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## **Variability in Heavy Metal Levels in River Water Receiving Effluents in Cape Town, South Africa**

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Additional information is available at the end of the chapter

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### **1. Introduction**

One of the most critical problems of developing and developed countries is improper management of vast amount of wastes generated by various anthropogenic activities. Though, very pronounced in the developing countries due to availability of potable water sources. More challenging is the unsafe disposal of these wastes into the ambient environment. Water bodies especially freshwater reservoirs are the most affected. This has often rendered these natural resources unsuitable for both primary and/or secondary usage [1]. Water shortage is an important concern in arid areas such as Africa, Southern Asia and Middle East and even in some parts of the World which it may lead to a war crisis [2].

On the other hands continued population growth, increased per capital water consumption and increased water requirements for industry and irrigation result in considerable decrease of usable water resources [3]. Therefore, treated wastewater recycling into the hydrological cycle is of significant importance and has many benefits. The major uses of treated wastewater are in agricultural irrigation, industrial activities and groundwater recharge. With respect to public health, principles of engineering economy, aesthetic standards and more importantly public acceptance, wastewater reuse can be developed.

However, incomplete removal of organic compounds and heavy metals from treated effluents can cause long term effects on the ecosystem even when the impact is not immediately feasible [4-6]. Although, a number of studies have been conducted on heavy metals in river in association with intensive farming and industrial activities in South Africa, most especially in the Guateng Province, no study has reported levels of heavy metals in relation to wastewater treatment plants in Cape Town. Thus, the main objectives of this study were to assess: (i) levels of heavy metals in river water receiving treated effluents from wastewater treatment plants

(ii) identification of the possible point source pollution of heavy metals from wastewater treatment plant if any and (iii) compare if reported levels are in compliance with the South Africa and other guidelines for freshwater management.

## 2. Materials and method

### 2.1. Methods

All the determinations were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) located at the geology Department, University of Stellenbosch. The 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; Helium gas: 5.3 mlmin<sup>-1</sup> for ICPMS. The isotopes of the elements determined were: <sup>52</sup>Cr, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>111</sup>Cd, <sup>75</sup>As, <sup>208</sup>Pb, <sup>202</sup>Hg, <sup>66</sup>Zn.

### 2.2. 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 (As, Cd, Cr, Co, Cu, Pb, Ni Hg and Zn) to check for instrument performances and AuCl<sub>3</sub> were obtained from Merck, South Germany. Ultrapure nitric acid (65 %) and 32 % hydrogen peroxide were obtained from Fluka Kamika, Switzerland. 1000 mgL<sup>-1</sup> of metal stock standard solution (As, Cd, Cr, Co, Cu, Pb, Ni Hg and Zn) was supplied by Sigma-Aldrich.

### 2.3. Study areas

Final effluent (at the discharge point) of six wastewater treatment plants namely; Athlone, Bellville (which consist of the Old and New plants), Kraaifontein, Potsdam, Stellenbosch and Zandvliet) were investigated for heavy metals. Five of these WWTPs were located in the City of Cape Town, while one is located in Stellenbosch. Rivers associated with each treatment plant are: Athlone-Vygekraal River; Bellville-Kuils River; Kraaifontein-Mosselbank River; Potsdam-Diep River; Zandvliet-Kuils River and Stellenbosch-Veldwachters River. All the sampled WWTPs receive wastewater from both domestic and industrial effluents, except kraaifontein that receives mainly (about 90 %) domestic wastewater. Samples were taken at the point of discharge, as well as upstream and downstream from point of discharge (about 1-2km) to evaluate the possible impact of effluent on heavy metals and organic compounds load on the aquatic.

### 2.4. River water collection and digestion

Samples were collected from eighteen sampling sites consisting of upstream, discharge point, downstream and a control site (Kirstenbosch Botanical Garden). Samples were collected in 1litre plastic container which 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 three times with MilliQ water. At the sampling sites, containers were rinsed three times with the water samples before being filled with the samples. The samples were preserved by adding few drops of conc.  $\text{HNO}_3$  to each sample bottle and the pH adjusted to 2.0 by the use of pH meter. The samples were transferred on ice chest to the laboratory prior to storage in a refrigerator at about  $4^\circ\text{C}$  before analysis. As samples may contain particulate or organic materials, pretreatment in the form of digestion is required before analysis. Nitric acid digestion was employed [7]. A few drops of  $\text{AuCl}_3$  were added to 100 mL of unfiltered river water samples to keep Hg ion in solution prior to digestion. Water sampling for heavy metals analysis commenced in January 2010 and ended in December 2010.

## 2.5. Quality control

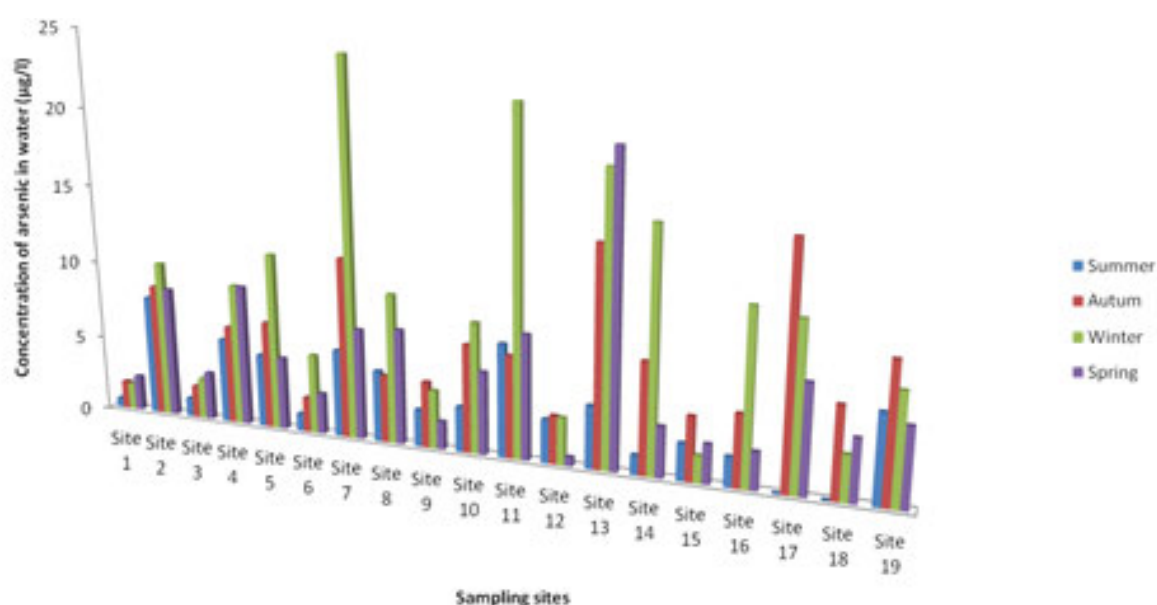
The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of known additions and analysis of replicates. All the analyses were carried out in triplicate and the results were expressed as the mean. The instrument calibration was checked with SRM 1643a (Trace elements in water) purchased from NIST, Gaithersburg, USA. The instrument reproducibility was checked using in-house prepared drift standard ( $1\ \mu\text{g L}^{-1}$  of all the trace and rare earth elements and  $1\ \text{mg L}^{-1}$  of Na, K, P, Ca and Mg). The elemental concentrations and accuracy of the certified reference materials SRM 1643a. The instrument drift was very negligible as measurement gave a ratio of 0.89 to 1.05. The result of the SRM 1640a (Trace elements in water) was acceptable to validate the calibration.

