

## Spatial and temporal distribution of PAHs in the North Saskatchewan River, Alberta, Canada

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**Abstract** Northern Canadian Rivers provide a broad range of ecosystem services, but increasing pressures from development and resource extraction have negatively impacted the ecology and water quality of many of these relatively pristine river systems. The North Saskatchewan River (NSR) drains an area of 57 000 km<sup>2</sup> in northern Alberta and provides water for multiple uses. However, landscape disturbance has increased the flux of a variety of sediments and associated contaminants in this river. To evaluate the spatial (gradient from headwater to downstream sites) and temporal (inter-annual) variation of PAHs in the NSR, grab samples of fine-grained river bed/bank sediment deposits were collected in 2010 and 2011 at 20 monitoring sites over a distance of 1000 km from Rocky Mountain House to Lloydminster. An additional 10 samples were collected in 2011 at the confluence of the main river with tributaries of varying land use. Individual congeners of 16 PAHs were extracted from sediment samples and analysed for PAHs. Compared to data reported for other northern Canadian rivers, PAH levels in the NSR are comparatively low (7 to 40 ng/g) and well below the sediment quality guidelines consensus-based Threshold Effect Concentration (TEC). PAHs in NSR sediment are primarily of pyrogenic origin and likely originate from mining processes, combustion of fossil fuels and some industrial discharges.

**Key words** polycyclic aromatic hydrocarbons; sediment; North Saskatchewan River, Canada; sediment quality guidelines

### INTRODUCTION

Many large river ecosystems in the world are under increasing pressures due to a wide range of natural and anthropogenic disturbances that influence flow characteristics, water quality and ecosystem health at a variety of spatial and temporal scales (Wrona *et al.*, 1996; Davies *et al.*, 2000; Walling & Fang, 2003). Relatively little is known about the impact of these disturbance effects in large rivers that drain northern temperate regions of the globe, primarily because of the large spatial scales involved, the lack of empirical data and poor theoretical understanding of these systems (Stanley & Boulton, 2000). Many northern river basins in Canada drain vast areas that integrate widespread atmospheric contaminant deposition and point-source inputs (Wrona *et al.*, 1996; MacDonald *et al.*, 2000). Studies investigating the quality of sediment in these rivers report elevated levels of persistent organic contaminants such as dioxins/furans (Culp *et al.*, 2000) and polycyclic aromatic hydrocarbons (Yunker *et al.*, 1993, 1996, 2002; Kurek *et al.*, 2013).

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 organic compounds with fused aromatic carbon rings that are widely distributed in the environment (Harvey, 2011). Because of their carcinogenic and mutagenic properties, the US EPA has classified 16 PAH congeners as priority pollutants (Gremm & Frimmel, 1994). These compounds can originate from geological deposits (petrogenic origin) but are mainly derived from processes such as combustion (pyrogenic origin) or microbial degradation (diagenic origin) (Sporstol *et al.*, 1983; Masplet *et al.*, 1987; Colombo *et al.*, 1989; Yunker *et al.*, 1993). PAHs are hydrophobic and preferentially bind to organic coatings of small particles in aquatic sediments and soils (Yang *et al.*, 2011). Accordingly, PAHs are present in many ecosystems and can enter the environment along multiple pathways that include releases to air, water, soil and sediment (US EPA 1996; 1997). The environmental impacts of PAH exposure to fish and humans are well documented (MacDonald *et al.*, 2000).

The North Saskatchewan River (NSR) receives inputs of sediment-associated contaminants from multiple sources including municipal and industrial wastewater discharges, storm and combined sewer discharges, tributary inputs, diffuse overland sources and river erosion (Donahue, 2009; AECOM, 2011). However, the chemical, physical and biological characteristics of sediment in the NSR have not been fully evaluated and additional information is required to assess their

provenance, storage (short and long term), fate and environmental impact (bioavailability and toxicity). The objectives of the present study were to: (1) evaluate the spatial and temporal variability of PAHs in sediment samples collected at 20 sampling stations in the NSR and an additional 10 key tributaries and (2) compare NSR PAH data with other related studies in northern Canadian rivers to provide a broader regional context. The data are presented and discussed in the context of their spatial (gradient from headwater to downstream sites) and temporal (inter-annual) variation. An assessment for sediment quality conditions in the NSR is provided by comparing the contaminant data (PAHs) to sediment quality guidelines (SQGs) that include the consensus-based Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) reported by MacDonald *et al.* (2000).

