



Nitrogen Removal from Mining Dewatering and the Fate of Water Release to a River

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Abstract Seepage water in underground mining voids arises from interception with aquifers that may become contaminated with nitrogen (N)-based explosive during underground blasting operations. The nitrogen-contaminated water may be pumped from underground mining voids and stored at the surface or discharged to a nearby river without treatment if sufficient dilution is achieved to minimize effects on the aquatic environment and pastoral activities. Maximum N concentration in dewatering water was observed to be 200 times the receiving water of the nearby river when compared against ANZECC/ARMCANZ (2000) water quality guidelines. This study sought to identify sources of N contamination of underground seepage water, pumped to the surface for discharge to the nearby river. The level of protection (for an aquatic ecosystem) specified the water quality objectives to be achieved following water release. The ANZECC/ARMCANZ (2000) has three levels of aquatic ecosystem protection, and ‘Level 2 Aquatic Ecosystem’ was selected being described as applying to slightly–moderately disturbed systems including rural streams receiving runoff from land disturbed to varying degrees by grazing or pastoralism, nearby or adjacent to urban areas. The study considered river flow data, underground dewatering production, discharge rates, and river water quality for upstream and downstream of the discharge point, as well as quantities of explosives used underground at specified % N in explosives estimated to remain following blasting. The most important nitrogen form present in the mine discharge wastewater was found to be oxidized-N (>93%). Only 0.54 % of end-of-pipe discharge was measurable in the downstream river and indicated that rapid dilution and removal of oxidized-N (nitrate/nitrite) by biota could be achieved. The level of oxidized-N expressed as load discharged to the river showed that the quantity of N discharged was similar in magnitude to the spillage of 4% explosive.

Keywords nitrogen, explosive, mining, dewatering, discharge, cattle, aquatic species

INTRODUCTION

Seepage water in underground mining voids arises from interception with aquifers that may become contaminated with nitrogen-based explosives during underground blasting operations. Ammonium nitrate used commonly as an explosive is the same as the common fertilizer. Nitrogen (N)-contaminated water may be pumped from underground mining voids and stored at the surface for treatment or discharged to a nearby river without treatment if sufficient dilution is achieved to minimize effects to the aquatic environment and pastoral activities and can be demonstrated and approved by Government regulators. Existing nitrogen (N)-contaminated water added upstream arises from local agricultural and urban activities and may affect the aquatic ecosystem. This study sought to identify sources of nitrogen contamination of underground mining seepage water, pumped to the surface for discharge to the nearby river and if additional nitrogen (N)-contaminated water pumped to the river gives further effects on the aquatic ecosystem. The level of protection (for an aquatic ecosystem) specified the water quality objectives to be achieved following water release follows the ANZECC/ARMCANZ (2000) levels of aquatic ecosystem protection.

OBJECTIVE

The objective of this study is to identify sources of N contamination of underground seepage water from a mining operation that is pumped to the surface for discharge to a nearby river and to identify if the level of protection (for an aquatic ecosystem) of the specified water quality criteria can be achieved following water release.

METHODOLOGY

The study is based on a site in Queensland, Australia, and considered river flow data, underground dewatering production from mining, discharge rates, and river water quality upstream and downstream of the discharge point (Noller, 2006).

The level of protection (for an aquatic ecosystem Environmental Value - EV) is the level of aquatic ecosystem condition specified by water quality objectives (WQOs) to be achieved for the intended water. The Queensland Water Quality Guidelines (QWQG, 2006) were developed concurrently with the EVs and water quality objectives (WQOs) and release process. These are technical guidelines for deriving WQOs for rivers in Queensland and include locally and regionally relevant water quality data for fresh, estuarine, and marine waters.

The ANZECC/ARMCANZ (2000) established three levels of aquatic ecosystem protection that are applied by QWQG (2006). The levels of aquatic ecosystem protection are: (i) Level 1: High ecological/conservation value ecosystems - effectively unmodified or other highly valued systems; (ii) Level 2: Slightly–moderately disturbed ecosystems - ecosystems in which aquatic biological diversity may have been adversely affected to a relatively small but measurable degree by human activity; and (iii) Level 3: Highly disturbed ecosystems - measurably degraded ecosystems of lower ecological value. The EVs and WQOs identified that the study river is: A level 2 Aquatic Ecosystem. This is described by ANZECC/ARMCANZ (2000) as an ‘Ecosystem in which aquatic biological diversity may have been adversely affected to a relatively small but measurable degree by human activity’. The biological communities remain in a healthy condition and ecosystem integrity is largely retained. Typically, such systems have slightly to moderately cleared catchments and/or reasonably intact riparian vegetation. Slightly–moderately disturbed systems could include rural streams receiving runoff from land disturbed to varying degrees by grazing or pastoralism. This description fits the surrounding area of the study mine and river.

