1997年の黒潮・親潮混合領域における栄養塩・炭酸系諸量の分布の季節変動

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Seasonal Variation in the Distributions of Carbonate Properties and Nutrients in the Kuroshio/Oyashio Interfrontal Zone Observed From January to August 1997

Tsuneo Ono*, and Katsuyuki Sasaki

Abstract: Distributions of nutrient and carbonate properties along 144°E section in the Kuroshio/Oyashio Interfrontal Zone were observed repeatedly on January, May, and August in 1997. Nitrogen and silicate decreased significantly in the mid layer of the Oyashio area from January to May, which was followed by a decrease in the alkalinity and complete depression of nitrogen from May to August. The export production estimated from the observed inventory change of nutrients during this time was similar to that of the previous estimation made in 1991. Significant seasonal variations of chemical properties were observed, even in the $\sigma_t = 26.60$ density surface, despite the fact that the density surface do not outcrop in the observation area. This result forced us to re-consider the previous estimations of cross-gyre transport across this area, as these estimates were based mainly on spring/summer data.

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*National Research Institute of Fisheries Science, Fukuura, Kanasawa, Yokohama 236-8648, Japan
The Kuroshio/Oyashio Interfrontal Zone (K/O Zone: Yasuda et al., 1996) is a key area in the transport of chemical substances across the subpolar front in the North Pacific. Complex mixing of the subtropical-gyre-oriented Kuroshio water with the subarctic-gyre-oriented Oyashio water occurs in this zone and results in effective cross-gyre transport (Talley, 1993; Talley et al., 1995; Yasuda et al., 1996; Maksimenko et al., 1997; Yasuda, 1997; Yoshinari and Yasuda, 1998). The transport of anthropogenic substances (CFCs, anthropogenic carbon, etc.) from the subarctic surface to the subtropical subsurface is of particular importance as an oceanic feedback process to anthropogenic perturbations (Tsunogai et al., 1993; Tsunogai, 1995, 1997; Ono et al., 1998a). The K/O Zone is also characterized as one of the most highly productive areas in the world. Such productivity is supported by the transport of nutrients from surface and/or the subsurface layers of the Oyashio in the K/O zone through the complex mixing processes.

Regardless of the above importance, there is little detailed analyses about the seasonal variation in the chemical compositions in the K/O Zone, especially for the subsurface layers. For carbonate properties such as total carbonate, observed data themselves have been limited for this region (e.g., Rogachev et al., 1996). Ono et al. (1998b) first detailed the distribution and dynamics of carbonate properties in the spring K/O Zone, however seasonal variation of the carbon cycle in this zone remains still unclear.

The K/O Zone encompasses the westernmost part of the Western Subarctic Gyre, but its water properties in the K/O Zone are significantly different from those of the subarctic gyre body due to interactions between the Okhotsk Sea water and/or the Kuroshio Extention water in adjacent to the K/O Zone (e.g., Kono, 1997; Kono and Kawasaki, 1997; Yasuda, 1997). Information regarding seasonal variation in the carbonate properties in the K/O Zone may be also useful as a reference for the future time-series studies as being occupied at the Station KNOT (44°N, 155E; Nojiri et al., 1998).

From January 1997 to April 1998 we conducted six cruises along 144°E in the K/O Zone to observe how distributions of nutrients and carbonate properties varied seasonally. We report preliminarily the results from the first three cruises of this program, referring particularly to the transition in the distribution of chemical properties during spring. This study is partly supported by the projects "Subarctic Gyre Experiment (SAGE)" financed by the Japan Science and Technology Agency and "Carbon Cycle in the Kuroshio/Oyashio Interfrontal Zone" also financed by the Japan Science and Technology Corporation.
Fig. 1. a) Sampling locations for each cruise. The surface temperature field at the b) SY9701 (January), c) SY9705 (May), and d) SY9708 (August) cruises are also shown. Each temperature field is reproduced from JHD (1997).
Fig. 1. (continued)
Observations

The data used in this paper were obtained during the cruises SY9701, SY9705, and SY9708 of the R/V Soyo Maru of our institute. On each cruise, samplings were made along 144°E with 0.5°N interval. Sampling locations for each cruise are shown in Fig. 1a, and the sea surface temperature fields during each cruise in Figs. 1b-1d.

