



## Distributions, speciation and stable isotope composition of organic matter in the southeastern Bering Sea

Laodong Guo<sup>a,\*</sup>, Tomoyuki Tanaka<sup>a</sup>, Deli Wang<sup>a</sup>, Noriyuki Tanaka<sup>a</sup>, Akihiko Murata<sup>b</sup>

<sup>a</sup>International Arctic Research Center, University of Alaska Fairbanks, Fairbanks, AK 99775, United States

<sup>b</sup>Japan Marine Science and Technology Center, Yokosuka, Kanagawa 237-0061, Japan

Received 30 November 2003; received in revised form 6 July 2004; accepted 7 July 2004

Available online 11 September 2004

### Abstract

Seawater samples were collected from the southeastern Bering Sea for determinations of dissolved (DOC, <0.7  $\mu\text{m}$ ), colloidal (COC, 1 kDa–0.7  $\mu\text{m}$ ) and particulate organic carbon (POC, >0.7  $\mu\text{m}$ ), dissolved organic nitrogen (DON), particulate nitrogen (PN), and dissolved carbohydrate (DCHO) species, as well as stable isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of suspended particulate organic matter (POM). DOC concentrations ranged from 61 to 92  $\mu\text{M}$  (average  $76 \pm 9 \mu\text{M}$ ) with increasing concentrations from outer shelf to inner shelf along  $166^\circ\text{W}$ . DOC concentrations were significantly inversely correlated with salinity, indicating that the DOC distribution was predominantly controlled by water mixing although primary production is the ultimate source of organic matter. DON concentrations averaged  $6.4 \pm 0.9 \mu\text{M}$ , ranging from 4.3 to 8.4  $\mu\text{M}$ , resulting in an average DOC/DON ratio of  $12 \pm 2$  (ranging from 8 to 15). Total dissolved carbohydrates (TDCHO) comprised  $13 \pm 3\%$  of bulk DOC, with  $35 \pm 15\%$  of TDCHO in the polysaccharide and  $65 \pm 15\%$  in the monosaccharide fractions. Suspended POM had an average C/N ratio of  $7.4 \pm 1.1$ , significantly lower than the average DOC/DON ratio ( $12 \pm 2$ ). There was a significant correlation between chlorophyll-*a* and POC concentrations. However, Chl-*a* concentration was not closely coupled to DOC abundance. On average, POC comprised  $14 \pm 5\%$  of the total organic carbon (TOC) pool in the water column, and COC comprised  $34 \pm 8\%$  of the TOC, leaving  $52 \pm 5\%$  of the TOC in the <1 kDa low-molecular-weight dissolved phase. Values of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in the suspended POM ranged from  $-27.1\text{‰}$  to  $-23.4\text{‰}$  (average  $-24.5 \pm 0.9\text{‰}$ ) and from  $2.8\text{‰}$  to  $9.9\text{‰}$  (average  $6.0 \pm 1.9\text{‰}$ ), respectively. Interestingly, particulate  $\delta^{15}\text{N}$  values were negatively correlated with nitrate ( $\text{NO}_3$ ) concentrations at low  $\text{NO}_3$  concentrations ( $\leq 5 \mu\text{M}$ ) but positively correlated with  $\text{NO}_3$  concentrations when  $\text{NO}_3$  concentrations were  $>5 \mu\text{M}$ , indicating the effects of nutrient drawdown in surface waters and diagenesis below the euphotic zone on the isotope fractionation. POM containing lighter C and N isotopes appeared to be decomposed preferentially during their transport from upper water column to bottom sediments.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Dissolved organic carbon; Colloidal organic carbon; Dissolved organic nitrogen; POC; Stable isotopes; Carbohydrates; Bering Sea; Continental shelf

\* Corresponding author. Tel.: +1 907 474 2794; fax: +1 907 474 2679.

E-mail address: [guol@iarc.uaf.edu](mailto:guol@iarc.uaf.edu) (L. Guo).

## 1. Introduction

Dissolved organic carbon (DOC) is a key component in the marine carbon budget and global carbon cycle and plays an important role in the biogeochemical cycles of many bioactive elements and contaminants in marine environments (Siegenthaler and Sarmiento, 1993; Hansell and Carlson, 2002 and references therein). However, DOC in the ocean continues to be the least understood reduced carbon pool on Earth (Hedges, 2002). The interplay between organic matter speciation, composition and reactivity in seawater is still largely unknown. Quantifying DOC inventories, composition, reactivity and interactions with other organic carbon species, as well as responses of various carbon species to environmental change, is essential for understanding organic carbon cycling in the ocean (e.g., Wheeler et al., 1997; Bauer et al., 2002; Vlahos et al., 2002; Dittmar and Kattner, 2003). Over the past years, the biogeochemical cycling of organic carbon in the Arctic has received increasing attention (e.g., Wheeler et al., 1997; Opsahl and Amon, 1999; Skoog et al., 2001; Amon, 2003). Despite their importance, the biogeochemical cycles of dissolved and particulate organic matter in the Bering Sea have received surprisingly little attention, although a vast amount of work has been published in the areas of fisheries, water chemistry and physics (e.g., National Research Council, 1996; Loughlin and Ohtani, 1999 and references therein; Takahashi et al., 2000).

The Bering Sea ecosystems provide one of the world's most abundant biological resources, contributing over half of the United States' fishery production (Springer et al., 1996 and references therein). Being heavily influenced by Pacific waters and seasonally by sea ice, the Bering Sea is the gateway for seawater exchange between the Pacific and the Arctic Ocean. It has been suggested that the polar region and the northern ecosystems are sensitive to global climate and environmental change (e.g., Manabe and Stouffer, 1994). Such changes may have profound impacts on the flux and biogeochemical cycling of carbon and other bioactive elements in the arctic region (Amon, 2003; Dittmar and Kattner, 2003). Indeed, recent studies have shown that there has recently been a shift in plankton species and community structures in the

Bering Sea, likely related to ongoing climate and environmental change in the region (Napp and Hunt, 2001). Changes in the plankton community dynamics may have altered organic carbon cycling pathways in the Bering Sea, but the biogeochemical consequence of environmental change is largely unknown. It is thus important to establish a baseline data set for trend analyses and for better understanding of marine carbon cycling and environmental change.

Naidu et al. (1993) reported stable organic carbon isotope composition of sediments from the north Bering Sea. Cooper et al. (1997) used nutrient and stable oxygen isotopic composition to examine the water exchange between Bering and Chukchi Seas waters. Recently, Smith et al. (2002) reported the stable C and N isotope composition of sinking particles from time series samples collected over the southeastern Bering Sea Shelf. Their results showed a strong spatial and temporal variability in stable-isotope composition of sinking particles, indicating a dynamic cycling of organic matter in the Bering Sea. However, reports on measurements of DOC and particulate organic carbon (POC) are still very scarce, especially in the eastern Bering Sea. To our knowledge, the only report on DOC distributions is by Agatova et al. (1999) for the Western Bering Sea. The lack of sampling and determinations of organic carbon species exposes a critical gap in our understanding of carbon dynamics, and the ecosystem as a whole, in the southeastern Bering Sea.

This study aimed to investigate the cross-shelf variability in the concentration, distribution, phase partitioning, and stable-isotope composition of organic matter in the southeastern Bering Sea. Samples were collected during August/September 2001 on board the *R/V Mirai* along a transect at 166°W. In order to better understand the dynamics of carbon and nitrogen on the Bering Sea Shelf, determinations were carried out of concentrations of DOC, colloidal organic carbon (COC), POC, dissolved organic nitrogen (DON), particulate nitrogen (PN), and dissolved carbohydrate species, including monosaccharides (MCHO) and polysaccharides (PCHO), as well as stable isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of suspended particulate organic matter (POM).

## 2. Materials and methods

### 2.1. Study area and sampling

The Bering Sea is a semi-enclosed, high-latitude sea with seasonal ice coverage. It has been shown to be sensitive to climate and environmental change (Napp and Hunt, 2001). Major rivers entering the Bering Sea include the Yukon River and the Kuskokwim River in the United States and the Anadyr River in Russia. Water masses on the Bering Sea Shelf can be divided into outer, middle and inner shelf waters (Stabeno et al., 2002). A growing body of literature describes work carried out in the southeastern Bering Sea region with either along- or cross-shelf sampling (e.g., Murata and Takizawa,

2002; Smith et al., 2002; Stabeno et al., 2002; Tanaka et al., 2004).

Seawater samples were collected using a CTD/Rosette system onboard the *R/V Mirai* during August/September 2001. Stations were occupied along a transect at  $\sim 166^\circ\text{W}$  (Table 1). Notice that station AV-01 is the most outer shelf station while station AV-09 is the most inner shelf station.

