MONITORING OF CONTAMINATION OF THE LUBLIN REGION WETLANDS USING MALLARDS (ANAS PLATYRHYNCHOS) AS A VECTOR OF THE CONTAMINATION BY VARIOUS CONDITIONALLY TOXIC ELEMENTS

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Abstract

Objectives of the research included: determination of concentration levels of selected conditionally toxic elements (Zn, Cu, Mn, Cr) in the organs and tissues of mallards (Anas platyrhynchos); identification of risks and dangers to the environment in the Lublin region associated with the contamination of selected organs of mallards by some conditionally toxic elements; an attempt to identify the organs that would enable quick and conclusive establishment of the mallards' condition, resulting from the accumulation of conditionally toxic elements; and evaluation of the edibility of mallard muscle tissue in terms of permissible standards and regulations binding in Polish law. Over a time span between 2001 and 2002, a total of 120 birds were examined. The concentration of polluting elements in collected samples of organs and tissues was ascertained using atomic absorption spectrometry (AAS). The results obtained were subjected to further statistical analysis. Significance of the correlation coefficient was analysed using Student's t-test. The highest concentration of copper (Cu) and manganese (Mn) was found in livers, and the highest concentration of zinc (Zn) was observed in muscles. It was also observed that the concentration of chromium (Cr) in the livers, kidneys and muscles of examined birds was comparable. The highest concentration of conditionally toxic elements was observed for ducks bred in the animal farm in Przytoczno. The concentration of conditionally toxic elements in organs of mallards depends significantly on their habitat. The quality of fodder used in mallard farming should be continuously monitored in order to reduce the risk of contamination with conditionally toxic elements. The high concentration of conditionally toxic elements in examined organs of mallards found in some cases justifies further monitoring of the environment. Based on the present study, it is not possible to determine organs that would enable quick and conclusive establishment of mallards' health resulting from the accumulation of conditionally toxic elements.

Key words: mallard, concentration, conditionally toxic elements

Various toxic elements penetrating the biosphere are included in the trophic chain. Toxic elements upset the biological equilibrium of existing ecosystems (Pain and Pienkowski, 1997; Walker et al., 2002). Previous research conducted in various parts of the world established strict links between the environment and the levels of heavy metals found in living organisms (Gochfeld, 1997). Since birds are higher in the trophic chain, they are superior to non-vertebrates in reflecting contamination hazards to humans (Furness and Greenwood, 1993). Conditionally toxic chemicals include elements such as chromium (Cr), zinc (Zn), manganese (Mn), and copper (Cu).

Vast amounts of chromium are delivered by tannery sewage, manufacturers of chromium-based pigments, municipal sewage, dust, ashes, and clinkers, especially in industrial districts (Wolak et al., 1995). High levels of chromium in fresh water (exceeding 0.05 mg/litre) may be toxic for fish and non-vertebrates such as snails and worms (Scheuhammer, 1991). The toxicity of chromium compounds depends on the level of chromium oxidization. Hexavalent chromium, i.e. chromium (VI), is 3–5 times more easily absorbed in the intestine than trivalent chromium (III) (Merian, 1984). Excessive amounts of chromium in food may lead to the development of cancers (cancerogenesis). On the other hand, chromium deficiency in animal food results in inhibited insulin action (Anderson, 1995; Scheuhammer, 1991).

Copper is essential for proper development and growth of both humans and animals (Dańczak et al., 1994). Copper contamination of the environment is significantly higher in places where copper is mined and processed (especially where copper works are located). An important source of copper contamination are fungicides containing organic and non-organic compounds of copper used in agriculture (Chmielnicka, 1999; Dańczak et al., 1994). Copper deficiency, especially in young organisms, leads to anaemia, growth inhibition, diarrhoea, hair pigmentation disorders, lowered synthesis of keratin, and degeneration of elastin in the vessels. High levels of copper in animal organs bring about hepatic icterus and result in changes in the kidneys, brain tissue, blood vessels and heart (Grys, 1988).

