

Spatial distribution of labile and total forms of copper and zinc in sediments from the Port of Gdansk

Barbara Radke^{1,3}, Grażyna Dembska², Barbara Aftanas²
Aneta Kowalczyk¹, Jerzy Bolałek^{1,4}

¹*University of Gdansk, Department of Marine Chemistry and Marine Environmental Protection, Al. Piłudskiego 46, Gdynia 81-378, Poland*

²*Maritime Institute, Department of Environmental Protection
Ul. Długi Targ 41/42, 80-958 Gdansk, Poland*

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Abstract

Sediment cores were collected from a number of sites in the Port of Gdansk in 1997 and 1998. The samples were segregated by depth then dried, homogenised and sieved into four grain size fractions (>2.00 mm, 2.00 - 0.063 mm, 0.063 - 0.032 mm, and 0.032 mm) Small-grained sand with a low admixture of silt predominated in all samples, whilst the amount of organic matter and water varied between samples. The 2.00 – 0.063 mm size fraction was the most abundant; and also showed the highest accumulation of trace metals. In the <2.00 mm size fraction the mean concentration of labile forms of copper was 9.06 mg kg⁻¹ DW, while the concentration of total forms was 12.73 mg kg⁻¹ DW. The mean concentrations of labile and total forms of zinc in this fraction were 31.79 and 46.27 mg kg⁻¹ DW, respectively. The widest ranges of concentrations for both labile and total forms of the metals were found in the near-surface sediment layers (0-20 cm). Sediments collected from highly industrialized locations contained the highest concentrations of metals.

³ Corresponding autor: bradke@ocean.ug.gda.pl

⁴ e-mail: jerzyb@sat.ocean.univ.gda.pl

INTRODUCTION

Industrialisation in the Gulf of Gdansk, including the harbor facilities, negatively impacts on the water and sediment qualities of the area, and has resulted in an increased content of trace metals in these two environmental compartments. Despite the implementation of legal regulations (inter alia, HELCOM Recommendation 13/1 from 1993 which has been transposed into Ordinance no. 9 of the Director of Maritime Office in Gdynia, dated 1 June 1996, position 87 of the Official Journal of Gdansk Voivodship; the document advises the measurement of concentrations of metals in the <2.00 mm size fraction) and a partial decline of the shipyard industry, the ports still pose a threat to the marine ecosystem of the Gdansk area. This is particularly true of the removal of accumulated sediments from harbor canals (so-called dredged spoils) and their storage in specially designated areas on land (Papai 1995) or at sea (Korzeniewski 1998).

The present legal acts regulate the dumping of dredged spoils enriched in, among others, trace metals (decree of the Minister of the Environment on the type and concentrations of substances that contaminate dredged spoils [Dz.U. no. 55, pos. 498, dated 16.04.2002], according to which labile forms of toxic substances should be determined in the <2.00 mm size fraction). However, until 1990 dumping of dredged spoils was conducted without any obligation to undertake chemical tests (Dembska et al. 2001a), and therefore without any control over the quality of the dumped material.

The near-bottom hydrodynamics of the Gulf of Gdansk differ from the hydrological and sedimentation conditions in the Port of Gdansk (Pustelnikovas et al. 2005). Dredged spoils containing contaminants and stored in dumping sites at sea undergo a slow process of dispersion into the water column, and thus constitute a threat to living organisms. The associated contamination disrupts the Gulf of Gdansk ecosystem, and, in turn, impacts on components of the overall energy and mass balance of the southern Baltic Sea.

It is therefore important that the evaluation of prospective dredging in the harbor and harbor canal should be based on stringent analyses that will determine the sedimentation rate and chemical composition of the sediments in question.

In this study the content of labile and total forms of copper and zinc in sediments from the Port of Gdansk after granulometric fractionation into the <2.00 mm, 2.00-0.063 mm, 0.063-0.032 mm and <0.032 mm size fractions was estimated. Sediment samples were collected from Wiślane Quay, Obrońców Poczty Polskiej Quay, Oliwskie Quay and Paliw Płynnych Quay and separated into depth layers. The spatial distribution of metals was hence reconstructed in both vertical and horizontal profiles. The results were compared to the

environmental standards and indicators that have been in force in Poland since 1 January 2003 (Dz.U. no. 62). The analytical procedures used were adapted from the HELCOM guidelines (1993), which were obligatory in Poland at that time.

