

Sediments in the Szczecin Lagoon: Selected elements and macrozoobenthos

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Introduction

The Szczecin Lagoon (Oderhaff) is strongly affected by anthropogenic activities - industry, shipping trade, agriculture and tourism. In this area, investigations are carried out since many years, but there were still a lot of unrecognized problems e.g. geochemistry and mineralogy of sediments and suspended matter. An important task is the investigation of concentrations of heavy metals and other contaminants in the water and the bottom sediments and their impact on the environment.

The investigations of sediments and macrozoobenthos were carried out within the GOAP project throughout 1994-97. Investigations of sediments in Szczecin Lagoon were carried out in close cooperation of the University of Greifswald (Germany) and the University of Szczecin (Poland). From the University of Greifswald Reinhard Lampe, Hinrich Meyer (Institute of Geography), Jürgen Eidam (Institute for Geosciences) participated and from the University of Szczecin, (Institute of Marine Science) Stanislaw Musielak, Andrzej Osadczuk, Krystyna Osadczuk, Brygida Wawrzyniak-Wydrowska, Zbigniew Piesik, Henryk Majewski were included.

Methods

Sediment samples were collected from both parts of the lagoon (Grosses Haff and Kleines Haff, [Fig.1](#)). Sampling sites were located by GPS Trimble Navigation. The samples were taken only from the uppermost layer of the bottom sediments (0-5 cm). 88 samples from both parts of the lagoon were examined geochemically, granulometric analyses were carried out in 99 samples from Grosses Haff. Some samples were examined mineralogically.

Grain-size analysis of sediments was performed by wet screening (Fritsch set) after H₂O₂ treatment. The fine-grained fraction (< 63 μm) was analysed by means of a laser particle sizer after H₂O₂ treatment, too. Some important grain-size parameters were calculated using a graphical method and the formulas according to Folk & Ward (1957).

The fraction below 63 μm was intended to geochemical and mineralogical analyses. The results of the chemical analyses of this fraction were recalculated to the complete sediment mass, taking into consideration the amount of this fraction in the whole sample. Contents of calcium carbonate were determined by the Scheibler method. Bio-silica contents were determined by spectrophotometric methods using UV/VIS SPECTROMETER PERKIN ELMER LAMBDA 12/2.0 nm. The amount of organic matter was estimated as loss on ignition (550 °C) and C_{org} (using a CHN-analyzer). Contents of sulfur were determined by the thermal analyser METALYT CS 100/1000. The determination of main and trace metals was carried out by ICP methods after 0,5 N HCl leaching. These analyses were made in the laboratories of E-M-A-University of Greifswald. A sequential extraction of metals from silty sediments was made in the laboratory of the Institute of Ecology in Police, using a method described by Tessier et al. (1979). Laser analysis of particle size was made in the Institut für Ostseeforschung, Warnemünde and in the Geological Institute in Sopot. Mineralogical investigations were carried out in the University of Szczecin by use of polarizing and electron microscopy, electron microanalysis, derivatography and X-ray diffraction.

All maps were performed with SURFER for Windows, Golden Software, Inc. For an interpretation and presentation of the results such other software were used as: EXCEL[®] Microsoft Corporation, GRAPHER[®] Golden Software,

Results

Sediments

Based on the amount of the $63\mu\text{m}$-fraction in the sediment samples, four granulometric sediment types were separated: silts, sandy silts, silty sands and sands. The map of the sediment distribution is presented in Fig. 2. Silts and sandy silts together cover 54 % of the bottom surface (that are ~360 km²). These sediments are located in deeper parts of the lagoon, below 3,5 meters in general, but in some parts of the basin with depths below 5-6 m we observed also sandy silts, mainly in the trough between Grosses and Kleines Haff, Fig. 2a. Silty sediments of the Grosses Haff are poorly and very poorly sorted. Sands are usually medium or poorly sorted. The granulometric features show a sedimentary environment of higher dynamics characterized by frequent resuspension and redeposition. In the northern part of the Grosses Haff we observed significant influences of the sea backwaters. The sandy sediments predominate here. In the central and southern part of the Grosses Haff deposition occurs under dominant influence of river transport. Silty sediments predominate here, but in the nearshore zone.

