

# Natural Decay of ANFO-Derived Nitrate in Pit Lakes: Insights from the Golden Bar Pit Lake, Macraes Gold Mine, Otago, New Zealand

*L. Navarro-Valdivia<sup>1</sup>, P.A. Weber<sup>2</sup>, J. Tuck<sup>3</sup>, and C. Hillman<sup>4</sup>*

1. Senior Environmental Geochemist, Mine Waste Management, Christchurch, Canterbury: email: [leo.navarro@minewaste.com.au](mailto:leo.navarro@minewaste.com.au).
2. Principal Environmental Geochemist, Mine Waste Management, Christchurch, Canterbury: email: [paul.weber@minewaste.com.au](mailto:paul.weber@minewaste.com.au).
3. Water Engineer, GHD, Christchurch, Canterbury: email: [jeff.tuck@ghd.com](mailto:jeff.tuck@ghd.com).
4. Environmental Geochemist, Mine Waste Management, Christchurch, Canterbury: email: [carlos.hillman@minewaste.com.au](mailto:carlos.hillman@minewaste.com.au).

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## ABSTRACT

Pit lakes resulting from mining activities often face challenges associated with mine-impacted waters, including nitrogen-rich residues from explosives such as ANFO (Ammonium Nitrate Fuel Oil). This study examines the natural decay of ANFO-derived nitrogen within the Golden Bar Pit Lake at Macraes Gold Mine to gain insights into the processes influencing nitrogen concentrations over time. Nitrogen removal processes, particularly nitrification and denitrification, were investigated to understand the effect of such processes on pit lake nitrogen concentrations.

Results indicate that ANFO blasting residues contributed significantly to initial nitrate ( $\text{NO}_3^-$ -N) concentrations in the pit lake with a peak of 30 mg/L and an initial nitrate load of 400 kg. However, it was found that nitrate is not a conservative contaminant and undergoes natural decay over time due to biochemical processes (20-30% per year). Nitrification initially increased nitrate concentrations, while denitrification reduced nitrate concentrations. Ammoniacal nitrogen (Amm-N) exhibited rapid decay attributed to nitrification. A model was constructed, which indicated that the estimated ANFO-derived nitrogen flush from pit surfaces was 5.35 g/m<sup>2</sup> on a plan area basis.

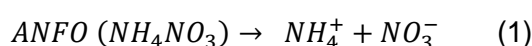
The observed decrease in nitrate concentrations over time indicates the potential for designing pit lakes to act as natural reactors for nitrate treatment, promoting eco-friendly and sustainable mining practices.

## Background

Pit lakes associated with pit closure at mining sites are often affected by mine-impacted waters, including nitrogenous compounds derived from blasting residues, e.g., ANFO (Ammonium Nitrate Fuel Oil). Due to its cost-effectiveness and high energy yield, ANFO is widely employed as a blasting agent. However, the residues of incomplete ANFO detonation (Eq. 1) can provide a reservoir of nitrogen that can affect pit lake water quality. In this study, we investigate the natural decay of ANFO-derived nitrogen in the Golden Bar Pit Lake at Macraes Gold Mine to understand the processes influencing nitrogen concentrations over time.

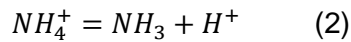
Nitrogen removal from waters including the processes of nitrification and denitrification have been widely studied in natural water ecosystems (e.g., Seitzinger, 1988; Seitzinger et al., 2006; Pina-Ochoa et al., 2006), however, literature on these processes within pit lakes is more limited. Some studies for pit lakes have concluded (from sand-quarries) that pit lakes can play a role in mitigating nitrogen loads from agriculture and act as nutrient filters to reduce nitrogen loads to downstream ecosystems (Nizzoli et al., 2020). However, is not clear if that data can be extrapolated to mine pit lakes.

Water run-off and rainfall that interacts with the pit walls and other surfaces containing blasting residues, can dissolve  $\text{NH}_4$  and  $\text{NO}_3$  blasting residues (Eq. 1) flushing them into the evolving pit lake.

