

Do sediments from coastal sites accurately reflect time trends in water column phytoplankton? A test from Himmerfjärden Bay (Baltic Sea proper)

Abstract—Long-term (1977–2000) ecological biomass data for total phytoplankton, diatoms, and cyanobacteria, based on plankton samples from Himmerfjärden Bay (Baltic proper), were compared to the historical sediment record using diagnostic plant pigment biomarkers. Radionuclides (^{210}Pb and ^{137}Cs) were used to determine chronology, sedimentation, and carbon burial rate. Despite high resolution sampling, using crust-freeze sampling, of sediment layers representing annual varves, no significant correlations between pigments preserved in sediments and phytoplankton biomass in plankton samples were detected for periods of 1–4 yr. This lack of correspondence was probably at least partly due to the importance of resuspension events in Himmerfjärden. When sedimentary pigments were averaged over longer time intervals (5 yr) averages of annual diatom biomass in the Himmerfjärd inlet were positively correlated to down-core concentrations of fucoxanthin ($r^2 = 0.98$) and diatoxanthin ($r^2 = 0.62$). This indicates that pigment biomarkers can still be used to interpret longer term development of eutrophication-related blooms in such estuarine systems. In contrast, zeaxanthin concentrations were not significantly correlated ($p > 0.05$, $r^2 = 0.05$) to cyanobacterial biomass as a 5-yr average. Using fossil pigments to determine relative differences in phytoplankton biomass composition in the absence of historical ecological patterns of phytoplankton composition can be misleading due to selective losses of pigments such as the epoxy-carotenoids. However, while the use of fossil pigments in laminated sediments alone may not allow for detailed interpretations of past phytoplankton communities, it does allow for the simple determination of the presence of significant biomass of phytoplankton classes, for which unique biomarker pigments exist.

There is increasing evidence that primary production in the Baltic Sea has increased in the second half of the 20th century due to enhanced nutrient loadings (Larsson et al. 1985; Stigebrandt 1991). These indications of eutrophication in the Baltic Sea resulted in large-scale efforts to address the issue of eutrophication in coastal waters (Rosenberg et al. 1990). One of the water bodies used for examining the effects of nutrients from municipal wastewater and runoff from agricultural land on coastal eutrophication in the 1980s was Himmerfjärden, an enclosed bay located in the southern archipelago of Stockholm. Since 1974, this bay had been receiving treated municipal wastewater from the Himmerfjärden sewage treatment plant, which served some 240,000 inhabitants in the southern Stockholm area in 1993 (Elmgren and Larsson 1997, 2001). Approximately biweekly collections of water for analysis of nutrients, phytoplankton production, and phytoplankton composition in Himmerfjärd Bay started in 1976 (Elmgren and Larsson 1997), and continue still. Macrofauna have been monitored annually in Himmerfjärden bay since 1972 (Elmgren and Larsson 1997). Most benthic macrofauna disappeared from the deepest part of the inner bay during an anoxic event in 1976, resulting

in the deposition of well-defined laminated sediments from this time (Schaffner et al. 1992). Although large-scale temporal changes in nutrients and phytoplankton dynamics of the Baltic Sea proper have thus been documented, the nutrient and production status of the Baltic and its coastal areas prior to anthropogenic inputs (pristine stage) can only be approximately inferred (Elmgren 1989).

Laminated sediment chronologies of organic and inorganic phosphorus, nitrogen, and carbon, as well as biogenic silica and carbon have been used to study the long-term development of eutrophication in lacustrine systems (Edmondson 1974; Conley et al. 1993) and in the open Baltic Sea (Jonsson et al. 1990). Plant pigments have also been used effectively as paleoindicators of historical changes in phytoplankton assemblages in lacustrine systems, where laminated sediments provide excellent environments for pigment preservation (Watts and Maxwell 1977). More specifically, fossil pigments have been used as indicators of a broad spectrum of processes in paleolimnology such as past production, algal and bacterial community composition, trophic levels, redox changes, lake acidification, and past UV radiation (Leavitt and Hodgson 2001). In estuarine ecosystems, highly variable physical controlling parameters, extreme spatial gradients, and bioturbation have limited the application of these techniques (Nixon 1988). In spite of these limitations, sediment cores have been used to interpret the long-term historical trends of eutrophication in estuaries that have long-term ecological records such as the Chesapeake Bay, over time scales of 100 to 300 yr (Cornwell et al. 1996; Zimmerman and Canuel 2000) to 2,500 yr (Cooper and Brush 1991). Recent work has also used stable carotenoid biomarkers, such as zeaxanthin, to reconstruct the historical occurrences of cyanobacterial blooms in the open Baltic Sea for the past 8,000 yr (Bianchi et al. 2000; Poutanen and Nikkilä 2001). However, to date no attempt has been made to compare the historical changes in phytoplankton assemblages obtained from pigment biomarkers in dated sediment cores in an estuarine system with the historical long-term ecological data sets that are available.

The laminated sediments of Himmerfjärden Bay provide a unique opportunity to examine the relationship between long-term ecological data (i.e., phytoplankton biomass composition, nutrients, and benthos) and plant pigment biomarkers preserved in laminated sediments. Thus, the objectives of this study were (1) to use radionuclides (^{210}Pb and ^{137}Cs) to determine chronology, sedimentation, and carbon burial rates at the core site in Himmerfjärden Bay; (2) to compare long-term data sets of total phytoplankton, diatom, and cyanobacterial biomass based on microscopical counts of plankton samples collected from 1977 to 2000 in Himmerfjärden Bay to the historical sediment record of diagnostic plant pigment biomarkers in a crust-freeze sediment core;

