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THE ANALYSIS OF ALGAL PIGMENTS AND THEIR DEGRADATION PRODUCTS USING HPLC, WITH DATA FROM SUSPENDED AND SINKING PARTICULATE MATTER IN PRYDZ BAY, ANTARCTICA

IL NOH

Department of Ocean Engineering, Korea Maritime University,

Pusan 606-791, Korea

Photosynthetic pigments and their degradation products in suspended and sinking particles collected from the Southern Ocean surface waters were measured using High Performance Liquid Chromatography (HPLC). The short-term variations in flux rates of chlorophylls and carotenoid pigments as well as their degradation products were compared at several locations in Prydz Bay, Antarctica, during austral summer 1987-88. In Prydz Bay, chlorophyll a accounted for approximately half of the pigments measured. A series of five phaeophorbide a derivatives, which are probably produced by zooplankton grazing, were the dominant degradation products in porphyrins. Among the carotenoid pigments, fucoxanthin dominated in both water column and sediment trap samples.

The flux rate of chlorophyll a at Outer Prydz Bay sites was generally highest (20 μg m^{-2} day^{-1}) at 50 m, and approximately double the flux rates at deeper horizons, however, at Inner Bay sites, the mean flux rate of chlorophyll a at 200 m was four times higher than that at the 50 m. Such anomalously high fluxes at 200 m imply that grazers were locally abundant between 100 m and 200 m at these sites closest to land, and this hypothesis is supported by visual evidence of lots of fecal pellets in the 200 m trap. Turnover rates for algal pigments in Prydz Bay, computed as standing stocks divided by measured flux, were negligible (generally >500 days). Thus, suspended particulate material in Prydz Bay was not recycled rapidly.

INTRODUCTION

Despite intense interest among scientists from a variety of disciplines in the processes

that drive the production, distribution and transport of particulate organic matter in the oceans, we still have but limited quantitative data on how much and what kind of biogenic particulate organic matter escapes from the surface waters of the Southern Ocean.

It is now generally agreed that the dominant mechanism for the vertical transport of organic matter into the deep sea is the relatively rapid settling of large particles (McCave, 1975), which recent studies have shown is dominated by "marine snow" and other uncompacted aggregates, as well as by compact fecal pellets and fecal strings. Such particles are ubiquitous in the oceans (Urrere and Knauer, 1981) and they are involved in many chemical and biological processes (Knauer et al., 1982; Karl et al., 1984). In general, the amount of organic material escaping from the euphotic zone increases as a function of primary production (Eppley and Peterson, 1979), while particulate organic carbon (POC) residence times decrease (Eppley et al., 1983). Recently, a number of sediment trap studies have confirmed that a strong predictive relationship between primary production rates and the particle flux out of the euphotic zone exists for areas that are widely separated geographically (Deuser et al., 1981; Honjo, 1982). Consequently, there is a continuing need for accurate, direct measurements of the flux of particulate organic matter out of the euphotic zone, to see whether this has global predictive value, as we seek to more fully understand upper ocean biological processes.

The present research focused on the measurement of photosynthetic pigments and their degradation products in suspended and sinking particles collected from Southern Ocean surface waters during austral summer 1987-1988. Participation in Ocean Drilling Program (ODP) Leg 119 allowed me to investigate short-term (day-to-day) variations in particle flux, and to see how these compared in different locations of the Indian Ocean sector of the Antarctic Ocean during the course of the same austral summer.

The Southern Ocean is characterized by high nutrient concentrations, marked seasonal variations in irradiance, low water temperatures, and comparatively little near-surface density stratification, which facilitates frequent mixing (Tilzer et al., 1986). Phytoplankton biomass and productivity in Antarctic waters are highly variable (Holm-Hansen et al., 1977). Previous studies have shown that localized physical processes were the important factors in

phytoplankton biomass accumulations in Southern Oceans (1984; Marra and Boardman, 1984; Smith and Nelson, 1985). However, the specific factors controlling the distribution of Antarctic phytoplankton on broader spatial and temporal scales have not been fully resolved (Hayes et al., 1984).

Although it is well recognized that : 1) there is a positive functional relationship between primary production and the downward flux of particulate organic matter and 2) the degree of this relationship depends strongly on trophic interactions that take place in the euphotic zone (Eppley and Peterson, 1979), the amount of production that is recycled versus exported from surface waters of the Southern Ocean is still incompletely understood. In particular, detailed knowledge regarding the flux rates of photosynthetic pigments from the near-surface mixed layer and the degree to which individual compounds are remineralized as a function of depth is an area of active research. Because we now suspect that large particle production plays a central role in water column biogeochemistry, upper ocean sediment trap studies can serve to allow clearer insights into the time scales over which new production and sinking are coupled in Southern Ocean. Moreover, since such research integrates geochemical processes with biological processes, it represents a useful first step in unraveling the complex interplay of oceanographic factors which influence particulate transport and sedimentation in the Southern Ocean.

MATERIALS AND METHODS

Field Collections

Suspended and sinking particles were collected in January-February 1988 during ODP Leg 119 to the Indian Ocean sector of the Antarctic Ocean (Fig. 1). My field work was carried out at four sampling sites in Prydz Bay. Two of these sites were located in the Outer Bay, and two in the Inner Bay. At the four locations, a total of ten deployments of a sediment trap array were made.

Description of Sediment Traps

Sinking particulate matter was collected with conical sediment traps (Fig. 2) that were designed and fabricated by Dr. R. B. Dunbar of Rice University (Dunbar, 1984). These traps were deployed on a drifting array which had three sediment traps suspended on braided nylon mooring line below a primary flotation sphere. To this sphere, a tracking buoy was tethered, which was outfitted with radio beacon, flashing strobe, radar reflector and flag. The radio beacon (Novatech, Model RF 700B), which broadcast at a VHF frequency of 156 MHz, could be tracked at least 6-7 miles away from the ship on channel 68 of a commercial RDF unit. After 20-37 hours, as weather allowed and/or depending on the drift rate of the arrays and the tending duties of the ice escort vessel, arrays were recovered and redeployed.

Made of gel-coated fiberglass, Dunbar traps weigh only about 8 kilograms. Valved holes in the sides of the cone allow most of the water overlying the collection chamber to be drained off prior to hauling each trap on board, and with a simple manual block and tackle rig one can get a multiple trap array back aboard easily.

Dunbar traps have a collecting cross section of 1600 cm^2. The baffle material used in the traps is an impregnated nylon honeycomb mesh with cells 1 cm wide by 4 cm deep. Laboratory flume studies indicate that a baffle with these dimensions prevents the penetration of turbulent eddies into the trapping chamber (Dymond et al., 1981). My experience on Leg 119 confirmed this, for material in the cod-end chamber was not visibly resuspended back into the cone, even when the trap was surging near surface during recoveries in seas of 1-2 meters.

Collection Depths and Sample Processing

The shallow trap collected sinking material at 50 m, close to the base of the mixed layer; the two additional traps collected from the upper pycnocline, at 100 m and at 200 m.

Based on collections made during Leg 113 in the Weddell Sea, it was anticipated that drifting traps in Prydz Bay would intercept between 0.1 and 1 gm m^{-2} day^{-1}. Accordingly, it was planned that enough material would be trapped in 24 hours so that each collection could

be split into fourths (or eighths) to give an archive aliquot, as well as 3 or more working aliquots for analysis of plant pigments and other substances. The archive aliquot was preserved in 4 % buffered formaldehyde for analysis of particle morphology and for phytoplankton enumerization and taxonomy. The remaining aliquots were used for the analysis of the following biochemical constituents such as plant pigments, biogenic silica, organic carbon, organic nitrogen, amino acids, $d^{13}C$ and $d^{15}N$.

Analysis of Plant pigments

For HPLC pigment analysis, filters frozen at sea were transported frozen on "blue ice" in an insulated chest. The samples were processed 2-6 weeks after the cruise, at Texas A & M University, as follows;

The filters were individually ground (glass/glass homogenizer) in 2 ml of 90 % acetone, allowed to extract for 48 hours, and centrifuged to remove suspended particles. In order to separate the dephytolated pigments, ion-pairing solution was added to the sample prior to injection into the HPLC system (Mantoura and Llewellyn, 1983).

