Baltica

www.geologin.lt/baltica

Baltica 15 (2002) 49-62

Normalisation as a tool for environmental impact studies: the Gulf of Gdansk as a case study

Jan Ebbing, Joanna Zachowicz, Szymon Uścinowicz, Cees Laban

Geochemical maps of the Gulf of Gdansk, based on data obtained using partial extraction techniques on the <200 µm fraction of sea bed sediments, show patterns of metal distribution that are closely related to sediment grain size, with low concentrations in the sandy coastal zone and high concentrations in the muddy central part of the Gulf. This reflects the commonly observed relationship between clay mineral content and trace element concentration. Normalisation to Al, as a proxy for clay mineral content, lead to the recognition of five geochemical anomalies with suspected anthropogenic origin. Analysis of new samples from the anomalous sites, using total concentration techniques on the <2 mm (whole sediment) fraction, together with data on contaminant sources, hydrodynamics, salinity profiles and water stratification (obtained from local authorities) verified and helped explain four of the anomalies: Cd, Cr and P near the mouth of the Vistula River; Cd, P, Ni, Pb and Zn east of the Hel Peninsula; P, Pb and Zn south-east of the Hel Peninsula; and Cd, Cr, P, Pb and Zn in Puck bay. Thus geochemical data not fully 'fit-for-purpose' can be used in environmental studies to establish potential anomalies that can be verified by follow-up sampling. This reduces research and monitoring costs by minimising the number of samples that need to be processed by the more expensive 'total' concentration methods. Using data on deposition rates and sedimentological characteristics at the anomalous sites, local background concentrations and enrichment factors (EF) were estimated for the sea bed sediments of three different sedimentation areas in the Gulf. After correction for variations in grain size, each sedimentation area was found to have different EFs.

☐ Inventory study, environmental study, normalisation, heavy metals, Aluminium, background values, enrichment factor, sedimentology, Baltic Sea, Gulf of Gdansk.

☐ Jan Ebbing [j.ebbing@nitg.tno.nl], Cees Laban [c.laban@nitg.tno.nl], The Netherlands Institute of Applied Geoscience, Departments of Groundwater and Geo-Marine and Coast, P.O.Box 80015, 3508 TA Utrecht, The Netherlands; Joanna Zachowicz [jzachowicz@pgi.gda.pl], Szymon Uúcinowicz [suscinowicz@pgi.gda.pl], Polish Geological Institute, Branch of Marine Geology, Koscierska 5 st., 80-328 Gdansk, Poland.

☐ Received 24 September 2002; accepted 3 December 2002.

INTRODUCTION

Domestic and industrial developments in Poland have, over many years, resulted in major pollution of large parts of the Gulf of Gdansk. The Vistula River is one of the main sources of this pollution (Fig.1). A joint geological and geochemical sea bed monitoring programme was carried out in the gulf, by the Polish Geological Institute (PGI) and the Geological Survey of the Netherlands (TNO-NITG), in order to gain an insight into the historical build-up of sea bed sedimentation and contamination. The programme was planned with the aim of identifying and describing pollution 'hot spots', as well as establishing a suitable data base for modelling purposes. In this way, it was hoped to create a suitable framework for identifying the requirements for remediation and abatement of this pollution.

In 1992 the PGI began to work on the "Geochemical Atlas of Poland" (scale 1:500,000), based on experience gained during the production of the Geochemical Atlas of Warsaw (Lis 1991) and of the Geochemical Atlas of Warsaw and Environs (Lis 1992). At the same time, the Marine Geology Branch of the PGI began compiling the "Geochemical Atlas of the Southern Baltic" (scale 1:500,000) dealing with the seabed surface, which covered an area of 30,532 km^2 of the

Polish Exclusive Economic Zone (Szczepańska, Uścinowicz 1994). For this purpose about one hundred sites within the Gulf were sampled. The < 200µm fraction of the samples was analysed for Al, As, Cd, Cr, Cu, Hg, Mg, P, S, V, Zn, Pb, Ni, Fe and Mn, a limited amount of the samples was also analysed for Li and Co. The total organic carbon (TOC) content and the amount of the <63 µm fraction in the sediment were also established.

Since the PGI dataset comprises the most reliable existing data on the chemical composition of sediments at the seabed surface in the Gulf of Gdansk, and also covers the area with a sufficiently fine grid, it was considered to provide the most useful dataset for a first environmental inventory of the study area. However, only the < 200 µm fraction was analysed after a partial extraction, which raises problems concerning the grain size effect and reproducibility (as explained later).

The aim of this study is to demonstrate that a dataset not ideally suited for the purpose, a very common problem, can be used for a first environmental inventory when treated in a correct way. In this specific case normalisation of part (P, Cd, Cr, Cu, Ni, Pb, and Zn) of the PGI data relative to Al was used as a possible tool to establish "anthropogenically" induced geochemical anomalies. In order to check the validity of the methodology, new cores were taken in both 'anomalous' and 'background' areas. In combination with existing knowledge on pollution sources, hydrodynamics, salinity profiles, water stratification and sedimentation rates, geochemical data from new cores were used to provide accurate information on local background values and enrichment factors for anomalous elements.

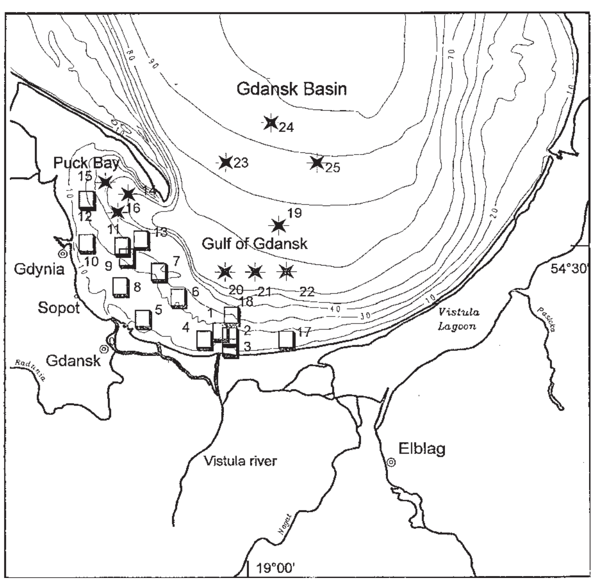

Fig. 1. The study area (the Gulf of Gdansk) at the northeast coast of Poland, the verification locations are indicated with asterisk (dominantly clayey) and boxes (dominantly sandy). The location numbers correspond to the core numbers (e.g. 1 stands for 01). Note the Vistula River as a major source for pollution and the semi-enclosed Puck Bay.

GEOGRAPHY AND GEOLOGICAL SETTING

The Gulf of Gdansk is a southern embayment of the Baltic Sea, located largely on the north coast of Poland, but with its eastern margin fringing the Russian coast. The Vistula, a major European river that drains a very large area of Poland, flows into the Gulf. More extensive information on the geography of the Gulf can be found in Glasby & Szefer (1998).

Domestic and industrial developments in Poland have, over many years, caused major pollution problems and this pollution extends into a large area of the Gulf of Gdansk (e.g. in Puck Bay, protected from the Baltic by the Hel Peninsula).

Geologically, the Gulf of Gdansk includes the southern part of the Gdansk Basin (Fig. 1). The oldest Holocene deposits in the Gdansk basin are grey-brown and light grey clays of the Yoldia Sea and Ancylus Lake (the early phases in the development of the Baltic Sea). These sediments were deposited during Preboreal and Boreal times. These are overlain by olive-grey, sometimes dark-grey or black muds of the Litorina and Postlitorina seas, deposited during Atlantic, Subboreal and Subatlantic times. The average thickness of the Yoldia Sea and Ancylus Lake sediments is ca. 2-3 m, and that of the overlying Litorina and Postlitorina seas deposits ca. 4-6 m (Kramarska et al. 1995).

In the near-shore shallow water zone of the Gulf of Gdansk the Holocene sediments were deposited in two different sedimentary environments namely: (a) continental, before the Atlantic transgression and (b) marine, during and after the Atlantic transgression. Above of the Pleistocene, marine sandy sediments accumulated during the Middle and Upper Holocene in the western part of the Gulf, whilst Lower Holocene deltaic and lagoonal continental deposits were deposited in the southern and eastern part (Uścinowicz et al. 1988).

