

Pilarczyk B., Pilecka-Rapacz M., Tomza-Marciniak A., Domagała J., Bąkowska M., Pilarczyk R. 2015. Selenium content in European smelt (Osmerus eperlanus eperlanus L.) in Pomerania Bay, Gdansk Bay and Curonian Lagoon. J. Elem., 20(4): 957-964. DOI: 10.5601/jelem.2015.20.1.876

SELENIUM CONTENT IN EUROPEAN SMELT (OSMERUS EPERLANUS EPERLANUS L.) IN POMERANIA BAY, GDANSK BAY AND CURONIAN LAGOON

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Abstract

Migratory smelt (Osmerus eperlanus eperlanus L.) may be perceived as a valuable indicative organism in monitoring the current environmental status and in assessment of a potential risk caused by selenium pollution. The aim of the study was to compare the selenium content in the European smelt from the Bay of Pomerania, Gdansk, and the Curonian Lagoon. The experimental material consisted of smelt samples (muscle) caught in the bays of Gdansk and Pomerania and the Curonian Lagoon (estuaries of the three largest rivers in the Baltic Sea basin: the Oder, the Vistula and the Neman). A total of 133 smelt were examined (Pomerania Bay n = 67; Gdansk Bay n = 35; Curonian Lagoon n = 31). Selenium concentrations were determined spectrofluorometrically. The data were analyzed statistically using one-way analysis of variance, calculated in Statistica PL software. The region of fish collection significantly affected the content of selenium in the examined smelts. The highest content of selenium was observed in smelt caught in the Bay of Gdansk (0.236 μ g g⁻¹ w.w.), then in smelt from the Pomeranian Bay $(0.165 \ \mu g \ g^{-1} \ w.w.)$, and the lowest in smelt obtained in the Curonian Lagoon (Lithuania) $(0.104 \ \mu g \ g^{-1} \ w.w.)$. The low concentrations of selenium recorded in the smelt show that there is a deficiency of this element, especially in the Curonian Lagoon (Lithuania). Geochemically, Poland and Lithuania are selenium deficient areas. Migratory smelt may serve as indicative organisms of environmental levels of selenium.

Keywords: smelt (Osmerus eperlanus), selenium, Pomerania Bay, Gdansk Bay, Curonian Lagoon.

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INTRODUCTION

Environmental protection in the European Union is considered an integral part of sustainable development policy. The economic growth of the Member States requires constant care of the environment. An essential element of these actions is assessment of the current state of the environment. The Baltic Sea is a shelf inland water body in Northern Europe, with Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland, Germany and Denmark lying on its coast. The Vistula, Neman, Oder, Lule, Kemi, Angerman and Daugava are the main rivers debouching to the Baltic Sea. The Baltic Sea contains waters whose properties are typically heavily modified by human activity.

Elevated concentrations of selenium may lead to a reduction in fish growth, reproductive disorders, gill damage and increased fish mortality (LEMLY 1993, 1997). This element can be taken up through the gills (respiration), gastrointestinal tract (with food, water and bottom sediment particles) and by absorption through body surfaces (VINNI et al. 2004, KRAUSE, PALM 2008, SHEPPARD et al. 2012).

The distribution of fish in the Baltic Sea depends on anthropogenic factors and existing habitat conditions. The numerous rivers flowing into the Baltic Sea are the primary cause of pollution. Identification of pollution sources is of particular importance in the case of elements extracted up to the land surface during the exploitation of minerals, such as arsenic, cadmium, lead, mercury or selenium. The coastal zone of the sea is most severely exposed to such pollution, mainly at individual points of pollution: urban wastewater collectors, estuaries, ports and other industrial centers. The content of selenium in the water depends on factors such as the geochemical environment, leeching from rocks and possible contamination. Selenium emissions from industrial sources, mostly from the combustion of coal and oil play an important role.

The main factors determining the species composition of the coastal zone fish fauna are the salinity of water and, to a lesser extent, the temperature of the water. Freshwater fish prefer warmer waters, which allow them to stay in the coastal waters throughout the year. However, certain freshwater species such as whitefish or smelt require colder water, so they avoid the coastal waters in summer and return in cooler periods for spawning and wintering.

FERNANDEZ-MARTINEZ, CHARLET (2009) believe that the most important factor involved in the circulation of selenium and responsible for its potential toxicity in aquatic ecosystems is the ability of aquatic organisms to accumulate selenium in high concentrations. The uptake of selenium by algae, bacteria and other aquatic invertebrates causes a rapid removal of the element from the water, which may give a false impression of the low concentration of this element in the water, hence obscuring the actual state and the effects of specific exposure (HAMILTON, LEMMY 1999). According to LEMLY (1999), a high content of selenium was found in the tissues of fish obtained from waters with a high concentration of this element (exceeding the geochemical background). Therefore, migratory smelt (*Osmerus eperlanus eperlanus* L.) may be a valuable indicator organism to be used for monitoring the environment and assessment of potential risks associated with selenium pollution. Geochemically, Poland and Lithuania are areas poor in selenium. A deficiency of this element is often found in terrestrial animals from this region (PILARCZYK et al. 2010, NOWAKOWSKA et al. 2014, JANKOWIAK et al. 2015). However, there are no data in available literature on the concentration of Se in tissues of smelt caught in the Baltic Sea.

