THE HIDDEN DRAGON: NITRATE POLLUTION FROM OPEN-PIT MINES – A CASE STUDY FROM THE LIMPOPO PROVINCE, SOUTH AFRICA

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ABSTRACT

Although nitrate is considered to be the most wide-spread groundwater contaminant, and nitrification of water resources can have potential serious health effects, the assessment of nitrate-related impacts are often over-simplified and ascribed to 'inadequate sanitation' without further consideration of the nitrogen-cycle and the identification of other potential sources or pathways, including open-pit mining, which can contribute to this problem. Global indicators used to indicate the effects of mining on surface and groundwater are mainly sulphates, chlorides, nitrates and cyanide, which, depending on the geology, the pH and the mining product, could be combined with increased levels of certain heavy metals. However, the focus of mining-related impact assessment is primarily on pH, sulphate, and some heavy metals, and nitrate is not usually found on the list of 'chemicals of concern' prepared by specialists predicting impacts associated with mining. Resulting from this oversight, the effects on the South African population resulting from mining-related nitrification of water resources are underestimated.

Due to the serious health effects of high nitrate in drinking water, and the consequent detrimental effects on communities that make use of groundwater so affected, it would be prudent for responsible mining companies to investigate the possibility of nitrate pollution being caused by their mining activities, so that this potential serious problem can be properly managed.

This paper puts the spotlight on this 'hidden dragon' in the context of a case study from the Limpopo Province in South Africa, where serious nitrification (57mg/l) of a community drinking water supply was found near an open-pit mine, which was identified as the cause of the contamination, after other potential sources have been eliminated. Based on the findings in this case study, some recommendations are made regarding impact prediction to identify nitrate resulting from mining activities as a potential pollutant of especially groundwater resources, and solutions that could potentially 'manage the dragon' are outlined.

1. INTRODUCTION

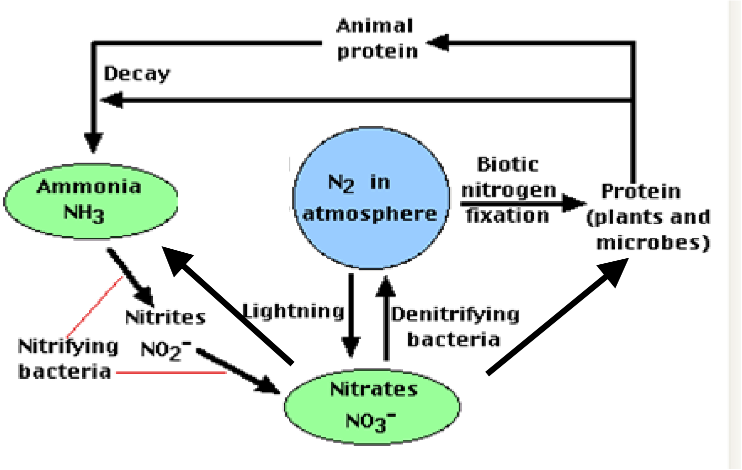
When nitrification occurs in the groundwater sources of communities near mines, the cause of this problem is almost always ascribed to 'poor or inadequate sanitation'. For most instances, that would be the correct identification of the problem. However, in some cases, especially for mines that are located in complex geology that contains high levels of elemental Nitrogen, the practice of open pit mining can lead to nitrification of shallow aquifers (Zaitsev, Mettänen, and Langwaldt, 2008). Similar to the processes leading to high sulphate concentrations in water, elemental nitrogen can be released as nitrate during excavations for mining, especially into local groundwater resources. In addition, the process of extraction of the minerals from the excavated rock involves nitrogen-based chemicals, and this process can generate effluents that can contribute further to increased nitrate levels in water resources, once it is disposed or discharged.

In November 2007, a number of samples were collected from community drinking water sources in a village that is located in close proximity to a platinum mine in the Limpopo Province, which has been in existence since 1926, and at which mining activities intensified and expanded since the late 1990's. The results of the analysis on the samples indicated alarmingly high levels of nitrate, and for one specific sample, taken at the Primary School in the village, it was determined unambiguously through a process of elimination that the activities at the mine is the cause of this contamination (Action Aid, 2008).

