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Running Head: Metals in Farmed and Wild Salmon

Corresponding Author: Jeffery A. Foran, 5005 N. Palisades Rd. ,Whitefish Bay, WI 53217. E: Jforan@wi.rr.com P: 414-963-9299 F: 414-273-7293

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A Survey of Metals in Tissues of Farm-raised and Wild Salmon

Short Communication

Jeffery A. Foran†, Ronald A. Hites‡, David O. Carpenter§, M. Coreen Hamilton||, Amy Mathews-Amos#, Steven J. Schwager††

† School of Natural Resources and Environment, University of Michigan, and Citizens for a Better Environment, 5005 N. Palisades Rd., Whitefish Bay, WI 53217

‡ Environmental Science Research Center, School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, IN 47405

§ School of Public Health and Institute for Health and the Environment, University at Albany, Rensselaer, NY 12144

|| Axys Analytical Services Ltd., P. O. Box 2219, 2045 Mills Road, Sidney, British Columbia, Canada V8L 3S8

Turnstone Consulting, 205 N. Edgewood Street, Arlington, VA 22201

†† Department of Biological Statistics and Computational Biology, 434 Warren Hall, Cornell University, Ithaca NY 14853

Abstract

Nine metals were measured in farm-raised and wild salmon from the United States, Canada, Chile, and Norway. Only organic arsenic was significantly higher in farm-raised compared to wild salmon, and none of the contaminants exceeded federal standards or guidelines.

Key Words: Metals, Farmed Salmon, Wild Salmon

Introduction

The occurrence of persistent and bioaccumulative chemicals in tissues of freshwater and marine organisms is a problem of global significance. In the U.S., every state except Colorado and Alaska has issued fish consumption advisories for specific bodies of water. In 2000, there were 2,242 such advisories based on mercury, 726 advisories based on PCBs, and lesser numbers based on chlorinated pesticides and dioxins (http://www.epa.gov/OST/fishadvice/) [1].

This problem has been documented most thoroughly in regions such as the Great Lakes where fish tissue concentrations of PCBs, mercury, and other organic and inorganic compounds have been monitored for more than twenty years [2,3,4]. Recently, this problem became more widely publicized as a result of warnings issued by the U.S. Food and Drug Administration (http://www.cfsan.fda.gov/~dms/admehg.html) for women and children to reduce or eliminate consumption of commercially sold shark, swordfish, mackerel, and tilefish due to mercury contamination.

Salmon, which was not included in the recent FDA consumption advisory, is a very popular fish for human consumption and is a healthy source of protein and omega-3 polyunsaturated fatty acids. [5,6]. Over the last several years, commercially-sold salmon (salmon purchased in stores and restaurants as opposed to those caught by sport anglers) has become increasingly popular due to its availability and lower price, which are the result of a practice commonly referred to as fish farming or aquaculture. Today, farm-raised salmon comprise the majority of fish consumed in commercial markets [7]. However, despite this increasing popularity, only minimal attention has been paid to contaminants in farmed salmon.

We conducted the first global analysis of over 40 contaminants in farm-raised and wild salmon, and have reported the results for organic contaminants in the tissues of these fish [8]. We also measured metals from a smaller set of farmed and wild salmon and report here the results of this analysis and a comparison of levels with federal regulatory thresholds and non-regulatory guidance.

Methods and Materials

Sampling

All fish sampled in this study were farm-raised or wild salmon. Farm-raised Atlantic salmon (*Salmo salar*) were purchased from commercial suppliers in the United States and Canada and were selected to include salmon farmed in Canada, Chile, Maine, the United States, and Norway. Three suppliers provided fish from each region. For comparison purposes, four suppliers provided wild Pacific salmon from the United States and Canada. The wild fish included Chum (*Oncorhynchus keta*) and Coho (*Oncorhynchus kistuch*). The viscera from all fish were removed before they were shipped and the heads and gills were left on the fish.

All samples came to the analytical laboratory (Axys Analytical in Sidney, British Columbia) fresh or frozen on ice or gel-packs. The fish were thawed and inspected by a fisheries biologist to verify species. Each fish was weighed and its length was measured. In each case, ten fish were ground and re-ground together to make a homogenous composite.

