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Relating temporal and spatial patterns of DMSP in the Barents Sea to phytoplankton biomass and productivity

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Abstract

Dimethylsulfoniopropionate (DMSP), produced by many marine phytoplankton, is the main precursor of the climate relevant gas dimethylsulfide (DMS). Currently, it is generally accepted that the relationship between DMSP and phytoplankton biomass (as chlorophyll *a*), while not representative of the absolute magnitude of the DMSP pool, is a good indicator of ecosystem structure. In this study we test the strength of the relationships between DMSP and various phytoplankton parameters in Arctic shelf waters of the Barents Sea. Our objective is to assess the predictive value that traditional phytoplankton carbon parameters have on DMSP. We discuss C:DMSP-S variability as a function of seasonality, water masses, grazing and nutrient limitation. For this purpose we analyze data from 5 cruises including winter, spring and summer conditions and across the seasonal ice zone at the time of the study. Highest phytoplankton DMSP concentration was usually measured at the ice edge. Marked seasonal variability was observed in phytoplankton carbon biomass and production but not necessarily in the particulate fraction of DMSP (DMSPp), resulting in seasonally varying C:DMSP-S. High winter DMSPp concentrations, when chlorophyll *a* and primary production were lowest and flagellates dominant, suggest a heterotrophic source. The production of extracellular carbon and the pool of dissolved DMSP (DMSPd) followed similar seasonal trends, with enhanced concentrations in spring, and we suggest that high dissolved primary production induced by nutrient limiting conditions resulted in high DMSPd concentrations. Mesoscale changes in total DMSP (particulate + dissolved) may be modeled from basin-wide total phytoplankton primary production (rather than from phytoplankton biomass) at seasonal and interannual scales. We conclude there is predictive power of DMSP concentrations in the Barents Sea based on seasonality, the position of the ice edge and the distribution of phytoplankton variables.

Keywords: Carbon; Sulfur; Dimethylsulfoniopropionate; Arctic; Polar; Climate; Seasonal and interannual variability; Barents Sea; Primary production; Phytoplankton

1. Introduction

Marginal ice zones (MIZ) belong to the most biologically important region in polar oceans, as sites of enhanced biomass and growth of many groups of organisms (e.g., Niebauer and Alexander, 1985; Rey and Loeng, 1985; Smith and Nelson, 1986). MIZ are also

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physically dynamic regions where mesoscale and submesoscale features modulate particle, gas and heat exchange, forming the northern boundary of the area seasonally affected by the melting sea ice, or seasonal ice zone (SIZ). In this article, we examine the role of scale in the patterns of dimethylsulfoniopropionate (DMSP) abundance as a function of phytoplankton biomass and productivity in the SIZ of the Barents Sea where potential changes in the planktonic ecosystem and associated carbon and sulfur fluxes due to climate change make prediction of possible biogeochemical responses highly speculative.

DMSP, produced by many marine phytoplankton, is the main precursor of the climate relevant gas dimethylsulfide (DMS) (Keller, 1989). DMS is the most abundant volatile sulfur compound in seawater and is widely accepted as dominating the flux of biogenic sulfur to the atmosphere, which is important for the global sulfur cycle and climate (Andreae, 1990; Scholes et al., 2003). Interest in the biogeochemical cycle of DMS increased sharply when a hypothesis linking biogenic DMS emission and global climate was proposed (Charlson et al., 1987; Schwartz, 1988). In this feedback, DMS produced by marine phytoplankton and the food web enters the troposphere and is oxidized there to sulfate particles, which influence cloud albedo and, consequently, climate. Large-scale climate change, in turn, affects phytoplankton abundance in the oceans and thereby completes the proposed feedback loop. From a climate perspective, the Arctic region is particularly sensitive and important to regional and global radiation balance due largely to positive feedbacks involving surface albedo and reduced sea ice extent or thickness (Morison et al., 2000; Overpeck et al., 2005).

Initially, investigators examined the variability of DMS concentrations in a locality as a function of phytoplankton abundance, composition, and/or physiology. The last decade has provided mounting evidence that DMS and DMSP are products of complex food web dynamics, coupled to interactions with the physical and chemical fields of the oceans. DMSP production in the ocean is so significant that perhaps 3–10% of the primary production flows through DMSP in some regions (Kiene et al., 2000; Simo and Dachs, 2002). Furthermore, it is the availability of DMSP, along with temperature, sunlight exposure and, in particular, ultraviolet radiation, that appears to control the yield of DMS (Kiene et al., 2000). Of the DMS formed in the ocean, perhaps 10–20% escapes to the atmosphere (Bates et al., 1994) making the emission of DMS a small leak from a major marine biogeochemical cycle. Thus, to understand the controls on DMS production one must understand the coupling between DMS and DMSP dynamics, and hence the controls on, and variability of, the DMSP pool (Simo, 2001).

The central Barents Sea is a productive, high-latitude marine ecosystem, with an extended shelf and a complex hydrography (Loeng, 1991; Loeng et al., 1997), including warm, NE-flowing Atlantic waters from the South and cold, SW-flowing Arctic waters from the North that converge at the Polar Front. According to Sakshaug (2004), this ecosystem accounts for more than 40% of the total primary production occurring on Arctic shelves underlining the importance of this sector for Arctic Ocean biogeochemistry. The presence of relatively nutrient-rich waters and a seasonal ice cover in the central and north-eastern part of the Barents Sea support a plankton bloom of long duration in the SIZ as the ice recedes northward during spring and summer (Sakshaug and Skjoldal, 1989; Wassmann et al., 1999; Wassmann, 2002). Progressively older stages of the bloom will be found southwards, in the previously ice-covered SIZ, providing an ecological, north–south spatial gradient similar to the temporal succession observed at any one location of the transect traveled by the receding ice (Rey and Skjoldal, 1987). This scenario provides a unique alternative to extensive temporal sampling of the ecological, chemical and physical factors determining sulfur and carbon fluxes as DMSP cycles over the entire plankton bloom. Matrai and Vernet (1997) observed high DMSP and variable DMS concentrations over most of the Barents Sea, from ice-free waters to the ice edge, suggesting that the physiological state of the spring bloom, rather than its species composition, played a major role in the cycling of DMSP and DMS in this region. Ecological modeling of the food web–DMSP–DMS system suggests that a longer seasonal sampling of the processes involved is necessary (Gabric et al., 1999). This paper aims towards predicting phytoplankton DMSP from carbon biomass and productivity at seasonal and interannual temporal scales, detected at spatial mesoscales, but not necessarily seen at small scale (<10 km) as exemplified by an earlier, complementary study done in 1993 (Matrai and Vernet, 1997; Andreassen and Wassmann, 1998; Wassmann et al., 1999) in the central Barents Sea.

2. Methods

2.1. Sample collection

Sampling took place during 4 cruises (see Table 1) on board the R/V *Jan Mayen* (Fig. 1). A South–North transect was followed from permanently ice-free waters

Table 1
Location and sampling dates for transect and profiling stations during the cruises

Cruise date	Station date	Cruise	Ending transect station	Research vessel	Profiling 24-h stations
13–29 May 1993	19 May	Barents-93	76° 32.2′N	Jan Mayen	73.73° N, 31.00° E (St. 4)
	21 May		32° 55.5′E		75.99° N, 31.68° E (St. 3)
	23 May				75.82° N, 32.50° E (St. 2)
	25 May				76.38° N, 32.73° E (St. 1)
16–24 March 1998	19 March	ALV-1	76° 23′N	Jan Mayen	72.55° N, 30.98° E (St. 3)
	21 March		33° 20′E		73.77° N, 31.88° E (St. 2)
	22 March				76.39° N, 33.21° E (St. 1)
18–30 May 1998	20 May	ALV-2	76° 04′N	Jan Mayen	72.50° N, 30.95° E (St. 5)
	22 May		32° 51′E		73.79° N, 31.64° E (St. 4)
	24 May				74.80° N, 34.46° E (St. 3)
	25 May				75.61° N, 33.06° E (St. 2)
	28 May				76.02° N, 32.99° E (St. 1)
29 June–9 July 1999	2 July	ALV-3	78° 12′N	Jan Mayen	73.80° N, 31.74° E (St. 5)
	4 July		33° 20′E		75.13° N, 32.48° E (St. 4)
	5 July				77.07° N, 33.82° E (St. 3)
	7 July				77.67° N, 34.32° E (St. 2)
	9 July				78.22° N, 34.38° E (St. 1)
3–14 July 2001	5 July	AOE-01	77° 54′N	Oden	77.83° N, 29.93° E (St. 1)
			29° 41′E		

The transect started at 72.5°N, 30.59° E for all cruises but AOE-01, which started at 72.5°N, 20.55°E.

