UPPSALA UNIVERSITET

NITROGEN TRANSFORMATIONS AT THE KIRUNA MINE

The use of stable nitrogen isotopes to trace nitrogen-transforming processes

Lino Nilsson

Abstract

Nitrogen transformations at the Kiruna mine
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Release of different nitrogen compounds can cause eutrophication in lakes and rivers which can lead to oxygen-free environments in bottom water and in the sediment and can in turn lead to fish-deaths. Ammonium can be toxic to biota and nitrate can in high concentration even be toxic to humans. WHO has released a limit for nitrate concentration in drinking water of 10mg/l.

The LKAB mine in Kiruna is the largest underground iron mine in the world and is prospecting, mining and refining iron ore, with an annual production of around 28 million tons. Release of different nitrogen compounds as a result of the explosives used during the mining operations has been a known problem for some time; however the processes affecting nitrogen during the water transport have never been fully investigated.

The main objective of this MSc thesis is to determine if changes in nitrogen and oxygen isotope composition can be used as a tracer for nitrogen transformation processes in the mine water at LKABs underground mine in Kiruna.

Water samples were collected at key points in the water transport system and were analyzed for isotopic composition. Isotopic and chemical data revealed two different sources of nitrate and ammonium, undetonated explosives and leachate from waste rocks. Three different nitrogen changing processes affecting concentration of nitrate and ammonium were found: ammonium volatilization, nitrification and sorption. It was not possible to quantify these processes individually. No processes which decrease the nitrate concentration were found.

Referat

Kväveförändrande processer i Kiruna gruvan
Användningen av stabila kväveisotoper för att spåra kväveomvandlande processer.

Lino Nilsson

Utsläpp av olika kväveföreningar kan orsaka övergödning i sjöar och floder vilket kan leda till syrefria förhållanden på bottnar och i sediment, vilket leder till att fiskar dör. Ammonium kan vara toxiskt för biota och nitrat kan i höga koncentrationer till och med vara toxiskt för människor. WHO har satt ett gränsvärde för nitratkoncentration i dricksvatten på 10mg/l.

LKABs gruva I Kiruna är den största underjordsgruva i världen som bryter järn. LKAB i Kiruna har en årlig produktion på 28 miljoner ton järn. Utsläppen av olika kväveföreningar till följd av användandet av sprängämnena som används är ett känt problem, dock har processerna som påverkar kvävet genom vattentransporten aldrig blivit utrett.

Huvudmålet med det här projektet var att bestämma om ändringar i isotopsammansättningen för kväve och syre kan användas för att spåra kväveförändrande processer i gruvvattnet i LKABs underjordsgruva i Kiruna.

Vattenprover samlades vid olika platser i vattentransportsystemet och analyserades för isotopsammansättning. Resultaten visade på två olika källor för kväve, odetonerade sprängämnen och läckage från gråbergshögar. Tre olika kväveomvandlande processer hittades: ammonium förångning, nitrifikation och sorption. Det var inte möjligt att kvantifiera dessa processer individuellt. Inga processer som sänkte nitratkoncentrationen upptäcktes.

Popular science review

Release of nitrogen compounds can cause eutrophication in lakes and rivers which, if progressing over time, causes an oxygen-free environment in the sediment. The nitrogen compounds ammonia and nitrate are two common forms; ammonia is in high concentration toxic to biota and nitrate is in high concentration toxic to humans.

LKABs mine in Kiruna, Sweden, is the largest underground iron mine in the world. Ammonium-nitrate based explosives are used for ore blasting. Boreholes are charged with the explosives and are later detonated. It can take up to months from charging to detonation. During this time groundwater can infiltrate and dissolve some of the explosives into ammonium and nitrate. Groundwater accumulates in the mine very quickly and a pump system is used to pump all the water up from the mine. The water is later on used as process water in the mineral processing plants. The water used in the different processing stages is then collected in a dam system where suspended particles have a chance to settle. Some of this water is then discharged through the outlet to the recipient, Kalixälven, and some water is recirculated and used as process water again.

During the water transport some processes are affecting the concentration of nitrate and ammonium, processes such as nitrification, denitrification and ammonium volatilization. These processes have been examined using stable nitrogen isotopes as a tracing method, the basic principle of using isotopes as a tracer is that every nitrogen-changing process has a signal that can be identified by examining how the isotopic composition shifts during the water transport. The investigation was carried out by collecting water samples at key locations in the mine, and analyzing the samples for nitrate and ammonium concentrations, as well as the isotopic composition in nitrogen for ammonium and isotopic composition in nitrogen and oxygen for nitrate.

Using this method, three different nitrogen-transforming processes were found:

- Nitrification, a process which transforms ammonium into nitrate, increasing the nitrate concentration while lowering the concentration of ammonium.
- Ammonium volatilization, a process where ammonium transforms into ammonia. Ammonia in the water is very volatile and will escape the system as ammonia gas.
- Sorption, a process where compounds such as ammonium and nitrate electrostatically bind to suspended particles in the water.

Given the three found processes, all of which only reduce the ammonium concentration, and one of which increases the concentration of nitrate, the nitrate concentration in the mineral processing system increases.

Populärvetenskaplig sammanfattning

Utsläpp av olika kväveföreningar orsakar övergödning i sjöar och floder vilket, om det pågår under en längre period, leder till syrefria förhållanden på bottnar. Detta leder i sin tur till många olika miljöproblem, exempelvis fiskdöd. Sprängämnen med två vanliga kväveföreningar, nitrat och ammonium, används i de svenska gruvorna. Utsläpp av ammonium kan i höga koncentrationer vara toxiskt för biota och nitrat i höga koncentrationer kan vara toxiskt för människor.

LKAB's gruva i Kiruna är världens största underjordsgruva för brytning av järnmalm. I brytningsprocessen används ammoniumnitrat-baserat sprängmedel. Borrhålen laddas med sprängämnen och det kan ta månader innan de laddade borrhålen detoneras. Under den här tiden kan grundvatten flöda in och lösa upp delar av sprängämnet i ammonium och nitrat. Grundvatten ansamlas fort i gruvan och ett pumpsystem används för att pumpa upp allt vatten. Det uppumpade vattnet används sedan som processvatten under de olika anrikningsprocesserna. Vattnet samlas sedan upp i ett damsystem där större suspenderade partiklar sedimenterar, en del av vattnet släpps sedan ut till recipienten, Kalixälven, och resten av vattnet återcirkuleras och används som processvatten igen.

Under vattentransportsystemet förändras koncentrationen av ammonium och nitrat av olika kväveförändrande processer, exempelvis nitrifikation, denitrifikation eller ammonium förångning. Dessa processer har undersökts med hjälp av stabila kväveisotoper som spårningsmetod. Principen med att använda stabila isotoper som spårningsmetod är att alla kväveförändrande processer har en signal som kan identifieras genom att undersöka hur isotopsammansättningen förändras under vattentransporten. Studien utfördes genom att ta vattenprover vid olika punkter i vattentransportsystemet och analysera proverna för nitrat- och ammonium- koncentrationer, samt isotopsammansättningen för kväve och syre i dessa kväveföreningar.

Metoden visade på tre olika kväveförändrande processer:

- Nitrifikation, en process som omvandlar ammonium till nitrat.
- Ammoniakavgång, en process där ammonium övergår till ammoniakgas. Gasen är flyktig och kan lämna systemet vid övergång till atmosfären.
- Sorption, en process där föreningar som ammonium och nitrat binder elektrostatiskt till större suspenderade partiklar.

Av de tre funna processerna så minskar samtliga ammoniumkoncentrationen, medan en process, nitrifikation, ökar nitratkoncentrationen. Ammoniumkoncentrationen i utsläppsvattnet är låg medan nitratkoncentrationen är betydligt högre. Detta är delvis en effekt av att nitrat har ackumulerats i mineralförädlingsprocessen där ingen process som minskar nitratkoncentrationen har identifierats.

Preface

This project is master thesis of 30 ECTS within the Master of Science program in Aquatic and Environmental engineering at Uppsala University. Supervisor has been Anders Widerlund at Luleå University of Technology, Division of Geosciences. Subject reviewer was Roger Herbert at the Department of Earth Science, Division of Air, Water and Landscape Sciences. Examiner was Fritjof Fagerlund at the Department of Eart Science, Division of Air, Water and Landscape Sciences.

This project has been done for Luleå University of Technology as a pilot study and was funded by *Hjalmar Lundbom Research Centre (HLRC)* and *LKABs stiftelse för främjande av forskning och utbildning vid Luleå tekniska universitet*. The assistance provided by LKAB during fieldwork and water sample analysis is gratefully acknowledged

I would like to give a huge thanks to my supervisor, Anders Widerlund, who's been answering all my questions and provided me with helpful tips and comments throughout the entire project. I would also like to thank Anders for the opportunity to assist during the water sample collection; it was a fun, and freezing, experience.

Uppsala 2013

1. Introduction

Ammonium-nitrate based explosives are used in the mining operations in northern Sweden. Infiltration of groundwater into the boreholes packed with explosives can lead to the dissolution of ammonium and nitrate into the water. Groundwater from the mine is pumped for dewatering and stored in a dam system. This water eventually discharges from these dams to natural rivers. As this discharge water contains nitrogen compounds, there is concern that the release of nitrogen compounds from the mine can cause eutrophication which may lead to oxygen-free environments and eventually fish-kills (Kendall, 1998). Ammonia (NH_3) can be toxic to biota, and nitrate (NO_3^-) can in high concentrations even be toxic to humans. WHO has released a limit for nitrate concentration in drinking water of 10 mg/l (WHO, 2011). A high concentration of nitrate in drinking water can cause methemoglobinemia (blue baby disease) (Kendall, 1998).

1.1 Objective

The main objective of this MSc thesis is to determine if changes in nitrogen and oxygen isotope composition can be used as a tracer for nitrogen transformation processes in the mine water at LKABs underground mine in Kiruna. The isotope analysis method relies on different nitrogen-transforming processes having unique isotopic signals. Stable nitrogen and oxygen isotopes have been used as a tracer method before (Kendall, 1998), though the focus has generally been on nitrogen processes in soil or river-bed sediment. The water transport system at the LKAB Kiruna mine is complex. Due to necessary simplifications, the details of nitrogen transforming processes occurring in the system cannot be shown. The possibility of quantifying these processes are examined and discussed in this study.

This study will include field sampling collection and sample preparation, data analyses and data interpretation. The water transport system and the current view of how the water flows through the mine will also be examined and checked for validity.

This MSc thesis is a part of a study conducted by Luleå University of Technology as a pilot study funded by Hjalmar Lundbom Research Centre.

1.2 Delimitations

This MSc thesis is limited to field sampling and data interpretation, and does not include the sample analysis, which is done by accredited laboratories. Another limitation is that only measurements performed in June 2012 and October 2012 will be analyzed. Data from a measurements conducted in March 2013 were not available in time to be included in this report.

2. Background

The study will examine processes that are affecting nitrogen from ammonium nitrate explosives during the water transport from the Kiruna mine to the tailings dams. In this section the study site as well as the sampling points will be described. The different nitrogen changing processes will be explained as well as the current view of the water transport system.

2.1 The LKAB Kiruna mine

LKABs mine in Kiruna is located in the sub-arctic northern part of Sweden (lat. 67° 50.9'; long. 20° 11.7') with an annual average temperature of -2°C (SMHI, 2013, internet). The landscape is dominated by mountains, Kirunavaara being the highest mountain in the local area (733 m a.s.l). The vegetation in the catchment area is dominated by peat land and deciduous forest (Figure 1).

The LKAB Kiruna mine is the largest underground iron mine in the world, with an annual ore production of 27.7 million tons (LKAB, 2013, internet). The ore is mined using sublevel caving. The mine is located in northern Sweden (Figure 1), approximately 200 km north of the Arctic Circle.

The main source of nitrate and ammonium in the mine water is undetonated ammonium nitrate-based explosives. It can take up to months from the loading of explosives into boreholes to detonation of the charges. During this time some of the explosives can dissolve in infiltrating groundwater, and subsequently enter the process water flow in the form of dissolved ammonium and nitrate. This is the major source of ammonium and nitrate in the process water. In addition, ammonium and nitrate are most likely also leached from waste rock. Waste rock is a term for rock depleted from iron ore; these waste rock piles are stored on the surface.

