Original Research

Chemometric Assessment of Chemical Element Distribution in Bottom Sediments of the Southern Baltic Sea Including Vistula and Szczecin Lagoons – An Overview

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Abstract

The distribution of Ca, Mg, K, Na, Si, P, S, Al, V, Mn, Fe, Co, Cu, Ni, Zn, Sr, Mo, Cd, Sb, As, Bi, Pb, Tl, Th, U, Ti, Cr, Ba and REE (determined by ICP-MS, ICP-AES, XRF and AAS methods) in bottom sediments of the southern Baltic as well as the Vistula and Szczecin Lagoons were discussed. Based on enrichment factors (EFs) the accumulation of the chemical elements in surficial sediment with respect to their concentration in Earth's crust showed that Cd, Pb, Cu, Zn and Ag in coastal regions seem to be generally anthropogenic in origin. It is shown that the sediments of the Szczecin Lagoon are the most polluted by heavy metals, especially Cd, Zn and Pb, and that the degree of heavy-metal pollution decreases substantially on passing from the Szczecin Lagoon to the Pomeranian Bay and then on passing to the Bornholm Deep and Słupsk Furrow. Fluffy material from the Oder estuary appears to be the main source of heavy metals in the muddy sediments of the Bornholm Deep. The distribution of the rare earth elements (REE) in sediments of the Polish EEZ is more complex than previously thought and may be controlled by the input of Fe-organic colloids from rivers and the presence of detrital material in the sediments. The rare earth element (REE) patterns in sediments from the study region do not appear to have been greatly modified during transport from their source into the southern Baltic. In each of the study areas, there is a slight enrichment in the LREE relative to the HREE in the sediments compared to the NASC. The lack of significant anomalies for the redox-sensitive elements such as Ce and Eu implies that redox processes have marginal significance in modifying the distribution of the REE in the sediments studied. Chemometric techniques (FA, EMA) appeared to be useful for interpreting the spatial differences of chemical element concentrations in the study area.

Keywords: chemometric analysis, chemical elements, sediments, southern Baltic

Introduction

The anthropogenic input of trace elements into the coastal and estuarine zones of the southern Baltic Sea has possibly resulted in changes in the ecological equilibrium in this area. Since both natural and anthropogenic material have accumulated together, it is difficult to identify what proportion of the measured concentration of the elements in the sediments is natural and what is anthropogenic. This problem is exacerbated by the variable inputs of elements originating from these two sources, which may vary by several orders of magnitude, as well as the dependence of the

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element concentrations on factors such as sediment grain size, mineralogy and organic carbon content [1].

To compensate for the influence of grain size on element variability in various size fractions of the sediments, a number of granulometrical and geochemical techniques have been developed [2]. According to this author, the physical and chemical factors can alter significantly the distribution pattern and concentration of trace elements associated with both suspended and bottom sediments.

The granulometric approach concerns normalization of trace element data relative to the different size fractions of the bulk sediment, such as < 100 μm [3, 4], < 80 μm [5], < 63 μm [6-9], 60-20 μm (10], < 20 μm [11] and < 2 μm [12].

The geochemical methods include normalization of the element concentrations in the sediment relative to Al as a terrigenous normaliser [9, 13, 14], Fe [15-17], Sc [18, 19], Rb [20], Li [1], middle rare earth elements (Eu) or the heavy REE (Yb, Lu) [8, 21, 22], Mg [23] and K [24]. These conservative elements are dominantly lithogenous in origin.

The pollution status of the Gulf of Gdańsk, Puck Bay and the Vistula Lagoon has been overviewed by Glasby and Szefer [25]. The aim of this paper was to overview the relationship between chemical element concentration in the surficial and core sediments as well as identification of their potential sources in the sediments of the Gulf of Gdańsk and the southern Baltic Sea, including lagoon sediments.

Horizontal Distribution

In order to evaluate to what extent the analyzed elements are enriched in surficial sediments, the Enrichment Factor (EF) for each element in each area has been calculated using the formula given by Szefer et al. [26, 27]:

$$EF = (C_x/C_{Al})_s/(C_x/C_{Al})_c$$

...where symbols C_x and C_{Al} mean the concentrations of elements x and Al in the surface sediments (s) and Earth's crust (c), respectively. The concentrations of elements in the earth's crust are taken from Riley and Chester [28]. The EF's have been calculated for the average composition of sediments from each area. EF's >>1 are generally taken to reflect high levels of pollutants.

These data confirm that the sediments in each of the study areas are subject to heavy-metal enrichment being in the sequence Cd > Pb > Zn > Cu except for the Bornholm Deep and Słupsk Furrow, where the sequence is Pb > Cd > Zn > Cu. The former sequence is the same those previously reported for sediments from the Gulf of Gdańsk and Puck Bay [26, 27]. The data also confirm that As and Sb are significant pollutants in the sediments of the southern Baltic [22]. Based on the EF data, the degree of heavy-metal pollution in each area changed in the sequence is: Szczecin Lagoon >> Pomeranian Bay ≈ inner shelf area > Gulf of

