

# Heavy metals in the Ventspils Harbour: normalization based on a multi-parameter dataset

Bärbel Müller-Karulis · Rita Poikāne · Valdis Segliņš

**Abstract** Heavy metals were investigated in the sediments of the Ventspils Harbour located in north-west Latvia (eastern Baltic Sea). Sediment samples were analysed for major and trace metals by ICP-AES, supplemented by inorganic and organic carbon as well as grain-size distributions. Principal component analysis of the data resulted in two main parameter clusters associated with Ca- and Al-rich material and indicated differing behaviour of Pb, Cu, Zn, N and P. Normalization with respect to Ca and Al by least absolute values regression removed the spatial pattern of sediment metal content in the harbour. High residual concentrations at individual sites were associated with local contaminations, whereas the overall concentration pattern was governed by the transport of riverine fine material. Dilution with coarser, quartz-rich marine sediments led to a pronounced heavy metal concentration drop towards the harbour gates. High mixing was an important feature of sediment dynamics in the Ventspils Harbour, hampering contaminant source identification and sediment monitoring.

**Keywords** Harbour · Heavy metals · Monitoring sediments · Normalization · Sediment mixing

## Introduction

Contaminated sediments in harbour areas do not only pose risks for aquatic life, but because many harbours are located in relatively shallow waterways, the need for regular dredging causes additional problems to manage and safely dispose off large volumes of dredged materials (Engler and others 1991a, 1991b). At the same time, pollution is a common phenomenon in harbours and therefore at least a smaller portion of the dredged material is contaminated and requires further treatment (International Maritime Organization 1995). As many harbours are located in urban, often heavily industrialized areas, local point and non-point sources contribute to the sediment pollution, together with contaminant inputs from boat traffic (United States Environmental Protection Agency 1997). In order to minimise the amount of contaminated material, knowledge about contaminant sources affecting the harbour sediments is essential (International Maritime Organization 1995). While total contaminant input determines the average pollution level in the harbour, sediment transport and possibly also geochemical processes can be expected to influence contaminant distribution in the harbour area itself.

Heavy metals are characteristic pollutants in urban areas (United States Environmental Protection Agency 1997), where also most harbours are located. However, differing sediment heavy metal contents do not necessarily indicate varying degrees of pollution, but reflect also dissimilarities in grain size (Förstner 1987; Kersten and others 1994; Kern and Westrich 1995; Szefer and others 1996; Nikodemus and others 1997) and mineralogical composition of the parent material (Kersten and others 1994; Loring and Asmund 1996; Abraham 1998). Normalization with respect to characteristic elements used as proxies for grain size or differing sediment sources is often used to distinguish anthropogenic pollution effects from natural variability (Schneider and Davey 1995; Summers and others 1996; Zwolsman and others 1996; Balls and others 1997; Donoghue and others 1998). Typical normalization approaches identify one or several reference elements, relative to which trace metal concentrations are interpreted. A variety of regression methods ranging from simple linear regression (for example Summers and others 1996) to multivariate (Donoghue and others 1998) and stepwise multiple models (Schneider and Davey 1995) as well as principal component analysis (Kern and Westrich 1995; Negrel

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B. Müller-Karulis (✉) · R. Poikāne  
Marine Monitoring Centre,  
Institute of Aquatic Ecology,  
University of Latvia, 8 Daugavgrīvas, 1007 Riga, Latvia  
E-mail: baerbel@monit.lu.lv

V. Segliņš  
Faculty of Geographical and Earth Sciences,  
University of Latvia, 10 Alberta, 1010 Riga, Latvia

1997; Ausili and others 1998) have been applied for normalization and statistical analysis of heavy metal data. This study employs a tiered approach, where a statistical method – principal component analysis – was used to select relevant reference elements from a multi-element ICP-AES dataset of total metal concentrations in the Ventspils Harbour sediments, supplemented by sediment organic matter content and sediment grain-size. The concentrations of six toxic heavy metals (Co, Cr, Cu, Ni, Pb, Zn) were then normalized to the selected reference elements (Al, Ca) using least absolute values (LAV) regression. This approach suggested that transport processes governed heavy metal distribution in the Ventspils Harbour and identified isolated polluted sites.

## Materials and methods

### Study area

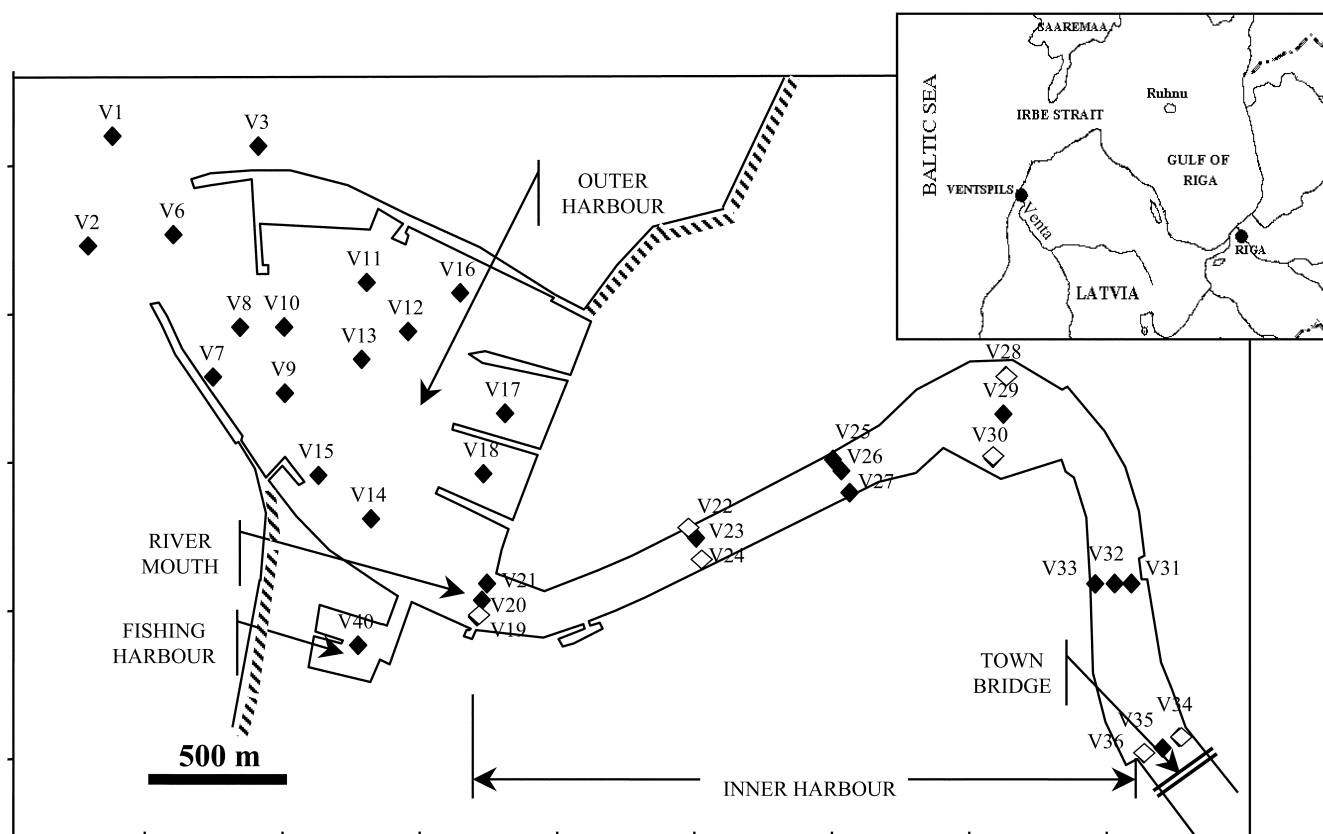
The Ventspils Harbour is located in north-west Latvia at the coast of the Baltic Sea (Fig. 1). The harbour gained its economic significance in the late 19th century as the only ice-free Baltic port in the czarist Russian empire. Today Ventspils ranks among the leading ports in the Baltic Sea region according to cargo turnover (34.1 million tons in