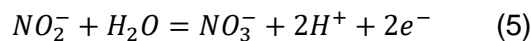
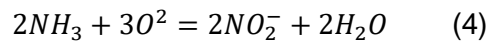
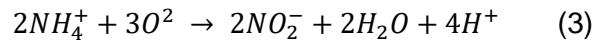


When ammoniacal nitrogen (Amm-N) is released into the water, it exists in two primary forms: unionized ammonia ( $\text{NH}_3$ ) and its ionized counterpart, ammonium ( $\text{NH}_4^+$ ) (Eq. 2). The equilibrium

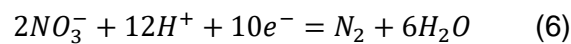
between these two forms is influenced by factors such as pH, temperature, and the concentration of dissolved oxygen.



In oxygen-rich waters, the dissolved oxygen ( $O_2$ ) readily reacts with Amm-N, leading to a process known as nitrification. Nitrification is a two-step microbial process that involves the conversion of ammonium ( $NH_4^+$ ) to nitrite ( $NO_2^-$ ) and then to nitrate ( $NO_3^-$ ). The first step is carried out by ammonia-oxidizing bacteria, which oxidize Amm-N to  $NO_2^-$  (Eq. 3 - 4), while the second step is facilitated by nitrite-oxidizing bacteria, converting  $NO_2^-$  to  $NO_3^-$  (Eq. 5).



Nitrifying bacteria are aerobic organisms requiring oxygen to convert ammonium to nitrate. As a result of nitrification, the concentration of ammonium in the water decreases while nitrate concentrations increase. Denitrification, on the other hand, is a microbial-driven process that involves the reduction of nitrate ( $NO_3^-$ ) to nitrogen gas ( $N_2$ ), as shown in Eq. 6, or other nitrogenous gases, ultimately leading to the removal of fixed nitrogen from the water column.



In lakes, denitrification typically occurs under anoxic (low- or zero- oxygen) conditions. As oxygen becomes limited, certain groups of microorganisms, known as denitrifiers, become active and utilize nitrate as an electron acceptor in their metabolic processes, however, denitrification has also been reported to occur under aerobic conditions (Robertson and Cherry, 1995).

## Study Location

Water quality data were available for the Golden Bar Pit Lake at the Macraes Gold Mine in Otago, New Zealand. The Golden Bar Pit (Figure 1) is no longer an active mining area at present and has a plan surface area of 131,000  $m^2$  (Figure 2). After mining ceased, the pit lake began filling in 2005 with water spill to the nearby stream occurring from as early as 2015. Data indicates the lake pH is neutral to alkaline with sulfate concentrations below 280 mg/L.

Elevated nitrogen concentrations were identified during the early stages of pit lake filling. The primary source of nitrate and ammonia in the Golden Bar Pit Lake are assumed to be derived from ANFO blasting residue as water quality data indicates only a small fraction of the nitrogen is associated with groundwater, surface waters, and rainfall.



Figure 1: Golden Bar Pit Lake (March 2023).

## Material and Methods

A water balance model was created in the GoldSim platform to represent hydrological processes, including rainfall, evaporation, groundwater flows, and surface runoff from contributing catchments. The model operates on a daily timestep and was calibrated against in situ pit lake level data provided by OceanaGold using measured rainfall data near the site.

A water quality data set was available and consists of water samples collected from the Golden Bar Pit Lake from 2005 to the present. Using standard analytical techniques, the samples were analysed for nitrate concentrations, ammoniacal nitrogen, and other relevant water quality parameters. The nitrogen loads were estimated as a product of nitrogen concentration and contributing flows to the pit lake as determined from the water balance model.

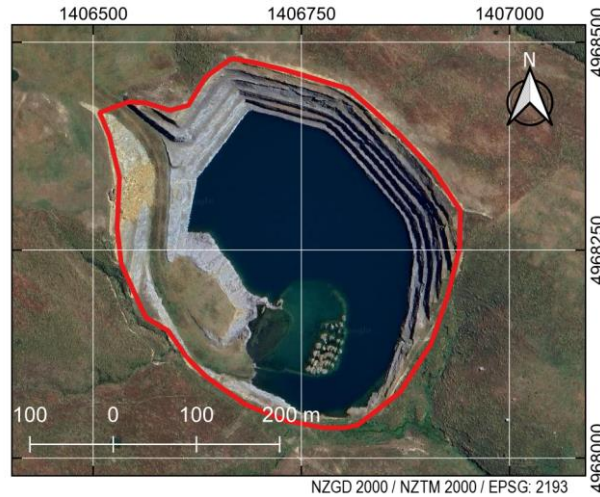


Figure 2: Aerial photo (Google Earth) for the Golden Bar Pit Lake. The delimited zone (red) represents an area of ~131,000 m<sup>2</sup> being the plan area of the pit void.

