



DISTRIBUTION AND ORIGIN OF ORGANIC MATTER IN THE BALTIC SEA SEDIMENTS DATED WITH ^{210}Pb AND ^{137}Cs

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Received 1 May 2011

Accepted 2 November 2011

Abstract: Organic carbon deposited in marine sediments is an important part of the global carbon cycle. The knowledge concerning the role of shelf seas (including the Baltic Sea) in the carbon cycle has increased substantially, however organic carbon accumulation rates in the Baltic sediments still require clarification.

This paper describes methods used for assessing organic carbon and nitrogen accumulation rates in six sediment cores collected in the sediment accumulation areas in the Baltic Sea. Mass sediment accumulation rates were based on ^{210}Pb method validated by ^{137}Cs measurements. The organic carbon accumulation rates ranged from 18 to 75 $\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. The C/N ratios and $\delta^{13}\text{C}$ were used to assess sedimentary organic matter provenance. The C/N ratios in the investigated cores vary in the range from 7.4 to 9.6, while $\delta^{13}\text{C}$ ranged from -24.4‰ to -26.4‰. Results of the terrestrial organic matter contribution in the sedimentary organic matter were calculated basing on $\delta^{13}\text{C}$ using the end member approach. Large proportion (41-73%) of the sedimentary organic carbon originates on land.

The obtained results indicate the Baltic Sea sediments as an important sink for organic carbon. Substantial fraction of the sedimentary load originates on land.

Keywords: accumulation rates, marine sediments, organic carbon, nitrogen, stable carbon isotopes.

1. INTRODUCTION

The carbon cycle is one of the major biogeochemical cycles as regards the flow of matter and energy in the environment. The main constituent of the carbon cycle is carbon dioxide (CO_2). In recent decades a significant increase of carbon dioxide in the atmosphere due to fossil fuel burning has been observed, resulting in global warming (Chen and Borges, 2009; HELCOM, 2007; IPCC, 2007).

It is believed that almost 35% of anthropogenic CO_2 emission is absorbed by seas and oceans (Takahashi *et al.*, 2009). Almost $\frac{1}{3}$ of this load is absorbed by shelf seas. During the last decade, knowledge about the role of shelf seas, in the carbon cycle has increased considerably. It has been estimated that the shelf seas are responsible for approximately 20% of marine organic matter production and about 80% of the total organic matter load deposited to marine sediments (Borges, 2005). The Baltic Sea plays a significant role among the shelf seas in this context (Thomas *et al.*, 2010).

The Baltic Sea is described as an autotrophic semi-enclosed brackish sea (Thomas *et al.*, 2003). Considera-

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ble amounts of nutrients, mostly from agriculture and industry, enter the sea from rivers, making the Baltic Sea one of the most productive marine ecosystems (Emelyanow, 1995; Gudelis and Jemielianowa, 1982; HELCOM 2006; Thomas *et al.*, 2003). The most important sources of organic matter in the Baltic Sea are: primary production, river runoff and import from the North Sea (Wasmund and Uhlig, 2003; Kuliński and Pempkowiak, 2011). However, it must be remembered that the Baltic Sea is a net source of organic matter for the North Sea (Kuliński *et al.*, 2011; Kuliński and Pempkowiak, 2012). A large part of the Baltic Sea catchment area includes agricultural areas that export large amounts of nutrients (Emelyanow, 1995; Gudelis and Jemielianowa, 1982). The increase of nutrients enhances the „biological pump” that causes CO₂ absorption and assimilation to organic matter by phytoplankton. A large part of organic matter both produced in the sea and brought to the sea is incorporated in the sediments (Kuliński and Pempkowiak, 2008). Existing data are insufficient to quantify the load of organic carbon that is accumulated in sediments. Preliminary estimates indicate that the amount of organic carbon deposited into the sediments is about 3.9 Tg C_{org} yr⁻¹ (Tg = 10¹² g) (Pempkowiak, 1985). However, the exact value is unknown (HELCOM, 2004; Kuliński and Pempkowiak, 2012). Estimates are uncertain due to limited amount of data on both sediment accumulation rates and the range of organic carbon concentrations in bottom sediments.

Nitrogen is an important biogenic element that is believed to be a limiting factor for organic matter primary production in the Baltic Sea (Dzierzbicka-Głowacka *et al.*, 2011; Hongisto, 2011). Although, sources of nitrogen to the Baltic are well established, deposition to sediments still requires further quantification (Łysiak-Pastuszak, 2000; Thomas *et al.*, 2003).

Using mass sediment accumulation rates, derived from ²¹⁰Pb and ¹³⁷Cs profiles, and concentrations in sediments of organic carbon and total nitrogen, accumulation rates of both these elements in the sediments of the Baltic Sea were calculated. The study was carried out on sediment cores collected from depositional areas of the sea. The results are essential for carbon and nitrogen budget calculations in the Baltic Sea.

