



Seasonal Variations in Sources of Organics to the Athabasca River and its Tributaries

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Summary

- The objective of this study was to evaluate sources and pathways of organic loading to the Athabasca River and its tributaries and assess how contributions vary seasonally.
- Dissolved organic profiles of atmospherically derived organics present on snow were compared to profiles of samples from the Athabasca River and its tributaries to evaluate seasonal contributions of atmospherically derived organics to surface water bodies in the AOSR.
- Hydrograph separations, based on monthly stable water isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) data, in some cases dating back to 2002, were used to evaluate the source contributions of snow, rain, groundwater and surface water to streamflow in the Athabasca River and its tributaries.
- Combined, these two techniques may provide insights into the underlying causes for seasonal changes in organic loading to the Athabasca River and its tributaries as organic transport may be more closely controlled by the origin of the streamflow than by the total discharge.

Introduction

Understanding the sources and pathways of organic transport to surface water bodies in the Athabasca Oil Sands Region (AOSR) is critical to assessing the risk to aquatic receptors and ensuring sustainable development in the region. Organic contaminants from natural and anthropogenic sources (i.e. forest fires, weathering of soil and bitumen, stack emissions, tailings ponds, vehicle emissions) may be transported to surface water bodies by either atmospheric (Cho et al., 2014, Kurek et al., 2013) or water-borne (Hall et al., 2012, Wiklund et al., 2012) pathways, however the contribution of each pathway to the overall organic load present in the Athabasca River and its tributaries remains unknown.

Atmospherically derived organics are deposited and accumulate on snow over the course of the winter season. During the spring freshet, meltwater and the accompanying organics are released from snowpack as either infiltration or runoff. The organics present in snowmelt may eventually reach surface water bodies either by surface or groundwater flowpaths. Increased erosion of rock, soil and bitumen during this dynamic hydrologic event may also result in the addition of various organic constituents to surface water bodies.

In this study, Electrospray Ionization Fourier Transform Ion Cyclotron Mass Spectrometry (ESI-FTICR MS) was used to characterize the dissolved organics present in snowpack and evaluate the seasonal contributions of atmospherically derived organics to the Athabasca River and its tributaries. Seasonal variations in the contributions of snow, rain, groundwater and surface water to streamflow in the Athabasca River and its tributaries were evaluated using hydrograph separations based on stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). Combined, these two techniques may provide insights into the underlying causes of seasonal water quality changes in the Athabasca River and its tributaries.

Theory and/or Method

Sample Collection

In February 2013, Alberta Environment and Sustainable Resource Development (AESRD) collected 67 snow samples from sites across the AOSR. A subset of 47 samples were analyzed using ESI-FTICR MS. River water samples from the Athabasca River and its tributaries were collected monthly between 2012 and 2014 as a part of AEMERA's Long-Term River Network (LTRN) monitoring program. A total of 110 river water samples from 18 sites in the Athabasca River and its tributaries were analyzed using ESI-FTICR MS.

The stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) used in the hydrograph separations were obtained from various sources. Like the samples collected for ESI-FTICR MS, stable water isotopes of river water data were obtained from LTRN sites across the Athabasca River and its tributaries. Monthly data from as far back as 2002 was available for some locations. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data for snowmelt was obtained from analysis of the 67 snow samples collected by AESRD as a part of this study. Rainfall $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures were obtained from a Cumulative Environmental Management Association (CEMA) funded event sampling program conducted in 2011-2012. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures for lakes were obtained from 50 lakes in the region over a period of 9 years (Gibson et al., 2015).

Analytical Methods

ESI-FTICR MS provides for the detection and characterization of thousands of dissolved polar organic compounds at very low concentrations. ESI-FTICR MS was conducted at the Proteomic Centre at the University of Victoria in British Columbia using a 12-Tesla Apex-Qe hybrid quadrupole FTICR MS (Bruker Daltonics, Billerica, USA). The machine was operated in ESI(-) mode to characterize the dissolved acidic polar organics which include naphthenic acids, oil sands extractable organics and a wide range of other nitrogen and sulfur containing compounds.

Stable isotope analysis ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was conducted either at the University of Waterloo (pre-2009) using a Micromass IsoPrime Dual Inlet/Gas Chromatograph or at Alberta Innovates – Technology Futures (post-2009) using a Thermo Scientific Delta V Advantage Dual Inlet/HDevice system. Results were reported in δ notation in permil (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW).

Data Analysis

Principle component analysis (PCA) was used to compare the thousands of organic compounds detected by ESI-FTICR MS. The PCA was carried out based on the relative concentrations of the samples to eliminate the effects of large differences in absolute concentration between samples.

Hydrograph separations were conducted using mass balance calculations to separate instantaneous streamflow into its source components. Instantaneous streamflow discharge (Q) was calculated as the sum of the contributions from the streamflow sources (x_1, x_2, x_3).

$$Q = x_1 + x_2 + x_3 \tag{1}$$

Mass balance equations were also used to represent the mass conservative tracers, $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

$$Q\bar{\delta}^{18}_Q = x_1\bar{\delta}^{18}_1 + x_2\bar{\delta}^{18}_2 + x_3\bar{\delta}^{18}_3 \quad (2)$$

$$Q\bar{\delta}^2_Q = x_1\bar{\delta}^2_1 + x_2\bar{\delta}^2_2 + x_3\bar{\delta}^2_3 \quad (3)$$

Solving the equations resulted in the fractional contributions of the streamflow assuming April and May streamflow contained contributions of snowmelt, groundwater and surface water, June to October streamflow contained contributions of summer rain, groundwater and surface water and November to March streamflow contained contributions of snowmelt, groundwater and surface water.

Examples

PCA analysis of the dissolved organic compositions of the 47 snow samples and the 110 samples from the Athabasca River and its tributaries showed compositional differences between the two sample types. In general, snow samples are dominated by O_2 , O_3 , and O_4 compound classes while Athabasca River and Tributary samples are dominated by O_6 to O_8 compound classes. The river samples showed a strong seasonal variation and most resembled the snow samples in March, April and September when O_2 classes became more pronounced. A general trend of increasing numbers of peaks from March to September indicated a greater variety in the dissolved organics over the course of the open water season.

The hydrograph separations revealed that seasonal variations in source contributions differ for the various locations in the Athabasca River and for the different tributaries. Certain tributaries were identified as being groundwater dominated (Steepbank, Muskeg, Firebag) while others were classified as surface-water dominated (Clearwater, Mackay, Ells). The Athabasca River showed an increase in the proportion of surface water downstream.

The seasonal variations in organic compositions can be compared to the seasonal changes in source contributions derived from the hydrograph separations to provide insights to the causes of seasonal water quality changes in surface waters in the AOSR.

Conclusions

- PCA analysis of the organic profiling results reveal large differences in the dissolved organic profiles of snow and river water.
- The months with the greatest similarity in organic composition between snow and surface water occur during periods of low river discharge (March, April, and September) and not during the peak of the spring freshet (May and June).
- This suggests that the impact of atmospheric organics accumulated on snowpack on the Athabasca River and its tributaries is not as straightforward as direct transfer of organics during the spring freshet. There may be a delay between when atmospheric organics are released from the snowpack and when they arrive in surface water bodies, or some of the organics that characterize atmospheric deposition on snow may be similar to the organics that characterize baseflow.
- Hydrograph separations combined with organic characterization may provide a useful means of correlating organic contributions to particular streamflow contributions.

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