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ALGAL PIGMENTS AND THEIR DEGRADATION PRODUCTS IN SUSPENDED AND SINKING PARTICULATE MATERIAL IN THE GULF OF MEXICO

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Photosynthetic pigments and their degradation products in suspended and sinking particles collected from the Gulf of Mexico waters 1987-88, were measured using High Performance Liquid Chromatography (HPLC). The short term variations in flux rates of chlorophylls and carotenoids as well as their degradation products were compared at the mesoscale cyclonic and anticyclonic circulation features (cold core ring and warm core ring). Chlorophyll a was the predominant porphyrin of suspended particulate matter at both CCR and WCR. Among carotenoid pigments, 19' hexanoyloxyfucoxanthin, which is a biomarker of prymnesiophytes, was dominant pigment at both rings. Phaeophorbide a, which is produced through the grazing processes of grazers, was the predominant degraded pigment in sinking particles at the study area. Total pigment flux in CCR was an order of magnitude higher than that in WCR. Less than 1 % of the standing stock of the pigments measured sank out of the upper 200 m of the WCR on any given day. Thus, suspended particulate matter in Gulf of Mexico was not recycled rapidly.

INTRODUCTION

The Gulf of Mexico is a marginal sea which experiences relatively small seasonal changes in irradiance, and its near-surface water is generally warm and stratified for most of the year. Accordingly, it has long been classified as a nutrient and plankton poor, oligotrophic subtropical ocean (Bogdanov et al.; 1969). Within the last two decades, however, we have also seen that mesoscale anticyclonic circulation features (warm-core rings) are regularly shed by the Loop Current in this subtropical region, and that as these advect into the western Gulf of Mexico they often are found to have companion cyclonic circulations (cold-core rings) near their periphery (Lewis and Kirwan, 1985; Kelly et al., 1986 and 1987). It has also been reported

that the zone(s) of interaction between anticyclonic and cyclonic circulation features are regions which are species rich, with higher than average biological stocks (Wormuth, 1982; Biggs et al., 1984; Cummings, 1984).

Since 1987, TAMU-sponsored Training and Research cruises of R/V Gyre have been measuring plankton production and standing stocks in warm- and cold-core mesoscale circulations which occur over the northwest continental slope of the Gulf of Mexico. Biggs et al. (1988) documented the nutrient-poor nature of the warm-core rings, but they showed that nutrient-rich water lies quite close to the surface in cold-core features. They also speculated that the frequent occurrence of cyclonic circulation regions over the continental slope of the NW Gulf is probably responsible for literature reports that primary production there averages 2-5 fold higher than that of other oceanic regions of the Gulf of Mexico, rivaling that of the continental shelf (El-Sayed, 1972).

A better description of transformations from suspended into sinking materials in the upper water column is an important first step in understanding the role which warm- and cold-core rings play in the biogeochemical cycling of carbon and nitrogen in the Gulf of Mexico, I made a direct comparison of the concentration of suspended algal pigments in upper water column with that of the flux of sinking algal pigments in a warm- and a cold-core ring in the NW Gulf of Mexico. I tested the following null hypotheses (H_0):

1) there is no difference in the concentration of suspended algal pigments in the upper water column between a cold-core ring and a warm-core ring in the NW Gulf of Mexico;

2) there is no difference in the fluxes of sinking algal pigments in the upper water column between a cold-core ring and a warm-core ring in the NW Gulf of Mexico;

3) the turnover of suspended algal pigment stocks caused by sinking in the upper water column of the NW Gulf of Mexico is rapid.

This paper will characterize the photosynthetic pigments and their degradation products in suspended and sinking particles collected from Gulf of Mexico surface waters during November-December 1987, and during October 1988. Collections of suspended and sinking material were made in both warm- and cold-core rings on three different cruises of R/V Gyre: Cruise 87G-11 (18-23 Nov 1987) (Fig. 1A), 87G-12 (28 Nov-5 Dec 1987) and 88G-05 (15-24 Oct 1988) (Fig. 1B). The types and the fluxes of algal pigments obtained from short-term deployments of floating sediment traps will be contrasted with those intercepted by a 39 day deployment of moored sediment traps, to better understand day to day variations of the algal

pigments sinking out of the oligotrophic subtropical ocean.

MATERIALS AND METHODS

1. Sediment Trapping

Sinking particles were subsampled from several deployments:

1) a 23 hour collection with a 2 floating trap array in a cold-core ring, on 30 Nov-1 Dec 87 during Gyre Cruise 87G-12;

2) two consecutive deployments of a 3 floating trap array in a warm-core ring, on 18-19 and 19-20 Oct 88 during Gyre cruise 88G-05. Collecting times lasted 20 hours and 18 hours, respectively;

3) a 39 day collection with a moored sediment trap array , which collected sinking materials from 4 December 1987 to 12 January 1988. Five traps attached to the mooring at depths of 636, 936, 1236, 1352 and 1404 m collected sinking particulate matter at 26 56.8′ N and 94 46.1′ W in 1450 m of water in the northwest Gulf of Mexico.

Sediment traps deployed in the cold-core ring during Gyre cruise 87G-12, as well as those deployed on a mooring during Gyre cruise 87 G-12, were cylindrical in shape, with a 5:1 aspect ratio. They had an intercepting area of 731 cm^2. By comparison, sediment traps deployed in the warm-core ring during Gyre cruise 88G-05 were conical in shape.

During Gyre cruise 87G-12, the 2-trap drifting array in the cold-core ring collected sinking material close to the base of mixed layer at 50 m, as well as from the upper pycnocline at 150 m. During Gyre cruise 88G-05, the 3-trap drifting array in the warm-core ring collected sinking particles close to the base of mixed layer at 50 m, and from the upper pycnocline at 100 m and at 200 m.

2. Analysis of Plant Pigments

For analysis of pigments and their degradation products in both suspended and sinking particulate material from the Gulf of Mexico, I employed the same Varian/Rainin HPLC analytical system that I used to process samples of suspended material from ODP Leg 119 (Noh, 1991). With this system, I could distinguish chlorophyll a from chlorophylls b and c, as well as from its degradation products chlorophyllide a, phaeophorbide a, and phaeophytin a. However, the Rainin column did not allow ideal separations of some of the carotenoids (e.g. 19′-butanoyloxyfucoxanthin and 19′-hexanoyloxyfucoxanthin overlapped that of fucoxanthin) and zeaxanthin

coeluted with lutein.

From the floating sediment trap samples on 87G-12, a 1:6 unpreserved aliquot was analyzed by HPLC from each depth, and a 1:4 unpreserved aliquot from the traps on 88G-05. From the five moored trap samples, a 1:16 aliquot preserved with sodium azide (NaN^3) was analyzed by HPLC.

RESULTS

1. Vertical Profiles of Suspended Algal Pigments during Gyre Cruise 87G-11

Chlrorophylls (see Fig. 2)

At CTD #12, which was within the cold core ring, chlorophyll a and b were both present in the upper 120 m, but no degradation products could be detected. The highest concentrations of chlorophylls a and b occurred at 40-60 m depth. In this subsurface maximum, the concentration of chlorophyll a reached 0.2 μg liter ^{1}. In contrast, chlorophyll b showed a less distinct subsurface maximum, being similar in concentration from 40 m to 100 m. At 120 m, though, chlorophyll b was not detected.

At CTD #19, which was "slope" water outlying either the warm or the cold core ring, chlorophyll a and b were again detected in the upper 100 m, without any of their degradation products. Subsurface concentrations of chlorophyll a in the upper 80 m were similar to those in the upper 60 m at CTD #12 in the cold-core ring, ranging from 0.17 to 0.2 μg liter^{-1}. Outside the cold-core ring, however, chlorophyll b was restricted to the deeper waters, being detected only at 80 and 100 m (0.07 and 0.03 μg liter ^{1}, respectively).

