ORIGINAL ARTICLE

Potential ecological risk assessment of a stream in Shamva, Zimbabwe

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Abstract

Water bodies are the final sinks of all pollution with more than 90% of contaminants found in suspended particulates and bottom sediments. Only less than 10% is retained in the water column yet it attracts and receives great research attention. The pollution status and the potential ecological risk of three pools of water along a stream due to heavy metal enrichment from a nearby active gold mining tailings dam were assessed. The upstream-downstream and sedimentological approaches to ecosystem health assessment were used. Potential uses of pool water were also evaluated based on measured water quality parameters. Heavy metals in water and sediment were determined using Flame Atomic Absorption Spectrometry. Results revealed that salinisation, acidification and heavy metals were exported from a mining tailings dam to the stream. The degree of contamination of pool water by heavy metals dictated water uses. Heavy metal concentrations imposed water use restrictions for aquatic life in a pool which directly received discharge from the mine tailings dam. The average heavy metal concentrations in sediments were lower than the standard shale values. Sediment quality guidelines and pollution indices showed that the stream was not polluted with heavy metals, thus posed no potential ecological risk. Continuous monitoring of tailings discharge and wash off is important to safeguard aquatic ecosystem and public health.

Keywords: metal, pollution, sediment, tailings, risk

1. Introduction

Fine particulates of mining tailings are subject to environmental manipulation thus potentially release heavy metals into the aquatic system (Ciszweski et al. 2013) of which more than 90% are found in sediments and suspended materials (Calmano and Forstner 1993). Sediments play an important role in heavy metal cycling in aquatic environments (Ongley 1996). Some heavy metals are essential for plant and animal nutrition but they may be toxic at elevated concentrations (Forstenr and Wittmann 1981). Public health effects of heavy metals are well documented (Jaishankar et al. 2014; WHO 2011b) are well documented. Sediment-associated heavy metals are not expected to present a direct ecological risk provided they remain immobilised by encapsulation (Singh et al. 2005). However, they are subject to remobilisation into the water column by in-stream hydrodynamic processes and external factors

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(Eggleton and Thomas 2004). Once remobilised and conditions permitting, heavy metals may become bioavailable to aquatic organisms and get exported to the terrestrial environment via the food chain. The analysis of heavy metals in bed sediments of water bodies near human settlements becomes crucial, not only to establishing anthropogenic impacts on the aquatic ecosystem, but also to investigating water use options (Yi et al. 2011).

Municipal and industrial sewage discharges into watercourses and reservoirs have dominated river water quality research in Zimbabwe, especially in urban settlements. Most of the work seems to have focused on the pollution status of the water column (e.g. Jonnalagadda and Mhere 2001; Nhapi and Tirivarombo 2004; Nyamadzawo et al. 2007; Kibena et al., 2014). None of these studies seem to have linked heavy metal content of bed sediments to the potential health of aquatic ecosystems. The sedimentology approach is an alternative way of assessing the health of aquatic ecosystems to laboratory assays which can be expensive, and to measuring ecosystem structure and abundances which can be time-consuming (Maher et al. 1999).

Sediment quality with respect to heavy metals, has been used to evaluate the pollution status and ecological health of watercourses and reservoirs using pollution indices (Mohiuddin et al. 2011; Majnoni et al. 2015), sediment quality guidelines (SQGs) (Maher et al. 1999; Soliman et al. 2015) and the ecological risk index (RI) (Liu et al. 2005). Four indices were used in this study (CF, PLI, Igeo and RI) to assess the pollution status of three pools of water along a stream that passes near (<100m) an active gold mining tailings dam. Heavy metal concentrations in sediments were compared to SQGs. The up-and downstream approach was used to establish the contribution of the tailings dam drainage to the concentration of heavy metals in water and sediment. We hypothesised that heavy metal concentrations in pools of water were above threshold limits for various uses. Continuous monitoring of heavy metals in water, soil and vegetation near mining tailings dams becomes important since some heavy metals are toxic, persistent and bioaccumulate, thus posing environmental and public health risks.

2. Materials and Methods

2.1. Description of the study area

The study was done in Shamva district (17˚19S 31˚3E) of Zimbabwe within the greenstone belt of the Shamvaian sediments whose ore bodies mineralisation according to Shoko and Tobani (2001) consists predominantly of pyrite (>90%) with minor sphalerite, galena, chalcopyrite, pyrrhotite and arsenopyrite. The annual rainfall range is 750-1000mm and the mean annual temperature varies from 19-30ºC. Mushambanyama Stream feeds into Magobo dam. Under normal rainfall events the stream is perennial. The poorly vegetated and unlined active tailings dam drains into the stream.

