Journal of Environmental Monitoring

Cite this: J. Environ. Monit., 2011, 13, 699

www.rsc.org/jem

PAPER

Geographic differences in organic contaminants and stable isotopes $(\delta^{13}C, \delta^{15}N)$ in thick-billed murre (*Uria lomvia*) eggs from Alaska[†]

Stacy S. Vander Pol,^{*a} Keith A. Hobson,^b Paul R. Becker,^a Rusty D. Day,^a Michael B. Ellisor,^a Rebecca S. Pugh^a and David G. Roseneau^c

Received 19th July 2010, Accepted 1st December 2010 DOI: 10.1039/c0em00347f

The contents from thick-billed murre (*Uria lomvia*) eggs collected at four Alaskan colonies in 2002 were analyzed for organic contaminants and carbon (δ^{13} C) and nitrogen (δ^{15} N) stable isotopes. Contaminant concentrations in the eggs varied from below detection limits to 230 ng g⁻¹ wet mass for 4,4'-DDE in one egg from St Lazaria Island in the Gulf of Alaska. Eggs from this colony generally contained higher levels of contaminants and exhibited significantly different patterns compared to eggs from the Bering and Chukchi seas. Stable isotope values also varied geographically; however, these differences appeared to be related to differences in C and N baselines in the food webs instead of differences in prey. Contaminant and stable isotope correlations were inconclusive, suggesting that better information on regional food web differences and differential offloading of contaminants and stable isotopes to the eggs must be obtained before these kinds of data can be fully incorporated into seabird egg contaminant monitoring programs.

Introduction

Murre (*Uria* spp.) eggs are good tools for monitoring contaminants for several reasons. In contrast to many species of birds, murres stay at northern latitudes year-round, and Alaskan birds winter in the Bering Sea and Gulf of Alaska.^{1–3} As a result, murres acquire contaminants from relatively discrete regions and, as piscivores, they feed near the top of the food chain and accumulate these substances at levels that can be easily

† Electronic supplementary information (ESI) available: Individual thick-billed murre egg results. See DOI: 10.1039/coemoo347f

measured. Murres lay single eggs, which avoids the potential problem posed by laying order on variability in contaminant loads,⁴ and the eggs are large enough (about 100-120 g or 12% of body weight) to provide sufficient amounts of material for both real-time and retrospective analyses and long-term specimen banking.5 Contaminant levels in the eggs also reflect the females' diets at the time of laying,⁶ and because murres arrive on their breeding grounds up to 4-6 weeks or more before laying begins,^{5,7-9} contaminants in their eggs reflect what is present in these areas. Furthermore, because murres are abundant and approximately 80% of the pairs that lose eggs early in the nesting season relay them within 14-15 days,1,5,10 collecting small numbers of eggs for contaminant monitoring programs does not detrimentally affect nesting populations. This study is part of the Seabird Tissue Archival and Monitoring Project (STAMP), a multi-agency, decadal-long program initiated in 1999 that is designed to collect and bank seabird tissues that can be used for both real-time and retrospective analyses. Recent work found that concentrations of organic contaminants in common murre

Environmental impact

This work presents the analyses of organic contaminants in an internationally recognized biomonitoring material, thick-billed murre (*Uria lomvia*) eggs, and examines correlations with egg stable-carbon and nitrogen isotope values that act as proxies for source of feeding and trophic level of laying birds. This combined isotope and contaminants approach over a large sampling region provided a means of controlling for dietary variations and baseline isotopic differences in food webs. Further research is now needed on metabolic pathways linking contaminants in diets and endogenous stores to seabird eggs. Monitoring programs should routinely analyze both contaminant and isotopic data in biomonitors like seabird eggs.

^aNational Institute of Standards and Technology, Analytical Chemistry Division, Hollings Marine Laboratory, 331 Fort Johnson Road, Charleston, South Carolina, 29412, USA. E-mail: stacy.vanderpol@nist. gov; Fax: +1-843-762-8742; Tel: +1-843-762-8994

^bEnvironment Canada, 11 Innovation Boulevard, Saskatoon, Saskatchewan, S7N 3H5, Canada

^cUS Fish and Wildlife Service, 95 Sterling Highway, Suite 1, Homer, Alaska, 99603, USA

(*Uria aalge*) eggs not only differed throughout Alaska, but also from levels in thick-billed murre (*U. lomvia*) eggs obtained at the same colonies.¹¹ To determine if thick-billed murre eggs collected in 2002 exhibited similar concentration and spatial patterns, organic contaminants and stable-carbon and nitrogen isotopes were measured in these specimens. Previously, δ^{15} N measurements have been used to help describe trophic levels in seabirds, and δ^{13} C levels have been used to differentiate between nearshore/benthic and offshore/pelagic diets.¹² Isotope assays have also proven useful in interpreting relationships between contaminant levels and feeding behavior.^{13,14}

This paper reports results of the organic contaminant analyses for polychlorinated biphenyls (PCBs), and organochlorine pesticides in the 2002 thick-billed murre eggs and uses the δ^{13} C and δ^{15} N data to describe geographical differences in contaminant loads.

