Characterizing the PAHs in surface waters and snow in the Athabasca region: Implications for identifying hydrological pathways of atmospheric deposition

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HIGHLIGHTS

- The highest PAH concentrations in the Athabasca River occur during high discharge.
- The PAH species present in river samples are different from those present on snow.
- Release of PAHs present on snow to surface waters is not the major source of PAHs.
- Snowmelt may contribute indirectly to increases in PAHs due to runoff and erosion.
- Understanding the fate of PAHs in catchments is needed for oil sands monitoring.

GRAPHICAL ABSTRACT

Principal Component Analysis of relative PAH abundances in snow and surface water in the Athabasca Oil Sands Region show that the organics present in rivers are compositionally different from those deposited on the snowpack.
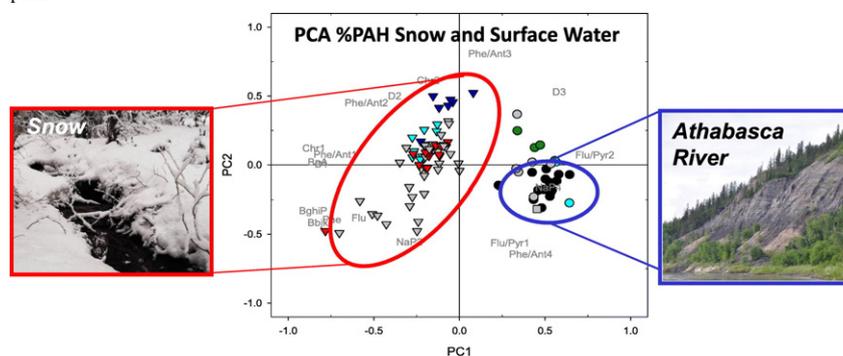
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ABSTRACT

The composition of polycyclic aromatic hydrocarbons present in snow and surface waters in the Athabasca Oil Sands Region (AOSR) was characterized in order to identify major contributors to the organics detected in rivers and lakes in the region. PAH concentrations, measured by three monitoring programs in 2011, were used to compare the PAH compositions of snow and surface waters across the AOSR. The 2011 dataset includes total (dissolved + particulate) concentrations of thirty-four parent and alkylated PAH compounds in 105 snow, 272 river, and 3 lake samples. The concentration of PAHs in rivers varies seasonally, with the highest values observed in July. The timing of increases in PAH concentrations in rivers coincides with the high river discharge during the spring freshet, indicating that this major hydrological event may play an important role in delivering PAHs to rivers. However, the composition of PAHs present in rivers during this period differs from the composition of PAHs present in snow, suggesting that direct runoff and release of PAHs accumulated on snow may not be the major source of PAHs to the Athabasca River and its tributaries. Instead, snowmelt may contribute indirectly to increases in PAHs due to hydrological processes such as erosion of stream channels, remobilization of PAH-containing sediments, increased catchment runoff, and snowmelt-induced groundwater inputs during this dynamic hydrologic period. Better understanding of transformations of PAH profiles during transport along surface and subsurface flow paths in wetland-dominated boreal catchments would improve identification of potential

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sources and pathways in the region. The compositional differences highlight the challenges in identifying the origins of PAHs in a region with multiple potential natural and anthropogenic sources particularly when the potential transport pathways include air, soil and water.

1. Introduction

Understanding the impacts of human activities on aquatic ecosystems in the Athabasca Oil Sands Region (AOSR) is required to ensure sustainable resource development in northeastern Alberta, Canada and to assess the economic benefit of oil sands development. Of particular concern in the AOSR is the release of polycyclic aromatic hydrocarbons (PAHs) because of the negative effects many PAH compounds have on human health (Delfino, 2002; Flowers et al., 2002; Perera et al., 2009; Chen et al., 2016) and the health of terrestrial and aquatic organisms (Colavecchia et al., 2004; Martin et al., 2005; Saunders et al., 2003; Vehniäinen et al., 2003). Given the negative effects of many PAH compounds on human and ecosystem health, it is important to understand the sources and pathways of PAH transport in the AOSR. PAHs are a group of over 100 different organic compounds commonly found in the environment (ATSDR, 1995). PAHs contain two or more fused aromatic rings (Harvey, 1997) and are classified as either parent PAHs, which contain only fused conjugated ring structures (e.g. Naphthalane and Chrysene), or alkylated PAHs, which contain various alkyl groups (e.g. C1 Naphthalene). PAHs can be categorized into pyrogenic and petrogenic groups (Wang et al., 2008; Yunker and Macdonald, 2003). Petrogenic PAHs originate from petroleum sources, including crude oil, fuels, lubricants and their derivatives (Saber et al., 2005). Pyrogenic PAHs are those formed by incomplete combustion of carbon-containing fuels such as wood, grass, coal, and diesel. Different sources yield different distributions of PAHs (Guo et al., 2011; Lopes and deAndrade, 1996). PAHs are present in water samples as either particulate or dissolved phases. The sum of both the particulate and dissolved phases is referred to as the total PAH concentration. The solubility and volatility of PAHs depend on the molecular weight. Solubility decreases as molecular weight increases, but PAHs are in general hydrophobic compounds that have a strong affinity to particulate matter and are often transported with sediment (Belles et al., 2016).

Within the AOSR there are multiple natural and anthropogenic PAH sources and multiple pathways for these PAHs to reach aquatic ecosystems. Anthropogenic sources of PAHs in the AOSR include the emissions from upgrading of bitumen to synthetic crude oil, the evaporation of process-affected water from tailing ponds (Parajulee and Wania, 2014; Kurek et al., 2013; Galarneau et al., 2014), blowing petcoke (Zhang et al., 2016) and the operation of fleet vehicles. Natural sources of PAHs in the region include forest fires (Gabos et al., 2001) and erosion of bitumen laden sediments by the Athabasca River and its tributaries (Akre et al., 2004; Headley et al., 2001). PAHs from these different anthropogenic and natural sources may be transported by air-borne pathways and deposited on the land surface or on the snowpack (Kelly et al., 2009; Cho et al., 2014), deposited directly onto surface water bodies, or carried to water bodies from the land surface by water-borne pathways. Understanding sources of PAHs in the AOSR and pathways by which PAHs arrive at surface water receptors locally and in downstream ecosystems, has been a scientific challenge due to the similar origins of some of the anthropogenic and natural sources (e.g. bitumen), lack of complete source characterization for all of the potential anthropogenic sources, the potential for multiple sources in close proximity, and transport pathways that involve transport by air, over land and by water.

Elevated concentrations of PAHs have been detected in the snowpack (Cho et al., 2014; Kelly et al., 2009; Manzano et al., 2016) in an area extending about 50–80 km from the centre of oil sands development. There is general consensus from these studies is that the higher

concentrations of PAHs in atmospheric deposition within this footprint are associated with industrial activities. However, studies aimed at determining the fate and impact of these PAHs on local and downstream aquatic receptors have yielded variable results and interpretations depending on the media studied (e.g. lake sediment archives, river and lake samples) and proximity to development (e.g. local or distal).

Studies using modern lake sediments to detect spatial distribution of PAHs in lakes (Evans et al., 2016) or lake cores to reconstruct time-series of PAH loadings (Hall et al., 2012; Jautzy et al., 2013, Jatuzy et al., 2015; Kurek et al., 2013; Elmes et al., 2016) have differed in their results depending on the proximity to development. The concentrations of PAHs in sediment cores from lakes near oil sands development (<55 km) have shown increasing PAH concentrations that with correspond to the timing of oil sands industry expansions (Jautzy et al., 2013; Kurek et al., 2013). However, other studies conducted using longer lake sediment cores from the Peace Athabasca Delta, located >200 km downstream of oil sands development and outside of the oil sands deposition area, have concluded that PAH delivery to the delta has not increased significantly over the past century and that the source of PAHs reaching the delta are more consistent with erosion of natural bitumen with no evidence of PAHs originating from atmospheric transport (Hall et al., 2012). Similar results have been reported for lake sediments in the Slave Delta, which are even farther from oil sands development (Elmes et al., 2016). Analysis of lake sediment PAH data collected as part of the Regional Aquatic Monitoring Program (RAMP) show spatial trends similar to those noted in the PAH atmospheric deposition fields, with higher concentrations of PAHs measured in lake sediments close to oil sands activities (<55 km) and lower concentrations with greater distances from oil sands activities (Evans et al., 2016).

Detecting potential impacts of oil sands activities on the Athabasca River and its tributaries has been more challenging due to the short residence times of these waters and substantial upstream watershed influences (Evans et al., 2016). Kelly et al. (2009) used dissolved PAH concentrations collected on permeable membrane devices (PMDs) to evaluate whether oil sands development contributed PAHs to the Athabasca River and its tributaries. They were unable to detect temporal variations in PAH concentrations in the river that could be attributed to a pulse of PAHs released with snowmelt, but increased concentrations of PAHs in tributaries downstream of oil sands activities were identified as evidence that catchment disturbances due to oil sands activities could be a source of PAHs. Data on PAH concentrations from bulk river sediment samples collected in the Athabasca River Delta and some of the Athabasca River tributaries collected as part of RAMP were used to identify whether there have been increases in the PAH concentrations (Evans et al., 2016; Timoney and Lee, 2011). The original interpretation of the sediment PAH concentrations from the Athabasca Delta over the 1999–2009 monitoring period was that increasing concentrations were an indication of impacts from oil sands development (Timoney and Lee, 2011). Using periodic grab samples river sediment to identify changes in PAH loadings to and transported by rivers is a challenge because of uncertainty regarding the time intervals represented by these samples and the potential for sediment remobilization and redistribution (Timoney and Lee, 2011). Nonetheless, the original study, and a reinterpretation of a longer time-series of RAMP/JOSM sediment PAH data for the Athabasca River Delta (Evans et al., 2016) found that total PAH concentrations have increased over the 1999–2014 period with evidence of increased contribution of combustion sources. The river and lake sediment data was consistent with increasing influence from oil sands development in the immediate oil sands

development area, with weaker evidence for any impacts in the Athabasca River Delta and Lake Athabasca (Evans et al., 2016).

