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A Review: Assessment of Trace Metals in Municipal Sewage and Sludge: A Case Study of Limpopo Province, South Africa

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Abstract

Trace metals including nanosilver in our aquatic environment are on the increase in part due to discharge from municipal sewage and indirectly from leaching from abandoned mine tailings and from sludge spread on farmland. The presence of the trace metals will likely impact negatively on the aquatic environment in excess of background levels. This review reports on the concentration of trace metals in municipal sewage in Limpopo province and the impact on fish and human health. Human health risks associated with the consumption of contaminated fish are discussed. The presence of silver is also highlighted and the remedial actions that are available in reducing the health risks including positive outcomes are discussed. The source of silver may be from the use of silver nanoproducts. There is a need for a paradigm shift of zero effluent discharge and start with harvesting of metals from the sewage effluent and sludge in order to protect the environment.

Keywords: trace metals, bioaccumulation, biomagnification, fish consumption, human health

1. Introduction

Trace metals in our aquatic environment are on the increase due to discharge from municipal sewage, active and abandoned mine tailings, and non-point pollution sources. Here, the trace metals may originate from metal fabrication industry [1], road runoff stormwater drains that are connected to municipal sewage plants [2–4], tannery industry [5], and from domestic households where zinc/copper scrubbers are used [6]. Trace metals have been known to originate from active and abandoned mine tailings, and these trace metals enter the aquatic

environment during rainy events [7–9] or windy events [10]. Some of the non-point pollutions are as follows: trace metals also leaching from sewage sludge spread on farmland [11] and discharge of bath water to the terrestrial environment where there is leaching to the aquatic environment. In rural areas of developing countries, there is no municipal sewer system, and the communities practicing disposal of wastewater to the terrestrial environment is common. Silver and silver nanoparticles have been found in the terrestrial environment and in municipal sewage as a result of the human use of silver deodorant products and silver nanoproducts [12, 13]. The sewage sludge disposal and the fate of silver nanoparticles and trace metals and their possible effects to the environment are reviewed. The presence of the trace metals will likely impact negatively on the aquatic environment in excess of background levels (**Figure 1**).

However, the municipal sewage sludge and sewage wastewater are also a source of trace metals that are essential for plant and human growth. The municipal sewage sludge is applied on farmland in order to improve land fertility, and irrigation of crops/vegetables with sewage wastewater is also beneficial. We choose Limpopo province for the following reasons. The Limpopo province is the fifth gross domestic product (GDP), based on 2010 figures, of South Africa based on commercial agriculture, mining, manufacturing, goods and services, and tourism with world renowned Kruger National Park [14, 15]. Secondly, the Limpopo province has experienced a surge in crocodiles and fish mortalities in freshwater

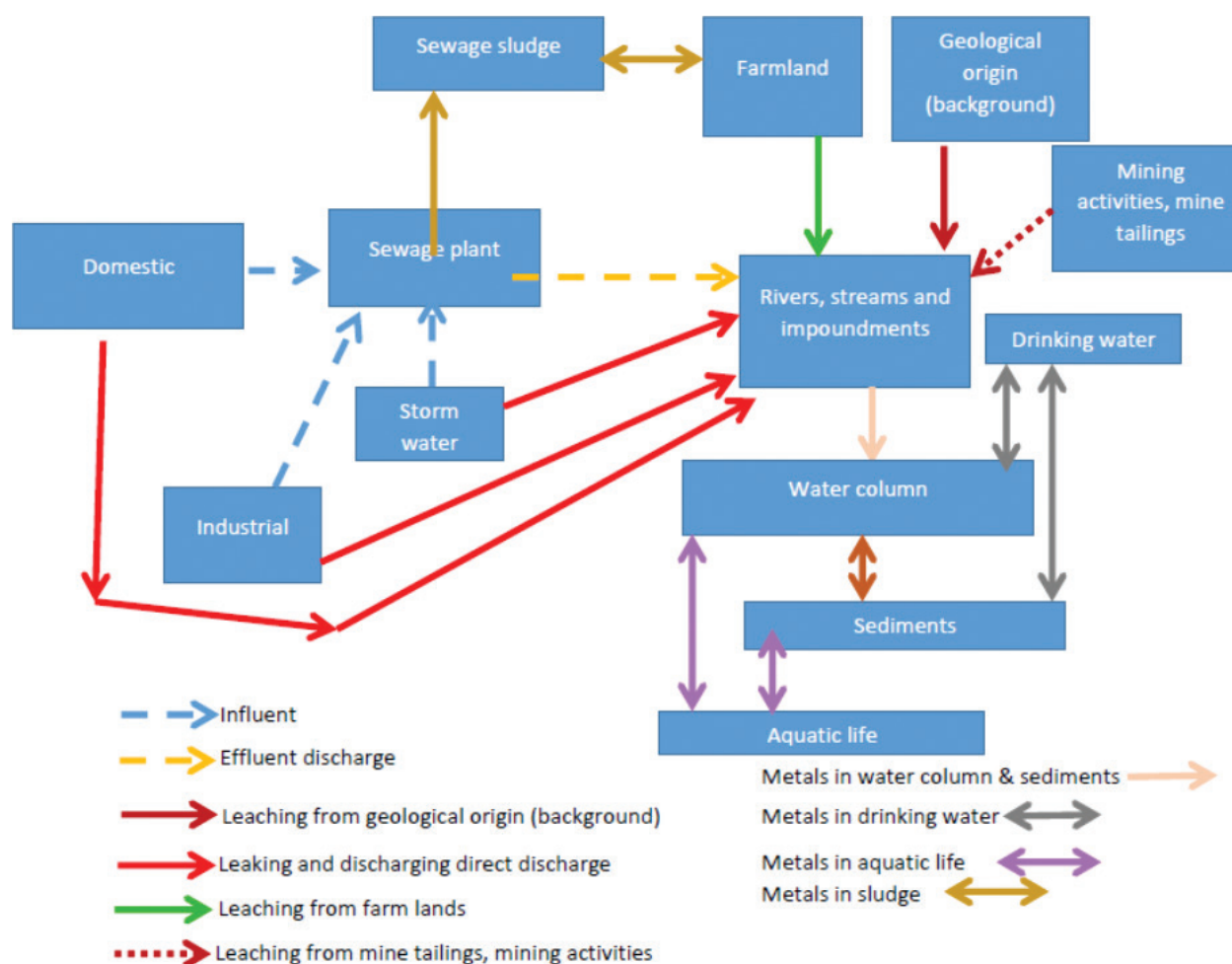


Figure 1. Schematic diagram illustrating the movement of trace metals toward freshwater environment.

