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**THE ANALYSIS OF HEAVY METAL CONCENTRATIONS IN EGGS OF COLLARED FLYCATCHERS, *FICEDULA ALBICOLLIS* (PASSERIFORMES, MUSCICAPIDAE), AND TITS, *PARUS MAJOR*, *PARUS CAERULEUS* (PASSERIFORMES, PARIDAE), IN DIFFERENT AREAS OF NORTH-EASTERN UKRAINE**

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**The Analysis of Heavy Metal Concentrations in Eggs of Collared Flycatchers, *Ficedula albicollis* (Passeriformes, Muscicapidae), and Tits, *Parus major*, *Parus caeruleus* (Passeriformes, Paridae), in Different Areas of North-Eastern Ukraine.** Chaplygina, A. B., Yuzyk, D. I. — Collared flycatchers (*Ficedula albicollis* Temminck, 1815), have more opportunities to accumulate heavy metals due to migration but they are more resistant to contamination in contrast to tits, (*Parus major* Linnaeus, 1758, *Parus caeruleus* Linnaeus, 1758). This research aimed to detect concentrations of some trace elements in eggs of the collared flycatcher, great tit and blue tit in different areas. There were found differences in heavy metal concentrations in the eggs among species and study areas. For collared flycatchers there were not established consistent patterns of changes in element concentrations among areas. The highest heavy metal levels were found in tits in samples of egg contents from a forest park (Pb —  $3.1410 \pm 0.3249$ , Cu —  $19.3290 \pm 1.4840$ , Zn —  $66.9612 \pm 17.6665$ , Fe —  $249.5513 \pm 40.2800$ , Mn —  $6.9032 \pm 0.2946$ , Ca —  $8298.3570 \pm 0.1080$ , Sr —  $17.6032 \pm 0.7512$ , Ni —  $0.5177 \pm 0.0220$ ). The lowest concentrations were found in egg contents of tits in Hetmanskyi National Nature Park (Cu —  $4.3492 \pm 0.2079$ , Fe —  $44.6647 \pm 0.2627$ , Mn —  $1.3194 \pm 0.2374$ , Ca —  $998.7001 \pm 0.0006$ , Ni —  $0.2443 \pm 0.0439$ , Cr —  $0.1466 \pm 0.0424$ ). The results indicate that heavy metals accumulated differently in shells and contents of eggs of collared flycatchers and tits in each of the study area. Some of microelements (zinc, mercury, iron, manganese, selenium and iodine) in small amounts are required for normal growth and development of birds. Heavy metal concentrations in egg shells and egg contents of all species did not exceed permissible levels.

**Key words:** heavy metals, eggs, collared flycatcher, great tit, blue tit.

## Introduction

The most of heavy metals (hereinafter HM) are contaminants, toxic and hazardous for living organisms. They are released to the environment from air emissions of plants (Kabata-Pendias, 2004, Messadeh, Al-Safi, 2005), motor vehicles (Timmer et al., 2004), use of mineral fertilizers and pesticides, forest fires (Aronsson, Ekelund, 2004, Fowler et al., 2004). Nowadays lead and cadmium environmental pollution has reached critically dangerous levels and encompassed the entire biosphere, impairing physiological state of animals and human health (Hansen et al., 2001, Timmer et al., 2004).

Pied flycatchers (*Ficedula hypoleuca* Pallas, 1764) and great tits (*Parus major* Linnaeus, 1758) store such elements as As, Cd, Cu, Ni, Pb and Se in their liver tissue (Berglund et al., 2012). Flycatchers are known to accumulate excessive amounts of cadmium and lead that may cause pathological changes and physiological dysfunctions of their organs, reduction of clutch size, elevated embryonic and bird mortality, decrease in haemoglobin and hematocrit levels. The extent of biological effects on a population generally depend on the dose, time of exposure (Nyholm, 1994) and distance from the source of pollution (Eeva et al., 2000). Nestlings accumulate HM more rapidly than adults (Rodzin et al., 2000). Lack of calcium in the areas contaminated with heavy metals may lead to the thinning of shell, reduction in sizes of eggs and clutches, delay in ossification of nestling limb bones (Eeva, Lehtikoinen, 2004). Mercury, lead and aluminium may impair the shell structure (Nyholm, 1994) that is often used as an indicator for heavy metal environmental pollution, for mercury in particular (Gilyasov, 1993). However, small amounts of such microelements as zinc, mercury, iron, manganese, selenium and iodine are required for the normal growth and development of bird embryos (Savage, 1968).