2.2. Sampling and sample analysis

Two pools of water; L2 and L3 were considered 600 and 1200m downstream respectively and L1, 100m upstream (Fig. 1). At each sampling site (pool) four grab water samples were randomly collected from just below the surface (10cm) in acid-cleaned polyethylene bottles (100ml). Water samples were filtered through 0.45μm pore diameter membrane filters (Chapman and Kimstach 1996) and separated into two subsamples; acidified with 2ml dil. HNO_3 (1:1; H_2O) for dissolved heavy metal analysis and unacidified for organic matter (OM) determination, and preserved on ice (Yi et al. 2011). Thirty-six water samples were collected from the three sites in September, October and November, 2015. Water pH and EC were determined on site using a calibrated multi-parameter tester 35 (Eutech Instruments, USA). Water samples were preconcentrated before analysis following procedures described by Divrikli et al. (2007). An acidified water sample (300ml) was put in a beaker and the pH was adjusted to 9 using 0.1MNaOH. The sample was passed through a cellulose nitrate membrane filter

(0.45µm pore size and 47mm diameter) under suction. The membrane filter and collected analytes were dissolved in conc. HNO_3 (0.5ml) at 80°C. The final solution was diluted to 10ml with deionised water and analysed for selected heavy metals using Flame Atomic Absorption Spectrometry (FAAS).

The sampling and pre-treatment of sediment samples were done following procedures described by Singh et al. (2010). Three grab sediment cores (0-10cm) were sampled from each pool where water was sampled using a polypropylene corer (1m long with extensions, 10cm internal diameter) into polyethylene bags. Samples were air dried and screened (63µm nylon sieve). The pH of sediment solution was determined by agitation and equilibration (10g sediment) with double distilled water (50ml) by stirring at regular intervals (1h) then measured with a tribuffer-calibrated (pH4, 7 and 10) pH meter (AD 1020 pH/mV/ISE and temperature meter). The OM content was determined by wet oxidation-redox titration using acidified dichromate solution. Dry sieved sediments (305g) were added to a 500ml conical flask. Concentrated H_2SO_4 (20ml) and $1N K_2Cr_2O_7$ (10ml) were added and the mixture was allowed to react for 30min. After diluting to 200ml, the sample was titrated with 0.4N ferrous $(NH_4)_2SO_4$ using a ferrion indicator to determine OM content. Total heavy metals were extracted from a split dry sample (1g) of sediment in open acid-mixture (conc. HCl: HNO_3:$HCLO_4$; 3:1:1, 20ml v/v) digestion over a hot plate. Cooled digests were filtered into a 50ml volumetric flask using deionised water for washings and made to the mark. No rainfall events occurred during the study.