### 2.2. Sample filtration and organic matter size fractionation

Total organic carbon (TOC) in seawater includes dissolved, colloidal and particulate organic carbon (i.e.,  $\text{TOC}=\text{DOC}+\text{POC}$ ). The traditionally defined DOC contains both COC and low-molecular-weight

Table 1

Concentrations of dissolved (DOC), colloidal (COC) and particulate organic carbon (POC), particulate nitrogen (PN), dissolved monosaccharides (MCHO) and total dissolved carbohydrates (TDCHO) along with stable isotopic composition of suspended particulate organic matter

Station	Lat ( $^\circ\text{N}$ )*	Depth (m)	DIC ( $\mu\text{M}$ )	DOC ( $\mu\text{M}$ )	DON ( $\mu\text{M}$ )	COC ( $\mu\text{M}$ )	MCHO ( $\mu\text{M C}$ )	TDCHO ( $\mu\text{M C}$ )	POC ( $\mu\text{M}$ )	PN ( $\mu\text{M}$ )	$\delta^{13}\text{C}$ ( $\text{‰}$ )	$\delta^{15}\text{N}$ ( $\text{‰}$ )
AV-01	55.003	0	1989	83	5.5	30	5.9	8.4	24	4.0	-25.27	4.83
		5	1992	72	6.4	–	7.9	10.7	16	2.9	-24.13	4.56
		10	1998	69	6.0	–	7.5	10.1	12	2.2	-24.05	3.60
		30	2045	65	5.4	–	4.5	7.9	4.0	0.46	-24.93	4.64
		50	2114	61	4.3	–	5.3	6.9	3.1	0.40	-24.61	7.19
		100	2185	65	5.5	–	1.7	5.8	5.1	0.64	-23.92	8.58
		131	2190	66	5.4	–	4.6	8.7	6.5	0.81	-24.25	7.61
AV-03	55.999	5	1971	72	6.9	32	5.1	10.3	13	2.2	-23.53	4.64
		10	1965	79	7.4	–	3.6	7.5	12	2.1	-24.06	4.86
		30	2030	68	6.6	–	4.2	5.9	5.0	0.66	-25.09	2.95
		50	2070	68	6.0	–	3.4	5.0	3.6	0.44	-24.60	2.86
		100	2158	64	5.5	–	4.3	9.2	5.3	0.59	-24.13	5.58
		106	2156	72	6.3	36	5.8	7.3	5.2	0.55	-23.41	5.16
AV-05	56.998	5	1950	83	7.5	38	12.1	13.8	10	1.6	-25.60	6.15
		10	1949	82	7.4	–	7.8	15.8	11	1.5	-25.99	5.38
		30	2091	69	8.4	–	7.4	7.9	5.3	0.67	-25.77	4.98
		50	2092	71	8.3	–	3.9	5.5	7.8	0.96	-25.88	5.49
		65	2091	74	7.7	33	5.2	8.9	8.9	1.0	-27.17	5.23
		106	2156	72	6.3	36	5.8	7.3	5.2	0.55	-23.41	5.16
AV-07	57.998	5	1962	88	5.8	32	6.3	10.7	15	1.9	-24.25	7.28
		10	1984	90	6.7	–	7.4	11.6	16	1.8	-24.30	5.83
		30	2049	81	6.9	–	6.7	7.8	7.8	0.99	-23.55	6.04
		51	2048	77	6.5	31	8.3	11.1	7.4	0.91	-24.50	5.71
		106	2156	72	6.3	36	5.8	7.3	5.2	0.55	-23.41	5.16
AV-09	58.999	5	1988	84	5.5	26	8.3	13.7	17	2.7	-24.08	8.62
		10	1986	87	6.2	–	5.6	13.9	18	2.9	-23.97	9.03
		20	1989	85	5.6	–	9.6	12.6	20	3.3	-23.85	9.98
		25	1988	92	5.9	27	9.0	11.9	19	3.0	-23.88	9.35
		106	2156	72	6.3	36	5.8	7.3	5.2	0.55	-23.41	5.16

\* Long ( $^\circ\text{E}$ ) is the same for all stations at  $194.00^\circ\text{E}$ . Station AV-01 is the most outer shelf station while station AV-09 is the most inner shelf station.

“–” means not determined.

(LMW) DOC. Therefore,  $\text{TOC} = \text{LMW DOC} + \text{COC} + \text{POC}$ . According to the filters used, POC was defined here as the organic carbon fraction  $>0.7 \mu\text{m}$  and bulk DOC as the  $<0.7 \mu\text{m}$  fraction. COC was operationally defined as the fraction between 1 kDa and  $0.7 \mu\text{m}$ , while the LMW DOC was the  $<1 \text{ kDa}$  fraction.

Both filtration and ultrafiltration were used to collect particulate, colloidal, and dissolved organic matter samples. In short, seawater ( $\sim 6\text{--}12 \text{ l}$ ) was filtered through pre-combusted glass fiber filters (GF/F, Whatman) with a pore size of  $0.7 \mu\text{m}$  to separate POC from DOC. Filter samples were frozen for determination of POC and total particulate nitrogen (PN) concentrations. Aliquots of filtrate were then collected for determination of DOC and DON concentrations.

For surface and bottom-water samples, aliquots of seawater filtered through GF/F filters were ultrafiltered to size fractionate the bulk DOC into COC and the  $<1 \text{ kDa}$  LMW DOC fractions. The ultrafiltration system was equipped with a Millipore ultrafiltration cartridge (Amicon, S1Y1) with a molecular weight cutoff of 1 kDa and other Teflon-wares, including tubing, fittings, and a 2-l Teflon jar. Before ultrafiltration, the cartridge was conditioned with  $\sim 1 \text{ l}$  of filtered seawater. A similar concentration factor (8–10) was used for ultrafiltration. After ultrafiltration, aliquots of both retentate and ultrafiltrate were sampled for a DOC mass balance (Guo et al., 1995; Guo and Santschi, 1996). Cartridge-cleaning and calibration procedures are described in Guo et al. (2000).

### 2.3. Measurements of nutrients, DOC, DON, and dissolved carbohydrate concentrations

Nutrients, including nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), ammonium ( $\text{NH}_4^+$ ), phosphate ( $\text{PO}_4^{3-}$ ), dissolved silicate ( $\text{Si(OH)}_4$ ), were measured on board with an auto-analyzer (TRACSS-800) using standard methods of Grasshoff et al. (1983) with some modifications. Dissolved oxygen (DO) was determined by the Winkler method. Dissolved inorganic carbon (DIC) concentrations were measured by methods described in Murata and Takizawa (2002).

Concentrations of DOC and COC were determined by the high temperature combustion method with a Shimadzu TOC-V analyzer, using procedures described in Guo et al. (1995). Immediately after

sample collection, all DOC samples, including GF/F filtrates, 1 kDa ultrafiltrates, and 1 kDa retentate, were acidified with concentrated HCl to bring the pH down to  $\leq 2$  (about 2 drops for 20 ml of seawater in a pre-combusted glass ampoule). Acidified DOC samples were kept in a refrigerator ( $2\text{--}4 \text{ }^\circ\text{C}$ ) until analysis. Total DOC blank, including water blank and instrument blank, was on the order of  $2\text{--}6 \mu\text{M}$ . Water blank was evaluated using a TC blank check program in our Shimadzu TOC analyzer. This water blank, not the total blank, was subtracted accordingly (Guo et al., 1995). Guaranteed reagent grade potassium biphthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ , Kanto Chemical) was used as a TOC standard. Analytical precision, in terms of coefficient of variation, was within 1–4% depending on samples' DOC concentrations.

Samples for DON analysis were filtered through a  $0.7\text{-}\mu\text{m}$ -pore-size GF/F glass fiber filter using a glass syringe equipped with a stainless steel filter holder. Total dissolved N was measured by a TNM-1 total-nitrogen unit interfaced with a Shimadzu TOC analyzer. Potassium nitrate (Wako) was used as a standard. Dissolved inorganic N (DIN, including nitrate, nitrite and ammonia) was then subtracted from total dissolved N to calculate the DON concentration. Precision expressed as coefficient of variation for DON concentrations after error propagation was in the range of 4–8% depending on samples.

Dissolved carbohydrate species were determined on a spectrophotometer using a modified colorimetric method (Hung et al., 2003a). Concentrations of MCHO were determined after oxidizing free reduced sugars with the 2,4,6-tripyridyl-s-triazine (TPTZ), while total dissolved carbohydrate (TDCHO) concentrations were determined after hydrolysis of 4 ml of filtered seawater with HCl at  $150 \text{ }^\circ\text{C}$ . The concentration of PCHO was then calculated from the difference between TDCHO and MCHO concentrations (in  $\mu\text{M C}$ ). The reagent blank in Milli-Q water was subtracted before calculating the final concentration of the MCHO. The variation coefficient was  $<5\%$  (Hung et al., 2003a).

### 2.4. Determinations of POC, PN, and stable isotope composition

Concentrations and stable isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of POC and PN were determined

on an elemental analyzer interfaced with an isotopic ratio mass spectrometer (Guo et al., 2003). Filter samples were acid fumed (HCl) before the analysis of POC and PN. Stable carbon and nitrogen isotope ratios were calculated in terms of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ,  $(R_{\text{sample}}/R_{\text{standard}}-1)\times 1000$ , where  $R$  is the ratio of  $^{13}\text{C}/^{12}\text{C}$ , or  $^{15}\text{N}/^{14}\text{N}$ , in suspended POM samples or standard (PDB for carbon and atmospheric  $\text{N}_2$  for nitrogen). Peptone was used as a standard material for both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  (with 44.3% of C and 15.8% of N;  $\delta^{13}\text{C}=-15.8\text{‰}$  and  $\delta^{15}\text{N}=7.0\text{‰}$ ). The precision and accuracy of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analyses were 0.1‰ and 0.2‰, respectively, as determined by replicate analyses of standards and samples.

### 3. Results and discussion

#### 3.1. Characteristics of hydrographic parameters

Hydrographic parameters determined in the water column over the southeastern Bering Sea Shelf included water temperature, salinity, nutrients (N, P and Si), and dissolved oxygen. Salinity showed a general decrease from the outer shelf (station AV01) to the inner shelf (station AV09) and an increase from surface to bottom waters (Fig. 1). Temperature, on the other hand, showed an increase from outer to inner shelf stations with a cold water mass located in the middle shelf region, likely isolated from the previous winter's cold water (Tanaka et al., 2004). A  $T$ - $S$  (temperature-salinity) diagram plotted for all stations along the transect revealed a dynamic mixing regime with different water masses at different stations showing a clear transition from outer shelf to inner shelf, and from surface waters to bottom waters (Fig. 1).

