academicJournals

Vol. 15(23), pp. 1101-1135, 8 June, 2016
DOI: 10.5897/AJB12.1723
Article Number: 6BC23B358794
ISSN 1684-5315

http://www.academicjournals.org/AJB

African Journal of Biotechnology

Full Length Research Paper

Variation in levels and removal efficiency of heavy and trace metals from wastewater treatment plant effluents in Cape Town and Stellenbosch, South Africa

Olujimi, O. O.[1,2]*, Fatoki, O. S.[3], Odendaal, J. P.[1], Daso, A. P.[2] and Oputu, O. U.[3]

[1]Department of Environmental and Occupational Studies, Cape Peninsula University of Technology, Cape Town, South Africa.
[2]Department of Environmental Management and Toxicology, Federal University of Agriculture, P. M. B. 2240, Alabata Road, Abeokuta, Ogun State, Nigeria.
[3]Department of Chemistry, Cape Peninsula University of Technology, South Africa.

Accepted 1 November, 2012; Accepted 25 September, 2013

This study focused on one year monitoring campaign to monitor the occurrence and removal of Endocrine Disruptive Metals (EDMs) and trace metals from selected wastewater treatment plants (WWTPs) in Stellenbosch and Cape Town. Composite water samples were collected from the WWTPs from January 2010 to December 2010 on a quarterly basis and concentrations determined using inductively coupled plasma-mass spectrometry (ICP-MS) after open beaker digestion. A total of 432 water samples consisting of raw, primary effluent, secondary effluent and final effluents were collected and analyzed. The general abundance distribution pattern for metals was Zn > Cu > Pb > Cr > Ni > As > Co > Cd > Hg. The removal efficiency ranged from 1.5% for Hg at Zandvliet WWTP plant during winter to 98.27% for Cu at Athlone WWTP treatment plant during summer. The final effluent concentration for most of the metals were within South African water quality guidelines while As, Hg, Cd and Pb concentration were higher than maximum limits set by the Canadian Council of Ministers of the Environment. Potsdam WWTP showed to be the most effective at heavy metals removal as compared with the other five treatment plants investigated in this study. The effluent metal concentration over time could pose health risk if used for agricultural irrigation.

Key words: Seasonal variation, endocrine disrupting metals, wastewater treatment plants, effluents, coupled plasma-mass spectrometry (ICP-MS), Cape Town.

INTRODUCTION

The presence of metals in wastewater is one of the main causes of water and soil pollution (Chanpiwat et al., 2008, 2010). The accumulation of these metals in wastewater depends upon several local factors (Oliveira

---

*Corresponding author. E-mail: olujimio@funaab.edu.ng

et al., 2007; Ogunfowokan et al., 2008). Metal composition in urban wastewater in Brazil, China, Iran and Poland had been reported to be both complex and highly varying and according to the prevailing economic activities and the living pattern (Kulbat et al., 2003; Oliveira et al., 2007; Rajbanshi, 2008; Chanpiwat et al., 2010). It has been stated that metal input in wastewater treatment systems is so variable that even down to an hour-by-hour scale it remains unpredictable (Ogunfowokan et al., 2008). Major sources of sewage wastewater include households, drainage water, businesses, atmospheric deposition, pipe sediment, building materials and traffic (Sorme and Largerkrist, 2002). Moreover, metal concentrations in wastewater can be affected by people's lifestyles and their awareness of the impacts on the environment. Metal removal efficiency depends on the metal concentration, its speciation, the reactivity of the available biopolymers or biomass, and the composition of other wastewater components (Wang et al., 1999). With emphasis on the improvement of stream and river water quality, the treatment plants must achieve greater efficiency in the treatment process. No study has reported on the concentrations of heavy metals most especially metals classified as Endocrine Disrupting Metals (EDMs) (that is, cadmium, arsenic, lead and mercury) in the influent and effluent wastewater from wastewater treatment plants in Western Cape Province, South Africa.

Previous studies have largely concentrated on the water, sediment and plant samples from Diep and Berg rivers (Jackson et al., 2007, 2009; Shuping, 2008; Ayeni et al., 2010). Though a nationwide survey was carried out in 1989 and 2002 to assess levels of heavy metals in sewage sludge from 77 wastewater treatment plants, the country's population had increased and there has been rural-urban migration, thus, pressure on wastewater treatment plants (WWTPs) facilities has increased over the last decade (Jaganyi et al., 2005). Paucity of information on the available endocrine disrupting metals, other trace metals and public outcry on poor performance of WWTPs facilities necessitated the need for this study to establish: 1) The occurrence and distribution pattern of endocrine disrupting metals and other trace elements; and 2) to access the impact of seasonal changes on EDMs availability and removal from wastewater effluents.

This study follows the preliminary investigation into the possible impact of wastewater treatment plant effluents on freshwater systems in Cape Town (Olujimi et al., 2012).

MATERIALS AND 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 were 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^{-1} for ICPMS. The isotopes of the elements determined were ^{111}Cd, ^{75}As, ^{208}Pb, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu and ^{66}Zn.

Reagents

Water (resistivity 18.2 MΩ cm) was de-ionized by the use of a Milli-Q system (Millipore, Bedford, MA, USA). Certified standard of all the metal (As, Cd, Cu, Co, Cr, Hg, Ni, Pb and Zn) were obtained to check for instrument performances from Merck, South Germany. $AuCl_3$, ultrapure nitric acid (65%) and 32% hydrogen peroxide were obtained from Fluka Kamika, Switzerland.

Study area and sampling protocol

Six wastewater treatment plants were investigated for the occurrence of heavy metals and for the effectiveness of the WWTPs in removing them from waste stream. Five of these WWTPs were located in the City of Cape Town, while one is located in Stellenbosch. Geographical locations and design properties of the investigated treatment plants are presented in Table 1. 24 h composite water samples were collected from the wastewater treatment on quarterly basis to observe the possible impact of seasonal variation on heavy metals in wastewater treatment plants. Sampling for heavy metals analysis commenced in January 2010 and ended in December 2010.

Wastewater digestion

Water samples for the heavy metals analysis were collected in 1 L plastic containers which were initially washed with detergent and rinsed with distilled water. The containers were finally soaked in 10% nitric acid overnight and rinsed with Milli-Q water prior to use. The samples were preserved by adding a few drops of concentrated HNO_3 to each sample bottle and pH adjusted to 2.0 by the use of pH meter. The samples were stored in a refrigerator at about 4°C, 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 in accordance with Akan et al. (2008). A few drops of $AuCl_3$ were added to the water samples to keep Hg ions in solution.

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:

$$\varepsilon(\%) = \left(\frac{EDCi/Mi - EDCe/Me}{Mi}\right)\times 100\% = \frac{QiCi - QeCe}{QiCi}\times 100\% = \frac{Ci - Ce}{Ci}\times 100\%$$

Table 1. Description of the six waste water treatment plants investigated.

WWTP ID	Geographical Location of plant	People Equivalent	Source	Treatment process	Associated River
A	S 33.5709° E 18.3048°	900,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew -	Vygekraal River
B	S 33.5923° E 18.4332°	591,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew -	Kuils River
C	S 33.82539° E 18.70442°	133,000	Domestic	S + G + Sed + AS (N) + Sed + Chl + AD + Dew	Mosselbank River
D	S 33.5070° E 18.3108°	385,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew	Diep River
E	S 33.94345° E 18.82492°	N/K	Domestic Industrial	S + G + Sed + FB + AS (BNR) + Sed + Chl + AD + Dew	Veldwachters River
F	S 34.0312° E 18.4259°	400,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew	Kuils River

With *EDCi/e* or *Mi/e* = the metal flux in influent/effluent (mgd^{-1}); *Ci/e* = the metal concentration in influent/effluent (mgl^{-1}); *Qi/e* = the mean flow rate of influent/effluent (l d^{-1}).

Statistical analysis

Statistical analysis was performed using SPSS 19.0. Normality of the distribution was tested by means of the Kolmogorov-Smirnov test of normality ($\alpha = 0.05$). As metal concentrations in the water were not normally distributed, significance of difference between raw wastewater, settling tank and effluents were assessed by means of non-parametric Wilcoxon tests ($\alpha = 0.05$). Seasonal effects were analyzed by means of the non-parametric Kruskal-Wallis rank test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Occurrence, distribution and removal pattern of heavy metals in wastewater treatment plants

Arsenic

Seasonal variation of arsenic at the Athlone WWTP is shown in Table 2, while Figure 1a presents the annual distribution pattern in the WWTP. The percentage removal of arsenic in treatment plants ranged from 22.14 to 68.44%. The annual mean removal efficiency of the plant for arsenic was 43.78% (Figure 2). Statistical analysis showed no significant difference ($P>0.05$) in the level of arsenic received at the plant during the studied period. However, it is noteworthy that the plant was not functioning optimally during the second and fourth sampling seasons. For the studied period, the removal efficiency of the plant could be adjudged ineffective as less than 50% of the total arsenic influx was removed from the waste stream. The annual distribution trend showed that about 20% of arsenic was removed at the primary settling tank, while the secondary settling tank accounted for about 60% (Figure 1). The ineffective removal of arsenic from the Athlone WWTP could be attributed to plant overload and frequent breakdown of the treatment plant. The arsenic concentrations in old and new Bellville plants (old Bellville plant received wastewater from domestic sources, while new plant received wastewater from both domestic and industrial sources) ranged from 4.62 to 9.2 µgL^{-1} and 6.01 to 43.76 µgL^{-1}. Effluent concentrations ranged from 2.57 to 4.69 µgL^{-1} and 1.12 to 5.10 µg L^{-1} in new and old plants, respectively (Table 2). For the two plants, there was significant differences ($P<0.05$) in seasonal arsenic concentrations. Also, there was significant differences in arsenic concentrations within the plant during summer and autumn seasons due to different plant treatment processes for old and new plants. The annual distribution pattern of arsenic in the WWTPs is presented in Figure 1b and c.