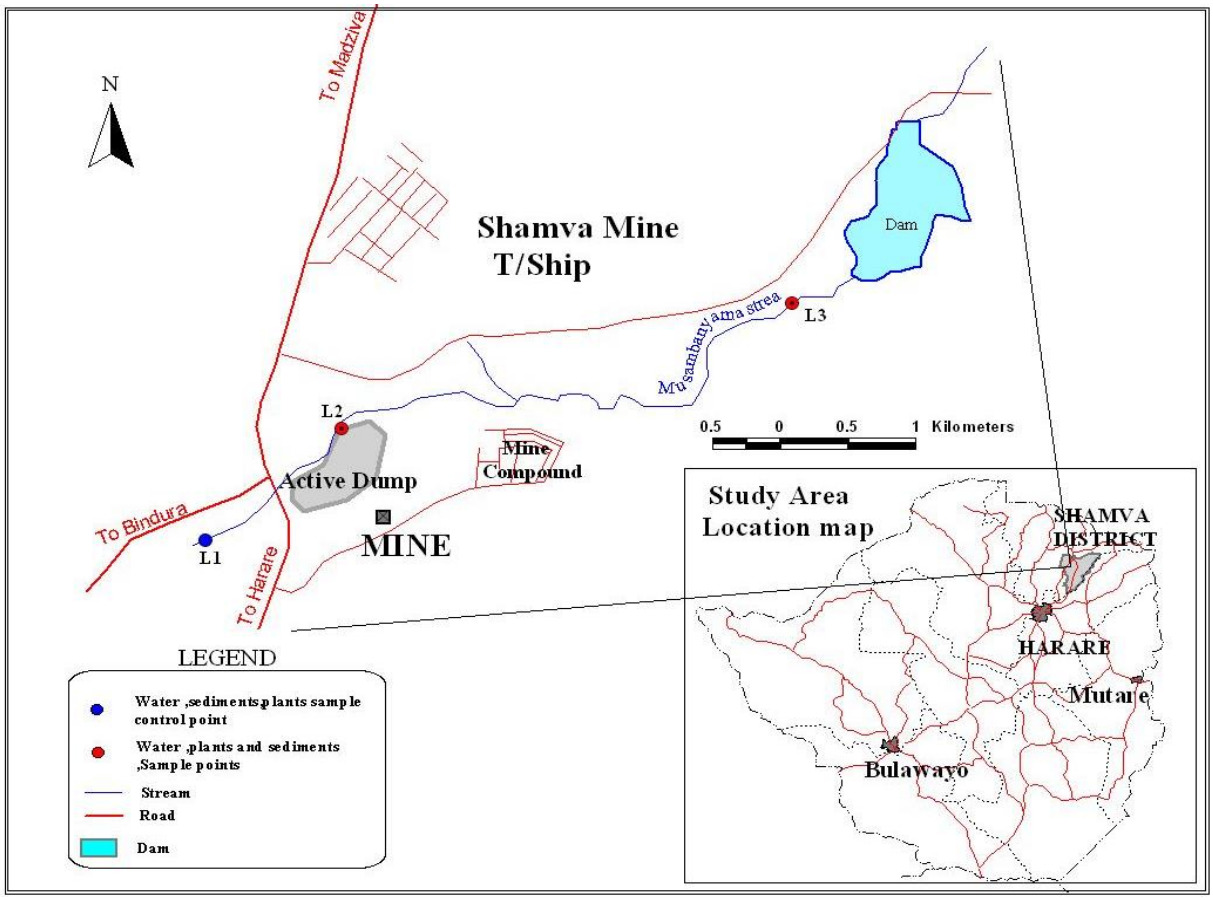

Fig. 1 The study area showing the location of pools of water along the stream under study.

2.3. Data analysis

Pollution indices and the potential ecological risk were determined using equations 1-4 and interpretation guidelines (Tab. 1).

$$Cf = \frac{c_s^i}{c_n^i} \qquad Eq.\ 1$$

C^i_s and C^i_n represent the content of heavy metal (i) in the test sample (s) and the background sample (n) respectively. Background values that were used were the geochemical average shale: 6.6, 90, 45, 46700, 850 and 20 for As, Cr, Cu, Fe, Mn and Pb respectively (Turekain and Wedpohl 1961).

$$PLI = (Cf1 * Cf2 * Cf3 * Cfn)^{1/n} \quad Eq.\ 2$$

Cf is the contamination factor for heavy metal 1, 2, 3 measured in sediment; *n* is the number of heavy metals whose concentration was measured.

$$I - geo = log_2(Cm|1.5 * Bm) \quad Eq.\ 3$$

C_m is measured concentration of trace element 'm' in sediment and *Bm* represents the geochemical background value trace element 'm' in average shale.

$$RI = \sum E^i_r = \sum T^i_r * C^i_f = \sum T^i_r * \frac{C^i_s}{C^i_n} \quad Eq.\ 4$$

C^i_s and C^i_n represent the content of heavy metal (i) in the test sample (s) and the background sample (n) respectively. T^i_r represents the toxic response factor for heavy metal (i) with values 10, 2, 5 and 5 mg/kg for As, Cr, Cu and Pb respectively (Forstner 1989). E^i_r represents the potential ecological risk index of each heavy metal and *RI* is the sum of the potential risk of all individual heavy metals studied.

2.4. Quality control procedures

Polythene water sampling bottles were pre-treated by soaking in dil. HNO_3 overnight and repeatedly rinsed with double deionised water. Samples were replicated three times. Samples for trace element analysis were preserved by acidifying with conc. HNO_3 to pH<2. Sample blanks were used in between analyses (every batch of ten) and sample standards were analysed again after the analysis of a ten sample batch. Certified reference material CRM) (channel sediment BCR 320R: 0083, European Commission Community Bureau of Reference) was used to check the precision of the analytical procedure. Three replicates of the CRM were digested and analysed for total heavy metals using the same procedures. Water pH and EC were determined *in situ*.

