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Episodic acidification of 5 rivers in Canada's oil sands during snowmelt: A 25-year record

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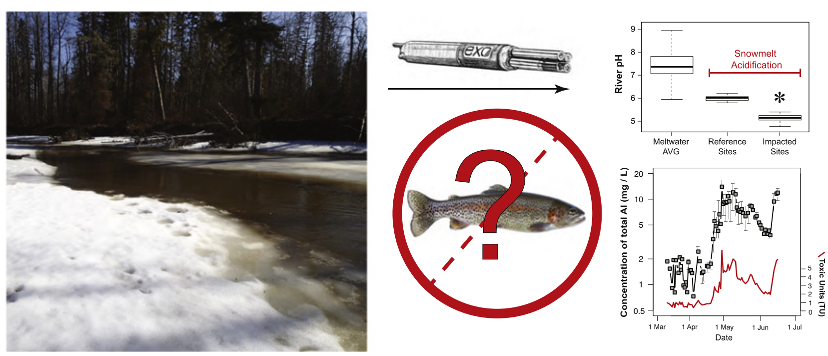
HIGHLIGHTS

- Surface water acidification during snowmelt was assessed using 25 years of automated data from Canada's oil sands region.
- Surface water acidification occurred in 39% of snowmelt events.
- Aluminum and 11 priority pollutants were greatest during snowmelt acidification episodes.
- Aluminum and copper during these episodes may be high enough to pose a risk to rainbow trout.
- Long-term monitoring in the oil sands region will ideally include the snowmelt period.

GRAPHICAL ABSTRACT



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ABSTRACT

Episodic acidification during snowmelt is a natural phenomenon that can be intensified by acidic deposition from heavy industry. In Canada's oil sands region, acid deposition is estimated to be as much as 5% of the Canadian total and large tracks of northeastern Alberta are considered acid-sensitive because of extensive peatland habitats with poorly weathered soils. To identify the frequency, duration and severity of acidification episodes during snowmelt (the predominant hydrological period for delivery of priority pollutants from atmospheric oil sands emissions to surface waters), a 25-year record (1989 to 2014) of automated water quality data (pH, temperature, conductivity) was assembled for 3 rivers along with a shorter record (2012–2014) for another 2 rivers. Acidic episodes ($pH < 7$, $ANC < 0$) were recorded during 39% of all 83 snowmelt events. The severity (duration x magnitude) of episodic acidification increased exponentially over the study period ($r^2 = 0.56$, $P < 0.01$) and was strongly correlated ($P < 0.01$) with increasing maximum air temperature and weakly correlated with regional land development ($P = 0.06$). Concentrations of aluminum and 11 priority pollutants (Sb, As, Be, Cd, Cr, Cu, Pb, Se, Ag, Tl and Zn) were greatest ($P < 0.01$) during low (<6.5) pH episodes, particularly when coincident with high discharge, such that aluminum and copper concentrations were at times high enough to pose a risk to juvenile rainbow trout (*Oncorhynchus mykiss*). Although low pH ($pH < 6.5$) was observed during only 8% of 32 acidification episodes, when present, low pH typically lasted 10 days. Episodic surface water acidification during snowmelt, and its potential effects on aquatic biota, is therefore an important consideration in the design of long-term monitoring of these typically alkaline ($pH = 7.72 \pm 0.05$) rivers.

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1. Introduction

Episodic acidification of waterways is a global phenomenon associated with high stream flows during periods of snowmelt or rain events (e.g., Jeffries et al., 1979; Cooper et al., 1987; Schindler, 1988; Davies et al., 1992; Wigington et al., 1996; Kowalik et al., 2007). Episodic acidification is typically brief (hours to weeks) and defined as periods when a water body can no longer neutralize incoming acid (i.e., when the acid neutralizing capacity, or ANC, is <0). Mild to moderate acidification of surface water during periods of snowmelt can occur naturally as a result of flushing or seepage of organic acids from soil (Wellington and Driscoll, 2004) and dilution of acid neutralizing base cations such as Ca^{2+} and Mg^{2} (Wigington et al., 1996). Acidic rainfall or pre-existing acidic deposition in the snow pack exacerbates these natural processes and, together, can result in acidic episodes of even greater severity with increases in both magnitude (decreases of 1 or more pH units) and extent (days-to-weeks) (e.g., Johannessen and Henriksen, 1978; Jeffries, 1990).

In streams and rivers, low pH episodes are often associated with elevated concentrations of contaminants such as metals because acidity increases their solubility (e.g., Davies et al., 1992; Wigington et al., 1996; Gensemer and Playle, 1999). For example, Al and Cd have been shown to mobilize from stream sediments in response to surface water acidification, resulting in increased stream water concentrations (e.g., Likens, 1985). Metals can also be mobilized from soils and then transported as a mixture of mineral- and organically-bound forms in surface runoff to adjacent streams (John and Leventhal, 1995; Driscoll and Postek, 1996; Vance et al., 1996). Organic matter, particularly dissolved organic carbon (DOC), can reduce the toxicity of metals such as aluminum. However, acidity during snowmelt yields conditions where Al is rapidly bioavailable from organic fractions and resupplied by inorganic Al contained in alkaline minerals (Campbell et al., 1992; Wesselink et al., 1996). Consequently, acidic conditions along with the dilution of stream water by metal-enriched snowmelt (due to soil mobilization or atmospheric deposition) could pose a toxic risk to aquatic life.

