

Original Research

# Chemical Forms and Distribution of Heavy Metals in Core Sediments from the Gdańsk Basin, Baltic Sea

M.J. Belzunce Segarra<sup>1\*</sup>, P. Szefer<sup>2</sup>, M.J. Wilson<sup>3</sup>, J. Bacon<sup>3</sup>, J. Bolalek<sup>4</sup>

<sup>1</sup>Marine Research Division (AZTI-Tecnalia), Muelle de la Herrera, Recinto Portuario s/n. 20110 Pasajes, Spain

<sup>2</sup>Department of Food Sciences, Medical University of Gdańsk, al. Gen. J Hallera 107. PL 80-416 Gdańsk, Poland

<sup>3</sup>Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen AB15 8QH, Scotland

<sup>4</sup>Department of Oceanography, University of Gdańsk, al. Marsz. Piłsudskiego 48. PL 81-378 Gdynia, Poland

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## Abstract

Short sediment cores (30 cm length) were taken along a transect of the Gdańsk Basin from the mouth of the Vistula River out into the Baltic Sea in June 1996. The chemistry and mineralogy of surficial and buried sediments were determined and Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analyzed in total and in fractions using a sequential extraction procedure. The bulk and clay mineralogy of the sediments were determined by XRD and SEM. The concentrations of some of the trace metals in sediments are above pre-anthropogenic background. In particular, the surficial samples are substantially enriched in Cu, Pb and Zn, suggesting an anthropogenic origin. The concentrations of Cu, Pb and Zn range from 21-71  $\mu\text{g}\cdot\text{g}^{-1}$ , 56-210  $\mu\text{g}\cdot\text{g}^{-1}$  and 21-83  $\mu\text{g}\cdot\text{g}^{-1}$ , respectively. Unexpectedly, the concentrations of trace metals increase seawards within the Gdańsk Basin. The forms of binding are different for each metal. Cobalt, Cr and Fe are mainly associated with the residual mineral fraction of the sediment, although in samples with high Fe concentrations there is a significant correlation with organic compounds. In contrast, Mn, Ni, Pb and Zn are predominantly associated with oxides and the organic fractions, with a significant percentage associated with the carbonate and exchangeable cation fractions, whilst Cu is mainly bound with the organic fraction.

**Keywords:** Gdańsk Basin, sediment cores, clay minerals, organic carbon, heavy metals, sequential extraction

## Introduction

The Baltic is particularly susceptible to an accumulation of pollutants in surficial sediments because it is a semi-enclosed sea surrounded by industrialized countries. There are many published data on metal pollutants in the Baltic Sea [1-7] and in general these studies have demonstrated that pollution is indeed a serious problem. In some areas, pollution may be even such a serious cause that bottom sediments are completely devoid of

marine life [8]. Heavy metal pollution of the Baltic Sea has long been recognized as a particular problem and in the past to a large extent this has been attributed to anthropogenic inputs from Poland. It has been shown that mining and smelting operations have caused significant environmental contamination in the hydrological system which flows into the Baltic Sea. For example, it is reported [9] that, in the Upper Silesian Zn-Pb district, water discharge supplies and appreciable amounts of base metals, up to 2  $\text{g}\cdot\text{m}^{-3}$  of mostly Zn and Pb. There is a decrease of metal contents in the Vistula River sediments downstream of Cracow. The Vistula River drains the Upper Silesian Mining and Metallurgical Industrial

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\*Corresponding author; e-mail: jbelzunce@pas.azti.es

District; hence there is a particularly strong accumulation of metals in the river sediments of this region. In the sediment of the Upper Vistula River along a distance of about 200 km > 99% of both Cd and Pb and > 90% of Zn are of industrial origin. The sediment sampled from the Gulf of Gdańsk showed decreasing metal concentrations by factors of about 10 for Zn, 20 for Cd and 5 for Pb and Cu [9]. In 1989, the Vistula discharged 2930 t of Zn, 12.8 t of Cd, 196 t of Pb, 233 t of Cu and 15.5 t of Hg to the Baltic [2]. The total metal concentrations in Baltic sediments have been reported by several authors [10-20].

The Gdańsk Basin is an interesting object of the present investigations, particularly with respect to the heavy metal status of the bottom sediments. Although the distribution of heavy metals in Baltic Sea sediments has received increasing attention in recent years, there are still various aspects that require further investigation. For example, bearing in mind that natural and anthropogenic materials accumulate together in sediments, the relative proportion of heavy metals from these two sources requires clarification, as do the actual forms in which the heavy metals are carried [21]. Therefore, it was decided to study a series of sediment cores taken along a transect in the Gdańsk Basin northwards from the mouth of the River Vistula. In order to assess the distribution of selected heavy metal forms and the extent of heavy metal pollution, both the surface and deep core segments were studied using sequential extraction techniques, combined with preliminary investigations of mineralogy and organic matter. A particular point of the investigation was to determine whether the heavy metals would be largely associated with fine mineral or organic particulates acting as potentially major carriers.

## Materials and Methods

### Sampling

Four sediment cores were collected on board the naval craft "Kopernik" during an oceanographic cruise in June 1996 in the Gdańsk Basin. Sample locations are shown in Fig. 1 and the coordinates, depths and properties of the sediment samples are shown in Table 1. The transect studied covers a distance of 42 km from sample K-6 (9.4 km from the river mouth) to sample K-1 (51.4 km from the river mouth). At each station ten cores were collected to perform different analytical procedures (mineralogy, metals, nutrients, sulphates, iron, redox potential, pH, humidity and organic matter). The results obtained on nutrients, iron, redox potential, pH, humidity and organic matter have been published already by Bolalek and Frankowski [22]. From the surface the sediment cores were sliced into 4 segments of 2.5 cm thickness and from this point to the bottom of the core in segments of 5 cm thickness. The subsamples obtained were placed in plastic bags and stored at 4°C until analysis. The sediment samples were oven-dried at 60°C for 24 hours [23] and the coarser material (> 2 mm) was removed using dry sieving through nylon mesh. The fresh samples contained 39 to 89% weight of water.

