ORIGINAL ARTICLE

Geographical and habitat differences in concentrations of copper, zinc and arsenic in eggshells of the Rook Corvus frugilegus in Poland

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Received: 8 April 2009 / Revised: 11 August 2009 / Accepted: 21 September 2009 / Published online: 10 October 2009 Dt. Ornithologen-Gesellschaft e.V. 2009

Abstract Levels of copper, zinc, and arsenic were analyzed in the Rook Corvus frugilegus eggshells from 43 breeding colonies located in different parts of Poland. The average [95% confidence interval (CI)] level of copper was found to be 8.13 (0.64–15.62) ppm, of zinc 13.81 (7.99– 19.62) ppm, and of arsenic 32.57 (25.60–39.54) ppm. The concentration levels of these metals varied widely in the surveyed shells, with the difference between extreme values being 90-fold for copper, 57-fold for zinc, and 36-fold for arsenic. General linear model (GLM) analysis revealed that the accumulation of copper in eggshells from urban rookeries was significantly higher than that in eggshells from rookeries in villages [average 19.31 (4.57–43.20) vs. 2.74 (2.36–3.12) ppm, respectively]. In comparison, the concentration of zinc in eggshells of urban colonies was only close to being significantly higher than that in eggshells of rural colonies ($P = 0.07$), and the arsenic levels in eggshells of rural and urban colonies were similar. No significant differences were found for any of the metals between rookeries located in the areas of intensive (western

Communicated by P. H. Becker.

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Poland) and extensive (eastern Poland) agriculture. Based on a comparison of our data with published data on arsenic contamination in different biota, including tissues and bird eggs of terrestrial and aquatic animals, the level of arsenic in Rook eggshells found in our study can be regarded as extremely high and is most likely due to the widespread use of pesticides containing arsenic.

Keywords Agricultural contaminants Arsenic · Biomonitoring · Bird eggs · Pesticides · Rookeries · Soil contamination · Trace elements

Introduction

The Rook Corvus frugilegus is a species of bird strongly associated with agro-ecosystems, especially in Central and Eastern Europe where by far the majority of rooks nest within farmed landscapes. Their diet is mainly based on Coleoptera and cereal grains that are found in the arable fields (Jabłoński [1979](#page-7-0); reviewed by Cramp [1998](#page-6-0); Kasprzykowski [2003](#page-7-0); Orłowski et al. [2009\)](#page-7-0). The strong link between the Rook and arable areas may make the species prone to the adverse or even lethal effects of agriculturally related contaminants, especially pesticides and heavy metals (Malmberg [1973\)](#page-7-0). Although the Rook is a common species in Central and Western Europe (Brenchley and Tahon [1997\)](#page-6-0), there have been no recent ecotoxicological studies on this species, and those that were carried out in the past only looked as single or, at the most, several rookeries (reviewed in Beyerbach et al. [1987\)](#page-6-0).

There is a shortage of studies investigating the level of contamination among different populations within the same species in the field of ecotoxicological research. Revolutionary changes in the intensification of agricultural

productivity, including the introduction of new fertilizing methods and the application of technologically advanced pesticides, focus attention on the acute need to determine the level of contaminants in the tissues of species strongly associated with agricultural areas. It is also of crucial importance to compare the level of contamination in the birds themselves with that of the environment.

In agricultural areas, the main source of heavy metal contamination, including copper (Cu) and zinc (Zn), are manure and slurry (Dach and Starmans [2005](#page-6-0)). An increase in livestock numbers and faulty utilization of large amounts of animal feces containing chemical remnants of food additives (mainly Cu and Zn) are considered to represent the main threats to the environment within the framework of the intensification of agricultural productivity in Europe (de Vries et al. [2002;](#page-6-0) Dach and Starmans [2005](#page-6-0)). The contamination of agricultural areas with arsenic (As) is linked to the massive use of pesticides containing this metal, which is believed to have started around the end of the nineteenth century (Murphy and Aucott [1998](#page-7-0); Peryea [1998;](#page-7-0) reviewed by Mandal and Suzuki [2002\)](#page-7-0). Copper (as copper hydroxide and copper sulfate) is similarly applied in many different kinds of pesticides (Epstein and Bassein [2001\)](#page-6-0), while As appears nowadays mainly in the form of monosodium methanearsonate (MSMA), monomethylarsocic acid (MMAV), and dimethylarsinic acid (DMAV) from which herbicides, including defoliants, are manufactured. Two other As compounds (lead arsenate and copper acetoarsenite), which have been in use for a considerably longer time, are the base for insecticide production. Arsenic and its derivatives affect biota and human health, and their biogeochemical cycles are currently being studied in many countries of the world (Mandal and Suzuki [2002](#page-7-0); Sierra-Alvarez et al. [2006\)](#page-7-0).

