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Metal and organic residues in addled eggs of least terns and piping plovers in the Platte Valley of Nebraska

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The threatened piping plover and the endangered interior least tern breed on the Platte River in Nebraska from the city of North Platte to the confluence with the Missouri River at Plattsmouth (Faanes 1983, Sidle *et al* 1988).

Major riverine nesting areas are the reaches from Lexington to Grand Island and from Columbus to Plattsmouth (Fig 1). Nesting habitat is sparsely vegetated or unvegetated islands, sandbars, or shorelines of the river.

An additional and important habitat is on the banks and islands within sand pits made by sand and gravel operations along the river.

In the initial nest of the year, piping plovers usually lay four eggs. and least terns lay two or three and sometimes four eggs. Piping plovers will commonly renest if the initial nesting attempt is unsuccessful; least terns will renest infrequently if the initial attempt is unproductive. When renesting, piping plovers usually lay three to four eggs, and least terns lay two eggs. Least terns feed primarily on small fish (Anderson and Hubert 1988). Piping plovers feed on small aquatic invertebrates and terrestrial insects.

Throughout the Platte River system, tern and plover eggs are most often lost to predation by mink, raccoons, and birds. Flooding and sandbar erosion are the second greatest cause of nest failure.

Rising water levels may directly flood nests located close to the water line, and changes in river velocity and course sometimes may destroy nests by erosion. Human disturbance is the third most important cause of nest failure. In addition to direct destruction of eggs, human activity near the nest can cause abandonment or can interrupt incubation, which results in egg mortality due to exposure (Lingle 1989).

Egg survival also may be influenced by environmental contaminants. Contaminants of concern along the Platte River are selenium, mercury, cadmium, DDT and its breakdown products, polychlorinated biphenyls (PCBs), and chlordane. Unpublished data in other studies conducted by the U.S. Fish and Wildlife Service (USFWS) indicate that selenium concentrations are high enough in tern and plover eggs to be of concern, and that mercury, chlordane, and PCBs may also be present in the environment.

Selenium is a naturally occurring trace element that is essential for vertebrates in small quantities but is toxic at higher concentrations. Weathering of Cretaceous marine shale or coal deposits can release high levels of selenium to soil, and natural precipitation on or irrigation of seleniferous soils can easily leach out selenium. The leached selenium can accumulate in surface waters, and lead to toxicity in fish and wildlife species via direct intoxication or intoxication through bioaccumulation and/or biomagnification (Lemly and Smith 1987, Ohlendorf 1989).

Once selenium enters an aquatic environment, it does not break down chemically, but continues to increase in concentration and recycle within the system. Irrigation return flows to Kesterson National Wildlife Refuge (NWR) in California were implicated in selenium-caused deformations and mortalities in unhatched water bird chicks and deaths of adults, among other manifestations (Ohlendorf and Skorupa 1989).

Kesterson, where selenium problems were first widely publicized, is not the only irrigation area in the western U.S. exhibiting such problems.

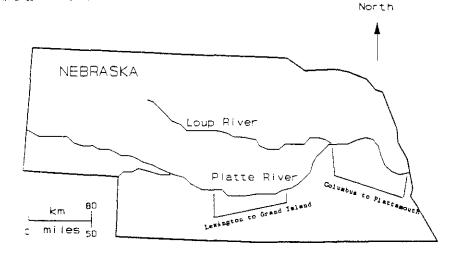


Fig 1. General nesting areas for interior least terms and piping plovers on the Platte River of Nebraska.

Mercury is one of the few metals that is strongly bioconcentrated and biomagnified. It is a carcinogen, mutagen, and teratogen, with no beneficial functions in fish or wildlife. Mercury is easily transformed from the inorganic to a more toxic organic form in fish and wildlife tissues. Increased synthesis of metallothionein in response to mercury exposure may help animals acquire a somewhat increased tolerance.

Sources of mercury are varied, but many sources releasing small amounts of mercury can have a cumulative impact on a small river, due to mercury's persistence. Leachates of municipal landfills contain mercury, possibly from disposal of items such as mercury batteries, thermometers, and electrical switches.

Cadmium also is a biologically nonessential element. All cadmium compounds are potentially harmful or toxic to a variety of species of fish and wildlife. Cadmium causes behavior, growth, and physiological problems in aquatic life at sublethal concentrations. Major sources of cadmium are incineration of fossil fuels, fertilizers, wastewater discharges, electroplating, and battery manufacturing.

