Characterizing the Organic Composition of Snow and Surface Water Across the Athabasca Region: Phase 2

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Oil Sands Research and Information Network

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REPORT SUMMARY

This study was conducted to characterize the composition of polar dissolved organic compounds 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 an important contributor to the dissolved organics detected in surface waters in the AOSR.

The Phase 1 OSRIN study (2013) was a pilot scale project conducted in 2011-2012 to evaluate whether Electrospray Ionization (ESI) coupled with Fourier Transform Ion Cyclotron Mass Spectrometry (FTICR MS) would be a useful analytical technique to characterize the dissolved organics in snow. Although a limited number of samples (i.e., 7 snow samples) were used in the Phase 1 study, the results indicated differences in organic signatures between the snow samples closest to oil sands activities and the more far-field samples.

The Phase 2 project includes a similar comparison of the composition of organics present in snow and surface water as was conducted in Phase 1, but is based on a more spatially and temporally comprehensive set of samples which allows a more extensive investigation of the spatial, temporal and species variations in snow and river water. Phase 2 also combines hydrometric data with the stable isotopic composition of snow and river water to identify when snowmelt appears in river discharge.

The dissolved organic composition results identified three snow groups. Group 1 snow tended to have O_2 as the dominant compound class, followed by O_4 compound classes. The snow samples from locations farthest from industrial activities had Group 1 organic profiles. The organic profiles for Group 2 had O_4 as the most abundant compound class and a pattern of decreasing relative contributions from the O_4 to O_{12} classes. There were only six Group 2 snow samples, but they were collected from either the geographical centre (GC) or near mining activities. The remaining snow samples that did not have similar dissolved organic compositions as Group 1 or Group 2 were categorized as Group 3 and were obtained from various locations.

The organic profiles obtained for the 110 river samples (84 tributary samples and 26 main stem Athabasca River samples) showed large differences between the composition of dissolved organics present in river water and those present in snow. River samples tended to have a greater relative contribution of O_6 to O_8 and S_2O_n ($n = 4$ to 9) compound classes than snow samples. More subtle differences in organic profiles were also evident between the individual river samples related to sampling location and season. Comparing the organic profile results between the river and snow samples show the different types of relationships that exist between river and snow dissolved organic compositions. The monthly river samples collected from the main stem Athabasca River and from one tributary sampling location (i.e., Muskeg 8) tend to have organic compositions that become more similar to Group 1 snow samples over the open water season. The other tributary sampling locations tended to have dissolved organic compositions that become more similar to Group 2 or Group3 snow compositions over the open water season. The river samples differed from snow in that the dissolved organics present in river water are dominated by O_6 to O_8 classes in oxygen containing compounds, and contain a greater relative contribution S_2O_n ($n = 4$ to 9).

Also, the Athabasca River samples had slightly different organic compositions than the tributaries, with higher relative contributions of O_2 class compounds than in the tributaries. The main stem Athabasca River samples also contained some SO_3 compounds that were not detected in the tributary samples.

All of the river samples showed seasonal variations in dissolved organics, with larger variations in the Athabasca River than in tributaries. The distribution of compound classes in the river samples did not change significantly between May and September, but the dominance of O_2 classes becomes more pronounced in September, particularly in the Athabasca main stem sample.

The river discharge and stable water isotope data indicate that snowmelt was a major component of the May river samples, but the dissolved organics present in the May river samples did not resemble those present in snow. The months with the greatest similarity between snow and river organic compositions were low flow periods in March, April, and September, which could indicate significant delays between when atmospheric organics are released from the snowpack and when they reach the rivers, or that some of the organics present in snow are similar to organics that characterize baseflow.

In summary, the results of this comprehensive profiling of organics in snow and river water across the AOSR suggest that nitrogen and sulphur containing compounds may be the most useful in improving our understanding of the sources and fate of atmospherically derived organics in the oil sands region. There are still some endmembers that need improved organic characterization, including baseflow (groundwater inputs and soil water in disturbed and undisturbed watersheds) to the Athabasca River and its tributaries. Direct sampling of dissolved organics that can be attributed to natural and anthropogenic atmospheric sources of organics (e.g., forest fire, stack emissions, fugitive emissions) are also needed.

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1 INTRODUCTION

Minimizing the contribution of contaminants derived from oil sands mining and processing activities is an important component of ensuring sustainable development in Alberta's Athabasca Oil Sands Region (AOSR). Previous investigations have revealed the presence of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) in snow and rivers in the AOSR and attributed them to atmospheric deposition (snow) and land disturbances (river) due to oil sands activities (Kelly et al. 2009). Various transport pathways of organics to aquatic receptors have been proposed in the AOSR including atmospheric (Cho et al. 2014, Kurek et al. 2013, Timoney and Lee 2011) and waterborne pathways (Hall et al. 2012, Wiklund et al. 2012). However the contribution of each pathway to the overall organic load present in the Athabasca River and its tributaries remains unknown.

Snow surveys provide a method of sampling atmospherically derived organics deposited during the winter months. During the spring freshet, meltwater and accompanying solutes either infiltrate into the ground or travel across the ground surface as runoff eventually reaching surface water receptors. If atmospheric deposition is a significant pathway of organic transport to surface water bodies in the region, water samples collected from the Athabasca River and its tributaries would be expected to contain organics with a similar composition as those present in snow deposited in the watershed.

In 2011 and 2012, Alberta Environment and Sustainable Resource Development (AESRD) conducted snow surveys to evaluate the distribution of PAHs and metals in the AOSR. Alberta Innovates – Technology Futures (AITF) and AESRD collaborated to investigate the contribution of atmospherically derived organics to the Athabasca River and its tributaries using AESRD and Regional Aquatic Monitoring Program (RAMP) snow and water samples. In the OSRIN Phase 1 study (hereafter referred to as Phase 1; Birks et al. 2013, Yi et al. accepted 2014), PAH concentrations and dissolved organic compositions were determined using Electrospray Ionization (ESI) coupled with Fourier Transform Ion Cyclotron Mass Spectrometry (FTICR MS) in snow, lake, river and tributary samples from the AOSR.

The results of Phase 1 showed that 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. Both the PAH data from 2011 and ESI-FTICR MS results from 2012 indicated differences in the composition of organics present in snowpack closest to oil sands activities and in far-field areas. Spatial trends within these data suggested that these methods may be useful for improved understanding of the different sources of atmospheric organics. Seasonal variations were observed in the organic compositions of Athabasca River samples throughout the open water season. There were only seven snow samples available for ESI- FTICR MS analysis in Phase 1, but the small dataset indicated differences in organic signatures between the snow samples closest to oil sands activities and the more far-field samples, suggesting that ESI-FTICR MS may be a promising technique for distinguishing different sources of atmospherically derived organics. In this study we use ESI-FTICR MS to characterize the dissolved acidic polar organics. This category of organics includes naphthenic acids and oil sands acid extractable organics (O_n compound classes), but also includes a wide range of other sulfur and nitrogen containing classes.

The objective of the Phase 2 project is to better 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 and rivers can be used to identify linkages between atmospheric organics and those detected in rivers. The Phase 2 project includes a similar comparison of the composition of organics present in snow and surface water as was conducted in Phase 1, but is based on a more spatially and temporally comprehensive set of samples (eight times more samples) which allows a more complete investigation of the spatial and species variations within the organic composition of snow. Phase 2 also combines hydrometric data with the stable isotopic composition of snow and river water to identify when snowmelt appears in river samples.

2 BACKGROUND

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 of solutes and particulates in the remaining snow. During the initial melt period, the ground is typically frozen so increases in infiltration and the subsequent increases in 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. Weathering of rock, soil and bitumen in the watershed can result in additions of various constituents to snowmelt.

Rivers are very dynamic systems providing a spatially integrated signal of water quality over their catchments, with strong seasonal variations. The dissolved organics present in the Athabasca River and its tributaries can originate from a combination of atmospheric deposition over the upstream portion of the catchment and surface and groundwater inputs. Both the atmospheric deposition and the surface and groundwater inputs can include natural (e.g., forest fire deposition, natural organic rich groundwater seeps) and anthropogenic sources (e.g., emissions from oil sands activities, increased organics from watershed development). The position of a river sampling location will determine the portion of the watershed contributing to runoff (including snowmelt) at that sampling location. Multiple sampling locations along a river each will integrate a different portion of the watershed runoff. 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.

Most of the recent research on atmospherically derived organics in the AOSR has focused on PAHs (Cho et al. 2014, Hall et al. 2012, Jautzy et al. 2013, Kelly et al. 2009, Kurek et al. 2013). Other types of organic atmospheric emissions have been identified and monitored from oil sands activities (i.e., VOCs from airborne surveys, fugitive emissions) (Percy 2012), but the Phase 1 study is the first that we are aware of that more broadly characterizes the full spectrum of organics present in atmospheric deposition in the AOSR. Although based on a limited number of samples (n = 7), the results of the ESI-FTICR MS analysis (ESI negative mode; ESI(-)) conducted as part of Phase 1 (Birks et al. 2013, Yi et al. accepted 2014) identified compositional differences in dissolved organics between snow samples collected from sites within 5 km of the geographic centre of operations (GC) and those collected from more remote far-field locations.

New analytical techniques, like ultrahigh resolution mass spectrometry, have greatly improved our ability to detect and characterize polar organic compounds in environmental samples (Headley et al. 2011, 2013, Mazzoleni et al. 2010). ESI-FTICR MS provides more comprehensive characterization of the dissolved polar organic compounds due to its extremely high resolution and mass accuracy, allowing for an improved ability to identify different organic species, particularly at very low concentrations such as those found in snowmelt and some surface waters. ESI-FTICR MS has been used to characterize the organics present in oil sands process waters, and some samples from lakes and rivers (Barrow et al. 2010, Grewer et al. 2010, Headley et al. 2011, 2013, Nyakas et al. 2013), however the Phase 1 study is the only previous example of using ESI-FTICR MS to profile snow.

The stable isotopes of water, $\delta^{18}O$ and $\delta^{2}H$, are naturally occurring and incorporated within the water molecule ($H_2{}^{18}O$, ${}^{1}H_2H^{16}O$). They are particularly useful tracers of water cycling as they undergo measureable and systematic fractionation as water is transported, evaporates and exchanges among phases in the water cycle. These fractionations result in differing isotopic labelling of precipitation, groundwater and surface waters that can be used to identify water sources, mixing, flow pathways, and have great potential for quantitative evaluation of water balance. Values are reported in per mil relative to Vienna Standard Mean Ocean Water (V-SMOW). The $\delta^{18}O$ and $\delta^{2}H$ values in river water can be used to identify when water originating from snowmelt appears in the river and to quantify the contribution of snowmelt to river discharge. In northern Alberta, snow typically has very negative $\delta^{18}O$ and $\delta^{2}H$ values and a distinctive meteoric signature compared to surface water, which has more positive $\delta^{18}O$ and $\delta^{2}H$ values depending on the degree of evaporative enrichment (Gibson and Edwards 2002, St. Amour et al. 2005).

3 METHODS

3.1 Sample Collection

3.1.1 *Snow Samples*

AESRD collected 67 snow samples from 56 sampling sites as part of their annual snow survey. Snow samples were collected in February 2013 (Figure 1), using a stainless steel corer (10.2 cm in diameter and 91 cm in length). The snow from the corer was emptied into Teflon bags, and subsequently melted in a dark room. All 67 snow samples were submitted for stable water isotope (SWI – $\delta^{18}O$ and $\delta^{2}H$) analysis at the AITF Isotope Laboratory in Victoria, British Columbia (Table 1), and a subset of 47 samples was selected for organic characterization using ESI-FTICR MS. These samples were selected based on the available sample volumes and geographical location.

3.1.2 *River Samples*

Monthly sampling of the Athabasca River main stem and tributaries was conducted by AESRD at 18 sampling locations between 2012 and 2014 (Figure 1). The outlines of the Steepbank, Muskeg and Firebag watersheds are shown in Figure 1 for reference. In total, 117 river samples were collected, including 26 from the Athabasca River main stem and 91 samples from tributaries. The river samples were collected from the centre of the river, at approximately 2/3 depth from the water surface. Eight of these sampling sites only collected river samples, the other eleven were sites where both snow and river samples were collected (co-location sites discussed below). A subset of 110 river samples was selected for ESI-FTICR MS analysis. An additional 61 were submitted for SWI analysis (Table 1). All samples were collected in pre-cleaned 250 mL glass amber bottles[1] and transported to AITF for analysis.

Information about whether each of the monthly river samples were taken during periods of high river (e.g., the spring freshet) or low (e.g., winter baseflow) river discharge can be inferred from discharge data available from the Regional Aquatics Monitoring Program (RAMP) (RAMP 2014). Daily river discharges (in m^3/s) collected during the 2013 season at Atha2 (main stem) and the Mus3 (tributary) are presented in Figure 2. Due to logistical difficulties, river discharges under ice were not reported.