Although significant progress has been made to date, a comprehensive understanding of the sources and pathways of PAHs within the AOSR is still needed (Parajulee and Wania, 2014). Improved understanding of PAH sources and transport pathways is required to better understand the relative role and transport pathways of natural and anthropogenic organics to the overall PAH load in the Athabasca River, tributaries and lakes.

There are a variety of hydrological pathways that can bring atmospherically derived organics to aquatic receptors in the AOSR. Atmospheric deposition deposited during the winter season will accumulate on the snowpack. During snowmelt, water, solutes and particulate matter present in the snowpack are released and either infiltrate the soil or pool and runoff depending on whether the ground is frozen. Sublimation can result in the loss of snowpack, but any solutes or particulates present in the snowpack remain and are concentrated. In northern climates, the ground is usually frozen during the initial melt period, so there is typically little opportunity for infiltration. Once depression storage is exceeded most of the snowmelt will flow as surface runoff, or very shallow interflow (Ireson et al., 2013). As the subsurface thaws, both surface and groundwater flow paths will become active, and both can contribute to increased runoff in tributaries and rivers. The melting of the snowpack, the spring freshet, is the dominant hydrological event in the region and results in the highest peak flows in rivers and tributaries along with significant flushing of the catchments (Gibson et al., 2016). During spring melt, increased overland flow and flow volume in rivers and tributaries can also lead to increased erosion and entrainment of sediment. Solutes and particulates are not expected to travel conservatively with meltwater either on the landscape or in tributary channels as they may be attenuated, stored, or remobilized by physical, chemical, or biological interactions during transport. Various constituents may also be added to flow along the way by weathering of rocks, soil and bitumen, by erosion, or by biological activity.

Rivers are very dynamic systems providing a spatially integrated signal of water quality from their contributing areas that may be strongly dependent on seasonal variations in the hydrological cycle. Surface water quality will vary depending on the sampling location, since each river water sample will integrate all of the water quality controls over the upstream contributing area. In terms of PAHs, the water samples from the Athabasca River and its tributaries should differ based on differences in sources and pathways contributing to different upstream catchment areas. Surface runoff and groundwater contributing to rivers may include organics attenuated, stored and later released from a variety of sources including geologic or biological sources within the catchment and historical airborne deposition. Temporal variations in river discharge that occur in response to individual storms and seasonal variations in flow are large, and so more frequent sampling is required to capture variations in water quality and organics. Variations in contributing areas may also be influential. Surface water samples from lakes will likely integrate atmospheric deposition from over the catchment area and will also include inputs from surface runoff and groundwater, but will not have the same temporal variations as rivers.

In this study, the composition of PAHs present in the snowpack was used to characterize atmospherically-derived PAHs deposited across the region and to evaluate whether PAH compositions of snow and surface waters can be used to identify pathways of PAH transport to aquatic ecosystems. Compositions of PAHs in snow and surface waters across the AOSR were compared to investigate the contribution of atmospherically-derived PAHs transported by snowmelt to the overall PAH loading in surface waters in the AOSR. Since river inputs are strongly dependent on seasonal variations in the hydrological cycle, seasonal sampling of PAHs was used to evaluate how seasonal water quality changes are related to variations in surface water inputs. This question is of particular concern as the transport of PAHs to surface water bodies during the spring melt could contribute PAHs in concentrations that are toxic to aquatic organisms at a time that coincides with spawning season (Kelly et al., 2009; Hall et al., 2012). This study is one of the first to directly investigate the relationship between atmospherically-derived PAHs present on snow and the PAHs observed in surface water receptors in the AOSR. The results of this study provide a greater understanding of the sources and pathways by which PAHs are transported to the Athabasca River and its tributaries. This information is valuable for developing targeted monitoring programs aimed at understanding and mitigation of oil sands impacts.

2. Methods

2.1. Data sources and compilation

PAH concentration data were compiled from three provincial monitoring programs and included data from snow and surface water samples collected throughout 2011. The snow data were collected by Alberta Environment and Parks and were discussed previously in Cho et al. (2014), and the river and lake datasets were compiled from data from the Regional Aquatic Monitoring Program (RAMP, 2011) and Alberta Environment and Parks Long-Term River Network (Alberta Environment, Parks, 2012) (Note that these three major databases used in this study are summarized in Table S1). The snow and surface water sampling locations are shown in Fig. 1. Snow sampling locations included 94 sites located approximately 5 km apart along eight directional transects that radiated outwards in the north, north-east, east, south-east, south, south-west, west, and north-west directions, respectively, from an approximate geographical centre of oil sands operations (GC: 57.005528 N, 111.455222 W). An additional 11 snow sampling sites were co-located with Alberta Environment LTRN water quality monitoring stations. Snow samples were collected in February 2011 according to the sampling protocol provided in Cho et al. (2014). The snow dataset includes samples with elevated PAH concentrations collected near oil sands operations and used to define the footprint of atmospheric impacts, as well as samples located distal from oil sands operations with background PAH concentrations (Cho et al., 2014). River water samples included 82 samples collected from the Athabasca River between the city of Fort McMurray and the confluence with the Firebag River. An additional 190 samples were collected from nearby tributaries. The Athabasca River and tributary samples were collected as grab samples, on a monthly (AEP) or seasonal (RAMP) basis between May and September 2011. Lake samples were collected during a single three-site sampling visit in September 2011. Summary of snow and surface water sampling site codes and description are listed in Table S2. With the exception of the samples from the Firebag River (FR-1, FR-2), McClelland Lake (MCL-1), Wapasu Creek (WAC-1) and the headwaters of the Muskeg River and North Steepbank River, all of the other surface water sampling locations were located within the area of elevated PAH deposition (PAH loading > 146 μg/m^2; Manzano et al., 2016) (Fig. 1b).

The different data sources for snow and surface waters included analyses of slightly different suites of PAHs from two laboratories. The AEP snow survey data reported 39 PAH compounds, the AEP Athabasca River and tributary data included 50 species, and the RAMP water quality data included 43 PAH compounds. Thirty-four PAH compounds were found to be common across all three data sources (Table 1) and were used. Thirty-four PAH compounds were found to be common across all three data sources (Table S3) and were used. The PAH analyses for the AEP-snow and river datasets were obtained using EPA method 625 whereas the RAMP data were obtained using Method MLA-021 (corresponds to a combination of EPA Method 1625B and 8270C/D). Both methods are a standardized gas chromatography/mass spectrometry procedure recommended by the USEPA for detection and measurements of organic pollutants in aquatic environments (USEPA, 1993). The two laboratories had similar QA/QC protocols and the PAH analyses performed by both are accredited by the Canadian Association for Laboratory Accreditation (CALA). Both labs routinely participate in PAH
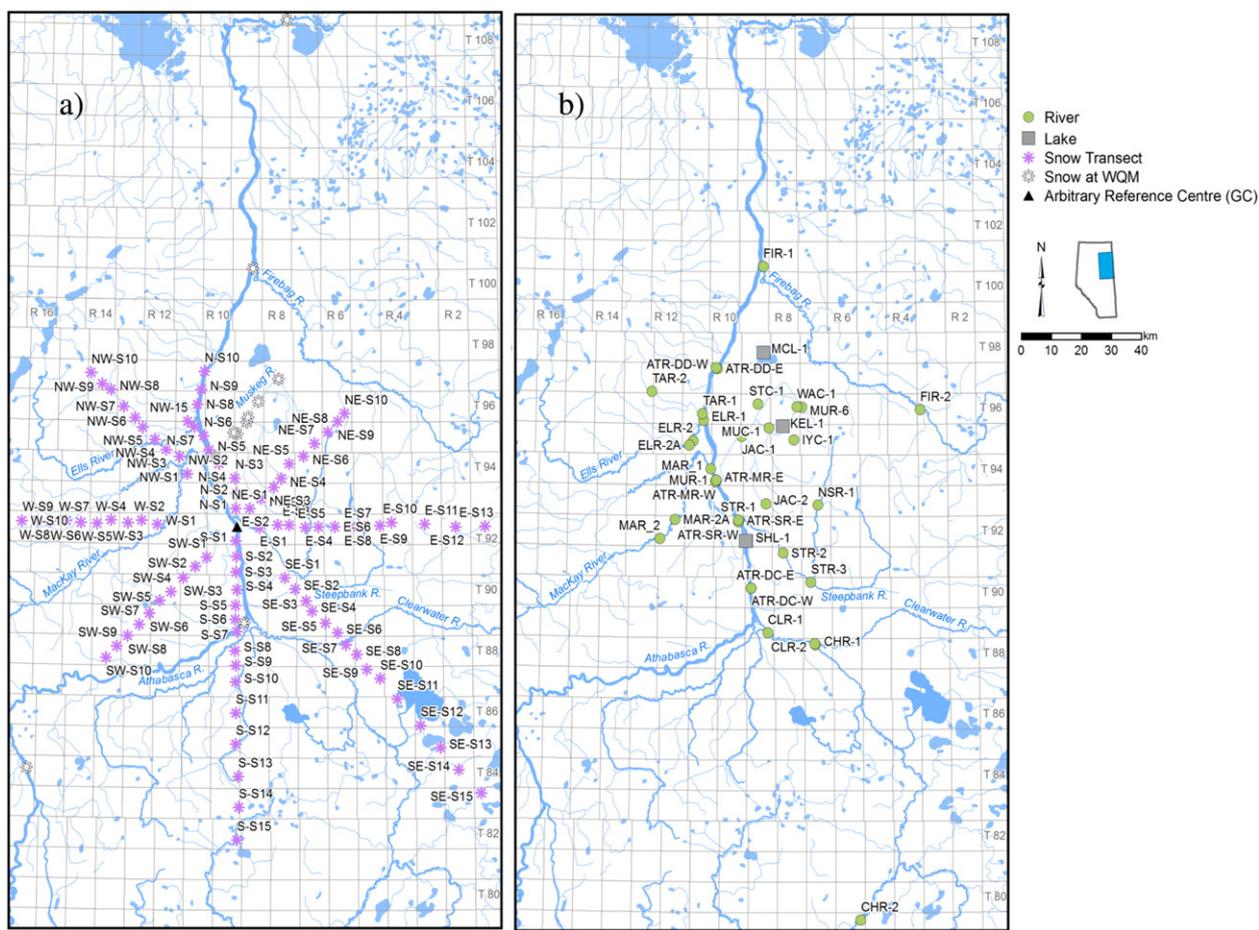
Fig. 1. Sampling locations of a) snow and b) surface waters including samples from the Athabasca River, tributaries and lakes.

