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Temporal and spatial distribution of dimethylsulfide in the subarctic northeast Pacific Ocean: a high-nutrient–low-chlorophyll region

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ABSTRACT

Dimethylsulfide (DMS) was measured in the upper 400 m of the northeast Pacific from February 1996 to June 2001. The sampling took place along Line P (48°34.5′N, 125°30′W to 50°N, 145°W). DMS concentrations increased diurnally from a pre-dawn low to a mid-day maximum and from coastal waters to open ocean, in a high-nutrient–low-chlorophyll-*a* (HNLC) water mass. The mean surface DMS in winter was 2 nM, in spring 6 nM and in summer 10 nM. Our June surface DMS amounts were comparable with those obtained by the Pacific Marine Environmental Laboratory. A sea to air flux of DMS at Station P (50°N, 145°W) was high in the summer of 1997 and the early autumn of 1998 and 2000 and was significantly higher than at other Line P stations. The average flux along Line P was 27 μmol m^{-2} d^{-1} by Wanninkhof's formula while that by Liss and Merlivat was 16 μmol m^{-2} d^{-1}. DMS profiles showed a decreasing trend with depth, as did temperature and chlorophyll-*a* (Chl-*a*), but an increasing trend with salinity and nitrate. Average DMS concentrations at mixed-layer depth (DMS_{MLD}) were low in winter at an average of 2.4 nM, moderate in spring at 8 nM and high in summer at 16 nM. For open ocean stations P20 and P26 DMS_{MLD} was high, while Chl-a_{MLD} was low for late spring and early summer during 1996–1998. That is the "summer paradox" phenomenon. The ratio of DMS_{MLD} to Chl-a_{MLD} was out of phase with the mixed-layer depth. Our data confirm the high DMS concentrations previously reported for this region and suggest that this is characteristic of the subarctic HNLC region.

1. Introduction

The surface ocean plays an important role in the global sulfur biogeochemical cycle. Phytoplankton release dimethylsulfoniopropionate (DMSP) when they age (Matrai and Keller, 1993), are grazed by zooplankton (Dacey and Wakeham, 1986; Cantin et al., 1996) or are attacked by viruses (Bratbak et al., 1995). A portion of the dissolved DMSP produced is then cleaved into DMS and acrylate by algal and bacterial DMSP lyases (Wolfe et al., 1994). As the major oceanic volatile sulfur compound, DMS contributes significantly to the atmospheric sulfur budget (Andreae, 1986). Once in the atmosphere DMS is oxidized to produce aerosol particles and nuclei for water droplets, which bring about absorption and scattering of solar radiation (Andreae and Crutzen, 1997). With an increase in atmospheric aerosol particles, the density of cloud condensation nuclei (CCN) would also increase which, in turn, would increase cloud cover. Hence, this effect would have a major impact on the Earth's radiative balance and climate. Charlson et al. (1987) suggested that this could have a cooling effect, of a magnitude as large as one-third of the warming for a doubling of atmospheric CO_2. Thus, sulfate aerosols are thought to have the next largest influence on climate after greenhouse gases (Turner et al., 1996). According to Penner et al. (2001), 70% of the sulfur is from anthropogenic flux due to burning of coal and oil and 30% from natural sources. Of natural sources of sulfur, 8% was due to volcanoes, <1% from coastal wetland, 1% from land and 21% from the ocean, with an uncertainty factor of two. Our knowledge of the global distribution of DMS is far from complete. Penner et al. (2001) pointed out that DMS as an oceanic biogenic sulfur source remains highly uncertain in seasonal coverage and some areas are sparsely sampled. This is definitely true for the northeast Pacific where the DMS global database of Kettle et al. (1999) shows a scarcity of data. The goal of the present study is to fill the gaps with a seasonal time-series of winter (January, February and March), spring (April, May and June) and summer (July, August and September). We measured the DMS concentrations together with other oceanographic variables over 6 yr along a transect

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between the west coast of Canada and station PAPA (50°N, 145°W) in the Gulf of Alaska. The results of this long-term survey are potentially valuable to oceanographers as a means of calibrating basin-scale ecosystem models that are becoming an important component of Earth system models. On a smaller scale, archived data from ocean station PAPA has been frequently used for 1-D model investigations and the information here will certainly help the scientific community to understand the workings of the upper ocean marine ecosystem at this location and its link with DMS. The value of this data set is comparable with a previous time-series (1992–1993) collected by Dacey et al. (1998) for the Bermuda Atlantic Time Series Study (BATS). The study also offers a unique opportunity to assess the influence of El Niño and La Niña regimes in a HNLC oceanic region.

2. Study area and methods

The study area was in the Gulf of Alaska in the northeast Pacific Ocean, mainly in the waters traditionally covered by the research ships of the Institute of Ocean Sciences, Fisheries and Oceans, Canada. This area is in the Pacific subarctic gyre(east) [PSAG(E)], with its southern boundary at 45°N and western boundary at 175°E in a scheme of biogeochemical provinces as defined by Longhurst et al. (1995). In summer, it is characterized by the east-flowing North Pacific Drift, originating from the Kuroshio Current, which bifurcates at about 130°W to 150°W with the clockwise California Current and the anticlockwise Alaska Current. A northward Davidson Current flows along the coast in winter. During spring, relatively fresher water from the Juan de Fuca Strait flows along the coast, primarily within the shallower continental shelf of bottom depth <200 m (Thomson, 1981; Bates et al., 1994). This would affect both the seasonal and spatial variability to be discussed later.

The study period was from February 1996 to June 2001 along Line P in waters off the coast of Vancouver Island at Station P26 (also called Station P or PAPA) and stations P04, P12, P16 and P20 (Table 1 and Fig. 1). Water properties of temperature, salinity, pressure or water depth, oxygen, silicate, phosphate, nitrate and chlorophyll-*a* (Chl-*a*) were also examined.

Sea water samples for DMS were collected using a General Oceanic rosette frame with 10 l Niskin PVC samplers coupled to

Table 1. Positions of Stations along Line P

Station number	Latitude	Longitude	Approx. depth (m)	Distance (km) from P01 (48°34.5′N, 125°30′W)
P04	48°39.0′N	126°40′W	1300	87
P12	48°58.2′N	130°40′W	3300	380
P16	49°17.0′N	134°40′W	3550	672
P20	49°34.0′N	138°40′W	3890	961
P26	50°00.0′N	145°00′W	4200	1420

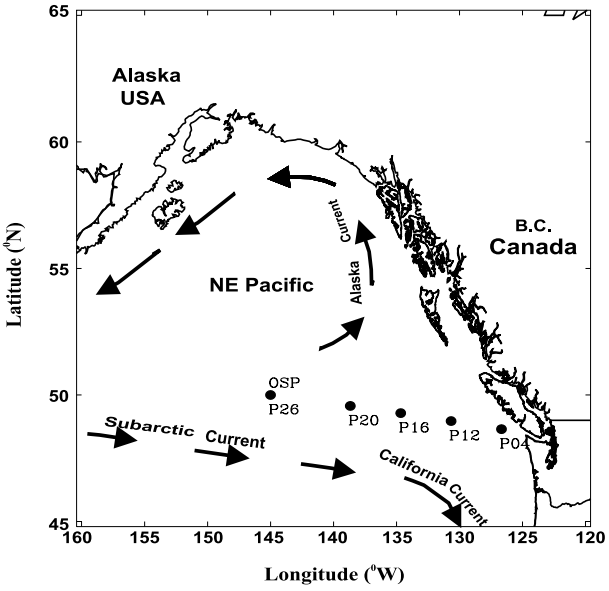

Fig. 1. Locations of the stations P04, P12, P16 and P20 along Line P and Station P (P26) and surface currents in the northeast Pacific Ocean.

a CTD (conductivity, temperature, depth) system, model SBE 11 plus (Seabird Electronics, Seattle, Washington, USA). A Technicon AutoAnalyzer™ was used to determine the concentrations of silicate, phosphate and nitrate. Sea water samples for Chl-*a* were collected with DMS sampling whenever possible. Chl-*a* was determined by filtering sea water through a Whatman GF/F glassfibre filter to retain phytoplankton cells, which were then extracted with 90% acetone for fluorometric determination (Wong et al., 1995).