### Mineralogical Analysis

The mineral composition of the sediments was studied by x-ray powder diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy. A total number of 12 samples: surface (0-2.5 cm), 10-20 cm and basal (25-30 cm) segments of the core sediments were selected for min-

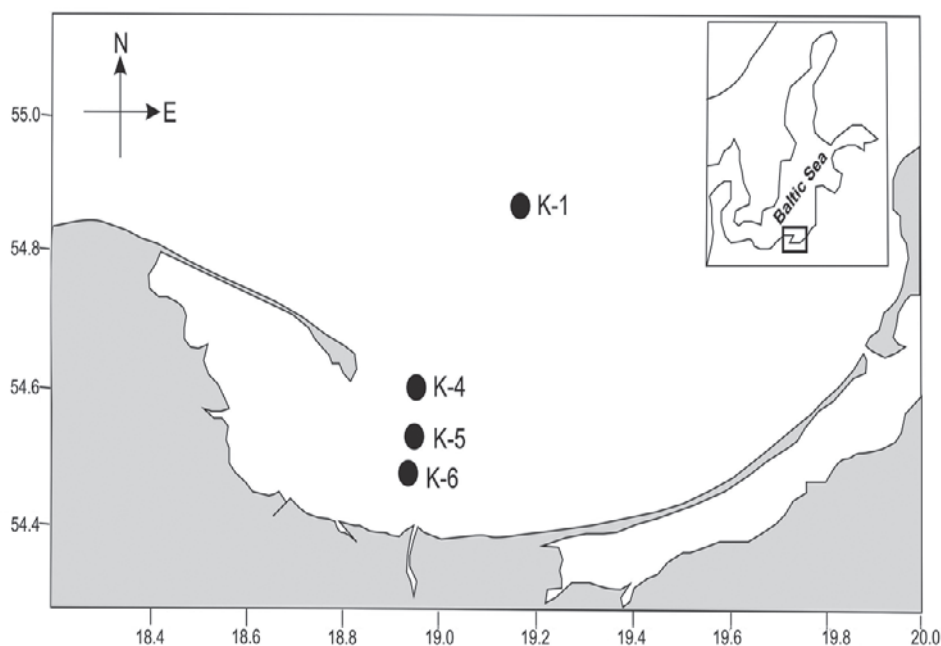


Fig. 1. Schematic map showing the location of the sampling sites.

Table 1. Coordinates position and depths of the sampling stations. The properties of the sediment samples are also indicated.

Sample	Latitude (N)	Longitude (W)	Depth (m)	Properties
K-1	54° 52'	19°10'	104	Black mud. Change in colour at 20 cm below surface. H <sub>2</sub> S smell. 30 cm length
K-4	54°35'87''	18°57'87''	78	Black mud. 30 cm length
K-5	54°30'57''	18°5757''	65	Black in colour, silty. No reduced sections. 30 cm length
K-6	54°27'44''	18°56'82''	60	Coarse particle size. Change in colour at 20 cm below surface. 45 cm length

eralogical studies. XRD analyses were made of random a mounts of whole samples for qualitative determination of non-clay minerals, and of oriented mounts of the < 2 µm fraction for a precise determination of clay minerals. The samples were washed free from salts in deionized water. Bulk fractions were ground to < 20 µm and packed into holders in a non-oriented form. Clay fractions were separated by centrifuge according to Stokes Law. The obtained suspensions enriched in clays were dried onto glass slides so as to form oriented aggregates. These samples were run after air drying, using ethylene glycol solvation to distinguish expandable clays and heating to 300°C for 2 hours to distinguish chlorite in the clay mineral assemblage. XRD patterns were recorded on a D5000 Siemens diffractometer using Co K $\alpha$  radiation at scan rates of 2° 2 $\theta$  per minute. Most samples were scanned through the range 2-45° 2 $\theta$ . For SEM studies a particle size greater than 63 µm, separated by wet sieving, was used. The instrument used was a Philips XL 20 scanning electron microscope fitted with an Oxford EXL II energy dispersive microanalysis system. Preliminary studies of the mineral composition of the samples were performed using a standard optical microscope and the fractions above 75 and 53 µm used here were separated by wet sieving.

### Chemical Analysis

Prior to chemical analysis, subsamples of the dried < 2 mm fraction were used to separate the grain size fraction < 63 µm by wet sieving. A total number of 8 subsamples, surface (0-2.5 cm) and basal (25-30 cm) segments of each selected core, were chosen for chemical analysis.

#### C, N Analysis

Total N and organic C were determined by combustion at 1020°C in a Carlo Erba Nitrogen Analyzer 1500 apparatus. Prior to analysis, the inorganic carbon was removed by subsequent additions of 1 N HCl.

#### Total Metal Analysis

1 g of dry weight sediment sample was digested in platinum crucibles with an acid mixture of 2 cm<sup>3</sup> of concentrated HClO<sub>4</sub> and 10 cm<sup>3</sup> of concentrated HF and heated on a hot

plate until dryness. After the addition of the same volume of these acids, the mixture was heated again until dry. Finally, 1 cm<sup>3</sup> conc. HClO<sub>4</sub> was then added and the mixture heated until evaporation with the appearance of white fumes. The final residue was dissolved with 12 N HCl, filtered (Whatman No. 540) and diluted to 50 cm<sup>3</sup>. The resulting solutions were stored for analysis of Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by atomic emission spectroscopy in an ICP (Inductively Coupled Plasma) Analyzer ARL 3580 B.

#### Sequential Extraction

The sequential extraction method described by Tessier *et al.* (24) was followed to determine the partitioning of the studied metals in five operationally defined fractions:

- *Exchangeable* (MgCl<sub>2</sub>)
- *Acid-extractable (bound to carbonates)* (NaOAc)
- *Reducible (bound to Fe/Mn oxides)* (NH<sub>2</sub>OH·HCl)
- *Oxidizable (bound to organic matter and/or sulphides)*: this fraction was extracted using three reagents: HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and NH<sub>4</sub>OAc
- *Residual*: the final extracted residue was digested with an acid mixture of HClO<sub>4</sub> and HF (1:5) following the same procedure used for the total analysis described above. After evaporation until dryness, the samples were dissolved in 12 N HCl and diluted to 25 cm<sup>3</sup>.