impoundments and rivers inside the Kruger National Park and other nature conservation areas directly and indirectly linked to metal pollution [15]. In the 2013 Green Drop assessment by the Department of Water Affairs (DWA), Limpopo province was forth from last on assessment performance [16]. Lastly, the drinking water sources for major urban areas such as Polokwane rely on groundwater for additional water supply sources which are recharge with wastewater effluent [18], and rural areas rely on surface water and groundwater sources for human consumption. The review investigates the studies that have occurred looking at the discharge of sewage effluent in terms of metal content and the environmental impact of these metals on aquatic fauna and flora. The study also investigates the metal content of trace metals of the municipal sewage sludge in the selected sewage plants in the study period.

2. Methodology

The review is based on articles between 2012 and 2018. The keywords were sewage, wastewater, Limpopo, crocodile, metals, effluent, fish, risk assessment, and human health.

3. Characteristics of the study area

The major river systems in the Limpopo province are the Nyl River, the Sand River, the Nzhelele River, and the Luvuvhu River; Oliphant River and these are some of the tributaries of the Limpopo River in South Africa. The municipal sewage plants are located near these major rivers or their tributaries. The Nyl River system is fed by the Klein and Groot Nyl Rivers and has a floodplain and a Ramsar wetland. The likely source of metal pollution is sewage plants from Modimolle and Mookgophong that discharge their effluent into the Nyl River [17]. The Sand River originates from Drakensberg Mountains and flows past Polokwane city and flows northward, past farming areas, formal and informal residential areas, mines, nature reserves, and joins the Limpopo River [18]. The Seshego township sewage plant discharges its effluent into the Blood River. The Polokwane sewage plant serving the Polokwane city discharges its effluent into the Sand River. Thus, the source of metal pollution of the Sand River is effluent discharged from sewage plants. The Luvuvhu River originates in Soutpansberg Mountains, flows into Albasini and Nandoni dams, and joins the Limpopo River. There are formal and informal residential and towns, subsistence and commercial farming that are taking place along the Luvuvhu River. Thohoyandou town is the major urban settlement, and the Thohoyandou sewage plant discharges its effluent into Mvudi River [19]. Other sewage plants are located in Waterval Township and urban area of Elim and these discharge their effluent into the Mudzwiriti and Doringspruit Rivers which flow into the Luvuvhu River and Albasini dam, respectively [20].

The Nzhelele River originates from Soutpansberg Mountains, meanders past rural communities, and flows past Nzhelele dam northwards into the Limpopo River. The sources of metal pollution are Siloam and Makhado oxidation ponds which discharge their effluent into the Nzhelele River [21, 22]. The area is characterized by urban settlements of Biaba and residential houses, some with pit latrines, subsistence and commercial farming and nature reserves. On the Oliphant River catchment, there are a number of municipal sewage plants

that discharge effluent either directly into the Oliphant River [15] or via some of tributaries such as the Elands River [23] and Ga-Selati River [24]. The Oliphant River is the most polluted river in South Africa and this is mainly due to mining activities, especially acid mine drainage, commercial and subsistence farming, and formal and informal residential discharges from municipal sewage plants [15, 25].

4. Results and discussion

4.1. Evidence of trace metal in freshwater environment

South Africa is a dry country, and rivers and streams flow during the rainy seasons. However, the location of sewage plants near streams and rivers means that the effluent is discharged into the streams and rivers and this contributes to base flow even during periods of no rainfall [20, 25]. The inflow from sewage effluents contributes to the build-up of trace metals in the freshwater environment. There are a number of studies that have shown the presence of trace metals on the freshwater environment (rivers and impoundments) in the Limpopo province of South Africa [15, 18–21, 24, 26–28]. In some cases, the trace metals are in excess of background levels, and the trace metals may become toxic to aquatic life and contaminate drinking water sources (**Table 1**). The pH values in the study sites were generally near the neutral, and therefore there was no contribution of metals due to the dissolution of bedrock or mining activities.

4.1.1. Aluminum (Al)

The study by Greenfield et al. [17] on the Nyl River system showed that the Al levels are higher than the target water-quality range (TWQR) of 10 µg/l during the study period. The presence of Al was attributed in part due to discharge of sewage effluent into the Groot Nyl River, a tributary of the Nyl River, and rainfall-induced erosion of local bedrock. The study by Edokpayi et al. [19, 21, 24] showed variation in the Al level in the Ga-Selati, Nzhelele, Mvudi, and Dzindi Rivers in excess of the target water-quality range. The high level of Al may be attributed to the Thohoyandou sewage plant which discharges treated effluent into the Mvudi River and Vuwani oxidation ponds which discharge into Dzindi River [19, 20, 29]. Nibamureke [27] found that high levels of Al in Albasini dam in excess of TQWR aquatic life guidelines were probably linked to a combination of leaching of bedrock (geology of area) by high rainfall and discharge of sewage effluent from Elim oxidation ponds [20]. The Al target water-quality range was established to safeguard the aquatic environment against the effect of toxic metals [30]. The high Al levels are a hazard to aquatic organism affecting their respiratory function and osmotic balance [17].

