ISOTOPIC FINGERPRINTING OF GROUNDWATER NITRATE SOURCES AROUND ANGLO PLATINUM'S RPM MOGALAKWENA OPERATION (LIMPOPO PROVINCE, SOUTH AFRICA)

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ABSTRACT

In response to allegations made by the NGO ActionAid in early 2008 that the highly elevated nitrate levels found in groundwater in communities adjacent to Anglo's RPM Mogalakwena operation originate from activities at the platinum mine, Anglo American conducted isotope studies (both in-house and through independent researchers) with the aim to identify the natural and anthropogenic groundwater nitrate sources in the area. Results of the in-house study are presented in this paper.

The results of this study demonstrate that at least three isotopically distinct nitrate end-member sources exist in the area and that mixing between these end-members can readily explain the observed compositional variations in the dataset. One of the identified end-member sources is nitrate from community-related septic waste or manure, and contamination from this source is shown to be the most likely cause of highly elevated groundwater nitrate contents in Ga-Molekana village. In contrast, effluents from the mine can be ruled out as a source of nitrate in groundwaters at Ga-Molekana on the basis of the isotopic/hydrochemical data and the westerly/south-westerly groundwater flow direction in the area.

Another important nitrate end-member source identified in the area is isotopically consistent with nitrate from soil or possibly from waste rock material, as suggested by leachate data for rock material from a blast site in the Zwartfontein South Pit. The limited data available to date suggest that the source of this end-member may lie within the mine area. Mixing calculations suggest, however, that prior to the addition of nitrate from this end-member the waters must have already had highly elevated nitrate concentrations, probably due to contamination with nitrate from community-related septic effluents or manure upstream from the operation. The extent to which nitrate fluxes from the soil/waste rock end-member to the groundwater are natural or are enhanced/caused by mining-related activities is the subject of ongoing investigation.

1. INTRODUCTION

In early 2008 the NGO ActionAid International released a report in which it made damaging and emotive allegations with regard to the negative environmental and socio-economic impact of Anglo Platinum's operations in Limpopo province. One of these allegations was that highly elevated groundwater nitrate values in communities adjacent to Anglo's RPM Mogalakwena operation originate from blasting and other activities at the platinum mine.

Although mine explosives represent a potential source of groundwater nitrate (Forsberg and Åkerlund, 1999) and earthmoving activities at mining operations may lead to the enhanced release of soil nitrate into the groundwater (Tredoux, 2004), as suggested by ActionAid, other important natural and anthropogenic nitrate sources exist. The latter include N-containing organic and inorganic fertilizers, animal manure, and discharge of human sewage (Kendall, 1998).

Effective control and management of nitrate contamination of water requires an understanding of the specific nitrate source(s). The latter, however, generally cannot be identified and differentiated using routine chemical analysis of waters alone. In contrast, isotopic analysis of nitrogen and oxygen in nitrate often provides more conclusive information for the fingerprinting of nitrate sources (Kendall, 1998).

In order to identify the sources of groundwater nitrate around the RPM Mogalakwena operation and to address the allegations made by ActionAid, Anglo American conducted isotope studies, both in-house and through external, independent researchers. Results of the in-house study are presented here.

Geological and Hydrological Setting

The study area is located ~30 km northwest of the town of Mokopane and straddles the NNW striking and WSW dipping footwall contact of the northern limb of the Bushveld Complex, which separates ultramafic/mafic cumulate rocks of the Bushveld Complex in the western part of the area from underlying Lower Proterozoic dolomites and Archaean granites/gneisses in its eastern part. Ultramafic/mafic intrusive bodies related to the Bushveld magmatic event occur within the footwall package. PGE-rich magmatic sulfide mineralisation is found along the footwall contact of the complex within a pyroxenitic sequence known as the Platreef.

The aquifers within the study area are highly heterogeneous with poor hydraulic interconnectivity. Most groundwater occurs in pockets of weathering and within steeply inclined fracture systems which are discontinuous, thereby giving the aquifers a semi-confined to confined character.

The groundwater level is generally between 15 and 30 m below the surface and is a subdued reflection of surface topography (Figure 1). Most groundwater flow occurs in the shallow aquifer within 50 m below the groundwater level and only 10% of groundwater flow takes place at depths greater than 50 m. The transmissivity of the shallow aquifer approximates 45 m^2/day and decreases with increasing depth to 10 m^2/day at a depth of 140 m below the water table.

Groundwater flow is predominantly in a south-westerly to westerly direction, as indicated by the yellow arrows on Figure 1. Groundwater abstraction around the tailings dam results in an increased groundwater gradient towards the tailings dam, in particular on its eastern side, and thereby draws water southwest/westwards towards the mine as suggested by numerical modelling.

Sample Collection

Ground- and surface water sampling was carried out in late June 2008 at 15 sites within and around Anglo Platinum's RPM Mogalakwena operation, which were selected for this study by local Anglo Platinum staff.

The sampling locations include the boreholes at the Podile Primary School and the Langalibalele Secondary School in Ga-Molekana village (east of the operation), as well as the Sandsloot creek and windmill well in Old Ga-Pila village (southwest of the operation).

To assess whether any groundwater contamination may be caused by leakage from the tailings dam or the adjacent return water dam, water from the tailings dam and from 5 monitoring boreholes (i.e., RWD-3, RWD-6, RWD-9, RWD-10 and P3) around the two dams was sampled. Furthermore, a sample was collected from borehole OY (Overysel) which is located in an area where, at the time of sampling, surface stripping and drilling was in progress for the development of a new open pit operation.

