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## A regional approach for mineral soil weathering estimation and critical load assessment in boreal Saskatchewan, Canada

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#### HIGHLIGHTS

- ▶ Weathering of boreal forest mineral soil was investigated in Saskatchewan, Canada.
- ► An empirical model was developed to predict base cation weathering rates.
- ▶ Weathering was predicted to be lowest downwind of major S emission sources.
- ▶ Soils in nine of 45 ecodistricts could be classified as highly acid-sensitive.

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#### ABSTRACT

In boreal regions of the province of Saskatchewan, Canada, there is concern over emerging acid precursor emission sources associated with the oil sands industry. Base cation weathering rates (BC<sub>w</sub>) and steady-state critical loads of sulfur (CL<sub>S</sub>) were identified for upland forest soil plots (n = 107) in 45 ecodistricts according to a new method for approximation of BC<sub>w</sub> in the region. This method was developed by regression of simple soil and site properties with BC<sub>w</sub> calculated through application of a soil chemical model (PROFILE). PROFILE was parameterized using detailed physicochemical data for a subset (n = 35) of the sites. Sand content, soil moisture and latitude emerged as important predictive variables in this empirical regression approximation. Base cation weathering varied widely (0.1–8000 mmol<sub>c</sub>m<sup>-3</sup> yr<sup>-1</sup>) across the study sites, consistent with their contrasting soil properties. Several sites had lower rates than observed in other acid-sensitive regions of Canada owing to quartz dominated mineralogy and coarse-textured soils with very low surface area. Weathering was variable within ecodistricts, although rates were consistently low among ecodistricts located in the northwest of the province. Overall, half of the forest plots demonstrated CL<sub>S</sub> less than 45 mmol<sub>c</sub>m<sup>-2</sup> yr<sup>-1</sup>. Historically, the acidification risk in this region has been considered low and monitoring has been limited. Given the very low CL<sub>S</sub> in many northern ecodistricts and the potential for increased acid deposition as oil sands activities expand, soil acidification in these regions warrants further study.

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#### 1. Introduction

In recent years the focus on acid rain in Canada has shifted west, as the oil sands industry in north-eastern Alberta (AB) is the largest contributor of sulfur (S) to the atmosphere (Environment Canada, 2004), while nitrogen (N) emissions from the industry are comparable to other major sources in the country (McLinden et al., 2012). The industry, which uses energy intensive practices to extract bitumen from sedimentary geologic formations, is anticipated to grow further in AB (Timilsina et al., 2005), and possibly expand into Saskatchewan (SK). Further increases in the release of S and N to the atmosphere could result, despite anticipated process efficiencies. As such, there are emerging concerns over impacts on

acid-sensitive ecosystems in the region that may arise due to sustained levels of elevated atmospheric deposition. In north-western SK, which is downwind of existing emissions sources in AB, acid-sensitive lakes are common (Jeffries et al., 2010; Scott et al., 2010). Lake sensitivity to acidic deposition is strongly influenced by catchment processes, which suggests that the terrestrial environment may also be sensitive to acidic deposition.

In contrast to the comprehensive studies including hundreds of lakes in the boreal region of SK, relatively little is known about forest soil acid-sensitivity. Assessments of terrestrial acidification in SK are limited to a national survey (CCME, 2008). This assessment used a soil texture approximation (STA) method based on clay content and parent material (UBA, 2004) that while widely applied, has not been tested for the region. Further, the soil data were derived from coarse resolution soil maps, thus site-specific variation was not accounted for. Nonetheless, the results suggested that critical loads of acidity, the highest deposition that can be sustained over the long-term without detrimental impacts to sensitive

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biota (e.g. Nilsson and Grennfelt, 1988), in northern SK are low (CCME, 2008). Critical loads (CL) have been used widely in Europe (Hettelingh et al., 2007) and Canada (Environment Canada, 2004) to identify the potential for impacts resulting from elevated levels of acidic deposition. As weathering of forest soils is the key determinant of acid-sensitivity (Wilson, 1986), it is integral to CL calculation. By necessity, regional CL assessments rely on prediction of mineral soil weathering rates from simple soil data (e.g. STA). Recent studies have highlighted the importance of regional adaptation of the STA approach in order to improve weathering rate predictions (Koseva et al., 2010; Whitfield et al., 2010a). It follows that CL assessments quantifying base cation weathering rates (BC<sub>w</sub>) according to site-specific data and region-specific relationships should be favored.

The motivation for this study was the emergence of acid precursor emissions in boreal regions of western Canada, and the limited capacity to assess terrestrial acid-sensitivity for the boreal forest of SK due to a scarcity of soil data. Upland soils were targeted through a field campaign in three predominantly forested ecoregions of the province. A range of landscape types, discrete subdivisions of the ecoregions known as ecodistricts, spread across a wide geographic area comprising approximately a third of the province (~250,000 km<sup>2</sup>) were sampled. The resulting data were used to assess whether simple soil properties can be related to weathering rates calculated with the soil chemical model PROFILE (Warfvinge and Sverdrup, 1992) across the spectrum of soils sampled in the region. The central objective of the study was to develop an empirical regression approximation (ERA) for prediction of BC<sub>w</sub> across a large number of sites in boreal SK using simple soil data. Weathering rates calculated with PROFILE formed the basis for ERA development. The estimated weathering rates were used to calculate CL and to test the hypothesis that the risk of soil acidification is highest for northern regions of boreal SK.

