FURTHER ASSESSMENT OF ENVIRONMENTAL CONTAMINANTS IN AVIAN PREY OF THE PEREGRINE FALCON IN BIG BEND NATIONAL PARK, TEXAS

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ABSTRACT—A small resident population of peregrine falcons (*Falco peregrinus anatum*) in the Big Bend region of Texas has suffered reproductive failures since 1990. To continue our assessment of the effects of environmental contaminants on the peregrine falcon, we collected representative avian prey species during 2001 at Mariscal Canyon, Big Bend National Park. The avian carcasses were analyzed for inorganic and organochlorine contaminants. Concentrations of Se and Hg were present at high levels (up to 11 and 2.2 μg/g dry weight, respectively) in some avian prey and could be implicated in reproductive failures of the peregrine falcon in Big Bend National Park. All other inorganic elements were below concentrations known to affect reproduction or to be associated with other deleterious effects in birds. Of all the organochlorines analyzed, only DDE and total PCBs were present above detection limits in all species, although at low concentrations. Our study provides further support to the hypothesis that contaminants in potential avian prey of the peregrine falcon in the Big Bend region are implicated in the productivity failures observed in this species since 1990.

RESUMEN—Una población pequeña del halcón peregrino (*Falco peregrinus anatum*) residente en la región de Big Bend ha tenido fracasos reproductivos desde 1990. Para continuar nuestra evaluación de los efectos de los contaminantes ambientales en el halcón peregrino colectamos especies de aves representativas como presa durante el año 2001 en el cañón de Mariscal, en el Parque Nacional de Big Bend, Los cadáveres de aves se analizaron por contaminantes inorgánicos y organoclorados. Observamos concentraciones de Se y Hg a niveles elevados (hasta 11 y 2.2 μg/g peso seco, respectivamente) en algunas especies presa y podrían estar implicados en los fracasos reproductivos del halcón peregrino en el Parque Nacional de Big Bend. Todos los demás elementos inorgánicos se observaron a concentraciones debajo de las que se sabe que afectan la reproducción o que han sido asociadas con otros efectos dañinos en aves. De todos los compuestos organoclorados analizados, solamente DDE y PCBs totales se encontraron por arriba de los límites de detección en todas las especies, pero a bajas concentraciones. Nuestro estudio proporciona apoyo adicional a la hipótesis de que los contaminantes en aves que son presa potencial del halcón peregrino en la región de Big Bend están posiblemente implicados en los fracasos reproductivos observados en la especie desde 1990.

The peregrine falcon (*Falco peregrinus anatum*) was removed from the U. S. Endangered Species List in 1999 (Federal Register, 25 August 1999). Although the species is believed to have recovered significantly throughout most of the United States, a small resident population (around 20 territories) in the Big Bend region of Texas has continued to experience reproductive failures since 1990 (Siegel, 1997; unpublished report). The highest productivity was recorded during 1978 (2.5 young fledged/nesting pair), and the lowest productivity occurred during 1995 (0.14 young fledged/nesting pair) (Siegel, 1997; unpublished report). The number of young fledged/nesting pair was above a sustainable level only during 4 y within the period 1990 to 2003 (Siegel, 1997; unpublished report). A productivity of 1.25 to 1.5 young fledged/nesting pair is expected to result in a sustainable population with potential for growth (Grier and Barclay, 1988; Wootton and Bell, 1992). Some recruitment of peregrine falcons into Big Bend might be occurring from a nesting population south of the Rio Grande in Maderas del Carmen, Coahuila, Mexico.

Low productivity of peregrine falcons during 1993 to 1996 was associated with low rainfall

(Siegel, 1997), similar to what has been observed in other regions (Newton and Mearns, 1988). However, previous studies suggested that reproductive failure of peregrine falcons in Big Bend also could be linked to high concentrations of contaminants in their prey (Mora et al., 2002). Potentially significant levels of contaminants in this area originate from past mining activities and agricultural practices in the vicinity of Big Bend near the Rio Grande and south of the border in Mexico.

There have been various studies documenting the impact of prey contaminated with DDE (a metabolite of DDT, a pesticide used in agriculture until 1972) on peregrine falcon reproduction (Enderson and Berger, 1968; Enderson et al., 1982, DeWeese et al., 1986; Elliott et al., 2005). Field observations and laboratory studies suggest that peregrine falcons feeding on prey containing as little as 0.5 μg/g wet weight of DDE could be negatively affected in their reproduction (Elliott et al., 2005). DDE produces eggshell thinning leading to increased egg breakage and reduced reproductive success (Anderson and Hickey, 1972).

