

Tracking Nitrate Sources at a Platinum Mine – Putting the puzzle together

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Abstract Elevated nitrate may be associated with mining activities but can also be attributed to the application of fertilizers, human and animal waste and other sources. Nitrogen readily undergoes biologically mediated reactions. This transformation and the mixing and evaporation processes that occur with reuse of water underground renders distinguishing between the origins of the nitrate in water a complex task.

This case study from a platinum mine in South Africa demonstrates how the hydrochemistry and the hydrogeological evidence, combined with evidence from stable isotope analysis, allowed for the identification of the source areas contributing to elevated nitrate in the water resources.

Key words Hydrochemistry, nitrate contamination, nitrogen isotopes, source identification

Introduction

Nitrate concentrations can typically vary from <1 to >45 mg/L as N in groundwater in the northern provinces of South Africa where the study area is located (Tredoux et.al 2009). Local nitrate concentrations can therefore exceed the South African drinking water quality standard of 11 mg/L as N (SANS 241- 2015). Although there is some debate as to the appropriateness in linking illness rates with nitrate levels in drinking water (Fewtrell 2004); the nitrate concentration standard was established as a conservative quality limit to reduce the risk of methaemoglobinaemia from drinking water in babies under 1 year of age (DWA 1996).

Nitrate sources

According to Brochu 2009 and Degnan et al. 2015, nitrate can be introduced into the groundwater resources through the incomplete ignition of explosive compounds such as ammonium nitrate, the injection of nitrogenous gases during blasting, and nitrification (oxidation) of reduced nitrogen components of explosives. Additional sources of nitrate in the mining environment can include the leaching of blasting residues from waste rock, tailings and/or dirty water impoundments, inadequate control of sewage and the dissolution of ammonium nitrate explosives or waste explosives due to poor handling, storage and loading. The interaction of the chemicals used in metallurgical plants (nitric acid, hydrochloric acid, iron chloride, ammonium chloride, sodium bromide and ammonium hydroxide) can also contribute to increased ammonia, nitrate and chloride concentrations in the groundwater by Bosman 2009.

Nitrate may also be naturally present as a result of soil nitrification processes from the mineralization and mobilization of nitrate from natural soil or host rock lithologies, (DWA 1996; Tredoux 2009, Bosman, 2009). Other possible sources of nitrogen in the water resources (ammonia and/or nitrate) unrelated to mining activities can also include sewage

sludge application or waste water irrigation or discharge, pit latrines or septic tank systems and domestic animal wastes (from feed lots (“kraals”). Extraneous sources may also include fertiliser application, fireworks and the degradation of cyanide where used as an industrial chemical in electroplating or ore processing (gold mines). Nitrate has also been noted to occur in rain downwind of sources such as coal-fired power plants, veld and forest fires. Tilling of soil in land previously left fallow for the winter months or long periods, deforestation and land clearing have also been indicated as providing additional nitrate to groundwater (Tredoux, 2009).

The various nitrogen species (ammonium, nitrate, nitrite and nitrogen) can convert readily from one to the other depending on the redox conditions and availability of a carbon source. This is often referred to as the “Nitrogen Cycle”. These biologically mediated reactions result in interactions and transformations of nitrogen that vary with changing conditions along the surface and groundwater pathways, within water dams and in waste impoundments. These transformations, the mobility of nitrate in water and the mixing that occurs with the reuse of water within the mining environment, make distinguishing between the origins of the nitrate in water a complex task, particularly where there are likely to be a number of different sources contributing to the nitrogen load in the water resource. Studies have shown that a multi-faceted approach using stable isotopes of oxygen, nitrate, hydrochemistry, and hydrogeologic evidence can assist in the identification of nitrate sources, (Degnan et.al 2015, Pasten-Zapata et.al 2014, Ihlenfeld et.al 2009, Zhang et.al 2015). This paper uses a case study from a platinum mine in South Africa to demonstrate how the combined evidence from isotopes, hydrochemistry and the hydrogeological setting was used to identify the sources contributing to the nitrate load in the river.

Materials and Methods – Case Study

Site Description

Platinum mines target platinum group metals from chromitite seams of the upper part of the Critical Zone and the lower part of the Main Zone of Bushveld Igneous Complex (BIC). There are three main areas in the mine area. These include Old Shaft (including an open cast pit, shaft complex and a waste rock dump (WRD), Process Plant (including a concentrator plant, workshops, a small sewage plant and process water dams and a more recent shaft complex), and a tailings and return water dam (termed the TSF). Old Shaft is located upstream of the Process Plant. The TSF is located in the hanging wall of the platinum seam downstream of the Process Plant. Flow in the ephemeral tributary (Tributary) starts downstream of Old Shaft near the WRD and flows past the Process Plant before discharging to the River and flowing past the TSF. Communities are located downstream of the mine area. Livestock were observed to be using the water downstream of the catchment.