The ground-dwelling prey of pied flycatchers (ants, centipedes, beetles) accumulates higher levels of HM than the grey tit's prey which is caught on the leaves (caterpillars, aphids). It may lead to disorders of calcium metabolism in the first species (Grue et al., 1986). The pied flycatcher, therefore, has a stronger reaction to contamination than the great tit (Eava, Lehtikoinen, 1995). The effect of heavy metals on the abundance of arthropods (Zvereva, Kozlov, 2010), earthworms (*Lumbricus terrestris* Linnaeus, 1758, *Nicodrilus roseus* Savigny, 1826), indirectly rooks (*Corvus frugilegus* Linnaeus, 1758) (Lebedeva, Minkina, 1998) and other birds is also known. The highest levels of contaminants are stored by omnivorous, fish-eating birds and birds of prey often ending a food chain (Burger, 2002) and thereby making most bird species reliable indicators of the environment (Lebedeva, 2001). This fact stipulates the urgency of our studies carried out for the first time in the region.

The aim of the research was to analyze heavy metal concentrations in egg shells and egg contents of collared flycatchers (*Ficedula albicollis* Temminck, 1815) and tits (*Parus major*, *P. caeruleus* Linnaeus, 1758) in different areas of North-Eastern Ukraine.

## Material and methods

The research was conducted in Ukraine over the period 2012–2014 in Hetmanskyi National Nature Park (Trostanets District, Sumy Region 50°24'55" N 35°04'16" E), the site called "Vakalivshchyna" (Sumy District, Sumy Region 51°01' N 34°55' E), and a forest park (Kharkiv 50°02'27" N 36°15'27" E).

We analyzed egg samples of collared flycatchers (long-distant migrants) and great and blue tits (sedentary birds). All these species are hole-nesting.

The heavy metal contamination is demonstrated by levels of Zn, Cu, Fe, Mn, Se, Co, Ca, Pb, Sr, Ni, Cr, Br in eggs of collared flycatchers and tits.

The experiment complied with bioethical norms, only eggs remained in the nests after hatching or those from abandoned clutches were selected for the analysis. A total of 122 eggs were collected, belonging to the collared flycatcher (52 eggs), great tit (46) and blue tit (24).

The eggs contents and egg shells were weighted and twice dried in a drying oven at the temperature of 60 °C, then reduced to fine particles. The received ash was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> adding water to get the volume of 50 ml. The results are expressed in mg/kg dry weight (egg contents, shell).

For statistical purposes the data were logarithmically transformed because they were not normal distributed. Microsoft Excel was used for calculations.

The presence of heavy metals in bird eggs was checked in a scientific laboratory of the Institute of Stock-Raising, NAS of Ukraine.

## Results and discussion

Food is the main source of contaminants entering the body. Migratory flycatchers accumulate them primarily during the winter and breeding seasons. Metals stored in tissues of female bodies may be transferred to the eggs, and then in small amounts are taken by the embryos from the yolk and albumin. The urban environment is a priori more contaminated with heavy metals. Thus, concentrations of lead, cobalt, manganese, nickel, copper, aluminium and chromium are higher in the earthworms collected in the city compared to those from suburban areas (Lebedeva, Minkina, 1998). In Finland, it has been tested the effect of reduced pollutant emissions on accumulation of heavy metals in pied flycatchers and great tits. It was noticed that for 20 years the accumulation of such elements as As, Cd, Cu, Ni, Pb and Se in the liver tissue had dropped from 58 to 95 % (Berglund et al., 2012).