## 3. Result and discussion

### 3.1. Arsenic

In this study, the seasonal concentrations of arsenic in water of the selected river systems receiving wastewater effluent were determined for samples taken from points about 1-2 km up and downstream from the point of final discharge. The range of the annual mean of arsenic in water for all sampling sites in comparison with other studies is presented in Table 1. The graphical forms of the seasonal variation at each sampling point for water is presented in Figure 1. The average levels of arsenic in water samples obtained from the river system ranged from  $0.56\ \mu\text{g L}^{-1}$  to  $23.78\ \mu\text{g L}^{-1}$  for the nineteen sampling points. The highest level of arsenic was obtained at sampling point 7 (Bellville WWTP downstream) during winter and the lowest at sampling point 12 (Stellenbosch WWTP discharge point) as depicted in Figure 1. The annual mean concentration of arsenic from each sampling point ranged from  $1.62\ \mu\text{g L}^{-1}$  (Site 1) to  $13.7\ \mu\text{g L}^{-1}$  (Site 13). The seasonal trend of arsenic in water shows that the summer samples had the least concentration while the winter had the highest concentration for most of the sampling sites except for sites 8, 11 and 15. Studies in several countries reported levels of arsenic in water ranging from  $1.25\ \mu\text{g L}^{-1}$  to  $5114\ \mu\text{g L}^{-1}$  [8-17] (Table 1). When comparing the findings of this study with other reported values, it was obvious that the result of this study was generally low except for sites 7, 11 and 13 where reported values were higher than the South Africa water

quality guidelines. Reported concentrations were within the human consumption (except for 7, 11 and 13), livestock watering, irrigation and aquaculture uses [18,19]. Generally, the wastewater treatment plants are believed to be one of the possible routes of organic and inorganic pollutants into the river systems. However, from this study, the annual mean values for arsenic at the discharge point was lower compared to the upstreams and downstreams values of the river, but higher than the values at the control site (Site 1). The high concentrations of arsenic at site 7 may be attributed to defeacating by cattle in the water as the water is used for livestock management in the area. Another possible means of arsenic in this section of the river may be attributed to the use of sodium salt of arsenous acid to treat tick infestations on cattle [20] and waste tyres dump. At sites 11 and 13, the high concentration of arsenic recorded may be attributed to seepage of landfill leachate into the river systems at site 11. The high concentration at site 17 may be attributed to channelization of the upstream and informal settlement around the sampling point. There is also possibility of storm water contamination as many rivers in Cape Town are known to receive storm water carrying industrial effluents, wastes from home and farms or seepage from groundwater [21]. Sites 7 (Bellville wastewater downstream) and 14 (Zandvliet wastewater upstream) are sampling points on Kuils River. Site 7 is located far upstream of site 14 which is about 2 km of Zandvliet point of discharge. High arsenic level at this portion of this river may be due to storm and wastewater effluent from the biggest informal settlement in Cape Town (Khayelitsha) with over 1.2 million inhabitants.



**Figure 1.** Seasonal trend in arsenic concentration ( $\mu\text{g/L}^{-1}$ ) in river water receiving waste effluent from WWTPs Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

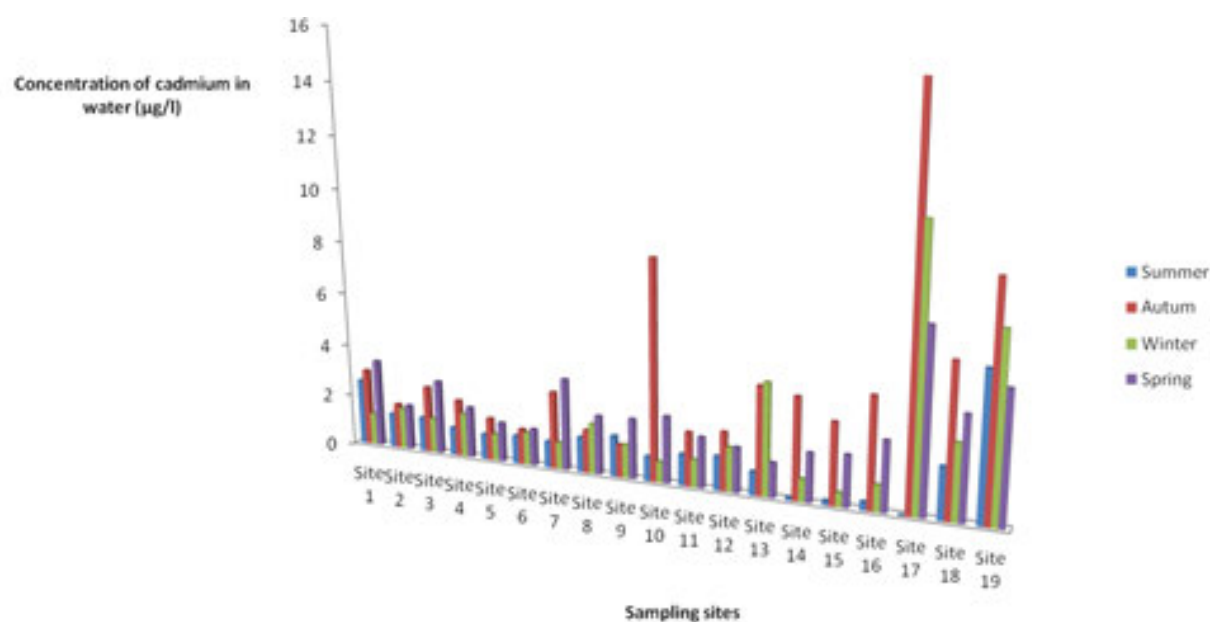
Water	WHO	Range	Year (Mean $\pm$ SD)	Reference
Cape Town		1.62-13.70	-	this study
Pakistan			97.5-78.5	[16]
Longeng Lake			0.06-0.23	[17]
China		<100 (86.2)		[18]
Shihezi (China) (Tributary of the Gobi)		1.25-5.14	90.3	[19]
Tanzania		0.01-18.37	-	[20]
Bangladesh		0.2-0.27		[21]
Tanzania		1-57	21-10	[22]
Japan		0.21-0.18	0.45	[23]
China		8.7-28.81	-	[24]
Mexico		70-160	-	[25]

