Original Research

Lead and Cadmium Levels in Muscle, Liver, and Kidney of Scaup *Aythya marila* from Szczecin Lagoon, Poland

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> Received: 26 November 2009 Accepted: 30 April 2010

Abstract

Concentrations of lead (Pb) and cadmium (Cd) were determined in breast muscle, liver, and kidney of adult scaups (*Aythya marila*) wintering in the Polish part of Szczecin Lagoon (southwestern Baltic) in 2002 (n=17) and 2004 (n=17). Significant discrepancies were observed for Cd, but not Pb concentrations in all the tissues between 2002 and 2004. Geometric means of Pb levels were calculated for all the analyzed birds (except one, n=33). Concentrations of Pb were similar in muscle, liver, and kidney (2.29, 2.38, 2.55 mg/kg dry weight, dw, respectively). Concentrations of Cd in the examined materials differed significantly (muscle, liver, kidney 0.27, 2.59, 10.31 mg/kg dw, respectively). Performed analysis of Pb and Cd concentrations in these eatable parts of duck showed exceeded maximum levels of toxic metals determined for foodstuffs in EU document No. 1881/2006. Concentrations exceeding maximum levels were detected in 65-100% of the samples (depending upon the examined material), most frequently in the case of Pb in the muscle.

Keywords: lead, cadmium, scaup, duck, human food

Introduction

Some waterfowl species such as mallard *Anas platyrhynchos*, teal *A. crecca*, long-tailed duck *Clangula hyemalis*, goldeneye *Bucephala clangula*, and scaup *Aythya marila* display a wide distribution area [1]. These species can be found, among other places, in Eurasia and North America. With such occurrences ecotoxicological comparisons can be made in order to describe the causes of frequent and dramatic decreases of some duck populations. The scaup was subjected to a distinct decrease of 50% and 30% of its population size in Europe and North America, respectively [2-5]. These alarming trends were the premise

for entering *Aythya marila* on the IUCN Red List of Threatened Species, assigning them the category of Least Concern, LC [6]. Scaup have their own breeding areas in the arctic and subarctic regions of Palearctic and Nearctic, but spends the winter at lower geographical latitudes, primarily around shallow marine and coastal reservoirs [1, 7]. In Europe, the Baltic Sea, especially its southwestern regions (including the Polish coast covering Pomeranian Bay, Szczecin Lagoon, and Gdańsk Bay), is the most important wintering site for the scaup and other sea ducks [8-10]. Due to the large concentrations of migrating and wintering birds, the aforementioned Baltic and coastal reservoirs were included in the European Ecological Network Nature 2000, involving countries of the European Union, according to the Birds Directive [11]. At the same

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time the Baltic Sea is highly polluted with important concentrations of harmful anthropogenic substances (including mercury, Hg, lead, Pb, and cadmium, Cd) coming from Poland [12, 13]. These substances are carried from the interior of Poland to the Baltic Sea by the waters of two main rivers: the Vistula and Odra, with the latter supplying Szczecin Lagoon. In winter, the basic food of scaup is mesozoobentos, which can comprise 90% of its diet [14, 15]. The habitat and food quality have a key role in the general condition, health, and very existence of both birds and mammals, including humans. Heavy metals accumulated in the bodies of birds can indirectly reveal the quality of the habitat in which they feed [15-19], enable estimations of the degree of intoxication in the birds themselves [20-26]. Moreover, it should be remembered that such game birds do pose health hazards to humans. Game birds consumed by people (primarily meat and to a lesser degree offal) may contain dangerous quantities of toxic elements such as Pb, Cd, and Hg, which is why eatable parts of duck should be analyzed closely with regard to these elements [27-29].