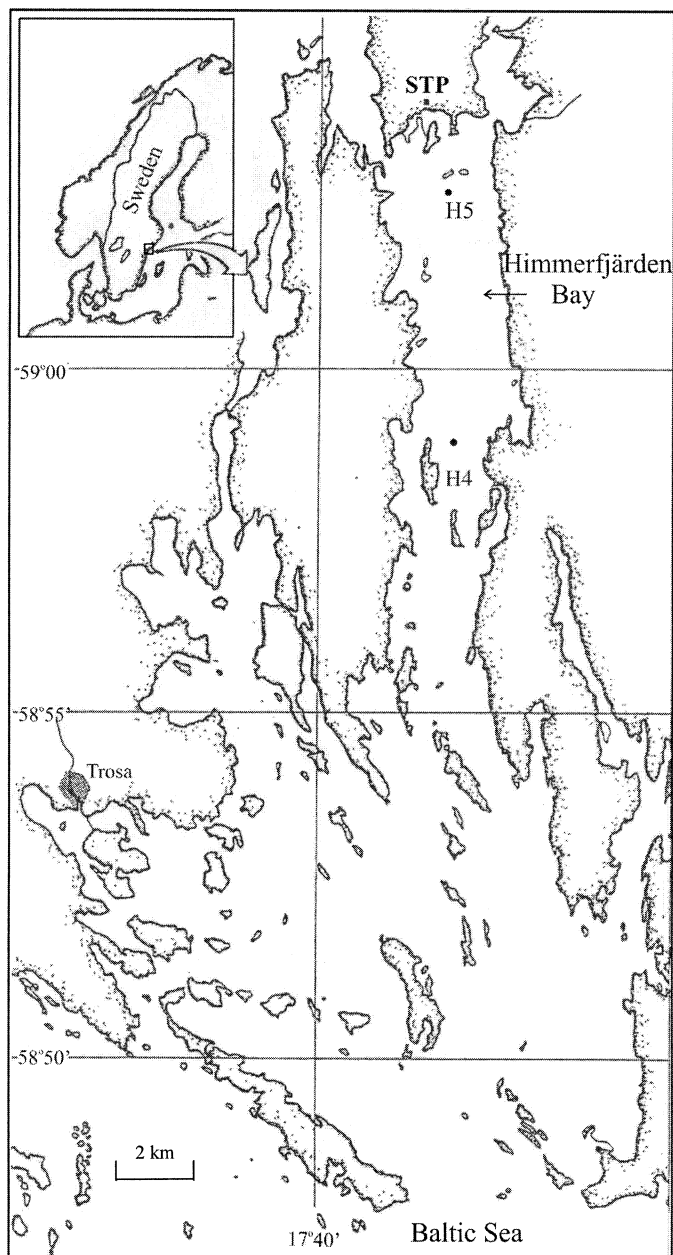


Fig. 1. Map showing the Himmerfjärden area, Sweden, with the location of the H-4 plankton collection station, the H-5 sediment core site, and the sewage treatment plant (STP).

(3) to evaluate the usefulness of pigment biomarkers in the sediment record for reconstructing the eutrophication history of estuarine environments.

Materials and methods—Site description and field sampling: The field site for sediment core collection was located within Himmerfjärden Bay, a brackish coastal bay (174 km², Elmgren and Larsson 1997) located in the southern Stockholm archipelago (Fig. 1). The core station (H-5) in Himmerfjärden has an average salinity of 6‰ and a water depth of 25 m (Elmgren and Larsson 1997).

A series of cores were collected from station H-5 in Oc-

tober 2000 using a box corer (Blomqvist and Boström 1987) with minimal disturbance to surface layers. The presence of *Beggiatoa*, a bacterium living at the reduced sediment–water interface, attests to collection of little disturbed surface sediments. A single core showing the highest resolution of laminations over a depth range of 29 cm was selected for analysis. A subcore was collected within the box core using a modified crust-freeze sampler (Renberg 1980). The core was sliced according to varves (annual laminations) using a scalpel, lyophilized, and analyzed for total carbon and nitrogen, plant pigments, and radionuclides.

Phytoplankton analyses: Phytoplankton samples have been collected from a 0–14-m depth interval using an integrating hose (inner diameter 25 mm) at a nearby station (H-4, in the same basin, but 7 km south of H-5) at approximately biweekly intervals (20–25 times yr⁻¹) from 1976 onward (Hajdu unpubl. data). Sediment cores collected at the H-4 site were not well laminated, so our comparisons between phytoplankton biomass in plankton samples and pigment biomarkers in sediments had to be based on H-5 sediments, the closest location where laminations were found. Samples were preserved using acidified Lugol's solution and counted in a NIKON inverted microscope using phase contrast at ×100 to ×600 magnification. Cell volumes were calculated from cell geometry based on optical measurements of cell size. For calculation of carbon content, plasma volume of diatoms and cell volume of all other algae were multiplied by a factor of 0.11 (for armored dinoflagellates by 0.13). Counting, cell volume, and a carbon biomass calculation followed the recommendations in HELCOM (1988). Loss of many samples from 1991 left that year without annual phytoplankton averages, so an average of 1990 and 1992 was used instead.

Sediment pigments: Plant pigments were extracted and analyzed by high-performance liquid chromatography (HPLC) according to the methods of Wright et al. (1991), as modified by Bianchi et al. (2000). The method allowed for adequate resolution of dominant peaks of interest: fucoxanthin (a biomarker for diatoms), chlorophyll *a* (a general biomarker for overall biomass; Wright et al. 1991), and zeaxanthin (a biomarker for cyanobacteria). A high-purity HPLC standard for chlorophyll *a* was obtained from Sigma Co. Fucoxanthin, zeaxanthin, and diatoxanthin standards were obtained from DHI Co. in Denmark. Pheopigment standards (pheophytin *a* and *b*, and pyropheophorbide *a* and *b*) were made in our laboratory based on the procedures of Bianchi et al. (2000). All pigments were normalized to total carbon content in the sediments to reflect the relative importance of different phytoplankton classes to total inputs of phytodetritus over time.

Organic carbon and nitrogen measurements: Organic carbon and nitrogen were measured on an elemental analyzer (Carlo Erba 1500 Series 1). Valine (48 % C, 10% N) and Merck Gel (38% C, 13% N) were used as standards. Precision was always <5% for both C and N.