At CTD #26, which was located just inside the warm-core ring, water samples collected from 4 subsurface depths (40, 60, 80 and 100 m) were analyzed post-cruise by HPLC. Only chlorophyll a and b were detected. Between 60-100 m, the concentration of chlorophyll a ranged from 0.13 to 0.25 μg liter^{-1}, with the subsurface maximum at 80 m. As at CTD #19 and #26, chlorophyll b was detected at only 80 and 100 m, where it averaged 0.07 μg liter^{-1}.

In summary, in November 1987 the DCMs were generally located at depths between 60 m and 100 m in the northwest Gulf of Mexico. However, the distribution pattern of chlorophylls in the cold-core ring was somewhat different from that within the warm ring, or in the outlying slope water.

First, the DCM at the cold-core ring site was shallow. High chlorophyll a concentrations at 40-60 m had decreased rapidly by 80 m, so that chlorophyll a was significantly lower (pairwise t-test, p=0.05) at this depth than chlorophyll a concentrations at CTD #19, 21 or 26. Second, only at the cold-core ring station was chlorophyll b present in detectable levels above 80 m. Elsewhere, chlorophyll b was generally restricted to the 80 m and 100 m collection depths.

Carotenoids (see Fig. 3)

19'-hexanoyloxyfucoxanthin, 19'-butanoyloxyfucoxanthin, zeaxanthin/lutein, β-carotene and diadinoxanthin were commonly detected at all of the CTD stations in the northwest Gulf of Mexico in November 87. 19'-hexanoyloxyfucoxanthin was generally the dominant carotenoid. Zeaxanthin/lutein was also common, but only rarely did it occur in high concentration at 100 m or at 120 m. Diatoxanthin and fucoxanthin were relatively less important carotenoids in the study area. These two carotenoids were generally present in low amount (< 0.01 μg liter^{1} for each), and not at every CTD cast or at all of the sampling depths.

Within the cold-core ring (CTD #12), 19'-hexanoyloxyfucoxanthin reached maximum concentrations subsurface at 40 and 60 m (0.06 μg liter^{-1}), and then decreased from there with depth. With the exception of a low concentration at 40 m, the distribution pattern of 19'-butanoyloxyfucoxanthin was quite similar to that of 19'-hexanoyloxyfucoxanthin. The maximum concentration of 19'-butanoyloxyfucoxanthin was 0.04 μg liter^{-1} at 60 m. Zeaxanthin/lutein and β-carotene exhibited similar vertical distribution patterns to that of 19'-hexanoyloxyfucoxanthin, showing that their maximum concentrations (0.02 μg liter^{-1}) at 40 and 60 m.

At the slope water location (CTD #19), the vertical distribution pattern of 19'-hexanoyloxyfucoxanthin, 19'-butanoyloxyfucoxanthin and β-carotene were all quite similar, reaching subsurface maxima at 80 m (0.06 μg liter^{-1} for 19'-butanoyloxyfucoxanthin; 0.05 μg liter^{-1} for 19'-hexanoyloxyfucoxanthin; 0.02 μg liter^{-1} for β-carotene). However, zeaxanthin/lutein had a broader and more shallow subsurface maximum.

In the warm-core ring (CTD #26), 19'-hexanoyloxyfucoxanthin was the most abundant of carotenoids. The subsurface 19'-hexanoyloxyfucoxanthin maximum was 20-40 m deeper here (60-100 m) than in the cold-core ring (40-60 m).

In summary, 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin were the two most abundant carotenoids in the

northwest Gulf of Mexico in November 1987. As with chlorophyll a, they reached their subsurface concentration maxima between 40-60 m in the cold ring, but this deepened to 60-100 m in the warm ring and adjacent slope water. Zeaxanthin/lutein was also a common carotenoid throughout this study area, reaching locally highest concentrations in the upper 60 m regardless of sampling within, or outside of, rings.
β-carotene, on the other hand, generally tracked the fucoxanthins, peridinin and chlorophyll a, reaching a subsurface maximum at 40-60 m in the cold-core ring, and at 60-100 m outside.

2. Vertical Profiles of Suspended Algal Pigments during Gyre Cruise 88G-05

Water samples were collected by rosette sampler for post-cruise analysis by HPLC at three CTD stations made within a warm-core ring (Sta #22, #23, #27). Since all three of these CTD casts were made at nearly the same location inside the ring, they provide insights about variation on a time scale of hours as well as variations on a spatial scale of a few kilometers within the WCR.

Chlorophylls (see Fig. 4)

All three CTD casts performed within the warm-core ring showed similar trends in the composition and vertical distribution patterns of chlorophylls. Both Chlorophylls a and b were present, but none of their degradation products were detected. Chlorophyll a concentrations were relatively low in surface waters (< 0.1 μg liter^{-1}), but these averaged two-fold higher (0.2 μg liter^{-1}) in the DCM, which generally occurred below 80 m. Chlorophyll b was quite rare in surface waters (< 0.01 μg liter^{-1}) but reached a broad subsurface maximum of about 0.05 μg liter^{-1} from 90-120 m.

Carotenoids (see Fig. 5)

19'-hexanoyloxyfucoxanthin, 19'-butanoyloxyfucoxanthin, fucoxanthin, zeaxanthin/ /lutein, β-carotene, diadinoxanthin, and diatoxanthin were detected within the warm ring. 19'-hexanoyloxyfucoxanthin was the most abundant carotenoid (0.02 μg liter^{-1} at its maximum), with 19'-butanoyloxyfucoxanthin and zeaxanthin/lutein also common in all of the CTD casts. Diadinoxanthin and

diatoxanthin were the least abundant of the carotenoids (both < 0.01 μg liter^{-1}).

At CTD #22, the vertical distribution patterns of 19′-hexanoyloxyfucoxanthin, 19′-butanoyloxyfucoxanthin and β-carotene were quite similar to those of chlorophyll a, reaching their subsurface maxima at the 100 m analytical depth. By contrast, zeaxanthin/lutein did not show a sharply defined subsurface maximum, instead averaging 0.01 μg liter^{-1} from 30 m down to 100 m, before decreasing sharply at the 120 m analytical depth.

In summary, the vertical distribution patterns of suspended algal pigments sampled near the center of the warm-core ring in October 1988 were quite similar, and individual pigments varied in concentration by less than a factor of two within sampling times of hours to days on sampling scales of a few kilometers. The distribution patterns of chlorophylls and carotenoids generally coincided with those measured the year previously, within a warm-core ring sampled in October 1987 during Gyre cruise 87G-11.

3. Pigment Composition of Sinking Particulate Material Collected by Drifting Sediment Traps during Gyre Cruise 87G-12

Chlorophylls (see Fig. 6A)

Chlorophyll a, chlorophyll c and phaeophorbide a were detected in the material intercepted by the sediment traps at both 50 m and 150 m. The flux of chlorophyll a was greatest at 50 m (47.7 μg m^{-2} day ^{1}) , but this decreased with depth so that the flux of chlorophyll a at 150 m was only 14 % of that at 50 m. Similarly, the flux of chlorophyll c was 3.5 μg m^{-2} day^{-1} at 50 m, but less than 0.1 μg m^{-2} day ^{1} at 150 m. The flux of phaeophorbide a averaged 20 % of the flux of chlorophyll a, decreasing from 9.3 μg m ^{2} day^{-1} at 50 m to 2.1 μg m ^{2} day ^{1} at 150 m.