AREA OF INVESTIGATION

The Port of Gdansk is located on the shore of the Gulf of Gdansk near the mouth of Martwa Wisła (Dead Vistula). The length of the water basin spreading between Przegalina and Nowy Port is 27 km (plus 2.5 km of Śmiała Wisła; Brave Vistula). Mean current speeds range from 2 to 5 cm s⁻¹, whilst the salinity ranges from 6.13 to 2.48 PSU (Majewski 1990). In the near-bottom layer of the river an inflow of saline water from the sea occurs.

The area under the management of the Port of Gdansk Authority S.A. is 660 hectares which includes a 6-ha Władysława IV Basin (Eko - Konsult 1998; Fig. 1). The harbor comprises of:

- the main port basin used for the berthing and passage of vessels
- a land area equipped with cranes for loading and unloading cargo, warehouses, transportation and environmental protection facilities
- quays and piers that protect the main port basin from wave action.

Samples of sediments were collected from the following loading and unloading quays (Mamuszka 1988):

- **Wiślane Quay** loading and unloading of general cargo, grain elevator, etc.,
- **Obrońców Poczty Polskiej Quay** (also known as Siarkowe Quay) loading and unloading of sulfur,
- **Oliwskie Quay** loading and unloading of general cargo, e.g. vegetables and fruits,
- **Obrońców Westerplatte Quay** cargo loading and unloading, cleaning of vessels,
- **Capt. Tadeusza Ziółkowskiego Quay** (which is an extension of Oliwskie Quay) cargo loading and unloading. This harbor canal is also an entry way to the port,
- **Port Północny** (Northern Port) basin (2.5 km away from the coastline) which is the most extended into the sea part of the Port of Gdansk. It is located north-east from the main port facilities, close to Martwa Wisła, Stogi housing estate and the Gulf of Gdansk. As described by Kreft (1996), coal and liquid cargoes, e.g. crude oil, gasoline, and diesel and heating fuels are loaded and unloaded in the Northern Port.

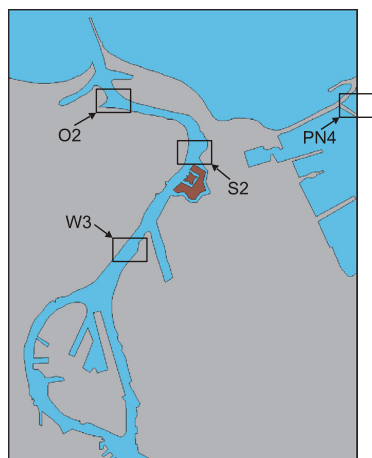


Fig. 1. Map of the Port of Gdansk where O1 denote sampling sites at Oliwskie Quay; S2 at Obrońców Poczty Polskiej Quay (also know as Siarkowe Quay); W3 at Wiślane Quay; and PN4 at Paliw Płynnych Quay.

MATERIALS AND METHODS

Sediments for analysis were collected in 1997 onboard r/v Dr Lubecki, a vessel belonging to Instytut Morski, from the following locations: Oliwskie Quay, Obrońców Poczty Polskiej Quay, Paliw Płynnych Quay and Wiślane Quay. In each location four cores of 100 to 140 cm length were extracted with a vibratory corer of 10-cm diameter. Cores were macroscopically examined (color, smell and admixtures) and split into 20-cm sections with a plastic spatula. For each core section the water content and loss on ignition were determined. Each section was split into two equal sub-samples; one sub-sample was used for granulometric analysis and the other for chemical analyses, in order to determine the content of labile and total forms of copper and zinc. Metal sieves of 2.00, 0.500, 0.125, 0.063 and 0.032 mm mesh size, and plastic sieves of 2.00, 0.063 and 0.032 mm mesh size were used for grain-size analysis and chemical analysis, respectively.