Experimental

Sample collection and preparation

Thick-billed murre eggs were collected from nesting colonies at St Lazaria Island in the southeastern Gulf of Alaska, St George Island in the southeastern Bering Sea, St Lawrence Island in the northern Bering Sea, and Cape Lisburne in the eastern Chukchi Sea during 20 June to 7 July 2002 (Fig. 1). Methods developed by York *et al.*¹⁵ were used to collect and process the samples. After the eggs were weighed and measured at the US Geological Survey (USGS) Alaska Science Center in Anchorage, Alaska, the contents were removed from the shells under a positive-pressure laminar flow hood, sealed in Teflon bags, frozen, and shipped to the National Institute of Standards and Technology (NIST) Marine Environmental Specimen Bank (Marine ESB) in Charleston, South Carolina in liquid nitrogen (LN₂) vapor dry shippers for cryohomogenization, analyses, and long-term storage in LN₂ vapor freezers at -150 °C.¹¹

Organic contaminant analysis

Six eggs were randomly chosen from each colony and homogenized at the Marine ESB. Approximately 3 g of material from

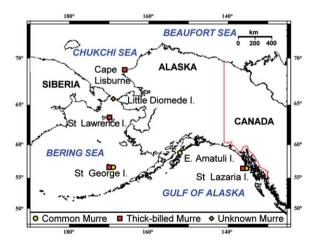


Fig. 1 Locations of the nesting colonies where murre (*Uria* spp.) eggs were collected in 1999 and 2002.

each of these samples was analyzed for organic contaminants using the procedures reported by Vander Pol et al.¹⁶ Briefly, the aliquots were extracted by pressurized fluid extraction (PFE), cleaned up using size-exclusion chromatography (SEC) and solid phase extraction (SPE), and analyzed by gas chromatography/ mass spectrometry (GC/MS) in two injections. The first injection used PTV onto a 30 m \times 0.18 mm \times 0.18 μm i.d. DB-XLB column (J&W Scientific, Folsom, California) with a 5 m \times 0.25 mm retention gap added to the beginning of the column and the MS was in electron impact (EI) mode. The oven was initially set at 80 °C with a 1.5 min hold, then ramped up to 170 °C at 25 °C min⁻¹ with a 0 min hold, then ramped up again to 270 °C at 2.0 °C min⁻¹ with a 0 min hold, and then ramped up to a final setting of 325 °C at 25 °C min⁻¹ with a 10 min hold (67.3 min total run time). The second injection used the same GC injector and column with the MS in negative ion (NCI) mode. All other conditions were as described by Vander Pol et al.¹⁶ Aliquots of SRM 1946 Lake Superior Fish Tissue and Murre Egg Control Material,¹⁷ a procedural blank, and six calibration solutions were prepared and analyzed along with the egg samples for quality assurance and control.

Stable isotope analysis

Five gram aliquots from the samples were sent to the Environment Canada in Saskatoon, Saskatchewan, in LN_2 vapor dry shippers for stable-carbon and nitrogen isotope analyses using the procedures described by Hobson *et al.*¹⁸ Briefly, the aliquots were freeze-dried and the lipids were extracted using a 2:1 chloroform : methanol soak and rinse. The resulting extracts were dried under a fume hood for 24 h before they were powdered and subsampled for the analytical work.

Stable-carbon and nitrogen isotope ratios were obtained by loading approximately 1 mg of the powdered subsamples into tin cups and combusting them at 1200 °C using continuous-flow isotope ratio mass spectrometry (CFIRMS) involving a Europa 20:20 IRMS interfaced with a Robo Prep combustion system. Stable isotope ratios were expressed in delta (δ) notation relative to the Vienna Pee Dee Belemnite (VPDB) or AIR standards for carbon and nitrogen, respectively.¹² Using within-run replicate measurements on an in-house albumen standard, the analytical uncertainty (SD) was estimated to be $\pm 0.3\%$ for δ^{15} N and $\pm 0.1\%$ for δ^{13} C.

Statistics

To meet assumptions of normality, Multivariate Analysis of Variances (MANOVAs) were conducted on a lipid mass basis for all compounds that did not have values below detection limits (4,4'-DDE, α -, β -, and γ -hexachlorocyclohexane [HCH], *cis*-chlordane, oxychlordane, heptachlor epoxide, hexachlorobenzene [HCB], pentachlorobenzene, octachlorostyrene [OCS], and PCB IUPAC congeners 28 + 31, 56, 63, 66, 74, 99, 105, 107, 118 + 106, 138, 146, 153, 156, 158, 163, 170, 172, 178, 180 + 193, 183, 187, 199, and 209). PCB congeners were summed because of limited degrees of freedom. If results were statistically different (*i.e. P* < 0.05), individual ANOVAs and Tukey *post hoc* tests were used to determine which compounds were different. Principal components analysis was conducted on the percentage

of total of these compounds to help visualize patterns. Major pesticides and Σ PCBs were correlated on a lipid mass basis to δ^{13} C and δ^{15} N values. To examine potential baseline trophic differences among water bodies, literature values for copepod and fish δ^{15} N values as reviewed by Point *et al.*¹⁹ were used to convert the δ^{15} N values of the thick-billed murre eggs to trophic levels. These trophic levels were then correlated to the contaminants as well. Adjustments were not made for multiplecomparisons, as recommended by Rothman.²⁰ All statistical tests were conducted using commercially available software (SAS Institute, JMP 7.0.2, Cary, North Carolina).