Concentrations of nutrients ( $\text{NO}_3$ ,  $\text{PO}_4$ , Si) also showed a general increase from the inner to the outer shelf stations and from surface to bottom waters (Fig. 1). There was a significant correlation between salinity and nutrients ( $p<0.001$  and  $R^2=0.68$ , 0.70 and 0.58 for  $\text{NO}_3$ ,  $\text{PO}_4$  and Si, respectively), and freshwaters from pristine Alaska rivers contained low nutrient concentrations (e.g., Guo et al., 2004a). Thus, nutrient sources to the shelf region appeared to be mostly from outer shelf bottom waters. The lowest nutrient ( $\text{NO}_3$ ,  $\text{PO}_4$ , Si) concentration was

found in surface waters at middle shelf stations, coinciding with the existence of a cold water mass and low N/P ratios in this area. The overall low inorganic N/P ratio suggested an N-limited ecosystem in the southeastern Bering Sea. Bottom waters at the middle shelf stations had elevated  $\text{NH}_4$  concentrations compared with the outer shelf station (Fig. 1). Dissolved oxygen concentrations consistently decreased with increasing water depth and from inner to outer shelf bottom waters.

#### 3.2. Concentrations of DOC, DON, POC, PN and carbohydrate species

DOC concentrations in the water column varied from 61  $\mu\text{M}$  at the outer shelf station (AV-01) to 92  $\mu\text{M}$  at the inner shelf station (AV-09), with an average of  $75\pm 9$   $\mu\text{M}$  (Table 1; Fig. 2). These DOC concentrations were considerably lower than those reported previously for the western Bering Sea and Anadyr Gulf (Agatova et al., 1999), but agreed well with those measured for other continental shelf waters (e.g., Guo et al., 1994, 1995; Hopkinson et al., 1997; Vlahos et al., 2002; Hung et al. 2003b). Higher DOC concentrations reported previously for the western Bering Sea could be due to either high DOC inputs from Russian Rivers or possible sample contamination problems. However, there are very limited DOC data available for further comparison in the Bering Sea.

DON concentrations ranged from 4.3 to 8.4  $\mu\text{M}$ , with an average of  $6.4\pm 0.9$   $\mu\text{M}$ . Using these DOC and DON concentrations, a molar DOM C/N ratio can be calculated. Calculated C/N ratios are in the range of 8–15, with an average of  $12\pm 2$ . These C/N ratios are higher than the Redfield ratio, but similar to C/N ratios observed for other coastal waters (e.g., Hopkinson et al., 1997; Hung et al., 2003b), and slightly lower than C/N ratios reported for open ocean environments (e.g., Loh and Bauer, 2000; Hansell and Carlson, 2001; Church et al., 2002).

POC concentrations varied from 3 to 25  $\mu\text{M}$  with an average concentration of  $11\pm 6$   $\mu\text{M}$ , while PN concentrations varied from 0.4 to 4.0  $\mu\text{M}$  with an average of  $1.6\pm 1.1$   $\mu\text{M}$ . The resulting particulate C/N ratio ranges from 5.6 to 9.4 with an average of  $7.4\pm 1.1$ . These particulate C/N ratios are close to the Redfield ratio and significantly lower than the DOM

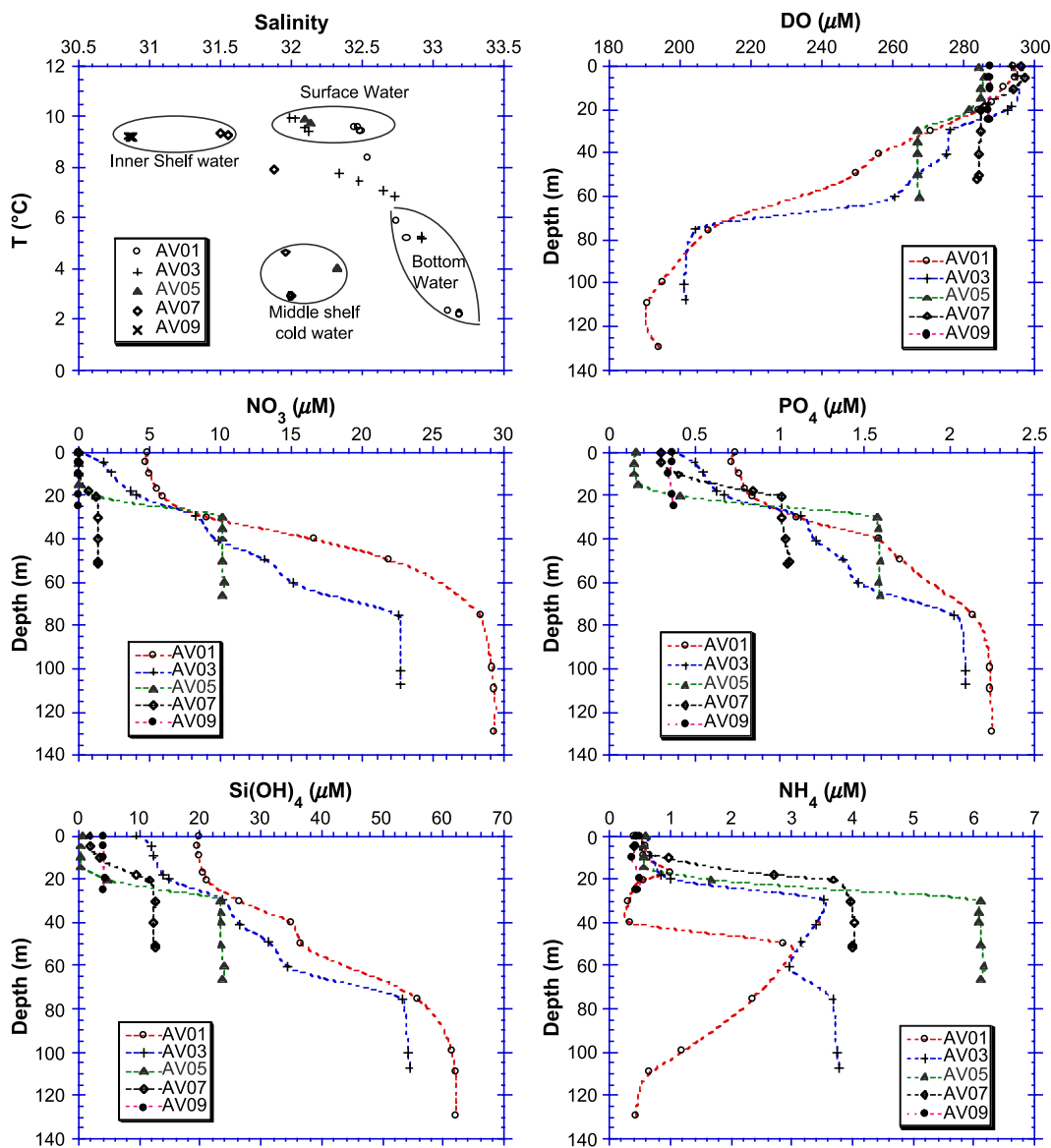


Fig. 1. A  $T$ - $S$  diagram, distributions of nutrients ( $\text{NO}_3$ ,  $\text{PO}_4$ ,  $\text{Si(OH)}_4$ ,  $\text{NH}_4$ ), and dissolved oxygen (DO) in the water column over the southeastern Bering Sea Shelf (during August/September, 2001 onboard the R/V Mirai).

$C/N$  ratios ( $12 \pm 2$ ) in the same water samples.  $C/N$  ratios could be a useful indicator of diagenetic status of marine organic matter (Guo and Santschi, 1997; Hedges et al., 2002). Many recent studies have reported  $\text{DOC}/\text{DON}$  ratios considerably higher than the Redfield ratio (e.g., Church et al., 2002), while  $C/N$  ratios in both POM and marine plankton have been reported to remain close to the Redfield ratio

(e.g., Kortzinger et al., 2001; Hedges et al., 2002; Hung et al., 2003b). It is known that N-containing organic compounds can be preferentially decomposed. Thus, water column DOC, with a higher  $C/N$  ratio, could be largely derived from water column POM, with a lower  $C/N$  ratio. If DOM and POM are derived from the same sources, a higher  $\text{DOC}/\text{DON}$  ratio compared to the  $\text{POC}/\text{PN}$  ratio indicates a more

