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Reports

CONTAMINANTS IN
INTERIOR LEAST TERN EGGS
FROM QUIVIRA
NATIONAL WILDLIFE REFUGE,
KANSAS, IN 1990 AND 1991

**KANSAS** 



QUIVIRA NATIONAL WILDLIFE REFUGE



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U.S. FISH AND WILDLIFE SERVICE Fish and Wildlife Enhancement 315 Houston Street Manhattan, Kansas 66502

# CONTAMINANTS IN INTERIOR LEAST TERN EGGS FROM QUIVIRA NATIONAL WILDLIFE REFUGE, KANSAS, IN 1990 AND 1991

by

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### SUMMARY

- ▶ Flooded or abandoned eggs of interior least terns (*Sterna antillarum*) nesting at Quivira National Wildlife Refuge in central Kansas were collected in 1990 and 1991. Four eggs were analyzed for metals and organochlorine contaminants in 1990. Two eggs were analyzed for metals in 1991.
- ► Concentrations of all metals analyzed were below the levels at which harmful effects on hatchability or survival are likely to occur.
- ▶ The only organochlorine compound detected in the eggs from 1990 was p,p'-DDE. The very low concentrations detected were unlikely to have caused any observable effects on productivity.
- ▶ The stage of incubation of the eggs collected was variable, and no conclusions relating contaminant levels to incubation stage should be drawn from the analyses.
- ▶ The information from the limited number of eggs analyzed indicates that there are no contaminants problems for interior least terns nesting at the refuge.

# **ACKNOWLEDGMENTS**

I appreciate the efforts of Dr. Roger Boyd and his field assistants, who were instrumental in collecting the eggs for these analyses. I also appreciate the efforts of Dave Hilley, Dan Schaad, Pat Gonzalez, and volunteers at the refuge. Tom Jackson and Dr. Gene Hansmann were very helpful in arranging funding for these analyses. I thank Dick Ruelle, Cathy Henry, Dr. Dan Welsh, Dr. Tim Fannin, and Dan Martin for their helpful reviews of this report.

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### INTRODUCTION

The interior population of the least tern (Sterna antillarum) was listed as endangered in 1985 (50 Federal Register 21,784-21,792). Therefore, the U.S. Fish and Wildlife Service (Service) and other agencies are involved in efforts to increase the population of the interior least tern, as outlined by Sidle and Harrison (1990). The major reason for listing the interior least tern as endangered was population reductions that apparently were due primarily to changes in the historic flow regimes along central U.S. rivers. However, wintering areas of interior least terns include Central American and South American coastlines (Sidle and Harrison 1990). The potential for interior least terns to accumulate contaminants from other locations suggests that evaluation of contaminant levels in eggs should be conducted, when possible.

Quivira National Wildlife Refuge is one of the two remaining nesting locations for least terns in Kansas, and the Service has undertaken several measures to enhance least tern nesting at the refuge (D. Hilley, personal communication). Biologists at the refuge collected least tern eggs for contaminants analyses in 1990 and 1991. This report presents the results of those analyses.

### STUDY AREA AND METHODS

Quivira National Wildlife Refuge is located in Stafford, Reno, and Rice counties in south-central Kansas. The refuge was purchased from private landowners in 1959. The Service owns surface rights to refuge lands, but mineral rights still belong to others. Numerous oil production facilities were in place when the refuge was purchased. Oil production has continued and some new production facilities have been developed. Two recent studies (Allen 1991, Allen and Wilson 1990) indicated that there are no major contaminants problems on the refuge. However, a Kansas Geological Survey study has indicated that selenium contamination should be a concern (Sophocleous 1992, Sophocleous and Perkins 1992).