Subsurface sea water samples were collected from 10 l Niskin PVC samplers mounted on a rosette/CTD system. Sea water was drawn from the Niskin samplers directly into 100 ml precision ground-glass syringes, which were then immersed in a bucket of surface sea water stored in the dark. An aliquot of 20 ml was transferred to a 50 ml gas stripper and purged with ultra-high-pressure nitrogen flowing at 100 ml min^{-1} for 5 min. Gas transfer lines were made of Teflon tubing, except for the portion of fused silica-lined stainless steel located between the extraction system and the gas chromatograph. Water vapour was removed by a cold jacketed condenser set at 4 °C. DMS was captured by a trap (30 cm × 3.2 mm internal diameter, stainless steel) packed with Tenax TA, and immersed in an ethanol cold bath at −25 to −30 °C. The trap was quickly heated to 100 °C to release the DMS into a Hewlett-Packard 5880A gas chromatograph equipped with a flame photometric detector and a Chromasil 330 (Sulpelco 1-1496) packed column that was kept at a constant oven temperature of 50 °C. The primary standard was prepared once a week from a stock solution of dimethylsulfide (Aldrich 471577) in isopropanol. The intermediate and working standards were made up fresh daily in purged, double Milli-Q water and run immediately before analysing each station

profile. The detection limit was 0.08–0.1 nM with an accuracy of >10%. The precision was 23% (*SD* ±21%) for concentrations <0.2 nM, 15% (*SD* ±14%) for concentrations 2–10 nM, 8% (*SD* ±9%) for >10 nM. The overall precision for our data set was 18% (*SD* ±17%). The DMS analytical method and calibration followed Uher (1999), who also described sampling and storage.

3. Results

Our results reveal significant variations in DMS concentrations at all timescales investigated (diurnal, seasonal and interannual) as well as spatially along Line P.

3.1. Diurnal profiles of DMS

Diurnal vertical profiles of DMS for the 0–160 m depth range are displayed in Figs 2a–g for 19–22 May and 27–29 August 1996 at P26, 14–16 June 1997 at P26, 12 June 1998 at P26, 8–11 June and 14 September 2000 at P26 and 21 June 2001 at P20, respectively.

3.2. Surface concentrations of DMS, Chl-a and sea surface temperature

Figures 3a–e show surface concentrations of DMS, Chl-*a* and sea surface temperature for stations P04, P12, P16, P20 and P26 from 1996–2001.

3.3. Profiles of DMS, Chl-a and sea water temperature

Figures 4a–f are profiles of DMS, Chl-*a* and sea water temperature for stations P04, P12, P16, P20 and P26 during winter cruises (January, February and March), spring cruises (April, May and June) and summer cruises (July, August and September) 1996–2001.

4. Discussion

Our study area is in high-nutrient–low-chlorophyll (HNLC) waters. The SERIES (Subarctic Ecosystem Response to Iron Enrichment Study) iron fertilization experiment (Boyd et al., 2004) confirmed that this low chlorophyll is due to a deficiency of iron in sea water around the P26 area. Although the stations along Line P are in the PSAG(E) of Longhurst et al. (1995) they exhibit different characteristics due to their locations and the direction of surface currents in the vicinity. Our stations P04 and P12 are in the coastal waters, P16 in transitional zone and P20 and P26 in the open ocean. The DMS-producing plankton species are different in these zones. Coastal waters are iron-rich, from land runoffs and rivers, which favour diatoms. The open-ocean species are mainly smaller plankton including dinoflagellates and coccolithophorids, particularly *Emiliania huxleyi*, which are good producers of DMSP and DMS (Keller, 1989).

4.1. Diurnal variations

Although not all the diurnal casts were within 24 h, they were from the same water mass as we had verified by density plots

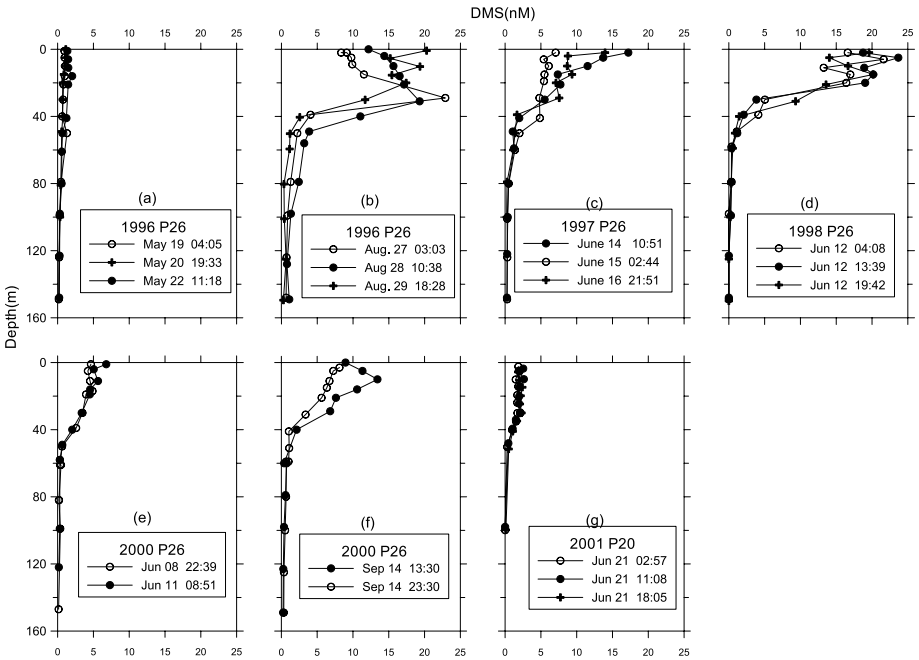

Fig. 2. Diurnal profiles: open circles are for pre-dawn data, solid circles for noon and crosses for dusk. Time is in local time which is 9 h behind UTC (Universal Time Code) during late spring (after April) and summer at P20 and P26.