A modification of the Tessier method was introduced in the fourth phase to avoid any vigorous reaction and subsequent loss of material. The addition of H<sub>2</sub>O<sub>2</sub> was made at cold temperature and the samples were left overnight.

All the material used for the experiments was carefully washed in 5% Decon bath overnight followed by 0.6 M HNO<sub>3</sub> bath overnight. Ultra-high pure water was used to rinse the material. All reagents used in this study were analytical grade.

Metal analyses were performed in a laboratory which is accredited by UKAS (United Kingdom Accreditation Service) for the analyses undertaken in this study. Process blanks, included with each batch of samples, were below the detection limits (Table 2). As no certified reference material exists for the Tessier sequential extraction scheme, it was practice to repeat samples from a previous analysis to ensure that consistent results were obtained. An additional check was to compare the sum of the concentration in the individual fractions with the results of the total digestion to confirm that good recovery had been obtained.

Table 2. Limits of detection (defined as three times the standard deviation of blank reagent) in the different matrices. Concentrations are  $\text{mg}\cdot\text{l}^{-1}$  in the solution analysed.

	$\text{MgCl}_2$	$\text{NaOAc}$	$\text{NH}_2\text{OH}\cdot\text{HCl}$	$\text{NH}_4\text{OAc}$	$\text{HCl}$
Cd	0.0209	0.0125	0.0600	0.0190	0.0171
Co	0.0237	0.0110	0.0200	0.0028	0.0169
Cr	0.0353	0.0063	0.0200	0.0155	0.0072
Cu	0.0500	0.0062	0.0024	0.0028	0.0032
Fe	0.0149	0.0078	0.0129	0.0116	0.0139
Mn	0.0031	0.0011	0.0028	0.0023	0.0062
Ni	0.0562	0.0134	0.0334	0.0423	0.0229
Pb	0.2180	0.0630	0.3609	0.2378	0.1339
Zn	0.0108	0.0032	0.0122	0.0071	0.0046

## Results and Discussion

### Morphology and Mineral Composition

The  $> 63 \mu\text{m}$  fraction was used for SEM studies which demonstrate the variety of components and shapes found in the sand fraction of the sediments. In general, the sediments are dominated by coarse grains of quartz and feldspars with occasional dolomite and mica-like particles. Biogenic material is sometimes present in the form of organic matter, plant debris and siliceous material covering and aggregating the clays, particularly in the deepest sample (K-1) compared with that taken near the mouth of the Vistula river (K-6). SEM micrographs also illustrate a particle size gradation with the coarser sediments near the coast and the fine particles and organic matter increasing in a seaward direction. (Figs. 2a-2d)

Optical microscopy shows a dominance of quartz with potassium feldspars, plagioclase feldspars, rock fragments and occasional opaque minerals. Chlorite occurs rarely. Fragments of diatomites and plant debris are common, especially in sample K-1 sited furthest from the coast. Some minerals show a cloudy surface suggestive of weathering.

The XRD patterns of the bulk samples are essentially similar being characterized by mixtures of quartz, feldspars, layer silicate minerals and carbonate minerals. Quartz yields the most intense reflection in all samples and both types of feldspar may also be abundant. The  $3.19 \text{ \AA}$  peak for plagioclase feldspar is more intense than that at  $3.24 \text{ \AA}$  for K-feldspar in all samples except K-6, near the Vistula mouth. Traces of pyrite are observed most noticeably in sample K-1. Muscovitic mica occurs in all samples, as does kaolinite, which yields a distinct, broad peak at  $7 \text{ \AA}$ . The same mineralogy is found at the bottom of the cores although the diffraction peaks are better re-

solved, suggesting an admixture of amorphous material or organic matter in surface samples (Fig. 3).

The XRD patterns of  $< 2 \mu\text{m}$  fractions show that all samples are similar with mica and kaolin being dominant (Fig. 3). The kaolin mineral yields a rather broad 001 reflection at about  $7.20 \text{ \AA}$  and would seem to represent a poorly ordered kaolinite. In all samples, except in K-4, the presence of expandable clays are evident, especially in the bottom section of the core and in sample K-6. A broad diffraction maximum occurs at about  $14.30 \text{ \AA}$ , which moves to  $17.37 \text{ \AA}$  after ethylene solvation. In some cases, however, a broad  $14 \text{ \AA}$  peak may remain which, combined with a peak at  $4.71 \text{ \AA}$ , suggests the presence of chlorite. Heating at  $300^\circ\text{C}$  invariably increases the intensity of the  $10 \text{ \AA}$  peak relative to that at  $7 \text{ \AA}$  but again in some instances a weak  $14 \text{ \AA}$  peak remains.

### C and N Analyses

The results of C and N analyses and their distribution are shown in Fig. 4. As expected, the values of C and N are higher in the uppermost 5 cm of the core samples and diminish with depth. Concentrations of C vary between 1.54% in the bottom sediment and 6.22% at the surface and N values are between 0.12 and 0.76% in the bottom and surface layers, respectively. In general, the content of organic C and N gradually increases seawards with the distance from the coast. These changes range from 1.61 to 6.22% C in the surface layers and 1.54 to 3.52% C in the bottom layers in the seaward direction. Similarly, the content of N varies from 0.20 to 0.76% at the surface and from 0.17 to 0.43% in the bottom section of the cores. It is observed that sample K-1, composed of fine grained material, shows the highest content of C and N and that the lowest concentrations occur in K-6, a coarse marginal