Results and discussion

Contaminant levels

Contaminant values in the reference materials fell within previously reported ranges indicating that the analyses were accurate.^{17,21} Percent lipids in the thick-billed murre egg homogenates ranged from 9.1% to 13.2% and did not vary significantly among colonies (Table 1 and ESI†); however, statistics were applied on a lipid–mass basis to meet assumptions of normality. Contaminant levels varied from below detection limits (0.1 ng g⁻¹ wet

mass) to 230 ng g⁻¹ wet mass for 4,4'-DDE in one of the St Lazaria Island eggs (see ESI[†]). Contaminants were lower than those found in the common murre eggs obtained at the same colonies in 1999, thick-billed murres collected in 2000 (Fig. 2), and gull eggs obtained in 2005.^{11,16} PCBs and DDTs tended to be higher in the Gulf of Alaska, and HCB tended to be higher in the Bering Sea, while HCHs and chlordanes were similar among regions (Table 1 and Fig. 2). These patterns were similar to the patterns found in the 1999 common murre eggs (Fig. 2) indicating a temporal consistency that is probably related to the regional food webs and atmospheric and oceanic transport of these contaminants. In fact, similar contaminant patterns have been found in walleye pollock (Theragra chalcogramma), a known prey item for murres, in the Gulf of Alaska and Bering Sea.²² Also, slightly higher levels of PCBs and DDTs have been detected in the air and water of the Gulf of Alaska, compared to the Bering Sea.23

Geographical comparisons

PCB patterns among thick-billed murre colonies exhibited the same pattern found in the common murre eggs collected in 1999, with the highest proportion of the more chlorinated congeners

Table 1 Mass fractions (means \pm standard deviations with ranges shown in parentheses in ng g⁻¹ lipid mass) of major contaminants used in the MANOVA for thick-billed murre (*U. lomvia*) eggs collected from Alaska in 2002 (n = 6 for each colony). Lipid, stable isotopes, and trophic levels were not included in the MANOVA