Manganese is a trace element required for the proper functioning of human and animal organisms (Indulski, 1987). Major manganese polluters are steel works and steel alloy manufacturers, producers of iron products, fertilizers, fungicides, as well as sediments produced in sewage treatment plants. In plants manganese is accumulated in young leaves, while crops such as rye and wheat accumulate manganese in the seeds. Excessive content of manganese in food may result in serious disturbances in metabolism and absorption of other elements such as copper, phosphorus, and iron, while manganese deficiency in animal food is manifested in deformation of bones, growth inhibition, and motion coordination disorders (ataxia) (Dańczak et al., 1994).

Zinc is an important component of many enzymes (metallothioneins) produced by humans and animals (alcohol dehydrogenase, alkaline phosphatases, and carboxypeptidases) (Kulikowska et al., 1991). Zinc deficiency accompanies disorders such as growth inhibition, underdevelopment of sexual glands, and lowered secretion of hormones by adrenal glands. In chickens, zinc deficiency results in skin disorders such as peeling, lowered feather growth, decreased egg production, as well as embryo development disorders. Moreover, zinc has protective effects in lead poisoning by decreasing lead absorption and stimulating removal of lead from liver, kidneys and blood (Das et al., 1984). The main objectives of the research included:

1. Determination of concentration levels of selected heavy metals (Zn, Cu, Mn, Cr) in the organs and tissues of mallards (*Anas platyrhynchos*).

2. Identification of risks and dangers to the environment in the Lublin region associated with the contamination of selected organs of mallards by some conditionally toxic elements.

3. An attempt to identify the organs that would enable quick and conclusive establishment of the mallards' condition, resulting from the accumulation of conditionally toxic elements.

Material and methods

The research material was collected in 4 reservoirs located in Przytoczno, Częstoborowice, Tuligłowy and Mosty. A total of 120 birds were examined over 2001 and 2002.

In 2001, 10 specimens were collected from Przytoczno, 16 from Częstoborowice and 16 from the Mosty reservoir. In 2002 samples were taken from 9 mallards from the Przytoczno reservoir, 24 samples from the Częstoborowice reservoir, 24 samples from Tuligłowy and 21 samples from the reservoir in Mosty.

The mallards were culled in the hunting districts in autumn respecting closed seasons (between 15 August and 20 December) using a double-barrelled gun cal. 12 and the lead shot Nos. 4 and 6. The research reference group was composed of 19 mallards culled in the animal farm in Przytoczno.

The concentration of polluting elements in collected samples of organs and tissues was ascertained using atomic absorption spectrometry (AAS). The AAS limit of detection (LOD) is 0.001 μ g/g for chromium, 0.008 μ g/g for copper, 0.009 μ g/g for manganese, and 0.009 μ g/g for zinc.

The detected concentrations of heavy metals were converted to wet weight (w.w.) values. The results obtained were subjected to further statistical analysis. Mean value (X), standard deviation (\pm SD) and range of variation (min-max.) were calculated separately for studies conducted in 2001 and 2002. This was followed by the examination of the correlation between the content of elements in the organs. The t-Student distribution was employed to assess the relevance of correlation coefficient.

Three levels of relevance were established: $\alpha = 0.05$; $\alpha = 0.01$; $\alpha = 0.001$. For the correlation coefficient ranges, relevances were as follows: highly significant: ***P ≤ 0.001 ; significant:**0.001 $\leq P \leq 0.01$; lowly significant:*0.01 $\leq P \leq 0.05$

Results

Chromium (Cr) concentration in the skeleton muscles, kidneys, hearts, and livers of mallards examined in 2001 and 2002 was similar and ranged from 0.01 to 0.03 μ g/g (Table 1). The highest chromium concentration was observed in the kidneys of mallards collected in 2002 from the Częstoborowice reservoir (1.53 mg/kg). The lowest average concentration of chromium was found in the muscles of mallards collected in 2001 from the Mosty reservoir (0.009 mg/kg).