RECENT SEDIMENTATION PROCESSES AND MARINE SEDIMENTS

An important feature of Baltic waters is their thermohaline stratification. The upper water layer is characterised by seasonal changes in temperature and by low salinity (in the Gdansk Basin ca. 7 per mille.). The lower water layer is characterised by a stable temperature of 3-4°C and higher salinity (in the Gdansk Basin ca. 11-12 per mille). A halocline is present in the Gdansk Basin at a depth of about 60-70m (Görlich et al. 1989). The stratification in the water column leads to a variation in oxygen content. Above the halocline, the saturation varies from 100% at the sea surface to 70% at the halocline, but below the halocline the saturation is less than 20%. In the Gdansk Basin, anaerobic conditions periodically occur at or near the sea bed. Temperature and salinity distribution determine the water density. In the period from May to November there is a distinct density rise (pycnocline), which is related to the summer thermocline. By contrast the deepwater pycnocline is related to the halocline and shows no seasonal variability, but depends solely on the advection of inflows from North Sea. Sandy deposits cover the sea floor down to the water depth (30-50 m) at which the pycnocline is present. Currents and waves, occurring in the water layer above the pycnocline, make permanent deposition of silty and clayey fractions in such areas impossible and normally the content of the <63 µm fraction is less than 0.5%. At depths under the direct influence of storm waves and where currents are active, sandy sediments are often redeposited.

In the zone where the pycnocline makes contact with the sea bottom, dominantly muddy sands and sandy muds occur while muddy deposits are present below the pycnocline. The sedimentation rate of mud depends on the amount of suspended matter and on the dynamic conditions in the near bottom layer. In the Gulf of Gdansk the sedimentation rate is in general between 1 and 2 mm per year (Pempkowiak 1991; Walkusz et al. 1992; Szczepańska & Uścinowicz 1994). Rates are higher in the central part of the gulf, but decrease towards the margins and also on local bottom elevations in the basin, where the thickness of the deposited mud may be only a few centimetres (indicating a sedimentation rate well below 1 mm per year, probably due to erosion). A lithological map of the seabed sediments has been prepared by Uścinowicz and Emelyanov (1993).

METHODOLOGY

Sampling by PGI and PGI/TNO-NITG

Initial sampling was carried out by PGI in observation squares of 100 km^2 arranged in a regular grid. Muds and sandy muds were sampled using a Niemistö gravity corer, from which 80 cm long (virtually undisturbed) cores were obtained, and a Kajak type corer with which up to 26 cm long cores could be taken. Sand and muddy sand deposits were sampled with a Van Veen grab sampler, with which disturbed samples of the first 5 cm below the sea bed can be taken. Subsamples were taken on site, stored in airtight plastic boxes and frozen at -20°C.

Additional sampling was carried out by PGI and TNO-NITG after selection of new sample locations based on the evaluation of the regular (PGI) data set. 25 locations (Fig. 1) were chosen with varying sedimentological composition and also including sites at potential "hot spots" e.g. dumping and anchorage sites, harbour entrances, and prodelta deposits of the Vistula River. At each location a sample of very high quality (completely undisturbed) was taken with a boxcorer. The average recovery of the cores was 0.30 m, the maximum being 0.44 m and the minimum being 0.15 m. Special tubes enabled subsamples to be taken for various purposes: notably description of the sea bed and organic and inorganic chemical analysis. The samples for geochemical analysis were stored in a transportable refrigerator and taken to the TNO-NITG laboratories within a week of collection.

Analytical methods

The initial (PGI) survey samples were divided into two parts, one of which was prepared for granulometric analysis and the other for chemical analysis. After removing organic matter with hydrogen peroxide, grain size analysis was carried out using an Analysette 22 laser particle sizer (muds, sandy muds and muddy sands) and using sieves with 1f unit spacing (sands). The second separate portion of the sand was put through a 200 µm nylon sieve, yielding approximately 2 g sample for chemical analysis.

Chemical analysis was carried out after drying at room temperature and powdering. Subsequently the samples were leached for 30 minutes in HNO_3/H_2O 1+1 in an MDS-81D microwave. Determination of the elements was carried out using the ICP method with an emission spectrometer PV8060 and plasma excitation using the flame atomic absorption method with spectrometers PU-9100X and SP9-800. The validity of the analytic methods was checked by analysing international reference samples and also by interlaboratory comparison. The following relevant detection limits were established:

- for Al 0.001% and for P 0.005%.
- trace elements in ppm: Cd (0.5), Cr (1), Cu (1), Ni (1), Pb (5), and Zn (1).

Total organic carbon content (TOC) was determined by a modified coulometric method, using a Coulomat 702 apparatus (precision 1.6%).

Whole sediment samples from the additional (PGI and TNO-NITG) sampling were dried overnight at 105°C. Pressed powder Tablets were automatically prepared of 10 g samples with 7 wax pills (1.2 g, containing EMU-Pulver 120 FD and wax) as binder. The sample material was ground together with the wax pills for 60 seconds in a Herzog swing mill with a tungsten-carbide vessel. Al, P,Cr, Cu, Ni, Pb, and Zn were analysed on pressed powder Tablets by X-ray fluorescence methods (XRF) using an ARL 8410 spectrometer. Pressed powder Tablets of international rock standards were used for calibration. The following detection limits were established:

- for Al 0.1%, and for P 0.01%.
- trace elements in ppm: Cr (5), Cu (10), Ni (1), Pb (5), and Zn (5).

For analysis of the extractable (»total) Cd, the following method was used: 2.5 g of a dry sample was soaked in 20 ml of 10% HCl on a boiling water bath for 3 hours. After dilution to 50 ml with distilled water, the tube was centrifuged at 20,000 rmp for 3 minutes, leaving a clear solution above the residue. After dilution (50 times) with 0.05 N HCl the Cd content was determined using a Scintrex AAZ-2 Atomic Absorption Spectrometer with Zeeman background correction. International standards were used for quality control. The lower detection limit of the analysis is 0.02 ppm Cd.

Mapping of the data

Contour maps of element distributions were prepared using the Surfer (version 4), software package from Golden Software Inc. To avoid the contour package correlating points lying on opposite sides, north or south, of the Hel Peninsula some false points were introduced. The points lie on the Hel Peninsula itself and have hypothetical low element content, analogous to almost pure quartz sand.

Al-normalisation

Grain size is an important factor controlling the distribution of both natural and anthropogenic components in sediments (Kersten et al. 1992; Loring & Rantala 1992). A general recommendation is that only sediments with more than 20% of <63 μm sediment fines should be considered for monitoring trends because only these sediments are sufficiently muddy to carry an appreciable contaminant load and are sufficiently homogeneous to minimise within-sample variability (JMG, 1992). Although this study is mainly a baseline and monitoring study, there is no overriding requirement to adopt this criterion because regionally relevant background concentrations can be determined from sandy cores. Nevertheless, many trace elements, especially metals, are associated with particle surfaces and differences in metal concentrations at sites, or even within a sediment core at the same site, can result from differences in the particle size distribution of the sediments.

To compensate for this problem, sediment data can be normalised by dividing the raw concentration data by the weight of the fine-grained fraction. This assumes that no contaminant metals are associated with sand-sized particles and that the only effect of sand in a sample is to dilute the level of contamination. However, granulometric normalisation alone is inadequate to explain all the natural trace metal variability in the sediments, since sedimentary components often can be mineralogically (and thus geochemically) different. In order to improve the interpretation of variability in composition, it is also necessary to distinguish the sedimentary components with which the metals are associated throughout the grain size spectrum. Since it is extremely difficult to effectively separate and analyse individual sediment components (Kersten & Förstner 1989), consideration of such associations must rely on indirect evidence from element co-relationships.

