Characterizing the Organic Composition of Snow and Surface Water in the Athabasca Region

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October 2013

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This report may be cited as:

Birks, S.J., Y. Yi, S. Cho, J.J. Gibson and R. Hazewinkel, 2013. Characterizing the Organic Composition of Snow and Surface Water in the Athabasca Region. Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alberta. OSRIN Report No. TR-40. 62 pp.

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REPORT SUMMARY

This pilot study was conducted by Alberta Innovates – Technology Futures (AITF) to characterize the composition of organics present in snow and surface waters in the Athabasca Oil Sands Region (AOSR) with the goal of identifying whether atmospherically-derived organics present in snow are a significant contributor to the organics detected in rivers and lakes in the region. This study is divided into two parts, each describing a different approach to characterizing the organics present in snow and surface waters. In Part 1, we interpret existing polycyclic aromatic hydrocarbon (PAH) concentration data, collected from various monitoring programs in 2011, to compare the composition of PAHs in snow and surface waters across the AOSR. In Part 2, we interpret new ultra-high resolution mass spectrometry analyses of snow and surface water samples collected in 2012 to compare the dissolved polar organics present in snow and surface waters in the Athabasca Oil Sands region (AOSR).

The first approach applied in this study uses existing data from snow, river and lake monitoring programs conducted during 2011 which measured total (dissolved + particulate) PAH concentrations in snow and surface waters in the region. The 2011 dataset includes total (dissolved + particulate) concentrations for 34 parent and alkylated PAH species for 105 snow, 272 Athabasca River and tributary, and 3 lake samples. These data were compiled so that the composition of PAHs in the Athabasca River, its tributaries and a small number of lakes could be compared with that of snowmelt. The snow data show compositional differences between the PAHs present in snow sampled from areas closest to oil sands activities (i.e., near-field sites) and from more distant (i.e., far-field) snow sampling locations. Despite large concentration variations in snow along geographic gradients, the composition of PAHs are found to be similar among near-field sites, but change significantly at far-field sites. Both the near- and far-field snow samples have PAH compositions that are different from the PAHs present in the Athabasca River, its tributaries and lakes. Compositional differences in PAH assemblages are also evident between tributaries and the Athabasca River. PAH concentrations in rivers are found to vary seasonally, with peak concentrations observed in July 2011 when Athabasca River levels were at their highest. However, the composition of PAHs present in July 2011 do not resemble the composition of PAHs identified in snow, suggesting that direct transfer of PAHs accumulated on snow from atmospheric deposition to Athabasca River and its tributaries in the area is not a major source of PAHs present in surface waters. The timing of peak PAH concentrations in rivers, which coincides with a high flow period during freshet, does suggest that snowmelt may contribute indirectly to increases in PAH concentrations due to processes such as increased catchment runoff, erosion of stream channels, and snowmelt-induced groundwater inputs during this dynamic hydrologic period.

The second approach applied in this study uses Electrospray Ionization Fourier Transform Mass Spectrometry (ESI-FTICR MS) to characterize the dissolved polar organic composition of snow and surface water samples provided by various Alberta Environment and Sustainable Resource Development (AESRD) programs conducted in 2012. The 2012 samples analyzed by ESI-FTICR MS include 7 snow samples, 73 Athabasca River and tributary samples, and 6 lake samples. This profiling method identified thousands of dissolved polar compounds including the

acidic organic components in negatively charged ESI(-) mode, and basic components in positively-charged ESI(+) mode. Although based on a limited number of samples, the organic profiles obtained for the snow samples in ESI(-) mode show compositional differences in the dissolved organics present in snow sampled from sites closest to oil sands activities (<5 km) and those sampled from more distant locations. There are also very significant compositional differences between the dissolved polar organics present in snow and surface waters in the AOSR. The composition of dissolved organics present in the Athabasca River upstream of the AOSR (i.e., Athabasca River at Athabasca) are found to be different from samples obtained from downstream sites in the vicinity of AOSR (i.e., Athabasca River at Fort McMurray and Athabasca River at Firebag confluence). The upstream Athabasca River sites tend to share some compositional similarities with far-field snow deposition, while the downstream Athabasca River sites are more similar to local tributaries. This contrast likely indicates shifts in the relative importance of regional snowmelt versus local inputs from small tributaries.

The results of these two separate approaches, which characterized different components of the organics present in snow and surface waters in the AOSR, leads to some similar conclusions. Both show compositional differences between the organics present in the snowpack near the centre of oil sands activities compared with more far-field locations and between the Athabasca River and its tributaries. The compositional differences between organics present in snow and those sampled in surface waters in the region suggest that even though the spring freshet is a period when elevated PAHs have been found in the Athabasca River the organics released directly from snow are not the dominant inputs during this peak discharge. These compositional differences may be useful tools for differentiating air-borne vs. water-borne organics away from the AOSR. The two methods used show the usefulness of PAH composition (i.e., relative concentrations of PAHs) and polar organic profiling in differentiating sources of organics in the region. The role of potential transformations of PAH and ESI-FTICR MS composition profiles during spring melt and during interactions along typical surface and subsurface flowpaths within wetland-dominated catchment areas typical of the region remains to be better understood.

ACKNOWLEDGEMENTS

The Oil Sands Research and Information Network (OSRIN), School of Energy and the Environment (SEE), University of Alberta provided funding for this project.

This report benefitted from comments made by Kusumakar Sharma. The authors wish to thank Shelley Manchur and Jessica Di Maria (Alberta Environment and Sustainable Resource Development) for collecting the samples and coordinating the field component and Don Jones (AITF) for assisting with sample handling and database management.

1 INTRODUCTION

Understanding impacts of human activities on aquatic ecosystems in the Athabasca Oil Sands Region (AOSR) is required to ensure sustainable development in northeastern Alberta and to assess the economic benefit of oil sands development to Alberta and Canada. Elevated concentrations of polycyclic aromatic hydrocarbons (PAH) have been identified in river water and sediments in the AOSR and airborne pathways have been implicated as the main conduit for transport of these contaminants from the AOSR industrial development into the aquatic ecosystem (Kelly et al. 2009, Kurek et al. 2013, Timoney and Lee 2011). Other studies have suggested that transport of PAHs by the Athabasca River, a waterborne pathway, is the main conduit for bringing PAHs to the Peace Athabasca Delta located approximately 200 km downstream of major oil sands development (Hall et al. 2012, Wiklund et al. 2012). Accordingly, we conceptualize that organics can take various pathways to reach aquatic ecosystems, including atmospheric deposition, and surface or groundwater flowpaths. The contribution of atmospherically-derived organics to the overall organic load present in the Athabasca River, tributaries and lakes is not known and improved understanding of differences in these sources and transport pathways is required.

Snow surveys provide a means of collecting an integrated sample of atmospherically-derived organics deposited during the winter season. Here we use the composition of organics present in snowmelt to characterize atmospherically-derived organics deposited across the region. 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 (Woo and Thorne 2003). During snowmelt, water, as well as solutes and particulate matter present in the snowpack, are released and become either infiltration or runoff depending on the condition of frozen ground. Sublimation may also account for loss of snowpack water in some cases; although this is not a pathway for movement of solutes or particulates, it leads to further concentration. During the initial melt period, the ground is typically frozen so increases in infiltration, mixing and resulting increases in groundwater levels and groundwater discharge to rivers may be limited or delayed. Once active, both surface and groundwater flow paths may contribute to increased runoff in tributaries and rivers, and typically result in 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 during transport by physical, chemical, or biological interaction. 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 over all or a portion of their catchments, with strong temporal variations. Water samples from the Athabasca River and its tributaries are therefore considered to generally contain an organic signature that integrates sources derived from atmospheric deposition over all or a portion of their respective catchment areas, as well as inputs from surface and groundwater sources. Surface runoff and groundwater 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 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. Water samples from lakes are considered to integrate atmospheric deposition over their catchment and also include inputs from surface runoff and groundwater but will not have the same temporal variations as rivers.

By comparing the organics present in snow (representative of atmospheric sources of organics) with these different surface water samples, each capturing a different combination of input from atmospheric, catchment and groundwater-derived organics, we anticipate that we can gain insight into differences in the organic composition of these waters and better understanding of the contribution of atmospherically-derived organics to surface waters across the region.

In 2011 and 2012 multiple water quality monitoring programs collected data on the organic composition of surface waters in the AOSR including the Athabasca River, its tributaries and a small number of lakes. These individual programs focused on atmospheric deposition or surface water quality, and separately have contributed to improved characterization of organics in snow and surface waters across the AOSR, but the various datasets have not been integrated to look at the footprint of organics across the Athabasca region. As a result, comparisons between these atmospheric and surface water organic data to look at the regional footprint of organics across the AOSR have not yet been made. This project makes use of existing sampling and monitoring programs to compile results and to obtain samples from snow and surface water to develop this comparative study.

Because this study takes advantage of existing data and opportunistic sampling, we had little control over the sampling locations. Trying to co-locate water sampling locations that exactly corresponded with snow sampling locations from various datasets was not possible, so our approach was instead to try to compile a large database with broad spatial and temporal coverage to provide a regional view or first approximation of the range and variability of organics present in snow and surface waters across the region.

The objective of this project is to use two completely separate approaches to characterize the composition of organics present in snow and surface waters in the AOSR and to see if similarities and/or differences in the composition of organics present in snow, rivers or lakes can be used to identify linkages or potential sources. Given the recently documented atmospheric organic footprint of oil sands operations that results in elevated concentration of PAHs in snow over areas in the AOSR (Cho et al., in submission), this study was conducted to test if a similar footprint, directly related to this atmospheric input, could be detected in surface waters.

- In Part 1 we use existing PAH data from snow and surface water collected in 2011 in the AOSR to compare the composition of PAHs deposited on snow with those detected in the Athabasca River, its tributaries and lakes.
- In Part 2 we conduct a pilot investigation to evaluate whether using ultra-high resolution mass spectrometry to profile the dissolved organic compounds in snow and surface waters collected during 2012 across the region can be used to further differentiate the sources of organics.

2 BACKGROUND

PAHs are a group of organic compounds commonly found in the environment and over 100 different PAH species have been identified. They contain two or more fused aromatic rings (Harvey 1997). Parent PAHs refer to PAH species with fused conjugated ring structure only such as Naphthalene and Chrysene. Alkylated PAHs are PAHs with various alkyl groups attached such as C1-Naphthalene and C1-Chrysene. Petrogenic PAHs are generated during the conversion of steroids to aromatic hydrocarbons in crude oil and coal deposits. Pyrogenic PAHs are those formed by incomplete combustion of carbon-containing fuels such as wood, grass, coal, and diesel. Different types of pyrogenic sources yield different distributions of PAHs (Guo et al. 2011, Lopes and deAndrade 1996). The solubility and volatility of PAHs depends 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. 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.

There is considerable interest in PAHs in the AOSR because of the negative effects many PAH species have on human health (Delfino 2002, Flowers et al. 2002, Perera et al. 2009) and terrestrial/aquatic organisms (Colavecchia et al. 2004, Martin et al. 2005, Saunders et al. 2003, Vehniäinen et al. 2003). The United States Environmental Protection Agency (US EPA) has classified 16 PAH species as “priority pollutants” because of their potential for carcinogenic, mutagenic, or teratogenic effects (ATSDR 2005).

In the AOSR, anthropogenic sources of PAHs include the upgrading of bitumen to synthetic crude oil, the evaporation of process-affected water from tailing ponds, or the operation of fleet vehicles. There are also natural sources of PAHs in the region including forest fires (Gabos et al. 2001) and natural erosion of bitumen laden sediments by the Athabasca River and its tributaries (Headley et al. 2001). PAHs from these different anthropogenic and natural sources may be transported in air and deposited on the snowpack (Kelly et al. 2009) or transported in water and eventually sequestered into soil and sediments (Nam et al. 2008). Given the negative effects of many PAH species on human and ecosystem health, it is important to understand spatial and temporal distribution of PAHs in atmospheric deposition and aquatic receptors. Previous work has documented the presence of PAHs originating from oil sands activities in the snowpack and has suggested that transfer of these PAHs to rivers may be a significant loading to aquatic ecosystems (Kelly et al. 2009, Timoney and Lee 2011).

PAHs are just one of category of organics that can be associated with industrial activities. Studies on the potential impacts from development in the AOSR have focused on PAHs and naphthenic acids because of their well-known toxicity, but there is growing concern that the potential environmental impacts of some of the other dissolved organic compounds should also be considered (Barrow et al. 2010, Grewer et al. 2010). AITF recently developed applications of ESI-FTICR MS to characterize dissolved organics present in rivers, lakes, groundwater and oil sands process-affected water (OSPW) in the AOSR (Gibson et al. 2011). The results of this research have shown that OSPW and some of the natural, organic-rich waters in the region contain complex mixtures of dissolved organics, of which naphthenic acids are only a small component. PAHs have been the focus of previous and current snow and surface water sampling campaigns and monitoring programs, but the composition of other organics have not been as well characterized. The application of ultra-high resolution analytical techniques, like ESI-FTICR MS provide new opportunities to detect and profile dissolved organic and inorganic compounds.

3 PART 1: SNOW AND SURFACE WATER PAH DATA FROM 2011

The first phase of this project compares PAH data measured in snow and surface water bodies in 2011 across the AOSR to identify similarities and differences in the PAHs deposited atmospherically on snow with those detected in the Athabasca River and its tributaries.

3.1 Methods

3.1.1 *Sources of PAH Data*

Multiple provincial programs collected surface water or snow samples to monitor PAH concentrations during 2011. Table 1 lists the three major databases that were used to compile a 2011 database of PAH compositions and concentrations in snow and surface waters (i.e., Athabasca River, its tributaries, and lakes) in the AOSR. AESRD had an intensive snow survey (AESRD-SS) that included analysis of PAHs, as well as their on-going water quality monitoring network that sampled the Athabasca River and tributaries (AESRD-AT) for a broad suite of water quality parameters including PAHs (Figure 1 and Table 1). RAMP water quality monitoring (RAMP-WQ) was also on-going in 2011, and included PAH results for water samples from Athabasca River, tributaries and a few lakes[1] (Figure 1). The AESRD-SS snow survey included sampling sites that were 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 arbitrary reference point (known as geographical center, GC, of oil sands operations) located at the approximate midpoint between the Syncrude Canada Ltd. and Suncor Energy Inc. bitumen upgraders (Figure 1). The snow survey sampling locations included 94 sites along the directional transects and 94 snow sampling sites that were located at Water Quality Monitoring stations. More detailed information about snow sampling protocol, analytical method and sampling locations is provided in Cho et al. (in submission 2013).

Collectively we refer to the entire 2011 PAH dataset as the snow and surface water dataset, but the surface waters included are predominantly from the Athabasca River and its tributaries; data from only 3 lakes were available.

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[1] These data are readily downloadable from http://www.ramp-alberta.org/ramp/data.aspx

Table 1. List of available 2011 data sources for compilation.

Dataset	Organization	Medium	Number of Samples
Snow Survey	AESRD	Snow	105
Athabasca and Tributaries	AESRD	Athabasca River	62
		Tributaries	158
Water Quality	RAMP	Athabasca River	20
		Tributaries	32
		Lakes	3

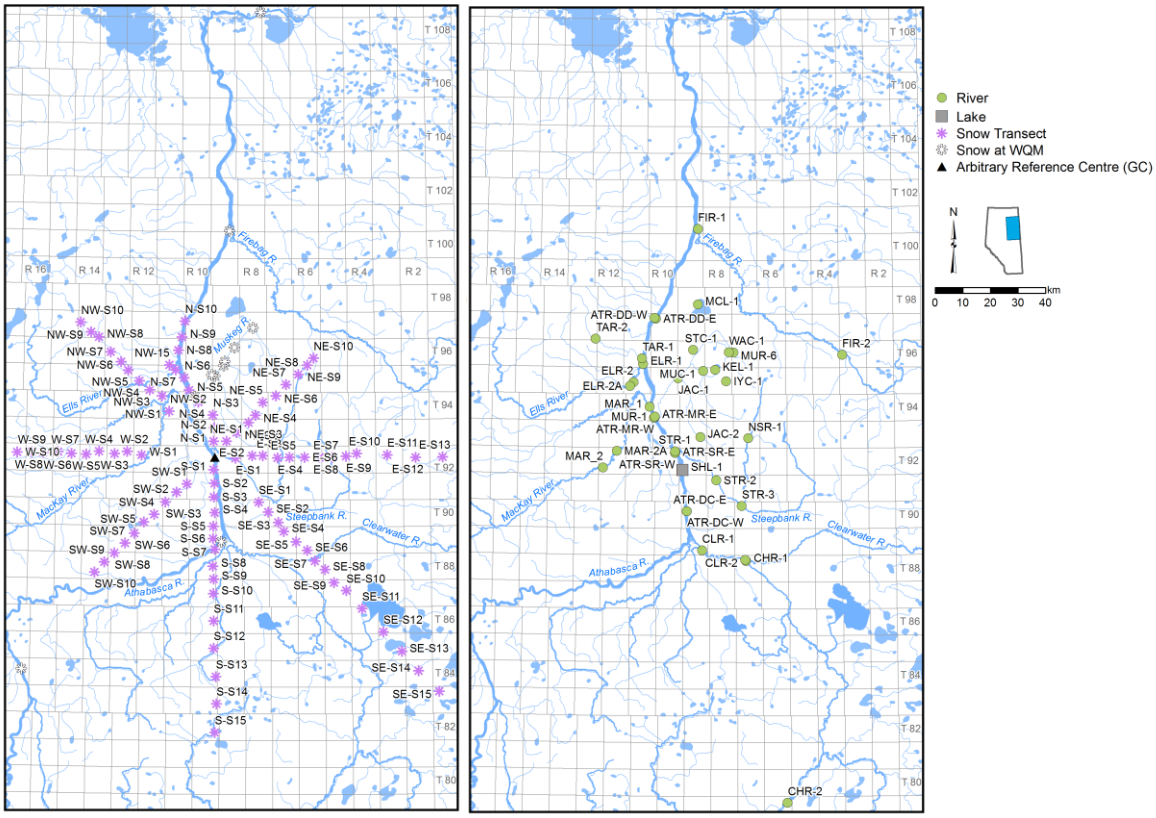

Figure 1. Location of 105 snow, 272 river and 3 lake samples available in the 2011 datasets.