2. EXPERIMENTAL

Study area

The Baltic Sea is the second largest brackish water body in the world. It extends between the 10-30°E and 54-64°N. The surface area of the Sea is equal to 415 000 km² (including Kattegat) (HELCOM 2007; Lass and Matthäus, 2008). The brackish nature of the Baltic Sea is due to the combination of the high river water discharge and the limited inflows of saline water from the North Sea. The inflows of saline water lead to a stable stratification of water in the Baltic basins where water depth ex-

ceeds about 80 m. Water budget of the sea is further influenced by precipitation that exceeds evaporation. Halocline resulting in limited mixing of water masses, and the progressive eutrophication, are the cause of oxygen deficits due to mineralization of organic matter. Direct discharges of treated sewage are of importance due to the load of nutrients they carry. Increasing eutrophication also implies phytoplankton blooms, enhancing the „biological pump” phenomenon (Dzierzbicka-Głowacka *et al.*, 2010).

The Gotland Deep (250 m depth) is a flat bottom basin with both gentle and steep slopes and with predominantly soft bottom (silty and muddy sediments) in the Eastern Gotland Basin, and both soft and hard bottom, equally distributed, in the Western Gotland Basin. The stratification of the water column causes a decrease of oxygen concentration with depth and promotes bottom water oxygen depletion. In the Eastern Gotland Basin, halocline and pycnocline are located at the depth of 60-70 m, while in the Western Gotland Basin – at the depth of 50-60 m (Hagen and Feistel, 2004; Walter *et al.*, 2006; Voipio, 1981).

The Gdańsk Deep is a circular, flat bottom basin covered by silty and muddy sediments. Inflows of saline water lead to the formation of halocline at the depth of 60-70 m and cause a deficiency of oxygen, accompanied by an occurrence of hydrogen sulfide. The surface water layers are characterized by low salinity of 7.1 psu and by seasonal fluctuations of temperature. The subsurface layers are characterized by stable temperature and salinity in the range of 9-11 psu (Ebbing *et al.*, 2002; Emelyanow, 2002; Leipe *et al.*, 2011; Szczepańska and Uściłowicz, 1994).

Materials and methods

Sediment cores were collected using Niemisto and GEMAX corers (equipped with two 50 cm long, 10 cm diameter core tubes) during the Oceania cruises, at 6 selected stations in the southern part of the Baltic Sea, in 2007 (**Table 1, Fig. 1**). Five sediment cores were collected from the areas characterized by steady sedimentation (Gotland Basin and Gdańsk Basin), while one sediment core was collected between the Oland Island and the Swedish coast, where the water dynamics have a strong impact on sedimentation processes. Profiles of salinity and temperature against depth measured using a CTD profiler proved water stratification at the study sites. All sediment cores were muddy, and characterized by an intensive smell of hydrogen sulfide. The sediment cores were brownish at the surface layers changing to grey and dark grey in the deeper sediment layers. Water from above the sediment surface was analyzed for basic parameters like salinity, O₂ and redox potentials. Immediately after collecting cores were sliced into 10 mm thick layers and frozen at -20°C. After thawing in laboratory sediment samples were freeze-dried at 60°C and homogenized. Before analysis sediments samples were passed

through 0.063 mm mesh sieve, the <0.063 mm fraction was further analyzed. The following analyses were carried out: moisture (bulk sediments), loss of ignition, C_{org} , N_{tot} , activity concentrations of ^{210}Pb and ^{137}Cs , carbon stable isotopes.

The moisture was calculated using the formula:

$$M = \frac{m_w - m_d}{m_w} \cdot 100\% \quad (2.1)$$

where: M is moisture (%), m_w is wet sample mass in grams (g), m_d is dry sample mass (g).

Sediment porosity was calculated according to the formula:

$$P = \frac{w_m}{d_w \cdot V} \quad (2.2)$$

where: P is sediment porosity, w_m is water weight in the sample (wet sample weight – dry sample weight), d_w is water density (1.00 g cm^{-3}) and V is vial volume.

Loss of ignition (LOI) was determined by burning dry samples in a muffle oven at 450°C for 8 hours.

Organic carbon and total nitrogen concentrations, and stable carbon isotopes composition ($\delta^{13}C$) were measured in an Elemental Analyzer Flash EA 1112 Series com-

bined with the Isotopic Ratio Mass Spectrometer IRMS Delta V Advantage (Thermo Electron Corp., Germany). The reference gas was pure N_2 and CO_2 gas calibrated against IAEA standards: CO-8 and USGS40 for $\delta^{13}C$ and N-1 and USGS40 for $\delta^{15}N$. The standard deviation was less than 0.15‰ and 0.20‰ for $\delta^{13}C$ and $\delta^{15}N$ respectively. Quality control of C and N concentrations measurements was carried out with standard materials supplied by the Thermo Electron Corp. The used methodology proved satisfactory accuracy and precision (average recovery 99.1% for C and 98.5% for N). Before analysis, carbonates were removed from the samples by acidification (HCl_{conc}) for 24 hours.

