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Chlorophyll *a* and its derivatives in deep Baltic sediments

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Grażyna Kowalewska
Institute of Oceanology,
Polish Academy of Sciences,
Sopot

Boris Winterhalter
Department of Surficial Geology,
Geological Survey of Finland,
Espoo, Finland

Joanna Konat
Institute of Oceanology,
Polish Academy of Sciences,
Sopot

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Abstract

Deep sediments (to 660 cm) from the Baltic Sea, collected in 1996–1997, were analysed for content of chlorophyll *a* and its immediate derivatives (chlorins: phaeophytin, pyrophaeophytin, phaeophorbides and steryl chlorin esters) using the diode-array HPLC method. These compounds were generally well preserved. The concentrations of both particular and total chlorins varied greatly depending on the sediment layer and were surprisingly high in some cases, comparable to concentrations in contemporary Baltic sediments (0–1 cm layer).

1. Introduction

Research on chlorophyll *a* and its derivatives in old marine sediments gave rise to a new branch of chemistry – organic geochemistry (Treibs, 1936). These were the first compounds to be regarded as 'biological markers'

(Eglinton and Calvin, 1967). To a great extent, it is the environmental conditions that influence the structure of chlorophyll derivatives occurring in sediments, so these compounds can act as paleoindicators (Baker and Palmer, 1978). On the basis of such studies much can be inferred about the history of sediments and their origin. However, since chlorophyll transformation processes are affected by a number of factors, there is still a dearth of knowledge about how the occurrence of particular chlorophyll derivatives is related to environmental conditions. The studies mentioned above were primarily concerned with highly transformed chlorophyll derivatives (porphyrins). The immediate chlorophyll *a* transformation products (chlorins) have received much less attention, especially with respect to quantitative analyses, owing to their instability and the technical difficulties involved. Indeed, it is only the recent development of HPLC techniques that has made such analyses possible (Jeffrey *et al.*, 1997).

The Baltic Sea is a very interesting basin for following the routes of chlorophyll transformation. Nevertheless, though recent sediments (0–10 cm surface layer) from the southern Baltic Sea have been analysed for the possible occurrence of chlorophyll *a* derivatives (Eckardt *et al.*, 1992; Kowalewska, 1994, 1997), the deep sediments have not been previously studied.

2. Experimental

Baltic Sea sediments were collected in the North Central Baltic Basin (NCB) – two cores: NCB–2 (0–256 cm – with a heavy gravity corer, during the cruise of r/v 'Petr Kottsov' in September 1996) and NCB–LL17 (0–60 cm – with a short Niemistö-gravity corer, during the cruise of r/v 'Aranda' in October 1996), and in the Bornholm Basin (BB) (0–657 cm – with a vibrohammer corer, during the cruise of r/v 'Aranda' in April 1997). For comparison, recent sediments (0–10 cm) were collected in the Gulf of Gdańsk, in the deepest part of the southern Baltic Sea ($\sim$100 m water depth) and near the port of Gdynia ($\sim$26 m depth). The location of the sampling stations is given in Fig. 1.

Details of extraction and further analysis have been described previously (Kowalewska, 1994, 1997; Kowalewska *et al.*, 1996). A frozen sample (*ca* 1–10 g) was left to thaw and the excess water was removed by centrifugation. The samples were extracted ultrasonically with acetone. Next, tetrapyrroles from the acetone extract were re-extracted to benzene. The benzene extract was evaporated to dryness, the residue dissolved in a small amount of acetone (200–1500 μl) and analysed by HPLC. Particular pigments were identified by comparing their retention times and spectra with the relevant values of standards. They were quantified on the basis