## Results

The following results are presented for the Golden Bar Pit Lake investigations.

### Water Balance

The water balance model provides continuous pit lake water levels and water volumes from 2005 to the present. This water balance model indicates that once the overflow level was reached (500 mRL) in 2018, there was discharge to the downstream receiving environment. The model indicates there were no losses from the Pit Lake to groundwater during the simulated model period. The evolution of the lake level and volume are shown in Figure 3.

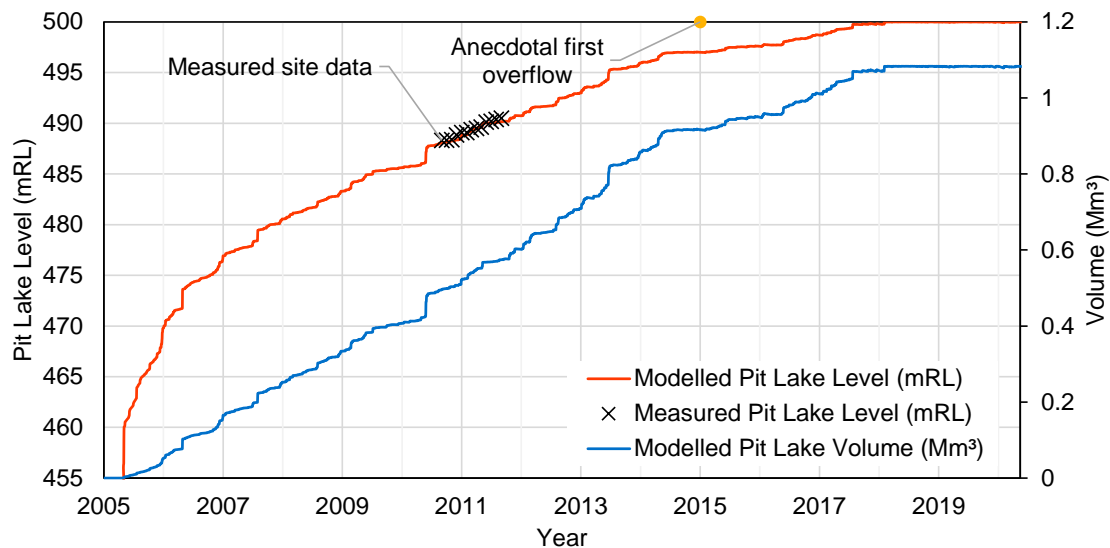


Figure 3: Model results for the Golden Bar Pit Lake filling reconstruction.

Water quality data at monitoring location GB02 below the GPL discharge point suggest pit lake spilling or seepage from the lake could have occurred from 2015 onwards.

### ***Nitrogen Concentrations and Loads***

Concentration data for nitrogenous compounds ( $\text{NO}_3$  - N; Amm-N) are shown in Figure 4 with the following observations noted:

- Pit Lake water quality data show a significant initial  $\text{NO}_3$  - N concentration in the pit lake of ~30 mg/L, attributed to the introduction of ANFO-derived residues from mining activities.
- $\text{NO}_3$  - N was not conservative. Nitrate load data indicates that it increases in the early stages of pit lake filling (due to ANFOs residue dissolution and nitrification of Amm-N) and then decreases with time.
- The  $\text{NO}_3$  - N load peaked at around 400 kg<sup>1</sup> in the year 2007, two years after pit lake filling commenced.
- Approximately 20-30% of the  $\text{NO}_3$  - N load is lost annually after the peak loads were observed, and the  $\text{NO}_3$ -N load approaches zero by the year 2018. This is assumed to be a function of biochemical denitrification processes. This means that 100% of the nitrate was removed by the year 2018, 13 years after the pit lake began filling.
- Although there is a data gap between 2011 and 2018,  $\text{NO}_3$  - N load approaches zero by 2018 with a clear decreasing trend.
- Amm-N also exhibits a sharp decaying trend, with concentrations and loads decreasing to zero within a year (by 2005) from a concentration peak of approximately 10 mg/L and a total load of 170 kg<sup>1</sup>. The decrease is assumed to be associated with biochemical nitrification processes (Eq. 3 – Eq. 5).

These findings show that nitrogen is not a conservative contaminant and is removed from solution (i.e., the pit lake), as evidenced by the decrease in load prior to the lake overtopping. This is most likely due to biochemical processes. This observation is important as it indicates that nitrate concentrations in pit lakes will decrease relatively quickly (e.g., 20-30% per year).