(72° 30′ N, 30° 21′ E) through the seasonal ice zone into ice-covered waters (50–80% ice coverage), sampling surface waters (0–3 m). Stations were occupied in a regular fashion, every 20 nautical miles, to determine the state of the bloom in relation to water masses distribution. From this survey, three to five process stations were chosen (Sts. 1–5, north to south) and occupied for 36 h each for vertical profiles and *in situ* experiments, following a drifting buoy (1993–1999 cruises only). During the transect, surface waters were sampled for temperature, salinity, irradiance, DMSP, primary production (except in 1993) and chlorophyll *a* (chl *a*) while six fixed depths were sampled for cell counts and chl *a*. At each of the process stations, standard hydrography, nutrients, primary production, suspended biomass (particulate organic carbon and chl *a*), phytoplankton identification and counts, and DMSP in the water column as well as sedimentation were investigated. Biomass and primary productivity are integrated to 50 m depth. This depth corresponded to 5%,<0.01% and <0.01% of surface irradiance in winter, spring and summer, respectively. A 5th cruise, on board the Icebreaker *Oden*, followed a similar transect, from 72° 30′ N, 20° 33’ E northwards transiting into the pack ice in July 2001 (Fig. 1). Only surface waters (0–3 m) were sampled but for one vertical station at the ice edge; surface waters were sampled only for DMSP. Stations during the Barents-93 cruise were sampled according to light depths, from surface to 0.01% surface irradiance (ranging 30–60 m deep). Sampling details other than those presented here are described in Matrai and Vernet (1997), Vernet et al. (1998), Andreassen and Wassmann (1998), Wassmann et al. (1999), Reigstad et al. (2002), Rat’kova and Wassmann (2002), and Olli et al. (2002).

Standard hydrographic sampling was done with a General Oceanics Rosette equipped with a Neil Brown Mk III or a Seabird CTD-profiler, an *in situ* SeaTech fluorometer, a Biospherical Instruments QSP-200L underwater sensor, and 5-l Niskin bottles fitted with Teflon coated stainless steel springs.

2.2. Analytical methods

Particulate and dissolved DMSP (DMSPp and DMSPd, respectively) were determined in separate fractions (Matrai and Vernet, 1997). Particulate material from the water column was collected onto Whatman GF/C glass fiber filters while the dissolved fraction was represented by the material in the filtrate passing through the Whatman GF/C, but GF/F in July 2001. DMSPp samples were basified and run at sea. DMSPd samples ($\leq$5 ml) were gravity filtered quickly into baked scintillation vials and stored frozen until later analysis during the cruise or back in the laboratory.

DMSP analysis was done with a purge and trap system in line with a gas chromatograph with a flame-photometric detector. DMSP was converted to DMS after the addition of 5N NaOH. The DMS evolved was sparged, cryotrapped and finally thermally desorbed. Chromatographic separation was achieved with a Supelco

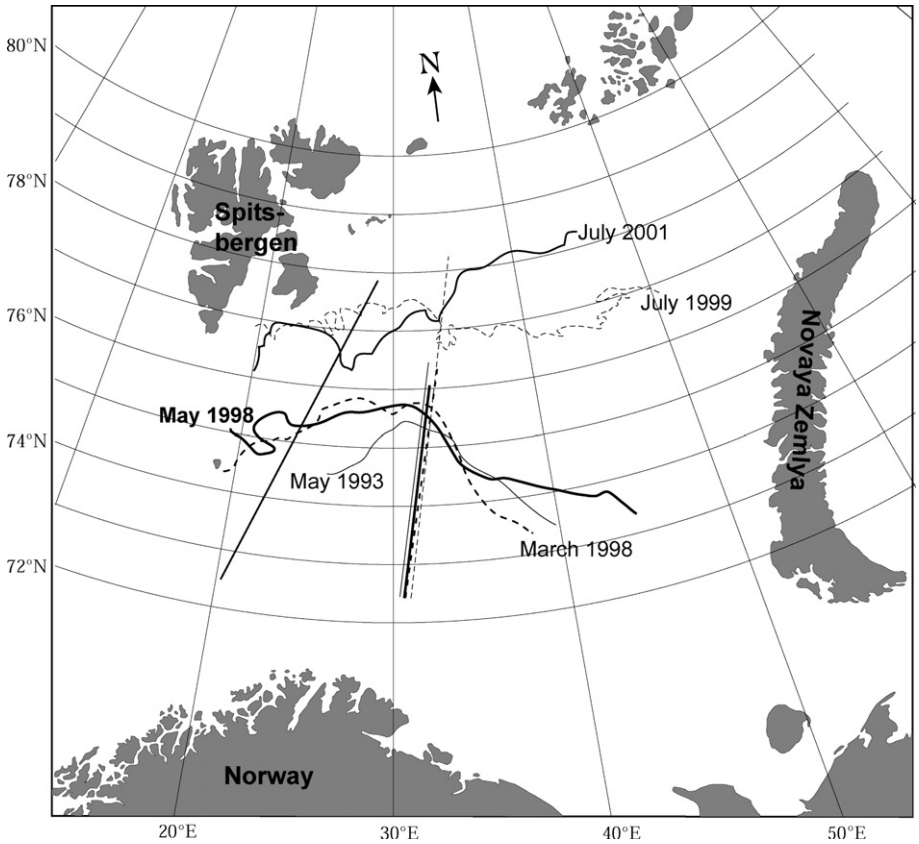

Fig. 1. Cruise transects for May 1993, March and May 1998, July 1999 and July 2001. Also indicated is the monthly mean positioning of the ice edge for the various cruises.

Chromosil 330 column at 85 °C with He as carrier gas at 40 ml min^{-1}. Liquid standards for DMS and DMSP were treated as described above. Analytical precision of triplicate standards and sample runs, determined as coefficient of variation, was better than 5% for most of the working range including the lowest concentrations of DMSP encountered here (Matrai and Keller, 1993).

Chl *a* samples were collected onto Whatman GF/C glass fiber filters (except for GF/F filters used in July 2001), extracted in 90% methanol kept cold and dark over 24 h, centrifuged prior to reading with a Turner Designs AU-10 fluorometer, and calibrated with pure chl *a* (Sigma Biochemicals); precision, determined as the coefficient of variation for triplicate standards, was better than 3% (Wassmann, 1991; Matrai and Vernet, 1997). Comparison between biomass estimation using Whatman GF/F (effective pore size of 0.7 μm) vs. GF/C filters (effective pore size of 1.0 ìm) revealed no significant difference (Vernet et al., 1998).

Primary production was measured with 24-h *in situ* and simulated *in situ* incubations as described in Vernet et al. (1998). Samples from Niskin bottles were used to fill 125-ml bottles, which were injected with 5 or 10 μCi of ^{14}C-labelled sodium bicarbonate (ICN Biochemicals). The bottles were incubated for 24-h either on deck, in a transparent Plexiglass incubator flushed with running seawater (during transect; only surface samples), or hung *in situ* from a polycarbonate line (process stations). Incubations started around the clock during transects and around midnight at the process stations. Primary production was measured as the difference in incorporation of ^{14}C between the average of two light and one dark bottle incubated at each depth (dark bottles were sometimes kept at 4 °C in a refrigerator in the dark). Two samples were taken from each bottle: (a) 3 ml of untreated sample was used to measure total radiocarbon assimilation, and (b) 100 ml of the sample was filtered onto a 25-mm Whatman GF/C at <15 mm Hg to collect cells and let through the dissolved carbon (Matrai et al., 1995). The material retained on the filter measured radiocarbon assimilated only into particulate carbon. Both samples

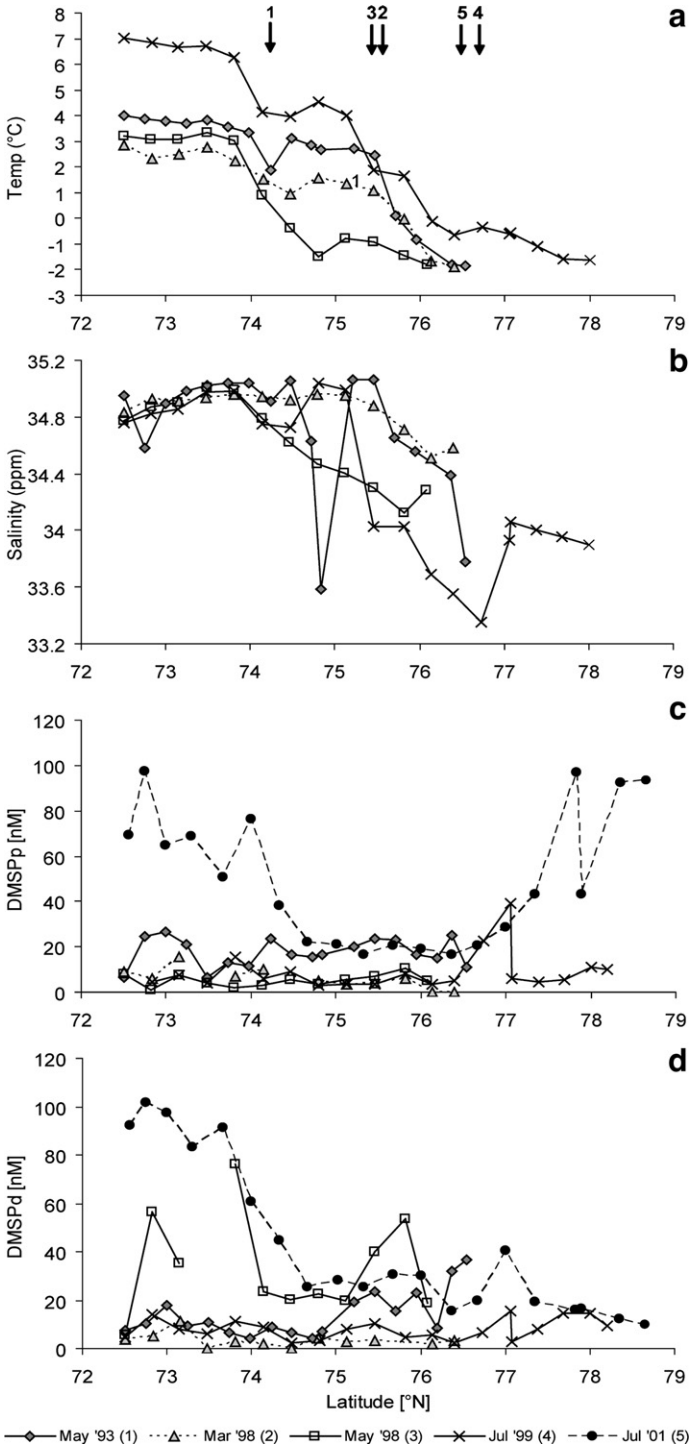

Fig. 2. Temperature (a), salinity (b), particulate (c) and dissolved (d) DMSP concentration in surface waters of the Barents Sea during March 1998, May of 1993 and 1998, and July of 1999 and 2001. The arrows indicate the location of the southernmost extent of the Polar Front.