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[1] For more information on the effects of storage containers on naphthenic acid analysis see Mahdavi, H., H. Mian, S. Hepperle and Z. Burkus, 2014. Standard Operating Procedures for Analysis of Naphthenic Acids from Oil Sands Process-Affected Water. OSRIN Report No. TR-62. 67 pp. http://hdl.handle.net/10402/era.40181

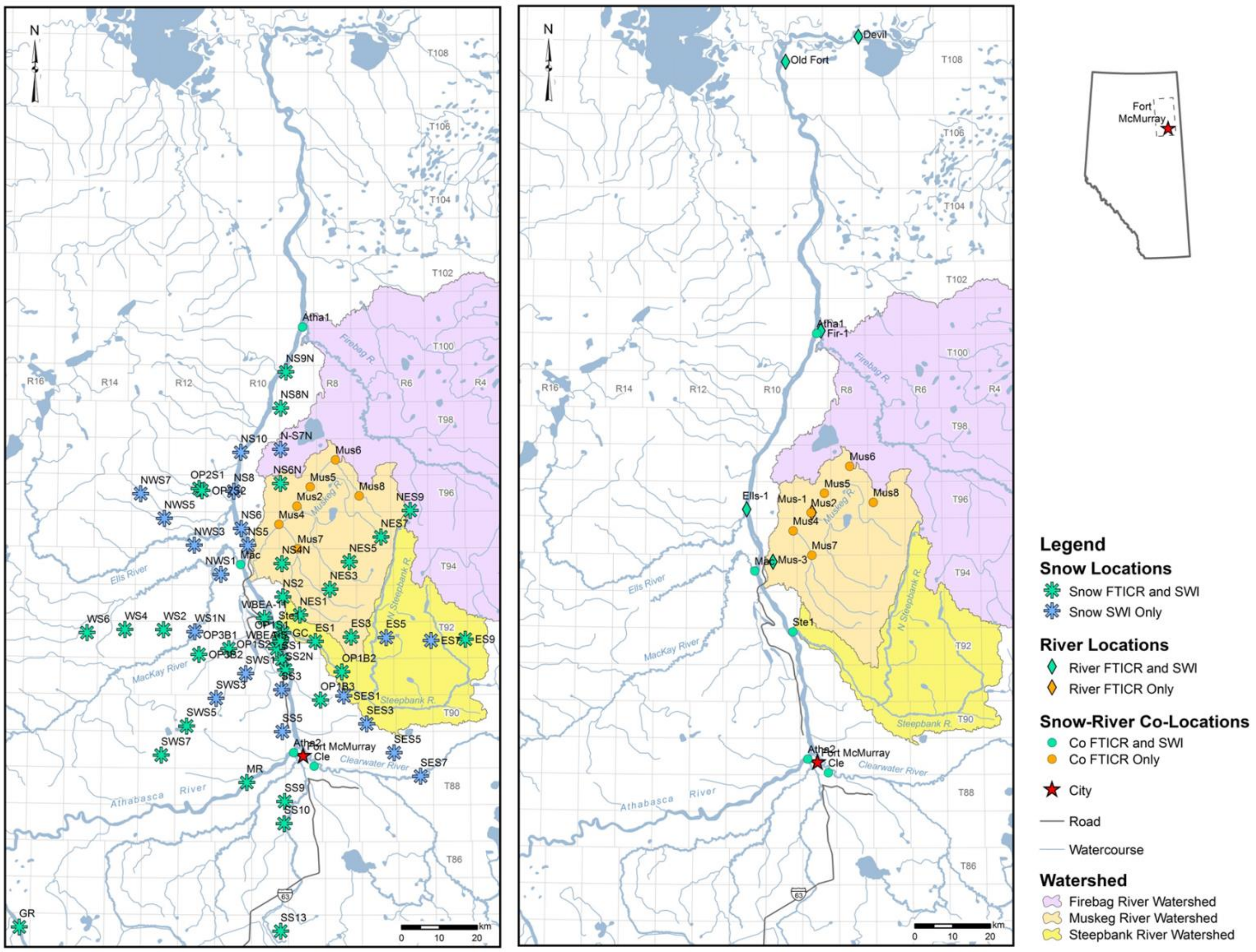

Figure 1. The location of snow sampling sites (left panel) and river sampling sites (right panel).
Co-location sites are locations where both snow and river samples were obtained.
Colours correspond to the type of analyses conducted (ESI-FTICR MS or SWI).
Atha3 is not shown as it is located well upstream of the other sampling locations.

Table 1. Summary of snow and river samples collected during the 2013 campaign. Samples submitted for ESI-FTICR MS and SWI were counted separately. The number of samples does not include duplicated samples collected for QA/QC purposes.

		# of Sites	**Collected Samples**	**ESI-FTICR MS**	**SWI**
Snow		56	67	47	67
River	Main Stem	5	26	26	26
	Tributaries	13	91	84	35

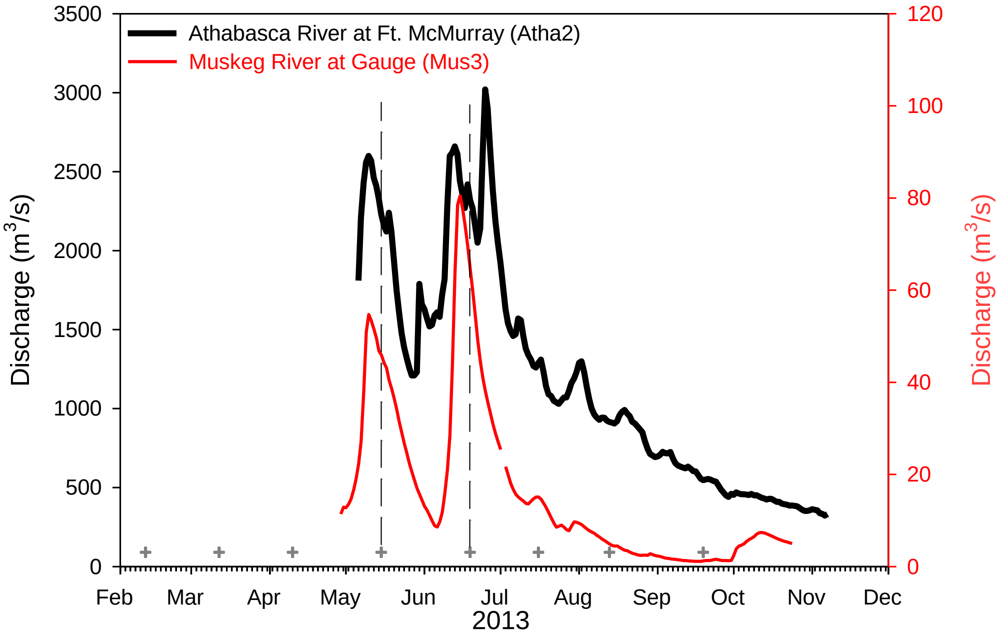

Figure 2. Hydrograph at main stem of the Athabasca River (Atha2) and the Muskeg River (Mus3) for 2013.
The grey crosses indicate dates when river samples were obtained.
The sampling periods at the peak discharge events in early May and mid-June are highlighted with dashed lines.

Figure 2 shows that samples from the May and June sampling events at Atha2 and Mus3 were collected in the falling limb of the hydrograph, days after peak flow conditions at these sampling locations. However, it is important to note that the exact sampling date varied from site to site due to logistical reasons and these slight differences in sampling date result in some samples for the same month being on either the rising or falling limb of the hydrograph. For example, the Atha3 samples were collected approximately one week before the other sites, and could actually be sampling in the raising limb of the hydrograph. The river samples used in this study are from a wide range of hydrological flow conditions (grey crosses on Figure 2) that include under ice samples, samples close to both discharges peaks, as well as on the falling limb of the hydrograph and during low flow conditions in the fall.

3.1.3 *Snow-River Co-Location Sites*

There were 11 locations where both snow and river samples were collected by AESRD (Figure 1). The sampling methods were the same as described above, but at these locations the snow sample was collected near the river sampling location. A total of 68 river samples and 11 snow samples were submitted for ESI-FTICR MS from the co-location sites.

3.2 Analytical Methods

3.2.1 *ESI-FTICR MS Analysis*

The detection and characterization of dissolved organics in snow and river samples via ESI-FTICR MS[2] was conducted at Proteomic Centre, University of Victoria, British Columbia. Samples were pretreated with liquid-liquid extraction (LLE) to separate and enrich organic extracts prior to analysis (Gibson et al. 2011). Each extract was then directly infused into a 12-Tesla Apex-Qe hybrid quadrupole FTICR MS (Bruker Daltonics, Billerica, USA) with a syringe pump at a flow rate of 3 µL/min. The instrument was operated in ESI(-) within a scan range of m/z 150 to 1,100. Each mass spectrum was recorded from an accumulation of 400 scans with broadband acquisition and a data acquisition size of 1 megabyte per second. Typical ESI-MS parameters were: capillary electrospray voltage of 3,800 V; spray shield voltage of 3,500 V; source ion accumulation time of 0.1 seconds; and, collision cell ion accumulation time of 0.2 seconds.

3.2.2 *Stable Water Isotope Analysis*

The $\delta^{18}O$ compositions were analyzed using a Delta V Advantage mass spectrometer and a GasBench II peripheral. Prior to analysis, water samples were allowed to equilibrate with 0.3% CO_2 in headspace. The CO_2 was then sampled using a CTC Analytics autosampler and the measured $\delta^{18}O$ values in CO_2 are used to calculate $\delta^{18}O$ values for the sample which is equilibrate with measured CO_2. $\delta^{2}H$ samples were analyzed using a Delta V Advantage mass spectrometer and an HDevice peripheral. 1 µL of sample was injected into the HDevice using a CTC Analytics autosampler. Chromium metal at 900°C is used as catalyst to quantitatively pyrolyze water to H_2 gas, which is measured for isotopic composition in the mass spectrometer. Isotopic results ($\delta^{18}O$ and $\delta^{2}H$) are reported in δ values (‰) relative to international reference V-SMOV (Coplen 1996). Analytical uncertainties are ±0.05‰ for $\delta^{18}O$ and ±0.3‰ for $\delta^{2}H$.

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[2] For more information on analytical methods for naphthenic acids 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

3.2.3 *Duplicate Samples*

Standard laboratory quality assurance and quality control procedures are followed at the ESI-FTICR MS and SWI laboratories. These include using international references to monitor isotopic measurements, running blanks between samples to ensure no carry over between samples, and performing internal mass calibration prior to data processing in ESI-FTICR MS. For ultrahigh resolution mass spectrometry, peaks with a signal-to-noise ratio greater or equal to ten were considered.

Duplicate samples were also submitted for both isotopic and ESI FT-ICR MS analyses. The results from the duplicate samples are included in Appendix 1.

3.3 Data Processing and Statistical Analysis

The data acquired from ESI-FTICR MS can include intensities for thousands of compounds (identified by their mass to charge ratio; m/z) detected in a single sample. This large volume of data needs to be processed before the results can be readily presented and discussed. Raw mass spectra were processed using a combination of DataAnalysis® (Bruker Daltonik, Brement, Germany), LabView® (National Instruments, Austin, TX) and a customized VBA script to produce a dataset reporting the molecular weights and the corresponding intensity for each individual sample. Details of raw spectra processing were described in Birks et al. (2013).

Molecular formulae of the detected homologues were further computed based upon the accurately measured masses with a custom algorithm written in the Matlab® (MathWorks Inc. Natick, Massachusetts). Homologues are 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, and they can be used to infer molecular formulae. The ability to infer molecular formulae from accurate measurement of mass is the most important advantage of ultrahigh resolution mass spectrometry (i.e., ESI-FTICR MS). Similar to the discussion of the Phase 1 results, the organic profiling results will focus on homologues. Since the output includes the intensities for thousands of different compounds a useful parameter to calculate is the relative contribution (RC). The RC is calculated as the intensity of a single peak, divided by the total intensity of all detected peaks.

There are a few different ways to visualize the output from ESI-FTICR MS analyses including:

Kendrick Mass Defect (KMD) Plots: These KMD 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. In a KMD plot homologues plot along a straight horizontal line.

Compound Class Plots: 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. 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.

Principle component analysis (PCA) Plots: The PCA was carried out based on the RC values to statistically characterize and compare compositional differences between samples. The sample scores (PC1 vs PC2) from PCA are presented in this report. PCA analyses are performed using SIMCA-P+ (V12.0, Umetrics AB Umeå, Sweden). PCA is a multivariate statistical technique that can be used to extract relevant information from a large data matrix (Mardia et al. 1989). Scores for the primary principal component (PC1) and the secondary principal component (PC2) are frequently used as indicator of similarity between samples. The closer the two samples are in a PCA plot the more similar their organic composition.

4 RESULTS AND DISCUSSION

4.1 Organic Profiles of Snow Samples

The ESI-FTICR MS organic profiling detected thousands of compounds in the 47 snow samples using ESI(-) mode (Table 2). The total number of detected compounds in the snow samples ranged from 1,920 to 5,450 with an average of 3,485.

About 30% of the detected compounds were homologues. The number of detected homologues varied between sampling sites and ranged from 458 to 1,951 with an average of 1,170 homologues detected across all sites. The presence of homologues is closely correlated with the number of total detected compounds. The mass distribution of homologues commonly resembles that of all detected compounds and the presence of homologues improves our ability to infer molecular compositions. For these reasons we will focus our interpretation of the ESI-FTICR MS results on homologues.

PCA was used to look at similarities and differences within the snow ESI-FITCR MS results. The snow samples show a wide range in dissolved organic compositions (Figure 3). There are two main groups that differ along the PC1 axis. Most of the snow samples have negative PC1 scores, and PC2 scores near zero, and we will refer to them as Group 1 (PC1<0). The snow samples that plot in Group 2 are characterized by high scores in both PC1 and PC2 and plot in the upper-right quadrant in the score plot (PC1>4, PC2>4). The samples that do not plot in either of these clusters are referred to here as Group 3, and they generally plot in the lower-right quadrant of the PCA plot.

Table 2. Summary of the number of individual peaks and homologues detected in the 47 snow samples (36 snow samples and 11 co-location sites).

