

Article

# Analysis of the Distribution of Some Potentially Harmful Elements (PHEs) in the Krugersdorp Game Reserve, Gauteng, South Africa

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Abstract: The Mintails Mogale Gold (MMG) and the Rand Uranium (RU) are two large-scale mining consortiums active in re-mining old tailings dams and dumps in Krugersdorp and are a source of mine discharge feed into the Krugersdorp Game Reserve (KGR). This has resulted in a noticeable accumulation of potentially harmful elements (PHEs) over a number of years. Efforts were implemented to interpret the concentration levels of PHEs in soils of the study areas of which a total of 36 georeferenced soil samples were collected (in triplicate) from the MMG, RU and KGR, including samples from farmlands and waterways adjacent to the mining sites. Samples were then analysed by both inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) for 36 elements. From the 36 elements of this study, detailed evaluations of the occurrence of 12 selected elements were discussed. The geochemical landscape at the KGR is shown to be in flux. The major mediating influences on the behaviour of As, Co, Cu, Hg and Pb, as they enter the KGR largely in the form of acid mine drainage (AMD), are the geological substrate (mostly in carbonate form). Analysis of the soils showed high levels of contamination for As and Co in ppm. The mean maximum of As ranged from (5.00–170.30) with the highest level found in the Krugersdorp site. The mean maximum of Co ranged from (46.00–102.30) with the highest level found in MMG. All of these values were well above the recommended maximum acceptable concentration (MAC) values, i.e., As (15–20) and Co (20–50). The mean maximum values for Pb (12.40–92.30); Cu (18.50–115.30) and Hg (12.40–92.30) content in surface soils of all four segments studied falls well within the MAC range for agricultural soils i.e., Cu (60–150); Hg (0.5–5) and Pb (20-300).

**Keywords:** potentially harmful elements (PHEs); Krugersdorp; maximum acceptable concentration (MAC); acid mine drainage (AMD)

## 1. Introduction

Krugersdorp Game Reserve (KGR) in the Gauteng Province of South Africa is one of the country's most important wildlife parks in terms of the revenue it generates from tourism and related activities. The Reserve is juxtaposed to two major mining outfits, Mintails Mogale Gold (MMG) and Rand



Uranium (RU) at Krugersdorp, and smallholdings (SH). This makes the total environment an ideal setting for investigating the impact of mining and ore processing activities on the health of neighbouring wildlife communities, and other nearby ecosystem components.

Krugersdorp (26°6′0″ S; 27°46′0″ E), Figure 1, also referred to as Mogale City, is located in the West Rand of the Gauteng Province of South Africa. It has a population of close to half a million inhabitants. It is flecked with a number of abandoned gold (with Mn, Fe, asbestos and lime) mines and boasts an industry that contributes significantly to the economic activity of the Gauteng region. MMG and RU are two large-scale mining consortiums active in re-mining of old tailings dams and dumps in Krugersdorp.

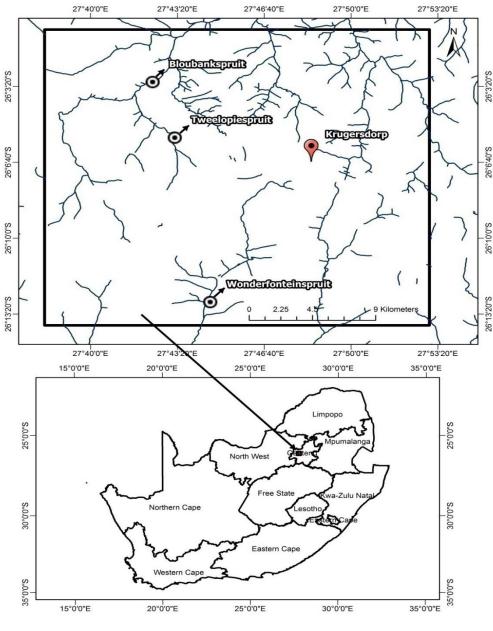


Figure 1. The study area.

Although a comprehensive literature search revealed extensive published information on the hydrochemical environment and soil geochemistry at MMG, RU and SH, as well as wildlife health at KGR, information regarding any on soil geochemistry is scarce [1]. The main aim of this study was to

provide a comprehensive data base of the occurrence and levels of potentially harmful elements (PHEs) in the study area, which is not available anywhere, rather than only focus on a few selected elements.

Heavy metals are a natural occurrence in nature all around the world or as a result of anthropogenic activities through emissions from the rapidly escalating industrial areas, mine tailings, discarding of high metal wastes and atmospheric deposition [1–4]. The metals commonly found in soil as a result of these activities include copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), cobalt (Co), mercury (Hg) and cadmium (Cd). Some of these metals are essential in small doses for use in living organisms for their normal physiological functioning. However, large concentrations can tend to destabilize ecosystems due to bioaccumulation in organisms causing toxic effects through metabolic interference and mutagenesis [1,5–7]. In addition, their accumulation in soils persists for a long period of time after their introduction, contributing to contamination of ecosystems [1,8,9]. Arsenic in particular, is quite toxic and readily absorbed by plants from groundwater and soil [10]. Mining of gold minerals, as seen in the mining consortiums in Krugersdorp is related to acid drainage problems that can cause long-term damage to waterways and biodiversity. Acid mine drainage (AMD) occurs when sulfide-bearing material are exposed to oxygen and water and typically ensues in iron sulfide-aggregated rocks. Although this process occurs naturally, mining can stimulate AMD generation merely through increasing the measure of sulfides exposed. Furthermore, naturally-occurring bacteria can hasten AMD production by supporting the breakdown of sulfide minerals [11]. The obvious concern is the deterioration of water and soil quality from the impact of AMD from the West Rand Basin, which inspired the need to garner more detailed information on the distribution characteristics and fate of the heavy metals around the mining area at Krugersdorp and to establish their levels of concentration. The above considerations provided motivation for the present study, which is aimed at investigating and documenting the PHE- and other element additions from mine effluents (AMD). This study reports on the distribution and concentration of heavy metals due to RU and MMG mining activities in the Krugersdorp region and their migration to surrounding smallholdings and the KGR, focusing on cobalt (Co), mercury (Hg), aluminium (Al), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), cadmium (Cd) and arsenic (As). This information is vital in formulating intervention measures such as mitigation (AMD neutralisation), rehabilitation and soil amendment.

#### Soils

Soils of Krugersdorp are mainly reddish brown to red and belong to the Hutton form (orthic topsoil on red apedal subsoil, usually on rock). The soils range in texture from clayey silt through silty clay to loam. During the field studies, sandy clay was also encountered at a few sites, but the sand content was always less than 10%. The soils are predominantly light textured (15%–25% clay), and vary in depth from less than 400 mm to over 1.2 m.