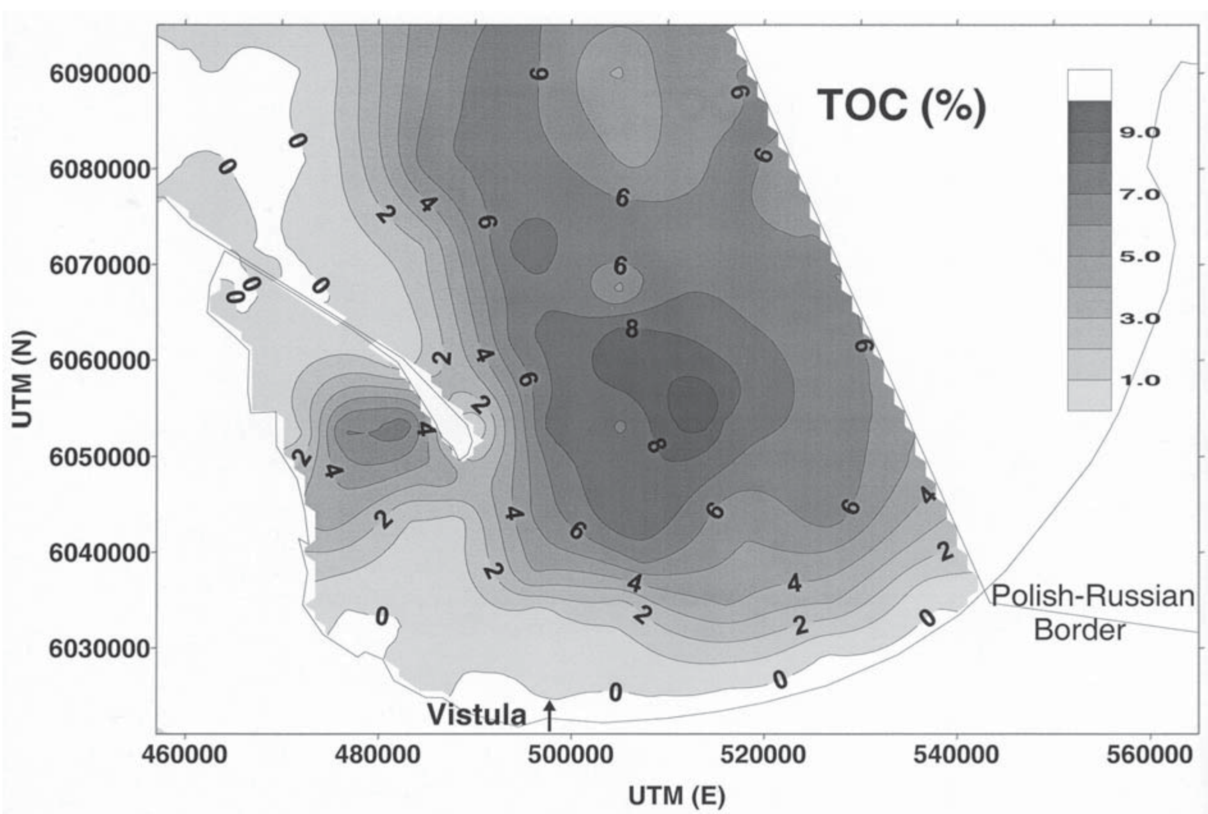

Fig. 2. Contour map of the TOC content (%) in sea bed surface sediments. The map is a reproduction of a part of a map presented by Szczepańska and Uścinowicz (1994).

Various geochemical approaches used for the normalisation of trace metal data have been reviewed by Loring and Rantala (1992) and have been incorporated in the JMG guidelines (JMG 1992). Since contaminants are mainly associated with the clay minerals, iron and manganese oxy-hydroxides and organic matter (in decreasing order), additional information can be obtained by measuring the concentrations of the representative elements of these components in the samples. An inert element such as aluminium, a major constituent of clay minerals, may be chosen as an indicator of the clay fraction. Aluminium is regarded as a conservative major element, which, unlike iron and organic carbon, is not significantly affected by early diagenetic processes, or strong redox effects such as are frequently observed in estuarine and coastal sediments (e.g. Kersten & Förstner 1991). However, the relationship between the concentration of trace metals and Al in anoxic strata may be weak due to entrainment of trace metals in secondary sulphide phases (Baeyens et al. 1991). Normalisation with the total organic carbon (TOC) concentration is not appropriate for this approach because TOC also acts as a contaminant itself. TOC concentrations in sediments are usually log normally distributed and skewed towards low concentrations, in a similar matter to metal contaminants (Fig. 2).

Aluminium (Al) normalisation (e.g. Windom et al. 1989; Os van 1993) is based on the fact that there is a natural relationship between trace metals and Al that exists in the absence of any human influences (since Al is a major component of clays its concentration is always assumed to be a natural concentration). The method is similar to normalisation based on the fine-grained fraction because Al concentrations follow grain size distribution (Windom et al. 1989). This is demonstrated for the data used in this study, by correlation coefficients between Al and the fraction <63 µm of 0.811 for the PGI (old) samples and 0.742 for the PGI/TNO-NITG additional (new) samples. In areas where erosional products of glaciers are a major source of sediment, as is possibly the case in the Gulf of Gdansk, Li may be more suitable for normalisation (Loring & Rantala 1992). However in this study, insufficient Li data were available to test this hypothesis.

THE EFFECT OF AL-NORMALISATION ON THE ORIGINAL PGI DATA SET

The selection of elements presented in this paper is based mainly on environmental considerations. Phosphorous (P) is chosen as an important parameter in eutrophication processes, cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) as members of the heavy metal group and Al and TOC as a link to grain size distribution and or contaminants. The original PGI data set can be found in the report of Laban et al. (1994), where the concentration of the various elements is presented in the form of Tables. It should be borne in mind that this PGI data was obtained after partial digestion of the <200 µm fraction of the sediment.

The geochemical map for aluminium, given by Szczepańska and Uścinowicz (1994) and reproduced in this study (Fig. 3a), is based on the data listed in the report of Laban et al. (1994). The comparison between the seabed sediment map (Uścinowicz & Emelyanov 1993) and this map shows a good correlation with the lowest Al values (0.2%) occurring near the coast in association with the coarser sediments and the highest values (around 3.0%) being found in the clayey area in the central part of the gulf. Puck Bay also has a clayey area with a higher Al content. Despite the partial digestion method used to leach the samples, it is apparent that a good correlation exists between the grain size distribution and the Al content (r=0.811), although grain size distributions were available for only 80% of the samples. The concentration of Al measured in this dataset varies between 0.07 and 3.47%.

A direct comparison between the grain size distribution, or in this case Al (Fig. 3a) and the TOC (Fig. 2) content might be considered unlikely because of the generally lognormal distribution of TOC in sediments. However, a first glance at the maps suggests a rather good correlation, with generally increasing TOC from the sandy coastal zone (low Al-content) towards the more clayey central part (high Al-content) of the gulf. High TOC values are observed in the clay of Puck Bay as well as in the central and northern part of the gulf (Fig. 2). Closer inspection reveals that the central part has values up to more than 9% while the northern part, which is more clayey (Uścinowicz & Emelyanov 1993), displays values of only up to 7%. Comparison of the Al content with the TOC content reveals another striking feature. In the central part of the gulf, there is an area with relatively low Al values of 1.6%, but TOC values of 8% are present. This poor correlation leads to a low r-value of 0.64 between TOC and Al, possibly indicating that the organic carbon (organic matter) settles from the water column at an earlier stage than other fine particles. The reason may be that once outside the Hel Peninsula the water becomes more open marine and hence more saline, resulting in flocculation of organic matter together with fluvial mud. Salomons and Eysink (1981) describe the process[1] and,

[1] Salomons & Förstner (1980) described other processes which could be scavengers of contaminants such as: adsorptive bonding on fine-grained material, precipitation of the elements in discrete compounds, coprecipitation of the element with hydrous Fe- and Mn-oxides and -carbonates, and incorporation in crystalline material. A model that stresses the importance of the authigenic formation of iron-minerals was developed by Görlich et al. (1989) for the Gulf of Gdansk. They point for instance to the importance of the immediate precipitation of amorphous $Fe(OH)_3$ across the salinity barrier and the formation of lepidocrocite (g-FeOOH) when freshwater is introduced into a marine environment.

mention a salinity of 5 and 15 per mille as an important boundary in the river Scheldt estuary. This may have serious environmental implications since contaminants are often strongly bounded to organic matter.

The TOC content in the surface sediments of the Gulf of Gdansk varies between 0.03 and 10.24%.

In comparing the P content with the grain size distribution, the correlation at first sight is less evident. The correlation of P with Al is also lower (r=0.52). This is expected since P is usually irregularly distributed across the different grain sizes of the sediment. However, in general there is still some relationship with the P content increasing from sands to muds, although in some localities in the Gulf of Gdansk there is a steep increase in P content (Szczepańska & Uścinowicz 1994).

The concentration of P varies from 0.03 to 0.40%.

If Cd, Cr, Cu, Ni, Pb, and Zn are compared with the sediment map (Uścinowicz & Emelyanov 1993) the correlation is evident with increasing contents from sands to muds and the same holds true for the comparison of these elements with Al. The following r values have been calculated between these elements and Al: Cd=0.91, Cr=0.85, Cu=0.91, Ni=0.90, Pb=0.82, and Zn=0.88. As an example of the distribution patterns of these elements in the sea bed sediments, the geochemical map for Pb is shown (Fig. 3b). The similarity of the distribution patterns of Pb and Al is striking (compare with Fig. 3a), especially considering that Pb has the lowest correlation (r=0.82) with Al of all the heavy metals mentioned. The maps for the other elements have a similar appearance (Szczepańska & Uścinowicz 1994).