Following the methods of Bidigare et al. (1985), algal pigments were separated with an HPLC system consisting of two Varian Model 2510 isocratic pumps, Model 2584 static mixer and a sample injector (Rheodyne Model 7125, 500 μl sample loop). A reverse-phase Microsorb C_{18} column (10 cm bed L x 4.6 mm ID, 3 μm particle size, Rainin Co.) was used for the pigment analysis, fitted with a guard column (1.5 cm bed L x 4.6 mm ID, 3 μm particle size, Rainin Co.).

A gradient solvent system (solvent A of 80:15:5 of methanol:distilled water:IP solution; solvent B of 100 % methanol) was employed for the elution of algal pigments. Solvent delivery was programmed at 100 % solvent A for the initial condition, then a linear gradient to 100 % solvent B at 2 min, followed by an isocratic hold (100 % B) until phaeophytin a peak was eluted (36.5 min). The flow rate was held constant at 1.2 ml/min. The peaks of chlorophylls and their degradation products were quantified using a fluorescence detector (Waters Associates, Model 420), by exciting at 434 nm and measuring the emission at above 600 nm. Carotenoid peaks were quantified using an absorption detector (Varian, Model

2550 Variable 1 Detector) at 436 nm. The HPLC was calibrated according to the procedures outlined by Bidigare (1989) and American Public Health Association (1989).

Chlorophyll a and chlorophyll b standards (Sigma Chemical Co.) were prepared in 90 % acetone and calibrated spectrophotometrically (Jeffrey and Humphrey, 1975). Phaeophytin a and phaeophytin b standards were prepared by the acidification of chlorophylls a and b with 1 N HCl, and concentrations were corrected for Mg^{++} loss (Strickland and Parsons, 1972). A chlorophyllide a standard was prepared from a dense culture of *Skeletonema costatum* that had reached stationary phase. This was extracted for 30 min in 50 % acetone, and then purified by Thin Layer Chromatography (TLC) (Barrett and Jeffrey, 1971; Jeffrey, 1981) and then calibrated spectrophotometrically using serial dilution. A phaeophorbide a standard was prepared by the acidification of chlorophyllide a, purified by TLC, and then calibrated spectrophotometrically. Chlorophyll c was extracted from *Sargassum* weed from the Gulf of Mexico, purified by TLC, and calibrated spectrophotometrically in 90 % acetone. Fucoxanthin, diadinoxanthin and diatoxanthin were extracted from *Skeletonema costatum* batch cultures by TLC, and standards prepared by calibrating spectrophotometrically in 100 % ethanol. Peridinin was extracted from *Gymnodinium* culture, purified by TLC, and then calibrated spectrophotometrically in 100 % ethanol.

For identification purposes, 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin were extracted from subtropical coccolithophorids and silicoflagellates, respectively, purified by TLC, and then injected into the HPLC system to allow their retention times (R_t) to be compared with that of fucoxanthin. Zeaxanthin was extracted from *Synechococcus* spp., purified by TLC, and calibrated spectrophotometrically in 100 % ethanol. b-carotene standard was purchased from Sigma Chemical Co., and calibrated spectrophotometrically in 100 % ethanol.

The following formula was used to calculate the individual pigment concentrations:

$$C_i = A_S \times (1/R) \times (1/IV) \times (EV) \times (1/SV)$$

where,

C_i = individual pigment concentration (ng per liter)

A_S = area of individual pigment peaks computed by Varian 4270 integrator

R = standard response factor (peak area divided by ng pigment per 0.5 ml standard)

IV = injection volume (0.5 ml)

EV = extraction volume (in milliliters)

SV = sample volume (in liters)

RESULTS

Water Column Structure in Prydz Bay

Distributions of salinity (Practical Salinity Units: PSU) and temperature (^{o}C) measured in Prydz Bay are shown in Figure 3. Based on T/S curve similarities between Sites 739 and 742, I have grouped these as Outer Prydz Bay. Similarly, I have grouped Sites 740 and 741 as Inner Prydz Bay.

Note that temperature in the upper 200 m at both locations generally varied by only 3 ^{o}C (+1 ^{o}C to -2 ^{o}C) and salinity by only 1 PSU (33.5 to 34.5 PSU). However, because temperatures in the upper 50 m of the Inner Bay ranged from 0 ^{o}C to +1.5 ^{o}C, the near-surface water there was relatively warmer than that at Outer Bay sites. In addition, note that salinity in the Inner Bay generally ranged between 34.0 to 34.5 PSU, with little variation down to 200 m. Thus, Inner Bay sites were relatively saltier throughout the upper 200 m than were Outer Bay sites, at which salinity in the upper 50 m reached as low as 33.7 PSU. These facts indicate that the sea ice had melted more recently at Outer Bay sites, which agrees with time-series satellite imagery of the ice cover in Prydz Bay (see Fig. 2 in Biggs et al., 1989). Thus, Inner Bay sites, which were ice-free longer than Outer Bay sites, had more time for upper waters to warm.

Pigment Composition of Suspended Particulate Matter

This section summarizes some general trends that can best be seen when sampling sites are grouped into Inner Prydz Bay (740, 741) versus Outer Prydz Bay (739, 742).

While the vertical distribution of chlorophylls a and c showed basically the same pattern at Inner and Outer Prydz Bay sites, the marked difference in the average amount of chlorophyll a and c is readily seen in Fig 4A and 4B. Generally Inner Prydz Bay sites had about 3 times higher chlorophyll a concentration, and about 5 times higher chlorophyll c than Outer Bay sites. The vertical distribution patterns for degradation products of chlorophyll a at Inner and Outer Bay sites were basically similar as well, but again the Inner Bay sites averaged 3.7, 3.5 and 2.2 times higher in average concentration of phaeophorbide a, chlorophyllide a and phaeophytin a, respectively

The distribution of fucoxanthin (Fig. 5A) in the Inner versus Outer Bay sites was quite similar to that of chlorophylls a and c. The concentration of fucoxanthin at Inner Bay locations was 4-5 times higher than that at Outer Bay locations, and the concentration of peridinin in the Inner Bay averaged 2.4 times higher than that in the Outer Bay. Note, however, that while peridinin in the Outer Bay usually had a subsurface maximum, with highest concentrations at the depths 33 m and 76 m (Fig. 5B), in the Inner Bay peridinin showed a bimodal pattern, with a local minimum in concentration at 33 m at 5 of the 6 Inner Bay cast locations.

The distribution of diadinoxanthin in Outer versus Inner Bay (Fig. 5C) showed the same pattern as chlorophyll a in the Inner versus Outer Bay. Highest concentrations were generally found at 10 m, 25 m, and 33 m. Note that the diadinoxanthin concentration in the Inner Bay averaged 4.6 times higher than that in the Outer Bay.

In Inner Prydz Bay, the distribution pattern of diatoxanthin tracked that of diadinoxanthin. In contrast, although the distribution of diatoxanthin in the Outer Bay usually showed a subsurface maximum at 33 m, at 76 m and 100 m depths, there was generally higher diatoxanthin than at 0 m, 10 m and 25 m depths (Fig. 5D). In general, the concentration of diatoxanthin at Inner Bay sites averaged 1.5 times that at Outer Bay sites.

At both Inner and Outer Bay sites, concentration of zeaxanthin/lutein below 25 m was higher than that in the shallower depths, and Inner Bay sites averaged 4.2 times more zeaxanthin/lutein than Outer Bay sites.

Pigment Composition of Sinking Particulate Matter Collections by Floating Sediment Traps

Six sediment trap deployments were performed in the Outer Prydz Bay Sites 739 and 742 on 19-22 Jan and 1-2 Feb 88, respectively, and four sediment trap deployments were performed in the Inner Prydz Bay Sites 740 and 741 on 25-27 Jan 88.

Because of the abundance of fecal pellets in the 200 m trap at Site 740, the mean flux pattern of chlorophylls (Fig. 6) in the Inner Bay was highest at 200 m for almost all the chlorophyll species. The mean flux of chlorophylls a and c at 200 m was at least 2-3 times higher than at 50 m or 100 m, and for the phaeopigments, the ratios of deepest layer flux to the shallowest exceeded 3:1. In contrast, the flux at 50 m for chlorophylls was generally similar or slightly higher than that at 100 m.

The mean carotenoid fluxes (Fig. 7) in the Inner Bay were also greatest at 200 m (and usually over 3 times higher than the fluxes at 50 m and 100 m). In contrast, in the Outer Bay the chlorophyll fluxes were highest at the shallowest depth (50 m), and the fluxes decreased with increasing depth. The carotenoid fluxes in Outer Bay showed the same tendency.