analysis proficiency tests organized by CALA (see Supplemental Information for more detailed information on laboratory intercomparability). Previous studies have demonstrated good agreement between the methods (e.g. Shepherd et al. (1992) reported good agreement for phenanthrene and naphthalene analytical results) the two methods and the CALA proficiency tests provide support for comparability of the parent PAH analytical methods. The EPA method 1625 is generally preferred due to lower detection limits, but is also more expensive as it requires isotope dilution and labelling. The laboratory QA/QC results for both labs are discussed in more detail in the Supplemental information (Section 1.1) but a review of the sampling procedures, sample handling methodologies and analytical procedures, supported by the results of 2011 PAH proficiency tests, suggest that the results from the two labs are comparable, with the main difference being the lower detection limits for the river and lake data reported by RAMP, compared with the snow and river data reported for the AEP samples (see Table S3).

Before these data could be compiled into a single dataset and analyzed statistically, a technique for treating non-detect values in the database had to be selected. Two techniques for the treatment of below detection limits in multivariate statistical analysis were considered: 1) constant substitution where all below detection limit results are replaced by a constant value. The value chosen is often based on a fraction of the detection limit, but because the different laboratories used in the different surveys had such large differences in detection limits a constant value of zero was used, 2) variable replacement, where below detection limit results are replaced using an algorithm implemented by SIMCA-P + so that the resulting dataset is close to a normal (or lognormal) distribution (Wold and Sjöström, 1977). The two methods for treating values below the detection limit (BDL) were evaluated by

comparing PCA results which were not found to be significantly different for the two techniques. For the sake of simplicity (Aruga, 1997), the constant substitution technique was used. Table 1 lists the PAH compounds common to the snow and surface water datasets.

2.2. Relative PAH concentrations

In this study, both absolute concentrations of individual PAH compounds and the PAH compositions (expressed based on relative PAH concentrations) were examined. The relative PAH concentration (%PAH) was determined as the percentage of each PAH compounds relative to the sum of the common thirty-four PAH compounds and was used to identify compositional differences among different samples. The relative concentration of a given PAH compounds in a sample was calculated using:

$$\%PAHx = (PAHx)/\Sigma PAH \tag{1}$$

where x is the absolute concentration of PAHx and ΣPAH is the sum of the concentrations of the thirty-four PAH compounds common to all of the datasets.

2.3. Statistical analysis

PCA is a multivariate statistical technique that transforms and extracts meaningful information from large datasets with many variables (Mardia et al., 1989). After the data transformation, the first principal component (PC1), a linear combination of the original variables, explains the largest amount of variation in the dataset, and the second principal component (PC2), another linear combination of variables, describes the next largest

Table 1

List of PAH compounds and abbreviations common to the three compiled snow and surface water datasets that were used in this study. Parent PAHs are indicated with an asterisk.

PAH name	Abbreviation	#Benzene and total rings[a]	Molecular weight (g)[a]	Solubility at 25 °C[a] (µg/L)	Vapour pressure at 25 °C[a] (mm Hg)	Log K_{OW}[a]
Naphthalene*	NaP	2	128.2	12,500 to 34,000	1.8×10^{-2}	3.37
C2-Naphthalene	NaP2	2				
C3-Naphthalene	NaP3	2				
C4-Naphthalene	NaP4	2				
Acenaphthylene*	Acy	2	152.2	3420	10^{-3} to 10^{-4}	4.07
Acenaphthene*	Ace	2	154.2			3.98
Fluorene*	Fl	2	166.2	800		4.18
C1-Fluorene	Fl1	2				
C2-Fluorene	Fl2	2				
C3-Fluorene	Fl3	2				
C1-Dibenzothiophene	D1	2				
C2-Dibenzothiophene	D2	2				
C3-Dibenzothiophene	D3	2				
C4-Dibenzothiophene	D4	2				
Phenanthrene*	Phe	3	178.2	435	6.8×10^{-4}	4.46
Anthracene*	Ant	3	178.2	59	2.4×10^{-4}	4.5
C1-Phenanthrene/anthracene	Phe/Ant1	3				
C2-Phenanthrene/anthracene	Phe/Ant2	3				
C3-Phenanthrene/anthracene	Phe/Ant3	3				
C4-Phenanthrene/anthracene	Phe/Ant4	3				
Fluoranthene*	Flu	3	202.3	260		4.9
Pyrene*	Pyr	4	202.1	133	6.9×10^{-7}	4.88
C1-Fluoranthene/pyrene	Flu/Pyr1	4				
C2-Fluoranthene/pyrene	Flu/Pyr2	4				
C3-Fluoranthene/pyrene	Flu/Pyr3	4				
Benz(*a*)anthracene*	BaA	4	228.3	11	1.1×10^{-7}	5.63
Chrysene*	Chr	4	228.3	1.9		5.63
C1-Chrysene	Chr1	4				
C2-Chrysene	Chr2	4				
Benzo(*b,j,k*)fluoranthene*	BbjkF	4				
Benzo[*a*]pyrene*	BaP	5	252.3	3.8	5.5×10^{-9}	6.06
Dibenz(*a,h*)anthracene*	DahA	5	278.3	0.4		6.86
Indeno(1,2,3-cd)pyrene*	IcdP	5	276.3			6.58
Benzo(*g,h,i*)perylene*	BghiP	6	276.4	0.3	1×10^{-10}	6.78

[a] The values were obtained from Nagpal, N.K., 1993 (Table 1).

variation remaining in the dataset, and so on. As the first few principal components (PCs) account for a large part of the variability in the dataset, we can use these PCs to represent the data without losing important information. When presenting PCA results, the projection of individual samples onto the axis defined by a PC is termed the "score", whereas the coefficient for each variable in the linear combination is called the "loading" of the variable. In this study, we use PCA as an exploratory tool for information extraction. PCA analyses were performed using SIMCA-P + (V12.0, Umetrics AB Umeå, Sweden). Note that the compiled 2011 snow and surface water dataset included 379 samples with analytical results for thirty-four PAH compounds. These data were used for descriptive statistics and plotting. Since a considerable proportion of results were reported as below detection limits (BLD), a preliminary untargeted screening of samples with >80% of reported variables was taken, which led to a total of 160 samples containing twenty-eight species selected for PCA. Two options were further evaluated for representing remaining BLD in the PCA analysis, including using a "0" value, or using half of the detection limit. The PCAs produced using these two different methods did not differ significantly, so "0" values were used to represent BDL (See more in Supplementary information). PCA was performed using both absolute (µg/L) and relative (%) PAH concentrations to statistically characterize and compare the snow and surface water samples in this study. Both the absolute and relative PAH concentrations were positively skewed, so both datasets were log transformed prior to PCA analysis to achieve normal (or log normal) distributions and reduce the effects of extreme values.

2.4. Diagnostic ratios

Use of diagnostic PAH ratios for source apportionment has limitations since the approach relies on the assumptions that the relative proportions of PAH compounds in each potential source is unique, and that the relative proportions of species are conservative in the environment as they move from source to receptor (Galarneau, 2008; Kim et al., 2009; Zhang et al., 2005). They are nonetheless informative for providing insight into compositional differences in the PAHs present in different samples. In this study a variety of diagnostic ratios typically used to differentiate between pyrogenic and petrogenic PAHs were calculated for the snow and surface water samples to identify broad compositional differences across these media.

2.4.1. Pyrogenic index (PI)

The PI is defined as the ratio of selected 3–6 ring parent PAHs to the total of 5 target alkylated PAH homologues (Stogiannidis and Lane, 2015; Wang et al., 2008; Wang et al., 2014) and was determined using:

$$PI = \frac{Acy + Ace + Ant + Flu + BaA + BeP + BghiP + IcdP + DahA}{NaP(1-4) + Phe/Ant(1-4) + D(1-4) + Fl(0-4) + Chr(0-4)} \quad (2)$$

PI ranges from 0.8 to 2.0 have been found for pyrogenic sources and much lower values have been reported for petrogenics (<0.01 for crudes and <0.05 for heavy oils and fuels) (Stogiannidis and Lane, 2015). The PI can be useful for distinguishing heavy fuels from crude oil, or light refined products and soot from crude oils or petroleum products. For pyrogenic PAH sources high molecular mass 4–6 ring PAHs are typically more prevalent than the 2–3 ring PAHs.

2.4.2. Flu / (Flu + Pyr) and BaA / (BaA + Chr)

Ratios of selected parent PAHs have been found useful for differentiating between pyrogenic and petrogeic sources (Yunker et al., 2002).