Compound	Gulf of Alaska St Lazaria I		S. Bering Sea St George I		N. Bering Sea St Lawrence I		Chukchi Sea Cape Lisburne		F Ratio Probability
Lipid (%)	10.4 ± 0.70 (9.69 - 11.6)		11.4 ± 1.4 (9.89 - 13.2)		10.4 ± 1.0 (9.07 - 12.2)		10.8 ± 0.81 (9.51 - 11.8)		1.31 0.299
δ ¹³ C (‰)	(-18.5 ± 0.73) (-19.217.4)	А	-20.9 ± 0.44 (-21.620.3)	В	(-18.7 ± 0.88) (-19.517.0)	А	-20.1 ± 0.93 (-21.419.1)	В	13.6 < 0.0001 ^a
δ ¹⁵ N (‰)	(-15.217.4) 14.3 ± 0.62 (13.4 - 15.2)	В	(-21.020.5) 12.8 ± 2.8 (11.5 - 18.5)	В	(-19.517.6) 15.2 ± 0.66 (14.4 - 16.2)	AB	(-21.415.1) 16.8 ± 0.94 (15.5 - 18.2)	А	7.17 0.0019 ^a
Trophic Level (copepod)	(13.4 - 13.2) 3.72 ± 0.16 (3.50 - 3.97)		(11.3 - 18.5) 3.36 ± 0.74 (3.01 - 4.87)		(14.4 - 10.2) 3.21 ± 0.17 (3.00 - 3.48)		(15.3 - 18.2) 3.63 ± 0.25 (3.28 - 4.00)		2.07. 0.137
Trophic Level (fish)	(3.50 ± 3.97) 3.67 ± 0.16 (3.45 - 3.92)		(3.01 - 4.37) 3.23 ± 0.74 (2.88 - 4.74)		(3.00 - 3.48) 3.44 ± 0.17 (3.24 - 3.71)		(3.28 - 4.00) 3.61 ± 0.25 (3.28 - 4.00)		1.42 0.267
∑PCBs	(5.43 - 5.92) 1600 ± 410 (858 - 2080)	А	(2.88 - 4.74) 466 ± 220 (234 - 856)	В	(5.24 - 5.71) 618 ± 140 (496 - 861)	В	(5.23 - 4.00) 562 ± 65 (481 - 639)	В	27.8 < 0.0001 ^a
4,4'-DDE	1790 ± 310	А	(234 - 830) 628 ± 180 (420 - 913)	В	523 ± 180	В	457 ± 95	В	<0.0001 55.7 <0.0001 ^a
НСВ	(1290 - 2130) 270 ± 30 (228 - 202)	В	296 ± 140^{-1}	В	(317 - 725) 410 ± 130 (205 - 527)	В	(352 - 620) 646 ± 200 (261 - 865)	А	9.27
Pentachlorobenzene	(228 - 302) 18.7 ± 3.4	В	(143 - 504) 19.3 ± 11 (2.55 - 27.0)	В	(205 - 537) 32.2 ± 12	AB	(361 - 865) 46.4 ± 20	А	0.0005 ^a 6.05
Octachlorosytrene	(14.9 - 23.5) 9.65 ± 3.4	В	(9.55 - 37.0) 9.27 ± 3.0	В	(15.5 - 48.5) 12.3 ± 2.9	В	(17.8 - 72.6) 18.2 ± 3.2	А	0.0042 ^a 10.5
Mirex	(5.45 - 15.2) 20.1 ± 3.9	А	(6.89 - 15.1) 10.9 ± 3.2	В	(9.33 - 16.9) 12.6 ± 4.5	В	(14.1 - 21.7) 17.4 ± 5.7	А	0.0002 ^{<i>a</i>} 5.60
Oxychlordane	(13.6 - 24.9) 58.3 \pm 22		$\begin{array}{c} (8.12 - 15.6) \\ 38.2 \pm 11 \\ \end{array}$		(8.42 - 19.9) 43.8 ± 9.8		(9.85 - 22.1) 55.3 ± 9.2		0.0059 ^a 2.79
cis-Chlordane	(26.8 - 81.2) 2.82 ± 0.86		(30.8 - 58.8) 3.65 ± 1.4		(34.3 - 56.7) 2.84 ± 0.81		$\begin{array}{c} (43.9-68.3) \\ 2.74\pm0.65 \\ \end{array}$		0.067 1.19
Heptachlor epoxide	(1.58 - 3.82) 32.0 ± 21		(2.10 - 5.86) 15.3 ± 8.5		(1.56 - 3.86) 20.6 ± 5.8		(2.13 - 3.80) 25.8 ± 8.9		0.339 1.97
α-НСН	(11.1 - 71.1) 35.0 ± 14		(10.3 - 32.4) 29.4 ± 15		(12.5 - 27.7) 21.0 ± 8.4		(17.8 - 41.9) 27.4 ± 13		0.151 1.20
β-НСН	(19.4 - 60.4) 218 ± 85		(10.9 - 54.1) 142 ± 93		(10.2 - 29.8) 187 ± 61		(12.3 - 47.0) 197 ± 89		0.334 0.896
ү-НСН	(121 - 342) 5.78 \pm 2.6 (3.70 - 11.1)		(78.6 - 323) 4.67 ± 2.2 (1.62 - 7.19)		(112 - 260) 3.35 ± 1.2 (1.73 - 4.78)		(110 - 337) 3.79 ± 1.7 (1.66 - 5.81)		0.460 1.69 0.201

^{*a*} ANOVAs were significantly different (P < 0.05). Colonies that do not share a letter were significantly different from each other based on Tukey–Kramer *post hoc* tests.

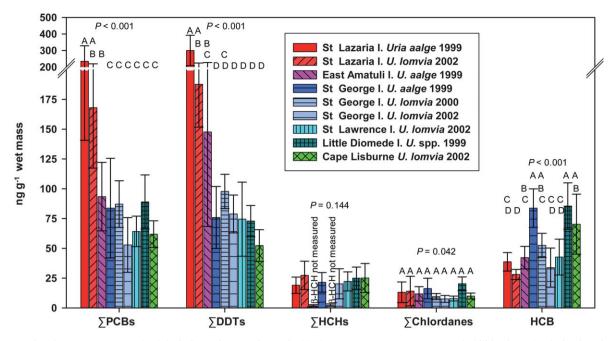


Fig. 2 Mass fractions (means \pm standard deviation) of contaminants in Alaskan murre (*Uria* spp.) eggs. Probabilities from Analysis of Variances and Tukey–Kramer *post hoc* tests conducted on lipid mass basis to meet assumptions of normality are also shown. Colonies that do not share a letter were significantly different (P < 0.05) from each other.

occurring at St. Lazaria Island (see Fig. 3 and Vander Pol *et al.*¹¹). Fractionation of the more heavily chlorinated PCB congeners is expected to occur more frequently at lower latitudes, as indicated from recent modeling of physical and chemical properties needed to transport these contaminants;²⁴ however, there appears to also be a regional differentiation of the PCB congeners between the Bering Sea and the Gulf of Alaska. This may possibly be explained by the differences in precipitation among the sites as higher chlorinated PCBs have been shown to be preferentially scavenged by rain.²⁵ The southeastern Gulf of Alaska region receives substantially more precipitation than the rest of Alaska,^{26, 27} possibly explaining the higher proportion of more chlorinated PCBs in eggs from St. Lazaria Island.

Colonies differed significantly in egg contaminant profiles (Wilk's $\lambda = 0.0011$, approximate $F_{42,21.5} = 4.59$, P = 0.0002). The highest levels of Σ PCBs and 4,4'-DDE were found at St Lazaria Island (individual PCB congeners exhibited the same pattern, with the exception of 28 + 31, 63, and 99), while the highest concentrations of HCB, pentachlorobenzene, and octachlorostyrene were detected at Cape Lisburne (Table 1). Mirex levels were higher at St Lazaria Island and Cape Lisburne than at the Bering Sea (St George and St Lawrence islands) colonies (Table 1 and ESI†).

