Analysis of Shallow Groundwater Monitoring Data of a Platinum Mine, Bushveld Complex, South Africa – Implications for Post-Closure

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Abstract

Elevated total nitrogen (N_T) and sulfate (SO_4^{2-}) concentrations in shallow groundwater on platinum mine sites are a ubiquitous phenomenon. This is considered from mostly a regulatory perspective to be a serious water contamination problem and mining companies are forced to implement expensive mitigation and post-closure remediation measures. This work shows that natural biogeochemical processes have the potential to reduce N_T and SO_4^{2-} concentrations to below regulatory guideline values. Rates of N_T and SO_4^{2-} decrease in a post-closure scenario have been calculated from existing monitoring data.

Ten shallow groundwater monitoring data points from a platinum mine on the Western Limb of the Bushveld Complex, South Africa, representing a maximum period from February 2005 to October 2020 and 280 observations, were analysed. In addition to the standard timeseries and statistical analysis, a new analysis method was tested on the data. The method is termed "Plume-and-Pulse" analysis and entails identifying N_T and SO_4^{2-} pulses within a pollution plume from a timeseries plot of monitoring data and using the measured concentrations together with the proportion of nitrogen species i.e., nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), of individual pulses and the differential change between analysis points to calculate rates of change of N_T and SO_4^{2-} species. These rates are statistically analysed and a distribution of post-closure N_T and SO_4^{2-} decrease rates estimated.

The main findings are that N_T and SO_4^{2-} show decreasing concentrations in shallow groundwater boreholes associated with mineral waste facilities, (i.e. tailings and waste rock), that have been intermittently operated over the monitoring period. The periods of inactivity represent post-closure scenarios. The Plume-and-Pulse analysis indicated a N_T range of decrease rates between $5.25{\times}10^{-10}$ (635 µg/L/d) and $9.54{\times}10^{-14}$ M/s (1 µg/ L/d), with a median of $2.39{\times}10^{-12}$ M/s (3 µg/L/d). The sulfate decrease rates range from $7.32{\times}10^{-10}$ (6 075 µg/L/d) to $1.24{\times}10^{-12}$ M/s (10 µg/L/d), with a median of $1.26{\times}10^{-11}$ M/s (105 µg/L/d). The decrease of N_T may be caused by gasification as well as microbial reduction of dissolved N-species. The reduction of SO_4^{2-} is most probably caused by microbial S-reducers and precipitation of metal sulfides in the anaerobic groundwater aquifer matrix.

The implication of this work is that post-closure remediation of N_T and SO_4^{2-} may not be necessary, if decrease rates are rapid enough. If decrease rates are not rapid enough, simple augmentation of shallow groundwater aquifers by the relevant microbial species may be a sufficient, long-term, post-closure mitigation.

Keywords: Mine Pollution, Post-Closure, Nitrogen, Sulfate, Plume-and-Pulse Method

Introduction

Elevated concentrations of total nitrogen (N_T), from ammonium nitrate explosives (Brooks *et al.*, 2019), and sulfate (SO_4^{2-}), from oxidising metal sulfides in water draining from precious metal mine waste facilities is ubiquitous. The sources and geochemical behaviour of these constituents in the mine reticulation system

during the mining operational phase are generally well understood. However, as more mines are reaching the end of their lifetimes and are closing, knowledge of the fate of N_T and SO_4^{2-} in the natural environment, particularly in surface water and groundwater, is becoming increasingly important. From a biogeochemical perspective, the processes controlling the speciation and mobility in the impacted environment are less well understood.

With the advent of biogeochemistry as a scientific discipline from geochemistry by Vladimir Vernadsky and co-workers in the late 1990s (Schlesinger and Bernhardt, 2020), came the realisation that geochemical processes are more complex than previously thought. Life, especially microbial (e.g., bacterial), and algal species, exert major controls on the rate of geochemical processes in natural and anthropogenically impacted environments (Schlesinger and Bernhardt, 2020). This is especially true for essential bio-nutrients such as N_T and SO_4^{2-}.