The metals can penetrate and permeate the entire tissue of birds following ingestion of heavy metal-contaminated prey or cereal grains (Best and Fisher [1982;](#page-6-0) Schafer et al. [1983\)](#page-7-0). The As level in Coleoptera, which constitute the main prey of the Rook (Orłowski et al. [2009\)](#page-7-0), may be very high after pesticide application (Morrissey et al. [2007](#page-7-0)). Female birds can eliminate surplus heavy metals in the eggshells (Burger [1994](#page-6-0); Dauwe et al. [2005\)](#page-6-0). Some pesticides contribute to the accumulation of the heavy metals in bird tissues; for example, the addition of dichlorodiphenyldichloroethylene (DDE) to the diet of the Black Duck Anas rubripes resulted in an increased Cu content in the eggshells (Longcore et al. [1972](#page-7-0)). According to Dauwe et al. ([1999\)](#page-6-0), the eggshell is a suitable indicator of heavy metal contamination, especially in the case of As, the level of which is higher in eggshells from contaminated breeding sites. However, the content of metals in eggs varies from species to species, and the contamination level is different in the shell than in the content of the egg itself (Burger

[1994](#page-6-0); Morera et al. [1997;](#page-7-0) Dauwe et al. [1999;](#page-6-0) Mora [2003](#page-7-0)). Mora [\(2003\)](#page-7-0) demonstrated that the eggshells of small Northern American passerines contained higher As and Cu concentrations that did the egg contents, while the reverse was true for Zn. In contrast, Morera et al. [\(1997](#page-7-0)) found relatively lower concentrations of Zn and Cu in the egg content of Audouin's Gull Larus audouinii. However, Swaileh and Sansur [\(2006](#page-7-0)) showed that the concentrations of Cu and Zn in the eggshell and the egg content of the House Sparrow Passer domesticus were highly correlated.

The aim of this study was to define the level of three heavy metals (As, Cu, and Zn) in the eggshells of rooks nesting in Poland. The study compared metal concentrations according to geographical position (western vs. eastern Poland) and rookery location (rural vs. urban habitat). Current growth in the intensification of agricultural production and the differences between western and eastern Poland (i.e., intensive vs. extensive agriculture, respectively) were expected to be factors causing differences between the levels of agriculture-related contaminants in the different colonies. Therefore, due to intensive agricultural practices in the western part of Poland, we expected the level of As to be higher in eggshells from colonies in western Poland than in those from colonies in eastern Poland. Accordingly, due to the high production of manure in rural areas, we expected the concentration of Zn and Cu to be higher in eggshells from rural rookeries than in those from urban rookeries.

Materials and methods

Rook eggshells were collected in the spring of 2005 in 43 rookeries (number of nests in particular colonies ranged from 5 to 480) located in Poland. The shells were picked up from the ground under nests. Membrane remnants and visible external dirt were removed from the eggshells before they were stored in glass containers for subsequent heavy metal analysis. All samples from different geographical locations, with varying intensities of agricultural production intensity and different habitat types, were collected for testing in the same manner.

The results of the analyses were categorized according to colonies located in the west (intensive agriculture) or east (extensive agriculture) of Poland as well as according to urban or rural sites. The river Vistula was the major geographic feature used to divide Poland into its eastern and western parts as it flows through the middle of Poland (Fig. [1\)](#page-2-0). Eight agricultural statistics were used to define intensive verus extensive agriculture: (1) the number of farm workers per kilometer; (2) milking capacity and (3) livestock number; (4) mineral fertilization intensity; (5) the number of available tractors and (6) harvesters; (7) the area

Fig. 1 Distribution of breeding colonies of the Rook Corvus frugilegus in Poland surveyed for copper, zinc, and arsenic levels in eggshells. Rookeries numbered as in [Appendix.](#page-5-0) The river Wisła (Vistula) is the border between western and eastern Poland (intensive vs. extensive agriculture; see [Materials and methods\)](#page-1-0)

sown in cereal crops, and (8) farm size (according to Chylarecki et al. 2006). Urban (cities, $n = 14$) and rural sites (villages, $n = 29$) were defined on the basis of the number of inhabitants in each locality, with 50,000 people taken as the threshold for defining a city (after Orłowski and Czapulak [2007\)](#page-7-0).

Due to the rather small amount of shells successfully collected in some rookeries, the metal concentration for each colony was determined using just two different shells or their fragments. In practice, large pieces of shells were used to ensure that the samples came from different eggs. Prior to the chemical analysis, all eggshells were rinsed twice with water containing detergent and air dried. They were then mineralized in a mixture of nitric and hypochloric acid in a high-pressure microwave digestion system (MARS-5; CEM, Matthews, NC). Atomic absorption spectroscopy (SpectrAA FS220; Varian, Palo Alto, CA) was used to determine the metal content. The measurement process was validated using reference material, DOLT-2 (fish liver) and DORM-2 (fish muscles), provided by the National Research Council of Canada Institute for National Measurement. The precision of the method, taken to be the degree of conformity between the results of multiple analyses performed on the same sample, corresponded to 5% (relative standard deviation, RSD). The measurements for the reference material were 25.8 ± 1.1 , 85.8 ± 2.5 and 16.6 ± 1.1 ppm for Cu, Zn, and As, respectively; in comparison, the average determined values (six measurements on 0.9-g samples) were 25.24 ± 0.25 , 87.20 \pm 0.35, and 17.6 \pm 1.0 ppm, respectively. All concentrations of metals were expressed in milligrams per kilogram (mg kg⁻¹ or parts per million; ppm) of dry mass (DW) at an accuracy of two decimal points.

