Regional spatial distribution of elements in the Vaal primary catchment using stream sediments geochemistry: Implication on anthropogenic and geogenic source

Netshitungulwana, K.T.R[1], B. Yibas[2], C. Gauert[3], D. Grobbelaar1, R. Lusunzi[1]

[1]*Council for Geoscience, 280 Pretoria Rd, Silverton, 0184, South Africa;*

[2]*Faculty of Natural and Agricultural Sciences, University of the Free State, 205 Nelson Mandela Drive, Parkwest, Bloemfontein, 9300;*

[3]*Geological Survey of Saxony-Anhalt, Department of Applied Geoscience, 38 Rothener Street, 06118 Halle (saule), Germany*

Abstract

The aim of this paper is to highlight the spatial distribution of major and trace element contaminants in the Vaal Primary Catchment (VPC). The VPC is the largest primary catchment in South Africa, occupying the central area of the country. The VPC is bordered to the east by Eswatini and to the west by Kuruman in the Northern Cape. To the north-west, the VPC is bordered by Botswana and the Limpopo and Olifants catchments. To the south-east, the VPC is bordered by Lesotho and to the south-west by the Orange catchment. The VPC is by far the most important in South Africa because it contains the country's most economic mineral resources, such as gold and coal, not only in Gauteng Province but also in the mining districts of the Free State (Welkom) and Northern Cape (Sishen and Postmasburg). The paper examines whether the source of the contaminants can be attributed to mining or other sources.

A total of 245 stream sediment data points were collected, representing the upper, middle, and lower VPC. The composite sediment samples were collected at a fraction of >2 mm, dried at room temperature, crushed, and ground to a fraction of -75 µm. The stream sediment samples were analysed for major and trace chemical elements by XRF. The upper Vaal results indicate that the Witwatersrand basin anomalies are characterised by elevated uranium (U) and chalcophile elements, with maximum arsenic (As) concentrations of 25 mg/kg. It is also worth noting that the coalfields around Ermelo, Bethal, Secunda, and Springs in the upper Vaal are characterised by elevated chalcophile and rare earth elements. The middle Vaal shows elevated U and chalcophile elements in areas of major gold mining in the towns of Klerksdorp, Bothaville, and Welkom, with a maximum As concentration of 334 mg/kg in the middle Vaal, which exceeds the threshold for sediment quality guidelines even at extreme concentrations of 33 mg/kg.

The elemental loadings of the stream sediments indicate contributions from either geogenic or anthropogenic sources. The lower Vaal indicates low metal concentrations. Therefore, the elevated concentrations can be attributed to anthropogenic sources due to mining. The areas of anthropogenic influence are supported by sulfate concentrations that are above 600 mg/L, exceeding South African water quality guidelines. The geogenic source may be associated with the undeveloped resources, which include but are not limited to the U-fields south of Bloemfontein and the ultramafic signatures in the lower Vaal.

Introduction

The Vaal River drainage basin covers an area of approximately 194249 km² and includes parts of the Northern Cape, North West, Mpumalanga, and Gauteng provinces, as well as much of the Free State. The Vaal catchment is the largest of nine primary catchments in southern Africa and drains most of the Kaapvaal craton (Erickson et al. 2011). Almost all the area south of the Vaal River itself is underlain by rocks of the Karoo Supergroup, but much of the northern Vaal consists of pre-Karoo rocks, mainly the Transvaal Supergroup and the Witwatersrand Basin, over which the tributaries flow in a southerly direction (Fig. 1–3). The Karoo Supergroup is a thick sequence of sedimentary rocks deposited between 300 and 180 Ma ago (Cairncross 2001; Banks et al. 2011). The Vaal River Basin is an economically important area in the interior of South Africa (SA), where a wide range of commodities such as gold and uranium, coal, and industrial, domestic, and intensive agricultural activities are mined (Masindi and Abiye 2018). The upper Vaal covers part of four provinces: Gauteng, Free State, Mpumulanga, and North West. The main rivers are the Vaal and its tributary, the Wilge. Other major tributaries are the Klip (Free State), Liebenbergsvlei, Waterval, Suikerbosrand, Klip (Gauteng), and Mooi rivers. The Middle Vaal lies in the central part of South Africa, in the Free State and North West Provinces. The Middle Vaal lies between the Upper and Lower Vaals and borders the Crocodile West, Marico, and Upper Orange areas. The main tributaries are the Skoonspruit, Rhenoster, Vals, and Vet rivers. The lower Vaal lies in the North West, Northern Cape, and Free State provinces. The lower Vaal borders Botswana to the north. In the southeast, the Vaal River is the only major river, and the Harts River is the only relevant tributary. Most of the region lies within the catchment area of the Molopo River, a tributary of the Orange River.

