Preliminary Investigation into Occurrence and Removal of Arsenic, Cadmium, Mercury, and Zinc in Wastewater Treatment Plants in Cape Town and Stellenbosch

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Abstract

The results of metals determination using inductively coupled plasma mass spectrometry (ICP-MS) for wastewater, sludges, freshwater, and sediment from six treatment plants and rivers in Cape Town and Stellenbosch are presented. The possible impacts of waste effluent on the freshwater systems are also assessed. The concentrations of the respective metals can be ranked in the order mercury < cadmium < arsenic < zinc. Occurrence of metals in influent wastewater ranged from 4.04-28.19, 1.64-17.39, 0.64-2.2, and 684.94-5128.31 $\mu g \cdot l^{-1}$ for arsenic, cadmium, mercury and zinc, respectively. Average metal removal efficiency in WWTP is listed as mercury > zinc > cadmium > arsenic, with removal efficiency ranging from 28% for arsenic at Plant B and 90.25% for As at Plant D. Sludges from the six treatment plants exhibited particularly high contents of heavy metals, above the permissible utilization and disposal of sewage sludge guidelines. Metal content of sediment and freshwater samples were also above the acceptable limits for aquatic ecosystems.

Introduction

Difference authors have defined heavy metals differently. Simply put, heavy metals is a collective term for metals of high atomic mass that are toxic and cannot be processed by living organisms, such as lead, mercury, and cadmium [1-3]. Toxic metals and their associated compounds have been found to be toxic, subjected to biomagnifications (since they are not biodegradable) and are persistent environmental contaminants [4, 5]. The environmental impact of heavy metals was previously mostly connected to industrial sources. Recently, environmental pollution due to heavy metals has decreased in many European countries due to legislation, improved cleaning technology, and altered industrial activities. But many developing nations still face this challenge [6, 7].

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Wastewater is water that has been used, as for washing, flushing, or in a manufacturing process, and so contains waste products and/or sewage. Major industrial sources of wastewater include surface treatment processes with elements such as As, Co, Cu, Zn, Ni, Cd, Pb, Hg, and Cr, as well as industrial products that, at the end of their use, are discharged into WWTP facilities [8, 9]. Major urban inputs to WWTPs include household effluents, drainage water, business effluents (e.g. car washes, medical uses), atmospheric deposition, and traffic-related emissions (e.g. vehicle exhaust, brake linings, tires, asphalt wear, gasoline/oil leakage) transported with storm water into the sewage.

Toxic metals in wastewater are one of the main causes of river water and sediment pollution. Accumulation of these metals in wastewater depends on many local factors such as types of industries in the region, people's way of life, and awareness of the impacts on the environment due to careless disposal of wastes. As the focal point, wastewater treatment plants are expected to control the discharge of heavy metals into a river system.

During wastewater treatment, a large amount of sludge is produced; generally, about 1% of the total dry weight but in some cases as much as 4% [8, 10, 11], while the remaining 99% is water. Since the heavy metals present in the influent wastewater stream become concentrated in the sludge, disposal of heavy metal-laden sludge presents an environmental hazard [8, 12]. For wastewater treatment authorities, sludge management options include: wet air oxidation, landfilling, incineration, ocean disposal and land application (agricultural, forest, and disturbed land).

Heavy metals are often released into the aquatic environment through atmospheric deposition or anthropogenic sources. The impacts of heavy metals on aquatic ecosystems are well documented. South Africa has been described as a water scarce nation with steadily declining water quality due to increases in urbanization and industrialization [13-15]. Wastewater from waste treatment plants had been used for irrigating farmland in many countries of the world, including middle Olifants sub-basin in South Africa [16]. Also, the land application method for dewatered and treated sludges in agricultural land, forest, disturbed, or landfill sites had been a normal practice around the globe [12, 17].

The aim of our study was to investigate the efficiency of WWTPs at removing heavy metals from wastewater. Also, to determine the levels of heavy metals in sewage sludge and to assess the impact of wastewater treatment effluent on freshwater systems downstream from the WWTPs.

Materials and Methods

Sampling and Study Areas

Six wastewater treatment plants (A, B, C, D, E, F) were investigated for their effectiveness in removing heavy metals from raw wastewater samples. Five of these WWTPs are located in the city of Cape Town, while one is located in Stellenbosch. Rivers associated with each treatment plant are:

Plant A – Vygekraal River
Plant B – Kuils River 1
Plant C – Mosselbank River
Plant D – Diep River
Plant E – Kuils River 2
Plant F – Veldwachter River