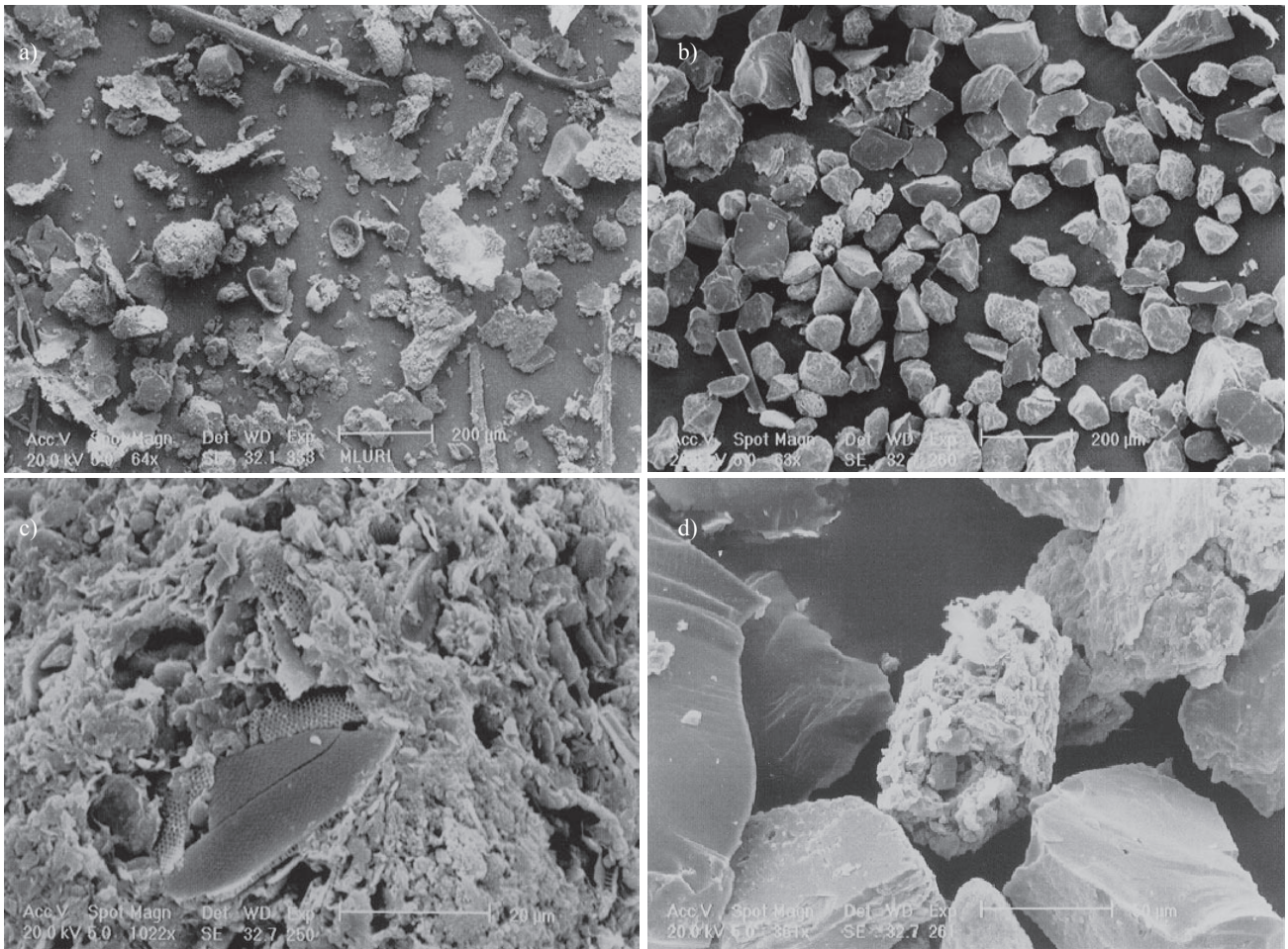


Fig. 2. SEM micrographs: (a) surface sample K-1: organic matter plant debris type; (b) surface sample K-6: mineral grains and absence of organic matter; (c) bottom sample K-5: siliceous material aggregating micaceous minerals; (d) surface sample K-6: quartz and feldspars mineral grains.

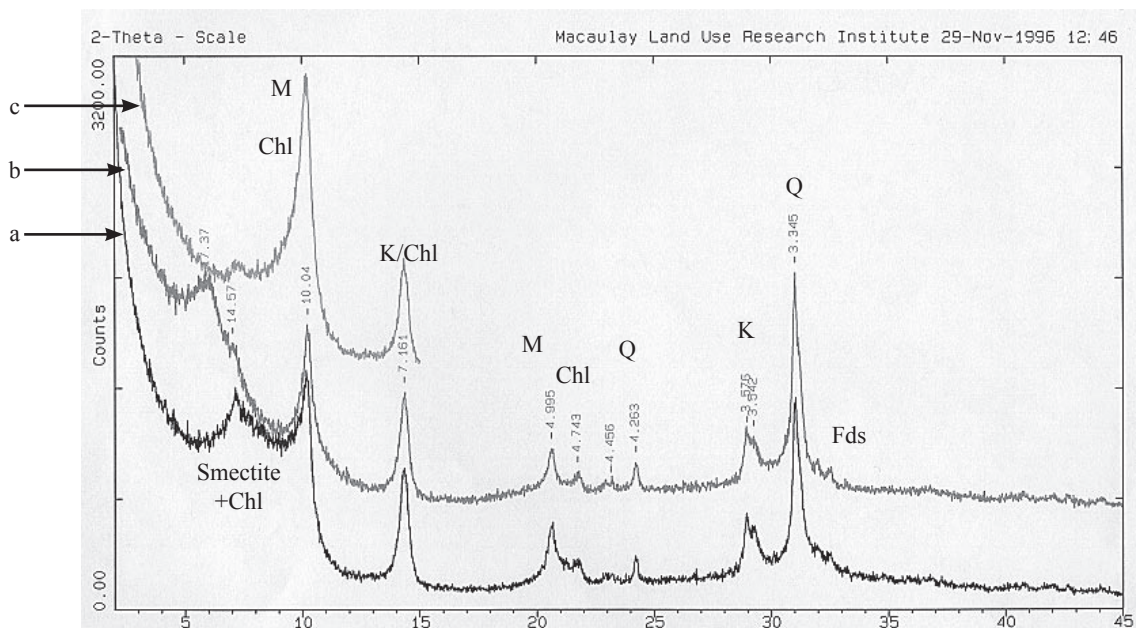


Fig. 3. XRD patterns of the clay fraction of K-6 sample: a) oriented prepare; b) after ethylene glycol solvation; c) after heating at 300°C/2 h.