Location	Site Description	Peaks	Homologues
Atha1	Athabasca River u/s Firebag R	2,496	992
Atha2	Athabasca R u/s Ft McMurray (LTRN)	3,480	1,554
Mus8	Muskeg River 27.5 km u/s Stanley Creek	3,127	1,380
Mus6	Muskeg River 11 km u/s Stanley	2,782	1,162
Mus5	Muskeg River u/s Stanley	4,307	1,718
Mus2	Muskeg River u/s Muskeg Creek	3,948	1,691
Mus4	Muskeg River u/s Jackpine Creek	3,939	1,608
Mus7	Jackpine Ck 16.5 km u/s Muskeg River	3,787	1,403
Mac	McKay River at mouth	3,083	1,130
Ste1	Steepbank River at mouth	3,646	1,164
Cle	Clearwater u/s Waterways	2,874	818
GR	Athabasca River u/s Grande Rapids	2,818	693
MR	Athabasca River @ Mountain Rapids	2,716	762
ES9	E-S9	2,599	633
SS9	S-S9	3,083	458
SS10	S-S10	2,212	678
SS13	S-S13	1,920	696
NS8N	N-S8	3,803	1,485
NS9N	N-S9	3,406	1,337
NES9	NE-S9	3,350	1,179
ES3	E-S3	3,406	755
NES3	NE-S3	3,028	797
NES5	NE-S5	3,483	999
NES7	NE-S7	3,223	1,033
NS4N	N-S4	4,076	1,470
NS6N	N-S6	5,268	1,777
NES1	NE-S1	3,293	1,094
ES1	E-S1	4,248	1,763
NS2	N-S2	3,702	1,409
SS1	S-S1	3,451	1,284
WBEA-5	Near ambient monitoring station 1	3,218	1,101
WBEA-11	Near ambient monitoring station 2	3,823	1,370

Location	Site Description	Peaks	Homologues
SS2N	S-S2	3,228	1,153
WS2	W-S2	2,893	883
WS4	W-S4	2,675	825
WS6	W-S6	3,159	569
SWS5	SW-S5	3,686	1,158
SWS7	SW-S7	3,286	836
OP3B1	Operator 3 Border Site 1	3,262	969
OP3B2	Operator 3 Border Site 2	3,185	852
OP1B3	Operator 1 Border 3	3,089	839
OP1S1	Operator 1 Site 1	3,978	1,423
OP1S2	Operator 1 Site 2	4,808	1,740
OP2S1	Operator 2 Site 1	5,460	1,951
OP2S2	Operator 2 Site 2	4,974	1,636
OP1S2	Operator 1 Border 2	3,613	1,515
GC	Geographic Centre	4,889	1,685

u/s = upstream.

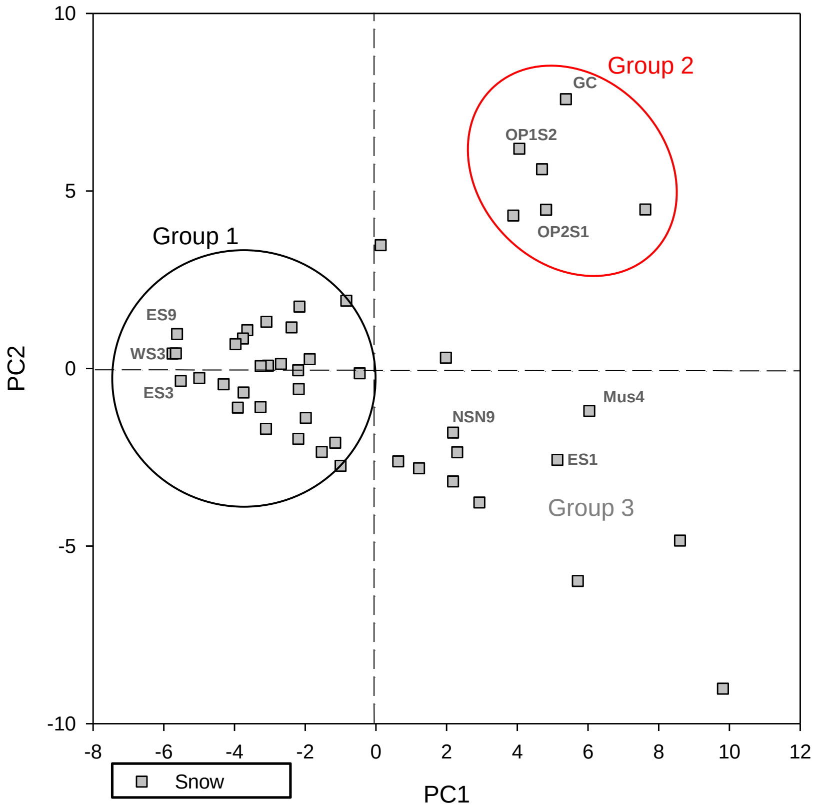

Figure 3. PCA analysis of the ESI-FTICR MS results for snow.
PC1 accounts for 37.1% of the variation and PC2 accounts for 21.0% of the variation.
Ellipses show the samples included in Group 1 and Group 2. All other samples are categorized as Group 3.

Comparing the distribution of compound classes from selected samples representative of the different snow groups highlights the types of compounds that differentiate the three groups (Figure 4). The samples presented for each group were selected based on the PCA (Figure 3). In particular, the oxygen containing compounds (O_n) appear to show systematic differences between groups. In the three Group 1 snow samples presented (ES9, ES3, WS6), the most abundant class is generally O_2, which is followed by the O_4 class in relative contributions. In Group 1 samples there is a pattern of decreasing relative contribution with increasing numbers, for compounds containing more than 6 oxygen (O_n, $n \geqq 6$) (Figure 4a). For Group 2 snow, the most abundant class is the O_4 class and there is a decreasing pattern in the relative contribution of O_4 to O_{12} classes (Figure 4b). Three samples that plotted in the bottom right hand quadrant of Figure 3 were selected to represent Group 3 snow in Figure 4c. These samples share some similarity with Group 1, such as relative abundance of O_2 classes, but also some similarities with Group 2, such as the distribution of O_4 to O_{12} classes, as well as the presence of S_2O_n (n = 4 to 8) classes.

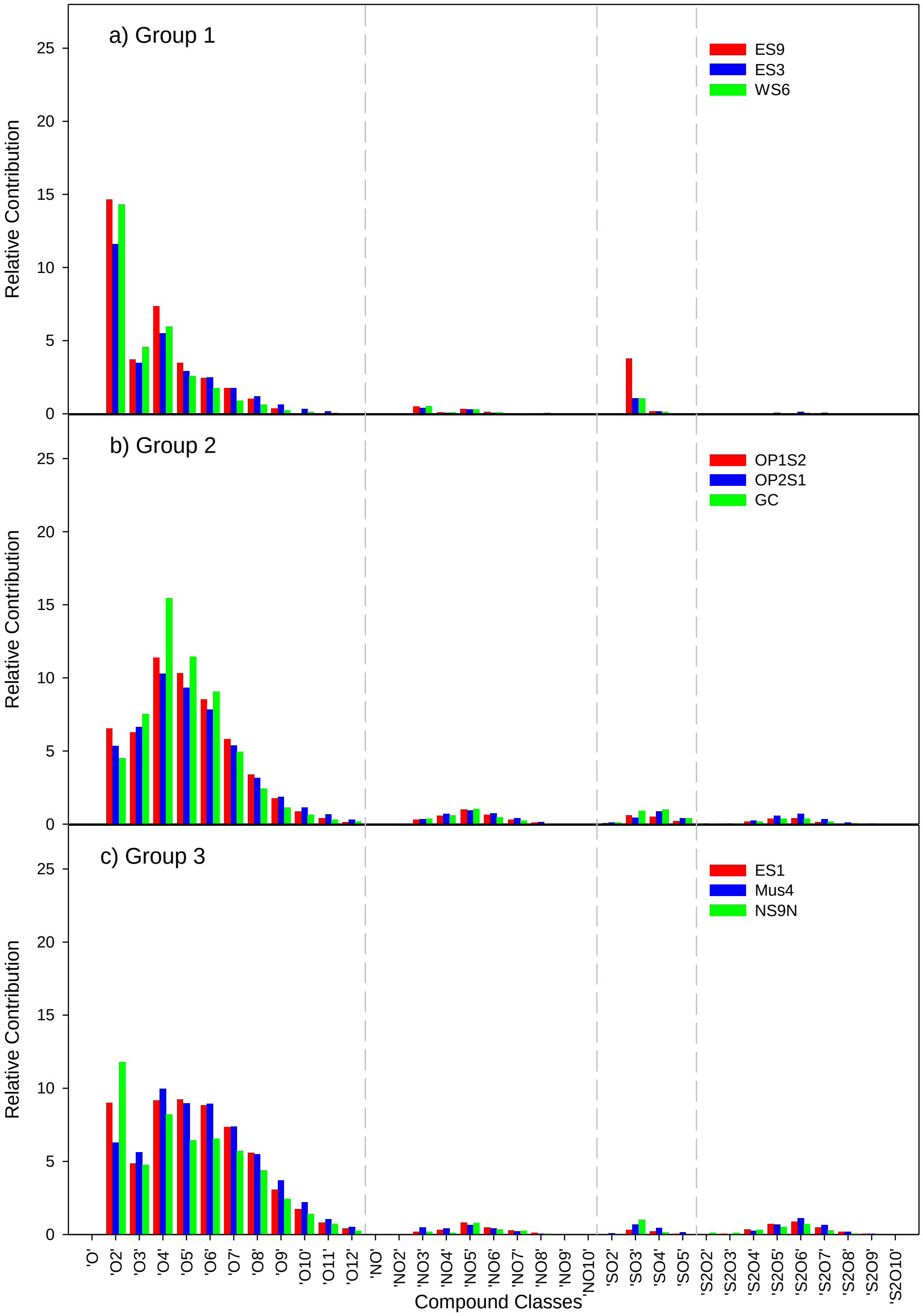

Figure 4. Distribution of dissolved organic compound classes in snow samples. The organic compositions of snow samples are presented three groups: a) Group 1 samples represented by ES9, ES3 and WS6, b) Group 2 samples represented by OP1S2, OP2S1 and GC, and c) Group 3 represented by ES1, Mus4 and NS9N.

There are also differences between the snow groups in the relative contribution of NO_n, SO_n and S_2O_n (n = 4 to 7) compounds. The NO_n (n = 3 to 7) and S_2O_n (n = 4 to 7) compounds are only present in trace amounts in Group 1, but SO_3 compounds have a much larger relative contribution. The presence of SO_3 compounds may distinguish Group 1 snow from the other snow groups (Figure 4a). The profiling results of Group 1 snow samples are similar to the far field snow samples from the Phase 1 study, in the high relative contribution of O_n (n = 2 to 4) compound classes.

Samples from Groups 2 and 3 are similar in the distributions of NO_n (n = 3 to 7), SO_n (n = 2 to 5) and S_2O_n (n = 4 to 8) compound classes (Figure 4 b & c). The main distinction between the compound classes present in Group 2 snow and Group 3 snow are the O_n (n = 2 to 4) classes, and distribution of SO_n (n = 3 to 5) classes.

Mapping the spatial distribution of the three snow groups shows that the snow samples farthest from the geographical centre (GC) tended to have Group 1 organics whereas Group 2 samples tend to be from snow located on lease areas (Figure 5). Group 2 samples do not appear to have any strong spatial patterns or distribution that suggest a single source, but instead are randomly distributed in on-lease areas. There were eight samples obtained near activities on lease areas, and four of these had Group 2 organics, one had Group 3 organics, and the remaining three had Group 1 organics. Even though the snow sample at the geographical center of oil sands mining activities has a Group 2 organic characterization, very nearby snow samples have Group 1 composition. For example, the two nearest samples (NES1 and SS1) to the GC have Group 1 compositions.

There are no clear patterns in the distribution of the Group 3 samples, which tend to be located along the main north-south transect from Fort McMurray northward through areas of mining activities.

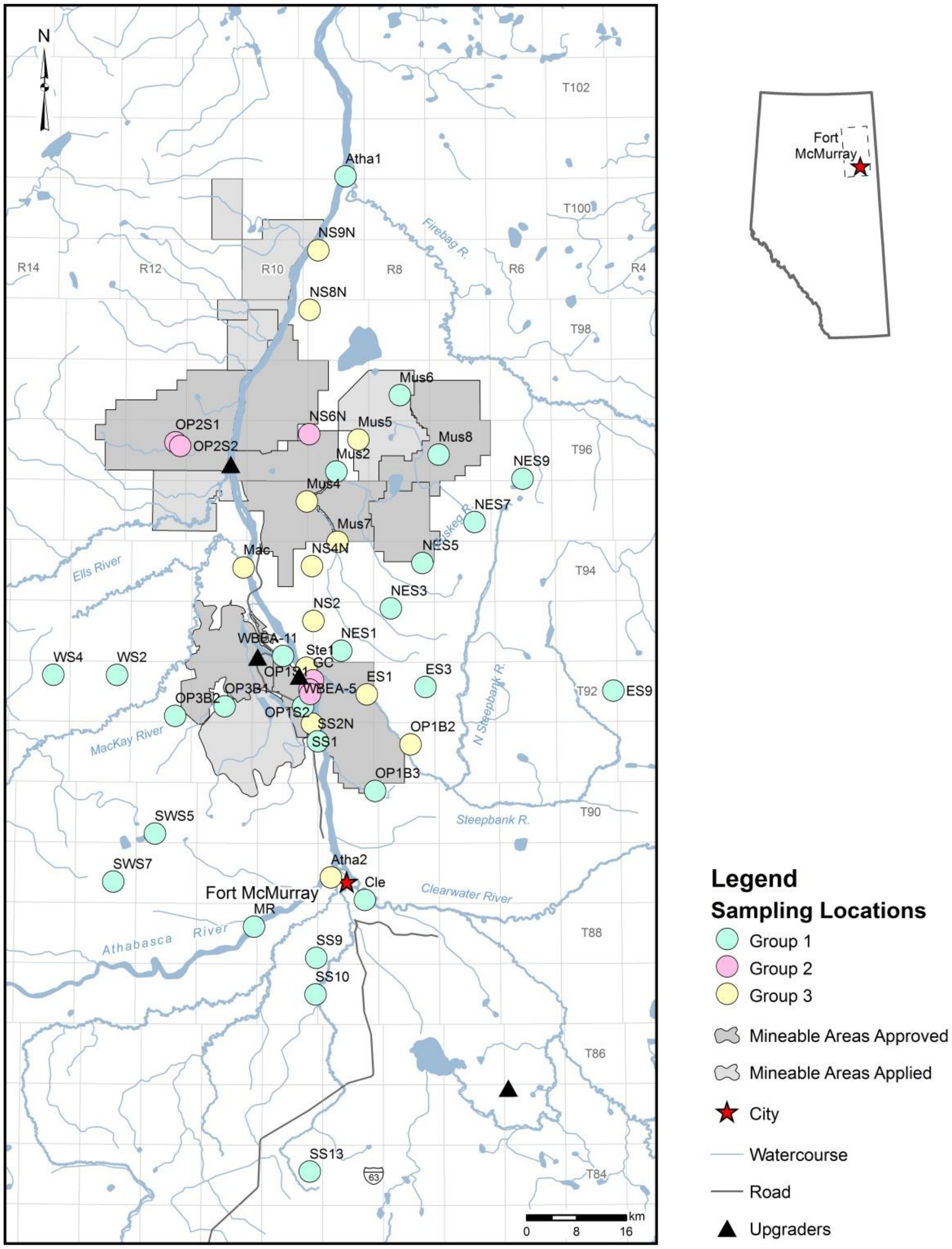

Figure 5. Map showing the locations of the Group 1, Group 2 and Group 3 snow samples.

