

Original Research

Assessment of Heavy Metal Pollution in the Blyde and Steelpoort Rivers of the Olifants River System, South Africa

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Abstract

The Olifants River System has been subjected to prolonged and cumulative ecosystem stress as a result of human activities such as mining, agriculture, industry and human settlements in the catchment. The objectives of the study were to assess pollution in the water and sediment by seven heavy metals and possible sources of pollution in two major tributaries of the Olifants River: the Blyde and Steelpoort rivers. The mean concentrations of the seven heavy metals in the water were low. The mean concentrations in the sediments were very high in both rivers. The results showed high levels of As and Mn in the Blyde River, and Cr, Fe, Mn and Zn in the Steelpoort River. The As and Mn in the Blyde could be from fertilizers, pesticides and other agricultural products, and Cr, Fe, Mn and Zn in the Steelpoort could be mainly from mining and agricultural discharge. The sediment analyses indicated a highly significant difference between the two rivers with the exception of As and Pb. The results of the enrichment factor (EF) and geo-accumulation index (I_{geo}) indicated pollution by Mn and Cr in the Blyde, and Cr, Fe, Mn, Ni and Zn in the Steelpoort. Thus, the results showed that there was a greater accumulation of heavy metals in the sediments of the Steelpoort than in the Blyde. The study demonstrates the need for a holistic approach to monitor pollution in the Steelpoort and a comprehensive strategy to prevent health risks in humans – especially communities that rely on the river for water and food.

Keywords: enrichment factor, geo-accumulation index, heavy metal pollution, sediment quality

Introduction

Globally, freshwater ecosystems have been subjected to several types of pollution mainly from anthropogenic activities such as mining, agriculture and industry [1-3]. In addition, urbanization and other human activities are

contributors of pollution in water bodies [4]. Among the most serious water pollutants are heavy metals, which can have deleterious effects on aquatic organisms and humans, even at trace concentrations [5-7].

Heavy metals are easily adsorbed to sediments, which can act as a sink and secondary source of these contaminants in water and aquatic biota [8]. Heavy metals are known for their toxicity and persistence in the environment [9]. Metals also have the tendency

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to bio-accumulate in living tissues, such as fish, to concentrations that can compromise the normal physiological processes of these organisms and those that feed on them such as humans [10].

South Africa is experiencing a steep increase in water demand with three major sectors driving the demand, agriculture, municipal and industrial sectors. The Olifants River is one of the major river systems in South Africa. It provides water for industrial, agricultural and domestic use. However, due to the various activities in its catchment, the river has turned out to be one of the most polluted rivers in the country [11]. Many of the impoundments and tributaries of the river's system are said to be contaminated with heavy metals, inorganic nutrients such as sulphates and nitrates from agricultural fields, mine drainage and wastewater treatment plants [12].

The Blyde and Steelpoort rivers are important tributaries of the Olifants [13]. The Blyde is known for its continuous flow and good water quality and provides water mainly for agricultural and domestic purposes [14]. The Steelpoort has been impacted by anthropogenic activities in the catchment – especially mining (e.g., ferrochrome and platinum), agriculture and human settlements. The increasing activities in the catchments has resulted in the release of pollutants into the rivers, including heavy metals [2].

The study was conducted to assess heavy metal pollution in water and sediments of the two rivers, to investigate the degree of contamination and pollution

using pollution indices such as enrichment factor (EF) and geo-accumulation index (*I*_{geo}), and to identify pollution patterns (if any) across study sites. Comparative study of these two rivers is important to prioritise pollutants entering the Olifants River from catchment areas. This is essential in designing proper management programmes to monitor water quality of the rivers as human activities continue to increase in the catchments.