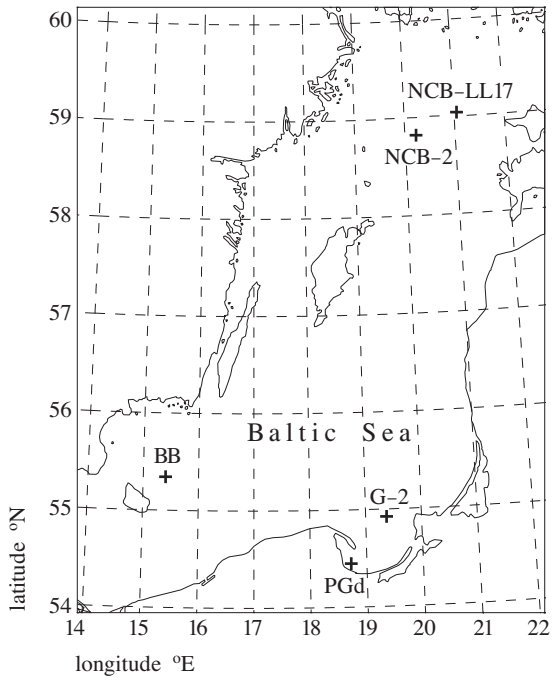

Fig. 1. Location of the sampling stations

of UV–VIS spectrophotometric measurements of an acetone extract at a wavelength corresponding to the maximum absorption of a pigment, and the ratio of the area under the peak corresponding to the pigment to the total integrated area of all the peaks (as a percentage) in diode-array HPLC chromatograms, at the same wavelength. In the case of fluorescence measurements, very low concentrations of chlorins were quantified by means of the calibration curve obtained from spectrophotometric and HPLC (both diode-array and fluorescence) measurements for the same extract. For these measurements an HPLC set (Knauer) with two detectors, a diode-array (Barspec Chrom-a-Scope) and a fluorescence detector (Shimadzu RF–551) were used. The HPLC standards were prepared by TLC (CAMAG-Linomat IV).

3. Results and discussion

The chlorins in the study samples were generally well preserved, an indication of reducing conditions and a high sedimentation rate. The sum of chlorins *a* concentrations (chlorophyll *a*, phaeophytin *a*, pyrophaeophytin *a*, phaeophorbides and steryl chlorin esters) varied from 0.42 to 172.25 nmol g^{-1} and was independent of the sediment layer depth, *e.g.*

at a depth of 100–250 cm in the North Central Basin these concentrations were comparable to those of contemporary sediments in the Gulf of Gdańsk (Fig. 2).