were immediately acidified with 0.25 ml of 10% HCl for 24 h. Finally, a 0.1 ml sample was taken from each incubation bottle and mixed with 0.25 ml of 10% NaOH to estimate radiocarbon specific activity. After 24-h acidification, water was added as needed to bring final sample volume to 3 ml. Subsequently, 7 ml of

Universol ES were added to all vials and samples stored on board ship. Radioactivity in the samples was measured in a Beckman liquid scintillation counter at the University of Tromsø, within 1 month of sample collection. All counts were corrected using an external quenching curve. In this way, carbon assimilated into particulate matter was measured from the radiocarbon activity retained in the Whatman GF/C filter and extracellular carbon incorporation (cell or colonial mucilage and dissolved organic matter) was calculated from the difference between total and particulate carbon incorporation.

3. Results

3.1. Horizontal gradients

Surface concentrations summarized the spatial and seasonal distribution of plankton-derived sulfur and carbon compounds along the transect during the growth season (Figs. 2 and 3). Furthermore, transects sampled during two spring and two summer seasons provide a glimpse of the interannual variability that can be expected in the Barents Sea (Table 2).

Winter concentrations of DMSPp in surface waters were low and fairly invariant throughout the transect but significant at all stations. Strikingly, the levels observed were as high as those observed in spring 1998 and summer 1999. Interannual variability in DMSPp along the entire transect showed higher concentrations in spring 1993, especially in southern Atlantic waters and at the ice edge, by as much as 6-fold. Summer concentrations of DMSPp increased at the ice edge in July 1999 when they exceeded those observed in spring, decreasing again northward. In July 2001, DMSPp concentrations were significantly higher than the previously sampled summer period, with maximal concentrations of 100 nM at both ends of the transect in Atlantic and Arctic waters and lower at the MIZ.

DMSPd showed a similar seasonal pattern to DMSPp, with lowest concentrations in winter (Table 2, Fig. 2). Surface stocks were slightly higher in southern Atlantic water than further north in Arctic water. Spring concentrations were clearly higher along the entire transect in May 1998. A large interannual variability was seen between the two summer samplings since the July 2001 surface DMSPd values reached 100 nM in the Atlantic end of the transect and only matched the July 1999

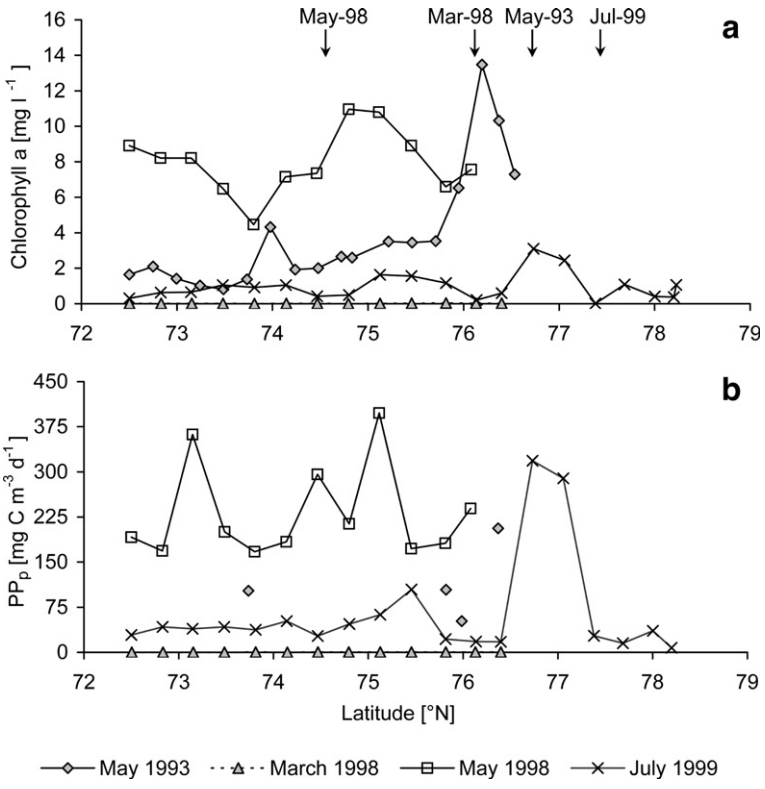

Fig. 3. Chlorophyll *a* concentration (a) and particulate primary production (b) in surface waters of the Barents Sea during March 1998, May of 1993 and 1998, and July of 1999. The arrows indicate the location of the southernmost extent of the Polar Front.

Table 2
Average values and standard deviations (in parenthesis) for all stations (n=12–21 stations per cruise) in surface waters (0–3 m) of a transect in the Barents Sea, from 72.5° to 78°N, sampled once during late winter, twice in spring and twice in summer

	March '98	May '93	May '98	July '99	July '01
DMSPp [nM]	5.9 (4.4)	17.6 (6.3)	5.2 (2.7)	9.5 (8.8)	50.0 (29.9)
DMSPd [nM]	3.4 (2.9)	14.0 (9.5)	22.2 (16.3)	7.9 (4.2)	43.0 (32.1)
DMSPt [nM]	10.0 (6.8)	31.7 (12.7)	39.2 (19.5)	17.6 (11)	93.0 (50.6)
Chl *a* [mg m^{-3}]	0.01 (0.01)	3.8 (3.2)	7.9 (1.8)	0.9 (0.7)	
PPpart [mg C m^{-3} d^{-1}]	0.2 (0.1)	116.0 (64.6)[a]	231.1 (78.8)	65.0 (86.9)	
PPdiss [mg C m^{-3} d^{-1}]	0.2 (2.8)	64.2 (60.0)	183.6 (182.5)	61.5 (36.5)	
POC [mg C m^{-3}]	52.7 (13.5)		559 (209)	265 (40)	
C:S [mg mg^{-1}]	317 (14)		2961 (209)	873 (40)	
DMSPp: chl *a*	905 (670)	7.5 (5.5)	0.7 (0.4)	11.6 (8.1)	
DMSPd: chl *a*	473 (418)	5.1 (3.5)	4.9 (4.4)	50.5 (174.2)	
DMSPt: chl *a*	1270 (1078)	12.6 (8.3)	5.6 (4.4)	86.4 (276.5)	
DMSPp:DMSPd	1.57 (1.36)	1.7 (0.9)	0.6 (0.2)	1.4 (1.2)	2.0 (2.5)

PP=primary production; C:S=POC/DMSPp-S; other abbreviations as in text.
[a] N=4 stations.

DMSPd levels under the ice. Otherwise, the July 1999 DMSPd levels were much lower and intermediate between winter and spring concentrations.

Chl *a* concentrations were very low at all stations during late winter (Fig. 3a) as was surface primary production (Fig. 3b, Table 2). Both chl *a* and primary production increased as the seasons progressed with maximum values found during the spring. Spring of 1998, however, was characterized by significantly higher chl *a* concentrations and primary production levels than the spring of 1993 along most of the transect, except at the North end, in Arctic waters. Chl *a* concentrations were highest at the ice edge bloom, located in Arctic waters during spring. Chl *a* and primary production decreased further North, under the ice. In summer, chl *a* concentrations were lower than during spring periods in Atlantic and Arctic waters, but the increase in the MIZ was still present. A corresponding pattern is observed for primary production in summer, with increased carbon uptake in the MIZ.

3.2. Vertical gradients

The vertical distribution of plankton-derived sulfur and carbon compounds in the Barents Sea also changed seasonally (Figs. 4 and 5). In general, surface values were similar to deep values during low production periods, and thus good estimators of overall concentration. On the other hand, surface and subsurface values were, on the average, higher than at depth (>50–75 m) during productive periods. Similar to surface transects, vertical profiles showed spatial and interannual variability. The most salient points are summarized below.

3.2.1. DMSP gradients

Winter concentrations of DMSPp (March 1998) were low and uniform with depth (Fig. 4a). In the spring, DMSPp values were either higher (May 1993) or similar (May 1998) (Fig. 4b,c) to winter values. In May 1993, the North–South gradient showed maximum surface and subsurface values in the MIZ, with intermediate values at the ice edge (Station 1) and lowest in the South (Station 4). Lower, winter-like values were observed at depths deeper than 50–80 m. In contrast, DMSPp in May 1998 did not show vertical or horizontal structure, did not surpass winter values, and higher subsurface values were seen only in some stations (Fig. 4c).

Summer concentrations of DMSPp showed vertical structure as well as a North–South gradient, with maximum subsurface values in the southern stations (Fig. 4d), unlike chl *a* (Fig. 4h). The vertical structure was shallower, with higher concentrations in the upper 20 m, than during productive periods in spring; the exception was the southernmost Station 5 where concentration remained high down to 80 m. In summary, DMSPp maxima were seen in spring and summer. Because of the relatively high winter DMSPp values that can be seen also at depth in all seasons (Fig. 4a), the maximum values of 40 nM were only about 10 times the minimum concentration.