Interior least terms nest on the Big Salt Marsh at the refuge (Figure 1). Nesting is monitored each year, and in 1990 and 1991 biologists collected abandoned or flooded eggs. In 1990, four eggs suitable for analyses were collected. Three of the eggs were from the same clutch. The eggs were analyzed individually for arsenic, mercury, and selenium using atomic absorption spectroscopy by the Research Triangle Institute (RTI) of Research Triangle Park, North Carolina. Other metal concentrations were determined with inductively coupled plasma emission spectroscopy (ICP) without preconcentration. Detection

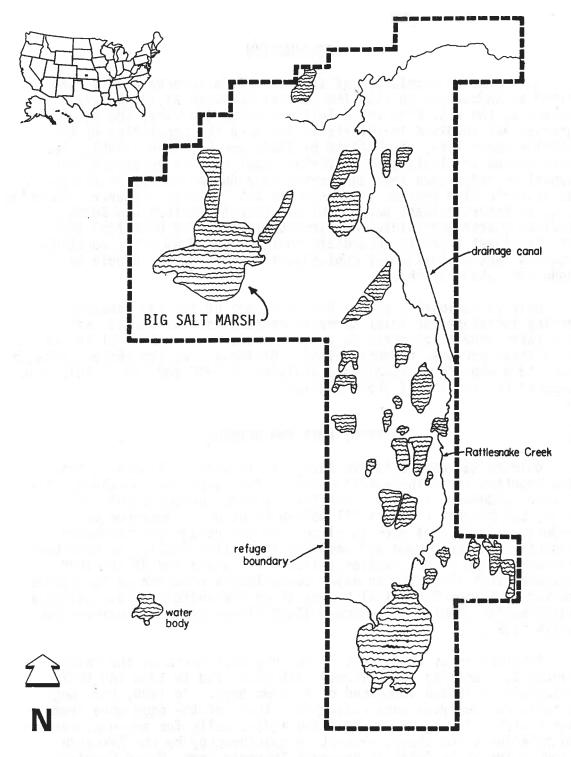


Figure 1. Big Salt Marsh least tern egg sampling location at Quivira National Wildlife Refuge, Kansas, in 1990 and 1991.

limits for the metals analyzed are shown in Table 1. RTI reported dry weight concentrations. Wet weight concentrations were calculated by multiplying the dry weight concentrations by [1 -( % moisture/100)].

Table 1. Detection limits in  $\mu g/g$  dry weight for metals in interior least tern eggs from Quivira National Wildlife Refuge, Kansas, in 1990 and 1991.

Element	Detect	tion Limit
	RTI	ETSRC <sup>2</sup>
aluminum	5.0	3.0
arsenic	0.3	0.2
barium	0.5	0.1
beryllium	0.1	0.01
boron	0.5	2.0
cadmium	0.1	0.02
chromium	0.5	0.1
copper	0.5	0.2
iron	10	1.0
lead	1.5	0.4-0.5
magnesium	20	0.1
manganese	0.5	0.2
mercury	0.02	0.005-0.07
molybdenum	0.8	1.0
nickel	0.8	0.1
selenium	0.3	0.2
strontium	0.5	0.1
tin	5.0	0.2
vanadium	0.5	0.3
zinc	1.0	
21110	1.0	0.2

<sup>1</sup> Research Triangle Institute, Research Triangle Park, North Carolina.

Aliquots of the 1990 eggs were analyzed for organochlorine compound concentrations by the Mississippi State Chemical Laboratory (MSCL) in Mississippi State. The concentrations were determined using electron capture gas chromatography. MSCL analyzed for alpha-benzene hexachloride (BHC), beta-BHC, delta-BHC, gamma-BHC, hexachlorobenzene, alpha-chlordane, gamma-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, heptachlor epoxide, dieldrin, endrin, mirex, toxaphene, o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, and total PCBs. Wet weight concentrations were reported for organochlorines. The detection limit was 0.01 microgram per gram ( $\mu$ g/g, 1 part per million)

<sup>2</sup> Environmental Trace Substances Research Center, Columbia, Missouri.

wet weight for all organochlorines except PCBs and toxaphene, for which the detection limit was 0.05  $\mu$ g/g. Lipid-normalization of organic compounds does not improve data reporting (Huckins *et al.* 1988, Schmitt *et al.* 1990), so I do not report lipid concentrations.

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Only two eggs suitable for analyses were collected in 1991. The eggs were from different clutches. The eggs were individually analyzed for metals by the Environmental Trace Substances Research Center of Columbia, Missouri. Atomic absorption spectroscopy and ICP analyses were done as had been done in 1990. ETSRC reported dry weight and wet weight concentrations.