4.2 Organic Profiles of River Samples and Comparisons with Snow

The composition of dissolved organics present in snow are compared to those measured in river samples to see if the dissolved organics present in river water resemble the dissolved organics present in the snowpack. Similarities between the two can be used to evaluate whether the dissolved organics present in snowmelt contribute significantly to the organic loading in the main stem Athabasca River and its tributaries.

The number of peaks and homologues detected in the river samples varied between months (Table 3). The average number of peaks in all of the snow samples (3,485) is lower than the average in all of the river samples (4,212).

The monthly variations included a general trend of increasing numbers of peaks from March to September. A greater number of detected peaks can indicate a greater variety in the dissolved organics present in the samples. The number of detected compounds was relatively low in March with an average of 4,058 detected compounds in all samples, ranging from 2,789 to 4,594. The highest average number of detected compounds was in June with an average of 4,347 ranging from 4,051 to 4,907. In September an average of 4,236 compounds was detected with a range of 3,677 to 4,587. Similar to what was observed for the snow samples, approximately 30% of the compounds detected in river water samples were homologues.

A plot of the PCA results for the entire snow and river dataset highlights the overall groupings in dissolved organics in the dataset (Figure 6). Snow samples are plotted as grey squares and river samples have symbols that indicate whether they are from the main stem of the Athabasca River, (red diamonds) or one of its tributaries (circles, colour-coded by tributary).

Differences in composition of dissolved organics present between most of the river and snow samples is clearly evident in the large separation along the PC1 (x-axis). Snow samples are characterized by high PC1 values, whereas most of the river samples are characterized by low PC1 values, similar to the results of Phase 1. The three groups of snow samples that were observed in Figure 3 are also evident in Figure 6. Note that the positioning of the samples in a PCA score plot depends on the samples included in the PCA. In Figure 3, which included just the snow samples, the positioning of the snow groups is different than in the PCA that includes both the river and snow samples (Figure 6).

Table 3. Summary of the number of individual peaks and homologues detected in river samples. Results of snow samples collected at the same location are also presented.

Location	Site Description	February (Snow)		March (River)		April (River)		May (River)		June (River)		July (River)		August (River)		September (River)	
		Peaks	Homo	Peaks	Homo	Peaks	Homo	Peaks	Homo	Peaks	Homo	Peaks	Homo	Peaks	Homo	Peaks	Homo
Atha1	Athabasca R u/s Firebag R	2496	992	3604	1428	3691	1495					4011	1573	3911	1577	3731	1504
Atha2	Athabasca River u/s Fort McMurray (LTRN)	3480	1554	3908	1601	3653	1421	4172	1593	4140	1549	4064	1565	3914	1503	3677	1408
Mus8	Muskeg River 27.5 km u/s Stanley Creek	3127	1380	4202	1555	4227	1609	4272	1612	4398	1630	4441	1643	4513	1688	4413	1686
Mus6	Muskeg R 11 km u/s Stanley	2782	1162	4414	1587	4540	1674					4488	1657	4583	1698	4573	1678
Mus5	Muskeg River u/s Stanley	4307	1718	4594	1688	4395	1626					4151	1483	4255	1660	4302	1674
Mus2	Muskeg R u/s Muskeg Ck	3948	1691	4314	1638	4311	1660			4348	1663			4486	1694	4587	1733
Mus4	Muskeg R u/s Jackpine Ck	3939	1608	3919	1480	4152	1450	4005	1485	4123	1554	4088	1530	4365	1600		
Mus7	Jackpine Creek 16.5 km u/s Muskeg River	3787	1403	4214	1479	4095	1505	4113	1479	4112	1458	4658	1424	4327	1471	4441	1507
Mac	McKay River at mouth	3083	1130	4305	1452	4691	1638	4605	1520	4677	1508	4579	1484	4670	1488	4412	1483
Ste1	Steepbank River at mouth	3646	1164	4182	1376	4280	1421	4748	1390	4907	1461			4429	1462	4279	1430
Cle	Clearwater u/s Waterways	2874	818	2789	733	3659	1124	4295	1294	4307	1342	4398	1323	4730	1321	4269	1291
Atha3	Athabasca River at Athabasca			3630	1247	3716	1295	4157	1497	4051	1409	3845	1318	3929	1385	3871	1320
Devil / OF	Athabasca River at Devil's Elbow			3992	1393	3934	1416	4096	1539	4191	1561	4053	1535	3963	1335	3788	1243
Mus3	Muskeg River at Gauge			4196	1440	4494	1527	4297	1469	4299	1472	4257	1459	4285	1492	4497	1631
Mus1	Muskeg creek at confluence			4344	1499	4621	1471	4371	1555	4365	1564	4511	1557	4408	1527	4446	1556
Ells1	Ells River at mouth			4268	1458	4629	1525	4581	1621	4528	1499	3048	954	4134	1481	4180	1464
Fir1	Firebag river near mouth			4107	1382	4080	1377	2388	804	4407	1525	4332	1474	4317	1495	4304	1469

Note that blank in the table indicate no sample were collected in the month at specified location.

Homo = homologues; u/s = upstream.

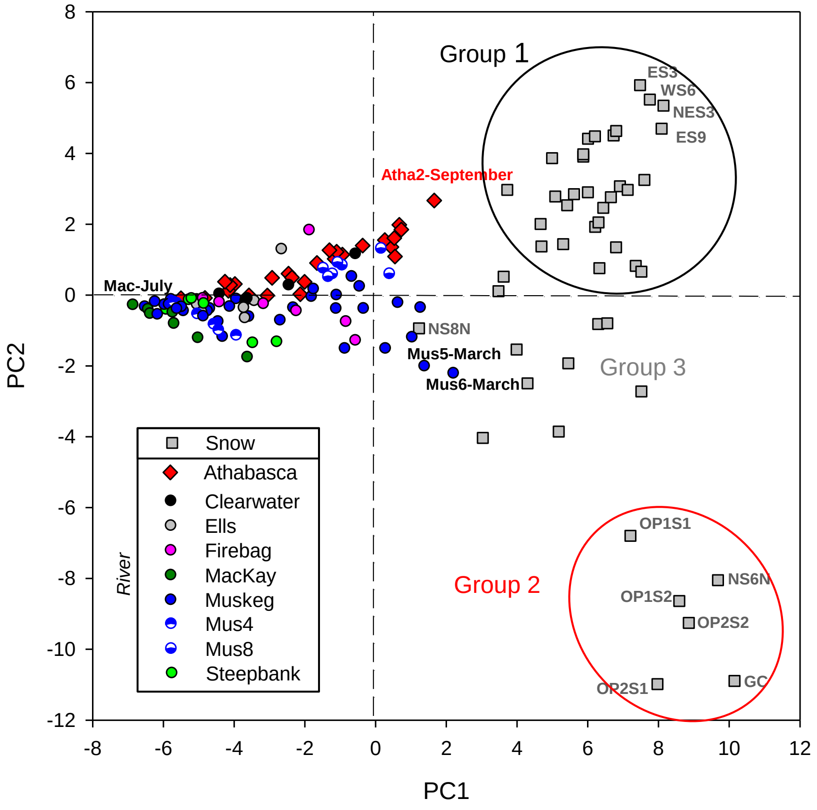

Figure 6. PCA analysis of all of the ESI-FTICR MS profiling results for snow and river samples (all months).
River samples have symbols that correspond to the main stem Athabasca (red diamonds) or from its tributaries (circles, colour coded by location).
Snow samples are grey squares with ellipses to indicate the same grouping identified in Figure 3.
PC1 accounts for 50.2% of the variation and PC2 accounts for 15.6% of the variation.

Separating the PCA results presented in Figure 6 into two figures that show the main stem Athabasca River samples (Figure 7 a) and the tributaries samples (Figure 7 b) individually, more clearly show the different types of relationships between river and snow dissolved organic compositions. The main stem Athabasca River samples have very little variation along the PC2 (y-axis) and are differentiated primarily along the PC1 (x-axis). River waters collected from the main stem Athabasca River tend to vary along a trend line towards the Group 1 snow samples (towards higher PC1 and PC2 scores) (Figure 7 a). The sample collected in September at sampling location Atha2, plots closest to the Group 1 snow composition. The sample from the mouth of the MacKay River in July (Mac-July) has the lowest PC1 score and is the most distinct from any of the snow compositions.

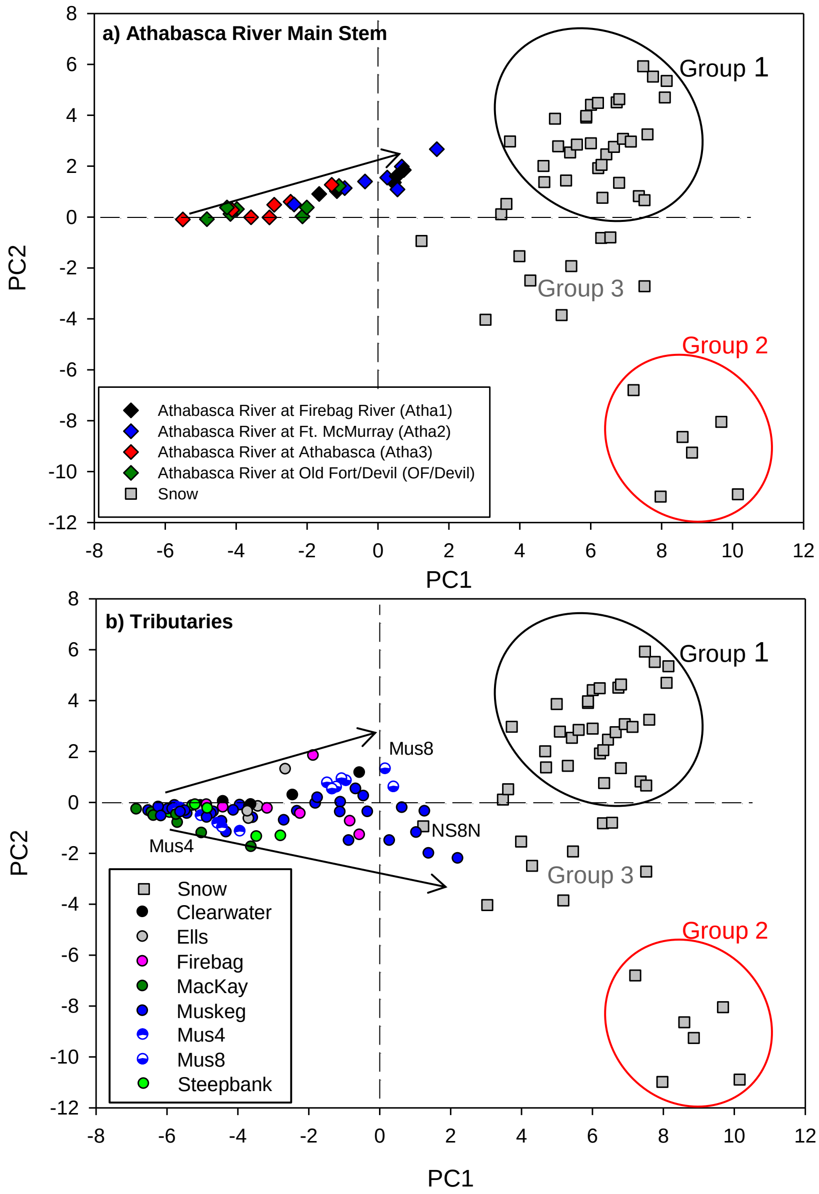

Figure 7. Main stem Athabasca River (a) and tributaries at the mouth (b) in PCA score plots. Two main trends are evident; one towards Group 1 snow, the other towards Group 2 snow.