The vertical and seasonal distribution of DMSPd was more closely related to overall phytoplankton biomass (as chl *a*) than DMSPp. In general, lower values were measured in winter, highest in spring (both in 1993 and 1998) and intermediate values in the summer (Fig. 5a–d). In winter, DSMPd concentrations were low but had some variability in the upper 30 m (Fig. 5a), and concentrations reached 20 nM. In the spring,

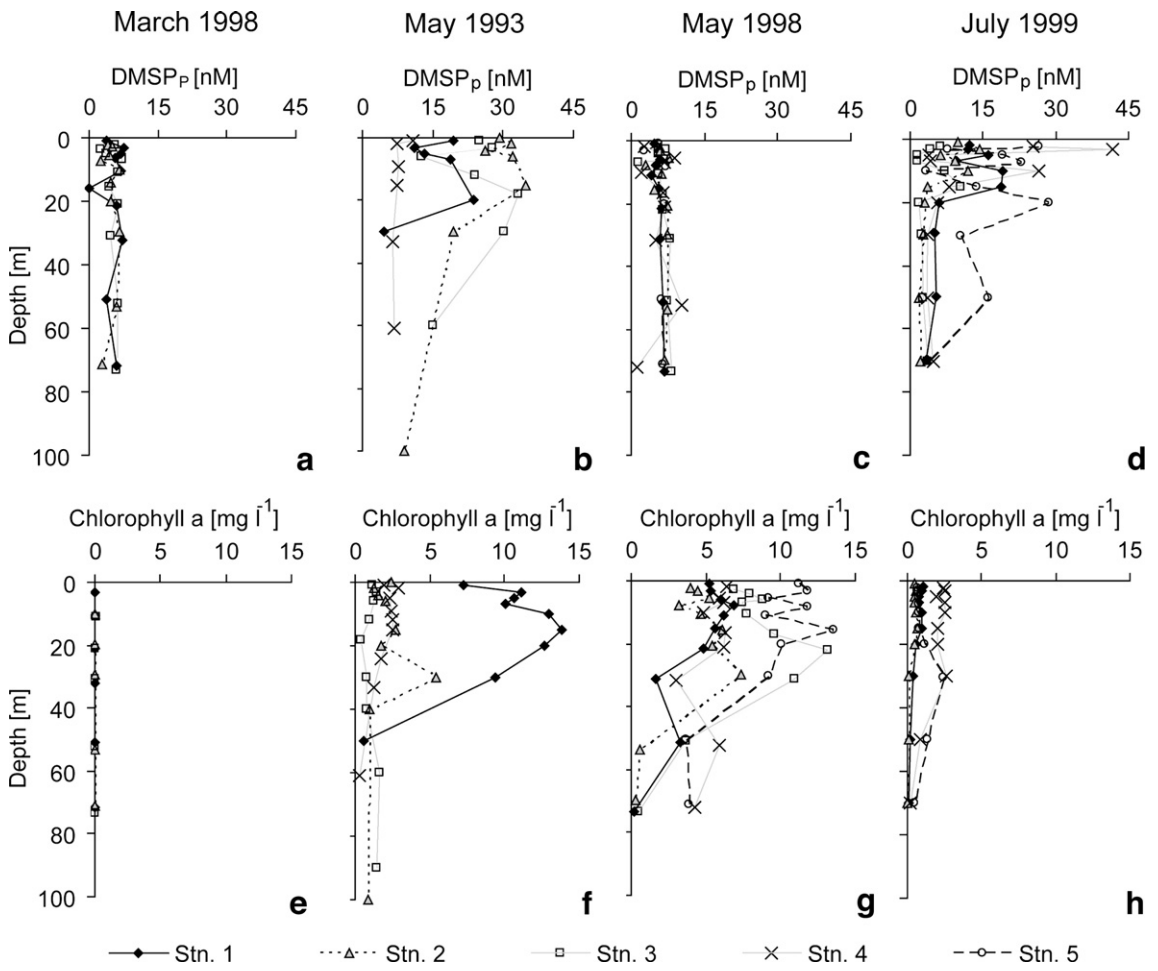

Fig. 4. The vertical distribution of DMSPp and chlorophyll *a*, respectively, in late winter (March 1998) (a,e), spring (May 1993 and 1998) (b and c; f and g), and summer (July 1999) (d, h) from the marginal ice zone (St. 1) to ice-free waters (St. 5). Chl *a* data for St. 3 in July 1999 is not available.

DMSPd either showed subsurface or surface maxima (stations 2 and 3 in Fig. 5b). In May 1998, DMSPd concentrations were similar to those of May 1993 (Fig. 5c), except for the southernmost, ice-free station where maximum concentrations of 80 nM were measured at 18 m depth. Summer values were higher in the upper 40 m but the vertical gradients were not pronounced (Fig. 5d). Deep summer values (>50–80 m) were similar to upper water column winter values, as in the case of DMSPp. In summary, the horizontal and vertical variability of DMSPd was higher than for DMSPp (Table 2), with a range of concentrations measured across 2 orders of magnitude.

Vertical concentrations found in the ice edge (Fig. 6) followed the seasonal pattern of distribution observed throughout the Barents Sea and did not show different dynamics. The most salient points were the higher DMSPp and DMSPd concentrations in summer, similar to spring values, and the highest overall phytoplankton production and biomass of the region.

3.2.2. Chlorophyll a and primary production gradients

Winter phytoplankton biomass, measured as chl *a* concentration, was very low and constant with depth (Fig. 4e). Maximum values were seen in spring, with highest overall values in May 1998. May 1993 showed a stronger North–South gradient (Fig. 4f) where only the station at the ice edge had large phytoplankton accumulation. The summer chl *a* distribution is quite homogeneous in the upper 20 m of the water column, with some indication of subsurface chl *a* maxima (Fig. 4h). In summary, surface chl *a* values were representative of subsurface (0–70 m) values, and the North–South gradient seen in Fig. 3a was representative of water column biomass. The range of chl *a* concentrations included spring values over 100 times the winter values

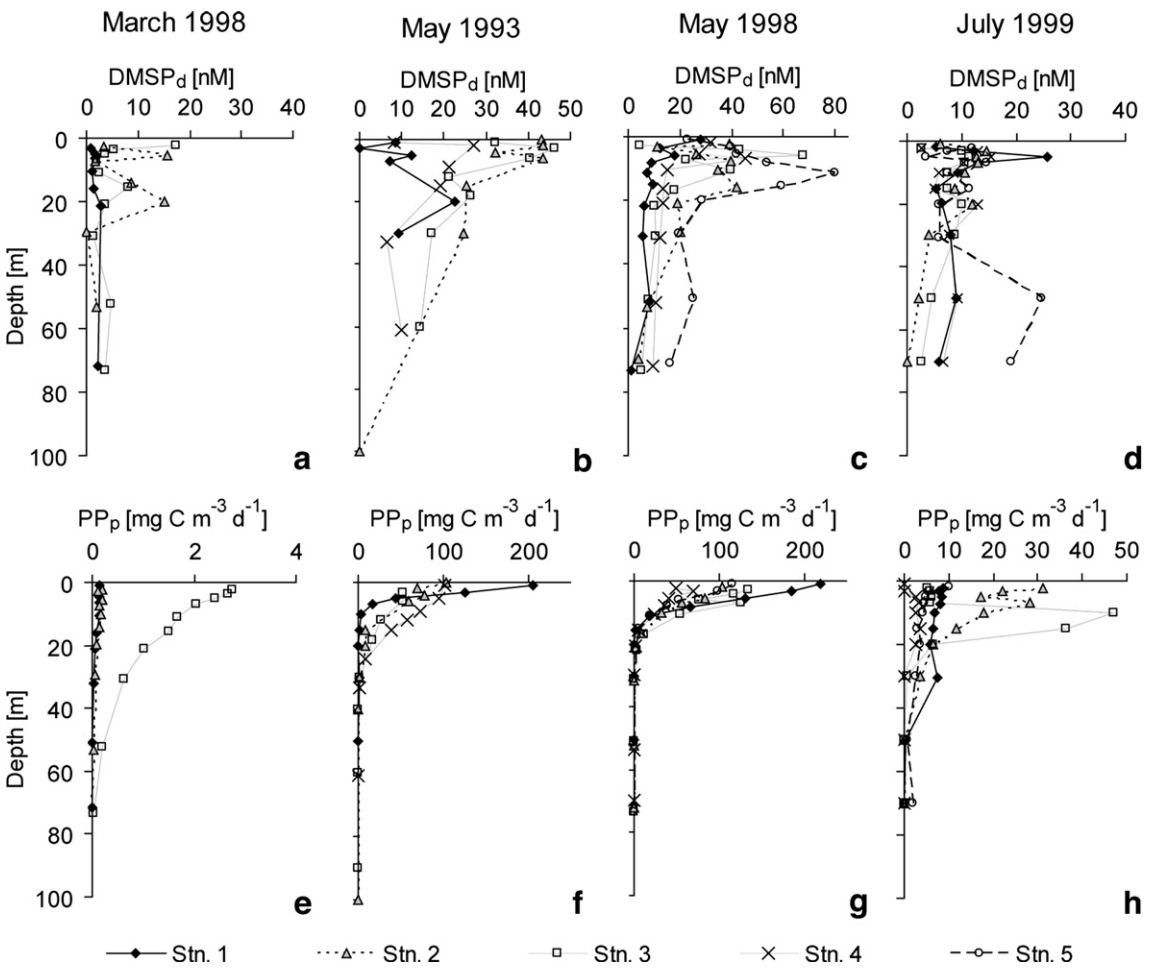

Fig. 5. Vertical distribution of DMSPd in (a) March 98, (b) May 1993, (c) May 1998, (d) July 1999 and particulate primary production for the same periods (e–h, respectively) from the marginal ice zone (St. 1) to ice-free waters (St. 5).