Since the interpretation of nitrate results is often over-simplified, this paper firstly highlights the complexities of the Nitrogen Cycle in the context of nitrate-chemistry and water resources, and secondly uses the case study as example to illustrate how the Nitrogen Cycle should be used in the interpretation of nitrate results and isotope studies. Sources and pathways associated with the elements of the Nitrogen Cycle at open-cast mining activities are discussed to outline considerations for impact prediction. Lastly, some recommendations are made regarding the management and monitoring of these sources and pathways, before some conclusions are summarised.

2. THE NITROGEN CYCLE AND NITRATE CHEMISTRY

The Nitrogen Cycle refers to the inter-conversion between nitrogen (N), nitrite (NO_2^-), nitrate (NO_3^-), ammonia (NH_3), and ammonium (NH_4^+) in the environment. A simplified illustration (Internet Reference #1) of the natural (not altered by anthropogenic activity) nitrogen cycle is outlined in Figure 1 below:



Nitrate (NO_3^-) is the end product of the oxidation of elemental nitrogen (N), ammonium (NH_4^+) and/or nitrite (NO_2^-) and is measured either as the salt, NO_3^-, or as the amount of Nitrate-Nitrogen (NO_3N). Natural soil is generally Nitrate-rich. Nitrates and Nitrites occur together in soil from natural erosion of geological Nitrogen. In normal geological processes such as erosion, desertification and soil formation, nitrate release occurs slowly over long periods of time, allowing the release of low levels of nitrogen that is essential for the formation of fertile soil. Metasedimentary and metavolcanic lithologies, such as greenstone and slate, typically contain high levels of elemental Nitrogen which could be released as nitrate in this manner.

The Nitrogen Cycle thus entails the uptake of atmospheric or soil Nitrogen by plants or animals, and the conversion and use there-of by plants and animals as essential building blocks for amino-acids and genetic material. As a result of animal excretion and plant decay, ammonia (NH_3) or ammonium (NH_4^+) is formed, which readily oxidises to nitrite (NO_2^-) and nitrate (NO_3^-) under aerobic (presence of oxygen) conditions (process of nitrification). Denitrifying bacteria can convert nitrate back to ammonium, ammonia, or atmospheric Nitrogen under reducing circumstances (process of de-nitrification).

The Nitrogen cycle is modified by anthropogenic activities such as the introduction of oxidizing or reducing circumstances or chemicals, or by the large scale disturbance of Nitrogen-rich geological formations. Ammonium (NH_4^+) will convert to nitrite (NO_2^-), and nitrate (NO_3^-) under oxidising conditions, such as aeration or excavation, while nitrate (NO_3^-) will convert to ammonium under reducing circumstances, or in the presence of a reducing agent, such as acids. Large scale anthropogenic disturbances to the natural Nitrogen Cycle are a serious cause of concern, since this can cause nitrate to be released in large quantities into water resources, which has significant detrimental ecological and human health effects.

The Occurrence of Nitrate in Water Resources

As discussed above, soil is naturally nitrogen-rich. Water resources, on the other hand, are naturally nitrogen-poor. Because nitrate has low concentrations in uncontaminated water resources (typically less than 5mg/l as NO_3N) and is liberated by human activity, it serves as an indicator of human impact on water resources (Adamski, 1997; Davis and Bell, 1998; Hem, 1985). Many USA States use the mere presence of Nitrate in water resources as pollution "indicator", some citing 1 mg/L NO_3N as a trigger level. Elevated levels of nitrate are the main cause of eutrophication in surface water resources (US EPA, 1998).

Human health is the norm used for nitrate in the South African Drinking Water Standard and Target water quality guideline for domestic use, which is set at 6 mg/L as NO_3N. The reason for this is that Nitrate readily converts in the gastrointestinal tract to nitrite as a result of bacterial reduction. Nitrite, upon absorption, combines with haemoglobin, the oxygen carrying red blood pigment, to form methaemaglobin, rendering the blood incapable of carrying oxygen – a disease known as methemoglobinanemia. Arterial blood with elevated methaemaglobin levels has a characteristic chocolate-brown colour as compared to normal bright red oxygen containing arterial blood. Values between 6 and 20mg/L could lead to methaemaglobinanemia in infants, while values above 20mg/L will cause methaemaglobinanemia in children, and mucus membrane irritations in adults. Signs and symptoms of methemoglobinanemia (methaemaglobin >1%) include shortness of breath, cyanosis, mental status changes, headache, fatigue, exercise intolerance, dizziness and loss of consciousness. Severe methemoglobinanemia (methaemaglobin >50%) patients have dysrhythmias, seizures, coma and death. Metabolically, nitrates may also react with amines and amides, commonly found in food such as meat to form nitrosamines, which are known carcinogens (cancer causing agents), and which can lead to especially stomach cancer (South African Water Quality Guidelines, 1996).

