THESIS

TEMPORAL CHANGES OF ORGANIC MATTER IN DISSOLVED AND PARTICULATE FORMS IN THE COASTAL OCEAN

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December 2004

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沿岸海洋における溶存態および粒子態有機物の時間変化

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2004 年 12 月

ABSTRACT

Temporal variation of organic matter in the coastal seawater was researched every few months in 2000-2002 at the center of Suruga Bay, Japan. These concentrations were measured as dissolved and particulate forms divided by filtration with glass fiber filter. Dissolved organic carbon and nitrogen (DOC and DON) concentrations ranged from 91.3 to 40.4 μM C and from 9.9 μM N to detection limit, respectively, and particulate organic carbon and particulate nitrogen (POC and PN) concentrations ranged from 30.1 to 0.5 μM C and from 4.8 μM N to detection limit from the surface to 200 m depth, respectively. DOC and POC concentrations decreased with depth. DOC concentration varied in the surface layer (shallower than 50 m depth) through years and its variation was synchronized with the variation in DON. Temporal changes of DOC co-varied also with particulate organic matter (POM): These concentrations were high during spring and summer and decreased to winter. A clear seasonal variation appeared especially in DOC, which was similar to those of chlorophyll *a* concentration and was contrary to the nutrients. This indicates that biological processes regarding to photosynthesis contributes to the seasonal variation in organic matter. In order to research the behavior on the organic matter at short time scale, water samples were collected three times per day (midday, night and predawn) mainly during September 2000 to October 2001. Diel variation in DOC concentrations, among the three sampling times, was greater in the upper 20 m, with a maximum difference of 21.7 μM C in July 2001, and reflected in diel DOC inventory variations from the surface to 50 m. Diel variations in DOC were controlled by both

physical and biological factors. DOC concentrations were significantly correlated with potential density in the deeper layers (100-1000 m), indicating that the distribution of DOC concentrations in the deeper layer was mainly decided by mixing. Most DOC concentrations in the upper layer (0-50 m) did not display the same relationship as in the deeper layer. Using the relationship with potential density at 100-1000 m, the DOC concentration in the upper layer, due simply to mixing, was calculated. The difference between the calculated and observed DOC was used to estimate biological contribution. The biological contributions to the depth-integrated DOC in the upper layer (0-50 m) were found greatly in November 2000 and April 2001 (0.37 and 0.29 mol C m^{-2}, respectively). This indicates that excess DOC accumulated, by biological processes, in the upper layer during these periods. In November 2000, excess DOC in the inventory was constant throughout the sampling days, whereas diel variations of DOC in the vertical profile were large and contrary to the variation between 10 and 20 m. This suggests that the excess DOC was contributed biologically during daytime in the uppermost layer and reached to the 50 m depth due to deeper mixing. As a result, the inventory appeared to be stable over a day because of the compensating effects of DOC production and consumption throughout 50 m. In contrast, in spring and summer, there was a distinct diel inventory decrease in the nighttime, with apparent rates ranging from –0.61 to –0.35 μM C h^{-1}. It is probable that the DOC, which accumulated during the daytime, was mostly labile, with a turnover time of a few hours. The results indicate that dynamics of diel DOC variations differed in each season, and suggest that these diel variations need to be considered when estimating seasonal DOC pools in the coastal ocean. DOC concentration increased in the surface layer from spring to summer with large dial changes. While diel change was little

in autumn, there was abundant DOC contributed by biological processes, but these accumulation disappeared in winter from the surface layer, indicating that DOC having more longer time scale was accumulated in the surface layer and transported to deep by water column convection in winter. Seasonal observations of DOC and DON allowed estimating amount of DOM exported to deep during winter. This shows that considerable amount total DOM (710 mmol C m^{-2} for DOC) which was constructed of resident DOC in the surface layer prior to the convection event and freshly produced DOC during the convective period, was exported to deeper layer (50-200 m) in February 2001. This exported DOC accounted for one third of annual flux of sinking particles (2290 mmol C m^{-2} for POC). On the other hand, the freshly produced DON could not detected during the overturn period. Any total DOC and DON could not be exported in the next year, suggests it is possible that there was annual difference in quality of DOC produced and it causes variation of the amount of exportable DOM.

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LIST OF ABBREVIATIONS

BA	Bacterial Abundance
BP	Bacterial Production
Chl-*a*	Chlorophyll *a*
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
NO_2	Nitrite
NO_3	Nitrate
PN	Particulate Nitrogen
PO_4	Phosphate
POC	Particulate Organic carbon
POM	Particulate Organic Matter
PP	Primary Production
$Si(OH)_4$	Silicate (Silicon hydroxide)
TDN	Total Dissolved Nitrogen
TOC	Total Organic Carbon

I. GENERAL INTRODUCTION

The oceans cover three-quarters of the Earth's surface, and thereby are important in materials cycles, especially, C, N, P, S and O which play significant roles biogeochemically in controlling the global environment because they are essential elements for organisms (Chester, 2000). In recent century, researchers have been paying attention to carbon as a constituting element of the 'greenhouse' gasses (CO_2 and CH_4) causing global warming. CO_2 is the least effective 'greenhouse' gas per kilogram emitted to the atmosphere for 'greenhouse' gasses, however, 1990s annual emission for 'greenhouse' gases have been estimated to be: CO_2 (6.4 PgC: fossil fuel, cement) >> CH_4 (600 Tg) >> N_2O (16.4 TgN), >> CF_3CH_2F (~25 Gg) (Prentice *et al.*, 2001; Ehhalt *et al.*, 2001). Consequently, CO_2 has the greatest potential contribution (55%) to global warming and its increase of concentration in the atmosphere is the most important single agent in the radiative forcing of the climate.

The oceans are a major reservoir of carbon (Fig. I-1). The total amount of carbon in the ocean is about 50 times greater than that in the atmosphere. Thereby, the role played by the oceanic carbon flux in the global carbon cycle has received increasing attention. Besides of carbon cycles, the ocean play the dominant role in the determining climate to redistribute heat by oceanic current for their capacity for the heat storage (Chester, 2000). The exchange of CO_2 between the atmosphere and the surface ocean is extremely important and on the time-scale of decades, or more, the CO_2 concentration of the atmosphere is controlled mainly by exchange with ocean water. Around 15 times as

much as CO_2 is exchanged by natural marine processes than the total produced by the burning of fossil fuel, deforestation and other human activities. The ocean effectively takes up much more CO_2 than other anthropogenic gasses because of the solubility and chemical reactivity of CO_2. Fig. I-2 summarized carbon cycling in the ocean. CO_2 dissolved in seawater occurs as three main forms: (non-ionic) dissolved CO_2, bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}). These species is termed DIC (dissolved inorganic carbon). The role of ocean in carbon cycle has been viewed in terms of a series of 'pump' that initially draw CO_2 down into the surface seawater: 'solubility pump', and then transport it within the system out of the surface layer as carbon: 'physical pump' and 'biological pump'. The most important role associated with organic matter is as 'biological pump'. It plays a role which the fixed carbon is transferred from surface water via the vertical gravitational settling of the biogenic debris produced in the euphoric zone. Part of the newly fixed carbon by photosynthesis returns to DIC and is released in dissolved form (dissolved organic carbon: DOC) through metabolism. The remainder, i.e., net primary production is consumed by zooplankton and bacteria, becomes detritus or DOC. Sinking of particulate organic carbon (POC) that includes dead organisms and detritus and vertical transfer of DOC by downward advection and diffusion create a downward flux of organic carbon from the shallower ocean to the deep ocean, which is known as 'export production'. Recent estimates for global export production range from roughly 10-20 PgC yr^{-1} (Falkowski *et al.*, 1998; Laws *et al.*, 2000). The net effect of the 'biological pump' is to reduce the partial pressure of CO_2 (pCO_2) in surface waters, causing an enhancement in the drawdown of CO_2 from the atmosphere initiated by phytoplankton growth. At depth, part of exported organic carbon is remineralized by heterotrophic

organisms and turns back to the form of DIC. This DIC is upwelled eventually into the surface layer again. Consequently, the fraction of production that escapes recycling, and the material transported to deep water can be returned to the surface only by water-mass transport associated with the thermohaline system. Once carbon is exported to depth as DOC, POC or DIC, the carbon remain there for a relative long time-scale because the deep-water is covered with the surface water like as a cap, and is therefore out of contact with the atmosphere for as long as 1000 yr. In addition of production of organic carbon, the calcium carbonate ($CaCO_3$) shells are formed by marine organisms and these sink and accumulate in sediments. Because this process tend to increase pCO_2, surface water pCO_2 and air-sea fluxes are in counter to the effect of organic carbon production. Therefore, the relation between the export of organic carbon and the export of calcium carbonate is a critical factor controlling overall effect of biological activity on the surface ocean pCO_2.

The carbon flux of export production is smaller than the physical transport (Fig. I-2) but there is a possibility that the flux of export production is enhanced by increasing of primary production, because primary production is controlled largely by nutrients supply from deep water and from rivering inputs in coastal ocean.

DOC is the largest pool of organic carbon in the ocean (680-700 Pg C: Williams & Druffel. 1987; Hansell & Carlson, 1998a), which is larger than land biota. The carbon pool of DOC is approximately the same magnitude as the pool of atmospheric CO_2 (Hedges, 1992). With regard to absorption and exchange of CO_2 between ocean and atmosphere, understanding the dynamics of the DOC pool is essential for modeling the global carbon cycle. In addition, the concept of the microbial loop (Azam *et al.*, 1983, Fig. I-3) makes the role of DOC in marine ecosystems particularly important. DOC

production and consumption processes link to organisms on almost all trophic levels, and involve with chemical process, moreover (Fig. 1-4). Organic matter in seawater is distributed in a wide range of continuous size (Fig. I-5). For analytical convenience, the fraction of organic matter passing through a filter (usually glass fiber filters with nominal pore size of 0.7 μm) is named dissolved organic matter (DOM), and its carbon content is classed as DOC (Ogawa & Tanoue, 2003). Actually, DOM contains small bacteria and viruses, and therefore does not mean true dissolved form. More than half of DOM, however, remains uncharacterized at the molecular level (Hedges *et al*., 2000). Generally, the abundance of DOM has been determined as DOC because carbon is a major element of organic matter. Based on data from time-series observations and incubation experiments, DOC was generally separated into at least three fractions, depending on biological lability (Kirchman *et al*., 1993; Carlson & Ducklow, 1995). These fractions are usually termed refractory, semi-labile and labile. Fig. I-6 shows the conceptual drawing of vertical distribution of these fractions in marine DOC. Deep-water DOC can be quite old (over 1000 years), and refractory in nature (Bauer *et al*., 1992). The semi-labile pool turns over on a seasonal time scale, varying from months to a year. The compounds of labile DOC include lipids, dissolved free amino acids and carbohydrates which have short turnover times, from minutes to days, because they are rapidly consumed by microbes.

Methodological developments and comparisons of analytical methods (Sharp *et al*., 2002) allow accurate and precise measurement of DOC concentrations, thereby increasing our knowledge of the detailed distribution of DOC concentrations in various aquatic systems. DOC in the deep ocean has long been considered to be uniformly distributed (Martin & Fitzwater, 1992) and hence largely refractory to biological decay but Hansell &

Carlson (1998a) demonstrated that DOC concentrations in deep ocean decreased by 14 μM C from the northern North Atlantic Ocean to the northern North Pacific Ocean. Time-series observation in the Western Mediterranean revealed that DOC accumulates in spring, and advects to deeper water by winter mixing. This DOC export flux is comparable to observations of annual particulate carbon flux from the euphotic zone (Copin-Montégut & Avril, 1993). In the Sargasso Sea, DOC accumulated in the surface water, is considerably exported to the deeper ocean in winter (Carlson *et al*., 1994; Hansell & Carlson, 2001). Many investigations have been investigated on the daily, weekly and seasonal variations in DOC concentration (Williams, 1995; Peltzer & Hayward, 1996; Børsheim & Myklestad, 1997; Hansell & Carlson, 1998b; Børsheim *et al*., 1999; Carlson *et al*., 2000; Álvarez-Salgado *et al*., 2001; Hansell & Carlson, 2001; Skoog *et al*., 2001; Church *et al*., 2002), while few observations on shorter time scales of hours are available (Sieburth *et al*., 1977; Kaplan & Bott, 1982; Hansell *et al*., 1993). DOC concentrations are not expected to vary greatly over short time scales because close coupling between production and consumption should keep labile DOC concentrations low. In contrast, refractory DOC is assumed to occur uniformly (about 40 μM C) through while water column in recent reports (Kirchman et al., 1993; Carlson & Ducklow, 1995). Accordingly, diel variability of DOC concentration in the ocean has been insufficiently investigated. Søndergaard & Middelboe (1995), however, found that the concentration of labile DOC increased from oligotrophic to eutrophic systems, implying a possibility that DOC acts dynamically on short time scales in highly productive areas.

Turnover time and proportion of DOC fraction available to organisms have been evaluated from laboratory experiments (e.g. Carlson & Ducklow, 1996; Cherrier *et al*.,

1996; Hopkinson *et al.*, 2002). This approach is less complicated than field experiments; however, it cannot predict the fate of DOC because dynamic cycling of DOC in the ocean is controlled by biogeochemical and physical processes. One of the aims in this study was to observe, in situ, diel variations of DOC concentrations in the upper layer of the coastal ocean, at Suruga Bay and determine the net diel biological contribution to the bulk DOC pool, after it had been distinguished from physical contributions. Time-series observations were conducted in the center of Suruga Bay in a fixed sampling station. Diel profiles of DOC collected over all seasons were analyzed to assess the significance of short time scale variations by biological processes for annual dynamics of DOC. Moreover, behavior of organic matter in coastal ocean was demonstrated by seasonal observations in Suruga Bay with comparison between dissolved organic matter (DOM) and particulate organic matter (POM). Finally, DOM export to deep layer was estimated from comparison of the inventory observed through years between the surface and deeper layers.

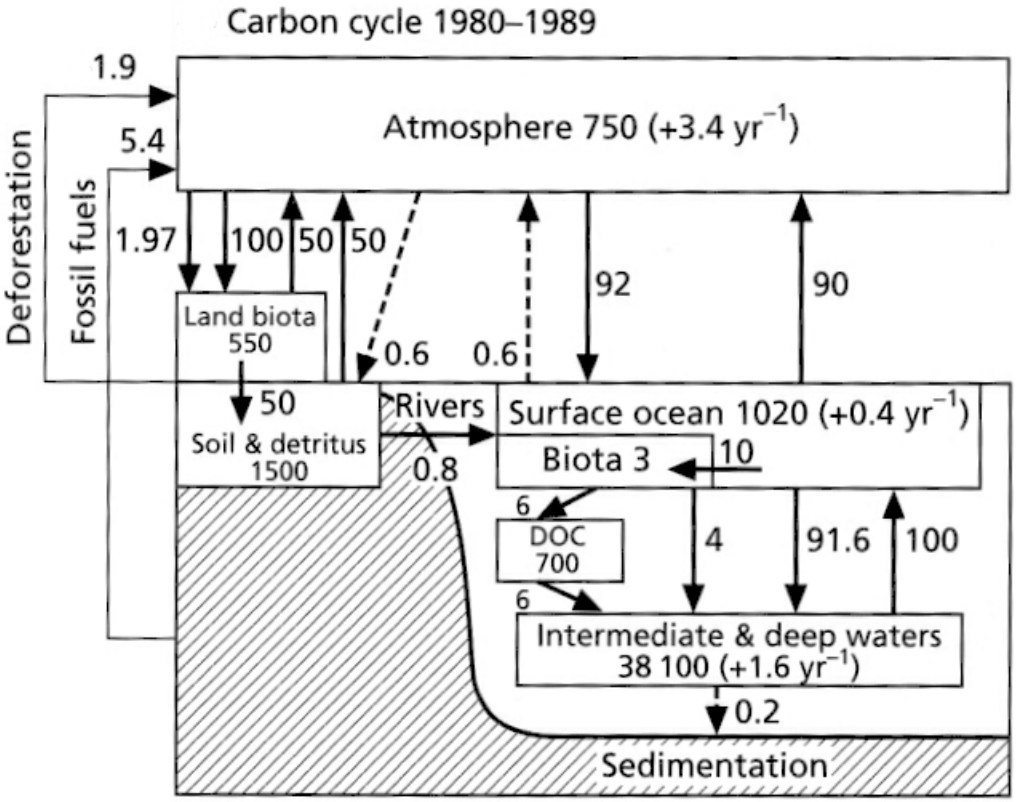

Fig. I-1: Global carbon cycle. Units: reservoir (GtC), fluxes (GtC yr^{-1}). [from Chester, 2000]

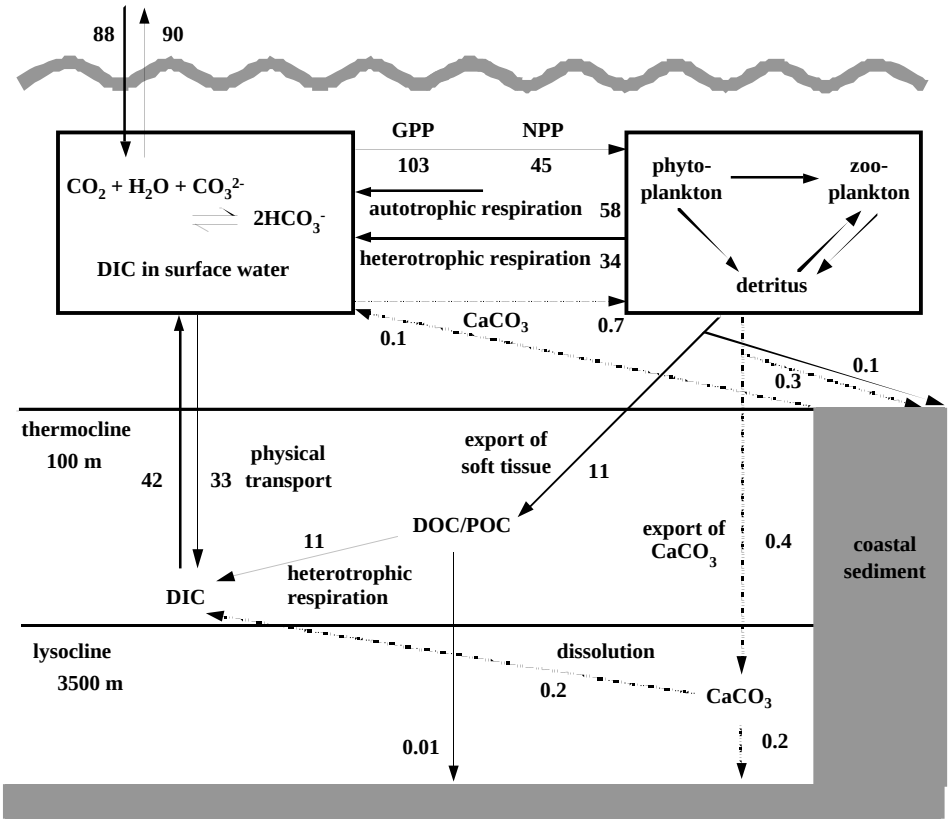

Fig. I-2: Carbon cycling in the ocean. CO_2 that dissolves in the ocean is found in three main forms (CO_2, CO_3^{2-}, HCO_3^-, the sum of which is DIC). DIC is transported in the ocean by physical and biological processes. Gross primary production is the total amount of organic carbon produced by photosynthesis; net primary production is what remains after autotrophic respiration, i.e., respiration by photosynthetic organisms. Sinking of DOC and particulate organic matter (POC) of biological origin results in a downward flux known as export production. This organic matter is transported and respired by non-photosynthetic organisms (heterotrophic respiration) and ultimately upwelled and returned to the atmosphere. Only a tiny fraction is buried in deep-sea sediments. Export of $CaCO_3$ to the deep ocean is a smaller flux than total export production (0.4 PgC yr^{-1}) but about half of this carbon is buried as $CaCO_3$ in sediments; the other half is dissolved at depth, and joins the pool of DIC. Also shown are approximate fluxes for the shorter-term burial of organic carbon and $CaCO_3$ in coastal sediments and the re-dissolution of a part of the buried $CaCO_3$ from these sediments. [from Prentice *et al.*, 2001]

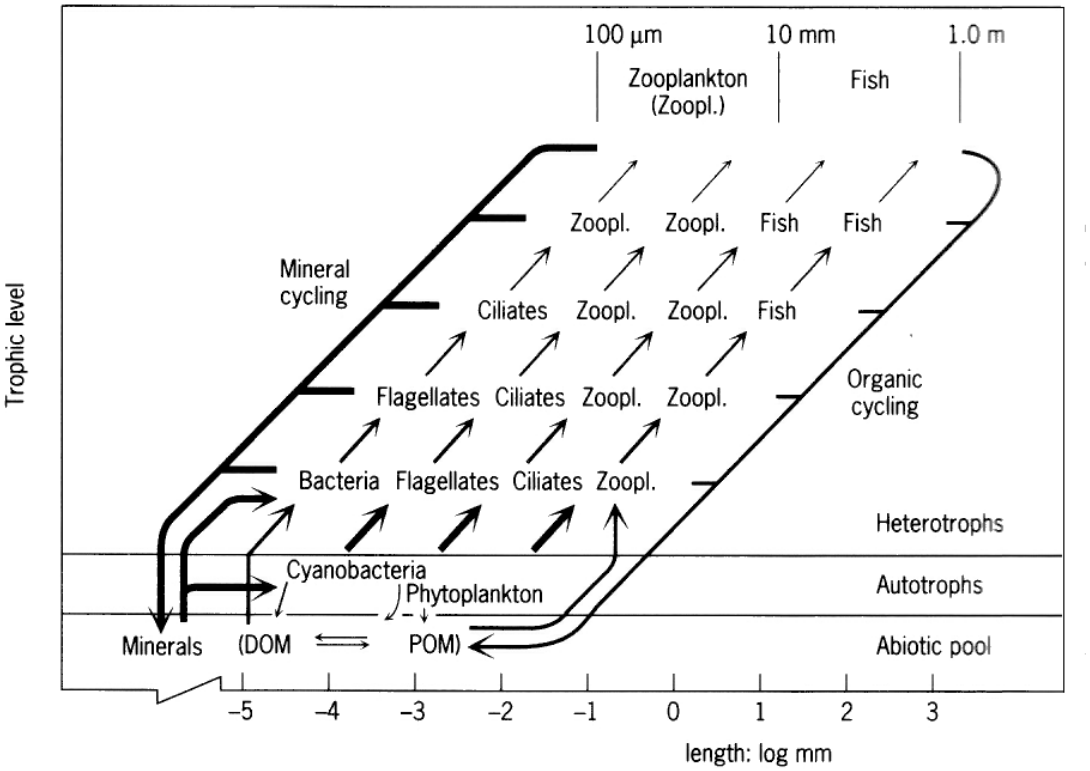

Fig. I-3: Semiquantitative model of planktonic food chains. Solid arrows represent flow of energy and materials; thick arrows, flow of materials alone. It is assumed that 25% of the net primary production is channelled through DOM and the "microbial loop", bacteria, flagellates and other micro-zooplantkon (e.g. ciliates). It is further assumed that the most efficient predator prey size ratio is 10:1, hence the slope of lines relating trophic status to log body length is 1:1. The food chain base represents a size range 3 orders of magnitude. [from Azam *et al.*, 1983]

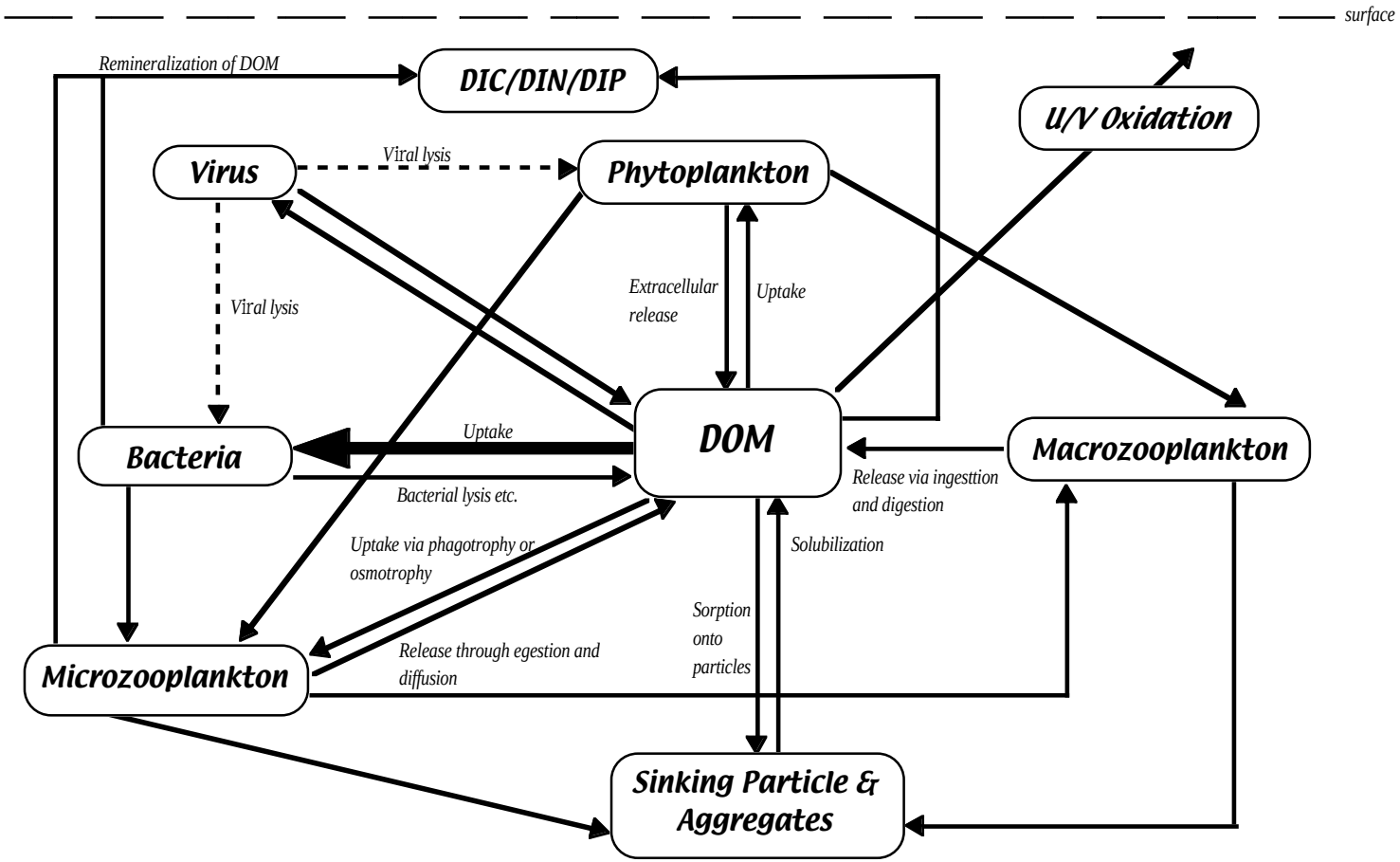

Fig. I-4: Schematic representation of the various DOM production and consumption processes in marine systems. The broken arrows associated with viruses represent viral infection and its effect on DOM production via cell lysis. The dark arrow represents dominant biotic removal process. [from Carlson, 2002.]

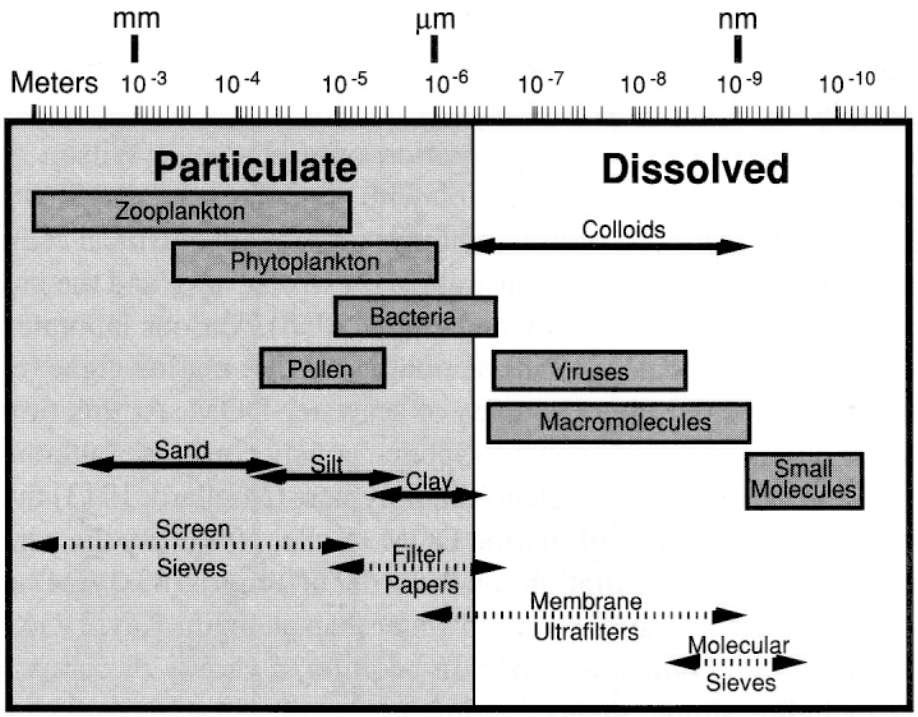

Fig. I-5: The continuum of size and separation methods for organic matter in seawater. [from Hedges, 2002]

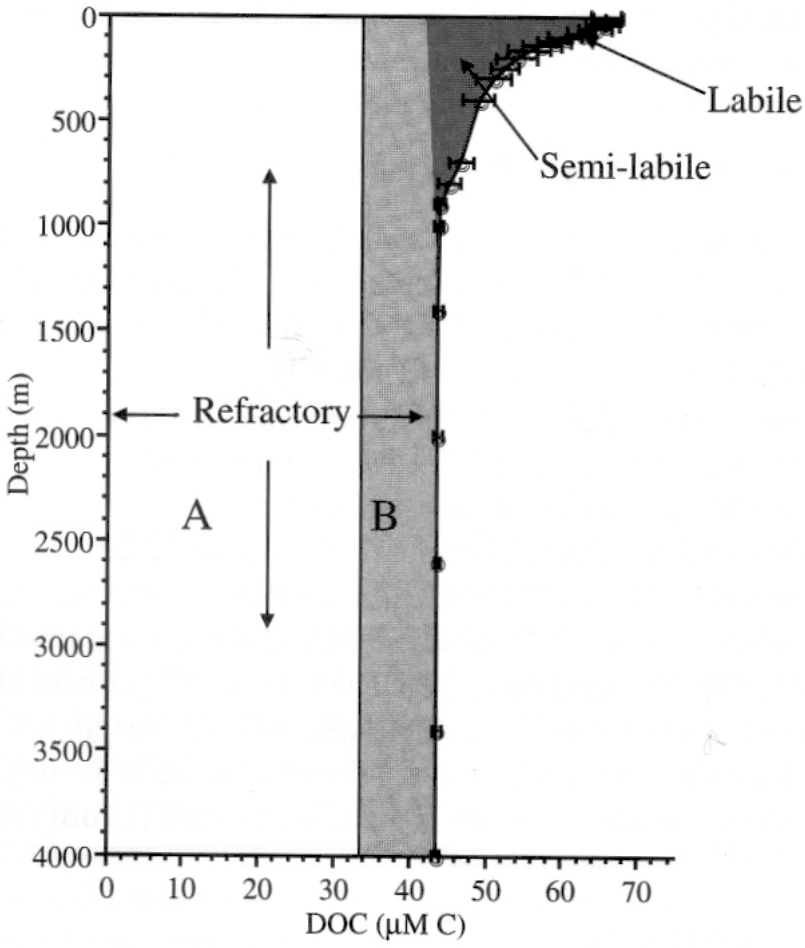

Fig. I-6: Conceptual cartoon of the various pools of refractory, semi-labile, and labile DOC in the open ocean. [from Carlson, 2002]

II. OBSERVATIONS

A. OCEANOGRAPHIC FEATURE OF SURUGA BAY

1. Feature of study area

Suruga Bay is open to the Pacific Ocean and has a submarine trough, deeper than 1000 m in depth, which runs from south to north in nearly center of the bay. This feature infers that the water structure of Suruga Bay is influenced by oceanic water originated from the surface water of the Kuroshio current (Inaba, 1981; Nakamura 1982; Toyota, 1985). Western side slope is leaded from the Izu peninsula and is connected to the trough. The eastern side is quite steep, whereas the bottom slope on western side is gentle, makes a shoal (shallower than 200 m), Seno-Umi. On the northeastern side, a shallow and flat inlet shallower than 100 m, Uchiura Inlet, connects to the main body of Suruga Bay. The current pattern in Suruga Bay has been studied by many researchers (Kimura, 1950; Sato, 1967; Nakamura & Muranaka, 1979; Inaba, 1981). They have reported that a counter-clockwise circulation dominates in the main body of the bay and shown that this pattern occurs with frequency of 75%, but other patterns including clockwise circulation also occur. Thereby, river water spreads on the western side, due to runoff of large rivers into Suruga Bay. Macroscopically, the water originated from open ocean, flows into Suruga Bay and runs northward along the eastern side. As the water is mixing with river water at

the head of the bay, following a counter-clockwise circulation, it outflows into the eastern side.

