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# Interspecific distribution and co-associations of chemical elements in the liver tissue of marine mammals from the Polish Economical Exclusive Zone, Baltic Sea

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**Abstract**

Concentrations of Al, B, Ba, Cd, Co, Cr, Cu, Fe, Ga, Hg, Li, Mn, Mo, Ni, Pb, Se, Si, Sr, Tl, V, Zn, Ca, K, Mg, Na and P in the livers of marine mammals obtained from by-catches or stranded on beaches on the Polish Baltic coast were determined by ICP-MS or ICP-AES and CV AAS. Interspecific diversity with respect to the contents of these elements was found in cetaceans and pinnipeds. The diverse Cd contents in the livers of these mammals can be attributed to the variable concentrations of this element in their food. Mercury was correlated with age and can reach high concentration associated with higher level of Se in older specimens. No significant relationships were found between concentration of the chemical elements studied and nutritional status/condition of the Baltic harbour porpoises as well as between their concentration in specimens from the Gulf of Gdańsk and open Baltic. It seems that the nutritional and health status of the specimens studied is generally enough good since the specimens studied were not stranded on beach because of starvation but almost incidentally caught in salmon gill nets. Strong correlations were found between the macroelements analysed, i.e. for the Ba–Ca–Sr, Ca–K, Ca–Mg, Mg–P, Zn–Mg and Zn–P assemblies. Significantly higher content of Al was found in males of harbour porpoises.


*Keywords:* Trace elements; Macroelements; Marine mammals; Baltic Sea

## 1. Introduction

By the end of the Second World War, the stocks of marine mammals living off the coast of Poland had fallen dramatically. In recent years, however, sightings of live animals have increased considerably, as have by-catches and strandings. This is due to the intensive programme of searches and a publicity campaign to encourage people to keep a lookout for such animals (Skóra et al., 1988; Skóra, 1991; Skóra and Kuklik, 2003).

The are four species of marine mammals in the Baltic: the harbour porpoise (*Phocoena phocoena*), a cetacean, and 3 pinniped species—the grey seal (*Halichoerus grypus*), the common seal (*Phoca vitulina*) and the ringed seal (*Phoca hispida*). Other species make only sporadic appearances in the Baltic (Skóra, 1991).

Since the 1980s epidemics caused by viral infections have been recorded among marine mammals (Kennedy, 1998). The question whether human pressures affect the state of health of porpoises, dolphins and seals is still an open one. The Baltic has long been recognised as one of the most polluted seas on the planet, so this question takes on a special significance in this region. Because marine mammals occupy the top level of the trophic web, have a considerable longevity as well as a long biological half-time of toxin elimination, they accumulate substantial quantities of organochlorine compounds and heavy

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metals (Das et al., 2003). De Swart et al. (1994, 1995, 1996) found that in common seals fed on Baltic herrings, several immune parameters were impaired in comparison to a group of seals fed on Atlantic fish. According to these authors, the impairment of NK cells and T lymphocytes in the animals fed on Baltic fish is probably due to pollution by organochlorine compounds. However, toxic heavy metals were not analysed in this work, so it is hard to discount their contribution to the impairment of immunity. There were few studies that tried to link marine mammal health to metal levels (Das et al., 2004; Bennett et al., 2001; Siebert et al., 1999). A severity of lesions and mercury levels were associated with the health state of the individuals (Siebert et al., 1999).

Although it has not been proved that trace metals influence marine mammals health status in a way which may contribute to the mortality observed in the last years, such hypothesis could not be neglected. According to recently published results by Kakuschke et al. (2005), the existence of metal-induced immunopathies has been shown among the harbour seals from the North Sea.

Heavy metals are among the toxic chemical contaminants which man has introduced into the world's ecosystems. Anthropogenic factors have disturbed the geochemical cycling of metals to a significant extent, on both a regional and a global scale (Nriagu and Pacyna, 1988). Szefer (2002) discusses in detail the problems arising out of the occurrence and distribution of metals, metalloids and radionuclides in the Baltic ecosystem with respect to marine mammals.

Aim of the study was to assay relationship, if any exists, between hepatic concentration of chemical elements and health/nutritional status of harbour porpoises from the Polish coast of the Baltic Sea as well as examine content of several toxic, micro- and macroelements in view of factors that govern their bioaccumulation.

## 2. Materials and methods

The liver samples from marine mammals used in thus study were obtained from specimens incidentally caught in salmon gill nets or stranded on beach in the estuarine Polish Baltic Sea between 1996 and 2003 (Fig. 1). The samples were taken from 14 harbour porpoises, two striped dolphins (*Stenella coeruleoalba*), two grey seals and one ringed seal. The sampling and biometrical data are given in Table 1. For Hg analysis 5 additional seals samples were taken (three from *H. grypus,* one sample from *P. hispida* and one from *P. vitulina*).

