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Partitioning and mobility of trace metals in the Blesbokspruit: Impact assessment of dewatering of mine waters in the East Rand, South Africa

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Abstract

A suite of trace metals was analyzed in water and sediment samples from the Blesbokspruit, a Ramsar certified riparian wetland, to assess the impact of mining on the sediment quality and the fate of trace metals in the environment. Limited mobility of trace metals was observed primarily because of their high partition coefficient in alkaline waters. Nickel was most mobile with a mean K_d of $10^{3.28}$ L kg^{-1} whereas Zr was least mobile with a mean K_d of $10^{5.47}$ L kg^{-1}. The overall trace metal mobility sequence, derived for the Blesbokspruit, in increasing order, is: Zr < Cr < Pb < Ba < V < Cu < Zn < Sr < Mn < U < Mo < Co < Ni. Once removed from the solution, most trace metals were preferentially associated with the carbonate and Fe–Mn oxide fraction followed by the exchangeable fraction of the sediments. Organic C played a limited role in trace metal uptake. Only Cu was primarily associated with the organic fraction whereas Ti and Zr were mostly found in the residual fraction. Compared to their regional background, Au and Ag were most enriched, at times by a factor of 20–400, in the sediments. Significant enrichment of U, Hg, V, Cr, Co, Cu and Zn was also observed in the sediments.

The calculated geoaccumulation indices suggest that the sediments are very lightly to lightly polluted with respect to most trace metals and highly polluted with respect to Au and Ag. The metal pollution index (MPI) for the 20 sampled sites varied between 2.9 and 45.7. The highest MPI values were found at sites that were close to tailings dams. Sediment eco-toxicity was quantified by calculating the sediment quality guideline index (SQG-I). The calculated SQG-I values (0.09–0.69) suggest that the sediments at the study area have low to moderate potential for eco-toxicity.

1. Introduction

The Witwatersrand Basin, made up of the East, Central and West Rand basins, in South Africa is famous for its prolific Au, coal and U deposits and mining has been going on in the basin since the late eighteen hundreds (Handley, 2004). Records of water ingress into underground mines in the East

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Rand date back to 1909 (Scott, 1995). To keep the mines operational, mine water was pumped out from the shafts on a recurrent basis and disposed of in the surrounding environment. As mining developed and the underground operations became interlinked, so the task of dewatering was carried by fewer mines. Most of the mines on the East Rand are currently inactive, closed or abandoned, and mining areas are inaccessible as water was allowed to flood the lower workings. Currently Grootvlei Gold Mine is one of the major mines in the area that regularly dewaters their underground workings and disposes of the effluent in the Blesbokspruit (Spruit – an Afrikaans word for a stream) to keep their operations going.

The Blesbokspruit, a Ramsar certified wetland site, is under potential threat of metal pollution from dewatering actions of the mines in the area. The wetland was put on the Montreux record in 1996 (www.ramsar.org/key_montreux_record.htm) because of uncontrolled disposal of untreated mine effluent. Since then, however, disposal of treated mine effluent has been strictly regulated. Mining in the East Rand basin has produced rock piles, sand and tailings dumps on the surface, and backfill rock piles underground. The Witwatersrand rocks contain varying proportions of sulfide minerals, the predominant being pyrite (Wittmann, 1979). The other base metal sulfides in the reef (pyrrhotite, arsenopyrite, chalcopyrite, galena, cobaltite and gersdorffite), in addition to Fe, contain elements such as; Ni, Pb, Cu, Co and As, while some of the leachable oxides are U-bearing (Scott, 1995; Wittmann, 1979). Groundwater seepage through the mineral reef, therefore, has high Fe, SO_4 and trace metal content and effluent pumping subsequently results in disposal and dispersal of trace metals in the surface water system. For example, Förstner and Wittmann (1976) and Wade et al. (2000) found metal enrichment in aquatic sediment caused by effluent from Witwatersrand gold mines which they ascribed to the presence of ore minerals, containing Cr, Zn, Pb and Co or processing additives containing Hg, Zn and Pb. Apart from this direct route, trace metals are also introduced into the surface water system from seepage through massive tailings dams, from mineral beneficiation plants associated with the Au mines in the area and via atmospheric fallout of fine particulates from the tailings dams. In Blesbokspruit, however, metals are also introduced by sources other than mining, as the stream flows through settlements and industrial areas before it passes through the wetland. The situation of Blesbokspruit is of increasing concern as over the years the stream has changed from being influent to effluent and now recharges the local dolomite aquifer (Scott, 1995). The poor water quality of Blesbokspruit therefore is likely to impact the freshwater resources in the area on a long term basis.

Once introduced into the aquatic environment trace metals have little degradation potential, and because of their low solubility and high partition coefficient under E_h–pH conditions of neutral waters, they tend to accumulate in sediments which form metal-rich repositories. With continued accrual, metal concentration in the sediment often exceeds environmental thresholds causing intrinsic toxicity level (Schulin et al., 1995). Furthermore, a change in biogeochemical conditions can easily remobilize sequestered trace metals making the metal-rich sediment repositories a potential long term source of pollution from where the metals can move along the food chain causing genotoxicity among living organisms (Patra et al., 2004).

Numerous studies have looked at trace metal dynamics, partitioning and subsequent impact on the biomes around active and abandoned mines (Ahn et al., 2005; Bruce et al., 2003; Coates, 2005; Dushenko et al., 1995; Kim and Jung, 2004; Lee and Correa, 2005; Leybourne et al., 2000; Roussel et al., 2000; Wong et al., 1999); however, despite prolific mining activities, little information is available from South Africa on pollution and fate of trace metals in surface waters or sediments, primarily because of a lack of stringent regulatory guidelines in the past and instrumental limitations. There have been a few studies made that describe the effect of salinity pollution from the mine effluent and its management in the Blesbokspruit catchment (Geldenhuys, 1997; Pilson et al., 2000), but to the authors knowledge, no one has previously performed a comprehensive chemical characterization of the sediment–water system or trace metal contamination in the wetland to evaluate the impact of anthropogenic activities on the quality of the wetland with respect to metal pollution. Here an environmental quality assessment is presented of the Blesbokspruit, a riparian wetland, affected by mining and associated activities. In particular, the article examines the partitioning of trace metals between surface water and sediments and their fate within the sediments.

2. Site description

The study area is situated in the East Rand near Johannesburg, South Africa (Fig. 1). Many years of regular pumping and disposal of large amounts of mine waters from Grootvlei Gold Mines and adjacent smaller mines in the area (Fig. 1) has resulted in the development of a riparian wetland along Blesbokspruit. A number of tailings dams associated with the mines are scattered along the stream (Fig. 1). Some of them have been reclaimed and reworked in the recent past (Mrs I. Lea, pers. com.). Many of the smaller mines have now been consolidated and function as one large unit. Hence, since 1995 groundwater is primarily discharged by Grootvlei Gold Mines from a single point near the sample point M14 (see Fig. 1).

The wetland was designated a Ramsar Site because of its ecological importance in supporting a bird sanctuary and an approximately 25 km long

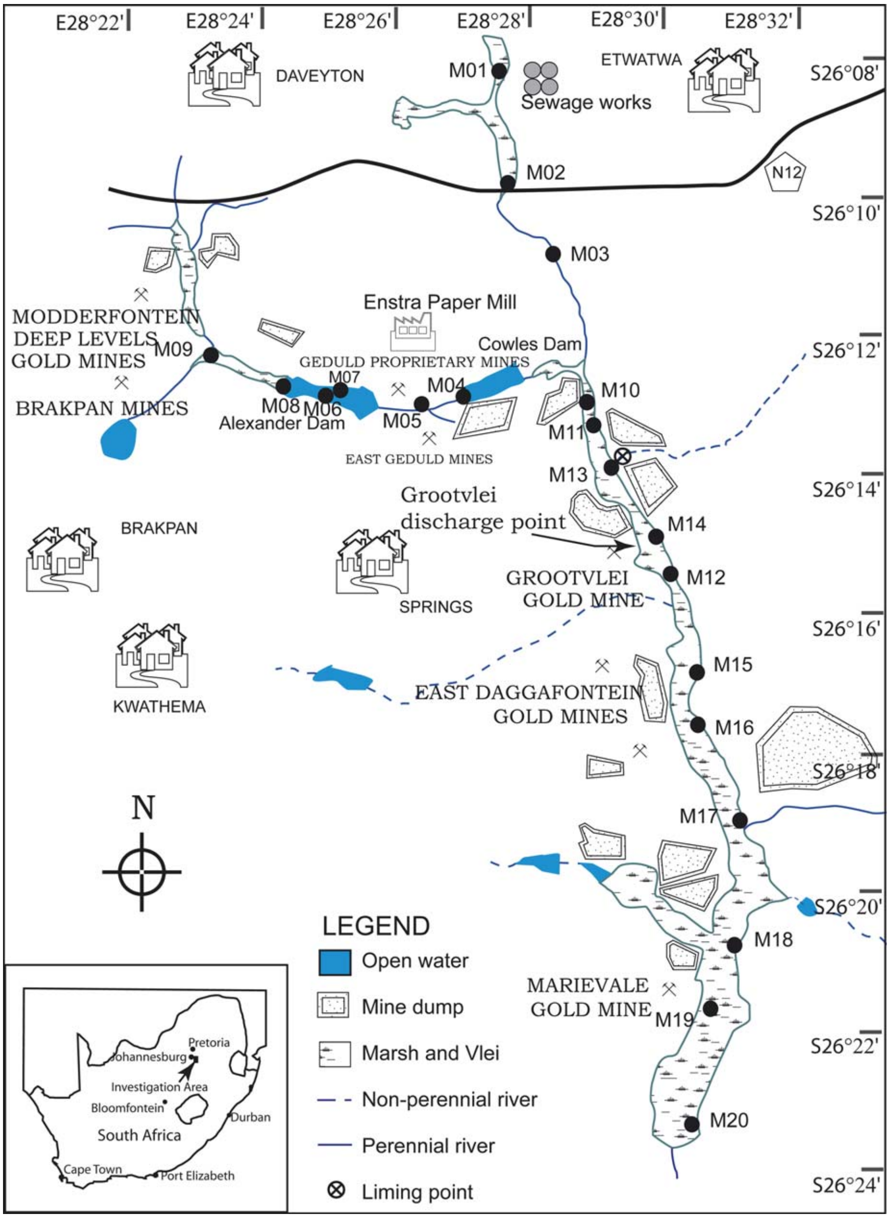

Fig. 1. Map showing site details and sampling locations.

green belt rich in hydrophytes, in otherwise semi-arid conditions. Mine water effluent flowing through the wetland ultimately discharges into the Vaal River, one of the major sources of fresh water supply to the Gauteng Province. The Blesbokspruit has eroded through sandstones and shales of both the Vryheid and Dwyka formations exposing the Chuniespoort Group dolomites which outcrop at surface. The dolomites alternate between being chert-rich and chert-poor (Barnard, 2000). The stream flows almost North-South through the study area and because of its low gradient, the river is swampy for most of its course (Scott, 1995). The marshes occur from Cowles Dam to beyond Marievale, a distance of 22 km (Fig. 1). Most of this reach of the river is covered with *Typha* and *Phragmites* with slowly moving or standing water on alluvium covered dolomite.

