

# Seasonal Metal Speciation in the Sabie River Catchment, Mpumalanga, South Africa

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**Abstract** - The present study investigated the hydrochemical characteristic changes of the Sabie River catchment. Water sampling was done in November and December (wet season, 2019) and July (Dry season, 2020). Physicochemical parameters and metal speciation were analyzed to assess their impact on water quality and fitness for human consumption. The hydrochemical characteristics of Sabie catchment showed variation of quality with seasons when compared with drinking water guidelines. Seepage from Nestor tailings storage facility (TSF) was also collected during wet season. In both season, aqueous metal speciation was done using the PHREEQC geochemical modelling code. Higher concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  were found in mine water while the dominant anion and cation were  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  in surface water samples. Additionally, the seasonal variation in the Sabie catchment quality characteristics was attributed to various activities taking place around the catchment and except for mine water, the water quality in the Sabie catchment did satisfy the guidelines postulated.

**Keywords**— wet and dry seasons, Sabie River, metal speciation, surface water, tailings storage facility, geochemical modeling

## I. INTRODUCTION

Originating in the upper reaches of the town Sabie in Mpumalanga Province of South Africa, the Sabie River passes through Sabie where entities such as York Timber Sawmills, wastewater treatment works and now-defunct underground mines of Transvaal Gold Mining Estate (TGME) are situated. The river further flows through Hazyview and Mkhuhlu and other residential areas before entering Kruger National Park (KNP), Mozambique and Indian Ocean respectively.

The Sabie-Pilgrim's Rest goldfields have rich history of gold mining dating back to 1872. Currently, there are no mining activities except for illegal (artisanal) mining on old diggings and tailings storage facilities (TSFs). Apart from mining, there are other different activities that are taking place within the Sabie catchment area ranging from commercial forestry, agricultural, and wastewater treatment works. There are also residential areas along the catchment (Simile, Hazyview and Mkhuhlu) which are also having potential impact to the quality

of water.

Various anthropogenic sources which include mining, agricultural activities and industrial wastewater contribute to pollution of surface water [1], [2]. Various factors that influence the mobility of the likely or definite contaminants from anthropogenic activities such as mining and mineral processing activities had been described [3] and [4]. These factors include occurrence, abundance, reactivity and hydrology. The term species had been defined as different forms of a particular element or its compounds [5]. For this study, the term speciation had been used to indicate the distribution of species in samples from the Sabie catchment. For a system containing both metal and ligand, the distribution of species will depend on the concentrations, pH, Eh, stoichiometry and ionic strength [6]. The subject of chemical speciation had gained favor in the field of environmental geochemistry because toxicity, availability and reactivity of element depend on chemical forms in which it occur [7]. Also, the bioavailability and toxicity of an element are highly influenced by the change in oxidation state. For example, Cr(III) is essential for regular glucose metabolism but Cr(VI) is genotoxic and may cause cancer [8], [6]; the more reduced form of As, As(III) had been described as more toxic than As(V) [6], [9];  $\text{Ba}^{2+}$  is highly toxic while  $\text{BaSO}_4$  is harmless and can be consumed [10].

Various studies had been undertaken in South Africa to determine speciation in surface water [11], [12], [13], [14], [15]. The present study was aimed at assessing the speciation of metal pollutants and impact on their potential dispersion.

## II. MATERIALS AND METHODS

### A. Site Description

There are various activities within the Sabie catchment area including agriculture, forestry and mining (abandoned TSFs and illegal mining). Located within Inkomati water Management Area, the Sabie River system is one of the largest rivers in Mpumalanga Province. It originates at an altitude of 2207 m.a.s.l., and enters Kruger National Park (KNP) 81.3 km downstream from its source (Fig. 1). The upper reaches are dominated with commercial forestry, sawmills, trout farms and fishing areas, Sabie town area, agricultural and industrial activities to a small extent. There are also abandoned mines located in the upper reaches of the Sabie catchment with illegal mining taking place.