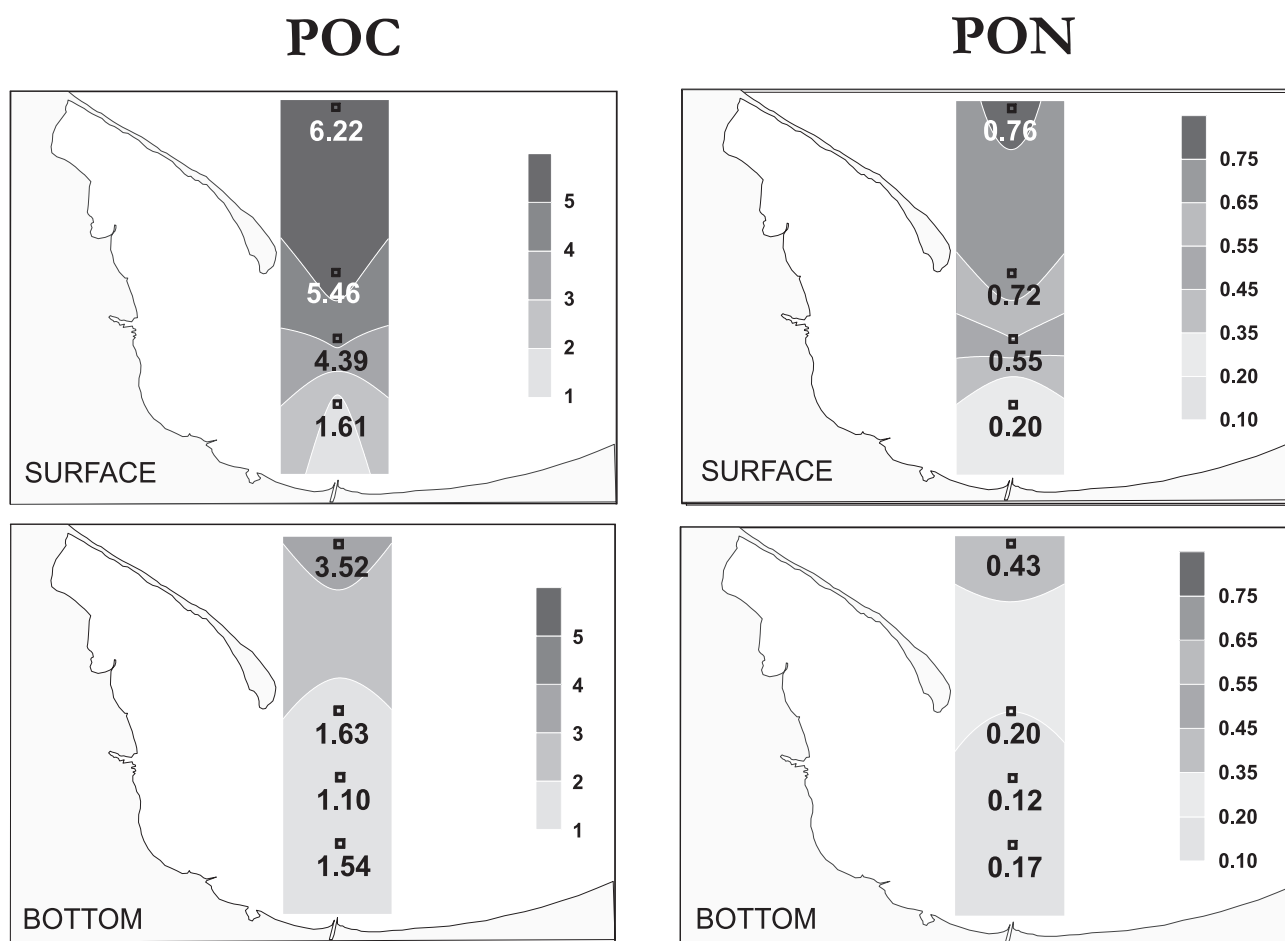


Fig. 4. Distribution of POC and PON at the surface and bottom sections of the core samples: values on maps correspond to samples K-6, K-5, K-4 and K-1 from the coast towards the sea.

sample. This suggests that organic matter is transported in the form of fine particulates, either freely or associated with clays.

#### Total Metal Content

Total metal contents of the sediments are summarized in terms of mean and ranges in Table 3. Concentrations of nearly all metals, in both surface and sub-surface samples, increase from the Vistula mouth towards the sea. Samples from K-1 are the most enriched, samples from K6 least enriched, whilst samples from K5 and K4 often show similar concentrations. Some metals, namely Cr, Cu, Zn and possibly Pb show higher concentrations in the surface sections of the core samples than in the bottom sections, although Fe, Mn and Co differ in this respect. The surface sediments of the Gdańsk Basin are moderately enriched in Cu, Pb, Zn and Cr with concentrations varying from 22 to 71  $\mu\text{g g}^{-1}$  for Cu, 38 to 83  $\mu\text{g g}^{-1}$  for Pb, 102 to 210  $\mu\text{g g}^{-1}$  for Zn and 65 to 107  $\mu\text{g g}^{-1}$  for Cr. These contents decrease down core, with values ranging between 21 to 44  $\mu\text{g g}^{-1}$  for Cu, 21 to 60  $\mu\text{g g}^{-1}$  for Pb, 56 to 108  $\mu\text{g g}^{-1}$  for Zn and 67 to 97  $\mu\text{g g}^{-1}$  for Cr.