Analysis

Analyses were conducted by Frontier Geosciences Inc., Seattle, Washington. Arsenic, copper, cobalt, strontium, cadmium, selenium, lead, and uranium were measured as follows: Approximately 0.5 g of the homogenized fish tissue was digested in 10-mL of concentrated nitric acid for 5 hours and diluted to 40 mL with reagent water. Metals were quantified by argon inductively coupled plasma mass spectrometry (ICP-MS) on a Perkin-Elmer ELAN 6000 instrument. Scandium was used as the internal standard for cobalt and copper; indium was used as the internal standard for arsenic, strontium and tin; and platinum was used as the internal standard for lead and uranium. The arsenic ion at m/z 75 was corrected for a small interference from the plasma due to ArCl. Total inorganic arsenic was quantified using hydride generation, cryogenic trapping, gas chromatography, atomic absorption spectrometry at a sample pH < 2.

For mercury analysis, approximately 0.5 g of the fish tissue was digested in 10-mL of 25% KOH/methanol for 2 hours at 60 °C and diluted to 40 mL with methanol. A 10-mL aliquot of the original digestate was diluted with 30 mL of 50% 0.2 N BrCl to oxidize all of the mercury to Hg^{++}. Total mercury was determined by $SnCl_2$ reduction, and dual gold amalgamation using cold-vapor atomic fluorescence spectrometry (CVAFS). Methyl mercury was then determined on a separate aliquot of the digestate using aqueous phase ethylation purging onto Carbotrap, isothermal GC separation, and CVAFS. Calibration standards were NIST certified or traceable to NIST certified materials. Methyl mercury (MeHg) standards were made from pure powder and calibrated for MeHg (equal to total mercury minus ionic mercury) against NBS-3133 and cross verified by analysis of NRCC DORM-2, a fish muscle reference sample from the National Research Council of Canada (NRCC). The majority of the mercury in muscle tissue is methylated and measurements for total mercury and methyl mercury gave similar results for each sample; thus, these measurements were considered duplicate measurements and were averaged.

QA/QC

All metals analyses were conducted in accordance with Frontier Geosciences accredited QA/QC program. The analysis batch of 18 samples also included the following QA/QC samples: four procedural blanks, two reference samples (DORM-2 and DOLT-3 supplied by the NRCC), a spiked matrix and a spiked matrix duplicate, and an analysis duplicate. The sample results were reviewed and evaluated in relation to the QA/QC samples worked up at the same time. All blank measurements were near or below the detection limits; hence, blank values were never subtracted from the sample measurements. Results for reference samples and spiked matrix samples were in the range of 75 to 125% recovery. Duplicate analyses differed from each other by less than 25%.

Results and Discussion

Concentrations of nine metals are presented in Table 1 in milligrams of contaminant per kilogram wet weight of whole fish (mg/kg), except for concentrations of methyl mercury, which are reported in nanograms per gram wet weight (ng/g wet). As it was not our purpose to isolate variations in contaminant concentrations among suppliers or geographic regions, we treated all farmed salmon as replicates and all wild salmon as replicates. Each measured sample was the composite of 10 individual fish; and a total of 180 fish were analyzed. The averages and standard errors of the replicate measurements were compared using Student's *t*-test. The critical values for these *t*-statistics vary with the appropriate degrees of freedom specified by the Welch modified two-sample *t*-test for unequal variances [9].

Total arsenic concentrations in the farm-raised fish were higher (at the $\alpha = 0.05$ significance level) than in the wild fish. However, inorganic arsenic was not detectable (the limit of detection was 4 ng/g wet weight) in these samples, consistent with other analyses indicating that arsenic is present in fish tissues in the relatively non-toxic organic form (www.epa.gov/ost/fishadvice/volume2/v2ch5.pdf). Methyl mercury concentrations were higher in the wild than in farm-raised salmon, although the difference is not statistically significant. There were no statistically significant differences between farmed and wild salmon for any other metal.

Concentrations of organic contaminants, including PCBs, dioxin, PBDEs, and several organic pesticides are highly and significantly elevated in farm-raised compared with wild salmon [8]. This difference appears to be, at least in part, a function of the feed provided to farmed salmon [8, 10]. Farm-raised salmon are also significantly larger, heavier, and fatter [8]. These differences do not, however, appear to have an effect on metal concentrations in farmed or wild salmon.