The main mineral constituents of silts are fine grains of quartz (more than 50% usually). Very important constituents of silts are detrital calcite (scraps of the shells of molluscs and Ostracoda), amorphous silica (diatoms) and amorphous organic matter as well. A lot of Ostracoda shells were found in the samples from stations 4, 13, 16, 18, 21, 44 and NW. They amounts to more than ten percents. In the samples from stations 49, 54, 56, 66 and R, shells of Ostracoda were not noticed.

Investigations conducted by use of X-ray diffraction and electron microscopy show also small amounts of such minerals as pyrite, dolomite, some clay minerals (illite, kaolinite, saponite, stilpnomelan), allophanes, iron and manganese oxides (hematite, goethite, manganosite, bixbyite) and sulphates (gypsum, anhydrite, bassanite, rozenite), some phosphates (taranakite, arrojadite, dickinsonite) and heavy minerals (amphiboles, pyroxene, garnets). Peculiar forms of pyrite were observed under the electron microscope. Similar framboidal forms of pyrite were noticed in the sediments of Venice Lagoon by Frizzo et al. (1991) and Bertolin et al. (1995). Characteristic constituents of silts are amorphous (non-crystalline) micro-grains of allophanes which are considered by Stoch (1974) as initial stage of clay minerals (Fig.3). The presence of iron in the composition of these mineral substances point out ferri-allophanes. In some samples of silts idiomorphic grains of gypsum were observed (Fig. 4). The idiomorphic forms of these grains suggest their authogenic origin, but we can not exclude an industrial waste heap of phospho-gypsum in the nearby chemical plant "Police" as a source of these minerals. Some parts of the heap material can be blown away to the Odra river or directly to the Szczecin Lagoon. The investigation of Odra river sediments nearby this heap, carried out by Niedzwiecki et al. (1993) showed also the possibility of eluate infiltration from the heap to the Odra. Rydzynski (1987) emphasized the significant influence of the uncontrolled pollutant load from the chemical plant on the chemism of the bottom sediments of the Szczecin Lagoon.

Table 0a. Chemical composition of silts selected from different part of Szczecin Lagoon

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	S	sum
	%	%	%	%	%	%	%	%	%	%	%	%
13	65,50	8,30	3,10	13,30	1,60	0,23	1,50	1,60	0,50	0,31	1,16	97,10
74	61,20	10,50	5,00	9,80	2,00	0,20	1,70	1,60	0,66	0,35	1,12	94,13
62	66,70	9,70	6,15	7,80	1,90	0,26	2,90	1,10	0,52	0,25	1,40	98,68
252	59,60	8,30	4,50	15,50	2,20	0,27	3,30	1,20	0,61	0,23	1,24	96,95

>From the chemical point of view, main constituents of silty sediments are silica, calcium carbonate and organic substances. Silts are usually composed of about 60 % of silica. Some parts of the total amount of silica in silts originates from diatoms (organic silica). The content of calcium carbonate varies in a broad range, from 0,6% to 32,2% - depending on the sample location. The least amounts of CaCO₃ were observed in the north-eastern part of

the Grosses Haff (Fig. 5). Organic silica occurs in various quantities, from 0,7% to 13,5%. The highest concentration of $\text{SiO}_{2\text{org}}$ was found in the south-western part of Grosses Haff, including the area of the trough between both parts of Oderhaff (Fig. 6).