Statistical analysis of the collected material was performed using Statistica ver. 7.0 (StatSoft [2006\)](#page-7-0) and Excel software. The statistical significance level was 0.05. The differences between heavy metal concentrations of specified data sets were tested using general linear model (GLM) analysis, with two values of metal concentration for each rookery used in each analysis. The combined effect between the levels of metals, taking into consideration an interaction between geographic and habitat divisions, was analyzed in GLM (StatSoft 2006), resulting in Wilks λ . The Spearman rank correlation coefficient (r_s) was used to define relationships between the analyzed metals. Data are presented as means with the 95% confidence interval (CI).

Results

The average (95% CI) concentration of Cu, Zn, and As in the Rook eggshells analyzed was 8.13 (0.64–15.62), 13.81 (7.99–19.62), and 32.57 (25.60–39.54) ppm, respectively. The concentrations of these heavy metals in eggshells collected from the various colonies survey varied enormously, with the difference between extreme values being 90-fold for Cu, 57-fold for Zn, and 36-fold for As [\(Appendix\)](#page-5-0). Extremely high concentrations of one specific metals were obtained only in a few colonies. Extremely high levels of Cu (>8 ppm) were measured in three rookeries located in two cities (633,000 and 71,000 inhabitants) in western Poland (two rookeries in Wrocław and one in Głogów; [Appendix](#page-5-0)); in the other 40 (93%) rookeries surveyed, the concentration of Cu did not exceed 7.60 ppm. Similar results were obtained for Zn: the concentration of Zn did not exceed 20.38 ppm in 40 rookeries, and extreme values were measured only in three rookeries in western Poland ([Appendix\)](#page-5-0). Arsenic concentration was more stable, and despite the lack of extremely high values, a very high concentration $(>=20 \text{ ppm})$ was recorded in 30 (70%) rookeries.

Statistically significant correlations among metal concentrations were recorded for Zn and Cu (Spearman rank correlation coefficient, $r_s = 0.22$, $P = 0.04$). For the other pairs of metals, these relationships were insignificant (Cu and As, $r_s = -0.16$, $P = 0.14$; As and Zn, $r_s = 0.10$, $P = 0.37$).

The accumulation of Cu in the eggshells of town-nesting rooks was significantly (sevenfold) higher than that in village-nesting rooks (Table [1](#page-3-0)). The concentration of Zn was also twofold higher in the eggshells of urban rookeries

Metal	Concentration	GLM				
	Average $(95\% \text{ CI})$	Min-max	Average $(95\% \text{ CI.})$	Min-max	F	P value
	Villages ($n = 29$)		Towns $(n = 14)$			
Cu	$2.74(2.36-3.12)$	$1.67 - 7.21$	19.31 (4.57–43.20)	1.93-150.45	9.772	0.002
Zn	$11.94(4.23 - 19.64)$	1.98-113.53	$17.77(8.60-26.73)$	2.64–59.58	1.741	0.190
As	35.32 (26.09–44.55)	2.45–87.30	26.86 (16.26–37.47)	3.40-58.06	2.703	0.104
	West $(n = 28)$		East $(n = 15)$			
Cu	$11.02(0.58-22.63)$	$1.67 - 150.45$	$2.74(2.49-3.00)$	$2.08 - 3.48$	2.320	0.131
Zn	$16.52(7.72 - 25.31)$	2.55–113.53	$8.75(5.36 - 12.13)$	1.98-20.16	3.377	0.070
As	30.94 (22.77-39.12)	$30.40 - 80.49$	35.6 (21.30–49.90)	2.45-87.30	0.829	0.365

Table 1 Results of the general linear model analysis on the concentrations (ppm) of copper, zinc, and arsenic in eggshells of the Rook Corvus frugilegus from breeding colonies located in villages and towns and in areas of intensive (west) and extensive agriculture (east) in Poland

GLM, General linear model; Cu, copper; Zn, zinc; As, arsenic; CI, confidence interval; Min, minimum; max, maximum

than in those of rural rookeries; however, this difference was only close to being statistically significant ($P = 0.07$). Arsenic levels were similar in both rural and urban colonies. No significant differences were found for any of the metals between the colonies located in the areas of intensive (western Poland) and extensive (eastern Poland) agriculture (Table 1).

An analysis of combined effect among the levels of metals in the surveyed rookeries, after their geographical and habitat categories had been taken into consideration, revealed a statistically significant interaction only in the case of Cu (GLM: Wilks $\lambda = 0.89$, $df = 83$, $P = 0.01$); for Zn and As, the combined effects were not statistically significant (GLM for Zn: Wilks $\lambda = 0.95$, $df = 83$, $P = 0.16$; GLM for As: Wilks $\lambda = 0.97$, $df = 83$, $P = 0.26$).