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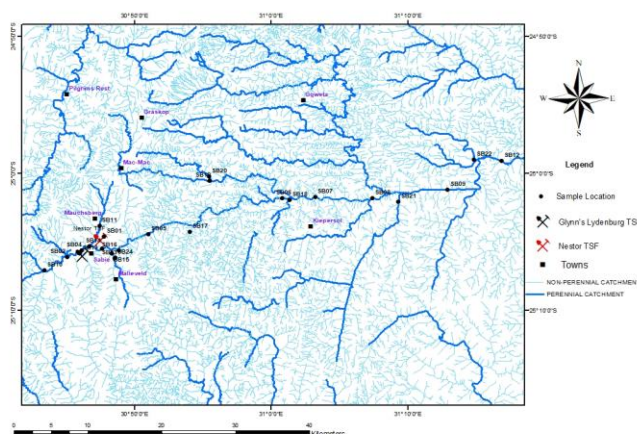


Fig. 1 : Location of Sabie catchment area (CGS 1: 250 000)

### B. Sample collection and analyses

A total of 22 surface water samples were collected from the Sabie River including its tributaries during wet season (November/December, 2019) and dry season (July/August 2020). Seepage from Nestor TSF was also collected during wet season. Sampling sites were predetermined and covered upstream to downstream of the Sabie River to Kruger National Park as well as connected streams. The sampling sites were chosen to determine the contribution of anthropogenic activities such as mining, forestry and agriculture, to the pollution of the Sabie catchment area. Sampling was done according to standard procedures [16] during dry and wet seasons. Water samples were collected using 100 mL polyethylene bottles. Sample bottles were rinsed at least three times using the water that is to be sampled. The samples were filtered using 0.45  $\mu\text{m}$  filter membrane for elemental (major, minor and trace element) and anion analyses. Elemental analysis samples were acidified using 3M nitric acid ( $\text{HNO}_3$ ) for preservation purpose. Immediately upon collection, samples were placed in a cooler (at 4°C) for transportation and storage. The following key variables were analyzed on-site, as they are likely to change with time or during transportation: pH, redox-potential (Eh), electrical conductivity (EC), temperature (T), dissolved oxygen (DO), total dissolved solids (TDS) and salinity following the South African National Standard (SANS) 5011 method. These variables were measured using a WTW multi 3430 measurement meter. Chemical analyses were carried out using inductively coupled plasma mass spectrometry (ICP-MS) and Ion chromatography (IC) analytical techniques. Coordinates of each sample site were recorded using global positioning system (GPS) device.

### C. Data analysis

Multivariate statistical analysis was performed using Microsoft Office Excel 2016®, focusing on the coefficient of variation (CV) and correlation analysis. The PHREEQC geochemical modeling software was used to predict the speciation of metals in water. The MINTEQA4.DAT was used for the ion interaction approach as it was able to incorporate all the selected parameters. Input data used for modeling program were pH, temperature, Eh (pE), and determined concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , Fe, As, Ca, Mn, Cu, Cl<sup>-</sup>,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . The output results of the model are presented in Table 4.

## III. RESULTS AND DISCUSSION

Seasonal variation of parameters analyzed onsite and alkalinity are presented in Table 1. For both seasons, the pH values were alkaline in all surface water samples with mean values of 7.5 in wet season and 7.9 in dry season respectively. However, seepage collected from Nestor TSF had low pH of 2.5, high EC and Eh recorded at 3890  $\mu\text{S}/\text{cm}$  and 270.2 mV respectively (SB00). All pH values recorded in both seasons were within acceptable limit for [17] with the exception of mine water. The values of pH measured from Sabie catchment area is a direct function of its total dissolved solids (TDS) and indicates concentrations of soluble salts in water. All values recorded in the Sabie River were within SANS (2015) limits. However, values recorded at SB11 located next to Glynn's Lydenburg TSF and SB12 (Klein Sabie River) were slightly above recommended limits with higher values recorded at Nkambeni and Bega Rivers (295  $\mu\text{S}/\text{cm}$  and 547  $\mu\text{S}/\text{cm}$  respectively). High values of EC in these sites can be attributed to human activities as there was evidence of dumping of waste at those sites. The values of DO were above recommended limit by WHO (2011) for both seasons and this can be attributed to aerobic conditions prevailing in the Sabie catchment area. According to [18] the concentrations of DO indicate changes in the redox state and microbial activity of water samples. The values of Eh ranged from -75.9 to -2.6 in both seasons with the mean of -35.9 during wet season and -47.41 in dry season. These low values of Eh can be attributed to the alkaline pH within the Sabie catchment. This is supported by high values (270.2 mV) recorded at Nestor TSF seepage sample which had acidic pH (2.5).