Nitrate is considered to be the most widespread groundwater contaminant. Sources of nitrate in natural waters results primarily from one or more of three causes:

- the disposal or discharge of human and animal debris and excrement into water resources (Internet Reference #2, Tredoux, 2004);
- agricultural activities such as the large-scale concentration of livestock or the over-use of nitrate-based fertiliser, for example KAN, LAN, etc (Gormly and Spalding, 1979);
- activities that influences the oxidising or reducing circumstances in the Nitrogen-cycle, such as aeration or acidification; or
- activities that disturbs bedrock which is high in elemental nitrogen (N) such as excavation, ploughing, building, and mining (Holloway and. Dahlgren, 1999; Kreitler and Jones, 1975; and Haschemeyer and Williard, 2008).

High levels of nitrate and ammonia combined with increased bacteriological contaminants, such as faecal coliforms and E.coli, would be indicative of pollution of water resources as a result of human or animal debris and excrement. Elevated levels of nitrate and/or ammonia together with increased phosphate concentrations would be indicative of fertiliser-related causes of the contamination (Scheierling, 2007). Sulphate is globally accepted as an indicator of mining-related bedrock disturbance. Elevated levels of nitrate and/or ammonia, together with levels of sulphate and chloride that are higher than background concentrations, would be indicative of pollution of water resources as a result of mining activities (Bros and Loredo, 2008).

3. CASE STUDY: HIGH NITRATE LEVELS IN A LIMPOPO VILLAGE WATER SUPPLY

The Limpopo Village under discussion is a typical South African rural traditional village, where people make a living from subsistence farming. It is however set apart from other villages in that people have been living here for at least two centuries. Important to note is that very few of the villagers are employed by the adjacent mine. The community is fairly self-reliant, and has established its own water supply through the establishment of boreholes near a little non-perennial stream that runs through the village and the mine, as well as the construction of a dam for livestock watering. The reason for the monitoring exercise was that a number of complaints have been received from villagers that related to fatigue, stomach cramps, nausea, etc., and they were concerned about their water supplies. The area around the village is outlined in Figure 2 below:

