

ORIGINAL RESEARCH ARTICLE

Limitation of lignin derivatives as biomarkers of land derived organic matter in the coastal marine sediments

Janusz Pempkowiak*

Marine Chemistry Department, Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland

Received 5 April 2020; accepted 21 April 2020

Available online 20 May 2020

KEYWORDS

Lignin phenols;
Stable carbon isotopes;
 $\delta^{13}\text{C}$;
End members;
Nonlinear analyses;
Gdańsk Bay;
Southern Baltic

Summary Lignin oxidation products (vanillyl, syringil and cummaryl phenols), and $\delta^{13}\text{C}$ were measured in a variety of land and marine samples collected in Inner Puck Bay – dominated by marine vascular plants, small river run-off, and shallow bottom, and in Gdańsk Bay – characterized by large river run-off, small marine vascular plants population, and the average depth exceeding euphotic zone. Both study areas are parts of the Gdańsk Basin, Southern Baltic. Typical $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} = -28\text{‰}$) and both composition and concentrations of lignin phenols were measured in samples originating from land. Small, yet easily measurable amounts of lignin phenols were found in marine vascular plants biomass ($\Sigma 8 = 90 \mu\text{g}/100 \text{mg}$ organic matter). The biomass was characterized by exceptionally high $\delta^{13}\text{C}$ values (-12‰). No lignin phenols and typical $\delta^{13}\text{C}$ values (-22‰) were measured in marine phytoplankton biomass. $\delta^{13}\text{C}$ and both composition and content of lignin phenols in organic matter of surface sediments collected in the study area fall in the range marked by the end members. The proportion of land derived organic matter calculated using lignin phenols, or $\delta^{13}\text{C}$ in Gdańsk Bay were comparable, while in Puck Bay they differed substantially. It was concluded that a) in areas with substantial bottom coverage with vascular plants the two end members approach, usually employed to establish the contribution of organic matter sources, is insufficient, b) organic matter originating from three sources: riverine, phytoplankton, and vascular plants contribute to sedimentary organic matter in Puck Bay with the respective proportion 30:40:30.

* Corresponding author at: Marine Chemistry Department, Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81–712 Sopot, Poland.

E-mail address: pempa@iopan.gda.pl

Peer review under the responsibility of the Institute of Oceanology of the Polish Academy of Sciences.



Production and hosting by Elsevier

<https://doi.org/10.1016/j.oceano.2020.04.004>

0078-3234/© 2020 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

© 2020 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Organic matter content in marine sediments most often is below 15%. Despite this organic matter is regarded as an important component of sediments. Both contribution to carbon cycling in the earth crust and the influence on physical, biological and chemical properties of sediments are mentioned in this respect (Bianchi et al., 2018; Hedges, 1992).

Amounts and properties of marine sedimentary organic matter depend on the proportion of allochthonous-land derived organic matter, since it differs greatly from autochthonous-marine biota produced organic matter (Jex et al., 2014). The former enters the marine environment mainly with the river run-off, although aerial transport may be of importance in case of specific substances (Chester, 2003; Cragg et al., 2020). Riverine organic matter load is generally composed of organic and organic-mineral, dissolved and particulate matter, washed out from the soil and, to a much smaller extent, from aquatic plants debris. Therefore, it reflects the properties of soil organic matter that is strongly influenced by the regional vegetation and climate (Hedges, 1992; Sun et al., 2017). This organic matter fraction is also relatively biochemically stable.

It has been well documented that terrestrial organic matter makes up a large proportion of sedimentary organic matter in the marine shelf areas (Gordon and Goni, 2003; Hedges et al., 1982; Hedges and van Geen, 1982; Miltner et al., 2005; Winogradow and et al., 2019). For example, in the Baltic Sea it constitutes up to 70 per cent of sedimentary organic matter (Miltner and Emeis, 2000; Pempkowiak and Pocklington, 1983; Staniszewski et al., 2001; Winogradow and Pempkowiak, 2014). This is because most of the terrestrial organic matter transported into the sea is deposited near the mouth of rivers and adjoining areas on the shelf (Gough et al., 1993; Hedges et al., 1988; Ji et al., 2020). Thus, the proportion of terrestrial organic matter in marine sediments decreases with increasing distance from land (Hedges et al., 1988). In the Baltic, most of the riverine organic matter load is transported to depositional basins (Miltner and Emeis, 2001; Pempkowiak and Pocklington, 1983; Staniszewski et al., 2001).

Identifying organic matter origin in sediments of a particular basin is essential in constructing material fluxes and budgets and understanding sedimentary processes. Elemental composition, stable carbon and nitrogen isotopes and chemical markers (chemical compounds that are lacking in either terrestrial or marine environments) have been used in determining the proportion of terrestrial organic matter in sediments (Bordovsky, 1965; Gardner and Menzel, 1974; Hedges and Ertel, 1982; Jex et al., 2014; Pempkowiak, 1983; Staniszewski et al., 2001). A typical component of terrestrial organic matter, believed to be lacking in marine plants, and therefore frequently utilized as a marker,

is lignin (Hautala et al., 1997; Hedges et al., 1988; Miltner and Emeis, 2001; Pradhan et al., 2014).

Lignin bio-macromolecules are high molecular weight phenolic polymers. They are major constituents of vascular plant cell walls (Merdy et al., 2002; Sederoff et al., 1999; Ye et al., 2001). The chemical structure of lignin is troublesome for analysis, owing to difficulties in isolating and de-polymerizing. We do know, however, that they are polyphenols consisting of monomers with a characteristic isopropyl benzoic carbon structure (Donaldson, 2001). Isopropyl benzoic monomers, usually contain methoxy groups bound to aromatic rings (Hedges and Ertel, 1982; Hedges and Mann, 1979).

Lignin polymers in plant tissues, soils, and sediments are not a subject to direct chemical analysis without prior isolation and derivatisation. Samples containing lignin are first subjected to chemical degradation, in order to release small molecules. Then the degradation products are extracted from the reaction mixture and quantified, following derivatization, by a variety of chromatographic techniques (Hedges and Ertel, 1982; Hedges et al., 1982; Staniszewski et al., 2001). When cupric oxide is used as the oxidant the predominant products of lignin oxidation are phenolic aldehydes and phenolic acids. Most often 8 major lignin-derived CuO oxidation products are quantified (Table 1). Chemical structure of the degradation products is presented in Figure 1. These belong to the following groups of phenols: syringyl (S – 3 compounds), vanillin (V, 3), and cynammyl (C, 2) (Farella et al., 2001; Hedges and Ertel, 1982; Hedges et al., 1982; Hu et al., 1999; Miltner and Emeis, 2001; Pempkowiak and Pocklington, 1983; Staniszewski et al., 2001; Wilson et al., 1985). The sum of the 8 lignin oxidation products recalculated to 100 mg of organic material ($\Sigma 8$), or/and to 10 g of sample (Δ) has been used to characterize yield of lignin phenols (Hedges and Mann, 1979). The lignin burden in mineral sedimentary material may be characterized by ' Δ ' – the sum of the 8 lignin phenols recalculated to 10 g of organic matter free material (Pempkowiak et al., 2006).

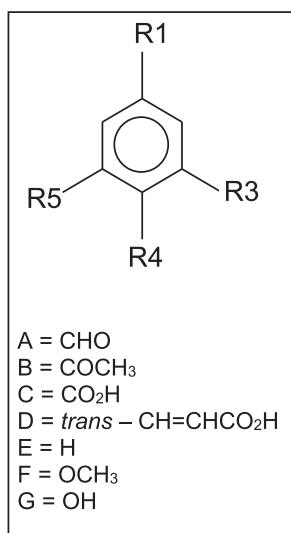
Ratios of specific phenolic aldehydes and phenolic acids may be used to characterize sources of lignin in sedimentary organic matter. The most often applied indexes include: the ratio of syringyl to vanillyl phenols (S/V) – an indicator of angiosperms plants, the ratio of cynammyl to vanillyl phenols (C/V) – an indicator of nonwoody plant tissues, the ratio of vanillic acid to vanillyl aldehyde (Ad/Al)_v – an indicator of diagenetic changes in lignin (Hedges et al., 1982; Miltner et al., 2005). The ratio of methoxyphenols to vanillin phenols (H/V), an indicator of aquatic plant contribution (Wilson et al., 1985), is seldom used.

