# Investigation of nitrate contamination of ground water associated with chromite mining in the Kroondal area, South Africa

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## Declaration

I, Kenneth Sayed Remofiloe Milanzi, declare that the thesis hereby submitted by me for the degree Magister Scientiae at the University of the Free State, is my own independent work and has not previously been submitted by me at another university/faculty.

I furthermore cede copyright of the thesis in favour of the University of the Free State.

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January 2013

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# List of Abbreviations

| | |
|---|---|
| CEC | Cation Exchange Capacity |
| DME | Department of Minerals and Energy |
| DWA | Department of Water Affairs |
| EC | Electric Conductivity |
| EMP | Environmental Management Plan |
| EMPR | Environmental Management Program Report |
| IWULA | Integrated Water Use License Application |
| MMT | Mehylcyclopentadienyl Manganese Tricarbonyl |
| PGE | Platinum Group Element |
| SANAS | South African National Accreditation System |
| SWMP | Storm Water Management Plan |
| TDS | Total Dissolved Salts |

# Abstract

Although naturally occurring in groundwater, nitrate presence is generally attributed and regarded as a contaminant. Elevated nitrate levels pose a threat once converted to nitrite, causing methaemoglobinaemia. This investigation serves to establish the origin, quantify the extent, distribution, and elucidate possible amelioration methods of nitrate in ground and surface waters of a chrome mine in Kroondal, South Africa. Already existing surface water and borehole (groundwater) points were sampled and monitored from 2011 to 2012. An independant sample collection was conducted twice during the year of 2012. ICP and isotope (hydrogen, oxygen and nitrogen) analysis were employed to see nitrate level behaviour. In 2011 and 2012, nitrate level elevations varied from acceptable to unacceptable, with maximums of up to 81.51 mg/l in both ground and surface waters (well above the Department of Water Affairs and Forestry domestic requirements of 10 mg/l). Hydrofacies plots attribute water chemistry to: calcium/magnesium bicarbonate, opencast mine, low sodium high salt and unpolluted waters. Domination in Mg cations occurs as would be expected within Bushveld Igneous Complex aquifers. This is a result of the abundance within mafic and ultramafic igneous rocks. Increased Nitrate concentrations in surface waters are suspected to be primarily a result of runoff from waste rock dumps, high in nitrate explosive residues. In groundwater, increased concentrations are suspected to be primarily a result of high nitrate concentrations in explosive residues from underground blasting, highly mobilised once in contact with water. A secondary cause is seepage from the tailings dam, waste rock, as well as from surface water, high in nitrate concentrations. Possible remediation strategies identified include Reverse Osmosis, Eco-Dosing and Biological De-Nitrification.

**KEYWORDS:** NITRATE, GROUND WATER MONITORING AMELIORATION

# Chapter 1 Introduction

## 1.1 Background

Ground water is defined as any and all water beneath the ground surface; with subsurface water being below the ground water table and accounted for as the sum of soil moisture above the ground water table and ground water below the ground water table (Younger, 2007). Subsurface water constitutes about 99% of the total volume of fresh water presently circulating planet Earth (L'vovich, 1979). The use of glaciers as a secondary source of fresh water resources may deem problematic and also influence marine biodiversity negatively (L'vovich, 1979; Safran, 2007 and Koç et al., 2009). Table 1-1 motivates the importance in protecting ground water, for the sustenance of life and the hydrological system.

**Table 1-1** *The hydrosphere (Modified after L'vovich, 1979).*

| Parts of the hydrosphere | Volume of water ($10^3$ km) | Total volume (%) | Share in total volume of freshwater (%) |
|---|---|---|---|
| **World ocean** | 1 370 323 | 93.96 | |
| **Ground water** | 60 000 | 4.12 | 14 |
| **Ground water and zone of active water exchange** | 4 000 | 0.27 | |
| **Glaciers** | 24 000 | 1.65 | 85 |
| **Lakes** | 280* | 0.019 | 0.6 |
| **Soil moisture** | 85** | 0.006 | 0.3 |
| **Vapours in atmosphere** | 14 | 0.001 | 0.05 |
| **River water** | 1 | 0.0001 | 0.004 |
| **Total** | 1 454 193 | 100 | 100 |

*Including about 5 000 km$^3$ of water in storage reservoirs

**Including about 2 000 km$^3$ applied through irrigation

Despite its natural occurrence in ground water (Hess and Jacobson, 1981; Arumi *et al*., 2005; and Stadler *et al*., 2008) the presence of nitrate in ground water is considered as a contaminant, due to its potential of harm to the environment. It is considered to be the most ubiquitous chemical contaminant in the world's aquifers and the levels of contamination are projected to increase (Fried, 1991; Goodchild, 1998; Joosten *et al*., 1998; Birkinshaw and Ewen, 2000; Liu *et al*., 2005). Nitrate in ground water result primarily from one or more of these sources:

- Agricultural activities such as the large-scale concentration of livestock or the over-use of nitrate-based fertiliser (Gormly and Spalding, 1979; Baker, 1992; Tredoux, 2004; Chowdary *et al*., 2005)

- Disposal or discharge of human and animal debris and excrement into potable water sources (MacQuarrie *et al*., 2001; Taylor, 2003; Tredoux, 2004)

- Explosives generally have a major component of nitrate (Revey, 1996; Kramer, 2001 and Meyer *et al*., 2007)

- Activities that influences the oxidising or reducing circumstances in the nitrogen cycle, such as aeration or acidification; or activities that disturb bedrock (high in elemental nitrogen) such as excavation, building, and mining (Revey, 1996; Vitousek *et al*., 1997 and Yaussy *et al.*, 2004)

Currently the Department of Water Affairs (DWA) 1996 regulations have set the standards of nitrate in ground water as 0-6 mg/l for domestic use and 0-100 mg/l for agriculture livestock. Nitrate in drinking water is detrimental to health once converted in the gastrointestinal tract to nitrite as a result of bacterial reduction (DWA, 1996; Addiscott & Benjamin, 2004 and Tredoux *et al*., 2009). Methaemoglobinemia occurs once the conversion takes place.

## 1.2 Significance and context of the study

It is understood that the elevated nitrate concentrations of Xstrata Kroondal mine are attributed to underground and opencast blasting, including residues from previously rehabilitated opencast areas. Nitrate explosive residue is highly soluble and easily dissolves into both surface and ground water (CHEMC, 2010). Nitrate in drinking water is a health concern as already mentioned. There is a cause for concern for some sites at Kroondal Mine with respect to their elevated nitrate levels (Table 1-2). Xstrata Alloys is committed to ensuring that the specific closure objectives of their chrome mine are reached. The specific closure objectives include ensuring that:

- The health and safety of people and animals is safeguarded from hazards (resulting from the suspended mining operations)

- The land is rehabilitated to achieve a condition approximating its natural state, or so that the envisaged end use of the land is able to be achieved

- The physical and chemical stability of the remaining structures should be such that risk to the environment through naturally occurring forces is eliminated

**Table 1-2** *Previous ground water monitoring results of nitrate levels (mg/l) at Xstrata Kroondal mine.*

| | **Non rainy months** | | | **Rainy months** | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Jul-08** | **Jul-09** | **Jul-10** | **Sep-00** | **Oct-06** | **Oct-08** | **Oct-09** | **Oct-10** |
| **KMB 01** | | | | **21.20** | | | | |
| **KMB 03** | 0.22 | -0.34 | 2.26 | 9.30 | | 9.30 | 5.11 | 3.05 |
| **KMB 03s** | | 0.34 | 2.72 | | | 0.50 | 3.83 | 5.38 |
| **KMB 05** | 0.30 | 2.79 | 1.45 | | | | 2.36 | 0.47 |
| **KMB 06** | | | | 7.60 | | 7.60 | | |
| **KMB 10** | | | | **12** | | **12** | | |
| **KMB 11** | | | | **22.20** | **37.1** | **22.20** | | |
| **KMB 13** | | | | 4.43 | | 4.43 | | |
| **KMB 16** | | | | | **10.7** | | | |
| **KMB 17** | -0.22 | | | | | | 0.28 | |
| **KMB 18** | | **25.10** | 6.78 | | | **14.90** | **19.40** | 5.33 |
| **KMB 19** | | | | | | **11.20** | | |
| **KMB 20** | | 4.42 | | | | | | |
| **KMB 21** | | 7.32 | 8.38 | | | | 8.18 | |

Understanding the origin, behaviour, distribution, monitoring and possible on-site treatment better at Xstrata Alloys is needed. This project also forms part of the Inkaba-ye Africa research programme, of which Inkaba-ye Africa has granted funding.

## 1.3 Methodology

A judgemental sampling design was undertaken; using sampling units on the basis of expert knowledge and professional judgement. This type of design, as opposed to the probability sampling design was cheaper and easier to implement. In judgmental sampling, the selection of sampling units (i.e., the number and location and/or timing of collecting samples) is based on knowledge of the feature or condition under investigation and on professional judgment without any type of randomization (EPA, 2002). Judgmental sampling is useful when there is reliable historical and physical knowledge about a relatively small feature or condition. Water samples were collected in 500 ml plastic containers and held for a maximum of 24 hours. The following water analyses were conducted: ion analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and alkalinity analysis by titration. Isotope analysis was conducted by analysing for hydrogen and oxygen isotopes at the University of Kwa Zulu Natal in South Africa; and nitrogen and oxygen isotope ratios were analysed at the Northern Arizona University in the United States of America. High levels of nitrate and ammonia combined with increased bacteriological contaminants, such as faecal coliforms and E.coli, were used to indicate 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 were used to indicate fertiliser-related causes of the contamination (Scheierling, 1996). Elevated levels of nitrate and/or ammonia, together with levels of sulphate and chloride that are higher than background concentrations, were used to indicate pollution of water resources as a result of mining activities (Bosman, 2009).

## 1.4 Scope

The two major parts conducted were nitrate contamination analysis and decision making towards managing elevated nitrated levels. This project started off with a desktop study and a site study. Following the aforementioned was a sample collection to establish data and delineate and analyse contamination. Once the problem extent had been characterised better, the possible sources of contamination were identified in order to efficiently set up management options.

## 1.5 Purpose of the study

- Determine the origin of nitrate in the ground and surface water of Kroondal chromium mine
- Quantify the extent and distribution of nitrate levels in the ground and surface water
- Elucidate possible amelioration methods of nitrate levels in both the ground and surface water

## 1.6 Layout of thesis

- Chapter 1 Introduction: introducing the subject of nitrate in ground water, giving a brief motivation and outlining the objectives of the study
- Chapter 2 Literature review: varying views of authors on the nitrate issue and a general direction in which research has been geared towards
- Chapter 3 Site description: geology and past work conducted in study area
- Chapter 4 Methodology
- Chapter 5 Results: information gained from analyses and monitoring presentation
- Chapter 6 Discussion
- Chapter 7 Conclusion and recommendations

# Chapter 2 Literature review

## 2.1 Nitrogen chemistry

### 2.1.1 Nitrogen

Nitrogen is a major constituent (78%) of the earth's atmosphere (Galloway, 1998 and Tagma *et al*., 2009) and occurs in various forms such as elemental nitrogen ($N_2$), nitrate ($NO_3^-$), nitrite ($NO_2^-$) and ammonia ($NH_3$). Roswall (1981) opposes the distribution of nitrogen on Earth (Table 2-1) by stating that, "Although abundant on earth, 96 per cent is found in the lithosphere and does not take part in the biogeochemical cycle. In terrestrial systems, only four per cent of the nitrogen occurs in biomass, while 96 per cent is found mainly in soil organic matter." Roswall is backed by several authors who attribute nitrogen primarily from a source other than the atmosphere (Bartholomew and Clark, 1965; Soderlund and Svensson, 1976).

**Table 2-1** *Distribution of nitrogen on Earth. All values in Tg ($10^{12}$g) (adapted fromRobinson., 1978).*

| | Nitrogen (Tg) | Proportion (%) |
|---|---|---|
| **Lithosphere** | $574 \times 10^8$ | 93.80 |
| **Atmosphere** | $38 \times 10^8$ | 6.20 |
| **Hydrosphere** | $0.23 \times 10^8$ | 0.04 |
| **Biosphere** | $0.003 \times 10^8$ | 0.001 |

Natural reactions of atmospheric forms of nitrogen with rainwater result in the formation of nitrate and ammonium ions (ESA, 1997; Galloway, 1998 and Tredoux *et al*., 2009). Nitrogen is an essential component of proteins, genetic material, chlorophyll, and other key organic molecules. All organisms require nitrogen in order to live. It ranks fourth behind oxygen, carbon, and hydrogen as the most common chemical element in living tissues (Vitousek *et al*., 1997; Dinnes *et al*., 2002 and Keeney and Hatfield, 2008). Most plants and animals cannot use nitrogen gas directly from the air as they do carbon dioxide and oxygen. Instead, the $NH_4^-$ and $NO_3^-$ anionic complexes are used in the nitrogen cycle (ESA, 1997).

### 2.1.2 Nitrate

The nitrate ion has a molecular mass of 62.0049 g/mol. This ion always has the same chemical structure (Figure 2-1), in which the nitrogen atom and the three oxygen atoms lie in the same plane in a symmetrical trigonal arrangement (Addiscott, 2005). This chemical structure is referred to as a resonance structure. Resonance structures of a molecule or ion are two or more structures with identical arrangements of the atoms but different arrangements of the electrons (Hart *et al.*, 2010).

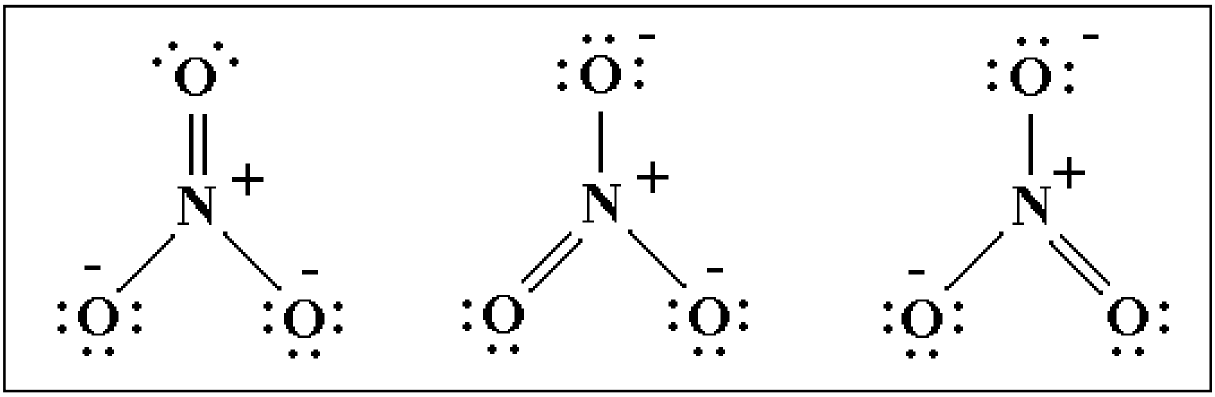


**Figure 2-1** *Nitrate resonance structures (McCarron and McCarron, 2008).*

The salts formed by nitrate are generally soluble (Addiscott, 2005). Cations generally occurring in ground water (Table 2-2) are likely to be calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), iron (Fe) and aluminium (Al), and the salts they form with nitrate are all highly soluble (Weast, 1964). Extreme solubility such as that of ammonium and calcium salts, have two consequences:

1. Virtually all the nitrate encountered in the environment is dissolved in water (Addiscott, 2005)
2. Solubility does not limit nitrate concentrations in natural waters (contamination vulnerability) (DeSimone and Howes, 1998; Addiscott, 2005 and Chowdary *et al*., 2005)

**Table 2-2** *Solubilities of the salts of nitrate in cold water (Weast, 1964).*

| | | **Solubility ($g/m^3$)** | |
|---|---|---|---|
| **Cation** | **Salt** | **Salt** | **Nitrate** |
| **$Ca^{2+}$** | $Ca(NO_3)_2{\cdot}4H_2O$ | $2.66 \times 10^6$ | $1.40 \times 10^6$ |
| **$Mg^{2+}$** | $Mg(NO_3)_2{\cdot}6H_2O$ | $1.25 \times 10^6$ | $0.61 \times 10^6$ |
| **$K^+$** | $KNO_3$ | $0.32 \times 10^6$ | $0.18 \times 10^6$ |
| **$Na^+$** | $NaNO_3$ | $0.92 \times 10^6$ | $0.67 \times 10^6$ |
| **$NH_4^+$** | $NH_4NO_3$ | $1.18 \times 10^6$ | $0.91 \times 10^6$ |
| **$Fe^{2+}$** | $Fe(NO_3)_2{\cdot}6H_2O$ | $0.84 \times 10^6$ | $0.36 \times 10^6$ |
| **$Fe^{3+}$** | $Fe(NO_3)_3{\cdot}6H_2O$ | $1.50 \times 10^6$ | $0.80 \times 10^6$ |
| **$Al^{3+}$** | $Al^{3+}(NO_3)_3{\cdot}9H_2O$ | $0.64 \times 10^6$ | $0.32 \times 10^6$ |

### 2.1.3 Ammonium and ammonia

According to Addiscott (2005), ammonium is often paired with nitrate as ‘mineral nitrogen’ among soil scientists. This is because it is so readily converted to nitrate by soil microbes, in a process known as nitrification. The relation between ammonia, water and ammonium can be expressed as follows (Addiscott, 2005):

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH4^{4+} + OH^{-}$$

## 2.2 The Nitrogen Cycle

### 2.2.1 Introduction

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 (Bosman, 2009). A simplified illustration of the natural (not altered by anthropogenic activity) nitrogen cycle is outlined in Figure 2-2. Two of the major natural sources of nitrogen entering the nitrogen cycle are nitrogen fixing organisms and lightning. Nitrogen-fixing organisms include a relatively small number of algae and bacteria. Lightning may also indirectly transform atmospheric nitrogen into nitrate, which rain onto soil (ESA, 1997 and Vitousek *et al*., 1997).

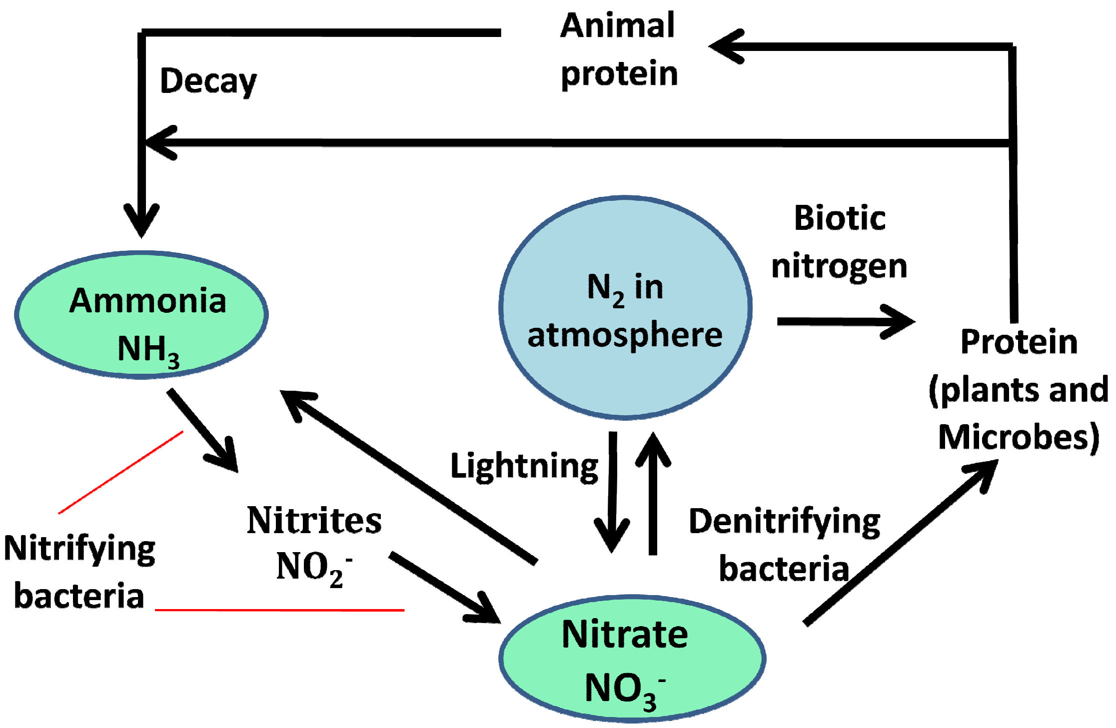


**Figure 2-2** *Simplified natural Nitrogen cycle (modified after Bosman, 2009).*

### 2.2.2 The process of the nitrogen cycle

The nitrogen cycle entails the uptake of atmospheric or soil nitrogen by plants or animals, and the conversion and use thereof by plants and animals. Processes involved are; fixation, mineralisation, nitrification and denitrification (Table 2-3). The processes within the nitrogen cycle do not occur in a fixed or systematic order as expressed in Table 2-3. From natural erosion of geological nitrogen, nitrate and nitrites occur together in soil. 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 (Stadler *et al*., 2008). Animal excretion and plant decay result in ammonia ($NH_3$) or ammonium ($NH_4^+$) being formed, which readily oxidise 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 denitrification). 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 (ESA, 1997; Vitousek *et al*., 1997 and Bosman, 2009).

**Table 2-3** *The Nitrogen Cycle process summarised (ESA, 1997; Vitousek et al., 1997 and Addiscott, 2005).*

| | **Process** | **Result** |
|---|---|---|
| **1** | $N_2$ conversion for plant use | Fixation<br>• Symbiotic bacteria<br>• Lightning (sometimes)<br>• Industrially at HT (600 $^{O}C$) and HP |
| **2** | Decomposition of plants and animals | Mineralisation or Ammonification |
| **3** | Under aerobic conditions:<br>$NH_3$ and $NH_4^+$ readily oxidise to $NO_2^-$ and $NO_3^-$ | Nitrification |
| **4** | Under reducing conditions:<br>Conversion of $NO_3^-$ back to $NH_4^+$, $NH_3$ or $N_2$<br>Direct conversion of $NO_2^-$ and $NH_4^+$ to $N_2$ | Denitrification<br>Anaerobic ammonium oxidation |

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.

### 2.2.3 Natural contribution

The lithosphere serves as the main nitrogen reservoir in the global context with an estimated 93.8 per cent of the total (Bartholomew and Clark, 1965). This includes the organically bound soil nitrogen which amounts to approximately 0.15 % of the total (Soderlund and Svensson, 1976). The large quantity of nitrogen contained in the rock mass only becomes available very gradually through weathering and the atmosphere (with two percent of the reserves) together with the soil nitrogen are the main sources of nitrogen for most biogenic reactions. The presence of geological nitrogen in reducing environments such as glacial till and carbonaceous shale, has been documented for other continents (Power and Scheepers, 1989) and this may also be the case in the Karoo (Tredoux, 2004). Ground water in contact with these rocks leaches ammonia that is oxidized to nitrate when redox conditions change.

### 2.2.4 Anthropogenic contribution

Humans can and are altering the global cycle of nitrogen via combustion of fossil fuels, production of nitrogen fertilizers, cultivation of nitrogen-fixing legumes, and other actions (ESA, 1997; Vitousek *et al*., 1997 and Galloway, 1998). Anthropogenic contribution to altering the global nitrogen cycle cannot be ignored (Table 2-4).

**Table 2-4** *Human contribution to the alteration of the global nitrogen cycle (after Vitousek et al., 1997).*

| **Human Contribution** | **Process** | **Tg/y** | **Comments** | **Example** |
|---|---|---|---|---|
| **N-fertiliser** | Industrial fixation | 80 | Human increase=food demand | |
| **N-fixing Crops** | N-fixation | | Derive $N_2$ directly from atmosphere | Soybeans, peas, alfalfa |
| **Fossil fuel burning** | Nitric oxide back | 20 | Previously stored fixed nitrogen released | |
| **Stored N mobilisation** | | >40 | $N_2$ from long-term biological storage pools liberated | Burning forests |
| | | 10 | | Draining of wetlands |
| | | 20 | | Land clearing for crops |

Industrial fixation from nitrogen fertilisers reaches up to 80 Tg/y. Human activities have at least doubled the transfer of nitrogen from the atmosphere into the land-based biological nitrogen cycle (Vitousek *et al*., 1997). Anthropogenic inputs increase the soil nitrogen pool to such an extent that leaching of nitrate is enhanced (Tredoux, 2009). Increasing nitrogen availability also generally reduces the biological diversity of affected ecosystems, and changes the rates and pathways of N cycling and loss (Tilman, 1987; Vos and Opdam, 1993; and Aber *et al*., 1995). Nitrate can leach through soils to stream water and ground water, depleting soil minerals, acidifying soils, and altering downstream freshwater and coastal marine ecosystems (Likens *et al*., 1996 and Nixon *et al*., 1996). One major consequence of human-driven alterations in the nitrogen cycle has been regional and global change in the chemistry of the atmosphere: specifically, increased emissions of nitrogen based trace gases such as nitrous oxide, nitric oxide, and ammonia (Vitousek *et al*., 1997). Vitousek *et al*., (1997) believes that human alterations of the nitrogen cycle have:

1. Approximately doubled the rate of nitrogen input into the terrestrial nitrogen cycle, with these rates still increasing
2. Increased concentrations of the potent greenhouse gas $N_2O$ globally, and increased concentrations of other oxides of nitrogen that drive the formation of photochemical smog over large regions of Earth
3. Caused losses of soil nutrients, such as calcium and potassium, that are essential for the long-term maintenance of soil fertility
4. Contributed substantially to the acidification of soils, streams, and lakes in several regions; and
5. Greatly increased the transfer of nitrogen through rivers to estuaries and coastal oceans.
6. Accelerated losses of biological diversity, especially losses of plants adapted to efficient use of nitrogen, and losses of the animals and microorganisms that depend on them; and
7. Caused changes in the composition and functioning of estuarine and near shore ecosystems, and contributed to long term declines in coastal marine fisheries

## 2.3 The nitrate issue

The nitrate issue is of global concern (Colleen, 1993; Spalding and Exner, 1993; Goodchild, 1998; Birkinshaw and Ewen, 2000; Aghzar *et al*., 2002; Liu *et al*., 2005 and Tagmal *et al*., 2009). “Ground water nitrate pollution has become a widespread problem which affects all countries regardless of their development level” (Tagmal *et al*., 2009). The environmental problems associated with nitrate, include excessive growth of water plants in freshwater, algal blooms in coastal and estuarine waters and ozone destruction in the stratosphere caused by the release of nitrous oxide from nitrate (Addiscott and Benjamin, 2004). On site sanitation generates nitrate problems, especially in rural areas and jeopardizes the socio-economic development of the country (Tagmal *et al*., 2009). Elevated nitrate concentrations occurring in ground water present a serious threat to infants (methaemoglobinaemia) and livestock (Kross *et al*., 1993 and Tredoux *et al*., 2009). Such situations may become worse in arid and semi-arid areas where water resources are recharged slowly, irrigation returns are re-used intensively and evaporation rates are high (Tagmal *et al*., 2009). Many studies primarily attribute increase of nitrate pollution to anthropogenic activities: such as mineral fertilizers and products of organic compounds from agriculture, septic systems and cattle manure (Power and Scheepers, 1989; Guimerà, 1998; Widory *et al*., 2004; Liu *et al*., 2005 and Tredoux *et al*., 2009). Nitrogen from anthropogenic sources includes fertilizers, biological nitrogen-fixation, ammonia volatilization, combustion and activities that bring nitrogen from long-term storage pools such as forests have been estimated by several groups to be close to the same order of magnitude (Table 2-5) as the nitrogen from natural (pre-industrial) sources (Jordan and Weller, 1996 and Vitousek *et al*.,1997).

**Table 2-5** *Estimates of annual nitrogen fixation (Adapted from Vitousek et al., 1997).*

| Source | 1960 (MMT of N) | 1990 (MMT of N) |
|---|---|---|
| **Legume crops** | 30 | 40 |
| **Fossil fuel emissions** | 10 | 15 |
| **Fertilizer** | 20 | 80 |
| **Total** | 60 | 145 |
| **Natural N fixation** | 80-130 | 80-130 |

Globally, nitrogen fertilizer is largely used for cereal grain production and accounts for an estimated 40% of the increase in per capita food production in the past 50 years (Mosier *et al*., 200I). Given the world's needs for food, the great ability of annual grains to produce the needed food (and animal feed) and the economic returns from nitrogen fertilizers; change on the larger scale will be slow and requires policy changes as well as economic assessments that include externalities (Keeney and Hatfield, 2008). The nitrogen fertiliser has increased significantly over time (Table 2-6). From 1960 to 1986, a vast gap between the developing and developed countries was experienced in nitrogen fertiliser consumption. Concern for the environment, humans and animals is highlighted once nitrate is converted to nitrite.

**Table 2-6** *Nitrogen fertiliser consumption (MMT) in the world, developed and developing countries, 1960-2003 (Adapted from Keeney and Hatfield, 2008).*

| Years | 60/61 | 70/71 | 75/76 | 80/81 | 85/86 | 90/91 | 95/96 | 00/01 | 02/03 |
|---|---|---|---|---|---|---|---|---|---|
| **World** | 10.80 | 31.75 | 43.90 | 60.78 | 70.37 | 77.56 | 78.07 | 81.19 | 85.11 |
| **Developed** | 8.55 | 23.13 | 30.79 | 35.79 | 38.86 | 33.07 | 29.88 | 29.07 | 28.71 |
| **Developing** | 2.28 | 8.61 | 13.11 | 24.90 | 31.51 | 42.39 | 49.18 | 52.12 | 56.40 |

## 2.3.1 The effects of nitrate on human beings

Nitrate in drinking water is widely but mistakenly believed to be responsible for two health concerns: methaemoglobinaemia and stomach cancer (Addiscott and Benjamin, 2004). Nitrate in drinking water are believed to attribute to methaemoglobinaemia (Comly, 1987; Johnson *et al*., 1987 and Rail, 1989), stomach cancer (Hill *et al*., 1973) and non-Hodgkin's lymphoma (Bogardi and Kuzelka, 1991), but substantial evidence accounts for the former and not the latter attribute (Addiscott and Benjamin, 2004 and Tredoux *et al*., 2009). There is no correlation between methaemoglobinaemia and nitrate ingestion in food and water by infants. (Addiscott, 2005) Methaemoglobinaemia or 'blue-baby syndrome' is a condition suffered by infants up to about one year old, and it is caused by nitrite, not by nitrate (Addiscott and Benjamin, 2004; Tredoux, 2004 and Hatfield and Forlett, 2008). Methaemoglobinemia most often affects infants of less than six months in age because infants possess much less oxidizable haemoglobin than adults. Also, nitrite ions may be more strongly bound by infantile haemoglobin due to immaturity of certain enzymes and that the kidneys of infants have inferior excretory power which may favour retention of nitrite for longer periods of time (Comly, 1987). In methaemoglobinaemia; one nitrite molecule reacts with two molecules of haemoglobin to form methaemoglobin (Comly, 1987; Adiscott and Benjamin, 2004 and Tredoux, 2004). In acid mediums, such as the stomach, the reaction occurs quite rapidly (Comly, 1987). This altered blood form protein prevents blood cells from absorbing oxygen. This results in suffocation of the infant and may lead to death (Gustafson, 1993). Oxygen deprivation results in the infant often taking on a blue or purple tinge in the lips and extremities, hence the name, blue baby syndrome (Comly, 1987). Other signs of infant methaemoglobinemia include gastrointestinal disturbances such as vomiting and diarrhoea, relative absence of distress when severely cyanotic but irritable when mildly cyanotic and chocolate-brown coloured blood (Comly, 1987 and Johnson *et al*., 1987).