Carotenoids (see Fig. 6B)

Diadinoxanthin, 19′-hexanoyloxyfucoxanthin, peridinin, zeaxanthin/lutein and fucoxanthin were detected in the sinking particulate material intercepted at 50 m. The fluxes of carotenoids showed patterns similar to that of chlorophyll a. The most abundant carotenoids in the sediment trap were diadinoxanthin and 19′-hexanoyloxyfucoxanthin. Fluxes of both were 15 μg m^{-2} day^{-1} at 50 m, and at 150 m the fluxes of both had

decreased about two fold. Similarly, at 150 m, the fluxes of fucoxanthin, and zeaxanthin/lutein were 47 %, and 59 % of that trapped at 50 m. For peridinin, measurable flux was only detected at the 50 m depth. For β -carotene, the concentration at 50 m was lost because of an experimental error during the HPLC run.

4. Floating Sediment Trap Collections during Gyre Cruise 88G-05

Chlorophylls (see Fig. 7 A & B)

From FST-1, the first sediment trap deployment, the HPLC chromatogram of the sample intercepted at 50 m was lost due to a problem with the HPLC integrator. However, at 100 m chlorophylls a and b, phaeophorbide a, and phaeophytins a and b were all detected. At 100 m the flux of chlorophyll a was 1.2 μg m^{-2} day^{-1}, and at 200 m this had decreased to 0.85 μg m^{-2} day^{-1}, 70 % of that at 100 m. For its degradation products phaeophorbide a and phaeophytin a, measurable fluxes were only detected at the 100 m depth. These were similar (1.2 and 1.3 μg m^{-2} day^{-1}) and about an order of magnitude less than the flux of chlorophyll a.

Rather unexpectedly, the flux of chlorophyll b at 100 m was greater than that of chlorophyll a plus that of its degradation products.

From FST-2, the second sediment trap deployment, chlorophyll a and phaeophorbide a were detected at 50 m and at 100 m, but phaeophorbide a was below the limits of detection at 200 m. In contrast to the first deployment, chlorophyll a was the dominant algal pigment in the sediment trap samples at all depths. Chlorophyll b was not detected at 100 m from FST-2, but the flux of chlorophyll b at 50 m was 0.6 μg m^{-2} day^{-1}, and 0.7 μg m^{-2} day^{-1} at 200 m.

Carotenoids (see Fig. 7 C & D)

From both the first and second sediment trap deployments, 19'-hexanoyloxyfucoxanthin, 19'-butanoyloxyfucoxanthin, diadinoxanthin, diatoxanthin, zeaxanthin/lutein, β-carotene were detected at all depths. In FST-1, 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin were the two most abundant carotenoids at 100 m, with fluxes of 2.4 μg m^{-2} day^{-1} and 1.7 μg m^{-2} day^{-1}, respectively. However, these fluxes were greatly reduced at 200 m, to only 4 % and 13 % of that at 100 m. The fluxes of diadinoxanthin, zeaxanthin, diatoxanthin and β-carotene were relatively low at 100 m (0.7, 0.4, 0.3 and 0.3 μg m^{-2} day^{-1}, respectively), and these were

even lower at 200 m.

DISCUSSION

1. Phytoplankton Taxonomic Composition

Because different taxa of phytoplankton have different types or different combinations of algal pigments, pigments can serve as chemotaxonomic "biomarkers". My HPLC data indicate that in fall 1987 and fall 1988 the phytoplankton community of the northwest Gulf of Mexico was a mixed assemblage, with prymnesiophytes (19'-hexanoyloxyfucoxanthin), chrysophytes (19'-butanoyloxyfucoxanthin), cyanobacteria (zeaxanthin), chlorophytes, prasinophytes and/or prochlorophytes (chlorophyll b), dinoflagellates (peridinin), along with diatoms (fucoxanthin + diadinoxanthin).

For example, because a zeaxanthin/lutein peak was consistently present in the upper 50 m and in concentration ranked third, after 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin, it implies that the material was zeaxanthin, the taxonomic marker for cyanobacteria. On the other hand, had this peak been most abundant below 50 m and well-related with a local maximum in chlorophyll b, it would likely have been lutein, from prochlorophytes.

2. Chlorophylls b and c, and Carotenoids

Until rather recently, it had been believed that chlorophyll b was rare in the oceanic marine environment. However, reports have appeared from investigators showing the presence of chlorophyll b in both open-ocean and coastal regions (Jeffrey, 1974, 1976; Bidigare et al., 1986; Hooks et al., 1988; Chisholm et al., 1988). In the NW Gulf of Mexico, the presence of the chlorophyll b indicates that prasinophytes and prochlorophytes and other green alga (chlorophytes) were present, and that these were most abundant at light intensities of 3-0.1 % I_o that are characteristically found from 60-100 m there (Sanchez, 1991).

Trees et al. (1986) reported that the chlorophyll b maxima generally coincided with chlorophyll a maxima, and that chlorophyll b seemed to be a persistent feature in the deep samples. In the present study, chlorophyll b generally was most abundant between 60 m-100 m, except within the cold ring, where it was found shallower, presumably as a consequence of upwelling. Earlier, Jeffrey (1976) had speculated that chlorophyll b-containing prasinophytes probably had adapted to survival in continuously low light

deep waters, but she also raised the question whether the *in vivo* blue absorption band of chlorophyll b is sufficient to harvest the energy required by these organisms at depth, or whether some light-harvesting carotenoid should be implicated. In fact, there may be multiple mechanisms which allow survival in deep waters, such as complementary chromatic adaptation (blue-green light increasing the concentration of blue green light-absorbing carotenoids), and/or increasing the total amount of light-harvesting chlorophylls and carotenoids (Jeffrey, 1980).

Chlorophyll c was detected far less commonly than chlorophyll b in the NW Gulf of Mexico. However, a contributing factor may have been the short Rainin HPLC column that I used, which did not always produce a sharp chlorophyll c peak. Complicating this was the electronic integrator that I had available to me, which did not always detect a broad and smooth peak, instead of a narrow and sharp peak in the fluorescence chromatograms at the retention time of chlorophyll c. Difficulties in separating other less common compounds from background probably apply as well to the chlorophyllous degradation products phaeophorbide a, phaeophytin a, and phaeophytin b. Nonetheless, such degradation products could not possibly have been overlooked if present at concentrations > 0.02 μg liter^{-1}, for they show up clearly in standards diluted down to these levels. Two conclusions thus emerge:

1) In samples in which the concentrations of chlorophyll a were relatively low (0.1-0.2 μg liter^{-1} at maxima), the concentrations of its degradation products such as phaeophorbide a, phaeophytin a and phaeophytin b were certainly lower. If these latter averaged an order of magnitude less abundant than chlorophyll a, they would indeed have been below the detection limit in the one-liter to four-liter samples that were filtered in the oligotrophic northwest Gulf of Mexico;

2) The phytoplankton community in the northwest Gulf of Mexico was apparently quite healthy. In fact the overall rarity of chlorophyllous degradation products in the study area agrees well with the data of Ondrusek (1989), who reported degradation products of chlorophyll a were quite uncommon in the upper 150 m of the subtropical North Pacific Ocean.

Among the carotenoids, 19'-hexanoyloxyfucoxanthin was usually the most abundant, dominating at most depths throughout the study area. However, because there was seldom a great difference in concentration between 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin in most samples, it indicates that chrysophytes as well as prymnesiophytes were important components of the phytoplankton community of the northwest Gulf of Mexico. In fact, 19'-butanoyloxyfucoxanthin was most

abundant between 60-100 m, within the core of the DCM. β-carotene, which is a carotenoid component of diatoms (Jeffrey, 1976; Stauber and Jeffrey, 1988), was present generally throughout the whole water column, rather than being restricted to either near surface or to DCM depths.