Discussion

The As concentration in the eggshells of 30 of the 43 rookeries surveyed in this study exceeded 20 ppm DW (see [Appendix](#page-5-0)). Based on published data on the level of As contamination in biota, including tissues of terrestrial and aquatic animals and bird eggs (Dauwe et al. [1999,](#page-6-0) [2005](#page-6-0); Kubota et al. [2002](#page-7-0); Mandal and Suzuki [2002](#page-7-0); Mora [2003](#page-7-0)), we consider the level of this metal to be extremely high. High levels of As in Rook eggshells should be linked with its long-term accumulation in the soil due the use of pesticides containing this metal (Murphy and Aucott [1998](#page-7-0); Peryea [1998\)](#page-7-0). The high usage of pesticides in Poland (total weight of insecticides, fungicides, rodenticides, and others) has appeared to be stable since the beginning of the 1960s $(in 1960: 45,013^{-3}$ kg; in 2005: $44,130^{-3}$ kg; GUS [1970–](#page-7-0) [2007\)](#page-7-0). However, it is difficult to relate pesticide usage to the absolute amount of active ingredients (currently used determinants), as the total usage of pesticides was defined in the past using different determinants. This is the primary reason why data on the combined weight of pesticides used in 1960 in Poland is incomparably higher than those that reported for Western Europe, where an almost tenfold increase of pesticide use was recorded between 1957 and 1995—based the amount of active ingredients (review in Sotherton and Holland [2003\)](#page-7-0).

Mora ([2003\)](#page-7-0) established the average As concentration (± standard deviation, SD) in the shells of two species of North American woodland passerines to be 2.1 (± 0.4) and 1.3 (\pm 0.2) ppm DW. The level of As in the shells of the Great Tit Parus major and the Blue Tit P. caeruleus living in contaminated areas in Belgium did not exceed 4.2 ppm (Dauwe et al. [1999](#page-6-0)), while the As concentration in tissues and egg contents in the Black-tailed Gull Larus crassirostris from Japan did not exceed 2.91 ppm DW (Kubota et al. [2002](#page-7-0)). According to the data of Erry et al. ([1999\)](#page-6-0), the As concentration in the organs of birds of prey originating from the UK did not exceed 0.346 ppm DW, while the highest concentrations described in the literature (56 ppm DW and 40.6 ppm DW) were found in the liver of a dead Osprey Pandion haliaetus (Wiemeyer et al. 1980) and Brown-headed Cowbird Molothrus ater (NAS [1977](#page-7-0)). According to Mandal and Suzuki [\(2002](#page-7-0)) an average level of As measured in freshwater fish amounts to 0.54 ppm in wet weight, although some values reach as up to 77 ppm. Equally high levels of As in the natural environment have been recorded only in soil, particularly in areas of As geological origin or in regions heavily contaminated by industry or agriculture (Mandal and Suzuki [2002](#page-7-0); Hossain [2006](#page-6-0)). The As level in unpolluted soils from various countries has been found to range from 0.1 to 40 ppm. In comparison, in some areas contaminated by pesticides or mining activity, it has been measured at between 57 and 2470 ppm (review in Hossain [2006](#page-6-0)), and in south-western Poland it was found to up to 800 ppm (WIOS [2008\)](#page-7-0).

In contrast to the As levels, the concentrations of Zn and Cu in the Rook eggshells analyzed in our study (excluding three extreme values for both metals; see [Appendix\)](#page-5-0) were not considerably different from the results obtained by other scientists studying the level of these metals in eggshells. The average level of Cu and Zn in eggshells of two small woodland passerines from Arizona was 3.0 and 6.2 ppm (Cu) and 9.5 and 46.2 ppm (Zn) (Mora [2003](#page-7-0)). The average concentration of Cu and Zn in eggshells of House Sparrow originating from the Middle East amounted to 1.0 (range 0.9–1.2 ppm) and 20.0 ppm (range 14.3–25.5) ppm, respectively (Swaileh and Sansur [2006](#page-7-0)). The average level of Cu and Zn in shells of the Great Tit and Blue Tit living in a contaminated area in Belgium was 3.2 and 32 ppm, respectively (Dauwe et al. [1999](#page-6-0)). The mean level of Cu in eggshells of the Grey Heron Ardea cinerea, Night Heron Nycticorax nycticorax, and Audouin's Gull nesting in Turkey was 6.75 and 1.37 ppm for the first two species and 1.85 and 10.20 ppm for the last species (data for two breeding colonies) (Ayas [2007](#page-6-0); Ayas et al. [2008](#page-6-0)). However, the eggshells of Grey Heron nesting in three different colonies in Poland in unpolluted areas had an average level of Cu ranging between 4.13 and 5.27 ppm, and of Zn ranging from 1.62 to 2.24 ppm (Dmowski [1999\)](#page-6-0). In two oceanic species, the Short-tailed Albatross Phoebastria albatrus and Black-footed Albatross, Ph. nigripes, found in Japan, the average Cu and Zn concentration in eggshells was 0.77– 0.78 and 3.39–5.61 ppm, respectively (Ikemoto et al. [2005](#page-7-0)).

