Bull. Environ. Contam. Toxicol. (2003) 71:163–169

DOI: 10.1007/s00128-003-0144-8

Bulletin of Environmental Contamination and Toxicology

Organochlorine Pesticides in Eggs of Birds of Prey from the Stavropol Region, Russia

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Received: 12 January 2003/Accepted: 15 April 2003

Birds of prey became legally protected in the USSR in 1964, but a decade later Galushin (1977) reported evidence that eagle, sea eagle, peregrine falcon *Falco peregrinus*, osprey *Pandion haliaetus* and even black kite *Milvus migrans* populations continued to decline. For the species with continued declines, Galushin suggested that destruction of habitat, use of pesticides, disturbance, occasional shooting and nest destruction may be important factors.

To determine the extent of chemical contamination in Russian birds of prey, we made a series of egg collections. Eggs of the peregrine falcon, a species that rapidly declined in Russia, were collected above the Arctic Circle on the Kola Peninsula in 1991 and adult females were fitted with satellite transmitters to determine wintering localities in 1994 (Henny et al 1994, Henny et al 2000), Osprey eggs were collected along the Upper Volga River in 1992 (Henny et al 1998a), and 12 species of raptor eggs were collected in three southcentral European Regions (Lipetsk, Voronezh and Saratov) in 1992 and 1993 (Henny et al 1998b). This paper, the fifth in the series, presents results of organochlorine pesticide analyses conducted on eggs of nine species of birds of prey collected in the Caucasus Mountains of southwestern Russia near Stavropol.

MATERIALS AND METHODS

In 1995, 39 eggs (one egg per clutch) were collected from raptor nests in the Stavropol Region. This portion of southwestern European Russia is located between the Black Sea and the Caspian Sea. The common kestrel *Falco tinnunculus* and red-footed falcon *F. vespertinus* accounted for 20 of the eggs. Eight of the common kestrel eggs came from within 15 km of Stavropol, with the other four from 230 km E., 90 km NE, 80 km NW, and 100 km NW of Stavropol. The red-footed falcon eggs were all collected from 20 to 70 km N or NW of Stavropol. Ten long-eared owl *Asio otus* eggs included three within 8 km of Stavropol, five 50-120 km NW, and two 220 km E of Stavropol. Three northern marsh harrier *Circus aeruginosus* eggs were collected 15 km NW, 90 km NW, and 70 km NE of Stavropol, and both scops owl *Otus scops* eggs 40 km NW of Stavropol. The Eurasian sparrowhawk *Accipiter nisus* and northern goshawk *A. gentilis* eggs were collected at forested edges within the city

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of Stavropol, but the goshawk nest was near abandoned (at least 5 years) orchards (pears, walnuts, apples). The only common buzzard *Buteo buteo* egg was collected 12 km NW of Stavropol, and the only lesser spotted eagle *Aquila pomarina* egg in the Kislovodsk Area 160 km SE of Stavropol. The general land use in the Stavropol Region was agriculture (wheat, barely, corn and other row crops) with planted forest strips, woodlands, isolated groves, forested bottoms associated with rivers, and grasslands. None of the nests could be monitored to evaluate their success.

The collected eggs were opened in Russia, placed in chemically cleaned jars and frozen for preservation. Egg contents were analyzed at the Mississippi State Chemical Laboratory. Ten gram tissue samples were thoroughly mixed with anhydrous sodium sulfate and soxhlet extracted with hexane for seven hours. The extract is concentrated by rotary evaporation; transferred to a tared test tube, and further concentrated to dryness for lipid determination. The weighed lipid sample was dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues were partitioned into petroleum ether which is washed, concentrated, and transferred to a glass chromatographic column containing 20 g of Florisil. The column was eluted with 200 ml 6% diethyl ether / 94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether / 85% petroleum ether (Fraction II). Fraction II was concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. Fraction I was concentrated and transferred to a silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions were eluted from the silicic acid column. Each was concentrated to appropriate volume for quantification of residues by packed or megabore column, electron capture gas chromatography. Polychlorinated biphenyls (PCBs) were located in Fraction II. Eggs were analyzed for alpha-hexachlorocyclohexane (α-BHC), β-BHC, Δ-BHC, lindane, hexachlorobenzene (HCB), heptachlor epoxide (HE), oxychlordane, gamma chlordane, alpha chlordane, *trans*-nonachlor, *cis*-nonachlor, dieldrin, endrin, mirex, p,p′-DDE (DDE), p,p′-DDD (DDD), p,p′-DDT (DDT), o,p′-DDE, o,p′-DDD, o,p′-DDT, toxaphene, and total PCBs. Spiked and duplicate samples were also analyzed (10% of total). Recovery rates of spiked samples were 90 to 105% except for HCB (70-75%). The detection limits were 0.05 ppm for toxaphene and total PCBs, and 0.01 ppm for all other pesticides and metabolites. When a contaminant was not detected, half of the detection limit was used to calculate the geometric mean. However, a geometric mean was not calculated if ≥ 50% of the samples were below the detection limit. Residue concentrations in eggs were corrected to an approximate fresh wet wt. (ww) using egg volumes (Stickel et al 1973); all organochlorines in eggs were expressed on a fresh ww basis.

