

Speciation of Metals in Sediments of the Sabie River System by Sequential Extraction

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Abstract

The speciation of ten metal species (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in tailings and sediments along the Sabie River system were investigated. Their total concentration and geochemical phase distribution were determined using sequential chemical extraction. Representative samples from the mine tailings storage facilities (MTSFs) and stream sediment were selected and the objectives were to analyse the total concentration of metal species and their distribution in the different geochemical phases, and to determine their association with the sediment components.

Results of the mine wastes from the Nestor MTSF indicated that two fractions were bioavailable. These fractions are the exchangeable metal-bound (F1) as well as Fe and Mn-bound (F2), with a possibility of the metals in these phases being remobilised under changing ambient conditions. Aluminium and iron were found to have the highest bioavailability, followed by Mn>As>Zn>Cr>Cu>Co>Pb in decreasing order. The highest average concentration of the investigated metal species in mine wastes and stream sediment samples is in silicate fraction (F4), which implies the geogenic origin of these elements. The primary mechanism responsible for this geochemical scavenging is adsorption into Fe, Mn and Al-hydroxide precipitates that are clearly in the Nestor Mine drainage path flowing towards the Klein Sabie River. The results showed that the sediments of the Sabie River System are of good quality compared to sediment quality guidelines standards. Only under the presence of strong reducing agents will the metals within sediments become bioavailable as most of the metal concentrations were recorded at 3rd and 4th fractions.

The study confirmed the attenuation of trace metals both by dilution and precipitation from the water into sediments. Sediments of the Sabie River system are of good quality as the majority of elements are partitioned on the third and fourth fractions, which are not bioavailable. Consequently, AMD mediated release from the Nestor MTSF is not considered to have a significant impact on the surrounding Sabie River system.

Keywords: Bioavailability, Potential Toxic Elements, Speciation, Sabie River System, Geochemical modelling

Introduction

The increased accumulation of trace elements (TEs) in soils because of anthropogenic activities poses a number of risks to human and ecosystem health, including bio- and water resources (Adriano *et al.*, 2004). Excess trace element exposure can endanger human health through the food chain or through direct contact with or ingestion of soil borne TEs, such as the soil-human or soil-water-

human pathways. In addition, because of the toxicity of TE contaminants to plants and soil-dwelling organisms, environmental risks may arise (Mench *et al.*, 1998; 2000). Recently, the environmental impacts of the seepages of elevated metal species, sulfate-rich, low pH water from gold mine tailings storage facility (MTSF) of Nestor in the Sabie, South Africa have been reported (Lusunzi, 2018). In addition, the tailings from the Nestor

MTSF were classified as acid producing based on the acid base accounting (ABA) and mineralogical data compared to the adjacent Glynns Lydenburg MTSF (Lusunzi *et al.*, 2018). The remediation of contaminated sediments and soil requires a detailed in situ characterization of the speciation of the potential toxic elements (PTEs) and their transformation with respect to time and spatial distribution.

In this study, the use of sequential extraction was combined with speciation-solubility as well as inverse modelling in order to understand better the partitioning and transport of metal species emanating from gold MTSFs in the Sabie Goldfield as well as the Sabie River system.

Study Area

The Sabie River system is in South Africa's Mpumalanga Province (Fig. 1). There are MTSFs from abandoned mines as well as forestry and agricultural activities in the catchment area. Furthermore, the area

includes rural and semi-urban residential areas, wastewater treatment plants, and waste disposal sites.

Methods

The Sabie River system included a reprocessing mine tailings storage facility (MTSF) and a tailings pond that collected rainwater. During the winter (dry) season (July/August 2020), tailings (NS01 and GL00), water, and stream sediment samples were collected.