DISCUSSION

Phytoplankton Community Structure of the Water Column

Throughout the Prydz Bay bottle cast samples, chlorophyll a, chlorophyll c, and fucoxanthin were the dominant pigment species. This indicates that the phytoplankton community of the study area was dominated by diatoms, a prediction confirmed by Kang (1989), who by counting phytoplankton numbers in subsamples fixed by Lugols from the same bottle casts that were analyzed by HPLC, found direct evidence of a diatom bloom that was dominated by *Nitzschia cylindrus* and *N. closterium*. Moreover, because the carotenoid 19'-hexanoyloxyfucoxanthin was the second most abundant carotenoid, it indicates that prymnesiophytes (e.g. *Phaeocystis* spp.) were also very abundant in the study area. In some

recent years *Phaeocystis* has been especially abundant in the Weddell Sea (Garrison and Buck, 1985) and in the Ross Sea (Palmisano et al., 1986). However, even after they have been fixed in Lugols, Antarctic prymnesiophytes seldom remain intact enough to allow quantitative enumeration.

The presence of peridinin throughout the study area indicates that the dinoflagellates, as well, contributed to the phytoplankton bloom.

Algal Pigment Distribution of the Water Column

Chlorophylls

Temperature-salinity-density structure of the water column strongly influenced the vertical distributions of algal pigments in the study area. Specifically, when the mixed layer depth was shallow, it provided favorable conditions for the ambient phytoplankters to bloom.

At Outer Bay Site 739, a deep chlorophyll maximum (DCM) was located between 25-75 m. In CTD casts #4-6 here, where the average mixed layer depth was only 15 m, the DCM was sharply defined. However, in CTD cast #7, where wind-mixing and/or horizontal advection caused the mixed layer to extend down to 40 m, no distinct DCM was defined and chlorophyll a was distributed almost evenly from surface down to 100 m.

At the other Outer Bay Site 742, the MLD extended to 35 m, on average. Here, there was no sharply defined DCM; instead pigment concentrations generally were rather uniformly distributed from the surface down to 50 m. This may reflect recent mixing of the upper water by wind and/or horizontal advection (i.e. between 22 Jan and 1 Feb) and consequent dilution of the average algal pigment concentrations.

At Inner Bay sites 740 and 741, where the mixed layer depth was only 15 m on the average, a DCM was well defined at 25-35 m. Lesser wind-mixing and warmer near-surface temperatures here presumably provided enough water column stability and to allow phytoplankton to reach higher concentrations.

By comparing chlorophyll a concentrations in Prydz Bay with those measured during ODP Leg 113 (Biggs et al., 1988), it can be seen that surface chlorophyll a concentrations throughout much of the Weddell Sea in austral summer 1987 were less than 0.05 $\mu g\ liter^{-1}$.

That is, they were generally 1-2 orders of magnitude lower than that present in Prydz Bay in austral summer 1988. However, in austral summer 1987, the surface chlorophyll concentrations averaged double the regional mean at the two sites which were nearest the continental land mass. The investigators speculated that such inshore increase reflected neritic influence, and/or the fact that both of the sites where chlorophyll was highest had been more recently covered by pack ice than had the other sampling regions. The same factors should, of course, influence algal pigment concentrations within Prydz Bay. Because the surface chlorophyll in Prydz Bay was much higher in concentration at Outer as well as Inner Bay sites than that in the Weddell Sea (i.e. 0.2-0.5 μg liter^{-1} at Outer, and 1.5 μg liter^{-1} at Inner Bay sites), it is an indication that Prydz Bay is more productive than most of the adjacent deep water. It is also likely that surface chlorophyll concentrations in Prydz Bay increased as austral summer continued, after our sampling there was ended.

Hayes et al. (1984) have reported that the near surface chlorophyll a concentrations around the Antarctic Peninsula, in the Drake Passage, and in the Scotia Sea and Weddell Sea during austral summer 1978-79 averaged 0.8, 0.3, 1.2 and 0.7 μg liter^{-1}, respectively. The surface chlorophyll a concentrations of the inshore waters were consistently over 3 times higher than those in offshore waters measured from January to March. For example, in January, their inshore and offshore chlorophyll a concentrations averaged 2.5 and 0.8 μg liter^{-1}, respectively. Such differences are similar in magnitude to what I am reporting for Prydz Bay, although their distinction between the inshore and offshore (distinguished by 1000 meters water depth in the former report) doesn't apply within Prydz Bay, where Inner versus Outer regimes are distinguished by their geographical proximity to the continental land mass, and by different near-surface T/S conditions.

In their investigation of the distribution of algal pigments in relation to temperature and optical variability in the Southern Ocean in January-February 1984, Bidigare et al. (1986) correlated the highest chlorophyll a concentrations (>0.8 μg liter^{-1}) in the Weddell and Scotia Seas to local areas where thermal stratification was more pronounced. Other previous Antarctic studies have also shown that increased water column stability helps maintain phytoplankton within the euphotic zone, thus promoting growth and subsequent biomass accumulation (El-Sayed and Taguchi, 1981; Smith and Nelson, 1985).

In fact, Smith and Nelson (1985) reported that extremely high concentrations of chlorophyll a (> 6 μg liter^{-1}) were measured in the vicinity of a receding ice edge off the coast of Victoria Land in the Ross Sea in January and February 1983. These investigators concluded that enhanced vertical stability of the water column, produced by low salinity melt water, created favorable conditions for biomass accumulation. The investigators also suspected that the epontic algae (those associated with the pack ice) that were released from melting ice may have inoculated the bloom.

Chlorophyll c is the second most abundant of the chlorophyll pigments in diatoms, dinoflagellates and chrysophytes (Jeffrey, 1980), and chlorophyll c generally co-varies with chlorophyll a in its vertical distributional profile in marine environments (Bidigare et al., 1986). Chlorophyll c:a ratios (mol:mol) for healthy diatoms in culture generally fall within the range of 0.2-0.4 (Gallagher et al., 1984). Similarly, chlorophyll c:a ratios (mol:mol) investigated by Bidigare et al. (1986) in the Weddell/Scotia Sea in austral summer 1984 averaged 0.23 ± 0.08.

Table 1 summarizes the ratio of mean chlorophyll c:a and mean chlorophyllide a to chlorophyll a (mol:mol) versus depth for suspended material at each site in the Prydz Bay study area. As is seen in this table, the ratio of chlorophyll c:a generally increased from the surface to the DCM, with the ratio at the DCM depth very similar to that (0.23 ± 0.08) reported by Bidigare et al. (1986) from previous HPLC survey work in the Weddell/Scotia Sea. In general, at the sites where a DCM was conspicuous and located between 25-76 m, the ratio of chlorophyll c:a exhibited maximum values in the DCMs.

Note that the ratio of mean chlorophyllide a to chlorophyll a in near-surface water of both the Outer and Inner Bay generally ranged from 0.04 to 0.13 μg liter^{-1} (mol:mol) except at Site 742, where chlorophyllide a was not detected below 25 m. At 25 m at Site 742, the ratio of chlorophyllide to chlorophyll a (0.61) was markedly higher than at other depths and sites. This anomalous ratio may reflect either a local accumulation of unhealthy cells around 25 m, or it may be an experimental artifact of filtration. For example, the chlorophyllase activity is enhanced when phytoplankton cell membranes are damaged (Jeffrey, 1974).

The physiological state of a natural phytoplankton assemblage may also be assessed by ratioing the concentrations of phaeophorbide a to chlorophyll a (Bidigare et al., 1986). Gowen

et al. (1983) measured chlorophyll a and its degradation products by thin-layer chromatography in two Scottish sea-lochs to monitor the progress of a spring bloom. During the initial stages of the bloom in February-March, chlorophyll a accounted for 70-90 % of the total pigments. As the bloom progressed in April, the proportion of chlorophyllide a increased to 40-50 %, indicating the onset of senescence. However, after this, by May, phaeophorbide a accounted for 40-60 % of the total pigments. Interestingly, phaeophytin a concentration remained low throughout that time series, and it never exceeded 4 % of the total pigment concentration.

