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Snowpack deposition of trace elements in the Athabasca oil sands region, Canada

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HIGHLIGHTS

- Loadings of 29 contaminants measured at 91 sites in the Alberta's Oil Sands region.
- Self organizing map applied to resolve the variation in metal mass loadings.
- The maximum metal loadings found along the river and northern transects.

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ABSTRACT

The total recoverable and dissolved concentrations of 29 metals and metalloids were analyzed in snowpack collected at 91 sites in the Athabasca oil sands region, Canada in winter 2011. Based on deposition pattern from geographical centre, three groups were found: Type-1 metals (i.e. dissolved and total recoverable V; Mo) showed a significant exponential decrease with distance, suggesting oil sands development sources; Type-2 elements (e.g. Al, Sb, As, Ba, Fe, Ni, Tl, and Ti and Zn) showed exponentially decline patterns but with some local point sources; Type-3 elements (e.g. Cd, Cl, Cr, Mn, Sr and Th) deposition pattern represented local sources. A self-organizing map showed that sites with the highest elemental concentrations (Cluster I) were mainly located in the vicinity of upgrading facilities and along the north-south transects. The lowest elemental concentration sites (Cluster III) were the most distal sites or located in the western region of the study area.

1. Introduction

Snow can be considered as an integrator of atmospheric pollutants based on the smaller size of snowflakes relative to rain droplets. A number of studies have used snow deposition for the identification of pollutant sources over long range transport (e.g (Barrie and Kovalick, 1980; Carling et al., 2012; Cereceda-Balic et al., 2012; Kirk et al., 2014; Thamban and Thakur, 2013; Timoney and Lee, 2009; Cho et al., 2014)). Less information is available about aerial transport of various air pollutants in mining and industrial settings.

Bitumen oil in northern Alberta represents the world's third largest crude oil reserve and is one of the major drivers of the Canadian economy (Alberta Government, 2014). However environmental concerns about water/air quality and quantity as well as public health have grown over the past decades (Dillon et al., 2011; Schindler, 2010, 2014). Environmental issues result mainly from surface mining and upgrading facilities which can be the sources of various contaminants including metals (Conly et al., 2007; Evans and Talbot, 2012; Guéguen et al., 2011; Headley et al., 2005; Kelly et al., 2010; Kirk et al., 2014) and polycyclic aromatic compounds (Cho et al., 2014; Kelly et al., 2009; Kurek et al., 2013) in the vicinity of the industrial activity. Kelly et al., (2010) used the exponential decay method to examine both the concentration and loading of thirteen inorganic priority pollutants as listed by the US Environmental Protection Agency in snowpack at 31 sites along the Athabasca River and tributaries and found that most of these

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contaminants had elevated concentrations and loadings near bitumen upgraders and the major oil sands developments. Kirk et al., (2014) also examined the spatial distribution of snowpack concentrations and loads of mercury, methylmercury and several metals using exponential decay and kriging techniques to develop deposition maps of contaminants to the AOSR. Both studies found elevated metal concentrations in snowpack collected within 50–85 km of major oil sands facilities (Kelly et al., 2010; Kirk et al., 2014), suggesting local sources related to oil sands development.

Spatial visualization of sparse measurements and/or irregularly distributed in space can be complex. Kriging is a univariate interpolation method and thus its visualization capabilities are limited to single metals and estimation accuracy is highly dependent on the number of measurements as well as their spatial distribution. Although principal component analysis (PCA) has been frequently used to extract multivariate source signatures, PCA assumes a multivariate normal distribution, which is frequently violated by geochemical data (Reimann and Filzsmoser, 2000). PCA is also sensitive to outliers, and the interpretation of components and the corresponding influence of variables is often challenging. On the other hand, Kohonen's self-organizing map (SOM (Kohonen, 2001)) is a powerful analytical tool for organizing large, multivariate sample data into patterns based on spatial deposition by arranging the data into groups with similar characteristics. SOM are also robust to noise, and component planes facilitate the simultaneous visualization of all variable distributions amongst the samples (Kohonen, 2001). The application of k-means clustering to an SOM further groups sets of samples that have similar multivariate patterns, facilitating the distinction of areas with different levels of contamination that may arise from a single source, even when the contamination level differs with direction and distance (Vesanto and Alhoniemi, 2000). The SOM technique has been previously applied in studies of air quality (e.g (Cuss and Guéguen, 2016; Mari et al., 2010; Pearce et al., 2011; Samecka-Cymerman et al., 2007, 2009)), but not yet for the study of metal deposition in snowpack.

