U.S. FISH AND WILDLIFE SERVICE MAINE FIELD OFFICE SPECIAL PROJECT REPORT: FY07-MEFO-6-EC



Environmental Contaminants in Tern Eggs from Monomoy National Wildlife Refuge and Seal Island National Wildlife Refuge Mission Statement U.S. Fish and Wildlife Service

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Environmental Contaminants in Tern Eggs from Monomoy National Wildlife Refuge and Seal Island National Wildlife Refuge

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Abstract

During the 2005 breeding season, six non-viable common tern (*Sterna hirundo*) and three roseate tern (*Sterna dougallii*) eggs were collected from Monomoy National Wildlife Refuge (NWR) in Massachusetts and Seal Island NWR in Maine. Eggs were formed into three 3-egg species-specific composites – one common tern sample and one roseate tern sample from Monomoy NWR, and one common tern sample from Seal Island NWR. All composite samples were analyzed for 26 organochlorine compounds and 19 trace elements.

At Monomoy NWR, Total Polychlorinated Biphenyl (PCB) concentrations in common tern and roseate tern composite egg samples were 0.67 and 1.13 parts-per-million (ppm), fresh wet weight, respectively. Total PCB in the common tern composite egg sample from Seal Island NWR was 0.34 ppm. DDE, a metabolite of the pesticide DDT, was found at 0.03 ppm in both the common and roseate tern samples from Monomoy NWR, and at 0.05 ppm in the common tern sample from Seal Island NWR. Concentrations of Total PCB and DDE were below suggested toxic effect threshold levels. Twenty-four other organochlorine compounds were below detection limits or in the low parts-per-billion (ppb) range.

Mercury was detected at 0.14 ppm and 0.11 ppm in roseate tern and common tern egg samples from Monomoy NWR, respectively. At Seal Island NWR, the common tern egg composite sample had a mercury concentration of 0.09 ppm. Concentrations in all three samples were well below a suggested avian reproductive effect threshold for mercury (0.80 ppm). Of the eighteen other trace elements in the analytical scan, ten were below detection in all samples. Although detected in all samples, levels of arsenic, copper, iron, magnesium, manganese, selenium, strontium, and zinc were not elevated compared to other regional tern studies and to suggested threshold effect levels.

Keywords: common tern, roseate tern, PCB, mercury, contaminants

PREFACE

This report provides documentation of environmental contaminants in nonviable common tern and roseate tern eggs collected from Monomoy National Wildlife Refuge, Massachusetts, and Seal Island National Wildlife Refuge, Maine. Analytical work was completed under U.S. Fish and Wildlife Service (USFWS) Analytical Control Facility Catalog 5100013 - Purchase Orders 94420-06-Y585 (Organics) and 94420-06-Y586 (Trace Elements).

Questions, comments, and suggestions related to this report are encouraged. Written inquiries should refer to Report Number FY07-MEFO-6-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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Acronyms and Abbreviations

Al	aluminum
ARTE	Arctic tern
As	arsenic
B	boron
Ba	barium
Be	beryllium
BHC	benzenehexachloride
Cd	cadmium
CGC	capillary gas chromatography
COTE	common tern
Cr	chromium
Cu	copper
DDD	dichlorodiphenyldicloroethane
DDE	dichlorodiphenyldicloroethylene
DDT	dichlorodiphenyltricloroethane
DEQ	Division of Environmental Quality (USFWS)
Fe	iron
FUD	Formerly Used Defense site
GERG	Geochemical and Environmental Research Group
Hg	mercury
μg/g	micrograms per gram (or parts-per-million)
MEFO	Maine Field Office (USFWS)
Mg	magnesium
Mn	manganese
NAS	National Audubon Society
ng/g	nanograms per gram (or parts-per-billion)
Ni	nickel
NWHC	National Wildlife Health Center (USGS)
NWR	National Wildlife Refuge
Pb	lead
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
ppb	parts-per-billion
ppm	parts-per-million
QA/QC	quality assurance / quality control
ROST	roseate tern
Se	selenium
Sr	strontium
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
Zn	zinc

1. Background

In 2004, U.S. Fish and Wildlife Service (USFWS) biologists at Monomoy National Wildlife Refuge (NWR) in Massachusetts and National Aububon Society (NAS) biologists at Seal Island NWR in Maine were concerned about a variety of abnormal symptoms in juvenile terns (e.g., unable to extend right or left wing, tight patagium, inability to fly, spinning in circles, droopy heads, emaciation, or lethargy) and multiple deaths within the same cohort. Symptoms appeared in common terns (*Sterna hirundo*; alpha code COTE) and Arctic terns (*Sterna paradisea*; alpha code ARTE) at Seal Island NWR, and in common terns and some roseate terns (*Sterna dougallii*, alpha code ROST) at Monomoy NWR. Carcasses were submitted to the U.S. Geological Survey National Wildlife Health Center (NWHC) in Madison, Wisconsin, for diagnostic examinations.

In 2005, the symptoms persisted within the colonies and additional carcasses were submitted to the NWHC. Non-viable tern eggs were also present at both refuges, and a few were collected in 2005 for environmental contaminant analyses. This report documents the results of the egg analyses.

Tern eggs have been used in several contaminant studies in response to reports of abnormalities (Hays and Riseborough 1972, Gilbertson *et al.* 1976), declines in reproductive success (Custer *et al.* 1983a, Kubiak *et al.* 1989, Castillo *et al.* 1994), or as bioindicators of temporal trends in contaminants (Burger and Gochfeld 2004). Egg concentrations generally reflect contaminant uptake of the female tern foraging near the nesting colony prior to egg-laying (Burger 1993, Burger 2002, Burger *et al.* 1992, Becker and Cifuentes 2004).