Many species of ducks are game birds, and in EU countries significant legal regulations concerning this issue are included in the Birds Directive [11] (Annex II/1 and II/2. Scaup is mentioned in Annex II/2, which means that in some EU countries, mostly where they appear in large numbers (for example in winter in Germany, Denmark, the Netherlands, and Latvia), this species may be hunted. Among Baltic EU countries the duck may not be hunted in Finland, Lithuania, Poland, or Sweden. In Russia, however, scaup are on the list of game species. Russia has considerable access to the Baltic, and the Russian territories host the largest breeding-grounds of scaup wintering in Europe. In game birds killed during hunting, and ones which survive being shot, Pb pellets and their fragments can be found in the breast muscles [27, 29-33]. Moreover, some amount of this Pb is drawn into muscles, the liver, kidneys (responsible for detoxification processes), and bone, where this metal accumulates over the whole life of the bird. This built-in Pb fundamentally originates from pellets and/or sinkers which have been swallowed by waterfowl, as socalled gastrolites, and is well documented in literature [20, 25, 34-36].

The constant increase and high ubiquity of anthropogenic Cd are deeply worrying [37, 38]. This element has a high affinity to kidneys (as a so-called nephrotoxin) and accumulates therein in the greatest amounts, with the liver coming in second. Ecotoxicological research from the previous dozen or so years show that the greatest concentrations of this nephrotoxin are found in sea-birds (including migratory diving ducks), which have their own breedinggrounds in the arctic and subarctic regions of the northern hemisphere [39-43]. Besides Cd of anthropogenic origin, considerable amounts of this metal have a geochemical origin. For organisms living in those regions, uptake of Cd is mostly explained by food ingestion [44-46]. Moreover, migrating sea ducks, such as scaup could also accumulate significant amounts of Cd at wintering sites [15, 23].

In ecotoxicological studies concerning Pb and Cd accumulation in waterfowl, the most frequently investigated organs are the liver and kidneys, because of their key role in the detoxification processes. However, with reference to human exposure to these toxic metals, it is essential to determine their concentrations in the principle edible parts of game birds, most importantly in breast muscles. Interestingly enough, Pb and especially Cd concentrations in these parts are very seldom investigated. The aim of the current study was to determinate concentrations of Pb and Cd in the muscle, kidneys and liver obtained from scaup wintering in Szczecin Lagoon. Another aim was to examine if the concentrations of these metals cross the maximum levels for certain contaminants in foodstuffs, valid in the European Union, were determined by the Commission Regulation (EC) from 2006 [47].

Material and Methods

Study Area and Sampling Strategy

Investigated birds came from Szczecin Lagoon. This lagoon is the so-called inner coastal waters of the Baltic Sea (~687 km²), being a reception pool for the mouth of the river Odra (catchment area of 120,000 km²). Depending on the direction and power of the wind, waters carried by this river mix with the waters of the Baltic Sea. Szczecin Lagoon includes a Polish-German border (Fig. 1).

In this study were used 34 adult scaup Aythya marila representing one of the diving duck species (tribe Aythyini). These birds wintered in the Polish part of Szczecin Lagoon in 2002 (2 females and 15 males) and 2004 (1 female and 16 males). The diving ducks perished (respectively March and April) by having become entangled in fishing nets while diving for food (molluscs, crustaceans, insect larvae). Prior to dissection, the ducks were stored at -20°C. In the laboratory the defrosted birds were dried with a filter paper. Age and sex were determined of all birds by gonad examination and the development of the bursa of Fabricius [48]. Individuals from 2004 were weighed within an accuracy of 10 g. The absolute masses of the liver and kidneys (right and left together) were also measured within an accuracy of 0.1 g, and their relative sizes expressed as a percentage of body mass.

Analytical Methods

Cadmium and Pb were assayed in the breast muscle, liver, and kidneys collected from each individual. The biological materials were dried at 105°C to a constant weight. The dried tissues were crushed in an agate mortar and 0.5-1.0 g samples were weighed out (to 0.0001 g). The biological samples were burned in glass vessels of a Velp Scientifica and mineralized in a 4:1 mixture of 65% nitric acid (HNO₃) and 70% hyperchloric acid (HClO₄) (Suprapur Merck*). Following mineralization, the samples were diluted and brought to 10 ml with bidistilled water. Concentrations of lead and cadmium were determined using induction-coupled argon plasma atomic emission spectrometry (ICP AES) in a Perkin-Elmer Optima 2000