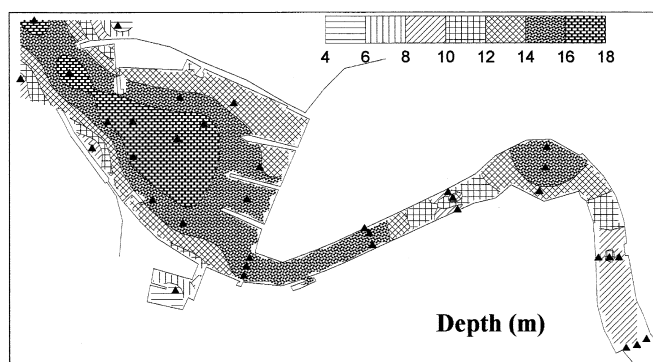
1999). About 70% of the processed cargo are crude oil and oil products. Other main commodities are potassium fertilizers and metals. With the establishment of a free economic zone in 1997 the harbour is currently expanding (Ventspils Harbour Authority 2000).

The harbour area is shaped by the Venta River estuary (Fig. 1). The inner harbour takes up 3.75 km along the lower reach of the Venta River from the Ventspils town bridge to the Venta mouth. The outer harbour is formed by two converging jetties of 1,480 and 2,060 m length that were constructed on the coastal slope (Ulsts 1998). The Venta is a medium-sized river draining western Latvia (average annual discharge 92.8 m<sup>3</sup>/s, drainage area 11,800 km<sup>2</sup>). To accommodate increasingly large vessels in the shallow river mouth area, the inner and outer harbour were successively dredged from their natural depth of 6 m to approximately 16 m. In 1998, when sampling was carried out, the outer harbour had a simple bowl-shaped depth profile (Fig. 2), with a deeper (16–18 m) vessel turning area in the centre and shallower basin edges (8–10 m). During our study, in the inner harbour, the most recent deepening was still proceeding and the final depth of 16 m had not been reached yet in a more shallow section (8–10 m depth, with a slightly deeper central shipping channel) downstream from the vessel turning basin in the Venta knee. Also, upstream of the Venta knee the harbour was only 8–10 m deep with a slightly deeper central shipping channel. In addition to the deepening operations during our study, continuous siltation requires constant maintenance dredging in the harbour, where the Venta is considered to be the main source of sediment.

Fig. 1

Harbour location and sampling sites. *Filled diamonds* Station sampled for chemical parameters and grain-size distribution; *unfilled diamonds* station sampled only for grain-size distribution





**Fig. 2**

Water depth in the Ventspils Harbour. Isocontours were constructed by kriging using Surfer software

Glacial sediments covered by more recent marine and riverine deposits characterize the geologic structure of the Ventspils area. Both harbour and town are located on a sandy lowland coast in the northern part of an old (Litorina) lagoon, which used to be separated from the sea by a narrow sand barrier. Therefore, in the Ventspils area sand deposits from the Litorina barrier overly clayey silt and clay of the Ancyclus Lake and Yoldia Sea. Occasionally varved clay deposited in a local lake during the last de-glaciation occurs in the lower part of these sediments. The total thickness of the ancient basin deposits varies from 9 to 20 m. Below, till from the second to last glaciation occurs.

The coastal slope in the Ventspils area is covered predominantly by fine sand and silt. At 12–15 m depth, and north of the harbour area at even 6–8 m depth, some areas are covered with boulders and pebbles. Along the coast, the East Baltic sediment flow transports debris derived from eroded parts of the coast and underwater slopes. In the Ventspils area, the minimum volume of the sediment flow is estimated at 600,000 to 800,000 m<sup>3</sup> annually (Knaps 1966).

### Sediment sampling and analysis

Sediment samples for trace metal, organic matter and grain-size analysis were taken in summer 1998 (29–30 July 1998 and 2–3 September 1998). As no prior information on sediment properties in the Ventspils Harbour was available, sampling stations (Fig. 1) were planned along a loose grid in the outer harbour (13 stations) and along six river cross sections (11 stations, 7 stations additionally sampled only for grain-size analysis). Because the actual sampling locations were sometimes moved to avoid harbour traffic, spatial coverage in the outer harbour was not completely homogeneous. The fishing harbour (station V40) was included to characterize conditions prior to the recent harbour deepening because this area is not dredged regularly. Marine stations adjacent to the harbour gates (three stations) served to characterize sediments outside the harbour area. Soft sediments were collected with a gravity corer (16 stations); sandy material with a van Veen grab (12 stations). Sediment subsamples were taken at standard

depths of 0–2 cm (28 samples) and 10–12 cm (12 samples). A 2-cm depth interval was sampled at the bottom of cores shorter than 10 cm (nine samples). Additional subsamples between the standard depths were included from six cores, where changes in colour or texture suggested intermediate layers of different material, as well as two subsamples below 12 cm depth (15–17 and 16–18 cm, respectively). From 11 stations with sandy sediments only surface material could be taken. For subsampling, gravity cores were gently pushed out of the liner, surplus sediment was cut off from the top with a Plexiglas sheet and samples were scooped off from the core with a polyethylene spoon. When possible, box cores were cut in half with a Plexiglas sheet and subsamples were again scooped off carefully within a 2-cm depth interval. From coarse-grained box cores only surface material was sampled. Subsamples for heavy metal analysis were stored in polyethylene containers, while subsamples for CHN analysis were stored in glass tubes. All material was immediately refrigerated and transferred to a freezer in the laboratory.

Sediment cores and grab samples were described according to colour and textural units. All subsamples were checked for odour. Samples for determination of total metal, phosphorus, carbon and nitrogen content were oven-dried at 105 °C at the Marine Monitoring Centre. With the exception of Hg, which was determined only at one station each in the outer harbour (V13), Venta mouth (V20) and the inner harbour (V35) to get a rough overview of concentration levels, major and trace elements were determined in all samples collected. Sample digestion and further analysis was performed by XRAL Laboratories (Canada), a ISO 9002 certified analytical laboratory. Samples were digested with HCl/HClO<sub>4</sub>/HF in Teflon beakers on a hot plate until all fluid evaporated. The remaining salts were dissolved in HCl, diluted with distilled water and the content of 31 elements (Ag, Al, As, Ba, Be, Bi, Cd, Ca, Cr, Co, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Sn, Sr, Ti, W, V, Y, Zn, Zr) was then analysed by ICP-AES (Fisons ICP-ARL 3560). Average deviation between duplicate samples was 2.4%. Hg-analysis was performed by XRAL using a cold vapour technique on a LEEMAN PS200 Automated Mercury Analyzer. Total carbon and nitrogen content were determined with a Fisons EA 1108 Elemental Analyzer at Bergen University. Inorganic carbon content (C<sub>in</sub>) was titrated as HCl soluble Ca and Mg by Balt-Ost-Geo, a licensed Latvian laboratory originating of the former central laboratory of the State Geological Survey. Organic carbon (C<sub>org</sub>) was calculated as difference between total and inorganic carbon. Grain size distribution was determined from the same material used for chemical analysis by sieving and pipette analysis. The granulometric analysis consisted of nine size fractions (<0.005 mm, 0.005–0.01 mm, 0.01–0.05 mm, 0.05–0.063 mm, 0.063–0.1 mm, 0.1–0.18 mm, 0.18–0.25 mm, 0.25–0.5 mm, >0.5 mm), which followed the mesh system commonly used in the former USSR to ensure comparability with earlier studies in the region. Sediment water content and density were measured by standard weight analysis (Fadееjev 1951, Preobrazenski and Sarkisyan 1954).

