FISH MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS IN ALBERTA, CANADA

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Introduction

The major routes of human exposure to polycyclic aromatic hydrocarbons (PAHs) are ingestion and inhalation. From a public health perspective, consumption of PAHs contaminated food is the most significant source of exposure for the general population. Particular interest has been shown for fish in the Alberta oil sands region. Fifteen priority PAHs have been adopted to assess either environmental effects or human health risks. Human health concerns are mostly associated with exposure to four to six ring PAHs shown to exhibit carcinogenic activity in experimental animals. Benzo[a]pyrene exposure may increase the risk of occurrence of some types of cancer in humans. Between 2009–2012, we have conducted a fish monitoring program to assess potential human health risks associated with the consumption of PAHs tainted fish including Lake Athabasca, downstream from the oil sands region of Alberta, Canada. The environmental and public health impacts of the oil sands have been particularly controversial[1]. Some studies have suggested that oil sands development is responsible for increasing PAHs levels in the Athabasca River[2,3,4] while others have attributed PAHs levels to background contributions from natural oil sands formations[5]. In either case, downstream consumers are understandably concerned about the potential health risks of consuming fish contaminated with PAHs.

Based on their molecular structures and weights, the 15 priority PAHs are divided into three groups: low molecular weight (LMW), medium molecular weight (MMW), and high molecular weight (HMW). LMW PAHs are those PAHs with three rings, Acenapthylene (ACY), Acenaphthene (ACE), Fluorene (FL), Phenanthrene (PH) and Anthracene (AN). MMW PAHs are those with four rings, Pyrene (PY), Fluoranthene (FLU), Benzo[a]anthracene (B[a]A) and Chrysene (CH). HMW PAHs are those with five or six rings, Benzo[b]fluoranthene (B[b]FLU), Benzo[k]fluoranthene (B[k]FLU), Benzo[a]pyrene (B[a]P), Indeno[1,2,3-c,d]pyrene (IP), Dibenz[a,h]anthracene (D[a,h]A) and Benzo[g,h,i]pyrene (B[g,h,i]P).

Materials and methods

The field collection of fish was conducted by gill-netting, angling and electrofishing between 2009 and 2012. The ten fish sampling sites were various lakes in Alberta including Lake Athabasca that receives the Athabasca River flowing through the oil sands. The fish species collected included northern pike (*Esox Lucius*), lake trout (*Salvelinus namaycush*), lake whitefish (*Coregonus clupeaformis*), walleye (*Hiodon alosoides*), brook trout (*Salvelinus fontinalis*), and rainbow trout (*Oncorhynchus mykiss*). These are all sport fish that are likely to be consumed by humans. Each fish sample was wrapped in solvent-rinsed aluminum foil, placed into a container with ice packs, and sent to the laboratory for analysis. Fish samples were kept at -20°C until PAHs analysis. The PAHs testing in fish muscle and liver samples was performed using an approach based on EPA method 3545A, 2007 for sample extraction and EPA method 8270D version 4, 2007 for GC/MS analysis. Five grams of homogenized fish tissue was mixed with 20 g of anhydrous sodium sulfate to remove moisture, then transferred into a 33 ml stainless steel accelerated solvent extraction cell, spiked with PAH surrogate (acenaphthene-d10, chrysene-d12, 1,4 dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10, Accustandard, New Haven, CT, USA) and topped up with Ottawa sand (Fisher Scientific Canada). The extractions were carried out using dichloromethane (DCM, Optima grade, Fisher) as the extraction solvent with a Dionex Accelerated Solvent Extraction ASE 200 system (Dionex, Sunnyvale, CA, USA). The DCM extracts were then dried with combusted sodium sulfate and concentrated down to 5 ml by nitrogen evaporator. The concentrated extracts were loaded on to a gel permeation chromatography system (GPC, Automated Gilson GX-271GPC clean-up system) equipped with an Envirosep ABC GPC column, (350 x 21.2 mm, Phenomenex, Torrance, CA, USA) to remove lipids in the extracts. The PAH fractions collected from GPC were blown down under nitrogen gas near to dry, reconstituted with 2 ml hexane (Optima grade, Fisher) and loaded onto the 30 cm silica gel column for further sample clean-up. The PAH fractions were eluted using 1:1 DCM/pentane and concentrated to 1 ml by nitrogen evaporation prior to gas chromatography mass spectrometry (GC-MS) analysis.

