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HEAVY METALS IN SOUTHERN BALTIC FISH: PRESENT SITUATION AND FUTURE TRENDS

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Herring (*Clupea harengus*) and cod (*Gadus morhua*) from three Southern Baltic areas were studied. Mercury content was determined with CV AAS and assays of the remaining metals were carried out with flame AAS.

A correlation between the fishing area and contents of Hg, Cd, Cu, and Zn in fish tissues was revealed. Interspecific differences are considered as well.

A noticeable decrease in Hg, Cd, Pb, and Cr and an increase in Cu and Zn can be observed over the recent several years in certain organs of herring and cod. In most cases, the changes taking place are better described by curvilinear (logarithmic) equation than by a linear one.

Correlations between contents of different metals in fish organs were detected, which points out to interactions between the metals during their uptake and release.

INTRODUCTION

Heavy metals are metallic elements of atomic number higher than 20 (Kabata-Pendias and Pendias 1979) or – according to another definition – of density higher than 6 g/cm^3 (Fõrstner and Mũller 1974). Most studies have so far concerned mercury, cadmium, lead, copper, and zinc. Their presence in the environment and organisms is inherent. However, as a result of ore mining and metal processing, and also during fuel combustion, environment can become contaminated with these metals and, in consequence, their levels in plants and animals increase. These are well-known relationships, observerd in fish ad well (Brown and Chow 1977; Chodyniecki and Protasowicki 1978; Johnels et al. 1967; Lucas et al. 1970; Protasowicki and Chodyniecki 1980).

As a semi-enclosed water body, the Baltic Sea is greatly exposed to anthropogenous pollution with heavy metals. This is best evidenced by the increase in their levels in sediments, starting with layers dating back to the beginning of this century (Suess and Erlenkeuser 1975; Skwarzec et al. 1985).

According to the mass balance calculations presented by Morozov and Petukhov (1981), an annual anthropogenous input of heavy metals to the Baltic Sea amounts to 1200 tonnes of zinc, 640 tonnes of copper, 280 tonnes of lead, 51 tonnes of cadmium, and 33 tonnes of mercury.

The objective of this paper is to present, based on our published and unpublished data, the current level of heavy metal pollution in selected Baltic fish, to follow trends in changes, and to indicate certain patterns in bioaccumulation of the elements in question.

MATERIALS AND METHODS

The studies were made on herring (*Clupea harengus*) and cod (*Gadus morhua*) caught in three Southern Baltic areas: 1) the Pomeranian Bay; 2) the Kołobrzeg-Darłowo fishing grounds; 3) the Władysławowo fishing grounds (Fig. 1).

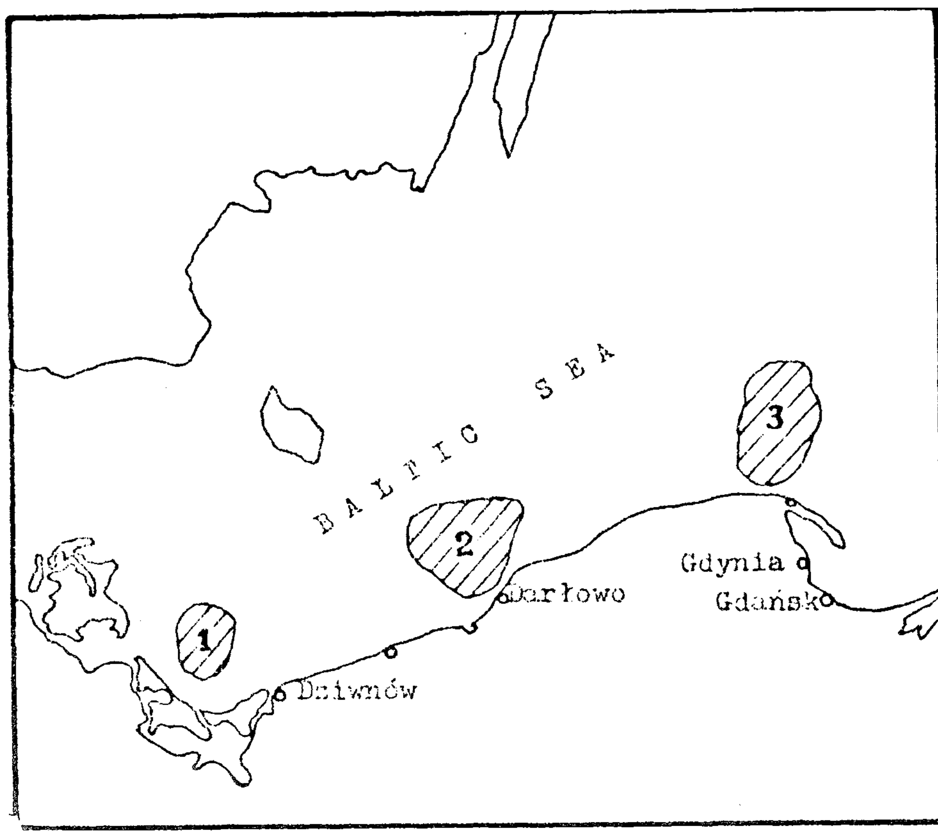


Fig. 1. Fishing areas

Mercury assays were made with CV AAS following combustion in HNO_3 + $HClO_4$ (3.5 : 1.5) (Adrian 1971); the remaining metals were analysed with flame AAS after dry combustion and solution in 15% HNO_3 (Protasowicki 1985).

