

## ENVIRONMENTAL CONTAMINANTS IN SURROGATE BIRDS AND INSECTS INHABITING SOUTHWESTERN WILLOW FLYCATCHER HABITAT IN ARIZONA

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**Abstract.** Several deformed Southwestern Willow Flycatchers (*Empidonax traillii extimus*) were reported in Arizona during the last few years. Environmental contaminants, particularly persistent bioaccumulative pollutants, have been associated with deformities in other birds from diverse areas of the United States. One objective of this study was to determine if environmental contaminants could be linked to deformities of the Southwestern Willow Flycatcher in Arizona. We measured levels of selected inorganic and organic contaminants in potential insect prey of the Willow Flycatcher and in avian surrogate species at selected sites within the San Pedro River and in Roosevelt Lake. DDE and PCBs were the only organochlorine compounds quantified above detection limits in all samples. None of the mean concentrations of DDE and PCBs in eggs, nestlings, or adult birds were near or above the threshold for potential detrimental effects on the birds themselves or on predators that may feed on them. Also, none of the concentrations of metals and metalloids in eggs, nestlings, and adults were at levels known to affect reproduction or that have been associated with deformities. Selenium was relatively elevated in bird samples (up to 5.8  $\mu\text{g/g}$  dry mass); however, these levels were still below those that have been associated with deformities in birds. We detected high concentrations of Sr (up to 450  $\mu\text{g/g}$  dry mass) in whole eggs of Yellow-breasted Chats (*Icteria virens*) that could affect eggshell strength, but more research is needed. Overall, the contaminants reported in this study are not likely to be implicated in the deformities observed in Southwestern Willow Flycatchers in the Lower San Pedro River and Roosevelt Lake.

**Key Words:** Arizona, contaminants, DDE, *Empidonax traillii extimus*, inorganic elements, insectivorous birds, PCBs, Southwestern Willow Flycatcher.

The lower San Pedro River, including adjacent downstream reaches of the Gila River (San Pedro-Gila rivers) and Roosevelt Lake in Arizona provide important nesting habitat for many passerine birds, including the federally endangered Southwestern Willow Flycatcher (*Empidonax traillii extimus*). Environmental contaminants such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins, polychlorinated dibenzo-furans, and selenium have been associated with deformities in birds from diverse areas of the United States (Ohlendorf et al. 1986, Giesy et al. 1994). Some of the most common deformities are crossed bills, small or missing eyes, and clubbed feet, but other types of deformities also occur (Gilbertson et al. 1991). Although fish-eating birds and birds at the top of the food chain are usually the most affected by persistent bioaccumulative toxicants (Hoffman et al. 1996), insectivorous birds may also be affected (McCarty and Secord 2000). Terrestrial and emerging aquatic insects in the lower San Pedro River and Roosevelt Lake may accumulate toxicants from agricultural pesticides, mining by-products, and wastewater treatment effluent. Therefore, insectivorous birds breeding on riparian corridors in both regions may accumulate toxicants from feeding on insects or other diets.

Between 1996 and 2000, 12 adult, one fledgling, and two nestling Willow Flycatchers were

found with bill or eye deformities in Arizona, Colorado, and New Mexico (Sogge and Paxton 2000). The mandible and beak deformities were characteristic of those observed in fish-eating birds from the Great Lakes, which have been attributed primarily to dioxins and PCBs (Giesy et al. 1994). Because environmental contaminants may be affecting the Willow Flycatcher and other wildlife of the lower San Pedro River, it is important to evaluate environmental contaminants to determine if there is a connection with flycatcher deformities in Arizona.

The objectives of this study were to determine levels of selected inorganic and organic contaminants in potential insect prey of the Southwestern Willow Flycatcher and in avian surrogate species at potentially impacted sites within the San Pedro River riparian zone and Roosevelt Lake. Specifically, we determined concentrations of persistent environmental contaminants to provide useful insights for evaluating causes of deformities in Willow Flycatchers in Arizona. We selected surrogate species that occupy the same habitat and have diets similar to those of the Willow Flycatcher in Arizona (Drost et al. 1998, Yard 1998). Therefore, we expected that contaminant burdens in adults, nestlings, and eggs of surrogate species should reflect those of the Willow Flycatcher. We analyzed for contaminants in adults, nestlings, eggs, and insects in order to establish the chemical dynamics from