The estimated daily intake (EDI) was calculated by the equation: EDI = C * IR * BF / BW, where IR is the rate of fish consumption (kg/d). The IR (kg/d) was classified into four groups for this study as: high (> 0.100 kg/day), medium (0.033–0.099 kg/day), low (0.005–0.029 kg/day), and very low (<0.004 kg/day). BF is the bioavailability factor (assumed to be 100% unit less, which is the maximum possible and most conservative assumption for this factor). BW is average body weight in humans (kg). Self-reported adult average weights for Albertans are 76.8, 85.7, and 67.2 kg for adults, males, and females, respectively. The body weights used in this study are 77 kg for adults, 67 kg for female adults, and 33 kg children (1 - 8 years old). C is a representative measure of PAH concentrations in fish muscle (ng/g, wet weight) expressed as TEQ. The TEQ is the sum concentration of the measured PAHs and the total mean TEQ is the average of all TEQs calculated from a fish tissue sample. The 50^{th} and 90^{th} percentile of the total mean TEQ concentrations were used for estimating exposure ratios. PAHs contaminant concentration is determined by multiplying the concentration of a particular PAHs analyte with its respective toxic equivalent factor (TEF) relative to benzo-a-pyrene (B[a]P).

Fifteen priority PAHs compounds for screening purpose were selected based on environmental effects and toxicological data (USEPA 2000). The TEFs for these PAHs was set by Health Canada. This agency regards an upper bound lifetime cancer risk level (LCR) of 1 in 100,000 (the maximum individual reference risk level, MIRRL) to be an essentially negligible cancer risk. The equation used to calculate upper bound lifetime carcinogenic risk for a given ongoing lifetime exposure scenario is LCR = EDI x CSF where EDI is the estimated daily intake continuing over a lifetime (mg/kg bw/day); and CSF is a cancer slope factor (mg/Kg bw/day)$^{-1}$. The oral cancer slope factor (CSF) of 2.3 (mg/kg bw/day)$^{-1}$ provided by Health Canada was used. An ER can be calculated as a ratio of what the calculated LCR is versus the MIRRL of 1 in 100,000 lifetime cancer risk: ER = LCR / MIRRL. Consumption limits may be produced to provide fish advisories. The equation for calculating lifetime average daily consumption limits is provided by the USEPA (USEPA, 2000) and is presented as: CR_{LIM} = (MIRRL* BW) / (CSF * C), where CR_{LIM} is a maximum allowable fish consumption rate (kg/day); MIRRL and BW as defined above, CSF is a cancer slope factor (mg/kg bw/day)$^{-1}$, and 2.3 (mg/kg bw/day)$^{-1}$ was used, and C is a measured concentration of chemical contaminant (as TEQ) in fish species (mg/kg).

