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Geochemical and Minerological Characterization of Mine Residue Deposits in the Komati/Crocodile Catchment, South Africa: an Assessment for Acid/Alkaline Mine Drainage

Novhe N. O.[1], Yibas B[2], Netshitungulwana R[3] and Lusunzi R[4]
Council for Geoscience, Environmental Geoscience Unit, 280 Pretoria Rd, Silverton, 0184, South Africa,
1.onovhe@geoscience.org.za, 2.byibas@geoscience.org.za,3.robertn@geoscience.org.za,
4.rlusunzi@geoscience.org.za

Abstract This study involved geochemical and mineralogical characterization of gold and coal mining wastes in the Komati/Crocodile river catchment area. The study reveals that Sabie-Pilgrim's Rest Goldfield is characterised by both potential acid-generating and non-acid generating mine residues, and this is attributed to variations in the mineralogy of source rocks. In the Barberton Greenstone Belt the majority of the mine residues show no potential to generate acid, but the field investigation revealed that old tailings deposits discharge acid drainage. The mine residues from the Kangwane Coalfield are classified as potential non-acid generating, whereas Ermelo Coalfield mine residue deposits are classified as potential acid-generating. The study conducted has been used to prioritise mine pollution hotspots at a catchment scale, for further detailed investigation and management.#

Keywords acid/alkaline mine drainage, mineralogy, mine residue deposits, tailings deposits

Introduction

Acid mine drainage (AMD) is a major environmental problem facing the South African mining industry. To guide development of an appropriate remediation scheme, a nation-wide mine drainage assessment is being conducted using a catchment area based approach. The results of the geochemical and mineralogical investigation of mine residue deposits for the assessment of the quality of the current mine drainage and its potential to generate acid/alkaline mine drainage in Komati-Crocodile river catchment area, situated in Mpumalanga Province, is the subject of this paper (fig. 1). The catchment borders on Mozambique in the east and on Swaziland in the south-east. The mine residue deposits which are the subject of this paper belongs to Sabie-Pilgrim's Rest Goldfield, Barberton Greenstone Belt, Kangwane and Ermelo Coalfields.

Material and methods

Fieldwork and sampling have been conducted to identify and characterise pollution sources in the area. Mine residue samples, such as tailings, waste rock and discard coal, were collected using handheld/truck-mounted auger and analysed by means of XRF analytical techniques for metal loadings, as well as XRD for mineralogical analysis. For XRF analyses samples were dried, crushed and milled to <75 μm. Simultaneous X-Ray Fluorescence Spectrometer (S-XRF) was used. For XRD analyses samples were scanned from 2 to 65° 2θ $\mathrm{Cu}_{\mathrm{K}\alpha}$radiation at a speed of 0.02° 2θ and generator settings of 40 kV and 35mA. Phase concentrations were determined as semi-quantitative estimates, using relative peak heights/areas proportions.In addition, acid base accounting tests have been conducted to estimate the samples potential to generate acid mine drainage. Seepages from mine residues were also collected using 100ml plastic bottles to assess the status of current mine drainage from the mine residue deposits. The seepage samples were filtered using 0.45 μm filter. Samples were acidified using 3M nitric acid (HNO_3) for analysis of cations. Analyses were done by means of ICP-MS and IC analytical techniques and the elements concentrations were compared to the South African water quality standard guidelines.