The purpose of the study was to compare the selenium content in the European smelt (*Osmerus eperlanus eperlanus* L.) from the Pomerania Bay, Gdansk Bay and the Curonian Lagoon

MATERIAL AND METHODS

Material

The experimental samples (muscle) were from smelt (Osmerus eperlanus eperlanus L.) caught in the Gdansk Bay, Pomerania Bay and the Curonian Lagoon (estuaries of the three largest rivers in the Baltic Sea basin: the Oder, Vistula and Neman) – Figure 1. The fish were sourced from commercial catches conducted in the specified waters. The 133 migratory smelt used in the study were caught in Pomerania Bay (n = 67, September 2011), Gdansk Bay (n = 35, October 2012) and the Curonian Lagoon (n = 31, December 2011) – Table 1.

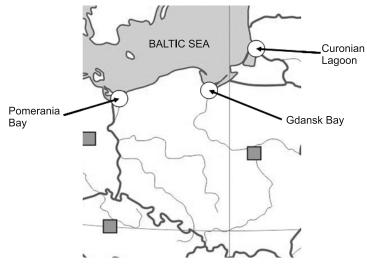


Fig. 1. Smelt (Osmerus eperlanus) sampling sites

Table 1

Estuary	n	Lengt	h (cm)	Weight (g)		
		range	$mean \pm SD$	range	$mean \pm SD$	
Pomerania Bay (Poland)	67	7.800 - 9.400	8.400 ± 0.42	2.260 - 4.760	3.010 ± 0.55	
Gdansk Bay	35	7.700 - 11.20	8.600 ± 0.9	2.700 - 9.600	5.010 ± 1.81	
Curonian Lagoon (Klaipeda, Lithuania)	31	12.20 - 20.00	15.20 ± 1.9	19.70 - 85.60	39.80 ± 16.5	

Biological characteristics of smelt (Osmerus eperlanus eperlanus L.)

Migratory smelts prey in estuarial zones of rivers, so the waters of the selected river affect them also in their foraging areas (and it is a continuous effect because smelts do not recede much from the feeding location and remain in the estuary). After entering puberty (usuallny during the second year of life), smelts migrate upstream to spawn, and afterwards they return to feeding locations. The studied fish were mature: the individuals from Poland were 2-3, and from Lithuania 3-5 years old.

The fish were stored frozen in polyethylene bags until chemical analyses.

Chemical analysis

All the chemicals were of analytical reagent grade. Most were obtained from Chempur, except 2,3-diaminonaphtalene (DAN), which was obtained from Sigma Aldrich, and Selenium Standard Solution purchased from Merck. Certified reference material SRM 1946 – Lake Superior Fish Tissue, was obtained from the National Institute of Standards and Technology (NIST).

Selenium concentrations in tissues were determined using the spectrofluorometric method (GRZEBUŁA, WITKOWSKI 1977). The samples of fish tissues (~1 g) were digested in HNO₃ at 230°C for 180 min and in HClO₄ at 310°C for 20 min. Then, HCl (9%) was added to the mineralized samples to reduce the selenates (Se VI) to selenites (Se IV). Then, selenium was derivatized with 2,3-diaminonaphtalene under conditions of controlled pH (pH 1–2) with the formation of a selenodiazole complex. This complex was extracted into cyclohexane. EDTA and hydroxylamine hydrochlorine were used as masking agents. An Se concentration was determined fluorometrically using a Shimadzu RF-5001 PC spectrofluorophotometer. Fluorescence in the organic layer (cyclohexane) was measured at an emission wavelength of 518 nm and an excitation wavelength of 378 nm. In parallel to the experimental samples, blank samples (reagent) were also measured.

The accuracy of the analytical method for the tissues was tested by the analysis of SRM 1946 reference material (NIST). Recovery values ranged from 93 to 98% of the reference value.

Statistical analysis

The data were analyzed statistically using one-way analysis of variance, calculated in Statistica PL software. The significance of differences between the groups was calculated using the Duncan's test. Prior to the analyses, the data were examined to determine their distribution using the Shapiro-Wilk W test.