In Prydz Bay, the vertical distribution of phaeophorbide a co-varied with that of chlorophyll a at most of the sampling sites in both the Inner and Outer Bay. This supports the observation of Bidigare et al. (1986) that chlorophyll a and phaeophorbide a concentrations in the upper 200 m in the Weddell/Scotia Sea displayed a positive linear relationship, and it indicates that a tight coupling probably exists between phytoplankton production and zooplankton grazing. Table 2 presents the ratio of mean phaeophorbide a to chlorophyll a (mol:mol) in suspended matter at both Outer and Inner Prydz Bay sites. Although the ten-fold lower abundance of phaeophorbide a relative to chlorophyll a was the major pattern in my data, it can be seen that the ratio of phaeophorbide a to chlorophyll a generally tended to increase with depth. This agrees well with Yentsch's pioneering observation (1965) that the ratio of phaeopigments to chlorophyll a increased with decreasing light intensity. However, the ratios of phaeophorbide a to chlorophyll a at the surface in the Inner Bay were ~2-fold higher than those immediately below (10 to 76 m). This suggests that the zooplankton grazing pressure may have been locally higher in this surface waters in the Inner Bay, as well as near the 200 m horizon. Another notable result is that at 25 m at Site 742, where the ratio of chlorophyllide a to chlorophyll a was unexpectedly high, the ratio of phaeophorbide a to chlorophyll a was locally high as well.

Phaeophytin a was rarely detected in suspended material in Prydz Bay, and it was by far the least common chlorophyll a degradation product throughout the study area. Similarly, Bidigare et al. (1986) detected phaeophytin pigments in only ~1% of a total of 533 samples they analyzed in the Weddell/Scotia Sea.

Chlorophyll b, a chemotaxonomic marker of green algae which allows enhanced light absorption in the blue region of the visible light spectrum, was also below detection limit in most of the Prydz Bay samples. This indicates that green algae were not an important phytoplankton component in the study area. The literature indicates that the chlorophyll b:a ratio of marine green algae is highly variable, with a reported range from 0.3 to 1.0 (Lorenzen, 1981). Where chlorophyll b was detected (CTD casts #4 and 5 in Outer Bay as well as over the Kerguelen Plateau in CTD casts #16 and 17), its concentrations ranged from 0.01-0.08 μg liter^{-1}. This implies that chlorophyll b distribution might be an indicator of oceanic rather than neritic conditions in the Southern Ocean.

Carotenoids

The fact that fucoxanthin was the most abundant of the carotenoids in suspended particulate matter throughout the study area is independent evidence, as stated previously, that the Prydz Bay sites were dominated by diatoms. This is supported by the fact that the accessory pigments present in diatoms (chlorophyll c, fucoxanthin and diadinoxanthin) were co-abundant in most of the samples. In general, as Table 2 shows, fucoxanthin co-varied with chlorophyll a in vertical distribution pattern. Note that while the ratio of fucoxanthin to chlorophyll a was highly variable with depth, the mean ratio in near-surface water in the Inner Bay (1.1, mol:mol) tended to be higher than that for the Outer Bay (0.7, mol:mol). The overall mean ratio of fucoxanthin to chlorophyll a in Prydz Bay was 0.9 (mol:mol). The higher fucoxanthin:chl a ratios may reflect a larger contribution by diatoms to the algal communities sampled.

Diadinoxanthin and diatoxanthin, two carotenoids also found in diatoms, were also present in most of the samples. As Stephens (1989) has reported, diatoxanthin shows a tight coupling with diadinoxanthin in vertical distribution [DT:DN xanthophyll cycle; Jeffrey, 1980]. In Prydz Bay, the concentration of diadinoxanthin was approximately twice the concentration of diatoxanthin at most depths in most samples. This ratio of diatoxanthin to diadinoxanthin agrees with that determined by Stephens (1989) (0.4 on average, expressed in mol:mol) in the open water phytoplankton collected at Anvers Island in the austral summer 1987.

Peridinin, which is a chemotaxonomic marker for the dinoflagellates, was generally more common at mid-depths (76-100 m) than at shallower depths in Prydz Bay, with the exception of CTD cast #4. This indicates that dinoflagellates in Prydz Bay generally were more abundant below the DCM. Even though peridinin concentrations were an order of magnitude lower than those of fucoxanthin in most of the samples, however, peridinin was present in almost every water column sample in Prydz Bay.

The carotenoid 19'-hexanoyloxyfucoxanthin, which is a chemotaxonomic marker of prymnesiophytes (e.g. *Phaeocystis*, as well as the subtropical coccolithophore *Emiliania huxleyi*), was generally rare above 25 m. Because it was the second most abundant carotenoid (after fucoxanthin) in the zone 25-75 m, if its co-elution with fucoxanthin was not too great, it indicates that the optimum niche for prymnesiophyte populations in Prydz Bay was subsurface, both coincident with and below the DCM. By contrast, 19'-butanoyloxyfucoxanthin was not detectable in most of the study area.

Zeaxanthin, which coeluted with lutein in our HPLC system, is a chemotaxonomic marker of cyanobacteria. Because zeaxanthin is thought to be a photoprotectant for cyanobacteria, its highest concentrations are usually found at or near the surface. However, while cyanobacteria are generally present in the near-surface water of many oceanic environments (Ondrusek, 1989), they have been reported to be less abundant in the surface waters of Southern Ocean (Letelier and Karl, 1989). In fact, Marchant et al. (1987) suggested that cold temperatures are the principal factor limiting cyanobacterial abundance in the Southern Ocean. In Prydz Bay, while the overall concentration of zeaxanthin/lutein was low, it generally exhibited a deeper water rather than a near-surface maximum. The most likely explanation for the deeper water presence and near-surface rarity of zeaxanthin/lutein, apart from the obvious conclusion that cyanobacteria were probably rare there, is that prochlorophytes, rather than cyanobacteria, were present. Prochlorophytes contain lutein as their accessory pigment, and while information about their distribution in the Southern Ocean is limited, these nanoplankton have been found in other oceans to be most abundant deeper rather than shallower in the photic zone.

In summary, Inner Bay sites had 3-5 times greater concentrations of suspended algal pigments than at Outer Bay sites. Locally greater water column stability imparted by the local

temperature-salinity-density structure was probably the main factor responsible for the bloom conditions within Inner Prydz Bay.

Algal Pigments in Material Sinking Out of Prydz Bay

Sediment trap collections reported by Dunbar (1984) from Bransfield Strait had mass fluxes 5-7 times higher than the highest flux at each site of the Prydz Bay areas (Table 3). Dunbar described that during the summer season of high productivity in Bransfield Strait, the dominant component of the vertical flux of sediment at nearly all depths was fecal pellet material. In contrast, Dunbar reported that fecal pellets were not a very common component of the vertical flux collected from different regions in the Ross Sea. Rather, low-density gelatinous aggregates of organic material and diatom tests were common in the Ross Sea collections, and mass fluxes there were at least 10-fold lower than in his Bransfield collections.

Interestingly, the fluxes at 50 m and 100 m were not markedly greater at Inner versus Outer Bay sites, even though the mean concentration of suspended algal pigments in Inner Prydz Bay was 3 times higher than that in the Outer Bay.

In general, at most of the Leg 119 sites, the particle flux was greater at 50 m than at 200 m. For instance, at Leg 119 Sites 739 and 742, the pigment fluxes at 100 m were 40-60 % of at 50 m, and the pigment fluxes at 200 m were 20-30 % of those at 50 m. This presumably reflects the higher primary production rate in the shallower depth strata, as well as the increasing importance of remineralization between 50-100 m, and between 100-200 m.

At Inner Bay Site 741 the flux pattern was similar, with flux greatest at 50 m, intermediate at 100 m, and lowest at 200 m. However, because of the abundance of fecal pellets at Site 740 on Leg 119, the mean fluxes at 200 m for Leg 119 averaged 6 fold greater than that at 50 m, and an order of magnitude higher. Such anomalously high fluxes at 200 m imply that grazers were locally abundant between 100 m and 200 m at these sites closest top land, and this hypothesis is supported by visual evidence of lots f fecal pellets in the 200 m trap.

CONCLUSION

The pigment flux out of the upper 200 m, relative to the integrated standing stock (integrated standing stock in $\mu g\ m^{-2}$ divided by the flux in $\mu g\ m^{-2}\ day^{-1}$), ranged from 0.1-1.5 % (average 0.3 %) at Outer Bay Sites and from 0.1-1.4 % (average <0.1 %) at Inner Bay Sites (see Table 3). These data do not support my null hypothesis that particulate material in Prydz Bay was recycled rapidly. On the contrary, phytoplankton standing stocks appeared to be very healthy, so that the amount of material settling out of the euphotic zone was also negligible, compared to that produced daily by photosynthesis.