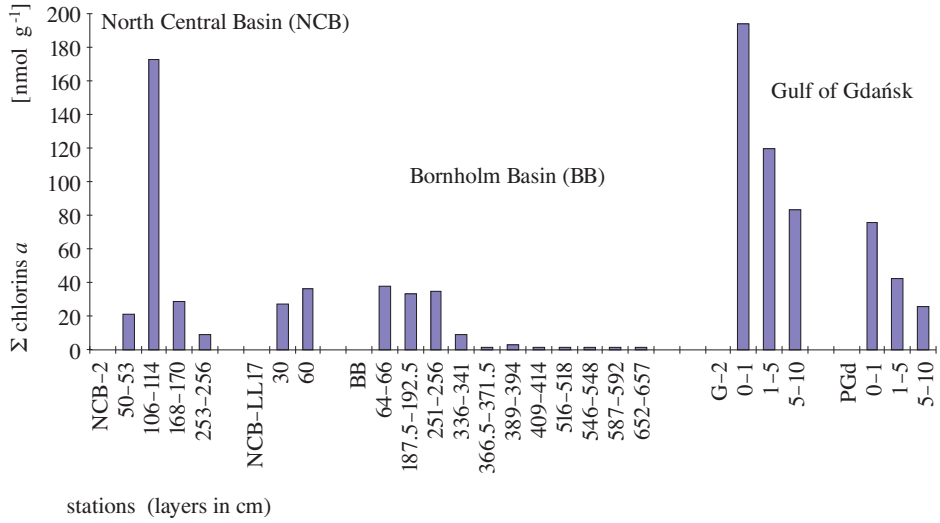

Fig. 2. Sum of chlorins *a* in the Baltic sediments

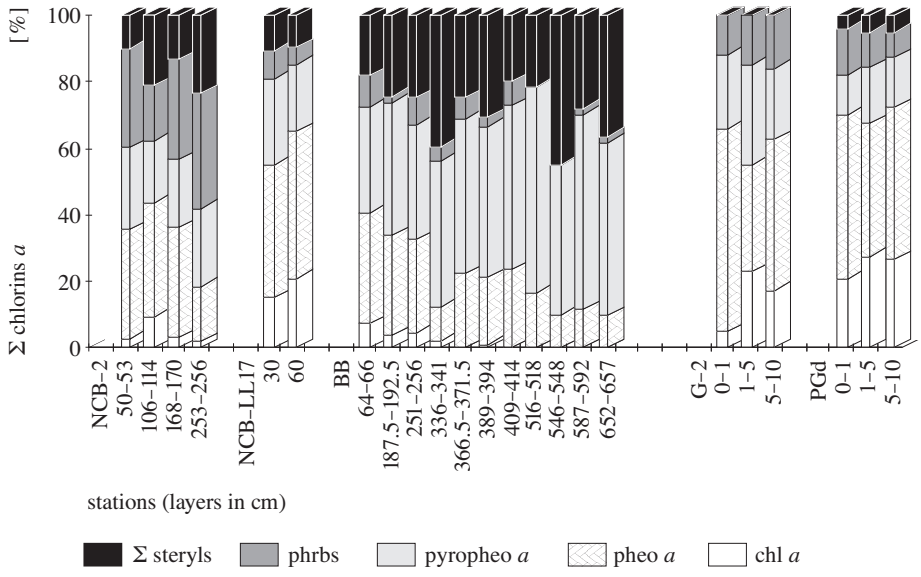

Fig. 3. Percentage of particular chlorins *a* in the sum of chlorins *a*; chl *a* – chlorophyll *a*, pheo *a* – phaeophytin *a*, pyropheo *a* – pyrophaeophytin *a*, phrbs – phaeophorbides, Σ steryls – sum of steryl chlorin esters

Concentrations of particular compounds also varied; their proportions in the sum of chlorins *a* are shown in Fig. 3. The transformation of chlorophyll *a* passed through phaeophytin and phaeophorbides to pyrophaeophytin and steryl chlorin esters. Undecomposed chlorophyll *a* was found in considerable amounts down to a depth of 370 cm and *e.g.* in the North Central Basin the concentration of chlorophyll *a* at a depth of *ca* 100 cm in the sediment was similar to that in recent sediments from the Gulf of Gdańsk. This could have been due to rapid accumulation, a high rate of primary production at the time of sediment formation, and low temperatures and anoxic conditions in and above the seafloor at that time and afterwards. Such a slow deterioration of chlorophyll also suggests a lack of micro-organisms in the sediment layer examined.

References

Baker E. W., Palmer S. E., 1978, *Geochemistry of porphyrins*, [in:] *The porphyrins*, D. Dolphin (ed.), Acad. Press, New York–San Francisco–London, 486–552.

Eckardt C. B., Pearce G. F., Keely B. J., Kowalewska G., Jaffé R., Maxwell J. R., 1992, *A widespread chlorophyll transformation pathway in the aquatic environment*, Org. Geochem., 19, 217–227.

Eglinton C. B., Calvin M., 1967, *Chemical fossils*, Sci. Am., 216, 32–43.

Jeffrey S. W., Llewellyn C. A., Barlow R. G., Mantoura R. F. C., 1997, *Pigment processes in the sea: a select bibliography*, [in:] *Phytoplankton pigments in oceanography*, S. W. Jeffrey, R. F. C. Mantoura and S. W. Wright (eds.), UNESCO Monogr. Oceanogr. Meth., Paris, 173–174.

Kowalewska G., 1994, *Steryl chlorin esters in sediments of the southern Baltic Sea*, Neth. J. Aquat. Ecol., 28, 149–156.

Kowalewska G., 1997, *Chlorophyll a and its derivatives in recent sediments of the southern Baltic Sea*, Oceanologia, 39 (4), 413–432.

Kowalewska G., Witkowski A., Toma B., 1996, *Chlorophylls c in bottom sediments as markers of diatom biomass in the southern Baltic Sea*, Oceanologia, 38 (2), 227–249.

Treibs A., 1936, *Chlorophyll and hemin derivatives in organic materials*, Angew. Chem., 49, 682–686.