Snow was sampled in February 2011 and surface water samples were collected between May and September 2011. The Athabasca River and tributaries river and lake samples were collected monthly between May and September 2011 and lake samples were collected during a single sampling visit in September 2011. In 2011, peak flows in the Athabasca occurred in early July and were higher than mean historical data for that period (Figure 2).

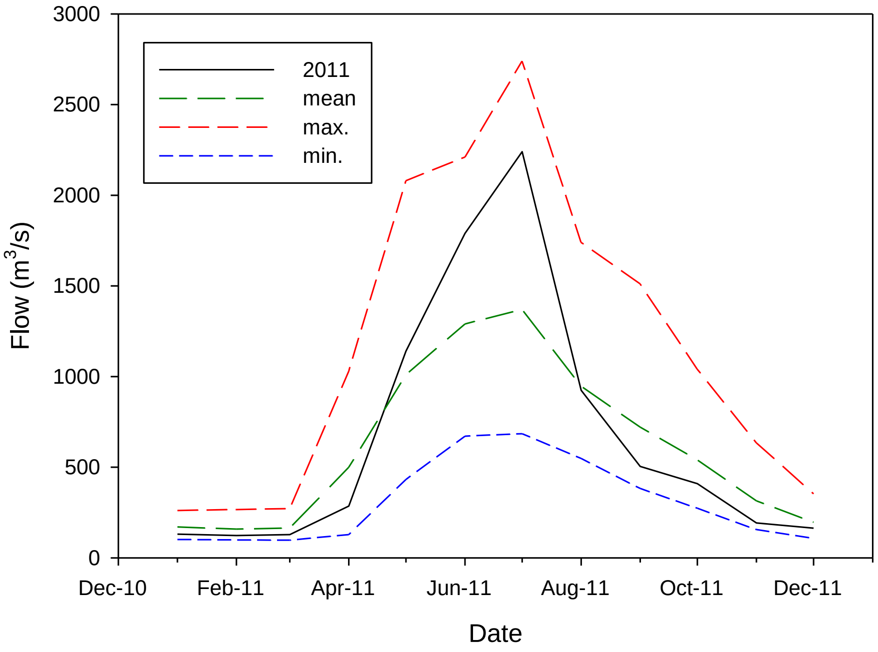

Figure 2. Streamflow data for the Athabasca River below Fort McMurray (WSC gauge 07DA001).

3.1.2 *Compilation of PAH Data*

The snow and surface water PAH data available for 2011 were compiled from different sources and as a result included different PAH species (Table 2). It is also important to note that three datasets included measurements made at two different laboratories with different detection limits. The AESRD-SS snow survey reported 39 PAH species, while AESRD-AT Athabasca River and tributary data included 50 species. The RAMP-WQ water quality dataset included 43 PAH species (Table 2). Thirty-four PAH species were found in all three data sources (Table 2). The compiled 2011 snow and surface water dataset only contains the 34 common species (highlighted in the table) to facilitate cross program comparison. Common abbreviations are included in Table 2 and were used to refer to these PAH species in the text and figures. All of the reported PAH data are for total PAHs in unfiltered samples, so we are not able to distinguish between PAHs present in the dissolved or solid phases.

Table 2. PAH species reported by source database.

Compound	**Abbreviation**	**AESRD Athabasca and Tributaries (AT)**	**AESRD Snow Survey (SS)**	**RAMP Water Quality (WQ)**
		50 Species	39 Species	43 Species
Acenaphthene*	Ace	√	√	√
Acenaphthylene*	Acy	√	√	√
Anthracene*	Ant	√	√	√
Benzo(a)pyrene*	BaP	√	√	√
Benz(a)anthracene*	BaA	√	√	√
Benzo(b,j,k)fluoranthene*	BbjkF	√	√	√
Benzo(g,h,i)perylene*	BghiP	√	√	√
Chrysene*	Chr	√	√	√
Dibenz(a,h)anthracene*	DahA	√	√	√
Fluorene*	Fl	√	√	√
Fluoranthene*	Flu	√	√	√
Indeno(1,2,3-cd)pyrene*	IcdP	√	√	√
Naphthalene*	Nap	√	√	√
Pyrene*	Pyr	√	√	√
Phenanthrene*	Phe	√	√	√
C1-Chrysene	Chr1	√	√	√
C2-Chrysene	Chr2	√	√	√
C1-Dibenzothiophene	D1	√	√	√
C2-Dibenzothiophene	D2	√	√	√
C3-Dibenzothiophene	D3	√	√	√
C4-Dibenzothiophene	D4	√	√	√

Compound	**Abbreviation**	**AESRD Athabasca and Tributaries (AT)**	**AESRD Snow Survey (SS)**	**RAMP Water Quality (WQ)**
C1-Fluorene	Fl1	√	√	√
C2-Fluorene	Fl2	√	√	√
C3-Fluorene	Fl3	√	√	√
C1-Fluoranthene/pyrene	Flu/Pyr1	√	√	√
C2-Fluoranthene/pyrene	Flu/Pyr2	√	√	√
C3-Fluoranthene/pyrene	Flu/Pyr3	√	√	√
C2-Naphthalene	NaP2	√	√	√
C3-Naphthalene	NaP3	√	√	√
C4-Naphthalene	NaP4	√	√	√
C1-Phenanthrene/anthracene	Phe/Ant1	√	√	√
C2-Phenanthrene/anthracene	Phe/Ant2	√	√	√
C3-Phenanthrene/anthracene	Phe/Ant3	√	√	√
C4-Phenanthrene/anthracene	Phe/Ant4	√	√	√
C3-Chrysene	Chr3	√	√	
C4-Chrysene	Chr4	√	√	
C4-Fluoranthene/pyrene	Flu/Pyr4	√	√	
C4-Fluorene	Fl4	√	√	
C1-Naphthalene	NaP1		√	√
Retene (1-Methyl-7-isopropyl Phenanthrene)	Ret	√		√
C1-Acenaphthene	AcP1			√
C1-Benzofluoranthenes/Benzopyrene	BeF/BeP1			√
C1-Biphenyl	BP1			√
C2-Benzofluoranthenes/Benzopyrene	BeF/BeP2			√

Compound	**Abbreviation**	**AESRD Athabasca and Tributaries (AT)**	**AESRD Snow Survey (SS)**	**RAMP Water Quality (WQ)**
C2-Biphenyl	BP2			√
1-Methylnaphthalene	MeN1	√		
2-Methylnaphthalene	MeN2	√		
3-Methylnaphthalene	MeN3	√		
7,12-Dimethylbenz(a)anthracene	DMA	√		
Acridine*	Acr	√		
Benzo(c)phenanthrene*	BcPh	√		
Benzo(e)pyrene*	BePy	√		
Dibenzo(a,h)pyrene*	DahPy	√		
Dibenzo(a,i)pyrene*	DaiPy	√		
Dibenzo(a,l)pyrene*	DalPy	√		
Perylene*	Per	√		

* indicates parent PAH

Another challenge in compiling the 2011 snow and surface water PAH dataset was the large number of results that were reported as below detection limits (BDL) and the variations in detection limits between analytes and between labs. For each dataset, we calculated a PAH detection ratio (i.e., percentage of above detection limit measurements in total number of measurements) of ~60% for the AESRD-SS dataset, ~3% for the AESRD-AT dataset; and ~49% for the RAMP-WQ2011 dataset. These differences in PAH detection ratios reflect lower detection limits used in the analyses of surface waters in the RAMP data (WQ2011). The PAH analyses for the AESRD-SS and AESRD-AT were obtained using EPA method 625 whereas the RAMP-WQ was obtained using EPA method 1625/8270. The two methods are considered equivalent, but the RAMP-WQ analysis was conducted with a lower detection limit (0.1 ng/L) compared to the AESRD-AT (10 ng/L) possibly due to differences in matrix effects and sample volumes analyzed.

Before these data could be compiled into a single dataset and statistically analyzed 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 we used a constant value of zero.
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 effect of the two methods for treating BDL was evaluated by comparing PCA results using the two different techniques. Comparison of PCA results for the dataset using the two techniques (not shown) generally did not produce significant differences in PCA results for the 2011 PAH data. For the sake of simplicity (Aruga 1997), the constant substitution technique was used.

3.1.3 *Absolute and Relative PAH Concentrations*

In our discussion of the compiled 2011 snow and surface water PAH dataset we refer to absolute concentrations as well as relative concentrations. Relative concentrations were determined as the percentage of each PAH species in the sum of all PAH species present (sum of 34 species) and were used to identify major compositional differences present in different samples. The relative concentration for a given PAH species in a sample was calculated using:

$$\%PAHx = (PAHx)/\Sigma PAH(34)$$

> Where x is the absolute concentration of PAHx and ΣPAH(34) is the sum of the concentrations of the 34 PAH species common to all datasets.

For example, the absolute concentrations of Chr1, a commonly abundant PAH species in snow, show significant decreases (~8 fold) in absolute concentration between sites S-S1 (1.8921 μg/L) and S-S5 (0.2302 μg/L), but the relative concentration of Chr1 remained similar at the two locations (S1 = 13%, S5 = 12%). The use of relative concentrations downplays the effect of high concentrations and focuses instead on the overall composition of PAHs present in the samples, rather than the absolute concentrations.

3.1.4 *Statistical Analyses*

Principle component analysis (PCA) was performed using both absolute (µg/L) and relative PAH concentrations (%) to statistically characterize and compare similarities between the snow and surface water samples. PCA is a multivariate statistical technique that transforms and extracts meaningful information from large datasets with many variables (Mardia et al. 1989). In general, PCA looks for a few linear combinations which can be used to extract relevant information from a large data matrix. 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 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 significant information, thus reducing the data dimension. 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. The sample scores (PC1 vs. PC2) from PCA were employed to illustrate a statistical overview. PCA analyses are performed using SIMCA-P+ (V12.0, Umetrics AB Umeå, Sweden).

After substituting the BDL values with zeros, the compiled 2011 PAH snow and surface water dataset contained a large number of samples with concentrations of individual PAHs listed as zero. To avoid excessive bias from these substituted values, we limited our Principal Component Analysis (PCA described below) to the samples that met the condition of having greater than 80% of the variables detected (i.e., at least 27 of 34 PAH compounds) for 80% of the observations. We focused our efforts on identifying compositional differences in samples where PAHs were detected. We were interested in determining if the assemblages of PAHs present in surface waters were similar to those detected in snow, so this bias towards including only those samples with PAHs detected was considered valid. Furthermore, our interpretation did not rely on determining averages across the dataset or use the absolute concentrations for any calculations, so excluding samples with few detectable PAHs did not affect any calculated parameters. Because our focus was on relative PAH concentrations (discussed below), we excluded samples with very few detected PAHs. Using this method to remove the data with very few detects for PAHs reduced the number of samples used in our statistical analyses to a total of 160 samples. Notably, once this criterion was applied Shipyard Lake was the only included in the PCA analysis.

3.2 Results and Discussion

3.2.1 *Summary of PAH Concentrations*

The compiled 2011 snow and surface water PAH dataset contained 379 samples covering 34 PAH species (both parent and alkylated PAHs). The absolute concentrations of parent PAH species in the entire dataset ranged from BDL to 0.5526 µg/L in snow samples, while they varied between BDL and 0.1540 µg/L in surface waters. The distribution of concentrations are skewed towards the lower concentrations as shown by the position of 25 to 75 percentiles (the box) relative to the 95% and 5% whiskers (Figure 3 and 4).

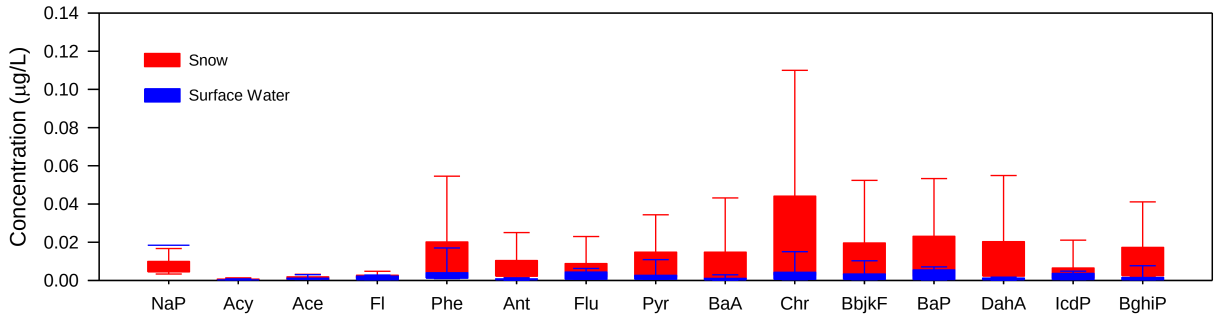

Figure 3. Summary of absolute concentrations of parent PAH species in the 2011 PAH dataset including snow (red) and surface waters (blue).
The box represents the range of 25 and 75 percentile, while the whiskers represent 5 and 95 percentile.

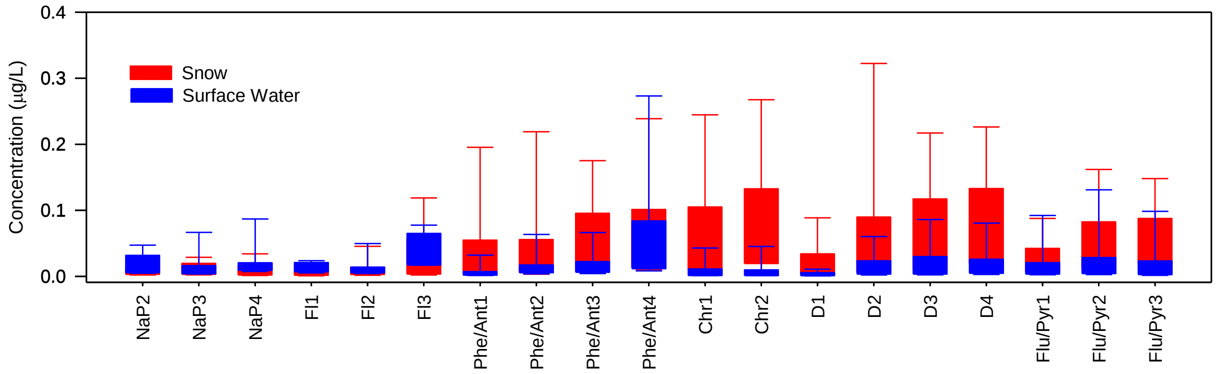

Figure 4. Summary of absolute concentrations of alkylated PAH species in the 2011 PAH dataset, including snow (red) and surface waters (blue).
The box represents the range of 25 and 75 percentile, while the whiskers represent 5 and 95 percentile.

The range of concentrations covered by the 25 to 75 percentiles was fairly narrow, but there were PAH species where there were individual samples that had concentrations much higher than the 25 to 75 percentile bounds. The concentrations of most parent PAH species were significantly higher in snow than in the surface water samples (Figure 3). The exception to this is Acenaphthylene (Acy) which had very low concentration in both snow and surface water, but with very similar concentration ranges in snow and surface waters.

The absolute concentrations of alkylated PAH species ranged from BDL to 1.8921 µg/L in snow, while they varied between BDL and 0.3760 µg/L in surface waters. Species, such as C4-

Phenanthrene/Anthracene (Phe/Ant4) and C3-Fluorene (Fl3) were the dominant PAHs present in surface water samples (Figure 4). It is also important to note that there are several species that had similar concentrations in both snow and surface water samples including:

- C1-Fluorene (Fl1)
- C2-Fluorene (Fl2)
- C3-Fluorene (Fl3)
- C2-Naphthalene (NaP2)
- C3-Naphthalene (NaP3) and,
- C4-Naphthalene (NaP4).

The Canadian Council of Ministers of the Environment water quality guidelines (CCME 2007) include recommendations for 16 PAH species, although only four of these species were included in the 2011 PAH snow and surface water dataset (i.e., Acy, BaA, Flu and Phe). The PAH concentrations in the 2011 surface water samples did not exceed the water quality guidelines (Table 3).

Table 3. Comparison of measurements of PAHs species concentrations in the 2011 surface water dataset (i.e., AESRD-AT and RAMP-WQ data for the Athabasca River, tributaries and lake samples in Table 1) with Canadian water quality guidelines for the protection of aquatic life (CCME 2007).

Species	**Name Code**	**Water Quality Guideline (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

For each sample, the absolute concentrations of 34 PAH species were summed to give a summed PAH concentration in each sample that we'll refer to as "ΣPAH(34)". The ΣPAH(34) concentrations varied between BDL and 1.8725 µg/L in surface waters, while they ranged from

0.0064 to 14.4602 µg/L in snow. ΣPAH(34) concentrations were generally higher in snow than in surface water samples. Box and whisker plots of the ΣPAH(34) concentrations for snow and surface water (Figure 5) show that the 25 to 75 percentile concentration range for surface water samples are comparable to the range of 0.009 to 0.202 µg/L reported by Kelly et al. (2009) for the dissolved PAH concentrations in Athabasca River samples. The high ΣPAH(34) concentrations (> 0.5µg/L) in some samples highlights the need for monitoring of PAH concentrations and better understanding their sources. The ΣPAH(34) concentrations calculated here only include the 34 PAHs species common to all three data sources; the ΣPAH that would be obtained if all of the PAH species in Table 2 were included is likely higher.

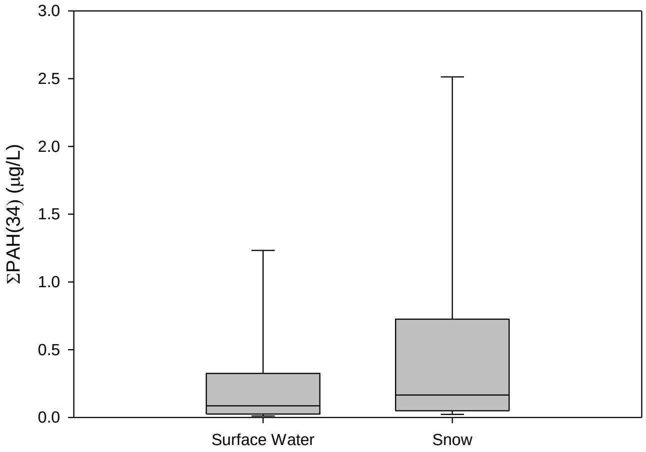

Figure 5. Comparison of ΣPAH(34) concentrations in the 2011 snow and surface water dataset.
The box represents the 25 to 75 percentile range, while the whiskers represent 5 and 95 percentile.

