

Horizontal and vertical distribution of lignin in surface sediments of the Gdańsk Basin*

OCEANOLOGIA, 43 (4), 2001.
pp. 421–439.

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KEYWORDS

Baltic Sea
Organic matter
Oxidation provenience

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Manuscript received 14 November 2001, reviewed 19 November 2001, accepted 21 November 2001.

Abstract

The aim of this study was to identify and quantify lignin transported from the River Vistula to the accumulation area in the Gdańsk Basin. Sediment samples collected along the Vistula mouth–Gdańsk Deep transect were analysed for lignin.

Lignin was characterised by oxidative degradation, cupric oxide being chosen as the most suitable oxidising agent. The polar functional groups of the oxidation products were silylated and the derivatives analysed by capillary gas chromatography on fused capillary silica columns with flame ionisation detection.

Lignin-derived oxidation products were quantified in the range from 3 to 20 $\mu\text{g g}^{-1}$ dry wt. for phenolic acids and from 6 to 12 $\mu\text{g g}^{-1}$ dry wt. for phenolic aldehydes. Differences in oxidation products contents are assigned to different lignin sources in the marine environment.

The horizontal and vertical gradients of these compounds in the sediments of the Gdańsk Basin are documented. The results are discussed in terms of the origin and fate of organic matter in the Gdańsk Basin. The measured differences in quality and quantity of the identified oxidation products provide insight into diagenetic processes in the surface marine sediments.

* The study was carried out as part of the Sopot Institute of Oceanology's statutory programme No. 3.1.

1. Introduction

The contents and functions of organic matter in the marine environment have been investigated for decades (Hedges & Ertel 1982). The presence of organic matter (including humic acids) affects processes taking place in the marine environment and modifies the behaviour of many compounds, for example heavy metals and pesticides (Förster & Salomons 1981, Pempkowiak 1997, Staniszewski et al. 2000). The extent of these influences depends on the content as well as on the physical and chemical properties of the organic matter (origin, age).

Quantification of terrestrial organic matter in marine sediments is of particular importance in shelf seas, which have been significantly affected by land use changes and anthropogenic impact over the last hundred years. One example is the Baltic Sea, which is characterised by a freshwater surplus of $1800 \text{ m}^3 \text{ s}^{-1}$ (Omstedt 1990) in the north, and inflows of saline ($\sim 35\text{‰}$) water from the North Sea via the Kattegat connection in the south. The resulting salinity gradient (from 2‰ in the Gulf of Bothnia to 25‰ in the Danish Straits) and the permanent halocline are other notable features. Red-ox conditions in the water and sediments below the halocline depend on intrusions of oxygenated water from the North Sea. This is because the oxygen below the halocline is rapidly consumed by suspended matter abundant in organic matter. The bottom topography of the Baltic consists of a series of basins separated by sills restricting bottom water circulation and material exchange between the basins. Those basins below the halocline ($\sim 30\%$ of the seafloor) are depositional areas, the other areas are non-depositional or erosional (Miltner & Emeis 2001).

Also characteristic of the Baltic Sea are the large production of organic matter, significant run-off, low average water temperature and low degree of organic matter mineralisation (Gudelis & Jemielianow 1982). However, the content, origin and sources of the organic matter are still poorly understood. It is difficult to quantify these sources because of the chemical, biological and physical dynamism of the sea system (Vanderbrucke et al. 1985, Pempkowiak 1989).

It is well known that terrestrial organic matter makes up a large proportion of the organic matter in the Baltic Sea (Pempkowiak & Pocklington 1982, Miltner & Emeis 2001). However, the available data are insufficient for identifying the origin of organic matter in particular basins. One way of determining the proportion of terrestrial organic matter is to apply chemical markers (Hedges & Ertel 1982). Lignin provides the best way of differentiating between terrestrial and marine organic matter, since only higher plants, common on land, contain it. Lignin compounds, which are phenol-like polymers, are major constituents of vascular plant cell walls.

As a result of their natural abundance, wide distribution and resistance to degradation, lignins are also commonly found in soil and sedimentary organic matter. However, analysis of the chemical structure of lignins is troublesome, owing to difficulties in isolating and depolymerising them. We do know that they are polyphenols consisting of monomers with a characteristic propylbenzoic carbon structure. Propylbenzoic monomers usually contain methoxy groups bound to aromatic rings (Pempkowiak 1989). Several bonding structures, including ether (C–O–C) and hydroxyl (C–OH), are found in the complex lignin macromolecule. Despite the limited number of base monomers, lignin macromolecules demonstrate enormous structural complexity (Stevenson 1982). The qualitative and quantitative analysis of organic compounds characteristic of higher plant tissues provides an opportunity to determine quantitatively the allochthonous organic matter fraction (Miltner & Emeis 1999). Components of terrestrial and marine organisms proved that lignins are very selective in this respect (Gardner & Menzel 1974, Waleńczak 1987).

Lignin polymers in plant tissues, soils, and sediments are not subject to direct chemical analysis without prior isolation and derivatisation. However, lignin in such samples can be characterised by chemical degradation to release small molecules and then can be extracted from the reaction mixture and quantified by a variety of chromatographic techniques. Phenolic aldehydes and phenolic acids are the predominant products of lignin oxidation and are often used for characterising lignins in marine sediments (Hedges & Ertel 1982).

The aim of this work was to establish the composition of lignin oxidation products in the surface and subsurface sediments of the Gdańsk Basin. Lignin oxidation products from ^{210}Pb dated layers of sediment cores were analysed by gas chromatography and the contents were used for evaluating the origin of organic matter in the southern Baltic.

2. Materials and methods

2.1. Sediment sampling

Sediment cores were collected during cruises of r/v 'Oceania' in the Gdańsk Basin. The locations of the sampling stations and their characteristics are given in Fig. 1 and Table 1.

Cores I5/A00 and I8/A00 were taken with a Niemistö type corer designed to collect soft sediments without disturbing the sedimentary stratification (Niemistö 1974). A Reneck-type box corer was used to collect sandy sediments from stations BCI11/A00 and BCI14/A00.