Epidemiological evidence does not provide any strong support for the hypothesis that the concentrations of nitrate in Britain pose a significant risk of stomach cancer (Burt *et al.*, 1993). The highest rates of stomach cancer were found by Burt *et al*. (1993) to be in the north and west of the country, whereas it is in the south and east that nitrate concentrations are highest. . There is evidence that nitrate intake is greater social classes I, II, III, whereas mortality from stomach cancer is highest in classes IV and V (Burt *et al*., 1993). The correlation of nitrate ingestion and stomach cancer is also disputed by Addiscott and Benjamin (2004) with the support of the following authors:

1. Foreman *et al*. (1985) in Addiscott and Benjamin (2004)
2. Beresford (1985) in Al-Dabbagh *et al*. (1986): negative relation between nitrate concentrations in 229 urban areas of the United Kingdom and stomach cancer
3. Van Loon *et al*. (1998) in Addiscott and Benjamin (2004): a study of 120 000 people failed to identify one person to associate stomach cancer and nitrate ingestion
4. Al-Dabbagh *et al*. (1986): a study conducted on workers in a nitrate fertilizer plant showed no difference between their mortality from stomach cancer and that of comparable workers in other jobs

The World Health Organisation (W.H.O., 2003) has stated that there isn't enough proof to substantiate nitrate attributing to stomach cancer. Contrary to all the negativity relating nitrate to our health, it has generally been accepted that humans produce nitrate in their bodies (Mitchell *et al*., 1916 and Green *et al*., 1981) and that a concentration of nitrate in saliva occur (Duncan *et al*., 1995). The nitrate in the saliva is rapidly changed (reduced) to nitrite in the mouth by bacteria, which live on the surface of the tongue (Duncan *et al*., 1995). Each day we produce about one litre of saliva, which we swallow. This saliva contains large amounts of nitrite, which will become nitrous acid when it reaches a normal human stomach (Mitchell *et al*., 1916 and Addiscott and Benjamin, 2004). Even someone on a nitrate free diet has an appreciable nitrate concentration in their blood plasma and a much greater concentration in their urine (Addiscott and Benjamin, 2004). An active transport mechanism occurs in the kidneys that pumps nitrate back from the urine into the blood (Kahn *et al*., 1975).

### 2.3.2 The effects of nitrate on animals

Elevated levels of dietary nitrate interfere with normal thyroid function, deficiency in livestock by destroying carotene or by interfering with utilisation of Vitamin A, reduced weight gain and reduced milk or egg production (Burt *et al*., 1993). Ingestion of nitrate reduces the lifespan, inhibits growth and increases abortion and infertility of cattle (Davison *et al*., 1964). The loss of two herds of cattle at individual wells was the resultant of high nitrate in Runnels County, Texas, in the summer of 1969 (Kreitler and Jones, 1975). In Botswana approximately 200 heads of cattle died of nitrate poisoning in the Ghanzi area in October 2000. It is noteworthy that all the recorded instances of livestock losses concerned pregnant heifers (Tredoux, 2004). According to Mahler *et al*. (2007), nitrate poisoning is most likely to occur in ruminant animals such as cattle and sheep. This is ascribed to the bacteria in the rumen's ability to convert nitrate to nitrite. Tredoux (2004) highlights the importance of noting that "Livestock can adapt toleratively high nitrate levels but cannot tolerate a sudden increase in the total nitrate intake, either from the fodder or the drinking water". Nitrate limits for stock watering are set considerably higher than for human consumption (in Namibia, the limit for stock-watering is set at 110 mg/l and in South Africa 90,3 mg/l is used as a guideline value for the watering of dairy cows) (Tredoux, 2004).

### 2.3.3 The effects on nitrate on the environment

The environmental problems associated with excessive nitrate include; excessive growth of water plants in freshwater, algal blooms in coastal and estuarine waters and ozone destruction in the stratosphere caused by the release of nitrous oxide from nitrate (Jordan and Weller, 1996; Vitousek *et al*., 1997; Addiscott and Benjamin, 2004 and Keeney and Hatfield, 2008;). Nutrient enrichment of surface waters (primarily nitrogen and phosphorous) is undesirable both as a result of the changes in the freshwater or marine ecosystem. Control of eutrophication depends on which nutrient (usually nitrogen or phosphorous) is growth-limiting (Burt *et al*., 1993). Lakes, coastal waters, and estuaries, overloaded with biologically available nitrogen, produce organic materials in abundance (Stadler *et al*., 2008). The nitrogen atom gets connected to carbon, but the unwanted effects of excess growth and subsequent decay create anaerobic conditions (Keeney and Hatfield, 2008). Rivers, lakes and ground water with excess in nitrogen can be toxic to humans and causes water quality problems in natural water systems (Hallberg and Keeney, 1993; Dinnes et al., 2002; Keeney, 2002 and Townsend, 2003). An excess of nitrogen in the estuaries of oceans enhances growth of aquatic organisms to the extent that water quality is affected and dissolved oxygen levels are lowered (Turner and Rabalais, 1991; Rabalais *et al*., 1996 and Howarth, 2000). This affects the metabolism and growth of oxygen requiring species, causing a condition referred to as hypoxia (Rabalais et al, 1996). When the atmosphere receives more nitrous oxide than it can assimilate, it results in stratospheric ozone destruction. Nitrous oxide and ammonia are greenhouse gases (Keeney and Hatfield, 2008).

## 2.4 Nitrate in Ground water

### 2.4.1 Occurrence and Distribution of Nitrate in Ground water

Mineral deposits of nitrate are rare due to the high water solubility of nitrate, although large deposits of sodium nitrate (saltpetre) occur in the desert regions of Chile (DWA, 1996). Elevated nitrate concentrations have been recorded in ground water of mostly uninhabited regions around the world with special reference to semi-arid settings (Aranibar *et al*., 2003 and Walvoord *et al.*, 2003). Elevated nitrate concentrations are generally associated with anthropogenic activities from areas of dense population (Razowska-Jaworek and Sadurski, 2004 and Wakida and Lerner, 2005), nitrate tends to increase in shallow ground water sources in association with agricultural and urban runoff, especially in densely populated areas (DWA, 1996). According to Tredoux *et al*. (2009), nitrate occurs extensively in ground water in southern Africa. Figure 2-3 shows that elevated nitrate concentrations occur both locally at isolated points as well as in vast areas regionally. Mainly the three northern provinces (Limpopo, North West and Northern Cape provinces) in South Africa are seriously affected by nitrate (Figure 2-4).

### 2.4.2 Nitrate Accumulation in Ground water

It is not easy to decide what constitutes an excessive concentration of nitrate in water, because this depends on whether or not the water also contains any bacteria and on the overall health of the consumer (Addiscott et al., 1991). The main cations in ground water are likely to be calcium, magnesium, potassium, sodium, iron, aluminium and the salts they form with nitrate are highly soluble (Weast, 1964). Solubility of nitrate gives a high mobility and potential for loss from the unsaturated zone by leaching (DeSimone and Howes, 1998; Chowdary *et al*., 2005). Increased nitrate levels in ground water or in rural and municipal water supplies usually occur as a result of contamination by organic wastes from animals or humans, or by nitrogenous fertilisers (Razowska-Jaworek and Sadurski, 2004 and Wakida and Lerner, 2005).

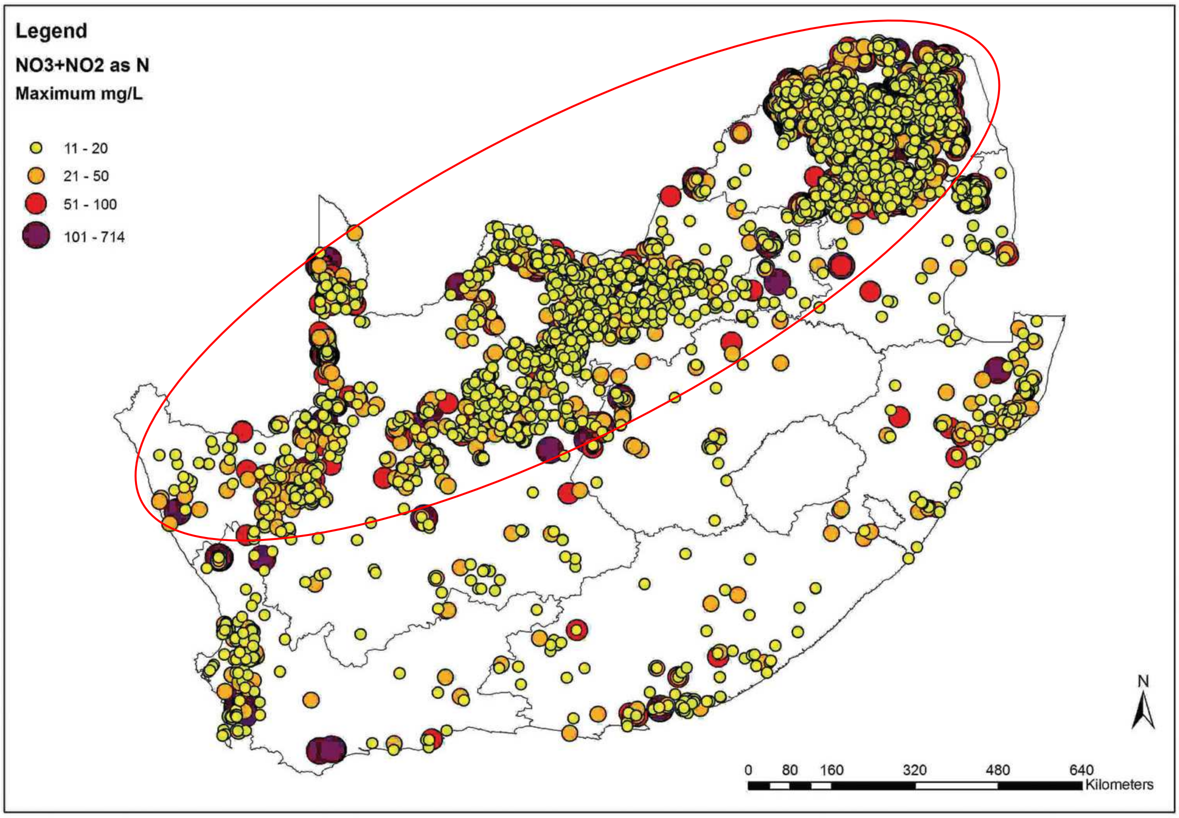


**Figure 2-3** *Maximum concentrations greater than 10 mg/L of nitrate and nitrite as nitrogen, from 1990-2008 (Modified from Israel et al., 2011).*

#### *2.4.2.1 Natural occurrence of nitrate in ground water*

Loss of nitrate from soil can occur by two main processes: leaching and denitrification; whereby leaching causes problems in the water environment and denitrification in the atmosphere (Addiscott, 2005). The fate of nitrate lost from the soil is shown in Figure 2-5 and leaching ultimately reaches ground water or surface waters.

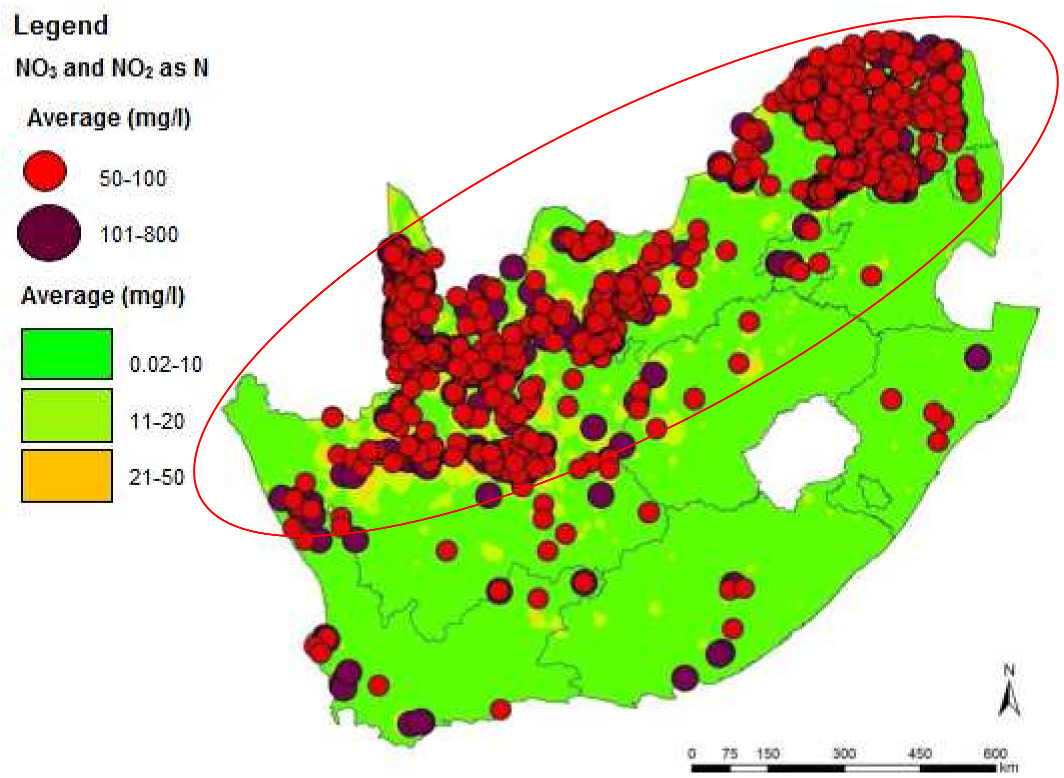


**Figure 2-4** Sampling points with a *maximum $NO_3$_N+$NO_2$ as N greater than 50 mg/L on an interpolated N map (Modified from Maherry et al., 2009).*

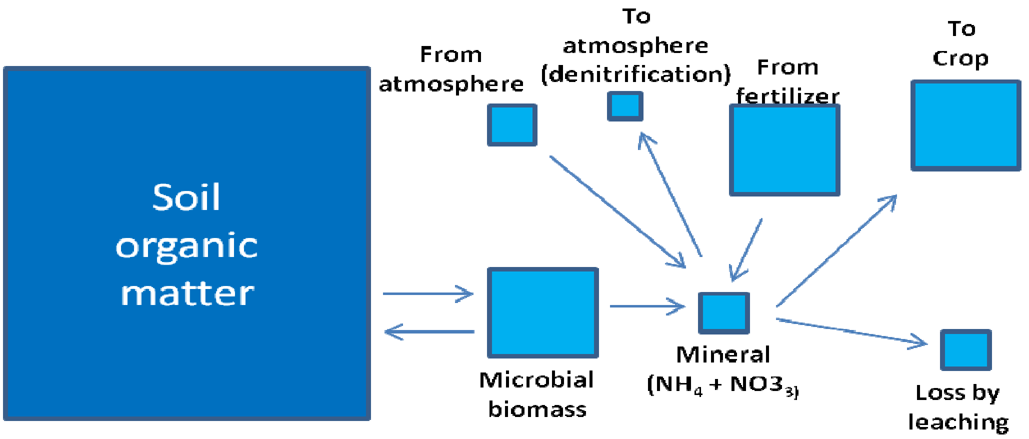


**Figure 2-5** *The four ultimate fates of nitrate (The size of the square is proportional to the quantity of nitrogen involved) (Modified from Addiscott et al., 1991).*

Only a small proportion of this nitrate (Figure 2-5) may have come from fertilizer (Addiscott, 1991). The rest will have come from mineralization in the soil, some from the ploughing up of old grassland, some from grazing animals or the application of manures and some from the deposition of various forms of nitrogen from the atmosphere (Addiscott, 2005 and Almasri, 2006). The three major routes for nitrate movement out of a soil profile are (Burt *et al*., 1993):

1. Upwards, crop uptake and gaseous loss

2. Sideways, via surface/subsurface flow
3. Downwards, as profile leaching

Tredoux (2004) summarises the environmental conditions under which natural leaching of nitrate from the soil zone and accumulation in ground water that have been observed in Table 2-7.

**Table 2-7** *Environmental conditions for natural leaching of nitrate from soil zone (adapted from Tredoux, 2004).*

| Cause | Effect |
|---|---|
| **Vegetation** | Nitrogen fixation by specific plant species |
| **Soil** | Low C:N ratio for mineralisation |
| **Rainfall** | Adequate to support the required vegetation type(s) |
| | Relatively low (150-250 mm/a) to cause semi-arid conditions |
| | Storm events large enough to ensure rapid natural recharge and nitrate leaching |
| **Temperature** | Sufficiently high to ensure microbiological nitrification (oxidation) |
| **Hydrology** | Absence of active open drainage systems (i.e. rivers ending in pans) |

#### *2.4.2.2 Anthropogenic occurrence of nitrate in ground water*

Whereas agriculture is the main source of nitrate in the highly developed countries such as Europe and the USA, on site sanitation is seen as the main anthropogenic source of nitrate in Southern Africa (Tredoux *et al*., 2009). The main inputs of nitrate to ground water (Table 2-8) are generally derived from anthropogenic activities (Gormly and Spalding, 1979; Baker, 1992; MacQuarrie *et al*., 2001; Taylor, 2003 and Tredoux, 2004; Chowdary *et al*., 2005). Pollution sources may include; application of fertilisers (Addiscott *et al.*, 1991), sewage sludge application to soil (MacQuarrie *et al*., 2001; Taylor, 2003 and Tredoux, 2004) and explosives in mines (Revey, 1996; Kramer, 2001 and Meyer *et al.*, 2007). Many studies correlate agriculture and nitrate concentration in ground water (Joosten *et al*., 1998; Jordan and Smith, 2005 and Liu *et al*., 2005). Using fertilizers extensively is regarded as a main non point source of nitrate leaching into ground water (Baker, 1992, DeSimone and Howes, 1998; Chowdary *et al*., 2005 and Liu *et al*., 2005). Fertilizer and manure application are considered non-point sources of nitrogen from agricultural practices (Chowdary *et al*., 2005 and Almasri, 2006), including dissolved nitrogen in precipitation, irrigation return flows, and dry deposition (Almasri and Kaluarachchi, 2005); while point sources of nitrogen such as septic systems are shown to contribute to nitrate pollution of ground water (MacQuarrie *et al*., 2001). Waste materials such as sites used for industrial waste and disposal of human and animal sewage are one of the anthropogenic sources of nitrate contamination of ground water (Tredoux, 2004). Septic tanks are another example of anthropogenic source nitrogen contamination of the ground water (Hallberg and Keeney, 1993 and Tredoux, 2004). Many areas of the United States and other countries have reported significant contamination of ground water from septic tanks, with ground water contamination usually related to the density of septic systems (Hallberg and Keeney, 1993).

**Table 2-8** *Anthropogenic occurrence of nitrate in ground water.*

| **Application** | **Cause** | **Effect** |
|---|---|---|
| Fertilizer (Addiscott *et al*., 1991 and Tredoux, 2004) | Cease absorption of nitrate upon ceasing growth | Vulnerability to leaching nitrate from soil |
| | | RSA fertilizer rates are low (no leaching of nitrate to ground water) |
| Farming-livestock (Tredoux, 2004) | Point source of nitrate at watering points, and septic tanks with drainage systems near water supply boreholes | High concentrations of nitrate and other pollutants (e.g. pathogens) in ground water |
| Pit latrines (Lewis *et al*., 1980; Hesseling *et al*., 1991; Jacks *et al*., 1999 and Tredoux, 2004) | Minerals/nutrients from waste accumulate | Vulnerability to nitrate seepage |
| Explosives (Forsyth *et al.*1995 and Revey, 1996). | Spillage (transportation), leaching (wet blastholes) and undetonated explosives (after blast) | Vulnerability of nitrate leaching |

Most commercial blasting agents contain from 70-94% ammonium nitrate. The most commonly used blasting agent within the mining industry is ANFO. ANFO is a mixture of 6% #2 diesel fuel oil and 94% ammonium nitrate. It readily dissolves in water, releasing both ammonia and nitrate (Table 2-9). Emulsion and water gel-based explosives also contain a large amount of ammonium nitrate and other oxidising salts that can leach nitrates to ground water. The rate at which nitrate leaches from different explosives (Table 2-9) varies based on the compositions of the explosives. The emulsion has the lowest leach rate over time as compared to the quickest leaching rate of ANFO.

**Table 2-9** *Percentage of nitrate leached from explosives (Modified after Revey, 1996).*

| Time (hrs) | ANFO | ANFO (water-resistant) | Water gel | Emulsion |
|---|---|---|---|---|
| **0.1** | 25 | - | - | - |
| **1** | >50 | 25 | - | - |
| **6** | - | - | 24.60 | 0.60 |
| **144** | - | - | >75 | 1.20 |

The water resistant ANFO is second to normal ANFO in leaching time. This is explained by Revey (1996) as follows: The leaching rate for emulsion explosives is much lower, because the ammonium nitrate is contained in an aqueous phase that is surrounded by an oil or (oil and wax) fuel phase. Hence when water contacts undetonated emulsions, the ammonium nitrate is protected by the relatively impervious oil and wax matrix. Despite their relatively low leaching rates, emulsions (when given enough water exposure time) can produce significant levels of nitrates and ammonia. By comparison, spilled ANFO will quickly dissolve in water and release all its ammonia and nitrates. If continuously spilled, the daily level of nitrates and ammonia released by any type of explosive that is exposed to water will eventually become significant. As mentioned earlier, explosives can introduce nitrate into the water in the mine or a waste rock disposal site. This can be attributed to spillage during explosive transportation or charging, leaching of explosives in wet blastholes or undetonated explosive in broken rocks after the blast. Explosive use can be divided into two types, small quantity or high frequency (Forsyth *et al.*, 1995). Examples of the first use would be drifting, raising and shaft sinking. Example of the second type would be stope or bench blasting. According to Forsyth *et al.* (1995), the potential for introduction of nitrogen into the water system is dependent on the following:

1. The explosives used
2. The water conditions
3. The handling and management of the explosives
4. The efficiency of the blasting operations

Forsyth *et al.* (1995) goes on to express that the specific explosive chosen will control the absolute amount of available nitrogen, the potential rate of release in the water system. This ranges from ANFO with high nitrogen content and very low water resistance to film wrapped emulsions with lower nitrogen content and a much higher water resistance. The handling of the explosive product has the most significant influence on the quantity of nitrogen entering the water system. In the case of ANFO, losses occur as spillage during filing of explosive loading losses could amount to between 5% and 15%of total ANFO used. The efficiency of the blasting operation will control the amount of nitrogen available from undetonated explosives. Blast holes may fail to detonate due to proximity effects such as dislodgement.

## 2.5 Management, remediation and treatment approaches of nitrate contamination in ground water

Several methods (physical, biological and chemical) have been proposed and implemented (Table 2-12). Although these techniques are effective at the removal of nitrate from contaminated water, pilot scale operation is expensive and with only limited potential application (Kapoor and Viraraghavan, 1997; Ayyasamy *et al*., 2007; Zaitsev *et al*., 2008). Such include; reverse osmosis (Kim and Benjamin, 2004; Mahler *et al*., 2007; Israel *et al.*, 2011), ion exchange (Matosic *et al*., 2000; Kim and Benjamin, 2004), catalytic reduction (Reddy and Lin, 2000; Maia *et al*., 2007), electrodialysis (Elmidaoui *et al*., 2002, Sahili *et al*., 2006), activated carbon process (Sison *et al*., 1995), land disposal (Ayyasamy, 2007), chemical denitrification (Lin and Wu, 1996; Hu *et al*., 2001) and microbial treatment (Ayyasamay *et al*., 2007; Zaitsev *et al*., 2008). The United States Environmental Protection Agency has recognized only three water treatment unit processes as best available technology treatment techniques for nitrate removal (Israel *et al*., 2011). These are ion exchange (IX), reverse osmosis (RO), and electrodialysis (ED) (Table 2.10). Other processes include Nanofiltration (NF), Point of use (POU) devices using RO, NF, distillation, and IX. Chemical or biological denitrification, either above ground in tanks or wetlands (*ex-situ* treatment) or below ground in the soil/water matrix (*in-situ* treatment) can be effective using RO, ED and IX technologies (Israel *et al*., 2011). The Department of Water Affairs and Forestry (1996) states that nitrate can’t be readily removed from domestic water supplies due to solubility. Some reduction of nitrate may be achieved using slow sand filtration, but the method is not reliable. Biological reduction of nitrate to nitrogen gas (denitrification) is feasible in the presence of a suitable carbon source, but the increase in carbonaceous matter is not compatible with a high quality water supply. Non-specific methods of removing nitrate according to the Department of Water Affairs include ion-exchange and reverse osmosis.

**Table 2-10** *Nitrate removal methods used (modified from Israel et al., 2011).*

| Method | Basic methodology | Advantages | Disadvantages | Removal Efficiency |
|---|---|---|---|---|
| **Ion Exchange** | Ions from a resin are exchanged for ions in feed water | • Ease of operation;<br>• Highly reliable<br>• Lower initial cost;<br>• Resins will not wear out with regular regeneration,<br>• Most effective and most efficient;<br>• Widely used<br>• Suitable for small and large installations | • Doesn't completely eliminate all $NO_3$,<br>• Can't remove non ionic dissolved species or microbes,<br>• Requires frequent monitoring for nitrate removal,<br>• Requires salt storage,<br>• Strongly basic anion resins are susceptible to organic fouling;<br>• reduced life and thermodynamically unstable | 80-99% |
| **Reverse Osmosis** | Physical process directing purer water through a semi-permeable membrane | • Produces highest water quality<br>• Effectively treats wide range of dissolved salts and minerals, turbidity, health and aesthetic contaminants, and certain organics;<br>• Some highly maintained units are capable of treating biological contaminants<br>• Compact and self contained,<br>• Single membrane units are available for small installations | • Relatively expensive to install and operate,<br>• Frequent membrane monitoring and maintenance;<br>• Temperature, and pH requirements to meet membrane tolerances;<br>• May be chemically sensitive<br>• High energy requirement | 50-96% |
| **Bio-remediation PRBs, injection, etc.** | Impacted ground water amended to stimulate biochemical reaction to convert nitrate to nitrogen gas | • Cheap and very fast,<br>• Natural process complete plume remediation,<br>• New technology | • Impact to geochemistry;<br>• Regulatory;<br>• Biomass build up | 70-95% |
| **Electro-dialysis** | Electrochemical process in which ions migrate through an ion selective semi-permeable membrane | • ED can operate without fouling or scaling, or chemical addition;<br>• Suitable for higher TDS sources,<br>• Low pressure requirements;<br>• Typically quieter than RO,<br>• ED extends membrane life and reduces maintenance | • Can't remove non ionic dissolved species or microbes,<br>• Unsuitable for high levels of Fe and Mn, $H_2S$, chlorine, or hardness,<br>• Limited current density;<br>• Current leakage;<br>• Back diffusion | 30-50% |

**Table 2-10** *Nitrate removal methods used (modified from Israel et al., 2011).*

| | | | | |
|---|---|---|---|---|
| **Pump and treat** | Impacted ground water pumped and treated | • Plume containment,<br>• Mass removal,<br>• Re-use of clean water,<br>• Injection of clean water | • Long-term engineering cost,<br>• Water rights issues,<br>• Treatment system potentially expensive,<br>• Hazardous concentrated waste stream | 50-90% |
| **Denitrification in combination with other contaminants** | During anaerobic bioremediation of other contaminants, nitrates serve as an electron acceptor | Fortuitous nitrate reduction in the presence of other organic contaminants if nitrate is present in an organic contaminant plume, and conditions are anaerobic, denitrification most likely will occur | • Reducing conditions must be present,<br>• Carbon source must be present,<br>• monitoring to determine, denitrification must be ascertained | 70-95% |
| **Distillation** | Boiling, collecting steam free of Contaminants | • Removes most impurities from water including viruses,<br>• Less expensive than bottled distilled water | • Best suited for municipal water;<br>• Rural waters of high mineral content will cause excessive scaling and increase maintenance,<br>• Receiving containers may be contaminated again,<br>• Regular cleaning and de-scaling of the elements of the boiler are required,<br>• Produces flat tasting water devoid of all minerals,<br>• Expensive to purchase and maintain,<br>• System is large and bulky, and not portable,<br>• Slow production of water (water must be stored) | 90-98% |

## 2.6 Previous nitrate study at Xstrata Kroondal mine

A nitrate contaminant plume migration was simulated by GCS water and environmental consultants (2012). For the contaminant plume migration, values higher than 6 mg/l were considered to be elevated. The sources of nitrate contamination for the site were identified as the two tailings dams and the blast residue from the mine operations. Figure 2-6 shows the current nitrate contaminant plume extents. The results should be viewed with caution as a layered homogeneous aquifer has been assumed. Heterogeneities in the aquifer are unknown and the effect of this cannot be predicted. Furthermore, no chemical interaction of the sulphate with the minerals in the surrounding bedrock has been assumed. Currently boreholes KMB 03, KMB 03s, KMB 06, and KMB 19 are within the simulated contaminant plume extents. Boreholes KMB03, KMB 03s and KMB 06 were shown to be affected by the eastern tailings dam and showed simulated nitrate values of 10 mg/l.

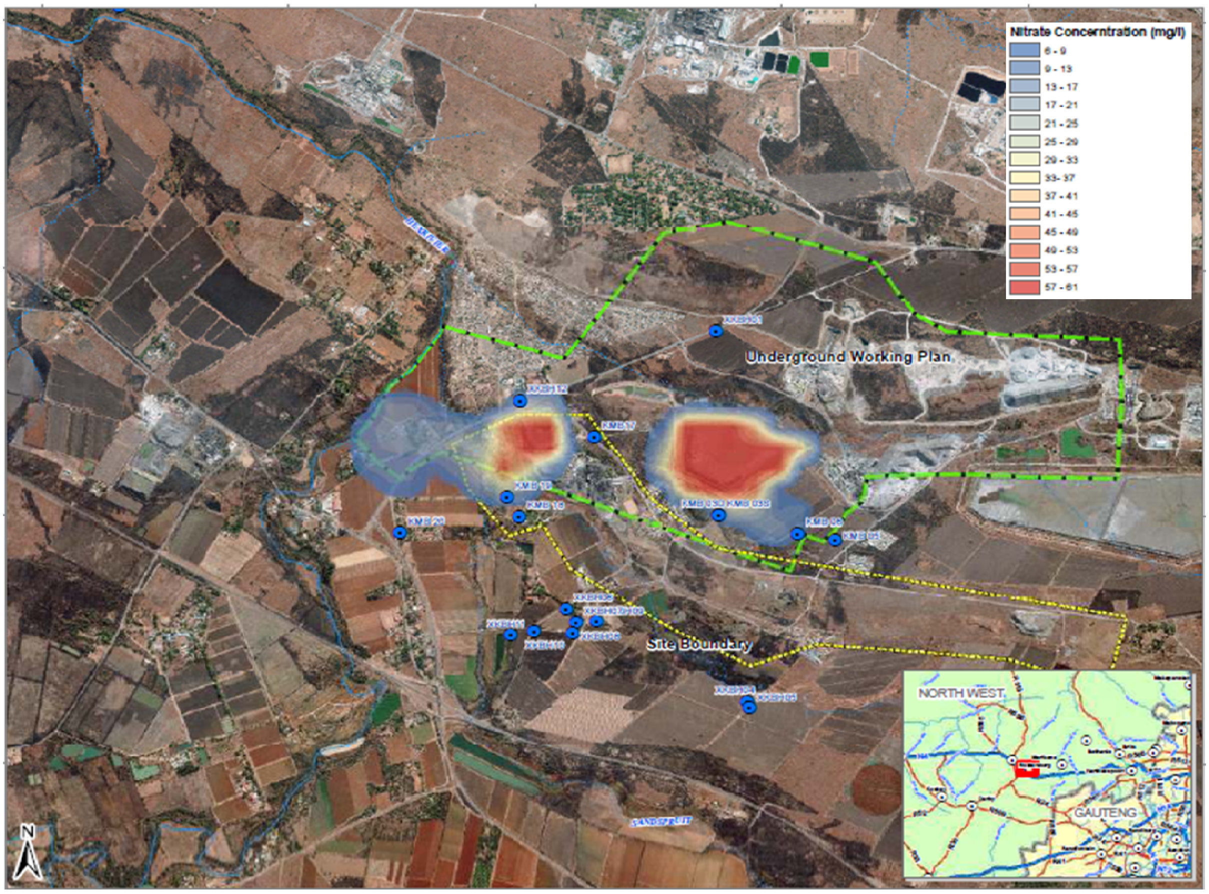


**Figure 2-6** *Current simulated contamination plume extents (GCS, 2012).*

Borehole KMB 19 was affected by the eastern tailings, showing simulated nitrate values of 20 mg/l. Despite being elevated, none of the effected boreholes exceed the DWA (6 mg/l) or SANS 241 (11 mg/l) limits for drinking water quality. Once the new equilibrium ground water flow conditions have been re-instated (i.e. ground water levels have recovered to initial conditions), nitrate contaminant plume migration will be controlled by natural flow gradients and intrinsic aquifer parameters (GCS, 2012). The nitrate contaminant plumes were simulated for 25, 50, 75 and 100 years after mine closure. Experience has shown that the plume stagnates after about 80-100 years, and no further movement after such time is expected (GCS, 2012). No chemical interaction of the sulphate with the minerals in the surrounding bedrock has been assumed in this regard. The overall impact on ground water quality for the post-closure phase was determined as medium.

