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

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There are multiple potential sources and pathways for natural and anthropogenic organics to reach aquatic ecosystems. Are there tracers?
Potential Sources of Organics

Atmospheric deposition of organics originating from oil sands operations are a potential source of organics.

Detailed measurement of PAHs in snow is an important aspect of monitoring in the AOSR.
Objectives

Can new organic profiling techniques improve our ability to identify atmospheric sources of organics?

Are atmospheric derived organics a significant contribution to surface waters?

OSRIN Phase 1: Birks et al., 2012; Yi et al., 2014

OSRIN Phase 2: Birks et al., 2014
Methods: Organic Profiling

Electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS)

- > 500,000 FWHM with broadband detection
- Simultaneous detection of 10,000 compounds in a single acquisition

- Highest broadband mass resolution power and mass accuracy available, making it possible to identify individual compounds in a complex mixture of organics.
Methods: Organic Profiling

Mass to charge ratio (m/z) (ln weight of compound)
Snow & Surface Water Samples

- 79 surface water samples
  - 73 Athabasca River and tributary samples, and
  - 6 lake samples
- 7 snow samples.
- Samples were collected by ESRD during various snow and surface water monitoring programs.
Snow & Surface Water Samples

- **Snow**
  - March 2012

- **Rivers:**
  - Monthly samples March 2012 to Sept 2012.

- **Lakes**
  - Aug. 2012
Snow & Surface Water Samples

Discharge of Athabasca Downstream of Fort McMurray

- 2012 Data
- Max
- Min

Snow

Rivers

Lakes
Results

- What dissolved organics were detected?

<table>
<thead>
<tr>
<th></th>
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<th># of Peaks</th>
</tr>
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<tbody>
<tr>
<td>Snow</td>
<td>Far-Field</td>
<td>1738</td>
</tr>
<tr>
<td></td>
<td>Near-Field</td>
<td>2120</td>
</tr>
<tr>
<td>Rivers</td>
<td>Athabasca</td>
<td>2816</td>
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<tr>
<td></td>
<td>Tributaries</td>
<td>3183</td>
</tr>
<tr>
<td>Lakes</td>
<td>Lakes</td>
<td>3009</td>
</tr>
</tbody>
</table>

- The # of peaks detected in river samples increased from March (under-ice) to Sept.
Near field snow is different from background snow.

Dissolved organics present in surface water are different from near field snow.
Results

- Different compound classes are present in:
  - Snow and surface water
  - Near and far field snow
- Near-field snow samples have $N_2O_n$ and $S_2O_n$ compound classes, which are absent in far-field snow

Naphthenic acids, $C_nH_{2n+z}O_2$
Results: New Tracers?

- Can we use these results to identify potential tracers of natural and anthropogenic sources of organics in the AOSR?
- Interest in using $O_2:O_4$ as a tracer of OSPW.
Results: New Tracers?

- Importance of characterizing all of the potential endmembers and multi-tracer approach.

Frank et al., 2014

Yi et al., 2014
Summary

- Near-field snow samples were compositionally different from far-field snow.

- The dissolved organic composition of upstream Athabasca River is similar to far-field snow.

- No evidence that Athabasca River become more similar to near-field snow.

- Compound classes potentially indicating sources in AOSR have been identified:
  - Near-field snow samples have $\text{N}_2\text{O}_n$ and $\text{S}_2\text{O}_n$ compound classes, which are absent in far-field snow.
Next Steps: Streamflow Partitioning

- Determining underlying causes of water cycle variability
- Source-apportionment
- Better understanding of water quality-water quantity relationships
- Role of snowmelt, groundwater or wetlands in determining water quality
Potential Applications of Results

- Ultrahigh resolution organic profiling may provide a way of identifying atmospherically derived organics.
- Identified compound classes present in near-field snow that are not present in far-field snow.
- Benefits of combining research with monitoring
  - Access to samples and expertise
  - Linking applied research with policy
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Combining isotopic and organic profiling we have found that the dissolved organics present in rivers during the peak of snowmelt do not show evidence of a significant contribution of atmospheric organics.