Six points were sampled at each wastewater treatment plant (Fig. 1): raw water (RW), primary settling tank water (PST), secondary settling tank water (SST), primary sludge (PS), secondary sludge (SS), and final effluents (FE). All the sampled WWTPs receive wastes from both domestic and industrial effluents, except one that receives mainly domestic wastewater (Plant C). In addition to samples from water treatment plants, water and sediment samples were collected from rivers that receive the final effluent from the WWTPs. Samples were taken at the point of discharge, as well as upstream and downstream from point of discharge to evaluate the possible impact of effluent on heavy metal load on the aquatic environment. Samples were collected between January and March 2010 on a weekly basis from all the treatment plants.
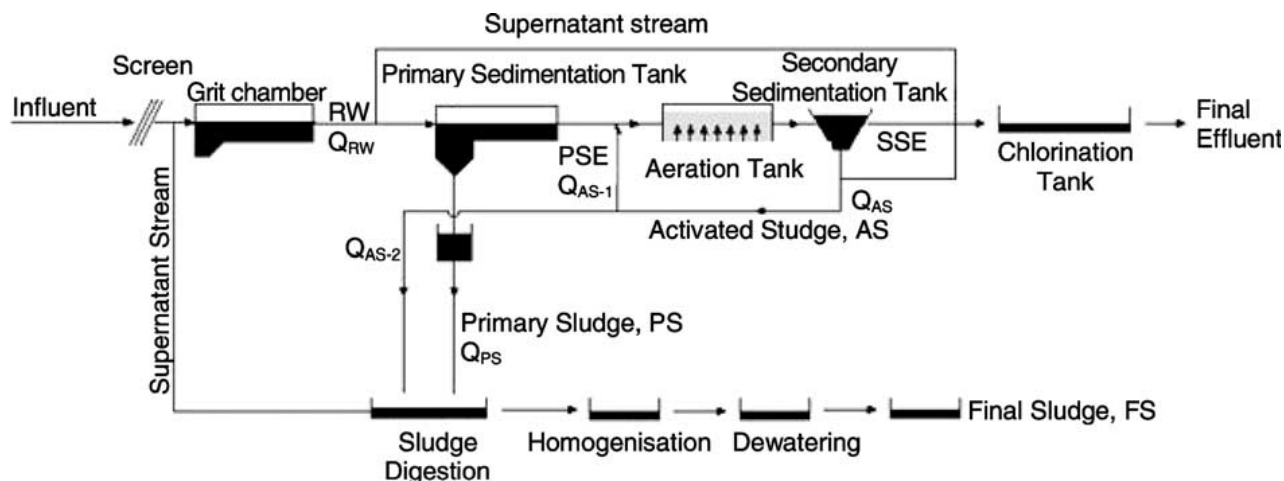

Fig. 1. Schematic diagram of wastewater treatment system. RW – raw water, PSE – primary sedimentation effluent, SSE – secondary sedimentation effluent, PS – primary sludge, AS – Activated secondary sludge.

Instrumentation

All the determinations were carried out by inductively coupled plasma mass spectrometry (ICP-MS) located at the geology department, University of Stellenbosch. An Agilent 7700 instrument was used with a Meinhardt nebulizer and silica cyclonic spray chamber with continuous nebulization. The operation parameters are: Plasma RF power, 1550 W; sample depth, 8.0 mm; carrier gas, 1.08 L/min; nebulizer pump, 0.10 rps; and helium gas, 5.3 mL/min.

Reagents

Water (resistivity 18.2 MΩ cm) was de-ionized by use of a Milli-Q system (Millipore, Bedford, MA, USA), certified standard of all the metals (arsenic, cadmium, mercury and zinc) to cheek for instrument performances and $AuCl_3$ were obtained from Merck, southern Germany. Ultrapure nitric acid (65%) and 32% hydrogen peroxide were obtained from Fluka Kamika, Switzerland.

Measurement of Physicochemical Parameters for Water and Sediment Samples

The pH, conductivity, and temperature of river water and wastewater were determined on-site with a dual pH and conductivity meter supplied by Merck NT Laboratory Pty Ltd and a thermometer. The organic matter content were assessed using the method described by Santisteban et al. [18] after the sludge and sediment were oven dried at 60ºC for 24 hours [19]. The pH was determined using 1:5 sediment-water suspension (15.0 g of sediment for 75 ml of MilliQ water and 0.01 M $CaCl_2$) by shaking in a mechanical shaker (Labotec Model 202) at 200 rpm for 1 hour and allowed to stand for another hour for pH measurement. Organic matter content was determined using loss on ignition method. 5 g of sediment samples were burned in a muffle furnace at 550ºC for 4 hours and organic matter content calculated gravimetrically based on weight difference.

Wastewater and River Water Digestion

Water samples for the toxic metals and arsenic analysis were collected in 1 L plastic containers that were initially washed with detergent and rinsed with distilled water. The containers were finally soaked in 10% nitric acid. The containers were then rinsed at least 3 times with MilliQ water. At the sampling sites, containers were rinsed 3 times with the water samples before being filled with the samples. The samples were preserved by adding conc. HNO_3 to each sample bottle and the pH adjusted to 2.0 by the use of a pH meter. The samples were stored in a refrigerator at about 4ºC before subsequent analysis. As samples may contain particulate or organic materials, pretreatment in the form of digestion is required before analysis. Nitric acid digestion was employed according to the method described by Akan et al. [20]. A few drops of $AuCl_3$ were added to 100 ml of unfiltered wastewater and river water samples to keep Hg ion in solution prior to digestion.

Sediment and Sludge Digestion

Sediment and sludge samples were collected into well-labeled Zip-Lock bags. The collected sediment and sludge samples were dried in an oven at 60ºC for 24 hr [19], and ground using porcelain pestle and mortar. The samples were sieved through a 1 mm sieve, discarding the fraction > 1 mm and eliminating stones, roots, and fragments of plastic and metal. The sieved samples were kept in well labeled pre-cleaned dried plastic containers. For the analysis, 1 g of both sediment and sludge samples were weighed using a fine analytical balance (RADWAG) into a test-tube and 10 ml of 1:1 HNO_3/water was added. The slurry was covered with wash glass and digested at 95ºC±5ºC after the addition of a few drops of $AuCl_3$ to stabilize Hg ions that may be present using a Grant dry-block heater for 30 min (USEPA 3050B). The sample was allowed to cool down, and 5 ml of HNO_3 was added and watch glass replaced. The samples were returned to the block heater and further heated for 2 hours. The samples were cooled down and 2 ml of water and 3 ml of hydrogen peroxide was added and the cover immediately replaced to prevent volatilization of mercury and samples heated for another 2 hours. A blank (control) of reagents without the samples were treated the same way as for samples. The samples were cooled to room temperature, filtered with 0.45 µm cellulose nitrate ultra-filtration membrane filters (Whatman) into 100 mℓ volumetric flasks, and made up to a volume with MilliQ water. The digested samples (water, sediment, and sludge) were analyzed using ICP-MS using the parameters stated.