Ondrusek (1989) reported that 19'-hexanoyloxyfucoxanthin, which is the dominant accessory pigment for cosmopolitan prymnesiophyte *Emiliania huxleyi*, was the most abundant carotenoid (on a total weight basis) in oligotrophic, subtropical North Pacific waters. My Gulf of Mexico data support Ondrusek, for 19'-hexanoyloxyfucoxanthin was common at most of the depths throughout the subtropical NW continental slope. Zeaxanthin/lutein was also commonly found in the NW Gulf of Mexico. However, unlike 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxyfucoxanthin, it was more abundant in near surface waters, from the surface to 60 m, rather than at DCM depths. This strongly suggests the compound was zeaxanthin rather than lutein, and that presence is an indicator of cyanobacteria, which are common in high irradiance, near surface subtropical (as well as tropical and temperate) regions. Gieskes and Kraay (1983) reported that zeaxanthin was the most abundant carotenoid in surface samples in the oligotrophic tropical Atlantic and in the Caribbean seas, where it reached concentrations of 0.1-0.2 μg $liter^{-1}$. They argued that the relative abundance of zeaxanthin in open-ocean samples in which chlorophyll b was absent or scarce was indicative of the ecological importance of cyanobacteria in oceanic systems. In the present study, at most sites in the NW Gulf of Mexico where only surface water was collected, zeaxanthin was likewise the most abundant carotenoid.

3. Sinking Particulates

Both in quality and quantity, the pigment composition of samples trapped in the cold ring in November 1987 was markedly different from that trapped in the warm ring in October 1988. In terms of kinds of materials present, the chlorophyll composition of the sediment trap samples intercepted at both 50 m and 150 m in the cold core ring was more simple than those intercepted at 50 m and 100 m in a warm core ring (see Table 1). Specifically, the cold ring samples lacked detectable phaeophytins a and b, as well as chlorophyll b. This might imply that the degradation mechanisms in the warm core ring were more complicated, compared to those in the cold core ring. However, since it is not possible to separate differential degradation from interannual variability, this observation therefore needs further investigation. In addition, note that diadinoxanthin,

19'-hexanoyloxyfucoxanthin, fucoxanthin and peridinin dominated the sinking carotenoids in the cold core ring, whereas in the warm core ring, the carotenoid flux was generally proportional to the concentration of the various carotenoids suspended in the water column.

In terms of quantity, both total pigment flux as well as the flux of individual compounds in the cold core ring was an order of magnitude higher than that in the warm core ring. This observation supports our current paradigm that primary production as well as other biological processes such as zooplankton grazing and biological decomposition, etc., were more active in the more nutrient-rich cold core ring. However, note that the flux of phaeophorbide a leaving the 50 m horizon in both cold and warm rings was only 20 % of that of chlorophyll a, which was the most abundant component in the falling material. This suggests that the zooplankton grazing pressure in the northwest Gulf of Mexico was not strong, compared to other marine environments. In addition, while pigment fluxes at 50 m in the cold ring were 2-7 times higher than those at 150 m, there were no large differences in flux between 50 m and 100 m in the warm core ring.

In samples collected by the moored traps, phaeophorbide a was the predominant chlorophyllous pigment (Fig. 8). Fluxes of phaeophorbide a in the moored samples were much higher than those trapped in the upper 200 m by short-term deployments. They were approximately an order of magnitude higher than those of chlorophyll a in the moored samples, whereas the fluxes of chlorophyll a obtained both in the cold-core ring (87G-12) and warm-core ring (88G-05) were only about 5 times greater than that of phaeophorbide a. This means that in deeper waters of the Gulf of Mexico, the main component of the sinking algal pigments was phaeophorbide a, assuming that the preservative in the moored traps did not result in the loss of chlorophyll a. In fact, the 2-week laboratory experiment with sodium azide (NaN^3) added as a preservative to *Skeletonema costatum* culture confirmed that the total amount of chlorophyll a plus degradation products was conserved after either one day or twelve days (Table 2). However, there was evidence for minor interconversions in the amount of each chlorophyll after one day and 12 days.

Because the most abundant carotenoid in most of the moored traps was fucoxanthin, the bulk of the plant material intercepted by the mooring appears to have been diatoms. In this sense, the moored traps collected a more simple suite of carotenoids than did the shallow, short-term, drifting sediment traps. Only 19'-butanoyloxyfucoxanthin and β-carotene were detected in addition to fucoxanthin in the moored samples. In the traps at

936 m and 1236 m, the flux of 19'-butanoyloxyfucoxanthin was almost equal to that of fucoxanthin.

4. Standing Stock versus Sinking Material

As Table 3 shows, less than 0.1 % of the standing stock of chlorophyll a sank out of the upper 200 m of the warm-core ring on any given day. For accessory pigments as well, the percentages were generally less than 0.5 %. Thus I must reject the null hypothesis that the standing stock of suspended particulates turned over rapidly by sinking out in the warm-core ring in the NW Gulf of Mexico. Unfortunately, however, because water column sampling was not coupled with sediment trap sampling in the cold-core ring in December 1987, the conclusion above may or may not be applicable to cold-core rings in the NW Gulf of Mexico.

5. Estimation of "new production " in the Gulf of Mexico from pigment fluxes

In an ideal steady-state system, the cycling of nutrients through a planktonic food web will continue indefinitely, with measurable phytoplankton standing stocks undergoing only minor stochastic variations. However, in the real ocean, there are bound to be net losses of nutrients from near-surface waters, such as the flux of sinking fecal materials and cast off exoskeletons out of the euphotic zone to deep water, or from fish catch and seabirds feeding in the ocean but depositing guano on land. Such nutrient losses must be replaced by external inputs to prevent a decline in the productivity of the system. Among the methods of renewal in the ocean there are the flux of nitrate from deep water, fixation of molecular nitrogen by free-living and symbiotic blue-green algae, and the nitrogen from terrestrial and atmospheric sources (Eppley and Peterson, 1979). This is so-called "new production" (Dugdale and Goering, 1967). In theory, it can be exported from the system without its reducing its overall productivity, and it is this which drives both the fish catch and the downward flux of organic matter to bathypelagic and benthic food web. By corollary, if we measure this export as the sinking of particulate organic matter out of surface waters in the ocean, the exports (i.e. flux of particulate organic matter) is equal to "new production" by the definition of Dugdale and Goering (1967).

Because the fluxes of algal pigments out of the surface waters of the Gulf of Mexico have been measured in the present study, pigment fluxes can be converted to the total carbon flux to compare the "new production"

with those in other investigations. A C:CHL weight ratio of 50 will be utilized for this comparison, which previous investigators have reported is a reasonable summary of carbon content to chlorophyll a in laboratory as well as field-collected Antarctic phytoplankton cells (Sakshaug and Holm-Hansen, 1984; Tilzer et al., 1985).

Table 4 presents the estimated carbon flux using a carbon to chlorophyll a weight ratio of 50. The estimated "new production" in terms of carbon in the Gulf of Mexico cold-core ring is approximately 7 times higher than that in the warm-core ring.

Knauer et al. (1990) reported that the *f*-ratio (the ratio of new production to total production) appeared to be inversely related to primary production. They obtained the lowest estimates (0.11-0.16) during periods of highest productivity. Thus, we can approximate the total carbon production from sediment-trapped CHL pigment fluxes if we assume an average *f* ratio of 0.15.