4.1.2. Chromium (Cr)

Water samples showed high levels of total Cr of 3679 µg/l at Nysvley in August 2001, and this sample point is downstream of Modimolle sewage plant [17]. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Cr (total) in the Nzhelele, Ga-Selati, Mvudi, and Dzindi rivers in excess of the target water-quality range with the Mvudi River having

Reference	[27]	[23]	[17]	[28]	[19]	[26]	[21]	[24]	[24]	[33]	[30]
Dam or river	^a Albasini dam	^b Flag Boshielo dam	^c Nyl River	^d Sand River	^e Mvudi River	^f Dzindi River	^g Mandzoro River	^h Nzhelele River	ⁱ Ga-Selati River	^j Mawoni River	TQWR µg/l
Name of River	Doringspruit	Elands & Oliphant	Nyl	Sand	Mvudi	Tshishushuru	Mandzoro	Nzhelele	Ga-Selati	Mawoni	
Name of sewage plant	Elim	Marble Hall	Modimolle	Polokwane	Thohoyandou	Vuwani	Malamulele	Siloam	Phalaborwa & Namakgale	Makhado	
pH	7.5 ± 0.1	8.28 – 9.42	5.52 – 9.95	7.49 – 8.48	7.72 – 7.7	7.47 – 7.53	6.7 ± 0.3	7.21 – 7.76	7.72 – 9.81	7.35 – 9.07	6.5 – 9
A1	280 ± 0.075	10.5 – 11.9	0 – 2089	–	393 – 13810	200 – 400	–	1172 – 29094	350	1.99 – 265.9	10
Cr (total)	2 ± 0	–	0 – 3679	–	12 – 593	30 – 110	–	45 – 396	60	0.58 – 46.04	Cr ⁶⁺ 7 and Cr ³⁺ 12
Mn	6 ± 8	0.5 – 10.0	0 – 5047	50 – 680	29 – 675	80 – 200	–	52 – 545	210	1.02 – 2271.48	180
Fe	382 ± 62	2.4 – 27.5	0 – 19901	10 – 140	425 – 5070	790 – 1720	546 ± 50	1028 – 4991	730	25.34 – 6000.83	*
As	–	–	0 – 79	–	–	–	–	–	–	0.43 – 3.10	10
Cd	2 ± 1	–	0 – 24	10	0.2 – 4.3	–	<0.1	0.4 – 2	10	0.01 – 0.27	0.25**
Cu	–	–	0 – 729	10	11 – 567	30 – 50	420 ± 240	25.7 – 66	–	2.38 – 83.51	0.8**
Zn	3 ± 2	–	0 – 1350	10 – 20	1 – 548	50 – 210	88 ± 38	42 – 131	–	0.97 – 113.4	2
Pb	2 ± 1	–	0 – 175	90	bdl – 46	10 – 50	22 ± 0.09	1 – 13	60	0.01 – 3.40	0.5**
Se	–	–	0 – 11	–	–	–	–	–	–	2	2

Notes: – not available; bdl below detection limit; *not more than 10% of background value; **medium water hardness of CaCO₃ with range 60 – 119 mg/l, ^aaverage of three samples on the Albasini dam basin; ^bconsidered the sample point FBI; ^cconsidered the sample points along the Nyl River; ^drange in values; ^erange is values from Jan to Jun 2014; ^gdownstream sample point; ^hdownstream sample point; ⁱconsidered the sum of wet and dry seasons; ^jconsidered the downstream sample point

Table 1. Concentrations for trace metals (range OR mean) in selected freshwater impoundments and rivers in Limpopo receiving sewage effluent.

higher Cr levels. The high levels of Cr in the rivers were attributed to sewage effluent discharge into the rivers as a result of inefficient metal removal during the wastewater treatment process [29]. The Cr level is in excess of the TWQR of Cr⁶⁺ (70 µg/l) and Cr³⁺ (120 µg/l) and is a threat to aquatic fauna [30, 31]. In the study by Shibambu et al. [32], the wastewater effluent flowed past a natural wetland which removed some of Cr and thus reducing Cr in the river water.

4.1.3. Manganese (Mn)

At Mosdene sample point, the manganese levels were 5047 µg/l in March 2002 (a period of high rainfall), indicating that part of Mn origins is geological other than sewage effluent discharge [17]. This sample point Mosdene is also downstream of the Modimolle sewage plant, and part of the increased levels is probably from the sewage inflows. The studies of [18, 33] for the Sand and Mawoni Rivers also found that high levels of Mn were probably due to rainfall erosion of bedrock. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Mn in the Nzhelele, Ga-Selati, Mvudi, and Dzindi Rivers in excess of the target water-quality range as a result of sewage discharge. The Mn level is in excess of the TWQR of 189 µg/l and is a threat to aquatic fauna especially fish [30, 33] and is an essential component in physiological processes of living organisms such as algae at trace levels [34].

4.1.4. Iron (Fe)

The Fe levels of 19,000 µg/l were recorded at Mosdene, in March 2002 (a period of high rainfall), indicating that part of Fe origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Fe in the Nzhelele, Ga-Selati, Mvudi, and Dzindi Rivers during the rainfall months of January to March 2014 and the Mvudi River having higher Fe levels and sewage effluent discharges. The studies of [18, 26, 32] for the Mandzoro, Sand, and Mawoni Rivers also found that high levels of Fe were probably due to rainfall erosion of bedrock. Nibamureke [27] found that high levels of Fe in water in excess of TQWR aquatic life guidelines were probably linked to a combination of leaching of bedrock (geology of area) by high rainfall and discharge of sewage effluent from Elim oxidation ponds [20]. The Fe level is within the guideline value range of 500 and 50,000 µg/l for freshwater [17]. Fe at trace level is an essential component of living organism including hemoglobin and myoglobin [35].

