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Development of a murre (*Uria* spp.) egg control material

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Abstract The Seabird Tissue Archival and Monitoring Project (STAMP) is a collaborative Alaska-wide effort by the US Fish and Wildlife Service's Alaska Maritime National Wildlife Refuge (USFWS/AMNWR), the US Geological Survey's Biological Resources Division (USGS/BRD), the Bureau of Indian Affairs Alaska Region Subsistence Branch (BIA/ARSB), and the National Institute of Standards and Technology (NIST) to monitor long-term (decadal) trends in environmental contaminants using seabird eggs. To support this effort, a matrix- (seabird egg) and concentration-specific control material was needed to ensure quality during analytical work. Although a herring gull egg quality assurance (HGQA) material is available from Environment Canada (EC), contaminant concentrations in this material tended to be higher than those observed in Alaskan murre (*Uria* spp.) eggs. Therefore, to prepare a more appropriate control material, a total of 12 common murre (*U. aalge*) and thick-billed murre (*U. lomvia*) eggs from four Bering Sea and Gulf of Alaska nesting locations were cryohomogenized to create 190 aliquots each containing approximately 6 g. This new control material was analyzed by different methods at NIST and EC facilities for the determination of concentrations and value assignment of 63 polychlorinated biphenyl (PCB) congeners, 20 organochlorine pesticides, and 11 polybrominated diphenyl ether (PBDE) congeners. The total PCB concentration is approximately 58 ng g^{-1} wet mass. Results obtained for analytes not listed on the certificates of analysis of the previously used control materials, HGQA and NIST's Standard Reference Material (SRM) 1946 Lake Superior Fish Tissue, are also presented.

Keywords Control material · Seabird · Egg · PCBs · PBDEs · Organochlorine pesticides

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Introduction

The Seabird Tissue Archival and Monitoring Project (STAMP) is a collaborative Alaska-wide effort by the US Fish and Wildlife Service's Alaska Maritime National Wildlife Refuge (USFWS/AMNWR), the US Geological Survey's Biological Resources Division (USGS/BRD), the

Bureau of Indian Affairs' Alaska Region Subsistence Branch (BIA/ARSB), and the National Institute of Standards and Technology (NIST) to monitor long-term (decadal) trends in environmental contaminants using seabird eggs. STAMP began in 1999 and has collected 891 egg clutches through 2005 from 41 colonies. To support the analytical chemistry quality assurance work associated with STAMP, a matrix- (seabird egg) and concentration-specific control material was needed. Although a herring gull egg quality assurance (HGQA) material is available from Environment Canada (EC), contaminant concentrations in this material tended to be higher than those observed in Alaskan murre (*Uria* spp.) eggs. Previous analyses of STAMP eggs used the HGQA and NIST's Standard Reference Material (SRM) 1946 Lake Superior Fish Tissue, which also tended to have higher concentrations than the murre eggs, as control materials. Therefore, to more closely address the analytical needs associated with the STAMP program, 12 common murre (*U. aalge*) and thick-billed murre (*U. lomvia*) eggs collected for STAMP were used to create a new control material characterized for organic contaminants. This paper summarizes the value assignments of the new egg control material (CM) and presents values for compounds that were not previously value assigned in the HGQA and SRM 1946.

Experimental

Sample collection and preparation

Seabird eggs were collected for long-term archival and contaminant analysis following protocols established for STAMP [1, 2]. Twelve Alaskan murre (*Uria* spp.) eggs were used to create a new control material for use in STAMP-related analyses. The eggs were from colonies where greater than ten eggs were archived or the numbers of eggs archived were too small to be used for statistical comparisons and included 4 *U. lomvia* eggs from St. Lawrence Island (collected 23 June 2003) and 8 *U. aalge* eggs: 1 from St. George Island (collected 28 June 2001), 5 from Middleton Island (collected 12 June 2003), and 2 from Bluff (collected 14 June 2003). The eggs were individually cryogenically homogenized [1], mixed together, and subdivided in 190 aliquots of fresh frozen powder, each approximately 6 g. The aliquots were placed in a −80 °C upright mechanical freezer for long-term storage. Specific procedures used to prepare the frozen egg homogenate have been described in detail by others [3].