Water residency has been recognized as a critical factor controlling the proportion of denitrified N inputs (Seitzinger et al., 2006). Figure 5 presents a dataset for nitrogen removal versus water residence time. The denitrification data for Golden Bar Pit Lake is also presented in Figure 5, with the residence time calculated as the difference between when the pit lake was completely denitrified (2018) and when it began filling (2005), i.e., 13 years. The denitrification rates for the Golden Bar Pit Lake align with the compiled dataset Figure 5.

The datasets support the notion that water residence time plays a crucial role in controlling the denitrification process in the Golden Bar Pit Lake, as it occurs in natural lakes. This finding highlights the significance of considering water residence time as a key factor in managing and predicting nitrogen dynamics within the pit lakes.

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<sup>1</sup> Where load was derived from concentration and the water volume (as presented in Figure 3).

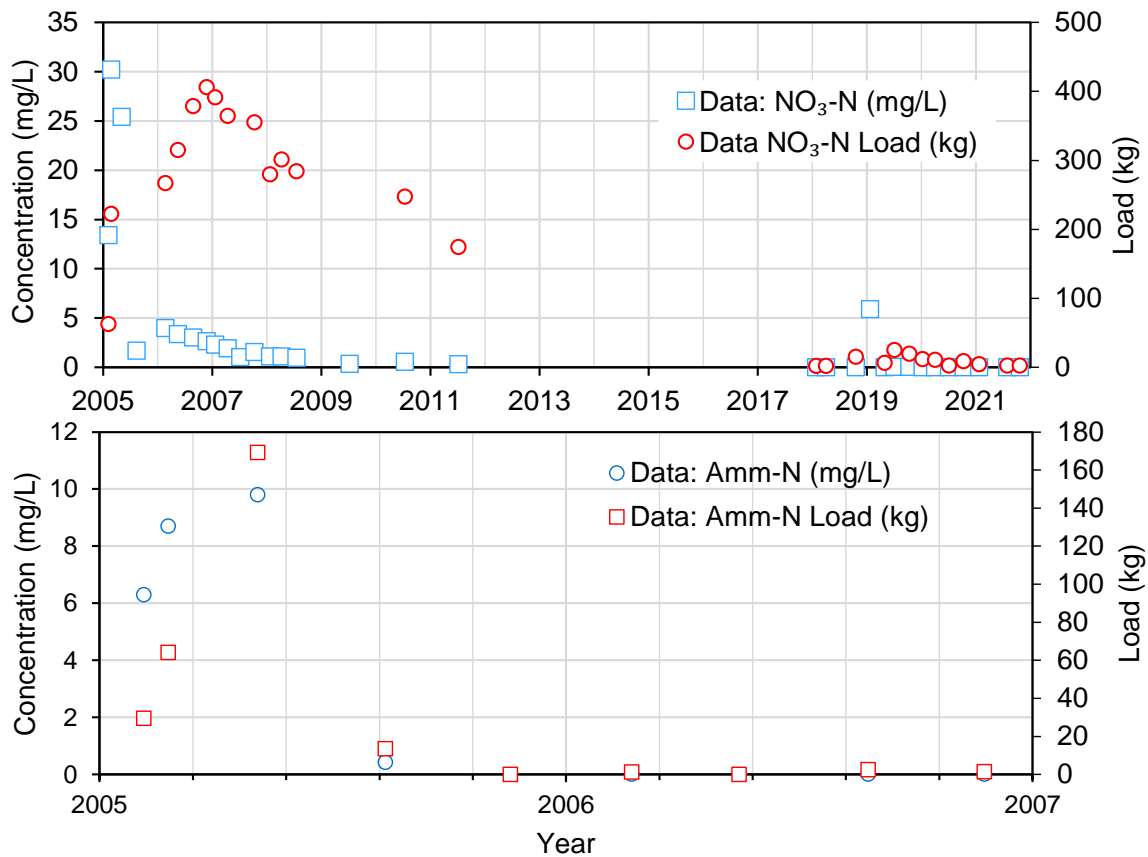


Figure 4: Golden Bar Pit Lake nitrate nitrogen and ammoniacal nitrogen concentration and loads over time.