Samples were also collected from the groundwater seep at the bottom of the Zwartfontein South pit and from the Pollution Control Dam North. At the time of sampling, the latter received water from the Mogalakwena Central pit as well as collected run-off from waste rock dumps during rainfall events.

The samples collected from boreholes SRK-4 and P31 represent background water assumed to be unaffected by anthropogenic inputs.

In addition, samples were also collected of fine-grained rock material from a site in the Zwartfontein South pit where blasting occurred 7 days prior to sampling. Isotopic analysis of water-extractable nitrate from this rock material was considered to be a potential proxy for the isotopic composition of nitrate derived from blasting in the mine.

At each site, separate sample aliquots were collected for the various hydrochemical and isotopic analyses (i.e., cations, anions, alkalinity, dissolved organic carbon, δD and $\delta^{18}O$, $\delta^{34}S$ and $\delta^{18}O$ of sulfate, $\delta^{15}N$ and $\delta^{18}O$ of nitrate). While both filtered (<0.45 μm) and unfiltered water samples were collected and analysed, all data presented in this paper are for filtered samples only. The aliquots for cation analysis were acidified with ultra-pure nitric acid to a pH of <2. The aliquots for isotopic analysis of dissolved nitrate were preserved by addition of appropriate amounts of mercuric chloride.

All samples were kept refrigerated (~4°C) from the time of sample collection in the field until analysis. In line with sampling best practice, duplicate samples were collected at two of the 15 locations to assess the reproducibility of the analytical results. To monitor any potential contamination of the samples by the sampling procedure two blank samples were collected and analysed. Certified reference materials

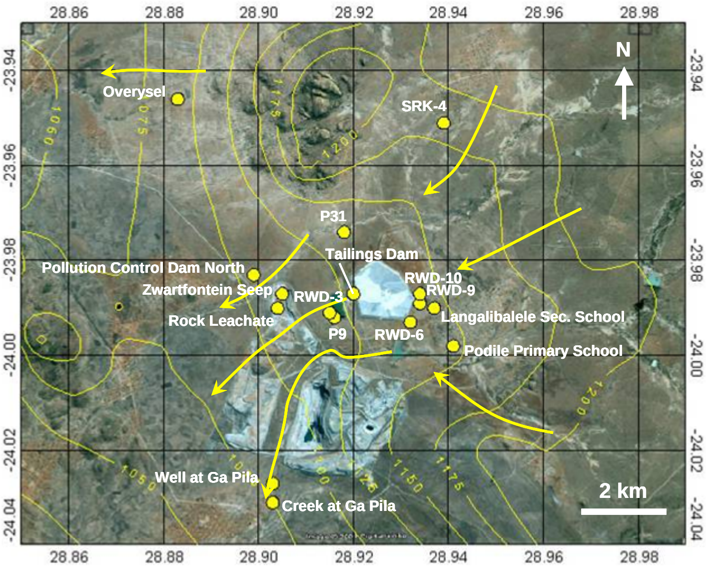


Figure 1. Map of the area around RPM Mogalakwena showing the sampling sites for this study. Also shown are elevation contour lines (25 m intervals) and general groundwater flow directions (yellow arrows). The background image was downloaded from Google Earth. Please note that the Google Earth scene was taken in mid-2004, and thus the outlines of pits, waste rock dumps etc. shown on the image do not reflect their extent at the time of sampling in June 2008.

(TROIS-94 and TM-23.3 issued by Environment Canada) were submitted and analysed along with the samples to assess the overall accuracy of the analytical data.

Water temperature, pH and specific electric conductivity were measured on site. Alkalinity was determined by titration within a few hours of sample collection.

In cases of boreholes with an installed pump (i.e., boreholes P9, P31, OY, Podile Primary School) water was pumped from the borehole for a sufficient time to ensure that the stagnant water in the borehole was replaced by ‘fresh’ water from the aquifer prior to sampling. In cases of boreholes without an installed pump (i.e., boreholes RWD-3, RWD-6, RWD-9, RWD-10, SRK-4, Langalibalele Secondary School) sampling was carried out using a bailer, and thus purging of the borehole prior to sample collection was not possible. However, no systematic chemical differences can be observed between the two types of borehole samples, and therefore it is assumed that the results presented in this paper are not significantly biased by the groundwater sampling procedure.

Detectives of the South African police force were present throughout the 3-day sampling program to oversee sample collection. At each sampling site, all collected sample aliquots were placed together into a numbered forensic bag which was subsequently sealed by the overseeing police detective. After completion of the sampling program, the sealed forensic bags were dispatched by refrigerated courier service to ACME Analytical Laboratories Ltd. in Vancouver (Canada) and to Queen’s University in Kingston (Canada).

Sample Analysis

Cation and anion analyses were carried out at ACME Analytical Laboratories Ltd. in Vancouver, Canada. Apart from nitrate which was determined by ion chromatography, all elements were analyses by ICP-MS. Alkalinity was determined by titration.