DV apparatus in the laboratory of the Department of Poultry and Ornamental Birds of the West Pomeranian University of Technology in Szczecin. Detection limits (µg/l) of the apparatus for Pb and Cd are 1.0 and 0.1 respectively. The concentrations of the examined metals were expressed in mg/kg dry weight (dw). To cross-check the analytical procedures applied, a Standard Reference Material (SRM) 1577b Bovine Liver, manufactured by the National Institute of Standards and Technology (USA) was assayed. Three samples of the reference material were analyzed. Levels of Pb and Cd were studied, specified by the SRM 1577b Bovine Liver manufacturer (CR) and the corresponding values measured in our laboratory (OL). They are listed below:

- CR for Pb and Cd: 0.129±0.004 and 0.50±0.03 mg/kg dw, respectively
- OL for Pb and Cd: 0.231±0.029 and 0.49±0.02 mg/kg dw, respectively.

Recovery of Cd assays was good (98%), but the Pb result was not (>0.20 mgPb/kg dw), which is an almost 180% recovery compared to the manufacturer-specified concentrations. However, Pb concentrations in the kidneys and liver of wild ducks were generally much higher than 0.5 mg/kg dw, and the error of determination of higher Pb concentrations was much lower.

Statistical Methods

Mean concentrations of Pb and Cd are presented as geometric mean and arithmetic mean, both commonly used in ecotoxicological studies. As concentrations of trace metals frequently deviate from the expected normal distribution, a non-parametric test was used in the performed comparisons (Mann-Whitney test, M-W). Due to the low number of females in the samples, no between-sexes differences were analyzed. In addition, Spearman's correlation coefficients were calculated for:

- a) concentrations of the two metals in the muscle, liver and kidneys;
- b) concentrations of each metal in two different biological materials.

All the calculations were performed, following recommendations from Sokal and Rohlf [49] and Moran and Solomon [50], with Statistica 8.0 software.

Human Health Hazards

The obtained results were compared with maximum levels for Pb and Cd in meat, liver, and kidneys, determined in an official European document: Commission Regulation

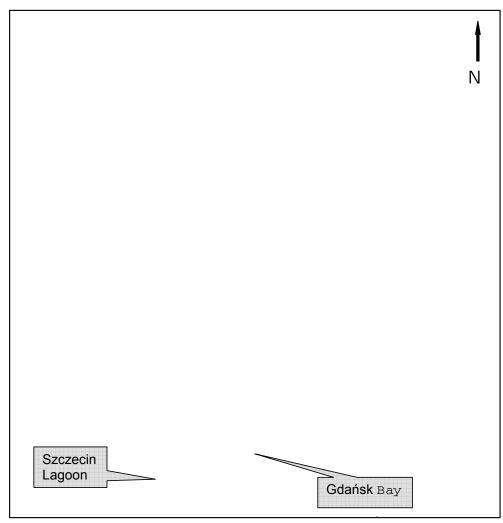


Fig. 1. Geographical location of the Szczecin Lagoon (scaup collection site) and Gdańsk Bay.

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Table 1. Concentration of lead and cadmium (mg/kg dw) in muscle, liver, and kidney of scaup from Szczecin Lagoon, Poland.