Sediment samples were collected concurrently with water samples, and samples containing a large amount of water were centrifuged to extract pore water. The Communities Bureau of Reference method (BCR) was used for sequential extraction (Rauret *et al.*, 1999). The leaching protocol was used to determine the environmentally extractable metal fractions, which were exchangeable (F1), reducible (F2), oxidisable (F3), and residual (F4) (F4). Metal species concentrations in the resulting leachates and acidic solutions were determined

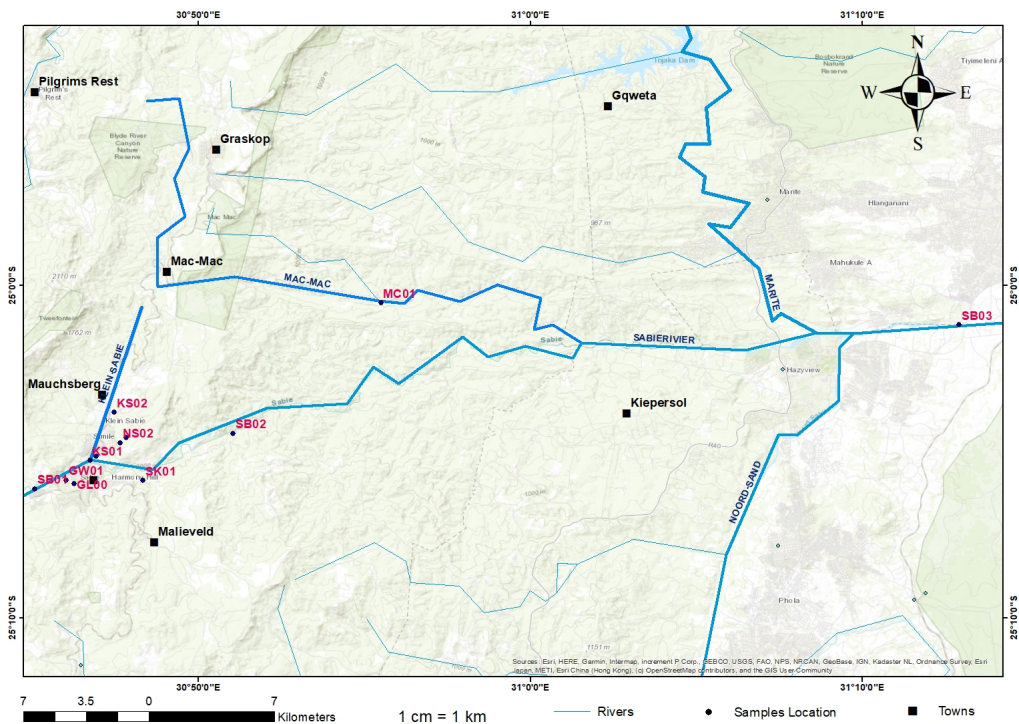


Figure 1 Location of the study area



Table 1 Range of highest percentages of speciated forms of metals measured in seepages water from the Nestor Mine

Element	Speciated forms	% Range
Ca	CaSO ₄ (aq)	66,2
	Ca ²⁺	35,3
	MgSO ₄ (aq)	61,1 38,9
Fe	FeSO ₄ (aq)	67,3
	Fe ²⁺	32,7
Al	AlF ²⁺	56,3
	Al(SO ₄) ²⁻	11,7
	AlSO ₄ ⁺	9,4
	Al ³⁺	2,4
Cr	Cr ²⁺	98,4
	CrOH ⁺	1,6
Cu	CuSO ₄ (aq)	66,3
	Cu ²⁺	31,9

using inductively coupled plasma mass spectrometry (ICP-MS). The PHREEQC geochemical modelling software was used for speciation-solubility, inverse, and forward modelling (Chalton and Parkhurst, 2002).

Results and discussion

Overview of water analyses

Table 1 summarises the onsite measurements of the water samples collected along the Sabie River system. The water samples (seepages) from the Nestor MTSF has low pH (2.34) together with dissolved oxygen (5.99 mg/L), high redox potential (253.0 mV) and electrical conductivity (24500 µS/cm) compared to surface water from the Sabie River system. However, water decanting from the Ritfontein Mine adit (RT00) has alkaline pH (9.05), low redox potential (-123.8 mV) and EC (167.7 µS/cm). Based on the PHREEQC geochemical modelling results, the most cations from the Nestor MTSF have abundant sulfate species, namely, Ca, Mg, Fe, and Cu while Cr is mostly present as a free cation.

