Tracing industrial emissions in the Athabasca oil sands region (Alberta, Canada) using stable isotope techniques

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The Athabasca oil sands region (AOSR) in northeastern Alberta, Canada, is one of the world's largest oil reservoirs. Its heavy oil will become increasingly important as conventional energy resoures decline. Due to the rapid industrial development in the AOSR, there have been increasing concerns about the impact of the emissions from the oil sands operations on the surrounding terrestrial and aquatic ecosystems. Stable isotope techniques may help to assess such impact in the case where industrial emissions are isotopically distinct from background components. In order to trace nitrogen (N) and sulfur (S) emissions released by the oil sands industry, we have determined chemical and isotopic compositions of various N and S compounds in emissions and several environmental receptors.

Potential source materials such as untreated oil sand, bitumen, elemental sulfur from the sulfur storage block, coke and the by-product ammonium sulfate were analyzed for either $\delta^{34}S$, $\delta^{15}N$ values or both. We also determined stable isotope ratios of sulfate ($\delta^{34}S$, $\delta^{18}O$), nitrate ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) and ammonium ($\delta^{15}N$) of stack emitted $PM_{2.5}$ [1]. The nitrogen and triple oxygen isotopic composition ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) of atmospheric nitrate in bulk deposition and throughfall as well as $\delta^{15}N$ of atmospheric ammonium, and $\delta^{18}O$ and $\delta^{34}S$ of atmospheric sulfate in throughfall and bulk deposition were also measured. Bio-indicators such as lichens and pine needles were collected and analyzed for total N content, $\delta^{15}N$, total S content and $\delta^{34}S$. Industrial N and SO_4 emissions were found to be isotopically distinct. $\delta^{18}O$ and $\Delta^{17}O$ of atmospheric nitrate deposition and $\delta^{18}O$ values of atmospheric sulfate deposition showed trends towards lower values with increasing nitrate and sulfate deposition rates allowing for the quantification of industrial contributions to atmospheric nitrate [2] and sulfate deposition in the AOSR. Lichens responded to elevated N and S deposition in close proximity to the oil sands operations, whereas chemical and isotopic compositions of N and S in pine needles showed no significant industrial impact.

In addition to "traditional" stable isotope techniques, we have investigated the suitability of $\delta^{98/95}Mo$ as an environmental tracer in the AOSR and determined its value in Athabasca bitumen and air filters. Preliminary results reveal that industrial activities are associated with Mo isotope fractionation, providing a potential new tracer for industrial activities in the AOSR.

[1] Proemse, B., Mayer, B., Chow, J., and J. Watson (in review). [2] Proemse, B., Mayer, B., and M. Fenn (in review).

Chemical imaging of isotopic spikes in hard tussues using LA-ICPMS

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Laser ablation ICPMS is a widely established method to directly monitor and image the elemetal distribution on solid surfaces with small lateral resolution. The minimal sample preparation and the fact that any solid surface can be analzed irrespective of its nature and composition, has made the method a versatile tool in many areas of science. In addition, the ability of detecting isotope specific information has increased the variety of applications sigificantly. E.g. human and animal teeth as well as otoliths are often used for migration studies.

Beside monitoring the natural isotopic variation, isotopically enriched spikes can be used in natural systems to monitor uptake and distribution of isotopic spikes by hard tissues after administration.

Here, we present the use of Sr isotope spikes for comparing calcium and strontium metabolism in the living organism and tracer distribution within hard tissues (i.e. bones, teeth, otoliths). Our results give new insights into Sr metabolism and turnover. The investigations bear an analytical challenge as spectral interferences have to be accounted for when analysing Sr and Ca isotope ratios with high spatial resolution using LA- ICPMS.