## METHODS

### Study area

Source waters of the NSR originate from the Saskatchewan Glacier in Banff National Park, Alberta. The NSR (1287-km long) flows across three Canadian provinces and drains an area of 122 800 km<sup>2</sup>. Mean annual discharge of the NSR at the Alberta Saskatchewan border is approx. 7 billion m<sup>3</sup>. In Alberta, the main tributaries of the NSR in the headwaters are the Brazeau, Ram and Clearwater rivers. The Sturgeon and Vermillion rivers contribute flow downstream of Edmonton. Two dams (Brazeau and Bighorn) located in the upper reaches of the NSR regulate river discharge. Winter flows are low but they increase dramatically in late spring and early summer during snowmelt and rain events. Flow regulation has altered seasonal flow patterns and resulted in somewhat lower summer flows and higher winter flows. The NSR basin drains a wide range of physiographic settings that differ in climate, geology, soils and landscape, elevation and natural vegetation. The regions include the Rocky Mountains, Foothills, Boreal Forest and Grassland regions, but the majority of the NSR drainage area is within the Central Parkland Natural Region (Donahue, 2009; AECOM, 2011).

### Sediment sampling

Grab samples of fine-grained river bed/bank sediment deposits were collected at 20 long-term river network (LTRN) monitoring sites along the NSR from Rocky Mountain House to Lloydminster in 2010 and 2011. An additional 10 samples (fine-grained river bed/bank sediment) were collected at the confluence of 10 tributaries of the NSR. The location of NSR and tributary study sites are shown in Fig. 1.

### PAH analysis

Sediment samples were frozen and then transported to Activation Labs located in Ancaster, Ontario, for PAH analysis. Individual congeners for the standard list of 16 PAHs were extracted in sediment samples (about 2 g) for 16 h with 100 ml acetone/dichloromethane/n-hexane (1:1:1, v/v/v) in Soxhlet apparatus (US EPA, 1996a). The concentrated extract was cleaned using a florisil column according to the EPA Standard Method 3620B (US EPA, 1996b). Deuterated PAHs [naphthalene-d<sub>8</sub> (d<sub>8</sub>-Nap), acenaphthene-d<sub>10</sub> (d<sub>10</sub>-Ace), phenanthrene-d<sub>10</sub> (d<sub>10</sub>-Phe), chrysened<sub>12</sub> (d<sub>12</sub>-Chr) and perylene-d<sub>12</sub> (d<sub>12</sub>-Per)] were used as internal standards for quantification. Extracts were analysed for PAHs using a Hewlett-Packard (HP) 6890N gas chromatograph (GC) coupled with an HP-5973 mass selective detector (MSD) and a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column using EPA Standard method 8270C (US EPA, 1996c). PAHs detected by GC with mass spectrometry (GC-MS) include naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene+benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. Benzo(b)fluoranthene and benzo(k)fluoranthene were co-eluted and quantified together.