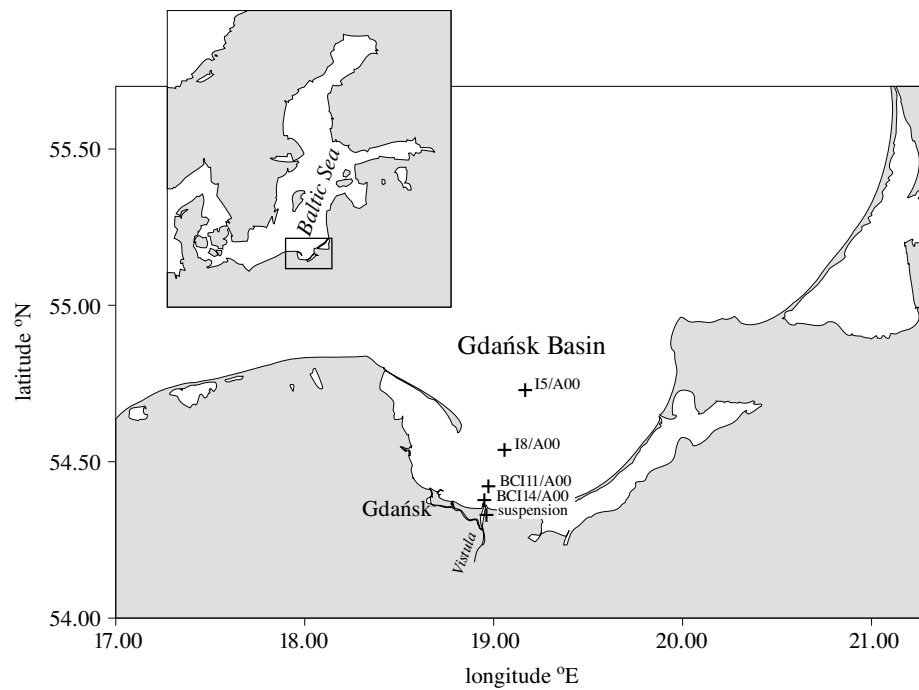


Fig. 1. Location of sampling stations in the Gdańsk Basin

Table 1. Characteristic of sampling stations

| Location of sampling station | Station | Geographic coordinates | | Water depth [m] | Sediment core length [cm] | Sample type |
|------------------------------|-----------|------------------------|--------------|-----------------|---------------------------|-------------|
| | | latitude °N | longitude °E | | | |
| Gdańsk Deep | I5/A00 | 54°42.94' | 19°15.06' | 100 | 40 | mud |
| Gdańsk Deep | I8/A00 | 54°30.03' | 19°04.05' | 70 | 32.5 | mud |
| Gulf of Gdańsk | BCI11/A00 | 54°23.03' | 19°00.01' | 40 | 12 | fine sand |
| Vistula estuary | BCI14/A00 | 54°22.05' | 18°57.06' | 13 | 10 | fine sand |
| Vistula mouth | VM | | | 0.5 | | |

The sediment core samples were cut into slices 10 mm (surface) or 25 mm (the subsurface segments of sediment cores) thick, transferred to plastic bags and kept in a deep freezer until analysis on shore.

A sample of about 500 litres of water was collected from the River Vistula, 2 km upstream from the river mouth. Suspended matter was decanted, centrifuged and freeze-dried to yield 2500 mg of dry material.

2.2. Analytical methods

The following parameters were analysed in the laboratory: moisture, organic matter, ^{210}Pb , fine grain fraction content, and lignin oxidation products.

Every other layer (from 5 cm below the water-sediment interface downwards) was analysed from cores I5/A00 and I8/A00, while all layers obtained from cores BCI11/A00 and BCI14/A00 were analysed.

Prior to analysis, the fine fraction ($< 67 \mu\text{m}$) was wet-sieved from the sandy sediments in the BCI11/A00 and BCI14/A00 cores with a $67 \mu\text{m}$ mesh polyethylene net and MilliQ water. Moisture (60°C , 24h) and loss on ignition (450°C , 8h) were measured in each sample.

The cores taken from 100 m and 70 m depth were dated using the natural radioisotope ^{210}Pb . The ^{210}Pb activity was measured in the sub-samples according to a method adapted from Flynn (1968). This technique has been frequently used for dating marine and lacustrine sediments (El-Daoushy et al. 1991, Pempkowiak 1991). 200 mg of freeze-dried sediment sample was wet digested (HF-HClO_4), ^{210}Po was spontaneously deposited on to a silver disc and measured by α -spectrometry using a Si surface barrier detector. Added to the sample prior to the digestion with acids, ^{209}Po was used as an internal standard for following the recovery rates of ^{210}Po in all the samples analysed. The recovery, in the range from 79 to 106%, was used to calculate the actual activities of ^{210}Po . The ^{210}Pb activity was then established assuming isotopic equilibrium with its granddaughter ^{210}Po . Repeat analyses of ^{210}Pb demonstrated the same activity, which thereby validated the assumption. The sedimentation rates were calculated from the ^{210}Pb profile according to the constant rate of supply model and least squares procedure (Robbins 1978, Joshi & Shukla 1991).

Lignin oxidation products were analysed by applying a CuO oxidation procedure (Hedges & Ertel 1982) modified by Hautala et al. (1998). Oxidation was carried out in glass test tubes with Teflon caps at a temperature of 170°C under nitrogen. The test tubes were loaded with sediment sample comprising 50 mg organic matter, 400 mg of powdered CuO, 100 mg of $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 6(\text{H}_2\text{O})$ and 3 ml of NaOH (2M). After 3 h at 170°C , the contents of the test tubes were centrifuged and rinsed with water. The combined supernatants were acidified to pH 1.5 with 6M HCl and centrifuged again. The precipitate was rinsed with acidified water. The combined acidified supernatants were extracted three times with ethyl acetate. The ethyl acetate was then evaporated off and the dry residues were stored in a desiccator at 4°C for derivatisation and GC analysis.

The polar functional groups of the oxidation products were silylated in order to obtain more highly volatile products. The dried products were dissolved in pyridine ($250 \mu\text{l}$) before the addition of $150 \mu\text{l}$ of the silylating

reagent [BSTFA – bis(trimethylsilyl)trifluoroacetamide] and derivatised for 1h at room temperature (Miltner & Emeis 1999). The derivatised products were analysed in a gas chromatograph (Shimadzu 17A) on fused silica capillary columns (Phenomenex ZB-5, 30 m × 0.25 mm × 0.50 μm) with flame ionisation detection.

The GC–FID analyses were performed under the following conditions: initial oven temperature 120°C/2 min, rate of oven temperature increase 3°C/min, final oven temperature 250°C/2 min; temperature of injector and detector: 240°C; carrier gas: helium with a flow rate of 1 ml/min.

Degradation products were quantified with commercial type phenolic acids and phenolic aldehydes (Fluka AG). Calibration curves and recovery rates based on internal standards (2-naphthoic acid) and standard addition of analysed compounds were used for quantitative analyses. The average recovery was $78 \pm 3\%$.

3. Results

The sedimentation regimes, characterised by mixing depth and sedimentation rate in the sediment cores, are presented in Table 2. The results of granulometric analyses given as percentages of fractions in the given diameter range are presented in Tables 3 and 4.