Radionuclides: sample preparation and analysis: Dry ground sediment samples for radiochemical analyses

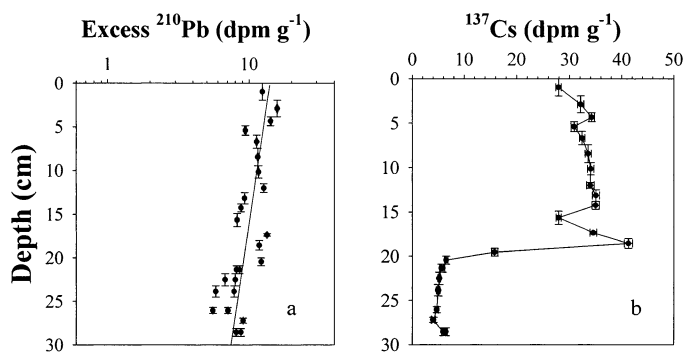


Fig. 2. (a) Excess ^{210}Pb versus cumulative mass and (b) ^{137}Cs concentration (dpm g^{-1}) profile in sediments collected at station H-5 in the Himmerfjärden area, Sweden.

($^{210}\text{Pb}_{\text{excess}(x_s)}$ and ^{137}Cs) were sealed in vials and equilibrated for three weeks. Activities of radionuclides were determined using gamma spectroscopy on a closed-end coaxial well detector. Detector efficiency as a function of material density for each radionuclide was determined from a series of standards covering the range of densities observed in the study area. Total ^{210}Pb activity was directly determined by measuring the 46.5-KeV gamma peak. Supported levels of ^{210}Pb were determined by measuring the gamma activity of ^{214}Pb (295 and 352 KeV) and ^{214}Bi (609 KeV). Self-absorption corrections were made on each sample following the technique of Cutshall et al. (1983). ^{137}Cs activities were determined by measurement of its 662-KeV gamma peak. ^{137}C is an impulse tracer (produced from atmospheric nuclear tests), which was first introduced into the environment in significant amounts in the early 1950s and had peak input in 1963. In addition, the study area received a more recent ^{137}Cs input as a result of the Chernobyl nuclear reactor accident in 1986. A geochronology was established using the down-core distribution of excess ^{210}Pb activities (22.3-yr half-life) using a constant initial concentration model (Appleby and Oldfield 1992) and by assigning a date of 1986 to the ^{137}Cs impulse peak (DeMaster et al. 1985).

Statistical analyses: The program Sigma Plot (Version 5.0) was used for regression analysis in order to test for significant relationships between biomarker pigments and phytoplankton biomass estimates.

Results— ^{210}Pb and ^{137}Cs profiles: The excess ^{210}Pb activities decrease systematically from 15.8 dpm g^{-1} in the surface layer to values of $6\text{--}9 \text{ dpm g}^{-1}$ at the bottom of the core (Fig. 2). The ^{137}Cs activities in the sediment cores ranged from 27.9 dpm g^{-1} at the surface to a distinct peak of 41.3 dpm g^{-1} at a depth of 18.55 cm (Fig. 2). Below the peak, ^{137}Cs activities decrease sharply to values of $4\text{--}5 \text{ dpm g}^{-1}$ at the bottom of the core.

Total carbon and nitrogen: Percent total nitrogen and carbon in H-5 sediments (0–28 cm) ranged from 0.2 to 0.4 and 2.1 to 3.2, respectively (Fig. 3). Molar C:N ratios generally ranged from 7.2 to 9.1, indicative of phytoplankton inputs.

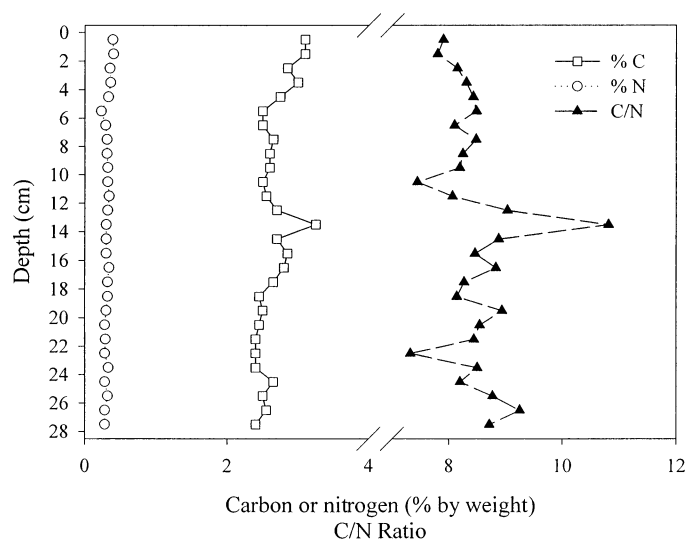


Fig. 3. Percent total nitrogen and carbon, and C:N molar ratios in sediments at station H-5 in the Himmerfjärden area, Sweden.

Plant pigments: Chlorophyll *a* concentration profiles in H-5 sediments ranged from 88 to $431 \text{ nmol (g organic carbon)}^{-1}$ and revealed two clear subsurface peaks in 1980/81 and 1988/89, followed by the most recent deposition layer of phytodetritus in 2000 (Fig. 4). There was clearly a diagenetic loss of chlorophyll *a* in the top 4 cm. High concentrations of pheopigments (pheophytin, pyropheophorbide) in the surface layers and at depth reflected the loss of parent chlorophyll *a* to these decay products. Fucoxanthin (a biomarker for diatoms) concentrations in the top 4 cm also showed diagenetic losses with the most prominent subsurface peak ($103 \text{ nmol (g organic carbon)}^{-1}$) occurring in 1985/86 (Fig. 4). Although diatoxanthin (a biomarker for diatoms) showed less diagenetic alteration in surface layers, it generally followed the same depth profile as fucoxanthin with a high subsurface peak ($212 \text{ nmol (g organic carbon)}^{-1}$) in 1985/86. Concentrations of zeaxanthin (a biomarker for cyanobacteria) ranged from 15 to $99 \text{ nmol (g organic carbon)}^{-1}$ and showed minor diagenetic effects in surface layers, with the two most prominent subsurface peaks occurring in 1985/86 and 1988/89 (Fig. 4).