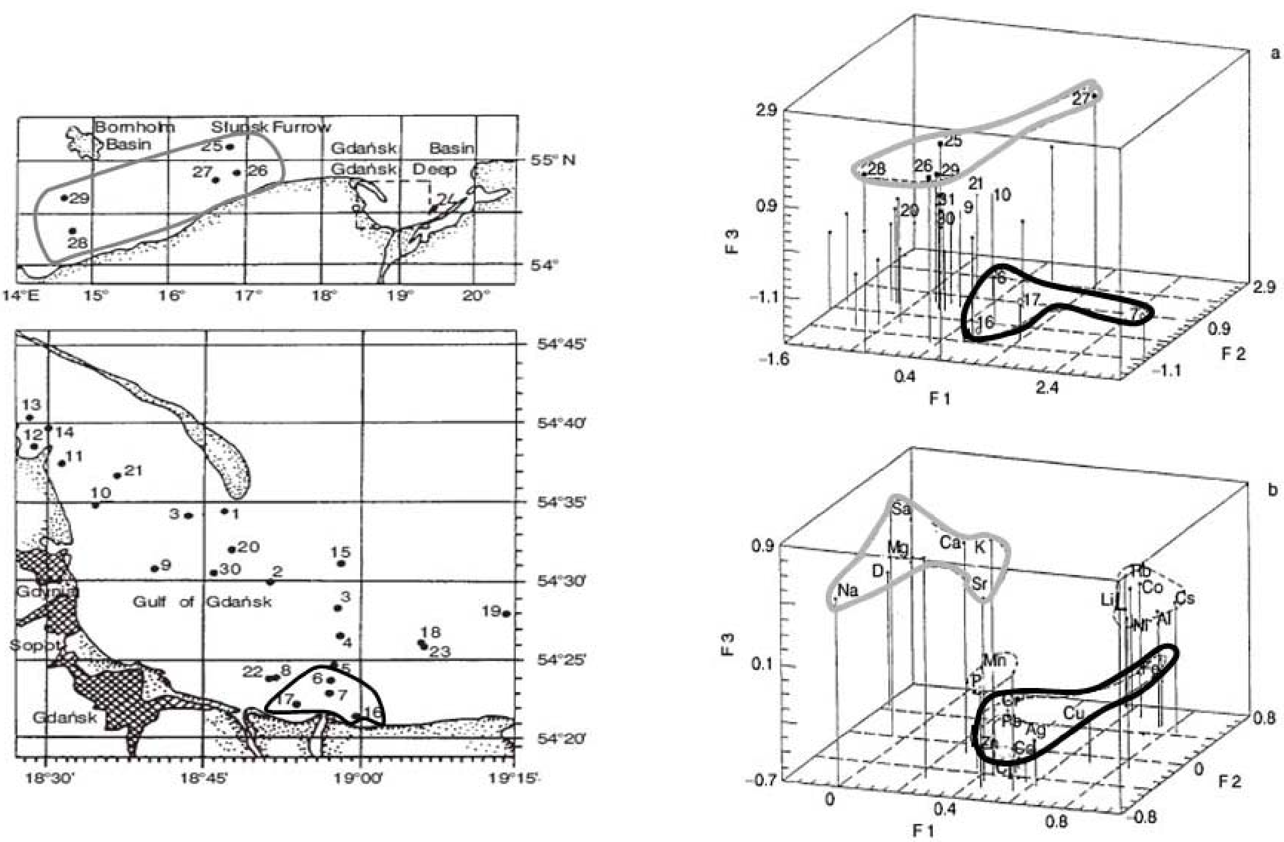


Fig. 1. Location of sediment sampling sites in the Southern Baltic and three-dimensional scatterplot of object sample scores (a) and loadings by individual variables (b) obtained for acid (concentrated HNO_3-$HClO_4$) leachates of sediment (fraction < 80 μm) sample data. Sa = salinity; D = depth of water; Ch = chlorophyll-a. Samples (nos. 6, 7, 16, 17) originating close to the subarea of the Vistula estuary (open circles) and from the open-sea region (filled circles) are indicated.

Gdańsk ≈ Bornholm Deep > Vistula Lagoon > Słupsk Furrow [9]. The distribution pattern of chemical elements in bottom sediments of the Southern Baltic has been presented by Szczepańska and Uścinowicz [29].

Fig. 1 illustrates factorial distribution of object scores in the three-dimensional scatter plot. It can be seen that open-sea samples (Nos. 25-29) form a separate cluster (with the highest values of F3) clearly distinguished from the grouping of points (with the lowest values of F3) represented by typical estuarine samples (Nos. 6, 7, 16 and 17). The remaining samples are located in mid-distance between the estuarine and open-sea clusters. It can be concluded that this intermediate region is less influenced by the influx of material of the riverine origin. The factorial distribution of loadings (variables) shows that the open sea object samples, corresponded to K, Mg, Ca, Na, Sr as well as parameters like salinity and depth of water (with the highest values of F3), are well isolated from the estuarine cluster - down located, consisted of Zn, Cd, Ag, Cu, Cr, Pb, chlorophyll-a and Fe. The localization of the latter (described by lower values of F3) substantiates identification of samples originating from the Vistula River's mouth (characterized also by lower values of F3). The intermediate cluster groups mainly elements such as Al, Li, Rb, Co, Cs and Ni and identifies the Puck Bay samples [5].