2. Sampling station and periods

Observation was conducted aboard the research vessel, *Suruga-maru* (Shizuoka Prefectural Fisheries Experiment Station, Fig. II-1b). Regular observations were conducted in 4 stations: 3, F, E and 2 (Fig. II-2) on 34˚51'N line crossing the bay, in 10-11 July, 28-29 August, 20-21 September and 27-28 November 2000, 19-20 February, 25-26 April, 11-12 July, 15-16 October and 12-13 December 2001, and 20-21 February, 14-15 May, 23-24 July and 18-19 September 2002. Temperature and salinity were measured by CTD (SBE 9 plus; Sea-Bird Electronics) every 1 dbar between the surface and the depth above 20 m from the sea bottom (B-20 m). The details of the sampling depths at each station are as follows; 2, 10, 20, 30, 50, 70, 100, 125, 150, 200, 300 and B-20 m depth at Sta. 3; 10, 20, 50, 70, 100, 125, 150, 200, 300, 400, 600 and B-20 m depth at Sta. F; 10, 20, 30, 50, 70, 100, 125, 150, 200, 300, 400 and B-20 m depth at Sta. E; 10, 20, 50, 100, 150, 200, 300, 400, 600, 800, 1000 and B-20 m depth at Sta. 2. Additional sampling depths were introduced at St.2; 30, 40, 60, 125 and 175 m depth in May 2002 and 30, 40, 60, 125 and 1288 m depth in July 2002. Seawater was collected with a carousel multi-sampler system equipped with 10-l Niskin bottles (Fig. II-1a); surface water was collected with a plastic bucket. CTD, nutrients and chlorophyll *a* data were collected at all station.

Diel observations were conducted at Sta. 2, which is located center of the bay and

just above the trough. The depth of Sta. 2 is over 1600 m. Diel sampling were conducted, mainly in the upper layer, at midday (~11:00), night (~22:00), and the next predawn (04:00-06:00), mainly in 21-22 September, 27-28 November 2000, 19-20 February, 25-26 April, 11-12 July, and 15-16 October 2001. The samples for DOM, POM, bacteria abundance, and incubations were collected besides the routine sampling at Sta. 2 mainly from August 2000 to December 2001.

3. Hydrological characteristics of the study area

a. Structure of water masses

The water masses in Suruga Bay were standardized by analyzing the monthly and seasonal oceanographic feature by Nakamura (1982). He classified the water column into 5 water masses (Fig. II-3): the coastal water originated from river water (water mass: A) at the depth less than 10-20 m; main offshore water originated from the Kuroshio (C), which is characterized by the maximum salinity (34.4-34.6) between 100-200 m; the surface water (water mass: B) defined as mixture of the upper coastal water mass (A) and below main offshore water (water mass: C); the intermediate water mass (D) characterized by the minimum salinity (34.2-34.4) having its origin in the Subarctic region, which distributes throughout year between 200-1200 m; the bottom water mass (the Pacific Deep Water mass: E, below 1200 m) which is considered to be modified water originated from the Antarctic Ocean. The coastal water (water mass: A) distributes from the bay head to the

western coastal region due to counter-clockwise circulation. Furthermore, the surface water is classified into two categories: the surface mixed water, retaining much of the characteristics of the coastal water mass, which distributes upper 50 m depth and the offshore surface water, retaining much of the Kuroshio water, which distributed in the upper 100 m depth. However, water masses of B and C can not be identified clearly in winter on the bases of salinity and temperature due to deep convective overturn.

b. The relationships between potential temperature and salinity, and temporal and spatial distributions of potential temperature and salinity

The θ/S diagrams which are profiles of salinity (S) plotted against potential temperature (θ) in each sampling period at Sta. 2, categorized each season (Fig. II-4). Here, the potential temperature (θ) is termed the temperature, which water would have at the surface under atmospheric pressure if seawater was brought to the surface from depth, without exchanging heat with its surrounding. Potential temperature is now calculated using *in situ* temperature. As potential temperature is not a function of depth, it is a more useful parameter than *in situ* temperature for characterizing water masses and vertical motion in the oceans (Chester, 2000).

The θ/S diagrams show obvious differences among seasons and clearly the occurrence of water masses described above. It is easy to distinguish two main water masses from two inflection points in the θ/S diagrams: the main offshore water originated from the Kuroshio appears at high salinity (higher than 34.5) and high temperature (around 15˚C); the intermediate water mass occurs at lower salinity (34.2-34.4) and temperature

(around 5˚C) through the year. Furthermore, the θ/S diagrams for summer and autumn reached higher temperature and lower salinity from the main offshore water, which shows that the main offshore water is mixed with the surface water which has characteristics of the coastal water, whereas this did not appear clearly in winter and spring due to convection of water column. The θ/S diagrams show that the intermediate water mass was mixing with the water mass having higher salinity and lower temperature, called the Pacific Deep Water. Both deeper water masses are stable through the years in contrast with upper water masses. The offshore water mass varied largely over sampling periods. The diagrams shifted to higher salinity and temperature than in the other periods in September 2000, July and September 2002 and weakly in May 2002.

Contour plots of salinity and potential temperature at the surface to bottom from July 2000 to September 2002 at Sta. 2 are shown Fig. II-5. The surface water (salinity: lower than 34.4) thickened from summer to autumn and deepened to coastal site up to around 50 m in depth (from Sta. 2 to Sta. 3; Fig. II-6), but thereafter, the surface water could not be identified due to deep convective overturn in winter and spring. As the surface water mass developed, the offshore water (salinity: higher than 34.4) sank to shallower than 150 m, and moreover, the below water mass, the intermediate water, became more deepened. Similar pattern was shown also in contour plot of temperature: the boundary between the offshore water and the intermediate water, 11˚C isopleth, deepened from the end of summer to autumn. Furthermore, the core of the intermediate water mass (salinity: lower than 34.3) became thin and disappeared occasionally. This appeared clearly at the western sites while the bottom water mass (water temperature: lower than 3˚C, salinity: higher than 34.5) was almost stable through the years (Fig. II-6). In addition to seasonal

variation, annual variations of salinity and water temperature were shown particularly in the upper 200 m: when compared between years, the offshore water mass was thinner in 2001 than in 2000 and 2002; the core of the offshore water mass (salinity: higher than 34.6) occurred in both 2000 (at Sta. 2 and E) and 2002 (at all Stas., Fig. II-6), indicating a strong influence of offshore water to more coastal region. This is also shown in the θ/S diagrams as the shift to higher salinity and temperature. Iwata *et al*. (2004) suggested that the intensity of inflow of the offshore water is related to the route of the Kuroshio current, i.e. distance between the axis of the Kuroshio current and Japanese coast.

The vertical distributions of salinity and potential temperature in each sampling period are shown by the cross sections from the center (Sta. 2) to the west (Sta. 3) of Suruga Bay at 34˚51'N line (Figs. II-6 and 7). The lower salinity distributed around Sta. 3 except for winter and spring periods, indicating inflow of river water. In July and September 2000, and July 2002, lower salinity (salinity: lower than 33.7) distributed shallower than 10-20 m and spread around to Sta. 2. This indicates that the inflow from rivers was enhanced due to increase of precipitation or dilution by rainwater. Fig. II-8 shows the monthly precipitation in Shizuoka during 2000 to 2002. The precipitation during summer (June – August) in 2000 and 2002 are relatively large in comparison with summer of 2001. Especially, precipitation of July 2001 was extremely low. This indicates fresh water (river water and rainwater) had little influence on the surface water at the time. The seasonal thermoclines were observed clearly in summer, particularly in July 2001. The potential temperature was 2-4˚C lower in July 2001 than in the same month in the other years.

The north-to-south observation was conducted on cross lines, 138˚33' E and 138˚38'

E in the bay at 28 May 2002, in addition to regular observations. Fig. II-9 shows the cross sections for vertical distributions of salinity and potential temperature from north to south on the line connecting Stas. E, 4, C and 5 (138˚33'E), which locate along the slope of Suruga Trough from center to the mouth of the bay, and on the line connecting Stas. 2, 6 and 7 (138˚38'E), which extends in the center of the trough. In the last regular observation at 14 May 2002, water column was still mixed deeply due to winter convective overturn, thus, the distributions of salinity were relatively uniform throughout 200 m (Fig. II-6); the water column at the next observation after two weeks was been already restratified (Fig. II-9). Although slight higher salinity (higher than 34.64) was observed in the mouth of the bay in cross section on 138˚33'E: this indicates reflection by the ocean current, the Kuroshio, the salinity and potential temperature distributions were not different vertically between two lines from north to south, and the obvious effects of the rugged shape of the bottom on the spatial distributions were not detected. Therefore, the stationary station 2 was a representative site for the body of Suruga Bay.

a

b

c

Fig. II-1: a) The photograph of a carousel multi-sampler system equipped with 10-l Niskin bottles and CTD (SBE 9 plus; Sea-Bird Electronics), b) The research vessel *Suruga-maru* (Shizuoka Prefectural Fisheries Experiment Station). c) The photograph when DOM were collected on board from the Niskin bottles by gravity-filtration with a silicone tube and a polypropylene filter holder connected directly to the spigots of the Niskin bottles.

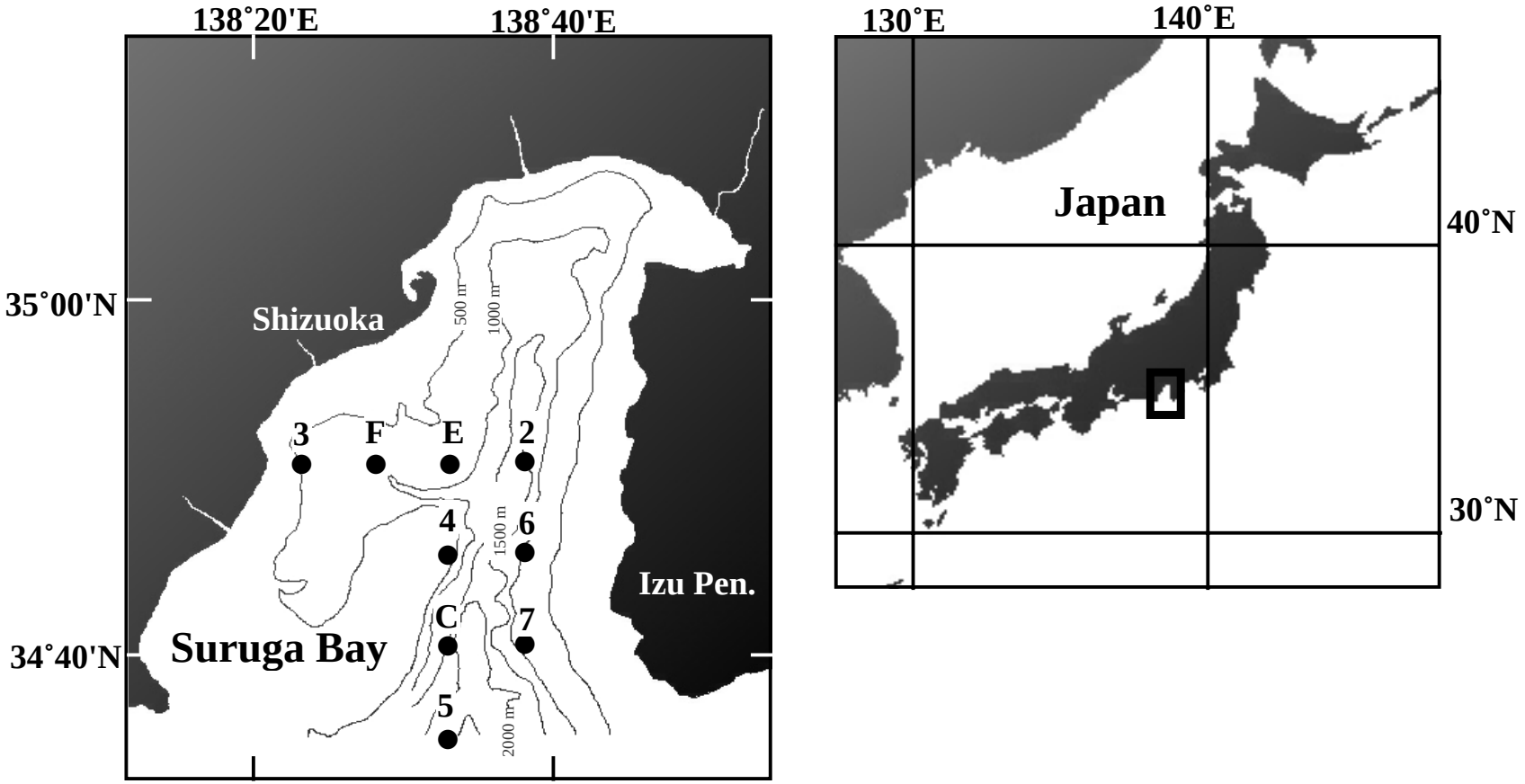

Fig. II-2: Sampling stations in Suruga Bay.

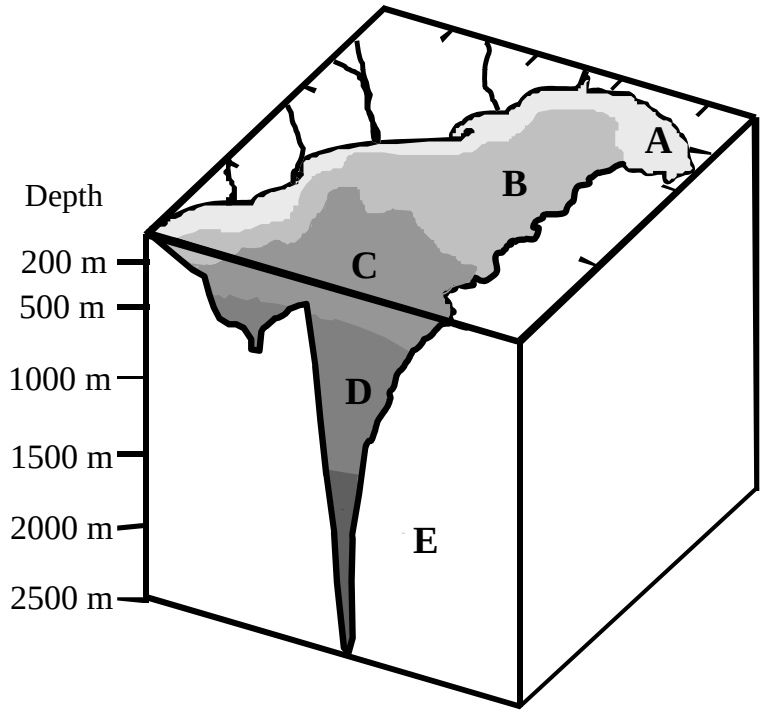

Fig. II-3: Schematic representation of water masses in Suruga Bay; A: Coastal Water originated from river water, B: Surface Water originated from Coastal Water and Offshore Water, C: Offshore Water originated from Kuroshio, D: Intermediate Water originated from Subarctic Zone, E: Pacific Deep Water [from Nakamura, 1982].

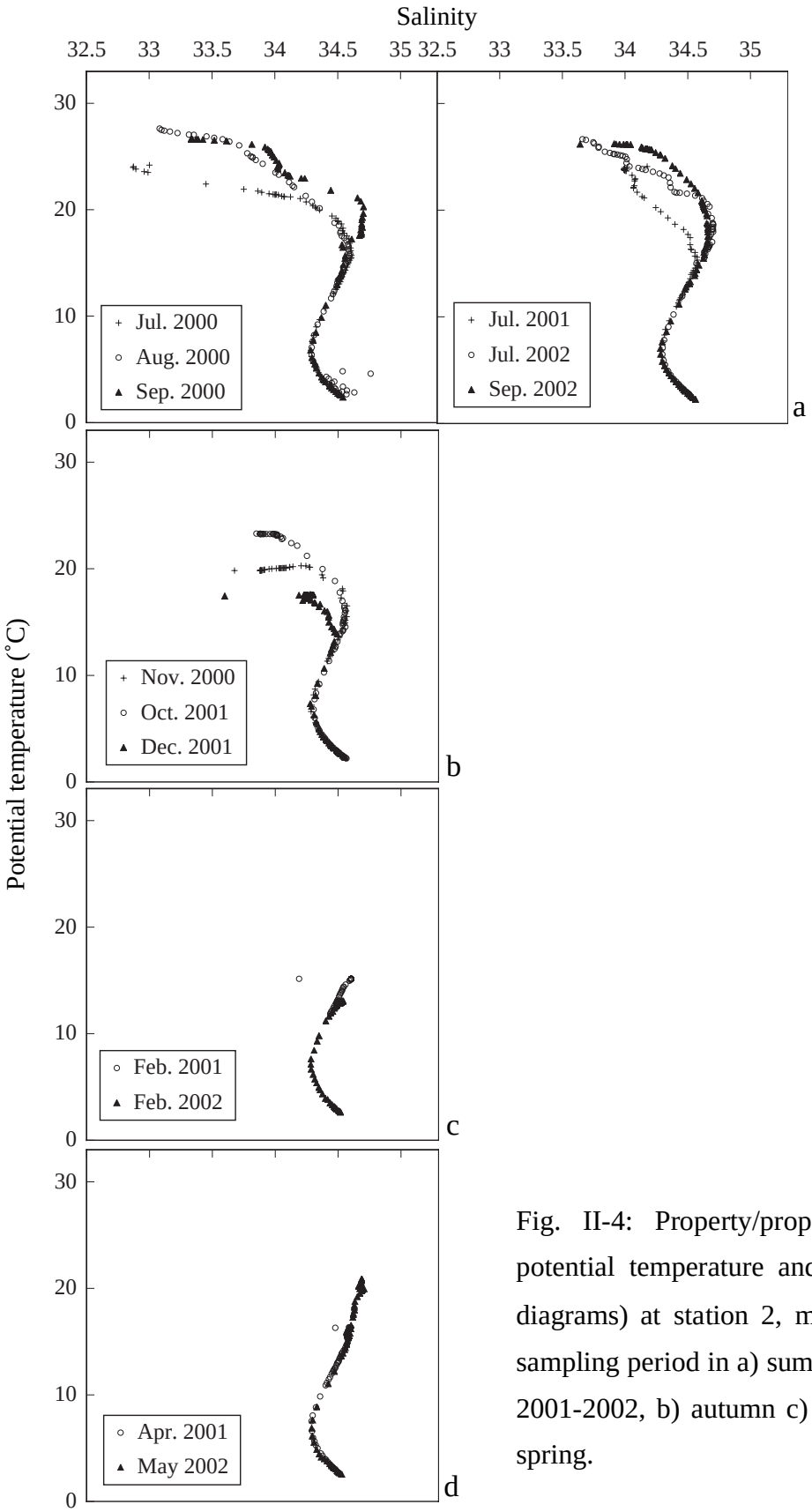

Fig. II-4: Property/property plots of potential temperature and salinity (θ/S diagrams) at station 2, midday in each sampling period in a) summer, 2000 and 2001-2002, b) autumn c) winter and d) spring.

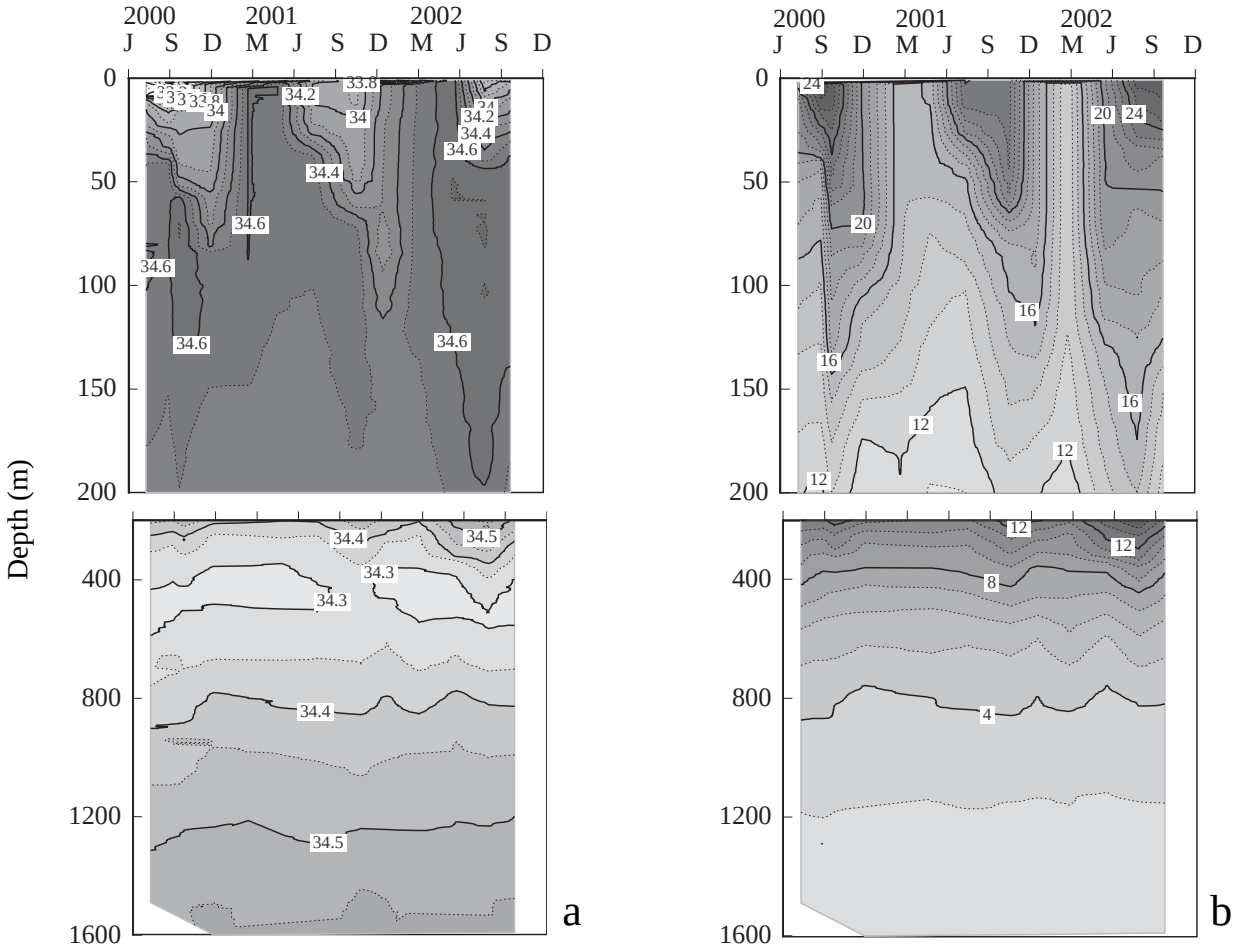

Fig. II-5: Contour plots of a) salinity, and b) potential temperature (˚C) in the surface-bottom from July 2000 to September 2002 at midday, station 2.

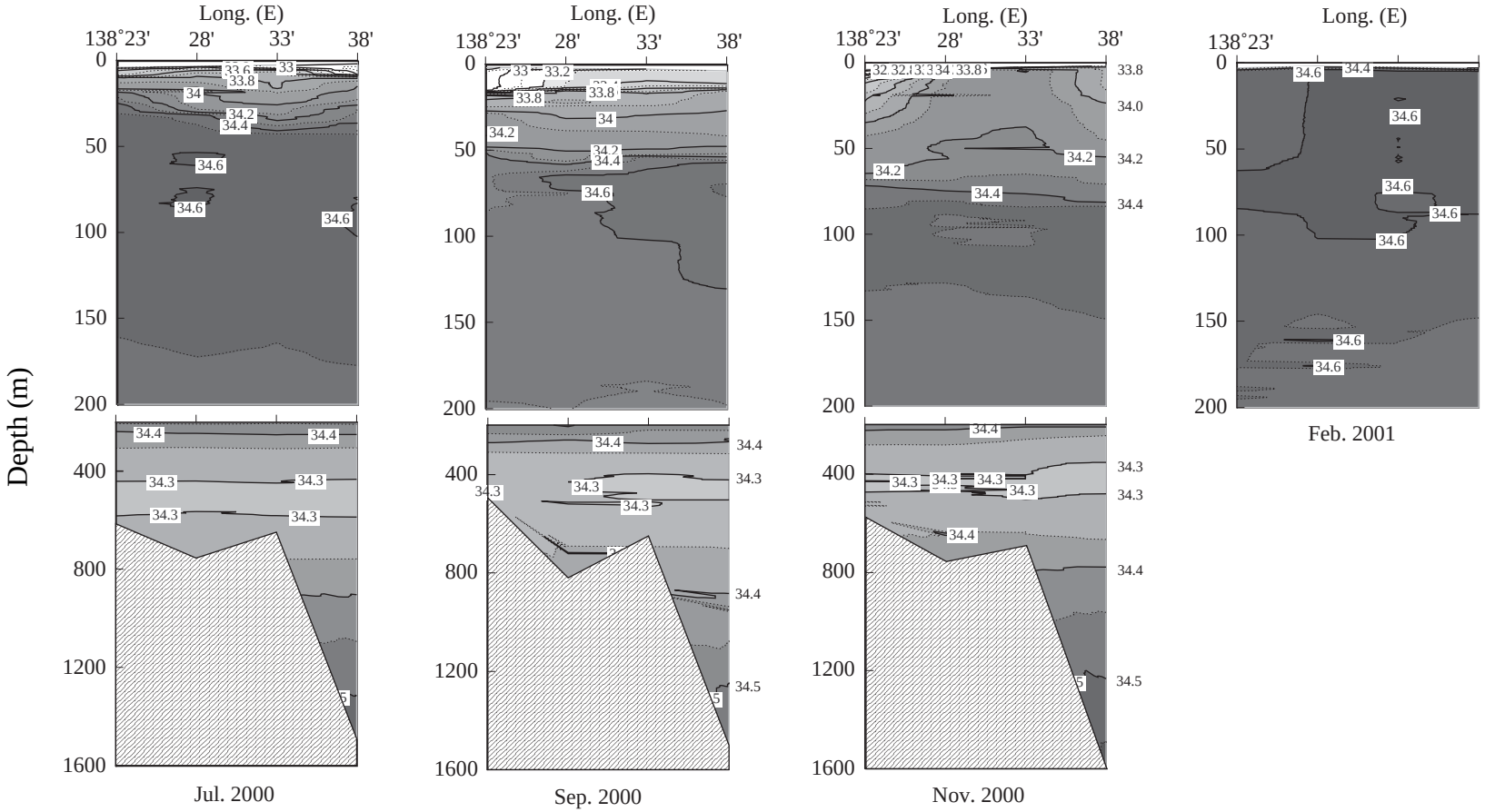

Fig. II-6: Vertical cross-sections of salinity in each sampling period from Sta. 3 (138˚23’E) - F (138˚28’E) - E (138˚33’E) - 2 (138˚38’E) along 34˚51’N line.

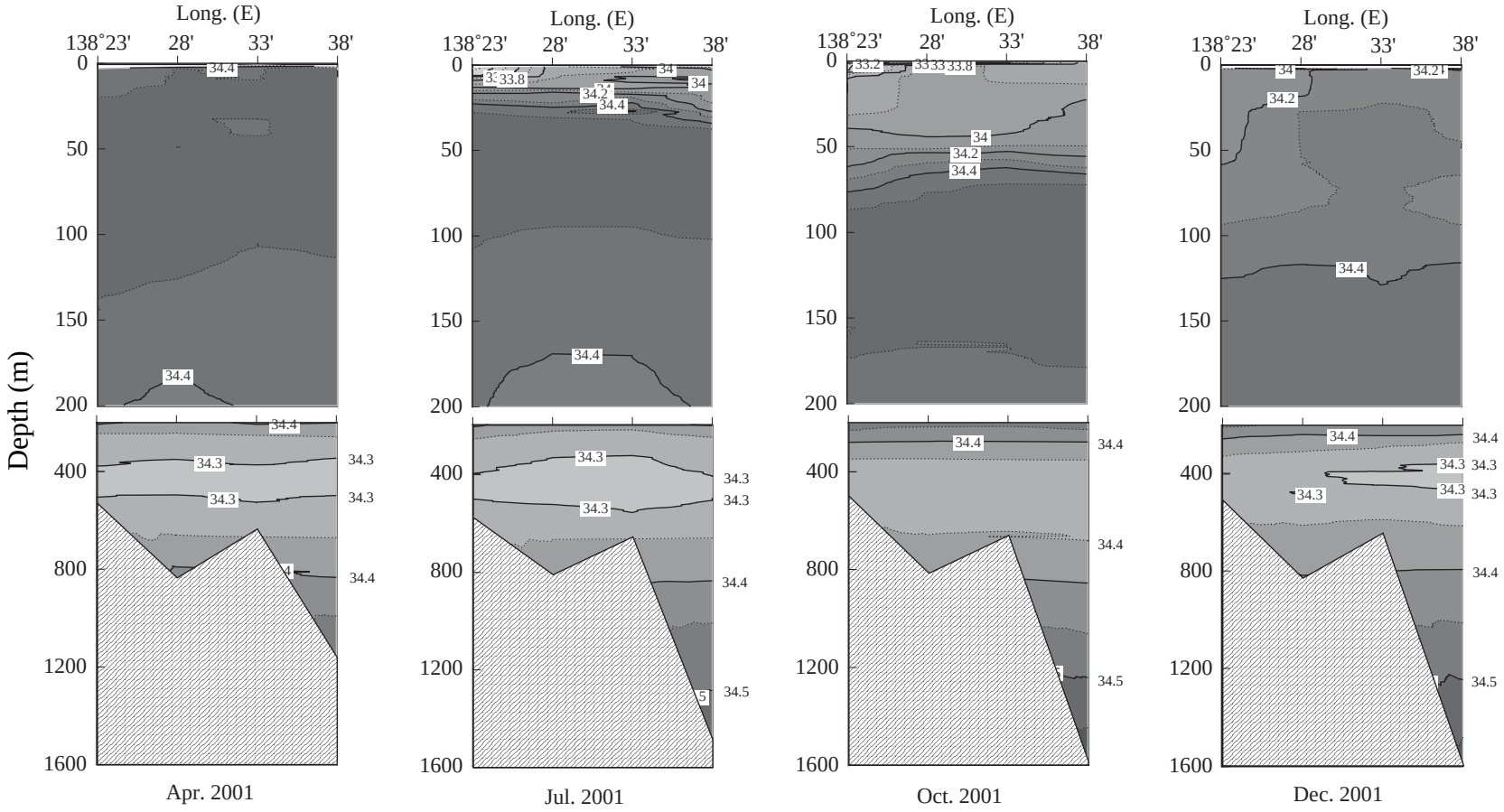

Fig. II-6: Continued.