### Statistical methods

Statistical analysis was performed on all major and trace element data, except for Hg, as only seven measurements were available, and Ag, As, Cd, Mo, Sb and W, for which data were at least in part below the detection limit of the analytical method. Two grain-size parameters were included – sand ( $>63 \mu\text{m}$ ), and the finest grain-size fraction measured ( $<5 \mu\text{m}$ ) – to represent coarse and fine material deposited in the harbour. STATISTICA software (StatSoft Inc, '99 version) was used for all statistical analysis. All parameters were checked for normal distribution (Shapiro–Wilk's  $W$  test) and parameters that contradicted the normality hypothesis ( $P < 0.10$ ) were not considered further (La, Mg, Y, Zr). Sand content ( $>63 \mu\text{m}$ ) was normalized by square-root transformation ( $\sqrt{\text{sand}}$ ). Therefore, the final dataset for statistical analysis consisted of 24 major and trace element concentrations supplemented by two grain-size parameters. Differences between element concentrations measured at several depths within the same core were compared by ANOVA. For principal component analysis and normalization by LAV regression only surface data were used because spatial coverage was highest at the surface layer (28 samples) and only the surface layer was believed to represent the current sedimentation conditions in the Ventpils Harbour after the recent dredging. Within the surface layer samples, data were missing only at station V3 for  $C_{\text{org}}$  and N and at V7 for  $C_{\text{org}}$ . Additionally, one outlier (Pb at station V33, where Pb concentrations deviated by +4.9 standard deviations from the mean) was removed from the dataset to assure normality. All data were standardized by subtracting the sample mean and dividing by the sample standard deviation. Standardization is recommended for multivariate statistical techniques to give equal weight to data with different variance (Sharma 1996). Missing data and the outlier removed for Pb were replaced by the sample mean for the respective parameter. Principal component analysis was followed by factor rotation (varimax normalized) to achieve a factor structure, in which each variable should have high loadings on only one factor and low loadings on all other factors (Sharma 1996). To further investigate the behaviour of trace metals in the Ventpils Harbour, six toxic heavy metals (Co, Cr, Cu, Ni, Pb, Zn) were chosen from the dataset and least absolute values regression (Grant and Middleton 1998) was applied to their standardized concentrations. Least absolute values regression (LAV) is a normalization technique that minimizes the sum of absolute instead of squared residuals to fit a linear relationship between parameters. Samples with high residual concentrations affect slope and intercept of the regression line, therefore, much less than in standard sum of square techniques (Grant and Middleton 1998).

## Results

### Sediment texture

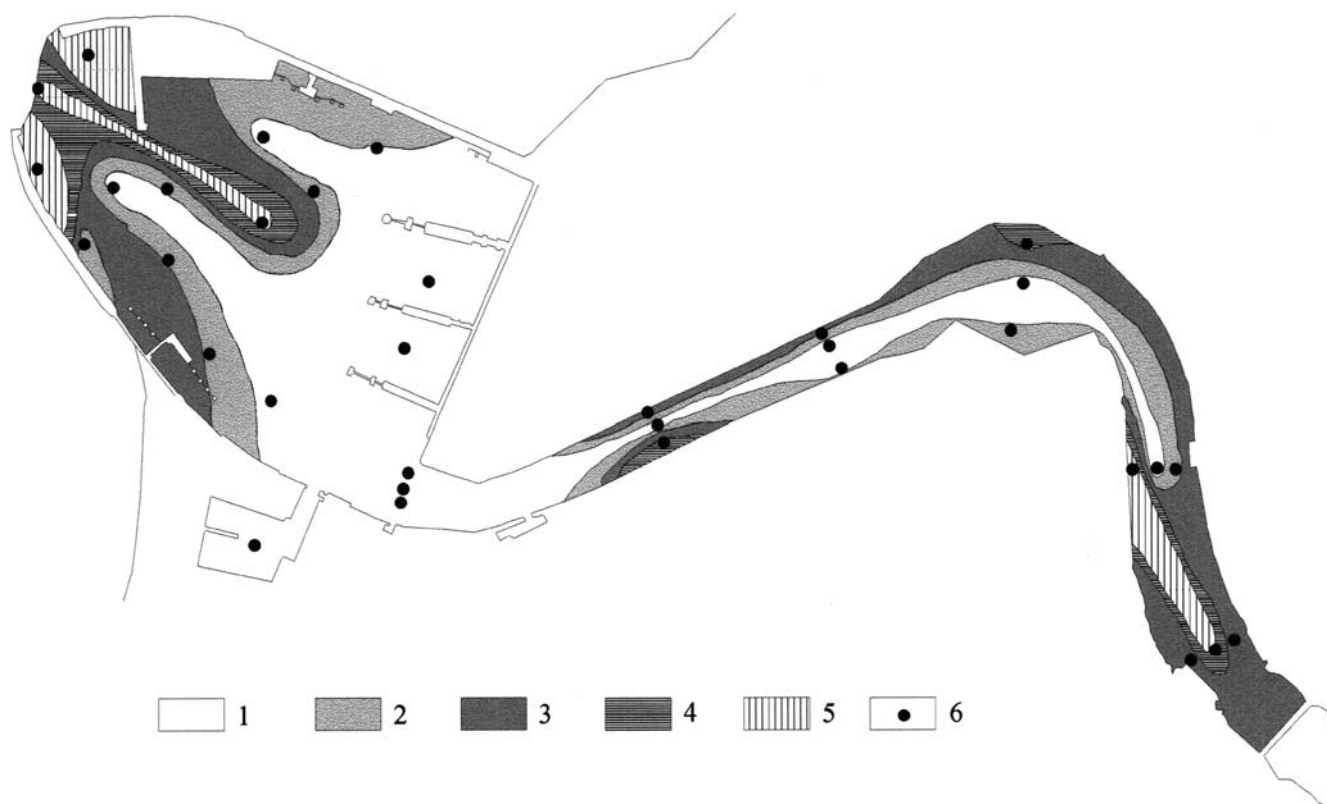
The riverbed of the Venta, including the mouth area, was covered predominantly by muddy silt with admixtures of

plant detritus. Areas of mixed sediments – sandy silt, silty mud and sand – occurred rarely. In the outer harbour, a yellowish layer of fluid consistency formed the top 2–3 cm of the sediments. Below, sediments were dark grey to black and their consistency gradually changed from semi-fluid to soft. In the inner harbour, muddy or occasionally silty sand covered the lower part of the Venta River, the shipping channel in the centre of the Venta and the river mouth area. These sediments were black or dark grey with admixtures of plant detritus. At an average water content of 69% and a corresponding sediment density of  $1.76 \text{ g/cm}^3$ , the sediments were of liquid or fluid consistency. Isocontours for the 0.25–0.1 mm (Fig. 3), 0.1–0.05 mm, and 0.05–0.01 mm (not shown) fractions were drawn to characterize the mechanical differentiation of the alluvium. The contour plots demonstrate a gradual mechanical differentiation of the alluvium in the outer harbour, which was most pronounced for the fine sand fraction (0.25–0.1 mm), but clearly evident in all three grain-size intervals. Sediment texture generally coarsened towards the harbour gates. For example, highest fine sand content ( $>30\%$ , Fig. 3) was observed as a narrow tongue reaching from the harbour gates into the outer harbour, accompanied by elevated fine sand contents (5–20%) along both breakwaters. In the central shipping channel of the inner harbour the mechanical differentiation of the alluvium was insignificant and the river bed was covered predominantly by muddy silt. At the river banks sediments tended to be coarser than in the shipping channel.

