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Abstract. Organochlorine chemical residues and elemental contaminants were measured in northern pike (*Esox lucius*), longnose sucker (*Catostomus catostomus*), and burbot (*Lota lota*) from 10 sites in the Yukon River Basin (YRB) during 2002. Contaminant concentrations were compared to historical YRB data and to toxicity thresholds for fish and piscivorous wildlife from the scientific literature. A risk analysis was conducted to screen for potential hazards to piscivorous wildlife for contaminants that exceeded literature-based toxicity thresholds. Concentrations of total DDT (sum of *p*,*p*′-homologs; 1.09–13.6 ng/g), total chlordane (0.67–7.5 ng/g), dieldrin (<0.16–0.6 ng/g), toxaphene (<11–34 ng/g), total PCBs (<20–87 ng/g), TCDD-EQ (≤1.7 pg/g), arsenic (0.03–1.95 μg/g), cadmium (<0.02–0.12 μg/g), copper (0.41–1.49 μg/g), and lead (<0.21–0.27 μg/g) did not exceed toxicity thresholds for growth and reproduction in YRB fish. Concentrations of mercury (0.08–0.65 μg/g), selenium (0.23–0.85 μg/g), and zinc (11–56 μg/g) exceeded toxicity thresholds in one or more samples and were included in the risk analysis for piscivorous wildlife. No effect hazard concentrations (NEHCs) and low effect hazard concentrations (LEHCs), derived from literature-based toxicity reference values and avian and mammalian life history parameters, were calculated for mercury, selenium, and zinc. Mercury concentrations in YRB fish exceeded the NEHCs for all bird and small mammal models, which indicated that mercury concentrations in fish may represent a risk to piscivorous wildlife throughout the YRB. Low risk to piscivorous wildlife was associated with selenium and zinc concentrations in YRB fish. Selenium and zinc concentrations exceeded the NEHCs and LEHCs for only the small bird model. These results indicate that mercury should continue to be monitored and assessed in Alaskan fish and wildlife.

The Yukon River is among the largest rivers in North America. Originating in northwestern British Columbia, Canada, it flows 3219 km through the Yukon Territory and central Alaska into the Bering Sea (Brabets *et al.* 2000). The Yukon River Basin (YRB), which comprises 854,700 km^2, receives most of its inflow as runoff from rainfall, snowmelt, and glacial melt and is the major contributor of water and solutes to the Bering Sea (Aagaard and Carmack 1989; Brabets *et al.* 2000; Schumm and Winkley 1994). The Yukon River and its tributaries are also the major transportation corridors of interior Alaska and provide food for subsistence living and drinking water for many rural villages. The YRB supports an array of habitats important to the diverse Alaskan fish and wildlife fauna, including salmon spawning areas (Eiler *et al.* 2004) and summer breeding grounds for migratory birds (NPS 2005; USFWS 2005).

Although much of the YRB is considered pristine, extraction and processing of natural resources, including precious metals, minerals, coal, oil, and natural gas, are important economic activities that can affect water quality (Brabets *et al.* 2000). Alaska's mining industry has a cumulative annual value of more than $1 billion, and expenditures for mining exploration and development have been increasing (Szumigala *et al.* 2003). In 2003, $7.5 million (26%) of exploration investments and $26.1 million (67%) of development investments were spent in the YRB near the Tanana River upstream of Fairbanks, an area rich in gold and other precious metals (Szumigala *et al.* 2003). This region in eastern Alaska has the largest number of placer mines and the greatest amount of exploratory drilling in the state, and the Fairbanks and Circle mining districts are among the top gold producers (Szumigala *et al.* 2003). Mineral exploitation will increase when the Pogo Mine, one of the largest underground gold mines, becomes operational in 2006 (Szumigala *et al.* 2003). In addition to gold, large coal deposits near Healy have been mined for 60 years, and mining of new deposits began in 2003 (Szumigala *et al.* 2003). Coalbed seams, which underlay many rural villages in the YRB, are being drilled to determine if methane could be an alternative fuel in remote areas of the YRB (Alaska Division of Geological and Geophysical Surveys 2005). Exploitation of these natural resources may release contaminants into YRB waters.

Mining for gold, other precious metals, including lead and zinc, and coal have caused trace metal contamination and habitat degradation for anadromous fish in the YRB (Buhl and Hamilton 1990; Salomone and Bergstrom 2004; USFWS 1986, 1991). Oil exploration and transportation are also

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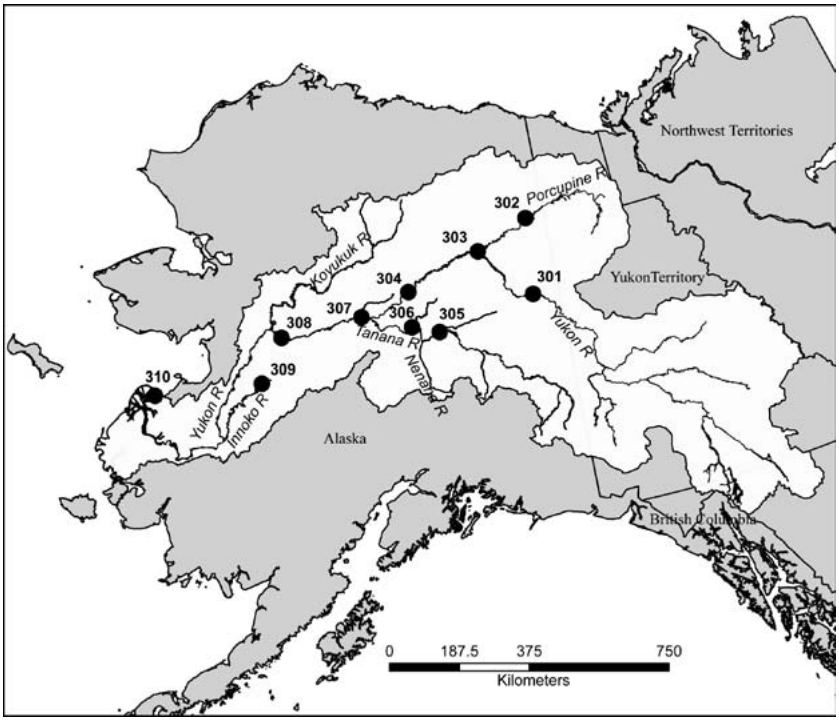

Fig. 1. Map of the Yukon River Basin illustrating waterways, state and territory boundaries, and locations sampled

potential contaminant sources (USBLM 2002). Organochlorine contaminant concentrations have been low historically (Schmitt *et al.* 1999; Snyder-Conn 1992) and primarily associated with military facilities near Fairbanks (Alaska Department of Environmental Conservation 2003; Mueller and Matz 2000; USEPA 1998). The YRB ecosystem might be susceptible to a variety of organochlorine contaminants, including *p,p′*-DDT, toxaphene, chlordane, and polychlorinated biphenyls (PCBs) introduced by long-range atmospheric transport (Barrie *et al.* 1992; Braune *et al.* 1999; Evans *et al.* 2005; Muir *et al.* 1999). In addition, the relationship between mercury emissions and methylmercury accumulation in aquatic food chains is poorly understood in arctic and subarctic regions (Mason *et al.* 2005).

In spite of the potential for multiple contaminant sources, monitoring contaminants in fish from the Alaska part of the YRB has been limited (Schmitt *et al.* 1999). Therefore, the objectives of this study were to document organochlorine and elemental contaminant concentrations in YRB fish and to evaluate the risk of these contaminant concentrations to fish and piscivorous wildlife. These objectives were achieved by collecting and preparing samples of fish from the YRB, measuring organochlorine and elemental contaminant concentrations, and assessing the risks of contaminants through comparisons with toxicity thresholds from the scientific literature and risk analysis modeling.

Methods

An overview of the methods is presented here. More detail is provided by Hinck *et al.* (2004a).

Sampling Sites and Field Collection

Adult northern pike (*Esox lucius*; henceforth, pike) or burbot (*Lota lota*) and longnose sucker (*Catostomus catostomus*; henceforth, sucker) were collected by hook and line, gill net, or fyke net at 10 sites from early May to mid-October 2002 (Fig. 1 and Table 1). Fish were wrapped in aluminum foil and frozen (−20°C) for analysis of organochlorine residues, elemental contaminants, and dioxin-like activity.

Laboratory Analyses

Individual fish were ground to a fine texture, and 15% of the total body weight was subsampled (42–1200 g) to maintain the proportional size representation of each fish in a composite sample. The ground subsamples were grouped by site, species, and gender and reground to create an homogenous composite sample. The composite sample was then subsampled (200 g) and refrozen (−20°C). All fish collected were included in a composite sample, and the number of fish in each composite sample ranged from 1 to 15. All equipment was disassembled and chemically cleaned between composite samples to prevent cross-contamination.