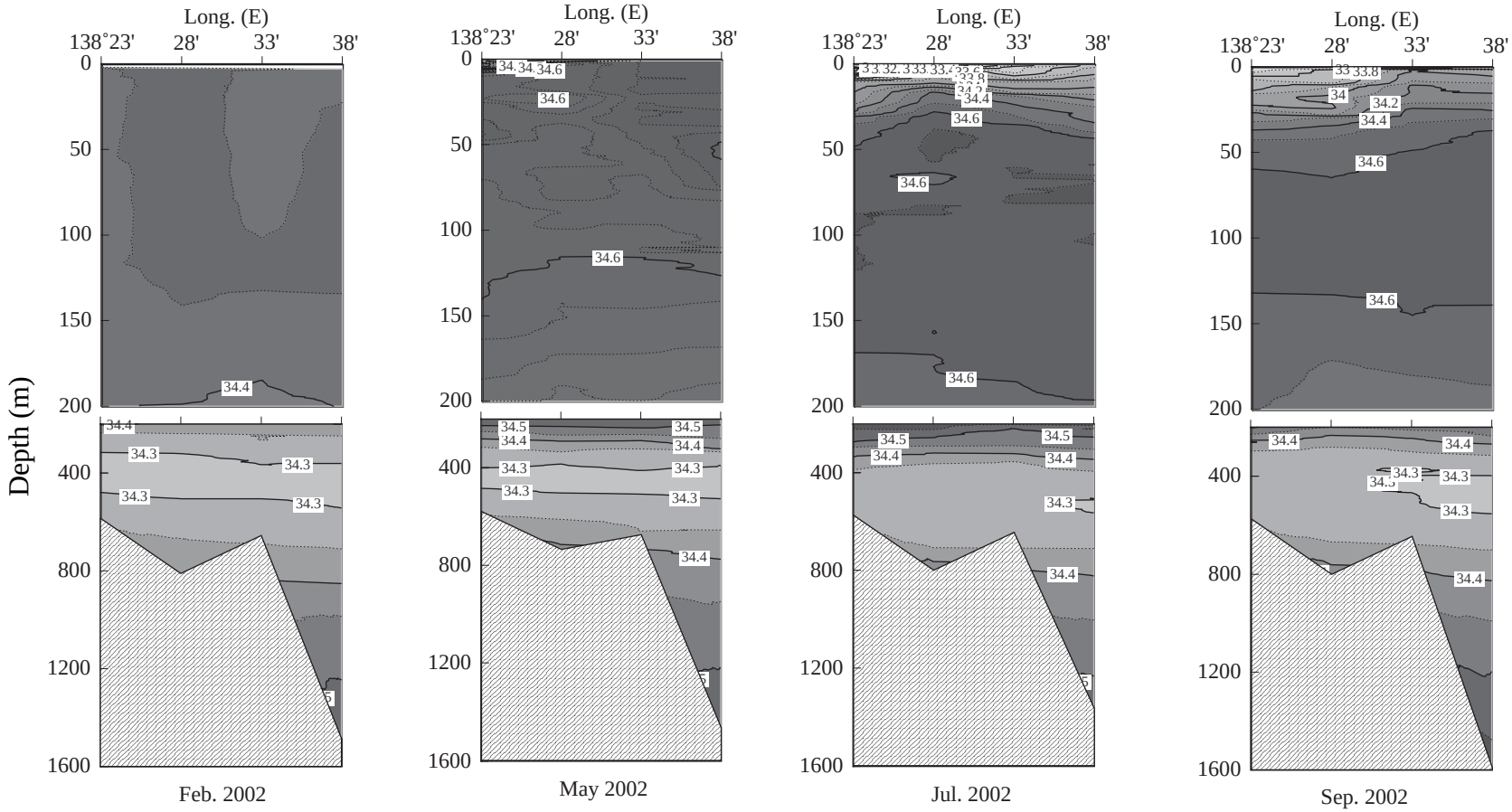

Fig. II-6: Continued.

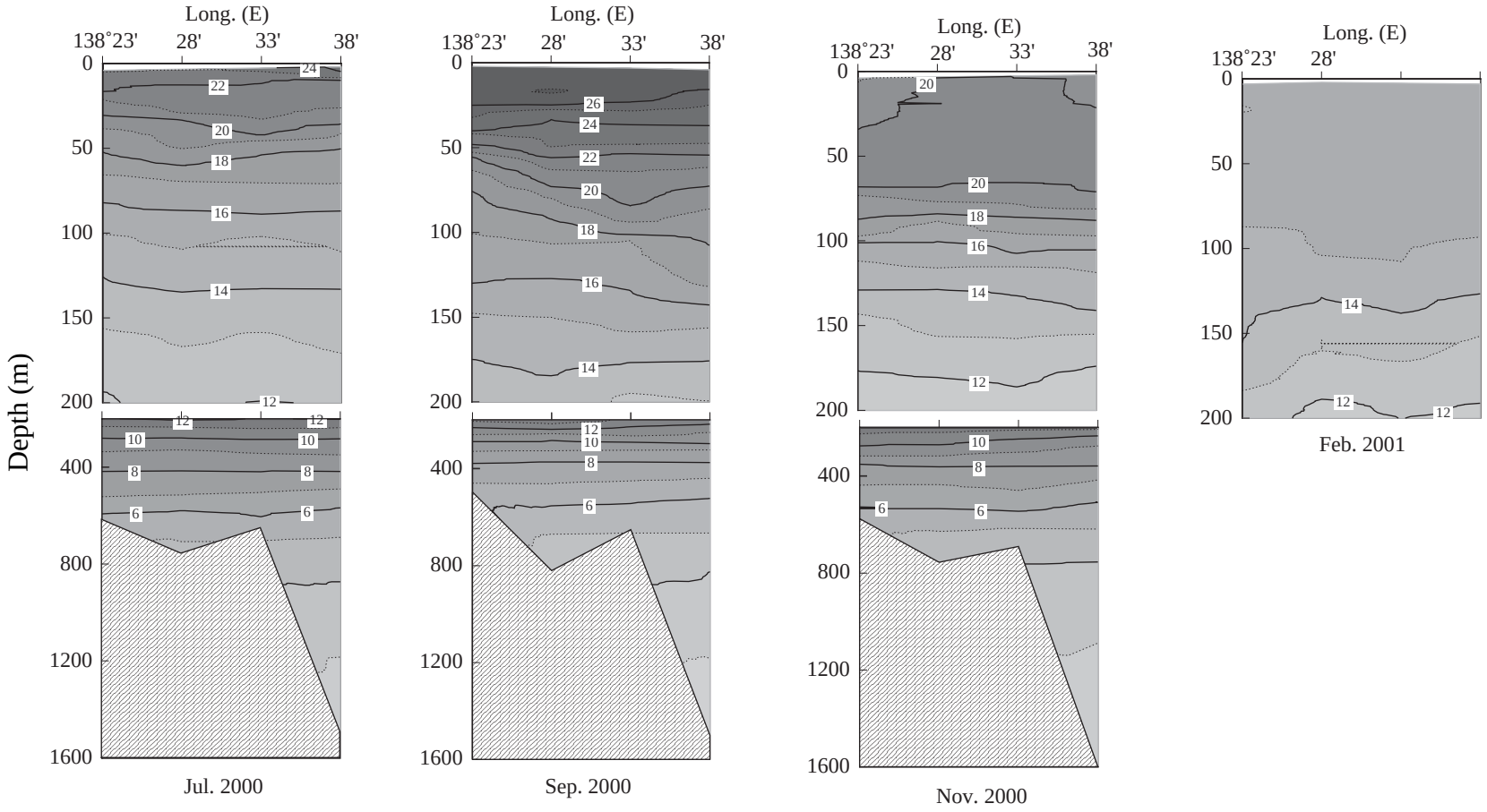

Fig. II-7: Vertical cross-sections of potential temperature (˚C) in each sampling period from Sta. 3 (138˚23’E) - F (138˚28’E) - E (138˚33’E) - 2 (138˚38’E) along 34˚51’N line.

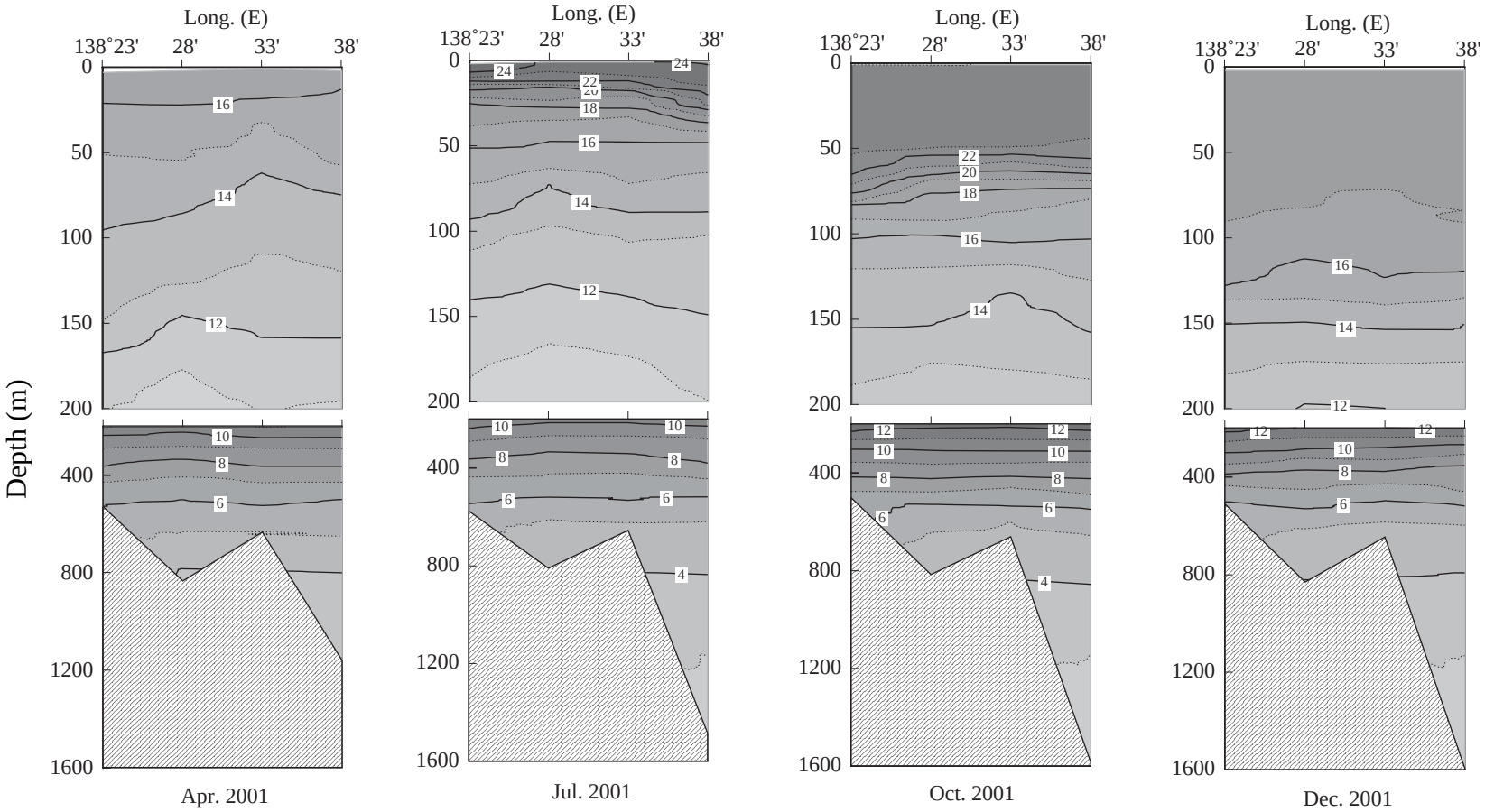

Fig. II-7: Continued.

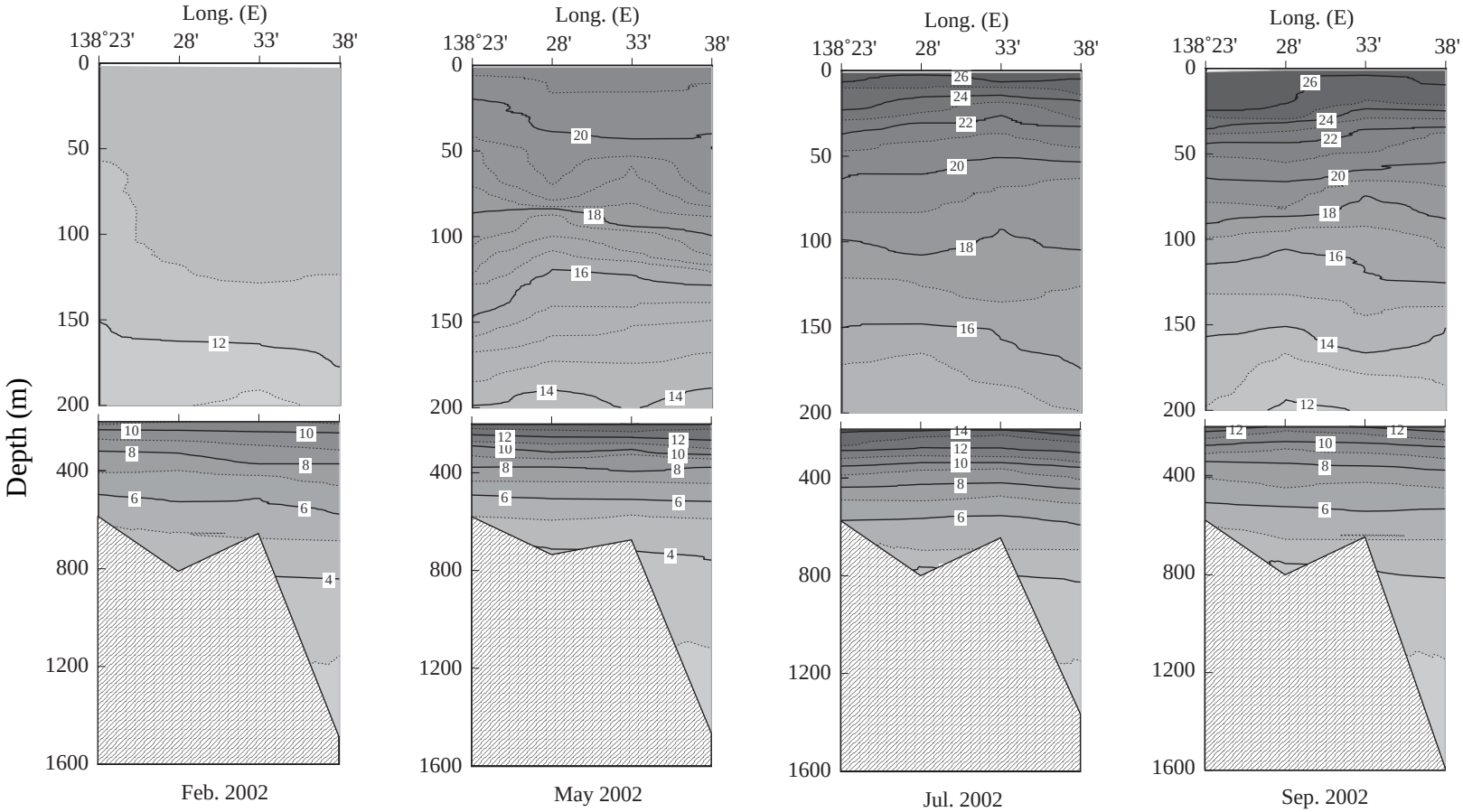

Fig. II-7: Continued.

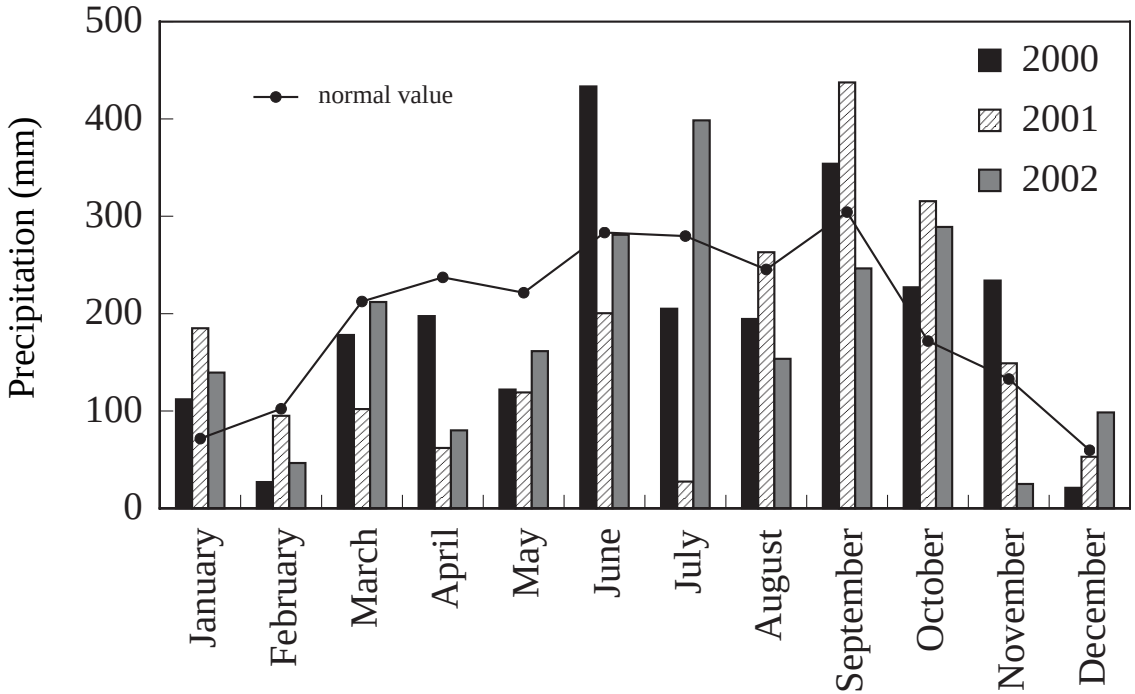

Fig. II-8: Monthly precipitation in Shizuoka during 2000 to 2002. [from Japan Meteorological Agency, http://www.data.kishou.go.jp/index50.htm]

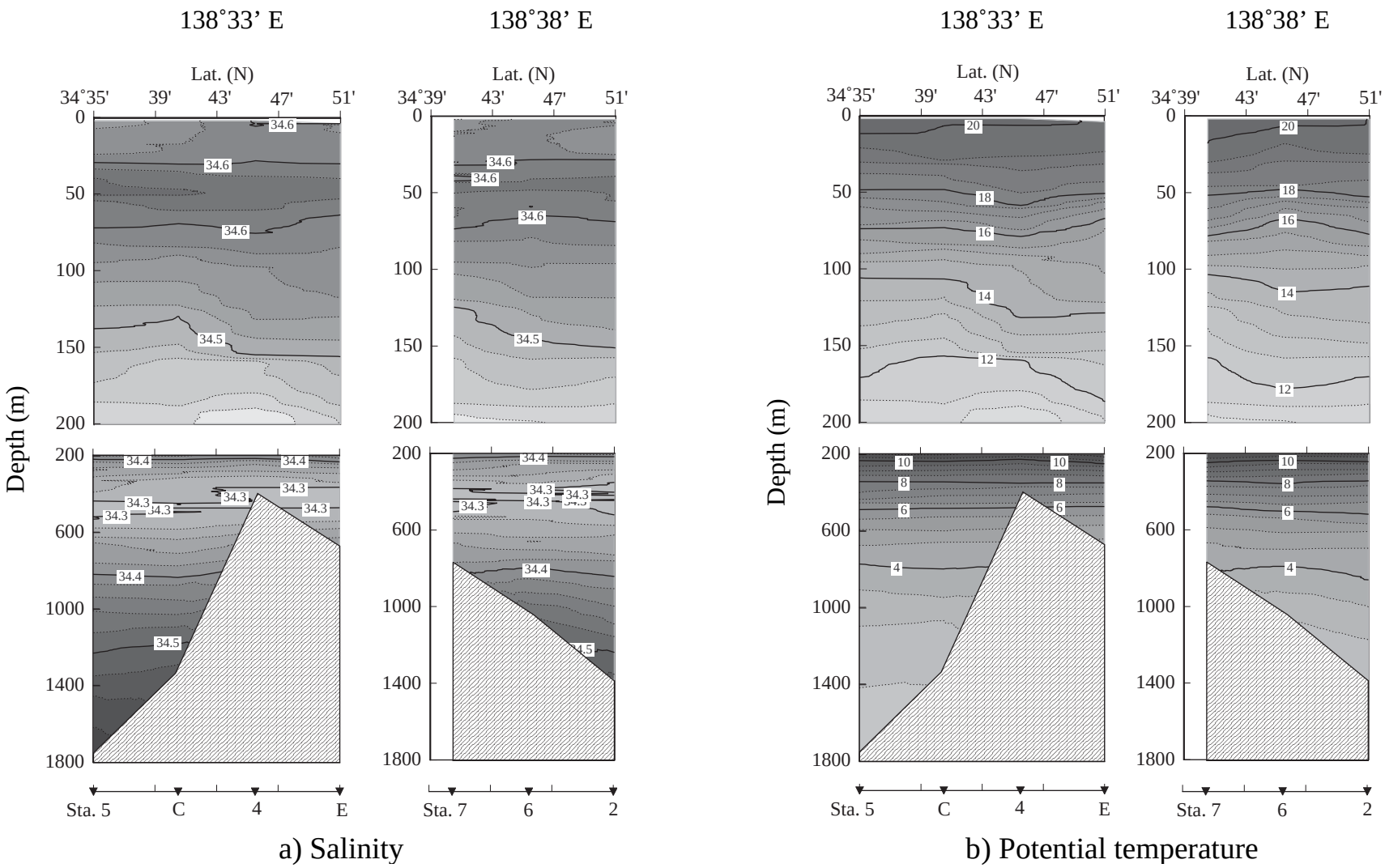

Fig. II-9: Vertical cross-sections for a) salinity and b) potential temperature (˚C) from north to south on the line connected with stations from E-4-C-5 along 138˚33’E line and from 2-6-7 along 138˚38’E line.

B. SAMPLING AND MEASUREMENTS

1. Dissolved organic carbon and nitrogen

DOM concentration is extremely low in seawater, so that, sampling should be conducted very carefully to avoid contamination from equipment and ambient environment.

Samples for DOM were taken by gravity-filtration with a silicone tube and a polypropylene filter holder (PP-25, TOYO ROSHI) connected directly to the spigots of the Niskin bottles. The filter holder contained double glass fiber filters (GF-75, TOYO ROSHI, equivalent to GF/F type, Whatman) precombusted at 500 ˚C for 4 h. All equipment for DOC samples was cleaned with Extran® (Neutral detergent, MA02, Wako Pure Chemical Industries), 3 N HCl solution and Milli-Q water. Milli-Q water was produced by passing distilled water through a Milli-Q SP TOC reagent water system (Millipore). After three rinses, the filtrate was collected in glass vials, washed with 3 N HCl solution and Milli-Q water, and precombusted (500 ˚C, 4 h) for removal of organic matter. The vials were immediately sealed with Teflon-lined caps and stored frozen until analysis. Validity of this sampling procedure was verified comparing with other procedure using glass equipment cleaned by washed with Extran®, 3 N HCl solution and Milli-Q water, and precombusted (500 ˚C, 4 h). In the procedure using glass, seawater was collected in 100-ml glass conical flask from Niskin bottle and filtrated by using glass funnel connected base putting double glass fiber filters (GF-75) between those. Filtrate

was dropped into a glass beaker setting in glass bell jar vacuumed by an aspirator. Filtrated sample was withdrawn with a Pasteur pipette to glass vials for preservation. When compared between these two sampling procedures, there was not significant difference ($p > 0.05$, $n = 3$) in the concentrations of both DOC in seawater treated with both procedures. Therefore, the former procedure using silicone tube and a polypropylene filter holder was chosen because it is easier due to simple equipment. This way also allowed me to collect quickly filtered samples and permitted me high efficiency to collect many samples in the short time with the advantage to prevent degradation of DOM during sampling.

Concentrations of DOM were determined by a high-temperature catalytic combustion (HTC) method, using a Sumigraph TOC-90 (Sumika Chemical Analysis Service) equipped with a non-dispersive infrared gas analyzer (Model 880; Rosemount Analytical), for precise detection of CO_2 and chemiluminescence NOx Analyzer (Model 2108; Desibi environmental corp.). A quartz combustion tube was filled with copper oxide wire, sulfix (mixture of AgO and CoO; Kishida Chemicals) for elimination of halogenated and sulfur compounds, and 3% platinum catalyst. The system for DOC analysis is detailed in Suzuki *et al*. (1992); Suzuki & Sugimura (1985). The combustion tube was conditioned by continuous injections of Milli-Q water over 1-2 days until peak areas of Milli-Q water were reduced to a constant low level. After frozen samples were thawed ultrasonically, a sample of 10 ml was acidified with 100 µl of 3 N HCl solution and sparged for 15 min with ultra-pure air (CO_2 < 0.1 ppm) to remove inorganic carbon. Then 200 µl seawater was injected into the quartz combustion tube heated at 680 ˚C; this was repeated five times for each sample. DON concentration was determined by

subtracting DIN (dissolved inorganic nitrogen: nitrite and nitrate were measured by TRAACS 2000, but ammonium was not measured in this study) from TDN (total dissolved nitrogen) detected by the chemiluminescence NOx Analyzer. Average analytical errors of DOC and TDN measurement were 0.85 and 0.63% as coefficient of variation or 0.42 μM C (range: 0.03-2.18) and 0.13 μM N (range: 0.00-0.89) as standard deviation (DOC: n = 330, TDN: n = 325), respectively. The variation in sample replication was checked and was within the range of analytical error (1.93 μM C as standard deviation). The system was standardized daily, before operation, with a four point calibration curve using EDTA–2Na solution in Milli-Q water. Total blank was determined from the intercept and slope of the calibration curve, and averaged 13.1 ± 1.8 μM C (n = 34) and 1.20 ± 1.71 μM N (n = 29). Deep Sargasso Sea water, provided by the Bermuda Biological Station (BBS, USA) as part of an international certified reference material program for DOM measurement by Hansell Laboratory, was measured as a daily reference material. The average of the reference material was 46.7 ± 1.3 μM C (n = 9) and 20.4 ± 0.5 μM N (n = 9). DOC and TDN concentrations were determined by subtracting the intercept and dividing by the slope of the each calibration curve.

2. Nutrients

Nutrient samples were collected into 100 ml polypropylene bottles from the Niskin bottles and kept in freezer (-30 ˚C) until analysis. Measured nutrients were as for nitrate (NO_3), nitrite (NO_2) phosphate (PO_4) and silicate ($Si(OH)_4$) with TRAACS 2000

(BRAN+LUEBBE) (Hansen & Koroleff, 1999). $Si(OH)_4$ was measured only in the samples taken between November 2000 and July 2002. Precision of nutrient analysis was ± 0.2%, ± 0.5%, ± 0.8% and ± 0.5 % as for NO_3, NO_2, PO_4 and $Si(OH)_4$, respectively estimated from coefficient of variation of the replicated (n = 5) analysis of the seawater sample which contained 13.90 µM of NO_3, 0.0 µM of NO_2, 0.92 µM of PO_4 and 18.83 µM of $Si(OH)_4$. Detection limit was estimated by multiplying 3 by standard deviation (SD) of the replicated (n = 5) analyses of 3.5% NaCl solution and the values were 0.05 µM, 0.01 µM, 0.02 µM and 0.03 µM as for NO_3, NO_2, PO_4 and $Si(OH)_4$, respectively (Iwata *et al.*, 2004; Iwata, personal communication).

3. Chlorophyll *a*

Concentration of chlorophyll *a* was measured in the samples taken at the depths of 0, 10, 20, 30, 50, 100, 150 and 200 m depth at Stas. 3, E and F and 0, 10, 20, 50, 100, 150 and 200 m depth at Sta. 2. Samples were collected into dark polyethylene bottles from the Niskin bottles, and 300 ml of the samples were immediately filtered through GF-75 glass fiber filter (TOYO ROSH) with suction (~200 hPa). Filter samples were kept in freezer (-30 ˚C) until the analysis after pigment extract using 10-ml *N*, *N*-dimethylformamide (Suzuki & Ishimaru, 1990). Chlorophyll *a* concentration was measured with a spectrofluorometer (RF-5300PC; Shimadzu), taking readings before and after acidifiation (Holm-Hansen *et al.*, 1965). The spectrofluorometer was calibrated with a chlorophyll *a* standard derived from *Spirulina* (Waco Pure Chemical Industries). On the analysis of the

standard containing 50 μg l^{-1} of chlorophyll *a*, SD of fluorescence read was ± 0.4 μg l^{-1} (*n* = 4), which is equivalent to ± 0.01 μg l^{-1} after divided by a concentration factor [filtration volume (300 ml) / extraction volume (10 ml)] of the samples. Precision of analysis was ± 0.7% estimated by coefficient of variation of the replicated (*n* = 4) analyses of the same standard solution and detection limit was 0.04 μg l^{-1} estimated by multiplying 3 by SD.