2.5. Statistical analyses

Normalised data were subjected to ANOVA to compare means of variables from different sampling sites. The Tukey B *post-hoc* procedure was used to separate measured means at $p<0.05$ using the Paleontological Statistical Software Package (Hammer et al. 2001). Estimated water quality parameters were compared to international guidelines for various water uses using a one sample *t*-test: (i) drinking water quality guidelines (WHO 2011a), (ii) Water quality requirements for agriculture (FAO 1985) and (iii) fresh water quality requirements for aquatic life of biota (CCME 2008). Measured sediment quality data were compared with SQGs (CCME 2001) using a one sample *t*-test. A Pearson correlation test was used to determine the strength of association between measured parameters of water, sediment and between water and sediment.

3. Results

There were no background levels of heavy metals in sediments for this study therefore the geochemical composition of shale was used. Reagent blanks showed no contamination during the analytical procedure and standard solutions had negligible deviations. Heavy metal recoveries of the

certified reference material were 93.34±0.02 (Pb) and 103.76±0.03% (Cu). Both water and sediment quality data showed no significant temporal variation over three months ($p>0.05$).

3.1. Heavy metal concentration in water and potential water uses

Table 2 shows the variation of physicochemical parameters of water samples taken from three pools of water along Mushambanyama Stream. Results show that As, Cr, Cu and Pb were not detected upstream (L1) and further downstream (L3). The concentrations of Fe and Mn at L1 and L3 showed the trend L1=L3<L2 while EC and pH recorded at the three pools showed: L1<L2>L3 and L2<L1<L3 respectively. The values of measured parameters from the three pools of water L1, L2 and L3 were within the water quality requirements for the four different uses which are potable, irrigation, fresh water life and watering livestock. However, EC at L2 did not meet the water quality requirement for irrigation. At L2, Cr and Fe did not meet the water quality requirement for fresh water life.

3.2. Characteristics of sediment and sediment quality guidelines

Table 3 shows the variation of physicochemical parameters of sediment samples taken from three pools of water along Mushambanyama Stream. Results show that the concentrations of As, Cr and Pb were below the detectable limit (ND) in sediments from L1. Arsenic was also below the limit of detection at L3. The concentrations of heavy metals in sediments from the three pools of water were below ($p<0.05$) the lower threshold values for sediment quality (TEL). Sediments from L2 contained the highest content of OM and the highest EC ($p<0.05$). They also showed the lowest pH which was acidic. The variation of sediment parameters across sampling points showed a trend: L1<L3<L2, except for As and Cu.

3.3. Sediment quality using indices

Table 4 shows the computed values for evaluating sediment quality and the potential ecological risk of three pools of water due to heavy metals up-and-downstream of Mushambanyama Stream relative to a nearby active gold tailings dam. Results reveal that the CFs for As, Cr, Cu, Fe, Mn and Pb were all below unity. The PLI was also below unity. Computed I-geo values put all sediments in class 0. The E_i^r and RI values (Tab. 4) put sediments from all the three sites in the <40 and <150 index ranges (Tab. 1) respectively.

Table 6 shows the strength of associations between water-water, water-sediment and sediment-sediment parameters using Pearson correlation coefficients considered significant at $p<0.05$, $p<0.01$ and $p<0.001$. All water and sediment quality parameters showed significant ($p<0.001$) and positive correlation with EC_w except with Cr_w ($p<0.05$), pH and pH_w (negative), As, and Cu_w (not significant, $p>0.05$). On the contrary, pH_w had significant ($p<0.001$) but negative correlation with the same parameters except with pH (positive) and with As, Pb_w, AS_w and Cr_w (Not significant, $p>0.05$). The following pairs of parameters for water and sediment showed significant ($p<0.001$) positive associations: pH/pH_w, EC/EC_w, Cu/Cu_w, Fe/Fe_w and Mn/Mn_w. However, As/As_w, Cr/Cr_w and Pb/Pb_w pairs showed weak negative correlations which were not significant ($p>0.05$). These heavy metals were not detected in water at the reference point upstream (L1) and further downstream (L3). Organic matter and pH which potentially influence the complexation or mineralisation of heavy metals in sediments were negatively and significantly ($p<0.001$) correlated.

Tab. 1 Calculation and interpretation of pollution indices and the potential ecological risk index of heavy metal-bound sediments from three pools of water in Mushayanyama Stream.