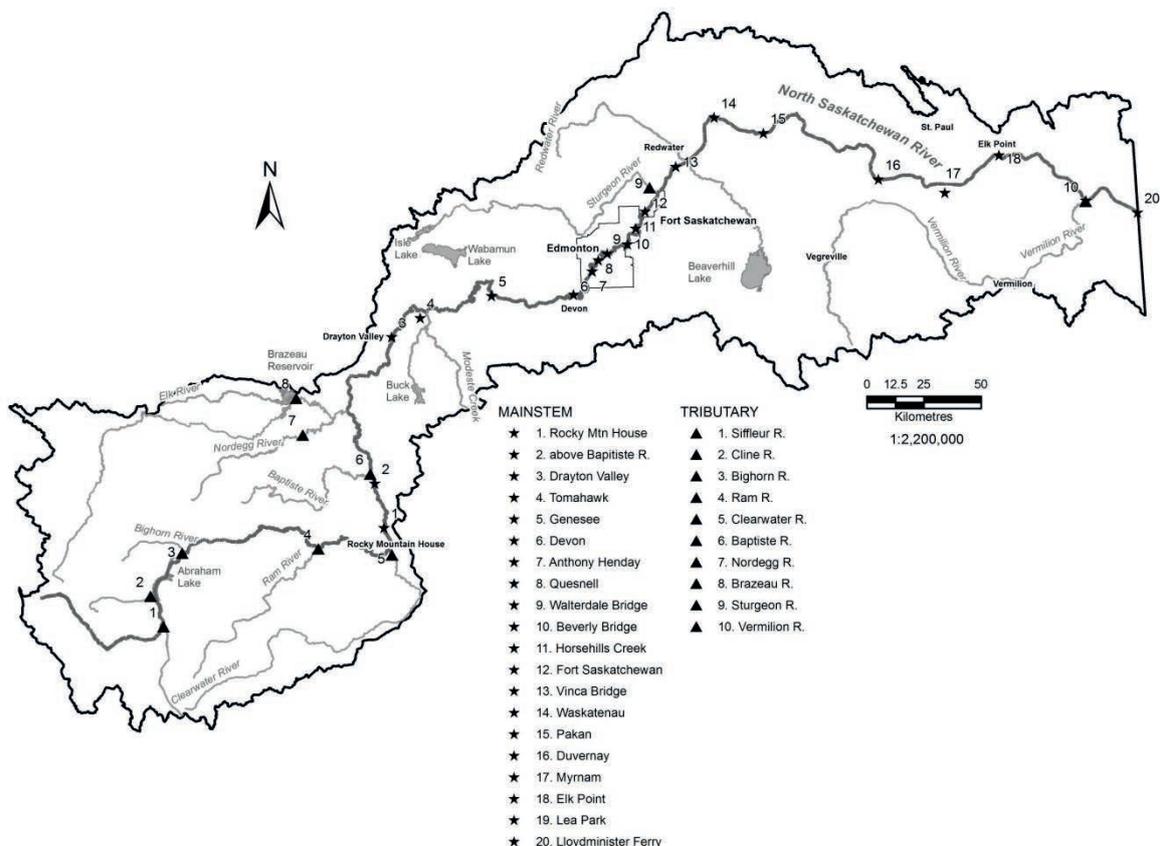


Fig. 1 Location of the study sites in the North Saskatchewan River and major tributaries.

## RESULTS AND DISCUSSION

### Total PAHs

In an early study of the global distribution of PAHs in recent sediments, LaFlamme & Hites (1978) reported that these organic contaminants are widely distributed in a range of aquatic systems. They found that the qualitative PAH pattern was remarkably constant for most of the locations studied and that total PAH abundance typically increases with proximity to large urban/industrial centres. More recently, several studies have been conducted globally to document the concentration and sources of PAHs in river sediment. Guo *et al.* (2007) investigated the spatial distribution PAHs in surface water, suspended particulate matter (SPM) and sediment in the Daliao River watershed, China. They reported that total PAH concentrations ranged from 946 to 13 449 ng/L in surface water, 317 to 238518 ng/g in SPM and 62 to 841 ng/g in sediments. In a study of PAH distribution in 29 Malaysian riverine and estuarine sediments, Zakaria *et al.* (2002) reported total PAHs concentrations ranging from 4 to 924 ng/g and the major sources were dumping of waste oil and urban runoff. Santschi *et al.* (2001) examined the historical contamination of PAHs in sediment cores from the Mississippi River Delta, Galveston Bay and Tampa Bay. They found trace organic contaminant levels in surface sediments at these three sites were lower than sediment deposited between 1940 and 1970. Tampa Bay was an exception where elevated levels of total PAHs were attributed to local sources due to the proximity to shore. These studies demonstrate the important role of particulate matter in the global distribution and fate of PAHs in the environment (atmospheric, terrestrial and aquatic) and the importance of proximity to PAH sources.