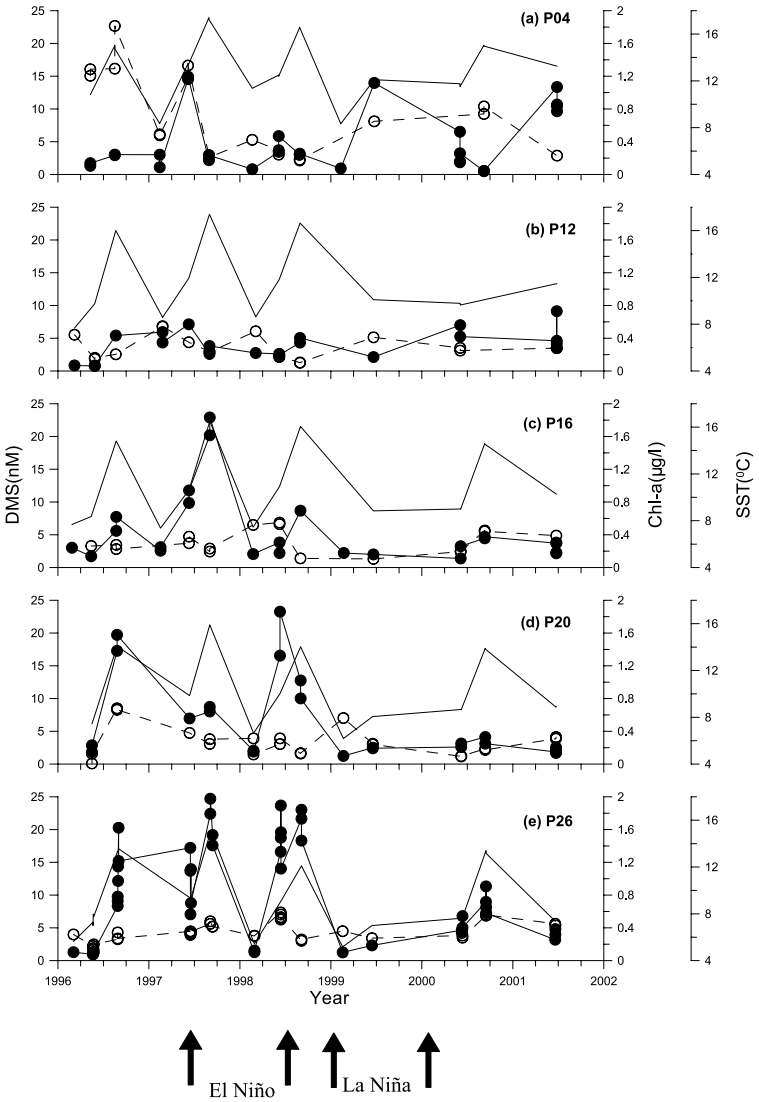

Fig. 3. Surface concentrations for DMS (solid circles), Chl-*a* (open circles) and sea surface temperature (solid line) for stations P04, P12, P16, P20 and P26 from 1996–2001.

(not shown). They can be regarded as quasi-diurnal. Such quasi-diurnal data for different stations, seasons and years are displayed in Figs 2a–g. A few cases are truly diurnal: 12 June 1998 at P26, 14 September 2000 at P26 and 21 June 2001 at P20. The smallest quasi-diurnal changes are in May 1996 at P26 (Fig. 2a), June 2000 at P26 (Fig. 2e) and June 2001 at P20 (Fig. 2g) probably due to the smaller biological changes in spring months. The June 1997 DMS at P26 (Fig. 2c) shows a surface DMS dawn–day–dust change of 10 nM, (7 to 17 nM) with much smaller changes if DMS down to 40 m depth is considered, a range of quasi-diurnal change of just 3 nM. The 12 June 1998 DMS at P26 (Fig. 2d) exhibits a similar pattern with a daytime maximum in the upper 5 m with a range of change of 11 nM, but at 40 m the change is only 3 nM. June 1997 to June 1998 was an El Niño event with high DMS. The summer diurnal change of DMS at P26 (Fig. 2f) has a much larger afternoon DMS and a shallow subsurface maximum. DMS is of biological origin (Andreae, 1986; Leck et al., 1990) and varies with light (Bates et al., 1994; Griffiths et al., 1999) and with photosynthesis by phytoplankton. Summer noon DMS concentrations would have been even higher were it not for the DMS photolysis effect (Toole et al., 2003) due to greater incident UV irradiance during summer daytime.

4.2. *Surface distribution*

Sea surface DMS was high in summer and low in winter. In winter, the mean DMS was 2 nM (0.8–6, $n = 20$). In spring, the mean DMS was 6 nM (0.8–24, $n = 79$). In summer, the mean was 10 nM (0.5–25, $n = 47$).

Time-series of surface DMS, Chl-*a* and temperature were plotted for the five stations on Line P as in Figs 3a–e. In Fig. 3a for station P04 in summer 1996, Chl-*a* is high at 1.8 μg l^{-1} and

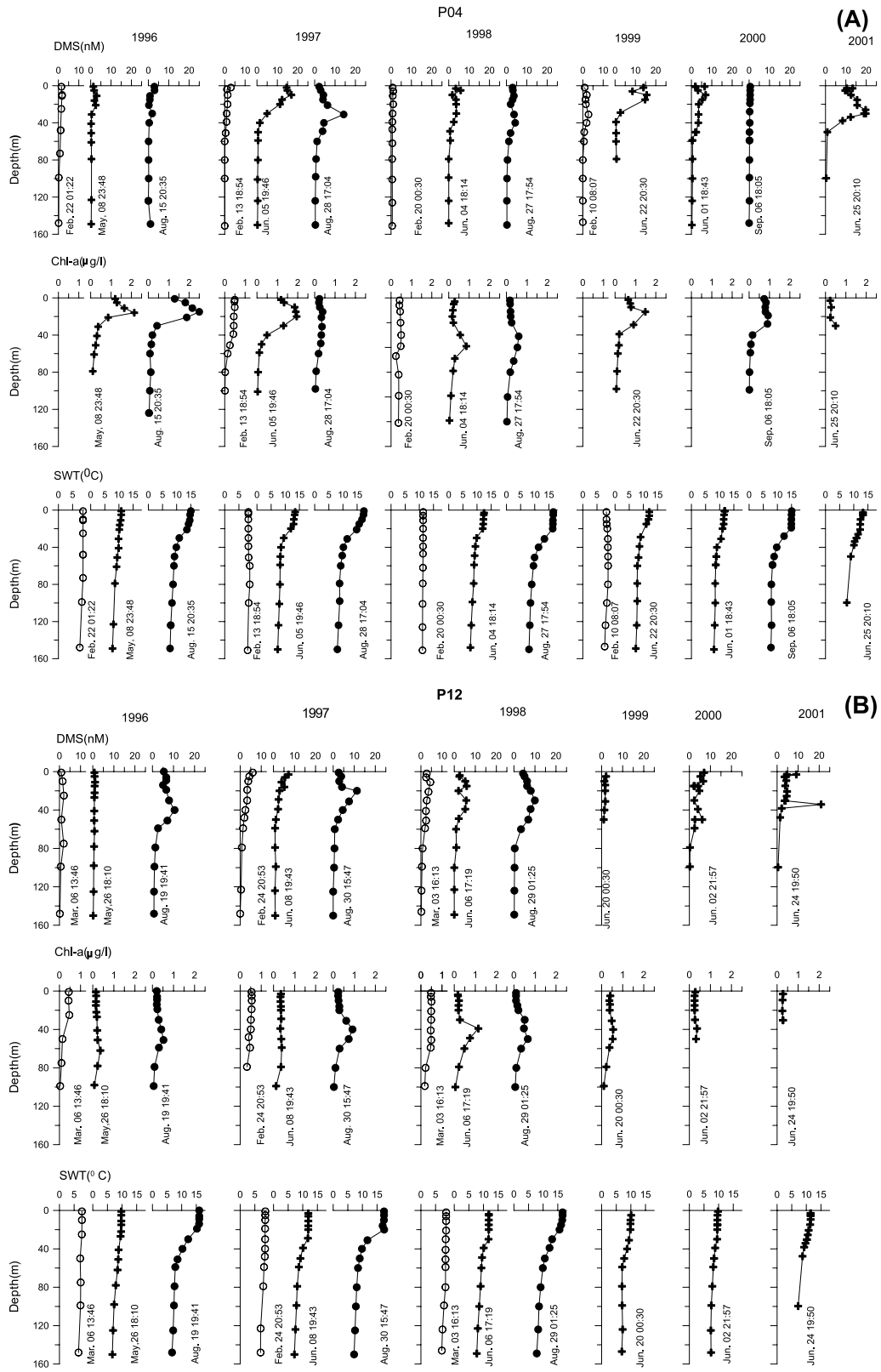

Fig. 4. Profiles of DMS, Chl-*a* and SWT for stations P04 (A), P12 (B), P16 (C), P20 (D) and P26 (E) from 1996–2001. Open circles are for winter (January, February and March) cruises, crosses for spring (April, May and June) cruises and solid circles for summer (July, August and September) cruises and time is in UTC.