It is clear that the geochemical maps (except for TOC, because of its often strong association with contaminants) do not give any indication of the existence of locations with anthropogenic influenced sediments. They all show, as expected, more or less a good correlation with the grain size

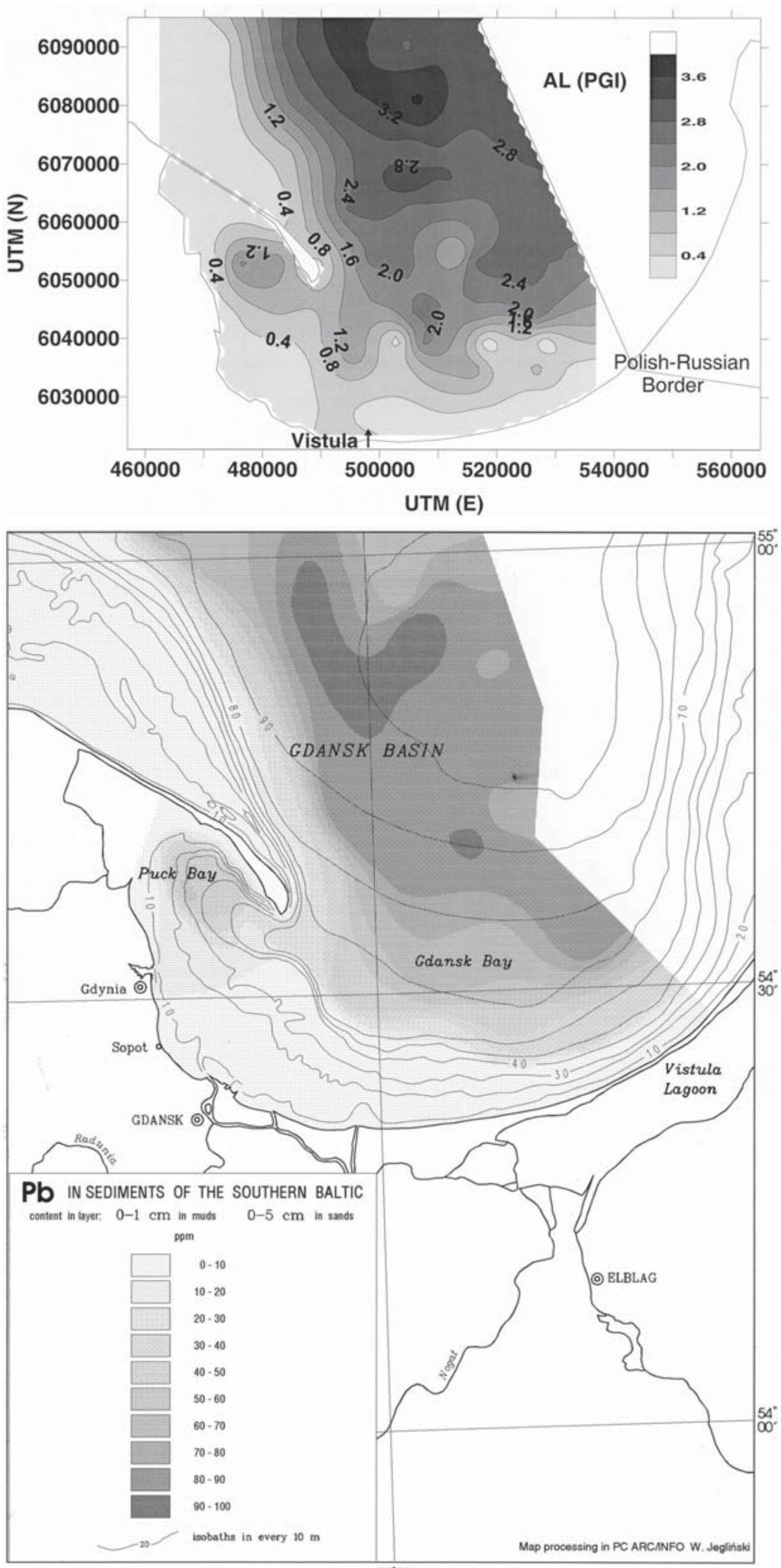

Fig. 3a-b. Contour maps of the Pb and Al concentration (ppm) in the sea bed surface sediments of the study area, whereas the map for Al has been drawn with the aid of the Surfer software and the map for Pb is the original one after Szczepańska and Uścinowicz (1994). Notably the increase in Pb and Al content is going from the coastal zone (sands) to the centre of the Bay (clays), where as Gdansk Bay stands for the Gulf of Gdansk.

distribution and Al content of the sediments. By normalising the data set with Al, as explained earlier, it is to be expected that additional information can be extracted from this data set.

The validity of the above statement is demonstrated with three examples (for P, Cr and Pb) from the original PGI data set.

The P/Al ratios (where P has been multiplied by 100 for presentation purposes) lie between 5 and 15 in most of the study area, largely without a significant pattern (Fig. 4a). Only in the coastal zone, where the sediment is sandy, are higher ratios found. This effect is enhanced since the absolute amount of P and Al is low in this type of sediments. Thus having implications for the error in measurements, as some samples will have contents of P and/or Al near or even below the detection limit. One striking anomaly lies at the outlet of the Vistula River (A in Fig. 4a), which appears to be shifted to the east (compare with Fig. 1). In the coastal area between Gdansk and Gdynia and in the coastal area in the north-west, higher P/Al ratios are present (B in Fig. 4a).

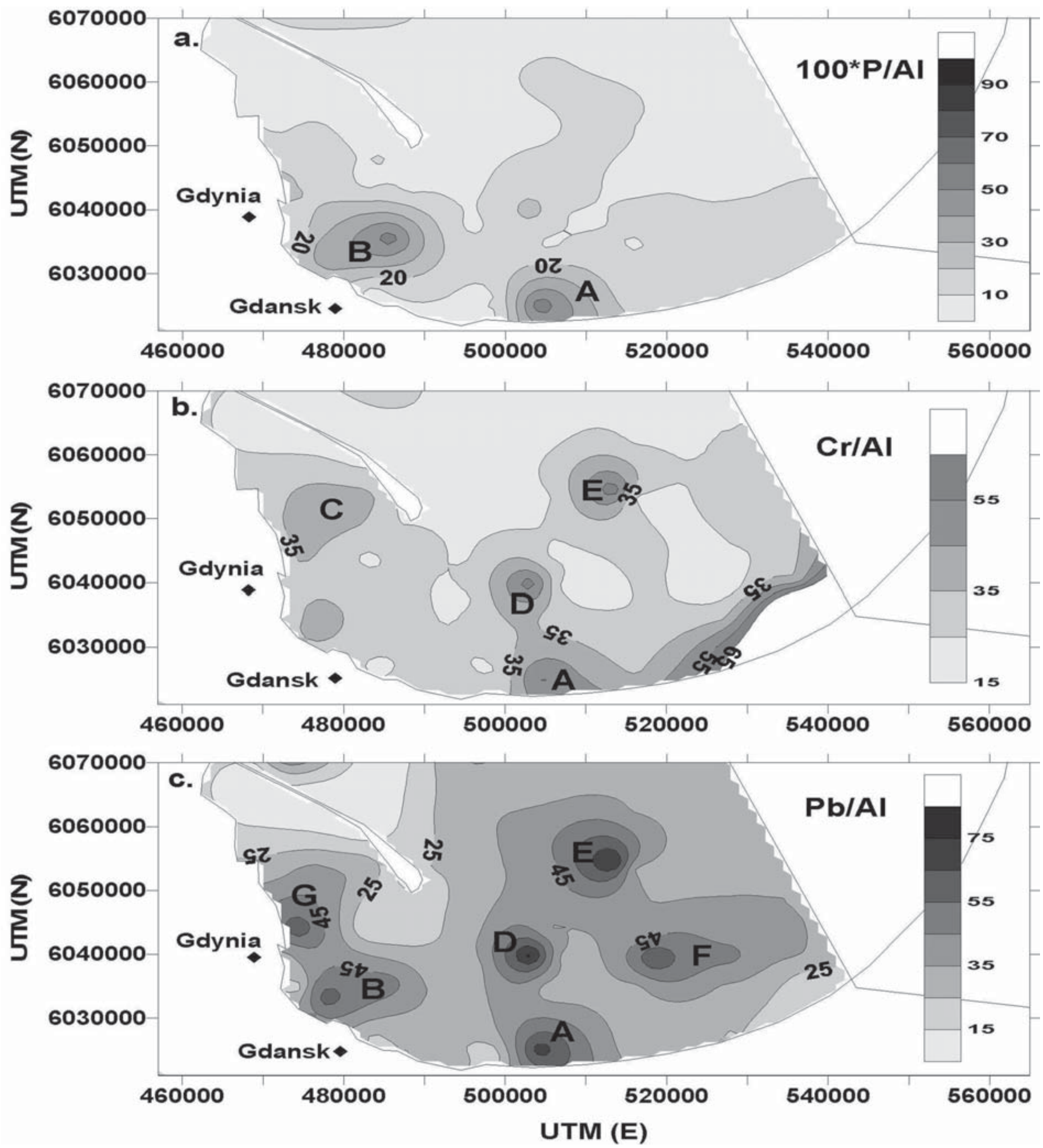

Fig. 4a-c. Contour maps of the P, Cr and Pb content normalised relatively to Al in the sea bed surface sediments, five to seven anomalies are more or less pronounced visible in the Gulf. The anomaly in the extreme northwest is probably partly induced by measurements lying close to the detection limit.