RESULTS AND DISCUSSION

Segments of the Stavropol Region are now farmed, and many of the buzzards, kestrels, falcons, harriers, goshawks, and owls nest in close association with agriculture. We considered all species to be migratory in at least portions of their range and, therefore, could accumulate contaminants on wintering grounds which sometimes are great distances from nesting areas (see Henny et al 1998b).

The large series of 12 common kestrel eggs were divided into two categories, those collected within 15 km and those from 80-230 km of Stavropol (Table 1). DDE and β-BHC were detected in 11 and 10 of the 12 eggs, respectively. The only other contaminant detected was 0.03 ppm α-BHC in the egg with the highest concentration of β-BHC (0.30 ppm). Geometric mean DDE concentrations (0.02 vs. 0.03 ppm) and mean β-BHC concentrations (0.02 vs. 0.07 ppm) were similar between the two locations. The red-footed falcon eggs contained DDE (0.05 ppm) and β-BHC (0.03 ppm) concentrations similar to the common kestrel.

Ten long-eared owl eggs all contained DDE (geo. mean 0.41 ppm) and 9 of 10 had β-BHC (geo. mean 0.04 ppm). No pattern for DDE was apparent among locations with five eggs containing 0.06 to 0.21 ppm, and five eggs 0.99 to 4.58 ppm -- they contained either extremely low or moderate concentrations. β-BHC was uniformly low, with two eggs also containing low concentrations of α-BHC (0.03 and 0.07 ppm). Two other long-eared owl eggs had low concentrations of HCB (0.06 and 0.41 ppm). Only DDE (geo. mean 0.11 ppm) was detected in the two scops owl eggs from the same general area.

The three northern marsh harrier eggs all contained DDE (geo. mean 1.00 ppm), DDD (geo. mean 0.02 ppm) and β-BHC (geo. mean 0.07 ppm). The only common buzzard egg contained low concentrations of DDE (0.07 ppm) and β-BHC (0.03 ppm), with the lone lesser spotted eagle egg containing only slightly higher concentrations of both contaminants (0.15 and 0.06 ppm, respectively).

On 13 April 1995, a pair of nesting northern goshawks with 4 eggs was observed, but an egg was not collected. The nest was destroyed by corvids and a second 4-egg clutch was laid about one month later (a few days into incubation when egg collected on 13 May 1995). The northern goshawk egg from the second clutch contained the most contaminants recorded during this study (DDE 3.08 ppm, DDD 0.13 ppm, β-BHC 0.55 ppm, HCB 0.04 ppm, and toxaphene 0.09 ppm). The goshawk nest was near orchards, which were possible sources for the organochlorine pesticides detected. The Eurasian sparrowhawk egg contained lower concentrations of DDE (1.82 ppm) and DDD (0.05 ppm), but also the parent-DDT (0.02 ppm) and β-BHC (0.21 ppm).

The common kestrel, red-footed falcon, long-eared owl, northern goshawk and common buzzard comprised 32 of the 39 raptor eggs collected in Stavropol, but other eggs from the same species were collected at one or more locations in Russia in 1992 (Table 2). DDE and β-BHC were the most common contaminants found in the common kestrel and red-footed falcon and were uniformly low in the Stavropol Region and the other Russian sites. Other contaminants in the two species were

Table 1. Organochlorine pesticides in birds of prey eggs from Stavropol Region, Russia, 1995.