RESULTS AND DISCUSSION

The previously published literature survey (Protasowicki 1987), revealed heavy metals contents in muscles of the two fish species caught in the Baltic to range within 0–1.39 (mercury); 0.002–0.4 (cadmium); 0.016–1.33 (lead); 0.02–2.8 (copper); and 1.4–32.4 (zinc), all the values being in µg per g wet weight.

Studies on mercury content in herring and cod from the three areas have been carried out in our laboratory since 1974; the remaining metals have been studied since 1978. Mean contents of the metals over the period of study are presented in Table 1.

Table 1

Mean contents of heavy metals in herring (*Clupea harengus*) and cod (*Gadus morhua*) in the Southern Baltic

Species Organ	Content (µg/g w.w.) *				
	Hg	Cd	Pb	Cu	Zn
Herring					
muscles	0.019±0.010 (73)	0.062±0.026 (53)	0.48±0.20 (56)	0.91±0.22 (59)	9.00±2.98 (60)
liver	0.037±0.029 (31)	0.615±0.287 (32)	0.70±0.60 (32)	5.35±1.99 (32)	35.31±20.32 (32)
Cod					
muscles	0.022±0.014 (69)	0.052±0.031 (58)	0.43±0.18 (57)	0.30±0.08 (60)	4.65±1.13 (60)
liver	0.021±0.018 (29)	0.048±0.030 (33)	0.26±0.13 (33)	8.83±3.85 (33)	16.80±5.22 (33)

* mean ± standard deviation (no. of batches, 5–50 individuals each, in parentheses)

The values presented are within the limits of heavy metals concentrations reported by other workers. The large standard deviation found indicates extensive temporal variability and association between the heavy metal content and a fishing ground. These problems have been discussed earlier (Protasowicki 1986, 1987): for example, the highest mercury content was recorded in herring caught from the easternmost fishing ground (3), while levels of cadmium, lead, and copper in fish caught from areas exposed to river runoff (1 and 3) were higher than those found in the Kołobrzeg-Darłowo fishing ground (2).

Additionally, it was pointed out that changes in cadmium, lead, and copper contents in the Pomeranian Bay and river Odra mouth fish proceeded in a similar manner and were strongly intercorrelated (r = 0.637–0.962).

Apart from interspecific differences in heavy metal contents, visible in the Table 1, differences between the organs studied are apparent as well, particularly with respect to the contents of cadmium, copper, and zinc.

Differential heavy metal accumulation in various organs has been dealt with by Bierman (1967), Rehwoldt et al. (1976), Wright (1976), and other workers. My own studies (Protasowicki 1987) confirmed that when heavy metal contents in 14 body organs of cod and flounder were compared. Exceedingly high contents of heavy metals,

