ORIGINAL RESEARCH ARTICLE

Temporal changes in Hg, Pb, Cd and Zn environmental concentrations in the southern Baltic Sea sediments dated with ^{210}Pb method

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Summary The article presents data on heavy metal — Hg, Pb, Cd and Zn — distribution in the layers of marine sediments from the off-shore areas of the southern Baltic Sea: Gdańsk Deep, SE Gotland Basin and Bornholm Deep. Depth profiles of metal concentrations were converted to time-based profiles using the ^{210}Pb dating method and verified by ^{137}Cs distribution in the vertical profile. The linear sedimentation rates in the Gdańsk Deep and SE Gotland Basin are similar, 0.18 cm yr^{-1} and 0.14 cm yr^{-1}, respectively, while the region of the Bornholm Deep is characterized by a greater sedimentation rate: 0.31 cm yr^{-1}. Regarding anthropogenic pressure, Gdańsk Deep receives the largest share among the analyzed regions. The maximal metal concentrations detected in this area were Zn — 230 mg kg^{-1}, Pb — 77 mg kg^{-1}, Cd — 2.04 mg kg^{-1} and Hg — 0.27 mg kg^{-1}. The least impact of anthropogenic pressure was noticeable in SE Gotland Basin. The combination of sediment dating with the analysis of vertical distribution of heavy metals in sediments benefited in the determination of target metal concentrations used in environmental status assessments. Reference values of heavy metal concentrations in marine sediments were determined as: Zn — 110 mg kg^{-1}, Pb — 30 mg kg^{-1}, Cd — 0.3 mg kg^{-1} and Hg — 0.05 mg kg^{-1} from the period of minor anthropogenic pressure. Basing on the determined indices: enrichment factor

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(EF), geoaccumulation indicator (I_{geo}) and contamination factor (CF) the status of marine environment was assessed regarding the pollution with heavy metals.

1. Introduction

Intensification of human activities regarding new technologies, especially inventing new substances, progress in medicine and pharmaceutical industry and the extension of needs in progressing civilization in general, results in increasing anthropogenic pressure on the natural environment. The release of large amounts of chemical substances to the environment poses currently one of the serious problems as neither their effects nor their distribution among the environment components is well recognized. Therefore, the assessment of the environmental status became the key issue at present in order to support appropriate decisions on measures aiming at reduction of the pressures and restoration of the undisturbed functioning of the ecosystem. The HELCOM Baltic Sea Action Plan (HELCOM, 2007) is an example of such a voluntary initiative of countries wishing to have back a healthy sea, and the Water Framework Directive (WFD) (Anon., 2000) and the Marine Strategy Framework Directive (MSFD) (Anon., 2008) are the examples of strong legal actions that bind countries to undertake measures aiming at protection of the marine environment. Nonetheless, the first stage in any counter-measure is the appropriate assessment of the current environmental status and comparison with certain reference status assumed as the desired one. In the case of pollutants — hazardous substances — the parameters used to define the good/desired environmental status are usually certain target values of concentrations. It is assumed that concentrations lower than the target are innocuous. It is then of great importance to determine the environmental target for any harmful substance. One of the possible ways is the determination of contaminant (e.g. heavy metal) concentrations related to moderate anthropogenic impact that would next allow to determine the reference conditions/background values.

It was pointed out that the determination of background levels of the analyzed heavy metals is very important regarding the choice of the appropriate assessment metrics; hence, it is the key issue in the final assessment result, e.g.: geoaccumulation index — I_{geo} or enrichment factor — EF (Carvalho Gomes et al., 2009; Pempkowiak, 1991; Pempkowiak et al., 1998; Rubio et al., 2000; Zahra et al., 2014). The determination of reference values for heavy metals in sediments of the assessed area is an optimal solution in this case; however, relying solely on geochemistry-based investigation might not be sufficient, and sediment dating seems to supply unequivocal information on the period which has to be considered for the identification of background values (Álvarez-Iglesias et al., 2007; Carvalho Gomes et al., 2009; Díaz-Asencio et al., 2009; Ruiz-Fernández et al., 2004; Sanchez-Cabeza and Druffel, 2009). Sediments are the sole environmental elements that reflect the changes ongoing in a marine environment in a systematic and nearly permanent way. This feature is of particular interest regarding the distribution and accumulation of contaminants whose concentrations are subject to intense variability in seawater and marine organisms. The changes observed in pollution of the marine environment become permanently preserved in the sediments. The mechanism directly responsible is the fact that contaminants, including heavy metals, show a significant affinity to suspended organic matter (Pempkowiak et al., 1999; Roussiez et al., 2005; Rubio et al., 2000), and having been adsorbed and/or bioaccumulated in organic matter, they are amassed in the sediments due to vertical transport and sedimentation processes (Álvarez-Iglesias et al., 2007; Carvalho Gomes et al., 2009; Díaz-Asencio et al., 2009; Ruiz-Fernández et al., 2004). Therefore, sediments may act as a record of human impact in areas where the formation of consecutive layers proceeds in an unperturbed way. Combining information on contaminant changes in sediments with sediment dating based on the analysis of the lead isotope — ^{210}Pb presents us with versatile application prospects.

Since 1963, when Goldberg (1963) presented his method of sediment dating by ^{210}Pb, a number of authors have further developed the method and its application as a geochronological tool in sediment studies in various environmental systems (lakes, estuaries, marine areas) (Appleby and Oldfield, 1992; Appleby, 1997; Díaz-Asencio et al., 2009; Matsumoto, 1987; Mulsow et al., 2009; Pfitzner et al., 2004; Suplińska and Pietrzak-Flis, 2008; Zaborska et al., 2007, 2014; Zajączkowski et al., 2004). The method of sediment dating based on an analysis of ^{210}Pb concentration changes makes it possible to characterize the scale of 100–150 years back, i.e. the period of intensive industrialization and increase of human activities in all aspects of existence. Sediment dating allows the identification of potential pollution sources and the examination of contamination changes related to transport (Álvarez-Iglesias et al., 2007; Ayrault et al., 2012; Carvalho Gomes et al., 2009; Díaz-Asencio et al., 2009; Li et al., 2012; Ruiz-Fernández et al., 2004).

The presented study focused on the application of the dating method, based on the vertical distribution of ^{210}Pb in marine sediments, to the determination of sedimentation rates and the dating of serial sediment layers in the areas of the southern Baltic Sea characterized by undisturbed sedimentation. By combining this information with results on heavy metal Hg, Cd, Pb and Zn distribution in the sediments it was possible to establish environmental target concentrations of heavy metals: Hg, Pb, Cd; the priority hazardous substances taken into account in environmental status assessment. Basing on the determined indices: enrichment factor (EF), geoaccumulation indicator (I_{geo}) and contamination factor (CF) the status of marine environment was assessed regarding the pollution with heavy metals.