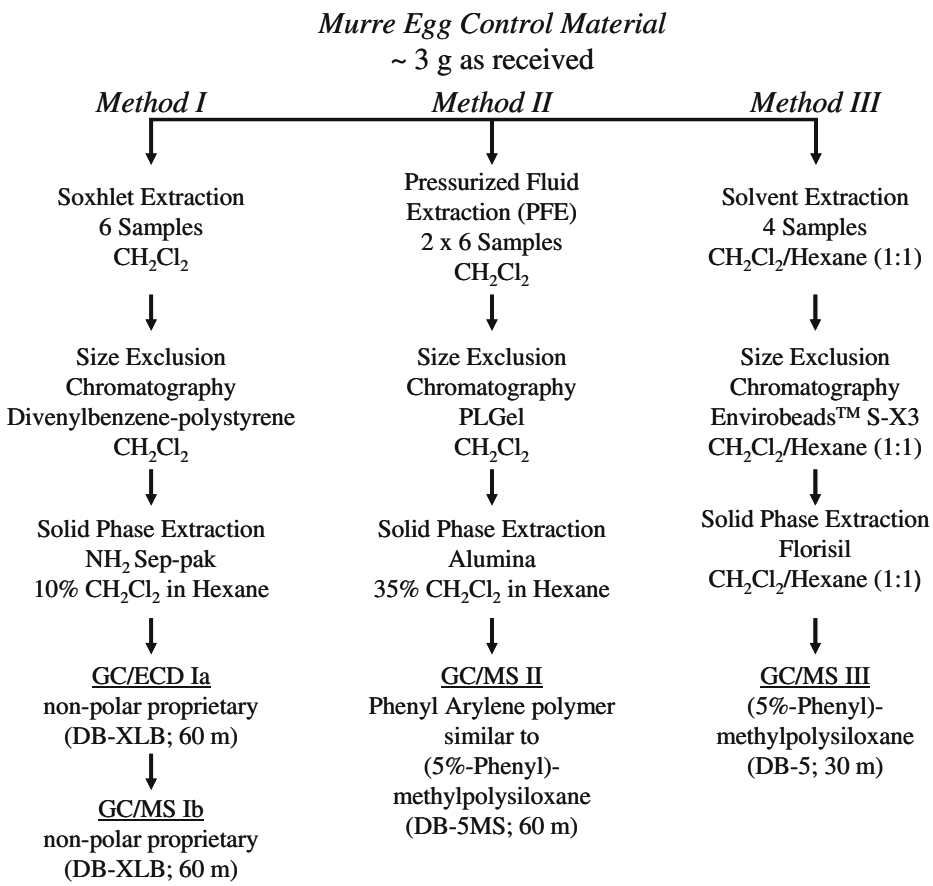

Fig. 1 Analytical scheme for value assignment of murre (*Uria* spp.) egg control material

Table 1 Results with means (ng g^{-1} wet mass) and 95% confidence intervals (CIs) for compounds not listed on the certificate of analysis for SRM 1946 with range of values obtained for the herring gull egg quality assurance material (HGQA) and its reference values (ng g^{-1} wet mass)