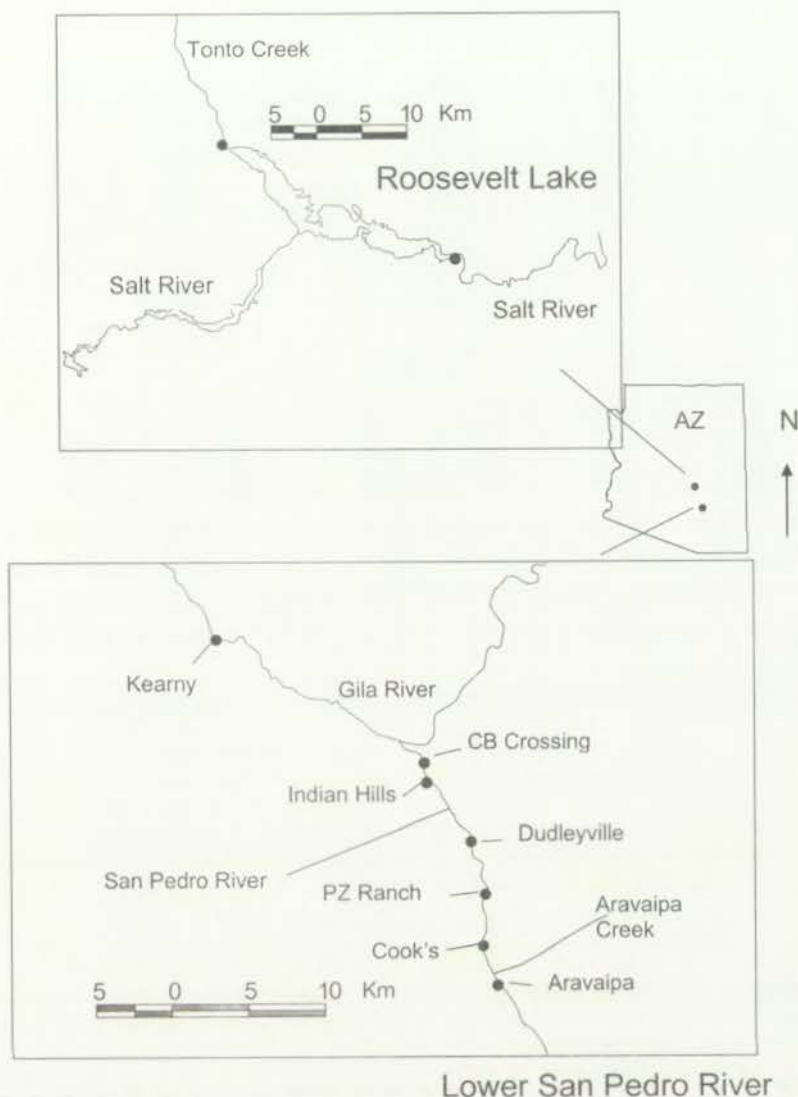


FIGURE 1. Location of contaminant sampling sites along the Lower San Pedro-Gila rivers riparian zone and Roosevelt Lake, Arizona.

the potential food source to adults, eggs, and young and to discern whether contaminants were more likely to come from local or migratory routes.

## MATERIALS AND METHODS

### STUDY AREAS AND SAMPLE COLLECTION

We collected 62 samples consisting of insects, carcasses, and eggs of surrogate bird species in the summer 1999 from several Willow Flycatcher nesting locations within the riparian zone at the San Pedro-Gila rivers (Pinal County), and from Roosevelt Lake (Gila County) in central Arizona (Fig. 1; Table 1). We captured adult Yellow Warblers (*Dendroica petechia*), Yellow-breasted Chats (*Icteria virens*), and Common

Yellowthroats (*Geothlypis trichas*) with mist nets and euthanized them immediately by cervical dislocation. Nestlings were removed from the nest and euthanized also by cervical dislocation. Adult and nestling carcasses were weighed, wrapped in aluminum foil, stored in plastic bags, and kept on ice until taken to the laboratory for storage at  $-20^{\circ}\text{C}$ . Yellow-breasted Chat eggs were collected from nests (mostly full clutches), wrapped in aluminum foil, and stored in a commercial refrigerator until further processing (some broken eggs were stored in glass jars at  $-20^{\circ}\text{C}$ ).