(Table 2), well exceeding the DMSPp range observed throughout the growth season.

Phytoplankton primary productivity showed the highest vertical and seasonal gradients. Winter rates were lowest, with measurable production only in ice-free waters (Stn. 3, Fig. 5e). Both springs (1993 and 1998) had the highest rates, always with a surface maximum. However, while primary production was highest at the southernmost station in May 1998 (Fig. 5g), it was highest at the ice edge in May 1993 (Fig. 5f), followed by production in ice-free waters. Summer primary production levels were between winter and spring values, as for chl *a*, with a similar overall seasonal range of maximum values of over 100-fold. Summer was the only time when pronounced subsurface maxima of productivity were observed; otherwise, the rates were uniform in the top 20 m of the water column.

3.3. Interactions within and between sulfur pools and carbon pools and production

When data are combined ($n=250$), two well-defined trends between DMSPp and DMSPd become apparent (Fig. 7). One relationship includes stations sampled in March 1998, May 1993 and July 1999 (DMSPd:DMSPp ratio ~1) while the second relationship includes stations from May 1998 (DMSPd:DMSPp ratio ~5). If DMSPp and DMSPd values for July 2001 are included, they fall also in the first group with similar proportions of both DMSP pools. These relationships are still clear when integrated values are used (Fig. 8a).

The relationship between integrated DMSPp and phytoplankton biomass (Fig. 8b), measured as chl *a*, also shows two populations: stations from March 1998, most of May 1993 and July 1999 when higher DMSPp is associated with higher chl *a* (DMSPp:chl *a* ~11)

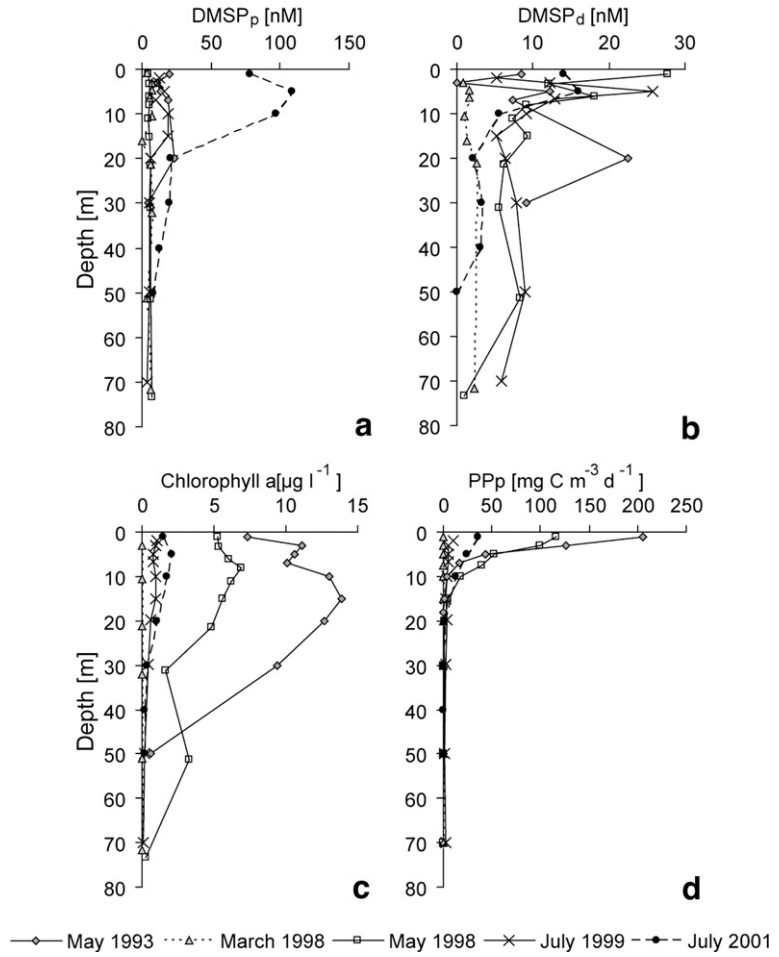

Fig. 6. Ice edge vertical gradients of carbon and sulfur in March 1998, May 1993 and 1998 as well as July 1999 and 2001; (a) DMSPp, (b) DMSPd, (c) chlorophyll *a*, (d) particulate primary production.

while a second population has a rather constant range of values of DMSPp at all chl *a* concentrations (DMSPp: chl *a* <1). This second group includes stations from May 98 and an ice edge station from May 1993; May 1998 had exceptionally low DMSPp to chl *a* ratio, due to low DMSPp concentrations (similar to winter values) and high chl *a* concentrations.

The relationship between integrated DMSPd and chl *a*, on the other hand, does not show any grouping of stations (Fig. 8c). In general, data from March 1998, May 1993 and July 1999 are concentrated over low chl *a* values and stations from May 1998 are towards high chl *a* concentrations. However, the cruise averages of integrated data (Fig. 8c) provide an average DMSPd:chl *a* ratio of ~5.

As expected, there is a positive correspondence among total particulate carbon (POC), chl *a* and primary

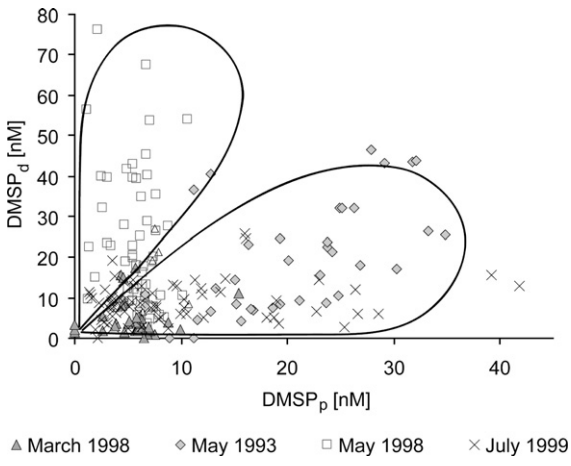

Fig. 7. Surface concentrations of DMSPd vs. DMSPp in the sampled transects for March 1998, May 1993 and 1998, and July 1999.

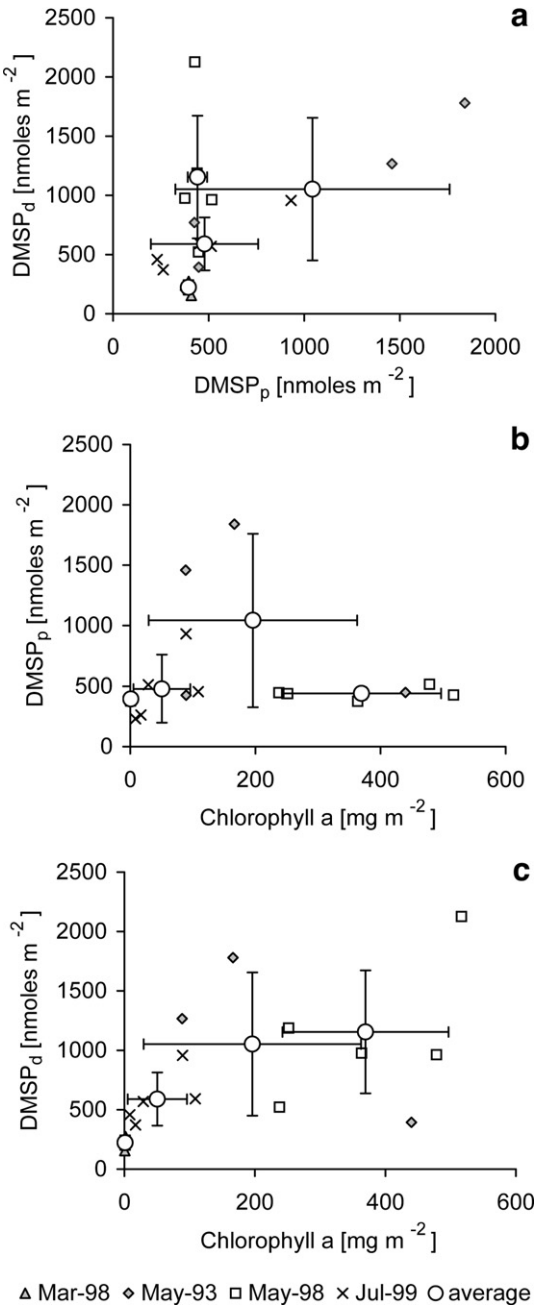

Fig. 8. Integrated values per station and cruise averages for (a) DMSPd vs. DMSPp, (b) DMSPp vs. chlorophyll *a* and (c) DMSPd vs. chlorophyll *a* in the sampled transect for March 1998, May 1993 and 1998, and July 1999.

production over the euphotic zone, indicating phytoplankton was a major contributor to suspended carbon. Although POC was present when chl *a* was undetected in late winter, POC accumulated slower than chl *a* over the seasons, i.e., the SIZ was enriched in chl *a* (Fig. 9a).