The concentrations of ammonium and nitrate change with the flow of process water from the mine, through the mineral processing plants and into the tailings dams (Figure 6). However, the nitrogen transforming processes in the system are poorly known. Processes such as ammonia volatilization, nitrification, and denitrification are likely to occur (see section 2.2.2). It is also likely that nitrogen (mainly as dissolved nitrate) is leaching into the mine from waste rock piles (Figure 6). All these processes will affect the isotopic composition of the nitrogen in the water, and may be possible to trace using nitrogen isotope analysis.
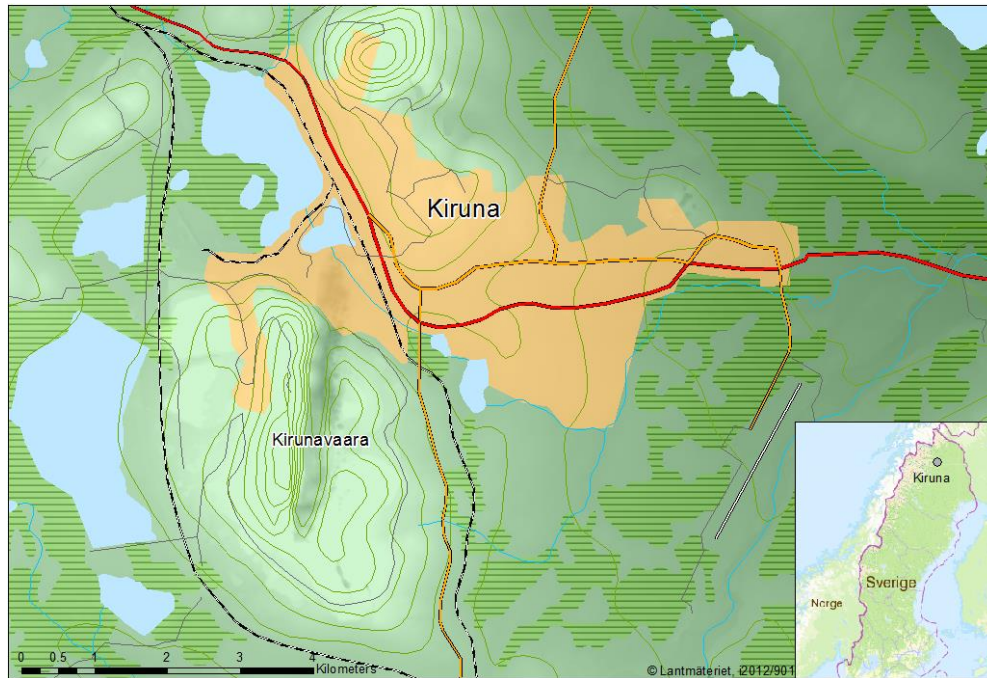
Figure 1. *The location of the Kiruna mine in northern Sweden. Hatched green is peat land, and solid green is dominated by deciduous forest.*

2.2 Nitrogen transformations and isotope analyses

Isotope analysis is a powerful tool for tracing and identifying nitrogen sources and transformation processes. Isotope analysis has been used previously to trace nitrogen transforming processes (Kendall, 1998). However, the focus has seldom been on mine water – process water systems. The main idea behind nitrogen isotope analysis is that processes affecting nitrogen concentrations change the isotopic composition of the residual nitrogen. The data interpretation is complex when two or more different processes affect the isotopic fractionation. In these cases it is difficult to make an accurate determination of nitrogen transforming process based on isotope analysis alone.

2.2.1 Major nitrogen transformations

Figure 2 shows major nitrogen transforming processes in a soil or lake system (Kendall, 1998). All of the nitrogen sources and transformations shown are most likely not present in a mine – process – pond water system. For example "plant N uptake" is a very important process in soil, but may be of minor importance in mine water, since the mine water contains little to no algae or macrophytes.
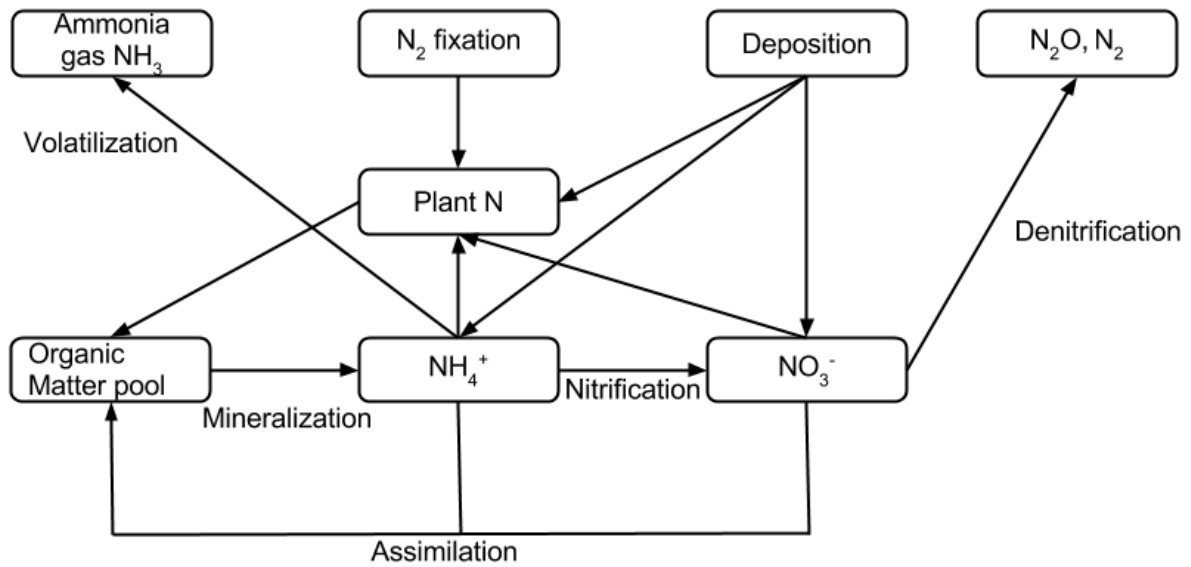
Figure 2. Major nitrogen-transforming processes.

Deposition

Deposition is not a nitrogen transforming process. This term is used to explain sources of nitrogen that are not related to nitrogen-fixation. At the Kiruna mine this process would correspond to dissolution of undetonated explosives, and nitrogen leaching from waste rock.

Nitrification

Nitrification is a process that transforms ammonia and ammonium to NO-compounds. Equations 1 - 3 show that this is a multi-step process, which involves autotrophic bacteria (Kendall, 1998). Autotrophic bacteria extract energy from these reactions and use the gained energy for their metabolism.

$$NH_4^+ + H_2O \rightarrow NH_2OH + 2[H] + H^+ \tag{1}$$

$$NH_2OH + O_2 \rightarrow NO_2^- + [H] + H^+ \tag{2}$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \tag{3}$$
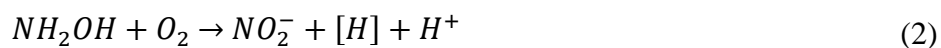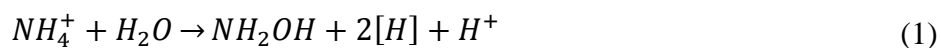
The first two steps of the nitrification process (Equation 1, 2) are catalyzed by the bacteria Nitrosomonas, and the third step (Equation 3) by Nitrobacter. An important parameter when identifying nitrification is bacterial mass, since the reactions can't occur without the presence bacteria. The collective name for the bacteria that are catalyzing nitrification is ammonium

oxidizing bacteria (AOB). A number of different tests for bacterial mass were conducted at each sampling point at the Kiruna mine.

Volatilization

A difficult aspect of identifying nitrification is that ammonium can transform to ammonia, given that the system has a high pH value. This reaction is described by Equation 4 (Vlek & Craswell, 1981). Some of the ammonia in the aqueous phase will go to gas phase according to Equation 5 (Vlek & Craswell, 1981) and are leaving the water transport system.
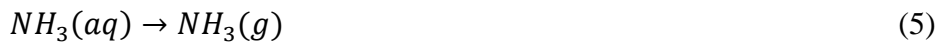
$$NH_4^+(aq) \leftrightarrow NH_3(aq) + H^+ \tag{4}$$

$$NH_3(aq) \rightarrow NH_3(g) \tag{5}$$

Although the presence of ammonia gas is easily confirmed by the characteristic smell of $NH_{3(g)}$ (which is the case at the Kiruna mine), it is difficult to estimate how much ammonia is in gas phase compared to aqueous phase. It is possible to calculate how much ammonium that transforms to ammonia; this is explained in detail in Materials and Methods (section 3.3.1).

Denitrification

Denitrification produces nitrogen gas (N_2) from nitrate, and only occurs in oxygen free environments (Carlson & Ingraham 1983). This process is used in sewage treatment plants to clear nitrate from waste water. Equation 6 shows the different N phases that can be produced in intermediate steps of the reaction.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO(g) \rightarrow N_2O(g) \rightarrow N_2(g) \tag{6}$$
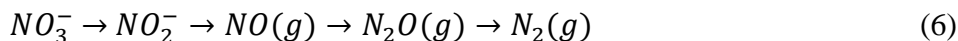
In soil, lake sediments and wetlands where lots of organic matter is available, the following reaction is the major cause of denitrification (Kendall, 1998).

$$4NO_3^- + 5C + 2H_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 \tag{7}$$

Where C is organic matter.

Since this process requires an oxygen-free environment, it is highly unlikely that denitrification occurs in the well-mixed process waters at the Kiruna mine. However, it is likely that oxygen-free zones exist in the pond system, most likely in the tailings of the ponds. Tailings are leftover from when iron has been separated from rock and are transported with the water from the processing plants into the tailings pond.

Sorption

Sorption and desorption are processes where ammonium and nitrate binds electrostatically to charged surfaces of suspended particles. How much ammonium and nitrate that is adsorbed is determined by factors such as pH, concentrations of dissolved ammonium and nitrate, and the characteristics of the adsorbent, for example specific surface area and mineral composition. The most likely place to find sorption processes are where a lot there are a lot of suspended particles in the water, since this means more surface area that ammonium and nitrate can bind to.

2.2.2 Isotopes

Three different elements are used for the isotope analysis for this project; nitrogen, oxygen and hydrogen. Isotopic composition is usually expressed as a fractionation between the sample and a reference. The reference for nitrogen is air where the average abundance of heavy nitrogen (^{15}N) is constant, for oxygen and hydrogen the Vienna Standard Mean Ocean Water (VSMOW) is used.

Nitrogen has two stable isotopes, ^{14}N and ^{15}N. The other isotopes of nitrogen (for instance ^{16}N and ^{13}N) are unstable with half-lives of minutes (Kendall, 1998). Oxygen has three stable isotopes; ^{16}O, ^{17}O and ^{18}O. Hydrogen has three; ^{1}H, ^{2}H (deuterium) and ^{3}H (tritium). Tritium is a radioactive isotope and has a half-life of 12.4 years.

The fraction between two stable isotopes can be used to identify nitrogen transforming reactions. Different reactions cause the proportion between the two isotopes to shift, giving insight into which reactions are occurring (Kendall, 1998).

In large systems, where several reactions occur simultaneously, affect the isotope fractionation differently for each reaction. To give additional insight and working around this problem the dual isotope analysis technique can be used, where, for example, the isotopic composition of oxygen and nitrogen in nitrate is determined. By knowing how the isotopic composition of oxygen as well as nitrogen in nitrate are changing gives additional clues about ongoing processes, and can help identify nitrate-transforming processes in the system.

The proportion between the light isotope and the heavy is usually expressed as:

$$\delta^y X_{sample} = \left\{ \left[\left(\frac{^yX}{^zX} \right)_{sample} \middle/ \left(\frac{^yX}{^zX} \right)_{reference} \right] - 1 \right\} * 1000 \qquad (8)$$

For example the isotopic composition of nitrogen is written as δ^{15}N, and the unit is per mil (‰). All the isotopes in this project are expressed as the example above except for tritium (^{3}H) which has its own unit called Tritium Units (TU); one TU means one tritium atom per 10^{18} hydrogen atoms.

