Mine Water and the Environment (2024) 43:278–293
https://doi.org/10.1007/s10230-024-00980-8

TECHNICAL ARTICLE

Tracing Mine Water Flows in a Dolomite Quarry, South Africa, Using Hydrochemistry and Stable Isotopes

Roger Diamond[1] · Christel van Staden[2] · Matthys Dippenaar[2]

Received: 21 August 2023 / Accepted: 22 April 2024 / Published online: 23 May 2024

Abstract
South Africa has a growing population, a relatively dry climate, and abundant mining activity, all of which increase the importance of water management. The Mooiplaas Dolomite Quarry, south east of Pretoria, has been mining metallurgical grade dolomite since 1969, within the productive karst aquifers of the Malmani Subgroup, Transvaal Supergroup. This study was conducted to elucidate the flow of water around the site, including the mine water and groundwater. The site was investigated by sampling precipitation, surface water, groundwater, and mine water for hydrochemical and stable isotope analysis from 2011 to 2017, totalling over 400 samples. Levels of nitrate in groundwater and mine water were marginally above drinking water limits, from explosives residues, and ammonia in the nearby Hennops River was unacceptably high due to municipal sewage outfalls, but otherwise, water quality was very good. Alkalinity from rock weathering, aided by crushing of dolomite, was the main control on water chemistry. Combined analysis of dissolved matter (TDS, nitrate, Mg, etc.) suggested that the dewatering of the mine and resultant recharge from the slimes dams caused an aerated zone of groundwater, which mixed with regional groundwater flowing beneath the site. Stable isotopes, with an evaporated signature from the mine open water bodies, also showed how mine operations cause recharge to groundwater and subsequent seepage back into the pit lakes. The mine appears not to contaminate the regional groundwater; however, mine designs should avoid situations where process water flows via groundwater back into pits, causing excessive dewatering costs.

Keywords Groundwater · Mining · Hydrogen and oxygen isotopes · Evaporation

Introduction

Water resources globally are under threat from the growing human population (Kåresdotter et al. 2022; Kummu et al. 2010). The global population of approximately 8 billion people not only consume fresh water, but also produce pollution that taints many freshwater resources (Simonovic 2002). In addition to these direct effects, indirect effects of ecological destruction and climate change are threatening water resources and the ability of humans to provide for their needs (Nhemachena et al. 2020).

Groundwater occurs in much larger quantities than surface water (Poeter et al. 2020), but a lot of this is too deep to easily exploit and often too salty for most uses (Gleeson et al. 2015). Despite this, groundwater supplies many billions of people and much of the agricultural and industrial activity of humans (Jasechko and Perrone 2021). Importantly, surface water resources are often absent, polluted, or not easily stored or distributed, so groundwater often provides a better, or the only water supply. It is estimated that 50% of the global urban population rely on groundwater for their personal use (UNESCO 2022).

Karst aquifers are some of the strongest groundwater resources, providing major water supplies to human activities and the environment in many parts of the world (Doveri et al. 2021; Gao et al. 2011; Schrader and Winde 2015). South Africa has relatively minimal carbonate rock, but where it does occur, aquifers of regional significance are found, in particular the dolomites of the Malmani Subgroup that occur from Pretoria westwards to the border with Botswana (Meyer 2014).

South Africa is a relatively dry land, with a mean annual precipitation of around 450 mm/a (Dent et al. 1989), which

✉ Roger Diamond
roger.diamond@uct.ac.za

[1] BIOGRIP, University of Cape Town, Cape Town, South Africa

[2] Department of Geology, University of Pretoria, Pretoria, South Africa

is not much over half the global figure of 750 mm/a (Oki and Kanae 2006). Groundwater use is not well measured or managed in South Africa (Pietersen 2006), but estimates are that about 15% of the total amount of water used by humans is groundwater, two-thirds of which is for irrigated agriculture, with nearly 300 towns fully dependent on groundwater (Knüppe 2011).

Water quality is as important as the amount of water available. Most human activities have the ability to impact water quality negatively, including domestic activities (Baloyi and Diamond 2019), urban areas (Germishuys and Diamond 2022), and mining (Winde 2013). Both underground and open pit mines affect water quality, with the nature of the pollution dependent on the mineralogy, water chemistry, rock structure, climate, and other environmental factors (Nordstrom 2011). The effects on groundwater quality from mining have been studied widely (Eary 1999), including in karst environments (Gao et al. 2011). Stable isotopes of water (hydrogen and oxygen) or dissolved constituents (such as NO_3^- or SO_4^{2-}) can be used as tracers of water flow, or to identify the sources of the water or dissolved matter (Cook 2020).

This study made use of hydrochemistry and the stable isotopes of water to help understand the flow of water in and around the Mooiplaas Dolomite Quarry. We evaluated the effect of the quarry on the groundwater of the area and suggest ways to improve site water management, as well as ideas for further study.

Site Description

Location

The Mooiplaas Dolomite Quarry has been mining metallurgical and aggregate grade dolomite since 1969. It is currently operated by Pretoria Portland Cement and is located on the south-western edge of Pretoria in Gauteng Province, South Africa (Fig. 1). Gauteng is the smallest of nine provinces in South Africa, but the most populous at about 16 million (Wikipedia 2022), and is mostly covered by the urban areas associated with Johannesburg in the south and Pretoria in the north.

Geology

The city of Pretoria, located 15 km north-east of the quarry, is underlain by the Pretoria Group, a lightly metamorphosed volcano-sedimentary sequence. This is underlain by the Chuniespoort Group, which includes the dolomites and cherty-dolomites of the Malmani Subgroup, all part of the Transvaal Supergroup, a relatively undeformed Archean to Proterozoic platform sequence forming part of the Kaapvaal Craton (Eriksson et al. 2006).

Mooiplaas mines mainly the Lyttleton Formation, a 100–150 m thick, chert-poor formation, which lies above the Monte Christo Formation and below the Eccles Formation, both of which are chert-rich, and all of which are part of the Malmani Subgroup. The final product, after milling, of metallurgical grade dolomite contains less than 3.5% SiO_2 and 0.5% Al_2O_3 (Page and Du Plessis 1986). The geology of the region dips gently northwards at 10–15°, a tilt caused by crustal subsidence after the intrusion of the Bushveld Igneous Complex around 2 Ga ago. Faults and mafic intrusions complicate the geology somewhat (Figs. 1 and 2).

Climate

The climate of the region is subtropical, with moderate temperature seasonality, but strong rainfall seasonality. Winters (May to July) have cold nights with minimums around 5 °C and warm days with maximums around 20 °C and negligible rainfall, whereas summer lasts from October to March, when temperatures are similarly 16 °C and 28 °C and monthly mean rainfall is around 100 mm (Fig. 3) (CSAG 2022). Total mean annual rainfall is about 700 mm. Winds are light, except for brief downdraughts associated with summer thunderstorms (SAWS 2021).

Geomorphology

Gauteng Province is a relatively flat area with gentle topography of rolling hills or low rocky ridges, typically up to 200 m above the surrounding plains. The whole region, however, is at high elevation, ranging from 1200 to 1800 masl.

Hydrology

The continental watershed runs east-west through central Johannesburg, with southward-flowing streams entering the Vaal River before joining the Gariep (Orange) River and flowing west to the Atlantic Ocean. Northward-flowing streams enter the Crocodile River before joining the Limpopo and flowing north and then east to the Indian Ocean. The Hennops River that flows past Mooiplaas Quarry is part of the latter catchment (Fig. 1).

Hydrogeology

The Malmani Subgroup dolomites are mildly karstified, with minimal surface water features, common sinkholes and dolines especially in the chert-rich formations, pinnacles, and grykes developed to several metres depth, and highly porous gryke infill called WAD (weathered altered dolomite) (Dippenaar et al. 2019). They form a high yielding

