DOMINANT CHLOROPHYLLS AND CAROTENOIDS IN MACROALGAE OF THE BALTIC SEA (BALTIC PROPER): THEIR USE AS POTENTIAL BIOMARKERS

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Plant pigments extracted from eleven different macroalgae from the Baltic proper were analyzed using high performance liquid chromatography (HPLC). Distinct pigment ratios found in the Phaeophyceae, Chlorophyceae, and Rhodophyceae may provide useful markers to differentiate between macroalgal versus planktonic inputs to subtidal regions of the Baltic. Fucoxanthin/chlorophyll-*a* (Chl-*a*) ratios in Phaeophyceae ranged from 0.34 to 0.64 compared to values typically greater than 1.00 in fucoxanthin containing phytoplankton. Similarly, the Chlorophyceae had Chl-*b*/*a* ratios that ranged from 0.20 to 0.30 while that typically found in single-celled chlorophytes is 0.9. Although we were not able to resolve dominant phycobilin pigments in the Rhodophyceae using this HPLC method, the zeaxanthin/Chl-*a* ratio may prove useful in distinguishing between phytoplankton inputs. Finally, the higher concentrations of the photoprotectant pigment β,β,-carotene in the gametic versus vegetative tissues of the brown algae *Fucus vesiculosus* may suggest that this plant has evolved a mechanism for protecting its genetic material from UV radiation while growing at the surface. Pigment ratios of these macroalgae may prove extremely useful in distinguishing between macroalgal versus planktonic inputs to the benthic communities of the Baltic Sea.

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INTRODUCTION

When compared to estuarine regions of the world the Baltic Sea is characterized by a low diversity with only few species of macroalgae (KAUTSKY & KAUTSKY 1989; WALLENTINUS 1991). This low diversity has primarily been attributed to stable and low salinity conditions, prevailing in the largest brackish waterbody in the world. The recent geological age of the system, about 3000 years, has also contributed to the paucity of both animal and plant species in this sea (RUSSELL 1985; WALLENTINUS 1991). Benthic primary production in coastal regions of the Baltic proper constitutes 33 % of the total coastal production (KAUTSKY 1995). Filamentous algae (i.e. *Pilayella littoralis*, *Cladophora glomerata*, and *Ceramium tenuicorne*) represent a major fraction of this production (75 % annually), while the perennial *Fucus vesiculosus* only contributes 10 % to the benthic primary production (KAUTSKY 1995). A significant fraction of the filamentous algal production remains detached from substratum (WALLENTINUS 1979; ANEER 1987) and by the end of June, this material is typically transported to coastal sediments, where drifting algal mats are formed on the sediment surface (BONSDORFF 1992). These mats can comprise as much as 50 % of the annual input of particulate organic matter to the sublittoral zone (KAUTSKY 1995). Moreover, macroalgae have been shown to represent important food resources for benthic and pelagic communities in estuarine and marine ecosystems (ELMGREN 1978, 1984; HILL et al. 1993). While there have been recent studies that have examined the coupling of phytoplankton blooms to the nutrition of benthic communities in the Baltic, the role of macroalgal inputs has largely been ignored. Although there are few species of macroalgae in the Baltic it remains a difficult task to document temporal and spatial variability of inputs of macroalgal-derived carbon to the benthos.

Characteristic plant pigments from different classes of algae have been used as biomarkers to determine sources of carbon input to aquatic ecosystems (MANTOURA & LLEWELLYN 1983; BIANCHI & FINDLAY 1990; MILLIE et al. 1993). Several good markers have already been identified for different types of phytoplankton. For example, the carotenoid fucoxanthin is a marker for diatoms (WRIGHT & JEFFREY 1987), while zeaxanthin, oscillaxanthin,