#### Metal Partitioning

Fig. 5 shows the contribution of each heavy metal in the extracted fractions expressed as a percentage of the sum of fractions. There was generally good agreement between the totals calculated from the sum of the fractions with totals determined separately.

Lead is distributed principally between the oxidizable and reducible fractions and on average about 20% of Pb is found in the residual phase and ~80% in the more mobile phases, this being made up of 34% in the organic/sulphide fraction, 36% in the Fe/Mn oxide/hydroxide fraction and 10% in the carbonate and exchangeable cation fraction. With increasing distance from the Vistula River mouth the oxidizable fraction increases and the reducible and residual phases decrease. This trend is particularly evident in the surface layers but can also be seen in the samples from the base of the cores.

Zinc is mainly associated with Fe/Mn oxide/hydroxide compounds, organic matter/sulphides and carbonate phases. Residual Zn ranges from ~15% in the surface layers to ~40% in the basal samples. There is a considerable contribution from the carbonate phase varying from ~25% at the surface to ~5% in the subsurface. In general

Table 3. Total metal concentrations, mean, range, standard deviation (SD,  $\mu\text{g g}^{-1}$  dry wt., Fe in %) and relative standard deviation (RSD,%) in the sediments of the Gdańsk Basin.

Sample cod	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Surface								
K6	9	65	22	1.79	188	20	38	102
K5	11	93	35	2.45	255	28	44	128
K4	11	92	46	2.41	247	33	65	140
K1	19	107	71	4.23	419	46	83	210
Mean	13	89	53	2.96	277	31	58	145
Range	9-19	65-107	22-71	1.79-5.19	188-419	20-46	38-83	102-210
SD	4.2	17	21	1.52	99	11	21	46
RSD	33	19	39	51.25	35	35	35	32
Basal								
K6	13	85	21	2.17	225	27	21	56
K5	12	73	24	2.44	293	24	42	75
K4	11	67	31	2.44	273	25	60	102
K1	21	97	44	4.23	434	48	51	108
Mean	14	80	30	2.82	306	31	44	85
Range	11-21	67-97	21-44	2.17-4.22	225-434	24-48	21-60	56-108
SD	5	13	10	0.95	90	12	17	24
RSD	32	16	34	33.59	29	38	38	28

and in contrast to Pb, lower percentages of Zn are associated with the oxidizable fraction in the surface layers than in the bottom layers of the sediment cores. There is a corresponding increase of the reducible and easily reducible phases in surface sediments compared with bottom samples. According to these observations, the increase in the total content of Zn observed in the surface layer of the sediment is mainly associated with an increase in the extractable carbonate fraction.

Manganese shows a marked decrease in the percentage contribution of the residual fraction towards the sea, decreasing from ~50% near the river mouth to ~20% in the deepest sample (K-1). Correspondingly, there is an increase in the other fractions, especially the oxidizable and exchangeable fractions, rising from ~45% of Mn in labile fractions at the river mouth to ~80% in the most seaward sample. Thus, the deepest sample, K-1, shows the lowest contribution of Mn to residual phase (~20%) but the highest to the oxidizable (50%) and exchangeable (14%) fractions. Reducible and easily reducible (carbonates) fractions represent 11 and 5% of the total Mn, respectively, in the K-1 sample. Comparing the bottom sediments with those at the surface, the former have slightly higher contents of Mn in their oxidizable fractions, whereas the latter are more strongly associated with the potentially more mobile phases associated with the first three extracts.

Copper seems to be homogeneously distributed in the samples and no differences were observed corresponding to sediment depth and distance from the river mouth. More than 70% Cu is found associated with organic compounds or/and sulphides, 28% with the residual matrix of the sediment and only about 2% with Fe/Mn oxides/hydroxides, carbonates and exchangeable phases.

Nickel is usually associated with organic/sulphide material, Fe/Mn oxides/hydroxides and carbonates and on average more than 60% of this metal is found in these forms. About 40% of Ni occurs in the residual form, decreasing slightly in surface layers and with distance from the Vistula mouth. The more labile fractions show a corresponding increase. Reducible and carbonate phases increase in surface layers while the oxidizable diminishes.

Iron contributes principally to the residual, oxidizable and reducible fractions with mean percentage values up to 53, 25 and 18%, respectively. The partitioning of Fe is usually homogeneous between surface and bottom sediments, although there is a significant increase in reducible iron in the surface layers. There is a seawards increment in the oxidizable and reducible fractions but a decrease in the residual fraction.

Cobalt is mainly related to the residual fraction, varying from 45% in the deepest sample (K-1 surface) to 78% in sample K-6 (surface). It is also significant that the per-