Dichloromethane extracts (0.1 g) of a 10-g subsample were analyzed gravimetrically for lipid content. Samples were analyzed by high-resolution capillary gas chromatography with electron capture detection (GC-ECD) for 29 organochlorine pesticide residues and total PCBs after size exclusion and adsorption column cleanup procedures (Hinck *et al.* 2004a). Total PCBs were reported as the sum of 137 congeners (001, 003, 004, 005, 006, 007, 008, 009, 010, 015, 016, 017, 018, 019, 020, 022, 024, 025, 026, 027, 028, 031, 032, 033, 034, 035, 037, 040, 041, 042, 043, 044, 045, 046, 047, 048, 049, 051, 052, 053, 054, 055, 056, 059, 060, 063, 064, 066, 067, 069, 070, 071, 072, 074, 075, 082, 083, 084, 086, 087, 090, 091, 092, 094, 095, 096, 097, 099, 101, 102, 105, 109, 110, 114, 115, 117, 118, 119, 122, 123, 124, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 141, 144, 146,

Table 1. Location and fish collection dates in the Yukon River Basin, Alaska

River	Station No.	Location	Collection dates	Latitude, longitude
Yukon	301	Near Charley–Kandik Confluence	6/5/02–6/6/02	65°22′28.56″N, 142°30′20.88″W
Porcupine	302	Fish Hook Bend	8/14/02–8/16/02	67°12′50.94″N, 142°09′58.56″W
Porcupine	303	Fort Yukon	6/12/02–6/14/02	66°35′21.06″N, 145°19′59.40″W
Ray	304	Near the Dalton Highway Bridge	6/4/02–6/7/02	65°53′01.26″N, 149°48′00.72″W
Tanana	305	Fairbanks	5/30/02–5/31/02, 6/28/02, 10/10/02	64°45′02.52″N, 148°03′15.84″W
Tolovana	306	Tolovana	6/4/02–6/6/02	64°56′56.40″N, 149°44′13.44″W
Yukon	307	Tanana	6/5/02–6/7/02	65°08′09.72″N, 152°24′54.72″W
Yukon	308	Galena	6/10/02–6/14/02	64°41′56.22″N, 156°58′36.30″W
Innoko	309	Innoko Refuge Field Station	7/15/02–7/17/02	63°38′33.66″N, 158°00′43.56″W
Yukon	310	Kotlik	5/9/02–5/12/02	63°02′12.18″N, 163°34′22.56″W

147, 149, 151, 153, 156, 157, 158, 163, 164, 166, 167, 170, 171, 172, 173, 174, 175, 176, 178, 179, 180, 183, 185, 187, 189, 190, 191, 193, 194, 195, 196, 197, 198, 199, 200, 202, 203, 205, 206, 208, and 209). Toxaphene residues were quantified on the basis of 20 component peaks of a technical toxaphene standard. Quality assurance (QA) measures for the organochlorine pesticide and PCB analyses included the analysis of blanks, triplicate, and fortified samples, use of internal standards to monitor recoveries of each sample, and the confirmation of residue identities by dual-column GC-ECD. Samples were fortified with pesticide and PCB surrogates to monitor recoveries through the entire analytical procedure. Surrogate recoveries (mean ± SD) were 103 ± 15% for organochlorine pesticides and 86 ± 6% to 99 ± 5% for total PCBs. Matrix spike recoveries (mean ± SD) were 90 ± 19% for DDTs, 91 ± 30% for chlordanes, 70 ± 16% for HCH compounds, 88 ± 35% for endosulfans, 86 ± 10% for toxaphene, and 96 ± 5% for total PCBs. The limit-of-detection (LOD) for each compound was calculated by adding the average procedural blank concentration to three times the procedural blank standard deviation. The nominal LODs were ≤0.8 ng/g wet weight (ww) for individual compounds, 20 ng/g ww for total PCBs, and 11 ng/g ww for toxaphene.

Subsamples for elemental analyses (~100 g) were freeze-dried. Percent moisture was determined as weight lost during lyophilization. One portion of the dried material was digested in nitric acid and analyzed by inductively coupled plasma–mass spectroscopy (ICP-MS) for cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). A second portion was dry-ashed (magnesium nitrate–nitric acid–HCl) and analyzed by hydride generation–atomic absorption spectroscopy for arsenic (As) and selenium (Se). A third portion was analyzed directly for total Hg using thermal combustion, amalgamation, and atomic absorption spectroscopy. QA measures for elemental determinations included the analysis of reagent blanks, replicate samples, certified reference materials, and fortified samples. Nominal LODs were 0.026 μg/g dry weight (dw) for As, 0.002 μg/g dw for Hg, 0.013 μg/g dw for Se, 0.1 μg/g dw for Cd, and 1.0 μg/g dw for Pb. Elemental concentrations (including LODs) were converted from dry weight to wet weight (ww) for statistical analysis and reporting using the moisture content of each sample.

A third subsample (10 g) was solvent-extracted and subjected to reactive cleanup for use in the H4IIE bioassay (Tillitt *et al.* 1991; Whyte *et al.* 2004). Concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalent doses (TCDD-EQ; pg/g ww) were determined by slope ratio assay as modified by Ankley *et al.* (1991). QA measures for the H4IIE bioassay included analysis of duplicate samples and reference materials. The LOD was 1.7 pg/g.

Dataset Composition and Statistical Analyses

A total of 217 fish representing three species and 10 stations were collected and examined. Pike (n = 158) were collected from all stations, sucker (n = 46) from five, and burbot (n = 13) from two. Pike (n = 19), sucker (n = 9), and burbot (n = 3) composite samples were analyzed for organochlorine chemical residues, elemental contaminants, and TCDD-EQ. For pike and sucker, differences in length, weight, and age among sites were tested with analysis of variance (ANOVA) using Fisher's protected least significant difference (LSD). Differences among stations for length ($F_{78,9} = 1.27$, $p = 0.27$), weight ($F_{78,9} = 1.69$, $p = 0.11$), and age ($F_{67,9} = 1.02$, $p = 0.44$) were not significant in female pike (Table 2). In male pike, differences among stations for length ($F_{59,8} = 3.09$, $p < 0.01$), weight ($F_{60,8} = 3.78$, $p < 0.01$), and age ($F_{55,8} = 2.14$, $p = 0.05$) were significant. Male pike were smaller from Stations 303 and 309 than Stations 306 and 307 and younger from Stations 303, 308, and 310 than Station 307 (Table 2). Differences among stations for age ($F_{26,4} = 4.45$, $p < 0.01$) and weight ($F_{26,4} = 2.95$, $p = 0.04$) but not length ($F_{26,4} = 1.04$, $p = 0.41$) were significant in female sucker. Female sucker from Station 306 weighed less than those from other stations, and females from Station 305 were younger than those from Stations 301 and 306 (Table 2). Length ($F_{10,3} = 1.36$, $p = 0.31$), weight ($F_{10,3} = 2.75$, $p = 0.10$), and age ($F_{9,3} = 0.96$, $p = 0.45$) did not differ significantly among stations in male sucker (Table 2).

All results for analytes in composite samples were converted to, reported as, and analyzed statistically as wet weight concentrations. Concentrations of many organochlorine contaminants were less than the LOD and were not analyzed statistically. Elemental contaminant concentrations were greater than the LOD in all samples analyzed statistically. Because concentrations of total Hg in predatory fish increase with size, age, or both (Evans *et al.* 2005; Wiener *et al.* 2002), $\log_{10}$-transformed length-adjusted (HgL) and weight-adjusted (HgW) concentrations were computed as described by Brumbaugh *et al.* (2001). Spatial differences in concentrations of Hg, HgL, HgW, Se, and Zn were examined statistically using ANOVA. A nominal α-level of 0.05 was used in all statistical tests unless otherwise indicated.

Wildlife Risk Analysis

Risk to piscivorous wildlife was evaluated with food chain models that incorporate food ingestion rates, uncertainty factors, and toxicity reference values (TRVs) for mammalian and avian wildlife (USEPA 1993). Both the no observed adverse effect level (NOAEL) and lowest observed adverse effect level (LOAEL) TRVs from the scientific literature were used (Sample *et al.* 1996). The most conservative wildlife risk estimates (*i.e.*, greatest risk) are typically obtained with a scenario in which the receptor is a small piscivorous bird or mammal that consumes a diet composed entirely of the most contaminated organism(s) from the study area. Models assuming that 100% of contaminant exposure was from a diet of 100% fish were developed to screen for risk. Site-specific data for other exposure pathways such as water and sediment were not available. A hazard concentration (HC) was calculated for each model species using the equation HC (μg/g) = [TRV (mg/kg/d) × body weight (kg)]/food ingestion rate (kg/kg/

Table 2. Mean ± standard error of length, weight, and age of northern pike, longnose sucker, and burbot from the Yukon River Basin, Alaska

	Female				Male			
Species and Station	*n*	Length (mm)	Weight (g)	Age (year)	*n*	Length (mm)	Weight (g)	Age (year)
Northern pike								
301 — Charley–Kandik	4	639 ± 40	1553 ± 281	5.8 ± 0.5	2	654 ± 25	1568 ± 202	8.5 ± 1.5
302 — Fish Hook Bend	15[a]	608 ± 21	1295 ± 133	5.8 ± 0.5	5[b]	591 ± 21	1162 ± 159	6.0 ± 0.4
303 — Fort Yukon	11[c]	537 ± 25	829 ± 96	4.5 ± 0.7	11[d]	498 ± 15	646 ± 60	4.2 ± 0.5
304 — The Bridge	7[e]	725 ± 94	2923 ± 1056	7.0 ± 1.2	2	579 ± 100	1200 ± 620	6.0 ± 3.0
305 — Fairbanks	3	615 ± 42	1440 ± 496	5.0 ± 1.0	0	—	—	—
306 — Tolovana	11[c]	661 ± 50	2061 ± 657	6.3 ± 1.7	10	609 ± 31	1479 ± 219	5.7 ± 1.3
307 — Tanana	12	615 ± 43	1704 ± 289	6.3 ± 0.9	8	642 ± 51	2069 ± 459	8.9 ± 1.5
308 — Galena	8[f]	629 ± 23	1525 ± 160	4.9 ± 0.6	12	591 ± 12	1325 ± 74	4.9 ± 0.5
309 — Innoko	9[c]	665 ± 63	2163 ± 572	7.5 ± 1.0	10	521 ± 24	945 ± 167	6.7 ± 0.9
310 — Kotlik	9[c]	588 ± 22	1372 ± 216	4.6 ± 1.0	8[f]	581 ± 19	1236 ± 108	4.6 ± 0.8
Longnose sucker								
301 — Charley–Kandik	11	457 ± 8	738 ± 41	3.4 ± 0.2	1	435	540	3.0
304 — The Bridge	2	474 ± 35	930 ± 190	3.5 ± 0.5	0	—	—	—
305 — Fairbanks	9	434 ± 15	672 ± 64	2.4 ± 0.2	11[f]	395 ± 6	488 ± 22	2.7 ± 0.2
306 — Tolovana	2	425 ± 46	550 ± 100	4.0 ± 1.0	1	394	500	3.0
308 — Galena	7	457 ± 13	900 ± 72	2.4 ± 0.4	1	415	700	2.0
Burbot								
305 — Fairbanks	8	700 ± 62	2387 ± 669	10.6 ± 1.1	4	589 ± 65	1100 ± 300	9.5 ± 2.1
310 — Kotlik	0	—	—	—	1	565	1080	7.0