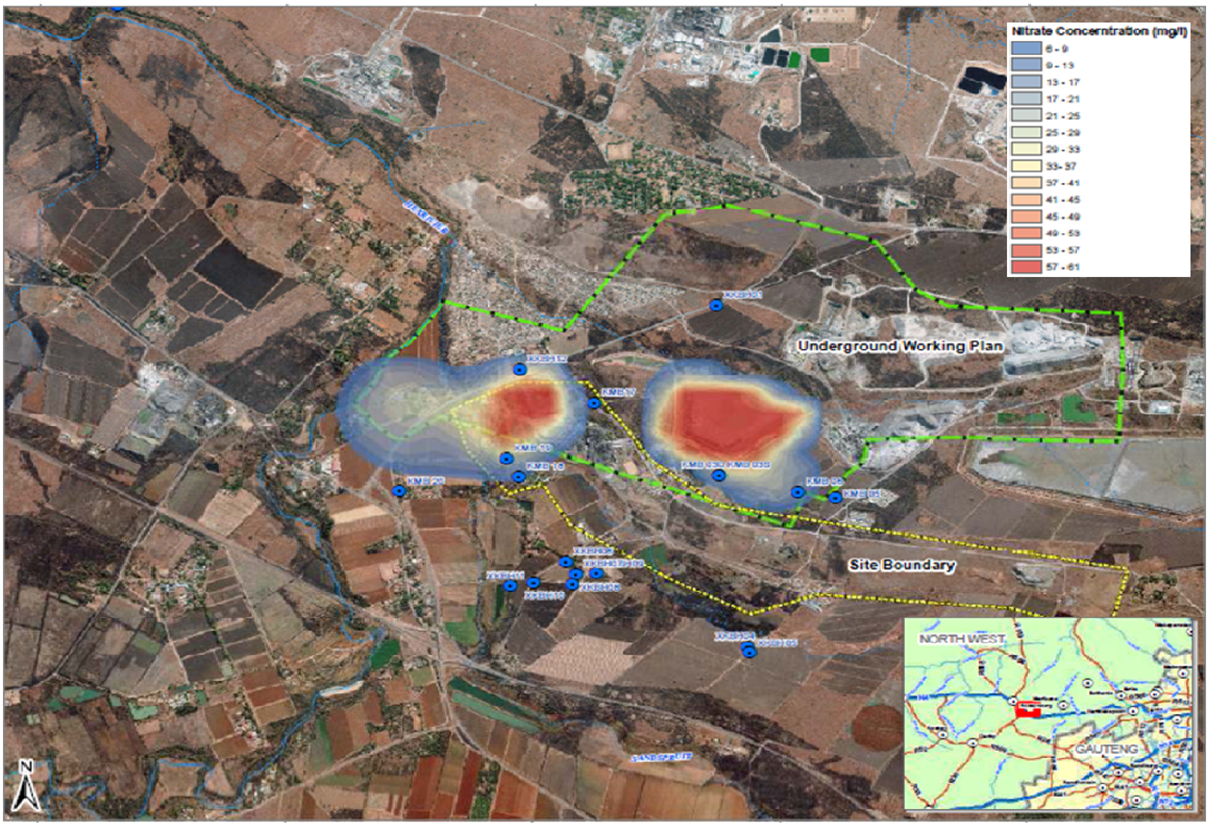


**Figure 2-7** *Simulated 100 year post closure contamination plume extent (GCS, 2012).*

The following can be deduced from the ground water contaminant plume modelling:

- Nitrate concentrations are simulated to decrease over time
- Nitrate concentrations in KMB 03, KMB 03s, KMB 06, KMB18 and KMB 19 will remain elevated
- Nitrate contamination from the tailings dams and slurry pond will migrate downward toward the abandoned mine workings over time (still remaining localized to the site area)

Although the nitrate levels in boreholes KMB 03, KMB 03s, KMB 06, KMB18 and KMB 19 will be elevated, the concentrations remain within the limits of the relevant DWA and

SANS241 standards for drinking water quality. Although various nitrate sources are attributable, ground water management is required irrespective of whom contamination is attributed to. GCS (2012) also proposed additional boreholes to be drilled (Figure 7-3). A total of 10 new boreholes are recommended to be drilled of which two should be drilled into the underground mine workings (shallow) and two of the existing monitoring boreholes (KMB 17 and KMB 18) are to be re-drilled. The Kroondal primary school borehole should be incorporated into the mine monitoring network to observe the effects of mine dewatering and contaminant migration. GCS (2012) identified a total of 52 boreholes within the study area during the hydroensus. The water level elevations measured show a 90% correlation with surface topography. 15 of the boreholes visited were used for domestic or agricultural water supply. A geochemical assessment was conducted on the mine waste material. No sulphide minerals were detected in the waste rocks, tailings or ROM (fresh product from the underground workings taken from conveyor offload point) through means of XRD and LECO furnace. The waste rock, ROM and tailings samples all classify as having no potential to generate acid-mine drainage with potentially no/low salt load that will emanate from the residue dumps. Seepage from the tailings dam will not become acidic.

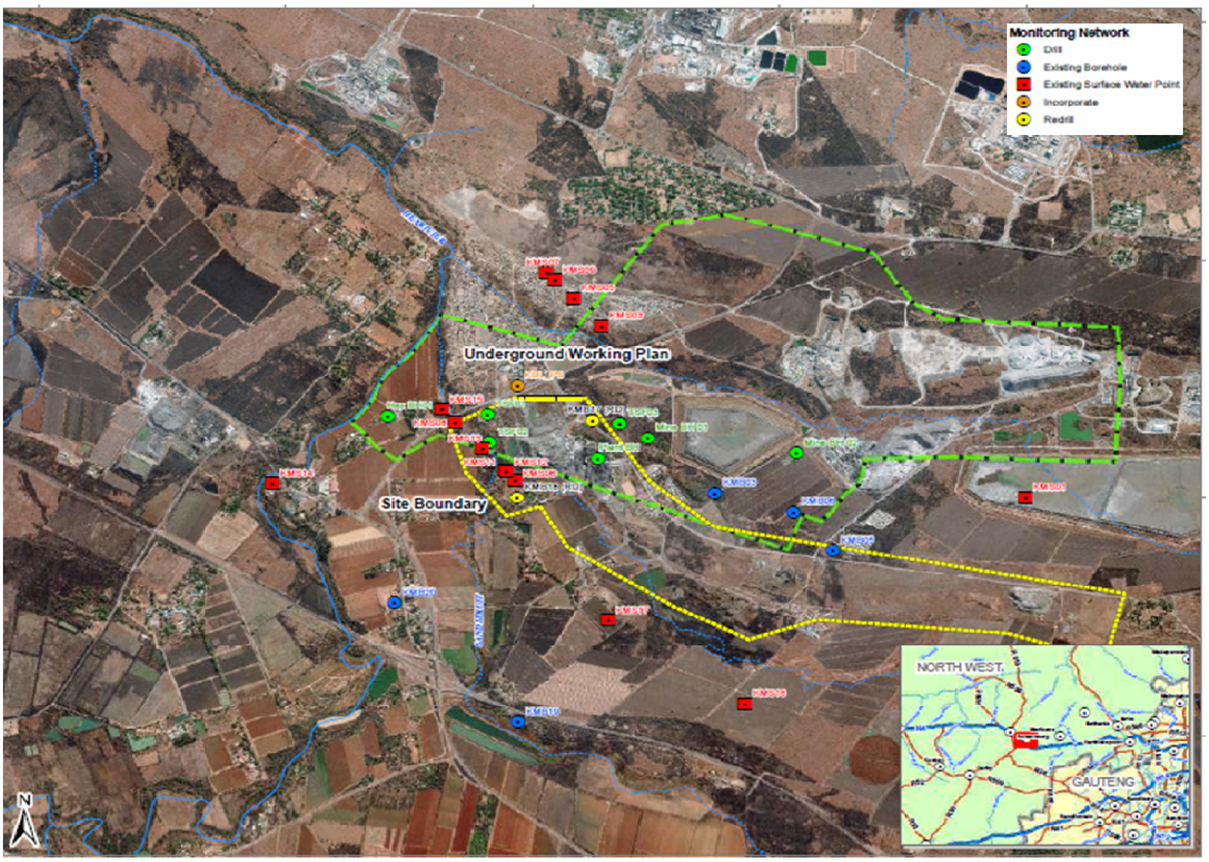


**Figure 2-8** *Proposed monitoring network (GCS, 2012).*

From ABA test results, GCS (2012) showed that the waste rock, ROM, ore stockpiles and tailings do not have a net acidification potential (because of the absence of sulphide minerals). No elevation in metals is expected to occur in the seepage at non-compliant concentrations from the waste rock, ROM, ore stockpiles and tailings as seepage will stay at near neutral conditions (based on leaching test results). Based on the leaching test results, GCS (2012) does not foresee that any anions will be elevated in seepage from either the residue dumps or the product stockpiles (except for nitrate that may be present in tailings water). The majority of boreholes currently impacted on by the mine operations are mine monitoring boreholes, however, borehole KMB 20 is being used as a supply points for a residential property. Boreholes KMB 18 and KMB19 were affected by the eastern tailings and slurry dams. The overall impact on ground water quality for the operational phase was determined to be low (for waste handling and nitrate due to blasting activities) and medium (for tailings dam activities). Efficient rehabilitation of the tailings dams and waste rock dumps is essential to ensure contaminant sources are reduced post mine closure. Possible mitigation measures for contaminant limiting contaminant plume migration include the reclamation of the tailings dam product, which will result in the removal of the source for contamination. Alternatively (GCS, 2012), a pump-and-treat approach could be taken where dewatering of the mine workings could be continued to remove contaminated water from the system and the water is stored in lined pollution control dams to be treated at a later stage.

# Chapter 3 Site Description

## 3.1 Regional Geology

The Xstrata Kroondal chrome mine is underlain by the Rustenburg Layered Suite of the Bushveld Igneous Complex (BIC) (Figure 3-1), which is a layered sequence of mafic rocks. This suite underlies a significant portion (about 65 000 km$^2$) of the region previously known as the Transvaal (Eales, 2001). Quartzite and shales (Magaliesberg formation) of the Transvaal supergroup form the floor rocks to the Bushveld Igneous Complex. Norites, which form the Chill Zone of the Complex lie in contact with metamorphosed quartzite and shales and are overlain in the vicinity of Rustenburg and to the south and south east of Rustenburg by a sequence of bronzitites and minor harzburgites. These form the Lower Zone of the Complex. The succeeding Critical Zone rocks are of more varied composition and contain economically important layers which are mined for their chrome and platinum group metals (Eales, 2001). The Rustenburg Layered Suite is subdivided into 5 zones and has diagnostic mineral associations within each subdivision (Table 3-1). Figure 3-2 shows the locality of Kroondal mine with respect to the Bushveld Igneous Complex.

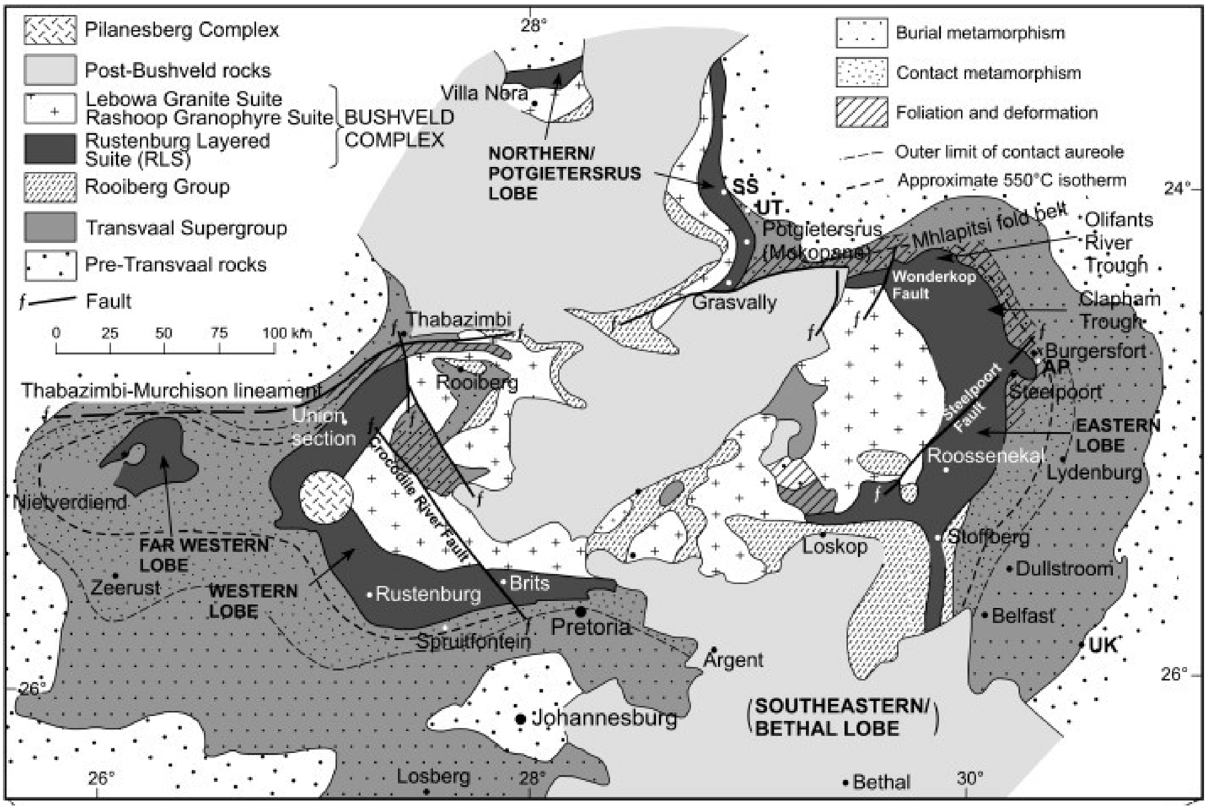


**Figure 3-1** *The Bushveld Igneous Complex (Cawthorne et al., 2006).*

**Table 3-1** *Zonal subdivision of the Rustenburg Layered Suite (Modified after Eales, 2001).*

| **Zone** | **Diagnostic Mineral association** | | **Dominant Rock types** |
|---|---|---|---|
| **Upper zone** | Fe-rich clinopyroxene | | Various Gabbros |
| | Fe-rich olivine | | Anorthosite |
| | Plagioclase | | Magnetite |
| | Alkali feldspars | | Diorite |
| | Magnetite | | |
| | Apatite | | |
| **Main zone** | Orthopyroxene | | Gabbronorite |
| | Clinopyroxene | | Gabbro |
| | Plagioclase | | Anorthosite |
| **Critical Zone** | **Upper** | **Lower** | |
| | Orthopyroxene | Orthopyroxene | Orthopyroxenite |
| | Plagioclase | | Norite |
| | Chromite | Chromite | Chromitite |
| | Olivine | | Hartzburgite |
| | | | Anorthosite |
| **Lower Zone** | Olivine | | Dunite |
| | Orthopyroxene | | Hartzburgite |
| | | | Orthopyroxenite |
| **Marginal zone** | Orthopyroxene | | Orthopyroxenite |
| | Olivine | | Hartzburgite |
| | Plagioclase | | Norite |

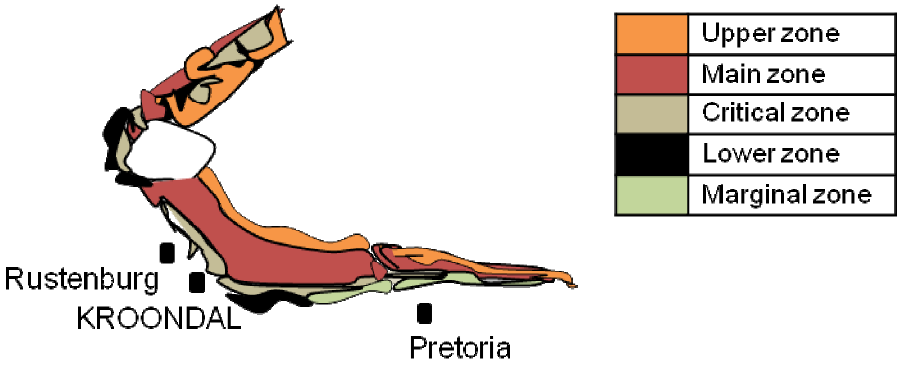


**Figure 3-2** *Locality of Kroondal mine in BIC (Modified after Eales, 2001).*

## 3.2 Stratigraphy

At Xstrata Kroondal chrome mine, pyroxenites with minor anorthosite layers overlie the bronzitite/harzburgite sequence and are succeeded by a thick sequence of interlayered norites and anorthosites (Figure 3-3). It is within this zone that the LG6 chrome seam is found, which is mined at the Xstrata Kroondal chrome mine. A prominent pyroxenite layer which contains the economically important Merensky reef mined for its PGEs to the north of the former Rustenburg chrome mine, marks the top of the Critical Zone.  A thick sequence of gabbro-norite assigned to the Main Zone of the Bushveld Igneous Complex overlies the Merensky reef to the north and north east of Rustenburg (CHEMC, 2010).  Chrome ore is mined and occurs as layers in the host rock pyroxenite, in the lower critical zone of the Bushveld Igneous Complex.  The chromitite layers are confined to the critical zone and were grouped from the bottom upwards, into lower, middle and upper groups.  The lower group contains seven, the middle group four and the upper group two chromitite layers. The LG6 chromitite layer occurs in the lower group of chromitite layers of the critical zone.  The lower group consists of seven chromitite seams of which the sixth seam numbered from bottom to top, namely the LG6 and LG6A are being mined.

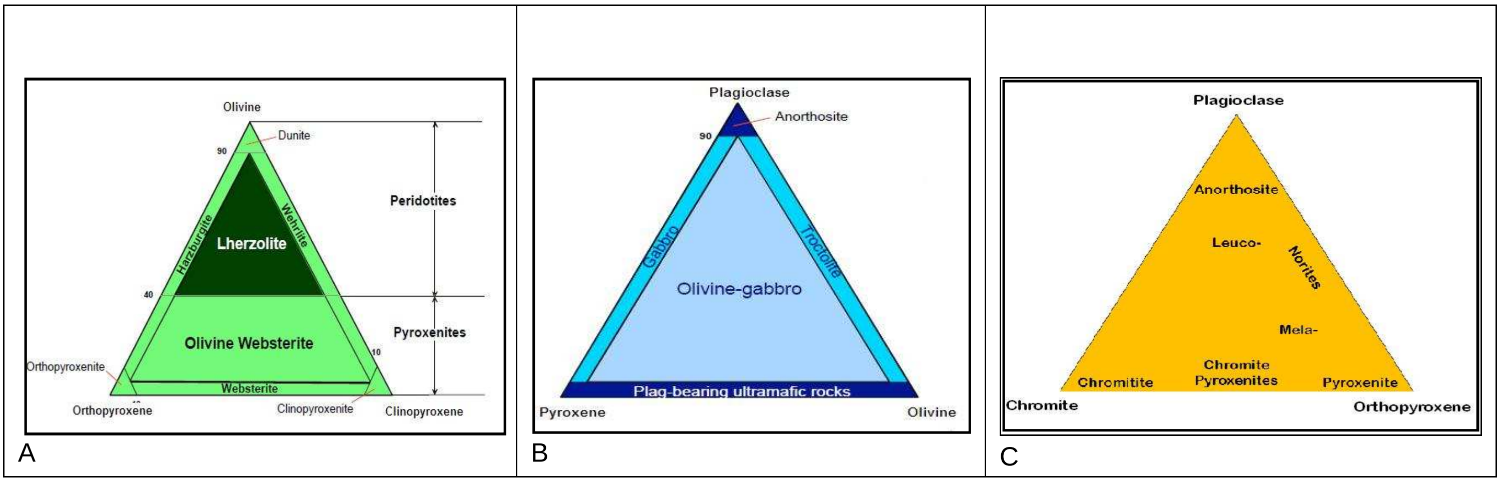


**Figure 3-3** *Classifications of A: Ultramafic rocks, B: Gabbroic rocks and C: Chromitite plot in gabbroic rocks (Pichler and Schmitt-Riegraf, 1997).*

## 3.3 Location and accessibility of study area

Xstrata Kroondal chrome mine can be accessed using the R104 road from Rustenburg and using the N4 road from Pretoria (Figure 3-4).    The mine is located 2 km east of Kroondal township and 10km east of Rustenburg on portions of the farm Kroondal 304 JQ (Figure 3-5).  Rustenburg is in the North West province of the Republic of South Africa.

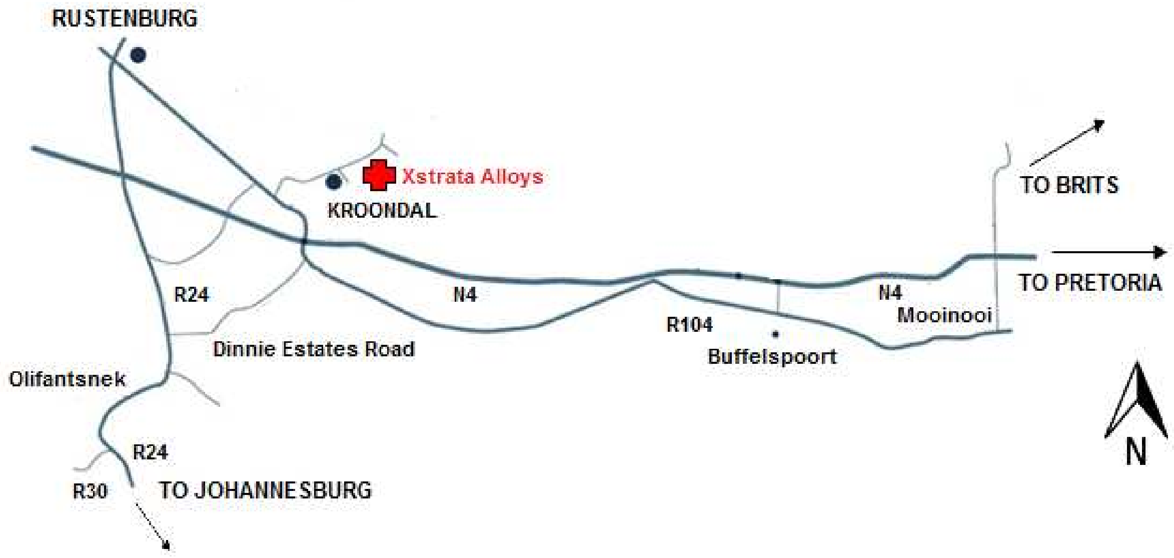


**Figure 3-4** *Directions to Xstrata Alloys Kroondal chrome mine (modified after ammsa.org.za, 2011).*

## 3.4 Climatic conditions

According to the Xstrata Kroondal EMPR (CHEMC, 2010), the annual average rainfall for the Rustenburg region is approximately 600 mm, mainly occurring as a result of thunderstorms between October and March, peaking in January. Hail can be expected, on an average of four times a year. Average daily maximum temperatures are about 32°C in January and 22°C in July. Average daily minima are about 18°C in the summer months and 4°C in July. Winds are mainly light to moderate and blow from the north-easterly direction except for short periods during thunder storms or weather changes when they have a southerly component. More site specific rainfall and evaporation information is available in the following sections.

### 3.4.1 Temperature

January is typically the hottest month with July being the coldest (Table 3-2 and Figure 3-6). The mean maximum temperature ranges from approximately 21.1 to 30.1°C and mean minimum temperatures range from 3.2 to 17.3°C (CHEMC, 2010).

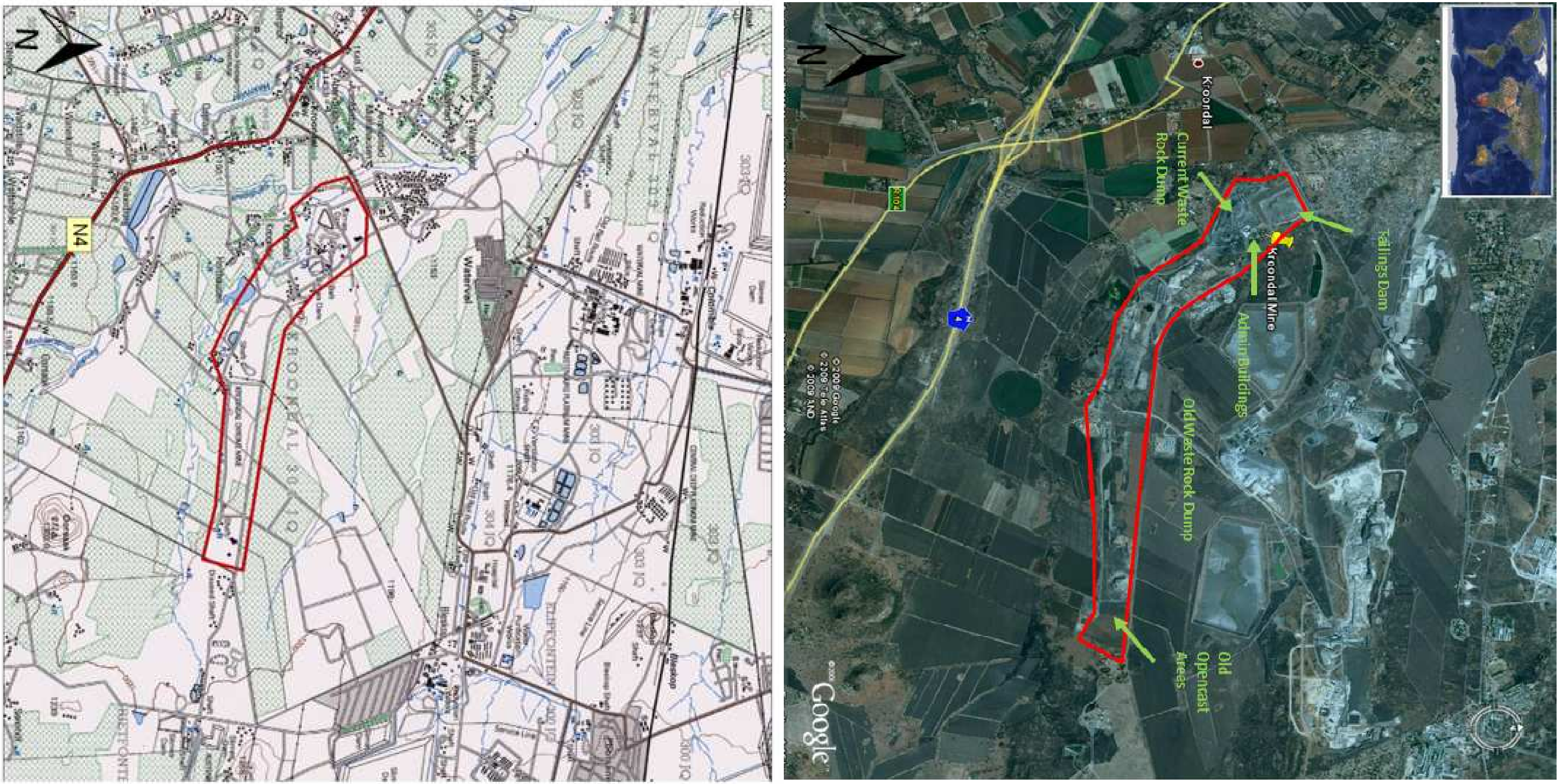


**Figure 3-5** Maps of *1:50 000 and aerial view of Xstrata Alloys Kroondal chrome mine (Modified after CHEMC, 2010).*

**Table 3-2** *Mean monthly, maximum and minimum temperatures from1993-2003 (CHEMC, 2010).*

| Month | Max ($^{0}$C) | Min ($^{0}$C) | Mean ($^{0}$C) |
|---|---|---|---|
| **January** | 30.10 | 17.20 | 23.60 |
| **February** | 29.50 | 17.30 | 23.40 |
| **March** | 28.60 | 15.70 | 22.20 |
| **April** | 26.30 | 11.60 | 19 |
| **May** | 23.20 | 7 | 15.10 |
| **June** | 21.50 | 3.40 | 12.50 |
| **July** | 21.10 | 3.20 | 12.20 |
| **August** | 23.80 | 5.90 | 14.90 |
| **September** | 28 | 10.90 | 19.50 |
| **October** | 29 | 14 | 21.50 |
| **November** | 28.80 | 15.40 | 22.10 |
| **December** | 29.70 | 16.80 | 23.30 |
| **Year** | **26.60** | **11.50** | **19.10** |

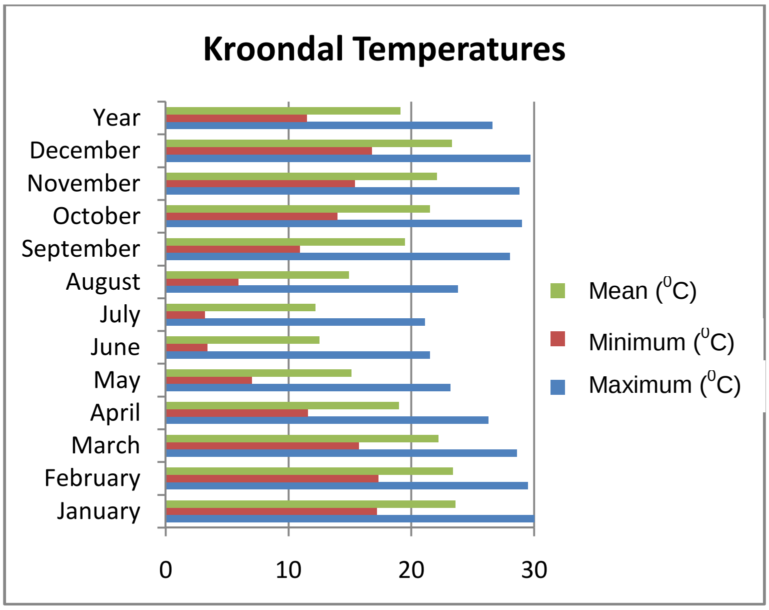


**Figure 3-6** *Kroondal temperatures*

### 3.4.2 Rainfall

Rainfall for the site was considered from various sources including various weather stations managed by both the South African Weather Services (SAWS) and the Department of Water Affairs and Forestry (DWA). The stations considered together with their proximity to site. The most appropriate rainfall station selected for use of data was DWA station A2E008 located at Kroondal, approximately 1.5km west of the Kroondal Operation with a rainfall record length of 53 years. Table 3-3 and Figure 3-7 are a summary of the monthly rainfall distribution at this station.

