

An Attempt of Heavy Metals Load Estimation During Sedimentation of Sludges in the Szczecin Lagoon

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1. Introduction

Heavy metals, diluted in water, are usually in ionic or colloidal form. They are partly taken in by water organisms into their cells and tissues and partly absorbed by inorganic particles in suspension. Organic matter, released into water after the decay of bacteria, plants and animals containing a certain amount of heavy metals absorbed earlier can additionally absorb more metals from the water. With time organic and inorganic suspension falls down forming bottom sediments. Although a certain amount of heavy metals can be released into water in this process, a considerable amount of them is deposited in bottom sediments permanently. Many authors used bottom sediments to study to what extent the development of industry and other kinds of human activities have disturbed the heavy metal cycle in nature.

Bottom sediments section shows a clear increase of heavy metals content beginning with the deepest layers (the oldest) – to the surface ones (the newest). This phenomenon was recorded in many parts of the world e.g. the North Sea (Försttner and Reineck 1974) the Baltic Sea (Suess and Erlenkeuser 1975) and the Szczecin Lagoon (Protasowicki et al. 1993).

In the accessible literature there is not much information about the load of heavy metals transported during sedimentation process in the Szczecin Lagoon, what was the reason for undertaking this research. Our purpose was an attempt to determine the load of heavy metals in the sedimentation process in this area, belonging to the Odra estuary.

2. Materials and methods

The material falling down on the bottom of the Szczecin Lagoon was collected by collectors which were placed for 4 months, from July to November 1992 in 5 places: 1 – border buoy, 2 – I Brama Torowa, 3 – II Brama Torowa, 4 – navigation sign, 5 – Chełminek (Fig. 1). The collector funnel (Fig. 2) was 232 cm² in area and was about 35 cm above the bottom.

In the collected material the content of heavy metals - Hg, Cd, Pb, Cu, Zn, Cr, Ni, Fe and loss on ignition were determined. Prior to heavy metal determination, the samples were burnt in a mixture of nitric and perchloric acids (Adrian 1971, Protasowicki et al. 1999). Chemical elements were analysed by the method of atomic absorption spectrometry (AAS), mercury by means of the cold vapour technique (CV AAS) and other metals after atomization by air-acetylene flame (FAAS). All the determinations were made in three parallel replications and relative error was below 5%.

3. Results and discussion

Detailed results of the studies on the content of heavy metals and the loss on ignition in the material collected after 4 months are presented in Table 1.

Table 1. The content of heavy metals in the sediments collected in the Szczecin Lagoon
Tabela 1. Zawartość metali ciężkich w osadach pobranych z Zalewu Szczecińskiego

Place*	Content, µg·g ⁻¹ dry weight								Loss on ignition, %
	Hg	Cd	Pb	Cu	Zn	Cr	Ni	Fe	
1	0.636	3.336	81.5	33.6	551	13.9	10.2	23730	14.01
2	0.476	2.035	35.8	29.0	299	11.4	13.6	6490	11.18
3	0.838	4.556	335.0	59.8	1427	20.0	22.9	31330	18.69
4	0.684	2.754	46.3	37.8	318	11.0	12.4	20570	15.22
5	1.324	6.227	97.6	65.1	678	27.1	20.1	16160	18.24

* see "material and methods" and Fig. 1.

The data show a certain differentiation in the loss on ignition depending on the place. Although the content of heavy metals in the collector material differed from the content recorded in the surface bottom sediments it was within the range of the recorded concentrations (Protasowicki et al. 1993, Niedźwiecki et al. 1998).