2. Study Purpose

Determine contaminant concentrations in non-viable tern eggs collected from Monomoy NWR and Seal Island NWR.

3. Study Areas

3.1 Monomoy NWR is an 8-mile long, 7,604-acre barrier island. It is located in southeastern Massachusetts south of the City of Chatham, Barnstable County, at the elbow of Cape Cod (Figure 1). Monomoy is a former World War II era U.S. Navy gunnery range and listed as Formerly Used Defense (FUD) Site No. D01MA0245. The site was principally used for machine gun target practice, and bullets and fragments can still be found on the refuge (T. Prior. 2007. Personal communication). The refuge is currently classified as a wilderness area and no other known contaminant sources are believed to be present.

Monomoy NWR provides habitat for federally protected roseate terns and piping plovers (*Charadrius melodus*), other seabirds and shorebirds, wading birds, and waterfowl. The refuge supports the second largest nesting colony of common terns on the Atlantic Seaboard and is the largest gray seal (*Halichoerus grypus*) haul-out site on the seaboard.

3.2 Seal Island NWR is a narrow 65-acre island located off of mid-coast Maine approximately

20 miles southeast of the Town of Rockland (Figure 2). The island is within Criehaven Township, Knox County. Seal Island is a former World War II era U.S. Navy bombing target and rocket gunnery range, and listed as FUD Site No. D01ME0032. The site has undergone a site assessment under the Department of Defense's Military Munitions Response Program. Due to past discoveries of munitions and explosives of concern, and the presence of munitions constituents (nine metals and one explosive, 2,6-dinitrotoluene) found during a 2007 site assessment (Alion Science and Technology 2007), a remedial investigation and feasibility study has been recommended.

Seal Island is an important breeding site for common tern, Arctic tern, Atlantic puffin (*Fratercula arctica*), black guillemot (*Cepphus grylle*), and common eider (*Somateria mollissima*). Roseate tern, razorbill (*Alca torda*), great cormorant (*Phalacrocorax carbo*), double-crested cormorant (*Phalacrocorax auritus*), great black-backed gull (*Larus marinus*), and herring gull (*Larus argentatus*) also nest on the island.

4. Methods

Nine non-viable eggs were collected in June and July 2005. On the Monomov NWR, three roseate tern eggs from Minimoy Island (N 41° 38' 07" / W 069° 58' 23"; Figure 1) and three common tern eggs from South Monomoy (N 41° 33' 24" / W 070° 00' 20"; Figure 1) were collected. Three common tern eggs were collected from Seal Island NWR (N 43° 53' 15" / W 068° 44' 24"; Figure 2). USFWS and NAS staff collected these eggs under provisions allowed by their Federal Migratory Bird Permits.

Tern eggs were refrigerated at 5° C immediately after collection. Prior to processing, eggs were cleaned of dirt, feces, and surface debris using a paper towel soaked with deionized water. Basic egg metrics were recorded (e.g., total weight, length, breadth). Volume was determined from length and breadth measurements (Hoyt 1979). Each egg was scored at the equator with a stainless-steel scalpel. Egg contents were extracted, weighed, and formed into species-specific 3-egg composites and placed in chemically clean jars. Composite samples were frozen and later shipped to analytical laboratories.

Egg contents were analyzed for 26 organochlorine compounds by the Geochemical and Environmental Research Group in College Station, Texas. Organochlorine compounds in the analytical scan were total polychlorinated biphenyl (Total PCB), four hexachlorocyclohexanes (*alpha* BHC, *beta* BHC, *delta* BHC, *gamma* BHC), seven chlordane compounds (heptachlor, heptachlor epoxide, oxychlordane, *alpha* chlordane, *gamma* chlordane, *cis*-nonachlor, *trans*nonachlor), metabolites and isomers of DDT (o,p'-DDD, o,p'DDE, o,p'DDT, p,p'-DDD, p,p'DDE, p,p'-DDT), aldrin, endrin, dieldrin, hexachlorobenzene (HCB), endosulfan II, mirex, pentachlor-anisole, and toxaphene. Residues were quantified by capillary gas chromatography with flame ionization, electron capture, or mass spectrometer detectors. Detection limits were 0.01 µg/g wet weight for Total PCBs and toxaphene, and 0.001 µg/g wet weight for all other organochlorine compounds. Total PCB was determined by the sum of congeners. Percent lipid was also measured in each composite sample. Determinations for 19 trace elements were made by Laboratory and Environmental Testing, Inc., in Columbia, Missouri. Elements included in the scan were aluminum, arsenic, boron, barium, beryllium, cadmium, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, lead, selenium, strontium, vanadium, and zinc. Most elements were quantified using inductively coupled plasma mass spectrometry (ICP-MS). Arsenic, lead, and selenium were measured through graphite furnace atomic absorption (GFAA). Mercury levels were determined with cold vapor atomic absorption (CVAA). Detection limits - in $\mu g/g$ wet weight - were 0.02 for mercury, cadmium, and beryllium; 0.05 for arsenic, barium, lead, selenium, and strontium; 0.07 for copper; 0.10 for chromium, manganese, nickel, vanadium, and zinc; and 0.50 for aluminum, boron, iron, magnesium, and molybdenum.

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 data packages.