#### 2. Methods

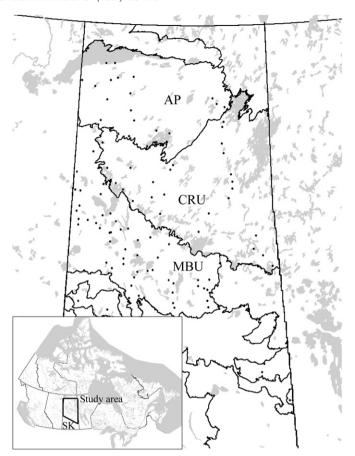
#### 2.1. Field survey

During the summer of 2011, mineral soils at 107 sites were sampled in three boreal ecoregions of SK (Fig. 1). Site selection was conducted with a goal of sampling multiple sites in each ecodistrict (n=45); uplands (moderately to well drained hillslopes) with mature forests (>30 years post-harvesting or fire) were targeted, and efforts were made to sample sites of different character (e.g. dominant vegetation, soil drainage) and to geographically distribute the sites within each ecodistrict. The sites were located distant (>100 m) from roadways wherever possible. Sites were accessed by road or by air, with the Mid-Boreal Upland (MBU; n=62) and Churchill River Upland (CRU; n=26) largely accessed by road, and those in the Athabasca Plain ecoregion (AP; n=19) by air. Site distribution within the ecodistricts was influenced in part by accessibility and aerial sampling efficiency (i.e. range of aircraft). Logistical challenges limited sampling of some ecodistricts to one or two sites.

At all sites a single soil pit was excavated in order to conduct horizon-based sampling of the mineral soils comprising the rooting zone and subsoil (e.g. A–C horizons). Mineral horizon type and depth were recorded in the field, and a bulk density ( $\rho$ ) sample was collected from each horizon using a volumetric sampling ring and hammer corer. Sub-samples for moisture analysis were also collected from unexposed soil of each horizon. Composite samples were collected for each horizon using soil from all sides of the pit. Stone content and rooting zone depth were estimated visually. Soil samples were stored (unrefrigerated) in labeled plastic bags and shipped to Trent University. Geographic coordinates were recorded in the field using a handheld GPS.

#### 2.2. Laboratory analyses

All composite and  $\rho$  samples were air-dried within two weeks of sample collection, prior to conducting further analyses. Bulk density



**Fig. 1.** Location of the study sites (filled circles) in the Athabasca Plain (AP), Churchill River Upland (CRU) and Mid-Boreal Uplands (MBU) ecoregions of Saskatchewan (SK). Shaded areas represent bodies of water. Note that the Mid-Boreal Uplands ecoregion is discontinuous. Location of the study area in the province of SK is shown on the inset map of Canada.

cores were sieved to 2 mm and weighed to determine  $\rho$  of the mineral soil. Likewise, the composite samples were sieved such that all analyses were specific to the soil fraction (<2 mm) of the mineral substrate. The moisture sub-samples underwent gravimetric analysis of water content to quantify volumetric water content ( $\theta$ ) according to Black (1965).

All rooting zone mineral horizons were analyzed to determine organic matter content (OM), particle size, and pH. Organic matter content was determined by measurement of loss-on-ignition after heating oven-dried soils at 375 °C for 16 h in a muffle furnace (Ball, 1964). Soil pH was measured in deionized water after a 60 minute equilibration period (Lozano et al., 1987). The proportions of particles in the clay, silt and sand size classes (<2 µm, 2–60 µm and 0.06–2.0 mm, respectively) were measured in triplicate (~1 g each) by laser ablation (Horiba Partica LA-950) and averaged for each soil horizon.

For a subset of the sites representing the potential range in weathering rate ( $n\!=\!35$ ; 30 selected randomly and five selected to ensure representation of range in texture and geographic location), additional analyses for mineralogy and specific surface area (SSA) were conducted. These analyses provided information on input parameters required for calculation of mineral weathering rates using a kinetic soil chemical model (PROFILE). Mineralogical content of the dominant horizons ( $n\!=\!1\!-\!2$ ) at each of these sites was quantitatively determined by X-ray diffraction (Siemens (Bruker) D5000 Bragg-Brentano diffractometer) using the Rietveld method. For these horizons, corresponding measurements of SSA of the soil were also conducted using a BET  $N_2$  adsorption isotherm (Micromeritics $^{\text{TM}}$  Gemini VII Analyzer). Prior to SSA analysis, the soils underwent sodium hypochlorite oxidation to remove the organic material (e.g. Kaiser and

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