Agricultural use of DDT has been banned in the U.S. since 1972, and most remaining residues presumably have broken down into DDD, DDE, and other chemicals. However, DDT is still manufactured and used in some countries; aerial transport and atmospheric deposition of DDT may account for its presence in some areas.

The biological effects of DDT are well known, and include reproductive impairment and eggshell thinning in raptors and other fisheating birds. The breakdown products have deleterious properties similar to those of DDT, and past use of DDT in the intensively cultivated Platte River valley may be a significant source of these products in the local environment.

PCBs are very stable compounds. Their accumulation in all levels of

the food chain is rapid, and depuration from contaminated organisms is lengthy. Because they are readily biomagnified, PCBs are particularly hazardous to predators. Predatory fish and wildlife are at risk since such a large percentage of their diet consists of other species of fish and wildlife. In predatory birds such as bald eagles (Haliaeetus leucocephalus), PCBs affect normal growth, reproduction, metabolism, and behavior. PCBs have effects on reproductive success and eggshell thinning similar to those of DDT.

Many of the effects documented for raptors may also be occurring in other types of birds, although information about effects of PCBs on most other species is needed.

The insecticide chlordane has been severely restricted by the U.S. Environmental Protection Agency and has been cancelled for most uses. It has a relatively long half life; upon decomposition, many of the metabolites are more toxic than the parent compound. Technical chlordane is a hazardous mixture of chemicals (α -chlordane, γ -chlordane, heptachlor epoxide, cis-nonachlor, trans-nonachlor, and oxychlordane) which tend to accumulate in fatty tissues.

It is rapidly accumulated by aquatic organisms, tends to be biomagnified in the food chain, and has been shown to be an animal carcinogen. A major past use of chlordane was as a termiticide.

During tern and plover nesting studies conducted in 1989 and

1990, addled tern and plover eggs from two sections of the Platte River were delivered to the USFWS in Grand Island. Eggs from sand pits along the central Platte River from Lexington to Grand Island were collected by the Platte River Whooping Crane Critical Habitat Maintenance Trust. Widely fluctuating water levels in the reach repeatedly flushed the river nests in 1989, so no addled eggs were available for analyses from river nests that year (Lingle 1989). Eggs from river colonies and sand pit colonies in the lower reach of river from Central City to Plattsmouth were collected by the Nebraska Game & Parks Commission in 1989 and 1990.

The eggs were refrigerated immediately upon receipt. A USFWS technician measured length, width, and volume (by immersion), total mass, and mass of the contents. Between individual dissections, opening and dissection apparatus were rinsed once in tap water and acetone, and three times in distilled water. The contents of each egg were put into a chemically clean glass jar, and did not touch any foreign materials during processing. The technician recorded presence and condition of embryos, putrefaction, color, and other physical characteristics of the contents of each egg. After processing, the eggs were frozen at -20 C until they were shipped. In 1989, eggs collected were screened for a broad range of contaminants. Often, the number of eggs required for the analyses could not be obtained from one nest. In those cases, eggs found in neighboring nests of each species were composited

for analyses. Composite samples consisted of eggs from only one species. In 1990, eggs were analyzed individually for a smaller number of residues.

Samples were shipped to Research Triangle Institute in North Carolina for inorganic analyses or to the Mississippi State Chemical Laboratory for organochlorine analyses. Arsenic and selenium analyses were conducted using graphite furnace atomic absorption spectroscopy (GFAA). Lead was determined by both GFAA and by inductively coupled atomic emission spectroscopy (ICP). Mercury was quantified with cold vapor atomic absorption spectroscopy. All other inorganic residues were determined with ICP. Egg contents for organochlorine analyses were extracted with hexane, the extract was concentrated and fractionated, and residues were determined by electron capture gas chromatography (GC) on a packed or megabore GC column.

Accuracy and precision of determinations were tested by instrument blanks, matrix blanks, duplicate determinations, and tests of standard references and spiked samples. Concentrations of hexachlorobenzene (HCB), antimony, silver, and tin were low, and little confidence can be placed in these results. All other analyses passed ISFWS quality assurance/ quality control criteria.