	SRM 1946						HGQA	
	GC-ECD 1	GC-ECD 2	GC/MS 1	GC/MS 2	Mean	95% CI	Range	Reference values
PCB 92+84+89	10.4	9.01	7.55	7.89	8.71	1.3	4.21–4.67	4.88±0.63
PCB 130			7.13	7.21	7.17		13.3–13.8	8.40±2.37
PCB 137			6.08	5.39	5.74		8.92–9.00	13.2±3.87
PCB 151			9.68	9.75	9.72		4.37–4.55	3.84±1.69
PCB 157	4.81	4.64	4.53	4.32	4.58	0.20	4.14–4.63	5.42±2.06
PCB 172			7.56	7.96	7.76		14.1–14.9	13.7±2.19
PCB 177			15.1	15.0	15.1		25.3–25.4	22.1±2.92
PCB 178			12.6	12.7	12.7		13.5–14.3	13.8±3.62
PCB 196+203			21.0	19.8	20.4		29.2–31.6	27.3±4.82
PCB 199			15.4	16.3	15.9		25.4–26.2	23.9+3.87
PCB 202			5.95	5.81	5.88		4.86–5.09	6.18±1.45
PCB 207			1.52	1.36	1.44		1.49–1.69	9.11±2.62
PCB 208			1.78	1.69	1.74		2.35–2.36	12.7±3.22
Octachlorostyrene			4.22	3.81	4.02		2.18–2.431	76±0.469

Determination of PCBs, PBDEs, and organochlorine pesticides

Murre egg control material

The murre egg homogenate was analyzed by NIST and EC to determine the concentrations for value assignment of 63 polychlorinated biphenyl (PCB) congeners, 20 organochlorine pesticides, and 11 polybrominated diphenyl ether (PBDE) congeners. Methods used for analyses are summarized in Fig. 1. An aliquot of the extract was used to gravimetrically determine total extractable organics (TEOs; "lipids"). Statistical methods used for value assignment have been described elsewhere [4]. Similar approaches have been used for the determination of certified and reference concentrations of organic contaminants in environmental matrix SRMs including fish and mussel tissue SRMs as well as marine sediment SRMs [5–7].

SRM 1946 and HGQA

Both SRM 1946 and HGQA were used as reference materials together four times when analyzing STAMP eggs, allowing analytes without values on the respective certificates of analysis to be measured. The last two batches were analyzed using method II presented here (see Fig. 1) and the first two batches were handled the same way through step 2, but then were fractionated using a semi-preparative aminopropylsilane column with F1 in hexane and F2 in 25% CH_2Cl_2 in hexane (volume fraction) and analyzed using a gas chromatograph with dual micro-electron capture detectors (GC-ECD) with a 60-m DB-XLB column (J&W Scientific, Folsom, CA) and a 60-m DB-5 column (J&W Scientific). Further details for this method were previously described [8]. Along with the switch between instruments, new analytes were added to the method and co-elutions of compounds varied (e.g., PCB 132 co-eluted with PCB 153

Table 2 Results with means (ng g^{-1} wet mass) and 95% confidence intervals (CIs) for compounds not value assigned for the herring gull egg quality assurance material (HGQA) with range of values obtained for SRM 1946 and the values listed on its certificate of analysis (ng g^{-1} wet mass)

	HGQA						SRM 1946	
	GC-ECD 1	GC-ECD 2	GC/MS 1	GC/MS 2	Mean	95% CI	Range	Certificate values
PCB 18	0.155	0.111	0.151	0.163	0.145	0.023	0.273–0.834	0.84±0.11
PCB 107	1.72	1.74	1.98	1.97	1.85	0.14	8.76–9.02	8.86±0.20
PCB 132	0.943	0.819			0.881		5.28–5.67	5.83±0.76
PCB 163	53.1	57.3	49.1	48.1	51.9	4.1	32.0–32.7	31.8±0.8
PCB 193	7.24	7.95			7.60		4.30–5.01	5.78±0.72
PCB 209	2.67	2.31	2.25	2.35	2.40	0.18	0.994–1.20	1.30±0.21
2,4′-DDE	0.258	0.29	0.281	0.299	0.282	0.017	0.705–1.07	1.04±0.29

Table 3 Summary of analytical results for TEOs, PCBs and organochlorine pesticides (mean (standard deviation) in ng g^{-1} wet mass, except TEOs in %) in murre (*Uria* spp.) egg control material homogenate

