

Stable isotope tracing of sources of nitrate in aquatic systems: examples from rivers in southern Alberta

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Summary

Widespread nitrogen (N)-based organic and inorganic fertilizer application as well as N in urban runoff and wastewater effluents from municipalities are causing increasing problems with groundwater and surface water quality worldwide (Spalding & Exner 1993). These anthropogenic N-inputs result in increased nitrate (NO_3) loading of aquatic systems, leading potentially to severe environmental and health impacts. NO_3 source identification is an important step in preventing pollution of aquatic ecosystems with N-containing compounds, or for remediating contaminated groundwater and surface water. Stable isotope tracer techniques have been used as a method to fingerprint sources of pollutants. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 have been used for identification of nitrate sources in previous riverine studies in southern Alberta. However, due to NO_3 lost during denitrification and overlap in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of some nitrate sources, unique source identification is not always possible. Therefore, we evaluate the use of boron as a co-tracer by measuring the $\delta^{11}\text{B}$ values of major nutrient sources such as synthetic fertilizers, wastewater treatment plant effluents, and manure and in water of receiving riverine systems in southern Alberta. Preliminary results found that NO_3 concentrations in the Bow River ranged between <1 and 8 mg/L, increasing with increasing downstream distance from the headwaters at Lake Louise. In conjunction with increasing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values this trend appears to be partially caused by wastewater treatment plant (WWTP) effluents. Boron concentrations range from 1 to 8 ppb within the Bow River, 300 ppb in cow manure, and samples of WWTP effluent are as high as 17 ppb. The emerging $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrate and the $\delta^{11}\text{B}$ values will be used in mixing models to determine the efficacy of boron as a co-tracer for identifying the major sources of nitrate to riverine systems.

Introduction

Nitrate from different sources may have distinct nitrogen and oxygen isotope ratios ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) that can be used to fingerprint the origin of NO_3 in aquatic systems (Rock and Mayer 2004; Xue et al. 2009; Widory et al. 2004). A literature review indicates, however, that there is some overlap in isotopic signatures of nitrate sources. In addition, denitrification is accompanied by isotope effects that may cause additional difficulties in the fingerprinting of NO_3 sources. These challenges may be addressed by using an additional, more conservative isotopic tracer to fully characterize NO_3 sources and sinks in aquatic systems. Boron is present in traceable amounts in wastewater effluents, inorganic fertilizers, and manure and may act conservatively in many natural settings (Widory et al. 2004; Vengosh et al. 1994). The objective of this ongoing study is to test the efficacy of boron isotope ratios ($\delta^{11}\text{B}$) as a co-tracer of NO_3 sources and sinks within the Bow and Oldman River in Southern Alberta. Measuring the boron and nitrate isotopic ratios in combination for potential nutrient sources and for aquatic receptor systems may provide advantages over using nitrate isotope signatures alone for conclusively identifying the sources responsible for degradation of water quality.

Methods

A number of key tasks were undertaken in order to assess the usefulness of $\delta^{11}\text{B}$ values as a co-tracer of nitrogen pollution in the Bow and Oldman River. These included:

- A literature review on what is known and what is not known about using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 and $\delta^{11}\text{B}$ values as isotopic tracers in aquatic systems;
- Determine the $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$ values of NO_3 -bearing wastewater effluents, synthetic fertilizers, and cow manure to characterize the end-members isotopically;
- Conduct a seasonal sampling campaign of the Bow and Oldman Rivers downstream of nutrient inputs to watersheds in order to assess and compare changes in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 and $\delta^{11}\text{B}$ values;
- Combine chemical, hydrological and isotope data to assess the usefulness of nitrate and boron isotopic compositions as a tracer of nutrient sources alone and in combination.

NO_3 concentrations of water samples were determined in the laboratory using ion chromatography (IC). $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrate were measured using continuous flow isotope ratio mass spectrometry (CF-IRMS). Boron concentrations were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-OES). Boron in water samples is subsequently concentrated to >5 ppb using ion exchange resins. The concentrated boron samples are then analyzed by thermal ionization mass spectrometry (TIMS) in order to determine the $\delta^{11}\text{B}$ value.

Key Findings

The literature review found that there are overlapping $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 derived from animal manure and wastewater effluents (Aravena et al. 1993). In contrast, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 -based synthetic fertilizers, atmospheric NO_3 , and NO_3 from soil nitrification have distinct isotopic signatures (Aravena et al. 1993, Kendall 1998, Wassenaar 1995). Rock and Mayer (2004) demonstrated the usefulness of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in identifying nitrate from natural soil nitrification and manure-derived nitrate as the main sources of NO_3 in the Oldman River. Chao (2011) used the same methods to demonstrate that NO_3 in the Bow River is mainly sourced by soil nitrification and effluent from wastewater treatment plants. Boron isotope ratios measured in combination with $\delta^{15}\text{N}$ values of NO_3 yield unique combinations of isotopic fingerprints for wastewater effluents, animal manure and synthetic fertilizers (Accoe et al. 2009, Leenhouts et al. 1998, Saccon et al. 2013, Seiler 2005, Widory et al. 2004, Widory et al. 2013), but have not been previously used in river studies in southern Alberta.