Labile forms of metals were separated via extraction of sediment fractions with 1M HCl (Luoma, Bryan 1981). Total concentrations of metals were determined by mineralisation of sediment samples with concentrated HF and HNO₃ in a microwave oven. Final determinations were performed by means of a Flame Atomic Absorption Spectrometry with a SpectrAA PLUS spectrometer (Varian).

RESULTS AND DISCUSSION

In total 919 samples were analyzed from the Port of Gdansk. The most abundant sediment type observed in the samples was small-grained sand with

infrequent lamellae of mud and clay. This sediment structure indicates that multiple, active processes of mechanical mixing have taken place, most likely in connection with the deepening and extension of specific harbor canals. An increased content of organic matter was associated with higher metal contents in the port sediments. The most abundant sediment type contained 10% organic matter, and was characterized by the highest metal concentrations. The lowest metal concentrations were found in sediments containing less than 1% organic matter, indicating a close affinity of labile forms of metals to organic matter (Dembska et al. 2001a). Additional analyses showed a strong correlation ($r = 0.79$, $p < 0.05$) between the water content and organic matter content in the sediments. This relationship became prominent in the sediments with very variable water contents (i.e. 2.5 – 85.3%), as previously reported by Fergusson (1990).

Sequential analysis of the sediments by the Tessier method (Tessier et al. 1979), estimating the amount of metal bound to different sediment size fractions, showed that in the <2.00 mm fraction 60% of copper was bound to organic matter, 14% to carbonates, about 5% to each of hydrated iron and manganese oxides, with some present in the exchangeable form. The immobile form of copper amounted to 16% of the total and was most likely bound to aluminosilicates (Fig. 2) (Dembska et al. 2001b).

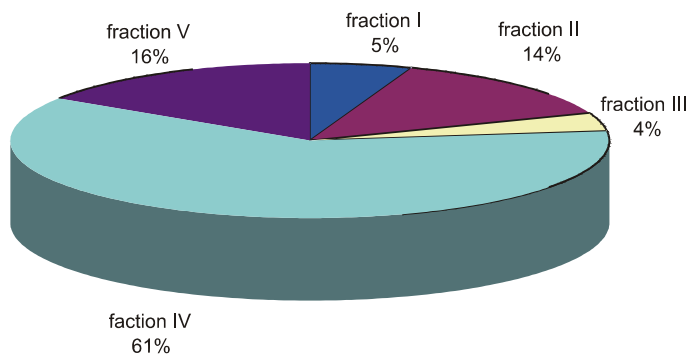


Fig. 2. Percentages of specific forms of copper in benthic sediment from Szczecińskie Quay. Core I: form I is exchangeable, form II bound to carbonates, form III bound to hydrated Fe-Mn oxides, form IV bound to organic matter, and form V bound to aluminosilicates (Dembska et al. 2001b).

Zinc was present in significant amounts in all the determined forms (as exchangeable, and bound to carbonates, hydrated iron and manganese oxides, organic matter, and aluminosilicates) (Fig. 3). It was predominantly bound to

aluminosilicates (ca. 38%) and carbonates (35%), with other forms constituting from 6 to 14% of the total. The content bound to organic matter was only 6%. Labile forms were primarily bound to carbonates, therefore under suitable conditions the metal might be released into the water column (Dembska et al. 2001b).

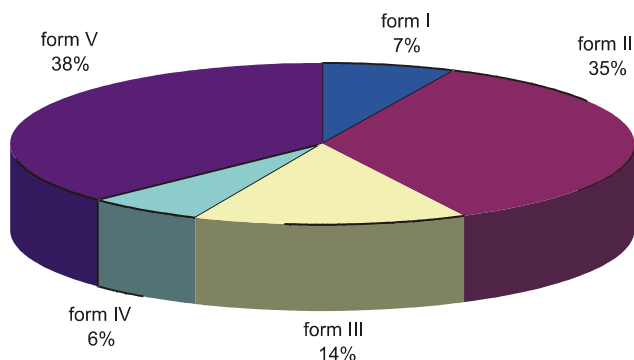


Fig. 2. Percentages of specific forms of zinc in benthic sediment from Szczecińskie Quay. Core I: form I is exchangeable, form II bound to carbonates, form III bound to hydrated Fe-Mn oxides, form IV bound to organic matter, and form V bound to aluminosilicates (Dembska et al. 2001b).