This paper investigates the spatial distribution of elements in the VPC to better understand the sources of elevated metal levels in stream sediments and water quality, as well as to determine whether the contaminant source can be attributed to mining or other sources.

Methodology

The spatial distribution of the 245-stream sediment (0–20 cm depth) and surface water samples were collected at the VPC

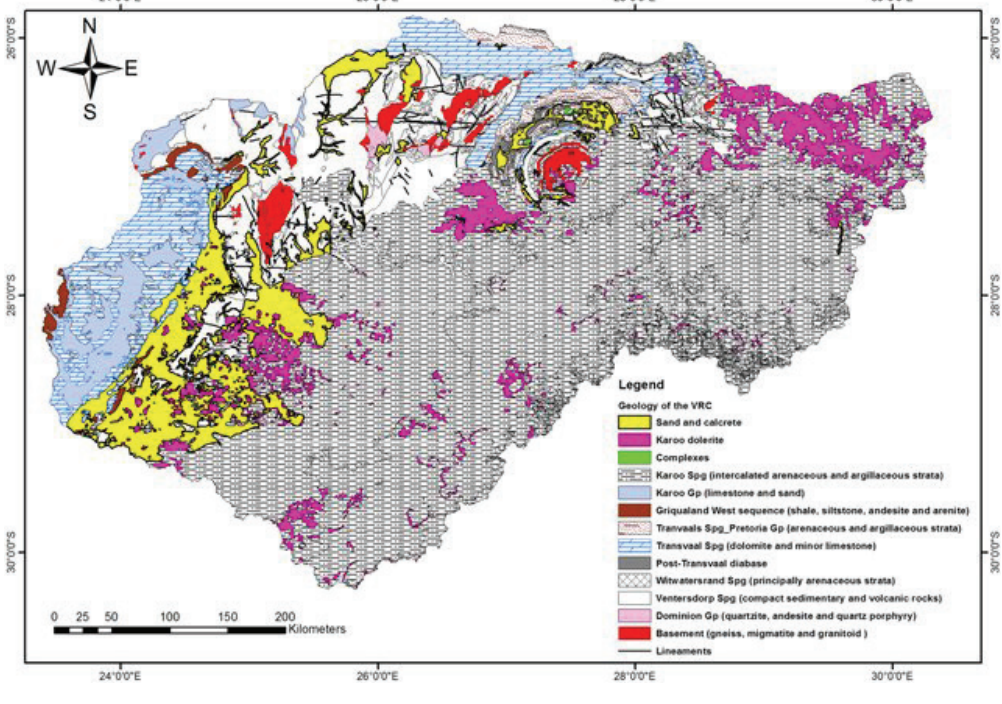

Figure 1 Simplified geological map of the Vaal Primary Catchment, South Africa (after Masindi and Abiye, 2018)

(Fig. 2–3). Some leachate samples from the mine tailings were also collected and compared to assess the quality of the water. The stream sediment sampling density was three samples per 10 km2. A composite sediment sample was collected at several locations, approximately 5–10 points, within approximately 50m. The minus 2mm fraction was collected as a bulk sample. The sample was later homogenized, and a bulk sample of approximately 5 kg was collected and stored in the polyethylene bag. The fine to clayey sediments collected as this fraction are where most metals are adsorbed (Salminen et al. 2005; Alexakis 2008; Netshitungulwana et al. 2013; Netshitungulwana 2022). The crusted sample was then crushed using a 3x4-inch jaw crusher. The samples were dried at room temperature of 27 °C to prevent the clay component of the sample from crusting after drying. The samples were then split in a rotary splitter and ground to < 75 µm. The samples were analysed for chemical composition by an X-ray fluorescence spectrometer (XRF). Water samples were analysed by inductively coupled mass spectrometry (ICP-MS).