2.2.3 Isotope dilution

In some cases a water sample is a mix of two or more waters with different isotope signals, for instance if explosives are dissolved in water and transported to a reservoir where mixing with e.g. groundwater occurs. In cases where one of the signals is unknown (Figure 3), it may be possible to calculate the unknown signal via an isotope dilution formula (Aravena et al., 1993), which is derived from the absolute weight of an element, this is explained in 3.3.3. To get an accurate description of the unknown signal it's important to take any ongoing nitrogen transforming process in the reservoir into account.
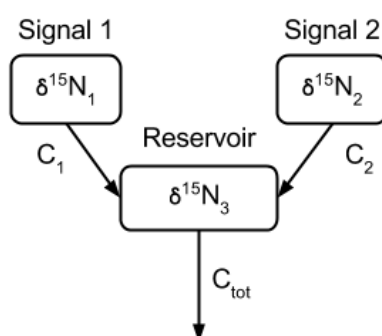

Figure 3. *Schematic overview of a situation where an unknown source isotope signal of nitrogen (Signal 2) can be calculated. C_1 and C_2 is the concentration originating from signal 1 and 2 respectively. C_{tot} is set according to: $C_{tot} = C_1 + C_2$.*

2.2.4 Dual isotope analysis

The dual isotope analysis method is used to trace different sources of nitrate and nitrate transforming processes and reactions. The basic principle is to analyze the isotopic composition of oxygen as well as nitrogen in nitrate. Different sources of nitrate have unique signals on both the nitrogen and oxygen isotopic composition. The main source of nitrate in this project is undetonated explosives, and perhaps some nitrate leached from waste rock and infiltrating into the mine. As mentioned in Section 2.2.1, the isotopic signal in water from the mine should match that of the explosives if this is the major source of nitrate, both for the $\delta^{15}N$ and $\delta^{18}O$ values.

Another source of nitrate is nitrification, which transforms ammonium in explosives into nitrate, as was described earlier in this chapter. Since the product nitrate from nitrification will have a lower $\delta^{15}N$ value than the residual ammonium, nitrate formed through nitrification can in some cases be traced. Nitrification can also be identified from $\delta^{18}O$ in nitrate. Two of the oxygen atoms in nitrate originate from water and one from air (Equation 1 - 3). By using the isotopic mixing formula mentioned in the previous section the fraction of nitrate originating from nitrification can be calculated (Aravena et al., 1993).

2.3 Water transport

One of the main objectives of this study was to investigate the current water transport model. It's important to have a correct view of the water transport before determining nitrogen affecting processes. Unknown fluxes could affect both isotopic composition and concentration.

The water balance in Figure 4 is based on the most recent data for the water flows through the mine, processing plants, and pond system (SWECO, 2010). Figure 4 only shows the discharge from the different key points, and does not show a high altitude reservoir placed in front of the processing plants. Mine water and the recirculated pond waters are pumped to a high elevation reservoir and from there transported down to the processing plants. The outlet from the processing plants is to the tailings pond, where most of the suspended matter settles. Overflow water is constantly discharged from the tailings pond to the clarification pond, and then to a large extent recirculated back into the processing plants. A minor amount (5.8 Mm^3/yr) is discharged to the recipient, Kalixälven.
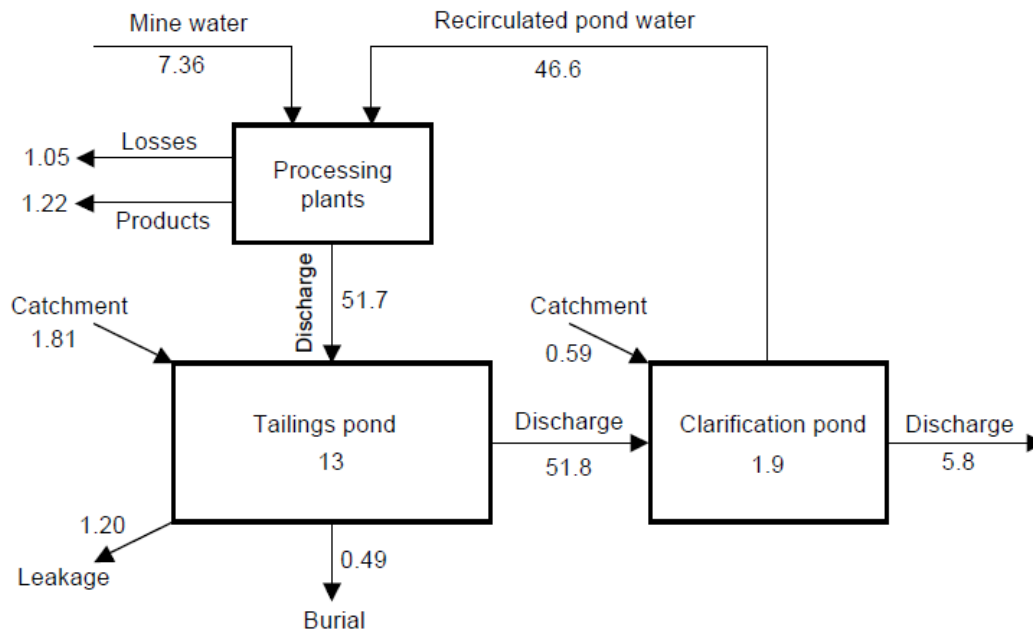
Figure 4. Simplified illustration of the water balance at the Kiruna mine. The unit is Mm^3/year for water flows, and pond volumes are in Mm^3 (data from SWECO, 2010)

2.3.1 Groundwater

The water transport from the surface to the mine is suspected to be rapid due to fractured rock with high hydraulic conductivity in the hanging wall of the mine. It is reasonable to believe that this fractured rock, a result of the sub level caving mining method, effectively transports infiltrating surface water into the mine. It is of interest to examine groundwater transport since its likely leaching nitrogen compounds from waste rock to the groundwater.

2.3.2 Local meteoric water line

The local meteoric water line (LMWL) is a function that can be used to describe the origin of water samples. LMWL is based on the same principles as the global meteoric water line (GMWL), which describes the relationship between δ^2H and $\delta^{18}O$ in precipitation. Equation 9 describes the GMWL based on global precipitation data, with an R^2 value of 0.95 (Clark & Fritz, 1997).

$$\delta^2H = 8 \cdot \delta^{18}O + 10 \qquad (9)$$

This equation shows the relation between δ^2H and $\delta^{18}O$ in waters of pure meteoric origin, and if no further reactions occur during the transport to the sampling point (Clark & Fritz, 1997).

Reactions that can cause the water sample to deviate from this relationship are:

- Evaporation, resulting in a reduced slope of the regression line. This is because the rate of exchange constant differs between $\delta^{18}O$, $\delta^{16}O$ and δ^2H (Clark & Fritz, 1997), and more $\delta^{16}O$ accumulates in water vapor.
- Geothermal exchange causing an increase in $\delta^{18}O$. At high temperatures the water can exchange isotopes with rocks to approach isotopic equilibrium (Clark & Fritz, 1997)

The LMWL is a relationship similar to GMWL, but based on local meteoric water composition, parameters such as elevation, latitude and inland location affects $\delta^{18}O$ and δ^2H values (Clark & Fritz, 1997). Jonsson et al. (2009) conducted a study to determine the LMWL in northern Sweden. Equation 10 describes the LMWL, which had an R^2 value of 0.84 (Jonsson et al., 2009):

$$\delta^2H = 7.2 \cdot \delta^{18}O + 0.3 \qquad (10)$$

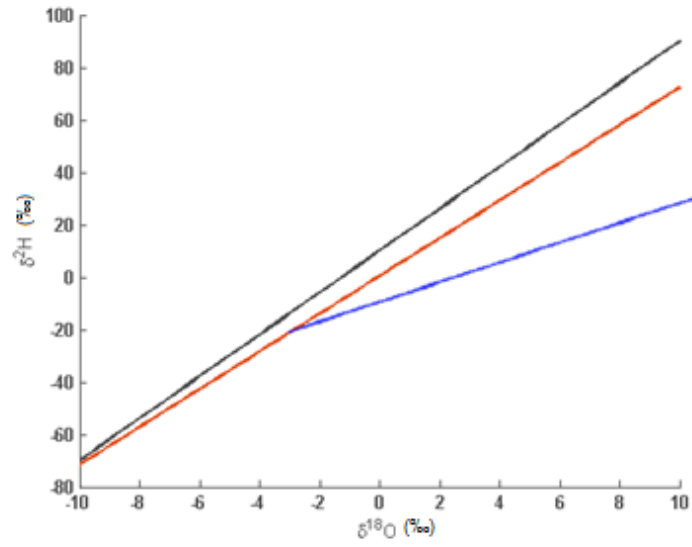The difference between the LMWL and GMWL is shown in Figure 5.

Figure 5. *Difference between LMWL in northern Sweden (red line) and GMWL (gray line). LMWL is based on data from Jonsson et al. (2009). The blue line represents an example of an evaporation trend, with $\delta^{18}O$ accumulating in liquid water.*

3. Materials and methods

In this chapter field sampling and sample preparation are explained (Section 3.1), and a brief description of analytical methods is given in Section 3.2. In Section 3.3 various nitrogen-transforming processes and how they affect the isotopic composition of nitrogen are explained. Section 3.4 discusses methods to estimate the residence time of water in the Kiruna mine and to detect uncertainties in the water balance.

3.1 Field Sampling

Water samples were collected in June and October 2012 from different sampling points located at key points along the water flow. Below follows a brief explanation of the seven sampling points used in this study (location, water type, and sampling strategy) (Figure 6). KVA stands for "Kiruna vatten" or Kiruna water, KEP stands for "Kiruna extra punkt" or Kiruna extra point. The sample points will be referred to by their acronym for the remainder of this report.
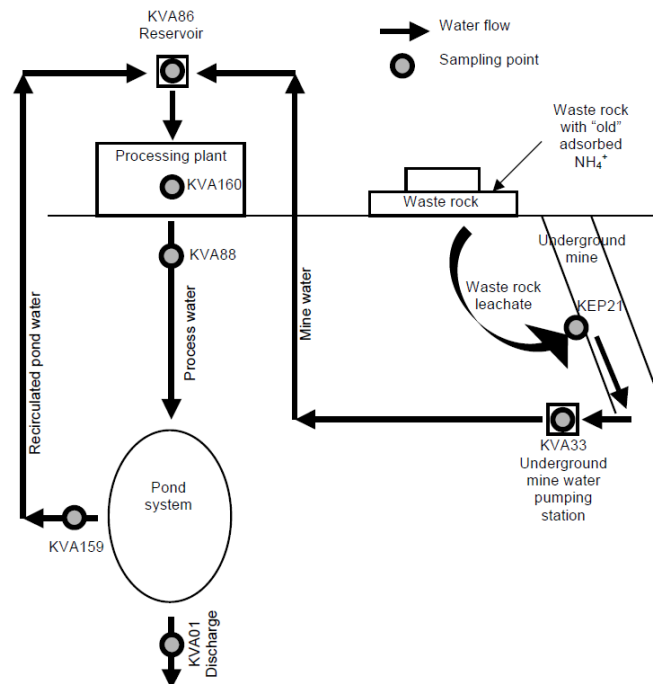
Figure 6. Simplified illustration of the water transport at the Kiruna mine and the seven sampling points used in this study

KEP21

This sampling point is located approximately 240m below the top of Kirunavaara, which is equivalent to about 60m below the ground surface. It is located below a waste rock pile, thus indicating if nitrate or ammonium is leaching from the waste rock into the mine. This point also represents water that is unaffected by processes occurring in the mine (e.g. dissolution of undetonated explosives).

KVA33

KVA33 represents water collected at a pump station pumping all the incoming groundwater to the surface. This water is pumped to KVA86, a high elevation reservoir from which the water enters the mineral processing plants. It is important to note that all water in the mine is essentially groundwater that has been pumped up via this station.

KVA86

This is the high elevation reservoir where water is briefly stored before it enters the mineral processing plants. This water is a mix between the mine water pumped directly to this reservoir, and recycled water from KVA159, which is water from the clarification pond. The majority of the water in this reservoir is water from KVA159, which is about 86% of the total incoming water (Figure 4). This sampling point represents water that enters the mineral processing plants.

KVA160

KVA160 is located in one of the processing plants, and represents water enriched in NH_4 that has been washed from ore material.

KVA88

The water in KVA88 is the discharge water from the mineral processing plants. Having this as a sampling point gives insight into the overall water quality change in the mineral processing plants. The water at KVA88 can be described as slurry, with suspended solids in the range 10–20 g/L.