At each station, 21 water samples were taken from the sea surface to 1500 m depth with 2.5-l Niskin bottles attached to a CTD-RMS. Subsamples for dissolved oxygen, nutrients (phosphate, nitrate+nitrite, and silicate), titration alkalinity, and total carbonate were taken from each bottle. At several stations in each cruise salinity subsamples were also taken from each bottle. These salinity samples were measured with an Auto-Sal analyzer on land and were used to calibrate the salinity values measured by CTD in each cruise.

The subsamples for dissolved oxygen (DO) were kept in 100 ml Fram bottles and measured with a HIRAMA ART-3DO-1 auto-titilator within 12 hours after sampling. The average difference between duplicate samples was 1.5 μmol/kg. For the SY9701 cruise, bottle DO samples were measured only at half of the stations because of instrumentation problems. In this case, the DO values measured by CTD were calibrated by those bottle measurements results and were used for the following analysis.

Nutrient subsamples were kept in 50 ml centrifuge tube, then 10 ml of each subsample was filtrated with a MILLEX®-HV 0.45 μm disposable cartridge filter unit and kept in 12 ml polypropylene tubes. These filtrated subsamples were stored at -20°C, and phosphate (P), nitrate+nitrite (N), and silicate (Si) were measured with a TRACCS-800 autoanalyzer in our laboratory within 6 months after each cruise.

Subsamples for titration alkalinity (TA) were kept in 100 ml grass bials with an aluminum-sealed butyl rubber plug and stored at room temperature. The TA values were measured on land by the modified one-point titration method (Ono et al., 1998a) within six months of sampling. The average difference among the duplicate samples was 3 μeq./kg.

Subsamples for total carbonate (TC) were kept in the grass bials as for the TA sampling. At 5 seconds after overflow, 1 ml of head space sample was removed and 400 μl of 5g HgCl₂/100 ml aq. solution was added. Each subsample was then sealed with a butyl rubber plug and aluminum sealing apparatus and stored at 1°C until measurement. The measurements of TC were made by the extraction-coulometric method following the procedure of Ono et al. (1998a) within 6 months of sampling. The stability of stored TC samples was determined at ±4.6 μmol/kg for the first month (Ono et al., 1998b). The stability of samples stored for longer periods was
Fig. 2. Distributions of TC on the $\sigma_z = 27.50$ density surface during each cruise.

estimated by determining variation in TC values among neighboring samples in the $\sigma_z = 27.50$ density surface, where small-scale latitudinal variation of TC was thought to be as small ($\pm 3 \mu mol/kg$ for the on-board measurement results at 165°E, Ono, 1997) as analytical errors (Fig. 2). If samples were unstable, isopycnal TC values would vary between stations where sample storage time was significantly different. As shown in Fig. 2, the standard deviations of all 3 neighboring data in the isopycnal profile were not larger than $4 \mu mol/kg$ for each cruise, and the degree of deviation between the neighboring 2 data had no correlation between the difference of storage time between 2 stations (data not shown). This indicated that the stability of TC samples after six months was similar to that after one month of storage. In the following discussion, we assume that the precision of TC measurements in each cruise was within $\pm 4.6 \mu mol/kg$.

The reference seawater certified and provided by the Scripps Institution of Oceanography (SIO-CRM; DOE, 1994) were measured along with TA and TC to correct for systematic differences among the stations and/or cruises. The overall mean precision of SIO-CRM measurement results was $2.3 \mu eq/kg$ for TA and $1.8 \mu mol/kg$ for TC, and detailed measurement results are shown in Fig. 3.
Fig. 3. Results of the measurement of SIO-CRM (Batch #35, Certified value for TC = 2111.62 ± 0.82 μmol/kg and TA = 2354.05 ± 0.50 μmol/kg) for a) TC and b) TA. The cruise/station No. at which CRM-measurement was done is used for X-axis. The solid line shows the average value and dashed line shows ±1σ.
Density structure and salinity distributions along 144°E The distributions of potential density along 144°E sections in three cruises are shown in Figs. 4a - 4c. The distributions of salinity, apparent oxygen utilization (AOU), N, TA, and TC in each section are shown in Figs. 5a - 5c, 6a - 6c, 7a-7c, 8a - 8c, and 9a - 9c, respectively.