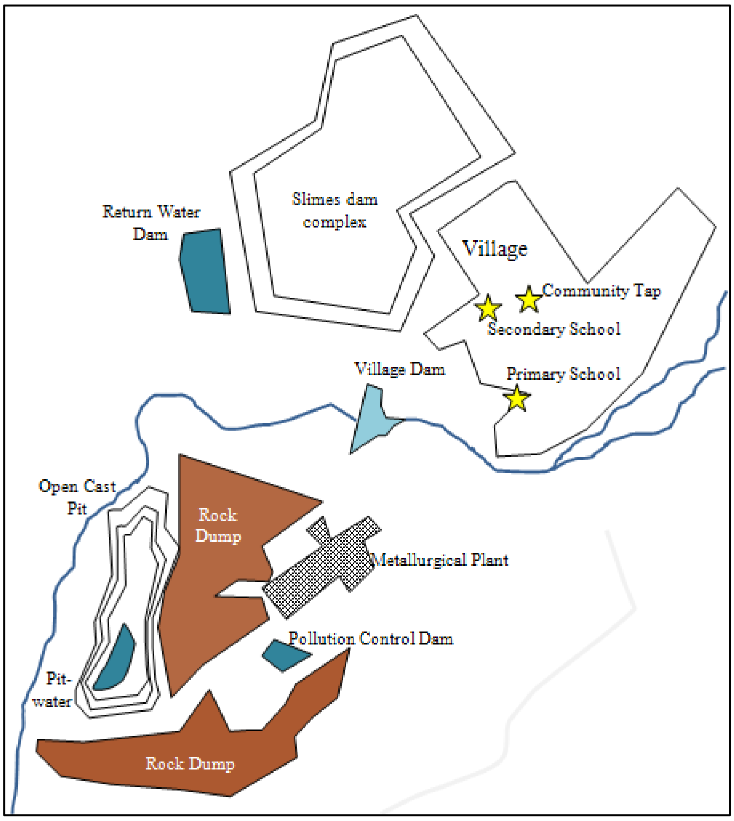


Figure 2. Schematic outline of Village and surrounds

The geology of the area is quite complex, as it forms part of the Bushveld Igneous complex, with numerous dolerite dyke intrusions and fractures. Aquifers are highly heterogeneous, and the faults and dykes display varying water-bearing characteristics (Tredoux, 2001). Fracture systems are predominantly vertical in nature, with some poorly developed horizontal fractures. Both shallow and deep aquifers have been identified, with the shallow aquifer occurring at between 20 to 30m below natural ground level. The mine abstracts water from this shallow aquifer for use in the metallurgical plant, at a yield of up to 11L/s from an unknown location. Un-surveyed data suggests a drawdown away from the village resulting from the mines' well-field, but the model used looses significance due to the heterogeneousness of the aquifer system and the vertical nature of fractures.

To determine if the complaints of villagers, namely that their water supplies was the cause for their ailments, were valid, samples were taken from the various sources of water supply for the village, namely:

- The Village Dam, used primarily for livestock watering; and
- Drinking water supply boreholes at the Primary and Secondary Schools, and a community tap.

At the time when the samples were taken, nitrate was not yet identified as a possible cause for concern, and hence these samples were analysed for all macro-chemicals, microbiological contaminants, and heavy metals at a SANAS accredited laboratory. For the purposes of this discussion, relevant results obtained from the monitoring exercise are outlined in Table 1 below:

Table 1. Analysis of Water Samples taken in Village

Variable	Unit	SANS Std*	Primary School	Secondary School	Community Tap	Village Dam
TDS	mg/L	500#	1634	770	940	272
Calcium	mg/L	80	99	72.9	66.7	19.3
Sodium	mg/L	100	365	84.3	118	53.6
Chloride	mg/L	100	336	139.8	132.8	29.2
Nitrate	mg/L	-	254.9	95	92.3	<0.3
NO_3 as N	mg/L	6	57.6	21.5	20.9	0
Sulphate	mg/L	200#	114	19.3	26.2	9.9
Phosphate	mg/L	-	<0.8	<0.8	<0.8	<0.8
Total coliforms	#/100 mL	0	0	Not measured	400	Not measured

* SANS 2001:241 Drinking Water Standard for Class 0 water

1996 SA WQ Guidelines for domestic use were used in cases where SANS 2001:241 did not specify a value

Discussion of Results

The quality of water from the Village Dam was quite good, although it is not used for drinking purposes, and this sample was used as background indicator. All samples of Village drinking water supplies exceeded the South African Drinking Water Standard of 6 mg/L NO_3N. The concentration of nitrate (57.6 mg/L NO_3N) in the sample taken from the borehole used by the Primary School exceeds this standard almost tenfold. Subsequent analysis by another party found similar results in the Primary School borehole – extremely high nitrate values, and no faecal microbial contamination. This is of particular concern, as such high nitrate levels could lead to serious health effects, especially to children in their developmental years, who were using this water at the time of sampling. It was hence critically important to determine the cause of these elevated levels of nitrate.

Based on the initial sampling results, a process of elimination was followed to determine the cause for the elevated nitrate levels in the Village drinking water supplies, as follows:

- As none of the samples had elevated phosphate levels, it was concluded that the overuse of fertiliser in agricultural activities is not a possible cause for the elevated levels of nitrate in any of the samples.
- The high levels of total coliforms in the sample taken at the Community Tap indicated that the most probable cause for the high levels of Nitrate at the Community Tap could be related to sewage contamination. Although total coliforms was not measured at the Secondary School, the similarities between the chemical compositions of the Community Tap and the Secondary School, and the close proximity of these two sampling locations, indicated that the most probable cause for the high levels of Nitrate at the Secondary School could also be related to sewage contamination.
- The samples at the Community Tap and the Secondary School had levels of both sulphate and chloride that were elevated from the background levels as observed in the Village Dam. Since the mobility of especially chloride in groundwater is quite high, the elevation of both these constituents above background levels could indicate a potential influence as a result of mining activities.
- The Primary School sample, in which the highest concentration of Nitrate were determined, did not have any total coliforms or detectable phosphate present, and also showed sulphate and chloride levels elevated above

background, and at higher levels than at the Community Tap and the Secondary School. The sulphate in this sample (114mg/L), while still within the SANS Standard, showed an increase of more than tenfold above the background values of 9.9mg/L in the Village Dam.