KVA159

This sampling point is located at the clarification pond, and represents water that is recycled back into the mineral processing plants. This water is pumped back to KVA86, which is the high elevation reservoir.

KVA01

This point is located downstream of the dam system, and represents water that is discharged to the recipient system (Rakkurijoki and the Kalix River). Measuring at the very end of the dam system gives a measure of water quality differences between the outlet and the recipient.

3.1.1   Analyses

Water temperature and oxygen concentrations were measured directly in the field to avoid changes during the transport. The collected water was prepared as explained later on in this section. Water samples were sent to four different laboratories to be analyzed for the compounds listed in Table 1.

LKAB	SLU	ALS	uwEilab
Temperature	ng DNA/ml	K	$\delta^{18}O$ (H_2O)
Nitrate as nitrogen	RNA/ml	Na	δ^2H (H_2O)
Sulphate	AOB/ml		^3H (H_2O)
Alkalinity	CrAr/ml		$\delta^{15}N$ (NO_3)
pH			$\delta^{18}O$ (NO_3)
Nitrogen, total			$\delta^{15}N$ (NH_4)
Ammonium as nitrogen			
Conductivity			
Suspended materials			
Oxygen			

As seen in Table 1 many different parameters are measured at the four laboratories. Most of these parameters are self-explanatory. The data measured at SLU are ng DNA molecules per ml water sample; RNA is the amount of genome copies per ml water sample; AOB is amount ammonium oxidizing bacteria, and CrAr is amount of crenerarchaea. The microbiological data was analysed since, as mentioned in 2.2.1, some nitrogen transforming processes are catalyzed by bacteria.

The collected water samples were prepared for isotope analysis as well as for the microbiological analysis. The nitrate and the ammonium isotope analysis samples were filtered through a 0.45µm filter to avoid suspended matter in the sample. The ammonium sample was also acidified to 4-5 pH with H_2SO_4. For the microbiological samples 200 – 600 ml water was filtered through a 0.22µm membrane filter, the filters were then frozen and sent to SLU for analysis.

3.2 Analytical methods

The laboratory work for determining the isotopic composition of the water samples was not a part of this study and will not be explained any further than the sample preparation. For more information about determining the isotopic composition in nitrate see Silva et al. (2000) for nitrate, and Brooks et al. (1989) for ammonium. All isotopic analyses in this study were conducted by University of Waterloo Environmental Isotope Laboratory, Ontario, Canada.

The size of microbial communities was quantified by real-time PCR, performed at the Department of Microbiology, Swedish University of Agricultural Sciences (SLU), Uppsala.

3.3 Nitrogen transformations

3.3.1 Nitrogen processes and their effect on the isotopic fractionation

Below follows explanations of how the isotopic fractionation changes with the major nitrogen transforming processes mentioned in Section 2.2.2. The calculation of reaction rates is also explained.

Nitrification

As mentioned in Section 2.2.1, nitrification is mediated by a number of different bacteria. Since bacteria prefer to use the lighter (^{14}N) isotope (Kendall, 1998), the δ^{15}N value will be lower in the product than in the reactant.

The nitrification rate is strongly correlated with both pH and temperature, with the generally quoted optimal temperature for nitrification being 25-35º C (Malhi & McGill 1982). It's difficult to define a pH range where nitrification rate is optimal, the general idea is that a high pH affects the nitrification rate positively, meaning a higher rate of nitrification at higher pH (Ste-marie & Pare 1999).

Equation 11 describes the nitrification rate as

$$U = \frac{k \cdot N}{K_N + N} \tag{11}$$

Where k is the maximum rate of nitrification, 1.15 mg l^{-1} day^{-1}; N is NH$_4$-N concentration and K_N is the half saturation constant, 5.14mg/l (Dinçer & Kargi 2000). This equation is illustrated in Figure 7. This reaction also depends on pH and temperature, since bacteria is involved, Equation 11 assumes optimal conditions (Dinçer & Kargi 2000).
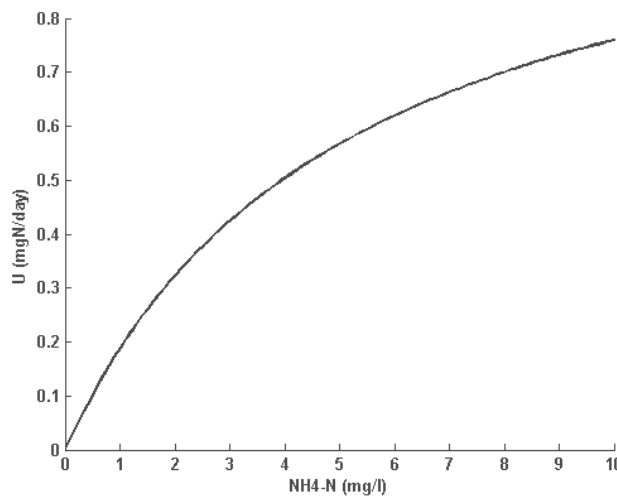

Figure 7. Nitrification rate as a function of available ammonium

Volatilization

Ammonia volatilization will increase the $\delta^{15}N$ of the residual aqueous ammonium, the equilibrium fraction change between the aqueous ammonium and the gaseous ammonia is as high as 34‰ (Kreitler, 1979), meaning that the lighter isotope leaves the system easier.

It is possible to calculate how much ammonium that transforms to ammonia. Equation 12 explains the relation between ammonium, pH and ammonia (Vlek & Craswell 1981).

$$[NH_3] = \frac{TAN}{1 + \frac{[H^+]}{Ka}} \tag{12}$$

where TAN is total ammonium nitrogen, $[H^+]$ is hydrogen ion concentration and Ka is 9.2397. This function can be plotted, as seen in Figure 8, as concentrations of ammonia and ammonium vs. pH.
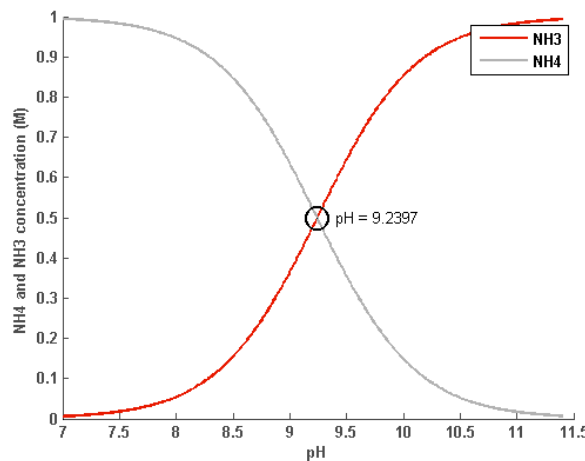
Figure 8. *Relation between ammonium and ammonia vs. pH. The initial concentration of TAN is set to 1M*

From measurements of pH and ammonium, the concentration of ammonia can be calculated, and by assuming that all ammonia instantly is transformed to $NH_{3(g)}$, an estimate of the relative importance of ammonia volatilization compared to nitrification can be made. Nitrification and volatilization have the same effect on both ammonium concentration and the residual isotopic composition (Kendall, 1998). Because of this, the two processes can be difficult to separate, although some characteristics can be used to identify each process individually:

- During nitrification ammonium is transformed into nitrate, while ammonia volatilization decreases the total N concentration in a system. Thus, the nitrate concentration increases during nitrification.
- Nitrification requires ammonium oxidizing bacteria to be present.

The conditions in the mine and process water favor ammonia volatilization (high pH and good ventilation). This reduces the gaseous pressure of ammonia, which increases the ammonia volatilization rate (Vlek & Craswell 1981).

Denitrification

Since bacteria are involved in the denitrification process, $\delta^{15}N$ will increase in the residual nitrate with increasing reaction progress (Kendall, 1998).

The rate at which denitrification can occur depends on a set of different variables, such as pH, temperature, the amount of organic matter present, and water retention time. More easily decomposed organic matter generally means a higher denitrification rate (Dinçer & Kargi 2000), as do longer water retention times. Denitrification rates tend to vary, because of the many different parameters that are involved in the reaction.

Sorption

Sorption and desorption of ammonium and nitrate onto electrically charged surfaces can result in minor N isotope fractionation effects. For ammonium, ions with the heavier ^{15}N tend to be adsorbed, whilst for nitrate, ions with the lighter ^{14}N tend to be adsorbed (Kendall, 1998). The rate at which this reaction occurs depends on a number of different variables such as available surface area and composition of the adsorbent, and pH (Sharifnia et al. 2012).

Research has been performed on many different soil types to determine at which pH sorption of ammonium is most efficient. A recent study (Sharifnia et al. 2012) suggested that the optimal pH for sorption of ammonium is around 7-8. This study was conducted with LECA (light expanded clay aggregate) as adsorbent, which had a grain size of around 4-8 mm. Other studies have shown similar pH ranges for optimal ammonium sorption (e.g. Sarioglu 2005).

Sorption of ammonium is the only process, apart from some cases of deposition, which will actually decrease the $\delta^{15}N$ value of the residual ammonium.

3.3.2 Rayleigh equations

Lord Rayleigh's equations describe how the isotopic composition in the product will change from that in the substrate, if the change in concentration is known (Kendall, 1998). Since all processes change the isotopic composition a little differently, an enrichment factor (ε) unique to the process is added according to equation 13:

$$\delta = \delta_0 + \varepsilon \cdot \ln(f) \qquad\qquad (13)$$

Where δ is the isotopic composition at time t, δ_0 is the initial isotopic composition; ε is the enrichment factor and f is a factor describing the progress of the process. f can be written as:

$$f = \frac{c(t)}{c_0} \tag{14}$$

c(t) is the concentration at time *t* and *c₀* is the initial concentration. ε (‰) in Equation 13 can be written as:

$$\varepsilon = 1000 \cdot (\alpha - 1) \tag{15}$$

Where α is the mean difference in isotopic weight from the substrate to the product.

In many cases the isotopic composition as well as the concentration difference is known before and after a reaction. For identifying a process the enrichment factor can be calculated and compared to literature values.

3.3.3 Isotope dilution

The isotope dilution method is used to calculate if any process is affecting the nitrate concentration from when the groundwater dissolves the undetonated explosives until it's pumped up from the underground pumping station, KVA33. It's unknown how much nitrate is originating from the undetonated explosives and how much are from nitrification. As mentioned in 2.2.3 it's possible to concentration fraction between signal 1 and signal 2 (Figure 3), below follows a derivation of how to calculate unknown signals.

First to calculate the abundance ^{15}N, Equation 8 is rewritten as:

$$\left[\left(\frac{\delta^{15} N_x}{1000} \right) + 1 \right] \left(\frac{^{15}N}{^{14}N} \right)_{air} = \left(\frac{^{15}N}{^{14}N} \right)_x \tag{16}$$

Equation 17 describes how to calculate the absolute atomic mass (Gramlich et al, 1973) from knowing the fraction of the two isotopes ^{14}N and ^{15}N, we substitute $\left(\frac{^{15}N}{^{14}N} \right)_x = x$ for clarity:

$$[x \cdot M_{15N}] + [(1 - x) \cdot M_{14N}] = \overline{M_N} \tag{17}$$

Where *M* is the atomic mass for each isotope. In Table 2 the atomic mass expressed in atomic units are reported for the isotopes of interest.