| Material | Parameter | 2002 (n=17) | | 2004 (n=16) | | Total (n=33) | | M-W test 2002 vs. 2004 | |
|-----------|-----------|----------------|-------------|----------------|------------|--------------|-------------|---------------------------|----------|
| | | Pb | Cd | Pb | Cd | Pb | Cd | Pb | Cd |
| | GM | 2.29 | 0.34 | 2.29 | 0.21 | 2.29 | 0.27 | NS p≤0.0001 | |
| Muscle, M | AM±SD | 2.31±0.34 | 0.36±0.10 | 2.30±0.18 | 0.21±0.02 | 2.30±0.27 | 0.29±0.10 | | p≤0.0001 |
| | Range | 1.82-3.02 | 0.20-0.56 | 1.98-2.60 | 0.18-0.26 | 1.82-3.01 | 0.18-0.56 | | |
| Liver, L | GM | 2.34 | 4.94 | 2.42 | 1.30 | 2.38 | 2.59 | NS | p≤0.0001 |
| | AM±SD | 2.40±0.62 | 5.45±2.37 | 2.46±0.50 | 1.65±1.03 | 2.43±0.56 | 3.60±2.65 | | |
| | Range | 1.79-4.50 | 1.32-11.65 | 2.00-4.19 | 0.26-3.35 | 1.79-4.49 | 0.26-11.65 | | |
| Kidney, K | GM | 2.44 | 20.98 | 2.67 | 4.85 | 2.55 | 10.31 | NS | p≤0.0001 |
| | AM±SD | 2.48±0.44 | 23.77±11.08 | 2.74±0.78 | 7.79±5.86 | 2.60±0.64 | 16.02±11.97 | | |
| | Range | 1.81-3.54 | 5.03-51.70 | 2.15-5.57 | 0.35-16.50 | 1.81-5.57 | 0.35-51.70 | | |
| M-W test | | | | | • | | | | |
| M vs. L | | NS | p≤0.0001 | NS | p≤0.0001 | NS | p≤0.0001 | | |
| M vs. K | | NS | p≤0.0001 | p≤0.01 | p≤0.0001 | p≤0.05 | p≤0.0001 | | |
| L vs. K | | NS | p≤0.0001 | p≤0.05 | p≤0.01 | p≤0.001 | p≤0.0001 | | |

The statistical comparison between materials and years was notified (GM – geometric mean, AM – arithmetic mean, SD – standard deviation, p – significance level of Mann-Whitney's test, NS – no significant difference).

(EC) No 1881/2006 of 19 December 2006, valid in EU since 1 March 2007 [47]. To convert the content of metal in 1 g dw to 1 g wet weight (ww) the following conversion rates were applied: 0.29 for the muscle, 0.28 for the liver and 0.27 for the kidneys (with respect to the water content in the samples). Cases with exceeded maximum levels were divided into three subgroups: by 50%, between 50% and 100%, and more than 100%.

Results

Body and Organ Size Characteristics

The mean body weight (and its standard deviation, ±SD) of the scaup obtained in 2004 (n=17) from Szczecin Lagoon was 1180±10 g, and the liver and kidneys weighed 41.4±4.6 and 14.7±2 g, respectively. The liver was 3.5±0.3% and the kidneys 1.2±0.1% of the body weight. Masses of the liver and kidney were on average 3.5±0.3% and 1.2±0.1% of the body weight, respectively. Because the ducks came from fishing nets, they were partly soaked with water and hence their body mass could be a little overstated, and the relative size of organs understated. The breast muscle, liver and kidneys contained 71.2±0.4%, 72.3±1.2%, and 73.1±1.0% water, respectively.

Metal Assayed

From statistical calculations, one individual from the year 2004 was excluded because its body contained very

large amounts of Pb (in the liver, kidneys and muscle, respectively, 45.32, 44.47, and 3.23 mg/kg dw), though concentrations of Cd in these parts were low (0.52, 1.62, and 0.17 mg/kg dw).

Mean concentrations of the examined metals in individuals from the years 2002 and 2004, as well as all the ducks taken together, are presented in Table 1. In the ducks from 2002, concentrations of lead in all the investigated body parts were similar. Geometrical means ranged from 2.29 mgPb/kg in the muscle to 2.44 mgPb/kg in the kidneys. Concentrations of Cd were significantly different between tissues. Kidney accumulated the highest amount of this element, followed by liver and to a lesser extent by muscle (about 21, 5, and 0.3 mgCd/kg, respectively). In the birds from 2004, mean concentrations of Pb in all the soft materials varied from ~2.3 to 2.7 mgCd/kg, with statistically significant differences in Pb concentrations between the kidneys and muscle, kidneys, and liver. Similar to the ducks from 2002, the birds from 2004 also had the greatest amount of Cd in the kidney, and the smallest in muscle (<5 and <0.5 mgCd/kg, respectively).

No discrepancies were observed between concentrations of Pb in analogous tissues in 2002 and 2004 (Table 1). In the case of Cd, significant differences appeared between years. The highest amount of Cd was found in birds collected in 2002.