A broad horizontal pycnocline was observed around 40°N - 41°N in the surface layers in January 1997 (Fig. 4a), which formed the front between the Kuroshio-oriented subtropical waters and the Oyashio-oriented subpolar waters. A horizontal pycnocline was also observed at around 38°N in May (Fig. 4b), while it was observed around 36°N in August (Fig. 4c). These fronts were also observed as the thermal fronts in the surface temperature fields (Figs. 1b - 1d). In January, a dome-like structure appeared around 33.5°N - 36.5°N, which seemed to represent the intrusion of a cold water tang from off-Japan coast around 37.5°N observed in Fig. 1b. Such dome-like structures, thus cold water tang, seemed remained in the subsurface layers around 34°N in both the May and the August sections (Fig. 4b and 4c). In the northern region, a warm core ring (WCR) was observed around 41°N in May and August (Fig. 4b and 4c), with a pycnostad of $\sigma_s = 26.5-26.6$ at its core. This seemed to have originated from the warm water tang observed just south of 38°N in January (Figs. 1b - 1d). This WCR or warm water tang seemed to divide the subpolar-side watermass in each section; i.e., the Oyashio First Branch north of WCR (or warm water tang) and the Oyashio Second Branch between the WCR and KE core.

The depth of the mixed layer (ML) reached 125 m both north and south of the density front in January, with the maximum density at the bottom of the ML being $\sigma_s = 26.4$ to the north of 40°N while being $\sigma_s = 25.5$ to the south of 40°N (Fig. 4a). In May the ML depth became shallower at around 20 m and 75 m to the north and south of the density front, respectively, due to the formation of a seasonal pycnocline (Fig. 4b). Maximum densities at the bottom of the ML were $\sigma_s = 26.1$ and $\sigma_s = 25.1$ north and south of the surface front at around 38°N, respectively. In August, the ML depth was around 20 m and 50 m, with maximum densities of $\sigma_s = 24.2$ and 22.8, north and south of the surface front, respectively.

The salinity section of each cruise showed a significant latitudinal gradient at the subpolar front from the surface to 500 - 750 m depth (Figs. 5a - 5c). South of the front, salinity values at the ML ranged from 34.6 to 34.7 psu in the January and May sections, whereas it ranged from 34.1 to 34.5 psu in the August section. To the north of the front, salinity distribution above 600 m showed quite complex variation, with ML salinity values ranging from 33.0 to 34.9 in January and from 32.6 to 33.9 in May and August.

In the August salinity section, several patch-like structures were observed in the
Fig. 4. Distribution of potential density ($\sigma_z$) along the 144°E section observed at a) January, b) May, and c) August cruise.
Fig. 5. Same as Fig. 4 but for salinity (psu)
Fig. 6. Same as Fig. 4 but for AOU (μmol/kg)
Fig. 7. Same as Fig. 4 but for N (μmol/kg).
Fig. 8. Same as Fig. 4 but for TA ($\mu$eq./kg)
Fig. 9. Same as Fig. 4 but for TC (μmol/kg)
Seasonal transition of carbonate/nutrients in Kuroshio/Oyasio

250 - 750 m depth layer south of 36°N, more numerous than those observed in the May section (Figs. 5b and 5c). Such low salinity patches were also observed in the January section, although the relative differences in salinity were not as great as in other seasons (Fig. 5a). Many studies have investigated low salinity patches and their relationship to cross-gyre transport in the K/O Zone (i.e., Rogachev et al., 1996; Yasuda et al., 1996; Maksimenko et al., 1997; Ono et al., 1998b), but observations in these studies were limited to spring. Our observations suggest that the formation processes of such patch-like structure in summer K/O Zone is the same as in the well-studied spring season, and is significant even in mid-winter.