Table 2. Atomic mass for elements of interest expressed in atomic units (data from wolfram alpha)

Element	Atomic mass (au)
14N	14.00307400478
15N	15.00010889823
16O	15.99491461956

18O   17.99916100100

While equation 17 expresses the mass for an element with a known fraction, the mixing of two of these inputs (Figure 3), which equals the resulting isotopic fraction, can be written:

$$\frac{C_1}{C_{tot}}([x_1 \cdot M_{15N}] + [(1 - x_1) \cdot M_{14N}])_{Source1}$$

$$+$$

$$\frac{C_2}{C_{tot}}([x_2 \cdot M_{15N}] + [(1 - x_2) \cdot M_{14N}])_{Source2} \qquad (18)$$

$$=$$

$$([x_{tot} \cdot M_{15N}] + [(1 - x_{tot}) \cdot M_{14N}])_{Product}$$

$$C_1 + C_2 = C_{tot} \qquad (19)$$

These two equations describe three different mean values for atomic mass, the left hand side is the two sources and the right hand side is the product. The concentration terms are for creating a weighted mean value. Since the calculation is calculated per liter of water no volume term is required. Equation 18 can be rewritten to describe the unknown fraction:

$$Subst. \begin{cases} ([x_1 \cdot M_{15N}] + [(1 - x_1) \cdot M_{14N}])_{Source1} \rightarrow S_1 \\ ([x_{tot} \cdot M_{15N}] + [(1 - x_{tot}) \cdot M_{14N}])_{Product} \rightarrow P \end{cases}$$

$$Subst. \begin{cases} \frac{C_1}{C_{tot}} \rightarrow C_1 \\ \frac{C_2}{C_{tot}} \rightarrow C_2 \end{cases}$$

$$C_1 \cdot S_1 + C_2([x_2 \cdot M_{15N}] + [(1 - x_2) \cdot M_{14N}]) \;\; = P \;\; \rightarrow$$

$$([x_2 \cdot M_{15N}] + [(1 - x_2) \cdot M_{14N}]) \;\; = \frac{P}{V_2} - \frac{C_1 \cdot S_1}{C_2} \;\;\;\; \rightarrow$$

$$x_2 = \left. \left(\frac{P}{C_2} - \frac{C_1 \cdot S_1}{C_2} - M_{14N} \right) \middle/ (M_{15N} - M_{14N}) \right. \qquad (20)$$

This method can be used for the [18]O fraction as well; the only difference is the reference fraction in air:

$$\left[\left(\frac{\delta^{18}O_{air}}{1000} \right) + 1 \right] \left(\frac{^{18}O}{^{15}O} \right)_{air} = \left(\frac{^{18}O}{^{15}O} \right)_x \qquad (21)$$

Where $\left(\frac{^{18}O}{^{15}O} \right)_x$ is 2005.2 ppm according to WSMOW.

3.4 Water transport

3.4.1 Ground water

The water transport from the surface to groundwater appears to be rapid in the Kiruna mine. Due to the mining method used – sublevel caving – the rocks in the hanging wall are heavily fractured. The resulting high hydraulic conductivity results in rapid groundwater infiltration (Eriksson et al. 2005).

Tritium (^{3}H) can be used to calculate the transport time from precipitation to groundwater. The tritium levels of the precipitation are known through the IAEAs (International Atomic Energy Agency) project GNIP (Global Network of Isotopes in Precipitation). Tritium is a radioactive isotope with a half-life of 12.4 years (Kazemi et al. 2006) and the formula for radioactive decay can be used to calculate tritium concentrations in groundwater according to:

$$C(t) = C_0 e^{-\lambda t} \tag{22}$$

Where C(t) is the concentration at time t, λ is the decay constant and C_0 is the tritium level in the precipitation. Since the aim here is to calculate the residence time of the groundwater in the mine, Equation 22 is rearranged to:

$$\frac{\ln(\frac{C(t)}{C_0})}{-\lambda} = t \tag{23}$$

With this formula it's possible to calculate the decay time from precipitation to mine water collected at KVA33 (Figur 2). This is also a measure of the residence time for the mine water.

3.4.2 Process water circulation at LKAB Kiruna

In this section different methods to discover and quantify any uncertainties in the water transport model (Figure 4) will be explained. As previously mentioned, to spot any uncertainties in the water transport system is fairly easy given the measured parameters. The water balance (Figure 4) shows that water is recycled back into the processing plants from KVA159 to KVA86, i.e. from the clarification pond to the high elevation reservoir. Water in KVA86 also receives water pumped up from KVA33, the mine water. This means that water in KVA86 is a mix of the two, and that the water quality should be similar to that in KVA159, since most water in KVA86 originates from KVA159.

Comparing the parameters in KVA86 to those of KVA159 and KVA33 shows whether KVA86 is a pure mix of the two waters, or if there are unaccounted-for fluxes in the water balance model.

Two methods for examining the existing water balance model can be used:

1. Conservative elements

Conservative elements can be used for tracing water transport. Conservative elements are elements displaying concentration changes related only to dilution in a system. They can thus be measured at different sample points to get information about water transport, inflows and outflows, and mixing processes.

The basic principle is simple, if water is added or subtracted from the system, either from evaporation or some unaccounted-for water inflow, the concentration of the conservative elements will change. All the water used in the mineral processing is essentially groundwater that has been pumped up from the mine. Some water is also directly added to the clarification- and tailings ponds from their respective catchment area. The only sampling point that does not directly interact with the rest of the water transport system is KEP21, which represents infiltrating ground water.

The key thing in conservative mixing is that the element is sufficiently inert in the system, with dissolution, precipitation, and particle interaction resulting in little or no concentration changes. Usually an element that is known for being conservative is added as a tracer and measured at suitable sampling points (Dulski et al. 2000).

2. Mixing

Using conservative elements, water mixing at the high elevation reservoir, KVA86, can be estimated, and the expected dilution calculated. The measured values at KVA86 should be close to calculated mixing values if simple mixing of two components occurs in the reservoir. The difference between expected value (Equation 24) and the measured value can give insight into any deviations from two-component mixing during the transport according to:

$$c_1 V_1 = c_2 V_2 + c_3 V_3 \qquad\qquad (24)$$

Where c_1 and V_1 is the concentration and volume in the mixed water, c_2, c_3, V_2 and V_3 are the concentration and the volume from the two sources. Since the water only is stored in KVA86 for a brief time and no evaporation affects the water during time the outgoing water volume is the same as the incoming; $V_1 = V_2 + V_3$. Water volumes are given from the most recent investigation of the water transport (Figure 4).

4. Results

In this section the results from the field sampling are presented in graphs and further explained in the text. The investigation of the water transport is explained in section 4.1, the water chemistry is presented in section 4.2, the nitrogen data and isotope data is presented un section 4.3, The results from the microbiological data is presented in section 4.4. In the diagrams and figures, the sampling points are ordered in the water flow direction though the mine, processing plants, and pond systems (i.e. from KEP21 to KVA01, see Figure 6).

4.1. Water balance

The water balance was examined in KVA86, where water is supposed to be a mixture of water from KVA33 and KVA159 (Figure 6). The dilution formula (Equation 24) was used to calculate expected values in KVA86, using measured parameters and the volume of the incoming water from the different sampling points (Figure 4).

Measured values in KVA86 are expressed as a fraction between the calculated expected values and measured. A value around 100% is to be expected, since according to the current view of the water transport, the water is transported into KVA86 from the two other sampling points. As can be seen in Figure 9, very few parameters follow the expected values. Measured aluminum for instance is around 850% higher than expected for June 2012.
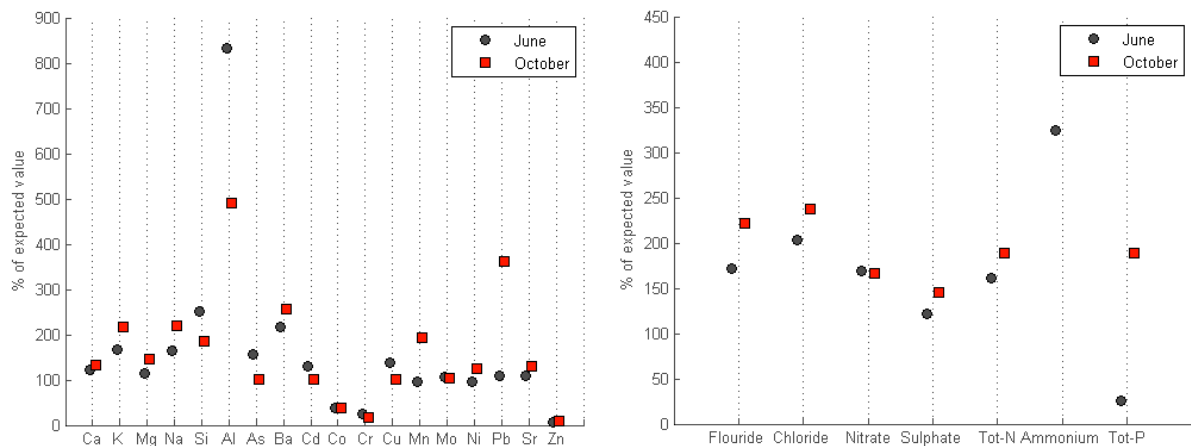
Figure 9. *Measured concentrations at KVA86 expressed as % of expected values for a two-component mixture of water from KVA33 and KVA159*

Figure 10 shows the assumed conservative elements plotted along the water flow path through the system. A clear trend is visible showing a near constant value through the system around 0.45, the exception being KEP21, which is expected since water is added between KEP21 and KVA33 as groundwater (Figure 6). The ratio between two conservative elements were used to further secure the presicion of the analysis, since it would require that incoming water has the exact same ratio of K/Na to not show up in this analysis.

21
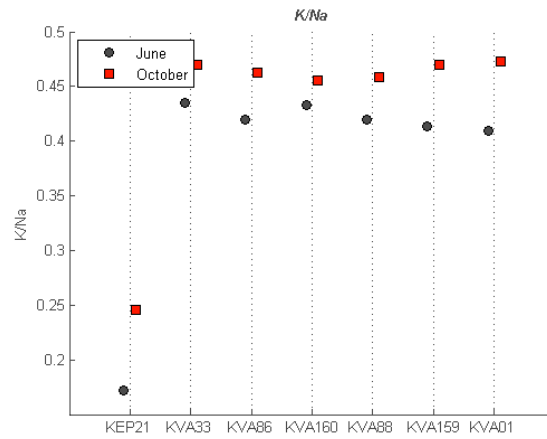
Figure 10. The proportion between the two assumed conservative elements K and Na from KEP21 to KVA01.

4.1.1. Residence time of mine water

Tritium data for precipitation is available from Station Naimakka (about 70 km north-east of Kiruna) for the period 1990 to 1995 (Figure 11), data from IAEAs GNIP.
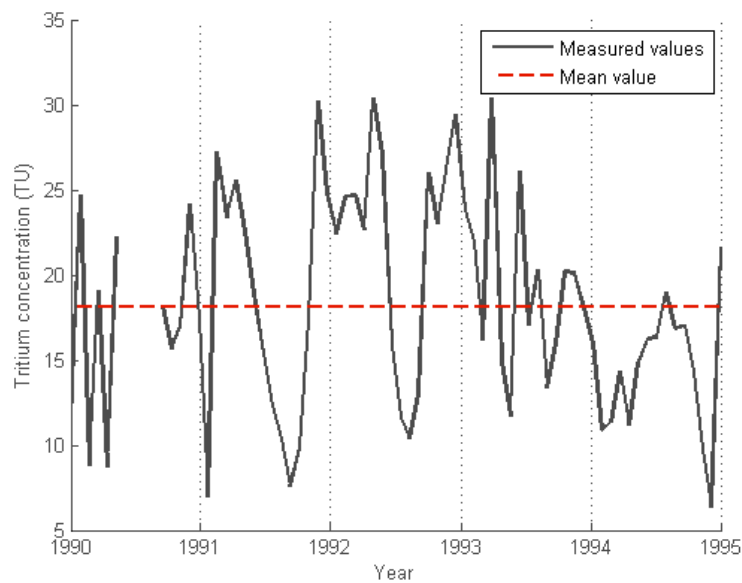
Figure 11. Tritium concentration (TU) in precipitation collected at Station Naimakka in northern Sweden.

Using the simplification that the tritium concentration in precipitation is fairly constant at ~17 TU (Figure 11), the residence time of mine water collected at KVA33 can be estimated (Table 3). The residence time was calculated using the formula for radioactive decay (Equation 23).

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Table 3. Calculated average residence times of mine water from the two sampling points KEP21 and KVA33 in the Kiruna mine.