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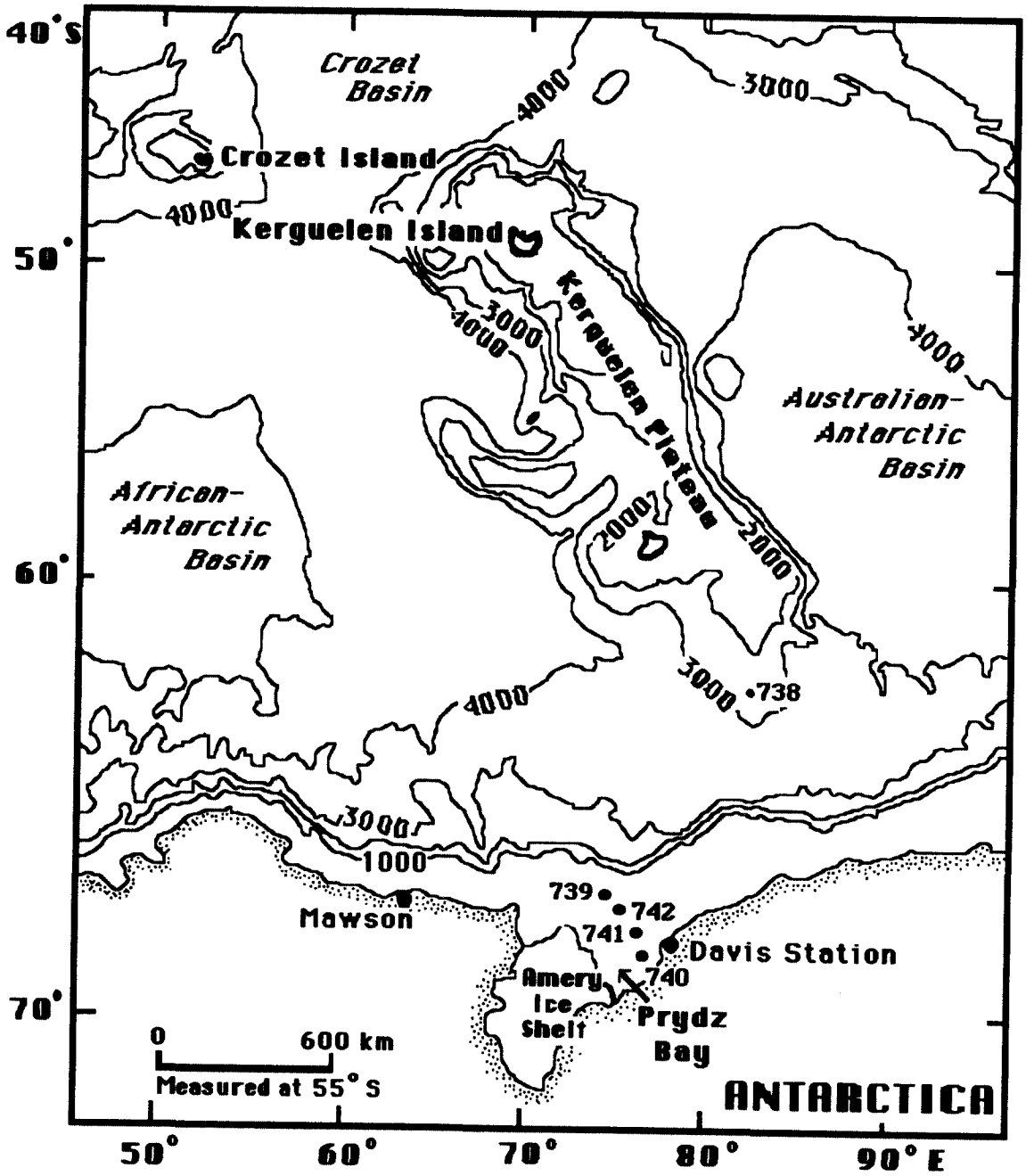

Fig. 1. Floating Sediment Traps (FSTs) were deployed in Outer Prydz Bay (Sites 739, 742) and Inner Prydz Bay (Sites 740, 741) during Ocean Drilling Program (ODP) Leg 119 in January-February 1988. FSTs were also deployed but could not be recovered south of the Kerguelen Plateau (Site 738).

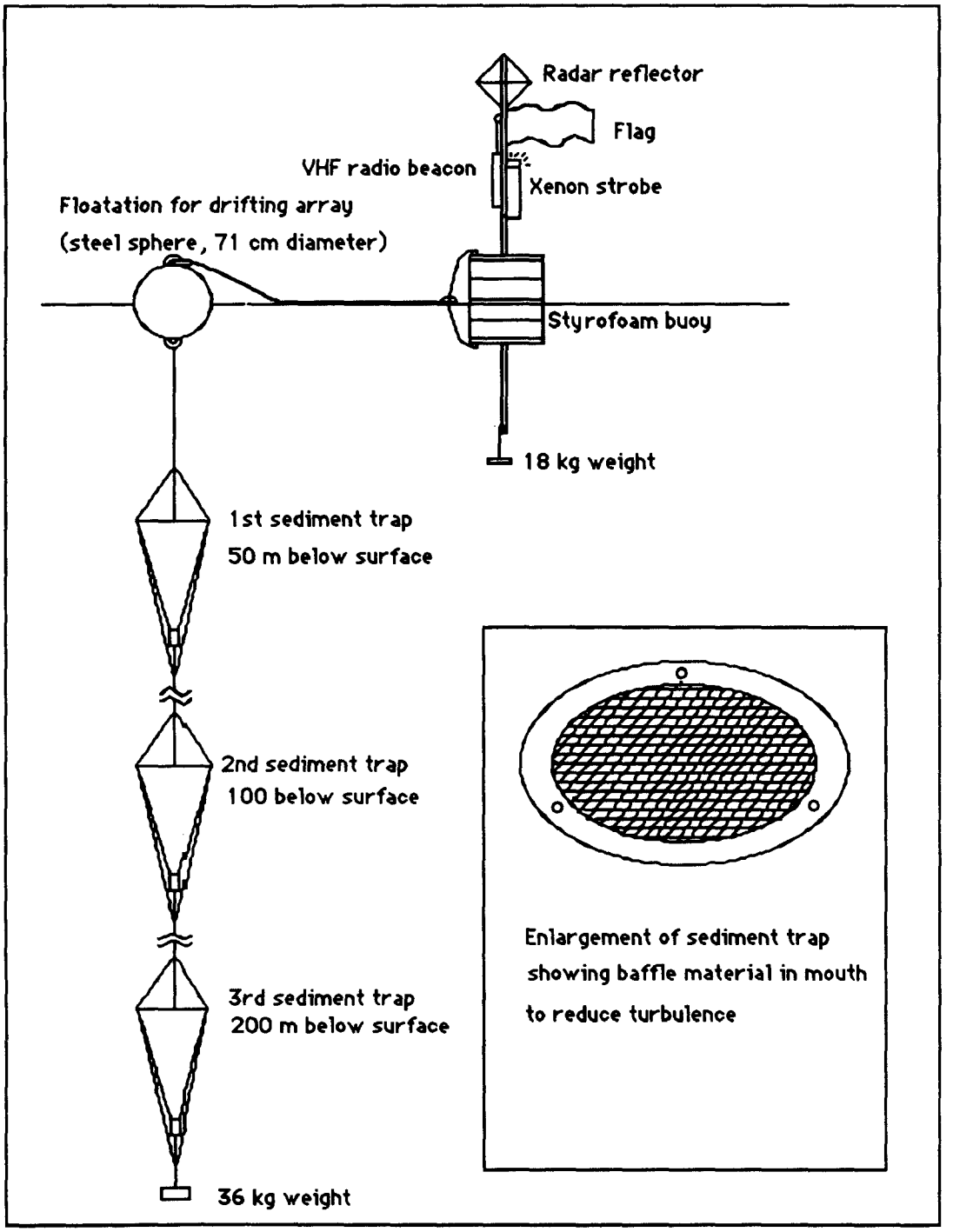

Fig. 2. Floating Sediment Trap drift array used for Prydz Bay collections (after Biggs et al., 1988).