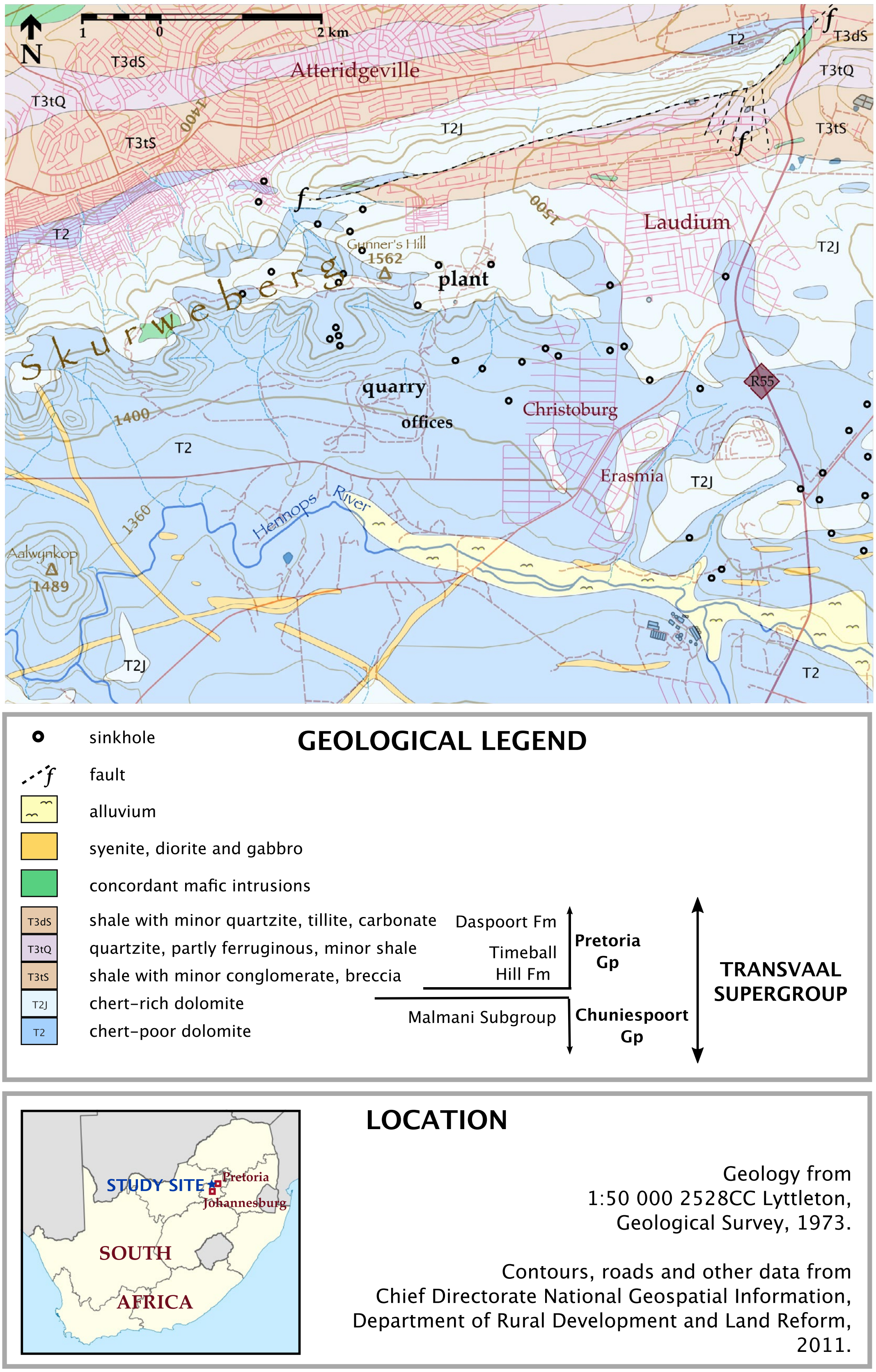

Fig. 1 Location and geology of the study area

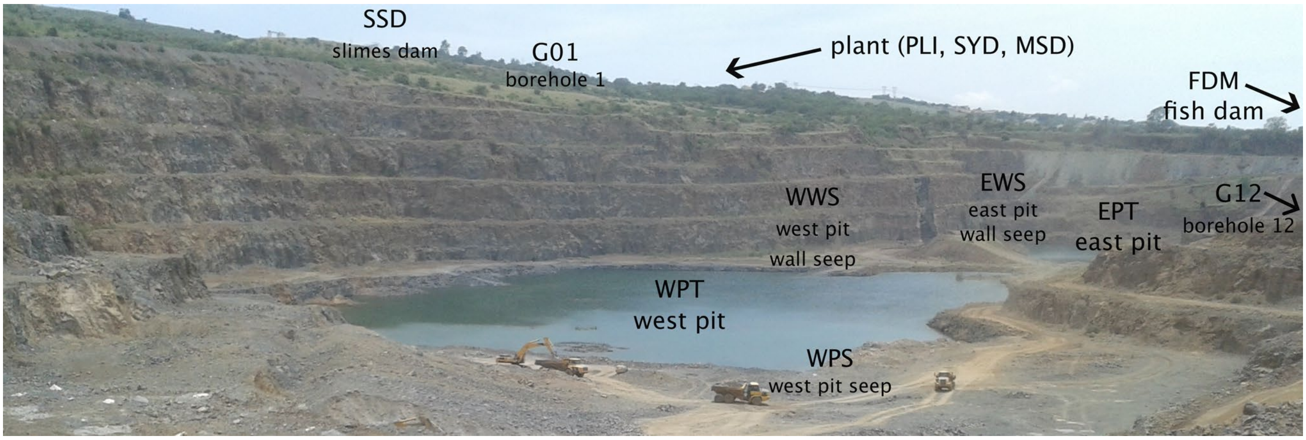

Fig. 2 View northeastwards over the Mooiplaas Dolomite Quarry, showing most of the sample locations used in this study. Note the vertical mafic intrusion (about 10m wide) in the far wall of the quarry, which separates the east and west pits

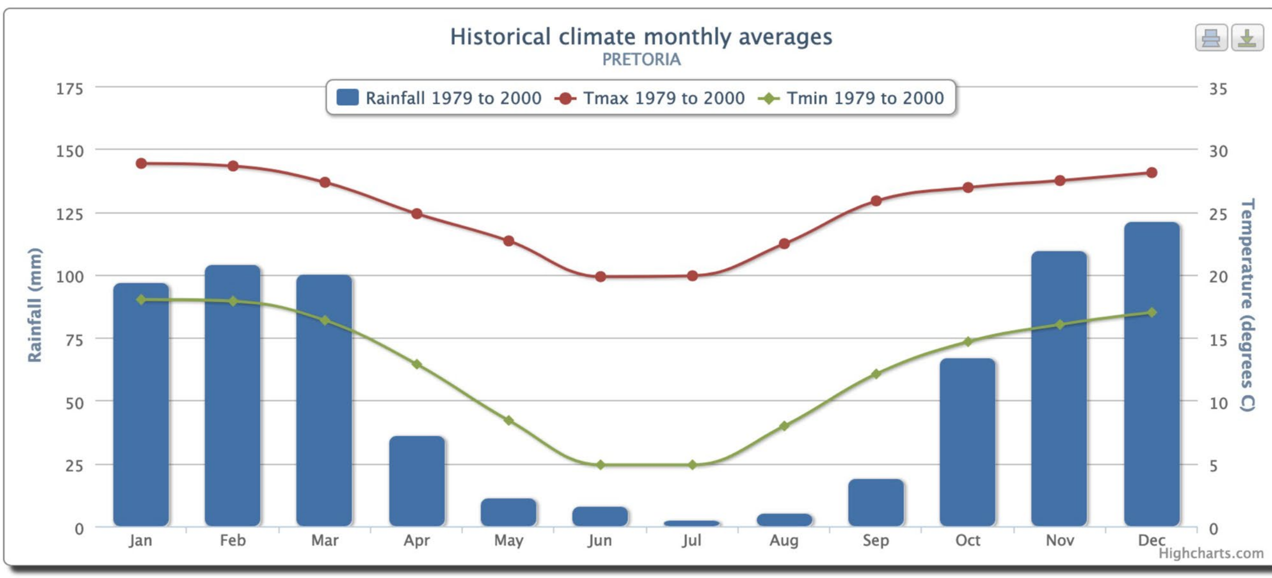

Fig. 3 Climate of the region (CSAG 2022)

aquifer that is utilized for agriculture, domestic, and public water supply (Meyer 2014). Borehole yields are typically over 5 L/s (DWAF 1999). Many springs emerge from the dolomites where they abut less permeable formations, some of which are today used for Pretoria's water supply (Dippenaar et al. 2019), and in the past were part of the reason our ancestors inhabited the Cradle of Humankind World Heritage Site, north-west of Johannesburg (Hobbs and De Meillon 2017).

The large gold mining operations in the Witwatersrand Supergroup near Johannesburg had to dewater tremendous volumes from the dolomites to allow mining, and now that much of the gold mining is over, water levels are recovering, and springs are starting to flow again, although often with poor water quality due to acid mine drainage (Schrader et al. 2014). Water quality in the dolomite aquifers is generally excellent, but effects from mining, agriculture and urban areas, often via polluted rivers, are likely to be increasing (Meyer 2014).

Methods

Field Work

Water samples were taken of rain, surface water, and groundwater at 20 locations in and around Mooiplaas Quarry from 2011 to 2017, totalling 407 samples.

Precipitation

Rain (and hail) was collected from December 2016 until May 2017 in Monument Park, 15 km to the east of Mooiplaas, totalling seven samples (two were taken in February—see Table 1). A standard plastic rain gauge was used to collect all precipitation, the amount of which was noted daily, after which all the water was placed into a larger bottle to create a composite sample for each month. Each month's sample was analysed for hydrogen and oxygen stable isotopes and select samples were analysed for dissolved matter.

Surface Water

The only natural surface water locations sampled were two sites on the Hennops River, upstream and downstream of the quarry (HRU and HRD), totalling 49 samples.

Groundwater

The distinction between surface water and groundwater is not simple at a quarry. For example, the pit lakes are open to the air and so qualify as surface water but are at the level of the water table and represent groundwater. Nonetheless, 17 locations were sampled for surface water/groundwater, of which six are boreholes, three are seeps and eight are various points in the water cycle of the quarry, including the pit lakes, various slurry or slimes dams, and sumps or inlets, totalling 352 samples.

Table 1 Sample abbreviations, names and locations

Id	Sample location	Latitude °S	Longitude °E	Elevation mamsl
RWR	Rain water	25.80282	28.22426	1440
HRU	Hennops River upstream	25.82131	28.07969	1375
HRD	Hennops River downstream	25.81579	28.02603	1350
SMP	Sump	25.80796	28.07617	1410
PLI	Plant inlet	25.79770	28.07933	1520
SYD	Slurry dam	25.79753	28.07961	1520
MSD	MDV slurry dam	25.79497	28.07974	1530
SSD	Slimes dam	25.80195	28.07548	1440
WPT	West pit	28.80630	28.07168	1350
EPT	East pit	25.80659	28.07285	1350
FDM	Fish dam	25.80821	28.07515	1400
G01	Groundwater (borehole) 1	25.80170	28.07590	1445
G02	Groundwater (borehole) 2	25.81780	28.07297	1380
G12	Groundwater (borehole) 12	25.80757	58.07333	1390
G13	Groundwater (borehole) 13	25.80697	28.07266	1380
WPS	West pit seep	25.80749	28.06747	1365
WWS	West pit wall seep	25.80469	28.07291	1360
EWS	East pit wall seep	25.80516	28.07470	1360
EBN	Exploration borehole north	25.80596	28.06521	1410
EBS	Exploration borehole south	25.80766	28.06531	1395

Laboratory Work

Hydrochemistry

Analysis was performed at Aquatico Laboratories in Pretoria. Electrical conductivity (EC) and pH were measured potentiometrically with an autosampler, where a Mode d'Emploi 2-pole conductivity cell was used for EC and a Red Rod pH probe was used for pH. TDS was measured gravimetrically after filtering out > 2 µm suspended solids and then evaporation in a pre-weighed dish, according to APHA (2005) procedures. Alkalinity, Cl, SO_4, PO_4, $N0_3$, and NH_4 were analysed using a KoneLab automated spectrophotometer, and Br using a desktop Hach spectrophotometer (APHA 2005). Na, Mg, K, and Ca were analysed with a Perkin Elmer Optima 7300DV or Optima 8300 ICP-OES (inductively coupled plasma optical emission spectrometer).

