

# Release of Explosives Originated Nitrogen from the Waste Rocks of a Dimension Stone Quarry

Teemu Karlsson and Tommi Kauppila

*Department of Land Use and Environment, Geological Survey of Finland*

## ABSTRACT

Emissions of nitrogen compounds, including  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , from mining areas can have detrimental effects on the environment through either eutrophication or direct toxicity. Besides environmental effects, contamination by nitrogen originated from explosives may be problematic, depending on definitions and classifications of inert waste. In certain jurisdictions, nitrogen contamination of otherwise mineralogically and chemically inert waste rocks of good technical quality may hinder utilization of these product streams. This is an important economic and environmental issue, especially at dimension stone quarries.

To study the amount of nitrogen contamination in waste rocks produced by these types of quarrying operations, two 1 m<sup>3</sup> lysimeters were installed at a selected quarry. The test units were filled with fresh waste rock immediately after the excavation of a block of dimension stone. The rainwater flowing through the test units was collected in separated plastic tanks and sampled regularly over a one year period.

The results indicate that the “first flush” of recharge water occurs rapidly, only after a few weeks, after which the nitrogen drainage settles to near natural rainwater levels. Calculations on the amount of nitrogen leached out of the test units and the remaining nitrogen detected on the rocks after the monitoring period suggest that a little more than half of the explosive residuals had remained within the waste rock material. The total amount of nitrogen derived from explosives in the waste rock material at a dimension stone quarry seems to be in the order of 0.1 mg/kg, which is well below the amounts commonly detected in waste rocks produced by larger scale mines and thus indicate that the environmental risks associated with these type of waste rocks are relatively low.

**Keywords:** Explosives, nitrogen, waste rock, dimension stone

## INTRODUCTION

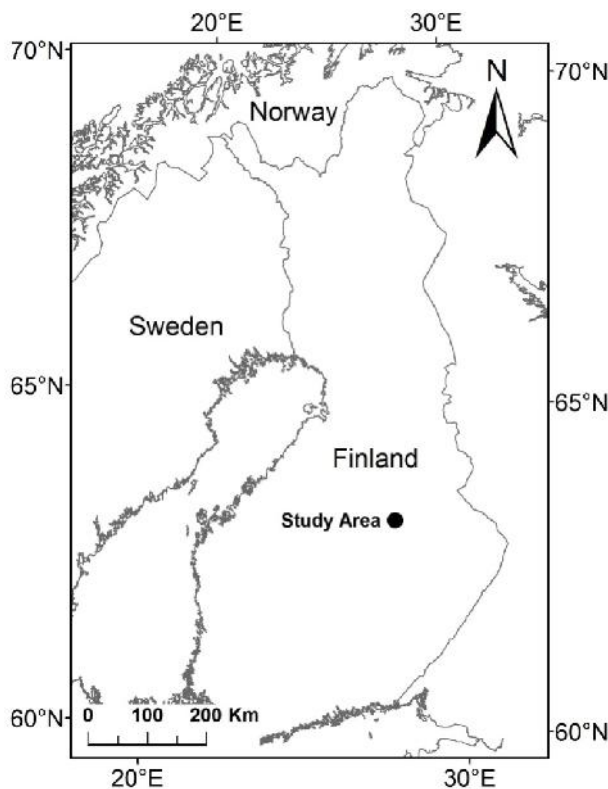
The presence of nitrogen compounds in mining areas can have detrimental effects on the environment through eutrophication or direct toxicity (Forsyth et al. 1995). Use of explosives is one of the main sources of nitrogen emissions in the mining industry (Morin & Hutt 2009). Besides environmental effects, contamination by nitrogen compounds derived from explosives may be problematic due to varying definitions and classifications of inert waste. Nitrogen contamination of otherwise mineralogically and chemically inert waste rocks of good technical quality may hinder the utilization of these product streams, which is an important economic and environmental issue at several quarries and mines.

To study the rate of dissipation and amount of nitrogen contamination on waste rock surfaces and to investigate the reactivity of the materials, a long term field study was conducted at a selected quarry.

## METHODOLOGY

The study area was a dimension stone quarry located in Varpaisjärvi in the Lapinlahti municipality in the region of Northern Savonia (Figure 1).