Lignin phenols are frequently used as markers of land derived material in the aquatic environment in general (Bianchi et al., 1997; Cragg et al 2020; Farella et al., 2001; Hautala et al., 1997; Hedges et al., 1988), and in the coastal marine environment in particular (Gardner and Men-

Table 1 Names and occurrence of lignin degradation products in various plant classes.

| No. | Compound | Name of group | Plant sources* | | | |
|-----|-----------------------|---------------|----------------|---|---|---|
| | | | G | g | A | a |
| 1 | m-hydroxybenzoic acid | H | + | + | | + |
| 2 | p-hydroxybenzaldehyde | | + | + | | + |
| 3 | p-hydroxybenzoic acid | | + | + | | + |
| 4 | vanillin | V | + | + | + | + |
| 5 | acetovanillone | | + | + | + | + |
| 6 | vanillic acid | | + | + | + | + |
| 7 | syringaldehyde | S | | | + | + |
| 8 | syringic acid | | | | + | + |
| 9 | acetosiringone | | | | + | + |
| 10 | p-cumaric acid | C | | + | | + |
| 11 | ferulic acid | | | + | | + |

* Plant sources: G – gymnosperm woods, g – nonwoody gymnosperm tissues, A – angiosperm wood, a – nonwoody angiosperm tissues.



| Typical oxidation products of lignin | Structure | | | |
|--------------------------------------|----------------|----------------|----------------|----------------|
| | R ₁ | R ₂ | R ₃ | R ₄ |
| benzoic acid | C | E | E | E |
| p-hydroxybenzaldehyde | A | E | E | G |
| vanillin | A | E | F | G |
| m-hydroxybenzoic acid | C | E | G | E |
| p-hydroxyacetophenone | B | E | F | G |
| p-hydroxybenzoic acid | C | E | E | G |
| syringaldehyde | A | F | F | G |
| vanillic acid | C | E | F | G |
| acetovanillone | B | F | F | G |
| syringic acid | C | F | F | G |
| p-cumaric acid | D | E | E | G |
| ferulic acid | D | E | F | G |

Figure 1 The chemical structure of lignin phenols.

zel, 1974; Gouth et al., 1993; Hedges et al., 1982; Miltner and Emeis, 1999; Pradhan et al., 2014; Staniszewski et al., 2001). The assumption is that aquatic plants do not comprise lignin units, and therefore organic matter derived from them may dilute lignin phenols concentration (thus influencing both $\Sigma 8$ and Δ) whereas the composition of lignin oxidation products remains unaltered (Gardner and Menzel, 1974; Hedges and Mann, 1979; Merdy et al., 2002). To quantify the proportion of allochthonous organic matter in marine sediments the so-called ‘end members approach’ is adopted (Hedges and Mann, 1979; Thorton and MsManus, 1994). Concentrations of lignin oxidation products (either Σ or Δ) in land-derived (LL), ‘pure’ marine (MM), and actual marine (ML) samples, are combined into a simple formula for the purpose of calculating proportion of allochthonous organic matter component – L (%), in a given sample:

$$L(\%) = \frac{LL - ML}{LL - MM} \cdot 100.$$

Since an assumption was adapted that no lignin phenols are yielded from ‘pure’ marine samples the equation has

been abbreviated to:

$$L(\%) = \frac{LL - ML}{LL} \cdot 100.$$

Based on this approach land derived organic matter was estimated to comprise a substantial proportion of marine sedimentary organic matter: 30–70% in the Baltic Sea (Bianchi et al., 1997; Miltner and Emeis, 1999, 2001; Pempkowiak and Pocklington, 1983; Staniszewski et al., 2001; Winogradow and Pempkowiak 2018; Winogradow et al., 2019), and 10–90% in the Columbia River estuary (Hedges, 1992), Amazon River estuary (Sun et al., 2017) and off India (Pradhan et al., 2014). However, the occurrence of typical lignin derivatives was reported in oxidation products of material originating from marine vascular plants (Cragg et al., 2020; Staniszewski, 2005). Therefore, the applicability of such an approach should be thoroughly investigated.

Estuarine ecosystems are composed of relatively heterogeneous biologically diverse subsystems: water column, mud and sand flats, bivalve reefs and beds, seaweeds and seagrass meadows that are connected by mobile animals

and currents. Together the systems form one of the most productive natural systems in the biosphere. These systems function as traps for all kinds of suspended and dissolved materials, nursery grounds for organisms including many commercially important species and recreational zones for humans. They are also complex systems that exchange matter and energy with terrestrial and marine ecosystems. Unlike seaweeds, submerged hydrophytes (vascular plants, seagrasses) do actually root themselves in the sediments at the bottom of the ocean floor, and they have leaves and flowers, just like terrestrial plants. There are four different groups of seagrasses: Zosteraceae, Hydrocharitaceae, Posidoniaceae and Cymodoceaceae, representing 72 different species.

Seagrass is often characterized as the ‘lungs of the ocean’ because of its capacity for absorbing carbon dioxide and generating oxygen. One square meter of seagrass can generate 10 liters of oxygen every day. Seagrasses tend to live in shallow water about 1 to 3 meters deep, but some can grow at depths of 58 meters (Jørgensen and Fath, 2008). The seafloor area covered by seagrass worldwide is reported in the range of 0.3–0.6 10^6 km² (Duarte and Chiscano, 1999). On the average the seagrass biomass is equal to 460 g dry weight/m², while net production is equal to 2.7 g DW/m² day – more than boreal forest (2.4), and much more than phytoplankton (0.3) (Duarte, 1991). About 25% of the net primary production is exported to beach ecosystems, while 55% is mineralized soon after the plants’ death (Duarte, 2010; Duarte and Cebrián, 1996; Duarte et al., 2005; Haddad and Martens, 1987; Jørgensen and Fath, 2008). It is estimated that 83 g/m² are buried in sediments (Duarte and Cebrián, 1996) – a subject to further mineralization as no accumulation of carbon in shallow, coarse-grained sediments takes place (Winogradow and Pempkowiak, 2019).

The motivation for the survey reported here was twofold. For one thing, it was investigating the occurrence of lignin phenols in the oxidation products of ‘pure’ marine samples: vascular plants, algae, mussels soft tissue. Moreover, the assessment was carried out to what extent this occurrence may affect the land derived organic matter proportion, calculated basing on lignin oxidation products, in actual marine sediments. Stable carbon isotopes ratio $\delta^{13}\text{C}$ was applied to verify the conclusion of the study.

The results indicate that typical lignin phenols do occur at small concentrations in the oxidation products of marine vascular plants. Moreover, their contribution must be taken into account in areas with large loads of organic matter originating from marine vascular plants and a small supply of terrestrial organic matter. A simple three-member approach was applied to establish a proportion of organic matter originating from three different sources in such a system. The sources considered were terrestrial, marine vascular plants, and marine phytoplankton.

2. Study area

The study was performed using samples collected from the Gdańsk Basin, Southern Baltic (Figure 2). Gdańsk Deep, Gdańsk Bay and Puck Bay are parts of the basin (Majewski, 1990).

Gdańsk Bay is a southeastern bay of the Baltic Sea. The western part of Gdańsk Bay, sheltered from the open sea by the Hel Peninsula, is formed by waters of Puck Bay, while the western-most shallow part of the latter is called Inner Puck Bay or the Puck Lagoon. Gdańsk Bay is enclosed by a large curve of the shores of the Hel Peninsula and the Sambian Peninsula. The coast of the bay features two very long sand spits, the Hel Peninsula and the Vistula Spit. The first one defines Puck Bay, the latter one defines the Vistula Lagoon. The maximum depth is 120 m, salinity ranges from 3 to 7 PSU (0.3–0.7%). The major ports and coastal cities are Gdańsk, Kaliningrad and Gdynia.

The main river entering Gdańsk Bay is the Vistula with a yearly run-off of about 40 km³. Gdańsk Bay receives the waters of the Vistula directly via the Przekop, whereas the Śmiała Wisła, and the Martwa Wisła are inactive. To the west of the Vistula river, several streams discharge waters to the bay with the yearly runoff equal to 0.09 km³. The Pregola discharges waters to the bay indirectly, through the Vistula Lagoon. Most of the suspended matter load is retained in the lagoon, influencing the bay to a small extent.

Inner Puck Bay receives waters of several streams. The major ones are the Płutnica and the Zagórska Struga. Total river runoff to Puck Bay equals 0.03 km³/annum.