The regional aquifer is a minor aquifer with higher yields associated with areas of preferential weathering along major lineaments such as faults and open joint systems. Groundwater levels vary from 3 to 27 mbgl, averaging at 11 mbgl. Despite a localised cone of depression around Old Shaft and some mounding around the TSF; the regional water levels do not

appear to have changed significantly from those recorded pre-mining. The regional groundwater flow directions therefore follow the topography towards the River. A local spring is noted at the toe of the WRD which could be due to the dyke which is orthogonal to the pseudo-layering of the BIC lithologies.

Problem Statement

Nitrate concentrations (around 17 mg/L as N) are reported in the river downstream of the platinum mine. As a number of rural communities are located around the mine; it was postulated that inadequate sanitation and livestock subsistence farming could be contributing to the elevated nitrate concentrations in the river. Concentrations of <20 mg/L as N could result in a slight chronic risk to babies drinking this water, but is likely to be well tolerated by livestock (DWAF 1996). The risk to infants is considered limited

Description of data used in the study

Water quality representative of the surface and groundwater resources before the current mining activities, were sourced from historical reports. Nitrate concentrations were < 10 mg/L as N except in the area around the current TSF. Nitrate concentrations were higher (median of 23 mg/L as N) pre-construction of the TSF due to historical mining (unrelated to the current mine activities).

Selected samples were analysed for pH, electrical conductivity (EC), nitrate, ammonia, sulfate and stable isotopes of hydrogen (^2H and ^1H) and oxygen (^{18}O and ^{16}O). Additional information was obtained from the routine monitoring obtained within a similar time frame and from the time series data. A sub-set of the samples was selected for analyses of the nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}_{\text{NO}_3}$).

The samples assessed included:

- Samples representing possible nitrate sources included fissure water (FW and FW_P), process dams (PW), treated sewerage (SEWER), seepage at the toe of the waste rock dump (WRD), tailings penstock water (TSF1), toe drain (TOE), return water (RWD1) and seepage around the tailings and RWD (TDSeep).
- Samples that would be likely to represent the ambient or background groundwater water quality where obtained from historical records and boreholes upgradient to mine activities.
- Surface samples from the tributary where R1 is at top of the catchment, R4 represents the point downstream of Old Shaft and Plant and R6 downstream of the TSF area all the mine activities. R7 represents the water quality at the most downstream point in the River.
- Groundwater samples from boreholes down-gradient of the mining activities.

Discussion and Results

Nitrate distribution

Surface water profiling (fig 1) demonstrates that the nitrate concentrations are highest at the top of the catchment near the Old Plant (R2 and R3) and are assimilated downstream (R4 to R7). Sodium and chloride concentrations increase downstream of the Process Plant (R4). Nitrate, sodium and chloride concentrations remain within a similar order downstream of the TSF (R6 and R7). This implies that the main source of nitrate is near the Old Shaft but there is an additional source of salinity from the Process Plant to the river. Nitrate concentrations in the sources and boreholes located around Old Shaft are similarly higher than around the Plant and TSF areas. Higher concentrations of sodium and chloride (salinity) are observed in the sources and boreholes around the Plant and TSF. A local distribution of higher nitrate is observed in the boreholes downstream of the RWD. These boreholes are located within a similar area adjacent to a dry drainage line. The higher concentrations may be associated with seepage from the RWD along a preferential flow path where the baseline pre-construction was already elevated.

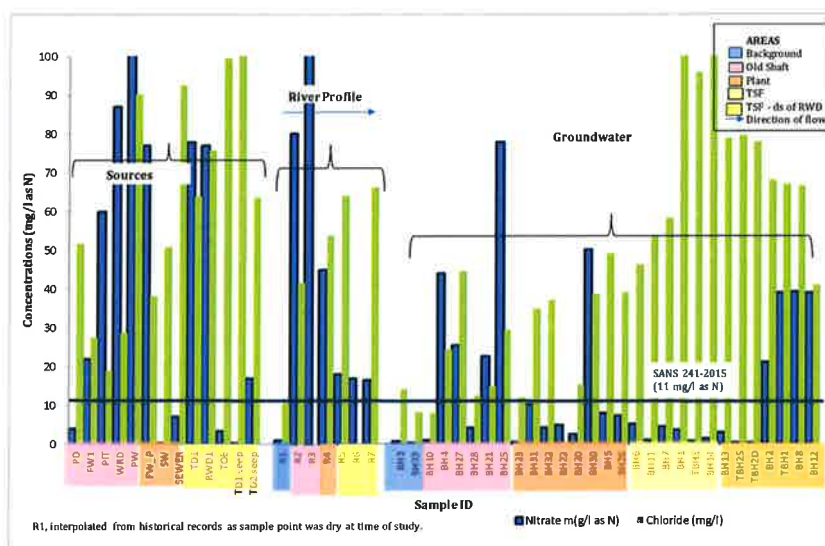


Figure 1. Bar chart presenting concentrations of nitrate (as N), chloride and sodium in the Study area