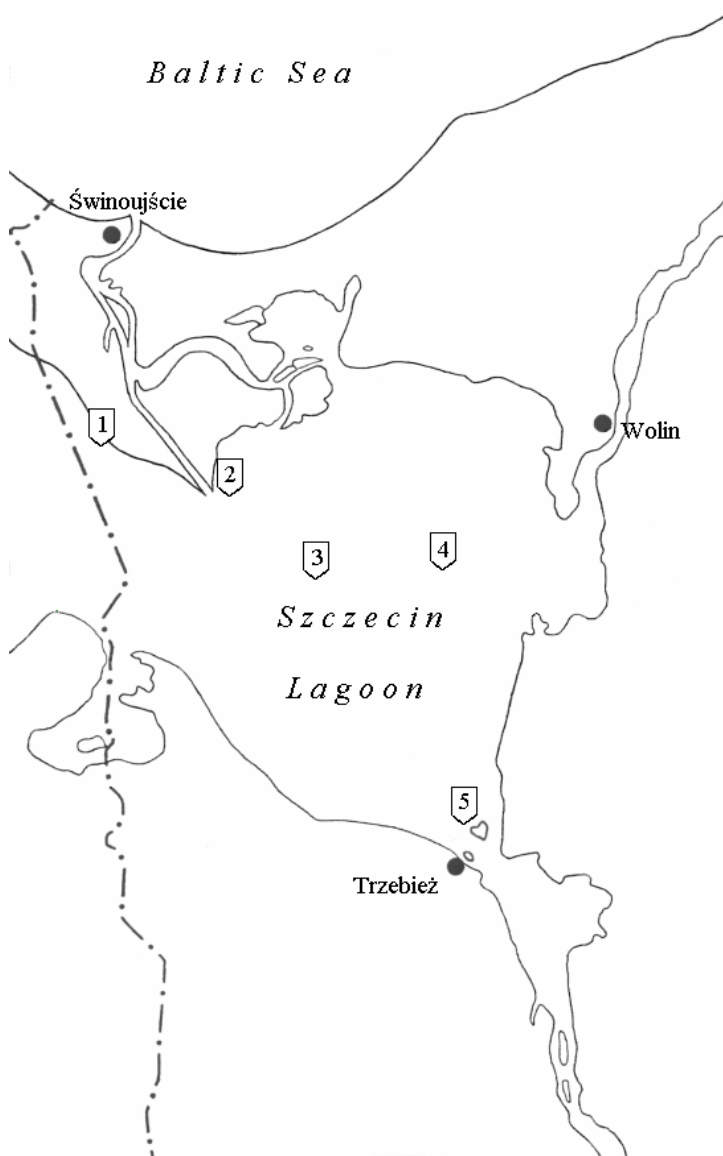


Fig. 1. Sampling points in the Szczecin Lagoon; 1 – border buoy, 2 – I Brama Torowa, 3 – II Brama Torowa, 4 – navigation sign, 5 – Chełminek

Rys. 1. Punkty poboru prób w Zalewie Szczecińskim; 1 – pława graniczna, 2 – I Brama Torowa, 3 – II Brama Torowa, 4 – boja nawigacyjna, 5 – Chełminek