Stable Isotopes

Analysis was performed at iThemba Labs in Johannesburg using a Los Gatos Research DLT-100, according to the procedures outlined by the IAEA (2009). This instrument fills a cavity with a vapourised sample and then fires a laser into the cavity with high reflectivity mirrors, generating a path length of kilometres, such that water molecules of different isotopic composition cause different degrees of absorption.

Data Correction and Validation

Hydrochemistry

In addition to laboratory calibration procedures, blanks (distilled water) and duplicates of field samples were submitted blind (unknown to the laboratory) with every batch of samples. The relative percent difference (RPD) for analytes was calculated for duplicate samples. Over 80% of the duplicate analyses had RPD < 10%. In addition, the charge balance was calculated, comparing the sum of cations to the sum of anions as milliequivalents, and it was found the RPD for charge balance was < 10% for all samples.

Stable Isotopes

Laboratory standards were inserted with every batch of samples, to allow correction to the international standard, SMOW (Standard Mean Ocean Water). In addition, blind duplicates were inserted with the samples to provide a check on the laboratory's precision. According to iThemba Labs, their analytical precision is approximately 1.5‰ for δ^2H and 0.5‰ for $\delta^{18}O$. Analysis of duplicates showed that RPD was < 10% for all duplicates.

Results

Hydrochemistry

Water Quality Assessment

Table 2 shows the mean values for each analyte at each sample location, and overall for the study. Shading indicates where values exceed ideal, acceptable, and maximum allowable drinking water quality guidelines for South Africa (SABS 2001). As can be seen from the table, the water quality around Mooiplaas is generally very good. The major exceptions are ammonia, which is moderately elevated in the Hennops River, the sump, and the two exploration boreholes, and nitrate which is slightly elevated in a few of the sample locations.

The ammonia in the Hennops River is likely to be from wastewater from sewage treatment works that discharge into the River (Rimayi et al. 2019). The presence of ammonia in the exploration boreholes is discussed later. The elevated nitrate, which is found in most of the mine water samples, is probably from explosives used for mining (Nilsson and Widerlund 2017).

Hydrochemical Trends

Several scatter plots have been drawn (Figs. 4, 5, 6, 7) showing the most interesting hydrochemical patterns. In Fig. 4, a very clear positive correlation exists between alkalinity and total dissolved solids (TDS). Alkalinity at the circumneutral pH's of this site is largely bicarbonate ions (HCO_3^-), which form during the process of rock weathering. In this process, atmospheric or soil CO_2 dissolves into rain or soil water, forming a solution of weak carbonic acid (H_2CO_3), which dissociates into hydrogen and bicarbonate ions, the H^+ then being exchanged for a metal cation (e.g. K^+) in a mineral. In addition to this process, which operates everywhere at the earth's surface where there is rain, the study area is underlain by dolomite. The dissolution of dolomite ($CaMgCO_3$) releases CO_3^{2-} ions into the water, most of which will be converted to bicarbonate from hydrogen ions available in the mildly acidic rain/soil water. By this mechanism, natural waters increase in metal cations and bicarbonate ions over time. The strong correlation of alkalinity with TDS proves the control that rock weathering has on water quality, and the gradient of 0.57 seems to show that nearly 60% of the dissolved matter can be accounted for by the alkalinity. In

Table 2 Mean values for hydrochemical parameters per sample location, and overall means, minimums and maximums

site	n	pH	EC	TDS	Na	K	Mg	Ca	Cl	SO_4	alkalinity as $CaCO_3$	NO_3-N	NH_4-N	PO_4	F	Br	SI dol
			mS/m	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
RWR	6	6.18	3.2	14	0.7	0.7	0.4	1.9	1.5	4.2	2	0.8	0.74	0.07	0.15	0.01	-9.9
HRU	26	7.82	69.1	382	64.7	10.2	15.7	38.7	66.2	48.1	199	1.5	10.18	1.21	0.25		-0.1
HRD	23	7.87	66.1	364	58.7	9.8	16.3	39.2	57.9	47.6	193	2.1	9.08	0.97	0.26		0.1
SMP	16	7.81	56.6	318	30.1	10.1	34.8	38.8	26.5	21.1	248	0.9	2.06	3.28	0.46		0.45
PLI	7	8.52	50.5	322	13.1	0.7	39.3	45.2	23.6	31.8	212	8.6	0.09	0.05	0.18	0.33	1.79
SYD	9	8.43	61.0	401	16.8	2.5	57.8	32.2	35.4	32.7	205	21.9	1.10	0.04	0.19	0.07	1.57
MSD	6	8.77	57.1	359	17.7	3.2	62.8	19.6	37.8	32.0	225	10.8	0.13	0.05	0.21	0.19	2.18
SSD	6	8.59	44.8	289	12.0	2.0	44.4	20.9	26.1	29.2	163	12.3	0.37	0.03	0.23	0.09	1.5
WPT	28	8.47	52.3	306	12.2	0.6	37.5	48.2	21.4	27.4	203	9.8	0.11	0.03	0.21	0.20	1.77
EPT	29	8.52	53.4	307	12.2	0.7	40.9	44.6	22.7	32.5	198	9.7	0.06	0.03	0.20	0.23	1.74
FDM	27	8.39	53.0	308	12.4	0.7	40.9	44.2	22.8	32.5	207	7.5	0.10	0.09	0.21	0.25	1.59
G01	59	7.94	89.9	547	19.3	1.1	64.3	91.6	66.2	84.6	320	5.7	0.09	0.05	0.24	0.60	1.39
G02	60	8.18	56.2	326	10.6	0.6	39.0	55.4	22.0	32.4	219	8.5	0.08	0.03	0.20	0.40	1.33
G12	63	7.91	65.7	383	9.9	0.9	45.0	70.4	23.7	40.5	263	8.7	0.10	0.03	0.21	0.50	1.04
G13	24	7.90	67.2	376	9.9	1.4	45.5	69.9	22.7	39.9	263	8.5	0.15	0.03	0.23		1.04
WPS	4	8.22	54.5	341	13.7	0.6	37.3	53.7	21.9	24.1	211	13.9	0.08	0.02	0.16	0.26	1.27
WWS	5	8.57	65.5	434	17.6	1.2	59.6	45.8	38.9	36.7	229	21.2	0.04	0.03	0.13	0.48	2.16
EWS	3	8.49	80.5	553	14.9	0.2	64.4	71.0	67.3	76.7	226	27.1	0.04	0.04	0.13	0.58	2.12
EBN	2	7.52	23.5	154	1.1	3.1	13.1	28.7	2.7	2.0	153	0.8	5.21	0.56	0.24	0.01	-0.96
EBS	4	7.70	50.2	307	2.8	2.7	37.2	57.3	4.2	26.4	277	0.5	4.37	0.03	0.27	0.01	0.57
min		5.90	1.8	5	0.2	BD	BD	0.8	0.9	0.1	1	BD	BD	BD	0.09	0.01	
max		9.02	140.0	807	166.0	28.5	77.7	139.0	205.0	122.0	520	29.3	28.10	13.70	1.67	0.86	
mean	407	**8.09**	**62.8**	**368**	**19.0**	**2.4**	**41.7**	**56.4**	**34.1**	**42.1**	**233**	**7.6**	**1.40**	**0.30**	**0.20**	**0.30**	

Shading indicates ideal (no shading), acceptable (light orange), allowable (medium orange) and above maximum allowable (dark orange) limits according to South African drinking water standards (SABS 2001). In the minimum values row, BD indicates the lowest value was below detection. The dolomite saturation index is given in the last column, as calculated using the preceding hydrochemical averages for each location and PHREEQC software