Species (N)[a]	Clutch Size (N)[b]	Geo. Mean (ppm wet wt)					
		DDE	DDD	DDT	β-BHC	α-BHC	HCB
Common Kestrel							
≤ 15 km Stavropol (8)	5.00 (7)	0.02	_	_	0.02	_	_
Range	4-6	ND[c]-0.39	ND	ND	ND-0.18	ND	ND
≥80 km Stavropol (4)	2.67 (3)	0.03	_	_	0.07	NC[d]	_
Range	1-5	0.03-0.04	ND	ND	0.02-0.30	ND-0.03	ND
Red-footed Falcon (8)	3.50 (4)	0.05	_	_	0.03	_	_
Range	2-4	0.02-0.55	ND	ND	0.01-0.08	ND	ND
Long-eared Owl (10)	4.57 (7)	0.41	_	_	0.04	NC	NC
Range	4-6	0.06-4.58	ND	ND	ND-0.27	ND-0.07	ND-0.41
Northern Marsh Harrier (3)	3.00 (2)	1.00	0.02	_	0.07	_	_
Range	2-4	0.65-1.28	0.01-0.02	ND	0.04-0.14	ND	ND
Scops Owl (2)	_	0.11	_	_	_	_	_
Range	_	0.08-0.14	ND	ND	ND	ND	ND
Eurasian Sparrowhawk (1)	_	1.82	0.05	0.02	0.21	ND	ND
Northern Goshawk (1)[e]	4.00 (1)	3.08	0.13	ND	0.55	ND	0.04
Common Buzzard (1)	3.00 (1)	0.07	ND	ND	0.03	ND	ND
Lesser Spotted Eagle (1)	_	0.15	ND	ND	0.06	ND	ND

[a] Number of eggs analyzed.
[b] Mean includes egg collected for analysis, but excludes nests with fresh eggs (possibly incomplete clutches).
[c] ND = none detected.
[d] NC = Not calculated if ≥50% of the samples below detection limit.
[e] Also contained toxaphene (0.09 ppm).

Table 2. A comparison of DDE, β-BHC, and PCBs in birds of prey eggs collected at Stavropol and other locations in Russia, 1992-1995.

Species/Location	N	Year	Geo. Mean (ppm wet wt) DDE	β-BHC	PCBs	Source
Common Kestrel						
Stavropol (≤ 15 km)	8	1995	0.02	0.02	< 0.05	This Study
Stavropol (≥ 80 km)	4	1995	0.03	0.07	< 0.05	This Study
Voronezh	3	1992	0.03	0.01	0.02	Henny et al (1998b)
Lipetsk	5	1992	0.06	0.01	0.05	Henny et al (1998b)
Sarotov	12	1992	0.03	0.02	0.02	Henny et al (1998b)
Red-footed Falcon						
Stavropol	8	1995	0.05	0.03	< 0.05	This Study
Sarotov	2	1992	0.03	0.01	0.02	Henny et al (1998b)
Long-eared Owl						
Stavropol	10	1995	0.41	0.04	< 0.05	This Study
Sarotov	1	1992	0.07	< 0.01	0.04	Henny et al (1998b)
Northern Goshawk						
Stavropol	1	1995	3.08	0.55	< 0.05	This Study
Voronezh	1	1992	1.14	0.08	0.26	Henny et al (1998b)
Lipetsk	1	1992	1.37	0.04	0.41	Henny et al (1998b)
Common Buzzard						
Stavropol	1	1995	0.07	0.03	< 0.05	This Study
Voronezh	4	1992	0.15	0.01	0.06	Henny et al (1998b)
Lipetsk	5	1992	0.20	0.02	0.22	Henny et al (1998b)

seldom detected, but when detected were always at low concentrations. PCBs were not detected in any species during this study, but our detection limit (0.05 ppm) was slightly higher than in the earlier studies (0.01 ppm) in Lipetsk, Voronezh and Saratov (Henny et al 1998b). The 10 long-eared owl eggs from Stavropol presented an interesting dichotomy with half showing extremely low DDE (0.06 to 0.21 ppm), and the others moderate concentrations (0.99 to 4.58 ppm), with β-BHC uniformly low. The only other long-eared owl egg collected (at Sarotov) had low DDE and no β-BHC. From a comparative perspective, 21 long-eared owl eggs collected in Oregon, USA, between 1978 and 1980 contained a geometric mean of 0.24 ppm DDE, no β-BHC, and PCBs only in one egg (but detection limit 0.50 ppm) with excellent reproductive success (Henny et al 1984). The northern goshawk egg from near Stavropol had 3.08 ppm DDE, second only to the 4.58 ppm DDE in a long-eared owl. The 3.08 ppm was higher than reported in lone eggs from both Voronezh and Lipetsk, but may be accounted for by the orchards nearby that traditionally received high pesticide use. The lone common buzzard egg from Stavropol contained low concentrations of DDE and β-BHC which were similar to those reported at Lipetsk and Voronezh.