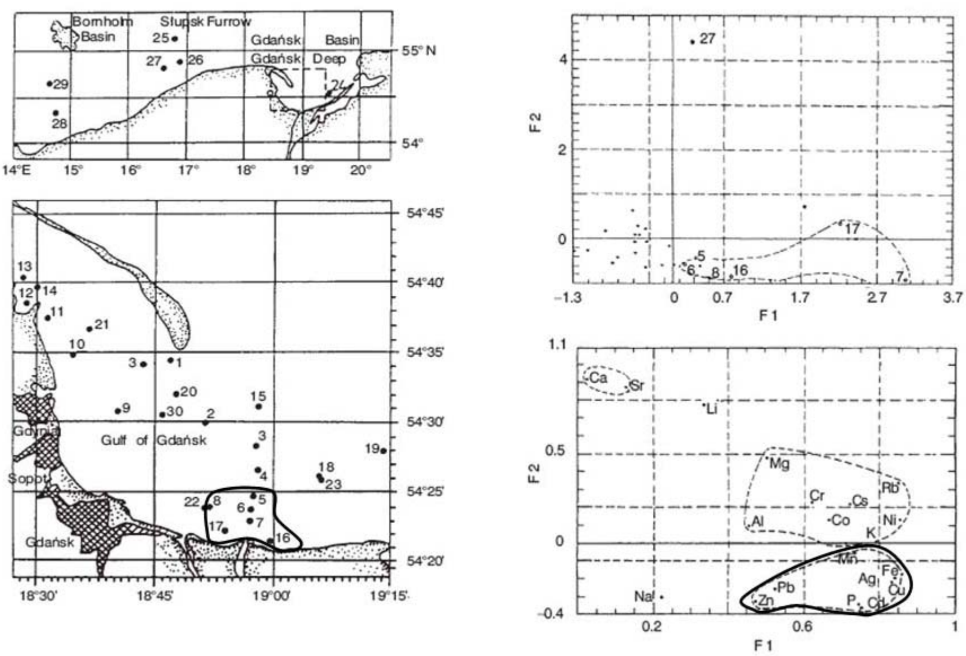


Fig. 2. Scatterplots of object sample scores (a) and loadings by individual variables (b) in space spanned by axes F1 and F2 obtained for acid (1 M HCl) leachates of sediment (fraction < 80 μm) sample data.

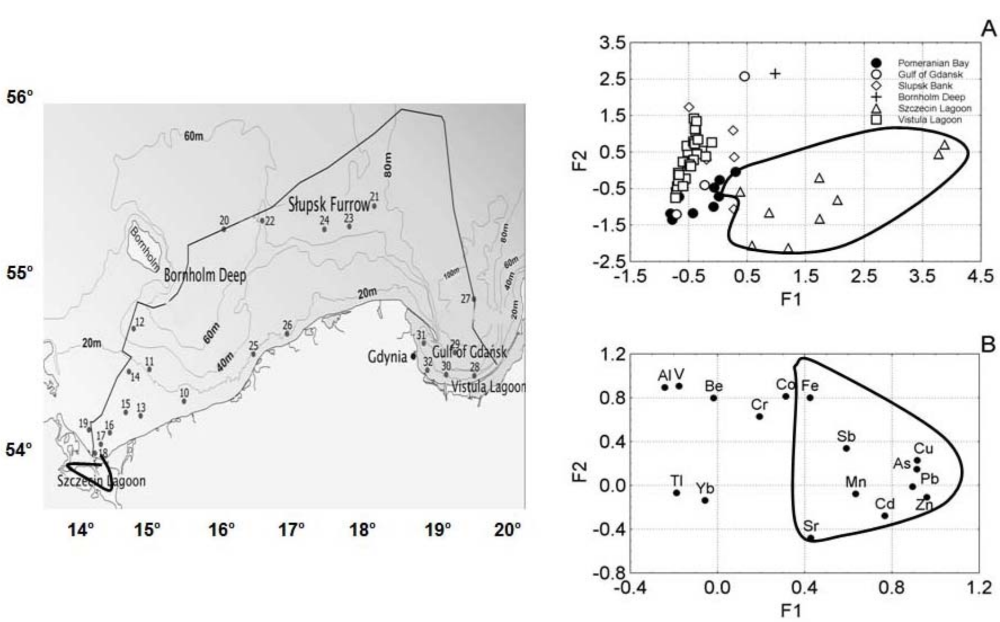


Fig. 3. Schematic map displaying the positions of the sediment sampling sites in Southern Baltic, Vistula Lagoon and Szczecin Lagoon, and scatterplots of object sample scores (A) and loadings by individual variables (B) obtained for sediments sample data from different areas of the Southern Baltic.

In order to recognize labile species of metals in sediments, chemical analyses of both the acid and basic extracts have been performed. The first three factors extracted 41, 16.7 and 9.2% of the total variance, respectively [5]. The results obtained are presented in two-dimensional scatter-plot (Fig. 2). The Ca-Sr cluster associated with the open-sea samples may reflect the presence of biogenic carbonates in the surface sediments. Since Fe-Mn and Al clusters are well isolated from each other it is suggested that 1 M HCl leached elements which are split into two major phase groups, i.e. Fe and Mn hydroxide/carbonate group (Ag, Cd, Cu, P, Pb, Zn and Fe with Mn) and the aluminosilicate group (Co, Cr, Cs, K, Mg, Ni, Rb with Al). The latter bounds the group of elements accompanied Al in Puck Bay area while the Fe-Mn phase is responsible mainly for the deposition of labile, easily extractable forms of Zn, Cd, Pb, Cu, Ag and P in the Vistula estuary. These elements, probably anthropogenic in origin, could be scavenged by this phase at the hydrological front where mixing of the Vistula river water with the brackish Baltic Sea water takes place.

