2015 AMAP Assessment of Temporal Trends in Persistent Organic Pollutants

A2.3 US-Alaska – Seabirds

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Introduction

The Seabird Tissue Archival and Monitoring Project (STAMP) has banked over 1900 seabird eggs collected from Alaska since 1999. Common murre (*Uria aalge*) and thick-billed murre (*U. lomvia*) make ideal biomonitors as abundant, circumpolar, essentially non-migrating, piscivores that only lay one egg (Vander Pol and Becker, 2007). Glaucous gull (*Larus hyperboreus*) and glaucous-winged gull (*L. glaucescens*) egg clutch banking began in 2004 at the request of subsistence harvesters and to correlate with other circumpolar studies. STAMP began as a joint project of the US Fish and Wildlife Service Alaska Maritime National Wildlife Refuge (USFWS-AMNR), the US Geological Survey Biological Resources Division (USGS-BRD), and the National Institute of Standards and Technology (NIST) to monitor long-term trends in environmental quality by (1) collecting seabird tissues (mainly eggs) at Alaskan seabird colonies without inadvertently contaminating them, (2) processing and banking the samples under conditions that ensure chemical stability during long-term (decadal) storage, and (3) analyzing subsamples of the stored material for anthropogenic contaminants (see York et al., 2001). Egg collections and processing are conducted by USFWS-AMNR and collaborating researchers (including Bureau of Indian Affairs Alaska Regional Subsistence Branch, BIA/ARSB; and local subsistence harvesters), and the banking of egg contents and contaminant analyses are conducted by NIST in its facilities at the Hollings Marine Laboratory, Charleston, South Carolina. In addition, carbon and nitrogen isotope analysis for food-web determination is now being conducted by Environment Canada and all eggshells are being archived at the Museum of the North, University of Alaska in Fairbanks. Additional support has been provided by the North Pacific Research Board.

Methods

Eggs are collected, measured and contents harvested using standard protocols (York et al., 2001; Rust et al., 2010). All egg contents are banked at the national Marine Environmental Specimen Bank (ESB) at NIST where until 2005 (for gull eggs) or 2008 (for murre eggs), the contents were cyohomogenized and aliquoted into Teflon jars (see York et al. 2001; Vander Pol et al., 2003, 2009a), after which the contents were fresh homogenized using various hand blenders and finally a bag-mixer (Interscience, St Nom la Bretêche, France) to increase the 'real-time analysis' potential into both Teflon jars and polypropylene cryovials to allow for analysis of perfluorinated chemicals (PFCs; see Vander Pol et al., 2009a,b, 2012; Rust et al., 2010). All aliquots are stored in liquid nitrogen vapor freezers and are available to other researchers under a formal access policy. Sample metadata are available[1].

Since 1999, 475 eggs have been analyzed for persistent organic pollutants (POPs) and mercury (Hg) by scientists at NIST to help advance the third goal of STAMP. Mercury analysis originally comprised microwave digestion followed by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICPMS; see Christopher et al., 2002; Day et al., 2006, 2012a). Since 2010, Hg analysis has moved to direct measurements (Milestone, Shelton, Connecticut; Bryan et al., in prep.) again to allow for more 'real-time analysis' potential. The creation and use of a control material (Vander Pol et al., 2007) ensures consistency between instrumental

[1] Sample metadata are available at: http://batchgeo.com/map/2e4a316a78e6f5a19b0c56b81db323fb [*Stacy: We hope to move this to a NIST site, but the software is still in legal. Please let me know if we can change it right before printing if the new site is available.*]

methods and batches (prior to the creation of this matrix-matched control material, SRM 1946 Lake Superior Fish Tissue was used). Likewise, for analysis of organic contaminants – polychlorinated biphenyls (PCBs), organochlorine pesticides, and since 2001 polybrominated diphenyl ethers (PBDEs) – methods have changed from pressurized fluid extraction (PFE) followed by size exclusion chromatography (SEC) and semi-preparative aminopropylsilane liquid chromatography (LC) fractionation with gas chromatography (GC) coupled to dual electron capture detectors (ECD; see Vander Pol et al., 2003, 2004), to PFE followed by SEC and solid phase extraction (SPE) with pressure temperature vaporization (PTV) GC coupled to mass spectrometer detector (MSD; see Vander Pol et al., 2009a,b, 2011, 2012) to decrease preparation time and increase analysis sensitivity.