In South Africa, mining companies are required to gather surface water and ground-water monitoring data for key parameters at key locations on the mine site during their operation. This data is sent to the relevant government departments and is meant to ensure compliance with conditions set out in the mine's water use licence. Often, this is the only purpose for which the monitoring data are used. In addition to compliance with regulations, monitoring data are also a record of biogeochemical processes and changes occurring at the mine site as well as in the surrounding environment. With sufficient knowledge, the monitoring data can be placed in a broader biogeochemical context, revealing the fundamental governing processes on specific constituents. Once the governing processes are known, their long-term behaviour can be determined and, if required, the appropriate remedial methods applied.

The aim of this study was to bring the continuous groundwater monitoring data at a Bushveld platinum mine, South Africa, into a biogeochemical context to identify impacts and whether remedial action in a post-closure scenario is required.

Methods

Timeseries data from 10 groundwater monitoring points representing a maximum monitoring period of just over 15 years and 280 observations were provided by an operational platinum mine located in the Bushveld Complex, South Africa. The N_T and SO_4^{2-} data were analysed. The database contained data for three N species, NO_3^-, NO_2^- and NH_4^+.

The monitoring points were selected downgradient of mine mineral waste facilities (i.e., waste rock and tailings) and down-gradient of historically mined open pits and shafts. The data was analysed on three scales. Rates of change were calculated between several points of increasing and decreasing N_T and SO_4^{2-} concentration for each pulse. The individual pulse data was compiled for each monitoring point as well as for the entire mine site and analysed. Descriptive statistics, histograms and box plots were used as part of the data analysis process.

Results and Discussion

Pulses of N were identified using the timeseries monitoring data. An example is fig. 1 which shows a borehole downgradient from a tailings facility. It is evident from the plot that the dominant N species is NH_4^+ and that there appears to be an inverse correlation between NH_4^+ and SO_4^{2-}. The interpretation of the timeseries monitoring data can be aided by the conceptual model in fig. 2. In fig. 2 the plume is shown as it is usually depicted in textbooks and publications. However, the plot at the bottom of fig. 2, which represents the monitoring data signal as measured over the monitoring period, and the actual data plot in fig. 1, shows that elevated N concentrations reach the monitoring borehole as pulses and is not a constant, continuous, homogenous input of N, and SO_4^{2-}, into the shallow groundwater system. The implication of the pulses of elevated N_T and SO_4^{2-} concentrations rather than a constant continuous input is that data from the analysis of individual pulses provide information on longer term trends of increasing or decreasing N_T and SO_4^{2-}. Analysis of a single pulse cannot provide information on the longer-term

biogeochemical behaviour of the system. The pulse-nature of the N_T and SO_4^{2-} plumes dictated that multiple pulses from multiple monitoring boreholes be analysed.

A total of 381 differential analysis points for N_T and 182 for SO_4^{2-} from 24 pulses in the 10 monitoring boreholes were analyses. The results of the analysis is shown in tab. 1 and graphically in fig. 3.
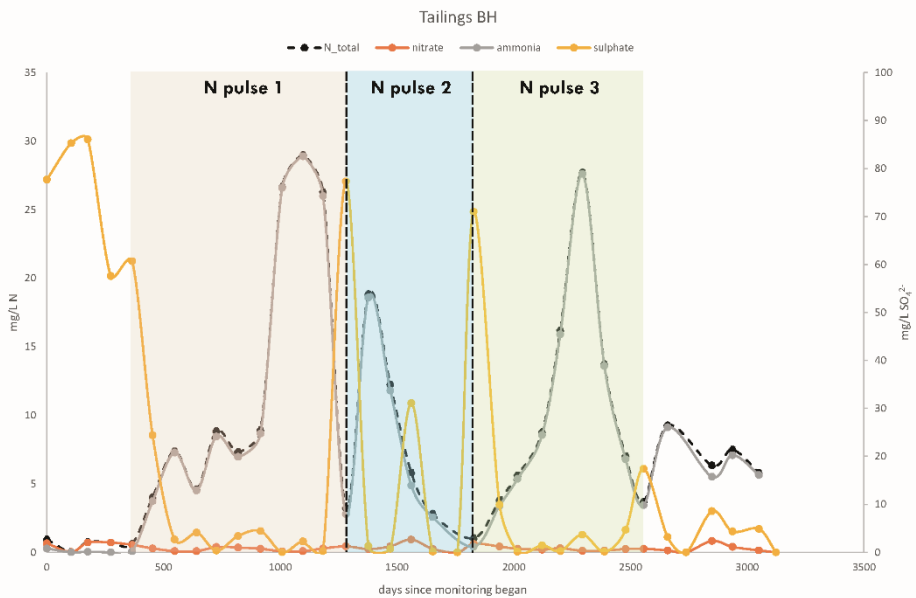