### Metals and organic matter

Metal and organic matter concentrations in the Ventpils Harbour varied considerable and deviated on average 30% about their mean (Table 1). Low relative standard deviations were found for Ba (9%), K (15%) and Sc (16%). Highest variability was observed for Pb (48%), Zn (44%) and N (41%).

At the surface layer (0–2 cm) all parameters investigated followed a similar distribution pattern, which Fig. 4 exemplifies for two major (Al, Ca) and two trace metals (Cr, Pb). In the Venta River upstream of the harbour area intermediate to high metal and organic matter concentrations as compared with the other stations visited were found. Within the inner harbour, sediment metal contents were lower at the river banks than in the central shipping channel. Metal concentrations in the inner harbour tended to increase towards the Venta mouth, starting from the vessel turning area in the knee of the inner harbour and gradually continuing towards the Venta mouth. The distribution of lead deviated slightly from the general pattern observed with low concentrations throughout the lower reach of the inner harbour. Highest metal and organic matter contents were generally found in the outer harbour immediately downstream from the Venta mouth. An area of higher metal concentrations also stretched along the eastern and northern edge of the outer harbour. In the centre and at the south-western edge of the outer harbour concentration levels decreased noticeably towards the sea, but lowest values within the dataset were generally



**Fig. 3**

Fine sand content (0.25–0.1 mm) in the sediment surface layer (0–2 cm), 1 <5%, 2 5–10%, 3 10–25%, 4 20–30%, 5 >30%, 6: sampling site. Isocontours were plotted using AutoCAD software

observed close to the southern breakwater. Concentrations at the marine stations were distinctly lower than in the harbour for all parameters investigated.

At 10–12 cm depth, metal and organic matter concentration patterns were generally similar to the sediment surface (data not shown). The concentration decrease towards the seaward stations was, however, less pronounced and the concentration maximum observed right downstream from the Venta mouth for the surface layer was found right in the Venta mouth for most parameters. Within the same core, differences between element concentrations in surface material (0–2 cm), subsamples at intermediate depth intervals, and material from the lower standard sampling depth (10–12 cm) were in most cases statistically not significant (ANOVA,  $P < 0.05$ ). Exceptions were Ba where concentrations at all other subsampling depths were significantly lower than at the sediment surface, and K, and Mn, where concentrations at the lower standard depth (10–12 cm) were significantly lower than at the sediment surface.

Further analysis of the dataset focused on heavy metal and organic matter distributions at the sediment surface (0–2 cm). Firstly, chemical and grain-size surface data was available from 28 stations, and secondly only the surface layer was believed to represent the sedimentation conditions in the Ventspils Harbour after the recent deepening, while deeper layers represented unknown time periods of sediment deposition.

#### Parameter interrelations

Metals, organic matter concentration and the proportion of fine-grained material (<5  $\mu\text{m}$ ) were highly correlated with each other (Table 2), as the average correlation coefficient (Spearman's  $r$ ) between the individual parameters was 0.78. Nearly perfect correlation ( $r \geq 0.99$ ) was found for Al/Ti, Al/V, Cr/V, Ni/V, Fe/V, Ti/V, Fe/Ni, Fe/Sc, Ni/Sc, Ti/Sc and Ca/ $\sqrt{\text{sand}}$ . Low correlation coefficients ( $\leq 0.50$ ) characterized the pairs Pb/Ba, Pb/C<sub>in</sub>, Pb/C<sub>org</sub>, Pb/Ca, Pb/Mn, Pb/N, Pb/Sr, Pb/<5  $\mu\text{m}$ , Pb/ $\sqrt{\text{sand}}$ , Cu/Ba, Cu/C<sub>in</sub>, Cu/C<sub>org</sub>, Cu/N, Ba/N and <5  $\mu\text{m}$ /N.

#### Principal component analysis

Principal component analysis extracted two factors with eigenvalues >1.0 from the dataset. After normalized varimax rotation the model explained 86.9% of the total variance in the data. The first principal component (factor 1) extracted as much as 80.1% of the total variance, the second principal component (factor 2) only 6.8%. Factor loadings (Fig. 5) grouped most parameters into two narrow clusters, while loadings for Pb, Cu, Zn, Na, P and N were spread throughout the parameter space. High correlation with factor 1 (0.69–0.94) and low correlation with factor 2 (0.24–0.42) characterized the proportion of fine material (<5  $\mu\text{m}$ ), square-root transformed sand content, organic and inorganic carbon and the elements Ba, Ca, Sr and Mn (group 1). The elements Al, Be, Co, Cr, Fe, K, La, Ni, Sc, Ti and V (group 2) fell within a narrow cluster with intermediate loadings on both factor 1 (0.69–0.77) and factor 2 (0.60–0.70). For the remaining parameters, high loadings on factor 1 (0.74–0.91) combined with variable, but low loadings on factor 2 (0.10–0.55) were found for Pb,

**Table 1**

Metal and organic matter concentrations in the Ventspils Harbour sediments

Parameter	Samples	Mean	Minimum	Maximum	SD
Ag (mg/kg)	49 <sup>a</sup>	0.53	<0.2	0.8	0.15
Al (%)	54	4.03	2.04	7.09	0.91
As (mg/kg)	54	<3			
Ba (mg/kg)	54	352	267	474	32.2
Be (mg/kg)	54	1.3	0.6	2.5	0.35
Bi (mg/kg)	54	<5			
C <sub>in</sub> (%)	53	0.40	0.16	0.61	0.11
C <sub>org</sub> (%)	52	3.19	0.60	6.00	1.10
Ca (%)	54	4.98	1.88	9.97	1.48
Cd (mg/kg)	54	<1	<1	2	
Co (mg/kg)	54	8.5	2	17	2.79
Cr (mg/kg)	54	41	12	71	14
Cu (mg/kg)	54	16.2	2.8	28.9	6.00
Fe (%)	54	2.11	0.59	3.77	0.72
Hg (µg/kg)	7	41.9	14	65	16.2
K (%)	54	2.19	1.33	3.12	0.33
La (mg/kg)	54	25.3	10.6	43.9	6.55
Mg (%)	54	1.42	0.37	2.34	0.47
Mn (mg/kg)	54	537	162	1120	203
Mo (mg/kg)	54	<1	<1	1	
N (%)	51	0.18	0.03	0.36	0.07
Na (%)	54	0.77	0.49	1.03	0.13
Ni (mg/kg)	54	19.7	5	35	6.94
P (%)	54	0.07	0.03	0.12	0.02
Pb (mg/kg)	54	12.7	3	44	6.13
Sb (mg/kg)	54	<5			
Sc (mg/kg)	54	6.2	1.7	11.9	2.06
Sn (mg/kg)	54	<10			
Sr (mg/kg)	54	125.2	74.1	168	20.58
Ti (%)	54	0.22	0.07	0.39	0.06
V (mg/kg)	54	49	13	102	18
W (mg/kg)	54	<10			
Y (mg/kg)	54	16.2	6.8	23.7	3.93
Zn (mg/kg)	54	80.1	16.9	254	35.58
Zr (mg/kg)	54	105.8	42.5	130	21.17