4.1.5. Arsenic (As)

The As levels of 79 µg/l were recorded at Mosdene on Nyl River, in August 2002 (a period of no rainfall), indicating that part of As origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The study by Shibambu [32] found low As levels in the Mawoni River downstream of a natural wetland showing the As removal as this was within the TWQR guideline values. The As level is in excess of the TWQR of 10 µg/l and is a threat to aquatic fauna especially fish [17, 30] and aquatic freshwater invertebrates such as *Daphnia magna* and *Ceriodaphnia dubia* [36].

4.1.6. Cadmium (Cd)

The Cd levels of 21 and 22 µg/l were recorded at Klein and Groot Nyl rivers, respectively, in August 2002 (a period of no rainfall), indicating that part of As origins is geological other than sewage effluent discharge [17]. The sample point is also upstream of the Modimolle sewage plant. The studies by Seanego [18] and Edokpayi et al. [21, 24, 28] found high Cd levels in the Sand, Ga-Selati, Nzhelele, and Mvudi Rivers and attributed the high Cd values to discharge of sewage effluent to these rivers. The Cd level is in excess of the TWQR of 0.25 µg/l and is a threat to aquatic fauna especially fish [30, 37] and aquatic flora such as altering small heat shock protein (HSP) genes in aquatic midge *Chironomus riparius* [38].

4.1.7. Copper (Cu)

The Cu levels in the range of 0–729 µg/l were recorded at Klein and Groot Nyl Rivers, respectively, in November 2001 (a period of rainfall), indicating that part of Cu origins is geological other than sewage effluent discharge [17]. High levels of Cu at 150 µg/l were recorded at Nysvley in November 2001, and this sample point is downstream of Modimolle sewage plant [17]. The studies of [18, 19, 21, 26, 28, 33] also found high Cu levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Cu values to discharge of sewage effluent to these rivers. The Cu level is in excess of the TWQR of 0.30 µg/l and is a threat to aquatic fauna especially fish [17, 30]. Copper is an essential component of aquatic organisms' enzymes and co-enzymes [39].

4.1.8. Zinc (Zn)

At Mosdene, the Zn levels of 1350 µg/l were recorded in August 2002 (a period of no rainfall), indicating that part of Zn origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The studies of [18, 19, 21, 26, 28, 33] also found high Zn levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Zn values to discharge of sewage effluent to these rivers. Nibamureke [27] found Zn levels just in water in excess of TQWR aquatic life guidelines and were unlikely to be a threat to aquatic life. The Zn level is in excess of the TWQR of 2 µg/l and is a threat to aquatic fauna especially the functioning of gills in fish [17, 30]. Zn at trace level is an essential component for biochemical and physiological processes in aquatic organisms [39].

4.1.9. Lead (Pb)

The Pb levels in the range of 2–175 µg/l were recorded at sewage plant and other Nyl River sites, respectively, in November 2002 (a period of rainfall), indicating that part of Pb origins is geological other than sewage effluent discharge (Greenfield et al. [17]). The studies of [18, 19, 21, 26, 28, 33] also found high Pb levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Pb values to discharge of sewage effluent to these rivers. Nibamureke [27] showed that low levels of Pb in water were within the TQWR aquatic life guidelines and were no threat to aquatic life. The Pb level is in excess of the TWQR

of 0.5 µg/l and is a threat to aquatic fauna especially the functioning of gills in fish [17, 30] and is considered a non-essential component in biological systems [39].

4.1.10. Selenium (Se)

The study by Greenfield et al. [17] found low Se levels in the Nyl River and attributed Se content to factors such as diffuse pollution and chemical weathering of bedrock. The leaching of Se from farmlands into the aquatic environment is a result of rainfall or irrigation that is practiced in the study area. Se is found in synthetic pesticides used in the study area. Shibambu [33] showed low levels of Se in the Mawoni River and were within the TQWR aquatic life guidelines and also showing the removal of Se by the natural wetland. However, high Se levels are toxic and may induce skeletal deformities in animals [17].

4.2. Trace metals in sludge of selected municipal sewage plants in Limpopo

A number of studies have been conducted in Limpopo to determine the metal removal efficiency of municipal sewage plants [18, 19, 26]. The metal efficiencies were generally low for these metals as high levels were found in the dried sludge (**Table 2**). The trace metals, Zn, Pb, and Cu, exceed the maximum permissible Department of Water Affairs & Forestry (DWA) guidelines, and the metals have a significant environmental impact.

The studies by Baloyi et al. [26] and Shamuyarira [41] showed that Cu and Zn contents were very high. The application of sludge rich in Cu and Zn as this case to agricultural land may result in leaching to the aquatic environment in the event of rainfall event or during irrigation. At minute quantities, Cu and Zn are essential elements and are necessary for plant growth [11]. Thus, a careful application of sludge to agricultural land is required in order to safeguard the aquatic environment, taking into account the presence of Cu or Zn content of the land. The Co content was variable among the sewage plants and showed no discernible trend. At high levels, Co is harmful to plants but is an essential element at trace levels in enzymatic biochemical reactions [42].

The Pb content in sludge was generally low with the exception of Louis Trichardt which had Pb content greatly exceeding the maximum DWA guidelines [40]. Pb has no known nutritional function in plant growth and thus is a potential hazard to the plants and crops that may be grown on the agricultural land. The presence of Cu, Zn, and Fe in wastewater streams and eventually in the sludge may be due to household use of brass (copper and zinc), copper, and iron scrubbers in washing of cooking pots [26].

The presence of high Pb in wastewater and then in the sludge for Polokwane and Louis Trichardt may be due to a dense vehicular traffic. In a 15-year study by Iglesias et al. [43] in Spain, they showed that the sludge application to agricultural land resulted in an increase in Pb, Hg, Zn, and Ag in treated soils and Cu, Pb, and Zn contents in maize and barley crops which was similar to the control site. In a similar study in South Africa, Ogbazghi et al. [44] also found a similar trend of increase in metals, Zn, Cd, Ni, and Pb soils, amended with sludge in a 10-year study.