3.2.2 *PAHs in the Athabasca River and its Tributaries*

PCA was used to provide an overview of the variability and groupings of PAH concentrations and compositions within the 2011 samples (see Figure 1b for sample locations). For example, the PCA analysis of absolute PAH concentrations in surface waters (including Athabasca River, tributary and lake samples) clearly show that the four Athabasca River samples collected in July 2011 (2 from ATR-DC and 2 from ATR-DD) are different from the other Athabasca River and tributary samples (Figure 6). Samples from ATR-DC and ATR-DD taken during other months plot in a similar position to the other tributary samples on the PCA plot, showing only minor shifts along the second axis (PC2). The Athabasca River samples from July (2 from ATR-DC and 2 from ATR-DD) are distinct from the other locations and other times because of higher PAH concentrations. The timing of highest PAH concentrations coincides with the period of maximum streamflow (Figure 2). The other anomalous Athabasca River sample was collected in September, 2011 (ATR-SR-W) when water levels were much lower (Figure 2). This sample is distinguishable along the PC2, which accounts for only 1.8% of total variability.

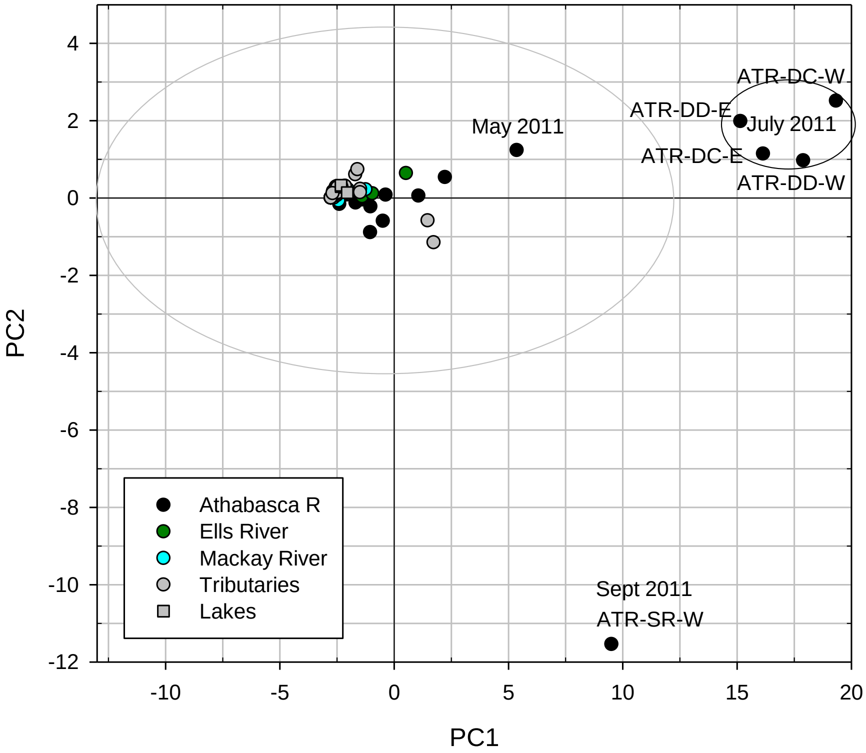

Figure 6. PCA analysis of PAH absolute concentrations from the 2011 surface water samples which included 27 stream samples and 1 lake.

The PAH species present at one of these anomalous Athabasca River sampling locations (ATR-DC; Figure 6) are examined in more detail in Figure 7. The concentration of July samples (red and blue bars in Figure 7) are consistently higher than the concentrations measured in May and September for this location. The concentrations of the alkylated PAHs included in Figure 7 were highest in July, followed by May and then September. The concentrations of the parent PAHs in May and September for these samples were too low to have visible bars in Figure 7, so only the July values (red and blue bars) are visible in the plot. Higher PAH concentrations were also measured in the July 2011 sample from the ATR-DD site than any of the other months measured. The higher concentration of PAHs in July is also consistent with Kelly et al. (2009) who found higher concentrations of total dissolved polycyclic aromatic compounds in Athabasca River and its tributaries during summer than during winter.

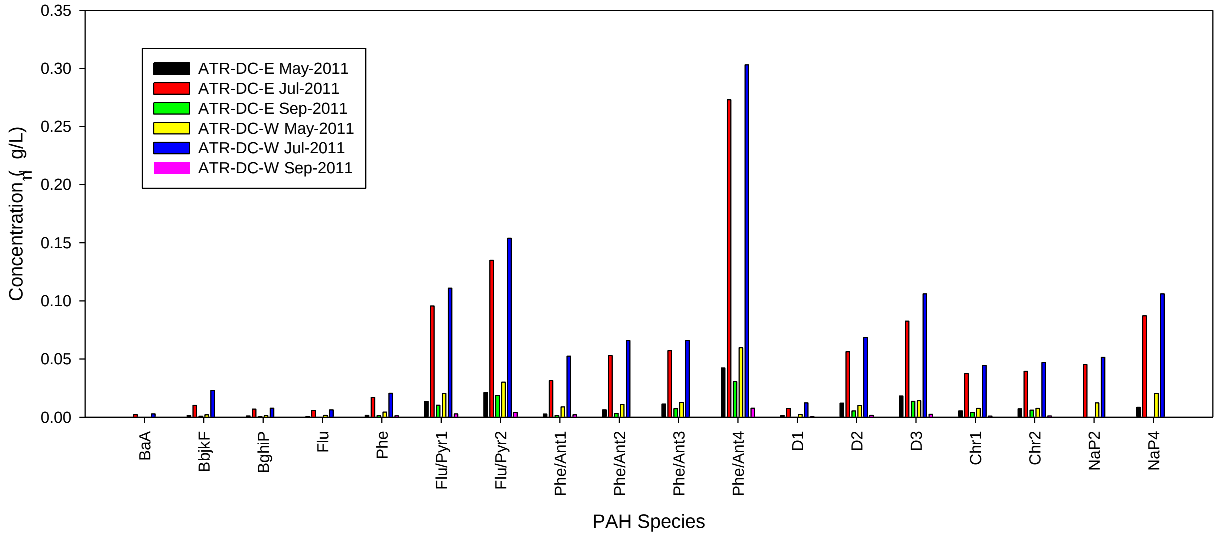

Figure 7. Absolute concentrations of selected PAH species at ATR-DC.
ATR-DC-E and ATR-DC-W indicate west and east bank of the river channel respectively.
Bars represent different sampling months: May, July and September 2011.

In addition to temporal variations, there were also interesting spatial patterns in PAHs in the 2011 surface water samples. Examining the concentrations of selected PAH species from the Ells River upstream sampling locations (ELR-2A, ELR-2) and the downstream site (ELR-1) (Figure 8), shows increases in PAH concentrations for many PAH species, especially alkylated PAHs. This pattern of increasing PAH concentrations along the Ells River was present in the September 2011 data, but it is not clear if this pattern persists over time. At the upstream site (ELR-2A), the concentrations of PAHs was higher in July 2011 than in September 2011 (Figure 8), similar to the Athabasca River (Figure 7).

Input of PAHs from the tributaries alone cannot explain the high concentration of PAHs in the Athabasca River in July 2011. The data for tributary sites showed that the ΣPAH(34) concentrations varied between 0.0002 µg/L and 0.4351 µg/L, while the ΣPAH(34) in the Athabasca River ranged from 1.5473 to 1.88725 µg/L. There is a significant gap between the maximum ΣPAH(34) concentration measured in tributaries and the minimum ΣPAH(34) concentration found in the Athabasca River in July, which suggests sources of PAHs other than just input from the tributaries.

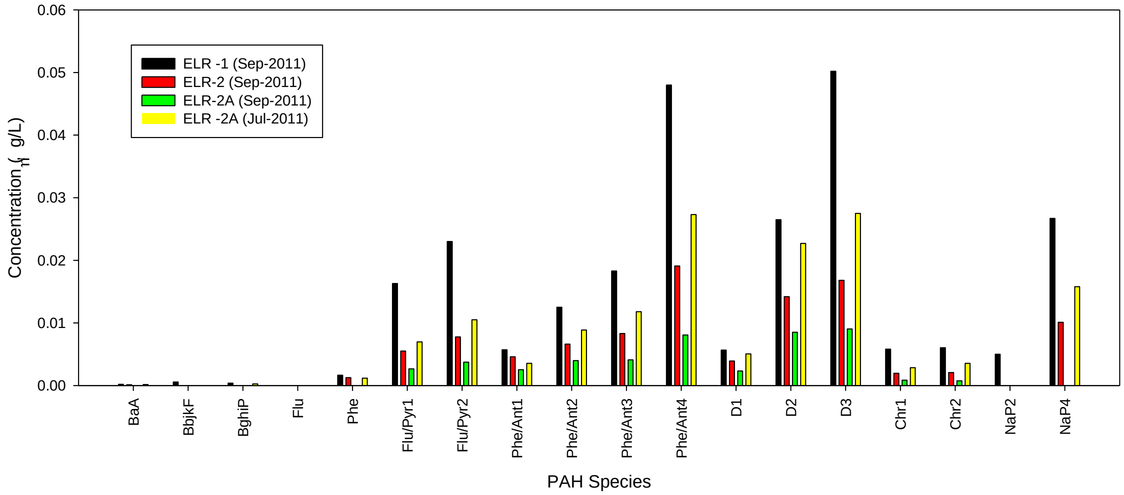

Figure 8. Absolute concentrations of selected PAH species along the Ells River. Sampling locations include two upstream locations (ELR-2A, ELR-2) and one downstream (ELR-1) location for September 2011. One of the upstream sites (ELR-2A) was also sampled in July 2011.

Closer examination of the relative concentrations of the 34 PAH species in the 2011 surface water dataset show compositional differences between the PAHs present in the Athabasca River and its tributaries (Figure 9). PCA analysis of the relative concentrations of PAH for the surface water dataset (Figure 9) shows that the Athabasca River samples (solid black circles) have greater relative concentrations of Chr1, Chr2, and Flu/Pyr1, whereas the tributaries (green, blue and grey circles) have greater relative concentrations of Phe/Ant3, D2 and D3 (Figure 9). In the analysis of PAHs in sediment cores from the Peace Athabasca Delta, Hall et al. (2012) identified D2 and D3 as species associated with flooding in the Delta. It is likely that flood-linked sediments were generated during local catchment runoff, which bear the signature of local tributaries rather than sediments eroded from the channel of Athabasca River. Some of the tributaries, including MacKay, Tar and Steepbank Rivers, showed compositional similarity to the Athabasca River during some months (labeled MAR, TAR and STR respectively in Figure 1b). The two anomalous Athabasca River samples (ATR-DC-W, ATR-SR-W) that differ in both the PCA1 and PCA2 axes were sampled in September 2011. The Shipyard Lake sample (grey square) is compositionally different from the samples from the tributaries or the Athabasca River.

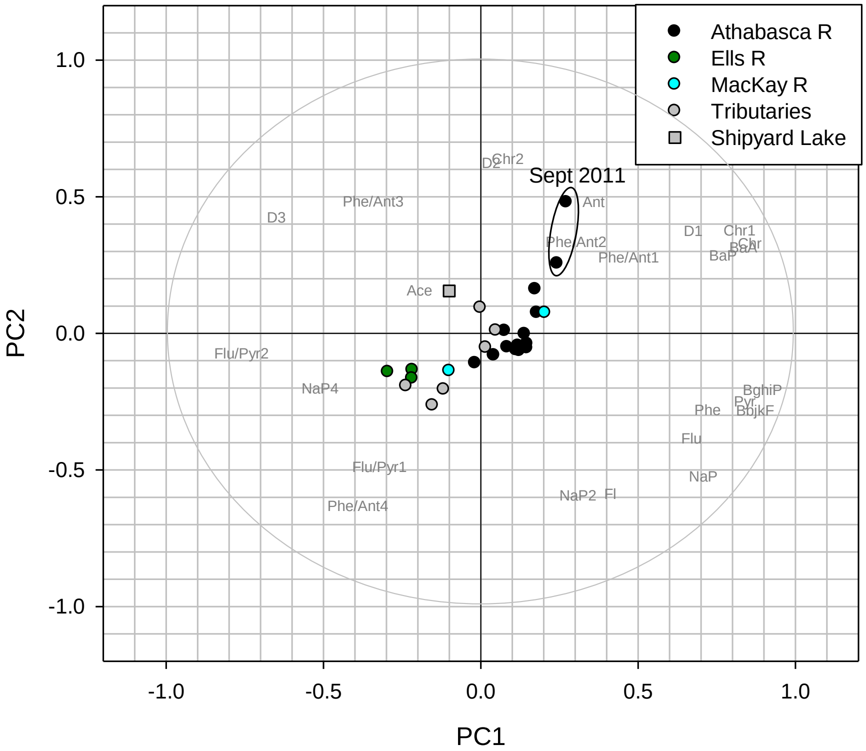

Figure 9. PCA analysis of relative PAH concentrations for stream waters as well as Shipyard Lake.
Grey labels indicate PAH species responsible for separation.

3.2.3 *PAHs in Snow*

The results of the PAH concentrations measured for the 2011 snow campaign are the focus of on-going research being conducted by AESRD (Cho et al. in submission 2013). The PAH data from the 2011 snow survey show a spatial pattern of decreasing PAH concentrations with increasing distance from the geographical center (GC) of oil sands activities (Cho et al. in submission 2013).

The relative concentrations of individual PAHs in the snow dataset also show some spatial trends that can be used to try to identify compositional changes in the assemblages of PAHs present across the AOSR. Even though there are large concentration differences evident in the 2011 snow dataset (Cho et al. in submission 2013), the relative concentrations along some transects show very little alteration (Figure 10). The snow samples from along the main north south transects, and from the WQM sampling locations cluster in the PCA of PAH relative concentrations (Figure 10 top panel). The composition of PAHs present in snow from the other transects show far greater variability (Figure 10 bottom panel).

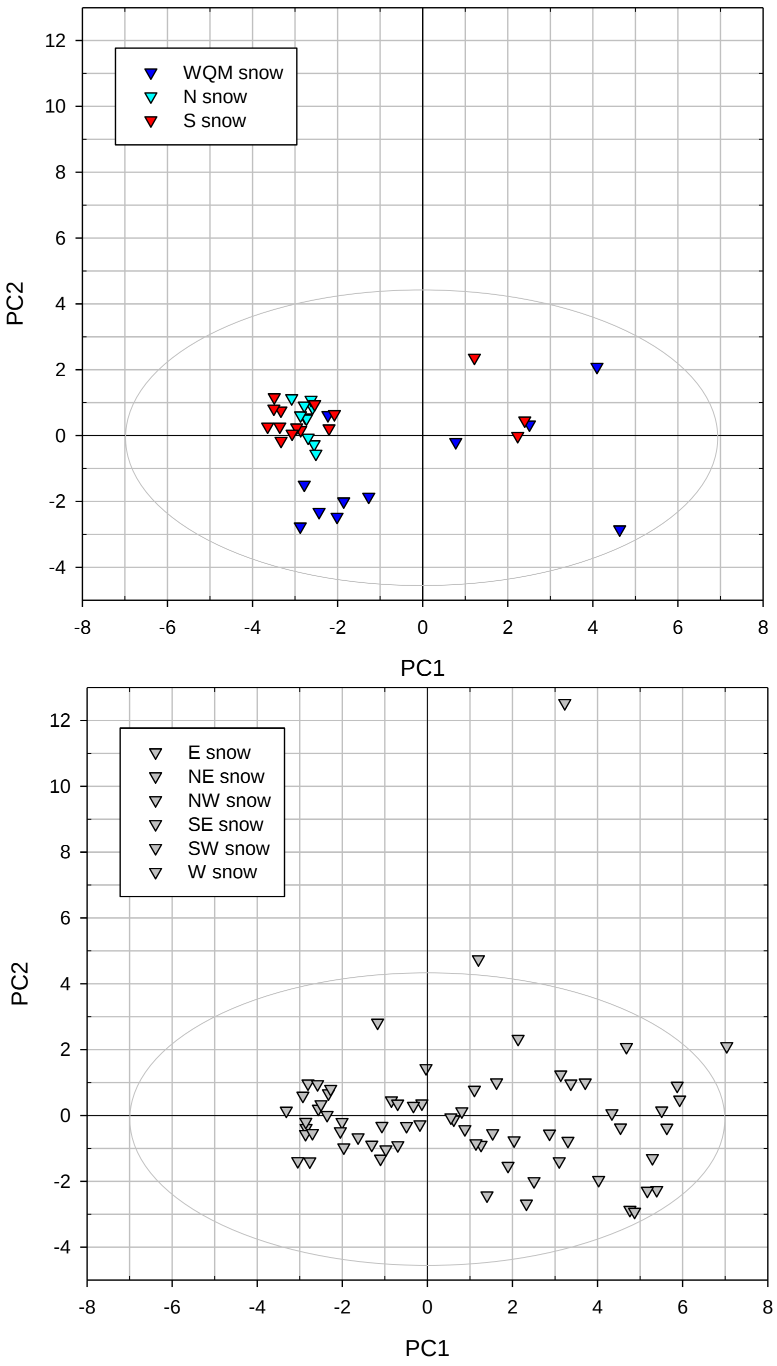

Figure 10. PCA analysis of PAH relative concentrations in snow samples from the 2011 survey. The top panel shows the PCA results for samples from along the south, north, and Water Quality Monitoring (WQM) transects. Bottom panel shows the PCA results from all other transects. Both plots include the results of a single PCA on the same dataset, however samples from specific transects are presented separately to allow spatial variations to be better identified.

Using the relative PAH concentrations in snow sampled at E-S1 (8 km from the GC) and E-S12 (73 km from the GC) as examples, the proportion of Chr1 increases from 8.56% to 24.81% as you move away from GC, while Phe/Ant1 decreases from 6.20% to 0% over the same transect. Moving eastward along the east sampling transect (Figure 1), Chr1 becomes more dominant; while Phe/Ant1 becomes less dominant in snow. The compositional changes could indicate transformations of PAHs or effects of multiple sources. This suggests that PAH compositions given by their relative concentrations are probably more useful than absolute PAH concentration in tracing sources and deposition of PAHs over short distances. However, PAHs transported over long distances may change composition if transformations or additions of organics occur along the transport pathway.