The specific aims of this study were (1) to compare the metal deposition in snowpack in the AOSR with that found in other cold regions worldwide, and (2) to evaluate the spatial variability of concentrations of 29 elements (Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cl, Co, Cu, Cr, Fe, Pb, Li, Mn, Mo, Ni, Se, Ag, Sr, Th, Sn, Ti, Tl, U, V, Zn) using SOM technique. In this study, 91 sampling sites were located along four transects (Cho et al., 2014) where elevated metal deposition in snowpack was previously reported (Kelly et al., 2010; Kirk et al., 2014). More sampling sites coupled with more elements measured in this study (29 vs. 8 and 13 in previous studies (Kelly et al., 2010; Kirk et al., 2014)) will allow us to better clustered the distributions of deposited metal loadings, and thereby identify possible sources of atmospherically derived pollutants in the AOSR.

2. Material and methods

2.1. Study area and sampling

The accumulated snowpack samples were collected during the last two weeks of February 2011 in the Fort McMurray region at eighty sites along 4 transects (N–S, W, SE–NW, SW–NE) covering a distance of ~200 km (Fig. 1). Linear distance to an arbitrary geographical center (GC; 57° 1.5′ N, 111° 33.0′ W) was calculated using ArcGIS (Cho et al., 2014). Each transect was labelled from 1 (the closest to GC) to 10–15 (the further away from GC). Eleven sites located along the main waterways (i.e. Athabasca River: R1–2, R10–11; Muskeg River watershed: R2–9) were also sampled as part of the Alberta Environment and Sustainable Resource Development's Water Quality Monitoring. Sixteen sites were located south of Fort McMurray (R2, Fig. 1), outside of the ~50 km radius

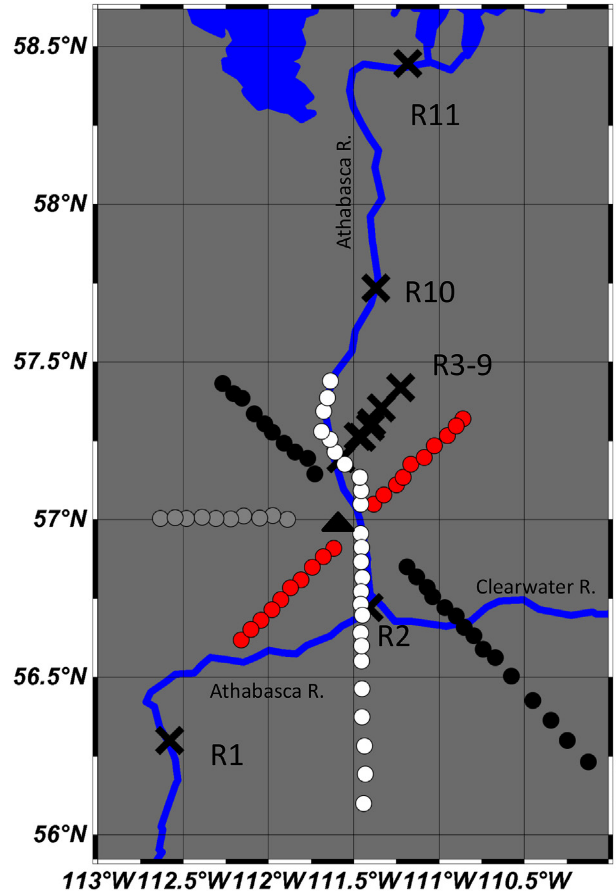

Fig. 1. Snow sampling locations (o) along 4 transects (S–N white; SW–NE, red; W, gray; NW–SE, black) in February 2011. The river snow samples (R1–R11; x) are indicated. GC is represented by the triangle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surrounding site GC. Ambient daytime temperatures ranged from −5 to −27 °C during snowpack sampling (Government of Canada (2012)). Wind density in the area surrounding site GC were predominantly from the north and south during the period prior to sampling (Cho et al., 2014), consistent with Kelly et al., (2010). Sampling sites were carefully selected to avoid areas of direct human activity (i.e. dirty snow, footprint) and the samples were collected at least 100 m upwind from the helicopter landing site to avoid any associated contamination. Clean clothing and sterile nitrile gloves were worn during all the sampling steps.

An aluminum corer with a stainless steel cutter (Prairie Corer; 7 cm diameter and 111.75 cm length) was used to collect samples down to a depth varying from 25 to 70 cm (mean 53 ± 10 cm). Aluminum samplers were previously used for snow sampling heavy metals (Snyder-Conn et al., 1997). To further reduce the potential for snow contamination between sites, the corer was “snow rinsed” when arriving at a new site by extracting a first core which was immediately discarded. More detailed snow sampling procedures and protocols can be found from Cho et al., (2014). Only the subsequent five cores collected at the same site were kept double bagged in expanded polypropylene boxes and shipped frozen to the laboratory at Alberta Innovates Technology Futures (AITF) in Vegreville, Alberta. The samples were kept frozen until sample processing and analysis. The concentrations of Al in AOSR snowpacks were comparable to previous studies (Table 1; (Kang et al., 2007; Thamban and Thakur, 2013)), suggesting no significant contamination from the corer.