Washing out of metals from sediment was rather localized, with areas closest to the quays being most active. Moreover, a tendency of decreasing metal concentrations with increasing depth was observed in some cases. This was true of concentrations of both labile and total copper in the <2.00 mm size fraction of sediments collected from Wiślane and Obrońców Poczty Polskiej Quays. A similar pattern was observed for the labile form of zinc from Wiślane, Obrońców Poczty Polskiej and Oliwskie Quays, and for its total form in samples collected at Wiślane Quay. Considering that the analyzed sediments are relatively recent this decreasing trend has not been treated as an indicator of the lower environmental contamination of an earlier time (Bolalek et al. 1999). Rather, it is considered to be the result of strong binding of metals with the sediment, as under reducing conditions sulfides can form stable compounds with metals (Papai 1995).

The analyses of distribution of copper and zinc concentrations in the Port of Gdansk (Table 1) show that the sediments from Wiślane and Oliwskie Quays have the highest concentrations of labile and total forms of these metals (Fig. 4); both quays are highly industrialized and heavily exploited. The lowest copper

Table 1

Concentrations of labile and total forms of copper and zinc (mg kg^{-1} d.w.) in sediments from different quays in the Port of Gdansk

Metal	Statistical parameters	Wiślane Quay		Oliwskie Quay		Siarkowe Quay		Paliw Płynnych (Liquid Fuels) Quay	
		labile	total	labile	total	labile	total	labile	total
Cu	N	18	5	27	22	20	14	16	12
	Mean [mg kg^{-1} DW]	25.07	32.80	5.57	16.08	1.74	4.41	6.14	7.92
	Minimum [mg kg^{-1} DW]	0.70	0.94	0.10	1.00	0.10	0.61	1.30	1.77
	Maximum [mg kg^{-1} DW]	85.30	130.5	21.00	124.85	7.20	14.41	25.30	23.72
	SD [mg kg^{-1} DW]	25.01	56.01	5.25	26.52	2.18	4.57	6.97	7.38
Zn	N	18	5	26	21	16	13	20	12
	Mean [mg kg^{-1} DW]	89.92	115.46	21.87	58.76	11.46	24.79	8.59	18.91
	Minimum [mg kg^{-1} DW]	1.00	1.12	0.80	3.05	0.50	2.61	0.80	0.99
	Maximum [mg kg^{-1} DW]	339.20	333.74	117.80	281.53	67.90	49.10	49.10	50.61
	SD [mg kg^{-1} DW]	100.61	158.51	31.55	71.11	17.87	21.46	14.02	18.18

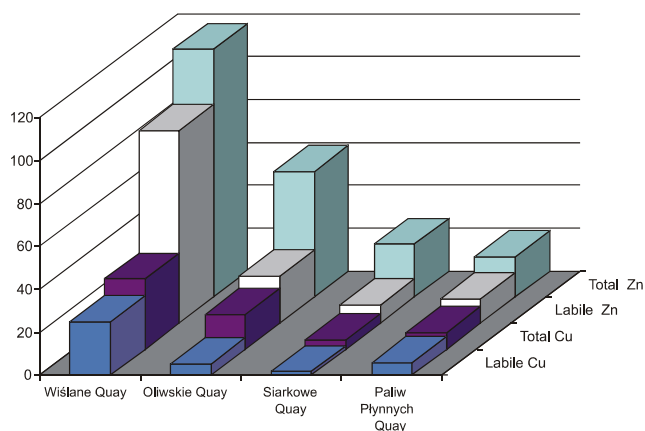


Fig. 4. Comparison of the concentrations (mg kg^{-1} d.w.) of labile and total forms of copper and zinc in the <2.00 mm size fraction of sediments from different quays in the Port of Gdansk.

and zinc concentrations were determined in the sediments from Obrońców Poczty Polskiej and Paliw Płynnych Quays.