3.2.4 *Differences in PAH Composition in Snow and Surface Waters*

PCA analyses were conducted on the relative PAH concentrations for the 2011 snow and surface water dataset to identify any compositional differences between the PAHs present in these samples (Figure 11). The largest statistical separation along the PC1 axis in Figure 11 is between snow and surface water samples (including tributary and lake water samples). The PAH species that account for the separation between snow and surface water compositions are Flu/Pyr2, NaP4, CHR1, Phe/Ant1, D1 and the parent PAH species (grey text in Figure 11). 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 species have greater relative concentrations in snow samples than in the surface water samples. It is interesting to note that parent and C1-alkylated PAHs have greater relative concentrations in snow samples, whereas some (not all) C2-through C4-alkylated PAHs have greater relative concentrations in river samples. Hall et al. (2012) also suggested a similar pattern in sediments – that C2-C4 alkylated PAHs were more prevalent in flood-prone intervals of their sediment cores; whereas parent naphthalene, C1 naphthalenes and retene and Nap1 are more prevalent for non-flood prone 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 the snow and surface water data (Figure 11), there is further separation along the PC2 axis. The snow samples sampled from the WQM sites plot in a fairly tight cluster, as do the snow samples from the south (with one exception) and north transects, reflecting similar PAH compositions. Despite the strong concentration gradient along the south and north transects, the similarity in PAH composition along these transects (Figure 11) could suggest a common source with limited transformation occurring during transport. The east and west snow sampling transects show far more variability in PAH composition, possibly indicating a variety of sources and/or transformation along the pathway.

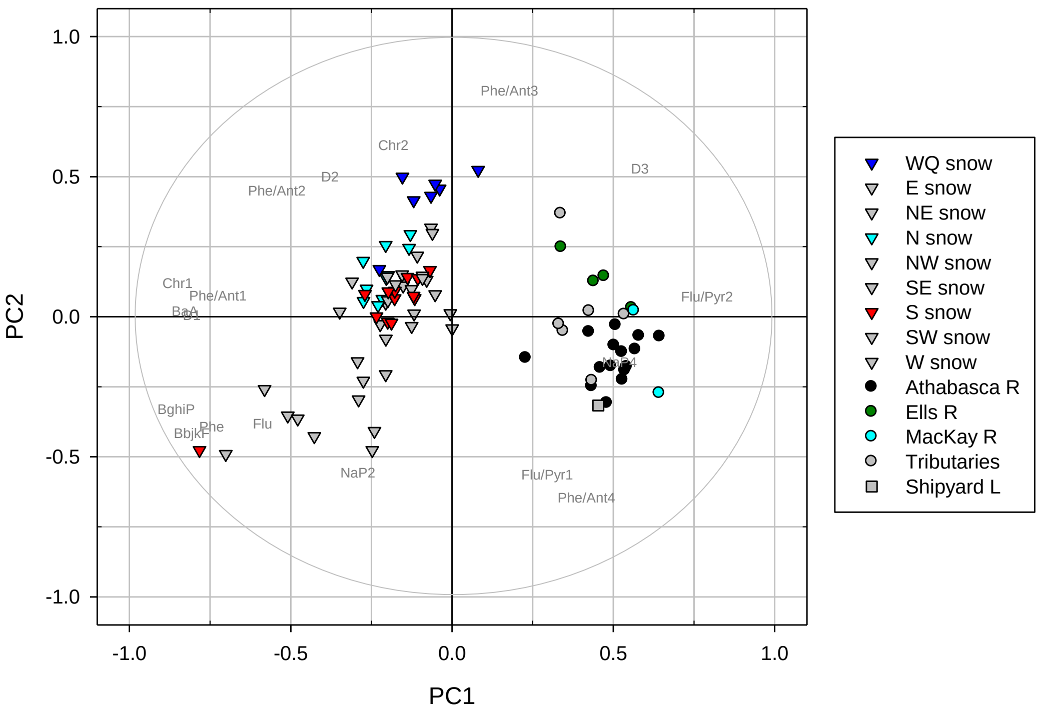

Figure 11. PCA biplots of snow and surface water PAH relative concentrations. Grey lettering indicates the abbreviation of the PAH species responsible for separation.

Variations in the composition of PAHs in surface waters are far less than the snow (Figure 11). The compositional differences between the PAHs in the Athabasca River and tributary samples are still visible (Figure 11), but this contrast is secondary compared to the compositional differences between river and snow samples. Tributaries show a wider range in PAH composition compared to clustering of samples from the main stem of the Athabasca River. The tributary samples are from smaller drainage basins and the composition of PAHs in discharge from those basins will depend on sources of PAHs within that basin, including different anthropogenic and geological sources. Differences in geology and activities within these small tributary basins and seasonal variations in stream flow may result in the large spatial and temporal variability. 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 in surface water PAHs (Figure 11) are mainly due to different relative concentrations of D3, Phe/Ant4 and Flu/Pyr1.

3.3 Limitations of the Dataset

This review of data was intended to integrate current PAH data for snow and surface water in the AOSR as a first step towards better understanding the composition of organics in the region and to identify possible linkages between atmospheric sources of organics and those present in aquatic ecosystems. As discussed in the introduction, the sampling locations and time periods for snow and surface water data did not always coincide but our approach was to try to provide a large enough spatial and temporal overview to identify main similarities and differences. The available data for 2011 included only information about total (dissolved + particulate) PAH compositions in snow and surface waters so this comparison did not distinguish between whether the PAHs were present in the dissolved or particulate phase. Given the affinity of PAHs for sediment, this type of analysis would be improved if data on both phases were available, particularly since the timing of maximum total PAHs in the Athabasca River and tributaries coincides with the spring freshet when catchment runoff and erosion would be greatest. Compositional changes in the dissolved and particulate PAHs would be expected as infiltrating snowmelt or atmospherically deposited organics infiltrate and interact with the soil matrix, and may account for some of the shifts identified between snow and surface water compositions. However the potential for interaction would be least during the rapid melt associated with the spring freshet so comparisons between snowmelt and surface waters immediately after the freshet should be when the potential transfer from snow to surface water would be the most direct.

4 PART 2: ESI-FTICR MS CHARACTERIZATION OF DISSOLVED ORGANICS IN SNOW AND SURFACE WATER IN THE AOSR

The second approach to characterizing the organics present in snow and surface water across the region uses ultra-high resolution profiling of the dissolved organic compounds using Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI-FTICR MS) analyses of snow and surface water samples collected by AESRD during 2012. The types of samples available from 2012 for this analysis are similar to the 2011 snow and surface water PAH dataset, in that we compare the organic composition of snow with surface waters including the Athabasca River, its tributaries and lakes, but the type of organics profiled and the numbers of samples and sampling locations were different. ESI-FTICR MS provides detailed characterization of the dissolved polar compounds and consequently does not profile the dissolved PAHs present in the snow. This analytical technique has not previously been used to profile the organic component of snow and one of the objectives of this pilot-scale investigation was to investigate whether using this new ultra-high resolution mass spectrometry profiling of the dissolved organic compounds in snow and surface water can be used to differentiate sources of organics.

The snow sampling program conducted by AESRD in 2012 did not include the spatial coverage of the 2011 snow program, but it did include snow samples from close to the center of oil sands activities (<5 km) where PAH deposition in snow was fairly high and samples from outside of the atmospheric organic footprint areas. Similar to the approach in Part 1, the composition of organics present in the snow samples was used to characterize the composition of atmospheric deposition. The composition of dissolved organics present in snow was compared with the composition of dissolved organics present in monthly samples from the Athabasca River, its tributaries and lakes in the region.

We assumed that the organics would be deposited across the region (possibly with higher concentrations in the footprint) on top of the snowpack as well as during the rest of the year. During the spring freshet melting of the snowpack would result in the release of the organics present in the snowpack to catchment runoff and possibly infiltration, resulting in increased discharge in the rivers and lakes in the area. Trying to co-locate water sampling locations that exactly corresponded with snow sampling locations or obtaining the samples during the melt was not possible so our approach is instead to try to obtain a large number of spatially distributed surface water samples across the region to characterize the composition of dissolved organics in the surface waters and compare them with the organics present in the snowpack. The surface water sampling locations do not correspond directly with the snow sampling locations, but we do have monthly river samples located upstream and downstream of development as well as along the major tributaries. Our approach was to try to conduct a wide spatial survey that would include enough spatial and temporal sampling to capture the range of organics present in surface waters over the open water season.

4.1 Methods

4.1.1 *Collection of Snow and Surface Water Samples in 2012*

The 2012 samples obtained by AITF from AESRD included 7 snow samples, 73 Athabasca River and tributary samples, and 6 lake samples (Figure 12). These samples were analyzed using ESI-FTICR MS to provide detailed characterization of the dissolved organic components of these waters.

The snow sampling campaign conducted by AESRD in March 2012 focused on method comparisons and as a result it was far less spatially extensive and included fewer samples than the 2011 AESRD snow sampling campaign described in Part 1. Seven snow samples were obtained during the AESRD 2012 snow survey program (Figure 12). The snow sampling methodology used by AESRD was the same as that used for the 2011 snow survey (described in Cho et al. in submission 2013). The seven snow sampling locations included three samples that correspond directly to the sampling locations in the 2011 survey (NW-S8, E-S7, NW-S2) that were located on the transects outside of the main PAH deposition area (61 km, 38 km and 30 km from GC respectively), and four sampling locations along the Athabasca and Steepbank Rivers (KAR-4, KAR-6a, KAR-16 and KST-2) much closer to the centre of oil sands activities (2 km, 4 km, 4 km and 2 km from GC respectively) where higher atmospheric deposition rates are expected.

The river samples were obtained from many of the sample sampling locations described in Part 1, but the 2012 samples also included a few upstream (Atha-3) and downstream (Old Fort AB07DD0010; and Devils Elbow AB07DD0105) samples, that were outside of the geographic range covered by the 2011 monitoring (Figure 12). Monthly river samples were collected between March 2012 and September 2012 from the centre of the river, at approximately 2/3 depth from the water surface.

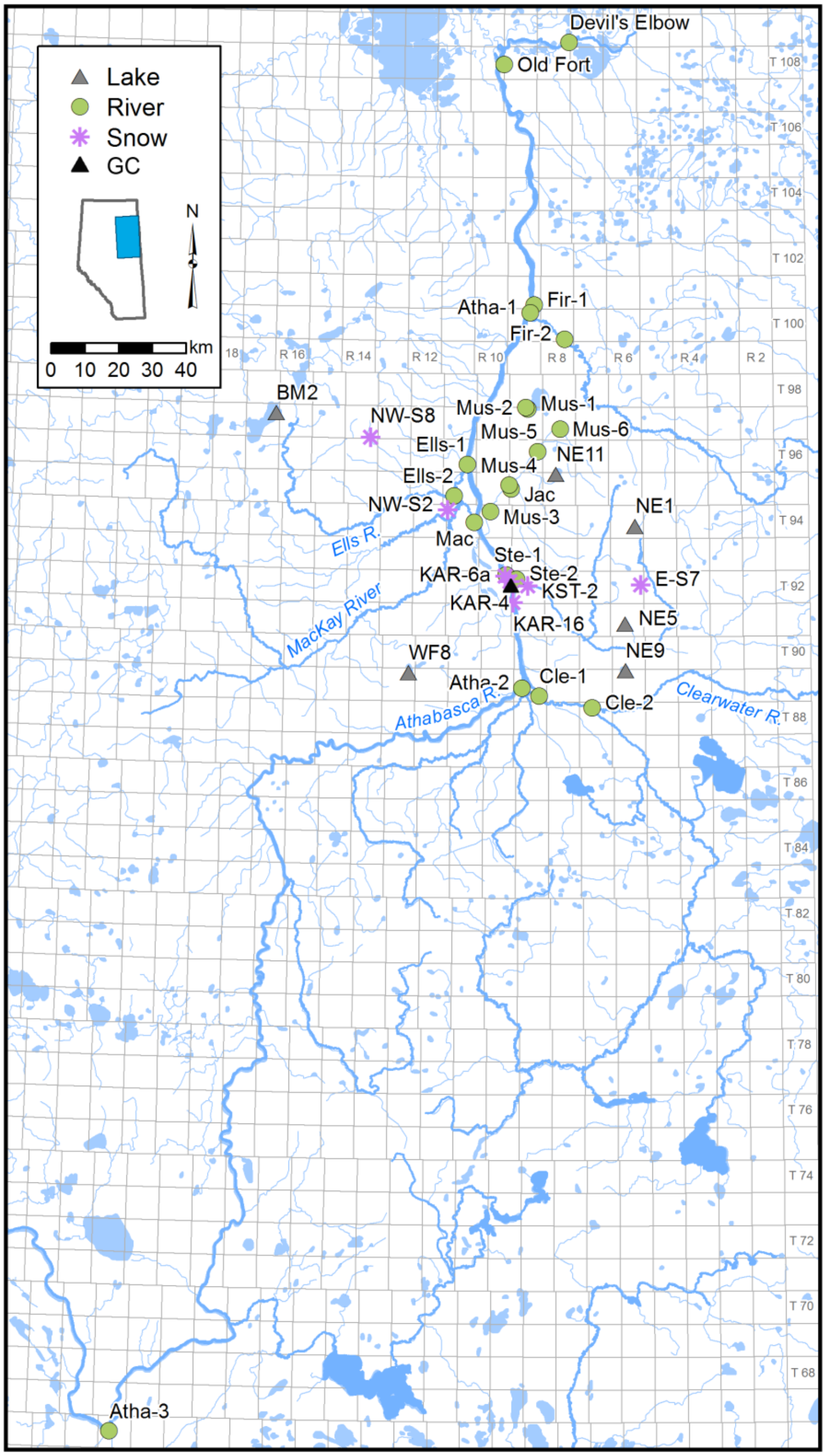

Figure 12. Sampling locations of snow, river and lake samples obtained in 2012 and analysed by ESI-FTICR MS.

Lake samples were collected in August 2012 from 6 lakes. The water sample was taken from about 10 cm below the water surface at the centre of the lake during helicopter surveys.

All samples were sealed in pre-cleaned, 250 ml amber glass bottles, and temporarily stored in coolers with icepacks and transported to AITF where they were refrigerated at 4°C prior to analysis.

4.1.2 *ESI-FTICR MS Analysis*

Samples for organic profiling using ESI-FTICR MS were pretreated with liquid-liquid extraction (LLE), followed by analysis on ultrahigh resolution Fourier Transform Ion Cyclotron Mass Spectrometer (Gibson et al. 2011)[2]. The LLE was performed to separate and enrich organic compounds into various organic extracts. Each extract was then directly infused into a 12-Tesla Apex-Qe hybrid quadrupole FTICR mass spectrometer (Bruker Daltonics, Billerica, USA). The instrument was operated in either (+) or (-) Electrospray Ionization (ESI) mode with a detection range of mass to charge ratio (m/z) 150 to 1,100. Mass spectra were recorded with an accumulation of 200 scans with broadband acquisition and a data acquisition size of 1 megabyte per second. For the ease of reference, we use “Organic Negative” and “Organic Positive” to refer to profiling results obtained in ESI(-) and ESI(+) ion mode, respectively. All of the results presented are for the dissolved organic component.

ESI(-) and ESI(+) modes profile different types of compounds present in a given sample. ESI(-) mode profiling includes dissolved acidic components, where deprotonated acids can be readily ionized and detected. ESI(+) mode is more suitable for the characterization of basic components (Barrow et al. 2010). Because the different ESI modes profile different types of compounds, the results for a single sample will differ, but can be used to provide different perspectives on the overall organic composition present in the water sample.

4.1.3 *Data Processing and Statistical Analysis*

The data acquired from ESI-FTICR MS include intensities for the thousands of compounds (identified by their mass to charge ratio; m/z) detected in each sample in both ESI(+) and ESI(-) ion modes. These large volumes of data need to be processed before the results can be readily presented and discussed. Mass spectra were batch-processed using a custom VBA script, which has been described elsewhere (Han et al. 2008), within the instrument vendor’s data processing software suite, DataAnalysis®. Basically, the raw mass spectra acquired in either the positive or the negative ion mode (ESI(+) or ESI(-)) were internally calibrated with the reference masses of the standard “ESI tuning mix” solution. Monoisotopic peaks corresponding to the isotopic distribution patterns were determined and those with signal-to-noise ratios ≥10 were picked to generate two-dimensional (m/z versus intensity) data matrices. The spectra obtained from the field blanks were also processed, and the peaks detected in the field blanks were subtracted from

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[2] For more info on this analytical method and others see Zhao, B., R. Currie and H. Mian, 2012. Catalogue of Analytical Methods for Naphthenic Acids Related to Oil Sands Operations. OSRIN Report No. TR-21. 65 pp. http://hdl.handle.net/10402/era.26792

the data matrices regardless of peak intensity. The resulting individual mass lists were further processed with another custom software program (LabView®, National Instruments, Austin, TX) for peak alignment, which generates multi-sample datasets combining allowable masses within 2 ppm. The dataset containing the m/z values and the corresponding intensities is reported for data illustration and statistical analyses.

Within the thousands of compounds detected by FTICR MS there are subgroups which are characterized by the same numbers of heteroatoms (nitrogen, oxygen and sulfur) but different numbers of CH_2 groups. These compounds are referred as homologues and can be readily identified as compounds that plot along a horizontal line in Kendrick plots (e.g., Figure 13). The mass distribution of homologues commonly resembles that of all detected compounds and the presence of homologues improves our confidence to infer molecular compositions. For these reasons we will focus our interpretation of the ESI-FTICR MS results on homologues.

The ESI-FTICR MS results for each individual sample can be viewed using Kendrick Mass Deficit (KMD) plots (e.g., Figures 13, 15 and 19). These plots provide a graphical representation of the mass distribution of the large number of compounds detected by ESI-FTICR MS. More importantly, because the mass measurements reported in Système international d'unités (SI) are rescaled to the Kendrick mass scale (Kendrick 1963), this graphical technique allows for easy identification of homologues.