Materials and Methods

Study Area and Description

The study was undertaken at two tributaries (Blyde and Steelpoort rivers) of the Olifants River (Fig. 1). Seven sampling sites were selected in the Blyde: Site 1 (BS1): Swadini Resort 24.516 S, 30.799 E; Site 2 (BS2): 24.504 S, 30.836 E; Site 3 (BS3): near a commercial farm (24.311 S, 30.834 E); Site 4 (BS4): near Hoedspruit town (24.405 S, 30.798 E); Site 5 (BS5): near a citrus farm (24.325 S, 30.831 E); Site 6 (BS6): near a wildlife estate (24.384 S, 30.806 E); and Site 7 (BS7): the confluence with the Olifants River, near an estate (24.258 S, 30.837 E). Sites represent four different groups of land use practices: domestic (BS1 & BS2), agricultural (BS3 and BS4), industrial (BS5) and 'pristine' areas (BS6 and BS7). Four sites were selected in the Steelpoort on the basis of catchment characteristics and land use activities: Site 1 (SS1) is located upstream of the river

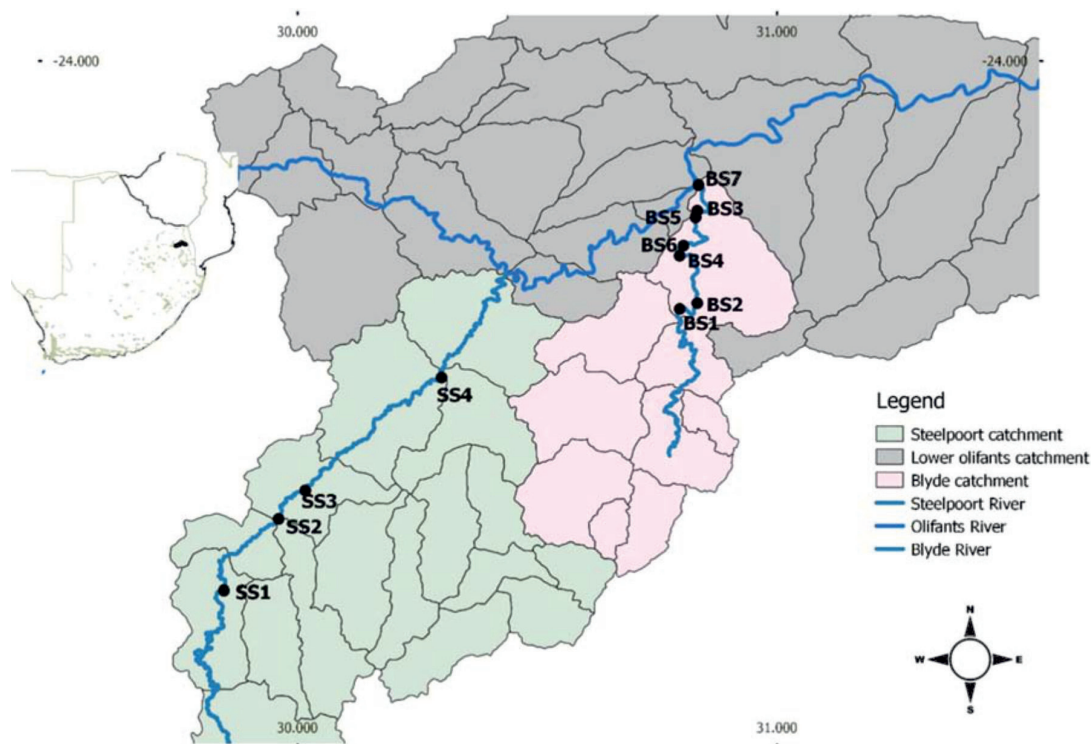


Fig. 1. Map of the study area showing the location of the seven sampling sites in the Blyde and four sampling sites in the Steelpoort of the Olifants River System.

with little agricultural activity (25.101 S, 29.847 E); Site 2 (SS2) is near a mine (24.953 S, 29.961 E); Site 3 (SS3) is near a mine and metal smelter (24.894 S, 30.017 E); and Site 4 (SS4) is near Steelpoort town close to the smelter (24.659 S, 30.302 E).

Water and Sediment Sampling

Water and sediment samples were collected bi-monthly from January to November 2018 at seven sites in the Blyde and four sites in the Steelpoort. Water samples were collected in 100 ml acid pre-treated polyethylene bottles and stored in a refrigerator (4°C) prior to analysis. Physicochemical constituents of water such as temperature, pH, dissolved oxygen, total dissolved solids (TDS), electrical conductivity and salinity were measured in the field using YSI equipment (Model 554 Datalogger with a 4 m multiprobe).

