

*Original Research*

# Evaluating Physicochemical Parameters, Heavy Metals, and Antibiotics in the Influent and Final Effluents of South African Wastewater Treatment Plants

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## Abstract

The waste generated from antibiotics as influents or effluents in important waters from the rivers over their increased usage is quickly leading to societal health problems. To avoid increased accumulation of these antibiotics and their waste matter, new methods and materials are required to solve the problems before escalation. This paper aimed at evaluating treated wastewater effluent quality of three wastewater treatment plants in South Africa's Vaal Triangle: Sebokeng, Rietspruit, and Leeuwkuil. The influents and effluents were collected and analysed for heavy metals, and eight antibiotic substances for human use (erythromycin, ampicillin, cimetoprim, tetracycline, ciprofloxacin, doxycycline, chloromphenol, and sulfamethoxazol). The physicochemical parameters were also measured and the results showed that Rietspruit influent (Riet IN) had the highest salinity, total dissolved solids (TDS), electrical conductivity (EC), and turbidity. Sebokeng was found to have the lowest values for all the measured parameters except for pH, which was lowest in Leeuwkuil influent (Lee IN). All the antibiotics were below the detection limit in all three wastewater treatment plants (WWTPs), except for sulfamethoxazole. The average concentration of sulfamethoxazole in the influents and effluents for the three investigated WWTPs ranged 39–47.8 ng L<sup>-1</sup>. The lowest concentrations of magnesium (8.60 mg L<sup>-1</sup>) and copper (0.054 mg L<sup>-1</sup>) were found in Rietspruit (Riet MID) and Lee EFF, respectively. Lee IN had the highest concentrations of Na (27.98 mg L<sup>-1</sup>), K (7.48 mg L<sup>-1</sup>), Mn (0.249 mg L<sup>-1</sup>), Cu (0.208 mg L<sup>-1</sup>), Fe (0.396 mg L<sup>-1</sup>), Ni (2.271 mg L<sup>-1</sup>), and Ca (28.60 mg L<sup>-1</sup>), while Riet IN had the highest Co concentration of 0.324 mg L<sup>-1</sup>. Sebo EFF and Sebo IN showed 11.82 mg L<sup>-1</sup> of Mg and 2.437 mg L<sup>-1</sup> of Zn, respectively. The abundance of the metal concentrations follows the order

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The reuse of treated effluent that has been discharged into the environment from municipal wastewater treatment plants (WWTP) is increasing due to the ever-increasing demands for water as the available supplies of freshwater are decreasing due to natural disasters such as droughts and the rapid growth of the global population [1]. The final effluents from WWTPs will pose a health risk to both humans and animals when not properly treated, as they could contain several contaminants, including pharmaceuticals such as antibiotics and heavy metals. Heavy metals such as cadmium ( $\text{Cd}^{2+}$ ) and lead ( $\text{Pb}^{2+}$ ) are toxic inorganic contaminants found in the environment released from industries such as metal plating, mining, cadmium-nickel and lead battery production, smelting, phosphate fertilizers, and the paint industry. Their bioavailability is influenced by such physical factors as temperature, adsorption, and sequestration, as well as chemical factors that influence complexation kinetics, speciation, and lipid solubility [2].

Antibiotics are chemotherapeutic agents that inhibit the growth of microorganisms such as bacteria, protozoa, and fungi. They are complex molecules that may have different functionalities within the same molecule, meaning that under different pH conditions they can be cationic, anionic, neutral, or zwitterionic [3]. While antibiotics save millions of lives globally each year,

their indiscriminate use poses an increasingly serious threat to public health [4]. The major pathway whereby antibiotics from human use enter the environment is the WWTP, since conventional plants do not completely remove pharmaceuticals [5]. The antibiotics end up in WWTP due to improper disposal of expired drugs (directly throwing in toilets), pharmaceutical residues from manufacture spill accidents, poultry processing, and agriculture and excretion via urine or faeces since many antibiotics are not completely metabolized and absorbed [6, 7].