2. Material and methods

2.1. Study area

The areas selected for the study: Bornholm Basin, Gdańsk Basin and SE Gotland Basin (Fig. 1), are characterized by the occurrence of silt-clay sediments, i.e. the Baltic olive-gray mud, containing mainly fractions finer than 0.063 mm. The bottoms of these areas are frequented by the occurrence of strong oxygen deficit and anaerobic conditions, and laminated deposits without bioturbation structures reflect the annual sedimentary rhythmicity. The accumulation rate of the silty-clay can vary in a relatively wide range from 0.5 to 2 mm yr^{-1} (Uścinowicz, 2011).

2.2. Sampling

Sediment samples were collected at three sampling stations located in the southern Baltic Sea: P5 of 87 m depth in the Bornholm Deep, P140 of 89 m depth in the Gotland Basin and P1 ca. 107 m depth in the Gdańsk Deep (Fig. 1). The samples were taken with a Niemistö corer with inner diameter of 5 cm onboard r/v Baltica during routine monitoring cruises.

For the purpose of heavy metal determination, three parallel cores were collected, each then divided into 2 cm slices down to 10 cm depth, and deeper 2 cm slices were selected at every 5 cm length of the core. Eventually, the three parallel cores were divided into the following samples: 0—2, 2—4, 4—6, 6—8, 8—10, 15—17, 22—24, 29—31 and 36—38 cm. The selection of sediment layers and the number of samples sufficient to assess heavy metal distribution in the sediment core was assumed based on multiyear experience gained in monitoring activities of the Baltic Sea. The wet

sediment samples were preserved by deep-freezing onboard the vessel and were then freeze-dried, homogenized and stored for further analyses on arrival at the land laboratory.

For the purpose of sediment age determination, six parallel sediment cores were taken at each station. The cores were divided into 1 cm wide slices down to 5 cm depth and deeper into slices of 2 cm width. This yielded the following sediment layers: 0—1, 1—2, 2—3, 3—4, 4—5, 5—7, 7—9, 9—11, 11—13, 13—15, 15—17 and 17—19 cm. The corresponding slices/layers from the six parallel cores at the sampling station were integrated to produce a single analytical sample. These samples were initially deep-frozen onboard the ship and freeze-dried and homogenized in the land laboratory prior to the exact analysis.

2.3. Models for ^{210}Pb sediment dating

^{210}Pb identified in sediment samples originates from two sources. A certain fraction is the result of radium (^{226}Ra) radioactive decay and this is called supported ^{210}Pb (^{210}Pb$_{supp}$); its activity along the vertical sediment profile practically does not change. The other source of ^{210}Pb deposited in marine sediments is atmospheric fall-out. The activity of ^{210}Pb unsupported or excess (^{210}Pb$_{ex}$), originating from the atmospheric deposition, decreases with the sediment depth. This activity forms the basis in the determination of rates of sediment accumulation: mass accumulation rate (MAR) and linear accumulation rate (LAR) and in the age determination of particular sediment layers. The ^{210}Pb$_{ex}$ activity concentration is determined from the total activity of this isotope (^{210}Pb$_{tot}$) in the analyzed layer by subtracting the activity of one of the products of ^{226}Ra decay, e.g. ^{214}Bi or ^{214}Pb. In the present study, determinations of sedimentation
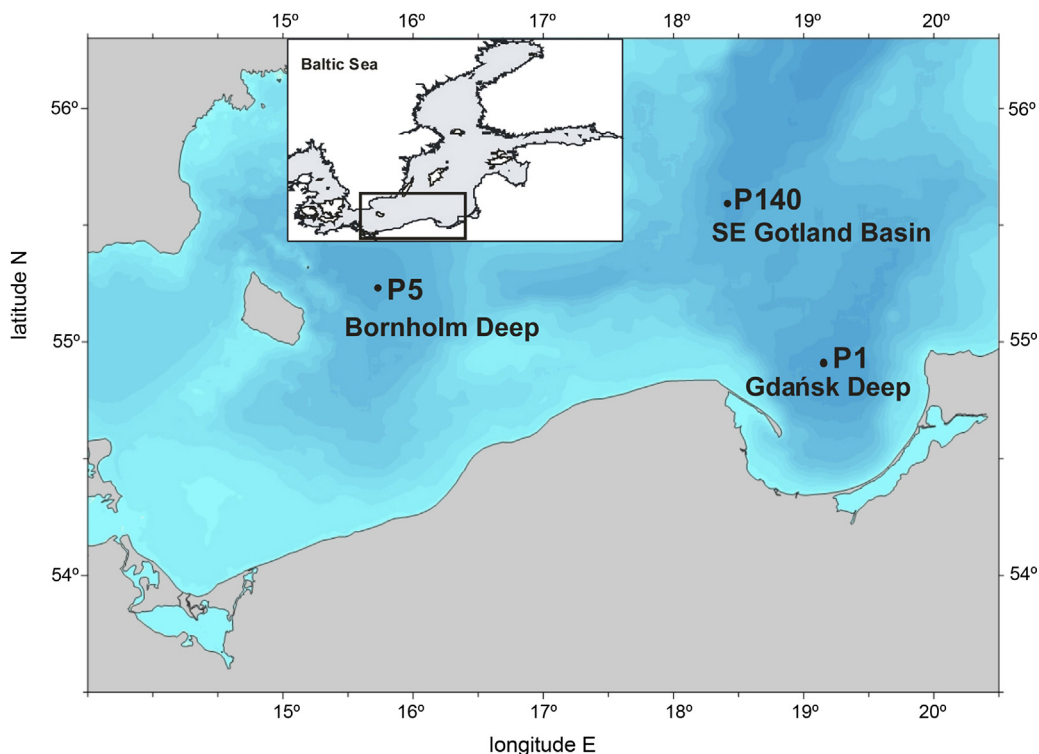

Figure 1   Localization of stations for sediment investigation.

rates and sediment age along the vertical profiles were done using two models (Appleby and Oldfield, 1992; Appleby, 1997; Boer et al., 2006; Carvalho Gomes et al., 2009; Díaz-Asencio et al., 2009; Robbins, 1978; Szmytkiewicz and Zalewska, 2014). The first model — the Constant Rate of Supply (RSC) model — is based on the assumption that the supply of ^{210}Pb to the sea surface is constant, while the sedimentation rate might vary. This model seems to apply to most sedimentary systems where sediment supply may vary in response to climatic or anthropogenic changes. The second model — the Constant Flux Constant Sedimentation Rate (CF:CS) model — assumes a constant dry-mass sedimentation rate (Szmytkiewicz and Zalewska, 2014).