Spearman's correlation coefficients (r_s) were determined between Pb and Cd in the muscle (M), the liver (L) and the kidneys (K). Positive correlations were observed between these metals only in the liver of the ducks from

| Relationships | 2002 (n=17) | 2004 (n=16) | 2002 and 2004 (n=33) |
|-----------------|-----------------|-----------------|-------------------------|
| $Cd_{M}-Cd_{L}$ | 0.60 (p≤0.05) | 0.76 (p≤0.001) | 0.89 (p≤0.0001) |
| $Cd_{M}-Cd_{K}$ | 0.72 (p≤0.01) | 0.76 (p≤0.001) | 0.91 (p≤0.0001) |
| $Cd_L - Cd_K$ | 0.90 (p≤0.0001) | 0.94 (p≤0.0001) | 0.97 (p≤0.0001) |

Table 2. Spearman's correlation coefficients of cadmium in analyzed biological materials of scaup.

M - muscle, L - liver, K - kidney.

2002 (Pb_L - Cd_L: r_s =0.52, $p \le 0.05$) and in the kidneys of the scaups from 2004 (Pb_K – Cd_K: r_s =0.54, p≤0.05). In all the examined individuals (n=33), in the analyzed tissues no significant relations between these elements were found. A lot more positive and statistically significant coefficients of correlation were found between concentrations of the same metal, but in different body parts. In the case of Pb analyzed in the ducks from 2002 (but not from 2004) statistically significant correlations were found between: Pb_M - Pb_L $(r_s=0.78, p\le 0.001), Pb_M - Pb_K (r_s=0.62, p\le 0.01), and Pb_K -$ Pb_L (r_s =0.82, p≤0.0001). In the joint duck group (both groups taken together, n=33) the above-mentioned correlations were also significant, though their values were smaller (r_s <0.60). Concentrations of Cd in all three body parts correlated significantly and positively with one another, in ducks from 2002, 2004, and both groups considered as one. Values of correlation coefficients for these compounds are presented in Table 2.

Concentrations of Pb and Cd According to European Document No. 1881/2006

Concentrations of Pb and Cd determined in all the examined scaups were divided into two groups – below and above maximum admissible levels presented in European document No. 1881/2006, setting maximum levels for certain contaminants in foodstuffs. In the document, concentrations of metals (including Pb and Cd) are expressed in mg/kg ww, and in the present work in mg/kg dw. That is why we established equivalents of maximum Pb and Cd levels for dw.

Among the 34 individuals analyzed, the maximum levels of Pb in the muscle, liver, and kidneys were exceeded by 100%, 88%, and 90% in the scaups, respectively (Table 3). In the muscle, the norm was exceeded most frequently and to the greatest extent – it ranged from 4.5 to 7.7 times greater. In the liver and kidneys it was usually exceeded by below 50%, and concentrations exceeding the norm by 50% and more were detected in only 4 individuals (11.8 %). In the case of Cd, almost 75% of individuals had an exceeded level in the muscle, almost 65% in the liver, and 79% in the kidneys. The maximum admissible Cd concentration was exceeded in 11 muscle samples, 17 liver samples and 24 kidney samples, 36.4%, 54.5%, and 72.7% of all the examined individuals, respectively.

Discussion

In ecotoxicological research on waterfowl, toxic metals such as Pb and Cd are most often found in the liver and kidneys due to temporary deposition and the role of these organs in detoxification. The risk of Pb poisoning (from shot pellets and, less frequently, sinkers) in anseriforms varies across the world and is well documented [20, 36, 51, 52]. Such poisonings mostly involve herbivorous and omnivorous birds feeding on the permanent pastures, shore and in shallow water reservoirs with a hard bottom. Geese, swans, dabbling, and diving ducks intake small stones, grit and metallic Pb fragments as gastrolites together with their food [36]. These materials facilitate the grinding of hard food by the stomach muscles (gizzards). Game birds, including anseriform, galliform and doves, presented a high prevalence of embedded shot which could represent a source of Pb intoxication for birds itself, human consumers, birds of prey, and scavengers [29-33, 53, 54]. Moreover, Pb intake together with contaminated food and sediments is permeated throughout the vascular system of birds from pellets, is later built into their tissues and organs [36, 55, 56]. This Pb, sometimes accumulated in considerable quantities, also holds a certain threat for organisms at the end of the food-chain, including humans.