Ammonium nitrate is the key explosive used in the underground workings at the study mine. The quantities of ammonium nitrate explosives with specified % N used at the underground mine gave an estimate of remaining explosives following blasting. As a general rule, 1 tonne of rock uses 1 kg of explosive. Some ammonium nitrate may be spilt during charging and was estimated to be 4% based on collecting residues and weighing them (Noller, 2006).

Water quality was collected and analyzed for dewatering from an underground source, to the discharge point, following discharge to a local river, upstream and downstream at the following sites: (i) Dewatering from underground; (ii) Dewatering storage tank at exit to discharge pipe before discharge to the local river; (iii) Downstream local river beyond mixing zone; and (iv) Upstream of the local river, including an historical gauging site of 40 years operation. Water samples were collected by mine staff and water quality data was measured by the mine laboratory for pH, total dissolved solids (TDS), suspended solids (SS), N forms as total unfiltered nitrogen, total filtered N, nitrite and nitrate (oxidized-filtered), particulate N (>0.45 µm), organic-N (total - oxidized-N) and ammonium ion (filtered). Filtration for N was conducted on-site using 0.45 µm cartridge membrane filters with a plastic syringe.

The site water budget included water quality of water consumed on site, water discharged quantities, and surface runoff from sub-catchments on site. The Queensland regulator has a large number of monitoring sites and gauging stations on the study site river (N and M, 2006). An upstream gauging station with 40 years of records was selected as having the most complete and relevant set to the discharge of the study mine (Noller, 2006).

RESULTS AND DISCUSSION

Table 1 gives the average monthly river flow (ML) for September to February at the main upstream gauging station which corresponds to the release of water from the mine. January and February and the annual summer rains (see Table 1 for rainfall during the study period). The data record for monthly flow at the upstream gauging station over 40 years had the corresponding average monthly flow for the period ending 2,400 hrs. and was $68,970 \pm 178,630$ ML. According to the Queensland Environmental Authority water from the mine must not be discharged to the river when the flow rate at the main upstream gauging station is less than 20 ML (Noller, 2006). For the period November–December (Table 1) the total underground transfer from the discharge tank to the river was 11,222 kL/month, based on a rate of 362 kL/day. The accumulated groundwater from the mine that was discharged to the river contained a consistently high total N level that was primarily oxidized-N.

Table 1 Monthly River flow (ML) at the main upstream gauging station over 40-years period

Month	Mean ^a	Standard deviation ^a	Percent (%)	Monthly rainfall (mm) at mine ^b
September	14,575	23,850	44.41	
October	17,384	27,491	1.34	134
November	31,678	47,532	15.17	216
December	50,762	11,106	16.52	141
January	115,284	319,054	15.64	-
February	210,310	379,291	8.79	-

Source and explanation: a. NR&M (2006); b. Noller (2006)

Table 2 gives a summary of ammonium nitrate used by the mine during the period from September to February. It is noted that all explosives were consumed in the explosion, apart from spillage (Noller, 2006). Assuming that spillage was 4%, 2,009 kg ammonium nitrate was dissolved in the underground water system from September to February. The established guide of 4,000 kg/month was equivalent to 1,400 kg-N/month and the loss of 160 kg is 56 kg-N. The calculated load of N released from the rising water main, discharge tank, and via the pipe was compared with the total ammonium nitrate used and spillage at the mine (Table 2). Percent N in explosives gave a total N budget, together with an estimate of how much remains following blasting.

