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GAUTENG PROVINCIAL GOVERNMENT, SOUTH AFRICA

**PROJECT TITLE**

**ESTABLISHMENT OF A MONITORING SYSTEM FOR  
SURFACE WATER AND GROUNDWATER  
IN THE CRADLE OF HUMANKIND  
WORLD HERITAGE SITE**

**REPORT TITLE**

**SEDIMENT CHEMISTRY ASSESSMENT**

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**BIQ005/2008**



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# **EXECUTIVE SUMMARY**

## **INTRODUCTION**

The Management Authority (MA) of the Cradle of Humankind World Heritage Site (COH WHS) commissioned project BIQ005/2008 to develop a water resources monitoring programme for the COH WHS. In order to successfully achieve this objective, the study included an assessment of sediment chemistry. This was precipitated by the comparatively sparse data of this nature for the drainages that receive and carry raw and/or treated mine water and treated municipal wastewater effluent. The ‘once-off’ sampling campaign took the form of an occurrence survey.

Sediment samples were collected at eight localities in the southern portion of the study area to determine the chemical composition of streambed material at various positions along the Tweelopie, Riet, Blougat and Bloubank spruits. The sampling localities targeted the inflow ends of dams where possible, or else the streambed where flow conditions are conducive to sediment deposition. They included a pristine karst spring for background/reference analysis. The depth of sampling ranged from 200 to 500 mm, mostly beneath a water column of  $\leq 1$  m. Typically, two samples were collected at each locality. The aggregation of certain samples sought to obtain a more representative single ‘site’ sample, and also reduce analytical costs at this screening level of investigation. The sampling protocol emulated that used by the CGS elsewhere on the Witwatersrand when sampling mining-related wetlands. The analyses were carried out on unsieved samples following standard procedures employed by the CGS. The samples were analysed as follows:

- X-ray fluorescence to determine major and trace elements, i.e. total chemical composition,
- batch leach, toxicity characteristic leaching procedure (TCLP) and acid rain leaching tests to determine the mobility and bio-availability of metals represented by their extractable fractions, and
- X-ray diffraction on one sample to determine the mineralogic composition.

## **RESULTS**

Since South Africa does not yet have freshwater sediment guidelines or legislated limits for most contaminants in soil, values from the European Union and the National Nuclear Regulator were used in a Tier 1 risk assessment for U and Ni. These variables are used as characteristic trace metals associated with mining. The ranking employed describes the following circumstances:

- risk quotients below 0.5 pose no risk,
- values between 0.5 and 2 allow for any sampling and/or laboratory errors, and
- risk quotients that are above 2 definitely pose a risk.

The risk quotients are based on the total concentration as measured by XRF analysis. It is not implicit that all of this concentration is extractable and/or mobilizable, as is shown by the leach tests. Nevertheless, the results indicate that both U and Ni display risk quotients of  $>2$  at the first two sampling localities, namely the Hippo and Lion Camp dams in the Krugersdorp Game Reserve. Further, that Ni also poses a risk at the next two sampling localities downstream also receiving only mine water, as well as below the confluence of the Riet and Blougat spruits.

The leach test results show that the TCLP method consistently mobilized the greatest fraction, followed by the acid rain and the batch leach methods. A highest Ni concentration of ~12% (71 mg/kg) of total concentration was extracted, followed by ~9% (28 mg/kg) and ~7% (13.7 mg/kg). The extractable fraction of ~71 mg/kg (by the TCLP method) is twice the regulatory limit of 35 mg/kg proposed by the EU. These results also put those of the Tier 1 risk assessment into perspective, especially in regard to Ni, since it is probable that a Tier 1 risk assessment based on extractable concentrations (as opposed to total concentrations) will return a greater number of Ni risk quotients in the range 0.5 to 2, rather than >2.

None of the leach tests extracted a U concentration higher than the regulatory limit of 16 mg/kg as proposed by the NNR. A highest U concentration of ~5% (5.4 mg/kg) was extracted, followed by ~2.5% (1 mg/kg) and 2% (0.02 mg/kg). The reference/background sample yielded no extractable U or Ni for any of the three leach tests employed. This site did, however, yield extractable fractions of Al, Fe, Mn and Cu for at least two of the three leach tests. It is therefore likely that sediments associated with 'pristine' karst groundwater sources in the study area may produce extractable metal concentrations despite the natural (pristine) chemical composition of the water produced.

## **CONCLUSION**

The finding that the measure of extractable U and Ni concentrations is an order of magnitude lower (smaller) than the total observed concentrations provides a measure of mitigation of the risk associated with the mobilization/remobilization of sediment-bound trace/heavy metals. However, the cumulative mass/volume of sediment contained in the various impoundments cautions against minimization or downplaying of the associated risk.