<sup>a</sup>Only values above the detection limit (0.2 mg/kg) are included

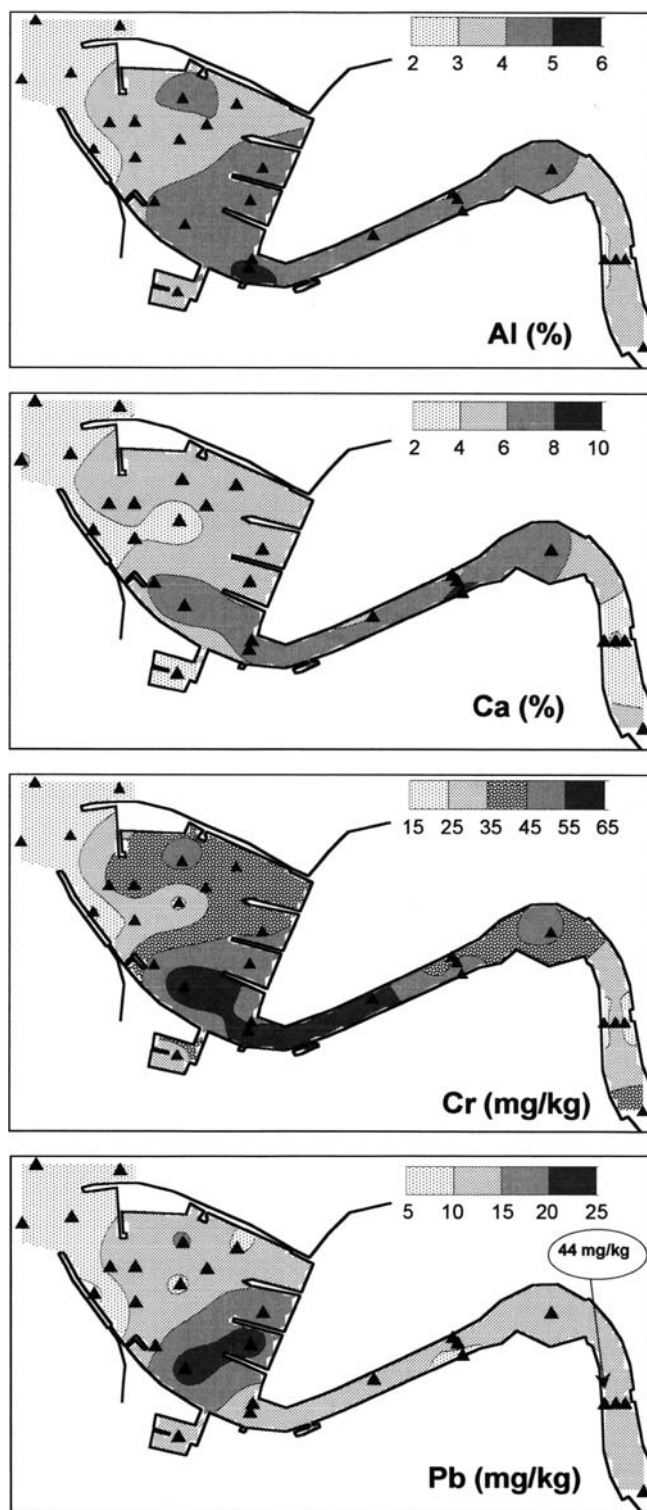
Cu, Zn, Na and P, whereas nitrogen had low loadings for both factor 1 (0.54) and factor 2 (0.44).

#### Least absolute values regression

As principal component analysis divided trace and major element concentrations into two narrow clusters with only few 'outliers', the clusters were thought to reflect the main features of metal dynamics in the Ventspils Harbour.

Accordingly, for normalization purposes, one parameter from each cluster was chosen as a reference element. Ca, which had the highest loading on the first principal component, was selected to represent group 1 elements, while Al was chosen to represent group 2. Al is a major component of clay minerals and, therefore, is considered to indicate the presence of fine-grained material (Kersten and others 1994). Al has consequently been used for normalization purposes in many studies (Kersten and others 1994; Summers and others 1996; Balls and others 1997; Abraham 1998; Trimble and others 1999).

Normalization with respect to both Ca and Al fits the data to a regression plane of the form  $[X]=a*[Ca]+b*[Al]+c$ , where symbols in square brackets denote the respective element concentrations,  $a$  and  $b$  define the slope of the regression plane, and  $c$  is the intercept that corresponds to

**Fig. 4**

Spatial distribution of Al, Ca, Cr and Pb in the sediment surface layer (0–2 cm). Isocontours were constructed by kriging using Surfer software

the concentration of element X at zero Ca and Al content. LAV regression (Grant and Middleton 1998) was used for normalization in order to minimize the influence of outliers on the slope of the regression plane. To make regression parameters and residual concentrations

**Table 2** Correlation coefficient matrix (Spearman's  $r$ ) for parameters determined in the surface layer (0–2 cm) of the Ventspils Harbour sediments. Correlation coefficients not significant at  $P < 0.05$  are printed in bold

	Al	Ba	Be	C <sub>in</sub>	C <sub>org</sub>	Ca	Co	Cr	Cu	Fe	K	Mn	N	Na	Ni	P	Pb	Sc	Sr	Ti	V	Zn	<5 $\mu\text{m}$		
Ba	0.78																								
Be	0.96																								
C <sub>in</sub>	0.78	0.65	0.77																						
C <sub>org</sub>	0.73	0.64	0.69	0.73																					
Ca	0.83	0.74	0.82	0.87	0.76																				
Co	0.94	0.75	0.87	0.73	0.67	0.80																			
Cr	0.98	0.70	0.96	0.79	0.73	0.82	0.92																		
Cu	0.78	0.50	0.78	0.50	0.49	0.51	0.73	0.81																	
Fe	0.98	0.75	0.96	0.81	0.79	0.88	0.93	0.97	0.80																
K	0.98	0.81	0.91	0.74	0.73	0.79	0.91	0.93	0.71	0.94															
Mn	0.90	0.77	0.88	0.86	0.81	0.97	0.85	0.89	0.63	0.95	0.86														
N	0.62	0.26	0.60	0.62	0.77	0.62	0.59	0.68	0.46	0.68	0.54	0.66													
Na	0.84	0.53	0.79	0.66	0.53	0.62	0.76	0.84	0.67	0.78	0.80	0.69	0.68												
Ni	0.98	0.76	0.95	0.81	0.77	0.86	0.93	0.98	0.80	0.99	0.93	0.93	0.69	0.82											
P	0.87	0.55	0.83	0.69	0.68	0.70	0.86	0.89	0.79	0.90	0.85	0.79	0.66	0.80	0.88										
Pb	0.65	0.45	0.67	0.39	0.37	0.35	0.56	0.68	0.78	0.63	0.61	0.47	0.48	0.75	0.67	0.69									
Sc	0.99	0.75	0.97	0.80	0.74	0.84	0.93	0.99	0.79	0.99	0.91	0.67	0.67	0.84	0.99	0.88	0.66								
Sr	0.87	0.72	0.85	0.86	0.73	0.96	0.83	0.86	0.55	0.89	0.84	0.95	0.68	0.78	0.89	0.77	0.49	0.88							
Ti	0.99	0.76	0.96	0.83	0.75	0.87	0.93	0.98	0.75	0.98	0.96	0.93	0.66	0.83	0.98	0.87	0.62	0.99	0.90						
V	0.99	0.75	0.97	0.80	0.76	0.85	0.93	0.99	0.80	0.99	0.94	0.92	0.69	0.81	0.99	0.88	0.66	1.00	0.89	0.99		0.90			
Zn	0.90	0.59	0.87	0.65	0.60	0.63	0.84	0.92	0.90	0.88	0.84	0.74	0.65	0.87	0.90	0.89	0.85	0.90	0.73	0.88	0.90		0.68		
<5 $\mu\text{m}$	0.82	0.68	0.77	0.77	0.67	0.66	0.76	0.76	0.62	0.80	0.81	0.73	0.46	0.59	0.79	0.59	0.38	0.80	0.66	0.80	0.88	0.80	0.68		
$\sqrt{\text{sand}}$	0.86	0.73	0.84	0.87	0.73	0.99	0.83	0.85	0.53	0.89	0.82	0.97	0.61	0.68	0.88	0.75	0.40	0.87	0.98	0.90	0.90	0.88	0.67	0.66	