Results

The Principal Component Analysis (PCA) results for the stream sediments indicate five groupings from factor 1 to 5 as follows: F1: As, Ce, Mo, Nd, Ni, Th, U, Y, and Yb; F2: Cu, Pb, Se, Ta, Tl, Zn; F3: Ga, Nb, Rb; F4: Hf, Zr, V; F5: Ge, W. It is evident that the elements listed in each of the five groupings are highly positively correlated (with R2 > 0.6) and spatially distributed within the VPC area. Table 1 shows that the highest concentrations of elements are mainly located in the middle Vaal catchment, such as samples MV18, 67, and 70. This area includes the major Au-U ores (Witwatersrand reefs of the Central Rand) mining towns of Klerksdorp and Welkom. The main distribution of elements in the region is represented by F1 and F2 factor loadings. Gold mining in the Witwatersrand Basin, including upstream of the Upper Vaal, may have contributed to the enrichment of these elements in the region. The highest concentrations of Pb, Cu, and Zn, as shown in Table 1, suggest that gold is associated with sulfide mineralization, which is above 2 wt.% for the chalcophiles listed. Surface water quality, where seepage

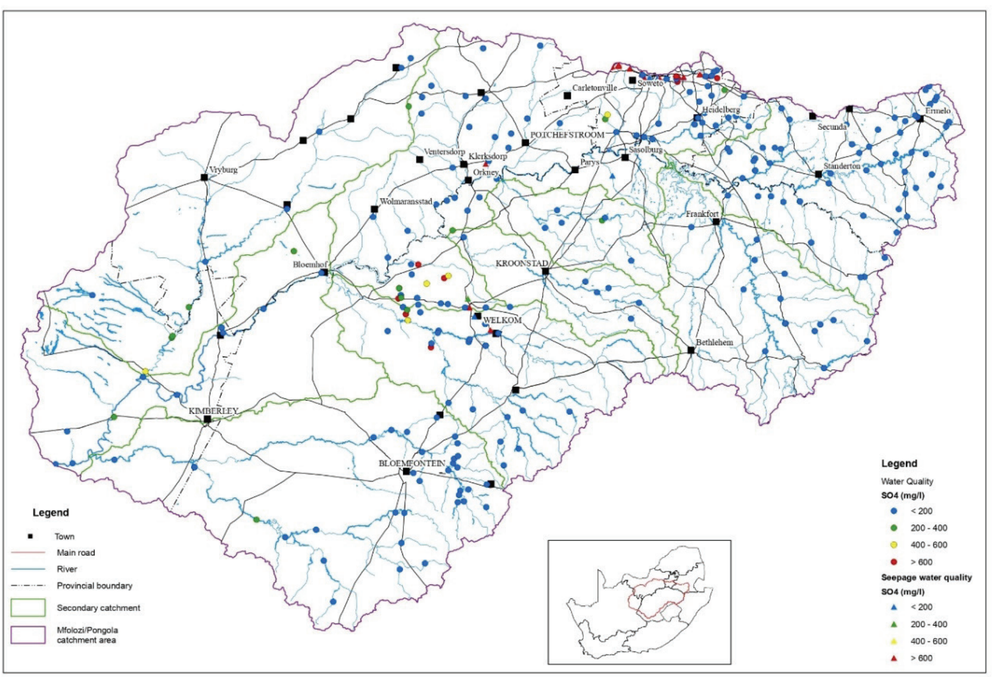

***Figure 2** Spatial distribution for SO42- on stream and seepage water quality in the Vaal Primary Catchment*

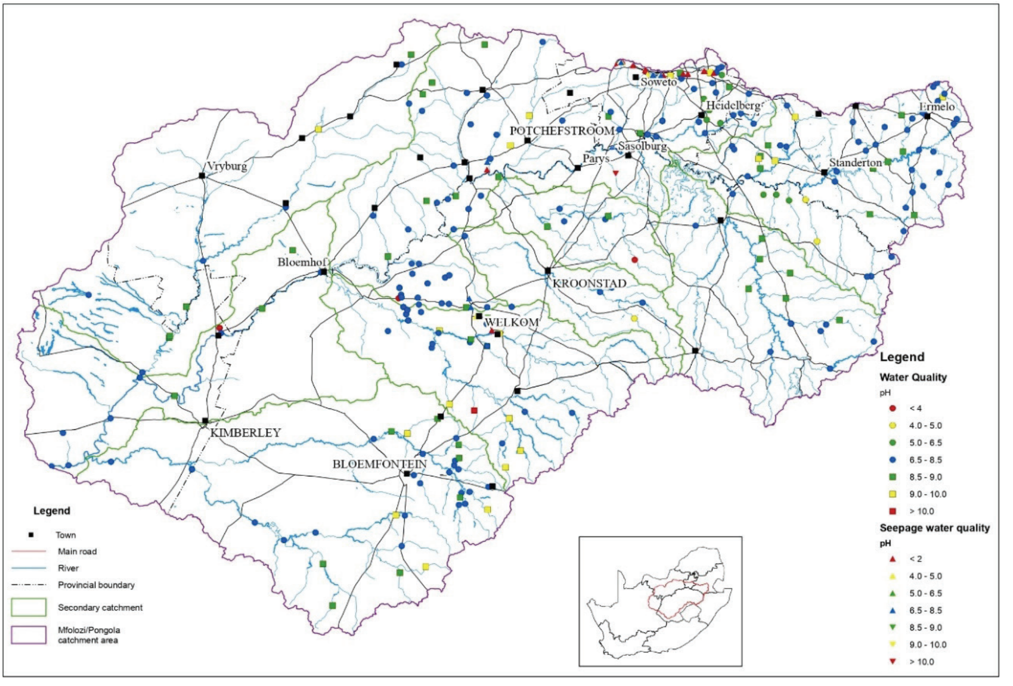

Figure 3 *Spatial distribution of pH on stream and seepage water quality of the Vaal Primary Catchment*

is possible, indicates areas of mining activity and elevated concentrations of elements that exceed South African water quality guidelines. This is evident in the upper and middle Vaal where mining occurs, such as Johannesburg, Klerksdorp, and Welkom, where sulfate (SO42-) concentrations exceed 600 mg/L (Fig. 2). Fig. 3 shows a similar trend in the spatial distribution of pH. Fig. 4 shows a holistic representation of the geo-environmental concerns in the VPC catchments. The sites are located in the upper, middle, and lower Vaal. As a result, Fig. 4 highlights the areas of the VPC with geo-environmental impacts.

Conclusions and Recommendations

The presence of sulfides may be the primary cause of the elevated element concentrations in stream sediments. The chalcophiles associated with sulfides have concentrations up to 334 mg/kg As, 49800 mg/kg Cu, 24127 mg/kg Pb, and 24487 mg/kg Zn, which are above the extreme effects of the sediment quality guidelines, with the maximum being 33 mg/kg As, 820 mg/kg Zn, 149 mg/kg Cu, and 250 mg/kg Pb (MacDonald et al. 2000). The higher concentrations of these elements downstream of the mining area can be attributed to the anthropogenic factors downstream of the mines (Fig. 4). The contribution of mining is also evidenced by higher sulfate concentrations, which exceed the SA Water Quality Guidelines and are mainly distributed in the mining region.

Acknowledgements

The authors would like to thank the Council for Geosciences for all the support they have provided.

References

Alexakis, D (2008) Geochemistry of stream sediments as a tool for assessing contamination by Arsenic, chromium, and other toxic elements: East Attica region, Greece. European Water 21/22: 57–72.

Banks, VJ, Palumbo-Roe B, Van Tonder D, Davies J, Fleming C, Chevrel S (2011) Conceptual models of Witbank coalfield, South Africa, Earth observation for monitoring and observing Environmental and Social impacts of mineral resource exploration and exploitation. Project no: 244242, Theme 6, Topic ENV.2009.4.1.3.2.