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liver M 0.02 0.02 0.03 0.01 0.03 0			max	0.03	0.07	0.05	0.09	0.04	3.63	0.08
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max 1.81 3.36 2.14 M 9.53 A 6.59 3.96 B min 5.16 1.83 1.09 max 17.40 17.00 9.04 2.87 M 1.8 2.87 2.11 2.11 min 1.46 7.09 0.90 9.04 2.11 min 1.46 7.09 0.90 0.90 0.90 max 2.13 1.14 3.22 0.90 0.90 0.90 0.90			min	0.61	0.16	0.92	1.47	1.54	1.08	0.61
M 9.53 A 6.59 3.96 B min 5.16 1.83 1.09 max 17.40 17.00 9.04 2.11 M 1.8 2.87 2.11 2.11 min 1.46 7.09 0.90 9.04 2.11 min 1.46 7.09 0.90 0.90 0.90 max 2.13 1.14 3.22 0.90 0.90 0.90			max	1.81	3.36	2.14	7.55	6.78	7.14	2.67
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max 17.40 17.00 9.04 2.11 M 1.8 2.87 2.11 min 1.46 7.09 0.90 max 2.13 1.14 3.22			min	5.16	1.83	1.09	2.13	3.39	2.08	0.86
M 1.8 2.87 2.11 min 1.46 7.09 0.90 max 2.13 1.14 3.22			max	17.40	17.00	9.04	22.40	8.88	30.90	11.40
1.46 7.09 0.90 2.13 1.14 3.22		heart	Μ	1.8	2.87	2.11	4.23	3.97	3.06	2.72
2.13 1.14 3.22			min	1.46	7.09	0.90	3.07	2.72	0.40	0.38
			max	2.13	1.14	3.22	7.22	5.82	5.94	8.61

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n n kidnevs	mim Max M	0.21 0.14 0.31 1.64	0.29 0.02 1.38	0.23 0.07 1.05 0.55	0.23 0.13 0.39 0.49	0.18 0.06 0.31 0.89	0.25 0.13 0.47 1.11	0.25 0.09 0.79 1.02	
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M min max		39.3 25.20 50.90	20 16.80 25.40	43.1 33.50 51.40	43.4 28.40 51.40	29.7 26.40 35.70	20.6 15.30 26.40	41.26 34.40 51.20	
M min max		24.3 19.70 33.80	12.4 8.79 15.10	15 11.30 19.40	13.3 9.76 14.80	17.9 15.30 22.80	13.7 9.87 17.20	22.1 17.30 28.30	

In 2001 the highest concentration of copper was found in the livers of mallards collected in the animal farm in Przytoczno (9.53 mg/kg), while the livers of mallards culled in Mosty had the lowest concentration of copper (3.96 mg/kg). The observed difference is statistically significant. In 2002 the highest concentration of copper was identified in the livers of mallards culled in Częstoborowice (13.20 mg/kg). Copper concentration in the livers of other specimens was 8.37 mg/kg in the mallards culled in Tuligłowy and 5.89 mg/kg in the mallards collected from the animal farm in Przytoczno, while the lowest concentration of copper was found in the livers of mallards culled in Mosty (3.95 mg/kg). Statistically significant differences were observed between the concentration of copper in the livers of mallards culled in Częstoborowice and those collected in the Przytoczno animal farm and the Mosty reservoir.

As regards the concentration of manganese in the livers of examined mallards, we found significant differences between specimens collected in different places. In 2001 the lowest concentration of manganese was found in the mallards culled in Częstoborowice (2.04 mg/kg), and lower concentration was observed in the mallards collected in the Przytoczno animal farm (1.60 mg/kg) and the specimens collected in Mosty (0.88 mg/kg). Furthermore, it was observed that the levels of manganese concentration in the kidneys and livers are similar. As regards the concentration of manganese in livers, statistically relevant differences were found between specimens collected in Częstoborowice. Moreover, statistically relevant differences were found between the concentration of manganese in the kidneys of specimens collected in Częstoborowice and Mosty. In 2002 manganese concentration levels in the mallard livers varied from 2.15 to 0.98 mg/kg, while manganese concentration in the kidneys was similar and ranged from 1.11 to 0.49 mg/kg.