The major concern of antibiotics release into the environment is the development of bacteria resistance and the resulting implications in human health [8]. Among the different classes of antibiotics, sulfamethoxazole is a representative compound of the sulfonamide bacteriostatic antibiotic family. WWTP-treated effluents are a significant source of antibiotic-resistance gene release into the downstream environment. The South African Water Act was established in 1956 and aimed to treat wastewater effluent to an acceptable standard prior to discharge into receiving water bodies. The aim of this study was to determine the occurrence of antibiotic residues in raw and treated sewage effluents from three different sewage treatment plants (Sebokeng, Rietspruit, and Leeuwkuil) in the Vaal Triangle, South Africa. Antibiotic sulfamethoxazole was used to monitor the efficacy of sewage plants to remove antibiotics.

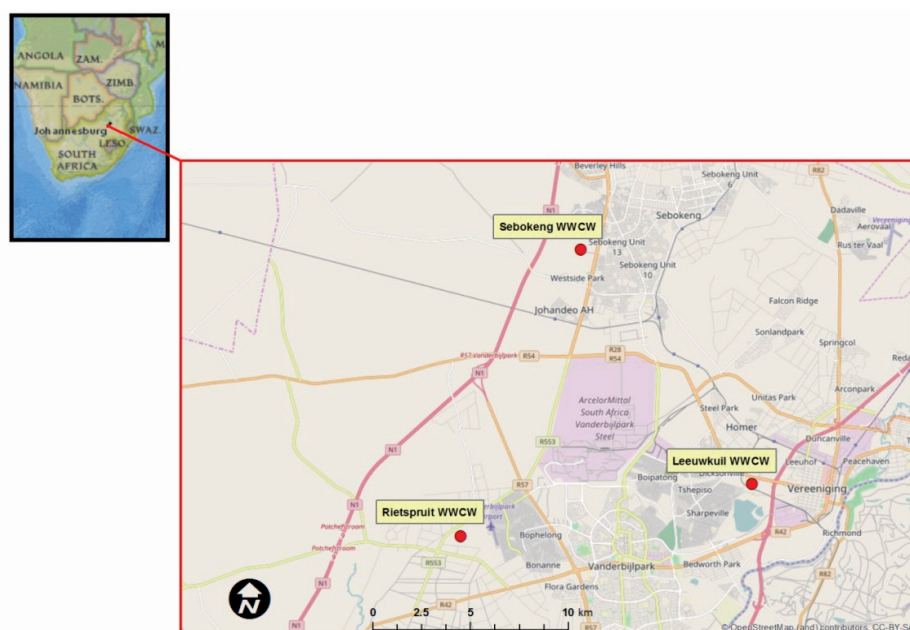


Fig. 1. Study area map showing locations of the WWTP sampling points.

## Materials and Methods

### Study Area Description

This research was carried out in Vaal Triangle on Sebokeng, Rietspruit and Leeuwkuil wastewater treatment plants in South Africa as shown in Fig. 1. The Sebokeng plant (SWWTP) is situated approximately 18 km northwest of Vereeniging, at approximately 26°34'29.03"S and 27°49'2.64"E. The catchment area includes some areas of the Emfuleni Local Municipality and Johannesburg Metropolitan Municipality. The catchment area includes Evaton, Evaton West, Palm Springs, Evaton North, Lakeside, Iron syde, Evaton side, Sebokeng Hills, Beverley Hills, Boitumelo, Johandeo, Poortje, Lenasia, and Orange Farm. The catchment area so far is mainly for housing, hence the origin of the wastewater is assumed to be mainly domestic. The catchment areas of the Leeuwkuil plant (LWWTP) include Sharpville, Tshepiso, Bedworth Park, Vereeniging, Three Rivers, Waldrif, and Roshnee; and Rietspruit (RWWTP) includes Bophelong, Louisrus, Movhango, and Vanderbijlpark. The final treated water from SWWTP and RWWTP is discharged into the Rietspruit River, whereas the LWWTP discharges its treated water into the Vaal.