The significantly higher average level of Cu in eggshells in Rook colonies located in towns was primarily due to extremely high Cu concentrations in three rookeries in south-western Poland (see [Appendix\)](#page-5-0). Exclusion of the data from these three sites resulted in very similar Cu values in both habitats (villages 2.74 ppm, towns 3.08 ppm). The extremely high Cu concentration in the eggshells from these three rookeries in south-western Poland is likely related to the geology of the area where a number of intensively exploited copper deposits are located. The average level of Cu in Rook eggshells in Poland (with the exception of these three extreme values) was found to be 2.83 (min–max 1.67–7.21) ppm (see [Appendix](#page-5-0)), which is considerably lower than the minimal value established as the lowest indicator (indices on a fiveclass scale from 0 to 5: \geq 100 ppm) of soil contamination in Poland (IOS 2003). A similar picture emerges for Zn, as its level in the Rook eggshells analyzed, following exclusion of the three extreme values, was found to be 9.41 ppm (min–max 1.98–20.38). This concentration is also considerably lower than the minimal value (50 ppm) reported as the lowest indicator of soil contamination in Poland (IOS^{[2003](#page-7-0)}). The three extremely high Zn levels were noted in the heavily industrialized cities in western Poland. Based on this result, we conclude that the Zn contamination does not originate from agriculture, a conclusion supported by the fact that the level of Zn in the soil exceeded the highest contamination class $(>=500$ ppm; accumulation data presented by WIOS^{2008}).

The extremely high level of As in the Rook eggshells analyzed here indicates that this metal can be regarded as a potential threat to the proper growth and development of birds. The lack of confirmation for our preliminary expectations of higher metal concentration in the eggshells of birds nesting in western Poland may be due to this species' biology and also to the fact that this species' winters in areas distant from their breeding areas. Rooks originating in Poland winter for several months mainly in Western Europe (Gromadzki and Mokwa [2005](#page-6-0)). Hence, the contamination level in eggshells of the Rook and other migratory bird species may be linked to a lesser degree with the contamination around the nesting sites than it is in resident species (Dmowski [1999](#page-6-0)). However, studies conducted on domesticated hens indicate that both the bioaccumulation and excretion of As is fast––birds fed on food with a high As content (up to 100 ppm) reached a maximum concentration in the sixth week, while the excretion of As by the birds was completed by 2 weeks after the experiment (Daghir and Nariri [1977](#page-6-0)). The two main As derivatives which have been applied as pesticides (arsenobetaine and dimethylarsinic acid) can permeate the eggshell to the inside of the bird eggs, and the former compound may account for as much as 95% of the total As content (Kubota et al. [2002](#page-7-0)). Arsenic accumulation in nestlings' tissues may lead to weight reduction; however, no effect of As on hatching success or on teratogenic activities has yet been reported (Stanley et al. [1994](#page-7-0)). According to Camardese et al. ([1990\)](#page-6-0), an extremely high As concentration (up to 430 ppm DW) in the vegetable food of Mallard Anas platyrhynchos nestlings increased nesting time and decreased overall nestling growth. It must be emphasized that despite the methodical inconveniences with assessing local contamination levels due to the Rook's migration cycle, the eggshells of this species should be used as a tool in monitoring agricultural contamination, especially that of pesticides and their remnants. The constant threat of heavy agricultural contamination indicates that there is an acute need for further studies on defining relations between the level of As in the environment, the amount in different tissues, and nestlings' condition.

Zusammenfassung

Geographische und Habitatunterschiede in den Konzentrationen von Kupfer, Zink und Arsen in Eierschalen der Saatkrähe Corvus frugilegus in Polen

Der Gehalt von Kupfer, Zink und Arsen wurde in Eierschalen der Saatkrähe Corvus frugilegus aus 43 in verschiedenen Teilen Polens gelegenen Brutkolonien

analysiert. Der durchschnittliche (95%-Konfidenzintervall) Gehalt von Kupfer betrug 8,13 (0,64-15,62) ppm, der von Zink 13,81 (7,99-19,62) ppm und der von Arsen 32,57 (25,60-39,54) ppm. Die Metallkonzentrationen in den untersuchten Eierschalen schwankten stark. Im Falle von Kupfer bestand ein 90-facher Unterschied zwischen den Extremwerten, für Zink war er 57-fach und für Arsen 36-fach. Eine allgemeine lineare Modellanalyse zeigte, dass die Anreicherung von Kupfer in Eierschalen aus Krähenhorsten in Städten signifikant höher war als aus Horsten in Dörfern (Mittelwerte (95%-Konfidenzintervall) 19,31 ppm (4,57-43,20) bzw. 2,74 ppm (2,36-3,12)). In den Eierschalen von in Städten nistenden Saatkrähen war die Zinkkonzentration gerade eben nicht signifikant höher $(P = 0.07)$. Die Arsenkonzentrationen in Kolonien auf dem Land und in der Stadt waren ähnlich. Für keines der Metalle bestanden signifikante Konzentrationsunterschiede zwischen Horsten in Regionen intensiven (Westpolen) und extensiven (Ostpolen) Ackerbaus. Im Vergleich mit anderen Daten zur Arsenbelastung verschiedener Biota, einschließlich der Gewebe und Eier landlebender und aquatischer Vögel, sollte der Gehalt dieses Metalls in den Eierschalen von Saatkrähen als extrem hoch angesehen werden. Dies ist wahrscheinlich auf den weitverbreiteten Gebrauch von arsenhaltigen Pestiziden zurückzuführen.