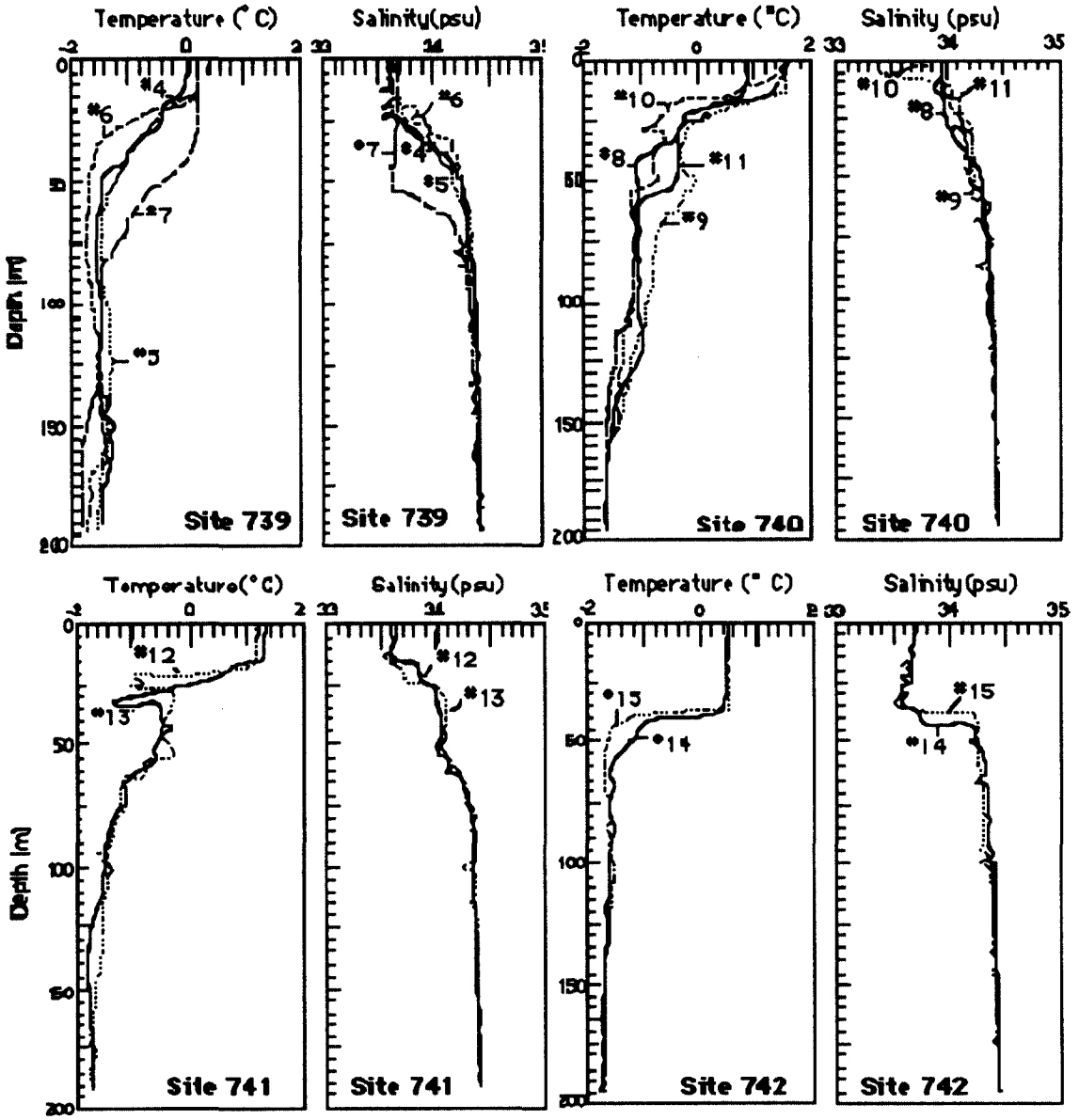

Fig. 3. Temperature and salinity structure of the upper 200 m of Outer and Inner Prydz Bay (from Biggs et al., 1988).

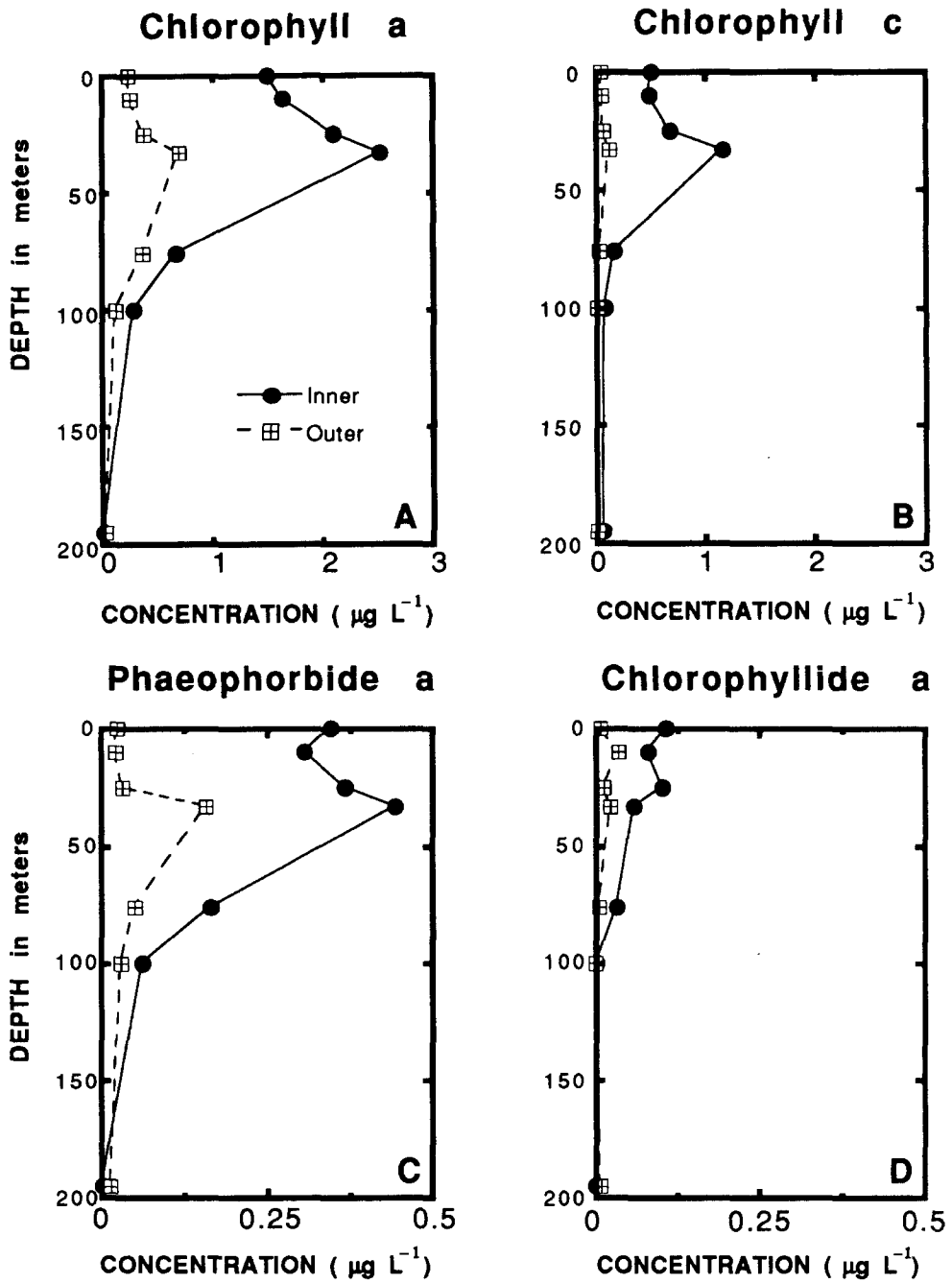

Fig. 4. A comparison of the average vertical distribution of chlorophylls at Inner versus Outer Prydz Bay sites.