The KGR is primarily grassland, with shrub thickets, small forests and fynbos found in the valley and close to the small dams. The only information that refers to soil quality, and is relevant to the present study, is the description of agricultural potential of the proposed route of the Westgate substation, west of KGR [12].

Although Krugersdorp is designated as an agricultural hub in the Gauteng Province, the general potential for agricultural development remains relatively low. Based on soil factors (not climatic conditions), Paterson (2008) describes areas of moderate or high agricultural soils [13].

#### 2. Materials and Methods

#### 2.1. Sampling Technique and Sample Preparation

A comprehensive literature search was used to garner published information on the hydrochemical environment and soil geochemistry at MMG, RU and SH. Some data were found to exist on hydrochemistry and wildlife health [1], but hardly any on soil geochemistry. Therefore, in order to complement the existing hydrochemical data, a total of 36 soil samples were collected for analysis (in

triplicate) from cultivable and uncultivable lands at the MMG and RU gold mine fields, and the KGR and adjacent SH to provide information on the soil geochemistry.

The map of the study area with sample sites is shown in Figure 2. At the mining sites (MMG and RU) soil samples were collected on a grid using pre-determined Global Positioning System (GPS) points. Adjacent to the mines and at the KGR, soil samples were taken at random intervals and at a distance of 15 m on either side of minor roads or footpaths (not shown) running approximately in the direction of rivers draining the two mining areas into the KGR (Figure 2). A distance of 15 m on either side of the paths was considered sufficient in minimizing anthropogenic influence on element fluxes in soils in the non-cultivable sectors of the land.

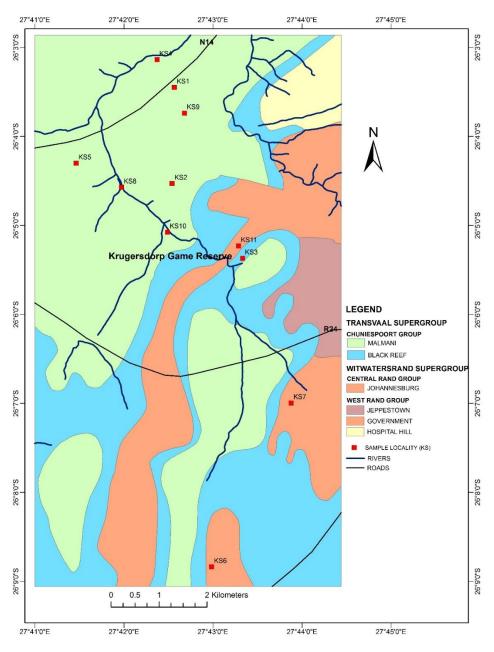


Figure 2. Geology and soil sampling points. KS = soil sampling points.

This sample design was selected in order to determine concentration levels and migration characteristics of PHEs in pollution trails emanating from the mine sites and entering the Krugersdorp ecosystem, to provide a comprehensive data base of the occurrence and levels of PHEs in the study area.

The GPS coordinates as well as other geoenvironmental characteristics such as geology, topography, vegetation, pedology and hydrological characteristics were carefully recorded at each sampling site. The soil sampling protocol comprised of the construction in an undisturbed area, of a 1 m  $\times$  1 m pit to a depth of 40 cm using pick and shovel. A composite near-surface soil sample (30 cm below A0) was collected and stored in pre-labelled Kraft paper envelopes in accordance with The International Geological Correlation Programme (IGCP) 259 recommendations [13], modified for application in tropical conditions by [14].

#### 2.2. Soil Sample Preparation and Analysis

Each soil sample was oven-dried (30 °C) for about 12 h, homogenized and then quartered in the Biochemistry Laboratories of the Mangosuthu University of Technology. Following disaggregation, the soil samples were sieved to <180  $\mu$ m (80 mesh). The samples were then stored in plastic vials and shipped to the headquarters of ACME Laboratories in Vancouver, Canada, for analyses. ACME's sample preparation method comprised of the weighing out of a 30 g split followed by an Aqua Regia dissolution technique. Following soil sample digestion, a range of nutritional and PHEs were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) techniques, but only the PHEs of As, Co, Cu, Hg and Pb were selected for this study.

#### 2.3. Quality Assurance Evaluation

Commercially available standards and previously analysed internal standards, as well as reagent blanks were included to check accuracy and precision. Triplicates were randomly incorporated into all analytical batches. The data were accepted if the relative standard deviation was <15% at five times the limit of detection for the triplicate samples. Triplicate samples comprised 16% of total samples. Standard solutions of all the elements were prepared by diluting their corresponding 1000 mg/L certified standard solutions. The blank reagents and standard reference materials (SRMs) of the metals were used to verify the accuracy and precision of digestion, while in view of data quality assurance, each sample batch was analysed in triplicate under standard opt-ionizing conditions within the confidence limit of 95% (see www.acmelab.com for further details).

#### 2.4. Soil Fraction Analysed

The fine fraction of 180  $\mu$ m (80 mesh) was considered suitable for the present study. A number of studies have determined that metals in the coarse-grained soils are mainly derived from parent materials, and metals in the fine fraction are mostly anthropogenic [15,16]. Other studies [5,17–19] have classified the fraction where enrichment of PHEs take place in (contaminated) soils as clay- and silt-sized. The high specific surface area and charge of fine particles are the probable factors that account for the high contamination levels seen in the fine fraction [20]. The Aqua Regia technique used for decomposition of soil samples (in this study) is a partial dissolution procedure able to release metals associated with a recent pollution source, and could be released to the soil solution with input of water (non-silicate-bound forms); but would not dissolve metals associated within the solid phases, i.e., within the structure of the insoluble minerals [21]. As such, the method is deemed suitable for the assessment or prediction of crop plant metal content, plant growth and plant deficiency or toxicity [22,23]. The method could therefore be considered a suitable tool in the assessment of the long-term potential risk of heavy or toxic metals entering the biosphere.

### 3. Results and Discussion

As pointed out in the introduction, the main aim of this study was to provide a comprehensive data base of the occurrence and levels of PHEs in the study area, which is not available anywhere, rather than only focus on a few selected elements (refer to Table 1). These are presented in Tables 2–4.

#### 3.1. Total Content of Selected Heavy Metals

Some soil pollution water sources and parameters are sighted in this section. February 2011 evidence of ADM in the Krugersdorp area involving the Tweelopie stream is shown in Figure 3. Previous (2006) KGR water hydrochemical parameters are outlined in Table 1 [24]. The general analytical results of the thirty-six (36) elements in Table 2 range from 9.22% (for Fe) to less than 0.1 ppm. From the 36 elements of this study, detailed evaluations of the occurrence of 12 selected elements are presented in Table 3. Of these, five heavy metals, namely As, Co, Cu, Hg and Pb, the data of which is presented in Table 4, from the respective study sites, were considered for a comparative analysis of their concentrations in the soil samples. The concentrations obtained in the study sites are compared with the reference values for background concentrations, Johnson [25] after Wedepohl [26].