### Water Sampling

Water samples were collected from each study site on the same day. The influents and effluents were collected in prewashed polyethene bottles. Each bottle was filled to the top to exclude air that could oxidize the dissolved organics in the samples. The samples were kept in the refrigerator at 4°C prior to analysis. Physico-chemical water parameters, which include electrical conductivity (EC;  $\mu\text{S cm}^{-1}$ ), pH, total dissolved solids (TDS;  $\mu\text{g L}^{-1}$ ), dissolved oxygen concentration (DO in  $\text{mg L}^{-1}$ ), total suspended solids (TSS), salinity, and turbidity were measured using a Hanna multi-parameter probe (HI 9828) at  $\pm 20$  cm below the water surface.

### HPLC Analysis

QA Bischoff HPLC with a UV detection system was used to separate and quantify the antibiotics. The wavelength ( $\lambda_{\text{max}}$ ) for analysis of the antibiotics was set at 254 nm and the column temperature was 20°C. The mobile phase composition was 50% water and 50% methanol, which was pumped at a flow rate of 2  $\text{mL min}^{-1}$ .

### Determining Selected Antibiotics

In separate vials, eight antibiotics were weighed (14 mg). They were then dissolved in methanol in 10 mL volumetric flasks. With ciprofloxacin, a solution of methanol: acetic acid 1:9 (v/v) was used. A mixture of the stock solution was made from these eight

individual antibiotic solutions by transferring 1.78 mL into a 100 mL volumetric flask and topping up to the mark with methanol.

### Heavy Metals Concentration Determination

For metals' analysis we used an ICP-OES Spectro Genesis End-on-plasma from Spectro Analytical Instruments (Pty.) Ltd. (Johannesburg, South Africa). Real samples were collected from three different wastewater treatment plants under study. In the laboratory, the samples were sonicated for 15 min before filtering through the 0.45  $\mu\text{m}$  filter paper. The solution was divided into two equal portions for metal ion determination and the other portion for organic compound analysis. The solution for metal ion analysis was then acidified with 5% (v/v). Both samples were kept in the fridge at 4°C until time of analysis.

## Results and Discussion

The physicochemical parameters were measured and it was found that Rietspruit influent had the highest salinity, total dissolved solids (TDS), electrical conductivity (EC), and turbidity. Sebokeng effluent was found to have the lowest values in all the measured parameters except pH, which was lowest in Leeuwkuil. Sebokeng influent had the highest pH of 7.07 and total dissolved solids (TSS) of 92, yet its effluent had the lowest TSS of 3, implying that the operation was efficient. Dissolved oxygen (DO) is an important parameter used for water quality control. The DO levels of the effluents (which are recommended to range between 8 and 10  $\text{mg L}^{-1}$  by the EU) were less than 5  $\text{mg L}^{-1}$ , except for Sebokeng. This level affects the aquatic ecosystem adversely. In a similar study by Momba and co-workers, (2006) in Buffalo City and Nkonkobe Municipalities, Eastern Cape, South Africa, levels of DO oxygen were found to be less than 5  $\text{mg L}^{-1}$ , except for East London and Fort Beaufort treatment plants [9].

### Antibiotics Analysis

The chromatograms (Fig. 2) for the inlet where the WWTP receives the raw water from industrial and

Table 1. Capacity, average inflow, and effluent of LWWTP, SWWTP, and RWWTP.

Plant name	Design capacity (ML/day)	Average inflow per day (ML)	Final effluent per day (ML)
Leeuwkuil	36	38.75	37.06
Rietspruit	36	30.53	22.28
Sebokeng	100	110.32	107

ML: Megalitres

Table 2. Physicochemical properties of both inflow and final effluent of Sebokeng, Rietspruit, and Leeuwkuil WWTPs.