Determination of ^{210}Pb activity concentration was performed assuming secular equilibrium between ^{210}Pb and ^{210}Po , according to the method developed by Flynn (1968) and adopted by Pempkowiak (1991). 100 mg of dry sediment was spiked with known activity of ^{209}Po , subsequently the sample was digested with 2 cm^3 of perchloric acid followed by 4 cm^3 of fluoric acid. The so obtained solution was transferred, with 6M HCl, to a Teflon vessel and evaporated to dryness. The dry residue was dissolved in $0.5 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid and ^{209}Po and ^{210}Po were spontaneously deposited onto silver disks of 15 mm diameter (90°C , 4 hours, continuous stirring). The disks were counted for 20 hours in an alpha spectrometer, type 7200-02, equipped with a silicon detector (Canberra). Counting error (1σ) was lower than 10%.

The ^{137}Cs was introduced into the environment as a consequence of nuclear weapons tests in the period from 1950-1976 (Abril, 2003). The significant quantities of ^{137}Cs were introduced also as a result of the Chernobyl accident in 1986 (Kankaanpaa *et al.*, 1997; Lima *et al.*, 2004; Suplińska, 2002; Suplińska, 2008). The ^{137}Cs specific activity was determined in a gamma spectrometer equipped with a Canberra high-purity Ge detector. The analyses were carried out on 20 g samples packed in vials of a cylindrical standard geometry ($65 \text{ mm} \times \phi 20 \text{ mm}$). Calibration of the counter was performed based on the reference materials obtained from IAEA (IAEA-300 and IAEA-315). The counting time was at least 24 h. Counting error (1σ) was lower than 10%. No correction for ^{137}Cs decay was applied as the useful information used was just the presence of the radionuclide at a given depth.

Sediment accumulation rates (SAR in $\text{cm} \cdot \text{yr}^{-1}$) were determined from profiles of excess ^{210}Pb activity concentrations versus porosity-corrected depth in sediments.

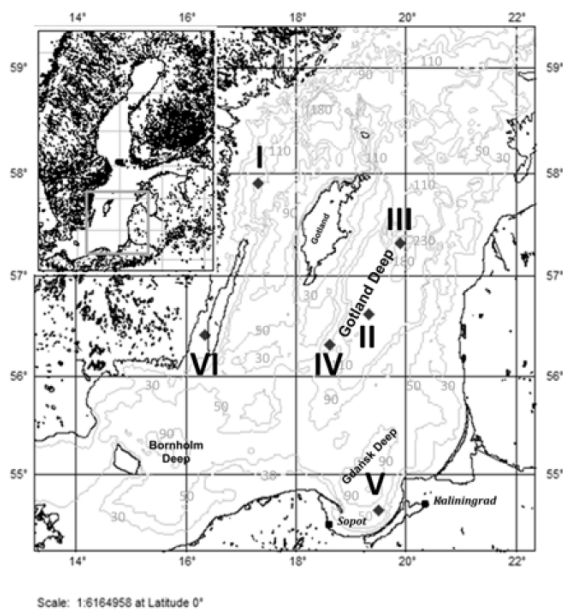


Fig. 1. Location of the sampling station.

Table 1. Location of cores sampling sites and sediment bulk properties.

Station	Latitude °N	Longitude °E	Depth (m)	Core length (cm)	Porosity
I	57°54	17°18	80	25	0.76-0.89
II	56°37	19°20	135	28	0.81-0.98
III	57°19	19°54	230	23	0.76-0.97
IV	56°19	18°36	85	23	0.70-0.93
V	54°37	19°30	55	42	0.81-0.95
VI	56°03	16°02	47	35	0.86-0.94

The supported $^{210}\text{Pb}_{\text{supp}}$ activity concentration was calculated as the mean of activities in layers, below the decay zone, with constant radiolabel activity. In the case of surface mixing, sediment accumulation rates were calculated from the part of profiles below mixed zone.

$^{210}\text{Pb}_{\text{ex}}$ activity concentration was calculated as the difference between total $^{210}\text{Pb}_{\text{tot}}$ and $^{210}\text{Pb}_{\text{supp}}$ activities:

$$^{210}\text{Pb}_{\text{ex}} = ^{210}\text{Pb}_{\text{tot}} - ^{210}\text{Pb}_{\text{supp}} \quad (2.3)$$

Sediment accumulation rates were calculated according to the formula:

$$A_t = A_0 e^{-\lambda t} \quad (2.4)$$

where A_t is the ^{210}Pb activity at time t , A_0 is the activity at time 0, λ is the radionuclide decay constant (for $\lambda = 0.031 \text{ 1/y}$).