3. Materials and methods

3.1. Surface water and sediment sampling

Surface water and sediment samples were collected from 20 randomly chosen sites that were geographically dispersed throughout the marsh (Fig. 1). Care was taken to include sites both upstream and downstream of a liming plant that treats and ultimately drains the effluent from tailings dams into the wetland, and the site where mine water from Grootvlei Gold Mine is discharged into the Blesbokspruit (Fig. 1). Sites M03, M04 and M06-M08 were located within the stream bed with little vegetation and site M05 was located on a secluded water body in a trough, probably a remnant of an old reworked mine dump. At each site, two surface water samples were collected and filtered through a 0.45 μm nylon membrane filter using a hand-held vacuum pump. One of the samples was acidified with 3 M HNO_3 to a pH of less than 2 to prevent metal precipitation. The water samples were stored in plastic bottles pre-rinsed with HNO_3 and deionized water. The bottles were sealed and stored at 4 °C before analysis.

At each of the 20 sample sites, surface sediments were sampled close to the sediment–water interface by completely inserting an inverted 50 mL polypropylene centrifuge vial. After digging the vial out, they were capped without leaving any head space. Care was taken to prevent further exposure of the sample to the atmosphere by storing the vials in an anaerobic jar where anoxic conditions were maintained using a BBL® gas pack. The jars were stored on ice for transportation to the laboratory for further analyses.

3.2. Water chemistry

At each sampling site, surface water pH, electrical conductivity (EC), dissolved O_2 (DO), redox potential (E_h) and temperature were measured using a WTW Sentix 41 pH-electrode, WTW TetraCon® 325 sensor, WTW galvanic CellOx 325 sensor and a SENTEK combination Pt electrode, respectively. Each of the electrodes was connected to a WTW Multi 340i Universal Pocket Meter for recording the measurements. The major anions and cations were determined in filtered, unacidified water samples using an ion Chromatograph (Dionex, DX500) and atomic absorption spectrophotometry (Varian AA10), respectively. Trace metal concentrations were determined in filtered and acidified water samples using an ICP-MS (Perkin Elmer/Sciex Elan 6000). To assess any external contamination while sampling, a trip blank was analyzed.

3.3. Sediment chemistry

Bulk sediment samples were analyzed for their trace metal content as well as the partitioning of trace metals among various phases. For determining bulk trace metal concentration, approximately 50 mg of dried sediment sample was treated with 4 mL of a 4:1 mixture of 28 M HF and 14 M HNO_3. Samples were digested for 48 h at 50–60 °C with occasional agitation before evaporation to complete dryness. A further 2 mL of 14 M HNO_3 was added and samples digested at 50–60 °C until complete dissolution followed by evaporation to dryness at approximately 75 °C. This latter procedure was repeated. After cooling, samples were diluted 1000 times with an internal standard. A syenite reference sample, STM-1, from the U.S. Geological Survey was analyzed simultaneously to determine the percentage systematic analytical error. Values for this sample have been published by Gladney and Roelandts (1988).

Partitioning of trace metals among various phases was determined using a 5-step sequential extraction scheme proposed by Tessier et al. (1979). The first three steps of the extraction process were conducted inside a glove bag under N_2 atmosphere to keep the sediments anoxic. Leachate from each step was analyzed for a suite of trace metals using an ICP-MS. In order to minimize the matrix effect caused by the presence of leachate within the supernatant of the first 4 fractions during ICP-MS analysis of trace metals, the calibration standards for each of the first 4 fractions were matrix matched to the samples. This was achieved by including the respective extractive reagent during the preparation of the calibration standards.

Sediment samples were analyzed for their grain size following a protocol adopted from the non-affiliated soil analysis work committee (Anon., 1990) and from Moore and Reynolds (1997). Organic C content was determined using a CHN analyzer. Prior to the analysis, 0.5 g of wet sediment samples were first treated with 2 mL of 50% (vol/vol) HCl to dissolve any carbonate fraction. The carbonate free sediment was washed with 5 mL of 1 M $HCOONH_4$ and dried at 40 °C. Subsequently, a known weight of dried sediment sample was combusted in the CHN analyzer to determine the organic C content.

3.4. Sediment quality

The sediment quality of the Blesbokspruit was assessed by calculating a number of indices:

3.4.1. Enrichment factor (E_f)

E_f was determined by calculating the amount of trace metal accumulated compared to the background concentration (see Table 3) of the same trace metal (Sinex and Helz, 1981):

$$E_f = \frac{C_{TM}/C_{Zr(Sample)}}{C_{TM}/C_{Zr(Background)}}. \quad (1)$$

The trace metal concentrations (C_{TM}) were normalized to the concentration of Zr (C_{Zr}) both in the background and in the sample as Zr was least mobile and was primarily associated with the residual fraction. Normalization in this manner accounts for the accumulation affected by the variation in the mobility of different trace metals.

3.4.2. Geoaccumulation index (I_{geo})

I_{geo} was calculated following the procedure proposed by Muller (1981) and Ruiz (2001):

$$I_{geo} = \log_2 \frac{C_{TM(sample)}}{1.5 \times C_{TM(Background)}}, \quad (2)$$

where C_{TM} denotes the concentration of trace metal and the factor 1.5 takes account of the variation of the trace metal in the background materials due to lithogenic effects (Ruiz, 2001).

3.4.3. Metal pollution index (MPI)

MPI is the geometric mean of the concentration of various trace metals present in the studied area (Usero et al., 1996):

$$MPI = \left(C_{TM_1}, C_{TM_2}, C_{TM_3}, \ldots, C_{TM_n}\right)^{\frac{1}{n}}, \quad (3)$$

where C_{TM_n} denotes the concentration of trace metal n expressed in mg/kg of dry weight.

3.4.4. Sediment quality guideline index (SQG-I)

SQG-I was calculated to determine the ecological risk caused by pollution from multiple metals present at the same site. The formula was modified after Fairey et al. (2001):

$$SQG\text{-}I = \frac{\sum_{i=1}^{n} C_{TM_i}/C_{TM_i\text{-threshold}}}{n}, \quad (4)$$

where $C_{TM_i\text{-threshold}}$ denotes the concentration of the ith trace metal beyond which its eco-toxicological effects are observed. SQG-I was calculated by both using the intervention values as well as the background concentration or target value of the trace metals as a threshold concentration. Here the target value is defined as the regional background value; the concentration of trace metal that one should strive to achieve after site remediation. The intervention value denotes the trace metal concentration above which eco-toxicity ensues and clean-up is mandatory according to Dutch regulations. SQG-I values based on target values; however, do not relate to eco-toxicity and merely provide a measure of the extent of pollution by multiple trace metals with respect to the background.

4. Results

4.1. Surface water samples

Surface water samples range from neutral to alkaline (pH ranging from 7 to 9.2) and were oxic ($DO = 2.5–10.8\ mg\ L^{-1}$) (Table 1). The high pH is maintained as the stream primarily flows over a dolomitic terrain. The EC of the water samples ranges between 521 and 2400 $\mu S\ cm^{-1}$ and shows considerable difference between the samples collected above and below the discharge point of the Grootvlei mine effluent (Table 1). The EC increases by almost a factor of 3 to 4 below the liming plant. Sample M05 shows somewhat anomalous behavior (see Table 1) as it was collected from a secluded shallow pond within a reworked

Table 1
Chemistry of surface water samples from the Blesbokspruit

Sample	pH	DO (mg/L)	E_h (mV)	EC (mS/cm)	Temp. (°C)	Anions (mg/L)							Cations (mg/L)			
						F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
M01	9.2	6.1	297	521	11	–	28	–	–	188	–	111	69	14	33	17
M02	7.1	8.4	470	630	15.9	–	89	–	–	26	–	126	80	13	23	10
M03	5.6	5.8	187	586	11.3	–	84	–	–	10	–	109	75	9	21	9
M04	7.2	3.7	538	698	11.4	0.1	74	–	–	13	–	82	87	13	35	10
M05	6.9	6.6	108	9660	12.4	–	67	28	–	73	–	4194	855	32	171	43
M06	7	5.4	118	787	14.1	–	106	–	–	17	–	105	115	21	34	11
M07	9.2	10.1	108	670	14.8	–	81	–	–	42	–	90	78	14	34	10
M08	9	10.1	203	790	18.5	–	114	–	–	24	–	100	110	17	36	10
M09	7.4	8.5	155	733	10.6	–	100	–	–	4	–	73	109	16	29	10
M10	8.1	7.1	190	1393	16.1	–	140	3	–	69	–	130	245	16	50	17
M11	8.1	6.1	200	1344	16.3	–	150	–	–	19	–	129	238	15	49	16
M12	7.5	2.5	na	2250	9.2	–	148	–	–	17	–	628	275	18	158	50
M13	8.2	10.8	187	1395	13	–	155	–	–	26	–	102	225	15	55	18
M14	7.9	9.8	218	2120	17	–	139	–	8	1	–	509	270	16	158	46
M15	8.1	6.8	54	2300	24.2	–	137	2	2	10	–	602	259	18	179	51
M16	8	9.3	454	2400	5.7	–	161	–	–	4	–	702	285	19	195	54
M17	8.1	9.3	180	2220	11.1	–	148	–	–	42	–	647	276	17	188	50
M18	8.2	8.6	279	2240	16	–	154	–	–	16	–	675	256	17	186	51
M19	8.2	10.3	462	2220	15	–	140	2	2	26	–	613	246	17	183	56
M20	8.4	9.1	192	2300	17.7	–	155	–	–	5	–	700	253	18	193	56

– not detected.

tailings dam and the water may have been affected by evaporation.