Intoxication with Cd could be related to the ingestion of contaminated food and sediments. The levels of Cd accumulated by seabirds in internal tissues are frequently higher than those which cause toxic effects in terrestrial bird species (for example galliforms) or in those connected with inland waters, such as waterfowl [24, 27, 41, 42, 57, 58]. However, as opposed to Pb, few researchers have focused on the possibility of transferring Cd to a human body as a result of eating the meat of game birds [46, 59-62]. Ecotoxicologists most often examine concentrations of Pb and Cd in the kidneys and livers of birds, accumulating there in the complicated processes occurring between the habitat and the animal bodies, but people mainly consume the muscles of game birds, breast muscles and, to a lesser degree, leg muscles. Offal (mainly the liver, stomach, heart, and seldom the kidneys) is only a small part of a birds' bodies and not always used for food. From an ecotoxicological point of view, it seems justified to determine the concentrations of these metals in the muscles of birds as well.

Studies investigating Pb and Cd content in the muscles of diving ducks are rare. Moreover, studies led on scaup are few in Europe, North America, and Japan [15, 17, 40, 63-66].

Table 3. The number of scaups (percentage in brackets) with Pb and Cd concentrations below and above admissible levels determined for edible poultry parts in the EU document Commission Regulation, EC, No. 1881/2006 (n=34).

| Crossed maximum levels of toxic metals | Muscle | Liver | Kidney | |
|--|----------------|---------------|----------------|--|
| | max. level | max. level | max. level | |
| Lead | 0.10 mg/kg ww | 0.50 mg/kg ww | 0.50 mg/kg ww | |
| | 0.40 mg/kg dw* | 2.0 mg/kg dw* | 2.05 mg/kg dw* | |
| below max. level | 0 | 4 (11.8%) | 3 (8.8%) | |
| over max. level | | | | |
| <50% | 0 | 26 (76.5%) | 27 (79.4%) | |
| 50-100% | 0 | 1 (2.9%) | 2 (5.9%) | |
| >100% | 34 (100 %) | 3 (8.8%) | 2 (5.9%) | |
| | max. level | max. level | max. level | |
| G 1 : | 0.05 mg/kg ww | 0.50 mg/kg ww | 1.00 mg/kg ww | |
| Cadmium | 0.20 mg/kg dw* | 2.0 mg/kg dw* | 4.10 mg/kg dw* | |
| below max. level | 9 (26.5%) | 12 (35.3%) | 7 (20.6%) | |
| over max. level | | | | |
| <50% | 14 (41.2%) | 5 (14.7%) | 3 (8.8%) | |
| 50-100% | 8 (23.5%) | 5 (14.7%) | 2 (5.9%) | |
| >100% | 3 (8.8%) | 12 (35.3%) | 22 (64.7%) | |

^{*}In the document 1881/2006, the maximum admissible concentrations were presented for wet weight (ww), which in this work are converted into a dry weight scale (dw); for scaup they are rounded up and made greater by about 10% with relation to the maximum levels given in the aforementioned document.

In this context, comparison between data obtained in the current study and available literature could bring some insight.

Lead

Lead concentrations in breast muscles, leg muscles, liver, and kidneys were previously determined in the 1980s in Poland in scaup from another part of the Baltic Sea coast (Gdańsk Bay) [65]. Birds sampled died entangled in fishing nets, similar to the current study. In both groups of muscles (both in females and males) were observed similar, small quantities of Pb (mean values from 0.09 to 0.12 mg/kg dw). In comparison with data obtained on scaup wintering in Gdańsk Bay [65], the concentration of Pb in the muscle of scaup observed at the beginning of the 21st century in Szczecin Lagoon was above twenty times greater (2.29 mg/kg dw, Table 1). About 25 years ago, male livers and kidneys of scaups from Gdańsk Bay had far smaller concentrations of this metal (0.23 and 0.27 mgPb/kg, respectively) than males investigated in the current study (2.38 and 2.55 mgPb/kg, respectively). Previous authors have demonstrated this increase in Pb concentrations in bones and gristle of analogous groups of scaup from the Polish Baltic Sea [63]. These data also confirm unfavorable tendencies; an increase in the concentrations of Pb in their bodies.