The highest total phytoplankton biomass values were recorded between 1980 and 1984 (Fig. 5). Chlorophyll *a* and/or chlorophyll *a* plus pheopigments in sediments did not show any significant correlations with total phytoplankton biomass in the water column. Diatom biomass in plankton samples, collected from 1977 to 2000 at station H-4, indicated that the highest annual average values occurred between 1982–1985 and 1989 (Fig. 5). The most prominent fucoxanthin and diatoxanthin subsurface peaks in sediments from H-5 were also observed at 1985/1986—just following the peak of diatom biomass in 1982–1985 (Fig. 5).

Regression analyses between sediment pigment concentrations of specific biomarkers versus microscope counts of corresponding phytoplankton classes were performed based on all data and averaged for 5-yr intervals—covering the span of years from 1980 to 2000. When using the finest time resolutions (1–4 yr) of all pigment data in sediments versus

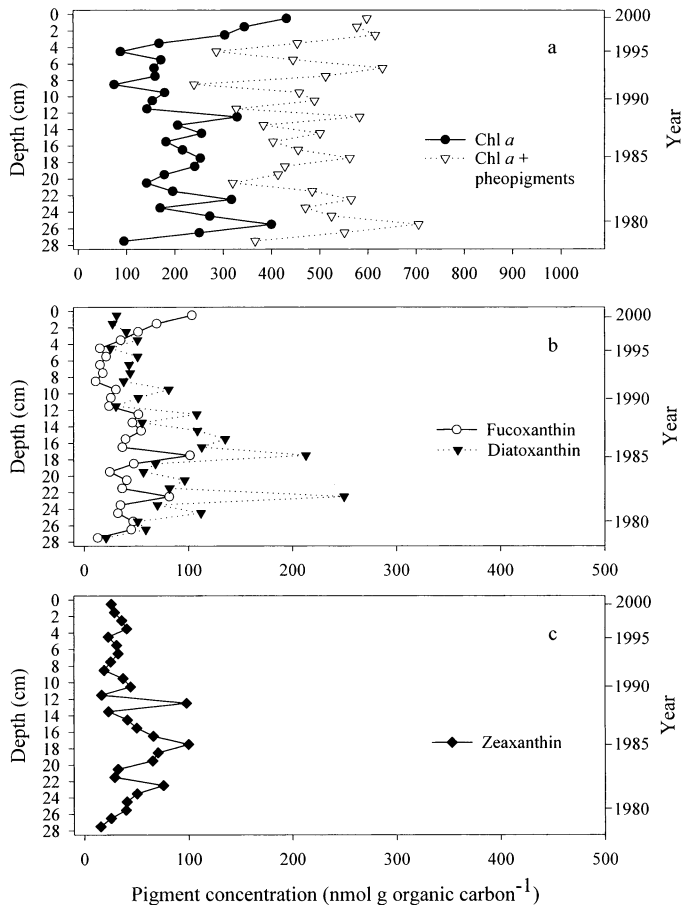


Fig. 4. (a) Concentration profiles ($\text{nmol g organic carbon}^{-1}$) of chlorophyll *a*, (b) fucoxanthin, and (c) zeaxanthin in sediments collected at station H-5 in the Himmerfjärden area, Sweden.

selected phytoplankton biomass data from plankton samples, there were no significant correlations (Fig. 6). However, when combining the data in 5-yr intervals of time we did find significant correlations with certain carotenoids but not with chlorophyll (Fig. 7). For example, while chlorophyll *a* in sediments versus total phytoplankton biomass in plankton samples was not significantly correlated ($r^2 = 0.12$), chlorophyll *a* and dominant pheopigments (pheophytin and pyrropeophytin) combined showed a more significant trend ($r^2 = 0.46$) (Fig. 7). However, it should be noted that the clustering of points at one end of the regression versus one point at the other range of concentrations makes this relationship very weak. Fucoxanthin and diatoxanthin showed significant correlations between sediment concentrations and diatom biomass in plankton samples ($p < 0.05$, $n = 5$, $r^2 = 0.98$) and ($p < 0.05$, $n = 5$, $r^2 = 0.62$), respectively (Fig. 7). In contrast, zeaxanthin was not correlated ($p > 0.05$, $n = 5$, $r^2 = 0.05$) to cyanobacterial biomass even as a 5-yr average.

Discussion—Sediment chronology: The observed scatter in excess ^{210}Pb profile is likely due to a non-steady state sedimentation regime on a decadal time scale (i.e., annual sediment fluxes that vary from year to year). The pattern of regular fluctuations in ^{210}Pb activity downcore has been ob-

