Nitrogen Forms, Leaching and Fate at Elk Valley Resources' Coal Operations in the Elk Valley

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Acknowledgements

- These findings reflect a highly collaborative effort between Elk Valley Resources (formally Teck Coal) and its consulting teams to understand natural forms of nitrogen and the influence of step changes in blasting agent management.
- The main objective was to numerically quantify both the effect of improvements in blasting agent management and the residual effects of leaching of natural nitrogen. The findings were used in the 2023 update to the Regional Water Quality Model for the Elk Valley.

Topics

- Occurrence of nitrogen
  - Naturally-occurring nitrogen
  - Nitrogen derived from blasting agents and effect of blast hole liners
- Leaching of nitrogen
- Fate of leached nitrogen
  - Nitrification, denitrification and the use of stable isotopes
  - Different waste disposal environments

Introduction

- For about four decades, the focus of understanding and quantifying nitrogen sources and leaching was entirely on blasting agents (Ferguson and Leask 1988).
- The significance of naturally-occurring nitrogen became apparent in recent years particularly as efforts to reduce losses of blasting agents have been fruitful.
- Considerable research has occurred to quantify naturally-occurring nitrogen and to quantify the benefits of measures to reduce losses of blasting agents.
- Analytical and interpretation tools to characterize sources of nitrogen and its fate were developed specifically for this work.

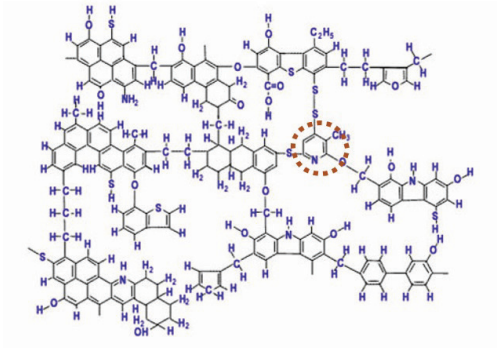
Naturally-Occurring Nitrogen

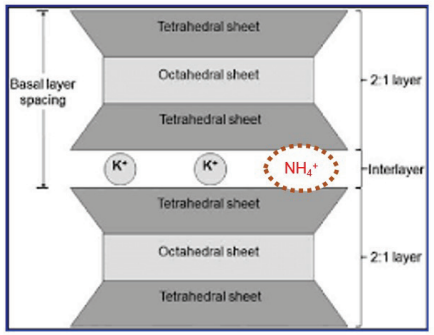
Origin

- The coal and associated sedimentary rocks were formed in deltaic swamps.
- Nitrogen became incorporated into the rocks due to decomposition of vegetation.
- Nitrogen is generally expected to be correlated with organic matter, and low-oxygen depositional environments (low flow conditions).

Forms of Naturally-Occurring Nitrogen

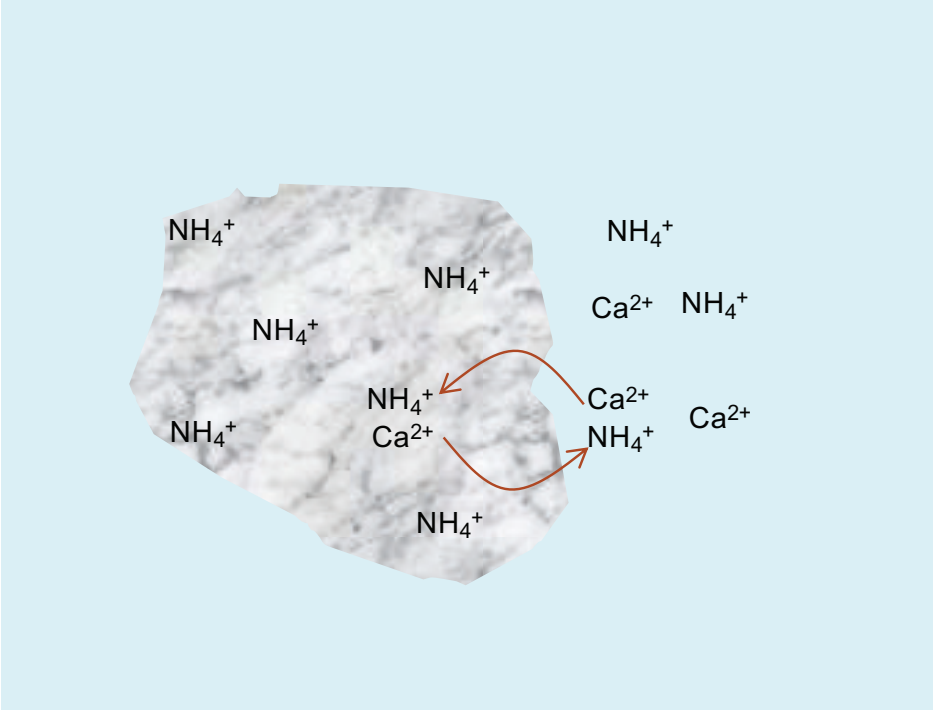
- Two main forms of natural nitrogen have been identified:
  - Covalently bound in large organic molecules ("organic form")
    - This is the most abundant form but it is also the least available under typical waste disposal environments due to the high energy required to break the covalent bonds.
  - Occurring as ammonium in layered clay silicate minerals ("exchangeable ammonium", exNH_4)
    - Its abundance is much lower than the organic form but it is readily leachable.
    - Correlates with the abundance of the clay mineral illite.