Tern Egg Number	Species	Total Egg Weight	Length	Breadth 1	Breadth 2	Mean Breadth	Egg Content Weight	Egg Volume	% Lipid
		(g)	(mm)	(mm)	(mm)	(mm)	(g)		
SMN-501	COTE	18.3	41.2	29.3	29.4	29.4	16.3	18.1	
SMN-502	COTE	18.6	41.4	30.0	29.9	30.0	16.1	18.9	
SMN-503	COTE	16.8	42.1	27.7	27.7	27.7	<u>14.8</u>	<u>16.5</u>	
SMN-501C ^a		Composite Sample Weight & Volume				47.2	53.5	6.20%	
MIN-501	ROST	18.1	41.4	28.8	28.7	28.8	15.4	17.5	
MIN-502	ROST	18.0	41.9	29.0	28.9	29.0	15.3	17.9	
MIN-503	ROST	18.9	42.4	29.2	29.0	29.1	<u>16.6</u>	<u>18.3</u>	
MIN-501C ^a		Composite Sample Weight & Volume				47.3	53.7	7.20%	
SEA-E501	COTE	15.5	39.3	28.9	28.7	28.8	14.2	16.6	
SEA-E503	COTE	18.4	41.3	30.5	30.3	30.4	17.0	19.5	
SEA-E505	COTE	17.8	40.7	29.7	29.8	29.8	16.6	18.4	
SEA-501C ^a			Composite	Sample Weig	ht & Volume		47.8	54.5	5.00%

 Table 1. Metrics of individual tern eggs and percent lipids in composites

^a Sample Number

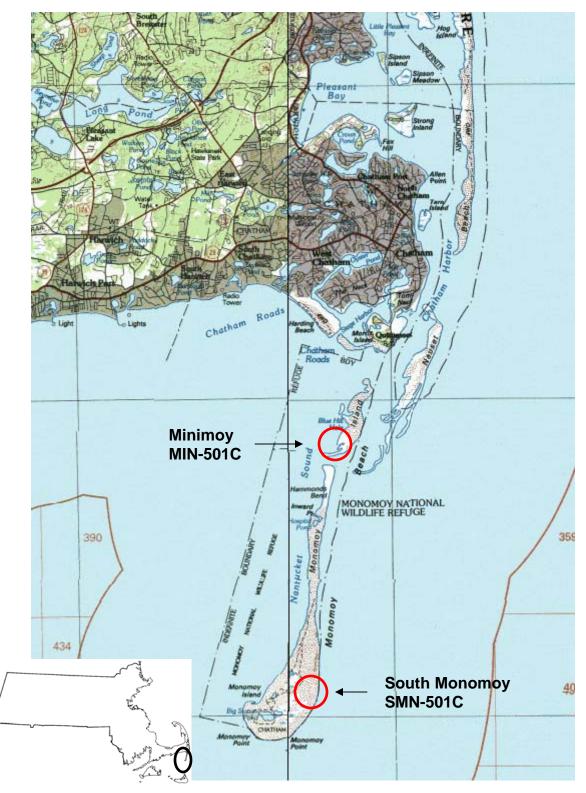


Figure 1. Sample locations – Monomoy NWR

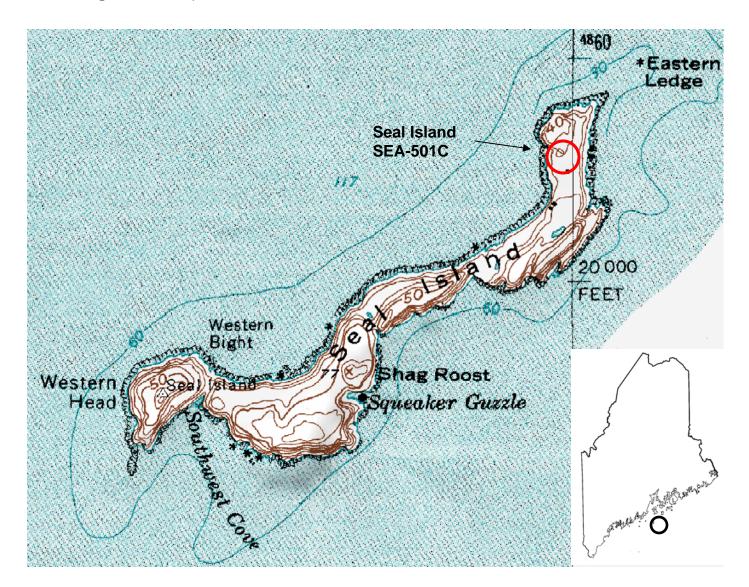


Figure 2. Sample location – Seal Island NWR

5. Analytical Results

Analytical results are presented in Table 2 (Organochlorine Compounds) and Table 3 (Trace Elements). Concentrations are presented $\mu g/g$ (parts-per-million) for organochlorine compounds and trace elements. Results are presented on a fresh wet weight basis to account for moisture loss after egg laying (Stickel *et al.* 1973). Total PCB concentrations are also presented on a lipid weight basis to facilitate comparisons with other regional studies (Table 4).

6. Discussion

Non-viable eggs were collected opportunistically within the tern colonies and the laying sequence of these eggs is not known. Common tern eggs may have higher or lower levels of certain contaminants depending on whether they are the first or last egg laid (Nisbet 1982, Becker 1992). Since only a very small number of eggs was collected for this study, data in this report should be viewed with some caution. Greater sample sizes would be required to adequately assess current contaminant exposure in eggs from the Seal Island and Monomoy tern colonies. Contaminant concentrations in tern egg composite samples from Seal Island NWR and Monomoy NWR were qualitatively compared to suggested biological effect benchmarks or threshold levels described in several studies and to contaminant concentrations reported in other tern egg studies for Massachusetts, Maine, and other states.

Concentrations in this report are presented in $\mu g/g$ wet weight on a fresh weight basis (i.e., corrected for moisture loss). To facilitate comparisons with other studies that reported concentrations on a dry weight basis or in ng/g (i.e., parts-per-billion), values in those studies were converted to wet weight using dry weight divided by three (Burger and Gochfeld 2004) and, if necessary, converted to $\mu g/g$ (1 $\mu g/g = 1,000$ ng/g). It should be noted, however, that the dry weight to wet weight conversion would not account for differences between wet weight and fresh wet weight concentrations. Generally, fresh wet weight concentrations would be slightly lower than wet weight levels.