### 3.4.3. Evaporation

As per the rainfall data selection, evaporation for the site was considered from various sources including various weather stations managed by both the South African Weather Services (SAWS) and the Department of Water Affairs and Forestry (DWA). It was decided to use the same weather station as was used for rainfall recordings (DWA station A2E008) in order to maintain a consistent approach, as well as to use a weather station with a reliable record length of 53 years. Table 3-4 and Figure 3-8 is a summary of the monthly evaporation distribution (lake evaporation) at this station.

**Table 3-3** *Monthly Rainfall Distribution of Kroodndal (SLR Consulting, 2011).*

| Month | Rainfall (mm) |
|---|---|
| **January** | 120 |
| **February** | 101 |
| **March** | 71 |
| **April** | 48 |
| **May** | 16 |
| **June** | 10 |
| **July** | 3 |
| **August** | 6 |
| **September** | 19 |
| **October** | 55 |
| **November** | 91 |
| **December** | 106 |
| **Total** | **645** |

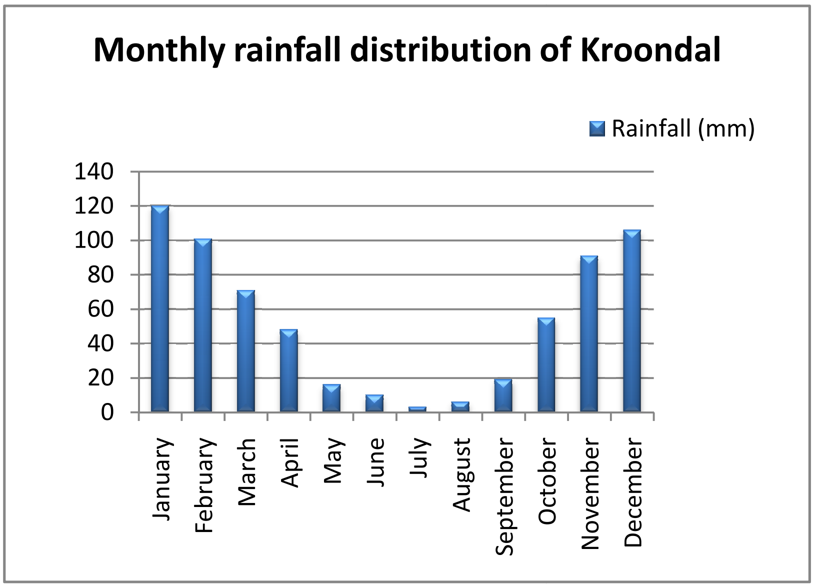


**Figure 3-7** *Monthly rainfall distribution of Kroondal*

**Table 3-4** *Monthly evaporation distribution of Kroondal (SLR Consulting, 2011).*

| Month | Evaporation (mm) |
|---|---|
| **January** | 156 |
| **February** | 136 |
| **March** | 133 |
| **April** | 100 |
| **May** | 88 |
| **June** | 68 |
| **July** | 76 |
| **August** | 98 |
| **September** | 129 |
| **October** | 147 |
| **November** | 146 |
| **December** | 157 |
| **Total** | **1434** |

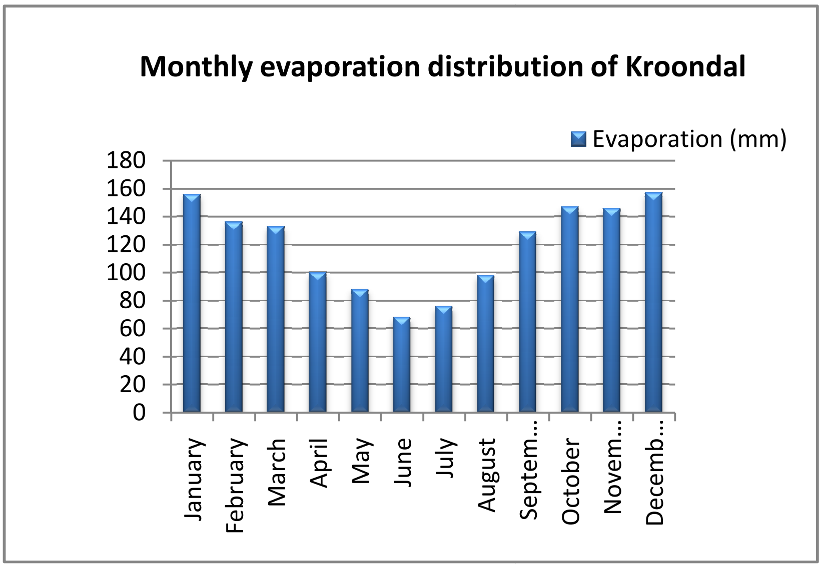


**Figure 3-8** *Monthly evaporation distribution of Kroondal.*

### 3.4.4 Wind

Wind data covers the period 1992–2003. This weather station data indicates that the predominant wind directions are north-westerly and north-easterly. The most frequently occurring wind speeds are in the range of 5,4km/h–11.9km/h (CHEMC, 2010).

### 3.4.5 Extreme weather conditions

Incidents of extreme weather conditions recorded at Rustenburg weather station (number 05115234) are frost, hail, drought and high winds. Hail can be expected on an average four times a year. The rainfall is somewhat unreliable and in about 12% of all years rather severe drought conditions occur. The incidence of high winds is low. Frost can occur during cold winters when temperatures drop below $0^0$C (CHEMC, 2010).

## 3.5 Soils

Two soils surveys have been conducted for Kroondal: A soil and vegetation survey was conducted by Mr Albie Gotze, of Environment research Technology CC in March 2003. The soil was investigated with an auger and then determining the soil form in 200 x 200m grids throughout the study area. A more recent study was compiled by the Institute of Soil, Climate and Water (2007). The area is predominantly comprised of black top soils with strong structure and heavy texture (>35% clay). The soils in this unit belong to the Arcadia (Ar) soil form. The analysis results show the clayey nature of the soils (many of the Arcadia soils in this area show much higher clay contents) and associated high CEC levels, mainly due to the Ca and Mg present in the soil (Institute of Soil, Climate and Water, 2007). The soils are alkaline, but show no signs of previous fertilization, with low P levels. The mainly smectitic nature, with consequent shrinking and swelling properties, of the Arcadia (turf) soils means that there is a narrower moisture range for cultivation than most other agricultural soils. Black clay soils are naturally fertile, with high cation exchange capacities and moderately high organic carbon contents.

## 3.6 Catchment Hydrology

### 3.6.1 Topography and Land Cover

The topography of the mining area is flat, with the average slope of 2.0% (Figure 3-9). The mining area is located at approximately 1155m MAMSL, with a variation in elevation of about 16m from the lowest to highest point. The majority of the land cover at Kroondal has been disturbed due to mining operations and associated activities. Under natural conditions the land cover would be classified as thornveld. Both the topography and land cover of the site are regarded as important considerations in the determination of runoff generated during flood events (SLR Consulting, 2011).

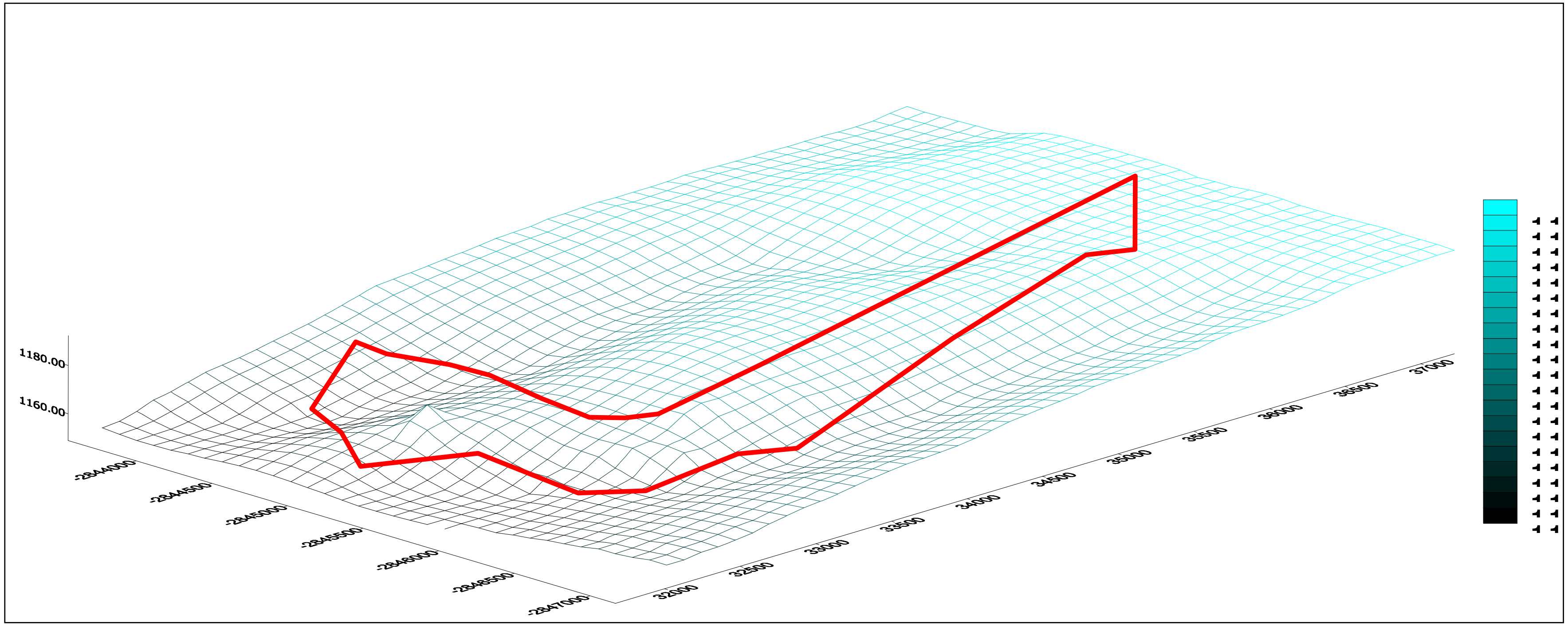


**Figure 3-9** *Topography of the Kroondal mine (Geo Hydro technologies, 2000).*

### 3.6.2 River Systems

The hydrographic basin of the area is almost entirely formed by the northern slopes of the Magaliesberg. Four main streams and their tributaries drain the area northwards to the low lying areas where the whole drainage system enters the Crocodile River. These four streams are the Crocodile itself (across the area of Brits), the Elandspruit, and Sterkstroom River (across the area of Mooinooi/Marikana) and the Hex River (CHEMC, 2010). The Xstrata Kroondal chrome mine falls under the primary drainage region A and in quaternary sub-catchment A22H (Midgley *et al*., 1990).

### 3.6.3 Aquifer Classification and Description

According to Environmental and Energy Management (2003), the geohydrology of the study area is that of an intergranular and fractured aquifer type, namely the Rustenburg Layered Suite to the north of the Magaliesberg. The mainly mafic rocks include norite, gabbro, magnatite gabbro, anorthosite and pyroxenite. Ground water occurrence is associated mainly with deeply weathered and fractured mafic rocks. More than 80% of the boreholes yield less than 2 l/s (Environmental and Energy Management, 2003). This is a result of the low permeability (~$10^{-6}$ cm/s) of the clay rich soils (i.e. black turf soils) that reduce recharge to underlying aquifers. The depth to ground water rest level typically occurs between 5m and 40m below surface. The mean water quality for this aquifer type shows that salinity can be a problem in these aquifers (average EC values of 105 mS/m). The aquifer of Kroondal is described in Table 3.5.

**Table 3-5** *Kroondal aquifer characteristics (Modified after Environmental and Energy Management, 2010).*

| Kroondal Aquifer Characteristics | |
|---|---|
| **Lateral Extent** | Distance to Sand Spruit<br>• 700m (west and south)<br>• 1500m (southeast)<br>• SE-NW tributary to Sand Spruit is <600m north |
| **Thickness** | 10 m |
| **Minor Aquifer system** | Fractured or potentially fractured rocks<br>(No high primary permeability or variable permeability) |
| **Vulnerability** | Low |
| **Susceptibility** | Low |
| **Protection Classification** | Low<br>(Ground water Quality Management Index = 4) |

## 3.7 Site history

As part of Xstrata's commitment to comply with their approved Environmental Management Plan (EMP), a surface and ground water monitoring program has been implemented for many years with appropriate monitoring undertaken by Aquatico Scientific. It is understood by Xstrata that this is an important commitment in obtaining an approved IWULA from DWA. From the past water monitoring results, it is evident that nitrate levels in both surface and ground water are of concern at the Kroondal operation, reaching concentrations above the allowable DWA limits. It is understood that the concentrations are elevated due to underground and opencast blasting, including residues from previously rehabilitated opencast areas. Nitrate explosive residue is highly soluble and easily dissolves into both surface and ground water (Table 2-10).

### 3.7.1 Previous and current activity

Historically, mining at Kroondal has consisted of both opencast and underground mining (Figure 3-10). Currently, all opencast mining has ceased and these areas have been rehabilitated. Only underground mining remains. As can be seen in Figure 3.4, Xstrata's Kroondal Mine is just one of several mining operations in the nearby vicinity. Existing structures on the past Gemini property included shafts, a small reservoir and power lines. Opencast areas have been rehabilitated and the mine is currently awaiting the rehabilitation certificate from DME indicating approval of the measures undertaken. The old infrastructure consisted of 3 incline shafts (Main, Conveyor and Chairlift) and modifications have been done on the old main shaft entrance. The old infrastructure consisted of 3 old ventilation shafts and there were seven septic tanks in operation, but are no longer used. The pre-mining land use was primarily agriculture and grazing. Kroondal chrome mine is operated by means of room and pillar underground mining.

### 3.7.2 Hydrocensus

The majority of boreholes have a pump set-up on surface that prevents the obtaining of ground water level and depth. The average depth of the water table in the area under investigation is 15 mbgl, but varied from 5 to 40 mbgl. It must be kept in mind that a great part of the existing boreholes do not have any borehole information. According to the local and mine personnel, the ground water levels in this area are variable with the rainfall, yet constant over the period of several years (CHEMC, 2010). Geohydro Technologies (2000) conducted a hydro-census (Table 3-6) of boreholes and surface water at the mine and surrounding areas (1km radius around the mining activities). Boreholes were randomly selected to be sampled where it was possible.

**Table 3-6** *Borehole census information of Kroondal mine area (Geohydro Technologies, 2000).*

| Borehole / Spring | Longitude (M) | Lattitude (M) | Depth (mbgl) | Description | Water Usage |
|---|---|---|---|---|---|
| **KMB01** | -35125.69 | 2846228 | 17.83 | South of Germini, next to old incline | Production |
| **KMB02** | -35130.89 | 2846581 | 6.16 | South of eastern Germini section, next to Stream | Production |
| **KMB03** | -33181.17 | 2845406 | 21.47 | North west of Germini section in crop field. | Production |
| **KMB04** | -33181.67 | 2845420 | - | North west of Germini section 2m north of KMB 03 | Production |
| **KMB05** | -34012.04 | 2845430 | 22.13 | Old windmill north of Germini section | None |
| **KMB06** | -33614.57 | 2845543 | - | Old mine pump into northern part of old mine works – proposed de-water borehole. | None |
| **KMB07** | -33604.36 | 2845537 | 20.85 | Old mine pump into northern part of old mine works, next to KMB06-proposed de-water. | None |
| **KMB08** | -33554.67 | 2846334 | 11.46 | At old mine village, south of Germini section | Production |
| **KMB09** | -33522.16 | 2846366 | - | At old mine village, south of Germini section | Production |
| **KMB10** | -33498.3 | 2846334 | - | At old village, south of Germini section | Production |
| **KMB11** | -33273.88 | 2846583 | - | South of stream next to irrigation field | Production |
| **KMB12** | -32066.924 | 2846279 | 9.93 | Behind Mr Van Zyl's house, next to white building | None |
| **KMB13** | -32044.008 | 2846364 | 8.78 | Behind Mr Van Zyl's house, next to white building | Production |
| **KMB14** | -33280.9 | 2846575 | 8.19 | Disused borehole south of stream next to irrigation field | Domestic |
| **KMB15** | -32204.246 | 2846273 | - | Behind Mr van Zyl's house next to worker's huts. | None |

The mine mainly uses stormwater, effluent and water pumped from underground. Rand Water is mainly used as a supplement for the closed water system of the mine. Ground water is abstracted from the underground mine workings (Environmental and Energy Management, 2003). Ground water at Kroondal is currently monitored on a quarterly basis and are provided by Aquatico Scientific.

### 3.7.3 Ground water Monitoring Borehole Localities

Section 26 (1) of the National Water Act, 1998 (Act 36 of 1998) provides for the development of regulations to, amongst others:

- Require that the use of water from a water resource be monitored, measured and recorded
- Regulate or prohibit any activity in order to protect a water resource or in-stream or riparian habitat; and
- Prescribe the outcome or effect, which must be achieved through management practices for the treatment of waste, or any class of waste before it is discharged into or allowed to enter a water resource.

Aquatico Scientific was commissioned by Xstrata Western Chrome Mines to conduct monthly surface water and quarterly ground water quality evaluations. The primary objective of the monitoring program is to determine the impact (quantitative and qualitative) that the activities of Xstrata Western Chrome Mines have on the receiving water environment. Another objective of the evaluation of a water quality database is to assess the necessity and effectiveness of the water monitoring localities, as well as the physical and chemical variables that are being analysed. Water monitoring can be an expensive exercise and has to be adjusted to adapt to the changing conditions that are normally associated with mining and industrial processes (Groundwater Complete, 2012). There are 21 ground water monitoring sites which have been established at Kroondal Mine, although some of these have been discontinued. Locations for many of these boreholes are illustrated in Figure 3-11 and their descriptions are presented in Table 3-7.

## 3.8 Current Treatment/Management of Ground water

At present, a surface and ground water monitoring network is in place and stormwater management on surface has been conducted. Possible nitrate removal strategies which have been contemplated by SLR Consulting include; Reverse Osmosis, Eco-Dosing and Biological Denitrification. The mine mainly uses Stormwater, effluent and water pumped from underground. Rand Water is mainly used as a supplement for the closed water system of the mine. Ground water is abstracted from the underground mine workings.

### 3.8.1 Surface and Ground water Monitoring Network

Aquatico Scientific currently undertakes the surface and ground water monitoring for Xstrata to meet the EMP requirements. Xstrata is committed continually to identify risks to the environment and will ensure that potential contamination resulting from any mining related infrastructure or activity is identified as a pollution source, monitored and managed accordingly. Therefore, the monitoring network for both surface and ground water needs to be constantly revisited and updated according to associated risks.

**Figure 3-10** *Surface water monitoring points focussed around Kroondal Chrome Mine (CHEMC, 2010).*

**Figure 3-11** *Ground water monitoring points in the greater area around Kroondal Chrome Mine (CHEMC, 2010).*

**Table 3-7** *Names and descriptions of ground water monitoring sites at Xstrata Kroondal chrome mine (CHEMC, 2010).*

| Locality | Description |
|---|---|
| **KMB01** | South of Eastern Gemini Section - Next to old incline |
| **KMB02** | South of Eastern Gemini Section - Next to stream |
| **KMB03** | North West of Gemini Section - Next to crop field |
| **KMB03s** | North West of Gemini Section - Next to crop field |
| **KMB05** | North of Gemini Section - Crop Field |
| **KMB06** | Old Mine Pump - Northern Part of old mine workings |
| **KMB08** | At old mine village - South of Gemini Section |
| **KMB11** | South of Eastern Gemini - Opencast Kroondal |
| **KMB16** | Andru Opencast - Tap at Office |
| **KMB17** | Upstream borehole - At Mine Entrance Gate |
| **KMB18** | Crocodile Farm - Into Main Cement Dam |
| **KMB19** | Crocodile Farm - Into Breeding Dam |
| **KMB20** | Crocodile Farm - Owners House Not |
| **KMB21** | Goose Neck Pipe - Water from Underground |

### 3.8.2 Storm water Management at Surface

According to SLR Consulting (2011), increased nitrate concentrations in surface waters are suspected to be primarily a result of runoff from waste rock dumps, high in nitrate explosive residues. At present, the management of stormwater following significant rainfall events is not ideal, with facilities typically undersized. Once the conceptual stormwater management plan is implemented, with infrastructure appropriately sized and lined, stormwater high in nitrate concentrations can be managed as dirty water and appropriately contained and treated. Further to this clean water will not be mixed with dirty water to further reduce the quantity of dirty water requiring management.

# Chapter 4 Methodology

## 4.1 Sampling and monitoring procedures

The surface and ground water at Xstrata Kroondal chrome mine is monitored by Aquatico Scientific. Monitoring data over the years of 2011 and 2012 were obtained from Aquatico Scientific (KMB03, KMB03s, KMB05, KMB18, KMB19 and KMB20) and used in this research to further investigate nitrate at Xstrata Kroondal chrome mine. Having gone to Xstrata Kroondal chrome mine, samples were collected during one of Aquatico Scientific's quarterly visits (Figure 4-1 and Figure 4-2).

**Figure 4-1** *Surface water sample collection.*

**Figure 4-2** *Water level reading.*

During the course of this project, an underground visit at Xstrata Kroondal mine for sample collection was conducted. Collection was conducted on two separate occasions from seepages and 'natural' living water underground as indicated by the mineworkers. The first collection was in July 2012, having collected six water samples; KDL 01, KDL 02, KDL 03, KDL 04, KDL 05 and KDL 06. The second collection was in September. It is in this time it was learnt that KDL 02 and KDL 03 were not natural waters and advice was given by the mine engineer to sample KDL 07 and KDL 08. The mine engineer also showed more source orientated water points of samples previously collected. Samples which were collected (Figure 4-3 to Figure 4-8) were analysed at the Institute of Groundwater Studies (IGS) at the University of the Free State for ions; using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for ions and titration for alkalinity. The IGS laboratory is accredited (ISO 17025). All samples were contained and sealed in transparent 500ml plastic bottles and sent to the laboratory within 24 hours. For isotope analyses, samples were also packaged (frozen) and sent to the Northern Arizona University for $^{15}$N-NO$_3$ + $^{18}$O-NO$_3$ analysis via Isotope-ratio mass spectrometry (GB-IRMS). Hydrogen and oxygen were analysed at the University of Kwa Zulu Natal (UKZN). At UKZN, each sample and standard was sub-sampled and analysed six times using a Los Gatos Research (LGR) DT-100 Liquid Water Isotope Laser Analyser. The accuracy of the standards calibration is presented in Appendix H1. The LGR DT-100 analyser does not report δ values on a V-SMOW scale, but as 2H/H and 18O/16O ratios. Post processing (temperature variation, sub sample density and deviation of the 2H/H and 18O/16O ratio) required determining these ratios for the standards, developing a relationship between the known V-SMOW δ values and the measured ratios of the standards (see Appendix H2) and then applying the relationship to the sub-sample measured ratios.

**Table 4-1** *Collected ground water samples and their locality.*

| Sample | Locality |
|---|---|
| **KDL 01** | MKA 77 Panel“Drom pomp FS” |
| **KDL 02** | MKC 56 Madala site |
| **KDL 03** | MKA old 53 |
| **KDL 04** | MKD Roadway |
| **KDL 05** | Dam R11 |
| **KDL 06** | Main shaft roadway |
| **KDL 07** | Old Rustenburg fissures |
| **KDL 08** | R19 Borehole |

All fieldwork from Aquatico Scientific is conducted according to the protocols and specifications, and code of practice within the SABS ISO 5667-1-15. These international standards address all aspects from the program design, sampling methods as well as sample preservation. Adhering to the norms as set out in the SABS standards is not always possible due to certain practicalities such as two of the following:

1. No pH, EC, or temperature readings are taken *in situ*
2. Boreholes are not purged before sampling

Aquatico Scientific’s laboratory in Pretoria is a SANAS Accredited Testing Laboratory (No T0374) and also takes part in the SABS inter laboratory Testing Scheme is also a SANAS.