The ESI-FTICR MS results from individual samples can also be compared by grouping the compounds detected into the major groups of dissolved organic compounds based on their heteroatom classes (e.g., Figure 22 and Figure 23). Homologues were categorized into five major heteroatom classes based upon their elemental compositions, including O_n, NO_n, N_2O_n, SO_n, and S_2O_n (where n = 1 to 12 in all cases), consistent with the classification scheme used by Headley et al. (2011). For example, SO_n refers to compounds that contain only one sulphur and multiple (varying from one to twelve) oxygen atoms. Other compound classes are defined analogously. By grouping hundreds of compounds into classes and summarizing total relative contributions for each class, we transform the results of profiling into a matrix tabulation of compounds which allows us to summarize the overall chemical composition of individual samples.

Similar to the relative PAH concentrations used to identify compositional differences in the 2011 PAH data described in Part 1, here we use relative contributions to overall peak intensity to identify compositional differences in the dissolved organic compounds detected by ESI-FTICR MS. For each compound identified, a relative contribution (RC) value was calculated as the intensity of individual peaks divided by the total intensity of all detected peaks. These RC values were used to characterize the composition of the organics, but we should note that the RC values cannot be treated as an accurate measure of absolute concentration. This is because different compounds may have different ionization efficiencies and the relative contribution of one particular compound is affected by its own transformation and that of other species. However, RC values do generally reflect composition changes in a complex mixture of organics (Hughey et al. 2007). Principle component analysis (PCA) was carried out on the RC values to statistically characterize and compare compositional differences between samples (e.g., Figures 14, 16, 18, 20 and 21) in a similar way as for the PAH relative concentration data in Part 1. The sample scores (PC1 vs. PC2) from PCA were employed to illustrate a statistical overview. PCA analyses are performed using SIMCA-P+ (V12.0, Umetrics AB Umeå, Sweden).

4.2 Results and Discussion

4.2.1 *Athabasca River and Tributaries*

The results of the organic profiling of the 2012 surface water samples conducted using FTICR MS in ESI(-) and ESI(+) modes provide information about different components of the dissolved organic composition. The ESI(-) results are better at characterizing the acidic component (e.g., sulfur and oxygen containing dissolved organic compounds), whereas the ESI(+) results are preferred for characterizing basic components including some nitrogen containing compounds (Barrow et al. 2010).

4.2.1.1 ESI(-) Mode Organic Profiling Results

Thousands of organic compounds were detected in river water using ESI-FTICR MS operated in ESI(-) mode (Table 4). Spatial and temporal patterns are evident in the distribution of these compounds. There was a general increase in the variety of dissolved organic constituents detected in river water over the open water season. The total number of detected organic compounds ranged between 2,512 and 3,028 compounds in March 2012 but increased to between 2,746 and 3,479 for September 2012 (Table 4). This general trend of increasing types of dissolved organics from March 2012 to September 2012, included some exceptions, most typically in June and July when the number of peaks was most variable between stations. Approximately 30% of detected organic compounds were identified as homologues. The presence of homologues was closely correlated with the total number of compounds detected. On average, 904 homologues are detected in the Athabasca River and tributary samples, varying within the range of 713 to 1,017.

Table 4. Summary of number of detected compounds and homologues using FTICR MS in ESI(-) mode in river samples.

	ESI(-) Results	**Mar 2012**		**Jun 2012**		**Jul 2012**		**Aug 2012**		**Sep 2012**	
Site Code	Site Description	All Peaks	Homo	All Peaks	Homo	All peaks	Homo	All Peaks	Homo	All Peaks	Homo
Fir-1	Firebag river near mouth			2,864	889	2,949	829	3187	987	3,358	952
Mus-1	Muskeg creek at confluence	3,026	840	3,342	976	3,197	877			3,479	948
Mus-2	Muskeg River above Muskeg Creek	2,660	789	3,103	873	2,703	777	3,503	1007	3,350	947
Atha-1	Athabasca River u/s Firebag			2,831	927	2,725	801	3,056	949	3,302	992
Mus-3	Muskeg River at Gauge	2,933	818	3,358	959	3,302	862	3,420	969		
Jac	Jackpine Creek above Muskeg River	2,780	785	3,334	963	3,345	856			3,426	936
Mus-4	Muskeg River u/s Jackpine Creek	3,028	855	3,441	1,015	3,275	870			3,463	931
Mus-5	Muskeg River u/s Stanley Creek	2,771	821	3,505	987	3,351	879			3,412	957
Mus-6	Muskeg River 11km u/s Stanley Creek	2,713	784	3,353	1,003	3,277	864			3,437	976
Atha-2	Athabasca River u/s Fort McMurray			2,728	910	2,782	815	2,872	934	2,864	929
Atha-3	Athabasca River at Athabasca			2,921	952	2,168	713	2,790	917	2,569	886
Mac	MacKay River at HWY 63			3,399	1,009	3,287	848	3,412	938	3,387	959
Ells-1	Ells River at Mouth			3,115	962	3,007	841	3,189	953	3,036	954
Ste-1	Steepbank River at Mouth			3,327	1,017	3,344	868	3,500	979	3,285	941
Mus-7	(Muskeg River) at Jackpine Creek			3,394	993	3,225	860			3,218	908
Mus-8	Muskeg River			3,339	991	3,281	896			3,223	934
Cle-1	Clearwater River			3,181	980	3,039	858	3,203	965	3,203	965

	ESI(-) Results	**Mar 2012**		**Jun 2012**		**Jul 2012**		**Aug 2012**		**Sep 2012**	
Site Code	Site Description	All Peaks	Homo	All Peaks	Homo	All peaks	Homo	All Peaks	Homo	All Peaks	Homo
Fir-2	Firebag River near Winter Road	2,393	762								
Ste-2	Steepbank River @ 5 km u/s confluence Atha River	2,763	797								
Cle-2	Clear River d/s 2 km d/s Christina	2,512	806								
Ells-2	Ells River @ Fort McKay Pumphouse	2,883	820								
Dev	Athabasca River at Devil's Elbow					2,969	865				
Old Fort	Athabasca River at Old Fort									2,746	852

Comparing Kendrick plots (Figure 13) from a tributary sample (e.g., Muskeg River; Fig. 13 a) and an upstream Athabasca River sample (Athabasca River at Athabasca; Fig. 13 b) highlights some of the similarities and differences in the homologue compositions in these two samples. Both samples have a similar distribution of mass ranges (x-axes) ranging between 200 and 600 Da (Figure 13), and both samples are also generally characterized by positive mass defect (i.e., KMD values, y-axes). Although both samples have bullseye patterns in the mass distribution (Figure 13), there are subtle differences. The most abundant species in the upstream Athabasca River sample (indicated by dark red shading) are limited to compounds of mass <400 Da (x-axis) and KMD < 300 (y-axis), while the bullseye appears to be broader in the tributary sample, including compounds of mass >400 Da and KMD > 300. The broad and extensive bullseye pattern in the tributaries is also consistent with the observation that more homologues tend to be detected in tributaries (Table 4). The Kendrick plots provide a visual method for comparing the composition of hundreds of compounds present in individual samples, however they are not as useful for identifying similarities and differences among multiple samples.

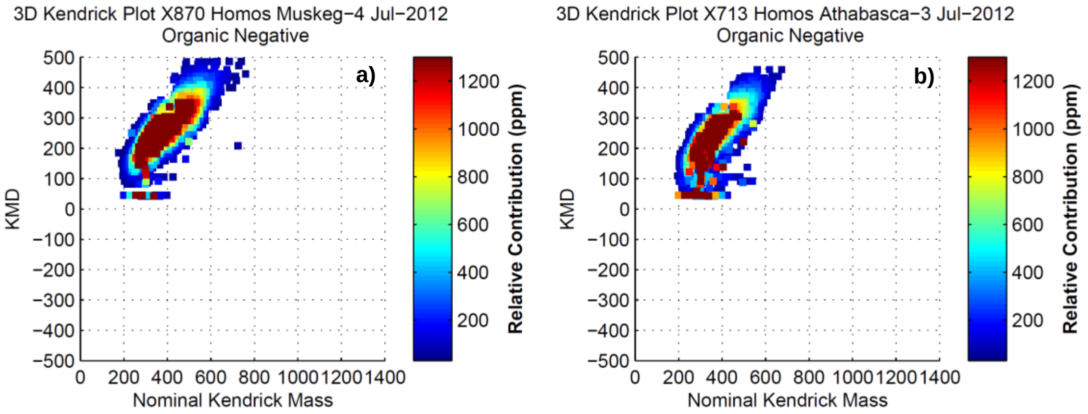

Figure 13. Kendrick plots of homologues found in (a) Muskeg River u/s Jackpine Creek (Mus-4) (a) and (b) Athabasca River at Athabasca (Atha-3) in ESI(-) mode. Both samples were collected in July 2012.

To compare the results of the ESI-FTICR MS analyses between multiple samples we use PCA analyses. The PCA analyses of the ESI(-) results for the 2012 surface water samples for ESI(-) mode are presented in Figure 14. The plots included in Figure 14 are based on the same PCA, but are plotted for individual months so that temporal variations can be more clearly identified. The most obvious temporal variation in the ESI(-) data is for the tributary samples from March 2012. This indicates that the homologue composition in the dissolved organics present in this month was significantly different from those sampled in August and September 2012, particularly along the PC2. We should note that only tributary samples were available for March, so we are unable to see if the Athabasca River composition changed as well.

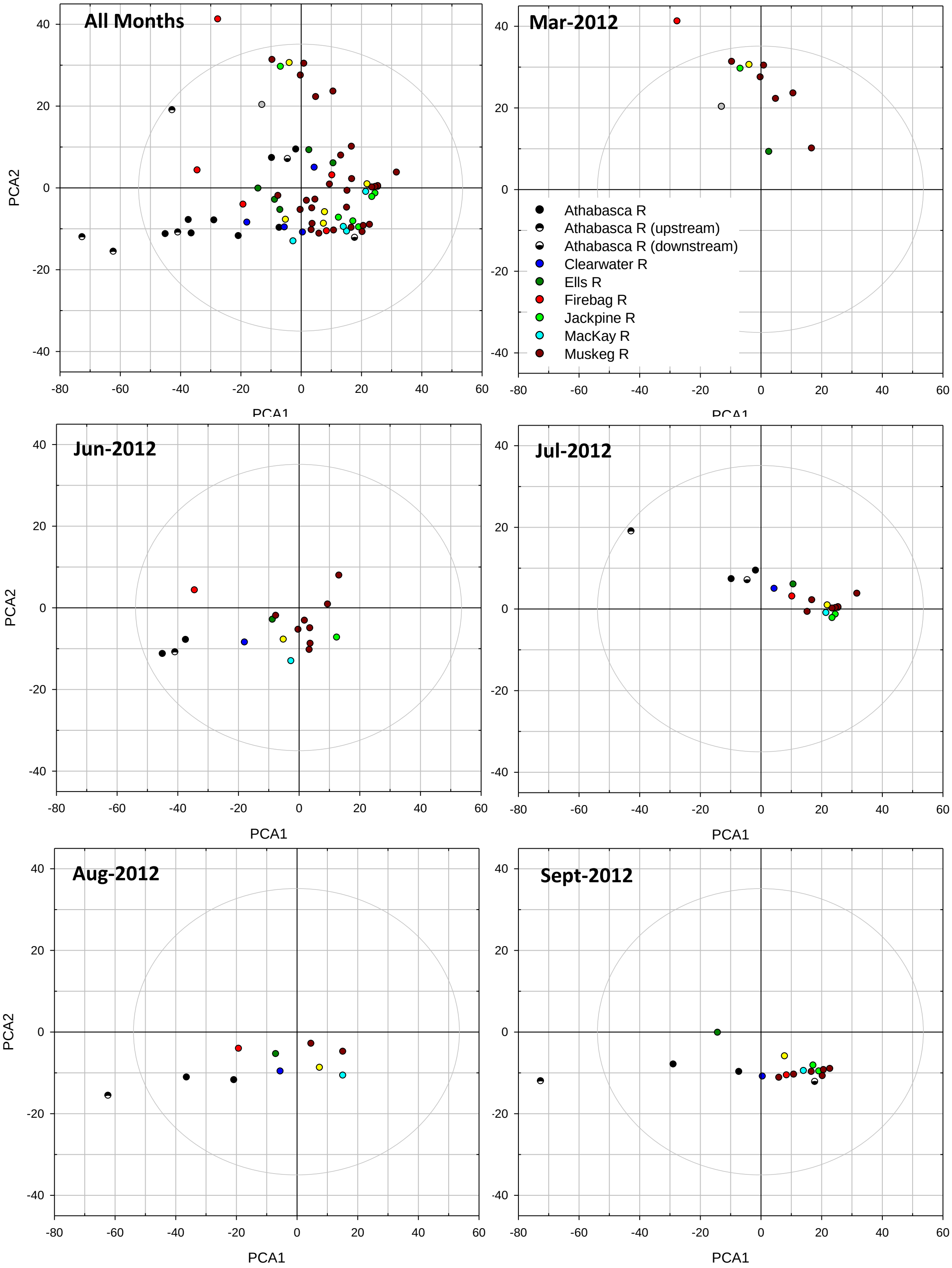

Figure 14. PCA analysis of homologue composition in river waters under ESI(-)mode. The first axis (PC1) explains 37.1% of variability, while the second axis (PC2) explains 13.4% of variability.
All of the plots include the PCA results of the same dataset, however samples from specific months are presented separately to allow temporal variations to be better identified.

The homologue distribution for July 2012 is also distinct from other months, with significant variations in PC2 (Figure 14). Even though there are small temporal variations in the homologue composition, the PCA shows that these temporal variations are not as large as the spatial variations between Athabasca River samples and its tributaries. The Athabasca River samples deviate from the tributaries along the PC1. There are also variations along the Athabasca River, with the most upstream site (i.e., Athabasca at Athabasca) being the most distinct, followed by samples from Fort McMurray and Firebag confluence. The ESI(-) results suggest a compositional shift in the dissolved organics present in the Athabasca River samples in July 2012, particularly for the upstream Athabasca location (Figure 14). Similar to the results of the PCA analysis of the 2011 PAH composition (Figure 9), the PCA results for the ESI(-) mode of the organic profiling also indicate distinct assemblages of dissolved organics present in the Athabasca River and the tributaries. Temporal variations, superimposed on top of this basic spatial pattern, contribute to a dynamic and complex overall system.

4.2.1.2 ESI(+)Mode Organic Profiling Results

The results of the ESI(+) mode profiling provide information about the basic dissolved organic compounds, including some nitrogen containing compounds. The total number of compounds detected in Athabasca River and tributary samples is found to vary between 1,596 and 1,942 in March 2012. For September 2012, the number of detected compounds increased to between 2,522 and 2,654 (Table 5). The temporal trend of increased dissolved organic substances in the river water appears to be consistent in both negative (Table 4) and positive (Table 5) profiling modes. June and July 2012 also had high variability in number of compounds detected, which may be related to higher streamflow during this period resulting in a more variable hydrological regime. Approximately18% of detected compounds were homologues, with an average of 413 homologues detected in rivers (including main channels and tributaries, min = 223, max = 555). Fewer compounds and fewer homologues are detected in the positive mode (Table 5) than in the negative mode (Table 4).

Unlike the spatial patterns identifiable in the ESI(-) results, temporal changes appear to dominate the profiling results in the positive mode. Comparing Kendrick plots from a single Athabasca River sampling location (Athabasca River at Athabasca) at two different months (July and September, Figure 15) shows the large temporal composition changes identified in the ESI(+) results for Athabasca River samples. This sampling location is upstream of oil sands development and the two samples were collected in different seasons (July and September 2012). Because the Kendrick plots for the ESI(+) results are not as structured as those for the ESI(-) results (Figure13), visual identification of differences is more difficult. There are no clear bullseye patterns, and the high abundance species (indicated by the dark red shading) are more sporadic. From July to September 2012, the number of homologues detected in ESI(+) mode increased significantly. The compounds that were identified in the September 2012 sample included compounds with Da>600 (x-axis) and KMD > 200 (y-axis) that were not present in the July 2012 sample.

Table 5. Summary of number of detected compounds and homologues (Homo) using ESI-FTICR MS under ESI(+) mode in river samples.

	ESI(+) Results	**Mar 2012**		**Jun 2012**		**Jul 2012**		**Aug 2012**		**Sep 2012**	
Site Code	**Site Description**	All Peaks	Homo	All Peaks	Homo	All peaks	Homo	All Peaks	Homo	All Peaks	Homo
Fir-1	Firebag River near mouth			2,181	437	1,812	257	2,615	549	2,574	504
Mus-1	Muskeg Creek at confluence	1,880	261	2,499	499	1,816	259			2,593	547
Mus-2	Muskeg River above Muskeg Creek	1,755	223	2,377	481	1,797	269	2,533	542	2,641	554
Atha-1	Athabasca River u/s Firebag			2,350	471	1,764	267	2,541	549	2,587	498
Mus-3	Muskeg River at Gauge	1,855	239	2,374	457	1,808	279	2,575	534		
Jac	Jackpine Creek above Muskeg River	1,872	255	2,168	422	1,996	281			2,654	555
Mus-4	Muskeg River u/s Jackpine Creek	1,744	262	2,361	469	1,894	279			2,575	512
Mus-5	Muskeg River u/s Stanley Creek	1,942	295	2,222	445	1,923	275			2,586	533
Mus-6	Muskeg River 11 km u/s Stanley Creek	1,762	253	2,480	519	1,891	282			2,616	533
Atha-2	Athabasca river u/s Fort McMurray			2,486	521	1,773	254	2,374	495	2,546	522
Atha-3	Athabasca River at Athabasca			2,397	496	1,601	236	2,517	515	2,522	522
Mac	MacKay River at HWY 63			2,542	523	1,924	267	2,498	488	2,522	507
Ells-1	Ells River at Mouth			2,594	496	2,021	296	2,678	538	2,596	523
Ste-1	Steepbank River at mouth			2,622	525	1,968	277	2,544	509	2,650	514
Mus-7	(Muskeg River) at Jackpine Creek			2,569	522	1,882	268			2,649	532
Mus-8	Muskeg River			2,526	535	1,874	269			2,549	484
Cle-1	Clearwater River			2,550	552	1,915	261	2,579	543	2,579	543
Fir-2	Firebag River near Winter Road	1,734	260								
Ste-2	Steepbank River @ 5km u/s confluence Atha River	1,596	234								
Cle-2	Clear River d/s 2 km d/s Christina River	1,796	274								
Ells-2	Ells River @ Fort McKay Pumphouse	1,700	249								
Dev	Athabasca River at Devil's Elbow					1,812	262				
Old Fort	Athabasca River at Old Fort									2,423	491

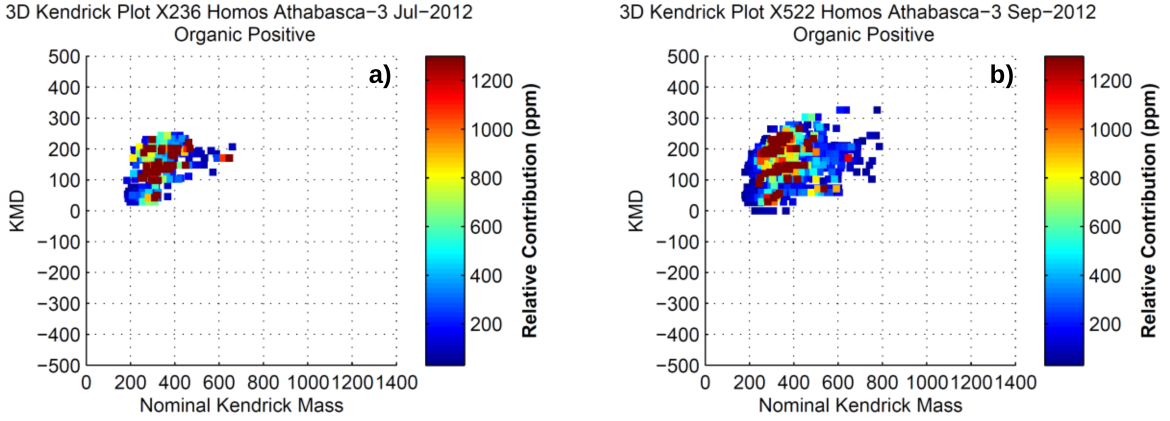

Figure 15. Kendrick plots of homologues found in the upstream Athabasca River sampling location (Atha-3) in ESI(+) mode in (a) July 2012 and (b) September 2012.