Lead (Pb) is a major contaminant in the study areas and very toxic for birds especially at the early stage of their development (Pain, 1995). Mean Pb concentration in egg contents of collared flycatchers ranges from  $0.2958 \pm 0.1533$  mg/kg (forest park) to  $4.6407 \pm 0.0026$  mg/kg (Vakalivshchyna), in egg shells — from  $1.6440 \pm 0.0830$  mg/kg (Hetmanskyi NPP) to  $3.5179 \pm 0.0690$  mg/kg (Vakalivshchyna). For collared flycatchers we did not found consistent patterns of changes in the Pb concentration among areas. Perhaps, it is due to the species ability to accumulate contaminants during migration. In tits, Pb prevails in egg shells with a significant increasing trend from  $2.5843 \pm 0.1462$  mg/kg (Vakalivshchyna) and  $0.0038 \pm 0.0002$  mg/kg (Hetmanskyi NPP) to  $7.8848 \pm 0.0530$  mg/kg (forest park) among areas. The egg contents of tits had lower concentrations of Pb and a significance of differences was revealed when compared Vakalivshchyna and the forest park ( $3.1410 \pm 0.3249$  mg/kg) (table 1). Thus, Pb concentrations differ among species and areas, in contrast to the reference site in Southern Poland, where the analysis of heavy metal

**Table 1. Lead concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	4.6407 ± 0.0026	3.5179 ± 0.0690
	Hetmanskyi NNP	4.1150 ± 0.0010	1.6440 ± 0.0830
	Forest park	0.2958 ± 0.1533	2.3977 ± 0.0250
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	0.3760 ± 0.0055**	2.5843 ± 0.1462*
	Hetmanskyi NNP	3.2741 ± 0.0021	0.0038 ± 0.0002*
	Forest park	3.1410 ± 0.3249**	7.8848 ± 0.0530*

\* Significance of differences at  $p < 0.001$ ; \*\* significance of differences at  $p < 0.05$ .

levels in tissues of collared and pied flycatchers has shown that the mean Pb concentration in eggs exceeded that of Cd (from 0.14 to 0.59 mg/g) and was rather similar between years. The highest Pb level was found in pectoral muscles (from 0.10 mg/g in 1991 to 0.76 mg/g in 1990). In 1991 the lead level in blood of the flycatchers was lower than in 1990 (0.0134 and 0.03595 mg/ml, respectively). So, there was a difference in concentrations in muscles and liver between years. However, the lead level in liver was similar in all years and did not exceed 1.09 mg/g (Swiergosz et al., 1998).

Cu level in egg contents of collared flycatchers ranged from  $5.4662 \pm 0.6630$  (Hetmanskyi NPP) to  $7.5426 \pm 0.7000$  (forest park) and in egg shells — from  $1.0117 \pm 0.8486$  (Hetmanskyi NPP) to  $2.4185 \pm 0.2920$  mg/kg (Vakalivshchyna). In tits, the highest level of Cu was detected in egg contents, with concentrations significantly increasing from  $8.0206 \pm 0.5406$  (Vakalivshchyna) to  $19.3290 \pm 1.4840$  mg/kg (forest park). The lesser amount of Cu was found in egg shells, with concentrations slightly different among areas: from  $4.8646 \pm 0.6190$  (Vakalivshchyna) to  $5.2565 \pm 1.6620$  mg/kg (forest park; table 2). Thus, there are differences in Cu concentrations among species and areas. However, in Southern Poland the mean copper concentration in eggs of collared and pied flycatchers did not exceed 5.8 mg/g (Swiergosz et al., 1998). The researchers did not found any significance of differences between years in tissues. The Cu level varied from 6.1 mg/g to 25.4 mg/g in the breastbone and liver, respectively.