Table 1: Preliminary concentration and isotope data for NO_3^- and B in effluents from waste water treatment plants, synthetic fertilizers and manure in Southern Alberta. n.d. - not yet determined

Source	$[\text{NO}_3]$ (mg/L)	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)	[B] (mg/L)	$\delta^{11}\text{B}$ (‰)
WWTP					
a) Lake Louise	23.34	3.2	-11.6	0.009	n.d.
b) Banff	13.40	15.3	-5.2	0.003	n.d.
c) Canmore	60.80	7.2	-11.3	0.011	n.d.
d) Bonnybrook	59.85	9.6	-8.2	0.014	n.d.
e) Pine Creek	20.30	14.9	-2.0	0.017	n.d.
f) Lethbridge	5.70	13.2	-1.8	0.017	n.d.
Fertilizer	n/a	-0.5	n/a	n.d.	n.d.
Manure	37.8	n.d.	n.d.	0.30	n.d.

Preliminary NO_3 concentrations and isotopic compositions of the main potential nitrate pollution sources in Southern Alberta (wastewater effluent, manure, and inorganic fertilizer) are summarized in Table 1 suggesting that nitrate from waste water treatment plant effluents has elevated concentrations and high $\delta^{15}\text{N}$ values. In contrast, nitrate from synthetic fertilizers and from natural nitrification of soil organic matter has low $\delta^{15}\text{N}$ values. Nitrate concentrations and $\delta^{15}\text{N}$ values for Bow River water are shown in Figure 1, indicating low nitrate concentrations (~ 1 mg/L) in the headwater regions and increasing nitrate concentrations (> 2 mg/L) further downstream. $\delta^{15}\text{N}$ values indicate that in the upstream regions NO_3 is derived from soil nitrification, but contributions from synthetic fertilizers would have the same $\delta^{15}\text{N}$ value. Nitrate from wastewater effluents appears to be the reason for increasing nitrate concentrations and $\delta^{15}\text{N}$ values with increasing downstream distance in the Bow River (Figure 1), but nitrate from manure would have the same $\delta^{15}\text{N}$ value.

