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Environmental Contaminants in Two Composite Samples of Piping Plover Eggs from Delaware

Fish and Wildlife Service

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Executive Summary

During June of 2009, eleven non-viable piping plover (*Charadrius melodus*) egg were collected from nests located at the northern end of Cape Henlopen State Park in Delaware. The eggs were combined into two composite samples and analyzed by the U.S. Fish and Wildlife Service for organochlorine compounds and trace metals.

Elevated concentrations of organochlorine compounds were not detected in the two composite egg samples. Polychlorinated biphenyls (PCBs, maximum concentration 362.0 parts-per-billion wet weight), DDE (max. 139.9 ppb, wet weight), and polybrominated diphenyl ether (max. 221.1 ppb, wet weight) concentrations were well below suggested adverse effect thresholds. Twenty-four other organochlorine compounds were detected in the low parts-per-billion range (< 11 ppb, wet weight) or were below analytical detection limits.

The analytical scan for trace metals included 19 elements. Mercury was detected at 0.116 parts-per-million (ppm, wet weight) and 0.106 ppm wet weight in the two piping plover composite egg samples. These mercury levels were similar to concentrations reported in other piping plover egg studies from the Atlantic Coast population and well below a suggested adverse effect threshold for sensitive bird species (0.25 ppm, wet weight). Selenium levels in the two composite samples (0.53 ppm, 0.60 ppm; wet weight) were also well below a suggested adverse effect threshold (3 ppm, wet weight).

Concentrations of strontium in Delaware piping plover eggs (28.4 ppm, dry weight) appeared elevated compared to studies of other mid-Atlantic coast bird species and to an effect level in black-crowned night heron embryos (11.3 ppm, dry weight). Once an ecotoxicological threshold for strontium has been established, strontium concentrations in piping plover eggs may warrant additional study.

PREFACE

This report provides documentation of environmental contaminants in non-viable piping plover eggs collected from Delaware. Analytical work was completed under USFWS Analytical Control Facility Catalog 5100039 and Purchase Orders 94420-09-Y002 (Organics) and 94420-09-Y003 (Trace metals).

Questions, comments, and suggestions related to this report are encouraged. Written inquiries should refer to Report Number FY10-MEFO-2-EC and be directed to:

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This report complies with the peer review and certification provisions of the Information Quality Act (Public Law 106-554, Section 515).

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1. Background

During June of 2009, eleven non-viable piping plover (*Charadrius melodus*) egg were collected from nests located at the northern end of Cape Henlopen State Park in Sussex County, Delaware (N 38° 48' 14" / W 075° 05' 39"; Figure 1). Since relatively little contaminant information is available for piping plover eggs from the Atlantic Coast population (Mierzykowski 2009), the U.S. Fish and Wildlife Service analyzed egg contents for residues of organochlorine compounds and trace metals.

2. Methods

Prior to processing, eggs were cleaned of sand and surface debris using a paper towel soaked with de-ionized water. Egg metrics were recorded (e.g., total weight, egg content weight, length, breadth) and volumes were calculated (Hoyt 1979). Eggs were scored at the equator with a stainless steel scalpel. Egg contents were extracted, placed in chemical clean jars, and weighed. The eleven eggs were combined into two composite samples – one of six eggs and one of five eggs. Composite samples were frozen and later shipped to analytical laboratories.

Composite egg samples were analyzed for organochlorine compounds (n = 27) by the Geochemical and Environmental Research Group in College Station, Texas. Trace metal determinations (n = 19 metals) were made by Laboratory and Environmental Testing, Inc. in Columbia, Missouri. Percent lipid and percent moisture were also measured. Quality assurance and quality control (QA/QC) procedures at both laboratories included procedural blanks, duplicates, spike recoveries, and certified reference material. The USFWS Analytical Control Facility reviewed QA/QC results and accepted both laboratory data packages.

Figure 1. Piping plover egg collection location, Delaware 2009 (N 38º 48’ 14” / W 075º 05’ 39”).