Figure 1 Timeseries plot of N and SO_4^{2-} data from a shallow groundwater monitoring borehole downgradient from a tailings facility showing the three N pulses analysed for differential changes in N species concentration.
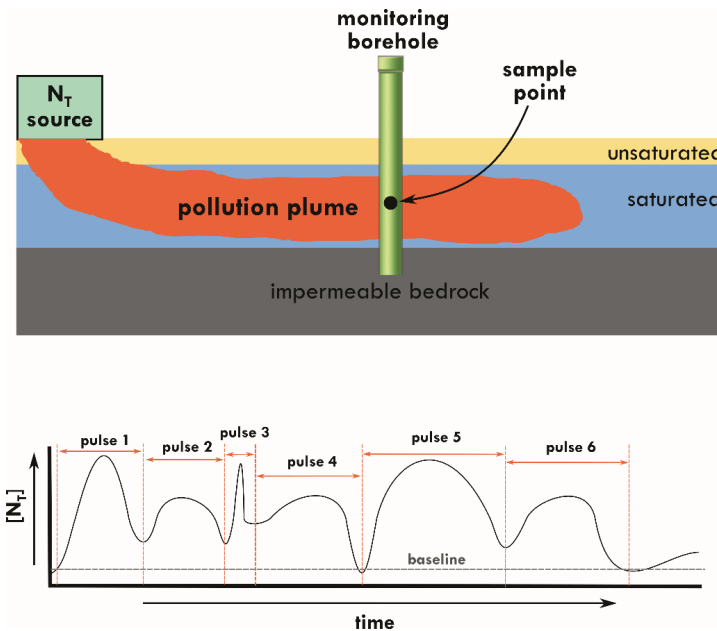

Figure 2 Conceptual model indicating the relationship between the signal in the timeseries monitoring data plot (bottom of the figure) and the plume emanating from a N-source e.g., tailings facility (top of figure).

Table 1 *Summary of concentration rates of change calculated from pulses in shallow groundwater monitoring borehole timeseries data.*