Relatively few studies have been conducted to determine the spatial distribution and temporal variability in PAHs in northern Canadian river systems. Studies to date indicate the presence of sediment-associated PAHs in large northern rivers in Canada (Yunker *et al.*, 1993, 1996, 2002) and their deltas (Milburn & Prowse, 1997; Timoney & Lee, 2011). Yunker *et al.* (1993) conclude

that relatively high PAH concentrations in the Mackenzie River and Beaufort Sea are primarily derived from petroleum or natural bitumen sources. In a study of PAHs in the Fraser River, Yunker *et al.* (2002) reported that remote regions of the Fraser River basin were lightly impacted but near Vancouver, vehicle emissions as well as storm and wastewater discharge were predominant sources of contamination. Timoney & Lee (2011) investigated the distribution of PAHs in water and sediments of the Athabasca Delta and Lake Athabasca. They reported that PAH concentrations increased at a rate of  $0.05 \pm 0.02$  mg/kg/year between 1999 and 2009. In their study, observed annual increases were correlated with annual bitumen production and mined sand volume, the extent of landscape disturbance and particulate emissions as well as total organic carbon in sediment and discharge of a major tributary of the Athabasca River. In suspended sediment samples collected from the Slave River by centrifuge at Fort Smith, McCarthy *et al.* (1997) detected PAH concentrations of concern ( $>650$  ng/g). About 100 km downstream of Fort Smith in the Slave River Delta, Milburn & Prowse (1997) reported that PAH levels ranged from 6 to 460 ng/g. In a recent study of PAH levels in six lakes near the Alberta oils sands operations, Kurek *et al.* (2013) report that total PAH fluxes are 2.5–23 times greater than ~1960 levels. They also report that PAH levels at one site impacted by oil sands operations have exceeded Canadian interim sediment quality guidelines since the mid-1980s. Based on the paucity of studies conducted to date, relatively high PAH levels have been measured in northern Canadian rivers that integrate widespread atmospheric contaminant deposition and point-source inputs within their drainage basins (Yunker *et al.*, 1996; Taylor *et al.*, 1998; Evans *et al.*, 2002; Timoney & Lee, 2011; Kurek *et al.*, 2013).

Compared to data reported for other northern Canadian rivers discussed above, PAH levels in NSR sediments are comparatively low (Table 1). Total PAH levels (sum of 15 congeners) ranged from 7 to 40 ng/g and were at concentrations well below the consensus-based TEC (Fig. 2). The mean  $\pm$  standard deviation of PAHs for 2010 and 2011 NSR samples were  $17.1 \pm 9.4$  ng/g and  $16.1 \pm 8.3$  ng/g, respectively. Similar values ( $15.4 \pm 12.5$  ng/g) were observed for the NSR tributaries. Total PAH levels in three tributaries (Vermillion, Ram and Bighorn) were  $>35$  ng/g.

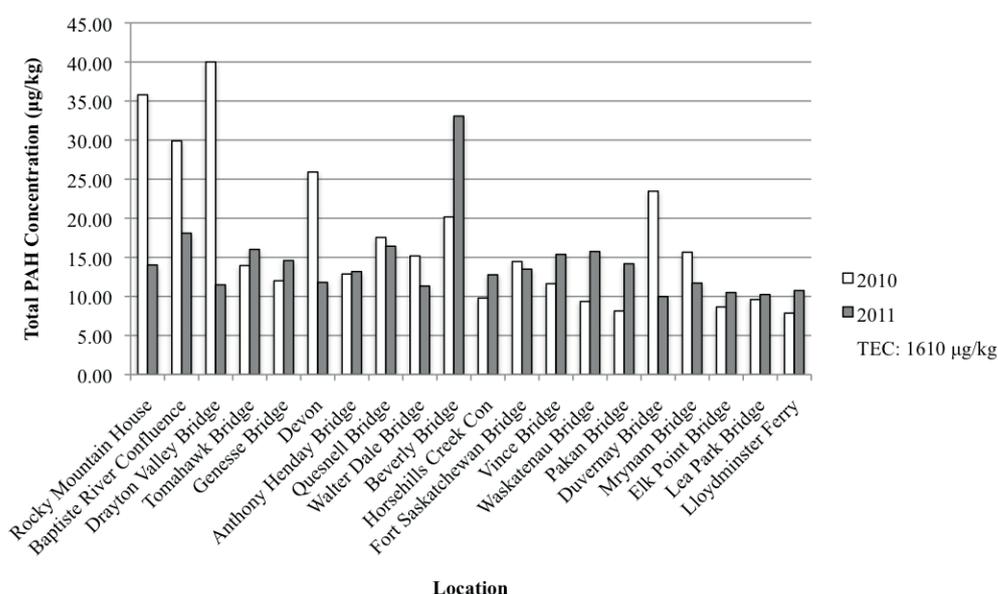
The environmental fate of PAHs is related to: (1) the partitioning of the chemical between environmental media, (2) the transport properties of the media, and (3) the transformation rate (Harvey, 2011). Since PAHs preferentially bind to fine particulate matter in aquatic systems, their fate is strongly influenced by the physical and chemical properties of particulate matter (Timoney & Lee, 2011). Accordingly, monitoring programmes that preferentially sample fine-grained river bed/bank sediment deposits may bias results of PAH analysis and produce values lower than expected due to the presence of silt and sand size fractions. *In situ* centrifuge samplers or Phillips samplers (Phillips *et al.*, 2000) are deployed to preferentially collect fine sediment ( $<100$   $\mu\text{m}$ ). Because of the influence of grain size distribution on PAHs, it may be possible that PAH levels would have been higher than reported herein had these *in situ* samplers been deployed in the NSR.