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## DEFINITION OF SYMBOLS, ACRONYMS AND ABBREVIATIONS

~	approximately
>	greater than
≤	less than or equal to
%	per cent (parts per hundred)
%ile	percentile
°E	degree(s) East (longitude)
°S	degree(s) South (latitude)
Al	aluminium
As	arsenic
Ba	barium
Ca	calcium
Cd	cadmium
Ce	cerium
CGS	Council for Geoscience
Cl	chloride
Co	cobalt
Cr	chromium
Cu	copper
DWA	Department of Water Affairs
EC	electrical conductivity
EPA	Environmental Protection Agency
EU	European Union
Fe	iron
Ga	gallium
HCO <sub>3</sub>	bicarbonate
K	potassium
La	lanthanum
m	metre(s)
Mg	magnesium
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per litre
mm	millimetre(s)
Mn	manganese
mS/m	milliSiemens per metre
N	nitrogen
Na	sodium
Nb	niobium
Nd	neodymium
Ni	nickel
NNR	National Nuclear Regulator
NO <sub>2</sub>	nitrite nitrogen
NO <sub>3</sub>	nitrate nitrogen
n.s.	not specified
Pb	lead

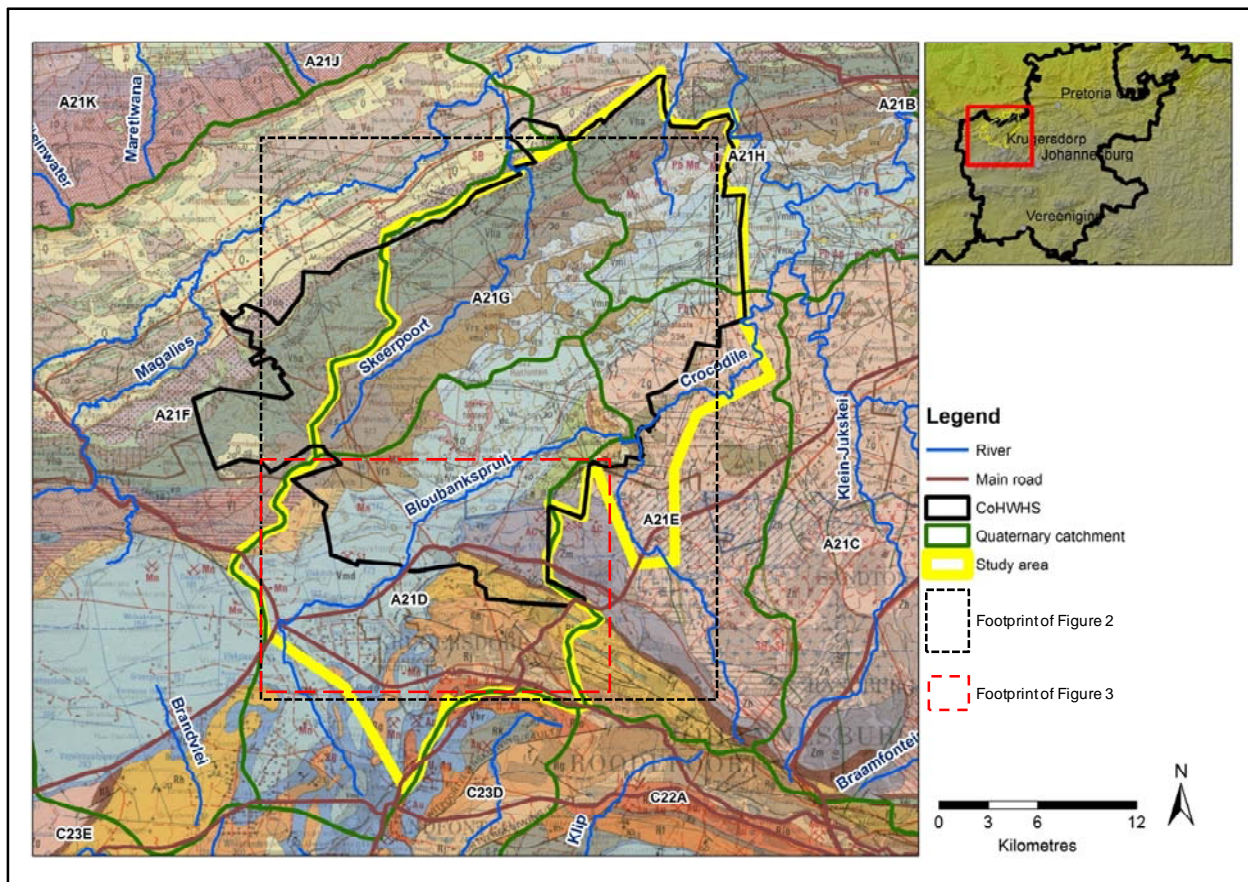
PO <sub>4</sub>	phosphate
Rb	rubidium
SANS	South African National Standard
Sc	scandium
Si	silicon
SO <sub>4</sub>	sulphate
Sr	strontium
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved salts
Th	thorium
U	uranium
US	United States (of America)
V	vanadium
WWTW	wastewater treatment works
XRD	X-ray diffraction
XRF	X-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium



# 1 INTRODUCTION

The Management Authority (MA) of the Cradle of Humankind World Heritage Site (COH WHS) commissioned project BIQ005/2008 to develop a water resources monitoring programme for the area (Figure 1). In order to successfully achieve this objective, the study included an assessment of sediment chemistry precipitated by the comparative sparseness of such data. The ‘once-off’ sampling and analysis campaign by the Council for Geoscience (CGS) took the form of an occurrence survey.