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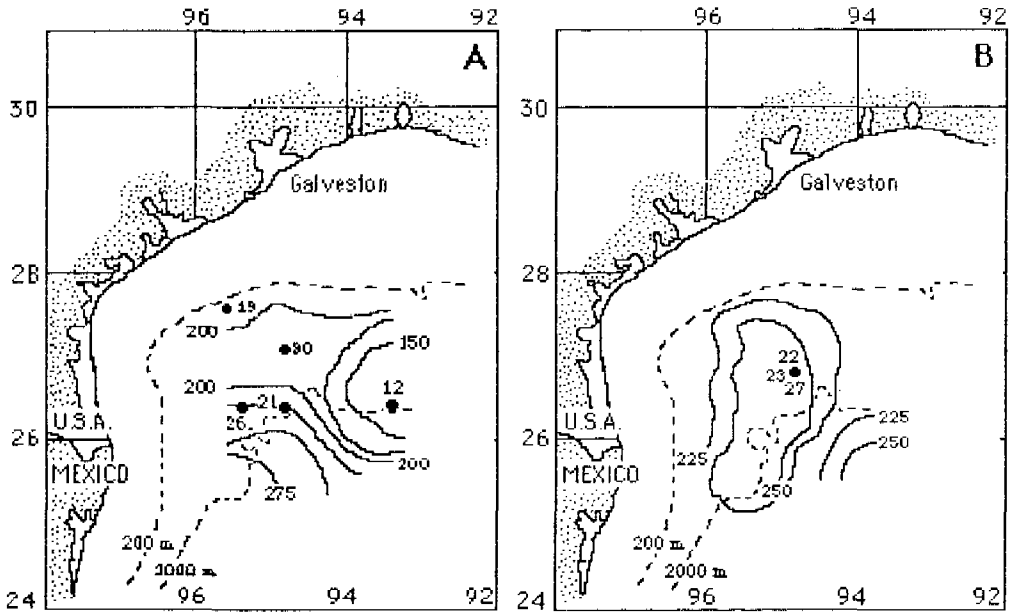

Fig. 1. Sampling locations in the northwest Gulf of Mexico for Gyre cruises A) 87G-11 in the fall 1987 and B) 88G-05 in the fall 1988.Contour lines show depth (m) to the 15°C isotherm; dashed lines show 200 m and 2000 m bathymetry.

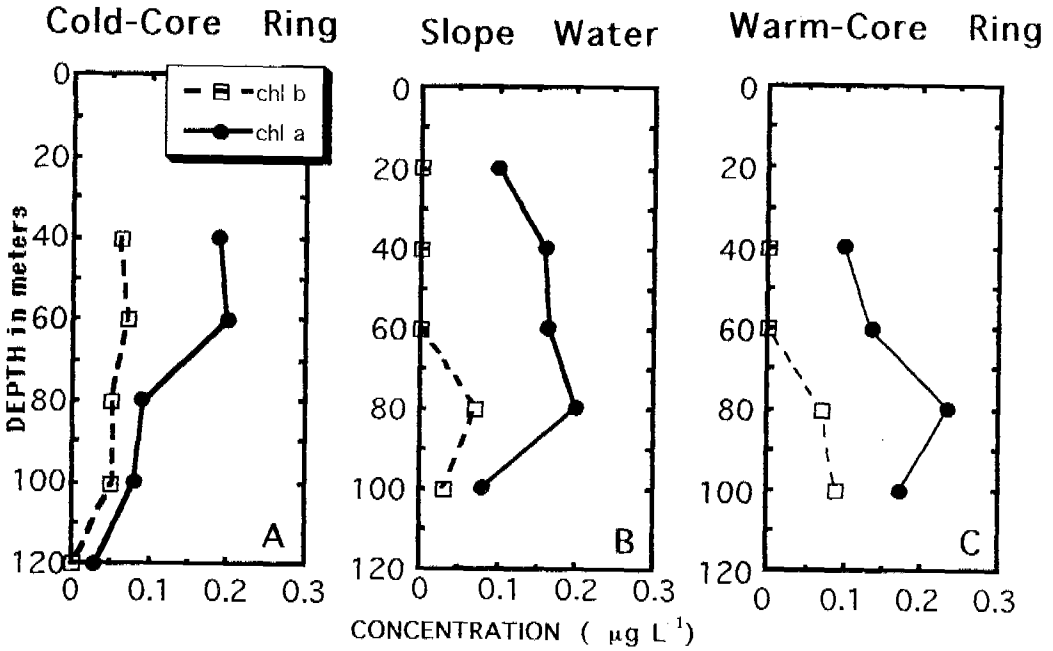

Fig. 2. Vertical distribution of chlorophylls in the northwest Gulf of Mexico in November 87 (Cruise 87G-11) at CTD stations 12 (Cold-Core Ring), 19 (Outlying Slope), and 26 (Warm-Core Ring).

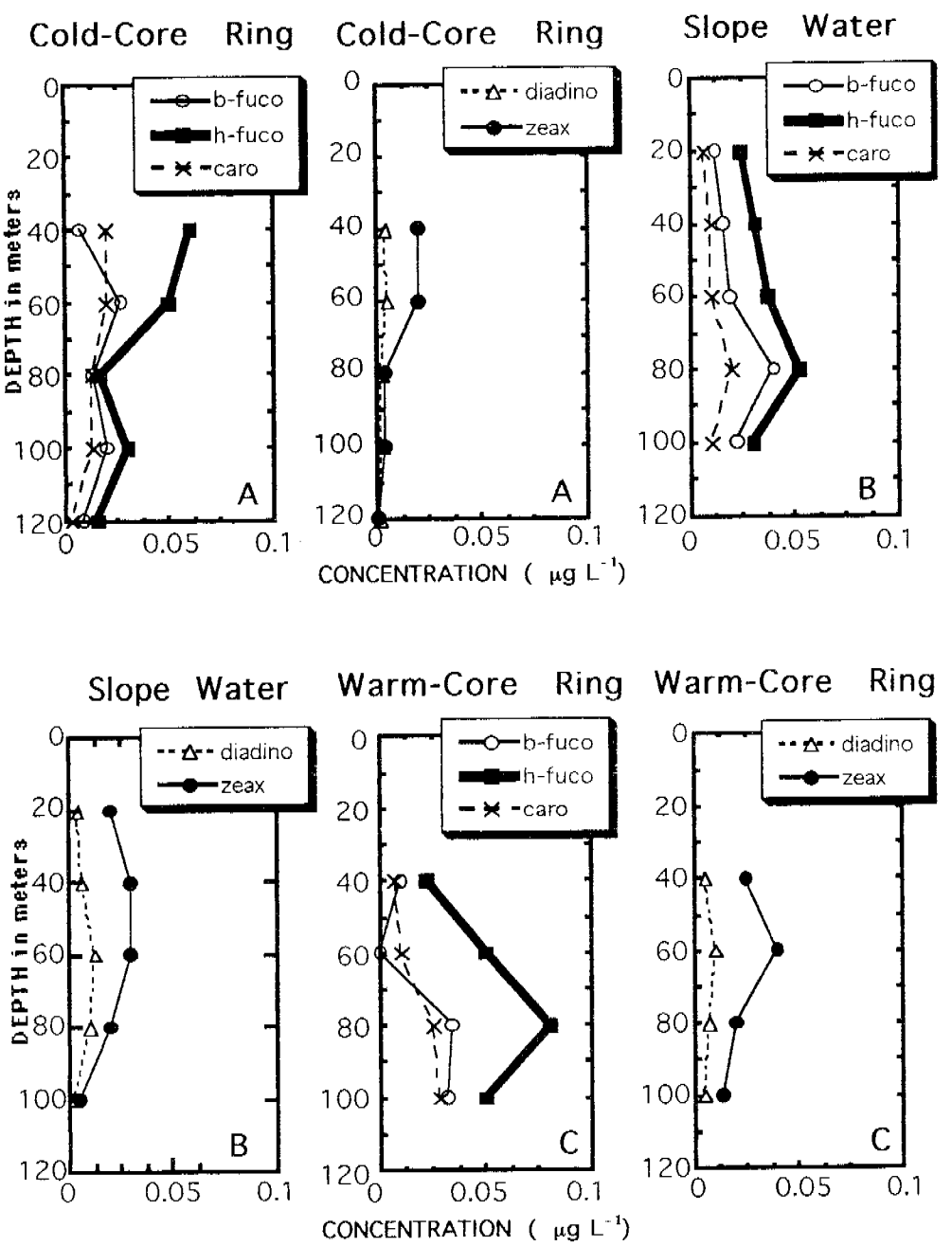

Fig. 3. Vertical distribution of carotenoids in the northwest Gulf of Mexico in November 87 (Cruise 87G-11) at CTD stations 12 (Cold-Core Ring), 19 (Outlying Slope), and 26 (Warm-Core Ring).