TABLE I: SEASONAL VARIATION OF PARAMETERS MEASURED IN SITU AND ALKALINITY ( $\text{MG}/\text{L CaCO}_3$ ) MEASURED IN SURFACE WATER IN THE VICINITY OF SABIE CATCHMENT

Sample number	pH		EC ( $\mu\text{S}/\text{cm}$ )		Eh (mV)		DO (mg/L)		Alkalinity (mg/L $\text{CaCO}_3$ )	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
SB01	7.8	8.3	78.3	64.7	-37.0	-64.5	7.5	9.5	33.6	29.1
SB02	7.9	7.8	130.0	105.0	-46.2	-40.0	7.4	8.5	55.2	49.8
SB03	8.1	8.3	153.1	149.1	-50.5	-64.2	7.3	8.7	61.1	60.4
SB04	8.3	8.2	168.0	141.0	-66.9	-64.5	7.8	8.3	59.5	54.6
SB05	8.0	8.2	142.4	101.0	-55.0	-63.2	7.2	9.6	56.2	52.1
SB06	7.3	8.0	120.0	120.5	-41.4	-49.8	6.8	9.1	47.1	50.7
SB07	8.0	8.1	135.4	125.1	-45.9	-50.2	7.1	9.2	37.1	126.0
SB08	7.7	8.1	108.0	119.1	-16.2	-58.4	7.3	9.5	49.9	46.8
SB09	8.0	8.1	128.0	238.0	-55.4	-60.5	6.7	8.3	47.0	87.2
SB10	7.3	8.5	83.7	67.4	-3.6	-75.9	7.1	8.6	39.1	20.0
SB11	6.7	7.5	174.0	174.3	26.9	-30.5	6.2	8.9	72.3	82.9
SB12	7.5	7.6	176.9	183.0	-23.0	-30.7	6.3	9.5	58.1	80.0
SB13	8.3	7.9	140.0	134.5	-51.6	-46.2	8.0	9.0	64.0	64.0
SB14	8.2	8.0	74.0	68.3	-65.9	-50.5	7.1	9.3	32.9	28.0
SB15	7.2	7.7	188.4	194.9	-2.6	-36.8	7.2	7.9	44.3	440.0
SB16	7.8	7.8	93.0	83.7	-44.0	-42.0	6.0	8.3	59.9	24.0
SB17	7.5	7.8	150.6	162.6	-20.7	-40.9	7.6	8.7	33.5	64.6
SB18	8.0	7.5	108.0	109.9	-55.6	-20.9	7.4	9.6	48.7	50.4
SB19	7.7	7.4	44.0	38.8	-37.3	-17.6	6.8	9.2	17.9	16.7
SB20	7.5	7.8	295.0	455.0	-20.2	-32.8	6.5	7.3	72.8	51.5
SB21	7.8	8.1	547.0	610.0	-41.3	-55.6	6.5	8.1	185.0	220.0
Mean	7.7	7.9	154.2	164.1	-35.9	-47.4	7.0	8.8	56.0	80.9
SD	0.4	0.1	104.1	133.9	23.4	15.7	0.5	0.1	32.7	93.3
SANS*	5-9.7		1700		N/A		N/A		N/A	
WHO*	7.0-									
WHO*	8.5		N/A		N/A		N/A		N/A	

Note: BDL, below detection limit; SD, standard deviation; SANS 241:2015; WHO (2011).

In the surface water of Sabie catchment,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  were the dominant cation and anion respectively (Table 2).

However,  $\text{SO}_4^{2-}$  is the dominant anion in mine water with  $\text{Ca}^{2+}$  still the dominant cation.