The results of the PCA analysis also clearly show temporal groupings in the surface water samples in ESI(+) mode. The river water samples plot in two distinct groups: the river samples collected in March and July 2012 plot in one group, whereas June, August and September 2012 samples plot in another group (Figure 16). While the strong temporal difference between early season (March) and late season (August and September) is reasonable, it is puzzling that similar differences were observed between June and July. Further work is required to understand the strong temporal pattern observed in positive mode profiling.

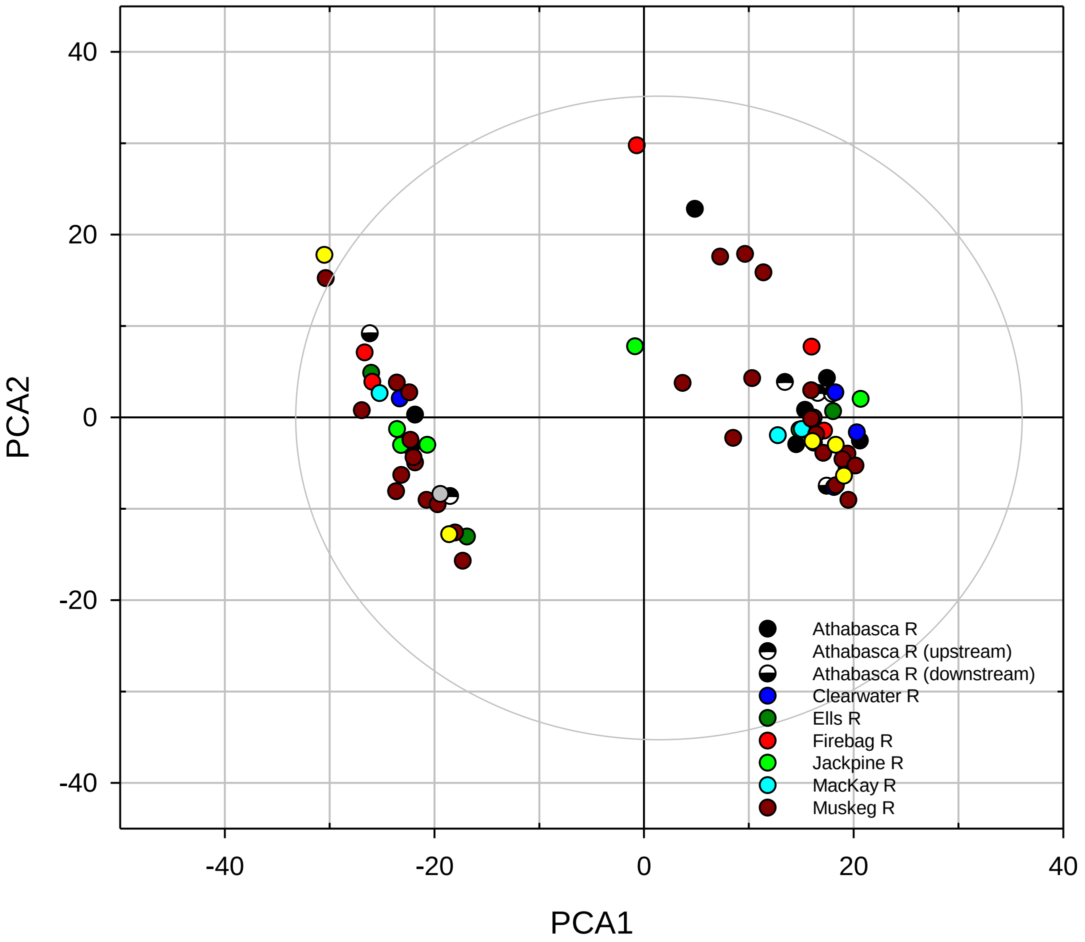

Figure 16. PCA analysis of homologues composition in river waters under ESI(+) mode. The first axis (PC1) explains 49.4% of variability, while the second axis (PC2) explains 9.3% of variability.

4.2.2 *Snow and Lake Samples*

Organic profiling using ESI-FTICR MS was also performed on 6 RAMP lakes (sampled in August 2012) and 7 snow samples (sampled in February 2012). Table 6 summarizes all peaks and homologues detected in both ESI(+) and ESI(-) modes. In ESI(-) mode, there was an average of 3,009 compounds detected in lake water, which was significantly more than the average number of compounds (1,956) detected in the snow samples. Accordingly, slightly more homologues were identified in lake water (828 on average) than in snow (710 compounds) and homologues comprised ~30% of the detected compounds. Approximately 1,900 compounds were detected in positive mode for lake water, which is less than the average of 2,353 compounds detected in snow samples. More homologues are also reported for snow samples (465) than for lake water (295 on average). In the positive mode, ~18% of detected compounds are homologues. The number of peaks detected in the lake samples ESI(-) mode are within the range found for river samples, but the number of peaks detected for lakes in ESI(+) mode is less than the range found for river samples. Despite these slight differences the percentage of homologues in lake and snow samples (in both negative and positive modes) is comparable to the percentage of homologues in river water.

Table 6. Summary of number of detected compounds and homologues under both positive and negative modes in lake and snow samples.

Sample ID	Type	Sample Date	Negative Mode		Positive Mode	
			All Peaks	Homo	All Peaks	Homo
NE1	Lake	Aug-26-2012	3,206	818	1,947	281
NE5	Lake	Aug-26-2012	3,286	884	1,958	283
NE9	Lake	Aug-26-2012	2,880	806	1,859	273
NE11	Lake	Aug-26-2012	3,131	851	2,051	334
BM2	Lake	Aug-30-2012	2,652	789	1,808	314
WF8	Lake	Aug-29-2012	2,897	819	1,779	283
NW-S8	Snow	Mar-1-2012	1,594	627	2,462	498
NW-S2	Snow	Mar-1-2012	1,941	717	2,367	462
Kar-6a	Snow	Mar-1-2012	2,074	734	2,575	552
KST-2	Snow	Mar-1-2012	2,318	816	2,174	413
Kar-4	Snow	Mar-1-2012	2,016	714	2,428	453
Kar-16	Snow	Mar-1-2012	2,074	737	2,259	457
E-S7	Snow	Mar-1-2012	1,678	625	2,205	421

4.2.2.1 ESI(-) Organic Profiling Results

The compounds detected in ESI(-) mode in lake water samples are different from those detected in snow (Figures 17 and 18). Comparing Kendrick plots for a lake water sample (NE1) (Figure 17a) and a snow sample (E-S7) (Figure 17b) located only 12 km apart show significant differences in the composition of dissolved organics. The lake water is characterized by compounds with KMD values >100, including quite a few with KMD > 300 (y-axis). The molecular mass of the high abundance species (indicated by the dark red color) ranged from 200 to 600 Da (x-axis), with a substantial number of compounds showing greater than 200 KMD (Figure 17). In comparison, a majority of high abundance species in snow were within the narrower mass range of 200 to 400 Da (x-axis). The high abundance snow KMD values are usually <200, suggesting less hydrogen content in the molecular structure (Figure 17).

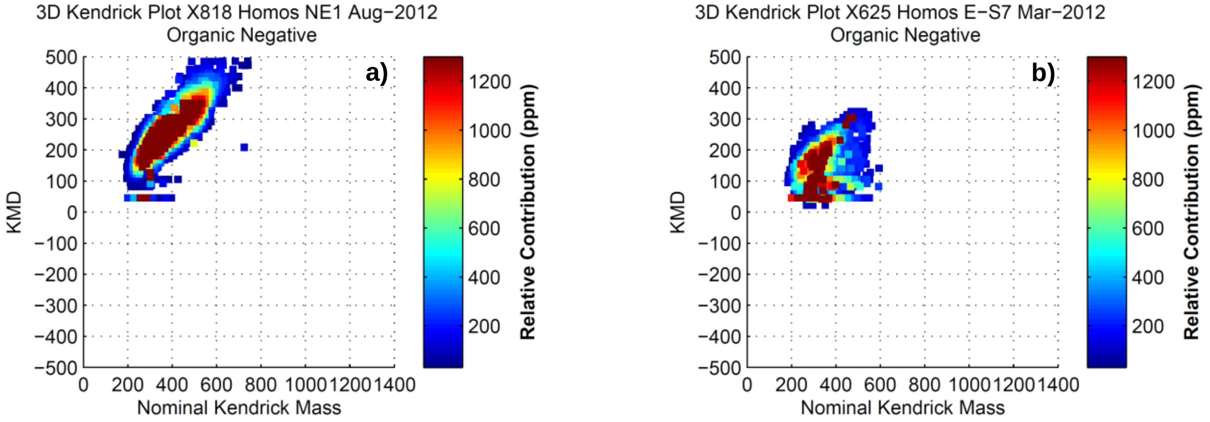

Figure 17. Kendrick plots of homologues found in (a) NE1 (Lake) and (b) E-S7 (Snow) under negative mode.

The PCA analysis of the ESI(-) results also suggests strong differences between the dissolved sulfur and oxygen containing organic compounds in snow and lake water samples (Figure 18). The snow samples (triangles) and the lake water (squares) can be readily differentiated along the PC1, which accounts for a majority (66.7%) of total variability. There is little variation between the homologues present in lakes, but the 7 snow samples are grouped in two clusters along the PC2 (Figure 18).

The two clusters of snow samples consist of one group (NW-S8, E-S7 and NW-S2) that were sampled from far-field locations outside of the high PAH deposition area (Cho et al. in submission 2013), while the other group of snow samples (KAR-6a, KAR-16, KAR-4 and KST-2) are mainly samples collected from snow along the Athabasca River bank near the GC in the 2011 north-south transect and within the high PAH deposition area. Even though there were only 7 snow samples available for organic profiling using ESI-FTICR MS, the geographical clustering of the samples from within the high PAH deposition areas (KAR-6a, KAR-16, KAR-4 and KST-2) and the far-field samples (NW-S8, E-S7 and NW-S2) suggests that the dissolved organic compounds present in snow within the immediate vicinity of major oil sand activities are distinct from the dissolved organics present in far-field snow depositions. Similar to the compositional differences in PAHs present near the GC and in far-field sites (Figure 10), the ESI-FTICR MS results of the 7 samples also indicate geographical clustering in the composition of dissolved organics. This suggests organic profiling may provide improved characterization of the dissolved organics present in atmospheric deposition that may be used to better understand and identify the origin of organics.

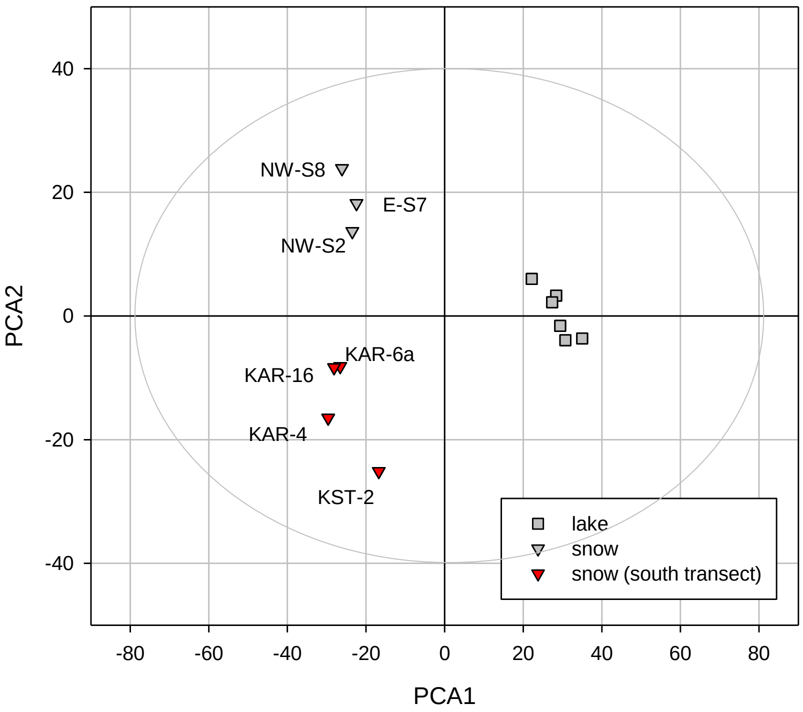

Figure 18. PCA analysis of homologues composition in lake and snow under ESI(-) mode. The first axis (PC1) explains 66.7% variability, while the second axis (PC2) explains 15.6% of variability.

4.2.2.2 ESI(+) Mode Organic Profiling Results

Similar to the ESI(-) mode results, the homologue compositions detected in ESI(+) mode show noticeable differences between lake water and snow. The Kendrick plots for NE1 (Lake) and E-S7 (Snow) (Figure 19) show that more homologues were identified in the snow than in the lake water and that the snow had on average a higher mass range. The homologues in snow extend well beyond the mass range of 600 Da, while the majority of compounds in lake water are limited to masses < 400 Da (Figure 19). The most abundant species in lake water (indicated by dark red color in Figure 19) had KMD values <200, whereas in snow the most abundant species had KMD values > 200. Although the profiling results from ESI(+) mode (Figure 19) are less structured compared to results from ESI(-) mode (Figure 17), there were still clear differences between the dissolved organics in snow and lake waters.

The PCA analysis of the ESI(+) results also indicates clear differences in the dissolved organic compounds present in lake water and snow (Figure 20). Similar to the PCA of the results from the ESI(-) mode (Figure 18), the lake water samples are compositionally different from snow, however the ESI(+) results do not show the same geographical clustering for snow samples detected in ESI(-) mode (Figure 20).

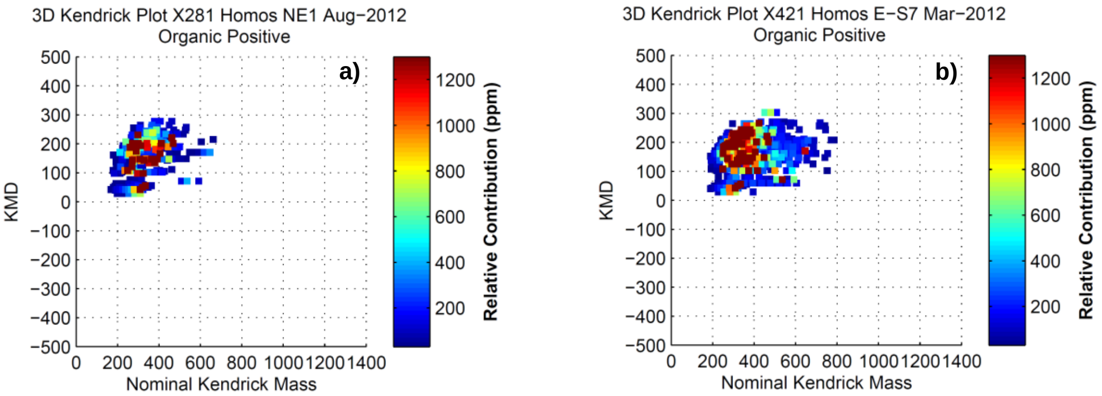

Figure 19. Kendrick plots of homologues found in (a) NE1 (Lake) and (b) E-S7 (Snow) in ESI(+) mode.