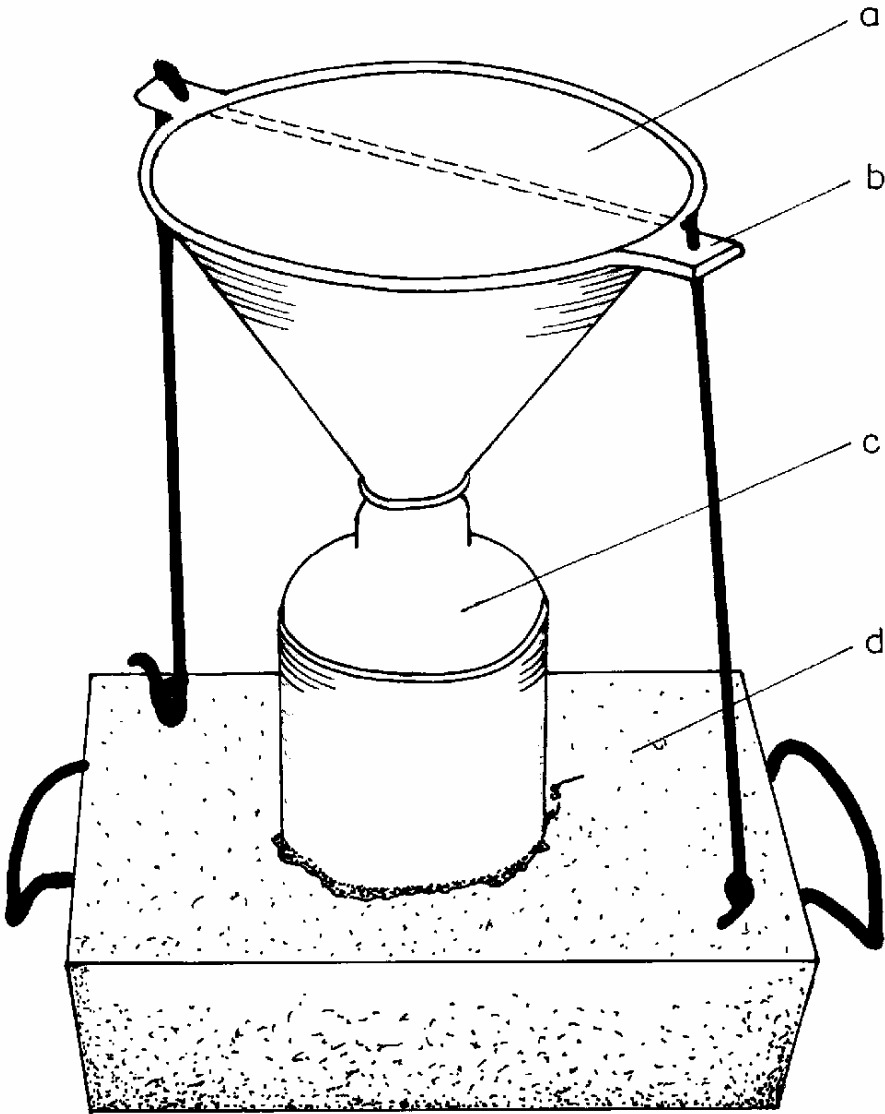


Fig. 2. The sediment collector: a – funnel, b – rope, c – bottle, d – concrete block

Rys. 2. Urządzenie do pobierania osadu: a – lejek, b – lina, c – butelka, d – blok betonowy

The ratio of maximum to minimum concentration level was as follows: Hg - 2.78; Cd - 3.06; Pb - 9.36; Cu - 2.24; Zn - 4.77; Cr - 2.46; Ni - 2.25; Fe - 4.83. Apart from a few exceptions the material collected in the area where the Odra flows into the Szczecin Lagoon (Chełminek) have the highest concentrations while the lowest is at a place near to Kanał Piastowski (I Brama Torowa).

It is worth pointing out that the observed differences cannot be explained by a different amount of organic matter (estimated on the basis of the loss on ignition) since the ratio of maximum : minimum level was 1.67.

The presented data fully confirm our earlier founding that heavy metal contamination of the Szczecin Lagoon is decreasing with the distance from Szczecin, which is the result of a self-purification processes in this aquatic area (Protasowicki 1991, Protasowicki and Niedźwiecki 1993).

Depending on the place, the collectors contained from 62-376 g of the sediment with the dry matter content within the range 27.82 - 41.77%, which allowed the calculation of the mass of the matter (dry matter) falling down to the bottom and the load of heavy metals (Table 2).

Table 2. Assessment of a matter and a heavy metal load yearly deposited on the bottom of the Szczecin Lagoon

Table 2. Oszacowany ładunek materii oraz metali ciężkich rocznie odkładanych na dnie Zalewu Szczecińskiego

Place*	Matter load, g·cm ⁻²	Heavy metal load, µg·cm ⁻² of bottom							
		Hg	Cd	Pb	Cu	Zn	Cr	Ni	Fe
1	0.418	0.266	1.394	34.1	14.0	230	5.8	4.3	9919
2	0.493	0.235	1.003	17.6	14.3	147	5.6	6.7	3200
3	0.107	0.090	0.487	35.8	6.4	153	2.1	2.5	3352
4	0.115	0.079	0.317	5.3	4.3	37	1.3	1.4	2366
5	0.476	0.630	2.964	46.5	31.0	323	12.9	9.6	7692

* see "material and methods" and Fig. 1.

The comparison of the data from Table 2 shows that despite similar matter loads in the places labelled 2 and 5 the amounts of heavy metal contents are definitely different. This finding confirms the previous one that a considerable amount of these elements is deposited within the Szczecin Lagoon and does not reach the Baltic Sea.