Table 0b . Content of main chemical constituents in fraction below 63 μm of sediments from Szczecin Lagoon

	Fraction <63 μm	LOI	CaCO_3	SiO_2 org.	S	C	C org.	N	H	Mg	Ca	Fe	Al	P
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
SANDS														
n	17	15	12	14	10	16	11	16	5	15	15	15	15	15
min.	0,1	0,6	1,5	0,69	0,38	0,15	0,59	0,01	0,23	0,02	0,07	0,16	0,07	0,01
max.	49,1	27,6	32,2	9,12	4,07	13,6	11,22	1,38	1,25	0,56	7,70	3,92	1,56	0,27
mean	22,0	14,4	12,0	4,5	1,5	6,6	5,9	0,6	0,8	0,3	2,5	2,2	0,8	0,1
median	25,3	13,8	12,9	4,6	1,2	6,6	5,7	0,7	1,0	0,4	2,8	2,0	0,8	0,1
st.dev.	17,4	10,6	9,9	2,8	1,1	5,3	4,0	0,5	0,4	0,2	2,4	1,3	0,6	0,1
SILTS														
n	71	71	71	70	68	71	71	71	24	71	71	71	71	71
min.	53,1	13,8	0,6	3,1	0,58	5,31	4,66	0,48	0,33	0,29	0,79	2,02	0,62	0,05
max.	98,7	35,2	31,8	13,5	4,88	14,4	12,28	1,57	1,80	0,64	10,36	5,67	2,27	0,57
mean	84,9	23,3	17,5	6,5	1,9	11,2	9,1	1,1	1,0	0,5	4,1	3,3	1,4	0,2
median	88,0	23,3	19,0	6,1	1,8	12,0	9,3	1,2	1,0	0,5	4,3	3,2	1,4	0,2
st.dev.	11,3	4,4	7,9	1,6	0,7	2,1	1,7	0,2	0,5	0,1	1,3	0,6	0,3	0,1

The amount of organic matter in silts is different. Loss on ignition of samples of silty sediments ranges from 13,8% to 35,2% and the contents of organic carbon in silts range from 4,66% to 12,3%. The relationship between organic carbon and the loss on ignition can be described as:

$$C_{\text{org}} = 0,887 + 0,354 \cdot \text{LOI}.$$

The highest concentrations of organic matter in silts are observed in the south-western part, the least in the north-eastern part of the Grosses Haff (Fig. 7). The C/N ratio indicates a polygenic character of the organic substances in the sediments of the Szczecin Lagoon. In the Kleines Haff authogenic (C/N usually below 8) while in the Grosses Haff allogenic substances predominate (C/N over 9 generally). The highest C/N ratio (10-11,5) we have noticed in the vicinity of the Odra river mouth (Fig. 8).

There are very specific distributions of phosphorus and manganese; the highest concentrations of these elements in sediments we observed along the shipping channel and in the trough between Grosses and Kleines Haff. The Spearman rank correlation show a strong relationship between the occurrence of these elements (Tab. 1).

Tab. 1 Spearman rank correlation of chemical constituents of bottom sediments from Szczecin Lagoon

Iron was found in sediments in significant quantities. Its concentration vary from 2,02% to 5,67% in silts and from 0,16% to 3,92% in sands. The highest concentration of iron we observed in the Grosses Haff, especially in those parts where fine-grained silts are located. Iron can be bound with various chemical phases in the sediments of the Szczecin Lagoon: oxides (hematite), hydroxides (goethite), sulphides (pyrite), sulphates (e.g. rozenite) and phosphates (e.g. arrojadite). It depends, among other things, on the redox conditions.

Sulphur, like iron, can be bound with various phases. A S-Fe correlation coefficient of $r=0,48$ indicates that apart sulphides, sulphur can be bound with other chemical phases, for example sulphates. Low concentration of sulphur in the south-western part of Grosses Haff, where the concentration of iron is high, seems to confirm this.

The distribution of trace metals is very characteristic; the highest concentrations of such metals as [zinc](#), [lead](#), [copper](#), nickel, cobalt and chromium are located in the south-western part of the Grosses Haff. In the same area we detected also the highest quantities of organic matter in the sediments. Spearman rank correlations confirm the relation between the occurrence of trace metals and organic matter ([Tab. 1](#)). In the case of lead, we found high concentration also in the Kleines Haff. The lowest concentrations of trace metals we observed in the north-eastern part of the Grosses Haff.