All isotope analyses for this study were performed at the Queen’s University Facility for Isotope Research (QFIR) in Kingston, Canada. Chemical preparation for analysis of nitrogen and oxygen isotopes in nitrate followed the method of Silva et al. (2000). The chemical preparation and analysis of sulfur and oxygen isotopes in sulfate followed a slightly modified version of the procedures of Rye et al. (1992) and Arehart et al. (1992). The analysis of oxygen and hydrogen isotopes of water followed routine procedures (i.e., CO_2 equilibration method for $\delta^{18}O$ and thermo-chemical reduction for $\delta^{2}H$).

To ensure QA/QC each sample measurement was performed in duplicate. Furthermore, a suite of certified chemical materials (Fisons^{tm} sulfanilamide and cistina for chemical compositions of N, S and O) as well as a suite of isotopic composition reference materials (NIST, IAEA, USGS and NBS) and in-house isotopic standards were utilized to calibrate each IRMS technology and to normalize sample measurements in order to cover the broad range of isotopic signatures. Reference materials included NIST 8548 and NIST 8550 for ^{15}N calibration (relative to $\delta^{15}N_{air}$), VSMOW and SLAP for ^{18}O calibration and NBS 123 and NBS 127 for ^{34}S normalization relative to CDT (Canyon Diablo troilite). All sample measurements were bracketed with reference materials and in-house standards such that the total numbers of standard measurements were 15-20%. All isotopic standards were measured to within 0.25‰ and all chemical standards to within 2% of their accepted values. In addition, wet-chemical preparations were routinely carried out on blanks and standards. Measurements were performed on Finnigan MAT^{tm} and ThermoFinnigan^{tm} continuous flow IRMS technologies.

For analysis of the fine-grained rock material from the blast site in the Zwartfontein South pit, two sub-samples of the material were immersed in ultra-pure water and agitated for 90 minutes in an ultrasonic bath. After sonication the samples were centrifuged and the supernatant solution decanted into separate bottles for isotope, cation and anion analysis. Analysis of nitrogen and oxygen isotopes of nitrate were carried out at Queen's immediately after sample preparation according to the method outlined above. Aliquots for cation (acidified to pH <2) and anion analysis were sent to ACME Vancouver, and were analysed within a few days after preparation at Queen's University.

2. RESULTS

Pertinent physical, chemical and isotopic data for the water samples collected as part of this study are summarised in Table 1. The sampled waters are moderately saline with EC values ranging from 540 to 3850 µS/cm. The pH of most water samples is circum-neutral to slightly alkaline (7.1-8.5). More acidic and more alkaline pH values are only observed for the tailings dam (6.3) and the Pollution Control Dam North (9.3), respectively. Water temperatures are in most cases in the range from 19 to 27 °C.

While the major cation and anion chemistry of the waters is generally dominated by Mg-Na and HCO_3-Cl, the anion chemistry tends to develop towards SO_4-Cl or SO_4-HCO_3 dominance with increasing salinity. Nitrate is a major or the dominant anion in some samples.

As summarised in Table 1 and shown on Figure 2, the highest NO_3^- concentrations are observed for the Pollution Control Dam North (685 mg/L), the windmill well and the creek at Old Ga-Pila village (422 and 324 mg/L) as well as the Podile primary school in Ga-Molekana village (294 mg/L). The tailings dam, the groundwater monitoring wells around the tailings dam, and background borehole SRK-4 show very low concentrations (mostly <1 mg/L). Intermediate nitrate values are observed for boreholes P31 and OY (38 and 44 mg/L), the Langalibalele Secondary School (60 mg/L) and the groundwater seep in the Zwartfontein South Pit (96 mg/L). The fine-grained rock material from the blast site in the Zwartfontein South pit contains ~60 mg of water-extractable NO_3^- per kg of rock.

The measured nitrogen and oxygen isotopic compositions of nitrate in the collected samples are summarised in Table 1 and shown on Figure 3. All isotopic results are reported in standard per mil δ-notation relative to air ($\delta^{15}N$) and VSMOW ($\delta^{18}O$). Unless indicated otherwise, all reported $\delta^{18}O$ values throughout this paper refer to $\delta^{18}O$ of nitrate. As can be seen on Figure 3, the collected samples broadly fall into two groups in terms of the observed variations in $\delta^{15}N$ and $\delta^{18}O$. The first group (hereafter referred to as 'Group I'), which comprises the majority of the collected samples, is characterised by limited variability in $\delta^{15}N$ (20.5 to 23.0 ‰) but large variability in $\delta^{18}O$ (9.7 to 31.2 ‰), defining a sub-vertical array that extends from the top right corner of the diagram to the bottom right corner. The second group (hereafter referred to as 'Group II'), which comprises the samples of the Pollution Control Dam North (2 duplicate samples) and the windmill well and creek (2 duplicate samples) at Old Ga-Pila village, has significantly lower $\delta^{15}N$ values than the first group (8.8 to 13.5 ‰) and a more limited variability in $\delta^{18}O$ (6.8 to 18.5 ‰).

The lowest $\delta^{15}N$ and $\delta^{18}O$ values (3.0 to 3.6 and 1.1 to 2.5 ‰, respectively) are observed for water-extractable nitrate from the fine-grained rock material collected at the blast site in the Zwartfontein South pit.