The diet of the peregrine falcon in North America includes over 400 species of birds and a few mammals (White et al., 2002). In the Big Bend region, the remains of 38 avian species were identified in 2 peregrine falcon eyries during 1977 (Chihuahuan Desert Research Institute, 1977). Among the prey species were ducks (*Anas*), mourning doves (*Zenaida macroura*), and several swallow and wren species. In a previous study, we reported concentrations of contaminants in potential prey (birds and bats) of the peregrine falcon from several locations in west Texas (Mora et al., 2002). The results of this study indicated that mercury (Hg), selenium (Se), and possibly DDE could be implicated in the reduced reproductive success of peregrine falcons in Big Bend National Park. DDE was elevated only in one species, whereas Hg and Se were elevated in most species ($n = 5$) (Mora et al., 2002). The high potential for bioaccumulation and biomagnification of these chemicals in the food chain makes top predators, such as the peregrine falcon, highly susceptible to their deleterious effects (Newton, 1979).

In this follow-up study, we report more recent contaminant data on potential avian prey of the peregrine falcon, including additional species from Mariscal Canyon, along the Rio Grande in Big Bend National Park. The objective of this study was to provide additional support to the hypothesis that some contaminants, particularly Se and Hg, might be implicated in reproductive failures of the peregrine falcon in Big Bend National Park. We also determined differences in concentrations of contaminants among 3 locally abundant prey species to ascertain the contribution by each species, particularly mourning doves, to the peregrine falcon diet.

Methods—During May 2001, we collected 21 carcasses from 8 avian species in Mariscal Canyon, along the Rio Grande, Big Bend National Park. Mariscal Canyon was selected because it was the easiest to access and there were 2 active territories in this section of the park. We collected the following species with a shotgun and steel shot: mourning dove, cliff swallow (*Petrochelidon pyrrhonota*), northern rough-winged swallow (*Stelgidopteryx serripennis*), black phoebe (*Sayornis nigricans*), Say's phoebe (*S. saya*), canyon wren (*Catherpes mexicanus*), and mallard (*Anas platyrhynchos*). Five of these species were identified as prey of the peregrine falcon in the Big Bend region (Chihuahuan Desert Research Institute, 1977). Black and Say's phoebes were not identified among the prey remains; however, they are common in the area and could be potential prey. Immediately after collection, specimens were weighed, wrapped in aluminum foil, and kept in plastic bags on ice until returned to the laboratory.

Chemical Analysis—In the laboratory, we processed the bird carcasses by removing the feathers, tail, beak, legs, wings, head, and stomach contents. The remaining carcass was homogenized with a Teckmar tissumizer (Pro Scientific, Oxford, Connecticut), and a portion (5 to 10 g) of the homogenate was analyzed for organochlorine compounds and selected heavy metals and metalloids by the Geochemical and Environmental Research Group, Texas A&M University. The organochlorine compounds analyzed included hexachlorobenzene (HCB), hexachlorocyclohexane (α, β, γ, and δ-HCH) chlordane (α and γ isomers), cis-nonachlor, trans-nonachlor, dieldrin, endrin, heptachlor epoxide, mirex, oxychlordane, toxaphene, DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane], DDE [1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene], DDD [1,1-dichloro-2,2-bis(p-chlorophenyl)ethane], and polychlorinated biphenyls (PCB).

Organochlorine analysis was performed according to methods previously described (Brooks et al., 1989; Sericano et al., 1990). Briefly, 2 g of sample homogenate were mixed with anhydrous sodium sulfate and extracted with hexane. The extracts were purified by silica-alumina column chromatography and with HPLC. Residues were quantitated by gas chromatography and electron capture detector, GC-ECD (^{63}Ni) in splitless mode (Hewlett Packard 5890A, Palo Alto, California), with a DB-5 (30 × 0.25 mm ID) fused-silica capillary column (Agilent/J&W Scientific, Folsom, California). Ten percent of the samples were confirmed by second injection on a DB-17 capillary column or by GC-MS. Percent recoveries of organochlorines in reference and spiked samples were greater than 80% in all cases; variation between duplicates was below 15%. The lowest detection limit for *p,p'*-DDE was 0.4 ng/g wet weight (ww). Percent moisture was determined by weight loss after drying approximately 2 g of homogenate in an oven at approximately 75°C for about 42 h or until constant weight. Percent lipid was determined with a small fraction of the homogenate extract, allowing the extract to evaporate, and then weighing the remaining solid on a microbalance.