Pyrene is favoured over fluoranthene under fossil fuel formation conditions (Stogiannidis and Lane, 2015), and so Flu / (Flu + Pyr) ratios are typically lower for petrogenic sources. In general Flu / (Flu + Pyr) ratios <0.5 are characteristic of petrogenic sources and ratios above 0.5 are characteristic of grass, wood or coal combustion (Yunker et al., 2002). However, caution should be used when applying Flu / (Flu + Pyr) in heavily industrialized areas because some combustion sources such as liquid fossil fuel (vehicle and crude oil) combustion exhibit a ratio of approximately 0.4 to 0.5 which is similar to petrogenic sources. In general, the Flu / (Flu + Pyr) ratio is fairly stable because both fluoranthene and pyrene degrade at similar rates in the atmosphere (Stogiannidis and Lane, 2015). Benz[*a*]anthracene is produced in a greater proportion than chrysene during combustion and therefore higher BaA / (BaA + Chr) ratios are indicative of combustion sources (Stogiannidis and Lane, 2015). In general, BaA / (BaA + Chr) ratios above 0.35 are indicative of combustion sources, ratios between 0.20 and 0.35 are indicative of either petroleum or combustion sources and ratios below 0.20 are attributed to petrogenic sources (Yunker et al., 2002).

2.4.3. C_0 / $(C_0 + C_1)$ ratios

The distribution of alkylated PAH homologues can also be used to distinguish pyrogenic and petrogenic sources. A maximum PAH homologue at C0 (i.e., Flu/Pyr) often indicates combustion sources while a maximum at C1 (i.e., Flu/Pyr1) often indicates petrogenic sources (Yunker et al., 2002). The C_0 / $(C_0 + C_1)$ ratios within the fluoranthene/pyrene series (Flu/Pyr) and the phenanthrene/anthracene series (Phe/Ant) are commonly used diagnostic ratios for differentiating petrogenic and pyrogenic sources of alkylated PAHs (Yunker et al., 2002).

3. Results and interpretation

3.1. PAH concentrations in surface waters and snow

Box (i.e., 25th and 75th percentiles) and whiskers (i.e., 5th and 95th percentiles) plots of concentration distributions in snow and surface waters (Athabasca River, tributaries and lakes) show the differences in total PAH concentrations in the different components (Fig. 2). In the snow samples there are individual outliers with anomalously high total PAH concentrations, but the 25th and 75th percentile bounds and median PAH concentrations are fairly similar for snow and the Athabasca River samples. The ΣPAH concentrations measured in tributaries and lakes are much lower (Fig. 2a).

Snow typically included a lower percentage of alkylated PAHs than surface waters (Fig. 2b) and lower ratios of alkylated to parent PAHs (Fig. 2c).

Comparing the concentration of individual PAH compounds between snow and surface waters provides more insight into the compositional differences of the waters (Fig. 3). Compared to surface waters, snow tends to have higher concentrations of D1–D4, and the 4–5 ring parent PAHs (BbjkF, BaP, DahA, IcdP, BghiP) (Fig. 3a). As was evident in the ΣPAH (Fig. 2a), the concentrations of PAHs in lakes included here were lowest of all surface waters, with non-detects for most species except NaP4 and D1–D4. Concentrations of PAHs were lower in the tributaries than in the Athabasca River (Figs. 2a and 3c) but the distribution of PAH compounds were fairly similar (Fig. 3c). In the Athabasca River samples, the alkylated PAHs like C4-Phenanthrene/Anthracene (Phe/Ant4) and C3-Fluorene (Fl3) had the highest concentrations. These PAH compounds are consistent with the species that are present in the highest concentrations in sediment sampled around natural exposures having the highest concentrations of Fl2, Fl3, C3-Phenanthrene, C4-Phenanthrene/anthracene, and D2, D3 and D4 (Akre et al., 2004; Headley et al., 2001). All of the surface water PAH concentrations measured in 2011 are below the Canadian Council of Ministers of the Environment guidelines (CCME, 2007) used for surface waters in Alberta (Table 2).

Differences in PAH concentration and compositions in snow and surface water were also evaluated using PCA on absolute PAH concentrations
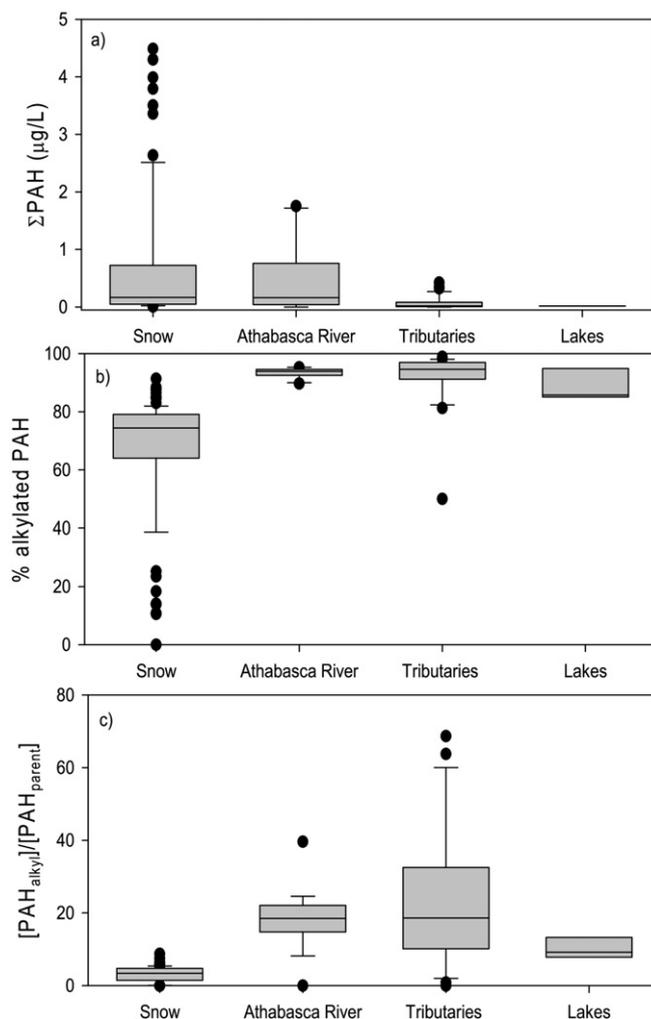

Fig. 2. Comparison of a) Σ PAH concentrations, b) % alkylated PAHs, and c) [PAH_alky/[PAH_parent].

(Figs. S2 and 4). The individual PCA biplots for snow (Fig. S2a) and surface waters (Fig. S2b) provide greater detail into anomalous samples in these datasets. A similar PCA analysis of the absolute PAH data for snow have been discussed in Cho et al. (2014) and they identified three main groupings of PAH concentrations based on geographical proximity to oil sands activities (Fig. S2a). Snow samples with anomalously high PAH concentrations tended to be from the north-south transect and located at sites close to the GC (Cho et al., 2014). The PCA biplot based on the absolute concentrations of PAHs of just surface water samples (Fig. S2b) highlight surface water samples with PAH concentration anomalies. Most of the tributary and main-stem Athabasca River samples plot close to the origin, but the July 2011 samples from the main-stem Athabasca plot as distinct anomalies, due to elevated concentrations of Phe/Ant4, and Fly/Pyr1–3, and to a lesser extent higher concentrations of D2–D4, and NaP2–4 (Fig. S2b). The ATR-DD-W sample collected in May 2011 plotted intermediary between the July samples and the rest of the river samples, due to slightly higher concentrations of the same PAHs (also evident in Fig. S1). The ATR-DD-W sample, collected in September 2011 was also compositionally distinct from the other Athabasca River and tributary samples due to lower concentrations of PAHs (see Figs. S1, and S2).

The PCA biplot comparing the absolute concentrations of PAHs in both snow and surface water (Fig. 4) reveals the anomalous snow and Athabasca River samples which had elevated concentrations of Flu, Phe, Fl, Chr2 and BbijkF and were sampled from snow sampling locations close to the GC along the north-south and water quality transects that align approximately with the Athabasca River (also described in
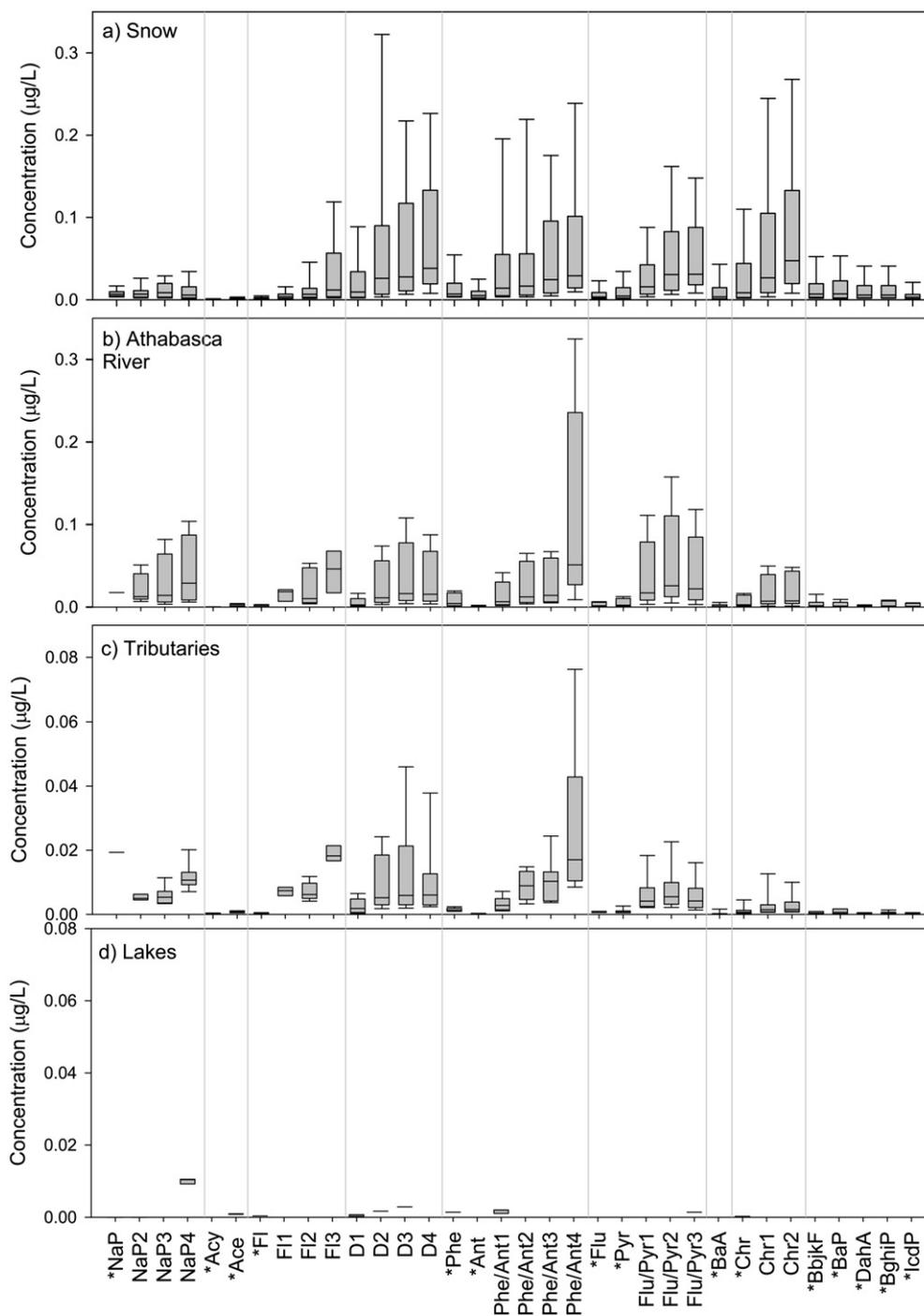
Fig. 3. Concentration distribution of PAH species in a) snow, b) the Athabasca River, c) tributaries and d) lakes. Notes different scale differences for tributaries and lakes. Parent PAHs are indicated by *, and PAHs are grouped by number of benzene rings.