borehole (downgradient)	pulse	$\Delta[SO_4^{2-}]$ increase	$\Delta[SO_4^{2-}]$ decrease	$\Delta[N_T]$ increase	$\Delta[N_T]$ decrease
			M/s		
Tailings BH 1	1	2.61×10^{-11}			-3.60×10^{-12}
	2		-1.26×10^{-11}		-1.19×10^{-13}
	3		-4.05×10^{-14}		-1.79×10^{-12}
Tailings BH 2	1		-6.43×10^{-11}	3.61×10^{-12}	
	2	4.73×10^{-11}			-2.39×10^{-12}
	3	5.59×10^{-11}			-1.02×10^{-12}
Tailings BH 3	1		-8.71×10^{-12}		-1.00×10^{-13}
	2		-2.44×10^{-12}	1.39×10^{-13}	
	3	7.86×10^{-12}		2.32×10^{-12}	
Tailings BH 4	1	8.81×10^{-12}		5.99×10^{-13}	
	2	4.28×10^{-12}		1.47×10^{-13}	
	3		-1.04×10^{-11}		-8.83×10^{-14}
Tailings BH 5	1	2.19×10^{-12}		7.60×10^{-12}	
Waste Rock BH 1	1	8.82×10^{-12}		2.59×10^{-13}	
	2		-7.88×10^{-12}	-1.88×10^{-11}	
	3	5.51×10^{-12}			-6.50×10^{-13}
Tailings BH 6	1		-1.01×10^{-09}	1.28×10^{-10}	
Tailings BH 7	1		-1.09×10^{-10}		-6.26×10^{-10}
	2	1.18×10^{-10}			-2.09×10^{-10}
Waste Rock BH 2	1	1.02×10^{-09}		0	
	2		-4.57×10^{-10}		-4.57×10^{-10}
	3	2.02×10^{-10}		2.06×10^{-12}	
Waste Rock BH 3	1	1.79×10^{-10}			-5.20×10^{-12}
	2		-3.08×10^{-10}		-5.84×10^{-12}

The histograms and box plots of the N_T and SO_4^{2-} rate of change data indicates that the variation of the rates is within the same order of magnitude and that there are few outliers. It also shows that although the rates of increase and decrease of N_T and SO_4^{2-} overlap, the rates of decrease tend to be higher than the rates of increase, indicating a general trend towards decreasing concentrations of N_T and SO_4^{2-}. NT decrease rates are between 5.25×10^{-10} (635 μg/L/d) and 9.54×10^{-14} M/s (1 μg/L/d), with a median of 2.39×10^{-12} M/s (3 μg/L/d). The sulfate decrease rates range from 7.32×10^{-10} (6 075 μg/L/d) to 1.24×10^{-12} M/s (10 μg/L/d), with a median of 1.26×10^{-11} M/s (105 μg/L/d). The similarity between the order of magnitude of the rates of the increasing and decreasing concentrations indicate that the N_T and SO_4^{2-} redox processes may be coupled by biogeochemical processes.