Reports on Pb concentrations in the breast muscles of scaup living in North America are scant. Only two groups of authors have reported data in the USA [15, 66]. In one individual shot in New York State, 2.00 mgPb/kg ww was detected [66], but in the breast muscles of 9 male scaups from the state of Connecticut no detectable quantities of Pb were found, except in one individual (0.33 mgPb/kg dw) [15]. Low Pb levels were found in the livers and kidneys of scaup from Connecticut (0.74 and 0.94 mg/kg dw, respectively) [15]. Similar levels of this metal (0.50-1.0 mgPb/kg dw) in the livers of scaup from different regions of North America were reported by some authors [17, 67, 68] or higher value (1.0-5.0 mgPb/kg dw) by others [69, 70]. Scaup living in North America only sporadically had Pb concentrations higher than 5 mg/kg in the liver and/or kidneys [17, 66]. In this study, only one individual had very high concentrations of this metal in the liver and kidneys, which exceeded 40 mgPb/kg dw, indicating plumbism. Usually, Pb concentrations in the liver and kidneys that are higher than 2 and 6-20 mg/kg ww, respectively, are assumed as critical [51]. It seems that Pb concentrations in the muscles of scaup examined in the current study, compared with the data for this species from Gdańsk Bay [65] and the data concerning A. marila living in North America [15, 67, 68], have worryingly high values. It shows the present exposure to Pb among the European populations of

scaups, probably from wintering sites (mainly Baltic Sea area), fall areas, and breeding grounds. To a great extent it may be due to two main sources. The first is the presence of Pb in food (e.g. molluscs and other invertebrates obtained from the bottom of the Baltic and its coastal reservoirs, including Szczecin Lagoon), and the second are Pb pellets, still used in Russia and southern Baltic countries of the European Union: Estonia, Latvia, Lithuania, and Poland [13, 71].

Cadmium

The biological half-life of Cd reachs 20 years or more in humans and long-lived homoiotherms such as scaup, which can live for 20 years [1, 24, 37, 38]. Toxic effects of Cd in those vertebrates are diverse and include kidney damage, testicular atrophy, and disturbances in essential element metabolism (Cu, Fe, Zn). Additionally, birds show suppression of egg production and eggshell thinning [72, 73]. The metal is accumulated in the renal cortex and even fairly low levels of dietary Cd (5-10 ppm) ingested by warm-blooded organisms over a long period of time may be toxic for them and act as a stressful substance [24, 57, 74, 75]. Concentrations of Cd >10 mg/kg ww (approximately 30-40 mgCd/kg dw) in vertebrate liver and kidneys indicate possible Cd contamination [72]. Hepatic concentration >3 mgCd/kg dw in freshwater duck is considered elevated [24]. Damage of kidney occurs in birds when nephric Cd concentration reaches 100-200 mg/kg ww (~350-700 mg/kg dw). Cadmium, as a nephrotoxin, is most often investigated in the kidney, and then the liver. A comparison of the current results concerning scaup from Gdańsk Bay [65] confirms other reports that in diving ducks, including Aythya marila, Cd accumulates mostly in the kidney and in a lower degree in the liver [15, 24, 76]. The muscle of the scaup and other ducks is a minor site of Cd accumulation [65, 75]. However, research on scaups from different regions of the southern Baltic show essential differences. Concentrations of Cd in male scaups from Gdańsk Bay (GB) are clearly smaller in the breast muscle, liver and kidneys than average values for all individuals from Szczecin Lagoon, SL (GB: 0.03, 0.41, 1.29; SL: 0.27, 2.77, 10.31 in mgCd/kg dw, respectively). Similar tendencies were observed for the hard tissues of scaups from Gdańsk Bay and scaup from Szczecin Lagoon [63, 64].