The chemical composition of sediments in environments impacted by mining activities on the Witwatersrand has been reported on by Coetzee et al. (2002; 2006), Robb and Robb (1998b), Rösner et al. (2001) and Wade et al. (2002), amongst others. Whilst the majority of these studies has understandably focussed on the presence of radionuclides in sediments, the presence of heavy metals such as Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn is of equal concern. For example, Von der Heyden and New (2004) identify precipitation (Fe, Al and Cu) and adsorption (Co, Ni and Zn) of metals onto suspended solid surfaces, and their subsequent settling within a wetland, as primary processes leading to metal accumulation within sediment. More significantly, these authors show the sediment to be a potentially important source of pollutants, with downstream pollution possibly continuing for a century after the cessation of effluent discharge into the wetland. This is a concern under circumstances where the drainages in the south-western portion of the COH WHS receive and carry raw and/or treated mine water as in the case of the Tweelapie Spruit, or treated municipal wastewater effluent in the case of the Blougat Spruit. The chemical composition of these waters has been extensively documented and studied also in regard to trace element concentrations.



**Figure 1. Definition of the study area in regard to the geology, surface water drainages and quaternary catchments in the COH WHS area and environs.**

## 2 PREVIOUS STUDIES

The study by Awofolu et al. (2007) provides results of trace metal analyses (Cd, Pb, Mn, Zn, Ni and Cu) of sediment samples collected at the sampling locations S1 to S4 shown in Figure 2 and Figure 3. The results are presented in Table 1 for each of the metals listed.

**Table 1. Concentrations of selected trace metals in streambed sediments downstream of the Percy Stewart WWTW (from Awofolu et al., 2007).**

Trace Metal	Concentration		Observations by PSP
	Minimum (mg/kg)	Maximum (mg/kg)	
Cd	Trace	0.12 ± 0.001	Lowest concentration of trace metal selection at all four stations on all four sampling occasions.
Pb	Trace	0.71 ± 0.03	Next lowest concentration of trace metal selection (after Cd) at all four stations on all four sampling occasions.
Mn	12.3 ± 0.14	2957 ± 18.4	Maximum value observed at station S1 on 4 <sup>th</sup> sampling occasion. S1 also returned highest values on all four sampling occasions.
Zn	0.13 ± 0.01	2.57 ± 0.03	Maximum value observed at station S2 on 4 <sup>th</sup> sampling occasion. Highest values distributed between all four stations on all four sampling occasions.
Ni	0.39 ± 0.001	1.96 ± 0.04	Maximum value observed at station S2 on 4 <sup>th</sup> sampling occasion. S2 also returned highest values on three sampling occasions.
Cu	0.18 ± 0.001	2.84 ± 0.03	Maximum value observed at station S3 on 3 <sup>rd</sup> sampling occasion. Highest values shared by S2 (1 <sup>st</sup> and 2 <sup>nd</sup> sampling occasions) and S3 (3 <sup>rd</sup> and 4 <sup>th</sup> sampling occasions).

Manganese (Mn) returned the highest concentration of all six elements at all three sampling localities on each of the four sampling occasions. Further, the sediment at sampling locality S1 on the Blougat Spruit and therefore closest to the Percy Stewart WWTW (Figure 2 and Figure 3), consistently returned the highest Mn concentration. This is in keeping with the statistical analysis of surface water chemistry in this drainage (Table 2), which reflects exceedances of the mean, median and 95%ile Mn values in a population of 44 analyses in the period June 2004 to May 2008 at the DWA station 188048 (Figure 3).

**Table 2. Water quality statistics for station 188048, Blougat Spruit.**

Variable	Statistical Parameter for the period of record 06/2004 to 05/2008							SANS 241: 2006 <sup>(1)</sup>
	n	5%ile	Mean	Median	95%ile	Std Dev	CoV (%)	
pH	42	4.1	6.4	6.7	7.8	1.1	17.1	5.0 – 9.5
EC (mS/m)	41	54.9	89.3	85.2	<b>158.0</b>	29.0	32.4	<150
TDS (mg/L)	40	380.0	550.0	498.5	940.1	177.8	32.3	<1000
Ca (mg/L)	42	34.6	56.3	53.3	77.3	16002	28.2	<150
Mg (mg/L)	42	6.6	9.1	9.4	12.3	1.8	20.1	<70
Na (mg/L)	42	51.4	86.1	88.5	119.5	22.1	25.6	<200
K (mg/L)	42	8.32	13.26	13.42	19.86	3.83	28.9	<50
Cl (mg/L)	42	44.7	65.2	65.8	79.6	13.5	20.7	<200
SO <sub>4</sub> (mg/L)	42	66.8	194.8	159.2	<b>434.1</b>	125.8	64.6	<400
HCO <sub>3</sub> (mg/L)	41	11.3	55.9	46.8	117.1	44.8	80.3	n.s.
NO <sub>3</sub> +NO <sub>2</sub> (mg N/L)	41	0.26	<b>11.92</b>	<b>10.63</b>	<b>26.72</b>	9.11	76.5	<10
PO <sub>4</sub> (mg P/L)	40	0.700	3.841	2.742	11.881	3.257	84.8	n.s.
Si (mg/L)	41	3.49	6.67	6.76	9.41	2.40	36.0	n.s.
Fe (mg/L)	44	0.006	<b>0.700</b>	0.079	<b>4.691</b>	2.03	290.6	<0.2
Mn (mg/L)	44	0.009	<b>0.937</b>	<b>0.267</b>	<b>2.045</b>	3.69	394.5	<0.1
Al (mg/L)	44	0.008	0.157	0.035	0.279	0.68	434.8	<0.3
Electrical balance (%)	41	-11.6	<b>5.5</b>	<b>5.6</b>	20.3	9.3	169	±5

(1) Recommended limit for Class 1 drinking water quality.  
 Bold text denotes values that exceed the SANS (2006) recommended limit for Class 1 drinking water.