6.1 Organochlorine compounds. Fifteen of the 26 organochlorine compounds included in the analytical scan were found above detection limits (Table 2). Only two will be discussed. All hexachlorocyclohexane compounds, *alpha* chlordane, *gamma* chlordane, *o*,*p*[']-DDE, *o*,*p*[']-DDT, *p*,*p*[']-DDD, pentachloro-anisole, and toxaphene were below detection limits in all samples. Other organochlorine compounds were detected slightly above detection limits in some or all egg composite samples (max. 0.010 μ g/g), but levels were an order of magnitude or more below suggested embryotoxicity thresholds. Because of their persistence in the environment and biological tissues, and known toxicological significance, Total PCB and DDE are discussed below.

<u>6.1.1 Total Polychlorinated Biphenyls (PCBs)</u> – PCBs were used for decades as a coolant and insulating agent in electrical transformers and capacitors (Eisler 1986). Although PCBs were banned in the United States in 1979, the compound persists in the environment as a legacy contaminant from historic discharges and improper disposal practices. Incineration of PCB-contaminated material has also spread the compound worldwide through atmospheric deposition.

PCBs, particularly PCBs with dioxin-like activity, adversely affect survival, growth, reproduction, metabolism, and accumulation in wildlife (Eisler and Belisle 1996).

Tern egg composite samples had Total PCB concentrations of 1.126 μ g/g (roseate tern, Minimoy Island), 0.671 μ g/g (common tern, South Monomoy), and 0.343 μ g/g (common tern, Seal Island). The common tern egg composite Total PCB level from Seal Island was similar to 50 individual common tern eggs collected from five islands in a broader Gulf of Maine tern contaminant study conducted during the same time period (mean 0.364 ± 0.192 μ g/g, Mierzykowski *et al.* 2008). The Seal Island sample Total PCB concentration appeared lower compared to an earlier study conducted near the Maine border. In 1986, seven common tern eggs from the Great Bay Estuary, NH, had a mean Total PCB level of 0.886 ± 0.259 μ g/g and a range of 0.450 to 1.160 μ g/g (Carr and von Oettingen 1989).

Total PCBs have been measured in tern eggs at Monomoy NWR for several years (Table 4). Seven roseate tern eggs collected in 1981 from Monomoy NWR had a geometric mean Total PCB level of $1.96 \mu g/g$ (range: $1.29 - 5.53 \mu g/g$; Custer *et al.* 1983b). In comparison, the Monomoy roseate tern egg composite sample from 2005 had a Total PCB level of $1.126 \mu g/g$ (Table 2, Table 4). Nisbet and Reynolds (1984) analyzed individual and composites of common tern eggs at Monomoy NWR throughout the 1970s (Table 4). Compared to their study, the Total PCB level in the Monomoy common tern egg composite appears to show a decrease by a factor of 3. As noted earlier, additional samples would need to be analyzed to confirm this apparent decrease. A decrease in Total PCBs at Monomoy NWR would be consistent with findings in nearby Buzzards Bay. Jayaraman *et al.* (2007) reported a 4.5-fold decrease in Total PCBs in Buzzards Bay common tern eggs between 1972 and 2005.

Total PCBs concentrations in eggs between 8 and 25 μ g/g have been associated with decreased hatching success in terns, cormorants, and eagles (Hoffman *et al.* 1996). Total PCB levels in tern composite samples from the two refuges were well below this threshold.

Total PCB concentrations on a lipid weight basis were also calculated for the egg composite samples (Table 4). On a lipid weight basis, Total PCB in the three composite egg samples from the two refuges ranged from 6.86 to 15.64 μ g Total PCB per g Lipid. In a study of feminization in common terns in Buzzards Bay, Hart (1998) suggested that formation of ovotestes in male tern embryos is more likely to occur at a threshold level > 100 μ g Total PCBs/g lipid, but cautioned that more study was needed. The three egg composite samples from the two refuges were also well below this suggested lipid-based threshold.

<u>6.1.2 Dichlorodiphenyldichloroethylene (DDE)</u> – DDE is a breakdown metabolite of the pesticide dichlorodiphenyltrichloroethane (DDT). DDT was banned from use in the United States in 1972 after it was implicated in avian eggshell thinning. Residues of DDT metabolites persist in the environment for decades, however, with the *para*, *para* (*p*,*p*²) isomer of DDE being detected most often in wildlife tissues. Terns are relatively sensitive to DDE and elevated egg levels (> 1.9 µg/g) may affect eggshell and embryo development (Nisbet 2002).

DDE in tern egg composite samples from the two refuges ranged from 0.030 to 0.046 μ g/g

(Table 2). Samples collected over two decades earlier from Monomoy had 5-fold higher DDE levels. Seven roseate tern eggs collected in 1981 from Monomoy NWR had a geometric mean DDE level of 0.16 μ g/g (range: 0.14 – 0.30 μ g/g; Custer *et al.* 1983b). The 2005 Monomoy NWR roseate tern egg composite sample had a DDE level of 0.03 μ g/g. Of the three egg composites, the highest DDE level was found in the sample from Seal Island NWR (0.046 μ g/g). DDE levels in 50 common tern eggs from five other coastal Maine islands ranged from 0.013 to 0.138 μ g/g with a mean of 0.043 ± 0.022 μ g/g (Mierzykowski *et al.* 2008), so the DDE level in the common tern sample from Seal Island is unremarkable. DDE levels in all three composite eggs samples from the two refuges were well below a 1.9 μ g/g hatching failure concentration reported by Nisbet and Reynolds (1984).

6.2 Trace elements. Nine of 19 trace elements in the analytical scan were detected in tern egg composites (Table 3). Aluminum, boron, barium, beryllium, cadmium, chromium, molybdenum, nickel, lead, and vanadium were below detection limits in all samples and will not be discussed.