	Method 1a GC-ECD DB-XLB-60 m	Method 1b GC/MS DB-XLB, 60 m	Method 2 GC/MS DB-5MS, 60 m	Method 3 GC/MS DB-5, 30 m	Percentage difference[a]	Consensus mean ±expanded uncertainty[b]	STAMP eggs range[c]
TEOs			10.9 (0.24)	12.68 (0.74)	14	11.8±1.1	6.94–16.0
PCB 28[d]	2.34 (0.12)	2.46 (0.066)		1.61 (0.12)	34	2.14±0.49	1.30–5.86
PCB 28+31	2.86 (0.23)	2.65 (0.13)	2.83 (0.047)	1.61 (0.12)	44	2.49±0.51	1.30–6.10
PCB 52		0.231 (0.032)	0.140 (0.0090)	0.30 (0.060)	53	0.234±0.095	<0.100–4.16
PCB 56			0.791 (0.040)	0.70 (0.050)	12	0.746±0.059	0.761–14.2
PCB 66	2.75 (0.40)	2.51 (0.067)	2.34 (0.070)	2.26 (0.14)	18	2.41±0.12	1.25–10.9
PCB 70		0.217 (0.022)	0.188 (0.0093)	0.21 (0.010)	13	0.205±0.018	<0.100–1.88
PCB 74		1.90 (0.026)	1.88 (0.054)	1.97 (0.090)	5	1.92±0.061	<0.100–6.40
PCB 99		3.84 (0.13)	3.85 (0.084)	4.11 (0.19)	6	3.93±0.17	1.35–23.7
PCB 101		0.610 (0.077)	0.345 (0.016)	1.55 (0.080)	78	0.835±0.7	<0.100–8.50
PCB 105	1.52 (0.28)	2.64 (0.14)	1.63 (0.037)	1.55 (0.12)	42	1.84±0.47	1.32–12.2
PCB 118	8.60 (1.0)	6.21 (0.17)	5.85 (0.081)	5.73 (0.35)	33	6.53±1.1	4.00–35.4
PCB 128	0.800 (0.14)	0.834 (0.084)	0.718 (0.023)	0.92 (0.090)	22	0.809±0.077	<0.100–19.0
PCB 130			0.305 (0.021)	0.29 (0.030)	5	0.298±0.018	Not determined
PCB 138		5.35 (0.24)	4.69 (0.18)	7.24 (0.52)	35	5.76±1.5	1.68–44.0
PCB 146	2.40 (0.45)	2.53 (0.11)	2.46 (0.063)	2.58 (0.27)	7	2.47±0.022	1.23–19.8
PCB 149			0.316 (0.025)	0.49 (0.020)	36	0.403±0.1	<0.100–12.9
PCB 153+132	11.4 (1.2)	11.2 (0.27)	10.8 (0.19)	11.58 (1.3)	7	11.0±0.26	3.90–85.1
PCB 156		0.646 (0.054)	0.585 (0.022)	0.44 (0.030)	33	0.557±0.12	<0.100–5.00
PCB 157		0.212 (0.029)	0.219 (0.016)	0.20 (0.010)	9	0.210±0.014	<0.100–1.36
PCB 158		0.370 (0.063)	0.270 (0.017)	0.31 (0.050)	27	0.317±0.063	<0.100–3.23
PCB 163	2.01 (0.45)	2.07 (0.13)	1.91 (0.050)		8	2.00±0.16	1.35–17.5
PCB 167			0.445 (0.020)	0.49 (0.050)	10	0.468±0.037	Not determined
PCB 170		2.21 (0.29)	0.979 (0.042)	1.22 (0.17)	56	1.47±0.72	0.142–9.54
PCB 172			0.362 (0.018)	0.38 (0.050)	4	0.371±0.028	Not determined
PCB 177			0.320 (0.026)	0.47 (0.060)	32	0.395±0.092	Not determined
PCB 178			0.418 (0.019)	0.44 (0.030)	5	0.429±0.02	Not determined
PCB 180	1.97 (0.31)	2.00 (0.050)		2.43 (0.34)	19	2.13±0.3	0.150–34.1
PCB 180+193	2.28 (0.43)	2.39 (0.099)	2.17 (0.10)		9	2.28±0.18	0.200–35.5
PCB 183	0.960 (0.16)	0.772 (0.031)	0.737 (0.027)	0.93 (0.050)	23	0.838±0.094	0.148–9.26
PCB 187	2.91 (0.46)	3.03 (0.11)	2.88 (0.075)	3.04 (0.50)	5	2.94±0.09	2.23–29.9
4,4′-DDE	60.0 (4.5)	67.6 (2.0)	77.1 (1.5)	72.68 (3.1)	22	69.5±6.3	33.0–433
α-HCH			1.03 (0.053)	1.29 (0.18)	20	1.16±0.18	0.214–4.06
β-HCH	20.8 (1.4)	25.9 (1.5)	28.1 (0.77)		26	24.9±4.3	7.13–39.6
Heptachlor epoxide	4.70 (1.0)	4.32 (0.17)	4.76 (0.38)	4.06 (0.22)	15	4.41±0.3	<0.100–9.85
Oxychlordane	8.36 (0.67)	7.12 (0.23)	6.99 (0.15)	6.28 (0.35)	25	7.16±0.7	1.96–17.7
cis-Chlordane			0.238 (0.014)	0.27 (0.030)	13	0.254±0.024	<0.100–1.41
cis-Nonachlor		2.29 (0.19)	1.46 (0.088)	2.07 (0.090)	36	1.94±0.48	<0.100–10.1
trans-Nonachlor			0.422 (0.037)	0.54 (0.15)	21	0.481±0.1	<0.100–13.9
Dieldrin			3.06 (0.18)	3.62 (0.32)	16	3.34±	0.289–13.5
Mirex		1.75 (0.19)	1.51 (0.088)	1.49 (0.080)	15	1.58±0.16	<0.100–7.49
HCB	25.3 (3.1)	38.2 (1.7)	38.5 (2.2)	33.80 (2.2)	34	34.0±5.3	12.0–123
Pentachlorobenzene			2.34 (0.38)	1.51 (0.18)	36	1.93±0.5	Not determined
Octachlorostyrene			0.985 (0.040)	0.84 (0.040)	14	0.913±0.087	Not determined