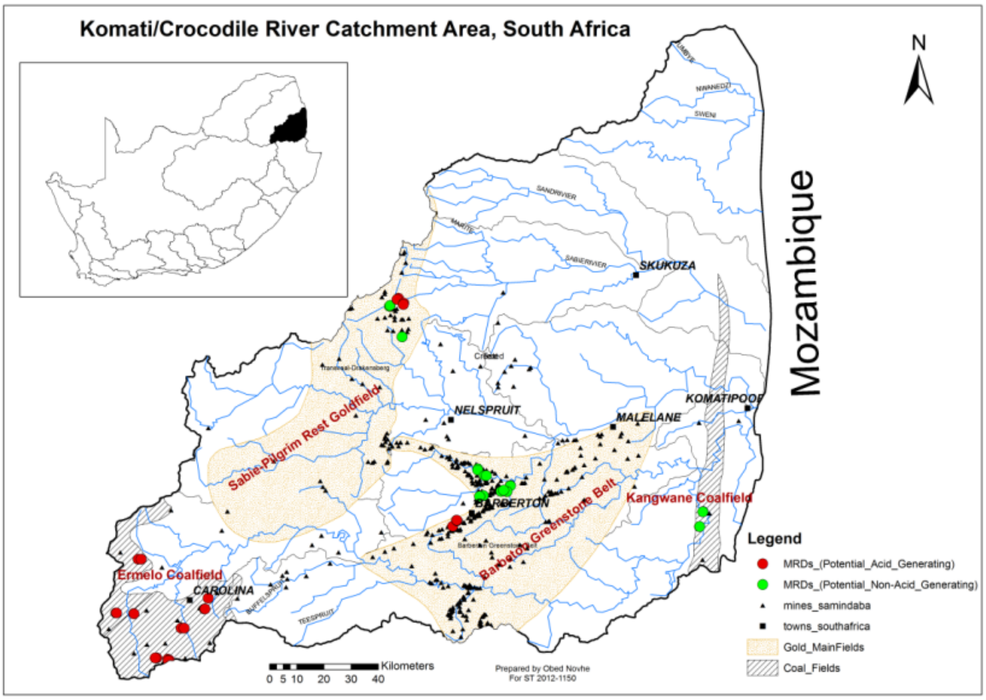

Fig. 1 *Distribution of mine residue deposits from the major mining gold and coal fields within Komati-crocodile primary river Catchment areas. In set shows the location of the catchment within South Africa.*

Results and discussions

Geochemical data

XRF results for major, minor and trace elements are presented in table 1. SiO_2 is a dominant oxide in the Sabie-Pilgrim's Rest goldfield (SPG) tailings (ranging from 61.99 – 91.45 wt.% at an average of 77.55 wt.%), followed by Fe_2O_3 and Al_2O_3 (in a range of 4.81 – 11.27; 1.78 – 6.82 wt.%, respectively). CaO, K_2O, MgO, MnO, TiO_2 and Cr_2O_3 also occur in lesser amount. Trace elements such as arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) occur in significant amount (table 1).

Predominant oxides in the Barberton Greenstone Belt (BGB) samples include: SiO_2 (52.63 - 71.63 wt.%, averaging at 61.82 wt.%) , Al_2O_3 (7.26 – 10.29 wt.%, averaging at 8.97 wt.%), Fe_2O_3 (3.87 – 10.46 wt.%, averaging at 7.01 wt.%) and MgO (3 – 14.60 wt.%, averaging at 6.85 wt.%). Other oxides that occur in lesser amount, in order of decreasing, include: CaO, K_2O, TiO_2, Cr_2O_3, MnO and P_2O_5 (in average of 3.62; 2.35; 0.43; 0.15; 0.14, and 0.06 wt. %respectively). Trace metals such as As, Cr, Cu, Ni, and Pb occur in significant amount (table 1).

Predominant oxides in the Ermelo Coalfield (EC) samples include: SiO_2 (17.30 – 62.32 wt.%, averaging at 34.33 wt.%), Al_2O_3 (3.71 – 14.82 wt.%, averaging at 8.35 wt.%), and Fe_2O_3 (1.28 – 10.81 wt.%, averaging at 3.37). Other oxides that are available in lesser amount include: CaO, K_2O, TiO_2, MgO, P_2O_5, MnO and Cr_2O_3(in average of 1.05; 0.80; 0.44; 0.30; 0.07; 0.02 and 0.01 respectively). In addition, As, Cr, Cu and Pboccur in significant amount (table 1).

Predominant oxides in the Kangwane Coalfield (KC) samples include: SiO_2 (23.20 – 47.11 wt.%, averaging at 34.49) and Al_2O_3 (6.03 – 13.66 wt.%, averaging at 10.18 wt.%). Other oxides that occur in lesser amount include: CaO, K_2O, MgO, TiO_2, P_2O_5, MnO, and Cr_2O_3 (in average 1.63; 1.29; 0.51; 0.05; 0.03; and 0.01wt.% respectively). Cr, Cu and Pb also occur in significant amount (table 1).