Figure 3. Tweelopiespruit (TLS) flowing out of Aviary Dam, Krugersdorp Game Reserve (KGR, 3 Feb 2011). Source: [27].

**Table 1.** Hydrochemical parameters of water from the KGR inlet (i.e., "treated water") for August and September 2006 in relation to the Department of water Affairs and Forestry (DWAF) Directive requirements. Source: Du Toit, 2006 [24].

Variables	Directive	August, 2006	September, 2006
pН	6.5-8.4	5.1 *	9.2 *
Conductivity (EC) (ms/m)	70	493 *	438 *
Sulphate (SO4) (mg/L)	200	3230 * ** ***	3000 * ** ***
Chloride (Cl) (mg/L)	36	50 *	43 *
Aluminium (Al) (mg/L)	0.06	0.70 *	0.88 *
Managnese (Mn) (mg/L)	0.07	85.18 * ** ***	18.28 * ** ***
Iron (Fe) (mg/L)	0.1	74.67 * ** ***	12.47 * ** ***

Note: \*—Not complying with DWAF's Directive; \*\*—Not complying with the Minimum Requirements of DWAF for Livestock Watering; \*\*\*—Not complying with the Minimum Requirements of DWAF for Domestic Use.

In the KGR, surrounding smallholdings and RU, Mn had the highest mean concentration followed by Cr. These three study sites also had a similar trend for the four lowest heavy metal concentrations, Pb > As > Cd > Hg (Tables 3 and 4). The soil samples from the KGR had mean heavy metal concentrations of 93.41, 4280.33, 17.37, 64.73, 35.07, 88.56, 0.17, 0.12, 11.55, and 7.56 mg·kg<sup>-1</sup> for Cr, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb, and As respectively. In the soils from MMG, the trend was Mn > Zn > As > Cr > Cu > Ni > Pb > Co > Cd > Hg (Table 3). The higher standard deviation reveals higher variations in heavy metal distributions from the point source of discharge to the adjacent areas.

		Analyte	Mo	Cu	Pb	Zn	Ag	Ni	Со	Mn	Fe	As	Au	Th
		Unit	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	PPM	PPB	PPM
	-	MDL	0.1	0.1	0.1	1	0.1	0.1	0.1	1	0.01	0.5	0.5	0.1
	Sample	Туре												
1	KS1A	Soil	0.9	15.8	5	23	< 0.1	29.5	11	2679	3.69	6.8	2.6	2.7
2	KS1B	Soil	1	11.8	4.8	15	< 0.1	24	11.2	3128	2.74	5.2	3.6	2.2
3	KS1C	Soil	1	16	6.4	18	< 0.1	26.3	11.6	2648	3.4	6.1	2.9	3.6
4	KS1D	Soil	0.9	10.1	4.6	15	< 0.1	16.4	9.3	1801	2.14	5.2	3.8	2.2
5	KS2A	Soil	0.5	16	7.5	25	< 0.1	38.5	10.5	5056	2.38	4.1	4.9	3
6	KS2B	Soil	1.1	29.5	15.1	54	< 0.1	91.1	18	>10,000	4.24	5.5	7.9	4
7	KS2C	Soil	0.8	27.9	15.8	79	< 0.1	97.1	14.4	>10,000	4.92	6.6	12.4	6.1
8	KS2C2	Soil	0.8	28.7	16.4	84	< 0.1	97.2	14.9	>10,000	4.74	6.7	11.8	5.7
9	KS2D	Soil	1.6	42	13.5	216	< 0.1	444.8	15.3	>10,000	8.23	8.6	8.8	4.4
10	KS3A1	Soil	0.9	40.6	6.3	25	< 0.1	49.3	11.1	3625	4.15	6.5	15.7	4
11	KS3A2	Soil	0.7	41.1	6.5	27	< 0.1	50.3	11.8	3960	4.23	6.4	15.5	4.2
13	KS3B	Soil	0.9	43.1	7.1	30	< 0.1	61.4	11	9233	4.32	7.4	13.1	4.1
14	KS3C	Soil	0.8	43.4	10.2	54	< 0.1	54.5	10.8	2956	4.85	7.3	14.6	5
15	KS3D	Soil	0.9	49	10.6	54	< 0.1	59.9	14.1	3401	4.85	7.6	11.1	4.5
16	KS4A	Soil	1	29.8	12.4	202	< 0.1	273.1	93	7644	2.86	6.4	442.2	2.8
17	KS4B	Soil	0.9	13.5	7	12	< 0.1	23.2	10.4	3226	2.59	3.6	4.7	3
18	KS5A	Soil	0.7	20.1	9.2	13	< 0.1	21.7	11.4	1558	2.95	4	4	4.8
19	KS5B	Soil	0.5	16.1	5.9	12	< 0.1	19.6	6.4	1082	2.47	3.3	3.8	4.3
20	KS6A	Soil	0.7	18.5	12.4	15	< 0.1	29.7	16.2	812	3.23	5	5.5	4.9
21	KS6B	Soil	0.9	13.7	6.3	32	< 0.1	61.5	46	451	2.1	2.9	3.4	3.6
22	KS7A	Soil	1.9	122.9	72.7	153	0.2	86.8	48.4	7086	3.74	140.7	272.8	4
23	KS7B1	Soil	1.7	115.3	92.3	1129	0.2	97.6	48.3	3011	4.31	170.3	407.7	7.1
24	KS7B2	Soil	1	61	50	690	0.1	59.6	26.9	1717	3.55	79.2	329.4	6.7
25	KS8A	Soil	0.7	80	18.4	736	<0.1	110.2	48.7	9290	4.01	16.8	354.9	3.2
26	KS8B	Soil	0.8	91.4	14.6	281	<0.1	77.4	102.3	7866	3.87	14.1	257.2	3.2
27	KS9A	Soil	0.9	18.6	7	19	<0.1	29.5	13.7	2366	2.71	4.7	15.4	3.7
28	KS9B	Soil	0.9	17.6	8.2	21	<0.1	27.5	13.3	2628	2.44	4.7	16.3	3.6
29	KS9C	Soil	0.6	20	5.2	16	<0.1	30.4	10.3	1807	2.82	3.9	21.1	4.3
30	KS9D	Soil	0.7	20	3.6	10	<0.1	31.6	9	1122	3.4	3.2	13.2	4.7
31	KS 10 A	Soil	1	93.2	79.6	446	4.7	117.6	39.4	8990	4.27	15.9	488.7	2.2
32	KS 11 Anthill sample	Soil	1	47.3	13.2	33	<0.1	39.3	11.8	527	6.39	7.5	60	2.2
33	KS 11 Allulii sample KS 11 Al	Soil	0.8	18.8	6.3	35 16	<0.1	19.8	4.8	256	2.83	11.5	26.5	2.9
33 34	KS 11 A2	Soil	1	18.5	6.1	15	<0.1	19.6	4.5	230	2.63	11.5	30.7	1.9
34 35	KS 11 A2 KS 11 B	Soil	0.7	10.5	3.6	10	<0.1	13.9	2.8	115	2.62 1.67	7.6	30.7 19.6	1.9
36	KS 11 C	Soil	0.7	36	6.6	26	<0.1	39.6	12.9	630	9.22	4.2	19.0	3
30 37	KS 11 D	Soil	0.8 1.1	55.3	0.0 9.6	20 36	<0.1	59.6 51.9	20.6	1273	9.22 9.08	4.2 8.5	30	3.8

**Table 2.** Full table of Krugersdorp Game Reserve soil samples analytical potentially harmful elements (PHEs) results.

Table 2. Cont.