FA was also applied for evaluating of the distribution of As, Cd, Co, Cr, Cs, Cu, Ba, Bi, Ga, In, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V, Zn, RRE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) in surface sediments of the Vistula Lagoon sediments (Polish sector) as well as Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, REE in the three sectors of the southern Baltic Sea [8, 22]. Uścinowicz and Zachowicz [30] have reported the distribution of chemical elements in surficial sediments of the lagoon. As can be seen in Fig. 3, the Szczecin Lagoon samples form a separate cluster which is closely fitted to the Pomeranian Bay samples. On the other hand, the Vistula Lagoon object scores accompanied those represented by the Gulf of Gdańsk (properly Puck Bay) sediments [31]. This scatter-plot clearly illustrates a great dissimilarity between geochemical composition of the Szczecin and Gdańsk Lagoon sediments. The Szczecin Lagoon and the Pomeranian Bay are elements of the Odra River estuary, while the Vistula Lagoon with the Gulf of Gdańsk, excluding its western inner part (Puck Bay), are supplied with the Vistula River. Bereft of topographical barriers, the Pomeranian Bay is exposed to permanent, intensive water exchange between itself and the neighbouring Arkona and Bornholm Basins and its exchange with the Central Baltic represented by the Słupsk Bank takes only about 3 weeks. Such long-distance water exchange is possibly reflected by overlapping of the object scores corresponding to the Pomeranian Bay and the Słupsk Bank. The distribution of

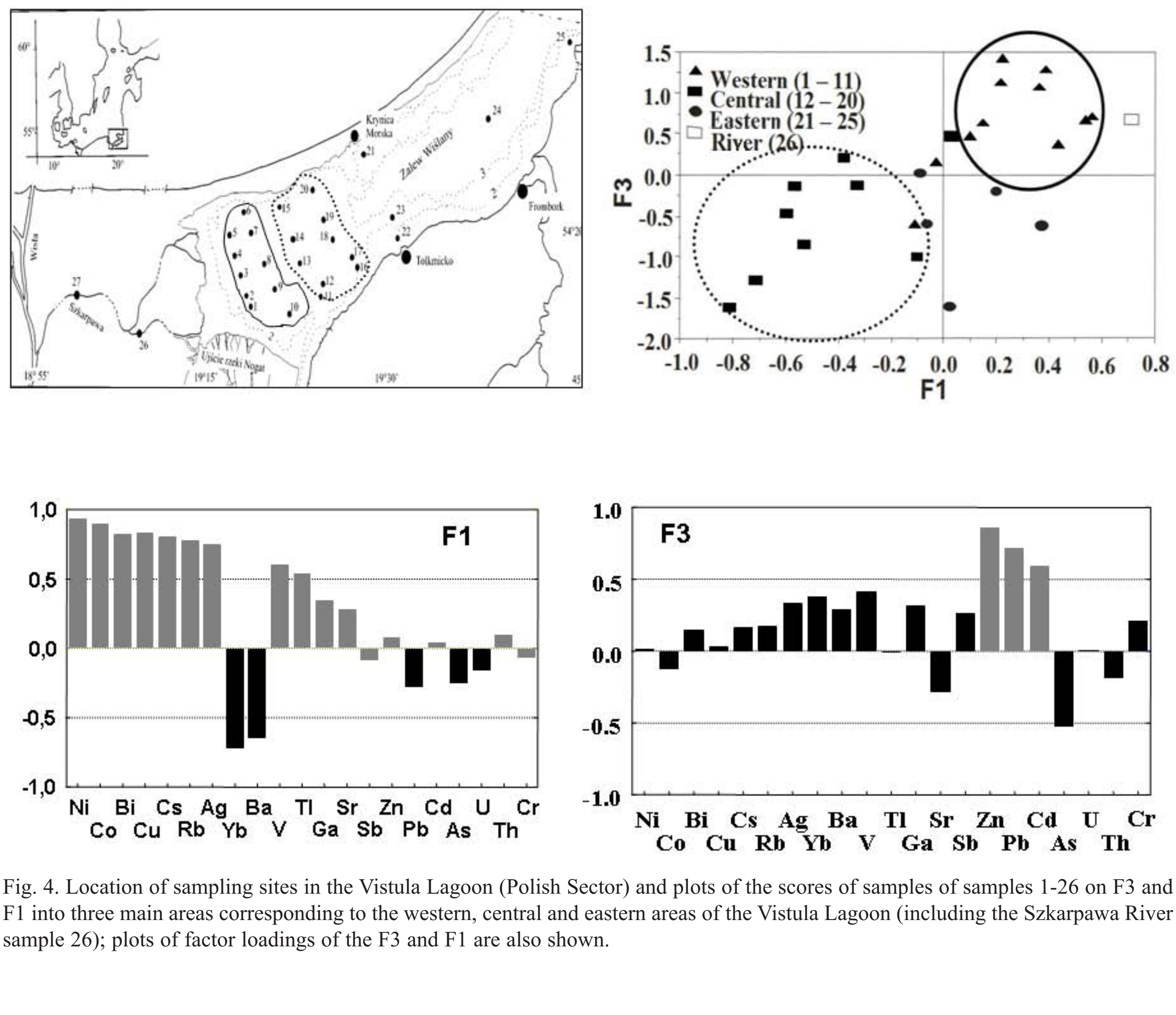


Fig. 4. Location of sampling sites in the Vistula Lagoon (Polish Sector) and plots of the scores of samples of samples 1-26 on F3 and F1 into three main areas corresponding to the western, central and eastern areas of the Vistula Lagoon (including the Szkarpawa River sample 26); plots of factor loadings of the F3 and F1 are also shown.

loadings (variables) in two-dimensional scatter plot indicates that elements such as Zn, Cu, As, Pb, Cd, Sb, Mn, Fe and Sr (described by high values of F1) are isolated from the cluster represented by Al, V, Tl, Be and Yb (characterised by lower values of F1, Fig. 3). Since Yb and Al are typically terrigenic elements in origin, and Cd and Pb belong to anthropogenically derived metals, it means that the Pomeranian Bay, and especially the Szczecin Lagoon, are the most polluted areas of the southern Baltic [8, 31].