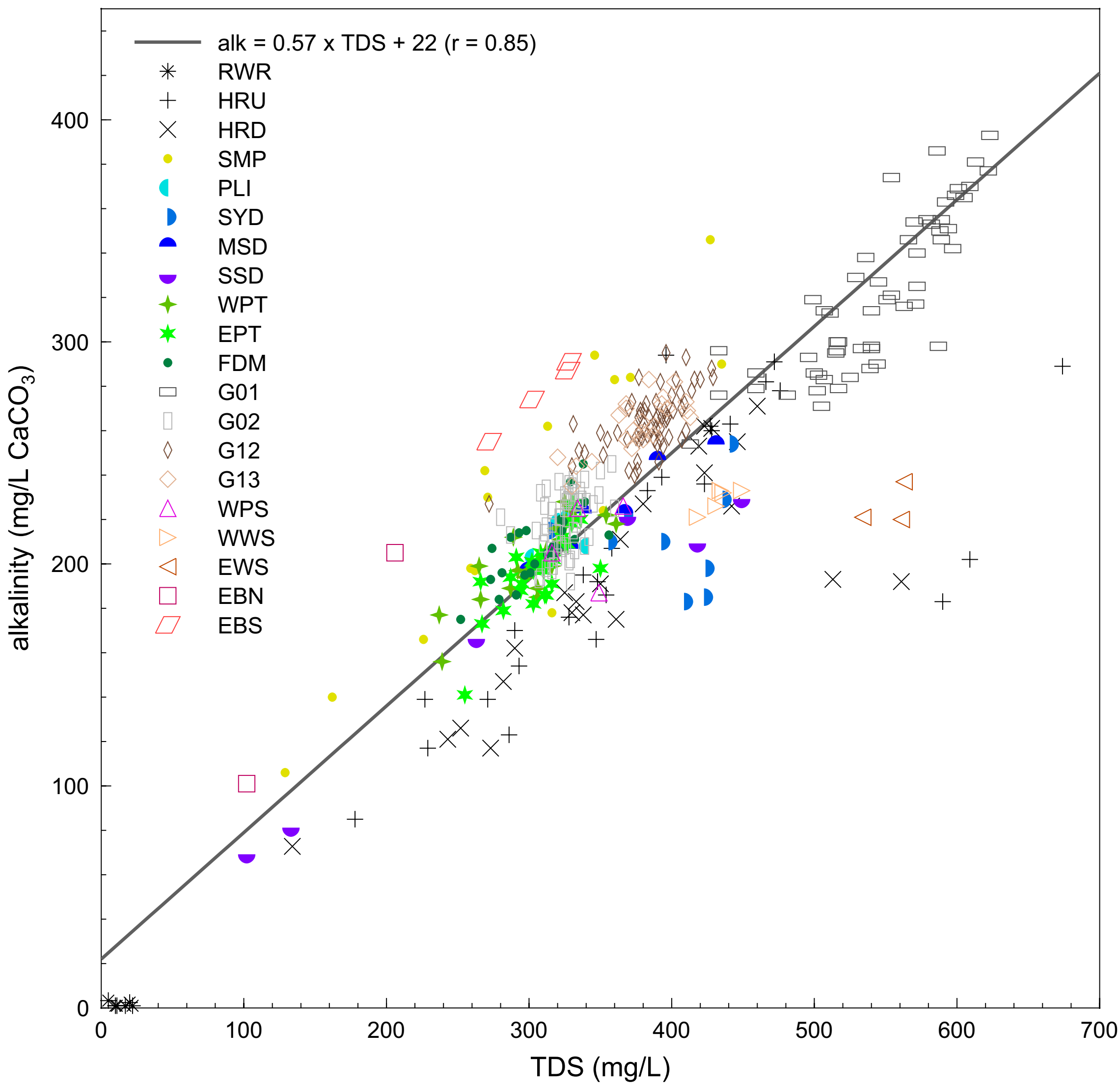

Fig. 4 Plot of alkalinity (reported as $CaCO_3$) against TDS (total dissolved solids). The strong correlation shows alkalinity is a major control on the water quality. Alkalinity is, in turn, largely influenced by rock weathering

actual fact, because the alkalinity is reported as $CaCO_3$, only 60% of this mass is actually carbonate or bicarbonate. As 60% of the 0.57 correlation is approximately 0.4, this means the alkalinity actually accounts for approximately 40% of the TDS (Table 2 and Fig. 4).

In contrast, the other major anion, chloride, which also correlates well with TDS, is at a much lower slope of 0.24 (Fig. 5). This slope would be even lower, if not for five outlier samples from the Hennops River, probably representing sewage spills of highly evaporated wastewater with high salt contents. The lower chloride content is typical of inland locations, such as Pretoria, where marine aerosol input is minimal (Van Wyk et al. 2011). What is also noticeable from Fig. 5 is the distinctly higher chloride contents of the Hennops River, compared to the mine water. This is because the mine area water chemistry is more strongly influenced by rock dissolution, encouraged by the blasting and crushing of dolomite.

For the cations, Ca and Mg are the dominant ions (see Table 2), which is typical of inland settings where dissolution of dolomite dominates over marine aerosol. Further evidence for dolomite dissolution being a strong control on the hydrochemistry is the dolomite saturation indices, as calculated using PHREEQC (Table 2). These mostly reveal the water to be supersaturated (*SI dol* > 0) in dolomite. The lowest groundwater or mine water *SI dol* values are found in the exploration boreholes, suggesting that the natural groundwater is less saturated in dolomite.

Figure 6 shows the nitrate and ammonia concentrations. There is a strong contrast between the Hennops River

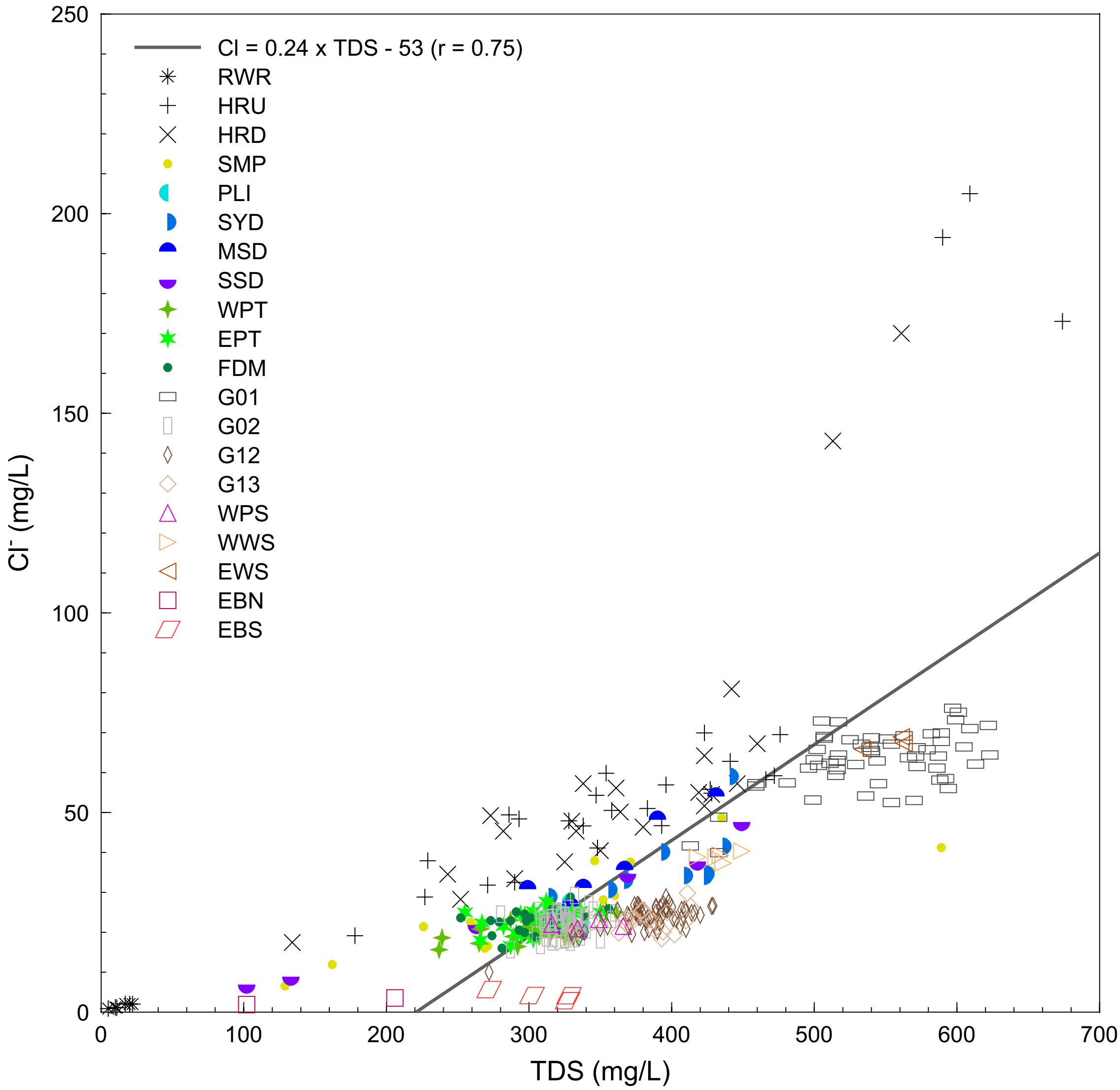

Fig. 5 Chloride concentrations plotted against TDS (total dissolved solids). The low gradient shows that Cl has a lesser role in the dissolved water quality components than alkalinity. This is to be expected for inland locations, far from the sea. Relatively high Cl samples from the Hennops River are likely from sewage spills from municipal waste water treatment works

samples where ammonia dominates, and virtually all of the other samples, where nitrate dominates. The likely reasons for the pattern in this study are twofold. First, the aerated state of groundwater in and around the mine is to be expected from the quarrying operations, where groundwater is being pumped out and recharged and generally circulated strongly through the pit lakes, the plant, various slurry dams, and so on. Second, the Hennops River receives treated and untreated sewage with a high organic matter content, which translates into a high COD (chemical oxygen demand; Rimayi et al. 2019). This decaying organic matter consumes the available oxygen in the water, causing the reduced form of nitrogen (ammonia) to dominate over the oxidised form (nitrate).