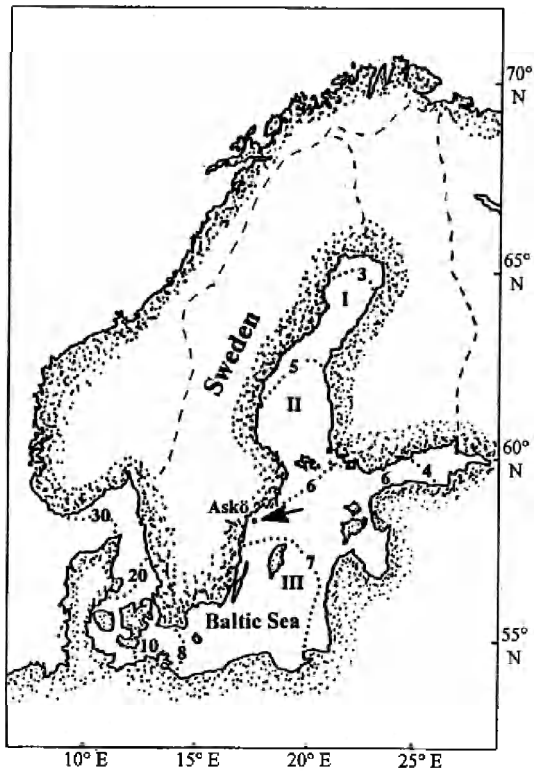

Fig. 1. Regions of the Baltic Sea. I: Bothnian Bay, II: Bothnian Sea, III: Baltic proper. Arrow shows collection area. Dotted lines show typical salinities.

echinenone, and myxoxanthophyll can serve as a markers for cyanobacteria (Hertzberg & Liaaen-Jensen 1969 a,b; Hertzberg et al. 1971; Leavitt & Carpenter 1990). Many macrophytes contain Chl-*b* which is not found in diatoms or cyanobacteria (Rowan 1989). Bianchi & Findlay (1990) showed that the Chl-*b*/lutein ratio was significantly higher in emergent than in submergent macrophytes in the Hudson River, and thus, could be used to differentiate between inputs from these two sources. Although there have been a few studies on the application of plant pigments as biomarkers of macrophytes and macroalgae, much of the work to date has centered on phytoplankton sources in freshwater and marine ecosystems (see review, Millie et al. 1993).

The concentration and distribution of photoprotective plant pigments vary with season in micro- and macroalgae and with tissue type in macroalgal species (i.e. vegetative versus reproductive) (Paerl et al. 1983; Paerl 1984; Rowan 1989). Carotenoids such as zeaxanthin and β,β-carotene have been shown to function as photoprotectants by quenching singlet oxygen which prevents peroxidation reactions (Foote et al. 1970; Foote 1974; Harbour & Bolton 1978). In cyanobacterial blooms that accumulate as scums in surface waters, prolonged exposure to UV irradiation result in enhanced carotenoid production which subsequently increased Chl-*a*-specific photosynthetic O_2 production (Paerl et al. 1983; Paerl 1984). While photoprotectant effects of carotenoids are better documented in microalgae, the reproductive tissues (particularly male gametes) of fucoid macroalgae have been shown to have higher concentrations of β,β-carotene than vegetative tissues (Carter et al. 1948). However, the possible role of carotenoids as photoprotectants for sensitive reproductive cells was not invoked as a basis for these differences (Carter et al. 1948).

In this study we examine differences in concentrations and ratios of carotenoids and chlorophylls in eleven dominant macroalgae collected from the Baltic proper. These ratios provide a distinct 'pigment signature' that may be used to differentiate between phytoplankton-derived versus macroalgae-derived inputs into the water column and sediments of this region. We briefly discuss how certain pigment ratios may be used to address carbon transport questions in the Baltic proper. We also present data that show how the concentration and distribution of photoprotectant pigments in fucoid macroalgae differ in vegetative and reproductive tissues.

MATERIAL AND METHODS

Site description

The Baltic Sea is one of the largest bodies of brackish water in the world. The entire system is relatively shallow (ca 56 m) and can be divided into three distinct basins, the Bothnian Bay, Bothnian Sea and Baltic proper (Fig. 1). The Baltic proper has a typical salinity range of 6 to 8 ‰ and the tidal range is almost negligible. However, there are considerable changes in the water levels along the Baltic coast, primarily due to changes in air pressure as well as wind strength and direction (Johannesson 1989). The water level can vary up to 1 m over the year which together with ice scouring may affect the zonation pattern and diversity of macroalgae (Kautsky & Kautsky 1989).