Note.—: not applicable.
[a] $n = 13$ for age.
[b] $n = 4$ for age.
[c] $n = 8$ for age.
[d] $n = 9$ for age.
[e] $n = 6$ for age.
[f] $n = 7$ for age.
[g] $n = 10$ for age.

day) for both a no effects HC (NEHC) and a low effects HC (LEHC). Piscivorous wildlife may be at risk from a contaminant if the measured concentration in the fish composite sample exceeds the NEHC and LEHC. Model species considered in the risk analysis included three sizes of piscivorous birds (belted kingfisher [*Ceryle alcyon*]; osprey [*Pandion haliaetus*], bald eagle [*Haliaeetus leucocephalus*]) and two piscivorous mammals (mink [*Mustela vison*] and river otter [*Lutra canadensis*]), which represented species or size classes of species native to the YRB. Organochlorine chemical residues and elemental contaminants were included in the risk analysis only if concentrations in at least one composite fish sample exceeded toxicity thresholds from the scientific literature.

Results

Organochlorine Pesticides, Total PCBs, and H4IIE-Derived Dioxin Equivalents

Lipid and moisture content were similar among species and sites. Lipid content was 1–6% in pike, 2–6% in sucker, and 3% in burbot. Moisture content was 63–78% in pike, 74–77% in sucker, and 78–80% in burbot.

Concentrations of most organochlorine pesticides were <10 ng/g (Table 3), and none exceeded toxicity thresholds for fish or piscivorous wildlife. Concentrations of *p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD were greatest (>4.0 ng/g) in samples from Station 305 but were lower than historical concentrations (<10–570 ng/g) at this site (Schmitt *et al.* 1999). Concentrations of *p,p′*-DDT were greater than the LOD only in female pike (4.7 ng/g) and male sucker (9.1 ng/g) from Station 305 (Table 3). Total DDT (*p,p′*-homologs) concentrations (1.10–13.6 ng/g) were less than effects thresholds for fish (>500 ng/g; Jarvinen and Ankley 1999) and piscivorous wildlife (>150 ng/g; Anderson *et al.* 1975; Blus 1996; Newell *et al.* 1987). Total DDT concentrations were also less than the protective guidelines for piscivorous aquatic birds (1000 ng/g; IJC 1987). The greatest total DDT concentrations (13.2 ng/g in sucker and 13.6 ng/g in pike from Station 305) approached the Canadian wildlife protective criterion of 14.0 ng/g (Environment Canada 2003). In addition, *p,p′*-DDT accounted for 36% and 67% of the total DDT in sucker and pike, respectively, from Station 305 (Fig. 2). The occurrence of proportionally high concentrations of *p,p*'-DDT at Station 305 might have signified recent inputs of unweathered insecticide (Aguillar 1984) and was higher than the proportion reported in the 1980s (Schmitt *et al.* 1999). All concentrations of *o,p′*-homologs were ≤1.33 ng/g (Table 3) and were not considered to represent a hazard to YRB fish and wildlife.

Concentrations of the seven measured chlordane-related compounds (*cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, heptachlor, and heptachlor epoxide) were ≤3.82 ng/g (Table 3). Total chlordane concentrations (sum of the seven) were 0.67–10.3 ng/g, which is less than the effects threshold (100 ng/g) for fish and piscivorous birds (Eisler 1990). Dieldrin concentrations (0.17–0.58 ng/g) were also below toxicity thresholds (120–2130 ng/g) for freshwater fish (Jarvinen and Ankley 1999;

Table 3. Limits-of-detection (LODs), percent of samples exceeding LOD, range of detected 2002 concentrations, and range of historical concentration for organochlorine chemical residues in composite samples of male (M) and female (F) northern pike (NP), longnose sucker (LS), and burbot (B) from the Yukon River Basin, Alaska

Organochlorine contaminant	LOD range (ng/g)	Samples >LOD (% of 31)	2002 Concentration range (ng/g)	Station with maximum concentration	Sample with maximum concentration	Historical concentrations[a] (ng/g)
p,p′-DDT	1.4–1.6	6	4.7–9.1	305	F, NP	<10–420
p,p′-DDD	0.38–0.43	58	0.46–6.64	305	F, LS	<10–520
p,p′-DDE	0.39–0.42	81	0.46–4.68	305	F, LS	10–570
Total *p,p′*-homologs	NA	NA	1.09–13.6	305	F, NP	30–1230
o,p′-DDT	0.12–0.13	42	0.20–1.10	305	M, LS	NR
o,p′-DDD	0.61–0.70	6	0.65–0.84	305	M, LS	NR
o,p′-DDE	0.15–0.16	26	0.16–1.33	309	F, NP	NR
Aldrin	NA	100	0.13–1.11	304	F, LS	ND
Dieldrin	0.16	35	0.17–0.58	304	F, LS	≤10
Endrin	0.11–0.12	35	0.15–0.80	301	F, LS	≤10
cis-Chlordane	0.19–0.22	29	0.22–1.12	306	F, NP	<10
trans-Chlordane	0.31–0.35	58	0.33–2.40	307	M, NP	<10
cis-Nonachlor	0.08–0.09	90	0.11–2.38	305	M, LS	<10
trans-Nonachlor	0.21–0.23	45	0.34–2.47	306	F, NP	<10
Oxychlordane	0.08–0.09	58	0.25–2.89	301	F, LS	<10
Heptachlor	0.19–0.21	19	0.24–3.82	304	F, NP	<10
Heptachlor epoxide	0.19–0.21	16	0.31–0.95	305	F, B	<10
Total chlordanes[b]	NA	NA	0.67–10.3	304	F, NP	NR
Toxaphene	11	35	12–34	302	F, NP	<100
Mirex	0.01	32	0.08–0.30	302	M, NP	<10
Pentachlorobenzene	0.05–0.06	13	0.06–0.10	302	F, NP	ND
Hexachlorobenzene	2.1–2.5	0	NA	NA	NA	<10
Pentachloroanisole	0.23–0.25	55	0.33–2.16	304	F, NP	<5
α-Hexachlorocyclohexane (HCH)	0.18–0.20	61	0.21–3.04	302	M, NP	<5–120
β-HCH	0.17–0.19	48	0.32–3.68	308	M, LS	ND
λ-HCH (Lindane)	0.39–0.44	52	0.46–8.87	301	F, LS	<10
δ-HCH	0.10–0.11	84	0.15–2.28	302	M, NP	ND
Dacthal	0.29–0.32	19	0.41–2.77	302	M, NP	<10
Endosulfan I	0.34–0.39	10	0.58–0.68	301	M, LS	ND
Endosulfan II	0.14–0.19	16	0.27–1.51	304	F, LS	ND
Endosulfan sulfate	0.79–0.90	3	1.05	308	F, LS	ND
Methoxychlor	1.7–1.9	13	2.0–3.0	306	F, NP	ND
Total PCBs[c]	20	83	21–87	305	F, LS	<100–5300[d]

Note. NR = not reported; ND = not determined; NA = not applicable

[a] Whole-body fish concentrations from 1969 to 1986 (Schmitt *et al.* 1999).

[b] Sum of *cis*- and *trans*-chlordanes and nonachlors; oxychlordane; heptachlor; and heptachlor epoxide, with censored values represented as 50% LOD.

[c] Sum of 137 congeners.

[d] Aroclor 1254 concentrations.

Macek *et al.* 1970; Peakall 1996; Shubat and Curtis 1986). Toxaphene concentrations in pike from Stations 301, 302, and 306 (29–34 ng/g) approached protective thresholds (35–900 ng/g) for growth and reproduction in freshwater fish (Eisler and Jacknow 1985; Jarvinen and Ankley 1999; Mayer *et al.* 1975, 1978).

Concentrations of total PCBs and TCDD-EQ were also low in all samples. Total PCB concentrations ranged from 19 ng/g to 87 ng/g and were >50 ng/g only in sucker and burbot from Station 305 and pike from Station 306 (Table 3). All PCB concentrations were less than conservative wildlife guidelines (100–110 ng/g) available for fish (IJC 1987; Newell *et al.* 1987). TCDD-EQ was less than or equal to the LOD (1.7 pg/g) in all samples (*i.e.*, dioxin-like activity was not detected in any sample), and all TCDD-EQs were less than the dietary toxicity thresholds for mammals (4.4 pg/g; Heaton *et al.* 1995; Tillitt *et al.* 1996) and birds (5.0 pg/g; Nosek *et al.* 1992).