Table 2. Sedimentation regimes in the investigated cores

| Layer [cm] | I5/A00 | | I8/A00 | |
|---------------|------------------|--|------------------|--|
| | age [year] | sedimentation rate [mm year ⁻¹] | age [year] | sedimentation rate [mm year ⁻¹] |
| 0–3 | mixed | 2.1 | mixed | 1.8 |
| 3–4 | 4.5 | | | |
| 4–5 | 13.6 | | | |
| 6–7 | 22.8 | | 12.3 | |
| 8–9 | 31.9 | | 24.5 | |
| 10–11 | 41.0 | | 36.8 | |
| 12–13 | 50.0 | | 49.0 | |
| 14–15 | 59.2 | | 61.4 | |
| 16–17 | 68.3 | | 73.6 | |
| 18–19 | 84.2 | | 95.1 | |
| 20–22.5 | 107.0 | | 125.8 | |
| 25–27.5 | 129.7 | | | |
| 30–32.5 | background value | | background value | |
| core length | 40 | | 32.5 | |

Table 3. Granulometric analyses of sediments from the BCI11/A00

| Sediment layer [cm] | Particle diameter [mm]* | | | |
|------------------------|-------------------------|----------------|----------------|----------------|
| | f ₁ | f ₂ | f ₃ | f ₄ |
| | contribution [%] | | | |
| 0–2 | 0.43 | 2.13 | 46.77 | 51.32 |
| 2–4 | 0.06 | 0.53 | 31.3 | 68.12 |
| 4–6 | 0.1 | 1.89 | 38.26 | 60.82 |
| 6–8 | 0.05 | 1.07 | 38.36 | 60.52 |
| 8–10 | 0.07 | 1.42 | 37.07 | 59.30 |
| 10–12 | 0.13 | 3.61 | 43.85 | 52.41 |

* f₁ > 1; 0.6 < f₂ < 1; 0.4 < f₃ < 0.6; 0.056 < f₄ < 0.4 (mm).

Table 4. Granulometric analyses of sediments from the BCI14/A00

| Sediment layer [cm] | Particle diameter [mm]* | | | |
|------------------------|-------------------------|----------------|----------------|----------------|
| | f ₁ | f ₂ | f ₃ | f ₄ |
| | contribution [%] | | | |
| 0–2 | 0.19 | 0.67 | 6.81 | 92.32 |
| 2–4 | 0.1 | 0.64 | 5.74 | 93.5 |
| 4–6 | 0.19 | 1.76 | 4.46 | 94.6 |
| 6–8 | 0.53 | 1.5 | 8.15 | 89.82 |
| 8–10 | 0.65 | 2.72 | 8.47 | 88.15 |

* f₁ > 1.0; 0.6 < f₂ < 1; 0.4 < f₃ < 0.6; 0.056 < f₄ < 0.4 (mm).

The sediments of both cores are remarkable for the very small contribution of the fraction larger than 1 mm: $0.14 \pm 0.14\%$ and $0.3 \pm 0.24\%$ respectively in cores BCI11/A00 and BCI14/A00. On the other hand, the respective contributions of the fraction 1.00 – 0.4 mm in both cores are very different: $41 \pm 6.28\%$ and $8 \pm 2.16\%$ in cores BCI11/A00 and BCI14/A00. As a consequence, the fine fraction content (> 0.056) differs substantially in the sandy cores: 51.2% in the core BCI11/A00 and 94.6% in BCI14/A00.

Moisture, organic matter content and lignin oxidation products recalculated per 1 g dry weight of sediment (fraction < 0.67 μm) are presented in Tables 5, 6, 7, 8, 9 and 10.

The moisture content varies from 55.05 to 90.68%, decreasing with increasing depth below the sediment-water interface in the I5/A00 and I8/A00 cores. It remains steady in the cores collected from two other locations.

Table 5. Moisture, organic matter and lignin oxidation products in the I5/A00 core

| Sediment layer [cm] | Moisture [%] | Organic matter [%] | Oxidation products* [$\mu\text{g g}^{-1}$ dry wt.] \pm SD | | | |
|---------------------|--------------|--------------------|--|--------------|-------------|---------------|
| | | | A | B | C | D |
| 0–4 | 90 | 22.4 | 7 ± 1 | 62 ± 4 | 42 ± 6 | 57 ± 5 |
| 5–8 | 86.7 | 20.1 | – | 140 ± 8 | 54 ± 12 | 92 ± 8 |
| 9–12 | 82.5 | 17.3 | – | 140 ± 8 | 52 ± 8 | 96 ± 8 |
| 13–16 | 79.2 | 14.2 | – | 170 ± 10 | 70 ± 10 | 4.0 ± 0.5 |
| 17–20 | 65.1 | 13.6 | – | 160 ± 10 | 80 ± 12 | 98 ± 8 |
| 22.5–30 | 73.6 | 12.8 | – | – | 60 ± 9 | 109 ± 9 |
| 37.5–40 | 73.2 | 12.1 | – | 145 ± 9 | 70 ± 10 | – |

*oxidation products:

A – 4-hydroxybenzaldehyde;

B – 4-hydroxy-3-methoxybenzaldehyde (vanilline);

C – 4-hydroxybenzoic acid;

D – 4-hydroxy-3,5-dimethoxybenzoic acid (syringil acid);

SD – standard deviation.

Table 6. Moisture, organic matter and lignin oxidation products in the I8/A00 core

| Sediment layer [cm] | Moisture [%] | Organic matter [%] | Oxidation products* [$\mu\text{g g}^{-1}$ dry wt.] \pm SD | | | |
|---------------------|--------------|--------------------|--|-------------|--------------|--------------|
| | | | A | B | C | D |
| 0–4 | 89.2 | 21.4 | 44 ± 9 | 118 ± 7 | 150 ± 24 | 170 ± 15 |
| 5–8 | 89.2 | 17.2 | 200 ± 41 | – | 150 ± 31 | 300 ± 26 |
| 9–12 | 76.7 | 19.0 | 41 ± 8 | – | 210 ± 31 | 150 ± 13 |
| 13–16 | 74.5 | 15.9 | 46 ± 9 | 90 ± 5 | 250 ± 37 | 180 ± 15 |
| 17–20 | 71.0 | 13.8 | 42 ± 8 | 27 ± 1 | 140 ± 20 | 72 ± 6 |
| 22.5–30 | 60.8 | 7.0 | – | – | 320 ± 48 | 218 ± 19 |

* oxidation products: for explanations of A, B, C, D, see Table 5.

In this study, loss on ignition (LOI) was used as a measure of organic matter. This is substantiated by the high correlation coefficient between organic carbon and loss on ignition found in the Baltic Sea surface sediments (Pempkowiak et al. 1987, Persson & Jonsson 2000). A decrease in LOI with increasing sediment layer depth was found in the investigated sediment cores. LOI ranged between 22.45% in the 0–1 cm layer of the I5/A00 core and 7.03% in the deepest layer of the 8/A00 core.