Results and discussion

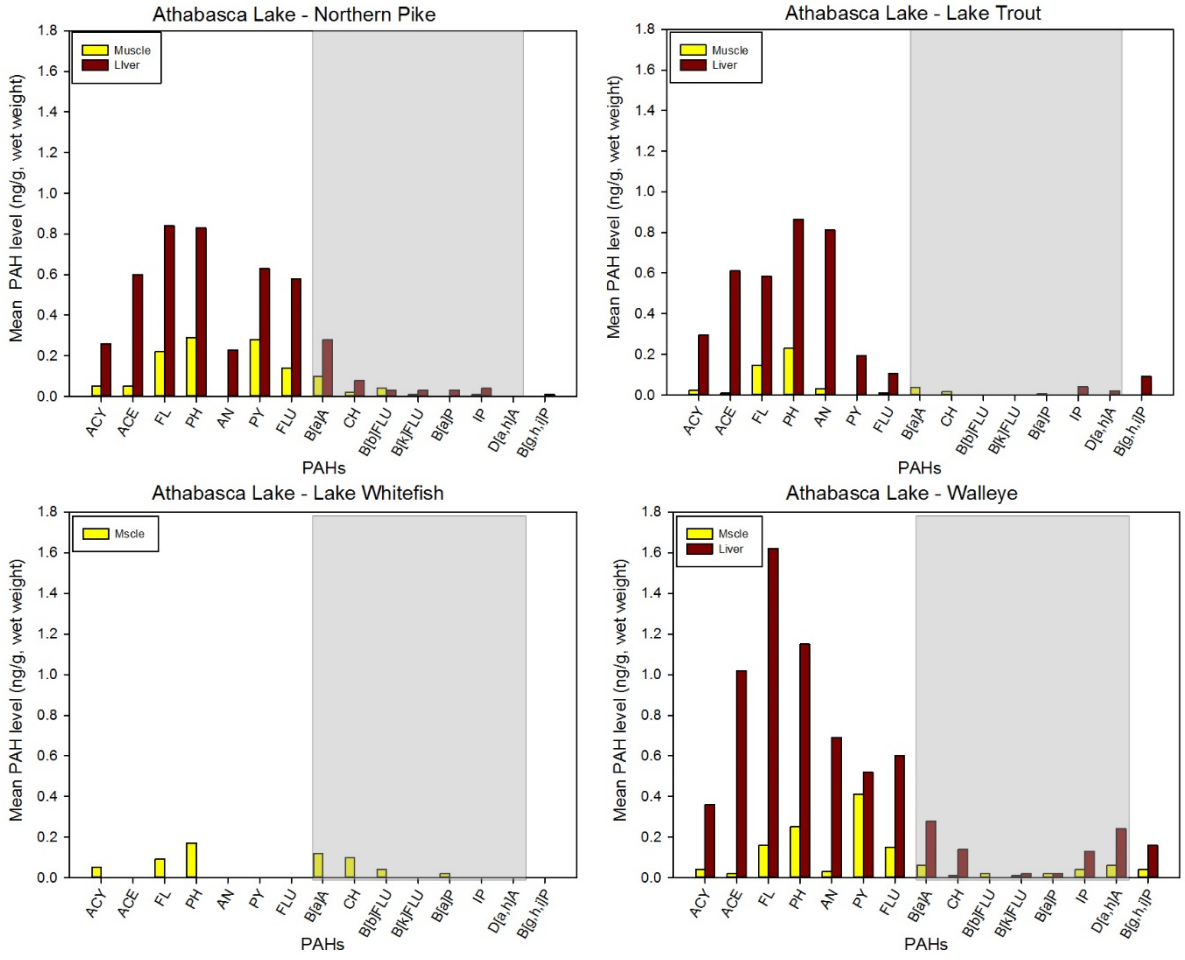
The sum of total PAH concentration (∑PAH) as expressed in lipid weight (ng/g) is shown in the table below.

Species	Year	Muscle (N=110)		Liver (N=44)	
		Mean	Range	Mean	Range
Lipid content (%)		1.55	0.35 – 15	15	1.7 – 31
Lake Athabasca					
Northern pike	2009	213	nd – 687	55	28 – 106
Lake trout	2010	13	nd – 82	27	3.7 – 142
Lake whitefish	2010	68	5.4 – 121	n/a	n/a
Walleye	2009	161	2.4 – 459	35	26 – 74
Sturgeon Lake					
Northern pike	2009	8.7	nd – 35	19	2.4 – 34
Walleye	2009	26	3.7 – 43	n/a	n/a
Chrystina Lake					
Brook trout	2010	101	28 – 332	n/a	n/a
Isle Lake					
Walleye	2009	52	7.6 – 100	n/a	n/a
Calling Lake					
Walleye	2009	13	nd – 33	n/a	n/a
Touchwood Lake					
Northern pike	2009	110	nd – 286	16	7.5 – 34
McGregor Lake					
Walleye	2009	166	57 – 234	n/a	n/a
Dickson Trout Pond					
Rainbow trout	2012	50	nd – 325	n/a	n/a
Little Bow Reservoir					

Northern pike	2010	99	48 – 130	25	20 – 31
Crawling Valley Reservoir					
Northern pike	2009	409	16 – 752	n/a	n/a
Walleye	2009	45	nd – 145	n/a	n/a