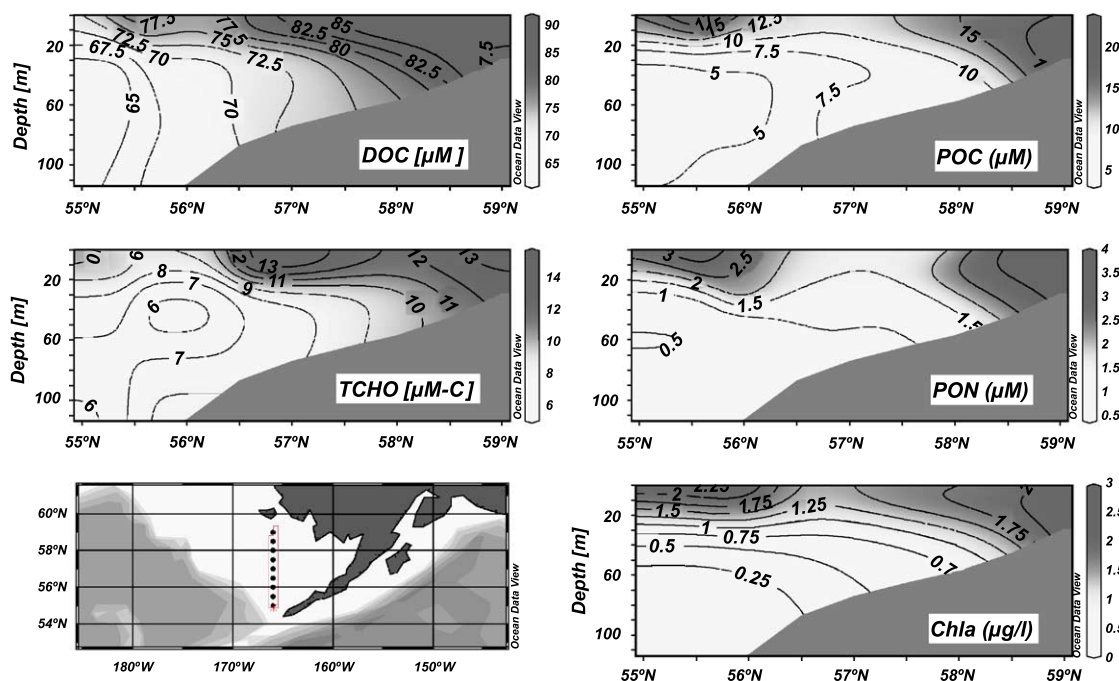


Fig. 2. Section profiles of dissolved organic carbon (DOC), particulate organic carbon (POC), particulate nitrogen (PN) concentrations (in  $\mu\text{M}$ ), and total dissolved carbohydrate (TCHO, in  $\mu\text{M C}$ ) and chlorophyll-*a* (Chl-*a*, in  $\mu\text{g/l}$ ) concentrations along  $166^\circ\text{W}$  in the water column over the southeastern Bering Sea Shelf.

recycled or diagenetically altered DOM pool. This conclusion is consistent with other observations in marine environments based on degradation rates, radiocarbon concentrations, and C/N ratios (e.g., Amon and Benner, 1996; Guo et al., 1996; Guo and Santschi, 1997).

The average concentration of TDCHO was  $9.6 \pm 2.9 \mu\text{M C}$ , ranging from 5 to  $16 \mu\text{M C}$  in the water column (Table 1). MCHO concentrations varied from 1.7 to  $12 \mu\text{M C}$ , with an average of  $6.2 \pm 2.3 \mu\text{M C}$ . PCHO concentrations were lower than those of MCHO, and ranged from 0.6 to  $8.3 \mu\text{M C}$ , with an average of  $3.4 \pm 1.9 \mu\text{M C}$ . Concentrations of TDCHO in the Bering Sea were similar to those reported previously for other marine environments (Bhosle et al., 1998; Hung et al., 2003a), but somewhat lower than those measured for coastal and bay waters (Burney and Sieburth, 1977; Borsheim et al., 1999). For example, Bhosle et al. (1998) reported a TDCHO concentration of  $7\text{--}13 \mu\text{M C}$  in the Arabian Sea and Hung et al. (2003a) reported concentrations of TDCHO ranging from 4 to 22

$\mu\text{M C}$  in the Gulf of Mexico. The results from these studies are close to the results from our measurements on the Bering Sea Shelf. Others reported a mean TDCHO concentration of  $12\text{--}33 \mu\text{M C}$  from Trondheimsfjord (ranging from 12 to  $74 \mu\text{M C}$ , Borsheim et al., 1999) and  $15\text{--}67 \mu\text{M C}$  from Narragansett Bay (Burney and Sieburth, 1977). Higher TDCHO concentrations in bay waters could be an effect of higher DOC concentrations, since the ratios of TDCHO to DOC were similar between different marine environments. Sources of carbohydrates in seawater are largely from marine organisms (Myklestad, 1974; Passow, 2002) and the difference in the concentrations of TDCHO between study areas could result from the difference in primary productivity and microbial and planktonic species (Hung et al., 2003a; Santschi et al., 2003). Indeed, our data also showed a significant correlation between TDCHO and chlorophyll-*a* (Chl-*a*) concentrations ( $R=0.58$ ,  $p<0.002$ ). More measurements are needed to better understand sources of carbohydrates and their role in organic carbon cycling.

### 3.3. Distributions of organic carbon species

The distributions of DOC, POC, PN, TDCHO and Chl-*a* concentrations in the water column at stations along 166°W are shown in Fig. 2. In general, concentrations of both DOC and TDCHO increased from outer shelf to inner shelf and decreased from surface water to bottom waters (Fig. 2). These distribution patterns were broadly similar to accompanying hydrographic parameters. Indeed, concentration of DOC was significantly correlated to salinity ( $R^2=0.68$ ,  $p<0.001$ , Fig. 3). This suggested that water mixing was important in controlling the overall distribution of DOC in the water column, even though biological production and microbial degradation are also important processes in controlling DOC distribution on shorter time scales. Our results are consistent with observations for other coastal marine environments, where a significant relationship between DOC concentration and salinity was observed (e.g., Guo et al., 1995; Pettine et al., 1999; Ogawa et al., 2003).

In southeastern Bering Sea Shelf waters, TDCHO concentrations were usually higher in surface waters than in deep waters (Fig. 2), which has also been observed for oceanic environments (Pakulski and Benner, 1994). TDCHO concentrations also increased from mid water column to bottom waters, except for the most shallow station, station AV-09 (Table 1). Similar to the DOC vertical distribution, the somewhat elevated TDCHO concentrations in bottom waters likely resulted from benthic DOM and POM decomposition in bottom waters. Unfortunately, we do not have quantitative fluxes from sediment to overlying waters.

Both POC and PN showed similar distribution patterns, with elevated concentrations in the upper water column of both outer and inner shelf regions and lower concentrations in the middle shelf area (Fig. 2). Chl-*a* concentrations had a similar distribution pattern to those of POC and PN concentrations. As shown in Fig. 3, there was a significant correlation between POC and Chl-*a* concentrations ( $R^2=0.83$ ,  $p<0.001$ ). However, the correlation between DOC concentration and Chl-*a* was relatively weak ( $R^2=0.42$ ,  $p<0.05$ ) (figure not shown). The difference in correlation coefficients in the relationship between Chl-*a* and POC (or DOC) indicated that a higher Chl-*a* concentration or higher biomass could result in a higher POC concentration but not necessarily a higher DOC concentration in the

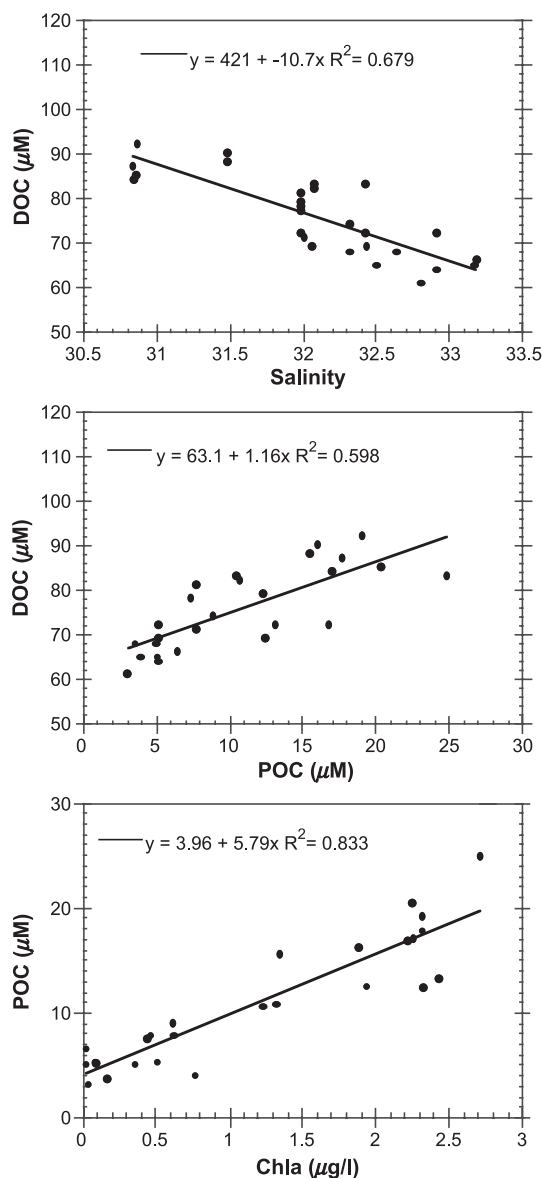


Fig. 3. Relationship between dissolved organic carbon (DOC), salinity, particulate organic carbon (POC), and chlorophyll-*a* (Chl-*a*) concentrations.

water column. This is somewhat surprising since DOC concentration was also broadly correlated to POC concentration (Fig. 3). Thus, microbial processes and grazing activity appeared to be more important than Chl-*a* concentration in controlling the water column DOC concentration (e.g., Strom et al., 1997; Wetz and Wheeler, 2003).

### 3.4. Phase partitioning of C, N and carbohydrate species

The partitioning of C and N between inorganic and organic and dissolved and particulate phases was examined by measuring different C and N species. Carbon species considered here included DIC, LMW DOC, COC, and POC. Similarly, total nitrogen (TN) in seawater contained DIN (including nitrate, nitrite and ammonia), DON and PN.