[a] Percentage difference=[max−min]/[max]×100%
[b] Expanded uncertainty about the mean (k=2, approximately 95% confidence); see ref. [4] for details
[c] Previously analyzed murre (*Uria* spp.) egg concentrations; see refs. [2, 8] for details
[d] PCB congener numbers are based on the IUPAC system

on the GC/MS). The calibration solution for all batches contained SRMs 2261 (Chlorinated Pesticides in Hexane), 2262 (Chlorinated Biphenyl Congeners in Isooctane), 2274 (PCB Congener Solution-II in Isooctane), 2275 (Chlorinated Pesticide Solution-II in Isooctane), and PCB Congener Solution III (PCBs 45, 56, 63, 70, 74, 82, 92, 107, 132, 146, 157, 158, 163, 174, and 193). The last two batches also included PCB Congener Solution IV (PCBs 79, 106, 113, 114, 119, 121, 127, 130, 137, 159, 165, 166, 167, 172, 175, 176, 177, 178, 185, 189, 191, 193, 196, 197, 200, 199, 202, 203, 205, 207, and 208, and pentachlorobenzene), 14 PBDE Congener Solution (PBDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209), Hexabromocyclododecane Solution (α-, β-, and γ-HBCDD), and octachlorostyrene.

Quality assurance/control

Compounds were quantified based on external calibration curves and internal standards added to the calibration standards and the samples. In addition method blanks and reference materials were employed to ensure method accuracy. The analyses by NIST were performed under the NIST quality system and the analysis by EC was preformed according to published methods [9].