Cho et al., 2014). As described above, the anomalous values were based on samples from the Athabasca River in July and they differ from the other surface water samples and snow samples due to higher concentrations of Phe/Ant4 (Fig. S3). Comparison of PAH compounds present in snow and the Athabasca River reveals compositional differences between PAH compounds in peak flow and snow samples with high PAH concentrations. The snow samples with elevated PAH concentrations were from locations centered along the north-south transect around the GC of oil sands activities typically had higher concentrations of PAH compounds including: D2–D4, Phe/Ant1–3, Chr, Chr, and Chr2, whereas the distinguishing feature of the Athabasca River July samples were much higher concentrations of Phe/Ant4.

3.2. Comparison of relative concentrations and compositions of PAHs in snow and surface waters

Relative concentrations of %PAH compounds were used to remove the effects of different PAH concentrations and better identify compositional changes in the PAH compound distributions. PCAs conducted on the relative concentrations (%PAH) were used to group samples that have similar relative %PAH distributions present but at different concentrations, identifying samples that are compositionally different. For example, the PCA conducted on the absolute concentrations of PAHs (Fig. 4 and Fig. S2a) identified samples with anomalously high PAH concentrations but the PCA based on %PAH (Fig. 5a) indicated very limited

Table 2
Comparison of measurements of PAHs species concentrations in the 2011 surface water dataset with Canadian water quality guidelines for the protection of aquatic life (CCME, 2007).

PAH species	Abbreviation	Water Quality Guideline (CCME, 2007) (µg/L)	Surface water		
			Mean (µg/L)	Maximum (µg/L)	N
Acenaphthene	Ace	5.8	0.0011	0.0041	29
Anthracene	Ant	0.012	0.0006	0.0030	21
Benz(a)anthracene	BaA	0.018	0.0011	0.0109	29
Benzo(a)pyrene	BaP	0.015	0.0024	0.0115	19
Fluoranthene	Flu	0.04	0.0022	0.0063	16
Fluorene	Fl	3.0	0.0010	0.0030	21
Naphthalene	NaP	1.1	0.0184	0.0193	2
Phenanthrene	Phe	0.4	0.0039	0.0206	35
Pyrene	Pyr	0.025	0.0030	0.0132	29

compositional differences between samples. Despite differences in concentrations (Fig. 4), the PCA conducted using %PAH relative abundances (Fig. 5a) shows that the composition of PAHs in snow are fairly consistent along the north-south transect which could indicate a similar source, present at differing concentrations due to dilution. The greatest compositional differences within the snow samples were from the east and west transects. Moving eastward along the east sampling transect (Fig. 1a), Chr1 becomes more dominant (increases from 8.56% to 24.81% from E-S1 to E-S12) but Phe/Ant1 becomes less dominant (decreases from 6.2 to 0% from E-S1 to E-S12). The compositional changes could indicate transformations of PAHs or effects of multiple sources. This suggests that %PAH may be more useful than absolute concentrations for tracing sources and deposition of PAHs over short distances, where compositional changes along the transport pathway are not expected.

The PCA conducted using %PAH for surface water data indicated compositional differences between the PAH's present in the Athabasca River, compared to the tributaries (Fig. 5b). The Athabasca River samples tended to have greater relative proportions of Chr1, Chr2, and Flu/Pyr1, whereas the tributaries had greater proportions of Phe/Ant3, D2 and D3. Some temporal variations in PAH compositions is also evident, with most of the Athabasca River and some tributary samples from May and July plotting near the origin, indicating similar relative abundances of PAHs common to the entire dataset. However, the fall samples from the Athabasca River (ATR-DC-W, ATR-SR-W) have

different relative abundances of PAHs compared to the tributaries, evident in the separation between these two groups of samples along the PC1 axis (Fig. 5b). The PCA of the absolute concentrations for surface waters (Figs. 4 and S2b) identified the anomalously high concentrations present in four of the July samples from the Athabasca River, but the PCA of %PAH for the surface water samples shows that the relative abundances of PAHs in these samples were similar to the May and July samples and differ mainly in their concentrations (Fig. 5b; see also Fig. S2). The concentrations of PAHs in the Shipyard Lake sample were low compared to most of the Athabasca River and tributary samples (Fig. 3d) and differed compositionally in the greater relative abundance of NaP4 and Phe/Ant1 (Fig. 5b).

The PCA biplot comparing the relative abundances of %PAHs in snow and surface water (Fig. 5c) indicates compositional differences between the PAHs present in snow and surface water samples, shown by the separation along the PC1 axis. This compositional distinction is due to differences in the relative concentration of Flu/Pyr2, NaP4, Chr1, Phe/Ant1, D1 and the parent PAH compounds between snow and surface waters. The Athabasca River, tributaries and the lake sample have greater relative concentrations of Flu/Pyr2 and NaP4 than the snow samples, whereas Chr1, Phe/Ant1, D1 and most of the parent PAH compounds have greater relative concentrations in snow than in surface water. In general, parent and C1-alkylated PAHs have greater relative concentrations in snow, whereas some C2-through C4-alkylated PAHs have greater relative concentrations in rivers (circles, Fig. 5c). Hall et al. (2012) also observed that C2–C4 alkylated PAHs were more prevalent in flood-prone intervals of their sediment cores, while parent naphthalene, C1 naphthalenes, retene and Nap1 were more prevalent for non-flood intervals. The C2–C4 alkylated PAHs have also been found at high concentrations in sediment from Athabasca River tributaries like the Ells River (Akre et al., 2004; Headley et al., 2001). Within each cluster of snow and surface water samples there is further separation along the second principal component (PC2, y-axis). The snow samples from the WQ snow sites plot in a fairly tight cluster indicating similar relative concentrations of PAHs, similar to most of the snow samples from the south-north transect. Although variations in the composition of PAHs in surface waters are evident, the compositional differences between the PAHs in the Athabasca River and tributary samples (Fig. 5b) are secondary when compared to the compositional differences between river and snow samples (Fig. 5c). Despite absolute PAH concentrations being anomalously high in the Athabasca River samples in July and September (Fig. S1, and S2b) the relative concentrations of PAHs present in the
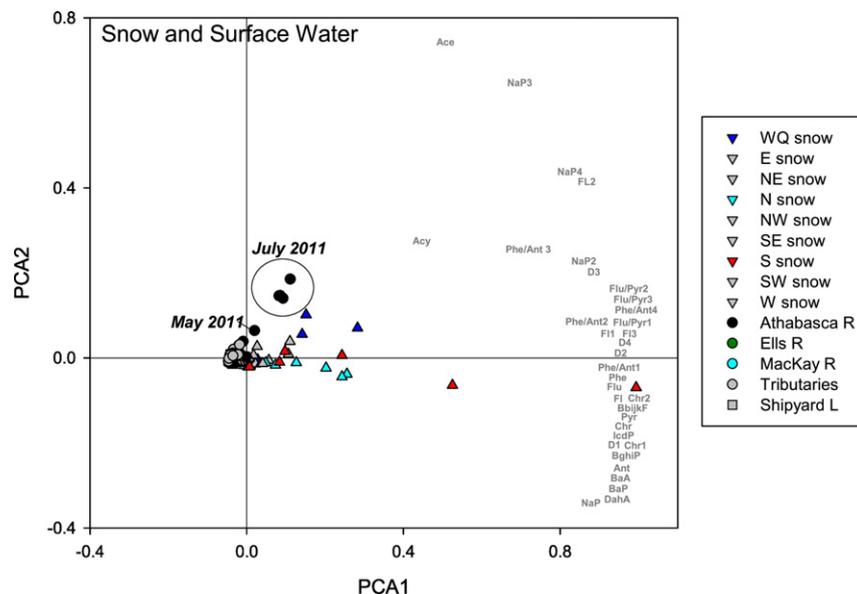