Table 1 Static Test Result

	Min	Max	Median	Average	Stdev	Mean+Sdev	Mean+2Stdev	Valid n
As	1,1	334,0	4,0	9,5	24,6	34,1	58,8	245
Ce	10,0	472,0	54,0	63,1	45,6	108,7	154,3	245
Cu	5,2	49800,0	28,0	239,6	3179,4	3419,0	6598,4	245
Ga	1,4	26,0	11,5	11,3	4,5	15,8	20,3	245
Ge	0,5	3,0	1,0	1,2	0,3	1,6	1,9	245
Hf	1,4	16,0	6,5	6,6	2,7	9,3	12,1	245
Mo	2,0	16,0	2,0	2,2	1,1	3,3	4,4	245
Nb	1,0	19,0	7,9	8,0	2,8	10,8	13,7	245
Nd	7,7	167,0	23,0	25,7	15,4	41,1	56,4	245
Ni	5,4	1625,0	39,0	70,3	149,9	220,2	370,1	245
Pb	2,4	24127,0	15,0	119,9	1540,3	1660,2	3200,6	245
Rb	2,0	120,0	47,0	50,6	24,8	75,4	100,3	245
Se	1,0	208,0	1,0	1,9	13,3	15,2	28,4	245
Th	2,1	82,0	5,3	6,2	5,5	11,8	17,3	245
Tl	3,0	60,0	3,0	3,2	3,6	6,9	10,5	245
U	2,0	993,0	2,1	8,8	64,2	73,1	137,3	245
V	7,2	434,0	89,0	98,1	51,7	149,9	201,6	245
W	3,0	9,9	3,0	3,1	0,6	3,7	4,3	245
Y	2,4	273,0	18,0	19,8	18,3	38,1	56,4	245
Yb	1,6	29,0	3,0	3,4	1,8	5,2	7,0	245
Zn	8,8	24487,0	52,0	181,4	1567,0	1748,4	3315,4	245
Zr	6,2	562,0	196,0	205,3	84,3	289,6	373,9	245

Eriksson, PG, Hatting PJ, Alterman W (1995) An overview of the geology of the Transvaal Sequence, the Bushveld Complex, South Africa. Mineralium Deposita 30, 98–111.

Masindi, K and Abiye T (2018) Assessment of natural and anthropogenic influences on regional groundwater chemistry in a highly industrialised and urbanised region: a case study of the Vaal River, South Africa. Environmental Earth Science, 77: 722pp.

MacDonald, DD, Ingersoll CG, Berger TA (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology 39:20–31.

Netshitungulwana, R, Yibas B, Novhe ON, and Motlakeng, T (2013). Stream sediment geochemistry of the areas impacted by mining around Emalahleni (formerly known as Witbank), South Africa: Fingerprinting AMD potential point sources. In: Brown, A., Figueroa, L., Wolkersdorfer, Ch., (Eds). Reliable Mine Water Technology. Denver, Colorado, USA (Publication Printers) I: 1–778.

Netshitungulwana KTR, (2023). Geochemical and mineralogical characterization of the lithological units of the geodehoop colliery in the Witbank coalfield to fathom the source and the receptor of metals in the riet-olifants catchment, South Africa. PhD Thesis, University of the Free State, South Africa. https://scholar.ufs.ac.za/items/10675432-bc32-4586-a545-aa00a890ce5a.

Netshitungulwana R, Yibas B, Novhe ON, Motlakeng T (2013) Stream sediment geochemistry of the areas impacted by mining around Emalahleni (formerly known as Witbank), South Africa: Fingerprinting AMD potential point sources. In: Brown A, Figueroa L, Wolkersdorfer Ch (eds) Reliable Mine Water Technology. Denver, Colorado, USA (Publication Printers), I: 1–778.

Salminen, R, Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W, Duris M, Gilucis A, Gregorauskiene, V, Halamic J, Heitzmann P, Lima A, Jordan G, Klaver G, Klein P, Lis J, Locutura J, Marsina K, Mazreku A, O'Connor PJ, Olsson S, Ottesen RT, Petersell V, Plant JA, Reeder S, Salpeteur I, Sandström H, Siewers U, Steenfeldt A, Tarvainen T (2005). FOREGS Geochemical Atlas of Europe, Part 1 – Background information, methodology and maps: Geological Survey of Finland, Espoo, 525p.