The general trend in the Cr/Al distribution shows higher ratios in the more sandy areas (Fig. 4b). An exception to this is the area in front of and to the west of the mouth of the Vistula River, where values seem to equate more closely with values found further offshore in the more clayey part of the gulf. There is no obvious explanation for this pattern, although as in the case of P the expression of the river seems to be shifted towards the east (A in Fig. 4b, compare with Fig. 4a). The values for Cr lie well above the detection limit (1 ppm) and in this respect the pattern for Cr is probably reliable. While Puck Bay displays a weak anomaly (C in Fig. 4b), stronger anomalies can be seen in the central part of the gulf, notably one south-east of the head of the Hel Peninsula (D in Fig. 4b) and one to the east of the Hel Peninsula (E in Fig. 4b). The first site is probably related to the relatively low Al values in that area (Fig. 3A) while the second site seems to correlate closely with an anomaly mentioned at the same position on the TOC map (Fig. 2). This latter observation suggests a strong relation between organic carbon and Cr.

A strong relationship between Pb and grain size distribution is not very apparent in the Pb/Al map (Fig. 4c), nor is the Pb/Al increase in the coastal zone distinct contrary to evidence from other elements. Some increase in Pb/Al ratios can be noted near the mouth of the Vistula River (with an eastward shift, A in Fig. 4c) and is visible in the coastal area between Gdynia and Gdansk (B in Fig. 4c). The sandy coastal zone in general has, however, low absolute Pb values. These are near the detection limit thus placing confidence in the anomalies doubtful. The two anomalies in the central part of the gulf (D and E in Fig. 4c) are more reliable and correlate well with the two anomalies for Cr in the same area. Anomaly D is related to a low Al content as was the case for Cr, whilst anomaly E correlates well with a TOC anomaly discussed earlier (see discussion of the TOC map). Two additional anomalies (F and G in Fig. 4c) become evident on the Pb/Al ratio map. They probably are caused by a very low Al content (see Fig. 3a) and Pb values near to the detection limit, and are thus unreliable. They were not taken into further consideration during this study.

The Al-ratio distribution patterns for P, Cr, and Pb point to at least five anomalies (Fig. 4), as do the results for some other elements (Cd, Cu, Ni, Zn) (Laban et al. 1994):

A. Near the mouth of the River Vistula (with its expression shifted to the east) for all elements mentioned, in accordance with Szefer et al. (1995).

B. The coastal zone between Gdynia and Gdansk, for Cd, Pb, (Cr) and P.

C. In the muddy part of Puck Bay a weak anomaly is present for Cr, Cu, and Ni.

D. Southeast of the head of the Hel Peninsula for Cr, Pb, and Zn.

E. East of the head of the Hel Peninsula for Cr, (Cu), Ni, Pb, and Zn coinciding with a strong anomaly for TOC.

VERIFICATION AND CAUSES OF THE ANOMALIES

Verification

To verify the above-mentioned anomalies and to establish whether they are of anthropogenic origin, new cores (verification samples) were taken (see Fig. 1). The results are given in Table 1, recalculated as ratios relative to Al to correct for grain size differences. From the new cores a seabed surface sample (Upper) and reference sample (Lower) were taken. Sediments deposited prior to the industrial revolution are considered as reference samples. With an average mud sedimentation rate of 1-2 mm per year in the Gulf (Pempkowiak 1991; Walkusz et al. 1992; Szczepańska & Uścinowicz 1994) mud samples taken at a depth of around 20 cm or deeper have an age between 100 and 200 years and fulfil this criterion, considering the anthropogenic influence on the sediments in the basin as being limited before 1900. For the sandy coastal sediments the sedimentation rate is less clear, although in this stable setting the sedimentation rate will be low, except for the mouth of the Vistula River, where a delta progressively builds out during recent times. An additional problem in the near shore area is the constant reworking by waves. Nevertheless, reference samples were taken at depths of between 18 and 36 cm, with the knowledge that the samples taken near the mouth of the Vistula River do not represent a pre-industrial reference level and that other sandy L-samples must be treated with care.

The verification samples for Cr indicate that for surface sediments (U-samples), anomalies occur near the mouth of the Vistula River and in Puck Bay. Sample 07L (nearshore) gives a very high reference value, probably due to reworking by anchors (Zachowicz et al., pers. comm.). In general the verification samples display a pattern (Fig. 5) of higher values for the upper samples (sea bed) than for the lower samples (reference). The difference between the upper and lower sample is, however, normally small. An additional observation can be made for the anomalous areas found in the centre of the gulf (see Cr/Al map Fig. 4b). The verification samples (20-25) for Cr (see Fig. 5), do not support identification of these areas as anomalous. This is not entirely unexpected since Cr is considered a detrital element in the study area, as Ni and Cu are (Glasby & Szefer 1998). Thus, differences in Cr/Al ratios probably reflect differences in lithology. And since the differences between upper and lower samples are relatively small it can be concluded that the sedimentation environment has been stable over the period of deposition. Sample 07, already identified as being disturbed, is an obvious exception.

The verification results for P do not agree completely with the P/Al ratio results given above (compare Fig. 5 with Fig. 4a). The higher ratios in the coastal area are less explicit, although still visible. More important is the relatively high ratio for the upper samples in Puck Bay compared with the contour map, given by Laban et al. (1994). This seems to indicate anthropogenic influences. From Table 1 and Fig. 5, it becomes clear that all the samples, excepting sample 07, have significantly higher ratios in the upper samples than in the lower samples. The obvious reason for this is an anthropogenic contamination; most probably by waste water effluent emanating from Gdynia, Gdansk and Wladyslawowo harbour and the Vistula River.

The verification results for Pb confirm anomalies (potential hot spots) in the two areas in the centre of the gulf (samples 20-25 in Fig. 5). The upper samples from these verification sites show especially high Pb/Al ratios. Another ano-maly is present in Puck Bay (samples 14-16 in Fig. 5). The area near the mouth of the Vistula River is unusual in that the lower sample values are much higher than the sea bed surface values (samples 01-04 and 17 in Fig. 5). The significance of this is not clear, unless the signal corresponds to a lessening of the amount of Pb pollution, perhaps since the introduction of unleaded fuel. If this is true it could prove to be a po-werful aid in the calculation of sedimentation rates in that specific sandy area. The sam-ples taken in this study are not suited for this purpose, since the sampled cores are to short and the subsam-pling interval is not adequate. The other sites suggest anthropogenic enrichment at the top.

The verification data presented in Table 1 and Fig. 5 confirm all five anomalies identified on the Al-ratio maps (Figs. 4a-c and Laban et al. 1994), although the anomalous elements found with the new samples do not always completely correspond with those found with the aid of the Al-ratio maps.

A. In the sandy sediments near the mouth of the Vistula River an anomaly is evident for Cd, Ni and Cr, but is less distinct for P and absent for Cu (values for Cu lie below the detection limit of the analytical method used). The results for Pb and Zn indicate an anomaly only in the L samples. If the origin of Pb and Zn is considered to be largely anthropogenic, the relative low values in the U-samples point to an environmental improvement and a relatively high sedimentation rate, this however requires further research.

