



## Preservation conditions and the use of sediment pigments as a tool for recent ecological reconstruction in four Northern European estuaries

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### Abstract

Down-core sediment pigment concentrations from four Northern European estuaries were measured using high-performance liquid chromatography (HPLC) to investigate phytoplankton community structure and preservation conditions over the last ca. 100 years where all sites have experienced different levels of eutrophication. Phytoplankton pigments have been shown to be useful biomarkers for phytoplankton community structure and abundance due to their taxonomic specificity. The pigment concentrations and sediment pigment inventory showed large variation between the four sites. Concentrations ranged from more than 6000 nmol/g OC to less than 100 nmol/g OC and the inventory integrated over the top 10 cm from more than 300 nmol/cm<sup>2</sup> to less than 30 nmol/cm<sup>2</sup> for total identified pigments. Good pigment preservation in Mariager Fjord (Denmark) reflected the almost permanently anoxic conditions. Pigments in Laajalahti (Finland) showed peak concentrations around the time of highest nitrogen loading events known from historical and modelled records over the past 100 years. In contrast, poor down-core preservation of pigments (especially carotenoids) was observed in the Ems-Dollard (The Netherlands) and Himmerfjärden (Sweden) estuaries. The Ems-Dollard site is an intertidal mudflat that experiences daily exposure to light and air, which enhances pigment degradation. In Himmerfjärden, resuspension is an important process affecting both the sedimentation rate and degradation properties. The different preservation conditions at the four sites were supported by the differences in two degradation indicators; the ratio of pheopigment-*a* to chlorophyll-*a* and total carotenoids to total pigments. Class-specific carotenoid pigments represented the dominant algal groups reported from each site, however, no distinct down-core changes in the pigment composition were observed at any of the four sites. This indicated that changes in plankton community structure on the group level have been limited over this time period or masked by low preservation of pigments.

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## 1. Introduction

Pigments preserved in sediment have been shown to be useful indicators of historical changes in phytoplankton production and assemblages (Sanger, 1988; Millie et al., 1993; Leavitt and Hodgson, 2001), and can therefore potentially provide the long-term records needed for interpreting current changes in the environment caused by eutrophication. This is critical, not only in Europe, but around the world where many estuaries have experienced problems with eutrophication (Rabalais and Nixon, 2002). However, it is well known that the majority of pigments are degraded in the water column and in the uppermost sediment before being incorporated into the fossil record (Furlong and Carpenter, 1988; Hurley and Armstrong, 1990; Leavitt, 1993; Bianchi et al., 2002b). Absolute concentrations of pigments should be used with care and interpreted on the basis of the sediment regime at the study site. Factors influencing the sediment pigment record include photo- and chemical oxidation as well as herbivore digestive processes in the water column during deposition and post depositional degradation in the sediment. Changes in grazing pressure can affect both the digestive degradation and preservation through escape from oxidation in the water column by faster downward transport in faecal pellets (Leavitt, 1993; Cuddington and Leavitt, 1999), while the presence of anoxia at the sediment–water interface and lack of benthic macrofauna has been shown to substantially increase the preservation of pigments in sediments (Sun et al., 1993; Bianchi et al., 2000b). The preservation of pigment biomarkers may improve over time with increased primary production reducing oxygen concentrations in the bottom waters, a phenomena that can be difficult to distinguish from an increase in biomarker concentration from simple increases in primary production (Leavitt, 1993).

Extensive work has been carried out on lake sedimentary pigments, which have been shown to reflect changes in the plankton community structure and biomass as a result of eutrophication, changes in grazing pressure and many other processes such as acidification and UV radiation (Leavitt and Hodgson, 2001). Relative to lakes, less extensive work on the preservation and accumulation of sedimentary pig-

ments has been carried out in estuarine and marine environments. For example, studies of pigments preserved in Baltic Sea sediments have demonstrated the occurrence of cyanobacterial blooms over thousands of years (Bianchi et al., 2000a) and changes in concentration of chlorophyll derivatives have been linked to changes in primary production, preservation conditions and climatic phenomena (Kowalewska et al., 1999; Kowalewska, 2001). In addition, the sediment pigment record has recorded fluctuations in plankton community structure in Himmerfjärden, Sweden (Bianchi et al., 2002a), and over a glacial cycle in Antarctica (Hodgson et al., 2003). In the Black Sea and Gulf of Mexico, sediment bacterial pigments have been used to investigate anoxygenic primary production and extent of anoxia, respectively (Repeta, 1993; Chen et al., 2001).

Individual carotenoids can be used as indicators of specific algae classes (Jeffrey et al., 1997). Indicator carotenoids include fucoxanthin (diatoms), diatoxanthin and diadinoxanthin (diatoms, dinoflagellates), alloxanthin (chryptophytes), lutein (green algae and higher plants), and zeaxanthin (cyanobacteria), while  $\beta$ -carotene and chlorophyll-*a* are more general indicators of total algal abundance. However, selective loss of pigments with different stabilities during deposition can affect the relative abundance of specific carotenoid pigments (Sanger, 1988; Hurley and Armstrong, 1990; Leavitt, 1993; Cuddington and Leavitt, 1999; Bianchi et al., 2000b). Examination of pigments individually relative to historical down-core maxima and minima has therefore been suggested as the most reliable method of interpreting the sediment pigment record (Leavitt, 1993). This study focuses on the sediment pigment record as a tool for investigating preservation conditions and possible changes in phytoplankton community over the last 100 years in different estuarine systems. We investigated four estuaries in Northern Europe, each representing different physical and chemical characteristics. The work was carried out as an integrated part of the EU funded MOLTEN project, which collected other multi-proxy evidence from these  $^{210}\text{Pb}$  dated sediment cores, including inorganic biomarkers and biological data (diatom remains, dinoflagellate cysts), some of which are published elsewhere (Vaalgamaa, 2004; Weckström et al., 2004).

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