Some of the tributaries have the occasional monthly sample that plots along the trend towards Group 1 snow (e.g., Firebag River, Ells River) (Figure 7 b). The only tributary sampling location that had a consistent trend towards Group 1 snow organic compositions was the Mus8 sampling location, which was at the headwater of the Muskeg River. The rest of the tributary samples plot along a trend line towards Group 3 or Group 2 snow.

Runoff (e.g., snowmelt) generated in a given watershed will follow the topographic gradient until it reaches a stream, then the water will follow the stream network from the headwaters towards the mouth. The samples from the headwaters of the Muskeg River (Mus8) indicate at this location the river water shows similarities with Group 1 snow, whereas at the downstream location (Mus4) the river water shows similarities with Group 3 or Group 2 snow.

The snow sample collected at NS8N plots separately from some of the other snow samples, and more closely resembles river water samples collected from the Muskeg River from two of the upstream sites (Mus5 and Mus6) collected in March 2013. The compound class distribution for these snow (NS8N) and river samples (Mus5 and Mus6) (Figure 8) highlight these similarities. The relative contributions of O_n (n = 3 to 12) compounds are very similar in the snow and river samples except for the O_2 compounds. The composition of snow at NS8N is different from typical Group 1 and Group 2 snow samples in that S_2O_n (n = 4 to 10) compounds were detected, which may contribute to the similarity between the NS8N snow samples and Muskeg River water samples.

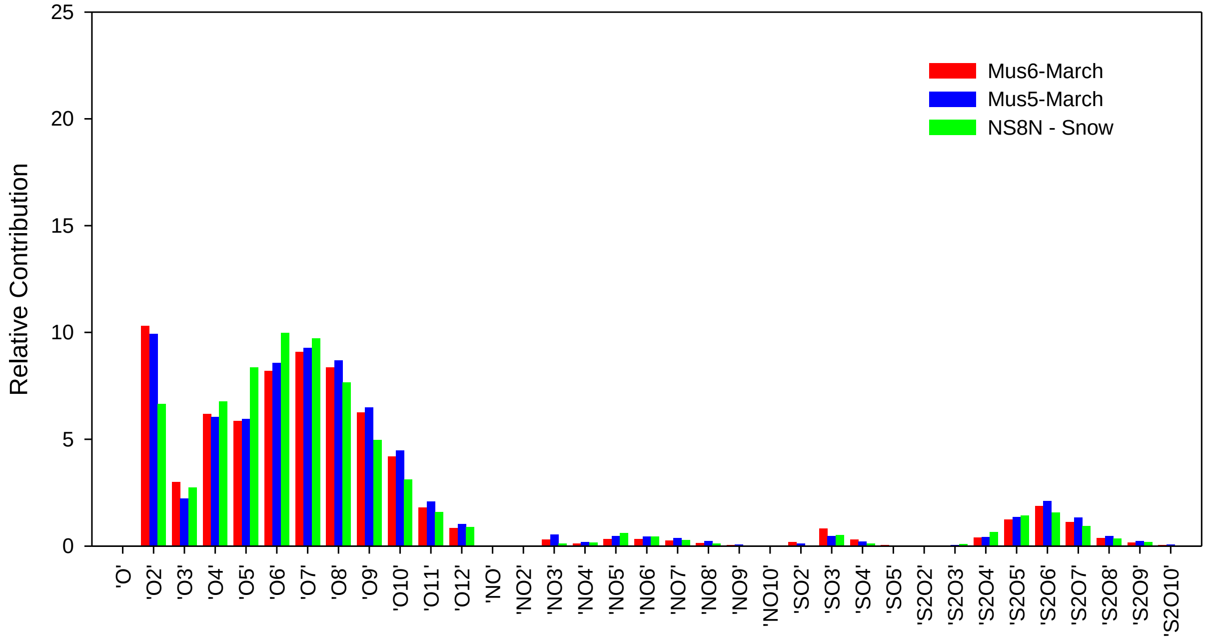

Figure 8. Distribution of compound classes in three samples showing similarity between the snow sample at this location and some river samples.

Better understanding of the differences in dissolved organics present in snow and river samples can be achieved by visual comparison of their KMD plots (Figure 9). Samples representative of a typical tributary sample (Mac-July), an Athabasca River sample (Atha2-Sep), a Group 1 snow sample (ES9) and a Group 2 snow sample (represented by GC) were chosen to represent the most distinct endmembers within these categories, based on the PCA plot (Figure 6).

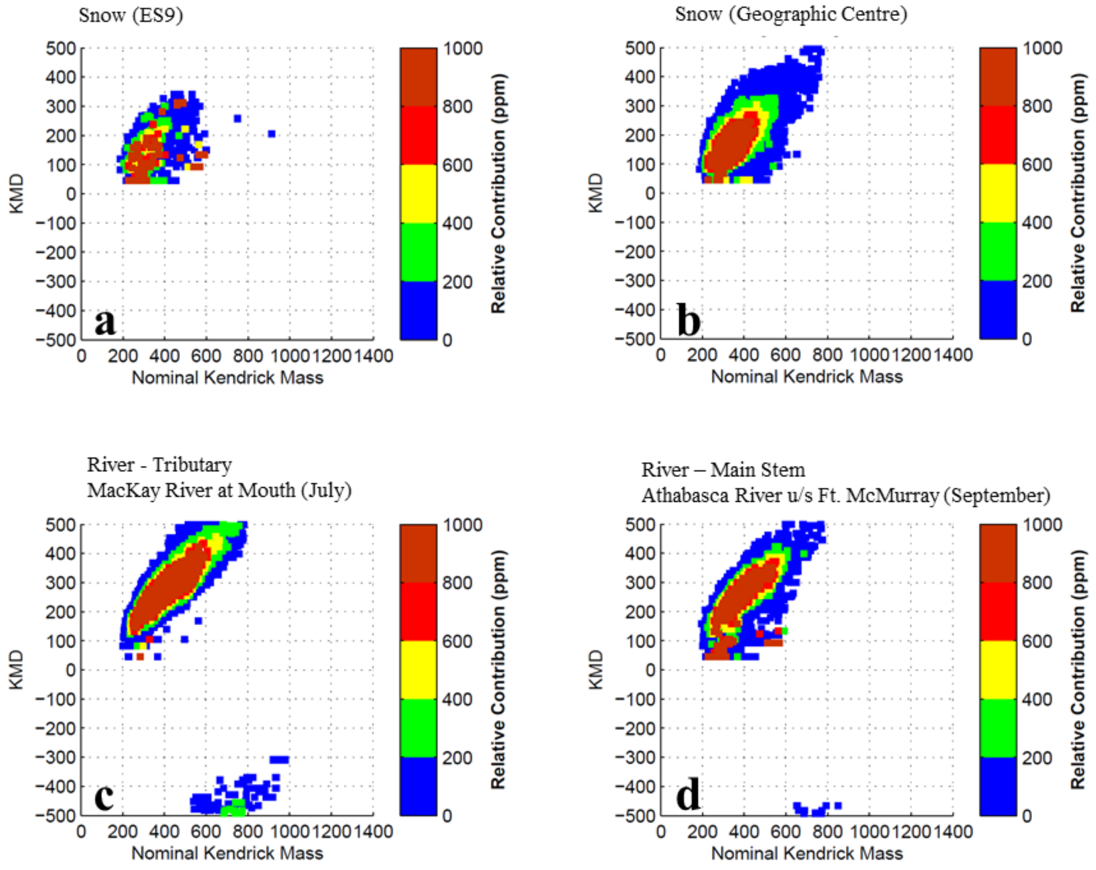

Figure 9. Kendrick plot showing organic composition of representative snow (a) ES9 (Group 1), (b) GC (Group 2), and river samples (c) Mac-July (tributary) and (d) Atha2-September (main stem Athabasca).

The river samples are characterized by a bullseye pattern indicating high relative contributions of organic compounds with a nominal Kendrick mass range (x-axis) between 200 and 600 Da. These high abundance species also have a fairly wide range of KMD values (y-axis) from 100 to 400. In contrast, the most abundant species in snow samples generally have a much smaller range in compound mass and KMD values. Compound mass values in the snow samples range from approximately 200 to 400 Da and KMD values vary between approximately 100 and 200. Differences between individual snow samples are also evident. The snow from GC has a solid bullseye pattern, consistent with the presence of a large number of homologues (1,685), but the snow from more distant locations (ES9, located approximately 50 km from GC) has a more irregular pattern consistent with fewer homologues (633).

The differences between snow and river samples, and variations within these groups, can also be compared using compound class plots (Figure 10). To give a better feel for the variability between different types of samples, compound class plots for three samples are included for each water type. River samples for May and September are presented, based on the endmembers observed in the PCA (Figure 6). Representative samples were selected to maximize the difference between the different categories.

The differences in compound classes between the various snow groups (Group 1 to 3) has already been discussed in Figure 4, but are included in Figure 10 (a, b, c) so that they can be compared with the results from different river samples. Figure 10 also includes compound class distributions for typical Athabasca River and tributary samples, for contrasting hydrological periods (spring freshet in May and low flow in September).

In general, the Athabasca River samples (represented by Atha2, Atha3 and Devil/OF) (Figure 10 d, f) and tributary samples (represented by Mac, Mus3, and Fir1) (Figure 10 e, g) are dominated by O_6 to O_8 classes in oxygen containing compounds. The Athabasca River samples differ from the tributary samples in that O_2 class compounds tend to have a higher relative contribution in the main stem than in the tributaries, consistent with the organic profiling results for the Athabasca River conducted during Phase 1. The main stem Athabasca River samples also contained some SO_3 compounds that were not detected in the tributary samples. The distribution of compound classes in the river samples did not change significantly between May and September, but the dominance of O_2 classes became more pronounced in September, particularly in the Athabasca main stem sample, but also to a lesser degree in some tributary samples (e.g., Fir1).

Comparing the distribution of compound classes in snow (Figure 10 a, b, c) with those in river samples (Figure 10 d, e, f, g) shows the compound classes responsible for the distinctions in the PCA (Figure 6). The dominant oxygen containing compounds in Group 1 snow are O_2 compound classes, and O_4 and O_5 compound classes in Group 2 and 3 snow (Figure 10 a, b). In rivers, with the exception of some Athabasca River samples with high relative contributions of O_2 compound classes, the dominant oxygen containing compounds in the river samples are O_6 to O_8 compounds. River samples also have a greater relative contribution S_2O_n ($n = 4$ to 9) compounds whereas SO_n ($n = 3$ to 4) compounds have a greater relative contribution in snow samples.

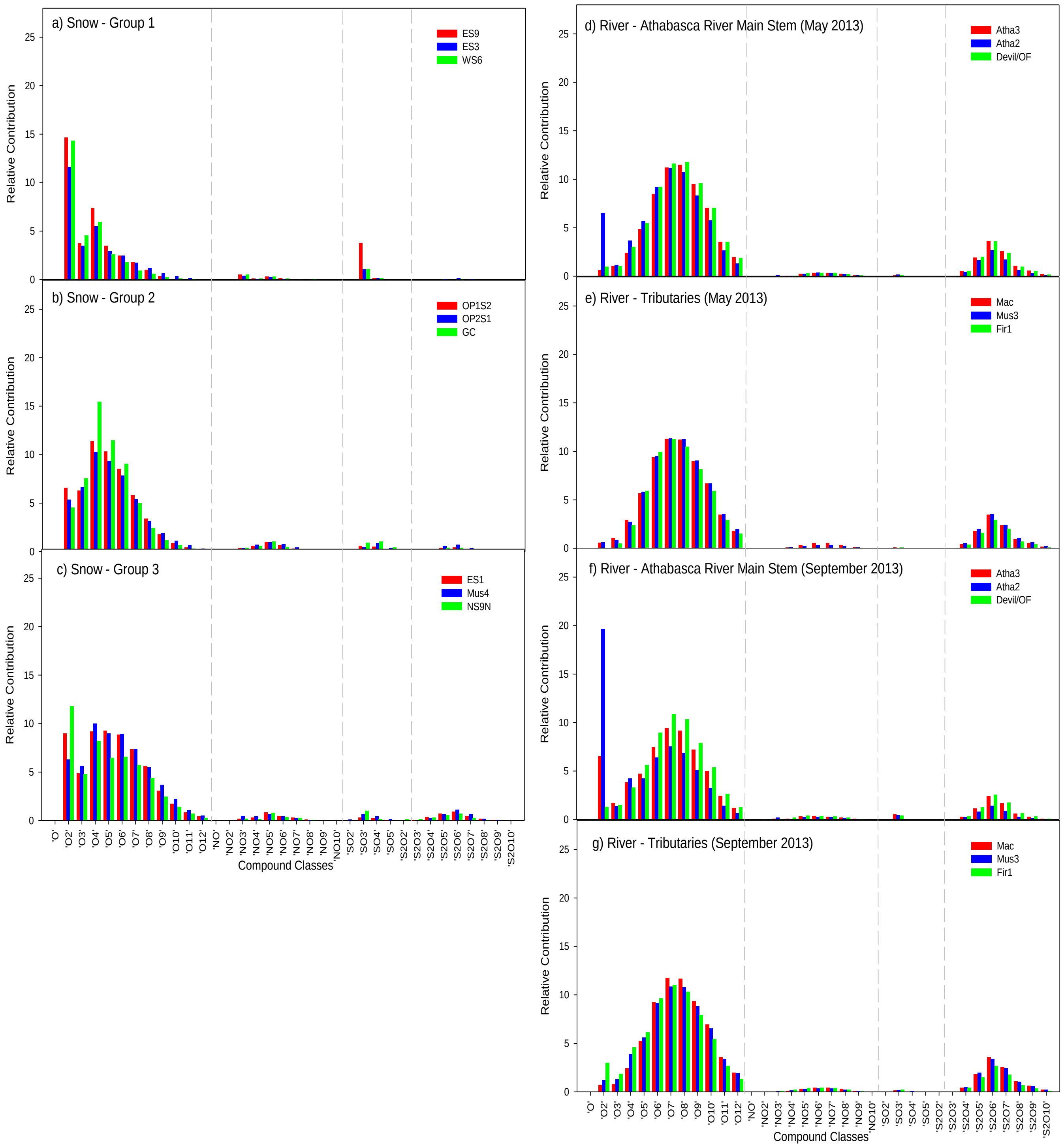

Figure 10. Compound class plots.
(a) Group 1 snow
(b) Group 2 snow
(c) Group 3 snow
(d) the Athabasca River main stem in May
(e) tributaries in May samples
(f) from the Athabasca River main stem in September, and
(g) the tributaries in September.
The river sampling locations have monthly data available, so the results from May and September are presented to show the temporal variability.