The absence of phosphate and total coliforms indicted that neither agricultural over-use of fertiliser, nor sewage contamination from humans or livestock concentration, could be the cause of the high levels of nitrate in the Primary School sample. The absence of phosphate and total coliforms in the Primary School sample, combined with the elevated levels of sulphate and chloride, indicated that mining-related activities had a definite influence on the high Nitrate concentration in the Primary School borehole.

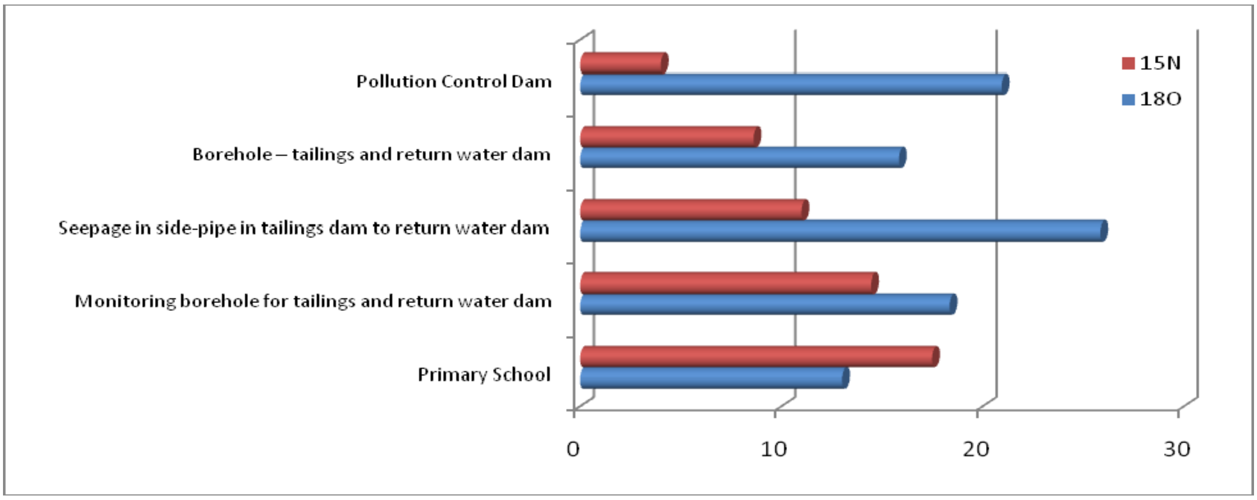
Isotope Studies

Usually, the sources of nitrate contamination can be relatively easily determined by means of isotope studies. Hence, an isotope study (δ15N and δ18O) was conducted by another party subsequent to the initial sampling, and the results obtained are outlined in Table 2 below:

Table 2. δ15N and δ18O Results of Water Samples

Description	**^{15}N**	**^{18}O**
Pollution Control Dam	4.01	20.95
Pollution Control borehole between tailings & return water dam	8.62	15.84
Seepage in side-pipe in tailings dam to return water dam	11	25.85
Monitoring borehole for tailings and return water dam	14.46	18.36
Primary School	17.49	13.02

Reactions such as nitrification and de-nitrification cause fractionation of both N and O, resulting in a greater % of ^{15}N and ^{18}O than the source. Should de-nitrification be the only process that takes place, a set of samples from a similar source and at different stages of de-nitrification will plot a typical straight line for both ^{15}N and ^{18}O. Plotting the data from Table 2 indicates a linear relationship for ^{15}N, as illustrated in Figure 3 below. However, the ^{18}O isotope data does not display the same linear relationship:



The reasons for the lack of the linear relationship for the ^{18}O isotope data becomes evident when the Nitrogen-cycle at an opencast mine is considered. Firstly, the process of de-nitrification is not the only process that takes place, as nitrification also occurs in the presence of nitrifying bacteria, incorporating oxygen from the atmosphere. In addition, there a number of different possible sources of nitrogen at the mine, which all has different origins, and will have different isotope signatures. The sources of nitrogen at the mine include:

- Geological nitrogen released during the blasting and excavation process;
- Pitwater and the use of ammonium-nitrate explosives;
- Various disposal facilities, such as Pollution Control Dams, Rock Dumps, Tailings Dams, etc.; and
- Different industrial Nitrogen-containing chemicals used in minerals processing, including nitric acid (HNO_3), and ammonium-chloride (NH_4Cl) and ammonium hydroxide (NH_4OH).