Daily primary production increased with chl *a* concentration, peaking at an optimum biomass of ~200 mg chl *a* m^{-2} and decreasing thereafter (Fig. 9b). The pattern of particulate and dissolved carbon production followed each other, although a higher proportion of dissolved production was observed after the peak of activity. Finally, primary production and POC correlated linearly

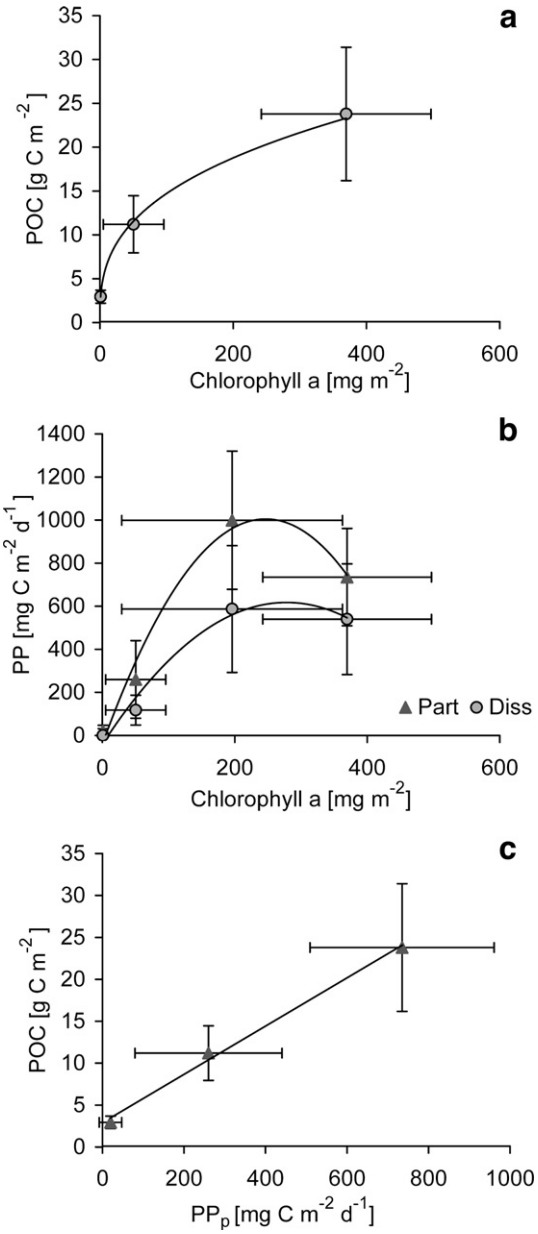

Fig. 9. Large-scale spatial and temporal relationships between integrated, cruise averaged phytoplankton estimators in the Barents Sea. (a) POC vs. chlorophyll *a*, (b) primary production vs. chlorophyll *a*, and (c) POC vs. primary production. Error bars indicate 1 standard deviation.

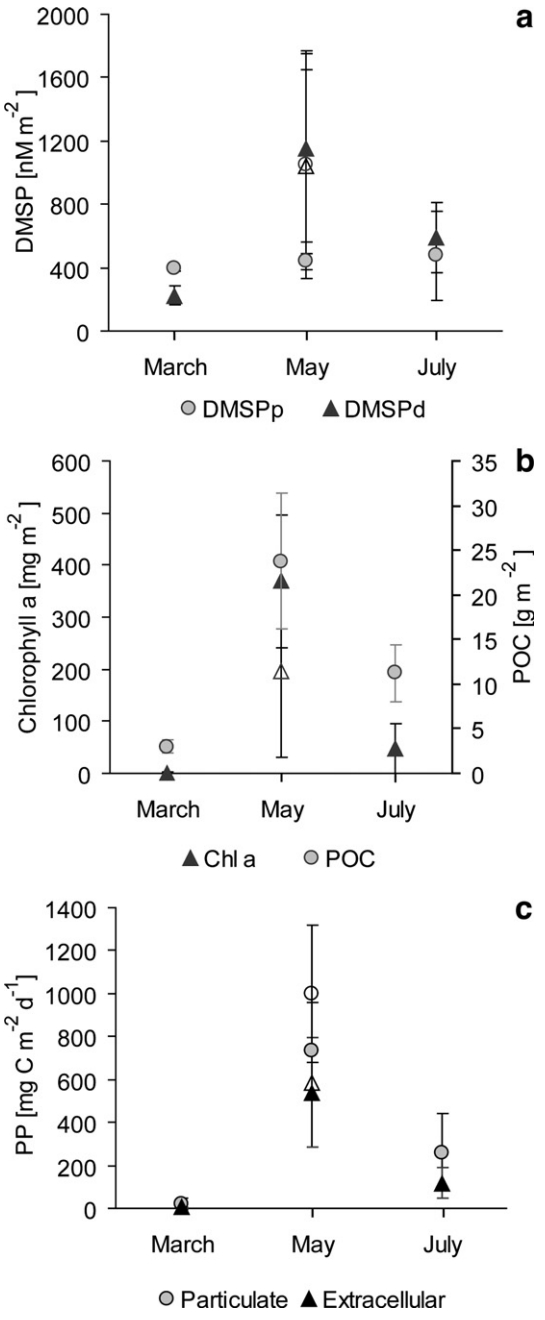

Fig. 10. Seasonal means and standard deviations of integrated particulate and dissolved DMSP (a), chlorophyll *a* and particulate organic carbon (b), and particulate and extracellular primary production (c) in the Barents Sea for winter 1998, spring of 1993 (open symbol) and 1998, and summer of 1999. POC data for May 1993 is not available.

(Fig. 9c) with a background POC value of 2.5 mg m^{-2} from the winter (Fig. 10c) that was not related to chl *a* or primary production.

4. Physical and chemical characteristics of the SIZ

The transects covered permanently ice-free waters dominated by Atlantic water in the South to waters subjected to the ice melt, the Polar Front and finally the ice-covered Arctic waters (Fig. 2a,b). The transect's northward extension increased from late winter to summer and was strictly a function of ice cover. The winters of 1993 and 1998 had normal-to-intermediate ice cover, while the winters of 1999 and 2001 had below average ice cover (Reigstad et al., 2002). The hydrography of the study area in 1993 and 1998/99 has been described in detail by Wassmann et al. (1999) and Reigstad et al. (2002), respectively, and is summarized below. Similar data are not available for July 2001.

In general, the transition from Atlantic water in the south to Arctic water in the north was observed regardless of the season; however, the northward inflow of Atlantic water appeared to be stronger in summer of 1999 (Reigstad et al., 2002). Early thermal stratification in Atlantic waters and the presence of a shallow halocline further north characterized both spring periods sampled (May 1993 and 1998); a southward displacement of the Polar Front as well as intrusions of Central Bank water were also observed at this time. In July 1999, the stratification had increased even further, with warmer and saline waters observed up to the Polar Front and a strong melt water surface layer further north.

Nutrient concentrations in March of 1998 were high, characteristic of winter values (i.e., 5–6 μM silicic acid and 10–12 μM nitrate) (Sakshaug et al., 1994) and homogeneously distributed with depth. A North–South nutrient gradient was evident in spring, with nutrient depletion observed in the mixed layer and being strongest in ice-covered Arctic waters. An exception was observed at the ice edge, within the fluctuating MIZ, where nutrient concentrations were still measurable. In May 1998, MIZ waters had somewhat lower average nutrient concentrations than in 1993. The strong thermal stratification in July 1999 was also reflected by a strong nutrient depletion in surface waters along the entire transect (although ammonium concentrations from the Barents Sea are largely unknown, see Kristiansen et al., 1994), except, again, at the ice edge where higher nutrient concentrations were measured, similarly to the spring cruises (Reigstad et al., 2002).

5. Discussion

The new data presented here give for the first time a glimpse of large-scale organic sulfur dynamics in Arctic shelf waters. First, seasonality was observed, as expected.

Second, summer values must be considered in Arctic organic sulfur budgets, as shown by the July 2001 values, indicating historical sampling emphasis during the spring bloom (Rey and Loeng, 1985; Matrai and Vernet, 1997; Sakshaug, 1997; Vernet et al., 1998; Kogeler and Rey, 1999; Wassmann, 2002) is insufficient to describe the growth season. Third, there seemed to be an out of phase temporal dynamics between carbon and sulfur biomass as represented by chl *a* and DMSPp pools. This translated into variable POC:DMSPp-S ratios at different times of the year (Table 2). Carbon signals showed a better defined and more conspicuous spring maximum while a less defined signal was seen in the pools of DMSPd and DMSPp. Fourth, winter DMSPp concentrations were high, suggesting other sources in addition to phytoplankton. Finally, the ratio of DMSPp:DMSPd was unexpectedly low under certain conditions of nutrient limitation and high phytoplankton accumulation.

Variability in the sulfur and carbon organic pools was observed spatially and seasonally. Mesoscale variability was high, and surface concentrations changed, when crossing into different water masses, from the Norwegian Coastal Current to Atlantic waters going from South to North (Figs. 2 and 3), and into different ice regimes. The expected enhanced biomass and growth earlier described for the Barents Sea MIZ (Niebauer and Alexander, 1985; Rey and Loeng, 1985; Smith and Nelson, 1986) changed seasonally (Fig. 10), especially at the ice edge where the relative importance of the phytoplankton biomass and production to the overall regional production was also a function of the time of the year (Table 3). This is to be expected if spatial distribution of the phytoplankton bloom is a proxy for its temporal development, as shown previously (but see Rey and Skjoldal, 1987; Falk-Petersen et al., 2000; Reigstad et al., 2002; Wassmann, 2002). Here we discuss the underlying factors determining the spatial and temporal variability in carbon and sulfur and the resulting POC:DMSPp-S relationships, within the context of what is known of phytoplankton dynamics in the Barents Sea.