Table 2 Total ammonium nitrate (as % of explosive use) consumption over a 6-month period

Explosive Accounting period (% Explosive use) ^a	Total ammonium nitrate (kg) ^a	Spillage ammonium nitrate estimated at 4% (kg) ^a	Total ammonium nitrate-N (kg) ^b	Spillage-N estimated at 4% (kg) ^b
May	7,467.4	299	2,614	104.5
October	11,778.9	471	4,122	164.9
November	4,099.1	164	1,435	57.4
December	6,435.7	257	2,253	90.1
January	10,714.8	426	3,750	150.0
February	11,784.2	471	4,124	165.0
Total	52,280.0	2091	18,298	731.85

Source and explanation: a. Noller (2006); b. Factor for ammonium nitrate - N = Total x 0.35; molecular weight = 80

Table 3 gives the calculated and measured loads of N from underground dewatering and discharged to the river, including a summary of the oxidized-N discharged from the mine to the river, showing that the quantity of N discharged was similar in magnitude to the spillage of 4% explosive. Table 4 gives the predicted and measured oxidized-N concentration in the river based on end-of-

pipe discharge and river mean flow. The difference between measured and calculated concentrations indicates lower recent flow in the river compared with the historical record. Some particulate forms of N arose from the mine dewatering, but most N present was filterable, as expected from explosive residues. Some particulate N (100 µg/L) was also present in river water (Noller, 2006), but data was not included in Tables 3-5.

Table 3 Calculated and measured loads of nitrogen from underground dewatering

Month	End of pipe discharge (kL) ^a	Measured nitrite-nitrate-N end of pipe (µg/L) ^a	Nitrogen discharged end of pipe (kg-N) ^a	Spillage of 4% explosive as -N (kg) ^a
October	5,260	21,800	114.7	269.4
November	11,222	19,800	222.2	297.5
December	7,157	17,600	126.0	(Nov-Jan)
January	9,030	18,900	170.7	165.0
Sum	-	-	633.6	731.85

Source and explanation: a. Noller (2006)

Table 4 Predicted and measured nitrate and nitrate – N concentration in river

Month	River mean monthly flow (ML) ^a	End of pipe discharge (kL) ^b	Measured Oxidized -N end of pipe (µg/L) ^b	Dilution ratio ^b	Predicted Oxidized -N river (µg/L) ^b	Measured Oxidized-N river (µg/L) ^b
October	17,384	5,260	21,800	3,305	6.6	997
November	31,678	11,222	19,800	2,823	7.0	254
December	50,762	7,157	17,600	7,093	2.5	166
January	115,284	9,030	18,900	12,767	1.5	12
Range					1.5-7.0	997-12

Source and explanation: a. NR&M (2006); b. Noller (2006)

Table 5 Nitrogen in underground seepage water and following discharge to river

Site	Total N ^a	Total N (filtered <0.45µm) ^a	Oxidized-N ^a	Ammonia-N ^a
Rising water main (µg/L)	20,900	19,200	20,000	270
Discharge Tank (µg/L)	19,900	20,500	31,300	0.10
End of pipe discharge (µg/L)	20,200	18,700	18,700	130
River upstream 10m (µg/L)	500	400	50	60
River downstream 10m (µg/L)	1,100	0.50	0.17	70
River main upstream gauging station 40 years (µg/L)	750	-	0.29	21
Queensland water quality guideline (µg/L) ^{b,c}	<250	-	<10	<10

Source and explanation: a. Noller (2006); b. QWQG (2006) annual median; c. QWQG (2006) guideline for Organic-N <200µg/L =total-N – oxidized-N

Table 5 gives N in underground seepage water and following its discharge to the river. The most important N form present in the mine discharge wastewater was found to be oxidized-N (>93%). Only 0.54 % of end-of-pipe discharge was measurable in the downstream river and indicated that rapid dilution and removal of oxidized-N by biota could be achieved. The level of oxidized-N expressed as load discharged to the river showed that the quantity of N discharged was similar in

magnitude to the spillage of 4% explosive. The accumulated groundwater from the mine that is discharged to the river contains a consistently high total N level that is primarily oxidized-N.

The historical upstream gauging station data for the river (Table 5) shows that total N has been consistently higher than the Queensland water quality guideline Level 2 water quality guideline, including upstream of the mine, for a long period of time. The results in Tables 5 and 6 show that the river has had a consistently high nitrogen load that exceeds the current guideline. An additional load to the river was added by the mine discharge. Table 6 gives water quality in underground seepage water and following discharge to the river for pH, total dissolved solids, and suspended solids. pH was marginally lower than the mine dewatering which also contributed to salinity. Suspended solids remained at or lower than the guideline.