Methylmercury (Davis et al., 2004), butyltin (Vander Pol et al., 2009a) and Hg isotopes (Point et al., 2011; Day et al., 2012a) have also been analyzed in selected samples. Stable carbon and nitrogen isotopes have been analyzed at Environment Canada to aid in the interpretation of the contaminant results (Vander Pol et al., 2011, 2012; Day et al. 2012a,b). Future work will include analysis of other heavy metals and trace elements and genetic analysis to distinguish eggs from unidentified murre species as these sympatric species nest in some of the same areas, and the eggs appear similar.

Data reported here have been analyzed using principal components analysis (PCA) for the compounds with no values below detection limit (PCB congeners 28+31, 66, 99, 105, 118, 138, 146, 153+132, 163, 170, 180+193, 183, 187;, 4,4'-DDE; oxychlordane; mirex; hexachlorobenzene, HCB; Hg). The compounds were summed for each egg and the proportion of that compound to the total was used for the PCA. The resulting eign value for each principal component (PC) compound was multiplied by the proportion of that compound to the sum in the egg. These values were summed to obtain the PC for each egg. Multivariate Analysis of Variances (MANOVA) was conducted to compare these compounds by combined region/species to limit type 1 errors. As the MANOVA was significant, individual analysis of variances (ANOVAs) and post-hoc Tukey HSD tests were used to further determine differences among colonies. All statistics were analyzed with JMP (SAS Institute, Cary, North Carolina) software and plotted using SigmaPlot (SPSS Inc., Chicago, Illinois) software. In addition to the PIA temporal analysis, means and standard errors of the colony data per year were plotted against the Pacific Decadal Oscillation (PDO[2]) index mean and standard error between February and May (when the eggs should be forming) to compare changes observed with oceanographic changes.

Summary of program results

Based on the PCA, Norton Sound murre eggs were generally separated from the Bering and Chukchi seas eggs due to higher proportions of Hg compared to mid-chlorinated PCBs (PC 1 explained 41.1% of the total variation; Fig. A2.1). The gull eggs are also slightly separated along PC1, but are also dominated by higher proportions of heavier chlorinated PCBs, similar to Gulf of Alaska murre eggs, which are generally separated from Being and Chukchi seas murre eggs along PC2 (24.3% of the total variation). PC2 appears to follow the global distillation/fractionation theory of heavier chemicals dominating lower latitudes and lighter chemicals moving toward the polar regions.