It is evident that, compared to sediments collected close to the shore, offshore sediments contain large amounts of lignin.

The data obtained indicate that lignin is most abundant in the muddy sediments of the Gdańsk Deep, while the fine-grained fraction of the sandy sediments contain small amounts of lignin (Tables 5–8). The vertical

Table 7. Moisture, organic matter and lignin oxidation products in the BCI14/A00 core

| Sediment layer [cm] | Moisture [%] | Organic matter [%]* | Organic matter [%] | Oxidation products*** [$\mu\text{g g}^{-1}$ dry wt.] \pm SD | | | |
|---------------------|--------------|---------------------|--------------------|--|-----------------|---------------|-------------|
| | | | | A | B | C | D |
| 0–2 | 84.7 | 0.7 | 16.6 | Bdl** | 10 \pm 0.6 | 10 \pm 1 | 15 \pm 1 |
| 2–4 | 86.5 | 0.4 | 16.4 | – | – | 1 \pm 0.1 | 7 \pm 0.6 |
| 4–6 | 88.5 | 0.3 | 15.8 | 5 \pm 1 | 3 \pm 0.2 | 7 \pm 1 | 7 \pm 0.6 |
| 6–8 | 84.9 | 0.2 | 15.5 | 0.22 \pm 0.05 | 0.43 \pm 0.03 | 1.1 \pm 0.2 | 1 \pm 0.1 |
| 8–10 | 84.6 | 0.2 | 14.9 | – | 0.82 \pm 0.05 | 2.3 \pm 0.3 | 2 \pm 0.2 |

*before fractionation; **below detection limit;

***oxidation products: for explanations of A, B, C, D, see Table 5.

Table 8. Moisture, organic matter and lignin oxidation products in the BCI11/A00 core

| Sediment layer [cm] | Moisture [%] | Organic matter [%]* | Organic matter [%] | Oxidation products** [$\mu\text{g g}^{-1}$ dry wt.] \pm SD | | | |
|---------------------|--------------|---------------------|--------------------|---|---------------|------------|---------------|
| | | | | A | B | C | D |
| 0–2 | 55.0 | 0.6 | 11.5 | 5 \pm 1 | 5.2 \pm 0.3 | 12 \pm 2 | 14 \pm 1 |
| 2–4 | 74.6 | 0.5 | 16.8 | 5.3 \pm 0.9 | – | 12 \pm 2 | 13 \pm 1 |
| 4–6 | 72.1 | 0.4 | 17.1 | 4.6 \pm 0.9 | 3.2 \pm 0.2 | 7 \pm 1 | 7.4 \pm 0.6 |
| 6–8 | 70.5 | 0.5 | 14.2 | 3.5 \pm 0.5 | 3.7 \pm 0.1 | 7 \pm 1 | 7.2 \pm 0.6 |
| 8–10 | 60.7 | 0.6 | 10.0 | 4.1 \pm 0.9 | 12 \pm 0.7 | 26 \pm 4 | 18 \pm 1 |
| 10–12 | 67.5 | 0.4 | 9.9 | 3.5 \pm 0.7 | 20 \pm 1 | 21 \pm 3 | 17 \pm 1 |

*before fractionation;

**oxidation products: for explanations of A, B, C, D, see Table 5.

Table 9. Lignin oxidation products normalized to organic matter in the suspended matter isolated from the Vistula river water

| Moisture [%] | Organic matter [%] | Oxidation products* [$\mu\text{g g}^{-1}$ o.m.] \pm SD | | | |
|-----------------|-----------------------|---|------------|--------------|--------------|
| | | A | B | C | D |
| 18.94 | 78.78 | 120 ± 25 | 35 ± 2 | 120 ± 19 | 170 ± 15 |

*oxidation products: for explanations of A, B, C, D, see Table 5.

Table 10. Percentage of allochthonous organic matter in sediments basing on lignin oxidation products

| Station* | Contribution of terrestrial organic matter [%] | | |
|-----------|---|------------|--------|
| | surface | subsurface | entire |
| I5/A00 | 50.0 | 55.4 | 53.0 |
| I8/A00 | 39.0 | 17.5 | 24.7 |
| BCI11/A00 | 6.3 | 10.3 | 8.3 |
| BCI14/A00 | 4.6 | 2.2 | 3.2 |

*The location of sampling stations is given in Fig. 1.

distribution of the oxidation products appears to be irregular. 4-hydroxybenzoic acid followed by 4-hydroxy-3,5-dimethoxybenzoic acid (syringil acid) are the most abundant oxidation products, while 4-hydroxybenzaldehyde is the least abundant one. The results of the quantification of lignin oxidation products in the Vistula suspended matter are presented in Table 9.

4. Discussion

The decreasing downward content of organic matter in sediments can be best explained as the effect of the biochemical mineralisation of organic matter. Surface sediments are more abundant in organic matter owing to the constant flux of organic-rich particulate matter from the water column. Since mineralisation under the oxic conditions, typical of sandy sediments is faster, there is less organic matter in the sandy sediments distributed close to the shore (cores BCI11/A00 and BCI14/A00). The organic matter content in the Baltic Sea is closely related to the content of the fine-grained fraction of sediments (Voipio 1981). This is caused both by sorption on mineral particles and by sedimentation of organic and inorganic colloids in the so-called depositional areas, which are situated in the deeps (Emylyanov 1995).

Lignin-derived oxidation products normalised to organic matter (o.m.) in sediment samples ranged from 0.7 to 330 $\mu\text{g g}^{-1}$ o.m. for phenolic acids and from 0.2 to 204 $\mu\text{g g}^{-1}$ o.m. for phenolic aldehydes (Figs. 8, 9, 10, 11).

Differences in the content and composition of the lignin oxidation products are most often attributed to the various sources of lignin (Hedges & Ertel 1982, Miltner & Emeis 1999, 2001). The measured differences in the quality and quantity of the identified oxidation products, as depicted in Fig. 2, provide additional insight into diagenetic processes in the surface sediments of the Gdańsk Basin. The specific composition of the products can be linked to certain types of terrestrial plants. The cinnamic to vanillic (C/V) and syringic to vanillic (S/V) ratios are usually used (Miltner & Emeis 2001).

The S/V ratios are shown in Fig. 2 as vertical profiles in the investigated cores.