Elemental Contaminants

Concentrations of As, Cd, Cu, and Pb in YRB fish were universally low and did not exceed toxicity thresholds (Table 4). Arsenic concentrations were 0.03–0.95 μg/g (Table 4), which did not exceed concentrations (5.4–11.6 μg/g) associated with reduced survival and growth in freshwater fish (Gilderhus 1966; McGreachy and Dixon 1992). Concentrations of Cd in pike and burbot were less than the LOD, but Cd was detected (0.04–0.12 μg/g) in all sucker samples (Table 4). All Cd concentrations were less than toxicity thresholds, including those that are potentially lethal (>5 μg/g) or associated with decreased spawning and reproduction (2–8 μg/g; Eisler 1985; Jarvinen and Ankley 1999). Copper concentrations were 0.41–1.49 μg/g (Table 4) and were generally greater in sucker (0.63–1.49 μg/g) than in pike (0.41–0.67 μg/g). Because Cu is highly regulated and does not bioaccumulate in fish, few

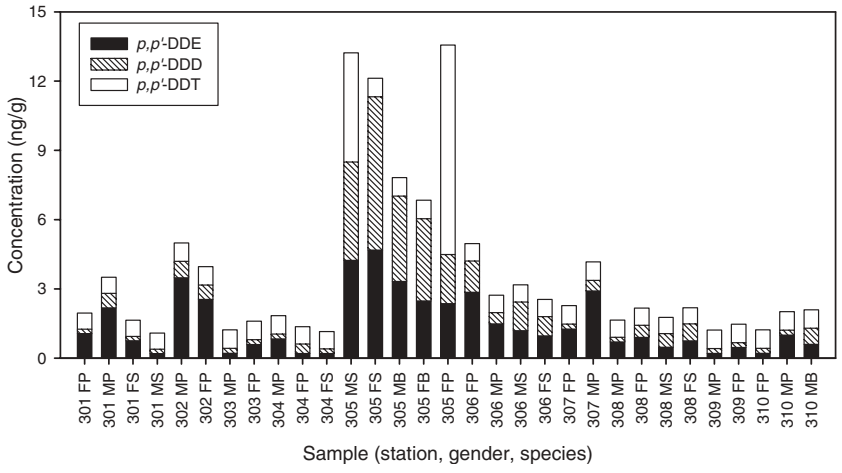

Fig. 2. Concentrations of DDT homologs including *p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDE in whole-body composite samples of male (M) and female (F) northern pike (P), longnose sucker (S), and burbot (B) in the Yukon River Basin, Alaska

Table 4. Range of 2002 concentrations, historical concentrations, and the minimum toxicity threshold for elemental contaminants in whole-body composite samples of male (M) and female (F) northern pike (NP), longnose sucker (LS), and burbot (B) from the Yukon River Basin, Alaska

Element	2002 Concentration range (μg/g)	Station with maximum concentration	Sample with maximum concentration	Historical YRB concentrations (μg/g)	Minimum toxicity threshold (μg/g)	Reference for toxicity threshold
Arsenic	0.03–1.95	310	M, B	0.02–9.11[a,c,d]	5.4–11.6	McGreachy and Dixon (1992); Gilderhus (1966)
Cadmium	<0.02–0.12	301	F, LS	<0.01–0.35[a,b,c,d]	2–8	Eisler (1985); Jarvinen and Ankley (1999)
Copper	0.41–1.49	301	F, LS	0.37–1.76[a,c,d]	11.1–11.7	Stouthart *et al.* (1996)
Lead	<0.21–<0.27	NA	NA	<0.02–4.46[a,b,c,d]	0.4	Holcombe *et al.* (1976)
Mercury	0.08–0.65	306	F, NP	<0.01–0.23[a,b,c,d]	0.1–0.3	Barr (1986); Heinz (1979)
Selenium	0.23–0.85	305	M, B	0.28–3.51[a,c,d]	0.75–1.0	Lemly (1996); Hamilton (2004)
Zinc	11–56	309	F, NP	9–73[a,c,d]	40–64	Spehar (1976)

Note. NA = not applicable.
[a] Whole-body concentrations from West and Deschu (1984).
[b] Whole-body concentrations from Mueller *et al.* (1995).
[c] Whole-body concentrations from Schmitt *et al.* (1999).
[d] Whole-body concentrations from Northern Contaminants Program (2004).

studies have measured Cu concentrations in whole-body fish (Eisler 1998; Jarvinen and Ankley 1999). Copper concentrations in YRB fish were less than those associated with reduced survival of carp (*Cyprinus carpio*) larvae (11.1–11.7 μg/g; Stouthart *et al.* 1996). Lead concentrations were less than the LOD (0.21–0.27 μg/g) in all samples, which were less than available toxicity thresholds from the scientific literature (Table 4).

Mercury was detected (>0.01 μg/g) in all samples at concentrations of 0.08–0.65 μg/g (Table 4). Total Hg concentrations differed significantly among stations only in pike (Table 5). Concentrations were significantly greater in pike from Station 304 than from Stations 302, 303, 305, or 310 (Table 5). Length-adjusted Hg concentrations were also significantly greater in pike from Station 304 than from Stations 303 and 310 (Table 5). Mercury concentrations were greater in heavier pike and did not differ significantly among stations after accounting for weight differences (Table 5). Dietary Hg concentrations of 0.1–0.3 μg/g have been associated with reproductive impairment in common loons (*Gavia immer*; Barr 1986) and mallards (*Anas platyrhynchos*; Heinz 1979). Mercury concentrations in all pike from Stations 304, 306, 307, and 308 and in burbot from Station 305 were >0.3 μg/g, and at least one sample from all stations exceeded 0.1 μg/g (Fig. 3). Other Hg guidelines in fish tissues range from 0.033 μg/g to 0.5 μg/g for the protection of piscivorous wildlife (Environment Canada 2003; IJC 1987).

Selenium was also detected in all samples at concentrations of 0.23–0.85 μg/g (Table 4). The greatest Se concentrations (>0.7 μg/g) were in pike from Stations 301 and 302 and burbot from Station 305 (Fig. 3). Among-station differences for concentrations of Se were significant in pike but not in sucker or burbot (Table 5). Selenium concentrations were significantly greater in pike from Stations 301, 302, and 303 than from Stations 308, 309, and 310 (Fig. 3 and Table 5). Toxicity thresholds associated with Se tissue concentrations are relatively low because of this element's high toxicity and potential to bioaccumulate. Whole-body Se concentrations should not exceed 4 μg/g dw (1.0 μg/g ww assuming 75% moisture) to avoid toxicity to larval fish and 3 μg/g dw (0.75 μg/g ww) to protect piscivorous wildlife (Hamilton 2004; Lemly 1996, 2002). Only male burbot from Station 305 exceeded 0.75 μg/g (Fig. 3).

Zinc was detected in all samples. Zinc concentrations were greater in pike (36–56 μg/g) than burbot (<16 μg/g) or sucker

Table 5. Least-squares mean concentrations (all wet weight) of total mercury (Hg), length-adjusted Hg (HgL), weight-adjusted Hg (Hg), selenium (Se), and zinc (Zn) that exceeded minimum toxicity thresholds in at least one composite sample[a]

Species and station	Hg (μg/g)	HgL (μg/g/m)	HgW (μg/g/kg)	Se (μg/g)	Zn (μg/g)
Northern Pike					
301 — Charley–Kandik	0.25 abc	0.38 abc	0.16 a	0.56 de	40.4 a
302 — Fish Hook Bend	0.23 ab	0.39 abc	0.19 a	0.72 e	45.1 a
303 — Fort Yukon	0.15 a	0.30 ab	0.22 a	0.56 de	46.5 a
304 — The Bridge	0.51 c	0.78 c	0.27 a	0.45 cd	47.7 a
305 — Fairbanks	0.19 ab	0.30 abc	0.13 a	0.56 cde	52.3 a
306 — Tolovana	0.42 bc	0.66 bc	0.25 a	0.46 cd	44.1 a
307 — Tanana	0.39 bc	0.63 bc	0.21 a	0.44 cd	43.4 a
308 — Galena	0.33 bc	0.55 bc	0.24 a	0.37 bc	44.3 a
309 — Innoko	0.25 abc	0.42 abc	0.17 a	0.24 a	50.7 a
310 — Kotlik	0.12 a	0.20 a	0.09 a	0.26 ab	42.7 a
Longnose sucker					
301 — Charley–Kandik	0.17 a	0.37 a	0.26 a	0.55 a	25.7 b
304 — The Bridge	0.19 a	0.41 a	0.21 a	0.60 a	19.6 ab
305 — Fairbanks	0.12 a	0.30 a	0.22 a	0.56 a	19.2 ab
306 — Tolovana	0.10 a	0.25 a	0.20 a	0.57 a	17.6 a
308 — Galena	0.10 a	0.23 a	0.12 a	0.50 a	15.6 a
Burbot					
305 — Fairbanks	0.26 a	0.40 a	0.16 a	0.77 a	12.9 a
310 — Kotlik	0.13 a	0.22 a	0.12 a	0.54 a	10.5 a
ANOVA					
F (*df* 16,14)	7.80	3.93	0.98	10.74	36.51
P value	<0.01	0.01	0.52	<0.01	<0.01

Note. Within each species–station group, means followed by the same letter are not significantly different ($p < 0.01$, Fisher's protected LSD). Also shown are ANOVA *F*-values, degrees-of-freedom (*df*), and statistical significance.