Additional factors that can indirectly influence the horizontal distribution of elements are dynamic environmental conditions and the granulometric composition of the sediments (Dembska et al. 2001a).

Distribution of copper and zinc in specific sediment layers is variable; this variability depends largely on the grain-size distribution of the sedimented

material. Of the <2.00 mm size fraction the 2.00-0.063 mm fraction was (92.84%), followed by the 0.063-0.032 mm fraction (5.39%), with the <0.032 mm fraction present in the smallest amount. The highest concentrations of metals were found in the <0.032 mm fraction, followed by the 0.063-0.032 mm fraction (Table 3).

Table 3

Concentrations (mg kg⁻¹ d.w.) of labile and total forms of copper and zinc in specific size fractions of sediments from the Port of Gdansk

Metal	Statistical parameters	Grain size fraction [mm]							
		< 0.032		0.063-0.032		2.00-0.063		< 2.00	
		labile	total	labile	total	labile	total	labile	total
Cu	N	48	5	76	61	78	63	81	53
	Mean [mg kg ⁻¹ DW]	43.93	149.01	33.80	52.13	8.90	13.46	9.06	12.73
	Minimum [mg kg ⁻¹ DW]	5.40	86.81	3.90	6.21	0.10	0.29	0.10	0.61
	Maximum [mg kg ⁻¹ DW]	189.60	231	200.50	260.00	105.10	158.17	85.30	130.50
	SD [mg kg ⁻¹ DW]	21.18	59.25	41.32	61.00	17.30	25.25	15.12	24.69
Zn	N	48	1	76	57	77	64	80	51
	Mean [mg kg ⁻¹ DW]	138.23	505.57	83.68	143.70	24.27	44.25	31.78	46.28
	Minimum [mg kg ⁻¹ DW]	18.6	507.57	3.20	12.02	0.30	1.13	0.50	0.99
	Maximum [mg kg ⁻¹ DW]	618	507.57	534.70	684.47	336.10	423.29	339.2	333.74
	SD [mg kg ⁻¹ DW]	176.45	-	121.26	172.46	49.79	72.19	60.30	71.13

where SD is a standard deviation

The highest loads of metals were accumulated in the 2.00-0.063 mm size fraction, i.e. for copper it was 69 and 76% of total and labile form, respectively, and for zinc 72 and 77% (Fig. 5). The lowest load of metals was found in the <0.032 mm fraction, i.e. 15 and 7% of total and labile form of copper, respectively, and 8% of labile zinc. One exception was the total content of zinc for which the lowest percentage share (13%) occurred in the 0.063-0.032 mm size fraction. The <0.032 mm fraction constituted only 1.77% of total collected material therefore it has to be assumed that larger size fractions (2.00-0.063 mm) contain the main pollution load. Based on this finding, the recommendation can be formulated that metal concentrations should be determined in the <2.0 mm fraction, which contains both large-particle fractions and silt. Such determinations would most reliably reflect the real pollution load in the sediment (Dembska et al. 2001a).

The percentage share of labile forms in the total content of metal was also determined in the collected sediment samples. In the <0.032 mm fraction 29.48 and 27.34% of the total contents of copper and zinc, respectively, were labile