Surface sediment samples were collected at a depth of 0-10 cm using a hand trowel. Three to five samples were taken and composited before being transferred to the 500 ml acid pre-treated polyethylene sampling bottles. The samples were placed in plastic bags, transported to the laboratory and frozen prior to analysis. Sediment samples were dried, and metal concentrations determined using nitric acid digestion and analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Measurements were reported in mg/kg dry weight by an accredited chemical laboratory (WaterLab (Pty) Ltd).

Assessment of Sediment Contamination

The degree of contaminants in the river was evaluated using an enrichment factor (EF). Iron (Fe) was used as the normalizing element to determine the EF-values [15] using the formula:

$$\text{Enrichment factor} = (C_n/\text{Fe})_{\text{sample}} / (C_n/\text{Fe})_{\text{background}}$$

...where C_n is the concentration of element "n". The background value is that of average shale [16]. Elements which are naturally derived have an EF value of near unity, while elements of anthropogenic origin have EF values of several orders of magnitude. Six categories are recognised: <1 background concentration, 1-2 depletion to minimal enrichment, 2-5 moderate enrichment, 5-20 significant enrichment, 20-40 very high enrichment and >40 extremely high enrichment [17].

The geo-accumulation index (I_{geo}) values were calculated for the different elements [18] using the formula:

$$I_{geo} = \log_2 (C_n / 1.5B_n)$$

...where C_n is the measured concentration of an element in the sediment and B_n is the geochemical background value in average shale of the element n, and 1.5 is the background matrix correction due to Terrigenous effects. The geo-accumulation index

Table 1. Mean metal concentrations (mg/l) of Blyde and Steelpoort river water.

Metal	As	Cr	Fe	Mn	Ni	Pb	Zn
BS1	0.007	0.008	0.08	0.02	0.10	0.001	0.012
BS2	0.004	0.003	0.07	0.01	0.06	0.001	0.008
BS3	0.006	0.016	0.01	0.03	0.03	0.002	0.005
BS4	0.007	0.005	0.02	0.05	0.12	0.001	0.017
BS5	0.004	0.008	0.03	0.07	0.03	0.001	0.006
BS6	0.009	0.009	0.03	0.08	0.05	0.002	0.004
BS7	0.001	0.005	0.09	0.07	0.14	0.002	0.017
SS1	0.006	0.002	0.23	0.06	0.09	0.002	0.034
SS2	0.003	0.005	0.21	0.03	0.026	0.001	0.054
SS3	0.003	0.009	0.40	0.05	0.030	0.002	0.031
SS4	0.003	0.004	0.31	0.04	0.046	0.002	0.037
Guideline values	0.01 ¹ ; 0.005 ³ ; 0.01 ⁴	Cr III: 0.012 ¹ ; 0.0089 ³	0.3 ³	0.18 ¹ ; < 1.3 ²	< 0.47 ⁴	0.0002-0.0012 ¹ ; 0.007 ³	0.002 ¹ , 0.03 ³ < 0.12 ⁴ 0.04 – 0.115 ² ;

References:

- 1 – [20]
- 2 – [37]
- 3 – [26]
- 4 – [38]

classification consists of seven classes (0-6): <0 (class 0) background concentration, 0-1 (class 1) unpolluted, 1-2 (class 2) moderately polluted, 2-3 (class 3) moderate to high pollution, 3-4 (Class 4) heavily polluted, 4-5 (Class 5) highly to very highly polluted, and 5-6 (Class 6) very heavily polluted [19].

Results and Discussion

Heavy Metal Distribution in the Water

The physicochemical parameters of water in both Blyde and Steelpoort rivers are presented in Table 1. Blyde acidity values ranged from 8.3 to 8.7 and were within the South African recommended range [20]. Mean electrical conductivity (EC): 270.75 at BS1 to 460.6 mS/m at BS4; total dissolved solids (TDS): 132.9 at BS1 to 152.9 mg/l at BS7; and dissolved oxygen (DO): 8.7 at BS5 to 11.5 mg/l at BS1. Steelpoort acidity ranged from 7.8 at SS1 to 9.0 at SS5. EC: 191.7 at SS2 to 446.5 mS/m at SS5; TDS: 90.8 at SS2 to 214.8 mg/l at SS3; and DO: 8.6 at SS3 to 10.7 mg/l at SS1. There were no significant differences in physicochemical properties between the two rivers ($p>0.05$).