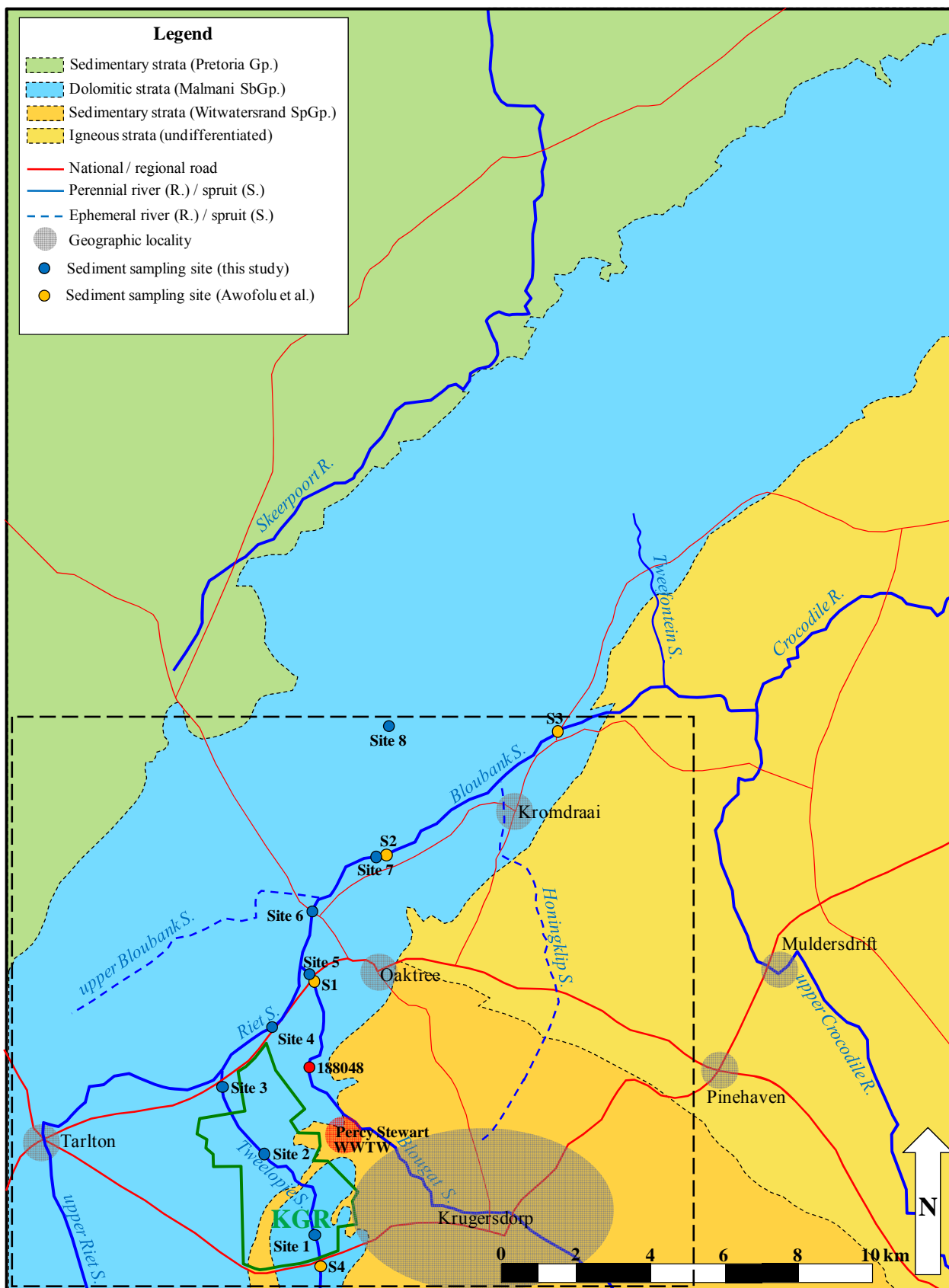


Figure 2. Geological map showing sediment sampling localities and other salient features. Footprint of Figure 3 represented by rectangular pecked line.

### 3 COH WHS STUDY

Greater detail describing the sediment sampling and analysis exercise is documented in the CGS report on this activity (Venter et al., 2010).