The heavy metal and metalloid analyses included aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), vanadium (V), and zinc (Zn). Approximately 0.5 g of sample homogenate was digested with nitric and perchloric acids. The digestate was analyzed for most elements with a Perkin Elmer, Model ELAN 5000 (Norwalk, Connecticut) inductively coupled plasma-mass spectrometer (ICP-MS). Arsenic and Se were analyzed with a Varian VGA-76 hydride generation accessory mounted to an atomic absorption spectrophotometer, AA Perkin Elmer, Model 3030 (Norwalk, Connecticut). Mercury was analyzed by the standard cold vapor atomic absorption method. The lowest detection limits for trace elements varied from 0.006 μg/g dw for Cd, 0.02 for Hg, 0.5 for Se, and 2 μg/g dw for Al. Percent recoveries of inorganic elements in spiked samples and certified reference materials were above 70% in all cases. Mean percent differences between duplicates in concentrations of selected elements were below 10%.

Statistical Analysis—Comparisons of concentrations of contaminants were possible for only 3 species and were conducted with the use of GLM ANOVA. Significant differences between species were determined by the Tukey multiple comparisons procedure. We used *t*-tests to compare concentrations of DDE, Hg, and Se between 2 collection years, 1997 (data in Mora et al., 2002) and 2001 (this study), for black phoebes and cliff swallows. Organochlorine and inorganic element data were log transformed to meet the assumptions of normality. All statistical analyses were performed with the use of SAS (SAS 8.2 for Windows, SAS Institute, Inc., Cary, North Carolina). The significance level was established at $P < 0.05$.

RESULTS—Concentrations of Al, Cd, Cr, Mn, Mo, Pb, and Sr were similar among 3 species (mourning dove, cliff swallow, and black phoebe) for which statistical comparisons were possible (Table 1). However, concentrations of B ($F_{2,14} = 8.4$, $P < 0.01$), Ba ($F_{2,14} = 15.8$, $P < 0.001$), and Zn ($F_{2,14} = 15.7$, $P < 0.001$) were significantly greater in cliff swallows than in black phoebes. Concentrations of Ba, Cu ($F_{2,14} = 4.7$, $P < 0.05$), and Zn were also greater in cliff swallows than in mourning doves. Mercury ($F_{2,14} = 210.6$, $P < 0.0001$) and Se ($F_{2,14} = 10.6$, $P < 0.01$) were significantly higher in black phoebes than in cliff swallows and mourning doves. Concentrations of

TABLE 1—Geometric mean concentrations and ranges (for $n > 1$) of heavy metals and metalloids (μg/g dry weight) in carcasses of avian prey of the peregrine falcon (*Falco peregrinum anatum*) in Big Bend National Park, Texas, 2001. Within columns, values that do not share the same letter are significantly different (top 3 species only).

Species[a]	n	Al	B	Ba	Cd	Cr	Cu	Hg	Mn	Mo	Pb	Se	Sr	Zn
MODO	5	21.9 A	1.23 A	1.22 B	0.12 A	1.01 A	6.5 B	0.05 C	3.34 A	0.13 A	1.05 A	1.67 B	26.1 A	57.2 C
		(7.0–38.1)	(1.0–1.50)	(0.86–1.51)	(0.02–2.09)	(0.57–1.78)	(5.02–7.22)	(0.04–0.08)	(2.54–4.83)	(0.01–0.66)	(0.13–24.7)	(0.87–3.84)	(13.6–46.0)	(49.4–73.2)
CLSW	6	33.5 A	1.51 A	3.23 A	0.09 A	0.63 A	9.5 A	0.15 B	3.5 A	0.12 A	0.26 A	2.8 B	14.9 A	85.0 A
		(19.9–50.4)	(1.0–2.32)	(2.24–6.26)	(0.03–0.15)	(0.51–1.10)	(5.18–15.0)	(0.09–0.19)	(2.51–4.4)	(0.01–0.61)	(0.14–0.39)	(1.8–11.0)	(8.3–21.3)	(73.1–98.4)
BLPH	6	35.4 A	0.61 B	1.2 B	0.07 A	1.2 A	9.4 A	1.61 A	3.11 A	0.23 A	0.25 A	6.7 A	25.9 A	70.2 B
		(26.1–56.2)	(0.25–1.45)	(0.63–1.93)	(0.05–0.18)	(0.63–2.77)	(8.51–9.91)	(1.24–2.24)	(2.5–5.08)	(0.01–0.62)	(0.17–0.39)	(6.2–7.9)	(21.5–35.1)	(65.6–75.8)
NRWS	1	56.2	1.11	3.12	0.03	0.67	10.62	0.36	5.04	0.41	0.34	7.89	43.7	78.3
SAPH	1	13.6	0.80	1.99	0.08	1.06	10.14	1.87	3.00	0.25	0.21	5.12	20.9	66.1
CANW	1	142.4	0.51	5.01	0.07	0.88	9.43	1.87	6.01	0.62	0.72	7.09	32.8	104.4
MALL	1	32.7	1.04	14.03	0.22	0.80	14.06	1.26	5.74	0.29	0.81	9.88	51.9	82.7
All species[b]	21	33.0 ± 12.7	1.2 ± 0.5	2.0 ± 1.4	0.2 ± 0.5	1.0 ± 0.6	8.8 ± 2.5	0.7 ± 0.8	3.4 ± 0.8	0.3 ± 0.2	1.9 ± 5.9	4.2 ± 2.9	23.3 ± 10.0	72.0 ± 13.8