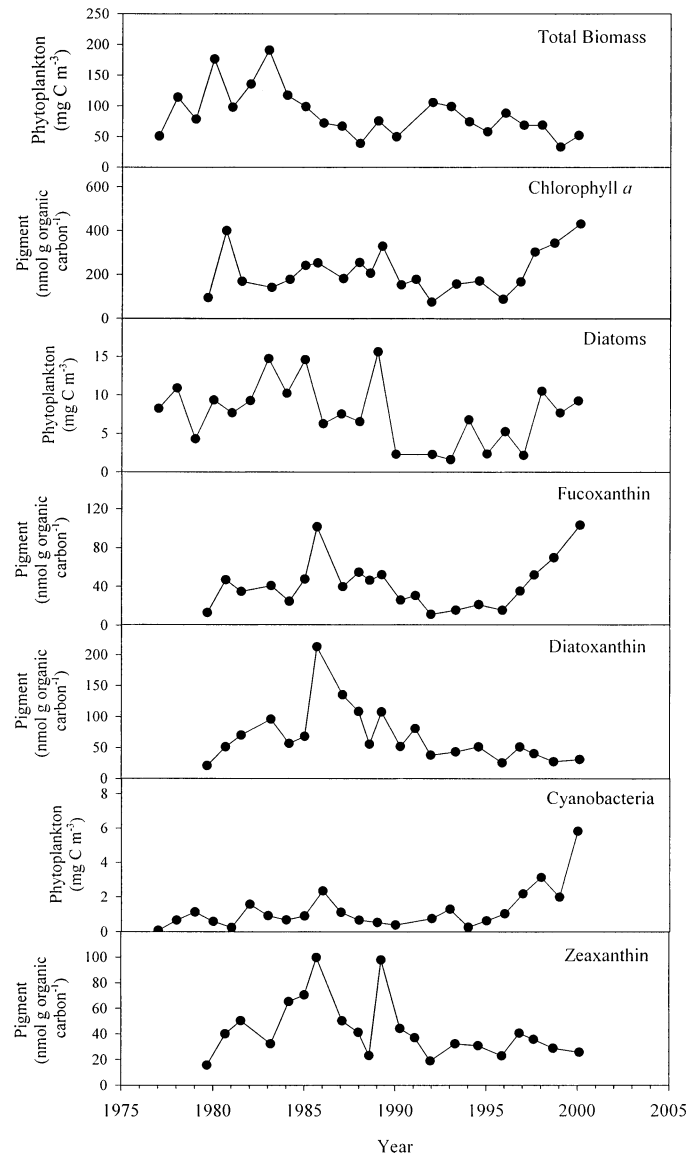


Fig. 5. Plant pigment (chlorophyll *a*, fucoxanthin, diatoxanthin, and zeaxanthin) concentrations ($\text{nmol g organic carbon}^{-1}$) in annual sediment layers (dated using radionuclides) at station H-5 and average annual total phytoplankton, diatom, and cyanobacterial biomass ($\mu\text{g C m}^{-3}$) at station H-4 in Himmerfjärden, Sweden, during the years 1977 to 2000.

served in other environments where the seasonal or inter-annual supply of particulate material varies (e.g., Kuehl et al. 1986). A regression ($r^2 = 0.51$) yields a mean sedimentation rate of 1.36 cm yr^{-1} for the 29 cm core, corresponding to a time interval of approximately 20 yr. If a date of 1986 (corresponding to the Chernobyl accident) is assigned to the depth interval where the peak ^{137}Cs activity is observed, the resulting sedimentation rate is 1.32 cm yr^{-1} . Therefore, the excess ^{210}Pb and ^{137}Cs chronologies closely agree. Sampling intervals ranged from 0.3 to 2.0 cm, depending on the thickness of the lamination that was dissected. Lamination counts place the peak ^{137}Cs value in 1987, not 1986, as also observed in the Stockholm Archipelago (M. Meili pers.

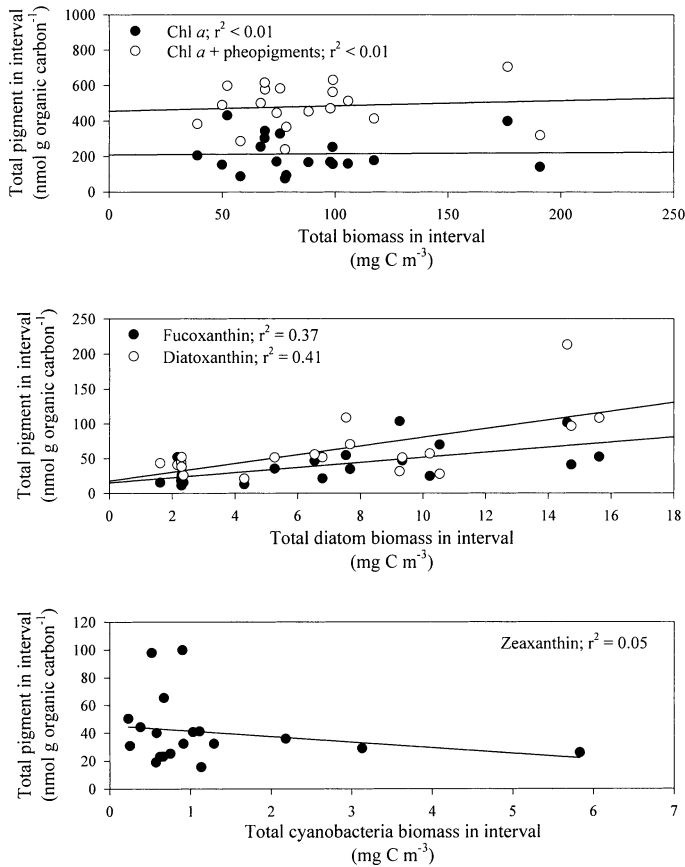


Fig. 6. Regressions of plant pigment (chlorophyll *a*, fucoxanthin, diatoxanthin, and zeaxanthin) concentrations (nmol g organic carbon⁻¹) in annual sediment layers (dated using radionuclides) at station H-5 versus average annual biomass ($\mu\text{g C m}^{-3}$) of total phytoplankton, diatoms and cyanobacteria at station H-4 in Himmerfjärden, Sweden, for the years 1979 to 2000.

comm.), which is still in good agreement with radioactive datings. The activities of excess ²¹⁰Pb and ¹³⁷Cs in the surface interval (0–1.95 cm) were lower than in the intervals immediately below, which is usually indicative of active mixing to this depth. The regular fluctuations in the ²¹⁰Pb profiles are consistent with resuspension and redeposition of surface sediments in the study area and the resultant homogenization of tracer activities within the affected surface interval.