Fig. 4. PCA biplots of absolute PAH concentrations for snow and surface waters. Grey lettering indicates the abbreviation of the PAH species responsible for separation.
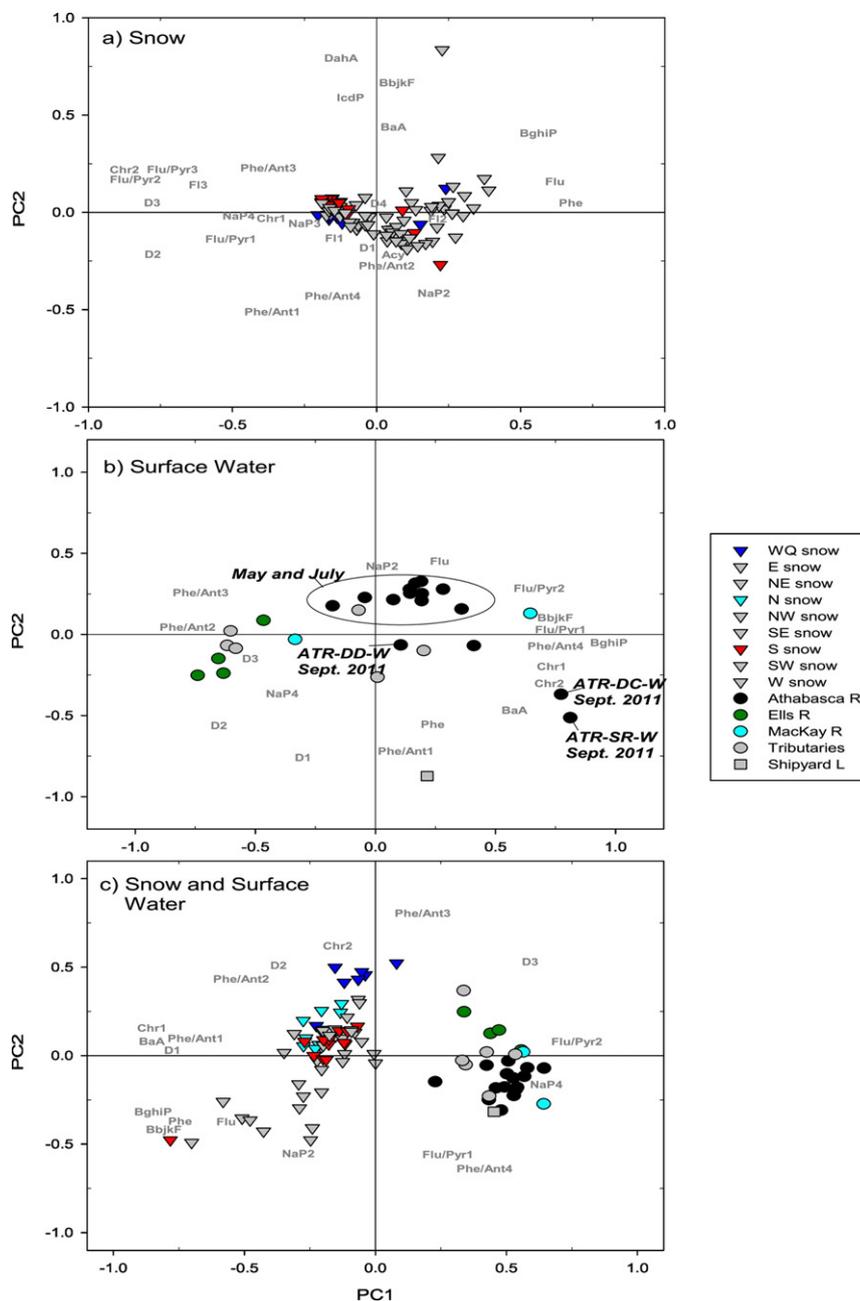
Fig. 5. PCA biplots of the relative concentrations of PAHs in a) snow, b) surface waters, and c) snow and surface waters. Grey lettering indicates the abbreviation of the PAH species responsible for separation.

main-stem remains fairly consistent over the year. The relative concentration of PAHs in each tributary is variable, possibly due to differences in geology and anthropogenic activities within these small catchments and seasonal variations in stream flow. In contrast, the large drainage basin area for the Athabasca River may integrate and average organics resulting in a less variable PAH composition. The compositional variations of PAHs in surface water are mainly due to different relative concentrations of D3, Phe/Ant4 and Flu/Pyr1 (PC2 in Fig. 5c).

The composition of PAHs in the Athabasca River samples were very similar (Figs. 5b, S1 a and b), but with higher absolute concentrations present in July and to a lesser extent May (Figs. 4, S1a and b). Both the May and July Athabasca River samples are compositionally different than the snow samples. The biplot for the snow and surface water samples identifies a group of parent PAH compounds (BghIP, BbjkF, Phe, and Flu; bottom left quadrant of Fig. 5c) that are responsible for some of the separation between the composition of PAHs in snow and surface water

samples. These 3–6 ring PAHs are typically detected in the first flush of effluent from urban snowmelt (Meyer et al., 2011). Phe is a very soluble 3-ring PAH (Table 1) and would likely be efficiently transfer to surface water via melt water and is often associated with the first melt from snowpack in urban areas (Meyer et al., 2011). The relative concentrations of these PAHs are not large in any of the river water samples (Fig. 5c), and the absolute concentrations are low during periods when the $\delta^{18}O$ composition of Athabasca River water indicate a high proportion of snowmelt (May 2011) (Fig. S3).

3.3. Diagnostic ratio results for PAH compounds in surface waters and snow

Differences in the composition of PAHs present in snow and surface water samples are also evident in the diagnostic ratios determined for these samples (Fig. 6). Characteristic ranges for pyrogenic and petrogenic PAHs are included for reference, but in this study these ratios were used
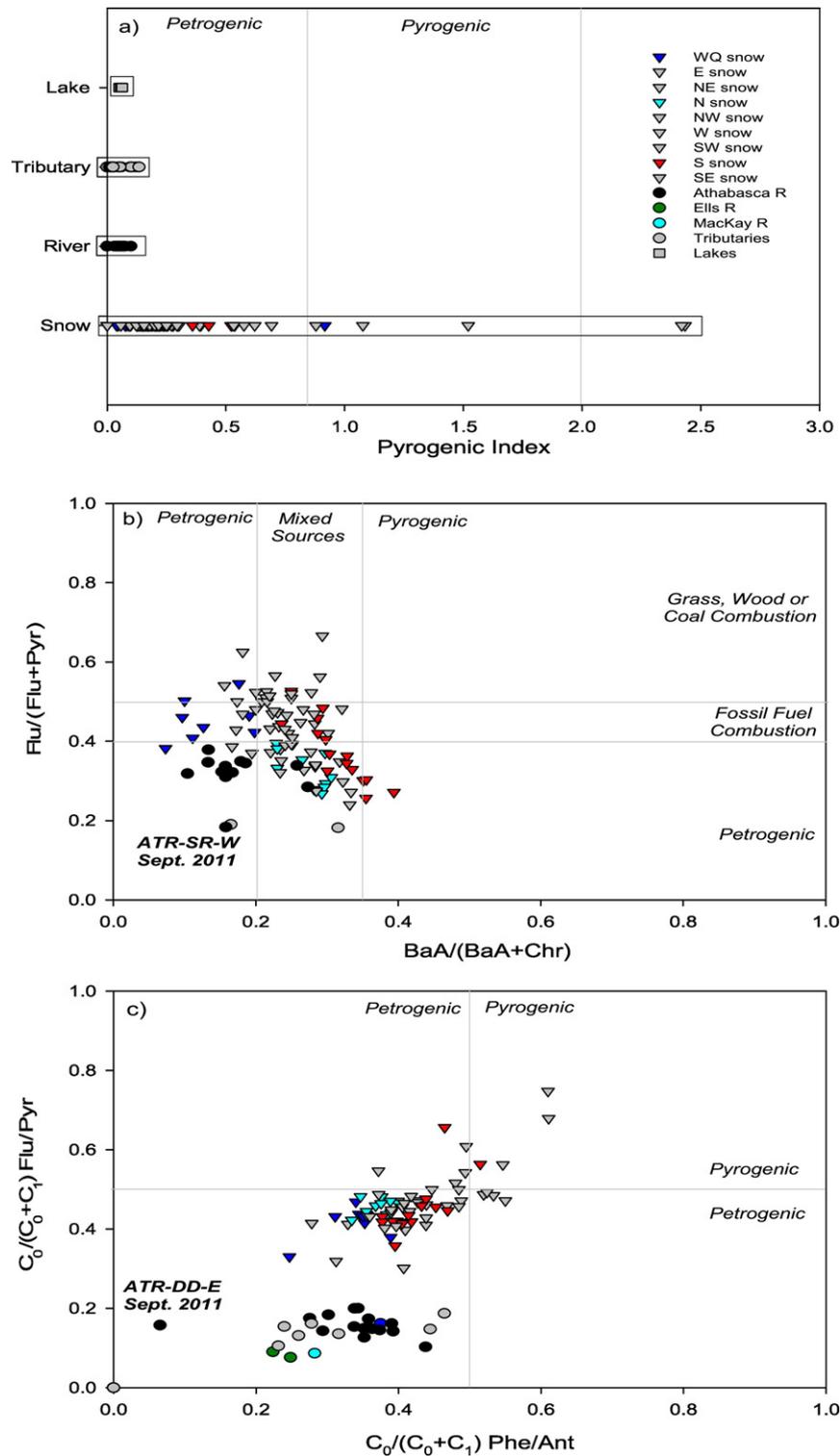
Fig. 6. Selected diagnostic ratios highlighting compositional differences in snow and surface waters, including a) pyrogenic index (PI) b) parent PAH ratios Diagnostic ratios for parent and c) alkylated ratios General ranges for pyrogenic and petrogenic PAHs are shown for reference (Yunker et al., 2002).

primarily to understand differences in composition and not for source apportionment. Various indicators of petrogenic and pyrogenic PAHs indicate more of a petrogenic source for PAHs detected in surface waters, compared to pyrogenic or mixtures of both.