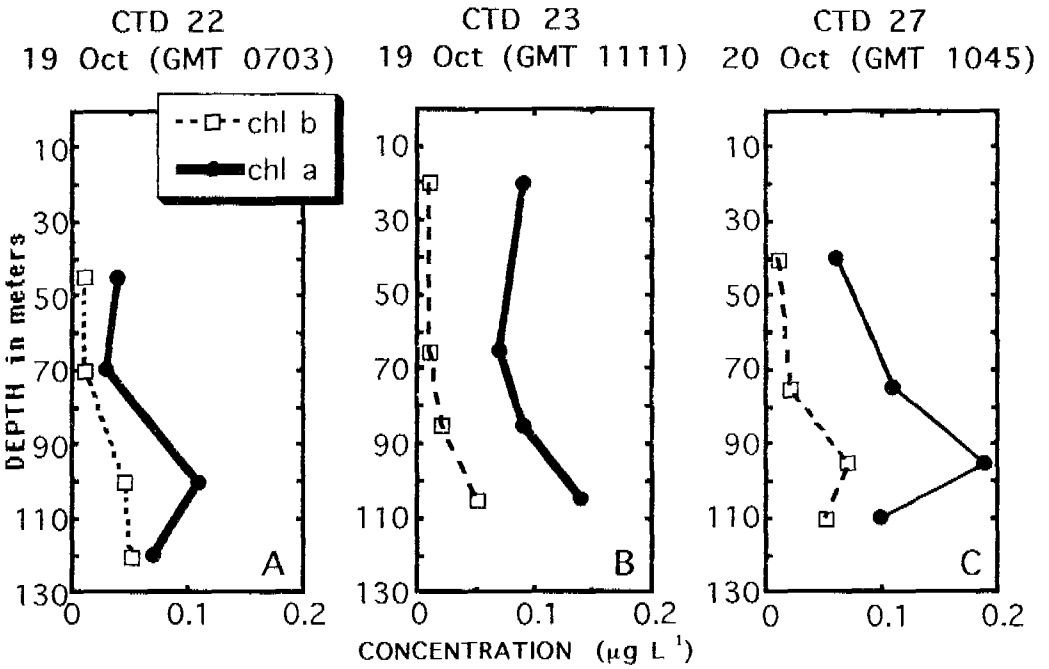

Fig. 4. Vertical distribution of chlorophylls in a Warm-Core Ring in the northwest Gulf of Mexico in October 1988.

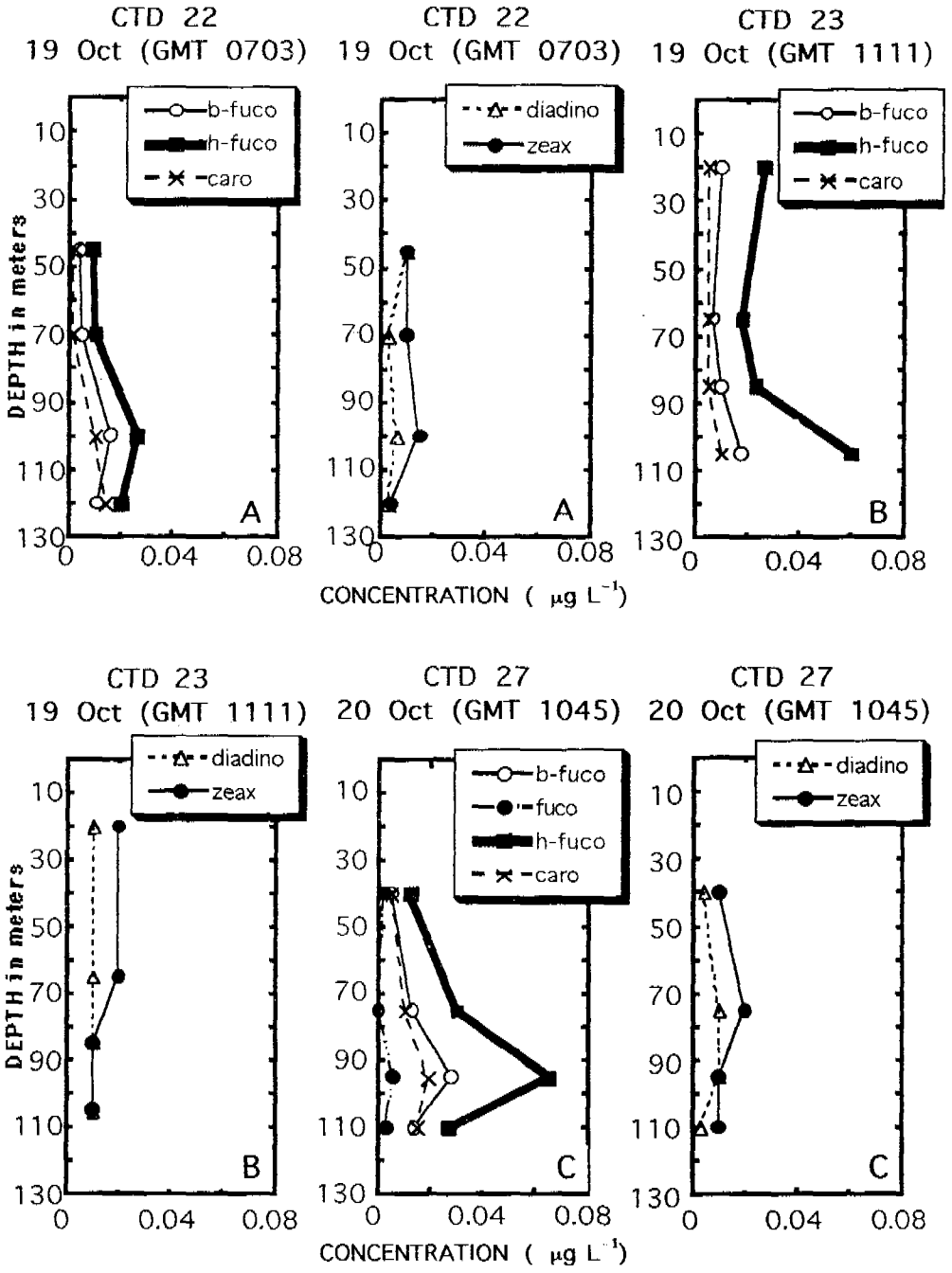

Fig. 5. Vertical distribution of carotenoids in a Warm-Core Ring in the northwest Gulf of Mexico in October 1988.