The main stone extracted at the selected quarry is black diabase, with an average density of 3 080 kg/ m<sup>3</sup>. The total amount of extraction is approximately 28 500 m<sup>3</sup>/year, of which around 24 000 m<sup>3</sup> i.e. 73 920 tons is waste rock. The use of explosives, mainly nitroglycol and diatomite containing K-pipecharges by Forcit Oy, is roughly 5 700 kg/year, the specific charge (powder factor) being around 0.065 kg / t. The average nitrogen concentration of K-pipecharge is 4.2 % (Forcit Oy 2013). The water resistance of K-pipecharges is reasonable, but the unexploded agent dissolves gradually into water. The waste rocks consist mainly of the same diabase material as the final products.



**Figure 1** The test site (a dimension stone quarry) is located in Varpaisjärvi in the Northern Savonia region of Finland

To evaluate the temporal changes in the quality of water emanating from waste rock produced by the quarry, two lysimeters were installed at the quarry site, and filled with waste rock material collected immediately after the excavation of a large diabase block. The rock material in both lysimeters was identical and the purpose of setting up two units was to examine the repeatability of the test. Unit 1 contained approximately 1 970 kg of rocks with 38 % porosity, and Unit 2 contained approximately 1 790 kg of rocks with 44 % porosity. The test units are shown in Figure 2.

The rain water flowing through the lysimeters was collected in separate 70-liter plastic tanks and analysed frequently, 9 times in total, between the 10th of October 2012 and the 16th of October 2013, excluding the winter months when the test units were frozen. The sampling interval was 2 weeks during the first month and once a month during the rest of the monitoring period.

The monitored parameters included nitrogen species ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and total-N),  $\text{Cl}^-$ , pH, Ec and temperature. Chloride ( $\text{Cl}^-$ ) is present in rock dust and in the blasting residuals (as sodium chloride) and is considered as a good indicator of the first flush of water through the test units (Bailey et al. 2013).

At the end of the observation period, the test units were filled (washed) with tap water and sampled three times (Unit 2 only once) to remove the remaining nitrogen of explosive origin and to determine the porosity and approximate weight of the rocks inside the test units. The chemical composition of the tap water used for washing was analyzed as well.



**Figure 2** The aging test units 1 (front) and 2 (behind). The rain water flowing through the units was collected in the green plastic tanks below. Photo: Lauri Solismaa / GTK

### Field measurements and sampling

The untreated samples were collected into HDPE sample bottles that had been triple-rinsed with sample water. The sample bottles were sent to the laboratory in a cool box during the sampling day. The samples arrived at the laboratory next morning and were analysed as soon as possible, to minimize the alteration of the samples, especially the sensitive NO<sub>2</sub>.

The pH, temperature, electric conductivity, nitrite and ammonium were measured in the field. The pH was measured by the Mettler Toledo SevenGo pH-meter. The electrical conductivity and temperature were measured with the WTW-electric conductivity meter Cond 340i. The nitrite and ammonium concentrations were analyzed with a portable Hach Lange DR2800 spectrophotometer using Lange cuvette tests LCK342 (0.6-6 mg/l NO<sub>2</sub>-N) and LCK 304 (0.015-2 mg/l NH<sub>4</sub>-N). The amount of rain water accumulated in the tanks was measured and the tanks were emptied after every sampling occasion.

Besides field measurements, the nitrogen species were also analysed in a laboratory to estimate the accuracy of the spectrophotometric measurements and to investigate the effects of transportation of the water samples to the laboratory. The results seemed to be similar with both methods although the portable spectrophotometer gave lower concentrations when the weather was colder.