**Table 1.** Concentration of arsenic in river water ( $\mu\text{gL}^{-1}$ ) in comparison with other globally published values

### 3.2. Cadmium

Seasonal concentrations change of cadmium in water of the river systems receiving wastewater effluents and Kirstenbosch Botanical Garden are presented in graphical form (Figure 2). For all the sites investigated, the average mean concentrations of Cd in water samples obtained from the river systems ranged from  $0.09 \mu\text{gL}^{-1}$  to  $14.78 \mu\text{gL}^{-1}$  for the 19 sampling points as placed in Figure 2. The highest level of cadmium in water was obtained at Site 17 (Athlone WWTP Upstream) during the autumn sampling season and the lowest at Site 14 (Zandvliet WWTP Upstream) during autumn. The annual average cadmium concentration found in this study ranged from  $1.44 \mu\text{gL}^{-1}$  Site 15 (Zandvliet WWTP discharge point) to  $7.96 \mu\text{gL}^{-1}$  Site 17 (Athlone WWTP downstream). In previous study conducted in South Africa, Fatoki *et al.* [21] reported concentration range of  $0.01$  to  $26 \text{ mgL}^{-1}$ , while another study [22] reported concentration range of between  $2$  and  $4 \mu\text{gL}^{-1}$ . Cadmium concentration had not been previously reported in the selected river systems in Cape Town as attention had been focus on other toxic metals and especially in sediment and soil samples. Similarly, in another study [23], cadmium was detected at about  $6 \mu\text{gL}^{-1}$  for upstream and downstream samples collected in the Eerste River for two sampling seasons. Elsewhere in South Africa, it was reported that levels of cadmium in water ranged from  $1.6 \mu\text{gL}^{-1}$  to  $260 \mu\text{gL}^{-1}$  as placed in Table 2 [21-28]. Annual values reported in this study were lower compared to previous finding in the Eastern Cape and Nigeria (Table 2). Cd concentrations in non-polluted natural waters usually are lower than  $1 \mu\text{gL}^{-1}$ , have been reported. On comparison with South Africa water quality guidelines, the reported levels of cadmium indicated that all sampling sites concentration were within the limits for human consumption except for site 17 and 19 while all sites, 17 and 19 inclusive were below the set limits of  $10 \mu\text{gL}^{-1}$  for livestock watering and irrigation of farmlands. However, in relation to protection of aquatic life's, reported concentrations for all the 19 sites were above the  $0.2 \mu\text{gL}^{-1}$  and  $0.017 \mu\text{gL}^{-1}$  limits by DWAF [18] and CCME [19] respectively.





**Figure 2.** Seasonal trend in Cd concentrations ( $\mu\text{gL}^{-1}$ ) in river water receiving waste effluent from WWTPs Sites are the same as listed in Figure 1

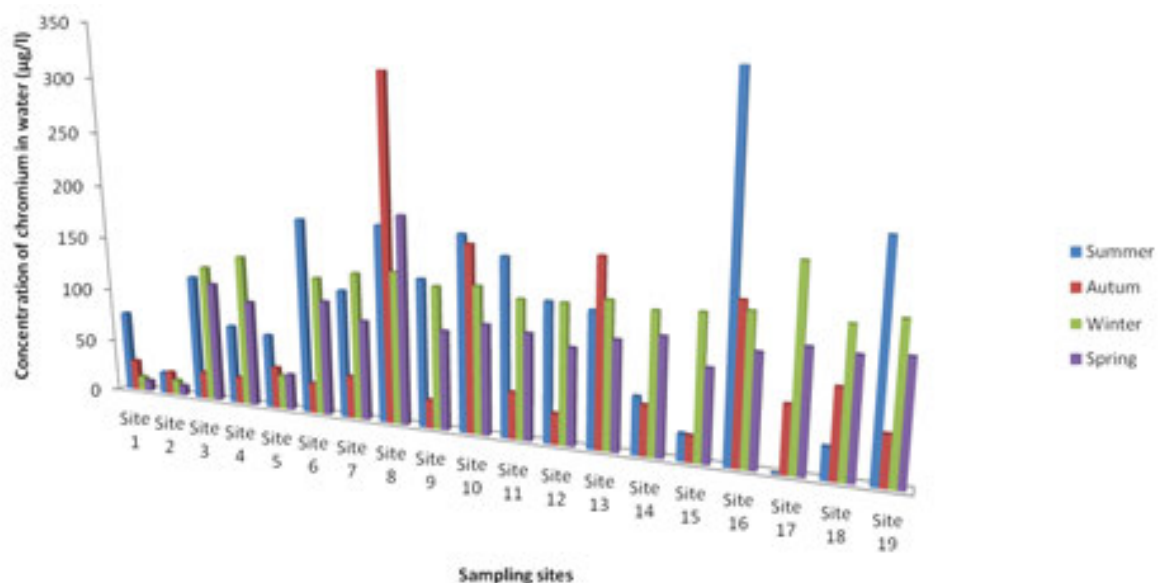
		Range	Mean (Mean $\pm$ SD)	Reference
Water	South Africa	2-4	-	[22]
	South Africa	0.0-2.0	-	[23]
	Cape Town	0.44-2.96	-	this study
	South Africa	0.1-1.1	-	[24]
	Mexico	-	14	[25]
	Egypt	<0.5-5.1	2.5	[26]
	India	0.07-5.0	-	[27]
	South Africa	-	6	[28]
	South Africa	0.04-1	-	[29]
	Nigeria	0.1-2.0	-	[30]

**Table 2.** Concentration of Cd in river water ( $\mu\text{gL}^{-1}$ ) and comparison with other globally published values

