

## **Arsenic Concentrations in House Wrens from Whitewood Creek, South Dakota, USA**

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About 100 million metric tons of gold-mill tailings were discharged into Whitewood Creek, near Lead and Deadwood, South Dakota, between 1876 and 1977 (Goddard 1989). A substantial portion of these wastes were deposited on the flood plains along Whitewood Creek. Also, an estimated 270,000 tons of arsenic, associated with gold ore in the form of arsenopyrite, were discharged into Whitewood Creek since 1920 (Goddard 1989). Although most of the trace elements known to be associated with the minerals present in gold ore seem to have weathered, arsenic concentrations were extremely elevated in Whitewood Creek sediments. For example, concentrations in uncontaminated sediments averaged 9.2 µg/g arsenic, whereas contaminated sediment samples averaged 1,920 µg/g arsenic (Goddard 1989).

Insectivorous birds feeding near Whitewood Creek may have elevated concentrations of arsenic, because arsenic was detected above background concentrations in benthic insects inhabiting Whitewood Creek (Cain et al. 1989). Additionally, arsenic accumulates rapidly in birds and may reach equilibrium in 10–30 days (Pendleton et al. 1995).

Cavity nesting birds are being widely used as indicators of local contamination (King et al. 1994, Bishop et al. 1995, Custer et al. 1998, Custer et al. 2000, Custer et al. 2001). One advantage of these species is that study sites can be established by placing nest boxes at locations of interest. Additionally, contaminant concentrations in eggs and chicks of these species seem to reflect pollutants found in the local environment. House wrens (*Troglodytes aedon*), which are cavity-nesting birds, have been used successfully as an indicator of local trace element contamination (Custer et al. 2001).

The objective of this study was to determine trace element exposure of house wrens nesting on Whitewood Creek, South Dakota. Specifically, we wanted to determine if arsenic concentrations were elevated in house wren samples from Whitewood Creek compared to a location not associated with arsenic contamination.

## MATERIALS AND METHODS

In 1997, nest boxes were positioned on metal posts along Whitewood Creek, SD (44° 38' 20" N, 103° 27' 25" W) and a reference site along the North Platte River near Casper, WY at Edness K. Wilkins State Park (42° 51' 30" N, 106° 51' 30" W). The boxes were checked once a week until eggs hatched and chicks had fledged. The species and number of eggs or young present was recorded at each visit. House wren eggs and chicks were collected from both locations.

A sample consisted of 2-3 eggs per box and 1-3 sibling 12-day-old chicks. Based on date of egg laying, the estimated date of hatching, and morphological features, the house wren chicks were estimated to be 12±2 days old. The day of hatching was considered as day zero. Egg contents were pooled by nest, emptied into chemically clean jars, and later analyzed for trace elements. Within two hours of collection, chicks were weighed (±0.1 g) and decapitated with a sharp pair of scissors. Immediately after death, the liver was removed from house wren chicks, weighed (±0.1 g), pooled by nest, and placed in chemically clean jars; contents of the upper gastrointestinal (GI) tract were pooled by site. Samples were frozen until they were analyzed for trace elements.

Egg contents, chick livers, and chick diet from the upper gastrointestinal tract were analyzed for trace elements by Research Triangle Institute, Research Triangle Park, NC, USA. Samples were freeze-dried, weighed, and then homogenized in a blender. Subsamples of freeze-dried livers were digested in stages with heat and nitric-perchloric acid and then analyzed for selenium (Se) and arsenic (As) by graphite furnace atomic absorption spectrophotometry, and for aluminum (Al), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), strontium (Sr), vanadium (V), and zinc (Zn) by inductively coupled plasma - atomic emission spectrophotometry. Separate subsamples were digested by nitric acid reflux and analyzed for total mercury by cold vapor atomic absorption spectrophotometry. Nominal levels of detection (µg/g dry weight) were as follows: Al = 5, As = 0.5, B = 2.0, Ba = 0.5, Be = 0.1, Cd = 0.1, Cr = 0.5, Cu = 0.5, Fe = 20, Hg = 0.1, Mg = 20, Mn = 0.5, Mo = 0.5, Ni = 0.5, Pb = 1.0, Se = 1.0, Sr = 0.5, V = 0.5, Zn = 1.0. The number of spikes, duplicates and blanks was 10% of the total number of samples analyzed. Concentrations were not adjusted for recovery, which averaged 102% overall for the various trace elements. Concentrations of trace elements are reported on a dry-weight basis; approximate wet-weight values can be calculated by using percent moisture values of 82.3% for eggs, 68.6% for livers, and 66.9% for diet from this study.