Zn in the flycatcher eggs ranged from  $19.6699 \pm 8.3333$  (forest park) to  $25.2304 \pm 0.1413$  (Vakalivshchyna) and in egg shells — from  $3.5832 \pm 0.0695$  (Hetmanskyi NPP) to  $7.4755 \pm 0.1808$  mg/kg (Vakalivshchyna). In tits, there was found a significant increasing trend for Zn in the egg contents from  $17.7877 \pm 0.1152$  (Hetmanskyi NPP) to  $66.9612 \pm 17.6665$  mg/kg (forest park). The tit egg shells had a lower Zn level, varying from  $12.8709 \pm 0.3355$  (Vakalivshchyna) to  $20.5372 \pm 0.1290$  (Hetmanskyi NPP) (table 3). It suggests the difference among species and areas in concentrations of this element. According to the research in Northern Poland the level of Zn in eggs ranged from 59 to 123 mg/g (Swiergosz et al., 1998) and the authors reported long-term fluctuations of Zn between years in all types of examined tissues (liver, breastbone and pectoral muscles), from 42 to 80 mg/kg.

**Table 2. Copper concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	6.1876 ± 0.2550	2.4185 ± 0.2920
	Hetmanskyi NNP	5.4662 ± 0.6630	1.0117 ± 0.8486
	Forest park	7.5426 ± 0.7000	1.5258 ± 0.8960
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	8.0206 ± 0.5406*	4.8646 ± 0.6190
	Hetmanskyi NNP	4.3492 ± 0.2079	5.0533 ± 0.2661
	Forest park	19.3290 ± 1.4840*	5.2565 ± 1.6620

\* Significance of differences at  $p < 0.001$ .

**Table 3. Zinc concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	25.2304 ± 0.1413	7.4755 ± 0.1808
	Hetmanskyi NNP	22.3562 ± 0.0543	3.5832 ± 0.0695
	Forest park	19.6699 ± 8.3333	6.1031 ± 1.0666
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	20.8660 ± 0.2996*	12.8709 ± 0.3355
	Hetmanskyi NNP	17.7877 ± 0.1152*	20.5372 ± 0.1290
	Forest park	66.9612 ± 17.6665*	16.8209 ± 1.9786

\* Significance of differences at  $p < 0.001$ .

**Table 4. Iron concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	63.3695 ± 0.3222	31.0013 ± 0.4124
	Hetmanskyi NNP	56.1361 ± 0.1239	12.9627 ± 0.1586
	Forest park	68.3270 ± 9.0000	22.0149 ± 2.4320
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	78.7017 ± 0.6831*	55.7402 ± 0.7650**
	Hetmanskyi NNP	44.6647 ± 0.2627	51.5698 ± 0.2942
	Forest park	249.5513 ± 40.2800*	70.4373 ± 4.5113**

\* Significance of differences at  $p < 0.001$ ; \*\* significance of differences at  $p < 0.005$ .

The statistical analysis has shown the differences in Fe concentrations among species and areas. Egg shells of collared flycatchers had from  $12.9627 \pm 0.1586$  mg/kg Fe in Hetmanskyi NNP to  $31.0013 \pm 0.4124$  mg/kg in Vakalivshchyna. The egg contents of flycatchers revealed Fe levels from  $56.1361 \pm 0.1239$  mg/kg (Hetmanskyi NNP) to  $68.3270 \pm 9.0000$  mg/kg (forest park). In tits, Fe prevailed in egg contents with a significant increasing trend from  $78.7017 \pm 0.6831$  (Vakalivshchyna) to  $249.5513 \pm 40.2800$  mg/kg (forest park). The tit egg shells had a lower level of Fe with a significance of differences between Vakalivshchyna ( $55.7402 \pm 0.7650$  mg/kg) and the forest park ( $70.4373 \pm 4.5113$  mg/kg) (table 4). However, according to the Northern Poland research, the differences between years were observed only for Fe in the breastbone, but was absent in the liver and pectoral muscles. Thus, concentrations of Cd, Cu and Fe were decreasing, and Zn was increasing in succeeding years but without a significance of differences between years (Swiergosz et al., 1998).