		Analyte	Мо	Cu	Pb	Zn	Ag	Ni	Со	Mn	Fe	As	Au	Th
		Unit	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	PPM	PPB	PPM
		MDL	0.1	0.1	0.1	1	0.1	0.1	0.1	1	0.01	0.5	0.5	0.1
	Sample	Туре												
38	* Pulp Duplicates													
39	KS 11 D	Soil	1.1	55.3	9.6	36	< 0.1	51.9	20.6	1273	9.08	8.5	30	3.8
40	KS 11 D	REP	1.1	57	9.5	37	< 0.1	53.9	21.7	1241	9.4	8.6	20	3.9
41	KS8B	Soil	0.8	91.4	14.6	281	< 0.1	77.4	102.3	7866	3.87	14.1	257.2	3.2
42	KS8B	REP	0.8	90.8	14.6	282	< 0.1	77.4	100.3	8027	3.93	14.2	258.4	3.3
42	Reference Materials													
44	STD DS10	STD	14	153.9	152.7	360	1.9	74	13.1	874	2.78	44.3	89.5	7.8
45	STD OXC109	STD	1.3	34.1	11.1	40	< 0.1	67.3	19.1	390	2.88	0.8	180.5	1.5
46	STD DS10	STD	14.4	148.6	152	326	2	71.6	12.7	840	2.58	43.3	88.8	7.9
47	STD OXC109	STD	1.5	34.7	11.8	39	< 0.1	69.5	19.1	385	2.71	0.7	189.1	1.6
48	BLK	BLK	< 0.1	< 0.1	< 0.1	<1	< 0.1	< 0.1	< 0.1	<1	< 0.01	< 0.5	< 0.5	< 0.1
50	Prep Wash													
51	G1	Prep Blank	0.1	3.1	3.6	45	< 0.1	3.5	4.1	517	1.79	0.5	< 0.5	5.8
52	G1	Prep Blank	0.2	2.8	3.5	45	< 0.1	3.2	3.8	523	1.82	< 0.5	0.7	5.6
		Analyte	Sr	Cd	Sb	Bi	v	Ca	Р	La	Cr	Mg	Ba	
		Unit	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	%	PPM	-
		MDL	1	0.1	0.1	0.1	2	0.01	0.001	1	1	0.01	1	
	Sample	Туре												
1	KS1A	Soil	3	< 0.1	0.3	0.1	42	0.02	0.014	6	64	0.02	54	
2	KS1B	Soil	1	< 0.1	0.2	0.1	31	< 0.01	0.013	6	47	0.02	62	
3	KS1C	Soil	4	< 0.1	0.4	0.2	46	0.02	0.014	7	67	0.02	74	
4	KS1D	Soil	<1	< 0.1	0.2	0.1	25	< 0.01	0.008	5	38	0.01	40	
5	KS2A	Soil	3	< 0.1	0.3	0.1	39	0.01	0.011	6	52	0.03	113	
6	KS2B	Soil	24	0.1	0.4	0.2	55	0.04	0.023	16	71	0.05	319	
7	KS2C	Soil	52	0.2	0.5	0.4	56	0.02	0.015	15	65	0.03	245	
8	KS2C2	Soil	52	0.1	0.5	0.4	53	0.03	0.015	14	60	0.03	239	
9	KS2D	Soil	387	0.5	0.5	0.2	54	0.07	0.017	21	57	0.07	226	
10	KS3A1	Soil	4	<0.1	0.2	0.1	85	0.02	0.02	10	107	0.02	67	
11	KS3A2	Soil	4	< 0.1	0.2	0.1	86	0.02	0.022	11	114	0.03	72	
11									0.021					
13	KS3B	Soil	22	< 0.1	0.3	0.1	88	0.02	0.021	11	100	0.03	113	

Table 2. Cont.