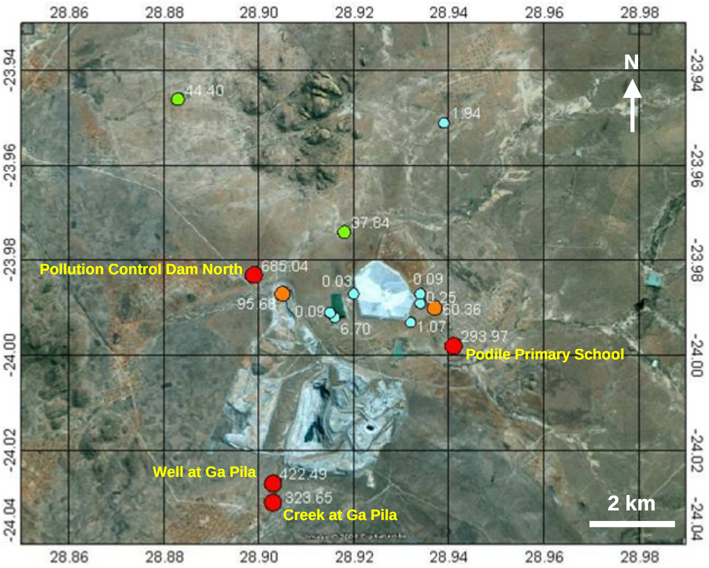


Figure 2. Map showing the spatial distribution of measured nitrate concentrations (in mg/L) in the sampled waters. Symbol colours are defined as follows: 0-25 mg/L (light blue), 25-50 mg/L (green), 50-100 mg/L (orange) and >100 mg/L (red). The background image was downloaded from Google Earth. Refer to the caption of Figure 1 for further comments regarding this image.

Table 1. Analytical results for the collected water samples.

Sample Site	**pH**	**EC** □S/cm	**Ca** mg/L	**Mg** mg/L	**Na** mg/L	**K** mg/L	**Cl** mg/L	**HCO$_3$** mg/L	**SO$_4$** mg/L	**NO$_3$** mg/L	**□^{15}N** ‰ (Air)	**□^{18}O** ‰ (VSMOW)
Tailings Dam	6.29	3850	198	106	495	11.9	577	78.0	1423	<0.05	20.9	17.0
Zwartfontein Pit South - Seep	8.45	1187	49.9	57.8	105	5.3	126	159	201	95.7	20.5	20.7
Pollution Control Dam North	9.29	2220	121	41.8	276	8.8	173	35.0	303	685	8.8	18.5
Pollution Control Dam North (Dup)	9.29	2320	124	44.6	277	9.1	175	34.0	312	685	9.1	17.0
Podile Primary School	7.39	2862	102	69.0	395	0.8	512	396	150	294	20.7	12.1
Langalibalele Secondary School	7.29	1209	71.4	54.5	83.8	5.8	172	291	24.0	60.4	22.7	19.2
Creek at Ga-Pila	8.28	2594	201	193	70.0	2.0	71.0	403	737	324	13.5	17.0
Creek at Ga-Pila (Dup)	8.28	2521	203	199	73.1	2.2	70.0	398	737	321	13.0	15.4
Well at Ga-Pila	7.74	2834	264	189	72.5	1.0	96.0	350	827	422	9.2	6.8
P-9	7.97	1533	65.5	119	72.2	6.1	209	348	189	6.7	22.3	14.9
RWD-3	7.99	874	13.8	51.3	89.3	7.0	127	216	62.9	0.09	23.0	17.8
RWD-6	7.12	3320	110	356	73.1	6.4	357	91.0	1324	1.1	22.0	9.8
RWD-9	8.08	1087	40.6	75.1	67.1	12.7	130	213	192	0.3	22.8	9.7
RWD-10	8.47	539	20.8	36.6	37.0	8.9	19.0	246	12.0	0.09	22.9	21.6
P-31	7.75	1181	39.7	83.3	100	3.3	89.0	383	92.9	37.8	22.0	25.1
SRK-4	7.14	1315	68.5	28.5	166	3.6	209	312	62.9	1.9	22.7	31.2
OY - Overysel	7.55	2342	83.5	60.7	317	1.7	508	295	195	44.4	22.0	18.0

3.

4. DISCUSSION

Denitrification is the process that poses most difficulties for simple applications of nitrate isotopes as a fingerprinting tool. Hence, for successful application of nitrate isotopes for tracing nitrate sources it is critical to determine if denitrification has occurred. Denitrification results in a systematic increase in both $\delta^{18}O$ and $\delta^{15}N$ with decreasing NO_3^- content, and on $\delta^{18}O$ vs. $\delta^{15}N$ plots produces trends with a slope of ~0.5 (e.g., Kendall, 1998). As can be seen on Figure 3, none of the data define such a trend. Furthermore, denitrification is expected to progress along the groundwater flow-path resulting in higher $\delta^{18}O$ and $\delta^{15}N$ values and lower NO_3^- contents at downstream sites. However, the reverse relationship is observed for the dataset of this study. Therefore, it is concluded that denitrification had either no or only a negligible effect on the observed variations in $\delta^{15}N$ and $\delta^{18}O$, and the latter are mainly controlled by mixing processes.

Sources of Nitrate

As can be seen on Fig. 3, the samples from the two background sites SRK-4 and P31, which are assumed to be unaffected by anthropogenic inputs, have fairly similar $\delta^{15}N$-$\delta^{18}O$ compositions that are distinct from those of the other samples. Furthermore, when combining the nitrate concentration data with the $\delta^{15}N$-$\delta^{18}O$ isotopic information (Figure 4), it can be seen that in general nitrate concentrations tend to increase away from these two background samples towards lower $\delta^{18}O$ and $\delta^{15}N$ values.