There are regulatory standards and guidance to address the health effects of some metals in fish tissues. The U.S. FDA has established action or tolerance levels for mercury, arsenic, cadmium, chromium, and lead, and U.S. EPA methods allow development of consumption advisories for arsenic, cadmium, methyl mercury, and selenium. The most stringent levels of these contaminants are reported in Table 2. None of the metals in farmed or wild salmon exceed FDA or EPA levels, and most concentrations were one or more orders of magnitude below these levels.

This paper addresses contaminants in whole salmon homogenates, which people generally do not eat, but which were analyzed to determine if there were sufficient grounds for the pursuit of a more elaborate study of salmon fillets. While our initial study did, indeed, trigger a larger effort to analyze organic contaminants in fillets [8], it did not warrant further research on metals.

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Table 1. Wet weight concentrations (mg/kg, mercury - ng/g) of 9 metals in farm-raised and wild salmon[a]

	Farmed Atlantic Salmon													**Wild Salmon**								
ocation	**BC**	**BC**	**Chile**	**Chile**	**Chile**	**ME**	**ME**	**ME**	**ME**	**Nor**	**Nor**	**Avg.**	**Std Error**	**Alaska**	**Alaska**	**Alaska**	**WA**	**WA**	**BC**	**Avg.**	**Std. Error**	***t*-**
ecies	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Atl**	**Chum**	**Coho1**	**Coho2**	**Chum**	**Coho**	**Chum**	**Wild**	**Wild**	
obalt	0.06	0.04	0.07	0.03	<	0.03	0.03	0.05	<	0.03	0.03	0.041	0.004	0.07	0.06	0.06	0.08	0.10	0.06	0.07	0.01	-
opper	0.40	0.61	0.42	0.46	0.44	0.36	0.42	0.41	0.39	0.37	0.57	0.441	0.024	0.62	0.68	0.56	0.58	0.56	0.61	0.57	0.04	-
rontium	10.1	15.0	12.8	22.1	14.6	14.2	11.1	9.9	25.0	14.7	27.2	16.06	1.80	15.3	1804	13.0	23.2	10.3	10.4	14.68	1.65	
admium	<	<	<	<	<	<	<	<	<	<	<	NA	NA	<	0.006	0.006	0.004	0.006	<	0.01	0.001	
lenium	0.013	0.005	0.005	0.004	0.013	0.005	0.008	0.006	0.008	0.004	0.011	0.007	0.001	0.005	0.012	0.007	0.007	0.005	0.005	0.01	0.001	0
ead	<	0.002	0.004	0.001	0.007	0.006	0.001	0.004	0.004	0.002	0.002	0.003	0.001	0.001	0.005	0.003	0.003	0.002	0.002	0.002	0.001	0
ranium	<	0.001	<	0.001	<0.001	<	0.002	<	0.003	<	0.008	0.002	0.001	0.004	0.001	<	0.004	<	0.002	0.001	0.002	-1
rsenic	0.49	0.39	0.45	0.51	0.33	0.38	1.06	0.48	1.41	0.51	1.44	0.678	0.126	0.41	0.38	0.49	0.29	0.38	0.30	0.39	0.03	<u>2</u>
eth Hg	18.4	13.2	11.9	19.8	17.9	18.6	38.7	15.4	25.5	28.9	13.6	20.17	2.42	30.0	21.0	27.0	21.0	17.0	27.0	23.8	2.0	-

a. Non-detects (<) are given as less than the detection limit, but statistical calculations used zero for these values. Detection Limits: Co – 0.03 mg/kg; Cd – 0.003 mg/kg; Pb – 0.001 mg/kg; Ur – 0.001 mg/kg

b. The *t*-test values are bold and underscored if the difference between the farm-raised and wild fish concentrations is significant with >95% confidence.

c. Abbreviations:

Atl – Farm-raised Atlantic Salmon

BC – British Columbia

ME – Maine

WA – Washington

Table 2. FDA action/tolerance levels, and the lowest contaminant concentration that would trigger a consumption advisory using U.S. EPA methods

Contaminant	**FDA Tolerance/ Action Level (mg/kg)**	**EPA Consumption Advisory Trigger (mg/kg)**
Arsenic (inorg)	76.0*	0.002[a]
Cadmium	3.0	0.088[b]
Selenium	NA	1.5[b]
Chromium	12.0*	NA
Methyl Hg	1.0	0.029[b]
Lead	1.5*	NA

* FDA Action/Tolerance not available for fish. Level for crustaceans.

a Based on cancer risk at the 1×10^{-5} risk level

b Based on non-cancer risk