Hence, samples taken near opencast mines where a nitrate problem has been identified will display complex and non-typical ^{15}N and/or ^{18}O isotope signatures, since both nitrification and de-nitrification processes of the Nitrogen-cycle are taking place, and because there are various different sources of Nitrogen present at such a mine (Motzer, W.E. 2006).

4. SOURCES AND PATHWAYS OF NITROGEN-NITRATE IN AN OPEN-CAST MINE

A number of potential sources of Nitrogen exist in an opencast mine, particularly the nitrate and ammonia species in the Nitrogen-cycle, depending on the specific circumstances at a particular source. Through the processes of nitrification and de-nitrification, nitrates could reach the surrounding aquifers via various pathways, and potentially cause nitrate pollution of drinking water resources. These sources and pathways include the following:

Bedrock Disturbance through Blasting, and Rock Dumps

Mining activities can be regarded as a liberator of elemental nitrogen (occurring in the soil or geological formations) as a result of disturbance of bedrock. Similar to the release of geological Sulphur (S) during the process of mining, high nitrate levels at mines typically results from the disturbance of bedrock that contains Nitrogen (N) through blasting. The presence of Sulphate (SO_4) is used worldwide as indicator of acid rock or acid mine drainage (AMD), since it originates from sulphur-containing minerals in the rock, which come into contact with water and the atmosphere upon being exposed during mining excavations, resulting in the formation of sulphuric acid (H_2SO_4), which readily dissolves in water, and, depending on the buffer-capacity of the water, could result in acidification of the water, and the associated solution of heavy metals from the rock into the water (USGS, Internet Reference #3, #4). In the same manner, nitrogen-containing minerals in the bedrock come into contact with water and the atmosphere upon being exposed during mining excavations, especially in opencast mining, resulting in the formation of nitrate (NO_3), which dissolves in water at an even faster rate than sulphate.

If the surrounding geology contains high levels of elemental Nitrogen, this elemental Nitrogen will therefore be released as Nitrate during the process of excavation and mining. Previous studies in the late 1980's have identified the high nitrate in this area, and have ascribed the high levels to geological changes resulting from anthropogenic activity. Such anthropogenic geological changes refer primarily to mining, or excavation, or both these activities, as is the case at an opencast mine. For this case study area, it must be noted here that mining is the only activity in the vicinity that disturbs the bedrock geology. These disturbances lead to increased oxidising conditions and the observation of nitrate increases over time, as the process of nitrification continues.

Once excavated, overburden rock and waste rock discard are disposed in large **Rock Dumps**, where the process of nitrification of geological Nitrogen continues as a result of exposure to the atmosphere. These Rock Dumps are often enormous, as for example up to 7 tons of rock needs to be processed to produce one ounce of platinum. When the nitrate in the rock dumps is dissolved due to exposure to rain, it leaches from the Rock Dumps and could enter surface and groundwater resources. In some cases, surface run-off from Rock Dumps are contained in a dirty-water system, but this is not always the case, and even when a dirty water system is in place, these systems are not lined, and the nitrate can reach the groundwater resources in the area. Rock dumps are therefore an additional potential source of nitrate in groundwater.

In addition to causing the geological disturbances discussed above, **blasting** often involves the use of **ammonia-based explosives**, which further contributes to elevated nitrate levels, especially in open-cast mining, as residues from the blasting is disposed with the waste rock, or remain behind in the excavation. Unused explosives are sometimes destroyed on a **burning ground**, which is often not lined, and once nitrification has occurred, nitrates can enter the groundwater environment from these disposal areas. Thus, the use of ammonium-based explosives can contribute to the levels of nitrate in surface- and groundwater around mines.

Pitwater

Upon the liberation of elemental geological nitrogen, in the presence of oxygen, the elemental nitrogen released from the bedrock will undergo nitrification, and nitrate will occur in high concentrations in the water collecting at the bottom of the excavation of opencast mines. This water originates from both rain-water collecting in the bottom of the excavation or 'pit', as well as ingress of the surrounding aquifers, as the water table is often reached in deep opencast mines, and is known as "**Pitwater**" (see Figure 4 below). As the released elemental Nitrogen is in direct contact with this pitwater, the concentrations of nitrate at a mine will be the highest in the pitwater, which is often in hydraulic connection with the surrounding aquifers, and can cause a pollution plume in a regional aquifer.