The surface water circulation in Gdańsk Bay is anticlockwise, and from west to the east. Moreover, there is a sandbar marking the eastern border of the shallow Inner Puck Bay (2.1 m average depth). Since there are no tides in the Southern Baltic the Vistula water is prevented from entering Puck Bay. Thus, two water bodies characterized by different hydrology can be distinguished: Gdańsk Bay and Inner Puck Bay. The former is characterized by large river discharge and substantial depth. The latter is separated from Gdańsk Bay by a sandbar, and is characterized by limited river runoff and shallow bottom (Majewski, 1990).

Puck Bay is characterized by an extensive population of aquatic vascular plants (*Zostera*, *Potamogeton*), and substantial phytoplankton primary production, while Gdańsk Bay has got comparable primary production, while the vascular plants population is of little importance there (Kruk-Dowgiatto, 2008; Majewski, 1990).

3. Material and methods

3.1. Sampling

The surface sediment samples were collected by means of a gravity corer from Gdańsk Bay at locations presented in Figure 2. The uppermost 0–2 cm layers were taken for analyses. Twice (May and October) samples of riverine suspended matter were recovered from about 600 liters of water which were collected from the Vistula river, about 2 km, and the Płutnica – about 0.3 km, upstream from the river mouth. The suspended matter was decanted, centrifuged and freeze-dried to yield 1.8–2.5 g of dry material. Marine suspended matter samples (some 0.3 g each) were collected by filtering some 200 dm³ of water through GF/F glass fiber filters.

Wood, leaf and moss samples were collected in autumn, from typical terrestrial plants (pine, oak, birch, maple) growing along Gdańsk Bay coast. Tissue samples provide, at

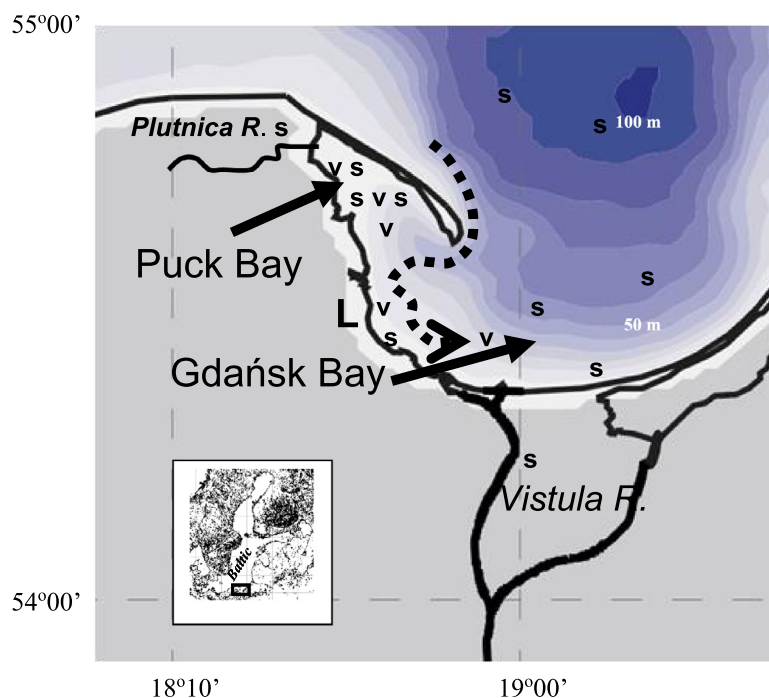


Figure 2 The study area (sampling stations: s – sediment, plankton and suspended matter samples, v – marine vascular plants, L – land vascular plants). Dashed arrow indicates direction of water circulation.

least, three examples from each of four categories of plant tissue types: woody (branch) and non-woody (leaf) tissues of gymnosperms and angiosperms.

Samples of marine biota including vascular plants (*Potamogeton* sp., Charophyta, *Zostera marina*), phytoplankton (*Chlorella vulgaris*, *Scenedesmus* sp., *Pilayella littoralis*, mixed plankton), mussels (*Mytilus trossulus*, *Mya arenaria*) were collected from the study area and stored dry till analyses.

Location of sampling stations is presented in Figure 2, while the characteristics of the collected samples are given in Table 2.

3.2. Analytical methods

The following properties of the collected samples were analyzed in the laboratory: moisture, organic matter, lignin oxidation products (C, V, S, H – phenols), and $\delta^{13}\text{C}$.

Moisture (60°C, 24 h) and loss on ignition (450°C, 4 h) were measured in each sample. Loss on ignition was used as a measure of organic matter (OM) concentration. It was recalculated to organic carbon (C_{org}) using the following formula: $C_{\text{org}} = 0.45 \times \text{OM}$ (Jonsson and Carman, 1994).

The analysis of lignin-derived phenols was performed after CuO oxidation according to a procedure developed by Hedges et al. (1982) and modified by Staniszewski et al. (2001). In short, steel bombs were loaded with various samples comprising about 50 mg organic matter (0.1 mg accuracy), 400 mg of powdered CuO, 100 mg of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6(\text{H}_2\text{O})$ and 3 ml of NaOH (2 mol/dm³). After 5 h at 180°C, the contents were centrifuged at $G=2400$ and rinsed with water several times. 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 derivatization and GC analysis. The dried products were dissolved in pyridine (250 μl) before the addition of 150 μl of the silylating reagent [BSTFA – bis(trimethylsilyl) - trifluoroacetamide] and derivatized for 1 h at room temperature. The derivatised products were analyzed in a gas chromatograph (Shimadzu 17A) on fused silica capillary columns (Phenomenex ZB-5, 30 m x 0.25 mm x 0.50 mm) with flame ionization detection. The GC-FID analyses were performed under the following conditions: initial oven temperature 120°C min, rate of oven temperature increase 3°C/min, final oven temperature 270°C; the temperature of injector and detector: 300°C; carrier gas: helium with a flow rate of 1.5 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 (3-etoxy,4-hydroxy-benzaldehyde) and standard addition of the analyzed compounds were used for quantitative analyses. The average recovery was $78 \pm 3\%$ ($n=5$). Blanks ran parallel to the samples proved the lack of signal at retention times characteristic of the analyzed samples. The limit of detection ranged from 0.1 to 0.8 $\mu\text{g/g}$ depending on the measured analyte, and never exceeded 2% of the analyte.

Stable carbon isotopes were analyzed according to a procedure described by Jędrysek et al. (2003). In short, a sample comprising some 3 mg of organic matter was combusted with CuO at 900°C in a glass ampoule. The evolving carbon dioxide was cryogenically purified and transferred to a model Finnigan Mat CH7 mass spectrometer equipped with a model Finnigan Mat Delta E detector. The PDB interna-

Table 2 List and short characteristics of collected samples.

| Sampling date | Place of sampling* | Type of sampling | Description |
|------------------|---------------------------------|---|--|
| 04.04. 07.09. | Vistula River Plutnica River | suspended matter | About 600 dm ³ of water was processed |
| 20.10. | Landscape Park | maple – branch maple – leaf oak – branch oak – leaf birch – branch birch – leaf pine – branch | Branches of trees with leaves still attached to them were collected |
| 13.10. 06.06. | Gdańsk Basin | <i>Pilayella littoralis</i> <i>Potamogeton</i> sp. Charophyta <i>Zostera marina</i> <i>Chlorella vulgaris</i> <i>Scenedesmus</i> sp. | Vascular plants were collected by a scuba diver. Phytoplankton samples were collected with a net towed with a speed 1.5 knot, mussels were collected with a dredge towed with a speed of 2.5 knots |
| 04.06. | | Plankton, mixed Tissues of mussels: <i>Mytilus trossulus</i> <i>Mya arenaria</i> | |
| 04.06. | Gdańsk Basin | Suspended matter | About 200 dm ³ were filtered through GF/F glass fiber filters |

* see map in Figure 2 for location of sampling grounds.

tional standard was used for calculating the stable carbon isotope ratio ($\delta^{13}\text{C}$) according to the formula:

$$\delta^{13}\text{C} = \frac{\left[\frac{^{13}\text{C}}{^{12}\text{C}} \right]_{\text{sample}} - \left[\frac{^{13}\text{C}}{^{12}\text{C}} \right]_{\text{standard}}}{\left[\frac{^{13}\text{C}}{^{12}\text{C}} \right]_{\text{standard}}}$$

Stable carbon isotopes ratio was measured with the 0.05‰ accuracy.