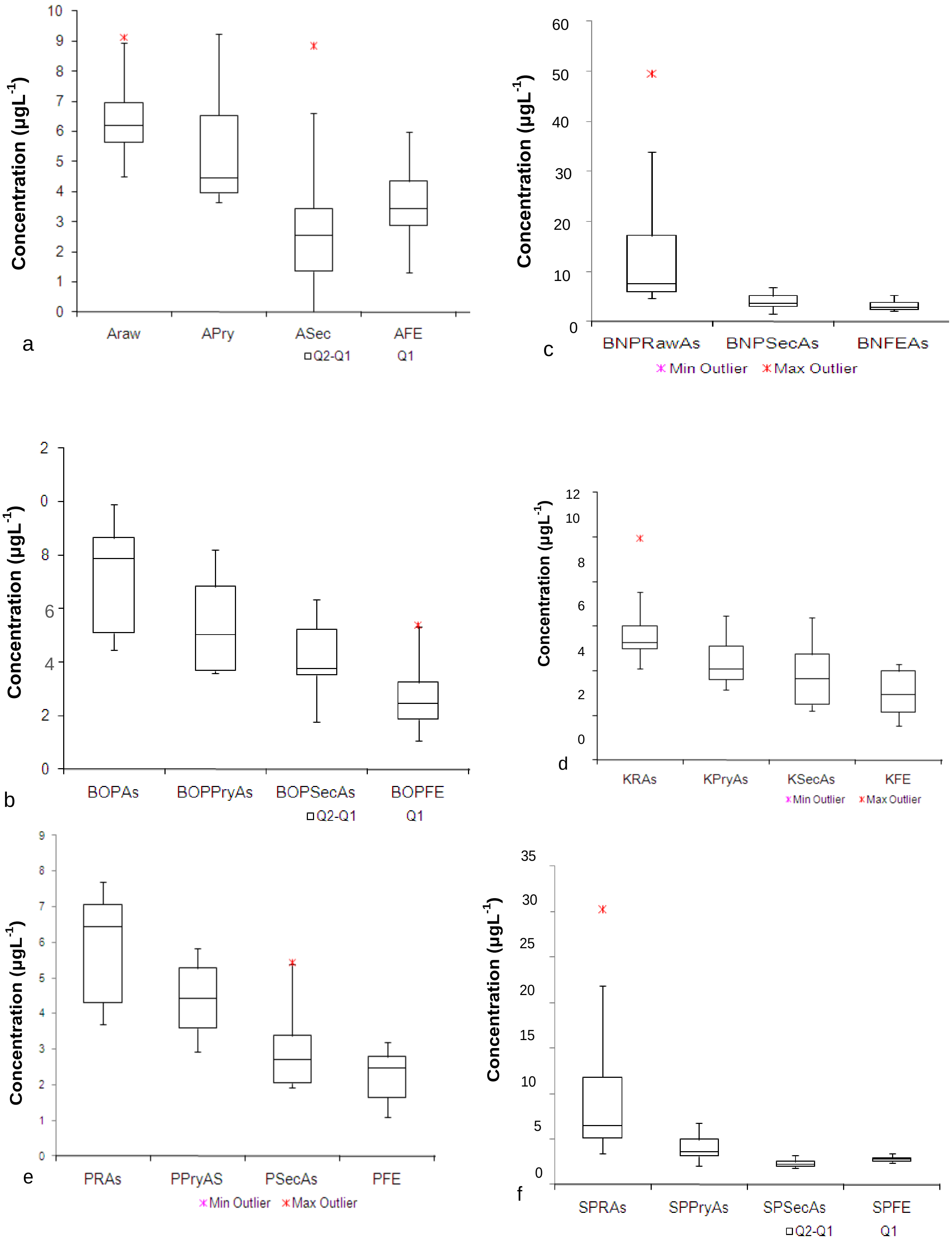
The seasonal removal efficiency of the plants ranged from 39.08 to 75.95% (old plant) and 40.31 to 94.12% (new plant) (Table 2). In the old plant, the primary settling tank accounted for about ¼% removal of arsenic on an annual basis, while the secondary settling tank removed

Table 2. Mean concentration (±SD) of As in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgl^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (µgL^{-1})				$\alpha_{\text{concentration}}$	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	6.21 ± 0.53	4.07 ± 0.42	2.02 ± 0.38	1.91 ± 1.03	*	68.44
	Autum ’10	8.24 ± 0.83	7.99 ± 1.21	6.09 ± 2.42	5.69 ± 0.47		30.93
	Winter ’10	6.14 ± 0.33	5.72 ± 1.17	2.83 ± 0.29	2.86 ± 0.29		53.42
	Spring ’10	3.95 ± 0.31	3.95 ± 0.31	N/A	3.89 ± 0.19	*	22.14
	α_{season}	*					
Bellville old	Summer ’10	4.62 ± 0.19	4.12 ± 0.48	3.71 ± 0.10	1.12 ± 0.06	*	75.67
	Autum ’10	9.35 ± 0.54	3.62 ± 0.02	2.71 ± 0.81	2.25 ± 0.22	*	75.97
	Winter ’10	8.38 ± 0.22	8.00 ± 0.34	6.04 ± 0.41	5.10 ± 0.48		39.08
	Spring ’10	6.16 ± 1.28	5.97 ± 0.60	4.62 ± 0.79	2.63 ± 0.17		57.35
	α_{season}	*					
Bellville new	Summer ’10	6.77 ± 2.36	NPST	4.60 ± 0.77	3.14 ± 1.13		53.67
	Autum ’10	43.76 ± 5.06	NPST	3.52 ± 0.20	2.57 ± 0.14	*	94.12
	Winter ’10	7.86 ± 0.74	NPST	5.91 ± 0.81	4.69 ±0.90		40.31
	Spring ’10	6.01 ± 0.27	NPST	2.19 ± 0.45	2.63 ±0.17		56.33
	α_{season}	*					
Kraaifontein	Summer ’10	4.27 ± 0.27	3.32 ± 0.16	2.38 ± 0.16	2.38 ± 0.15	*	44.28
	Autum ’10	5.27 ± 0.15	3.93 ± 0.22	2.98 ± 0.65	2.38 ± 0.10		54.87
	Winter ’10	8.88 ± 1.10	6.03 ± 0.47	5.16 ± 1.11	3.71 ± 0.31		58.27
	Spring ’10	5.27 ± 0.09	4.48 ± 0.47	4.44 ± 0.57	1.78 ± 0.21		66.27
	α_{season}						
Potsdam	Summer ’10	4.23 ± 0.16	3.11 ± 0.15	2.23 ± 0.21	1.20 ± 0.12	*	71.52
	Autum ’10	7.38 ± 0.10	5.53 ± 0.49	4.24 ±1.08	2.09 ± 0.31	*	71.64
	Winter ’10	6.59 ± 0.31	5.08 ± 0.54	3.27 ± 0.23	2.64 ± 0.07		59.96
	Spring ’10	5.28 ± 0.21	3.25 ± 0.31	2.00 ± 0.08	3.10 ± 0.09		41.18
	α_{season}	*		*			
Stellenbosch	Summer ’10	28.20 ± 3.43	4.20 ± 0.44	2.03 ± 0.07	2.75 ± 0.20	*	90.25
	Autum ’10	5.33 ± 2.17	3.26 ± 0.26	3.04 ± 0.21	2.91 ± 0.49		45.37
	Winter ’10	6.71 ± 0.47	6.49 ± 0.47	2.34 ± 0.12	2.98 ± 0.05		55.54
	Spring ’10	5.07 ± 0.47	2.60 ± 0.55	2.01 ± 0.29	2.56 ± 0.16		49.48
	α_{season}	*					
Zandvliet	Summer ’10	4.04 ± 0.38	NPST	3.3 ± 0.1	2.75 ± 0.20	*	42.63
	Autum ’10	4.07 ± 0.45	NPST	2.8 ± 0.1	2.6 ± 0.1		35.54
	Winter ’10	4.53 ± 0.24	NPST	2.3 ± 0.3	1.6 ± 0.8		62.77
	Spring ’10	7.36 ± 0.49	NPST	5.8 ± 1.0	2.56 ± 0.16		66.58

$\alpha_{\text{concentration}}$, Significant difference between the stages of WWTPs; α_{season}, significant difference of seasonal differences; *, difference is significant at $\alpha = 0.05$.