4. Particulate organic carbon and nitrogen

Seawater for particulate (organic) matter sampling was collected into polyethylene bottles from the Niskin bottles, and 2-5 liter of the water samples was immediately filtered through GF-75 glass fiber filter (TOYO ROSHI) with suction (~200 hPa). The filter samples kept in freezer (-30 ˚C) until the analysis. The filter was exposed to HCl vapor for a day to remove $CaCO_3$ and dried at ~50 ˚C in a drier or in a glass vacuum desiccator before analysis. Consequently, particle matter on the GF-75 glass fiber filter was detected as POC and PN and these concentrations were measured by SUMIGRAPH NC-90A (Sumika Chemical Analysis Service).

5. Bacterial abundance and carbon biomass

The seawater for bacterial abundance was collected in 50 ml-sterilized tube and fixed immediately with glutaraldehyde or neutralized formalin (final concentration, 2 %) and

preserved at 4 C˚, in darkness. Bacteria was stained with DAPI and counted under an epifluorescence microscope according to Porter & Feig (1980). Bacterial abundance was converted into carbon biomass using a factor of 30.2 fgC $cell^{-1}$ (Fukuda *et al*. 1998). The counting was conducted within 2 weeks of the collection

6. Bacterial production rate

Generally, bacterial production rate (BP) is often measured by incorporation of leucine (Kirchman *et al*., 1985) or thymidine (Furman & Azam, 1980 and 1982) labeled by radioisotopes. These methods are high sensitive and require only relative short time for incubation. However, the experiment using radioisotopes could not be carried out on board due to lack of on board hot laboratory, so the 'dilution' method (Landry & Hassett, 1982; Shinada *et al*., 2000; Shinada, 2002) was conducted instead. The 'dilution' technique allows simultaneous estimation of bacteria or phytoplankton growth rate and the grazing loss rates due to zooplankton with minimal manipulation of the natural plankton assemblages (Landry & Hassett, 1982; Shinada *et al*., 2000). One of the potential sources of error associated with the technique is the nutrient limitation during experiments on phytoplankton. Although nutrients were depleted during summer in the surface layer of Suruga Bay, Gifford (1988) reported that nutrients enrichments in natural plankton assemblages may result in some damage or change, therefore it was not added any nutrients on dilution experiments. Therefore, growth rate of phytoplankton estimated in this study might not exactly reflect potential rate. Apparent bacteria or phytoplankton

growth (μ_{net}, d^{-1}) and zooplankton grazing rates (g, d^{-1}) on bacteria or phytoplankton were estimated using Landry & Hassett (1982) model:

$$\mu_{net} = \mu_{max} - g \cdot x \qquad (1),$$

where x and μ_{max} are the proportion of diluted seawater ($x = 1$ is non-diluted treatment) and potential growth of bacteria or phytoplankton, respectively. Apparent growth rate (μ_{net}) was calculated for each bottles as

$$\mu_{net} = \ln(N_t/N_0)/t \qquad (2),$$

where N_0 and N_t are the initial and final bacteria abundance or chlorophyll *a* concentration , and t is the incubation time (d), respectively.

Rate of bacteria or phytoplankton growth and mortality duel to grazing can be inferred from observed changes in population density following incubations of different dilutions of natural seawater. The equation (1) is the appropriate equation describing the changes in population density over time, *t*. The observed rate of change in population density at the different dilutions is linearly related to the dilution factor (Fig. II-10). The negative slope of this relationship is the grazing coefficient g; the *Y*-axis intercept is the bacteria or phytoplankton growth rate, μ_{max}.

Samples for BP were collected from 2-5 m at night into two 10-litter polycarbonate bottles cleaned with HCl solution and Mill-Q water and immediately the one sample was filtered with polycarbonate filter (pore size: 0.2 μm) to remove bacteria. These samples were preserved in dark until arrival at land. In laboratory on land, natural (unfiltered) sample was diluted with filtered seawater with 0.2 μm filter. Dilution series of unfiltered to filtrated seawater (generally, the percentage of unfiltered water: 100, 50, 30, 20 and 10%) were prepared in 500-ml polycarbonate bottles in triplicates. The diluted samples

were incubated for a day in outdoor aquarium. Subsamples for bacteria abundance and chlorophyll *a* concentration were collected at initial and at the end of the incubation. Sample for bacteria abundance were fixed with glutaraldehyde (final concentration of 2%) and preserved at 4 ˚C, dark until counting bacteria abundance. Sample for chlorophyll *a* was filtrated with GF-75 filter, treated and measured as the same way described above.

7. Primary production rate

Sample water for measuring primary production rate (PP) was collected at 6 depths corresponded with 1, 5, 10, 20, 50, and 100% surface light irradiance (upper than 2 m). PP was calculated from uptake of labeled inorganic carbon ($H^{13}CO_3^-$) according to Hama *et al.*, 1983. Samples were collected in two cleaned 10-litter polycarbonate bottles (Nalgene) rinsed two times with the sample. In laboratory, sample was withdrawn from the 10-litter polycarbonate bottles into 500 ml-polycarbonate bottles cleaned Extran® and HCl solution and sterilized. The 500-ml polycarbonate bottles added 1 ml of stock solution of 10g l^{-1} of 99.9% $NaH^{13}CO_3$ were fixed to each light level according to the collected depths with black nets. These bottles were incubated in an outdoor acrylic aquarium circulating surface seawater during 24 hours from start time (12:00-16:00). After incubation, seawater was filtered with precombusted (500 ˚C, 4 h) GF-75 glass fiber filters. The filters were stored in freezer until analysis. After removed $CaCO_3$ and added $H^{13}CO_3^-$ by HCl vapor and dried in the same way for POC measurement, the isotopic ratio of carbon in particulate organic matter on the filter was analyzed with ThermoQuest

interfaced with ConFlo between EA1110 and delta plus XL (Thermo Electron).

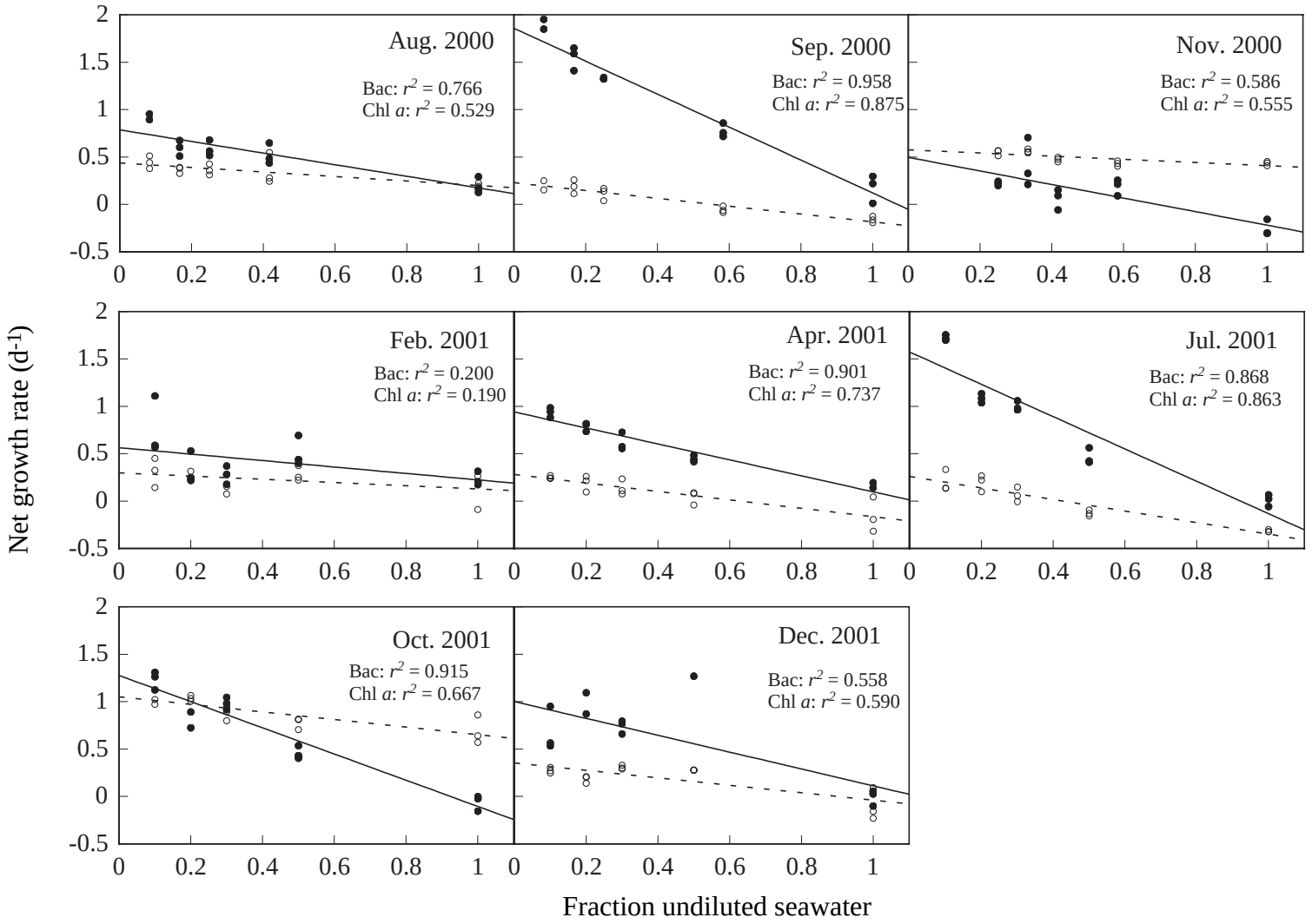

Fig. II-10: The results of dilution experiments. Solid and open circles represent net growth rate (d^{-1}) for bacteria and phytoplankton, respectively. Solid and broken lines represent liner regressions for bacteria and phytoplankton, respectively.

III. DYNAMICS OF ORGANIC MATTER IN SURUGA BAY

A. TEMPORAL AND VERTICAL DISTRIBUTIONS OF CHEMICAL AND BIOLOGICAL PARAMETERS

1. Spatial and temporal distributions of nutrients and chlorophyll *a*

Contour plots of temporal and vertical distribution (upper 200 m) of nutrients: nitrate, nitrite, silicate and phosphate, from July 2000 to September 2002 at Sta. 2 are shown Fig. III-1. Nutrients concentration showed nearly the reverse distribution of potential temperature and increased with depth except nitrite. Nutrients concentrations were low in the upper 50 m during spring to autumn (Nitrate: lower than 5 μM, Silicate: lower than 10 μM and phosphate: lower than 0.4 μM). On the other hand, nitrite decreased with depth and sometimes has the maximum at the subsurface between 30-70 m. The concentration ranged from under detection limit to 1.08 μM through observations and water column. Below 150 m, nitrite concentration was very low (lower than 0.22 μM). Nitrate was depleted upper around 20 m from spring to summer in 2000 and 2002, and thereafter nutrients increased in the surface layer of winter, because deep mixing raised them from deep to upper water. Vertical sections of nutrients from Sta. 3 to Sta. 2 along latitude 34˚51’ N in each sampling period (Fig. III-2) show that the magnitude of nitrate depletion became greater in the coastal station (toward Sta. 3: 138˚23’E): the depletion extended to

more deeper, layer in July and September 2000, April and July 2001, and May and September 2002, while silicate and phosphate were not depleted except for silicate in the upper 20 m, July 2001. This corresponds with a possibility that nitrogen is limiting factor for the phytoplankton in the offshore surface water during spring to autumn in Suruga Bay (Shiomoto & Hashimoto, 1999).

High concentrations of chlorophyll *a* were observed in the surface layer while below 100 m depth, chlorophyll *a* concentration was very low (lower than 0.2 μg l^{-1}) (Fig. III-3a). In the coastal stations, Sta. 3 and F, chlorophyll *a* concentration was higher than other stations (Fig. III-4). This suggests a possibility that nutrients input from river water into the coastal site enhance PP. Relatively high concentrations of nitrate (over 0 μM, i.e. no depletion) and silicate (over 4 μM) were observed at the surface, Sta. 3 in September and November 2000 (chlorophyll *a*: 1.6 and 1.8 μg l^{-1} in September and November 2000, respectively), but in the other sampling periods with more high concentration of chlorophyll *a*, such obvious rise in nutrients at the surface in coastal site could not be observed, concluding that high chlorophyll *a* concentration in more coastal site did not necessarily correspond with increase of nutrients at the surface. Vertical cross-sections of nutrients concentrations (Fig III-2) show, rather, the reverse distribution of chlorophyll *a* in almost periods: there was nutrients depletion when chlorophyll *a* concentration was high. Moreover, low salinity distributed around Sta. 3 corresponding with appearance of high chlorophyll *a* concentration in September and November 2000, October 2001, and May, July and September 2002 (Fig. III-2), suggesting that nutrients derived from river was used up by phytoplankton in the coastal site, resulting in high chlorophyll *a* concentration and low (depletion) nutrients at Sta. 3. Generally, nitrate concentration has significant reverse

correlation ($p < 0.05$) with chlorophyll *a* concentration upper 200 m depth in each sampling periods (Table III-1). Similar correlation was observed between silicate and chlorophyll *a*.

Observations every few months demonstrated clearly spring (in February and April 2001) and autumn blooms (in October 2001). Unfortunately, spring bloom in 2002 and autumn bloom in 2000 could not been detected from chlorophyll *a* distribution owing to the coarse intervals of observations. The blooms, however, might occur, especially in spring of 2002 because nutrients had been already depleted at the surface layer (lower than around 30 m) in May 2002 sampling, indicating that phytoplankton had consumed nutrients derived from deeper layer during sampling period in winter.

Nitrate that was supplied to the surface layer from deep by winter mixing was completely consumed by phytoplankton during spring, so that chlorophyll *a* concentration increased during spring (Fig. III-3a and III-4). In summer, the water column had been completely stratified, chlorophyll *a* concentration was low at the surface, whereas the distribution of chlorophyll *a* concentration showed the maximum concentration at the subsurface below the mixed layer. This was observed clearly in July 2001. The depth of subsurface chlorophyll *a* maximum was nearly corresponded with the bottom of the euphotic zone defined as the depth of at least 1% surface irradiance. There were enough nutrients in the depth, which was probably caused by that nutrients would be supplied by diffusion from the deeper layer, there and light inhibition in summer. In autumn, the mixed layer had been deepened, and then chlorophyll *a* became higher concentration due to mixing with the deeper water loaded abundant nutrients.

2. Temporal distributions of organic matter

Fig. III-3c and III-3d show the contour plots of POC and P(O)N from July 2000 to September 2002 upper 200 m at Sta. 2. Temporal distributions for both POC and PN co-varied and were similar to that of chlorophyll *a* and DOC concentration (Table III-1). Both POC and PN concentrations were highest in spring in the upper 50 m, whereas chlorophyll a showed high concentrations in both spring and autumn. The ranges throughout water column (up to bottom-20 m) for POC and PN were from 0.54 to 30.1 μM C and from under detection limit to 4.8 μM N, respectively. DOC concentration decreased with depth. Vertical profiles in each season through the water column are shown Fig. III-5. DOC concentration was almost uniform below 400 m (44.0 μM C (range: 39.0-50.1 μM C, n = 90) over seasons although DOC in the upper layer varied seasonally: DOC concentrations were highest in summer and lowest in winter. Vertical profiles of DON concentration seems to be high at the surface and decrease to 200 m but the ranges within season were large in comparison with DOC, therefore it is impossible to say that there were seasonal variation for DON. The range of DOC and DON concentration throughout water column at Sta. 2 was from 39.0 to 91.3 μM C and from under detection limit to 9.9 μM N, respectively. The contour plot for DOC (Fig. III-3e) was also nearly similar to those of POC and chlorophyll *a*. The relationship between DOC and chlorophyll *a* showed significant correlation ($p < 0.05$) in each periods except July 2001, and February and May 2002 (Tables III-1). DOC concentration showed the highest values in summer at the surface layer (above 20 m). As the surface water was diluted with deeper water having low DOC concentrations by convective overturn and

DOC was consumed, DOC concentration decreased in the surface layer from autumn to winter, consequently. The contour plot for DON shows a similar seasonal variation to DOC. DOC concentration in winter was almost constant but the water column when compared with other seasons. This temporal variation in DOC was contrary to the nutrients.

Fig. III-3b shows temporal and vertical distribution for bacteria abundance at Sta. 2 upper 200 m. Bacteria abundance decreased with depth and varied seasonally. The range of bacteria abundance was from 1.6×10^4 to 1.9×10^6 cells ml^{-1} throughout water column from August 2000 to November 2002. The concentrations were low and uniform in winter, and thereafter increased near the surface in spring, 2001. From summer to autumn in 2001, the bacteria were more abundant at the subsurface than the surface, whereas a lot of bacteria abundance was observed at the surface in autumn rather than spring, 2002. The temporal distribution of bacteria was considerably similar to the POC. The relationship between bacteria abundance and POC concentration showed a significant linear regression ([POC] = 8.2×10^{-3} [bacteria abundance] + 0.24, $r^2 = 0.74$, $n = 118$, $p < 0.001$), indicating that POC increased with bacteria. This result suggests that bacteria biomass of carbon contributed significantly to POC. Then, the bacterial carbon content was estimated using a conversion factor: 30.2 fg $cell^{-1}$ (Fukuda *et al.,* 1998). Assuming that the percentage of bacteria abundance passing through a glass fiber filter was 20% in average that was estimated from a comparison of bacteria abundance between unfiltered and filtered seawater (Table III-2), bacteria carbon biomass accounted for 26% in average (range: 6.7-64) of the POC in the depths range from surface to 400 m, while it accounted for only 6.1% in average (range: 1.9-20.3) of the POC in deeper than1000 m. In addition,

the difference in the contribution between deeper than 1000 m depths and the other upper depths was significant, which indicates that POC was dominated with detritus rather than bacteria. The seasonal or vertical variations of percentage of bacteria carbon biomass to the POC were not clear.

Table III-1: Summary of linear regression with chlorophyll *a* concentration fit to the model: [Chl-*a*] = a + b*x*.

	x = $[NO_3^-]$					x = $[Si(OH)_4]$					x = [DOC]					x = [POC]				
Period	*b*	*a*	r^2	*n*	*p*	*b*	*a*	r^2	*n*	*p*	*b*	*a*	r^2	*n*	*p*	*b*	*a*	r^2	*n*	*p*
Jul. 2000	-0.04	0.51	0.68	30	< 0.05											0.08	-0.001	0.67	7	<0.05
Aug. 2000	-0.03	0.47	0.51	21	< 0.05						0.02	-0.71	0.32	21	< 0.05	0.07	-0.04	0.51	21	<0.05
Sep 2000	-0.03	0.43	0.40	43	< 0.05						0.02	-0.86	0.53	18	< 0.05	0.07	0.05	0.58	12	<0.05
Nov. 2000	-0.05	0.94	0.54	44	< 0.05	-0.03	0.92	0.41	44	< 0.05	0.04	-1.78	0.70	20	< 0.05	0.17	-0.12	0.69	14	<0.05
Feb. 2001	-0.15	2.28	0.20	43	< 0.05	-0.08	2.06	0.14	43	< 0.05	0.06	-2.83	0.56	21	< 0.05	0.22	-0.17	0.91	14	<0.05
Apr. 2001	-0.08	1.43	0.61	45	< 0.05	-0.05	1.52	0.53	45	< 0.05	0.07	-3.02	0.63	21	< 0.05	0.06	0.16	0.72	14	<0.05
Jul. 2001	-0.02	0.53	0.25	45	< 0.05	-0.01	0.53	0.29	45	< 0.05	0.01	-0.06	0.04	21	> 0.05	0.02	0.06	0.29	14	<0.05
Oct. 2001	-0.10	1.45	0.59	43	< 0.05	-0.06	1.58	0.49	43	< 0.05	0.06	-2.94	0.62	20	< 0.05	0.20	-0.22	0.95	14	<0.05
Dec. 2001	-0.06	1.01	0.64	45	< 0.05	-0.04	1.04	0.64	45	< 0.05	0.04	-1.44	0.44	20	< 0.05	0.16	-0.18	0.64	14	<0.05
Feb. 2002	-0.08	1.46	0.77	45	< 0.05	-0.04	1.45	0.69	45	< 0.05	0.01	0.14	0.01	7	> 0.05	0.19	-0.17	0.94	7	<0.05
May 2002	-0.03	0.43	0.51	54	< 0.05	-0.02	0.49	0.47	54	< 0.05	0.01	-0.54	0.33	12	< 0.05	0.05	0.09	0.33	20	<0.05
Jul. 2002	-0.03	0.39	0.43	21	< 0.05	-0.02	0.40	0.37	21	< 0.05						0.03	0.12	0.28	20	<0.05
Sep. 2002	-0.05	0.67	0.44	53	< 0.05	-0.03	0.65	0.32	53	< 0.05	0.02	-0.93	0.63	10	< 0.05	0.05	0.06	0.59	17	<0.05
spring [a]	-0.05	0.78	0.27	99	< 0.05	-0.03	0.83	0.22	99	< 0.05	0.03	-1.14	0.22	33	< 0.05	0.06	0.06	0.68	34	<0.05
summer [b]	-0.03	0.50	0.33	213	< 0.05	-0.02	0.53	0.25	119	< 0.05	0.01	-0.44	0.19	70	< 0.05	0.04	0.09	0.35	91	<0.05
autumn [c]	-0.08	1.21	0.53	87	< 0.05	-0.05	1.23	0.41	87	< 0.05	0.05	-2.31	0.60	40	< 0.05	0.19	-0.18	0.89	28	<0.05
winter [d]	-0.08	1.42	0.19	133	< 0.05	-0.04	1.35	0.15	133	< 0.05	0.03	-1.07	0.24	48	< 0.05	0.16	-0.09	0.71	35	<0.05

Data from the surface to 200 m are used for calculation.
a: Apr. 2001 and May 2002.
b: Jul. Aug. and Sep. 2000, Jul. 2001, and Jul. and Sep. 2002.
c: Nov. 2000 and Oct. 2001.
d: Feb. and Dec. 2001, and Feb. 2002.

Table III-2: Comparison of bacteria abundance between unfiltered and filtered seawater.

depth (m)	unfiltered		filtered [a]					
			GF-75			GF/F		
	average	SD	average	SD	(%) [b]	average	SD	(%)
11	39.9	5.0	12.1	1.0	30	12.8	3.1	32
200	19.3	2.0	1.4	0.1	7	2.4	0.4	13

Seawater was collected in October 15, 2001. Unit is 10^3 cells ml^{-1}

a: Seawater was filtered with each glass fiber filter: GF-75 (TOYO ROSHI) and GF/F (Whatmann).

b: Percentage of bacteria abundance in filtered seawater to unfiltered seawater.

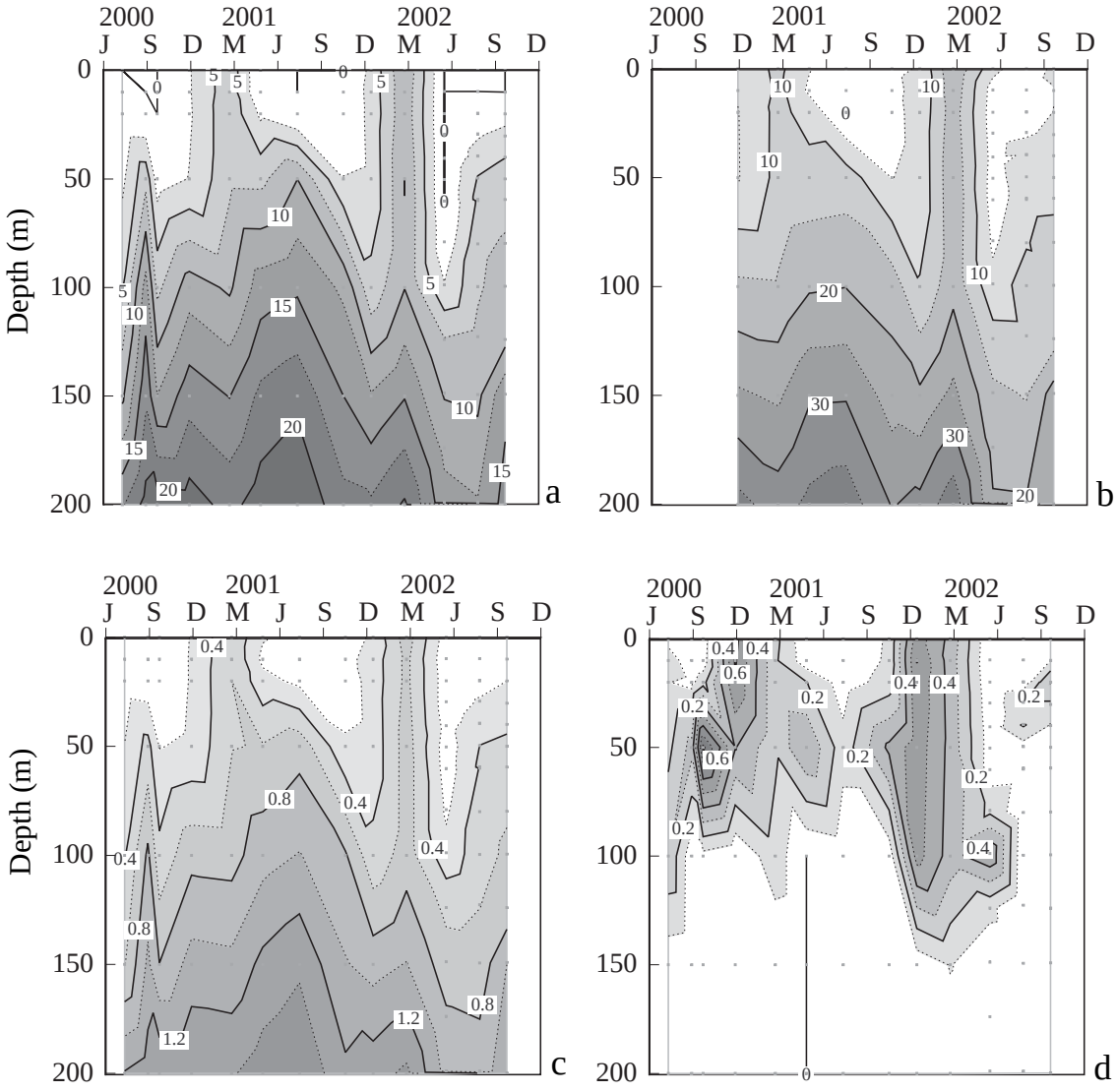

Fig. III-1: Contour plots of a) nitrate, b) silicate, c) phosphate and d) nitrite concentrations at midday, station 2. Data are shown from the surface to 200 m depth during July 2000 to September 2002 except silicate during November 2000 to September 2002. Unit: µM.

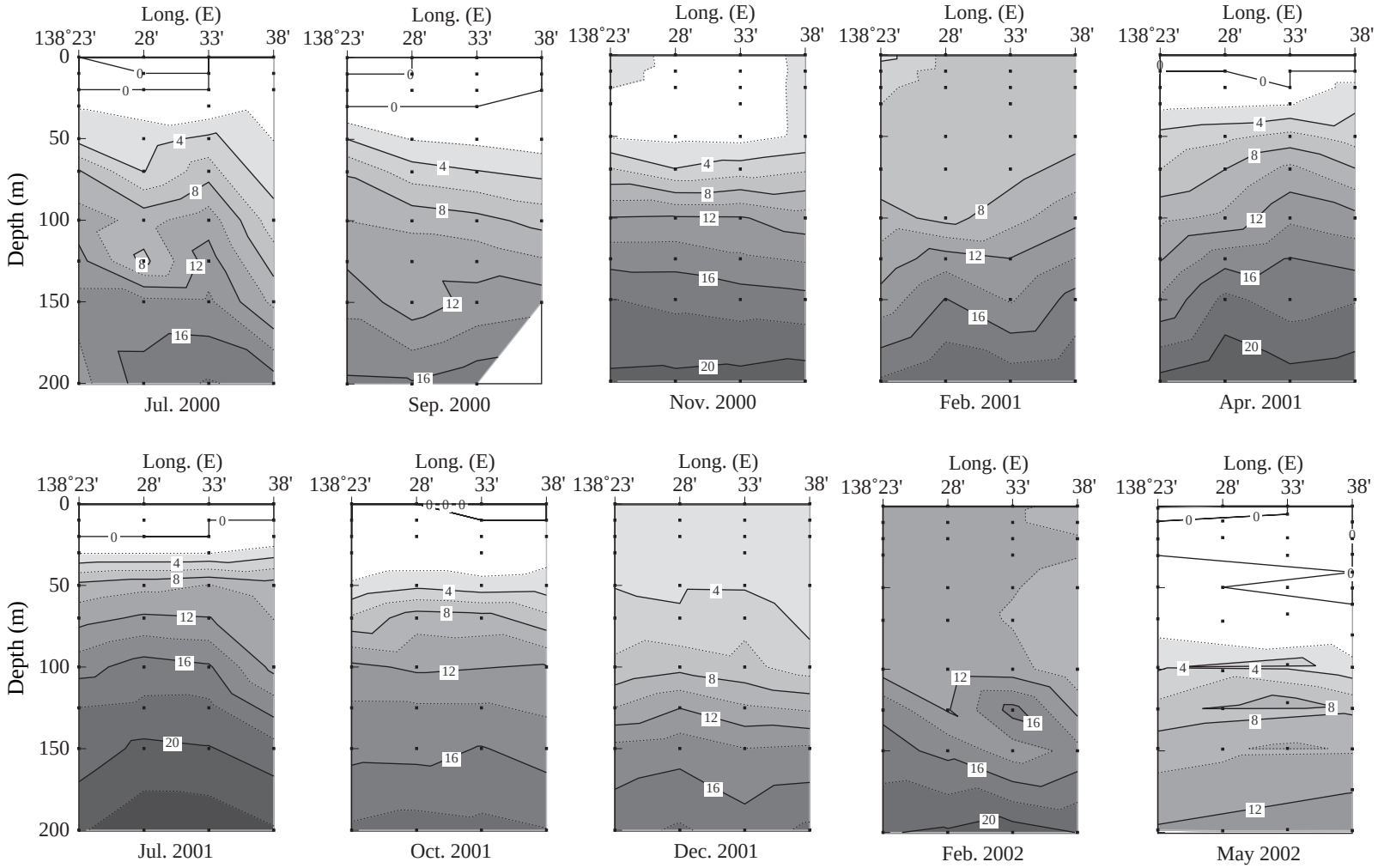

Fig. III-2: a) Vertical cross-sections of nitrate (μM) from Sta. 3 (138˚23'E) - F (138˚28'E) - E (138˚33'E) - 2 (138˚38'E) along 34˚51'N in each sampling period from the surface to 200 m depth.