Mean metal concentration ranges of Blyde water were as follows: As 0.001 at BS7 to 0.009 mg/l at BS6; Cr 0.003 at BS2 to 0.016 mg/l at BS3; Fe 0.01 at BS3 to 0.09 mg/l at BS7; Mn 0.01 at BS2 to 0.08 mg/l at BS6; Ni 0.03 at BS3 and BS5 to 0.14 mg/l at BS7; Pb 0.001 to 0.02 mg/l; and Zn 0.004 at BS6 to 0.017 mg/l at BS4 and BS7.

The mean metal concentration ranges of Steelpoort water were as follows: As was 0.003 mg/l at all sites except SS1 (0.006 mg/l), Cr 0.002 at SS1 to 0.009 mg/l at SS3, Fe 0.21 at SS2 to 0.40 mg/l at SS3, Mn 0.03 at

SS2 to 0.06 mg/l at SS1, Ni 0.026 at SS1 to 0.046 mg/l at SS4, Pb 0.001 to 0.002 mg/l, and Zn 0.031 at SS3 to 0.054 mg/l at SS2. There were no significant differences in metal concentrations between the two rivers (Table 1).

The source of high metal concentrations in the water could be natural (sediments in the case of environmental change) or from effluents of anthropogenic activities [21]. The water column and sediment layer are in direct contact, leading to an exchange of constituents, including metals [22]. In the Steelpoort, the high mean concentrations of Cr and Fe could be from Ferrochrome mining discharge, while the relatively higher As concentration in the Blyde could have come from fertilizers and pesticides due to the intensive agricultural activities in some parts of the catchment [23].

Heavy Metal Distribution in the Sediments

Mean heavy metal concentration ranges in Blyde sediment were as follows: As 1.4 at BS5 to 4.05 mg/kg at BS7, Fe 9457 at BS3 to 64771 mg/kg at BS7, Mn 280 at BS5 to 1016 mg/kg at BS4, Ni 9.84 at BS3 to 55.0 mg/kg at BS7, Pb 4.16 at BS1 to 6.76 mg/kg at BS3, and Zn 16 at BS6 to 69.1 mg/kg at BS4 (Table 2).

In the Steelpoort, As concentrations ranged from 1.03 at SS4 to 2.35 mg/kg at SS1, Fe 124917 at SS4 to 240528 mg/kg at SS2, Mn 1619 at SS3 to 2312 mg/kg at SS2, Ni 34 at SS1 to 185 mg/kg at SS4, Pb 2.66 at SS2 to 3.66 mg/kg at SS3, and Zn 122 at SS2 to 215 mg/kg at SS3 (Table 2). Similar to the water column, metal concentrations in sediments were higher in the Steelpoort except for As and Pb.

The concentrations of Cr exceeded the Canadian Council of Ministers of the Environment (CCME)

Table 2. Comparison of heavy metal concentrations (mg/kg, dry weight) in river sediments of the Blyde and Steelpoort rivers.

Metal	As	Cr	Fe	Mn	Ni	Pb	Zn
BS1	2.7	73.0	32899	607	38.0	4.16	49.0
BS2	1.7	50.0	28879	477	23.0	4.40	33.0
BS3	2.2	21.0	9457	437	9.8	6.80	20.0
BS4	2.9	62.0	49269	1016	50.0	5.50	69.3
BS5	1.4	30.0	10772	280	11.0	4.50	24.0
BS6	3.6	36.0	13050	699	19.0	5.90	16.0
BS7	4.1	218	64771	694	55.0	6.30	66.0
SS1	2.4	60.1	227827	2236	34.0	3.28	138
SS2	1.4	610	240528	2312	143	2.66	122
SS3	1.23	1461	137828	1619	121	3.66	215
SS4	1.03	477	124917	1717	185	3.55	149
Guideline value	na	37.3 ¹	na	na	na	35.0 ¹	123 ¹