The final hydrochemistry scatter plot, Fig. 7, shows magnesium plotted against TDS. Here there is substantial separation of samples and clear grouping of certain locations, as well as distinctly different trends between the Hennops River, mine water, and groundwater. The mine water circulates in the slurry and slimes dams, the plant inlet, and the pit lakes, while the groundwater was sampled from boreholes and seeps. Overall, both the mine water and groundwater show much higher Mg values than the Hennops River. This is likely due to the blasting and crushing of dolomite at the mine, which accelerates dolomite dissolution and the release of Mg into this water. However, even within the mine area, the groundwater has a lower Mg vs TDS trend than the mine water, which is more directly exposed to the broken-up

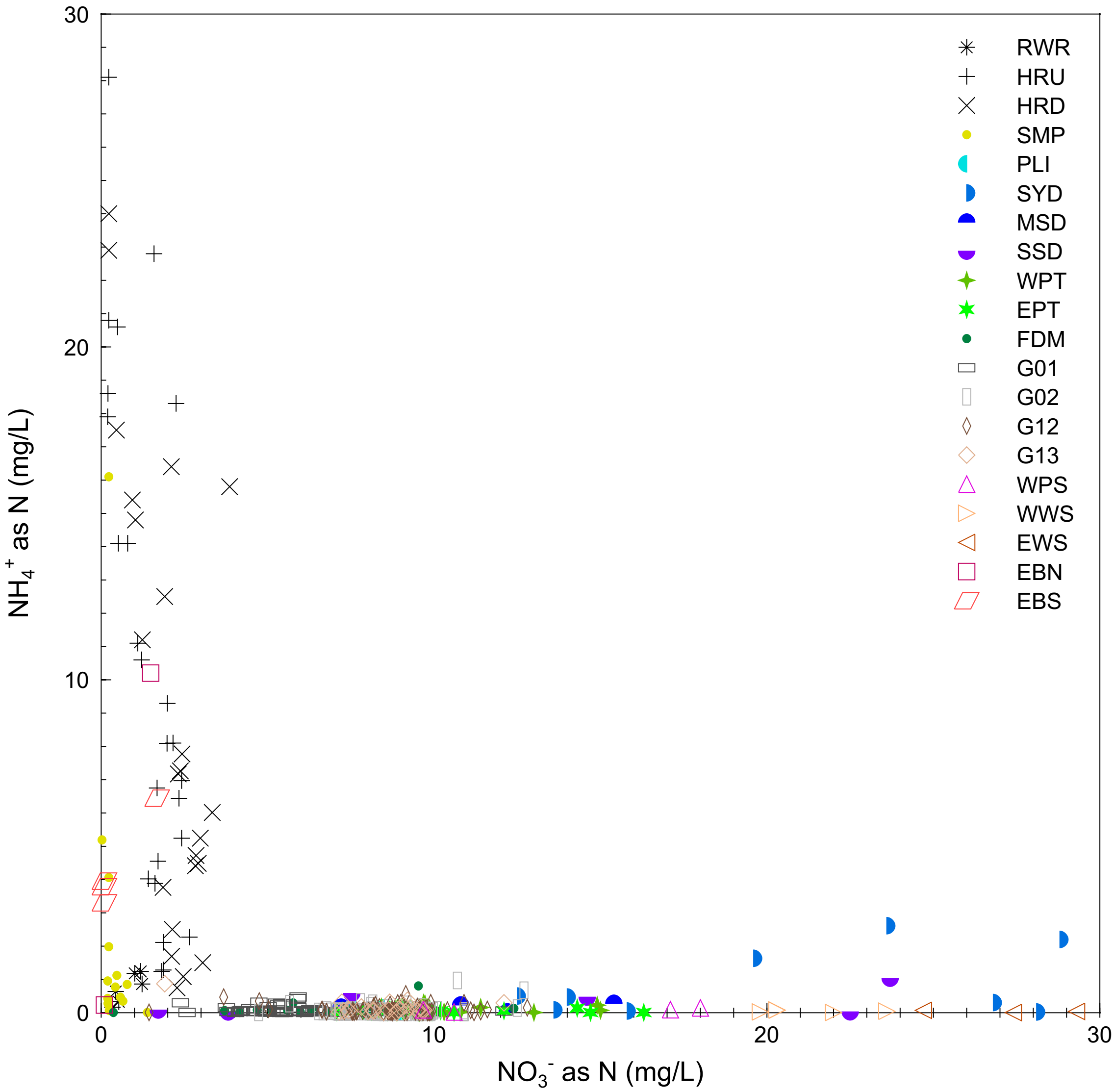

Fig. 6 Ammonium plotted against nitrate, revealing two distinct water types. Surface water in the Hennops River contains high ammonium, evidence for sewage spills, whereas most other water (surface and groundwater) near the quarry has elevated nitrate, most likely from explosives residues

dolomite. The slurry dams have the highest Mg contents, reflecting their position downstream of the plant and thus the highest exposure to fine dolomite particles.

However, the Mg and TDS levels are fairly low, still being within acceptable drinking water limits. This is partly due to the way in which dolomite dissolution is controlled by acidity. Once the acidity of the water has been used up (the mean pH for this study was 8), dolomite dissolution is negligible. This is confirmed by the high dolomite saturation indices, showing the water to be supersaturated in Ca-Mg-CO_3. The low TDS may also be partly due to the way in which the mine water interacts with the local groundwater and is diluted by the local to regional groundwater flowing through the site.

Stable Isotopes

The hydrogen and oxygen isotope results are given in Table 3 and plotted in Fig. 8. The rain isotope composition ranges from about − 70‰ δ^2H and − 10‰ δ^{18}O to almost + 10‰ δ^2H and 0‰ δ^{18}O. The LMWL (local meteoric water line) was calculated using these points and the reduced major axis form of regression, where both x and y are treated as independent variables, giving the result of $\delta^2H = 8.3\delta^{18}O + 12.2$. This line is slightly steeper than the GMWL (global meteoric water line; Craig 1961). Many LMWLs are at a gentler gradient than the GMWL (Diamond 2022), but some areas do have LMWLs with gradients around 8; the line calculated for this study is

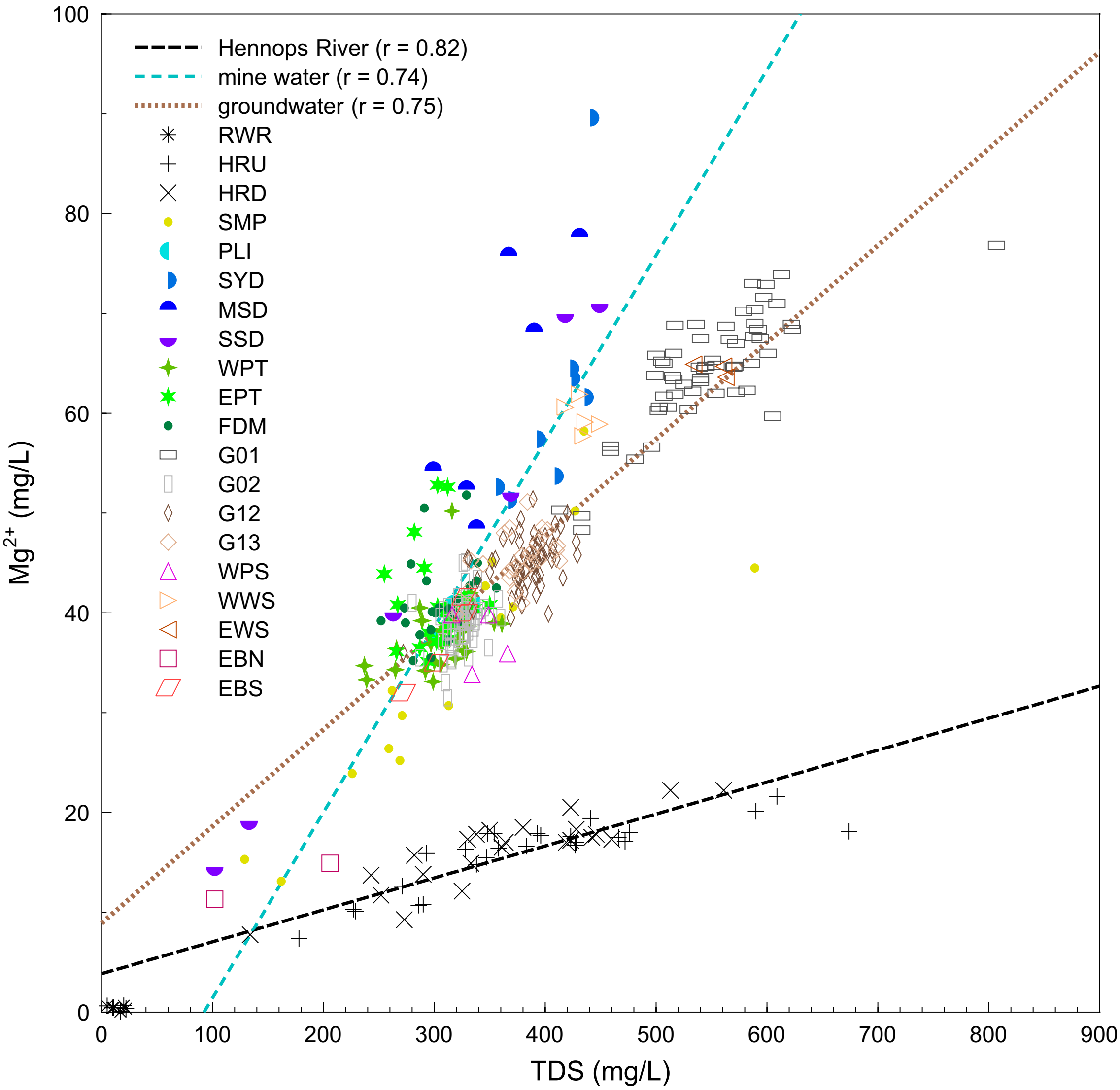

Fig. 7 Magnesium plotted against TDS. The three distinct trends reveal the effect of crushed dolomite and actively circulating groundwater in the mine area, to a high degree for the *mine water*, a moderate degree for the *groundwater*, and with no effect in the Hennops River

very close to that from Meyer (2014), who calculated a Pretoria LMWL of $\delta^2H = 8\delta^{18}O + 11.8$.