The research found that the average concentration of zinc in the organs of examined mallards varied notably. The highest concentration of zinc was observed in the livers (from 43.1 to 20.0 mg/kg). However, in 2001 the concentration of zinc was even higher in the skeleton muscles of mallards collected in the animal farm in Przytoczno (50.5 mg/kg). In 2002 the highest concentration of zinc in the livers was found in the mallards collected in Tuligłowy (43.4 mg/kg), while the lowest concentration of zinc occurred in the specimens collected in Częstoborowice (20.6 mg/kg).

Discussion

The average concentration of chromium in the organs of mallards culled in Częstoborowice in 2001 as well as those culled in Mosty and collected in the Przytoczno animal farm in 2001–2002 ranged from 0.01 to 0.03 μ g/g w.w. However, the average concentration of chromium in organs of mallards culled in Tuligłowy in 2000 and 2002 ranged from 0.02 to 0.04 μ g/g w.w. Cohen et al. (2000) carried out a research on 72 adult male greater scaups (*Aythya marila*), culled in winter 1996–1997 and spring 1997 in an area of Long Island. The average concentration of chromium in the livers was 2.4 ppm w.w. in scaups collected in winter and 1.6 ppm w.w. in those collected in spring (Cohen et al., 2000). Burger and Gochfeld (1985) examined

14 black ducks (*Anas rubripes*) culled by hunters in the Raritan Bay (New Jersey, USA) from December 1980 to January 1981 and found that the concentration of chromium in their livers averaged 2.051 μ g/g w.w. According to a regulation of the Minister of Health of 19 November 2002 on requirements for the quality of water intended for human consumption, the maximum concentration of chromium should be lower than 0.05 μ g/l.

Most animals demonstrate high copper tolerance, and only animals inhabiting areas where dust emissions produced by the copper industry are particularly high are vulnerable to copper and copper compounds poisoning (Monkiewicz, 1988). Moreover, copper poisoning may be caused by the use of chemicals in agriculture and occurs in habitats located in proximity to sewage treatment plants (Kabata-Pendias and Pendias, 1979; Kabata-Pendias and Pendias, 1993). The highest average concentration of copper was found in the livers of mallards culled in different years in selected habitats. Dańczak et al. (1997) in their research carried out in 1995 found that the average concentration of copper in kidneys and livers of male mallards was equal to 4.43 and $29.7 \,\mu g/g$ w.w. respectively, while in female mallards the average concentration of this element was 6.35 μ g/g w.w. in kidneys and 18.6 μ g/g w.w. in the livers. The research involved 14 specimens (10 male mallards and 4 female mallards) collected in the Słońsk sanctuary (Dańczak et al., 1997). It was found that the average concentration of copper in black ducks (Anas rubripes) collected in 1976-1980 in the area surrounding Chesapeake Bay was 14.2 µg/g w.w. in kidneys and 34.9 µg/g w.w. in livers (Di Giulio and Scanlon, 1984). Burger and Gochfeld (1985) examined 14 black ducks (Anas rubripes) culled by hunters in the Raritan Bay (New Jersey, USA) from December 1980 to January 1981 and found that the average concentration of copper in their livers was 8.508 µg/g w.w. Research carried out in 1993 on a sample of 30 dead long-tailed ducks (Clangula hyemalis) found on the Baltic Sea coast in the area of the Wolin National Park revealed that the average concentration of copper in the kidneys was 3.69 µg/g w.w. in males and 3.92 µg/g w.w. in females, and average concentration of copper in the livers was 7.38 μ g/g w.w. in males and 7.81 μ g/g w.w. in females (Dańczak et al., 1994). Cohen et al. (2000), who studied a sample of 72 adult male greater scaups (Aythya marila) culled in winter 1996–1997 and spring 1997 in an area of Long Island, found the concentration of copper in the livers to average 61.1 ppm w. w. in scaups collected in winter and 67.7 ppm w.w. in those collected in spring. Research carried out in 1988–1991 (Falandysz et al., 1994) examined poultry skeleton muscles, livers, and kidneys of chickens, turkeys, ducks, and geese bred in northern Poland and found that the average concentration of copper was highest in goose livers (80 mg/kg), medium in duck livers (58 mg/kg), and lowest in turkeys (4.7 mg/kg). As regards poultry kidneys, the average concentration of copper was 9.9 mg/kg in ducks and 3.0 mg/kg in turkeys. According to a regulation of the Minister of Health of 19 November 2002 on requirements for the quality of water intended for human consumption, the maximum concentration of copper should not exceed 2.0 μ g/l.