		Analyte	Sr	Cd	Sb	Bi	v	Ca	Р	La	Cr	Mg	Ba	
		Unit	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	%	PPM	
	-	MDL	1	0.1	0.1	0.1	2	0.01	0.001	1	1	0.01	1	
	Sample	Туре												
15	KS3D	Soil	8	< 0.1	0.3	0.2	97	0.14	0.035	18	122	0.04	141	
16	KS4A	Soil	7	0.5	0.3	0.1	47	0.1	0.026	7	100	0.03	125	
17	KS4B	Soil	3	< 0.1	0.2	< 0.1	44	0.02	0.015	7	84	0.02	99	
18	KS5A	Soil	6	< 0.1	0.2	0.2	62	0.04	0.015	15	107	0.04	94	
19	KS5B	Soil	3	< 0.1	0.2	0.2	53	0.02	0.013	13	95	0.03	73	
20	KS6A	Soil	3	< 0.1	0.2	< 0.1	71	0.03	0.017	7	99	0.02	83	
21	KS6B	Soil	2	< 0.1	0.1	< 0.1	46	0.02	0.016	6	73	0.02	29	
22	KS7A	Soil	64	0.3	1.4	0.6	46	0.14	0.065	20	88	0.04	405	
23	KS7B1	Soil	53	0.8	1	0.7	64	0.09	0.077	23	120	0.03	290	
24	KS7B2	Soil	29	0.4	0.5	0.4	61	0.06	0.051	18	99	0.02	162	
25	KS8A	Soil	11	0.7	0.4	0.2	70	0.16	0.025	17	96	0.09	150	
26	KS8B	Soil	11	0.4	0.3	0.1	59	0.08	0.032	11	80	0.06	169	
27	KS9A	Soil	1	< 0.1	0.3	0.2	48	< 0.01	0.016	10	69	0.02	78	
28	KS9B	Soil	2	< 0.1	0.3	0.2	40	0.01	0.016	9	64	0.02	89	
29	KS9C	Soil	2	< 0.1	0.3	0.2	51	0.02	0.016	10	73	0.02	84	
30	KS9D	Soil	2	< 0.1	0.3	0.2	63	0.02	0.016	13	91	0.02	73	
31	KS 10 A	Soil	21	0.7	1.5	5.3	59	0.27	0.145	15	113	0.06	258	
32 I	KS 11 Anthill sample	Soil	4	< 0.1	0.4	0.2	70	0.04	0.046	12	176	0.03	32	
33	KS 11 A1	Soil	2	< 0.1	0.5	0.2	42	0.01	0.019	6	79	0.02	15	
34	KS 11 A2	Soil	2	< 0.1	0.7	0.2	40	< 0.01	0.018	6	76	0.02	14	
35	KS 11 B	Soil	2	< 0.1	0.2	0.1	24	< 0.01	0.013	5	49	0.01	9	
36	KS 11 C	Soil	4	< 0.1	0.3	0.2	74	0.06	0.029	11	227	0.03	26	
37	KS 11 D	Soil	3	< 0.1	0.5	0.2	82	0.01	0.042	15	233	0.03	38	
38	*Pulp Duplicates													
39	KS 11 D	Soil	3	< 0.1	0.5	0.2	82	0.01	0.042	15	233	0.03	38	
40	KS 11 D	REP	3	< 0.1	0.5	0.2	86	0.01	0.046	15	232	0.04	38	
41	KS8B	Soil	11	0.4	0.3	0.1	59	0.08	0.032	11	80	0.06	169	
42	KS8B	REP	11	0.4	0.4	0.1	60	0.1	0.034	12	87	0.06	174	
42	Reference Materials													
44	STD DS10	STD	66	2.6	8.6	12.7	42	1.07	0.075	18	54	0.74	315	
45	STD OXC109	STD	130	< 0.1	< 0.1	< 0.1	44	0.62	0.095	12	55	1.36	54	
46	STD DS10	STD	68	2.7	9.4	12.6	40	1.02	0.075	18	52	0.75	348	
47	STD OXC109	STD	138	< 0.1	< 0.1	< 0.1	46	0.68	0.104	12	56	1.43	57	
48	BLK	BLK	<1	< 0.1	< 0.1	< 0.1	<2	< 0.01	< 0.001	<1	<1	< 0.01	<1	

Table 2. Cont.

		Analyte	Sr	Cd	Sb	Bi	v	Ca	Р	La	Cr	Mg	Ba		
		Unit	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	%	PPM	-	
		MDL	1	0.1	0.1	0.1	2	0.01	0.001	1	1	0.01	1	-	
	Sample	Туре													
50	Prep Wash														
51	G1	Prep Blank	45	< 0.1	< 0.1	< 0.1	38	0.45	0.073	10	7	0.5	158		
52	G1	Prep Blank	47	< 0.1	< 0.1	< 0.1	37	0.45	0.066	10	7	0.5	155		
		Analyte	Ti	В	Al	Na	К	W	Hg	Sc	T1	S	Ga	Se	Te
		Unit	%	PPM	%	%	%	PPM	PPM	PPM	PPM	%	PPM	PPM	PPM
		MDL	0.001	1	0.01	0.001	0.01	0.1	0.01	0.1	0.1	0.05	1	0.5	0.2
	Sample	Туре													
1	KS1A	Soil	0.017	<1	0.86	0.002	0.03	< 0.1	0.03	4.7	< 0.1	< 0.05	5	< 0.5	< 0.2
2	KS1B	Soil	0.014	<1	0.82	0.002	0.02	< 0.1	0.03	3.7	< 0.1	< 0.05	4	< 0.5	< 0.2
3	KS1C	Soil	0.017	<1	0.99	0.004	0.02	< 0.1	0.04	4.7	0.1	< 0.05	5	< 0.5	< 0.2
4	KS1D	Soil	0.01	<1	0.57	0.003	0.02	< 0.1	0.02	2.6	< 0.1	< 0.05	3	< 0.5	< 0.2
5	KS2A	Soil	0.018	<1	1.05	0.003	0.03	< 0.1	0.03	4.6	< 0.1	< 0.05	5	< 0.5	< 0.2
6	KS2B	Soil	0.029	<1	1.81	0.003	0.06	< 0.1	0.04	6.3	0.1	< 0.05	8	< 0.5	< 0.2
7	KS2C	Soil	0.04	1	1.43	0.004	0.06	< 0.1	0.07	8.6	0.1	< 0.05	8	< 0.5	< 0.2
8	KS2C2	Soil	0.038	2	1.46	0.004	0.06	0.1	0.08	8.4	0.1	< 0.05	9	< 0.5	< 0.2
9	KS2D	Soil	0.041	<1	1.73	0.006	0.07	0.1	0.5	6.9	0.1	< 0.05	13	< 0.5	< 0.2
10	KS3A1	Soil	0.033	<1	1.63	0.004	0.03	< 0.1	0.04	7.1	< 0.1	< 0.05	8	< 0.5	< 0.2
11	KS3A2	Soil	0.034	<1	1.8	0.004	0.03	< 0.1	0.03	7.2	< 0.1	< 0.05	8	< 0.5	< 0.2
13	KS3B	Soil	0.036	<1	1.76	0.003	0.04	< 0.1	0.04	6.7	< 0.1	< 0.05	9	< 0.5	< 0.2
14	KS3C	Soil	0.042	2	2.15	0.008	0.06	< 0.1	0.03	8.8	< 0.1	< 0.05	10	< 0.5	< 0.2
15	KS3D	Soil	0.035	3	2.37	0.007	0.05	< 0.1	0.04	8.9	< 0.1	< 0.05	10	< 0.5	< 0.2
16	KS4A	Soil	0.023	1	1.13	0.004	0.04	< 0.1	0.04	4.8	0.1	< 0.05	6	< 0.5	< 0.2
17	KS4B	Soil	0.025	<1	1.12	0.002	0.03	< 0.1	0.03	4.4	< 0.1	< 0.05	5	< 0.5	< 0.2
18	KS5A	Soil	0.027	<1	1.52	0.003	0.03	< 0.1	0.02	7	0.1	< 0.05	7	< 0.5	< 0.2
19	KS5B	Soil	0.026	<1	1.39	0.003	0.03	< 0.1	0.02	5.8	< 0.1	< 0.05	6	< 0.5	< 0.2
20	KS6A	Soil	0.027	<1	1.38	0.005	0.03	< 0.1	0.01	6.5	0.1	< 0.05	6	< 0.5	< 0.2
21	KS6B	Soil	0.02	<1	1.39	0.004	0.03	< 0.1	0.02	4.9	< 0.1	< 0.05	5	< 0.5	< 0.2
22	KS7A	Soil	0.022	3	1.16	0.014	0.05	0.2	0.33	5	0.1	0.15	6	1	< 0.2
23	KS7B1	Soil	0.034	3	1.71	0.012	0.05	0.2	0.26	6.9	0.1	0.09	9	0.6	< 0.2
24	KS7B2	Soil	0.025	1	1.79	0.007	0.04	0.1	0.15	6.8	< 0.1	0.05	8	< 0.5	< 0.2
25	KS8A	Soil	0.036	2	1.25	0.009	0.05	< 0.1	0.22	5.7	0.1	< 0.05	6	< 0.5	< 0.2

Table 2. Cont.