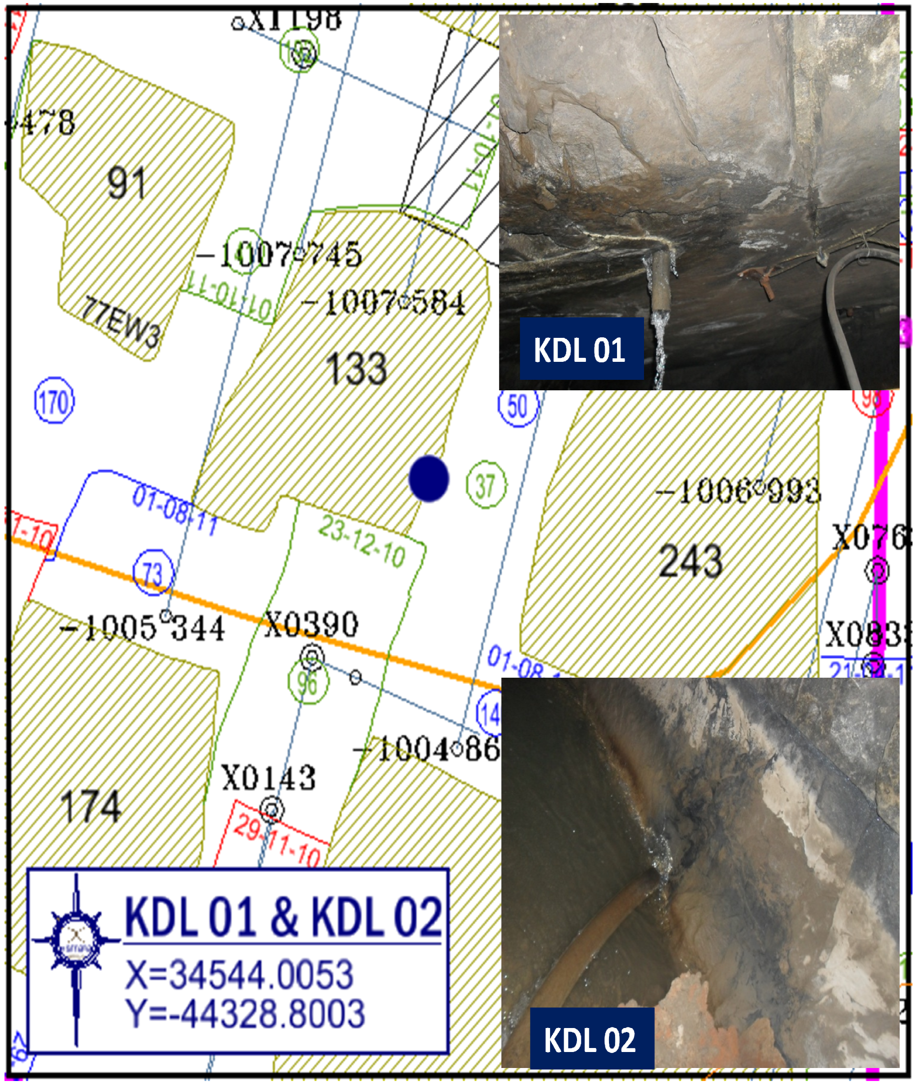


**Figure 4-3** *Locality of KDL 01 and KDL 02 underground.*

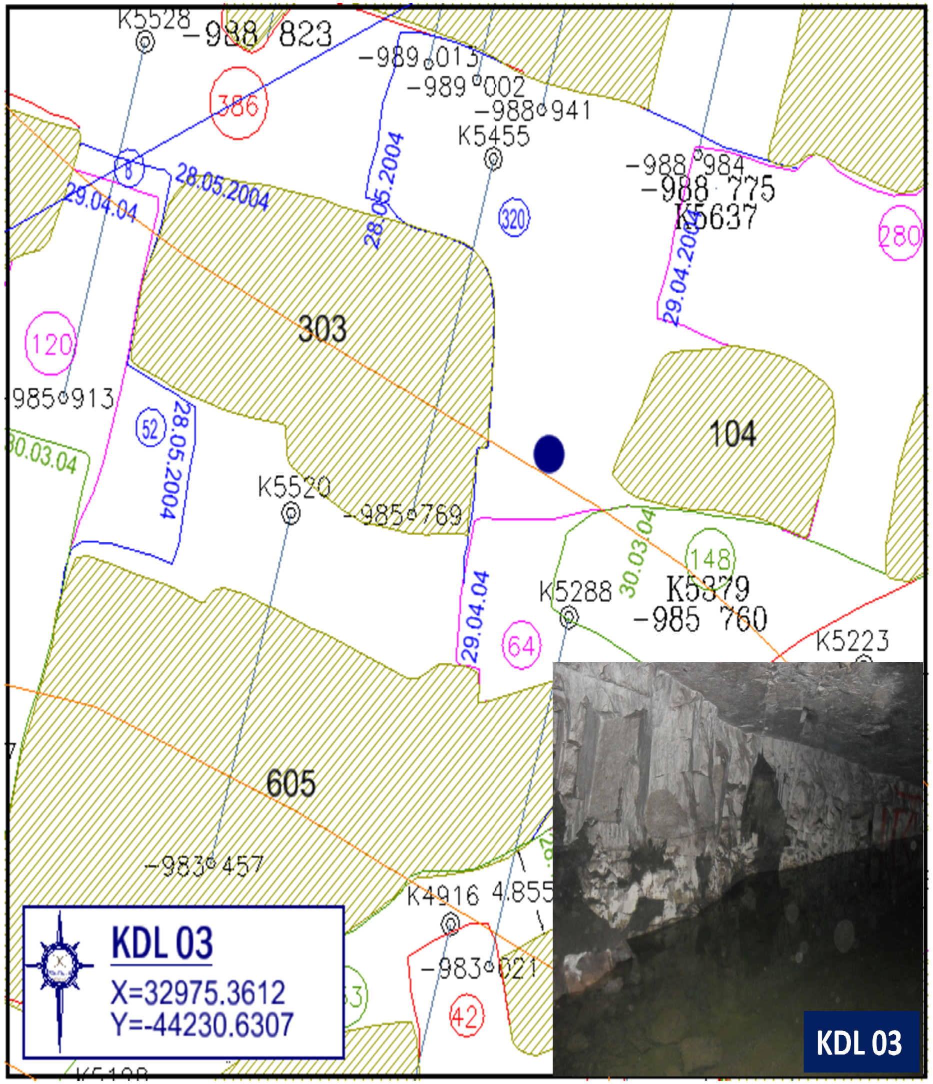


**Figure 4-4** *Locality of KDL 03 underground.*

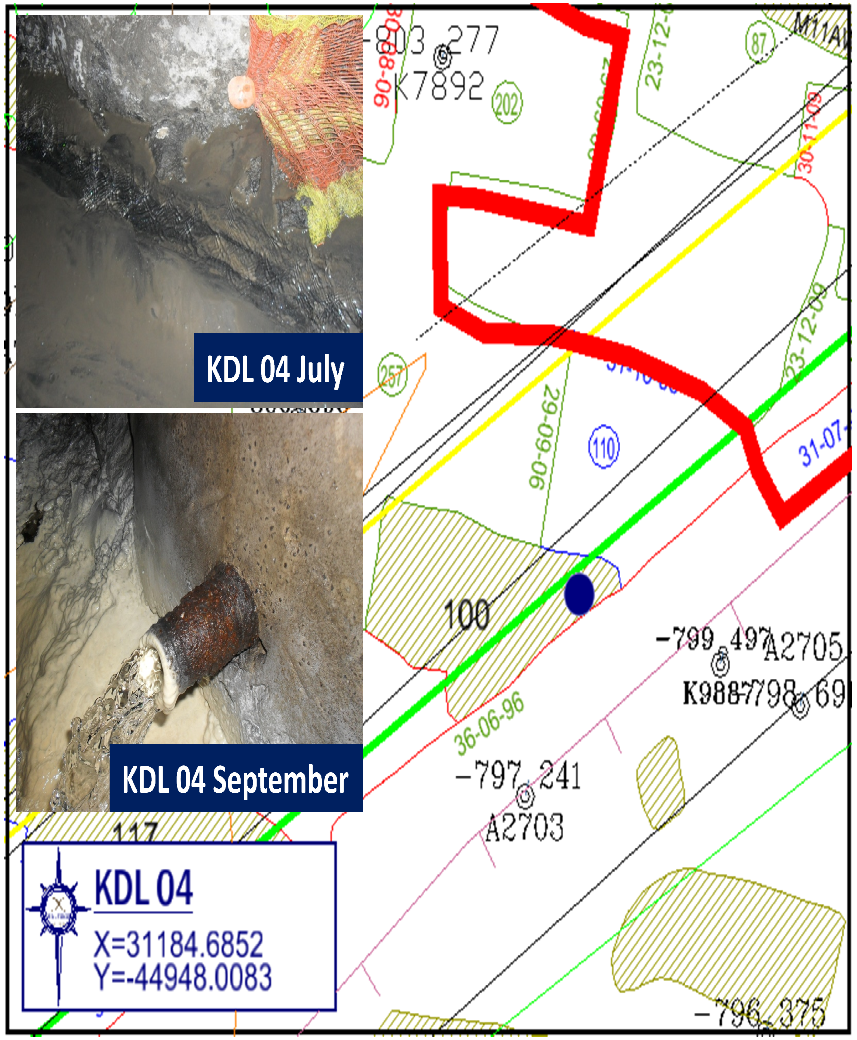


**Figure 4-5** *Locality of KDL 04 underground.*

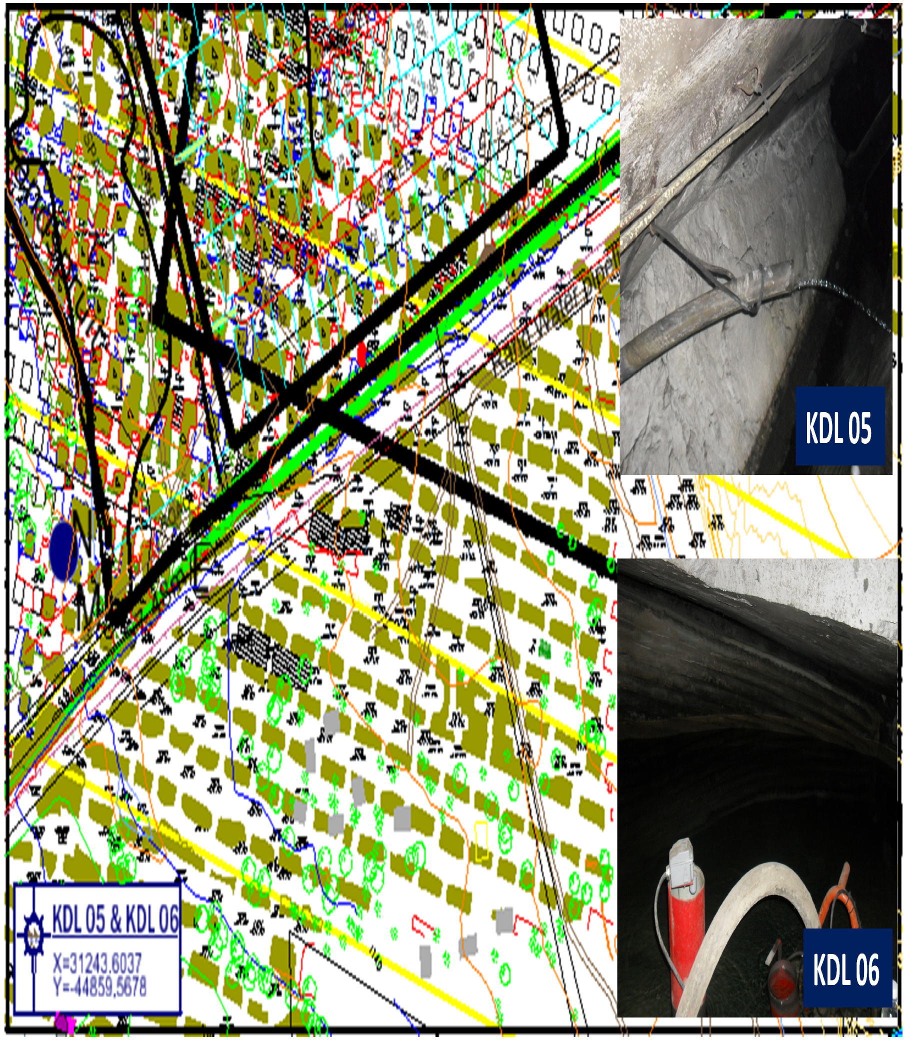


**Figure 4-6** *Locality of KDL 05 and KDL 06 underground.*

**Figure 4-7** Locality of KDL 07 **Figure 4-8** KDL 08 R19 borehole

## 4.3 Water quality evaluation

The water quality at Kroondal mine was evaluated against the DWA Exemption 2118B conditions by Aquatico Scientific for compliance purposes. This exemption was granted by DWA to Xstrata South Africa (PTY) LTD in terms of section 21(4) of the Water Act, 1956 (Act 54 of 1956). Evaluation was also against the DWA South African Water Quality Guidelines for Domestic Use. The South African Water Quality Guidelines (SAWQG) are used by the Department of Water Affairs (DWA) as its primary source of information and decision-making support to judge the fitness of water for use and for other water quality management purposes. Four broad categories of water use are recognised in the National Water Act, namely the use of water for:

- Domestic purposes
- Industrial purposes
- Agricultural purposes
- Recreational purposes

The South African Water Quality Guidelines for Domestic Use Guidelines and those for Agricultural Use were mainly used to discuss water of the receiving environment.

### 4.3.1 Conditions of exemption of water disposal

Xstrata Kroondal mine received exemption granted in terms of Section 21(4) of the Water Act, 1956 (Act 54 of 1956) in respect of the disposal of the purified or treated water *(Groundwater Complete, 2012-Annexture E)*, including water recovered from any effluent. The quality of effluent is prescribed as follows:

a) The impact of the contribution of the exemptee to the waste load in the Hex River determined upstream (KMS 14) and downstream (KMS 15) from the mining complex must comply with the target values (or any other applicable parameters according to the South African Water Quality Guidelines published by the Department of Water Affairs and Forestry. The exempted water quality values are shown in Table 4-2.

**Table 4-2** *Exempted water quality values (Aquatico Scientific, 2012).*

| **Parameter (mg/l)** | **KMS14 and KMS 15** | **KMS 11** |
|---|---|---|
| **pH** | 6-8.50 | 6-8.50 |
| **Electrical conductivity (mS/m)** | <70 | <150 |
| **$NO_3$_N** | <6 | <12 |
| **$SO_4$** | <200 | <400 |
| **F** | <1.50 | <1.50 |
| **$PO_4$** | <0.025 | |
| **Cl** | <100 | <200 |
| **Na (SAR)** | <1.50 | <1.50 |

b) Stormwater and effluent discharged into the Return Water Dam (KMS 11) and seepage from the system must comply with the standards below, as well as the quality requirements for parameters as specified in the General and Special Standard for Phosphate as prescribed by the minister of Water Affairs and Forestry in terms of section 21(1)(a) of the Act (Water Act, 1956) and published in Government Notice 991 of 18 May 1984, as amended from time to time.

## 4.4 Quantification of results

The software, WISH version 2.0 (Windows Interpretation System for Hydrogeologists) was used to quantify results from laboratory analysis. Using water quality data received from the laboratory, hydro-facies plots such as Piper, Durov, S.A.R, Stiff, Schoeller and Expanded Durov diagram amongst others were constructed.

### 4.4.1 Accuracy of chemical analysis-Electro Neutrality

The accuracy of the analysis (Appendix A1 to A3) for major ions is determined using the Electro Neutrality (EN) percentage. Cations used for calculation are $Na^+$, $K^+$, $Mg_2^+$ and $Ca_2^+$. Anions used are $Cl^-$, $HCO_3^-$, and $SO_4^{2-}$ . The EN should be less than 5% and the following formula was used:

**Equation 1** *Electro Neutrality.*

$$\text{E.N. (\%)} = \frac{\sum \text{cations (meq/l)} - \sum \text{anions (meq/l)}}{\sum \text{cations (meq/l)} + \sum \text{anions (meq/l)}} \text{ *100\% <5\%}$$

### 4.4.2 Accuracy of chemical analysis-Plausibility of electrical conductivity

This is only applicable to EC values less than 2000 µs/cm. The following formula was used to evaluate the plausibility of the Electrical Conductivity (Appendix B1 to B3):

**Equation 2** *Plausibility of electrical conductivity.*

$$\sum \text{anions (meq/l)} = \sum \text{cations (meq/l)} \sim \text{EC/100 (µS/cm)}$$

For EC < 2000 µS/cm

### 4.4.3 Hydrofacies diagrams

Piper, SAR and Schoeller diagrams were used to interpret the chemistry of the waters. Piper diagrams allow for many water analyses to be plotted on the same diagram and can be used to classify waters. Concentrations are however renormalized and this system cannot easily accommodate waters where other cations or anions may be significant (Crossey *et al*., 2009). Sodium concentration is an important criterion in irrigation water classification because sodium reacts with the soil to create sodium hazards by replacing other cations (Kumar, 2004). The extent of this replacement is estimated by Sodium Adsorption Ratio (SAR). A Schoeller Diagram is a semi-logarithmic diagram of the concentrations of the main ionic constituents in water. Concentrations of each ion in each sample are represented by points on six equally spaced lines and points are connected by a line. The diagram gives absolute concentration, but the line also gives the ratio between two ions in the same sample (Barbiero, *et al*., 2002).

# Chapter 5 Results

## 5.1 Introduction

Previous data (dating as far back as 2006), combined with the monitoring data (2011 and 2012) of surface water, ground water and bacteriological monitoring were used to establish trends and general water quality in Xstrata Kroondal mine. A monitoring point system was already in place and data was relayed from Aquatico Scientific. In addition to the monitoring points, ground water sample collections from fissures and seepages underground was privately collected in July and September 2012. The surface water monitoring was divided into process water (KMS 02, KMS 03, KMS 05, KMS 06, KMS 07, KMS 11 and KMS 16) and receiving environment (KMS 01, KMS 08, KMS 09, KMS 12, KMS 13, KMS 14, KMS 15 and KMS 17). Monitored ground water boreholes consisted of KMB 03, KMB 03s, KMB 05, KMB 18, KMB 19 and KMB 20. Bacteriological monitoring was conducted in KMS 02, KMS 03 and KMS 09. The private July and September sample collection comprised of KDL 01, KDL 02, KDL 03, KDL 04, KDL 05, KDL 06, KDL 07 and KDL 08.

## 5.2 General water quality

### 5.2.1 Sampling register

KMS 05 and KMS 06 were recorded as dry or stagnant for the majority of the annual period 2011. KMS01 was also recorded as dry occasionally during this period. In 2012, KMS01 and KMS12 were recorded as dry for more than six months throughout the annual period (Table 5-1). Locality KMS 05 was recorded as dry for the duration of the annual period. All remaining localities, with the exception of KMS 02 and KMS 13 which was recorded once as dry and stagnant respectively, recorded flow throughout the annual period. Of the 13 monitoring boreholes that are listed in the database only 6 (KMB 03, KMB 03S, KMB 05, KMB 18, KMB 19 and KMB 20) were monitored during the 2011 and 2012 monitoring years (Table 5-2). The reasons for the boreholes which weren’t sampled can be attributed to blocked boreholes and access issues.

**Table 5-1** *Surface water monitoring sampling register of 2011 and 2012.*

| Site | Description | Category | Jan-11 | Feb-11 | Mar-11 | Apr-11 | May-11 | Jun-11 | Jul-11 | Aug-11 | Sep-11 | Oct-11 | Nov-11 | Dec-11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KMS 01** | Upstream point of Kroondal tributary | Receiving | * | Stag | * | * | * | * | Dry | Dry | * | Dry | * | Dry |
| **KMS 02** | Sewage effluent (tank outflow) into KMS 03 | Process | * | * | * | * | * | * | * | * | * |  | * | Dry |
| **KMS 03** | Erickson dam (underground and return water dam) | Process | * | * | * | * | * | * | * | * | * |  | * |  |
| **KMS 05** | Settler dam | Process | * | * | Stag | Stag | Stag | Stag | Stag | Stag | * | Stag | * | Dry |
| **KMS 06** | Slimes dam seepage water | Process | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | * | Dry | * | * |
| **KMS 07** | Runoff plant water | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 08** | Downstream point of Sand Spruit tributary | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 09** | Outlet of crocodile farm | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 11** | Return water dam | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 12** | Kroondal tributary upstream of return water dam | Receiving | * | * | * | * | * | * | * | * | * | * | * | Dry |
| **KMS 13** | Sand Spruit, upstream of return water dam | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 14** | Hex River, downstream of Sand Spruit | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 15** | Hex River, upstream of Sand Spruit | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 16** | Vent shaft/old underground water pumped into pit dam | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 17** | Farmer's dam into which KMS 16 discharges | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **Site** | **Description** | **Category** | **Jan-12** | **Feb-12** | **Mar-12** | **Apr-12** | **May-12** | **Jun-12** | **Jul-12** | **Aug-12** | **Sep-12** | **Oct-12** | **Nov-12** | **Dec-12** |
| **KMS 01** | Upstream point of Kroondal tributary | Receiving | * | * | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry |
| **KMS 02** | Sewage effluent (tank outflow) into KMS 03 | Process | * | * | * | * | * | * | * | * | * | * | * | Dry |
| **KMS 03** | Erickson dam (underground and return water dam) | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 05** | Settler dam | Process | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry | Dry |
| **KMS 06** | Slimes dam seepage water | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 07** | Runoff plant water | Process | * | * | * | * | * | * | * | * | * | * | * | Dry |
| **KMS 08** | Downstream point of Sand Spruit tributary | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 09** | Outlet of crocodile farm | Receiving | Dry | * | * | * | * | * | * | * | * | * | Dry | * |
| **KMS 11** | Return water dam | Process | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 12** | Kroondal tributary upstream of return water dam | Receiving | * | Dry | Dry | Dry | Dry | Dry | Dry | * | * | * | * | * |
| **KMS 13** | Sand Spruit, upstream of return water dam | Receiving | * | * | * | * | * | * | * | * | * | Stag | * | * |
| **KMS 14** | Hex River, downstream of Sand Spruit | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 15** | Hex River, upstream of Sand Spruit | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |
| **KMS 16** | Vent shaft/old underground water pumped into pit dam | Process | * | * | * | * | * | * | * | * | * | * | Dry | Stag |
| **KMS 17** | Farmer's dam into which KMS 16 discharges | Receiving | * | * | * | * | * | * | * | * | * | * | * | * |

**Table 5-2** *Ground water monitoring register of 2011 and 2012.*

| Site | Description | Jan-11 | Apr-11 | Jul-11 | Oct-11 | Jan-12 | Apr-12 | Jul-12 | Oct-12 |
|---|---|---|---|---|---|---|---|---|---|
| **KMB03** | North west of Gemini section | * | * | * | * | * | * | * | * |
| **KMB03s** | North west of Gemini section | * | * | * | * | * | * | * | * |
| **KMB05** | North of Gemini section | Access | * | * | * | * | * | * | * |
| **KMB06** | Mine pump in northern part of old mine works | Access | Access | Access | Access | Access | Access | * | Access |
| **KMB17** | Upstream borehole (Mine entrance gate) | Blocked | Blocked | Access | Blocked | Blocked | Blocked | Blocked | Blocked |
| **KMB18** | Crocodile farm (into main cement dam) | * | Access | * | * | Access | * | * | * |
| **KMB19** | Crocodile farm (pipe in holding pen) | Access | Access | Access | * | Access | * | * | * |
| **KMB20** | Crocodile farm (owner's house) | Access | * | * | * | * | Access | Access | * |

## 5.2.2 Surface water monitoring

### 5.2.2.1 Process water

The process water quality (Table 5-3) revealed stable water quality conditions for all process water localities during January to December 2011. Notable fluctuations in salts (EC/TDS) and nitrate concentrations were seen at all the process water localities. The annual average profiles of all process water monitoring localities exceed condition 3.2 in terms of nitrate concentrations. The Electrical Conductivity (EC) and pH levels at some of the localities also exceeded the Exemption 2118B conditions. Based on the calculated annual average profiles, the general quality of process water at Xstrata Kroondal mine can be described as neutral to slightly alkaline, fresh (Appendix C1) and very hard (Appendix C2) with very high nitrate concentrations. Relatively stable major cation and anion water quality conditions for all process water localities during the January to December 2012 (Table 5-4) period were observed. Fluctuations in Salts (EC/TDS) and nitrate concentrations, especially at localities KMS06, KMS07 and KMS11, were noted. Exemption 2118B (Appendix C3) proposes that Kroondal process water monitoring localities comply with condition 3.2 of the Exemption. The annual average profiles of all process water monitoring localities exceed the permit condition 3.2 in terms of nitrate concentrations. The Electrical Conductivity (EC) and pH levels at some of the localities also exceeded the Exemption 2118B conditions. Based on the calculated annual average profiles, the general quality of process water at Xstrata Kroondal mine can be described as neutral to slightly alkaline, hard to very hard and saline to very saline with very high nitrate concentrations.

### 5.2.2.2 Receiving water

In the receiving water quality (Table 5-3), KMS 14 (Hex River, upstream of Sand Spruit) revealed stable conditions during the annual period of 2011, a slight change in the dominant cations in the month of August 2011. A noticeable increase in salinity (TDS and EC) and sulphate concentrations was seen for the annual period. Long term trends analysed for the database period also revealed improved, but steadily rising, conditions for salinity, total hardness and nitrate levels at this locality. When taking the annual average water quality profile into consideration, the water at KMS 14 can be described as relatively neutral, non-saline and moderately hard. The water quality of KMS 15 (Hex River, downstream of Sand Spruit) also showed a slight, but noticeable increase in salinity (TDS and EC) for the annual period. Nitrate concentrations at KMS 15 fluctuated throughout the annual period with the overall annual nitrate average remaining compliant with the Permit 3.1 Receiving environment conditions. KMS 15 presented a relatively neutral, non saline and moderately hard profile. A significant (in comparison to previous annual periods) impact in terms of the downstream water quality of the Sand Spruit was calculated for the recent annual period. Increased levels of sulphate, chloride, and nitrate were seen when comparing the annual average values between the Sand Spruit upstream of the mine (KMS 13) to the Sand Spruit downstream of the mine (KMS 08). The Xstrata Kroondal mine is the most likely contributor. Slight increased levels of ammonia were also recorded for the annual period. The noted rise in nitrate (3.5 mg/l) and chloride (6 mg/l) concentrations could possibly be attributed to the return water dam (KMS 11), having elevated nitrate levels, which overflowed and discharged into the Sand Spruit between these two monitoring localities. The water quality at the monitoring locality KMS 17 (Farmer’s dam) shows fluctuating trends. When the process water locality (KMS 16–Vent shaft underground water in dam) overflows, it discharges directly into KMS 17. The annual average results for KMS17 showed only EC levels that do not comply with the Exemption 2118B condition 3.1 guidelines. In 2012 (Table 5-4) KMS14 (Hex River, upstream of Sand Spruit) revealed stable conditions during the annual period. A noticeable increase in salinity (TDS and EC) concentrations is seen for the annual period. Long term trends analysed for the database period also reveal improved and steadily decreasing trends for salinity, total hardness, sulphate and nitrate levels at this locality. KMS14 can be described as relatively neutral, non-saline and hard. The water quality of KMS15 (Hex River, downstream of Sand Spruit) also show a slight, but noticeable increase in salinity (TDS and EC) for the annual period. Nitrate concentrations at KMS15 fluctuated throughout the annual period with the overall annual nitrate average exceeding the Permit 3.1 Receiving environment conditions. The high annual average nitrate concentration detected at locality KMS15 can be attributed to the high nitrate concentrations, in excess of 40 mg/l, measured in the months of May, June, August and December 2012. KMS15 presents a relatively neutral, non saline and moderately hard profile. Increased levels of TDS, Total Hardness, sulphate, chloride, nitrate, ammonium and phosphate was seen when comparing the annual average values between the Sand Spruit upstream of the mine (KMS13) to the Sand Spruit downstream of the mine (KMS08). Xstrata Kroondal mine was identified as the most likely contributor. The nitrate and chloride concentrations increased by 41.7 mg/l nitrate and 58 mg/l chloride between localities KMS13 and KMS08. The noted rise in nitrate and chloride concentrations could possibly be attributed to the return water dam (KMS11), having elevated nitrate levels, which overflowed and discharged into the Sand Spruit between these two monitoring localities. The water quality at the monitoring locality KMS17 (Farmer's dam) indicates stable major dominant cation and anion trends for the annual period. When the process water locality (KMS16 – Vent shaft underground water in dam) overflows, it discharges directly into KMS17. The annual average results for KMS17 shows pH, EC and phosphate levels that do not comply with the Exemption 2118B condition 3.1 guidelines.

In monitored surface water, the elevated nitrate extent is within the Kroondal mine surface boundary (Figure 5-1). This suggests that mining activity influences nitrate levels. More attention will be paid to KMS 01 in future monitoring because contamination upstream runs an inevitable risk of contaminant mobility downstream. Although downstream points may be elevated in nitrate levels, the other upstream points show acceptable levels.

**Figure 5-1** *Elevated nitrate extent in monitored surface water.*

**Table 5-3** *Annual average concentrations of monitored surface water at Xstrata Alloys in 2011.*

| | Permit: 2118B | | SANS 241:2 | Surface water monitoring localities | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Variable (mg/l)** | **3.1 Receiving** | **3.2 Process** | **DWA 2011** | **KMS 01** | **KMS 02** | **KMS 03** | **KMS 05** | **KMS 06** | **KMS 07** | **KMS 08** | **KMS 09** | **KMS 11** | **KMS 12** | **KMS 13** | **KMS 14** | **KMS 15** | **KMS 16** | **KMS 17** |
| **No. of records** | | | | **5** | **9** | **10** | **3** | **2** | **10** | **10** | **10** | **10** | **9** | **10** | **10** | **10** | **10** | **10** |
| **TDS** | NA | NA | 1200 | 339 | 649.40 | 573.90 | 624 | 875.50 | 641.60 | 213.30 | 720 | 656.30 | 479.80 | 185 | 169.90 | 170 | 602.60 | 375.40 |
| **pH** | 6-8.50 | 6-8.50 | 5-9.70 | 8.38 | **8.54** | **9.10** | **8.71** | 8.24 | 8.43 | 8.20 | 8.11 | 8.38 | 8.31 | 8.30 | 8.08 | 8.20 | 8.45 | **8.69** |
| **EC (mS/m)** | 0-70 | 0-150 | 0-170 | 67.94 | 131.50 | 115 | **152** | **204.70** | 146.20 | 44.20 | **142** | **153.60** | **94.98** | 34.20 | 30.09 | 35.19 | 122.20 | **72.36** |
| **Ca** | NA | NA | 0-150 | 31.12 | 59.42 | 45.87 | 52.31 | 87.35 | 58.52 | 20.43 | 47.30 | 60.17 | 39.19 | 19.70 | 17.86 | 17.09 | 51.76 | 31 |
| **Mg** | NA | NA | 0-100 | 55.9 | 98.40 | 98.93 | 90.31 | 107.90 | 94.83 | 35.36 | 119 | 95.16 | 83.28 | 31.30 | 25.67 | 29.09 | 116.10 | 67.20 |
| **Na** | NA | NA | 0-200 | 15.62 | 58.81 | 45.18 | 89.26 | 127.90 | 70.41 | 13.68 | 35.80 | 76.79 | 27.75 | 7.37 | 9.01 | 8.05 | 24.41 | 17.30 |
| **K** | NA | NA | 0-50 | 5.09 | 3.76 | 3.09 | 8.43 | 14.08 | 6.80 | 1.65 | 11.30 | 8.02 | 4.69 | 1.01 | 1.65 | 1.31 | 8.19 | 6.26 |
| **Cl** | 0-100 | 0-200 | 0-300 | 23.65 | 116.10 | 78.35 | 100.70 | 112.70 | 84.82 | 16.93 | 72.20 | 95.21 | 40.82 | 8.82 | 18.18 | 11.66 | 39.32 | 28.32 |
| **$SO_4$** | 0-200 | 0-400 | 0-500 | 81.89 | 116.90 | 111.30 | 103.50 | 183.70 | 124.30 | 29.92 | 116 | 128.90 | 90.10 | 24.3 | 28.26 | 22.37 | 136.30 | 84.97 |
| **$NO_3$-N** | 0-6 | 0-12 | 11 | **15.77** | **30.53** | **25.74** | **91.47** | **136.50** | **65.35** | **7.67** | 4.34 | **74.25** | **14.64** | 0.74 | 1.88 | 3.59 | **36.92** | **9.60** |
| **Total hardness** | NA | NA | NA | 307.80 | 553.60 | 521.90 | 502.70 | 662.50 | 536.70 | 196.60 | 606 | 542.20 | 440.80 | 1780 | 150.20 | 162.20 | 607.40 | 354.10 |

**Table 5-4** *Annual average concentrations of monitored surface water at Xstrata Alloys in 2012.*

| | **Permit: 2118B** | | **SANS 241:2** | **Surface water monitoring localities** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Variable (mg/l)** | **3.1 Receiving** | **3.2 Process** | **DWA 2011** | **KMS 01** | **KMS 02** | **KMS 03** | **KMS 05** | **KMS 06** | **KMS 07** | **KMS 08** | **KMS 09** | **KMS 11** | **KMS 12** | **KMS 13** | **KMS 14** | **KMS 15** | **KMS 16** | **KMS 17** |
| **No. of records** | | | | **2** | **11** | **12** | **0** | **12** | **11** | **12** | **10** | **12** | **6** | **11** | **12** | **12** | **10** | **12** |
| **TDS** | NA | NA | 1200 | 399.50 | 569.50 | 564.10 | - | 1090.8 | 1018 | 603.90 | 803.50 | 1081 | 606.20 | 376.60 | 243.80 | 418.30 | 682 | 620.60 |
| **Ph** | 6-8.50 | 6-8.50 | 5-9.70 | **8.90** | **8.80** | **8.90** | **-** | 8.1 | 8.3 | 8.10 | 8.30 | 8.20 | 8.20 | 8.50 | 8.20 | 8.30 | **8.60** | **8.70** |
| **EC (mS/m)** | 0-70 | 0-150 | 0-170 | 69.90 | 91.50 | 88 | **-** | **180.5** | **171.50** | **103.10** | **129.80** | **178.20** | **95.70** | 60.70 | 40.90 | 81.10 | **112.20** | **96.50** |
| **Ca** | NA | NA | 0-150 | 32.40 | 37.80 | 33.30 | - | 98.3 | 85.50 | 53.90 | 46.50 | 92.10 | 46 | 35.80 | 17.60 | 38.10 | 51.30 | 33.40 |
| **Mg** | NA | NA | 0-100 | 69 | 101.80 | 98.60 | - | 106 | 101 | 83.50 | 117.30 | 109.10 | 100.50 | 64.50 | 41.20 | 61.10 | **114.90** | **108** |
| **Na** | NA | NA | 0-200 | 15.50 | 26.40 | 26 | - | 123 | 106.40 | 43.20 | 48 | 127.70 | 22.50 | 9.60 | 6.30 | 22.10 | 25.50 | 22.10 |
| **K** | NA | NA | 0-50 | 7.10 | 2.10 | 2.40 | - | 14.7 | 10.70 | 5.70 | 9.90 | 19 | 4.80 | 0.90 | 0.80 | 2.40 | 7.90 | 8.50 |
| **Cl** | 0-100 | 0-200 | 0-300 | 27.20 | 37.30 | 36.50 | - | 191.8 | 142.10 | 69.60 | 60.60 | 181.10 | 33.90 | 11.30 | 14.70 | 38.50 | 35.90 | 35.70 |
| **$SO_4$** | 0-200 | 0-400 | 0-500 | 92.90 | 105 | 111.70 | - | 186.8 | 158.30 | 94.50 | 87.40 | 207.40 | 103.80 | 46.40 | 36.60 | 61.10 | 149.90 | 145.40 |
| **$NO_3$-N** | 0-6 | 0-12 | 11 | 2.74 | **14.28** | **12.96** | **-** | **119.23** | **111** | **42.01** | 2.34 | **120.23** | **6.11** | 0.30 | 2.14 | **24.50** | **31.79** | 5.06 |
| **Total hardness** | NA | NA | NA | 365 | 513.70 | 489 | - | 682 | 629.60 | 478.30 | 593.40 | 678.60 | 528.80 | 354.90 | 213.30 | 346.80 | 601.20 | 528.80 |

### 5.2.3 Bacteriological monitoring

KMS 02 (Sewage Effluent – tank outflow), KMS 03 (Erickson – Underground and return water) and KMS 09 (Outlet of crocodile farm) are monitored for bacteriological integrity. Bacteriological results recorded at these localities during January to December 2011 and January to December 2012 are presented in Table 5-5 and Table 5-6 respectively.

**Table 5-5** *Xstrata Kroondal mine bacteriological results for 2011.*

| | **KMS 02** | | | **KMS 03** | | | **KMS 09** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Heterotrophic Plate Count (HPC)** | **Total Coliform** | ***E. Coli*** | **HPC** | **Total Coliform** | ***E. Coli*** | **HPC** | **Total Coliform** | ***E. Coli*** |
| | (CFU per 100ml) | | | (CFU per 100ml) | | | (CFU per 100ml) | | |
| **Jan** | >391.2 | 900 | 30 | >15 000 | 140 | 6 | 15 000 | 100 000 | 100 000 |
| **Feb** | >391.2 | 32 000 | 200 | 3 700 | 1 600 | 3 | 15 000 | 100 000 | 100 000 |
| **Mar** | >15 000 | >100 000 | 2000 | >15 000 | 19 000 | <1 | 15 000 | 100 000 | 100 000 |
| **Apr** | >15 100 | 101 000 | 19000 | 15 100 | 101 000 | 1 300 | 15 000 | 100 000 | 100 000 |
| **May** | >15 000 | 600 | 19 | 4200 | 90 | 5 | 15 000 | 100 000 | 100 000 |
| **Jun** | >15 000 | 10 000 | 200 | >15 000 | 6 000 | 100 | 15 000 | 100 000 | 100 000 |
| **Jul** | >15 000 | 430 | 50 | 4 600 | 60 | 10 | 15 000 | 100 000 | 100 000 |
| **Aug** | >4 200 | 410 | 10 | 11 300 | 2 200 | <1 | 15 000 | 100 000 | 100 000 |
| **Oct** | >15 000 | 780 | 50 | >15 000 | 110 | 100 | 15 000 | 100 000 | 100 000 |
| **Dec** | Dry | | | >15 000 | 230 | <1 | 15 000 | 15 000 | 15 000 |

Total coliforms and E. coli are common to untreated sewage waste water and are generally used to indicate inefficient treatment processes. KMS 02 and KMS 03 indicated very high concentrations of HPC, mostly beyond detection limits, and elevated levels of total coliform bacteria and E.coli bacteria over the entire annual period 2011. When recorded with flow, KMS 09 also presented HPC, total coliform bacteria and *E.coli* bacteria beyond detection limits. The DWA guidelines are shown in Appendix C4. KMS02 had fluctuating counts of Heterotrophic Plate Count, total coliforms and *E.coli.* Varying *E.coli* and total coliform counts were recorded throughout the annual period at locality KMS02 ranging from unacceptable quality (March) to Ideal quality (August). No bacteriological sample was taken at locality KMS02 in the month of February 2012 as a result of no flowing conditions. Locality KMS03 indicated consistent marginal quality to poor quality conditions throughout the annual period as a result of varying very high E.coli, total coliforms and Heterotrophic Plate Counts. Dry conditions were recorded for locality KMS09 in the months of January and November 2012. In terms of bacteriological quality locality KMS09 consistently fell within unacceptable water quality limits as a result of extremely high total coliform, *E.coli* and heterotrophic plate count counts throughout the annual period.