Mineralogical data

Mineralogical analyses by means of XRD on the samples show a wide variation of both primary and secondary minerals. For tailings, Jambor (1994) defined primary minerals as the ore and gangue minerals that were processed and deposited in an impoundment without any changes other than reduction in grain size by comminution. Secondary minerals refer to those that have been formed by processes that can lead to precipitation, such as evaporation, oxidation, reduction, dilution, mixing, and neutralization (Alpers et al. 1994). Secondary minerals include efflorescent sulphate salts as well metal oxide, hydroxide, hydroxy sulfate, and sulphide minerals.

In the Sabie-Pilgrim's Rest Goldfield (SPG), tailings SPG 1 and 2 are comprised of the following primary minerals: quartz (SiO_2), mica [$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$], Plagioclase ($NaAlSi_3O_8$ – $CaAl_2Si_2O_8$), pyrite (FeS_2), Pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), Microcline ($KAlSi_3O$) and Kaolinite [$Al_2Si_2O_5(OH)_4$](in average 74; 10.6; 3.6; 2.3; 2; 1.5 and 1.2 wt.% respectively). The top layers of the tailings is dominated by the following secondary minerals: Jarosite $KFe^{3+}{}_3(SO_4)_2(OH)_6$ (in average 4.1 wt.%), Gypsum ($CaSO_4 \cdot 2H_2O$) (in average 1.9 wt.%) and Copiapite $Fe^{2+}Fe^{3+}4(SO_4)6(OH)_2 \cdot 20H_2O$ (in average 3.5 wt.%). Pyrite is a major acid producing mineral. Tailings dump SPG1 is associated with black reef quartzite mineralization, whereas tailings SPG2 is associated with Archean granite mineralisation. However, alumina silicate minerals such as Kaolinite, mica and plagioclase are also considered as potential acid neutralizers, but to a much lesser extent and reaction rate compared to carbonate minerals such as calcite (Jambor 2003).Mineral such as quartz on the other hand had no potential of acid neutralization, and this is mainly due to its physical property (hardness) (Kwong 1993). The secondary minerals result from oxidation of sulphides, and they precipitate during evaporation of acidic, iron, and sulphate-rich water within mine waste material and store acid generated by oxidation process. Although most of AMD from sulphide-bearing geological formations are from oxidation of sulphide minerals, the dissolution of soluble and less soluble iron sulphate minerals also contribute to the acidity of drainage (Lapakko 2002). The presence of jarosite, an iron-sulfate mineral, in soil or in mining waste is an indicator of acidic, sulphate rich conditions. Tailings dumps SPG 3 & 4 are comprised of quartz and Dolomite [$CaMg(CO_3)_2$] as major mineral assemblages (in range of 57.5 and 24.1 wt.% respectively). The presence of dolomite as a major acid consuming mineral is associated with the primary mineralisation host rocks i.e. malmani dolomite. Other primary minerals that are potential acid consuming include: pyrophyllite, mica, and plagioclase. Gypsum and geothite [$Fe^{3+}O(OH)$] also present as major secondary minerals. The absence of jarosite in SPG 3 & 4 could be attributed to less acidic conditions in the tailings due to high concentrations of carbonates i.e. dolomite.

In the Barberton Greenstone Belt (BGB), the samples are mainly comprised of quartz (in average 45 wt.%), talc (in average 31wt.%). Other minerals that occur in considerable amount include: dolomite (average 10wt.%), kaolionite (11.09 wt.%), amphibole (9.3 wt.%) , plagioclase (4.2 wt.%), k-feldspar (2.4 wt.%) and calcite (2%). Calcite and dolomite are the important neutralizing minerals. Secondary minerals include magnesite (average 11.72 wt.%), gypsum (2.9 wt.%) and hematite (2.5 wt.%). The absence of sulphate mineral such as jarosite in this regard, also indicates the presence of less acidic conditions due to abundant acid consuming minerals.

The samples in the Ermelo Coalfield (EC) are comprised of quartz, kaolinite and pyrite (in average of 42.6; 35.6 and 9.14 wt.% respectively). Other primary minerals include: calcite, k-feldspar and mica (in average of 6.8; 5.3; and 3.7 respectively).Calcite is the important buffer mineral, whereas pyrite is the primary acid producing mineral. Secondary minerals include: gypsum (6.2 wt.%), hematite (2.75 wt.%) and jarosite (3.1 wt.%).