Another trace metal of interest is silver and aluminum in municipal dried sludge, since in these urban towns, there are no heavy metal-intensive industries (**Table 2**). The presence of Ag in the sludge may be attributed to the use of silver nanopropducts. The study by Shamuyarira and

Reference	[41]	[41]	[41]	[41]	[41]	[26]	[40]	
Trace metals (mg/ kg dry mass)	Thohoyandou sewage plant	Polokwane sewage plant	Tzaneen sewage plant	Louis Trichardt sewage plant	Musina sewage plant	Malamulele sewage plant	DWAF*	
							Total maximum threshold	Maximum permissible level
Al	13388 ± 293	12238 ± 357	11953 ± 470	12583 ± 173	6958 ± 272	NA	–	–
Fe	29228 ± 491	10080 ± 57	18085 ± 509	19273 ± 223	8000 ± 750	11337 ± 1057	–	–
Mn	629 ± 10	263 ± 0	288 ± 7	1348 ± 29	201 ± 17	NA	–	–
As	2.6 ± 0.1	5.1 ± 0.1	4.2 ± 0.1	3.3 ± 0.2	4.8 ± 0.0	NA	2	20
Ni	33.9 ± 0.1	47.3 ± 1.3	31.3 ± 1.7	514 ± 0.6	35.2 ± 1.0	NA	150	200
Cr (total)	64.4 ± 0.7	134.5 ± 5.2	53.5 ± 2.4	97.1 ± 2.2	35.1 ± 1.6	NA	350	450
Cd	0.82 ± 0.03	3.11 ± 0.16	1.39 ± 0.06	1.66 ± 0.09	1.06 ± 0.04	2.7 ± 0.4	3	5
Pb	35.6 ± 0.1	103.8 ± 3.8	52.3 ± 2.4	172.9 ± 0.9**	21.3 ± 0.8	18.4 ± 3.6	100	150
Cu	378.0 ± 3.5**	324.8 ± 2.8	263.7 ± 9.1	499.3 ± 1.7**	626.0 ± 5.0**	178 ± 23	120	375
Zn	1193 ± 28**	1552 ± 35**	951 ± 36**	1732 ± 5**	1032 ± 21**	821 ± 124**	200	700
Ag	6.1 ± 0.1	6.9 ± 0.1	13.4 ± 0.5	21.9 ± 0.4	7.1 ± 0.0	NA	–	–
Hg	1.1 ± 0.0	1.2 ± 0.1	1.4 ± 0.1	1.7 ± 0.1	1.1 ± 0.0	NA	1	9
V	70.6 ± 0.6	39.3 ± 0.1	28.0 ± 1.1	57.4 ± 0.7	70.2 ± 2.0	NA	–	–
Se	4.1 ± 0.1	4.0 ± 0.4	4.1 ± 1.2	4.9 ± 0.4	5.4 ± 0.1	NA	–	–
Mo	3.0 ± 0.0	9.8 ± 0.2	5.0 ± 0.2	5.9 ± 0.0	20.1 ± 0.0	NA	–	–
Co	12.0 ± 0.0	53 ± 0.2	5.6 ± 0.2	12.6 ± 0.0	4.7 ± 0.3	NA	–	–

Notes: *DWAF guidelines for metal limit receiving high sludge loads; **Exceeds DWAF guidelines; – not available.

Table 2. Average concentrations for trace metals from selected sewage sludge in Limpopo.

Gumbo [6] of five selected municipal plants in the Limpopo province of South Africa found that silver was in the range of 6.13 ± 0.12 mg/kg dry mass to 21.93 ± 0.38 mg/kg dry mass. A recent study by Mackevica et al. [45] in Denmark showed that the maximum silver nanoparticles per toothbrush were released into the wastewater during a normal toothbrush exercise and were 10.2 ng silver content. The commercial toothbrushes are embedded with silver nanoparticles, and the adult and children toothbrush had a total silver content of 16.07 ± 0.11 and 13.53 ± 0.04 g for the whole tooth brush, respectively. Based on these studies, it can be assumed that most of the nanosilver and silver, which is used domestically, finds its way to the municipal sewage plants [6, 46] or to the environment if there is no municipal sewage plant connection as in most rural areas of developing countries [12]. The silver content of sewage wastewater is lower in comparison with sewage sludge since the silver is adsorbed onto sewage biomass to form insoluble silver sulfide (Ag_2S) [47]. Thus, the hazard may arise when the sludge is applied on farmland as fertilizer. A recent study by Wu et al. [13] in China, showed under pH conditions, metal promoters Cu and Zn, aerobic conditions, and the presence of sulfur-dominated amino acids, that the insoluble Ag_2S might become mobile and available for uptake by crops such as wheat mostly than in brown rice.

In South Africa, the Department of Water & Sanitation has not developed guideline values for silver in the sewage sludge or the disposal of sewage containing silver [48]. Elsewhere in the United States of America, the Environment Protection Agency has regulated silver ion generators as pesticides under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) but not silver in sewage sludge [36, 49]. In the European Union, the biosolids directive (sewage sludge directive 86/278/EEC) states that all biocides that contain silver should be screened and approved by May 14, 2014 [50].

Aluminium is another trace metal that is also found in high concentrations in the dried municipal sludge in excess of 6900 mg/kg (**Table 2**). The origin of Al in the domestic wastewater is probable probably the use of deodorants that contain Al as shown by the study of Modika [51] or the use of Al cookware where upon washing releases Al in the wastewater [52]. In a separate case studied by Modika [51], in South Africa, the Ag and Al contents in wastewater were in the range of 0.03–0.52 ppb and 0.03–0.21 ppm, respectively, over the 5-day period. The Ag and Al contents in soap B were found to be <0.032 ppb and 0.07 ppm, respectively. The Nivea deodorant spray had the silver and aluminum of 7.03 ppb and 124.88 ppm, respectively. The wastewater was disposed to the natural environment since in the village there is no municipal sewerage connection.