Chloride and SO_4^{2-} were the dominant anions (Table 1). Sulfate content in the Blesbokspruit ranges between 73 and 702 mg L^{-1} with an exceptionally high value at M05 of 4194 mg L^{-1}. Sulfate concentrations were generally highest in the main portion of the wetland between sites M13–M20, alongside the current mining operations. The Cl^- concentrations of the Blesbokspruit ranged between 28 and 161 mg L^{-1} with a general downstream increase. Surprisingly, NO_3^- was also high in many of the samples, although it is suspected that there was some NO_3^- contamination from the HNO_3 used to clean the vials as 35 mg L^{-1} of NO_3^- was measured in the trip blank. The dominant cations in the Blesbokspruit were Na^+ and Ca^{2+} with lesser amounts of K^+ and Mg^{2+} (Table 1). The Na^+ and Ca^{2+} content of the Blesbokspruit ranged from 69 to 855 mg L^{-1} and 21 to 195 mg L^{-1}, respectively. Their concentration increased downstream with the highest concentrations occurring in the main portion of the wetland (sites M10–M20). The Mg^{2+}content of the Blesbokspruit ranged from 9 to 56 mg L^{-1} whereas the K^+content varied from 9 to 32 mg L^{-1} with a high value of 32.0 mg L^{-1} measured at M05. Charge balance for all the samples was below the acceptable value of 10% (range: 0.1–9.8%), except for site M05 where major cations were underestimated resulting in a charge imbalance of 29%.

Trace metal concentrations measured in surface water are shown in Table 2. Simultaneous measurement of a standard (SRM 1640), treated in the same manner as the samples, shows that the systematic analytical error for all of the trace metals was below 9% except for Zn and Fe for which the measured error was 32.9% and 26.2%, respectively. Concentration of measured trace metals in Blesbokspruit was higher than the composition of the world average river water but for some of the trace metals it was less than the treated mine effluent, which is disposed of into the wetland (Table 2). In general trace metal concentrations increase downstream with clear step increases close to the tailings dams and the effluent discharge point.

4.2. Sediment characteristics and bulk trace metal concentrations

Sediments in Blesbokspruit consist predominantly of quartzose sand and silt with minor amounts of gravel and clay (Table 3). Overall, the grain size in Blesbokspruit decreases downstream. The upper portion of the wetland, M01–M09, appears to be sandier with varying amounts of

Table 2
Trace element concentration in surface water samples from the Blesbokspruit (μg L^{-1})

Samples	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	Nd[c]	30.8	0.6	1.5	71.4	197.8	12.2	6.8	3.8	157.5	2	0.5	119	0.3	6.6	0.9	0.1	64.8	0.5	1.1	2.1	0	2
M02	Nd	28.7	0.6	1.2	1711	481.5	4.4	3.7	Nd	155.9	0.2	0.2	81.7	0.1	0.1	1.2	0	45.1	0.3	0.8	0.1	0	Nd
M03	Nd	26.5	0.6	0.7	3128.5	559.6	2.6	2.4	2	272.7	0	0.2	88.7	0.1	0.1	1.3	0.1	79	0.3	0.6	0.3	Nd	Nd
M04	Nd	39.7	1	3.5	23.7	103.5	6.5	44.7	2.5	69.8	8	1.3	151	0.2	4.7	1.3	0.1	26.3	0.2	0.4	0.3	Nd	23.2
M05	Nd	324.3	1.2	4.3	2634.6	356.6	4250	41495	267	1119	4.4	41.3	485	0.3	6.6	1.7	1.5	31	0.5	0.3	0.4	0	15.5
M06	Nd	39.9	1	5.2	253.5	146.9	18.3	60.5	3.1	68.8	3.1	1.2	143	0.3	7.5	1.8	0.2	15.8	0	0.1	0.7	Nd	20
M07	Nd	39.9	1.2	2.2	101.3	88	2.9	37.9	3.1	10.1	8.2	0.7	147	0.3	4.8	1.8	0.1	14.4	0	0.1	7.6	Nd	24.3
M08	Nd	38.9	1.3	2.6	40.7	56.8	6.6	24.2	1.9	8.3	4.1	0.9	139	0.3	9.6	1.5	0.1	13	0.1	0.4	0.5	Nd	22.4
M09	Nd	34.1	2.3	3.6	31.3	73.5	8.1	19.5	0.8	21.2	7.1	1.8	171	0.3	15.6	1.3	0.2	16.7	0.1	0.3	1	Nd	2.8
M10	Nd	47.2	6.5	7	928.1	154.2	123	294.2	3.3	54.1	9.9	6.5	156	0.4	16.8	2	0.1	16.7	0.5	2.1	1.7	0	28.9
M11	Nd	40.2	7.2	2	275.7	152.5	14.7	65.6	2.1	25.4	8	5.9	142	0.3	12.5	1.6	0.1	25	0.3	1.3	2.3	0	10.6
M12	Nd	170.4	3.4	5.6	298.6	505.6	9.1	50.4	3	39.1	6	4.8	337	0.4	6.6	1	0.3	16.4	0.3	1	0.6	0	27.3
M13	Nd	47.6	5.8	5.8	282.5	151.1	14.6	65.6	5.4	20.7	9.4	5.9	156	0.4	11.6	1.4	0.2	20.9	0.4	0.7	1.8	0	15.9
M14	0	158.2	4.5	6.9	419.5	429.9	9.7	50.3	2.7	29.7	6.3	5.5	308	0.3	7.4	1.3	0.2	17.8	0.4	0.7	0.6	0	26.8
M15	0.1	179.1	3.1	3.2	365.9	464.5	11.3	41.7	0.1	28.1	5.4	3.4	324	0.3	3.8	1.4	0.3	25	0.2	0.5	0.3	Nd	32.6
M16	0.2	186.8	3.7	4.6	581.9	499.5	8	35.8	0.3	32.2	4.9	3.6	357	0.4	4.3	1.2	0.3	20.8	0.1	0.2	0.4	Nd	38.1
M17	Nd	186.6	4.4	4.6	686.4	487.4	11	48.4	0.9	32	4.8	4.3	340	0.3	5.6	1.2	0.3	32.7	0.1	0.4	0.5	Nd	34.9
M18	0.2	178.7	4.6	6.7	557.9	470.2	9.5	36.7	5.1	29.8	4.1	4.4	339	0.5	4.9	1.3	0.3	29.3	0	0.2	0.4	Nd	36.2
M19	Nd	192.2	3.3	4.4	395.8	496.8	6.4	30.9	4.1	31.9	4	4.4	341	0.4	4.4	1.2	0.3	25.5	0	0.2	0.3	Nd	39.9
M20	Nd	200.2	5.1	11.3	272.5	491.2	5.1	24.6	0.1	28.4	3.5	3.4	366	0.4	4.3	1	0.3	26.7	0.8	2.5	0.4	0.1	36.7
Treated effluent[a]	1	0	0	3384	3442	577	16	65	19	1694	4	5	689	521	2	0	1	207	0	14	152	3	0
World average[b]	**0.0089**	**0.489**	**0.71**	**0.7**	**34**	**66**	**0.148**	**0.801**	**1.48**	**0.6**	**0.62**	**0.07**	**60**	**0.04**	**0.42**	**NA**	**0.08**	**23**	**NA**	**NA**	**0.08**	**0.04**	**0.37**

[a] Chemical composition of treated mine water that is discharged into the Blesbokspruit from Grootvlei Gold Mines. Data provided by Grootvlei Gold Mines, a subsidiary of Petrex (Pty) Ltd.

[b] Average trace metal concentrations measured in major world rivers (Gaillardet et al., 2003).

[c] Not detected.

Table 3
Sediment properties and trace element concentration (in mg kg^{-1}) in bulk sediments of the Blesbokspruit

Sample	M01	M02	M03	M04	M05	M06	M07	M08	M09	M10	M11	M12	M13	M14	M15	M16	M17	M18	M19	M20	B[a]
%Gravel	44	6	27	1	8	14	2	0	0	3	3	0	0	0	0	0	3	1	1	0	
%Sand	33	31	61	64	52	67	31	66	85	21	32	16	11	50	21	24	21	34	17	63	
%Silt	18	45	8	26	37	12	29	24	9	73	59	54	47	40	73	71	47	43	56	27	
%Clay	5	18	4	9	4	7	38	10	6	4	6	29	43	10	6	4	30	23	26	10	
%OC	1.8	9.0	0.9	0.9	0.6	1.3	1.3	0.9	0.5	2.9	5.8	2.4	2.1	1.3	2.2	1.7	3.2	1.4	4.4	0.9	
Ti	3924	3427	1289	1314	1906	2929	5359	2568	1396	3880	3637	5108	4017	3061	4268	4436	5263	4252	4868	2337	**4600**[b]
V	119	90	110	33	53	94	238	68	39	89	82	103	153	70	78	105	107	85	109	48	**30**
Cr	192	155	532	79	219	164	339	111	146	214	218	130	304	104	167	178	180	124	210	62	**105**
Mn	2551	1470	3488	68	111	160	902	89	78	509	530	1207	908	473	806	1246	410	409	998	146	**272**
Fe	40,174	58,347	52,946	10,462	18,006	33,930	56,936	15,944	14,355	36,277	28,562	41,926	46,084	24,435	33,879	38,418	40,488	26,400	48,473	11,733	**47,200**[b]
Co	54.3	22.4	27.2	33.8	11.6	28.4	40.0	7.6	10.6	123.6	19.7	14.4	81.5	8.5	75.6	22.0	14.5	12.6	101.8	3.6	**9.8**
Ni	86.9	52.2	70.4	134.9	79.6	117.6	163.2	67.3	33.4	438.2	65.3	71.9	233.1	28.9	233.9	54.3	56.9	32.2	343.4	16.2	**36.1**
Cu	62.6	38.4	34.5	48.1	54.2	71.4	91.7	21.9	15.6	199.4	39.6	47.8	361.6	12.9	34.7	39.5	50.5	30.2	61.6	14.4	**16.9**
Zn	202.2	181.7	89.5	91.9	35.8	182.4	155.9	100.2	105.9	423.5	102.9	150.6	225.6	81.2	197.1	107.7	222.4	81.9	330.0	43.2	**97.7**
As	8.2	8.3	14.6	32.5	77.8	20.0	6.0	24.3	126.8	38.2	8.0	7.3	130.7	6.4	7.9	3.9	7.9	3.7	10.3	2.5	**13**[b]
Se	0.9	0.9	8.2	0.9	1.3	0.1	0.4	1.8	5.9	4.7	1.0	1.4	1.3	5.7	5.5	2.9	7.7	1.2	2.0	1.1	**0.6**[b]
Sr	96.7	67.7	25.3	9.1	41.5	14.7	17.6	13.0	30.1	30.9	47.3	49.4	52.5	17.8	21.5	45.1	32.8	25.8	43.1	16.4	**123.6**
Zr	109.7	83.4	42.1	26.5	51.2	74.2	97.1	58.6	64.4	118.1	106.5	125.9	103.1	103.8	117.6	120.2	175.7	124.0	135.5	66.0	**256.6**
Mo	1.3	1.6	2.1	0.8	1.2	1.3	1.9	0.7	1.9	2.7	1.0	1.4	1.4	2.0	1.1	0.5	1.4	0.7	1.4	0.5	**1.9**
Ag	0.7	0.6	10.2	0.3	0.3	0.3	0.5	0.3	0.9	1.1	0.5	0.6	1.2	1.1	1.2	0.6	1.5	0.5	0.7	0.3	**0.07**[b]
Cd	0.2	0.1	0.1	0.2	0.0	0.4	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.3	0.1	0.2	0.1	**0.3**[b]
Ba	1160.5	483.8	732.9	59.8	139.3	117.3	138.1	113.6	123.3	167.5	162.8	249.0	644.5	120.1	165.2	245.8	182.9	149.1	221.2	110.7	**547.6**
Au	0.1	0.3	1.7	0.4	0.1	0.2	0.2	0.2	0.9	1.0	0.2	0.1	0.3	0.4	0.4	0.1	0.6	0.1	0.6	0.1	**0.005**[b]
Hg	0.2	0.9	5.8	0.8	0.0	0.0	0.5	0.3	2.1	2.0	0.2	0.2	0.1	0.9	0.8	0.0	0.7	0.1	0.2	0.0	**0.4**[b]
Pb	38.7	36.1	35.5	11.6	25.4	19.3	12.3	8.2	13.1	21.0	22.3	20.6	24.4	13.5	14.6	16.0	19.6	15.2	17.5	7.4	**27.4**
Th	11.1	9.5	3.8	2.3	4.3	5.9	6.8	4.9	5.0	11.0	10.1	11.5	12.2	7.0	7.6	9.1	10.3	9.7	11.5	5.0	**15.3**
U	2.4	2.1	2.4	14.5	7.7	35.5	2.8	2.4	22.3	14.9	4.4	3.3	62.4	1.7	4.9	1.9	5.4	1.7	44.9	1.4	**5.1**