Historical bloom events: Averages of annual diatom biomass over 5-yr intervals in the Himmerfjärd inlet were positively correlated to down-core concentrations of fucoxanthin and diatoxanthin, which indicates that pigment biomarkers can be used to interpret the long-term bloom development in estuarine systems. Despite the high resolution sampling in crust-freeze sampling, significant correlations between pigments and phytoplankton total biomass averaged over 1–4 yr were not significant. Previous studies in lakes have shown good agreement between historical phytoplankton data and fossil pigments (Leavitt and Findlay 1994; Leavitt et al. 1999). In fact, Tunnicliffe (2000) successfully reconstructed a 130-yr record of organic carbon content and stable isotope composition using varved sediments from Saanich

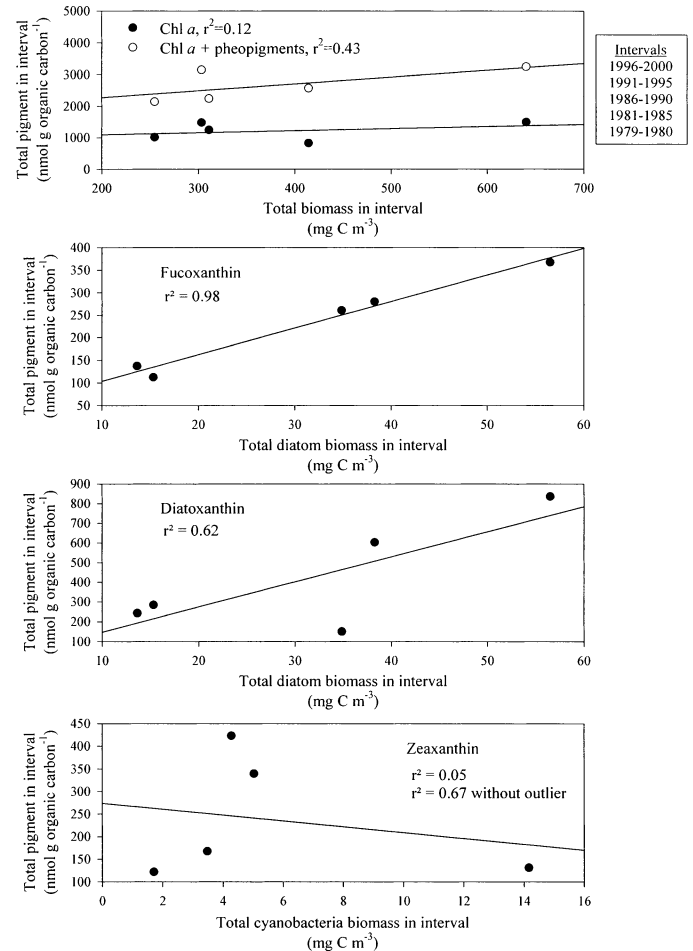


Fig. 7. Regressions of plant pigment (chlorophyll *a*, fucoxanthin, diatoxanthin, and zeaxanthin) concentrations (nmol g organic carbon⁻¹) in annual sediment layers (dated using radionuclides) at station H-5 versus average annual biomass ($\mu\text{g C m}^{-3}$) of total phytoplankton, diatoms and cyanobacteria at station H-4 in Himmerfjärden averaged over 5-yr intervals, Sweden, for the years 1979 to 2000.

Inlet, British Columbia. The lack of correlation between pigment concentrations and phytoplankton biomass data over intervals of 1–4 yr in this study was likely due to differential rates of phytoplankton cell settlement between classes and, perhaps most importantly, sediment resuspension and sediment transport in Himmerfjärden (Blomqvist and Larsson 1994). Based on plankton samples, the highest annual average diatom biomass for the period 1977–2000 occurred in 1982–1985 and 1989, and the highest recorded inorganic nitrogen load to the Himmerfjärden Basin (over 1,100 metric tons) occurred in 1985. The highest recorded input of phosphate (35 metric tons) occurred in 1984, due to an experimental increase in phosphorus loading conducted from November 1983 to October 1984, and higher than usual phosphate concentrations persisted into spring of 1985 (Elmgren and Larsson 1997). An exceptionally early spring bloom resulted in a very high annual average for diatom biomass in 1989. Despite the details that are available on annual changes in nutrient concentrations and phytoplankton

biomass, we were not able to reconstruct these annual changes in phytoplankton composition based on fine resolution sampling of pigments in sediments. The lack of correlation between phytoplankton biomass and pigments in sediments on an annual to semiannual basis may also stem from the fact that we are comparing phytoplankton samples from one location and sediments pigments from another within Himmerfjärden Basin—albeit only 7 km away.

Overall, there was no significant correlation between cyanobacterial biomass and sediment zeaxanthin concentrations. Picoplanktonic cyanobacteria, which are an important component of phytoplankton biomass in Himmerfjärden in summer (Larsson and Hagström 1982), were not included in the microscopic counts of cyanobacteria due to their small size, but may have contributed to sediment zeaxanthin input. Another possible reason for this lack of correlation may be the gas vacuoles of larger cyanobacteria, which mean that they sediment out of the water column less efficiently than diatom blooms and may lead to erratic patterns of sedimentation. Conversely, other studies in lake and coastal environments have used zeaxanthin as an effective biomarker of past changes in cyanobacterial biomass (Chen et al. 2001; Leavitt and Hodgson 2001)

Factors affecting pigment preservation: Significantly higher concentrations of zeaxanthin than of fucoxanthin in H-5 sediments are likely due to differences in the relative chemical stability of these pigment biomarkers. Factors controlling pigment inputs and preservation in sediments can be divided in predepositional (i.e., photooxidation, grazing, microbial decay) and postdepositional (i.e., bioturbation oxygen levels, microbial decay) processes (Leavitt and Hodgson 2001). If we assume that the inputs of zeaxanthin to H-5 sediments were lower than fucoxanthin, and the pigment (fucoxanthin or zeaxanthin) to biomass ratios were similar between diatoms and cyanobacteria at the time of deposition, the most likely reason for higher concentrations of zeaxanthin in sediments (with consistently lower annual biomass of cyanobacteria than of diatoms in the plankton) is the greater chemical stability of zeaxanthin.