Figure 4. Pitwater at a typical opencast mine

Pollution Control Dam

Pitwater is usually pumped out of the excavation to a holding or evaporation pond or **pollution control dam**. Concentrations of nitrate in the Pollution Control Dam will be similar to nitrate concentrations in the pitwater, as oxidising conditions continue to prevail in the Pollution Control Dam. From the isotope results discussed above, it is clear that the ^{15}N signature in the Pollution Control Dam reflects only the signature of geological Nitrogen, possibly combined with the signature of explosives. At this point, no other nitrogen species have been introduced.

Pollution Control Dams should be lined to prevent the release of contaminants into aquifers. If they are not lined, they could be a direct source of nitrate contamination of regional groundwater systems.

Metallurgical Process Plant

The extraction of valuable metals such as platinum from the excavated rock (which contains elemental nitrogen) is a complex process, as it often occurs in the presence of other metals. Preliminary treatment of the rock with aqua regia (a mixture of nitric acid, HNO_3, and hydrochloric acid, HCl) gives a solution containing complexes of gold and palladium as well as H_2PtCl_6. The gold is removed from this solution as a precipitate by treatment with iron chloride ($FeCl_2$). The platinum is precipitated out as impure $(NH_4)_2PtCl_6$ on treatment with ammonium chloride (NH_4Cl), leaving H_2PdCl_4 in solution. The $(NH_4)_2PtCl_6$ is burned to leave an impure platinum sponge. This can be purified by dissolving again in aqua regia, removal of rhodium and iridium impurities by treatment of the solution with sodium bromide, and precipitation of pure $(NH_4)_2PtCl_6$ by treatment with ammonium hydroxide, NH_4OH. This yields platinum metal by burning (Internet Reference #5).

This extractive process therefore takes place under reducing (acidic) circumstances, as it requires the addition of nitric acid, ammonium chloride, and ammonium hydroxide. Thus, in addition to geological nitrogen released during excavation and the ammonia-nitrate explosives used, the extraction process in a metallurgical plant adds to the available nitrogen in the nitrogen cycle at a mine. The reducing conditions in the metallurgical process will lead to de-nitrification, which will imply that the dominant species of the Nitrogen-cycle in effluent from the metallurgical process will be ammonia and ammonium, and not nitrate.

The use of various chloride-containing chemicals (hydrochloric acid, iron chloride, and ammonium chloride) in the metallurgical process is one of the reasons why elevated chloride concentrations are also indicative of contamination of groundwater as a result of mining activities. As chloride and nitrate are both more mobile than sulphate, the presence of these contaminants could indicate a pollution plume from a mine before sulphate reaches alarmingly high levels.

Tailings Dam

Following the extraction of the mineral being mined, the residues, effluent, and ‘tailings’, resulting from this extractive process, is pumped to a **residue or tailings dam**, which in this case is located in close proximity to, and upgradient of, the Primary School. Due to the nature of the extractive process, this effluent is quite acidic, and together with the presence of sulphuric acid created as a result of acid mine drainage, reducing factors and conditions exist on the tailings dam that will further the process of de-nitrification. It must be noted that leachate from the tailings dam will thus not contain any extractable nitrate but will exhibit high ammonia concentrations. This is to be expected, as the tailings dam is a reducing environment, and nitrogen will not be present as nitrate, but rather as the ammonia and ammonium-species.