TABLE II SEASONAL VARIATION OF CATIONS AND ANIONS IN THE VICINITY OF SABIE CATCHMENT

Sample number	Ca		Mg		Na		Cl		NO <sub>3</sub>		SO <sub>4</sub>		D
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	
SB01	7.32	5.29	4.67	3.16	2.13	1.50	1.52	1.46	1.04	2.09	1.58		
SB02	12.40	9.96	7.74	5.81	1.94	1.61	1.92	1.70	1.90	1.36	1.05		
SB03	14.70	12.70	9.21	7.50	2.63	2.13	2.37	2.36	Bdl	2.44	5.44		
SB04	14.00	11.70	8.64	6.57	3.04	2.35	5.83	2.56	Bdl	2.67	5.40		
SB05	12.90	11.20	7.90	6.42	3.58	3.12	3.88	3.49	2.32	2.50	5.09		
SB06	10.80	9.94	6.71	5.76	4.03	3.06	3.70	3.05	3.28	1.59	3.51		
SB07	10.80	27.60	6.77	15.50	4.36	21.00	4.06	7.27	1.21	1.13	3.92		
SB08	7.57	9.74	4.55	5.27	5.74	6.14	5.76	4.54	1.73	1.33	3.44		
SB09	8.75	24.20	6.01	9.24	7.14	7.43	7.04	7.27	0.93	1.13	3.33		
SB10	7.85	4.23	5.15	2.00	1.68	10.09	1.10	3.00	0.70	0.30	1.36		
SB11	17.30	19.96	10.80	7.60	3.23	10.09	2.94	3.18	0.92	1.98	10.00		
SB12	15.00	15.44	9.14	8.91	4.75	6.15	3.80	7.00	8.52	1.80	9.43		
SB13	14.00	14.17	8.65	8.53	1.24	2.34	1.37	3.00	1.16	0.40	Bdl		
SB14	6.27	5.36	4.15	3.45	1.98	2.66	1.56	4.00	0.63	0.20	Bdl		
SB15	19.20	5.48	7.61	3.68	4.41	2.29	3.79	5.00	2.90	1.00	32.10		
SB16	5.39	11.00	2.47	5.92	9.37	2.57	6.83	2.76	2.55	1.32	1.13		
SB17	10.50	11.50	9.76	8.03	4.97	6.66	4.83	8.06	1.39	1.11	5.36		
SB18	9.86	11.00	5.93	5.92	2.68	2.57	2.60	2.76	0.59	1.32	0.83		
SB19	2.80	3.38	1.35	2.63	4.60	5.08	3.58	2.91	2.57	0.47	0.00		
SB20	16.40	11.70	10.70	5.95	23.40	3.52	24.70	4.89	Bdl	1.65	19.80		
SB21	25.20	32.50	37.20	37.90	29.60	15.30	45.70	48.70	2.32	6.81	11.80		
Mean	14.42	12.76	8.37	7.89	5.77	5.60	8.46	6.14	1.67	1.65	5.93		
SD	13.07	7.63	1.47	7.46	1.51	4.99	2.82	9.94	0.39	1.38	7.69		
SANS*	—	—	400	—	200	—	≤300	—	≤0.9	—	≤500		
WHO*	—	—	—	—	40	—	—	—	50	—	—		

Note: BDL, below detection limit; SD, standard deviation; SANS 241:2015; WHO (2011)

Table 3 presents seasonal variation of trace metals in the Sabie River catchment. There is no significant difference in concentrations of measured species in both wet and dry seasons. On the other hand, seepage collected during wet season from Nestor TSF had elevated concentrations of species such as Fe, Al, As, Mn, Cu and Cr in increasing order.

