

Tracing nitrogen and sulfur emissions in the Athabasca Oil Sands Region, Alberta, Canada, using stable isotope techniques

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Abstract

The Athabasca Oil Sands Region (AOSR) in north-eastern Alberta, Canada, contains the world's largest bitumen reservoir and constitutes an enormous new energy source. However, the processing of bitumen is accompanied by significant nitrogen (N) and sulfur (S) emissions. The oxidation of N and S compounds in the atmosphere results in elevated nitrate and sulfate loads and there is increasing concern about the potential impact of elevated nitrate and sulfate deposition rates on the environment in the vicinity of the emission sources. Traditional stable isotope ratios of nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) have been previously used to identify nitrate and sulfate sources in various studies. In this ongoing study, we test whether we can use stable isotope techniques to determine the source and fate of anthropogenic N and S emissions in the vicinity of industrial emitters.

Nitrate (NO_3^-) and sulfate (SO_4^{2-}) in bulk precipitation and throughfall have been collected in the AOSR since 2007 and samples were taken at various distances from the main emission stacks near Fort McMurray (57.0479875 °N, 111.615502 °W), ca 450 km NE of Edmonton, Alberta, Canada. At each site, several ion exchange resin (IER) throughfall and open field samplers were installed. Throughfall samplers were mounted on tree branches, whereas open field samplers collected bulk precipitation. The resins were exposed from April 2007 to September 2007 ("summer 2007") and from October 2007 to May 2008 ("winter 2007/2008") at four different sites, and between May and October 2008 ("summer 2008") at 13 different sites.

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analyses of nitrate have shown differences in $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of atmospheric nitrate between summer and winter samples, and between throughfall and bulk precipitation. Winter samples had higher mean $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values with $0.6 \pm 1.7\text{‰}$ and $74.8 \pm 5.3\text{‰}$ ($n=41$), respectively, than summer samples with mean $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values of $-3.2 \pm 1.1\text{‰}$ and $66.9 \pm 5.3\text{‰}$ ($n=103$). For both summer and winter, mean $\delta^{15}\text{N}_{\text{NO}_3}$ values were higher in throughfall samples ($-1.3 \pm 2.4\text{‰}$) than in bulk precipitation samples ($-3.0 \pm 1.8\text{‰}$), indicating that throughfall contains dry deposited N from the tree canopy, likely with elevated $\delta^{15}\text{N}$ values. In contrast, $\delta^{18}\text{O}_{\text{NO}_3}$ values collected in summer 2008 were lower in all throughfall samples compared to bulk precipitation samples.

Throughfall also had higher $\delta^{34}\text{S}_{\text{SO}_4}$ values ($5.1 \pm 0.1\text{‰}$, $n=16$) than bulk precipitation ($3.4 \pm 1.2\text{‰}$, $n=18$) and is similar to the $\delta^{34}\text{S}$ value of elemental sulfur ($5.3 \pm 0.5\text{‰}$, $n=10$) from a large industrial sulfur block implying that anthropogenic S emissions may affect the isotopic composition of sulfate in throughfall in the vicinity of industrial emitters.