

Tracing the sources and fate of nitrogen at gold mine sites using stable isotopes of nitrogen and water

Rihem Jaïdi, Eric Rosa, Carmen M. Neculita, Vincent Cloutier, Thomas Genty, Daniel Blanchette

Research Institute on Mines and Environment (RIME), Université du Québec en Abitibi-Témiscamingue (UQAT)

Summary

Mine effluents can contain mixtures of various contaminants originating from different sources (mineral weathering, chemicals added during ore processing and water treatment, explosives). The discrimination of these sources is required to optimize water management and treatment. Although isotopic tracing approaches are widely used in environmental geochemistry, their applications in mining environment remain limited. In this context, the project aims to test an isotopic approach to discriminate the sources and fate of nitrogen compounds at active gold mine sites where N-based explosives and cyanides are used. Water samples were collected on two mine sites, from dewatering wells to the final effluents. The stable isotopes of nitrogen and oxygen in nitrate (for $\delta^{15}\text{N} - \text{NO}_3^-$ and for $\delta^{18}\text{O} - \text{NO}_3^-$) and in dissolved ammonium nitrogen ($\delta^{15}\text{N} - \text{NH}_4^+$) were measured, along with the concentrations of dissolved nitrogen compounds. Stable isotopes of the water molecule ($\delta^2\text{H} - \delta^{18}\text{O}$) were also analyzed. These isotopic tracers are jointly used to trace the source and fate of nitrogen at the mine sites.

Methods

Two mine sites were targeted for data acquisition. Both are active gold mines where the main sources of nitrous species are cyanides (and their derivatives) and explosives. Overall, 20 samples were collected from these two different mine sites. Sampling sites were selected to monitor the chemical evolution of water from pumping wells used for mine dewatering to the final effluents released to the environment. Physicochemical parameters (pH, redox potential (ORP), dissolved oxygen (DO), electrical conductivity (EC) and temperature) were measured on site using a YSI 556 Professional Plus multi-parameter probe. Samples for dissolved metal analyses were filtered on site using 0.45 μm membranes and acidified at pH 2 (using 2% v/v HNO_3), then analyzed by Inductively Coupled Plasma - Atomic Emission spectrometry (ICP-AES; Optima 3100 RL, Perkin Elmer, relative precision of 5%) and Inductively Coupled Plasma - Atomic Mass Spectrometry (ICP-MS). Samples for anions analyses were filtered on site using 0.45 μm membranes and analyzed by Ion Chromatography (Methrom, 881 Compact IC Pro) using a device coupled to an 863 compact autosampler and equipped with a Metrohm 6.1006.520 separation column. The $\text{NH}_3 - \text{N}$ concentrations were determined on filtered samples with an Orion 9512HPBNWP selective probe, following the standard method (APHA, 2012). Samples for $\delta^{15}\text{N} - \text{NO}_3^-$, $\delta^{18}\text{O} - \text{NO}_3^-$ and $\delta^{15}\text{N} - \text{NH}_4^+$ analyses were collected in 1 L HDPE bottles. For $\delta^{15}\text{N} - \text{NH}_4^+$ determination, water samples were filtered at 0.45 μm and acidified to pH < 2 using (1 % v/v H_2SO_4). The principle of laboratory protocol consisted in converting NH_4^+ to NH_3 gas and then trapping it as ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ on fiberglass membranes. The membranes were prepared using gloves, scissors and sheets of aluminum