**Table 5-6** *Xstrata Kroondal mine bacteriological results for 2012.*

| | **KMS 02** | | | **KMS 03** | | | **KMS 09** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Hetero-trophic Plate Count (HPC)** | **Total Coliform** | ***E. Coli*** | **HPC** | **Total Coliform** | ***E. Coli*** | **HPC** | **Total Coliform** | ***E. Coli*** |
| | (CFU per 100ml) | | | (CFU per 100ml) | | | (CFU per 100ml) | | |
| **Jan** | 7400 | 150 | 13 | 2700 | 360 | 2 | Dry | | |
| **Feb** | No flow | | | 10400 | 150 | 1 | 104200 | 603000 | 345000 |
| **Mar** | 3400 | 140 | 5 | 1210 | 89 | 6 | 174700 | 395000 | 197000 |
| **Apr** | 4400 | 540 | 90 | 2200 | 220 | 4 | >15000 | >99999 | >99999 |
| **May** | 1420 | 320 | 6 | 1490 | 210 | 4 | >15000 | >99999 | 84000 |
| **Jun** | | | | 1470 | 260 | 10 | >15000 | >99999 | >99999 |
| **Jul** | 15000 | 1600 | 9 | 700 | 50 | 3 | >15000 | >100000 | >100000 |
| **Aug** | 84 | -1 | -1 | 840 | 200 | 17 | >15000 | >100000 | >100000 |
| **Sep** | 980 | 69 | 1 | 790 | 260 | 7 | >15000 | >100000 | >100000 |
| **Oct** | 6100 | 420 | 10 | 3400 | 100 | 3 | - | - | - |
| **Nov** | 2400 | 120 | 17 | 3000 | 120 | 7 | Dry | | |
| **Dec** | 7700 | 620 | 39 | 15000 | 510 | 24 | 14900 | 4400 | 1500 |

### 5.2.4 Ground water monitoring

Four chemical parameters (TDS, nitrate, sulphate, and magnesium) were chosen from the full list of analytes as indicators of the type of contamination that could potentially occur at the Xstrata Kroondal operations. These parameters will be plotted for all the different areas and all boreholes where data exists. Although only the four parameters will be plotted in each case, all inorganic parameters were generally assessed and anomalies discussed.

In the average ground water quality (Table 5-6) for 2011, Total Dissolved Salts (TDS) concentrations remained well within ideal ranges for domestic use with averages varying between 360 and 800 mg/l. No significant increasing or decreasing concentration trends could be identified. Ground water nitrate concentrations fluctuated significantly throughout the monitoring year, but displayed no significant increasing or decreasing concentration trends. Anomalous high concentrations were measured in ground water monitoring boreholes KMB18 and KMB19 during the July 2011 and October 2011 sampling runs respectively, which exceeded the maximum permissible concentration of 20 mg/l. Average concentrations measured in the remainders of monitoring boreholes vary between 1 and 6 mg/l, which are within ideal limits. Average ground water sulphate concentrations vary between 60 and ± 120 mg/l, which are well within ideal ranges for domestic use. No significant increasing or decreasing concentration trends could be identified. Ground water magnesium concentrations measured in monitoring boreholes KMB19 (Crocodile Farm - Pipe in holding pen) and KMB20 (Crocodile Farm - Owners House) exceed the maximum permissible concentration with averages varying between 150 and 100 mg/l respectively. The remaining monitoring boreholes display averages varying between 70 and 90 mg/l, which are within ideal and recommended ranges for domestic use. No significant increasing or decreasing concentration trends could be identified. Domination in magnesium cations within igneous Bushveld Complex aquifers is a common phenomenon, which is the result of the abundance thereof within the mafic and ultramafic igneous rocks. The total hardness of 2011 and 2012 (Appendix D2) ranges from 453 mg$CaCO_3$ to 658 mg$CaCO_3$ and can be classified as very hard (>300 mg$CaCO_3$) based on classification ratings (Appendix C2). In 2012, ground water TDS concentrations remained well within ideal and recommended ranges for domestic use with averages varying between ± 490 mg/l and 910 mg/l. Slight concentration increases were measured in monitoring boreholes KMB03 and KMB 03S, which are located down gradient from the tailings dam. Average ground water sulphate concentrations vary between ± 90 mg/l and ± 260 mg/l, which are well within ideal ranges for domestic use. Significant concentration increases were again measured down gradient from the tailings dam. Ground water nitrate concentrations measured down gradient from the tailings dam in monitoring boreholes KMB 03 and KMB 03S displayed significant increasing concentration trends. An average of 23 mg/l was measured down gradient from the tailings dam, which exceeds the maximum permissible concentration of 20 mg/l. The maximum permissible concentration was also exceeded by KMB06, which is located in old mine workings. Concentrations measured in the remainders of boreholes remained within ideal and recommended ranges throughout the past monitoring period. Average groundwater magnesium concentrations measured in the majority of monitoring boreholes vary between ± 100 mg/l and 130 mg/l, hence exceeding the maximum permissible concentration for domestic use. Monitoring boreholes KMB05 and KMB20 are the exceptions with concentrations remaining within ideal and recommended ranges throughout the year. Significant concentration increases were measured in KMB03, 03S and 18.

**Table 5-7** *Average ground water quarterly monitoring quality of Xstrata Kroondal 2011.*

| Variable (mg/l) | SANS241:2<br>2011 | KMB 03 | KMB0 3S | KMB 05 | KMB 18 | KMB 19 | KMB 20 |
|---|---|---|---|---|---|---|---|
| **No. of records** | | **4** | **4** | **3** | **3** | **1** | **3** |
| **TDS** | **1200** | 670 | 614 | 603.33 | 592.33 | 799 | 465 |
| **pH** | **5-9.70** | 8.19 | 8.11 | 7.83 | 8.17 | 7.95 | 8.27 |
| **EC (mS/m)** | **0-170** | 117.93 | 113.23 | 115.10 | 110.07 | 145 | 89.23 |
| **Ca** | **0-150** | 75.75 | 66.50 | 92 | 41.67 | 49 | 27.33 |
| **Mg** | **0-100** | 80.50 | 82 | 61.33 | **121.33** | **152** | 93.33 |
| **Na** | **0-200** | 70.25 | 59 | 40.67 | 22.67 | 41 | 18.67 |
| **K** | **0-50** | 3 | 2 | 3 | 1.67 | 2 | 1.33 |
| **Cl** | **0-300** | 43.50 | 34.25 | 21 | 47.33 | 58 | 24.33 |
| **$SO_4$** | **0-500** | 97.50 | 76.75 | 97.33 | 92.67 | 115 | 89.67 |
| **$NO_3$-N** | **11** | 5.40 | 4.76 | 0.37 | **12.88** | **22.16** | 5.60 |
| **Total hardness** | **NA** | 520.75 | 503.75 | 482.33 | 603.33 | 747 | 453 |

**Table 5-8** *Average ground water monitoring quality of Xstrata Kroondal 2012.*

| Variable (mg/l) | SANS241:2 | KMB 03 | KMB 03s | KMB 05 | KMB 06 | KMB 18 | KMB 19 | KMB 20 |
|---|---|---|---|---|---|---|---|---|
| **No. of recorded** | **2011** | **4** | **4** | **4** | **1** | **3** | **3** | **3** |
| **TDS** | **1200** | 957.50 | 962 | 668.50 | 633 | 559.67 | 554 | 554 |
| **pH** | **5-9.70** | 7.90 | 8.02 | 7.72 | 8.09 | 8.47 | 8.47 | 8.47 |
| **EC (mS/m)** | **0-170** | 149.40 | 146.48 | 107.85 | 127.20 | 94.53 | 96.90 | 96.90 |
| **Ca** | **0-150** | 99.68 | 81.75 | 93.98 | 50.67 | 39.51 | 38.46 | 38.46 |
| **Mg** | **0-100** | **110.49** | **115.98** | **71.08** | **129.10** | **112.13** | **110.22** | **110.22** |
| **Na** | **0-200** | 89.35 | 106.93 | 64.54 | 23.45 | 26.71 | 25.83 | 25.83 |
| **K** | **0-50** | 2.85 | 2.17 | 2.29 | 8.92 | 1.92 | 2.56 | 2.56 |
| **Cl** | **0-300** | 75.37 | 69.58 | 24.63 | 33.04 | 36.64 | 36.34 | 36.34 |
| **$SO_4$** | **0-500** | 276.48 | 306.68 | 92.06 | 150.90 | 94.15 | 100.55 | 100.55 |
| **$NO_3$-N** | **11** | **24.94** | **25.71** | 1.10 | **28.60** | 8.57 | 8.75 | 8.75 |
| **Total hardness** | **NA** | 704 | 682 | 527.25 | 658 | 560.67 | 550 | 550 |

The 2011 Piper diagram for ground water monitoring in monitored ground water (Figure 5-2) reveals a water quality of unpolluted ground water in terms of cations and anions; and calcium/magnesium bicarbonate waters.

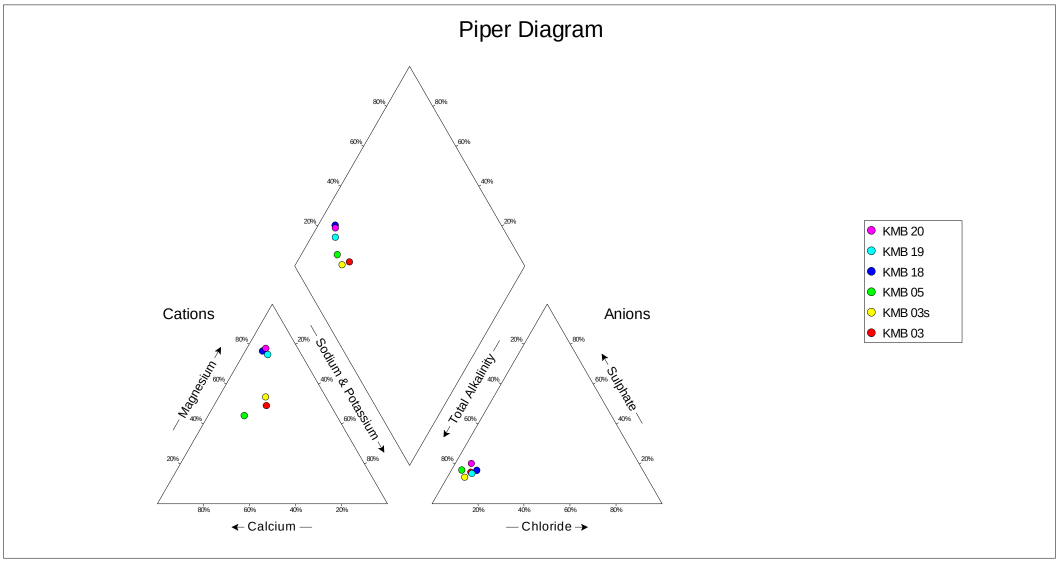


**Figure 5-2** *2011 Piper diagram of ground water monitoring.*

The SAR plot for monitoring ground water (Figure 5-3) classifies the underground waters as $C_3S_1$. In $C_3S_1$ water, this is regarded as a high salt and low sodium content classification of water. High salt content water can only be used in soils with a good drainage. Leaching is needed periodically and plants sensitive to brackish water must be avoided. Low sodium content water can be used for irrigation as it holds low brackish danger.

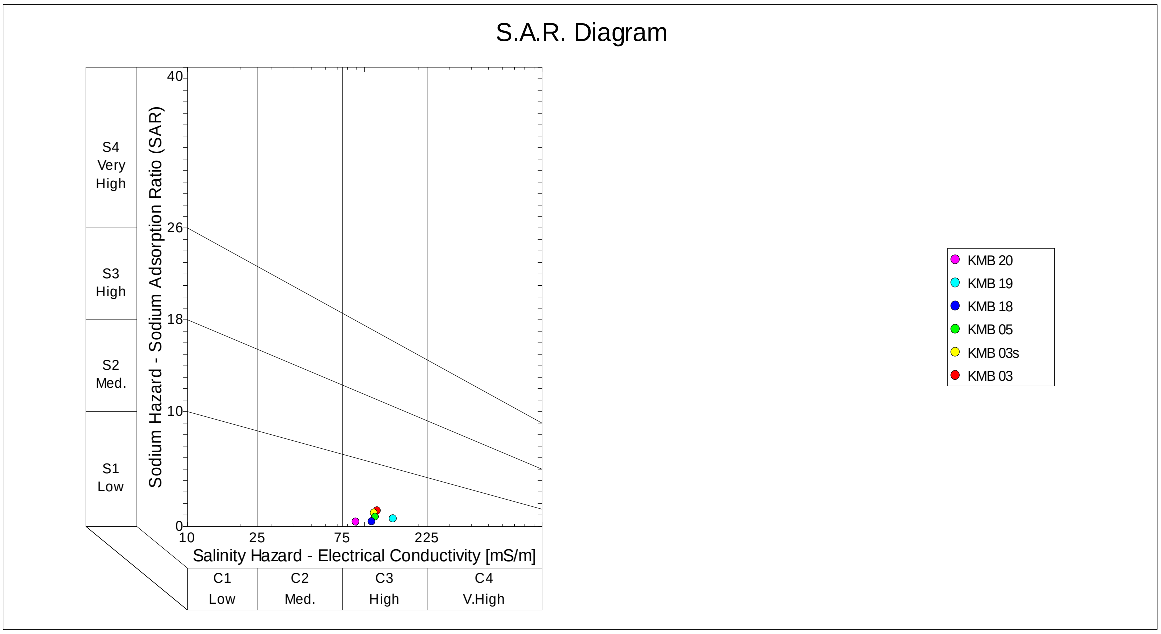
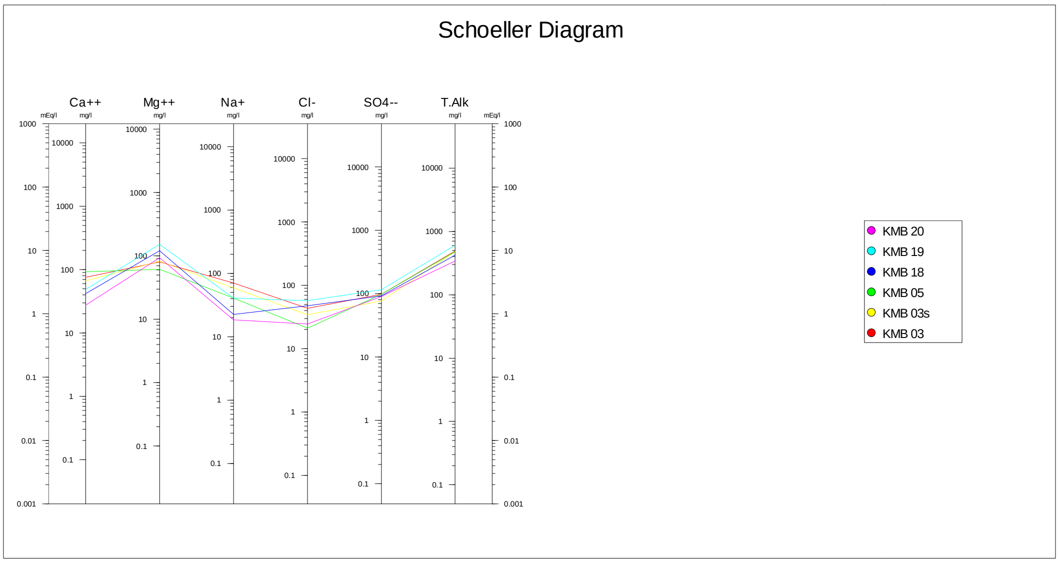


**Figure 5-3** *2011 SAR diagram of ground water monitoring.*

The major parameter values are displayed in the Schoeller plot (Figure 5-4) showing magnesium enrichment and verifying the Piper plot (Figure 5-2). In 2012; the hydrofacies plot as 2011.



The elevated nitrate extent in ground water can’t be sufficiently stated (Figure 5-4) due to an inconsistent monitoring programme in place. KMB 03, 06, 18 and 19 display elevated nitrate levels within the currently monitored boreholes.

**Figure 5-4** *2011* Schoeller *diagram of ground water monitoring.*

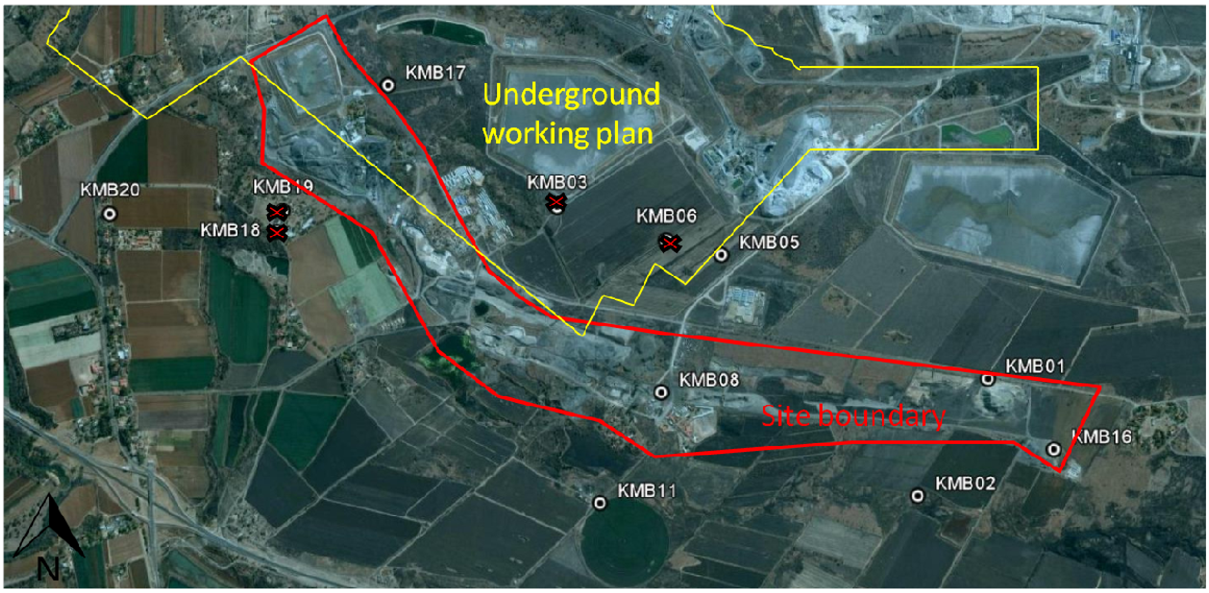


**Figure 5-5** *Elevated nitrate concentration extent.*

## 5.3.4 Collected ground water samples

In July sampling (Table 5-9), water was recorded as slightly alkaline waters with EC levels for KDL 01 and KDL 04 above DWA requirements.  KDL 02 and KDL 03 will not be discussed because the two localities are of known man made pollution and were substituted by sampling localities KDL 07 and KDL 08 in September.  Very magnesium rich waters with high nitrate values (up to 107.3 mg/l) were recorded.  The most likely cause for the high nitrate in ground water underground is explosives.  KDL 05 and KDL 06 showed acceptable nitrate values and all other parameters remained well within DWA requirements.

**Table 5-9** *July ground water quality of sample collection.*

| **Variable (mg/l)** | **Description** | **pH** | **EC (mS/m)** | **Ca** | **Mg** | **Na** | **K** | **Cl** | **$SO_4$** | **$NO_3$_N** |
|---|---|---|---|---|---|---|---|---|---|---|
| **SANS 241:2 2011** | | **5-9.70** | **0-170** | **0-150** | **0-100** | **0-200** | **0-50** | **0-300** | **0-500** | **11** |
| **KDL 01** | MKA 77 Panel | 7.99 | **185** | 136.10 | **116** | 60.70 | 2 | 141.68 | 169.22 | **107.30** |
| **KDL 02** | MKC old 56 | 8.60 | 101 | 17.40 | **120** | 29.30 | 4.80 | 46.41 | 113.28 | **20.11** |
| **KDL 03** | ` | 8.30 | 130 | 45.50 | **117.10** | 48.80 | 7.90 | 97.40 | 145.32 | **62.34** |
| **KDL 04** | MKD roadway | 8.08 | **174** | 100.90 | **140.10** | 86.60 | 3.60 | 158.21 | 218.06 | **94.58** |
| **KDL 05** | Dam R11 | 8.53 | 75 | 20.20 | 91 | 19.10 | 2.40 | 21.23 | 103.90 | 10.96 |
| **KDL 06** | Main shaft roadway | 8.53 | 92 | 32.60 | **118.10** | 18.70 | 2.90 | 23.05 | 91.40 | 5.51 |

In September sampling (Table 5-10), water was recorded as slightly alkaline waters with KDL 05 and KDL 06 EC levels above DWA requirements.  Magnesium rich waters were recorded from KDL 01, KDL 04 and KDL 05; with KDL 06 displaying enrichment in calcium, sodium and chloride.  Sulphate enrichment was observed in KDL 01 and KDL 05; whilst elevated nitrate recorded only in KDL 01.  All other parameters remained well within DWA requirements.

**Table 5-10** *September ground water quality of sample collection.*

| **Variable (mg/l)** | **Description** | **pH** | **EC (mS/m)** | **Ca** | **Mg** | **Na** | **K** | **Cl** | **$SO_4$** | **$NO_3$_N** |
|---|---|---|---|---|---|---|---|---|---|---|
| **SANS 241:2 2011** | | **5-9.70** | **0-170** | **0-150** | **0-100** | **0-200** | **0-50** | **0-300** | **0-500** | **11** |
| **KDL 01** | MKA 77 Panel | 7.92 | 90.9 | 24.4 | **103.8** | 14.2 | 2 | 29 | 209 | **23.2** |
| **KDL 04** | MKD roadway | 8.45 | 94.9 | 28.2 | **108** | 15.9 | 2.2 | 28 | 100 | 4 |
| **KDL 05** | Dam R11 | 8.52 | **172** | 29.6 | **217.1** | 24.4 | 2.4 | 137 | 265 | **52** |
| **KDL 06** | Mainshaft roadway | 6.86 | **812** | **645.1** | 10.6 | **819.7** | 4.9 | **2459** | 88 | 4.4 |
| **KDL 07** | Old Rustenburg fissures | 8.45 | 78 | 21.8 | 84.6 | 12.6 | 1.1 | 21 | 111 | 7.1 |
| **KDL 08** | R19 borehole | 8.46 | 77.9 | 22.2 | 91.5 | 13.2 | 1.2 | 22 | 112 | 7.2 |

Piper plots for the 2012 underground water averages (Figure 5-7) show fresh water quality of unpolluted ground water in terms of cations and anions; and calcium/magnesium bicarbonate waters. KDL 06 must be highlighted as it plots as plots as sodium chloride water or calcium/sodium sulphate waters.

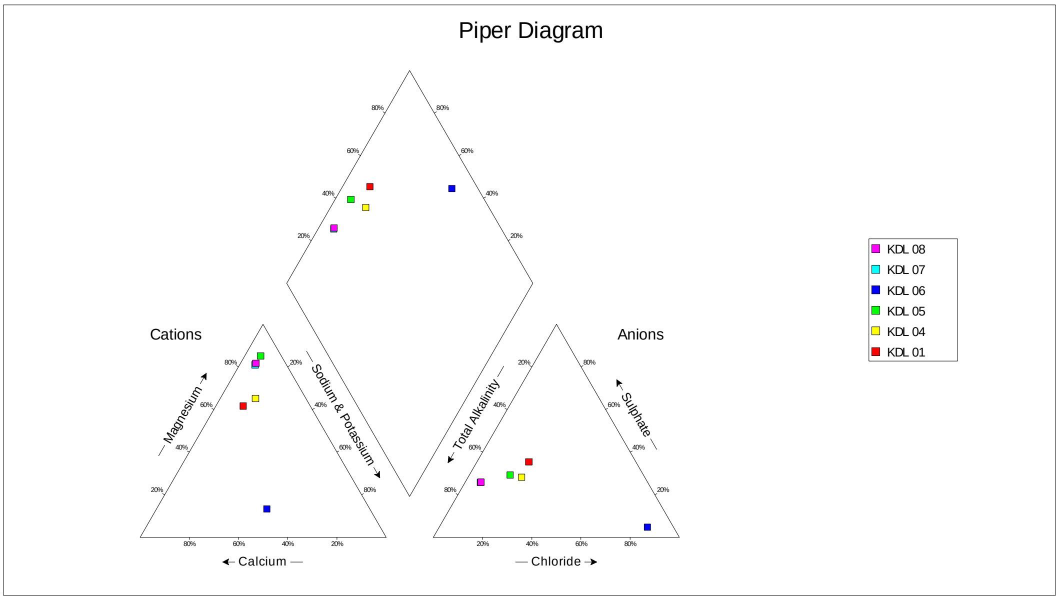


**Figure 5-6** *Piper diagram of collected ground water samples.*

The SAR plot for July collected ground water samples (Figure 5-8) classifies the underground waters as $C_3S_1$. In $C_3S_1$ water, this is regarded as a high salt and low sodium content classification of water. High salt content water can only be used in soils with a good drainage. Leaching is needed periodically and plants sensitive to brackish water must be avoided. Low sodium content water can be used for irrigation as it holds low brackish danger. KDL 06 plots as $C_4S_3$. In $C_4S_3$ water, this is regarded as a very high salt and high sodium content classification of water. Very high salt content water is not fit for irrigation under normal conditions. This water can be used in emergencies on sandy soils. High sodium content water should not be used on soil with limited drainage.

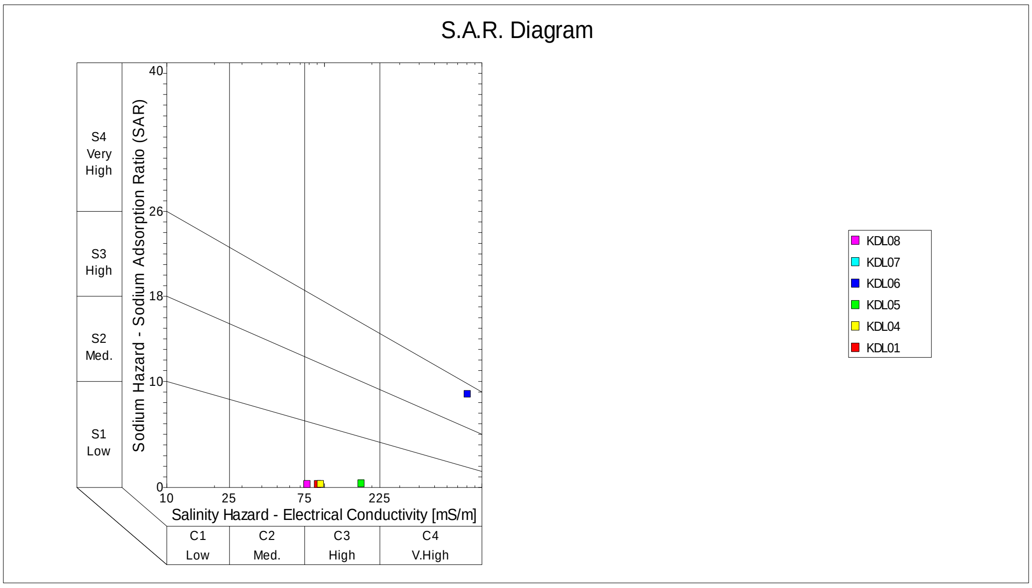


**Figure 5-7** *SAR diagram of collected ground water samples.*

The Schoeller plots (Figure 5-9) show a general magnesium and total alkalinity enrichment. All the collection sites have similar behaviour in chemistry with the exception of KDL 06, KDL 07 and KDL 08. KDL 06 is calcium and sodium rich, whilst KDL 07 and KDL 08 are display less chloride enrichment. KDL 01 and KDL 04 do not deviate from the general chemical behaviour just as in September. These plots suggest a further investigation into KDL 06 is required.

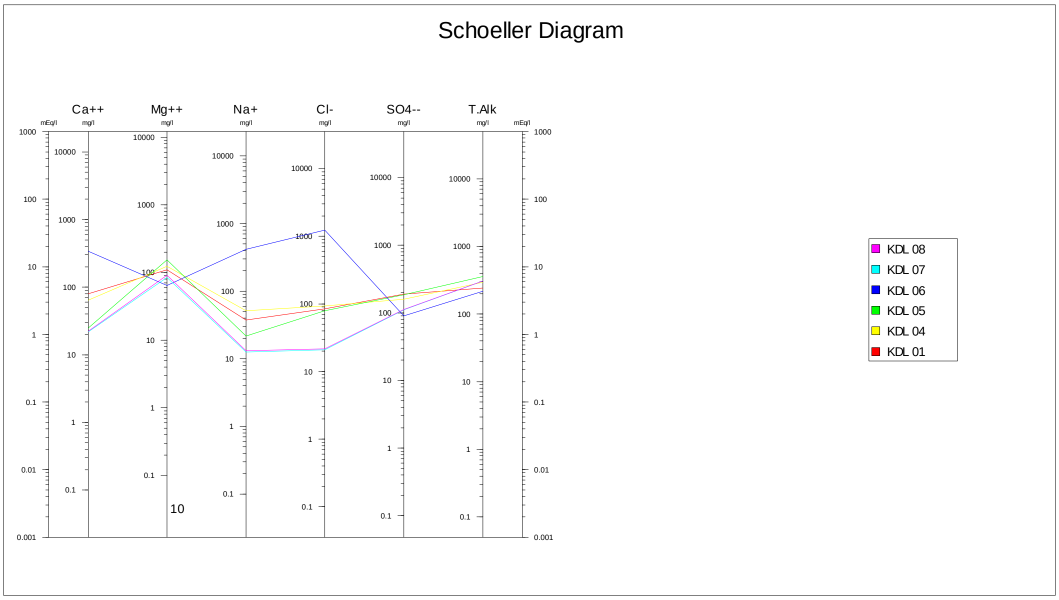


**Figure 5-8** *Schoeller diagram of collected ground water samples.*

### 5.3.5 Nitrate trends from monitoring

Under Exemption, the receiving environment water limit for nitrate is 6 mg/l (as of Permit: 2118B 3.1) and the process water limit for nitrate is 12 mg/l (as of Permit: 2118B 3.2). The other monitored water limit for nitrate is 11 mg/l (SANS 241:2 2011) and trends can be observed in Figure 5-9. Notable fluctuations in nitrate concentrations were seen at all the process water localities. The annual average profiles of all process water monitoring localities exceed condition 3.2 in terms of nitrate concentrations. All process water monitoring localities displayed elevated nitrate levels from 2011 to 2012. KMS 09, KMS 13, KMS 14 and KMS 15 are the only receiving environment water monitoring localities that displayed nitrate levels within acceptable ranges. KMS 01, KMS 08, KMS 12 and KMS 17 displayed elevated nitrate levels in this period. KMS 08 (downstream of Sand Spruit) although elevated in nitrate was minor (7.67 mg/l) and does not pose worry. KMS 12 (tributary upstream of return water dam) may possibly be affected by KMS 11's (Return water dam) elevated nitrate level. KMS 17 (Farmer's dam into which KMS 16 discharges) may possibly be affected by KMS 16's (Vent shaft/old underground water pumped into dam) elevated nitrate levels. In 2012, all the process water remained elevated in terms of nitrate levels and elevated Receiving environment water was observed in KMS 08, KMS 12 and KMS 15.