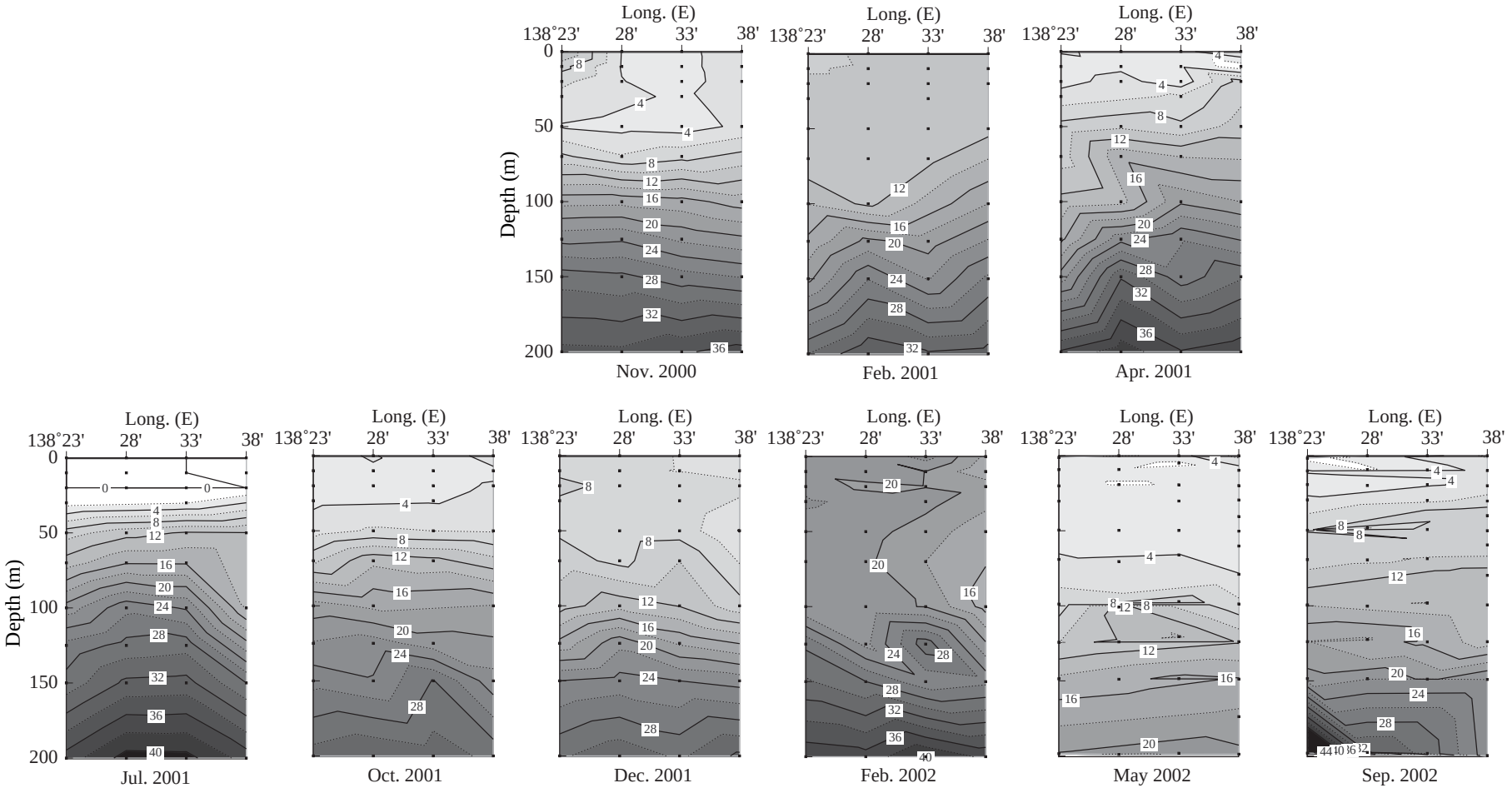

Fig. III-2: b) Vertical cross-sections of silicate (μM) from Sta. 3 (138˚23'E) - F (138˚28'E) - E (138˚33'E) - 2 (138˚38'E) along 34˚51'N in each sampling period from the surface to 200 m depth.

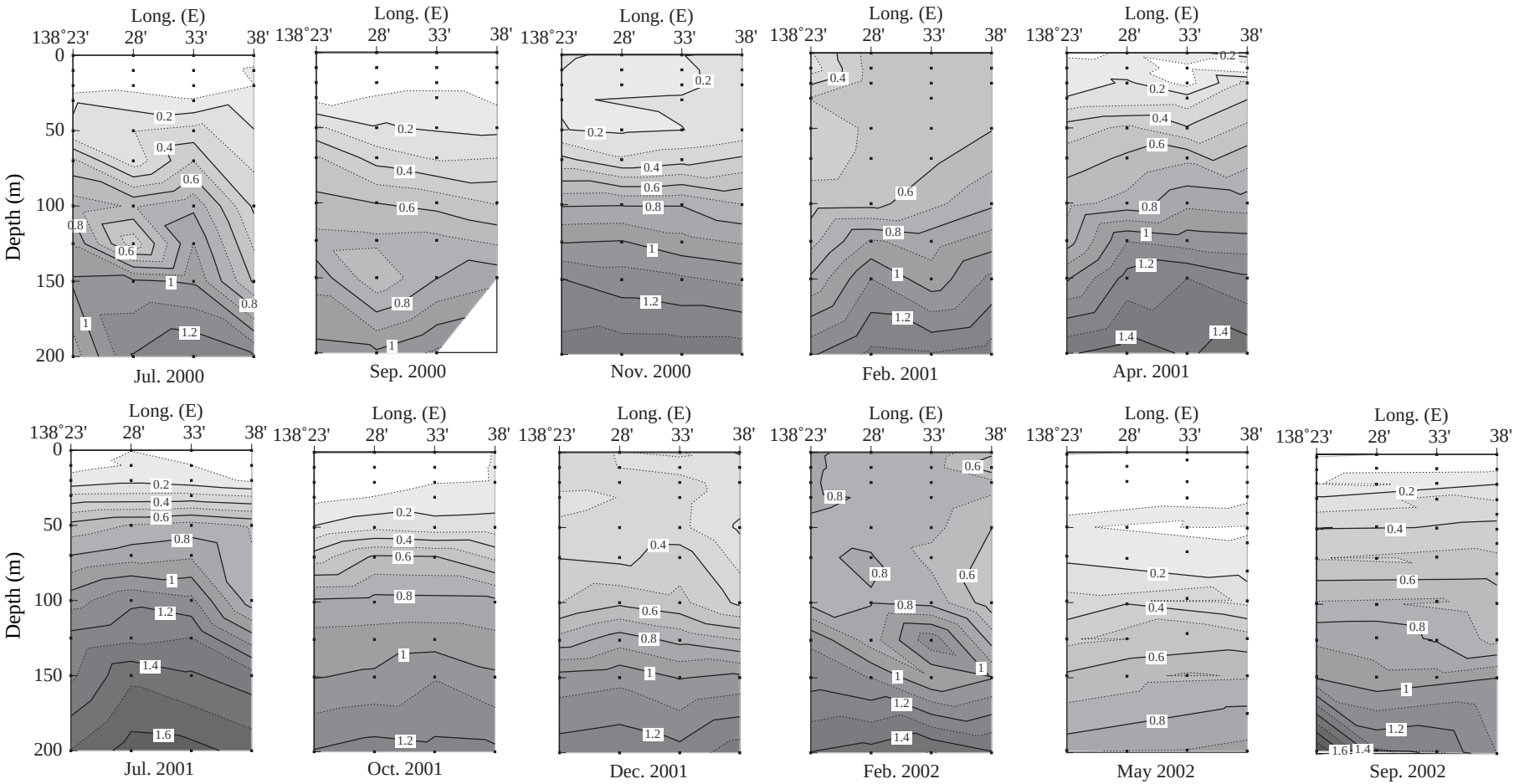

Fig. III-2: c) Vertical cross-sections of phosphate (μM) from Sta. 3 (138˚23'E) - F (138˚28'E) - E (138˚33'E) - 2 (138˚38'E) along 34˚51'N in each sampling period from the surface to 200 m depth.

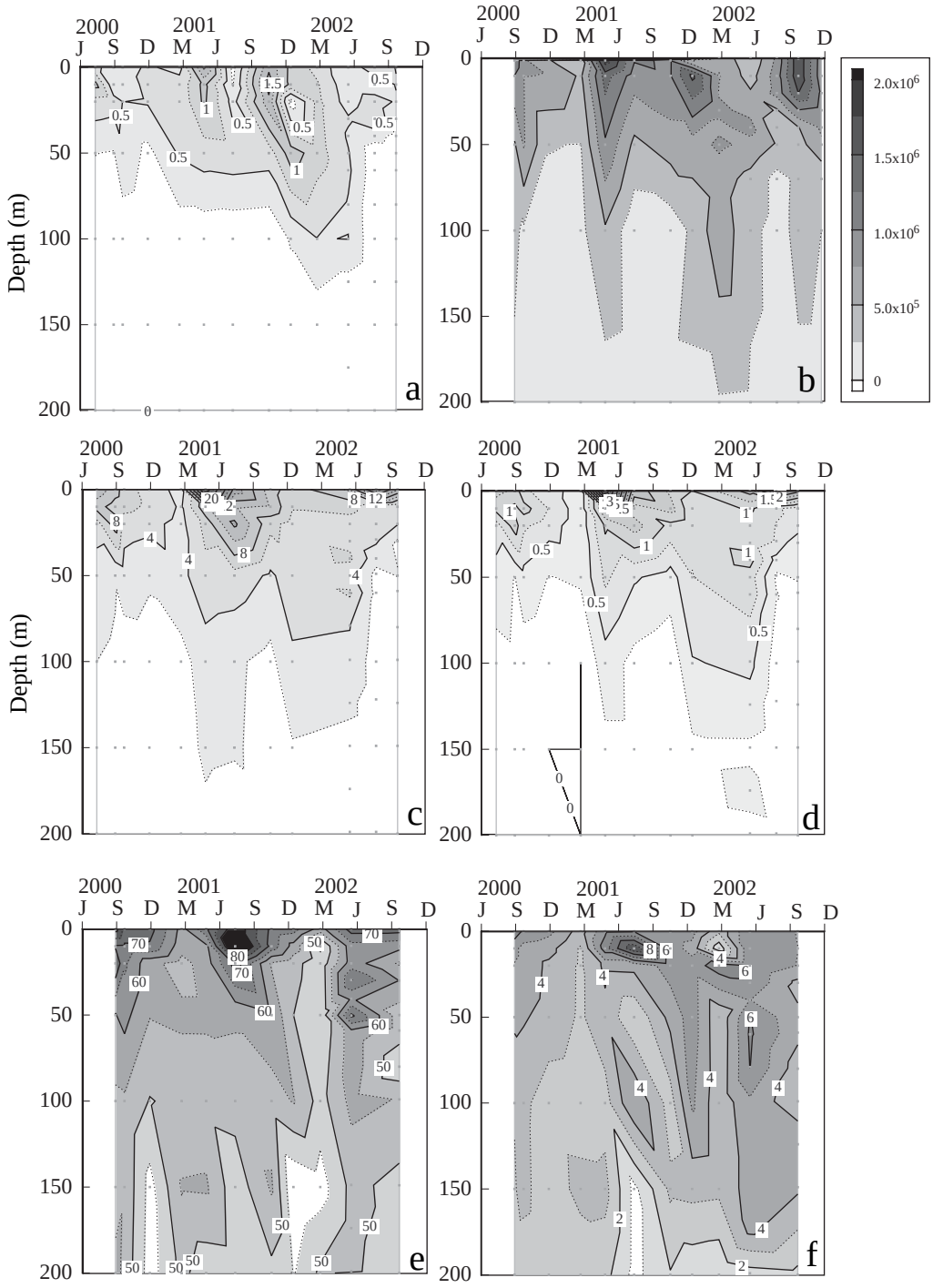

Fig. III-3: Contour plots from the surface to 200 m depth during July 2000 to September 2002 at station 2. a) chlorophyll *a* concentration (µg l^{-1}) at midday and b) bacteria abundance (cells ml^{-1}) at midday from July 2000 to February 2002 and at predawn from May 2002 to September 2002, c) POC (µM), d) PN (µM), e) DOC (µM), and f) DON (µM) at midday, but only data for DOC and DON in February 2002 is used at predawn.

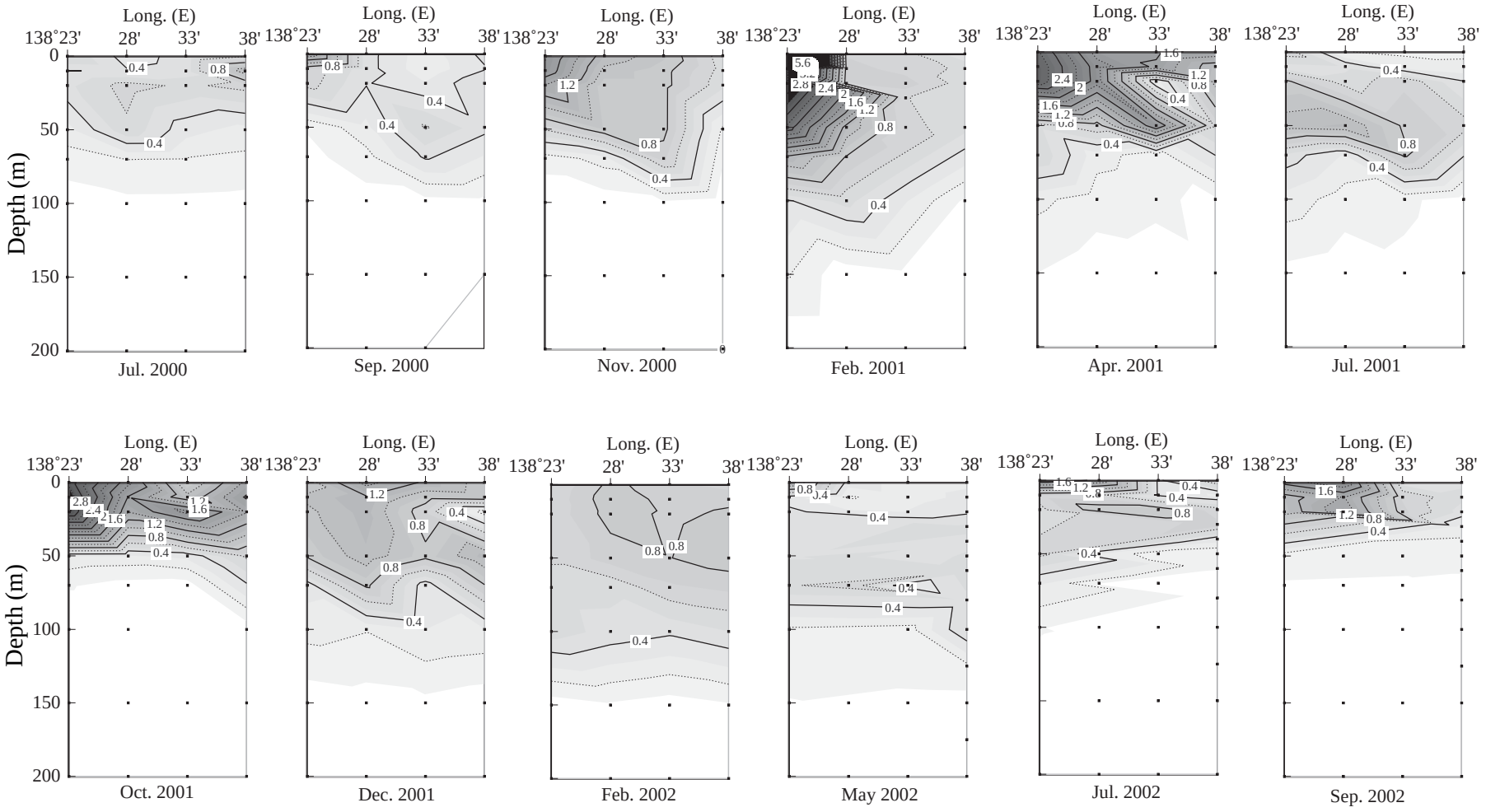

Fig. III-4: Vertical cross-sections of chlorophyll *a* concentration (μg l^{-1}) from Sta. 3 (138˚23'E) - F (138˚28'E) - E (138˚33'E) - 2 (138˚38'E) along 34˚51'N in each sampling period from the surface to 200 m depth.

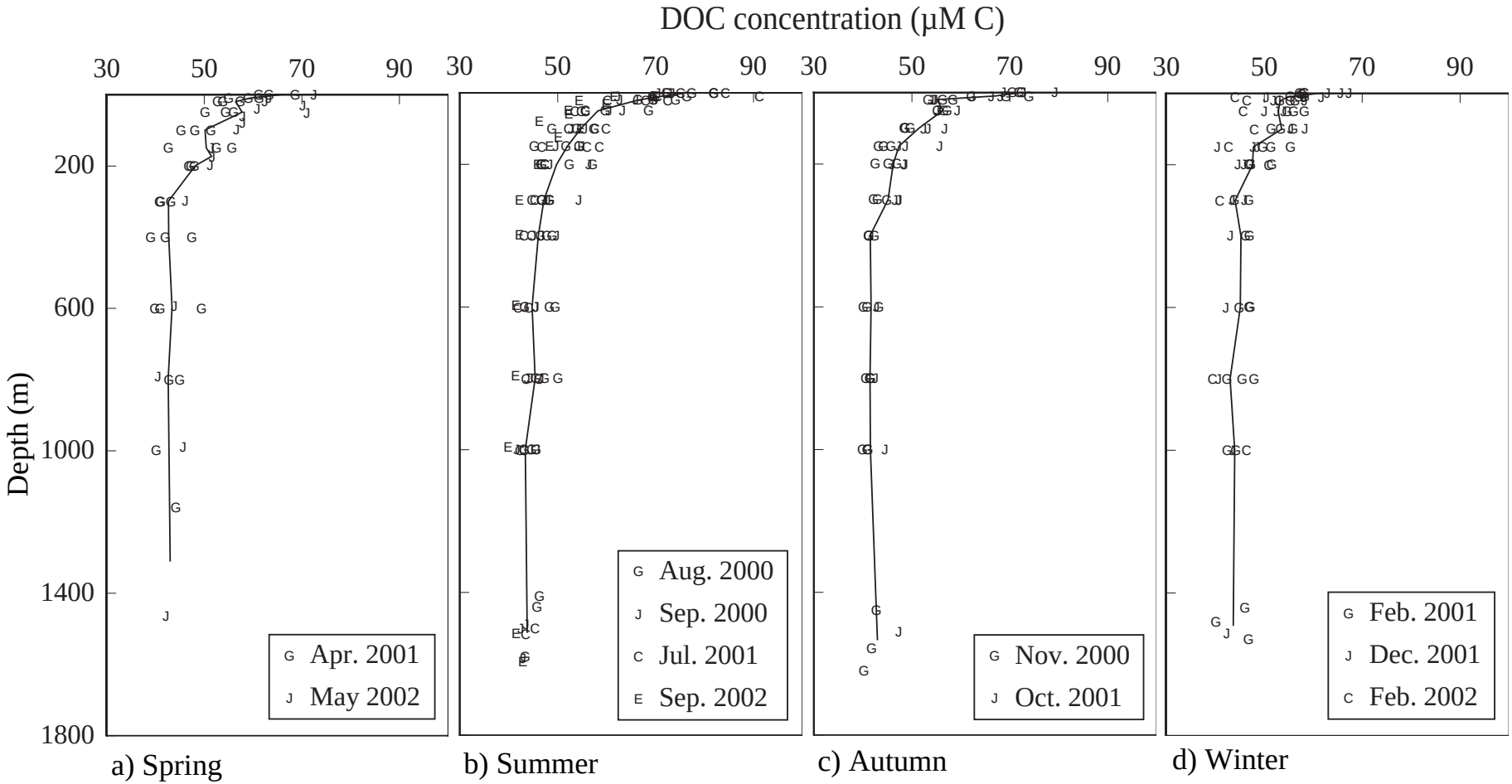

Fig. III-5: Vertical profiles of DOC (µM) in each season; a) spring, b) summer, c) autumn, and d) winter through the water column. Solid lines represent average for each season.

B. Evaluation of Diel Changes in DOC Caused by Biological Processes

1. Diel variations of vertical distribution of DOC in the upper layer

a. Vertical profiles of salinity, potential temperature and concentrations of DOC in the upper layer

Diel vertical profiles of salinity and potential water temperature in the top 100 m depth for each sampling period during September 2000-October 2001, are shown in Fig. III-6 and diel vertical profiles of DOC concentrations are shown in Fig. III-7.

DOC concentrations decreased with depth, ranging from 91.3 to 45.2 μM. In September 2000, DOC concentrations decreased from night to predawn ($p < 0.05$, *t*-test), except on the surface. Diel differences of over 7 μM C were observed at depths of 10 and 20 m. Both salinity and water temperature profiles varied diurnally, and the variations were above the accuracy of the CTD sensor (0.002 and 0.001 ˚C for salinity and water temperature, respectively). Salinity profiles showed comparatively large variations near haloclines. In November 2000, DOC concentrations were high on the surface and at 10 m (range: 62.1–73.9 μM C), but decreased sharply below 20 m. DOC concentrations at 10 m showed considerable diel variations. Diel change observed at 10 m from midday to night (11.8 μM C) was large compared to variations on the surface, and at 50 and 100 m. Salinity was rather high at predawn compared to the other two sampling times throughout

the 100-m range, while water temperature at predawn was lower below 50 m, with the maximum difference of 1.41 ˚C at 74 m. In February 2001, DOC concentrations were almost uniform (range: 51.5–58.3 µM C) throughout 100 m, and showed little change diurnally. Similarly, both diel vertical profiles of salinity and water temperature were uniform through 100 m, owing to deep convective overturn, and almost stable, in comparison with sensor accuracy. The mixed layer depth (MLD), during this period in February 2001, was calculated at 114 m (Table III-3). MLD was defined as the depth at which the water density (σ_t) is 0.125 units greater than the surface value (σ_t at 2-5 m in this study), according to Levitus (1982) and Taki & Suzuki (2001). DOC concentrations for April 2001 increased on the surface and at 10 m, but decreased at 50 and 100 m in comparison with DOC measurements for February 2001. It also varied among the three sampling times ($p < 0.05$, *t*-test) through 100 m, with diel variations ranging up to 7.5 µM C. DOC concentrations were higher at midday than night and predawn, except for 10 m. Below 40 m, temperature decreased gradually from midday to predawn, with a maximum diel difference of 0.93 ˚C at 55 m. Compared with September 2000, DOC concentrations for July 2001 were higher, despite being a similar season, and showed large diel variations, particularly in the upper 20 m. A DOC decrease of 21.7 µM C, from midday to night at 10 m, was the largest diel change in all sampling periods. Simultaneously, salinity and temperature varied considerably, among the three sampling times, above 40 m. Salinity was lower, while temperature was higher, at midday than the following night and predawn. The largest difference (0.27 and 3.28 ˚C for salinity and potential temperature, respectively) was detected between midday and predawn near 20 m depth. In October 2001, DOC concentrations varied diurnally on the surface and at 10 m (an increase of 10.6

μM C from midday to night), although salinity and temperature did not show such considerable variations as observed in July in the layer.

Vertical profiles of DOC concentrations varied among the three sampling times (midday, night and predawn). In most sampling periods, relatively larger diel variations in DOC concentrations were found in the upper 20 m range.

Diel distributions in bacteria abundance and chlorophyll *a* concentration from the surface to 100 m are shown Fig. III-8 and III-9. The ranges of bacteria abundance between the surface and 100 m were within 10^5 cells ml^{-1} (range: 1.2-8.8 × 10^5) from September 2000 to February 2001, while increased to 10^6 cells ml^{-1} at the surface in April 2001. Bacteria abundance in July 2001 ranged from 7.7 × 10^4 to 1.2 × 10^6 cells ml^{-1} between the surface and 100 m depth. There were not obvious diel differences in bacteria abundance in each sampling period during September 2000-October 2001. Chlorophyll *a* concentration showed somewhat diel variations because of grazing, mortality and doubling time for phytoplankton. Especially, great diel variations were observed in November 2000 and July 2001. In November 2000, chlorophyll *a* concentration increased from midday to night except the surface. The greatest difference between chlorophyll *a* concentrations in diel vertical distributions for six sampling periods, 1.1 μg l^{-1} was observed at 20 m in July 2001.

b. Relationship between potential density and DOC

Data from deeper layers were obtained, at the same time, for reference and comparative purposes with the upper layer. All measured concentrations of DOC were

plotted against potential density (σ_θ) for each sampling period (Fig. III-10). Data for σ_θ below 300 m at midday and night in February 2001 were not included owing to sensor malfunction. Values of σ_θ at depths from 1 to 5 m of CTD were applied to surface data. DOC concentrations from 400 to 1000 m at night in July 2001, and at midday and night in October, were not measured.

DOC concentrations were distributed inversely along σ_θ for all sampling periods. DOC concentrations correlated significantly ($p < 0.001$) with σ_θ for all sampling periods in deeper layers (100-1000 m) lying below the seasonal pycnocline. Regression lines were obtained by the least-squares method. On the other hand, DOC for lower density (i.e. in the upper layer) varied against σ_θ in some sampling periods. In November 2000 and October 2001, DOC in the upper layer (0-50 m, shown as solid circle) deviated conspicuously, and in April and July 2001, some values obtained from upper layers were also distributed above the regression lines.

c. Diel variations in depth-integrated DOC

Fig. III-10 shows that the behavior of DOC at 0-50 m depths seemed to be different from that at 100-1000 m depths. The deviations of DOC concentration against σ_θ in the upper layer resulted from the wide range of DOC concentrations in the mixed layer. The depth of the euphotic zone was defined as depths with at least 1% surface irradiance, and ranged from 33 to 62 m during September 2000 to October 2001. The euphotic zone roughly corresponds with the upper 50 m layer, which infers that there are biological processes involved in primary production. Therefore, DOC concentrations were

integrated with depth from the surface to 50 m (Fig. III-11), to compare the inventory between seasons; however, only a value of DOC in September 2000 at 50 m for midday was estimated by linear interpolation from the values at 20–100 m, owing to data loss during analysis.

DOC inventory showed that seasonal variation decreased from summer to winter and ranged from 2.73 to 3.62 mol C m^{-2}. Moreover, inventories of DOC varied diurnally in some sampling periods. Large diel differences in DOC inventories were observed from night to predawn in September 2000, and from midday to night in April (0.20 mol C m^{-2}) and July 2001 (0.39 mol C m^{-2}) , respectively. Inventory at midday in July 2001 was the largest of all, owing to high concentrations of DOC at midday in the upper 20 m (Fig. III-11). Diel difference occurred from night to predawn in October 2001. In vertical profile for November 2000, large diel variations in DOC concentrations were observed at 10 m (Fig. III-7); nevertheless, inventories for November 2000 did not show distinct diel variations. Similarly, in February 2001, diel differences of inventories could not be distinguished. Seasonal inventories of DOC in the upper layer showed a common diel pattern of decreasing to predawn.

2. Estimation of biological contribution to diel variations removing physical effects

a. Evaluation of net biological contribution to DOC inventory

Noticeable variations were observed in diurnal vertical profiles of DOC (Fig. III-7) in some periods. The largest diel change of 21.7 μM DOC at 10 m in July 2001 is about twice as large as previous reports of ~13 μM C on the surface (Sieburth *et al*., 1977; Zweifel *et al*., 1993). These diel changes in vertical profiles of DOC concentrations were reflected in inventories of DOC (Fig. III-11). Physical and biological factors, however, could not be identified in the diel variations because salinity and temperature profiles also showed similar variations during some sampling periods. Previous studies had examined the relationship between DOC concentrations and hydrological variables (e.g. Peltzer & Heyward, 1996; Hansell *et al.,* 1997; Santinelli *et al.,* 2002). In this study, DOC concentrations correlated significantly with σ_θ ($p < 0.001$) in the deeper layer (100-1000 m; Fig. III-10) in all sampling periods. In general, DOC in the deep ocean has an apparent mean ^{14}C age of several thousand years, indicating extremely slow remineralization (Bauer *et al*., 1992). DOC concentrations observed in the deeper layers of Suruga Bay displayed fewer temporal variables than the upper layer where there is a supply of fresh DOC. This indicates that, below a depth of 100 m, DOC is distributed along the mixing line between the upper water with high DOC concentration and deeper water with low DOC concentration.

Assuming that DOC concentration in the upper layer follows the same mixing

pattern observed in deeper layers, then DOC concentration, which is determined only by physical mixing between the upper layer and deeper water, can be estimated from the relationship between DOC and σ_θ in the deeper layer. A similar approach using mixing ratios for estimation of DOC concentration, determined by physical controlling, has been described previously (Suzuki, 1993; Peltzer & Heyward, 1996). The regression line between DOC and σ_θ, which was obtained in the deeper layer for each sampling period (Fig. III-10), was extrapolated to values of σ_θ in the upper layer to calculate a DOC concentration given simply by mixing. Figure III-12 shows vertical profiles of the calculated DOC (DOC (cal)) and observed DOC (DOC (obs)) in each sampling period. The error bar in calculated DOC concentration represents the standard deviation about the regression line, i.e. the range of concentration containing statistical variation caused by dispersion in the deeper layer. In September 2000, there were no significant differences between DOC (obs) and DOC (cal) ($p > 0.05$, *t*-test), except for a surface reading at midday. In contrast, DOC (obs) in November 2000 greatly exceeded DOC (cal), with differences ranging from 9.4 to 21.1 μM C on the surface and at 10 m. DOC (obs) for July 2001 varied from DOC (cal). DOC (obs) was higher than DOC (cal) at midday, but was lower than DOC (cal) at night and predawn, which differed from the readings for September 2000.

To compare DOC (cal) with DOC (obs) as an inventory, DOC (cal) was integrated with depths from surface to 50 m, and the integrated DOC (cal) was subtracted from DOC (obs), which was shown as a difference (Table III-4). Excesses over DOC (cal) were found in November, and at midday in April. On the other hand, inventories of DOC (obs) fell below DOC (cal) in October, and at night and predawn in July. The difference in

inventory between DOC (cal) and DOC (obs) means the net biological addition or removal of DOC, i.e. the net biological contribution to the DOC inventory, involving both production and consumption of DOC. Therefore it can be concluded that DOC accumulated by biological processes in the sampling period in November 2000 (diurnal average 0.37 mol C m^{-2}), and at midday in April 2001, which indicates that there was the net production of DOC at the time. On the other hand, DOC inventory was less than DOC (cal) in October 2001 (diurnal average –0.35 mol C m^{-2}), and at night and predawn in July 2001, which means there was a net consumption of DOC during these periods. On the contrary, there was little net biological contribution in September 2000.