about 40% of the total arsenic concentration. The new Bellville plant uses University of Cape Town design (UCT) tank accounted for about ¼% removal of arsenic on an annual basis, while the secondary settling tank removed about 40% of the total arsenic concentration. The new Bellville plant uses University of Cape Town design


a
Concentration (µgL-1)
0 1 2 3 4 5 6 7 8 9 10
Araw
APry
ASec
AFE
Q2-Q1
Q1
c
Concentration (µgL-1)
0 10 20 30 40 50 60
BNPRawAs
BNPSecAs
BNFEAs
Min Outlier
Max Outlier
b
Concentration (µgL-1)
0 2 4 6 8 0 2
BOPAs
BOPPryAs
BOPSecAs
BOPFE
Q2-Q1
Q1
d
Concentration (µgL-1)
0 2 4 6 8 10 12
KRAs
KPryAs
KSecAs
KFE
Min Outlier
Max Outlier
e
Concentration (µgL-1)
0 1 2 3 4 5 6 7 8 9
PRAs
PPryAS
PSecAs
PFE
Min Outlier
Max Outlier
f
Concentration (µgL-1)
0 5 10 15 20 25 30 35
SPRAs
SPPryAs
SPSecAs
SPFE
Q2-Q1
Q1

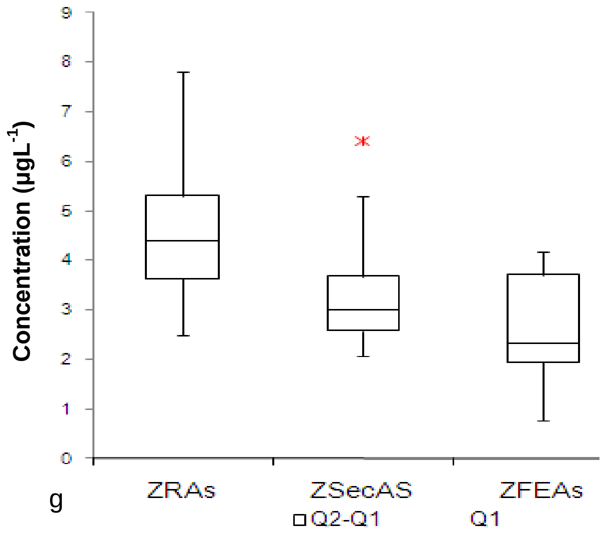


Figure 1. Box and whisker plot for annual spread of As concentration in WWTPs. a) Athlone b) Bellville old c) Bellville new d) Kraaifontein e) Potsdam f) Stellenbosch g) Zandvliet.

(UCT) system with returned activated sludge, raw effluent were pumped straight into the bioreactor with no primary settling tank. Secondary settling tank removed about 75% of the total influx of arsenic. The annual mean removal efficiency of this treatment plant (old and new systems combined) was about 62% and thus, could be rated above average in performance (Figure 2). Arsenic concentration at the Kraaifontein WWTP ranged from 4.27 to 8.8 µgL^{-1} in the influent waste and 1.78 to 3.71 µgL^{-1} in the final effluent (Table 2). The removal efficiency of the plant increased by about 22% over the sampling period (Table 2). The annual mean distribution pattern revealed that 25% of arsenic was removed at the primary settling tank, while 36.8% was removed at the secondary settling tank (Figure 1d). The annual mean removal efficiency of the plant was 55.92% (Figure 2). There was a significant difference in the concentration over the study period due to the treatment process.

The Potsdam WWTP arsenic concentrations varied between 4.23 to 7.38 µgL^{-1} in influent waste and 1.21 to 3.10 µgL^{-1} in the final effluent (Table 2). The annual mean with distribution pattern of arsenic is presented in Figure 1e. There was a significant difference ($P<0.05$) in arsenic level over the sampling period. The distribution and removal pattern showed that about 28% of arsenic in the wastewater was removed at the primary settling tank, while about 50% was removed at the secondary settling tank. The annual mean removal efficiency of the plant was 61.07% (Figure 2). This showed that the treatment plant was more effective at arsenic removal compared to Athlone and Bellville plants. The Stellenbosch WWTP received a concentration range of 5.07 to 28.20 µgL^{-1} for fourth and first quarter, respectively, in the influent wastewater while the final effluent had a concentration range of 2.56 to 2.98 µgL^{-1} (Table 2). The seasonal removal efficiency of the plants varied between 45.37 to 90.25% with an annual mean removal efficiency of 60.16%. There was significant difference in the arsenic concentration in the influent into the plant over the sampling period. An increase in concentration of arsenic in the Zandvliet WWTP was also observed from 4.04 to 7.36 µgL^{-1} in the raw effluent, while the final effluent concentrations ranged from 1.69 to 2.62 µgL^{-1}. This plant seasonal removal efficiency varied between 35.54 to 66.58% (Table 2). About 30% of arsenic concentration was removed at the secondary settling tank, while the remaining can be accounted for in the wastewater sludge.

The annual distribution pattern is presented in Figure 1g. Though, over 35% of arsenic concentration that enters the plant was removed, there was no significant difference ($P>0.05$) due to plant treatment processes except for summer season.

Cadmium

Cadmium concentration ranged from 2.21 to 3.38 µgL^{-1} and 0.52 to 2.31 µgL^{-1} in the influent and effluent wastewater of Athlone plant, respectively (Table 3). Generally, 65% of heavy metals in raw influent are believed to be removed at the primary settling tank (Chanpiwat et al., 2008). This assumption could not hold for cadmium in this plant as overall annual mean removal efficiency for the plant revealed that 25% of the total Cd concentration was removed at the primary settling tank,

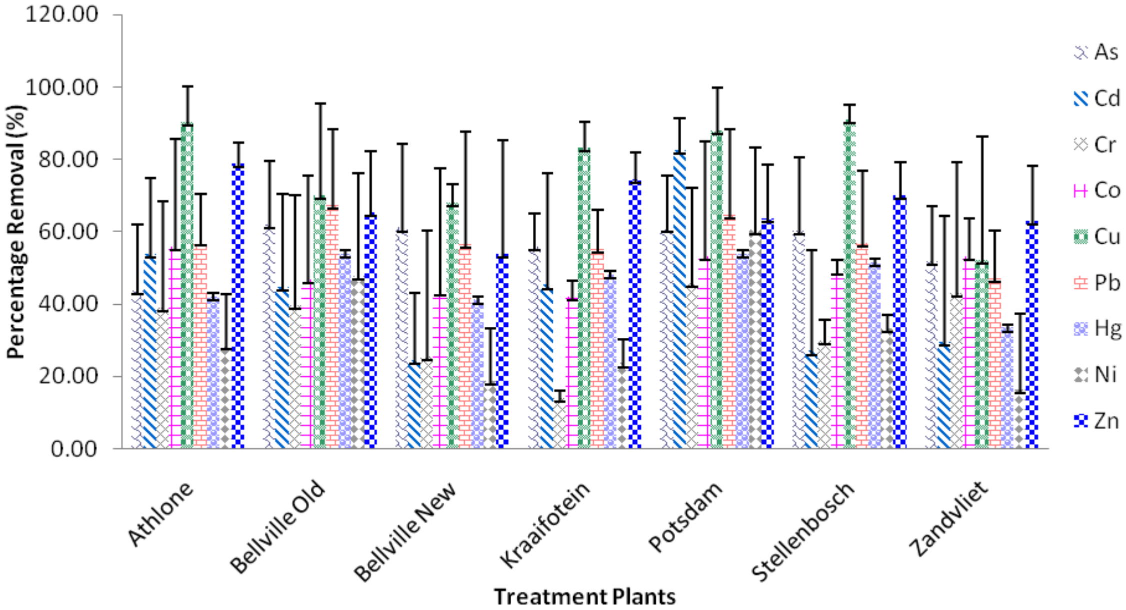


Figure 2. Comparison of annual removal efficiency for trace metals in WWTPs.

while about 35% was taken off the waste stream at the secondary settling tank. The annual distribution pattern of cadmium in the treatment plant and the annual removal efficiency are presented in Figure 3a and Table 3. Based on the removal efficiency, the plant could be rated average for cadmium removal. There was no significant difference in the influent cadmium concentrations in the plant over the study period. The influent concentrations of cadmium at the old Bellville plant varied between 1.53 and 5.52 µgL^{-1}, while the new plant concentrations varied between 1.64 and 3.55 µgL^{-1}. The final effluent concentrations ranged from 1.42 to 2.24 µgL^{-1} and 1.07 to 1.36 µgL^{-1} for the new and old plants, respectively (Table 3). The annual distribution pattern of cadmium in the two plants presented in Figure 3b and c indicated that 18.8% of cadmium concentration was removed at the Bellville old plant primary settling tank, while 28.9 and 25.22% were removed at the secondary settling tanks of the old and new plant, respectively. The annual mean percentage removal was 44.88 and 24.61% for the old and new plants, respectively (Figure 2). For the new plant, with the exception of the summer season, no significant difference in cadmium concentrations occurred over the study period or between the influent and effluent concentration.