[2] http://jisao.washington.edu/pdo/PDO.latest

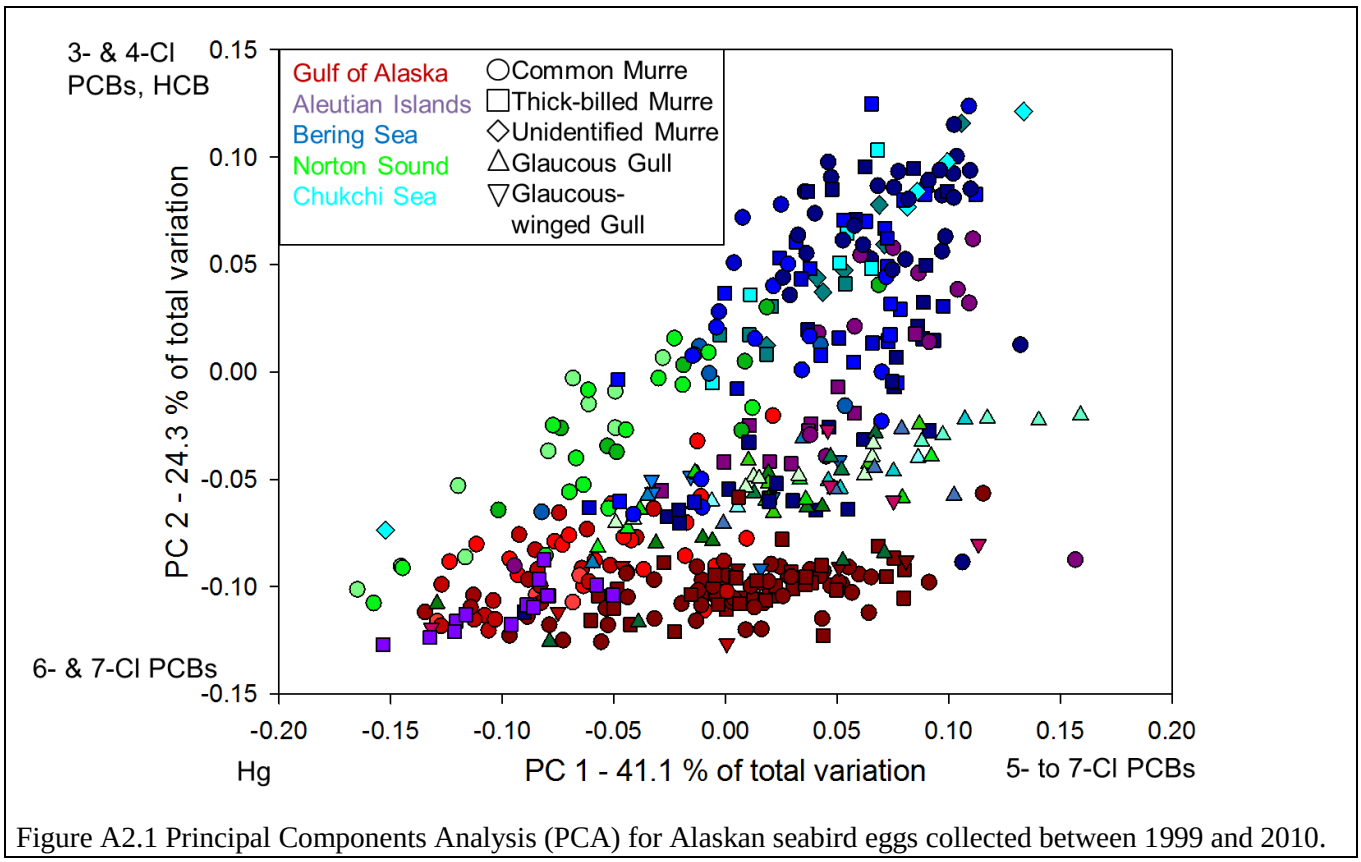

Figure A2.1 Principal Components Analysis (PCA) for Alaskan seabird eggs collected between 1999 and 2010.

The MANOVA comparing region/species combinations was highly significant (Wilk's $\lambda = 0.0123$, $F_{234, 4269} = 9.40$, $p < 0.0001$). All of the post-hoc ANOVAs were also highly significant ($p < 0.0001$). The 3-Cl PCBs were higher in the Chukchi Sea region and Norton Sound glaucous gull eggs and lower in the Norton Sound common murre and Bering Sea and Gulf of Alaska common and thick-billed murre eggs. The 7-Cl PCBs were highest in the Chukchi Sea glaucous gull and Gulf of Alaska thick-billed murre eggs and lowest in the Aleutian Islands thick-billed murre and Norton Sound and Bering Sea murre eggs. The Gulf of Alaska thick-billed murre eggs had the highest levels of 4,4'-DDE while the Bering Sea and Norton Sound murre eggs had the lowest. Eggs from these regions/species also had the lowest oxychlordane levels while the greatest were in the Chukchi Sea glaucous gull eggs. HCB is a lighter compound, and the lowest levels were observed in the Gulf of Alaska thick-billed and glaucous-winged gull eggs, while the highest were in the Chukchi Sea murre eggs. The highest levels of mirex were in the Chukchi Sea and Norton Sound glaucous gull eggs while the lowest were in the Bering Sea and Aleutian Islands murre eggs. Mercury was highest in the Norton Sound glaucous gull, Aleutian Islands thick-billed murre, and Gulf of Alaska common murre eggs and lowest in the Bering Sea murre eggs. While, BDE 47 was not included in the MANOVA due to missing values for the 1999–2001 eggs, a separate ANOVA was conducted for this important compound. The highest levels were in Chukchi Sea glaucous gull and Gulf of Alaska glaucous-winged gull eggs, and lowest in the Bering Sea and Norton Sound murre eggs. Overall, the highest contaminant levels were found in the Chukchi Sea and Norton Sound glaucous gull and Gulf of Alaska murre eggs and the lowest in the Bering Sea murre eggs (see Table A2.1).