Magnitudes of the net biological contribution to inventory differed within similar seasons. A large accumulation of DOC was found in November 2000, while DOC inventory was deficient in October 2001. Coincidentally, the primary production rate (Table III-3) was higher in November 2000 (21.0 mmol C m^{-2} day^{-1}) than in October 2001 (4.5 mmol C m^{-2} day^{-1}). These indicate that DOC supply, related to primary production, may contribute to the magnitude of net DOC accumulation. There was larger deficient of DOC at night and predawn in July 2001 in comparison with September 2000, although primary production rates were higher in July 2001 (38.3 mmol C m^{-2} day^{-1}) than in September 2000 (8.1 mmol C m^{-2} day^{-1}). This suggests that the accumulation or scarcity of DOC may not be related simply to the magnitude of primary production, but may involve difference in the quality of DOC supplied, such as variation of phytoplankton species composition and change of percent of extracellular release from phytoplankton, and subsequent removal processes: biotic consumption (mainly bacterial uptake) and photochemical mineralization (Mopper *et al.*, 1991; Moran & Zepp, 1997) of DOC and

sorption onto particles (Dreffel *et al.*, 1996).

b. Net biological contribution to diel variations in DOC inventory

In addition to DOC (obs), DOC (cal) inventories show large diel variations. A distinct diel change was detected between night and predawn in July 2001 (Table III-4). Diel variations in DOC (obs) inventories involve both biological and physical contributions, therefore the net biological contribution to these variations was estimated by subtracting the diel variations in the DOC (cal) inventories for each sampling interval (Table III-5). The fraction of 0.20 and 0.33 mol C m^{-2} for April and July 2001, respectively, was due to a diel decrease of observed DOC from midday to night, due to biological processes. DOC was abundant, compared with DOC (cal), at midday in the upper 10 m in July 2001 (Fig. III-12). This suggests that DOC production dominated consumption at midday, although it was only transient accumulation, and disappeared from the layer at night due to rapid consumption. Therefore the DOC accumulated at midday was most probably labile, and turned over on the time scale of the sampling interval (several hours). It seems that DOC was consumed throughout 50 m from midday to night with average apparent rates of –0.35 and –0.61 μM C h^{-1} in April and July2001, respectively (Table III-5). In contrast, variations in the subsequent interval (from night to predawn), by the biological contribution to inventories, showed a little increase at apparent rates of 0.12 and 0.03 μM C h^{-1} in April and July 2001, respectively. A rapid apparent change rate of –0.52 μM C h^{-1} appeared from night to predawn in September 2000 also. This suggests that the DOC, which accumulated during the daytime, may be rapidly

consumed in the afternoon or during the night, in spring and summer.

Table III-6 is shown amount of semi-labile DOC in Suruga Bay from result of degradation experiments (Hino *et al.*, 2002; Hino, 2004; Hino, personal communication). The experiments were focussed on the seasonal variation in amount of semi-labile DOC: seawater collected at 20 m contained more abundant bioavailable DOC, which is degraded during several weeks (fraction 1, Table III-6), especially in April and July, which is consistent with great diel change DOC, observed in April and July 2001. This result implied a possibility that a lot of more bioavailable DOC having more short turnover time occurred at the sampling periods. And this supports that the accumulated DOC in the surface layer in April and July 2001 may be consumed rapidly at time-scale of several hours.

Compared with DOC consumption rates in previous degradation experiments, our apparent decrease rates were higher than rates in the oceanic system (1.4 ± 2.0 - 4.4 ± 2.6 μM C d^{-1}, Cherrier *et al.*, 1996; 0.04-0.10 μM C h^{-1}, Carlson & Ducklow, 1996), but similar to rates in the coastal ocean (0.09-0.47 μM C h^{-1}, as bacterial production, Coffin *et al.*, 1993), except for summer. To account for DOC production, substantial consumption rates of DOC in Suruga Bay would be expected to become much higher than the apparent decrease rate. In the Atlantic Ocean, a similar high diel decrease rate of DOC (0.82 μM C h^{-1}) on the surface was reported as mean uptake rate of DOC (Sieburth *et al.*, 1977). Malone *et al.* (1991) evaluated the release rates of DOC in Chesapeake Bay using ^{14}C and found high release rates in summer (0.58-1.2 μM C h^{-1}). This supports the possibility, in this study, of an adequate supply of DOC to sustain a large consumption in coastal ocean.

On the other hand, the inventory for November 2000 showed little diel variation in

both observed and calculated DOC (Table III-4). In vertical profiles, however, DOC concentrations varied in the upper 10 m, where DOC (obs) differed largely from DOC (cal) (Fig. III-12). DOC concentrations increased from midday to night, and decreased from night to predawn at 10 m, while, at 20 m, the diel variation displayed an inverse pattern, i.e. DOC decreased from midday to night, and increased from night to predawn. MLD in November 2000 was 54 m, and deeper than the MLD for July and April (11 and 21 m, respectively, Table III-3). This indicates that DOC accumulated in the daytime in the uppermost layer was transported throughout the mixed layer by relative deep mixing in November, as described in Fig.III-12. Consequently, inventories appeared to be stable during the sampling day, since production and consumption of DOC balanced each other throughout 50 m. On the other hand, the net biological contributions to diel inventory variations were less in November 2000 than in spring and summer (Table III-5). This suggests that the excess DOC in November 2000, contributed by biological processes, turned over on the time scale of the daily cycle, although there is also the possibility that more labile DOC was produced and consumed so rapidly that it was not observed as a diel variation in DOC concentration or inventory.

A lot of excess DOC (0.36-0.37 mol C m^{-2}), contributed by biological processes in November 2000, however, decreased to under a half (0.11-0.20 mol C m^{-2}) by February 2001 (Table III-4). It seems possible that the seasonal decrease in excess DOC from autumn to winter, was caused not only by consumption in the layer, but also by transport to deeper layers (coinciding with an increase in MLD), if it was not already consumed owing to the relatively long turnover time, as described by Carlson *et al.* (1994) in the northwestern Sargasso Sea.

I have mainly discussed about contributions of mixing process as one of the physical processes in changing DOC concentrations, but also there was possibility of changing DOC concentration due to lateral advection. Fig. III-13 shows vertical profiles at Sta. 2, 5, 6 and 7 observed at 28 May 2002. Compared with DOC vertical profile at Sta. 2, large differences of DOC concentrations from at Sta. 2 were observed in the upper 20 m. At 10 m depth, DOC concentration at Sta. 5 and 7 was lower 7-8 μM C than at Sta. 2. At 20 m, DOC concentration at Sta. 6 was higher 10 μM C than at Sta. 2. Horizontal variation of DOC concentration seems to be comparable with diel change, but these data were collected at same day but not same time, therefore these differences reflected both of spatial and temporal variations. In this study, I do not have enough data to discuss the contribution of lateral advection in diel change of DOC concentration. Previous studies in the equatorial Pacific Ocean estimated DOC export by lateral advection: 0.5-3 mmol C m^{-2} d^{-1} (0.01-0.06 μM C in the upper 50 m, Taki & Suzuki, 2001), -1-5 mmol C m^{-2} d^{-1} (0.03-0.13 μM C in the upper 40 m, Peltzer & Hayward, 1996). They reported the advection velocity as 0.03-0.15 m s^{-1} in the region. Nakamura (1982) reported average of horizontal current velocity: 0.4-0.6 m s^{-1} in the upper 50 m of Suruga Bay, which was the 4-13 time larger than in the equatorial Pacific Ocean. This indicates that the influence to diel change of DOC concentration by lateral advection is likely to be a little but the change is fast than the open ocean.

c. Relationship of DOC diel changes contributed biologically with bacterial production

Potential bacterial growth rates (μ_{max}) determined by the 'dilution' method varied trough the year (Table III-7): potential bacteria growth rates were high in summer and low in winter and co-varied with grazing rates by zooplantkon on bacteria (r^2 = 0.91, n = 8, p < 0.001), while did not have a significant correlation with phytoplankton growth rates. This implies a possibility that bacterial production was controlled by grazing rather than phytoplankton productivity, although estimation of these potential growth rates might be underestimated due to the nutrients limitation in summer.

Bacterial production in the upper layer (0-50 m) in each sampling period was estimated from bacterial maximum growth rates (μ_{max}) from results of dilution experiments using 2-5 m seawater and bacteria abundance observed *in situ*. Assuming that bacteria increase throughout 50 m with the same growth rate (μ_{max}), increase daily of bacteria abundance (ΔN_t) was calculated following:

$$\Delta N_t = N_0 \cdot \mu_{max} - N_0 ,$$

where N_0 is initial bacteria abundance which are the values collected *in situ* at predawn because the collecting time of these samples were near to the actual initial time of the dilution experiments. Increase in bacteria abundance was converted into carbon biomass by a factor 30.2 fg C cells^{-1} (Fukuda *et al.*, 1998). In the 0-50 m layer, bacteria increased per day ranging from 0.14-1.8 × 10^{14} cells m^{-2} as abundance and from 0.34-1.8 mmol C m^{-2} as carbon biomass during August 2000 to December 2001 if there was absence of grazing.

DOC inventories in 0-50 m layer were high at midday and decreased to predawn in

most of sampling periods. Therefore, assuming difference of DOC between midday and predawn was apparent daily biological change of DOC, it was calculated by subtracting [DOC (obs) – DOC (cal)] at predawn from [DOC (obs) – DOC (cal)] at midday. DOC inventory changed biologically from midday to predawn ranging from –88 to 322 mmol C m^{-2} during August 2000 to December 2001 (minus values mean increase from midday to predawn). The differences in DOC inventory in the upper layer significantly related with daily bacterial production (Fig. III-14, $r^2 = 0.74$, $p < 0.01$) and the slope was around 1, implying that the apparent decrease, i.e. net consumption in DOC met potential bacterial production for a day. On the other hand, the regression line has a positive intercept, implying that bacterial production also contributed to DOC production. Bacteria contribute not only to consumption but also to production of DOC via bacterially induced lysis of phytoplankton, lysis of bacteria by virus infection, directly release DOM in the form of hydrolytic enzymes, and particle solubilization by attached bacteria (Carlson, 2002, Fig. I-4). Bacterial production estimated from the potential growth rate in the 'dilution' experiment was eliminated loss due to grazing in bacteria but was not concerned with its respiration. Therefore, this result supports broadly that diel change in DOC was significantly caused by biological processes and particularly implies significant of bacterial contribution to the diel changes in DOC. Actually, there are other biological processes concerned with DOC production and consumption by phytoplankton, virus and zooplankton. Diel vertical profiles of chlorophyll *a* concentration showed considerable variation among at midday, night and predawn, especially in the upper 50 m, November 2000 and at 20 and 50 m in July 2001 (Fig. III-9). This suggests a possibility that phytoplankton distributed heterogeneously, which might be driven by lateral advection, so

that this might cause remarkable diel change of DOC concentration.

Table III-3: The depth of mixed layer and euphotic zone and primary production rate in each observation.

Period	MLD (m)	Euphotic zone [a] (m)	PP [b] (mmol C m^{-2} d^{-1})
Jul. 2000	6	--- [c]	---
Aug. 2000	9	33	7.9
Sep. 2000	11	35	8.1
Nov. 2000	54	38	21.0
Feb. 2001	114	62	10.4
Apr. 2001	21	35	---
Jul. 2001	8	49	38.3
Oct. 2001	39	33	4.5
Dec. 2001	74	46	2.8
Feb. 2002	156	51	19.8
May 2002	22	49	7.8
Jul. 2002	4	35	7.4
Sep. 2002	12	51	24.7

a: The euphotic zone is defined as at least 1% surface irradiance.
b: Primary production (PP) is integrated with depth through euphotic zone.
c: no data.

Table III-4: DOC inventory from the surface to 50 m. DOC (obs) means observed DOC. DOC (cal) means calculated DOC from regression lines obtained from 100 to 1000 m. Difference means DOC (obs) - DOC (cal). Standard deviations are in parentheses.

Sampling period	Time	DOC (obs) (SD) (mol C m^{-2}) (A)	DOC (cal) (SD) (mol C m^{-2}) (B)	Difference (mol C m^{-2}) (A) - (B)
Sep. 2000	Midday	3.30 (0.01)	3.24 (0.13)	0.06
	Night	3.39 (0.01)	3.28 (0.13)	0.11
	Predawn	3.15 (0.01)	3.25 (0.13)	-0.10
Nov. 2000	Midday	3.01 (0.02)	2.64 (0.07)	0.36
	Night	3.01 (0.01)	2.64 (0.07)	0.37
	Predawn	3.00 (0.01)	2.63 (0.07)	0.37
Feb. 2001	Midday	2.77 (0.03)	2.65 (0.12)	0.11
	Night	2.79 (0.02)	2.64 (0.12)	0.14
	Predawn	2.85 (0.03)	2.65 (0.12)	0.20
Apr. 2001	Midday	2.92 (0.03)	2.64 (0.19)	0.29
	Night	2.73 (0.02)	2.64 (0.19)	0.09
	Predawn	2.76 (0.01)	2.62 (0.19)	0.14
Jul. 2001	Midday	3.62 (0.02)	3.55 (0.18)	0.07
	Night	3.23 (0.01)	3.50 (0.18)	-0.27
	Predawn	3.14 (0.03)	3.39 (0.18)	-0.25
Oct. 2001	Midday	3.00 (0.02)	3.29 (0.13)	-0.29
	Night	2.98 (0.01)	3.31 (0.13)	-0.33
	Predawn	2.89 (0.02)	3.31 (0.13)	-0.42

Table III-5: Differences from midday to night and from night to predawn in DOC inventory from the surface to 50 m. DOC (obs) means observed DOC. DOC (cal) means calculated DOC from regression lines obtained from 100 to 1000 m. Difference means DOC (cal) - DOC (obs). Change rate is calculated as follows: the difference (DOC (cal) - DOC (obs)) divided by interval of sampling times.

Period		ΔDOC (obs) (mmol C m^{-2}) (A)	ΔDOC (cal) (mmol C m^{-2}) (B)	Difference (mmol C m^{-2}) (B) - (A)	Change rate (μM C h^{-1})
Midday - Night	Sep. 21-22, 2000	-87	-37	50	0.09
	Nov. 27-28, 2000	-8	1	10	0.02
	Feb. 19-20, 2001	-21	7	27	0.05
	Apr. 25-26, 2001	196	1	-195	-0.35
	Jul. 11-12, 2001	386	51	-335	-0.61
	Oct. 15-16, 2001	19	-18	-37	-0.07
Night - Predawn	Sep. 21-22, 2000	241	31	-210	-0.52
	Nov. 27-28, 2000	14	13	-1	-0.003
	Feb. 19-20, 2001	-66	-6	61	0.15
	Apr. 25-26, 2001	-33	16	49	0.12
	Jul. 11-12, 2001	94	106	13	0.03
	Oct. 15-16, 2001	92	2	-90	-0.23

Table III-6: Estimation of semi-labile DOC in Suruga Bay.

Sampling date	Period (d) [a]		DOC (μ MC)					
			20 m			800 m		
	Fraction 1	Fraction 2	Initial ±SD	Fraction 1 [b] (%)	Fraction 2 [c] (%)	Initial ±SD	Fraction 1 (%)	Fraction 2 (%)
26 Apr. 2001	15	--- [d]	67.5	11.4 (17)	---	---	---	---
12 Jul. 2001	21	358	83.4 ±1.3	20.6 (25)	4.5 (5)	43.8 ±0.6	1.0 (2)	3.5 (8)
16 Oct. 2001	21	262	73.2 ±1.8	5.7 (8)	9.3 (13)	46.9 ±1.3	1.8 (4)	2.7 (6)
13 Dec. 2001	21	204	59.3 ±0.2	0.9 (2)	0.2 (0)	41.5 ±1.6	0.0 (0)	0.0 (0)
1 Feb. 2002	21	154	52.1 ±1.4	n.d.	2.7 (5)	38.8 ±1.3	n.d.	n.d.
15 May 2002	21	51	64.6 ±0.1	3.9 (6)	0.0 (0)	38.6 ±0.6	n.d.	0.3 (1)

a: The days of degradation experiment using for calculation.
b: The difference in concentrations between initial and 15 or 21 days of experiment. The percentage of initial concentration was shown in parentheses.
c: The difference in concentrations between 21 days and the end of experiment. The percentage of initial concentration was shown in parentheses.
d: no data.
e: not detected.
[from Hino *et al.*, 2002; Hino, 2004; Hino, personal communication]

Table III-7: Summary of the results of the dilution experiments, including bacteria abundance and chlorophyll *a* concentrations at the initial of the experiments, bacterial and phytoplankton growth rate (μ_{max}) and zooplankton grazing rate (g).

Period	Bacteria			Phytoplankton		
	Initial (10^6 cells ml^{-1})	g (d^{-1})	μ_{max} (d^{-1})	Initial ($\mu g\ l^{-1}$)	g (d^{-1})	μ_{max} (d^{-1})
29-30 Aug. 2000	0.93 ±0.06	0.61	0.79	0.10 ±0.00	0.24	0.44
22-23 Sep. 2000	0.52 ±0.10	1.81	1.91	0.26 ±0.01	0.42	0.24
28-29 Nov. 2000	0.76 ±0.14	0.71	0.49	1.06 ±0.02	0.17	0.58
20-21 Feb. 2001	0.23 ±0.04	0.34	0.56	0.43 ±0.01	0.17	0.30
26-27 Apr. 2001	1.58 ±0.08	0.84	0.94	0.71 ±0.02	0.45	0.28
12-13 Jul. 2001	1.22 ±0.15	1.70	1.57	0.26 ±0.01	0.61	0.26
16-17 Oct. 2001	0.94 ±0.14	1.38	1.28	1.19 ±0.01	0.40	1.05
13-14 Dec. 2001	0.63 ±0.04	0.89	1.00	0.76 ±0.03	0.39	0.35

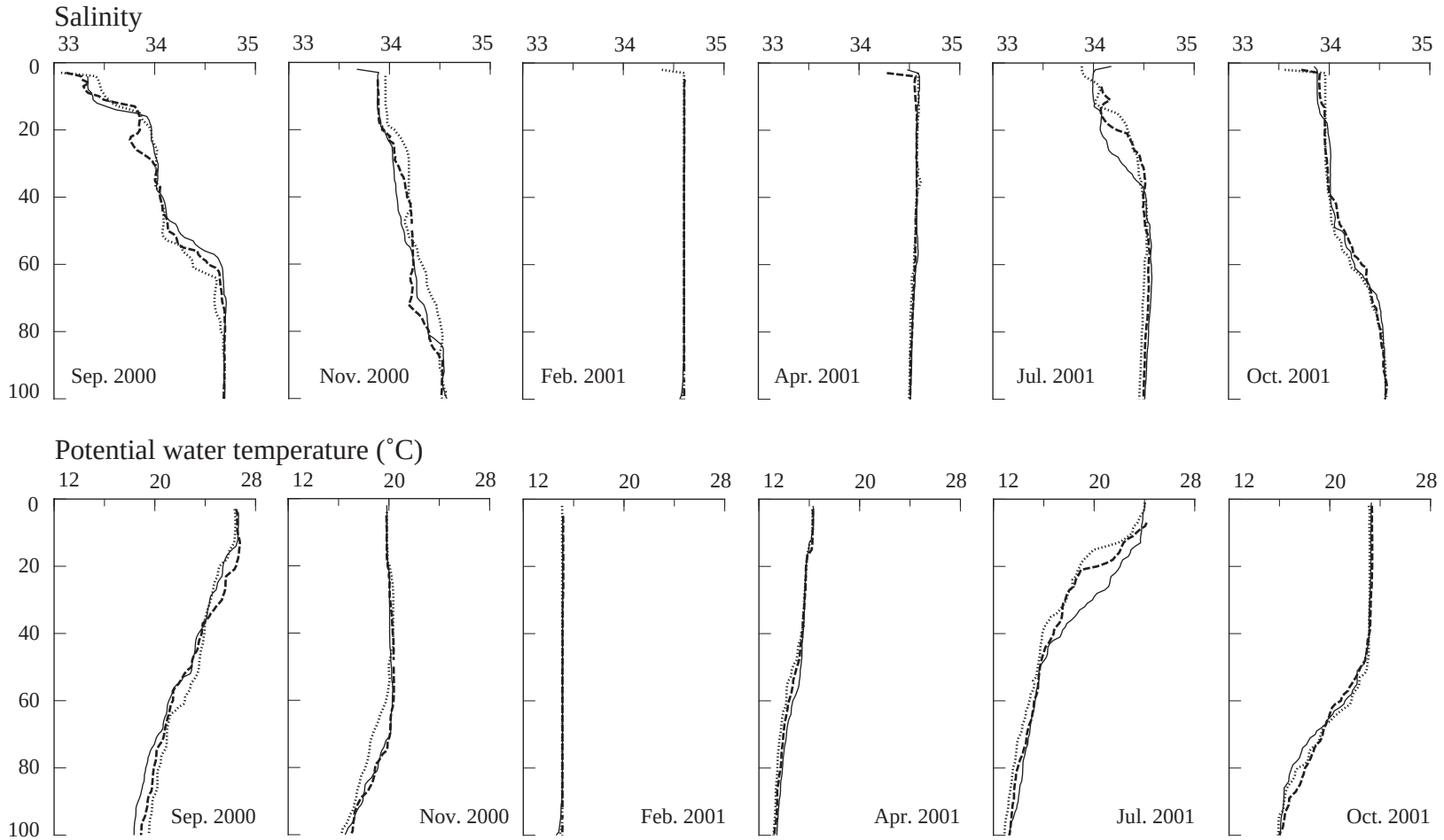

Fig. III-6: Vertical profiles of salinity and potential temperature, from the surface to 100 m, observed at midday (solid line), night (broken line), and predawn (dotted line), during September 2000-October 2001.

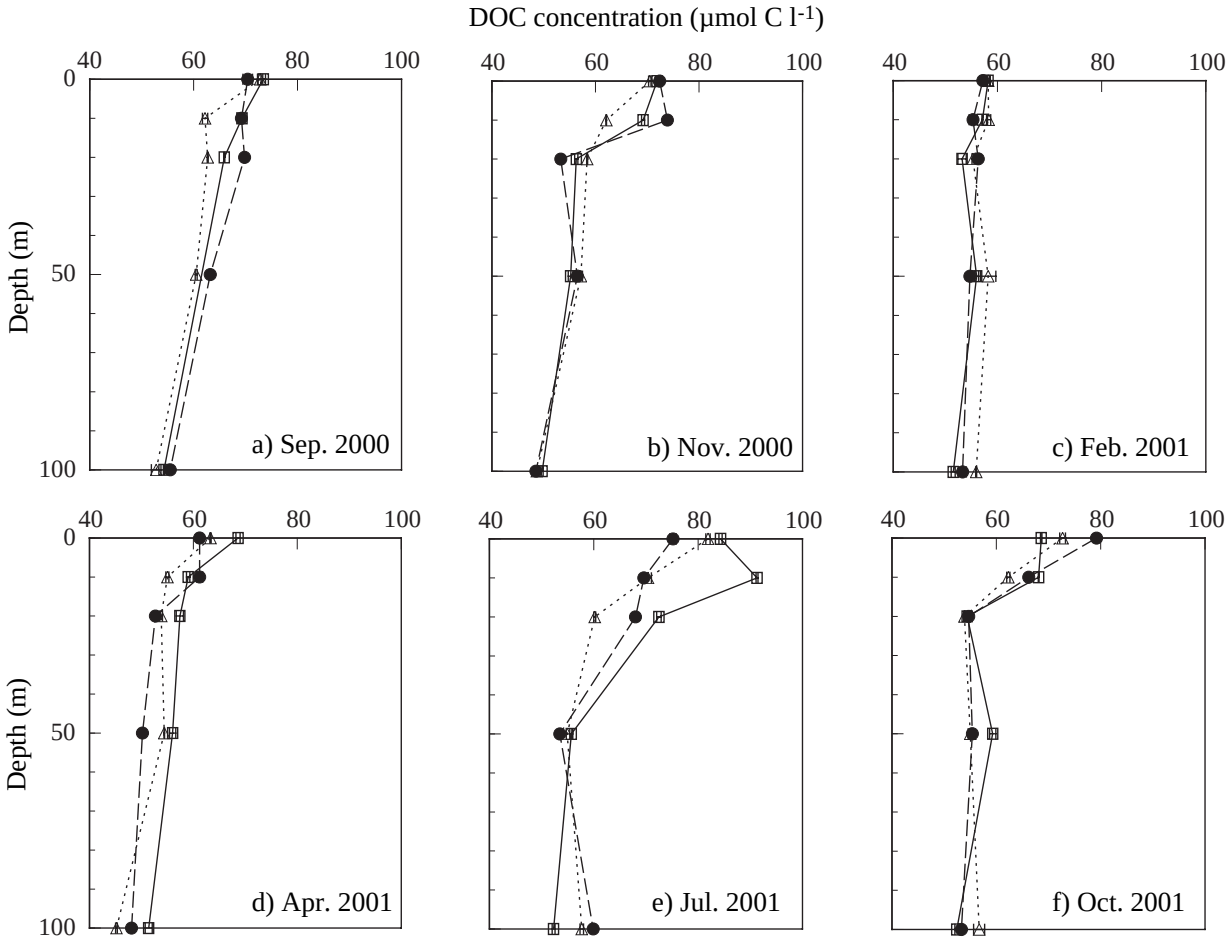

Fig. III-7: Diel vertical profiles of DOC concentrations, from surface to 100 m in a) September 2000, b) November 2000, c) February 2001, d) April 2001, e) July 2001, and f) October 2001. Open squares, solid circles and open triangles represent DOC concentrations collected at midday, night and predawn, respectively. Error bars represent standard deviations.

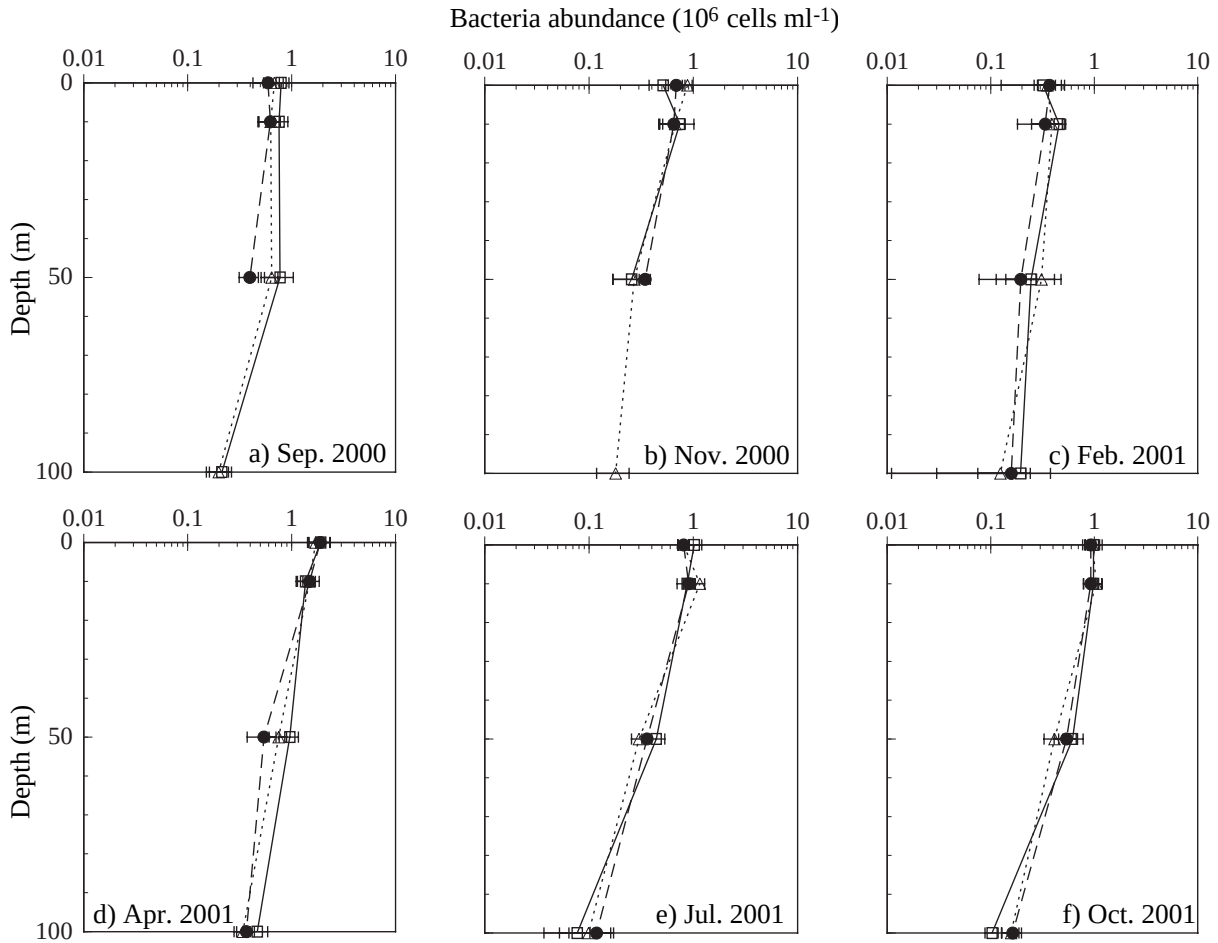

Fig. III-8: Diel vertical profiles of bacteria abundance from surface to 100 m in a) September 2000, b) November 2000, c) February 2001, d) April 2001, e) July 2001, and f) October 2001. Open squares, solid circles and open triangles represent bacteria abundance collected at midday, night and predawn, respectively. Error bars represent standard deviations.

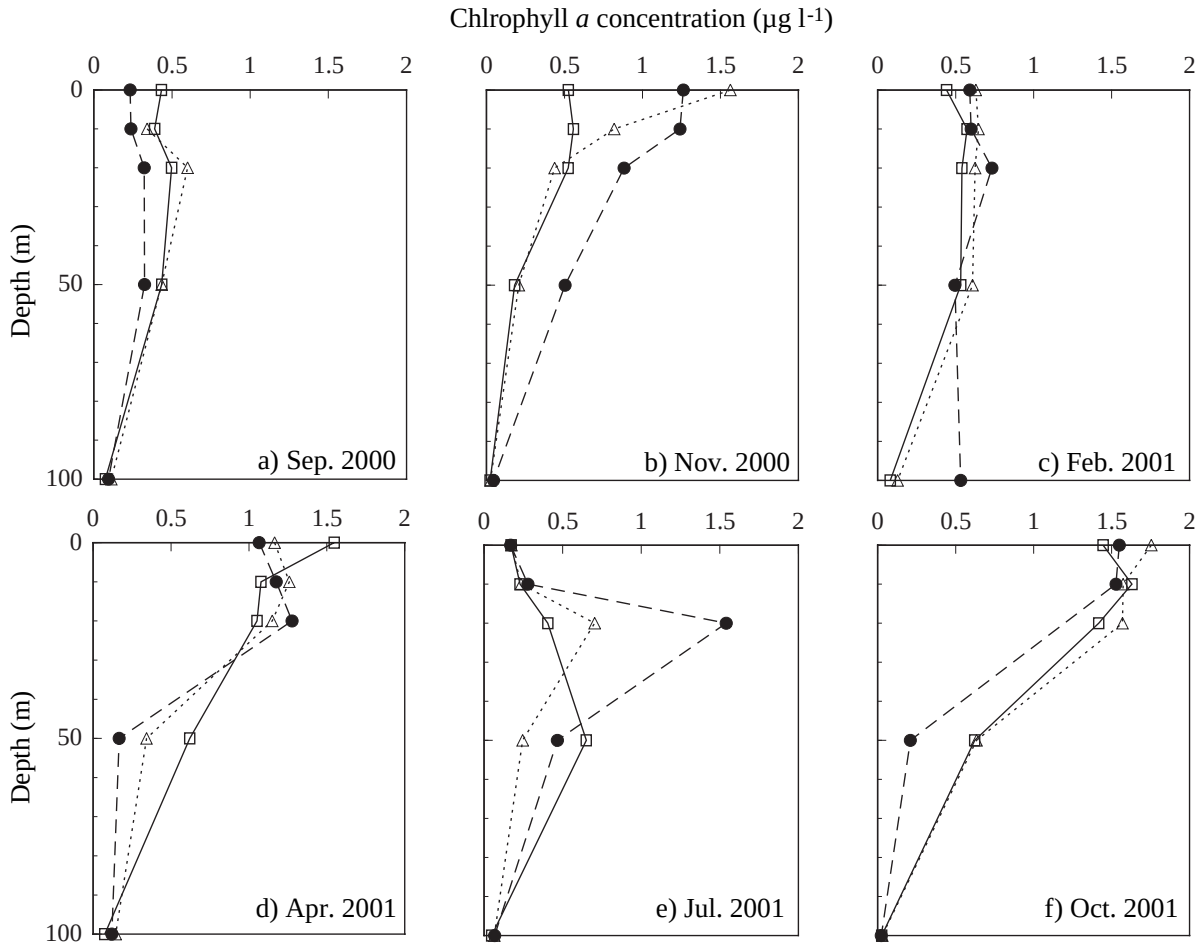

Fig. III-9: Diel vertical profiles of chlorophyll *a* concentrations from surface to 100 m in a) September 2000, b) November 2000, c) February 2001, d) April 2001, e) July 2001, and f) October 2001. Open squares, solid circles and open triangles represent chlorophyll *a* concentrations collected at midday, night and predawn, respectively.