When t is replaced by $t = x/v$ (x – depth of a given sediment layer, v – sedimentation rate) the above formula can be rewritten:

$$\ln A^{210}\text{Pb}_{\text{ex}}(x) = \ln A^{210}\text{Pb}_{\text{ex}}(0) - (\lambda/v) x \quad (2.5)$$

where: $A^{210}\text{Pb}_{\text{ex}}(x)$ is the activity at layer x , $A^{210}\text{Pb}_{\text{ex}}(0)$ is the activity at surface (layer 0), λ is the decay constant, v is the sediment accumulation rate.

The constant rate of supply (CRS) model was used throughout the calculations (Robins, 1978; Zaborska *et al.*, 2007).

$$A_x = A_0 e^{-\lambda t} \quad (2.6)$$

$$x/v = 1/\lambda \ln \Sigma(A_{\text{ex}})/\ln \Sigma(A_{\text{c0}}) \quad (2.7)$$

where ΣA_{ex} is the cumulative residual $^{210}\text{Pb}_{\text{ex}}$ activity beneath sediments of depth x , ΣA_{c0} is the total $^{210}\text{Pb}_{\text{ex}}$ activity in the sediment column, x is the cumulative depth (cm), v is the sediment accumulation rate ($\text{cm}\cdot\text{yr}^{-1}$), t is the age of the sediment (years).

Sediment mass accumulation rates (MAR in $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) were calculated using the $^{210}\text{Pb}_{\text{ex}}$ after transforming sediment depth to mass depth (Robins, 1978; Zaborska *et al.*, 2008). Cumulative dry mass depth was estimated according to the formula:

$$D_D = h \cdot D_S \cdot (1 - P) \quad (2.8)$$

$$\Sigma D_D = \Sigma (h_{i+1} - h_1) \cdot (1 - P_i) \cdot D_i \quad (2.9)$$

where D_D is the dry mass depth, h is the layer thickness, D_S is the dry sediment density and P is the layer porosity.

To validate the so obtained sediment accumulation rates, profiles of the man-made radionuclide ^{137}Cs were used. Actual (measured), and expected (basing on ^{210}Pb datings) depths of ^{137}Cs occurrence were compared. If both depths agreed (3 cores), sediment age determinations were accepted. If both depths were different (3 cores) then the mixing depth of surface sediments was

adjusted to give an agreement between the expected and the actual ^{137}Cs occurrence depths.

Organic carbon and total nitrogen accumulation rates were calculated as the product of mass sediment accumulation rates ($\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and organic carbon concentrations and total nitrogen concentrations respectively. Only the surface, above the mixed depth, organic carbon concentrations was used, to get the flux of a newly deposited organic carbon.

3. RESULTS AND DISCUSSION

Sediment accumulation rates

The highest total ^{210}Pb ($^{210}\text{Pb}_{\text{tot}}$) activity concentrations were measured in sediment samples from station VI, where they range from $906 \pm 15 \text{ Bq/kg}$ at the sediment surface to $211 \pm 11 \text{ Bq/kg}$ at the lower sediment section. The lowest total ^{210}Pb activity concentrations are measured in sediments collected at station I. They range from $172 \pm 10 \text{ Bq/kg}$ to $26 \pm 1.2 \text{ Bq/kg}$ (Fig. 2a). The high value of ^{210}Pb activity concentration in sediments from station VI could be due to the Emar river that enters the Kalmar Sund nearby the location of the sampling station.

Linear accumulation rates of sediments in the investigated cores vary in the range from $0.06 \text{ cm}\cdot\text{yr}^{-1}$ at station IV to $0.16 \text{ cm}\cdot\text{yr}^{-1}$ at station VI. Surface layers of cores from stations I, II, III and VI were mixed, which may be caused by bioturbation or by physical processes, e.g. wave induced water movement – strong enough to affect deposited sediments (e.g. station VI). In the course of mixing, sediments may be resuspended and the fine grained fraction may be washed out.

Mass sediment accumulation rates, below the depth of surface sediment mixing, vary from 159 to $534 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. The highest mass sediment accumulation rate was found at station I ($534 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and at station III ($461 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). While the mass sediment accumulation rate at station II reached a value of just $160 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (Table 2).

The results are well in the ranges reported earlier for the Baltic sediments (Hille *et al.*, 2006; Pempkowiak, 1991; Szczepańska *et al.*, 2009; Suplińska, 2008; Widrowski and Pempkowiak, 1986).

The activity concentrations of ^{137}Cs in sediments differ depending on sampling site and sampling depth (Fig. 2b). The highest concentration is observed at the station V, localized in the Gdansk Deep, amounting to about $430 \pm 18 \text{ Bq/kg}$ in the surface layer, while the lowest – at station IV where the activity concentration is about $80 \pm 6 \text{ Bq/kg}$ at surface sediments. Ranges of radiocesium activity concentrations in the surface sediments reported earlier (Pempkowiak, 1991; Suplińska, 2002) agree well with our results.