As species differences, especially at St. Lazaria Island in the Gulf of Alaska, seemed to vary over the past decade (see Fig. A2.2), potential relationships with oceanographic conditions (probably affecting prey availability) were examined. Several contaminants in thick-billed murre eggs at St. Lazaria Island generally correlated with the spring (February–May, when eggs should be forming) PDO indices, while common murre eggs at this location exhibited an opposing trend. None of the other long-term monitoring colonies exhibited this correlation with the PDO. However, this could be due to a lack of time sampling points. Possible explanations for the correlation are being examined and will be published once all the carbon and nitrogen stable isotope data are available.

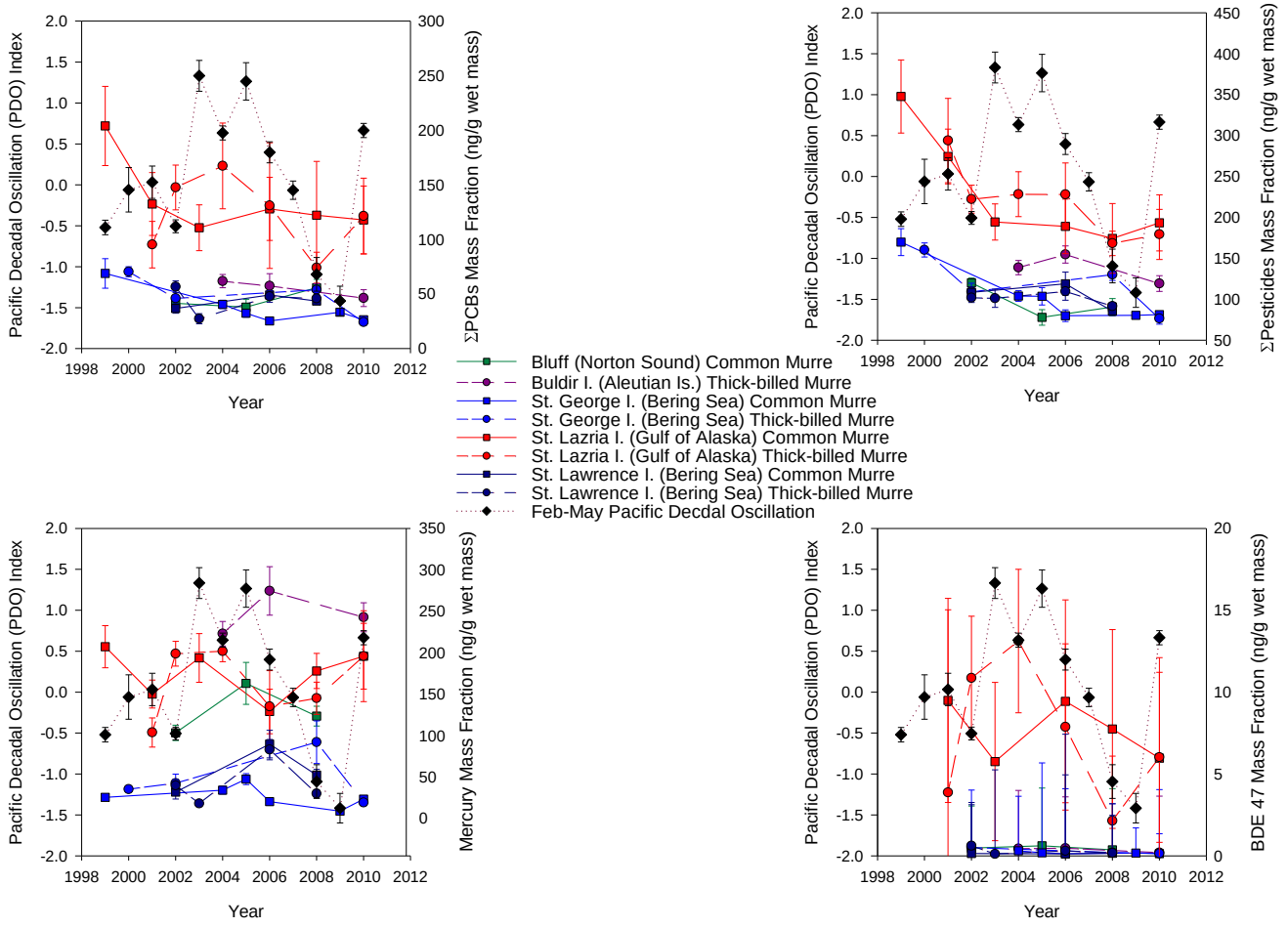

Figure A2.2 Mean concentrations (and standard errors) for a range of contaminants in Alaskan murre (*Uria* spp.) eggs compared to the February–May Pacific Decadal Oscillation.

Table A2.1 Post-hoc Tukey HSD results following highly significant ($p < 0.0001$) ANOVAs. Region/species that do not have overlapping letters were statistically ($p < 0.05$) different.

Region/Species	3-Cl PCBs (28+31)	4-Cl PCBs (66)	5-Cl PCBs (99, 105, 118)	6-Cl PCBs (138, 146, 153+132, 163)	7-Cl PCBs (170, 180+193, 183, 187)	4,4'-DDE	Oxychlordane	HCB	Mirex	Mercury	ΣPCBs	Σpesticides	Σcontaminants	BDE 47
Chukchi Sea														