The Kraaifontein plant received an influent concentration range of 1.85 to 8.88 µgL^{-1} and released effluent with a concentration range of 1.25 to 2.29 µgL^{-1} (Table 3). The removal efficiency of this treatment plant varied between 7.68 to 74.97% with an annual mean of 45.22% (Figure 2). The annual distribution pattern presented in Figure 3d revealed that 36.2 and 30.1% of total cadmium concentration were removed at primary and secondary settling tanks, respectively. The annual mean removal efficiency showed that the plant was below average for cadmium removal. Cadmium concentration in the influent of the Potsdam plant varied between 8.67 and 17.39 µgL^{-1} with an annual mean of 12.62 µgL^{-1}, while the effluent concentrations varied between 1.33 to 2.85 µgl^{-1} with annual mean of 2.02 µgL^{-1} (Table 3). The distribution of cadmium in the plant (Figure 3e) showed that 45.2 and 36.02% cadmium was removed from the waste stream at the primary and secondary settling tanks, respectively. The annual mean removal efficiency was 82.58% (Figure 2). The high concentration of cadmium in the influent could be due to high industrial effluent received at the plant. There were significant differences in cadmium concentration over the sampling period due to treatment processes during summer. The Stellenbosch plant's cadmium concentrations in the influent ranged from 1.68 to 2.96 µgL^{-1} with annual mean concentration of 2.45 µgL^{-1}, while cadmium concentration in the final effluent ranged from 1.29 to 2.23 µgL^{-1} with an annual mean of 1.65 µgL^{-1} (Table 3). The annual distribution pattern in Stellenbosch presented in Figure 3f shows that about 25% of the cadmium was removed at the primary settling tank, while 4.9% was removed at the secondary settling tank.

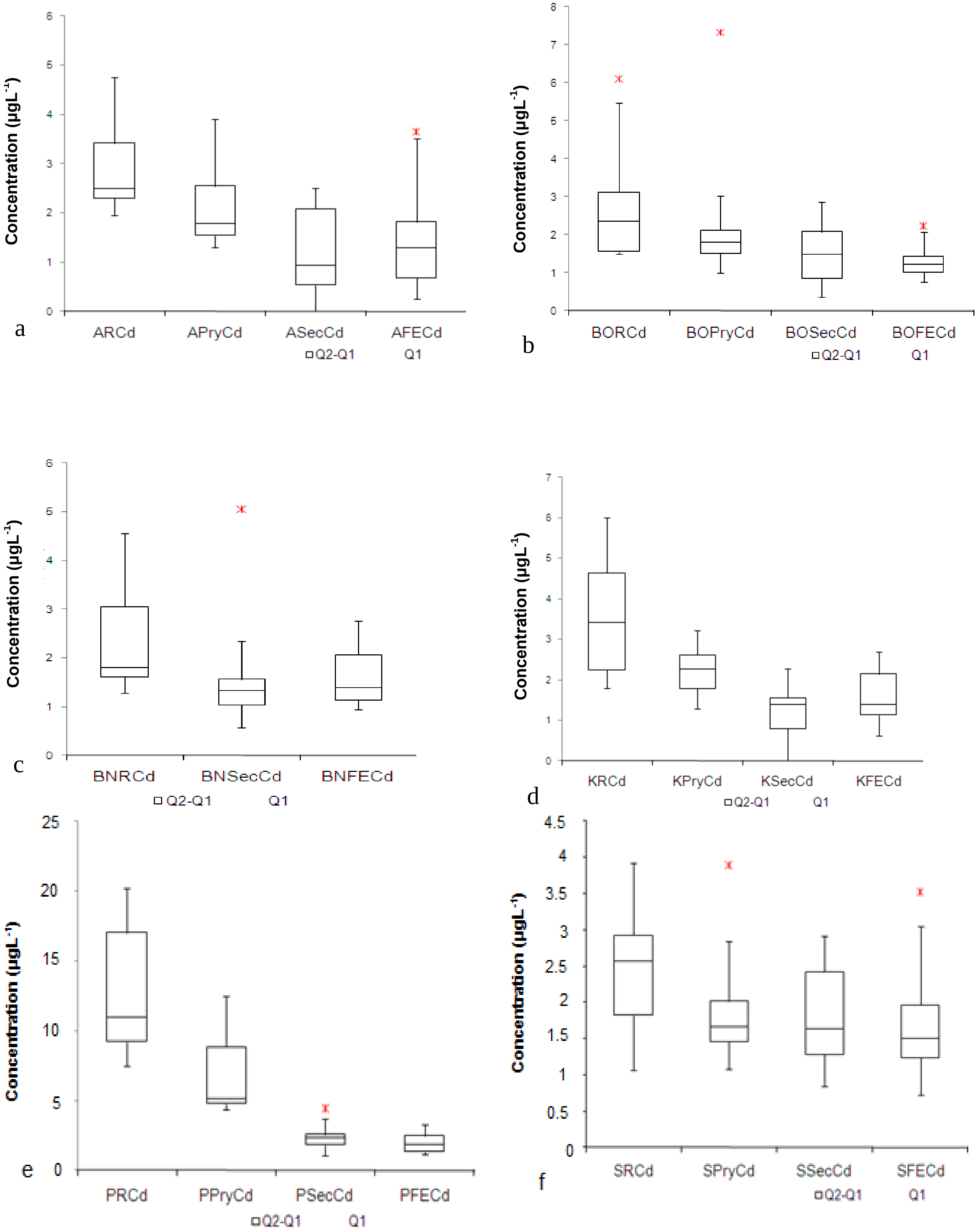
The annual mean removal efficiency was 29.17% (Figure 2). There was no significant difference due to seasonal change. However, there was significant difference due to treatment plant processes during the summer as the plant was constantly breaking down during the summer sampling protocol.

Table 3. Mean concentration (±SD) of Cd in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgl^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (µgL^{-1})				α $_{concentration}$	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	2.94 ± 0.31	1.35 ± 0.04	0.86 ± 0.15	1.01 ± 0.51		65.61
	Autum ’10	3.09 ± 0.69	2.64 ± 1.01	2.06 ± 0.5	1.80 ± 0.13		32.43
	Winter ’10	2.21 ± 1.10	1.86 ± 0.42	1.71 ± 0.76	0.52 ± 0.23		74.97
	Spring ’10	3.38 ± 0.1	2.91 ± 1.16	N/A	2.31 ± 1.27		7.68
	α $_{season}$						
Bellville old	Summer ’10	2.40 ± 0.26	1.74 ± 0.04	1.07 ± 0.15	1.07 ± 0.5		55.44
	Autum ’10	5.52 ± 0.69	4.10 ± 1.01	2.45 ± 0.49	1.36 ± 0.13		41.86
	Winter ’10	1.53 ± 0.24	1.50 ± 0.43	0.69 ± 0.76	1.25 ± 0.24		18.08
	Spring ’10	2.05 ± 0.54	1.97 ± 0.51	1.91 ± 0.38	1.42 ± 0.37		30.59
	α $_{season}$						
Bellville new	Summer ’10	1.64 ± 0.05	NPST	1.33 ± 0.25	1.18 ± 0.17	*	28.16
	Autum ’10	3.55 ± 0.87	NPST	3.36 ± 1.69	2.24 ± 0.23		36.81
	Winter ’10	1.68 ± 0.33	NPST	0.74 ± 0.24	1.64 ± 0.96		2.38
	Spring ’10	2.23 ± 0.98	NPST	1.31 ± 0.18	1.42 ± 0.38		36.11
	α $_{season}$			*			
Kraaifontein	Summer ’10	4.57 ± 0.31	2.69 ± 0.19	N/A	1.56 ± 0.9	*	65.78
	Autum ’10	1.85 ± 0.05	1.54 ± 0.23	1.27 ± 0.24	1.25 ± 0.10		32.43
	Winter ’10	8.88 ± 1.10	6.03 ± 0.47	1.71 ± 0.46	1.28 ± 0.72		74.97
	Spring ’10	2.48 ± 0.1	2.43 ± 0.41	1.65 ± 0.25	2.29 ± 0.49		7.68
	α $_{season}$	*	*				
Potsdam	Summer ’10	17.39± 0.55	4.49 ± 0.24	1.64 ± 0.91	1.33 ± 0.9	*	92.33
	Autum ’10	14.53± 5.10	12.14 ± 0.37	3.08 ± 1.19	2.57 ± 0.59		82.29
	Winter ’10	8.67± 1.62	4.91 ± 0.12	1.97 ± 0.62	1.35 ± 0.18		84.47
	Spring ’10	9.89± 1.35	6.15 ± 1.50	2.44 ± 0.15	2.85 ± 0.53		71.24
	α $_{season}$	*					
Stellenbosch	Summer ’10	2.96 ± 0.46	1.31 ± 0.29	0.96 ± 0.11	1.29 ± 0.36	*	
	Autum ’10	2.54 ± 0.57	1.57 ± 0.26	2.46 ± 0.62	2.23 ± 1.16		12.34
	Winter ’10	1.68 ± 0.52	2.33 ± 1.35	1.61 ± 0.31	1.61 ± 1.16		4.17
	Spring ’10	2.62 ± 1.33	2.42 ± 0.58	2.13 ± 0.58	1.47 ± 0.51		43.86
	α $_{season}$						
Zandvliet	Summer ’10	2.32 ± 0.23	NPST	0.84 ± 0.20	1.17 ±0.15		49.62
	Autum ’10	3.10 ± 0.54	NPST	2.17 ± 0.59	2.53 ± 0.43		18.39
	Winter ’10	1.07 ± 0.17	NPST	1.05 ± 0.45	0.53 ± 0.08		50.78
	Spring ’10	3.22 ± 0.38	NPST	1.96 ± 0.45	1.95 ± 0.65		39.62
	α $_{season}$						

α $_{concentration}$, Significant difference between the stages of WWTPs; α $_{season}$, significant difference of seasonal differences; *, difference is significant at α = 0.05; NA, not analysed; NPST, no primary settling tank.