To obtain the sludge and sediment concentrations, the ICP values were converted using the formula:

$$SMC = \left(\frac{ICP_{Reading} - C_{reading}}{WSS} \right) * DF$$

...where: *SMC* – soil or sludge concentration (ug·g^{-1}), *ICP* – inductively coupled plasma values, *C* – blank, *DF* – dilution factor, *WSS* – weight of soil or sludge sample (g).

Treatment Plants Removal Efficiency

Unfortunately, none of the WWTPs were monitored for both influent and effluent flow rates. The removal efficiency (ε) of each metal was calculated based on influent and effluent concentrations, on the assumption of steady-state conditions and that precipitation or evapotranspiration had minimal impact on the water storage as compared to inflow and outflow.

$$\varepsilon(\%) = \left(\frac{Mi - Me}{Mi} \right) \times 100\% =$$

$$= \frac{QiCi - QeCe}{QiCi} \times 100\% = \frac{Ci - Ce}{Ci} \times 100\%$$

...where: *Mi/e* – the metal flux in influent/effluent (mg·d^{-1})
Ci/e – the metal concentration in influent/effluent (mg·l^{-1})
Qi/e – the mean flow rate of influent/effluent (l·d^{-1})

Quality Assurance for Instrumentation and Analytical Method

The spiking method (standard addition method) was employed for water, sediment, and sludge samples due to non-availability of reference materials. For water samples, 100 ml of wastewater, freshwater, and MilliQ water were measured into 250 ml conical flasks and spiked with known concentration of the metal standard and digested as described above. 1 g of pre-digested sediment and sludge samples was also spiked and recovery determined following digestion outlined above. Triplicate analysis of each of the metals was carried out with water, sediment, and sludge samples along with blank samples.

Statistical Analysis

Data generated were subjected to one-way analysis of variance (ANOVA) for statistical differences at $P<0.05$. Pearson correlation and regression models were applied for possible relationships with other elements.

Results and Discussion

Percent Recovery and Physicochemical Parameters of Sediment and Water Samples

The results show that sediment pH ranged from 5.23±1.24 (Plant D discharge point) to 8.24±0.09 (Plant-F upstream) and from 6.47±0.08 (Plant-E discharge point) to 7.49±0.04 (Plant-F upstream) for water and $CaCl_2$ determination, respectively (Table 1). The organic matter content of the river sediment ranged from 0.69±0.04 (Plant-E upstream) to 2.842±0.011 (Plant-C upstream). The organic matter content in all the river sediment at the discharge points were generally compared to upstream and downstream sediment of the river systems investigated as presented in Table 1 with the exception of the Veldtwachter River, where the values increase downstream. This may be attributed to the dumping of demolished building materials in a portion of the upstream site. The amount of organic matter in this study for sediment is within the range prescribed by Radojevic and Baskin [21].

The percentage recovery of the analytical method is presented in Table 2. The mean percentage recoveries for metals range from 88.89±0.37 to 95.1±0.31; 89.9±0.06 to 101.3±4.61; 89.23±0.33 to 95±01; 72.6±0.12 to 96.2±8.1; and 90.4±4.6 to 97.7±3.6 for arsenic, calcium, cadmium, mercury, and zinc, respectively, in all the samples analyzed.

Influent and Effluent Metal Concentrations and Removal Efficiency of WWTPs

Generally, the results showed influent metal concentrations widely fluctuating and highly varied according to the area served by the treatment plants. The variations in the concentrations of the metals and metalloid investigated in the six treatment plants is presented in Tables 4-9. There was a significant difference in metal concentration between the influent and effluent of metals investigated in all the wastewater treatment plants ($P<0.05$) (Table 3), except for arsenic in Plant B (Table 5). Commonly, metals get adsorbed or absorbed into suspended solids in the WWTPs and are consequently removed through sludge formation. Based on the removal efficiency calculation, average metal removal efficiency in WWTPs is listed as mercury > zinc > cadmium > arsenic (Fig. 2).

Occurrence and removal of heavy metals in the influent and effluent of the treatment plants investigated in this study is compared to other studies in a few countries (Table 3). Except for France and Austria, the results showed that arsenic, cadmium, and mercury concentrations in the influent were higher than values reported in other studies for the countries listed in Table 3. Actually, heavy metal removal mostly occurs in the primary settling tank according to the complex nature and concentration of the influents. WWTPs are designed for organic matter removal through decomposition by microorganisms. Heavy metal removal through the WWTP process can be viewed as a side benefit [2]. The removal efficiency of the six plants agreed with previous studies in other countries [2].