Plant pigments

Eleven different macroalgal species were collected from the littoral zone of the Baltic proper in July 1994 (Table 1). Macroalgae chosen for this study represented the dominant forms of macroalgae in the region. The algae collected had no macroepiphytic growth, however, the presence of microepiphytes (i.e., benthic diatoms) growing on many of the algae was very likely. These microepiphytes did not create a problem in obtaining 'pigment signatures' because if we are to use these pigments as biomarkers in ecological studies we need 'signatures' that are characteristic of natural conditions, not pure cultures. Approximately two grams of wet material from each of the macroalgae were lyophilized, pulverized, reweighed and then extracted using 100 % acetone; see Bianchi

& FINDLAY (1990) for further details on extraction procedures.

Reversed-phase high-performance liquid chromatography (RP-HPLC) analysis was conducted using the method of WRIGHT et al. (1991), as modified by BIANCHI et al. (1995). Absorbance detection was achieved using a Waters model 600E solvent delivery system coupled with dual-channel detection, using a Waters model 996 photodiode array detector set at 438 nm; fluorescence was measured using a Shimadzu model RF-535 fluorescence detector with excitation set at 440 nm and emission at 700 nm. The injector was connected via a guard column to a reverse-phase C_{18} Alltech Adsorbosphere column (5 µm particle size; 250 mm × 4.6 mm i.d.). After injection (100 µl), a gradient program (1 ml min^{-1}) began isocratically with mobile phase A (80 : 20 methanol: 0.5 M ammonium acetate, aq.; 7.2 pH v/v) which then ramped to 100 % mobile phase B in 4 min (90 : 10 acetonitrile : HPLC grade water v/v) and then changed to 20 % B and 80 % mobile phase C (100 % ethyl acetate) in 14 min. This was followed by a return to 100 % B in 3 min with final ramping to 100 % A in 3 min. This gradient allowed for sufficient resolution of all dominant pigments; Chl-c_1 and c_2 were resolved as a single peak (Fig. 2). This gradient also allows for separation of the stereo-isomers lutein and zeaxanthin (WRIGHT et al. 1991).

High purity HPLC standards for Chl *a* and *b* were obtained from Sigma Co. Carotenoid standards were kindly provided by Hoffman LaRoche Co., Basel, Switzerland.

All peaks were quantified with calculated response factors.

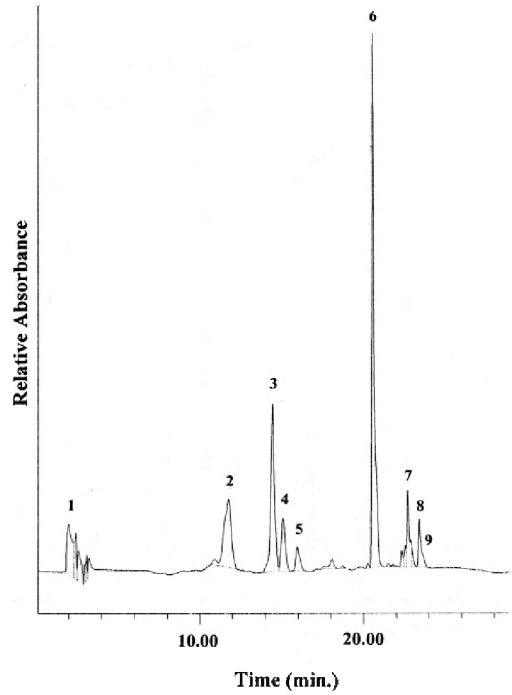

Fig. 2. Absorbance chromatogram of pigments in *Fucus vesciculosus* (male vegetative) collected from the Baltic Proper. The numbered peaks are identified (with known standards) as the following pigments: 1 - solvent front; 2 - Chl c_1, c_2; 3 - fucoxanthin; 4 - *cis*-fucoxanthin; 5 - *diadinoxanthin; 6 - Chl-*a*; 7 -* phaeophytin-*a*; 8 -*β,∈-carotene; 9 - β,β-carotene. Pigments with asterisks were not included as dominant pigments in this study.