Concentrations of COC (1 kDa–0.7  $\mu\text{m}$ ) were measured in the surface and bottom waters at each station. They varied from 26 to 38  $\mu\text{M}$ , with an average of  $32 \pm 4$   $\mu\text{M}$ . There was no significant difference in COC concentrations between surface and bottom waters at these shelf stations. This was likely due to the shallow water column and the presence of a benthic nepheloid layer and thus elevated DOC concentrations in the bottom waters, especially at inner shelf stations (Table 1; Fig. 2).

Within the <0.7- $\mu\text{m}$  dissolved phase, COC comprised, on average,  $40 \pm 7\%$  of the DOC, leaving  $60 \pm 7\%$  of the DOC in the LMW phase (Fig. 4). The colloidal fractions in the Bering Sea Shelf waters were similar to those reported previously for other coastal marine environments (e.g., Guo et al., 1995; Pettine et al., 1999). Within the TOC pool, on average,  $14 \pm 5\%$  (ranging from 7% to 23%) of the TOC was POC (>0.7  $\mu\text{m}$ ),  $34 \pm 8\%$  (ranging from 24% to 46%) was COC (1 kDa–0.7  $\mu\text{m}$ ) and  $52 \pm 5\%$  of the TOC (ranging from 48% to 58%) was in the <1 kDa dissolved phase (Fig. 4).

TDCHO comprised  $13 \pm 3\%$  of bulk DOC in the study area, with a range of 7–19%. In general, the ratio of TDCHO to DOC was somewhat higher in surface water than in the bottom water column. Within the TDCHO pool,  $65 \pm 15\%$  was measured in the MCHO fraction, and  $35 \pm 15\%$  was in the PCHO fraction. A slightly higher PCHO fraction was also observed in bottom waters, likely resulting from sediment resuspension in the benthic nepheloid layer. Within the bulk DOC pool, MCHO comprised  $8.1 \pm 2.6\%$  of DOC and PCHO comprised  $4.4 \pm 2.4\%$  of DOC, leaving  $87 \pm 3\%$  of DOC in the non-carbohydrate fraction (Fig. 4).

Ratios of TDCHO/DOC observed in the Bering Sea are within the range reported for other marine environments (Pakulski and Benner, 1994; Pettine et

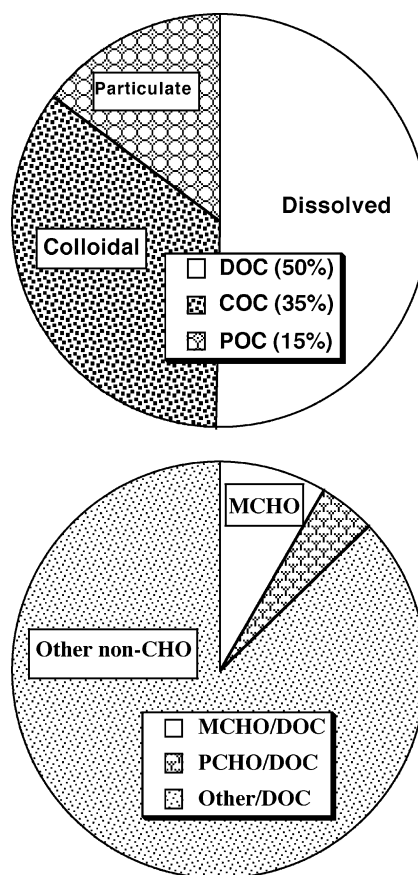


Fig. 4. Average partitioning of organic carbon between dissolved (<1 kDa), colloidal (1 kDa–0.7  $\mu\text{m}$ ), and particulate (>0.7  $\mu\text{m}$ ) phases, and the partitioning of monosaccharides (MCHO), polysaccharides (PCHO), and other non-carbohydrates (other non-CHO) in the bulk DOC pool.

al., 1999; Hung et al., 2003a). Many studies have also observed significant differences in the concentration of TDCHO and the ratio of TDCHO/DOC between seasons and between surface water and deep waters (Pakulski and Benner, 1994; Borsheim et al., 1999; Pettine et al., 1999; Hung et al., 2003a). For example, Hung et al. (2003a) observed a variable percentage in MCHO and PCHO fractions from nearshore to offshore stations. Pakulski and Benner (1994) found that the upper water column normally contained higher TDCHO concentrations and a higher ratio of TDCHO/DOC. In addition, they found that PCHO was a dominant form of carbohydrate in the upper water column whereas MCHO was the dominant form of carbohydrate in the bottom waters. In a different

study area, Bhosle et al (1998) observed predominately PCHO (average  $75 \pm 11\%$ ) in the TDCHO pool throughout the entire water column.

Carbohydrates are one of the major organic compound classes in oceanic DOC (Benner et al., 1992; Santschi et al., 1998). Most importantly, polysaccharides comprise a substantial fraction of the semi-labile DOC in seawater (Kirchman et al., 2001) and are an active component in marine organic carbon cycles. In Yukon river waters, Guéguen et al. (2004) found that the ratio of PCHO/TCHO in DOM pool decreased while the ratio of MCHO/TCHO increased from May to September. Accompanying this,  $^{14}\text{C}$  ages of DOM increased from May to September (Guo, 2004b). It is likely that fresher organic matter contains more polysaccharides while regenerated DOM contains more monosaccharides. The higher fractions of monosaccharides in the TDCHO pool measured for the southeastern Bering Sea during late summer/early autumn may point to a more recycled or refractory DOM pool, consistent with the higher C/N ratio observed for the DOM.

In seawater systems, DIC normally outweighs TOC (DOC+POC) (Table 1). Nitrogen, on the other hand, is more homogeneously partitioned between organic and inorganic phases. On average,  $42 \pm 30\%$  of the TN was present as DIN (including  $\text{NO}_3$ ,  $\text{NO}_2$  and  $\text{NH}_4$ ),  $45 \pm 21\%$  of the TN was present as DON and  $13 \pm 11\%$  of the TN was present as PN. While DIC remained the predominate C phase ( $96 \pm 1\%$  of the total C pool) throughout the entire water column,

TN demonstrated a more dynamic partitioning pattern between upper water column and bottom waters (Fig. 5). In the upper water column, on average,  $20 \pm 9\%$  of the TN was present as PN and  $58 \pm 14\%$  as DON, leaving  $22 \pm 19\%$  in the DIN pool. In bottom waters, only  $3 \pm 2\%$  of TN was present as PN, with  $28 \pm 13\%$  as DON and up to  $68 \pm 15\%$  as DIN. In other words, DON was the dominant N species in the upper water column while DIN was the dominant N species in lower water column (Fig. 5). This contrasting partitioning between C and N and between upper and lower water column indicated that transformation between N species was more intensive and hence N cycling in the water column was highly dynamic in the study area. Interestingly, while major nutrient species ( $\text{NO}_3$ ,  $\text{PO}_4$  and Si) were all significantly correlated with DO concentration ( $p < 0.001$ , not shown),  $\text{NH}_4$  concentrations were not significantly correlated with DO. This suggested that, in addition to water column processes, sedimentary and benthic processes were also greatly important in governing the distribution and cycling of DIN species (e.g., Tanaka et al., 2004).

### 3.5. Stable isotopic composition of particulate organic matter

Values of suspended POM  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are listed in Table 1 and are compared with different sample types from the southeastern Bering Sea Shelf region in Table 2. Values of  $\delta^{13}\text{C}$  ranged from

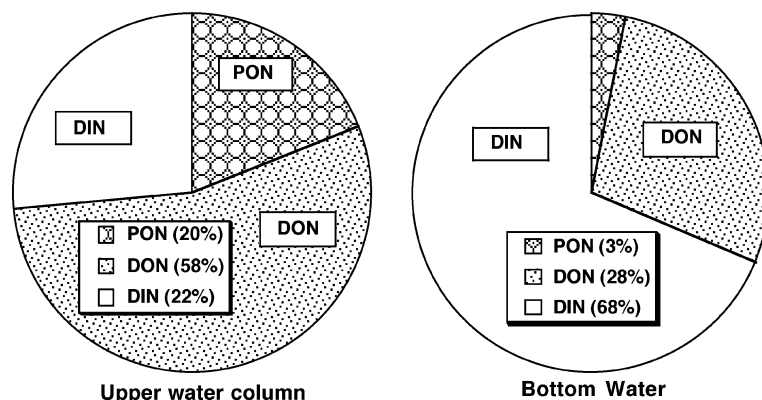


Fig. 5. Nitrogen partitioning between dissolved inorganic, dissolved organic, and particulate phases in the upper water column and bottom water column in the southeastern Bering Sea.

Table 2  
Stable isotopic composition in different sample types from the S.E. Bering Sea shelf

Sample type	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Reference
Surface sediments	−21.0 to −23.1	6.7–7.6	Smith et al., 2002
Settling particles	−20 to −26.2	6.2–15.1	Smith et al., 2002
Zooplankton	−19.7 to −25.1	8–15	Schell and Vinette, 1998
Net plankton	−18.2 to −26.5	6.6–13.2	Smith et al., 2002
Suspended POM	−23.4 to −27.1 (−24.5±0.9)	2.86–9.98 (6.0±1.9)	This work
Yukon River DOM	−27.68±0.44	−0.89±0.37	Guo, 2004b
Yukon River POM	−26.22±0.70	0.77±0.45	Guo, 2004b

−27.1‰ to −23.4‰ with an average of  $-24.5 \pm 0.9$ ‰. Values of  $\delta^{15}\text{N}$  varied from 2.8‰ to 9.9‰, with an average of  $6.0 \pm 1.9$ ‰.

