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## Atmospheric deposition of sulfur and inorganic nitrogen in the Southern Canadian Rocky Mountains from seasonal snowpacks and bulk summer precipitation

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## SUMMARY

This study quantified atmospheric deposition of sulfur (S) and nitrogen (N) in the alpine of the Southern Canadian Rocky Mountains and evaluated loads relative to critical limits for ecologic effects on alpine ecosystems from N saturation and acidification. Deposition was evaluated by collecting seasonal snowpack and summer bulk precipitation samples along elevational transects in the alpine Haig Valley and given regional context using snowpack samples from six additional glacier sites. S and N deposition were evaluated in terms of two conceptual models. Model 1 representing deposition from emissions that are mainly distant and Model 2 representing deposition from a mixture of distant and local to regional emissions. Annual S and N (including ammonium ( $NH_4^+$ ), nitrate ( $NO_3^-$ ) and nitrite ( $NO_2^-$ )) deposition in the alpine Haig Valley was  $0.74 \pm 0.18$  kg S ha<sup>-1</sup> and  $1.10 \pm 0.18$  kg N ha<sup>-1</sup> yr<sup>-1</sup>, which is sufficiently high for the occurrence of detrimental ecologic effects related to N saturation in the most sensitive alpine ecosystems, but lower than the critical limit for acidification. Snowpack S and N deposition was consistent with well mixed air mainly from distant sources (Model 1), therefore indicating S and N were largely transported within the precipitating air mass and or picked up by the air mass in transit to the alpine Haig Valley. Relatively consistent deposition of S and N in seasonal glacier snowpacks at sites extending 210 km along the Continental Divide and 100 km west of the divide supports the interpretation that Model 1 describes deposition in alpine glacier snowpack. Similar deposition values for the highest site in the Haig Valley and the mean from the regional snowpack study indicate the highest site in the Haig Valley represents regional conditions of S and N deposition. Summer deposition of sulfate  $(SO_4^{2-})$  and ammonium  $(NH_4^+)$  was also consistent with dominantly distant emission sources (*Model 1*). In contrast there was enhanced transport and deposition of nitrate  $(NO_3^-)$  and nitrite  $(NO_2^-)$  in the summer to low elevations in the Haig Valley from local to regional emissions (Model 2).

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# *Abbreviations:* N, inorganic nitrogen; NO<sub>3</sub><sup>-</sup>, nitrate; NH<sub>4</sub><sup>+</sup>, ammonium; NO<sub>2</sub><sup>-</sup>, nitrite; NO<sub>x</sub>, nitrogen oxides (NO<sub>x</sub> = NO and NO<sub>2</sub>); S, sulfur; SO<sub>4</sub><sup>2-</sup>, sulfate; [NO<sub>3</sub><sup>-</sup>], (square brackets designating concentration); NP, National Park; HDPE, high density polyethylene; DI, 18.2 Ω deionized water; masl, meters above sea level; HG2500, Haig Valley at 2500 masl; HG2640, Haig Valley at 2640 masl; HG2770, Haig Valley at 2770 masl; RB2500, Robertson Valley at 2500 masl; RB2800, Robertson Valley at 2800 masl; OP2400, Opabin Glacier at 2400 masl; WP2670, Wapta Icefield at 2670 masl; AT2820, Athabasca Glacier at 2820 masl; IC2490, Illicilewaet Glacier at 2490 masl; d.l., method detection limit; AWS, automatic weather station; RBAWS, Robertson Valley AWS; HGAWS, Haig Valley AWS; w.m., weighted mean; KS, Kananaskis Station; ppb, parts per billion; N–NO<sub>3</sub><sup>-</sup>, nitrogen component of ritrate; N–NH<sub>4</sub><sup>+</sup>, nitrogen component of ammonium; SWE, snow water equivalent; CL<sub>Ndep</sub>, critical loads of N deposition; kg N ha<sup>-1</sup>, kilograms of nitrogen per hectare; kg S ha<sup>-1</sup>, kilograms of sulfur per hectare.

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## 1. Introduction

Global levels of biologically available reactive inorganic nitrogen (N), which is mainly nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>), were four times higher than preindustrial (1860) levels by the early 1990s and are projected to be eight times higher by 2050 (Galloway et al., 2004). Anthropogenic emissions, mainly from fossil fuel combustion, also contribute about 73% of global atmospheric sulfur (S) (Sofen et al., 2011). Nitrogen is released to the atmosphere predominantly as nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) from fossil fuel and biomass combustion and as ammonia (NH<sub>3</sub>) from agricultural crop fertilization and animal excretion. NO<sub>x</sub> is oxidized in the atmosphere into HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup> while







564

 $NH_3$  is transformed into  $NH_4^+$ . Fossil fuel combustion and ore smelting are the main sources of atmospheric S.