¹ – [26]

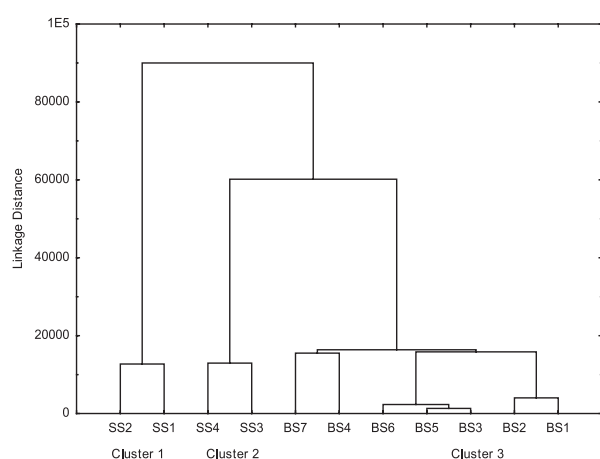


Fig. 2. Cluster diagram of sites obtained using the linkage method and Euclidean distance matrix (the distance reflects the degree of association between different sites based on the dissimilarity of metals of surface sediments).

sediment quality guidelines for the protection of aquatic life, which is 37.3 mg/kg at all sites for both rivers except at BS3, BS5 and BS6 along the Blyde. Similar to the water column, high concentrations of Cr at Steelpoort sites could be from ferrochrome mining discharge. Concentrations of Zn exceeded the CCME sediment quality guideline of 13 mg/kg at all sites of the Steelpoort River except site SS1. High concentrations of Zn in sediment from the Steelpoort may be attributed to the presence of unused remains of zinc sulphate in fertilizers [24] and wastewater [25].

A comparison of the mean concentration of heavy metals in sediments (Table 2) to CCME sediment quality guidelines [26] show that all Steelpoort study sites were heavily polluted with Cr (>37.3 mg/kg) and Zn (>123 mg/kg), while BS1, BS2 and BS4 of the Blyde were polluted with Cr. High levels of Cr in the Blyde are not unexpected, as fertilizers usually contain significant contents of Cr [27].

Based on the spatial similarities of metal concentrations in the sediments, three main clusters were identified (Fig. 2). Cluster 1 comprised two sites of the Steelpoort (SS1 and SS2), with relatively lower

metal concentrations in sediment samples. Cluster 2 also comprised the other two sites of the same river (SS3 and SS4), which are surrounded by heavy mining and smelter activities. Cluster 3 is comprised of all seven sites of the Blyde, depicting the main sources of pollution at these sites resulting from agricultural and domestic discharges.

Enrichment Factor

The degree of pollution in sediments can be assessed using indices such as enrichment factor (EF) and the geo-accumulation index. EF values for the metals together with their background average shale [16] are shown in Table 3. The EF index has been widely used to determine the pollution status and the sources of heavy metals in sediments of rivers, lakes and bays [28, 29]. According to the EF classifications, most of the metals showed deficiency to minimal enrichment in both rivers. However, Cr shows moderate (>2) to significantly high (>5) enrichment downstream in the Steelpoort, while Mn shows a moderate (>2) enrichment at BS3 and BS6 of the Blyde. Manganese compounds are used in fertilizers, varnishes, fungicides and as livestock feed supplements. Increased Cr values at SS3 and SS4 are strongly linked to the high ferrochrome mining associated with the catchment of the Steelpoort.

Geo-Accumulation Index

The geo-accumulation index is used to determine anthropogenic contamination in river sediments [30, 31]. The calculated *I_{geo}* values based on the average shale are presented in Table 4 and show that the majority of metals have an index value below zero. In the Blyde, all metals were below zero except Cr at site BS7, which had an *I_{geo}* value of between 0 and 1, and belongs to class 1. This indicates that the river sediment is uncontaminated at all the sites, except BS7, where the river joins the Olifants – an indication that the contamination is mainly from the Olifants. However, in the Steelpoort, only As and Pb had *I_{geo}* values below zero at all sites. The *I_{geo}* value for Cr ranged

Table 3. Enrichment factor for heavy metal in Blyde and Steelpoort river sediments.