Acknowledgments We are grateful to A. Wuczyński, P. T. Dolata, K. Kujawa, R. Kruszyk, J. Pietrowiak, M. Rachel, T. Mazgajski, R. Piekarski, S. Kuźniak, S. Jędrzejewski, A. Sokołowska, T. Wilżak, J. Ratajczak, P. Tryjanowski, T. Stawarczyk, M. Słupek, M and U. Martini, and the Management of Landscape Parks in Sieradz for participating in the ecotoxicological study of the Rook in Poland. We would also like to thank M. Sek for checking the English version of the text.

Appendix

Table 2.

Table 2 Concentration of Cu, Zn, and As in eggshells of the Rook C. frugilegus from the surveyed breeding colonies in Poland

Number ^a	Location	Region ^b	Status of colony ^c		Metal level (ppm) ^d					
			Village/town	West/east	Cu		Zn		As	
1	Wrocław (1)	D	$\mathbf T$	W	2.84	2.84	35.68	52.51	7.92	7.00
2	Wrocław (2)	D	$\mathbf T$	W	4.67	4.89	3.97	6.21	3.64	3.16
3	Wrocław (3)	${\bf D}$	$\mathbf T$	W	60.92	70.29	9.31	12.73	9.893	9.695
4	Wrocław (4)	${\bf D}$	$\mathbf T$	W	150.24	150.66	15.53	16.81	33.78	33.41
5	Pietrzykowice	${\bf D}$	V	W	2.91	2.83	10.62	15.41	26.99	24.62
6	Oleśnica	D	V	W	2.76	2.74	2.94	4.58	37.17	34.95
7	Środa Śląska	${\bf D}$	$\ensuremath{\mathbf{V}}$	W	2.78	2.81	3.24	5.13	15.23	15.04
8	Przerzeczyn Zdrój	${\bf D}$	$\ensuremath{\mathbf{V}}$	W	1.85	1.80	1.97	3.13	28.69	25.61
9	Ząbkowice Śląskie	D	V	W	3.76	3.71	15.59	21.66	39.25	33.89
10	Pszenno	D	\mathbf{V}	W	2.79	2.87	5.10	7.89	21.36	18.85
11	Borek Strzeliński	D	V	W	1.70	1.64	2.04	3.25	30.87	27.59
12	Zgorzelec	D	V	W	2.62	2.50	11.34	16.99	80.14	76.48
13	Zebrzydów	D	V	W	7.60	6.82	117.96	109.10	11.73	13.15
14	Strzelin	D	$\ensuremath{\mathbf{V}}$	W	2.88	2.93	4.65	7.55	79.99	81.00
15	Łagiewniki	D	V	W	2.58	2.55	5.20	8.49	37.16	33.10
16	Świdnica	D	$\mathbf T$	W	2.54	2.53	9.41	13.04	8.09	6.44
17	Głogów	D	$\mathbf T$	W	20.59	20.28	9.23	0.52	18.79	21.59
18	Gorzów Wlkp (1)	L	$\mathbf T$	W	2.15	2.11	55.17	64.00	49.86	52.73
19	Gorzów Wlkp (2)	L	$\mathbf T$	W	2.32	2.23	15.26	18.68	34.22	38.30
20	Wodzisław Śl.	Ś	$\mathbf T$	W	3.72	3.12	9.49	14.72	18.37	18.02
21	Gołębin Stary	W	\mathbf{V}	W	2.17	1.41	4.81	7.052	80.64	73.67
22	Żerków	W	V	W	2.09	2.06	6.98	10.35	10.58	8.56
23	Kępno	W	V	W	2.15	2.12	5.12	8.23	33.75	30.34
24	Laski	W	V	W	1.93	1.88	3.43	5.64	34.76	31.65
25	Warszawa (1)	M	$\mathbf T$	W	5.01	4.51	15.42	25.33	53.12	61.70
26	Warszawa (2)	$\mathbf M$	T	W	3.24	3.24	7.38	11.65	23.51	26.81
27	Warszawa (3)	M	T	W	2.01	1.86	12.54	17.58	24.16	27.72