Approximately 2–5 g of insects (flies, bees, wasps, true bugs, leafhoppers, and dragonflies, among others) were collected from Cook's Lake, Indian Hills, and Kearny in the lower San Pedro River and from Roosevelt Lake, with malaise traps containing a killing jar

TABLE 1. MEAN DDE AND PCBs ( $\mu\text{G/g}$  WET MASS) IN EGGS AND CARCASSES OF NESTLING AND ADULT INSECTIVOROUS BIRDS AND INSECTS FROM ARIZONA, 1999 (RANGE IN PARENTHESES)

Class	Species	Location	N	4,4' DDE	PCBs	
Adults	Yellow-breasted Chat	Cooks Lake	3	0.034 (0.019–0.051)	0.016 (0.014–0.018)	
		Indian Hills	7	0.126 (0.020–0.250)	0.021 (0.012–0.050)	
		Kearny	1	0.023	0.040	
		Roosevelt	5	0.031 (0.017–0.061)	0.012 (0.006–0.021)	
		Yellow Warbler	Cooks Lake	2	0.090 (0.055–0.125)	0.019 (0.016–0.022)
		Indian Hills	1	0.056	0.039	
		Kearny	8	0.143 (0.024–0.269)	0.141 (0.037–0.311)	
		Common Yellowthroat	Cooks Lake	3	0.125 (0.073–0.215)	0.025 (0.020–0.031)
	Nestlings	Yellow-breasted Chat	Cooks Lake	1	0.016	0.014
			Indian Hills	2	0.034 (0.025–0.044)	0.013 (0.008–0.017)
Roosevelt			2	0.017 (0.014–0.020)	0.007 (0.003–0.012)	
Yellow Warbler			Cooks Lake	1	0.180	0.022
		Kearny	2	0.058 (0.051–0.064)	0.161 (0.139–0.183)	
		Eggs	Yellow-breasted Chat	Cooks Lake	1	0.034
Indian Hills				3	0.165 (0.019–0.355)	0.033 (0.010–0.067)
			Dudleyville	3	0.035 (0.019–0.060)	0.033 (0.015–0.064)
	GRS-12		3	0.084 (0.078–0.093)	0.032 (0.023–0.048)	
		PZ Ranch	3	0.099 (0.049–0.161)	0.186 (0.024–0.491)	
		Roosevelt	6	0.027 (0.017–0.041)	0.026 (0.011–0.056)	
	Insects	Several	Cooks Lake	1	0.026	0.224
			Indian Hills	1	0.102	0.387
			Kearny	1	0.024	0.237
			Kearny	1	0.003	0.026
			Roosevelt	1	0.042	0.258

with a cloth soaked in acetone at the top. The traps were placed near the sites where the birds were collected and were left for one or more days until enough insect biomass was gathered. After collection, the insects were transferred to chemically cleaned glass jars and kept at  $-20^{\circ}\text{C}$  until chemical analysis.

#### CHEMICAL ANALYSIS

Bird carcasses, eggs, and insects were analyzed for organochlorine contaminants and inorganic elements. The carcasses were obtained by plucking feathers, removing head, legs, beak, and stomach contents. Eggs were analyzed whole (including eggshells) because some eggs were broken and frozen prior to separation of the eggshells. This occurred because eggs had to be carried around for several hours while searching for more nests. We also analyzed the whole egg to determine total depuration of contaminants from the adult female to the egg. Contaminant concentrations were not adjusted for possible moisture loss. After homogenization, about 2 g of sample were used for each analysis.

The samples were analyzed at the Geochemical and Environmental Research Group (GERG), Texas A&M University.

#### ORGANOCHLORINE COMPOUNDS

We analyzed the following organochlorine compounds: polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexane ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ -HCH) chlordane ( $\alpha$  and  $\gamma$  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], and DDD [1,1-dichloro-2,2-bis(p-chlorophenyl)ethane]. Approximately 2 g of sample homogenate were mixed with anhydrous sodium sulfate and extracted with hexane. The samples were extracted following the NOAA status and trends method (McLeod et al. 1985) with some modifications (Brooks et al. 1989). The extracts were



purified by silica/alumina column chromatography and with HPLC. Residues were quantitated by gas chromatography and electron capture detector, GC-ECD ( $^{63}\text{Ni}$ ) in splitless mode, with a DB-5 ( $30 \times 0.25$  mm ID) fused-silica capillary column (Sericano et al. 1990). Ten percent of the samples were confirmed by second injection on a DB-17 capillary column or by GC-MS. Spike recoveries were above 80% in all cases; variation between duplicates remained within 15%. The lowest detection limit for organochlorine compounds was approximately 1 ng/g wet mass (ww).