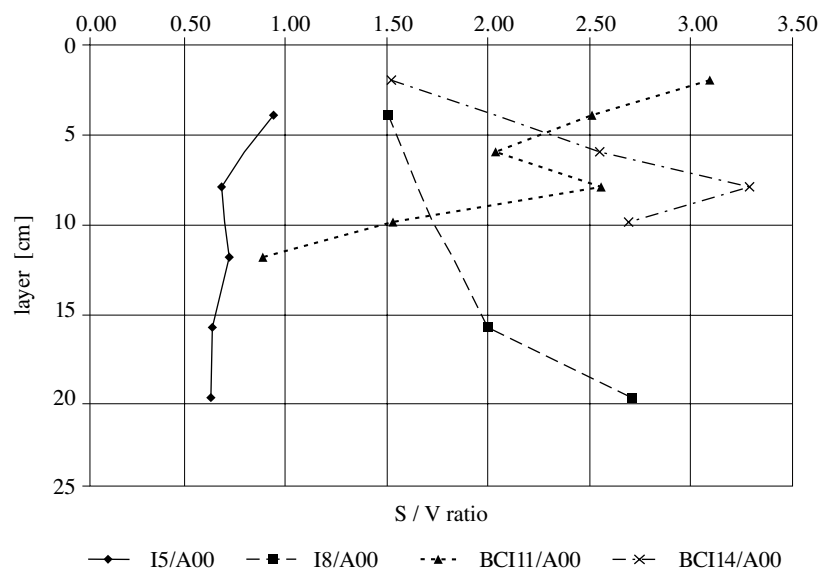


Fig. 2. The dependence of the syringil to vanilline phenol (S/V ratio) on the depth below sediment water interface in the investigated cores

The S/V ratio decreases with increasing depth (cores I5/A00 and BCI11/A00), indicating preferential degradation of syringil phenols and/or the variable origin of the lignin deposited in the sediments. The profiles drawn for the I8/A00 and BCI14/A00 cores indicate that the ratio increases downwards. This may be because both these sampling stations were located at a depth intermediate between the shallow (BCI11/A00) and deep (I5/A00) stations. It has been demonstrated that material deposited at

different depths in the Gdańsk Basin differ in origin (Emylyanov 1995). The observed differences in the S/V ratio in the transect from the river mouth to the Gdańsk Deep can also be attributed to the dependence of the deposited material on the distance from the shore and the depth of the sea.

The strong dependence between organic matter and the S/V ratio is noteworthy. Linear regression correlation coefficients of 0.85 and 0.73 respectively for the I5/A00 and BCI11/A00 cores were calculated (Fig. 3). The feature can be explained again as the preferential degradation of certain lignin fragments and/or as the dependence of the quality of organic matter on the load discharged into the sea. A similar explanation was provided by Louchourn et al. (1998) for the lignin variation in the sediment of the St Lawrence system. Strangely enough, there were no statistically significant correlation coefficients in the case of the two other investigated cores, indicating that the sedimentation regime was different there.

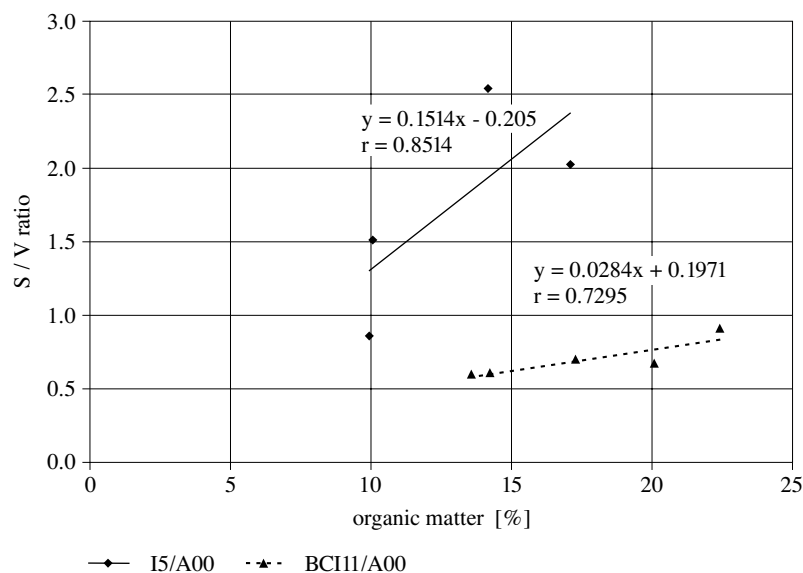


Fig. 3. The relationship between the syringil to vanilline phenol (S/V ratio) and organic matter content in cores I5/A00 and BCI11/A00

A lignin characteristic similar to that found in this study was reported for S/V values in the sediments of Lake Savojärvi in Finland (Hautala et al. 1997). The S/V values ranged from 0.92 to 5.54 (from 0.65 to 2.75 in this study), while in sandy sediments the ratio in Finland ranged from 0.69 to 0.89 (from 0.85 to 3.65 in this study). In the paper by Miltner & Emeis (1999), the values for the Pomeranian Bay in the Baltic Sea show that the ratio is independent of the distance from the shore, possibly because the

sediments are uniform there. The same researchers interpret the organic matter content of the sediments in the Arkona Basin, elevated as compared to the Pomeranian Bay, as the organic matter contribution from additional sources there (Miltner & Emeis 2001). It follows from the data obtained in this study that the lignin in the shallow sandy sediments originates from angiosperms. By contrast, the contribution of angiosperms as a source of lignin in the Gdańsk Deep sediments is small. This supports the conclusion that sedimentary material deposited at varying distances off shore differs with respect to its origin (Persson & Jonsson 2000).

Vanilline phenols were found in just three of the six sediment layers of the core I8/A00, a feature indicating a variable sedimentation regime in the area.

The phenols yields in the I8/A00 core are the highest of all the samples investigated. The total yield of phenols in the I5/A00 core, equal to $1708 \mu\text{g g}^{-1}$ o.m. is some 60% of the I8/A00 yield. This difference can be explained by the much smaller sedimentation rate.

Both cores collected from the sandy bottom sediments show a poor yield of lignin oxidation products (Fig. 7). This confirms the conclusion concerning efficient organic matter mineralisation in oxic environments.

The contents of aldehydic phenols and phenolic acids decrease with increasing depth below the sediment – water interface. This is due to the decreasing amount of organic matter (as a result of biochemical degradation in the sediments). Samples of BCI11/A00 (Fig. 6, 10) and BCI14/A00