TABLE III SEASONAL VARIATION OF TRACE METALS IN THE VICINITY OF SABIE RIVER CATCHMENT

Sample number	Al (mg/L)		As (mg/L)		Cu (mg/L)		Cr (mg/L)		Fe (mg/L)		Mn (mg/L)		Zn (mg/L)	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
SB00	72	—	16.1	—	5.39	—	0.71	—	500	—	8.28	—	3.19	—
SB01	0.02	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.02	Bdl	Bdl	Bdl	Bdl	Bdl
SB02	0.01	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
SB03	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.01	Bdl	0.04	Bdl	Bdl	Bdl
SB04	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03	Bdl	0.02	Bdl	Bdl	Bdl
SB05	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	Bdl	0.01	Bdl	Bdl	Bdl
SB06	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	Bdl	Bdl	Bdl	Bdl	Bdl
SB07	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.17	Bdl	0.16	Bdl	Bdl	Bdl
SB08	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.12	Bdl	0.02	Bdl	Bdl	Bdl
SB09	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.11	Bdl	Bdl	Bdl	Bdl	0.02
SB10	Bdl	0.02	Bdl	0.04	Bdl	Bdl	0.01	0.04	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
SB11	Bdl	0.01	Bdl	0.02	Bdl	0.08	Bdl	0.01	Bdl	Bdl	0.42	Bdl	Bdl	Bdl
SB12	Bdl	Bdl	Bdl	0.03	Bdl	0.03	Bdl	Bdl	Bdl	0.02	Bdl	Bdl	0.03	Bdl
SB13	0.04	Bdl	Bdl	0.02	Bdl	0.01	Bdl	0.01	Bdl	Bdl	0.00	Bdl	Bdl	Bdl
SB14	0.18	Bdl	0.04	0.03	0.01	0.01	Bdl	Bdl	Bdl	0.02	0.02	Bdl	0.01	Bdl
SB15	Bdl	Bdl	Bdl	Bdl	0.14	0.01	Bdl	0.01	Bdl	Bdl	0.30	Bdl	Bdl	Bdl
SB16	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.16	Bdl	Bdl	Bdl	Bdl	Bdl
SB17	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03	0.18	Bdl	0.05	Bdl	Bdl
SB18	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
SB19	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.11	0.08	Bdl	Bdl	Bdl	Bdl
SB20	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.07	0.09	0.06	Bdl	Bdl	Bdl
SB21	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.02	Bdl	0.06	Bdl	Bdl	Bdl
Mean	0.01	0.00	0.00	0.01	0.01	0.03	0.00	0.00	0.02	0.04	0.02	0.04	0.00	0.00
SD	0.04	0.01	0.01	0.01	0.03	0.03	0.00	0.00	0.04	0.06	0.07	0.10	0.00	0.00
CV	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
SANS*	0.3	—	0.01	—	≤	—	—	—	2	—	0.4	—	0.05	—
WHO*	0.1	—	0.01	—	—	—	—	—	0.1	—	0.4	—	2	—

Note: BDL, below detection limit; SD, standard deviation; SANS (2015); WHO (2011); —, not taken.

The input data for metal speciation in surface water in the vicinity of Sabie River catchment area is presented in Table 4 and Table V presents data for predicted species in mine water. These data were calculated using PHREEQC modeling program for understanding behavior of metals in the surface water.

The concentrations of Ca chemical species calculated for all water samples analyzed in both wet and dry seasons showed a dominance in the oxidation state II (>93%), the rest being complexes with carbonates ( $\text{CaHCO}_3$  &  $\text{CaCO}_3$ ), nitrate ( $\text{CaNO}_3$ ), sulphate ( $\text{CaSO}_4$ ) and chloride ( $\text{CaCl}$ ). In the case of magnesium, the most principal chemical species was  $\text{Mg}^{+2}$  (>94%) analyzed in both dry and wet seasons. Other chemical species of Mg were  $\text{MgOH}^+$ ,  $\text{MgF}^+$ ,  $\text{MgCl}^+$ ,  $\text{MgSO}_4$  and carbonates ( $\text{MgCO}_3$  &  $\text{MgHCO}_3$ ). Based on this results, bioavailability of both Ca and Mg is likely to occur, however, this will be decreased as they also form complexes with carbonates.

According to [19] the  $\text{Cu}^{2+}$  ions complexes  $\text{CuCO}_3$  (aq),  $[\text{Cu}(\text{HCO}_3)_2]$ ,  $\text{Cu}(\text{OH})_3^-$  and  $[\text{Cu}(\text{OH})_4]^{2-}$  are present in waters with high concentrations of hydrogen carbonates. From speciation modelling, Cu was predicted as being likely to precipitate as  $\text{CuCO}_3$  and  $\text{Cu}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ . The concentrations of  $\text{CuCO}_3$  ranged between 52.15-89.22% in wet season and 50.45-90.52% in dry season. On the other hand, the concentrations of  $\text{Cu}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$  ranged between 0.13 to 3.68% and 0.04 to 6.51 in both dry and wet seasons respectively. The other species predicted for Cu were free hydrated ion ( $\text{CuOH}$ ),  $\text{CuHCO}_3$  and precipitates ( $\text{CuSO}_4$  &  $\text{Cu}(\text{OH})_2$ ).