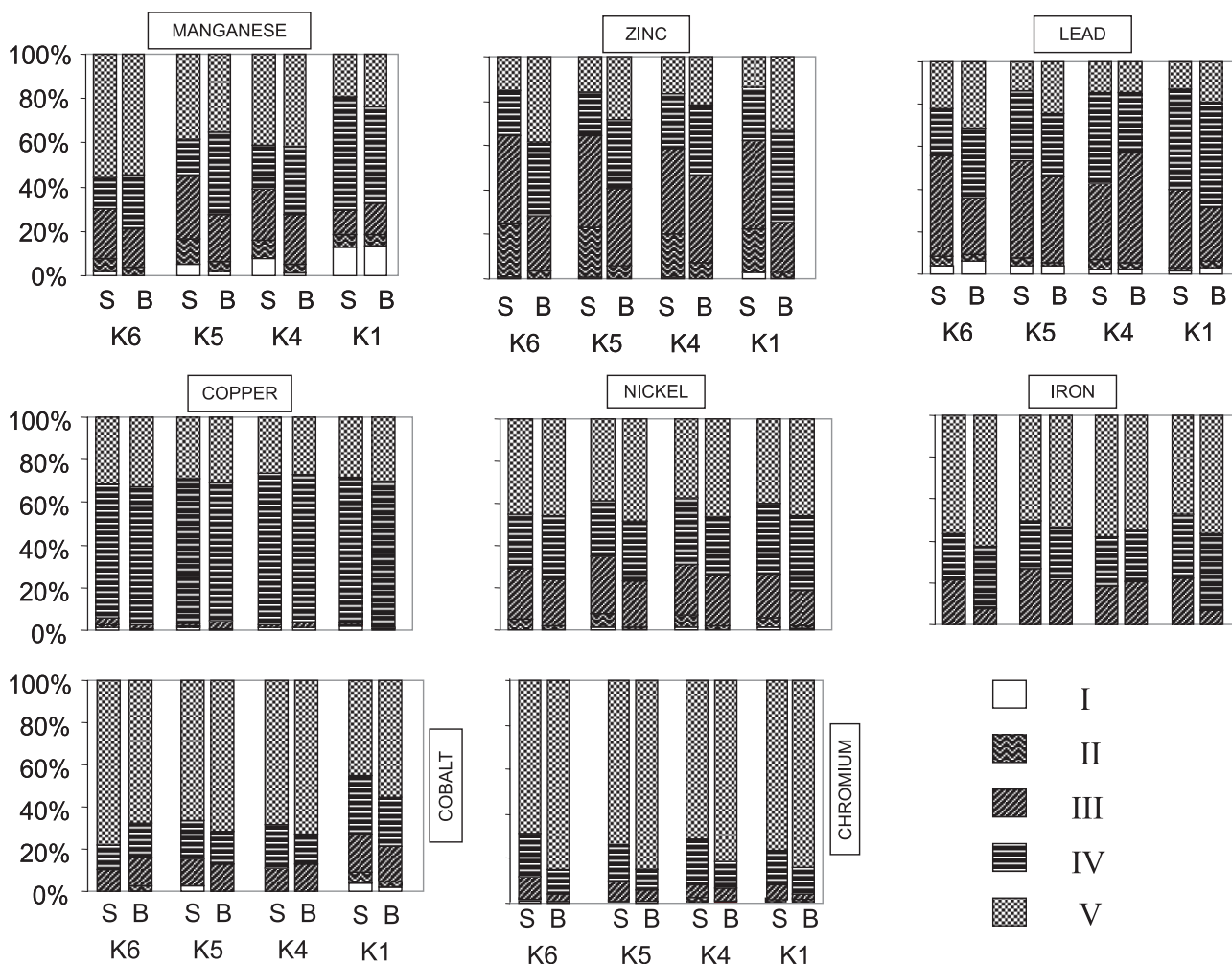


Fig. 5. Diagrams illustrating the heavy metals distribution in surface (S) and bottom (B) sediment samples, upon each stage of chemical extraction: I-exchangeable, II-acid extractable, III-reducible, IV-oxidizable, V-residual.

centage of Co associated with oxidizable and reducible phases increases with distance from the river mouth, with values up to 20 and 13%, respectively in sample K-1. The potential mobility of Co seems to increase with increasing distance from the Vistula River mouth and in the surface layers of the sediments, although the amounts are relatively small.

Chromium shows a distribution of forms in the sediments similar to that of Fe and Co. This distribution is rather homogeneous between the different core samples, with the highest contribution being in the residual phases (up to 70%). About 16% Co is associated with the oxidizable fraction and ~14% with the most labile fractions. There is a slight increase in the labile fractions in the surface layers of the cores compared with the bottom layers.

#### Origin and Availability of Heavy Metals

According to Belzunce-Segarra et al. [25], the sediments of the Gdańsk Basin are of riverine origin related to the settling of the load carried by the Vistula River, with

the coarsest sediments being concentrated near the river mouth and the finest transported and deposited further from the coast. The SEM observations presented here are consistent with this general picture and clearly illustrate the detrital nature of the mineral grains.

In general, the mineralogy of the sediments is quite homogeneous, with quartz, feldspars, micas and kaolin minerals being identified as the main components in both surface and basal samples. However, close inspection of the XRD traces reveals that there are some stratigraphic differences in mineralogy between surface and basal samples. Thus, expandable clays are more evident in the basal samples whereas the clay minerals in the surface samples, judging from the intensity and resolution of the various diffraction peaks, seem to be more poorly ordered. Probably, the latter observation can be explained by the higher content of organic matter found in the surface samples compared with the samples taken from the base of the sediment cores.

With regard to the organic matter (organic carbon and nitrogen content) status of the sediments, the mean organic C content of 4.42% for the surface sediments of the Gdańsk



Basin is rather lower than the mean value of 5.7% for the western Baltic, as well as for other semi-enclosed coastal areas characterized by high levels of contamination and close to large urban nuclei (6.7% in Arkona Basin) [26] or by high productivity and low levels of pollution (5-5.5% in West Spanish Coast) [27]. In fact, productivity of the Gdańsk Basin is very low at the beginning of summer when the sampling was made. The relatively high amounts of organic matter found in the surface sediments are, therefore, not attributed to biological activity but to an association with fine-grained terrigenous material (clay minerals, biogenic detritus) as is illustrated in the SEM micrographs (Figs. 2a, 2b). Bolalek and Frankowski [22] have related the organic matter content found in the Baltic sediments (17.8% median value) to anthropogenic sources. Thus, the gradual increase in C and N concentrations with distance from the mouth of the Vistula corresponds to the transport and deposition of these fine particles. In addition, high sedimentation rates are favoured by the water temperature (cold) as well as the absence of water stratification, as it was observed during the cruise, and in these circumstances the accumulation of organic matter is favoured over degradation. This results in high levels of organic matter compared with data for surface sediments in the Gulf of Gdańsk [28]. However, the decrease in organic C and N downwards to the sediment core suggests that degradation and mineralization processes do occur, which is contrary to the observations for the sediments of the Western Gulf of Gdańsk [29]. But it is in agreement with the reducing conditions found in the same area of study by Bolalek and Frankowski [22]. Under such conditions the oxidation of organic matter occurs by reduction of iron oxides and sulphates. The evolution of organic matter is also corroborated by SEM and XRD results (Figs. 2a, 2b and 3).