In the bottom sediments of Szczecin Lagoon we noted especially high concentrations of such metals as [zinc](#) and [lead](#). The mean concentration of lead in silty sediments (161 ppm) is 10 times, the mean zinc concentration (737 ppm) is 8 times and the zinc concentration in silts of south-western part of the Grosses Haff is even 14 times higher than the Clark value of earth's crust. Concentrations of other metals in the sediments of the Szczecin Lagoon are comparable to their Clark concentrations (Winogradow 1962).

The average concentrations of zinc and lead in the silty sediments of the Szczecin Lagoon are several times higher than their concentrations in the sediments of such typical lagoons as Aveiro (Portugal), Piratinga (Brazil) or Chilka (India) (Gomes & Delgado 1993, Huang et al. 1984, Panda et al. 1995). When compared with sediments from Kuršiu Marios Lagoon, the average concentration of zinc in the sediments of the Szczecin Lagoon is over 20 times, the concentration of lead 10 times higher (Pustelnikow et al. 1983). On the other hand, the concentration of zinc in sediments of the Szczecin Lagoon is comparable to its concentration in silts from lagoons under strong anthropopression e.g. Venice Lagoon (Menegazzo et al., 1989). The level of concentration of other trace metals (Cu, Ni, Co, Cr) in the sediments of the Szczecin Lagoon is similar to other lagoons.

Results of sequential extraction of metals show that the metals are bound in various chemical phases to different extent ([Fig. 9](#)). Such metals as copper, nickel, cobalt and chromium are bound first and foremost to the residual fraction. Such metals as iron, manganese and zinc are bound mostly to the oxides fraction. Lead is connected with the organic fraction as well as the oxides fraction. Therefore metals fixed to oxides (Mn, Fe, Zn) and organic substances (Pb) can be easily released under changing redox conditions. Metals bound to residual fraction - first of all Cu, Cr, Co, Ni - can not be remobilized.

To interpret the geochemical results factor and cluster analyses were performed. Using principal component method we obtained three main factors which explain 74% of variance. First factor shows high loadings for organic matter and trace metals. Second factor has high loadings for calcium carbonate, manganese and mainly lead. Third factor has high loadings for iron and sulphur. The highest values of the first "organo-metallic" factor we find in the south-western part of the Grosses Haff, ([Fig. 10](#)). The highest values of the second "carbonate" factor we observe in the Kleines Haff and the highest values of the third "sulphuric" factor in north-eastern part of Grosses Haff.

Using the tree diagram of geochemical similarity resulting of cluster analysis we can distinguish two main groups of sediments (A and B) and some subgroups ([Fig. 11](#)). Taking into account the results of the factor and cluster analyses we are able to separate four types of sedimentary geochemical facies in the Szczecin Lagoon ([Fig. 12](#)):

facies B (B1+B2) - with high contents of organic matter, amorphous silica and heavy metals;

facies A1a+A2 - with very low contents of organic matter, amorphous silica, heavy metals and calcium carbonate;

facies A1b1 - transition between B and A1a+A2 (intermediate quantities of above-mentioned constituents);
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facies A1b2 - rich in calcium carbonate, manganese and lead.
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There is a noticeable clear interdependence between the geochemical variability of the sediments and the specific cellular water circulation in the Szczecin Lagoon ([Fig. 13](#)). We may suppose that the geochemical variation of the

sediments is caused by processes of resuspension, sorption and resorption as a consequence of the strong and specific hydrodynamics of the Szczecin Lagoon.