[a] Regional background concentration of trace metals based on average composition of Vryheid Formation (Azzie, 2002).

[b] Background concentration based on average crustal shale (Turekian, 1972).

gravel, silt and clay. Downstream of sample M10, the sediments have more silt with greater proportions of clay and less gravel. The sediment organic C content ranges from 0.5% to 9.0% with an average of 2.3% (Table 3). In general, there appears to be a higher organic C content in samples collected from sites M10 to M20. This coincides with the establishment of major *Typha* and *Phragmites* (reed) beds within this portion of the stream.

ICP-MS analyses of digested sediment are depicted in Table 3. For a geostandard treated in the same manner as the samples, analytical error was below 10% for all of the elements for which certified values were available. The results confirm accumulation of a suite of trace metals in the wetland sediment. The highest concentrations were measured for Fe followed by Mn, Ti and Ba (Table 3). Other metals, such as, Au, Cr, Cu, Co, Hg, Ni, Pb, V, U and Zn, together with As, also showed a significant buildup in the sediment fraction. Highest concentration of trace metals were measured at site M13, situated close to the discharge point of the liming plant that collects the seepage from the surrounding tailings dams. At site M14, closest to the discharge point of effluent from Grootvlei Gold Mine, trace metal concentrations were low but gradually increased downstream. Another peak in trace metal concentrations was observed close to the site M19; however, the source of the trace metals is not apparent.

4.3. Sequential extraction and phase associations

Following the sequential extraction scheme of Tessier et al. (1979), varying proportions of different trace metals were extracted from the exchangeable, carbonate, Fe–Mn oxide, organic and residual fractions (Fig. 2). In Fig. 2, the results are presented in three groups by averaging metal concentration of the samples extracted from each fraction from sites M01–M09, M10–M14 and M15–M20, respectively. The sites with similar characteristics were grouped together to reflect the general apportionment of metals within the sediments. Although this simplifies the interpretation of the data, it also obscures some of the localized differences in metal partitioning that may exist.

In general trace metals at the site were associated with relatively unstable phases. At the northern end of the site (M01–M09), most of the trace metals were sequestered within the Fe–Mn oxide and carbonate fractions; followed by exchangeable and organic fraction (Fig. 2a). The residual fraction contained negligible amounts of trace metals except for Zr, 90% of which was found in the residual fraction. Titanium (39% of total Ti) and Th (21% of total Th) were the other two most abundant trace metals in the residual fraction. More than 50% of As, Cd, Pb and Zn was associated with Fe–Mn oxide whereas 60% of U, 55% of Ti and 46% of Cr precipitated as carbonates. Significant proportions of Ag, Au and Hg were associated with the exchangeable fraction and the largest amounts of Cu (60%) and Mo (42%) were found in the organic fraction (Fig. 2a). In the central portion of the marsh where reed beds were much more extensively developed (M10–M14), only Cu, Co and Ni showed a noteworthy change in their association with the organic fraction: 97% of Cu fractionated with the organics and 40% more Co and Ni was found in organics compared to the upstream portion of the marsh (Fig. 2b). A significant increase in trace metal content within the exchangeable fraction was also observed at these sites resulting in almost equal distribution of trace metals among the exchangeable, carbonate and Fe–Mn oxide fractions (Fig. 2b). Except for Zr and Ti, the residual fraction had negligible amounts of trace metals. In the lower portion of the site (M15–M20) where marshy conditions persist, many of the trace metals that were high in the exchangeable fraction in the midstream of the marsh were found in relatively more stable reservoirs (Fig. 2c). However, 60–70% of As, Sr and Hg was found in the exchangeable fraction at the downstream sites. No other significant change in the behavior of trace metals was observed between the middle and lower portion of the marsh except that more of the same trace metals (Cu, Ni, Co, Th) were found to be associated with the organic fraction and most of the Ti (80%) was found in the residual fraction (Fig. 2c).

5. Discussion

At the peak of mining activities in South Africa around 1955, there were 24 active mines and at least 90 shafts on the East Rand Basin alone (Scott, 1995). As mining operations closed, leaving behind a myriad of shafts and stopes underground, water flooded the underground openings and decanted to other deeper mines. To retain access to its mineral reserves, fewer and fewer mines were pumping large amounts of water to the surface. For example,

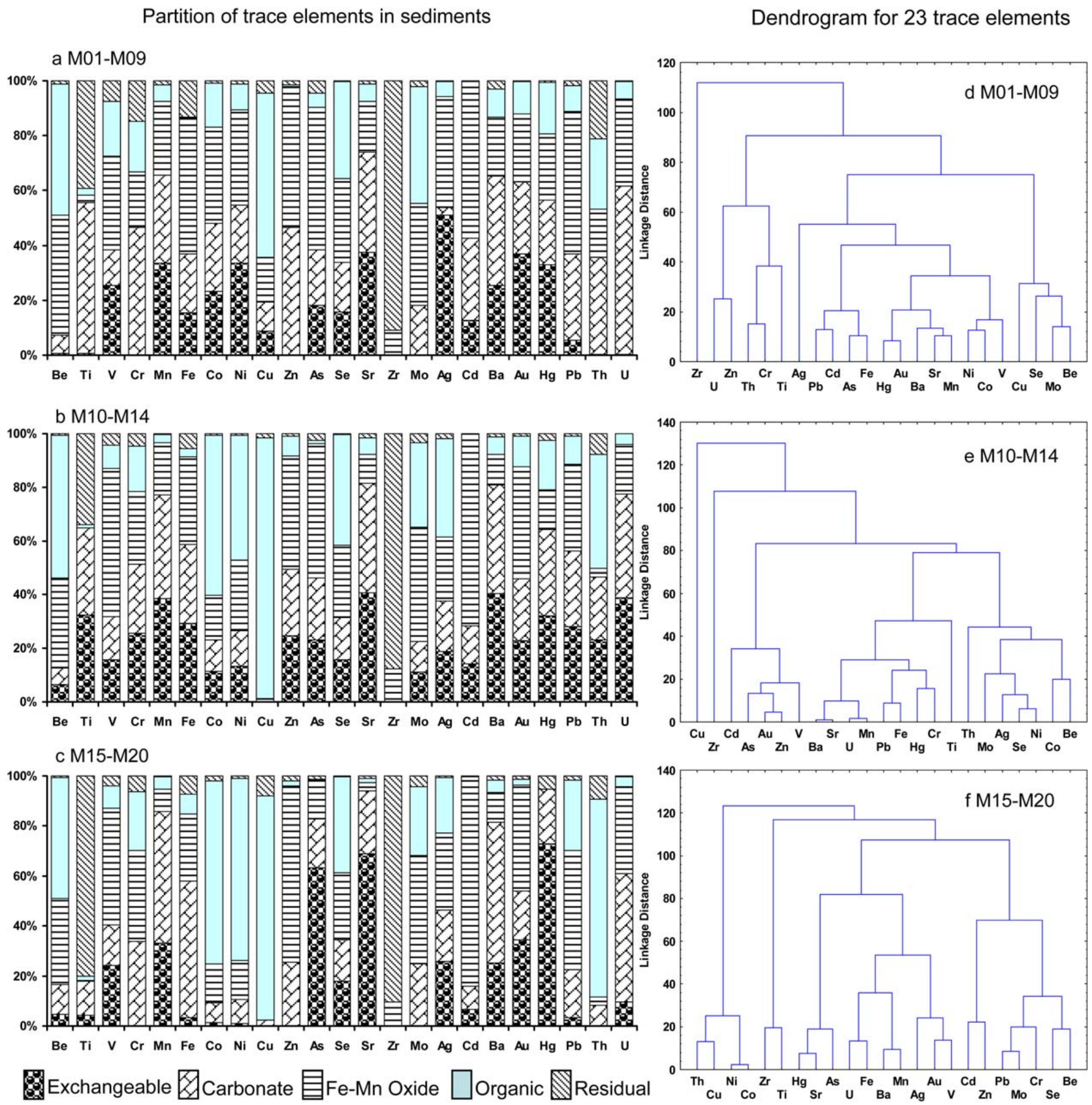

Fig. 2. Partitioning of trace elements in the solid phase as determined from sequential extraction of sediment trace elements for sites (a) M01–M09, (b) M10–M13 and (c) M14–M20. Results from cluster analysis of trace element data are plotted for the respective sites in (d) M01–M09, (e) M10–M13 and (f) M14–M20. Cluster analysis was performed using Euclidian distances and complete linkage.