		Analyte	Ti	В	Al	Na	К	W	Hg	Sc	Tl	S	Ga	Se	Te
		Unit	%	PPM	%	%	%	PPM	PPM	PPM	PPM	%	PPM	PPM	PPM
		MDL	0.001	1	0.01	0.001	0.01	0.1	0.01	0.1	0.1	0.05	1	0.5	0.2
	Sample	Туре													
26	KS8B	Soil	0.033	2	1.52	0.01	0.05	< 0.1	0.24	6.5	0.2	0.09	7	< 0.5	< 0.2
27	KS9A	Soil	0.019	<1	1.28	0.002	0.02	< 0.1	0.03	6	0.1	< 0.05	6	< 0.5	< 0.2
28	KS9B	Soil	0.017	<1	1.16	0.004	0.02	< 0.1	0.04	5.4	0.1	< 0.05	5	< 0.5	< 0.2
29	KS9C	Soil	0.02	<1	1.23	0.002	0.02	< 0.1	0.04	6.6	0.1	< 0.05	6	< 0.5	< 0.2
30	KS9D	Soil	0.023	<1	1.39	0.002	0.02	< 0.1	0.02	7	< 0.1	< 0.05	8	0.6	< 0.2
31	KS 10 A	Soil	0.028	2	1.59	0.008	0.06	0.4	1.36	5.1	0.1	< 0.05	7	0.5	< 0.2
32	KS 11 Anthill sample	Soil	0.025	1	1.57	0.006	0.04	0.1	0.06	8.8	< 0.1	< 0.05	8	< 0.5	< 0.2
33	KS 11 A1	Soil	0.014	<1	0.93	0.007	0.03	< 0.1	0.04	3.1	< 0.1	< 0.05	4	< 0.5	< 0.2
34	KS 11 A2	Soil	0.013	<1	0.93	0.006	0.03	< 0.1	0.03	3	< 0.1	< 0.05	4	< 0.5	< 0.2
35	KS 11 B	Soil	0.008	<1	0.65	0.007	0.03	< 0.1	0.03	1.8	< 0.1	< 0.05	2	< 0.5	< 0.2
36	KS 11 C	Soil	0.025	<1	1.44	0.005	0.02	< 0.1	0.04	8.2	< 0.1	< 0.05	8	< 0.5	< 0.2
37	KS 11 D	Soil	0.029	<1	2	0.005	0.04	0.2	0.05	11.5	0.1	< 0.05	10	< 0.5	< 0.2
38	*Pulp Duplicates														
39	KS 11 D	Soil	0.029	<1	2	0.005	0.04	0.2	0.05	11.5	0.1	< 0.05	10	< 0.5	< 0.2
40	KS 11 D	REP	0.029	<1	1.93	0.005	0.04	0.3	0.06	11.1	0.1	< 0.05	11	< 0.5	< 0.2
41	KS8B	Soil	0.033	2	1.52	0.01	0.05	< 0.1	0.24	6.5	0.2	0.09	7	< 0.5	< 0.2
42	KS8B	REP	0.037	3	1.67	0.01	0.06	< 0.1	0.26	6.8	0.2	0.1	7	< 0.5	< 0.2
42	Reference Materials														
44	STD DS10	STD	0.073	6	0.99	0.062	0.32	3.2	0.29	2.8	5.2	0.26	4	2.2	4.9
45	STD OXC109	STD	0.332	1	1.42	0.611	0.37	0.2	< 0.01	1	< 0.1	< 0.05	5	< 0.5	< 0.2
46	STD DS10	STD	0.077	7	0.98	0.065	0.31	3.5	0.28	2.7	4.8	0.26	5	2.2	5.3
47	STD OXC109	STD	0.387	2	1.46	0.654	0.4	0.2	< 0.01	1	< 0.1	< 0.05	5	< 0.5	< 0.2
48	BLK	BLK	< 0.001	<1	< 0.01	< 0.001	< 0.01	< 0.1	< 0.01	0.2	< 0.1	< 0.05	<1	< 0.5	< 0.2
50	Prep Wash														
51	G1	Prep Blank	0.105	<1	0.86	0.066	0.46	< 0.1	< 0.01	2.3	0.2	< 0.05	4	< 0.5	< 0.2
52	G1	Prep Blank	0.099	<1	0.89	0.064	0.45	< 0.1	< 0.01	2.1	0.3	< 0.05	4	< 0.5	< 0.2

\* Duplicate samples run for accuracy purposes.

Heavy	Metal			Kruger	Rand Uranium Mine	Mintails Mogale Gold	Smallh	oldings				
		KS1 ( <i>n</i> = 4)	KS2 ( <i>n</i> = 5)	KS3 ( <i>n</i> = 5)	KS8 ( <i>n</i> = 2)	KS9 ( <i>n</i> = 4)	KS10 ( <i>n</i> = 1)	KS11 ( <i>n</i> = 6)	KS6 ( <i>n</i> = 2)	KS7 ( <i>n</i> = 3)	KS4 ( <i>n</i> = 2)	KS5 ( <i>n</i> = 2)
	Mean	56.25	61.00	113.20	88.00	74.25	113.00	140.00	86.00	102.33	92.00	101.00
Cr	SD	17.02	7.31	9.83	11.31	11.76	N/A	81.99	18.39	16.26	11.31	8.49
(90.00) *	Min	38.00	52.00	100.00	80.00	64.00	N/A	49.00	73.00	88.00	84.00	95.00
	Max	67.00	71.00	123.00	96.00	91.00	N/A	233.00	99.00	120.00	100.00	107.00
	Mean	2564.00	9011.20	4635.00	8578.00	1980.75	8990.00	502.17	631.50	3938.00	5435.00	1320.00
Mn	SD	553.94	2211.02	2596.11	1006.92	667.08	N/A	425.64	255.27	2801.97	3124.00	336.58
(850.00) *	Min	1801.00	5056.00	2956.00	7866.00	1122.00	N/A	115.00	451.00	1717.00	3226.00	1082.00
	Max	3128.00	10,000.00	9233.00	9290.00	2628.00	N/A	1273.00	812.00	7086.00	7644.00	1558.00
	Mean	10.78	14.62	11.76	75.50	11.58	39.40	9.57	31.10	41.20	51.70	8.90
Со	SD	1.01	2.69	1.36	37.90	2.29	N/A	6.81	21.07	12.38	58.41	3.54
(19.00) *	Min	9.30	10.50	10.80	48.70	9.00	N/A	2.80	16.20	26.90	10.40	6.40
	Max	11.60	18.00	14.10	102.30	13.70	N/A	20.60	46.00	48.40	93.00	11.40
	Mean	24.05	153.74	55.08	93.80	29.75	117.60	30.52	45.60	81.33	148.15	20.65
Ni	SD	5.58	164.56	5.47	23.19	1.73	N/A	15.16	22.49	19.58	176.71	1.48
(68.00) *	Min	16.40	38.50	49.30	77.40	27.50	N/A	13.90	29.70	59.60	23.20	19.60
	Max	29.50	444.80	61.40	110.20	31.60	N/A	51.90	61.50	97.60	273.10	21.70
	Mean	13.43	28.82	43.44	85.70	20.05	93.20	31.17	16.10	99.73	21.65	18.10
Cu	SD	2.94	9.21	3.34	8.06	2.81	N/A	17.79	3.39	33.76	11.53	2.83
(45.00) *	Min	10.10	16.00	40.60	80.00	17.60	N/A	11.10	13.70	61.00	13.50	16.10
	Max	16.00	42.00	49.00	91.40	24.00	N/A	55.30	18.50	115.30	29.80	20.10
	Mean	17.75	91.60	38.00	508.50	18.25	446.00	22.67	23.50	657.33	107.00	12.50
Zn	SD	3.77	73.38	14.71	321.73	2.22	N/A	10.58	12.02	488.82	134.35	0.71
(95.00) *	Min	15.00	25.00	25.00	281.00	16.00	N/A	10.00	15.00	153.00	12.00	12.00
	Max	23.00	216.00	54.00	736.00	21.00	N/A	36.00	32.00	1129.00	202.00	13.00