### Laboratory measurements

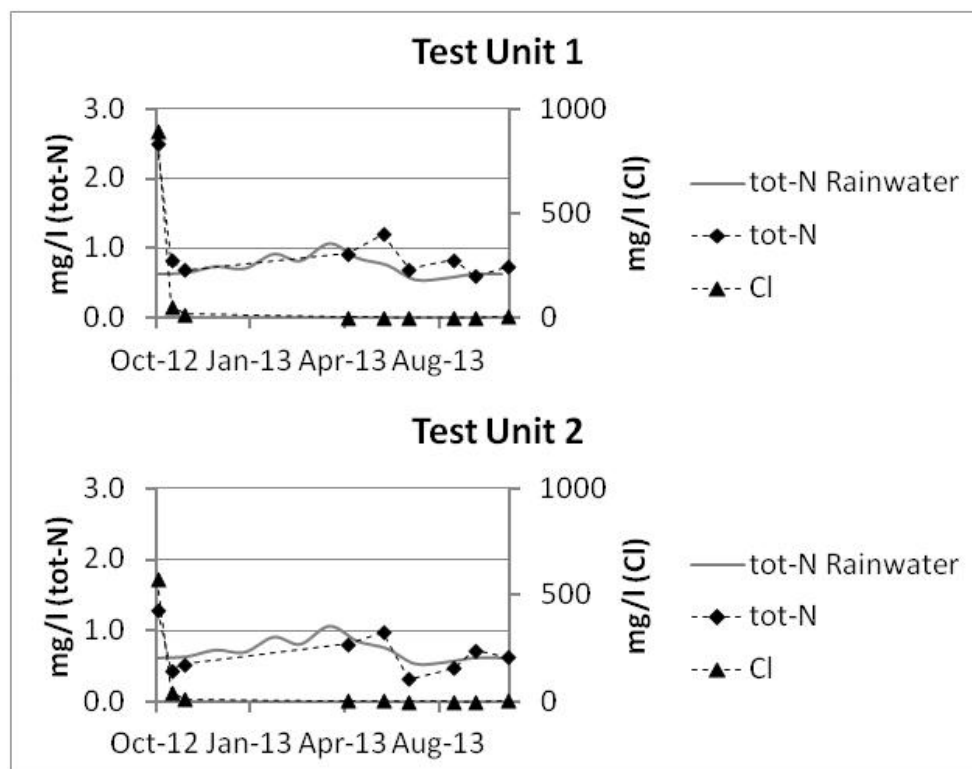
The laboratory measurements included total nitrogen, nitrite, nitrate and chloride in an accredited laboratory (Labtium Oy). The NO<sub>2</sub><sup>-</sup> was measured by spectrophotometry. The anions NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> were measured using ion chromatography (IC) according to the standard SFS-EN-ISO 10304-1. NH<sub>4</sub><sup>+</sup> was measured by the Aquakem analyser (salicylate-spectrophotometric method). Total nitrogen was measured by the peroxosulphate oxidation and Aquakem analyser (hydrazine reduction and spectrophotometric sulphanilamide method).

## RESULTS AND DISCUSSION

The monitored concentrations and values followed similar trends in both test units, but the concentrations were somewhat lower in Test Unit 2. At first the electric conductivity and concentrations, e.g. of total-N and Cl<sup>-</sup> were relatively high, but declined rapidly to the average local rain water values after the “first flush” (Figure 3). Cl<sup>-</sup> declined more sharply and remained low for the remainder of the study. The nitrogen concentrations were more erratic, but the absence of Cl<sup>-</sup> suggests that most of the nitrogen was delivered from rain water / atmosphere.

The most abundant nitrogen species was NO<sub>3</sub>-N, around 60 % of the total first flush N concentration. The NH<sub>4</sub>-N concentrations were relatively high during the first flush, around 40 % of the total N. Later, the proportion of the NO<sub>3</sub>-N increased to 67 – 94 % and the proportion of NH<sub>4</sub>-N decreased to 1 – 9 %. The field measurement values of NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> were mainly higher than those measured in laboratory, which may indicate the instability of these nitrogen species during transport.

The total-N concentrations in rainwater have been measured by the Finnish Environment Institute (SYKE) at the nearest weather station at Maaninka (about 40 km south west from Varpaisjärvi) during 2004 – 2012. The rainwater samples collected at the test units at Varpaisjärvi had similar total-N concentrations to Maaninka, around 0.6 mg/L. During two observation periods (30<sup>th</sup> of April 2013 and 20<sup>th</sup> of August 2013) the rainwater tanks were full and probably overflowed.



**Figure 3** Total-Nitrogen and Chloride concentrations in the recharge waters of the Test Unit 2 and total-N of rainwater in Maaninka (monthly averages during the years 2004-2012) measured by the Finnish Environment Institute

The amount of water required to fill the Unit 1 was 380 litres and 440 litres for the Unit 2 (i.e. the porosities were 38 % and 44 %). The rock masses of the units were calculated by the volume and density of the diabase (in Unit 1 approximately 1 970 kg and in the Unit 2 approximately 1 790 kg).