In order to verify the results of age determination by the ^{210}Pb method it is necessary to apply an additional tag whose concentration changes in the marine environment can be easily documented to specific events. In the case of the Baltic Sea, the most obvious tag is the totally anthropogenic isotope of cesium — ^{137}Cs. In the verification of the age determination method based on ^{137}Cs it is assumed that the described historical events (e.g. testing of nuclear weapons performed since 1945 with maximum deposition recorded in 1963 and the accident in the Chernobyl power plant in 1986) should be well marked, as an increase, in the curve of the isotope changes along the sediment core. Simultaneously, the results have to be interpreted cautiously, taking into account the complexity and large number of processes affecting the final result — the presentation of ^{137}Cs distribution in the sediment vertical profile. Therefore the isotope could be useful for verifying sediment chronology when post-depositional processes are not affecting this radionuclide (Díaz-Asencio et al., 2009).

2.4. Analysis of gamma emitters

^{210}Pb, ^{226}Ra and ^{137}Cs contents in marine sediments were analyzed by high-resolution gamma spectrometry using an HPGe detector with a relative efficiency of 40%, and a resolution of 1.8 keV for peak of 1332 keV of ^{60}Co. The detector was coupled with an 8192-channel computer analyzer (GENIE 2000). The samples were placed in plastic containers of geometry identical to those used for calibration. After reaching equilibrium between ^{226}Ra and its daughter nuclides (^{214}Bi, ^{214}Pb) the samples were ready for measurements. Time of measurements was 80,000 s for each sample. ^{210}Pb was determined by gamma emission at 46.5 keV, ^{226}Ra was determined by the emission of its daughter nuclides ^{214}Pb and ^{214}Bi at 352 keV and 609 keV respectively and ^{137}Cs was measured via its emission at 661.6 keV.

The reliability and accuracy of the applied method were verified by the measurement of certified sediment material IAEA-300 (Table 1).

2.5. Analysis of heavy metals

Mercury content in sediments was determined using cold vapor atomic absorption spectrometry in an AMA 254 mercury analyzer. In this method, a sample (ca. 100 mg) is placed in the burning chamber of the analyzer, where it is dried and burned in oxygen flame at 600°C. The released mercury is collected in a gold amalgam catalyst. Having completed the sample decomposition, the temperature is stabilized at 120°C and mercury content is measured with a detection limit of 0.05 ng.

Cadmium, lead, zinc and aluminum concentrations were measured in the sediments' mineralization, obtained by treating the sediment samples (ca. 1.5 g) with concentrated acids HNO_3 and HF. The mineralization was carried out in teflon vessels at elevated temperature. The concentrations of metals were measured using atomic absorption spectrometry (AAS); cadmium — in a Perkin-Elmer 4100 spectrometer with HGA 700 graphite furnace, and lead, zinc and aluminum were measured in a Shimadzu AA-6601F flame atomic absorption spectrometer.

The accuracy and precision of measurements were controlled using a certified reference material (Table 1), analyzed parallel to the sediment samples.

3. Results and discussion

3.1. Sediment geochronology

^{210}Pb$_{ex}$ activity along the sediment cores from the three sedimentation basins of the southern Baltic Sea was calculated as the difference between the ^{210}Pb$_{tot}$ activity and the ^{210}Pb$_{supp}$ activity; the latter being determined by measuring the activity of the radioactive decay products (^{214}Bi, ^{214}Pb) of ^{226}Ra which remain in radioactive equilibrium with

Table 1 Results of certified reference material analyses.

Certified reference material	Analyzed element	Certified value	Confidence interval	Measured value
IAEA − 300, Radionuclides in the Baltic Sea	^{137}Cs	1056.6 Bq kg^{-1} on reference date: 1.01.1993	1046−1080	1065 ± 24 Bq kg^{-1} on reference date: 1.01.1993
	^{210}Pb	360 Bq kg^{-1} on reference date: 1.01.1993	339−395	350 ± 40 Bq kg^{-1} on reference date: 1.01.1993
QTM045MS	Hg	0.103 mg kg^{-1}	—	0.103 ± 0.004 mg kg^{-1}
QTM080MS	Cd	0.490 mg kg^{-1}	—	0.463 ± 0.023 mg kg^{-1}
	Pb	48.80 mg kg^{-1}	—	47.29 ± 1.64 mg kg^{-1}
	Zn	148.99 mg kg^{-1}	—	145.93 ± 3.51 mg kg^{-1}

$^{210}Pb_{supp}$. In all three basins, activity concentrations of both $^{210}Pb_{tot}$ and $^{210}Pb_{supp}$ decline exponentially with the sediment depth, thus providing a basis for the application of both dating models CF:CS and CRS (Boer et al., 2006; Carvalho Gomes et al., 2009; Díaz-Asencio et al., 2009). Similar distribution was observed in Gdańsk Deep by Pempkowiak (1991). ^{214}Bi activities along the core profiles changed in relatively narrow ranges. The maximal differences in a given basin were up to 10 Bq kg^{-1}, with the mean at the level of 39 ± 3 Bq kg^{-1} in the Bornholm Deep, 35 ± 3 Bq kg^{-1} in the SE Gotland Basin and 45 ± 7 Bq kg^{-1} in the Gdańsk Deep.

The maximal activity concentrations of $^{210}Pb_{ex}$ were found in the surface sediment layer in the Gdańsk Deep (420 Bq kg^{-1}) and decreased rapidly to 5 Bq kg^{-1} at 21 cm depth of the sediment. In the SE Gotland Basin activity concentrations varied from 4 Bq kg^{-1} in the deepest sediment layers to 242 Bq kg^{-1} in the surface layer, while the youngest sediments of the Bornholm Deep showed the least activity of $^{210}Pb_{ex}$ (151 Bq kg^{-1}).