In the Kangwane Coalfield (KC), the samples are comprised mainly of quartz (in average 48.75 wt.%), palygorskite (12.5 wt.%) kaolionite (in average 11.3 wt.%), mica (8.5 wt.%), calcite (5.5 wt.%), dolomite (2,3 wt.%), and k-feldspar (3 wt.%). Secondary minerals include: jarosite and hematite (in average 4.7 and 4 wt.% respectively).

Acid base accounting (ABA)

Fig. 2shows subdivision based on acid potential (AP) and neutralizing potential (NP) of the mine residues samples collected at different mining sites in the Komati/Crocodile catchment areas. Sabie-Pilgrim's Rest goldfield (SPG) samples have both potential to generate acid and a potential to neutralize acid, depending on the mineralisation of the source rocks. SPG1 and SPG2 are characterised by high AP than NP, and their net potential ration is less than 1 (NPR<1) (Fig.2). Their AP ranges from 15.9 kg $CaCO_3$/ton to 31.3 kg $CaCO_3$/ton, whereas NP ranges from -6.5 kg $CaCO_3$/ton to 2.9 kg $CaCO_3$/ton. Based on the geochemical results samples contain considerable amount of sulphur (in a range of 0.5 to 1 wt.%), consistent the mineralogical data, which indicated the presence of pyrite as a primary acid producing mineral and jarosite as a secondary acid-generating mineral. Field observation, onsite test and laboratory results also revealed that these mine residues discharges acidic leachate with considerable concentration of SO_4, Fe, Mn,Al, Co,As, exceeding the limit as per South African water quality standard (table.2). However, the mine dumps that are associated with mineralisation within dolomite (SPG 3 and SPG 4)do not leach any drainage. Based on ABA results these MRDs have more NP than AP, and their NPR>2; and hence they are less likely to generate acid. Their AP ranges from 0.4 kg $CaCO_3$/ton to 40.7 kg $CaCO_3$/ton, whereas NP ranges from 6.7 kg $CaCO_3$/ton to 149 kg $CaCO_3$/ton. This is also confirmed by high paste pH which ranges from 7.7 -7.9.#

Barberton Greenstone Belt (BGB) Samples have high neutralisation potential than acid potential, and they plot at NPR>2 (fig.2). Net neutralisation potential is considerably high, ranging from 65 - 118 kg $CaCO_3$/ton. Paste pH is greater than 8, which indicates presence of buffer minerals. However, fieldwork observation, onsite analyses and laboratory results revealed that the newly established dumps leach out alkaline drainage, whereas the oldest dumps leach out acid water (table.2). This could be attributed to the rate of mineral reactivity over time. #

The classification criteria used based on the calculated parameters, such as NPR, NNP and percentage of sulphide sulphur indicate that samples from Kangwane Coalfield (KC) are potential non-acid generating. The sample have more neutralising capacity than acid generating capacity, and their NPR>2 (fig. 2).Old and newly established mine pits are characterised by very alkaline water, which shows a strong buffering capacity of the minerals contained in the coal spoils/discard.

Based on acid base accounting results, Ermelo Coalfield (EC) MRDs are classified as potential acid generating with most of the samples plot at NPR<1field (fig. 2). The acid potential of all the samples exceeds the neutralization potential. The acid potential (AP) ranges from 12.6 kg $CaCO_3$/ton to 221 kg $CaCO_3$/ton, whereas neutralization potential (NP) ranges from -5.9 kg $CaCO_3$/ton to 19 kg $CaCO_3$/ton. The sulphur percentage ranges from 0.9 to 8%, averaging at 2%.