C_i^f (Liu et al. 2005)		I-geo (Muller 1969)			E_i^r (Hakanson 1980)		RI (Hakanson 1980)	
Index range	Level	Index range	class	Level	Index range	risk	Index range	risk
$C_i^f < 1$	Nil	I-geo ≤ 0	0	Unpolluted	$E_i^r < 40$	low	RI < 150	low
$1 \leq C_i^f < 2$	suspected	0 < I-geo ≤ 1	1	Slight	$40 \leq E_i^r < 80$	moderate	150 ≤ RI < 300	moderate
$2 \leq C_i^f < 3.5$	slight	1 < I-geo ≤ 2	2	Moderate	$80 \leq E_i^r < 160$	considerable	300 ≤ RI < 600	high
$3.5 \leq C_i^f < 8$	very high	2 < I-geo ≤ 3	3	moderately severe	$160 \leq E_i^r < 320$	high	RI ≥ 600	very high
$8 \leq C_i^f < 27$	severe	3 < I-geo ≤ 4	4	Severe	< 320	dangerous		
$C_i^f \geq 27$	extreme	4 < I-geo ≤ 5	5	severely extreme				
		5 < I-geo ≤ 6	6	Extreme				

Tab. 4 Mean values (n=9) of indices used to assess sediment quality of pools of water along Mushambanyama Stream from September-November, 2015.

	Sampling site L1					Sampling site L2					Sampling site L3				
Index	Cr	Cu	Fe	Mn	Pb	As	Cr	Cu	Fe	Mn	Pb	Cr	Cu	Fe	Mn	Pb
CF	-	1E-03	2E-05	4E-04	-	2.E-03	3E-04	3E-03	8E-05	2.E-03	1.8E-03	2E-04	1.5E-03	3E-05	7E-04	7E-04
PLI	←		L1<1		→	←			L2<1		→	←		L3<1		→
Igeo	-	-10.6	-16.0	-11.8	-	-9.5	-12.4	-9.0	-14.2	-9.5	-9.7	-13.2	-10.0	-15.5	-11.2	-11.2
E_r^i	0.004	0.36	-	-	0.005	0.12	0.004	1.89	-	-	1.12	0.02	0.24	-	-	0.34
RI	←		0.364		→	←			3.134		→	←		0.60		→

Tab. 2 Physicochemical parameters of water sampled from three pools along Mushayanyama Stream from September-November, 2015. Values are reported as means of replicate (n=9) measurements (mean±SE). Units are mg/l for heavy metals unless specified.

Parameter	Statistic	Sampling site			Water use guidelines			
		L1	L2	L3	Drinking [1]	Irrigation [2]	Freshwater Life [3]	Watering livestock [4]
EC (µS/cm)	min - max	55 - 83	508 - 597	158 - 267				
	mean±SE	66.67±3.08	547.67±10.69	210.89±14.15	-	< 500	-	- (150-500)
	sig. difference	**a**	**b**	**c**		< 750		
pH(H_2O) ( )	min - max	7.13 - 7.15	6.25 - 6.28	7.26 - 87.31				
	mean±SE	7.14±0.002	6.23±0.004	7.29±0.006	6.5 – 8.4	6.5 – 8.4	6.5 – 9.0	6.0-8.5 **[5]**
	sig. difference	**a**	**b**	**c**				
As (µg/l)	min - max		1.10 - 2.80					
	mean±SE	ND	2.0±0.10	ND	10	100	50	25 (200)
Cr (µg/l)	min - max		2.9 - 3.8					
	mean±SE	ND	3.3±0.1	ND	50	100	2	50 (1000)
Cu	min - max		0.021 - 0.028	0.011 - 0.015				
	mean±SE	ND	0.025±0.0008	0.013±0.0005	2	0.2	2, 3 and 4**	0.5-5 (0.5)
	sig. difference		**a**	**b**				
Fe	min - max	0.15 - 0.23	0.93 - 1.11	0.17 - 0.28				
	mean±SE	0.19±0.008	1.02±0.02	0.22±0.01	-	5	0.3	0-10 **[6]** (-)
	sig. difference	**a**	**b**	**a**				
Mn	min - max	0.01 - 0.02	0.20 - 0.26	0.02 - 0.04				
	mean±SE	0.01±0.001	0.23±0.006	0.03±0.002	0.4	0.2	-	0-10 **[6]** (-)
	sig. difference	**a**	**b**	**a**				
Pb	min - max		0.010 - 0.018					
	mean±SE	ND	0.014±0.0008	ND	0.01	5	1, 2, 4 and 7*	0.1 (0.1)

1. WHO (2011a) Drinking water quality guidelines; **2**. FAO (1985) - Water quality for agriculture; **3**. CCME (2008) Freshwater for aquatic life; **4**. CCME (2005) - Livestock water quality guidelines; **5**. Agriculture and Agri-food Canada (2015) - Water quality impacts on livestock; **6**. Holmes (1996) - South African water quality guidelines; * in µg/L for water hardness values : 0-60, 60-120, 120-180 and >180mg/L ($CaCO_3$) respectively; ** in µg/L for water hardness values: 0-120, 120-180 and >180mg/L ($CaCO_3$) respectively; Values in brackets (not square) for watering livestock are maximum/upper limits for FAO (1985). Two values for EC for irrigation: <500 – for permeability problems of soil and, <750: for salinity problems. Letters **a, b, c** across a row for a parameter: if similar, there is no significant difference ($p>0.05$) and if they are different there is significant difference ($p<0.05$).