Decay constants have been shown to differ greatly among pigments, with very stable carotenoids such as β carotene (all plants) and zeaxanthin (cyanobacteria) versus labile carotenoids such as fucoxanthin (diatoms) and peridinin (dinoflagellates) (Repeta and Gagosian 1987; Bianchi et al. 1991, 2000). It has been suggested that the more labile epoxide-containing pigments such as fucoxanthin and peridinin undergo rapid degradation because of epoxide rearrangement that destroys the center of the conjugated double-bond system (Repeta and Gagosian 1987). Therefore, using fossil pigments to determine relative differences in phytoplankton composition, in the absence of historical ecological patterns of phytoplankton composition, can be misleading due to selective losses of pigments such as the epoxy-carotenoids (Leavitt and Hodgson 2001). While the use of fossil pigments alone may, thus, not allow for detailed interpretations of past phytoplankton communities, it does allow for the simple determination of the presence of different phytoplankton classes in laminated sediments and should also be useful for establishing between-year variability of algal

groups with unique pigment markers (Leavitt and Hodgson 2001), except in near-surface layers with rapid diagenetic changes.

Possible effects of resuspension: Resuspension events at this station typically account for much more than 50% of the gross sedimentation rate (Blomqvist and Larsson 1994). The common occurrence of resuspension events at the H-5 station may explain why a significant relationship was observed between diatom biomass in plankton samples and fucoxanthin and diatoxanthin concentrations in these sediments only for a time interval of 5 yr. It is likely that large and variable input of sediments resuspended from shallower bottoms prevented a correlation between fucoxanthin and chlorophyll *a* and the average water column diatom biomass for shorter time intervals. Owing to its greater chemical stability, more zeaxanthin may have remained in the resuspended material, masking any correlation with water column biomass. However, both zeaxanthin and fucoxanthin were found to be good indicators of increased eutrophication on the Louisiana shelf, an area where resuspension events are common (Chen et al. 2001). Moreover, that study was able to use bacteriochlorophylls as biomarkers of anoxygenic phototrophic green sulfur bacteria, which indicated past hypoxic events on the shelf. Thus, favorable redox conditions can clearly enhance the preservation of labile pigments, rendering them useful for historical reconstructions. Other studies have also used lipids as paleobiomarkers in environments where preservation was high due to periodic or more persistent conditions of low oxygen, such as the Chesapeake Bay (Zimmerman and Canuel 2000) and the Black Sea (Sun and Wakeham 1994), respectively.

Based on pigment biomarkers and the range of C:N ratios (7–11), much of the carbon input to this region is clearly derived from sedimentation of autochthonous production (i.e., phytoplankton blooms). That lamination counts dated the subsurface ^{137}Cs peak to 1987, rather than the Chernobyl year of 1986, may reflect a delayed ^{137}Cs input, since the greatest input of Chernobyl ^{137}Cs in the region occurred after an intense rainfall further north along the Baltic coast (Saxén and Ilus 2001). The carbon burial rate at H-5, based on vertical profiles of ^{210}Pb and ^{137}Cs , about $220 \text{ gC m}^{-2} \text{ yr}^{-1}$, was similar to the phytoplankton production of about $207 \text{ gC m}^{-2} \text{ yr}^{-1}$ at H4 (average of 1977–1992, Larsson et al. 1994). Since only a small fraction of phytoplankton production is normally sequestered in sediments, this attests to the importance of sediment resuspension and sediment focusing at the study site. While much of the spring diatom bloom settles out, later blooms give proportionally much less sedimentation, which may explain why we did not see a significant correlation between total phytoplankton biomass in plankton samples and total chlorophyll + pheopigments in sediments for any studied interval (1–5 yr).

In conclusion, phytoplankton biomass in Himmerfjärden Bay did not correlate with selective chlorophyll *a* concentrations in annually laminated sediments for a period of 1–4 yr and neither did biomass of select algal classes with their associated pigment biomarkers in sediments. This lack of correlation results from within-year variability in the settlement of plankton, resuspension of sediments, and differential

decay of specific biomarkers; it precludes annual scale reconstruction of phytoplankton biomass from sediment cores in coastal areas of the Baltic Sea. Five-year averaged diatom biomass in phytoplankton samples and concentrations of diatom pigment biomarkers in sediments were positively correlated in contemporaneously deposited sediment layers, indicating that pigment biomarkers do reflect longer term bloom development in estuarine systems with anoxic, laminated sediments. Finally, assuming that inputs of zeaxanthin to core site sediments were lower than fucoxanthin, the most likely reason for higher concentrations of zeaxanthin in sediments is its greater chemical stability.

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References

APPLEBY, P. G., AND F. OLDFIELD. 1992. Application of lead-210 to sedimentation studies. *In* M. Ivanovich and R. Harmon [eds.],