No anomalies were reported in the samples. Laboratory quality assurance and quality control were responsibilities of the Patuxent Analytical Control Facility of the Service. Precision and accuracy of the laboratory analyses were confirmed with procedural blanks, duplicate analyses, test recoveries of spiked materials, and reference material analyses. Round-robin tests among the analytical labs also were part of the quality control. Analytical results were not adjusted to reflect spike recoveries. Tests of reference standards were not done for organic compounds. With the exception of a low recovery for hexachlorobenzene in spikes at MSCL, all analyses met the QA/QC standards established by the Service.

The stage of incubation of the eggs collected was variable. No conclusions relating contaminant levels to incubation stage should be drawn from the analyses.

# RESULTS AND DISCUSSION

**METALS** 

Arsenic, beryllium, cadmium, lead, molybdenum, nickel, and vanadium, were not detected in any egg. Concentrations of chromium, copper, iron, magnesium, manganese, and zinc were within normal ranges. Those metals were not considered further. Mercury and selenium concentrations in the eggs are shown in Table 2. Concentrations of other metals are presented in Table 3.

Dietary mercury has been correlated with production of fewer eggs and lower productivity in birds (e.g. Heinz 1979, Spann et al. 1972). Fimreite (1971) found that mercury concentrations of 0.5 to 1.5  $\mu$ g/g wet weight in pheasant (Phasianus colchicus) eggs reduced hatchability. Borg et al. (1969) found that 1.3 to 2.0  $\mu$ g/g wet weight reduced hatchability in pheasants. Wiemeyer et al. (1984, 1988) used Fimreite's 0.5  $\mu$ g/g effect level to assess mercury effects on bald eagle (Haliaeetus leucocephalus) and osprey (Pandion haliaeetus) egg hatchability. Common tern (Sterna hirundo) eggs from a site in Ontario

Table 2. Mercury, and selenium concentrations in  $\mu$ g/g in interior least tern eggs from Quivira National Wildlife Refuge, Kansas, in 1990 and 1991.

		Element Concentration					
		Mer	cury	Selei	nium		
	Percent	Dry	Wet	Dry	Wet		
	Moisture	Weight	Weight	Weight	Weight		
1990 <sup>1</sup>	72.1	2.01	0.56	1.48	0.41		
1990 <sup>1</sup>	71.8	1.49	0.42	1.50	0.42		
1990 <sup>1</sup>	71.2	2.38	0.69	2.12	0.61		
1990	71.6	1.80	0.51	2.10	0.60		
1991	75.0	1.80	0.45	2.90	0.73		
1991	73.8	0.64	0.17	1.70	0.45		

<sup>1</sup> Eggs from the same nest.

at which fledging success was only 10 to 12 percent contained a mean mercury concentration of 3.65  $\mu$ g/g wet weight, compared to a mean of 1.00  $\mu$ g/g wet weight at a colony with normal fledging success (Fimreite 1974). King et al. (1991) found that wet weight mercury concentrations up to 0.91  $\mu$ g/g in eggs of Forster's terns (Sterna forsteri) and up to 0.74 µg/g in eggs of black skimmers (Rhyncops niger) did not affect reproductive success. White and Cromartie (1977) determined that mean wet weight concentrations in hooded merganser (Lophodytes cucullatus) eggs in the U.S. ranged from 0.16 to 1.49  $\mu$ g/g. They did not determine the effects of those concentrations on productivity. Heinz (1975) found that mallard (Anas platyrhynchos) ducklings from eggs that contained approximately 1  $\mu$ g/g mercury wet weight had poorer avoidance behavior than did controls. Peterson and Ellarson (1976) found mercury concentrations in oldsquaw (Clangula hyemalis) eggs from Hudson Bay that ranged from 0.09 to 0.44  $\mu$ g/g wet weight. Vermeer (1971) analyzed mercury content in aquatic bird eggs in Saskatchewan and Manitoba, and found that the highest levels were in eggs of fish-eating herring gulls (Larus argentatus). However, herring gull eggs containing 0.5 to 2.0  $\mu g/g$  wet weight hatched successfully. Egg concentrations up to 16  $\mu g/g$ wet weight did not appear to affect herring gull hatching or fledging success in Ontario (Vermeer et al. 1973). Henny and Herron (1989) found no relationship between white-faced ibis (Plegadis chihi) productivity at Carson Lake, Nevada, and geometric mean mercury concentrations in eggs of up to 1.06  $\mu$ g/g dry weight. King et al. (1980) found comparable concentrations in white-faced ibis eggs in Texas.