#### 3.1 Purpose and Rationale

Sediment samples were collected at eight localities (Figure 2, Figure 3 and Table 3) in the southern portion of the study area targeting the Tweelopie Spruit, the Riet Spruit, the Blougat Spruit and the Bloubank Spruit. The ‘once-off’ sampling campaign therefore took the form of an occurrence survey (Shelton and Capel, 1994). The sampling localities focussed on the inflow or upstream ends of surface water impoundments where possible, or else within the stream channel where flow conditions are conducive to sediment deposition. This site selection method is described by EPS (1994) as non-statistical, deterministic (or judgemental). The sites include a pristine karst spring to provide a background/reference analysis. Two of the sites (5 and 7) coincide with the localities S1 and S2 of Awofolu et al. (2007). The depth of sampling ranged from 200 to 500 mm, mostly beneath a water column of  $\leq 1$  m, and typically two samples were collected at each locality (refer Table 3 for greater definition). The aggregation of certain samples reflected in Table 3 (sites 2, 4, 5, 6, 7 and 8) sought to obtain a more representative single ‘site’ sample made up of two ‘subsite’ samples (Herr and Gray, 1997), and also reduce analytical costs at this screening level of investigation. The sampling protocol emulated that used by the CGS elsewhere on the Witwatersrand when sampling mining-related wetlands (McCarthy and Venter, 2006).

**Table 3. Description of sediment sampling localities.**

Site	Latitude Longitude	Description of and Rationale for Site Selection	Sample No.	Analysis Description
1	26.06452°S 27.69613°E	Hippo Dam inlet on the Tweelopie Spruit in the Krugersdorp Game Reserve. First impoundment downstream of the mine area receiving AMD.	JV10/001 JV10/002 JV10/003 JV10/004	BL/Alk./TCLP/AR/XRF BL/Alk./TCLP/AR/XRF BL/Alk./TCLP/AR/XRF XRD/ICPMS metals
2	26.10235°S 27.72122°E	Lion Camp entrance dam inlet on the Tweelopie Spruit in the Krugersdorp Game Reserve. Third impoundment downstream of the mine area receiving a mixture of AMD and better quality karst groundwater.	JV10/005 JV10/006	BL/Alk./TCLP/AR/XRF Combined with JV10/005
3	26.10345°S 27.72145°E	Krugersdorp Brickworks Dam inlet on the Tweelopie Spruit. Fifth impoundment downstream of the mine area receiving a better quality mixture of AMD and karst groundwater.	JV10/007	BL/Alk./TCLP/AR/XRF
4	26.08570°S 27.70988°E	Inlet of dam on Ptn. 8/2 of Sterkfontein 173IQ on the Riet Spruit. Seventh impoundment downstream of the mine area receiving a mixture of AMD and karst groundwater.	JV10/008 JV10/009	BL/Alk./TCLP/AR/XRF Combined with JV10/008
5	26.04800°S 27.71213°E	Lower end of the Blougat Spruit receiving treated municipal wastewater effluent from the Percy Stewart WWTW.	JV10/010 JV10/011	BL/Alk./TCLP/AR/XRF Combined with JV10/010
6	26.02203°S 27.72005°E	Bridge where the R563 crosses the Bloubank Spruit, receiving primarily the discharge from site #5.	JV10/012 JV10/013	BL/Alk./TCLP/AR/XRF Combined with JV10/012
7	26.04003°S 27.72110°E	Causeway over the Bloubank Spruit downstream of Makiti, receiving primarily the discharge from site #6.	JV10/014 JV10/015	BL/Alk./TCLP/AR/XRF Combined with JV10/014
8	25.97883°S 27.74323°E	Stilling basin of Danielsrust Spring. Off-channel natural spring serving as ‘pristine’ background sample.	JV10/016 JV10/017	BL/Alk./TCLP/AR/XRF Combined with JV10/016