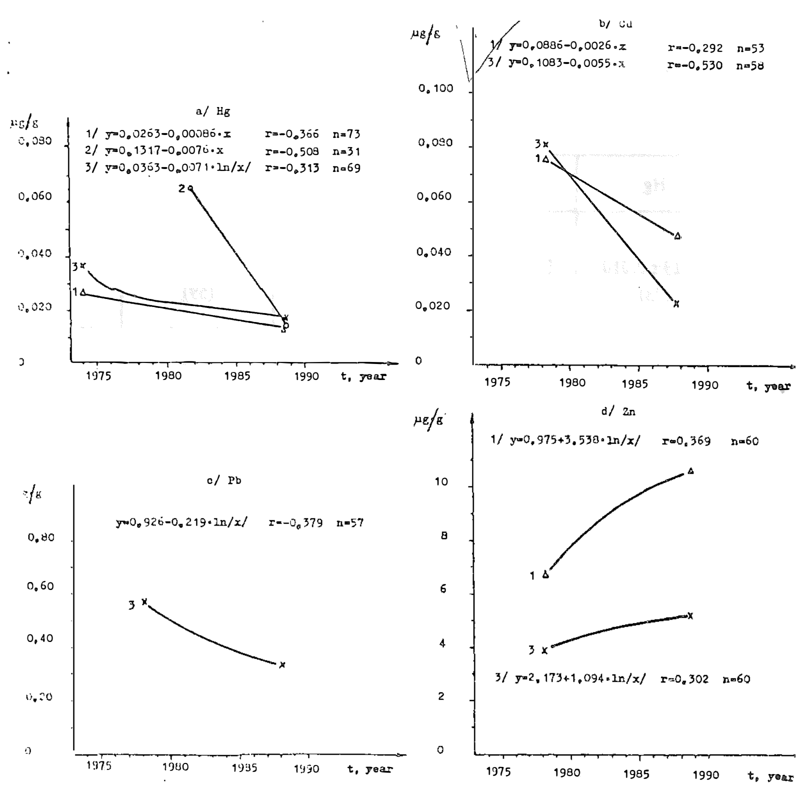


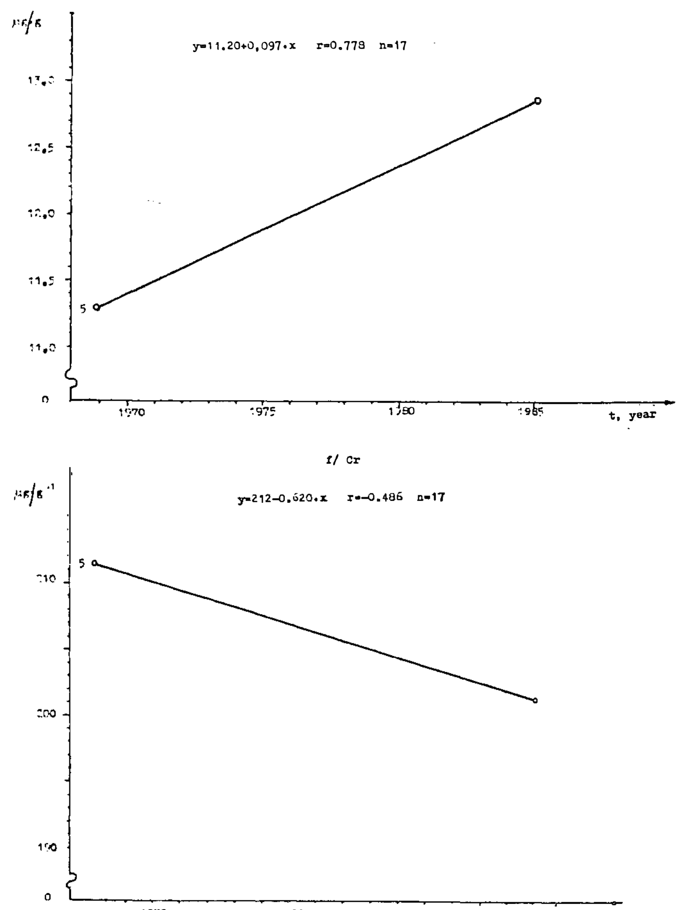
Fig. 2. Trends in changes of heavy metal content in the Southern Baltic fish: 1 – herring muscles, 2 – herring

cadmium, lead and copper in particular, in fish otoliths, coupled with the ease of storage of otoliths make them a very useful material for trend analyses. Such studies were made on otoliths of cod caught within 1969–1985 in the Władysławowo fishing ground (3). The levels of cadmium, lead, copper, zinc, and chromium were analysed (Protasowicki and Kosior 1987).

Increased copper level and decreased chromium contents were demonstrated, changes in contents of other metals showing no definite trend.

The analysis carried out in the present work reveals (Fig. 2) decreasing contents of mercury (herring muscles and liver, cod muscles), cadmium (herring muscles, cod muscles), and lead (cod muscles) over the period of study. On the other hand, the contents of zinc are observed to increase (herring muscles, cod muscles). In spite of some variation, the copper level did not show any definite trend.

The observed decrease in mercury content is doubtless related to a ban on mercury compounds in paper industry and agriculture of the Baltic countries. The trend was first observed by Westöö and Rydälv (1971). The decreasing trends in cadmium and



liver, 3 – cod muscles, 4 – cod liver, 5 – cod otoliths (for otoliths only, see Protasowicki and Kosior 1987) lead contents cannot be, as yet, tied up to any definite cause. The decrease in lead contents may be, perhaps, associated with increasing use of lead-free petrol in the western countries as the major part of the anthropogenous load of this metal deployed in the Baltic is derived from combustion of liquid fuels (Morozov and Petukhov 1981). No data on reduced cadmium inputs have been found in the literature.

In spite of a high annual input of zinc to the Baltic (Heybowicz and Rybiński 1988; Morozov and Petukhov 1988), the concentration of this metal does not seem to have doubled over the recent decade. Perhaps the slight increase in zinc content in the water significantly affected concentrations of zinc in fish muscles. Food is a more important source of zinc than water, as already observed by Hoss (1964) and Renfro et al. (1974).

