess CO_2 versus salinity at the σ_θ = 26.8 (A), σ_θ = 27.0 (B) and σ_θ = 27.2 (C) in the northwestern Pacific and the Okhotsk Sea. (■) AV-91 and AV-92; (◇) AL-95; (×) MR98-K01 cruises.

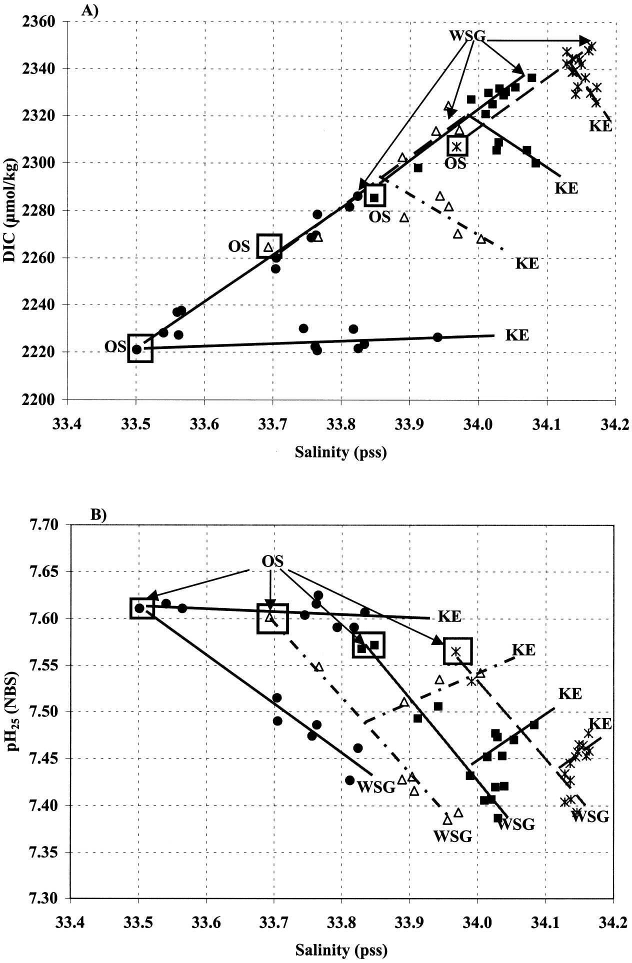

Fig. 7. Dissolved inorganic carbon (A) and pH (B) versus salinity at the σ_θ = 26.78–26.88 (●), σ_θ = 26.94–27.01 (△), σ_θ = 27.03–27.09 (■) and σ_θ = 27.15–27.19 (×) in the northwestern Pacific, OS - the Okhotsk Sea (the Bussol' Strait area), KE - Kuroshio Extension and WSG - Western Subarctic Gyre. Mixing is along straight lines on the DIC/Salinity and pH/Salinity diagrams.

$\sigma_\theta \approx 26.8$ (filled circles, Fig. 7) is transported to the subtropical region directly (without significant modification by mixing with WSG water) with the coastal branch of Oyashio.

Using the differences in excess CO_2 at isopycnal surfaces between the Okhotsk Sea, the western subarctic Pacific and subtropical regions, it is possible to roughly estimate the amount of excess CO_2 supplied to the subarctic Pacific from the Okhotsk Sea and the transport of excess CO_2 from the subarctic to the subtropical region.

According to Talley (1996), the Oyashio water transport to the intermediate water layer of the subtropical area is 3–5 Sv. The net exchange between the Okhotsk Sea and the subarctic Pacific is about 3–5 Sv (Talley, 1996).

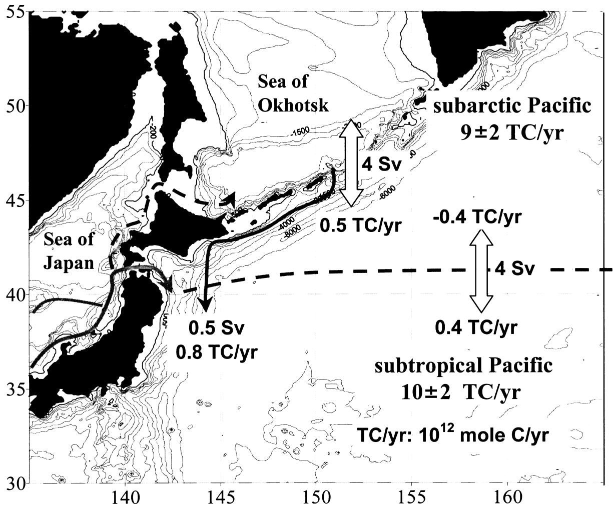

Fig. 8. Water and excess CO_2 exchange rates in the intermediate water layer of the northwestern Pacific.

The average difference in excess CO_2 concentrations between the western subarctic Pacific and the Okhotsk Sea waters (AL-95 data) and between the western subarctic Pacific and the Subtropical waters (AV-91 and AV-92 data) in the range of 26.7–27.5 σ_θ are –4 and 3 μmol/kg, respectively (Fig. 5(C)). Thus the net transport of excess CO_2 from the Okhotsk Sea to the subarctic Pacific and from the Pacific subarctic to the subtropical zone are about of 0.5×10^{12} mol/yr and 0.4×10^{12} mol/yr, respectively.