The predominance species of Fe was  $\text{Fe}^{+2}$  with concentrations ranging between 91.16 to 98.19 and 93.79% to 99.30% in wet and dry seasons respectively. The remaining Fe was predicted to be present as  $\text{FeOH}$ ,  $\text{FeSO}_4$  and  $\text{FeHCO}_3$ . Also showing similar dominance in terms of speciation was Mn which showed dominance in  $\text{Mn}^{+2}$  chemical species. The ranges for  $\text{Mn}^{+2}$  were 69.45 to 95.80 (wet season) and 59.01 to 91.03% (dry season). There is also likelihood of Mn species to precipitate as carbonate based concentrations of  $\text{MnCO}_3$  (up to 27.77% in wet season and 36.90% in dry season) and  $\text{MnHCO}_3$  (up to 3.53% in wet season and 3.15% in dry season). Some of the predicted chemical species of Mn are  $\text{MnOH}$ ,  $\text{MnSO}_4$  and  $\text{MnNO}_3$ .

Most of Al species were likely to dissolve as hydroxides. The main species predicted for Al was  $\text{Al}(\text{OH})_4^-$  which ranged between 57.698 to 99.02% in wet season and 89.31 to 98.88 during wet season. According to [20]  $\text{Al}(\text{OH})_4^-$  is more predominant in alkaline waters. Other predicted species of Al were  $\text{Al}(\text{OH})$ ,  $\text{Al}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ . Also, Cr was likely to precipitate as hydroxide ( $\text{CrOH}$ ) with concentrations ranging between 97.16 to 99.93% (wet season) and 99.55 to 99.93 (wet season); consistent with [21] at pH of about 8.  $\text{Cr}^{+2}$  was the other predicted chemical species of Cr with concentrations ranging between 0.07 to 2.84 (wet season) and 0.02 to 0.45% (dry season).

TABLE IV RANGE OF HIGHEST PERCENTAGES OF SPECIATED FORMS OF METALS MEASURED IN SURFACE WATER IN THE VICINITY OF SABIE CATCHMENT.

Element	Speciated forms	Wet season %Range	Dry season %Range				
					Al(OH) <sup>+</sup>	0.13-17.70	0.03-1.40
					Al(OH) <sub>3</sub> (aq)	0.97-23.10	1.08-6.22
					Al(OH) <sub>4</sub> <sup>-</sup>	57.70-99.02	89.31-98.88
Ca	Ca <sup>+2</sup>	94.21-99.41	93.55-98.88	Cr	Cr <sup>+2</sup>	0.07-2.84	0.02-0.45
	CaCl <sup>+</sup>	0.01-0.76	0.01-0.21		CrOH <sup>+</sup>	97.16-99.93	99.55-99.93
	CaSO <sub>4</sub> (aq)	0.01-4.01	0.15-2.53				
	CaNO <sub>3</sub> <sup>+</sup>	0.01-3.62	0.01-0.12	Cu	Cu <sup>+2</sup>	1.74-39.63	1.22-15.01
	CaOHCO <sub>3</sub> <sup>+</sup>	0.67-3.17	0.28-2.89		CuOH <sup>+</sup>	4.01-21.31	2.31-12.96
	CaCO <sub>3</sub> (aq)	0.03-1.26	0.03-1.68		CuOH <sub>3</sub> <sup>-</sup>	0.02-0.36	0.02-0.06
Mg	Mg <sup>+2</sup>	95.56-99.55	94.80-99.55		Cu(OH) <sub>2</sub> (aq)	0.02-3.47	0.12-1.92
	MgOH <sup>+</sup>	0.01-0.07	0.01-0.03		CuSO <sub>4</sub> (aq)	0.01-1.49	0.01-0.14
	MgF <sup>+</sup>	0.01-0.06	0.01-0.05		CuCO <sub>3</sub> (aq)	52.15-89.22	50.45-90.52
	MgCl <sup>+</sup>	0.01-0.10	0.01-0.06		Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup>	0.13-3.68	0.04-6.51
	MgSO <sub>4</sub> (aq)	0.12-2.30	0.14-1.28		CuHCO <sub>3</sub> <sup>+</sup>	0.10-2.53	0.10-0.58
	MgCO <sub>3</sub> (aq)	0.02-0.63	0.05-0.85	Mn	Mn <sup>+2</sup>	69.45-95.80	59.01-91.03
	MgHCO <sub>3</sub>	0.47-2.49	0.47-2.65		MnCO <sub>3</sub> (aq)	3.35-27.77	0.01-36.90
Fe	Fe <sup>+2</sup>	91.16-98.19	93.79-99.30		MnOH <sup>+</sup>	0.04-0.23	0.01-1.17
	FeOH <sup>+</sup>	0.10-6.15	0.29-2.98		MnF <sup>+</sup>	0.01-0.03	0.07-0.09
	FeCl <sup>+</sup>	0.03-0.05	0.06		MnCl <sup>+</sup>	0.01-0.36	0.01-0.07
	FeSO <sub>4</sub> (aq)	0.13-4.24	0.15-2.64		MnSO <sub>4</sub> (aq)	0.01-2.95	0.02-1.66
	FeHCO <sub>3</sub> <sup>+</sup>	0.39-3.18	0.26-1.71		MnNO <sub>3</sub> <sup>+</sup>	0.01-0.85	0.01-0.03
Al	Al <sup>+3</sup>	0.052			MnHCO <sub>3</sub>	0.60-3.53	0.76-3.15
	Al(OH) <sub>2</sub> <sup>+</sup>	0.01-1.40	0.03-2.48				