As far as the differentiation of the load of organic matter is concerned there are two clear zones of different sedimentation intensification. The points 1, 2 and 5 represent the outlet and the side area, with in comparison with the

point 3 and 4 in the central part of the area. Taking into consideration these differences we can state that the values for the points in the central part are most useful for estimating the load of heavy metals in the Szczecin Lagoon.

On the basis of the above mentioned data and the area of the Zalew Wielki which according to Majewski (1980) is 410 km² in area it was calculated that the total annual deposition is within the range (ton/year): matter 1,316,100÷1,414,500; mercury 0.972÷1.107; cadmium 3.899÷5.990; lead 65.19÷440.34; copper 52.89÷78.72; zinc 455.1÷1,881.9; chromium 15.99÷25.93; nickel 17.22÷30.75; iron 21,102÷41,230.

The comparison of these values with the load of heavy metal pollutants flowing into the Szczecin Lagoon with the Odra (PIOŚ 1993), confirms that they are deposited to a great extent in bottom sediments. For the complete balance it would be necessary to estimate the load of pollutants falling into water from atmosphere.

4. Conclusions

1. The material deposited in the sedimentation process at the bottom of the Szczecin Lagoon has a great load of heavy metal, as a result, the flow of these pollutants from the Odra estuary into the Baltic Sea is limited to a great extent.

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Próba oszacowania ładunku metali ciężkich w czasie procesu sedymentacji osadów w Zalewie Szczecińskim

Streszczenie

W celu bliższego poznania procesów sedymentacji w Zalewie Szczecińskim wystawiono kolektory powstającego osadu. Kolektory takie wystawiono na okres 4 miesięcy od lipca do listopada w 5 punktach zalewu. Powierzchnia kolektora wynosiła 232 cm² i znajdowała się na wysokości około 35 cm nad dnem. W kolektorach po upływie 4 miesięcy, w zależności od rejonu, zebrano się od 62 do 376 g osadu o zawartości suchej masy w przedziale 27,82÷41,77%. Pozwoliło to wyliczyć masę opadającej na dno materii.

W zebranych w kolektorze materiale oznaczono zawartość materii organicznej oraz metali ciężkich – Hg, Cd, Pb, Cu, Zn, Cr, Ni, Fe. Materię organiczną oznaczono na podstawie strat przy wyżarzaniu w temperaturze 5500°C. Próby przed oznaczeniem metali ciężkich spalano w mieszaninie kwasów azotowego i nadchlorowego (HNO₃ + HClO₄). Pierwiastki analizowano metodą absorpcyjnej spektrometrii atomowej (AAS), przy czym rtęć oznaczano techniką zimnych par (CV AAS), a pozostałe metale po atomizacji w płomieniu acetylenowo-powietrznym (FAAS).

Zawartości metali mieściły się w następujących granicach: Hg – 0,636÷1,324; Cd – 2,035÷6,227; Pb – 46,3÷335; Cu – 0,21÷8,71; Zn – 299÷1427; Cr – 11,0÷27,1; Ni – 10,2÷22,9 i Fe – 3686÷31326 µg·g⁻¹ suchej masy. Tak znaczne zróżnicowanie wynikało z faktu miejsca położenia kolektora. Odnotowano, że największe ilości stwierdzano w rejonie ujścia Odry do Zalewu Szczecińskiego lub w jego części centralnej.

Uwzględniając powyższe dane oraz powierzchnię polskiej części zalewu – Zalew Wielki, która wynosi 410 km² obliczono że, całkowita roczna depozycja mieści się w zakresie (ton/rok): materia 1316100÷1414500; rtęć 0,972÷1,107; kadm 3,899÷5,990; ołów 65,19÷440,34; miedź 52,89÷78,72; cynk 455,1÷1.881,9; chrom 15,99÷25,83; nikiel 17,22÷30,75 i żelazo 21102÷41230.

Porównanie tych wartości z ładunkiem zanieczyszczeń dopływającym do zalewu z wodami Odry (suma przekroju Krajnika i Goleniowa) podawanymi przez PIOŚ potwierdza, że są one w znacznej mierze odkładane w osadach dennych zalewu.