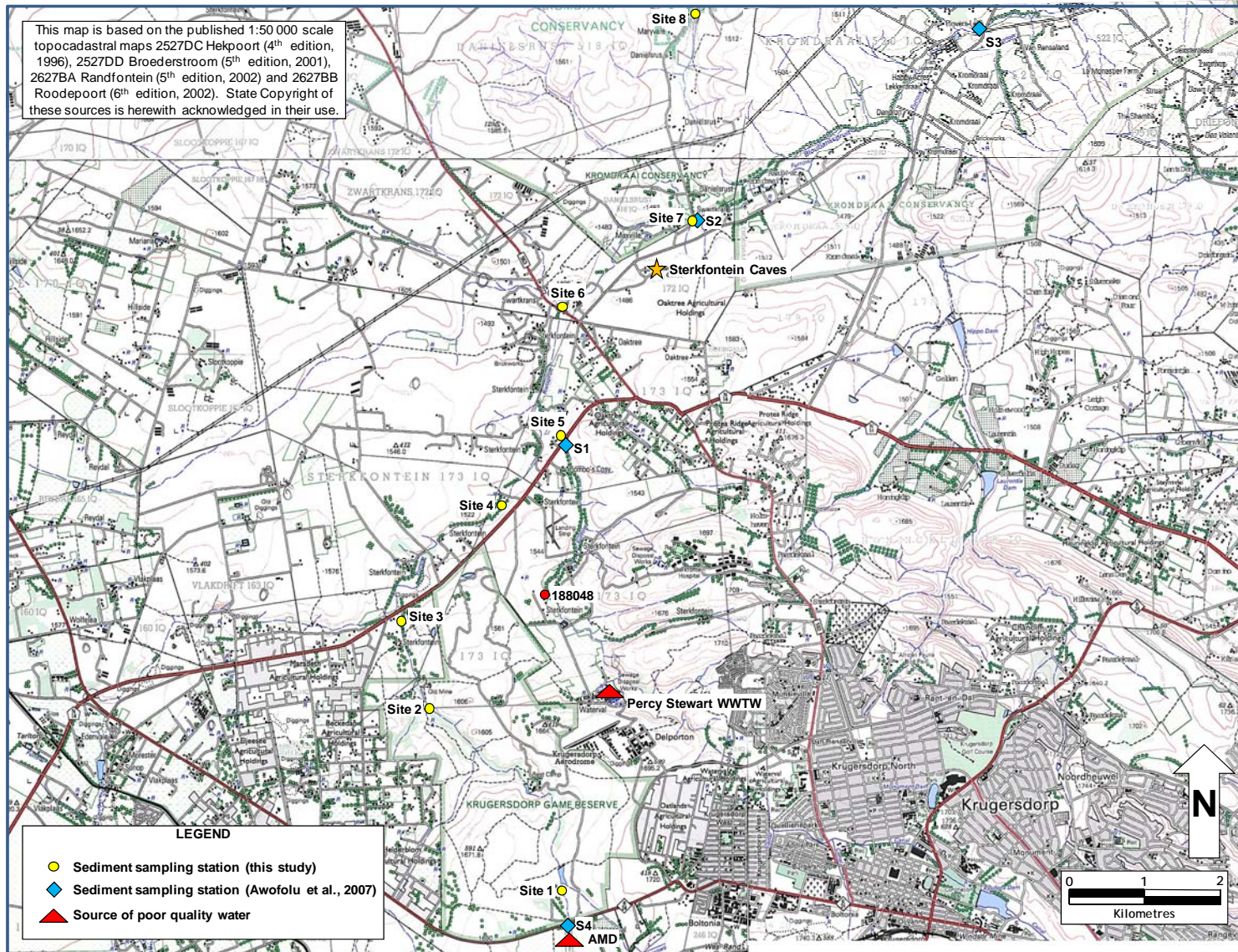


Figure 3. Large scale locality map of sediment sampling sites and other salient features.

The analyses were carried out on unsieved samples following standard procedures employed by the CGS. The samples were analysed as follows:

- X-ray fluorescence (XRF) to determine major and trace elements, i.e. total chemical composition,
- batch leach (BL), toxicity characteristic leaching procedure (TCLP) and acid rain (AR) leaching tests to simulate the likelihood of elements to be mobilised under certain environmental conditions, i.e. the mobility and bio-availability of metals as represented by their extractable fractions, and
- X-ray diffraction (XRD) on one sample to determine the mineralogic composition.

### 3.2 Results

The results of the analyses performed are presented in Venter et al. (2010). In order to assess whether downstream contamination is present, the US EPA Tier 1 risk assessment was applied to the data. This method is described by Wade et al. (2002). The trace metal concentrations determined from XRF analysis are ranked in order of decreasing maximum detected value in Table 4 for each of the samples and sites.

**Table 4. Ranking of trace metal concentrations in sediment samples according to maximum values.**

Variable	Site and Sample No. (preface the latter with JV10/ as per sample no. in Table 3)											Maximum Value (mg/kg)
	Site 1				Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	
	001	002	003	004	005	007	008	010	012	014	016	
Al <sup>(1)</sup>	48314	66014	38001	5088	56290	5897	41198	13037	50322	17144	5897	66014
Fe <sup>(2)</sup>	50579	9658	53900	19600	60900	4276	36934	18783	62916	34821	4276	62916
Mn <sup>(3)</sup>	4565	213	77	620	7850	120	4349	1057	8747	8498	120	8747
Zn	216	72	460	263	943	430	261	53	56	81	12	943
Ba	531	120	122	13	173	549	307	101	751	446	21	751
Ni	313	134	720	623	497	607	196	38	111	68	6.7	720
Cr	603	425	290	37	401	367	339	223	413	214	95	603
Co	119	17	202	227	154	149	72	11	28	25	1.7	227
Zr	227	213	143	16	197	154	164	61	177	50	21	227
Cu	105	60	135	34	174	49	57	15	46	35	4.2	174
V	126	137	100	15	116	99	84	30	97	51	9.6	137
Ce	100	126	130	29	83	100	48	<10	48	31	<10	130
U	41	35	107	13	50	6.3	9.9	<2	3.6	<2	<2	107
As	83	9.3	65	9.3	83	18	14	6.4	15	7.8	<4	83
Nd	30	61	73	20	61	46	29	10	27	10	<10	73
La	37	57	62	16	66	64	37	<10	33	18	<10	66
Pb	52	25	31	3.9	32	29	37	9.4	13	17	2.9	52
Sr	30	11	39	49	27	38	16	14	17	19	2.1	49
Rb	28	35	23	4.4	43	37	42	9.4	47	17	7.5	47
Y	18	31	36	7.4	41	26	18	4.8	18	7.6	1.9	41
Sc	16	19	17	11	17	16	14	5.1	16	7.4	<3	19
Ga	13	16	11	1.8	14	13	11	3.7	12	4.9	2	16
Nb	10	13	8.9	2.7	10	9.4	9	3.6	9.6	4	2.5	13
Th	10	8.6	8.7	<3	8.4	7	6.3	<3	7.2	3.7	<3	10

(1) Calculated from weight% concentration of Al<sub>2</sub>O<sub>3</sub>.  
(2) Calculated from weight% concentration of Fe<sub>2</sub>O<sub>3</sub>(t).  
(3) Calculated from weight% concentration of MnO.  
All values are as mg/kg.  
Shaded cells denote location of maximum element value.