Accumulation rates of organic carbon

Organic carbon concentrations measured in the all six investigated sediment cores are presented in Fig. 3a. The

highest organic carbon concentration (C_{org}), ranging from 10.13% at the surface to 4.56% in deeper layers was measured in sediments from station II, situated on the

southern side of the Gotland Deep. At station IV C_{org} concentration reached value of only 5.47% at the surface layer and decreased to about 3.73% in deeper layers.

Organic carbon accumulation rates ($g \cdot C \cdot m^{-2} \cdot yr^{-1}$) calculated as a product of the mass sediment accumulation rates and the organic carbon concentrations vary in the range from $18 g \cdot C \cdot m^{-2} \cdot yr^{-1}$ at station IV to $75 g \cdot C \cdot m^{-2} \cdot yr^{-1}$ at station VI (Table 2).

The average organic carbon accumulation rate observed at stations II and III (Gotland Deep) is about $33 g \cdot C \cdot m^{-2} \cdot yr^{-1}$. The value is within ranges obtained by Emeis *et al.* (2000) (about $27 g \cdot m^{-2} \cdot yr^{-1}$) and Struck *et al.* (2000) (about $30 g \cdot m^{-2} \cdot yr^{-1}$) for the southern Baltic.

The organic carbon accumulation rate result calculated for the station V amounts to $27 g \cdot C \cdot m^{-2} \cdot yr^{-1}$. The value is smaller than the literature values for the Gdańsk Deep (Emeis *et al.*, 2000, about $60 g \cdot m^{-2} \cdot yr^{-1}$), although the mass sediment accumulation rate value is similar to the literature values for this region (MAR at station V – $410 g \cdot m^{-2} \cdot yr^{-1}$, MAR obtained by Pempkowiak, 1991 – about $510 g \cdot m^{-2} \cdot yr^{-1}$). The difference is caused by low levels of organic carbon concentrations, measured in sediment samples from core number V, amounting to about 6.48% at the surface and just 2.87% in deeper segments of the sediment core. The low concentrations, most likely, are caused by location of the sampling site at the margin of the Gdańsk Deep.

Profiles of organic carbon concentrations in recent bottom sediments of the Baltic Sea indicate that organic matter concentrations decrease with sediments depth. This is attributed to the recent increased organic matter deposition caused by eutrophication (Emeis *et al.*, 2000; Voss *et al.*, 2000). Another important factor contributing to this phenomenon is mineralization of labile part of organic matter (Kuliński and Pempkowiak, 2012). Such a trend is observed generally at station II, III, IV and V. At station III the typical decrease is followed by an increase in the sub-surface sediment layers. This increase may suggest that 100-150 years ago, at this particular location, there occurred much higher deposition of organic matter that has been buried permanently in sediments since then. Another explanation might be different origin and associated different proportion of organic matter stable fraction deposited there due to resuspension and redeposition processes.

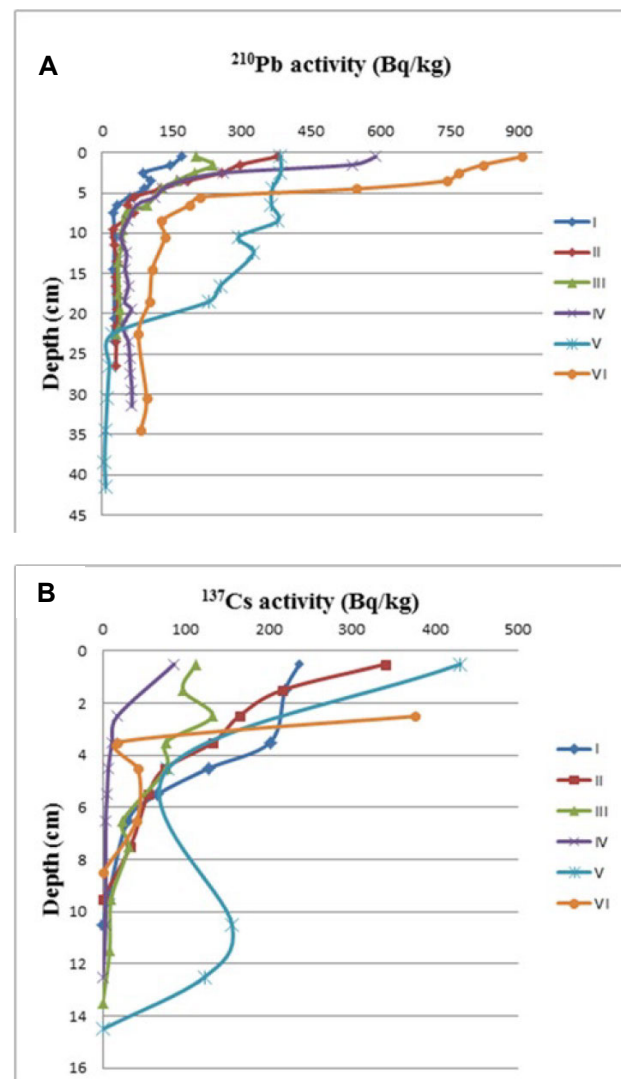


Fig. 2. A – ^{210}Pb activity concentrations against sediment depth in the core, B – ^{137}Cs activity concentrations against sediment depth in the core.