In 1989, 28 least tern and 16 piping plover eggs were collected. Including composites, the number of samples analyzed for inorganics in 1989 was five for least terns and four for piping plovers. Individual analyses in 1990 produced sample sizes of 15 and 3, respectively. For organochlorine analyses, four least tern and three piping plovers eggs were used in 1989, and one egg of each species was used in 1990.

In 1989 17 of the least tern eggs had an embryo in some stage of development; in 1990 only one did. Five piping plover eggs contained an embryo in 1989. In 1990, seven eggs contained an embryo in some stage of development. Determination of early embryonic development was confounded in many cases by putrefaction of the egg contents. No sufficiently developed embryos showed any gross external abnormalities.

Inorganic residues are expressed as dry weights in Tables 1 and 2. Organochlorine residues are given as wet weights in Tables 3 and 4. The average moisture content of piping plover eggs collected in 1989 was 72%; in 1990, 66%. Average moisture in least tern eggs collected in 1989 was 70%; in 1990, 69%. Dry weights may be converted to a wet weight via the formula:

Wet weight = Dry weight [100-(%Moisture/100)]

Inorganic elements not detected were aluminum, antimony, cobalt, chromium, molybdenum, silver, tin, and vanadium. Inorganic residues of interest include mercury, selenium, and cadmium. Mercury residues in piping plover eggs (Table 1) ranged from 0.12 $\mu g/g$ to 0.755 $\mu g/g$. In least tern eggs (Table 2), the range was 0.94

μg/g to 3.19 μg/g. Piping plover eggs ranged from 4.82 μg/g to 11.4 μg/g selenium. Selenium in least tern samples was found from 4.16 μg/g to 9.46 μg/g. Cadmium was not detected in least tern eggs, and was found at concentrations from 0.1 to 0.3 μg/g in piping plover eggs (Table 1).

Several organochlorine compounds were not present or, if present, were below limits of detection (α -BHC, β -BHC, γ -BHC, σ -BHC, γ -chlordane, toxaphene, o,p'-DDE, o,p'-DDD, endrin, cis-nonachlor, o,p'-DDT, and mirex). Residues of p,p'-

DDT in piping plover eggs (Table 3) were at detectable limits of $0.005 \,\mu g/g$; p,p'-DDD ranged from $0.005 \,\mu\text{g/g}$ to $0.02 \,\mu\text{g/g}$; p,p'-DDE ranged from 0.07 µg/g to 0.4 µg/g. Total PCBs ranged from $0.025 \mu g/g$ to $0.67 \mu g/g$ in piping plover eggs. Chlordane components were found generally near the limit of detection (0.01 μg/g). In the more piscivorous least tern (Table 4), egg residues of p,p'-DDT were 0.03 µg/g; p,p'-DDD ranged from 0.01 µg/g to 0.03 µg/g; p,p'-DDE ranged from $0.2 \mu g/g$ to $0.68 \mu g/g$. PCB residues in least tern eggs ranged from $0.86 \,\mu\text{g/g}$ to $1.90 \,\mu\text{g/g}$.

Chlordane component concentrations generally were found near the limit of detection.

Discussion

The biological significance and harmful threshold levels for reproductive effects from mercury residues are not well understood. For example, the difference in mercury levels in successful and unsuccessful bald eagle nests was only 0.04 µgHg/g wet weight (Eisler 1987). Background levels for eggs in piscivorous birds ranged from 0.24 µg/g to 63.2

Table 1. Elements in composite (1989) and individual (1990) samples of addled piping plover eggs collected from the Platte River valley, NE. All values are $\mu g/g$ dry weight; "ND" signifies not detected, N_c signifies the number of composite samples analyzed, and N_s signifies the number of individual samples analyzed.

1989 cond	entration					1990 cona	entration			
Element	N_c	Mean	Median	Min	Max	N_i	Mean	Median	Min	Max
ΑI		ND								
S b		ND								
Ba	4	4.86	3.20	2.74	10.3					
Be	4	0.025	0.025	0.025	0.025					
В	4	0.324	0.250	0.250	0.546					
Cď	4	0.151	0.100	0.100	0.302					
Co		ND								
Cr		ND								
Cu	4	4.29	2.53	2.28	9.82					
Fe	4	108	120	56.4	136					
Pb1		ND								
Pb ²	4	0.245	0.1	0.1	0.681		, ND			
Mg	4	4 84	505	353	571		, ND ∵			
Mn	4	2.94	2.43	1.46	5.46					
Мо		ND								
Ni	4	0.555	0.400	0.400	1.02					
Ag		ND							•	
Sr	4	13.3	13.5	11.2	14.9					
Sn		ND								
V		ND								
Zn	4	58.8	59.1	3 5	81.8					
As		ND					ND			
Hg	4	0.649	0.724	0.394	0.755	2	0.142	0.142	0.120	0.163
Se	4	7.87	7.01	6.04	11.4	3	6.72	6.85	4.82	8.5

¹ Analyzed by inductively coupled plasma emission spectroscopy.

