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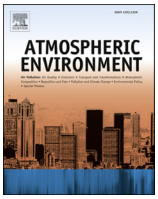

Summer deposition of sulfate and reactive nitrogen to two alpine valleys in the Canadian Rocky Mountains

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HIGHLIGHTS

- Sulfate was predominantly from distant sources.
- Local to regional hydrocarbon combustion strongly enhanced nitrate deposition.
- Large differences in deposition were observed between 2 opposing valleys.
- Preferential transport of local to regional pollutants to NNW facing valley.
- Rain within SE facing valley was relatively clean.

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ABSTRACT

Summer deposition of sulfate and reactive nitrogen (mainly nitrate, and ammonium) to two alpine valleys in the Southern Canadian Rocky Mountains was investigated to constrain their major sources and evaluate physiographic influences on deposition. The effects of elevation, aspect, and air mass trajectory were evaluated using stable isotope composition ($\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$, and $\delta^{34}S-SO_4^{2-}$) and major ion concentrations for bulk precipitation. Deposition in the two valleys was related to synoptic scale weather conditions and the route the air mass followed, the location of major emission sources relative to the study site, and atmospheric residence time. Distinct differences in deposition at a relatively small scale between two opposing alpine valleys was mainly related to the orientation of the two valleys relative to the physiography of the Western Canadian Cordillera and the dominant pathways of air mass transport. Sulfate was found to be dominantly from distant sources, while NO_3^- was strongly enhanced by emissions from local to regional combustion. Local to regional pollutants were preferentially transported to the NNW facing Robertson Valley during NW-upslope synoptic conditions while precipitation in the SE facing Haig Valley was from relatively clean air with minimal influence from local and regional pollutants particularly at the highest elevation site.

1. Introduction

Alpine terrestrial and aquatic ecosystem function are particularly susceptible to harmful effects from enhanced deposition of atmospheric sulfur (S) and reactive nitrogen (N_r). This is due to the overabundance of N_r (mainly nitrate (NO_3^-), and ammonium (NH_4^+)) as a nutrient (Bowman et al., 2006), and to acidification from sulfate (SO_4^{2-}) and NO_3^- (Baron et al., 2011). Chronically elevated N_r deposition leads to detrimental effects including reduced species diversity, eutrophication (excessive algae growth leading to oxygen depletion of the water body), changes in species dominance, and decreased resilience (Fenn et al., 2003; Vitousek et al., 1997). Acidification can leach soil nutrients and base cations, mobilize toxic metals, and destroy soil microorganisms (Schindler, 1999; Visgilio et al., 2007).

Summer rain typically has high solute levels (relative to snowpack) and makes a disproportionate contribution to annual solute loads in temperate alpine regions (Beem et al., 2010; Heuer et al.,

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Abbreviations: magl, meters above ground level; masl, meters above sea level; N_r, reactive nitrogen; [*X*], concentration of *X* (where $X = SO_4^{2-}$, NO_3^-, etc.); w.m., weighted mean.

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2000; Kuhn et al., 1998; Nickus et al., 1998; Wasiuta et al., 2014). Climate change has led to a progressively greater proportion of annual precipitation occurring as rain in the Canadian Rocky Mountains and in much of the Western Prairie Provinces a result of the later onset of snow deposition in the autumn and earlier snowpack melting in the spring (Schindler and Donahue, 2006). Independent of other influences, it is anticipated that S and N_r deposition in the alpine will increase due to this higher proportion of annual precipitation as rain, which has higher solute concentrations than the precipitation accumulated in the seasonal snowpack. Identifying the major sources and processes contributing to S and N_r deposition in the summer are therefore crucial to understanding total S and N_r deposition in alpine environments.

Increasing emissions of nitrogen oxides ($NO_x = NO + NO_2$) and ammonia (NH_3) in Western Canada are projected to continue mainly as a result of amplified emissions from oil and gas extraction, and coal-fired electrical power generation, as well as enhanced livestock and poultry production (Schindler et al., 2006). In contrast, decreasing S emissions in Canada and the US over the last 2 decades have led to a near-linear decrease in the concentration of SO_4^{2-} ($[SO_4^{2-}]$) in precipitation (Aherne and Shaw, 2010; Environment Canada, 2010a).

Numerous studies focused on S and N_r atmospheric deposition, emission sources, atmospheric transport, and ecologic effects of deposition have been carried out in alpine environments in the US Rocky Mountains and in Europe (e.g. Burns, 2004; Mast et al., 2001; Nickus et al., 1997; Wolfe et al., 2001). Despite increasing N emissions in Western Canada and a growing interest in the impacts of S and N_r deposition, there have been only a few studies to date focused on the alpine of the Western Canadian Cordillera (Aherne et al., 2010; Aherne and Shaw, 2010; Hobbs et al., 2011; Lafrenière and Sinclair, 2011; Murphy et al., 2010; Strang et al., 2010; Wasiuta et al., 2014). These studies indicate that summer bulk precipitation can account for more than 40% of total atmospheric S and N_r deposition (Lafrenière and Sinclair, 2011; Wasiuta et al., 2014) and that annual N_r deposition is similar to the mean deposition at monitored sites in the US Rocky Mountains (Wasiuta et al., 2014). There is evidence that N_r loads in alpine lakes have increased in recent decades (Hobbs et al., 2011), and N-excess and eutrophication is occurring in many Western Canadian alpine lakes (Murphy et al., 2010).