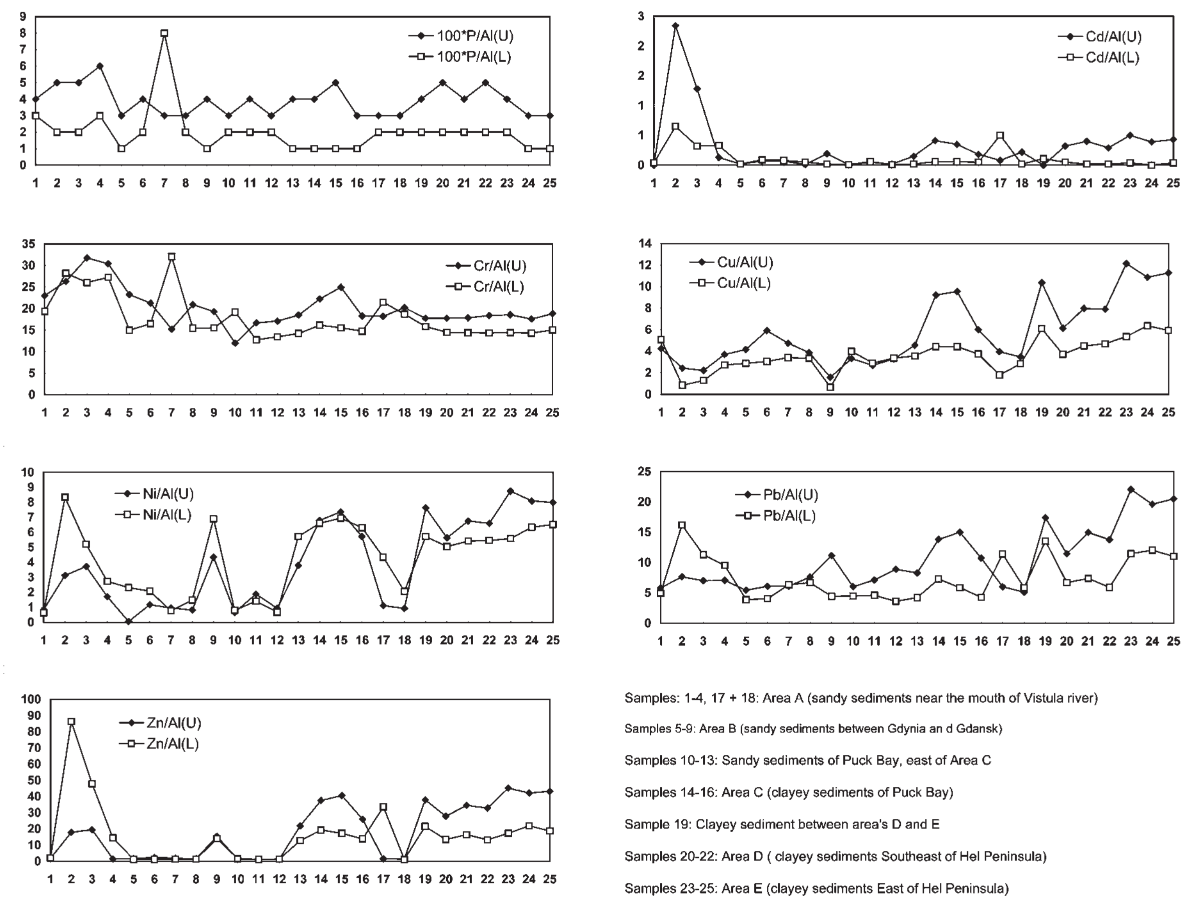

Fig. 5. Al ratio plots for P, Cd, Cr, Cu, Ni, Pb and Zn for all 25 verification samples taken. In the plots the Upper (sea bed) samples are plotted as closed boxes while the Lower (reference/background) samples are plotted as open boxes. The lower samples were taken at depths varying from 16 to 36 cm below sea bed (see also Table 1).

Table 1. The exact positions of the verification locations and the analytical results for Al and the calculated Al-ratios for P, Cd, Cr, Cu, Ni, Pb and Zn. All concentrations of the studied major and minor elements were obtained after analyses with XRF. The U-sample is taken at the sea bed surface and the L-sample is considered the natural background sample, the depth of sampling is indicated in cm.

SAMPLE	UTM(X)	UTM(Y)	Depth (cm)	Al (%)	P/Al	Cd/Al	Cr/Al	Cu/Al	Ni/Al	Pb/Al	Zn/Al
01U	496373,8	6026508	0-2	1,17	0,04	0,01	23,00	4,26	0,43	5,82	2,13
01L			18-20	0,98	0,03	0,04	19,34	5,09	1,02	4,95	2,54
02U	498137,9	6025803	0-4	2,05	0,05	2,34	26,29	2,43	3,12	7,67	17,88
02L			34-36	5,92	0,02	0,65	28,22	0,84	8,34	16,19	86,40
03U	499967,5	6024337	0-2	2,27	0,05	1,28	31,77	2,21	3,72	7,00	19,54
03L			38-40	3,92	0,02	0,32	26,05	1,28	5,20	11,32	47,77
04U	495127,8	6025378	0-2	1,35	0,05	0,13	30,40	3,71	1,70	7,06	1,85
04L			34-36	1,84	0,02	0,33	27,22	2,72	2,73	9,54	14,48
05U	483769,4	6028186	0-2	1,20	0,03	0,02	23,25	4,15	0,05	5,45	2,08
05L			30-32	1,74	0,01	0,02	14,98	2,88	2,31	3,89	1,44
06U	489722,3	6033677	0-2	0,85	0,04	0,07	21,26	5,91	0,59	6,11	2,95
06L			24-26	1,64	0,02	0,09	16,45	3,05	2,07	4,05	1,52
07U	485519,3	6037453	0-2	1,05	0,03	0,07	15,20	4,75	0,00	6,09	2,38
07L			20-25	1,47	0,08	0,08	32,05	3,41	0,68	6,36	1,70
08U	480941,4	6035040	0-2	1,29	0,03	0,01	20,91	3,87	0,77	7,64	1,94
08L			20-25	1,49	0,02	0,05	15,43	3,35	1,48	6,67	1,68
09U	480559,6	6041756	0-4	3,16	0,04	0,19	19,29	1,58	4,34	11,15	15,37
09L			25-30	7,54	0,01	0,02	15,51	0,66	6,90	4,43	14,04
10U	475139,8	6043006	0-2	1,51	0,03	0,01	11,94	3,32	0,33	6,02	1,66
10L			16-18	1,25	0,02	0,00	19,16	3,99	0,40	4,49	2,00
11U	480336,5	6045040	0-4	1,86	0,04	0,05	16,68	2,69	1,88	7,14	1,35
11L			16-18	1,73	0,02	0,06	12,75	2,90	1,41	4,61	1,45
12U	472558,9	6051404	0-4	1,52	0,03	0,02	17,08	3,28	0,66	8,90	1,64
12L			18-20	1,49	0,02	0,01	13,43	3,36	0,34	3,62	1,68
13U	482146,9	6044866	0-2	3,57	0,04	0,15	18,49	4,55	3,79	8,29	21,85
13L			22-24	6,76	0,01	0,02	14,20	3,57	5,72	4,22	12,81
14U	480630	6053199	0-4	4,95	0,04	0,41	22,21	9,22	6,80	13,83	37,60
14L			22-24	6,50	0,01	0,06	16,15	4,43	6,60	7,29	19,30
15u	476529,3	6055147	0-1	5,33	0,05	0,35	24,96	9,54	7,36	15,01	40,63
15L			22-24	6,90	0,01	0,06	15,52	4,43	6,95	5,86	17,28
16U	478434,5	6048609	0-2	5,42	0,03	0,18	18,28	6,01	5,72	10,74	25,92
16L			22-24	6,45	0,01	0,05	14,73	3,74	6,31	4,29	13,83
17U	510813,9	6026353	0-1	1,26	0,03	0,08	18,20	3,96	0,40	6,01	1,98
17L			24-26	2,80	0,02	0,50	21,46	1,79	4,34	11,41	33,62
18U	500000	6030012	0-2	1,43	0,03	0,22	20,21	3,48	0,00	5,12	1,74
18L			12-14	1,76	0,02	0,02	18,70	2,83	2,06	5,84	1,42
19U	509220,1	6046097	0-2	4,96	0,04	0,00	17,74	10,36	7,63	17,39	38,00
19L			22-24	5,43	0,02	0,11	15,83	6,09	5,72	13,53	21,51
20U	499924,4	6037412	0-2	4,22	0,05	0,32	17,76	6,14	5,63	11,46	27,83
20L			22-24	5,18	0,02	0,05	14,48	3,72	5,05	6,71	13,47
21U	505269,6	6037434	0-4	4,82	0,04	0,40	17,85	7,98	6,75	14,97	34,57
21L			20-22	5,85	0,02	0,02	14,35	4,50	5,41	7,39	16,46
22U	510765,9	6037499	0-2	4,68	0,05	0,29	18,38	7,90	6,60	13,78	32,85
22L			22-24	6,15	0,02	0,02	14,31	4,69	5,46	5,91	13,26
23U	500032,3	6057868	0-4	4,63	0,04	0,50	18,56	12,14	8,74	22,06	45,16
23L			22-24	5,77	0,02	0,04	14,40	5,36	5,58	11,48	17,30
24U	508027,8	6065275	0-2	5,41	0,03	0,39	17,57	10,87	8,09	19,61	42,18
24L			22-24	6,92	0,01	0,00	14,30	6,36	6,34	12,03	21,88
25U	516135,8	6057841	0-4	5,06	0,03	0,43	18,79	11,27	7,99	20,51	43,13
25L			22-24	6,79	0,01	0,04	15,02	5,93	6,52	11,02	18,74

B. The anomaly between Gdynia and Gdansk is confirmed for Pb, Cd and P (for these elements only in sample 09U). This could indicate that the anomaly is spatially rather restricted.