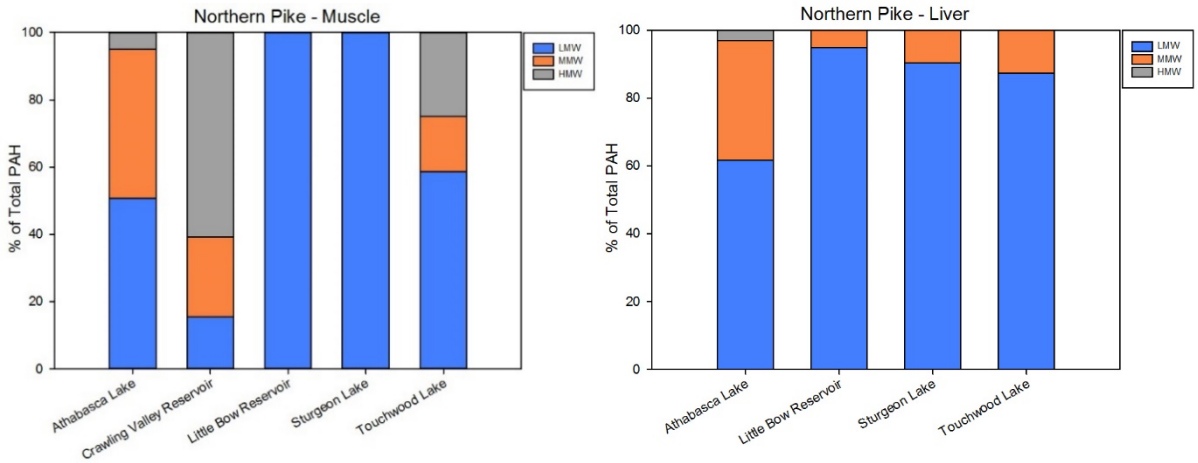
The mean of lipid-based ∑PAH ranged from 13 to 409 ng/g (lipid) for muscle samples and 16 to 55 ng/g (lipid) for liver samples. The lipid-based ∑PAH levels were higher in the muscles than in the livers ($p < 0.01$). The highest concentration (409 ng/g, lipid) was found in the muscle samples of northern pike collected from Crawling Valley Reservoir.

PAH profiles that have higher concentrations of low molecular weight (LMW) PAHs are characteristic of PAHs generated by petroleum, but this is best confirmed by a dominance of alkyl-substituted PAHs, data that were not available for our sample analyses. Source attribution for PAHs found in environmental media has attracted considerable attention with a variety of indicators or ratios proposed. A series of indicators were proposed based on individual PAHs and sub-groups of PAHs that could be used and various schemes of increasing complexity for attributing PAH composition to specific sources have been developed. The PAH patterns in fish from Lake Athabasca are shown in the graphs below.



One explanation for this PAH profile in fish is the physicochemical properties of PAHs. LMW PAHs are more soluble in water than HMW PAHs. In addition, HMW PAHs, such as B[a]P, are more lipophilic and so have a tendency to partition to sediment particles, which decreases the bioavailability of HMW PAHs in the water column for fish. As a result, LMW PAHs are more bioavailable in the water column, which means greater exposure and absorption of LMW PAHs among fish. This trend lowers the PAH risk to human consumers.

The proportion of PAHs on one fish species, northern pike from Lake Athabasca is shown in the graph below. Low molecular weight (LMW) PAHs include ACY, ACE, FL, PH and AN, medium molecular weight (MMW) PY, FLU, B[a]A, CH, and high molecular weight (HMW) are B[b]FLU, B[k]FLU, B[a]P, IP, D[a,h]A and B[g,h,i]IP).



The exposure ratios for adults and children in the high intake group were evaluated. All exposure ratios were less than one. Therefore, none of the samples would pose a significant cancer risk for humans. There is currently no need to issue a public health fish consumption advisory in relation to PAH levels in fish muscle nor liver.

The findings indicate that:

- The PAH levels in fish in Alberta water bodies were within the levels in similar fish species reported in other locations,
- The estimated human exposures to PAHs were low for local consumers,
- Baseline information on PAH levels in local fish was developed,
- Guidance for PAHs in fish was developed to support public health decision making.

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