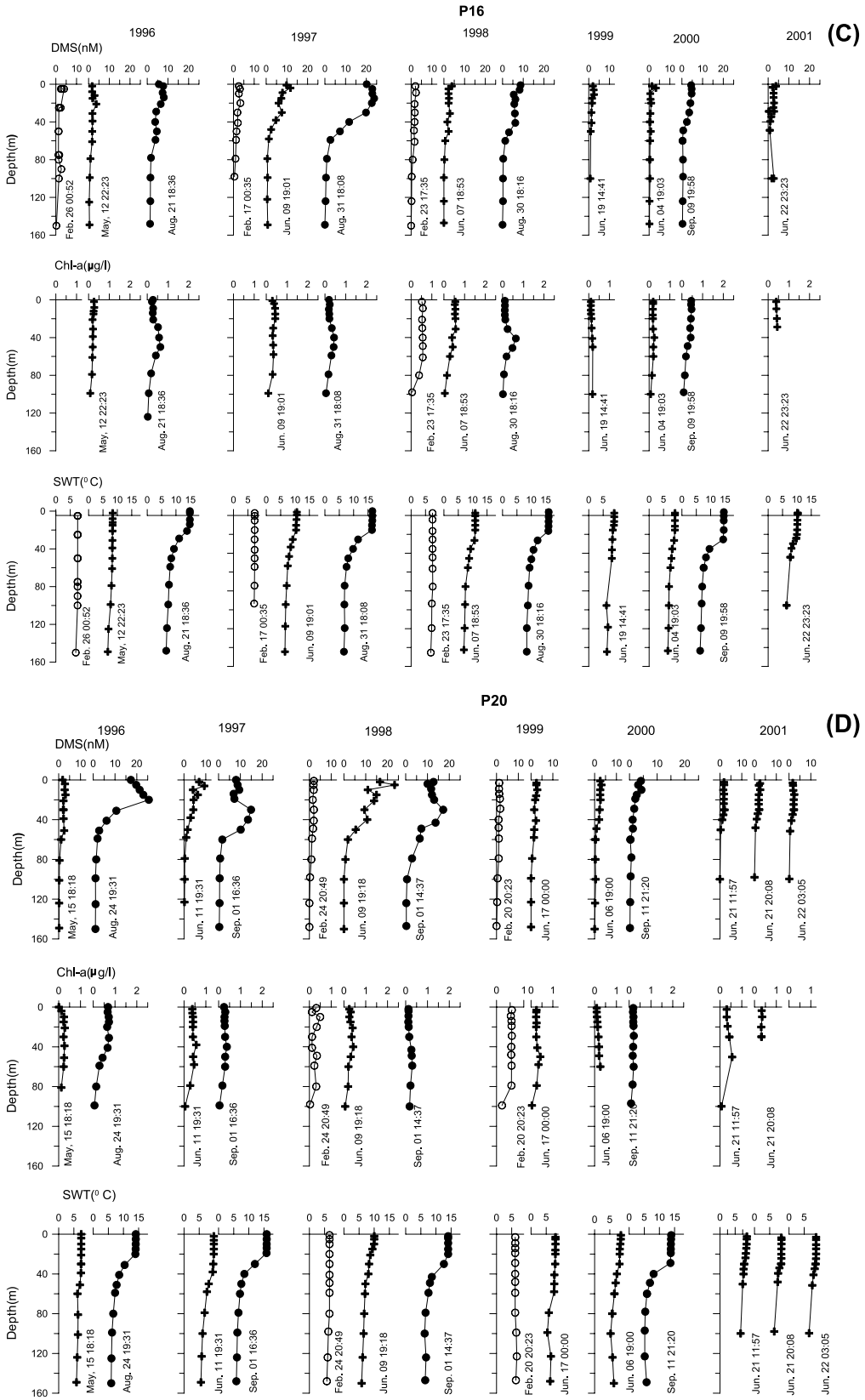
P16
(C)
1996
1997
1998
1999
2000
2001
DMS(nM)
Chl-a(µg/l)
SWT(° C)
Depth(m)
Feb. 26 00:52
May. 12 22:23
Aug. 21 18:36
Feb. 17 00:35
Jun. 09 19:01
Aug. 31 18:08
Feb. 23 17:35
Jun. 07 18:53
Aug. 30 18:16
Jun. 19 14:41
Jun. 04 19:03
Sep. 09 19:58
Jun. 22 23:23
P20
(D)
May. 15 18:18
Aug. 24 19:31
Jun. 11 19:31
Sep. 01 16:36
Feb. 24 20:49
Jun. 09 19:18
Sep. 01 14:37
Feb. 20 20:23
Jun. 17 00:00
Jun. 06 19:00
Sep. 11 21:20
Jun. 21 11:57
Jun. 21 20:08
Jun. 22 03:05

Fig. 4. (cont'd)

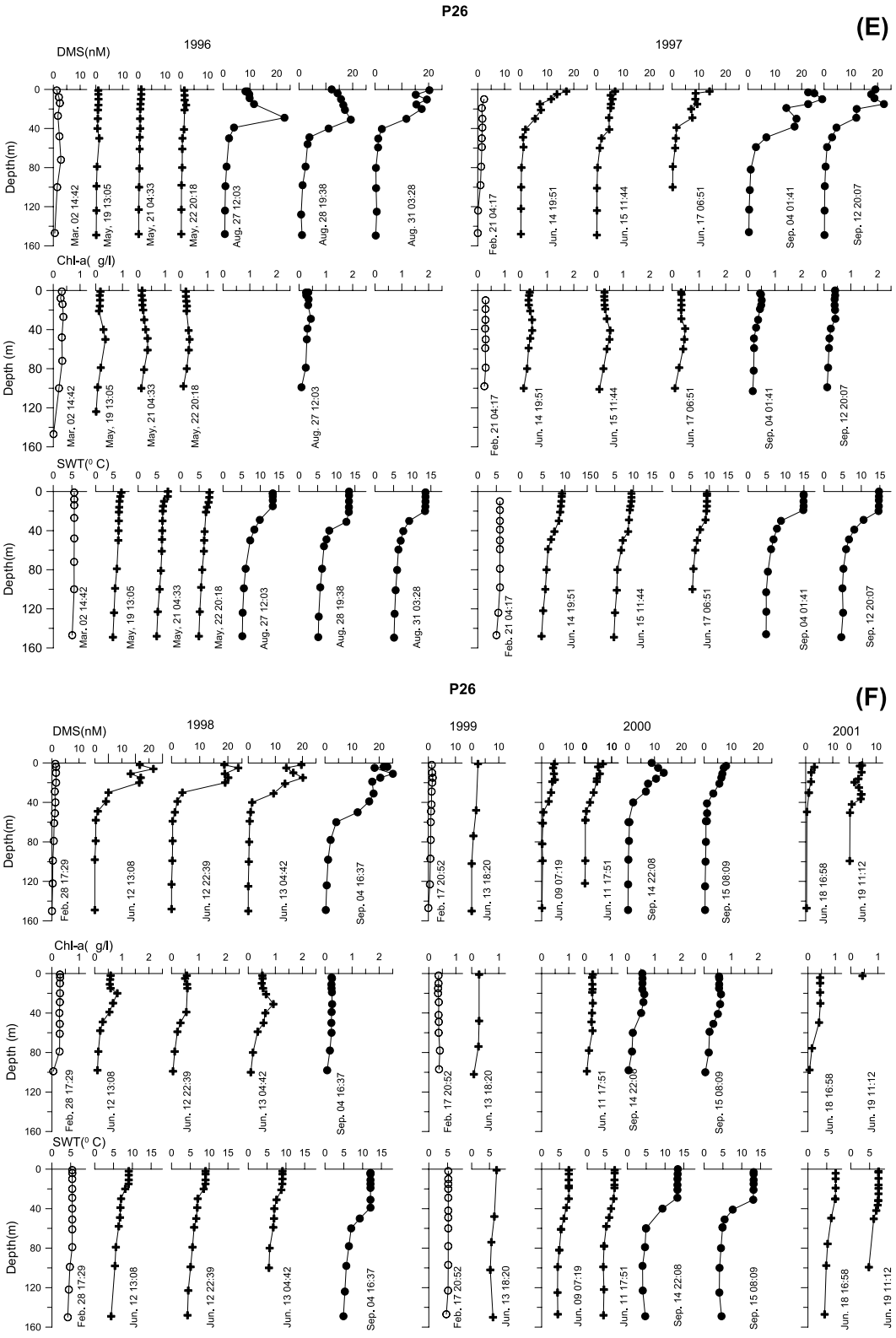
P26
(E)
1996
1997
DMS(nM)
Depth(m)
Mar. 02 14:42
May. 19 13:05
May. 21 04:33
May. 22 20:18
Aug. 27 12:03
Aug. 28 19:38
Aug. 31 03:28
Feb. 21 04:17
Jun. 14 19:51
Jun. 15 11:44
Jun. 17 06:51
Sep. 04 01:41
Sep. 12 20:07
Chl-a(g/l)
Depth (m)
SWT(° C)
P26
(F)
1998
1999
2000
2001
Feb. 28 17:29
Jun. 12 13:08
Jun. 12 22:39
Jun. 13 04:42
Sep. 04 16:37
Feb. 17 20:52
Jun. 13 18:20
Jun. 09 07:19
Jun. 11 17:51
Sep. 14 22:08
Sep. 15 08:09
Jun. 18 16:58
Jun. 19 11:12