The age of individual sediment layers was determined using the CRS model applying the cumulative depth instead of the real depth to eliminate the sediment compaction effect and related variable content of interstitial water (Fig. 2). The obtained statistically significant correlations between the age of sediment layer and cumulative depth were described with 2nd degree polynomial function in all three studied sedimentation basins. The correlation coefficients reached 0.980, 0.999 and 0.997 in the SE Gotland Basin, Bornholm Deep and the Gdańsk Deep, respectively, at confidence limit of p = 0.0000 (Fig. 2). The ages of sediment layers, and time of their formation, are quite close in the SE Gotland Basin and in the Gdańsk Deep — the deepest layers of formation in these basins were estimated at 1838 and 1858, respectively. The sediment layer at 21 cm depth in the Bornholm Basin comes from a decidedly later period — 1928, indicating a greater sedimentation rate. These observations were certified by the linear accumulation rate obtained from the CF:CS model. The linear accumulation rate determined in the Gdańsk Deep reached 0.18 cm yr^{-1} confirming earlier investigations (Pempkowiak, 1991) and was relatively close to that in the Got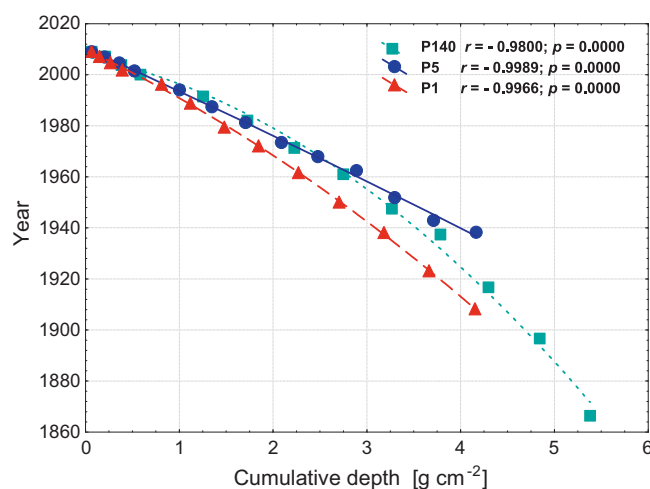land Basin (0.14 cm yr^{-1}). The corresponding mass accumulation rates in these basins were 0.032 g cm^{-2} yr^{-1} and 0.049 g cm^{-2} yr^{-1}. In the Bornholm Deep the identified linear accumulation rate and the mass accumulation rate were much higher, 0.31 cm yr^{-1} and 0.059 g cm^{-2} yr^{-1}, respectively. Fresh water discharge from rivers and the extent of riverine water in the sea are the factors directly influencing the amount of suspended matter in the water column and consequently affect the intensity of the sedimentation process. On one hand, riverine water is a source of large amounts of organic and mineral material discharged into the sea. On the other hand, the transported nutrients intensify primary production, which leads to massive phytoplankton blooms under favorable meteorological conditions. Taking into account riverine discharge and its impact on the amount of suspended organic and inorganic material in seawater, a more intensive influence of the Vistula river could be expected within the Gdańsk Deep area than the influence of the river Oder in the Bornholm Deep, where no prolific algal blooms have been observed and the input of terrestrial material and pollution is moderated, e.g. by filtering properties of the Szczecin Lagoon. It is therefore assumed that the larger sedimentation rate observed in the Bornholm Deep has to be related to a different structure of the sedimenting organic matter or specific hydrological conditions.

In order to validate the chronologies determined using ^{210}Pb dating, the vertical distribution of ^{137}Cs was related to the age of the sediment layers. The distribution of ^{137}Cs activity in the surface sediment layers reflects, to a large extent, the distribution of $^{210}Pb_{ex}$ (Fig. 3). The highest values were observed the Gdańsk Deep, where activity concentration exceeded 200 Bq kg^{-1} in the surface later, which was a little higher then found by Zaborska et al. (2014). The distinctly lower activities of ^{137}Cs measured in surface sediments from the Bornholm Deep (66.5 Bq kg^{-1} in the upper layer) show the effect of the frequent flushes of the North Sea (Zalewska and Lipska, 2006) saline inflows in the near bottom layer, the water in the North Sea having much lower content of ^{137}Cs. ^{137}Cs concentrations in surface sediments of the SE Gotland Basin were nearly twice as big, and reached 130.4 Bq kg^{-1}.

The curves illustrating changes of ^{137}Cs activity in respective sediment layers and the corresponding years lack unequivocal peaks (Fig. 3). This may be attributed to the redistribution of radiocesium within sediment column. The redistribution could be caused by two main processes: (i) physical and biological mixing at or near the sediment-water
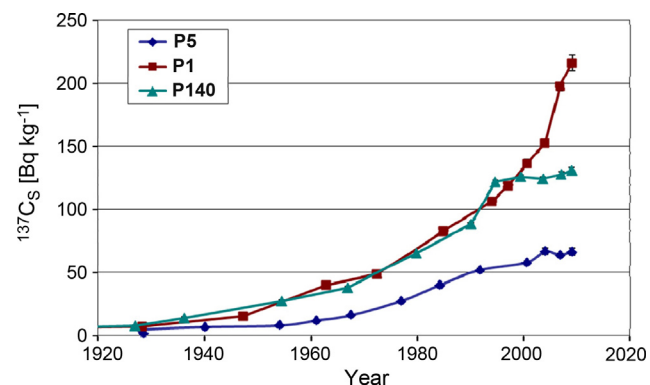

Figure 2 Correlation between estimated years and cumulative depth.

Figure 3 Deposition history of ^{137}Cs.

interface and (ii) chemical diffusion or advection within the porewater.

The initial specific increase in ^{137}Cs activity is observed since 1950, and this can be related to the beginning of atmospheric nuclear testing started in 1945. The increase in test intensity between 1958 and 1963 could be only visible as the continuous ascension of in the activity curve along the vertical profile. ^{137}Cs concentrations in sediments show a constant increase since that time, though note that in the entire range, the lowest activity rates are characteristic of the Bornholm Deep sediments. The marked change in the curve slope of the SE Gotland Basin occurred in 1990 as compared to 1980 (Fig. 3) and this is definitely the direct impact of ^{137}Cs input from the accidental release in the Chernobyl power plant in 1986. A change in the curve development, though less spectacular, was also detected in the Gdańsk Deep, and this was linked to the year 1994 as compared to the lower level — dated in 1984. This change indicates the same source of observed changes.

After 1995, ^{137}Cs activity in sediments in the SE Gotland Basin became stable as indicated by only an insignificant increase from 125.5 to 130.4 Bq kg^{-1} observed in 12 years. Similar stabilization of ^{137}Cs concentrations is noted in the Bornholm Deep, and between 2001 and 2006 the concentrations varied in a narrow range 63.8—66.5 Bq kg^{-1}. This stabilization has to be attributed to the continuous decline of the isotope concentrations in seawater. It is solely in the area of Gdańsk Deep that an increasing tendency of cesium concentrations is observed.

The presented trends in ^{137}Cs concentrations in sediment cores are acceptable to verify fidelity of the ^{210}Pb dating.

3.2. Heavy metal concentrations

Sediment layers, subjected to heavy metal determination, were dated using the ^{210}Pb chronology characteristics, taking into account the shift related to different dates of sediment sampling. In order to extend the range of dating, the results were extrapolated using a regression model beyond the depth of dating. The square fit (as established for the correlation between the age of sediment and the cumulative depth in the depth range of the cores where dating was performed) was applied for the results extrapolation. As a result of extrapolation, the deepest layers (36—38 cm) were assigned to the years 1625, 1751 and 1850 in the SE Gotland Basin, Gdańsk Deep and Bornholm Deep, respectively.