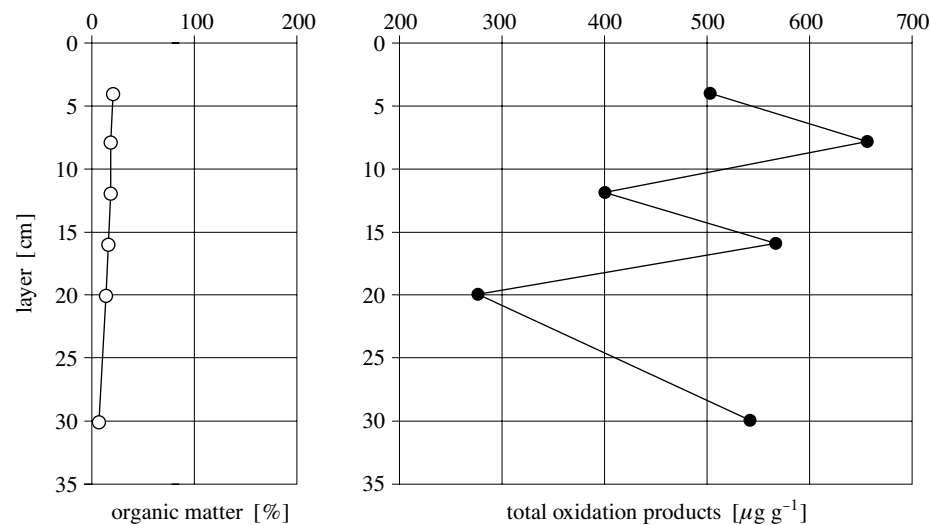


Fig. 4. Organic matter content and sum of lignin oxidation products in successive layers of the core I8/A00

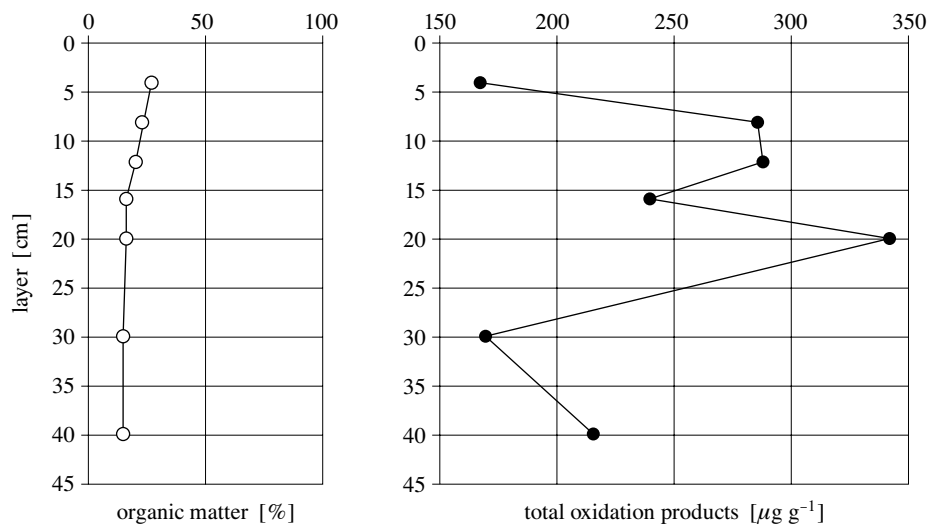


Fig. 5. Organic matter content and sum of lignin oxidation products in successive layers of the core I5/A00

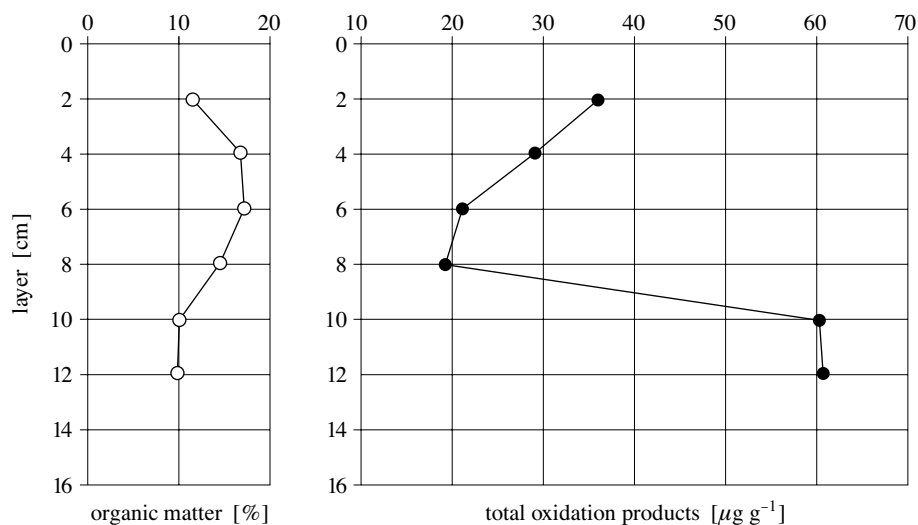


Fig. 6. Organic matter content and sum of lignin oxidation products in successive layers of the core BCI1/A00

(Fig. 7, 11) show different profiles of phenols, because oxidation product concentrations are lower in the surface layers (0–4 cm) than in the subsurface ones (> 8 cm). This might be caused by different precursors of lignin (different plant species) and/or physicochemical conditions.

Sediments located near the coast are poor in organic matter. The highest contents of aldehydic phenols and phenolic acids were measured in core I8/A00 (Fig. 4, 8) (as compared to the other samples), followed by core I5/A00 (Fig. 5, 9). This is probably caused by directed transport of organic matter originating from the Vistula estuary.

The contribution of organic matter from land decreases with increasing distance from the coast (Table 2). The total amount of phenolic compounds in the oxidation products of organic matter is usually related to the plant material from which it originates. In our work in calculating the amount of organic matter of different origin, it was assumed that organic matter brought to the sea with river run-off constitutes part of the marine organic matter. Based on this assumption, a simple method for estimating the percentage of terrestrial humics was developed using the end member approach (Hedges & Mann 1974, Pempkowiak & Pocklington 1983).

$$F_t(\%) = \frac{\Sigma PA_s - \Sigma PA_m}{\Sigma PA_t - \Sigma PA_m} \times 100 = \frac{\Sigma PA_s}{\Sigma PA_t} \times 100, \quad (1)$$

where

F_t is the percentage of terrestrial organic matter;

ΣPA_s is the sum of phenolic aldehydes and acids in the sample;

ΣPA_t is the sum of phenolic aldehydes and acids characteristic of allochthonous organic matter (river);

ΣPA_m is the sum of phenolic aldehydes and acids characteristic of autochthonous organic matter (equal to zero).