Oxygen and Deuterium Isotopes

The results for the samples analysed for the environmentally stable isotopes for hydrogen (^2H and ^1H) and oxygen (^{18}O and ^{16}O) are presented in the figure below (fig 2). According to Mook 2000, fractionation of oxygen and hydrogen in water during various processes often results in the development of a unique isotopic composition in the water. The relative abundance of these isotopes (expressed as a ratio relative to a standard) is used as an indicator of the source of the water, or the processes which it has undergone. The hydrologic connection between two samples, if found along a flow path, can therefore be proved if the samples are

isotopically similar or if the results plot along a mixing line between two isotopically distinct source waters (otherwise termed endmembers). The background groundwater samples plot in the lower negative quadrant, as is typical of groundwater, whilst the TSF provides an evaporative endmember in the positive top quadrant. A distinct mixing line is indicated between the TSF and groundwater samples confirming the impact of the TSF on the groundwater. Of note, is the similar grouping of the samples near Old Shaft (WRD, FW1 (fissure water), adjacent boreholes and stream samples (R2 and R3) which shares similar isotopic characteristics to the groundwater. This implies that the water at the toe of the WRD and water in the river is probably recharged by groundwater.

Gaye, 2001 suggests that a plot of relationship between $\delta^{18}\text{O}$ and salinity (TDS) can also be used to identify different salinization pathways. The TDS was estimated from the electrical conductivity reported for the samples and plotted against $\delta^{18}\text{O}$ (fig 3). The hydrochemical grouping identified around the WRD and groundwater is once again shown in the plot as is the mixing between the TSF sources and the groundwater.

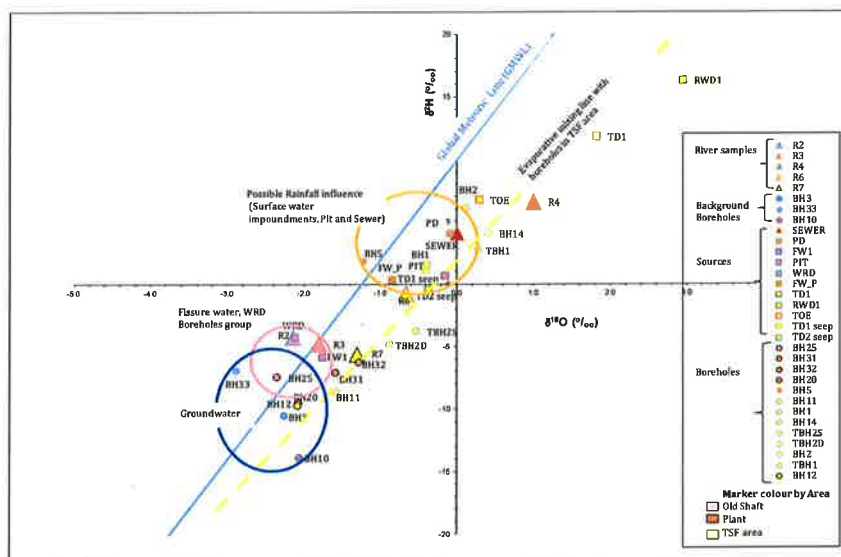


Figure 2 Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$

Nitrogen Isotopes

The relative abundance of nitrogen isotopes in water can be compared to reference values obtained from literature, to identify the likely water source. Kendall 1998 provides typical ranges of nitrate isotopes of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the nitrate ion, plotted in comparison to the study results (fig 4). The results from the study again show a similar grouping between the water in the tributary, the WRD seep, fissure water (FW) and groundwater boreholes located within the same area. These samples all plot within the range typical of a source relating to blasting activities. The stream samples T2 and T1 are also located within this area. The information further supports the observation that WRD seep is recharged by leachate

through the WRD and groundwater daylighting at the toe of the dump. This seep contributes to flow in the Tributary. The sewer sample plots within the range expected for animal or human waste and the TSF sample plots outside the typical ranges for nitrogen. These results further support the observations made based on the hydrochemistry that the water in the tributary is hydrochemically and isotopically similar to that of the groundwater within the area (fissure water and boreholes).