The Zandvliet plant’s influent cadmium concentrations were in the range of 1.07 to 3.10 µgL^{-1} with an annual mean influent concentration of 2.43 µgL^{-1}. The final effluent concentration ranged from 0.53 to 2.53 µgL^{-1} (Table 3). The annual distribution pattern for cadmium in the treatment plant revealed that 34 and 7% of cadmium in the wastewater was removed into primary and secondary sludge, respectively (Figure 3g). The annual mean removal efficiency for the plant shows that less than 40% of total cadmium concentration was removed


a
Concentration (µgL⁻¹)
0
1
2
3
4
5
6
ARCd
APryCd
ASecCd
AFECd
Q2-Q1
Q1
b
Concentration (µgL⁻¹)
0
1
2
3
4
5
6
7
8
BORCd
BOPryCd
BOSecCd
BOFECd
Q2-Q1
Q1
c
Concentration (µgL⁻¹)
0
1
2
3
4
5
6
BNRCd
BNSecCd
BNFECd
Q2-Q1
Q1
d
Concentration (µgL⁻¹)
0
1
2
3
4
5
6
7
KRCd
KPryCd
KSecCd
KFECd
Q2-Q1
Q1
e
Concentration (µgL⁻¹)
0
5
10
15
20
25
PRCd
PPryCd
PSecCd
PFECd
Q2-Q1
Q1
f
Concentration (µgL⁻¹)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
SRCd
SPryCd
SSecCd
SFECd
Q2-Q1
Q1

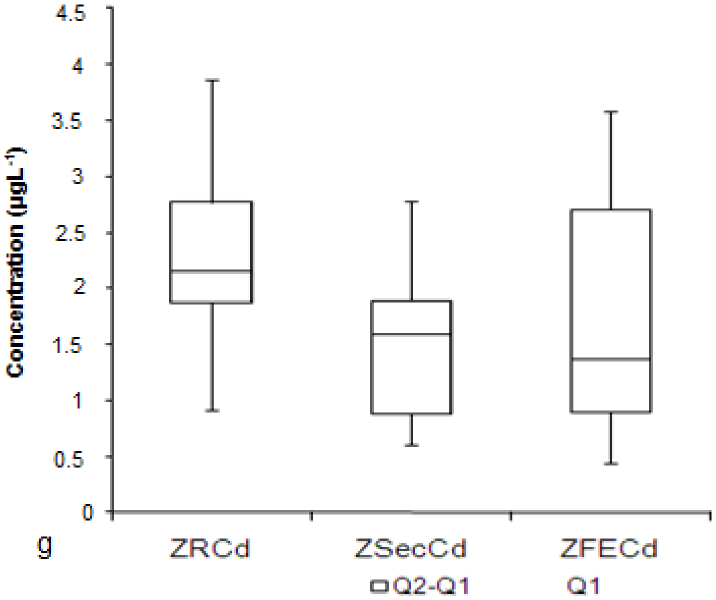


Figure 3. Box and whisker plot for annual spread of Cd concentration in WWTPs. a) Athlone b) Bellville old c) Bellville new d) Kraaifontein e) Potsdam f) Stellenbosch g) Zandvliet.

from the waste stream (Figure 2).

Cobalt

Cobalt influent concentrations into the Athlone plant ranged from 3.29 to 11.65 μgL^{-1}, while the final effluent concentration varied between 1.12 and 2.62 μgL^{-1} (Table 4). The annual distribution pattern of cobalt in the plant as depicted in Figure 4a showed that only 9.2% of cobalt concentration into the plant was removed at the primary settling tank while 77.5% removal took place at the secondary settling tank. The annual mean removal efficiency of the plant was 55.98% (Figure 2). There was significant difference in the seasonal concentration of cobalt received at the plant, also, significant difference due to treatment processes was noticeable during the summer season. The old and new Bellville plants received influent with 3.30 to 6.29 μgL^{-1} and 3.44 to 13.86 μgL^{-1} and released effluent containing between 1.13 to 3.23 μgL^{-1} and 1.54 to 3.23 μgL^{-1} of cobalt, respectively. The annual distribution patterns of cobalt in the two Bellville plants are presented in Figure 4b and c. 32.62% of the total concentration into the old plant was removed at the primary settling tank with a corresponding concentration of about 11% removed at the secondary tank. The new plant using the UCT system with only a secondary sedimentation tank removed about 55%. The mean annual removal efficiency was 46.74 and 43.5% for old and new plants, respectively (Figure 2). No significant difference was observed for the seasonal influent concentration at old plant. However, a significant difference due to the plant treatment processes was noticeable during the summer season. For the new plant, significant difference due to plant treatment processes and season was recorded. The Kraaifontein treatment plant received influent cobalt concentrations ranging between 0.34 and 3.98 μgL^{-1} and the final effluent concentration ranged from 0.18 to 2.14 μgL^{-1} (Table 4). The annual Co distribution pattern and removal efficiency are presented in Figure 4d. The distribution pattern shows that 27.45% was eliminated through the primary sedimentation tank while secondary sedimentation tank accounted for 32.35%. The annual mean removal efficiency of the plant was 42.07%. There was significant difference in the plant treatment processes.

The concentration range between 2.23 and 5.02 μgL^{-1} was received in the influent during the sampling seasons at the Potsdam treatment plant. The effluent concentration varied between 0.65 and 4.73 μgL^{-1} (Table 4). The annual mean influent concentration was 3.68 μgL^{-1} while the annual mean effluent concentration was 1.94 μgL^{-1}. The distribution pattern of cobalt in the plant (Figure 4e) indicated that 20.65% of total annual concentration was removed at the primary settling tank while about 17% was trapped into secondary sludge through the secondary sedimentation tank. The annual mean removal efficiency of the plant was 53.19%. A significant difference due to season and plant treatment processes was observed.

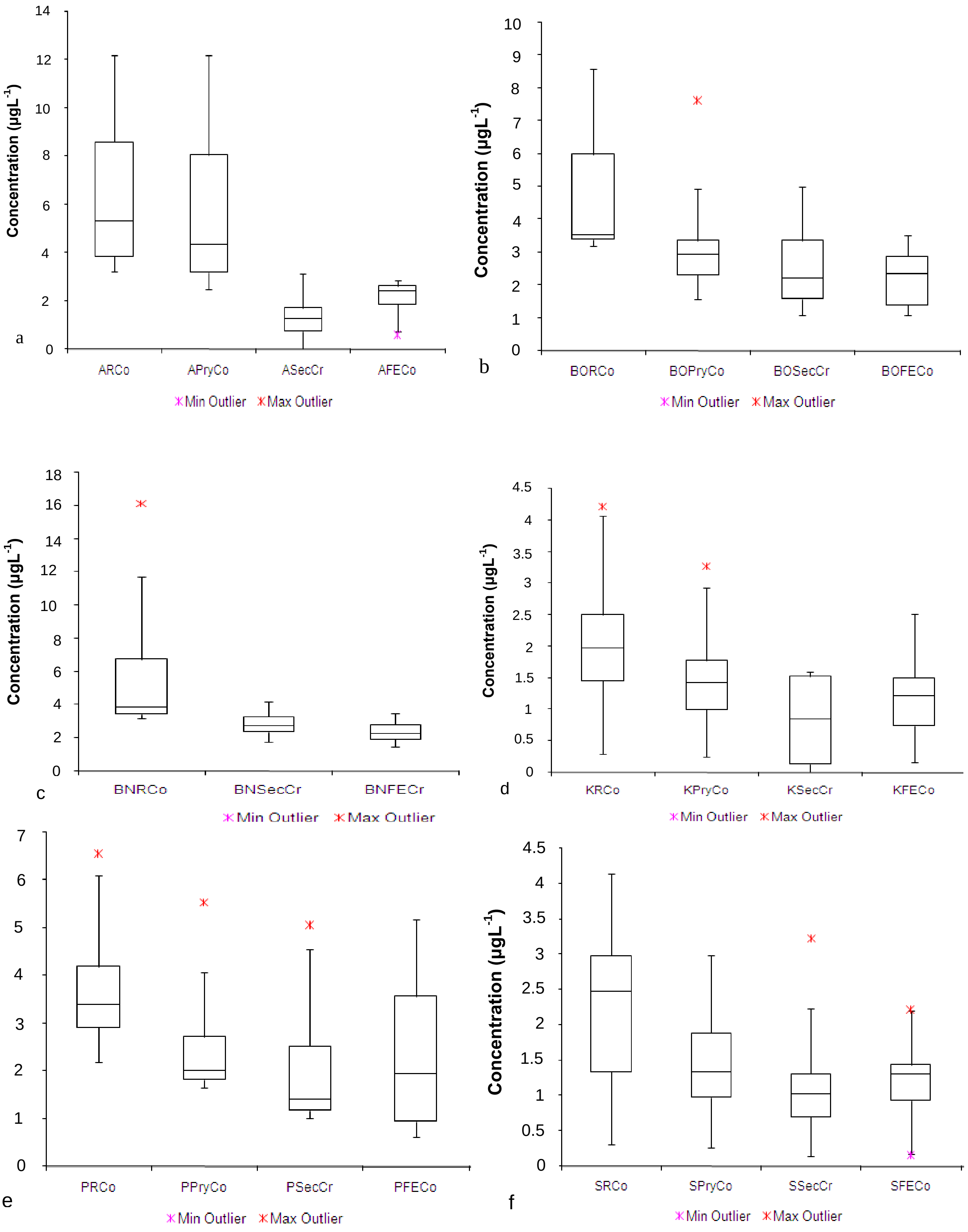
Stellenbosch and Zandvliet treatment plants influent concentration ranged from 0.35 to 3.17 μgL^{-1} and 0.34 to