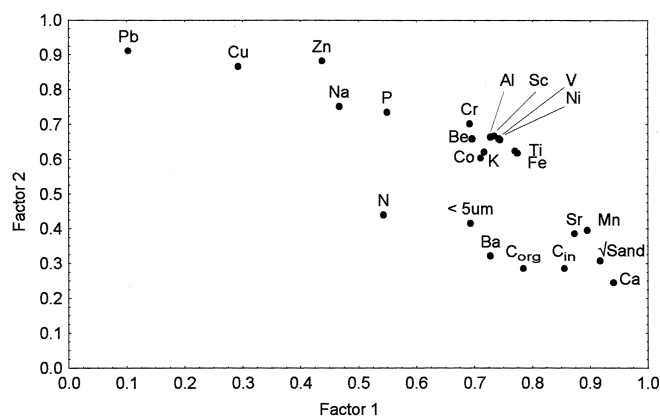
comparable among the different metals, standardized concentrations were used in the analysis rather than raw data. The LAV regression explained between 55 and 95% of the variance for the six metals investigated (Co, Cr, Cu, Ni, Pb, Zn). Regression coefficients (Pearson  $r$ , Table 3) ranged between 0.94 and 0.98 for the group 2 metals Co, Cr and Ni, but were distinctly lower for Cu and Pb (0.78 and 0.74). The normalization also explained the distribution of Zn fairly well ( $r=0.91$ ). For Co, Cr and Ni the slope coefficients were both positive with respect to Ca and Al, whereas Cu, Pb and Zn had negative slope coefficients with respect to Ca.

LAV regression residuals (Fig. 6) were distributed evenly over the harbour area and the pronounced metal concentration increase in the lower part of the inner harbour with the subsequent drop towards the sea was not reflected in the residual concentrations. A total of 97% of the residual concentrations ranged between  $\pm 1$  standard deviation of the original data. Higher residual concentrations were observed at separate stations (V33 for Pb and Cu, V40 for Cu, V20 for Zn).

## Discussion

Compared with data from the surface layer of sediments in the upper reach of the Venta river (Kļaviņš and others 1999, see Table 4), heavy metal concentrations in the Ventspils Harbour were approximately seven times higher for Cu, six times for Ni and two times for Co. The more complete digestion method used in this study might have contributed to these differences, but also Kļaviņš and others (1999) found elevated Pb and Ni concentrations in the lower reach of the Venta, right upstream of the Ventspils Harbour, indicating the influence of metal pollution in the Ventspils region. Still, Latvian pollution standards (Environmental Protection Commission of the Latvian Republic 1992), classify Ventspils Harbour sediments as 'clean' with respect to As, Be, Cd, Co, Cr, Cu, Hg, Mg, Ni, Pb, Sb, V and Zn. For Ba, Fe and Mn the concentration limits of the lowest contaminant class were exceeded, which might be because total metal digests were used in this study compared with the HNO<sub>3</sub> extractable metals on which the pollution standard is based. Compared with surface sediments of similar grain-size in the Klaipeda harbour (Jokšas 1994, see Table 4), another commercial port on the eastern coast of the Baltic Sea, concentrations in the Ventspils Harbour were higher for Co and Mn, but lower for Cr, Cu, Pb and Zn, and even distinctly lower for Hg. Cellulose and cardboard production (Jokšas 1994) contributed to the higher pollution load in the Klaipeda port area. Metal concentrations in the Ventspils Harbour were also often similar or even lower than in the sediments of the Gulf of Riga (Leivuori and others 2000), a near-by marine area. Thus, despite its urban setting, heavy metal pollution in the Ventspils Harbour was low.

The low metal concentrations in the Ventspils Harbour were not caused by the removal of potentially contaminated



**Fig. 5**  
Principal component loadings

sediments during the recent harbour deepening. Even after the dredging operations a modern sediment cover persisted in the harbour because, at most stations investigated, the recent sediments were at least 10 cm thick and the underlying periglacial sediments had been reached only at the deeper horizon (10–12 cm) of individual stations. Heavy metal concentrations in the harbour area prior to the deepening (Latvian marine administration, unpublished data) were similar to our study. Most likely, the current surface sediments were to a large part formed by pre-deepening material that dredging operations and vessel traffic redistributed in the harbour area. Also, the absence of depth gradients for most metals agrees well with frequent mixing of the harbour sediments.

The high correlations between individual metal concentrations and the analogous spatial distributions observed in the harbour area suggest that similar processes governed the behaviour of all metals. Also, principal component analysis confirmed the highly similar metal behaviour because a single factor model already explained 80.1% of the variance in the dataset. Correlation coefficients between parameter concentrations found in the Ventspils Harbour were generally higher than those found in similar studies in the Gothenburg harbour (Engström and Stevens 1999) and the Klaipeda area (Jokšas 1994). The smaller study area and the lack of tributaries in the Ventspils Harbour possibly contributed to the tight relationships within the dataset.

The principal component clusters one and two were separated only by minor differences, as parameters were

highly intercorrelated between both groups (average Spearman's  $r$  between group 1 and 2 parameters 0.82). Only Pb, Cu, Zn, as well as Na, P and N were found outside the two main principal component loading clusters and their relatively low correlations to all other elements suggest that additional factors influenced their distribution. The principal component groups reflected the geochemical characteristics of the measured parameters. While parameters in principal component group 1 (<5  $\mu\text{m}$ ,  $\sqrt{\text{sand}}$ ,  $C_{\text{org}}$ ,  $C_{\text{in}}$ , Ba, Ca, Sr, Mn) were mainly associated with calcite and co-occurring minerals, group 2 parameters (Al, Be, Co, Cr, Fe, K, La, Ni, Sc, Ti, V) represented aluminosilicate components. Thus group 1 contained the calcite constituents Ca and  $C_{\text{in}}$ , the common Ca substitute Sr (Van der Loeff and Boudreau 2000), and Mn, which also forms carbonate minerals (Stumm and Morgan 1981). Within group 2, Al and K are principal elements in feldspars and clay minerals, which are also known to contain Co, Ni, Ti and V (Norman and De Deckker 1990; Nikodemus and others 1997). Fe also clustered within this group, but the substantial Fe content of the samples (average 2.11%) as compared with Al (4.03%) suggests that Fe was not attributed solely to aluminosilicates. Sequential extraction results (Poikāne, unpublished data) showed Fe to be chiefly bound in ferric oxyhydroxides, which, according to the high correlation to the other group 2 parameters, behaved environmentally similar to aluminosilicate components.