Manganese (Mn) is an important microelement supporting main mechanisms in tissues (Drown et al., 1986). However, accumulation of Mn high concentrations in the air may cause neurological and respiratory diseases in people (Roels et al., 1992). The laboratory research on mammals have shown that increased Mn levels lead to death and fertility reduction (Laskey et al., 1982), cause decrease in motion activity, dysfunction of nervous system and convulsions (Ingersoll et al., 1995). In egg contents of collared flycatchers there was detected a significant increasing trend for Mn between Vakalivshchyna ( $1.8669 \pm 0.1080$ )

**Table 5. Manganese concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	1.8669±0.1080*	0.7805±0.9990
	Hetmanskyi NNP	1.6583±0.1120	0.3583±0.1433
	Forest park	4.0671±0.1390*	0.4359±0.1779
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	2.6317±0.2289**	1.5709±0.2563
	Hetmanskyi NNP	1.3194±0.2374	1.5549±0.2658
	Forest park	6.9032±0.2946**	1.5770±0.3299

\* Significance of differences at  $p < 0.005$ ; \*\* significance of differences at  $p < 0.05$ .

and the forest park ( $4.0671 \pm 0.1390$ ). Mean Mn levels in the egg shells varied from  $0.3583 \pm 0.1433$  (Hetmanskyyi NPP) to  $0.7805 \pm 0.9990$  mg/kg (Vakalivshchyna). In egg contents of tits, there was also found a significant increasing trend between areas from  $2.6317 \pm 0.2289$  (Vakalivshchyna) to  $6.9032 \pm 0.2946$  mg/kg (forest park). No significance of differences in Mn levels was found in the tit egg shells (table 5).

Out of all examined shells only the egg shells of collared flycatchers from the forest park had selenium (Se) and cobalt (Co), in rather small quantities —  $0.0218$  and  $0.4359$  mg/kg, respectively. Though, in contrast to selenium, scanty concentrations of cobalt were found in egg-yolk of collared flycatchers in Hetmanskyyi NPP and Vakalivshchyna,  $0.0082$  and  $0.0533$  mg/kg, respectively (table 6). It suggests that among the studied birds only the collared flycatcher is able to accumulate these elements, presumably during migration.

Calcium (Ca) prevails among heavy metals found in bird eggs. It is known that the total amount of calcium that is transferred to an egg from the female body affects the clutch size, thickness and weight of the shell (Eeva, Lehtikoinen, 1995). Mean concentrations of Ca in egg contents of collared flycatchers varied from  $1255.2001 \pm 3.3268$  (Hetmanskyyi NPP) to  $1538.8370 \pm 0.0510$  (forest park) and in egg shells — from  $430.8237 \pm 4.2584$  (Hetmanskyyi NPP) to  $655.6440 \pm 11.0718$  mg/kg (Vakalivshchyna). In tits, the highest level of Ca was found in egg contents with a significant increasing trend from  $1244.1882 \pm 0.0018$  (Vakalivshchyna) to  $8298.3570 \pm 0.1080$  mg/kg (forest park). In the tit egg shells the Ca concentrations are significantly increasing if compare Vakalivshchyna ( $1294.2881 \pm 0.0020$ ) and the forest park ( $1688.3936 \pm 0.1209$  mg/kg) (table 7).

The weight of the shell in the North-Western Finland was higher in the great tits near the plant, i.e. in the area more contaminated with heavy metals, compared to the pied flycatchers in the areas more distant from sources of pollution (Eeva, Lehtikoinen, 1995). This difference in concentrations of Ca in both species of birds may be related to differences in their foraging behaviour. In particular, *P. major* during the breeding season chiefly collects prey from leaves (Gibb, 1954), whereas *F. hypoleuca* prefers terrestrial insects (Silverin, Andersson, 1984). This difference in prey selection could explain the presence of high amounts of calcium in faeces of great tit nestlings in comparison with those of pied flycatchers in

**Table 6. Selenium and cobalt concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg content (Se)	Shell (Se)	Egg contents (Co)	Shell (Co)
		x $\pm$ SE			
<i>Ficedula albicollis</i> Temm.	Hetmanskyyi NNP	0.0000	0.0000	$0.0082 \pm 0.0005$	0.0000
	Vakalivshchyna	0.0000	0.0000	$0.0533 \pm 0.0035$	0.0000
	Forest park	0.0000	$0.0218 \pm 0.0086$	0.0000	$0.4359 \pm 0.0290$
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Hetmanskyyi NNP	0.0000	0.0000	0.0000	0.0000
	Vakalivshchyna	0.0000	0.0000	0.0000	0.0000
	Forest park	0.0000	0.0000	0.0000	0.0000

\* Significance of differences at  $p < 0.001$ ; \*\* significance of differences at  $p < 0.005$ .