The northern marsh harrier eggs at Stavropol (geo. mean 1.00 ppm DDE and 0.07 ppm β-BHC) were slightly higher than five Montagu's harrier *Circus pygargus* eggs from Voronezh (0.45 and 0.02 ppm, respectively) (Henny et al 1998). Extremely low DDE concentrations were found in the two scops owl eggs while the lesser spotted eagle had low concentrations of both DDE and β-BHC. The Eurasian sparrowhawk population in western Europe declined in response to organochlorine pesticides and responded favorably following the banning of most organochlorine products in the 1970s (Newton 1986). Thus, it was not unexpected that the Eurasian sparrowhawk egg collected at Stavropol would continue to have one of the higher DDE concentrations, although 1.82 ppm is not a concentration of concern.

Both DDE and β-BHC were generally found in the Stavropol Region at relatively low concentrations with few exceptions. A few other organochlorine contaminants were also detected, but at extremely low concentrations. Dieldrin, endrin, heptachlor epoxide, *cis*-nonachlor, gamma chlordane, *trans*-nonachlor, o,p′-DDE and o,p′-DDT, and PCBs were not detected during this study. Based upon the earlier studies in 1992 when reproductive success was monitored (Henny et al 1998b), it is doubtful that the contaminant concentrations we report were adversely influencing reproductive performance. During this series of studies in Russia between 1991 and 1995 (a single egg collected from 109 nests of 18 species including 4 eagle species), only peregrine falcon eggs contained concentrations of contaminants that warranted special concern, in this case both DDE and PCBs (Henny et al 1994, Henny et al 1998b). Medvedev & Markova (1995) also reported low concentrations of DDE and lindane in eggs of three species of gulls, the common tern *Sterna hirundo* and hooded crow *Corvus cornix* from southern Karelia, Russia, near the Finnish border.

Acknowledgments. We are grateful to Vladimir Flint and Alexander Sorokin (Russian Institute for Nature Conservation) and Steven Kohl (Office of International Affairs, U.S. Fish and Wildlife Service) for supporting this project. This study was conducted under Area V of the U.S.-Russia Environmental Agreement.

REFERENCES

Galushin VM (1977) Recent changes in the actual and legislative status of birds of prey in the U.S.S.R. Pp 152-159 In: Chancellor RD (ed) World Conference on Birds of Prey, Internat. Council Bird Preservation, London

Henny CJ, Blus LJ, Kaiser TE (1984) Heptachlor seed treatment contaminates

hawks, owls and eagles of Columbia Basin, Oregon. Raptor Research 18: 41-48
Henny CJ, Galushin VM, Kuznetsov AV (1998a) Organochlorine pesticides, PCBs, and mercury in osprey *Pandion haliaetus* eggs from the Upper Volga River, Russia. Pp 525-534 In: Chancellor RD, Meyburg BU, Ferrero JJ (eds) Holarctic Birds of Prey ADENEX- WWGBP, Merida, Spain
Henny CJ, Ganusevich SA, Ward FP, Schwartz TR (1994) Organochlorine pesticides, chlorinated dioxins and furans, and PCBs in peregrine falcon *Falco peregrinus* eggs from the Kola Peninsula, Russia. Pp 739-749 In: Meyburg BU, Chancellor RD (eds). Raptor Conservation Today, WWGBP and Pica Press, East Sussex, England
Henny CJ, Galushin VM, Dudin PI, Khrustov AV, Mischenko AL, Moseikin VN, Sarychev VS, Turchin VG (1998b) Organochlorine pesticides, PCBs and mercury in hawk, falcon, eagle and owl eggs from the Lipetsk, Voronezh, Novgorod and Saratov Regions, Russia, 1992-1993. J Raptor Research 32: 143-150
Henny CJ, Seegar WS, Yates MA, Maechtle TL, Ganusevich SA, Fuller MR (2000) Contaminants and wintering areas of peregrine falcons *Falco peregrinus* from the Kola Peninsula, Russia. Pp 871-878 In: Chancellor RD, Meyburg BU (eds.). Raptors at Risk, WWGBP and Hancock House Publishers, Ltd, Surrey, BC, Canada
Medvedev N, Markova L (1995) Residues of chlorinated pesticides in the eggs of Karelian birds, 1989-90. Environ Pollut 87: 65-70
Newton I (1986) The sparrowhawk. T & AD Poyser, Calton, England
Stickel LF, Wiemeyer SN, Blus LJ (1973) Pesticide residues in eggs of wild birds: adjustment for loss of moisture and lipid. Bull Environ Contam Toxicol 9: 193-196.