Comparing the removal efficiency of the treatment plants (Fig. 2), the removal efficiency of all plants for arsenic was poor except for plants D and E with 90.25 and 71.63%, respectively. Considering the possible health impact of arsenic, the worst scenario of not removing this metal from the waste stream will greatly be felt down-
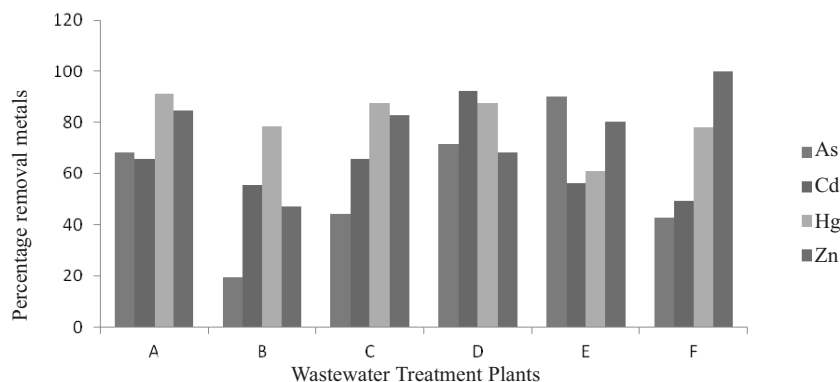

Fig. 2. Percentage removal of metals at the six treatment plants investigated.

Table 1. pH and organic matter (%LOI) of sediment samples.

Plants	Source	Sediment pH		Sediment organic matter, % LOI	Water		
		Water	CaCl$_2$		pH	Temp. (ºC)	Conducitivity
A	Upstream	N/A	N/A	N/A	N/A	N/A	N/A
	DP	N/A	N/A	N/A	N/A	N/A	N/A
	Downstream	7.84±0.14	7.17±0.01	1.91±0.32	7.50	27	1370
B	Upstream	CHN	CHN	CHN	7.80	30	850
	DP	CHN	CHN	CHN	7.50	28	840
	Downstream	8.08±0.64	6.81±0.05	1.91 ±0.11	7.60	30	910
C	Upstream	8.05±0.02	7.31±0.03	2.84 ±0.11	9.50	28	750
	DP	7.38±0.08	7.13±0.02	1.39 ±0.05	7.5	23	810
	Downstream	7.68±0.24	7.09±0.02	2.35 ±0.13	7.1	23	890
D	Upstream	6.42±0.67	7.12±0.05	1.85 ±0.08	7.2	26	590
	DP	5.23±1.24	6.62±0.03	0.94 ±0.28	8.0	25	870
	Downstream	6.72±0.19	7.14±0.09	1.29 ±0.12	7.5	26	1160
E	Upstream	6.9±0.24	6.55±0.04	0.69 ± 0.04	6.9	27	580
	DP	6.84±0.20	6.47±0.08	1.01 ± 0.31	7.0	28	580
	Downstream	7.27±0.30	6.80±0.05	1.71 ± 0.19	7.2	30	580
F	Upstream	8.24 ±0.09	7.49±0.04	2.57 ± 0.19	7.2	27	1312
	DP	6.75±1.38	7.31±0.02	1.43 ± 0.05	7.2	27	1096
	Downstream	7.50± 0.05	7.14±0.04	2.40± 0.03	7.2	27	1112

DP – Discharge point, CHN – Channelized, N/A – Not accessible

Table 2. Percentage recoveries of elements from spiked water, sediment, and sludge samples.

Elements	% Recovery from spiked freshwater samples	% Recovery from spiked wastewater samples	% Recovery from spiked sediment samples	% Recovery from spiked sludge samples
As	94.82±0.35	93.1±0.21	95.1±0.31	88.89±0.37
Ca	101.3±4.61	94.3±0.38	89.9±0.66	98.93±0.28
Cd	89.23±0.33	97.4±0.92	93.2±0.43	95.00±0.10
Hg	72.6±0.12	96.2±8.1	89.0±0.29	91.30±6.30
Zn	96.83±0.37	90.4±4.6	92.5±0.22	97.7 0±3.60

stream, where water is used for animal rearing as in the case of Plant B (Table 5). Generally, Plant D has the highest removal efficiency (Fig. 2) while Plant B has the lowest removal efficiency with less the 50% removal efficiency for arsenic and zinc. Plants B and F have less than 30 and 50% removal efficiency for cadmium, respectively – another heavy metal of great environmental concern.

Heavy Metals in River Systems

Calcium is not considered as toxic, but an excess amount of it in water could pose some challenges. Calcium concentrations ranged from 28.362±1.913 mg·l^{-1} (Veldtwachter River) to 130.451±5.67 (Kuils River 2) for upstream and 22.871±2.184 mg·l^{-1} (Kuils River 2) to 146.499±11.976 mg·l^{-1} (Kuils River 1) for downstream. Calcium was analyzed along with the metals, as it is known to reduce the toxicity of some metals [28]. However, calcium concentration in the river systems and wastewater treatment plants showed that the water exceeded the maximum limit of 32 mg·l^{-1} set by DWAF [29] for some sites.

Cadmium levels ranged from 0.71±0.19 μg·l^{-1} (Veldtwachter River) to 1.354±0.20 μg·l^{-1} (Mosselbank River) for upstream and 0.89 ± 0.16 (Veldtwachter River)

Table 3. Heavy metal concentrations in influent and effluents from other countries and investigated treatment plants in Cape Town.