Fig. 4. (cont'd)

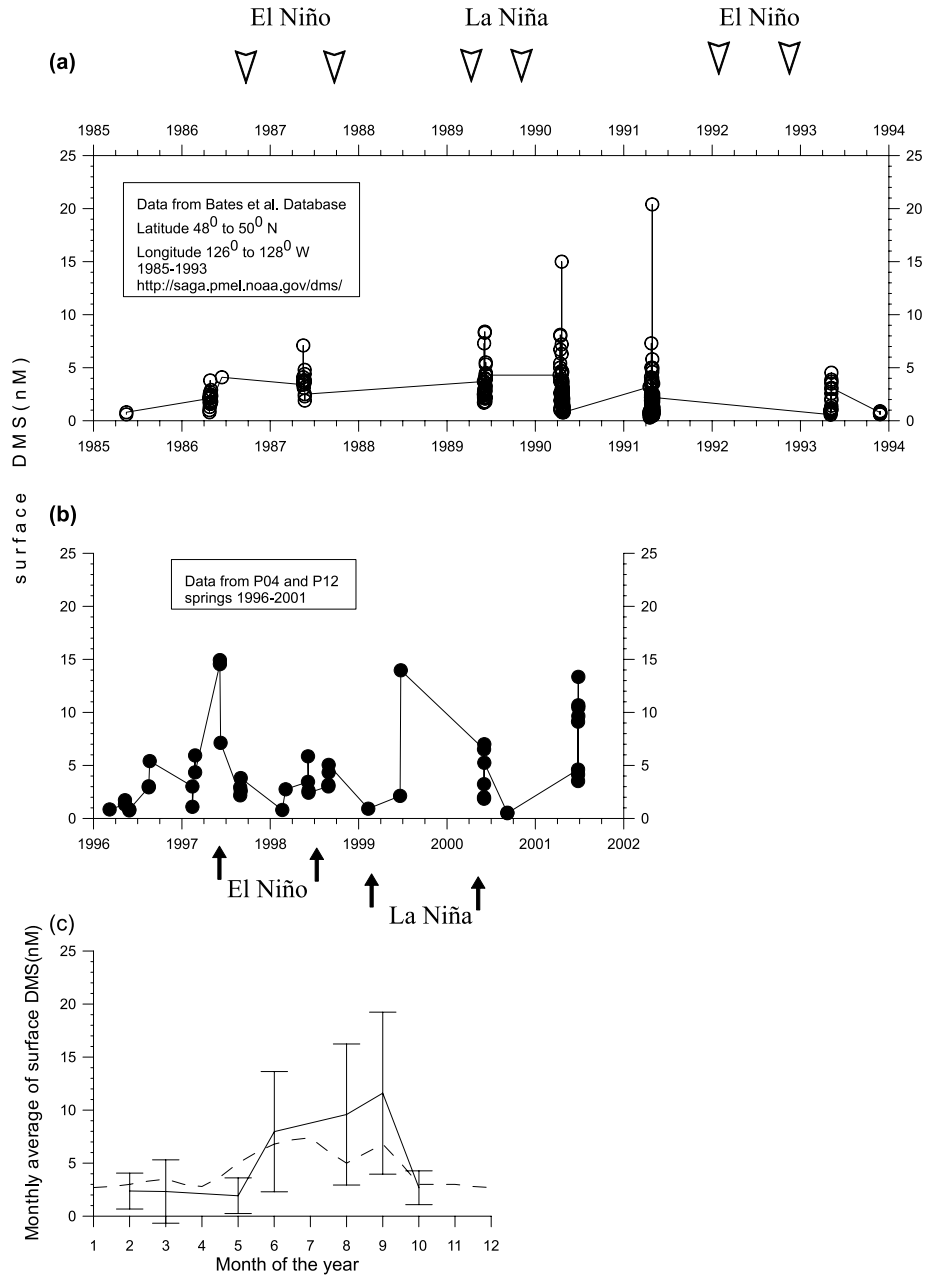

Fig. 5. Comparison of surface DMS concentrations from two different data sets. (a) Data from http://saga.pmel.noaa.gov/dms/. (b) Our data from P04 and P12 for spring 1996–2001. (c) Comparison of database of Kettle et al. (1999) (dotted line) and our monthly average results along Line P, 1996–2001 (solid line).

sea surface temperature (SST) at 15 °C but DMS is low at 3 nM. While in June 1997, DMS at 15 nM, Chl-*a* at 1.2 μg l^{-1} and SST at 13 °C are all high at the start of this El Niño year. In June 2001, both SST (13 °C) at about 1 °C above normal, and DMS (11 nM) are high, but Chl-*a* is low at 0.23 μg l^{-1}. In Fig. 3b, for station P12, SST is around 16–17 °C in the summer of 1996, 1997 and 1998 but Chl-*a* and DMS remain quite low during the same periods. In Fig. 3c, for station P16 in August 1997 during El Niño, both SST and DMS are high but Chl-*a* is low. In Fig. 3d for station P20 in June 1998, DMS is high with values above 20 nM. In Fig. 3e for station P26, September 1997, and June and September 1998, DMS is high at around 20 nM. These plots clearly indicate the large variation of seasonal and spatial distribution of DMS with Chl-*a* and SST. They also show that there are no simple relationships between DMS with either temperature or Chl-*a*.

Variation of DMS with Chl-*a* for both the surface microlayer and subsurface was studied by Yang (1999) in the South China Sea. However, the DMS in the subtropical waters is of the order

of 2 nM, substantially lower than the DMS in the colder HNLC waters in the northeast Pacific by a factor of eight.

4.3. Comparison with other databases

We compare our results with two data sets, one from the PMEL (Pacific Marine Environmental Laboratory) and another one from Kettle's database (Kettle et al., 1999).

Data from http:saga.pmel.noaa.gov/dms/ were downloaded for our study area. The only available data were for latitude 48° to 50 °N and latitude 128.2°W and a few at 140°W from 1985 to 1993 with most of them for spring, especially April cruises and a few for October. Kettle et al. (1999) built on this to compile their database. The data are plotted in Fig. 5a. This data set is mainly from PSI-3 (Pacific Sulfur/Stratus Investigation, 15–30 April 1991) at station 48°14′N, 128°20′W (Bates et al., 1994). We selected our spring data at stations P04 and P12 over our study period to match their data. Fig. 5b is a plot for spring data at P04 and P12 in this study. The PMEL database has an average 2 nM (0.3–20, $n = 472$) for spring (mainly in April) which is much lower than our result of 6 nM in June.

Our results were plotted against those from the database of Kettle et al. (1999) for their regime of PSAG(E) as in Fig. 5c. Our DMS concentrations are almost always higher for the spring and the summer but comparable to those of Kettle et al. (1999) within experimental errors.

