Science of the Total Environment 625 (2018) 264–274

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Meltwater from snow contaminated by oil sands emissions is toxic to larval fish, but not spring river water

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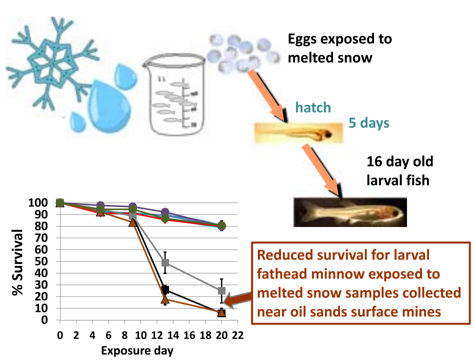
## HIGHLIGHTS

- Snow sampled near oil sands surface mining sites decreased larval fish survival.
- Snow sampled far from oil sands surface mining sites caused no chronic toxicity.
- Spring melt water sampled at industry sites was not toxic to exposed larval fish.
- Snow dilution and mixing with river water during spring melt was protective.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 13 October 2017
Received in revised form 22 December 2017
Accepted 23 December 2017
Available online xxxx

Editor: Jay Gan

*Keywords:*
Fathead minnow
Oil sands
Snow
Spring melt water
PAHs, toxicity

## ABSTRACT

To assess the toxicity of winter-time atmospheric deposition in the oil sands mining area of Northern Alberta, embryo-larval fathead minnow (*Pimephales promelas*) were exposed to snowmelt samples. Snow was collected in 2011–2014 near (<7 km) oil sands open pit mining operations in the Athabasca River watershed and at sites far from (>25 km) oil sands mining. Snow was shipped frozen back to the laboratory, melted, and amended with essential ions prior to testing. Fertilized fathead minnow eggs were exposed (<24 h post-fertilization to 7–16 days post-hatch) to a range of 25%–100% snowmelt. Snow samples far from (25–277 km away) surface mining operations and upgrading facilities did not affect larval fathead minnow survival at 100%. Snow samples from sites near surface mining and refining activities (<7 km) showed reduced larval minnow survival. There was some variability in the potencies of snow year-to-year from 2011 to 2014, and there were increases in deformities in minnows exposed to snow from 1 site on the Steepbank River. Although exposure to snowmelt from sites near oil sands surface mining operations caused effects in larval fish, spring melt water from these same sites in late March–May of 2010, 2013 and 2014 showed no effects on larval survival when tested at 100%. Snow was analyzed for metals, total naphthenic acid concentrations, parent PAHs and alkylated PAHs. Naphthenic acid concentrations in snow were below those known to affect fish larvae. Concentrations of metals in ion-amended snow were below published water quality guideline concentrations. Compared to other sites, the snowmelt samples collected close to mining and upgrading activities had higher concentrations of PAHs and alkylated PAHs associated with airborne deposition of fugitive dusts from mining and coke piles, and in aerosols and particles from stack emissions.

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https://doi.org/10.1016/j.scitotenv.2017.12.284

*Capsule:* Snow collected close to oil sands surface mining sites is toxic to larval fathead minnows in the lab; however spring melt water samples from the same sites do not reduce larval fish survival.



## 1. Introduction

Oil sands surface mining operations in northern Alberta release oil sands-related compounds (OSRCs) into the air from refinery process stacks (National Pollutant Release Inventory, Environment and Climate Change Canada, 2015). In addition, compounds may be released from large tailings ponds (Galarneau et al., 2014), coke piles (Zhang et al., 2016), and mining dusts (Jautzy et al., 2013; Kurek et al., 2013). Numerous studies have shown deposition of OSRCs near oil sands operations (Evans et al., 2016; Harner et al., 2013; Hsu et al., 2015; Jariyasopit et al., 2016; Kelly et al., 2010; Kelly et al., 2009; Kirk et al., 2014; Kurek et al., 2013; S.M. Li et al., 2017; Manzano et al., 2017; Manzano et al., 2016a; Schuster et al., 2015; Zhang et al., 2015).

Recent studies of atmospheric deposition to snow in the oil sands mining area of northern Alberta have shown significant deposition of polycyclic aromatic hydrocarbons (PAHs) and metals. Kelly et al. (2009) found high depositions of PAHs and alkyl-substituted PAHs (APAHs) in areas closest to oil sands stacks. Deposition of total PAHs + APAHs in snow near oil sands surface mining facilities was 2–8 mg/m$^3$, with about 95% in the particulate matter and 5% in the dissolved phase (Kelly et al., 2009). In a related study, these authors also found that deposition of certain metals was also highest close to oil sands stacks (Kelly et al., 2010). High concentrations of Be, Pb, Hg, Sb, As, Cd, Cr, Cu, Ni, Ag, Tl, and Zn were deposited in snow particulates close to (<50 km) oil sands upgrading facilities, and concentrations declined exponentially with distance from the source (Kelly et al., 2010). These studies have assessed the concentrations of OSRCs in melted snow, but have not thus far assessed if the mixtures of chemicals deposited with snow are associated with effects on aquatic organisms. The authors of these studies speculated that the concentrations of PAHs + APAHs in the snow melt pulse could cause toxicity in exposed biota (Kelly et al., 2009). Whether oil sands surface mines' atmospheric deposition of PAHs is sufficient to harm aquatic species is currently unknown (Hodson, 2013).