Possible processes include volatilisation through denitrification forming predominantly N_2 and N_2O gasses (Pina-Ochoa and Alvarez-Cobelas 2006, Korom 1992, Mateju *et al.* 1992) and the formation of ammonia through ammonification (Burger
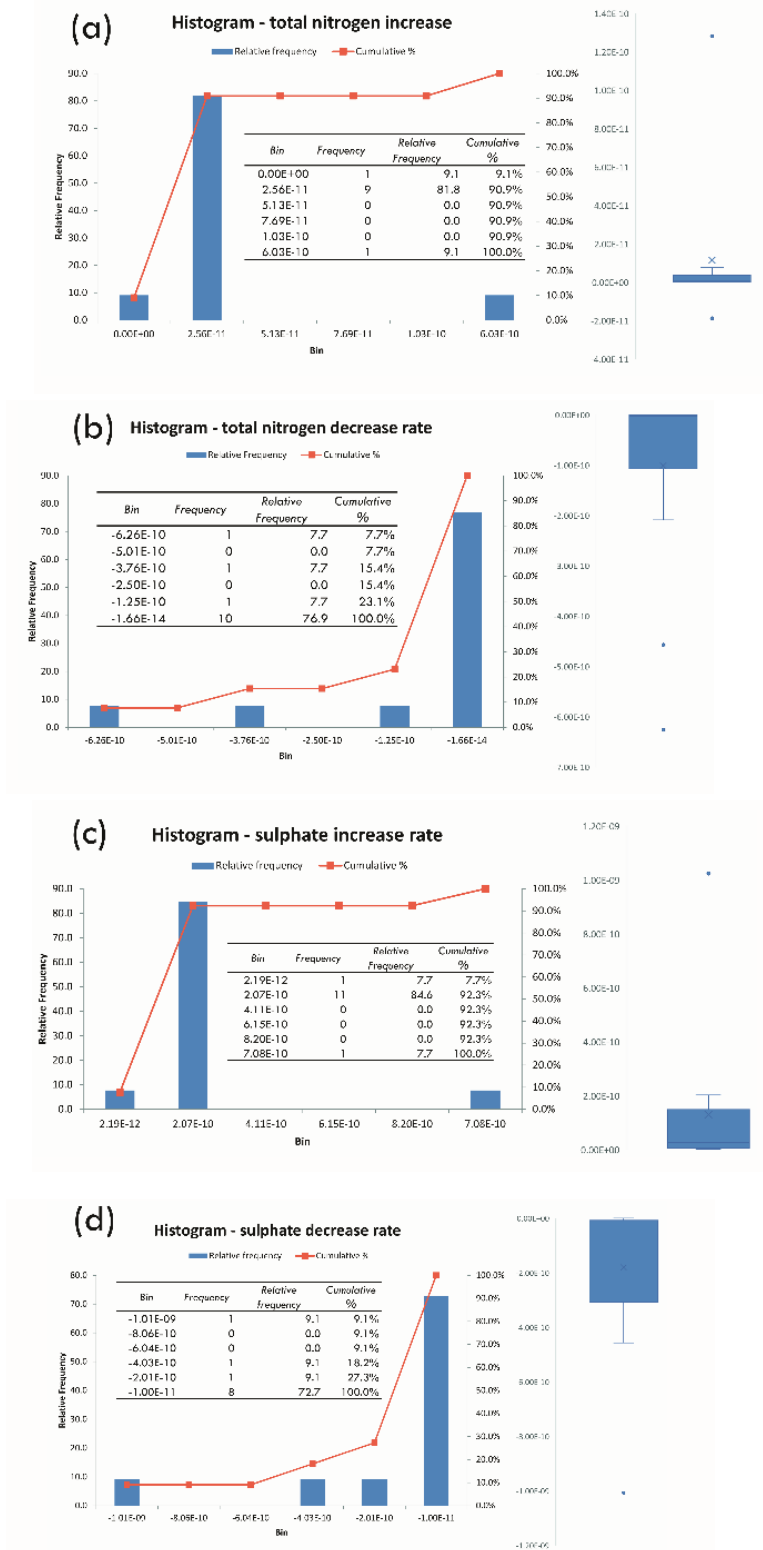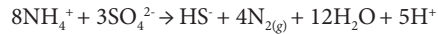
Figure 3 *Histogram and box plots of the rates of change data for N$_T$ (a and b) and SO$_4^{2-}$ (c and d).*

and Jackson 2003). The Henry constant for $NH_{3(g)}$ at 25°C per mole of gas dissolved is low (Rong *et al.* 2011) but can still be significant when considering the total mass of N_T in the system. Both processes can be microbially controlled and catalysed.
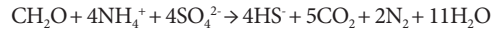
A potential mechanism by which SO_4^{2-} may be removed from at least the aquifer water column is reduction to sulfide (S^{2-}), which at pH values greater than 7 is in the form of the HS^- anion. The HS^- then reacts with dissolved metal ions, principally iron (Fe^{2+}) to form S^{2-} mineral precipitates e.g., pyrite [FeS_2], which settle and become part of the aquifer matrix. This process can also be microbially controlled and catalysed (Shen and Buick, 2004).