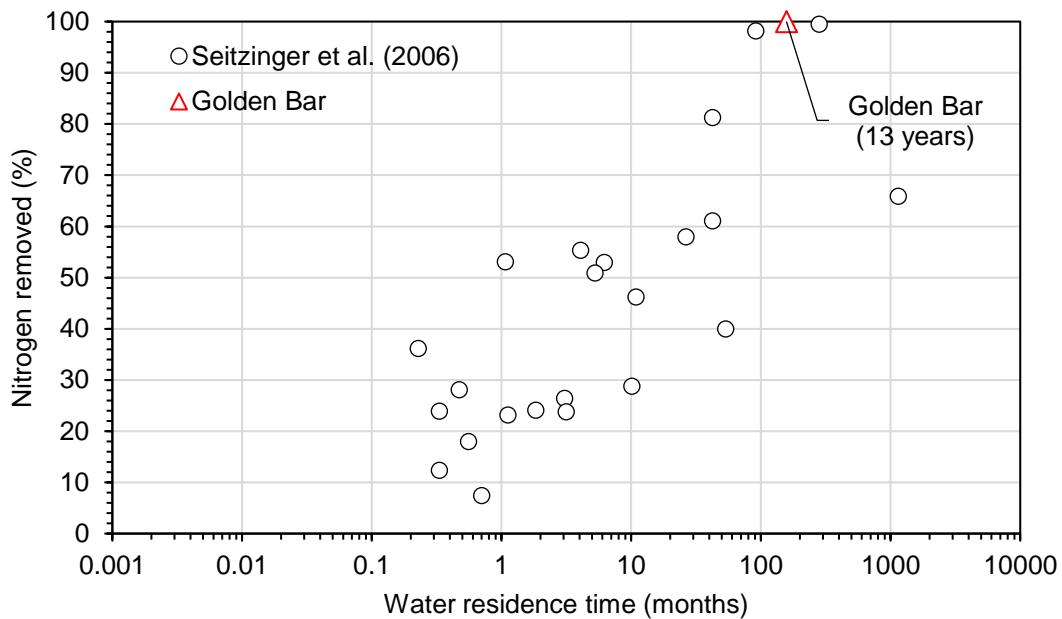


Figure 5: Lake water residence time and nitrogen removal. Data source: Seitzinger et al. (2006).

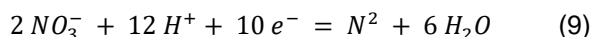
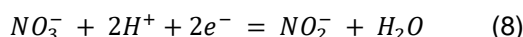
### Water Quality Model and the Estimation of ANFO-derived Nitrogen

A water quality model was developed for the Golden Bar Pit Lake using PHREEQC and includes all major ions and relevant elements. Moreover, the model incorporates kinetic equations to quantify the transformation rates of nitrogenous compounds within the lake. To achieve this, empirical data from the pit lake serves as the dataset to calibrate the nitrogenous concentrations, while nitrification and denitrification processes are also integrated into the model.

Both processes were included in PHREEQC from an empirical perspective; the only variables considered are time, nitrogen concentrations, and loads. Following the Amm.dat database approach



(Parkurst & Appelo, 2013), where  $\text{NH}_3$  is named Amm (from ammonia), the ammoniacal nitrogen is “uncoupled” from the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (in aqueous equilibrium reactions), and the key reactions that are modelled are listed below:



The first equation models the speciation between  $\text{AmmH}^+$  ( $\text{NH}_4^+$ ) and Amm ( $\text{NH}_3$ ). The second equation models the speciation of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . And the third equation models the reaction/change between  $\text{NO}_3^-$  and aqueous  $\text{N}_2$ .

The first kinetic process to include is denitrification, which converts aqueous  $\text{N}_2$  to Ntg (Nitrogen gas). By removing  $\text{N}_2$  from solution the model converts  $\text{NO}_3^-$  to  $\text{N}_2$  to compensate for the decrease in aqueous  $\text{N}_2$  (due to Eq. 9).

The second process is ammonia oxidation or nitrification, which converts Amm to  $\text{NH}_3$ . Due to  $\text{NH}_3$  not being defined in the database on purpose, the  $\text{NH}_3$  is assumed by PHREEQC to be speciated as the most stable species, which would be  $\text{NO}_3^-$  (in an aerobic environment). For denitrification, consumption of organic matter ( $\text{CH}_2\text{O}$ ) is assumed.