The grain-size parameters (<5  $\mu\text{m}$ ,  $\sqrt{\text{sand}}$ ) indicated a slight distinction in the affinity of major and trace elements to fine material. Square root transformed sand content characterized the absence of sand from a sample rather than high sand content, as the transformation assigned high values to samples with low sand content, while samples with more than 50% sand were given a low, constant value (Fig. 7). Especially the calcite components (Ca and  $C_{\text{in}}$ ) were more closely correlated to square-root transformed sand content than to material <5  $\mu\text{m}$ , whereas aluminosilicate parameters associated more strongly with fine material <5  $\mu\text{m}$ , confirming their clay mineral character. In the Ventspils Harbour low sand content was characteristic for silty and muddy deposits of riverine sediments. Also the carbonate character of principal component group 2 agreed well with the predominantly riverine origin of these elements, as both limestone and dolomite occur in Devonian and Permian sediments in the upper reach of the Venta River.

The typical spatial distribution pattern of metal concentrations in the Ventspils Harbour – increasing concentrations throughout the inner harbour and a pronounced drop towards the seaward part of the outer harbour (Fig. 4) – was entirely removed by normalization with respect to Al and Ca (Fig. 6) for the six toxic heavy metals investigated. LAV regression intercepts (Table 3) were close to zero for Co, Cr, Ni and Zn, and only slightly shifted to negative values for Cu and Pb. Thus, the sedimentation pattern and geochemical behaviour of Al- and Ca-rich material almost completely explained Co, Cr, Ni and Zn concentrations in the Ventspils Harbour and also a large part of the spatial variation of Cu and Pb. High LAV

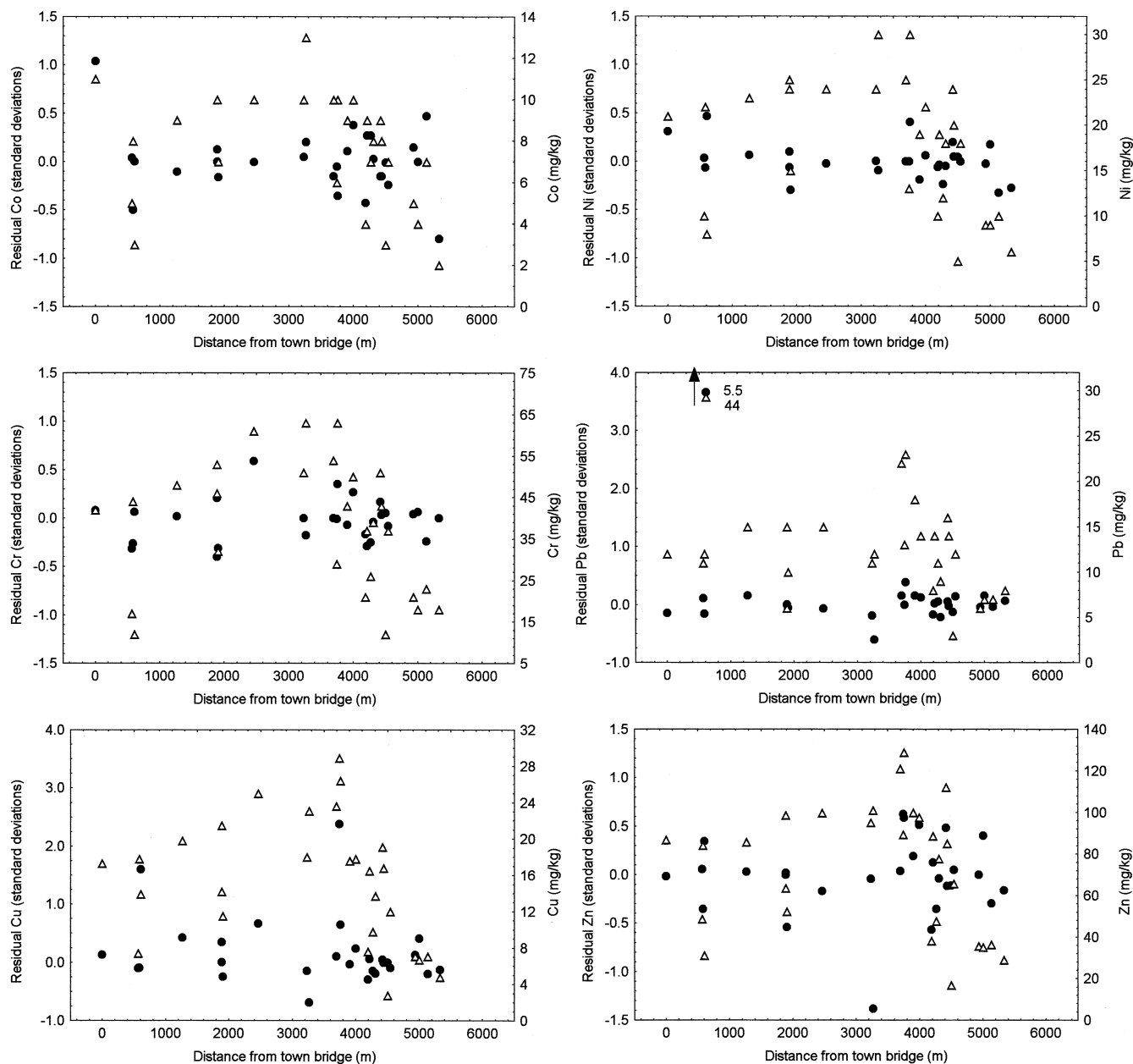
**Table 3**

LAV regression parameters for selected elements with respect to Ca and Al

	Co	Cr	Cu	Ni	Pb	Zn
$r$	0.94	0.97	0.78	0.98	0.74	0.91
a	0.07	0.09	-0.31	0.15	-0.24	-0.50
b	0.86	0.87	1.16	0.85	0.42	1.34
c	0.00	0.02	-0.18	-0.01	-0.19	0.02

a, b Slope coefficients with respect to Ca and Al, respectively; c Intercept of the regression plane;  $r$  Pearson correlation coefficient between predicted and observed values





