



## Tracing atmospheric nitrate in the Athabasca Oil Sands Region in north-eastern Alberta, Canada, using $\Delta^{17}\text{O}$

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The Athabasca Oil Sands Region (AOSR) in 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) emissions. The oxidation of N compounds in the atmosphere results in elevated nitrate loads and there is increasing concern about the potential impact of elevated nitrate deposition rates on the environment in the vicinity of the emission sources. Traditional stable isotope ratios of nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) have been previously used to identify nitrate sources in various studies. In this ongoing study, we test if the novel tracer  $\Delta^{17}\text{O}$  of nitrate provides further unique insights about atmospheric oxidation pathways of anthropogenic N emissions in the vicinity of industrial emitters.

Nitrate ( $\text{NO}_3^-$ ) in bulk precipitation and throughfall has been collected in the AOSR since 2007. Precipitation and throughfall, major sinks for atmospheric nitrate, have been sampled 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 using the "denitrifier method" 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.

The first results of  $\Delta^{17}\text{O}_{\text{NO}_3}$  in bulk precipitation samples ( $n=8$ ) and throughfall samples ( $n=2$ ) of nitrate collected in summer 2007 yielded non-zero  $\Delta^{17}\text{O}$  values, and therefore mass-independent oxygen isotope fractionation, ranging from 18.3 to 23.9‰ for bulk precipitation and from 15.3 to 21.1‰ for throughfall. The sampling location yielding nitrate with the lowest  $\Delta^{17}\text{O}$  value (15.3‰) registered the highest  $\text{NO}_3\text{N}$  deposition rate (4.5 kg/ha) and was closest to the main stack (6 km). Throughfall  $\Delta^{17}\text{O}$  values were 3.0 and 1.8‰ lower than those in the coexisting bulk precipitation sample.

Further  $\Delta^{17}\text{O}_{\text{NO}_3}$  analyses will test whether there is a trend towards lower  $\Delta^{17}\text{O}_{\text{NO}_3}$  values in throughfall compared to bulk precipitation, if seasonal variations can be observed, and which reactions are responsible for any observed trend. Additionally,  $\Delta^{17}\text{O}_{\text{NO}_3}$  may also help to reveal the fate of nitrate delivered with increased atmospheric deposition in terrestrial and aquatic ecosystems in the AOSR.