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- Uranium-series disequilibrium: Applications to Earth, marine and environmental sciences. Clarendon.
- BIANCHI, T. S., S. FINDLAY, AND D. FONTVIELLE. 1991. Experimental degradation of plant material in Hudson River sediments. I. Heterotrophic transformations of plant pigments. *Biogeochemistry* **1**: 17–33.
- , P. WESTMAN, C. ROLFF, E. ENGELHAUPT, T. ANDRÉN, AND R. ELMGREN. 2000. Cyanobacterial blooms in the Baltic Sea: Natural or human induced? *Limnol. Oceanogr.* **45**: 716–726.
- BLOMQUIST, S., AND K. BOSTRÖM. 1987. Improved sampling of soft bottom sediments by combined box and piston coring. *Sedimentology* **34**: 715–719.
- , AND U. LARSSON. 1994. Detrital bedrock elements as tracers of settling resuspended particulate matter in a coastal area of the Baltic Sea. *Limnol. Oceanogr.* **39**: 880–896.
- CHEN, C., T. S. BIANCHI, B. A. MCKEE, AND J. M. BLAND. 2001. Historical trends of hypoxia on the Louisiana shelf: Application of pigments as biomarkers. *Org. Geochem.* **32**: 543–561.
- CONLEY, D. J., C. L. SCHELSKE, AND E. F. STORMER. 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Mar. Ecol. Prog. Ser.* **101**: 179–192.
- COOPER, S. R., AND G. S. BRUSH. 1991. Long-term history of Chesapeake Bay anoxia. *Science* **254**: 992–996.
- CORNWELL, J. C., D. J. CONLEY, M. OWENS, AND J. C. STEVENSON. 1996. A sediment chronology of the eutrophication of Chesapeake Bay. *Estuaries* **19**: 488–499.
- CUTSHALL, N. H., I. L. LARSEN, AND C. R. OLSEN. 1983. Direct analysis of ²¹⁰Pb in sediment samples: Self-absorption corrections. *Nucl. Instrum. Methods* **206**: 309–312.
- DEMASTER, D. J., B. A. MCKEE, C. NITTRouer, Q. JIANGCHU, AND C. GUODONG. 1985. Rates of sediment accumulation and particle reworking based on radiochemical measurement from continental shelf deposits in the East China Sea. *Cont. Shelf Res.* **4**: 143–158.
- EDMONDSON, W. T. 1974. The sedimentary record of eutrophication of Lake Washington. *Proc. Natl. Acad. Sci. U.S.A.* **71**: 5093–5095.
- ELMGREN, R. 1989. Man's impact on the ecosystem of the Baltic Sea—energy flows today and at the turn of the century. *Ambio* **18**: 326–332.
- , AND U. LARSSON. 1997. Himmerfjärden: Förändringar i ett näringsbelastat kustekosystem i Östersjön. Swedish Environmental Protection Agency, Report **4565**: 1–197.
- , AND ———. 2001. Eutrophication in the Baltic Sea area: Integrated coastal management issues, p. 15–35. *In* B. von Bodungen and R. K. Turner [eds.], *Science and integrated coastal management*. Dahlem Univ. Press.
- HELCOM. 1988. Guidelines for the Baltic Monitoring Programme for the third stage. *Balt. Sea Environ. Proc.* **27D**: 1–161.
- JONSSON, P., R. CARMAN, AND F. WULFF. 1990. Laminated sediments in the Baltic—A tool for evaluating nutrient mass balances. *Ambio* **19**: 152–158.
- KUEHL, S. A., D. J. DEMASTER, AND C. A. NITTRouER. 1986. Nature of sediment accumulation on the Amazon continental shelf. *Cont. Shelf Res.* **6**: 209–225.
- LARSSON, U., R. ELMGREN, AND F. WULFF. 1985. Eutrophication and the Baltic Sea: Causes and consequences. *Ambio* **14**: 9–14.
- , AND Å. HAGSTRÖM. 1982. Fractionated phytoplankton primary production, exudate release and bacterial production in a Baltic eutrophication gradient. *Mar. Biol.* **67**: 57–70.
- , A. SJÖSTEN, AND K. SKÄRLUND. 1994. Himmerfjärdsundersökningen. Stockholm Univ. Department of Systems Ecology, Tech. Rep. **15**: 1–106.
- LEAVITT, P. R., AND D. L. FINDLAY. 1994. Calibration of fossil pigments with 20 years of phytoplankton data from eutrophic

- Lake 227, Experimental Lakes Area, Ontario. *Can. J. Fish. Aquat. Sci.* **51**: 2286–2299.
- , R. I. HALL, AND J. L. SMOL. 1999. Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: Evidence from paleolimnology. *Limnol. Oceanogr.* **44**: 757–773.
- , AND D. A. HODGSON. 2001. Sedimentary pigments, p 2–21. *In* J. P. Smol, H. J. B. Birks, and W. M. Last [eds.], *Tracking environmental changes using lake sediments*. Kluwer.
- NIXON, S. W. 1988. Physical energy inputs and the comparative ecology of lake and marine ecosystems. *Limnol. Oceanogr.* **33**: 1005–1025.
- POUTANEN, E.-L., AND K. NIKKILÄ. 2001. Carotenoid pigments as tracers of cyanobacterial blooms in recent and post-glacial sediments of the Baltic Sea. *Ambio* **30**: 179–183.
- RENBERG, I. 1980. Improved methods for sampling, photographing and varve-counting of varved lake sediments. *Boreas* **10**: 255–258.
- REPETA, D. J. 1989. Early diagenesis of carotenoids in recent marine sediments—II. Degradation of fucoxanthin to loliolides. *Geochim. Cosmochim. Acta* **53**: 699–707.
- , AND R. B. GAGOSIAN. 1987. Carotenoid diagenesis in recent marine sediments—I. The Peru continental shelf (15°S, 75°W). *Geochim. Cosmochim. Acta* **51**: 1001–1009.
- ROSENBERG, R., R. ELMGREN, S. FLEISCHER, P. JONSSON, G. PERS-SON, AND H. DAHLIN. 1990. Marine eutrophication case studies in Sweden—A synopsis. *Ambio* **19**: 102–108.
- SAXÉN, R., AND E. ILUS. 2001. Discharge of ¹³⁷Cs and ⁹⁰Sr by Finnish rivers to the Baltic Sea in 1986–1996. *J. Env. Radioactivity* **54**: 275–291.
- SCHAFFNER, L. C., P. JONSSON, R. J. DIAZ, R. ROSENBERG, AND P. GAPCYNKI. 1992. Benthic communities and bioturbation history of estuarine and coastal systems: Effects of hypoxia and anoxia. *Sci. Total Environ., Suppl. Mar. Coast. Eutrophication* 1001–1016.
- STIGEBRANDT, A. 1991. Computations of oxygen fluxes through the sea surface and the net production of organic matter with application to the Baltic and adjacent seas. *Limnol. Oceanogr.* **36**: 444–454.
- SUN, M. Y., AND S. G. WAKEHAM. 1994. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin. *Geochim. Cosmochim. Acta* **58**: 3395–3406.
- TUNNICLIFFE, V. 2000. A fine-scale record of 130 years of organic carbon deposition in an anoxic fjord, Saanich Inlet, British Columbia. *Limnol. Oceanogr.* **45**: 1380–1387.
- WATTS, C. D., AND J. R. MAXWELL. 1977. Carotenoid diagenesis in a marine sediment. *Geochim. Cosmochim. Acta* **41**: 493–497.
- WRIGHT, S. W., AND OTHERS. 1991. Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. *Mar. Ecol. Prog. Ser.* **77**: 183–196.
- ZIMMERMAN, A. R., AND E. A. CANUEL. 2000. A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: Anthropogenic influence on organic matter composition. *Mar. Chem.* **69**: 117–137.

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