The total contents of heavy metals in the sediments of the Gdańsk Basin determined in this study are somewhat lower than those found previously for the same area (Table 4 [25, 30, 2]), although these differences can result from variations in sediment texture, sources and other natural spatial differences, as well as improvements in the overall environmental quality of the Baltic Sea in recent years [17-20]. Nevertheless, some heavy metals, namely Cr, Cu and Ni, are in somewhat higher concentrations in the area of study higher than those reported for other polluted areas such as Cork Harbour in Ireland and Cardiff Bay in the UK (Table 4, references 31 and 32), and several authors have reported on considerable heavy metal inputs to the Basin as a result of industrial activities [9, 2]. Anthropogenic enrichment of the metals ( $AE > 1$ ) is also supported by their higher concentrations in the surface layers of the sediment, except Fe, Mn and Co, compared with the layers at the base of the cores. In the latter the metal concentrations approximate background levels for shales and clays [33], sub-recent Rhine sediments [34] and lacustrine sediments [35] (Table 4). Assuming that the metal concentrations found in the bottom sediments represent background levels, this means that the surface sediments were enriched in metals such as Zn (1.71), Cu (1.45) and Pb (1.32) in contrast to Cr (1.10), Ni (1.02), Mn (0.90), Co (0.91) and Fe (0.97). The AE values for Zn, Cu and Pb are similar to those reported by Szefer et al. [36] in Puck Bay, where recent layers of sediments are moderately enriched in Zn, Cu and Pb with respect to the background segments that correspond to "pre-anthropogenic era". Presumably, these metals are anthropogenic in origin while Cr, Co, Ni, Mn and Fe can be classified as terrigenous in origin.

Table 4. Average concentration of heavy metals ( $\mu\text{g g}^{-1}$  dry wt., Fe in %) in sediments in the study area and in other aquatic areas.

Region	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References (nr reference in the text)
Gdańsk Basin	48-86	79-212	32-161	3.1-5.0	297-535	35-164	70-155	121-1168	Belzunce-Segarra et al. (1987): [25]
Gdańsk Basin			67				256	264	Skwarzec et al. (1988): [30]
Gdańsk Deep			58				168	275	Skwarzec et al. (1988): [30]
Gdańsk Basin			27-79				11-80	80-429	Glasby and Szefer (1998): [2]
Gdańsk Basin	9-19	65-107	22-71	1.8-5.2	188-419	20-46	38-83	102-210	Present paper
Cork Harbour		12	17			14	36	95	Berrow (1991): [31]
Cardiff Bay		44	61	3.2	668	26	138	234	Hitchcock and Thomas (1992): [32]
Shales and clays	19	83	45	4.7	600	68	20	95	Turekian and Wedepohl (1961): [33]
Rhine sediments	16	47	51	3.2	960	46	30	115	Förstner and Müller (1974): [34]
Lacustrine sediments	16	62	45	4.3	760	66	34	118	Förstner (1978): [35]

However, the bioavailability of heavy metals depends upon their chemical form rather than upon total concentration [21, 37]. Sequential extraction analysis shows that the metals fall into two groups. In the first are Fe, Cr and Co which occur largely in the residual fraction and therefore in a non-available form. This is typical of what would be expected of metals that originate by lithogenesis, and this is confirmed by the fact that this group of metals show no surface enrichment (except for Cr) when compared with concentrations in samples from the base of the cores. The second group of metals consists of Cu, Mn, Ni, Pb and Zn, largely released during the sequential extraction procedure prior to the residual fraction stage. Copper, Zn and Pb are enriched in the surface sediments, presumably being to some extent of anthropogenic origin. Heavy metals of anthropogenic origin are typically more labile [38, 39]. Oxidizable and reducible phases represent the predominant forms of these labile metals, although a significant portion of Mn is released by the first extract (exchangeable cations) and of Zn by the second extract (carbonates). Most Cu is associated with the oxidizable (organic/sulphide) fraction, which is normally the case in contaminated soils and sediments.

Comparing the different forms of the metals at different core depths, it is found that there is an increase in the proportion of Mn, Ni and Zn in the first three extracts at the surface in comparison to the bottom. Lead shows a different behaviour with a greater proportion in the oxidizable (organic/sulphide) form at the surface than at depth. The proportion of both Pb and Mn in this form increases seawards, implying that these metals may be carried by organic matter.

Compared to data obtained several years ago [25], it is concluded that the total content of metals in the Gdańsk Basin have diminished; however, the potential mobility has increased for Ni, Fe, Co and Cr.

### Conclusions

The mineralogical results reveal the riverine origin of the sediments of the Gdańsk Basin, with the coarser mineral grains deposited near the river mouth and the finest terrigenous particles transported further from the coast. This fine material is the best carrier for the external inputs of organic matter, which is then transported and accumulated in surface sediments far from the coast. On the other side, the natural conditions of the Baltic sea favour the degradation and mineralization processes of organic matter resulting in its decline in the bottom sediments.

The heavy metal content of the Gdańsk Basin sediments sampled along a transect taken from the mouth of the Vistula River in a seawards direction shows considerable enrichment in both surface and basal samples. However, the total content of Cr, Cu, and Zn, and possibly Pb, tend to be higher in the surface samples, an enrichment that may be attributed to a recent anthropogenic contribu-

tion. With the exception of Cr, these metals occur in a non-residual (more labile) form. In contrast, Fe and Co show little enrichment at the surface and occur mainly in the unavailable (residual) form, although significant proportions of these metals still occur in more labile forms. Manganese shows no systematic enrichment in the surface sediments but the proportion of non-residual forms increases in the seaward direction. It is probable that Fe, Mn and Co are largely lithogenic in origin and that the seawards increased concentrations of heavy metals may be attributed to their association with fine particulate matter.

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