The inter-annual and longitudinal variation of total PAH levels in the NSR are shown in Fig. 2. With the exception of six of the 20 NSR sites investigated, PAH levels were comparatively similar between 2010 and 2011. In 2010, the highest total PAH concentrations were measured in the uppermost three NSR tributary sites, but these levels decreased in 2011. Increases in total PAH levels in 2010 were attributed to increased concentrations of naphthalene that decreased in 2011. There was no significant trend in PAH concentration with distance downstream.

The inter-annual and longitudinal variation of six of the most abundant PAH congeners measured in NSR sediment are shown in Fig. 3. PAH congeners whose levels were below the detection limit ( $<1$  ng/g) are presented as one half of the detection limit (0.5 ng/g). With the exception of the Drayton Valley site, phenanthrene was detected at all sites at levels  $<5$  ng/g. In 2010, naphthalene levels  $>10$  ng/g were measured at four sites (Rocky Mountain House, Baptise River confluence, Drayton Valley Bridge and Devon) but in 2011 they decreased to  $<7.5$  ng/g. Drayton Valley is the epicenter for oil and gas activity (including non-conventional fracking operations) in the NSR watershed. The Rocky and Bapsite subwatersheds have considerable oil and gas operations and this land use activity is likely responsible for slightly elevated naphthalene levels observed at these sites.

**Table 1** PAHs in NSR sediment (ng/g).

Compound	TEC	Aromatic ring	Median	Max	Min	% of samples >TEC
Napthalene	176	2	4.25	22.54	0.86	0
Acenaphthylene		3	0.50	1.81	0.50	
Fluorene	77.4	3	0.50	3.11	0.50	0
Phenanthrene	204	3	1.59	21.34	0.50	0
Anthracene	57.2	3	0.50	2.43	0.50	0
Fluoranthene	423	4	0.50	3.82	0.50	0
Pyrene	195	4	0.50	4.42	0.50	0
Benzo(a)anthracene	108	4	0.50	2.35	0.50	0
Chrysene	166	4	0.50	3.85	0.50	0
Benzo(b)fluoranthene		5	0.50	8.83	0.50	
Benzo(k)fluoranthene		5	0.50	2.86	0.50	
Benzo(a)pyrene	150	5	0.50	5.09	0.50	0
Indeno(123-cd)pyrene		5	0.50	1.30	0.50	
Dibenzo(ah)anthracene	33	6	0.50	3.26	0.50	0
Benzo(ghi)pyrene		6	0.50	6.36	0.50	

**Fig. 2** Spatial and temporal variation of total PAHs in NSR and tributary sediment.

### Source identification

Ratios of PAHs in sediment samples have been developed and are often used for source discrimination (Gschwend & Hites, 1981; Sicre *et al.*, 1987; Colombo *et al.*, 1989; Yunker *et al.*, 2002). The ability to discriminate PAH sources is based on knowledge of the relative thermodynamic stability of various PAH compounds as well as differences in the PAH source characteristics and changes in PAH composition that can occur in the environment (Yunker *et al.*, 2002). PAH ratios such as phenanthrene/anthracene (PHE/ANT) are commonly used for source discrimination because phenanthrene is the most thermodynamically stable tri-aromatic isomer. Because the PHE/ANT ratio is temperature dependent, low PHE/ANT ratios (4 to 10) represent compounds formed at high temperature (Gschwend & Hites, 1981). In contrast, higher PHE/ANT values represent compounds formed at lower temperatures where organic matter is transformed into petroleum (Soclo, 1986; Benner *et al.*, 1990). Accordingly, the PHE/ANT ratio can be used to define two broad classes of sediments: PHE/ANT > 10 for petrogenic inputs and PHE/ANT < 10 for the dominance of pyrolytic sources. Similarly, the flouranthene/pyrene (FLT/PYR) ratio has