	Sampling time	³H concentration (TU)	Time (years)
KEP21	June	6.6	18.1
	October	6.4	18.6
KVA33	June	10.8	9.3
	October	10.4	9.9

4.1.2. Local meteoric water line

Measured $\delta^{18}O$ and $\delta^{2}H$ values in H_2O at the sampling points are plotted with the LMWL in Figure 12. It's noticeable that no clear evaporation trend can be seen since the measured data does not deviate significantly from the LMWL (note the difference in scale between Figure 8 and 12).
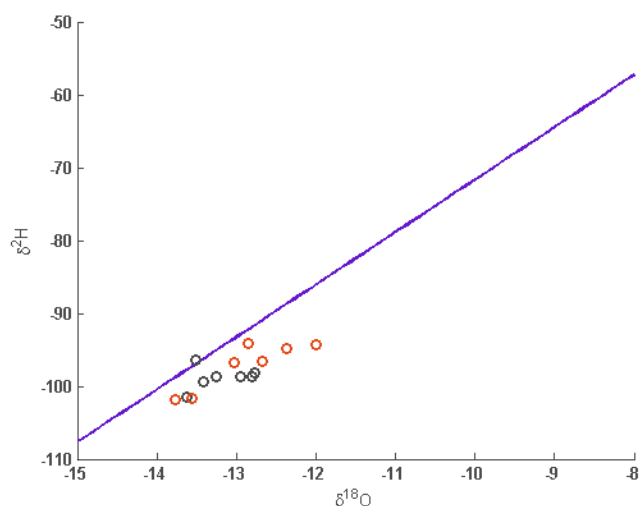
Figure 12. Measured $\delta^{18}O$ and $\delta^{2}H$ plotted with LMWL from Jonsson et al. (2009). The black circles are data from June and the red circles are from October

4.2. Water chemistry

Water quality parameters measured at the sampling stations are plotted in Figure 13 and 14. The water quality parameters are also plotted for the recipient, the Kalix River, which is the green dashed line in the plots. The Kalix River only receives water from KVA01 (the discharge point from the Kiruna mine). Water quality parameters that are studied are turbidity, temperature, pH, chloride and sulphate concentrations, and conductivity (Figure 13). Figure 14 shows measured oxygen as percent saturation (this parameters were not available for the recipient).
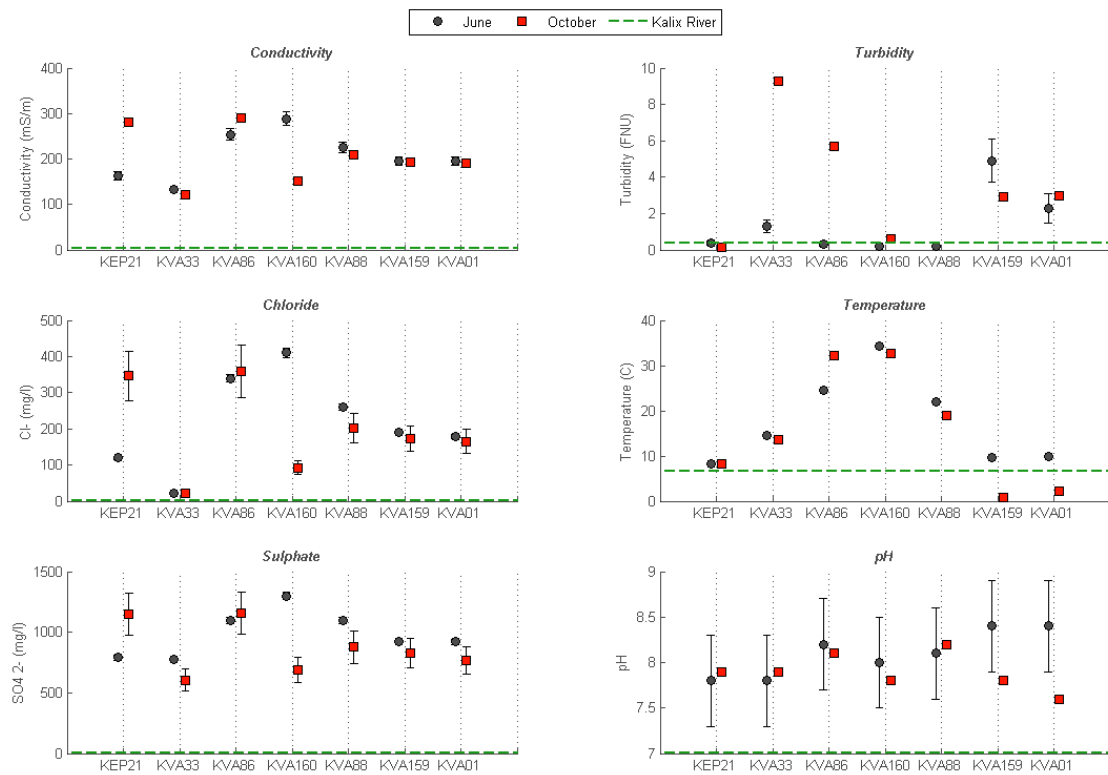
Figure 13. *Selected water quality parameters measured in this study.*

Figure 14. *Measured oxygen concentration expressed as percent saturation.*

The concentration of suspended matter is given in Table 4. It can be noted that the suspended matter concentration at KVA88 is very high (> 20 g/l), indicating the presence of mineral surfaces where ammonium may be adsorbed.

Table 4. *Concentrations of suspended matter at the sampling points, the concentration are given in mg/l*

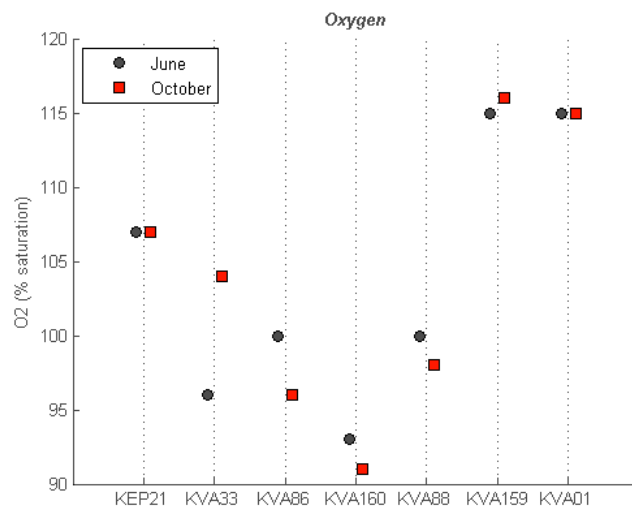|	June			October		
KEP21	<4	±	-	<2	±	-
KVA33	<4	±	-	19	±	-
KVA86	190	±	7.1	110	±	-
KVA160	130	±	5.5	41	±	-
KVA88	33000	±	1000	20000	±	-
KVA159	10	±	1.4	5.8	±	-
KVA01	9.8	±	1.4	5.2	±	-

4.3. Nitrogen data

4.3.1. Nitrogen concentration data

Nitrate and ammonium concentrations are plotted for each sampling point in Figure 15. The figure shows that ammonium has the higest concentration at KVA33, which is the recipient of the groundwater enriched in nitrate and ammonium from the explosives. The nitrate concentrations are lowest at KVA33 and higest at KVA86 and KVA88. Another thing that can be noted that the ammonium concentration decreases rapidly from KVA33 and along the water flow path to KVA01.
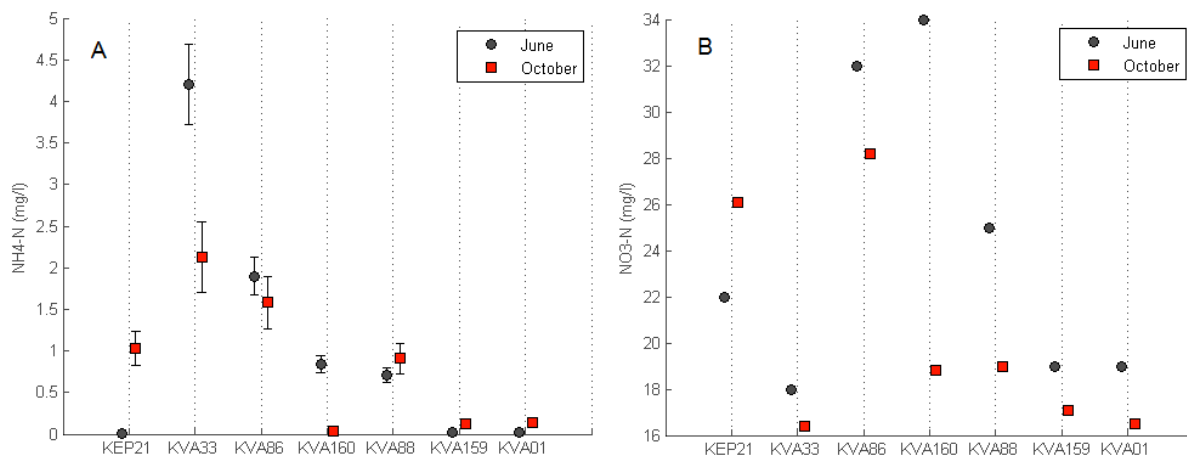

Figure 15. *Ammonium and nitrate concentrations in the sampling points KEP21 – KVA01. A is ammonium and B is nitrate*

4.3.2. Nitrogen isotope data

Table 5 shows isotope data from the sampling points and the ammonium nitrate-based explosives used in the mine. At some of the sampling points ammonium concentrations were too low to permit determination of $\delta^{15}N$.

Table 5. Isotopic composition in nitrate ($\delta^{15}N$ and $\delta^{18}O$) and ammonium ($\delta^{15}N$) in all sampling points as well as in the explosives used in the mine. bd means below detection limit.

		NO3	NO3	NH4
	Sampling point	$\delta^{15}N$	$\delta^{18}O$	$\delta^{15}N$
June	KEP21	5.15	14.23	bd
	KVA33	3.06	10.58	7.13
	KVA86	4.67	18.40	12.27
	KVA160	4.31	17.38	12.28
	KVA88	4.79	16.60	7.48
	KVA159	5.68	15.75	bd
	KVA01	5.45	15.41	bd
October	KEP21	4.78	12.88	3.53
	KVA33	4.90	11.29	8.28
	KVA86	4.63	16.41	14.95
	KVA160	5.27	16.73	bd
	KVA88	4.93	14.94	10.18
	KVA159	6.99	15.78	bd
	KVA01	6.43	15.31	bd
Explosives	S1	3.69	22.08	-7.58
	S2	3.18	23.41	-8.06
	S3	3.36	23.56	-7.96

Figure 16 shows $\delta^{15}N$ values for ammonium as well as the ammonium concentration at the different sampling points, with the decrease in ammonium concentration along the water flow path clearly visible. $\delta^{15}N$ values for ammonium increase from KVA33 (7.1 – 8.3 ‰) to KVA86 (12.3 – 15.0 ‰), and then decrease again to KVA88 (7.5 – 10.2 ‰).

Figure 17 shows the $\delta^{15}N$ values for nitrate and nitrate concentrations. The concentration of nitrate is low in KVA33 (4.2 – 2.3 mg/L) and then increases to the next sampling point. The values of $\delta^{15}N$ are generally high (5.5 – 7.0 ‰) in the tailings dam (KVA159 and KVA01).
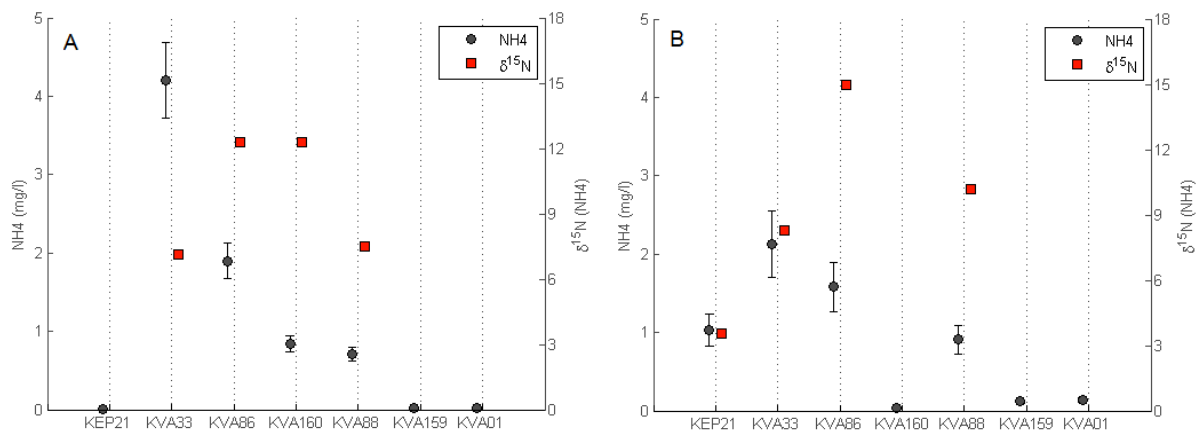
Figure 16. *Ammonium concentration (left axis) and d15N values (right axis) for A) June and B) October*
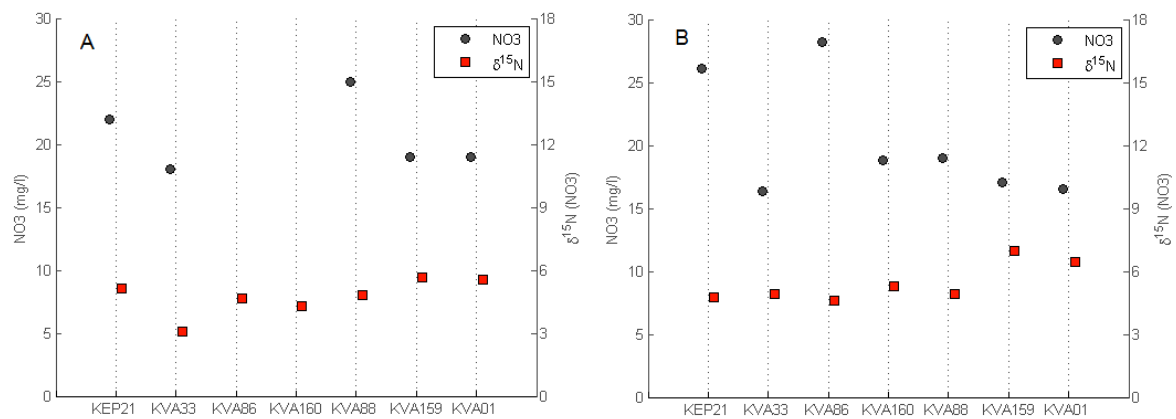
Figure 17. *Nitrate concentration (left axis) and d15N values (right axis) for A) June and B) October*