It is therefore suggested that the variations in $\delta^{15}N$ and $\delta^{18}O$ observed in the dataset can be explained by the addition of nitrate from two isotopically distinct end-member sources to the background waters. The proposed mixing relationships between the background waters and the two suggested end-members are indicated by the two mixing lines on Figures 3 and 4.

One of these two nitrate end-members is inferred to have high $\delta^{15}N$ (~18 to 23 ‰) and low $\delta^{18}O$ values (<10 %), consistent with the typical compositional range of nitrate derived from manure and septic waste (Kendall, 1998). Addition of nitrate from this end-member source to the background waters can explain the sub-vertical array defined by the Group I samples on Figures 3 and 4. As will be discussed in more detail below, the suggested mixing relationship implies that community-related septic effluents (or manure) are the dominant source of the elevated nitrate contents in the groundwater samples from Ga-Molekana village. The combination of elevated chloride (512 mg/L) and nitrate (294 mg/L) contents in the water sample from the Podile Primary School is fully consistent with this interpretation (McQuillan, 2004).

The other nitrate end-member is inferred to have low $\delta^{15}N$ (<5 ‰) and low $\delta^{18}O$ values (<10 ‰). Addition of nitrate from this end-member source to the background waters could explain the trend defined by the Group II samples on Figures 3 and 4. The inferred $\delta^{15}N$-$\delta^{18}O$ composition of this end-member source matches the typical compositional ranges of soil nitrate and nitrate derived from ammonium fertilizers (Kendall, 1998). To our knowledge local farmers do not use ammonium fertilizers, and thus the latter can be ruled out as a significant nitrate source in the study area. However, soils in semi-arid environments of southern Africa can be a natural source of elevated nitrate levels in groundwater, as demonstrated by the studies of Schwiede et al. (2005) and Stadler et al. (2008). Considering that all water samples with $\delta^{15}N$ values <20‰, i.e., all Group II samples, are from sites within and downstream of the mine area, it is possible that the source of the low-$\delta^{15}N$ / low-$\delta^{18}O$ nitrate end-member may lie within the mine area. Further work is currently in progress to verify this observation and to establish whether nitrate fluxes from the low-$\delta^{15}N$ / low-$\delta^{18}O$ nitrate end-member are natural or are possibly enhanced/caused by mining-related activities (e.g., blasting, earthmoving). A detailed sampling program is required to address this question since spatially complex nitrate distributions with localized clusters of elevated concentrations and steep concentration gradients between adjacent boreholes have been observed in areas of naturally elevated groundwater nitrate levels (Stadler et al., 2008).

Remarkably, the $\delta^{15}N$-$\delta^{18}O$ composition of water-extractable nitrate in the fine-grained rock material from the blast site in the Zwartfontein South pit falls within the inferred compositional range of the low-$\delta^{15}N$ / low-$\delta^{18}O$ end-member (Figures 3 and 4). The origin of nitrate in this rock material, however, is still unknown at this stage. While the spatial and temporal association with blasting could suggest that the nitrate in this material may be derived from explosives, the measured isotopic composition of the extracted nitrate is inconsistent with the limited published $\delta^{15}N$-$\delta^{18}O$ data for ammonium nitrate (Benson et al., 2009) and other explosives (Bordeleau et al., 2008). Since the sampled blast site was located on one of the upper benches of the Zwartfontein pit it is conceivable that the nitrate may have been soil-derived and may have become incorporated in the sampled material either through physical addition of soil components during blasting or through seepage from the soil. Considering that the rocks at the sampled site comprise mafic/ultramafic cumulates it is highly unlikely that the nitrate is derived from the rock material itself (Holloway and Dahlgren, 2002).

Despite the uncertainty regarding the ultimate source of nitrate in the blast site material, the δ^{15}N-δ^{18}O composition of nitrate in this material and its substantial content of water-extractable nitrate (~60 ppm) highlight the potential importance of waste rock material as a source of nitrate in the study area. The isotopic composition and high content of nitrate in the Pollution Control Dam North, which receives water from the Mogalakwena Central pit and run-off from waste rock dumps, support this suggestion. Further work is currently in progress to identify the origin of nitrate in the blast site material.