However, the predicted chemical species from Nestor TSF seepage calculated for wet season were different from the ones predicted for the Sabie catchment surface water (Table V).

Most cations were predicted to likely precipitate as sulfates, namely, Ca, Mg, Fe and Cu.

TABLE V RANGE OF HIGHEST SPECIATED FORMS OF METALS FROM NESTOR TSF SEEPAGE.

Element	Speciated forms	Wet season %Range
Ca	CaSO <sub>4</sub> (aq)	65.31
	Ca <sup>+2</sup>	34.47
	CaHCO <sub>3</sub> <sup>+</sup>	0.18
	CaCl <sup>+</sup>	0.04
Mg	MgSO <sub>4</sub> (aq)	60.01
	Mg <sup>+2</sup>	39.74
	MgHCO <sub>3</sub> <sup>+</sup>	0.17
	MgCl <sup>+</sup>	0.07
Fe	MgF <sup>+</sup>	0.02
	FeSO <sub>4</sub> (aq)	66.82
	Fe <sup>+2</sup>	33.00
	FeHCO <sub>3</sub> <sup>+</sup>	0.17
Al	AlF <sub>2</sub> <sup>+</sup>	55.71
	AlF <sup>+2</sup>	17.17
	Al(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	10.62
	AlF <sub>3</sub> (aq)	8.81
	AlSO <sub>4</sub> <sup>+</sup>	7.19
	Al <sup>+3</sup>	0.39
Cr	AlF <sub>4</sub> <sup>-</sup>	0.12
	Cr <sup>+2</sup>	99.89
Cu	CrOH <sup>+</sup>	0.11
	CuSO <sub>4</sub> (aq)	64.58
	Cu <sup>+2</sup>	34.24
	CuHCO <sub>3</sub> <sup>+</sup>	0.87
	CuHSO <sub>4</sub> <sup>+</sup>	0.28
	CuCl <sup>+</sup>	0.03
	CuF <sup>+</sup>	0.01

Under acidic conditions, soluble Al<sup>+3</sup> is dominant and insoluble Al(OH)<sub>3</sub> mostly occur in a neutral conditions [20]. Based on speciation, Al is likely to form complexes with both fluorine sulfate. The dominant species was AlF<sub>2</sub><sup>+</sup> (55.71%) followed by AlF<sup>+2</sup> (17.17%), Al(SO<sub>4</sub>)<sub>2</sub><sup>-</sup>, AlSO<sub>4</sub><sup>+</sup> (7.19%), AlF<sub>4</sub><sup>-</sup> and few concentrations of soluble Al<sup>+3</sup> (0.39%). For Cr chemical speciation, the most dominant species predicted was Cr<sup>+2</sup> at 99.89% and the remainder was CrOH (0.11%).

#### IV. CONCLUSION

From upstream to downstream of the Sabie catchment, the surface water is alkaline and the concentrations of metal species are within limit permitted by SANS and WHO. However, the seepage from Nestor TSF had low pH and elevated concentrations of metal species such as Fe, Al, As, Mn, Cu and Co exceeding limits for drinking water. It was observed from the study that there was no significant difference between physicochemical parameters measured in surface water samples collected in the wet and dry seasons. The results from PHRREQC modeling revealed that cation exchange played a significant role in regulating the chemistry of surface water in the Sabie Catchment area.

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Title: Geochemical and Mineralogical Characterization of Precipitates from Sabie-Pilgrim's Rest Goldfields for the Potential of Acid Mine Drainage

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