Table 3
Integrated values (surface to 50 m) for the ice edge in late winter, spring and summer

	March '98	May '93	May '98	July '99	July '01
DMSPp [nanomoles/m^2]	409.0	448.0	447.1	513.5	1931.8
DMSPd [nanomoles/m^2]	154.6	393.4	571.7	560.2	225.8
Chl a [mg/m^2]	0.74	439.9	237.6	29.0	40.7
POC [g/m^2]	2.14		34.4	13.3	16.3
PPpart [mg/m^2/d]	3.38	814.0	719.0	164.2	312.1
PPdiss [mg/m^2/d]	8.20	530.0	363.0	127.3	

PP = primary production; other abbreviations as in text.

5.1. Seasonal development

A modeling study (Gabric et al., 1999) predicted that spring phytoplankton bloom activity, including the conversion of DMSPd to DMS, would cease by late June (Matrai and Vernet, 1997), which field data no longer support. The system continues to synthesize DMSP through the summer and, if the July 2001 values are indicative, DMS fluxes could also be highest in summer. DMS concentrations are primarily a function of its precursor DMSPd concentrations, of biological consumption of DMS and DMSPd, and of ventilation (Simo, 2001). However, significantly reduced rates of DMSPd consumption have been reported at colder temperatures (4 °C), preferentially resulting in DMS production, rather than following the demethylation pathway (no DMS release) more commonly seen in temperate waters (Kiene and Service, 1991). Since DMSP was present in winter, spring and summer in the Barents Sea (Fig. 10a), the source dynamics of its main breakdown product, DMS, of climatic relevance, need to be incorporated in regional climate modeling (Anderson and Kaltin, 2001).

Our winter data suggest a heterotrophic source for DMSPp. It would explain late winter high concentrations (Fig. 2) when phytoplankton biomass was lowest and dominated by unidentified flagellates (Fig. 11), most likely heterotrophic (Rat'kova and Wassmann, 2002). Ice protists are known to seed the vernal bloom and some have high levels of DMSPp (Levasseur et al., 1994) while high concentrations of DMSP have been observed in sea ice (e.g., DiTullio et al., 1998; Trevena et al., 2003). Thus, ice micro-organisms recently released into the underlying water might also account for the enhanced DMSPp concentrations in late winter (but see Rat'kova and Wassmann (2002), Ratkova and Wassmann (2005)). The background POC of 2.5 mg m^{-2} observed in the winter also suggests that about 10% of the maximum water column POC (Fig. 10b) may be heterotrophic or detrital organic carbon. This interpretation is further supported by Verity et al. (2002) who reported as much as 47% of carbon as heterotrophic and/or detrital carbon, including bacteria, for the Barents Sea in summer 1999. A possible contribution of high DMSPp by co-occurring flagellates might not be ubiquitous in Arctic shelf waters, however. Flagellate biomass was not significant at any time during the April–September Arctic NOW polynya study, where continued diatom-dominance translated

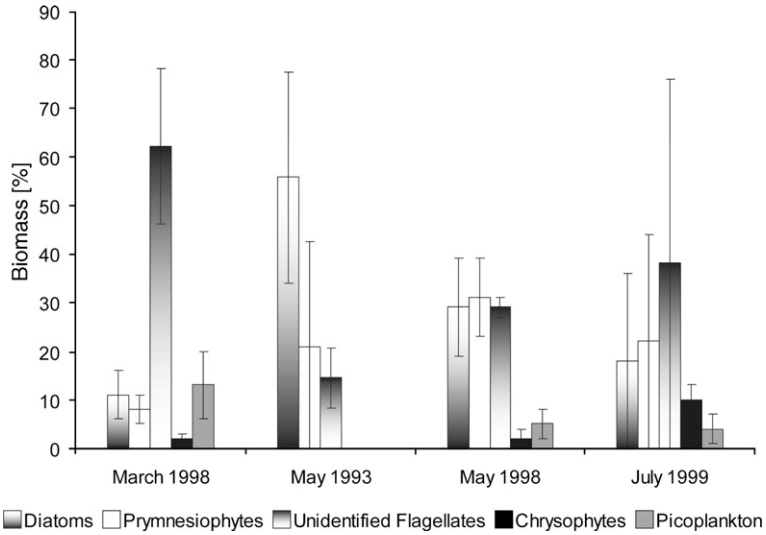

Fig. 11. Phytoplankton carbon biomass (%) (mean and standard deviation) in surface waters of the Barents Sea during winter/fall 1998, spring of 1993 and 1998, and summer of 1999.

into lower DMSP concentrations for the entire period (Bouillon et al., 2002; Lovejoy et al., 2002), unlike the Barents Sea observations.

5.2. Predicting DMSP-S from carbon dynamics

The particulate and dissolved pools of DMSP are connected in a dynamic manner by food web processes (Simo, 2001) such that changes in their combined (DMSPt) abundance and production may better reflect the biocomplexity of its cycling. In the Barents Sea, mesoscale DMSPt concentrations may be modeled from phytoplankton production (particulate and/or extracellular) (Fig. 12b), rather than from phytoplankton biomass. It is very interesting to note that there was a significant DMSPt pool in winter, not unlike those observed in spring and summer. DMSP was present despite an effectively non-existent chl *a* pool or any primary production (i.e., no autotrophic activity) (Fig. 3), but with some POC present (Fig. 12, Tables 2 and 3) that resulted in sulfur enrichment of the particulate organic matter and suggest pre-bloom conditions. Such winter DMSP concentrations are also comparable to values recorded year round in temperate and tropical regions (e.g., Dacey et al., 1998; Tang et al., 2000). As particle formation increased from winter to spring and summer, DMSPt levels increased as did chl *a*, POC levels and total primary production rates. The specific contribution of the particulate and dissolved DMSP pools in these relationships varied (Fig. 8b and c in the case of chl *a*), with the dissolved pool being larger.

5.3. Other sources of high DMSPd concentrations

The high values of DMSPd may also be explained by variables and processes not studied herein. For example, it has been indicated that grazing affects the DMSPt pool, promoting the release of DMSPd (e.g., Dacey and Wakeham, 1986; Tang et al., 1999; but see Wolfe et al., 1997). The low DMSPp:DMSPd ratio (0.8–1.1) observed in spring 1993 and 1998 and in summer 1999 at the ice edge could be explained by a grazing component. However, both the type of grazers (i.e., macro vs. microzooplankton) and prey (i.e., microphytoplankton vs. nanoplankton) can affect the partitioning of DMSP into particulate and dissolved pools. Ancillary data supports the dominance of microzooplankton during the 1999 summer in the Barents Sea (Olli et al., 2002) as proposed for other Arctic shelf seas, such as the Western Greenland, and Norwegian Seas, in spring (Hansen et al., 1996) and summer (Vernet, 1991; Rat'kova and Wassmann, 2002; Verity et al., 2002). The co-variability of microzooplankton grazers and high DMSPd in Arctic shelf waters indicates this is an important area of future research.

An alternative explanation for elevated levels of DMSPd, over DMSPp, may reside in the difficulty of accurately determining it, as this experimental procedure can affect certain phytoplankton cells, due to possible filtration artifacts, resulting in spurious release of extracellular material (e.g., Turner et al., 1990; Archer et al., 2002; Kiene and Slezak, 2006); however, in our case, the same filtration procedure was used in all

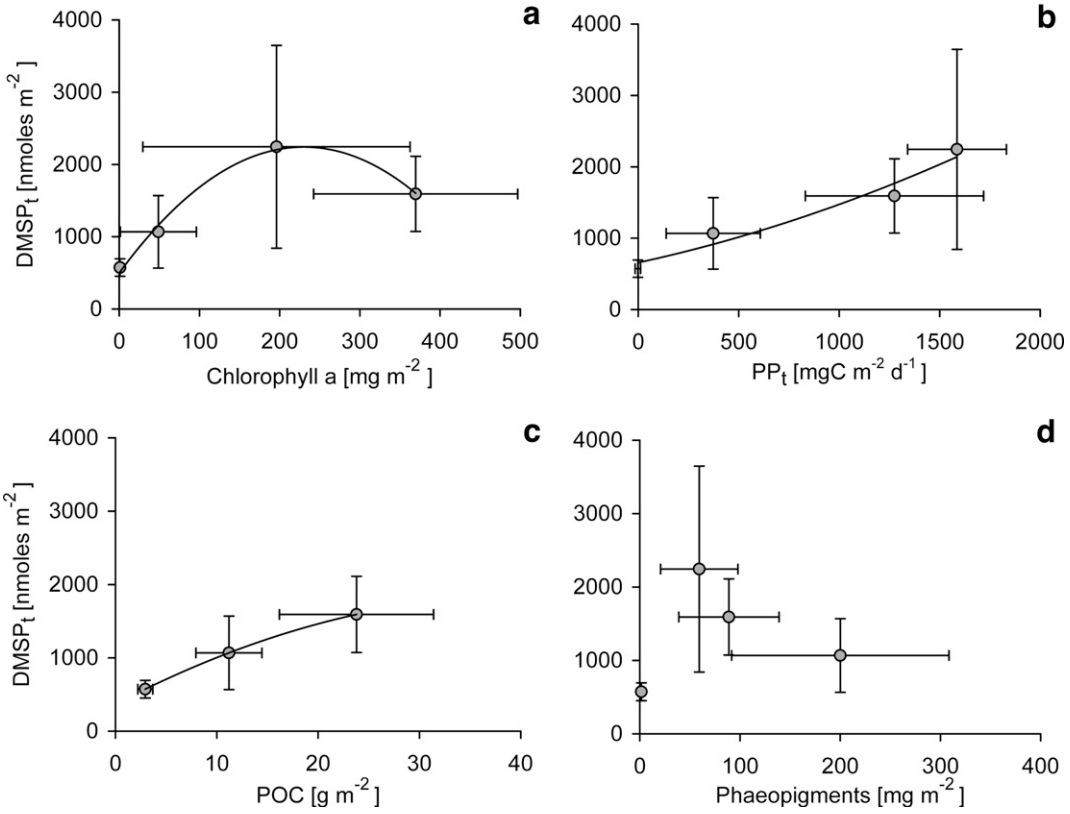

Fig. 12. Integrated, cruise averaged means and standard deviations of DMSP total vs. (a) chlorophyll *a*, (b) total primary production, (c) POC, and (d) phaeopigments. The lines represent a polynomial fit to the data.