[a] MODO = mourning dove (*Zenaida macroura*), CLSW = cliff swallow (*Petrochelidon pyrrhonota*), BLPH = black phoebe (*Sayornis nigricans*), NRWS = northern rough-winged swallow (*Stelgidopteryx serripennis*), SAPH = Say's phoebe (*Sayornis saya*), CANW = canyon wren (*Catherpes mexicanus*), MALL = mallard (*Anas platyrhynchos*).

[b] Arithmetic mean ± *SD*.

TABLE 2—Percent moisture and lipid (arithmetic mean ± *SD*) and *p,p′*-DDE and total PCB concentrations (geometric mean and range for $n > 1$, μg/g wet weight) in carcasses of avian prey of the peregrine falcon (*Falco peregrinus anatum*) in Big Bend National Park, Texas, 2001.

Species[a]	*n*	% moisture	% lipid	*p,p′*-DDE	Total PCB
MODO	5	69.2 ± 2.3	23.3 ± 13.0	0.002 B (0.001–0.008)	0.010 B (0.006–0.018)
CLSW	6	67.4 ± 2.0	18.6 ± 5.7	0.194 A (0.020–0.61)	0.036 A (0.025–0.045)
BLPH	6	68.3 ± 1.8	15.8 ± 7.5	0.180 A (0.095–0.501)	0.028 A (0.022–0.044)
NRWS	1	68.0	27.5	0.216	0.049
SAPH	1	68.1	6.2	0.062	0.018
CANW	1	68.7	20.2	0.063	0.057
MALL	1	73.3	6.5	0.022	0.005
All species[b]	21			0.180 ± 0.198	0.026 ± 0.013

[a] MODO = mourning dove (*Zenaida macroura*), CLSW = cliff swallow (*Petrochelidon pyrrhonota*), BLPH = black phoebe (*Sayornis nigricans*), NRWS = northern rough-winged swallow (*Stelgidopteryx serripennis*), SAPH = Say's phoebe (*Sayornis saya*), CANW = canyon wren (*Catherpes mexicanus*), MALL = mallard (*Anas platyrhynchos*). Within columns, values that do not share the same letter are significantly different (top 3 species only).

[b] Arithmetic mean ± *SD*.

Se and Hg were also elevated in other species; however, single values could not be compared to the mean values from other species.

DDE and total PCBs were the only organochlorine compounds quantified above detection limits; however, concentrations of both chemicals were relatively low in all species (Table 2). Concentrations of PCB and DDE were significantly greater ($F_{2,14} = 24.3$ and 31.8, respectively, $P < 0.0001$) in cliff swallows and black phoebes than in mourning doves. Concentrations of DDE and PCB in northern roughed-winged swallows and canyon wrens were within the range of those in cliff swallows and phoebes.

Concentrations of DDE were not significantly different between 1997 (data in Mora et al., 2002) and 2001 for black phoebes and cliff swallows, the only 2 species from which data from both years were available. However, Se concentrations decreased significantly ($P < 0.01$) in black phoebes and Hg decreased significantly ($P < 0.001$) in cliff swallows from 1997 to 2001.

DISCUSSION—Most heavy metals and metalloids in birds were above detection limits; however, only Se and Hg were of concern for potential deleterious effects on avian predators feeding on such prey. Lemly (1996) suggested that dietary concentrations of Se > 3 μg/g dw could have negative effects on fish and wildlife. All the bird species collected in 1997 had concentrations of Se greater than 3 μg/g dw (Mora et al., 2002). Selenium concentrations decreased significantly in black phoebes collected in 2001 compared to those collected in 1997; however, Se concentrations in birds collected in 2001 were still present at levels considered hazardous if ingested by predators such as the peregrine falcon. Six species in the present study had Se concentrations that approached the threshold value or were greater than 3 μg/g dw.