Figure 18 shows the dual isotopic composition of nitrate (δ^{15}N and δ^{18}O) at the sampling points. The δ^{18}O value for nitrate is low at KVA33 (10.6 – 11.3 ‰), and then increases to the next sampling point, KVA86 (18.4 – 16.4 ‰). The δ^{15}N value varies much less than δ^{18}O, and shows the highest values (5.5 – 7.0 ‰) at the last two sampling points (KVA159 and KVA01).
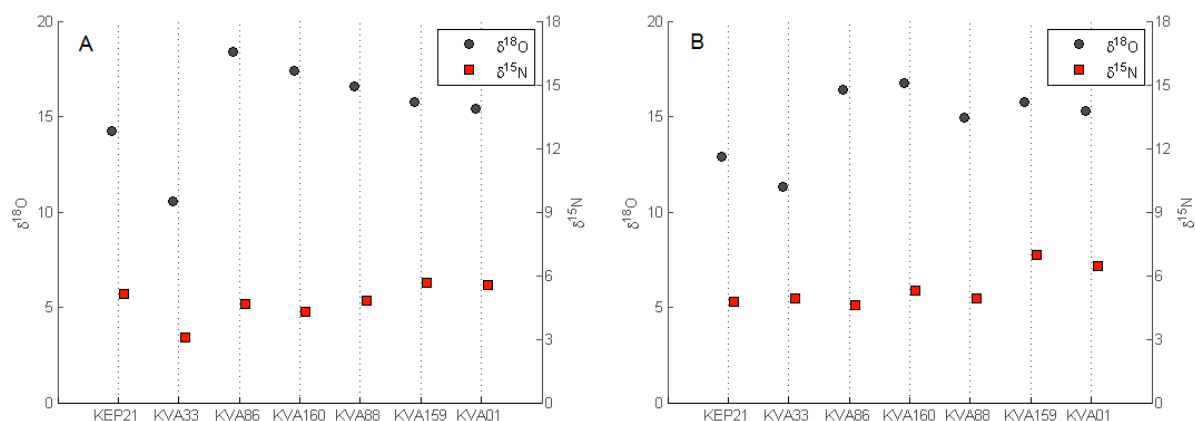
Figure 18. *Isotopic composition of nitrate ($\delta^{18}O$, left axis and $\delta^{15}N$, right axis) A) June. B) October*

4.3.3. Enrichment factors

Table 7 shows calculated enrichment factors found at or between the different sampling points. Isotope data was not available for all sampling points since the concentration of ammonium was below the detection limit at the last three sampling points (KVA88–KVA01). The enrichment factors are based on the concentration difference between the sampling points (Equation 13) shown in table 7.

Table 6. *Enrichment factors (ε) between different sampling points*

	From - To	ε (‰)
June	Explosives - KVA33	See Fig 19
	KVA33 - KVA86	-6.5
	KVA86 - KVA88	4.9
October	Explosives - KVA33	See Fig 19
	KVA33 - KVA86	-22.3
	KVA86 - KVA88	8.6

The concentration difference between the explosives and KVA33 is unknown, and a fixed value for the enrichment factor is not possible to obtain. The change in concentration can be plotted as a function of the enrichment factor since the isotopic composition is known in both KVA33 and in the explosives (Figure 19).

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Figure 19. *Concentration change in ammonium as a function of enrichment factor. C_0 is concentration of ammonium origin from undetonated explosives and C(t) is ammonium concentration in KVA33.*

4.3.4. Dual isotope analysis

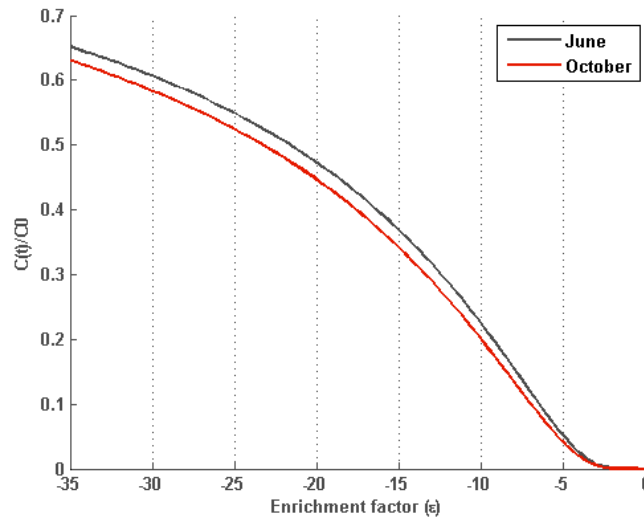The isotopic composition of oxygen ($\delta^{18}O$) in nitrate may serve as an indicator of nitrification (Aravena et al., 1993). This is particularly important in the warm parts of the mineral processing plants (KVA33, KVA86 and KVA160), since microbiological data suggest that nitrification may occur in this part of the system. Isotope mixing can be used to estimate how much of the nitrate was formed from nitrification, and also how much ammonium was transformed into nitrate.

As mentioned in Section 3.3.4, nitrate formed from nitrification will have a known isotopic composition of oxygen, since one oxygen atom in nitrate is from atmospheric oxygen, and two are from water (Aravena et al., 1993). $\delta^{18}O$ in atmospheric oxygen is +22 ‰, and $\delta^{18}O$ of water is approximately -13.7 ‰ at KVA33. Nitrate formed from nitrification thus will have an estimated $\delta^{18}O$ value of:

$$\frac{22+(2*-13.7)}{3} = -1.8$$

Assuming that nitrate in KVA33 originates from undetonated explosives and nitrification of ammonium; it's possible to calculate how much ammonium that has been transformed into nitrate using Equations 16 - 20. The isotopic composition of the product and the two source signals are known. The only unknown factor is the term for the weighted mean value, which in this case are the concentration fractions C_1 and C_2. A calculation of how much of the product nitrate that originates from nitrification and undetonated explosives is presented in Table 7. The calculation indicates that dissolution of explosives and nitrification each contribute approximately 50% of the nitrate present at KVA33.

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*Table 7.*Calculated concentrations of nitrate produced from ammonium lost due to nitrification in KVA33. C_{nitri} is the concentration of nitrate, C_{ex} is the concentration of nitrate that comes from explosives, $C_{tot} = C_{nitri} + C_{ex}$.

	C_{nitri}/C_{tot}	C_{ex}/C_{tot}	C (mg/l)	
			NO3	NH4
June	0.51	0.49	9.06	2.63
October			8.05	2.34

The calculated concentrations of ammonium in Table 7 show how much ammonium that has been nitrified to cause the fractionation difference between the explosives and the values measured in KVA33. The calculation in Table 7 represents a situation where no ammonia volatilization is occurring simultaneously with the nitrification.

4.3.5. Summary of nitrogen data

Table 8 summarizes nitrogen concentrations, the NH_4/NO_3 ratio, and isotope data for the sampling points. Possible nitrogen transforming processes mentioned under section 3.3.1 are shown as well.

Table 8. Summary of nitrogen concentrations, isotope data and possible N transformations

Station		Conc (mg/L)		NH_4/NO_3		$\delta^{15}N$ (‰)		Possible N transformations
		June	October	June	October	June	October	
Explosives	NH4:	-	-	-	-	-7.83		
	NO3:	-	-			3.4		
KEP21	NH4:	0.01	1.03	0.0005	0.03946	-	3.53	Nitrate leaching from waste rock
	NO3:	22	26.1			5.15	4.78	
KVA33	NH4:	4.2	2.13	0.2333	0.12988	7.13	8.28	Ammonia volatilization, Nitrification
	NO3:	18	16.4			3.06	4.9	
KVA86	NH4:	1.9	1.58	0.0594	0.05603	12.27	14.95	Nitrification, Ammonia volatilization
	NO3:	32	28.2			4.67	4.63	
KVA160	NH4:	0.84	0.04	0.0247	0.00213	12.28	-	
	NO3:	34	18.8			4.31	5.27	
KVA88	NH4:	0.71	0.91	0.0284	0.04789	7.48	10.18	Ammonium sorption
	NO3:	25	19			4.79	4.93	
KVA159	NH4:	0.016	0.117	0.0008	0.00684	-	-	
	NO3:	19	17.1			5.68	6.99	
KVA01	NH4:	0.016	0.139	0.0008	0.00842	-	-	
	NO3:	19	16.5			5.54	6.43	

4.4. Microbiological data

Table 9 shows the results from the bacterial analysis in the different sampling points. The parameters measured were mass of DNA (ng DNA/ml), amount of genome copies (RNA/ml), amount of ammonium oxidizing bacteria (AOB/ml) and amount of a crenerarchaea (CrAr/ml).

This data is also presented in Figure 20 as percent of the maximum value. The sampling points that have a high temperature (20-35 °C at KVA86, KVA160 and KVA 86) (Figure 13) have also the highest amount of bacterial mass. These are also the sampling points where ammonium oxidizing bacteria (AOB, Table 9) are most abundant, suggesting that nitrification should be possible at these sampling points.

Table 9. Mass of bacterial DNA and number of gene copies at the sampling points in October 2012. nd stands for not determined

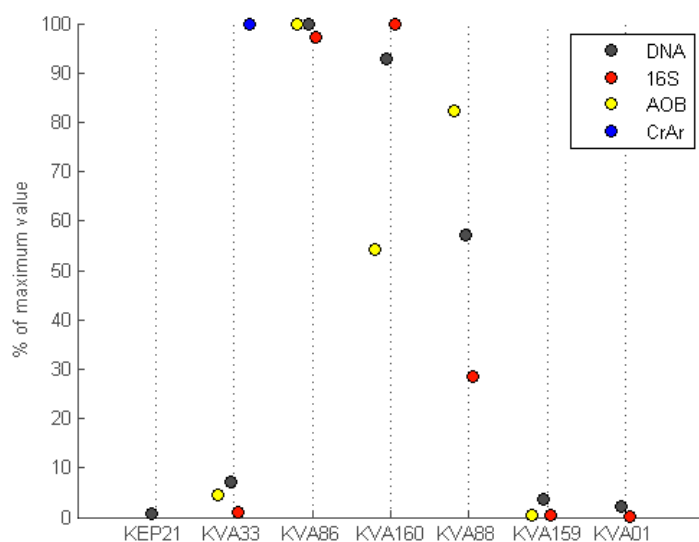| Sample	ng DNA/ml	16S/ml	AOB/ml	CrAr/ml
KEP 21	0.1			
KVA 33	1.0	$3.5 \cdot 10^5$	$7.9 \cdot 10^3$	$4.8 \cdot 10^2$
KVA 86	14.0	$3.4 \cdot 10^7$	$1.7 \cdot 10^5$	nd
KVA 160	13.0	$3.5 \cdot 10^7$	$9.2 \cdot 10^4$	nd
KVA 88	8.0	$1.0 \cdot 10^7$	$1.4 \cdot 10^5$	nd
KVA 159	0.5	$1.7 \cdot 10^5$	$7.9 \cdot 10^2$	nd
KVA 01	0.3	$7.1 \cdot 10^4$	nd	nd

Figure 20. Mass of bacterial DNA and number of gene copies at the sampling points in October 2012

5. Discussion

5.1. Water balance

The conservative elements analysis for the water transport (K/Na ratio, Figure 10) suggests that no new water is introduced into the system because of the constant proportions between the conservative elements. The only sampling point that shows a deviating K/Na ratio is KEP21, which is an external flow entering the mine water – processing plants – pond system. If there was an addition of water anywhere in the main water transport system this would be visible on this plot, except if the added water had the same K/Na ratio as the process water.