4.4. Sea to air DMS flux

DMS accounts for half of the natural sulfur emissions to the atmosphere (Kiene and Bates, 1990) even though they represent only about 1% of the total DMS loss (Bates et al., 1994). Based on Liss and Merlivat (1986) flux parametrization, and Wanninkhof and McGillis (1999) we computed DMS sea-to-air flux as flux(LM) and flux(WAN). Wind speeds for the Line P cruises for 1996–2001 came from several sources: SAIL (standard ASCII interface loop), COCC (sea pCO_2 sampling of the Center for Ocean Climate Chemistry) and BLOG (bridge log from ship's anemometer). For each cruise the most accurate, complete meteorological data available were the ones used. The computed fluxes and wind speed at 10 m height at P04, P12, P16, P20 and P26 are shown in Figs 6a–e. The spatial variability is

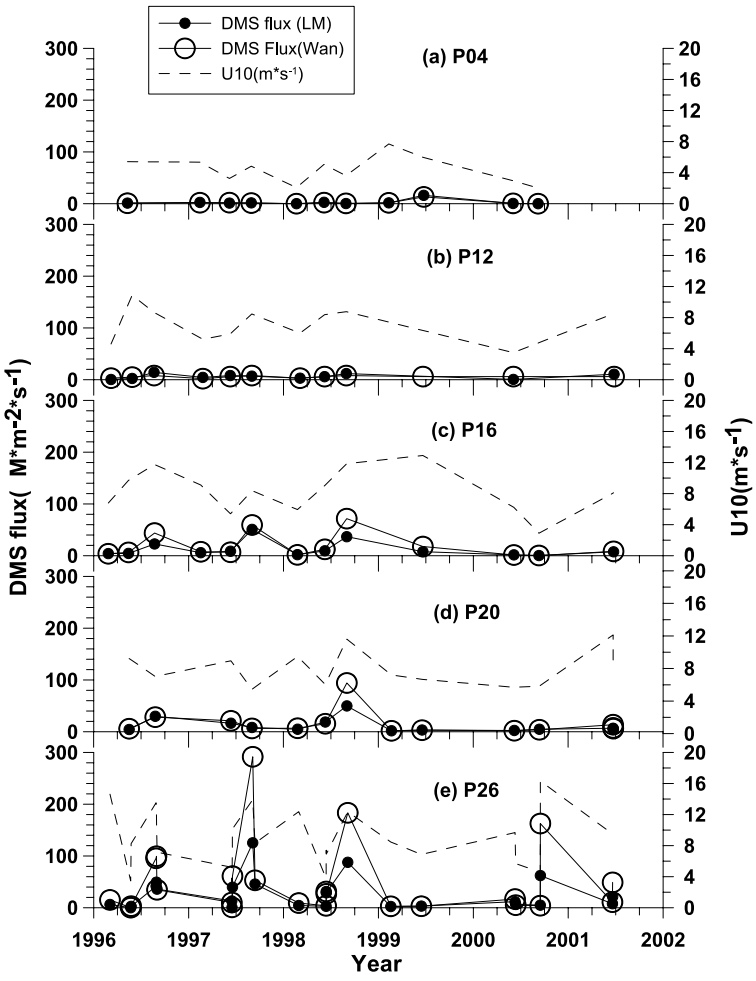

Fig. 6. Temporal and spatial variations of the DMS flux by the Liss and Merlivat (1986) parametrization(solid circles), DMS flux of Wanninkhof and McGillis (1999) (open circles) and wind speed at 10 m height (dotted lines) for stations (a) P04, (b) P12, (c) P16, (d) P20 and (e) P26 from 1996–2001.

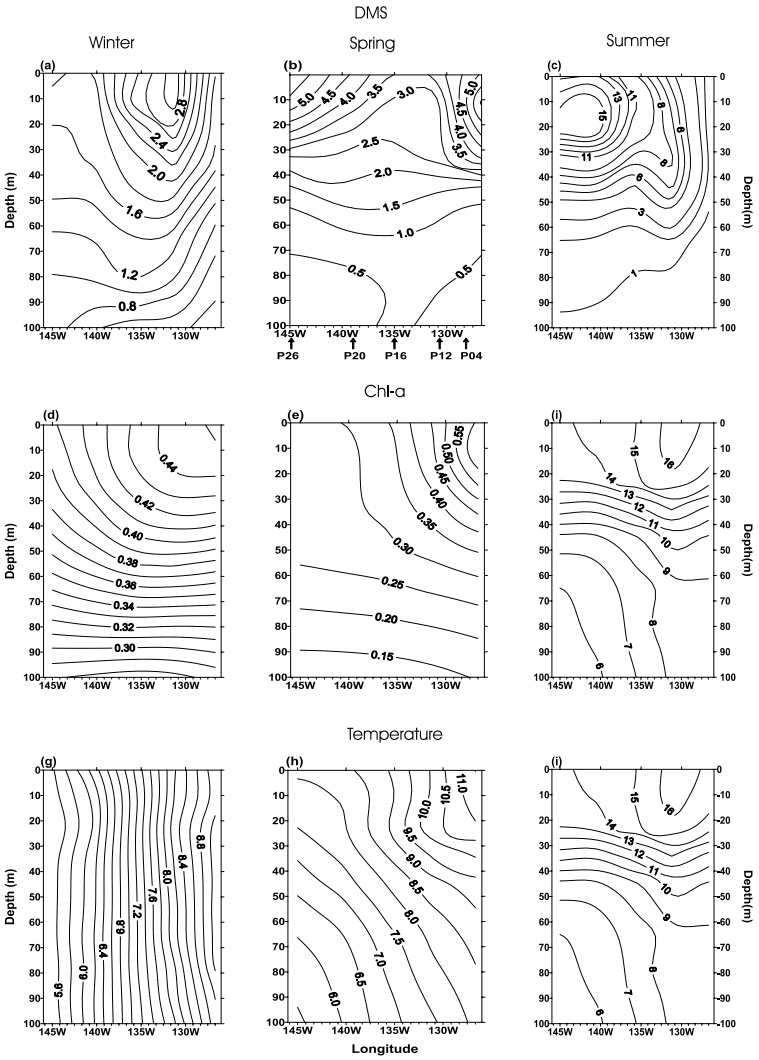

Fig. 7. (a–c) Contours of average DMS (nM) in 0–100 m for all stations along Line P from 1996–2001: (a) winter, (b) spring and (c) summer. Arrows indicate longitudes of P04, P12, P16, P20 and P26. (d–f) Contours of average Chl-*a* (μg l^{-1}) in 0–100 m for all stations along Line P from 1996–2001: (d) winter, (e) spring and (f) summer. (g–i) Contours of average SWT (°C) in 0–100 m for all stations along Line P from 1996–2001: (g) winter, (h) spring and (i) summer.

evident since flux at the offshore station P26 is significantly higher than those at other stations because of higher wind speed (P04, average wind speed at 10 m height = 4 m s^{-1}, range 1–7, $n = 13$, that for P26 = 9 m s^{-1}, range 3–16, $n = 24$) and higher DMS surface concentrations (P04, average DMS concentration = 5 nM, range 1–15, $n = 13$, that for P26 = 10 nM, range 1–22, $n = 24$). The high fluxes are observed for the months of August and September during the 1997–1998 El Niño year, and to a lesser extent in 2000, a La Niña year at P26. For each station, the seasonal variability is clear. During the El Niño year, the spring of 1997 and the autumn of 1998, the flux was lower than that in a La Niña year of 2000, and lowest in the normal year of 1996. Station P26 water was within 1 °C of the normal temperature in 1996. It was warmer in 1997 but cooler in 1998 and 1999, when regime shift was suspected to have occurred, similar to the shift in 1977 (Bond et al., 2003). This shift may lead to change in plankton species. For example, a decreasing dominance of coccolithophores, which favour a warmer phase, may lead to a change in DMS production. Enhancement of the new production at Station P occurs during El Niño years (Wong et al., 1998) could increase the biological production of DMS as well. At P04 and P12 flux(LM) and flux(WAN) agree very well. Starting at P16 and P20, when the wind speed is high, flux(WAN) are higher. At P26, flux(WAN) can be double that of flux(LM) due to high wind speed. The average flux(LM) is 16 μM m^{-2} d^{-1} (range 0.03–138, $n = 136$) and that for flux(WAN) is 27 μM m^{-2} d^{-1} (range 0.02–322, $n = 136$).