#### HEAVY METALS AND METALLOIDS

We quantified the following heavy metals and metalloids: aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), and strontium (Sr). Approximately 0.5 g of sample was digested with nitric and perchloric acids. The digest was analyzed for most elements with a Perkin Elmer, Model ELAN 5000, 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. Mercury was analyzed by the standard cold vapor atomic absorption method. The lowest detection limits for trace elements varied between 0.006  $\mu\text{g/g}$  dw for Cd and 2  $\mu\text{g/g}$  dw for Al. Percent recoveries of spiked samples and certified reference materials were above 90% in most cases. Mean relative percent differences between duplicates were <10%.

#### STATISTICAL ANALYSES

Yellow-breasted Chats were the main species collected from most locations; therefore, most comparisons among locations were performed only with chat data. We used the GLM procedure on ranked data (SAS Institute 1987) to test for differences in mean concentrations of organic and inorganic elements among all sites (within San Pedro and Roosevelt). The Tukey multiple comparisons procedure was used to determine which means were significantly different. We compared concentrations of organochlorine and inorganic compounds in adult chats with data from three locations and in eggs with data from five locations. We compared inorganic element concentrations among adults, nestlings, and eggs with data from Roosevelt and Indian Hills and all locations combined. We also compared concentrations of inorganic elements among species with combined data for adults from several locations. We tested for differences in mean concentrations of organochlorines between locations (San Pedro vs Roosevelt) and between species (chats vs. warblers) by two-sample comparison procedures. The level of significance was set *a priori* at  $P < 0.05$ .

#### ACCUMULATION FACTORS FOR METALS AND METALLOIDS

We estimated the proportion of inorganic contaminants that birds acquired through the diet, assuming that they were feeding on insects similar to those sampled in our study. We used mean inorganic element concentrations from Yellow-breasted Chats from specific locations (Indian Hills and Roosevelt) and from

all locations to obtain accumulation ratios from insects to adults and nestlings, adults to eggs, and eggs to nestlings. The accumulation factor represents the ratio of the concentration in a given compartment (e.g., carcass) divided by the concentration in another compartment (e.g., insects). The accumulation factor indicates whether a contaminant ingested in the food is potentially accumulated in adults, the proportion that is depurated by the female through the egg (including deposition in the eggshell), and accumulation in nestlings. A ratio  $\leq 1$  suggests no bioaccumulation, whereas a ratio  $> 1$  indicates bioaccumulation.

## RESULTS

#### ORGANOCHLORINES

DDE and PCBs were the only organochlorine compounds detected in all samples (Table 1). DDE concentrations were low (range 0.003–0.355  $\mu\text{g/g}$  ww) but were somewhat higher in adult birds and eggs than in insects and nestlings. Polychlorinated biphenyl concentrations also were low (range 0.006–0.491  $\mu\text{g/g}$  ww); however, PCBs were higher in insects and much lower in adults and nestlings. There were no significant differences (GLM of ranked data,  $P > 0.05$ ) in concentrations of DDE and PCBs among adult chats from Cooks Lake, Indian Hills, and Roosevelt Lake. DDE and PCB concentrations also were not significantly different (GLM of ranked data,  $P > 0.05$ ) among chat eggs from Dudleyville, Indian Hills, GRS-12 (by CB Crossing), and PZ Ranch, in the lower San Pedro River, and Roosevelt Lake. DDE and PCBs were not significantly different (t-test,  $P > 0.05$ ) between chat eggs or carcasses from the lower San Pedro River and Roosevelt Lake. DDE concentrations also were similar (t-test,  $P > 0.05$ ) between carcasses of adult chats and Yellow Warblers from the lower San Pedro River; however, concentrations of PCBs were significantly greater (t-test,  $P < 0.01$ ) in Yellow Warblers than in chats from the same locations.

#### METALS AND METALLOIDS

Insects had proportionally higher concentrations of Cr, As, Cd, and Ni than bird carcasses and eggs (Table 2). Mean concentrations of Cr, As, Cd, Ni, Sr, and Al were similar (GLM of ranked data,  $P > 0.05$ ) in adult chats from Cooks Lake, Indian Hills, and Roosevelt Lake. However, concentrations of Pb and Se were significantly higher (GLM of ranked data,  $P < 0.05$ ) in adult chats from Indian Hills than in adults from Roosevelt Lake, but were similar to chats from Cooks Lake. Copper concentrations were significantly higher (GLM of ranked data,  $P < 0.05$ ) in adult chats from Cooks Lake than in those from Indian Hills and Roosevelt Lake. Concentrations of Hg were significantly higher