Statistical analysis

An F_{max} was used prior to ANOVA analysis to check for homogeneity of variances. A one-way ANOVA was used to test for significant differences of pigments in algae and tissue type. When ANOVA differences were significant, a Scheffé multiple range test was performed to detect for differences between means.

RESULTS

Plant pigment concentrations

In the eleven macroalgae studied, five major carotenoids were identified in addition to Chl-*a*, *b*, and c (Table 1). There were significantly higher concentrations of chlorophyll-a ($p < 0.05$) in the Chlorophyceae than in all other macroalgae collected, except for Chl-*a* concentrations in the red algae *Rhodomela confervoides* (Table 1). As expected, Chl-*b* was only present in green algae. *Cladophora glomerata* contained significantly higher concentrations of chlorophylls and carotenoids ($p < 0.05$) than *Enteromorpha intestinalis*; perhaps most notable were the significantly higher concentrations of Chl-*b*. Fucoxanthin occurred in significantly higher concentrations ($p < 0.05$) than any other carotenoid in the Phaeophyceae (Table 1). *Pilayella littoralis* had significantly higher concentrations ($p < 0.01$) of fucoxanthin and cis-fucoxanthin than all other brown macroalgae. The only dominant carotenoids found in the Rhodophyceae were β,β-carotene, zeaxanthin, and lutein (Table 1). Unlike other carotenoids, zeaxanthin occurred only in the rhodophytes (Table 1). *Rhodomela confervoides* had significantly higher ($p < 0.05$) concentrations of Chl-*a* than all other red macroalgae.

Plant pigment ratios

The only pigment ratio that could be compared across all classes of macroalgae was the β,β-carotene/Chl-*a* ratio which was found to be considerably lower in the Chlorophyceae (Table 2). The violaxanthin/Chl-*a* ratio was generally higher in Phaeophyceae than in the Chlorophyceae (Table 2). *Chorda filum* had the lowest values for all pigment ratios when compared to other brown macroalgae. Similarly, *Rhodomela confervoides* had a lower lutein/Chl-*a* ratio than other red macroalgae. Conversely, *Phyllophora spp.* had the highest β,β-carotene/chlorophyll-a and zeaxanthin/Chl-*a* ratios when compared to other red macroalgae (Table 2).

Table 1: Pigment concentrations (µg g^{-1} dry wt) in eleven dominant macroalgae collected from the Baltic Sea (Baltic proper) in 1994. (ND = not detected, ± = SD, N = 4).

Algae	Chl-*a*	Chl-*b*	Chl-c_1, c_2	Fucoxanthin	cis-Fuco.	β,β-Carotene	Violaxanthin	Lutein	Zeaxanthin
CHLOROPHYCEAE									
Cladophora glomerata	431.8 ± 32.3	128.7 ± 21.4	ND	ND	ND	36.8 ± 11.2	54.6 ± 13.8	82.9 ± 18.4	ND
Enteromorpha intestinalis	393.5 ± 28.2	78.2 ± 15.3	ND	ND	ND	24.3 ± 6.9	38.9 ± 14.7	59.6 ± 10.2	ND
PHAEOPHYCEAE									
Chorda filum	296.7 ± 26.9	ND	42.6 ± 2.6	102.0 ± 16.9	28.9 ± 7.3	34.7 ± 12.6	52.6 ± 13.7	ND	ND
Dictyosiphon foeniculaceus	159.7 ± 13.8	ND	48.6 ± 9.6	86.7 ± 12.2	22.9 ± 5.6	46.9 ± 8.4	67.8 ± 12.4	ND	ND
Fucus vesiculosus	156.9 ± 32.6	ND	34.9 ± 12.2	101.0 ± 18.3	48.7 ± 8.9	42.8 ± 15.6	76.8 ± 13.6	ND	ND
Pilayella littoralis	269.5 ± 30.8	ND	64.9 ± 8.3	128.9 ± 15.6	81.4 ± 10.6	34.6 ± 12.8	98.6 ± 10.1	ND	ND
RHODOPHYCEAE									
Ceramium tenuicorne	242.0 ± 30.8	ND	ND	ND	ND	55.9 ± 11.8	ND	32.4 ± 8.9	82.9 ± 12.6
Furcellaria lumbricalis	228.0 ± 30.8	ND	ND	ND	ND	28.6 ± 9.6	ND	28.6 ± 10.4	86.8 ± 23.2
Phyllophora spp.	259.6 ± 15.8	ND	ND	ND	ND	67.9 ± 12.1	ND	14.9 ± 6.4	92.7 ± 29.6
Polysiphonia nigrescens	229.0 ± 25.8	ND	ND	ND	ND	49.6 ± 15.8	ND	26.5 ± 11.5	54.9 ± 23.6
Rhodomela confervoides	429.0 ± 26.9	ND	ND	ND	ND	86.9 ± 10.4	ND	18.9 ± 10.4	69.1 ± 34.8