Trace element concentrations were log transformed (using base 10 logarithms) to satisfy the assumption of homogeneity of variance. T-tests were used to compare trace element concentrations between locations (SD and WY) for egg and liver samples. T-tests were only used if ≥50% of samples had detectable values; one-half the detection limit was assigned to samples below the detection

limit. When less than one-half of the trace elements were detected, only the range of values is presented.

## RESULTS AND DISCUSSION

Arsenic, beryllium, cadmium, chromium, molybdenum, nickel, and vanadium were not detected in house wren eggs from either location (Table 1); all of the other trace elements were detected in two or more samples. Beryllium and vanadium were not detected in any house wren liver sample, but all of the other trace elements were detected in one or more samples. Beryllium, mercury, and vanadium were not detected in any diet sample, but all of the other trace elements were detected in at least one diet sample. Arsenic, chromium, lead, nickel, and selenium were not detected in the WY diet, but were detected in the SD diet.

**Table 1.** Trace element concentrations ( $\mu\text{g/g}$  dry weight) in house wren eggs, livers of house wren chicks, and diet of house wren chicks from Whitewood Creek, SD and the North Platte River near Casper, WY in 1997.

Trace element <sup>a</sup>	Range of concentrations ( $\mu\text{g/g}$ dry weight)					
	Eggs		Livers		Diet	
	SD (n=5)	WY (n=3)	SD (n=5)	WY (n=3)	SD (n=1)	WY (n=1)
Al	7.2-16	13-23	4nd-35 <sup>b</sup>	2nd-7	465	346
As	nd	nd	1.8-5.6	nd	103	nd
Ba	2.8-5.8	11-15	4nd-1.1	nd	19	20
B	13-31	14-25	9-32	18-22	28	82
Cd	nd	nd	nd	1nd-0.2	0.3	1.4
Cr	nd	nd	4nd-0.8	nd	1.3	nd
Cu	2.3-3.0	2.9-6.1	22-38	22-24	45	39
Fe	81-139	110-121	1872-5398	2020-4185	3540	342
Pb	nd	1nd-1.2	2nd-2.1	2nd-1.3	3.5	nd
Mg	297-506	293-534	653-783	672-750	1215	998
Mn	3.3-5.7	4.6-6.2	4.8-7.8	5.1-5.7	394	26
Hg	0.1-0.3	0.1-0.2	2nd-0.2	nd-0.1	nd	nd
Mo	nd	nd	2.6-3.5	3.4-4.3	1.4	3.1
Ni	nd	nd	4nd-0.6	2nd-1.0	2.8	nd
Se	3.0-3.8	4.3-6.3	5.2-7.0	7.0-12	0.9	nd
Sr	5.8-27	13-21	2nd-4.1	0.2-0.3	54	43
Zn	44-57	49-69	85-139	78-102	174	238

<sup>a</sup> Beryllium and V were not detected in eggs, livers, or diet.

<sup>b</sup> The number before nd is the number not detected. The number after the dash is the maximum concentration.

The data suggest that house wren chicks from Whitewood Creek, SD were locally exposed to arsenic, but chicks from the North Platte River, WY were not. Arsenic was detected in house wren livers and diet from Whitewood Creek but not in similar samples from the North Platte River (Table 1). Because arsenic was not detected in eggs, the transfer of arsenic from egg to chick was probably negligible and thus arsenic detected in chicks from Whitewood Creek originated locally.