3.3. Modeling contribution to sedimentary organic matter from various sources

The contributions of organic matter originating from various sources in the Bay of Puck sediments were established by means of nonlinear estimation (Kulinski and Pempkowiak, 2008; Pempkowiak et al., 2006a). The modelled contributions (**a** – riverine: *R*, **b** – marine vascular plants: *V*, **g** – phytoplankton: *P*) were calculated from linear regression equations independently for values of $\delta^{13}\text{C}$ and $\Sigma 8$ in sedimentary organic matter (OC_M), measured in actual samples.

$$\text{OC}_M \delta^{13}\text{C} = a * \delta^{13}\text{C}_{(R)} + b * \delta^{13}\text{C}_{(V)} + g * \delta^{13}\text{C}_{(P)}$$

$$\text{OC}_M \Sigma 8 = a * \Sigma 8_{(R)} + b * \Sigma 8_{(V)} + g * \Sigma 8_{(P)}$$

This is based on the following assumption: the total concentration of a given property (either $\Sigma 8$ or $\delta^{13}\text{C}$) consists of three portions contributed by each of the members in proportion to the mass contribution of organic matter originating from the sources.

The unknown contributions are calculated applying non-linear estimation. Statistica 5 software package was used to perform calculations.

4. Results and discussion

4.1. Lignin phenols in marine vascular plants

In Table 3 yields of phenolic aldehydes and acids from terrestrial and marine plants, from riverine and marine suspended matter, and from marine sediments are presented.

As for terrestrial plants, the yield of lignin phenols is in the range from 5000 $\mu\text{g/g}$ (maple leaf) to 21000 $\mu\text{g/g}$ (oak leaf), and from 8000 $\mu\text{g/g}$ (pine wood) to 11000 $\mu\text{g/g}$ (birch wood), respectively for soft and hard parts of the investigated plants. Moss was characterized by the exceptionally high yield of phenolic aldehydes and acids (22000 \pm 350 $\mu\text{g/g}$). Yields of the sum of vanillin, syringil, and cynammyl phenols recalculated to 100 mg organic carbon ($\Sigma 8$) are in the same range as reported earlier for plant tissues (Hautala et al., 1997; Hedges and Mann, 1979).

Marine planktonic material yielded none of lignin phenols, and neither did soft tissue of mussels collected in the Gdańsk Basin. It is interesting to see that $\Sigma 8$ phenols are practically lacking in the coastal surface suspended matter. This may be attributed to the lack of lignin phenols ($\Sigma 8=0$) in the planktonic material, dilution of riverine suspended matter by biomass originating from planktonic primary production and transport to the sedimentation basin

Table 3 Yields of lignin phenols and $\delta^{13}\text{C}$ in the analyzed samples.

| Sample | Lignin phenols/ \pm standard deviation | | | | | Lignin indexes | | $\delta^{13}\text{C}$ (‰) |
|---------------------------------|--|---------------|---------------|-----------------|------------------------------|-----------------|---------------|---------------------------|
| | V | C | S | H | $\Sigma 8$ | C/V | S/V | |
| | $\mu\text{g/g}$ | | | | $\mu\text{g}/100\text{ mgC}$ | | | |
| Gymnosperms¹ | | | | | | | | |
| - wood | 2741 \pm 87 | 3576 \pm 93 | 899 \pm 39 | 4911 \pm 112 | 1935 \pm 108 | 0.49 \pm 0.03 | 2.3 \pm 0.4 | -28.7 \pm 0.4 |
| - soft parts | 3576 \pm 118 | 899 \pm 27 | 807 \pm 27 | 11365 \pm 317 | 1450 \pm 36 | 0.06 \pm 0.01 | 2.8 \pm 0.6 | -28.5 \pm 0.3 |
| Angiosperms² | | | | | | | | |
| - wood | 6616 | 694 | 842 | 442 | 1630 | 0.16 | 0.13 | -26.0 |
| - soft parts | 3215 | 1921 | 652 | 892 | 893 | 0.59 | 0.20 | -27.2 |
| Suspended matter | | | | | | | | |
| - Vistula River ³ | 2871 | 2207 | 5536 | 4138 | 2120 | 0.77 | 1.9 | -26.4 |
| - Płutnica River ³ | 2530 | 2230 | 6320 | 1890 | 2350 | 0.90 | 2.5 | -27.1 |
| - Puck Bay ³ | 14 | 8 | BLD | BLD | 4.0 | 0.57 | - | -20.5 |
| - Gdańsk Bay ³ | 25 | 14 | 15 | 8 | 8.1 | 0.56 | 0.60 | -23.7 |
| - Southern Baltic | 14 | 12 | BLD | BLD | 5.2 | 0.86 | - | -22.2 |
| Marine biota | | | | | | | | |
| - vascular plants ^{4a} | 176 | 83 | 177 | 1529 | 89.8 | 0.52 | 1.05 | -11.7 |
| - phytoplankton ^{4b} | BLD | BLD | BLD | BLD | BLD | - | - | -22.0 |
| - mussels ^{4c} | BLD | BLD | BLD | BLD | BLD | - | - | - |
| Marine sediments | | | | | | | | |
| - Puck Bay ^{5a} | 1800 \pm 65 | 790 \pm 41 | 2150 \pm 76 | 1512 \pm 65 | 823 \pm 37 | 0.44 \pm 0.08 | 1.2 \pm 0.1 | -23.0 \pm 0.2 |
| - Gdańsk Bay ^{5b} | 1363 \pm 64 | 870 \pm 26 | 2760 \pm 82 | 1458 \pm 51 | 861 \pm 31 | 0.64 \pm 0.07 | 1.6 \pm 0.2 | -24.8 \pm 0.2 |

BLD – below detection limit.

¹ maple, oak, birch.

² pine.

³ average of 2 samples.

^{4a} *Potamogeton* sp., Charophyta, *Zostera marina*.

^{4b} *Scenedesmus* sp., *Chlorella vulgaris*, mixed phytoplankton.

^{4c} *Mytilus trossulus*, *Mya arenaria*.

^{5a} average of 3 samples.

^{5b} average of 5 samples.

of, lignin-rich, riverine suspended matter in the above bottom, nepheloid layer (Pempkowiak et al., 2002; Winogradow and Pempkowiak, 2018). Organic matter derived from unicellular algae (phytoplankton) constitutes almost 100% of primary production in the marine environment at a global scale, although in the coastal, shallow regions marine vascular plants can contribute substantially to the primary production (Chester, 2003; Cragg et al., 2020; Kruk-Dowgiałto, 2008).

Exceptionally large concentrations of hydroxyl phenols (H) in organic material derived from aquatic plants draw attention. It seems to be a specific feature of aquatic plants biomass. This was reported earlier by Hautala et al. (1997), and Hedges and Mann (1979) who concluded that hydroxyphenols must have yet another source but lignin polymer. In another study the hydroxyphenols were associated with high chlorophyll α concentrations, indicating a possible autochthonous source (Cotrim da Cunha et al., 2001).

It follows from the presented data that marine vascular plants yielded, on average, 435 $\mu\text{g/g}$ compounds in question (V+S+C). The range was from 300 to 500 $\mu\text{g/g}$ ($\Sigma 8=120\ \mu\text{g}/100\ \text{mgCorg}$). Of the three species studied the highest yield resulted from *Zostera marina*, although the differences between species are small. No reports on the occur-

rence of lignin phenols in the oxidation products of biomass produced by marine biota have appeared so far.

Terrestrial suspended organic matter is delivered to the sea, mainly, with river runoff. Composition of suspended matter isolated from river water provides indications on the amount and quality of such material. On average concentrations of particulate lignin phenols in the Vistula water fall in the range from 8000 to 10000 $\mu\text{g/g}$ dry matter. The yield and composition of the phenols derived from the Płutnica suspended matter are similar to these of the Vistula River suspended matter. The riverine suspended matter $\Sigma 8$ index measured in this study is equal to 2223 \pm 250 $\mu\text{g}/100\ \text{mg}$ organic carbon, close to other reported values (Farella, 2001; Staniszewski, 2001). Seasonal variations of both the yield and composition can be observed, possibly, due to the river water flow variations (Cortim da Cunha et al., 2001; Staniszewski et al., 2001; Sun et al., 2017).