Two precipitation samples are outliers. The upper outlier is for February 2017, during which there was precipitation in 25 of the 28 days, with a total of only 67 mm (Weather and Climate 2023a). These low rainfall events tend to suffer from raindrop evaporation as the rain falls to the ground, thereby generating more positive delta values. The lower outlier is from May 2017, during which there was a single rainfall event over 3 days, producing only 5 mm of rain, but in which temperatures plummeted 10 °C below the norm to 8 °C as a cold front moved across the country (Weather and Climate 2023b). This resulted in an unusually isotopically negative sample. Despite these outliers, the MWL for this study runs through the remaining five samples (one is somewhat obscured by the other data) convincingly.

All the samples except for the rainwater also plot along an excellent regression line ($r = 0.98$) with the equation $\delta^2H = 4.5\delta^{18}O - 3.5$. This line is at a lower gradient than the meteoric water lines and is typical of a local evaporation line (LEL). The groundwater samples tend to plot at the lower end of the line, and the lowest samples are in fact the two exploration boreholes. These are located to the west of the mining area and are the furthest removed from the pits, crushing plant, and various slurry dams, and so are least involved with the disturbed mine area. As such, they represent relatively undisturbed “natural” groundwater in terms of isotopic composition. It therefore makes sense that they plot close to the LMWL. The groundwater samples with the

Table 3 Hydrogen and oxygen stable isotope data for rain, groundwater and mine water

Date	RWR		PLI		SYD		MSD		SSD		WPT		EPT		FDM	
	Rain water		Plant inlet		Slurry dam		MSD slurry dam		Slimes dam		West pit		East pit		Fish dam	
	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Dec 2016	− 20.2	− 4.21														
Jan 2017	− 18.9	− 3.94														
Feb 2017	9.1	− 0.22														
21 Feb 2017	− 25.1	− 4.68														
Mar 2017	− 14.6	− 2.67														
Apr 2017	− 14.2	− 3.26	− 15.7	− 2.47	− 14.5	− 2.39	− 13.6	− 2.29	− 13.5	− 2.04	− 19.0	− 3.36			− 14.9	− 2.62
May 2017	− 72	− 9.88	− 15.6	− 2.74	− 15.1	− 2.75	− 13.2	− 2.20	8.0	2.93	− 18.7	− 3.34	− 16.1	− 2.75	− 15.8	− 2.52
Jun 2017			− 16.5	− 2.63	− 14.9	− 2.40	− 12.8	− 2.10	10.2	3.02	− 17.8	− 3.16	− 15.9	− 2.67	− 15.6	− 2.66
Jul 2017			− 15.6	− 2.68	− 14.7	− 2.46	− 14.6	− 2.37	− 14.2	− 2.33	− 18.7	− 3.27	− 16.0	− 2.70	− 15.6	− 2.58
Aug 2017			− 15.5	− 2.55	− 13.4	− 1.48	− 11.8	− 1.87	0.0	0.66	− 20.0	− 3.50	− 15.5	− 2.58	− 15.2	− 2.76
Sep 2017			− 14.5	− 2.66	− 13.4	− 2.23	− 11.4	− 1.83	− 6.5	− 0.82	− 16.6	− 2.89	− 14.9	− 2.49	− 14.8	− 2.43

Date	G01		G12		WPS		WWS		EWS		EBN		EBS	
	Borehole 1		Borehole 12		West pit seep		West pit wall seep		East pit wall seep		Exploration bh N		Exploration bh S	
	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Apr 2017	− 17.4	− 3.27	− 16.1	− 3.11	− 20.6	− 3.81					− 24.2	− 5.04	− 30.1	− 5.25
Mar 2017	− 16.9	− 3.31	− 15.5	− 3.03	− 20.6	− 3.82	− 15.7	− 2.36			− 25.1	− 5.31	− 29.4	− 5.13
Jun 2017			− 16.2	− 2.74	− 17.9	− 3.19	− 14.2	− 2.24	− 8.4	− 1.34				
Jul 2017	− 18.8	− 3.24	− 16.4	− 2.77			− 13.9	− 2.2	− 9.1	− 1.49				
Aug 2017	− 15.9	− 3.04	− 16.3	− 2.7			− 12.8	− 1.83	− 8.3	− 1.3				
Sep 2017			− 27.1	− 5										

All delta (δ) values in permille (‰) and corrected to SMOW (standard mean ocean water) as per international standards (Cook 2020)

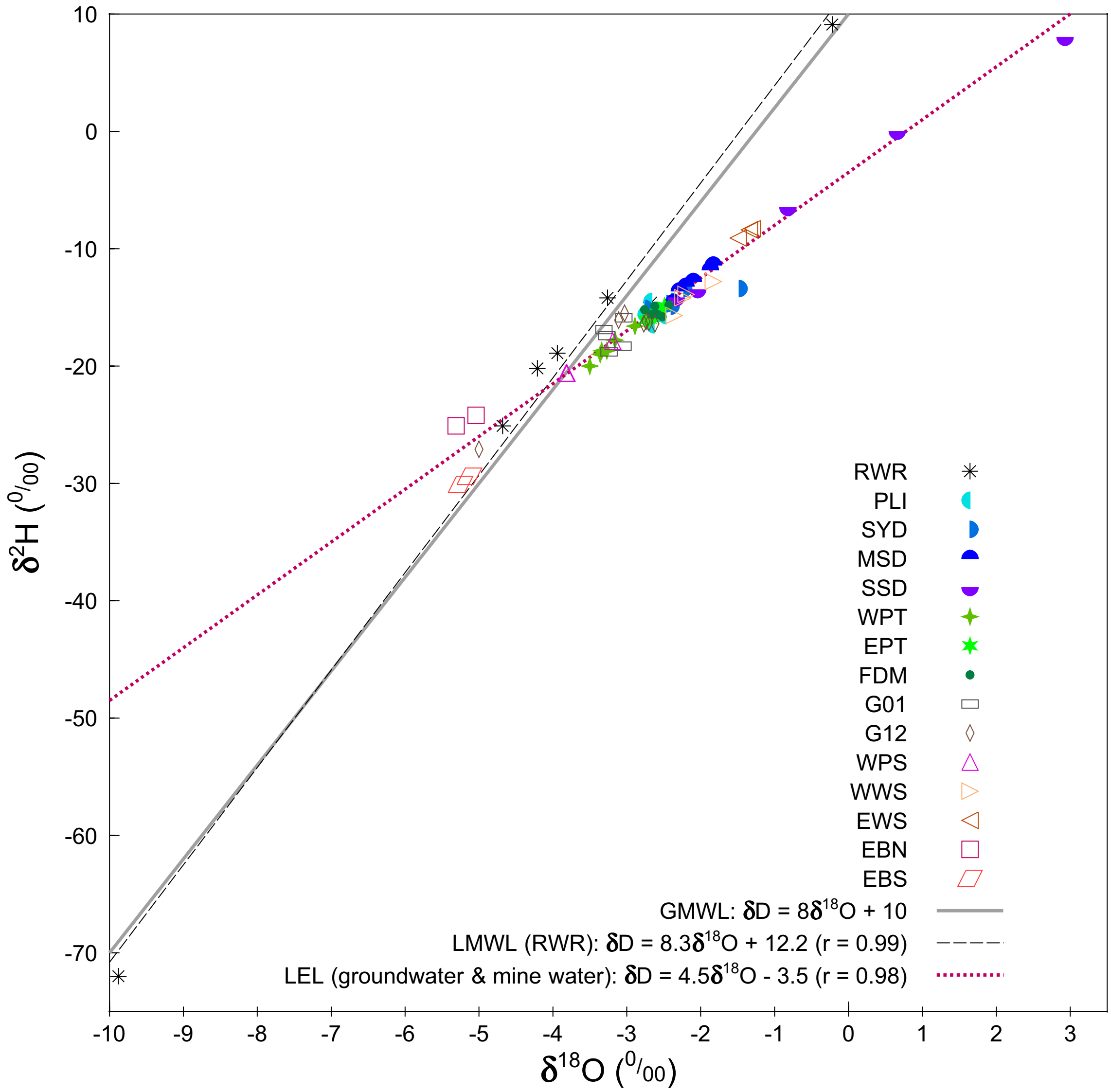

Fig. 8 Stable isotope composition of water samples from the study. The low gradient trend for all except the rain samples, reveals that evaporation is acting on much of the water around the mine site, with the least affected being the exploration boreholes (possibly reflecting natural groundwater of the area), through to the most evaporated samples in the slimes dam

highest δ values are the two pit wall seeps, where evaporation has acted on the water prior to sampling, possibly as the water drips down the exposed rock faces of the open pits. The G01 and G12 borehole samples plot close to the LWML, but with some tendency towards the right, suggesting mild evaporative effects.

In contrast to the groundwater, the mine water in the various pits and slurry dams has a moderate to highly evaporated isotope signature, plotting furthest from the LWML. This shows that much water is lost to evaporation during the quarrying process. It is also possible that the cause of the evaporated signature for the pit wall seeps (WWS and EWS) is not the final stages of dripping down the exposed pit walls, but rather the local groundwater mixing with some of the mine water. This would happen when water from the highly evaporated slurry dams infiltrates the ground and recharges the water table, and then mixes with the groundwater.

Discussion

The Mooiplaas dolomite quarry affects the local groundwater in several ways. The nitrate levels show that explosives residues dissolve into the groundwater. This nitrogen is almost all in the oxidized state (nitrate), with virtually no ammonia detected, indicating that the groundwater is well oxygenated by the mining activities. This happens through the dewatering of the east and west pits and seepage, re-infiltration, and recharge from the slurry and slimes dams and other ponds (see Fig. 9).

In contrast, the Hennops River shows high ammonia levels and negligible nitrate. This is due to the discharge of treated and untreated sewage, containing high organic matter contents, into the river, causing high COD and rendering the river water anoxic (Rimayi et al. 2019).