A principal components analysis (PCA) demonstrated that the St Lazaria Island organic contaminant and stable isotope

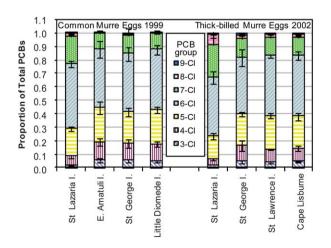


Fig. 3 Proportions of total PCBs (means \pm standard deviation) in Alaskan murre (*Uria* spp.) eggs.

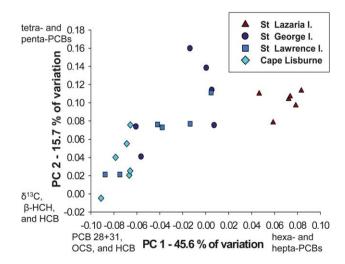


Fig. 4 Principal components analysis of thick-billed murre (*U. lomvia*) eggs collected at Alaskan nesting colonies in 2002. Compounds influencing the loadings are shown along the axes.

patterns differed from the other colonies (Fig. 4). The first two PC axes explained 61.3% of the total variation, with PC 1 explaining 45.6% and separating out St Lazaria Island because of higher proportions of hexa- and hepta-PCBs (21.3–30.3% of the PCA compounds) compared to the other colonies (11.6–23.7% of the PCA compounds). This pattern was similar to the pattern observed in the common murre eggs collected in 1999.¹¹

Stable isotope values also exhibited geographical variation. The most pelagic seabird colony, St George Island, expectedly had the lowest levels of δ^{13} C, but was not significantly different from the mainland based Cape Lisburne colony (Table 1 and ESI[†]). Zooplankton from these areas was also found to have lower δ^{13} C values.²⁸ Eggs from Cape Lisburne contained higher δ^{15} N values than those obtained at St Lazaria and St George islands (Table 1 and ESI[†]). Previous isotopic measurements of zooplankton off western Alaska have documented the effect of deep water upwelling across the Bering Shelf (near St George Island).²⁸ Zooplankton tend to become enriched in ¹⁵N (*i.e.*, higher δ^{15} N values) north of the Bering Shelf and this produces a gradient extending from the southern Bering Sea to the Chukchi Sea, a phenomenon that is supported by the current observations of progressively increasing $\delta^{15}N$ values from St George Island to St Lawrence Island to Cape Lisburne (Table 1). While not statistically significant, slightly higher δ^{15} N values were observed at St Lazaria Island compared to St George Island (Table 1 and ESI[†]). Similarly, δ^{15} N levels in bone collagen from harbor seals (Phoca vitulina) collected in 1995 in the southeastern Gulf of Alaska, near St Lazaria Island, were higher than levels found in the southern Bering Sea, near St George Island.²⁹

The overall pattern in baseline food web stable isotope values in the study area clearly indicates that before contaminant data can be corrected for among-colony comparisons, regional food webs will have to be normalized to common trophic levels and nearshore vs. offshore feeding models. This approach was used in a complementary study in the same region comparing $\delta^{15}N$ to mercury isotopes in murre eggs.¹⁹ Applying these techniques to the current samples resulted in similar trophic levels among colonies for both the copepod- and fish-based baseline values (Table 1). As the proportion of each prey item may vary by colony and/or individual murre, additional information such as fatty acid analysis would also be useful in determining the cause of the geographical differences in contaminant levels. However, as the isotope values that have been established for the colonies are useful for making temporal comparisons of contaminants within-colonies,30 it is recommended that these measurements become a routine part of any contaminant monitoring program using seabird eggs.

Relationship between contaminants and stable isotopes

Correlations between contaminants and uncorrected stable isotope values led to some unexpected results (Table 2). The negative correlations observed for the δ^{13} C values suggest that contaminants were higher in the local pelagic food web than in the nearshore food web. While some compounds such as β -HCH, oxychlordane, hexa- and pentachlorobenzene, and octachlorostyrene were positively correlated with δ^{15} N values, as expected, other contaminants produced negative correlations

Table 2 Correlations between major contaminants (on a lipid mass basis) and carbon and nitrogen isotope ratios found in the thick-billed murre (U. *lomvia*) eggs collected from Alaska in 2002 (n = 6 for each colony). Italicized values indicate negative slopes; significant correlations (P < 0.05) are shown in bold