4.3 Comparing Organic Profiles at Snow-River Co-Location Sites

There were 11 sites where a snow sampling location was co-located with a river sampling location. At these locations, snow was sampled in February, and the nearby river site was sampled monthly. These co-location sites were thought to provide the most direct comparison of organic compositions in snow and river water on a local scale.

The results shown in Figure 6 were filtered to just show the co-located snow and river samples to make it easier to compare the snow and river organic profile at a single location (Figure 11). The data in Figure 11 are from the same PCA, but only show the snow (square) and river (diamond, Athabasca main stem; circle tributaries) for the 11 co-location sites.

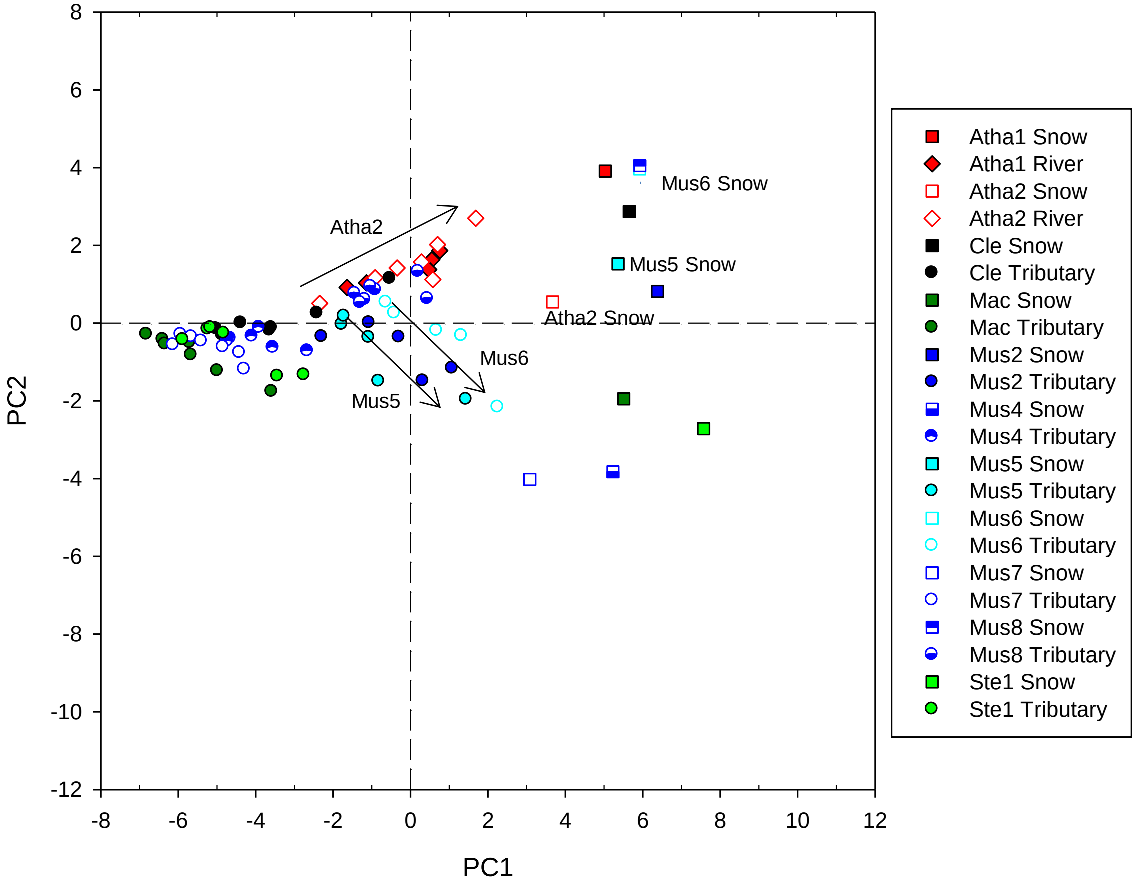

Figure 11. PCA score plot for the 11 snow and river co-location sites.
For each location the snow sample (squares) obtained in February, is shown with all of the monthly river data (diamonds, Athabasca main stem; circles tributaries) available for the same location
Sites where river samples do not become similar to adjacent snow sampling location are identified.

Comparing the composition of dissolved organics in river samples with the snow sample collected at the same location (Figure 11), shows the large separation along PC1 between river samples and the co-located snow sample that was evident in the complete snow and river dataset (Figure 6). The co-location dataset shows that in most cases river samples from a given location vary over time along a trendline towards a similar composition as the co-located snow sample. However, in some cases the river samples do not plot along a trendline towards the co-located snow sample (e.g. Mus5 and Mus6). Even though the rivers samples from Mus5 and Mus6 show some similarity with Group 1 snow (Figure 6), the river samples from Mus5 and Mus6 do not resemble the closest snow samples (snow from Mus5 and Mus6) (Figure 11). The river samples from Mus5 and Mus6 will include not only local runoff, but will also integrate runoff from upstream portions of the watershed. Similarly for the snow and River samples from Atha2, the river samples plot along a trendline towards Group 1 snow (Figure 6), but not necessarily the snow sampled from Atha2 (Figure 11).

This highlights the challenge in characterizing the linkages between snowmelt and river samples. Because river samples integrate not only runoff received at that immediate location, but all upstream locations within the watershed, sampling and interpretation of the data must also consider the position of the river sample within the watershed. Similarly, on a temporal scale, sampling different times over the open water period in a river may be necessary to characterize organics present in the river, since there will be differences in composition depending on whether the sample is from the freshet or baseflow.

4.4 Temporal Changes in River Organics

Temporal variations in the organic profile of river samples can be examined more closely by separating the PCA results shown in Figure 6 by month (Figure 12). In March and April, before the spring freshet, the organic composition of river water in the region appeared to vary significantly from site to site (Figure 12 a, b). In May and June, the organic profiles of river samples became more similar to each other and more distinct from snow (Figure 12 c, d). In August and September, the organic profiles of the main stem Athabasca River water and the tributaries become more similar to the snow organic profiles (Figure 12 e, f).

Temporal changes in organic profiles are more pronounced in the main stem of the Athabasca (Atha2) River than in the tributaries (Mac) (Figure 13). The temporal changes in the Athabasca include variations in the relative contribution of O_6, O_7 and O_8 compound classes. The relative abundance of O_2 to O_4, NO_3 and SO_3 compounds appears to increase over the open water season while the relative abundance of other O_n compounds, NO_5 to NO_8 and S_2O_n compounds decrease from May to September.

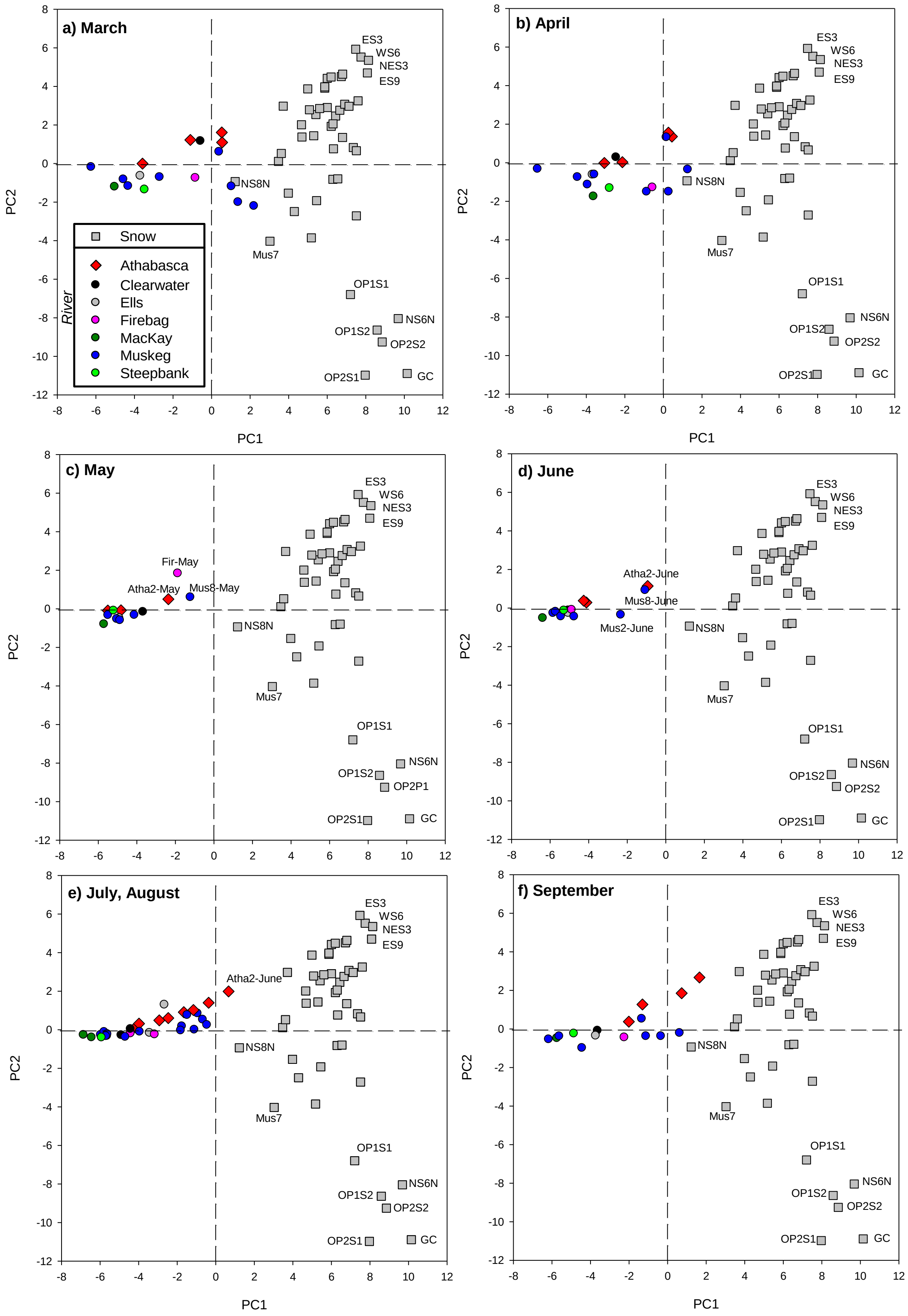

Figure 12. Monthly examples (based on same PCA as Figure 6) to show temporal changes in organic profiles in river samples.
The same snow data are shown on each for reference.

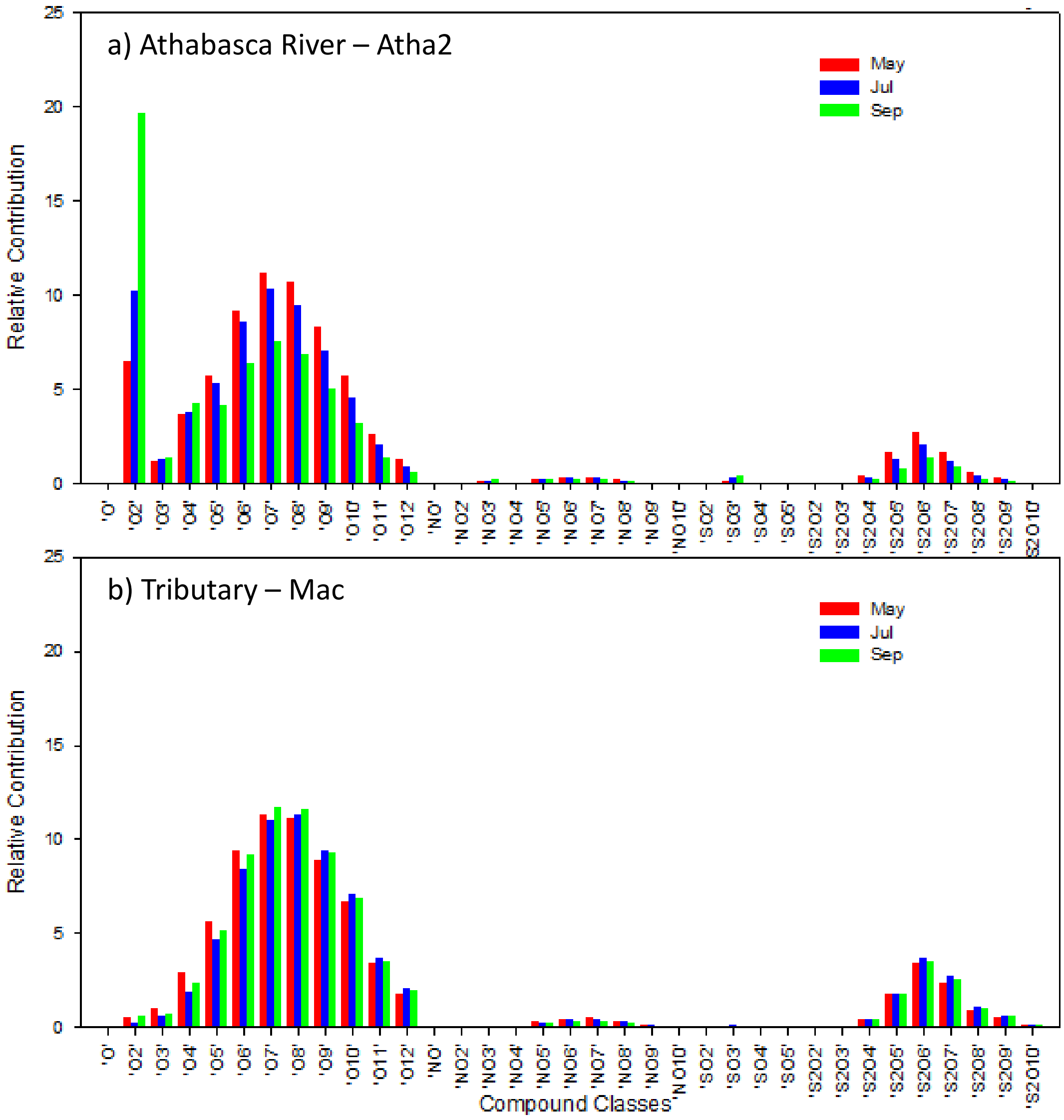

Figure 13. Temporal changes in relative abundance of organic compounds in (a) Athabasca River (main stem) (Atha2) and (b) tributary (Mac).