Photoprotectant pigments

Concentrations of chlorophylls and carotenoids in the male and female tissues of the fucoid algae *Fucus vesiculosus* were not found to be significantly different, except for the photoprotectant pigment β,β-carotene ($p < 0.05$) (Fig. 3). The highest concentrations of β,β-carotene occurred in the male gametic tissues. However, in both male and female tissues, β,β-carotene was significantly higher ($p < 0.05$) in gametic than in vegetative tissues.

DISCUSSION

Plant pigment as biomarkers

Selective plant pigment ratios in Phaeophyceae collected from the Baltic proper are significantly different from similar ratios typically found in dominant phytoplankton. For example, the range of fucoxanthin/Chl-*a* ratios in the Phaeophyceae of this region is 0.34 to 0.64 compared to values typically greater than 1.00 in fucoxanthin containing phytoplankton (i.e. diatoms) (Bianchi et al., unpublished data) (Table 2). Similar values of fucoxanthin/Chl-*a* ratios have been reported for seaweeds (Ramus et al. 1976, 1977) decreasing with depth from 0.42 at the surface to 0.34 at a depth of 4 m; thus, it is likely that there are even lower ratios in the subtidal *Fucus vesiculosus* population growing down to 8 m in the Baltic. Pure cultures of the diatom *Phaeodactylum tricornutum* have been shown to have ratios of 0.90 (Bidigare 1989). Fucoxanthin/Chl-*a* ratios among the different brown macroalgae are similar enough that it would not be possible to distinguish between different species (Table 2).

The relative importance of littoral-derived macroalgae versus subtidal benthic communities remains an important question in the Baltic. On a yearly cycle, the brown macroalgae *Pilayella littoralis* is detached from rocky bottoms along the Baltic coast (Wallentius 1979). However, it remains uncertain whether this carbon is transported to local sediments, remineralized, or transported to deeper waters. The rocky littoral zone has been shown (Kautsky 1995) to contribute 12-56 % of the annual primary production in coastal areas of the Baltic, with large variations over the year. For example, there is usually a peak in May-June consisting of brown algae (i.e. *Pilayella/Ectocarpus*) followed by a later pulse from the green alga *Cladophora glomerata*. Much of this material is believed to be transported and deposited in the soft-bottom sediments of the region. During the spring bloom, phytoplankton biomass equals that of macroalgae, while in summer it represents only about 15% of the total macroalgal biomass (Kautsky 1995). In late autumn, *Ceramium tenuicorne* is detached by storm events which may also tear off old fragments of

Table 2. Plant pigment ratios in eleven dominant macroalgae collected from the Baltic Sea (Baltic proper) in 1994. All ratios are based on the pigment concentrations listed in Table 1. Fuco. = Fucoxanthin, β,β-Caro. = β,β-Carotene, Vio. = Violaxanthin, Lut. = Lutein, Zea. = Zeaxanthin.