Compound	Country	Raw Water ($\mu g \cdot l^{-1}$)	Effluent ($\mu g \cdot l^{-1}$)	References
As	Spain	2.2	-	[22]
	Italy	0.3-31	0.5-9.2	[23]
	Israel	5.6	5.1	[24]
	South Africa	**4.04-28**	**1.20-3.72**	**this study**
Cd	Austria	< 20-60	< 20-60	[22]
	Poland	< 0.01	<0.01	[25]
	France	6-85	-	[22]
	Germany	0.4	0.1	[22]
	Greece	< 1-4.4	<1	[26]
	Israel	0.6	0.8	[24]
	Italy	0.2-1.8	0.1-1.6	[23]
	Spain	0.06-1.19	0.04-0.11	[27]
	South Africa	**1.64-17.39**	**0.94-1.33**	**this study**
Hg	Austria	<10	<10	[22]
	Spain	0.00-0.50	0.00-0.24	[27]
	France	1-8	-	[22]
	Germany	0.6	0.1	[22]
	Italy	<1	-	[22]
	Italy	0.2-147	0.1-9.5	[23]
	South Africa	**0.64-2.2**	**0.1-0.38**	**this study**
Zn	Poland	270-800	-	[2]
	Poland	270-300	90-120	[25]
	Austria	< 20-3,700	20-500	[22]
	Greece	330-3,200	20-900	[26]
	Israel	75	54	[24]
	Italy	100-900	-	[22]
	Italy	61-833	24-238	[23]
	South Africa	**684.94-5,128.31**	**133.71-909.38**	**this study**

to 4.52±0.55 $\mu g \cdot l^{-1}$ (Kuils River 2) for downstream, respectively. It ranged from 1.01 $\mu g \cdot l^{-1}$ (Plant A) to 1.56 $\mu g \cdot l^{-1}$ (Plant C) at the point of discharge from the treatment plants. Previous work by Jackson et al. [19] did not investigate the levels of cadmium in the Diep River. There is thus a paucity of information on the concentration of cadmium in the river systems investigated for this study. The concentrations

recorded show that Kuils River 2 downstream is more polluted compared to other rivers under investigation. This may be attributed to effluent from the largest informal settlement in Cape Town (Khayelitsha), where there is a waste cadmium battery dump site. For all the treatment plants investigated, no significant difference in cadmium concentration was observed between the final effluent and downstream water except at Plant F and Kuils River 2.

The level of cadmium was acceptable for use of irrigation 5.1 $\mu g \cdot l^{-1}$ [30]; 10 $\mu g \cdot l^{-1}$ [29] and livestock 10 $\mu g \cdot l^{-1}$ [29]; 80 $\mu g \cdot l^{-1}$ [30]. However, the observed concentration was higher than the recommended value of 0.2 $\mu g \cdot l^{-1}$ [29] and 0.017 $\mu g \cdot l^{-1}$ [30] for an aquatic ecosystem. The result of this study for cadmium is similar to the study of van Aardt and Erdmann [31], Davies et al. [32] (<0.001 $\mu g \cdot l^{-1}$), plus Fatoki and Awofolu [33]. The concentration was lower than the result reported by Fatoki et al. [34] and Fatoki and Mathabatha [35]. The concentration of cadmium at Veldtwachter River downstream was 96% of the recommended value and this could contribute to bioaccumulation of cadmium in aquatic life and, subsequently, biomagnifications in the food chain.

Cadmium concentration in river sediment ranged from 0.90±0.05 (Kuils River 2) to 4.07±0.22 $\mu g \cdot g^{-1}$ (Mosselbank River) for upstream and from 0.86±0.61 (Mosselbank River) to 1.59±0.18 $\mu g \cdot g^{-1}$ (Diep River) for downstream as presented in Tables 4 to 9. The result is similar to work reported elsewhere by Fatoki et al. [36] (0.011±0.002 to 0.033±0.004) and Adekoya et al. [3] (ND – 0.95 $\mu g \cdot l^{-1}$). The values were much lower than the findings of Fatoki and Mathabatha, [35] (12.7 to 183 mg·g⁻¹), [17] (7.0±1.2) and [37]. The level in sediment exceeded interim sediment quality guidelines (0.6 mg·kg⁻¹) and probable effect level (3.5 mg·kg⁻¹) set by the Canadian Council of Ministers for the Environment [30] to trigger health effects in some aquatic life.

The concentrations of Zn ranged from 191.52±3.54 $\mu g \cdot l^{-1}$ (Veldtwachte River) to 385.49±39.48 $\mu g \cdot l^{-1}$ (Kuils River 1) for upstream and from 155.73±13.34 $\mu g \cdot l^{-1}$ (Veldtwachte River) to 664.66±15.38 $\mu g \cdot l^{-1}$ (Vygekraal River) for downstream. This study shows that the level of zinc in freshwater is higher than the recommend concentrations of 0.03 mg·l⁻¹ [38], 0.036 mg·l⁻¹ [39], 0.0006 mg·l⁻¹ [40], and 0.009 mg·l⁻¹ [41] for safe aquatic ecosystems. The result were higher than values reported by van Aardt and Erdmann [31] (20 $\mu g \cdot l^{-1}$) and Awofolu et al. [42] (0.018±0.001 $\mu g \cdot l^{-1}$). The results of this study show that the concentration of Zn between final effluent and downstream water is significantly different (P<0.05) for all rivers, except the Veldtwachter. This shows the possible impact on water quality resulting from the wastewater effluent in the study areas.