Welsh and Mayer (1992) found that mercury concentrations in least

Table 3. Element concentrations in  $\mu g/g$  from ICP scans in interior least tern eggs from Quivira National Wildlife Refuge, Kansas, in 1990 and 1991.

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		Element Co	<u>ncentration</u>			
	Barium	Bo	Boron		Chromium	
Year	Dry W Weight Wei	et Dry ght Weight	Wet Weight	Dry Weight	Wet Weight	
1990 <sup>1</sup>	4.11 1.1	S ND	ND	ND	ND	
1990¹	4.48 1.2	26 0.57	0.16	ND	ND	
1990¹	3.28 0.9	94 ND	ND	ND	ND	
1990	ND N	D ND	ND	ND	ND	
1991 1991	1.40 0. 1.70 0.		ND 0.5	0.1 ND	0.03 ND	

		E	lement Co	ncentrati	on		
	Copi			Iron		<del></del>	
Year	Dry Weight	Wet Weight	Dry Weight	Wet Weight	Dry	Wet	
1990¹	1.37	0.38	129.0	36.0	452	126	
1990 <sup>1</sup>	2.40	0.68	131.0	36.9	465	131	
1990 <sup>1</sup>	2.50	0.72	92.5	26.6			
1990	2.40	0.68	113.0	32.1	308	87	
1991 1991	3.00 1.90	0.75 0.50	123.0 98.8	30.8 26.0	527 543	132 142	
	1990 <sup>1</sup> 1990 <sup>1</sup> 1990 <sup>1</sup> 1990	Year Dry Weight  1990¹ 1.37 1990¹ 2.40 1990¹ 2.50 1990 2.40  1991 3.00	Copper           Dry         Wet           Weight Weight           1990¹         1.37 0.38           1990¹         2.40 0.68           1990¹         2.50 0.72           1990         2.40 0.68           1991         3.00 0.75	Copper         Ir           Dry         Wet         Dry           Weight Weight         Weight           1990¹         1.37         0.38         129.0           1990¹         2.40         0.68         131.0           1990¹         2.50         0.72         92.5           1990         2.40         0.68         113.0           1991         3.00         0.75         123.0	Copper         Iron           Dry         Wet Weight Weight           1990¹         1.37         0.38         129.0         36.0           1990¹         2.40         0.68         131.0         36.9           1990¹         2.50         0.72         92.5         26.6           1990         2.40         0.68         113.0         32.1           1991         3.00         0.75         123.0         30.8	Year         Dry Weight Weight         Dry Weight Weight         Wet Weight         Dry Weight           1990¹         1.37 0.38 129.0 36.0 452           1990¹         2.40 0.68 131.0 36.9 465           1990¹         2.50 0.72 92.5 26.6 439           1990         2.40 0.68 113.0 32.1 308           1991         3.00 0.75 123.0 30.8 527	Copper         Iron         Magnesium           Dry         Wet Weight Weight Weight Weight Weight Weight Weight         Dry Wet Weight Weight Weight Weight Weight           1990¹         1.37         0.38         129.0         36.0         452         126           1990¹         2.40         0.68         131.0         36.9         465         131           1990¹         2.50         0.72         92.5         26.6         439         126           1990         2.40         0.68         113.0         32.1         308         87           1991         3.00         0.75         123.0         30.8         527         132

	W. 111	E1	ement Con	centratio	n	
	Manganese		Strontium		Zinc	
Year	Dry Weight	Wet Weight	Dry Weight	Wet Weight	Dry Weight	Wet Weight
1990 <sup>1</sup>	3.18	0.89	2.48	0.69	51.3	14.3
1990 <sup>1</sup>	3.11	0.88	3.53	1.00	59.3	16.7
1990 <sup>1</sup>	2.48	0.71	3.62	1.04	42.7	12.3
1990	0.96	0.27	2.85	0.81	41.9	11.9
1991	2.60	0.65	15.6	3.91	54.7	13.7
1991	1.40	0.37	27.9	7.31	45.2	11.8

<sup>1</sup> Eggs from the same nest.

tern eggs from sites on the Missouri River in North Dakota ranged from 0.08 to 1.48  $\mu$ g/g dry weight in 1990 and from 1.03 to 1.48  $\mu$ g/g dry weight in 1991. Those concentrations were lower than those in eggs from Quivira, but the larger concentrations from North Dakota eggs are comparable to those from Quivira. The maximum mercury concentration in least tern eggs from the Missouri River in South Dakota from 1988 through 1990 was 1.19  $\mu$ g/g dry weight (Ruelle 1992).