Factor analysis was also performed on the 26 samples from the Vistula Lagoon. The eigenvalue was set to 1.0 as a threshold in order to limit the number of extracted and rotated factors. Four factors (FI-FIV) were obtained which explained 64.3% of the total variance and accounted for 31.1, 12.4, 11.8 and 9.0% of the total variance, respectively [22]. As can be seen in Fig. 4 the object samples are clustering into two main areas, each corresponding to a geographically distinct zone. Samples from the western part of the lagoon (samples 1-11) and the Szkarpawa River (sample 26) with the highest values of F3, mostly influenced by the riverine input of anthropogenicaly-derived material, are generally characterized by the greatest concentrations of Zn, Pb and Cd (F3). Samples from the central area, characterised by the lowest values of F1, reflect detrital origin of Yb, Ba, Pb, As and U.

Based on the factorial analysis of the Szczecin Lagoon concentration data, the first three factors explained cumulatively 86.2% of the total variance. The factorial picture reported by Glasby et al. [8] is in good agreement with dendrograms showing patterns of element distribution in sediments from Szczecin Lagoon constructed by Osadczuk and Wawrzyniak-Wydrykowska [32]. The geographical distrib-

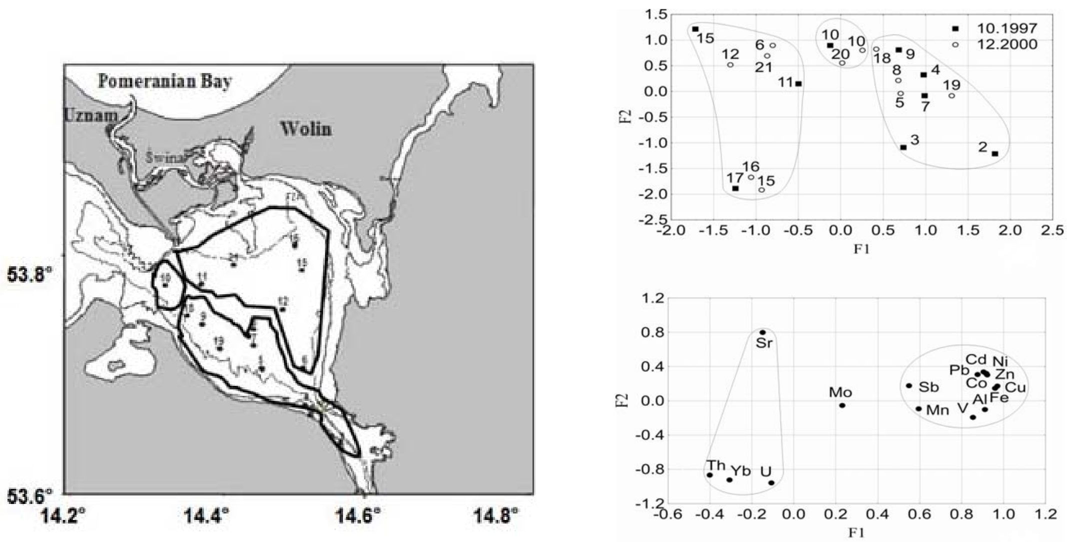


Fig. 5. Schematic map displaying the positions of the sampling sites in Szczecin Lagoon and biplots for object scores of factors F1 and F2 for 21 sediment samples and biplots for object scores and loadings of F1 and F2.

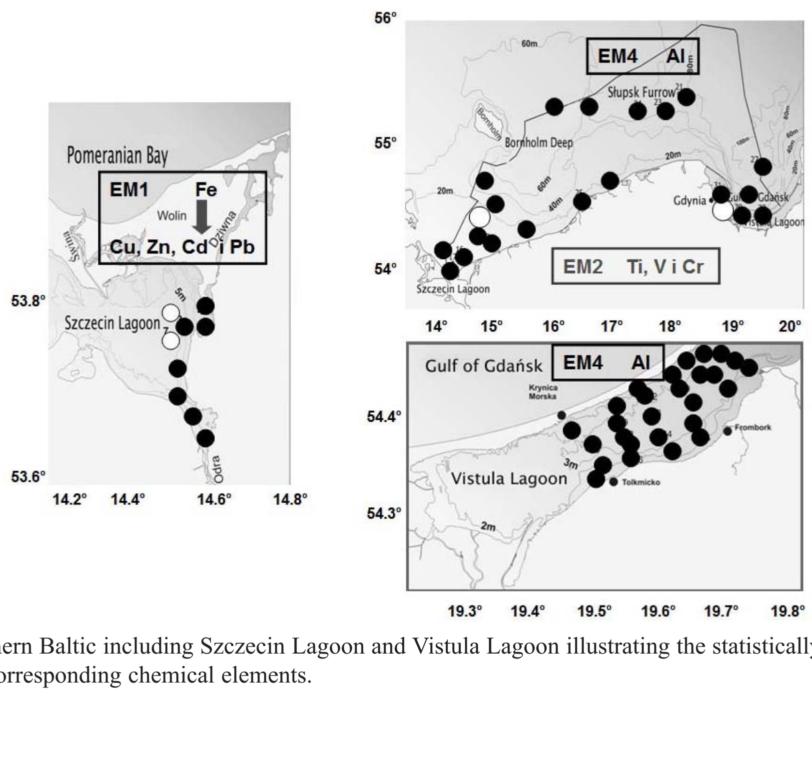


Fig. 6. Map of the Southern Baltic including Szczecin Lagoon and Vistula Lagoon illustrating the statistically significant EMA distribution of samples and corresponding chemical elements.