Table 2 continued

Number ^a	Location	Regionb	Status of colony ^c		Metal level $(ppm)^d$					
			Village/town	West/east	Cu		Zn		As	
28	Warszawa (4)	M	T	W	2.74	2.54	15.03	22.21	20.38	23.81
29	Podnieśno	P	V	E	3.21	3.23	3.50	5.50	15.82	12.21
30	Wyszków	P	V	E	2.63	2.65	11.76	13.34	18.33	14.71
31	Iganie	P	V	E	3.08	3.10	2.42	3.72	2.54	2.36
32	Biodry	P	V	E	2.11	2.04	4.20	6.64	3.55	2.48
33	Zelków	P	V	E	2.28	2.27	5.45	8.29	57.72	56.07
34	Czyżew	P	V	E	2.14	2.13	2.47	3.89	30.04	26.49
35	Zembrów	P	V	E	2.44	2.39	1.59	2.36	23.41	18.97
36	Stoczek Łukowski	P	V	E	2.14	2.09	5.62	8.62	39.23	35.34
37	Wizna	P	V	E	3.02	3.06	4.52	7.38	46.67	43.67
38	Siedlce	P	T	E	3.33	3.40	2.05	3.24	59.03	57.09
39	Oleśnica	P	V	E	2.87	2.92	9.78	12.60	78.49	80.20
40	Mokobody	P	V	E	2.95	3.00	18.63	16.67	24.51	25.48
41	Seroczyn	P	V	E	2.89	2.89	21.12	19.19	40.55	41.77
42	Mordy	P	V	E	2.58	2.57	19.41	18.27	87.36	87.25
43	Toczyska	P	V	E	3.45	3.51	8.03	12.13	19.97	16.66

Three highest concentrations are marked in bold

^a Designated number of a rookery, as in Fig. [1](#page-2-0)

^b Region: D, Dolnośląskie; L, Lubuskie; Ś, Śląskie; W, Wielkopolskie; M, Mazowieckie; P, Podlaskie