exNH$_4$ Leaching Process

- Exchange occurs between ions (Ca^{2+} and NH_4^+ in this example).
- It occurs until equilibrium between the pore water and ions in the solid is established. The process is therefore reversible.
- Exchange occurs within the solid by aqueous diffusion, and it is not instantaneous. NH_4^+ further from the surface of the particle takes longer to reach the pore water than ions near the surface.



Nitrogen from Blasting Agents

Current Understanding

- Blasting agents are based on ammonium nitrate (NH_4NO_3) which is water soluble.
- Interaction of blasting agents in the blast hole with groundwater allows dissolution to occur. NH_4NO_3 dissolves and leaves the blast hole as NH_4^+ and NO_3^- .
  - This component of the blasting agent cannot detonate.
- Major improvements in handling of blasting agents have practically eliminated the contribution of spillage to undetonated explosives.
- Also, misfires are a negligible contributor.
- The focus is therefore on minimizing interaction with groundwater using blast hole liners.

Investigations of the Effectiveness of Blast Hole Liners

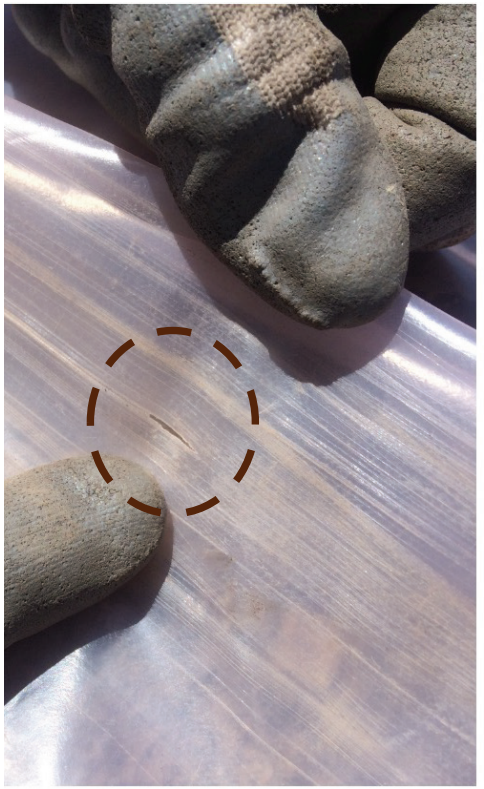
- Blast hole liners are plastic bags that go inside the blast hole

- Two major phased investigations have evaluated the effectiveness of blast hole liners

Investigation		Method
1	Test of the hypothesis that liners do not tear.	Sample water in blast holes before and after loading with explosives
2	A quantitative study to determine actual losses of blasting agents from blast holes	Use blast holes as a wellfield to measure loss from a central loaded blast hole