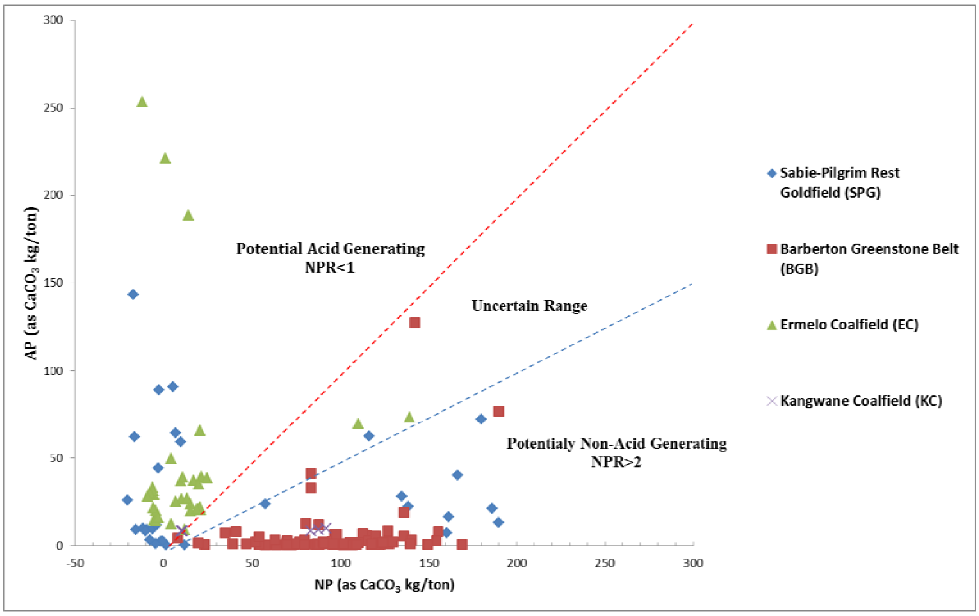

Fig. 2 *Acid potential and Neutralisation potential graph indicating areas of potential acid generating, uncertain range and potential non-acid generating for the mine residues.*

Conclusions

In this study mineralogy and bulk geochemical analyses that were undertaken showed a clear variation in chemistry of the samples and this conforms to the likely leachate from the samples as determined by static geochemical prediction techniques and the field/laboratory analyses. This has enabled prioritization of pollution hotspots at a catchment scale, for further detailed investigation and management.

Sabie-Pilgrim's Rest Goldfield is characterized by both potential acid-generating and non-acid generating mine residues, and this is attributed to variations in the mineralogy of host rocks. Fe, Mn, Al, As, Cr, Cu, Ni, Pb will probably be potential pollutants that may impact on the quality of water, provided the physic-chemical conditions prevailing at the site allow leaching of these metals in significant amount. Barberton Greenstone Belt mine residues are classified as potential non-acid generating, and this is attributed to the presence of considerable amount of buffer mineral species than acid generating species. However, some of the oldest mine residues leach out acid leachate and this could be attributed to the rate of mineral reactivity. The key leachable metals include As, Cr, Cu, Ni, Pb. In the Kangwane Coalfield, the anthracite mine pits (both old and new) are characterized by very alkaline water, which shows a strong buffering capacity of the minerals contained in the coal spoils/discard. This is also confirmed by acid base accounting results that indicate that the samples have high neutralization potential than acid potential, and hence the samples are less likely to generate acid. In the Ermelo Coalfield, both active and abandoned mines are currently generating acid mine drainage and they show the potential to continue generating. The acid mine drainage manifests itself in a form of seepages as well as run-off from mine residue deposits, such as discard coal dumps and slimes. Fe, Al, Mn, As, are the potential contaminants.

There is a need to conduct kinetic test to ascertain the rate of reaction, to determine the quality of leachate with time. In addition, there is an urgent need to carry out proper management and/or rehabilitation plan to minimise environmental impacts/contaminations that could result into cross border problems.

Table 1 Selected XRF major (wt. %) and trace elements (mg/kg) concentrations of the samples