All the surface water samples from the Sabie River system have alkaline pH (8.67 to 10.33) and low EC (78.9 to 267.0 µS/cm) that is within the SANS241 (2015) guideline as well as acceptable DO (7.52 to 8.67 mg/L) and redox potential (-123.8 and -60.3 mV). Most chemical species occurs as cations (Ca, Mg, Fe, and Mn) with the exception of Al, Cr, and

Cu that occurs as complexes with hydroxides (Al and Cr) and carbonate (Cu) respectively. The Al species is mostly AlOH₄⁻ in alkaline water (>80%).

Table 1 displays the analytical results of the water samples collected along the Sabie River system including mine water (leachates from the Nestor MTSF: NS01 & NS02; and water decanting from the Rietfontein Mine adit: RT00). Metal species in the seepages from the Nestor MTSF occurs in excess to the SANS2241 (2015) and WHO (2011) guidelines while the surface water from the Sabie River and connected streams are within the limits. The effect of the pH on metal mobility is obvious for the seepage sample from the Nestor MTSF (NS01) that has an average Fe concentration of 3004 mg/L whereas the dilution effect is evident on samples from the Sabie River system has acceptable Fe values of less than 1 mg/L.

Sequential extraction and speciation solubility

Results obtained for the sequential extraction in the Sabie River system are summarised in Table 3. The sample collected near the main Nestor MTSF (NS01) has all high metal species concentrated in the exchangeable fraction (F1) with an exception of As. However, the metal species are highly partitioned on the inert fraction at the Glynns Lydenburg MTSF (GL00), except Mn.

Table 2 Range of highest percentages of speciated forms of metals in surface water of the Sabie River system

Element	Speciated forms	% Range
Ca	Ca ²⁺	>98
	CaCl, CaSO ₄ , CaHCO ₃ ⁺	<1
Mg	Mg ²⁺	>98
	MgOH, MgF, MgCl	<1
Fe	Fe ²⁺	>96
	FeH ⁺ , FeCl, FeSO ₄ (aq), FeHCO ₃	<1
Al	AlOH ₄ ⁻	89,3
	Al ³⁺ , Al(OH) ²⁺ , AlOH	<1
Cr	CrOH ⁺	99,4
	Cr ²⁺	0,6
Cu	CuCO ₃ (aq)	56,4
	CuOH ⁺	13,6
	Cu ²⁺	5,6
Mn	Mn ²⁺	65,8
	MnCO ₃	5,6

Conclusions

All metal species from the Nestor MTSF are bioavailable as were found partitioned in the exchangeable fraction. The majority of metal species (As, Al, Fe, Co, Cr, Cu, Ni, Pb, and Zn) in the Sabie River system (including the Glynns Lydenburg MTSF) are apportioned on the residual fraction, implying that they are not bioavailable. There are high concentration of Mn partitioned on the exchangeable and Fe-Mn oxide fractions respectively, especially in the upstream of the Sabie River system. This is unimportant

because significant concentrations of Mn can co-precipitate with carbonates such as dolomite and calcite that are present. Based on onsite analyses and analytical results, acid mine drainage was confirmed at the Nestor MTSF. However, water from the Sabie River system was found to be neutral-alkaline with low metal species concentrations, implying that there is no acid mine drainage. The PHRREQC modelling results showed that cation exchange was important in regulating the chemistry of surface water in the Sabie Catchment area.

Table 3 Analytical results of water samples from the Sabie River system

Sample ID	Al (mg/L)	As (mg/L)	Ca (mg/L)	Cl (mg/L)	Cu (mg/L)	Cr (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)	SO ₄ (mg/L)
NS01	261.8	26.80	61,2	47.3	74.94	2.89	3004	7,66	8.09	15,47	3650
RT00	0.03	ND	11,99	4.1	0.06	0.007	ND	7,98	0.30	ND	6.0
SB01	0.01	0.01	4,37	1,5	0.02	0.02	0.05	3,3	ND	ND	1,7
SB02	0.08	ND	8,53	3,5	ND	0.01	0.12	5,82	0.05	0.01	5,2
SB03	1.53	0.02	8,53	5,8	ND	0.02	0.79	5,96	0.03	ND	3,4
GW01	0.09	0.04	18,23	3,3	0.04	0.01	0.88	12,57	0.11	ND	5,7
KS01	0.14	0.01	12,01	4,5	0.02	0.02	0.24	8,81	0.06	ND	9,1
KS02	0.03	0.02	13,43	5,7	0.01	0.02	0.32	9,34	0.01	ND	ND
MC01	ND	ND	10,01	4,4	0.003	0.004	0.123	5,9	0.005	ND	34,2
RT01	0.032	ND	12,35	2,7	0.058	0.007	ND	5,3	0.301	ND	1,1
SK01	0.042	ND	5,2	2,5	ND	0.006	0.071	4,8	0.025	ND	ND
SANS241 (2015)	0.3	0.01		≤300	0.02	0.005	2		0.4	0.05	≤500
WHO (2011)	0.1	0.01							0,4	2	