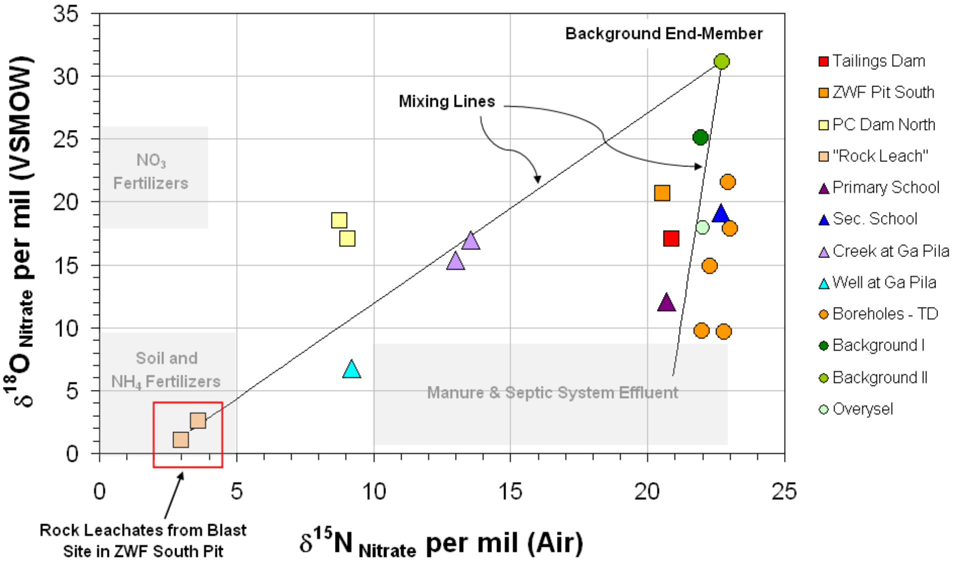


Figure 3. Diagram showing the measured □15N and □18O values of the collected water samples. The grey shaded fields represent typical compositional ranges of selected nitrate sources (after Kendall, 1998). The samples labelled 'Boreholes – TD' comprise the 5 monitoring boreholes around the tailings dam (i.e., RWD-3, RWD-6, RWD-9, RWD-10 and P-9). The two samples labelled 'Background I' and 'Background II' are boreholes P-31 and SRK-4, respectively. See text for discussion.

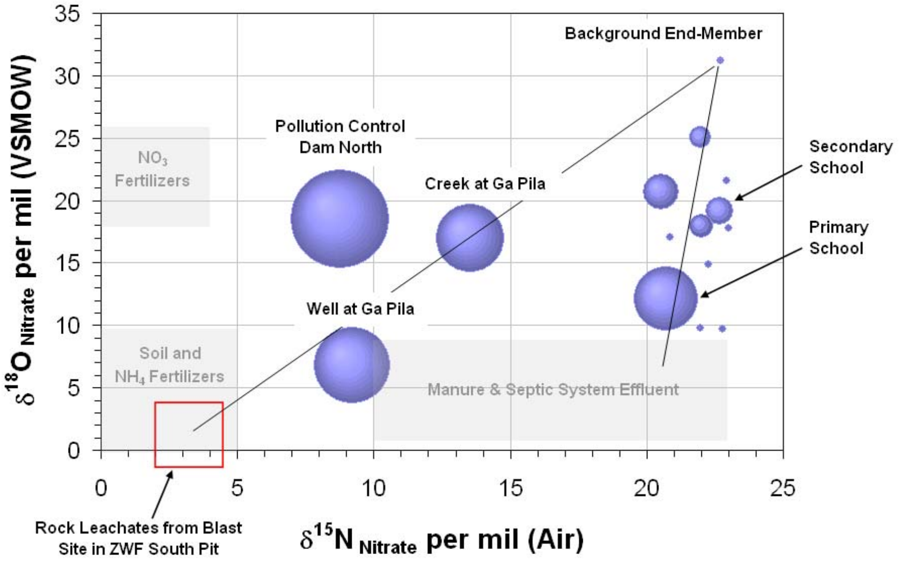


Figure 4. Bubble chart showing the measured □15N and □18O values of the collected water samples. The symbol size is proportional to the nitrate content of the respective sample. The grey shaded fields represent typical compositional ranges of selected nitrate sources (after Kendall, 1998).

Mixing Models

$\delta^{18}O_{Nitrate}$ vs. NO_3^- Relationships

Taking a closer look at the sub-vertical trend defined by the 'Group I' samples on Figure 4, it is noted that some of the samples plotting near the manure/septic waste field have very low NO_3^- contents similar to that of the background water from borehole SRK-4. At first glance, this observation appears to be inconsistent with the suggested two-component mixing model. However, as demonstrated on Figure 5, the observed variations in $\delta^{18}O$ and NO_3^- along the sub-vertical trend can be readily explained by mixing between background waters and a manure/septic waste end-member, assuming that the NO_3^- contents of the background waters vary between values of <1 mg/L and ~20 mg/L. The latter assumption appears to be reasonable on the basis of existing data on natural nitrate levels of groundwaters in the region (DWAF, 2003; Tredoux, 2004).

The grey curves on Figure 5 represent calculated mixing lines between an assumed manure/septic waste end-member ($\delta^{18}O$ = 10‰; NO_3^- = 390 mg/L) and two background end-members with the same $\delta^{18}O$ value of 31.2‰, corresponding to the isotopic composition of sample SRK-4, and variable NO_3^- contents of 0.6 mg/L and 20 mg/L, respectively. As can be seen on Figure 5, the curvature of the mixing line as well as the relative changes in $\delta^{18}O$ and NO_3^- of background-effluent mixtures are strongly dependent on the NO_3^- content of the background end-member.

The data and mixing relationships presented on Figure 5 also clearly demonstrate that mine water from the tailings dam cannot be the source of nitrate contamination in Ga-Molekana village. This conclusion is fully consistent with the information from other isotopic and chemical tracers (e.g., $\delta^{34}S$-$\delta^{18}O$ of sulfate; data not presented), as well as with the westerly to south-westerly groundwater flow direction.