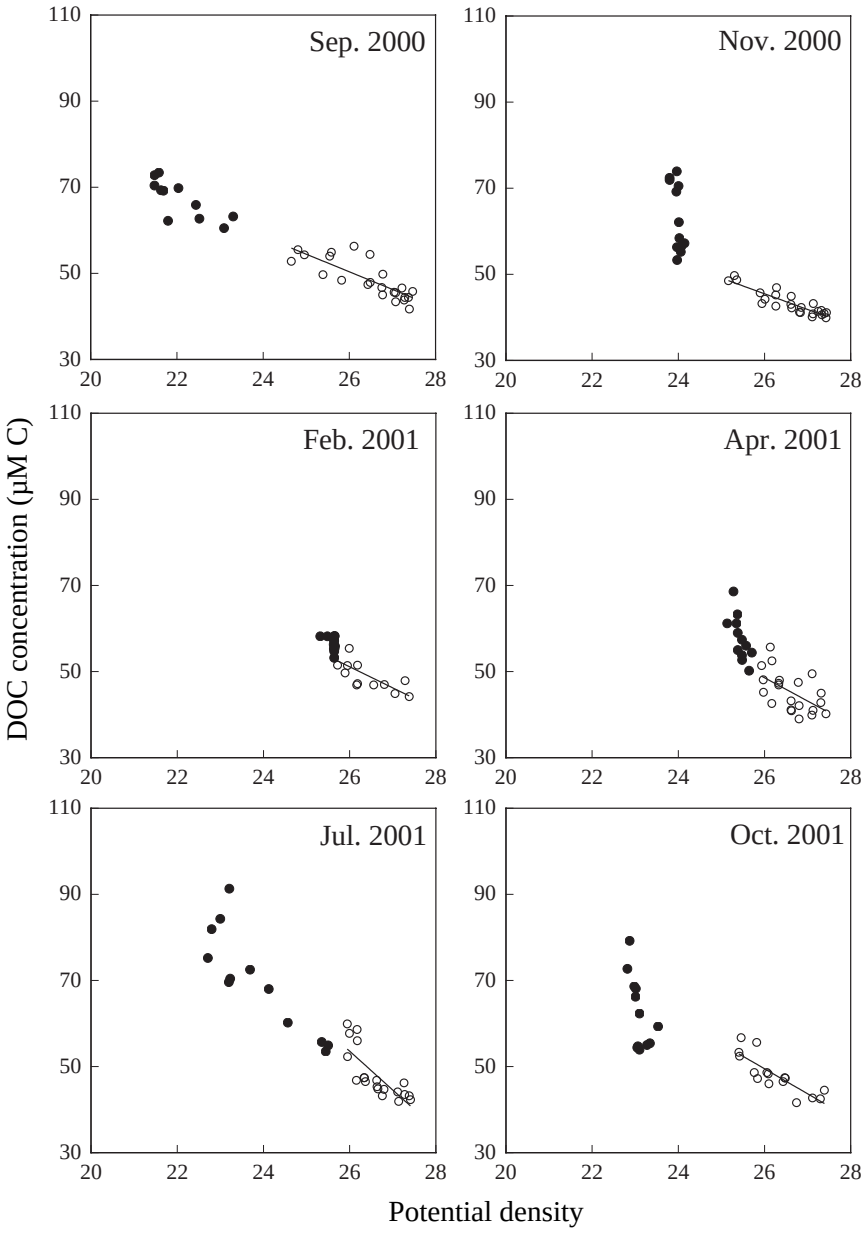

Fig. III-10: DOC concentration versus potential density for all data collected at midday, night and predawn during September 2000-October 2001. Solid circles represent data from surface to 50 m; data from 100 to 1000 m are represented as open circles. The solid lines represent linear regression between DOC concentration and potential density in the layer 100-1000 m: y = -4.1x+ 157 ($r2$ = 0.66, n = 23, p < 0.001) for September 2000; y = -3.6x + 140 ($r2$ = 0.80, n = 24, p < 0.001) for November 2000; y = -4.9x + 178 ($r2$ = 0.62, n = 14, p < 0.001) for February 2001; y = -6.9x + 228 ($r2$ = 0.47, n = 24, p < 0.001) for April 2001; y = -9.0x + 287 ($r2$ = 0.62, n = 24, p < 0.001) for July 2001; and y = -5.8x + 201 ($r2$ = 0.70, n = 16, p < 0.001) for October 2001.

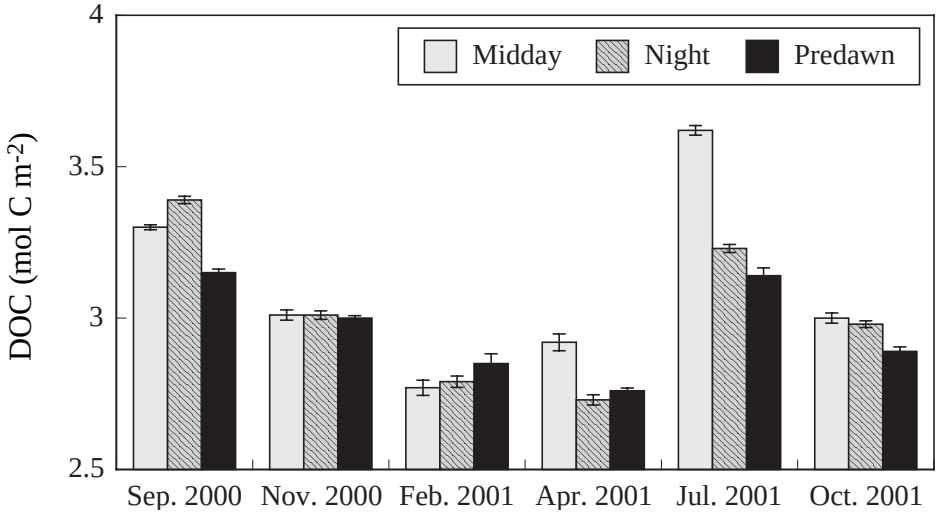

Fig. III-11: Integrated DOC with depth from the surface to 50 m, at midday, night and predawn. Error bar is normalized to area by integrating standard deviation in DOC concentration with depth.

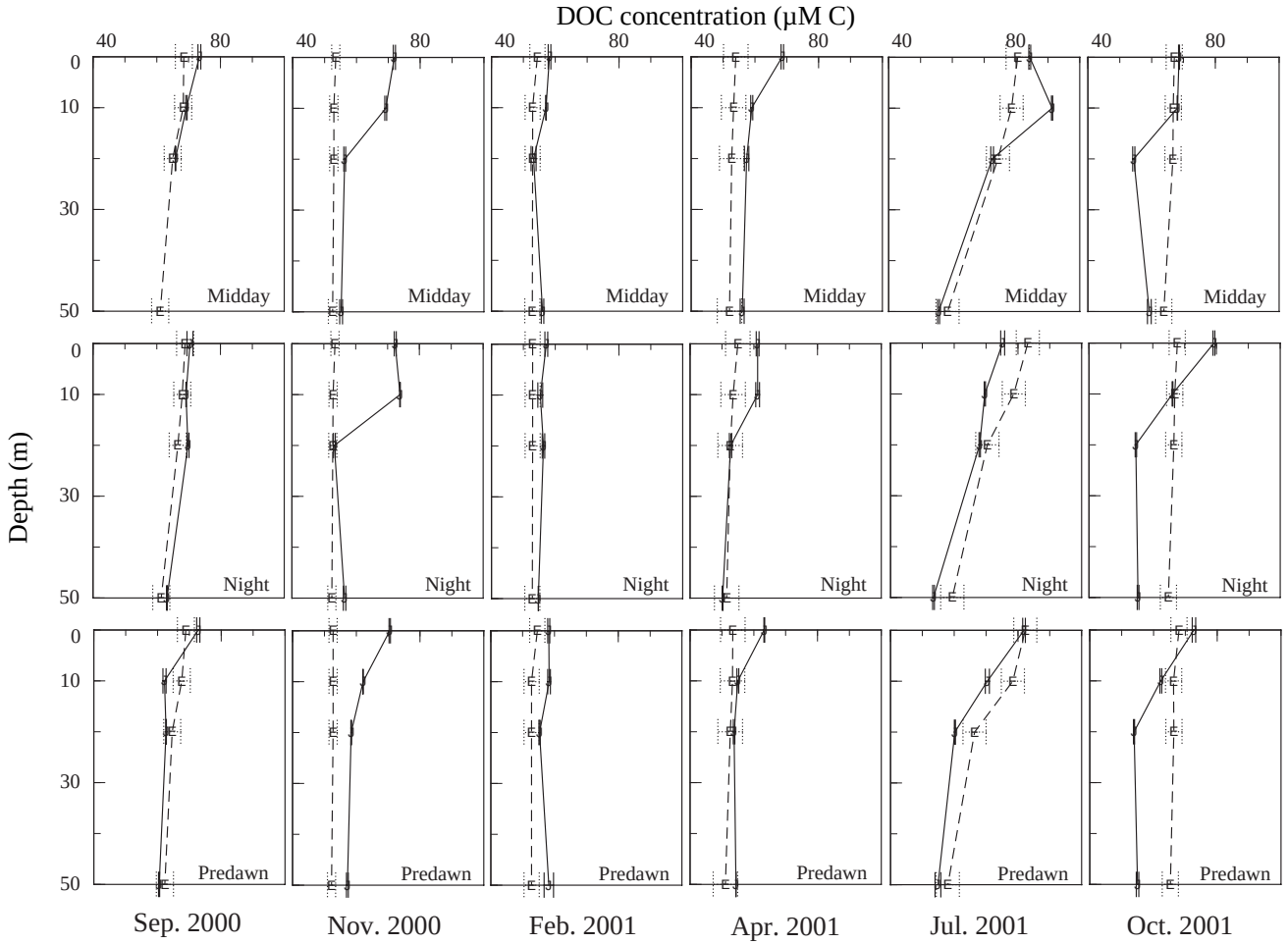

Fig. III-12: Vertical profiles from the surface to 50 m of DOC concentrations observed and calculated from regression lines obtained from 100 to 1000 m with potential density in September 2000-October 2001. Solid and open circles represent observed and calculated DOC concentrations, respectively. Error bars represent standard deviations.

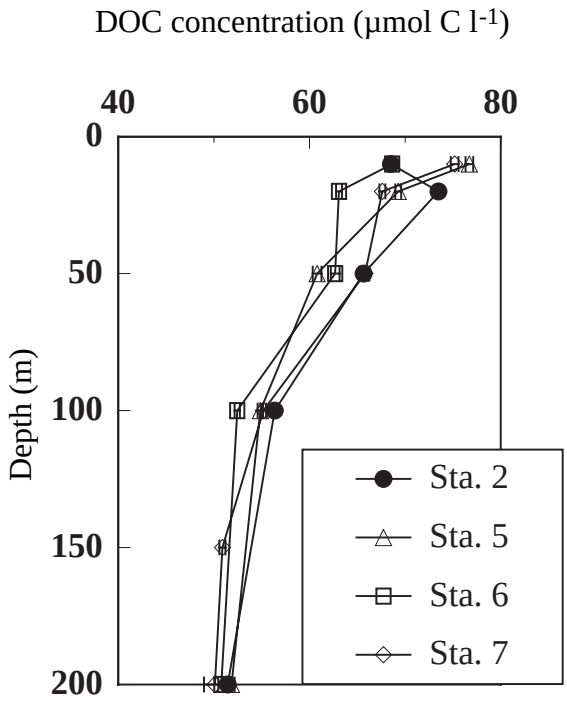

Fig. III-13: Vertical profiles of DOC concentrations from surface to 200 m at Sta. 2, 5, 6 and 7 in 28 May 2002. Error bars represent standard deviations.

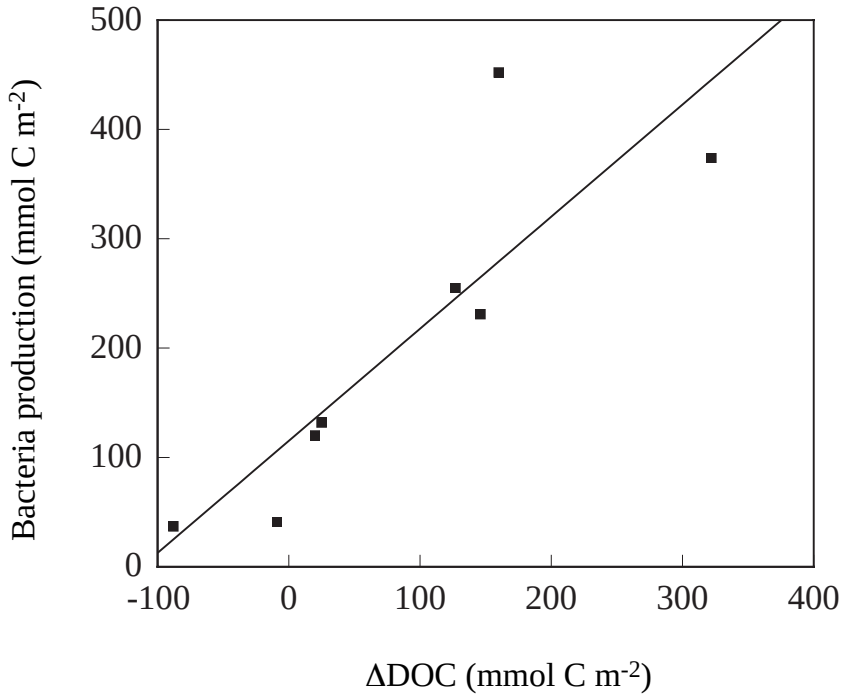

Fig. III-14: Relationship between bacterial production and apparent change in DOC inventory (0-50 m) contributed biologically from midday to predawn (ΔDOC).

C. Estimation of Seasonal Accumulation and Downward Export of Organic Matter

1. Comparison of seasonal inventory between the upper and middle layers

Inventories for nutrients, organic matter, chlorophyll *a* concentrations and bacteria abundance were calculated to integrate these concentrations with depths divided the two layers: the upper (0-50 m) layer and the middle (50-200 m) layer (Fig.III-15). The upper layer is roughly corresponded to the euphotic zone and the bottom of the middle layer, 200 m depth, is close to the deepest MLD (Table III-3) during our observation.

DOC inventory in the upper layer showed clearly seasonal change as decrease from summer to winter and increased from spring to summer, ranging from 2680 to 3620 mmol C m^{-2}. On the other hand, DOC inventory in the middle layer seems to be larger in spring and summer than winter (range: 6990-8620 mmol C m^{-2}), but such obvious seasonal pattern observed in the upper layer could not be found in the middle layer. DON inventory in the upper layer showed similar seasonal variation of the DOC. In the middle layer, the DON inventory decreased from August 2000 to April 2001 but thereafter was almost stable to October 2001. After the sharp increase in December 2001, the value of DON inventory of the middle layer decreased to the level of last winter-summer and increased again in May 2002. This sudden increase in December 2001 was also observed for nitrite, particulate matter, chlorophyll *a* and bacteria abundance although these

continued to be high values to May 2002. Nitrite inventory showed different seasonal variation from others: the peak in nitrite inventory in the upper layer was observed a few months earlier than other nutrients.

POC inventories in both layers were almost same of the PN. During February 2001 to April 2001, the inventories increased greatly. The increase in spring was observed also in 2002. POC and PN inventories decreased slowly during summer to autumn and ranged 153-505 and 14.3-72.6 mmol m^{-2}, respectively. Simultaneously, in the middle layer, inventories for POC and PN showed the increase in spring, although the increase in 2002 spring was larger than those in the upper layer and longer than in the last spring and continued during December 2001 to May 2002. Seasonal variations in chlorophyll *a* coincided with that of POC and PN. The inventory for bacteria abundance co-varied with the POC and PN. These indicate that biomasses of phytoplankton and bacteria contributed considerably to both elements of carbon and nitrogen in POM.

Table III-8 and III-9 showed summary of correlations among inventories in each surface-50 m and 50-200 m layer. The inventories for nutrients except nitrite showed significant negative correlation with DOC and DON in the upper layer. The values were largest in winter in the upper layer. Nutrients in the middle layer except for nitrite negatively related with DON but not DOC while nitrite showed positive relationship with DON.

The C:N ratio of DOM in inventory displayed almost same variation as the C:N ratio of PM (Fig. III-16). The range of C/N for DOC was 10.2-18.9 in the upper layer and about two times higher than the ratios of PM (range: 6.0-10.7), which is close to the ratio of phytoplankton (6-8). The C/N for DOM and PM inventories in the upper layer

increased from August 2000 to February 2001 and decreased suddenly to April 2001. After a peak in July 2001, the C:N ratio seemed to be stable in comparison with the ratios in last year. The ranges of ratios in the middle layer were larger than those in the upper layer, 11.1-23.0 and 5.9-31.4 for DOM and PM, respectively, although the trend of variation was similar to the upper layer. Each ratio had significant correlation with its nitrogen components rather than carbon (Tables III-8 and 9), therefore, the variation was strongly influenced with variation in nitrogen. While nitrogen of POM could be directly measured, DON was calculated by subtracting DIN from TDN, therefore the precision of DON depend on both measurements of DIN and TDN. In this study, DON concentration was shown without subtracting of ammonium concentration because ammonium concentration was very low (average: 0.11 μM, range: from under detection limit to 0.74 μM from the surface to 100 m, $n = 50$). Although DOC/DON in this study were close to the ratios in seawater reported previously (8.1-23 in the upper 150 m, Ross Sea, Carlson *et al.*, 2000; 11.5 - over 14 from the surface to deeper than1000 m in Sargasso Sea, Hansell & Carlson, 2001), it is necessary to discuss carefully the ratios of DOC:DON, especially at deep ocean, where nitrate concentration is extremely higher than DON.

DOC/DON was significantly correlated with C/N of PM ($p < 0.001$ for the upper layer and $p < 0.01$ for the middle layer) and bacteria abundance in both layers ($p < 0.001$). Bacteria abundance was related more significantly with PN and DON directly rather than the ratios (Tables III-8 and III-9). Needless is to say that bacteria abundance would be expected to relate with organic matter because particulate and dissolved matter include themselves organic matter originated from bacteria. Probably, it is rather speculated that the seasonal variation in both dissolved and particulate organic nitrogen as substance that

is consumed by bacteria concerned with bacteria growth. The seasonal organic nitrogen cycling was influenced by not only bacteria but also phytoplankton and its growth stage condition (Meon & Kirchman, 2001), and heterotrophic grazer (Bronk *et al*., 1998; Verela *et al*., 2003).

2. Estimation of downward export of organic matter

DOC inventory showed a clear seasonal variation: DOC inventory was high during spring and summer and decreased to winter in the upper layer (Fig. III-15). This indicates that the DOC was newly produced in the euphotic zone and accumulated in the surface layer because of almost no transport of water between the upper and lower layer due to the complete stratification of water column. During this period, DOC production exceeded over consumption in the surface layer: there was net DOC production. DOC inventory decreased with the deepening MLD. Diel variations of inventory in the upper layer were greater in spring and summer (August and September 2000, and April and July 2001) than in autumn. DOC inventories were almost stable during a day in November 2000 (Fig. III-11). This suggests that during spring and summer there was more abundant labile DOC having a shorter turnover time than in autumn where the labile DOC fraction was lower. In addition, this implies that the DOC occurred in the upper layer in autumn turned over at relative long time scale. Hansell & Carlson (2001) called the accumulated DOC present in the surface layer at the end of autumn seasons ‘resident’ DOC. The ‘resident’ DOC was deeper mixed during the overturn period. As a result, DOC concentration in the

upper layer was diluted with the deeper water having lower DOC concentration and the DOC was enriched in the deeper layer instead.

In Suruga Bay, there was seasonal variation for DOC inventories and obvious different concentrations between the upper and middle layer except winter, which was similar to the observed in the Sargasso Sea by Carlson *et al*. 1994 and Hansell & Carlson, 2001. They reported that when there was difference in concentrations between water at the surface and the depth mixed, DOC would be exported to deeper layer. Thereby, when there was an excess of DOC in the surface layer at the onset of the overturn event, it was necessary to downward export (Hansell, 2002). Then, the DOC downward export flux in Suruga Bay during the winter overturn event was estimated, following Carlson *et al.* (1994) and Hansell & Carlson (2001), according to the following: DOC concentrations for late autumn profile prior to deep overturn event (defined with MLD: deeper than 100 m because the MLD were deeper than 100 m but were shallower than 200 m in winter seasons, Table III-3) were integrated by the depth of mixed layer of winter, and the integrated DOC was normalized with the depth to convert into a mean concentration in the mixed layer. If DOC for autumn was redistributed homogeneously trough the mixed layers, the DOC inventory would be lower in the upper layer (0-50 m) and larger in the middle layer (50-200 m) than the values actually observed in autumn. The values calculated were summarized in Table III-10. The inventories used for calculation were average of data collected at midday, night and predawn, and range of values using data at each sampling time were shown in the parentheses. For observation period of 2000-2002, the overturn events were observed two times: at February 2001 and 2002. In the case of the overturn period in 2000-2001, DOC was integrated from the surface to the MLD (114

m) of February 2001 using the profile for November 2000 as the representative values prior to the deep mixing. The mean concentration trough the mixed layer was calculated at 55.4 μM C. The mean concentration was re-integrated from the surface to 50 m and DOC inventory of middle layer (50-200 m) was also recalculated subtracting the re-integrated value of the upper layer from the whole (0-200 m) inventory of November 2000 to compare with the value observed actually in February 2001. As a result, the re-integrated DOC of November 2000 was lower in the upper layer and larger in the middle layers, when compared with the values observed in November 2000. This indicates that DOC was diluted in the upper layer while DOC was enriched in the middle layer by physical mixing, i.e. 240 mmol C m^{-2} of the 'resident' DOC was exported into the middle layer. Observed DOC inventories in February 2001 were larger than the estimated DOC inventories using value of November 2000 which was redistributed to the MLD of February 2001: the differences were 30 and 470 mmol C m^{-2} in the upper layer and middle layer, respectively. This indicates that there was not addition from 'resident' DOC in the surface layer but freshly produced DOC 'fresh' DOC during the convective period. Hansell (2002) demonstrated that the spring bloom occurred at the same time of convective overturn because nutrients were loaded to the surface layer and phytoplankton could be supplied by enough light to growth in the middle latitude. Both primary production (Table III-3) and chlorophyll *a* distribution (Figs. III-3 and 4) showed an increase during the overturn period and particularly the abundance of phytoplankton demonstrated the occurring of spring bloom in Suruga Bay (Fig. III-17).

Actually, the exported DOC should be evaluated to take account of DOC consumption during the overturn period in addition of physical mixing. Consequently,

the exported total ('resident' + 'fresh') DOC into the middle layer was estimated at 710 mmol C m^{-2}. The DOC export during the overturn period was comparable to annual export DOC or TOC (total organic carbon: DOC + POC) reported in previous studies (400-1500 mmol C m^{-2} yr^{-1}, Copin-Montégut & Avril, 1993; Carson *et al.*, 1994; Hansell & Carlson, 2001).

In contrast with the overturn period in 2000-2001, the exported 'fresh' DOC could not be detected during the next overturn period, December 2001 to February 2002. The 'resident' DOC exported into the middle layer was 70 mmol C m^{-2}, was only one third of the last year but total exported DOC was not detected because the inventory in the 50-200 m layer of February 2002 was lower than the inventory of December 2001. In the same way of DOC, exported DON were calculated in the two years. DON was exported to the middle layer as only 'resident', 30 mmol N m^{-2} February 2001, but total exported DOC was not detected. On the other hand, any of exported DON was not detected in February 2002. Although the MLD was deeper in February 2002 (156 m) than in 2001 (114 m), the inventory observed in February 2002 was extremely lower than the estimated inventory using the profile for December 2001 even regarding net consumption. This implies that DOC was more accelerated to consume during the overturn period. This result was opposite to the conclusion by Hansell & Carlson (2001) which the amount of TOC exported depended largely on the depth of mixing. On the other hand, they indicated that the time required for exported TOC to mineralize associated with the shallow winter maximum MLD. Therefore, it is possible that most of the exported DOC had been consumed until observation in February 2002 faster than in the case of the last year. As a result, the exported DOC could not be detected owing to coarse intervals of observations.

Between DOM observed in February 2001 and 2002, there was the noticeable difference in C:N ratio (Fig. III-16): The ratios of DOC:DON in inventories were higher in February 2001 (18 and 21 in the upper and middle layer, respectively) than those in February 2002 (11 and 16 in the upper and middle layer, respectively), suggesting possibility of the difference of quality of DOM exported between in these overturn periods. This difference in quality of DOM in each period might be caused by variation in composition of phytoplankton. One of the source of DOC production in the sea is photosynthetic algae and their extracellular release is now established as a part of the primary production. The extracellular release rate from phytoplankton can vary among species and be changed by physiological factors, such as phases of growth, strength of light irradiance or variation in nutrients (Myklestad, 2000). It is possible that the difference in quality of DOC produced decides the fates of DOC.

The experiments for evaluation of sinking particle flux by using sediment trap were conducted for around two weeks, at three times, May-June 2001, October-November 2001 and July 2002. The sediment traps were placed at three depths, 100, 300 and 700 m in 2001, and 100, 300 and 500 m in 2002. Fig. III-18 shows the sinking particle fluxes during these periods. Table III-11 shows sinking particle fluxes in these experiments. The sinking particle fluxes ranged 0.50-24 g m^{-2} d^{-1} for total mass of sinking particles, 0.6-114 mmol C m^{-2} d^{-1} for POC, and 0.07-13 mmol N m^{-2} d^{-1} for PN. The C:N ratio of sinking particulate matter was average 10-11 (9.0-15) at three depths in May-June 2001 and October-November 2001, which was higher than the C/N of POM (as suspended form) and lower than DOC/DON (Fig. III-16). On the other hand, in July 2002, the C:N ratio of sinking particulate matter was lower (average 5.9-8.7) than in previous experiments, and

especially, the C:N ratio at 100 m was lowest (average 5.6), which was resulted from low C/N values collected at 5 times during the periods conducted the sediment trap (Fig. III-18). This annual trend that C/N decreased in 2002 coincided with DOM. The fluxes of organic carbon and nitrogen of sinking particulate increased with depth. To compare with DOM export, the all fluxes at 300 m, obtained from three times observations, were averaged and the average was converted to per year by multiplying 365 days. The average sinking flux at 300 m was 2290 mmol C m^{-2} y^{-1} for POC and 252 mmol N m^{-2} y^{-1} for PN its C/N was 9.1.

Total exported DOC and DON for February 2001 was 710 mmol C m^{-2}. Each value was corresponded to one third of the annual sinking POC flux. This indicates that organic carbon was significantly exported to deep as dissolved form during the overturn event, which was comparison to sinking particle flux in Suruga Bay while also suggests a possibility that the ability to export DOC varied annually.

This study inferred significance that organic carbon as dissolved form was able important role in the carbon cycle in the coastal area.

Table III-8: Relationships between depth-integrated dissolved organic carbon (DOC), dissolved organic nitrogen (DON), the C:N ratio of DOM (DOC/DON), silicate ($Si(OH)_4$), phosphate (PO_4), nitrate (NO_3), nitrite (NO_2), particulate organic carbon (POC), particulate nitrogen (PN), the C:N ratio of POM (POC/PN), chlorophyll *a* (Chl-*a*) and bacteria abundance (BA) from 0-50 m. Slopes of the regressions ($\pm r$) and correlation values are presented. n = 20-28.

	DOC	DON	DOC/DON	$Si(OH)_4$	PO_4	NO_3	NO_2	POC	PN	POC/PN	Chl. *a*	BA
DOC	1.000	0.409 [a]	0.168	-0.777 [c]	-0.630 [c]	-0.625 [c]	-0.416 [a]	0.306	0.179	0.058	-0.424 [a]	-0.105
DON		1.000	-0.815 [c]	-0.588 [b]	-0.670 [c]	-0.653 [c]	-0.275	0.556 [a]	0.644 [b]	-0.571 [b]	-0.002	0.473 [a]
DOC/DON			1.000	0.155	0.345	0.323	-0.001	-0.428	-0.618 [b]	0.740 [c]	-0.278	-0.633 [c]
$Si(OH)_4$				1.000	0.904 [c]	0.912 [c]	0.124	-0.202	-0.174	0.211	0.180	-0.108
PO_4					1.000	0.981 [c]	0.012	-0.176	-0.256	0.458 [a]	0.063	-0.233
NO_3						1.000	0.063	-0.231	-0.307	0.420	0.046	-0.280
NO_2							1.000	-0.430	-0.296	-0.208	0.190	0.040
POC								1.000	0.906 [c]	-0.112	0.287	0.550 [a]
PN									1.000	-0.473 [a]	0.388	0.683 [c]
POC/PN										1.000	-0.196	-0.456 [a]
Chl. *a*											1.000	0.408 [a]
BA												1.000

a: $p < 0.05$
b: $p < 0.01$
c: $p < 0.001$

Table III-9: Relationships between depth-integrated dissolved organic carbon (DOC), dissolved organic nitrogen (DON), the C:N ratio of DOM (DOC/DON), silicate ($Si(OH)_4$), phosphate (PO_4), nitrate (NO_3), nitrite (NO_2), particulate organic carbon (POC), particulate nitrogen (PN),the C:N ratio of POM (POC/PN), chlorophyll *a* (Chl-*a*) and bacteria abundance (BA) from 50-200 m. Slopes of the regressions ($\pm r$) and correlation values are presented. n = 19-28.