4.5. *Vertical distributions*

Figures 4a–f show vertical profiles of DMS, Chl-*a* and SWT of P04, P12, P16, P20 and P26 from 1996–2001. In general, winter values are low for all stations and for all years. High DMS which correlates with high biological production occurs in spring to

summer. The oceanic DMS concentrations of Bates et al. (1994) show that sea water DMS concentrations varied by a factor of 50 between the summer and winter in mid and high latitudes. This is confirmed by our results for 24 August 1996 at Station P20 at 20 m depth with DMS concentration as high as 30 nM, while on 24 February 1998 for the same station and same depth, DMS concentration was as low as 1.5 nM. The summer–winter variation was a factor of 20.

Figures 7a–c are the contours of average DMS casts from 1996–2001 for all stations along Line P, Figs 7d–f that of Chl-*a* and Figs 7g–i are sea water temperature. Figs 7a, d and g are for the winter, Figs 7b, e and h for the spring and Figs 7c, f and i for the summer. The spatial and seasonal variations are clear. In winter, DMS concentrations are low at all stations other than the high value at P12. In spring, DMS at P04 is comparable to that of P26, an open ocean station. In summer, DMS at P26 is high at 15 nM, three times that in spring and almost ten times that in winter. At P04, a coastal station, Chl-*a* concentrations are higher than at other stations for all seasons due to river run-offs. In Fig. 7c the summer DMS at station P26 is high while the corresponding Chl-*a*in Fig. 7f is low.

Figures 7g–i show the sea water temperature in the upper 100 m along Line P for winter (Fig. 7g), spring (Fig. 7h) and summer (Fig. 7i). Winter mixing and cold air over the ocean produce uniformly low temperature in the upper 100 m above the permanent halocline usually at 120 to 150 m depth. Offshore Station P26 is at ≈6 °C, while inshore stations along Line P got progressively warmer to about 9 °C near the west coast of Vancouver Island. For spring, warming spreads from inshore 11 °C downwards and towards offshore, now at 7.5 °C. In summer, the inshore waters near 130°W to 132°W reach 16 °C with the upper 20 m warmed up to 13 °C, while the deeper waters at 145°W stay at 8 °C.

We examined the correlation of DMS with temperature, Chl-*a*, salinity and nitrate. Figure 8 shows average summer casts of DMS, Chl-*a*, SWT, salinity and nitrate from 1996–2001 at station P26. DMS show the same trend of decrease with depth, as temperature and Chl-*a*, but an opposite trend to salinity and nitrate. DMS is high in shallow water but low in deep water, while salinity and nitrate are generally low in the mixed layer and high in deep waters. Phytoplankton production, which consumes nutrients, leads to higher Chl-*a* and lower nitrate in the euphotic zone. For most cases, DMS and temperature are highly correlated (average correlation coefficient R^2 is 0.81, range 0.26–0.98, $n = 79$) while DMS and Chl-*a* are less correlated (average R^2 is 0.43, range −0.9–0.93, $n = 69$).

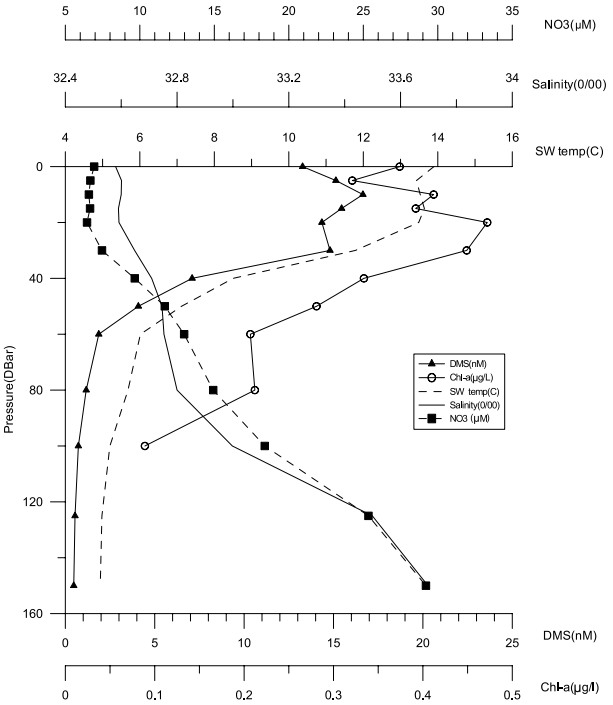

Fig. 8. Average summer profile for DMS and other parameters at P26, 1996–2001. Solid triangle for DMS (nM), solid line with open circles for Chl-*a* (μg l^{-1}), dotted line for sea water temperature (°C), solid line for salinity (‰) and dotted line with solid squares for NO_3 (μM).

4.6. DMS, Chl-a and the summer paradox

Figures 9a, c, e, g and i are the time-series of the average DMS at mixed-layer depth (DMS_{MLD}) and that of Chl-*a* (Chl-a_{MLD}) at P04, P12, P16, P20 and P26 respectively from 1996–2001. P26 is in HNLC waters suffering from iron limitation (Boyd et al., 2004). Chl-*a* concentrations are always low, even in summer. There were cases of the "summer paradox" in which DMS_{MLD} was high but Chl-a_{MLD} was low as suggested by Simò and Pedròs-Aliò (1999a) in the North Atlantic. This concept was later supported by Toole et al. (2003) using Dacey's 1992–1993 time-series in the Sargasso Sea (Dacey et al., 1998). DMS_{MLD} and Chl-a_{MLD} for P04 (Fig. 9a) and that for P12 (Fig. 9c), both coastal stations, showed no summer paradox for the years 1996–2001. At P16 (Fig. 9e) there was a summer paradox for the El Niño year (1997) only. For open ocean stations P20 (Fig. 9g) during 1996 and 1998, and for P26 (Fig. 9i), during 1996, 1997 and 1998, there was summer paradox. The results are summarized in Table 2 as late spring or early summer paradox. UTC time was added if the observation was for diurnal study.

Abiological processes of photolysis and chemical oxidation are an unlikely explanation for the "summer paradox", (Simò and Pedròs-Aliò, 1999b; Toole and Siegel, 2004). Plankton and bacteria contribute to DMS and DMSP. Plankton such as dinoflagellates and *E. Huxyli* supply 43% of the algal sulfur in June in the northern North Sea (Simò, 2004). Bacterial production is a major source of DMSP (Kiene et al., 1999, 2000). High DMS and DMSP also come from a bloom of planktonic coccolithophores in the North Atlantic (Burkill et al., 2002). At Station P, the bacterial population is relatively low in El Niño years of 1997 and