The increased concentration of Zn downstream in the Mosselbank River could be attributed to an open dump site close to the river. On average, the Zn concentration for the Vyekraal River downstream was higher than other rivers downstream, while the kraaifotein Mosselbank upstream was more contaminated than other rivers upstream. The result of this study is similar to other works [4, 31, 35, 42]. It was higher than results reported by Adekoya et al. [3], but

Table 4. Heavy metal concentrations at Plant A WWTP and the Vyekraal River (Mean±SD) (water – µg·L^{-1} sludge and sediment – µg·g^{-1}).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	N/A	N/A	N/A	N/A	N/A
Raw water	6.21±0.53^c	75,527.01±955.13^b	2.94±0.76^c	2.20±1.21^c	1,431.95±16.80^c
PST	4.067±0.42^{dc}	77,892±1,098.23^b	1.35±0.04^d	0.41±0.331^d	912.54±9.634^d
Primary sludge	17.65±0.77^b	98,823.13±23,172.82^a	8.91±1.16^b	7.64±1.05^b	7,859.86±320.11^b
SST	2.02±0.38^d	87,658.37±5,874.6^b	0.86±0.15^d	0.28±0.17^d	340.63±4.77^f
Secondary sludge	33.17±1.81^a	116,609.22±2,824.57^a	16.42±1.04^a	13.95±0.87^a	9,745.23±50.06^a
FE	1.96±1.03^c	87,454.25±16,641^{bc}	1.01±0.52^d	0.19±0.08^d	222.68±21.09^f
Downstream water	5.54±3.58^c	113,989.9±23,335.15^a	1.27±0.17^d	0.22±0.09^d	664.66±15.38^e
Downstream sediment	15.57±0.11^b	42,788.35±3,949.39^c	1.57±0.11^d	0.22±0.05^d	946.79±3.08^d

Same superscript indicates no significant difference, while different superscript indicates significant difference.

Table 5. Heavy metal concentrations at Plant B WWTP and the Kuils River 1 (Mean ± SD) (water – µg·g^{-1} sludge and sediment – µg·g^{-1}).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	4.74±2.10^{def}	77,143±2,203.52^{gf}	0.99±0.16^d	0.28±0.16^d	385.49±39.48^h
Raw water	4.62±0.19^{def}	87,214.2±8,612^{ef}	2.39±0.09^b	1.77±0.97^c	1004.75±0.82^d
PST	4.12±0.48^{ef}	63,733.98±4,368.6^g	1.74±0.09^{bc}	0.83±0.29^d	883.52±124.56^e
SST	3.71±0.09^{fe}	96,566.19±4,016.87^{ef}	1.07±0.33^c	0.125±0.07^d	699.64±8.48^f
Sludge	31.77±0.34^a	120,185.33±1,412.20^d	13.29±1.86^a	6.33±.72^a	20,164.09±23.24^a
FE	3.72±0.15^{fe}	125,530.91±2,516.38^d	1.07±0.11^c	0.38±0.13^d	533.77±15.17^g
Downstream water	5.61±0.35^{cde}	146,499.15±11,976.63^c	1.02±0.18^c	0.25±0.03^d	379.79±6.09^h
Downstream sediment	6.47±0.77^{cd}	34,415.06±4,035.69^h	1.07±0.16^c	0.01^d	478.22±9.41^g

Same superscript indicates no significant difference, while different superscript indicates significant difference.

lower compared to a study conducted on some sections of the Diep and Plankenburg rivers [19].

The level of zinc in the river sediment ranged from 152.85±10.43 µg·g^{-1} (Kuils River 2 upstream) to 2,574.71± 28.67 µg·g^{-1} (Mosselbank River), and 182.08±0.003 µg·g^{-1} (Veldtwachter River) to 947.79±3.08 µg·g^{-1} (Vygekraal River) for downstream while discharge point sediment ranged from 79.35±2.98 µg·g^{-1} (Diep River) to 464.69±22.51 µg·g^{-1} (Kuils River 2). Generally, the results of this study revealed high levels of sediment contamination. The reported values were higher than interim sediment quality guidelines of 123 mg·kg^{-1} and probable effect levels of 315 mg·kg^{-1} [30].

Arsenic concentrations were not significantly different for all the WWTPs investigated over the study period. The levels of arsenic varied between 4.56±0.16 µg·l^{-1} (Mosselbank River) to 7.72±0.2 µg·l^{-1} (Diep River) for upstream water and from 1.86±0.55 µg·l^{-1} (Kuils River 2) to 5.61±0.35 µg·l^{-1} (Kuils River 1) for downstream water, while it ranged from 1.21±0.12 (Plant-D, Table 7) to 3.72±0.15 µg·l^{-1} (Plant-B, Table 4) for final effluents. The concentration in water sample was below the guidelines set by DWAF [29] for human consumption, irrigation and live-

stock. The level is, however, higher than the standard set for aquatic life protection of 5 µg·l^{-1} [38]. There is significant difference ($P < 0.05$) in arsenic concentration between the final effluent and downstream water, which shows that the pollution could be related to the waste effluent from the treatment plants.

The arsenic concentration in the sediment ranged from 5.31±0.99 (Veldtwachter River) to 71.09±7.22 µg·g^{-1} (Mosselbank River) for the upstream, and 6.47±0.77 (Kuils River 1) to 24.64±10.02 µg·g^{-1} for the downstream sediment. Point-of-discharge concentration ranged from 3.94±0.41 µg·g^{-1} (Mosselbank River) to 18.24±0.55 µg·g^{-1} (Diep River). Level of occurrence differs significantly as observed for water samples. The levels of arsenic in the sediment samples were generally higher compared to values reported by Botes and van Staden [43] in Eastern Cape, South Africa. Also, the reported concentration of arsenic was higher than the limit of 5.9 mg·kg^{-1} interim sediment quality guidelines set by CCME [30]. There is a significant variation ($P < 0.05$) in the arsenic concentration between the influent and effluent of all the treatment plants in this study. Occurrence concentration was similar in all the plants except D.