**Distributions of properties along 144°E section** The distributions of AOU and N along 144°E section in each cruise (Figs. 6a - 6c and Fig. 7a - 7c) varied significantly, especially in the layers above 750 m. The patterns of variation are similar to those of potential density (Figs. 4a - 4c). In the May and August sections, several anomalous structures occurred where patch-like structures were observed in the salinity sections (Figs. 6b, 6c, 7b, and 7c), although their signals had faded due to the large vertical gradient of AOU and/or N in these layers. In the layers below 750 m depth vertical gradients of AOU and N were small, with its value around 260 - 280 μmol/kg for AOU and 40 - 42 μmol/kg for N.

In the January AOU section, a water mass with a significant negative AOU value (i.e., oversaturated with DO) was observed above 250 m depth north of 40°N (Fig. 6a). Such DO-oversaturated areas were also observed in the northernmost region of the ML in May and August sections (Fig. 6b and 6c). However, the area of oversaturation seemed somewhat smaller in May and August compared to that in January, although data north of 42°N lacked in the May and August sections. This implies that DO-oversaturation is not caused by in-situ biological activity, as biological productivity in the field is considerably larger in the May and August than in January. Interaction with the Oyashio Coastal water (Otani, 1989) may play some roles, causing a rapid change in water temperature which may lead to the temporal oversaturation of DO. If this is true, other properties of coastal origin (i.e., dissolved organic carbons and/or plankton of coastal origin) may also be transported into these water mass to some extent. Gas-exchange from wave-generated bubbles, which occurs extensively in the ocean in winter, may also contribute to the oversaturation of dissolved gases (e.g., Farmer et al., 1993).

Except these in the above mentioned area, AOU levels in the ML were almost zero in the May and August section. In the January section, AOU levels in the ML south of 40.5°N were positive, suggesting the injection of subsurface water by enhanced vertical mixing (Fig. 6a). Positive AOU in the ML even occurred south of the subpolar front, suggesting that the subsurface water injection was also significant on the
subtropical side of K/O Zone in winter.

N in the winter ML was also high, with values always greater than 2 \( \mu \text{mol/kg} \) except at in the core of the Kuroshio Extension (KE) (Fig. 7a). Highest N concentration in the ML was observed north of 42\(^\circ\)N, where N value was greater than 14 \( \mu \text{mol/kg} \). These high N values in the ML disappeared in the May and August sections (Fig. 7b), where the N in the ML was nearly always lower than 2 \( \mu \text{mol/kg} \) in the May section (Fig. 7b), and constantly lower than 1 \( \mu \text{mol/kg} \) in the August section (Fig. 7c). However, the N concentration in ML in the May section were more than 1 \( \mu \text{mol/kg} \) even in the south end of the section. The subarctic gyre was generally found to be a high-nutrient low-chlorophyll zone, and water transported from the gyre body to the K/O Zone contains a significant amount of nutrients even in May (e.g., Kono et al., 1997). This may maintain the significant nutrient level of ML in the May K/O Zone.

The distribution pattern of TA was similar to that of salinity in each cruise, although TA increased uniformly from the surface to 1500 m depth (Figs. 8a - 8c). TA increased even in the layers below 750 m depth, in contrast to the AOU and N distributions. This differences is because dissolution of calcite occurs in the deep layers of the North Pacific whereas degradation of organic matter occurs mainly in the shallow seasonal/permanent thermocline. The distributions of TC (Figs. 9a - 9c) resembled to those of N above 750 m layers, and those of TA in the deeper layer. This implies that TC variation in the upper 750 m layers is controlled mainly by biological degradation, whereas it is controlled mainly by dissolution of calcite in the layers below 750 m. TC values in the ML north of 40\(^\circ\)N exceeded 2080 \( \mu \text{mol/kg} \) in January, decreased to around 2000 \( \mu \text{mol/kg} \) in May, and further to around 1980 \( \mu \text{mol/kg} \) in August. This is mainly due to biological activity, but the interaction of coastal water (generally low TC) may also play a role as for the AOU. The seasonal change of TC in the ML was also observed in the region south of 40\(^\circ\)N, but the extent of the decrease was smaller than in the northern region.