² Analyzed by graphite furnace atomic absorption spectroscopy.

μg/g (Eisler 1987, Wiemeyer et al 1988). At Red Rocks Lake NWR in Montana, mercury levels in great blue heron (Ardea herodias) eggs ranged from 0.512 µg/g to $1.040 \,\mu g/g$ (Jones *et al* 1990); the range of mercury residues from least tern eggs found in our study was generally higher. For American coot (Fulica americana) and trumpeter swan (Cygnus buccinator) eggs from Red Rocks Lake NWR, mercury levels from <0.072 μg/g to 0.972 were detected; Platte River piping plover eggs had mercury residues in the same range. Mercury may have

adverse effects on avian reproduction at $0.9 \,\mu g/g$ wet weight (3.6 $\,\mu g/g$ dry weight, Eisler 1987). The maximum concentration of mercury we found in eggs of Platte River least terns was just below this value (3.19 $\,\mu g/g$). Note, however, that some results in our study are from composite samples, and that concentrations of mercury in some individual eggs would be greater than the highest concentration we report for the composite.

Our results support the general observation that mercury concen-

trations are greater in piscivorous birds than in other birds, and that mercury concentrations should be of more concern for least terns than for piping plovers. We do not know if least terns are particularly sensitive to effects of mercury contamination.

The tolerance of eggs from least terns and piping plovers to selenium toxicity is not known, but the birds' status as threatened or endangered species does not permit direct toxicity testing. Bird and egg tolerances to selenium toxicity and its effects are species

Table 2. Elements in composite (1989) and individual (1990) samples of addled interior least tern eggs collected from the Platte River valley, NE. All values are mg/g dry weight; "ND" signifies not detected, N_c signifies the number of composite samples analyzed, and N_i signifies the number of individual samples analyzed.

1989 Concentration				1990 Concentration						
Element	N _C	Mean	Median	Min	Max	Nj	Mean	M edian	Min	Max
Al		ND								
Sb		ND								
Ва	5	3.88	4.06	1.11	7.32					
Be		ND								
В		ND								
Cd		ND								
Co		ND								
Cr		ND								
Cu	5	3.08	3.34	1.58	4.11					
Fe	5	126.6	131	107	142					
Pb1		ND								
Pb ²	5	0.16	0.100	0.100	0.399		ND			
Mg	5	501.8	522	391	584					
Mn	5	3.056	3.18	2.17	3.57					
Mo		ND								
Ni		ND								
Ag		ND						•		
Sr	5	9.416	9.77	6.81	12.1					
Sn		ND								
		ND								
Zn	5	72.94	78.9	5 5.6	88.8					
As		ND				15	0.15	0.15	0.15	0.15
Hg	5	1.512	1.41	1.26	2.04	11	1.62	1.34	0.944	3.19
Se	5	7.18	7.06	6.27	8.54	15	7,14	6.98	4.16	9.46

¹ Analyzed by inductively coupled plasma emission spectroscopy.

² Analyzed by graphite furnace atomic absorption spectros∞py.

dependent. Eisler (1985a) found that normal selenium concentrations in freshwater bird eggs ranged from 0.8 to 3.0 µg/g dry weight, and Skorupa and Ohlendorf (1991) reveal that for field collected eggs of various avian species the upper normal boundary is 3.0 μg/g dry weight. While a precise relationship between selenium concentrations and hatching failure for various bird species is unknown, preliminary data indicate that selenium concentrations less than 3 µg/g in eggs are not associated with any effects; the range from 3 to 20 µg/g indicates an area of possible embryonic lethality without any gross embryonic deformities apparent; and, concentrations greater than 20 µg/g dry weight are generally associated with embryonic deformity (H. Ohlendorf, pers comm).