4.2. $\delta^{13}\text{C}$ in the analysed samples

In Table 3 the $\delta^{13}\text{C}$ values of the analyzed samples are presented. Except for pine wood ($\delta^{13}\text{C}=-26\%$) terrestrial plants material, and riverine suspended matter falls in the range from -28‰ to -30‰, typical of terrestrial

plants (Maksymowska et al., 2000; Opsahl and Benner, 1995). Organic material derived from marine vascular plants *Zostera marina*, and *Potamogeton* sp. is characterized by much higher $\delta^{13}\text{C}$ values (-12‰) than marine phytoplankton (-22‰), while marine suspended matter and marine sediments are characterized by $\delta^{13}\text{C}$ values falling in the range between marine phytoplankton and riverine suspended matter, except the Bay of Puck, where it is marginally higher (-21.5‰). The exceptionally high values for the marine vascular plants biomass were already reported earlier (Hamminga and Mateo, 1996; Hu and Burdige, 2007), and attributed to the ability of seagrasses to use bicarbonate as an inorganic carbon source (Raven et al., 2002). Sedimentary organic matter $\delta^{13}\text{C}$ signatures in both bays are typical of the Gdańsk Basin (Maksymowska et al., 2000; Winogradow and Pempkowiak, 2018), the Baltic (Miltner et al., 2005; Voss et al., 2000; Winogradow et al., 2019), and worldwide (Gordon and Goni, 2003; Pradhan et al., 2014; Requejo et al., 1986, 2003; Thorton and McManus, 1994).

The occurrence of lignin phenols and abundance of heavy carbon isotope in marine vascular plants biomass may be due to biased estimations of sedimentary organic matter provenience evaluated by means of the end member approach based on lignin residues and/or stable carbon isotopes.

4.3. The influence of marine vascular plants biomass on the sedimentary organic matter properties

Although the yield of $\Sigma 8$ phenols derived from marine vascular plants biomass is 10 to 50 times smaller than that from terrestrial plants biomass, the 'marine' biomass lignin phenols may influence the overall yield ($\Sigma 8$) in sediments comprising organic matter originating from both sources, if a load of marine plants biomass is substantial as compared to organic matter discharged to the sea from land. Therefore, the marine plants contribution cannot be entirely omitted when quantitative relations between marine and land originated organic matter pools are considered. This concerns especially coastal, shallow waters, characterized by restricted water exchange with the open sea, where organic matter derived from vascular marine plants can constitute not only a substantial proportion of primary production, but can overwhelm organic matter load discharged to the sea with river runoff (Kruk-Dowgiatto, 2008). Therefore, a possible influence of the marine vascular plants on the concentration and composition of lignin phenols in the coastal sediments was investigated in some detail in this study.

Not only are lignin phenols used to quantify the proportion of land derived organic matter in marine sediments. Ratios of specific lignin phenols or their groups are used to discriminate between taxonomic plant classes (gymnosperm vs. angiosperm) and tissue types (straw vs. woody tissue) and to diagnose the diagenetic state of lignin material (Jex et al., 2014; Pempkowiak et al., 2006; Reeves, 1995).

In the investigated samples the ratio of syringil to vanillin phenols (S/V) range from 2.8 (gymnosperms, soft parts) to 0.13 (pine wood). The S/V ratio in riverine suspended matter equals 1.9 and 2.5 respectively in the Vistula and the Płutnica suspended matter, indicating gymnosperms woody

material as a source of suspended organic matter, while the S/V ratio in sediments ranges from 1.2 (Puck Bay) to 1.6 (Gdańsk Bay) – values smaller than the ratio in the riverine suspended matter. One explanation for the S/V values could arise from the fact that in the surface sediments, the more degraded organic matter might be contained. It has been shown by several authors (Farella et al., 2001; Hedges et al., 1988; Jex et al., 2014; You et al., 2018) that in the course of degradation, lignin derivatives lose syringil units much faster than vanillin ones. This is unlikely in the presented case, however, considering that based on sedimentation rates in the area (Pempkowiak, 1991; Winogradow and Pempkowiak, 2014), surface sediments not older than 10 years were analysed.

In material derived from marine vascular plants, the S/V ratio equals 1.05 (Table 3), which means that the S/V ratio values in sedimentary organic matter may be influenced substantially in sediments rich with organic matter derived from vascular plants.

The C/V ratios of lignin phenols in the analysed samples are in the range from 0.49 (gymnosperms, wood) to 0.06 (gymnosperms, soft parts). In the riverine suspended matter the C/V ratio equals 0.77 and 0.90, while in the Gdańsk Basin sediments it ranges between 0.29 and 0.44. This indicates that the contribution of nonwoody plant fragments is small (Hedges and Mann, 1979; Opsahl and Benner, 1995). Since the ratio in the marine vascular plants biomass equals 0.55, the contribution of marine vascular plants is likely, although not as obvious an explanation as in the case of the S/V index. Modern pollen yielding high amounts of cinnamyl phenols (Hu et al., 1999) may be another factor influencing C/V ratio values.

The dependence of S/V vs C/V for both marine and terrestrial plants is presented in Figure 3. Terrestrial plants are characterized by large S/V values and small C/V values. Marine plants have small S/V values and both small and large C/V values. S/V ratios in the range from 0.1 to 1.0 are attributed to angiosperm plants material, while C/V ratios in the range from 0.1 to 0.4 are attributed to gymnosperm plants (Cragg et al., 2020; Hedges and Mann, 1979) Since S/V values are used to differentiate between angiosperm vs angiosperm plants, lowering S/V values due to contribution of marine vascular plants phenols may lead to misjudgment in this respect. It must be kept in mind, however, that the yield of lignin phenols from marine plants is smaller than that from terrestrial plants by an order of magnitude. Therefore, the influence will be manifested only in samples comprising a large fraction of V+S+C phenols derived from marine plants biomass.

The distribution of both the S/V and C/V indexes is yet another indication that contribution of marine vascular plants biomass to marine sedimentary organic matter should be taken into account when investigating provenience basing on lignin residues and/or stable carbon isotopes.

The extent of the influence depends both on the actual values of indexes ($\Sigma 8$, C/V, S/V), and on the proportion of organic matter derived from the marine vascular plants in the total sedimentary organic matter. This depends on the bottom coverage by marine vascular plants, biomass production by the plants and hydrology of a given water body. The resistance to biochemical degradation of V, S, and C phenols precursors is also an important factor here. These,

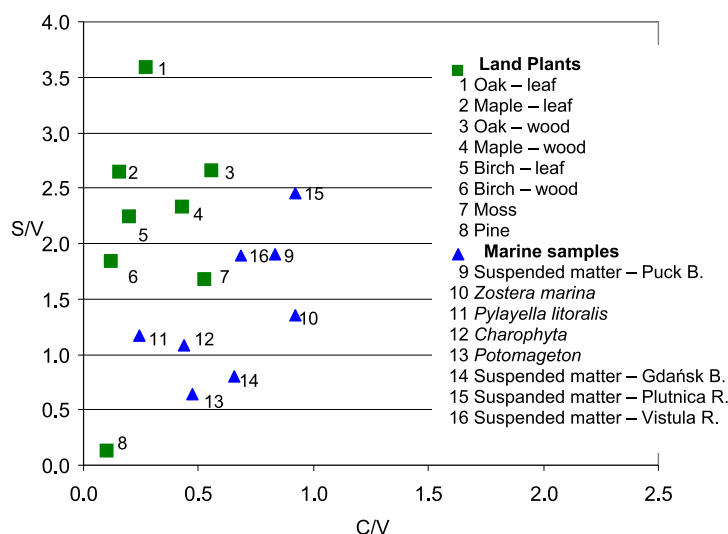


Figure 3 The plot of S/V vs. C/V indexes of the investigated samples.