Table 4 Speciation of metal species in the Sabie River system

Sample ID	Fraction	Concentration (mg/L)									
		As	Al	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
NS01	F1	615.1	1951	22	38	167	67110	264	50	1	77
	F2	6.08	1.2	0	0	0	329	0.1	0.2	0.1	0
	F3	2.2	0	0	0	0.4	49	0.2	0	0.04	0.2
	F4	135.88	46	0	0.5	1.2	906	3.1	4.7	0.92	18
GL00	F1	0.52	27	0	0	1	27	148	3.7	0.02	10
	F2	0.5	6.6	0	0	0	290	63	1.1	0.02	2
	F3	37.18	15	0.2	0.2	3.5	275	12	0.4	0.92	5.3
	F4	450.16	465	0	16	14	15718	72	14	5.92	89
SB01	F1	0.02	131	0.1	0	0	40	143	1.8	0.06	1
	F2	0.02	110	0	0	0	654	57	0.3	0.08	2
	F3	0.38	1339	2.2	8.7	3.9	617	18	2.7	1.84	2.3
	F4	7.2	11313	5	56	21	22811	107	28	3.84	81
SB02	F1	0.72	98	1.4	0	0.1	102	204	4.9	0.12	9.6
	F2	1.18	65	0	0	0	1183	46	0.3	0.18	5
	F3	8.44	925	1.3	5.9	31	585	18	3	2.72	3.8
	F4	151.4	8126	2.7	27	33	17596	72	17	5.16	67
SB03	F1	0.12	46	0	0	0	132	17	1.1	0.06	0.3
	F2	0.22	7.1	0	0	0	504	4.8	0.3	0.04	0.3
	F3	0.6	121	0	0.8	0	111	3.5	0.3	0.2	0.8
	F4	4.44	752	0	4.6	1.3	1728	14	3.1	0.48	36
GW01	F1	0.12	89	0	0.9	0	234	251	1.9	0.4	3.8
	F2	0.1	21	0	0	0	336	184	0.1	0.3	0.4
	F3	1.34	285	1.8	5.8	0	210	43	2.4	1.66	1.3
	F4	6.42	1652	0.5	28	2.3	4510	90	11	1.58	53
KS01	F1	0.82	116	3.6	0	3.6	37	377	8.7	0.12	46
	F2	1.12	52	0	0	0	1282	61	2	0.18	16
	F3	6.72	1555	3.3	8.6	25	1066	37	10	4.74	18
	F4	90.94	7611	2.4	32	34	20269	171	22	9.18	97
KS02	F1	0.08	105	0	0	0	80	62	1.7	0.08	0.2
	F2	0.08	9	0	0	0	579	13	0.3	0.04	0
	F3	0.56	144	0	0.7	0	96	6.3	0.3	0.2	0.2
	F4	3.7	908	0	6.3	1.4	1927	18	3.7	0.6	30
SP01	F1	0.22	52	2.3	0	9.3	15	246	3.4	0.46	2.5
	F2	0.18	20	8.8	0	1.6	447	301	2.3	0.42	1.1
	F3	5.62	382	7.6	3	14	209	107	6.3	3.14	2.6
	F4	76.94	3449	8.8	39	27	11804	180	26	6.64	62
RT01	F1	0.28	316	1.7	0	333	120	71	2.8	0.28	6.8
	F2	0.84	120	0	0	48.3	928	68	0.4	1.6	1.2
	F3	7.3	683	0.1	0.4	29	120	5.8	0.3	1.08	1
	F4	25.88	5020	0	3.6	26	4535	25	2.9	3.88	46

Acknowledgements

The authors would like to thank the Council for Geoscience for funding this study.

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