C. Cu and Cr (U samples) and Ni confirm the anomaly in Puck Bay, whilst in contrast to the Al-ratio maps, P, Cd, Pb and Zn in the verification samples also point to an anomaly in Puck Bay, especially for the U-samples.

D. The anomaly southeast of the Hel Peninsula is indicated by Ni and Zn, but not by Cr. For Cu, P, Pb and Cd it is indicated only for the U samples. In general all the elements studied seem to be enriched in the U samples.

E. The anomaly east of the Hel Peninsula is indicated by Ni, Pb, and Zn, but not by Cr. For Cu, P and Cd it is indicated only for the U samples. In general all elements studied seem to be enriched in the U samples.

Causes

♦ In the Vistula mouth/delta (area A) a direct input from the polluted Vistula River probably causes the anomaly for Cd, Pb, Zn, Pb, Ni and Cr, with the resulting signal in the sediments shifted to the east. An explanation for this shift (evident for all elements) may be the wind driven current pattern in the gulf. At and in front of the mouth of the Vistula River the current is directed generally eastwards, with winds dominantly coming from the west (Majewski 1990; Lauer 1992, 1993, 1994). This is also visible on the lithological map (Uścinowicz et al. 1993), where it seems that the delta builds out more strongly to the east. One sample (07), immediately east of the mouth, could play an important role in overstressing this factor. This sample has an extremely low Al content (0.07%), and may cause a particular strong anomaly in a ratio map.

♦ In the area near the harbours of Gydnia/ Gdansk (area B), material dredged from the harbours is being dumped and could probably cause an anomaly (Lewandowski & Szczepańska 1993), although this anomaly, for Pb, Cd and P, is only confirmed by the verification sample 09U.

♦ Puck Bay (area C) can be regarded as a semi-closed system that functions as a deposition centre for fines (+ contaminants) coming into that semi-enclosed area. The relatively high enrichment factors (Szczepańska & Uścinowicz 1994) point to a strong anthropogenic influence. This is confirmed by the high concentrations P, Cd, Pb, (Cr) and Zn in the U-samples only. The opinion given by Glasby and Szefer (1998) who consider Ni, Cu and Cr to be detrital elements is supported by these observations.

♦ East and Southeast of the Hel Peninsula (areas D + E) the anomaly for all elements is probably created by the flocculation of organic matter together with fluvial mud (Salomons & Eysink 1981) and/or the formation of iron-minerals (Görlich et al. 1989), both processes in combination with a contaminant load from the polluted freshwater plume of the Vistula River. It is also possible that the pycnocline works as a trap, since anoxic bottom waters can contain higher concentrations of heavy metals. Laban et al. (1994) noted in the same area a sharp increase in the organic pollutant content of the sea bed sediments. For the elements (Cu, P, Pb and Cd), which are especially anomalous in the U-samples, it seems likely that the enrichment has an anthropogenic source since the sedimentation environment and the sediment source has been fairly constant over the last few hundreds of years (see earlier and later discussion).

THE BACKGROUND LEVELS AND ENRICHMENT FACTORS

Enrichment of the surface sediment layer by heavy metals and other chemical components may result from natural geochemical/lithological properties of the sediment or from anthropogenic influences. Evaluation of the degree of contamination of the sea bed surface layer can be done by comparison to a reference layer, the so-called geochemical background. In order to determine the depth below sea bed of the geochemical background layer many natural factors should be taken into account such as: rate of sedimentation, depth of mixing of sediments caused by bioturbation and near-bottom current action, and rate and range of pore water diffusion. Also it must be borne in mind that natural processes of sediment accumulation may be disturbed by human activity e.g. fishing, shipping, military activities etc.

In accordance with the practice in PGI the subsamples taken during the verification sampling campaign at a depth varying from 20 to 40 cm are assumed to represent background samples (Szczepańska & Uścinowicz 1994). This combined with the knowledge that the sedimentation pattern in the gulf has not changed significantly during deposition of the upper 50 cm of sediment (Witkowski 1994; Pempkowiak 1991; Walkusz et al. 1992) leads to the following conclusion. The verification samples can be used to establish background values and enrichment factors if certain sedimentological constrains are taken into account.

In the central part of the Gdansk Basin, with a sedimentation rate of 1 to 2 mm/year, a 20 cm thick layer of mud has formed during the last 100 to 200 years. Macroscopic observations and X-ray photographs of cores have shown that contemporary bioturbation processes do not as a rule penetrate deeper than ca. 10 cm (Laban et al. 1994). Therefore, muds at 18-20 cm depth below the sediment water interface should have been laid down and deposited before the beginning of the intense industrial development in the Baltic Sea drainage area, and as a result should be free of anthropogenic contamination.

In the nearshore coastal zone the situation is more complicated. The sandy deposits in that area are undergoing constant reworking due to wave activity and the sedimentation rate is probably highly variable. As a result the selection of true geochemical background samples representing the coastal sands is much more difficult.

Taking these problems into account the following three groups of samples are selected as being representative of background values in specific depositional environments in the Gulf of Gdansk:

A. Background values for the sandy sediments belonging to the coastal zone are thought to be best represented by samples taken from cores 08-,10-, 11-,12-, and 18 (Table 1 and Fig. 1), and not by samples from in front of the mouth of the Vistula River. These sandy samples are not representative due to an uncertain deposition rate. Similar problems occur in the area between Gdynia and Gdansk, for core 07.

Table 2. The average contents in the sea bed surface sediments (I) and background values (II) for a selected group of samples, see text. The enrichment factor (E.F.) is calculated after normalisation relative to Al. The coastal sands, Puck Bay clays, and Central Bay clays stand respectively for A, B, and C, as mentioned in the text.

		Content of chemical elements							
Region	Code	Al %	P %	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Pb ppm	Zn ppm
A: Coastal sands	I	1,50	0,05	0,20	26,00	10,00	1,40	10,60	5,00
	II	1,50	0,03	0,20	27,00	10,00	1,50	7,50	5,00
	E.F.	-	1,50	1,00	0,94	1,00	0,90	1,42	1,00
B: Puck Bay clays	I	5,20	0,21	1,60	114,00	43,00	34,60	68,70	181,00
	II	6,60	0,07	0,36	101,00	28,00	45,00	37,50	107,00
	E.F.	-	4,00	6,20	1,43	1,98	0,99	2,32	2,15
C: Central Bay clays	I	4,80	0,19	1,61	87,00	46,00	35,70	83,30	183,00
	II	6,00	0,10	0,23	89,00	32,00	35,00	59,00	111,00
	E.F.	-	2,00	8,50	1,22	2,00	1,28	1,77	2,06

B. The background values for the clay deposits in the semi-enclosed Puck Bay are represented by samples taken from cores 14-, 15-, and 16 (Table 1). These cores have a uniform lithological composition.

C. The background values for the clay deposits in the central part of the Gulf are represented by samples taken from cores 19-, 20-, 21-, 22-, 23-, 24-, and 25 (Table 1). These cores also have a uniform lithological composition.

In Table 2 the average seabed surface and background values for the various inorganic components are given. By dividing the normalised sea bed surface data with the background data (Kersten et al. 1992) the enrichment factors for the various components in the three selected depositional environments are calculated (Table 2).

Not surprisingly, the sea bed surface and background values for the sands differ considerably from the clays. This is largely because the values presented represent the content in the bulk samples (total fraction). Only P and Pb seem to be enriched in the coastal sands whilst Cd, Cu and Zn have concentrations lying below or near to the detection limit (respectively 0.02, 10, and 5 ppm). For the clays in Puck Bay and the central part of the Gulf it is evident that all elements, except perhaps Ni and Cr, are enriched in the sea bed surface layer. This points to a strong anthropogenic influence, for Cu, Pb, Zn, and P in both Puck Bay and the central Gulf, whilst Cd is extremely enriched in Puck Bay (factor 6.20) and the central Gulf (factor 8.50). There are considerable differences in enrichment for P, Cd, and Pb, between Puck Bay and the central part of the Gulf. Indicating that in a coastal environment it is inadvisable to work with one background value and enrichment factor for a specific lithological unit. The sedimentological setting should always be considered. The generally low enrichment factor for both Cr and Ni (around 1) is probably related to their detrital origin (Glasby & Szefer 1998). These authors claim that the same holds true for Cu, but this is not confirmed in the current study which shows an enrichment factor of 2 for Cu in the clayey sediments.