The amounts of total nitrogen released from the test units were calculated by multiplying the amounts of water (litres) by the nitrogen concentrations (Table 1). The nitrogen concentrations of the first flush were determined by subtracting the background value (0.6 mg/L in October) from the measured concentrations. The first flush includes the first samplings in October 2012 when the concentrations were higher than the background values of rainwater (Unit 1 10<sup>th</sup> October 2012 and 25<sup>th</sup> October 2012, Unit 2 only 10<sup>th</sup> October 2012).

The amount of nitrogen originating from explosives was detected in Test Unit 1 was 138.8 mg i.e. 0.07 mg/kg Waste Rock and 32.5 mg i.e. 0.02 mg/kg Waste Rock in Test Unit 2. About half of the total nitrogen seemed to be left in the test units after one year of ageing. Presumably some traces of explosive nitrogen were also released after the first flush, but the nitrogen concentrations were so close to the average rain water values that assessment of exact numbers is difficult. Some small residual amounts probably also remained in the stone material after washing. Considering the uncertainty factors, the amount of nitrogen derived from explosives in the type of rock material used in this study is around 0.1 mg/kg or 0.1 g/t. Multiplying this by the annual average amount of waste rocks (24 000 m<sup>3</sup> i.e. 73 920 t) remaining at the test site results in blasting-related nitrogen load of around 7.4 kg/year from the waste rock pile.

**Table 1** The amounts of total nitrogen released from the test units during first flush and washing. \*NH<sub>4</sub>-N + NO<sub>2</sub>-N concentrations.

Sample	tot-N (mg/L)	Water (L)	Released N (mg)
<b>Test Unit 1</b>			
10.10.2012	1.9	28	53.2
25.10.2012	0.2	48	9.6
1 <sup>st</sup> wash	0.1	380	38
2 <sup>nd</sup> wash	0.1	380	38
3 <sup>rd</sup> wash	0.0	380	0
<b>Total N</b>			<b>138.8</b>
<b>Test Unit 2</b>			
10.10.2012	0.7	27.5	19.3
1 <sup>st</sup> wash	0.03*	440	13.2
<b>Total N</b>			<b>32.5</b>

Lysimeters used in this study were relatively small scale compared with the size fractions of normal waste rock material, which introduces a bias to the test setup. In addition, the residuals of explosives are heterogeneously distributed in a waste rock material as demonstrated by the differences between the test units. The rock material in the test units presented a "worst case"; real waste rock contains also larger boulders, so it has less surface area / kg (= less explosives-N / kg)

than the finer material in the test units. This indicates that in practice, the amount of leaching from the waste rock material should be less.

Waste rocks produced by the natural stone industry seem to contain less explosives originated nitrogen than waste rocks produced by larger mining activities. For example waste rock at the Diavik diamond mine in Canada contains tot-N around 4.6 mg/kg (Bailey et al. 2013) and ore and waste rocks at the Kemi chromium mine around 20 mg/kg (Mattila et al. 2007).

The leaching tests conducted in this study apply to the K-pipecharge explosives used at the test quarry, which contain relatively low amounts of nitrogen, about 4.2 %. Different types of explosives exist for different purposes and their nitrogen contents and solubilities may vary. In general, the nitrogen content of different rock blasting explosives varies between 20 – 30 % of total weight (Chloth 2011).

## CONCLUSIONS

Based on the observation period of more than a year the “first flush” of nitrogen occurs rapidly, during the first few weeks (or first rain events), after which the nitrogen drainage settles to natural rainwater levels. Based on the current results, the first flush removes approximately half of the total nitrogen, mainly in NO<sub>3</sub>-N and NH<sub>4</sub>-N forms.

Calculations on the nitrogen leached out of the test units during the observation period and the remaining nitrogen detected on the rocks after the test period indicate that some residuals of explosives remain within the test material. The remaining nitrogen is leached out fairly slowly, promoting loss to the atmosphere.

The two seemingly identical units had different nitrogen concentrations, which suggest that the undetonated explosives are heterogeneously distributed in a waste rock pile.

The total amount of nitrogen derived from explosives in the waste rock material of a dimension stone quarry seems to be on the scale of 0.1 mg/kg, which is well below the amount detected in waste rock produced by larger scale mines. The main reason for the difference is probably the moderate use of low nitrogen containing explosives in natural stone quarrying.

As the nitrogen contamination of dimension stone quarrying waste rock is relatively low to begin with and enhanced by the rapid flushing by rainwater, the residues of explosives should not be considered to prevent the utilization of otherwise mineralogically inert waste rocks of good technical quality.

## ACKNOWLEDGEMENTS

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