**Seasonal balance sheet of chemical properties in the K/O Zone Mixed Layer**  As seen in the previous section, seasonal variation in the distribution of chemical properties was significant, especially in the ML.

The hydrographic structure in the K/O Zone was highly complicated and varied between times. Signals of seasonal variations in the chemical properties of a water mass are often masked by hydrographic variation, if observations from a fixed station are used. Therefore, we used property-versus-salinity plots to analyze seasonal variations in the chemical properties in the K/O Zone. For this analysis, salinity is assumed to be an indicator of water types.

The horizontal distribution of potential density for each cruise at depth of 10 m,
Fig. 10. Distribution of potential density ($\sigma_s$) against salinity at a) 10m, b) 30m, c) 50m, d) 75m, and e) 100m depth along 144 $^\circ$E section. Open circles represents the data of January, x the May, and dots the August, respectively.

Fig. 11 Same as Fig. 10 but for N ($\mu$mol/kg).
Fig. 12. Same as Fig. 10 but for Si (μmol/kg).

Fig. 13 Same as Fig. 10 but for TA (μmol/kg).
Fig. 14. Same as Fig. 10 but for TC (μmol/kg).
30 m, 50 m, 75 m, and 100 m are plotted against salinity and shown in Figs. 10a - 10e, respectively. The distributions of N, Si, TA, and TC at each isodepth are also shown in Figs. 11a - 11e, 12a - 12e, 13a - 13e, and 14a - 14e, respectively.

The potential density in the 75 m layer was almost constant at around \( \sigma_s = 26.40 \) January to August in waters where salinity was less than 34.0 PSU (Fig. 10d). In layers shallower than 75 m, the potential density in August tended to be smaller than that in January and May at the same salinity, suggesting that the effect of seasonal warming reaches to 75 m depth in this area, at which ML salinities are less than 34.0 PSU. In the 100 m layer, in contrast, the potential density in May and August was greater than that in January (Fig. 10e). A seasonal pycnocline developed below 20 m depth in May and August in the Oyashio region (Figs. 4b and 4c), which corresponds to the area with ML salinities less than 34.0 PSU (Figs. 3b and 3c). Fig. 10c - 10e suggest that in the Oyashio region, hydrographic seasonal variations differs between the layers shallower than 75 m depth and deeper layers. In layers shallower than 75 m, hydrographic variation occurred mainly through seasonal heating in the summer. Below 75 m, in contrast, winter ML water was remained under the seasonal pycnocline and gradually mixed (probably mainly isopycnally) with the subsurface waters, which enhanced the density of under 75 m layer from winter to summer. The latter pattern of seasonal variation was also observed in the layers down to 125 m (data not shown), which was the bottom depth of the winter mixed layer in the Oyashio Region.

In waters where the salinity was greater than 34.0 PSU, the density distribution was relatively constant between the January and the May, but became significantly smaller in the August, even at the 75 m depth (Fig. 10d). Such a summer warming effect was also observed in the 100 m layer, but in water where the salinity was 34.2 - 34.6 PSU, the density in May and August was greater than that of January in this layer (Fig. 10e).

The concentrations of N in the layers shallower than 75 m (Figs. 11a - 11c) had decreased significantly in the May compared to January, especially in waters where salinity was smaller than 34.0 PSU. In waters of 33.0 PSU in the 10m layer, concentration of N decreased to around 2.0 \( \mu \text{mol}/\text{kg} \) in the May from around 12.0 \( \mu \text{mol}/\text{kg} \) in the January, but did not reach zero during this period (Fig. 11a). In August, concentrations of N decreased to almost 0 \( \mu \text{mol}/\text{kg} \) for the waters of all salinity ranges in the 10m and 30m layers with a few exceptions (Fig. 11b). Si in the 10-30 m layers also decreased in the May, and the extent of depression in this period seemed more severe for Si than that observed for N (Figs. 12a - 12c). In the 10m layer, Si decreased to almost 0 \( \mu \text{mol}/\text{kg} \) in May in the waters where salinity was less than 33.0 PSU (Fig. 12a). Si also decreased significantly in waters where salinity was around 33.5 - 34.0 PSU in the 30 m layer, and the Si depression observed during
May and August was not so significant around this area as that observed for the N distribution (Fig. 12b). This suggests that the biological consumption of silicate mainly occurred before the end of May in the K/O Zone in this year. Further, the remaining N in this area was consumed through the biological activities of Si-independent species to make the N depression observed in the end of August.