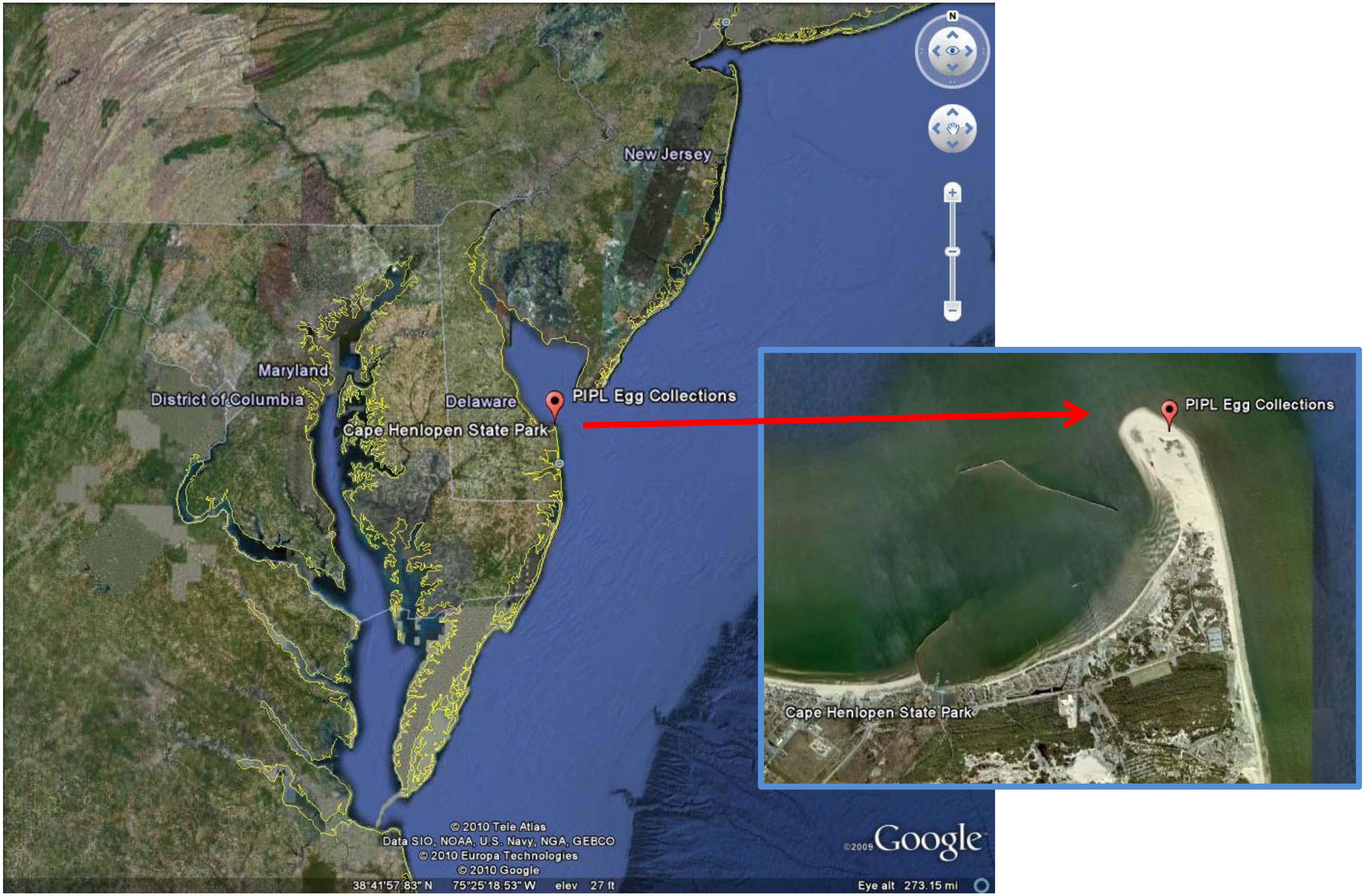

Table 1. Egg metrics and percent lipids for 2009 PIPL eggs from Delaware

Sample No.	Egg No.	Total Wt. (g)	Length (mm)	Equator 1 (mm)	Equator 2 (mm)	Mean Eq 1 & 2	Sample Wt (g)	Lipids (%)
DE-09-01	1	9.2	31.2	24.8	24.8	24.8	8.0	
(n=6 eggs)	2	9.4	32.1	24.8	24.8	24.8	7.9	
	3	8.3	31.3	24.2	24.1	24.2	7.4	
	4	10.9	33.3	25.3	25.5	25.4	9.4	
	5	10.2	32.3	24.7	24.8	24.8	8.9	
	6	8.7	32.2	24.0	24.0	24.0	8.1	
							49.7	7.85
DE-09-02	7	9.4	32.1	24.8	24.9	24.9	9.4	
(n=5 eggs)	8	9.4	32.9	24.8	24.9	24.9	7.4	
	9	9.5	32.8	24.7	24.6	24.7	8.5	
	10	9.3	33.2	24.5	24.5	24.5	8.1	
	11	10.2	33.1	24.5	24.5	24.5	8.3	
							41.7	8.83

3. Analytical Results

Analytical results are presented in Table 2 (Organochlorine Compounds) and Table 3 (Trace Metals). Concentrations are ng/g (parts-per-billion) for organochlorine compounds and in µg/g (parts-per-million) for trace elements. All results in the text, unless otherwise noted, are presented on a fresh wet weight basis to account for moisture loss after egg laying (Stickel *et al*. 1973).

In some journal publications, trace metals other than mercury may be presented on a dry weight basis. A second trace metal table (Table 4) is included in this report to facilitate data comparisons with dry weight data sets.

4. Discussion

Contaminant concentrations in the Delaware piping plover eggs were compared to suggested toxicity threshold effect levels described in several studies, a previous study of Delaware piping plover eggs (Munavali 1992) or to other Atlantic Coast piping plover contaminant investigations.

4.1 Organochlorine Compounds (Table 2)