that were first thoroughly cleaned using ethanol. Three drops of H_2SO_4 (8N) solution was then added to the fiberglass membranes. The latter were subsequently wrapped with a hydrophobic PTFE membrane. These membranes were placed in air tight bottles containing the water samples. The pH of the samples was increased to > 9 by adding $NaOH$ (5N), and the solutions were stirred continuously for 7 days to promote NH_4^+ to NH_3 (gas) conversion and the formation of $(NH_4)_2SO_4$ on the acidified membranes (method adopted from Sebiló et al., 2004). A method adapted from Silva et al. (2000) was used for $\delta^{15}N - NO_3^-$ and $\delta^{18}O - NO_3^-$ analyses. Nitrate was immobilized using *BioRad* anion exchange columns. The samples were percolated through the columns and eluted using HCl (3M). A total of 6.5 g of pre-treated silver oxide (Ag_2O) was added to the leachates to form silver nitrate and silver chloride (solid). The silver chloride was then recovered by filtration. Isotopic analyses were subsequently conducted at the GEOTOP laboratory¹, on silver nitrate, using isotope-ratio mass spectrometry. Samples collected for the analysis of $\delta^2H - \delta^{18}O$ of the water molecule were stored in 60 ml HDPE bottles and analyzed at the GEOTOP laboratory using a dual inlet *Micromass Isoprime™* isotope ratio mass spectrometer coupled to an *Aquaprep™* system. These data were then used to assess evaporation rates, according to the Craig and Gordon (1965) model, and to further identify the sources and fate of N-compounds at the scale of the studied sites using water isotopes mass balances.

Preliminary results and discussion

Nitrogen concentration data

Nitrate and ammonia nitrogen concentrations collected at mine site #1 are shown in Figs 1 and 2. Nitrate concentrations were relatively low (0.7 - 1 mg/L) in samples collected in the natural freshwaters from upstream and downstream of the final mine effluent discharge point (Figure 1A). However, the samples collected on the mine site showed significantly higher nitrate concentrations (49 - 498 mg/L) (Figure 1B). The highest NO_3^- concentration was detected at the outlet of the biological water treatment plant (Figure 1C) and in the groundwater pumped by mine dewatering wells (Figure 1D). The high NO_3^- concentration measured at the outlet of the biological treatment plant is mainly due to the biological nitrification process (using Moving Bed Biofilm Reactor (MBBR) and Rotating Biological Contactor (RBC) technologies] occurring under aerobic conditions and allowing the transformation of SCN^- and $NH_3 - N$ to NO_3^- (Villemur et al., 2015; Tanabene et al., 2018; Mulligan, 2019; Neculita et al., 2019; Saborimanesh et al., 2019). The NH_4^+ concentrations showed a maximum in basin #1 (Figure 2A) and in the groundwater pumped by mine dewatering wells (Figure 2B) (58.97 and 43.13 mg/L, respectively). The high NH_4^+ in groundwater pumped from dewatering wells is likely associated with the presence of undetonated explosives. Ammonium concentrations in the natural water upstream and downstream of the mine effluent discharge were lower (0.01 - 0.2 mg/L) (Figure 2C). In another study documenting nitrogen sources and fate at a mine site, the highest NH_4^+ concentrations were reported in waters collected from groundwater wells used for mine dewatering (Nilsson et al., 2017). Nevertheless, the authors of the last study reported low NO_3^- concentrations in these same waters and tentatively explained their findings by suggesting that NH_4^+ was not oxidised to NO_3^- . In the present study, NO_3^- concentrations in groundwater samples from mine dewatering

¹ <https://www.geotop.ca/en/laboratoires>

are relatively high, probably because the oxidation of NH_4^+ to NO_3^- occurs efficiently. To be noted that basin #1 (Figure 2A) receives all waters from the ore processing plant as well as from the high-density sludge (HDS) pond which might explain the high concentrations of NH_4^+ .

Figure 1 Dissolved NO_3^- and oxygen concentrations at different sampling stations from site #1