<u>6.2.1 Arsenic (As)</u> – Arsenic is a metalloid used in the production of pesticides and wood preservatives. Coal-fired power utilities and metal smelters annually release tons of arsenic into the atmosphere (Environment Canada 1993). Arsenic is a teratogen and carcinogen, which bioconcentrates in organisms, but does not biomagnify in food chains (Eisler 1994). In mallard dietary studies, arsenic exposure did not affect hatching success and was not teratogenic, but did delay egg laying, reduce egg weight, and cause eggshell thinning (Stanley *et al.* 1994).

Arsenic levels in tern composite egg samples were 0.06 μ g/g (common tern, Seal Island), 0.08 μ g/g (common tern, South Monomoy) and 0.09 μ g/g (roseate tern, Minimoy Island). The arsenic level at Seal Island was similar to concentrations found in common terns at five other Maine islands (0.07 ± 0.02 μ g/g, range: below detection – 0.11 μ g/g; Mierzykowski *et al.* 2008). In 35 common tern eggs from Barnegat, NJ, Burger (2002) reported an arsenic mean of 0.06 μ g/g (converted to wet weight using dry weight/3) and a maximum concentration of 0.14 μ g/g. In seven common tern eggs from the Great Bay Estuary, NH, mean arsenic was 0.04 ± 0.07 μ g/g and the range was 0.01 to 0.20 μ g/g (Carr and von Oettingen 1989). Arsenic levels in composite egg samples from the two refuges were similar to the means or within the ranges reported in these three studies.

Arsenic concentrations in biota are usually less than 1 μ g/g, with higher concentrations found in marine organisms particularly crustaceans (Eisler 1994). Libby *et al.* (1953) reported that domestic chicken (*Gallus gallus*) egg residues greater than 0.43 μ g As/g (converted to wet weight using dry weight/3) had no effect on hatchability or fertility. All composite egg samples from the two refuges had arsenic levels lower than the avian embryotoxic threshold suggested by Libby *et al.* (1953) and lower than the nominal level suggested by Eisler (1994).

<u>6.2.2 Copper (Cu)</u> – Copper is used in the preservation and coloring of foods, in brass and copper water pipes and domestic utensils, and in fungicides and insecticides (Gross *et al.* 2003). Copper is an essential trace nutrient that is required in relatively high concentrations (Gochfeld and Burger 1987). Copper is not carcinogenic, mutagenic, or teratogenic at environmentally realistic concentration (Eisler 1997).

Copper concentrations in common tern composite egg samples appeared similar at South Monomoy (0.74 µg/g) and Seal Island (0.79 µg/g). A higher copper concentration was found in the roseate tern composite egg sample from Minimoy Island (0.97 µg/g). At other Maine islands, the mean copper concentration in 50 common tern eggs was $0.61 \pm 0.09 \mu g/g$ with a range of 0.44 to 1.01 µg/g (Mierzykowski *et al.* 2008). Two earlier regional studies were located that reported copper concentrations in common tern eggs. Seven common tern eggs from the Great Bay Estuary, NH, had a mean copper concentration of $0.68 \pm 0.06 \mu g/g$ (range: $0.59 - 0.78 \mu g/g$, Carr and von Oettingen 1989). At Great Gull Island in Long Island Sound, NY, Connors *et al.* (1975) reported a mean copper concentration of $1.63 \mu g/g$ (converted to wet weight using dry weight/3) and range of 1.14 to $1.82 \mu g/g$ in nine common tern eggs. Morera *et al.* (1997, citing 3 studies) noted that copper concentrations in eggs of seabirds are usually low, between 0.15 and $1.8 \mu g/g$. Copper levels in the three egg composite samples from the two refuges fall within the concentration range presented by Morera *et al.* (1997). No data are available regarding copper toxicity to avian wildlife (Eisler 1997).

<u>6.2.3 Iron (Fe)</u> – Iron is a common component of rock and soils. It is mined and used in steel production, and also used in pesticides (e.g., iron phosphate). Iron, like copper, is an essential trace nutrient that is required in relatively high concentrations (Gochfeld and Burger 1987). Iron levels in tern composite egg samples from the two refuges were similar – 24, 25, and 26 µg/g. These iron levels appear analogous to results in two other tern studies. Fifty common tern eggs from five Maine islands had a mean iron concentration of $26 \pm 4.1 \mu g/g$ (Mierzykowski *et al.* 2008). Seven common tern eggs from the Great Bay Estuary, NH, had a mean iron level of $24.5 \pm 3.6 \mu g/g$ (range: $19.3 - 29.6 \mu g/g$, Carr and von Oettingen 1989). No biological effect level for iron in bird eggs was found in the literature.

<u>6.2.4 Magnesium (Mg)</u> – Magnesium is an essential element whose deficiency causes neuromuscular irritability, calcification, and cardiac and renal damage (Goyer 1986). It constitutes about 2% of the earth's crust, is a component of seawater, and is widespread in all living cells (Aikawa 1991). Magnesium is used in aluminum alloys (e.g., cans and containers), incendiary flares, electrical conductive material, corrosion protection, and as a reducing agent to obtain other elements (Goyer 1986, Aikawa 1991).

Magnesium level in composite tern egg samples were 84 μ g/g (common tern, South Monomoy), 96 μ g/g (common tern, Seal Island) and 112 μ g/g (roseate tern, Minimoy Island). In a study of five Maine islands, magnesium levels in 50 common tern eggs was 92.6 ± 9.24 μ g/g with a range of 66.8 to 109.1 μ g/g (Mierzykowski *et al.* 2008). Magnesium in the roseate tern composite sample from Monomoy NWR exceed this range, but the significance of this concentration is not known. An adverse biological effect level for magnesium in avian eggs was not found in the literature.