CONCLUSIONS

Normalisation of surface sediment compositional data (obtained after partial extraction of the <200 μm fraction) to Al has been to suppresses the grain size effect and allow geochemical anomalies to be established. In the Gulf five anomalies were revealed.

The five anomalies were evaluated after additional sampling in a verification programme, where the total-element content in whole sediment samples was analysed. This provided proof of the validity of all these anomalies:

(a) Near the mouth of the Vistula River, for Cd, Cr, less distinct for P, Pb and Zn.
(b) Coastal area between Gdynia and Gdansk, for Pb, Cd, and P.
(c) Puck Bay, for P, Cd, Cr, Cu, Ni, Pb, and Zn.
(d) South-east of the head of the Hel Peninsula, for P, Pb, Zn, Ni, Cu, Cd.
(e) East of the Hel Peninsula, for P, Pb, Zn, Ni, Cu, Cd.

The cause of the anomaly near the mouth of the Vistula River lies in the direct input of pollutants from the river itself. The anomaly lies east of the river mouth (possibly because of wind driven currents). Puck Bay works as a closed system for fines and their contaminant load. East and southeast of the Hel Peninsula an increase in salinity seaward, possibly results in the flocculation of organic matter together with fluvial mud and/or in the formation of iron-minerals, all with a contaminants load. The existing pycnocline could work as a trap.

In the Gulf of Gdansk three major depositional environments can be recognised:

- sandy sediments in the coastal zone.
- clays deposited in Puck Bay.
- clays deposited in the central part of the Gulf.

In these three areas enrichment factors (E.F.) can be established, again after normalisation to Al. The coastal sands are enriched in P (E.F.=1.5) and Pb (E.F.=1.42), while the detection limits for Cd, Cu, and Zn are too high for any conclusions regarding these elements to be drawn. The surface clays in Puck Bay and the central part of the Gulf are enriched in all elements, except for Ni and Cr. The level of enrichment differs between Puck Bay (e.g. P=4.0 and Cd=6.2) and the central part of the Gulf (e.g. P=2.0 and Cd=8.5), demonstrating the importance of establishing individual background values for different depositional environments.

Normalisation to Al allows existing datasets that are not ideally suited for environmental purposes to be used for preliminary assessment of an area. Anomalies established in this assessment can be conformed by later additional sampling and their nature established (anthropogenic or natural). The costs of environmental assessments can thus be minimised.

Acknowledgements. The authors thank Drs R.Taraškevičius (Institute of Geology and Geography, Vilnius) and J.Ridgway (BGS) for critically reading the last draft and for giving valuable advice for improvement. Drs G. Glasby and R. Swennen have been so kind to review the very first draft. This work was partly supported by the Ministry of Economic Affairs of The Netherlands through the funding of a PSO-project for the Gulf of Gdansk.

References

Baeyens W., Panutrakul S., Elskens M., Leermakers M., Navez J., Monteny F. 1991: Geochemical processes in muddy and sandy tidal sediments. *Geomarine Letters 11,* 188-193.

Glasby G.P, Szefer P. 1998: Marine pollution in Gdansk Bay, Puck Bay and the Vistula Lagoon, Poland: An overview. The Science of the Total Environment, March.

Görlich K., Görlich E.A., Tomala K., Hrynkiewicz A.Z., Pham Quac Hung. 1989: ^{57}Fe Mössbauer study of a sediment column in the Gdansk Basin, Baltic Sea: palaeoenvironmental application. *Marine Geology 88,* 49-69.

JMG 1992: Guidelines for the sampling and analysis of sediments under the Joint Monitoring Programme. *Report of the Joint Monitoring Group to the Oslo and Paris Commissions.*

Kersten M., Förstner U. 1989: Speciation of trace elements in sediments. *In* G. Batley(ed): *Trace element speciation Analytical Methods and problems*. CRC Press. Boca Raton, 245-317.

Kersten M., Förstner U. 1991: Geochemical characterization of pollutants mobility in cohesive sediments. *Geomarine Letters 11,* 184-197.

Kersten M., Balls P.W., v.Enk, R.J., Green, N., Kramer, K.J.M., Kriews, M., Monteny, F., Zuurdeeg, B., Akkerman, I., d.Vries, A., Moris, A., Ebbing, J., Zwolsman, J.J.G. 1992: Metals. *In* R. Laane (Ed): *Background concentrations of natural compounds.* Tidal Waters Report DGW-92.033.

Kramarska R., Uścinowicz Sz., Zachowicz J. 1995: Quaternary. *In* J.E. Mojski et al. (Ed.): *Geological atlas of the Southern Baltic, 1:500,000,* 22-30. Państw. Inst. Geol. Sopot–Warszawa.

Laban C., Ebbing J., Zachowicz J., Szczepańska T., Uścinowicz S. 1994: Geological and geochemical sea bed monitoring of the Gdansk Gulf area. Project within the framework of the Netherlands Support Program for Eastern Europe (PSO). Report published by the Geological Survey of the Netherlands, Haarlem.

Lauer Z. 1992: Currents. *In* Environmental conditions in the Polish zone of the Southern Baltic Sea during 1991, report 10, 36-52. Marine Branch IMGW, Gdynia (In Polish).

Lauer Z. 1993: Currents *In* Environmental conditions in the Polish zone of the Southern Baltic Sea during 1992, report 10, 41-53. Marine Branch IMGW, Gdynia (In Polish).

Lauer Z. 1994: Currents. *In* Environmental conditions in the Polish zone of the Southern Baltic Sea during 1993, report 10, 34-43. Marine Branch IMGW, Gdynia (In Polish).

Lewandowski A., Szczepańska T. 1993: Sediment Pollution in the Southern Baltic. *Land degradation and rehabilitation 4,* 307-315.

Lis J. 1991: Geochemical Atlas of Warsaw 1:100,000. Panstw. Inst. Geol., Warszawa.

Lis J. 1992: Geochemical Atlas of Warsaw and environs 1:100,000. Panstw. Inst. Geol., Warsaw.

Loring D.H., Rantala R.T.T. 1992: Manual for the geochemical analysis of marine sediments and suspended particulate matter. *Earth-Science Review 32*, 235.

Majewski A. 1990: Chapter 5: Hydrology and Hydrochemistry. *In* The Gulf of Gdansk, 150-153; MGW, Warsaw, Poland.

Os B. van 1993: PhD-thesis: Primary and diagenetic signals in Mediterranean sapropels and North Atlantic turbidites. Royal Faculty of Earth Sciences Utrecht, the Netherlands.

Pempkowiak J. 1991: Enrichment factors of heavy metals in the Southern Baltic surface sediments, dated with ^{210}Pb and ^{137}Cs. *Environmental International 71,* 421-428.

Salomons W., Eysink W.D. 1981: Pathways of mud and particulate trace metals from rivers to the southern North Sea. *Special Publication of the International Association of Sedimentology 5,* 429-250.

Salomons W., Förstner 1980: Trace metal analysis on polluted sediments. II Evaluation of environmental impact. *Environmental Technological Letters 1,* 506-517.

Szefer P., Glasby G.P., Pempkowiak J., Kaliszan R. 1995: Extraction studies of heavy-metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chemical Geology 120,* 111-126.

Szczepańska T., Uścinowicz S. 1994: Geochemical Atlas of the Southern Baltic, 1:500,000. Polish Geological Institute, Warsaw, Poland.

Uścinowicz S., Kramarska R., Przezdziecki P. 1988: The Quaternary of the South-west region of the Polish Baltic. *In* B.Winterhalter (ed.): *The Baltic Sea.* Geological Survey of Finland, Spec. pap. 6, 51-58.

Uścinowicz S., Emelyanov E.M. 1993: Bottom deposits of the Gdansk Bay. *In* C.Laban, J.Ebbing, J.Zachowicz, T.Szczepańska, S.Uścinowicz (eds.): *Geological and Geochemical sea bed monitoring of the Gdansk Gulf area*. Geological Survey of the Netherlands, Haarlem.

Walkusz J., Roman S., Pempkowiak J. 1992: Contamination of the Southern Baltic surface sediments with heavy metals. *Bulletin of Sea-fishery Institute 1(125),* 33-37.

Windom H.L., Schropp S.J., Calder F.D., Ryan J.D., Smith jr R.G., Burney L.C., Lewis F.G., Rawlinson C.H. 1989: Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environmental Science and Technology 23,* 314-320.

Witkowski A. 1994: Recent and fossil diatom flora of the Gulf of Gdansk, southern Baltic Sea. *Bibliotheca Diatomologica 28,* Berlin, Stuttgart.