The pyrogenic index (PI) determined for the snow and surface water samples (Fig. 6a) shows consistently low values for the lake, tributary and Athabasca River samples that are typically interpreted as an indicator of petrogenic sources of PAH. In contrast, the snow samples had a

very wide range of PI values, some with low values similar to the surface waters, and indicative of a petrogenic sources, but others that were clearly pyrogenic, or a mixture of the two.

The Flu / (Flu + Pyr) diagnostic ratio result showed little separation between snow and surface water samples (Fig. 6b). The surface water samples all had Flu / (Flu + Pyr) ratios typical of petrogenic PAHs, but the snow samples had values spanning the full petrogenic to pyrogenic range. However, some fossil fuel combustion sources have low Flu / (Flu

+ Pyr) ratios that overlap with petrogenic sources (Yan et al., 2006). In some industrial areas, diesel, gasoline and crude oil combustion sources have been found to have Flu / (Flu + Pyr) ratios that fall close to or within the range typical of petrogenic sources (<0.4, Yunker et al., 2002). Flu and Pyr are expected to have similar degradation in the environment (Stogiannidis and Lane, 2015) and therefore this ratio should be subject to less alteration along flowpaths compared to other diagnostic ratios.

The BaA / (BaA + Chr) ratios indicate compositional differences between snow and surface water samples with surface water samples being more consistent with petrogenic sources and snow samples having compositions more consistent with pyrogenic sources (fossil fuel combustion sources; Fig. 6b). None of the snow or surface water samples had BaA / (BaA + Chr) ratios as high as would be expected for grass or wood combustion (BaA / (BaA + Chr) $\approx 0.46 \pm 0.02$ and BaA $\approx 0.46 \pm 0.06$, Yunker et al., 2002). BaA degrades more rapidly than Chr (Stogiannidis and Lane, 2015), so caution should be used when interpreting BaA / (BaA + Chr) ratios. It is possible that the separation seen between snow and surface water BaA / (BaA + Chr) ratios may be due to transformations along the flowpath rather than differences in source.

Separation was seen between the snow and surface water samples in both the $C_0 / (C_0 + C_1)$ (Flu/Pyr) and $C_0 / (C_0 + C_1)$ (Phe/Ant) diagnostic ratios (with surface water samples appearing to be more petrogenic than snow samples (Fig. 6c). However almost all of the samples have $C_0 / (C_0 + C_1)$ (Flu/Pyr) and $C_0 / (C_0 + C_1)$ (Phe/Ant) ratios typical of petrogenic PAH sources. Again, this may be due in part to the overlap between the Flu / (Flu + Pyr) ratios from some industrial pyrogenic sources and petrogenic ranges (Yunker et al., 2002). Attributing sources using Phe/Ant is complicated by aging effects which can result in unreliability of this diagnostic ratio for source distinction. Ant is less stable than Phe during slow organic diagenesis, but is produced during combustion (Neff et al., 2005) and it is not clear how this could influence the $C_0 / (C_0 + C_1)$.

3.4. Athabasca River $\delta^{18}O$ time-series

The $\delta^{18}O$ of monthly river samples collected from the Athabasca River below McMurray (07DA001, Gibson et al., 2016) can be used with the stream discharge data to identify changes in hydrology and streamflow sources that could be contributing to the temporal changes in PAHs present in the Athabasca River. In particular, the $\delta^{18}O$ composition of river waters is a sensitive indicator of the relative contribution of snowmelt (St. Amour et al., 2005; Gibson et al., 2016). Comparison of the ΣPAH concentrations measured at the Athabasca River stations (ATR-DC, ATR-DD) with changes in river discharge and $\delta^{18}O$ composition of river water (Fig. 7) provides some insight into potential causes for these changes. The Athabasca River hydrograph (Fig. 7a) shows the fairly typical snowmelt related increases in discharge during April to June, with maximum discharge in July due to the combined effects of snowmelt and summer rains, followed by a gradual decrease in flow into the fall, and diminishing flows during the under ice period from November to April. However, 2011 was an anomalous year due to high summer precipitation that resulted in peak discharge being roughly two times greater than observed in previous years.

Prior to the start the rising limb of the hydrograph, the ΣPAH concentrations were below detection (March 2011). However, over the course of the open water season, the ΣPAH concentrations roughly follow stream discharge, with the highest concentrations occurring in July 2011 (Fig. 7b). The increase in daily discharge beginning at the end of April 2011 coincides with the shift to more negative $\delta^{18}O$ values measured in river water in May 2011, consistent with this rise in the hydrograph being mainly due to snowmelt contributions. The July PAH sample was collected from the Athabasca River after the main snowmelt peak and the $\delta^{18}O$ composition of this sample indicated that streamflow at this time was likely dominated by catchment runoff and summer rain. By September 2011, streamflow had returned to typical
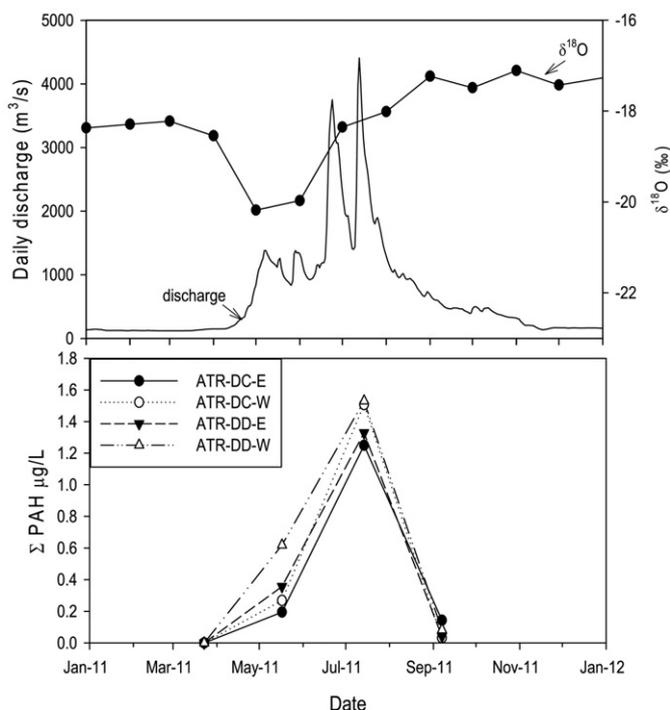

Fig. 7. a) Daily Athabasca River discharge and $\delta^{18}O$ (‰) of monthly river samples from the Athabasca River near Fort McMurray and b) the time-series of ΣPAHs measured at ATR-DD and ATR-DC (east and west bank samples).

fall values, ΣPAH had decreased and the $\delta^{18}O$ composition of the river indicated a return to groundwater and surface water contributions. The seasonality of PAH concentrations in the Athabasca River was also noted by Kelly et al. (2009) who found that polycyclic aromatic hydrocarbon concentrations in the Athabasca River and its tributaries tended to be higher during the summer (June to August) than during the winter (February to March) months.

4. Discussion

4.1. Compositional differences of PAHs in snow and surface waters

The concentrations identified in the 2011 snow and surface water datasets compiled for this study are within the ranges and consistent with previous reports focusing on each of these media separately. The lower total PAH concentrations measured in tributaries compared to the Athabasca River may be due to the lower concentrations of total suspended solids in smaller tributaries compared to the main-stem. Higher PAH concentrations have been measured in sediment in tributaries in the AOSR compared to the main-stem itself, and this has been attributed to the main-stem sediment being diluted by sediment from outside of the AOSR (Headley et al., 2001). PAH concentrations in snow were previously analyzed by Cho et al. (2014) and are consistent with the findings of Kelly et al. (2009). The difference in the distribution of alkylated and parent homologues in the snow and surface waters is consistent with the PAHs in surface waters having more of a petrogenic source than snow, since the alkylated PAHs are more abundant in petroleum and are more resistant to weathering than the parent compounds. Surface water samples contained higher concentrations of alkylated PAHs such as C4-Phenanthrene/Anthracene (Phe/Ant4) and C3-Fluorene (Fl3). These PAHs are consistent with compounds that are commonly present in sediment sampled around natural exposures (Fl2, Fl3, Phe3, Phe/Ant4, and D2, D3 and D4) (Akre et al., 2004; Headley et al., 2001). Cho et al. (2014) found that alkylated species of dibenzothiophenes, phenanthrenes/anthracenes, fluranthenes/pyrenes, chrysenes and fluorenes

were present at elevated concentrations in snow samples from near oil sands operations. Dibenzothiophenes are found in oil or bitumen sources while phenanthrenes and fluorenes are derived from coke combustion sources (Cho et al., 2014).

The diagnostic PAH ratios highlight some of the compositional similarities and differences between the PAHs present snow, lakes, tributaries and the Athabasca River and provide some general insights into possible sources. Although the PCA of the relative abundances of PAHs (%PAHs) in surface water indicates some variability in the 34 PAH compounds present in the samples both spatially and temporally (Fig. 5c), the diagnostic ratios for these samples all suggest a dominantly petrogenic origin (Fig. 6). In contrast, the PCA of the relative concentrations (%PAH) in snow (Fig. 5a) indicates limited variation in the composition for most of the snow samples; the various diagnostic ratios used here indicate a wide range of potential sources (Fig. 6) consistent with previous interpretations of the snow dataset (Cho et al., 2014). The differences in BaA / (BaA + Chr) (Fig. 5b), $C_0 / (C_0 + C_1)$ Flu/Pyr (Fig. 5c) and $C_0 / (C_0 + C_1)$ Phe/Ant (Fig. 5c) between snow and surface waters are consistent with the large separation seen in the PCA of the relative concentrations and could indicate that source differences might explain some of the compositional differences. These ratios are consistent with surface water having more petrogenic sources of PAH such as erosion of bitumen present naturally in alluvial sediment, while snow samples are more typical of a mixture of petrogenic and pyrogenic sources or combustion of fossil fuels.