Usually, most of the surface run-off and leachate will be captured in **return water dams.** If the tailings dam and/or return water dam is not lined, or is located on a geological anomaly, the ammonium-containing run-off and "leachate" from the tailings dam and/or return water dams will pass through the vadose (or unsaturated) zone, and due to the high solubility of ammonium in water, it will quickly reach the underlying aquifers. During the process of leaching through the vadose zone, the ammonia-containing leachate comes into contact with nitrifying bacteria and oxygen, and conversion to nitrite and nitrate (nitrification) occurs. It has been confirmed in various studies that nitrogen species are converted from ammonium-N to nitrate-N while moving through the vadose zone from unsaturated to saturated conditions . The higher value for the ^{15}N isotope results in the tailings dam monitoring borehole than in the tailings dam pollution control borehole confirms the initiation of this process of nitrification in the vadose zone (Peckenham, Nadeau, Amirbahman, Brutsaert, and Wilson 2004). The ^{15}N and ^{18}O isotope results for the monitoring borehole at the tailings and return water dam and for the Primary School are virtually identical, with the Primary School displaying a slightly heavier ^{15}N signature and a slightly less heavy ^{18}O signature. This is as a result of further **nitrification** from NH_4 to NO_3 occurring through the vadose zone, and the reduction in the ^{18}O isotope is as a result of the introduction of fresh atmospheric oxygen in this process, as the plume moves away from the tailings dam.

Exposure Pathways

Irrespective the source of the nitrogen-species, whether it from the disturbance of the geological nitrogen through blasting, the rock dumps, pitwater, pollution control dam, contamination of soil at the metallurgical process plant, or the tailings dam and return water dam, the pathways of exposure of local and regional aquifers are similar.

Since chloride, ammonia, and nitrate are relatively small ions, they will have higher mobility through the vadose zone than ions such as sulphate, which is a bigger, and less mobile, molecule. A pollution plume will hence have elevated levels of chloride and nitrogen-species before other mining contaminants, such as sulphate, are observed.

If no management measures are implemented that could prevent the movement of these nitrogen-species along these pathways, a pollution plume will be present in the underlying aquifers, and when communities are using these aquifers for their drinking water supplies, they are exposed to the detrimental health effects of especially nitrate.

5. RECOMMENDATIONS FOR NITRATE IMPACT MANAGEMENT AND MONITORING

On the bases of the preceding discussion, some recommendations can be made with regard to management and monitoring measures to prevent possible impacts resulting from exposure to species in the Nitrogen cycle from realising.

Management Measures

If mining occurs in an environment that contains high levels of geological Nitrogen, precautionary management measures should be implemented to prevent the release of species in the Nitrogen cycle such as ammonia and nitrate into the environment. These measures can include the following:

- Implementation of appropriate stormwater management around the excavation to prevent the ingress of run-off into the excavation. This will reduce the volume of pitwater that are contaminated with nitrate, which would reduce the costs associated with the management of this water.
- Implementation of appropriate stormwater management around rock dumps through the establishment of a clean and dirty water system, which would reduce the volume of run-off contaminated with nitrate from the rock dumps.
- Implementation of appropriate containment measures for all impoundments used to store contaminated water, such as pollution control dams, return water dams and tailings dams, such as clay and plastic linings.

Monitoring Measures

As the Nitrogen-cycle is fairly complex, and different nitrogen-species could be present or absent depending on the oxidising or reducing circumstances at specific sources on a mine, and also because nitrate contamination could have various different sources, great care should be taken with the design of monitoring programmes, and the interpretation of monitoring results. The following recommendations are of note in this respect:

- Groundwater pollution detection monitoring programmes around mines, in addition to the generally accepted variables of pH, electrical conductivity, sulphates, chlorides, cyanide, selected heavy metals and nitrates, should also include ammonia, total coliforms or E. Coli, and phosphate.
- Great care should be taken in the interpretation of monitoring data, especially as it relate to the presence or absence of the species in the nitrogen cycle. For instance, in the investigation referred to above, a conclusion was made that "*since no nitrate was found in samples taken from the tailings effluent, the tailings dam cannot be a source of nitrate in the community groundwater*". This interpretation is clearly incorrect, and indicates a

lack of consideration of the mechanics of the Nitrogen cycle, since in the reducing environment at the tailings dam, nitrogen is present as the ammonia species, and not as the nitrate species.

- Elevated levels of nitrate or ammonia in combination with higher than background sulphate levels should be identified as an early warning of a possible pollution plume, and further investigation should be initiated in order to act pro-actively to prevent such pollution plumes from reaching water supplies of users outside the mine boundaries.

6. CONCLUSION

Nitrate pollution can occur from various sources, including several activities on especially open-cast mines, and due to the serious health effects of high nitrate levels in drinking water, and the consequent detrimental effects on communities that make use of groundwater so affected, it would be prudent for responsible mining companies to investigate the possibility of nitrate pollution being caused by their mining activities, so that this potential serious problem can be properly managed.

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