3.3. Chromium

Results of seasonal concentration of chromium in both the river water and sediment are presented in graphical forms as depicted in Figure 3. The average chromium concentrations ranged from  $9.27 \mu\text{gL}^{-1}$  to  $327.29 \mu\text{gL}^{-1}$ . The highest concentration was at site 16 during summer while the least was at site 12 (Potsdam WWTP upstream) during the spring. The annual mean concentration in water ranged from  $16.19 \mu\text{gL}^{-1}$  (Potsdam WWTP upstream) to  $206.57 \mu\text{gL}^{-1}$  (Site 8, Kraaifontein Upstream). To the best of our knowledge, no work had reported Cr levels in selected river systems in Cape Town. Aside from Nigeria and Mexico, reported annual concentration ranges were higher than values reported in Egypt, Greece and China [15,26,29-31] (Table 3). The presence of Cr (III) in drinking water is unlikely due to low

solubility of the hydrated Cr (III) oxide. The more stable Cr (VI) may occur especially in the vicinity of industries which result in environmental pollution. The Target Water Quality Range (TWQR) for aquatic ecosystem is 7 µgL<sup>-1</sup> while the human consumption target is 50 µgL<sup>-1</sup> [18]. The average annual concentration of chromium for the sites exceeded the TWQR guideline for aquatic ecosystem while sites 1, 2 and 5 were within the 50 µgL<sup>-1</sup> limits for human consumption. The high concentration of Cr in the river systems may be due to high number of vehicle repair workshops, electro plating industries and paint industries in the City of Cape Town, as their waste effluents may enter the rivers as storm water. Also, from this study, a major route of Cr to the river systems in Cape Town and Stellenbosch are through wastewater treatment plants effluents and landfill site leachate (Figure 3). For all sites, Cr values also exceeded the recommended value of 2 µgL<sup>-1</sup> for aquacultural uses, while all sites except for sites 6, 8, 10, 11, 13, 16 and 19 are within the TWQR for irrigation purposes (100 µgL<sup>-1</sup>) but within the livestock watering guidelines. However, comparing with international standards, the reported values in this study exceeded the 8 µgL<sup>-1</sup> and 50 µgL<sup>-1</sup> for irrigation water and livestock water use [19].



**Figure 3.** Seasonal trend in Cr concentrations (µgL<sup>-1</sup>) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

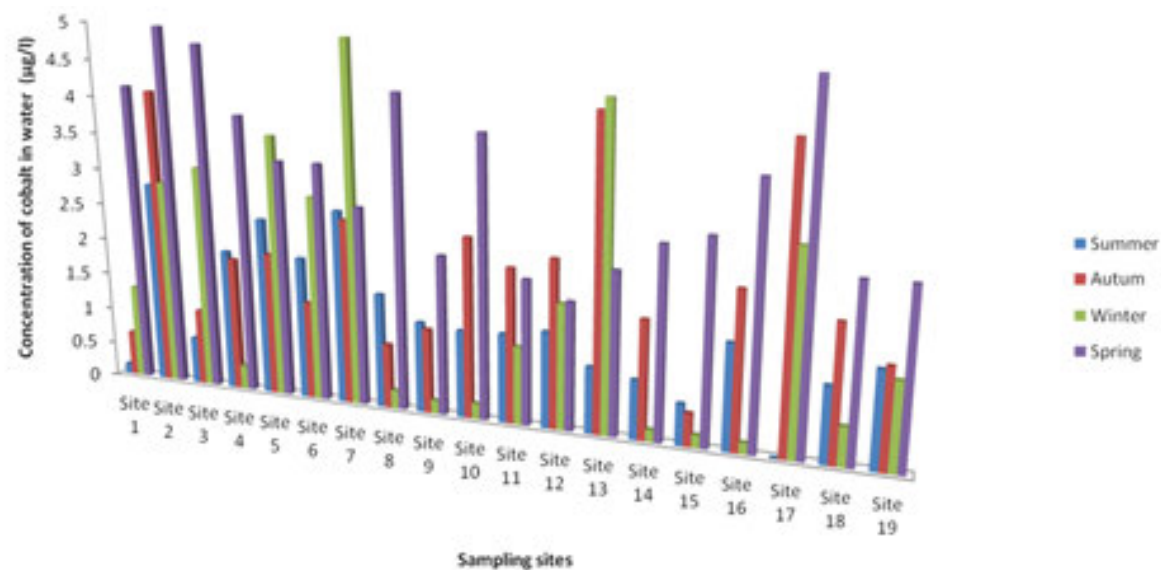
Water	Cape Town	Range	Mean (Mean ± SD)	Reference
		16.19-206.57	-	this study
	Nigeria	0.00-270	-	[26]
	Mexico	60-212	-	[15]
	China	6.67-20.44	-	[30]
	Greece	1.02-4.58	-	[29]
	Egypt	8-88	-	[31]

**Table 3.** Annual concentration (Mean) of Cr in river water (µgL<sup>-1</sup>) and comparison with other globally published values



3.4. Cobalt

The seasonal variation in Co concentrations from all the 19 sampling sites is presented in Figure 4. The graphical presentation shows that Co ranged from 0.15  $\mu\text{g/L}^{-1}$  to 4.95  $\mu\text{g/L}^{-1}$ . The highest concentration of Co was obtained at sampling site 2 (Potsdam WWTP upstream) during spring and the lowest was obtained at site 16 (Zandvliet WWTP downstream) during winter. The annual mean of Co concentration at each sampling site ranged from 0.96  $\mu\text{g/L}^{-1}$  (Site 15, Zandvliet WWTP discharge point) to 3.66  $\mu\text{g/L}^{-1}$  (Site 2, Potsdam WWTP upstream) (Figure 4). The values reported in this study were considerably lower when compared to previous studies in South Africa and elsewhere [15,24,28,32] (Table 4). Cobalt is considered an essential metal and form part of Vitamin B12, which is useful during the synthesis of red-blood cell. Ingestion of cobalt at concentration higher than 2000  $\mu\text{g/L}^{-1}$  may result in chronic human effect [24]. The reported concentration of cobalt in this study exceeded the unpolluted surface water quality guidelines [18]. However, the water is suitable for agricultural and livestock watering purposes.