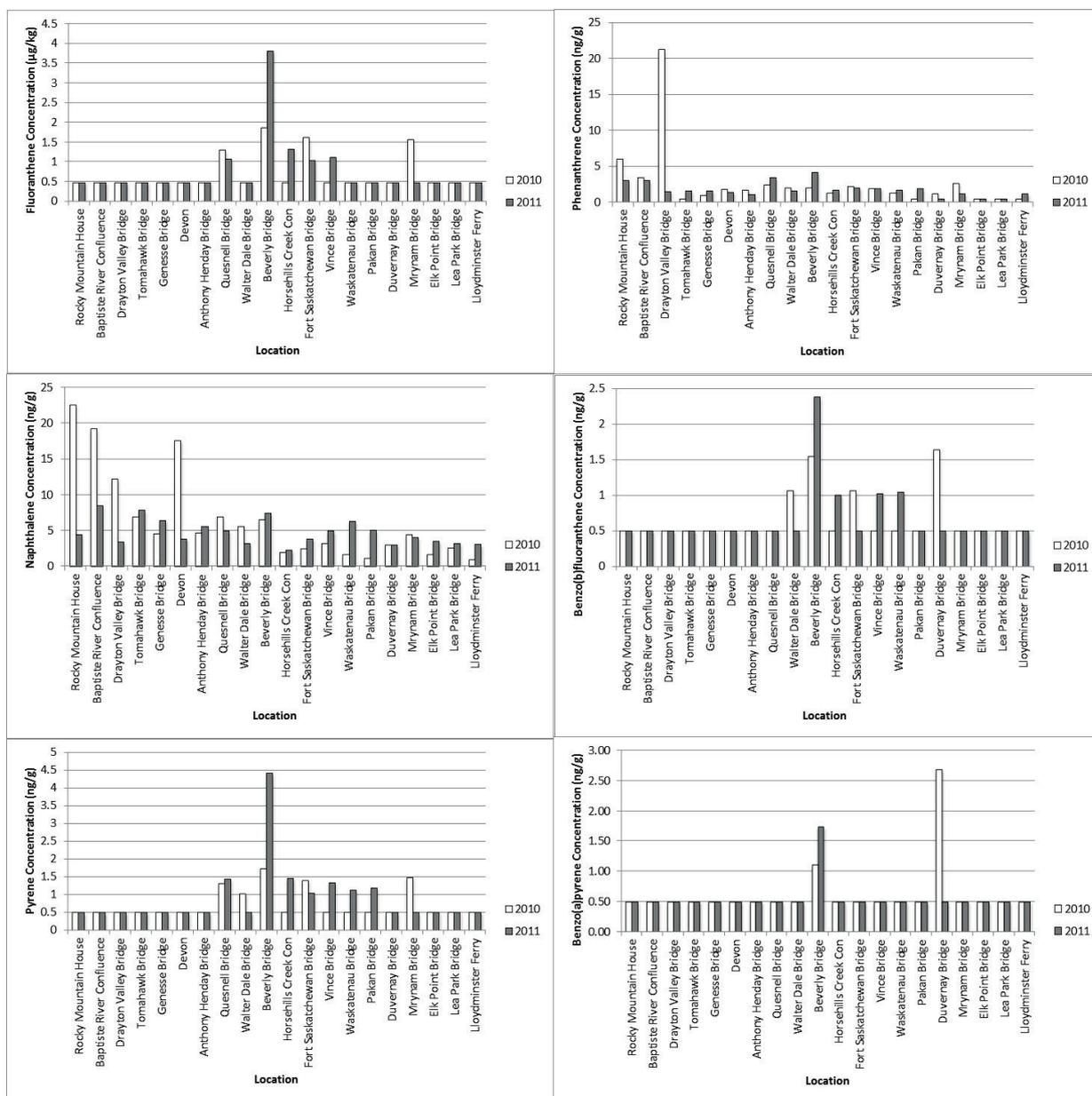


Fig. 3 Spatial and temporal variation of PAH congeners in NSR and tributary sediment.