ution of the geochemical facies determined by these authors corresponds strictly to the three main areas of the lagoon identified by FA [8]. As can be seen in Fig. 5, samples from the western part of the lagoon with high values of F1, mostly influenced by the riverine input (Oder river), have the highest levels of Cd, Pb, Cu, Zn, Co, Ni, V, Mn, Sb and Al. Clay minerals and organic matter (PM) can build aggregates and flocs which concentrate the trace elements and then sink to form the fluffy layer. This finding is supported by Löffler et al. [33], since the levels of trace elements are significantly correlated with particulate OM and Al. For instance, Pb and Cd are preferentially associated with clay mineral particles forming more or less stable aggregates with OM. It resulted in a strong relationship between OM, Al, Fe and trace elements, agreeably to the factorial distribution reported by Glasby et al. [8]. Specific factors influencing fluffy layer in the system (the Odra River - Pomeranian Bay – Arkona Basin) have been discussed by Pempkowiak et al. [34].

Samples from the eastern part of the lagoon (with low values of F1) were attributable to the enrichment of elements such as Yb, Th, U and Sr as terrigenous in origin.

The northwestern part of the lagoon is characterized by the presence of sediments that appear to be transitional in geochemical composition, possibly associated with Mo [8].

As reported by Renner et al. [35], endmember 1 (EM1) was the highest for Fe, Cu, Zn, Cd and Pb, EM2 for Ti, V, Cr and Cd, EM3 for Be, Mn Co, As, Sr, Mo and Sb and EM4 for Al. It has been shown that EM1 (11.1% of the total abundance) is dominant in samples 1-5 and 8-9 from the Szczecin Lagoon, EM2 (10.3% of the total abundance) in samples 14 from the Pomeranian Bay and 32 from the Gulf of Gdańsk and EM4 (75% of the total abundance) in all other samples. EM4 is therefore the most important in virtually all the samples from the Pomeranian Bay, Bornholm Deep, Słupsk Furrow, inner shelf area, the Gulf of Gdańsk and the Vistula Lagoon and is detrital in origin (Fig. 6).

As can be seen in Fig. 7 NASC (North American Shale Composition) – normalised REE patterns indicate that the REE distribution in the sediments has not been greatly modified during their riverine transport to Szczecin Lagoon and the Gulf of Gdańsk. The lack of significant Ce and Eu anomalies in the plots also suggested that redox processes have not played a significant role in modifying the distribution of the REE in these sediments [8, 9, 22].

Temporal trends in variations of element concentrations in surficial sediments were studied based on data reported by Szefer et al. [5] and those unpublished yet. The concentration of labile forms (extractable in 1M HCl) of heavy metals in surficial sediments (<63 μm) of the estuarine area of the Gulf of Gdańsk analyzed recently (unpublished data) are smaller than those reported previously for the same region. For instance, levels of Zn, Cd, Cu and Cr were ca. 10-, 6-, 5- and 2-times lower in extractable fraction of sediments collected along a transect of the gulf from mouth of the Vistula River as compared to those taken from the same area ca. 20 years ago [5]. This may be a result of recent reduction of anthropogenic emissions of these metals to the study area.

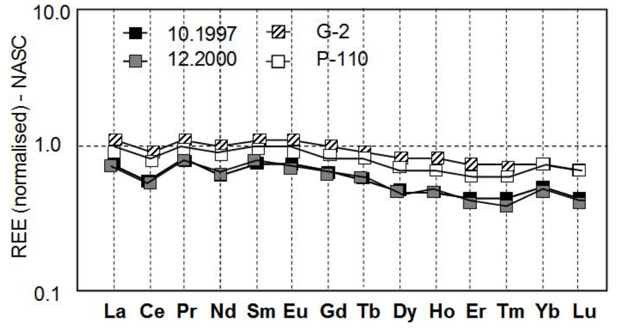
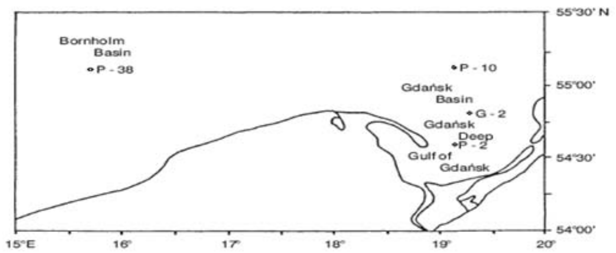


Fig. 7. Plots of the average North American Shale Composition (NASC) – normalised REE data for sediments from the Gdańsk Basin and Szczecin Lagoon (10. 1997, 12. 2000).



Object number*	Sample depth in core [cm]	Object	Sample depth in core [cm]
Core P-2		Core P-10	
2	0.7-2.0	1	0.0-1.6
4	3.0-4.0	3	2.6-3.9
6	5.0-6.0	5	5.5-7.4
7	6.0-7.0	6	7.4-9.2
8	7.0-8.0	7	9.2-11.4
10	10.0-12.0	8	11.4-14.1
11	12.0-15.0	9	14.1-17.8
12	15.0-20.0	10	17.8-21.5
13	20.0-25.0	11	21.5-25.8
14	25.0-30.0	12	25.8-31.3
Core G-2		13	31.3-34.8
1	0.0-1.0	Core P-38	
2	1.0-2.0	1	0.0-0.7
4	3.0-4.0	2	0.7-1.8
5	4.0-5.0	5	5.0-6.2
6	5.0-6.0	6	6.2-8.1
10	9.0-10.0	7	8.1-9.7
11	10.0-12.0	8	9.7-12.1
12	12.0-15.0		
13	15.0-20.0		
14	20.0-25.3		

Fig. 8. Map of the Southern Baltic indicating the localization of the sampling sites with listed tabularly the object numbers and depths of corresponding core segments.