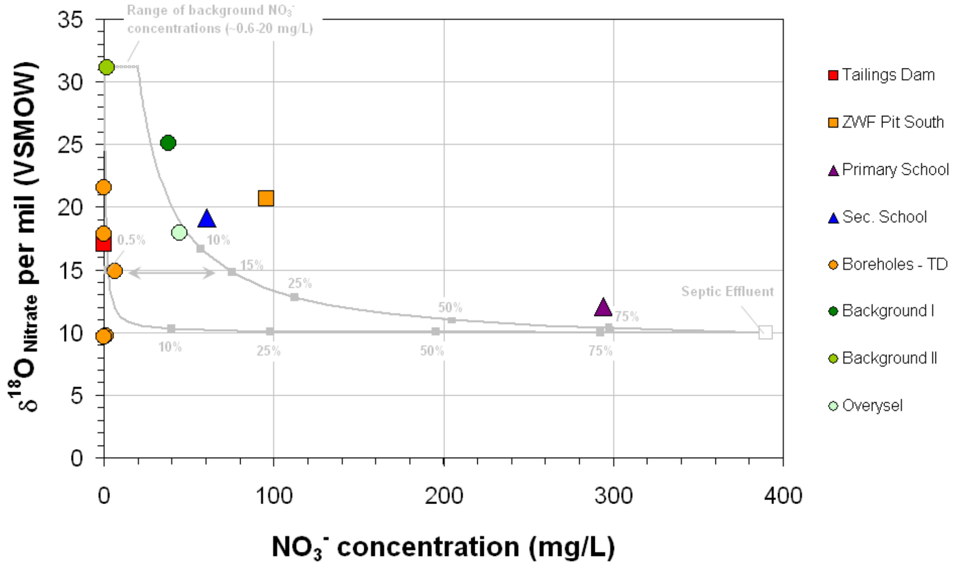
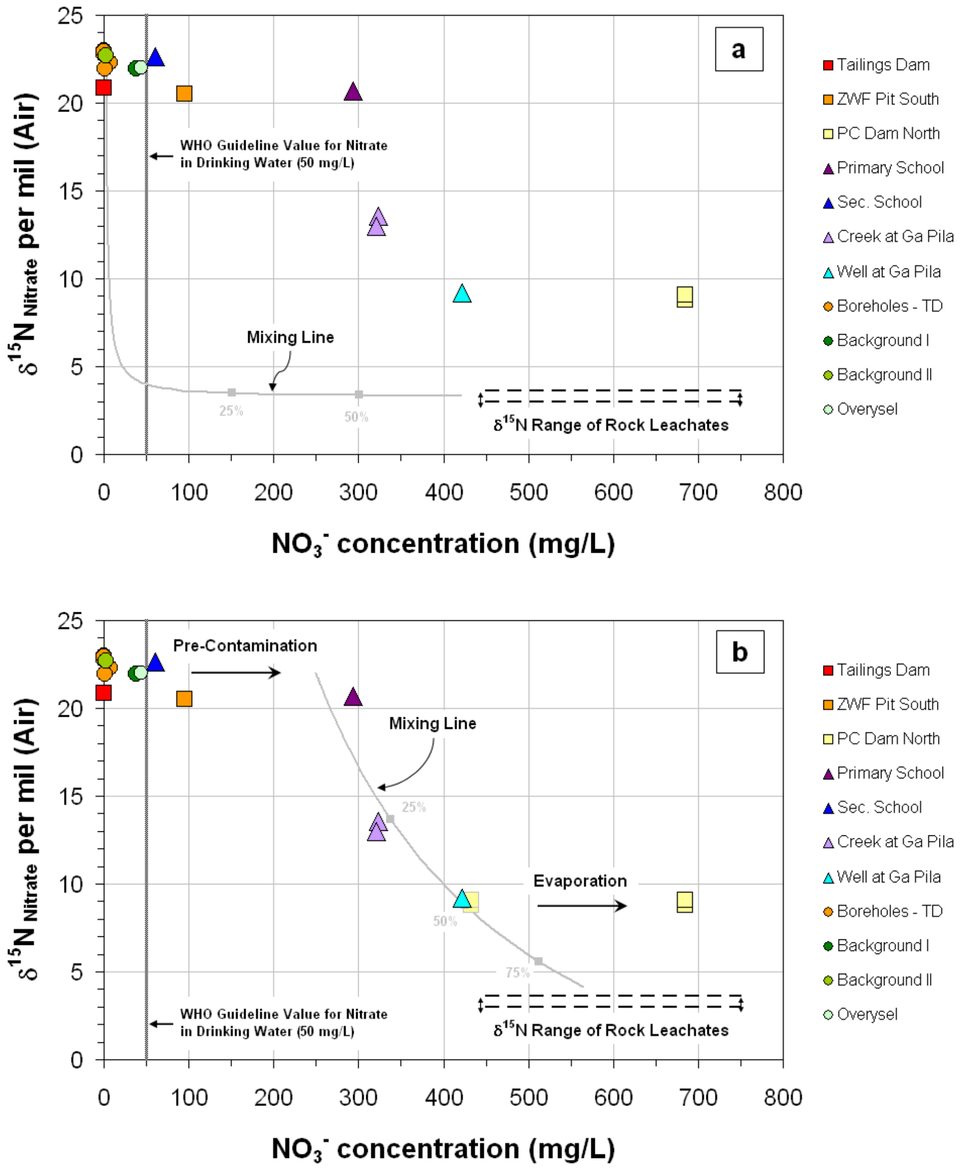


Figure 5. Diagram showing the variations in □18O of the collected water samples as a function of nitrate content. Please note that only 'Group I' samples plotting along the sub-vertical trend on Figures 3 and 4 are shown on this diagram. The grey curves represent mixing lines between a septic effluent end-member and two background end-members. Labels along these curves indicate the percentage of septic effluent in the mixture. For details on sample names refer to the caption of Figure 3. See text for discussion.