The metals show a strong affinity to the clay fraction of the sediment and its coating formation (e.g. organic matter, iron and manganese oxides) (Beldowski and Pempkowiak, 2003; Pempkowiak et al., 1998, 1999; Szefer et al., 1995; Zaborska et al., 2014). Because sediment composition, and therefore its grain size, are liable to vary depending on the sedimentation area, organic matter input from different sources, and also depending on meteorological and hydrological conditions, it is necessary to use normalization to eliminate the effect of grain size and mineralogy on the final result and its interpretation (Acevedo-Figueroa et al., 2006). The normalization procedure is based on the application of a clay mineral indicator, with concentrations of the analyzed metals then related to this indicator. We have applied Al as the normalizing element (Cheevaporn and San-Diego-McGlone, 1997; Zahra et al.,

2014). It is a conservative element and a major constituent of the clay minerals. The concentrations of heavy metals were related to 5% content of aluminum. The normalization level of Al was based on the observation that Al concentrations in sediment cores from the examined areas was relatively uniform and close to 5%, indicating a homogenic structure of sediments. The greatest variability in vertical distribution of Al in sediment core was found out in the Gdańsk Deep (station P1). This being the result of assorted organic matter transported with the riverine input with regard to both composition and amount, and the impact of transported riverine organic matter is maximal in the Gdańsk Deep area as compared to the other basins. In the Gdańsk Deep, the lowest content of Al was determined in the two uppermost sediment layers (4.72 and 4.95%), while the maximal content (6.34%) was determined at 32 cm depth. In the Bornholm Deep, Al concentrations varied in a very narrow range 5.01—5.41%, and the span of concentrations in the SE Gotland Basin was 3.97—4.62%.

Depth profiles of metal concentrations were converted to time-based profiles using a ^{210}Pb-derived vertical accretion rate (Fig. 4). Not surprisingly, the highest concentrations of all examined metals were detected in the Gdańsk Deep area; the pollutants deposited by the direct input from the Vistula river (Fig. 4). Zinc concentration in the surface layer reached 245 mg kg^{-1} and this was similar to the result obtained by Pempkowiak (1991) (233 mg kg^{-1} for the upper layers 2—4 cm) and by Glasby et al. (2004) (248 mg kg^{-1} for the upper layers 2.5—5 cm), but higher than quoted (148 mg kg^{-1}) by Szefer et al. (2009). In our investigation, the lead level in the same layer was estimated at 82 mg kg^{-1}, a comparable figure to 75 mg kg^{-1} obtained by Szefer et al. (2009). Much lower concentrations were measured in the case of cadmium and mercury, the metals of strictly anthropogenic origin. Their concentrations ranged from 0.17 to 0.05 mg kg^{-1}, respectively, in the deepest sediment core layers to 2.16 and 0.28 mg kg^{-1} in the upper most part. Similar results for Cd in the upper layer were obtained in this region by Pempkowiak (1991) — 1.51 mg kg^{-1} and Glasby et al. (2004) — 1.7 mg kg^{-1}. In the Gdańsk Deep, a slight increase of Cd and Hg took place between ca. 1830 and 1940, followed by a more pronounced change in these metals input into the marine environment marked by a steep change in the curves' slope. After 1980, the curves illustrate a substantial increment leading to a maximal level of mercury of 0.29 mg kg^{-1} and of cadmium, 1.99 mg kg^{-1}, occurring in the upper layers.

Zinc concentration in the sediment increased at a slow, nearly constant rate from 110 mg kg^{-1} in the deepest layer to 156 mg kg^{-1} in 1980, from which a steep increase to maximum value (246 mg kg^{-1}) reaching in the upper layer was observed. Lead showed a much faster, and also continuous, accumulation rate in this region, increasing from 7.2 to 43.6 mg kg^{-1} up to 1980. Past 1980, the increase in lead concentrations in the sediment shows a decidedly dynamic character. The reason for the more intensive input of Pb should be seen in an outburst of industrialization observed in Poland in 1960 and 1970. None of the metals analyzed in sediments from the Gdańsk Deep showed concentration decrease in recent years despite the significant reduction in their emissions to the atmosphere. The emission of mercury was reduced from 34 t yr^{-1} in 1996 to 16 t yr^{-1} in 2007, lead — from 960 t yr^{-1} in 1996 to 553 t yr^{-1} in 2007, and cadmium — from 91 t yr^{-1} to 40 t yr^{-1} in the same period
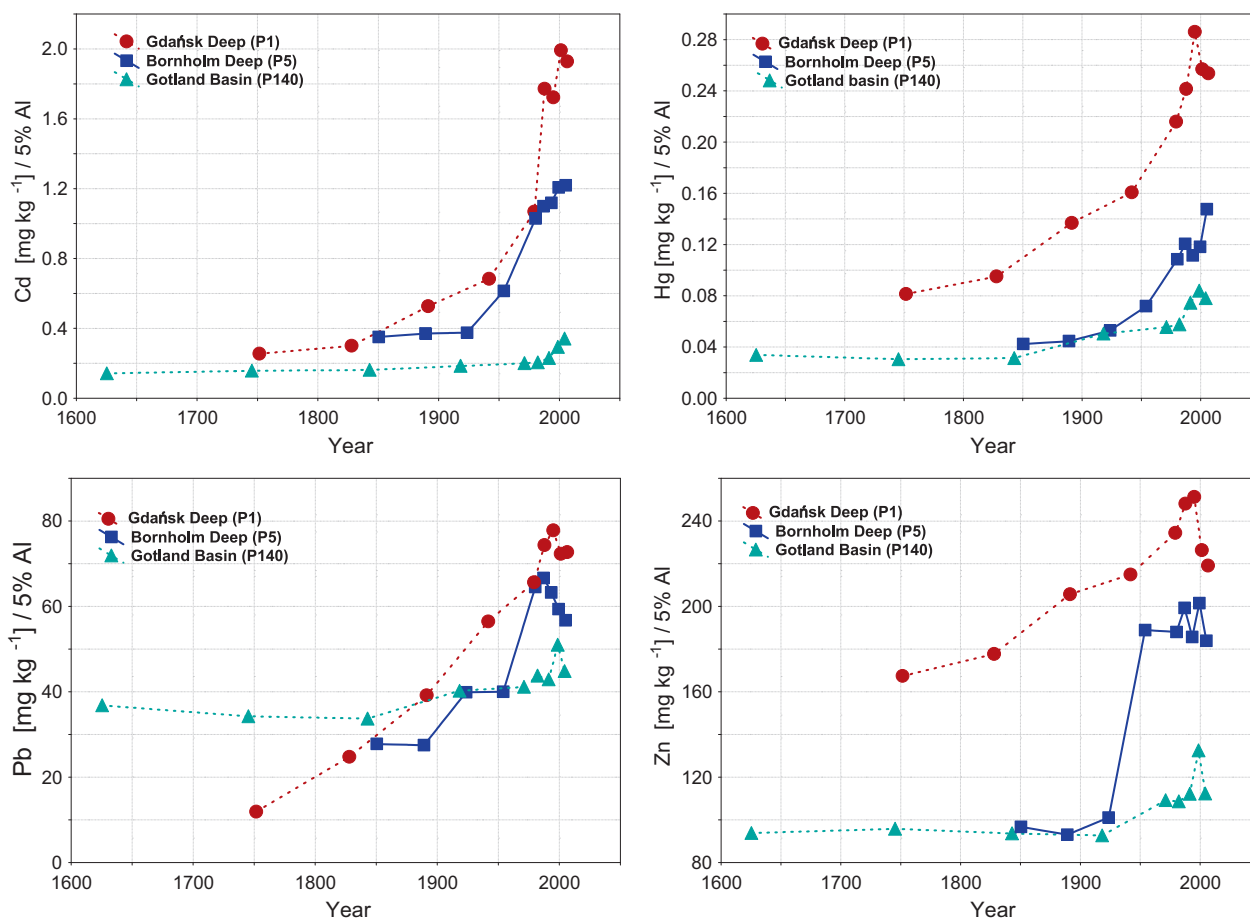
Figure 4 Deposition history of Cd, Hg, Pb and Zn.