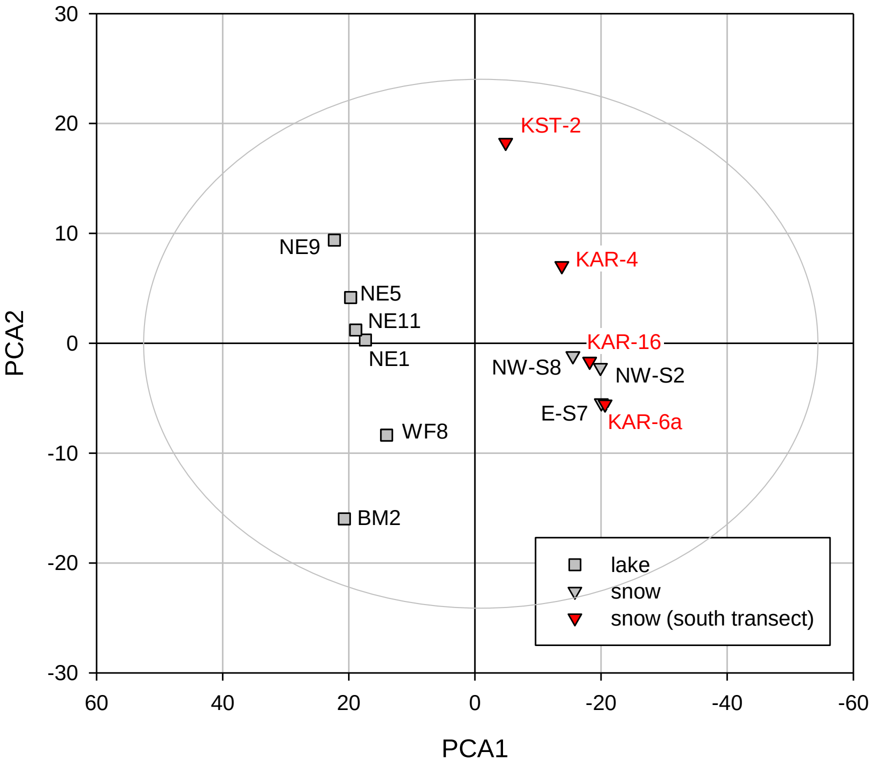

Figure 20. PCA analysis of homologues composition in lake and snow under positive mode. The first axis (PC1) explains 51.7% of variability, while the second axis (PC2) explains 10.6% of variability.

4.2.3 *Comparison of Organic Profiles of Surface Water and Snow*

Using PCA to compare the organic profiles obtained via ESI-FTICR MS for all of the snow and surface water samples available for 2012 illustrates differences in the dissolved organic components of these different types of water in the AOSR. We will limit our comparison to the results from ESI(-) mode, as ESI(+) results have more puzzling temporal variations. The ESI(-) results show the differences in the acidic oxygen containing dissolved organic compounds (e.g., sulfur and oxygen containing dissolved organic compounds) present in snow (triangles) and the surface water samples (circles and squares) (Figure 21).

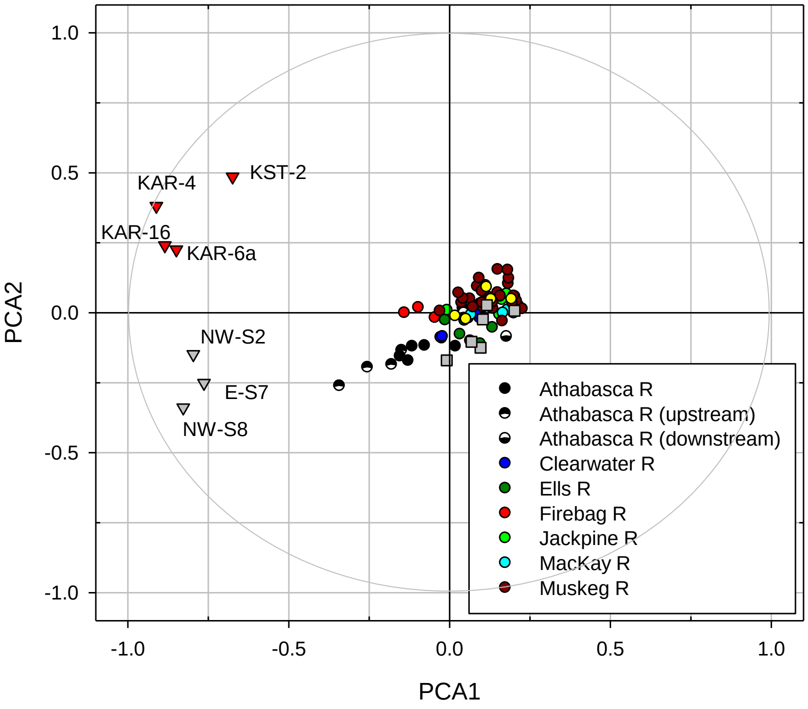

Figure 21. PCA of the ESI(-) results for snow and surface waters (including Athabasca River, tributary and lake samples).
Snow samples are labelled with downward triangles and colour coded to correspond with the 2011 transect locations and lakes are indicated with grey squares.
PC1 explains 52.1% of total variability of the dataset while PC2 explains 10.6% of the variability.

The most prominent grouping that emerges from the PCA results is the separation between surface water samples and snow (Figure 21). Lake waters (grey squares), are compositionally similar to tributary samples (coloured circles). The difference between the organic profile of the dissolved organics present in snow samples and the surface water samples suggests that the majority of dissolved organics present in surface water samples have different compositions, which may indicate different sources than the snow samples. Furthermore, the differences in dissolved organics present in snow and surface water suggest that it may be possible to use these profiles to distinguish atmospherically derived organics from those transported by streams and rivers. However, this PCA analysis only provides a statistical overview of the groupings present among the 1,259 homologues detected in negative mode. It is not yet clear which of these compounds could be the key indicator(s) of different sources of organics.

There are distinct spatial variations in the dissolved organic profiles present in Athabasca River samples (Figure 21). The Athabasca River samples are distinct from the tributary samples, and show compositional changes as you move from sites upstream of Fort McMurray (bottom-filled circles) through the development area (black circles) to more distal downstream sites (top-filled circles) (Figure 21). Temporal variations (not shown) are not as great as these spatial variations. The profiles of the dissolved organics present in the upstream site (i.e., Athabasca River at Athabasca) are different from the organics present in tributaries. As you move downstream along the Athabasca River (Athabasca River at Fort McMurray and at Firebag River) the dissolved organics present in the Athabasca River become more similar to those found in tributary samples. This is consistent with local runoff from tributaries contributing organics to the Athabasca River as it flows downstream across the region. The dissolved organics present in the upstream Athabasca samples are more similar to the organics present in the far-field snow samples (Figure 21). There are only a few tributary samples from the Firebag River (red circles) that show compositional similarities to snow found near the GC (red triangles). This contrast between the dissolved organics present in the Athabasca River and those present in the tributaries is consistent both for organic profiling using ESI-FTICR MS (Figure 21) and for PAH composition analyses (Figure 11). We hypothesize that organic profiles at the upstream site are likely linked more closely to snow and other sources at a regional scale, while signatures at downstream site (i.e., Athabasca River at Fort McMurray and Firebag confluences) are more likely to reflect inputs from tributaries and local sources of dissolved organics from subcropping bedrock.

4.2.4 *Differences in Chemical Compositions from ESI(-) Organic Profiling*

The results of the ESI(-) profiling were also used to identify the relative contribution of different categories of organics present in each sample to provide a way of summarizing the major compositional differences. For each sample the homologues were categorized based on their elemental composition and categorized using the classification scheme used by Headley et al. (2011) (Figure 22 and Figure 23). For example, SO_n refers to compounds that contain only one sulphur and multiple (varying from one to twelve) oxygen atoms. Other compound classes are defined analogously. By grouping hundreds of compounds into classes and summarizing total relative contributions for each class, we transform the results into a simpler summary of the chemical composition of individual samples. The PCA analysis (Figure 21) was used to select pairs of samples with large differences in the dissolved organics to highlight the compositional differences in the dissolved polar organics present in a tributary sample (Figure 22 a) and an upstream Athabasca River sample (Figure 22 b) as well as between a tributary sample (Figure 23a) and a far-field snow sample (Figure 23).

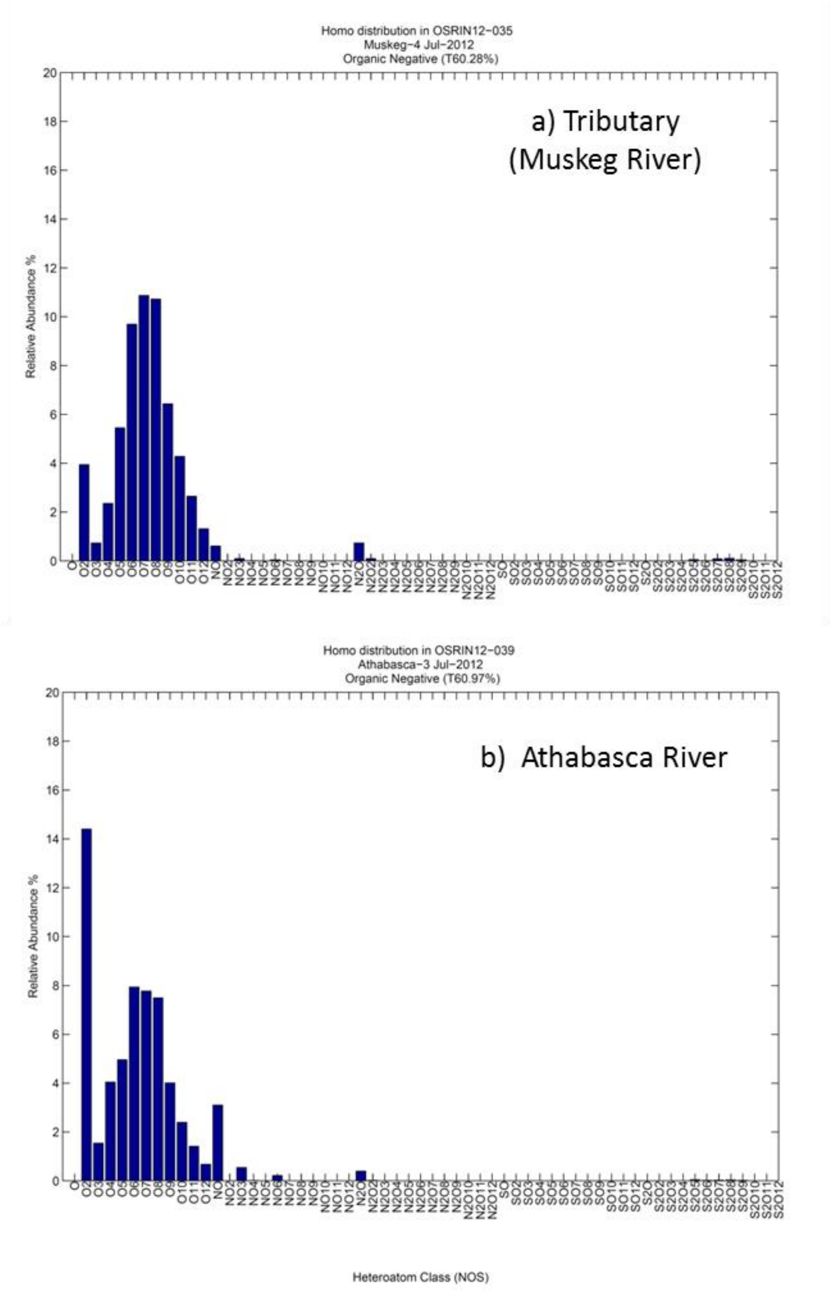

Figure 22. Differences between a) tributary (Muskeg-4) and b) Athabasca River main channel (Athabasca-3, Athabasca River at Athabasca, upstream) for samples obtained in July 2012.

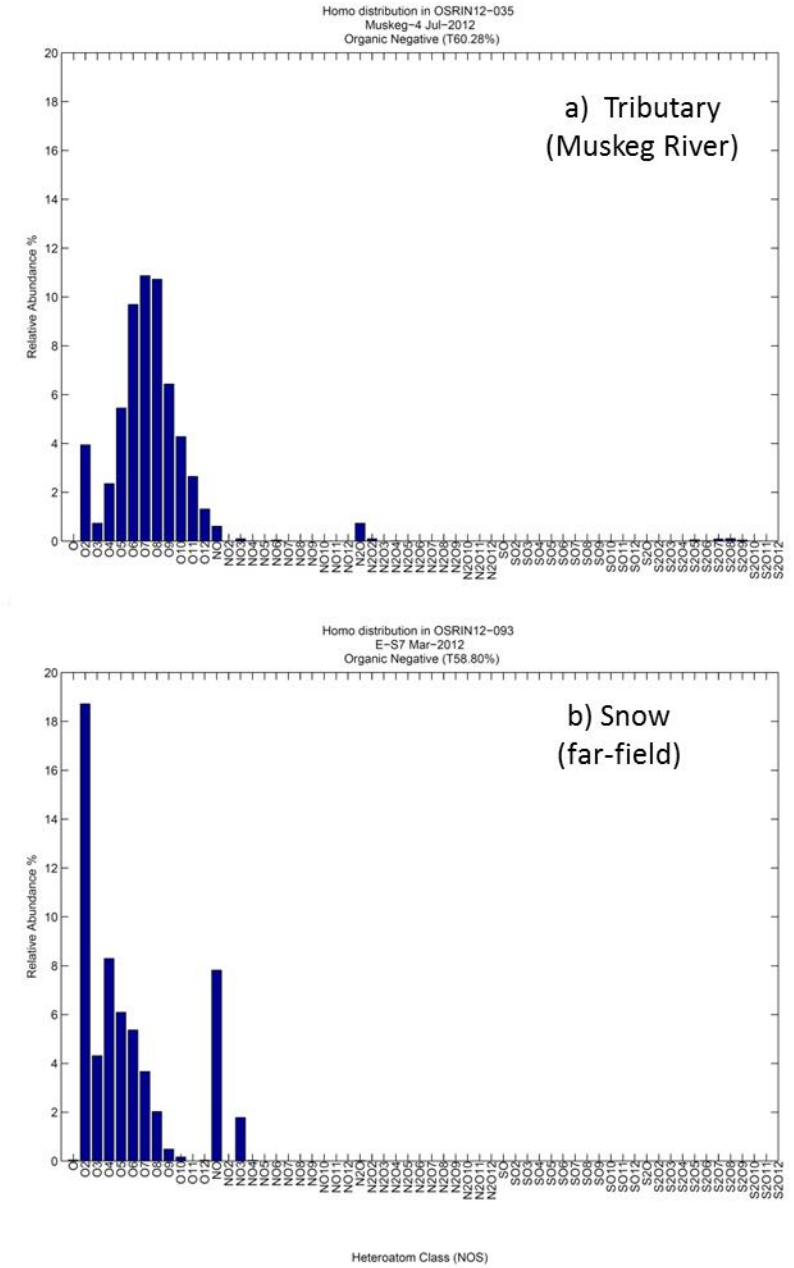

Figure 23. Differences between a) a tributary sample (Muskeg-4) and b) a far-field snow sample (E-S7).

The PCA of the ESI(-) results (Figure 21) identified large compositional differences between the dissolved organics present in the upstream Athabasca River (Atha-3) sample compared with those identified in one of the tributary samples from the Muskeg River at Jackpine Creek. Comparison of the composition of these two samples (Figure 22) shows that the upstream Athabasca River sample is dominated by oxygen-containing classes (O_n) with minor or absent nitrogen-containing classes (NO_n and N_2O_n) and sulphur-containing classes (SO_n and S_2O_n) and the separation between these samples in Figure 21 is likely the result of differences in the On class of compounds. The major difference between the upstream Athabasca River sample and this tributary example is in the greater relative abundance of O_2 compounds in the upstream Athabasca River sample. In the tributary sample, the O_6-O_8 compounds dominate (Figure 22). The O_2 class is commonly regarded as "classic" naphthenic acids, while Lee (1940) introduced the term "oxy-naphthenic acids" that describes compounds which are formed after mild oxidation of classic naphthenic acids. Han et al. (2009) reported mono- and di-oxide naphthenic acids (i.e., O_3 and O_4 classes) in extracts from oil sands process-affected water, and Grewer et al. (2010) reported detection of other oxidized acids, as they demonstrated for O_3-O_5 classes. The profiling of dissolved organics in this study presents a broad spectrum of oxy-naphthenic acids. The ratio of naphthenic acids (O_2) and oxy-naphthenic acids (O_{6-12}) may be useful for separating dissolved organics present in upstream Athabasca River samples and tributaries.

The PCA of the ESI(-) results (Figure 21) also indicated large compositional differences between the dissolved organics present in the far-field snow samples and the tributary samples from the Muskeg River. Comparing the chemical compositions of dissolved polar organics present in a tributary sample (Muskeg River) with those detected in a far-field snow sample show differences in the relative abundance of O_2 and the distribution pattern of O_n (n = 3-12) (Figure 23). In the tributary sample, the O_6-O_8 compounds dominate, whereas in snow the O_4 compounds dominate, and O_{11}-O_{12} compounds are absent. We also note that NO and NO_3 compounds are more prominent in snow than in tributaries. All of these observations contribute towards better understanding of the compositional differences between organics in different sources (i.e., tributaries and snow) feeding into the Athabasca River and other aquatic ecosystems in the region.

It is also interesting to note the similarity between the far-field snow (Figure 23b) and the upstream Athabasca River sample (Figure 22b), especially the relatively high abundance of the O_2 class. The upstream Athabasca River sample is most similar to the cluster of far-field snow samples in the PCA plot (Figure 21) and may be evidence that the dissolved organics present in the upstream Athabasca River may have inherited part of their dissolved organic signature from atmospheric organics deposited in the catchment outside of the AOSR (similar to far-field snow composition).

5 IMPORTANCE OF SPRING SNOWMELT

Both the absolute and relative PAH concentrations (2011 PAH dataset for snow and surface water described in Part 1) and the new profiling of the dissolved polar organic compounds (2012 ESI-FTICR MS results for snow and surface water described in Part 2), show spatial and temporal variations in organics present in snow and surface waters in the AOSR. The two approaches characterize two completely separate types of organics. PAHs, which are polycyclic aromatic hydrocarbons, are non-polar and so are not a type of organic included in the profiles from ESI-FTICR MS analysis.

The pathways for organics present in the snowpack to reach aquatic ecosystems includes release of dissolved and particulate components directly to aquatic ecosystems during the spring melt

(Meyer and Wania 2008, Sharma and McBean 2001) as well as accumulation on soils over the catchment area and gradual release to surface waters (Kelly et al. 2009). Hydrophobic organics that are typically associated with sediment particles (e.g.some PAHs) differ from hydrophilic organics (like the polar organics detected by ESI-FTICR MS) in how they are released and transported during snowmelt (Meyer and Wania 2008). Dissolved organics are often released first, followed by particle-bound species. The particle-bound species are often not transported as far and can be deposited near river mouths (Menzie et al. 2002) whereas dissolved phase species can be transported farther or infiltrate groundwater.