Water quality parameter	Sampling point					
	Sebo IN	Sebo EFF	Riet IN	Riet EFF	Lee IN	Lee EFF
pH	7.07	6.97	6.88	6.87	6.72	6.91
Salinity	0.28	0.16	0.34	0.23	0.27	0.28
TDS	289	166	343	234	273	288
EC	580	333	688	470	546	577
DO	2.13	8.90	2.70	4.01	2.79	3.04
Turbidity	102	4	90	16	72	38
TSS	92	3	75	14	71	34

TSS: total suspended solids, COD: chemical oxygen demand, EC: electrical conductivity, TDS: total dissolved solids, DO: dissolved oxygen, Sebo IN: Sebokeng inflow, Sebo EFF: Sebokeng effluent, Riet IN: Rietspruit inflow, Riet EFF: Rietspruit effluent, Lee IN: Leeuwkuil inflow, Lee EFF: Leeuwkuil effluent

domestic waste are dirty as observed at the Lee plant. Some of the peaks were difficult to quantify as they overlapped with the matrix. From the chromatograms of the sampled areas we observed that there were subtle differences in the peaks, implying that the treatment plants receive the raw water of almost the same quality. The broad shoulders on all chromatograms could be a result of the decaying biota, which results in humic substances.

In this study, the average concentration of sulfamethoxazole in the influents and effluents for the three investigated WWTPs ranged 39-47.8 ng L<sup>-1</sup>. This concentration range does not deviate from the concentrations of this antibiotic compared to other studied WWTPs in South Africa and the rest of the world. Antibiotics were detected in appreciable amounts at the inlet of the wastewater treatment plant. Example includes: a high concentration of sulfamethoxazole (59.28 µg L<sup>-1</sup>) was detected at the influent of the WWTP, Northern water works, Durban, South Africa [10]; among the 12 pharmaceutical compounds investigated by Qarni and co-workers (2016), sulfamethoxazole was found in

Table 3. Some analytical regression analysis data obtained for sulfamethoxazole analysis.

Parameter	Value
Retention time (min)	11.14
Regression equation	$y = 116.8x - 8.937$
R <sup>2</sup>	0.9951
LOD (mg L <sup>-1</sup> )	0.052
LOQ (mg L <sup>-1</sup> )	0.179
Linear dynamic range (mg L <sup>-1</sup> )	0.25-2.4

Table 4. Concentrations of sulfamethoxazole in different stages at WWTPs.

Site/location	Concentration (ng L <sup>-1</sup> )		
	Inlet	Middle	Outlet
Rietspruit	39.5	-	-
Sebokeng	-	-	15.0
Leeuwkuil	-	57.8	80.3

- : not detected

the influents and effluents of two hospital WWTPs in Saudi Arabia [11]; of the 22 representative antibiotics studied by Zhang et al. (2016), sulfadiazine (396 ng L<sup>-1</sup>) and sulfamethazine (382 ng L<sup>-1</sup>) were the dominating antibiotics in the influent, and the concentrations of selected antibiotics ranged from ND-41.8 ng L<sup>-1</sup> in the effluent-receiving river [12]; and in a nationwide groundwater survey conducted by the United States Geological Survey (USGS), sulfamethoxazole appeared in 23% of the samples at an average concentration of 1.11 µg L<sup>-1</sup>.

### Removal Efficiency of the Treatment Plants

The removal efficiencies of the WWTPs for the removal of the sulfamethoxazole were calculated using the following equation:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

...where C<sub>0</sub> and C<sub>e</sub> are the inlet and outlet concentrations of sulfamethoxazole (mg L<sup>-1</sup>).

The wide variation of the removal ability of the three WWTPs (-34.3% to >99%) is not surprising as this spread has been observed across the world. In a study by Bhandari et al. (2008) in various aqueous streams of four municipal WWTPs in the Midwestern United States, the average aqueous phase concentrations for sulfamethoxazole in the raw wastewater and effluents were 18.3 µg L<sup>-1</sup> and 3.25 µg L<sup>-1</sup>, respectively [13].

Sewage treatment plants are rarely equipped to filter these drugs from wastewater. Antibiotics are released into the water system and this often results in poor or

Table 5. Removal efficiency of the wastewater treatment plant for sulfamethoxazole.