Grootvlei Gold Mines, one of the few mines still active in the area, currently pumps mine water at an average rate of 75 M*l* day^{-1} (Anon., 2005). Pumping of such large volumes of water from a single point source has created a potentially hazardous situation by mobilizing the cumulative load of subsurface trace metal contaminated mine drainage to the surface environment.

5.1. Trace metals in water: mobility and partition coefficient

Trace metal concentrations measured in Blesbokspruit are, in general, higher than the world average concentrations measured in rivers (Table 2). This is expected as the stream is flowing through areas impacted by metal mining operations. In order to identify dominant processes responsible for mobilization of metals at the site, cluster analysis was performed. The analysis shows a complete decoupling of major and trace elements in Blesbokspruit (Fig. 3). This trend is exactly opposite to that observed by Dupré et al. (1996) in the river waters of the Congo Basin where a close interrelationship among the trace and major elements was observed indicating crustal weathering as the major source of the trace metals. The decoupling reflects anthropogenic processes as well as multiple sources of trace metals in the area. Before the mine water is discharged into the river, it is aerated in a high density separation plant to precipitate out excess Fe and then lime is added to adjust the pH of the effluent waters (Anon., 2005). Also, acidic seepage through tailings dams is captured and treated with lime before it enters the Blesbokspruit. Both these processes impact on the relative concentration of major and trace elements in the stream waters leading to their progressive decoupling.

Trace metal concentrations in Blesbokspruit normalized to the trace metal composition of the Vryheid Formation, when compared to Sr suggest that some are more mobile than others. The order of increasing mobility is Zr < Cr < Pb < Ba < V < Cu < Zn < Sr < Mn < U < Mo < Co < Ni. The mobility sequence was determined only for those trace metals for which a concentration in the Vryheid Formation was available (Table 3). An understanding of mobility potential of toxic trace metals and how it might change with human-induced conditions is essential for remediation planning. However, not all trace metals behave similarly under a given set of environmental conditions and different fluvial systems can respond to changing environ-

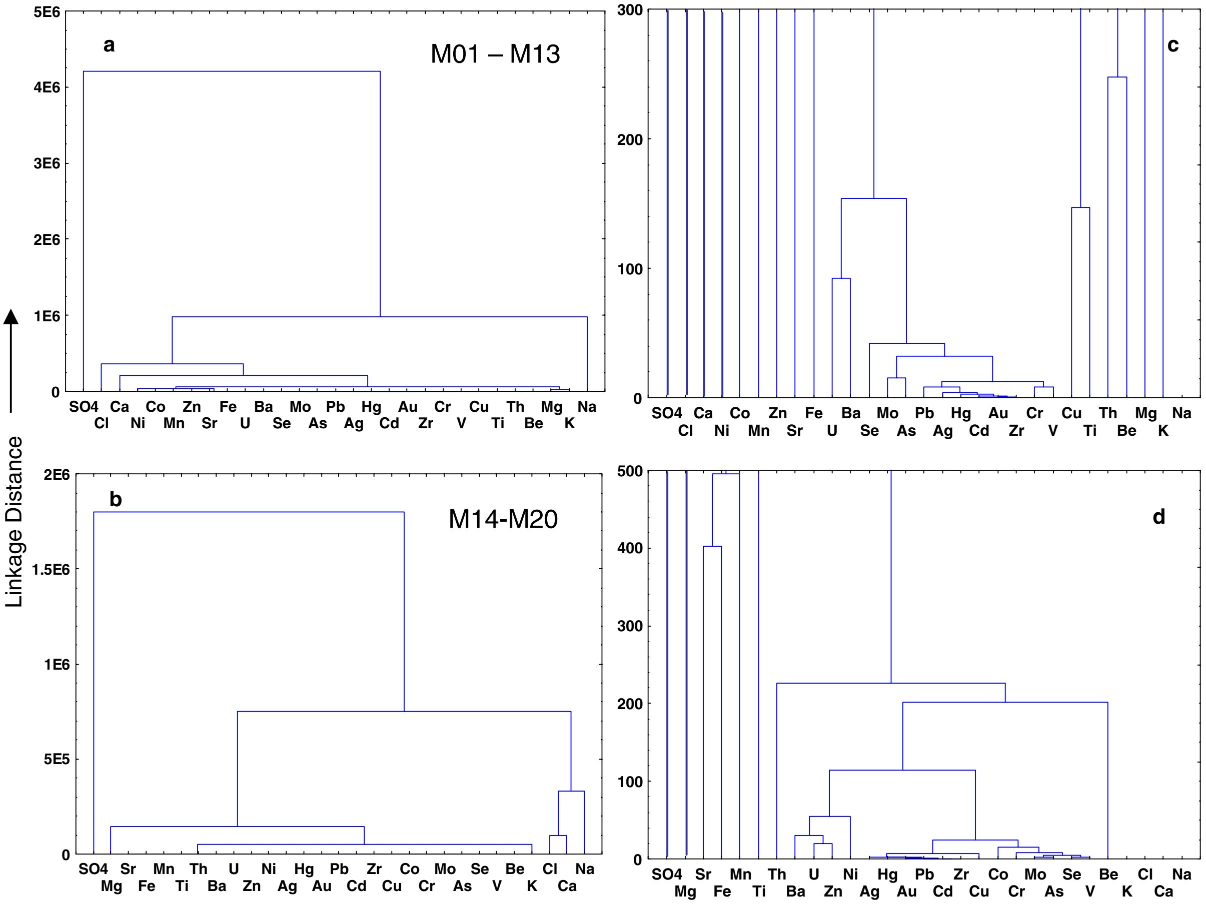

Fig. 3. Dendrograms showing the behavior of major and trace elements in stream water for sites (a) M01–M13 and (b) M14–M20. The same analyses are plotted at an enlarged scale for sites (c) M01–M13 and (d) M14–M20. Cluster analysis was performed using Euclidian distances and complete linkage. Please note that site M12 was included in M14–M20 for cluster analysis as it lies downstream of site M14.

mental conditions by an enhancement or attenuation of mobilities of trace metals (Siegel, 2002). For example, Cu and Zn are essentially immobile under basic pH conditions whereas Mo is mobile (Siegel, 2002). Scokart et al. (1983) report that a pH < 6 increases Cd mobility but Zn mobility increases only when pH < 5. Åström (1998) found that as a result of a drop in pH, Co, Mn and Ni were readily mobilized from sulfide bearing fine grained sediments whereas Cu was mobilized to a lesser degree and V had limited mobility.

Cluster analysis was further used to identify the collective mobility behavior of trace metals in Blesbokspruit. At a first glance the analysis suggests that all of the trace metals co-vary with each other (Figs. 3a and b). However, on a closer look several clusters are observed delineating trace elements with similar mobility (Figs. 3c and d). In the upstream regions, U and Ba, Mo and As, Cr and V, Cu and Ti, and Th and Be are closely interrelated. The closest coupling was observed between Pb, Ag, Hg, Cd, Au and Zr (Fig. 3c). Downstream, three separate clusters with elements having close affinity to each other are observed (Fig. 3d): (i) U, Zn, Ba and Ni; (ii) Ag, Hg, Au, Pb, Cd, Zr and Cu and (iii) Co, Cr, Mo, As, Se and V. All other trace metals are decoupled and form their own cluster.

To determine the impact of mixing of mine effluent with the water of the Blesbokspruit on trace metal mobility, trace metal concentrations were plotted against SO_4^{2-} concentration (Fig. 4). Sulfate was considered a conservative tracer as its concentrations were high enough to withstand minor changes. A mixing line, depicted by the broken lines in Fig. 4, denotes the concentration trend by simply mixing the treated mine water with the water of Blesbokspruit (composition similar to that measured at M13). Values that fall above the line denote addition to the water by mineral dissolution or desorption whereas values below the line reflect partitioning of metals into the solid phase. The graphs show that as the mine effluent mixes with Blesbokspruit water, most trace metals precipitate out; however, the sediments are acting as a source for

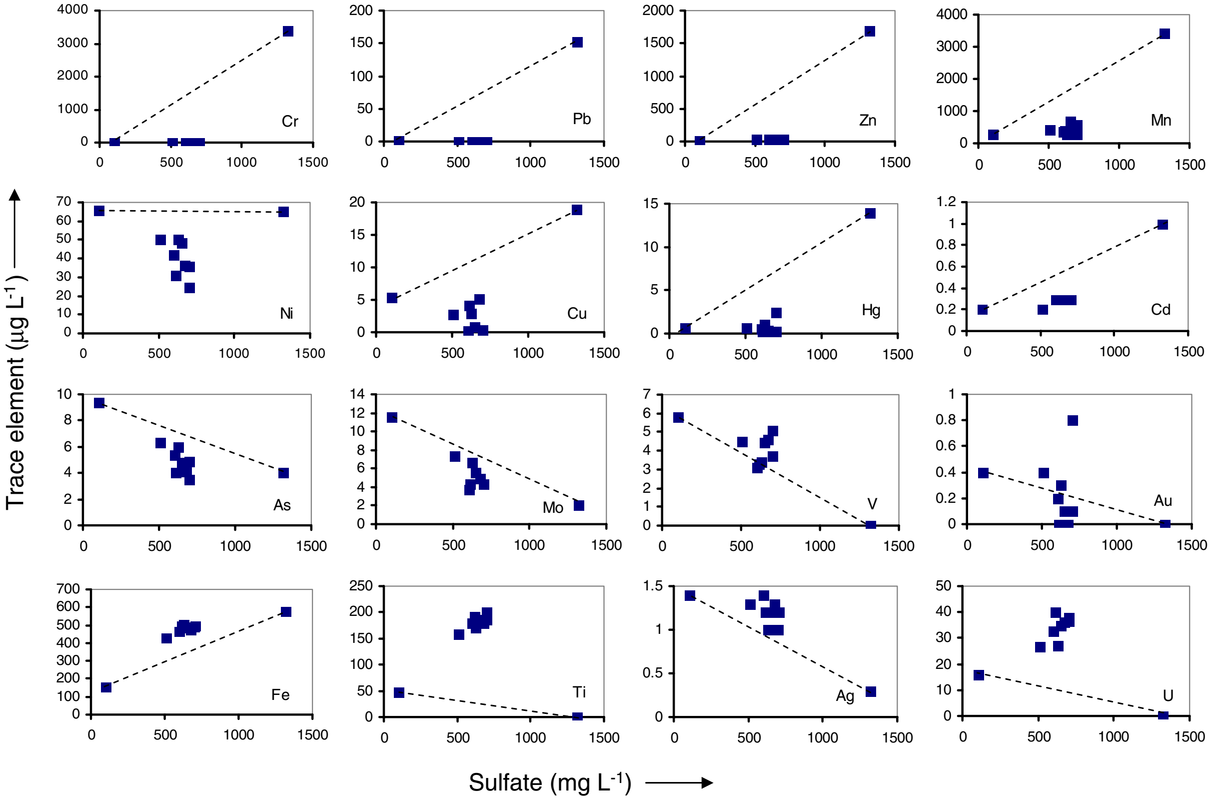

Fig. 4. Mixing line, denoted by the dashed line, represents concentration trend followed if mine effluent from Grootvlei Gold Mines is mixed with Blesbokspruit water having composition similar to that measured at site M13. Filled rectangles denote the measured concentration of individual trace elements in Blesbokspruit water between sites M14 and M20.