Table 4 Characteristics of lignin phenols in a two member system (riverine suspended organic matter and marine vascular plants biomass).

| Organic carbon composition RPC ¹ : MVPC ² | Expected ³ $\Sigma 8$ $\mu\text{g}/100 \text{ mgC}$ | Actual ⁴ $\Sigma 8$ | Expected/Actual | | |
|--|---|--------------------------------|---------------------------------|-----------|-----------|
| | | | % Terrestrial organic matter | S/V | C/V |
| 100 : 0 | 2100 | 2100 | 100/100 | 1.93/1.93 | 0.77/0.77 |
| 99 : 1 | 2079 | 2080 | 99/99 | 1.93/1.92 | 0.77/0.77 |
| 95 : 5 | 1995 | 1999.5 | 95/95 | 1.93/1.89 | 0.77/0.76 |
| 90 : 10 | 1895 | 1899 | 90/90 | 1.93/1.84 | 0.77/0.76 |
| 75 : 25 | 1575 | 1597.5 | 75/76 | 1.93/1.71 | 0.77/0.70 |
| 50 : 50 | 1050 | 1095 | 50/52 | 1.93/1.49 | 0.77/0.64 |
| 25 : 75 | 525 | 592.5 | 25/28 | 1.93/1.27 | 0.77/0.57 |
| 10 : 90 | 210 | 291 | 10/14 | 1.93/1.14 | 0.77/0.53 |
| 5 : 95 | 105 | 190.5 | 5/9 | 1.93/1.09 | 0.77/0.51 |
| 1 : 99 | 21 | 110.1 | 1/5 | 1.93/1.06 | 0.77/0.50 |
| 0 : 100 | 0 | 90 | 0/4 | 1.93/1.05 | 0.77/0.50 |

¹ Riverine Particulate Organic Carbon.

² Marine Vascular Plants Organic Carbon.

³ assuming the lack of lignin phenols in marine vascular plants ($\Sigma 8 = 0$).

⁴ assuming $\Sigma 8$ of lignin phenols as in Table 3 ($\Sigma 8 = 90$).

of course, depend on local environmental factors. Assuming just the two organic matter sources, theoretically, composition of sedimentary organic matter may range from 100% land- 0% marine vascular plants derived, to 0% land- 100% marine vascular plants derived. In Table 4, $\Sigma 8$, S/V and C/V indexes are presented of hypothetical sedimentary organic matter consisting, in varying proportions, of land derived and marine vascular plants derived components. Characteristics of the two end members ($\Sigma 8$, C/V, S/V) were taken from Table 3. It follows from the results of calculations presented in Table 4 that, as expected, the extent of the influence depends on the marine vascular plants contribution

to sedimentary organic matter. Up to some 50% contribution, the influence on $\Sigma 8$ is weak. It raises when contribution reaches some 60%. Actual values of both S/V and C/V indexes differ substantially from calculated already when the terrestrial contribution decreases to 75%. It can be concluded that both the calculated proportion of terrestrial organic matter in sedimentary organic matter and origin of lignin, judged by S/V and C/V indexes, can be seriously misjudged based on lignin derivatives alone (Table 4). It has been already pointed out that $\delta^{13}\text{C}$ cannot be trusted in areas with strong vascular marine plants biomass production, either. Therefore, a different approach is necessary for ar-

Table 5 The inflow of lignin phenols to the study area.

| Water body | Input V+S+C (kg/year) | |
|------------|-----------------------|------------------------|
| | Riverine | Marine Vascular Plants |
| Gdańsk Bay | 24750 ¹ | 231.2 ³ |
| Puck Bay | 825 ² | 462.4 ⁴ |

¹ Assuming: river runoff 1060 m³/s, suspended matter concentration 8 mg/dm³, organic matter in suspension 20%, yield of $\Sigma 8$ as in Table 3.

² Assuming: river runoff 2.8 m³/s, suspended matter concentration 7 mg/dm³, organic matter in suspension 14%, yield of $\Sigma 8$ as in Table 3.

³ Assuming: bottom covered by *Potamogeton* + *Zostera marina* + *Zanichella* – 6.1 km², biomass yield g/(m² year) *Potamogeton* – 32, *Zostera marina* – 26, *Zanichella* – 7.5, $\Sigma 8$ yield as in Table 3.

⁴ Assuming: bottom covered by *Potamogeton* + *Zostera marina* + *Zanichella* – 13.2 km², biomass yield as, in footnote no 3, above, $\Sigma 8$ yield as in Table 3.

Table 6 Average values of sedimentary organic matter origin indicators and proportion of land derived organic matter in Gdańsk Bay and Inner Puck Bay sedimentary organic matter (ML%), based on different indicators.

| Indicator | Unit | Gdańsk Bay ¹ | Puck Bay ² |
|--|---------------------------------------|-------------------------|-----------------------|
| $\delta^{13}C$ | ‰ | -24.8±0.2 | -23.2±0.1 |
| $\Sigma 8$ | mg V + S + C / 100 mgC _{org} | 861±45 | 823±37 |
| S/V | — | 1.60±0.15 | 1.20±0.10 |
| C/V | — | 0.64±0.03 | 0.40±0.02 |
| Proportion of terrestrial organic matter | | | |
| - based on $\delta^{13}C$ | % | 47 | 20 |
| - based on $\Sigma 8$ | % | 41 | 39 |
| - based on loads of lignin phenols | % | — | 35 |
| - based on the 'three end members' | % | 44 | 30 |

¹ average of 5 samples.

² average of 3 samples.

eas where a strong contribution from marine vascular plants is suspected.

4.4. Origin of sedimentary organic matter in the study area

One such area is Puck Bay, a shallow-bottom and well sheltered, north-west corner of the Gdańsk Basin. In Table 5 estimated inflow of autochthonous and allochthonous suspended organic matter is presented for Puck Bay, and Gdańsk Bay. The load of lignin residues discharged to the sea with the riverine suspended matter is comparable to a load of precursors derived from marine plants in Puck Bay, while in Gdańsk Bay a load of lignin phenols precursors derived from marine plants is two orders of magnitude smaller than the one brought to the bay with the Vistula runoff. Since both bays constitute two separate water bodies, sedimentary organic matter may reflect the mixed origin of lignin phenols precursors in Puck Bay as opposed to practically singular source in Gdańsk Bay.

In Table 6 terrestrial organic matter proportions (ML%) in the sedimentary organic matter, based on lignin phenols and $\delta^{13}C$, are listed. Values for Gdańsk Bay are close to one another independently of the applied indicator. However, Puck Bay land derived organic matter proportions differ by a factor of 2 (20% – based on lignin vs. 39% – based on $\delta^{13}C$). The $\Sigma 8$ index suggests a substantial contribution of land derived organic matter to the bay. Since the lignin phenols in the

riverine organic matter originate from woody gymnosperm plants, the S/V and C/V indexes should be equal to 2.6 and 0.49, respectively. However, the actual values are different (Table 3), confirming the substantial contribution of material comprising lignin phenols from a source differing with the quality of phenols from that in river runoff. Biomass of marine vascular plants is an obvious contributor of such material.

It is difficult to quantify the contributions, still there are several approaches to do it. One way of evaluating the contribution is comparing the V+S+C phenols loads derived from the inflow of terrestrial organic matter, and that derived from biomass production of marine vascular plants in the study area. The respective figures are presented in Table 5. The load of the V+S+C phenols originating from marine vascular plants is smaller than the riverine one in both the bays (Table 5). In Gdańsk Bay, the contribution is below 1%. Therefore, as explained earlier, on the regional basis no real threat of misusing lignins as biomarkers of terrestrial organic matter exist. However, in Puck Bay, the contribution is 35%. It may be concluded therefore that locally, in areas with substantial bottom coverage by the underwater meadows, and at the end of the growing season such a possibility exists, as the example of Puck Bay proves. In such an area substantial deviations from results of the two end-members approach based on lignin phenols could be expected and actually take place. Interestingly enough, also stable carbon isotopes ratio measured in samples collected

in the Bay of Puck shows high values. This may be well attributed to the exceptionally low values of $\delta^{13}\text{C}$ in organic material originating from marine vascular plants.

The gathered evidence suggests that in the Bay of Puck a three-member system would better reflect geochemistry of organic matter. The end members are: the riverine organic matter – R ($\Sigma 8=2500$, $\delta^{13}\text{C}=-28.5\text{‰}$), marine vascular plants – V ($\Sigma 8=90$, $\delta^{13}\text{C}=-12.0\text{‰}$), and marine phytoplankton – M ($\Sigma 8=0$, $\delta^{13}\text{C}=-22.0\text{‰}$). Basing on these characteristics the riverine – a, marine vascular plants – b, and marine phytoplankton – g, contributions to the sedimentary organic matter were calculated. The nonlinear estimation used for this purpose (Pempkowiak et al., 2006; Kulinski and Pempkowiak, 2008), proved the contributions to be, on average, 30% – a, 40% – b and 30% – c, for three samples of sediments collected in the bay. A need for introducing a three member approach was suggested earlier. Bianchi et al. (2002) and Gorgon and Goni (2003), noticed that distributions of sedimentary organic matter properties in the northern Gulf of Mexico can be explained by the separation of terrestrial organic matter into two fractions differing with the properties and distribution in sediments; while Requejo et al. (2003) suggested diversified terrestrial lignin sources at the Washington coast. The features may be attributed to fractionation of lignin residues due to specific surface area of sediment particles (Bergamasi et al., 1997), hydrodynamic factors (Ji et al., 2020) and bacterial activity (Yu et al., 2018). The phenomenon described here is based on entirely different mechanism, however.