TABLE 2. MEAN INORGANIC ELEMENT CONCENTRATIONS AND RANGES ( $\mu\text{g/g}$  DRY MASS) IN EGGS AND CARCASSES OF NESTLING AND ADULT BIRDS AND INSECTS FROM ARIZONA, 1999

Age Class	Species	Location	N	Cr	As	Cd	Pb	Se	Hg	Cu	Ni	Sr	Al
Adult	Yellow-breasted Chat	Cooks Lake	3	0.83 (0.53-1)	0.17 (0.10-0.22)	1.11 (0.83-1.40)	0.34 (0.13-0.46)	1.79 (1.31-2.1)	0.11 (0.1-0.12)	14.0 (10.6-19.6)	0.22 (0.15-0.27)	44 (39.4-51)	21 (18-20)
		Indian Hills	7	0.71 (0.32-1.9)	0.23 (0.11-0.35)	0.50 (0.26-0.64)	0.51 (0.28-1.04)	1.90 (1.1-2.4)	0.14 (0.1-0.23)	7.6 (5.2-10.4)	0.72 (0.01-3)	29 (15-46)	30 (12-58)
	Yellow Warbler	Kearny	1	1.35	0.26	1.15	0.52	2.08	0.48	10.6	0.35	21	21
		Roosevelt	5	0.79 (0.53-1.25)	0.18 (0.1-0.24)	0.49 (0.17-1.3)	0.18 (0.13-0.26)	1.04 (0.87-1.24)	0.36 (0.24-0.4)	7.2 (6.3-7.8)	0.15 (0.05-0.41)	21 (12.4-28)	20 (14.4-26.7)
	Common Yellowthroat	Cooks Lake	2	0.36 (0.27-0.44)	0.20 (0.12-0.27)	0.26 (0.23-0.29)	0.49 (0.30-0.67)	3.07 (2.91-3.23)	0.19 (0.17-0.21)	8.9 (8.6-9.2)	0.40 (0.26-0.53)	22 (16.2-28.7)	25 (19-32)
Nestling	Yellow-breasted Chat	Indian Hills	1	0.50	0.36	0.21	3.85	5.87	0.14	20.8	0.46	15	39
		Kearny	8	0.90 (0.5-1.7)	0.17 (0.11-0.23)	0.20 (0.07-0.63)	0.57 (0.42-0.8)	5.10 (2.1-6.6)	0.21 (0.13-0.31)	11.9 (10.1-15.9)	0.24 (0.05-0.54)	15 (10.3-22.4)	26 (13.2-42.4)
	Yellow Warbler	Cooks Lake	3	0.78 (0.27-1.18)	0.36 (0.09-0.81)	0.17 (0.1-0.21)	0.22 (0.16-0.26)	1.73 (1.41-2.05)	0.25 (0.13-0.32)	9.0 (8.7-9.2)	0.20 (0.08-0.46)	15 (12.8-15.9)	15 (13-17)
		Cooks Lake	1	0.27	0.17	0.17	0.09	1.09	0.13	8.2	0.17	45	30
	Yellow Warbler	Kearny	2	1.14 (0.96-1.32)	0.16 (0.15-0.17)	0.04 (0.04-0.04)	0.18 (0.11-0.26)	4.84 (4.55-5.14)	0.07 (0.06-0.07)	8.7 (8.3-9.05)	0.79 (0.72-0.85)	50 (38-63)	16 (14.8-16.8)
Eggs	Yellow-breasted Chat	Cooks Lake	1	0.16	0.54		0.17	3.53	0.02	2.3	1.65	257	28
		Indian Hills	3	0.30 (0.21-0.42)	1.00 (0.6-1.3)	0.02 (0.01-0.03)	0.17 (0.02-0.28)	3.90 (3.4-4.3)	0.02	2.2 (1.9-2.9)	0.71 (0.24-1)	313 (266-395)	10 (5.3-12.4)
	Yellow Warbler	Dudleyville	3	0.30 (0.16-0.57)	1.27 (1-1.43)	0.01	0.19 (0.05-0.39)	3.80 (3.2-5)	0.02	3.0 (2.3-4.1)	0.50 (0.28-0.80)	450 (324-579)	59 (2-149)
		GRS-12	3	0.38 (0.18-0.62)	0.82 (0.72-0.98)		0.12 (0.03-0.19)	4.51 (3.46-5.2)	0.02	3.4 (2.5-4.2)	1.30 (0.8-1.9)	243 (145-363)	14 (0.33-35.6)
	PZ Ranch	Roosevelt	6	0.56 (0.03-1.45)	0.94 (0.7-1.2)	0.01 (0-0.02)	0.26 (0.04-0.28)	2.70 (2.7-6.7)	0.12 (0.02-0.32)	2.7 (1.8-3.8)	0.33 (0.02-2.8)	396 (99-233)	27 (7-38)