Results and discussion

Additional analytes in SRM 1946 and HGQA

The results for compounds that were not previously value assigned for NIST's SRM 1946 Lake Superior Fish Tissue and EC's Herring Gull Egg Quality Assurance Material (HGQA) are reported in Tables 1 and 2, respectively. The interbatch variance was less than 10% for most compounds. PCBs 92+84+89 and 163 appear to have lower values with GC/MS compared to GC-ECD, potentially indicating co-elutions when using GC-ECD.

Murre egg control material

Results for the TEOs, PCBs and organochlorine pesticides with consensus means and expanded uncertainties for the murre egg CM are listed in Table 3. The consensus means and expanded uncertainties were compared to the two previous reference materials used for analysis of seabird eggs by STAMP: EC's HGQA and NIST's SRM 1946 (Figs. 2, 3 and 4). Contaminants in the murre egg CM with concentrations below the method detection levels are not reported here (PCBs 18, 29, 31, 44, 45, 49, 50, 63, 82, 87, 92, 95, 104, 107, 110, 114, 137, 151, 154, 174, 176, 188, 189, 193, 194, 195, 196, 199, 200, 201, 202, 206, 207, 208, and 209, and 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 2,4′-DDT, 4.4′-DDT, γ-HCH, and *trans*-chlordane). The PBDE values are a combination of the concentrations determined by methods 2 and 3 (Fig. 1), and only two replicates were used for method 2. Only consensus means and expanded uncertainties for the major PBDE congeners (PBDEs 47, 99, 100, and 138) were compared to SRM 1946 (Fig. 4). The remaining PBDE congeners were either near or below the methods' detection limits.

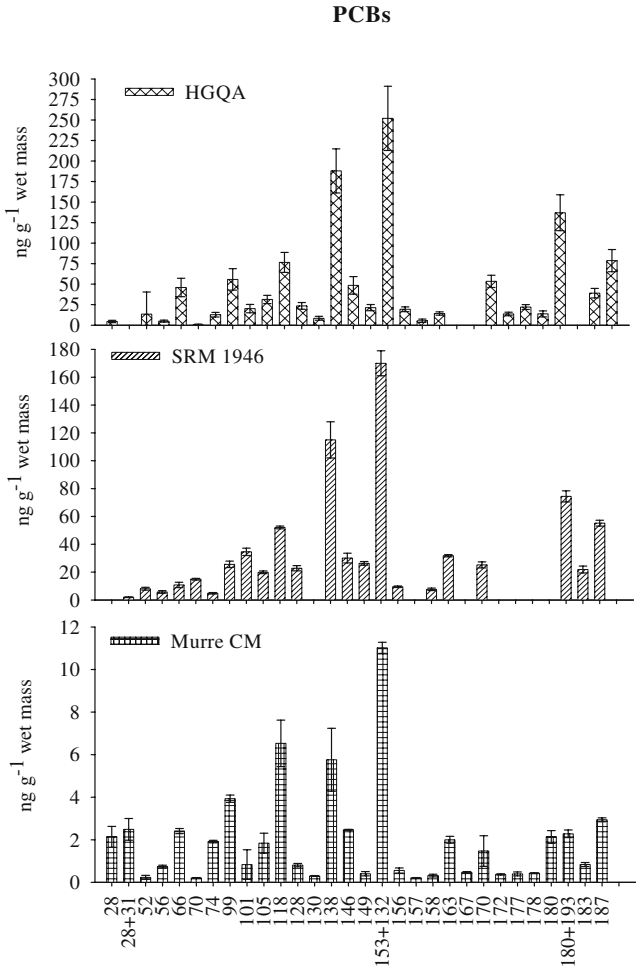

Fig. 2 Consensus means and expanded uncertainties for murre (*Uria* spp.) egg control material (CM) compared to SRM 1946 and herring gull egg quality assurance (HGQA) material reference values for PCB congeners based on IUPAC system