[a] $n = 2$ composite samples for all species–station group except northern pike from Station 305, longnose sucker from Station 304, and burbot from Station 310 where $n = 1$. See Table 2 for number of individual fish in each composite sample.

(15–31 μg/g; Fig. 3). Zinc concentrations differed significantly among stations in sucker but not in pike or burbot (Table 5). Concentrations of Zn were greater in sucker from Station 301 than from Stations 306 and 308 (Table 5). Zinc is highly regulated in fish (Bury *et al.* 2003), and few studies have measured Zn concentrations in whole-body fish (Jarvinen and Ankley 1999). Zinc concentrations in most pike were >40 μg/g, a concentration that has been associated with reduced growth and survival in larval and adult cyprinids (Spehar 1976).

Wildlife Risk Analysis

Because concentrations of Hg, Se, and Zn exceeded literature-based toxicity criteria for fish and piscivorous wildlife in one or more samples, HCs were calculated for three sizes of birds and two sizes of mammals. The risk from Hg increased as bird size decreased (Table 6). All Hg concentrations exceeded NEHCs for belted kingfisher (0.002 μg/g) and osprey (0.05 μg/g; Table 6). Mercury concentrations in samples from Stations 301, 304, 306, 305, 307, 308, and 309 also exceeded the NEHC for bald eagle (0.27 μg/g), mink (0.21 μg/g), or both, but no Hg concentrations represented a risk to river otter (Table 6). For LEHCs, Hg concentrations in all samples represented a risk to belted kingfisher (0.02 μg/g), and concentrations in pike from Stations 304 and 306 were potentially hazardous to osprey (0.50 μg/g).

Selenium and Zn concentrations were less than the NEHCs and LEHCs for all species except the belted kingfisher. Selenium and Zn did not represent a risk to larger birds or mammals in our model (Table 6). All Se concentrations were greater than the NEHC (0.12 μg/g) and LEHC (0.24 μg/g) for belted kingfisher. Zinc concentrations exceeded the NEHC (4 μg/g) in all samples and exceeded the LEHC (39 μg/g) in all pike samples for belted kingfisher (Table 6).

Discussion

Concentrations of most organochlorine chemical residues were relatively low (<10 ng/g) in our whole-fish samples, which is consistent with the findings of other YRB studies (Schmitt *et al.* 1999; Snyder-Conn 1992). Concentrations of aldrin, pentachlorobenzene, β-HCH, δ-HCH, endosulfan I, endosulfan II, endosulfan sulfate, and methoxychlor, which have not been measured previously in the YRB, were also low (<4 ng/g) in YRB fish. All organochlorine and TCDD-EQ concentrations were less than literature-based toxicity thresholds available for fish or piscivorous wildlife, but concentrations of toxaphene, *p,p′*-DDE, and total PCBs either approached toxicity thresholds or were relatively high in some samples and are discussed in more detail.

Declining concentrations of many organochlorines were recently documented in lake trout (*Salvenius namaycush*) from Yukon Territory lakes (Ryan *et al.* 2005), but elevated toxaphene concentrations have been reported in burbot and lake trout from Lake Laberge in the upper YRB (Braune *et al.* 1999; Kidd *et al.* 1998). Toxaphene concentrations in our fish from riverine sites were low (≤34 ng/g), but the LOD for

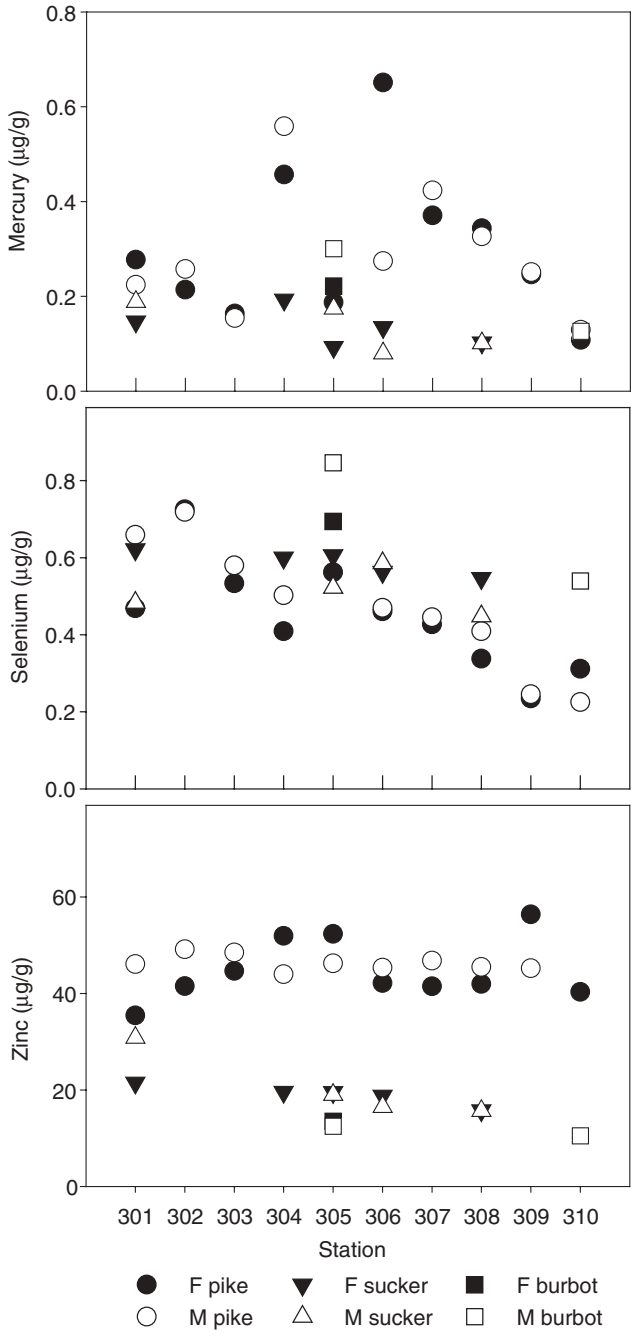

Fig. 3. Concentrations of total mercury, selenium, and zinc in whole-body composite samples of male (M) and female (F) northern pike, longnose sucker, and burbot in the Yukon River Basin, Alaska

toxaphene (11 ng/g) exceeded the Canadian wildlife guideline for the protection of piscivorous wildlife (6.3 ng/g; Environment Canada 2003). Although technical toxaphene is highly toxic to fish (Johnson and Finley 1980), adverse effects on freshwater fish have not been associated with whole-body residues <1000 ng/g in laboratory studies (Jarvinen and Ankley 1999). Environmentally weathered toxaphene residues are highly complex and variable, and higher-resolution methods are necessary to characterize their composition and potential toxicity in field studies (*e.g.*, Bidleman *et al.* 1993; Gooch and Matsumura 1987; Harder *et al.* 1983; Muir and de Boer 1993; Ribick *et al.* 1982; Swackhamer and Hites 1987).

Concentrations of *p*,*p*′-DDE were greater in pike (<10–93 ng/g) from the Mississippi River Basin (Schmitt 2002) and the Rio Grande Basin (Schmitt *et al.* 2004) compared to those in YRB pike (<0.4–3.5 ng/g). Residues of DDT and its metabolites remain present in the arctic as a consequence of atmospheric transport (Barrie *et al.* 1992; Braune *et al.* 1999; Muir *et al.* 1999) and because of historical use in the YRB (Mueller and Matz 2000). Ryan *et al.* (2005) reported that *p*,*p*′-DDE concentrations have decreased significantly in lake trout from the Yukon Territory over the last decade. A similar trend was evident in our data. Concentrations of *p*,*p*′-DDE in fish from Station 305 were much lower our study (2.4–6.6 ng/g) compared to historical concentrations (10–570 ng/g; Schmitt *et al.* 1999). However, we found that *p*,*p*′-DDT accounted for a comparatively high proportion of the total DDT in sucker (36%) and pike (67%) from Station 305. Such high proportions were not found historically at this site (Schmitt *et al.* 1999) and may signify recent inputs of unweathered *p*,*p*′-DDT (Aguillar 1984). DDT was used for mosquito control within the city of Fairbanks and nearby military facilities, and storage facilities at Fort Wainwright Army Base and Eielson Air Force Base near Fairbanks represent potential local sources of DDT contamination (Mueller and Matz 2000).

Total PCB concentrations were not detected in pike (<50 ng/g) from the Mississippi River Basin (Schmitt 2002) and the Rio Grande Basin (Schmitt *et al.* 2004) and were generally low in YRB pike (<20–87 ng/g). Relatively high concentrations were measured in fish from Station 305 (39–87 ng/g), where elevated PCB residues were previously reported in fish (<100–5300 ng/g; Schmitt *et al.* 1999). Remediation activities were initiated after contaminated sediments and wastes from Eielson Air Force Base, which is located upstream of Station 305, were identified as PCB sources (Alaska Department of Environmental Conservation 2003). PCB concentrations are expected to decrease further as remediation of sediment is completed. Other YRB studies measuring total PCBs in whole-body fish were not found. Total PCB concentrations were measured in lake trout muscle (3.5–328.3 ng/g) and burbot liver (26.7–1997.1 ng/g) from lakes in the upper YRB (Ryan *et al.* 2005). Although these tissue concentrations cannot be directly compared to whole-body concentrations, temporal trends in concentrations can be examined. Total PCB concentrations have decreased significantly in lake trout over the last decade, but concentrations in burbot have not changed significantly (Ryan *et al.* 2005).