<u>4.1.1 Polychlorinated Biphenyl (PCB)</u> - The PIPL egg samples from Delaware contained 278 ng/g and 362 ng/g of Total PCBs. A total PCB threshold effect level specific to piping plover eggs does not exist. Hoffman *et al*. (1996) reported that common terns (*Sterna hirundo*) with greater than 7,500 ng/g of total PCBs had decreased hatching success. Both egg composite samples from Delaware were well below the tern threshold level. The latest PCB concentrations in the 2009 Delaware plover egg composite samples were also lower than the levels reported for Delaware in 1991 (420 ng/g, reported as Aroclor 1254; Munavali 1992).

<u>4.1.2 Polybrominated Diphenyl Ether (PBDE)</u> - Total PBDE was markedly different in the two composite samples with 221 ng/g in the six egg composite (DE-09—01) and 22 ng/g in the five egg composite (DE-09-02). PBDE is considered a newly emerging contaminant, so little comparative data are available for the compound in piping plover eggs. Total PBDE in recent piping plover egg collections from Maine ranged from 20 ng/g to 210 ng/g (Goodale 2008 and 2009), the same range found in the 2009 Delaware samples. Six osprey (*Pandion haliaetus*) eggs collected in 2002 from the same region of Delaware as the piping plover eggs contained a range of 141 to 429 ng/g (mean 206 ng/g) of Total PBDE (Toschik *et al*. 2005).

An avian egg threshold effect level for total PBDE has not yet been established. McKernan *et al*. (2009) suggested a lowest observable effect level (LOEL) on American kestel (*Falco sparverius*) pipping and hatching success for total PBDE may be as low as 1,800 ng/g. PBDE concentrations in the Delaware piping plover composite egg samples were well below the LOEL suggested from kestrels.