The predominant compound for each contaminant group (PCB 153+132, 4,4′-DDE, and BDE 47) in the new murre egg CM were the same as in the previously used reference materials, but the patterns and values were different. Some of the pattern differences may be related to the higher latitudes where the murre eggs were collected. Several studies have correlated increases of HCB levels and

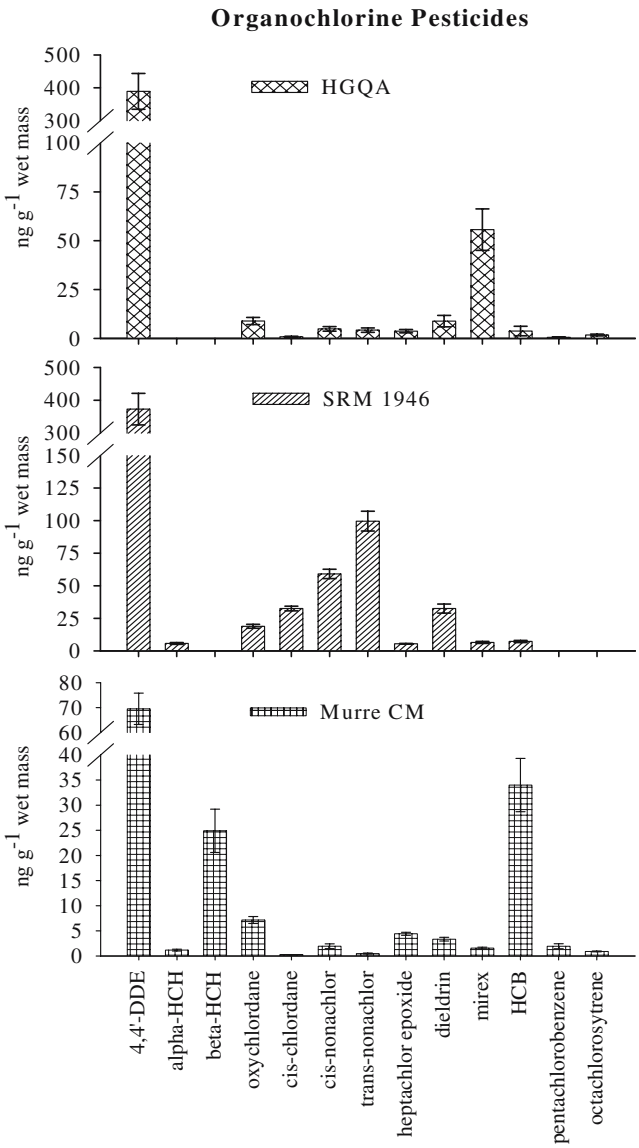

Fig. 3 Consensus means and expanded uncertainties for murre (*Uria* spp.) egg control material (CM) compared to SRM 1946 and herring gull egg quality assurance (HGQA) material reference values for organochlorine pesticides

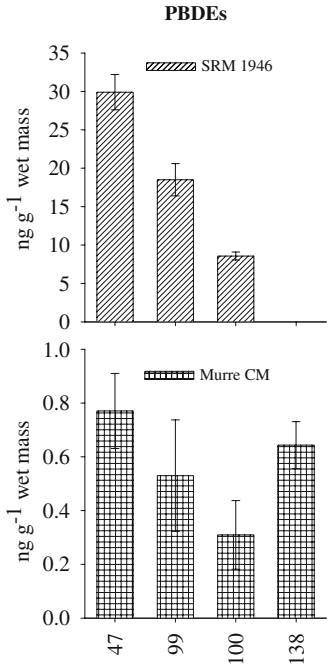

Fig. 4 Consensus means and expanded uncertainties for murre (*Uria* spp.) egg control material (CM) compared to SRM 1946 reference values for PBDE congeners

decreases in lower chlorinated PCB values to increases in latitude [10–12].

