CONGENER-SPECIFIC PCB ANALYSIS OF NATIVE FOODS FROM NUNIVAK AND ST. LAWRENCE ISLANDS, ALASKA

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Introduction

Many rural indigenous communities in Alaska rely on traditional foods for a significant portion of their dietary intake and cultural traditions. A survey of eleven Alaskan native villages in the late 1980's determined that a traditional subsistence diet provided nearly 50% of essential nutritional intake, including protein, iron, vitamin B_{12}, and omega-3 fatty acids[1]. Fish was determined to be the most common source of protein in native diets, accounting for a majority of the total food harvest[1]. In many villages significant cultural traditions are associated with the rituals of harvesting and consumption of native foods. Although the dietary and cultural importance of traditional food consumption has been established, little data is available on contaminant levels, associated dietary uptake, and potential health effects of organochlorine contaminants found in traditional foods. The purpose of this study was to provide a preliminary assessment of persistent and bioaccumulative organochlorine contaminants in a variety of traditional native foods from Nunivak and St. Lawrence Islands. Future work will integrate dietary surveys, contaminant exposure, and potential health effects to native populations.

Methods and Materials

Bering Sea native food samples were collected in the vicinity of Nunivak and St. Lawrence Islands, Alaska. Pacific halibut (*Hippoglossus stenolepis*), chum salmon (*Oncorhynchus keta*), Pacific herring (*Clupea pallasii*), tomcod (*Eleginus gracilis*), skate (genus *Raja*), and common murre (*Uria aalge*) eggs were collected for analysis. Tissue samples of muscle, liver, and composite whole fish and egg samples were analyzed for congener-specific polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), p-p' dichlorodiphenyldichloroethylene (DDE), and mirex at the Environmental Research Center of the State University of New York at Oswego. Bering Sea samples were collected as part of subsistence food harvests in the vicinity of Nunivak Island (NI), Alaska during the year 2000 field season by Larson King and Derek King. Murre eggs were collected by Wilfred Miklahouk and Douglas Gologergen during June 2001 from St. Lawrence Island (SLI), Alaska.

Homogenized samples were extracted for gas chromatographic analysis after methods developed at the SUNY Oswego Environmental Research Center[2]. Pre-cleaned anhydrous sodium sulfate (approximately 10 times sample weight) was added, and the sample extracted three times each with 50 mL hexane using a Brinkman Polytron homogenizer (Model PT 10/35) with large generator (PTA-10L). After each extraction, the hexane extracts were transferred into a volumetric flask and brought to volume. Lipid analysis was conducted by gravimetric procedures utilizing an aliquot (subsample) of the extracted sample. The remaining sample was used for congener-specific PCB analyses. The PCB sample extract was treated three times with concentrated sulfuric acid; and further treated with tetrabutylammonium hydrogen sulfate (TBA);

and condensed to 2 mL in a Kuderna-Danish (K-D) apparatus using a 3-ball Snyder Column on a steam bath for alumina adsorption column cleanup[3]. Column clean-up utilized 6-8 grams of alumina placed in a 10x350 mm Chromaflex column equipped with a 250 mL reservoir, with an upper layer (2 g) of anhydrous sodium sulfate held in place with silanized glass wool. The sample extract was added to the alumina column and eluted with 200 mL of hexane, which was concentrated in K-D apparatus to 1-2 mL for gas chromatographic analysis.

Congener-specific PCB, hexachlorobenzene (HCB), p-p' DDE, and mirex analyses were conducted based on capillary column procedures previously described[2,3,4]. Briefly, analytical instruments were calibrated every five samples, with a system blank and calibration check solutions analyzed during each analytical run. A Hewlett-Packard (HP) Model 5890II GC with an electron capture detector (ECD - Ni^{63}) and autosampler was used for data acquisition. The capillary column utilized was a HP Ultra II, 25 meter with 0.22 mm id and 0.33 *u*m film thickness. The calibration standard is a 1:1:1:1 mixture of Aroclors 1221, 1016, 1254, and 1260 each at 200 pg/uL, hexachlorobenzene (HCB) at 5 pg/uL, and p-p' DDE and Mirex each at 10 pg/uL (AccuStandard, Inc.), which allows for the analysis of 100 chromatographic zones of 132 congeners/co-eluters. Laboratory Quality Assurance/Quality Control at the SUNY Oswego ERC is based on a program developed from USEPA protocols[5]. The program consists of replicate analyses, surrogate analyte recoveries (IUPAC 14, 30 IS, 65, 166, and 209), matrix spikes/matrix spike duplicates and, method, reagent and system blanks at prescribed intervals.

Results and Discussion

Average analytical results for the Nunivak and St. Lawrence Island samples are presented in Table 1. Sample PCB concentrations ranged between 4.2 and 87.9 ng/g wet weight for the tissues. HCB, DDE, and Mirex concentrations ranged between 0.2-39.4, nondetected (nd)-78.2, and nd-1.8 (ng/g wet weight), respectively. As expected, comparison of the PCB and lipid results indicates a significant correlation (r = 0.9358) between sample lipid levels and wet weight total PCB values. The four highest lipid samples (herring, skate and halibut liver, and murre eggs) on average, have PCB and organochlorine concentrations ranging from 4-10X the remaining lower lipid samples. The relative magnitude of the select organochlorine pesticides measured for the NI and SLI samples warrants discussion. Interestingly, the average p-p' DDE and total PCB concentrations in the murre eggs are nearly equal, averaging ~ 80 ng/g – wet weight basis. Hexachlorobenzene was also found as a significant contaminant in the murre eggs and halibut livers, averaging 39.4 and 10.5 ng/g, respectively. Mirex, a contaminant generally associated with the Great Lakes/St. Lawrence River basin was identified in both liver samples (skate and halibut) and murre eggs at concentrations over 1 ng/g.