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	P_2O_5	Cr_2O_3	As	Co	Cr	Cu	Ni	Pb	V	Zn
SG-1	78.41	0.64	6.28	6.74	0.03	0.43	0.67	1.88	0.06	0.01	365	15	117	99	29	137	77	44
SG-2	78.34	0.17	4.65	6.76	0.04	1.62	2.09	1.50	0.05	0.01	2244	16	56	243	19	94	27	30
SG-3	91.45	0.08	1.78	4.81	0.70	0.14	0.13	0.27	0.04	0.01	132	26	119	177	221	40	40	93
SG-4	61.99	0.48	6.82	11.27	0.25	3.44	5.02	1.36	0.07	0.02	1558	29	147	40	73	30	99	164
BG-1	71.63	0.43	9.75	3.87	0.11	3.00	2.44	3.42	0.08	0.04	230	14	293	26	81	23	57	86
BG-2	66.05	0.40	8.67	5.55	0.13	4.82	2.85	2.21	0.06	0.14	264	20	1031	35	161	8	112	61
BG-3	60.19	0.43	9.42	8.39	0.17	8.45	4.19	1.72	0.07	0.15	632	45	1222	49	354	55	132	107
BG-4	52.63	0.37	7.26	10.46	0.15	14.60	3.03	1.47	0.04	0.21	1844	72	1651	98	871	57	106	132
BG-5	59.60	0.51	8.45	7.36	0.14	4.93	5.21	2.19	0.06	0.23	1600	30	1564	232	322	35	118	77
BG-6	60.82	0.44	10.29	6.45	0.14	5.28	4.00	3.12	0.07	0.13	527	28	913	89	242	22	90	53
EC-1	49.55	0.25	3.71	2.09	0.00	0.06	0.69	0.52	0.05	0.01	19	7	47	23	10	17	46	4
EC-2	23.39	0.53	10.42	2.39	0.02	0.40	1.67	0.51	0.04	0.01	9	10	52	22	21	25	48	21
EC-3	21.37	0.37	7.17	2.31	0.01	0.18	1.93	0.47	0.03	0.00	8	16	41	16	33	17	43	15
EC-4	47.87	0.32	7.43	10.81	0.03	0.22	0.52	0.91	0.04	0.01	35	39	87	17	52	34	63	26
EC-5	38.05	0.60	11.45	2.90	0.01	0.37	0.77	0.92	0.05	0.01	6	10	61	17	22	18	61	35
EC-6	26.93	0.52	9.18	1.79	0.01	0.33	1.03	0.55	0.13	0.01	7	6	43	13	19	12	44	12
EC-7	62.32	0.70	14.82	4.14	0.04	0.60	0.54	2.70	0.11	0.01	<4	16	77	21	30	29	91	71
EC-8	17.30	0.26	4.60	2.59	0.03	0.24	1.46	0.22	0.04	0.01	6	19	83	19	34	17	71	25
EC-9	22.19	0.40	6.39	1.28	0.01	0.29	0.86	0.40	0.14	0.00	5	8	37	8	23	8	36	9
KC-1	47.11	0.38	9.14	1.82	0.02	0.63	0.68	2.22	0.03	0.01	<4	15	45	10	28	22	48	31
KC-2	23.20	0.30	6.03	1.78	0.01	0.72	1.30	0.79	0.02	0.00	<4	24	29	8	31	13	33	11
KC-3	37.47	0.74	13.66	2.46	0.04	0.88	2.75	1.25	0.06	0.01	<4	9	51	22	24	19	53	31
KC-4	30.19	0.63	11.88	2.07	0.03	0.63	1.81	0.90	0.09	0.01	<4	8	46	14	22	16	45	21

***Table 2** Analytical data for selected seepage water samples from the mine residue deposits (EC as mS/m and other constituents as mg/L)*

Sample ID	pH	EC	As	Fe	Al	Cr	Mn	Cu	Zn	SO_4
	6-9*	0-70*	0.01*	0.1*	0.15*	0.05*	0.05*	0-1*	3*	200*
SPG-1	2.6	610	1.57	354.8	43.61	0.15	1.1	1.23	0.58	2,701
SPG-3	8.3	89	1.26	0.14	0.25	<0.005	<0.01	<0.02	<0.3	252
BGB-1	7.8	160	3.63	2.98	0.11	<0.005	0.32	3.87	0.54	2,947
BGB2	8.1	180	0.52	<0.1	1.49	<0.005	44.99	<0.02	<0.3	7,860
BGB3	2.6	610	2.76	486.61	32.91	0.79	23.19	6.75	11.25	6,393
EC-1	2.4	1017	0.98	3,307.23	820	1.15	264.62	2.12	7.38	21,493
EC-2	3	170	0.05	2.67	3.31	<0.005	42.33	<0.02	<0.3	1,244
EC-3	3	300	0.05	<0.1	1.35	<0.005	0.4	<0.02	<0.3	4,404
EC-4	5.1	100	0.05	0.45	<0.05	<0.005	0.11	<0.02	<0.3	20
KC-1	7.6	320	0.05	<0.1	<0.06	<0.005	<0.01	<0.02	<0.3	169
KC-2	8.9	270	0.05	<0.1	<0.07	<0.005	<0.01	<0.02	<0.3	412

***** *The South African Water Quality Guidelines for Domestic Water Use (DWAF, 1996)*

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