The values for the murre egg CM are within (although near the lower limit) the range of concentrations previously reported for STAMP murre eggs (Table 3) [2, 8]. As discussed elsewhere, contaminant concentrations in Alaskan murre eggs tend to be lower than values reported in Eastern Canada and Europe [8]. The BDE 47 and 99 values for the murre egg CM (mean of 0.77 and 0.53 ng g^{-1} wet mass, respectively) are also an order of magnitude lower than those reported for common murre eggs from the Baltic Sea (mean of 11 and 1.5 ng g^{-1} wet mass, respectively) [13]. At approximately 58 ng g^{-1} wet mass for total PCBs (63 congeners), the murre egg CM has a slightly higher concentration than recently reported for spectacled eider (*Somateria fischeri*) eggs from the Yukon-Kuskokwim Delta, Alaska (6.3–54.7 ng g^{-1} wet mass) [14].

STAMP will use the new murre egg CM in all future analyses of Alaskan seabird eggs. If other laboratories begin requesting samples of the new control material, a murre egg SRM may be developed to fulfill the demand.

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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.

References

1. York GW, Porter BJ, Pugh RS, Roseneau DG, Simac K, Becker PR, Thorsteinson LK, Wise SA (2001) Seabird Tissue Archival and Monitoring Project: protocol for collecting and banking seabird eggs. NISTIR 6735, Gaithersburg, MD
2. Vander Pol SS, Christopher SJ, Roseneau DG, Becker PR, Day RD, Kucklick JR, Pugh RS, Simac KS, York GW (2003) Seabird Tissue Archival and Monitoring Project: egg collections and analytical results for 1999–2002. NISTIR 7029, Gaithersburg, MD
3. Zeisler R, Langland JK, Harrison SA (1983) Anal Chem 55:2431–2434

4. Guide to the expression of uncertainty in measurement (1993) ISBN 92-67-10188-9, 1st edn. ISO, Geneva, Switzerland; see also Taylor BN, Kuyatt CE (1994) Guidelines for evaluating and expressing the uncertainty of NIST measurement results. NIST Technical Note 1297, US Government Printing Office, Washington, DC (available at http://physics.nist.gov/Pubs)
5. Poster DL, Kucklick JR, Schantz MM, Porter BJ, Leigh SD, Wise SA (2003) Anal Bioanal Chem 375:223–241
6. Poster DL, Kucklick JR, Lopez de Alda MJ, Porter BJ, Pugh RS, Schantz MM, Wise SA (2004) Anal Bioanal Chem 378:1213–1231
7. Wise SA, Poster DL, Schantz MM, Kucklick JR, Sander LC, Lopez de Alda MJ, Schubert P, Parris RM, Porter BJ (2004) Anal Bioanal Chem 378:1251–1264
8. Vander Pol SS, Becker PR, Kucklick JR, Pugh RS, Roseneau DG, Simac KS (2004) Environ Sci Technol 38:1305–1312
9. Won, HT, Mulvihill, MJ, Wakeford, BJ (2001) Multiresidue methods for the determination of chlorinated pesticides and polychlorinated biphenyls (PCBs) in wildlife tissues by gas chromatography/mass spectrometry. Technical Report Series No 335E, Canadian Wildlife Service, Headquarters, Hull Québec, Canada
10. Simonich SL, Hites RA (1995) Science 269:1851–1854
11. Ockenden WA, Sweetman AJ, Prest HF, Steinnes E, Jones, KC (1998) Environ Sci Technol 32:2795–2803
12. Sobek A, Gustafsson Ö (2004) Environ Sci Technol 38:2746–2751
13. Sellström U, Bignert A, Kierkegaard A, Häggberg L, De Wit CA, Olsson M, Jansson B (2003) Environ Sci Technol 37:5496–5501
14. Wang D, Huelck K, Atkinson S, Li QX (2005) Bull Environ Contam Toxicol 75:760–767