<u>4.1.3 Dichlorodiphenyldichloroethylene (DDE)</u> - The brown pelican (*Pelecanus occidentalis*) appears to be one of the most sensitive bird species with reproductive failure occurring when DDE residues in eggs exceed 3,700 ng/g (Blus 1996). DDE in the PIPL egg composite samples from Delaware (139 ng/g and 117 ng/g) were well below the 3,700 ng/g threshold associated with eggshell thinning. The DDE levels in the 2009 Delaware plover samples were also considerably lower than levels reported for eggs collected in Delaware in 1991 (450 ng/g, Munavali 1992).

<u>4.1.4 Other Organochlorine Compounds</u> - Other organic compounds in the analytical scan (e.g., chlordane compounds, hexachlorocyclohexanes, dieldrin, mirex, etc.) were in the low ng/g range (< 11 ng/g) or were below analytical detection limits.

Table 2. Organic compounds in 2009 PIPL composite egg samples from Delaware, ng/g fresh wet weight

	DE-09-01	DE-09-02
PCB and PBDE		
PCB-TOTAL	278.21	362.00
BDE-TOTAL	221.08	22.03
Hexachlorocyclohexanes		
alpha BHC	< 0.481	< 0.500
beta BHC	< 0.481	< 0.500
gamma BHC	< 0.481	< 0.500
delta BHC	< 0.481	< 0.500
Total BHC	BDL	BDL
Chlordane Compounds		
alpha chlordane	< 0.481	< 0.500
gamma chlordane	1.23	1.11
cis-nonachlor	< 0.481	< 0.500
trans-nonachlor	9.27	11.30
oxychlordane	8.08	8.68
heptachlor epoxide	1.44	1.97
heptachlor	< 0.481	< 0.500
Total Chlordane	20.02	23.06
DDT Metabolites		
o,p'-DDD	4.22	5.71
o,p'-DDE	< 0.481	0.86
o,p'-DDT	< 0.481	< 0.500
p,p'-DDD	0.49	1.19
p,p'-DDE	139.93	117.12
p,p'-DDT	0.81	1.15
Total DDT	145.45	126.02
Other Organochlorine Compounds		
aldrin	< 0.481	< 0.500
endrin	< 0.481	< 0.500
dieldrin	6.81	8.05
endosulfan II	< 0.481	< 0.500
HCB	1.31	2.23
mirex	2.19	3.59
pentachloro-anisole	< 0.481	0.43
toxaphene	< 9.62	< 10.0

ng/g = parts-per-billion, fresh wet weight = corrected for moisture loss
Values in red preceded by < symbol indicate non-detects and detection limits
Non-detects not included in sums for Total Chlordane and Total DDT
BDL = below detection limit

4.2 Trace Metals (Table 3 – Fresh Wet Weight, Table 4 – Dry Weight).

4.2.1 Mercury (Hg) - Mercury was detected at 0.116 µg/g and 0.106 µg/g in the two 2009 Delaware piping plover composite egg samples. In an earlier Delaware piping plover egg investigation (Munavali 1992), Hg was below the analytical detection limit of 0.180 µg/g. Mercury in a piping plover egg composite collected from Maine in 2003 had a similar Hg concentration of 0.170 µg/g (Mierzykowski and Carr 2004).

An avian egg threshold effect level for Hg has not been established for piping plovers, but several researchers have suggested mercury effect thresholds based on laboratory and field investigations with other bird species. Scheuhammer *et al*. (2007) suggested that egg Hg concentrations greater than 1 µg/g would be associated with impaired hatchability and embryonic mortality in a number of bird species. Lower Hg toxicity thresholds have been suggested based on studies with mallards (*Anas platyrhyncos*)(0.80 µg/g, Heinz 1979) and ring-necked pheasants (*Phasianus colchicus*) (0.50 µg/g, Fimreite 1971).