4.3. Trace metals in sediments of impoundments and rivers receiving sewage effluent

The sewage effluent rich in metals is discharged into rivers and streams, and the metals either stay in solution or are trapped in complex sediments and pollution sinks [53]. The metals in the sediments can be released back into the water column should the environmental conditions change, such as pH becoming acidic, with devastating consequences on aquatic life and human health [15, 54] or during flood conditions [55]. The pH values in the study sites were generally near the neutral to alkaline, and therefore there was no contribution of metals due to the dissolution of bedrock or mining activities (**Table 3**). The trace metals that are likely to have an impact on aquatic life are Cd, Cr, V, Pb, Ni, and Zn.

Trace metals (mg/kg dry weight)	^a [27] mg/kg dry weight Average concentration	^b [18] mg/kg dry weight range concentration	^c [28] mg/kg dry weight range concentration	^d [21] mg/kg dry weight range concentration	^e [15] mg/kg dry weight Average concentration	^e [15] mg/kg dry weight Average concentration	^e [15] mg/kg dry weight Average concentration	^e [15] mg/kg dry weight Average concentration	Australian and New Zealand (ANZECC) [56] mg/kg dry weight	
Name of River or dam	Doringspruit flows into Albasini dam	Sand	Mvudi	Nzhelele	Ga-Selati	Oliphant River @ Phalaborwa a barrage	Letaba River, enters KNP	Luvuvhu River, enters KNP	Low risk	High risk
Name of sewage plant	Elim	Polokwane	Thohoyandou	Siloam	Namakgale, Phalaborwa	Upstream sewage plants	Malamulele	Thohoyandou	Freshwater & reservoirs	
pH*	7.34 – 7.63	7.49 – 8.30	7.3 – 7.7	7.21 – 7.76	8.7	8.6	8.1	8.1	6.5	8.0
Al	136.660 ± NA	–	4080 – 9090	2331 – 4707	145392.94	93046.9	23865.48	36066.5	–	–
Cr (total)	0.337 ± 0.045	–	31.96 – 175	7.804 – 51.288	969.29	623.41	270.48	312.58	80	370
Mn	4.801 ± 0.185	39.3 – 225	160 – 2160	120 – 516	3295.57	1209.61	1352.38	2019.72	–	–
Fe	196.128 ± NA	25.6 – 256.4	2900 – 7460	1175 – 5252	164778.67	148875.04	62050.25	110603.95	–	–
As	–	–	–	–	18.42	16.75	14.96	15.15	20	70
Cd	0.058 ± 0.041	0.0192 – 0.0284	bdl – 2.189	0.006 – 4.056	0.16	0.09	0.19	0.12	1.5	10
Cu	0.260 ± 0.056	0.89 – 2.28	7.68 – 5690	2.182 – 566	174.47	195.4	68.41	158.69	65	270
Zn	0.412 ± 0.009	6.67 – 15	9.78 – 1524	2.605 – 202	155.09	139.57	71.6	88.96	200	410
Pb	0.426 ± 0.024	0.71 – 3.38	1.17 – 8.37	0.248 – 2.71	30.05	25.12	15.75	17.07	50	220
Ni	0.161 ± 0.033	–	–	–	562.19	334.97	116.15	175.52	21	52
Co	0.279 ± 0.006	–	–	–	135.7	84.67	5.75	81.75	–	–
V	0.583 ± 0.079	–	–	–	310.17	558.28	175.01	360.67	–	–

Notes: bdl: below detection limit; – not available; KNP: Kruger National Park; *pH is for water column above the sediments; ^arange is for the 2 samples sites; ^brange is for the 8 sample sites; ^c^drange is values from Jan to Jun 2014; ^enormalised to 10% taking into account background values.

Table 3. Concentrations for trace metals in sediments of selected freshwater impoundments and rivers in Limpopo receiving sewage effluent.

Nibamureke [27] found high levels of Fe and Al in sediments in excess of TQWR aquatic life guidelines which were probably linked to rainfall that may have occurred during the sampling trip (Table 4). However, the near neutral pH of the water samples would imply that the Al and Fe would not be available for uptake by the fish and cause harm especially to the gills. Nibamureke [27] showed that the high Cr (0.337 mg/l) levels would likely affect fish health as shown by changes in blood variables (hematocrit and plasma proteins) and were consistent with Cr exposure. The Cr ions are toxic since the alkaline pH contributes to the availability of Cr in sediments and becomes available in the water column.

Nibamureke [27] concluded that Cu levels were not harmful to fish health since the high Cu levels were transitional as a result of rainfall events that occurred during the sampling period. Also, other variables such as dissolved oxygen, total hardness metals (Ca and Mg), and Zn compete with Cu in fish physiology, thus reducing Cu toxicity [30]. Nibamureke [27] concluded that Mn levels in the sediments were likely to be harmful to fish health as a result of Mn becoming soluble due to alkaline pH. Though Mn is an essential metal in fish health, higher levels become toxic and cause reduced red and white blood cells, causing damage to kidney and spleen [27].

Nibamureke [27] showed that a high Pb level in the sediment is a cause of concern since Pb has been implicated in endocrine disruption chemical. However, other variables such as low DO levels and hardness (Ca and Mg) metals tend to inhibit Pb toxicity in fish, thus preventing its bioavailability [27]. Thus, the presence of Pb in the sediments may be linked to sewage inflows originating from Elim oxidation ponds and leaching from surrounding farms [20]. The levels of Cd in sediments are harmful to aquatic life. The Cd metal accumulates in the sediment and may become toxic to aquatic life such as *C. riparius* since these midge larvae live at the bottom sediments [38]. Their study showed that at laboratory exposure of 18.33 mg/l, Cd treatment altered the gene profile of small heat shock proteins (sHSPs). These sHSPs protect the organism against adverse conditions that may be encountered such as high Cd levels found in the sediments.