(HELCOM, 2009). The maximal riverine input of lead, 210 t yr^{-1}, was noted in 1994 (HELCOM, 2011), although this had decreased to 180 t yr^{-1} already in 1995, and continued to reach ca. 40 t yr^{-1} in 2006. Unfortunately, an increase in riverine discharges of lead was observed in 2007, to 80 t yr^{-1}, causing a reversal of the decreasing trend in the surface sediment layer. The absence of significant decrease in heavy metal concentrations in sediments from the Gdańsk Deep is probably related directly to the considerable amounts of heavy metals discharged to the sea by the Vistula river. Additionally, an adjournment of the response of heavy metal concentrations in surface sediments in relation to changes occurring in the discharge has to be considered, especially if thin (2 cm) sediment layers are studied. Well marked changes in concentrations of heavy metals in surface sediment layer were found out in the SE Gtoland Basin, where Pb and Zn concentrations show a clear descent since 1980, and Hg since 1990. Heavy metal concentrations in the sediment from the SE Gotland Basin are decidedly lower than that in the Gdańsk Deep. Particularly large differences are found in the case of Cd, Hg and Zn. Cadmium concentrations vary from 0.17 mg kg^{-1} in the deepest sediment layer to 0.51 mg kg^{-1} in the surface layer, with a significant increase since 1980. A similar pattern, as evidenced by an increase since 1980, was noted in Hg concentrations. Mercury concentrations spanned the range from 0.04 to 0.12 mg kg^{-1}, and visible decline is seen in the surface layer, since about 1990. In the case of zinc, its content increased significantly in the SE Gotland Basin sediments after 1918, and later after 1980, reaching a maximum of 188 mg kg^{-1} at 4—6 cm depth. In this region, zinc — similar to lead concentrations, decreased after 1990 to the level of 168 mg kg^{-1}. Lead content showed the lowest gradient between layers, attaining 43.2 mg kg^{-1} at 36—38 cm depth and maximal, 72 mg kg^{-1}, in 4—6 cm layer attributed to 1990.

In the Bornholm Deep, cadmium and mercury concentrations remained practically unchangeable up to 1923, at 0.30 and 0.04 mg kg^{-1}, respectively. Later, the sediment profiles show an unvarying increase of both metals up to their maximal levels, Cd — 1.21 mg kg^{-1} and Hg — 0.15 mg kg^{-1}, in surface layers. Cadmium concentration obtained in this study in surface sediments of the Bornholm Deep is in very good agreement with the value of 1.20 mg kg^{-1} presented by other authors (Szefer et al., 2009). Zn and Pb show a different (to Cd) pattern of changes in the Bornholm Deep sediments. The Pb curve indicated a considerable shift around 1890, from 24.5 mg kg^{-1} in the two deepest layers to 34.9 mg kg^{-1}, and the next steep increase was noted after 1950. About 1980, Pb concentration reached 56 mg kg^{-1} and stayed almost unchanged in the next layers up to the surface. In our study, the surface sediment contained 56.6 mg Pb kg^{-1}, a little lower level than, 85 mg kg^{-1}, presented in literature (Szefer et al., 2009). In the case of zinc, a jump from 88 mg kg^{-1} to 163 mg kg^{-1} was defined to take place between 1920 and 1950. Later on, Zn content

oscillates around 185 mg kg^{-1}; the literature data point out a quite similar level of 188 mg kg^{-1} (Szefer et al., 2009).

3.3. Enrichment factor (EF)

Enrichment factor is widely applied to differentiate metal sources: anthropogenic and natural origin (Carvalho Gomes et al., 2009; Zahra et al., 2014). Enrichment factor (EF) is defined as the ratio of the given metal concentration measured in the environment element to the concentration level regarded as the environmental target concentrations. Enhanced values of EF indicate the increased heavy metal concentrations resulting mainly from anthropogenic pressure. To illustrate the temporal changes of heavy metal concentrations, enrichment factors EF in particular sediment layers related to background levels from the deepest layer were calculated according to the formula:

$$EF = \frac{C_{ML}}{C_{MB}},$$

where C_{ML} — metal concentration (normalized to 5% Al) in sediment layer x, C_{MB} — metal concentration (normalized to 5% Al) in background layer.

As anticipated, the highest EFs were obtained for all four heavy metal species in surface sediments of the Gdańsk Deep (Fig. 5). In Fig. 5, the EF values are presented as calculated as a ratio of metal concentration in each sediment layer — C_{ML} to the target concentration of metal — C_{MT}. The highest enrichment factors were obtained for cadmium; its concentrations measured in 2009 were nearly 13-fold higher than the background level. Lead turned out to be the second pollutant with respect to concentration increase in the surface layer related to the deepest layer with EF >10. Mercury concentrations increased over five times, and zinc showed the least spectacular increment, with the maximal EF of 2.2.

The weakest changes in relation to reference conditions were noted in the SE Gotland Basin. EF values of Pb and Zn in this region varied within similar ranges, with a maximal point of 1.5 assigned about 1990. Quite similar EF records, though at a much lower level than that in the Gdańsk Deep, were found here also in the case of Cd with the maximum at 2.9 in the surface layer. In the case of mercury, the maximal EF of 3.0 was found around 1980.

In the Bornholm Deep, the build-up of Cd and Hg concentrations in sediment layers were shown to follow approximate patterns as evidenced by the maximal EF of 4.05 and 4.07, respectively, in the surface layer. The maximal EF levels of zinc and lead in the Bornholm Deep were 2.27 and 2.38, respectively.