The livers were lyophilised and homogenised. Approximately 0.6 g of this material (weight accurate to 4 significant figures) was mineralised with conc. nitric acid (Suprapur® MERCK) in closed 100 mL Teflon bombs tightened to 22.5 Nm. Digestion of these portions was carried out in a close microwave system (Milestone MLS 1200 Mega) with a procedure consisting of five steps: 250 W for 1 min; 0 W for 1 min; 250 W for 8 min; 400 W for 5 min; and 650 W for 5 min. The final determination of all of the elements was done on an inductively coupled plasma atomic emission spectrometer (Thermo Jarrell-Ash ICP-AES 9000, Babington nebulizer) and a time-of-ion-flow inductively coupled plasma mass spectrometer (LECO TOF-ICP-MS, Meinhard). In both apparatuses the power supplied to the plasma was 1.05 kW, the plasma gas (argon) flow rate was 16 $L \cdot min^{-1}$ (Plasma 16 L/min Ar-plasma gas flow rate), the nebulising gas flow rate (also argon) was 1 $L \cdot min^{-1}$, and the sample suction rate was 1.2 $mL \cdot min^{-1}$. The experimental conditions of the analysis were optimised in such a way as to obtain the maximum yield from the simultaneous determination of a number of elements. Monoelemental ICP standards from Merck (Darmstadt, Germany) were used for calibration. The slope of the calibration curve was checked after every tenth determination.

The results obtained for As, B, Co, Cr, Ga, Li, Ni, Pb, Se, Tl and V in most cases lay below the method's limit of detection. This procedure was verified with the use of TORT-2 reference material (lobster hepatopancreas), obtaining yields

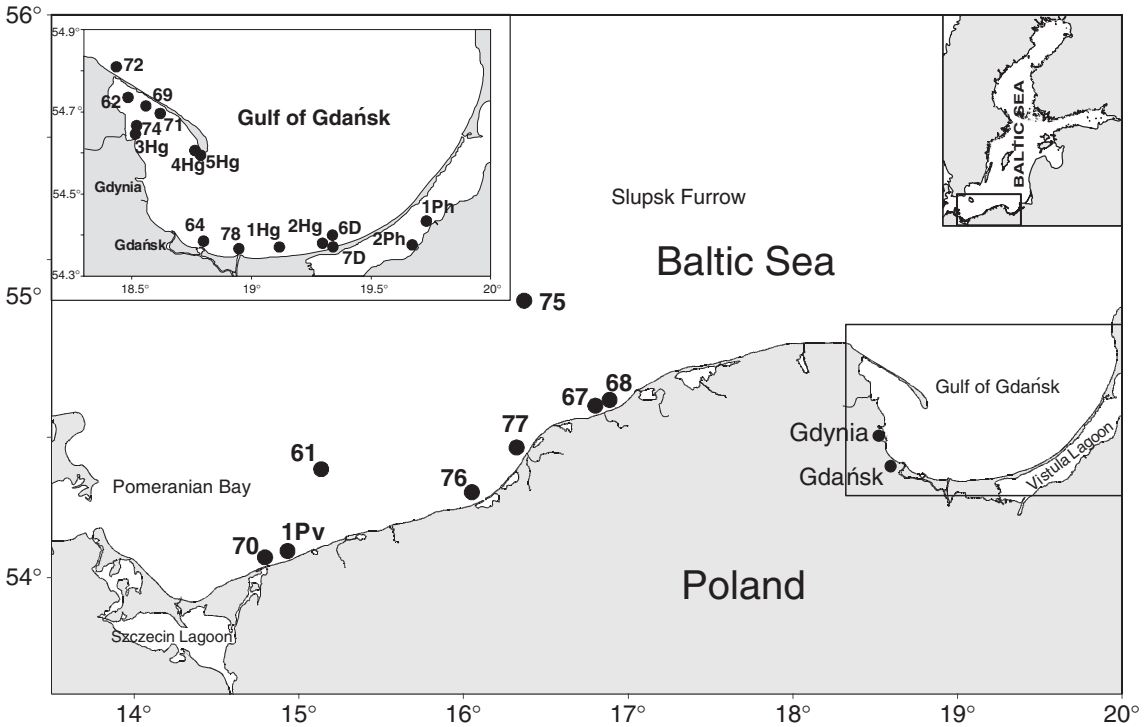


Fig. 1. Map of the Polish coast of the Baltic Sea with marked locations of the sampling sites.