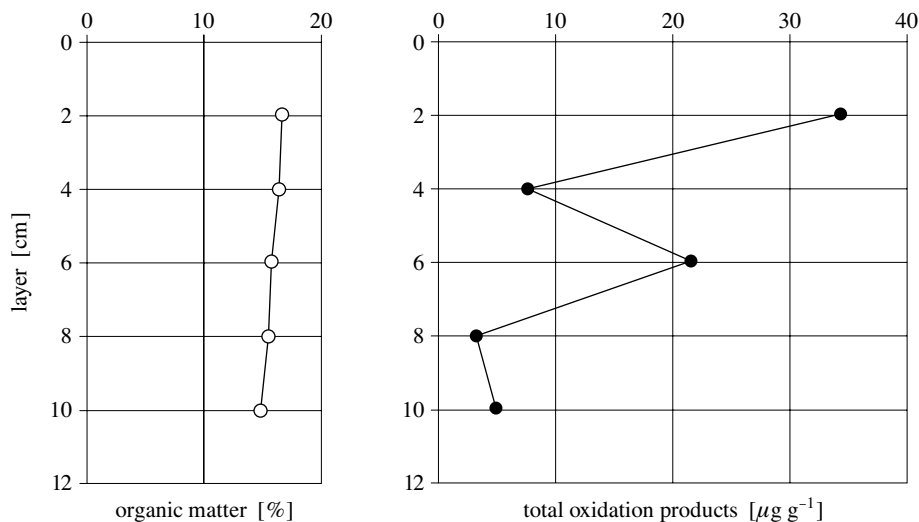


Fig. 7. Organic matter content and sum of lignin oxidation products in successive layers of the core BCI4/A00

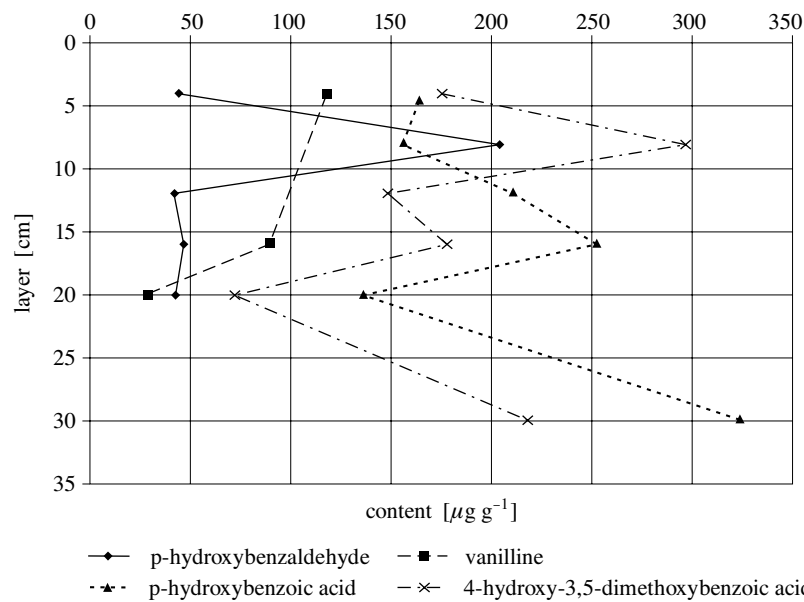


Fig. 8. Vertical profiles of lignin degradation products in the sediment core I8A/00

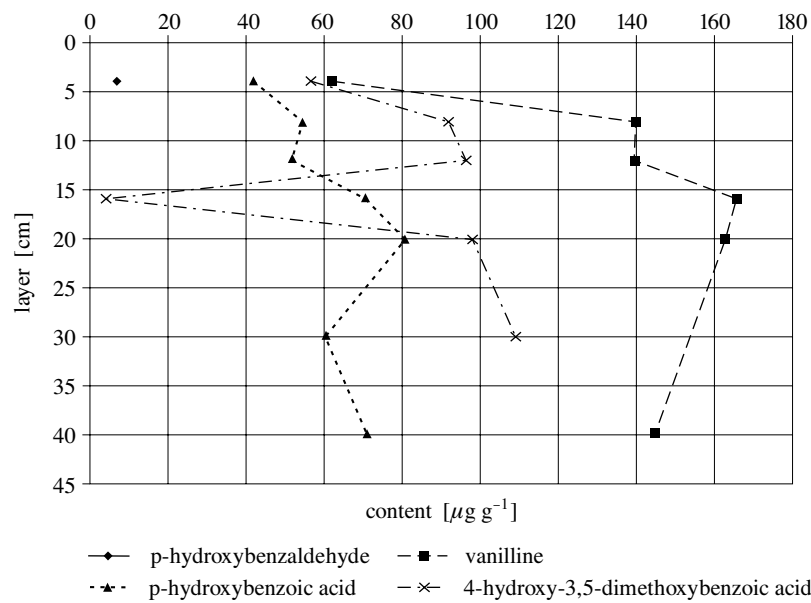


Fig. 9. Vertical profiles of lignin degradation products in the sediment core I5A/00

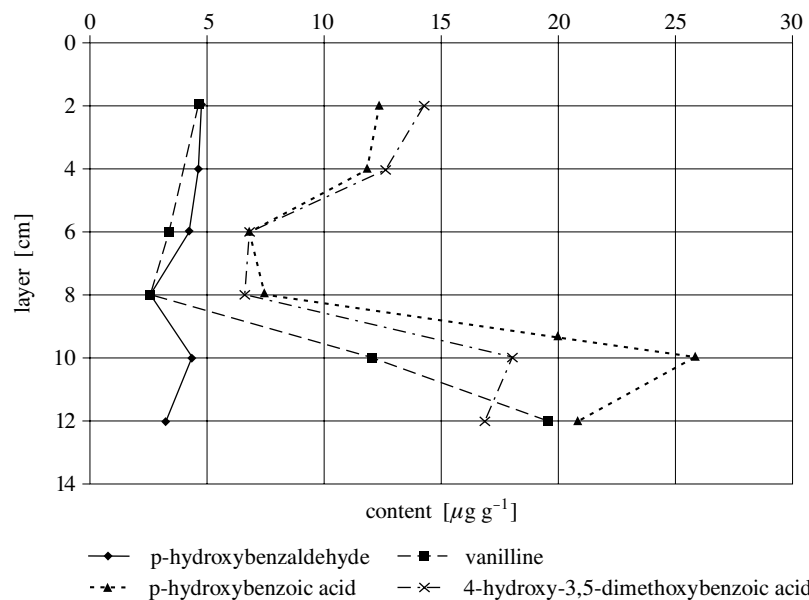


Fig. 10. Vertical profiles of lignin degradation products in the sediment core BCI11A/00

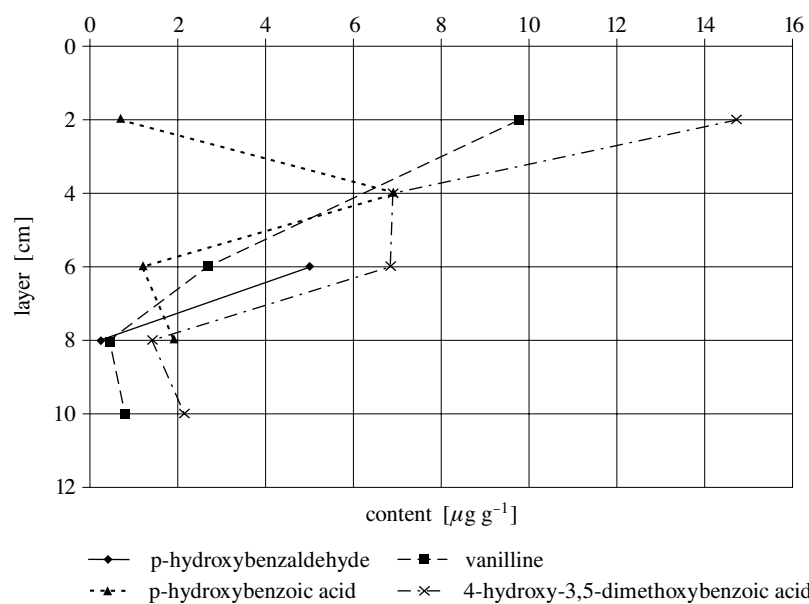


Fig. 11. Vertical profiles of lignin degradation products in the sediment core BCI14A/00