Macrozoobenthos

The Szczecin Lagoon, similarly to other parts of the River Odra estuary, has a complicated hydrology and is strongly affected by anthropogenic factors, pollution and eutrophication in particular. Excessive amounts of pollutants and nutrients, introduced into the Lagoon mainly by the Odra (from Poland, Germany, and Czech Republic) have contributed to a number of physico-chemical changes, observed in the area since the 1960s. The changes involved alteration of the pH, strong hyperoxygenation, as well as qualitative and quantitative changes among the aquatic communities (plankton, benthos, fish fauna) (e.g. Drzycimski 1986; Gizinski et al. 1980; Kompowski, Pienkowski 1986; Piesik 1992). Macrozoobenthos is an ecological entity useful in observations of biotic changes in an aquatic system, for which reason it has been selected as an object of comparative studies in the Grosses Haff, the largest area of the Szczecin Lagoon.

Macrozoobenthos of the Grosses Haff was sampled in June and July 1994. The samples were collected from 21 sites with a 635 cm² Van Veen grab. Two grabs per sites were retrieved; the sediment was sieved through a 1 mm mesh size sieve and the organisms retained were fixed in 4% formaldehyde. The animals were sorted, identified, and enumerated, the abundance being expressed as no. of individuals per 1 m² bottom area. Biomass was calculated by weighing the animals, after the external water had been removed by blotting, and referring the weights to 1 m² bottom area.

The samples were found to contain representatives of a total of 11 macrozoobenthic taxa, including the Nematoda, Oligochaeta, Hirudinea, Amphipoda, Diptera (larvae and pupae), and Lamellibranchia. Of all taxa found, only two (the Tubificidae and larval Chironomidae) were of a considerable importance in terms of abundance and biomass (Tab. 2, 3), indicative of a substantial eutrophication of the Lagoon. Other taxa occurred only rarely and in low numbers. The bivalve *Dreissena polymorpha* occurred at 2 out of the 21 (frequency F = 9.5%) sampling sites only. This results from the fact that favourable conditions for its life (sand, sand with mud or with shell debris) occurred only there.

The dominant chironomid larvae occurred at all the sites, regardless of the sediment type (F = 100%). The densities were unevenly distributed over the area and ranged widely from site to site (from about 190 to 15000 ind./m², Tab. 2). The chironomid larvae dominated also the macrozoobenthos biomass (Tab. 3) in the Lagoon (excluding biomass of Bivalve). Biomass values (wet weight) were found to vary along with the sediment type. Additionally, the biomass was found to increase along the south-north gradient in the Lagoon (Tab. 4).

Table 4. Summer biomasses (wet weight) of dominant macrozoobenthic taxon in the Grosses Haff (Szczecin Lagoon) in 1987, 1988, and 1994.

Year		Chironomidae larvae: wet weight [g / m ²], Grosses Haff			
		Southern part	Central part	Northern part	x
1987	*	11,92	4,42	2,97	6,64
1988	*	42,34	41,35	19,19	34,29
1994	**	16,77	19,29	39,85	25,3
		Oligochaeta: wet weight [g / m ²], Grosses Haff			
1987	*	5,04	1,75	1,83	2,87
1988	*	6,73	6,59	2,95	5,42
1994	**	12,53	3,40	1,94	5,96

* data of Wolnomiejski and Grygiel (1992), ** this study

The oligochaetes were represented by the Tubificidae. Tubificids proved to be a density and biomass subdominant of the macrozoobenthic assemblages studied. The frequency of occurrence was very high (85.7%), the densities varied widely from 0 to 6000 ind./m². Mean densities decrease along the south-north gradient. A similar gradient was detected in the biomass (Tab. 4).