Scaup populations living in North America displayed average concentrations of hepatic Cd, which usually do not exceed 10 mg/kg dw [15, 17, 59, 66, 67, 77]. In contrast to the liver, theirs had concentrations of nephric Cd several times higher, and value >80 mgCd/kg dw [23, 26, 68]. Interesting findings concerning scaups from the Californian coast during early and late wintering have been published [23, 26]. These diving ducks spent the winter season on the seacoast, which is polluted with heavy metals, and accumulate considerable quantities of toxic metals, including Cd in the kidneys. Among several analyzed groups, the highest average concentration of Cd was observed in scaup from Alameda (33.9 mgCd/kg dw) at the end of wintering [23].

Other duck species (sea ducks, especially eiders, genus Mergini) sometimes showed even higher concentrations of this metal in the kidneys, and even in the liver. For example in male Somateria fischeri from Alaska and arctic Russia, the average concentrations of Cd in those organs were 99.8 and 37.0 mgCd/kg dw, respectively. In some individuals of this species, the nephric concentration of Cd exceeded 350 mg/kg [42, 76]. Those molluscivorous birds naturally exposed to high concentrations of Cd in their diet may trigger a tolerance to Cd higher than other species. The tentative threshold for nephric Cd concentration was proposed for them 333 mg/kg dw [78]. In detoxification processes of Cd in birds, the kidneys and liver play a key role, especially their ability to synthesize of metallothioneins. Contamination of waterfowl by Cd resulted in an increase of nephric and hepatic metallothionein (the metal binding protein) production, which represents the main pathway of detoxification of Cd [23, 39, 75]. Besides excretion and metallothionein synthesis, presumably sea birds have the means to rid themselves of Cd from their systems by either physiological processes such as breeding and moulting, or seasonal variations in diet, facilitated by a more rapid turnover of Cd in the birds' bodies [41, 73, 79-81]. Probably European populations of scaup belong to that group because their winter food consists mainly of zebra mussels [82]. These molluscs are common in the Szczecin Lagoon and may be an important source of trace metals, including Cd [71, 83]. Very high Cd levels in liver and kidneys, over 50 and 100 mg/kg dw, respectively, have been reported not only from molluscivorous ducks, such as eiders from marine ecosystems [5, 42, 43], but also in inland herbivorous birds. Some plants (especially the willow, Salix spp.) growing on Cd-rich and/or Cd-polluted grounds may constitute another source of the metal for terrestrial birds, e.g. from the genus Lagopus [84-86]. Cadmium concentrations in kidney, liver, and breast muscle of the willow ptarmigan (Lagopus l. lagopus) from Norway were described about 10 years ago [85]. The highest levels of Cd were typically found in the oldest (>15 months) individuals (140±30.2, 13.8±5.5, 0.45±0.26 mgCd/kg dw in kidney, liver, and breast muscle, respectively). Also, a significant Spearman's correlation coefficient for muscle Cd and kidney Cd in all the birds studied (r_s =0.72, p<0.01, n=48) was reported. The authors of that study [85] suggested the relationship between Cd contents in kidney and breast muscle in birds to be of special interest, as it indicates an increase in Cd levels in breast muscle when kidney levels exceed about 80-90 mg/kg dw. In the current study, lower Cd concentrations were found in the three materials investigated, but a higher r_s value for the kidney vs. breast muscle Cd relationship $(r_s=0.90, p\leq0.0001)$. In both cases, the maximum muscle Cd level exceeded the standard set by relevant European regulation [47].

Unfortunately, there are few reports that examine concentrations of Pb and Cd in the muscles, liver, and kidneys at the same time, hence it is difficult to assess the threat to people posed by the presence of these metals in game birds. Considering Pb and Cd concentrations in the livers and kid-

neys, which are sometimes quite significant, it is difficult to estimate their levels in muscles and if they exceed permissible values. High correlation coefficients between the Pb concentrations, and especially between Cd concentrations in the muscles, liver and kidneys, can only be helpful here to a small extent [85, this work]. On the basis of the aforementioned studies and comparisons we may assume that the problem does exist, and is probably more serious than earlier thought, at least with reference to scaup in Europe.

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