TABLE 2. CONTINUED

Age Class	Species	Location	N	Cr	As	Cd	Pb	Se	Hg	Cu	Ni	Sr	Al
Insect	Various Species	Cooks Lake	1	0.91	0.38	0.81	0.62	1.33	0.07	29.1	10.80	9	89
		Indian Hills	1	3.91	1.04	1.60	0.89	0.96	0.16	37.4	2.75	8	123
		Kearny	1	13.71	0.31	0.38	1.07	1.21	0.09	27.9	0.22	13	185
		Kearny	1	0.55	0.88	1.18	0.57	1.39	0.12	44.6	0.08	117	46
		Roosevelt	1	2.25	1.98	0.70	0.77	0.12	0.16	27.1	2.55	8	141

( $P < 0.05$ ) in adult chats from Roosevelt than in those from Indian Hills and Cooks Lake.

Concentrations of Cr, As, Cd, Pb, Se, Cu, Ni, and Al were similar in chat eggs from five locations in the lower San Pedro River and Roosevelt Lake (GLM of ranked data,  $P > 0.05$ ). Concentrations of Sr, however, were significantly higher (GLM of ranked data,  $P < 0.05$ ) in chat eggs from Dudleyville and PZ Ranch in the lower San Pedro River than in Roosevelt Lake. Mercury was near detection limits in chat eggs.

Concentrations of Cr, As, Cd, Pb, Se, Hg, Ni, and Sr were similar between adults and nestling chats but differed significantly from concentrations in eggs (GLM of ranked data, see below). Concentrations of As, Se, Ni, and Sr were significantly higher (GLM of ranked data,  $P < 0.05$ ) in whole eggs than in adults or nestling chats; however, concentrations of Cr, Cd, Pb, and Hg were significantly lower (GLM of ranked data,  $P < 0.05$ ). Copper concentrations were significantly higher in nestlings than in adults or eggs (GLM of ranked data,  $P < 0.05$ ).

Concentrations of Cr, As, Hg, Ni, and Al were similar among carcasses of chats, warblers, and yellowthroats (GLM of ranked data,  $P > 0.05$ ). Cadmium and Sr were significantly higher (GLM of ranked data,  $P < 0.05$ ) in chat carcasses than in other two species. Copper and Hg were significantly higher (GLM of ranked data,  $P < 0.05$ ) in Yellow Warblers than in chats, but were similar to Common Yellowthroats.

#### METAL AND METALLOID ACCUMULATION FACTORS

Table 3 provides mean accumulation factors of metals and metalloids from insects to birds, nestlings, and eggs. The accumulation factor was  $>1$  in the following cases: from insects to adults for Se, Hg, and Sr; from adults to eggs for As, Se, Ni, and Sr; from insects to nestlings for Se, Hg, Cu, Sr, and Al; and from eggs to nestlings for Cr, Cd, Pb, Hg, Cu, and Al.

#### DISCUSSION

##### CONTAMINANT PATTERNS AND HAZARD ASSESSMENT

DDE concentrations in birds from Arizona were similar to those found in other insectivorous species collected recently in Big Bend National Park, but were about 30 times lower than the DDE residues found in Cliff Swallows (*Petrochelidon pyrrhonota*) collected along the Rio Grande near El Paso, Texas, during the same year (M. Mora, unpubl. data). None of the mean DDE concentrations in eggs, nestlings, and adult birds were near or above the threshold for potential detrimental effects on the birds themselves or on predators that may feed on them. Based on available studies, the Brown Pelican

TABLE 3. MEAN ACCUMULATION FACTORS (RANGES IN PARENTHESES) FOR METALS AND METALLOIDS BASED ON CONCENTRATIONS IN YELLOW-BREASTED CHATS AND INSECTS FROM ARIZONA