Among the studied marine sedimentation basins, the area of Gdańsk Deep remains under the most severe anthropogenic pressure. The EF increasing >1.0, indicating enhanced input of heavy metals to the marine environment, dates as far back as 1828, while the maximal increment gradient was noted after 1979. SE Gotland Basin is the area of the weakest anthropogenic impact; the initial ascent of EF values occurred here about 1850, and the subsequent about 1980. The Bornholm Deep EF values of Cd and Pb are lower than that in the Gdańsk Deep while those of Hg is quite close in both areas. The first peaking of EF values, particularly well discerned in the case of Pb, was noted here about 1890. The most substantial increase of EF values took place between

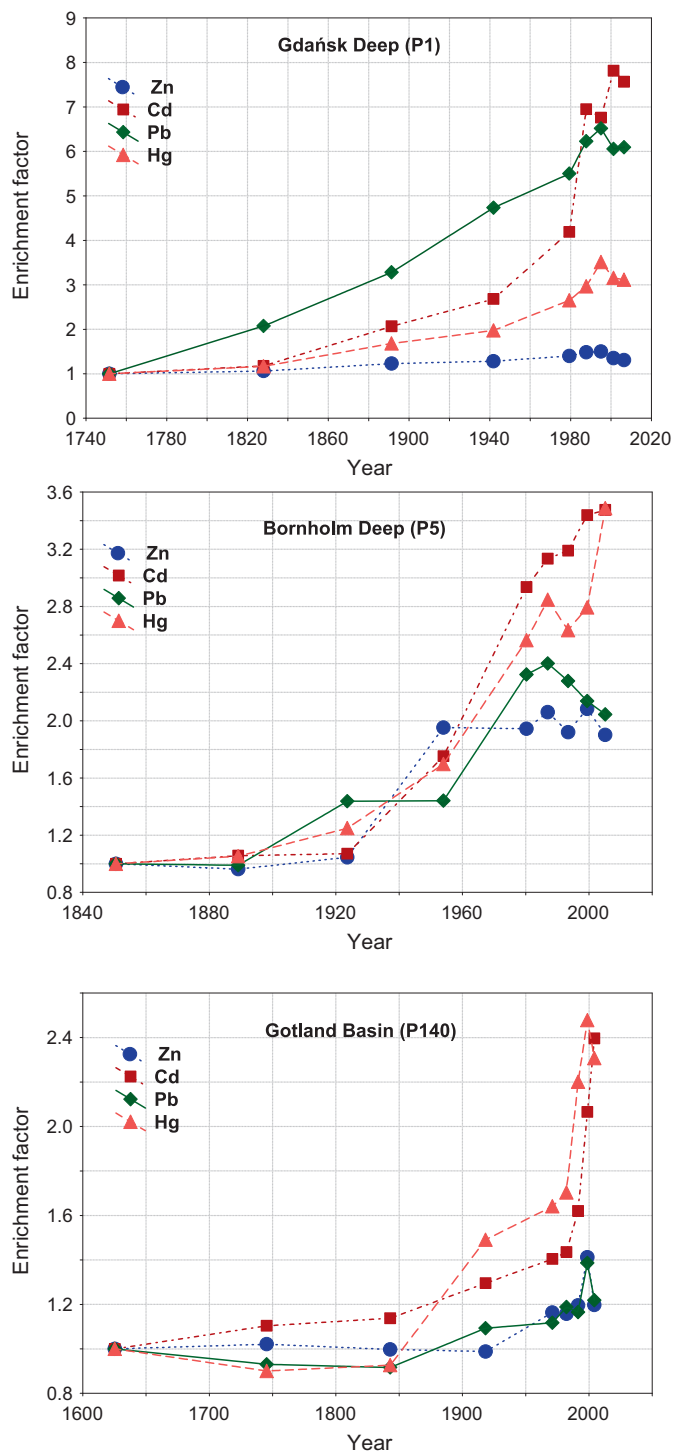**Figure 5** Enrichment factors estimated for Cd, Hg, Pb and Zn in investigated areas.

1920 and 1980, with Cd and Hg concentrations continuing to increase while Pb content started to stabilize.

3.4. Environmental status assessment regarding marine sediment pollution with heavy metals

Environmental quality assessment requires application of appropriate indicators, which would unequivocally reflect

the present situation. Regardless of the applied indicator, the key element in environmental quality assessments is the definition of reference conditions to which the contemporary values are related. Therefore it is very important to establish appropriate target concentrations; this target level could be determined as an innocuous concentration, not causing any biological effects in marine organisms. We have assumed that the metal concentrations in the deepest sediment layers, corresponding to the absence of or very limited anthropogenic pressure, fulfill the definition of target values. The mean concentration of each metal in the three deepest sediment layers (22—24 cm, 29—31 cm and 36—38 cm) was assumed as the method of target values setting for heavy metal pollution assessment in the southern Baltic Sea. The following target concentrations (C_T) were obtained: Zn —110 mg kg^{-1}, Pb — 30 mg kg^{-1}, Cd — 0.3 mg kg^{-1} and Hg — 0.05 mg kg^{-1}. The presented values are in considerable agreement with the average metal concentrations in shale, these reaching according to Turekian and Wedepohl (1961) and Zahra et al. (2014): Zn — 95 mg kg^{-1}, Pb — 20 mg kg^{-1} and Cd — 0.3 mg kg^{-1}.

The determined target values were applied to calculate the relevant indices further used in environmental status assessment (Carvalho Gomes et al., 2009; Zahra et al., 2014):

(1) Enrichment factor (EF)

$$EF = \frac{C_{M0}}{C_{MT}},$$

where C_{M0} — heavy metal concentration in the surface sediment layer, C_{MT} — target concentration of the metal.

The enrichment factors (EF), besides supplying the basic information on the contribution of anthropogenic pollutants, are also used in environmental status assessments as put forward in the classification presented in Table 2 (Birch and Olmos, 2008; Zahra et al., 2014).

(2) Geoaccumulation index (I_{geo})

$$I_{geo} = \frac{\log_2 C_{M0}}{1.5 C_{MT}}.$$

I_{geo} is a coefficient, proposed by Müller (1979), and quite widely applied in sediment studies (Carvalho Gomes et al., 2009; Zahra et al., 2014), including assessments of sediment pollution with heavy metals (Zahra et al., 2014).

(3) Contamination factor (CF)

The method of CF calculation is identical to EF calculation. This factor was applied in the Initial Assessment of the Polish marine areas within MSFD (Anon., 2008) implementation process.

The CF factor was applied to assess the status of marine environment based on 5-class scale, derived for the EU Water Framework Directive (FWD) (Anon., 2000) purposes of the marine transitional and coastal waters' status assessments (Table 2). However, the MSFD requires the classification to be

Table 2 Sediment quality classifications based on enrichment factor (EF), geoaccumulation index (I_{geo}) and contamination factor (CF).

EF classification[a]			I_{geo} classification[a]			CF classification			
EF ranges	EF classes	Status description	I_{geo} ranges	I_{geo} classes	Status description	CF ranges	CF classes	Status description according 5-classes assessment	Status according MSFD
$EF < 1$	I	No enrichment	$I_{geo} = 0$	0	Unpolluted	$0 < CF < 0.5$	5	Very good	
$EF < 3$	II	Minor enrichment	$0 < I_{geo} < 1$	1	Unpolluted to moderately polluted	$0.5 \leq CF < 1$	4	Good	GES (Good Environmental Status)
$3 < EF < 5$	III	Moderate enrichment	$1 < I_{geo} < 2$	2	Moderately polluted	$1 \leq CF < 5$	3	Moderate	
$5 < EF < 10$	IV	Moderately severe enrichment	$2 < I_{geo} < 3$	3	Moderately to highly polluted	$5 \leq CF < 10$	2	Poor	Sub-GES
$10 < EF < 25$	V	Severe enrichment	$3 < I_{geo} < 4$	4	Highly polluted	$CF \geq 10$	1	Bad	
$25 < EF < 50$	VI	Extremely severe enrichment	$4 < I_{geo} < 5$	5	Highly to very highly polluted	—	—	—	—
—	—	—	$5 < I_{geo} < 6$	>5	Very highly polluted	—	—	—	—

[a] Presented after Birch and Olmos (2008) and Zahra et al. (2014).