Algae	Chl-*b*/*a*	Chl-c_1,c_2/*a*	Fuco./Chl-*a*	cis-Fuco./Chl-*a*	*β*,*β*-Caro./Chl-*a*	Vio./Chl-*a*	Lut./Chl-*a*	Zea./Chl-*a*
CHLOROPHYCEAE								
Cladophora glomerata	0.30	-	-	-	0.08	0.13	0.19	-
Enteromorpha intestinalis	0.20	-	-	-	0.06	0.10	0.15	-
PHAEOPHYCEAE								
Chorda filum	-	0.14	0.34	0.10	0.12	0.18	-	-
Dictyosiphon foeniculaceus	-	0.30	0.54	0.14	0.29	0.42	-	-
Fucus vesiculosus	-	0.22	0.64	0.31	0.27	0.49	-	-
Pilayella littoralis	-	0.24	0.48	0.30	0.13	0.36	-	-
RHODOPHYCEAE								
Ceramium tenuicorne	-	-	-	-	0.23	-	0.13	0.34
Furcellaria lumbricalis	-	-	-	-	0.12	-	0.13	0.38
Phyllophora spp.	-	-	-	-	0.36	-	0.08	0.35
Polysiphonia nigrescens	-	-	-	-	0.22	-	0.12	0.24
Rhodomela confervoides	-	-	-	-	0.20	-	0.04	0.16

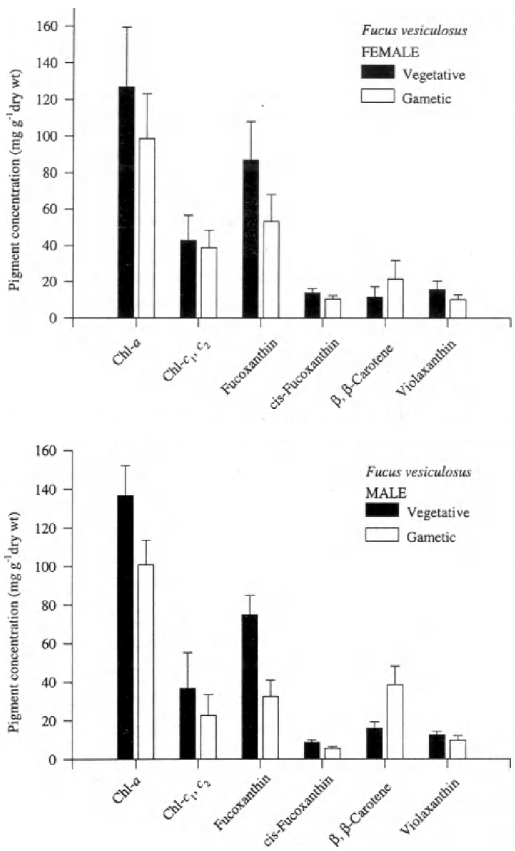

Fig. 3. Plant pigment concentrations in male and female tissues (vegetative and gametic) of *Fucus vesiculosus* collected from the Baltic Sea (Baltic proper). Error bars denote standard deviation (n = 4).

Fucus vesiculosus, a fraction accumulates along the shoreline and is typically found in the drift bank, or may be deposited in subtidal sediments.

Although pigment ratios can change during transport and decomposition of detritus, ratios in estuarine surface sediments have been shown to be useful in documenting 'fresh' source inputs, prior to any significant diagenetic effects (Bianchi et al. 1993; Bianchi et al. 1995). Recent laboratory work demonstrated that pigment decay rates in Baltic sediments were strongly influenced by the presence of oxygen, with higher decay rates in oxic versus anoxic sediments (Abele-Oeschger 1991; Bianchi et al., unpublished data). Despite the effects of post-depositional decomposition on pigment signatures, we have found a good correlation with sedimentary pigments and source inputs to sediments in the Baltic proper (Bianchi et al., unpublished data). Other studies have also shown that accumulation rates of selected carotenoids (i.e. lutein) in sediments of the Kiel Bight correlated well with horizontal transport of macrophytes (Abele-Oeschger 1991).

Low Chl-*b*/*a* ratios of the macrophytic Chlorophyceae in this region may be useful in distinguishing inputs from Chl-*b* and lutein containing phytoplankton, because there is a tendency for green algae to produce more Chl-*b* (Yokohama & Misonou 1980). The ratios typically observed in the macroalgae are 0.20 to 0.30 (Table 2), while that typically found in single-celled chlorophytes is 0.9 (Wood, 1979; Hooks et al. 1988). However, somewhat higher values have been observed in some green macroalgae (i.e. 0.64 at 10 m depth to 0.44 at 1 m in *Ulva lactuca,* and 0.63 in *Codium fragile)* (Ramus et al. 1976, 1977). Another ratio that would be needed to decipher these inputs would be the lutein/Chl-*b* ratio. Macrophytic chlorophytes from our study were in the range of 0.60 to 0.80 (Table 1), while the ratio typically found in single-celled phytoplankton for this region was greater than 1.00 (Bianchi et al. unpublished data). The Chl-*b*/lutein ratio also proved to be very useful in distinguishing between submerged versus emergent macrophytes in the Hudson River estuary (Bianchi & Findlay 1990).