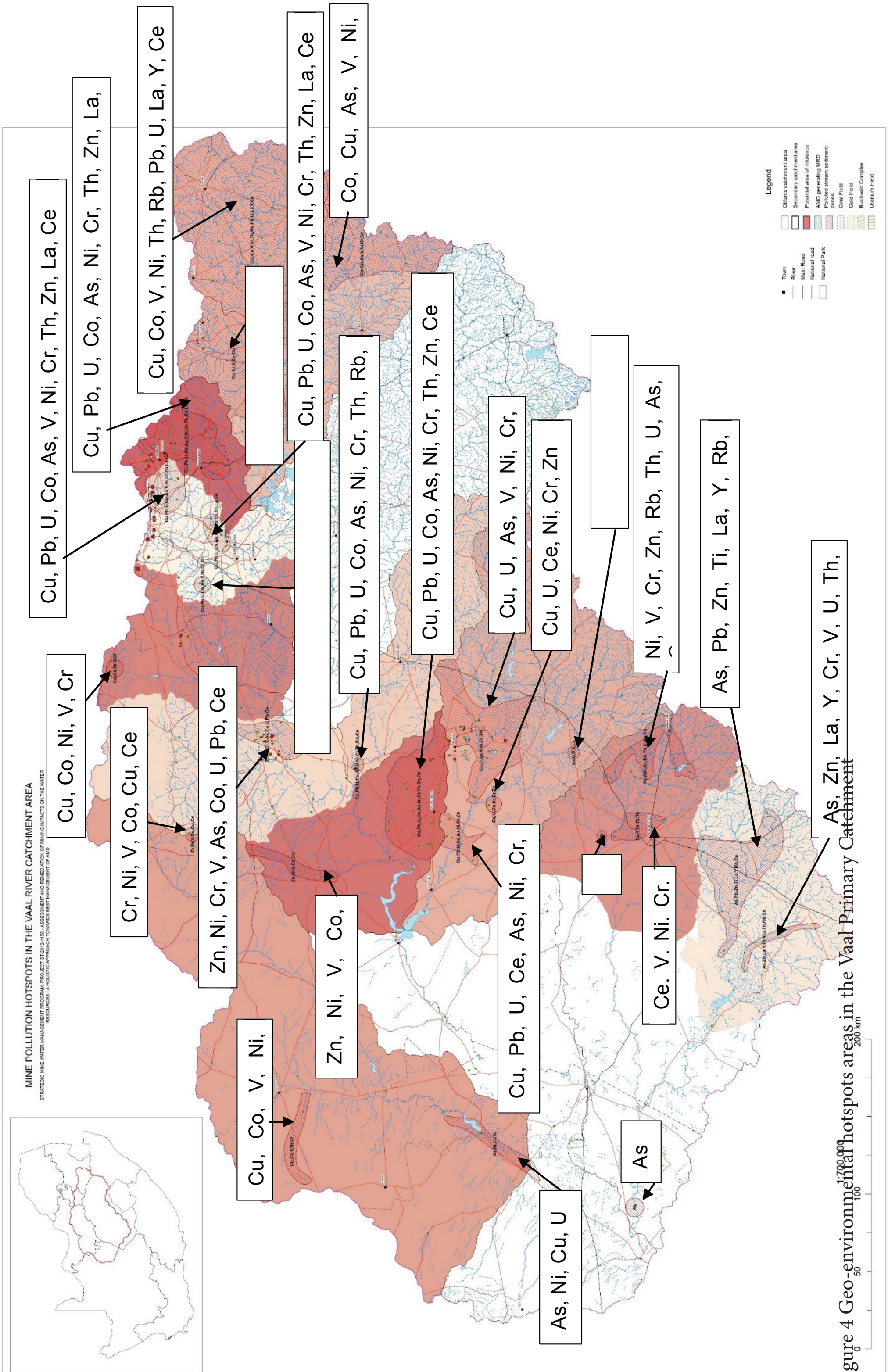

Figure 4 Geo-environmental hotspots areas in the Vaal Primary Catchment