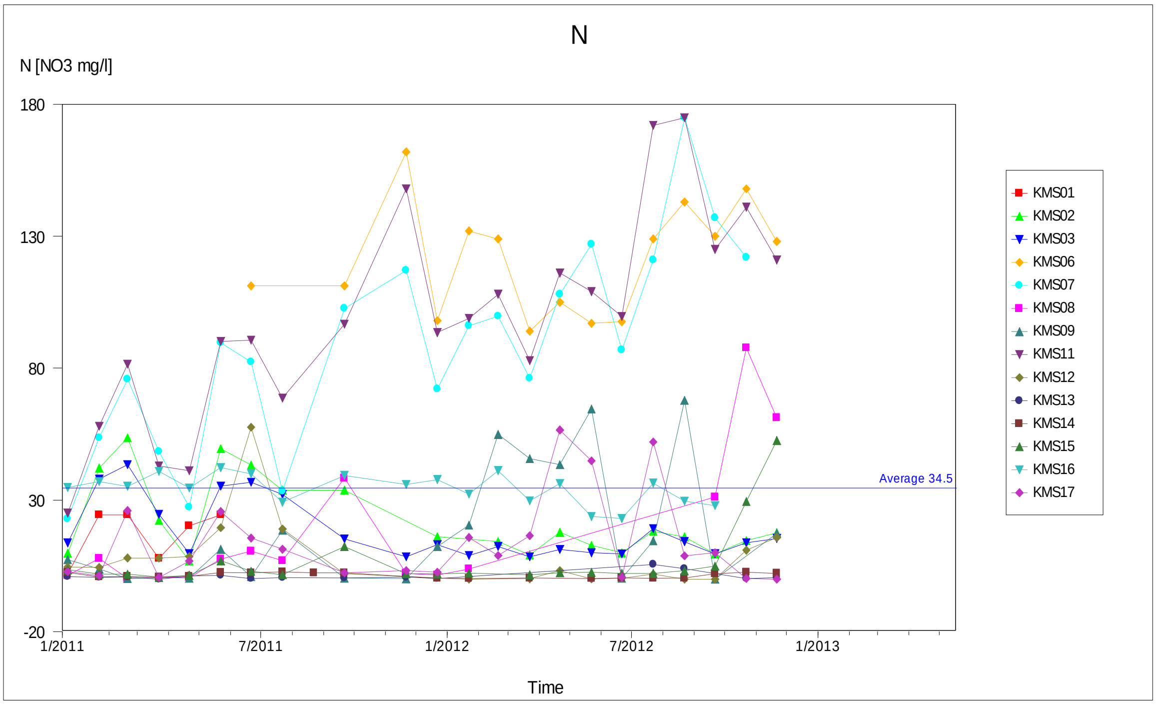


**Figure 5-9** *Surface water nitrate time-series graph.*

From 2011 to 2012 (Figure 5-10), significant nitrate increases were observed in KMB 03, KMB 03S and KMB 18. Plume monitoring refers to the groundwater quality monitoring points that have been committed specifically for determination of the extent, geometry, concentration and migration rate of a groundwater pollution plume downstream of a source. According to (Aquatico, 2012), a plume monitoring system measures the concentration distribution and migration rate of a groundwater pollution plume. If a pollution plume is detected in the monitoring boreholes down-gradient of potential pollution sources, additional boreholes will need to be developed to ensure that the concentration distribution and extent of the pollution plume is well understood and accurately definable. The groundwater nitrate content down gradient from the Kroondal tailings dam increased significantly throughout the 2012 evaluation period, which may be an indication of pollution plume movement.

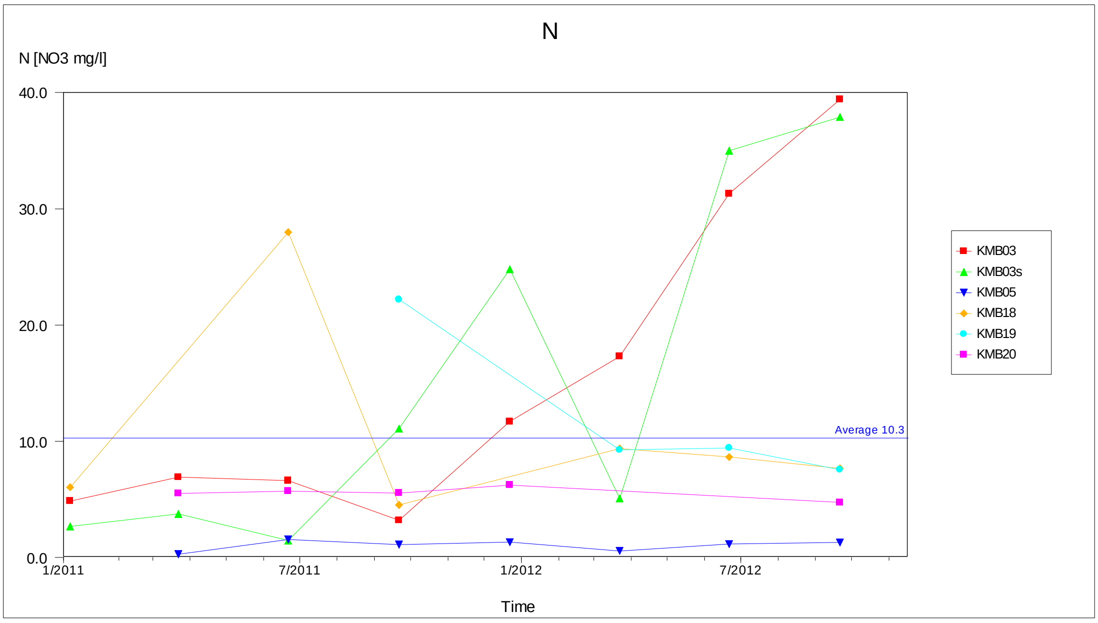


**Figure 5-10** *Ground water nitrate time-series graph*

In July (Table 5-11), the six collected samples all (with the exception of KDL 06) recorded as elevated nitrate levels above the DWA requirements with values of up to more than ten times the DWA range. As already mentioned, it was learnt that KDL 02 and KDL 03 weren't natural water and a resampling in September resulted in the introduction of KDL 07 and KDL 08. In September, only KDL 01 and KDL 05 showed nitrate levels exceeding DWA requirements. KDL 04, KDL 06, KDL 07 and KDL 08 remained well within the DWA requirements. Elevated nitrate levels underground are most probably sourced from explosives.

**Table 5-11** *July and September collected ground water samples.*

| Sample | July $NO_3$-N<br>mg/l | September $NO_3$-N<br>mg/l |
|---|---|---|
| **KDL 01** | **107.30** | **23.20** |
| **KDL 02** | **20.11** | |
| **KDL 03** | **62.34** | |
| **KDL 04** | **94.58** | 4 |
| **KDL 05** | **10.96** | **52** |
| **KDL 06** | 5.51 | 4.40 |
| **KDL 07** | | 7.10 |
| **KDL 08** | | 7.20 |

The September hydrogen and nitrogen isotopes of the collected ground water (Table 5-12 and Figure 5-11), show that denitrification did not occur (a linear relationship between oxygen and nitrogen doesn't occur). In many circumstances, isotopes offer a direct means of source identification because different sources of nitrate often have distinct isotopic compositions. Nitrogen isotopes (δ15N) have been used to identify nitrogen sources and processes in hundreds of studies over the past several decades (Heaton 1986). Since the early 1990s, nitrate isotope studies have often included analysis of the oxygen isotopes of nitrate (δ18O) (Kendall 1998).

**Table 5-12** *Hydrogen and Nitrogen isotope results of September collected ground water samples.*

| Sample | $NO_3$_N (mg/l) | 15 N Air (‰) | 18 O VSMOW (‰) |
|---|---|---|---|
| **KDL 07** | 7.10 | 6.85 | 4.17 |
| **KDL 08** | 7.20 | 7.43 | 5.44 |
| **KDL 01** | 23.20 | 11.27 | 15.03 |
| **KDL 05** | 52 | 13.10 | 8.71 |
| **KDL 04** | 4 | 14.34 | 13.97 |
| **KDL 06** | 4.40 | 31.22 | 33.35 |

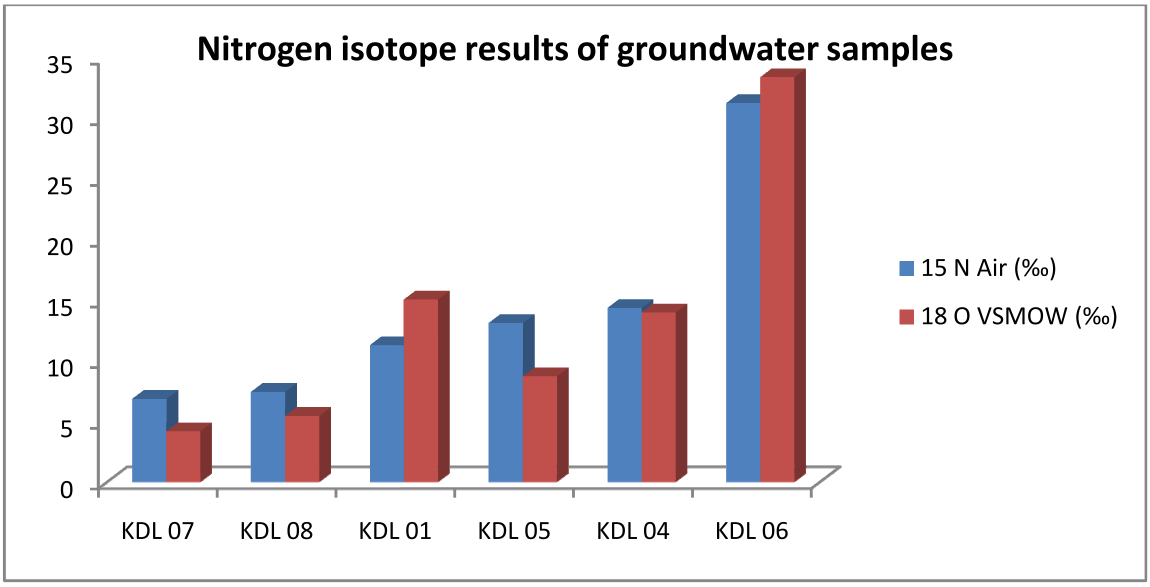


**Figure 5-11** δ15N and δ18O Isotope results of water samples

Isotopes of collected ground water samples in September (Figure 5-12) plots attribute (Kendall *et al*., 2007) KDL 07 and KDL 08 as soil ammonium. KDL 01, KDL 04 and KDL 05 are attributed as manure and septic waste. KDL 06 showed denitrification to have occurred.

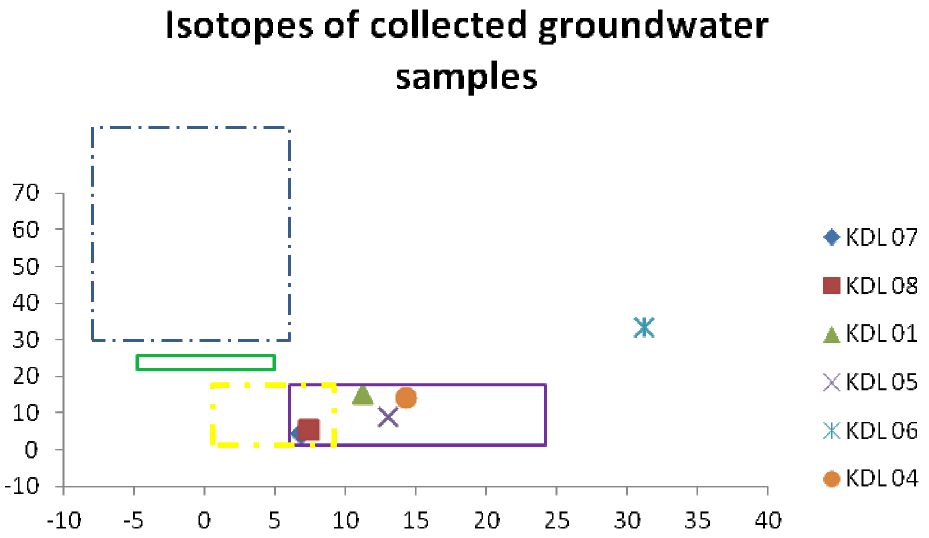


**Figure 5-12** *Isotope results of collected ground water samples and their possible sources.*

The hydrogen and oxygen results of the September underground water samples are expressed in Appendix D1 and D2. These results can be used as benchmark data for Kroondal underground water in future water studies (particularly post-closure). KDL 04 (MKD roadway) shows evaporation to have occurred.

# Chapter 6 Discussion

## 6.1 Background and project approach

The presence of nitrate in ground water is considered as a contaminant, despite its natural occurrence (Arumi *et al*., 2005; Hess and Jacobson, 1981 and Stadler *et al*., 2008). It was therefore important to get data on a background of the chemistry in the Kroondal area, to have an understanding of the mines contribution/influence to the current chemistry. Xstrata operations commenced from 2001 and the mine is just one of several mining operations in the nearby vicinity. It would also be beneficial to see ground water chemistry values of surrounding mines, but access to data of other mines was difficult (disclosure issues). Mainly the three northern provinces (Limpopo, North West and Northern Cape provinces) in South Africa (Figure 2-4) are seriously affected by nitrate (Israel *et al.*, 2011). Six borehole samples were obtained during Aquatico Scientific's field investigation in September 2000 (Table 6-1), which should be considered as a benchmark against which future monitoring results can be compared. Nitrate limits were considered 6mg/l at the time.

**Table 6-1** *Year 2000 Kroondal ground water monitoring water quality (Aquatico Scientific, 2012).*

| | **Variable (mg/l)** | **pH** | **EC (mS/m)** | **Ca** | **Mg** | **Na** | **K** | **Cl** | **$SO_4$** | **$NO_3$-N** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Description** | **SANS241: 2 2011** | **5-9.70** | **0-170** | **0-150** | **0-100** | **0-200** | **0-50** | **0-300** | **0-500** | **0-11** |
| South of Eastern Gemini Section (next to old incline) | **KMB01** | 8.53 | 106 | 34.2 | **127.6** | 17.4 | 1.9 | 16.75 | 134.3 | **21.2** |
| North West of Gemini Section (next to crop field) | **KMB03** | 7.81 | 118 | 115.5 | **141** | 19.2 | 2 | 42.5 | 165 | 9.3 |
| Old Mine Pump (Northern part of old mine workings) | **KMB06** | 7.56 | 127 | 122.4 | **183.3** | - | - | 40.6 | 180.2 | 7.6 |
| Old village ( south of Gemini section) | **KMB10** | 7.66 | 113 | 44.4 | **123.5** | 23.1 | 1.5 | 26.01 | 138.3 | **12** |
| South of eastern Gemini (Opencast Kroondal) | **KMB11** | 8.46 | 119 | 47.9 | **136.9** | 24 | 0.9 | 25.01 | 169.2 | **22.2** |
| Behind Mr van Zyl's house (next to white building) | **KMB13** | 7.58 | 80 | 21.6 | 97.3 | 14.1 | 0.5 | 23.27 | 68.13 | 4.43 |

The benchmark data (Table 6-1) displayed slightly alkaline water with EC values well within DWA requirements. The pH of natural waters is influenced by various factors and processes, including temperature, discharge of effluents, acid mine drainage, acidic precipitation, runoff, microbial activity and decay processes (DWA, 1996). The adjustment of pH in water will inevitably increase the salinity of the water by adding ions such as sodium, carbonate, hydroxyl, sulphate or chloride (DWA, 1996). Most natural waters will have pH values from pH 5.0 to pH 8.5. A pH that is too high is undesirable because free ammonia increases with rising pH (DWA, 1996). Magnesium rich water (except KMB 13) conditions were also observed, typical of the Bushveld Igneous Complex. Excess magnesium intake, particularly as the sulphate, results in diarrhoea (DWA, 1996). Calcium,sodium, potassium, chloride and sulphate values remained well within the DWA requirements nitrate for boreholes KMB 01, KMB 10 and KMB 11 exceeded the DWA requirements. From the benchmark data, only KMB 03 remains for monitoring to date and no other background data can be used as a frame of reference. Available water quality data (Table 6-2) from 2006 is not known as to when in the year it was taken and no data was found for the year 2007. Data in 2009 and 2010 is a lot more representative, having more samples taken during the year, compared to previous years.

**Table 6-2** *Sample registry of previous monitoring at Xstrata Kroodal mine.*

| Locality | Description | No. of records 2006 | No. of records 2008 | No. of records 2009 | No. of records 2010 |
|---|---|---|---|---|---|
| KMB 01 | South of Gemini (next to old incline) | ? | - | - | - |
| KMB 02 | South of eastern Gemini (next to stream) | ? | - | - | - |
| KMB 03 | North west of Gemini (crop field) | - | 1 | - | 4 |
| KMB 03S | North west of Gemini (crop field) | - | 1 | 4 | 4 |
| KMB 05 | Old windmill (north of Gemini) | - | 1 | 4 | 4 |
| KMB 06 | Old mine pump (northern part of old mine) | - | 1 | - | - |
| KMB 08 | (Old mine village, south of Gemini) | ? | - | - | - |
| KMB 10 | (Old mine village, south of Gemini) | - | 1 | - | - |
| KMB 11 | South of stream (next to irrigation field) | - | 1 | - | - |
| KMB 13 | Behind Mr van Zyl’s house (next to white building) | - | 1 | - | - |
| KMB 16 | Andru Opencast (tap at office) | ? | - | - | - |
| KMB 17 | Upstream borehole (mine entrance gate) | - | - | 3 | 1 |
| KMB 18 | Crocodile farm (main cement dam) | - | 1 | 4 | 3 |
| KMB 19 | Crocodile farm (breeding dam) | - | - | 1 | 1 |
| KMB 20 | Crocodile farm (owner’s house) | - | - | 2 | 1 |
| KMB 21 | Goose neck pipe (water from underground) | - | - | 2 | 1 |

Previous monitoring water quality data (Table 6-3) has displayed elevated magnesium levels, as would generally be expected in the Bushveld Igneous Complex. Only KMB 17 (upstream borehole at mine entrance) displayed elevated chloride levels. The DWA (1996) describe chloride as one of the major anions to be found in water and sewage. Its presence in large amounts may be due to natural processes such as the passage of water through natural salt formations in the earth or it may be an indication of pollution from sea water intrusion, industrial or domestic waste. Chloride is of concern in domestic water supplies because elevated concentrations impart a salty taste to water and accelerate the corrosion rate of metals. High concentrations of chloride can also be detrimental to chloride-sensitive garden plants. Elevated nitrate levels were notable in KMB 11 (irrigation field), KMB 18 (crocodile farm) and KMB 19 (crocodile breeding dam). KMB 11 has livestock influence and could possibly be a contributor to the elevated nitrate concentrations. KMB 18 and KMB 19 would be expected to have elevated levels due to urea and faeces of animals within the sampling area.

**Table 6-3** *Previous monitoring water quality data at Xstrata Kroondal mine*

| | **Year** | **pH** | **EC (mS/m)** | **TDS** | **Ca** | **Mg** | **Na** | **K** | **Cl** | **$SO_4$** | **$N\_NO_3$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **SANS 214:2 2011** | | **5-9.70** | **0-170** | **1200** | **0-150** | **0-100** | **0-200** | **0-50** | **0-300** | **0-500** | **0-11** |
| **KMB 01** | **2006** | 9.29 | 74 | - | 16.03 | 72.92 | 30.3 | 3.01 | 24.26 | 184.52 | - |
| **KMB 02** | **2006** | 8.97 | 83 | - | 14.3 | **103.91** | 18.04 | 0.95 | 16.02 | 91.18 | - |
| **KMB 03** | **2008** | 8.24 | 98.6 | 564 | 55.56 | 59.32 | 29.49 | 1.04 | 24.58 | 58.99 | 0.18 |
| | **2010** | 7.84 | 115.2 | 560.25 | 55.03 | 74.22 | 56.5 | 1.41 | 31.4 | 70.09 | 2.14 |
| **KMB03S** | **2008** | 7.93 | 115.9 | 654 | 74.35 | 69.72 | 34.11 | 0.75 | 38.25 | 65.29 | 0.5 |
| | **2009** | 7.63 | 109.08 | 640.5 | 86.48 | 87.14 | 41.45 | 0.95 | 38.74 | 96.24 | 1.05 |
| | **2010** | 7.88 | 128.30 | 696 | 84.79 | 88.39 | 52.82 | 1.52 | 40.24 | 159.26 | 3.86 |
| **KMB05** | **2008** | 7.93 | 100.80 | 550 | 57.94 | 44.37 | 51.42 | 2.42 | 12.32 | 22.04 | -0.1 |
| | **2009** | 7.54 | 91.63 | 490.25 | 79.76 | 59.6 | 30.4 | 1.67 | 13.37 | 44.2625 | 1.83 |
| | **2010** | 7.55 | 104.73 | 502.5 | 81.93 | 62.37 | 26.87 | 1.14 | 15.01 | 61.06 | 2.31 |
| **KMB06** | **2008** | 7.56 | 127 | - | 122.4 | **183.30** | - | - | 40.6 | 180.2 | 7.6 |
| **KMB 08** | **2006** | 8.22 | 198 | - | 139.63 | **220.55** | 29.44 | 0.89 | 140.04 | 843.81 | - |
| **KMB10** | **2008** | 7.66 | 113 | - | 44.4 | **123.5** | 23.1 | 1.5 | 26.01 | 138.31 | 12 |
| **KMB 11** | **2006** | 8.61 | 196.80 | - | 137.49 | **224.86** | 28.88 | 1.14 | 130.75 | 721.24 | - |
| | **2008** | 8.46 | 119 | - | 47.9 | **136.9** | 24 | 0.9 | 25.01 | 169.22 | **22.2** |
| **KMB13** | **2008** | 7.58 | 80 | - | 21.6 | 97.3 | 14.1 | 0.5 | 23.27 | 68.13 | 4.43 |
| **KMB 16** | **2006** | 8.67 | 90.30 | - | 33.28 | **114.19** | 10.57 | 2.18 | 12.75 | 105.35 | - |
| **KMB17** | **2009** | 7.61 | 175.70 | 1072.33 | 136.87 | 98.1 | 134.81 | 5.12 | 279.69 | 167.67 | 0.003 |
| | **2010** | 7.64 | 214.10 | 1442 | 162.2 | **116.1** | 179.9 | 8.32 | **371.1** | 270.7 | 3.49 |
| **KMB18** | **2008** | 8.22 | 139.60 | 820 | 38.2 | **110.1** | 37.52 | 1.47 | 61.52 | 225.6 | **14.9** |
| | **2009** | 7.94 | 125.83 | 705 | 46.08 | **135.17** | 44.8 | 1.45 | 59.04 | 149.77 | **20.1** |
| | **2010** | 7.98 | 141.47 | 646.33 | 47.98 | **125.95** | 25.1 | 1.35 | 52.66 | 130.24 | 9 |
| **KMB19** | **2008** | 7.83 | 154.20 | 938 | 49.99 | **141.3** | 17.21 | 1.61 | 48.62 | 178.23 | **11.2** |
| | **2009** | 7.53 | 129.90 | 731 | 54.51 | **162.9** | 16.09 | 2.22 | 65.2 | 174.51 | **33.4** |
| **KMB20** | **2009** | 8.08 | 91.30 | 525 | 29.56 | **108.9** | 16.37 | 1.4 | 26.22 | 93.79 | 3.13 |
| | **2010** | 7.89 | 86.70 | 528 | 29.69 | **105.7** | 12.66 | <0 | 29.4 | 89.38 | 0.34 |
| **KMB21** | **2009** | 8.39 | 91.45 | 463.5 | 23.95 | **103.74** | 21.91 | 2.02 | 38.03 | 82.72 | 7.27 |
| | **2010** | 8.39 | 86.70 | 477 | 18.66 | 94.5 | 19.78 | 2.72 | 36.07 | 71.16 | 8.38 |

Another important aspect to this project was to find the sources of the elevated nitrate levels in ground water chemistry. With a previous history of mining (including other surrounding mines), agricultural activity (including a neighbouring crocodile farm) and surrounding informal settlements; explosives, fertilisers and human/animal debris (Gormly and Spalding, 1979; Baker, 1992; Revey, 1996; Kramer, 2001; MacQuarrie *et al*., 2001; Taylor, 2003; Tredoux, 2004; Chowdary *et al*., 2005 and Meyer *et al*., 2007) cannot be ruled out as possible nitrate sources. Although this project investigated ground water, it was important to consider and use surface water in this investigation. Some of the major nitrate movements from soil profiles include; movement via surface/subsurface flow and profile leaching. It was therefore useful to look at surface water. Figure 3-7 shows January to March and October to December as rainy months for South Africa. One could then assume (Figure 6-1) that in the rainy months, concentrations would be diluted or appear lessened. Conversely, in the non rainy months, one would expect that concentrations would be elevated or revealed. Dilution is however not the solution to pollution. From the soil survey conducted in 2007; analysis results showed that the soil was high in calcium and magnesium (Institute of Soil, Climate and Water, 2007). The soils were also shown to be alkaline, but showed no signs of previous fertilization, with low phosphate levels. The Kroondal aquifer characteristics (Table 3-5) are of a low vulnerability and susceptibility. Therefore chances of impacting the aquifer are slim. Rehabilitated open cast sites were identified from one of the site visits at the Kroondal mine with Dr Fanie Botha. It is in this time that the previously opencast mined area (now rehabilitated) was seen. It is also within this time that the concept of the old Gemini shaft and open cast mine recharging into Kroondal mine ground water was considered as a likely possibility.

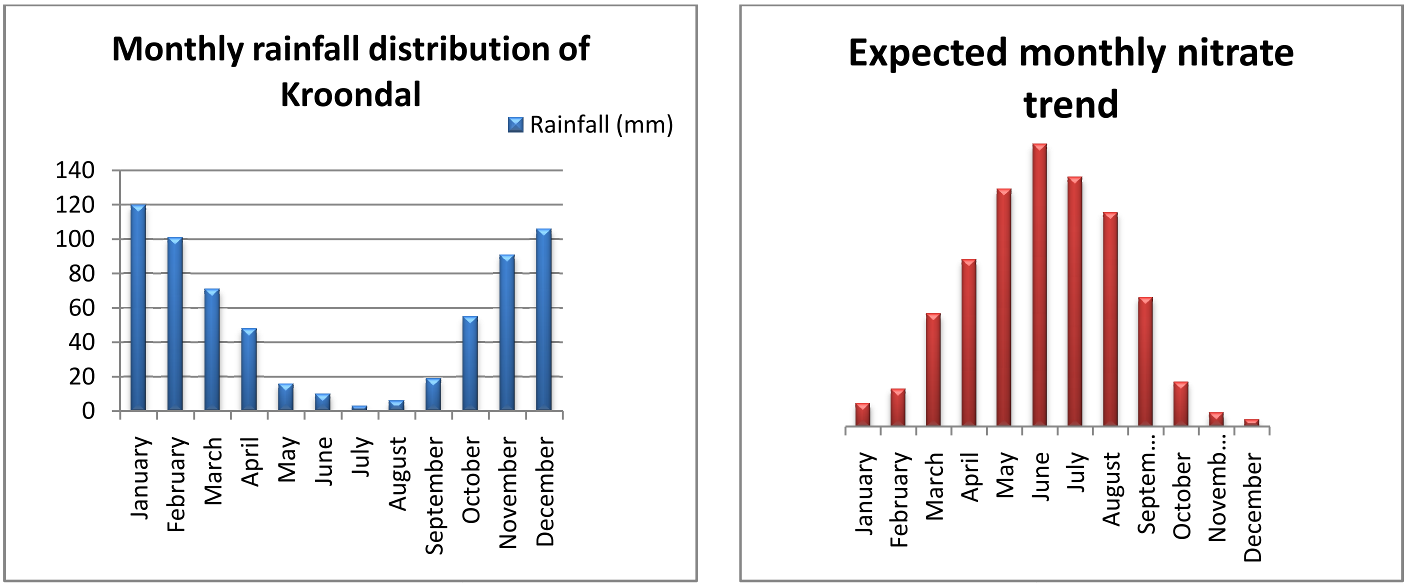


**Figure 6-1** *Anticipated monthly nitrate behaviour based on monthly rainfall distribution of Kroondal*

A list of assumed possible nitrate sources (looking at the study site and its immediate surroundings) was made and recorded as follows:

- Kroondal township pit latrines (human waste)
- Crocodile farm (animal waste)
- Explosives (ANFO)
- Kroondal farms (fertilisers)
- The mine plant (nitrogen cycle-fixation contribution)

The *E.Coli* analysis was chosen and seen as best fit within this investigation for exposing human and animal debris. Hydrogen and nitrogen isotopes for exposing nitrate sources, looking at phosphate levels for fertiliser contribution and the overall water chemistry to help conclude. Based on the fact that natural hardness is influenced by the geology of a catchment and the presence of soluble calcium and magnesium minerals (Pichler and Schmitt-Rietgraf, 1997); very hard water would then typically be attributed to elevated calicium/magnesium values. The dominance in magnesium cations was also expected to be relatively high as this is common within Bushveld Igneous Complex aquifers as a result of the abundance within mafic and ultramafic igneous rocks (Pichler and Schmitt-Rietgraf, 1997).

## 6.2 Results

### 6.2.1 Surface water monitoring: Process water quality

Elevated pH values for KMS 02 (Sewage effluent into Erickson dam in South-Eastern corner of Kroondal complex), KMS 03 (Erickson dam in South-Eastern corner of Kroondal complex for underground-return water) and KMS 05 (Settler dam in Kroondal plant area south of plant, next to braai lapa) were recorded as above DWA requirements for the annual averages from 2011 to 2012. There are at least 23 KMS 02 accounts, 22 KMS 03 accounts and nine KMS 05 accounts (since 2009) of monitoring points exceeding DWA pH requirements from 2006 to 2011. Elevated pH values range from 8.54 to 9.04. It is evident from the fore mentioned information that elevated pH values are not a new phenomena and date as far back as 2006. Treatment in this regard is required. The same can be mentioned with respect to EC. Elevated EC values for KMS 05, KMS 06 and KMS 11 were recorded as above DWA requirements from 2006 to 2011. There are at least 26 KMS 05 accounts, 49 KMS 06 accounts and 41 KMS 11 accounts of monitoring points exceeding DWA EC values from 2006 to 2011. Elevated EC values ranged from 151 to 354.80 mS/m. It is also evident from the fore mentioned information that elevated EC values are not a new phenomena and date as far back as 2006. Elevated process water EC values were recorded for KMS 05, KMS 06 and KMS 11 in 2011. KMS 05's (settler dam) progress could not be quantified due to non sampling in 2012. KMS 06 showed a decrease (204.70 to 180.50 mS/m) in EC values from 2011 to 2012. The 2012 EC data for KMS 06 is more representative (12 samples) compared to the exaggerated 2011 data for KMS 06 (two samples). KMS 07 (run off plant water) increased from a stable (146.20 mS/m) EC to an elevated (171.50 mS/m) EC. This rise can be attributed to the TDS values increasing from 2011 (641.60 mg/l) to 2012 (1018 mg/l).