Despite the fact that, due to the magnitude of the correlation coefficients, linear regression has been chosen to describe trends in most cases, curvilinear (logarithmic) regression seems to be generally more adequate because heavy metals contents never drop to zero, nor can they grow to infinity.

In the light of the data obtained, it is optimistic to note the progressing decreases in the contents of mercury, cadmium, and lead in fish, the metals being toxic. The monitoring should be, however, continued, because the correlation coefficients, albeit significant, indicate the trends observed to be rather weak.

Cadmium and other heavy metals in animal body are known to be bound mainly to metalothioneins, low molecular weight proteins (Noël-Lambert at al. 1978). The presence of one or more heavy metals in the environment induces synthesis of these proteins in fish body. Interactions between microelements are known to take place in organisms, too (Kabata-Pendias and Pendias 1979). The coexistence of some elements in the environment is widely known as well.

These facts were conducive to analyse correlations between different heavy metals in muscles and liver of herring and cod. The coefficients summarised in Table 2 demonstrate the strongest correlations to concern metal contents in herring liver (all 10 pairs), cod liver (5 pairs), and herring muscles (2 pairs). The relevant regression equations are given in Table 3.

The results suggest that changes in the contents of one metal may affect other metals. In most cases positive correlations were found, except for a negative relationship between mercury and zinc in cod liver. On the other hand, no correlation was found for cod muscles.

The correlation found for herring liver leads to suggesting that cadmium, present in high concentrations in the liver, triggers metalthionein synthesis, which in turn increases the organ's capacity to bind other heavy metals. A reverse situation occurs at low cadmium contents. This interpretation is confirmed by data reported by other authors (Noël-Lambert et al. 1978) and also by my studies (Protasowicki unpubl.): cadmium intoxication of fish was found to increase contents of some microelements in

Table 2

Correlations between contents of heavy metals in the Southern Baltic fish organs*

a) herring *Clupea harengus*

	Muscles (n = 56)				
	Hg	Cd	Pb	Cu	Zn
Hg		0.084	0.089	0.063	0.000
Cd	0.580[b]		0.496[c]	0.424[b]	0.100
Pb	0.508[b]	0.878[c]		0.202	0.197
Cu	0.418[a]	0.843[c]	0.773[c]		0.245
Zn	0.453[a]	0.904[c]	0.857[c]	0.844[c]	
	Liver (n = 28)				

b) cod *Gadus morhua*

	Muscles (n = 58)				
	Hg	Cd	Pb	Cu	Zn
Hg		−0.063	0.148	−0.105	−0.089
Cd	−0.256		0.253	0.000	0.187
Pb	0.000	0.0568[b]		0.122	0.239
Cu	−0.187	0.290	0.284		0.148
Zn	−0.428[a]	0.467[b]	0.400[a]	0.699[c]	
	Liver (n = 29)				

* n = no. of samples; correlation unmarked by a letter = nonsignificant; a = significant ($\alpha = 0.05$); b = highly significant ($\alpha = 0.01$); c = very highly significant ($\alpha = 0.001$)

Table 3

Regression equations describing relationships between individual heavy metals in Southern Baltic fish organs

Fish species, organ pair of heavy metals x – y	Regression equation
Herring *Clupea harengus*	
muscles	
Cd – Pb	y = 0.229 + 6.644x
Cd – Cu	y = 0.866 + 0.735x
liver	
Cd – Hg	y = 0.0040 + 0.0574x
Cd – Pb	y = −0.469 + 1.890 x
Cd – Cu	y = 1.785 + 5.805x
Cd – Zn	y = −4.279 + 65.152x
Hg – Pb	y = 0.271 + 11.062x
Hg – Cu	y = 4.256 + 29.085x
Hg – Zn	y = 25.327 + 329.435x
Pb – Cu	y = 3.653 + 2.475x
Pb – Zn	y = 16.032 + 28.683x
Cu – Zn	y = −11.309 + 8.222x
Cod *Gadus morhus*	
liver	
Cd – Pb	y = 0.156 + 2.408x
Cd – Zn	y = 13.143 + 80.015x
Hg – Zn	y = 19.702 – 127.705x
Pb – Zn	y = 12.625 + 16.190x
Cu – Zn	y = 8.572 + 0.949x

the internal organs. While accepting this explanation, simultaneous changes in heavy metal contents in the environment and fish food cannot be ruled out completely.

CONCLUSIONS

1. Contents of heavy metals in Baltic fish were found to be species – and fishing area-dependent and varied considerably over the recent years, the contents of mercury, cadmium, lead, and chromium showing a downward trend, while a rising trend was observed in zinc and copper.
2. Changes in the content of one metal affected the levels of other elements. This relationship was most conspicuous in fish liver and most often took a form of a positive correlation.

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