On the other hand, the concentrations of TA decreased significantly both from January - May and from May - August (Figs. 13a - 13c). Unlike N and Si, TA seemed to decrease even in the 75m layer from January to May (Fig. 13d) and thus some modification of the water mass might have occurred during this period which was not evident in the simple property - versus - salinity plots. Nevertheless, the decrease of TA during the cruises was more significant in layers above 50m than in the 75m layer, which indicates that a significant amount of TA was consumed during the observation period by some processes such as the formation of calcite/aragonite through biological activity.

The change in concentration of each substance during cruises in watermass where salinity was 33.5 psu in the 30 m layer were calculated from Figs. 11b - 14b and listed in Table 1. This water mass was selected as representative of Oyashio component water in the K/O Zone observed throughout the cruises (see also Figs. 3a - 3c). About two thirds of the winter N was consumed by the end of the May, with the remainder consumed from the May to the August. The consumption of N until the end of May was strongly correlated with Si consumption in spring, which had used about 90% of the winter Si before the May cruise. The consumption of N from May to August, in contrast, seemed to correlate with the significant TA depression from May to August (Table 1). As a consequence, the decrease of TC was similar for the January to May and May to August periods (50 μmol/kg of depression during each period, see Table 1).

If we assume that the change in concentration of each substance during these periods was constant throughout the upper 30 m of the water column, the corresponding depression of N and TC reached about 6.1 g N/m³ and about 37 g C/m³, respec-

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<td>50</td>
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<td>Jan.-Aug.</td>
<td>14</td>
<td>22</td>
<td>100</td>
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Table 1. Change in the concentration of N, Si, TA, and TC, in water salinity = 33.5 psu and depth = 30 m (μmol/kg). The right hand column shows the ratio of concentration change (C/N), after correction for the biological formation of carbonate tests.
tively, from January to August. Sasaki and Matsukawa (1991) estimated the export production of N and C from January to August for the top 50 m layer of Oyashio area in the K/O Zone as 3.2 g N/m² and 20 g C/m², respectively. The depressions of N&TC inventories in the Oyashio ML estimated above were very correspondent to their estimation, taking account that export production decreases exponentially with depth; or that the export flux at 50 m is roughly half of that at 30 m, as summarized by Honda et al. (1997). This suggests that the bulk of new production in the Oyashio ML from January to August is maintained by the consumption of nutrients which initially existed in the water mass in January. The nutrients additionally supplied from the bottom of the ML by vertical diffusion after the winter season did not seem to play significant role, in which case the bulk transport production should significantly exceed the apparent decrease of nutrients.

The concentration of N in the ML was zero in the August throughout the observed area. Therefore, nutrient supply by the vertical diffusion process should be more important for primary production in the observation area after this month, as observed in the subtropical area (e.g., McGillicuddy and Robinson, 1997).

We should note that we may not have observed exactly the same water mass on each cruise, even though they have the same T-S properties, as the residence time of a water mass in the K/O Zone is only several months or more shorter. Nevertheless, we should regard these water masses as a series of water masses which experienced similar processes in their formation and/or transport. The change in concentration of substances listed in Table 1 is thus thought to virtually represent the temporal sequence of a single water mass which pass through the Oyashio side of the K/O Zone. From January to May, the ratio of N depression to that of C (Table 1) was somewhat lower than the usual biological stoichiometry such as analyzed by Redfield et al. (1963) or Anderson and Sarmiento (1994). This may indicate that the values listed in this table show the in-situ concentration changes in a water mass only semi-quantitatively, although the high C/N ratio in the concentration change from May to August was also observed in the wider subarctic oceans (Sambrotto et al., 1993). In contrast, the C/N ratio in the concentration change from January to August was similar to that of usual open ocean values at about 6.6 (Redfield et al., 1963).