5. Conclusions

Oxidative degradation of marine vascular plants biomass yields vanillin, cynammyl, and syringil phenols. The average yield of eight analyzed phenols ($\Sigma 8$) is 90 $\mu\text{g}/100\text{ mg}$ organic carbon. In areas characterized by a large supply of marine vascular plants biomass and a small load of riverine organic matter, lignin concentration ($\Sigma 8$) and lignin indexes are strongly modified by phenols derived from marine vascular plants biomass. Since the marine vascular plants biomass is characterized not only by the specific composition of phenols, but by exceptionally high $\delta^{13}\text{C}$ values as well, a three members approach is better suited for evaluation of the sedimentary organic matter provenience in such areas. Using a nonlinear analysis of the sedimentary organic matter $\Sigma 8$ and $\delta^{13}\text{C}$ in Puck Bay, Southern Baltic, the contributions from the three sources in question were calculated to be 40%, 30% and 30% respectively in riverine POM, marine vascular plants, and phytoplankton.

Acknowledgements

This work was performed in the frame of the Institute of Oceanology statutory activities (Theme 3). Participation of the *r/v Oceania* in sampling is acknowledged. The author is grateful to O. M. Jędrysek for performing $\delta^{13}\text{C}$ measurements, and to A. Staniszewski for lignin analysis.

References

- Bergamashi, B., Tsamakidis, E., Keil, G., Eglinton, T., Montlucon, D., Hedges, J., 1997. The effect of grain size and surface area on organic matter, lignin and carbohydrate concentration, and molecular compositions in Peru Margin sediments. *Geochim. Cosmoch. Ac.* 61 (6), 1247–1260.
- Bianchi, T.S., Cui, Blair, X.Q., Burdige, N.E., Eglinton, D.J., Galy, T.I., Galy, V., 2018. Centers of organic carbon burial and oxidation at the land-ocean interface. *Org. Geochem.* 115, 138–155, <https://doi.org/10.1016/j.orggeochem.2017.09.008>.
- Bianchi, T.S., Siddhartha, M., McKee, B.A., 2002. Sources of terrestrially-derived organic carbon in lower Mississippi River and Louisiana shelf sediments: implications for differential sedimentation and transport at the coastal margin. *Mar. Chem.* 64, 211–223.
- Bianchi, T.S., Rolff, C., Lambert, C.D., 1997. Sources and composition of particulate organic carbon in the Baltic Sea: the use of plant pigments and lignin-phenols as biomarkers. *Mar. Ecol. Prog. Ser.* 156, 25–31. <https://doi.org/10.3354/meps156025>.
- Bordovsky, O., 1965. Accumulation and transformation of organic substances in marine sediments. *Mar. Geol.* 3, 3–114.
- Cotrim da Cunha, L., Serve, L., Gadel, F., Blazi, J.-L., 2001. Lignin-derived phenolic compounds in the particulate organic matter of a French Mediterranean river: seasonal and spatial variations. *Org. Geochem.* 32, 305–320.
- Chester, R., 2003. *Marine Geochemistry*. Blackwell Publ., Malden, 357–404.
- Cragg, S.M., Friess, D.A., Gillis, L.G., Trevathan-Tackett, S.M., Terrett, O.M., Watts, J.E., Distel, D.L., Dupree, P., 2020. Vascular Plants Are Globally Significant Contributors to Marine Carbon Fluxes and Sinks. *Ann. Rev. Mar. Sci.* 12, 469–497, <https://doi.org/10.1146/annurev-marine-010318-095333>.
- Donaldson, A., 2001. Lignification and lignin topochemistry – ultrastructural view. *Phytochemistry* 57, 859–873.
- Duarte, C.M., 1991. Seagrass depth limits Aquatic. *Botany* 40, 363–377.
- Duarte, C.M., Chiscano, C.L., 1999. Seagrass biomass and production: a reassessment. *Aquat. Bot.* 65 (1–4), 159–174.
- Duarte, C.M., Cebrián, J., 1996. The fate of marine autotrophic production. *Limnol. Oceanogr.* 41, 1758–1766.
- Duarte, C.M., Marbà, N., Gacia, E., Fourqurean, J.W., Beggins, J., Barrón, C., Apostolaki, E.T., 2010. Seagrass community metabolism: Assessing the carbon sink capacity of seagrass meadows. *Global Biogeochem. Cy.* 24 (4), GB4032, <https://doi.org/10.1029/2010GB003793>.
- Duarte, C.M., Middelburg, J.J., Caraco, N., 2005. Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences* 2, 1–8.
- Farella, N., Lucotte, M., Louchouart, P., Roulet, M., 2001. Deforestation modifying terrestrial organic transport in the Rio Tapajós. Brazilian Amazon. *Org. Geochem.* 32, 1443–1458.
- Gardner, W.S., Menzel, D.W., 1974. Phenolic aldehydes as indicators of terrestrially derived organic matter in the sea. *Geochim. Cosmochim. Ac.* 38, 813–822.
- Gorgon, E., Goni, M., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochim. Cosmochim. Ac.* 67, 2359–2375.
- Gough, M.A., Fauzi, R., Mantoura, C., Preston, M., 1993. Terrestrial plant biopolymers in marine sediments. *Geochim. Cosmochim. Ac.* 57, 645–964.
- Hautala, K., Peuravuori, J., Pihlaja, K., 1997. Estimation of origin of lignin in humic DOM by CuO – oxidation. *Chemosphere* 35, 809–817.
- Haddad, R., Martens, Ch, 1987. Biogeochemical cycling in the organic rich coastal marine basin: 9. Sources and accumulation