The ongoing denitrification/nitrification processes occur since the start of the model, even though the calculated loads of Amm-N and  $\text{NO}_3^-$  increase in the first years. To calibrate the ongoing processes, an initial nitrogen load of 700 kg (as  $\text{NH}_4\text{NO}_3$ ) was added as the “first flush” within the first three years of the model to match the empirical data and reach the  $\text{NO}_3^-$ -N peak of 400 kg in 2007. The results of the calibrated nitrate model are shown in Figure 6.

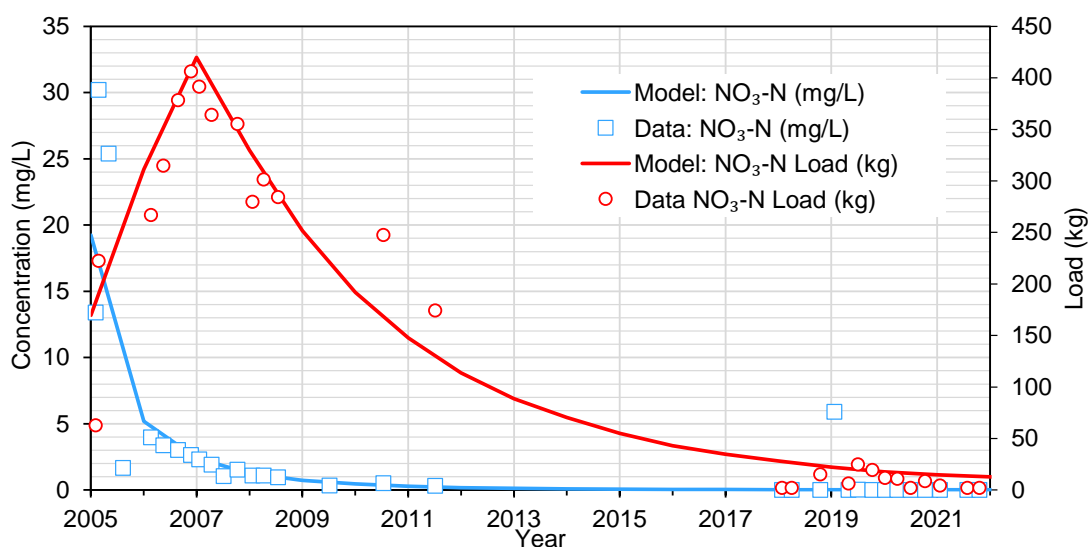


Figure 6: Nitrate nitrogen concentration and nitrate loads and the results of the model after calibration.

Using ~700 kg of  $\text{NH}_4\text{NO}_3$  being flushed off the pit walls to the pit lake and a pit void plan surface area of ~131,000  $\text{m}^2$ , it was estimated that 5.35  $\text{g}/\text{m}^2$  of nitrogen as  $\text{NH}_4\text{NO}_3$  was flushed from pit surfaces (i.e., ANFO blasting residue). It is proposed that this value can be used for quantifying  $\text{NO}_3^-$  loads and concentration at other pits at the Macraes mine. The resulting loads and concentrations are shown in Figure 6 using the calibrated initial load.

This study provides evidence of how nitrogenous compounds decrease with time within a pit lake environment. The results suggest that potentially, the process could be used to design a pit lake treatment system for nitrogenous compounds. With proper monitoring, a pit lake nitrate treatment

reactor could become an eco-friendly and sustainable solution for mitigating nitrate pollution in mining-affected water bodies.

## Conclusions

This study provides insights into the natural decay of ANFO-derived nitrogen in the Golden Bar Pit Lake:

- ANFO blasting residues have resulted in high initial concentrations of nitrate ( $\text{NO}_3 - \text{N}$  up to 30 mg/L) in the pit lake. However, our findings demonstrate that nitrate is not a conservative contaminant and is subject to natural removal processes over time (20-30% per year).
- Nitrification and denitrification processes play crucial roles in shaping the nitrogen concentrations in the pit lake. Nitrification led to an initial increase in nitrate concentrations, while denitrification facilitated the reduction of nitrate loads, especially after reaching the peak in 2007.
- Ammoniacal nitrogen also exhibited a rapid decay, primarily attributed to nitrification. This study highlights the importance of considering biochemical processes in pit lakes' water quality assessments and management strategies.
- The required amount of nitrogen (in the form of ammonium nitrate) was determined to be approximately 5.35 grams per square meter of the plan area of the pit.

## ACKNOWLEDGEMENTS

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