Table 2. Linear sediment accumulation rates ($cm \cdot yr^{-1}$), mass sediment accumulation rates ($g \cdot m^{-2} \cdot yr^{-1}$), organic carbon accumulation rates ($g \cdot C \cdot m^{-2} \cdot yr^{-1}$) and nitrogen accumulation rates ($g \cdot N \cdot m^{-2} \cdot yr^{-1}$) in the investigated sediments.

Sediment core	Linear sediment accumulation rate ($cm \cdot yr^{-1}$)	Mass sediment accumulation rate ($g \cdot m^{-2} \cdot yr^{-1}$)	Organic carbon accumulation rate ($g \cdot C \cdot m^{-2} \cdot yr^{-1}$)	Accumulation rate of nitrogen ($g \cdot N \cdot m^{-2} \cdot yr^{-1}$)	Ratio of carbon and nitrogen accumulation rates
I	0.14	534	34	4.4	7.7
II	0.11	198	23	2.3	10.0
III	0.10	461	43	5.0	8.6
IV	0.06	320	18	2.3	7.8
V	0.06	410	27	3.4	7.9
VI	0.16	874	75	8.8	8.5

Organic carbon concentration profiles and total nitrogen concentration profiles at all stations except station I exhibit similar shapes. It indicates that nitrogen, carbon and organic matter concentrations changes in the corresponding sediment layers are governed by similar processes. This is clearly seen at sediment core from station III, where the increase of nitrogen and organic carbon concentrations are measured at exactly the same sediment layer (16-17 cm), indicating untypical origin of sediments constituting the layer.

Accumulation rates of nitrogen

Total nitrogen concentrations in the investigated sediment samples range from 1.34% to 0.34%. The highest N_{tot} concentrations were measured in sediments from station II. These amounted to 1.34% in the surface layer

and to 0.48% in deeper part of the core. The lowest total nitrogen concentrations were measured in the sediment core collected at station IV (0.73-0.42%) (**Fig. 3b**).

Accumulation rates of nitrogen expressed in $\text{g}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ was calculated as a product of the mass sediment accumulation rates and the nitrogen concentration measured in sediments. The lowest nitrogen accumulation rate is observed at stations II and IV ($2.3 \text{ g}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). The highest nitrogen accumulation rate is observed at station VI ($8.8 \text{ g}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) (**Table 2**).

As it can be seen, the same trends are observed for nitrogen and organic carbon accumulation rates. The lowest and the highest values of organic carbon accumulation rates occurred in sediments from stations II and VI. However, ratios of C/N accumulation in sediments differ considerably, indicating perhaps that not all labile organic matter is actually mineralized in the surface sediments. The matter of C/N ratios is discussed, in some detail, below.

Origin of organic matter in the Baltic sediments

There are several indicators that may be used to assess sedimentary organic matter provenance. The most valuable ones are based on molecular composition of organic substances. Moreover, ratio of C/N abundance in the matter is frequently used for the purpose of differentiating land ($C/N > 12$) vs. marine ($C/N < 10$) origin. Redfield ratio of marine phytoplankton biomass ($C/N = 7$) is much smaller than sedimentary organic matter originating from pure marine sources. This indicates that preferential mineralization of organic nitrogen takes place in the course of sedimentation and early diagenesis. The C/N ratios encountered in the investigated cores vary in the range from 7.4 to 9.6 (**Table 3**). This would indicate predominantly marine character of sedimentary organic matter in the