Our analysis of the 2011 snow and surface water dataset found that the highest concentrations of PAHs in the Athabasca River occurred in July 2011, suggesting that spring/summer months may be a period of high fluxes of PAHs in the Athabasca River. Concentration measurements in July were higher than those in May and September 2011 (Figure 6 and Figure 7). The period of May to July is also the season of intensified flow in the Athabasca River. High snowmelt contribution during July 2011, as well as in the May to July interval in many years, is confirmed using a stable isotope record compiled for the Athabasca River below Fort McMurray (Figure 24). As shown for similar rivers in the Liard catchment (St. Amour et al. 2005), river discharge decreases in heavy isotope content (i.e., $\delta^{18}O$) during the spring freshet which is a sensitive indicator of the relative contribution of heavy-isotope depleted snowmelt. The July 2011 sample was collected from the Athabasca River on the receding limb of the hydrograph after peak discharge, but during a period when snowmelt was still significant. Rain was also likely a significant source of water to the river at this time based on meteorological records. As shown, peak discharge in 2011 was roughly two times greater than in previous years due to the combined effect of snowmelt and rain. Note that 2012 isotope analyses were not available at the time this report was compiled. 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.

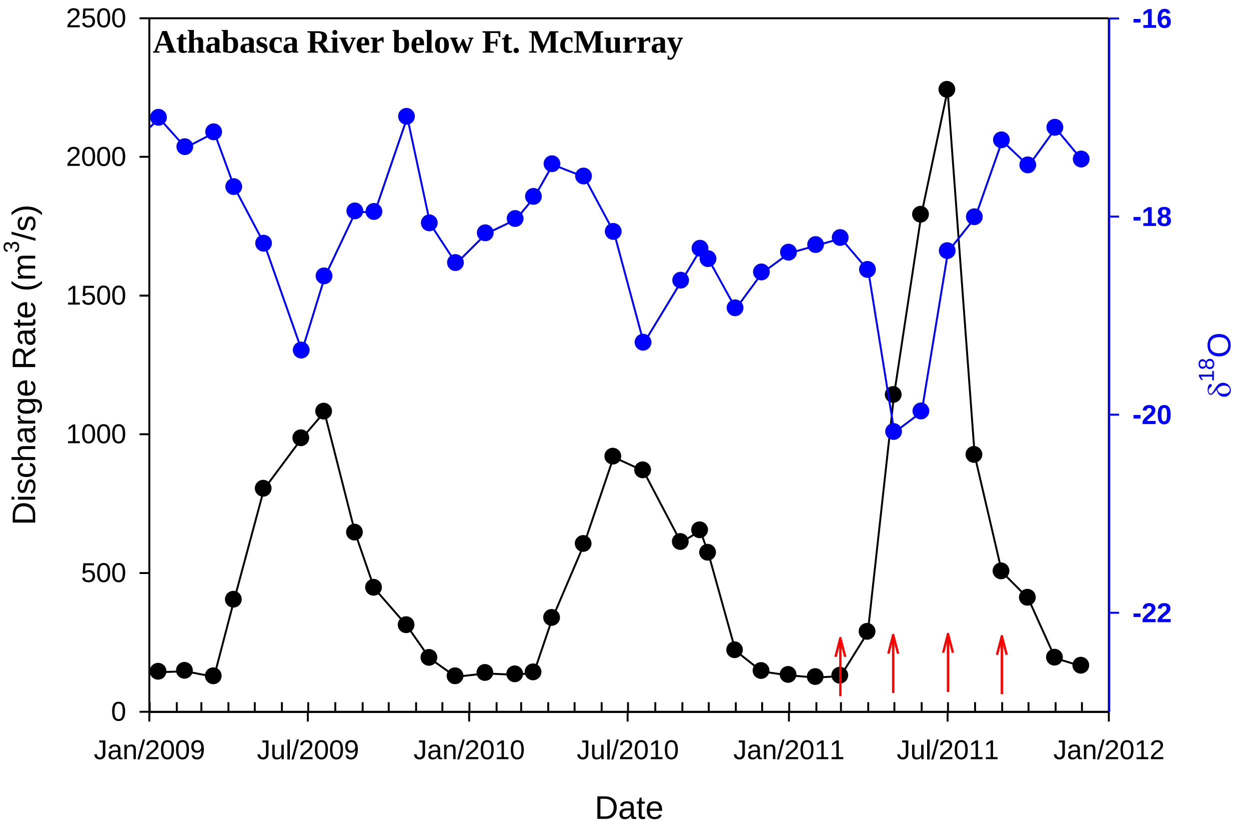

Figure 24. Monthly discharge of Athabasca River below Fort McMurray and temporal change of isotopic composition of the river as an indicator of impact of snowmelt. Sampling times during 2011 are indicated by red arrows.

The 2011 PAH dataset (Figures 3 to 5) indicates that PAH concentrations are generally higher in snow than in surface waters including the Athabasca River, its tributaries and lakes. The higher PAH concentrations in the Athabasca River water during the spring freshet combined with the presence of PAHs in the snowpack might suggest that elevated PAHs in Athabasca River during spring/summer could be attributed directly to snowmelt. However, the compositional differences between the organics identified in snow and surface water samples (identified using the relative PAH concentrations in Part 1, Figure 11 and using the ESI-FTICR MS results in Part 2, Figure 21) suggest that direct transfer of atmospherically-derived organics deposited on the snowpack to surface waters during snowmelt is not a significant component of the organics present the Athabasca River, its tributaries and lakes in the AOSR. Alterations in the relative PAH concentrations due to chemical partitioning of PAHs between dissolved and solid phases as snow melted and was transported over the catchment to the Athabasca River may account for some of the compositional differences between the PAHs present in snow and surface water. These alterations were not specifically addressed in this study because only total (dissolved +

particulate) PAH concentrations were available for the 2011 study period. However, the ESI-FTICR MS profiling of the polar organic compounds conducted in Part 2 also indicated compositional differences in the dissolved organics present in snow and surface water that would be less affected by the partitioning that occurs during snowmelt and transport. Even if the organics present in the snowpack are not a significant direct source of organics present in river discharge during the open water season, the timing of elevated PAH concentrations in surface waters with periods of peak flow suggest that the hydrological activity associated with snowmelt contributes indirectly to the organics present in the Athabasca River and its tributaries through mobilization or erosion of PAH-containing sediments, catchment run-off or groundwater inputs.

6 SUMMARY

The overall objective of this study was to characterize the composition of organics present in snowmelt and surface waters in the Athabasca Oil Sands Region (AOSR) with the goal of identifying whether atmospherically derived organics present in snowmelt are a significant contributor to the organics detected in lakes and rivers in the region.

The results of Part 1 are based on a compiled dataset of total (dissolved + particulate) PAH concentrations for snow, Athabasca River, tributary and lake samples from the AOSR. Our analysis shows that:

- Compositional differences are observed between the PAHs present in snow sampled from areas closest to oil sands activities and the more far-field snow sampling locations.
- Despite large concentration variations in snow along geographic gradients, the composition of PAHs remains similar among near-field sites, but changes significantly at far-field sites.
- Both the near- and far-field snow samples have PAH compositions that are different from the PAHs present in the Athabasca River, its tributaries and lakes.

- Compositional differences in PAH assemblages are also evident between tributaries and the Athabasca River. PAH concentrations in rivers are found to vary seasonally, with peak concentrations observed in July 2011 when Athabasca River levels were at their highest. However, the composition of PAHs present in July 2011 does not resemble the composition of PAHs identified in snow, suggesting that direct transfer of PAHs accumulated on snow from atmospheric deposition to the Athabasca River and its tributaries in the area is not a major source of PAHs present in surface waters. The timing of peak PAH concentrations in rivers which roughly coincides with peaks in river discharge associated with the spring freshet do suggest that snowmelt may contribute to increases in PAH concentrations due to more indirect processes like increased catchment runoff, erosion of stream channels, and/or snowmelt-induced groundwater inputs during this period of intense hydrological activity.
    - The absolute concentration of individual PAH species in surface water samples ranged from BDL to 0.3760 µg/L and the ΣPAH(34) concentrations varied between BDL and 1.8725 µg/L.
    - In the Athabasca River and its tributaries, the highest absolute PAH concentrations were in July 2011, when river discharge was at its maximum.
    - PAH concentrations increased from upstream to downstream along tributaries such as the Ells River, but this needs to be further confirmed by systematic sampling in other tributaries in the region.
    - The highest concentrations of PAHs in the tributary samples are less than the minimum concentrations of PAHs in the main Athabasca River channel, suggesting that inputs from the tributary catchments alone cannot be solely responsible for the PAHs in the main channel.
    - The composition of PAHs in Athabasca River samples is different from those sampled in the tributaries, indicating again that inputs from the tributary catchments alone cannot be solely responsible for the PAHs in the main channel.
    - The concentration of PAHs in snow is generally higher than in surface waters.
    - There are spatial trends in the composition of PAHs in snow samples. Snow samples from near-field locations (located near the geographical centre of oil sands operations) had a fairly uniform PAH composition, particularly along the north-south transects.
    - PAH composition in snow is different from PAH composition in the Athabasca River and its tributaries, supporting the idea that atmospheric PAH is not a significant component of the PAHs present in surface waters.

The results of Part 2 included new ESI-FTICR MS analyses of snow and surface water samples collected in the AOSR in 2012.

- The FTICR MS identified thousands of dissolved polar compounds including acidic organic components in ESI(-) mode and basic components in ESI(+) mode.
- Although based on a small number of snow samples (n = 7), the results of the ESI-FTICR MS analyses identified compositional differences in dissolved organics present in snow in the AOSR. The PCA of ESI(-) results indicated that the snow samples clustered in two distinct groups: one from the high PAH deposition area (<5 km from the GC along the north-south 2011 transect) and another group outside of the high PAH deposition area from more far-field locations. These results indicate that there are spatial variations in the anionic dissolved organic compounds present in snow in the AOSR.
- There were also significant compositional differences between the dissolved polar organics present in snow and surface waters in the AOSR.
- The composition of dissolved organics present in the Athabasca River upstream of the AOSR (i.e., Athabasca River at Athabasca) was different from the samples obtained from downstream sites in the vicinity of AOSR (i.e., Athabasca River at Fort McMurray and Athabasca River at Firebag confluence).
- The upstream Athabasca River sites tend to share some compositional similarities with far-field snow deposition, while the downstream Athabasca River sites are more similar to local tributaries. This contrast likely indicates shifts in the relative importance of regional snowmelt versus local inputs from small tributaries.
- The ESI(-) results also indicate compositional differences in the dissolved organics present in the Athabasca River and its tributaries. The upstream Athabasca River samples have a very distinct dissolved organic profile. The dissolved organics present in the downstream Athabasca River samples more closely resemble the dissolved organics present in adjacent tributaries.
- The ESI(-) results indicate large differences in the dissolved organic component of tributaries in March and slight shifts in the Athabasca River water in July, coinciding with the period of greatest discharge.

This study has provided improved characterization of the PAHs and dissolved organics present in surface waters in the AOSR, and therefore better insight into the potential sources and controls on organics in surface water bodies in the region. Combining the results from Part 1 and Part 2, characterizing the organics in snow and surface waters over the two years and using the two separate types of organics, provides some general insights into composition of organics in snow and surface waters in the AOSR and potential sources of organics to aquatic ecosystems:

- Both the PAH composition results and ESI-FTICR MS organic profiling results suggest that the relative concentrations and overall organic compositions may have additional value beyond absolute concentrations of individual compounds in identifying and separating different organic sources and their pathway to aquatic ecosystems.

- Both the PAH data from 2011 and ESI(-) results from 2012 indicate differences in the composition of organics present in snowpack closest to oil sands activities and in far-field areas. Spatial trends within these data suggest that these methods may be useful for improved understanding of the different sources of atmospheric organics.
- The ESI(-) results indicate anionic dissolved organic compounds present in the upstream Athabasca River sample are similar to the dissolved organics detected in far-field snow samples, those from sampling locations outside of the high PAH deposition area.
- The compositional differences in PAHs and dissolved polar organic compounds in snow and most surface water samples suggest that direct transfer of organics accumulated on snow from atmospheric deposition to the Athabasca River, its tributaries and lakes is not the dominant source of organics to these surface water bodies. The timing of peak PAH concentrations in rivers with peaks in river discharge associated with the spring freshet do suggest that snowmelt may contribute to increases in PAH concentrations due to more indirect processes like increased catchment runoff, erosion of stream channels, snowmelt-induced groundwater inputs during this period of intense hydrological activity.
- Both the PAH and ESI-FTICR MS results show compositional shifts in July that may be related to the peak river discharge associated with the spring freshet.
- Different compositions of PAHs and dissolved polar organics present in snow, compared with surface waters, suggest that these differences can be used to separate airborne vs. waterborne organics in the AOSR.

This study was intended as a first step towards better understanding the sources of organics to aquatic ecosystems in the region and the role that atmospherically derived organics play in the overall loading.

In Part 2 we took advantage of existing monitoring programs conducted by AESRD in 2012 and these programs determined the availability of snow, Athabasca River, tributary and lake samples. There were far fewer snow samples available in 2012 for the ESI-FTICR MS analysis, but the distinction in organic signatures between the snow samples closest to oil sands activities and the more far-field samples suggest that this may be a promising technique for distinguishing different sources of atmospherically derived organics, that would benefit from a more comprehensive spatial sampling campaign.

7 FUTURE RESEARCH

This project was used to assemble two comprehensive datasets of organics for snow and surface waters in the AOSR. The results of this pilot study have identified some intriguing organic signatures and spatial and temporal trends that can be used to better understand sources and transport of organics in the region. But there are still many aspects of these datasets that could be studied in detail. Our plans for future research include activities that could focus on existing data from 2011 and 2012 as well as new analyses. For the 2011 data we plan to further investigate the PAH species that distinguish the different groups and potential composition changes associated with transformations during atmospheric transport, catchment runoff or weathering. The new 2012 ESI-FTICR MS dataset will be further interpreted to focus on identifying the compounds present in the snow closest to oil sands activities that are absent from the more distant snow sampling locations to investigate whether there are atmospherically-derived organics (other than PAHs) that may be associated with development. The differences in organic composition between snow near the centre of oil sands activities and snow from more far-field locations may identify the dissolved polar organics present in the high-deposition areas that might be a useful indicators of oil sands activities.

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9 GLOSSARY

9.1 Terms

Absolute Concentration

Quantification of amount of a substance per volume in the sample. Absolute PAH concentrations are expressed as µg/L in this study.

Atmospherically-Derived Organics

Organics that originate from atmospheric deposition.

Detection Limit

The lowest quantity of targeted PAH compound that can be distinguished from the absence of that substance (a *blank value*). The detection limit is estimated from the mean of the blank, the standard deviation of the blank and some confidence factor.

Dissolved Organics

A broad term for organic compounds of varied origin and composition within aquatic systems. Distinct from particulates and organics attached to particulates, these compounds are dissolved in water and transported along with the water movement.

Far-field

Used qualitatively in this report to describe locations that are farther removed from the geographical centre (GC) of oil sands activities. A strict distance cut-off was not used, but the term was used to describe qualitative distances for the 2011 snow samples in Part 1. In Part 2 there were only 7 snow samples so far-field was used to describe the samples > 5 km from the GC.

Homologue

A series of compounds with a similar general formula, but varying by the length of a carbon chain (number of CH_2 groups). Because homologues typically have a fixed set of functional groups, these compounds have similar chemical and physical properties.

Near-field

Used qualitatively in this report to describe locations that are closer to the the geographical centre (GC) of oil sands activities. A strict distance cut-off was not used, but the term was used to describe qualitatively for the 2011 snow samples in Part 1. In Part 2 there were only 7 snow samples so near-field was used to describe the snow samples from locations < 5 km from the GC.

Polycyclic Aromatic Hydrocarbons (PAHs)

A group of organic compounds composed of two or more fused conjugated benzene rings. PAHs are non-polar and have varying degrees of hydrophobicity. They are commonly associated with fossil fuels, combustion of fuels and other complex carbon sources. These compounds can be found in air, water and sediments and many are considered to be toxic and carcinogenic. The PAHs can be loosely divided into unsubstituted or parent PAHs and alkyl-substituted or alkylated PAHs.

- Parent PAHs refer to PAH species with fused conjugated ring structure only such as Naphthalene and Chrysene.
- Alkylated PAHs refer to PAH species with various alkyl groups attached, such as C1-Naphthalene and C1-Chrysene.

Relative Concentration

The ratios of the amount of individual PAH compounds to total amount of PAHs in the sample. The relative concentration of one PAH (PAHx) was determined using

$$\%PAHx = (PAHx) / \Sigma PAH(34).$$

> Where x is the absolute concentration of PAHx and ΣPAH(34) is the sum of the concentrations of the 34 PAH species common to all datasets.

Spatial

Used in this report to describe patterns that vary depending on the geographical position within the study area.

Species

Used in this report to describe individual PAHs. In general the term can be used for a group of chemically-similar atomic or molecular structural units. Our use of the term PAH species refers to individual types of PAHs that fit the definition of having two or more fused conjugated benzene rings. For example Naphthalene is one of the 34 PAH species compiled for the 2011 snow and surface water PAH dataset.

Surface Waters

Refers to the Athabasca River, its tributaries and a small number of lakes in this report.

Temporal

Used in this report to describe trends that vary over time. These include patterns related to the sampling month, season or year.

9.2 Acronyms

AESRD	Alberta Environment and Sustainable Resource Development
AITF	Alberta Innovates – Technology Futures
AOSR	Athabasca Oil Sands Region
AT	Athabasca River and Tributaries
BDL	Below Detection Limits
CCME	Canadian Council of Ministers of the Environment
Da	Dalton
EPA	Environmental Protection Agency
ESI	Electrospray Ionization
ESI(-)	ESI Negative Mode
ESI(+)	ESI Positive Mode
ESI-FTICR MS	Electrospray Ionization Fourier Transform Ion Cyclotron Mass Spectrometry
GC	Geographical Center
KMD	Kendrick Mass Defect
LLE	Liquid – Liquid Extraction
NA	Naphthenic Acids
OSRIN	Oil Sands Research and Information Network
PAH(s)	Polycyclic Aromatic Hydrocarbon(s)
PCA	Principal Component Analysis
RAMP	Regional Aquatic Monitoring Program
RC	Relative Contribution

SEE	School of Energy and the Environment
SI	Système international d'unités
SS	Snow Survey
WQ2011	Water Quality 2011
WQM	Water Quality Monitoring
WSC	Water Survey Canada

LIST OF OSRIN REPORTS

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