The highest concentration of manganese was found in the kidneys $(3.39 \ \mu g/g \ w.w.)$ and livers $(3.86 \ \mu g/g \ w.w.)$ of the mallards culled in the Tuligłowy reservoir in 2000. A study carried out in 1993 (Dańczak et al., 1994) on a sample of 30 dead long-tailed ducks (*Clangula hyemalis*) from the Wolin National Park (Poland's Baltic Sea coast)

found that the average concentration of manganese in livers was 6.83 μ g/g w.w. in males and 7.48 μ g/g w.w. in females. Burger and Gochfeld (1985) examined 14 black ducks (*Anas rubripes*) culled by hunters in the Raritan Bay (New Jersey, USA) from December 1980 to January 1981 and found that the concentration of manganese in livers averaged 1.848 μ g/g w.w.

In 1988–1991, Falandysz et al. (1994) examined poultry skeleton muscles, livers and kidneys taken from chickens, turkeys, ducks and geese bred in northern Poland. They found that the average concentration of manganese was highest in duck livers (3.7 mg/kg), medium in goose livers (2.3 mg/kg), and lowest in turkeys (1.8 mg/kg). As regards poultry kidneys, the concentration of manganese averaged 2.1 mg/kg in ducks, 1.7 mg/kg in geese and 1.6 mg/kg in turkeys. According to a regulation of the Minister of Health of 19 November 2002 on requirements for the quality of water intended for human consumption, the maximum concentration of manganese should not exceed 0.05 μ g/l.

Health-threatening concentrations of zinc in organs occur rather rarely due to difficult resorption of this element from the alimentary canal (Wałkuska, 1999). The highest concentration of zinc was established in the muscles of mallards collected in 2001 in the animal farm in Przytoczno (50.5 µg/g w.w.). Dańczak et al. (1997) found in 1995 using a sample of 14 mallards (10 males and 4 females) collected in the Słońsk sanctuary that the average concentration of zinc in the kidneys and livers of the male mallards was 26.0 and 43.6 μ g/g w.w. respectively, while in the female mallards the average concentration of this element was $29.2 \,\mu g/g$ w.w. in kidneys and 53.9 μ g/g w.w. in livers. Di Giulio and Scanlon (1984) reported that the average concentration of zinc in black ducks (Anas rubripes) collected in 1976–1980 in the area surrounding Chesapeake Bay was 84 µg/g w.w. in kidneys, 136 µg/g w.w. in livers and in 117 µg/g w.w. in elbow bones. Burger and Gochfeld (1985), who examined 14 black ducks (Anas rubripes) culled by hunters in the Raritan Bay (New Jersey, USA) from December 1980 to January 1981, found that the average concentration of zinc in the livers of examined specimens was 4.0563 µg/g w.w. A study carried out in 1993 (Dańczak et al., 1994) on a sample of 30 dead long-tailed ducks (Clangula hyemalis) from the Wolin National Park established that the average concentration of zinc in kidneys was 22.56 μ g/g w.w. in males and 22.85 μ g/g w.w. in females. The average concentration of zinc in livers was 24.02 µg/g w.w. in males and 27.16 µg/g w.w. in females (Dańczak et al., 1994). Cohen et al. (2000) studied 72 adult male greater scaups (Aythya marila), culled in winter 1996–1997 and spring 1997 in an area of Long Island. The average concentration of zinc in the livers was 121.4 ppm w.w. in scaups collected in winter and 129.6 ppm w.w. in those collected in spring. In 1988–1991, Falandysz et al. (1994), who examined poultry skeleton muscles, livers, and kidneys taken from chickens, turkeys, ducks, and geese bred in northern Poland, found that the average concentration of zinc was highest in goose livers (58 mg/kg), medium in duck livers (51 mg/kg) and lowest in turkeys (37 mg/kg). As regards the kidneys, the average concentration of zinc was 29 mg/kg in ducks and 20 mg/kg in turkeys.