All Platte River samples with detectable selenium contained between 3 and 20 μ g/g. Based on ranges of effects derived from other studies of selenium toxicity in birds, selenium may be affecting reproduction of least terns and piping plovers in our study area. Also, because our samples were analyzed as composites of varying numbers of eggs, some of the eggs in the composite sample had higher concentrations than we report.

Selenium-caused mortality of a few eggs or chicks of an abundant species may be insignificant; on the other hand, selenium problems in threatened and endangered plovers and terns in the Platte River valley may be particularly significant because of the combination of other factors

Table 3. Organochlorine residues in composite (1989) and one individual (1990) samples of addled piping plover eggs collected from the Platte River valley, NE. All values are mg/g wet weight; "ND" signifies not detectable, missing values were not analyzed for; N_C signifies the number of composite samples analyzed.

Compound	N _c	1989 con Me an	centrations Median	M in	Мах	1990 concentrations Value
HCB a-BHC g-BHC b-BHC s-BHC	3	0.01	0.005	0.005	0.01	ND ND ND ND ND
Oxychlordane Heptachlor	3	0.02	0.02	0.01	0.04	0.01
epoxide g-Chlordane	3	0.03	0.02	0.01	0.07	0.02 ND
t-Nonachlor Toxaphene	3	0.03	0.01	0.01	0.06	0.01 ND
Tot.PCB's o,p'-DDE a-Chlordane	3	0.24	0.025	0.025	0.67	0.14 ND 0.005
p,p'-DDE	3	0.26	0.23	0.16	0.40	0.07
Dieldrin o,p'-DDD Endrin cis-Nonachlor o,p'-DDT	3	0.14	0.04	0.01	0.36	0.03 ND ND ND ND
p,p'-DDD p,p'-DDT Mirex	3	0.01	0.005	0.005	0.02	0.005 0.005 ND

(such as flooding and predation) that also inhibit recruitment.

The harmful threshold level for reproductive effects of cadmium in birds is not well known. However cadmium in eggs from unsuccessful nests of Cooper's hawks (Accipiter cooperii) was higher than the residue in eggs from successful nests (Eisler 1985b). At Red Rocks Lake NWR, cadmium residues in trumpeter swans and American coots ranged from $< 0.05 \mu g/g$ to 2.16 μg/g. Concentrations in eggs of American coots from refuges in South Dakota ranged from < 0.02 μ g/g to 0.04 μ g/g (USFWS 1990). Cadmium in eggs of piping plovers collected in the Platte River valley ranged from <0.1 μ g/g to 0.302 μ g/g. Cadmium concentrations in least tern eggs were below the detection limits.

Residues of DDT and its metabolites have been extensively documented in raptor eggs. In common terns (*Sterna hirundo*), thickness and structure of eggshells are not adversely affected at residue levels of <4 µgDDE/g (Switzer *et al* 1973, Fox 1976, quoted in Weseloh *et al* 1989). DDT is metabolized to DDD and DDE. Metabolism of DDT combined with its environmental degrada-

tion may account for the less frequent detection of DDT and the higher detection of DDE in addled eggs (Abou-Donia and Menzel 1968, quoted in Wiemeyer et al 1988). In least tern eggs from the Platte River valley, DDE levels ranged from 0.2 µg/g to 0.68 µg/g. Median DDE residues from piping plover eggs collected in the Platte River valley during our study were less than the 0.66 µg/g median concentration in piping plover eggs from the New Jersey Coast (USFWS 1991) (Table 5).

Although residue levels in Platte River eggs are from composite samples, and individual eggs may have levels greater than the reported value for the composite, it does not appear that DDE residues were sufficient to cause reproductive impairment in populations of least terns and piping plovers nesting along the Platte River in 1989 and 1990.

Residues of PCBs were found in all eggs in this study, supporting

Table 4. Organochlorine residues in composite (1989) and one individual (1990) samples of addled interior least tern eggs collected from the Platte River valley, NE. All values are mg/g wet weight; "ND" signifies not detectable, missing values were not analyzed for; N_C signifies the number of composite samples analyzed.