The depression ratio of Si to N also showed somewhat high value during the period from the January to the May (about 2.0, Table 1) compared to the world average value of around 1.0 (Brzezinski, 1985). Such apparently high Si:N ratio can be explained, however, if we assume high Si consumption by the NH₄-oriented regenerated production within the late-spring Oyashio area as suggested in Saito et al. (1998b). Although the results of Table 1 is only semi-quantitative, the observed Si depression prior to the N depression (Figs. 11 and 12) cannot be explained without the high Si
consumption relative to N. Our result thus confirms the Saito et al. (1998a)'s former model calculation.

**Seasonal change in the distribution of chemical properties along isopycnal surfaces** To investigate further the seasonal variation of chemical properties in waters below the seasonal ML, distributions of pressure, N, Si, TA, and TC were plotted against salinity on the four density surfaces with densities from $\sigma_s = 26.4$ to $\sigma_s = 26.8$ and are shown in Figs. 15a - 15d, 16a - 16d, 17a - 17d, 18a - 18d, and 19a - 19d, respectively.

On each surface with a density less than $\sigma_s = 26.6$, a significant depression of N, Si and TC was observed during January and May in waters where salinity was less than 34.0 psu (Figs. 16a, 16b, 17a, 17b, 19a and 19b). In the $\sigma_s = 26.6$ density surface, the extent of depression was greatest in waters where salinity was less than 33.6 psu, N had decreased by 5-6 $\mu$mol/kg, Si had decreased by 10 - 12 $\mu$mol/kg, and TC had decreased by 40 $\mu$mol/kg. Such seasonal depression was also observed in the $\sigma_s = 26.7$ density surface (Figs. 16c, 17c, and 19c), although the extent of depression for each substance was not so significant as that of $\sigma_s = 26.6$ density surface. The process of cross-gyre transport of fresh water and/or chemical properties across the K/O Zone has been investigated by several studies, but all were based on the data mainly collected in spring and/or summer (e.g., Talley, 1993; Talley et al., 1995; Rogachev et al., 1996; Yasuda et al., 1996; Maksimenko et al., 1997; Yasuda, 1997; Ono et al., 1998b; and Yoshinari and Yasuda, 1998). In these studies the transport of each property was estimated by assuming that 1) the volume transport of water is constant for each season, and that 2) the salinity and/or the concentrations of chemical substances in the Kuroshio/Oyashio end members are constant for each season. Our results shows, however, clearly that the assumption 2) is not true on the density layers of $\sigma_s \leq 26.7$. This study thus provides some constraints to the future estimations of cross-gyre chemical transport.

It should be noted that the density surface of $\sigma_s = 26.6$ did not outcrop in the ML, even in winter, in the 144°E section (Fig. 4a, see also the previous discussion), although Talley (1991) suggested that the density surface of $\sigma_s = 26.7$ may outcrop in the K/O Zone in winter. The cause of observed seasonal variation in this density surface is thus not explained by the ML processes in the K/O Zone along the 144°E section. Talley (1991) also suggested that the $\sigma_s = 26.6/26.7$ density surface outcrops in the Oyashio region upstream of K/O Zone, for example in the neighborhood of the Kuril islands, in winter. If these density surfaces in the upstream area are shallow even in spring, then the chemical properties of these waters may be changed by the effect of ML processes.

The slight decrease of pressure on the $\sigma_s = 26.6$ density surface pressure in the
Fig. 15. Distribution of pressure (db) against salinity at the density surface of a) \( \sigma = 26.4 \), b) \( \sigma = 26.6 \), c) \( \sigma = 26.7 \), and d) \( \sigma = 26.8 \), along the 144°E section. Open circles represent the data of January, x the May, and dots the August, respectively.

Fig. 16. Same as Fig. 15 but for N (\( \mu \text{mol/kg} \)).
Fig. 17. Same as Fig. 15 but for Si (μmol/kg).