Concentrations of As (0.03–1.95 µg/g), Cd (<0.02–0.12 µg/g), Cu (0.41–1.49 µg/g), and Pb (<0.21–0.27 µg/g) were low in YRB fish and did not exceed toxicity thresholds for fish or piscivorous wildlife. Our results confirm findings of previous YRB studies (Mueller *et al.* 1995; Schmitt *et al.* 1999; West and Deschu 1984). Concentrations of Hg, Se, and Zn exceeded toxicity thresholds for fish or piscivorous wildlife and were included in the piscivorous wildlife risk analysis. Mercury concentrations in YRB pike were among the highest measured in predatory fish when comparing similar monitoring studies. Mercury concentrations were lower in pike (<0.02–0.18 µg/g) from the Mississippi River Basin (Schmitt 2002) and the Rio

Table 6. Calculated hazard concentrations (HC; μg/g) of mercury (Hg), selenium (Se), and zinc (Zn) for piscivorous wildlife with a diet composed of 100% fish, and stations where measured contaminant concentrations in at least one YRB fish sample exceeded the HC

	No effects[a]		Low effects[a]	
Contaminant and model species	NEHC (μg/g)	Stations where concentrations >NEHC	LEHC (μg/g)	Stations where concentrations >LEHC
Mercury				
Belted kingfisher	0.002	All	0.02	All
Osprey	0.05	All	0.50	304, 306
Bald eagle	0.27	301, 304, 305, 306, 307, 308	2.66	None
Mink	0.21	301, 302, 304, 305, 306, 307, 308, 309	1.03	None
River otter	0.66	None	3.29	None
Selenium				
Belted kingfisher	0.12	All	0.24	All
Osprey	3.1	None	6.21	None
Bald eagle	17	None	33	None
Mink	1.29	None	2.12	None
River otter	4.12	None	6.79	None
Zinc				
Belted kingfisher	4	All	39	All
Osprey	112	None	1016	None
Bald eagle	601	None	5432	None
Mink	1029	None	2057	None
River otter	3293	None	6587	None

[a] Hazard concentration = threshold reference value × body weight/food ingestion rate for no effects (NEHC) and low effects (LEHC). Threshold reference values = no observed adverse effect level (NOAEL) and lowest observed adverse effect level (LOAEL) from Sample *et al.* (1996). NOAEL for Hg = 0.0064 mg/kg/day for birds and 0.032 mg/kg/day for mammals; Se = 0.4 mg/kg/day for birds and 0.2 mg/kg/day for mammals; and Zn = 14.5 mg/kg/day for birds and 160 mg/kg/day for mammals. LOAEL for Hg = 0.064 mg/kg/day for birds and 0.16 mg/kg/day for mammals; Se = 0.8 mg/kg/day for birds and 0.33 mg/kg/day for mammals; and Zn = 131 mg/kg/day for birds and 320 mg/kg/day for mammals. Body weight = 0.15 kg for belted kingfisher; 1.63 kg for osprey; 4.15 kg for bald eagle; 0.90 kg for mink; and 7.41 kg for river otter (USEPA 1993). Food ingestion rate = 0.50 kg/kg/day for belted kingfisher; 0.21 kg/kg/day for osprey; 0.10 kg/kg/day for bald eagle; 0.14 kg/kg/day for mink; and 0.36 kg/kg/day for river otter (USEPA 1993).

Grande Basin (Schmitt *et al.* 2004) compared to those in YRB pike (0.08–0.65 μg/g), and whole-body Hg concentrations >0.3 μg/g in any species were rare in other riverine monitoring studies (Hinck *et al.* 2004b; Schmitt 2002; Schmitt *et al.* 2004). Mercury concentrations in pike can be highly variable in subarctic and arctic waters (Evans *et al.* 2005; Jewett *et al.* 2003;) and can often differ with ecosystem structure and trophic dynamics (Cabana *et al.* 1994). The greatest Hg concentrations (>0.4 μg/g) were in fish from the central portion of the YRB, where potential Hg sources such as historical placer mines, wetlands, and subbituminous coal deposits are located (Brabets *et al.* 2000; Brumbaugh *et al.* 2001; Gray and Sanzolone 1996; Rudd 1995). Wetlands, which occupy 30% of the YRB, are a significant source of methylmercury (MeHg), the most toxic form of Hg to fish (Brabets *et al.* 2000; Brumbaugh *et al.* 2001). The amount of MeHg released from YRB wetlands and the effects in aquatic biota from a subsequent exposure are unknown. Mercury from atmospheric deposition may also contribute to the elevated Hg concentrations in YRB fish (Lockhart *et al.* 2005; Northern Contaminants Program 2003). Studies on long-range transport, deposition mechanisms, and biological exposure and effects are needed to understand Hg cycles in the YRB (Arctic Monitoring and Assessment Programme 2003; Mason *et al.* 2005).

Concentrations of Se (0.17–0.68 μg/g) and Zn (28.4–55.9 μg/g) in pike from the Mississippi River Basin (Schmitt 2002) and Rio Grande Basin (Schmitt *et al.* 2004) were similar to those in YRB fish. Zinc is an essential element and is actively regulated in fish, and Zn concentrations >20 μg/g are rare in most predatory fish (Schmitt *et al.* 1999). However, Zn concentrations were >30 μg/g in our pike. Schmitt *et al.* (1999) reported that Zn concentrations historically were >30 μg/g in pike from various US river basins, including the YRB, which indicates that concentrations are greater in pike than in many other species.

Piscivorous birds and mammals are present throughout the YRB and may be exposed to contaminants through the consumption of contaminated fish, water, and sediment. Our risk analysis, which only considered fish consumption, is conservative and should be used as a screening-level tool to determine where high contaminant concentrations might pose a risk to piscivorous wildlife. Our risk analysis determined that Se and Zn concentrations in the YRB may be hazardous to smaller birds such as the belted kingfisher but not to larger birds or mammals. The greatest risk was associated with Hg concentrations, which exceeded NEHCs, LEHCs, or both in all bird and mink models. Larger mammals such as the river otter were not at risk. This assessment is consistent with a mink study in the Yukon Territory, which determined that Hg concentrations were below levels of toxicological concern, although mink with higher proportions of fish in their diet were expected to have higher Hg concentrations compared to those feeding on small mammals (Gamberg *et al.* 2005).

Migratory piscivorous birds, including the Pacific loon (*Gavia pacifica*), arctic tern (*Sterna paridisaea*), herring gull (*Larus argentatus*), mergansers (*Mergus* spp.), and grebes

(*Podiceps* spp.), may be exposed to high Hg concentrations in the fish that they consume while nesting along rivers, lakes, and wetlands in the YRB (NPS 2005; USFWS 2005). Birds may be exposed to contaminants after arrival at breeding grounds, and differences in breeding area habitats and diet might also affect contaminant concentrations and associated risk from those contaminants (Ambrose *et al.* 2000). Studies have shown that common loons and herring gulls are particularly sensitive to contaminant exposure (Barr 1986; Tillitt *et al.* 1998). Hatchlings may be at greater risk to accumulative contaminants such as Hg in their diets due to their small size and high food ingestion rates compared to adult birds, and scavengers can be exposed to contaminants when consuming dead or dying fish associated with natural or anthropogenic events (Buehler 2000). Another study supports our conclusion that avian wildlife may be at risk to Hg in the YRB (Ambrose *et al.* 2000). Ambrose *et al.* (2000) reported that Hg concentrations in peregrine falcons (*Falco peregrinus anatum*) were significantly greater in unsuccessful nests in the YRB compared to those in other parts of Alaska, and Hg concentrations in eggs increased between 1988–1990 (0.33 μg/g) and 1991–1995 (0.53 μg/g). More data on other exposure pathways (*e.g.*, water, sediment), nonfish dietary components, and residence within the YRB are needed to more precisely determine the risk of Hg exposure to piscivorous wildlife.

Overall, concentrations of organochlorine chemical residues and elemental contaminants were low in YRB fish, but toxaphene, DDT, and other organochlorine chemical residues should continue to be monitored because of their threat to the health of arctic and subarctic ecosystems. Selenium and Zn originating from natural sources are potentially toxic to fish and piscivorous wildlife, but a greater risk is associated with relatively high Hg concentrations throughout the YRB. Our data indicate that Hg has the potential to be hazardous to piscivorous birds and other top predators in the YRB, and specific risks to piscivorous wildlife in the YRB need to be examined further. As energy exploration and development continues to expand in the YRB, the release of toxic trace elements into aquatic habitats may increase. Continued monitoring of contaminant concentrations is needed to document trends in fish, and studies describing Hg sources, exposure pathways, and effects in Alaskan fish and wildlife are warranted.