4.4. Impact of metal on aquatic environment

There are a number of studies that have shown the impact of trace metals on aquatic flora (plants) and aquatic fauna [15, 18, 27]. The study by Nibamureke [27] on fish species, *Clarias griepinus*, *Coptodon rendalli*, and *Oreochromis mossambicus* on their health from Albasini dam showed the presence of trace metals and so on. The source of trace metals is probably the effluent discharge from Elim sewage plant into Doringspruit River which then flows into Albasini dam [20].

The studies by Seanego [18] and Nibamureke [27] showed that the metals, Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Pb, V, and Zn, were present in fish body in various organs (Table 4). These metals contribute to the well-being of the fish at trace levels. However, there are two metals, Al and Fe that were in toxic levels and were likely to cause histopathological damage to the fish as shown from the study by Nibamureke [27]. The study by Seanego [18] on the Sand River, the Limpopo province of South Africa, also found high Fe levels in the body mass of *O. mossambicus* fish.

In another study in Loskop dam, South Africa, Oberholster et al. [58] showed that the Al and Fe bioaccumulate in algae which in turn is consumed by *O. mossambicus* as part of their diet and the Al and Fe are now present in the fish. In a separate study by Magonono [59] and

Trace metals (mg/kg)	Albasini dam [27] Average concentration		Sand River [18] range concentration	Flag Boshielo dam – [57] Average concentration	Phalaborwa barrage [57] Average concentration
Name of River	Doringspruit River		Sand River	Elands & Oliphant	Oliphant
Name of sewage plant	Elim		Polokwane	Marble Hall & upstream of Oliphant Rivers	Sewage plants upstream of Oliphant River
Fish muscle	<i>C. gariepinus</i>	<i>O. mossambicus</i>	<i>O. mossambicus</i>	<i>O. mossambicus</i>	<i>O. mossambicus</i>
Al	0.813 ± 0.199	0.911 ± 0.291	–	59.8	59.4
Cr (total)	–	–	–	36.9	13.5
Mn	0.012 ± 0.002	0.021 ± 0.009	113.6 – 290.9	5.3	15.3
Fe	0.241 ± 0.064	0.247 ± 0.079	1286 – 3429	647	125
As	–	–	–	0.7	0.0
Cd	–	–	0.0898	0.0	0.2
Cu	0.009 ± 0.001	0.012 ± 0.004	8 – 14	10.5	4.9
Zn	0.202 ± 0.025	0.243 ± 0.042	78 – 159	25.8	214
Pb	0.003 ± 0.000	0.003 ± 0.000	–	4	4.8
Ni	–	–	–	2	4.9
Co	–	–	–	2	0.4
Se	–	–	–	1.7	2

Notes: – not available.

Table 4. Average and range concentrations for trace metals in fish in freshwater impoundments and rivers in Limpopo receiving sewage effluent.

Gumbo et al. [20], they showed the presence of algae in the Sand River and the Albasini dam as a result of the availability of nutrients. The source of Fe in the body mass of *O. mossambicus* was in part attributed to bedrock of the Sand River which is dominated by the granite which on weathering produces Fe and Mn [18] and effluent discharge from Polokwane sewage plant rich in Fe and Mn since there are high levels of Fe and Mn in the sewage sludge [41].

Another hypothesis advanced by Oberholster et al. [58] was that the consumption of algae with Al led to a drop in pH to 2.9 in the stomach of *O. mossambicus*, thus contributing to the Al bioavailability. The same process of biomagnification in the food chain may be occurring with fish in Albasini dam and may account for the high Al and Fe levels in fish body muscles. Again in the same study by Oberholster et al., they found evidence of yellow fat which was associated with a high Al level in the *O. mossambicus* fish, and the yellow fat is associated with pansteatitis. The pansteatitis has been linked with the death of crocodiles and fish in the Kruger National Park [15]. The studies by Seanego [18] and Nibamureke [27] did not show if this condition of pansteatitis was occurring within the *O. mossambicus* fish in the Albasini dam or in the Sand River.

4.5. Human health-risk assessment

The consumption of fish by rural communities in South Africa is on the increase since fish is an affordable protein source in comparison with other animal or plant protein sources [60]. The fish are provided by illegal fisherman or from small-holder fish farms that are located in the Limpopo province [61, 62]. However, for wild stock fisheries, a number of studies in South Africa have shown that the popular *O. mossambicus* fish is contaminated with metals such as Al, Fe, and Pb at toxic levels [18, 27, 57, 58]. Thus, studies have been conducted to evaluate human health-risk assessment of the consumption of fish contaminated with toxic metal (**Table 5**).

The average daily dose (ADD) is expressed in mg/kg human body mass per day from this expression (1) as per the procedure by Addo-Bediako et al. [57].

$$ADD = \frac{(\text{average metal in fish muscle } (fw)) \times (\text{mass of fish consumed})}{(\text{adult body mass}) \times (\text{number of days in between fish meals})} \quad (1)$$

where the average metal concentration (mg/kg) in fish muscle, mass of fish consumed (kg) was 0.150 kg portion once per 7 days, adult body mass (kg) was 70 kg, and days is the number of day in between fish meals.

The hazard quotient (HQ) for fish from the Albasini dam and the Sand River was calculated from the data that were provided on the trace metals in the fish muscles based on the procedure by Addo-Bediako et al. [57]. The assumptions were that an individual would eat 150 g of fish per week and the adult body mass was 70 kg as per the study by Addo-Bediako et al. [57]. The studies clearly showed the high levels of trace metals in the fish muscle, and these metals, Cr, Pb, and Sb [57] and Fe and Pb [18], were likely to affect human health (**Table 5**). The human-risk assessment (HQ) was near 1 or was above 1 and thus posed hazard to fish consumers near the Phalaborwa Barrage, Flag Boshielo dam, and the Sand River.