The only two sample sites with significant ammonia, other than the Hennops River, are the exploration boreholes, which, as stated earlier, lie to the west of the active mining area (Fig. 9). The presence of ammonia in these boreholes could result from several factors. First, the informal settlements that occur north of the mining area and at a higher elevation (Fig. 1) have inadequate sanitation, so human waste, rich in ammonia, could be leaching into the ground. In addition, cows and goats are kept and their waste may contribute to the ammonia load. Also, since the exploration boreholes are removed from the most active mining area, they are less likely to receive recently pumped and oxygenated water, keeping the ammonia stable. The low nitrate levels in the groundwater in these two boreholes show that they are uninfluenced by the mining operations.

The highest nitrate levels were found in the slurry dams (mainly SYD & SSD), and in the two wall seeps in the east and west pits (EWS & WWS). As nitrates are extremely soluble, residual explosives from years ago would likely have been leached from the old benches and blast holes above the wall seeps, so the presence of high nitrate in these wall seeps suggests the groundwater being discharged at the wall seeps is being recharged by seepage from the slurry dams upslope to the north.

Crushing of dolomite, creating high surface area, enhances the release of Mg by weathering. This is revealed by comparing the two exploration boreholes, averaging 13 and 37 mg/L Mg^{2+}, against the mine water, with an average of ≈ 60 mg/L. When the Mg-enriched mine water mixes with regional groundwater, the resultant groundwater beneath the mine has intermediate Mg values, averaging 50 mg/L.

The stable isotope results show some remarkable patterns. All the groundwater and mine water samples sit along a LEL; each sample site tends to cluster quite well, and the clusters are fairly well ordered. The order of sample sites, from least to most evaporated, is shown in Fig. 10. As with the Mg data, the two exploration boreholes seem to be the closest to natural groundwater, with isotope compositions very similar to rain water and close to the local and global meteoric water lines. These are followed by the west pit seep, which is on the south-western side of the west pit and

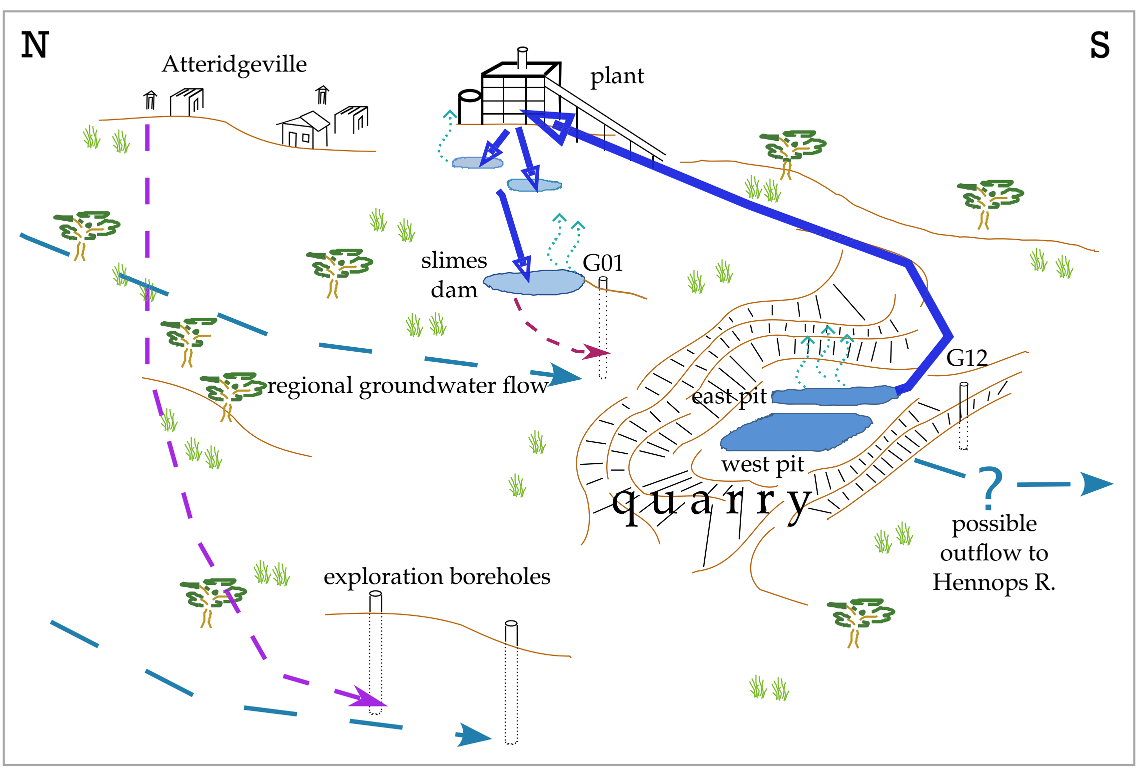

Fig. 9 Conceptual diagram of water flows around the Mooiplaas Dolomite Quarry. Groundwater is indicated with dashed lines and evaporation with dots. The exploration boreholes appear to be unimpacted by the mine activity, but may have urban pollution, accounting for their high ammonium levels. The slurry and slimes dams recharge groundwater, which then discharges via the pit wall seeps. This is detected with evaporated stable isotope signatures and high nitrate levels in the pit wall seeps

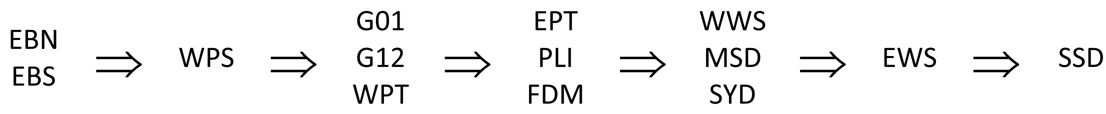

Fig. 10 Increasingly evaporated stable isotope values for sample sites (see Fig. 2). The two exploration boreholes, west of the active mining area, are most similar to meteoric water, followed by mostly groundwater samples and then mine water samples

furthest from the plant and various dams, and so is likely to be discharging relatively natural groundwater. Then come two boreholes, G01 and G12 and the west pit lake. Note that at this point, most of the samples are groundwater. The next group has more mine water samples, being the east pit lake, the plant inlet, and the fish dam. The last main group contains the west pit wall seep, the MSD slurry dam, and the slurry dam. The groundwater sample here, WWS, could be experiencing dramatic evaporation immediately prior to sampling, as the water trickles over rock slabs, but is also likely influenced by the evaporated water from the slurry dams upgradient (to the north), which recharge the groundwater. In a similar way, the east pit wall seep also shows a very evaporated isotope signature, and finally the slimes dam, which is the last point in the mine water cycle before that water recharges the groundwater.

Conclusion

The main control on water chemistry at Mooiplaas is alkalinity. In this karstic setting, most of the alkalinity is from dissolution of carbonate minerals, mostly dolomite, in the Malmani Subgroup, though weathering of silicates and other minerals also contributes. Ca and Mg are the main cations, also due to the dolomite-dominated geology and the distance from the coast, where Na tends to dominate.

Ammonia is elevated in the Hennops River (HRU & HRD) and the exploration boreholes (EBN & EBS), most likely due to sewage discharged into the former and poor sanitation in Atteridgeville in the latter. Nitrate is elevated in most of the mine water and groundwater samples, from explosive residues. Aside from these moderate ammonia and nitrate levels, the groundwater quality is generally good; however, trace element and bacterial analyses were not performed.

The presence of nitrate and absence of ammonia in the mine water and boreholes within the mining area is evidence of well-aerated groundwater, caused by dewatering, recharge, and active circulation of surface water and groundwater in the mine area. Higher TDS levels in all but the exploration boreholes suggests evaporative concentration, further supporting this model. In contrast, the two exploration boreholes have higher ammonia, indicating less aeration, and lower TDS, indicating less evaporation. This groundwater possibly reflects the regional groundwater condition, although the high ammonia is probably only a local effect from the nearby township and informal settlement.

There appears to be a mixing relationship between the mine water and groundwater based on dissolved Mg trends, as the actively circulated mine water (pits, dams, etc.) mixes with the regional groundwater flowing towards and beneath the mine area. The limited increase in TDS is also evidence for only minor evaporative enrichment due to a sustained regional flow of groundwater, preventing excessive salinisation of the site.

Stable isotopes reveal a strong evaporation trend acting on all of the mine water. The least evaporated samples are the two exploration boreholes, again suggesting these reflect regional groundwater conditions. From there, the various samples progressively show more evaporation, ending with the slurry and slimes dams. The moderately evaporated isotope composition of the east and west pit wall seeps (EWS & WWS) suggest recharge or leakage from the slimes or slurry dams (SSD & SYD), mixed with groundwater, is discharging into the east and west pits. High nitrate levels in the EWS and WWS corroborate this.

The quarry does not appear to contaminate the regional groundwater, although analysis of microorganisms and trace elements, such as Zn and Cd, would be desirable to confirm this. Pollution from sewage works and poor sanitation in nearby settlements probably present a greater risk to water quality.

The quarry does actively circulate water from the dewatering of pits, via the plant and various dams, recharging groundwater and then discharging back into the pits. The layout of the site contributes to this problem, with the plant and dams above the pits. Recirculation is, however, limited, as evaporation and salinity are only moderate, tempered by regional groundwater flow that keeps the groundwater and mine water fresh.

Recommendations

Recommendations for management of this and other mine sites include better planning of the site layout to prevent recirculation of mine water. In the event this is not possible, then lining of slurry dams to prevent infiltration could be a practical solution. Optimising explosives use, including storage and handling areas, may help reduce nitrate levels somewhat.