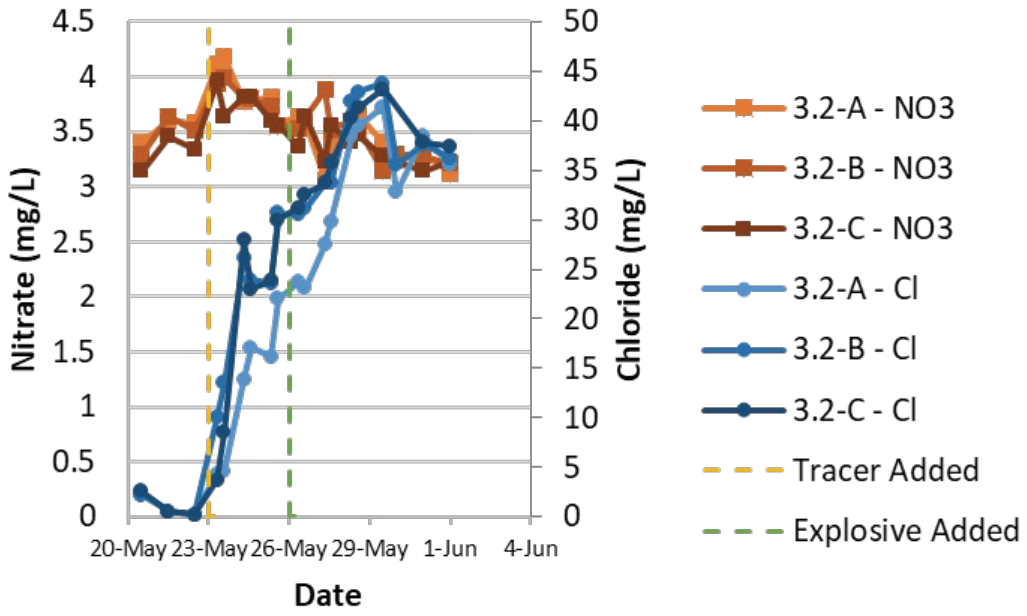
Investigation 1: Conclusions on Test of Liner Tearing

- On the order of 50% of liners tear to some degree.
- Very minor tears can influence water chemistry in the blast hole but might in reality represent low loss to groundwater.
- The study was designed to provide a yes/no on liner tearing. Quantification was not intended or possible from the data obtained.



Investigation 2: Quantification of the Effect of Liner Tearing

- The study methodology was effective.
- Liner tearing was confirmed.
- However, blasting agent losses from lined holes are less than 0.5% of loaded agent.
- This was an order of magnitude lower than unlined holes.
- The value of lining was demonstrated.



Comparison of Natural and Blasting Agent Nitrogen

$exNH_4$ Leaching

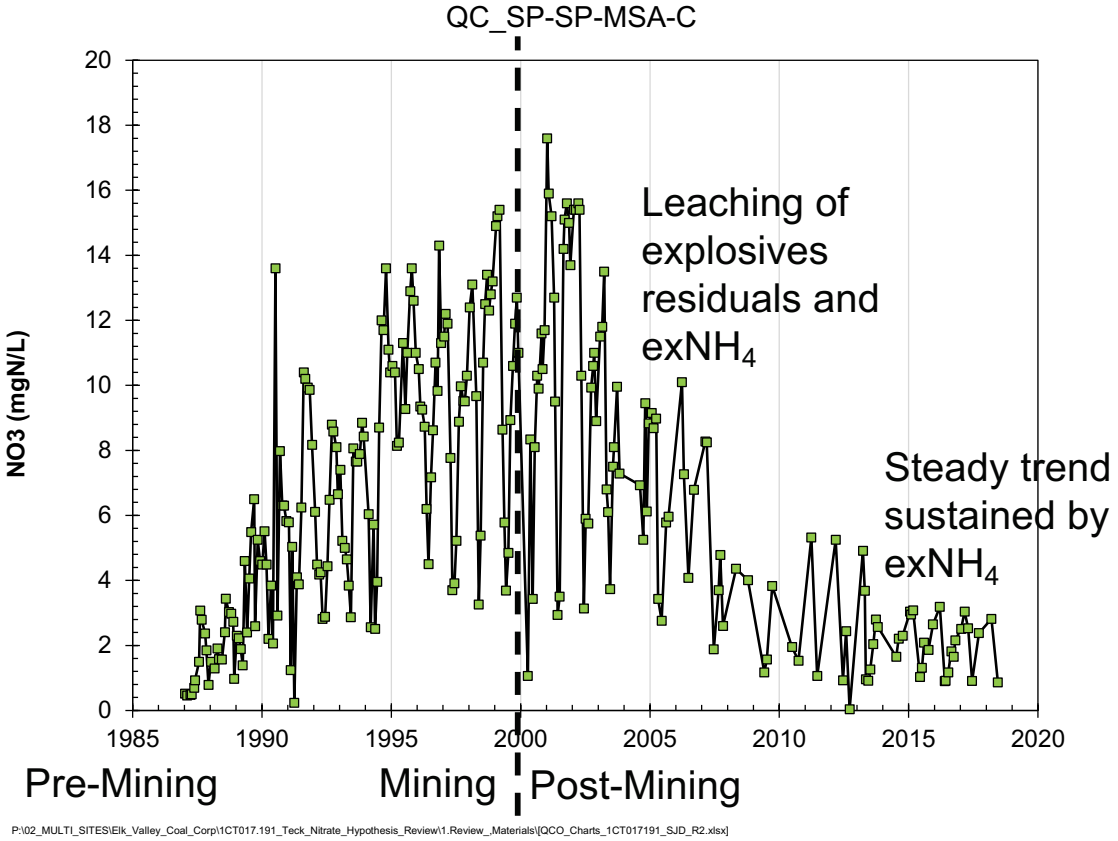
- $exNH_4$ concentrations are 10s to 100s mgN/kg.
- However, only $exNH_4$ in finer particles is available for “immediate” leaching because it occurs distributed throughout the rock.
- Absolute concentrations are not comparable due to the difference in occurrence and leaching mechanisms.
- Leaching of $exNH_4$ can continue for centuries but at low concentrations.