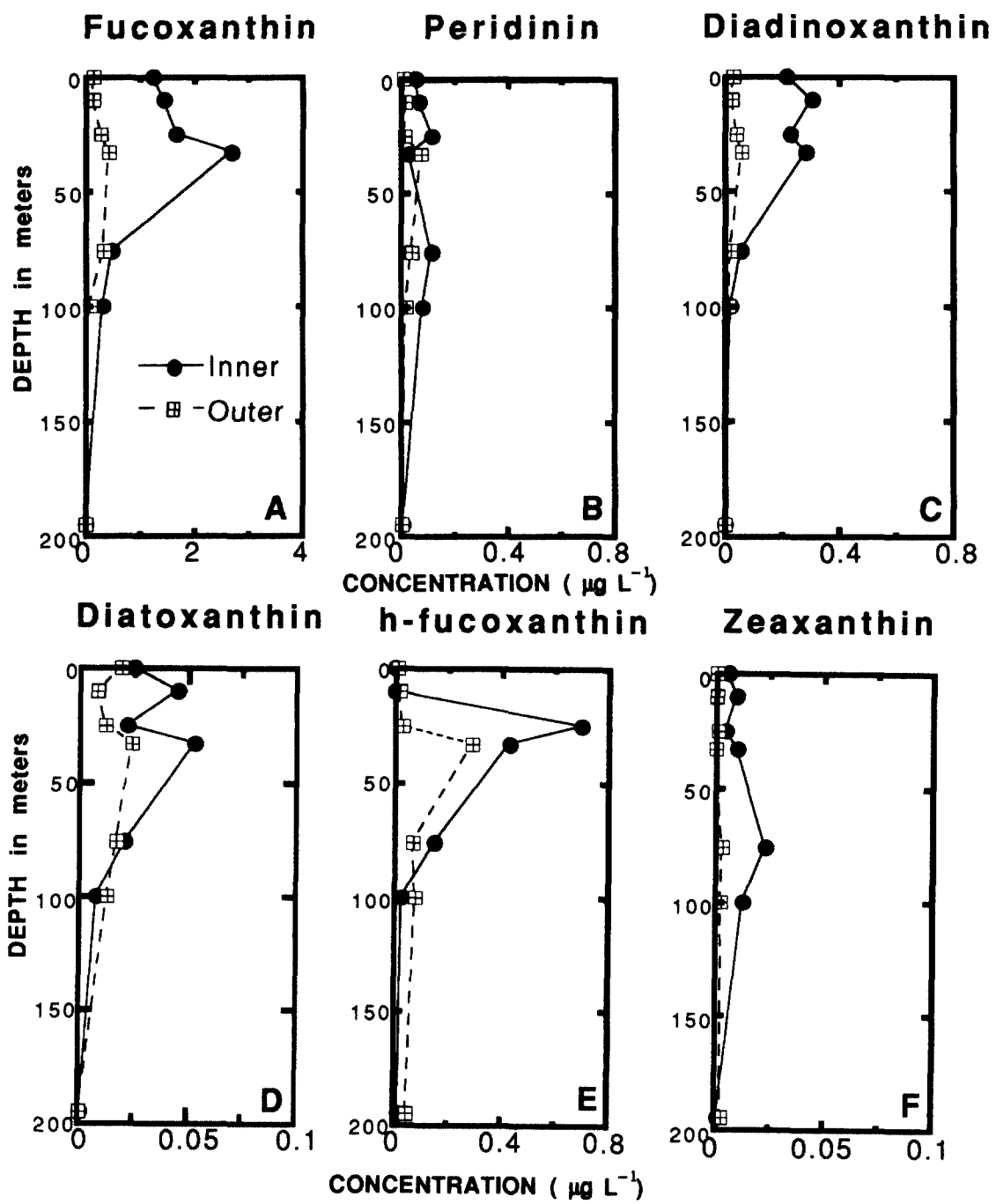

Fig. 5. A comparison of the average vertical distributions of carotenoids at Inner versus Outer Prydz Bay sites.

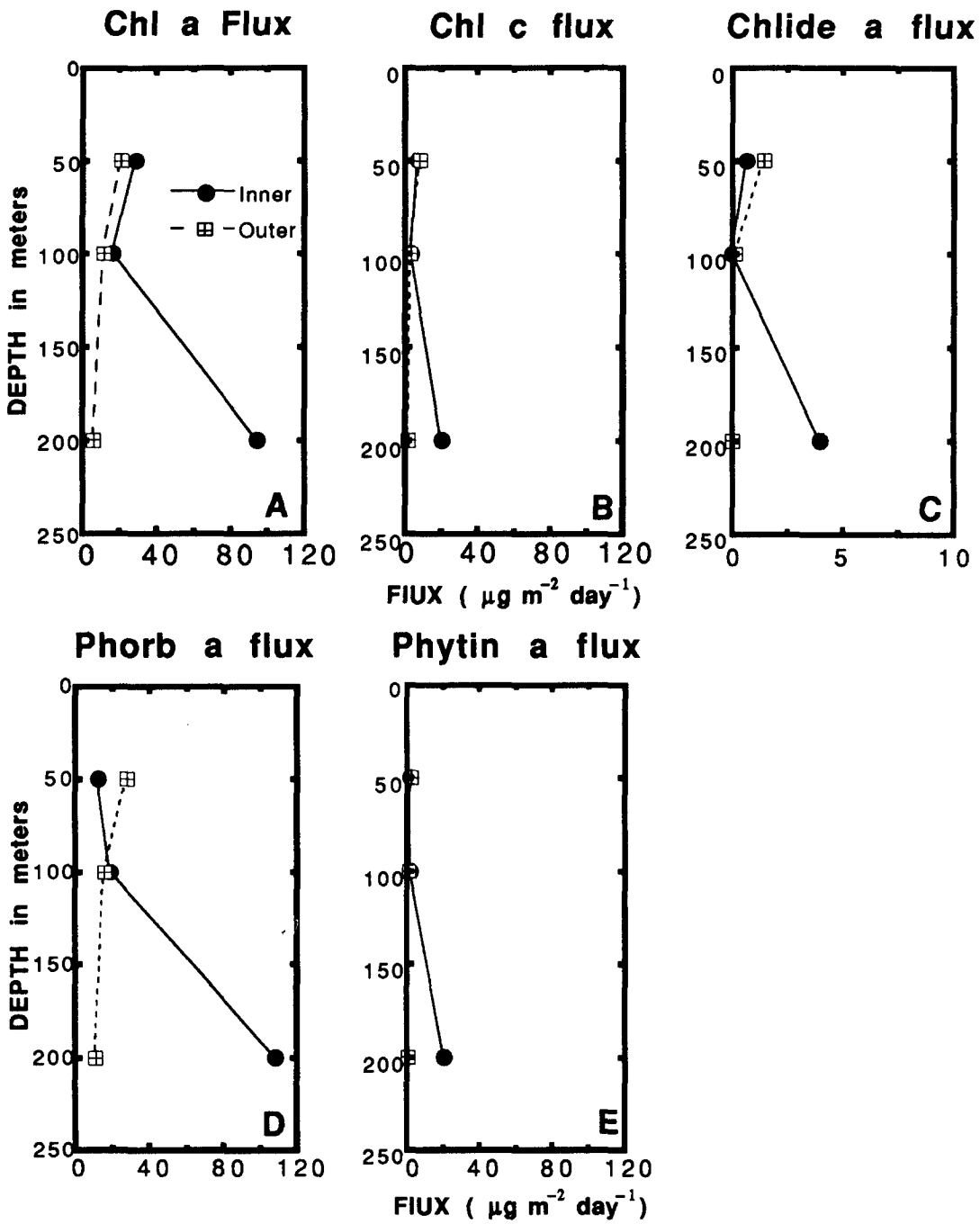

Fig. 6. Summary of mean fluxes of chlorophylls in Inner Bay versus Outer Bay Chlorophyll a degradation products are reported as chlorophyll a equivalent.