- rates of vascular plant-derived organic material. *Geochim. Cosmochim. Ac.* 51, 2991–3001.
- Hamminga, M., Mateo, M., 1996. Stable carbon isotopes in seagrasses: variability in ratios and use in ecological studies. *Mar. Ecol. Prog. Ser.* 84, 9–18.
- Hedges, J.I., 1992. Global biogeochemical cycles: progress problems. *Mar. Chem* 39, 67–93.
- Hedges, J.I., Clark, W.A., Cowie, G.L., 1988. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnol. Oceanogr.* 33, 1116–1136.
- Hedges, J.I., Ertel, J.R., 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Anal. Chem.* 54, 174–178.
- Hedges, J.I., Ertel, J.R., Leopold, E.B., 1982. Lignin geochemistry of a late Quaternary sediment core from Lake Washington. *Geochim. Cosmochim. Ac.* 46, 1869–1877.
- Hedges, J.I., Mann, D.C., 1979. The characterisation of plant tissues by their lignin oxidation products. *Geochim. Cosmochim. Ac.* 43, 1803–1807.
- Hedges, J.I., van Geen, A., 1982. A comparison of lignin and stable carbon isotope composition in quaternary sediments. *Mar. Chem.* 11, 43–53.
- Hu, F.S., Hedges, J., Gordon, E.S., Brubaker, L.B., 1999. Lignin biomarkers and pollen in postglacial sediments of an Alaska lake. *Geochim. Cosmochim. Ac.* 63, 1421–1430.
- Hu, X., Burdige, D., 2007. Enriched stable carbon isotopes in the pore waters of carbonate sediments dominated by seagrasses; Evidence for coupled carbonate dissolution and reprecipitation. *Geochim. Cosmochim. Ac.* 71, 129–144.
- Jędrysek, O.M., Krąpiec, M., Skrzypek, G., Kałużny, A., 2003. Air-pollution effect and paleotemperature scale versus $\delta^{13}\text{C}$ records in tree rings and in a peat core (Southern Poland). *Water Air Soil Pollut.* 145, 359–373.
- Jex, C.N., Pate, G.H., Blyth, A.B., Spencer, R., Hernes, P.J., Khan, S.J., Baker, A., 2014. Lignin biogeochemistry: From modern processes to Quaternary archives. *Quaternary Sci. Rev.* 87, 46–59.
- Jørgensen, S.E., Fath, B.D., 2008. *Encyclopedia of Ecology*. Elsevier, 1407–1413.
- Ji, Y., Feng, L., Zhang, D., Wang, Q., Pan, G., Li, X., 2020. Hydrodynamic sorting controls the transport and hampers source identification of terrigenous organic matter: A case study in East China Sea inner shelf and its implication. *Sci. Total Environ.* 706, 135699, <https://doi.org/10.1016/j.scitotenv.2019.135699>.
- Jonsson, P., Carman, R., 1994. Changes in deposition of organic matter and nutrients in the Baltic Sea during the twentieth century. *Mar. Pollut. Bull.* 28, 417–426.
- Kruk-Dowgiałło, L., 2008. Przyczyny i skutki wieloletnich zmian fitobentosu Zatoki Gdańskiej. *Inst. Morski, Gdańsk*, 132 pp.
- Kuliński, K., Pempkowiak, J., 2008. Dissolved organic carbon in the southern Baltic Sea: Quantification of factors affecting its distribution. *Estuar. Coast. Shelf Sci.* 78, 38–44.
- Majewski, A., 1990. *Zatoka Gdańska*. Wyd. Geol., Warsaw, 120–311.
- Maksymowska, D., Richard, P., Piekarek-Jankowska, H., Riera, P., 2000. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdańsk (Southern Baltic Sea). *Estuar. Coast. Shelf Sci.* 51, 585–598.
- Merdy, P., Guillon, E., Dumonceau, J., Aplincourt, M., 2002. Characterisation of a wheat straw cell wall residue by various techniques A comparative study with a synthetic and an extracted lignin. *Anal. Chim. Acta* 459, 133–142.
- 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.* 31, 57–66.
- Miltner, A., Emeis, K.C., 2000. Origin and transport of terrestrial organic matter from the Oder lagoon to the Arkona Basin. *Southern Baltic Sea, Org. Geochem.* 31 (1), 57–66.
- Miltner, A., Emeis, K., 2001. Terrestrial organic matter in surface sediments of the Baltic Sea, Northwest Europe, as determined by CuO oxidation. *Geoch. Cosmochim. Ac.* 65, 1285–1299.
- Miltner, A., Emeis, K.C., Struck, U., 2005. Terrigenous organic matter in Holocene sediments from the central Baltic Sea. *NW Europe. Chem. Geol.* 216 (34), 313–328.
- Opsahl, S., Benner, R., 1995. Early diagenesis of vascular plant tissues: Lignin and cutin decomposition and biogeochemical implications. *Geochim. Cosmochim. Ac.* 59, 4889–4904.
- Pempkowiak, J., 1983. C18 reversed-phase trace enrichment of short- and long-chain (C2-C8-C20) fatty acids from dilute aqueous solutions and sea water. *J. Chromatogr.* 258, 93–102, [https://doi.org/10.1016/S0021-9673\(00\)96401-X](https://doi.org/10.1016/S0021-9673(00)96401-X).
- Pempkowiak, J., 1991. Enrichment factors of heavy metals in the Southern Baltic surface sediments dated with ^{210}Pb and ^{137}Cs . *Environ. Int.* 17, 421–428.
- Pempkowiak, J., Pocklington, R., 1983. Phenolic aldehydes as indicators of the origin of humic substances in marine environments. In: Christman, R.F., Gjessing, E.T. (Eds.), *Aquatic and terrestrial humic materials*. Ann Arbor Sci., Michigan, 371–385.
- Pempkowiak, J., Beldowski, J., Staniszewski, A., Leipe, T., Emeis, K.-Ch., 2002. The contribution of the sediment fraction to the fluffy layer suspended matter. *Oceanologia* 44 (4), 513–527.
- Pempkowiak, J., Tylmann, W., Staniszewski, A., Gołębiowski, R., 2006. Lignin depolymerisation products as biomarkers of the organic matter sedimentary record in ^{210}Pb – ^{137}Cs -dated lake sediments. *Org. Geochem.* 37, 1452–1464.
- Pempkowiak, J., Walkusz-Miotk, J., Beldowski, J., Walkusz, W., 2006. Heavy metals in zooplankton from the Southern Baltic. *Chemosphere* 62, 1697–1708.
- Pradhan, U.K., Wu, Y., Shirodkar, P.V., Zhang, J., Zhang, G., 2014. Sources and distribution of organic matter in thirty-five tropical estuaries along the west coast of India – a preliminary assessment. *Estuar. Coast. Shelf Sci.* 151, 21–33.
- Raven, J.A., Johnston, A.M., Kubler, J.E., Korb, R., McInroy, S.G., Handley, L.L., Scrimgeour, C.M., Walker, D.I., Beardall, J., Vanderklift, M., Fredriksen, S., Dunton, K.H., 2002. Mechanistic interpretation of carbon isotope discrimination by marine macroalgae and seagrasses. *Funct. Plant Biol.* 29, 355–378.
- Reeves, A.D., 1995. The use of organic markers in the differentiation of organic inputs to aquatic Systems. *Phys. Chem. Earth* 2, 133–140.
- Requejo, A., Brown, J., Boehm, P., 1986. Lignin geochemistry of sediments from the Narragansett Bay Estuary. *Geochim. Cosmochim. Ac.* 50, 2707–2717.
- Requejo, A., Brown, J., Boehm, P., Sauer, T., 2003. Lignin geochemistry of North American coastal and continental shelf sediments. *Org. Geochem.* 17, 649–662.
- Sederoff, R.R., MacKay, J.J., Ralph, J., Hatfield, R.D., 1999. Unexpected variation in lignin. *Curr. Opin. Plant Biol.* 2, 145–152.
- Staniszewski, A., 2005. *Pochodzenie materii organicznej w osadach dennych Bałtyku Południowego* PhD Thes., IO PAN, Sopot, 185 pp.
- Staniszewski, A., Lejman, A., Pempkowiak, J., 2001. Horizontal and vertical distribution of lignin in surface sediments of the Gdańsk Basin. *Oceanologia* 43 (4), 421–439.
- Sun, S., Schefuß, E., Mulitza, S., Chiessi, C. M., Sawakuchi, A. O., Zabel, M., Baker, P. A., Hefter, J., Mollenhauer, G., 2017. Origin and processing of terrestrial organic carbon in the Amazon system: lignin phenols in river, shelf, and fan sediments. *Biogeosciences* 14, 2495–2512, <https://doi.org/10.5194/bg-14-2495-2017>.
- Thorton, S., McManus, J., 1994. Application of organic carbon and nitrogen stable isotopes as indicators of organic matter provenance in estuarine systems: evidence from the Tay estuary. *Scotland. Estuar. Coast. Shelf Sci.* 38, 219–233.

- Voss, M., Larsen, B., Leivuori, M., Vallius, H., 2000. Stable isotope signals of eutrophication in coastal Baltic sediments. *J. Marine Syst.* 25, 287–298.
- Wilson, J.O., Valiela, I., Swain, T., 1985. Sources and concentrations of vascular plant material in sediments of Buzzards Bay, Massachusetts, USA. *Mar. Biol.* 90, 129–137.
- Winogradow, A., Pempkowiak, J., 2014. Organic carbon burial rates in the Baltic Sea sediments. *Estuar. Coast. Shelf Sci.* 138, 27–36, <https://doi.org/10.1016/j.ecss.2013.12.001>.
- Winogradow, A., Pempkowiak, J., 2018. Characteristics of sedimentary organic matter in coastal and depositional areas in the Baltic Sea. *Estuar. Coast. Shelf Sci.* 204, 66–75, <https://doi.org/10.1016/j.ecss.2018.02.011>.
- Winogradow, A., Mackiewicz, A., Pempkowiak, J., 2019. Seasonal changes in particulate organic matter (POM) concentrations and properties measured from deep areas of the Baltic Sea. *Oceanologia* 61 (4), 505–521, <https://doi.org/10.1016/j.oceano.2019.05.004>.
- Ye, Z.H., Zhonga, R., Morrison, W.H., Himmelsbach, D.S., 2001. Caffeoyl coenzyme A O-methyltransferase and lignin biosynthesis. *Phytochemistry* 57, 1177–1185.
- Yu, T., Wu, W., Liang, W., Lever, M.A., Hinrichs, K.U., Wang, F., 2018. Growth of sedimentary *Bathyarchaeota* on lignin as an energy source. *Proc. Natl. Acad. Sci. USA* 115 (23), 6022–6027, <https://doi.org/10.1073/pnas.1718854115>.