The presence of Cr poses human health issues especially the Cr⁶⁺ ion which is toxic and carcinogenic to humans [39]. The presence of Pb is a serious concern in South Africa since the phased out of Pb in petroleum fuels is due to impairments of cognitive development in children [20, 39]. The presence of Fe is that the fish at these high levels poses a challenge since Fe is an essential element of human physiology hemoglobin, for instance, but may cause hemosiderosis (lung complications) [39]. The presence of Sb is a serious concern in South Africa since the Sb is a waste by-product of the manufacture of electronic circuitry and light-emitting diodes (LEDs) [63] and Sb origins maybe industrial waste or geological [64]. The Sb is not known to be essential to human health and has been associated with dermatitis, a skin disease [65], and cancer [66]. The presence of Ag is a serious concern in South Africa since the Ag may originate from the discharge of Ag-based nanoproducts in sewage effluent or in sludge [6]. Thus, there is a cause of concern since the sewage effluent continues to be discharged into these freshwater impoundments and rivers and the metal contamination of fish is likely to increase due to the detriment of rural fish consumers.

Fish species	Reference dose (RfD) (µg/kg)	Addo-Bediako et al. [57]			^a Nibamureke [27]			^b Seanego [18]								
		<i>O. mossambicus</i>		<i>O. mossambicus</i>	<i>C. gariepinus</i>			<i>O. mossambicus</i>								
Name of sewage plant		upstream of Oliphant River		Marble Hall & upstream of Oliphant Rivers			Elim			Elim			Polokwane & Seshego			
Name of river or dam		Phalaborwa barrage			Flag Boshielo dam			Albasini dam			Albasini dam			Sand River		
Trace metals		[Metal] (mg/kg fw)	Average daily (ADD) µg/kg	HQ	[Metal] (mg/kg fw)	Average daily dose (ADD) µg/kg	HQ	[Metal] (mg/kg dw)	Average daily dose (ADD) µg/kg	HQ	[Metal] (mg/kg dw)	Average daily dose (ADD) µg/kg	HQ	[Metal] (mg/kg dw)	Average daily dose (ADD) µg/kg	HQ
Al	1000	14.9	4.55	0.00	15.0	4.58	0.0	0.813	0.24	0.00	0.911	0.27	0.00	0	0	0
Fe	700	31.4	9.61	0.01	161.7	49.49	0.07	0.241	0.07	0.00	0.247	0.07	0.00	2550	744.45	1.06
Mn	140	3.8	1.17	0.01	1.3	0.4	0.0	0.012	0.00	0.00	0.021	0.01	0.00	206.2	60.21	0.43
Cu	40	1.2	0.37	0.01	2.6	0.81	0.02	0.003	0.00	0.00	0.012	0.00	0.00	0	0	0
Cr	3	3.4	1.04	0.35	9.2	2.82	0.94	0	0	0	0	0.00	0	0	0	0
Ni	20	1.2	0.38	0.02	0.5	0.15	0.01	0	0	0	0	0	0	0	0	0
Zn	300	53.6	16.4	0.05	6.4	1.97	0.01	0.202	0.06	0.00	0.243	0.07	0.00	131.8	38.5	0.128
Pb	0.057	1.2	0.37	6.14	1.0	0.31	5.12	0.003	0.00	0.015	0.003	0.003	0.015	3	0.88	14.365
Sb	0.4	0.3	0.09	0.23	5.0	1.52	3.79	0	0	0	0	0	0	0	0	0
V	5	53.6	0.15	0.05	7.7	2.37	0.47	0.004	0.00	0.00	0.005	0.005	0.00	0	0	0
As	0.3	0.01	0.00	0.01	0.2	0.06	0.19	0	0	0	0	0	0	0	0	0
Cd	3	0.0	0.01	0.00	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
Co	0.4	0.1	0.03	0.07	0.5	0.15	0.38	0	0	0	0	0	0	0	0	0
Ag	5	1.3	0.40	0.08	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0

Notes: Fw fresh wet; dw dry weight; ^aaverage dry weight of the fish; ^baverage of dry weight of four sample points.

Table 5. The hazard quotients (HQ) for the fish species in freshwater impoundments and rivers receiving sewage effluent.

4.6. Future management strategy dealing wastewater and sludge

The continued discharge of sewage effluent and sludge rich in trace metals is likely to continue in future as population increases in urban areas driven in part by rural to urban migration and naturally. Also, there is a need for more studies on other river catchments where there is lack of information in the Limpopo province. Other studies by Sibanda et al. [25], Shibambu [32], Gumbo et al. [68], and Olowoyo and Lion [69] have shown that the wastewater is rich in nutrients and essential traces such that the wastewater is usable for irrigation of crops, fruit trees, and vegetables. Limpopo province is a dry and arid region and the use of wastewater for irrigation is a welcome idea but there should be safeguards in place to protect the food consumers and irrigators from the negative impacts of wastewater reuse [68, 69]. The sludge may be used for innovative ways such as top soil cover (mined areas), biofertilizer, building materials, veld fire retardant and control, erosion control, forestry fertilization, and recovery of phosphorus [1]. Also, there is a need for a paradigm shift of sewage plants of just treating sewage to mining or to recover valuable and economic metals according to Mulchandani and Westerhoff [67]. The disposal of trace metals with engineered nanosized scale such as Ag, Ti, and Zn to sewage sludge is also on the increase worldwide as scientists develop and introduce new nanotechnological products. In order to safeguard the environment, there is a need to mine these trace metals from sewage sludge.

5. Conclusion

The municipal sewage plants continue to discharge effluent rich in trace metals to the aquatic environment. Some of these trace metals are harmful to the humans as they biomagnify through the food web such as the consumption of fish. The introduction of nanosized metals to the sewage effluent exacerbates the situation of metal pollution of the aquatic environment. There is a need for a paradigm shift where sewage plants discharge zero effluent and start harvesting the valuable trace metals in order to protect the environment.

Conflict of interest

The authors declare no conflict of interest.

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