Vertical Distribution

The vertical profiles of selected elements in southern Baltic sediment cores have been investigated by several authors [15, 27, 36, 37]. Among 14 cores, three granulometric fractions of < 2, 2-63 and 63-200 µm have been additionally analysed for concentrations of minor and major elements. Granulometric and mineralogical characteristics of the sediment cores as well as changes of the organic matter concentration in the particular segments with depth of their location are illustrated and discussed by Szefer et al. [27, 36, 37]. The data presented graphically show a decrease in the concentrations of Cd, Ag, Pb, Zn and Cu with depth in sediment column in most of the cores. The increase in heavy metals in the upper layers of Puck Bay, compared to the lower layers, reflects the onset of industrialisation, and the resultant increase in heavy-metal pollution, in Poland. By contrast, sediments from the estuarine core taken from near the mouth of the Vistula River have a much higher sedimentation rate than those from Puck Bay. Sedimentation rates for the upper layers of nearby sediments have been determined to be in the range 0.91-7.71 mm/yr. Assuming the average of these two values for the upper layers of sediments for the estuarine core, this implies that the sediments in the upper 20 cm of this core were deposited during the last 45 years or so (although this figure is subject to a wide margin of error). This corresponds to the period of heavy industrialisation in the Vistula Basin [26]. In addition, this stormy area has been exposed to extensive sediment resuspension, leading to mixing of the sediment. The lower levels of many elements in the depth range 5-15 cm in this core may reflect the stagnation of the Polish economy after 1980, when industrial production declined.

As expected, significant variations of metal concentrations in relation to sediment particle size were identified. The fine-grained (sub-colloidal) fraction is mainly enriched in the heavy metals, while the 63-200 µm fraction commonly exhibited the lowest levels of the metals analyzed.

The horizontal distribution of selected metals and their vertical profiles in southern Baltic sediment cores have been investigated widely using a dozen sediment cores [27, 36].

Concentration data of sediment cores collected from several sampling sites of the Southern Baltic (Fig. 8) have been processed by PCA. The distribution of principal component scores is similar to that of the principal component loadings (Fig. 9). Since C_{org} represents organic matter molecules and Al is a typical element of crustal origin, two antipathetic PC1 clusters indicate that C_{org}, N, Cu, Pb, Zn, Cd and possibly P (low values of PC1) are biogenic while Al, Fe, Ti, K, Mg, Th, Co and Ni (high values of PC1) are terrigenous in origin [38]. These two main groupings of loadings correspond to the surface (anthropogenically influenced) and to deeper (prehistoric background) layers of sediments, respectively. The clusters let us identify elements anthropogenic in origin (Pb, Cd, Zn, Cu and partly P) accumulated in recently formed top layers of sediments as well as elements terrigenic in origin (Al) deposited in the segments corresponding to precivilization era. Atypical distribution of object scores for the core P-2 reflects the occurrence of calcareous material in the core (2.3-3.7% Ca).