Recent research in Canada's oil sands region has shown that the snowpack receives significant loadings of priority pollutants such as heavy metals and hydrocarbons (e.g., Kelly et al., 2009, 2010; Kirk et al., 2014). The predominant pathway proposed to introduce contaminants into waterways near oil sands development is snowmelt (*Ibid*). When a snowmelt event is combined with acidification, contaminants will be more mobile compared to the remainder of the flowing water season when the rivers are highly alkaline (pH > 7.5). As such, acidic episodes may be important factors affecting water quality and, in turn, the status of aquatic organisms in Canada's oil sands region. Conventional monitoring that focuses on post-snowmelt grab samples of surface water chemistry likely underestimates the influence of episodic low pH episodes during the meltwater period.

Our objective was to identify and describe the frequency, duration, and severity of acidification episodes between late winter and early summer (2-March to 14-June) in 5 tributaries draining Canada's oil sands region using data collected over a 25 year period (1989–2014). Using contemporary (2012–2014) data, we also evaluated the effect of pH and stream flow on concentrations of 12 acid sensitive elements (11 USEPA priority pollutants, namely Sb, As, Be, Cd, Cr, Cu, Pb, Se, Ag, Tl, and Zn as well as Al). Finally, we conduct a preliminary assessment of the toxic potential of low pH episodes by comparing the combined toxic potential of aluminum and 11 priority pollutants to rainbow trout (*Oncorhynchus mykiss*), a standard test species.

2. Materials and methods

2.1. Study area

The study spanned 56° 44′ 33″ N × 110° 30′ 8.99″ W and 57° 13′ 39.9″ N × 111° 57′ 32.04″ W, an area of approximately 11,140 km^2 centered 20 km north and east of Fort McMurray, AB, Canada (Fig. 1). Northeastern Alberta is a region with a high anthropogenic acid deposition rate (estimated at ~300 t SO2 and ~200 t NOx per day; Davies, 2012). Annual precipitation ranges from 410 to 470 mm/y with approximately 81% falling as snow (range 62 to 100% between 2-March and 14-June since 1989; https://www.ec.gc.ca/natchem/) and an average annual snow depth of 30 to 49 cm (Atlas of Canada, 2009). The frost-free period is typically short, averaging 85 days per year. The ecoregion surrounding Fort McMurray is boreal mixed wood forests and mesotrophic peatlands with predominately dystric brunisol soils (Atlas of Alberta Lakes, 1990; Prior et al., 2013). Mesotrophic peatlands are considered highly sensitive to acid deposition (Holowaychuk and Fessenden, 1987).

A total of 18 sites on 5 tributaries of the Athabasca and Clearwater rivers were selected for assessment of low pH episodes, 4 of which (Firebag, Muskeg, Steepbank, and Mackay) were situated in areas of active oil sands development (Fig. 1, Table 1). High Hills, a tributary of the Clearwater is 44 km east of Fort McMurray and is considered a reference site, as it is not directly impacted by land cover changes associated with oil sands development. However, the High Hills site is within the 50-km deposition zone of multiple industrial activities to the north and west due to the prevailing wind direction in the region (east south-east; Chetner and Agroclimatic Atlas Working Group, 2003).

2.2. Data collection and screening

Automated (e.g., YSI-6600 or EXO sondes, Hoskin Scientific Ltd., Burlington, ON, Canada) water quality data consisting of water temperature and pH collected at 15-, 30- or 60-min intervals were obtained from Alberta Environment and Environment Canada. The dataset initially included 69 sites on 7 rivers and lakes in the oil sands region sampled

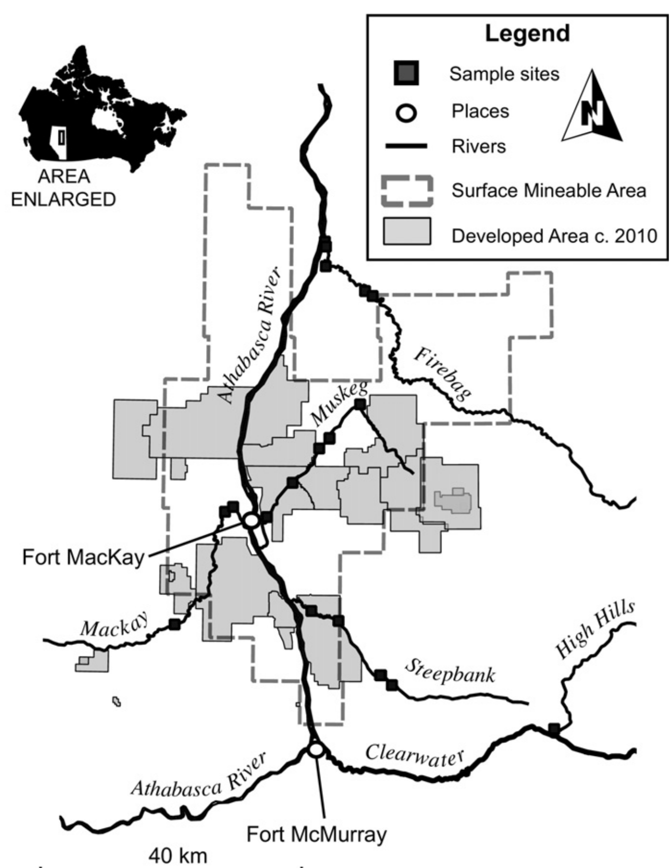

Fig. 1. Map of 18 sites on 5 rivers in the lower Athabasca region where automated sondes were deployed over a 25-year period (1989–2014).