The lack of arsenic detected in house wren eggs from Whitewood Creek may be a consequence of the type of arsenic present in prey items. Organic forms of arsenic predominate in food-chain organisms (Phillips 1990) and some organic forms do not accumulate in bird eggs (Dagher and Hariri 1977).

Because birds may be able to eliminate arsenic more effectively as they age (Stanley et al. 1994), it is difficult to interpret the significance of arsenic concentrations in livers based on laboratory feeding studies. Camardese et al. (1990) fed mallard (*Anas platyrhynchos*) ducklings a diet of 300  $\mu\text{g/g}$  dry weight arsenic for 10 weeks and found 1.3  $\mu\text{g/g}$  dry weight arsenic in the liver. They reported altered growth, development, and physiology of ducklings at this concentration. Based on that study, chronic effects on house wren chicks in our study may be expected because the pooled diet of house wrens was 103  $\mu\text{g/g}$  dry weight arsenic and the mean liver concentration was 2.9  $\mu\text{g/g}$  dry weight. However, the concentrations of arsenic in those ducklings were probably much higher when they were younger and a comparable age to the house wrens in our study. For example, ducklings fed 100 and 400  $\mu\text{g/g}$  dry weight arsenic in feed for two weeks resulted in 4.5 and 33  $\mu\text{g/g}$  dry weight arsenic in livers (Stanley et al. 1994). Additionally, ducklings fed 200  $\mu\text{g/g}$  dry weight arsenic in diet resulted in  $>6$   $\mu\text{g/g}$  dry weight arsenic (calculated from wet weight) in duckling livers after 4 weeks (Hoffman et al. 1992).

Arsenic concentrations in house wren chicks and diet from Whitewood Creek were elevated, but not to the level considered acutely toxic. Arsenic was detected in all 5 livers (range 1.8 to 5.6  $\mu\text{g/g}$  dry weight; 0.5-1.7  $\mu\text{g/g}$  wet weight) and the pooled diet sample (103  $\mu\text{g/g}$  dry weight) from Whitewood Creek and not in any sample from the North Platte River (Table 1).

Background arsenic concentrations in tissues are generally  $< 0.5$   $\mu\text{g/g}$  wet weight arsenic (Goede 1985); all samples from Whitewood Creek were above this level. Animals that died from arsenic poisoning had 2-10  $\mu\text{g/g}$  wet weight arsenic in tissues; tissues with  $>10$   $\mu\text{g/g}$  wet weight arsenic confirm arsenic poisoning (Goede 1985). Further studies are necessary to determine if chronic effects of arsenic are present in house wren chicks at Whitewood Creek.

Mean concentrations of aluminum, boron, copper, iron, manganese, mercury, strontium, and zinc in house wren eggs did not differ between Whitewood Creek and the North Platte River (Table 2). Barium and selenium concentrations were

significantly higher in eggs from the North Platte River than from Whitewood Creek. Mean concentrations of boron, copper, iron, magnesium, manganese, molybdenum, strontium, and zinc in house wren livers did not differ between the two locations. Selenium concentrations were significantly greater in house wren livers from the North Platte River compared to Whitewood Creek.

**Table 2.** Geometric mean trace element concentrations ( $\mu\text{g/g}$  dry weight) in house wren eggs and livers of house wren chicks from Whitewood Creek, SD and the North Platte River near Casper, WY in 1997.