Increased N delivery to terrestrial and aquatic ecosystems profoundly effects ecosystem function and biodiversity and contributes to a cascade of ecologic responses associated with ecosystem N saturation (Aber et al., 1998). Alpine ecosystems are particularly sensitive to enhanced N deposition and can show ecologically destructive responses at relatively low levels of deposition (Burns et al., 2008; Nanus et al., 2008) due to the harsh climate, large expanses of exposed bedrock and thin soils, low vegetation biomass, and rapid release of snowpack pollutants in spring melt (Baron et al., 2005). Ecosystems are often oligotrophic (rich in dissolved oxygen but poor in nutrients) so even small additions of a limiting nutrient can lead to marked changes (Baron et al., 2005). Studies in the US Rocky Mountains have documented: enhanced primary productivity, increased surface and groundwater  $[NO_3]$ . increased soil N mineralization and leaching, lowered lake acid neutralizing capacity, increased abundance of nitrophilous species, and decreased species diversity (Bowman et al., 2006; Williams et al., 1996; Wolfe et al., 2001). The acidifying role of atmospheric S and N are of also a concern to sensitive terrestrial ecosystems which can exhibit leaching of soil nutrients and base cations, mobilizing of toxic metals, and destruction of soil microorganisms (Schindler, 1999; Visgilio et al., 2007).

Although total Canadian emissions and deposition of S and N have decreased (from 1988 to 2007) (Environment Canada, 2010a; Zbieranowski and Aherne, 2011), emissions in Western Canada are increasing and projected to grow further due to increased oil, gas, and tar sand development, intensive agriculture activities, and population growth (Allen et al., 2006; Schindler et al., 2006). Despite a growing concern of the potential environmental impacts of these amplified emissions, evaluation of atmospheric S and N deposition to Western Canadian alpine regions have only recently been initiated (Aherne et al., 2010; Lafrenière and Sinclair, 2011). There is no ongoing measurement or monitoring of atmospheric S and N deposition in alpine regions of the Canadian Rocky Mountains or the interior ranges of British Columbia (to the authors knowledge) resulting in poor comprehension of current levels of alpine atmospheric S and N deposition and limited understanding of the major factors affecting deposition.

The aim of this research was to quantify atmospheric deposition of S and N to an alpine site in the Southern Canadian Rocky Mountains to: (1) consider whether atmospheric deposition occurs at levels that could be ecologically harmful; and (2) evaluate if deposited atmospheric S and N are derived from distant sources or if local and regional emissions of S and N influence atmospheric deposition to high alpine sites in the region.

Building on the first assessment of S and N deposition in the region for 2005/2006 that was conducted by Lafrenière and Sinclair (2011), this study provides a more robust evaluation of annual deposition and variation of S and N with altitude. This study also sought to use spatial variations in ion concentrations and in deposition with altitude and within the region to identify factors that influence S and N deposition (Rogora et al., 2006; Wasiuta et al., 2006). Precipitation accumulated in the 2009/2010 seasonal snowpack and summer 2010 bulk precipitation in the Haig Valley were used to determine annual atmospheric deposition and guantify altitudinal and seasonal variations. Snowpack S and N deposition measured at nine locations in the Rocky and Selkirk Mountains provide the first regional scale evaluation of winter alpine S and N deposition. The study of spatial variability provides regional context for the more detailed/extensive study in the Haig Valley. Baseline atmospheric S and N deposition presented here also provide a reference for studies of sites more directly affected by local and regional emissions.

### 1.1. Study sites

All field sites are relatively remote from large transportation corridors, communities, and point source emissions. The main site, the Haig Valley, lies in the Front Range of the southern Rocky Mountains in Peter Lougheed Provincial Park, Alberta, Canada (50° 42'33"N, 115° 18'00"W) (Fig. 1). It is 35 km south of the Bow Valley transportation corridor with the Trans-Canada Highway and the Canadian Pacific Railway, 40 km south of the closest communities (Exshaw, population 362, Canmore, population 12,288), (Statistics Canada, 2011) and 95 km SW of the closest city (Calgary, population 1,096,833) (Statistics Canada, 2011). The Haig Valley Glacier is the longest arm of the southernmost icefield in the region (Sinclair and Marshall, 2009). The upper glacier (at 2800 masl) forms a broad gently sloping plateau that flows southeast from the Continental Divide to approximately 2430 masl (Fig. 1). Six additional sites were sampled along a 210 km trajectory NW from the Haig Valley. The sites are 6–12 km from the closest roads, 14–95 km from the nearest communities, and  $\geq$  95 km from cities. Two sites were sampled in the adjacent NW facing Robertson Valley divided from the Haig Valley by a steep col that marks the Continental Divide. Three sites were sampled in the Canadian National Parks (NP). From south to north, these are the Opabin Glacier (Yoho NP), Wapta Icefield (Banff NP), and the Athabasca Glacier (Jasper NP). An additional site on the Illecillewaet Glacier (Glacier NP) lies  $\sim$ 100 km west of the Continental Divide (Fig. 1). This project focused on sampling glacier sites where the seasonal snowpack represents a large proportion of the annual precipitation (e.g.



**Fig. 1.** Map of sampling sites in the Haig Valley with regional sampling sites shown in the upper right insert map.

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