Since no water with a unique K/Na ratio appears to be added to the main mine water – processing plants – pond water flow system, the concentrations measured in KVA86 (Figure 9) are difficult to explain. If no water is added in KVA86, meaning that it's just a mix between KVA33 and KVA159, then the parameters should be close to those obtained via the mixing calculation (Figure 9), which they are not. This discrepancy suggests that additional water enters the system at KVA 86, although this is not indicated in the water flow path and water balance (Figure 6 and Figure 4).

5.2. Water discharge to the Kalix river

When examining the water quality in the Kiruna mine the important sampling point is the discharge to the Kalix river, a number of different water quality parameters were analyzed and compared to that of the recipient (Table 10).

Table 10. Comparison of water quality parameters between the outlet in the mine water transport system, KVA01, and the recipient, the Kalix River.

		KVA01	Kalix River
Calcium	(mg/l)	249	3.6
Sulphate	(mg/l)	843	4.2
Chloride	(mg/l)	173	0.84
Conductivity	(µS/cm)	193	0.33
Ammonium	(mg/l)	0.08	0.01
Nitrate	(mg/l)	18	0.23
pH		8	6.8

The water quality parameters are compared to a sampling point located in the recipient (Kalix River) upstream of the inflow of process water from the Kiruna mine (Figure 13 & Figure 14). The water quality of the outlet (KVA01) has high concentrations of calcium (242 – 256 mg/L), sulphate (920 – 766 mg/L) and chloride (180 – 165 mg/L), resulting in a high conductivity (195 – 191 µS/cm). The concentration of ammonium in KVA01 is around 0.016 – 0.139 mg/l which compared to the recipient that has a concentration of around 0.01 mg/l. The concentration of nitrate in the outlet is 16.5 – 19 mg/l and the concentration in the Kalix River is 0.23 mg/l. The pH is higher in KVA01 (pH 8.4 – 7.6) than in the recipient (pH 6.6 –

7.1). The most notable parameters in this project is the difference between ammonium and nitrate concentration in the discharge. There is virtually no leachate of ammonium to the Kalix river whereas the concentration of nitrate is well above that of the Kalix river.

5.3. Nitrogen transforming processes

5.3.1. Nitrogen sources

There are two main pathways for nitrogen-transfer from the explosives to the mine and process water:

- Nitrogen leaching from undetonated explosives
- Nitrogen leaching from waste rock piles (mainly nitrate)

The influence of undetonated explosives is most evident at KVA33 (the sampling point closest to the explosives used in the mine), where ammonium always shows maximum concentrations (Figure 15). The concentration of nitrate is however low in KVA33 and higher in most of the other sampling points (Figure 15). This is partly due to nitrification transforming ammonium into nitrate (discussed in Section 5.3.3).

The isotopic composition of the explosives is different from that measured in KVA33, particularly for $\delta^{15}N$ in ammonium. However, the $\delta^{15}N$ value in dissolved nitrate is fairly similar to that in the explosives (Table 5). The $\delta^{18}O$ value at KVA33 (+10.6–11.3 ‰) is about half that of the explosives (+22.1–23.6 ‰). Two different theories are proposed as possible explanations:

- Nitrate at KVA33 is a mix of nitrate from the explosives and nitrate originating from nitrification. Nitrate formed through the latter process contains oxygen from the surrounding water.
- Nitrate with a different isotopic composition is entering into the mine with groundwater leachate from waste rock piles.

The most likely explanation for the $\delta^{18}O$ value of nitrate in KVA33 is the first alternative. A mix between the oxygen in nitrate from explosives and the oxygen in water would explain $\delta^{18}O$ values of +10.6–11.3 ‰ in water at KVA33 (see Section 4.4.4).

The second process (N leaching from waste rock piles) is very likely also occurring, since it is difficult to explain all nitrate in KVA33 only with addition from explosives. The nitrate concentration in KVA33 is lower than expected. The nitrate concentration from the explosives can be calculated with the assumption that the ammonium concentration in KVA33 originates from undetonated explosives. Since the molar ratio between ammonium and nitrate in the explosives is close to 1:1, the total nitrate that comes from the explosives should be 7 – 14 mg/l based on an ammonium concentration of 2 – 4 mg/l, which is somewhat lower than that observed (16 – 18 mg/l).

The evidence for nitrate leaching from waste rock is the generally high concentration of nitrate in KEP21 (19–26 mg/L, Figure 15b). In contrast, the concentration of ammonium was

generally low (<0.01 mg/L; n = 2) or moderately high (1.0 mg/L; n = 1) (Figure 15a) in KVA33. Since KEP21 does not interact with the explosives used in the mine, there should be no addition of nitrate or ammonium from the explosives at this sampling point.

5.3.2. Nitrification

All sampling points had around 100% oxygen saturation (Figure 14). The oxygen saturation combined with high temperatures in KVA33, KVA86, KVA160 and KVA88 (Figure 13) provide good conditions for nitrification. A further indication of suitable conditions for nitrification is the pH at the different sampling points (Figure 14), which is around 7.5 – 8.5. As mentioned in Section 3.3.1, a high pH promotes higher nitrification rates. The pH range is also suitable for ammonium sorption, which has an optimal pH range of around 7 – 8, as explained in Section 3.3.1.

The high concentration of oxygen, the slightly alkaline environment, and the warm temperature in the process water offer good conditions for nitrification at KVA86-KVA88. This is further supported by microbiological data indicating the presence of ammonium oxidizing bacteria at these sampling points (Figure 20).

There is evidence pointing to nitrification occurring between KVA33 and KVA86. The amount of ammonium oxidizing bacteria as well as the DNA mass both show maxima at KVA86, indicating favorable conditions for nitrification in the warm (20 – 35 °C) parts of the mineral processing plants.

Another way to investigate if nitrification occurs between KVA33 and KVA86 is to calculate the nitrification rate (Figure 7), to see if nitrification can explain the change in concentration and isotopic composition of ammonium. The pH between the two sampling points (pH 7.8 – 8.2) favors nitrification. The specific reaction rate can be calculated via the ammonium concentration at the different sampling points. The ammonium concentration varies from about 1.5mg/l and 5mg/l, suggesting a nitrification rate of about 0.25 to 0.55 mgN/l/day (Equation 11) assuming that the calculated nitrification rates are applicable for this case. This means that the nitrification between KVA33 and KVA86 would require 4-7 days in June and 0-5 days in October.

The results presented in Section 4.3.4 indicate the presence of nitrification in KVA33. This is clearly noticeable on the way the isotopic composition of oxygen on nitrate is behaving from the undetonated explosives to KVA33. If all the nitrate in KVA33 originated directly from undetonated explosives the isotopic composition should match that from the explosives. The $\delta^{18}O$ value in the explosives is 23.1 and only 10.6 in KVA33 meaning that a process is affecting the isotopic composition of nitrate in KVA33.

As can be seen in Table 6 the enrichment factor between KVA33 and KVA86 was around -6 in June 2012 and -22 in October 2012 which is in the interval for both nitrification as well as ammonium volatilization (see below) (Kendall, 1998) and serves as further proof of those processes happening in these sampling points.

5.3.3. Volatilization

Ammonia loss via volatilization is likely to contribute to the isotopic shift of around +15 ‰ between ammonium in the explosives and at KVA33 (Table 5). Another process in the water system of the Kiruna mine that can explain a loss of ammonium is sorption, but as mentioned in Section 3.3.1 and 5.3.5, this process would decrease the $\delta^{15}N$ value.

The conditions for ammonium volatilization are favorable everywhere in the water transport system since, at pH values in the range 7.5 – 8.5, ammonium continuously transforms to ammonia. The rate of ammonia volatilization depends on the pressure of gaseous ammonia over the water surface (Kreitler, 1979). Thus, the good ventilation in the mine, or open-air water reservoirs, will provide environments with low gaseous pressure of ammonia favorable for ammonia volatilization.

This suggests that conditions for volatilization are favorable at KVA33 (mine ventilation) and at the sampling points KVA86 and KVA160 (open-air water reservoirs).

5.3.4. Denitrification

There was no clear evidence of denitrification at any of the sampling points. The change in $\delta^{15}N$ in nitrate was generally small. In some cases the $\delta^{15}N$ as well as the concentration of nitrate showed changes that could indicate denitrification, for example in the dam system. However, the $\delta^{18}O$ value of oxygen in nitrate did not show changes that were consistent with denitrification. Denitrification is an anoxic process, and should be of little or no significance in the mine – processing plant system, since at every sampling point the water was close to 100% oxygen saturation (Figure 14).

Denitrification is, however, likely to occur in the anoxic sediments in the pond system, where organic matter is present. At the sampling points in the clarification pond (KVA159 and KVA01), the highest $\delta^{15}N$ values for nitrate were measured and the concentration of nitrate was low (Figure 17). These water samples represent surface water from the pond, and it is possible that oxygen saturation, nitrate concentrations and $\delta^{15}N$ values for nitrate in the pond bottom water and sediment differ from those of the surface water. In addition, each pond has a catchment area, and nitrate addition from the catchment is very likely.

5.3.5. Sorption

The $\delta^{15}N$ value of ammonium decreases from KVA86 to KVA88 (Table 5), suggesting either an inflow of ammonium that changes the isotopic composition, or sorption of ammonium onto suspended matter in the process water. Since no water inflows are known in this part of the process, and the concentration of ammonium is decreasing as well, an inflow of ammonium can be ruled out.

According to previous studies of ammonium sorption (Kendall, 1998), the enrichment factor is around 4-8 for this process, which agrees with the ones calculated between KVA86 and KVA88 (4.9 − 8.6, Table 6).

Ammonium sorption requires a surface for the ammonium to bind to. The concentration of suspended matter at KVA88 is very high, sometimes up to 33g/l (Table 4), indicating the presence of surfaces where sorption of ammonium can occur. In addition, pH (8.1 − 8.2) is favorable for sorption of ammonium, and the ammonium concentration decreases from ~2 mg/l at KVA86 to ~0.5 mg/L at KVA88 (Table 8). From KVA88 this suspended matter is discharged to the tailings pond. It's reasonable to assume that some ammonium adsorbed to tailings gets buried in the tailings pond, which is a way for ammonium to leave the system and have no further interactions within the water transport system.

6. Conclusions

Below follows the conclusions that can be made from this project. The use of stable nitrogen isotopes to trace nitrogen transforming processes is a good method and can be used in the water transport system at the Kiruna mine.

- Measurements of the nitrogen isotope composition of dissolved nitrate and ammonium are technically possible in mine and process water at the Kiruna mine. The observed isotopic shifts can be interpreted in terms of ammonia volatilization, nitrification, and ammonium adsorption.
- Two different sources for nitrogen were identified: 1) nitrogen from waste rock piles (predominantly nitrate) leaching into the mine (observed at sampling point KEP21), and 2) undetonated explosives (observed at sampling point KVA33). Water infiltrates from the surface into the mine on a time scale of 9–18 years. Calculation of the fractions of nitrogen originating from source 1) and 2) is not possible with existing data.
- Ammonium oxidizing bacteria may account for some ammonium loss between KVA86 and KVA88 via nitrification. However, no quantitative estimate of nitrification could be made due to simultaneously occurring ammonium volatilization.
- Ammonia volatilization accounts for partial ammonium loss at KVA33. Quantitative interpretation of this process was not possible due to indication of nitrification also occurring at KVA33.
- Sorption of ammonium may occur where the suspended matter concentration is high, particularly at the discharge point KVA88.
- There was insufficient data to make quantitative estimates regarding denitrification, a process that mainly occurs in the pond system.
- One or several unknown processes/water flows are affecting the water between KVA159 and KVA86, since a two-component mixing model between mine water and recirculated pond water does not explain parameter values measured at KVA86.

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