The qualitative poverty of the macrozoobenthic communities studied, accompanied by a marked domination in abundance and biomass of two taxa only is a clear indication of the strong eutrophication of the Grosses Haff, similarly to other parts of the Lagoon and the entire Odra estuary (Hensel 1994; Wolnomiejski, Grygiel 1989, 1992, 1994; Gizinski et al. 1980; Masłowski 1992; Ochman et al. 1989; Czarnecki 1993). The eutrophication, increasing since the 1960s, brought about strong blooms of toxic cyanobacteria of the genus *Microcystis*, the genus dominating the phytoplankton in warmer seasons since 1983. This has caused negative effects in animal communities of the area (Piesik 1992). The abundance of oligochaetes and chironomid larvae increased considerably over that time. Table 5 represents quantitative data concerning the two taxa, collected since the 1950s. Compared to the '50s (Wiktor 1954, 1962), chironomid density increased 13-fold by 1975/76 (Gizinski et al. 1980); compared to 1984 the density was 24 times higher (Masłowski 1992). The mean chironomid density in 1986 was lower than that in the '50s to grow again and stabilise at the level of over 2000 ind./m² in the 1990s (Tab. 5). Comparing data from 1994 to the earlier data (from literature) concerning the bottom macrofauna of Szczecin Lagoon, it can be seen that no essential changes occurred in the composition of species; only qualitative changes are stated.

Table 5 Quantitative changes of the dominant macrozoobenthic taxa in the Szczecin Lagoon in different years

Reference year of study	Wiktor J., K. Wiktor (1954)	Wiktor (1962)	Gizinski et al. (1980)	Maslowski (1992)					Wolnomiejski, Grygiel (1992)				This Study
	1951	1954	1975-1976	1984	1985	1986	1987	1988	1987	1988	1989	1990	1994
Chironomidae larv.	205	215	2858	4989	4686	153	477	1816	976	2426	1572	2321	2789
Oligochaeta	62	101	4541	15498	7931	1488	659	1486	875	1794	4191	4591	1712

Using cluster analysis four main benthos communities were distinguished (Fig. 14). These communities correspond to of different part of the Szczecin Lagoon bottom. Plotting these groups from the original sampling sites shows that there is a clear gradient from the south to the north of the Lagoon (Fig. 15). Stations of group A are located in the southern part of the area which is the most extensively influenced by freshwater (Oder flows into the lagoon). The total number of taxa in this group was the highest (ranged from 2 to 8) when compared to stations of group B, C and D (it is single station). This group consisted mainly of Tubificidae, within this group *Dreissena polymorpha* was found. About 1 to 4 taxa were found per stations of group B. The taxa compositions is quite similar between sites. They are more similar to each other than stations of group A, C and site D. This group is characterised by the lowest density of organisms with a main taxon of Chironomidae. These stations were located mainly in the west-central part and the north-eastern part of the lagoon. In this group the mean biomass was also very low (excluding Bivalve).

Stations of group C are located mainly in the east-central part of the lagoon. Within this group the number of taxa was from 2 to 5. This group was characterised by a high density and biomass of Chironomidae and Tubificidae. A single station D is a little different from the others with its highest density and biomass of organisms. The highest density was recorded in Chironomidae. This station differs from the other groups of the most northern location, the lowest depth and the type of sediment (sand). On this site the highest biomass was recorded including and excluding biomass of *D. polymorpha*.

The community (group A, B, C and D) distribution reflected abrupt changes in environmental condition such as bottom sediment type (silt content and mean grain size), depth, organic content (C org.), heavy metals (Zn), P, CaCO₃ and SiO org. content. The highest value of this parameters were observed in group A (without depth), which is most extensively influenced by freshwater when compared to other groups. The lowest values were in station D (excluding P and CaCO₃) which is most influenced by salty water.

Conclusions

We can establish four different sedimentary areas in the Szczecin Lagoon:

- south-western part of Grosses Haff, where sedimentation is under the strong influence of Oder river input and its pollution;
- north-eastern part of the Grosses Haff, where sedimentation is under the prevailing influence of sea water;
- Kleines Haff, with relative stability of sedimentary processes as consequence of balanced sea and river influences;
- area of shipping channel in Grosses Haff, where natural sedimentary processes are strongly disturbed by navigation of big boats and dredging of channel.

The distribution of these areas reflects the specific hydrodynamics of Szczecin Lagoon which results from mixing of fresh and salt water in the shallow water basin. The main factor affecting the chemistry of sediments is the Odra river load.

The macrozoobenthos communities reflect changes in environmental condition such as sediment type (silts or sands), chemistry of sediments, depth and location towards Odra river mouth.

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