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References

Aagaard K, Carmack EC (1989) The role of sea ice and other fresh water in the Arctic circulation. J Geophys Res 94:14,485–14,498

Aguillar A (1984) Relationships of DDE/DDT in marine mammals to the chronology of DDT input into the ecosystem. Can J Fish Aquat Sci 21:840–844

Alaska Department of Environmental Conservation (2003) Alaska's Final Draft 2002/2003 integrated water quality monitoring and assessment report, August 2003. Division of Water, Juneau, Alaska

Alaska Division of Geological and Geophysical Surveys (2005) Alaska Division of Geological and Geophysical Surveys annual report 2004. State of Alaska Department of Natural Resources, Fairbanks, Alaska

Ambrose RE, Matz A, Swem T, Bente P (2000) Environmental contaminants in American and arctic peregrine falcon eggs in Alaska, 1979–95. US Fish and Wildlife Service, Northern Alaska Ecological Services, NAES-TR-00-02, Fairbanks, Alaska

Anderson DW, Jehl JR Jr, Risebrough RW, Woods LA Jr, DeWeese LR, Edgecomb WG (1975) Brown pelicans: improved reproduction off the southern California Coast. Sci 190:806–808

Ankley GT, Tillitt DE, Giesy JP, Jones PD, Verbrugge DA (1991) Bioassay-derived 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents in PCB-containing extracts from the flesh and eggs of Lake Michigan chinook salmon (*Oncorhynchus tshawytscha*) and possible implications for reproduction. Can J Fish Aquat Sci 48:1685–1690

Arctic Monitoring and Assessment Programme (2003) AMAP Assessment 2002: The influence of global change on contaminant pathways to, within, and from the Arctic. AMAP, Oslo

Barr JF (1986) Population dynamics of the common loon (Gavia immer) associated with mercury-contaminated waters in northwestern Ontario. Occasional Paper 56, Canadian Wildlife Service, Ottawa, Ontario

Barrie LA, Gregor D, Hargrave B, Lake R, Muir D, Shearer R, Tracey B, Bidleman T (1992) Arctic contaminants: sources, occurrence, and pathways. Sci Total Environ 122:1–74

Bidleman TF, Wall MD, Muir DCG, Stern GA (1993) Selective accumulation of polychlorocamphenes in aquatic biota from the Canadian arctic. Environ Toxicol Chem 12:701–710

Blus LJ (1996) DDT, DDD, and DDE in birds. In: Beyer WN, Heinz GH, Redmon-Norwood AW, (eds) Environmental contaminants in wildlife: interpreting tissue concentrations. Lewis Publishers, Boca Raton, FL, pp 49–71

Brabets TP, Wang B, Meade RH (2000) Environmental and hydrologic overview of the Yukon River Basin, Alaska and Canada. US Geological Survey, Water Resources Discipline, WRIR 99-4204, Anchorage, Alaska

Braune B, Muir D, DeMarch B, Gamberg M, Poole K, Currie R, Dodd M, Duschenko W, Eamer J, Elkin B, Evans M, Grundy S, Herbert C, Johnstone R, Kidd K, Koeing B, Lockhart L, Marshall H, Reimer K, Sanderson L, Shutt L (1999) Spatial and temporal trends in contaminants in Canadian Arctic freshwater and terrestrial ecosystems: a review. Sci Total Environ 230:145–207

Brumbaugh WG, Krabbenhoft DP, Helsel DR, Wiener JG, Echols KR (2001) A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients: bioaccumulation in fish. US Geological Survey, Biological Resources Division, BSR-2001-0009, Columbia, Missouri

Buehler DA (2000) Bald eagle (*Haliaeetus leucocephalus*). In: Poole A, Gill F (eds) The birds of North America Vol. 506. The Birds of North America, Inc, Philadelphia, pp 1–39

Buhl KJ, Hamilton SJ (1990) Comparative toxicity of inorganic contaminants released by placer mining to early life stages of salmonids. Ecotoxicol Environ Safety 20:325–342

Bury NR, Walker PA, Glover CN (2003) Nutritive metal uptake in teleost fish. J Exp Biol 206:11–23

Cabana G, Tremblay A, Kalff J, Rasmussen JB (1994) Pelagic food chain structure in Ontario lakes: A determinant of mercury levels in lake trout (*Salvelinus namaycush*). Can J Fish Aquat Sci 51:381–389

Eiler JH, Spencer TR, Pella JJ, Masuda MM, Holder RR (2004) Distribution and movement patterns of Chinook salmon returning

to the Yukon River basin in 2000, 2002. National Oceanic and Atmospheric Administration Technical Memo NMFS-AFSC-148. National Oceanic and Atmospheric Administration, Seattle, Washington

Eisler R (1985) Cadmium hazards to fish, wildlife, and invertebrates: Asynoptic review. US Fish and Wildlife Service Biological Report 85(1.2). US Fish and Wildlife Service, Laurel, Maryland

Eisler R (1990) Chlordane hazards to fish, wildlife, and invertebrates: a synoptic review. US Fish and Wildlife Service Biological Report 85(1.21). US Fish and Wildlife Service, Laurel, Maryland

Eisler R (1998) Copper hazards to fish, wildlife, and invertebrates: a synoptic review. US Geological Survey, Biological Resources Division Report BSR 1998-0002. US Geological Survey, Laurel, Maryland

Eisler R, Jacknow J (1985) Toxaphene hazards to fish, wildlife, and invertebrates: A synoptic review. US Fish and Wildlife Service Biological Report 85 (1.4). US Fish and Wildlife Service, Laurel, Maryland

Environment Canada (2003) Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic biota: summary table. In: Canadian tissue residue guidelines, Canadian Council of Ministers of the Environment, Water Quality Guidelines Task Group, Winnipeg, Manitoba, Canada. Available from http://www.ec.gc.ca/ceqg-rcqe (accessed December 2005)

Evans MS, Muir D, Lockhart WL, Stern G, Roach P (2005) Persistent organic pollutants and metals in the freshwater biota of the Canadian Subarctic and Arctic: An overview. Sci Total Environ 351–352:94–147

Gamberg M, Boila G, Stern G, Roach P (2005) Cadmium, mercury, and selenium concentrations in mink (*Mustela vison*) from Yukon, Canada. Sci Total Environ 351–352:523–529

Gilderhus PA (1966) Some effects of sublethal concentrations of sodium arsenate on bluegills and the aquatic environment. Trans Am Fish Soc 95:289–296

Gooch JW, Matsumura F (1987) Toxicity of chlorinated bornane (toxaphene) residues isolated from Great Lakes lake trout (*Salvelinus namaycush*). Arch Environ Contam Toxicol 16:349–355

Gray JE, Sanzolone RF (1996) Environmental studies of mineral deposits in Alaska. Survey Bulletin 2156. US Geological Survey, Denver, Colorado

Hamilton SJ (2004) Review of selenium toxicity in the aquatic food chain. Sci Total Environ 326:1–31

Harder HW, Carter T, Bidleman TF (1983) Acute effects of toxaphene and its sediment-degraded products on estuarine fish. Can J Fish Aquat Sci 40:2119–2125

Heaton SN, Bursian SJ, Giesy JP, Tillitt DE, Render JA, Jones PD, Verbrugge DA, Kubiak TJ, Aulerich RJ (1995) Dietary exposure of mink to carp from Saginaw Bay, Michigan: 2. Hematology and liver pathology. Arch Environ Contam Toxicol 29:411–417

Heinz GH (1979) Methylmercury: reproductive and behavioral effects on three generations of mallard ducks. J Wildl Manag 43:394–401

Hinck JE, Bartish TM, Blazer VS, Denslow ND, Gross TS, Myers MS, Anderson PJ, Orazio CE, Tillitt DE (2004a) Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental contaminants and their effect on fish in the Yukon River basin. US Geological Survey, Biological Resources Division, SIR 2004-5285, Columbia, Missouri

Hinck JE, Schmitt CJ, Bartish TM, Denslow ND, Blazer VS, Anderson PJ, Coyle JJ, Dethloff GM, Tillitt DE (2004b) Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental contaminants and their effect on fish in the Columbia River basin. US Geological Survey, Biological Resources Division, SIR 2004-5154, Columbia, Missouri

IJC (International Joint Commission) (1987) Revised Great Lakes Water Quality Agreement of 1978. Office of Consolidation United States and Canada, Ottawa, Canada

Jarvinen AW, Ankley GT (1999) Linkage of effects to tissue residues: Development of a comprehensive database for aquatic organisms exposed to inorganic and organic chemicals SETAC Press, Pensacola, FL

Jewett SC, Zhang X, Naidu AS, Kelley JJ, Dasher D, Duffy LK (2003) Comparison of mercury and methylmercury in northern pike and Arctic grayling from western Alaska rivers. Chemosphere 50:383–392

Johnson WL, Finley MT (1980) Handbook of acute toxicity of chemicals to fish and aquatic invertebrates: summaries of toxicity tests conducted at Columbia National Fisheries Research Lab, 1965–78. US Fish and Wildlife Service, Washington, DC

Kidd KA, Schindler DW, Hesslein RH, Muir DC (1998) Effects of trophic position and lipid on organochlorine concentrations in fishes from subarctic lakes in Yukon Territory. Can J Fish Aquat Sci 55:869–881

Lemly AD (1996) Selenium in aquatic organisms. In: Beyer WN, Heinz GH, Redmon-Norwood AW (eds) Environmental contaminants in wildlife: interpreting tissue concentrations. Lewis Publishers, Boca Raton, FL, pp 427–445

Lemly AD (2002) Symptoms and implications of selenium toxicity in fish: The Belews Lake case example. Aquat Toxicol 57:39–49

Lockhart WL, Stern GA, Low G, Hendzel M, Boila G, Roach P, Evans MS, Billeck BN, DeLaronde J, Friesen S, Kidd K, Atkins S, Muir DC, Stoddart M, Stephens G, Stephenson S, Harbicht S, Snowshoe N, Grey B, Thompson S, DeGraff N (2005) A history of total mercury in edible muscle of fish from lakes in northern Canada. Sci Total Environ 351–352:427–463