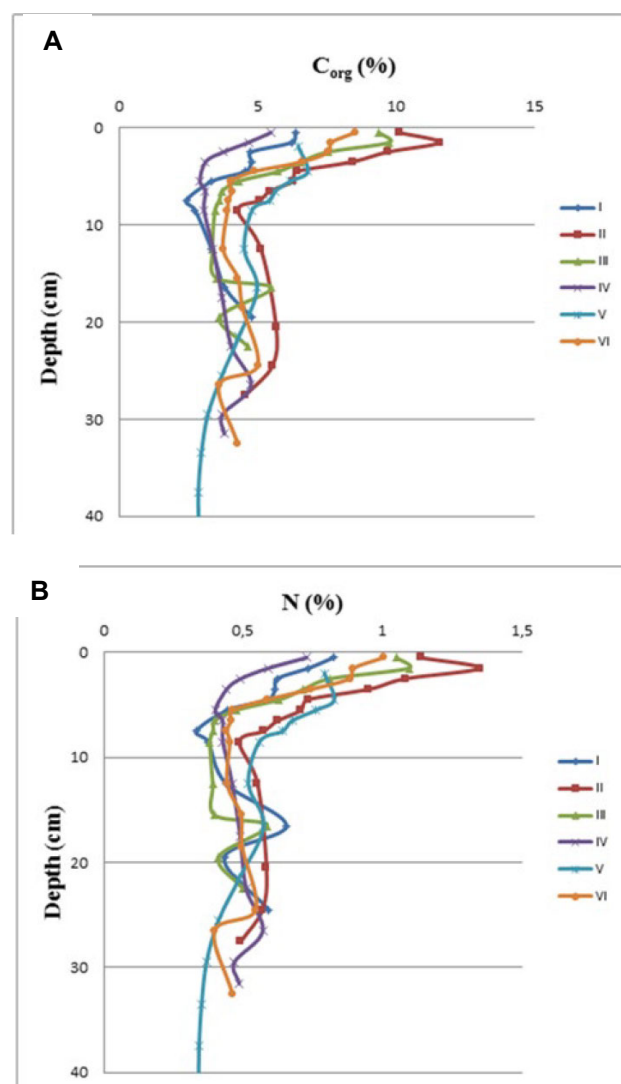


Fig. 3. A – organic carbon concentration against sediment depth, B – total nitrogen concentration against sediment depth.

Table 3. $C_{\text{org}}/N_{\text{tot}}$ ratios, $\delta^{13}\text{C}$ and terrestrial organic matter proportion in the surface (<10 cm) and subsurface (>20 cm) segments of the investigated cores.

Sediment core	Layers	C/N ratio	$\delta^{13}\text{C}$ (‰)	Terrestrial organic matter contribution (%)
I	Surface	8.6 ± 0.2	-24.70 ± 0.08	45.0
	Subsurface	9.6 ± 0.5	-24.68 ± 0.98	44.6
II	Surface	8.8 ± 0.1	-24.56 ± 0.20	42.7
	Subsurface	9.5 ± 0.2	-25.63 ± 0.10	60.5
III	Surface	9.1 ± 0.2	-24.70 ± 0.18	45.0
	Subsurface	9.0 ± 0.3	-26.36 ± 0.36	72.7
IV	Surface	7.4 ± 0.3	-24.78 ± 0.12	46.5
	Subsurface	8.0 ± 0.3	-24.63 ± 0.27	44.2
V	Surface	8.3 ± 0.1	-24.61 ± 0.22	43.5
	Subsurface	8.8 ± 0.2	-25.81 ± 0.08	63.5
VI	Surface	8.6 ± 0.2	-24.45 ± 0.21	40.8
	Subsurface	9.0 ± 0.2	-25.53 ± 0.06	58.8

* standard deviation

investigated sediments. However, due to the unknown molecular composition of both marine and land components just qualitative assessment as to the organic matter origin can be performed. Moreover, the ratios measured in the sediments may be biased due to the differing mobility of organic carbon and organic nitrogen mineralization products (CO_2 and $\text{NH}_3 \cdot \text{H}_2\text{O}$). Carbon dioxide largely diffuses out of the sediments to the overlying water, while ammonia is sorbed on sediments particles and thus is retained in sediments (Emeis *et al.*, 2000). Thus the C/N ratio can be used for quantitative assessment of organic matter origin, but cautiously (Table 3).

It is obvious, however, that C/N ratios in the uppermost segments of the cores (<10 cm) are much lower than these in the subsurface segments (>20 cm). The border between higher (subsurface) and smaller (surface) ratios is placed at the depths corresponding to deposition period 1930-1950, close to the period when eutrophication in the Baltic has started (Łysiak-Pastuszak, 2000; Voss *et al.*, 2000). For five of the six investigated cores these differences are statistically significant. The average C/N ratio in the surface sediments is 8.4. There is one core (IV) with C/N ratio (7.4) significantly lower than average, and one core (III) with C/N ratio (9.1) – significantly higher. In the latter case the differences seem to indicate increased contribution of terrestrial organic matter, originating possibly from the Bay of Riga, while the former case - accumulation of large quantities of sedimentary material rich with autochthonous organic matter, possibly due to redeposition or sediment slides.