Table 2 reveals the descriptive statistics for the principal contaminants found in the St. Lawrence Island murre eggs (N=11) based on wet weight. By far the most prevalent contaminant is the environmentally persistent organochlorine pesticide p-p'-DDE. Hexachlorobenzene is second on the list, with IUPAC PCB153 being the most common PCB congener, followed by PCB118, PCB138+163+164, PCB66+95, PCB99, PCB56+60+92, and PCB 146.

Table 3 displays the average mole % PCB homologue distribution and average number of chlorines per biphenyl (Avg. Cl/BP) for the NI and SLI samples. Homologue based mole percent PCB calculations are concentration independent, and correct for the substantial difference in PCB

molecular weights associated with increased PCB chlorination. The use of average total Cl/BP calculations allow an assessment of overall sample chlorination, which can be directly related to other samples or original technical Aroclor PCB mixtures. As you will note, nearly 80% of the PCBs found in the NI and SLI samples were found in PCB homologues with 4, 5, and 6 chlorines per biphenyl. The remaining PCB homologues are present in small concentrations, with the exception of a relatively enriched pattern in the di-chloro PCB homologue group for the halibut liver and herring samples. For comparison with the NI and SLI samples, the average number of chlorines per biphenyl (Cl/BP) for Aroclor 1248 and Aroclor 1254 standards measured in the ERC labs were 3.86 and 5.07 Cl/BP, respectively.

Table 1. Average results of Nunivak and St. Lawrence Island biota for % lipids, total PCB, HCB, DDE, and Mirex in ng/g (wet weight).

Average Sample	N	Lipids (%)	Avg. PCB (ng/g)	Avg. HCB (ng/g)	Avg. DDE (ng/g)	Avg. Mirex (ng/g)
Nunivak Island						
Chum Muscle	6	1.1	7.00	0.47	0.80	0.01
Chum Liver	6	1.4	5.67	0.43	0.18	0.02
Halibut Muscle	6	0.4	4.82	0.19	0.29	0.01
Skate Muscle	1	0.4	4.16	0.15	0.02	0.01
Tomcod Composite	2	1.5	7.30	0.36	0.00	0.00
Halibut Liver	5	27.7	79.55	10.48	10.14	1.22
Herring Composite	4	8.4	23.11	2.00	2.07	0.09
Skate Liver	1	17.1	87.91	6.64	1.47	1.75
St. Lawrence Island						
Murre Eggs	11	11.9	81.78	39.37	78.17	1.51

Table 2. Rank order and descriptive statistics for contaminants (ng/g - wet weight) measured in St. Lawrence Island murre eggs (N=11).

IUPAC	Avg.	Median	Min.	Max.	StdDev.
DDE	78.17	57.79	26.48	242.26	59.63
HCB	39.37	40.44	22.86	55.87	10.02
153	9.76	8.67	2.78	22.40	5.02
118	8.93	7.50	4.31	19.22	4.41
138+163+164	7.44	6.22	2.64	18.81	4.31
66+95	5.83	4.77	3.63	9.38	2.62
99	5.12	4.71	1.49	10.22	2.33
56+60+92	2.97	3.09	1.92	4.62	1.17
146	2.66	2.48	1.17	5.33	1.03

Table 3. Mole % and average number of chlorines per biphenyl (avg. Cl/BP) for Nunivak and St. Lawrence Island samples.

Mole %	Chum Muscle	Chum Liver	Halibut Muscle	Skate Muscle	Tomcod	Halibut Liver	Herring	Skate Liver	Murre Eggs
Cl 1	0.92	3.12	0.00	0.00	0.00	6.36	3.37	0.00	0.00
Cl 2	6.71	9.75	6.65	5.13	11.72	20.16	18.62	14.84	5.36
Cl 3	13.60	8.87	12.05	11.20	9.50	3.91	5.43	0.59	6.83
Cl 4	31.57	27.22	26.70	27.69	26.84	19.59	27.39	15.97	16.84
Cl 5	26.65	30.30	32.90	36.80	32.78	27.88	27.91	38.86	31.72
Cl 6	15.07	14.08	14.13	14.28	10.71	18.11	12.98	22.94	27.76
Cl 7	3.97	4.03	4.79	3.30	6.65	3.41	3.67	5.71	9.33
Cl 8	0.96	0.95	1.48	0.94	1.34	0.55	0.40	0.94	1.95
Cl 9	0.55	1.66	1.30	0.65	0.45	0.03	0.24	0.15	0.22
Avg. Cl/BP	4.46	4.45	4.63	4.61	4.49	4.13	4.15	4.76	5.07

Conclusions

The four highest lipid samples (herring, skate and halibut liver, and murre eggs) on average, have PCB and organochlorine concentrations ranging from 4-10X the remaining lower lipid samples. Murre eggs have significantly higher concentrations of the select organochlorine pesticides measured in this study.

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