Fig. 18. Same as Fig. 15 but for TA (μmol/kg).
Fig. 19. Same as Fig. 15 but for TC (μmol/kg).

Fig. 20. Typical vertical distribution of N in the Oyashio area, observed at 40°N, 144°E during January (open circles) and May (x).

summer K/O Zone (Fig. 15b) may cause change of the water properties in the density layer and may also cause chemical seasonal variation. However, the typical vertical profiles of N in the Oyashio area (Fig. 20) suggests that such a slight rise of the density surface by tens of meters is not insufficient to explain the observed concentration change in the density surface. Thus the changes in the density layers is not considered as the principal cause of seasonal variation of chemical properties. In the potential density and salinity sections along 144°E, these density layers were characterized by the intrusion of a WCR during winter and spring (Figs.
4a - 4c and 5a - 5c). However this also seemed not to have major contribution to the observed seasonal variation, because seasonal change of the chemical properties was even smaller around the core salinity values of the WCR, 34.0 psu at the $\sigma_s = 26.6$ density surface.

Unlike the other properties, the distribution of TA against salinity did not show significant seasonal variation in each density surface (Fig. 18a - 18d). This result suggests that the depression of TA observed in the seasonal ML from winter to summer (Fig. 13a - 13c) did not affect waters below the seasonal thermocline. This also indicates that process of biological carbonate formation may have not been significant in the area where seasonal depression of N, Si and TC occurred in the $\sigma_s = 26.6$ density surface.

Conclusion

Throughout this work, remarkable seasonal variation in the chemical properties are observed particularly in the ML of the Oyashio-side of the K/O Zone. Two successive processes are largely responsible for the observed seasonal variation; i.e., the Si-related biological processes largely decreased N and Si in the ML from January to May, then carbonate-related biological processes significantly decreased TA and completely consumed N in the ML on the Oyashio-side of the K/O Zone. The transport production by these processes is estimated to be the same as that observed previously by Sasaki and Matsukawa (1991).

A significant seasonal variation of the chemical properties is observed in the $\sigma_s = 26.60$ density surface on the Oyashio-side of the K/O Zone and also in the $\sigma_s = 26.70$ density surface to some extent. Although the cause of such variation is somewhat unclear and is not due to the ML processes within the observation area, the results forced us to re-consider former estimates of cross-gyre transport of salinity and/or chemical properties through the K/O Zone which were based on spring and summer data only.

Our study continued to include the later half of 1997, and results for the whole observation will be reported elsewhere. However, our data are limited to a single section along 144°E. Information about spatial differences in the seasonal variation pattern of the chemical field in the K/O zone therefore remains unknown. Our data should also be analyzed in conjunction with other datasets observed in other area within and/or around the K/O Zone, such as the repeated observation along the A-line off Hokkaido (e.g., Saito et al., 1998b) and the time-series observations at Station KNOT (e.g., Nojiri, 1998).
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References


DOE, 1994: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; ver. 2. Edited by A. G. Dickson and C. Goyet. ORNL/CDIAC-74.


Seasonal transition of carbonate/nutrients in Kuroshio/Oyasio

103, 30873-30883.


Tsunogai, S., T. Ono and S. Watanabe, 1993: Increase in total carbonate in the western North Pacific water and a hypothesis on the missing sink of anthropogenic carbon. J. Oceanogr., 49, 305-315.


1997年の黒潮・親潮混合領域における栄養塩・炭酸系諸量の分布の季節変動

小笠原夫・佐々木克之

1997年の1月～8月にかけて、黒潮・親潮混合領域の144° Eに沿った栄養塩・炭酸系諸量の分布を反復観測し、その季節変動を調べた。親潮域の混合層では1月から5月にかけてケイ素の枯渇と窒素の減少、続いて5月～8月間ではアルカリ度の減少と窒素の枯渇が観測された。このような季節変化は亜表層のσθ = 26.6 密度面付近でも観測されるため、春・夏期の観測値のみを基に見積もられた親潮・黒潮間の物質輸送の見積もり値を再考する必要性が示唆される。