Suspended matter isolated from Vistula river water was used as a terrestrial end member. The marine end member was set at zero, since no lignin occurs in marine plants. The results presented in Table 10 indicate that organic matter discharged into the Gulf of Gdańsk is transported to the Gdańsk Deep, while the organic matter of the near-shore sediments is almost entirely composed of autochthonous organic matter. Substantial primary production amounting to $250 \text{ g C m}^{-2}/\text{year}$ (Renk 1992) contribute to the observed phenomena.

References

- El-Daoushy F., Olsson K., Garcia-Tenorio R., 1991, *Accuracies in Po-210 determination for lead-210 dating*, Hydrobiologia, 214, 43–52.
- Emylyanov E.M., 1995, *Baltic Sea: geology, geochemistry, paleo-oceanography, pollution*, Acad. Nat. Sci., RF, Kaliningrad.
- Flynn W.W., 1968, *The determination of low levels of polonium-210 in environmental samples*, Anal. Chim. Acta, 43, 221–227.
- Föster U., Salomons W., 1981, *Metal pollution in the aqua environment*, Springer-Verlag, Berlin, 3–61.
- Gardner W., Menzel D., 1974, *Phenolic aldehydes as indicators of terrestrially derived organic matter in the sea*, Geochim. Cosmochim. Acta, 38, 813–822.
- Gudelis W., Jemielianow J., 1982, *Geology of the Baltic Sea*, Wyd. Geol., Warszawa, 413 pp., (in Polish).
- Hautala K., Peuravuori J., Pihlaja K., 1997, *Estimation of origin of lignin in humic DOM by CuO – oxidation*, Chemosphere, 35, 809–817.
- Hautala K., Peuravuori J., Pihlaja K., 1998, *Organic compounds formed by chemical degradation of lake aquatic humic matter*, Environm. Int., 24, 527–536.
- Hedges J., Ertel R., 1982, *Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products*, Anal. Chem., 174–178.
- Hedges J., Mann D., 1974, *The lignin geochemistry of marine sediments from the southern Washington coast*, Geochim. Cosmochim. Acta, 43, 813–822.
- Joshi S. R., Shukla B. S., 1991, *Ab initio derivation of formulations of Pb-210 dating of sediments*, J. Radioanal. Nucl. Chem., 148, 73–79.
- Louchouart P., Lucotte M., Canuel R., Gagne J., Richard L., 1997, *Sources and early diagenesis of lignin and bulk organic matter in the sediments of the Lower St. Lawrence Estuary and the Seguenay Fjord*, Mar. Chem., 58, 3–26.
- Miltner A., Emeis K., 1999, *Origin and transport of terrestrial organic matter from the Oder Lagoon to the Arkona Basin, southern Baltic Sea*, Org. Geochem., 57–66.
- Miltner A., Emeis K., 2001, *Terrestrial organic matter in surface sediments of the Baltic Sea, Northwest Europe, as determined by CuO oxidation*, Geochim. Cosmochim. Acta, 65, 1285–1299.

- Niemistö L., 1974, *A gravity corer for studies of soft sediments*, Merent. Julk./Havsfors., 238, 33–38.
- Omstedt A., 1990, *Modelling the Baltic Sea as thirteen sub-basins with vertical resolution*, Tellus, 42A, 286–301.
- Pempkowiak J., 1989, *Origin, sources and properties of humic substances in the Baltic Sea*, Ossolineum, Wrocław, 146 pp., (in Polish).
- Pempkowiak J., 1991, *Enrichment factors of heavy metals in the southern Baltic surface sediments dated with ^{210}Pb and ^{137}Cs* , Environm. Int., 17, 421–428.
- Pempkowiak J., 1997, *An outline of marine geochemistry*, Wyd. Uniw. Gdańsk, Gdańsk, 121–126, (in Polish).
- Pempkowiak J., Pocklington R., 1983, *Phenolic aldehydes as indicators of the origin of humic substances in marine environments*, [in:] *Aquatic and terrestrial humic materials*, R. F. Christman & E. T. Gjessing (eds.), Ann. Arbor Sci., Michigan, 371–385.
- Pempkowiak J., Grylicki H., Marko-Narloch H., 1988, *Correlation between major components of the Baltic surface sediments*, Proc. 16th Conf. Baltic Oceanogr., Inst. Mar. Res., Kiel, 2, 833–842.
- Persson J., Jonsson P., 2000, *Historical development of laminated sediments – an approach to detect soft sediment ecosystem change in the Baltic Sea*, Mar. Poll. Bull., 40 (2), 122–134.
- Piotrowska-Szypryt M., Pemkowiak J., 1997, *The comparison of the properties of humic acids from the surface and subsurface layers of marine bottom sediments*, Humic Sub. Environm., 1, 119–128, (in Polish).
- Renk H., 1992, *Primary production and the concentration of chlorophyll a*, Stud. i Mater. Oceanol., 61, 167–180.
- Robbins J. A., 1978, *Geochemical and geophysical application of radioactive lead*, [in:] *The biogeochemistry of lead in the environment*, J. O. Nriagu (ed.), Elsevier, Amsterdam, 285–393.
- Staniszewski A., Pazdro K., Beldowski J., Leipe T., Emeis K., Pempkowiak J., 2000, *Temporal and spatial changes of cadmium in near-bottom suspended matter in the Pomeranian Bay – Arkona Deep system*, Oceanologia, 42 (4), 483–491.
- Stevenson F. J., 1982, *Humus chemistry, genesis, composition, reactions*, A. Wiley Int. Publ., New York, 443 pp.
- Vanderbrucke M., Pelet R., Debyser Y., 1985, *Geochemistry of humic substances in marine sediments. Humic substances in soil, sediment and water*, G. Aiken, D. McKnight & R. Wershow (eds.), Wiley, New York, 249–274.
- Voipio A., 1981, *The Baltic Sea*, Elsevier, Amsterdam, 418 pp.
- Waleńczak Z., 1987, *Organic geochemistry*, Wyd. Geol., Warszawa, 72–75, (in Polish).