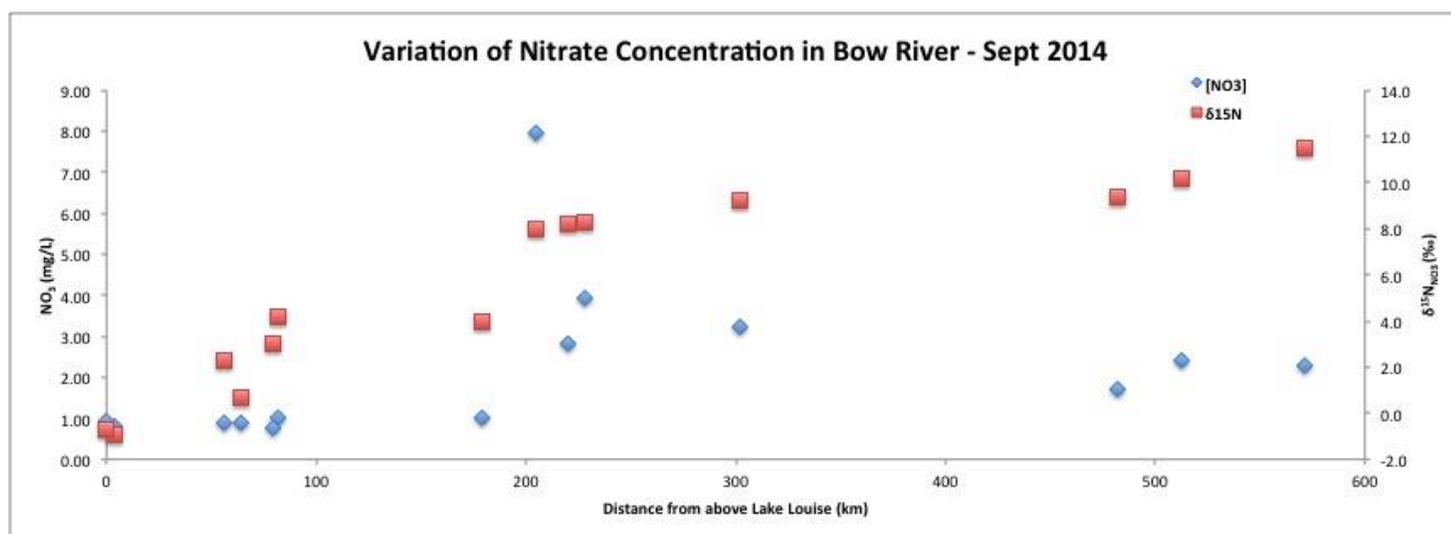


Figure 1: NO_3 concentrations (mg/L) and $\delta^{15}\text{N}$ values of surface water from Bow River sampling sites with distance from Lake Louise, AB. There is a trend of increasing NO_3 concentrations and $\delta^{15}\text{N}$ values with increasing downstream distance that is in part caused by wastewater effluents.

To further delineate potential nitrate sources, B concentrations and isotope ratios are currently investigated. Boron concentrations in the Bow River were below 8 ppb and as low as 1 ppb in some cases, while B concentrations in WWTP effluents were as high as 17 ppb and measured at 300 ppb in cow manure (Table 1). B isotope measurements for different nutrient sources are currently underway and it is hypothesized that boron concentration and isotope data may be useful to further differentiate between the different types of pollution sources that can not be resolved by nitrate isotope compositions alone. If so, this will enable wastewater effluent, synthetic and organic fertilizer end-members to be additionally characterized by their $\delta^{11}\text{B}$ values.

Conclusion

Concentration and isotope analyses revealed that low amounts of nitrate in the headwaters of the Bow River are predominantly derived from nitrification of soil organic matter. With increasing flow distance, increasing riverine nitrate concentrations appear to be caused predominantly by effluents from wastewater treatment plants, although manure-derived nitrate may be a secondary source causing elevated $\delta^{15}\text{N}$ values. We currently evaluate B concentrations and isotope ratios as additional fingerprints to better resolve contributions from these potential nutrient sources. This may allow precise boron- and nitrate-

source mixing models to be generated for these riverine systems to better understand nitrate sources and cycling, and to potentially mitigate nutrient contamination.

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References

- Accoe, F., Berglund, M., Duta, S., Hennessy, C. & Taylor, P. (2008). Source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B: a case study in Flanders (Belgium). *European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel*, EUR 23425 EN.
- Aravena, R., Evans, M.L., and Cherry J.A. (1993). Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Ground Water* 31, 180-186.
- Chao, J. (2011). *Stable isotope geochemistry of the Bow River, Alberta, Canada*. Unpublished master's thesis, University of Calgary, Alberta, Canada.
- Kendall, C. (1998). Tracing nitrogen sources and cycling catchments. In *Isotope tracers in catchment hydrology*. Edited by C. Kendall and J.J. McDonnell. Elsevier, Amsterdam, the Netherlands. pp. 534-569.
- Leenhouts, J.M., Bassett, R.L., & Maddock III, T. (1998). Utilization of intrinsic boron isotopes as co-migrating tracers for identifying potential nitrate contamination sources. *Groundwater* 36, 240-250.
- Rock, M., & Mayer, B. (2004). Isotopic assessment of surface water nitrate within the Oldman River basin, Southern Alberta, Canada. *Water, Air and Soil Pollution*, 4, 545-562.
- Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Bottcher, M.E., Savarino, J., Escher, P., Eisenhauer, A., & Erbland, J. (2013). Multi-isotope approach for the identification and characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area. *Applied Geochemistry* 34, 75-89.
- Seiler, R.L. (2005). Combined use of 15-N and 18-O of nitrate and 11-B to evaluate nitrate contamination in groundwater. *Applied Geochemistry* 20, 1626-1636.
- Spalding, R. F., & Exner, M. E. (1993). Occurrence of nitrate in groundwater-a review. *Journal of environmental quality*, 22(3), 392-402.
- Vengosh, A., Heumann, K.G., Juraske, S., & Kasher, R. (1994). Boron isotope application for tracing sources of contamination in groundwater. *Environmental Science Technology*, 28, 1968-1974.
- Wassenaar, L.I. (1995). Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^- . *Applied Geochemistry* 10, 391-405.
- Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., & Guinamant, J. (2004). Nitrate in groundwater: an isotopic multi-tracer approach. *Journal of Contaminant Hydrology* 72, 165-188.
- Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., & Boeckx, P. (2013). Improving the management of nitrate pollution in water by the use of isotope monitoring: the $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$ triptych. *Isotopes in Environmental and Health Studies* 49, 29-47.
- Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., & Boeckx, P. (2009). Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. *Water Research* 43, 1159-1170.