RESULTS

The content of selenium in the examined smelt was significantly affected by the region of fish collection. The highest selenium content was observed in smelt caught in the Bay of Gdansk (0.236 μ g g⁻¹ w.w.), then in smelt from the Pomerania Bay (0.165 μ g g⁻¹ w.w.), with the lowest content detected in smelt collected from the Curonian Lagoon (Lithuania) (0.104 μ g g⁻¹ w.w.), less than half of that from the Gdansk Bay. Statistically significant differences were found (p < 0.001) in the selenium content in the smelt between the three regions compared (Table 2).

Table 2

Region		Se content (µg g ⁻¹ w.w.)							
	n	mean	GM	median	minimum	maximum	SEM		
Gdansk Bay	35	0.236^{A}	0.235	0.241	0.200	0.284	0.006		
Pomerania Bay (Poland)	67	0.165^{B}	0.156	0.184	0.068	0.221	0.009		
Curonian Lagoon (Klaipeda, Lithuania)	31	0.104^{c}	0.102	0.102	0.078	0.139	0.003		
Total	133	0.154	0.142	0.134	0.068	0.284	0.007		

The content of selenium in smelt collected from different regions

AB,C – different letters indicate statistically significant differences at p < 0.001

DISCUSSION

Young smelt feed on diatoms, rotifers and nauplius *Copepoda*. The dominant zooplankton in the diet of older individuals is composed of cladocerans (*Chydorus* sp., *Bosmina coregoni*, *Daphnia* sp., *Bythotrephes longimanus*, *Leptodora kindtii*). In some water bodies, a large proportion of the diet consists of copepods of the order *Cyclopoida* and *Calanoida* (ROGALA 1992, STER-LIGOVA et al. 1995). According to GARNAS (1983), in the spring, with lower zooplankton abundance in the waters, smelt feed on chironomid larvae (*Tendipedidae*), moving from the bottom to the surface. The concentration of selenium in plankton is higher than the content in most invertebrates, which indicates the high ability of plankton to bioaccumulate this element from water (MUSCATELLO, JANZ 2009). Therefore, the smelt has a high ability to accumulate selenium and may be used to monitor the status of environmental selenium levels. Shellfish of the order *Amphipoda* and *Mysidacea* also comprise a large food source in brackish waters. As adult smelt are predators, the incidence of cannibalism can be rather high (EERDEN et al. 1993).

In our study, we found differences in selenium concentrations in the smelt relative to the sampling sites. The observed differences may be the result of human industrial and agricultural activity, and of geochemical conditions. Geochemically, Poland, like Lithuania, Latvia and Estonia, is a country that is poor in selenium in geochemical terms. The soil concentrations of selenium in these countries are comparable (GOLUBKINA et al. 1992, SURAI 2002). Selenium is a bio-element characterized by a narrow margin between physiological and toxic concentrations. Studying the selenium content in fish can be the basis for the identification of selenium deficiency or its toxicity.

Improvements of the water quality in the Oder, Vistula, and Neman rivers (and their tributaries), which have occurred over the last ten years, have significantly decreased the discharge of pollutants into the Baltic Sea (FANT et al. 2001). However, the significantly higher concentration of selenium in smelt from the Gdansk Bay and Pomerania Bay (Poland), compared to the Curonian Lagoon (Lithuania), may indicate some selenium contamination of the Oder and Vistula rivers and its tributaries, as the Se concentrations found in the fish from these bays were comparable with those obtained by BURGER et al. (2001) in an area which is not poor in this element (Catfish – 0.21 μ g g⁻¹ w.w.; Bowfin – 0.25 μ g g⁻¹ w.w.). The Se concentrations recorded were also comparable to the results obtained by MULDER et al. (2012) in fish from Lake Mjøsa. Fish from the upper South Atlantic contained much higher Se levels at 0.825 μ g g⁻¹ (FOSTER, SUMAR 1997).

The concentrations of selenium recorded in the smelt in this study show that there is an environmental deficiency of this element, particularly in the Curonian Lagoon (Lithuania). Migratory smelt constitute a food base for larger predatory fish and fish-eating birds, and in some countries (Lithuania, Latvia, Russia) they are of great economic importance. They are processed into canned fish and used in the production of fish oil and animal feed. Fairly rich fish fauna exists in the waters of the Gdansk Bay, Pomerania Bay and the Curonian Lagoon, dominated by freshwater fish with commercial shoals occurring seasonally during the spawning period (zander Sander lucioperca, bream Abramis bram, sichel Pelecus cultratus, herring Clupea herengus membras) (POVILANSKAS, MARGOŃSKI 2010). It should be expected that also the selenium content in those fish would be considerably lower than in the same species obtained from other regions. Fish are a recommended component of the human diet and a valuable source of selenium.

CONCLUSIONS

Migratory smelt may serve as indicative organisms of the selenium content in the environment. The region of fish origin had a significant impact on the content of selenium in the studied smelt. Our study has shown a deficiency of this element especially in the Curonian Lagoon (Lithuania).

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