A methylmercury dosing study showed species differences in the sensitivity of avian embryos (Heinz *et al*. 2009). Highly sensitive species with LC_{50}s less than 0.25 µg/g included white ibis (*Eudocimus albus*), snowy egret (*Egretta thula*), and tri-colored heron (*Egretta tricolor*). Moderately sensitive species with LC_{50}s greater than 0.25 µg/g, but less than 1 µg/g, included clapper rail (*Rallus longirostris*), common tern (*Sterna hirundo*), and royal tern (*Sterna maxima*). Low sensitive species with LC_{50}s 1 µg/g or higher included lesser scaup (*Aythya affinis*), Canada goose (*Branta canadensis*), and laughing gull (*Larus atricilla*). It is not known where piping plovers would reside within the three mercury sensitivity categories suggested by Heinz *et al*. (2009), but the Hg levels found in 2009 Delaware piping plover eggs would be below the suggested threshold level for the most sensitive species.

4.2.2 Selenium (Se) – Selenium levels in the two Delaware piping plover egg composites were 0.53 µg/g and 0.60 µg/g. Heinz (1996) suggested a 3 µg/g Se threshold for reproductive impairment in bird eggs. Both 2009 composite samples from Delaware were well below this Se threshold. The Delaware piping plover egg Se levels were higher, however, than a single composite piping plover egg sample from Maine in 2003 (0.41 µg/g, Mierzykowski and Carr 2004).

4.2.3 Strontium (Sr)[1] – An adverse effect threshold for Sr in bird eggs has not been established. In nine black-crowned night heron (*Nycticorax nycticorax*) embryos from Delaware, some effects on oxidative stress (i.e., increased concentrations of "reduced glutathione" GSH) were found at mean Sr concentration of 11.3 µg/g dry weight (Rattner *et al*. 2000). Both piping plover egg samples from Delaware had Sr levels (28.4 µg/g dry weight, Table 4) that were higher than the embryo effect level reported by Rattner *et al*. (2000). Compared to other piping plover studies, the two 2009 Delaware piping plover eggs composite samples were slightly higher than a single composite sample of piping plover eggs from Delaware in 1991 (25.7 µg/g dry weight, Munavali 1992), and a single composite piping plover egg sample from Maine in 2003 (21.4 µg/g dry weight, Mierzykowski and Carr 2004).

Too little information is currently available to characterize Sr concentrations in Delaware piping plover eggs as highly elevated. Considerably higher concentrations have been found in other bird species. Mora (2003) examined Sr in seventy eggs of eleven passerine species in Arizona and considered levels in yellow warblers (*Dendroica petechia*, 224 µg/g dry weight) and song sparrows (*Melospiza melodia*, 189 µg/g dry weight) as elevated. Mean Sr concentrations in the other nine passerine species ranged from 3.2 to 50.2 µg/g dry weight (Mora 2003). Schwarzbach *et al*. (2006) found Sr ranging from 11.1 to 176 µg/g dry weight in California clapper rail (*Rallus longirostris obsoletus*) eggs with embryo deformities associated with the highest Sr concentrations.

4.2.4 Other Trace Metals – Arsenic, barium, beryllium, copper, iron, magnesium, manganese, and zinc were also detected in piping plover eggs; but toxic effect thresholds have not been established for these elements, some of which are essential elements for biological systems.

[1] Dry weight concentrations are presented and discussed in the strontium (Sr) section.

Table 3. Trace metals in 2009 PIPL composite egg samples, µg/g fresh wet weight

FRESH WET WEIGHT

	DE-09-01	DE-09-02
Aluminum (Al)	< 0.50	< 0.50
Arsenic (As)	0.07	< 0.05
Boron (B)	< 0.50	< 0.50
Barium (Ba)	0.16	0.14
Beryllium (Be)	0.07	0.05
Cadmium (Cd)	< 0.03	< 0.03
Chromium (Cr)	< 0.10	< 0.10
Copper (Cu)	0.73	0.70
Iron (Fe)	22.4	21.3
Mercury (Hg)	0.116	0.106
Magnesium (Mg)	140.8	108.9
Manganese (Mn)	0.31	0.25
Molybdenum (Mo)	< 0.50	< 0.50
Nickel (Ni)	< 0.10	< 0.10
Lead (Pb)	< 0.05	< 0.05
Selenium (Se)	0.53	0.60
Strontium (Sr)	6.38	6.31
Vandadium (V)	< 0.10	< 0.10
Zinc (Zn)	14.2	14.2