Recommendations for further study include analysing the groundwater for trace elements and microbiology, to better quantify the water quality. Stable isotope studies benefit from long-term precipitation data. Setting up long term monitoring sites that include such parameters could benefit many researchers working in the natural sciences, but especially the water sciences. Other tracers and parameters could also be used to help understand the surface water-groundwater interaction, such as tritium, useful to date young groundwater, or radon, useful to differentiate groundwater from surface water.

Mining companies are generally reluctant to allow research on their sites or use of their data. We are very grateful to PPC Mooiplaas and hope that this research encourages other mines to open up to research, as this would benefit the broader research community, being able to share experiences and data, and in turn benefit society and the environment.

Acknowledgements The authors thank Pretoria Portland Cement Mooiplaas Dolomite Quarry for access to the quarry for sampling and agreeing to release historical data, Aquatico Laboratories for assistance with sampling, the Water Research Commission for funding, and Grant Hall and Stefan Woodborne at the University of Pretoria stable isotope laboratory for analytical assistance.

Funding Open access funding provided by University of Cape Town. Water Research Commission, South Africa.

Data availability Complete raw data is available from the corresponding author, upon request.

References

APHA (2005) Standard methods for the examination of water and wastewater. 22nd edition. Amer Pub Health Assoc, Washington DC

Baloyi RS, Diamond RE (2019) Variable water quality of domestic well emphasizes the need for groundwater quality monitoring and protection: Stinkwater, Hammanskraal, Gauteng. Water SA 45:216–224. https://doi.org/10.4314/wsa.v45i2.08

Cook P (2020) Introduction to isotopes and environmental tracers as indicators of groundwater flow. The Groundwater Project, Guelph, Ontario, Canada http://www.gw-project.org/ ISBN: 978-1-7770541-8-2

Craig H (1961) Isotopic variations in meteoric waters. Science 133:1702–1703

CSAG Climate Systems Analysis Group (2022) https://cip.csag.uct.ac.za/

Dent MC, Lynch SD, Schulze RE (1989) Mapping mean annual and other rainfall statistics over southern Africa. Technical Report 109/1/89. Water Research Commission, Pretoria

Diamond RE (2022) Stable isotope hydrology. Groundw Proj Guelph Ont. https://doi.org/10.21083/978-1-77470-043-3

Dippenaar MA, Van Rooy JL, Diamond RE (2019) Engineering, hydrogeological and vadose zone hydrological aspects of Proterozoic dolomites (South Africa). J Afr Earth Sci 150:511–521. https://doi.org/10.1016/j.afrearsci.2018.07.024

Doveri M, Natali S, Franceschi L, Menichini M, Trifiro S, Giannecchini R (2021) Carbonate aquifer threatened by legacy mining: hydrodynamics, hydrochemistry and water isotopes integrated approach for spring water management. J Hydrol 593:125850. https://doi.org/10.1016/j.jhydrol.2020.125850

DWAF (1999) Johannesburg, 1:500,000 hydrogeological map. Dept of water affairs and forestry, Pretoria

Eary LE (1999) Geochemical and equilibrium trends in mine pit lakes. Appl Geochem 14:963–987

Eriksson PG, Altermann W, Hartzer FJ (2006) The Transvaal Supergroup and its precursors, pp 237–260. In: Johnson MR, Anhaeusser CR, Thomas RJ, The Geology of South Africa. Geological Society of South Africa, Johannesburg and Council for Geoscience, Pretoria

Gammons CH, Brown A, Poulson SR, Henderson TH (2013) Using stable isotopes (S, O) of sulfate to track local contamination of the Madison karst aquifer, Montana, from abandoned coal mine drainage. Appl Geochem 31:228–238. https://doi.org/10.1016/j.apgeochem.2013.01.008

Gao X, Wang Y, Ma T, Hu Q, Xing X, Yu Q (2011) Anthropogenic impact assessment of Niangziguan karst water. Water Manag 164:495–510. https://doi.org/10.1680/wama.1000070

Germishuys R, Diamond RE (2022) Nitrogen isotopes of *Eichhornia crassipes* (water hyacinth) confirm sewage as leading source of pollution in Hartbeespoort Reservoir. South Africa SA J Sci. https://doi.org/10.17159/sajs.2022/11098

Gleeson T, Befus KM, Jasechko S, Luijendijk E, Cardenas MB (2015) The global volume and distribution of modern groundwater. Nat Geosci. https://doi.org/10.1038/NGEO2590

Hobbs P, De Meillon N (2017) Hydrogeology of the sterkfontein cave system, cradle of humankind, South Africa. SA J Geol 120:403–420. https://doi.org/10.25131/gssajg.120.3.403

IAEA (2009) Laser spectroscopic analysis of water samples for stable hydrogen and oxygen isotopes. Training Course Series 35, International Atomic Energy Agency, Vienna, Austria

Jasechko S, Perrone D (2021) Global groundwater wells at risk of running dry. Science 372:418–421

Kåresdotter E, Destouni G, Ghajarnia N, Lammers RB, Kalantari Z (2022) Distinguishing direct human-driven effects on the global terrestrial water cycle. Earth's Future. https://doi.org/10.1029/2022EF002848

Knüppe K (2011) The challenges facing sustainable and adaptive groundwater management in South Africa. Water SA 37:67–79

Kummu M, Ward PJ, De Moel H, Varis O (2010) Is physical water scarcity a new phenomenon? Global assessment of water shortage over the last two millennia. Environ Res Lett 5:034006. https://doi.org/10.1088/1748-9326/5/3/034006

Meyer R (2014) Hydrogeology of Groundwater Region 10: The Karst Belt. WRC report TT553/14. Water Research Commission, Pretoria

Nhemachena C, Nhamo L, Matchaya G, Nhemachena CR, Muchara B, Karuaihe ST, Mpandeli S (2020) Climate change impacts on water and agriculture sectors in Southern Africa: Threats and opportunities for sustainable development. Water 12:2673. https://doi.org/10.3390/w12102673

Nilsson L, Widerlund A (2017) Tracing nitrogen cycling in mining waters using stable nitrogen isotope analysis. Appl Geochem 84:41–51. https://doi.org/10.1016/j.apgeochem.2017.05.025

Nordstrom DK (2011) Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Appl Geochem 26:1777–1791. https://doi.org/10.1016/japgeochem.2011.06.002

Oki T, Kanae S (2006) Global hydrological cycles and world water resources. Science 313:1068–1072

Page DC, Du Plessis PG (1986) Chert free metallurgical grade dolomite in the southern Transvaal the Mooiplaas and Glen Douglas Mines, In: Anhaeusser CR, Maske S, Mineral Deposits of Southern Africa, Geological Soc of South Africa, Johannesburg pp 829–835

Pietersen K (2006) Multiple criteria decision analysis (MCDA): a tool to support sustainable management of groundwater resources in South Africa. Water SA 32:119–128

Poeter E, Fan Y, Cherry JA, Wood W, Mackay D (2020) Groundwater in our water cycle-getting to know Earth's most important fresh water source. Groundwa Proj Guelph Ont Canada. https://doi.org/10.21083/978-1-7770541-1-3

Rimayi C, Chimuka L, Gravell A, Fones GR, Mills GA (2019) Use of the Chemcatcher passive sampler and time-of-flight mass spectrometry to screen for emerging pollutants in rivers in Gauteng Province of South Africa. Environ Monit Assess 191:388. https://doi.org/10.1007/s10661-019-7515-z

SABS (2001) South African Standard SABS 241—Drinking Water. South African Bureau of Standards, Pretoria

SAWS (South African Weather Service) (2021) Regional weather and climate of South Africa: Gauteng. Unpublished report: WCS-CLS-REGIONAL_CLIMATE_GAUTENG.001

Schrader A, Winde F, Erasmus E (2014) Using impacts of deep-level mining to research karst hydrology—a Darcy-based approach to predict the future of dried-up dolomitic springs in the Far West Rand goldfield (South Africa). Part 1: a conceptual model of recharge and inter-compartmental flow. Environ Earth Sci 72:3549–3565. https://doi.org/10.1007/s12665-014-3263-0

Schrader A, Winde F (2015) Unearthing a hidden treasure: 60 years of karst research in the Far West Rand, South Africa. SA J Sci 111:2014–2144. https://doi.org/10.17159/sajs.2015/20140144

Simonovic SP (2002) World water dynamics: global modeling of water resources. J Environ Manag 66:249–267. https://doi.org/10.1006/jema.2002.0585

Sun J, Tang C, Wu P, Strosnider WH (2014) Hydrogen and oxygen isotopic composition of karst waters with and without acid mine drainage: impacts at a SW China coalfield. Sci Total Environ 487:123–129. https://doi.org/10.1016/j.scitotenv.2014.04.008

UNESCO (2022) The United Nations World Water Development Report 2022: Groundwater: Making the invisible visible. UNESCO, Paris

Van Wyk E, Van Tonder GJ, Vermeulen D (2011) Characteristics of local groundwater recharge cycles in South African semi-arid hard rock terrains - rainwater input. Water SA 37:147–154

Weather & Climate (2023a) Pretoria weather in February 2017. https://weatherandclimate.com/south-africa/gauteng/pretoria/february-2017

Weather & Climate (2023b) Pretoria weather in May 2017. https://weatherandclimate.com/south-africa/gauteng/pretoria/may-2017

Wikipedia (2022) https://en.wikipedia.org/wiki/gauteng

Winde F (2013) Challenges for sustainable water use in dolomitic mining regions of South Africa—a case study of uranium pollution part I: Sources and pathways. Phys Geogr 27:333–347. https://doi.org/10.2747/0272-3646.27.4.333

Zhu G, Wu X, Ge J, Lui F, Zhao W, Chu Wu (2020) Influence of mining activities on groundwater hydrochemistry and heavy metal migration using a self-organizing map (SOM). J Cleaner Prod 257:120664. https://doi.org/10.1016/j.jclepro.2020.120664