Table 4. Mean concentration (±SD) of Co in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgl^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (µg l^{-1})				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	11.7 ± 0.49	11.9 ± 0.25	1.4 ± 0.07	1.9 ± 1.12	*	84.01
	Autum ’10	7.06 ± 0.75	5.75 ± 0.99	1.13 ± 0.14	1.52 ± 0.72		78.53
	Winter ’10	4.18 ± 0.19	3.06 ± 0.50	2.92 ± 0.28	2.62 ± 0.10		37.27
	Spring ’10	3.29 ± 0.11	3.26 ± 0.41	N/A	2.50 ± 0.38		24.10
	α_{season}		*	*			
Bellville old	Summer ’10	3.50 ± 0.09	2.59 ± 0.15	1.72 ± 0.2	1.71 ± 0.3	*	51.04
	Autum ’10	6.29 ± 0.38	1.66 ± 0.15	1.41 ± 0.3	1.13 ± 0.1		82.03
	Winter ’10	3.30 ± 0.11	3.1 7 ± 0.07	2.89 ± 0.3	2.90 ± 0.2		12.22
	Spring ’10	5.54 ± 2.72	5.14 ± 2.2	4.54 ± 0.4	3.23 ± 0.4		41.68
	α_{season}						
Bellville new	Summer ’10	3.44 ± 0.12	NPST	3.43 ± 0.23	2.15 ± 0.08	*	37.55
	Autum ’10	13.86 ± 1.97	NPST	1.91 ± 0.13	1.54 ± 0.05	*	88.89
	Winter ’10	4.51 ± 0.47	NPST	2.81 ± 0.10	2.66 ± 0.34		41.05
	Spring ’10	3.46 ± 0.32	NPST	3.08 ± 0.97	3.23 ± 0.41		6.50
	α_{season}		*				
Kraaifontein	Summer ’10	1.94 ± 0.15	1.33 ± 0.09	N/A	1.23 ± 0.30	*	36.94
	Autum ’10	1.91 ± 0.08	1.53 ± 0.06	1.53 ± 0.04	1.15 ± 0.12		39.63
	Winter ’10	0.34 ± 0.04	0.28 ± 0.03	0.19 ± 0.01	0.18 ± 0.03		45.48
	Spring ’10	3.98 ± 0.27	2.78 ± 0.45	1.55 ± 0.04	2.14 ± 0.55		46.21
	α_{season}		*	*			
Potsdam	Summer ’10	2.23 ± 0.05	1.75 ± 0.07	1.19 ± 0.08	0.65 ± 0.04		70.62
	Autum ’10	3.31 ± 0.15	2.14 ± 0.15	1.62 ± 0.37	1.06 ± 0.03		67.94
	Winter ’10	4.16 ± 0.09	3.07 ± 0.10	1.94 ± 0.50	1.31 ± 0.24	*	68.43
	Spring ’10	5.02 ± 1.62	4.73 ± 0.75	4.47 ± 0.55	4.73 ± 0.38		5.79
	α_{season}		*				
Stellenbosch	Summer ’10	2.45 ± 0.13	1.29 ± 0.09	0.95 ± 0.08	1.27 ± 0.07	*	48.18
	Autum ’10	2.77 ± 1.27	1.48 ± 0.26	1.17 ± 0.13	1.34 ± 0.13		51.74
	Winter ’10	0.35 ± 0.04	0.28 ± 0.01	0.16 ± 0.01	0.17 ± 0.00		51.36
	Spring ’10	3.17 ± 0.26	2.76 ± 0.30	2.31 ± 0.90	1.76 ± 0.39		44.66
	α_{season}		*	*		*	
Zandvliet	Summer ’10	1.69 ± 0.36	NPST	1.66 ± 0.25	0.55 ± 0.07	*	67.59
	Autum ’10	0.89 ± 0.09	NPST	0.52 ± 0.07	0.44 ± 0.02		50.75
	Winter ’10	0.34 ± 0.02	NPST	0.22 ± 0.07	0.17 ± 0.0		51.36
	Spring ’10	3.23 ± 1.4	NPST	2.91 ± 0.4	1.86 ± 1.67		42.30
	α_{season}		*				

$\alpha_{concentration}$ denotes the significance of difference between the stages of WWTPs; α_{season} denotes the significance of difference of seasonal differences; *: difference is significant at α = 0.05; NA = not analysed; NPST = no primary settling tank.

3.23 µgL^{-1}, respectively (Table 4). The final effluent concentration ranged from 0.17 to 176 µgL^{-1} for Stellenbosch and 0.17 to 1.86 µgL^{-1} for Zandvliet. The annual distribution spread for the two plants are presented in


a
Concentration (μgL-1)
0
2
4
6
8
10
12
14
ARCo
APryCo
ASecCr
AFECo
Min Outlier
Max Outlier
b
Concentration (μgL-1)
0
1
2
3
4
5
6
7
8
9
10
BORCo
BOPryCo
BOSecCr
BOFECo
Min Outlier
Max Outlier
c
Concentration (μgL-1)
0
2
4
6
8
10
12
14
16
18
BNRCo
BNSecCr
BNFECr
Min Outlier
Max Outlier
d
Concentration (μgL-1)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
KRCo
KPryCo
KSecCr
KFECo
Min Outlier
Max Outlier
e
0
1
2
3
4
5
6
7
PRCo
PPryCo
PSecCr
PFECo
Min Outlier
Max Outlier
f
Concentration (μgL-1)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
SRCo
SPryCo
SSecCr
SFECo
Min Outlier
Max Outlier

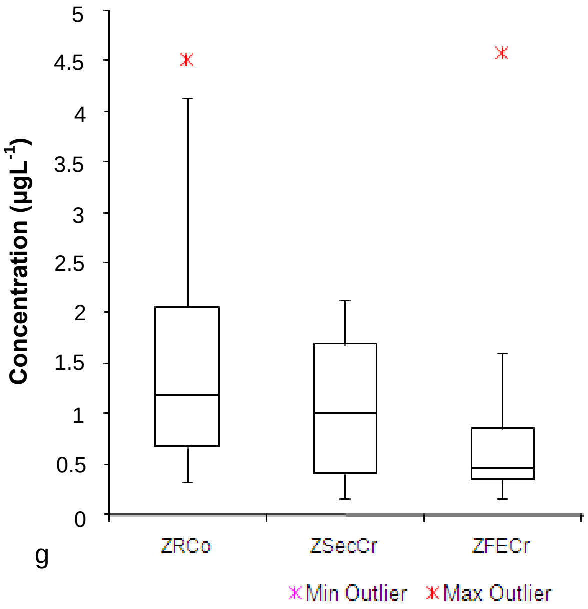


Figure 4. Box and whisker plot for annual Co concentration in WWTPs. a) Athlone b) Bellville old c) Bellville new d) Kraaifontein e) Potsdam f) Stellenbosch g) Zandvliet.

Figure 4f and g. The annual mean removal efficiency for the plants was 48.99% for Stellenbosch and 53.08% for settling tank of Stellenbosch, while 13.69 and 13.63% were removed at the secondary tanks of Stellenbosch and Zandvliet, respectively. Significant difference due to season and treatment process was observed for the plant over the study period.

Chromium

Chromium concentration in the influent waste into Athlone plant varied between 116.96 and 199.53 μgL^{-1} with an annual mean concentration of 144.82 μgL^{-1} (Table 5). The final effluent concentration ranged between 25.15 and 132.61 μgl^{-1} with an annual effluent mean concentration of 86.32 μgL^{-1}. The annual distribution pattern of chromium in the plant revealed that 37.04 and 19.62% were removed at the primary and secondary settling tanks (Figure 5a). The annual mean removal efficiency of the treatment plant fell below 40% (Figure 2). Significant difference due to treatment process was noticeable during summer season. The influent concentration of chromium into the Bellville old plant varied between 108.36 and 207.68 μgL^{-1}, while the new plant received between 106.4 and 159.61 μgL^{-1}. The effluent concentration ranged between 26.18 to 135.8 μgL^{-1} for old plant and from 30.25 to 153.44 μgL^{-1} for the new plant (Table 5). The distribution pattern (Figure 5b and c) showed that chromium was poorly removed from the waste effluent from the two plants as less than 26 and Zandvliet (Figure 2). The annual distribution of Co revealed that 33% was removed at the primary 40% were removed from old and new plants, respectively (Figure 2). There was a significant difference (P<0.05) during autumn due to plant treatment processes. The total influent concentration into the Kraaifontein plant ranged from 31.15 to 154.62 μgL^{-1} with an annual mean of 111.01 μgL^{-1} and the final effluent concentration varied between 26.14 and 130.5 μgl^{-1} with an annual mean effluent of 96.03 μgL^{-1} (Table 5). The percentage removal of Cr was below 20% over the study. The distribution pattern of total Cr in the plant presented in Figure 5d shows that 13.9% and about 4% was removed through primary and secondary settling tanks. The annual mean efficiency of the plant is presented in Figure 5. There was significant difference in the influent concentration due to seasonal change and plant treatment process.