<u>6.2.5 Manganese (Mn)</u> – Manganese is a component of the earth's crust, an essential trace element for animals, and is used in iron alloys, nonferrous alloys, and dry cells (Moore 1991). Airborne emissions from vehicle exhausts are a potential source of manganese. Manganese, as methylcyclopentadienyl manganese tricarbonyl, has been used as an additive in

gasoline and is currently under review by EPA (2008). In herring gull chicks (*Larus argentatus*), manganese exposure reduced growth, disrupted behavior, and thermoregulation (Burger and Gochfeld 1995).

Manganese levels in egg composites were $0.32 \ \mu g/g$ (common tern, Seal Island), $0.40 \ \mu g/g$ (common tern, South Monomoy), and $0.46 \ \mu g/g$ (roseate tern, Minimoy Island). Burger (2002) examined manganese in 35 common tern eggs from Barnegat Bay, NJ, and reported a mean level of $0.76 \ \mu g/g$ (converted to wet weight using dry weight/3) and a maximum of $1.38 \ \mu g/g$. In 50 common tern eggs from five islands in Maine, the mean manganese level was $0.50 \pm 0.16 \ \mu g/g$ with a range of 0.23 to $1.04 \ \mu g/g$ (Mierzykowski *et al.* 2008). An adverse effect level for manganese in avian eggs could not be located in the literature. Manganese levels in three egg composite samples from the two refuges appeared lower than the mean reported by Burger (2002) and similar to the mean reported by Mierzykowski *et al.* (2008).

<u>6.2.6 Mercury (Hg)</u> – Mercury is a global pollutant with biological mercury hotspots existing in the northeastern United States (Evers *et al.* 2007). Sources of mercury contamination include emissions from coal-fired energy facilities, incinerators, mining activities, operation of chloralkali plants, and disposal of mercury-contaminated products such as batteries and fluorescent lamps (Eisler 1987). Mercury is a mutagen, teratogen, and carcinogen which bioconcentrates in organisms and biomagnifies through food chains (Eisler 1987). The most toxic form or mercury is the organic form, methylmercury. Methylmercury may account for nearly all of the total mercury in bird eggs (Schwarzbach *et al.* 2006).

Mercury was detected at 0.14 µg/g and 0.11 µg/g in roseate tern and common tern egg samples from Monomoy NWR, respectively. At Seal Island NWR, the common tern egg composite sample had a mercury concentration of 0.09 µg/g. Mean mercury in 50 common tern eggs from five islands in Maine was 0.11 ± 0.03 µg/g with a range of 0.06 to 0.20 µg/g (Mierzykowski *et al.* 2008). In 35 common tern eggs from Barnegat Bay, NJ, mean mercury was 0.41 ± 0.05 µg/g with a range of 0.10 to 1.21 µg/g (converted to wet weight using dry weight/3; Burger 2002). Mean mercury in seven common tern eggs from the Great Bay Estuary, NH, was 0.19 ± 0.09 µg/g (range: 0.10 - 0.37 µg/g, Carr and von Oettingen 1989). In nine common tern eggs from Great Gull Island in Long Island Sound, NY, Connors *et al.* (1975) reported a mean mercury level of 0.09 µg/g and a range of 0.02 to 0.27 µg/g.

Several mercury concentrations or ranges for effects in avian eggs have been suggested. An often used reproductive effect endpoint for mercury in bird eggs is 0.80 µg/g (Heinz 1979, Henny *et al.* 2002), while other investigators and ecological risk assessors suggest 0.50 µg/g as an ecological effect screening benchmark value (Eisler 1986, RAIS 2006). Scheuhammer *et al.* (2007) suggested an egg-Hg concentration > 1 µg/g as associated with impaired hatchability and embryonic mortality in a number of bird species. Thompson (1996) summarized that mercury concentrations in eggs of 0.5 to 2.0 µg/g are sufficient to reduce egg viability, hatchability and embryo survival in birds. Elevated mercury exposure in fish-eating birds has been documented in Maine (bald eagle, Mierzykowski *et al.* 2006; common loon, Evers *et al.* 2003). However, among seabird species in the Gulf of Maine, common terns do not appear to have highly elevated mercury levels (Mierzykowski *et al.* 2005).

Mercury concentrations in tern egg composite samples from Monomoy and Seal Island NWRs were below suggested reproductive effect threshold values and within ranges reported in other studies.

<u>6.2.7 Selenium (Se)</u> – Selenium is a beneficial or essential element for some biota at trace amounts to parts-per-billion concentrations, but toxic at elevated concentrations (Eisler 1985). Selenium is present in rocks and soils. However, coal and oil combustion, nonferrous metal production, iron manufacturing, municipal and sewage refuse incineration, and production of phosphate fertilizers introduce greater amounts of selenium into the environment than natural sources (Ohlendorf 2003). Background selenium levels in eggs of freshwater and terrestrial bird species are < 1 µg/g (typically 0.5 to 0.8 µg/g), and maximum levels are < 1.67 µg/g, but levels may be more variable and higher in marine species (Ohlendorf 2003; converted to wet weight using dry weight/3).

Selenium levels in the three egg composites from the two refuges were similar: 0.59 μ g/g (roseate tern, Minimoy Island), 0.61 μ g/g (common tern, South Monomoy), and 0.67 μ g/g (common tern, Seal Island). In 50 common tern eggs from five Maine islands, the mean selenium level was 0.60 ± 0.09 μ g/g with a range of 0.37 to 0.83 μ g/g (Mierzykowski *et al.* 2008). In Barnegat Bay, NJ, common tern eggs, Burger (2002) reported a mean selenium concentration of 0.68 μ g/g (converted to wet weight using dry weight/3) and a maximum of 1.10 μ g/g. Carr and von Oettingen (1989) reported a mean selenium concentration of 0.50 ± 0.07 μ g/g and a range of 0.38 to 0.58 μ g/g in seven common tern eggs from the Great Bay Estuary, NH. Selenium levels in egg composites from the two refuges were similar to other tern studies and background levels (Ohlendorf 2003).