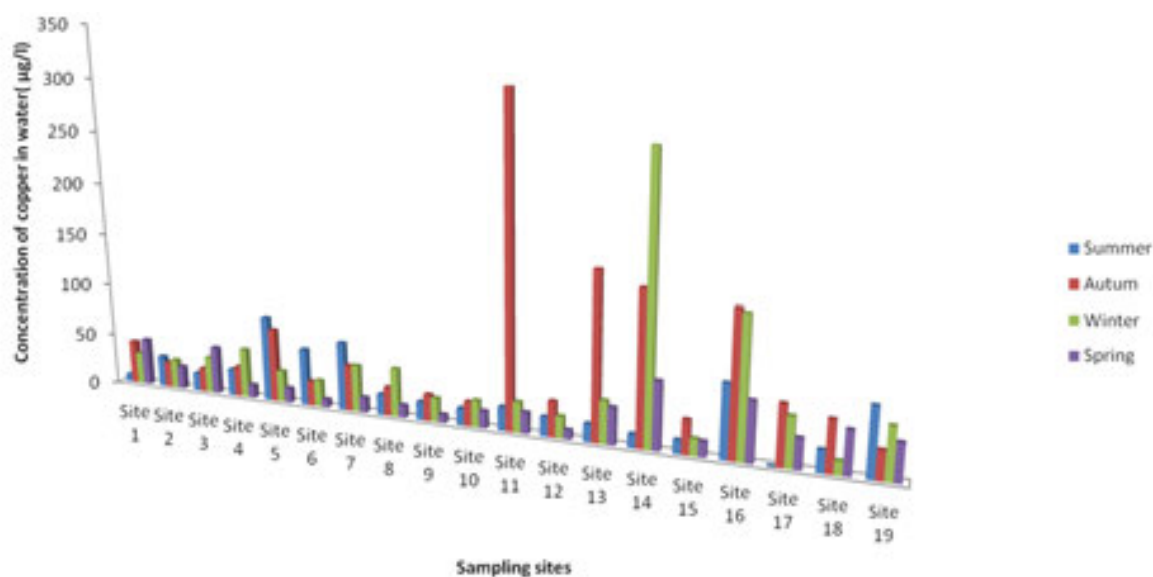
**Figure 4.** Seasonal trend in Co concentrations ( $\mu\text{g/L}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

		Range	Mean (Mean $\pm$ SD)	Reference
Water	South Africa	0.04-1.99	-	[32]
	<b>Cape Town</b>	<b>0.96-3.66</b>	-	<b>this study</b>
	Egypt	<5-43	-	[28]
	Mexico	2-8	-	[15]
	China	0.42-6.18	-	[30]
	South Africa	trace-62	-	[24]

**Table 4.** Concentration of Co in river water ( $\mu\text{g/L}^{-1}$ ) and comparison with other globally published values

### 3.5. Copper

The average concentrations of copper in water samples of the selected river system are graphical form as shown in Figure 5. The average levels of Cu in water samples obtained from the 19 sampling points ranged from 6.99  $\mu\text{g/L}^{-1}$  to 305.39  $\mu\text{g/L}^{-1}$ . The highest level of copper was obtained at sampling site 11 (Stellenbosch upstream) during autumn and the lowest at sampling point 1 (control site, Kirstenbosch botanical garden) during summer as depicted in Figure 5. The annual mean of copper concentration at each sampling site ranged from 18.23  $\mu\text{g/L}^{-1}$  (Site 9, Kraaifontein discharge point) to 120.52  $\mu\text{g/L}^{-1}$  (Site 14, Zandvliet upstream). Previous study on Eerste River [23] reported concentration range of 60-70  $\mu\text{g/L}^{-1}$  while studies elsewhere in South Africa reported Cu concentration of 2-530  $\mu\text{g/L}^{-1}$  [22,24,25] (Table 5). Copper concentration at Site 11 during autumn season may be attributed to leachate seepage into the river system and the dumping of the demolition material coupled with storm water from the landfill site. Levels at site 14 may be attributed to the closeness to an informal settlement. Reported Cu concentration were lower compared to studies elsewhere (Table 5). The annual average values in this study were within the South African water quality guideline for Cu in domestic water usage (DWAf, 1996). The TWQR limits for irrigation and livestock watering are 200  $\mu\text{g/L}^{-1}$  and 5000  $\mu\text{g/L}^{-1}$  with chronic impact on livestock expected between 1000 and 10,000  $\mu\text{g/L}^{-1}$  depending on the livestock [18]. Cu concentrations reported in this study were within these limits except for Site 11 (Stellenbosch upstream) during the autumn season. Generally, all the sampling sites values for Cu exceeded the set limits of 0.3  $\mu\text{g/L}^{-1}$  for the protection of aquatic life. Wastewater treatment plants shows to be one of the major routes of copper into the freshwater systems from this study.



**Figure 5.** Seasonal trend in Cu concentrations ( $\mu\text{g/L}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

Water		Range	Mean (Mean ± SD)	Reference
	<b>Cape Town</b>	<b>18.23-120.52</b>	-	<b>this study</b>
	South Africa	383-387	-	[24]
	Mexico	>200	-	[15]
	India	102.82-258.7	161.43	[27]
	South Africa	60-70	-	[23]
	South Africa	2-3	-	[25]
	Egypt	22-54	-	[31]
	Nigeria	0.00-1536	-	[26]
	South Africa	100-530	-	[21]