Tab. 3 Physicochemical parameters of sediment sampled from three pools of water along Mushayanyama Stream from September-November, 2015. Values are reported as means of replicate (n=9) measurements (mean±SE). Units are mg/kg for heavy metals unless specified.

Parameter	Statistic	L1	L2	L3	Sediment Quality Guidelines*	
					TEL	PEL
	min - max		0.011 – 0.017			
As	mean±SE	ND	0.014±0.009	ND	5.9	17.0
	min - max		0.020 - 0.029	0.013 - 0.017		
Cr	mean±SE	ND	0.025±0.0001	0.015±0.0004	37.3	90.0
	sig. difference		**a**	**b**		
	min - max	0.03 - 0.05	0.12 - 0.15	0.05 - 0.08		
Cu	mean±SE	0.04±0.002	0.14±0.004	0.07±0.003	35.7	197.0
	sig. difference	**a**	**b**	**a**		
	min - max		0.032 - 0.041	0.010 - 0.020		
Pb	mean±SE sig.	ND	0.04±0.001	0.013±0.002	35.0	91.3
	difference		**a**	**b**		
	min - max	1.02 - 1.18	3.29 - 4.04	1.47 - 1.61		
Fe	mean±SE	1.10±0.02	3.69±0.08	1.54±0.02	-	-
	sig. difference	**a**	**b**	**c**		
	min - max	0.31- 0.39	1.62 - 1.85	0.51 - 0.65		
Mn	mean±SE	0.35±0.009	1.75±0.002	0.57±0.02	-	-
	sig. difference	**a**	**b**	**c**		
	min - max	0.12 - 0.17	1.27 – 1.68	0.61 – 0.80		
OM (%)	mean±SE	0.14±0.006	1.47±0.05	0.69±0.02	-	-
	sig. difference	**a**	**b**	**c**		
	min - max	7.12 - 8.12	5.10 - 6.22	6.98 - 8.00		
pH(H_2O) ( )	mean±SE	7.12±0.12	6.23±0.13	7.27±0.12	-	-
	sig. difference	**a**	**b**	**c**		
	min - max	154 - 182	1 853 – 1 960	412 - 494		
EC (µS/cm)	mean±SE	166.00 ±3.41	1 909.11±12.06	445.44 ±9.70	-	-
	sig. difference	**a**	**b**	**c**		

***** CCME (2001)

Tab. 5 Results of other similar studies on heavy metal concentrations in water and sediments of streams and rivers.

Sampling site		Heavy metal concentration (µg/L for water, and mg/kg for sediment unless specified)						Other physico-chemical parameters			Reference
		As	Cr	Cu	Pb	Fe	Mn	pH	OM (%)	EC (µS/cm)	
Mukuvisi Stream,	W	-	-	210 - 250	10	-	-	6.8 - 7.0	-	-	Nyamangara
Harare, Zimbabwe,	S	-	-	45 - 85	15 - 50	-	-	5.9 - 7.1	-	-	et al. (2008)
Manyame River,	W	-	-	10 - 65	10 - 98	0 - 1 450	0 - 80	6.17 - 7.68	-	38 - 642	Kibena et al.
Harare, Zimbabwe,											(2014)
Stream	W	-	-	3.5 - 631.1	ND - 13	11.4 - 1 490	14.3 - 1 580	3.9 - 8	-	93 - 402	Kim et al.
Korea	S	-	-	75 - 900	35 - 450	1.5E04 - 1.1E05	500 - 4 200	-	-	-	(2007)
Tisza River	S	14.1 - 19.0	116. 0 -	61.6 - 88.9	42 - 56	40 496.3 -	464.7 -				Štrbac et al
Serbia			136.8			48 469.6	1 626.3				(2014)
Yangtze River,	W	0.97	1.3	2.8	0.02	-	-	-	-	-	Yi et al.
China	S	24.7	76.4	45.7	37	-	-	-	-	-	(2011)
Mlambomlwane River		-	-	0.77	1310 -	4 250 - 4 350	1 530 – 1 810	1.18 - 1.37	-	15.3 - 21.5	Nevulaudzi et
Mpumalanga, SA	W				1450						al. (2014)
Nyaba River, Enugu,	W	1.7 - 104	0.6 - 19.4	9 - 36	5.7 - 19	0.2 - 16.6	27 - 2 800	3.18 - 6.69	-	7 - 344	Nganje et al.
South-Eastern Nigeria											(2010)
Gomti River,	W	-	1 - 5.7	ND	19 - 39	34 - 117	13 - 53	8.1 - 8.6	-	437 - 539	Singh et al.
India	S	-	2.2 - 19.1	0 - 350	6.3 - 75.3	606 – 3 022	82.6 - 263.1	7.6 - 8.3	0.3 - 2.5*	-	(2005)
Mushambanyama	W	1.1 - 2.8	2.9 - 8.8	50 - 2 810	10 - 18	580 – 4 650	290 - 1 400	6.62 - 8.59	-	55 - 597	
Stream, Zimbabwe	S	ND - 0.017	ND - 0.029	0.03 - 0.15	ND - 0.041	1.02 - 4.04	0.31 - 1.85	5.10-8.12	0.61 - 1.68	154 - 1960	*This Study*