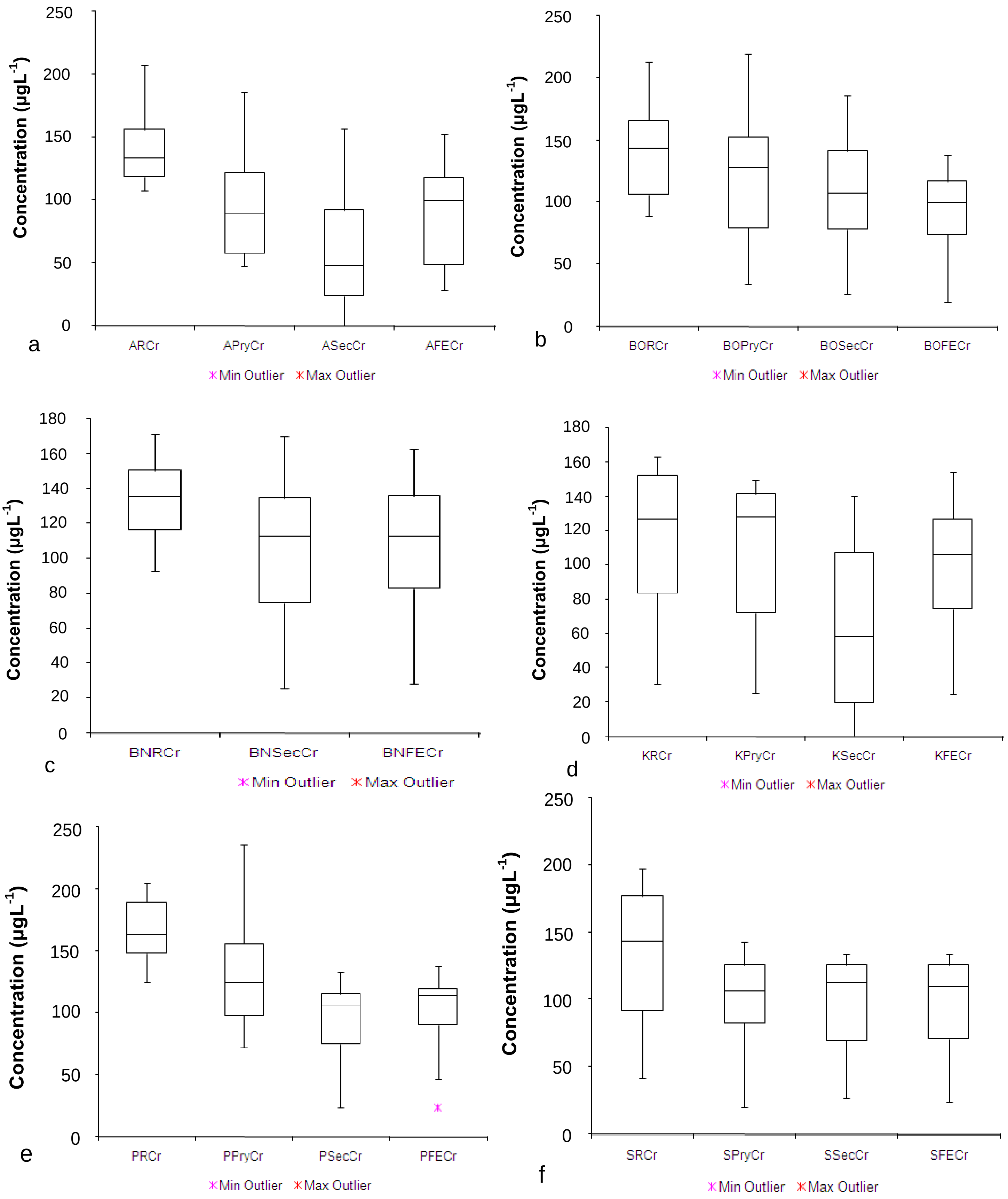
The Potsdam treatment plant received a concentration range of 146.94 to 223 μgL^{-1} in the influent and concentration in the effluent released ranged from 25.47 to 127.78 μgL^{-1} (Table 5). The annual mean concentration in the influent was 174.67 μgL^{-1}, while the annual mean concentration of chromium in the final effluent was 95.79 μgL^{-1}. The distribution pattern in the plant is presented in Figure 5e. The plant distribution pattern for chromium showed that about 29 and 25% of chromium in wastewater was removed at the primary and secondary settling tanks, respectively. The annual mean removal efficiency of the plant is presented in Figure 2. There was significant difference due to treatment process during summer season between influent and effluent

Table 5. Mean concentration (±SD) of Cr in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgl^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (µgL^{-1})				α concentration	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	135.8 ± 3.6	57.8 ± 2.4	35.9 ± 3.56	29.2 ± 1.2	*	78.54
	Autum ’10	126.9 ± 14.7	56.5 ± 15.4	65.71± 9.3	80.3 ± 36.9		36.80
	Winter ’10	199.5 ± 7.2	137 ± 30.0	149.3 ± 7.5	132.6 ± 24.0		33.54
	Spring ’10	116.9 ± 15.1	113.8 ± 7.8	N/A	108.2 ± 12.8		7.48
	α season						
Bellville old	Summer ’10	207.68 ± 5.9	190.6 ± 26.1	161.3 ± 21.5	95.8 ± 5.3		53.89
	Autum ’10	108.5 ± 9.1	39.6 ± 4.4	35.47 ± 10.7	26.2 ± 5.5	*	75.87
	Winter ’10	152.1 ± 1.6	146.5 ± 1.3	132.0 ± 9.8	131.9 ± 9.3		42.86
	Spring ’10	108.36 ± 24.5	106.4 ± 9.2	100.85 ± 2.4	112.8 ± 1.7		15.70
	α season						
Bellville new	Summer ’10	159.6 ± 12.7	NPST	157.9 ± 11.8	153.4 ± 8.0		3.86
	Autum ’10	134.2 ± 17.2	NPST	29.09 ± 2.6	30.25 ± 1.9	*	77.47
	Winter ’10	138.99 ± 13.0	NPST	127.1 ± 3.2	123.3 ± 11.7		11.33
	Spring ’10	106.4 ± 4.3	NPST	97.6 ± 6.4	96.6 ± 8.3		9.19
	α season		*				
Kraaifontein	Summer ’10	154.62 ± 8.1	144.2± 7.7	N/A	135.8 ± 17.5	*	12.17
	Autum ’10	31.15 ± 0.9	28.04± 2.4	26.94 ± 0.2	26.14 ± 0.9		16.06
	Winter ’10	154.1 ± 3.9	141.6± 1.9	134.0 ± 5.5	130.5 ± 9.5		15.36
	Spring ’10	104.2 ± 2.9	100.2± 18.4	95.72 ± 5.6	91.73 ±1.4		11.95
	α season		*	*		*	*
Potsdam	Summer ’10	177.32 ±16.3	114.54 ± 9.72	99.9 ± 9.9	99.9 ± 9.9	*	33.96
	Autum ’10	150.81± 4.3	77.76 ± 4.9	26.31 ± 3.2	25.47 ± 1.9		83.11
	Winter ’10	223.62 ± 8.2	198.85 ± 20.6	129.5 ± 5.8	127.8 ± 9.0		42.86
	Spring ’10	146.94 ± 21.3	133.32 ± 7.9	108.5 ± 3.7	112.8 ± 1.7		23.22
	α season						
Stellenbosch	Summer ’10	172.40 ± 11.2	120.7 ± 2.9	116.36 ± 7.7	126.52 ± 2.50	*	26.6
	Autum ’10	44.58 ± 3.7	35.9 ± 16.5	30.5 ± 5.1	28 ± 4.4	*	36.5
	Winter ’10	187.89 ± 12.1	138.9 ± 3.6	132.4 ± 1.61	126.6 ± 6.9		32.6
	Spring ’10	116.5 ± 9.1	93.7 ± 1.7^{g}	98.3 ± 23.1	89.1 ± 9.6		23.5
	α season		*	*		*	*
Zandvliet	Summer ’10	98.4 ± 7.8	NPST	68.0 ± 7.6	24.6 ± 3.3	*	74.92
	Autum ’10	87.24 ± 3.9	NPST	23.9 ± 0.5	23.8 ± 0.5		72.72
	Winter ’10	136.62 ± 2.6	NPST	133.5 ± 2.7	130.86 ± 3.9		4.22
	Spring ’10	105.5 ± 21.6	NPST	98.97 ± 5.1	89.1 ± 9.6		20.13
	α season					*	

α concentration, Significant difference between the stages of WWTPs; α season, significant difference of seasonal differences; *, difference is significant at α = 0.05; NA, not analysed; NPST, no primary settling tank.