	DOC	DON	DOC/DON	$Si(OH)_4$	PO_4	NO_3	NO_2	POC	PN	POC/PN	Chl. *a*	BA
DOC	1.000	0.375	-0.051	-0.341	-0.186	-0.223	0.106	0.050	-0.109	0.249	-0.024	0.133
DON		1.000	-0.925 [c]	-0.599 [c]	-0.631 [c]	-0.638 [c]	0.664 [c]	0.473 [a]	0.706 [c]	-0.525 [a]	0.408 [a]	0.674 [c]
DOC/DON			1.000	0.533 [b]	0.598 [c]	0.577 [b]	-0.628 [c]	-0.430	-0.756 [c]	0.676 [b]	-0.376	-0.731 [c]
$Si(OH)_4$				1.000	0.889 [c]	0.872 [c]	-0.321	0.160	-0.190	0.474 [a]	-0.044	-0.318
PO_4					1.000	0.984 [c]	-0.459 [a]	0.078	-0.280	0.460 [a]	-0.212	-0.320
NO_3						1.000	-0.521 [b]	0.026	-0.306	0.424	-0.317	-0.298
NO_2							1.000	0.446 [a]	0.535 [a]	-0.298	0.741 [c]	0.460 [a]
POC								1.000	0.809 [c]	-0.209	0.764 [c]	0.531 [a]
PN									1.000	-0.654 [b]	0.751 [c]	0.769 [c]
POC/PN										1.000	-0.226	-0.607 [b]
Chl. *a*											1.000	0.330
BA												1.000

a: $p < 0.05$
b: $p < 0.01$
c: $p < 0.001$

Table III-10: Estimation of DOC and DON exported to the 50-200m layer, and DOC and DON added to the 0-50 m layer during overturn event.

Fraction	Period	Export [a] (mmol C m^{-2})			Addition [e] (mmol C m^{-2})
		Total [b]	Resident [c]	Fresh [d]	
DOC	2000-2001 [f]	710 (480-940)	240 (230-250)	470 (220-700)	30 (0-80)
	2001-2002 [g]	n.d. [h]	70	n.d.	n.d.
DON	2000-2001	n.d.	30 (20-30)	n.d.	n.d.
	2001-2002	n.d.	n.d.	n.d.	n.d.

a: DOC or DON exported to the 50-200 m layer during winter overturn periods.
b: Average of total DOC or DON exported to the 50-200 m layer (observed integrated-DOC or DON in winter - observed integrated-DOC or DON in autumn). The numbers in parentheses show the range of values calculated using data at each sampling time: midday, night and predawn.
c: Re-distributed DOC or DON, which was resident until autumn, to winter mixed layer depth (calculated integrated-DOC or DON in autumn - observed integrated-DOC or DON in autumn).
d: Freshly produced DOC or DON during winter overturn period (observed integrated-DOC or DON in winter - calculated integrated-DOC or DON in autumn).
e: DOC or DON added to the 0-50 m layer from autumn to winter.
f: The period from November 2000 to February 2001 in the case of 2000-2001.
g: The period from December 2001 to February 2002 in the case of 2001-2002.
h: not detected.

Table III-11: Average and ranges of fluxes for particulate organic carbon, particulate nitrogen, average and ranges of these C:N ratios, and average and ranges of total mass in sinking particle collected by using sediment traps at depths of 100, 300, 500 (in July 2002) and 700 (in May-June 2001 and October-November 2001) m.

Period	Depth			
	100 m	300 m	500 m	700 m
Particulate organic carbon flux (mmol m^{-2} d^{-1})				
16 May - 10 Jun. 2001	4.0 (2.7-5.6)	6.4 (3.6-10)	--- [a]	9.7 (5.7-16)
23 Oct. - 15 Nov. 2001	1.7 (0.8-2.6)	4.0 (2.4-5.2)	---	11 (6.1-16)
20 Jul. - 28 Jul. 2002	1.4 (0.6-4.3)	8.5 (0.7-31)	25 (5.0-114)	---
Particulate nitrogen flux (mmol m^{-2} d^{-1})				
16 May - 10 Jun. 2001	0.39 (0.28-0.55)	0.61 (0.33-1.0)	---	0.92 (0.54-1.6)
23 Oct. - 15 Nov. 2001	0.16 (0.07-0.25)	0.37 (0.23-0.51)	---	1.0 (0.59-1.5)
20 Jul. - 28 Jul. 2002	0.23 (0.09-0.56)	1.1 (0.08-4.0)	2.9 (0.71-13)	---
C/N				
16 May - 10 Jun. 2001	10 (9.2-11)	10 (9.0-11)	---	11 (9.8-11)
23 Oct. - 15 Nov. 2001	11 (9.4-12)	11 (10-15)	---	11 (10-11)
20 Jul. - 28 Jul. 2002	5.9 (4.3-10)	8.0 (7.2-9.4)	8.7 (7.1-10)	---
Total mass flux (g m^{-2} d^{-1})				
16 May - 10 Jun. 2001	0.96 (0.71-1.4)	1.8 (1.0-2.6)	---	4.2 (2.5-5.7)
23 Oct. - 15 Nov. 2001	0.78 (0.50-1.2)	1.9 (1.3-2.9)	---	6.5 (4.3-8.8)
20 Jul. - 28 Jul. 2002	0.84 (0.59-1.3)	3.5 (0.77-14)	4.5 (1.2-24)	---

a: no data.

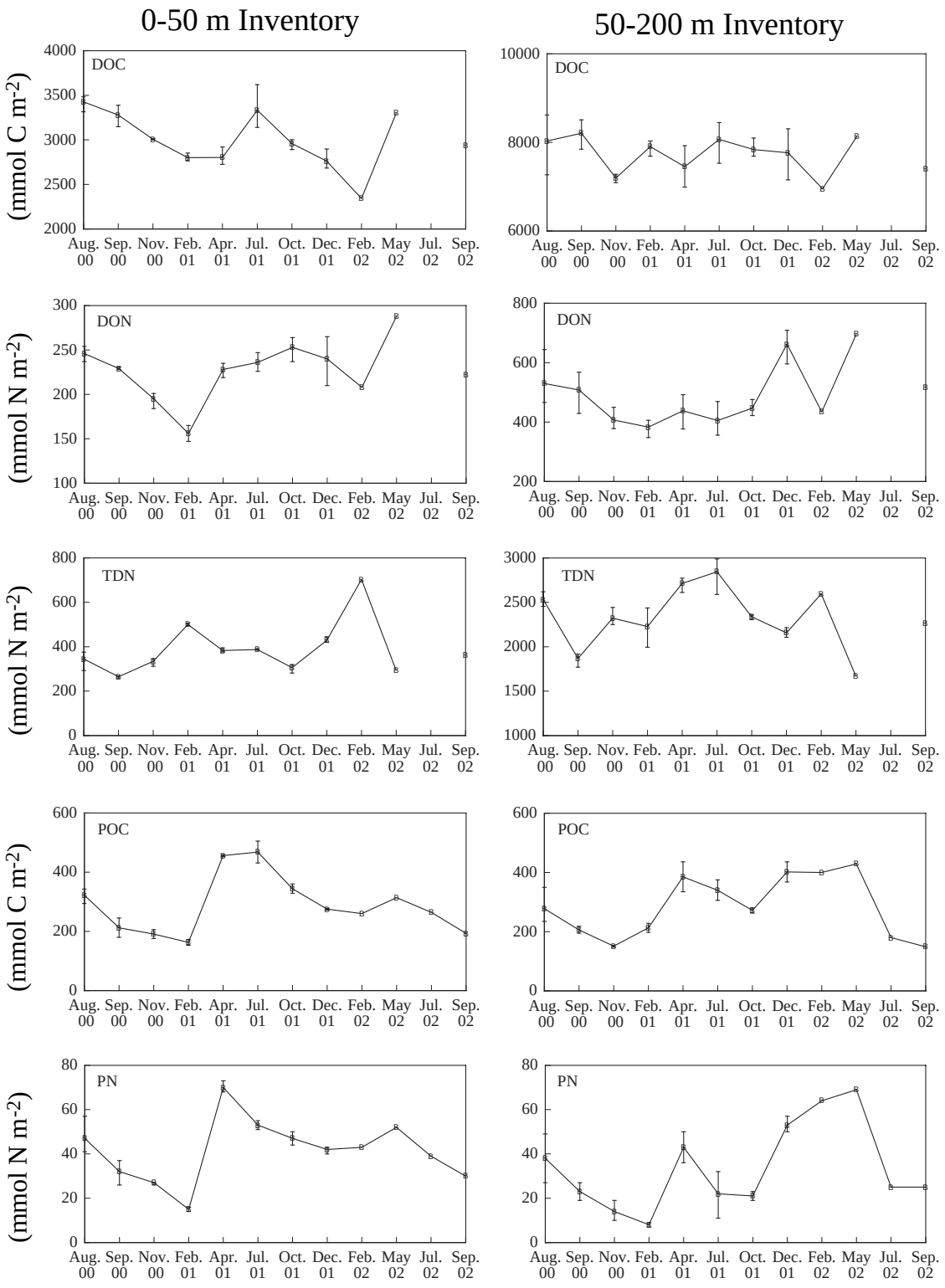

Fig. III-15: Seasonal variation in inventories of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), particulate organic matter (POC), particulate nitrogen (PN), silicate ($Si(OH)_4$), phosphate (PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-),

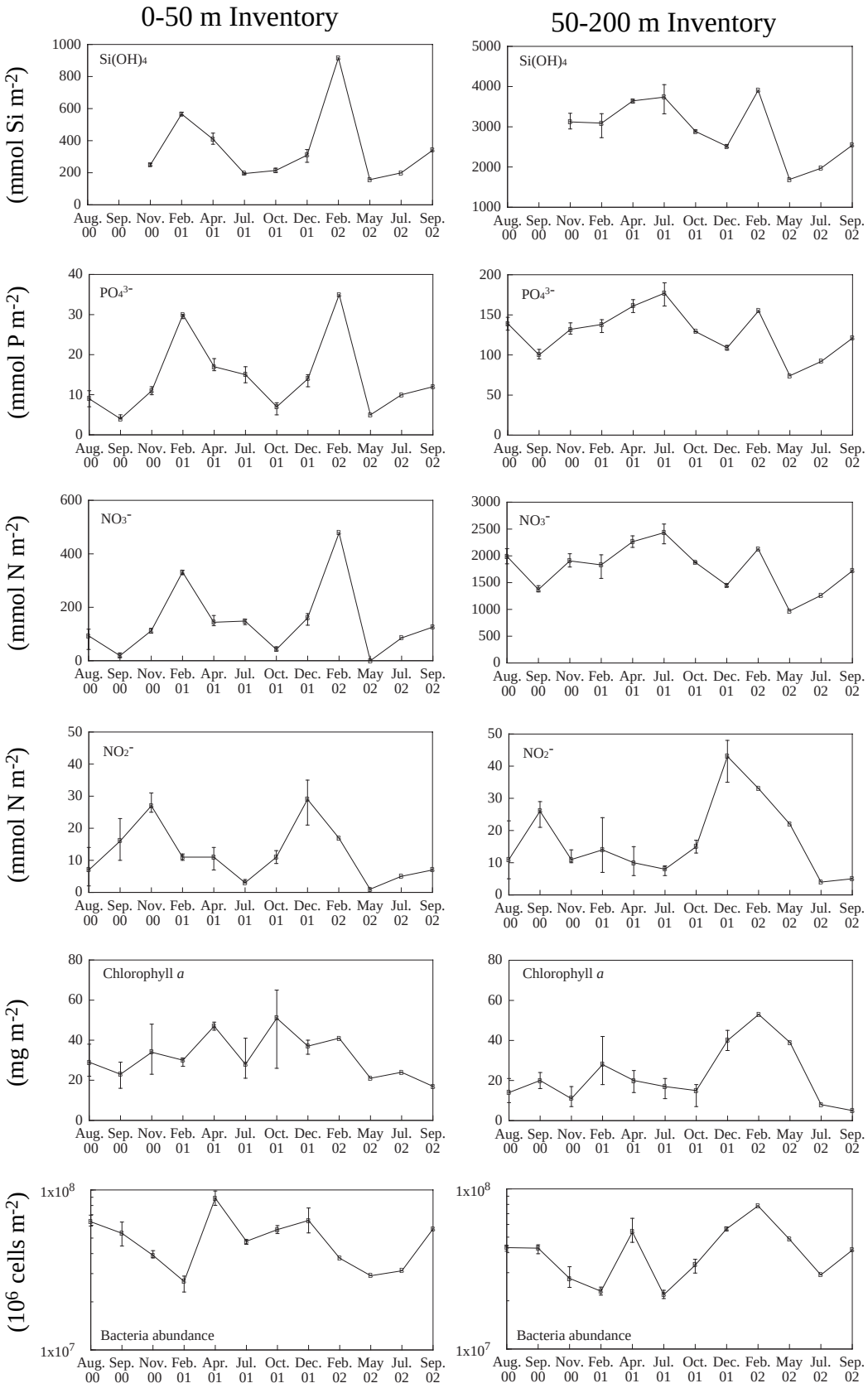

Fig. III-15: Continued.

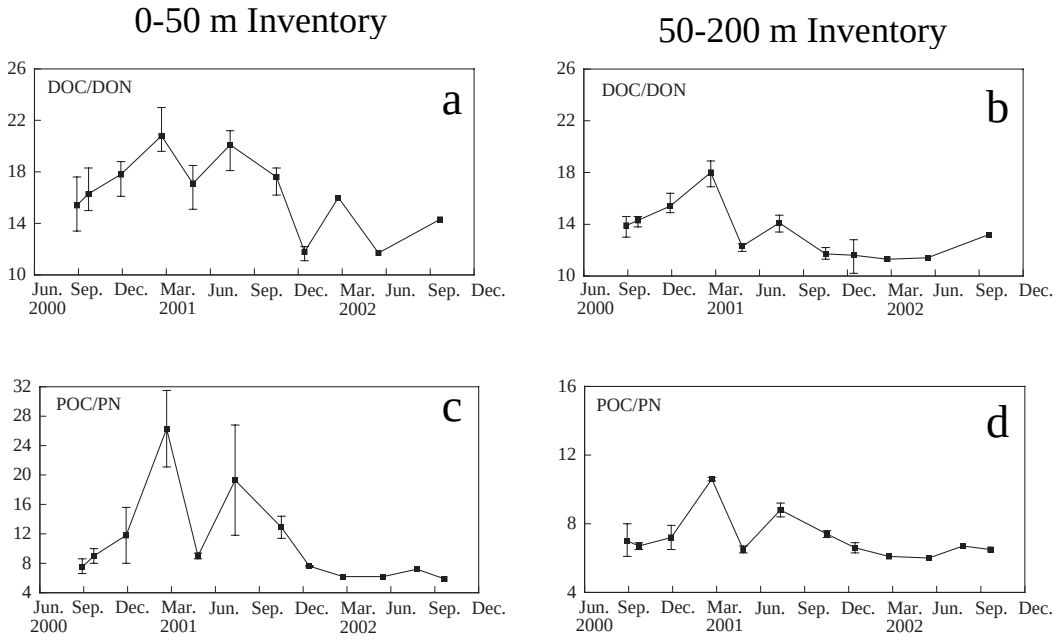

Fig. III-16: Seasonal variation in inventories of the C:N ratio of a) dissolved organic matter (DOM) in inventories of 0-50 m and b) 50-200 m and c) particulate (organic) matter (POM) in inventories of 0-50 m and d) 50-200 m. Values and bars during August 2000 to December 2001 represent average and range of data collected diurnally, respectively. The values during May 2002 to September 2002 are single data.

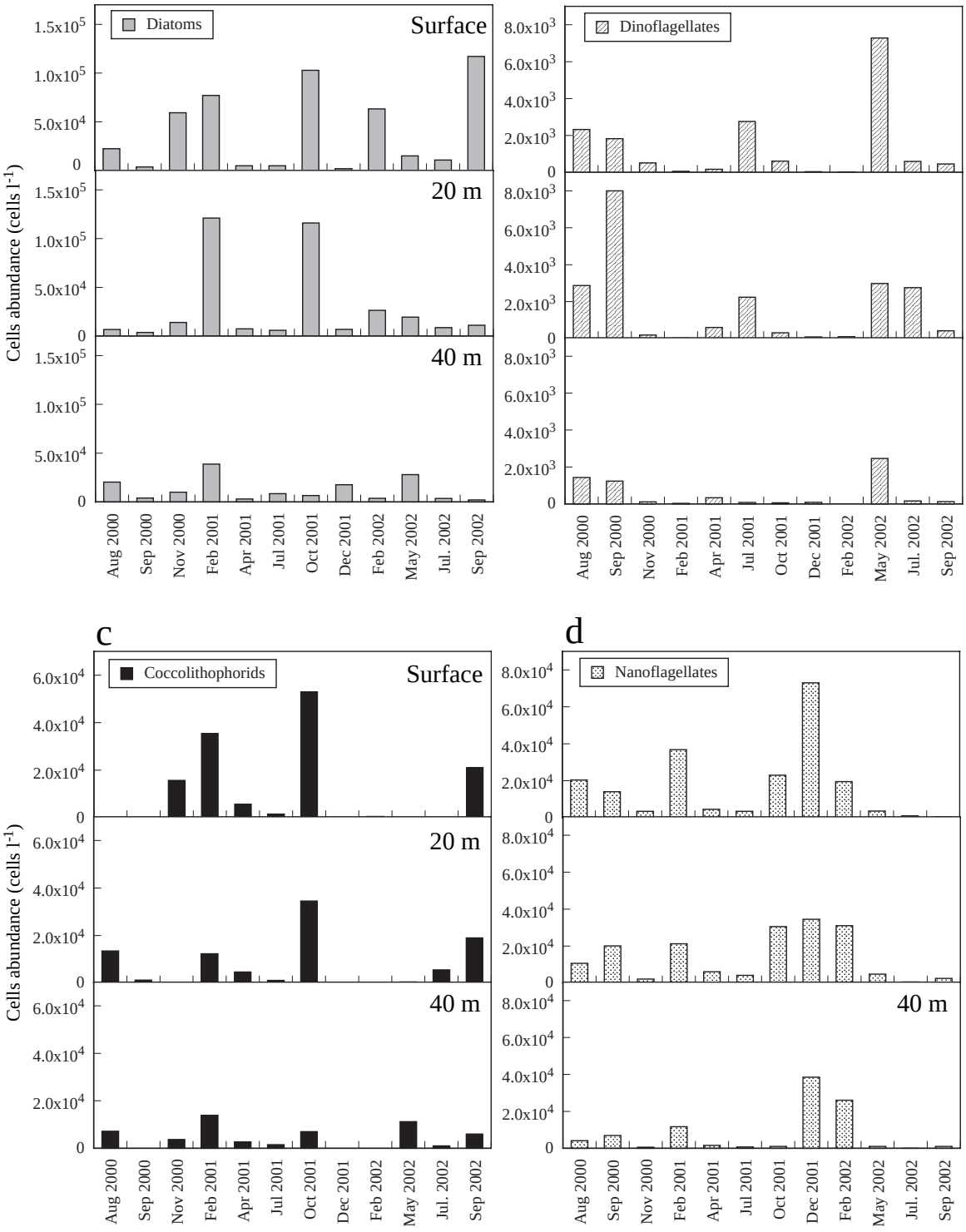

Fig. III-17: Seasonal variation in phytoplankton abundance of a) diatoms, b) dinoflagellates, c) cocolithophorids and d) nanoflagellates at the surface, 20 and 40 m.

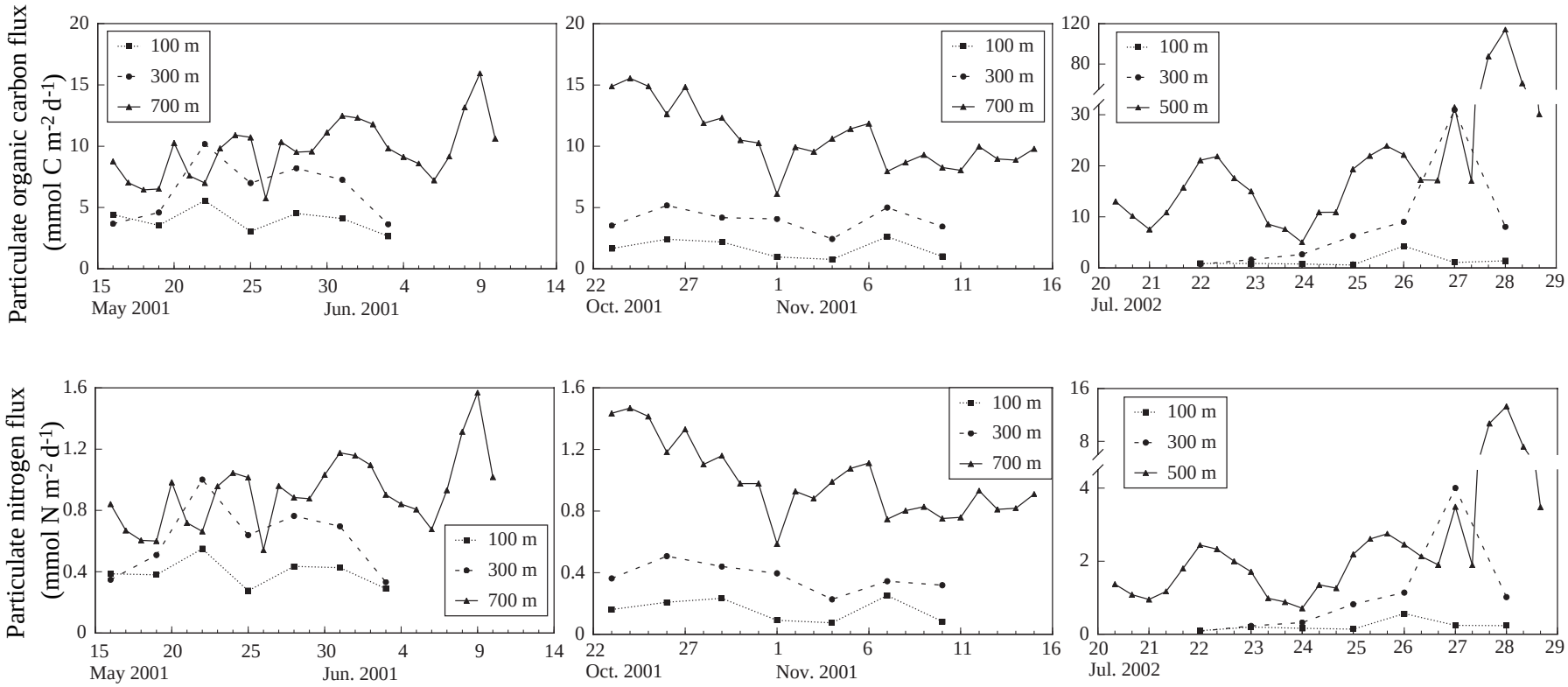

Fig. III-18: Time-series of sinking particle fluxes collected by sediment trap at 3 depths in May-June 2001, October-November 2001, and July 2001 for particulate organic carbon, particulate nitrogen and total mass and of these ratio of C:N.

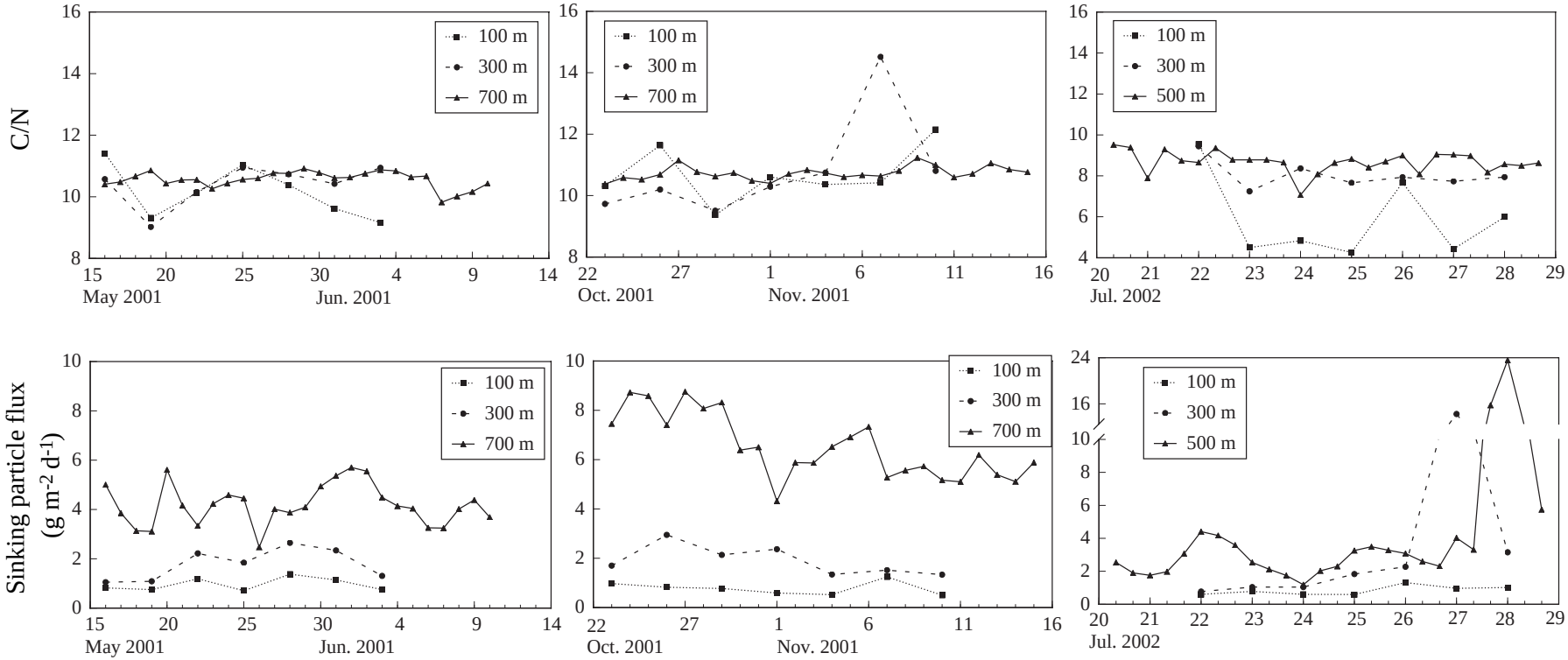

Fig. III-18: Continued.

IV. CONCLUSION

In Suruga Bay, DOC concentration showed remarkable diel changes in the upper 20 m with maximum change of 21.7 μM C at 10 m from midday to night in July 2001. The biological contribution to diel change of DOC was evaluated by comparing observed DOC concentration with calculated DOC concentration decided theoretically by water mixing. As a result, DOC accumulated biologically in the upper layer (surface to 50 m) in autumn (November 2000) with little diel variation in inventory of DOC in spite of remarkable diel change of DOC concentration. This indicates that production and consumption of DOC apparently compensated each other in the upper 50 m during a day, and DOC which accumulated biologically in the upper layer might turn over on the time scale of a day or more. In winter (February 2001), depth-integrated DOC (inventory) were lower than in autumn in the upper 50 m layer, suggesting that the excess DOC, contributed by biological processes, was consumed and/or exported downwards by deep mixing. The exported DOM was 710 mmol C m^{-2} as DOC but the exported DON was not detected during overturn event. Simultaneously, DOC was freshly produced through the mixed layer in February 2001 during overturn due to stimulated primary production by adequate light and supply of nutrients from deeper water by mixing. The 'fresh' DOM accounted for two-third of the total exported DOC in February 2001. This total amount of exported DOM was one-third of annual flux of sinking particle organic carbon in Suruga Bay. This suggests that DOC export was important as well as sinking particulate organic carbon in carbon cycle in Suruga Bay characterized by a deep trough. On the other hand, in the

next winter (2001-2002), the ‘fresh’ DOM exported was not detected and the exported DOC was only 70 mmol C m^{-2} as ‘resident’ DOC until autumn and any DON was not exported to deep. There was the noticeable difference in C:N ratio Between DOM inventories in February 2001 and 2002: The ratios of DOC:DON in inventories were higher in February 2001 than those in February 2002, suggesting a possibility of the difference of quality of DOM exported between in these overturn periods.

When the water column had stratified completely, the DOC inventory in the upper layer increased from spring to summer (April and July 2001), with large diel variations in inventory DOC. DOC accumulated in surface layer at midday, but it was reduced during night. The reduction during nighttime was probably mainly due to biological activity within the upper layer from relationship with daily bacterial production and apparent DOC decrease from midday to predawn causing by biological processes. In the following autumn (October 2001), however, DOC was depleted throughout the 0-50 m layer, in contrast to the previous autumn. The net consumption during the period might be caused by not only biological processes but also other processes, photochemical degradation. Moreover, this suggests a problem that it is not satisfied only by using one mixing line obtained from 100-1000 m depth to evaluate of the contribution to diel change DOC by biological processes.

Our results suggest that diurnal transient DOC accumulation, in spring and summer, can be regarded as labile because of its rapid disappearance. The magnitude of DOC accumulation in autumn may affect the downward flux of DOC from the upper layer in winter in Suruga Bay. Our observed considerable seasonal variation in diel DOC changes suggests that it is necessary to take diel variations into account when estimating seasonal

DOC pools in the coastal ocean. To demonstrate the global significance of the effect of biological activity on diel DOC variations in the field, it is necessary to evaluate biological contribution more precisely, in addition to detail investigations of temporal variability of DOC in various systems.

ACKNOWLEDGEMENTS

I would like to express my thanks to Professor Yoshimi Suzuki (Department of Biology and Geosciences, Shizuoka University) for his valuable scientific guidance and encouragement. He interested me in oceanography and gave me an opportunity to study in his laboratory. I am grateful to Professor Katsutoshi Ishikawa and Professor Hideki Wada (Department of Biology and Geosciences, Shizuoka University), Dr. Takeo Hama (College of biological sciences, second cluster of colleges, University of Tsukuba), Dr. Hiroshi Ogawa (Ocean Research Institute, University of Tokyo) and Professor Dennis A. Hansell (Rosenstiel School of Marine and Atmospheric Science, University of Miami) for their valuable comments to this study.

I wish to thank Dr. Beatriz E. Casareto (Laboratory of Aquatic Science Consultant Co., Ltd.) for her much help and encouragement and Professor Kimio Fukami (Faculty of Agriculture, Kochi University) for teaching the method of counting microbes. I thank Dr. S. Lan. Smith (Frontier Research System for Global Change) for correction of my paper and his valuable comments and Dr. Masato Hayashi, and Mr. Masahito Taki for their suggestions.

I am indebted to the staffs of Y. Suzuki laboratory, Department of Biology and Geoscience, Shizuoka University for accomplishment of this study. Especially, the members of research team of Suruga Bay, Mr. Tatsuya Iwata, Mr. Yuta Natori, Mr. Mamoru Hino and Miss Aya Haneda and Mr. Yusuke Tsuji, they gave me many advises for this study whenever I encountered difficulties, and supported me in research and

analysis. Very thanks Mr. Takahiro Hagawa for his help in finishing this thesis.

I thank Mr. Yasumasa Igarashi, Mr. Yoshitsugu Hagiwara, Mr. Takayuki Hanai, and the officers and crew of R. V. *Suruga-Maru,* and the other staff of Shizuoka Prefectural Fisheries Experiment Station for their help and support during sampling.

This work was funded by the Japan Ministry of Education, Culture, Sports, Science and Technology (Grant-in-Aid for Scientific Research 12793001).

Finally, I sincerely thank to my parents and sister for their support and encouragement.

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