Trace element <sup>a</sup>	Geometric mean concentration			
	Eggs		Livers	
	SD (n=5)	WY (n=3)	SD (n=5)	WY (n=3)
Al	10.5	15.6	-- <sup>a</sup>	--
As	--	--	2.9	--
Ba	4.1 A <sup>c</sup>	12.8 B	--	--
B	19.3	17.3	18.1	19.8
Cu	2.6	3.8	27.6	22.5
Fe	103	117	3087	2675
Mg	371	337	724	722
Mn	3.9	5.4	5.8	5.3
Hg	0.2	0.1	0.1	--
Mo	--	--	3.1	3.7
Se	3.4 A	4.9 B	5.9 A	9.7 B
Sr	10.5	15.8	0.3	0.3
Zn	49	58	98	91

<sup>a</sup> Dashed line indicates that no mean could be calculated

<sup>b</sup> Locations with concentrations that do not share the same letter are significantly different (t-tests eggs Ba  $p = 0.0007$ , Se  $p = 0.02$ ; for chicks Se  $p = 0.01$ )

Selenium concentrations in house wren eggs (means 3-5  $\mu\text{g/g}$  dry weight) and house wren livers (means 6-10  $\mu\text{g/g}$  dry weight) were higher from the North Platte River than from Whitewood Creek, but not to levels considered toxic. Background concentrations in bird eggs are generally < 5  $\mu\text{g/g}$  dry weight selenium and an embryo viability threshold is estimated at 10  $\mu\text{g/g}$  dry weight selenium (United States Department of Interior 1998). Background hepatic concentrations are typically < 10  $\mu\text{g/g}$  dry weight selenium and a threshold for juvenile and adult toxicity is estimated at 30  $\mu\text{g/g}$  dry weight selenium (United States Department of Interior 1998).

The source of selenium in the North Platte River is probably from irrigation return flow. Concentrations of selenium in biota collected from an upstream major irrigation project were elevated (See et al. 1992). Additionally, house wrens collected nearer to the irrigation project had higher selenium concentrations (geometric mean = 19 µg/g dry weight selenium, Custer et al. 2001) than reported here.

Mercury concentrations in house wren eggs (means  $\leq 0.2$  µg/g dry weight, maximum concentration = 0.3 µg/g dry weight) and house wren livers (means  $\leq 0.1$  µg/g dry weight, maximum concentration = 0.2 µg/g dry weight) were at background levels. Impairment of reproductive success has been associated with egg concentrations of 2.5 to 10 µg/g dry weight mercury (assuming 80% moisture, Thompson 1996). House wrens collected on the North Platte River 10 km upstream of our study had similar mercury concentrations (0.1 µg/g dry weight mercury in liver and not detected in eggs, Custer et al. 2001).

Strontium concentrations in house wren eggs (means 11-16 µg/g dry weight) and chicks (mean 0.3 µg/g dry weight, range nd-0.8) were elevated. Background concentrations of strontium in chicken eggs (*Gallus gallus*) were 2 µg/g dry weight (Puls 1994). Strontium is rarely detected in bird livers, but concentrations in American coot (*Fulica americana*) livers from San Francisco Bay varied between 0.45 and 0.79 µg/g dry weight (Hui 1998) and concentrations in lesser scaup livers varied from 0.4-1.0 µg/g dry weight in western Lake Erie (Custer and Custer 2000). House wrens collected on the North Platte River 10 km upstream of our study had equal or higher strontium concentrations (mean egg concentration = 23 µg/g dry weight, mean liver concentration = 0.5 µg/g dry weight, Custer et al. 2001).

Boron concentrations in swallow and house wren eggs (means 17-19 µg/g dry weight) were elevated based on pen studies of mallard ducks. Concentrations of 13-20 µg/g dry weight in eggs are considered elevated and 20 µg/g, dry weight is a threshold concentration associated with embryonic toxicity (Puls 1994). House wrens and tree swallow eggs collected on the North Platte River 10 km upstream of our study had even higher boron concentrations (means 58-59 µg/g dry weight, Custer et al. 2001).

Zinc concentrations in house wren livers varied from 70-130 µg/g dry weight. These values were well below levels associated with Zinc toxicity (1200 µg/g dry weight, Gasaway and Buss 1972). Copper, iron, magnesium, manganese, and molybdenum in livers of house wrens were within the normal range (Puls 1994).

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