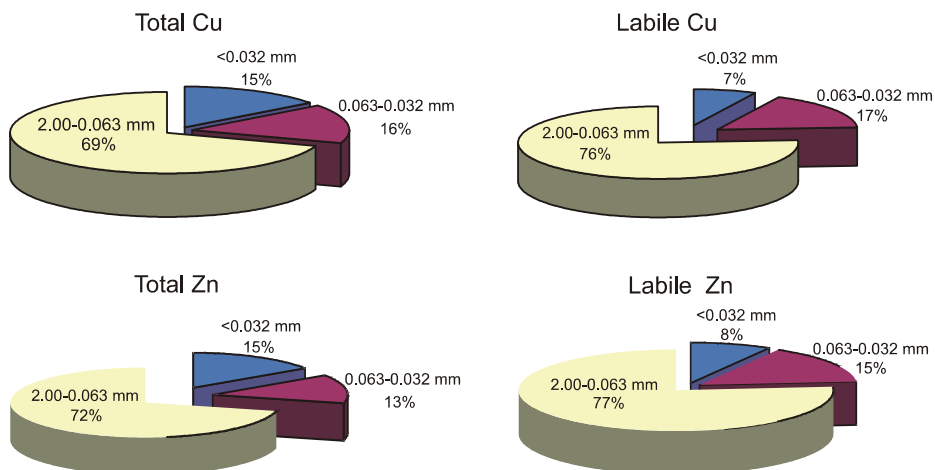


Fig. 5. Load (as %) of total and labile forms of copper and zinc in specific size fractions of the sediment.

forms. In the 2.00-0.063 and 0.063-0.032 mm fractions, labile forms of copper constituted about 65%, with labile zinc forms about 56% (Fig. 6).

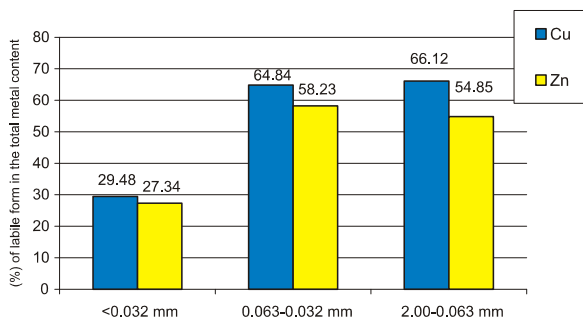


Fig. 6. Percentage share of labile forms of the total content of copper and zinc in sediments from the Port of Gdansk.

The determined values were compared to the recommended indicators for the labile forms of the metals in the <2.00 mm size fraction (Dz.U no. 55, pos. 498) and the appropriate indicators for total forms (HELCOM 1993) (Table 3). The obtained mean concentrations along the vertical and horizontal distribution profiles were lower than those admissible by Polish standards. The analyzed material can therefore be considered, with high probability, as not being contaminated with regard to copper and zinc contents.

Table 2

Comparison of mean concentrations (mg kg^{-1} d.w.) of labile and total forms of copper and zinc in the <2.00 mm size fraction of sediments from the entire area of the Port of Gdansk

Metal	Statistical parameters	Labile form	Total form	Required indicator acc. to Dz. U. no 62 pos. 498 for labile form	HELCOM's indicator for total form
Cu	N	81	53	150	40
	Mean [mg kg^{-1} DW]	9.058	12.73		
	Minimum [mg kg^{-1} DW]	0.10	0.61		
	Maximum [mg kg^{-1} DW]	85.30	130.50		
	SD [mg kg^{-1} DW]	15.12	24.69		
Zn	N	80	51	1000	350
	Mean [mg kg^{-1} DW]	31.79	46.29		
	Minimum [mg kg^{-1} DW]	0.5	0.99		
	Maximum [mg kg^{-1} DW]	339.2	333.74		
	SD [mg kg^{-1} DW]	60.30	71.13		

where SD is a standard deviation

SUMMARY

Sediment samples were collected with a vibratory corer in 1997 and 1998 from four areas of the Port of Gdansk: Wiślane Quay, Obrońców Poczty Polskiej Quay, Oliwskie Quay, and Paliw Płynnych Quay. Samples were split into four grain-size fractions, i.e. <2.00 , $2.00-0.063$, $0.063-0.032$ and <0.032 mm. These sediments consist of small-grained sand with a low admixture of silt, with the dominant size fraction being $2.00-0.063$ mm. The highest concentrations of copper and zinc were observed in <0.032 mm fraction, implying active sorption on silt minerals.

Copper and zinc in this environment are primarily of anthropogenic origin. The sediment surface layer (0-20 cm) was the most variable in regard to the concentration of the metals. This phenomenon is postulated to result from mechanical mixing due to passage of ships and dredging of canals. Sediment samples from Wiślane and Oliwskie Quays, the most industrialized port areas, contained the highest concentrations of copper and zinc. However, all the sediments tested contain copper and zinc in concentrations lower than the indicator values recommended by the Polish Ministry of the Environment and HELCOM.

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