$\delta^{15}N_{Nitrate}$ vs. NO_3^- Relationships

To further evaluate the suggested interpretation that the $\delta^{15}N$-$\delta^{18}O$ isotopic compositions of the Pollution Control Dam North and the well and creek at Old Ga-Pila village result from the addition of nitrate from a low-$\delta^{15}N$ / low-$\delta^{18}O$ end-member source, two mixing scenarios are illustrated on Figs. 6a and 6b. For both mixing scenarios, the $\delta^{15}N$ composition of the low-$\delta^{15}N$ nitrate end-member is defined by the average value of the rock leachates (i.e., $\delta^{15}N$ = 3.3‰), and its nitrate concentration is assumed to be 600 mg/L. In contrast, the composition of the high-$\delta^{15}N$ nitrate end-member is different for each of the two mixing scenarios. For the scenario on Fig. 6a the composition of this end-member is defined by that of background sample SRK-4 ($\delta^{15}N$ = 22.7‰ and NO_3^- = 1.9 mg/L, whereas for the scenario on Fig. 6b the composition is $\delta^{15}N$ = 22‰ and NO_3^- = 250 mg/L, reflecting the addition of NO_3^- from septic system effluents to background sample SRK-4.

As can be seen, the curvature of the mixing line on Fig. 6a is very high and the samples of the Pollution Control Dam North and the well and creek at Old Ga-Pila village do not fall on the calculated mixing line. Therefore, mixing between background water (as represented by sample SRK-4) and the low-δ^{15}N/high-NO_3^- end-member cannot account for the composition of these samples. In contrast, the samples of the well and creek at Old Ga-Pila village plot on or close to the mixing trend shown on Fig. 6b, which originates from the hypothetical pre-contaminated "background" end-member.



Figures 6a and 6b. Diagrams showing the variations in δ15N of the collected water samples as a function of nitrate content. The grey mixing curves on these diagrams illustrate two separate mixing scenarios. Labels along the mixing curves indicate the percentage of the low-δ15N end-member in the mixture. For details on sample names refer to the caption of Figure 3. See text for discussion.

It should be noted that after correction for the extensive evaporation experienced by the water in Pollution Control Dam North (~40% evaporative water loss, as estimated on the basis of $\delta^{2}H_{Water}$-$\delta^{18}O_{Water}$; data not presented), the positions of the two duplicate Pollution Control Dam samples on Fig. 6b are similar to that of the well sample from Old Ga-Pila village ($\delta^{15}N \approx 9$‰; $NO_3^- \approx 433$ mg/L), and thus the samples would also fall on the calculated mixing trend.

The important implications of these mixing calculations for data interpretation is that prior to the addition of low-δ^{15}N nitrate (e.g., from soils or waste rock dumps) to the waters of the Pollution Control Dam North and the well and creek at Old Ga-Pila village these waters must have had already highly elevated nitrate contents, probably due to contamination with nitrate from manure/septic system effluents.

Nonetheless, a proportion of the nitrate in the waters at Old Ga-Pila village may be derived from within the mine area. The suggested two-stage process in which background waters are first contaminated with nitrate from community-related septic waste or manure before receiving additional inputs from an isotopically distinct nitrate source within the mine area would be fully consistent with the westerly to south-westerly groundwater flow direction.

5. CONCLUSIONS

The results presented in this paper demonstrate that at least three isotopically distinct nitrate end-member sources exist in the study area. The suggested end-member sources comprise (1) a background end-member with low NO_3^- content and high $\delta^{15}N$-$\delta^{18}O$ values, (2) an end-member with high NO_3^- content and high $\delta^{15}N$ / low $\delta^{18}O$ values, corresponding to nitrate from manure/septic waste, and (3) an end-member with high NO_3^- content and low $\delta^{15}N$-$\delta^{18}O$ values, corresponding to nitrate from soil or possibly waste rock material. The latter is suggested by leachate data for rock material from a blast site in the Zwartfontein South Pit. The observed variations in $\delta^{15}N$-$\delta^{18}O$ and NO_3^- in the dataset can be readily explained by mixing between these three end-member sources.

The results indicate that the high groundwater nitrate concentrations at the Podile Primary School and the Langalibalele Secondary School in Ga-Molekana village are not caused by effluents from Anglo Platinum's operations but are most likely the result of contamination from community-related septic waste or manure. This interpretation is consistent with the westerly to south-westerly groundwater flow direction in the area, which renders a contribution from the operation to the groundwaters at Ga-Molekana village unlikely.

On the basis of the available data, the source of the low $\delta^{15}N$-$\delta^{18}O$ nitrate end-member may lie within the mine area. Mixing calculations suggest, however, that prior to the addition of nitrate from this end-member the waters must have already had highly elevated nitrate concentrations, probably due to contamination with nitrate from community-related septic effluents or manure upstream from the operation. The extent to which nitrate fluxes from the low $\delta^{15}N$-$\delta^{18}O$ nitrate end-member to the groundwater are natural or are enhanced/caused by mining-related activities is subject of ongoing investigation.

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