Sampling area	Removal efficiency (%)
Rietspruit	> 99
Sebokeng	-
Leeuwkuil	-34.3 <sup>a</sup>

<sup>a</sup>Calculated from the sample collected at sedimentation and the outlet



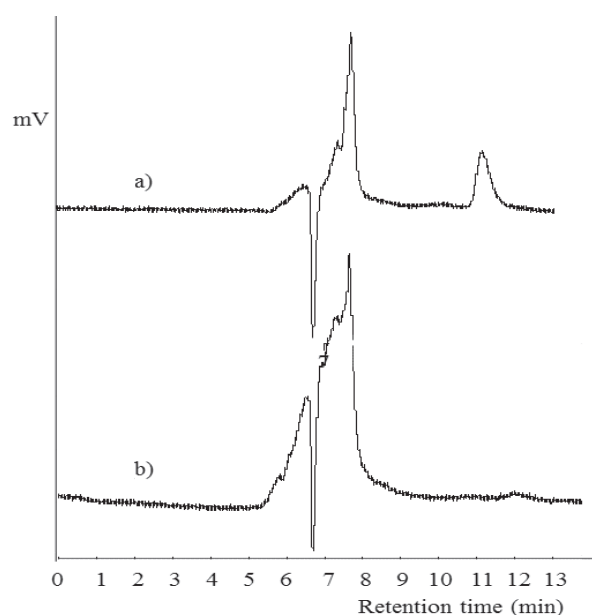


Fig. 2. Chromatograms of a) a standard solution  $0.25 \text{ mg L}^{-1}$  and b) sample.

negative removal efficiencies, as at the Lee WWTP (Table 4). The same trends were found by Zhang and co-workers (2016) in a series of the antibiotics where they observed the influent and effluent concentrations of ofloxacin to be  $214$  and  $274 \text{ ng L}^{-1}$ , respectively [12]. This resulted in a negative removal efficiency. The authors also observed that all investigated macrolides, like spiramycin, had a lower influent concentration compared to the effluent. A good percentage ( $> 90 \%$ ) of the antibiotics was removed after treatment [10]. The removal efficiencies of sulfamethoxazole using different methods such as activated sludge (AS) and membrane bioreactors (MBR) are shown in Table 6.

### Metal Analysis

The trace metals analysed in the water samples from the three wastewater treatment plants at different stages of water treatment are shown in Table 3. We observed that the least concentration of sodium ( $17.26 \text{ mg L}^{-1}$ ), cobalt ( $0.239 \text{ mg L}^{-1}$ ), manganese ( $0.022 \text{ mg L}^{-1}$ ), iron ( $0.105 \text{ mg L}^{-1}$ ), zinc ( $0.706 \text{ mg L}^{-1}$ ), and platinum ( $<0.065 \text{ mg L}^{-1}$ ) were found in the Sebo EFF water sample, whereas gold ( $0.240 \text{ mg L}^{-1}$ ), calcium

( $13.04 \text{ mg L}^{-1}$ ), arsenic ( $0.050 \text{ mg L}^{-1}$ ), and potassium ( $3.66 \text{ mg L}^{-1}$ ) were least in Sebo MID. The lowest concentrations of magnesium ( $8.60 \text{ mg L}^{-1}$ ) and copper ( $0.054 \text{ mg L}^{-1}$ ) were found in Riet EFF and Lee EFF, respectively. In a similar study, Cu levels in the effluent were found to range between  $0.002$  and  $0.011 \text{ mg L}^{-1}$  [16].