U, Ag, Ti, Fe and to some extent for V and Au in the stream water.

To what extent the trace metals are partitioned between the solution and the solid phase is quantified in terms of partition coefficient (K_d) and is calculated according to Eq. (5) (Zhang et al., 1994),

$$K_d = \frac{C_s}{C_w}, \tag{5}$$

where C_w and C_s denote the trace metal concentration in the water and solid phases, respectively. The sorption model assumes equilibrium and the K_d values are often calculated under controlled laboratory conditions. However, laboratory calculated values are often very different to what is observed in the field because of variations in the solvent characteristics; for example, under laboratory conditions non-complexing electrolytes are often used, whereas in the field the trace metals can form a complex in the solution resulting in low K_d values (Langmuir, 1997). Under field conditions, however, the K_d approach describes removal of trace metals from solution by multiple mechanisms such as, adsorption, precipitation and coprecipitation with major elements (Siegel, 2002). Such a lumped process approach provides a K_d value that is valid only for the system in which it is measured (Langmuir, 1997). When the contaminant of interest is already present in the sediments, the in situ K_d or apparent K_d values retrieved following the lumped approach are far more relevant, though (Langmuir, 1997).

The mean and the range of calculated apparent K_d values for various trace metals at Blesbokspruit are given in Table 4. The calculated K_d values are high and suggest that there is a large tendency for the trace metals to precipitate out from the stream waters or that the sediments have a large specific capacity to adsorb the trace metals. Consequently, this makes the Blesbokspruit wetland a potentially good metal repository. Note that the calculated K_d values were not very different than the range of K_d values calculated for these trace metals in major world rivers (Table 4). However, they were significantly larger than the K_d values calculated in a stream affected by acid mine drainage (Table 4). Interestingly though, barring few trace elements, K_d values follow the mobility sequence described above; for example, the lowest K_d value of $10^{0.28}$ L kg^{-1} was measured for the most mobile (Ni); whereas, the highest K_d value of $10^{5.92}$ L kg^{-1} was measured for the least mobile Zr. Even though at Blesbokspruit pH varies within a narrow range,

Table 4
Calculated in situ partition coefficient (log K_d in L kg^{-1}) of trace metals in the Blesbokspruit compared to K_d values measured at other riverine environments

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
Blesbokspruit																						
Mean	4.61	4.57	4.67	3.19	5.08	3.28	3.28	4.34	3.46	3.48	2.85	2.16	5.47	2.43	2.72	2.77	3.91	3.02	2.94	4.44	4.70	2.50
Min	3.77	3.97	3.74	1.63	4.38	0.44	0.28	2.31	1.51	2.85	1.51	1.65	5.12	1.87	2.25	1.35	3.36	1.81	2.21	3.21	4.70	1.58
Max	5.13	5.30	5.88	4.55	5.81	4.20	4.47	5.54	4.19	4.62	4.61	2.92	5.92	4.31	3.89	3.37	4.49	3.94	3.98	5.56	4.70	3.90
World Average[a]	5.75	5.34	5.00	5.11	6.08	5.00	5.26	4.82	5.70	3.10	4.00	3.40		3.78	2.37	4.70	4.00	3.10		6.00	5.54	5.34
Acid drainage stream, Adak[b]		2.56–4.02	2.47–3.82	0.43–2.97	1.23–3.95	0.32–3.33	1.27–3.67	0.62–3.36	0.45–2.39	1.86–4.30										1.52–3.12		
Huanghe[c]				5.30–6.10	5.88–7.47	5.53–6.29	4.76–5.16	4.04–4.40	5.02–5.98							4.90–5.99				5.46–6.15		
Changjiang[d]								4.33–4.49								5.09–5.23				5.81–5.95		
Mississippi[e]				5.20–6.30	6.95–7.62		4.35–4.69	4.15–4.27								4.60–4.98				5.23–5.62		
St. Lawrence[f]				5.32	5.96	4.95	4.43	4.53	4.6							4.09						
Nile[g]								5.15–5.25												5.17–5.31		

[a] Li (2000).
[b] Bhattacharya et al. (2006).
[c] Zhang et al. (1994).
[d] Zhang (1995, 1999).
[e] Trefry et al. (1986).
[f] Yeats and Bewers (1982).
[g] Abdel-Moati (1990).

the measured K_d values do not vary linearly with pH, suggesting that at Blesbokspruit sorption may not be the dominant process for segregating trace metals into the solid phase.

5.2. Trace metals in sediments

In the bulk sediments, trace element concentrations were by and large higher than the background at all of the sites (Table 3). At some sites the concentration of Ba, Sr, Th and Se were less than the background. Trace metal concentration measured in the Vryheid Formation were considered as background as the Blesbokspruit has eroded through this formation. For all of the trace elements measured here, local background values are not known. For those elements (Ti, Fe, As, Se, Ag, Cd, Au and Hg), world average shale composition was considered as the background concentration. Spatially, higher trace element concentrations were found in samples collected close to the liming plant at site M13. It seems that the adjacent tailings dams are acting as a major source of trace metals into the wetland. The trace metal concentrations decrease significantly just downstream of site M14 suggesting limited mobility of the trace metals within the wetland. Some of the trace metals were higher in the most upstream portion of the wetland, maybe because of its proximity to an informal settlement, a sewage plant and a paper mill. Another peak in trace metals was observed at site M19. However, no direct input of trace metals occurs close to this site. It is possible that the tailings dam just above the site is the source, although, for the lack of visible evidence it cannot be said for sure. Otherwise, no distinct spatial distribution pattern of trace metals is apparent within the sampled area.

In sediments, trace metal concentrations are considered to vary with sediment properties such as, percent organic C, grain size and Fe–Mn oxyhydroxide content (Adriano, 2001). In order to identify any covariation of trace elements among themselves or with sediment properties, a Pearson linear correlation matrix was generated (Table 5). Pairs having a correlation coefficient greater than 0.5 are highlighted in Table 5. Only Ti and V show any correlation with the clay content whereas Zr and Th were coupled to silt. Vanadium showed a stronger link to Fe than clay, though. Mn, Ba and Pb show an unexpectedly strong association with gravels. Surprisingly, no significant correlation was observed between the trace elements and the sediment organic C content. A number of trace metals (Ti, V, Cr, Sr, Ag, Ba, Hg and Pb) covaried with Mn and/or Fe, though. The strongest link was observed between Co and Ni that also covaried with Zn, Cu, and U. Arsenic was related to U and Cu but did not show any relationship with Ni and Co. Gold was found to be associated with Cr, Mo, Ag, Hg and Pb.

Partitioning behavior of trace metals within the solid phase varied in different parts of the wetland (Fig. 2). In general trace metals were preferentially associated with carbonate and Fe–Mn oxides compared to the organic fraction. Copper, Ni, Co and to some extent Th were the only elements that were preferentially associated with the organic fraction. Cluster analysis portrays the trace metal partitioning behavior in sediments succinctly. It is evident that some of the trace elements behave more closely with each other when compared to others. For example, at sites M01–M09, five distinct clusters, which closely relate the group of trace elements, are evident (Fig. 2d): (i) Th and Cr; (ii) Pb, Cd, As and Fe; (iii) Hg, Au, Ba, Sr and Mn; (iv) Ni, Co and V; and (v) Mo and Be. Each of these clusters are decoupled from one another and the rest of the elements form their own cluster, except Zn and U, which are primarily found associated with the carbonate and Fe–Mn oxide fractions, form their own cluster but their linkage probability is smaller compared to the trace metals in the other five clusters. Zirconium, as expected, is least related to any of the other trace elements as it is primarily found in the residual fraction.