^c T, Town; V, village; W, west; E, east

^d Metal levels from two analyzed shells per colony are shown

References

- Ayas Z (2007) Trace element residues in eggshells of grey heron (Ardea cinerea) and black-crowned night heron (Nycticorax nycticorax) from Nallihan Bird Paradise, Ankara, Turkey. Ecotoxicology 16:1573–3017
- Ayas Z, Celikkan H, Aksu ML (2008) Lead (Pb) and copper (Cu) concentration in the eggshells of Audouin's Gulls (Larus audouinii) in Turkey. Turk J Zool 32:1–6
- Best LB, Fisher DL (1982) Granular insecticides and birds: factors to be considered in understanding exposure and reducing risk. Environ Toxicol Chem 11:1495–1508
- Beyerbach M, Büthe A, Heidmann WA, Dettmer R, Knüwer H (1987) Chlorierte Kohlenwasserstoffe in Eiern und Lebern von Saatkrähen (Corvus frugilegus) aus niedersächsichen Brutkolonien. J Ornithol 128:277–290
- Brenchley A, Tahon J (1997) Rook Corvus frugilegus. In: Hagemeijer EJH, Blair MJ (eds) The EBCC atlas of European breeding birds: their distribution and abundance. T & AD Poyser, London
- Burger J (1994) Heavy metals in avian eggshells: another excretion method. J Toxicol Environ Health 41:207–220
- Camardese MB, Hoffman DJ, LeCaptain LJ, Pendleton GW (1990) Effects of arsenate on growth and physiology in mallard ducklings. Environ Toxicol Chem 9:785–794
- Chylarecki P., Jawińska D., Kuczyński L (2006) Common breeding bird monitoring in Poland: annual report 2003–2004. Polish Society for the Protection of Birds, Warsaw. Available at: <http://www.otop.pl>
- Cramp S (ed) (1998) The complete birds of the Western Palearctic on CD-ROM. Oxford University Press, Oxford
- Dach J, Starmans D (2005) Heavy metals balance in Polish and Dutch agronomy: actual state and previsions for the future. Agric Ecos Environ 107:309–316
- Daghir NJ, Nariri NN (1977) Determination of total as residues in chicken eggs. J Agric Food Chem 25:1009–1010
- Dauwe T, Bervoets L, Blust R, Pinxten R, Eens M (1999) Are eggshells and egg contents of great and blue tits suitable as indicators of heavy metal pollution? Belg J Zool 129:439–447
- Dauwe T, Janssens E, Bervoets L, Blust R, Eens M (2005) Heavy metal concentrations in female laying great tits (Parus major) and their clutches. Arch Environ Contam Toxicol 49:249–256
- de Vries W, Römkens PF, van Leeuwen T, van Bronswijk JJ (2002) Heavy metals. In: Hagyart PM, Jarvis SC (eds) Agriculture hydrology and water quality. CAB Int, Oxon, pp 107–132
- Dmowski K (1999) Birds as bioindicators of heavy metal pollution: review and examples concerning European species. Acta Ornithol 34:1–25
- Epstein L, Bassein S (2001) Pesticide applications of copper on perennial crops in California, 1993–1998. J Environ Qual 30:1844–1847
- Erry BV, Macnair MR, Meharg AA, Shore RF, Newton I (1999) Arsenic residues in predatory birds from area of Britain with naturally and anthropogenically elevated arsenic levels. Environ Pollut 106:91–95
- Gromadzki M, Mokwa K (2005) Migrations and wintering of the Rook Corvus frugilegus in Poland––analysis based on recoveries. In: Jerzak L, Kavanagh BP, Tryjanowski P (eds) Corvids of Poland. Bogucki Wydawnictwo Naukowe, Poznań, pp 319-331
- Hossain MF (2006) Arsenic contamination in Bangladesh––an overview. Agric Ecos Environ 113:1–16
- Ikemoto T, Kunito T, Tanabe S, Tsurumi M, Sato F, Oka N (2005) Non-destructive monitoring of trace element levels in shorttailed albatrosses (Phoebastria albatrus) and black-footed albatrosses (Phoebastria nigripes) from Torishima Island, Japan, using eggs and blood. Mar Pollut Bull 51:889–895
- IOS´ (2003) The State of Environment in Poland 1996–2001. Inspection for Environmental Protection, Warsaw
- Jabłoński B (1979) Food of the rook, Corvus frugilegus L. in different parts of its territory (in Polish). Przegl Zool 23:67–80
- Kasprzykowski Z (2003) Habitat preferences of foraging Rooks Corvus frugilegus during the breeding period in the agricultural landscape of eastern Poland. Acta Ornithol 38:27–31
- Kubota R, Kunito T, Tanabe S, Ogi H, Shibata Y (2002) Maternal transfer of arsenic to eggs of black-tailed gull (Larus crassirostris) from Rishiri Island, Japan. Appl Organomet Chem 16:463–468
- Longcore JR, Samson FB, Kreitzer JF, Spann JW (1972) Changes in mineral composition of eggshells from black ducks and mallards fed DDE in the diet. Bull Environ Contam Toxicol 6:345–350
- Malmberg T (1973) Pesticides and the rook Corvus frugilegus in Scania, Sweden between 1955 and 1970. Oikos 24:377–387
- Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235
- Mora M (2003) Heavy metals and metalloids in egg contents and eggshells of passerine birds from Arizona. Environ Poll 125:393–400
- Morera M, Sanpera C, Crespo S, Jover L, Ruiz X (1997) Inter- and intrclutch variability in heavy metals and selenium levels in Audouin's Gull eggs from the Ebro Delta, Spain. Arch Environ Contam Toxicol 33:71–75
- Morrissey CA, Albert CA, Dods PL, Cullen WR, Lai VW, Eliot JE (2007) Arsenic accumulation in bark beetles and forest birds occupying mountain pine beetle infested stands treated with monosodium methanearsonate. Environ Sci Technol 41:1494– 1500
- Murphy EA, Aucott M (1998) An assessment of the amount of arsenical pesticide used historically in a geographic area. Sci Total Environ 218:89–101
- NAS (1977) Arsenic: medical and biological effects of environmental pollutants. National Academy of Science, Washington, DC, p 332
- Orłowski G, Czapulak A (2007) Different extinction risks of the breeding colonies of Rook Corvus frugilegus in rural and urban areas of SW Poland. Acta Ornithol 42:145–155
- Orłowski G, Kasprzykowski Z, Zawada Z, Kopij G (2009) Stomach content and grit ingestion by Rook Corvus frugilegus nestlings. Ornis Fenn 86: (in press)
- Peryea FL (1998) Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation. In: Proc 16th World Congress Soil Sci (CD Rom). Montpellier. Available at: [http://soils.tfrec.wsu.edu/leadhistory.](http://soils.tfrec.wsu.edu/leadhistory.htm) [htm](http://soils.tfrec.wsu.edu/leadhistory.htm)
- Schafer EW Jr, Bowlers WA Jr, Hurlbut J (1983) The acute oral toxicity, repellency, and hazard potential of 998 chemicals to one or more species of wild and domestic birds. Arch Environ Contam Toxicol 12:355–382
- Sierra-Alvarez R, Yenal U, Field JA, Kopplin M, Gandolfi AJ, Garbarino JR (2006) Anaerobic biotransformation of organoarsenical pesticides monomethylarsonic acid and dimethylarsinic acid. J Agric Food Chem 54:3959–3966
- Sotherton N, Holland J (2003) Indirect effects of pesticides on farmland wildlife. In: Hoffman DJ, Barnett A, Rattner G, Burton GA, Cairns J (eds) Handbook of ecotoxicology, 2nd edn. CRC Press, Boca Raton, pp 1173–1192
- Stanley TR, Spann JW, Smith GJ, Rosscoe R (1994) Main and interactive effects of arsenic and selenium on mallard reproduction and duckling growth and survival. Arch Environ Contam Toxicol 26:444–451
- StatSoft (2006) Statistica (data analysis software system), version 7.1. StatSoft, Tulsa. Available at: www.statsoft.com
- Swaileh KM, Sansur R (2006) Monitoring urban heavy metal pollution using the house sparrow (Passer domesticus). J Environ Monit 8:209–213
- WIOŚ (2008) Ocena stopnia zanieczyszczenia gleb województwa dolnośląskiego w 2007 roku—obszary bezpośrednio zagrożone zanieczyszczeniami (The assessment of soil contamination level in the Lower Silesia region in 2007––areas directly threatened by contamination). Wojewódzki Inspektorat Ochrony Srodowiska we Wrocławiu, Wrocław. Available at: [http://wroclaw.pios.gov.](http://wroclaw.pios.gov.pl/pliki/gleby/ocena_2007.pdf) [pl/pliki/gleby/ocena_2007.pdf](http://wroclaw.pios.gov.pl/pliki/gleby/ocena_2007.pdf)
- Wydawnictwo GUS (1970–2007) Statistical yearbook of the Republic of Poland. Wydawnictwo GUS, Warsaw