Fish embryos and larval stages are particularly sensitive to the effects of PAHs and APAHs (reviewed in Hodson, 2017). Many of the fish species present in the Athabasca River and its tributaries spawn in the spring (late April through May). These species include walleye (*Sander vitreus*), northern pike (*Esox lucius*), longnose sucker (*Catostomus catostomus*), white sucker (*Catostomus commersoni*), and slimy sculpin (*Cottus cognatus*) (Bond, 1980; Bond and Machniak, 1979; RAMP, 2015, 2016; Tripp and McCart, 1979). Thus there is potential for exposure of sensitive fish embryos and larvae to PAHs and APAHs when OSRCs-impacted snow melts into the river.

To assess the potential impacts of atmospheric OSRC deposition on aquatic organisms, we investigated the response of exposure to melted snow collected in bulk from areas close to oil sands stacks and mines (in 2011, 2012, 2013, 2014) in 21-d bioassays using fathead minnow (*Pimephales promelas*) embryos and larvae. These embryo-larval fathead minnow exposures have been used in our laboratory previously to assess the toxicity of oil sands sediments containing PAHs and APAHs (Colavecchia et al., 2004) and naphthenic acid mixtures (Marentette et al., 2015b).

Snow and spring melt water samples were assessed to determine if aerial deposition was a potential pathway by which contaminants related to industrial oil sands surface mining practices could affect fish embryos and larvae. The sources of the contaminants in snow would be largely anthropogenic, and would be deposited over 4–5 months (during the autumn and winter) originating from fugitive mining dusts and coke piles, and in particles from industrial stack emissions. Fathead minnow embryos were exposed to the melted (ion-adjusted amended) snow for 5 days, and hatched minnows larvae were exposed for a further 7 to 16 days. Embryos and larvae were assessed for % hatch, % deformed fry, growth (length, weight, condition factor) and survival, after exposure to 25%, 50%, and 100% amended melted snow.

## 2. Methods

### *2.1. Site selection*

For snow and spring melt water sampling, study sites were chosen to be near (<7 km) industry mining and upgrading activities, or far from (>25 km) these locations (Fig. 1). Snow and spring melt water samples were collected from sites on the Athabasca River, and two major tributaries, the Ells and Steepbank Rivers. A list of sites with latitude and longitude and dates of sampling is provided in Table S1. Sites were chosen based on those sampled in Kelly et al., 2009, and were coordinated with a field campaign assessing spatial trends in atmospheric contaminant deposition in 2011, 2012, and 2013 (Kirk et al., 2014). In 2013 and 2014, snow sampling sites were chosen to focus on the Ells and Steepbank rivers to align with fish and invertebrate sampling sites carried out under the Joint Oil Sands Monitoring (JOSM) program. All snow samples were collected over ice on the river, and spring melt water samples (200 L collected by pump into 20 L stainless steel canisters) were taken directly from the river as the snow was melting, so that the results would represent snow that entered the river when snowmelt occurred, or actual spring melt water (see Supplemental data Table S1 of snow and spring melt water sampling sites and dates, and Fig. S1 of spring melt water sampling times on plots of daily discharge of Athabasca River).

The embryo-larval fathead minnow tests were designed to determine if snow and spring melt water had the potential to affect fish survival and growth. The relevance of any observed effects from the snowmelt exposures was further addressed in the testing of spring melt water, representing what fish would be exposed to in the real environment during spring snowmelt. Spring melt water was always tested at 100% concentration (i.e., undiluted) as this was the concentration to which wild fish would be exposed.

### *2.2. Snow and spring melt water sampling*

Since all snow samples were collected on thick river ice, we ensured that the snow collected (and the OSRCs contained in it) would have entered the river during melt. Bulk snow samples (0.37–0.74 M$^3$ from each site) were collected via helicopter and transported immediately to freezer trucks and kept frozen during shipment and in storage until fish exposures began in Burlington, ON, 2–5 months later. Spring melt water was collected through holes bored in ice that covered the river, and 200 L from each site was transported via helicopter, and then transported to Burlington via freezer truck at −20 °C until fish exposures began several weeks after collection.

Snow was sampled in March of each year so that we sampled during maximum snowpack depth but before any significant melting. Historical Fort McMurray snowpack accumulation data from Environment Canada's National Climate Data and Information Archive was reviewed to target sample collections for maximum snowpack depth. A 100 m$^2$ site far from the landing-circle disturbance of the helicopter's rotors (i.e., 50–100 m distance) was delimited, and snow was first sampled from five 1 m × 1 m areas, focusing initially on the corners and centre of the large square, followed by collection from additional 1 m × 1 m