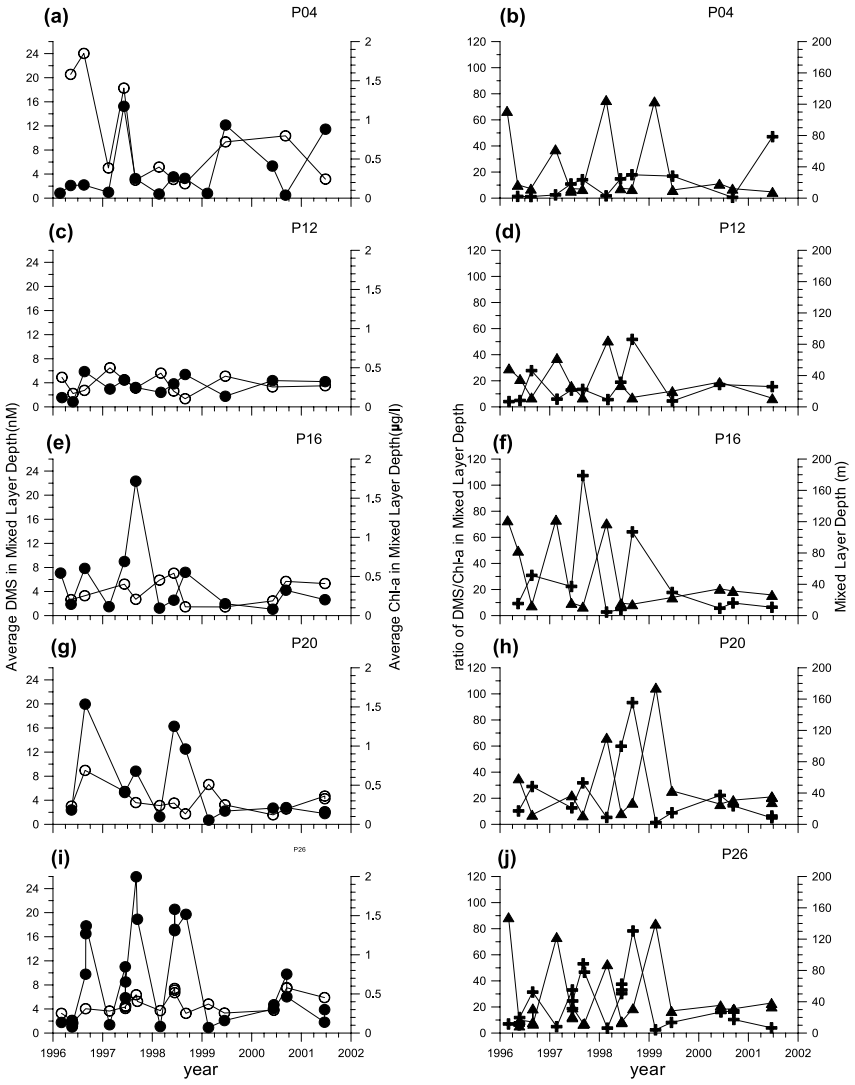

Fig. 9. (a, c, e, g, i) Time-series of DMS_{MLD} (solid circles) and Chl-a_{MLD} (open circles) at stations P04, P12, P16, P20 and P26 respectively from 1996–2001. (b, d, f, h, j) Time-series of ratio DMS_{MLD}/Chl-a_{MLD} (solid diamonds) and MLD (crosses) at stations P04, P12, P16, P20 and P26 respectively from 1996–2001.

1998 and even lower in La Niña years of 1999 and 2000 (Sherry, 2002). Grazing of bacteria by microzooplankton is unimportant due to the slow growth rates of bacteria in the cold waters relative to subtropical and tropical waters. Due to the low bacterial grazing, low bacterial biomass and productivity in subarctic waters, grazing of DMS-producing flagellates can be a factor in the high DMS production in summer. The relative balance between phytoplankton production and zooplankton at Station P (Frost, 1987) is keeping chlorophyll low, and because of low diatom numbers in HNLC waters, lack of competition leads to the flourishing of smaller high-DMS-producing flagellates and dinoflagellates. In HNLC waters of the subarctic North Pacific, diatoms are important in DMS production. Bucciarelli and Sunda (2003) proposed that the intracellular DMSP concentration is related to the level of oxidative stress linked to a specific growth rate and cellular Chl-*a* under nutrient limitations. Their nutrient-limited cultures of coastal diatoms indicated that intracellular DMSP increases during nutrient limitation. Thus, factors affecting the sources of emission of DMS to the atmosphere for cloud condensation nuclei are also linked to the state of health of plankton under stress and the ocean environment, particularly in HNLC waters in subarctic North Pacific as in this paper and in the Southern Ocean and the Antarctic Ocean (Turner et al., 1996).

Figures 9b, d, f, h and j show the time-series of mixed-layer depth (MLD) and the ratio of DMS_{MLD}/Chl-a_{MLD}. This agrees with Simò and Pedròs-Aliò (1999a) that DMS_{MLD}/Chl-a_{MLD} have an opposite trend with MLD for all stations for 1996–1999 but not for 2000–2001. The waters at Station P and Line P are subjected to effects of El Niño, La Niña and regime shift (Wooster and Zhang, 2004) causing warmer and colder phases. Starting in 1999, we experience a regime shift to a cold phase. Indeed, mixing exerts a profound effect on DMS production in

Table 2. Summary of the late spring or early summer paradox

Year	Month	Day	Station	MLD (m)	DMS_{MLD} (nM)	Chl-a_{MLD} ($\mu g\,l^{-1}$)	DMS $_{MLD}$/Chl-a_{MLD}	Comment
1997	6	5	P04	9.42	15.25	1.406	10.85	
1999	6	22	P04	10.37	12.14	0.719	16.89	
2001	6	26	P04	8.02	11.45	0.243	47.12	
1996	8	19	P12	11.96	5.86	0.211	27.77	
1998	8	29	P12	20.16	1.76	0.104	51.73	
1996	8	21	P16	13.09	7.84	0.254	30.87	
1997	6	9	P16	16.24	8.98	0.402	22.34	
1997	8	31	P16	11.44	22.33	0.208	107.36	
1998	8	30	P16	14.54	7.19	0.112	64.20	
1996	8	24	P20	12.25	19.96	0.689	28.97	
1997	9	1	P20	11.46	8.83	0.278	31.76	
1998	6	9	P20	14.23	16.28	0.272	59.85	
1998	9	1	P20	27.55	12.50	0.134	93.28	
1996	8	27	P26	14.12	9.77	0.311	31.42	
1997	6	14	P26	21.48	11.00	0.333	33.03	UTC 1951
1997	6	15	P26	20.13	5.87	0.314	18.69	UTC 1144
1997	6	17	P26	32.74	8.49	0.345	24.61	UTC 0651
1997	9	4	P26	11.90	25.95	0.489	53.07	UTC 0141
1997	9	12	P26	12.54	18.90	0.405	46.67	UTC 2007
1998	6	12	P26	13.84	17.23	0.570	30.23	UTC 1308
1998	6	12	P26	14.91	20.55	0.548	37.50	UTC 2239
1998	6	13	P26	14.52	17.01	0.516	32.97	UTC 0442
1998	9	4	P26	31.76	19.72	0.252	78.25	
2000	9	14	P26	30.87	9.78	0.576	16.98	UTC 2208
2000	9	15	P26	31.03	6.02	0.579	10.40	UTC 0809

the short term and on longer timescales (Simò and Pedròs-Aliò, 1999a).

5. Conclusions

Our surface DMS concentrations are higher than but comparable to those in the global database of Kettle et al. (1999) and the PMEL regional database. Kettle et al.'s database may have underestimated the DMS values in the northeast Pacific region and PMEL's was for April while ours is for June. Our DMS concentrations agree well with field data and modelling results from other investigators in that DMS increased diurnally from a pre-dawn low to a mid-day maximum, from low in coastal waters to high in offshore HNLC waters and from a winter low to a summer high in the upper mixed layer. DMS showed a decreasing trend with depth with temperature and Chl-*a* but an opposite trend to salinity and nitrate. DMS and Chl-*a* exhibit the "summer paradox" in open ocean for 3 yr of the 6 yr investigation. The ratio of DMS $_{MLD}$ to Chl-a_{MLD} is out of phase with the mixed-layer depth. The sea to air flux of DMS was significantly higher at Station PAPA compared with other stations along Line P. The short duration of the higher DMS flux at Station PAPA occurred in the summer of 1997 and the early autumn of 1998 and 2000. These short-term perturbations may make a substantial contribution to the picture of global DMS flux distribution.

Since the concentrations of DMS are related to so many factors prediction of the connection between climate change and DMS will involve complex models that require information about many biological, chemical and physical processes. Our 6 yr time-series on Line P offers a suitable database for testing time-varying models on a fixed location or section.

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Data used in this paper can be accessed at: http://www-sci.pac.dfo-mpo.gc.ca/osap/people/cswong/wong_e.htm

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