Since the HPLC method used in this study cannot resolve water soluble phycobilin pigments, such as phycoerythrin in rhodophytes, it is not ideal for documenting pigments of these algae. A suitable HPLC methodology for the separation and quantification of phycobilins from natural assemblages does not exist (Swanson & Glazer 1990). However, rhodophytes unlike many other macrophytes do contain zeaxanthin (Rowan 1989) (Table 1). The problem of cyanobacteria also containing zeaxanthin can be resolved by analyzing for the presence of other cyanobacterial pigments such as echinenone, myxoxanthophyll, and oscillaxanthin, which are absent in rhodophytes. Also, the zeaxanthin/Chl-*a* ratio can be used to determine inputs of Rhodophyceae versus cyanobacteria; the range found in rhodophytes from this study was 0.16 to 0.49 (Table 2), which is significantly lower than that typically found in cyanobacteria (greater than 0.50) (Bidigare et al. 1989).

Photoprotectant plant pigments

Significantly higher concentrations of the photoprotectant pigment β,β,-carotene in the gametic versus the vegetative tissues of the brown algae *Fucus vesiculosus* may suggest that this plant has evolved a mechanism for protecting its genetic material from UV radiation while growing near the surface. *Fucus vesiculosus* grows extensively in the depth interval from 0.5 to 8 m and subtidal regions of the Baltic Proper (Kautsky et al. 1992). When growing in shallow regions it is clearly evident that receptacles floating on the water surface have a distinctly brighter orange color in comparison to the blades of the plant. Based on pigment analyses, it appears that much of this color is attributable to the significantly higher concentrations of β,β-carotene in both

male and female structures of the plant (Fig. 3). Moreover, male gametes have significantly higher concentrations than female gametes, imparting a distinct bright orange color to sperm cells (personal observation). This protective pigment has also been observed (via the bright orange color) in the large surface blooms of cyanobacteria that occur in the Baltic each summer (personal observation). Previous work has shown that enhanced production of this carotenoid by cyanobacteria resulted in an increase in chlorophyll-a specific photosynthetic O_2 production (PAERL et al. 1983; PAERL 1984). Further work is needed to determine if the photosynthetic efficiency of *Fucus vesiculosus* is enhanced in plants containing more β,β-carotene, and to document whether there are differences in the fitness of male and female gametes containing different concentrations of β,β-carotene.

CONCLUSIONS

Selective plant pigment ratios in the Phaeophyceae (fucoxanthin/Chl-*a*) and Chlorophyceae (Chl-*b*/*a*) from macroalgae collected in the Baltic proper are significantly different from those found in dominant phytoplankton of the region. These differences may allow for the separation of macrophytic versus planktonic organic carbon inputs to subtidal sediments. The ramifications of using these biomarkers should prove useful in determining the relative importance of these two dominant source inputs to benthic communities in the Baltic proper. The Rhodophyceae may also provide some useful pigment ratios (zeaxanthin / Chl-*a*) in differentiating between macroalgal versus planktonic inputs. However, the dominant phycobilin pigments were not resolved by the current HPLC methodology. Significantly higher concentrations of the photoprotectant pigment β,β,-carotene in the gametic versus the vegetative tissues of the brown algae *Fucus vesiculosus* may suggest that this plant has evolved a mechanism for protecting its genetic material from UV radiation when growing in shallow waters. Finally, the series of peaks of detached brown macroalgal material in June, green algae in July, and a mixture of red and green algae in late autumn after storm events in the Baltic (KAUTSKY 1995), may create a sequence of potentially useful signals where these pigment biomarkers can be used to separate inputs from pelagic and benthic sources.

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