Compounds Correlated	Overall		St Lazaria I		St George I		St Lawrence I		Cape Lisburne	
	R^2	Р	R^2	Р	R^2	Р	R^2	Р	R^2	Р
δ^{13} C- δ^{15} N	0.0671	0.222	0.0140	0.824	0.194	0.323	0.288	0.272	0.839	0.0102
δ^{13} C-4,4'-DDE	0.192	0.0322	0.311	0.250	0.147	0.453	0.0682	0.617	0.347	0.218
δ^{13} C- α -HCH	0.053	0.279	0.198	0.377	0.0537	0.658	0.264	0.297	0.361	0.207
δ^{13} C- β -HCH	0.00801	0.678	0.0437	0.691	0.0289	0.748	0.117	0.507	0.857	0.0081
δ^{13} C- γ -HCH	0.0391	0.354	0.332	0.232	0.0181	0.799	0.189	0.390	0.693	0.0398
δ^{13} C- <i>cis</i> -Chlordane	0.134	0.0791	0.201	0.373	0.144	0.459	0.558	0.0881	0.199	0.375
δ^{13} C-Heptachlor epoxide	0.0255	0.456	0.0783	0.591	0.0143	0.822	0.0344	0.725	0.310	0.251
δ^{13} C-Oxychlordane	0.0772	0.189	0.105	0.530	0.00684	0.876	0.424	0.161	0.549	0.0921
δ^{13} C-Mirex	0.0777	0.187	0.0671	0.620	0.0350	0.723	0.817	0.0135	0.640	0.0561
δ^{13} C-Octachlorosytrene	0.0000178	0.984	0.802	0.0158	0.00700	0.875	0.483	0.131	0.342	0.223
δ ¹³ C-HCB	0.0784	0.185	0.348	0.218	0.000410	0.970	0.029	0.747	0.870	0.0067
δ^{13} C-Pentachlorobenzene	0.0597	0.250	0.569	0.083	0.00136	0.950	0.0858	0.573	0.781	0.0196
$\delta^{13}C-\sum PCBs$	0.295	0.0061	0.374	0.197	0.146	0.456	0.00533	0.891	0.535	0.0985
δ^{15} N-4,4'-DDE	0.0477	0.305	0.00169	0.350	0.0132	0.829	0.0213	0.782	0.124	0.494
δ^{15} N- α -HCH	0.00316	0.794	0.258	0.304	0.052	0.663	0.000562	0.964	0.500	0.116
δ ¹⁵ N-β-HCH	0.191	0.0330	0.218	0.938	0.915	0.0028	0.325	0.238	0.614	0.0651
δ^{15} N- γ -HCH	0.0145	0.575	0.363	0.206	0.0477	0.678	0.0369	0.715	0.780	0.0197
δ^{15} N- <i>cis</i> -Chlordane	0.0100	0.642	0.00604	0.884	0.0898	0.564	0.188	0.390	0.212	0.358
δ^{15} N-Heptachlor epoxide	0.139	0.0723	0.534	0.099	0.957	0.0007	0.0813	0.584	0.397	0.180
δ^{15} N-Oxychlordane	0.227	0.0185	0.567	0.084	0.813	0.0141	0.900	0.0039	0.671	0.0462
δ^{15} N-Mirex	0.0592	0.252	0.00174	0.980	0.172	0.414	0.475	0.130	0.682	0.0428
δ^{15} N-Octachlorosytrene	0.512	< 0.0001	0.169	0.418	0.894	0.0044	0.501	0.115	0.288	0.273
δ ¹⁵ N-HCB	0.333	0.0032	0.0464	0.682	0.558	0.0880	0.0740	0.602	0.640	0.0560
δ^{15} N-Pentachlorobenzene	0.273	0.0088	0.0139	0.824	0.664	0.0482	0.0360	0.719	0.474	0.131
δ^{15} N- \sum PCBs	0.00185	0.950	0.321	0.241	0.041	0.702	0.334	0.230	0.285	0.276

Table 3 Correlations between major contaminants (on a lipid mass basis) found in the thick-billed murre (*U. lomvia*) eggs collected from Alaska in 2002 (n = 6 for each colony) and trophic levels calculated from literature copepod- and fish-based baseline levels¹⁹. Significant correlations (P < 0.05) are shown in bold

	Trophic L (copepod)		Trophic Level (fish)		
Compounds Correlated	R^2	Р	R^2	Р	
4,4'-DDE	0.0755	0.194	0.0375	0.365	
α-HCH	0.0441	0.0325	0.0130	0.596	
β-НСН	0.226	0.0190	0.275	0.0085	
γ-НCН	0.0434	0.329	0.0135	0.589	
<i>cis</i> -Chlordane	0.00893	0.661	0.00087	0.891	
Heptachlor epoxide	0.227	0.0186	0.240	0.0152	
Oxychlordane	0.305	0.0052	0.308	0.0049	
Mirex	0.108	0.118	0.0912	0.152	
Octachlorosytrene	0.105	0.122	0.150	0.0616	
Pentachlorobenzene	0.00916	0.656	0.0318	0.405	
НСВ	0.0243	0.467	0.0405	0.319	
ΣPCBs	0.129	0.0845	0.110	0.114	

(Table 2). Even for oxychlordane, the within-colony correlation for Cape Lisburne was significantly negative. In fact, with the exception of cis-chlordane, all other contaminant-isotope ratio correlations were negative at this colony. In contrast, an intraspecific study of δ^{15} N values and contaminants in glaucous gull (Larus hyperboreus) hepatic tissue from Bjørnøya in the Barents Sea found only positive correlations, with HCB, 4,4'-DDE, and Σ PCBs being significant.³¹ Using the same literature values and equations as discussed in Point et al.,¹⁹ the calculated copepodand fish-based trophic levels were used in place of δ^{15} N values for the overall contaminant correlations among locations. All correlations were now positive, with heptachlor epoxide now significant (P < 0.05, Table 3). However, the correlations with hexa- and penta-chlorobenze and octachlorostyrene were no longer significant due to lower adjusted trophic level for Cape Lisburne compared to $\delta^{15}N$ (Tables 1–3), once again indicating that adjusting for baseline trophic level differences is important when making comparisons among different regions.