Cd

(0.30) \*

Hg (0.40) \*

Pb

(20.00) \*

As

(13.00) \*

v

(130.00) \*

Fe

(47,200.00)

\*

Heavy Metal

Mean

SD

Min

Max

Mean

SD

Min

Max

Mean SD

Min

Max Mean

SD

Min

Max

Mean

SD

Min

Max

Mean

SD

Min

Max

KS1 (n = 4)

0.10 0.00

0.10

0.10

0.03

0.01

0.02

0.04

5.20

0.82

4.60

6.40

5.83

0.78

5.20

6.80

36.00

9.70

25.00

46.00

29,925.00

6935.60

21,400.00

36,900.00

6.30

1.66

4.10

8.60

51.40

7.02

39.00

56.00

49,020.00

21,154.72

23,800.00

82,300.00

7.04

0.55

6.40

7.60

89.80

5.07

85.00

97.00

44,800.00

3430.74

41,500.00

48,500.00

15.45

1.910

14.10

16.80

64.50

7.78

59.00

70.00

34,900.00

989.95

38,700.00

40,100.00

				Table 3. Cont						
		Kruger	sdorp Game	Rand Uranium Mine	Mintails Mogale Gold	Smallholdings				
.)	KS2 ( <i>n</i> = 5)	KS3 ( <i>n</i> = 5)	KS8 ( <i>n</i> = 2)	KS9 ( <i>n</i> = 4)	KS10 ( <i>n</i> = 1)	KS11 ( <i>n</i> = 6)	KS6 ( <i>n</i> = 2)	KS7 ( <i>n</i> = 3)	KS4 ( <i>n</i> = 2)	KS5 ( <i>n</i> = 2)
	0.20	0.10	0.55	0.10	0.70	0.10	0.10	0.50	0.30	0.10
	0.17	0.00	0.21	0.00	N/A	0.00	0.00	0.27	0.28	0.00
	0.10	0.10	0.40	0.10	N/A	0.10	0.10	0.30	0.10	0.10
	0.50	0.10	0.70	0.10	N/A	0.10	0.10	0.80	0.50	0.10
	0.14	0.04	0.23	0.03	1.36	0.04	0.02	0.25	0.04	0.02
	0.20	0.01	0.01	0.01	N/A	0.01	0.01	0.09	0.01	0.00
	0.03	0.03	0.22	0.02	N/A	0.03	0.01	0.15	0.03	0.02
	0.50	0.04	0.24	0.04	N/A	0.06	0.02	0.26	0.04	0.02
	13.66	8.14	16.50	6.00	79.60	7.57	9.35	71.67	9.70	7.55
	3.61	2.09	2.69	2.02	N/A	3.36	4.31	21.17	3.82	2.33
	7.50	6.30	14.60	3.60	N/A	3.60	6.30	50.00	7.00	5.90
	16.40	10.60	18.40	8.20	N/A	13.20	12.40	92.30	12.40	9.20

8.48

2.79

4.20

11.60

55.33

23.11

24.00

82.00

53,016.67

33,853.53

16,700.00

92,200.00

3.95

1.49

2.90

5.00

58.50

17.68

46.00

71.00

26,650.00

7990.31

21,000.00

32,300.00

130.07

46.47

79.20

170.30

57.00

9.64

46.00

64.00

38,666.67

3955.17

35,500.00

43,100.00

5.00

1.98

3.60

6.40

45.50

2.12

44.00

47.00

27,250.00

1909.19

25,900.00

28,600.00

3.65

0.49

3.30

4.00

57.50

6.36

53.00

62.00

27,100.00

3394.11

24,700.00

29,500.00

34,000.00 \* The mean concentrations were compared to reference values (mg.kg<sup>-1</sup>) for background concentrations after [26].

4.13

0.72

3.20

4.70

50.50

9.54

40.00

63.00

28,425.00

4045.06

28,200.00

15.90

N/A

N/A

N/A

59.00

N/A

N/A

N/A

42,700.00

N/A

N/A

N/A

The sampling sites in the KGR (Table 3) showed a distinct migration pattern of heavy metal concentrations. Sampling sites KS8 and KS10 displayed higher mean concentrations than the other sampling sites in the KGR. This is interesting since KS8 and KS10 were located in close proximity to the TLS (Figure 1). The higher mean concentrations are to be expected since AMD first decanted into this waterway in September 2002 [28]. The sampling site KS1 in the KGR had predominantly the lowest mean heavy metal concentrations (Table 4). Again, this is to be expected, since this sampling site was the furthest from the point source of discharge (Figure 1).