been used to provide insight to the origin of PAH compounds. For example, values greater than 1 are typically related to pyrogenic origins (Sicre *et al.*, 1987). In atmospheric urban aerosols, pyrene levels are often greater than fluoranthene (FLT/PYR ~ 0.6 to 0.8) (Benner *et al.*, 1989). When plotted, PHE/ANT and FLT/PYR ratios provide a good indication of PAH sources from petrogenic or pyrolytic origin (Raoux, 1991).

In this study, PHE/ANT and FLT/PYR ratios indicate that most locations in the NSR exhibited a strong pyrolytic input (Fig. 4). The data suggest that the majority of PAHs in the NSR are likely due to mining processes, combustion of fossil fuels and some industrial discharges. Two exceptions in the data set are Drayton Valley Bridge (PHE/ANT 42.68) and Baptiste River near the mouth (PHE/ANT 33.02). PAHs at these two sites are likely of petrogenic origin from possible sources such as petroleum, crude oil and its refined products. Naturally occurring PAH sources in the NSR may include the natural erosion of coal or bitumen seams as well as forest fires, which can be frequent and severe in the head water regions of the basin.

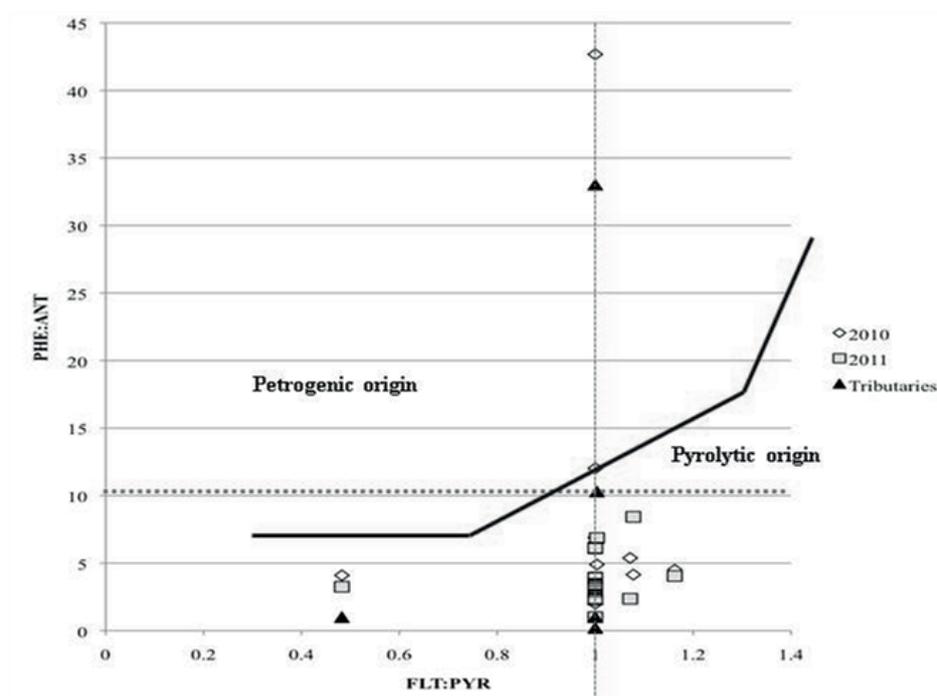


Fig. 4 PHE:ANT and FLT:PYR ratios for NSR and tributary sediments.

## CONCLUSIONS

A study was conducted to evaluate spatial and temporal distribution of PAH levels in fine grained bed/bank deposits on the NSR. Compared to data reported for other northern Canadian rivers, PAH levels in the NSR are comparatively low (7 to 40 ng/g) and well below the sediment quality guidelines consensus-based Threshold Effect Concentration (TEC). PAHs in NSR sediment are primarily of pyrogenic origin and likely originate from mining processes, wildfire, combustion of fossil fuels and some industrial discharges.

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