**Table 5.** Concentration of Cu in river water (ugL<sup>-1</sup>) and comparison with other globally published values

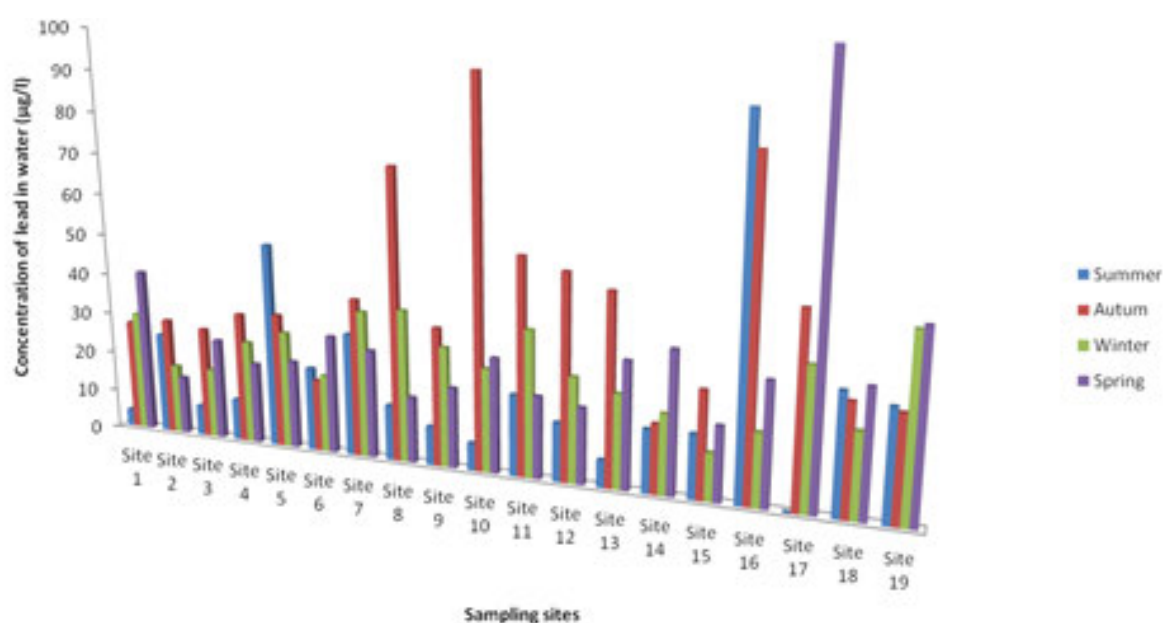
**3.6. Lead**

The result of seasonal concentrations of lead in water and sediment of the selected river systems receiving wastewater effluent are presented in Figure 6. The average values of Pb in water samples obtained from the river system ranged from 4.18 µgL<sup>-1</sup> to 86.73 µgL<sup>-1</sup> for the 19 sampling points as shown in Figure 6. The highest level of lead was obtained at Site 16 (Zanvliet WWTP point of discharge) during summer and the lowest at Site 1(control site, Kirstenbosch Botanical Garden) during summer. Meanwhile, the annual mean value of lead at each sampling site in this study for water ranged from 17.6 µgL<sup>-1</sup> to 52.9 µgL<sup>-1</sup>. Previous studies in South Africa had reported Pb concentration ranging below detection limit to 1110 µgL<sup>-1</sup> [21,23-26,28,29] (Table 6). Meanwhile, another study Reinecke *et al.* [23] reported 30 to 40 µgL<sup>-1</sup> of lead in the Eerste River. Effluent discharges from sewage treatment plant and industries had been suggested as possible routes of Pb into river systems. Thus, considering the values reported in the study, wastewater effluent is a factor to high lead concentration in the river system. Though, the study shows that the final effluent concentration were generally low for lead, and the effluent helps to further dilute the river water concentration, possible contamination source could not be ruled out. The recommended threshold level of lead for South Africa Rivers is 10 µgL<sup>-1</sup> [18]. The results shows that the annual average value of lead for all the sampling points of the river system and the control site were above the TWQR threshold level for human consumption and aquacultural purposes. However, reported values were within the TWQR for irrigation and livestock watering. The water is unsuitable for the protection of aquatic ecosystems as TWQR limits of 0.2 µgL<sup>-1</sup> was exceeded.

**3.7. Mercury**

In this study, the seasonal concentrations of mercury in water of the selected river system and control site are depicted in Figure 7. The average levels of Hg in water samples obtained from the 19 sampling sites ranged from 0.1 µgL<sup>-1</sup> to 8.09 µgL<sup>-1</sup> while the annual mean concentration for each sampling site ranged from 1.45 µgL<sup>-1</sup> to 2.58 µgL<sup>-1</sup> The highest level of mercury was obtained at sampling site 15 (Zandvliet discharge point) during the spring season and the lowest at sampling point 2 (Potsdam WWTP upstream) as depicted in Figure 7. Previous study in Eastern Cape had reported concentration of Hg 0.003 mgL<sup>-1</sup> [33]. While Retief *et al.* [32]

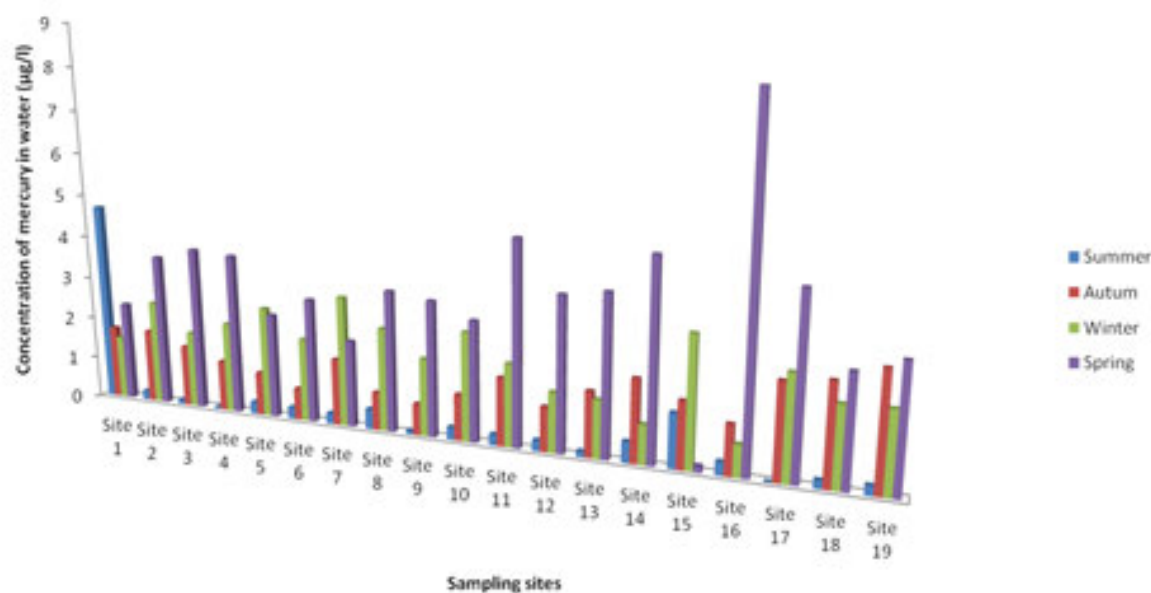
reported Hg concentration range of  $0.125 \mu\text{gL}^{-1}$  to  $0.513 \mu\text{gL}^{-1}$  in the Vaal dam, South Africa. Previous studies in several countries reported levels of mercury in water were ranged from not detected to  $1502 \mu\text{gL}^{-1}$  [27,34-37] (Table 7). The recommended TWQR threshold level of mercury for South African rivers for human consumption is  $1.00 \mu\text{gL}^{-1}$  [18]. The average values of mercury for all the samplings sites exceeded the limits, though there are instances during sampling period where Hg concentrations were below this guideline. Also, Hg concentration exceeded TWQR guideline for the protection of aquatic ecosystem, livestock watering and aquaculture uses. Considering the effect of ingesting Hg through the river water, the water system is unsafe for domestic, agricultural, livestock and aquaculture uses.