The baseline trophic level adjustments do not affect the withincolony comparisons. The overall results vary significantly depending on the colony, e.g., oxychlordane is significantly positively related to δ^{15} N at St George and St Lawrence island, but the relationship is not significant at St Lazaria Island and at Cape Lisburne it is significantly negative (Table 2). Potential explanations for these findings include possible decoupling between the δ^{15} N and δ^{13} C and contaminant datasets, given the fact that the isotope data represented the protein fraction of the diets and the contaminant data were based on the lipid fraction. If the birds obtain most of their lipids, and hence their contaminant loads, from the same prey types they obtain protein from, then close coupling between the $\delta^{15}N$ data and contaminants that accumulate at various trophic levels would be one of the expected outcomes. However, these couplings are not always present, and if the lipid component of the eggs is primarily derived from body stores obtained from lower trophic level prey, and the protein component comes from higher trophic level prey (or vice versa), then a negative correlation would be the expected result. Indeed, this has been found in common murre eggs obtained at a colony off central California.³² At this breeding location, murres accumulated organic contaminant loads from fish during winter and lower trophic level euphausiids during the nesting season. Currently, one hypothesis is that the Cape Lisburne females may be using a different nutrient allocation strategy during the egg development phase (*i.e.*, they may be differentially mobilizing contaminants, based on endogenous *vs.* exogenous reserves). Because Cape Lisburne clearly differs from the southern colonies, more information needs to be obtained on nutrient allocation strategies and their effects on contaminant burdens to help improve data interpretation.

Conclusions

Thick-billed murre eggs exhibited contaminant patterns similar to the patterns previously found in common murre eggs obtained at the same Alaskan colonies. In addition, eggs from the Gulf of Alaska contained higher levels of contaminants and had significantly different patterns compared to eggs from the Bering and Chukchi seas. Stable-carbon and nitrogen isotopes also exhibited geographical variations that appeared to be related to differences in baseline food web values rather than differences in murre trophic levels. Contaminant and stable isotope correlations were inconclusive, suggesting that better information on regional food web differences and differential offloading of contaminants and stable isotopes to the eggs must be obtained before these types of data can be fully incorporated into seabird egg contaminant monitoring programs.

Disclaimer

Certain commercial equipment or instruments are identified in this paper to adequately specify the experimental procedures. Such identification does not imply recommendations or endorsement by the National Institute of Standards and Technology nor does it imply that the equipment or instruments are the best available for the purpose.

Acknowledgements

We would like to thank the Alaska Maritime National Wildlife Refuge for supporting the STAMP program; Larua Greffenius, Susan Hatch, Arthur Kettle, Dean Kildaw, Alexis Paul and the residents of Little Diomede Island for collecting the 1999 common murre eggs; Adrian Gall, Earl Kingik, Jackson Mokiyuk, Leslie Slater, and Julie Snorek for collecting the 2002 thick-billed murre eggs; and Lesley Chappel and Kristin Simac for helping to process them. Blanca Mora Alvarez prepared the samples for stable isotope analyses and Myles Stocki made the isotopic measurements.

References

- 1 Handbook of the Birds of Europe, the Middle East and North Africa: the birds of the Western Palearctic, ed. S. Cramp, Oxford University Press, New York, 1st edn, 1985, vol. IV, pp. 170–195.
- 2 K. Kaufman, *Lives of North American Birds*, Houghton Mifflin Co., New York, 1st edn, 1996, pp. 267–271.
- 3 S. A. Hatch, P. M. Meyers, D. M. Mulcahy and D. C. Douglas, *Condor*, 2000, **102**, 145–154.
- 4 D. Pastor, L. Jover, X. Ruiz and J. Albaigés, *Sci. Total Environ.*, 1995, 162, 215–223.