Category	Cr	As	Cd	Pb	Se	Hg	Cu	Ni	Sr	Al
Adult/Insect	0.24 (0.18-0.35)	0.18 (0.09-0.22)	0.57 (0.31-0.70)	0.43 (0.23-0.57)	4.08 (1.61-8.65)	1.68 (0.90-2.26)	0.25 (0.20-0.27)	0.16 (0.08-0.26)	2.42 (0.93-3.56)	0.20 (0.14-0.24)
Egg/Adult	0.53 (0.42-0.71)	4.80 (4.36-5.34)	0.02 (0.01-0.03)	0.53 (0.33-0.79)	3.06 (2.05-4.63)	0.12 (0.06-0.16)	0.33 (0.30-0.38)	2.72 (0.98-5.19)	9.59 (7.85-10.9)	0.78 (0.33-1.03)
Nestling/Insect	0.58 (0.24-1.16)	0.20 (0.13-0.26)	0.33 (0.26-0.37)	0.30 (0.12-0.48)	1.36 (0.8-2)	1.01 (0.13-1.70)	1.14 (0.51-1.86)	0.11 (0.09-0.16)	3.54 (1.26-6.46)	2.35 (1.15-3.72)
Nestling/egg	3.98 (3.15-4.66)	0.25 (0.22-0.27)	37.86 (27-51)	1.50 (0.68-2.5)	0.19 (0.09-0.32)	6.16 (1-13.5)	16.21 (5.02-31)	0.39 (0.21-0.61)	0.15 (0.13-0.17)	21.94 (8.48-47.1)

(*Pelecanus occidentalis*) has been one of the most sensitive bird species to the eggshell thinning effects of DDE; levels of approximately 3  $\mu\text{g/g}$  ww in eggs increased egg breakage and decreased productivity. However, there is much variation in sensitivity to DDE among species (Blus 1996). The low levels of DDE in adult birds, nestlings, and insects suggested little, if any, accumulation along migratory routes; rather, they indicate possible accumulation from local sources.

Polychlorinated biphenyl concentrations also were very low. PCBs were higher in insects and much lower in adults and nestlings, also suggesting local sources rather than acquisition during migration or in wintering grounds. PCBs were greater in warblers than in chats from Kearny probably because warblers were feeding closer to the Kearny sewage ponds, the most likely source of PCBs in the area. The lowest concentrations of PCBs that have been associated with deformities in birds are approximately 3.5  $\mu\text{g/g}$  ww in eggs of Double-crested Cormorants (*Phalacrocorax auritus*; Yamashita et al. 1993). All PCB values in eggs, nestlings, and adult birds collected in Arizona were less than 1  $\mu\text{g/g}$  ww; thus, it is unlikely that PCBs are associated with deformities that have appeared in flycatchers in the area.

Most concentrations of metals and metalloids in eggs and carcasses of the three bird species also were not of concern for biological effects such as deformities in birds. None of the concentrations of Cr, As, Cd, Pb, Hg, Cu, Ni, and Al in eggs, nestlings, and adults were at levels known to affect reproduction or that have been associated with deformities (Heinz 1979; Eisler 1985a, 1986, 1987, 1988, 1998; Whitworth et al. 1991; Miles et al. 1993; McIlveen and Negusanti 1994). Additionally, some inorganic elements were retained in the eggshell since the eggs and eggshells were analyzed together; therefore, some elements were less likely to affect the embryos. Recent analyses indicate that except for Cu, Mn, Se, and Zn, concentrations of inorganic elements were 2-35 times greater in eggshells than in eggs (Mora in press). However, Burger (1994) found that concentrations of Pb and Cr were higher in egg contents than in eggshells of Herring Gulls (*Larus argentatus*) and Roseate Terns (*Sterna dougallii*). Thus, species differences in deposition of inorganic elements in eggs and eggshells need to be considered.

A concentration of 0.4  $\mu\text{g/g}$  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). The mean concentration of total Hg in insects in the Lower San Pedro River and Roosevelt Dam was



below 0.15  $\mu\text{g/g}$  dw, about 1/3 the maximum recommended level to protect wildlife. Insects from the same area also had Cu levels ranging from 27–45  $\mu\text{g/g}$  dw. No data on toxicity of Cu to wildlife are available; however, poultry studies indicate that adverse effects could occur when chickens are fed diets containing 350  $\mu\text{g/g}$  ww Cu for 25 days (Eisler 1998). Of the few studies with Ni, Outridge and Scheuhammer (1993) observed that a diet of 300  $\mu\text{g/g}$  ww caused reduced growth in newly hatched chickens. Nickel concentrations in insects from Arizona were all below 11  $\mu\text{g/g}$  dw. Aluminum concentrations in insects and nestlings from Arizona were somewhat high; however, dietary concentrations of Al of 200, 1000, and 5000  $\mu\text{g/g}$  ww administered to European Starlings (*Sturnus vulgaris*) did not affect their growth, reproduction, or survival (Miles et al. 1993).