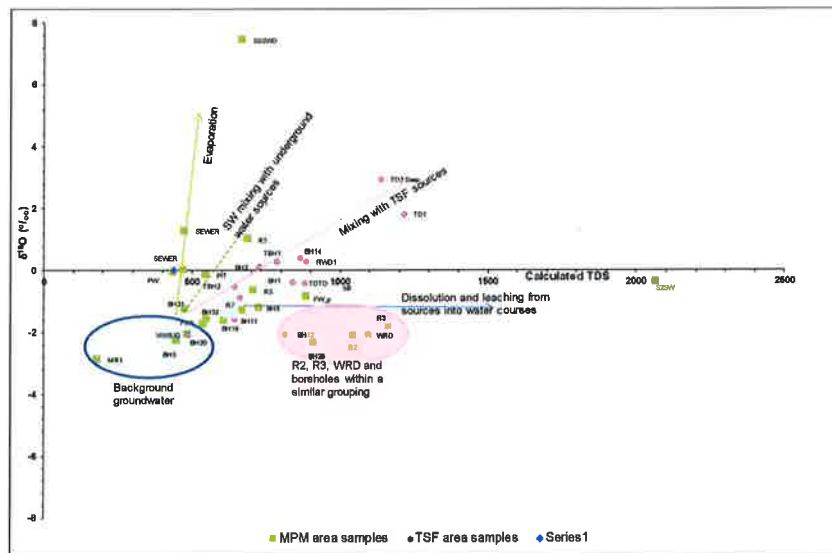


Figure 3 Plot of $\delta^{18}\text{O}$ versus salinity

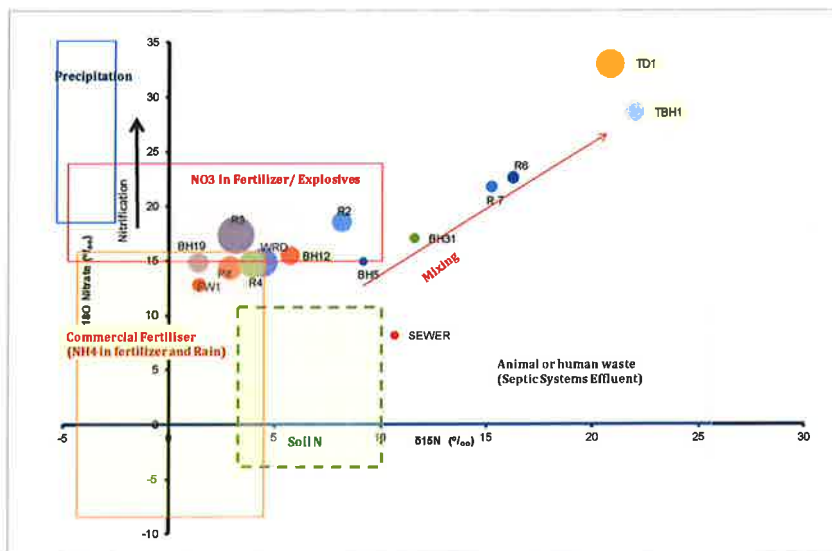


Figure 4. Plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}$ (reference areas after Kendall 1998)

Conclusions

The combined evidence from isotopes and hydrochemistry confirms that the main source of nitrate in the river down-stream is from blasting activities, is most likely related to the underground mining of the platinum reef. The findings are supported by comparison of the current water quality results to background water quality data collected prior to mining activities, and in boreholes located up-gradient of current activities.

The groundwater plumes are relatively localised, with higher nitrate concentrations associated with a potentially diffuse source from the underground workings in and around the Old Shaft and WRD. The isotope and hydrochemistry results suggest that poor quality groundwater is surfacing in the tributary, possibly due to a linear feature acting as a barrier to flow. The tributary water then mixes with the contaminated water leached from the WRD, before discharging to the river. A secondary diffuse source of nitrate, as well as increased salinity, is indicated by increasing concentrations along the stream length and is possibly from sources in the Plant area.

The tailings source samples are isotopically different from the other samples obtained during the study. A mixing line is apparent between the sample results for the TSF and the boreholes and seeps in the vicinity of the TSF, and implies that the groundwater quality is impacted by the TSF. The tailings and return water dams, although sources of nitrate themselves, were found to have less of an impact on the river as is indicated by the similar nitrate concentrations reported up and down-stream of the river, which is down-gradient of the TSF.

Recommendations

Water management for the mine should focus on reducing the nitrogen load in the tributary which discharges to the river. Management measures that could prove useful include changing the hydraulic dynamics of the Waste Rock Dump (WRD) to reduce rainfall infiltrating through the dump and/or intercepting the seepage from the WRD before it discharges to the Tributary, a biological system to bio-remediate or “polish” the water before it discharges to the river could also be considered and training of mine personnel to be aware of the implications of spillages of waste explosives and/or to optimise blasting procedures for efficient detonation of explosives.

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