µg/g = parts-per-million, fresh wet weight = corrected for moisture loss
Values in red preceded by < symbol indicate non-detects and detection limits
Non-detects not corrected for moisture loss

Table 4. Trace metals in 2009 PIPL composite egg samples, µg/g dry weight

DRY WEIGHT

	DE-09-01	DE-09-02
Aluminum (Al)	< 2.00	< 2.00
Arsenic (As)	0.3	< 0.200
Boron (B)	< 2.00	< 2.00
Barium (Ba)	0.69	0.62
Beryllium (Be)	0.3	0.2
Cadmium (Cd)	< 0.100	< 0.100
Chromium (Cr)	< 0.500	< 0.500
Copper (Cu)	3.2	3.1
Iron (Fe)	100	96
Mercury (Hg)	0.53	0.48
Magnesium (Mg)	628	492
Manganese (Mn)	1	1
Molybdenum (Mo)	< 2.00	< 2.00
Nickel (Ni)	< 0.500	< 0.500
Lead (Pb)	< 0.200	< 0.200
Selenium (Se)	2.4	2.7
Strontium (Sr)	28.4	28.4
Vandadium (V)	< 0.500	< 0.500
Zinc (Zn)	62.9	63.7

µg/g = parts-per-million
Values in red preceded by < symbol indicate non-detects and detection limits

5. Summary

Elevated concentrations of organochlorine compounds were not detected in two composite samples of non-viable piping plover eggs collected in Delaware in 2009. PCB (max. 362.0 ng/g), DDE (max. 139.9 ng/g), and polybrominated diphenyl ether (max. 221.1 ng/g) concentrations in 2009 Delaware piping plover egg samples were well below suggested adverse effect thresholds. Twenty-four other organochlorine compounds were detected in the low parts-per-billion range (< 11 ng/g) or were below analytical detection limits.

Mercury was detected at 0.116 µg/g and 0.106 µg/g in the two 2009 Delaware piping plover composite egg samples. These mercury levels were similar to concentrations reported in other piping plover egg studies from the Atlantic Coast population and well below a suggested adverse effect threshold for sensitive bird species (0.25 µg/g, Heinz *et al*. 2009). Selenium levels in the two composite samples (0.53 µg/g, 0.60 µg/g) were also well below a suggested adverse effect threshold (3 µg/g, Heinz 1996).

Concentrations of strontium in 2009 Delaware piping plover eggs (28.4 µg/g dry weight) were elevated compared to studies of other mid-Atlantic coast bird species (Table 5) and to a level that suggested oxidative stress in black-crowned night heron embryos (11.3 µg/g dry weight, Rattner *et al*. 2000). However, considerably higher strontium levels (> 100 µg/g dry weight) have been found in eggs of other bird species from the U.S. southwest (Mora 2003) and west coast (Schwarzbach *et al*. 2006). Strontium concentrations in bird eggs likely vary with concentrations detected in soil and water, and the northeast and upper Great Lakes regions of the U.S. have lower concentrations of strontium than areas in the southwest (Mora M.A. 2010. Personal communication).

Table 5. Strontium (Sr) in bird eggs from mid-Atlantic states, µg/g dry weight

Species	State	Year(s)	n	Individual Eggs or Composite Samples	Mean Sr Conc.
Piping Plover	DE	2009	2	Composites	28.4
Piping Plover	DE	1991	1	Composites	25.7
Black-crowned Night-heron	DE	1993 - 1997	31	Individual	8.0
Common Tern	MD	1994	10	Individual	3.3
Osprey	NJ	1994 - 1998	9	Individual	2.9
Peregrine Falcon	DE	1998	2	Individual	1.0

Data provided by Bruce Nierwienski, USFWS. Environmental Contaminants Data Management System (ECDMS)

Once an ecotoxicological threshold for strontium has been established, strontium concentrations in piping plover eggs along the Atlantic Coast may warrant additional study.

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