cruises and extensive testing of possible filtration disruption for the planktonic system of the Barents Sea showed no biasing between dissolved and particulate pools (Matrai and Vernet, 1997; Vernet et al., 1998; Vernet and Matrai, unpubl. data). We conclude that the high DMSPd values observed are real and resulted from ecological processes.

5.4. Nutrient limitation

We suggest that the reduced nutrient levels observed at the end of the spring bloom (Vernet et al., 1998; Reigstad et al., 2002) may regulate the release of DMSPd in the Barents Sea. Direct phytoplankton exudation of DMSP, whether active or passive, can result in elevated levels in the dissolved fraction (Laroche et al., 1999), similar to the previously mentioned effect of grazing. It should be noted that viral action and depressed bacterial consumption can also lead to high DMSPd concentrations (Simo, 2001) but such data are not available for the Barents Sea, except in May 1993 (Matrai and Vernet, 1997). In our results, May 1998 had a lower DMSPp: DMSPd ratio (Fig. 7), concomitant with a higher proportion of the carbon uptake being released extracellularly, than May 1993 (Table 2). May 1998 differed from May 1993 in that the onset of nutrient limitation occurred earlier (Reigstad et al., 2002) and that the main limiting nutrient was nitrate. This suggests that the SIZ spring bloom in 1998 was at a later stage of development, on the average, than in 1993. It is possible that nitrate limitation, affecting all algae, may result in stronger extracellular release at the community level than the mostly silicate limitation, affecting only diatoms, in May 1998 and thus explain the higher DSMPd.

A similar release of DMSPd has been observed in aging, nutrient-depleted phytoplankton cells kept in cultures (Matrai and Keller, 1994) as well as in late stage blooms of another prymnesiophyte *Emiliania huxleyi* (Malin et al., 1993; Matrai and Keller, 1994). Stefels (2000) also suggests that DMSP exudation may be enhanced under unbalanced growth conditions due to nutrient scarcity and mediated through algal and bacterial enzymes. Such DMSP-lyase activity has been reported for Antarctic waters (Harada and Kiene, 2005)

and enzymatic activity in general has been shown to be significant in Arctic waters (Huston and Deming, 2002).

Extracellular release is a ubiquitous characteristic of Barents Sea MIZ phytoplankton, which have been shown to release 36–55% of their total (particulate+dissolved) carbon uptake while healthily growing, especially in waters dominated by *Phaeocystis pouchetii*, *Chaetoceros socialis* and *Thalassiossira* sp. (Vernet et al., 1998). This pattern was repeated in the MIZ in spring of 1998 when 34–53% of the primary production was measured as extracellular carbon (mucilage and dissolved organic carbon), increasing from below detection in March 1998 to 735±226 mg C m^{-2} d^{-1} in spring of 1998, and was a factor of ca. 2 higher than in the summer (July 1999). The higher proportion of dissolved production observed after the peak of activity (Fig. 9b) suggests more of the newly formed carbon was excreted from the cell at high chl *a* concentration. This enhanced overall, extracellular carbon release can only increase the pool of DMSPd. Furthermore, the relationship between averaged, integrated DMSPd concentrations and dissolved primary production was highly significant (March 1998, May 1993 and 1998, July 1999) ($r^2=0.99$, $p<0.01$) (Fig. 10). Our data thus support using the average fraction of primary production measured extracellularly as an index of DMSPd exudation. Another related source of DMSPd is that released from the mucilaginous fraction in these waters (measured as 10–18% of the DMSPt pool in May 1993, Matrai and Vernet, 1997). Proposed mechanisms are the enzymatically-mediated release of DMSPd or a breakdown of the mucilaginous assembly (Chin et al., 1998).

Nutrient limitation in the Barents Sea may reduce overall community biomass and DMSPp levels, changing the DMSPp: chl *a* ratio. A higher DMSP: chl *a* ratio may be due to stronger representation by DMSP-producing plankton or to a short-term stress DMSP response by phytoplankton to nutrient limitation (Sunda et 2al., 2002). In our study, DMSPp and DMSPt were higher per unit phytoplankton biomass under relatively more nutrient-replete conditions (DMSPp:chl *a*=7–11), (i.e., May 1993 and July 1999, with silicate limitation and leftover nitrate) and lower during nitrate limitation (DMSPp:chl *a*=0.7) (i.e., May 1998) (Fig. 8b, Table 2). Such DMSPp:chl *a* spring ratios were higher than those reported for the NOW polynya with a very different phytoplankton composition (Bouillon et al., 2002) or for ice algae (DMSPp:chl *a*=0.5 in bottom ice) (Levasseur et al., 1994) but lower than those reported for cold, nutrient-replete, non-bloom Antarctic waters (DMSPp: chl *a*=16–60) (Turner et al., 1995 and refs. therein) or temperate waters of the Gulf of Maine in spring (DMSPp:chl *a*=20–100) (e.g., Keller et al., 2004). However, this ratio may also be high because of the presence of DMSPp in non-phytoplankton biomass, either microzooplankton (Tang et al., 2000; Simo et al., 2002), bacteria (Wolfe, 1996), fecal material (Kwint et al., 1996) or detritus (Belviso et al., 1993). Earlier paradigms limited DMSP cycling solely to phytoplankton (Andreae, 1984), resulting in the search for a general relationship between DMSPp and chl *a* that has not proven necessarily strong (Kettle and Andreae, 2000), except in the case of phytoplankton blooms. The lack of correlation between these variables on a global basis is usually attributed to only a subset of the phytoplankton containing DMSP, as indicated earlier (Dacey et al., 1998; Simo, 2001), or due to a vertical mismatch between pigment and DMSPp maxima resulting from different physiological adaptations. Currently, it is generally accepted that the DMSP: chl *a* ratio, while not representative of the absolute magnitude of the DMSP pool, is a good indicator of ecosystem structure (Simo, 2001). We suggest that the high DMSPp:chl *a* observed in the Barents Sea in winter and summer is due to a heterotrophic source and not to nutrient limitation while the high DMSPd:DMSPp ratio is due to nutrient limitation, particularly nitrate.

6. Conclusions

We propose two important factors controlling DSMP dynamics in the Barents Sea. First, nitrate limitation at the end of the spring bloom was the best predictor for low DMSPp:DMSPd ratio (spring 1998), and supports high DMSPd concentrations found under silicate limitation (spring 1993). Second, we propose a heterotrophic source of DMSPp to explain high winter concentrations.

There is predictive power of DMSP concentrations in the Barents Sea based on seasonality and biological variables (Figs. 4–10) but not on physical properties, such as temperature, salinity or water masses encountered along a North–South transect through the seasonal ice zone (Figs. 2 and 3). The predictions are variable and depend on the DMSP fraction as well as on the temporal and spatial scales considered. The surface seasonal signal was the strongest for predicting overall DMSP concentrations (changes in DMSP concentration by a factor of 6); in addition, interannual variability can be very high (changes in DMSP concentration by a factor of up to 10) (Table 2). Spatially, the strongest, most consistent predictor of high DMSP concentration was the ice edge. DMSPp and DMSPd distributions were not spatially related to each other and cannot be used as predictive; their ratio was divided in two main groups (Fig. 7), one of them enriched with DMSPd.

When considering the DMSP fractions independently, DMSPp concentrations were not predicted by chl *a*, total suspended carbon (POC) or primary productivity. DMSPd concentrations can be predicted by chl *a* at the local scale (individual station profile, Figs. 4 and 5) and also regionally (when integrated by depth and cruise, Figs. 8 9 10 and 12). The best prediction was obtained for concentrations of DMSP total at the average regional scale, being related linearly to total integrated primary production (particulate + dissolved) and non-linearly to integrated chl *a*. We recommend determinations of both particulate and dissolved primary production in addition to biomass (as chl *a*) and POC.

Spatial and temporal multi-year patterns of DMSP and other planktonic variables in the pan-Arctic Ocean are still limited. Thus, efforts to synthesize all available data should be supported. Denser data coverage is clearly required for planktonic parameters, extending past spring time, to sample the entire growth season and to establish better climatologies; relationships may then be established between DMSP and parameters which can be measured by, or derived from, remotely-sensed variables. This will help immensely in our understanding of seasonal and interannual DMS and DMSP variability, especially in regions with high spatial and temporal variability in the micro- and mesoscale.

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