Macek KJ, Rodgers CR, Stalling DL, Korn S (1970) The uptake, distribution and elimination of dietary ^{14}C-DDT and ^{14}C-Dieldrin in rainbow trout. Trans Am Fish Soc 99:689–695

Mason RP, Abbott ML, Bodaly RA, Bullock OR Jr, Driscoll CT, Evers D, Lindberg SE, Murray M, Swain EB (2005) Monitoring the environmental response to changing atmospheric mercury deposition. Environ Sci Technol 39:14A–22A

Mayer FL Jr, Merhle PM Jr, Dwyer WP (1975) Toxaphene effects on reproduction, growth, and mortality of brook trout. EPA-600/3-75/013 US Environmental Protection Agency, Washington, DC

Mayer FL Jr, Mehrle PM, Crutcher PL (1978) Interactions of toxaphene and vitamin C in channel catfish. Trans Am Fish Soc 107:326–333

McGreachy SM, Dixon DG (1992) Whole-body arsenic concentrations in rainbow trout during acute exposure to arsenate. Ecotoxicol Environ Safety 24:301–308

Mueller KA, Matz AC (2000) Organochlorine concentrations in burbot (*Lota lota*) livers from Fairbanks, Alaska, and Kanuti, Tetlin, and Yukon Flats National Wildlife Refuges, Alaska, 1998. US Fish and Wildlife Service, Northern Alaska Ecological Services, NAES-TR-00-01, Fairbanks, Alaska

Mueller KA, Snyder-Conn E, Scannell PO (1995) Metal and metalloid contaminants in water, sediments, fish, and mammals of Kanuti National Wildlife Refuge, Alaska, 1985–1990. US Fish and Wildlife Service, Northern Alaska Ecological Services, NAES-TR-95-02, Fairbanks, Alaska

Muir DCG, de Boer J (1993) Toxaphene: Analytical chemistry. Chemosphere 27:1827–1834

Muir D, Braune B, DeMarch D, Norstrom R, Wagemann R, Lockhart L, Hargrave B, Bright D, Addison R, Payne J, Reimer K (1999) Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: A review. Sci Total Environ 230:83–144

NPS (National Park Service) (2005) Bird species and distributions in Yukon—Charley Rivers National Preserve. Available from http://www.nps.gov/yuch/Expanded/key_resources/birds/inventory.htm (Accessed August 4, 2005)

Newell AJ, Johnson DW, Allen LK (1987) Niagara River biota contamination project: Fish flesh criteria for piscivorous wildlife.

New York State Department of Environmental Conservation, Division of Fish and Wildlife, Bureau of Environmental Protection Technical Report 87-3. New York State Department of Environmental Conservation, Albany

Northern Contaminants Program (2003) Canadian Arctic Contaminants Assessment Report Phase II. Indian and Northern Affairs Canada, Whitehorse, Yukon, QS-8526-010-EE-A1

Northern Contaminants Program (2004) Yukon Contaminants Database. Indian and Northern Affairs Canada, Whitehorse, Yukon

Nosek JA, Craven SR, Sullivan JR, Hurley SS, Peterson RE (1992) Toxicity and reproductive effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in ring-necked pheasant hens. J Toxicol Environ Health 35:187–198

Peakall DB (1996) Dieldrin and other cyclodiene pesticides in wildlife. In: Beyer WN, Heinz GH, Redmon-Norwood AW (eds) Environmental contaminants in wildlife: Interpreting tissue concentrations. Lewis Publishers, Boca Raton, FL, pp 73–98

Ribick MA, Dubay GR, Petty JD, Stalling DL, Schmitt CJ (1982) Toxaphene residues in fish: Identification, quantification, and confirmation at part per billion levels. Environ Sci Technol 16:310–318

Rudd JW (1995) Sources of mercury to freshwater ecosystems: A review. Water Air Soil Pollut 80:697–713

Ryan MJ, Stern GA, Diamond M, Croft MV, Roach P, Kidd K (2005) Temporal trends of organochlorine contaminants in burbot and lake trout from three selected Yukon lakes. Sci Total Environ 351–352:501–522

Salomone P, Bergstrom DJ (2004) Yukon river summer chum Salmon stocks status and action plan. Regional Information Report No. 3A04-03. Alaska Department of Fish and Game Division of Commercial Fisheries, Anchorage

Sample BE, Opresko DM, Suter GW (1996) Toxicological Benchmarks for Wildlife: 1996 Revision. Oak Ridge National Laboratory, Oak Ridge, TN, ES/ER/TM-86/R3

Schmitt CJ (2002) Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental contaminants and their effects on fish in the Mississippi River basin. US Geological Survey Biological Resources Division BSR 2002-0004. US Geological Survey, Columbia, Missouri

Schmitt CJ, Dethloff GM, Hinck JE, Bartish TB, Blazer VS, Coyle JJ, Denslow ND, Tillitt DE (2004) Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental contaminants and their effects on fish in the Rio Grande basin. US Geological Survey Biological Resources Division SIR 2004-5108. US Geological Survey, Columbia, Missouri

Schmitt CJ, Zajicek JL, May TW, Cowman DF (1999) Organochlorine residues and elemental contaminants in US freshwater fish, 1976–1986: National Contaminant Biomonitoring Program. Rev Environ Contam Toxicol 162:43–104

Schumm SA, Winkley BR (1994) The character of large alluvial rivers. In: Schumm SA, Winkley BR (eds) The variability of large alluvial rivers. American Society of Civil Engineers, New York, pp 1–9

Shubat PJ, Curtis LR (1986) Ration and toxicant preexposure influence dieldrin accumulation by rainbow trout (*Salmo gairdneri*). Environ Toxicol Chem 5:69–77

Snyder-Conn E (1992) Contaminant investigation of fish in Lake Minchumina, Alaska. US Fish and Wildlife Service, Northern Alaska Ecological Services, NAES-TR-92-03, Fairbanks, Alaska

Spehar RL (1976) Cadmium and zinc toxicity to flagfish (*Jordanella floridae*). J Fish Res Board Canada 33:1939–1945

Stouthart X, Haans J, Lock R, Wendelaar Bonga S (1996) Effects of water pH on copper toxicity to early life stages of the common carp (*Cyprinus carpio*). Environ Toxicol Chem 15:376–383

Swackhamer D, Charles J, Hites R (1987) Quantitation of toxaphene in environmental samples using negative ion chemical ionization mass spectrometry. Anal Chem 59:913–917

Szumigala DJ, Hughes RA, Harris RH (2003) Alaska's Mineral Industry 2003. Special Report 58. Division of Geological and Geophysical Survey, Fairbanks, Alaska

Tillitt DE, Giesy JP, Ankley GT (1991) Characterization of the H4IIE rat hepatoma cell bioassay as a tool for assessing toxic potency of planar halogenated hydrocarbons in environmental samples. Environ Sci Technol 25:87–92

Tillitt DE, Gale RW, Meadows JC, Zajicek JL, Peterman PH, Heaton SN, Jones PD, Bursian SJ, Kubiak TJ, Giesy JP, Aulerich RJ (1996) Dietary exposure of mink to carp from Saginaw Bay 3. Characterization of dietary exposure to planar halogenated hydrocarbons, dioxin equivalents, and biomagnification. Environ Sci Technol 30:283–291

Tillitt DE, Schmitt CJ, Weseloh DV, Bunck CM (1998) Organochlorine concentrations and trends in North American fish and wildlife. In: Cary J, Cook P, Giesy J, Hodson P, Muir D, Owens JW, Solomon K (eds) Ecotoxicological risk assessment of the chlorinated organic chemicals. SETAC Press, Pensacola, FL

US BLM (Bureau of Land Management) (2002) Final environmental impact statement renewal of the federal grant for the trans-Alaska pipeline system right-of-way. US Bureau of Land Management, BLM/AK/PT-03/005+2880+990, Washington DC

US EPA (Environmental Protection Agency) (1993) Wildlife exposure factors handbook. Office of Health and Environmental Assessment and Office of Research and Development, Washington, DC. EPA/600/R093/187

US EPA (Environmental Protection Agency) (1998) EPA superfund record of decision amendment: Eielson Air Force Base, EPA ID AK1570028646. Fairbanks, Alaska, EPA/AMD/R10-98/185

US FWS (Fish and Wildlife Service) (1986) Trace elements from placer mining in Alaskan streams are toxic to young salmonids. Research Information Bulletin #98. US Fish and Wildlife Service, Anchorage, Alaska

US FWS (Fish and Wildlife Service) (1991) Young salmon are sensitive to arsenite and mercury released by placer mining activities. Research Information Bulletin #30. US Fish and Wildlife Service, Anchorage, Alaska

US FWS (Fish and Wildlife Service) (2005) National Wildlife Refuges—Alaska Region. Available from http://alaska.fws.gov/internettv/nwrtv/maptv.htm (Accessed August 4, 2005)

West RL, Deschu NA (1984) Kantishna Hills heavy metals investigations, Denali National Park, 1983. US Fish and Wildlife Service, Interagency Agreement with the National Park Service 14-16-007-85-5524

Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM (2002) Ecotoxicology of mercury. In: Hoffman DJ, Rattner BA, Burton GA Jr, Cairns J Jr (eds) Handbook of Ecotoxicology, 2nd ed. Lewis Publishers, Boca Raton, FL

Whyte JJ, Schmitt CJ, Tillitt DE (2004) The H4IIE cell bioassay as an indicator of dioxin-like chemicals in wildlife and the environment. Crit Rev Toxicol 34:1–83