The denitrification, ammonification, and sulphate reduction process can also be coupled by the microbial sulfammox process. In recent years, laboratory studies on N and S biogeochemical processes show that N and S cycles can be linked in anaerobic environments found in marine and wetland sediments, by a SO_4^{2-}- reducing $NH_{3(aq)}$-oxidation (sulfammox) process (Liu *et al.*, 2021). The sulfammox process is facilitated by microbes and entails the coupled reduction of NH_4^+ and SO_4^{2-} to produce $N_{2(g)}$ and $N_2O_{(g)}$. NO_2^-, N_2H_4, NH_2OH and S_2^- are important intermediate species in this process. The net reaction for this process is given in eq. 1 (Liu *et al.*, 2021):

$$8NH_4^+ + 3SO_4^{2-} \rightarrow HS^- + 4N_{2(g)} + 12H_2O + 5H^+$$

Equation 1

In eq. 1, *g* denotes the gas phase. In the presence of organic matter, eq. 2 can be written (Liu *et al.*, 2021):

$$CH_2O + 4NH_4^+ + 4SO_4^{2-} \rightarrow 4HS^- + 5CO_2 + 2N_2 + 11H_2O$$

Equation 2

The sulfammox process occurs between pH values of 7 and 8.5 and at HCO_3^- concentrations < 1 000 mg/L (Liu *et al.*, 2021). A conceptual model of the process is shown in fig. 4.

Future work will be focussed on quantifying the biogeochemical processes responsible for the decrease of N_T and SO_4^{2-} in the platinum mine site groundwater system.

Conclusions

An analysis of the rates of change of N_T and SO_4^{2-} from shallow groundwater monitoring data from boreholes downgradient of mine mineral waste facilities, shows a trend towards decreasing concentrations over time, implying that mass of these constituents is removed from the groundwater column to either the gas phase or to the solid phase (i.e., the aquifer matrix). N_T decrease rates are between 5.25×10^{-10} (635 µg/L/d) and 9.54×10^{-14} M/s (1 µg/L/d), with a median of 2.39×10^{-12} M/s (3 µg/L/d). The sulfate
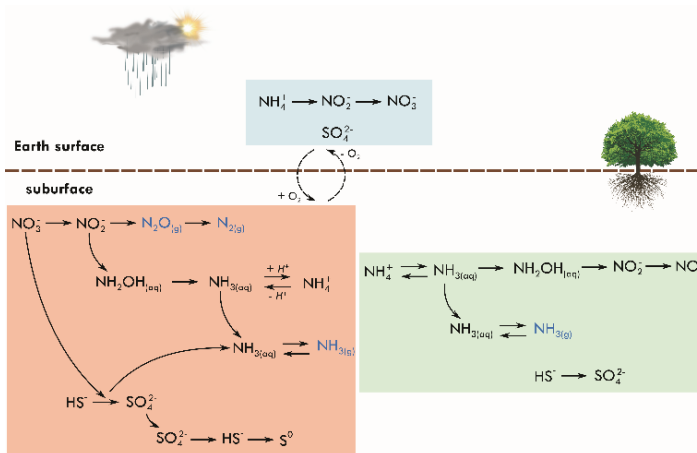
Figure 4 Reaction network diagram showing the sulfammox process on the left, which couples nitrogen and sulfur reduction and the ammification and sulfur oxidation process on the right. The balance within the network determines whether the concentration of N and S species decrease or increase over time.

decrease rates range from 7.32×10^{-10} (6 075 µg/L/d) to 1.24×10^{-12} M/s (10 µg/L/d), with a median of 1.26×10^{-11} M/s (105 µg/L/d).

The similarity between the order of magnitude of the rates of the increasing and decreasing concentrations indicate that the N_T and SO_4^{2-} redox processes may be coupled by biogeochemical processes.

Possible biogeochemical processes include denitrification forming N_2 and N_2O gas as product, ammonification, which causes degasification of N_T in the form of $NH_{3(g)}$ as well as the reduction of SO_4^{2-} to S^{2-} and the precipitation of metal sulfide minerals in the aquifer matrix. The denitrification and sulfate reduction may be linked by the sulfammox biogeochemical process. The implication of these results is that S and N can be expected to decrease in a post-closure scenario due to "natural" mitigation.

Future work will be focussed on quantifying the biogeochemical processes responsible for the decrease of N_T and SO_4^{2-} in the platinum mine site shallow groundwater system and the rates of decrease, focussed on a post-closure scenario.

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