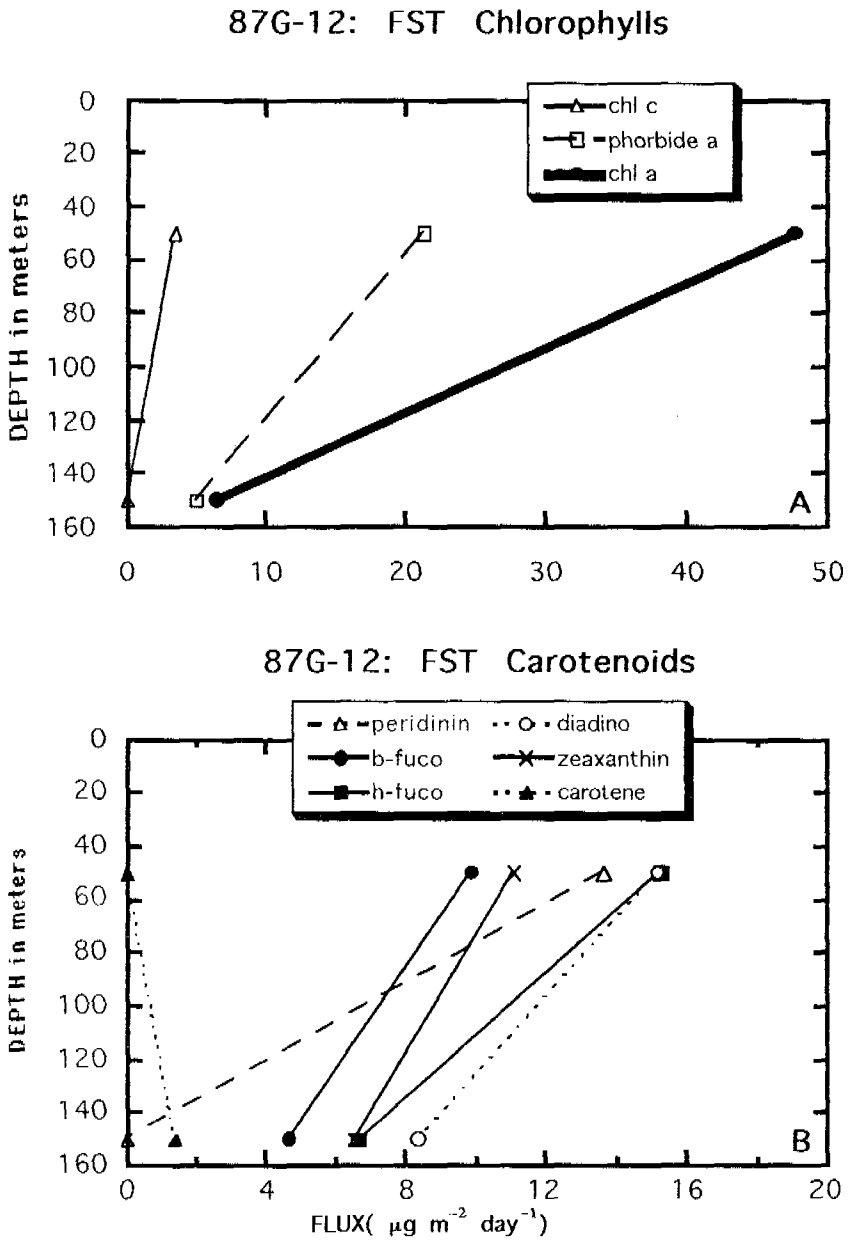

Fig. 6. Fluxes of chlorophylls and carotenoids collected by floating sediment traps at 50 m and 150 m in a Cold-Core Ring in the Northwest Gulf of Mexico in December 1987. Phaeophorbide a is reported as chlorophyll a equivalent.

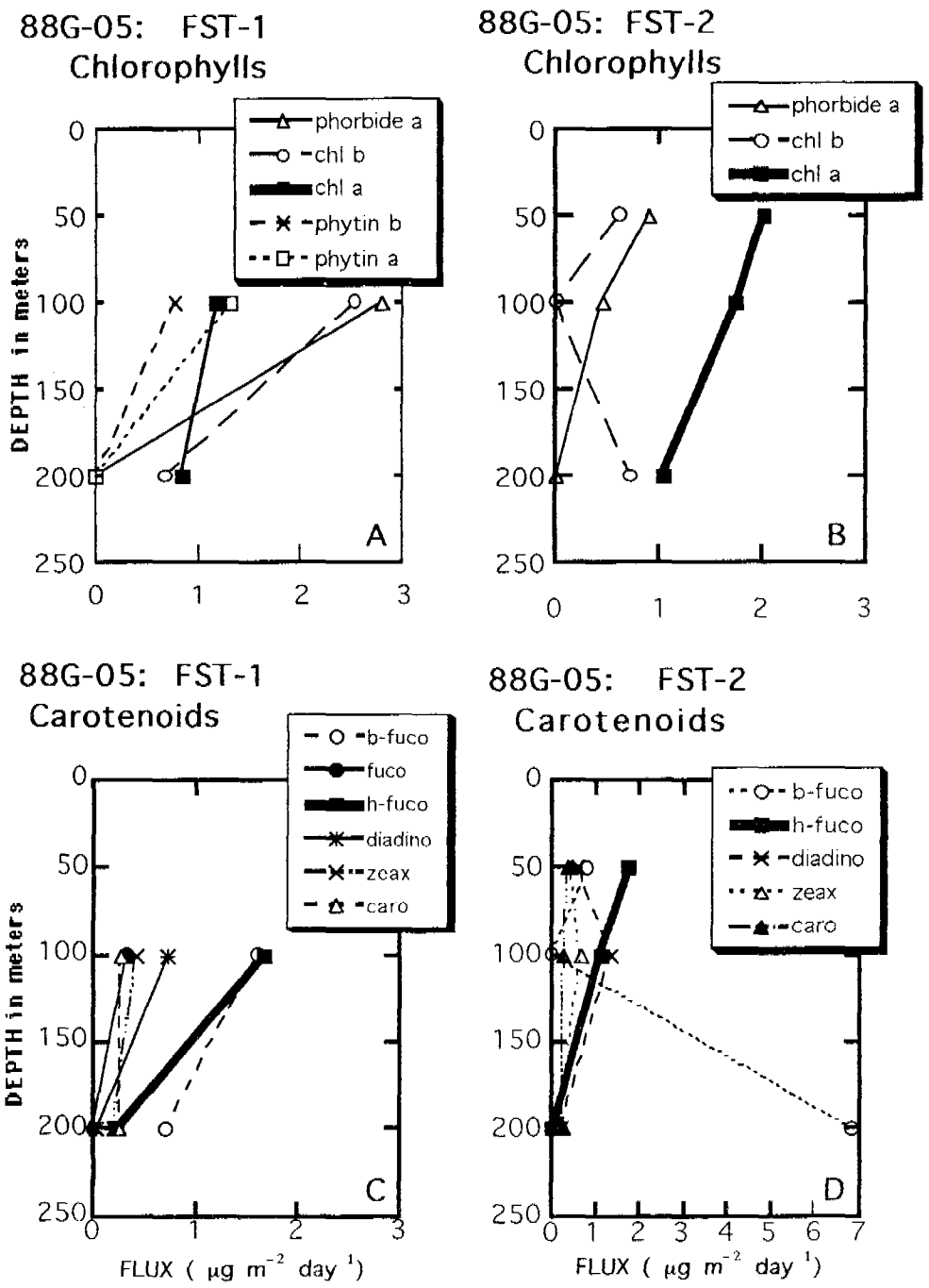

Fig. 7. Fluxes of chlorophylls(A and B) and carotenoids(C and D) intercepted by two deployments of floating sediment traps in a Warm-Core Ring in the northwest Gulf of