thick-billed murre	A	A-E	C-E	C-F	CD	EF	D-F	AB	C-G	C-F	C-F	C-E	B-D	BC
unidentified murre sp.	A	A-C	C-E	C-F	CD	D-F	C-E	A	B-E	C-F	D-F	B-E	B-D	BC
glaucous gull	A	A	A	A	AB	EF	A	B-D	A	A-D	A	AB	A	A
Norton Sound														
glaucous gull	A	A	B	B	A-C	BC	B	C-G	A	A	B	A-C	A	BC
common murre	B	E	D-E	E-F	D	F	F	C-E	C-G	BC	EF	E	CD	C
Bering Sea														
glaucous-winged gull	AB	A-D	B-D	B-E	A-D	B-F	BC	C-G	A-C	AB	B-F	A-E	A-C	BC
thick-billed murre	B	C-E	DE	E-F	D	F	F	C-G	F	EF	EF	DE	D	C
common murre	B	D-E	E	F	D	F	F	C	E-G	F	F	DE	D	C
Aleutian Islands														
glaucous-winged gull	B	A-E	B-D	A-D	A-D	A-E	B-F	E-G	AB	A-F	A-E	A-E	A-D	BC
thick-billed murre	B	A-D	C-E	D-F	D	B-E	D-F	C-G	D-G	A	D-F	B-D	AB	BC
common murre	AB	B-E	C-E	C-F	CD	C-F	D-F	BC	FG	D-F	C-F	C-E	CD	BC
Gulf of Alaska														
glaucous-winged gull	AB	AB	B-E	B-F	A-D	A-D	C-F	FG	C-G	A-E	B-F	A-E	A-C	A
thick-billed murre	B	A-C	C	BC	AB	A	D-F	G	CD	AB	BC	A	A	B
common murre	B	B-D	C	CD	BC	B	D-F	D-G	C-G	A	CD	BC	A	BC

Conclusions

The Seabird Tissue Archival and Monitoring Project –STAMP – has been successfully banking and monitoring seabird eggs in the Alaskan region since 1999. Aliquots of the eggs are available to other researchers. Contaminant patterns and concentrations differ by region and species and some of the temporal trends appear to be correlated with the PDO. STAMP will continue to use murre eggs to monitor changing contaminant trends in this region.

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