It is apparent that site 1 (the Hippo Dam) supports the maximum concentration of 16 of the 24 elements represented. Site 2 (the Lion Camp dam) supports a further four of the elements, leaving site 6 (the Bloubank Spruit at the R563 crossing) to support the remaining four elements.

The elevated Fe and Mn levels at site 6, compared to those at site 1 for example, are not readily explained. It is possible, however, that these circumstances reflect the historical impact of Percy Stewart WWTW effluent, with its characteristic elevated Fe and Mn concentrations (Table 2), on the downstream receiving drainages. The discharge from this facility via the Blougat Spruit has manifested a perennial (albeit artificial) flow regime in the long-term, compared to the much more recent ephemeral character of mine water discharge via the Tweelopie Spruit into the Riet Spruit.

It is important to note that the sample bearing the highest concentration of an element will not necessarily release the greatest extractable fraction of that element. Table 1 indicates that Awofolu et al. (2007) recorded maximum Zn, Ni and Cu values at site S2. A comparison of the results with those recorded for these elements at site 7 (the same locality) of the current study reveals significant differences. In all instances, the Awofolu et al. (2007) results are an order of magnitude lower.

### 3.2.1 Tier 1 Risk Assessment

In this method, the measured concentrations are compared to a regulatory standard. Since South Africa does not yet have freshwater sediment guidelines (Gordon and Muller, 2010) or legislated limits for most contaminants in soil (Coetzee et al., 2006), values from the European Union (EU) and the National Nuclear Regulator (NNR) were used. Venter et al. (2010) report Tier 1 risks for uranium (U) and nickel (Ni) respectively. These variables are used as characteristic trace metals associated with mining. A risk quotient of greater than 1 indicates areas where the measured concentration is larger than the regulatory standard, and will require follow-up studies and possible remedial action (Coetzee et al., 2006). The colour-coding used in the ranking by Venter et al. (2010) is replicated in Table 5, and describes the following circumstances:

- risk quotients below 0.5 pose no risk,
- values between 0.5 and 2 allow for any sampling and/or laboratory errors (risk quotients in this range might pose a risk and may warrant follow-up studies), and
- risk quotients that are above 2 definitely pose a risk.

**Table 5. Tier 1 risk quotients for U and Ni associated with each sediment sampling site.**

Site No.	Site Description	Tier 1 Risk Quotient	
		Uranium	Nickel
1	Hippo dam on the Tweelopie Spruit in the KGR	>2	>2
2	Lion Camp dam on the Tweelopie Spruit in the KGR	>2	>2
3	Krugersdorp Brickworks dam on the Tweelopie Spruit	<0.5	>2
4	Dam on Ptn. 8/2 of Sterkfontein 1731Q on the Riet Spruit	0.5 to 2	>2
5	Lower end of the Blougat Spruit	<0.5	0.5 to 2
6	Bridge where the R563 crosses the Bloubank Spruit	<0.5	>2
7	Causeway over the Bloubank Spruit downstream of Makiti	<0.5	0.5 to 2
8	Danielsrust Spring (background/reference site)	<0.5	<0.5

It should be noted that the risk quotients are based on the total concentration as measured by XRF analysis. It is not implicit that all of this concentration is extractable and/or mobilizable, as is shown in section 3.2.2.

### 3.2.2 Extractable/Mobilizable Fraction

Leach tests were conducted to determine the extractable (mobile) fraction of the total concentration of elements measured by XRF. The pie charts in Figure 4 and Figure 5 show the fraction (expressed as a % of the total concentration) of Ni and U, respectively, extracted from the sediment samples of each site by each of the leach test methods used. The results show that the TCLP method consistently mobilized the greatest fraction, followed by the acid rain and the batch leach methods.

The highest Ni concentration (~12% or 71 mg/kg) was extracted from the site 3 sample, followed by the site 1 sample (~9% or 28 mg/kg) and the site 4 sample (~7% or 13.7 mg/kg). Since the highest total Ni concentration was measured at site 1 (the Hippo Dam sample JV10/003), further investigations into site-specific conditions might explain this result. Site 3 is also the only site where the extractable fraction of ~71 mg/kg (by the TCLP method) is twice the regulatory limit of 35 mg/kg proposed by the EU (ANTEA, 2000 in Coetzee et al., 2006). These results also put those of the Tier 1 risk assessment quotients (section 3.2.1) into perspective, especially in regard to Ni.

It is probable that a Tier 1 risk assessment based on extractable concentrations (as opposed to total concentrations) will return a greater number of Ni risk quotient values in the range 0.5 to 2, rather than >2.