These C- and N-isotope ratios were within the ranges previously reported for settling particles and plankton species in the study area (Schell and Vinette, 1998; Smith et al., 2002; Table 2). However, the  $\delta^{13}\text{C}$  values in the Bering Sea are somewhat lighter than those observed for POC in tropical/subtropical regions such as the Pacific Ocean and Sargasso Sea (e.g., Druffel et al., 1992; Wang et al., 1998). Based on data synthesis, Hofmann et al. (2000) found that POC  $\delta^{13}\text{C}$  values decreased with increasing latitude in the oceanic environment. Thus, the differences in POC  $\delta^{13}\text{C}$  values between the Bering Sea and other regions are consistent with the latitudinal distribution pattern of POC  $\delta^{13}\text{C}$  in the ocean (Hofmann et al., 2000). The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of suspended POM from the inner shelf waters were usually heavier than those from the outer shelf waters (Table 1). Interestingly, the lowest  $\delta^{13}\text{C}$  values were observed at the middle shelf station (station AV-05), coincident with the presence of a cold water mass in this region (Tanaka et al., 2004). The lighter  $\delta^{13}\text{C}$  value in the middle shelf cold water mass may be related to the greater isotopic fractionation in low temperature environments (Sackett et al., 1965; Hofmann et al., 2000). In addition,  $\delta^{13}\text{C}$  values of suspended POM showed a general increase with increasing water depth (Fig. 6), and were lighter than those of surface sediments in the study area (Table 2), as observed in the western Arctic Ocean (e.g., Naidu et al., 1993; Shin et al., 2004; Guo et al., unpublished results). In comparison, there was little difference in  $\delta^{13}\text{C}$  values between plankton, POM, and sediments in the Pacific Ocean (e.g., Wang et al., 1998), and in some cases, POM  $\delta^{13}\text{C}$  values

decreased with increasing water depth in continental shelf/slope regions (e.g., Bauer et al., 2002). Heavier  $\delta^{13}\text{C}$  in surface sediments than in suspended particles suggest that organic components containing lighter C isotopes can be preferentially decomposed during

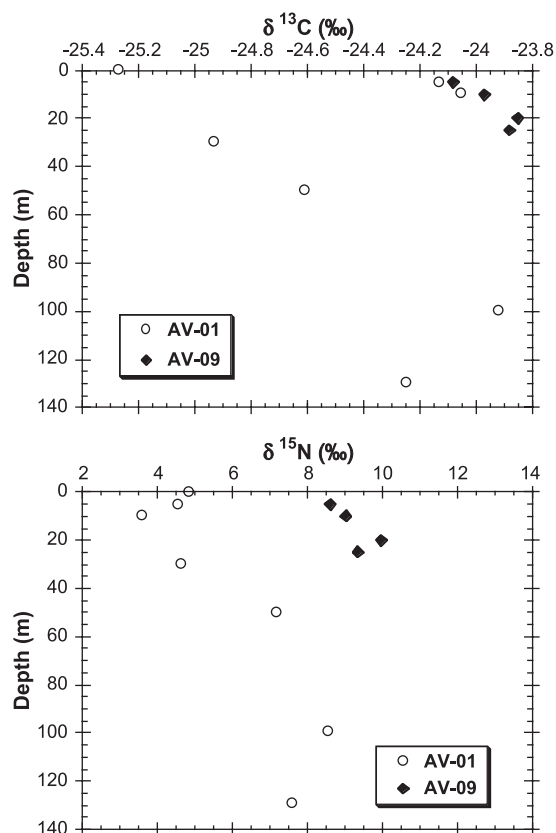


Fig. 6. Examples of vertical distributions of  $\delta^{13}\text{C}$  (upper panel) and  $\delta^{15}\text{N}$  (lower panel) of suspended particulate organic matter at an outer shelf station (AV-01) and an inner shelf station (AV-09).

their transport from the water column to the sediments or during their decomposition/regeneration in the sediment–water interface if sedimentary organic matter is derived from POM in the overlying water column.

Terrestrial organic matter from Yukon River waters has an average  $\delta^{13}\text{C}$  value of  $-27.7 \pm 0.4\text{‰}$  for DOM and  $-26.7 \pm 0.7\text{‰}$  for POM, respectively (Table 2). These values were about 2–3‰ lighter than the average  $\delta^{13}\text{C}$  value in the Bering Sea. It is less likely that terrestrial organic matter could have a noticeable impact on POM  $\delta^{13}\text{C}$  values observed in the study area. This is because the inner shelf waters with a lower salinity should have received more freshwater and terrestrial organic matter and thus have lighter  $\delta^{13}\text{C}$  values if the influence of terrestrial organic matter is significant. However, the opposite is true. The  $\delta^{13}\text{C}$  values of POM from inner shelf waters were usually heavier than those from outer shelf waters (Table 1).

The average  $\delta^{15}\text{N}$  value ( $6.0 \pm 1.9\text{‰}$ ) in the Bering Sea was up to 6‰ heavier than the terrestrial end-member values from the Yukon River DOM ( $-0.89 \pm 0.37\text{‰}$ ) and POM ( $0.77 \pm 0.45\text{‰}$ ) samples (Table 2). Therefore, higher  $\delta^{15}\text{N}$  values in the Bering Sea pointed to a predominately marine source for POM, consistent with its lower C/N ratios (average  $7.4 \pm 1.1$ ). Mino et al. (2002) reported that high-latitude regions in the north generally had somewhat higher POM  $\delta^{15}\text{N}$  values. Thus, our results showing somewhat higher  $\delta^{15}\text{N}$  values in the Bering Sea seemed consistent with the latitudinal distribution pattern of POM  $\delta^{15}\text{N}$  reported previously (Mino et al., 2002). In addition, values of  $\delta^{15}\text{N}$  showed a general increase with increasing water depth, especially at outer and inner shelf stations (Fig. 6), although there was an exception in the middle shelf region. The increase in  $\delta^{15}\text{N}$  values with increasing water depth suggested a preferential decomposition of organic components containing lighter N isotopes during the transport of organic matter from surface water to bottom waters, consistent with the vertical profiles reported previously for  $\delta^{15}\text{N}$  of POM and DOM in other marine environments (e.g., Altabet 1988; Guo et al., 2003). However, the middle shelf stations showed no consistent trend in the vertical distribution of  $\delta^{15}\text{N}$  values compared to those at outer and inner shelf stations (Table 1). The  $\delta^{15}\text{N}$  values in the sediments

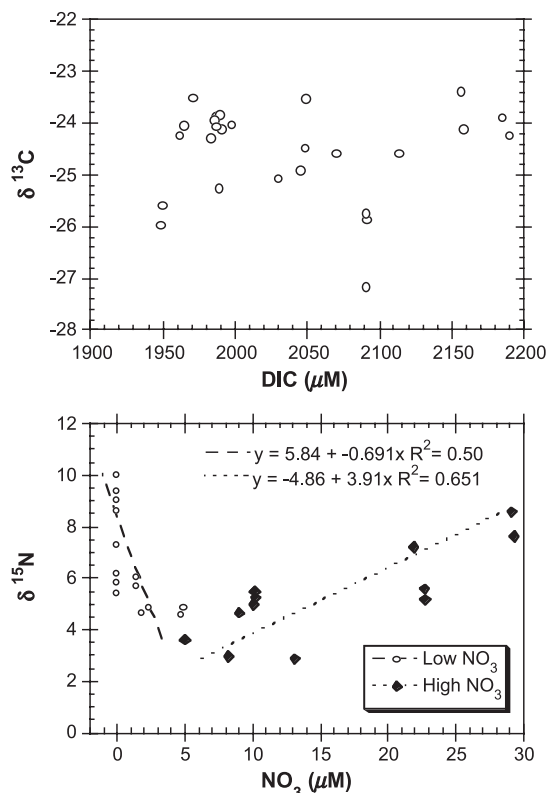


Fig. 7. Plots of particulate  $\delta^{13}\text{C}$  (‰) vs. total DIC concentration (upper panel) and particulate  $\delta^{15}\text{N}$  (‰) vs.  $\text{NO}_3$  concentration (lower panel) in the water column of the southeastern Bering Sea.

were slightly higher than the average  $\delta^{15}\text{N}$  value of our suspended POM (Table 2).

The relationship between particulate  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values was very weak (not shown), as was the relationship between  $\delta^{13}\text{C}$  (or  $\delta^{15}\text{N}$ ) and the particulate C/N ratio, likely resulting from the dynamic water mixing. This lack of correlation also indicated different biogeochemical pathways between C and N isotope fractionation in the water column.

In open ocean environments, POM  $\delta^{13}\text{C}$  can be highly correlated to  $\text{CO}_2(\text{aq})$  (e.g., Rau et al., 1992). However, we did not find a significant relationship between  $\delta^{13}\text{C}$  values and DIC concentrations in the water column (Fig. 7). The poor correlation between  $\delta^{13}\text{C}$  and DIC concentration indicated that isotopic composition of POM was not simply controlled by the DIC concentration or  $\text{CO}_2(\text{aq})$  in the shelf region. The relationship between  $\delta^{15}\text{N}$  values and  $\text{NO}_3$  (or DIN) concentrations in the water column was not straight-

forward (Fig. 7). However, if data points from the upper water column were separated from those of the lower water column, a V-type relationship was revealed. Upper and lower water columns showed a linear but opposite relationship between  $\delta^{15}\text{N}$  values and  $\text{NO}_3$  concentrations (Fig. 7). In the upper water column, where the  $\text{NO}_3$  concentration was low ( $<5 \mu\text{M}$ ), the  $\delta^{15}\text{N}$  values were inversely correlated with  $\text{NO}_3$  concentration. In contrast, the  $\delta^{15}\text{N}$  value was positively correlated with  $\text{NO}_3$  concentration in the bottom waters where  $\text{NO}_3$  concentration was higher ( $>5 \mu\text{M}$ ). These  $\delta^{15}\text{N}$  data clearly show the effect of nutrient drawdown in surface waters and diagenesis below the euphotic zone (e.g., Saino and Hattori, 1980; Altabet and Francois, 1994). It seemed that N isotopic fractionation during photosynthesis predominantly influenced the  $\delta^{15}\text{N}$  values of POM in the upper water column whereas POM decomposition/regeneration was important in controlling the POM  $\delta^{15}\text{N}$  value in the bottom water column.