Blasting Agent Loss

- 0.5% blasting agent loss (with liners) is equivalent to about 0.5 mg N/kg (total N as NH_4 and NO_3).
  - 5 mgN/kg at 5% loss,
- Blasting agent loss is immediately available for leaching because it is in the pore water not the rock.
- Typically think of residuals leaching fully over a time frame of a decade.

Example of Long-Term Nitrogen Leaching

- Leaching of $exNH_4$ can sustain nitrogen leaching at low levels above pre-mining conditions after blasting agent residuals have been flushed.
- Example from Quintette Coal, northeastern BC.



Conclusions on Source of Nitrogen

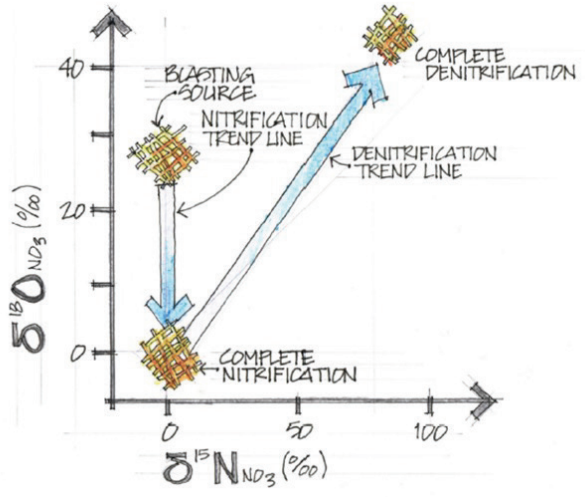
- Prior to lining of blast holes, losses of explosives and the natural source were probably comparable (i.e., roughly 50:50, explosives vs natural)
- Lining of blast holes has substantially reduced losses from explosives.
- As a result, the natural source now dominates (roughly 10:90).

Fate of Nitrogen

Stable Isotopes

- Relative concentrations of the stable isotopes of oxygen and nitrogen in nitrogen ions and oxygen and hydrogen in water are very useful for tracking the source of the nitrogen, and the progress of biotic and abiotic processes.

$$\delta^{18}O_{NO_3} = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \times 1000$$



Fate of Nitrogen

Oxic Environments

- Ammonium “nitrifies” (oxidizes) to nitrate (via nitrite) in a time frame of less than year. As a result, drainage from unsaturated waste rock is dominated by nitrate with lesser ammonium and nitrite.

Suboxic Environments

- In low oxygen environments, nitrification of leached NH_4^+ will be suppressed until it enters the surrounding oxygenated environments.
- Nitrate is “denitrified” (reduced) to nitrogen gas which occurs naturally and in specially engineered saturated and unsaturated environments.

Conclusions

- Natural leachable nitrogen occurs as exchangeable ammonium in the ubiquitous clay mineral illite.
- Covalently-bonded nitrogen is stable and is not expected to be a significant contributor to leachable nitrogen.
- exNH_4 leaches under any unsaturated or saturated waste disposal condition. Leaching is controlled by diffusion which occurs rapidly for particles finer than centimetres.
- Implementation of blast hole lining has reduced losses of blasting agents by an order of magnitude such that natural nitrogen is the dominant source of nitrogen loading.

Conclusions

- Under oxygenated conditions, nitrate is the dominant form of leached nitrogen because ammonium oxidizes rapidly.
- In low oxygen environments, nitrate is converted to nitrogen gas.

- These processes can be understood using stable isotopes.