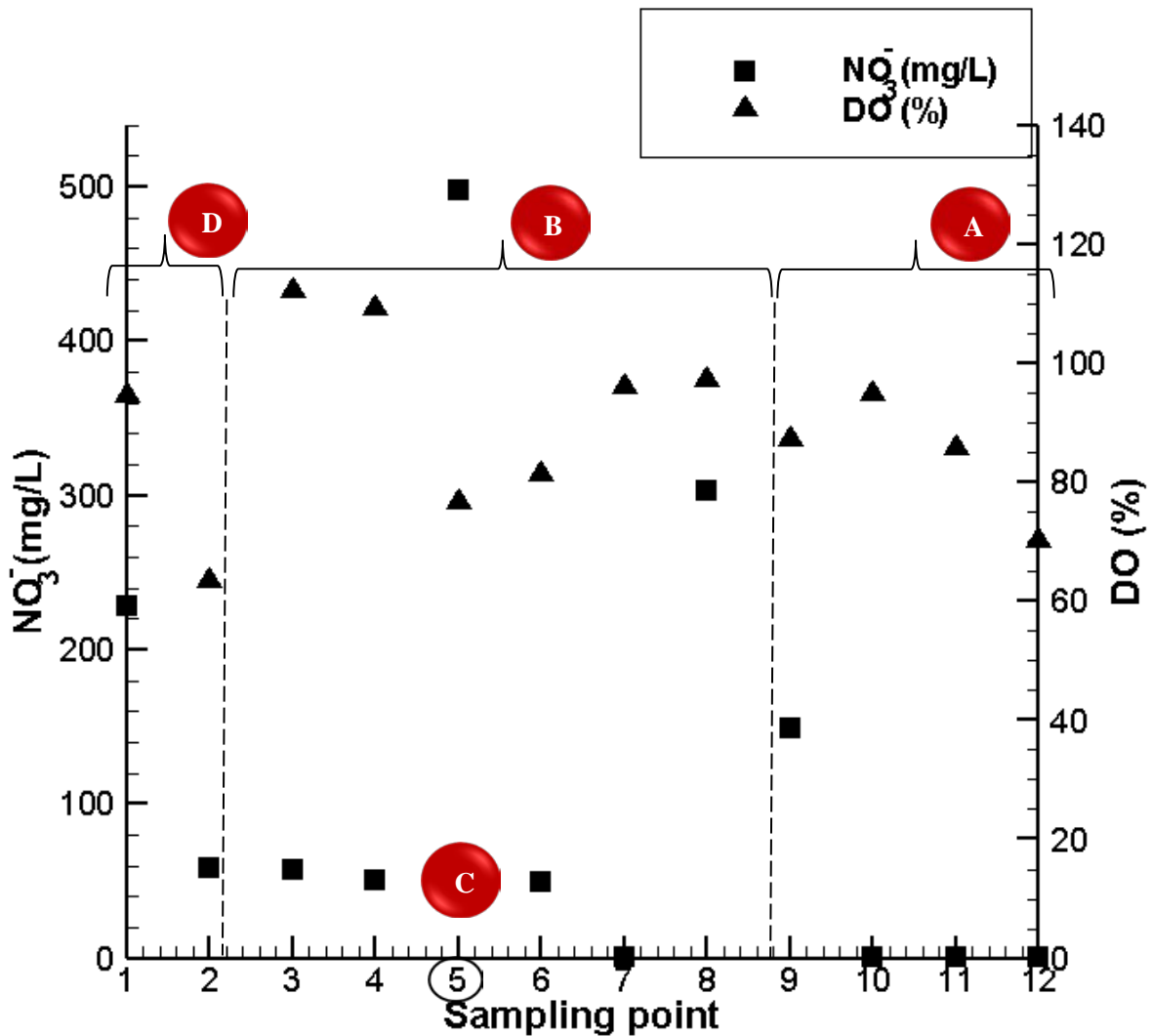
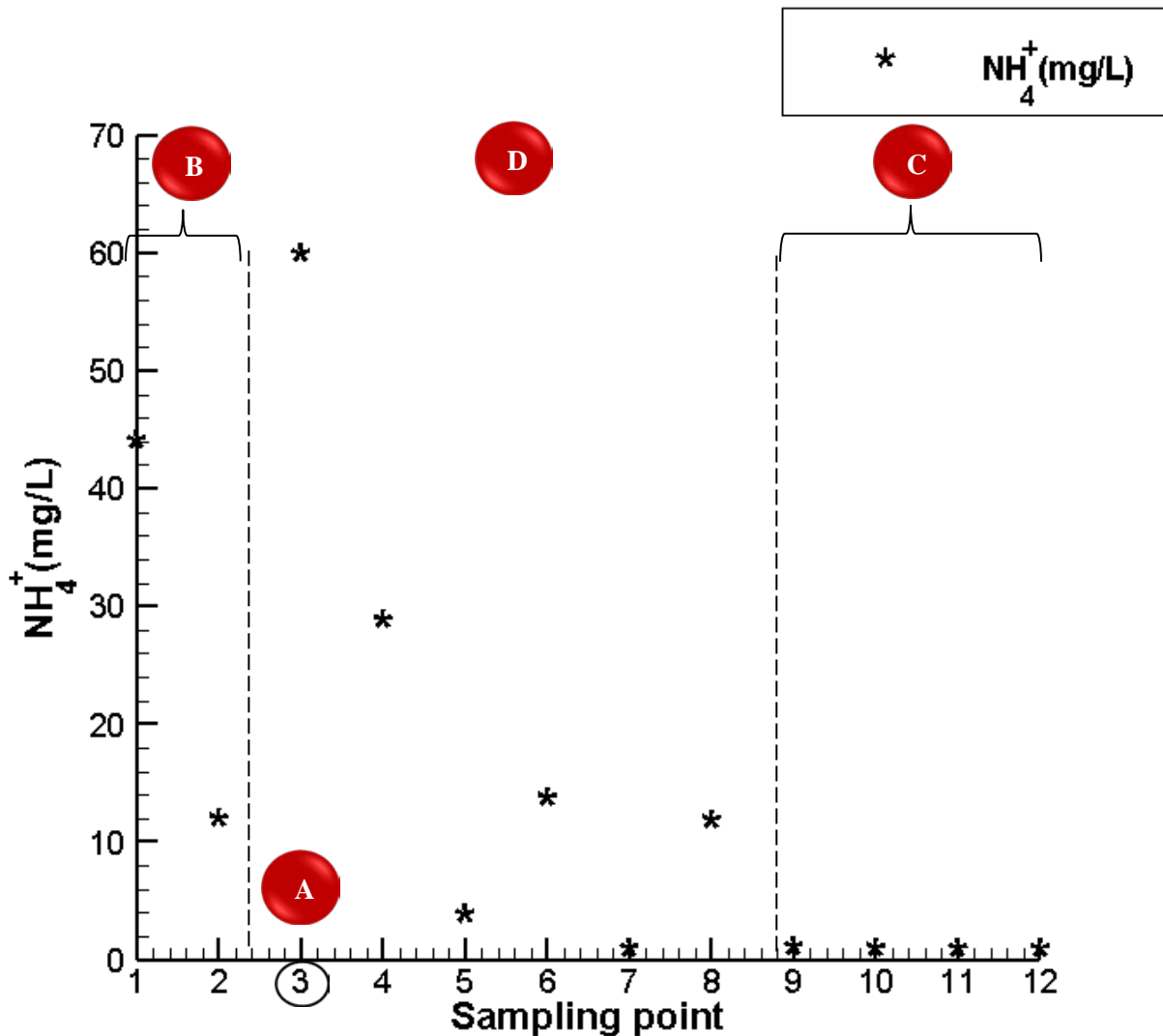


Figure 2 Dissolved NH_4^+ concentrations at different sampling stations from site #1



Isotopic data analysis

The stable isotopes analyses are currently being conducted at the GEOTOP laboratory. Nitrogen isotopes will mainly be used to evaluate the contribution of cyanide vs undetonated explosives to the final concentrations of NH_4^+ and NO_3^- measured at different sampling stations at the two studied mine sites. The stable isotopes of water (δ^2H - $\delta^{18}O$) will be used to further discuss the hydrological mass balance at the mine sites, with a focus on the timing of recharge and on the effects of evaporation.

Scientific outcomes

Ultimately, the results from the present study will improve the understanding and the discrimination of the sources and fate of nitrogen at the two active gold mine sites and allow for evaluating optimized effluent management and treatment approaches.

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