4.4.1 *Temporal Changes in River Discharge*

Understanding the hydrology of the Athabasca River main stem and its tributaries important for interpreting the changes in surface water organics over the course of the open water season.

The hydrograph data from the Athabasca River at Fort McMurray and the Muskeg River at Gauge presented in Figure 2 should be representative of most of the river samples included in our survey and can be used to help interpret the temporal variations in the river organic compositions. The 2013 open water season included two peaks in the hydrographs for the Athabasca River and the Muskeg River (Figure 2) and the river organic profile results are for samples from the under ice, low flow period, peak river flow, and from the falling limb of the hydrograph. The samples collected in March and April 2013 (Figure 12 a, b) are from a low flow period, when the rivers would still be ice covered and where most of the inputs would be from groundwater inputs (baseflow). The May and June river samples were collected during periods of peak discharge in the Athabasca River and tributaries. The July and August samples are from the falling limb of the hydrograph when the contributions of snowmelt and summer precipitation are decreasing. The September sample should be representative of a period of low flow in the river, but prior to any ice cover.

4.4.2 *Temporal Changes in River Stable Water Isotope Labelling*

The SWI composition ($\delta^{18}O$ and $\delta^{2}H$) of river samples can be used to identify the hydrological processes driving the seasonal variations in river discharge discussed above. SWI signatures provide a useful means to differentiate snowmelt from river water because snow is generally more depleted in $\delta^{18}O$ and $\delta^{2}H$ than surface water sources. Here SWI variations in river water are used to identify when snowmelt arrives at the different river sampling locations.

The stable isotope signatures of snow and river samples collected during the 2013 sampling program are shown in Figure 14, with data from regional lake surveys for comparison (Cumulative Environmental Management Association (CEMA) field campaign in 2013). $\delta^{18}O$-$\delta^{2}H$ signatures of snow samples are isotopically distinct from surface water samples (Figure 13). The isotopic composition of snow samples obtained during the 2013 sampling program vary from -25.60‰ to -29.03‰ in $\delta^{18}O$ (between -164.2‰ and -199.4‰ for $\delta^{2}H$) with average values of -27.14‰ and -206.7‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (as indicated by the red star in Figure 13). In the $\delta^{18}O$-$\delta^{2}H$ space, snow samples plot along the Local Meteoric Water Line (LMWL) suggesting meteoric origin. Summer precipitation, another important component of water resources in the region, is also of meteoric origin but with more enriched isotopic signatures. Although summer precipitation was not sampled for this report, its normal range of variation is indicated in Figure 14.

The sample collected from the geographic center (GC) of the study area is the most isotopically enriched of the snow samples ($\delta^{18}O$ = -25.60‰ and $\delta^{2}H$ = -199.9‰). This is interesting because a pattern of decreasing isotopic values with increasing latitude is generally observed in northern hemisphere (Dansgaard 1964). Although the overall range in latitudes in the snow samples in this survey is fairly narrow, this pattern is not observed in the snow samples collected for this study: the most isotopically enriched sample, GC, and the most isotopically depleted sample (E5; $\delta^{18}O$ = -29.03‰ and $\delta^{2}H$ = -206.7‰), occur at approximately the same latitude.

Compared to snow collected in the region, the isotopic compositions of river water are enriched with a range of -14.65‰ to -20.93‰ in $\delta^{18}O$ (between -123.13‰ and -160.3‰ in $\delta^{2}H$) and tend to plot along a Local Evaporation Line (LEL). Variations along the LEL reflect how much evaporation the sample has undergone, with samples further along the LEL indicating more significant evaporation, and therefore more enriched isotopic signatures.

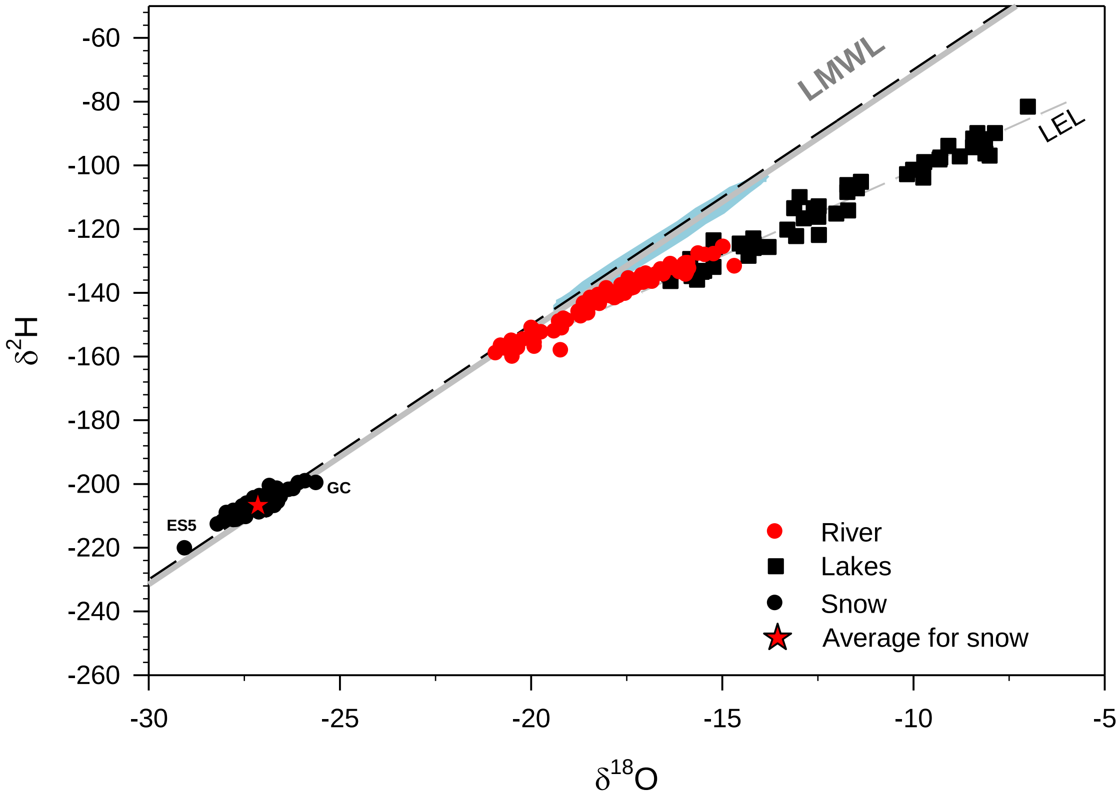

Figure 14. δ^{18}O-δ^2H signatures of snow, river water and lake water in 2013.
Clear distinctions between snow, river and lake waters can be used to label sources of water.
The red star indicates the average isotopic composition of snow based upon these samples. The grey solid line and black dash line indicate Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL), respectively. The grey long dash line shows the Local Evaporation Line (LEL). The light blue shading indicates the range for summer precipitation in the region.

The differences in isotopic signatures of snow and river samples can be used in conjunction with temporal variations in river discharge and isotopic signatures in individual rivers (Figure 15) to identify when snowmelt contributes to river discharge. The δ^{18}O signatures in tributaries at the main stem station generally become depleted in early May coinciding with the peak of river discharge (Figure 2). The depleted isotopic signatures in the Athabasca River main stem and its tributaries in May appears to indicate increased inputs of isotopically depleted snowmelt at a time when air temperature generally increases above zero and snowpack begins to disappear.

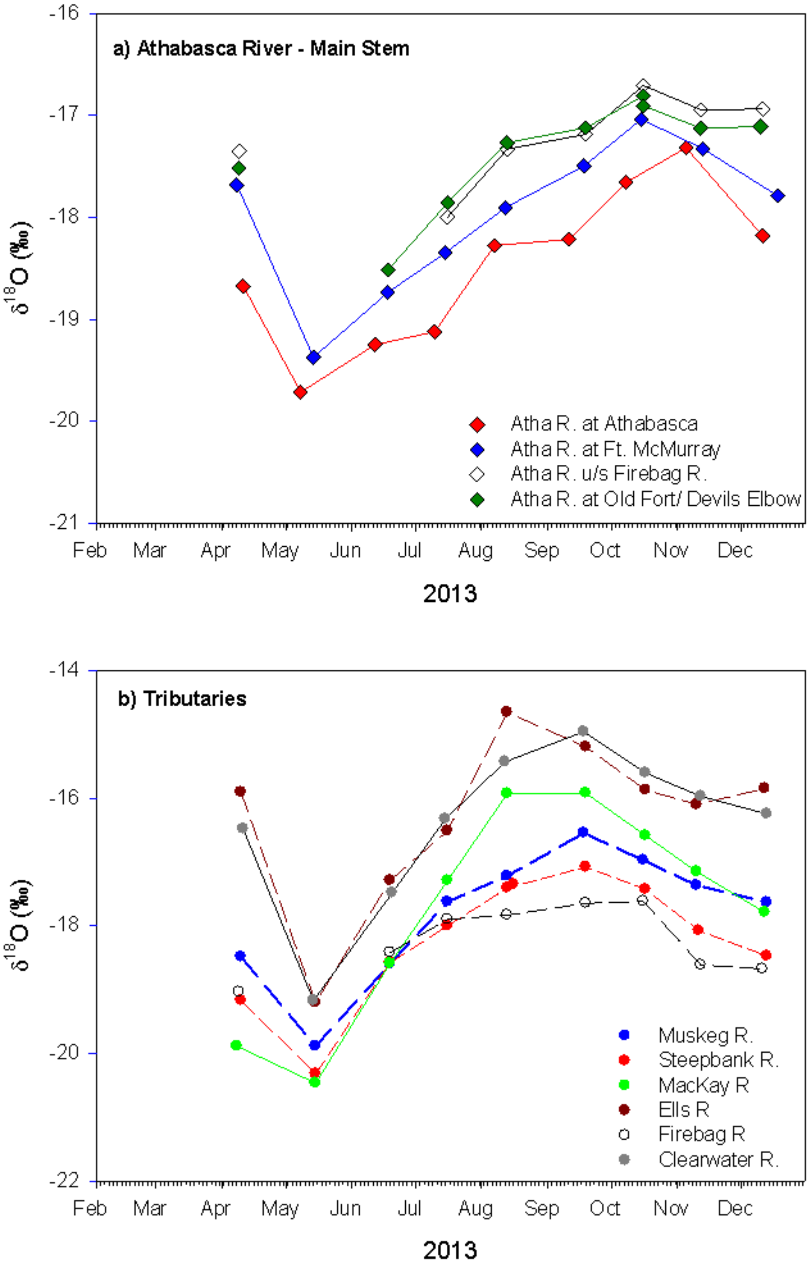

Figure 15. Temporal changes in $\delta^{18}O$ in river water from Apr-2013 to May-2014 in (a) tributaries and (b) main stem of Athabasca River.
Isotopic signatures in the main stem tend to be lower than signatures from tributaries. Isotopic compositions of tributaries vary between -20.47‰ and -14.65‰ in $\delta^{18}O$, while values from main stem vary between -20.90‰ and-16.71‰ $\delta^{18}O$.

Unlike the trends observed for the May hydrograph peak, the peak in mid-June (Figure 2) does not coincide with depleted isotopic signatures (Figure 15). Instead isotopic signatures continued to increase until early September (Figure 15). This indicates that snowmelt cannot be the main component of the hydrograph peak in mid-June. Instead, water sources with enriched isotopic signatures, such as summer precipitation (Figure 14) are more likely to be the major contributor. In addition, evaporation during the open water season also contributes to the enrichment of $\delta^{18}O$ in river water.

The shift towards more negative $\delta^{18}O$ and $\delta^{2}H$ values in May indicate the arrival of snowmelt to the river channels at this time (Figure 15). The snowmelt would have contributed to increased flow in both the tributaries and the main stem with peak flow occurring around May 10th 2013. In June 2013, river discharge reached a new maximum (peak in hydrograph in Figure 2), however this second peak must also include a large component of summer precipitation as indicated by the enriched isotopic signature. This information provides a clear timeline of snowmelt impacts to the river and aids in the interpretation and discussion of seasonal changes in organic compositions of river water.

4.4.3 *Role of Snowmelt in Temporal Changes in River Organics*

Combining the hydrometric data on river discharge with information about the contributions of snowmelt to that discharge from SWI can be used interpret some of the temporal changes in organic profiles found in the Athabasca River and tributary samples.