#### 3.2. Distribution of Soil Geochemical Data

Mean concentration ranges of Aqua Regia extractable As, Co, Cu, Hg and Pb fraction (pseudo-total fraction) of soil samples collected for this study were compared with the range of maximum allowable concentrations (MAC) for agricultural soils worldwide, as given in [29]. Quite unexpectedly, mean PHE concentrations in soils of the KGR and SH are well within the range of MAC for agricultural soils worldwide. Table 4 gives the statistical parameters of surface soil PHE data, including standard deviations and location of mean contents within the range of MAC given for agricultural soils worldwide [29]. High standard deviations signify wider variations in PHE distribution from the point source of discharge of AMD to the adjacent areas. Of the four study segments (KGR, SH, MMG and RU), only MMG gives a mean value for As (130.07 ppm) falling above the MAC range for agricultural soils worldwide (15–20 ppm). Mean As values for the other three segments fall well within the MAC range (Table 4). Similarly, Co, KGR and SH gave mean values for surface soils (102.30 ppm) and (93.00 ppm) respectively, that is above the upper threshold of the MAC range for agricultural soils (20–50 ppm) given in [29]. The other two study segments gave mean values well within this range.

The mean Cu content in surface soils of all four segments studied falls well within the MAC range for agricultural soils (60–150 ppm) given in [30]. The highest Cu values were again found in samples from the MMG segment, but with a mean value (99.73) far removed from the upper threshold (150 ppm) of the MAC range. The mean Cu concentrations decrease in the order: MMG (99.73 ppm) > KGR (35.07 ppm) > SH (19.88 ppm) > RU (16.10 ppm) (Table 4).

The mean Hg content in surface soils of all four segments studied falls well within the MAC range given for agricultural soils (0.5–5 ppm) in reference [29]. The highest Hg values were again found in samples from the MMG segment.

The mean Pb content in surface soils of all four segments studied falls well within the MAC range for Pb in agricultural soils (20–300 ppm) given in reference [29]. The highest Pb values were again found in samples from the MMG segment.

#### 3.3. Sampling Sites

KS8 and KS10, in close proximity to the Tweelopiespruit (TLS) (Figure 1), displayed higher mean concentrations of PHEs in surface soil compared to the other sampling sites in the KGR. This is unsurprising, given that the TLS is the waterway where AMD first decanted in September 2002 [14]. The sampling site KS1 in the KGR gave the lowest PHE concentrations. Again, this is to be expected, since this sampling site was the furthest from the point source of AMD discharge (Figure 2). The relatively low concentrations of Cu, Hg and Pb in surface soils of the KGR, explained both on the basis of improved quality of influent mine water and carbonate–water interactions in the soil, is taken to indicate that the potential supply of these elements to herbage and crops would be limited.

					Study Sites				
I	PHE	Krugersdorp Game Reserve	Smallholdings	Rand Uranium Mine	Mintails Mogale Gold	Range of MAC in Agricultural Soils <sup>a</sup>	Average Composition of Living Matter <sup>b</sup>	Comments	
	Mean	7.56	4.33	3.95	130.07				
	SD	3.54	1.41	1.49	46.47			Toxic; readily absorbed by plants	
As	Min	3.20	3.30	2.90	79.20	15-20	0.31	from groundwater and soil	
	Max	16.80	6.40	5.00	170.30			fiont groundwater and son	
	Ν	23	4	2	2				
	Mean	17.37	30.30	31.10	41.20				
	SD	19.45	41.86	21.07	12.38				
Со	Min	2.80	6.40	16.20	26.90	20-50	0.2	Microorganisms ( <i>Rhizobium</i> sp.);	
	Max	102.30	93.00	46.00	48.40			essential to animals	
	Ν	23	4	2	2				
	Mean	35.07	19.88	16.10	99.73			Vital to health of all living organism	
	SD	23.21	7.15	3.39	33.76			Necessary for haemoglobin and	
Cu	Min	10.10	13.50	13.70	61.00	60-150	60-150	2	melanin formation; component of
	Max	93.20	29.80	18.50	115.30			several blood proteins and enzyme	
	Ν	23	4	2	2			systems	
	Mean	0.12	0.03	0.02	0.25				
	SD	0.27	0.01	0.01	0.09				
Hg	Min	0.02	0.02	0.01	0.15	0.5–5	0.00	Toxic. Fish can contain unusual	
	Max	1.36	0.04	0.02	0.26			amounts	
	Ν	23	4	2	2				
	Mean	11.55	8.63	9.35	71.67				
	SD	14.26	2.87	4.31	21.17			Present in plants and animals; easil	
Pb	Min	3.60	5.90	6.30	50.00	20-300	0.51	absorbed and accumulates in	
	Max	79.60	12.40	12.40	92.30			different plant parts	
	Ν	23	4	2	2				

Table 4. As, Co, Cu, Hg and Pb (ppm) in agricultural soils and in living matter, compared with mean values in soils of the study localities. a [29]; b [30].

#### 4. Conclusions

Data from the hydrochemical literature as well as from current research on soil geochemistry indicate that large amounts of mine pollutants produced predominantly in the form of AMD have infiltrated soils and other environmental compartments of the KGR through ground- and surface waters, over several decades of gold mining. Analysis of the soils showed high levels of contamination for As and Co in ppm. The mean maximum of As ranged from (5.00–170.30) with the highest level found in the Krugersdorp site. The mean maximum of Co ranged from (46.00–102.30) with the highest level found in MMG. All of these values were well above the MAC recommended values, i.e., As (15–20) and Co (20–50). The mean maximum values for Pb (12.40–92.30), Cu (18.50–115.30), and Hg (12.40–92.30) content in surface soils of all four segments studied falls well within the MAC range for agricultural soils, i.e., Cu (60–150), Hg (0.5–5), and Pb (20–300). The major mediating influences on the behaviour of As, Co, Cu, Hg and Pb, as they enter the KGR largely in the form of acid mine drainage (AMD), are the geological substrate (mostly in carbonate form).

These pollutants can cause modifications to natural element cycling in the KGR- and adjacent soil environments. The fluxes of residual As, Co, Cu, Hg and Pb in soils from influent AMD that is available for plant uptake in KGR is considered to be determined largely by the nature of the underlying substrate (predominantly carbonate) and the level of treatment of decant from adjacent mining localities during any given season. The high As and Co contents found in most of the soils in our study areas provide a major motivation for proposing further investigation of the waters infiltrated by AMD contamination and comparing it to the soil values obtained to give a more comprehensive idea of the amount of PHE accumulation. Well-designed, quantitative research along these lines will enable the rehabilitation of metal-contaminated areas with appropriate indigenous species, allow identification of metal toxicities when they occur and allow for the effective regulation of metal emissions. This information is considered vital in the formulation of intervention measures such as mitigation, Acid mine drainage (AMD) neutralization, rehabilitation and soil amendment. Results from these kinds of studies would enable more informed decisions to be taken on site investigations, clean-up actions, and remedy selection. In accordance with the observations of DEAT [31], more research is required on the field impact of AMD on potentially receiving dolomitic (karst) environments and the re-activation of springs dried-up due to dewatering. Strategies should be evolved to utilize the storage potential of defunct/closed underground mine voids so as to optimally manage the generation of AMD and control its potential impact on the receiving surface and groundwater environments.

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