Metal	Shale	BS1	BS2	BS3	BS4	BS5	BS6	BS7	SS1	SS2	SS3	SS4
As	13	0.3	0.2	0.84	0.21	0.5	1.1	0.23	0.04	0.02	0.03	0.02
Cr	90	1.16	0.91	1.2	0.66	1.5	1.5	1.8	0.14	1.3	5.6	2.1
Fe	47200	1	1	1	1	1	1	1	1	1	1	1
Mn	20	1.02	0.92	2.6	1.15	1.44	3.0	0.6	0.54	0.53	0.65	0.8
Ni	850	0.8	0.55	0.72	0.7	0.71	1.1	0.6	0.1	0.41	0.6	1.03
Pb	68	0.3	0.36	1.69	0.26	0.26	1.1	0.23	0.03	0.01	0.1	0.1
Zn	95	0.74	0.57	1.1	0.7	0.7	0.61	0.51	0.3	0.3	0.8	0.6

Table 4. Geo-accumulation index for heavy metals in Blyde and Steelpoort river sediments.

<i>I_{geo}</i>	As	Cr	Fe	Mn	Ni	Pb	Zn
BS1	-2.80	-0.88	-1.10	-1.10	-1.41	-2.90	-1.60
BS2	-3.51	-1.42	-1.31	-1.43	-2.10	-2.14	-2.10
BS3	-3.23	-2.61	-2.87	-1.60	-3.33	-2.23	-2.52
BS4	-2.69	-1.13	-0.48	-0.32	-0.96	-2.50	-1.13
BS5	-3.48	-2.23	-2.71	-2.20	-3.22	-2.67	-2.58
BS6	-2.49	-1.90	-2.52	-0.89	-2.40	-2.41	-3.20
BS7	-2.40	0.68	-0.15	-0.91	-0.90	-2.40	-1.10
SS1	-3.12	-1.21	1.70	0.85	-1.62	-3.23	-2.31
SS2	-0.50	2.21	1.82	0.85	0.50	-0.15	-0.20
SS3	-4.10	3.41	0.96	0.40	0.26	-3.10	0.61
SS4	-4.32	1.82	0.55	0.43	0.85	-3.20	0.10

from 1.82 to 3.4 (class 1 to class 4). The *I_{geo}* value for Fe ranged from 0.55 to 1.82 (class 1 to class 2). The *I_{geo}* value for Mn ranged from 0.44 to 0.85 (class 1). The *I_{geo}* value for Ni was above zero from SS2 to SS4, and falls in class 1. The *I_{geo}* value for Zn was above zero only at SS3 and SS4 (class 1). The calculated *I_{geo}* class values in the Steelpoort were between 0 and 4 and the *I_{geo}* class values showed uncontaminated to heavily contaminated river sediments, while in the Blyde the *I_{geo}* class values for Cr showed uncontaminated to moderately contaminated river sediments [19].

Comparing the two rivers, the Steelpoort is more contaminated with the selected metals than the Blyde. The high levels of metals such as, Fe, Cr and Zn in the Steelpoort possibly originate from the smelting of ferrochrome in the area [2] and wastewater [32]. This is of great concern, as the levels of contaminants are likely to increase due to the rapid urbanization and industrialization in the area. Many studies have confirmed a link between urbanization and contamination by heavy metals in rivers [33-36].

Conclusion

Sediments actively accumulate heavy metals, which may somehow improve the quality of the water, but this phenomenon poses a risk of secondary water pollution by heavy metals under sediment disturbance and/or changes in sediment chemistry. The standard guideline, EF and *I_{geo}* values indicated widespread pollution by Cr, Fe, Mn and Zn in the Steelpoort sediments, and Cr and Mn in the Blyde sediments. In the Blyde, the *I_{geo}* values showed that sediments have background concentrations for all the metals except Cr, while in the Steelpoort the *I_{geo}* values (with the exception of As and Pb) exceeded the background concentrations.

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Conflict of Interest

The author declares no conflict of interest.

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