**Figure 6.** Seasonal trend in Pb concentrations ( $\mu\text{gL}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

Water		Range	Mean (Mean $\pm$ SD)	Reference
	<b>Cape Town</b>	<b>17.64-52.99</b>	-	<b>this study</b>
	Nigeria	10-2570	-	[26]
	South Africa	10.5-20.1	-	[25]
	Greece	ND-12.61	-	[29]
	South Africa	30-40	-	[23]
	South Africa	24-350	-	[24]
	South Africa	240-1110	-	[21]
	Egypt	5-57	-	[28]

**Table 6.** Concentration of Pb in river water ( $\mu\text{gL}^{-1}$ ) and comparison with other globally published values



**Figure 7.** Seasonal trend in Hg concentration ( $\mu\text{gL}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

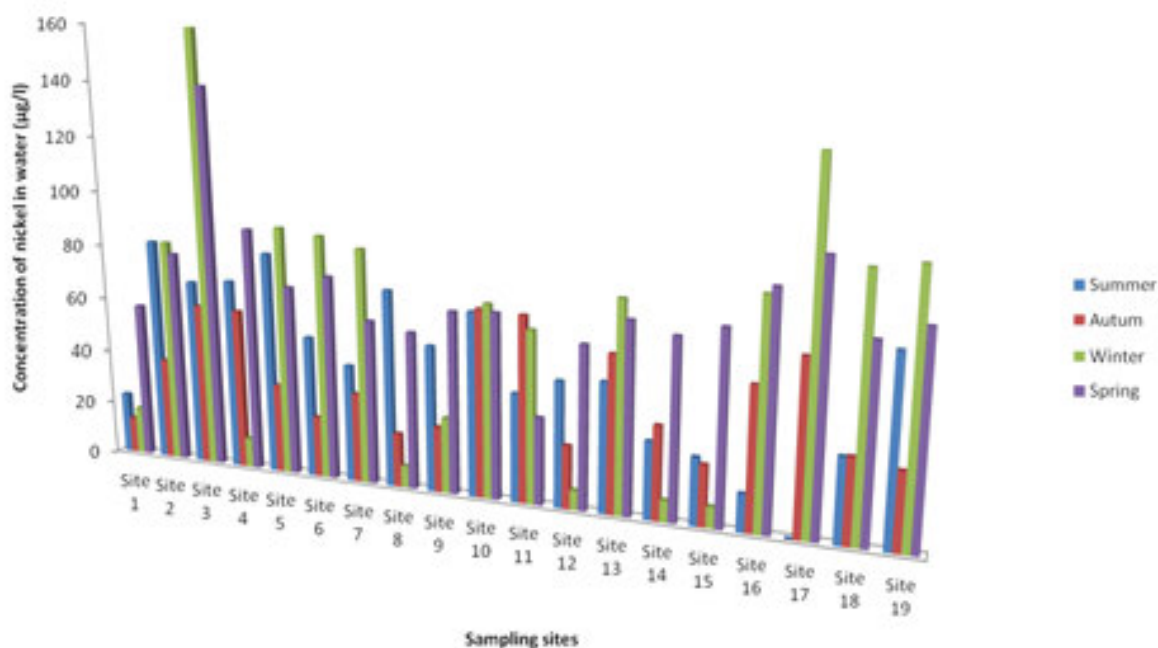
Water		Range	Mean (Mean $\pm$ SD)	Reference
	<b>Cape Town</b>	<b>1.45-2.58</b>	-	<b>this study</b>
	India	0.015-0.194	0.001	[27]
	South Africa	trace-3	-	[33]
	Spain	ND	-	[37]
	Turkey	1.50-1502	-	[36]
	Spain	ND-2.09	-	[35]
	Spain	2.80-5.70	-	[34]

**Table 7.** Concentration of Hg in river water ( $\mu\text{gL}^{-1}$ ) and comparison with other globally published values

3.8. Nickel

Seasonal concentrations of nickel in water, from all the 19 sampling locations are presented in Figure 8. The seasonal concentration ranged from  $7.7 \mu\text{gL}^{-1}$  to  $159.17 \mu\text{gL}^{-1}$ . The highest level of nickel was obtained at sampling point 3 (Potsdam discharge point) during winter and the lowest at site 15 (Zandvliet discharge point) during winter. Meanwhile, the annual average nickel concentration found in this study in the water samples ranged from  $27.62 \mu\text{gL}^{-1}$  to  $106.39 \mu\text{gL}^{-1}$  for Site 1 (Kirstenbosch Botanical Garden) and Site 3 (Potsdam discharge point), respectively. A study by Awofolu *et al.* [24], reported concentration of nickel found in Eastern Cape river to ranged from  $201 \mu\text{gL}^{-1}$  to  $1777 \mu\text{gL}^{-1}$ . Besides that, Retief *et al.* [32] reported a nickel concentration range of  $2.89 \mu\text{gL}^{-1}$  to  $27.2 \mu\text{gL}^{-1}$  in Vaal dam, South Africa (Table 8). Studies in several countries reported levels of nickel in water ranging from  $< 5 \mu\text{gL}^{-1}$  to  $300 \mu\text{gL}^{-1}$  [15,24,

28,31,32] There was no water quality guidelines set by South Africa Department of Water Affair and Forestry for human consumption, protection of aquatic ecosystem and for aquacultural uses. However, the reported concentrations in this study were still within the TWQR of 200  $\mu\text{gL}^{-1}$  and 1000  $\mu\text{gL}^{-1}$  for irrigation and livestock watering. From this study, WWTP acts as one of the major routes of nickel into the freshwater system as concentration downstream of the treatment plants was higher than concentration upstream. This also established the anthro-pogenic route of nickel introduction into the environment



**Figure 8.** Seasonal trend in Ni concentration ( $\mu\text{gL}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

		Range	Mean (Mean±SD)	Reference
Water	<b>Cape Town</b>	<b>27.62-106.39</b>	-	<b>this study</b>
	Mexico	160-300	-	[15]
	South Africa	201-1777	-	[24]
	China	0.14-6.13	-	[30]
	Egypt	<5-33	-	[28]
	South Africa	2.89-27.16	-	[32]