This study has documented some of the compositional differences between the PAHs present in snow and surface water, but attributing these differences to potential sources would benefit from better characterization of all of the potential sources. Rivers in the region may receive PAHs from variety of natural and anthropogenic sources. The composition of PAHs present in some of these potential sources have been characterized with varying levels of detail (e.g. atmospheric deposition, Cho et al., 2014; groundwater, Gue et al., 2015; river sediment, Akre et al., 2004 and Headley et al., 2001; petcoke, Zhang et al., 2016). But there are also potential PAH sources in the region that have not been as well characterized, including urban runoff, muskeg drainage, and catchment runoff from disturbed (mined) or fire-impacted catchments.

4.2. Evaluating the role of snowmelt

The more negative $\delta^{18}O$ values measured in the Athabasca River in May and June 2011 indicate that this is the time-period with the greatest proportion of snowmelt contributing to discharge. If PAHs were transferred directly from the snowpack to streamflow then this would be the period when their peak influence would be expected in the river. The composition of PAHs in the Athabasca River samples in May and July were very similar (Figs. 5b, S1 a and b), and they differ mainly in the higher absolute concentrations present in July (Figs. 4, S2 a and b). Both the May and July Athabasca River samples are compositionally different than the snow samples, suggesting that the direct transfer of atmospherically-derived PAHs deposited on the snowpack to surface waters during snowmelt is not a significant component of the PAHs present in the Athabasca River during this period. The biplot for the snow and surface water samples identifies a group of parent PAH compounds (BghIP, BbjkF, Phe, and Flu; bottom left quadrant of Fig. 5c) that are responsible for some of the separation between the composition of PAHs in snow and surface water samples. These 3–6 ring PAHs are typically detected in the first flush of effluent from urban snowmelt (Meyer et al., 2011). Phe is a very soluble 3-ring PAH (Table S1) and would likely be efficiently transfer to surface water via melt water and is often associated with the first melt from snowpack in urban areas (Meyer et al., 2011). The relative concentrations (%PAH) of these PAHs are not large in any of the river water samples (Fig. 5c), and the absolute concentrations are low during periods when the $\delta^{18}O$ composition of Athabasca River water indicate a high proportion of snowmelt (May 2011) (Fig. S3). Compositional

differences between the snow and surface water samples (Figs. 5b, S2a and b), particularly those for the spring freshet when snowmelt should be the greatest contribution, indicate that direct transfer of PAHs present on the snowpack to streamflow is not a major source of PAHs during this period. The composition of PAHs present in snowmelt is distinct when compared to any of the surface waters, due to the greater proportion of parent PAHs, and lower concentrations of PAHs associated with petrogenic sources.

The hydrograph and $\delta^{18}O$ time-series suggest that by September 2011 the Athabasca River discharge had returned to being primarily composed of groundwater contributions. This is the time period when some of the anomalous PAH compositions were noted (Figs. 5b, 6b and c, S2b). This shift in PAH composition that coincides with a period of less catchment runoff and a return to baseflow, may indicate compositional differences in the PAHs present in groundwater when compared to those present in surface water.

The various pathways for snowmelt to reach aquatic ecosystems include overland flow, and shallow macropore flow (Gibson et al., 2016) and flow along each of these pathways is governed by hydrological processes that can influence the retention or release of dissolved and particulate organics. During the spring freshet, snowmelt can flow to surface waters with minimal interaction with catchment materials, particularly for on-channel snowmelt, or near-channel overland flow (Meyer and Wania, 2008; Sharma and McBean, 2001). In some cases it may accumulate on soils over the catchment area and be gradually released to surface waters (Kelly et al., 2009; Nam et al., 2008). Hydrophobic organics that are typically associated with sediment particles (e.g. some PAHs) are differentiated from hydrophilic organics (like the polar organics detected by ESI-FTICR MS, Yi et al., 2015) in how they are released and transported during snowmelt (Meyer and Wania, 2008). Dissolved organics are often released first, followed by particle-bound species. Particle-bound species are often not transported as extensively and can be deposited near river mouths (Menzie et al., 2002), whereas dissolved phase species can be transported farther or may infiltrate groundwater.

Differences in PAH compositions in the river and snow during the spring freshet indicates that sources such as catchment runoff, erosion of stream channels, and snowmelt induced groundwater inputs should be considered in addition to atmospherically-derived organics n snowmelt as potential sources of PAHs to aquatic ecosystems.

4.3. Conservativeness of PAHs along hydrological pathways

Alterations in the relative PAH concentrations due to chemical partitioning of PAHs between dissolved and solid phases during snowmelt and transport over the catchment to the Athabasca River may also contribute to some of the compositional differences noted between the PAHs in snow and surface waters. These alterations were not specifically addressed in this study because only total PAH concentrations were available. However, the ESI-FTICR MS profiling of the dissolved polar organic compounds in snow and surface waters sampled in 2012 at many of the same locations as this study (Yi et al., 2015) also indicated compositional differences in the dissolved organics present in snow and surface water in the AOSR. The dissolved polar organics measured by Yi et al. (2015) would be less affected by the partitioning that can occur on PAH's during snowmelt and transport. Despite differences in the conservativeness and potential for transformation and retention, both the dissolved polar organics (Yi et al., 2015) and total PAHs (this study) indicate compositional differences between the atmospherically-derived organics present in snowmelt and the organics that are detected in rivers and lakes in the AOSR. Even if the PAH's present in the snowpack are not a significant direct source of organic loading to for rivers, the co-incident timing of elevated PAH concentrations in surface waters with periods of peak flow suggests that the hydrological activity associated with snowmelt contributes indirectly to the loadings of PAHs and other organics to the Athabasca River and its tributaries.

During periods of higher stream discharge, increased erosion of stream channels and remobilization of PAH-containing sediments, increased catchment runoff or snowmelt induced groundwater inputs could all result in increased loadings of total PAHs to rivers.

The findings of this study emphasize the need to better understand the transformations of PAHs along the potential pathways from snowmelt to streamflow. This study has identified significant compositional differences between the PAHs present in snow and those identified in surface water during periods of snowmelt. Identifying the types of compositional changes that should be expected due to differences in PAH volatility, water solubility and partitioning to organics and sediment, are necessary to develop monitoring approaches to identify PAHs from oil sands activities, and to improve models that to try to predict the fate and transport of atmospheric PAHs to surface water (Dayyani et al., 2016). The implications of non-conservative behaviour of PAHs in the atmosphere has been discussed for atmospheric source apportionment studies (Galarneau, 2008) and in multi-media fate studies focusing on identifying atmospheric sources of PAHs in soils (Zhang et al., 2005). However, predicting and identifying PAHs originating from atmospheric deposition from oil sands activities in downstream aquatic ecosystems also requires understanding of the conservativeness and partitioning of PAHs between air-sediment and water. Concurrent collection of water samples for analysis of stable isotopes in future monitoring studies may help to improve understanding of the relative contribution of water sources at the time of sampling in rivers and tributaries.

The results of this study have identified the need for improved understanding of processes affecting PAH composition along the pathway from atmospheric deposition, to snowmelt, to surface water receptors, including the relationship between dissolved and particulate PAH and other water quality parameters (e.g. pH, DOC, suspended solids).

5. Summary and conclusions

This study was conducted with the objective of characterizing the composition of PAHs present in snow and surface waters to identify whether atmospherically-derived PAHs present in snowmelt are a significant contributor to the PAHs detected in lakes and rivers in the AOSR. Our study highlights compositional differences in PAH assemblages present in snow and surface waters, and between tributaries and the Athabasca River. PAH concentrations in rivers are found to vary seasonally, with peak concentrations observed in July when Athabasca River levels and stream discharge were at their highest. The $\delta^{18}O$ composition of Athabasca River water indicates that spring and early summer are the periods with the greatest proportion of snowmelt contribution to streamflow. However, PAHs present in the Athabasca River during time of peak snowmelt contribution are different from the PAHs identified in snow, suggesting that direct runoff of PAHs accumulated on snow from atmospheric deposition to the Athabasca River and its tributaries at this time. The timing of the peak PAH concentrations in the Athabasca River roughly coincides with peak discharge during the spring freshet, which suggests an indirect link between these occurrences. Most likely snowmelt induces a general increase in catchment runoff and activation of a wide range of hydrological pathways leading to increased shallow groundwater and wetland contributions as well as potential for increase erosion of stream channels. There are also several potential sources of PAHs to rivers in the AOSR that have not yet been well-characterized (e.g. urban runoff, and runoff from disturbed, mined or fire-impacted catchments) whose potential contributions to the overall organic loading present in the surface waters in the region have not been assessed. All of these sources should be considered in addition to atmospherically-derived organics present on snowmelt as potential contributions to the over PAH loading in regional rivers. Contributions from these various sources should be considered collectively for monitoring efforts aimed at detecting and mitigating the effects of PAH loading on the Athabasca River and its tributaries.

Identifying the types of compositional changes to be expected as a consequence of variations in PAH volatility, water solubility and partitioning between organics and sediment, are necessary to develop monitoring approaches to identify PAHs from oil sands activities, and to improve predictions of the potential cumulative effects of atmospheric deposition to surface water across the region.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.06.051.

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