**Table 7. Calcium concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x $\pm$ SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	$1417.1716 \pm 8.6499$	$655.6440 \pm 11.0718$
	Hetmanskyyi NNP	$1255.2001 \pm 3.3268$	$430.8237 \pm 4.2584$
	Forest park	$1538.8370 \pm 0.0510$	$492.3929 \pm 0.0652$
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	$1244.1882 \pm 0.0018^*$	$1294.2881 \pm 0.0020^{**}$
	Hetmanskyyi NNP	$998.7001 \pm 0.0006$	$1153.2581 \pm 0.0006$
	Forest park	$8298.3570 \pm 0.1080^*$	$1688.3936 \pm 0.1209^{**}$

\* Significance of differences at  $p < 0.001$ ; \*\* significance of differences at  $p < 0.05$ .



**Table 8. Strontium concentrations (mg / kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg content	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	1.4936 ± 0.0864	1.9788 ± 0.1105
	Hetmanskyi NNP	2.3953 ± 0.1617	0.8431 ± 0.2069
	Forest park	0.1479 ± 0.0509	1.3078 ± 0.0651
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	0.1880 ± 0.0163*	3.1417 ± 0.0183
	Hetmanskyi NNP	1.9058 ± 0.3429*	1.2309 ± 0.3840
	Forest park	17.6032 ± 0.7512*	4.2052 ± 0.8413

\* Significance of differences at  $p < 0.001$ .

**Table 9. Nickel concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	0.3734 ± 0.0216	0.1099 ± 0.276
	Hetmanskyi NNP	0.3071 ± 0.0207	0.0211 ± 0.0265
	Forest park	0.2958 ± 0.0101	0.0218 ± 0.0129
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	0.3133 ± 0.0272	0.1013 ± 0.0305*
	Hetmanskyi NNP	0.2443 ± 0.0439	0.2591 ± 0.0492
	Forest park	0.5177 ± 0.0220	1.5770 ± 0.0247*

\* Significance of differences at  $p < 0.001$ .

reference areas near the plant. By now there had been no research detecting calcium in the insects being the prey of tits and flycatchers.

Strontium (Sr) in egg contents of the collared flycatcher ranged from  $0.1479 \pm 0.0509$  (forest park) to  $2.3953 \pm 0.1617$  (Hetmanskyi NPP) and in egg shells — from  $0.8431 \pm 0.2069$  (Hetmanskyi NPP) to  $1.9788 \pm 0.1105$  mg/kg (Vakalivshchyna). In tits, Sr prevailed in egg contents and significantly increased among areas from  $0.1880 \pm 0.0163$  (Vakalivshchyna) and  $1.9058 \pm 0.3429$  (Hetmanskyi NPP) to  $17.6032 \pm 0.7512$  mg/kg (forest park). In egg shells of tits Sr varied from  $1.2309 \pm 0.3840$  (Hetmanskyi NPP) to  $4.2052 \pm 0.8413$  mg/kg (forest park) (table 8).

Mean concentration of nickel (Ni) in egg shells of flycatchers varied from  $0.0211 \pm 0.0265$  (Hetmanskyi NPP) to  $0.1099 \pm 0.276$  mg/kg (Vakalivshchyna) and in egg contents — from  $0.2958 \pm 0.0101$  (forest park) to  $0.3734 \pm 0.0216$  mg/kg (Vakalivshchyna). In tits, there was found a significant increasing trend for Ni in egg shells when compared between Vakalivshchyna ( $0.1013 \pm 0.0305$  mg/kg) and the forest park ( $1.5770 \pm 0.0247$  mg/kg). In egg contents of tits concentrations of Ni varied from  $0.2443 \pm 0.0439$  (Hetmanskyi NPP) to  $0.5177 \pm 0.0220$  mg/kg (forest park) (table 9).