Table 6 Water quality in underground seepage water and following discharge to the river

Site	pH ^a	Total dissolved solids (mg/L) ^a	Suspended solids (mg/L) ^a
Rising water main	8.18	2,280	6
Discharge Tank	8.18	2,280	6
End of pipe discharge	8.16	913	2
River upstream 10m	7.90	247	4
River downstream 10m	7.8	260	5
River main upstream gauging station 40 years	7.7	-	-
Queensland water quality guidelines	6.5-8.2	-	<6

Source and explanation: a. Noller (2006); b. QWQG (2006) annual median.

Total N in river upstream water was 500 µg/L which exceeded the Queensland water quality guideline (Table 5). The river 10m below discharge was 1,100 µg/L Total N which also exceeded the guideline (QWQG, 2006). Some particulate N (100 µg/L) arose from the mine dewatering but most N present was filterable (Noller, 2006).

Ammonia in the river upstream (60 µg/L) and downstream river (70 µg/L) both exceeded the Queensland water quality guideline level of 10 µg/L (Table 5). The addition of ammonia from the mine to the river was therefore 10 µg/L and the level at the river downstream exceeded the QWQG (2006) guideline. The discharge of any ammonia from the mine dewatering was compromised by the existing river load.

Oxidized-N in the river upstream was 50 µg/L which exceeded the guideline (<40 µg/L). The river downstream level was 170 µg/L and indicated an addition of 120 µg/L oxidized-N to the river from mine dewatering. However, comparison with the end of pipe discharge and river downstream oxidized-N indicated efficient removal of oxidized-N. The oxidized-N discharged from the end of the pipe was in the key form of oxidized-N i.e., $18,700/20,200 \times 100 = 92.6\%$ of Total-N. However, the discharge of any oxidized-N like ammonia from mine dewatering was compromised by the existing river load. Although the oxidized-N at the end of the pipe was 18,700 µg/L, the difference between the river upstream and river downstream was only 120 µg/L.

Organic-N concentration, calculated as the difference between total and oxidized-N, was very low. The upstream river level was <100 µg/L compared with the river downstream level of 330 µg/L, the latter exceeding the QWQG (2006) guideline figure of 200 µg/L. This may be due to the presence of urea or a similar soluble organic form of nitrogen from pastoral and crop activities.

The most important N form present in the mine discharge was therefore the oxidized-N (>93%) and organic-N was less important. Some particulate-N was also present. The fact that only 0.54 % of end-of-pipe discharge remained measurable in the river downstream indicated that rapid dilution and removal of oxidized-N by biota was occurring. Maximum N concentration in dewatering water for this study was observed to be 200 times the receiving water of the nearby river when compared against ANZECC/ARMCANZ (2000) water quality guidelines and 'Level 2 Aquatic Ecosystem' that was selected for this river receiving runoff from land disturbed to varying degrees by grazing or pastoralism, nearby or adjacent to urban areas.

CONCLUSION

The study showed that accumulated underground groundwater from the mine dewatering being discharged to the river had a consistently high total N level that was primarily oxidized-N (>93%) and was derived from 4% ammonium nitrate spillage from blasting. Although only 0.54 % of end-of-pipe mine discharge was measurable in the downstream river and indicated that rapid dilution and removal of oxidized-N by biota could be achieved, the Total N in river upstream water was 500 µg/L which exceeded the QWQG (2006) water quality guideline (Table 5). The river 10m below discharge was 1,100 µg/L Total N which also exceeded the guideline (QWQG, 2006), but most N present was filterable (Noller, 2006). Ammonia in river upstream (60 µg/L) and downstream river (70 µg/L) both exceeded the QWQG (2006) water quality guideline level of 10 µg/L (Table 5).

The selected 'Level 2 Aquatic Ecosystem' Slightly–moderately disturbed ecosystems–ecosystems in which aquatic biological diversity may have been adversely affected to a relatively small but measurable degree by human activity for the receiving water of the nearby river when compared against ANZECC/ARMCANZ (2000) water quality guidelines for this river receiving runoff from land disturbed to varying degrees by grazing or pastoralism, nearby or adjacent to urban areas. However, the presence of excess Total N in the river water from upstream agricultural and urban activities compromised the mine water discharge. The discharge of any ammonia from the mine dewatering was also compromised by the existing river load.

Thus, treatment options for the mine-discharged water were required and focused on the removal of oxidized N. Ammonia was effectively removed by a shift in the equilibrium of its dissolved form prior to its transfer to the surface, i.e., the ammonia was either removed as nitrogen gas or converted to nitrate. The co-cations in the solution are alkaline and alkaline earth metals and not hydrogen ions as the pH are relatively high.

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