**Fig. 6**

LAV regression residuals (*filled circle*) and raw data (*empty triangle*) in relation to distance along the river downstream from the town bridge (for comparison: the Venta mouth and harbour gates are located 3,250 and 4,950 m downstream from the town bridge, respectively). Note the different scale for Cu and Pb

regression residuals at individual sites were mostly caused by local contamination. The highest Pb residual (+5.5 standard deviations), together with an elevated Cu residual (+1.6 standard deviations), was found at station V33 on the river bank. Sediments at this station were black, smelled of oil products and also contained construction debris. Oil contamination from rain-water drainage is a known problem in the Ventspils Harbour (Ventspils Harbour Authority 2000) and also heavy metals might have entered the harbour basin from rain-water drainage pipes. Elevated heavy metal concentrations caused by storm-

water inputs were, for example, found in a Sydney Estuary (Birch and Tyler 1999). Station V40, where a high Cu residual (+2.4 standard deviations) was observed, is located in the shipping harbour, which was used for removal of ship paints that often contain Cu (Trimble and others 1999). Additionally, the fishing harbour is not dredged regularly and sediments accumulate over longer time periods. A high, but negative residual Zn concentration (-1.38 standard deviations) occurred at station V20 located in the Venta mouth where the sediment was characterized by the highest Al and fine material content (5.5 and 40.8%, respectively) in the dataset. Under a thin surface layer olive clays of the Baltic Ice Lake occurred (Ulsts 1998) and thus the low Zn concentration was most likely caused by the admixture of mineralogically different material from the deeper sediment layers, which was also supported by the high Al concentration and the finer

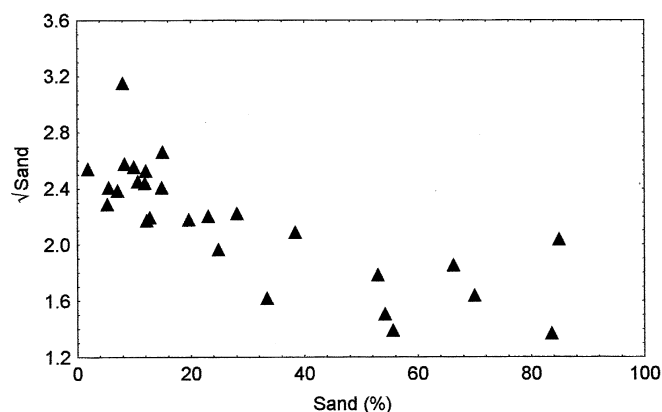
**Table 4**

Heavy metal concentrations in the Ventspils Harbour compared with neighbouring areas

Element	Ventspils Harbour mean <sup>a</sup>	Ventspils Harbour maximum <sup>a</sup>	Venta, upper reach <sup>b</sup>	Venta, lower reach <sup>b</sup>	Klaipeda Port, silt <sup>c</sup>	Gulf of Riga <sup>d</sup>
Cd (mg/kg)	<1	<2	0.87	1.68	1.19	0.73
Co (mg/kg)	8.5	17	3.42	3.82	4.45	
Cr (mg/kg)	41	71			87.5	82
Cu (mg/kg)	16.2	28.9	2.36	2.75	26.40	31
Hg ( $\mu$ g/kg)	47	65			800	100
Mn (mg/kg)	537	1,120			300	452
Ni (mg/kg)	19.7	35	3.29	9.10		41
Pb (mg/kg)	12.7	44	15.45	55.30	17.43	39
Ti (%)	0.22	0.39				0.42
V (mg/kg)	49	102				79
Zn (mg/kg)	80.1	254			171.30	146

grain-size. Therefore, unlike some environments in which Cu, Pb and Zn were identified as typical anthropogenic pollution indicators (Lottermoser 1998; Rice 1999), in the Ventspils Harbour only Cu and Pb were linked to contaminated sites, whereas the deviations in Zn concentrations were caused by differing parent material. Geochemical reactions most likely did not influence the distribution of the six heavy metals normalized to Al and Ca because both reference elements were geochemically inert at the neutral pH conditions (Yurkovskis, unpublished data) in the Ventspils Harbour. Therefore, except for the local disturbances discussed, mainly transport processes governed trace metal dynamics. The spatial distribution of heavy metals agreed well with the sedimentation pattern of fine material in the harbour. Areas with higher metal concentrations were found in the inner harbour and along the eastern and northern edge of the outer harbour basin, where fine material was deposited. As principal component analysis suggested both reference elements to be associated with fine-grained material, the dependence of heavy metal content on sediment grain-size was also consistent with the normalization results. From the lack of spatial pattern in the normalized heavy metal concentrations follows that either no significant metal pollution sources were present in the harbour area itself, that metals entered the harbour basin from disperse

sources that did not leave a spatial signature in the sediments, or that high sediment mixing had efficiently 'smeared out' contaminants over the harbour basin. The recent dredging operations, frequent vessel traffic, as well as back-flow caused by salt water intrusions, which periodically reach the inner harbour (Yurkovskis, unpublished data), added to the dynamic sedimentation conditions. The tongues of coarser material that stretched into the outer harbour from the harbour gates most likely corresponded to marine sediment influxes, because periodic influx of rather fine clastic material of marine genesis is a characteristic feature of the sedimentation conditions in the outer harbour (Ulsts 1998). A recent study showed the marine material to be quartz-rich, as sediment quartz content and quartz/feldspar ratios increased in the outer harbour towards the sea (Jonsson 2000). In addition to the lower surface area of coarse grained sediments, quartz also lacks sorption sites for heavy metals, which in oxic environments are mainly associated with clay minerals, iron and manganese oxides, and organic matter (Kersten and others 1994). Therefore, quartz-rich marine material could efficiently dilute more contaminated riverine sediments. Dilution of heavy metal concentrations by marine material has been described for example in the Rhine and Elbe estuaries, and has been linked both to inputs of relatively clean marine fine material (Groengroeft and others 1998) as well as to dilution with coarse marine sediments (Brügmann 1995). In the Ventspils Harbour, dilution of fine-grained sediments with quartz-rich coarse material of marine origin most likely was the chief influence factor on sediment heavy metal content. However, within this study it was not possible to quantify the role of the marine sediment influx in maintaining the low heavy metal concentrations observed in the Ventspils Harbour sediments.



**Fig. 7**  
Effect of square root transformation on the parameter sand

## Conclusions

Statistical methods – principal component analysis and normalization by LAV regression – identified sediment transport as the main factor determining heavy metal concentrations in the Ventspils Harbour. Principal component analysis suggested deviations from this pattern for

Pb, Cu and Zn, which LAV regression linked to individual contaminated sites, or – in the case of Zn – admixture of older sediments. Sediment grain size information proved vital for the successful interpretation of the heavy metal data because the mechanical differentiation of the alluvium in the outer harbour clearly showed the influx of coarser marine sediments through the harbour gates and suggested mixing of marine and riverine material as an important feature of sediment transport in the Ventspils Harbour. Mineralogical information, for example concentrations of minerals ‘typical’ for marine or riverine material, could be used in future studies of estuarine harbour settings to investigate the proportion of marine and riverine sediments more closely. In the case of the Ventspils Harbour, high correlations between all major and trace metals, especially with respect to the geochemically inert elements Al and Ca, indicated that metal distributions were not governed by geochemical reactions. This might be different in more complex harbour settings, where sedimentation conditions, especially with respect to organic matter input and redox conditions, are spatially more variable. As shown by the Ventspils Harbour example, potential contaminant sources within the harbour basin itself were impossible to identify from the spatial distribution of metals in the sediments. Sediments were continually disturbed by vessel traffic, dredging operations, and – in the case of the Ventspils Harbour – also by the estuarine circulation, smearing potential contaminant signals over the entire harbour area. The high sediment mixing also poses difficulties for sediment quality monitoring, as changes in pollutant inputs can be detected only after long time periods. Therefore, reliable inventories of contaminant inputs at their source are essential for successful environmental management of harbours.

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