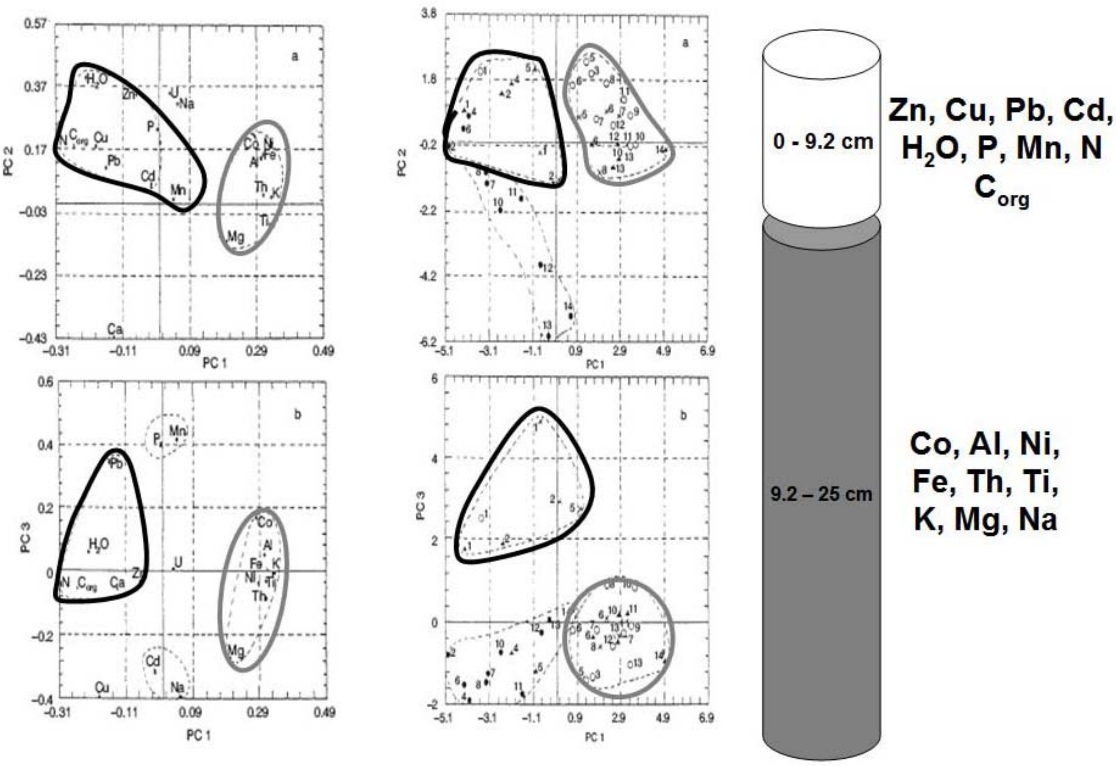


Fig. 9. Scatterplots of principal component segment scores. Samples originating from stations P-2 (close circles), P-10 (open circles), P-38 (x), and G-2 (triangles) are numbered as in the Table of the object numbers and depths of corresponding core segments listed below the map; (a) scores and loadings in space spanned by PC1 and PC2, (b) scores and loadings in space spanned by PC1 and PC3.

Metal Speciation and Mineralogical Forms of Fe

For most metals, e.g. Cu, Pb and Cd, the silicates and sulphides/organic phases are the dominant substrates in Baltic sediments [39]. In the clay fraction of sediments the metal-sulphides-organic matter complexes have been sporadically identified. Speciation of trace elements in the Baltic Sea sediments reflects a complex nature of different processes related to their precipitation or coprecipitation with carbonates and Mn-Fe-oxyhydroxides. They can form the complexes with organic and inorganic floculated particles – as well as be transported within the crystal lattice of minerals and on exchangeable sites of clay minerals. Their last two forms dominate in the clay fraction of sediments [39]. According to Belzunce Segarra et al. [40] Mn, Ni, Pb and Zn, are predominantly accumulated in Fe-Mn oxide/hydroxide and organic fractions of Gulf of Gdańsk sediment, especially in carbonate and cation-exchangeable fractions, while Cu is mainly associated with the organic fraction. Other elements such as Co, Cr and Fe are mostly found to be associated with the residual mineral component of the sediment, although in the case of samples enriched in Fe there was a significant contribution of these elements in oxidizable fraction, bound with organic matter. According to Pempkowiak et al. [41] the speciation of selected metals in the four fractions studied differed significantly between sediments from the Baltic Sea and the Norwegian Sea. In contrast to Norwegian Sea sediments, Baltic sediments contained substantial quantities of Cd, Pb and Zn – adsorbed on sediment particles or bound to Fe-Mn oxyhydroxides. Among the metals studied, Cu and secondarily Cd, Pb and Zn seem to be mostly bound to organic matter, especially in the Baltic sediments. This could be explained by high affinity of the metals, particularly Cu to Baltic humic substances, represented some fraction (20-80%) of natural organic matter.

Other major sediment determinants such as amorphic Fe-Mn oxyhydroxides, effectively contribute to accumulate of labile, easily extractable species of Cd, Cu, Pb and Zn in Baltic sediments, especially in estuarine areas [5, 42-44]. There is a distinctly marked salinity (hydrological) front ca. 10 km from the Vistula River mouth. Ferrous ions are located in ferrous hydroxide, an unidentified Fe^{2+}/Fe^{3+} hydroxide, monosulphides and authigenic siderite. Ferric ions are identified in fine-crystalline ferrihydrite, α- and γ-FeOOH. Iron in non-clay magnetic minerals changes its valency and mineral form along the sediment column [43]. The presence of lepidocrocite-ferrihydrite- Fe^{2+}/Fe^{3+} hydroxide (and siderite and FeS) parageneses and the Fe^{3+}/Fe^{2+} ratio higher than 2.0 indicate a brackish, stratified estuary-type basin. A ferrous hydroxide-goethite-dominated paragenesis with lower levels of FeS and a Fe^{3+}/Fe^{2+} ratio of lower than 1.0 substantiates identification of a freshwater environment while transitional conditions to or from brackish basins are identified by total Fe and siderite content peaks and enhanced levels of FeS [31, 43].

Conclusions

- Chemometric multivariate techniques, i.e. FA, PCA and EMA are recommended as effective statistical tools to simplify and visualize interpretation of the relationships between numerous elemental data.
- Vistula Lagoon sediments were locally polluted by Ag, Sb, As, Cd and Pb.
- Szczecin Lagoon appeared to be the area most polluted with heavy metals, especially Cd, Zn and Pb.
- The flood resulted in the enhanced transport of redox-sensitive and anthropogenic elements in the Odra River and their subsequent redeposition in the sediments of the Szczecin Lagoon.
- Amorphic Fe-Mn oxyhydroxide phase is responsible mainly for the deposition of labile forms of Zn, Cd, Pb, Cu, Ag and P in the Vistula estuary. These elements, probably anthropogenic in origin, could be scavenged at the hydrological front where mixing of the Vistula water with the brackish Baltic water takes place.
- Based on chemometric evaluation of the data obtained it is found that in sediment cores of the southern Baltic Al is a typical element of crustal origin and C_{org} represents organic matter molecules. Aluminium, Fe, Ti, K, Mg, Th, Co and Ni (positive values of PC) are terrigenous while C_{org}, N, Cu, Pb, Zn, Cd and possibly P (negative values of PC) are biogenic in origin.
- The terrigenous cluster corresponds with deeper segments – formed in the precivilization era while the biogenic cluster is attributable to surface segments (anthropogenically influenced) deposited in the civilzation era.
- NASC (North American Shale Composition) – normalized REE patterns indicate that the distribution of REEs in the sediments has not been greatly modified during their riverine transport to Szczecin Lagoon and the Gulf of Gdańsk.

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