Selenium, derived primarily from irrigation drainage of areas with marine sedimentary rocks of Late Cretaceous age (Seiler 1997), was relatively elevated in bird samples (up to 5.8  $\mu\text{g/g}$  dw); however, these levels were still below those that have been associated with deformities in birds (13–24  $\mu\text{g/g}$  dw; Skorupa and Ohlendorf 1991). Although Se may not be lethal or teratogenic at such levels, dietary concentrations of Se > 3  $\mu\text{g/g}$  dw may have negative effects on fish and wildlife (Lemly 1996). Concentrations of Se < 5  $\mu\text{g/g}$  dw in the diet of adult Screech Owls (*Otus asio*) resulted in oxidative stress in their nestlings (Wiemeyer and Hoffman 1996). Thus, raptorial birds feeding on songbirds or insectivore species along the San Pedro River and the Roosevelt Lake area could be affected by high concentrations of Se in their prey.

One important finding of this study was the elevated levels of Sr (up to 450  $\mu\text{g/g}$  dw) in eggs of chats from two locations on the San Pedro River. The unusually high concentrations of Sr, however, were present mostly in the eggshell (Mora in press) with little potential for association with deformities in birds. Notwithstanding, Sr mobilization is closely associated with Ca metabolism; thus, it is possible that a high deposition of Sr in the eggshell could affect eggshell strength and increase egg breakage (Mraz et al. 1967), but this deserves further documentation. The distribution of Sr in the environment is associated with potassium- or calcium-rich rocks. Some areas in Arizona south of the study area have been reported with high concentrations of Sr in stream sediments (Theobald and Barton 1988). Our findings point out the potential for accumulation of high concentrations of Sr in eggshells of passerine birds nesting in some regions of Arizona.

Except for Sr, which showed some geographic

differences in concentrations among samples from the San Pedro River, concentrations of most inorganic elements were similar between the lower San Pedro River and Roosevelt Lake. This suggests that the sources of inorganic contaminants are distributed somewhat uniformly throughout the nesting habitat in these two regions. This is also supported by similar concentrations of Cr, As, Hg, Ni, and Al among the three bird species from the lower San Pedro River. Additional collection of samples from other Willow Flycatcher locations would allow for increased sample sizes and more robust comparisons to better determine contaminant patterns and potential impacts on nesting insectivorous birds.

#### METAL DYNAMICS AMONG BIOTIC COMPARTMENTS

Analysis of the accumulation factors suggests that of all the inorganic elements, only Se, Hg, and Sr (ratio > 1) bioaccumulated from insects to adults. However, the presence of high concentrations of metals in insects suggested acquisition of other metals through the diet. The accumulation factors also indicate that adult birds deposited greater concentrations of As, Se, Ni, and Sr than other metals in eggs, relative to their body burdens. From insects to adults and then from adults to eggs, bioaccumulation factors were 12.5 for Se, and 23.2 for Sr (Table 3). As indicated earlier most Sr is deposited in the eggshell, whereas most Se absorbs directly in the egg contents (Mora in press). This study documents the significance of the eggshell for deposition of Sr by the laying female. The accumulation factors of metals from insects to nestlings were quite similar to those from insects to adults suggesting that the possible source of inorganic contaminants was local rather than from a distant source. These considerations assume that the insect samples analyzed represent the food source for the birds collected in the area and that the metal concentrations observed were average concentrations for the area.

#### CONCLUSIONS AND RECOMMENDATIONS

Overall, DDE, PCBs, metals, and metalloid concentrations reported in this study are not likely to be implicated in the deformities observed in Southwestern Willow Flycatchers in the Lower San Pedro River and Roosevelt Lake. Local Willow Flycatcher deformities may be due to other factors or to exposure to other contaminants to which the surrogate species were not exposed or that were not detected in our analysis. Southwestern Willow Flycatcher deformities appear to be occurring throughout their breeding



range (Sogge and Paxton 2000); therefore, sampling of surrogate species from other areas in Arizona and New Mexico should be conducted to determine differences and similarities in contaminants among sites. Environmental contaminants such as metals, organochlorines, and other persistent chemicals would be expected to exert their toxic and teratogenic effects on the developing embryo or young rather than on adults; therefore, we should be able to document mortality rates and deformities in young to better assess exposure and effects of contaminants on the Southwestern Willow Flycatcher. Additionally, the effects of high concentrations of Sr on

eggshell strength and potential increase in egg breakage in insectivorous birds should be investigated.

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