Table 6. Heavy metal concentrations at Plant C and the Mosselbank River (Mean±SD) (water – µg·l⁻¹ sludge and sediment – µg·g⁻¹).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	4.56±0.16[d]	73840.17±1867.90[b]	1.35±0.20[c]	0.47±0.22[b]	204.59±35.78[g]
Upstream sediment	71.09±7.22[a]	105585.49±10853.25[a]	4.07±0.32[a]	0.56±0.13[bc]	2574.71±28.67[a]
Raw water	4.27±0.27[d]	47465.32±2540.04[de]	4.57±0.31[a]	0.638±0.03[b]	1206.88±1.16[c]
PST	3.32±0.16[d]	45816.27±3951.89[e]	2.69±0.19[b]	0.31±0.11[bcd]	391.46±4.62[d]
Primary Sludge	9.43±0.10[c]	63916.12±8295.97[c]	3.27±0.32[b]	2.72±0.46[a]	2078.52±15.26[b]
Final effluent	2.78±0.16[d]	48829.39±5558.63[de]	1.56±0.90[c]	0.08±0.03[d]	208.29±17.31[g]
Point of discharge sediment	5.97±0.28[cd]	2777.64±1110.03[f]	0.92±0.10[c]	0.06±0.02[d]	205.83±2.36[g]
Downstream water	2.89±0.29[d]	56097.36±3362.31[f]	0.94±0.04[c]	0.29±0.11[d]	283.15±14.09[e]
Downstream sediment	20.10±0.69[b]	1964.63±1445.19[f]	0.86±0.61[c]	0.06±0.05[d]	240.31±3.21[f]

Same superscript indicates no significant difference, while different superscript indicates significant difference.

Table 7. Heavy metal concentrations at Plant D and the Diep River (Mean ± SD) (water – µg·g⁻¹ sludge and sediment – µg·g⁻¹).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	7.72±0.20[d]	61,018.49±33,212.3[d]	1.33±0.45[b]	0.21±0.18[d]	368.23±14.89[fe]
Upstream sediment	18.05±0.43[b]	38,123.64±4,611.62[e]	0.99±0.11[e]	0.01[d]	230.01±19.25[f]
Raw water	4.23±0.13[f]	71,982.88±4,897.38[cd]	17.39±0.55[c]	0.79±0.30[c]	822.99±1.49[c]
PST	3.11±0.18[g]	75,443.93±4,715.48[bcd]	4.49±0.61[d]	0.28±0.12[d]	626.33±181.34[d]
Primary sludge	11.83±0.17[c]	94,437.38±9,526.26[ab]	40.35±1.90[a]	3.89±0.77[a]	2,781.58±11.31[a]
SST	2.23±0.89[h]	8,449.48±14,536.81[bc]	1.64±1.21[e]	0.09±0.08[d]	341.31±47.93[fe]
Secondary sludge	20.31±0.69[a]	62,875.10±2,149.45[d]	37.87±0.76[b]	2.08±0.06[b]	2,550.66±31.89[b]
Final Effluent	1.21±0.12[i]	84,938.19±1,054.32[bc]	1.33±0.07[e]	0.10±0.06[d]	260.07±1.59[f]
Point of discharge sediment	18.24±0.55[b]	9,559.72±1,530.80[f]	0.77±0.12[e]	ND	79.35±2.98[g]
Downstream water	5.49±0.26[e]	111,865.79±17,513.99[a]	1.08±0.13[e]	0.04±0.001[d]	244.56±14.17[f]
Downstream sediment	7.55±0.20[d]	16,013.07±4,390.20[f]	1.59±0.18[e]	0.014±0.003[d]	422.50±11.76[e]

Same superscript indicates no significant difference, while different superscript indicates significant difference.

Mercury concentrations in water samples range from 0.21±0.18 (Diep River) to 0.49±0.34 µg·l⁻¹ (Kuils River 2) for upstream and 0.04±0.001 µg·l⁻¹ (Diep River) to 0.29±0.11 µg·l⁻¹ (Mosselbank River) for downstream water. The concentrations of mercury in this study are lower than the set standards for human consumption, livestock and irrigation purposes [29]. Comparing this study to other works, the result is shown to be lower than that reported by Fatoki and Awofolu [33] in the Eastern Cape Province of South Africa. The value obtained exceeded the limit of 0.026 µg·l⁻¹ [38] and 0.04 µg·l⁻¹ [29] for healthy aquatic ecosystems.

Heavy Metals in Sludge

Considering the systems adopted by treatment plants, primary, secondary, and treated sludges were analyzed for their heavy metal concentrations depending on the treatment plant design. The distribution pattern of the metals and arsenic concentration in sludge samples was similar to their occurrence in the influent. Zinc was the most abundant metal and, again, mercury was the least abundant. Treatment plants A and B received more heavy metal-laden waste than all the other four treatment plants investigated (Tables 4 and 5). Statistically, there is a significant difference (P<0.005) in metal concentrations in the primary and secondary sedimentation tanks of the investigated WWTPs. Metals in sewage sludge can be grouped according to the range of their average concentration as follows:
(a) Hg, (2.08-16.5 µg·g⁻¹)
(b) As, Cd (3.27-40.35 µg·g⁻¹)
(c) Zn (2078-20164 µg·g⁻¹)