Heinz (1996) suggested a 3 μ g Se/g threshold for reproductive impairment in bird eggs. All three tern egg composite samples from the two refuges had selenium levels well below this reproductive impairment threshold.

<u>6.2.8 Strontium (Sr)</u> – Strontium is an element of seawater (Bowen 1956) and essential in marine gastropod shell development (Bidwell *et al.* 1986). Strontium is used in fireworks, red signal flares, and on tracer bullets (Merck 1983).

Strontium levels in eggs appeared higher at Seal Island (common tern, 2.09 μ g/g) than at Monomoy (common tern, 1.50 μ g/g; roseate tern, 0.88 μ g/g), but many more samples would be needed to confirm a significant statistical difference. At five other Gulf of Maine islands, the mean strontium concentration in 50 common tern eggs was $1.20 \pm 0.51 \mu$ g/g with a range of 0.36 to 3.06 μ g/g (Mierzykowski *et al.* 2008).

A toxic effect threshold level for stable strontium in bird eggs was not found in the literature. In black-crowned night heron embryos, a strontium concentration of $3.76 \ \mu g/g$ (converted to wet weight using dry weight/3) was associated with increased oxidative stress using hepatic oxidized glutathione (Rattner *et al.* 2000). Mora (2003) considered strontium levels of 75 $\ \mu g/g$ (converted to wet weight using dry weight/3) and 63 $\ \mu g/g$ as elevated in yellow warbler and song sparrow

eggs, respectively. Compared to several other bird species examined by Mora (2003), strontium levels in eggs of yellow warblers and song sparrows were highest. Although the strontium level in the Seal Island composite egg sample appeared higher than the two samples from Monomoy, it was within the range found by Mierzykowski *et al.* (2008) and lower than the effect level reported by Rattner *et al.* (2000).

<u>6.2.9 Zinc (Zn)</u> – Zinc is used in galvanized metal alloys, paints, wood preservatives, fertilizers, and rodenticides (Opresko 1992, Eisler 1993). Zinc, like copper and iron, is an essential trace nutrient that is required in relatively high concentrations (> 10 μ g/g; Gochfeld and Burger 1987, Burger and Gochfeld 1988). Zinc is a cofactor of > 200 enzymes and has an important function in the antioxidant defense system that ameliorates the effects of environmental stress (Sahin and Kucuk 2003).

Zinc levels in tern egg composite samples were 14.7 μ g/g (roseate tern, Minimoy Island), 11.1 μ g/g (common tern, South Monomoy), and 14.0 μ g/g (common tern, Seal Island). In the Maine common tern study by Mierzykowski *et al.* (2008), the mean zinc level was 13.4 ± 2.14 μ g/g and the range was 9.1 to 18.3 μ g/g. Lower and higher zinc levels were reported in two earlier common tern studies. In 1986, seven common tern eggs from Great Bay Estuary, NH, had a mean zinc level of 10.3 ± 1.0 μ g/g and a range of 8.3 to 11.4 μ g/g (Carr and von Oettingen 1989). Nine common tern eggs from Long Island Sound, NY, in the early 1970s had a mean zinc level of 23.5 μ g/g (converted to wet weight using dry weight/3) and a range of 17.9 to 29.8 μ g/g (Connors *et al.* 1975). The zinc levels found at the two refuges are similar to levels found in the Maine study. A toxic effect threshold level for Zn in bird eggs was not found in the literature.

Location Sample No. Species	Minimoy Island, MA MIN-501C Roseate Tern	South Monomoy, MA SMN-501C Common Tern	Seal Island, ME SEA-501C Common Tern	
Polychlorinated Bipheny	1			
PCB-TOTAL	1.126	0.671	0.343	
Hexachlorocyclohexane	6			
alpha BHC	BDL	BDL	BDL	
beta BHC	BDL	BDL	BDL	
delta BHC	BDL	BDL	BDL	
gamma BHC	BDL	BDL	BDL	
Chlordane Compounds				
heptachlor	0.001	BDL	BDL	
heptachlor epoxide	0.002	0.002	0.002	
oxychlordane	0.002	0.003	0.002	
alpha chlordane	BDL	BDL	BDL	
gamma chlordane	BDL	BDL	BDL	
cis-nonachlor	BDL	0.001	BDL	
trans-nonachlor	0.006	0.008	0.001	
DDT Metabolites				
o,p'-DDD	0.009	0.010	0.002	
o,p'-DDE	BDL	BDL	BDL	
o,p'-DDT	BDL	BDL	BDL	
p,p'-DDD	BDL	BDL	BDL	
p,p'-DDE	0.031	0.030	0.046	
p,p'-DDT	0.007	0.006	BDL	
Other Organochlorine Co	ompounds			
aldrin	0.001	BDL	BDL	
endrin	0.003	0.004	BDL	
dieldrin	0.001	0.001	0.003	
HCB (hexachlorobenzene)	0.003	0.003	0.005	
endosulfan II	0.001	BDL	BDL	
mirex	0.005	0.002	0.007	
pentachloro-anisole	BDL	BDL	BDL	
toxaphene	BDL	BDL	BDL	

Table 2. Organochlorine compounds in tern egg composites, $\mu g/g$ fresh wet weight

Single 3-egg composite from each location $\mu g/g = parts-per-million$, fresh wet weight (i.e., corrected for moisture loss)