In the mid- and downstream portion of the sampled area, for many of the trace elements, a comparatively larger fraction is associated with the organic phase. In addition, at the southern end (M15–M20) some of the trace elements (Sr, As, and Hg) are increasingly partitioned in the exchangeable fraction (Fig. 2). At the central portion of the marsh (M10–M14) also, five clusters of trace elements behaving similarly are visible (Fig. 2e): (i) As, Au, Zn and V; (ii) Ba, Sr, U and Mn; (iii) Pb, Fe, Hg and Cr; (iv) Ag, Se and Ni and (v) Co and Be. Copper and Zr were least like others as they were primarily associated with the organic and residual fraction, respectively. At the southern end (M15–M20), the clusters were more stringy and the trace elements form nine different clusters (Fig. 2f): (i) Th and Cu; (ii) Ni and Co; (iii) Zr and Ti; (iv) Hg, Sr and As; (v) U and Fe; (vi) Ba and Mn; (vii) Au and V; (viii) Pb, Mo and Cr

Table 5
Person linear correlation matrix for trace elements and associated physico-chemical properties of sediments from the Blesbokspruit

	%Gravel	%Sand	%Silt	%Clay	%OC	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
%Gravel	■																										
%Sand	0.11	■																									
%Silt	−0.47	−0.79	■																								
%Clay	−0.32	−0.53	0.13	■																							
%OC	−0.07	−0.48	0.44	0.17	■																						
Ti	−0.17	−0.86	0.62	0.61	0.35	■																					
V	0.15	−0.53	0.07	0.65	0.10	0.64	■																				
Cr	0.41	−0.15	−0.15	0.15	−0.02	0.00	0.58	■																			
Mn	0.71	−0.23	−0.13	−0.04	0.15	0.06	0.39	0.68	■																		
Fe	0.27	−0.63	0.21	0.48	0.51	0.58	0.78	0.63	0.66	■																	
Co	0.06	−0.54	0.45	0.14	0.19	0.33	0.30	0.27	0.16	0.39	■																
Ni	−0.11	−0.47	0.47	0.15	0.14	0.30	0.26	0.22	−0.01	0.30	0.96	■															
Cu	−0.06	−0.46	0.23	0.48	0.04	0.23	0.43	0.33	0.02	0.32	0.63	0.59	■														
Zn	0.04	−0.58	0.45	0.24	0.37	0.50	0.32	0.14	0.10	0.49	0.87	0.86	0.53	■													
As	−0.14	0.22	−0.21	0.11	−0.25	−0.37	−0.12	0.13	−0.24	−0.22	0.14	0.14	0.55	0.02	■												
Se	0.02	0.07	0.04	−0.20	−0.15	−0.13	−0.15	0.31	0.24	0.06	0.04	0.02	−0.14	0.12	0.06	■											
Sr	0.53	−0.47	0.16	0.08	0.48	0.30	0.20	0.11	0.51	0.44	0.19	0.00	0.20	0.25	0.05	−0.22	■										
Zr	−0.15	−0.79	0.64	0.44	0.34	0.89	0.37	−0.08	0.02	0.42	0.30	0.25	0.15	0.53	−0.30	0.18	0.32	■									
Mo	0.17	−0.09	−0.03	0.07	0.12	0.03	0.29	0.47	0.27	0.43	0.42	0.44	0.30	0.52	0.22	0.47	0.05	0.09	■								
Ag	0.43	0.15	−0.29	−0.15	−0.13	−0.32	0.11	0.78	0.72	0.35	0.01	−0.05	−0.03	−0.07	−0.04	0.61	−0.08	−0.23	0.37	■							
Cd	0.17	−0.11	−0.03	0.10	0.04	0.32	0.24	−0.06	−0.11	0.21	0.36	0.38	0.13	0.56	−0.26	−0.03	−0.14	0.30	0.14	−0.15	■						
Ba	0.82	−0.23	−0.22	0.03	0.13	0.04	0.32	0.47	0.83	0.49	0.22	−0.01	0.28	0.16	0.05	0.02	0.75	0.03	0.17	0.41	−0.06	■					
Au	0.21	0.19	−0.20	−0.20	−0.05	−0.35	−0.04	0.62	0.44	0.23	0.27	0.26	0.05	0.26	0.16	0.76	−0.19	−0.17	0.64	0.83	0.02	0.18	■				
Hg	0.33	0.29	−0.32	−0.27	−0.11	−0.44	−0.03	0.66	0.57	0.23	0.06	0.04	−0.07	0.02	0.08	0.70	−0.16	−0.32	0.57	0.91	−0.13	0.27	0.94	■			
Pb	0.74	−0.25	−0.09	−0.08	0.43	0.00	0.20	0.52	0.75	0.58	0.17	0.01	0.19	0.21	0.02	0.05	0.76	0.03	0.34	0.44	−0.05	0.82	0.26	0.35	■		
Th	0.00	−0.86	0.62	0.47	0.53	0.80	0.41	0.01	0.19	0.54	0.47	0.36	0.45	0.63	−0.09	−0.10	0.64	0.84	0.14	−0.24	0.15	0.33	−0.20	−0.33	0.32	■	
U	−0.13	−0.14	−0.01	0.39	0.01	0.04	0.15	0.15	−0.15	0.14	0.53	0.52	0.70	0.45	0.61	−0.16	0.05	0.04	0.14	−0.10	0.27	0.07	0.09	−0.13	0.01	0.25	■

and (ix) Se and Be. In addition Cd and Zn show some similarities in their behavior.

5.3. Sediment quality

A number of methods are available for assessing sediment quality and each has its own pros and cons (Caeiro et al., 2005). Enrichment indices (E_f and I_{geo}) provide a simple way of comparing the extent of metal pollution among different sites. However, the main criticism against calculation of such indices is that they do not aggregate all the contaminants into one variable and it becomes difficult to compare the sites and interpret the data when multiple metals are in question (Caeiro et al., 2005). The enrichment factor further suffers from the fact that there are no threshold values for denoting the pollution level. I_{geo} on the other hand provides a classification system for the degree of pollution when compared to the background (Ruiz, 2001): $I_{geo} < 1$ – unpolluted; $1 < I_{geo} < 2$ – very lightly polluted; $2 < I_{geo} < 3$ – lightly polluted; $3 < I_{geo} < 4$ – moderately polluted; $4 < I_{geo} < 5$ – highly polluted; $I_{geo} > 5$ – very highly polluted.

The calculated E_f values show that most metals at the sampled sites are enriched compared to the background (Table 6). However, spatially the extent of enrichment varied. Highest enrichment was observed for Au followed by Ag. Significant enrichment was also observed for Hg and U. All of these elements are either associated with the ore being mined or are used in the processing of the ore. The extent of enrichment of precious metals has prompted small scale entrepreneurs to seek permits to re-mine the accumulated sediments in the smaller dams and the wetland

The calculated values for I_{geo} suggest that the sites are affected differently for different metals (Table 6). In general, the sites are *very lightly to lightly polluted* with respect to most trace metals. Some of the sites, however, are *highly polluted* with respect to Ag and Au (Table 6). Even though the absolute concentration of trace metals in Blesbokspruit seems high the I_{geo} values suggest low levels of pollution primarily because the background concentrations are also very high in this mineral rich zone.

To account for the presence of multiple metals at a site, MPI was calculated by taking the geometric mean of the trace metal concentration of multiple elements at one site (Eq. (3)). The calculated MPI values suggest that the site M10 is the most polluted followed by sites M13 and M19 (Table 6). Interestingly, all of the three sites are close to the tailings dams indicating their major role in mobilizing trace metals in the environment. Sites M15 and M16 did not show the same extent of pollution probably because the tailings dam next to the sites (see Fig. 1) has been reclaimed and reworked. Although, MPI aggregates all of the metals into one value and provides an easy way to compare one site from another, it suffers from the same drawback of not having any threshold value to denote the pollution level.

The sediment quality guideline index was calculated based on the target value and intervention value for various trace metals. The index provides a measure of risk to biota from metal pollution. A SQG-I > 1 based on target value suggests that clean-up is required whereas SQG-I > 1 based on the intervention value denotes that at the site, biota is prone to metal toxicity and clean-up is mandatory. Furthermore, if SQG-I is high (>1.5) sediments have a high probability of being toxic to biota, low probability of being toxic when SQG-I is low (<0.5) and moderately toxic when 0.5 < SQG-I < 1.5 (Fairey et al., 2001). For the lack of any specific guideline values for trace metals in wetland sediments in South Africa and the fact that intervention values are not available for all of the measured trace elements, the Dutch intervention values (in mg kg^{-1}) were used for As (55), Ba (625), Cd (12), Cr (380), Co (240), Cu (190), Pb (530), Hg (10), Mo (200), Ni (210) and Zn (720) (Adriano, 2001). In addition, eco-toxicity threshold values for U (100) and Se (4) were added from other sources (Hamilton, 2004; Sheppard et al., 2005). For the target values, same background values were used as given in Table 3. SQG-I$_{(target)}$ depicted in Table 6 therefore takes into account all of the measured trace elements whereas SQG-I$_{(intervention)}$ is based on trace elements for which the intervention value could be obtained. There are a number of good reasons for using Dutch intervention values for assessing the toxicity potential of the sediments. For example, the intervention values take into account both, human and eco-toxicological considerations and the soil type and local circumstances including, natural concentrations of the contaminants (Adriano, 2001).

SQG-I$_{(target)}$ values vary between 1.5 and 24.2 suggesting that all of the sites are contaminated and should undergo remediation. Although based on the intervention values, the sediments have a

Table 6
Sediment quality as determined from the calculation of enrichment factor (E_f), geoaccumulation index (I_{geo}), metal pollution index (MPI) and sediment quality guideline index (SQG-I)