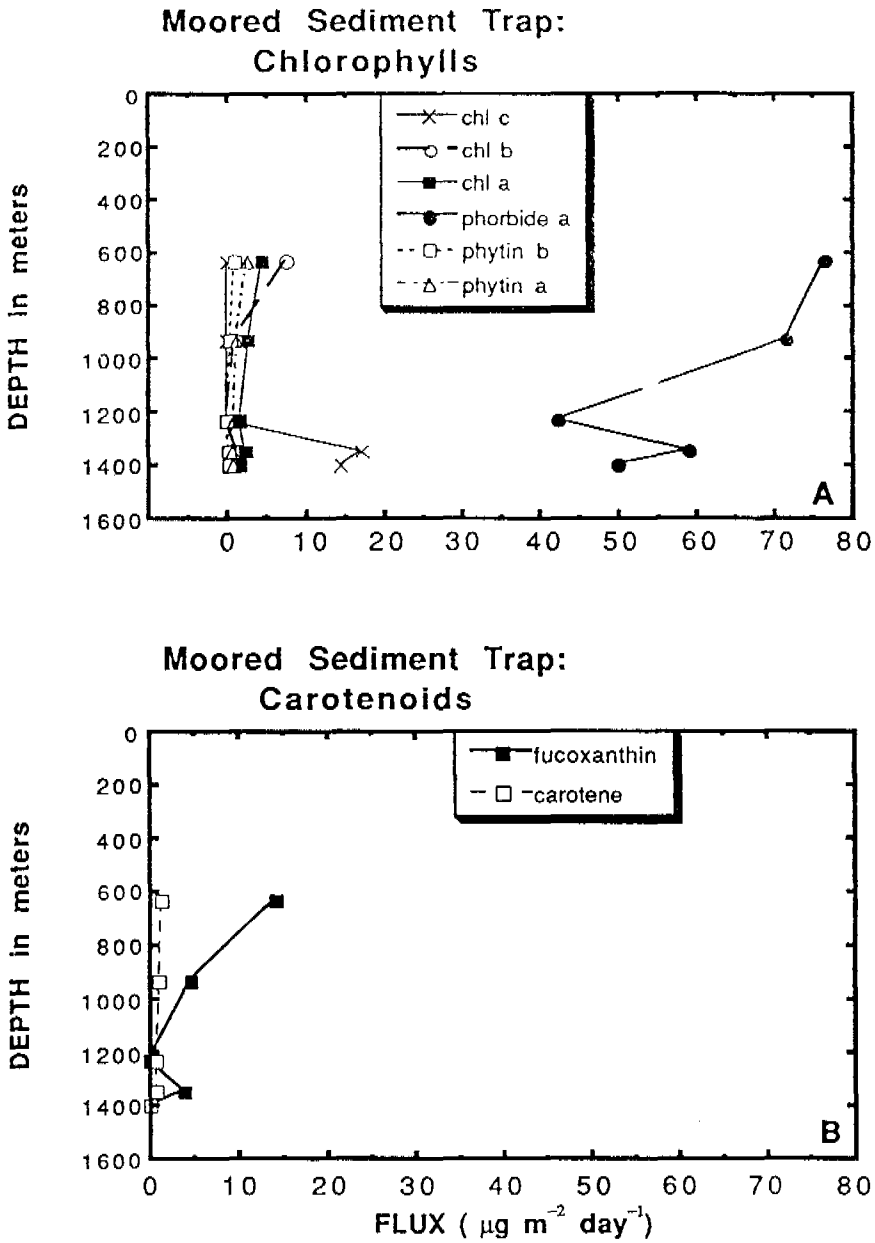

Fig. 8. Vertical profiles of chlorophylls (A) and carotenoids (B) collected by moored sediment traps in the northwest Gulf of Mexico from Nov 1987 to Jan 1988.

Table 1. A comparison of the mean flux of plant pigments and their degradation products ($\mu g\ m^{-2} day^{-1}$) collected by floating traps in a Cold-Core versus Warm-Core Ring.

Pigments	Flux				
	Cold Core ring		Warm core ring		
	50	150	50	100	200
chl a	47.7	6.5	2.0	1.5	0.9
chl b	-	-	0.6	1.3	0.7
chl c	3.5	-	-	-	-
phorbide a†	21.3	5.0	0.9	1.6	-
phaeophytin a†	-	-	-	0.7	-
phaeophytin b -	-	-	0.4	-	-
peridinin	3.6	-	-	-	0.4
b-fuco	9.9	4.7	0.8	0.8	3.8
fucoxanthin	15.2	6.6	-	0.3	-
h-fuco	-	-	1.8	1.4	0.1
diadinoxanthin	15.2	8.4	0.6	1.0	0.1
zeaxanthin	11.1	6.6	0.4	0.5	0.2
β-carotene	*	1.4	0.4	0.3	0.3

† Phaeophorbide a and phaeophytin a are reported as chlorophyll a equivalent

- Not detected

* the peak missed during HPLC run

Table 2. Results of a laboratory experiment in which NaN_3 preservative was added to *Skeletonema costatum* culture, expressed as the actual amounts after one and twelve days in preservative.

pigment	original	1 day	2 weeks
chlide a†	0.57	0.13	0
phorbide a†	5.81	6.11	6.61
chla allomerized	0.04	0.10	0.12
chl a	2.39	2.59	2.33
chl a'	-	-	0.02
phytin a†	-	-	0.03
Total	8.81	8.93	9.11

† Chlorophyll a degradation products are reported as chlorophyll a equivalent. The unit is expressed as μg.

- Not detected

Table 3. Integrated standing stocks (SS*i*) versus sinking materials in a Warm-Core Ring in the northwest Gulf of Mexico in October 1988.

Pigment	0-50 m			0-100 m			0-200 m		
	SS*i*[a]	Flux[b]	%[c]	SS*i*	Flux	%	SS*i*	Flux	%
chl a	2.2	2	0.1	6.4	3.5	<0.1	8.6	4.4	<0.1
chl b	0.4	0.6	0.2	1.5	1.9	0.1	2.5	2.6	0.1
phorb a[d]	ND	0.9	-	ND	2.5	-	ND	2.5	-
h-fuco	0.6	1.8	0.3	1.9	3.2	0.2	2.8	3.3	0.1
peri	0.5	ND	-	1.3	ND	-	1.8	0.4	<0.1
b-fuco	<0.1	0.8	2.7	0.1	1.6	1.6	0.2	5.6	2.8
diadino	0.3	0.6	0.2	0.7	1.6	0.2	0.8	1.7	0.2
zea	0.5	0.4	0.1	1.2	0.9	<0.1	1.4	1.1	<0.1
β-carotene	0.2	0.4	0.2	0.7	0.7	0.1	1.1	1.0	0.1

[a] Integrated standing stock, expressed as mg m^{-2}

[b] Flux, expressed as μg m^{-2} day^{-1}

[c] SS*i*/Flux, expressed as percentage

[d] Phaeophorbide a is reported as chlorophyll a equivalent.

Table 4. The estimated "new production" in the Gulf of Mexico.

	Cold-Core Ring	Warm-Core Ring
Chl a flux	7[a]	1[b]
Carbon flux	325	45

[a] 150 meter trap material was used to estimate the carbon flux in the cold-core ring, where the 1 % isolume ranged from 50 m to 70 m.

[b] 200 meter trap was used to estimate the carbon flux in the warm-core ring, where the 1% isolume ranged from 100-120 m

* the units are expressed in $\mu g\ m^{-2}\ d^{-1}$