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

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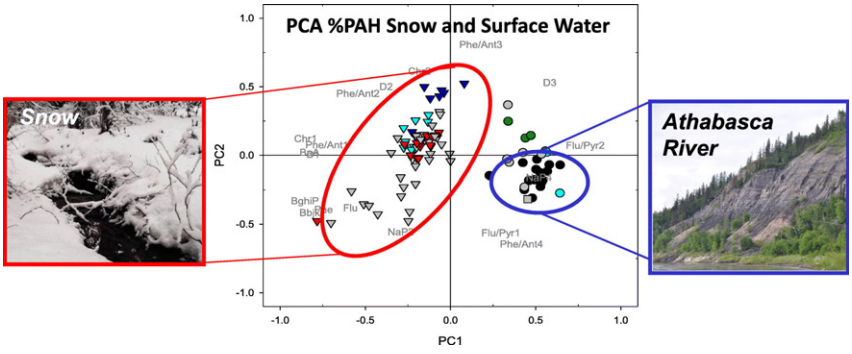
HIGHLIGHTS

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

GRAPHICAL ABSTRACT

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



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ABSTRACT

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

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

1. Introduction

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

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

Elevated concentrations of PAHs have been detected in the snowpack (Cho et al., 2014; Kelly et al., 2009; Manzano et al., 2016) in an area extending about 50–80 km from the centre of oil sands development. There is general consensus from these studies is that the higher concentrations of PAHs in atmospheric deposition within this footprint are associated with industrial activities. However, studies aimed at determining the fate and impact of these PAHs on local and downstream aquatic receptors have yielded variable results and interpretations depending on the media studied (e.g. lake sediment archives, river and lake samples) and proximity to development (e.g. local or distal).

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

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