Generally, the concentration of all heavy metals except Hg in the sludge from all the investigated treatment plants were above the South African permissible utilization and disposal of sewage sludge guidelines [44]. The results indicate that metal levels were proportional to the influent metal concentration. The result of this study is similar to

Table 8. Heavy metal concentrations at Plant-E and the Veldtwachter River (Mean±SD) (water – µg·l⁻1 sludge and sediment – µg·g⁻¹).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	7.15±0.56[c]	28,362±1,913.31[cd]	1.20±0.15[de]	0.26±0.09[b]	191.52±3.54[e]
Upstream sediment	5.31±0.99[c]	13,152.35±2,165.18[de]	0.96±0.16[de]	0.10±0.01[c]	167.52±10.7[efg]
Raw water	28.19±3.43[a]	42,260.41±1,800.79[cb]	2.96±0.46[c]	0.64±0.02[b]	684.94±16.58[c]
PST	4.19±0.44[c]	39,894.50±1,497[cb]	1.31±0.29[d]	0.48±0.08[b]	351.21±22.36[d]
Primary sludge	21.14±0.14[b]	47,751.36±1,967.48[bc]	3.84±0.37[b]	14.76±3.72[a]	2,738.67±37.65[b]
SST	2.03±0.07[dc]	45,241.84±1,931.72[cb]	0.96±0.11[de]	0.14±0.03[b]	128.53±13.85[h]
Secondary sludge	21.66±1.67[b]	42,992±2,641[bc]	4.65±0.22[a]	16.15±6.03[a]	2,931.09±28.63[a]
Final Effluent	2.75±0.21[c]	53,881.30±2,847.59[b]	1.29±0.36[d]	0.25±0.03[b]	133.71±13.36[gh]
Point of discharge sediment	3.94±0.41[c]	3,442.62±587.76[e]	0.75±0.09[e]	0.11±0.03[c]	162.71±13.13[efhg]
Downstream water	3.19±0.94[c]	50,780.18±2,856.54[b]	0.89±0.16[de]	0.13±0.02[b]	155.73±13.34[fgh]
Downstream sediment	24.64±10.02[ab]	105,799.43±34,772.66[a]	0.99±0.04[de]	0.14±0.07[b]	182.08±3.92[fe]

Same superscript indicates no significant difference, while different superscript indicates significant difference.

Table 9. Heavy metal concentrations at Plant F and Kuils River 2 (Mean±SD) (water – µg·l⁻¹ sludge and sediment – µg·g⁻¹).

Sampling point	As	Ca	Cd	Hg	Zn
Upstream water	4.22±0.63[e]	130451±5621.85[c]	0.71±0.19[f]	0.49±0.34[c]	346.43±21.34[h]
Upstream sediment	15.10±0.46[c]	320365.51±42050.71[a]	0.90±0.05[f]	0.09±0.02[c]	152.85±10.43[i]
Raw water	4.05±0.38[ef]	53159.02±818.13[d]	2.32±0.29[c]	0.69±0.09[c]	5128.31±10.20[a]
SST	3.33±0.05[f]	46725.53±4740.98[d]	0.84±0.20[ef]	0.30±0.07[c]	2119.95±11.84[d]
Untreated sludge	14.24±0.51[b]	40055.88±6266.85[d]	9.32±0.82[a]	7.06±2.61[a]	2566.52±36.66[c]
Treated Sludge	15.09±0.46[a]	39713.72±436.26[d]	9.71±0.20[a]	3.88±0.45[b]	2683.15±16.19[b]
Final Effluent	2.32±0.53[g]	66119.92±19841.15[dc]	1.17±0.15[def]	0.15±0.02[c]	909.38±23.08[e]
Point of discharge sediment	13.46±0.55[b]	231605.85±100966.21[b]	1.74±0.47[cd]	0.17±0.05[c]	464.69±22.51[g]
Downstream water	1.86±0.55[g]	22871.48±2184[d]	4.52±0.55[b]	0.31±0.14[c]	644.57±20.90[f]
Downstream sediment	11.52±0.33[d]	257791.62620.20[ab]	1.54±0.23[de]	0.23±0.07[c]	614.64±14.38[f]

Same superscript indicates no significant difference, while different superscript indicates significant difference.

other findings [45, 46], and values were lower than results reported by other authors in some Europeans countries [17, 24, 25, 27].

Employing Effluent to Agricultural Irrigation

Treated water from the WWTPs is either discharged into different rivers (Tables 4-9), used for irrigation (Plant C), or of cooling purposes in industries (Plant B). Previous studies had shown that plants irrigated with waste effluent uptake significantly metals into their tissue, and this could pose a health risk for humans through their consumption [12, 47]. All six WWTPs in some instances failed to comply with the national wastewater discharge act (DWA, 2010). Thus, effluent usage for irrigation, drinking, and other domestic uses over a long period can result in serious health risks [48-50].

Conclusion

Our study has attempted to assess and compare the level and removal efficiency of heavy metals from waste treatment plants using an activated sludge system. The removal efficiency of the wastewater treatment plants investigated was proportional to the level of metals in the influent wastewater. The removal efficiency of the plants is within the ranges reported in recent studies. It was established from the investigation that zinc was the most abundant, while mercury was the least prominent metal. Furthermore, the findings of this study showed that wastewater treatment plants and freshwater systems needs to be further monitored to assess the possible impact of seasonal variation and risk that the effluents could pose on water quality, aquatic life, and consumers.

Acknowledgements

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