None of the leach tests extracted a U concentration higher than the regulatory limit of 16 mg/kg as proposed by the NNR (Coetzee et al., 2006). The highest U concentration (~5% or 5.4 mg/kg) was extracted from the third of the site 1 samples, followed by the first of the site 1 samples (~2.5% or 1 mg/kg) and the site 5 sample (2% or 0.02 mg/kg).

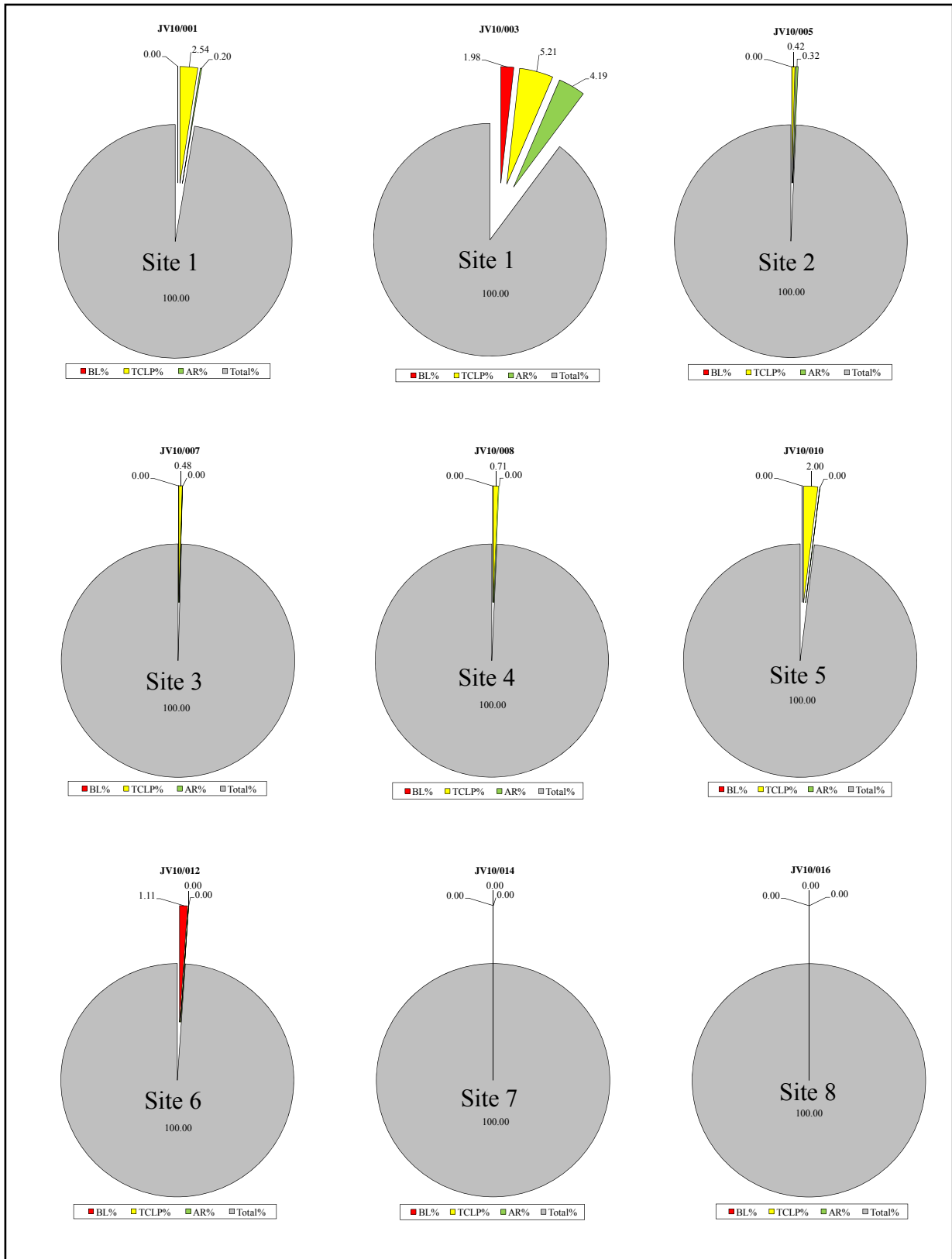
The reference/background site 8 (sample JV10/016) yielded no extractable U (unsurprising given the concentration reported in Table 4) or Ni for any of the three leach tests employed. This site did, however, yield extractable fractions of Al, Fe, Mn and Cu for at least two of the three leach tests. It is therefore likely that sediments associated with 'pristine' karst groundwater sources in the study area may produce extractable metal concentrations despite the natural (pristine) chemical composition of the water produced.

## 4 CONCLUSION

The finding that the measure of extractable U and Ni concentrations is an order of magnitude lower (smaller) than the total observed concentrations provides a measure of mitigation of the risk associated with the mobilization/remobilization of sediment-bound trace/heavy metals. However, the cumulative mass/volume of sediment contained in the various impoundments and river/stream courses cautions against minimization or downplaying of the associated risk.



**Figure 4. Pie charts of extractable (mobile) fractions of total nickel concentration per sediment sample as produced by the three leach test methods used. Note that each 'sliver' is a fraction of 100%.**



**Figure 5. Pie charts of extractable (mobile) fractions of total uranium concentration per sediment sample as produced by the three leach test methods used. Note that each 'sliver' is a fraction of 100%.**

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