Mean Hg levels in black phoebes collected during 2001 were similar to those reported in 1997 (Mora et al., 2002); however, Hg levels in cliff swallows decreased significantly from 1997 to 2001 ($P < 0.001$). Four of 7 species collected in the present study contained mercury residues that were above 0.5 μg/g dw. All the species collected in 1997 also had Hg levels above 0.5 μg/g dw (Mora et al., 2002). A concentration of 0.4 μg/g dw total Hg in the diet of fish-eating birds has been suggested as the threshold value at which no negative effects are known to occur (Eisler, 1987). Reduced egg laying and hatching success have been reported in mallards feeding on methyl Hg at 0.5 μg/g dw (Heinz, 1979). Abnormal behavior during reproduction was observed in common loons (*Gavia immer*) ingesting Hg in the diet at about 1 μg/g dw (Barr, 1986). The data from these studies suggest that Hg concentrations in potential prey of the peregrine falcon in Big Bend National Park might be high enough to be associated with potential reproductive failures or other detrimental effects. Mercury was much lower (mean = not detected to 0.35 μg/g dw) in swallows from several other locations in the Rio Grande (Mora et al., 2006).

Concentrations of PCB in all species collected from Mariscal Canyon were all below 0.1 μg/g during 2001. This was not surprising because most samples collected along the Rio Grande over the last 2 decades have shown relatively low concentrations of PCBs (Mora and Wainwright, 1998). However, we were surprised to find concentrations of DDE below 1 μg/g in avian carcasses. During 1997, concentrations of DDE in northern rough-winged swallows ranged from 0.18 to 15.5 μg/g dw (Mora et al., 2002). Unfortunately, there was only one northern rough-winged swallow analyzed in this study. However, swallows from other locations along the Rio Grande continue to have elevated concentrations of DDE. For example, recent work has shown mean DDE levels in cave swallows (*Petrochelidon fulva*) and cliff swallows to range from 0.5 μg/g ww at Falcon Lake to 12.4 μg/g ww at El Paso (Mora et al., 2005). These results indicate that more samples should be analyzed to determine if the DDE concentrations have indeed declined in swallows from the Big Bend region or if levels vary with season or are highly regionally associated.

Overall, the results of the present study are in agreement with our previous findings that Se and Hg are present at elevated levels in potential prey species of the peregrine falcon in Big Bend National Park and might be impacting reproduction (Mora et al., 2002). Earlier studies reported that DDE was possibly involved in potential reproductive failures of peregrine falcons nesting in the Big Bend region (Chihuahuan Desert Research Institute, 1977; Hunt et al., 1986). Although the current study results did not indicate elevated levels of DDE, elevated concentrations of DDE are still observed in potential avian prey of the peregrine falcon in several other regions of the Rio Grande (Mora et al., 2005); thus, the potential for associated eggshell thinning effects in raptors in this region should not be ignored.

Mourning doves are considered the main prey item in the peregrine falcon diet in several regions in North America (White et al., 2002, Ellis et al., 2004). Mourning doves are abundant in the Big Bend region and also were the cleanest of all the birds analyzed in this study. If peregrine falcons were feeding mostly on doves in the region, we would expect that they were minimally affected by contaminants, because they were feeding on the cleanest species. Elliott et al. (2005) estimated that peregrine falcons in British Columbia, Canada, would be successful breeders only if they consumed a diet based mostly on doves, and that eating as little as 10% of other species would provide enough DDE in the diet to impair their reproduction. All the potential prey species analyzed in this study had DDE levels below 0.5 μg/g ww, the critical concentration above which effects on reproduction of the peregrine falcon are suspected (Elliott et al., 2005).

Low productivity of peregrine falcons in the Big Bend Region from 1993 to 1996 coincided with a period of low rainfall (Siegel, 1997). It is known that extended drought periods and low food supply can seriously affect peregrine falcon reproduction (Newton and Mearns, 1988). However, we suggest that current reproductive failures of peregrine falcons in the region might be more likely associated with high concentrations of Hg and Se. However, it has been suggested that in some cases Se could have a protective effect on the toxicity of Hg in birds (Heinz and Hoffman, 1998). Thus, a more thorough assessment that considers the potential contribution of contaminants from each potential prey species in the diet is warranted. Additionally, further monitoring of sites adjacent to and throughout the park might help identify the potential sources of Hg and Se. The results could guide management decisions to mitigate or minimize exposure to local hotspots or to reduce the contribution from potential nearby sources.

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