#### 4. Summary and conclusions

Concentrations of organic carbon species (DOC, POC, and carbohydrates) in the water column increased, in general, from outer to inner shelf stations with elevated concentrations in surface waters. The significant correlation between DOC and salinity suggested that the DOC distribution in the water column was largely controlled by water mixing although biological processes are important in the production and decomposition of DOC.

TDCHO comprised, on average,  $\sim 13 \pm 3\%$  of bulk DOC. Within the TDCHO pool,  $35 \pm 15\%$  was PCHO and  $65 \pm 15\%$  was MCHO. DOM had higher DOC/DON and MCHO/TDCHO ratios than POM. This may have indicated that the DOM pool is more refractory and diagenetically older than the POM pool in the water column over the southeastern Bering Sea Shelf. Within the TOC pool, POC made up  $\sim 14 \pm 5\%$  and COC made up  $\sim 34 \pm 8\%$ , leaving  $\sim 52 \pm 5\%$  of the TOC in the  $<1 \text{ kDa}$  dissolved phase. Within the total N pool, DON was the dominant N species in the upper water column ( $58 \pm 14\%$ ), while DIN was the dominant N species in the lower water column ( $68 \pm 15\%$ ). In contrast, DIC remained the predominant C phase ( $96 \pm 1\%$ ) throughout the entire water column.

Chlorophyll-*a* concentrations were significantly correlated with POC concentrations but weakly correlated with DOC concentrations. This may indicate that a higher Chl-*a* (or higher biomass) did not necessarily result in an instantaneously higher DOC concentration in the water column. Instead, subsequent microbial and grazing processes may be more important in the production of DOC in the water column.

The overall low particulate C/N ratio, together with the significant relationship between POC and Chl-*a*, suggested a predominant marine source for POM. Relatively lower  $\delta^{13}\text{C}$  ( $-24.5 \pm 0.9\text{‰}$ ) and higher  $\delta^{15}\text{N}$  values ( $6.0 \pm 1.9\text{‰}$ ) of the POM in the Bering Sea compared to values in tropical/subtropical regions were consistent with the latitudinal distribution pattern of stable isotope composition in the ocean, and thus supported a dominantly marine source for POM in this shelf region. The average  $\delta^{13}\text{C}$  value of POM from the Bering Sea was 2–3‰ heavier than values of terrestrial POM and DOM from Alaska river waters. However, the average Bering Sea  $\delta^{15}\text{N}$  value was up to 6‰ heavier than average terrestrial POM/DOM  $\delta^{15}\text{N}$  values.

N-isotope composition of POM was highly related to the dynamic cycling of nutrients in the water column, and seemed to be controlled by isotopic fractionation processes during photosynthesis in the upper water column (low nutrient regime), but by regeneration/degradation processes in the bottom water (high nutrient regime). Overall, organic matter containing lighter C and N isotopes seemed to be decomposed preferentially during its transport and transformation in the water column.

#### Acknowledgements

We are grateful to chief scientist, Dr. S. Honjo, the captain and crewmembers of the *R/V Mirai*, and members of the science party from JAMSTEC and Marine Works Japan for their assistance in sample collection during the MR01-K04 Leg-01 cruise. We gratefully thank Munehito Kimura for performing the measurement of dissolved organic nitrogen, JAMSTEC for providing CTD, nutrients, chlorophyll-*a* and dissolved oxygen data, Candace O'Connor for careful reading of the manuscript, and Mark Altabet, Associate Editor, and two anonymous reviewers for

constructive comments and notations that improved the manuscript. This work was supported by Frontier Research System for Global Change/International Arctic Research Center.

## References

- Altabet, M.A., 1988. Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Res.* 35, 535–554.
- Altabet, M.A., Francois, R., 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nutrient utilization. *Glob. Biogeochem. Cycles* 8, 103–116.
- Amon, R.M.W., 2003. The role of dissolved organic matter for the organic carbon cycle in the Arctic Ocean. In: Stein, R., Macdonald, R. (Eds.), *The Organic Carbon Cycle in the Arctic Ocean*. Springer, New York, pp. 83–99. Chap. 4.
- Amon, R.M., Benner, R., 1996. Bacterial utilization of different size classes of dissolved organic matter. *Limnol. Oceanogr.* 41, 41–51.
- Agatova, A.I., Arzhanova, N.V., Torgunova, N.I., 1999. Organic matter of the Bering Sea. In: Loughlin, T.R., Ohtani, K. (Eds.), *Dynamics of the Bering Sea*. PICES, University of Alaska Fairbanks, Alaska, pp. 261–283. AK-SG-99-03.
- Bauer, J.E., Druffel, E.R.M., Wolgast, D.M., Griffin, S., 2002. Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope. *Deep-Sea Res.*, II 49, 4387–4419.
- Benner, R., Pakulski, J.D., McCarthy, M., Hedges, J.I., Hatcher, P.G., 1992. Bulk chemical characteristics of dissolved organic matter in the ocean. *Science* 255, 1561–1564.
- Bhosle, N.B., Bhaskar, P.V., Ramachandran, S., 1998. Abundance of dissolved polysaccharides in the oxygen minimum layer of the Northern Indian Ocean. *Mar. Chem.* 63, 171–182.
- Borsheim, K.Y., Mykkestad, S.M., Sneli, J.A., 1999. Monthly profiles of DOC, mono- and polysaccharides at two locations in the Trondheimsfjord (Norway) during two years. *Mar. Chem.* 63, 255–272.
- Burney, C.M., Sieburth, J.M., 1977. Dissolved carbohydrates in seawater. *Mar. Chem.* 5, 15–28.
- Church, M.J., Ducklow, H.W., Karl, D.M., 2002. Multiyear increases in dissolved organic matter inventories at station ALOHA in the North Pacific Subtropical Gyre. *Limnol. Oceanogr.* 47, 1–10.
- Cooper, L.W., Whitley, T.E., Grebmeier, J.M., Weingartner, T., 1997. The nutrient, salinity, and stable oxygen isotope composition of Bering and Chukchi Sea waters in and near the Bering Strait. *J. Geophys. Res.* 102 (C6), 12563–12573.
- Dittmar, T., Kattner, G., 2003. The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review. *Mar. Chem.* 83, 103–120.
- Druffel, E.R.M., Williams, P.M., Bauer, J.E., Ertel, A.J., 1992. Cycling of dissolved and particulate organic matter in the open ocean. *J. Geophys. Res.* 97, 15639–15659.
- Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim. 419 pp.
- Guéguen, C., Guo, L., Wang, D., Tanaka, N., Hung, C.-C., 2004. Chemical characteristics and origin of dissolved organic matter in the Yukon River. *Biogeochemistry* (revised).
- Guo, L., Santschi, P.H., 1996. A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater. *Mar. Chem.* 55, 113–127.
- Guo, L., Santschi, P.H., 1997. Isotopic and elemental characterization of colloidal organic matter from the Chesapeake Bay and Galveston Bay. *Mar. Chem.* 59, 1–15.
- Guo, L., Coleman Jr., C.H., Santschi, P.H., 1994. The distribution of colloidal and dissolved organic carbon in the Gulf of Mexico. *Mar. Chem.* 45, 105–119.
- Guo, L., Santschi, P.H., Warnken, K.W., 1995. Dynamics of dissolved organic carbon in oceanic environments. *Limnol. Oceanogr.* 40, 1392–1403.
- Guo, L., Santschi, P.H., Cifuentes, L.A., Trumbore, S., Southon, J., 1996. Cycling of high molecular weight dissolved organic matter in the Middle Atlantic Bight as revealed by carbon isotopic ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) signatures. *Limnol. Oceanogr.* 41, 1242–1252.
- Guo, L., Wen, L., Tang, D., Santschi, P.H., 2000. Re-examination of cross flow ultrafiltration for sampling aquatic colloids: evidence from molecular probes. *Mar. Chem.* 69, 75–90.
- Guo, L., Tanaka, N., Schell, D.M., Santschi, P.H., 2003. Nitrogen and carbon isotopic composition of high-molecular-weight dissolved organic matter in marine environments. *Mar. Ecol., Prog. Ser.* 252, 51–60.
- Guo, L., Zhang, J.-Z., Guéguen, C., 2004. Speciation and fluxes of nutrients (N, P, Si) from the upper Yukon River. *Glob. Biogeochem. Cycles* 18, GB1038. doi:10.1029/2003GB002152.
- Guo, L., et al., 2004. Isotope composition of dissolved, colloidal and particulate organic matter in the Yukon River (submitted for publication).
- Hansell, D.A., Carlson, C.A., 2001. Biogeochemistry of total organic carbon and nitrogen in the Sargasso Sea: control by convective overturn. *Deep-Sea Res.*, II 48, 1649–1667.
- Hansell, D.A., Carlson, C.A., 2002. *Biogeochemistry of Marine Dissolved Organic Matter*. Academic Press, San Diego. 774 pp.
- Hedges, J.I., 2002. Why dissolved organic matter? A marine retrospective. In: Hansel, D., Carlson, C. (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*. Academic Press, San Diego, pp. 1–33.
- Hedges, J.I., Baldock, J.A., Gelinas, Y., Lee, C., Peterson, M.L., Wakeham, S.G., 2002. The biochemical and elemental compositions of marine plankton: a NMR perspective. *Mar. Chem.* 78, 47–63.
- Hofmann, M., Wolf-Gladrow, D.A., Takahashi, T., Sutherland, S.C., Six, K.D., Maier-Reimer, E., 2000. Stable carbon isotope distribution of particulate organic matter in the ocean: a model study. *Mar. Chem.* 72, 131–150.
- Hopkinson, C.S., Fry, B., Nolin, A.L., 1997. Stoichiometry of dissolved organic matter dynamics on the continental shelf of the northeastern USA. *Cont. Shelf Res.* 17, 473–489.
- Hung, C.-C., Guo, L., Santschi, P.H., Alvarado-Quiroz, N., Haye, J., 2003a. Distributions of carbohydrate species in the Gulf of Mexico. *Mar. Chem.* 81, 119–135.