The water sample Lee IN measured the highest concentrations of Na ( $27.98 \text{ mg L}^{-1}$ ), K ( $7.48 \text{ mg L}^{-1}$ ), Mn ( $0.249 \text{ mg L}^{-1}$ ), Cu ( $0.208 \text{ mg L}^{-1}$ ), Fe ( $0.396 \text{ mg L}^{-1}$ ), Ni ( $2.271 \text{ mg L}^{-1}$ ), and Ca ( $28.60 \text{ mg L}^{-1}$ ), while Riet IN measured  $0.324 \text{ mg L}^{-1}$  of Co, Sebo EFF showed  $11.82 \text{ mg L}^{-1}$  of Mg, and Sebo INN  $2.437 \text{ mg L}^{-1}$  of Zn. The lower to moderate concentrations measured for water samples in this study may be due to less geological interaction since it is classified as surface water [17]. The concentrations of the trace metals Pb and Cd were below their respective detection limits of  $<0.01$  and  $<0.001$ , respectively. The reason for Pb concentrations being lower than the detection limit in this study could be due to the phasing out of leaded petrol in South Africa. Shamuyarira and Gumbo (2014) also found low concentrations of Pb in Limpopo province, South Africa [18].

Cr concentrations were also below detection limits of  $<0.020$  in the water samples, except for Lee IN and Lee MID with  $0.148 \text{ mg L}^{-1}$  and  $0.128 \text{ mg L}^{-1}$ , respectively. The chemical concentrations of analysed trace metals revealed substantial variability across the geographic spread of the sample points in the study sampling areas. The abundance of metal concentrations follows the order:  $\text{Ca} > \text{Na} > \text{Mg} > \text{K} > \text{Zn} > \text{Ni} > \text{Fe} = \text{Pt} > \text{Co} = \text{Au} > \text{Mn} > \text{Cu} > \text{Cr} > \text{As}$ , indicating higher concentration of Ca as  $28.60 \text{ mg L}^{-1}$  while As has the least value, which is  $0.075 \text{ mg L}^{-1}$ . The concentrations of the studied trace metals are higher for the inflow samples, which may be due to the transportation of wastewater from different anthropogenic activities with the runoff of rainwater and waste leachate. For the elements As, Cd, Cu, Cr, Pb, and Zn, the concentrations in the effluents are below National Water Act waste discharge standards, DWAF 2010 guidelines.

The concentration of As was highest in Sebo EFF and Lee MID ( $0.075 \text{ mg L}^{-1}$ ), which exceeded the WHO standard ( $0.010 \text{ mg L}^{-1}$ ) (Table 3). No permissible guidelines/limits have yet been established for Co. The concentration of Co in the effluent ranged  $0.239$ - $0.324 \text{ mg L}^{-1}$ . However, easily dissolved cobalt

Table 6. Removal efficiencies of sulfamethoxazole from different WWTPs.

WWTP	Country	Removal (%)	Reference
Northern Water works (Durban)	South Africa	$> 90$	[10]
HWWT MBR (pilot scale)	Switzerland	7	[14]
MWWTP AS + chlorination	Taiwan	20	[15]

HWWT: hospital wastewater treatment plants, MWWTP: municipal wastewater, MBR: membrane bioreactor, AS: activated sludge

Table 7. Trace metal concentration (mg L<sup>-1</sup>) at different stages of wastewater treatment.

Sample ID	As	Co	Na	K	Mg	Mn	Cu	Ni	Cr	Fe	Zn	Pt	Au	Ca	Pb	Cd
Lee IN	0.057	0.274	27.98	7.48	11.68	0.249	0.208	2.271	<0.020	0.396	1.121	0.396	0.274	28.60	<0.01	<0.001
Lee MID	0.075	0.264	23.78	5.32	9.28	0.168	0.070	0.260	0.128	0.292	0.941	0.292	0.264	23.82	<0.01	<0.001
Lee EFF	0.066	0.247	22.84	5.76	9.52	0.032	0.054	0.248	0.148	0.267	0.810	0.267	0.247	22.80	<0.01	<0.001
Riet IN	0.065	0.324	21.90	6.00	10.30	0.152	0.191	0.323	<0.020	0.283	1.072	0.283	0.324	20.74	<0.01	<0.001
Riet MID	0.069	0.307	21.40	5.22	8.60	0.023	0.165	0.304	<0.020	0.174	0.912	0.174	0.306	19.16	<0.01	<0.001
Riet EFF	0.072	0.305	19.82	5.36	9.50	0.023	0.123	0.303	<0.020	0.149	0.843	0.149	0.307	20.98	<0.01	<0.001
Sebo IN	0.053	0.265	22.86	4.72	10.36	0.064	0.192	2.241	<0.020	0.132	2.437	0.132	0.265	16.13	<0.01	<0.001
Sebo MID	0.050	0.240	18.48	3.66	9.82	0.064	0.192	0.268	<0.020	0.132	0.706	0.132	0.240	13.04	<0.01	<0.001
Sebo EFF	0.075	0.239	17.26	4.44	11.82	0.022	0.152	0.268	<0.020	0.105	0.706	<0.065	0.239	21.80	<0.01	<0.001
Maximum	0.075	0.324	27.98	7.48	11.82	0.249	0.208	2.271	0.148	0.396	2.437	0.396	0.324	28.60		
Minimum	0.050	0.239	17.26	3.66	8.60	0.022	0.054	0.241	0.128	0.105	0.706	0.132	0.240	13.04	<0.01	<0.001