In March and April, when the rivers were still under ice, the organic compositions of river water in the region varied significantly from site to site (Figure 12 a, b). The differences in organic compositions in river samples during this period may reflect differences in baseflow organics specific to each watershed. After the main spring freshet in May, and continuing through June when the second peak discharge period occurred, river water across the region became more similar in organic composition (Figure 12 c, d). Even though the very negative $\delta^{18}O$ and $\delta^{2}H$ values measured in river water in May indicate that snowmelt is the main component of discharge during this period, the organic composition of river water sampled in May is not similar to the composition of organics detected in the snow (Figure 11 c). This suggests that, when the peak of the snowmelt was passing through the system, the majority of the dissolved organics in the river did not originate directly from the snowpack.

In June, during the second and largest peak in river discharge, the $\delta^{18}O$ and $\delta^{2}H$ values indicate that summer precipitation contributed significantly to the increased river discharge. The dissolved organic present in river water during June remained similar to each other, and distinct from snow. After the main peak discharge periods, when river discharge receded back to low flow conditions (July to September, Figure 11 e, f), the dissolved organics in the river water samples became more similar in terms of organic composition to the snow sampled in February. This period is also when groundwater inputs become more important in maintaining streamflow (the lack of groundwater data does not allow this endmember to be separated). There are some ESI-FTICR MS data for saline groundwater discharges to the Athabasca River (Gibson et al. 2011), but these samples were not extracted using the same liquid-liquid extraction which was only recently developed, and are thus not directly comparable. There were some specific river samples, such as Fir1-May, Mus8-May, Mus8-Jun, Mus2-Jun, that plot as anomalies compared to other months at those locations, and may be due to site-specific conditions (e.g., activity within the watershed, extreme precipitation events).

Kelly et al. (2009) measured elevated concentrations of dissolved and particulate PAHs in the snowpack near oil sands upgrading facilities and elevated concentrations of dissolved PAHs in tributaries downstream of development and attributed these to oil sands development. The elevated dissolved PAH concentrations in tributaries in watersheds with oil sands development were more specifically linked to land disturbances within watersheds with recent mining activities. Their sampling did not include any river sampling during the spring freshet, but they suggest that the release of the organics present in the snowpack during the spring freshet could also be a significant source of organics to rivers and tributaries. They identified spring snowmelt and washout during precipitation events as important unknowns in understanding how organics can reach aquatic ecosystems in the Athabasca region. While our results are for polar dissolved organic compounds and not for PAHs, our dataset do not show clear evident to suggest that the snowpack organics are a dominant source of organics present in the Athabasca River or its tributaries during the peak of the spring freshet (May).

5 SUMMARY

The results of the ESI-FTICR MS analysis (ESI(-) mode) of 47 snow samples located within a 100 km radius from the geographical center (GC) of oil sands mining activities identified three main groups in terms of dissolved organic profiles:

- Group 1 snow samples tended to have O_2 as the dominant compound class, followed by the O_4 class in relative contributions. In Group 1 samples there is a pattern of decreasing relative contribution with increasing n numbers, for compounds containing more than 6 oxygens (O_n, $n \geqq 6$). Group 1 snow also had SO_n, S_2O_n (n = 4 to 7), NO_n (n = 3 to 7) and S_2O_n (n = 4 to 7) compounds detected in trace amounts, while SO_3 compounds are noticeably abundant. Most of the Group 1 samples were from the sampling locations farthest from development or any industrial activities, but there were also Group 1 samples located near Group 2 samples.
- For Group 2 snow, the most abundant class is the O_4 class and there is a decreasing pattern in the relative contribution O_4 to O_{12} classes. These samples included compounds containing nitrogen (NO_n) and sulphur (SO_n and S_2O_n) elements that may be the key to differentiating between snow groups. The six Group 2 snow samples included one sample from the GC, and five samples from on-lease areas near mining activities.
- Group 3 included snow samples that did not plot in the main clusters defined for Group 1 or Group 2. This group differed from Group 2 along the PC2 axis, and from Group 1 along the PC1 axis. The 13 Group 3 samples were from a variety of locations including near the city of Fort McMurray and near lease areas. There are no clear patterns in the distribution of the Group 3 samples, however they tend to be located along the main north-south transect from Fort McMurray northward through areas of mining activities.

The ESI-FTICR MS analysis of the 110 river samples (84 tributary samples and 26 main stem Athabasca River samples) identified overall differences between the compositions of river water and snow and some subtler differences within the river samples.

- The main distinction between the dissolved organics present in river water and snow are that river samples are dominated by O_6 to O_8 classes in oxygen containing compounds, and contain a greater relative contribution S_2O_n (n = 4 to 9) than snow.
- The Athabasca River samples differ from the tributary samples in that O_2 class compounds tended to have a higher relative contribution in the main stem than in the tributaries. The main stem Athabasca River samples also contained some SO_3 compounds that were not detected in the tributary samples.
- The PCA for the river data shows some groupings specific to watershed and sampling location.

Comparing the ESI-FTICR MS results for all of the river samples with the snow results show the different types of relationships between river and snow dissolved organic compositions. The monthly river samples collected from the main stem Athabasca River and from the tributary sampling location at Muskeg 8 tend to have organic compositions that become more similar to Group 1 snow samples over the open water season. The other tributary sampling locations tended to have dissolved organic compositions that become more similar to Group 2 or Group 3 snow compositions over the open water season.

All of the river results showed seasonal variations in dissolved organics, with larger variations in Athabasca River than in tributaries. The distribution of compound classes in the river results did not change much between May and September, but the dominance of O_2 classes becomes more pronounced in September, particularly in the Athabasca main stem site. Potential causes for some of the temporal variations in river organic composition were identified using hydrometric and SWI results.

- Before the spring freshet (March and April), while the rivers are still under ice, the different river sampling locations have distinct organic profiles. The greater variability in organic profiles for river samples during this period, may reflect distinct dissolved organic profiles specific to baseflow in each watershed.
- During the spring freshet (May) the $\delta^{18}O$ and $\delta^{2}H$ results show that this discharge peak was comprised primarily of snowmelt. The composition of dissolved organics at the different river sampling locations became more similar.
- During the second peak in river discharge (June) the $\delta^{18}O$ and $\delta^{2}H$ results show that this discharge peak had a much larger contribution of summer precipitation than in May, and the dissolved organic composition of the river samples remained similar to each other as was described for May.
- During the falling limb of the hydrograph (July and August) and during the low flow period starting in September, the composition of organics in the river samples shows

the greatest similarities with the snow profiles. The organics in river samples during this period show more variations between watershed and sampling location similar to what was observed in the March and April samples.

The differences between the dissolved organics present in snow and those detected in river water when the bulk of the snowmelt was flowing through the river (May-June), indicate that the direct transfer of organics deposited onto the snowpack to rivers, is not a major source of organics during the peak of the spring freshet. The months with the greatest similarity between snow and river organic compositions are periods of low river discharge (March, April, September) which could indicate possible delays between when atmospheric organics are released from the snowpack and when they transport to rivers, or that some of the organics present in snow are similar to organics that characterize baseflow.

The results of this comprehensive profiling of snow and river water suggest that nitrogen and sulphur containing compounds may be the most useful in improving our understanding of the sources and fate of atmospherically derived organics in the oil sands region.

There are still some endmembers that need improved organic characterization, including baseflow (groundwater inputs) to the Athabasca River and its tributaries. Characterizing the dissolved organics that can be directly attributed to natural and anthropogenic atmospheric sources of organics (e.g., forest fire, stack emissions, fugitive emissions) is challenges, are also needed[3].

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[3] For information on using satellite imagery to track wildfire smoke and industrial emissions in the AOSR see Marey, H.S., Z. Hashisho and L. Fu, 2014. Satellite Remote Sensing of Air Quality in the Oil Sands Region. OSRIN Report No. TR-49. 104 pp. http://hdl.handle.net/10402/era.38882

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7 GLOSSARY

7.1 Terms

Atmospherically-Derived Organics

Organics that originate from atmospheric deposition.

Baseflow

The portion of streamflow that is not due to surface runoff due and is primarily groundwater inputs to the river. This is the main source of river discharge during under-ice conditions in winter months in northern climates.

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.

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.

Main Stem

In hydrology, a main stem is the primary downstream portion of a river. It is also known as the "trunk". Tributaries are smaller rivers or streams that flow into the main stem.

Polar Organics

Polar organics: refer to organic compounds with differences in electronegativity between atoms in a bond creating an unequal distribution in their charge. This results in one end of the compound having a slightly positive charge and the other a slightly negative charge. Several function groups can lead to polarity within an organic compound, including: amide ($-CONH_2$), carboxyl (-COOH), and hydroxyl (-OH) groups. Alkanes (-H; hydrocarbons) are commonly considered as non-polar compounds.

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.

Spatial

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

Temporal

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

Tributary

A small river or stream that flows into a larger river. The larger river is the main stem.

7.2 Acronyms

AESRD	Alberta Environment and Sustainable Resource Development
AITF	Alberta Innovates – Technology Futures
AOSR	Athabasca Oil Sands Region
CEMA	Cumulative Environmental Management Association
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 Centre
KMD	Kendrick Mass Defect
LEL	Local Evaporation Line
LLE	Liquid – Liquid Extraction
LMWL	Local Meteoric Water Line
NA	Naphthenic Acids
OSRIN	Oil Sands Research and Information Network
PAH(s)	Polycyclic Aromatic Hydrocarbon(s)
PCA	Principal Component Analysis
QA/QC	Quality Assurance/Quality Control
RAMP	Regional Aquatic Monitoring Program
RC	Relative Contribution
SEE	School of Energy and the Environment
SI	Système international d'unités
SWI	Stable Water Isotope
V-SMOW	Vienna Standard Mean Ocean Water

WQM	Water Quality Monitoring
WSC	Water Survey Canada

APPENDIX 1: Quality Assurance/Quality Control (QA/QC)

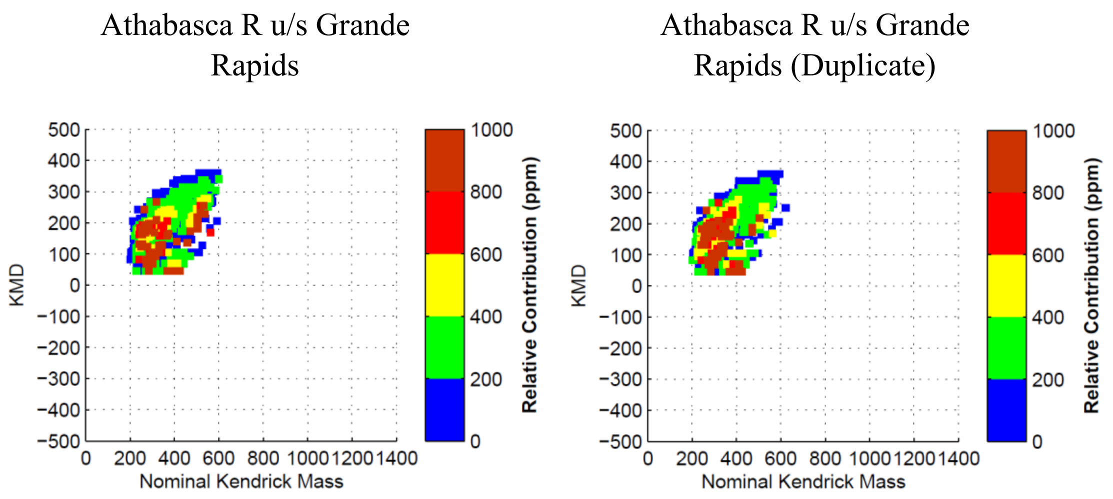
Duplicate samples collected during the snow campaign were submitted for both isotopic and ESI-FTICR MS analyses (QA/QC) (Table A1).

Table A1: $\delta^{18}O$ and number of peaks reported for four pairs of duplicated samples.

AITF ID	AESRD ID	Sample Description	Sampling Date	$\delta^{18}O$	Number of peaks
OSRIN2-96	T13-7085	Geographic Centre	12-Feb-2013	-25.61	4,860
OSRIN2-177	T13-7086	Geographic Centre (Duplicate)	12-Feb-2013	-25.08	4,889
OSRIN2-80	T13-7018	Athabasca River u/s Grande Rapids	11-Feb-2013	-26.89	2,818
OSRIN2-175	T13-7020	Athabasca River u/s Grande Rapids (Duplicate)	11-Feb-2013	-27.53	2,212
OSRIN2-161	T13-7091	Operator 1 Border 2	12-Feb-2013	-26.75	3,597
OSRIN2-176	T13-7092	Operator 2 Border 2 (Duplicate)	12-Feb-2013	-26.79	3,613

u/s = upstream.

Overall, the duplicated sample suggest that isotopic and organic results are reliable. The three pairs of duplicate samples show reasonably similar results in $\delta^{18}O$ and in the organic profiling. Using the duplicate samples from Athabasca River u/s Grande Rapids as an example, there was only a 0.64‰ difference in $\delta^{18}O$ values. Comparison of the ESI FT-ICR MS showed that 1,951 of the peaks were detected in both samples with a very similar mass distribution of compounds (Figure A1). In this report, only one sample from each duplicated pair is incorporated in the data reporting and analysis. The samples with the higher number of detected peaks were selected for inclusion.


Athabasca R u/s Grande Rapids

Athabasca R u/s Grande Rapids (Duplicate)

Figure A1. Kendrick plot, showing similar mass distribution of compounds in the pair of duplicated samples collected at Athabasca River upstream of Grand Rapids.

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