In collared flycatchers the Cr level in egg shells varied from  $0.2180 \pm 0.0128$  (forest park) to  $0.2199 \pm 0.0217$  mg/kg (Vakalivshchyna), and was not found at all in Hetmanskyi NPP. Mean Cr concentrations in egg-yolks of collared flycatchers ranged from  $0.1479 \pm 0.0100$  (forest park) to  $0.2134 \pm 0.0170$  (Vakalivshchyna). In egg shells of tits the

**Table 10. Chromium concentrations (mg/kg, dry wt.) in egg contents and egg shells**

Species	Area	Egg contents	Shell
		x ± SE	
<i>Ficedula albicollis</i> Temm.	Vakalivshchyna	0.2134 ± 0.0170	0.2199 ± 0.0217
	Hetmanskyi NNP	0.1843 ± 0.0200	0.0000
	Forest park	0.1479 ± 0.0100	0.2180 ± 0.0128
<i>Parus major</i> L., <i>P. caeruleus</i> L.	Vakalivshchyna	0.1880 ± 0.0360	0.2534 ± 0.0403
	Hetmanskyi NNP	0.1466 ± 0.0424	0.1944 ± 0.0474
	Forest park	0.0000	0.5257 ± 0.0224

chrome level varied from  $0.1944 \pm 0.0474$  (Hetmanskyi NPP) to  $0.5257 \pm 0.0224$  mg/kg (forest park). In egg contents of tits there were lesser amounts of Cr: from  $0.1466 \pm 0.0424$  (Hetmanskyi NPP) to  $0.1880 \pm 0.0360$  mg/kg (Vakalivshchyna) and it was not found at all in the forest park (table 10).

Brom (Br) was not found in samples.

Therefore, small quantities of some microelements (zinc, mercury, iron, manganese, selenium and iodine) are required for the normal growth and development of birds. Heavy metal concentrations that exceeded permissible limits and could lead to particular deceases and pathologies were not detected in egg shells and egg contents.