Eisler (1987) concluded that a safe maximum mercury concentration in bird eggs is 0.9  $\mu$ g/g wet weight. Based on that recommendation and the findings reported above, it appears that mercury contamination is not a significant hazard to least terns nesting at Quivira. However, the differences in mercury concentrations in eggs from different states indicate that the source(s) of mercury may be found in the nesting areas. This possibility should be studied.

Selenium is an essential trace nutrient for terrestrial and aquatic organisms, so it probably will be found in most analyses of biota. The tolerance of eggs of different species is variable (Heinz et al. (1987). Lemly and Smith (1987) concluded that the level of concern for selenium in bird eggs should be 15 to 20  $\mu$ g/g dry weight. Skorupa and Ohlendorf (1991) stated that approximately 10  $\mu$ g/g is the lower value for the concentration in individual eggs that reduced embryo viability in blacknecked stilts (Himantopus mexicanus). The nationwide upper boundary for normal mean dry weight concentrations in bird eggs is approximately 3  $\mu$ g/g (Eisler 1985). The maximum concentration found in any of the tern eggs collected at Quivira was less than 3  $\mu$ g/g, so selenium is not of concern in the least tern eggs collected.

Information on normal barium concentrations in wildlife is lacking, and I have no reference data for comparison to the concentrations found in least tern eggs from Quivira. The barium concentrations in eggs from Quivira can be compared to those from other locations. Only three of 27 barium concentrations in least tern eggs from South Dakota from 1988 through 1990 (Ruelle 1992) were greater than those found at Quivira.

A physiological need for boron in animals has not been determined. Mallard hens fed 1000  $\mu$ g/g boron in the diet laid eggs that contained from 26 to 81  $\mu$ g/g dry weight and in which embryo survival was impaired. Eggs from hens on the control diet contained boron concentrations of 3  $\mu$ g/g dry weight or less (Smith and Anders 1989), concentrations that are comparable to those found in least tern eggs from Quivira.

The effects of strontium on bird eggs have not been assessed. Skorupa and Ohlendorf (1991) indicated that strontium concentrations above 75  $\mu$ g/g are elevated. Because all strontium concentrations in eggs from Quivira were well below that level, I conclude that the concentrations were not harmful. The concentrations are comparable to those found in least tern eggs from South Dakota (Ruelle 1992).

## CHLORINATED HYDROCARBONS

The only chlorinated hydrocarbon detected in the eggs analyzed in 1990 was p,p'-DDE. The concentrations detected were 0.07  $\mu$ g/g in one egg, 0.08  $\mu$ g/g in one egg, and 0.09  $\mu$ g/g in the other two eggs. Zicus et al. (1981) considered wet weight geometric mean DDE concentrations of  $0.62 \mu g/g$  and  $0.52 \mu g/g$  in hooded merganser and common goldeneye (Bucephala clangula), respectively, to be low. Custer and Mitchell (1987) reported that for black skimmers nesting at a site on the Texas coast, in nests in which all eggs hatched the geometric mean wet weight DDE concentration was 1.9  $\mu$ g/g. In white-faced ibis eggs from Carson Lake in Nevada, Henny and Herron (1989) found that eggs were unlikely to be cracked during incubation if egg DDE concentrations were below 4  $\mu q/q$ wet weight. In evaluations of eggs from Carson Lake, Henny and Bennett (1990), found that eggshell strength and thickness were negatively correlated with DDE concentrations. Henny and Bennett used eggs with less than 0.40  $\mu$ g/g wet weight as controls for their analyses of eggshell strength. Custer and Mitchell (1989) found what they considered low geometric mean DDE concentrations (0.14 and 0.27  $\mu$ g/g wet weight) in white-faced ibis eggs from two locations in southern Texas. Clutch size and productivity were reduced in black-crowned night-herons in the western U.S. when DDE concentrations were above 8  $\mu$ g/g wet weight (Henny et al. 1984).

The DDE concentrations found in least term eggs from Quivira were low compared to the values from other studies. No detrimental effect on productivity is likely at the concentrations found.

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