W = water, S= sediment, * Total Organic Carbon (TOC)

Tab. 6 Pearson correlation coefficients for water and sediment quality characteristics.

	EC_w	pH_w	Cr_w	Mn_w	Fe_w	As_w	Pb_w	Cu_w	Fe	Mn	Cu	Pb	Cr	As	EC	OM	pH
EC_w	1.000																
pH_w	-0.900 ***	1.000															
Cr_w	0.761 *	-0.127 NS	1.000														
Mn_w	0.953 ***	-0.978 ***	-0.058 NS	1.000													
Fe_w	0.957 ***	-0.980 ***	0.076 NS	0.995 ***	1.000												
As_w	0.226 NS	-0.378 NS	0.113 NS	0.071 NS	0.307 NS	1.000											
Pb_w	0.200 NS	0.064 NS	0.086	-0.220 NS	-0.250 NS	0.728 *	1.000										
Cu_w	0.931 ***	-0.952 ***	0.243 NS	0.940 ***	0.925 ***	-0.687 *	-0.140 NS	1.000									
Fe	0.978 ***	-0.950 ***	0.676 *	0.978 ***	0.980 ***	0.160 NS	0.407 NS	0.951 ***	1.000								
Mn	0.976 ***	-0.958 ***	-0.220 NS	0.983 ***	0.987 ***	0.066 NS	-0.078 NS	0.941 ***	0.990 ***	1.000							
Cu	0.977 ***	-0.909 ***	0.043 NS	0.960 ***	0.962 ***	0.743 *	0.209 NS	0.882 ***	0.963 ***	0.970 ***	1.000						
Pb	0.941 ***	-0.947 ***	0.014 NS	0.948 ***	0.939 ***	-0.346 NS	-0.194 NS	0.935 ***	0.926 ***	0.938 ***	0.915 ***	1.000					
Cr	0.850 ***	-0.885 ***	-0.654 NS	0.873 ***	0.890 ***	0.093 NS	-0.180 NS	0.770 **	0.857 ***	0.913 ***	0.872 ***	0.818 ***	1.000				
As	0.393 NS	-0.555 NS	0.136 NS	0.038 NS	0.532 NS	-0.251 NS	-0.436 NS	-0.291 NS	0.084 NS	0.299 NS	0.143 NS	0.030 NS	0.125 NS	1.000			
EC	0.976 ***	-0.959 ***	-0.740 *	0.987 ***	0.987 ***	0.071 NS	0.097 NS	0.949 ***	0.992 ***	0.997 ***	0.970 ***	0.946 ***	0.896 ***	-0.206 NS	1.000		
OM	0.978 ***	-0.837 ***	0.738 *	0.910 ***	0.908 ***	0.138 NS	0.176 NS	0.945 ***	0.956 ***	0.942 ***	0.951 ***	0.943 ***	0.813 ***	-0.156 NS	0.949 ***	1.000	
pH	-0.900 ***	0.999 ***	-0.535 NS	-0.978 ***	-0.980 ***	-0.242 NS	0.173 NS	-0.953 ***	-0.951 ***	-0.960 ***	-0.909 ***	-0.949 ***	-0.886 ***	-0.263 NS	-0.959 ***	-0.839 ***	1.000