Table 3 Values of enrichment factor (EF), geoaccumulation index (I_{geo}) and contamination factor (CF) determined for each metal and aggregated sediment status assessment.

	Zn		Pb		Cd		Hg		Sediment status assessment			
	EF/CF	I_{geo}	EF/CF	I_{geo}	EF (CF)	I_{geo}	EF/CF	I_{geo}	Mean EF	Mean I_{geo}	Mean CF/5-classes assessment	Mean CF MSFD assessment
Gdańsk Deep (P1)	2.2	0.6	2.7	0.9	7.2	2.3	5.7	1.9	4.5 Moderate enrichment	1.4 Moderately polluted	4.5 Moderate	4.5 SubGES
Bornholm Deep (P5)	1.7	0.2	1.9	0.3	4.1	1.4	2.9	1.0	2.6 Minor enrichment	0.7 Unpolluted to moderately polluted	2.6 Moderate	2.6 SubGES
SE Gotland Basin (P140)	1.5	0.03	2.2	0.6	1.7	0.2	2.3	0.6	1.9 Minor enrichment	0.4 Unpolluted to moderately polluted	1.9 Moderate	1.9 SubGES

done in two categories only: Good Environmental Status (GES) and sub-GES (Table 2).

The CF coefficients have been calculated of all analyzed metal concentrations in surface sediment layers (Table 3) as the current environmental status was to be assessed. The obtained CF values were used to classify the environmental status in the three southern Baltic Sea areas with regard to heavy metal pollution. In the case of Zn and Pb the status of all three areas assessed on the basis of I_{geo} and EF has to be considered as unpolluted to moderately polluted as only minor enrichment regarding these metals occurs (Table 3). Cd and Hg present quite different case, as the values of their I_{geo} indicate a moderately to highly polluted status of sediments in the Gdańsk Deep, and moderately severe enrichment is observed according to the EF's values. In the Bornholm Deep, there is moderate enrichment as regard Cd and minor enrichment in the case of Hg. The SE Gotland Basin has to be considered as unpolluted to moderately polluted with Cd and Hg.

Taking into account the CF factor, the status of all areas classified with respect to all analyzed metals was moderate, in the 5-class scale and as sub-GES in the MSFD classification system.

To assess the aggregated impact of the analyzed metals an average of all indicators was calculated (Table 2), characterizing the assessed area. The obtained results pointed out the Gdańsk Deep to be moderately polluted, with moderate enrichment in heavy metals, while the Bornholm Deep and the SE Gotland Deep turned out to be unpolluted to moderately polluted with minor enrichment of heavy metals in sediments.

The obtained classification results, based on the applied indicators, fall in good agreement, particularly regarding the EF and I_{geo}. Wider ranges of EF and I_{geo} values make the classification scheme flexible, while the narrow range of CF values makes the classification more rigorous.

The most restrictive is, however, the use of 2-class system recommended by MSFD, as the sub-GES result of classification imposes an obligation of counter measures to be undertaken on land, though simultaneously the magnitude of the problem cannot be assessed properly.

4. Conclusions

The area of Gdańsk Deep remains under the most severe anthropogenic pressure among the studied sedimentation basins. Sediments from this region were characterized by the highest heavy metal concentrations, except for Pb — higher concentration of lead was found in SE Gotland Basin before 1880. The substantial, saltatory change in metal concentrations and the resulting EF values were observed in the Gdańsk Deep after 1979. The maximal metal concentrations here reached 232 mg kg^{-1} — Zn, 77 mg kg^{-1} — Pb, 2.04 mg kg^{-1} — Cd and 0.27 mg kg^{-1} — Hg; this resulted in enrichment factor values (related to the concentrations in the deepest layer) of 13 in the case of Cd, 10 — Pb and 5 — Hg. This pollution of Gdańsk Deep sediments with heavy metals is directly linked to their input via the fresh water discharge of the Vistula River.

The SE Gotland Basin is the area showing the weakest anthropogenic pressure, this being proved by both the actual heavy metal concentrations and the dynamics of their changes. The substantial increase in Cd and Hg accumulation in sediments took place after 1980, and this was even more dynamic than in the Gdańsk Deep. The maximal EF values observed here reached 1.5 in the case of Zn and Pb and about 3 in the case of Cd and Hg.

Metal concentrations in the Bornholm Deep sediments assumed intermediate levels; simultaneously the greatest differentiation was seen after 1920, when a significant increase in heavy metal input occurred in this region.

The determined target concentrations (C_T): Zn —110 mg kg^{-1}, Pb — 30 mg kg^{-1}, Cd — 0.3 mg kg^{-1} and Hg — 0.05 mg kg^{-1} are consistent with the mean concentrations specific of average concentrations in shale.

On the basis of assessment on geoaccumulation index — I_{geo}, enrichment factor — EF and contamination index, the area of the Gdańsk Deep is considered moderately polluted with moderate enrichment of sediments in heavy metals, while the areas of Bornholm Deep and SE Gotland Basin are unpolluted to moderately polluted with minor enrichment of sediments with heavy metals. In the case of assessment based

on CF factor, all areas were classified as having moderate status or sub-GES in the 2-class assessment.

The obtained results point to differences in characteristics and dynamics of sediment formation in the basins located in the eastern part of the Polish sector of the southern Baltic Sea — Gdańsk Deep and SE Gotland Basin and that in the western part — the Bornholm Deep. The periods of sediment formation in the Gdańsk Deep and SE Gotland Basin are very similar; the deepest layers were respectively dated in 1838 and 1858, while the deepest sediment layers from the Bornholm Deep denote a much later period, around 1928, pointing to a faster sedimentation rate in this area. The determined linear sedimentation rates in the Gdańsk Deep $(0.18 \, \text{cm} \, \text{yr}^{-1})$ and in the SE Gotland Basin $(0.14 \, \text{cm} \, \text{yr}^{-1})$ are quite close, and the corresponding mass accumulation rates reached: $0.032 \, \text{g} \, \text{cm}^{-2} \, \text{yr}^{-1}$ and $0.049 \, \text{g} \, \text{cm}^{-2} \, \text{yr}^{-1}$. In the Bornholm Deep higher values of both linear sedimentation $(0.31 \, \text{cm} \, \text{yr}^{-1})$ and mass accumulation $(0.059 \, \text{g} \, \text{cm}^{-2} \, \text{yr}^{-1})$ rates were determined.

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