- 5 The Atlantic Alcidae: the Evolution, Distribution, and Biology of the Auks Inhabiting the Atlantic Ocean and adjacent Water Areas, ed. D. N. Nettleship and T. R. Birkhead, Academic Press, London, Orlando, 1st edn, 1985, p. 574.
- 6 B. M. Braune, G. M. Donaldson and K. A. Hobson, *Environ. Pollut.*, 2001, **114**, 39–54.
- 7 P. R. Ehrlich, D. S. Dobkin and D. Wheye, *The Birder's Handbook:* a Field Guide to the Natural History of North American Birds: Including all Species that Regularly Breed North of Mexico, 1st edn, Simon & Schuster/Fireside Books, New York, 1988.
- 8 A. J. Gaston and J. M. Hipfner, in *The Birds of North America*, ed. A. Poole, Cornell Lab of Ornithology, Ithaca, 2000, vol. 497, DOI: 10.2173/bna.497.
- 9 A. J. Gaston and D. N. Nettleship, *The Thick-Billed Murres of Prince Leopold Island: a Study of the Breeding Ecology of a Colonial High Arctic Seabird*, Canadian Wildlife Service, Monograph Series, Ottawa, 1st edn, 1981, vol. 6, p. 350.
- 10 L. M. Tuck, *The Murres: their Distribution, Populations and Biology* a Study of the Genus Uria, Canadian Wildlife Service Monograph Series, 1st edn, 1960, vol. 1, p. 260.
- 11 S. S. Vander Pol, P. R. Becker, J. R. Kucklick, R. S. Pugh, D. G. Roseneau and K. S. Simac, *Environ. Sci. Technol.*, 2004, 38, 1305–1312.
- 12 K. A. Hobson, J. F. Piatt and J. Pitocchelli, J. Anim. Ecol., 1994, 63, 786–798.
- 13 B. M. Braune, G. M. Donaldson and K. A. Hobson, *Environ. Pollut.*, 2002, **117**, 133–145.
- 14 R. Dietz, P. M. Outridge and K. A. Hobson, *Sci. Total Environ.*, 2009, 407, 6120–6131.
- 15 G. W. York, B. J. Porter, R. S. Pugh, D. G. Roseneau, K. S. Simac, P. R. Becker, L. K. Thorsteinson and S. A. Wise, *Seabird Tissue Archival and Monitoring Project: Protocol for Collecting and Banking Seabird Eggs*, National Institute of Standards and Technology, Gaithersburg, Maryland, NISTIR 6735, 2001.
- 16 S. S. Vander Pol, P. R. Becker, M. B. Ellisor, A. J. Moors, R. S. Pugh and D. G. Roseneau, *Environ. Pollut.*, 2009, **157**, 755–762.

- 17 S. S. Vander Pol, M. B. Ellisor, R. S. Pugh, P. R. Becker, D. L. Poster, M. M. Schantz, S. D. Leigh, B. J. Wakeford, D. G. Roseneau and K. S. Simac, *Anal. Bioanal. Chem.*, 2007, **387**, 2357–2363.
- 18 K. A. Hobson, A. Fisk, N. Karnovsky, M. Holst, J.-M. Gagnon and M. Fortier, *Deep-Sea Res.*, *Part II*, 2002, **49**, 5131–5150.
- 19 D. Point, J. E. Sonke, R. D. Day, D. G. Roseneau, K. A. Hobson, S. S. Vander Pol, A. J. Moors, R. S. Pugh, O. F. X. Donard and P. R. Becker, *Nat. Geosci.*, in press, DOI: 10.1038/NGEO1049.
- 20 K. J. Rothman, Epidemiology, 1990, 1, 43-46.
- 21 SRM 1946 Lake Superior Fish Tissue, Certificate of Analysis, National Institute of Standards and Technology, Gaithersburg, MD, 2003, https://www-s.nist.gov/srmors/certificates/view_ certGIF.cfm?certificate=1946.
- 22 A. P. X. de Brito, D. Ueno, S. Takahashi and S. Tanabe, *Chemosphere*, 2002, 46, 401–411.
- 23 H. Iwata, S. Tanabe, N. Sakai and R. Tatsukawa, *Environ. Sci. Technol.*, 1993, 27, 1080–1098.
- 24 M. Scheringer, M. Salzmann, M. Stroebe, F. Wegmann, K. Fenner and K. Hungerbühler, *Environ. Pollut.*, 2004, **128**, 177–188.
- 25 J. C. Duinker and F. Bouchertall, *Environ. Sci. Technol.*, 1989, 23, 57–62.
- 26 P. J. Stabeno, N. A. Bond, A. J. Hermann, N. B. Kachel, C. W. Mordy and J. E. Overland, *Cont. Shelf Res.*, 2004, 24, 859–897.
- 27 J. M. Stafford, G. Wendler and J. Curtis, *Theor. Appl. Climatol.*, 2000, **67**, 33–44.
- 28 D. M. Schell, B. A. Barnett and K. A. Vinette, *Mar. Ecol. Prog. Ser.*, 1998, **162**, 11–23.
- 29 A. C. Hirons, D. M. Schell and B. P. Finney, *Oecologia*, 2001, 129, 591–601.
- 30 C. E. Hebert and D. V. C. Weseloh, *Environ. Sci. Technol.*, 2006, 40, 5624–5628.
- 31 K. Sagerup, E. O. Henriksen, J. U. Skaare and G. W. Gabrielsen, *Ecotoxicology*, 2002, 11, 119–125.
- 32 W. M. Jarman, K. A. Hobson, W. J. Sydeman, C. E. Bacon and E. B. McLaren, *Environ. Sci. Technol.*, 1996, **30**, 654–660.