In conclusion, the highest concentration of copper (Cu) and manganese (Mn) was found in the livers of wild ducks, while the highest concentration of zinc (Zn) was

observed in muscles. It was also observed that the concentration of chromium (Cr) in the livers, kidneys and muscles of examined birds was comparable. The highest concentration of heavy metals was observed for ducks bred in the animal farm in Przytoczno. The concentration of heavy metals in organs of wild ducks depends significantly on the place they live in. The quality of fodder used in wild duck farming should be continuously monitored in order to reduce the risk of contamination with heavy metals. The high concentration of heavy metals in the examined organs of some wild ducks justifies further monitoring of the environment. On the basis of the present findings it is impossible to identify the organs that would enable quick and conclusive establishment of the mallards' condition, resulting from the accumulation of conditionally toxic elements.

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Monitorowanie skażeń środowiska wodno-błotnego lubelszczyzny z wykorzystaniem kaczki krzyżówki (*Anas platyrhynchos*) jako wektora zanieczyszczeń wybranymi pierwiastkami warunkowo toksycznymi

STRESZCZENIE

Celem przeprowadzonych badań było: określenie poziomu stężenia wybranych pierwiastków warunkowo toksycznych (Zn, Cu, Mn, Cr, Ni) w narządach i tkankach kaczki krzyżówki (*Anas platyrhynchos*), poznanie stanu aktualnego zagrożenia środowiska województwa lubelskiego związanego ze skażeniem niektórymi pierwiastkami warunkowo toksycznymi wybranych narządów kaczek, próba określenia, który narząd kaczek pozwala na najszybsze i jednoznaczne określenie stanu ich zdrowia wynikającego z kumulacji pierwiastków warunkowo toksycznych, ocena przydatności spożywczej tkanki mięsnej kaczki krzyżówki w aspekcie dopuszczalnych norm i przepisów obowiązujących w ustawodawstwie RP.

W dwuletnim cyklu 2001–2002 r. do badań użyto łącznie 120 ptaków. Zawartość badanych pierwiastków w próbkach tkanek i narządów krzyżówek oznaczano metodą absorpcyjnej spektometrii atomowej. Wszystkie wyniki oznaczeń zawartości pierwiastków warunkowo toksycznych zostały podane w przeliczeniu na świeża masę. Otrzymane wyniki poddano analizie statystycznej. Do oceny istotności wartości współczynnika korelacji użyto rozkładu t-Studenta. W organizmach dzikich kaczek stopień kumulacji miedzi (Cu) i manganu (Mn) jest najwyższy w wątrobie, stopień kumulacji cynku (Zn) w mięśniach, natomiast skażenie chromem (Cr) jest porównywalne w wątrobie, nerkach i mięśniach badanego ptactwa. Najwyższe stężenia pierwiastków warunkowo toksycznych występują w badanych narządach dzikich kaczek hodowlanych zamieszkujących zbiornik w Przytocznie. Pomiędzy zawartością pierwiastków warunkowo toksycznych a miejscem pozyskiwania materiału do badań występuje istotna zależność. Należy zwrócić uwagę na zawartość pierwiastków warunkowo toksycznych w paszy stosowanej w gospodarstwach jako karma dla dzikich kaczek hodowlanych. Stwierdzone w jednostkowych przypadkach wysokie stężenia pierwiastków warunkowo toksycznych w narządach dzikich kaczek stanowią wskazanie do dalszego monitoringu skażenia środowiska tymi pierwiastkami. Na podstawie przeprowadzonych badań nie można określić u kaczek krzyżówek narządu, którego zbadanie pozwoli na szybkie i jednoznaczne określenie stanu ich zdrowia wynikającego z kumulacji pierwiastków warunkowo toksycznych.