BDL = below detection limit

Location Sample No. Species		Minimoy Island, MA MIN-501C Roseate Tern	South Monomoy, MA SMN-501C Common Tern	Seal Island, ME SEA-501C Common Tern
Element				
Aluminum	Al	BDL	BDL	BDL
Arsenic	As	0.09	0.08	0.06
Boron	В	BDL	BDL	BDL
Barium	Ba	BDL	BDL	BDL
Beryllium	Be	BDL	BDL	BDL
Cadmium	Cd	BDL	BDL	BDL
Chromium	Cr	BDL	BDL	BDL
Copper	Cu	0.97	0.74	0.79
Iron	Fe	25	24	26
Mercury	Hg	0.14	0.11	0.09
Magnesium	Mg	112	84	96
Manganese	Mn	0.46	0.40	0.32
Molybdenum	Мо	BDL	BDL	BDL
Nickel	Ni	BDL	BDL	BDL
Lead	Pb	BDL	BDL	BDL
Selenium	Se	0.59	0.61	0.67
Strontium	Sr	0.88	1.50	2.09
Vanadium	V	BDL	BDL	BDL
Zinc	Zn	14.7	11.1	14.0

Table 3. Trace elements in tern egg composite samples, μ g/g fww.

Each sample is a 3-egg composite.

 μ g/g = parts-per-million, fww = fresh wet weight (adjusted for moisture loss) BDL = below detection limit

Table 4. Total PCB results compared to other tern studies in the region

Locations	Species	Year of Collection	n	Total PCB μg/g fww	µg Total PCB per g Lipid	Data Source
Maine						
Seal Island	Common Tern	2005	One 3-egg composite	0.34	6.86	This study
5 islands (Stratton, Jenny, Po	Common Tern ond, Eastern Egg, Petit Ma	2004 + 2005 nan)	50 individual eggs	0.36 ± 0.19	5.99	Mierzykowski <i>et al</i> . 2008
3 islands (Stratton, Pond, Pe	Common Tern tit Manan)	2003	Three multi-egg composites	0.49	n.r.	Mierzykowski <i>et al</i> . 2004
Massachusetts South Monomoy	Common Tern	2005	One 3-egg composite	0.67	10.82	This study
		2000				The study
Minimoy Island	Roseate Tern	2005	One 3-egg composite	1.13	15.64	This study
Monomoy Island	Roseate Tern	1981	Seven individual eggs	1.96	n.r.	Custer et al. 1983b
Monomoy Island	Common Tern	1978	One 12-egg composite	2.13	n.r.	
Monomoy Island	Common Tern	1977	Seven individual eggs	2.77 ± 0.60	n.r.	
Monomoy Island	Common Tern	1977	Six individual eggs	3.14 ± 0.36	n.r.	Nisbet & Reynolds 1984
Monomoy Island	Common Tern	1976	Eight individual eggs	8.89 ± 15.0	n.r.	
Monomoy Island	Common Tern	1975	One 5-egg composite	4.90	50.00	
Monomoy Island	Common Tern	1973	Five individual eggs	3.69 ± 0.83	n.r.	

 μ g/g = parts-per-million, fww = fresh wet weight (i.e., corrected for moisture loss) n.r. = not reported

7. Summary and Management Recommendations

Although only a few eggs were analyzed in this study, contaminant levels in tern egg composites appear similar to results from other studies.

At Monomoy NWR, Total PCB concentrations in common tern and roseate tern composite egg samples were 0.671 and 1.126 μ g/g fresh wet weight, respectively. At Seal Island NWR, Total PCB in the common tern composite egg sample was 0.343 μ g/g. DDE, a metabolite of the pesticide DDT, was found at 0.031 and 0.030 μ g/g in common and roseate tern samples from Monomoy NWR, respectively, and at 0.046 μ g/g in the common tern sample from Seal Island NWR. Concentrations of Total PCB and DDE were below suggested toxic effect threshold levels. Twenty-four other organochlorine compounds were below detection limits or in the low parts-per-billion (ng/g) range.

Mercury was detected at 0.14 μ g/g and 0.11 μ g/g in roseate tern and common tern composite egg samples from Monomoy NWR, respectively. At Seal Island NWR, the common tern egg composite sample had a mercury concentration of 0.09 μ g/g. Concentrations in all three samples were well below suggested reproductive effect thresholds for mercury (0.05 - 0.80 μ g/g). Of the eighteen other trace elements in the analytical scan, ten were below detection in all samples. Although detected in all samples, ranges of arsenic (0.06 - 0.09 μ g/g), copper (0.74 - 0.97 μ g/g), iron (24 - 26 μ g/g), magnesium (84 - 112 μ g/g), manganese (0.32 - 0.46 μ g/g), selenium (0.59 - 0.67 μ g/g), strontium (0.88 - 2.09 μ g/g), and zinc (11.1 - 14.7 μ g/g) do not appear elevated compared to suggested biological effect thresholds or other studies.

Elevated levels of organochlorine and trace element contaminants were not found in tern egg samples from the study sites, however, periodic (e.g., 5-year) monitoring is recommended to track temporal changes in contaminant concentrations at these two refuges. While Total PCBs and DDE have exhibited declines in tern eggs since the 1970s (Nisbet 2002), levels of other contaminants such as polybrominated diphenyl ethers (PBDEs) have been increasing in terns (Jayaraman *et al.* 2007) and other bird species (Elliott *et al.* 2005). Future analyses of tern eggs should include determinations of PBDEs and newly emerging compounds such as perfluorooctane sulfonate.

Note: The precise cause of behavioral effects and death among tern fledglings could not be determined by the NWHC. At Monomoy NWR, salmonella (*Salmonella typhimurium*) was detected in five common tern fledglings. Abnormalities in the organs of the immune system were identified. At Seal Island NWR, salmonella was not found in single Arctic tern and common tern carcass samples. However, similar to the birds at Monomoy NWR, Seal Island tern carcasses exhibited a marked weakening of the immune system.

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