This study investigates summer deposition of S and N_r from two alpine valleys in the Southern Canadian Rockies with the aim of understanding the major sources and physiographic influences on deposition. Major ion concentrations and stable isotope values (for nitrate $\delta^{15}N{-}NO_3^-$ and $\delta^{18}O{-}NO_3^-$ and sulfate $\delta^{34}S{-}SO_4^{2-}$) from summer precipitation are used to constrain major emission sources and evaluate the effects of elevation, aspect, and air mass trajectory on deposition. The study is unique in the use of stable isotopes of NO_3^- and SO_4^{2-} to provide insights into S and N_r deposition at a remote alpine site. It is also the first investigation focused on factors controlling summer deposition of S and N_r in the Western Canadian Cordillera.

2. Background

2.1. Study area

The study site is located in the Front Range of the Southern Canadian Rocky Mountains in Peter Lougheed Provincial Park (Fig. 1) Alberta, Canada. Samples were collected along two opposing glaciated valleys that straddle the Continental Divide. The Haig Valley (50° 43′N, 115° 19′) is a broad open south-east (SE) facing valley while the opposing Robertson Valley is narrow, steep walled and faces north–north-west (NNW). Both are relatively remote from large transportation corridors, communities, and point source emissions; 35 km south of the Bow Valley transportation corridor with the Trans-Canada Highway and the Canadian Pacific Railway, about 40 km south of the closest communities (Exshaw, population 362, and Canmore, population 12,288 and 95 km SW of the closest city (Calgary, population 1,096,833 (Statistics Canada 2011))).

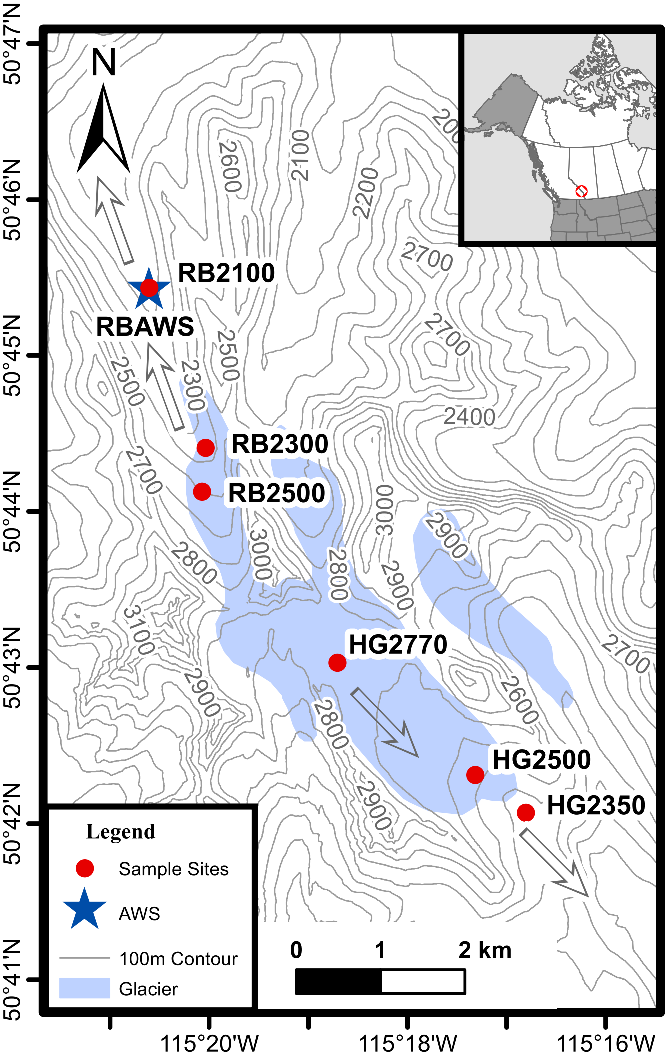

Fig. 1. Map of sampling sites in the Haig Valley and Robertson Valley, Peter Lougheed Provincial Park, Alberta, Canada. Arrows point down valley. Digital topographic data from 082j11 and 082j14 (NTDB, 2005).

2.2. Sources of atmospheric sulfur and nitrogen

Anthropogenic S emissions continue to dominate atmospheric loads although global emissions are declining (Klimont et al., 2013; Smith et al., 2011). The major source is fossil fuel combustion with S derived from organic compounds and contaminants in the fuel (Thode, 1991). Natural sources include volcanic emissions (SO_2), sea-salt (SO_4^{2-}), marine biogenic emissions (mainly dimethyl sulfide (DMS)), biologic decay (H_2S), and lithic dust (e.g. gypsum $CaSO_4{\cdot}2H_2O$). Sulfur is emitted into the atmosphere mainly as sulfur dioxide (SO_2), with emissions from reduced S oxidized in the atmosphere to SO_2. Further oxidation of SO_2 to sulfate (SO_4^{2-}) can occur through gas phase oxidation (homogenous) or aqueous phase oxidation (heterogeneous) which includes reactions on the surface of sea-salt and lithic aerosols (Alexander et al., 2009).