		M01	M02	M03	M04	M05	M06	M07	M08	M09	M10	M11	M12	M13	M14	M15	M16	M17	M18	M19	M20
Ti	E_f	2.0	2.3	1.7	2.8	2.1	2.2	3.1	2.4	1.2	1.8	1.9	2.3	2.2	1.6	2.0	2.1	1.7	1.9	2.0	2.0
	I_{geo}	−0.8	−1.0	−2.4	−2.4	−1.9	−1.2	−0.4	−1.4	−2.3	−0.8	−0.9	−0.4	−0.8	−1.2	−0.7	−0.6	−0.4	−0.7	−0.5	−1.6
V	E_f	9.3	9.2	22.4	10.6	8.9	10.8	21.0	10.0	5.1	6.5	6.6	7.0	12.7	5.8	5.7	7.5	5.2	5.9	6.9	6.2
	I_{geo}	1.4	1.0	1.3	−0.5	0.2	1.1	2.4	0.6	−0.2	1.0	0.9	1.2	1.8	0.6	0.8	1.2	1.2	0.9	1.3	0.1
Cr	E_f	4.3	4.6	31.0	7.4	10.5	5.4	8.6	4.6	5.6	4.4	5.0	2.5	7.2	2.5	3.5	3.6	2.5	2.5	3.8	2.3
	I_{geo}	0.3	0.0	1.8	−1.0	0.5	0.1	1.1	−0.5	−0.1	0.4	0.5	−0.3	1.0	−0.6	0.1	0.2	0.2	−0.3	0.4	−1.3
Mn	E_f	22.0	16.7	78.4	2.4	2.1	2.0	8.8	1.4	1.1	4.1	4.7	9.1	8.3	4.3	6.5	9.8	2.2	3.1	7.0	2.1
	I_{geo}	2.6	1.9	3.1	−2.6	−1.9	−1.3	1.1	−2.2	−2.4	0.3	0.4	1.6	1.2	0.2	1.0	1.6	0.0	0.0	1.3	−1.5
Fe	E_f	2.0	3.8	6.8	2.1	1.9	2.5	3.2	1.5	1.2	1.7	1.5	1.8	2.4	1.3	1.6	1.7	1.3	1.2	1.9	1.0
	I_{geo}	−0.8	−0.3	−0.4	−2.8	−2.0	−1.1	−0.3	−2.2	−2.3	−1.0	−1.3	−0.8	−0.6	−1.5	−1.1	−0.9	−0.8	−1.4	−0.5	−2.6
Co	E_f	13.0	7.0	16.9	33.4	5.9	10.0	10.8	3.4	4.3	27.4	4.8	3.0	20.7	2.1	16.8	4.8	2.2	2.7	19.7	1.4
	I_{geo}	1.9	0.6	0.9	1.2	−0.3	1.0	1.4	−1.0	−0.5	3.1	0.4	0.0	2.5	−0.8	2.4	0.6	0.0	−0.2	2.8	−2.0
Ni	E_f	5.6	4.4	11.9	36.2	11.1	11.3	11.9	8.2	3.7	26.4	4.4	4.1	16.1	2.0	14.1	3.2	2.3	1.8	18.0	1.7
	I_{geo}	0.7	−0.1	0.4	1.3	0.6	1.1	1.6	0.3	−0.7	3.0	0.3	0.4	2.1	−0.9	2.1	0.0	0.1	−0.7	2.7	−1.7
Cu	E_f	8.7	7.0	12.4	27.6	16.1	14.6	14.3	5.7	3.7	25.6	5.6	5.8	53.3	1.9	4.5	5.0	4.4	3.7	6.9	3.3
	I_{geo}	1.3	0.6	0.4	0.9	1.1	1.5	1.9	−0.2	−0.7	3.0	0.6	0.9	3.8	−1.0	0.5	0.6	1.0	0.3	1.3	−0.8
Zn	E_f	4.8	5.7	5.6	9.1	1.8	6.5	4.2	4.5	4.3	9.4	2.5	3.1	5.7	2.1	4.4	2.4	3.3	1.7	6.4	1.7
	I_{geo}	0.5	0.3	−0.7	−0.7	−2.0	0.3	0.1	−0.5	−0.5	1.5	−0.5	0.0	0.6	−0.9	0.4	−0.4	0.6	−0.8	1.2	−1.8
As	E_f	1.5	2.0	6.8	24.2	30.0	5.3	1.2	8.2	38.8	6.4	1.5	1.1	25.0	1.2	1.3	0.6	0.9	0.6	1.5	0.7
	I_{geo}	−1.2	−1.2	−0.4	0.7	2.0	0.0	−1.7	0.3	2.7	1.0	−1.3	−1.4	2.7	−1.6	−1.3	−2.3	−1.3	−2.4	−0.9	−3.0
Se	E_f	3.5	4.6	83.6	14.5	10.9	0.6	1.8	13.1	39.3	17.2	4.0	4.8	5.4	23.7	19.9	10.3	18.8	4.1	6.3	7.1
	I_{geo}	0.0	0.0	3.2	0.0	0.5	−3.2	−1.2	1.0	2.7	2.4	0.2	0.6	0.5	2.7	2.6	1.7	3.1	0.4	1.2	0.3
Sr	E_f	1.8	1.7	1.2	0.7	1.7	0.4	0.4	0.5	1.0	0.5	0.9	0.8	1.1	0.4	0.4	0.8	0.4	0.4	0.7	0.5
	I_{geo}	−0.9	−1.5	−2.9	−4.3	−2.2	−3.7	−3.4	−3.8	−2.6	−2.6	−2.0	−1.9	−1.8	−3.4	−3.1	−2.0	−2.5	−2.8	−2.1	−3.5
Zr	E_f	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	I_{geo}	−1.8	−2.2	−3.2	−3.9	−2.9	−2.4	−2.0	−2.7	−2.6	−1.7	−1.9	−1.6	−1.9	−1.9	−1.7	−1.7	−1.1	−1.6	−1.5	−2.5
Mo	E_f	1.6	2.6	6.6	4.1	3.2	2.4	2.6	1.6	4.0	3.1	1.3	1.5	1.8	2.6	1.3	0.6	1.1	0.8	1.4	1.0
	I_{geo}	−1.1	−0.8	−0.5	−1.8	−1.2	−1.1	−0.6	−2.0	−0.6	−0.1	−1.5	−1.0	−1.0	−0.5	−1.4	−2.5	−1.0	−2.0	−1.0	−2.5
Ag	E_f	23.4	26.4	886.9	41.5	21.5	14.8	18.9	18.8	50.2	34.7	17.2	17.5	42.7	39.1	35.9	18.3	31.6	14.8	18.9	16.7
	I_{geo}	2.7	2.5	6.6	1.5	1.5	1.5	2.3	1.5	3.1	3.4	2.3	2.5	3.5	3.4	3.5	2.5	3.8	2.3	2.7	1.5
Cd	E_f	1.6	1.0	1.6	6.5	0.0	4.6	1.8	1.5	1.1	1.7	0.8	0.7	0.8	0.6	1.3	0.7	1.4	0.7	1.3	1.3
	I_{geo}	−1.2	−2.2	−2.5	−1.2	-18.8	−0.2	−1.2	−2.2	−2.5	−0.9	−2.2	−2.2	−2.2	−2.6	−1.3	−2.2	−0.6	−2.2	−1.2	−2.2
Ba	E_f	5.0	2.7	8.2	1.1	1.3	0.7	0.7	0.9	0.9	0.7	0.7	0.9	2.9	0.5	0.7	1.0	0.5	0.6	0.8	0.8
	I_{geo}	0.5	−0.8	−0.2	−3.8	−2.6	−2.8	−2.6	−2.9	−2.7	−2.3	−2.3	−1.7	−0.3	−2.8	−2.3	−1.7	−2.2	−2.5	−1.9	−2.9

Au	E_f	46.8	184.6	2124.9	774.6	100.2	138.3	105.7	175.2	697.2	425.6	96.4	40.8	149.3	203.0	170.2	42.7	175.3	41.4	227.2	77.8
	I_{geo}	3.7	5.3	7.9	5.7	3.7	4.7	4.7	4.7	6.9	7.0	4.7	3.7	5.3	5.8	5.7	3.7	6.3	3.7	6.3	3.7
Hg	E_f	1.2	6.9	87.7	19.4	0.0	0.0	3.3	3.3	21.3	10.7	1.2	1.0	0.6	5.3	4.2	0.0	2.7	0.5	0.9	0.0
	I_{geo}	−1.6	0.6	3.3	0.4	-39.1	-39.1	−0.3	−1.0	1.8	1.7	−1.6	−1.6	−2.6	0.5	0.4	-39.1	0.3	−2.6	−1.6	-39.1
Pb	E_f	3.3	4.1	7.9	4.1	4.6	2.4	1.2	1.3	1.9	1.7	2.0	1.5	2.2	1.2	1.2	1.2	1.0	1.1	1.2	1.0
	I_{geo}	−0.1	−0.2	−0.2	−1.8	−0.7	−1.1	−1.7	−2.3	−1.6	−1.0	−0.9	−1.0	−0.8	−1.6	−1.5	−1.4	−1.1	−1.4	−1.2	−2.5
Th	E_f	1.7	1.9	1.5	1.5	1.4	1.3	1.2	1.4	1.3	1.6	1.6	1.5	2.0	1.1	1.1	1.3	1.0	1.3	1.4	1.3
	I_{geo}	−1.0	−1.3	−2.6	−3.3	−2.4	−2.0	−1.8	−2.2	−2.2	−1.1	−1.2	−1.0	−0.9	−1.7	−1.6	−1.3	−1.2	−1.2	−1.0	−2.2
U	E_f	1.1	1.3	2.9	27.5	7.6	24.1	1.5	2.1	17.4	6.3	2.1	1.3	30.5	0.8	2.1	0.8	1.6	0.7	16.7	1.1
	I_{geo}	−1.7	−1.9	−1.6	0.9	0.0	2.2	−1.5	−1.7	1.5	1.0	−0.8	−1.2	3.0	−2.2	−0.7	−2.0	−0.5	−2.2	2.6	−2.5
MPI		**29.3**	**25.9**	**37.4**	**15.3**	**3.1**	**6.3**	**24.9**	**13.9**	**22.0**	**45.7**	**20.4**	**22.5**	**42.5**	**18.1**	**28.8**	**6.2**	**30.0**	**15.1**	**36.4**	**2.9**
SQG-$I_{intervention}$		**0.20**	**0.15**	**0.31**	**0.21**	**0.28**	**0.22**	**0.27**	**0.14**	**0.34**	**0.58**	**0.15**	**0.14**	**0.69**	**0.09**	**0.26**	**0.13**	**0.17**	**0.09**	**0.37**	**0.05**
SQG-I_{target}		**3.1**	**4.3**	**24.3**	**4.7**	**2.1**	**3.3**	**3.7**	**2.7**	**9.9**	**12.4**	**3.0**	**2.4**	**6.9**	**5.3**	**6.0**	**2.4**	**7.8**	**1.9**	**8.1**	**1.5**

low to moderate probability of being toxic to biota suggesting that in general the pollution levels are low. These values, however, should not be taken at face value because for one, not all of the metals, including the ones causing most pollution (Au and Ag), were considered for calculating the SQG-$I_{(intervention)}$ values and second, these values are based on only the surficial sediments representing very recent events. It must be noted that many of the mines in the area have closed down in the last 50 years reducing their impact on the environment.

6. Conclusions

In Blesbokspruit, trace metals are primarily mobilized through mining activities either through the pumping of underground mine water or seepage from massive tailings dams that have accumulated over the years along the stream. Although, the mine water discharges trace metals directly into the stream it is comparatively a smaller source because (1) the pH of the water is naturally high from flowing through the local dolomite aquifer, and (2) the mine water undergoes high density separation followed by lime treatment before it is discharged. Both these factors promote precipitation of metals rather than dispersion and consequently the mobility of trace metals is relatively low in the studied area. The colossal waste heaps associated with historic mining activities pose a greater risk in promoting the dispersion of trace metals in the local environment both through the seepage of acidic waters and from atmospheric fallout.

The partition coefficient for all of the measured trace metals in Blesbokspruit is high, which leads to their accumulation in the wetland. It seems that in sediments, the trace metals are preferentially partitioned in the carbonate and the Fe–Mn oxide fraction compared to the organic or the exchangeable fraction. Therefore, precipitation and co-precipitation rather than sorption seem to be the main mechanisms for removing the trace metals from the solution phase. Even though the surficial sediments are enriched in trace metals compared to their regional background concentration, the extent of pollution in Blesbokspruit is still low to moderate from an eco-toxicological perspective.

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