Lee IN: Leeuwkuil inflow, Lee MID: Leeuwkuil middle, Lee EFF: Leeuwkuil effluent, Riet IN: Rietspruit inflow, Riet MID: Rietspruit middle, Riet EFF: Rietspruit effluent, Sebo IN: Sebokeng inflow, Sebo MID: Sebokeng middle, Sebo EFF: Sebokeng effluent

compounds in water are more harmful than those that are hard to dissolve in water. When cobalt is found in the body, it is dispersed into all tissues, such as the liver, kidney, and bones [19]. The concentrations of Na in the effluent samples ranged between 17.26 mg L<sup>-1</sup> and 27.98 mg L<sup>-1</sup> but have no health implications. According to WHO (2003), most water supplies contain less than 20 mgL<sup>-1</sup> of sodium (Na), but in some countries levels can exceed 250 mg L<sup>-1</sup> [20]. The concentration of potassium (K) in the final effluents ranged 3.66-7.48 mg L<sup>-1</sup>. Potassium ions in living cells play a significant role in many cell functions, like growth, metabolism, repair, and capacity regulation, as well as in the electric potentials of the cell [21]. The pattern of accumulation in the effluent was in the order Lee EFF > Riet EFF > Sebo EFF. Copper concentrations were below the WHO limit, ranging from 0.054 to 0.152 mg L<sup>-1</sup> in the final effluents. The maximum permissible limit by WHO is (2.0 mg L<sup>-1</sup>), which confirmed that Cu plays an important role in chemical and biological processes in the environment and that excessive exposure could lead to health hazards [22]. Copper enters the water system via mineral dissolution and industrial effluents, since it is used as algicide and insecticide, and through corrosion of copper alloy water distribution pipes. Cu is only potentially hazardous when present at elevated levels in environmental media.

In the collected effluent water samples, the concentration of nickel ranged from 0.248 to 0.303 mg L<sup>-1</sup>. This concentration was above the maximum permissible limit set by WHO (0.2 mg L<sup>-1</sup>). Increased concentration and long-term exposure of humans to Ni can lead to decreased body weight, liver and heart damage, and skin irritation [23]. Concentrations of Ni become a health concern in environments where pH is less than 4.5. Although nickel has been an essential trace element for human and animal health, an uptake of large quantities of nickel can result in birth defects, asthma, respiratory failure, and chronic bronchitis. It can also cause various kinds of cancer on different sites within the bodies of animals [24].

Cr was only found in Lee IN (0.148 mg L<sup>-1</sup>) and Lee Mid (0.128 mg L<sup>-1</sup>) above the maximum permissible limit of 0.1 mg L<sup>-1</sup>. It is reported that frequent ingestion of Cr-contaminated water can cause anaemia and stomach cancer [25]. High Cr concentration has been reported to increase body weight loss and cause a reduction in the percentage of body fat, resulting in weight loss in humans [26]. The concentration of iron in water samples ranged between 0.105 to 0.396 mg L<sup>-1</sup> and is present as Fe<sup>2+</sup> in drinking water and Fe<sup>3+</sup> in suspended form. The levels in the effluents were found in the following order: Lee EFF > Riet EFF > Sebo EFF. The maximum allowed concentration of iron in drinking water is 1.0 mg L<sup>-1</sup> [25]. Ingestion of Fe in large quantities results in a condition known as 'haemochromatosis,' which results in tissue damage due to high iron concentration [25].