- Hung, J.J., Chen, C.H., Gong, G.C., Sheu, D.D., Shiah, F.K., 2003b. Distributions, stoichiometric patterns and cross-shelf exports of dissolved organic matter in the East China Sea. *Deep-Sea Res.*, II 50, 1127–1145.
- Kirchman, D.L., Meon, B., Ducklow, H.W., Carlson, C.A., Hansell, D.A., Steward, G.F., 2001. Glucose fluxes and concentrations of dissolved combined neutral sugars (polysaccharides) in the Ross Sea and Polar Front Zone, Antarctica. *Deep-Sea Res.*, II 48, 4179–4197.
- Kortzinger, A., Koeve, W., Kahler, P., Mintrop, L., 2001. C:N ratios in the mixed layer during the productive season in the northeast Atlantic Ocean. *Deep-Sea Res.*, I 48, 661–688.
- Loughlin, T.R., Ohtani, K., 1999. Dynamics of the Bering Sea. University of Alaska Sea Grant, Fairbanks. AK-SG-99-03, 825 pp.
- Loh, A.N., Bauer, J.E., 2000. Distribution, partitioning and fluxes of dissolved and particulate C, N and P in the eastern North Pacific and Southern Oceans. *Deep-Sea Res.*, I 47, 2287–2316.
- Manabe, S., Stouffer, R.J., 1994. Multiple-century response of a coupled ocean–atmosphere model to an increase of atmospheric carbon dioxide. *J. Climate* 7, 5–23.
- Mino, Y., Saino, T., Suzuki, K., Maranon, E., 2002. Isotopic composition of suspended particulate nitrogen ( $\delta^{15}\text{N}_{\text{us}}$ ) in surface waters of the Atlantic Ocean from 50°N to 50°S. *Glob. Biogeochem. Cycles* 16 (4).
- Murata, A., Takizawa, T., 2002. Impact of a coccolithophorid bloom on the CO<sub>2</sub> system in surface waters of the eastern Bering Sea shelf. *Geophys. Res. Lett.* 29 (11) (Art No. 1547).
- Myklestad, S.M., 1974. Production of carbohydrates by marine planktonic diatoms: I. Comparison of nine different species in culture. *J. Exp. Mar. Biol. Ecol.* 9, 137–144.
- Naidu, A.S., Scalan, R.S., Feder, H.M., Goering, J.J., Hameedi, M.J., Parker, P.L., Behrens, E.W., Caughey, M.E., Jewett, S.C., 1993. Stable organic carbon isotopes in sediments of the north Bering–south Chukchi seas, Alaska–Soviet Arctic shelf. *Cont. Shelf Res.* 13, 669–691.
- Napp, J.M., Hunt, G.L., 2001. Anomalous conditions in the southeastern Bering Sea 1997: linkages among climate, weather, ocean and biology. *Fisheries Oceanogr.* 10, 61–68.
- National Research Council, 1996. *The Bering Sea Ecosystem*. National Academic Press, Washington, DC.
- Ogawa, H., Usui, T., Koike, I., 2003. Distribution of dissolved organic carbon in the east China Sea. *Deep-Sea Res.*, II 50, 353–366.
- Opsahl, S., Benner, R., Amon, R.M., 1999. Major flux of terrigenous dissolved organic matter through the Arctic Ocean. *Limnol. Oceanogr.* 44, 2017–2023.
- Pakulski, J.D., Benner, R., 1994. Abundance and distribution of carbohydrates in the ocean. *Limnol. Oceanogr.* 39, 930–940.
- Passow, U., 2002. Production of transparent exopolymer particles (TEP) by phyto- and bacterioplankton. *Mar. Ecol., Prog. Ser.* 236, 1–12.
- Pettine, M., Patrolecco, L., Manganelli, S., Capri, S., Farrace, M.G., 1999. Seasonal variations of dissolved organic matter in the northern Adriatic Sea. *Mar. Chem.* 64, 153–169.
- Rau, G.H., Takahashi, T., Des Marais, D.J., Repeta, D.I., Martin, J.H., 1992. The relationship between  $\delta^{13}\text{C}$  of organic matter and  $[\text{CO}_2(\text{aq})]$  in ocean surface water: data from a JGOFS site in the northeast Atlantic Ocean and a model. *Geochim. Cosmochim. Acta* 56, 1413–1419.
- Sackett, W.M., Eckelmann, W.R., Bender, M.L., Be, A.W.H., 1965. Temperature dependence of carbon isotope composition in marine plankton and sediments. *Science* 148, 235–237.
- Santschi, P.H., Balnois, E., Wilkinson, K., Buffle, J., Guo, L., 1998. Fibrillar polysaccharides in marine macromolecular organic matter as imaged by atomic force microscopy and transmission electron microscopy. *Limnol. Oceanogr.* 43, 896–908.
- Santschi, P.H., Hung, C.-C., Schultz, G., Alvarado-Quiroz, N., Guo, L., Pinckney, J., Walsh, I., 2003. Control of acid polysaccharide production and  $^{234}\text{Th}$  and POC export fluxes by marine organisms. *Geophys. Res. Lett.* 30 (2), 1044.
- Saino, T., Hattori, A., 1980.  $^{15}\text{N}$  natural abundance in oceanic suspended particulate matter. *Nature* 283, 752–754.
- Schell, D.M., Barnett, B.A., Vinette, K.A., 1998. Carbon and nitrogen isotope ratios in zooplankton of the Bering, Chukchi and Beaufort sea. *Mar. Ecol., Prog. Ser.* 162, 11–23.
- Siegenthaler, U., Sarmiento, J.L., 1993. Atmospheric carbon dioxide and the ocean. *Nature* 365, 119–125.
- Skoog, A., Lara, R., Kattner, G., 2001. Spring–summer cycling of DOC and DON and inorganic N in a highly seasonal system encompassing the northeast water polynya, 1993. *Deep-Sea Res.*, I 48, 2613–2629.
- Shin, K.H., Tanaka, T., Tanaka, N., McRoy, C.P., Murata, A., 2004. Shelf–basin interaction in the western arctic ocean: organic matter dynamics. *J. Oceanogr.* (submitted for publication).
- Smith, S.L., Henrichs, S.M., Rho, T., 2002. Stable C and N isotopic composition of sinking particles and zooplankton over the southeastern Bering Sea shelf. *Deep-Sea Res.*, II 49, 6031–6050.
- Springer, A.M., McRoy, C.P., Flint, M.V., 1996. The Bering Sea green belt: shelf-edge processes and ecosystem production. *Fisheries Oceanogr.* 5, 205–223.
- Stabeno, P.J., Kachel, N.B., Sullivan, M., Whitedge, T.E., 2002. Variability of physical and chemical characteristics along the 70-m isobath of the southeastern Bering Sea. *Deep-Sea Res.*, II 49, 5931–5943.
- Strom, S.L., Benner, R., Ziegler, S., Dagg, M.J., 1997. Planktonic grazers as a potential important source of marine dissolved organic carbon. *Limnol. Oceanogr.* 42, 1364–1374.
- Takahashi, K., Fujitani, N., Yanada, M., Maita, Y., 2000. Long-term biogenic particle fluxes in the Bering Sea and the central subarctic Pacific Ocean. *Deep-Sea Res.*, I 47, 1723–1759.
- Tanaka, T., Guo, L., Deal, C., Tanaka, N., Whitedge, T., Murata, A., 2004. N-deficiency in an oxygenated cold water mass in the Bering Sea Shelf: influence of sedimentary denitrification. *Cont. Shelf Res.* 24, 1271–1283.
- Vlahos, P., Chen, R.F., Repeta, D.J., 2002. Dissolved organic carbon in the Middle-Atlantic Bright. *Deep-Sea Res.*, II 49, 4369–4385.
- Wang, X.C., Druffel, E.R.M., Griffin, S.A., Lee, C., Kashgarian, M., 1998. Radiocarbon studies of organic compound classes in

- plankton and sediment of the northern Pacific Ocean. *Geochim. Cosmochim. Acta* 62, 365–378.
- Wetz, M.S., Wheeler, P.A., 2003. Production and partitioning of organic matter during simulated phytoplankton blooms. *Limnol. Oceanogr.* 48, 1808–1817.
- Wheeler, P.A., Watkins, J.M., Hansing, R.L., 1997. Nutrients, organic carbon and nitrogen in the upper water column of the Arctic Ocean: implications for the sources of DOC. *Deep-Sea Res., II* 44, 1571–1592.