4. Discussion

4.1. Heavy metal concentration in water and potential water uses

Salinisation, acidification and metal loading observed at L2 (Tab. 2) could have come from the active mining tailings dam drainage. Chapman and Kimstach (1996) reported that these changes in river water could arise from the release of acidic mining wastewater. The export of heavy metals from mining tailings dams into the aquatic environment has been reported elsewhere (Kovacs et al. 2012; Modoi et al. 2014). The presence of heavy metals at L2 but not at L1 may suggest that an external source introduced them. The source of heavy metals could be the tailings dam since there were no inflows from surface runoff and there were turbulent flows within pools of water. Turbulent flows can introduce heavy metals into the water column (Eggleton and Thomas 2004). The absence of heavy metals in detectable quantities downstream (L3) after they were recorded at L2 may suggest self-purification through dilution by the stream. In natural waters As, Cr and Pb are found in very small quantities of <1-2, <2 and <5µg/L respectively (WHO 2008). The concentration of As, Cr, Cu, Pb and the pH for the three pools of water (L1, L2 and L3) along Mushambanyama Stream dictate water use options. The EC of water which put a restriction on water from L2 for irrigation plays an important role in the salinity of soil (FAO 1985). In natural waters at pH 6-9 Fe and Mn rarely occur at concentrations above 1mg/l (Ongley 1996).

4.2. Characteristics of sediment and sediment quality guidelines

The higher concentrations of heavy metals in sediment at L2 than at L1 and L3 ($p<0.05$) suggest enrichment due to an external source. Metals showed strong significant correlation with pH and organic matter content. Sediment pH influences the mobilisation of heavy metals in sediments (Calmano and Forstner 1993).

Low pH releases more metal ions into solution. Organic matter form complexes with heavy metals limiting their bioavailability for plant and animal uptake (Hong et al. 2012). In their study, Idriss and Ahmad (2012) observed that the organic fraction had the second highest content of metal after the residual fraction. They explained the correlations between (1) organic matter and metals and (2) pH and metals, with respect to metal solubility, ultimately their availability. Huong et al. (2012) also observed correlations between organic matter and heavy metal concentrations in sediments. The water /sediment correlation for heavy metals Cu, Fe and Mn were strong and significant. This could be due to the metal equilibrium which exists between the water column and the sediment (Eggleton and Thomas 2004).

According to CCME (2001) measured concentrations of sediment quality are compared to sediment quality Guideline values (SQGVs) and interpreted as concentrations: ≤ SQGV: rare pollution, no ecological effects between SQGV and the probable effect level (PEL): moderate pollution with occasional negative ecological risks; >PEL: serious pollution with pronounced negative ecological effects. The concentrations of As, Cr, Cu and Pb in sediments from Mushambanyama Stream were below their respective interim sediment quality guidelines (ISQGs) $p<0.05$). The four studied heavy metals therefore represent concentrations where adverse biological effects could rarely occur.

4.3. Sediment quality using indices

The contamination factors for As, Cr, Cu, Fe, Mn and Pb were all below unity suggesting no contamination of sediments from the pools of water. The PLI was also below unity implying no pollution of the pools of water (Tomlison et al. 1980). Computed I-geo values put all sediments in class 0 suggesting no contamination (Tab. 1). Pollution indices were in agreement with the sediment quality

data in predicting no contamination for the pools of water with As, Cr, Cu, Fe, Mn and Pb. These data were also in agreement with ecological pollution risk indices which showed low ecological risk for the three pools of water along Mushambanyama Stream. Similarities and differences in the parameters studied for Mushambanyama Stream with other studies (Tab. 5) may be due to both in-stream and watershed processes, hydrogeology, climate and anthropogenic activities.

5. Conclusions

This study showed that the degree of impairment of water quality with heavy metals dictates the potential uses of water. The concentrations of Cr, Cu, Fe and Pb restricted water use at a pool directly receiving mining tailings discharge for aquatic life. Using the upstream-downstream approach we showed that natural sources of pollutants (at L1) and tailings dam discharges (at L2) enriched sediments from pools of water with heavy metals although to levels lower than the sediment quality guidelines. Pollution indices, SQGs and potential ecological risk indices showed that the three pools of water along Mushambanyama Stream were not polluted and posed no potential ecological risk. The continuous monitoring of the quality of river water and sediments is critical for both ecosystem and human health as it reveals the potential health risks associated with anthropogenic pollution which can be identified and remediated.

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