			,			1990
		-	ncentration			concentration
Compound	N _C	Me an	Me dian	M in	Max	Value
HCB	4	0.01	0.01	0.01	0.01	ND
a-BHC						ND
g-BHC						ND
b-BHC						ND
s-BHC						ND
Oxychlordane Heptachlor	4	0.03	0.02	0.02	0.06	0.03
epoxide	4	0.05	0.04	0.04	0.09	0.08
g-Chlordane						ND
t-Nonachlor	4	0.07	0.07	0.05	0.10	0.08
Toxaphene						ND
Tot.PCB's	4	1.44	1.50	0.86	1.90	1.5
o,p'-DDE						ND
a-Chlordane						0.05
p,p'-DDE	4	0.48	0.48	0.29	0.68	0.2
Dieldrin	4	0.16	0.15	0.06	0.27	0.12
o,p'-DDD						ND
Endrin						ND
cis-Nonachlor						ND
o,p'-DDT						ND
p,p'-DDD	4	0.02	0.03	0.01	0.03	0.02
p,p'-DDT						0.03
Mirex	-					ND

Table 5. Comparison of organochlorine residues in piping plover eggs collected on the New Jersey Coast 1 with residues in piping plover addled eggs from the Platte Valley of Nebraska. All values are mg/g wet weight; "ND" signifies not detectable, and missing values were not analyzed for.

Piping Plover, New Jersey coast					Piping Plover, Platte River Valley				
Compound	Mean	Median	Min	Max	N	Mean	Median	Min	Max
Oxychlordane Heptachlor	0.06	0.04	0.02	0.12	3	0.02	0.02	0.01	0.04
epoxide	0.04	0.04	0.02	0.08	3	0.03	0.02	0.01	0.07
t-Nonachior	0.08	0.06	0.03	0.14	3	0.03	0.01	0.01	0.06
a-Chlordane					1	0.005	0.005	0.005	0,0 05
cis-Nonachlor				0.02					
Total PCB's	4.4	3.8	3.3	6.9	4	0.205	0.14	0.005	0.67
p.p'-DDE	0.64	0.66	0.2	1.1	4	0.215	0.20	0.07	0,40

¹USFWS 1991. Environmental contaminants in New Jersey coast piping plover (*Charadrius melodus*) eggs. USFWS Region 5 Contaminants Report. USFWS, Pleasantville, NJ. 12pp + app.

Eisler's (1986) observation that measurable concentrations of PCBs can be found in most bird eggs.

This may be because PCBs are ubiquitous in the environment, and because the lipophilic PCBs are deposited in the high fat content of egg yolk. USFWS (1991) reported median PCB residues in piping plover eggs from the New Jersey coast that were greater than median PCB concentrations found in our study (Table 5). Total PCB residues in least terns from the Platte Valley are less than the 2.9 µg/g to 10.4 µg/g found in common terns along the Great Lakes by Weseloh *et al* (1989).

PCB residues in our study are well below documented levels in eggs exhibiting reproductive impairment in ringed turtle doves (16 μ g/g wet weight, or 64 μ g/g dry weight) and in chickens (20 μ g/g wet weight, or 80 μ g/g dry weight) (Heinz *et al* 1984 quoted in Eisler 1986).

Although species sensitivity may vary, and interpretation of toxicity for various PCB concentrations is confounded by a plethora of congeners and isomers, we do not believe that PCB residues are high enough to impair reproduction in least terms and piping plovers nesting in the Platte River valley.

Technical chlordane used for termite control consists of oxychlordane, heptachlor and its metabolite heptachlor epoxide, cis- and trans-nonachlor, and α - and γ -chlordane, and often other compounds. Trans-nonachlor mean residues in common tern eggs

from the Canadian Great Lakes ranged from $0.09~\mu g/g$ to $0.31~\mu g/g$ (Weseloh *et al* 1989), vs. a mean of $0.07~\mu g/g$ in least tern eggs in our samples. On the New Jersey coast, piping plover eggs carried residues comparable to those in piping plover eggs from the Platte River (Table 5). Although species sensitivity may vary, it does not appear that chlordane residues are high enough to adversely affect least tern and piping plover reproduction in the Platte River valley.

The concentration of most residues detected in eggs of least terns and piping plovers nesting in the Platte River valley are not a cause for alarm. However, selenium and mercury concentrations in addled eggs are a cause for concern. Selenium and mercury concentrations were elevated above background, and selenium in particular may be causing embryo mortality without gross embryological defects. More significantly, the impacts of contaminants combined with the physical degradation of habitat may further accelerate population declines for both of these species.

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