One of the most important factors in the excess CO_2 accumulation in the subtropical north Pacific is the transport of about 0.5 Sv of the Okhotsk Sea water (σ_θ = 26.7–26.8 and excess $CO_2 \approx 50$ μmol/kg) with coastal branch of Oyashio (Fig. 8). This transport of the Okhotsk Sea water to the subtropical Pacific represents the compensation flux for the surface subtropical waters supplied to the Okhotsk Sea from the Sea of Japan and modified the intermediate waters of the Okhotsk Sea (Talley and Nagata, 1995).

The annually averaged increase in the total dissolved inorganic carbon content of seawater from 1973 to 1991–1993 was 0.63 ± 0.15 mol/(m^2·year) in the northeastern Pacific (Slansky *et al.*, 1997), 0.7 ± 0.2 mol/(m^2·year) in the western subarctic Pacific and 0.58 ± 0.2 mol/(m^2·year) in the western subtropical Pacific (Ono *et al.*, 1999). Taking into account the surface area of the subarctic and subtropical Pacific to be 1.4×10^{13} and 1.85×10^{13} m^2, respectively, we estimated that the subarctic and subtropical Pacific have been accumulating about $9 \pm 2 \cdot 10^{12}$ mol and $10 \pm 2 \cdot 10^{12}$ mol of excess CO_2 per year. We indicated in Fig. 8 that about 10% of the excess CO_2 accumulation in the subtropical north Pacific is determined by water exchange with the subarctic and the Okhotsk Sea.

Based upon the field studies described above and discussions, we conclude that:

1) the Kuril Basin (Okhotsk Sea) and the Bussol' Strait area are characterized by the greatest concentrations of excess CO_2 and the lowest values of pH_{excess} at the isopycnal surfaces in the intermediate water layer of the northwestern Pacific;

2) the highest difference in excess CO_2 concentrations between the Okhotsk Sea and the western subarctic Pacific (about 8 μmol/kg) is found at the $\sigma_\theta = 27.0$;

3) the difference in excess CO_2 between the western subarctic Pacific and subtropical region is significant only in the upper part of the intermediate water layer ($\sigma_\theta = 26.7$–27.0); and

4) about 10% of the excess CO_2 accumulation in the subtropical north Pacific is determined by water exchange with the subarctic Pacific and the Okhotsk Sea.

Acknowledgements

We wish to thank the scientists and technicians of POI (Russia), IOS (Canada) and MWJ (Japan) for their efforts in the carbonate parameters analysis. We also thank the captains and crew members of the R/V "Mirai", R/V "Akademik Vinogradov" and R/V "Akademik Lavrentiev" for their assistant in this study. The authors would like to express their appreciation to Dr. P. Brewer and anonymous reviewers for instructive and valuable suggestions to improve the manuscript.

Appendix: The Uncertainty in the Excess CO_2 Calculation

In our calculation of the accuracy of excess CO_2 concentration, we assume that the coefficient between (ΔTCO_2(org.ox.) – $0.5\cdot\Delta TA$(org.ox.)) and AOU (equals to 0.78), temperature coefficient of Eqs. (12) and (13a), and the coefficient between (TA – TCO_2) and pH (Eq. (9)) are valid and constant. Since there is the uncertainty in the excess CO_2 calculation from TA – TCO_2 data (Eq. (12)) ($\sigma_{CO_2\text{excess}}(TA - TCO_2)$) depends on the accuracy of the TCO_2, TA and dissolved oxygen measurements, (σ_{TO_2}, σ_{TA} and σ_{O_2}) is expressed:

$$\sigma^2_{CO_2\text{excess}}\left(TA - TCO_2\right) \sim \sigma^2_{TCO_2} + \left\{0.5\cdot\sigma_{TA}\right\}^2 + \left\{0.78\cdot\sigma_{AOU}\left(\sqrt{\sigma^2_{O_2\text{equil.}} + \sigma^2_{O_2}}\right)\right\}^2. \tag{A1}$$

As the uncertainty in the excess CO_2 calculated from pH – TCO_2 data by Eq. (13a), ($\sigma_{CO_2\text{excess}}(pH - TCO_2)$) depends on the accuracy of the TCO_2, pH and dissolved oxygen measurements (σ_{TO_2}, σ_{pH} and σ_{O_2}) is expressed:

$$\sigma^2_{CO_2\text{excess}}\left(pH - TCO_2\right) \sim \left\{0.5\cdot\sigma_{TCO_2}\right\}^2 + \left\{180\cdot\sigma_{pH}\right\}^2 + \left\{0.78\cdot\sigma_{AOU}\right\}^2. \tag{A2}$$

Taking σ_{AOU}, σ_{pH}, σ_{TA} and σ_{TO_2} as, respectively, ±3 μmol/kg, ±0.007 pH unit, ±4 μmol/kg and ±3 μmol/kg, we obtained that $2\,\sigma_{CO_2\text{excess}}(pH - TCO_2) \approx 6.1$ μmol/kg and $2\,\sigma_{CO_2\text{excess}}(TA - TCO_2) \approx 8.6$ μmol/kg. These results suggest that if the Eq. (9) is valid, the uncertainty of the excess CO_2 calculation from pH – TCO_2 data by Eq. (13a) is lower than from TA – TCO_2 data by Eq. (12).

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