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## References

- Aronsson, K. A., Ekelund, N. G. 2004. A. Biological effects of wood ash application to forest and aquatic ecosystems. *Journal Environ. Qual.*, **33**, 1595–1605.
- Berglund Asa, M. M., Rainio Miia, J., Eeva, T. 2012. Decreased metal accumulation in passerines as a result of reduced emissions. *Environmental toxicology and chemistry*, **31** (6), 1317–1323.
- Burger, J. 2002. Food Chain differences affect heavy metals in bird eggs in Barnegat Bay, New Jersey. *Environmental Research Section A*, **90**, 33–39.
- Drown, D. B., Oberg, S. G., Sharma, R. P. 1986. Pulmonary clearance of soluble and insoluble forms of manganese. *J. Toxicol. Environ. Healths*, **17**, 201–212.
- Eeva, T., Lehikoinen, E. 1995. Egg shell quality, clutch size and hatching success of the great tit (*Parus major*) and the pied flycatcher (*Ficedula hypoleuca*) in an air pollution gradient. *Oecologia*, **102**, 312–323.
- Eeva, T., Lehikoinen, E. 2004. Rich calcium availability diminishes heavy metal toxicity in pied flycatcher. *Functional ecology*, **18**, 548–553.
- Eeva, T., Tanhuanpää, S., Råbergh, C., Airaksinen, S., Nikinmaa, M., Lehikoinen, E. 2000. Biomarkers and fluctuating asymmetry as indicators of pollution-induced stress in two hole-nesting passerines. *Functional ecology*, **14**, 235–243.
- Fowler, B. A., Whittaker, M. H., Lipsky, M., Wang, G., Chen, X.-Q. 2004. Oxidative stress induced by lead, cadmium and arsenic mixtures: 30-day, 90-day, and 180-day drinking water studies in rats: an overview. *Biometals*, **17** (5), 567–568.
- Gibb, J. 1954. Feeding ecology of tits, with notes on treecreeper and goldcrest. *Ibis*, **96**, 513–543.
- Gilyasov, A. S. 1993. Contents of metals in some birds of the Lapland reserve. In: Kozlov, M. V., Haukioja, E., Yarmishko, V. T., eds. Aerial pollution in Kola peninsula. *Kola Scientific Centre, Apatity*, 383–390.
- Grue, C. E., Hoffman, D. J., Beyer, W. N., Franson, L. P. 1986. Lead concentration and reproductive success in European starlings *Sturnus vulgaris* nesting within highway roadside verges. *Environ. Pollut. Ser. A*, **42**, 157–182.
- Hansen, K. H., Pedersen, A. J., Ottosen, L. M., Villumsen, A. 2001. Speciation and mobility in straw and wood combustion fly ash. *Chemosphere*, **45**, 123–128.
- Kabata-Pendias, A. 2004. Soil-plant transfer of trace elements — an environmental issue. *Geoderma*, **122**, 143–149.
- Laskey, J. W., Rehnberg, G. L., Hein, J. F., Carter, S. D. 1982. Effects of chronic manganese (Mn<sub>2</sub>O<sub>3</sub>) exposure on selected reproductive parameters in rats. *J. Toxicol. Environ. Health*, **9**, 677–687.
- Lebedeva, N. V., Minkina, T. M. 1998. Toxicant concentrations in a terrestrial food-web in South-West Russia. Pollution-induced changes in soil invertebrate food-webs edited by Ruslan O. Butovsky and Nico M. van Straalen. *Amsterdam and Moscow*, 99–196.
- Lebedeva, N. V. 2001. Birds as objects of bioindication. *Proc. of the XI International Symposium on Bioindicators. Syktyvkar, Komi Republic, September 17–21*, 226–236.
- Messadeh, A. M., Al-Safi, S. 2005. Analysis of cadmium and lead: their immunosuppressive effects and distribution in various organs of mice. *Biol. Trace Elem. Res.*, **108** (1–3), 279–286.
- Nyholm, N. E. I. 1994. Heavy metal tissue levels, impact on breeding and nestling development in natural populations of pied flycatcher (*Aves*) in the pollution gradient from a smelter. In: Donker, M. H., Eijssackers, H., Heimbach, F., eds. *Ecotoxicology of Soil Organisms*. Lewis Publishers, Boca Raton, USA.
- Pain, D. J. 1995. Lead in the environment. In: Hoffman, D. J., Rattner, B. A., Burton, G. A. J. & Cairns, J. J., eds. *Handbook of Ecotoxicology*. Lewis Publications, Boca Raton, FL, 356–391.
- Rodzin, E. V., Konstantinov, V. M., Fedorovskij, N. N. 2000. The content of heavy metals in the environment and in the body of gray crows *Corvus cornix* inhabiting on the Lyubertsy filtration fields in the suburbs of Moscow. *Russkij ornitologicheskij zhurnal*, **121**, 10–14 [In Russian].

- Savage, J. E. 1968. Trace minerals and avian reproduction. *Fed. Proc.*, **27**, 927–931.
- Silverin, B., Andersson, G. 1984. Föda hos svartvita flugsnappare *Ficedula hypoleuca*: en jämförelse mellan vuxna fåglar och boungar. *Vår Fågelvärld*, **43**, 517–524.
- Swiergosz, R., Sawicka-Kapusta, K., Nyholm, N. E. I., Zwolinska, A., Orkisz, A. 1998. Effects of environmental metal pollution on breeding populations of pied and collared flycatchers in Niepolomice Forest, Southern Poland. *Environmental Pollution*, **102**, 213–220.
- Timmer, L. W., Childers, C. C., Nigg, H. N. 2004. Pesticides registered for use on Florida citrus. In: Gainesville, F. L. Florida Citrus Pest Management Guide, SP-43, *University of Florida*.
- Zvereva, E. L., Kozlov, M. V. 2010. Responses of terrestrial arthropods to air pollution: A meta-analysis. *Environ. Sci. pollut. Res.*, **17**, 297–311.

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