**Table 8.** Concentration of Ni in river water ( $\mu\text{gL}^{-1}$ ) and comparison with other globally published values



3.9. Zinc

Seasonal variation in the concentration of Zn in water samples from all the 19 sampling sites is presented in Figure 9. The average seasonal concentration ranged from 25.15  $\mu\text{g/L}^{-1}$  to 909.38  $\mu\text{g/L}^{-1}$ . The highest level of zinc was obtained at sampling site 15(Zandvliet discharge point) during summer and the lowest at sampling site 12 (Stellenbosch discharge point). Meanwhile, the annual mean zinc concentration found in this ranged from 172.79  $\mu\text{g/L}^{-1}$  (Site 1, Kirstenbosch Botanical Garden) to 722.07  $\mu\text{g/L}^{-1}$  (Site 13, Stellenbosch downstream). Previous study in the Western Cape Province had reported various concentration of Zn in river water. Jackson *et al.* [38], reported zinc concentration ranging from 100  $\mu\text{g/L}^{-1}$  to 2100  $\mu\text{g/L}^{-1}$  in Berg River and Jackson *et al.* [39] reported concentration range of between 100  $\mu\text{g/L}^{-1}$  and 4400  $\mu\text{g/L}^{-1}$ for studies conducted on Plankenburg and Diep Rivers. However, studies elsewhere in South Africa had reported concentration range of 10  $\mu\text{g/L}^{-1}$  to 43  $\mu\text{g/L}^{-1}$  [21,23,24,33] (Table 9). Meanwhile, studies in several countries reported levels of zinc in water were ranged from <5  $\mu\text{g/L}^{-1}$  to 97  $\mu\text{g/L}^{-1}$  [22, 23,26,27,39-46] (Table 9). The reported values in this study were lower compare to previous studies in Cape Town. Aside from the geology of the catchment, zinc concentration in the river systems pointed towards WWTPs and storm water carrying both industrial and domestic effluents. The recommended TWQR for Zn in water for domestic purposes is 3000  $\mu\text{g/L}^{-1}$  [18]. Thus, from the reported values, no health effect is expected from domestic use of the water from the sampling sites. However, the TWQR for the protection of aquatic ecosystem, aquaculture purposes, livestock watering and irrigation of are 2  $\mu\text{g/L}^{-1}$ , 30  $\mu\text{g/L}^{-1}$ , 0 to 20  $\text{mg/L}^{-1}$  and 100  $\mu\text{g/L}^{-1}$ . From this study, water from the river systems and the control site is not suitable for the protection of aquatic ecosystem or use for aquaculture purposes.

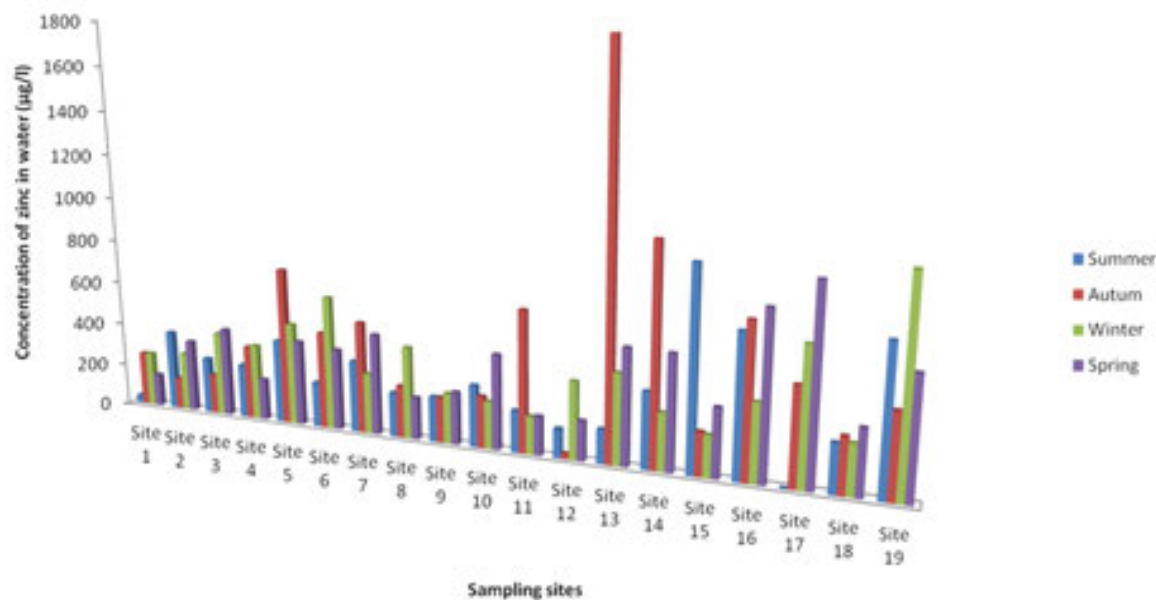


Figure 9. Seasonal trend in Zn concentrations ( $\mu\text{g/L}^{-1}$ ) in river water receiving waste effluent from WWTPs; Sites are the same as listed in Figure 1

Water	Range	Mean (SD)	Reference
Cape Town	49.1-1112	-	[43]
Cape Town	111.66-1413.13	-	this study
Cairo	24.0-121.68	80.82 (31.67)	[44]
Denmark	7-21240	-	[42]
Egypt	13.0-2712	-	[28]
South Africa	8.9-15340	-	[42]
Turkey	30.02-1871	-	[41]
Uganda	42.77-1968.43	-	[45]
India	128.29-46602	217.37	[46]
India	8.77-323.47	-	[47]
South Africa	26.0-11081.2	-	[48]
South Africa	42.5-77.5	-	[24]
South Africa	2.9-211.3	-	[49]

**Table 9.** Concentration of Zn in river water ( $\mu\text{g L}^{-1}$ ) and comparison with other globally published values

## 4. Conclusion

In the river water, arsenic and cadmium were within the normal level for human consumption but exceeded the limits for the aquatic life protection. Also, lead and mercury exceeded both limits for human consumption and sustainable aquatic life's. The trend in the levels of metals and arsenic in the river systems showed that the upstream and downstream are more polluted compared to the WWTP discharge points. This is an indication that the WWTPs might not completely be the pollution source of the river systems in the City of Cape Town. The reported trend may be attributed to waste dumping on the river course, indiscriminate wastewater discharge from industries, storm water runoff from agricultural lands and grey and domestic wastewater.

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