Stable carbon isotopes were also measured in the samples originating from the sediment cores and are presented as $\delta^{13}\text{C}$ in Table 2. The $\delta^{13}\text{C}$ values measured in the sediment samples ($\delta^{13}\text{C}_s$) range from -24.4‰ to -26.5‰. This is in good agreement with the earlier published data (Voss *et al.*, 2005). The measured values indicate that organic matter in the sediments is a mixture of terrestrial ($\delta^{13}\text{C}_t$ equal to -28‰) and marine ($\delta^{13}\text{C}_m$ equal to -22‰, Boutton, 1991) materials. The $\delta^{13}\text{C}$ values are frequently used for quantitative assessment of terrestrial organic matter (T%) contribution in the coastal marine environment (Voss *et al.*, 2005). An end member approach is applied for this purpose, based on the following formula:

$$T(\%) = \frac{\delta^{13}\text{C}_s - \delta^{13}\text{C}_m}{\delta^{13}\text{C}_t - \delta^{13}\text{C}_m} \times 100(\%) \quad (3.1)$$

Results of the so calculated terrestrial contribution to sedimentary organic matter are presented in the Table 3 and Fig. 5. The obtained values, for the surface sediments, are surprisingly uniform, indicating that terrestrial organic matter constitute between 40.8% and 46.5% of total organic matter in the surface sediments, independently of the location. Proportion of terrestrial organic matter in subsurface sediments ranges between 44.2% and 72.7% (Fig. 4). Thus it is both much larger and much more varying. This can be attributed to the recent

eutrophication of the sea and increased deposition to sediments of autochthonous organic matter (Łysiak-Pastuszak, 2000; Voss *et al.*, 2000). This explanation is supported by the high correlation coefficient of the relationship between $\delta^{13}\text{C}$ and C concentration (Fig. 5). A general agreement between $\delta^{13}\text{C}$ and C/N ratios, namely decreasing $\delta^{13}\text{C}$ parallel to increasing values of C/N, is also evident and most likely caused by mineralization of nitrogen – rich organic matter.

4. CONCLUSIONS

The presented study indicates substantial organic carbon and total nitrogen accumulation rates in the sediments of depositional areas of the Baltic Sea. The rates amount to, on average, $35 \text{ g} \cdot \text{C} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ and $4 \text{ g} \cdot \text{N} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$. The values are much higher compared to other shelf seas. This can be attributed to both substantial primary productivity

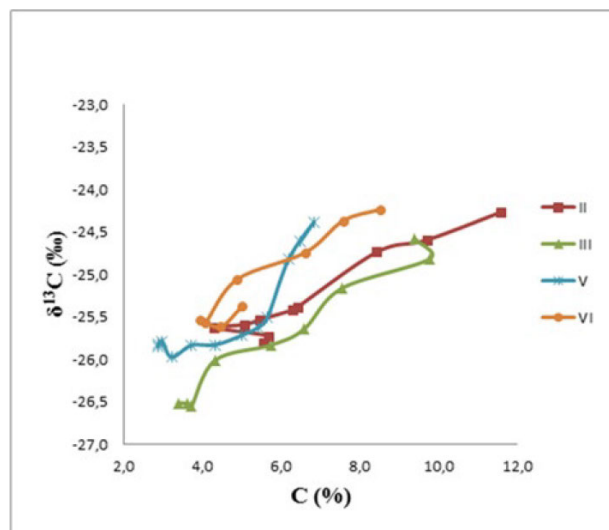


Fig. 4. Relationship between $\delta^{13}\text{C}$ (‰) and C (%) concentrations in the investigated sediments.

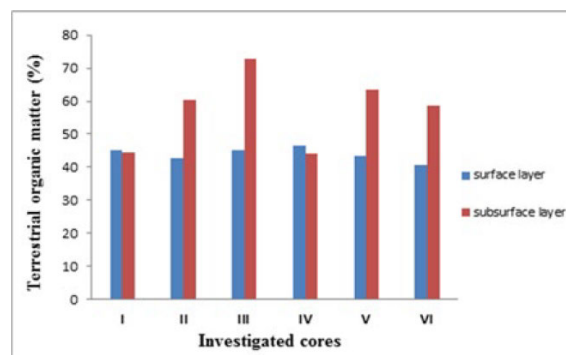


Fig. 5. Terrestrial organic matter contribution in the investigated cores.

and huge loads of organic matter discharged to the Baltic Sea with river run-off. The latter factor, although decreasing in the importance, still contributes nearly half (45±5%) of sedimentary organic matter in the Gotland Basin and Gdańsk Basin of the Baltic Sea. The obtained results indicate the Baltic Sea sediments as an important sink for organic carbon and total nitrogen. Significant amount of organic carbon accumulated in sediments has an important contribution in carbon cycle of the Baltic Sea.

ACKNOWLEDGEMENTS

This study was financially supported by the Baltic-C, a Bonus Plus founded project, the BALTEX project founded by the Ministry of Science and Higher Education in Poland, and the NN 306 407338 project founded by the Ministry of Science and Higher Education.

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