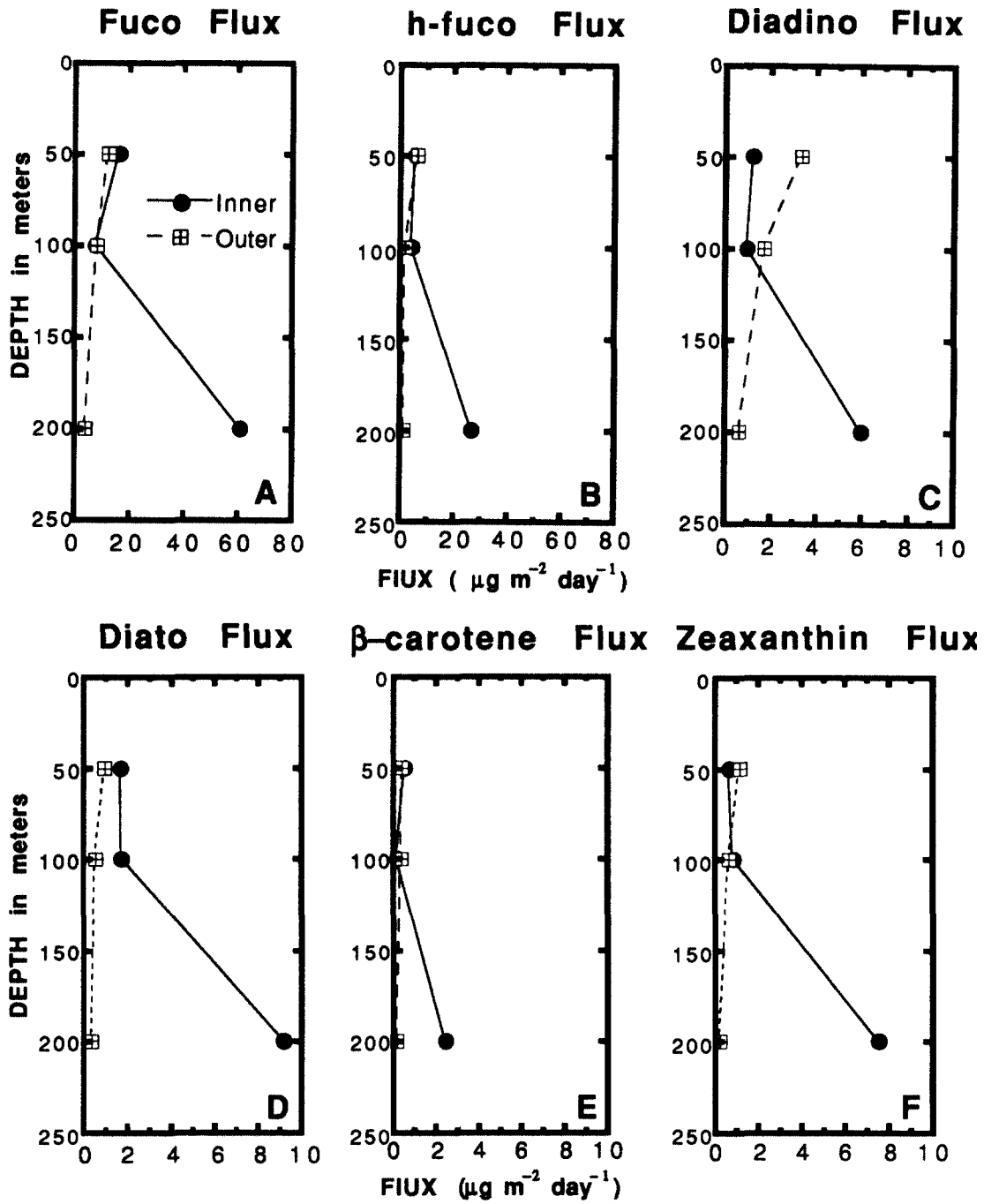

Fig. 7. Summary of mean fluxes of carotenoids in Inner Bay versus Outer Bay.

Table 1. Ratio of mean chlorophyll c:a (mol:mol) and mean chlorophyllide a to chlorophyll a (mol:mol) versus depth at each site in Prydz Bay.

Depth	Outer Site				Inner Site			
	739		742		740		741	
	c:a[a]	chlide:a[b]	c:a	chlide:a	c:a	chlide:a	c:a	chlide:a
0 m	0.12	0.04	0.71	0	0.57	0.10	0.40	0.13
10 m	0.23	0.06	NS*	NS	0.36	0.07	0.52	0.08
25 m	0.25	0.05	0.47	0.61	0.45	0.08	0.52	0.05
33 m	0.32	0.05	0.12	0	0.59	0.06	0.67	0.02
43 m	NS	NS	0	0	NS	NS	NS	NS
76 m	0.09	0	0.09	0	0.27	0.05	0.53	0.1
100 m	0.06	-	0	-	0.09	-	0.56	-
195 m	0.18	-	0	-	0	-	0	-

[a] c:a denotes the ratio of chlorophyll c to chlorophyll a.

[b] chlide:a denotes the ratio of chlorophyllide a to chlorophyll a.

* Not sampled

Table 2. Ratio of mean phaeophorbide a to chlorophyll a (mol:mol) and mean fucoxanthin to chlorophyll a (mol:mol) versus depth at each site in Prydz Bay.

Depth	Outer Site				Inner Site			
	739		742		740		741	
	ph:chl a[a]	fu:chl a[b]	ph:chl a	fu:chl a	ph:chl a	fu:chl a	ph:chl a	fu:chl a
0m	0.15	0.81	0.14	0.64	0.34	0.89	0.33	1.51
10m	0.09	0.82	NS*	NS	0.25	0.92	0.36	1.44
25m	0.13	0.76	0.30	0.48	0.29	0.99	0.22	1.22
33m	0.32	1.32	0.13	2.44	0.28	1.17	0.20	1.78
43m	NS	NS	0	2.91	NS	NS	NS	NS
76m	0.16	1.00	0.36	0.66	0.47	0.82	0.28	1.26
100m	0.21	0.90	0.40	0.19	0.75	1.09	0.47	2.94
195m	0.71	1.00	1.06	0.68	0.21	1.33	0	3.73

[a] ph:chl a denotes the ratio of phaeophorbide a to chlorophyll a.

b fu:chl a denotes the ratio of fucoxanthin to chlorophyll a.

* Not sampled

Table 3. Integrated Standing Stock of suspended pigments (SS*i*) in mg m^{-2} versus Sinking pigments (F) in μg m^{-2} day^{-1} in Prydz Bay in the austral summer 1988.

	0-50 m			0-100 m			0-200 m		
	SSi	F	%	SSi	F	%	SSi	F	%
Outer Bay									
chlide a	0.6	1.5	0.3	1.0	1.7	0.2	1.0	1.7	0.2
chl c	4.7	11.5	0.2	8.1	16.1	0.2	8.6	19.1	0.2
phorb a	2.8	24.8	0.9	5.7	39.6	0.7	6.8	49.4	0.7
chl b	0.1	ND*	0	0.3	ND	0	0.7	ND	0
chl a	27.8	26.4	0.1	52.8	42.1	<0.1	60.3	50.6	<0.1
phytin a	0.2	3	1.5	0.2	4.8	2.4	1.1	5.7	0.5
peri	2.3	5.3	0.2	4.9	7.5	0.2	5.6	9.4	0.2
b-fuco	0.2	1.4	0.7	0.4	1.7	0.4	0.5	1.8	0.4
fuco	17.1	15.9	0.1	35.4	26.8	<0.1	40.9	32.3	<0.1
h-fuco	4.3	8.3	0.2	9.3	10.8	0.1	12.2	12.8	0.1
diadino	2.6	4.7	0.2	4.4	7.0	0.2	5.1	8.0	0.2
diato	1.0	1.2	0.1	2.1	1.8	<0.1	2.9	2.3	<0.1
zea	0.1	1.5	1.5	0.2	2.2	1.1	0.6	2.5	0.1
β-carotene	0.1	0.6	0.6	0.2	1.2	0.6	0.2	1.5	0.8
Inner Bay									
chlide a	2.5	ND	0	3.8	ND	0	3.8	ND	0
chl c	44.9	4.4	<0.1	76.5	6.6	<0.1	84.1	8.7	<0.1
phorb a	10.8	5.8	0.1	18.4	13.7	<0.1	22.0	23.3	0.1
chl b	ND	ND	-	ND	ND	-	ND	ND	-
chl a	108.7	20.6	<0.1	177.1	29.8	<0.1	198.2	37.7	<0.1
phytin a	0.3	ND	0	0.3	ND	0	0.3	4.1	1.4
peri	3.0	1.3	<0.1	5.9	2.3	<0.1	10.4	3.2	<0.1
b-fuco	ND	ND	-	ND	ND	-	ND	ND	-
fuco	124.5	12.6	<0.1	208.4	19.3	<0.1	236.7	24.5	<0.1
h-fuco	ND	2.1	-	ND	3.8	-	ND	5.1	<0.1
diadino	16.1	0.6	<0.1	23.5	1.1	<0.1	24.3	1.5	<0.1
diato	2.6	0.8	<0.1	3.8	2.1	<0.1	4.1	2.9	<0.3
zea	0.7	ND	0	1.7	ND	0	2.5	0.2	0.1
β-carotene	1.2	0.4	<0.1	1.8	0.4	<0.1	1.8	0.4	0.1

* Not detectable