Table 8. Removal efficiencies of wastewater treatment plant for different metals.

Metal	Removal efficiency (%)		
	Lee	Riet	Sebo
As	-15.8	-10.8	-41.5
Au	9.9	5.2	9.8
Ca	20.3	-1.2	-35.2
Cd	-	-	-
Co	9.9	5.9	9.8
Cr	-	-	-
Cu	74.0	33.6	20.8
Fe	32.6	47.4	20.5
K	23.0	10.7	5.9
Mg	18.5	7.8	-14.1
Mn	87.1	84.9	65.6
Na	18.4	9.5	24.5
Ni	89.1	6.2	88.0
Pb	-	-	-
Pt	32.6	47.4	-
Zn	27.1	21.4	71.0

(-) Either the influent or effluent was below the detection limits

On the contrary, low iron concentration can lead to nose bleeding, gastrointestinal infection, and myocardial infarction [27].

The concentration of zinc in all the water samples ranged between 0.706 and 2.437 mg L<sup>-1</sup>. The permissible limit of zinc in water according to WHO standards is 3.0 mg L<sup>-1</sup>. The Zn levels in the effluents ranged between 0.706 to 0.843 mg L<sup>-1</sup> in the following order: Riet EFF > Lee EFF > Sebo EFF. Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. Very high concentrations may cause a bitter taste and opalescence in alkaline water [17]. Zinc may be added to the environment anthropogenically through industrial activities like engine wear, exhaust emissions, waste combustion, and the use of sewage sludge from industrial areas as fertilizer [28].

Calcium is a major constituent of different types of rock. Hence it is present in natural waters ranging from zero to several hundred milligrams per litre depending on the source and treatment of the water [17]. Causes for hardness in water and incrustation in boilers are due to the presence of calcium. Its levels in the studied effluents ranged in the order: Sebo EFF < Riet EFF < Lee EFF. The concentration was in the range 13.04 to 22.80 mg L<sup>-1</sup>.

The overall removal efficiency of metals at Leeuwkuil wastewater treatment plant was 30%, followed by Rietspruit (20.62 %) and lastly Sebokeng (17.32 %). For most individual metals, removal efficiency was very low (<<50 %), probably due to the operation of the treatment plants under stress, design weakness, and overloaded capacity. Sebokeng and Leeuwkuil treatments plants receive water that is more than the design capacity, as shown in Table 1. In another study by Morrison et al., (2001), they found that efficiency of the Keiskammahoe treatment plant was poor, resulting in the discharge of raw sewage due to inadequate treatment works, a malfunctioning pump station, and poor planning for expansion [29].

## Conclusions

Sulfamethoxazole was the only antibiotic out of the eight studied antibiotics that was detected in the wastewater of the three WWTPs and was above the LOD of 52 µg L<sup>-1</sup>. There was a wide spectrum of removal efficiencies, ranging from poor to good for LWWT (−34.8%) and RWWT (> 99%), respectively. The current wastewater treatment at the three sites studied during our study was not sufficient for the removal of heavy metals, since only three of the sixteen measured heavy metals at both LWWT and SWWT and one at RWWT were eliminated with efficiencies above 60%. The highest concentrations of most metals were found in Leeuwkuil wastewater. Among the metals studied, the most abundant element was Ca (28.60 mg L<sup>-1</sup>) and the lowest was arsenic (0.053 mg L<sup>-1</sup>). In future, we will investigate seasonal variations of the heavy metals detected in this study.

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## Conflict of Interest

The authors declare no conflict of interest.

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