### 6.2.2 Surface water monitoring: Receiving water quality

The pH values for KMS 01 (Upstream point of the Kroondal tributary) and KMS 17 (Farmer's dam receiving water from overflowing vent shaft dam) were recorded as above DWA requirements for the annual averages from 2011 to 2012. There are at least five KMS 01 accounts and 31 KMS 17 accounts of monitoring points exceeding DWA pH requirements from 2007 to 2011. Elevated pH values range from 8.51 to 9.77. The elevated pH values are not a new phenomena and date as far back as 2007. The increase (8.38 to 8.90) in KMS 01 pH from 2011 to 2012 appears due to a decrease from five to two sampling records from 2011 to 2012. KMS 17 remained elevated in both 2011 and 2012 and didn’t show significant change in elevated levels from 2011 (8.69) to 2012 (8.70). Elevated EC values for KMS 08 (downstream point of Sand Spruit tributary, near (downstream of) Return water dam), KMS 09 (discharge from crocodile farm into Sand Spruit tributary), KMS 12 (Kroondal tributary downstream of Crocodile farm, upstream of Return Water Dam), KMS 15 (Hex River downstream of Sand Spruit tributary) and KMS 17 (Farmer's dam receiving water from overflowing Vent shaft dam) was recorded as above DWA requirements from 2006 to 2011. There are at least 31 KMS 08 accounts, 34 KMS 09 accounts, 21 KMS 12 accounts, 21 KMS 15 and 32 KMS 17 accounts of monitoring points exceeding DWA EC requirements from 2007 to 2012. Elevated EC values ranged from 73 to 267.7 mS/m. Although elevated in EC values, KMS 09 showed decreasing EC values from 2011 (142 mS/m) to 2012 (129.80 mS/m). KMS 12 showed a slight increase from 2011 (94.98 mS/m) to 2012 (95.7 mS/m) and can be attributed to the sharp increase in TDS values from 479.8 to 606.20 mg/l. KMS 17 displayed a sharp rise in EC values from 72.36 to 96.5 mS/m and can also be attributed to TDS values almost doubling from 375.40 to 620.60 mg/l. KMS 08 elevated from 44.20 to 103.10 mS/m and is attributed to a very sharp TDS increase from 213.30 to 603.90 mg/l.

### 6.3.1 Ground water quality

Monitored ground water displayed elevated magnesium levels in boreholes KMB 18 and KMB 19 (monitored once). In 2012, elevated magnesium levels were observed in all the monitored boreholes KMB 05. Elevated magnesium levels are typical of the Bushveld

Igneous Complex and have been observed even in benchmark data. The ground water monitoring therefore displays fresh water with elevated nitrate. In 2011, KMB 18 and KMB 19 (sampled once) were elevated with values of 12.88 mg/l and 22.16 mg/l respectively. Values were however acceptable in 2012 as 8.57 mg/l and 8.75 mg/l respectively. An increase in nitrate from acceptable to unacceptable was observed in KMB 03, KMB 03s and KMB 06 (sampled once). The increase in KMB 03 from 2011 (5.40 and 4.76 mg/l) to 2012 (24.94 and 25.71 mg/l) is a significant one and further attention is required to investigate monitoring point KMB 03. EC levels ranged from acceptable to unacceptable. KDL 01 and KDL 04 displayed elevate EC levels of 185 and 174 mS/m in July respectively. However, the EC values were at acceptable levels in September with EC levels of 90.9 and 94.9 mS/m respectively. KDL 06 increased from July to September in elevated calcium, sodium and chloride values. The elevations above requirements are more than fourfold for calcium, sodium and chloride. Underground water sampling was conducted only in July and September and future sampling will prove beneficial to analysing water quality data.

### 6.3.2 Nitrate levels

In the receiving environment (surface water) of 2011; KMS 09, KMS 13, KMS 14 and KMS 15 remained within acceptable DWA nitrate levels. KMS 01 (two samples), KMS 09, KMS 13 and KMS 14 remained within acceptable DWA nitrate levels in 2012. A sharp increase from 2011 (3.59 mg/l) to 2012 (24.50 mg/l) was observed in KMS 15 (Hex River upstream of Sand Spruit). Ground water monitoring nitrate concentrations for KMB 05 (north of Gemini section) and KMB 20 (crocodile farm owner’s house) have remained well within the ideal nitrate ranges since 2006. Ground water sample collections in September 2012, only KDL 01 and KDL 05 showed nitrate levels exceeding DWA requirements of 23.2 and 52 mg/l respectively. Isotopes of collected ground water samples in September 2012 attribute the following sources:

- Soil $NH_4^+$ (KDL 07 and KDL 08).
- Manure and septic waste (KDL 01, KDL 04 and KDL 05)
- KDL 06 outlying behaviour

According to Usher and Pretorious (2008); stable nitrogen and oxygen isotopes are useful in indicating sources when nitrate is present in surface or ground water. Delta nitrate-nitrogen (δ15N nitrate) and nitrate-oxygen (δ18O nitrate) isotope ratios in water can be used to identify nitrate sources and their fate. Nitrogen has two stable isotopes: 14N, with a natural abundance of 99.63% and 15N, with a natural abundance of 0.37%. The wide difference in the isotopic abundance can be used to determine distinctive isotopic signatures to define specific natural occurrences and sources arising from human activities. An approach to isotope study is to analyse samples for both nitrogen and oxygen isotopes in the nitrate in the water. This so-called dual approach to identification of the nitrate origin was used in the investigation (Usher and Pretorious, 2008). Explosives are expected to show low δ15N nitrate and δ18O nitrate values (typical explosives signatures include a range of δ15N nitrate and δ18O nitrate of 3-3.6 and 1 to 1.1 respectively). The collected underground water samples did not reflect this.

## 6.4 Management options

The following options at Xstrata together with SLR Consulting (2011) have been considered for the treatment/management of ground water in the near future:

- Surface and ground water monitoring
- Stormwater management at surface
- Reverse Osmosis
- Eco- Dosing
- Biological De-Nitrification
- Effective Management of Ground water

### 6.4.1 Surface and ground water monitoring network

Aquatico Scientific currently undertakes the surface and ground water monitoring for Xstrata to meet the EMP requirements. The monitoring network for both surface and ground water needs to be constantly revisited and updated according to associated risks.

### 6.4.2 Stormwater management at surface

Increased nitrate concentrations in surface waters are suspected to be primarily a result of runoff from waste rock dumps, high in nitrate explosive residues. At present, the management of stormwater following significant rainfall events is not ideal, with facilities typically undersized (SLR Consulting, 2011). Once the conceptual stormwater management plan is implemented with infrastructure appropriately sized and lined; stormwater high in nitrate concentrations can be managed as dirty water and appropriately contained and treated. Further to this, clean water will not be mixed with dirty water to further reduce the quantity of dirty water requiring management.

### 6.4.3 Reverse Osmosis

Reverse Osmosis (RO) provides an option to treat contaminated water pumped from underground by feeding it to a clarifier with coagulant added (Israel *et al.*, 2011). According to SLR Consulting (2011), this will enable the sludge to settle and be removed as underflow into a pre-filtration tank where it is backwashed using clean water. Ozone can be added prior to further filtration with filter cake chemically inserted ready for disposal. The filtrate can then be combined with the clarifier overflow for further treatment in the RO plant. The solution will contain soluble salts and metals, with backwash water, ozone and chlorine added to produce clean water, of potable standard as well as chemically inert solids which can be safely disposed of.

### 6.4.4 Eco-Dosing

According to SLR Consulting (2011); Eco-Dosing (ED) provides a system consisting of an electron generator, coupled to an electrochemical reactor housing a specified number of confined metal electrodes which are configured to effect the predetermined de-pollution of a particular waste water stream. The reactor will treat waste water (called an electrolyte at this stage of the process) via confined metal electrodes being suspended in the electrolyte flow, allowing for the passing of an electric current, generating a number of reactive chemical species. These reactive species are engineered and manipulated to convert, destroy, react with or precipitate out the pollutants. The resultant product is then separated to produce clean water. The Xstrata Boshoek Smelter is currently testing the effectiveness of using the ED system to remove Chrome VI from their water. The result of this testing will provide the basis for the potential of treating dirty water at other Xstrata operations.

### 6.4.5 Biological De-nitrification

Biological De-nitrification (BD) is a process by which Nitrates are converted into Nitrogen which is then released into the ambient air (Lin and Wu, 1996). The BD process does however require the addition of carbon to act as a substrate for the microorganisms to metabolise. This can be done in a BD plant. According to SLR Consulting (2011), a natural alternative to the establishment of a BD plant is to develop an artificial wetland or reed-bed facility, successfully implemented in South Africa. These facilities act as biofilters removing both sediment as well as contaminants. The challenge is to establish an appropriately positioned sustainable low-energy facility. The low-energy of the wetland becomes a key consideration in the effectiveness of the facility in allowing sufficient filtration and reaction time for the removal of sediment and conversion of contaminants (nitrate).

### 6.4.6 Effective management of ground water

Increased nitrate concentrations in ground water are suspected to be primarily a result of high nitrate concentrations in explosive residues from underground blasting, highly mobilised once in contact with water. A secondary cause is seepage from the tailings dam, waste rock, as well as from surface water high in nitrate concentrations. According to SLR Consulting (2011), an effective management measure in this regard is to manage the ground water level at a point below the blasting/mining level. This would mean that mine dewatering should take place via strategically placed boreholes located a distance from the blasting/mining area, allowing for sufficient drawdown of ground water to a point below the blasting/mining area. This would not only allow for a reduced nitrate contamination in the ground water, but will also allow for a reduced clean water requirement currently supplied by Magalies Water. This is because dewatered water should be of a cleaner nature than present due to the limited exposure to the blasting/mining area and will not have high suspended solid counts. Platinum and chrome mines, as well as gold and coal mines, have for many years altered the hydrogeological and hydrological flows of the aquifers and catchments to create anthropogenic or “manmade” conditions (SLR Consulting, 2011). This typically results in artificial recharge (AR) zones where surface water percolates through to the ground water, exacerbating the problem of managing water in the underground mining area. It is therefore important to acknowledge the interaction between surface and ground water at previously rehabilitated opencast areas. Primary to surface flows are the destruction of the subsoil conditions, especially drainage channels with often much higher permeability after mining. During rainfall events this results in higher recharge into the subsoil and aquifers. Aquifer conditions also changed substantially. Pre-mining, most of the aquifers were semi-confined aquifers with low effective porosities of $10^{-5}$% (SLR Consulting, 2011), compared to the now backfilled open pits consisting mostly of fresh norite and anorthosite gravel and boulders with effective porosities of up to 25%. The pits are up to 40 mbgl whereas the natural ground water levels may range from 15 to 20 mbgl. As a result, ground water is continuously discharged from the semi-confined to the unconfined systems. Mining activities by default lead to enhanced recharge conditions and further to this large primary aquifers were created which store large volumes of water. The Kroondal operation is such a case already affected by AR and needs to develop site-specific strategies to manage it more effectively. Linked to this is a delicate salt balance and with mostly inert rocks, only natural cycles e.g. nitrate need to be managed, with no or limited acid rock drainage expected.

# Chapter 7 Conclusion and recommendations

Process water monitoring localities at Kroondal remained relatively stable during the annual periods of 2011 and 2012, but notable fluctuation in salts and nitrate concentrations were evident. The bacteriological monitoring localities presented significant levels of total coliforms and *E coli, indicating* inefficient treatment by the wastewater treatment plant.

In the receiving environment*;* the Hex River upstream from Kroondal revealed a stable profile during the annual periods of 2011 and 2012. Increasing concentrations (especially in terms of EC and TDS) could be seen for the annual periods at the upstream Hex River locality. The downstream locality exhibited stable to slightly increasing TDS and EC concentrations toward the end of 2012.

Groundwater quality within the Kroondal Chrome mining area varied from good to marginal with respect to potable quality guidelines. In some boreholes the chemical parameters exceeded the maximum permissible ranges for domestic use and significant increases in the groundwater sulphate, magnesium and nitrate content were measured down gradient from the tailings dam. Unlined surface water structures like dams, canals and trenches impact on the natural ground water level and inversely, mine voids cause the dewatering of the surrounding aquifer. The response of groundwater levels on seepage or dewatering has to be monitored to enable a good understanding of flow impacts, which in turn will directly influence ground water migration rate and direction. New monitoring boreholes should be developed in the place of demolished boreholes and a complete monitoring program that covers all known and potential sources should be reinstated. Ground water is a vital resource and requires constant protection and observation to ensure water remains as clean as possible. Possible origins of elevated nitrate levels in ground water (Table 7-1) were looked at and argued as previously rehabilitated opencast work, natural state chemistry and explosives.

**Table 7-1** *Possible causes of elevated nitrate levels at Kroondal chrome mine*

| Causes | Effects |
|---|---|
| Previously rehabilitated opencast work | Recharging into existing mine work |
| Natural state chemistry | Typical Bushveld Igneous Complex conditions |
| Low phosphate and ammonia values | Fertilisers an unlikely source |
| Low delta nitrogen and oxygen values | Fertilisers an unlikely source |
| High delta nitrogen and oxygen values | Manure and septic waste<br>Amonium soil |

The planned water management projects (Table 7-2) are already behind schedule and implementation of projects should commence as soon as possible. Currently a storm water management plan has been conducted but a water balance and implementation of the storm water management plan remains outstanding.

**Table 7-2** *Future work between SLR Consulting and Xstrata Kroondal mine.*

| **Date** | **Water resource management element** | **Description of activity** | **Deliverable** |
|---|---|---|---|
| Oct 2011 | Detailed design of SWMP | Design for use in construction | Detailed design of SWMP |
| Dec 2011 | Construction Phase 1 | Construction of upstream clean diversion | Constructed infrastructure |
| Nov 2011 | Update of dynamic water balance | Daily rainfall driven dynamic water balance | Dynamic water balance |
| Nov 2011 | Development of Integrated Ground water Resource Management Plan (IGRMP) | Use existing reports and site visits to develop IGRMP | Report capturing borehole positions and technical details |
| Jan 2012 | Phase 1: Drilling of dewatering boreholes | Drill and test boreholes at identified positions | 3 dewatering boreholes |
| Apr 2012 | Phase 2: study to allocate or treat bore water | Sample over 3 month period to view quality and identify appropriate use | Report specifying quality and recommend use |
| Jul 2012 | Phase 3: Infrastructure to manage bore water | Equipping boreholes and convey to user | Equipped boreholes/ small reservoir |
| Oct 2012 | Phase 4: Placement of impermeable layers | Layers will control artificial recharge | Sealed drainage area over rehabilitated areas |
| Feb 2013 | Construction Phase 2 | Construction of dirty water berms and channels | Constructed infrastructure |
| Oct 2013 | Construction Phase 3 | Construction of dirty storm water dams | Constructed infrastructure |

The options which have been considered for the treatment/management of ground water in the near future include:

- Surface and ground water monitoring
- Stormwater management at surface
- Reverse Osmosis
- Eco- Dosing
- Biological De-Nitrification
- Effective Management of Ground water

Currently surface and ground water monitoring programmes exist within the mine but management in this regard is important to monitor all boreholes in place. Storm water management at the surface is in its inception (design phase) and implementation thereof is to follow. Bio remediation seems the best treatment option in that it's a cheap, fast and natural process. Regulatory concerns and bio mass build up are of concern, but this method seems most viable. Possible mitigation measures for contaminant limiting contaminant plume migration include the reclamation of the tailings dam product, which will result in the removal of the source for contamination. Alternatively, a pump-and-treat approach could be taken where dewatering of the mine workings could be continued to remove contaminated water from the system and the water is stored in lined pollution control dams to be treated at a later stage. Different management options can however be investigated before closure.

It is important to eliminate the development of subsidence to surface through sound underground mine planning and leaving sufficient pillars and barrier zone along shallow sub outcrop zones. The footprint of dirty areas, such as the pollution control dams, stockpile areas, workshops and diesel storage areas will have to be minimised. The storm water management plans in place at the site should be adhered to and updated as new surface infrastructure is implemented in the future. Static ground water levels should be monitored as mentioned to ensure that any deviation of the ground water flow from any idealised predictions is detected in time. Monitoring results must be interpreted annually by a water specialist (hydrologist/geohydrologist) and network audited annually as well to ensure compliance with regulations. There are currently defunct shafts and old exploration boreholes (hydrocensus) which must be sealed off. Boreholes should be drilled into the mine workings so that the rate of flooding and water level recovery and quality could be established. Stage curves could also aid in the management of the closure phase. A detailed mine closure plan should be prepared during the operational phase, including a risk assessment, water resource impact prediction as stipulated in the DWA Best Practice Guidelines (EMPR, 2009). The implementation of the mine closure plan and the application for the closure certificate can be conducted during the decommissioned phase. Monitoring of mine/process water is critical in order to validate the geochemical assessment. A geochemical model could be constructed that assess the effectiveness of potential mitigation measures during the operational phase so that mitigation measures could be implemented. The following objectives are envisaged for the closure phase (EMPR, 2009):

- Obtain ground water closure objectives approved by government
- Continue ground water quality and level monitoring
- Minimise infiltration and run off from tailings

Negotiations will have to take place to obtain ground water closure objectives approved by government during the decommissioning phase of the project (based on the results of the monitoring information obtained during the construction and operational phases of the project, and through verification of the numerical model constructed for the project). Ground water quality and groundwater level monitoring for a period of two to four years after mining ceases will prove useful in order to establish post-closure ground water levels and quality trends. The monitoring information will have to be used to update, verify and recalibrate the predictive tools used during the study to increase the confidence in the closure objectives and management plans. It is recommended that water monitoring continue up to two years after production has stopped. This information should be used to update the long-term predictions. Infiltration of rain water into the tailings material must be minimised and ponding of rain water on top of the tailings dam must be prevented. Results of the monitoring programme could then be presented to Government on an annual basis, with the post closure monitoring programme re-evaluated on an annual basis in consultation with Government. Several action plans are required post closure of the mine, with the most obvious being to seal all the vent shafts. Multiple-level monitoring wells must be constructed to monitor base flow quality within the identified sensitive zones and to monitor ground water level behaviour in the underground workings. The results of the monitoring programme to should be used to confirm/validate the predicted impacts on ground water availability and quality after closure. A pollution control dam could be used to intercept polluted seepage water from rehabilitated tailings dams and waste rock dumps. This should be considered if it is found that the Hex River and the Sand Spruit and Kroondal tributaries are negatively affected by pollution (regular sampling of these surface water bodies is essential). The implementation of as many closure measures during the operational phase, while conducting appropriate monitoring programmes to demonstrate actual performance of the various management actions during the life of mine is needed. The ground water monitoring network design should comply with the risk based source pathway-receptor principle. A ground water monitoring network should contain monitoring positions which can assess the groundwater status at certain areas. Both the impact on water quality and water quantity should be catered for in the monitoring system. The boreholes in the network should cover the contaminant sources, receptors and potential contaminant plumes. Furthermore monitoring of the background water quality and levels is also required. Ground water monitoring should also be conducted to assess the impact of mine dewatering on the surrounding aquifers, ground water inflow into the mine works and ground water quality trends. This will be done by monitoring of ground water levels in the monitoring boreholes as well as measuring water volumes pumped from mining areas; and sampling of the ground water in the boreholes at the prescribed frequency. The position of the sealed shafts should be monitored visually to determine if any seepage emanates from these pathways.

In the process water, elevated pH and EC were observed. Elevated pH values for KMS 02, KMS 03 and KMS 05 were recorded as above DWA requirements for the annual averages from 2011 to 2012. Elevated pH values ranged from 8.54 to 9.04 with such elevated trends dating back to 2006. The same can be mentioned with respect to EC, elevated EC values for KMS 05, KMS 06 and KMS 11 were recorded as above DWA requirements. Elevated EC values ranged from 151 to 354.80 mS/m also dating back to 2006. Treatment in this regard is required. In the receiving water, elevated pH and EC were observed. The pH values for KMS 01 and KMS 17 were recorded as above DWA requirements for the annual averages from 2011 to 2012. Elevated pH values range from 8.51 to 9.77 dating from 2007. Elevated EC values for KMS 08, KMS 09, KMS 12, KMS 15 and KMS 17 were recorded as above DWA requirements from 2006 to 2011. Elevated EC values ranged from 73 to 267.7 mS/m. Although elevated in EC values, KMS 09 showed decreasing EC values from 2011 (142 mS/m) to 2012 (129.80 mS/m). Sharp increases in EC (KMS 12 and KMS 17) were directly proportional to the doubling in TDS values.

Monitored ground water displayed elevated magnesium and EC levels. In boreholes KMB 03, KMB 03s, KMB 05, KMB 06, KMB 18 and KMB 19 from 2011 to 2012. Elevated magnesium levels are typical of the Bushveld Igneous Complex and have been observed even in benchmark data. EC levels ranged from acceptable to unacceptable. KDL 01 and KDL 04 displayed elevated EC levels in July; however EC values were at acceptable levels in September. KDL 06 increased from July to September in elevated calcium, sodium and chloride values. The elevations above requirements are more than fourfold for calcium, sodium and chloride. Underground water sampling was conducted only in July and September and future sampling will prove beneficial to analysing water quality data.

In the receiving environment (surface water) of 2011; KMS 09, KMS 13, KMS 14 and KMS 15 remained within acceptable DWA nitrate levels. KMS 01, KMS 09, KMS 13 and KMS 14 remained within acceptable DWA nitrate levels in 2012. Ground water monitoring nitrate concentrations for KMB 05 (north of Gemini section) and KMB 20 (crocodile farm owner's house) have remained well within the ideal nitrate ranges since 2006. Ground water sample collections in September 2012, only KDL 01 and KDL 05 showed nitrate levels exceeding DWA requirements. Explosives are expected to show low δ15N nitrate and δ18O nitrate values (typical explosives signatures include a range of δ15N nitrate and δ18O nitrate of 3-3.6 and 1 to 1.1 respectively). The collected underground water samples did not reflect this.

Overall, the ground water monitoring displayed fresh water with elevated nitrate. In 2011, KMB 18 and KMB 19 were elevated, but values were however acceptable in 2012. An increase in nitrate from acceptable to unacceptable was observed in KMB 03, KMB 03s and KMB 06. The increase in KMB 03 from 2011 (5.40 and 4.76 mg/l) to 2012 (24.94 and 25.71 mg/l) is a significant one and further attention is required to investigate monitoring point KMB 03. It must be stressed that boreholes should be re-instated where monitoring no longer occurs and the surface and ground water monitoring network should be well managed.

# Chapter 8 References

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# Appendix

### Appendix A1 Electroneutrality of monitored surface water for 2011 and 2012.

| **2011** | | | **2012** | |
|---|---|---|---|---|
| **Site name** | **E.N. (%)** | **Accuracy** | **E.N. (%)** | **Accuracy** |
| **KMS 01** | -1.39 | Accurate | 1.05 | |
| **KMS 02** | 1.29 | Accurate | 0.12 | Accurate |
| **KMS 03** | 2.45 | Accurate | 0.24 | Accurate |
| **KMS 05** | 0.85 | Accurate | | |
| **KMS 06** | 1.47 | Accurate | 0.02 | Accurate |
| **KMS 07** | 1.37 | Accurate | 0.82 | Accurate |
| **KMS 08** | 0.61 | Accurate | 0.18 | Accurate |
| **KMS 09** | -1.88 | Accurate | -0.42 | Accurate |
| **KMS 11** | 1.16 | Accurate | -1.07 | Accurate |
| **KMS 12** | 0.84 | Accurate | -2.7 | Accurate |
| **KMS 13** | 0.95 | Accurate | 0.1 | Accurate |
| **KMS 14** | -0.19 | Accurate | 0.19 | Accurate |
| **KMS 15** | 0.47 | Accurate | 0.56 | Accurate |
| **KMS 16** | 1.96 | Accurate | -1.09 | Accurate |
| **KMS 17** | 2.46 | Accurate | -0.23 | Accurate |

### Appendix A2 Electroneutrality of monitored ground water for 2011 and 2012.

| **2011** | | | **2012** | | |
|---|---|---|---|---|---|
| **Site name** | **EN (%)** | **Accuracy <5%** | **Site name** | **EN (%)** | **Accuracy <5%** |
| KMB 03 | 0.4 | Accurate | KMB 03 | -2.6 | Accurate |
| KMB 03s | 0.6 | Accurate | KMB 03s | -0.6 | Accurate |
| KMB 05 | -3.2 | Accurate | KMB 05 | -1 | Accurate |
| KMB 18 | 1.8 | Accurate | KMB 18 | 3.1 | Accurate |
| KMB 19 | -2.6 | Accurate | KMB 19 | 4.1 | Accurate |
| KMB 20 | 0.6 | Accurate | KMB 20 | -4.2 | Accurate |

### Appendix A3 Elecroneutrality of collected ground water samples.

| **Sample** | **July EN (%)** | **Accuracy** | **Sample** | **Sept E.N. (%)** | **Accuracy (<5%)** |
|---|---|---|---|---|---|
| **KDL01** | -3.10 | Accurate | KDL 01 | 2.87 | Accurate |
| **KDL02** | 2.90 | Accurate | KDL 04 | -2.73 | Accurate |
| **KDL03** | 0.50 | Accurate | KDL 05 | 5.27 | Inaccurate |
| **KDL04** | 4.10 | Accurate | KDL 06 | -1.84 | Accurate |
| **KDL05** | 3.20 | Accurate | KDL 07 | -2.66 | Accurate |
| **KDL06** | 3.50 | Accurate | KDL 08 | 0.88 | Accurate |

## Appendix B1 Electric Conductivity of monitored surface water for 2011 and 2012.

| SiteName | 2011 | | | 2012 | | |
|---|---|---|---|---|---|---|
| | E.C. (µS/cm) | Cations (meq/l) | Anions (meq/l) | E.C. (µS/cm) | Cations (meq/l) | Anions (meq/l) |
| **KMS 01** | 6.8 | 6.97 | 7.17 | 6.99 | 8.17 | 8 |
| **KMS 02** | 13.15 | 13.77 | 13.42 | 9.08 | 11.6 | 11.58 |
| **KMS 03** | 11.5 | 12.49 | 11.89 | 8.66 | 11.18 | 11.13 |
| **KMS 05** | 15.2 | 14.72 | 14.47 | 17.34 | 19.74 | 19.74 |
| **KMS 06** | 20.47 | 20.88 | 20.27 | | | |
| **KMS 07** | 14.62 | 14.61 | 14.21 | 16.68 | 18.81 | 18.5 |
| **KMS 08** | 4.42 | 4.63 | 4.57 | 9.24 | 10.63 | 10.59 |
| **KMS 09** | 14.17 | 14.96 | 15.53 | 13.15 | 16.17 | 16.31 |
| **KMS 11** | 15.36 | 14.95 | 14.61 | 17.59 | 20.23 | 20.67 |
| **KMS 12** | 9.5 | 10.3 | 10.13 | 9.91 | 11.65 | 12.3 |
| **KMS 13** | 3.41 | 3.92 | 3.85 | 5.85 | 7.24 | 7.22 |
| **KMS 14** | 3.01 | 3.47 | 3.48 | 3.63 | 4.1 | 4.09 |
| **KMS 15** | 3.51 | 3.65 | 3.61 | 8.1 | 7.64 | 7.55 |
| **KMS 16** | 12.22 | 13.42 | 12.9 | 11.21 | 13.28 | 13.57 |
| **KMS 17** | 7.24 | 8 | 7.62 | 9.45 | 11.49 | 11.55 |

## Appendix B2 Electric Conductivity of monitored ground water for 2011 and 2012.

| Site Name | 2011 | | | 2012 | | |
|---|---|---|---|---|---|---|
| | E.C. (µS/cm) | Cations (meq/l) | Anions (meq/l) | E.C. (µS/cm) | Cations (meq/l) | Anions (meq/l) |
| **KMB 03** | 11.79 | 13.6 | 13.48 | 14.52 | 17.54 | 18.43 |
| **KMB 03s** | 11.32 | 12.71 | 12.56 | 14.13 | 17.88 | 18.09 |
| **KMB 05** | 11.51 | 12.38 | 12.3 | 10.5 | 13.11 | 13.34 |
| **KMB 06** | | | | 12.72 | 14.4 | 13.07 |
| **KMB 18** | 11 | 13.09 | 12.61 | 8.32 | 11.81 | 11.11 |
| **KMB 19** | 14.5 | 16.83 | 17.66 | 8.66 | 11.49 | 10.61 |
| **KMB 20** | 8.92 | 9.91 | 9.76 | 9.4 | 9.09 | 9.85 |

## Appendix B3 Electric Conductivity of collected ground water samples for July 2012.

| Sample | July | | | September | | |
|---|---|---|---|---|---|---|
| | EC (µS/cm) | Cations (meq/l) | Anions (meq/l) | E.C. (µS/cm) | Cations (meq/l) | Anions (meq/l) |
| **KDL01** | 18.5 | 19.03 | 12.56 | 81.2 | 10.42 | 9.84 |
| **KDL02** | 10.1 | 12.14 | 10.01 | | | |
| **KDL03** | 13 | 14.23 | 9.64 | | | |
| **KDL04** | 17.4 | 20.42 | 12.04 | 9.49 | 11.04 | 11.66 |
| **KDL05** | 7.5 | 8.89 | 8.02 | 17.2 | 20.46 | 18.41 |
| **KDL06** | 9.2 | 12.24 | 11.01 | 7.8 | 68.84 | 71.42 |
| **KDL 07** | | | | 7.79 | 8.62 | 9.1 |
| **KDL 08** | | | | 9.09 | 9.24 | 9.08 |

## Appendix C1 Saline water classification (Lehr, 1980).

| Classification | Total Dissolved Solids (mg/l) |
|---|---|
| **Freshwater** | 0 – 1000 |
| **Slightly saline** | 1 000 – 3 000 |
| **Moderately saline** | 3 000 – 10 000 |
| **Very saline** | 10 000 – 35 000 |
| **Briny** | >35 000 |

## Appendix C2 Hardness classifications (DWA, 1996).

| Hardness range (mg $CaCO_3$) | Description of hardness |
|---|---|
| 0-50 | Soft |
| 50-100 | Moderately soft |
| 100-150 | Slightly hard |
| 150-200 | Moderately hard |
| 200-300 | Hard |
| >300 | Very hard |

## Appendix C3 Permit 2118 for process and receiving water quality exemptions

| Variable (mg | 3.1 Receiving | 3.2 Process |
|---|---|---|
| **pH** | 6-8.5 | 6-8.5 |
| **EC** | <70 | <150 |
| **$NO_3$_N** | <6 | <12 |
| **$SO_4$** | <200 | <400 |
| **F** | <1.5 | <1.5 |
| **Cl** | <100 | <200 |
| **Na as SAR** | <1.5 | <1.5 |

## Appendix C4 DWA bacteriological water quality standards.

| Category | E. coli | Total Coliform | Heterotrophic |
|---|---|---|---|
| **Ideal** | 0 | 0 | 100 |
| **Good** | 0-1 | 0-10 | 1000 |
| **Marginal** | 1-10 | 10-100 | 10 000 |
| **Poor** | 10-100 | 100-1000 | >10 000 |
| **Unacceptable** | >100 | >1000 | - |

## Appendix D1 δ2H and δ18O Analysis (Standard deviation n=3)

| Sample Name | δ $^{2}$H Reportable Value (permil) | δ $^{2}$H Standard Deviation (permil) | δ $^{18}$O Reportable Value (permil) | δ $^{18}$O Standard Deviation (permil) |
|---|---|---|---|---|
| **KDL 01** | -9.89 | 0.91 | -2.02 | 0.15 |
| **KDL 04** | -3.45 | 1.63 | -0.93 | 0.11 |
| **KDL 05** | -4.29 | 0.4 | -1.54 | 0.28 |
| **KDL 06** | -17.99 | 1.33 | -3.59 | 0.15 |
| **KDL 07** | -8.56 | 1.92 | -2.15 | 0.25 |
| **KDL 08** | -10.24 | 1.76 | -2.13 | 0.17 |

## Appendix D2 Sample values against the global meteoric water line