concentration. The influent chromium concentrations at the Stellenbosch treatment plant varied between 44.58 and 187.89 µgL^{-1}, while the final effluent concentration ranged from 28.31 to 126.63 µgL^{-1} (Table 5). The annual spread for chromium is presented in Figure 5f while the annual mean percentage removal efficiency of the plant was below 40%. Based on this efficiency, the plant could be rated ineffective in chromium removal. Though the


a
Concentration (µgL-1)
0
50
100
150
200
250
ARCr
APryCr
ASecCr
AFECr
Min Outlier
Max Outlier
b
Concentration (µgL-1)
0
50
100
150
200
250
BORCr
BOPryCr
BOSecCr
BOFECr
Min Outlier
Max Outlier
c
Concentration (µgL-1)
0
20
40
60
80
100
120
140
160
180
BNRCr
BNSecCr
BNFECr
Min Outlier
Max Outlier
d
Concentration (µgL-1)
0
20
40
60
80
100
120
140
160
180
KRCr
KPryCr
KSecCr
KFECr
Min Outlier
Max Outlier
e
Concentration (µgL-1)
0
50
100
150
200
250
PRCr
PPryCr
PSecCr
PFECr
Min Outlier
Max Outlier
f
Concentration (µgL-1)
0
50
100
150
200
250
SRCr
SPryCr
SSecCr
SFECr
Min Outlier
Max Outlier

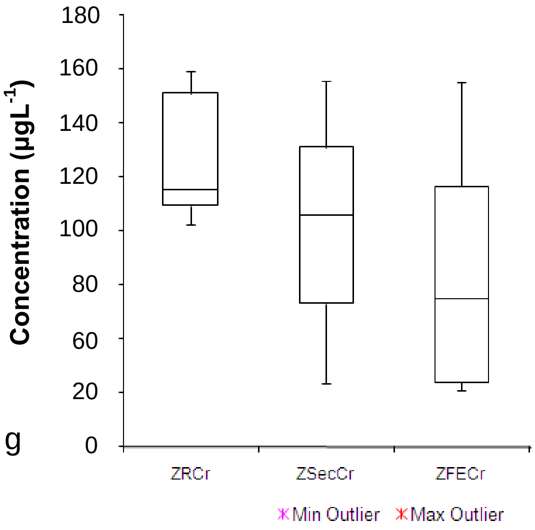


Figure 5. Box and whisker plot for annual Cr concentration in WWTPs: a, Athlone; b, Bellville old WWTP; c, Bellville new; d, Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet.

trapped in the secondary sludge. This was not the case for the new plant as it operates on UCT. 48.41% of the total copper was retained in the secondary sludge, while the balance was assumed to be present in the re-circulated activated sludge. The annual mean percentage removal efficiencies of the plants were 70.02 and 68.10% for old and new plants, respectively (Figure 2). With the exception of the spring season in the old plant, there was significant difference in the influent concentration and in concentration due to plant treatment process for all the seasons under study for the two plants.

Concentration of copper in wastewater received at the Kraaifontein varied between 96.56 and 135.76 µgL^{-1}, while the final effluent concentration ranged from 7.66 to 25.16 µgL^{-1} (Table 6). The annual distribution for copper in the plant is depicted in Figure 6d. The annual distribution pattern shows that 45.36% of the total copper concentration was removed at the primary sedimentation tank, while 35.15% was removed at the secondary settling tank which is often returned to the activated sludge. The annual mean removal efficiency was 83.28% (Figure 2). No significant difference in influent concentration was observed due to seasonal change but there was significant difference due to plant treatment process on influent concentration over the seasons. The Potsdam wastewater treatment plant exhibited significant difference in both the influent copper concentration (seasonal) and due to plant treatment process on the influent concentration. The plant copper concentration was the second highest after the Athlone plant (the second largest plant in Cape Town). The annual mean influent concentration was 484.04 µgL^{-1} while the annual mean final effluent was 30.25 µgL^{-1}. The seasonal variation is shown in Table 6 and the annual distribution in the plant is presented in Figure 6e. The plant distribution pattern showed that 50.19% of total influent concentration was removed at the primary settling tank while about 45% was removed at the secondary settling tank into their respective sludge. The annual removal efficiency was 87.99% (Figure 2).

Stellenbosch and Zandvliet plants received annual mean concentration of 221.57 and 54.33 µgL^{-1}, respectively. The seasonal influent and effluent concentrations in the two plants are presented in Table 6. The annual mean removal efficiencies were 91 and 55.26% for Stellenbosch and Zandvliet, respectively (Figure 6). The annual distribution pattern in the plants (Figure 6f and g) shows that 46.3 and 40.66% of total copper concentration was removed at the Stellenbosch primary and secondary sedimentation tanks while 58.1% was taken at the Zandvliet secondary tank. For the two plants, no significant difference due to seasonal change was noticeable; however, for Stellenbosch plant, there was significant difference between the influent and effluent concentration due to treatment process. Significant difference in Zandvliet was during summer and winter sampling seasons.

Lead

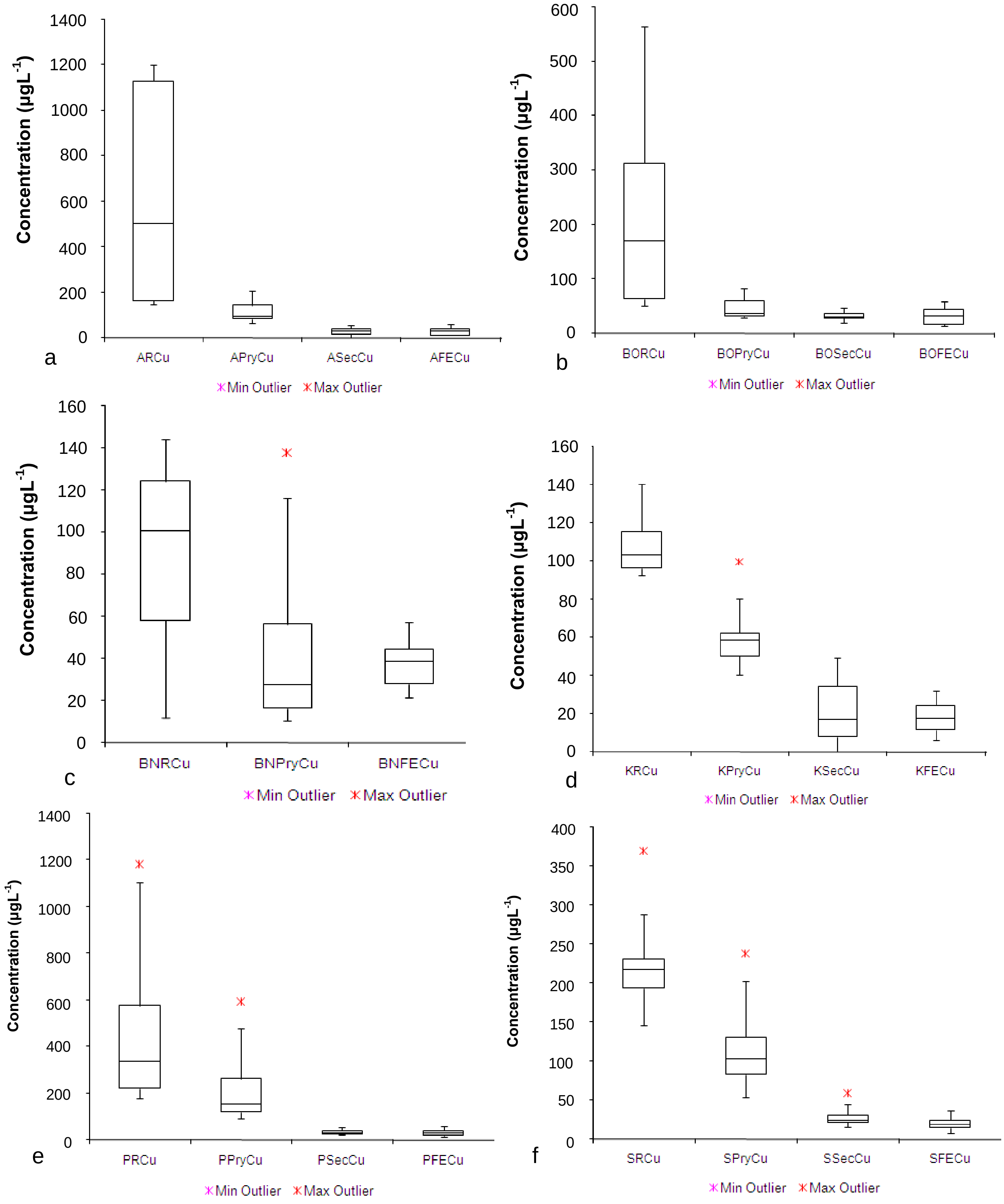
The Athlone lead influent concentration ranged from 49.61 to 81.89 µgL^{-1} and 20.40 to 30.31 µgL^{-1} in the final effluent (Table 7). Lead removal in the influent waste was above average for all the seasons except for the spring. Influent annual mean was 64.46% while annual mean in final effluent was 26.57 µgL^{-1}. The annual distribution pattern of Pb in the plant is presented in Figure 7a.

Table 6. Mean concentration (±SD) of Cu in the influent, primary, secondary and final effluent of WWTPs during the different seasons (μgL^{-1}) with associated total removal efficiency.

WWTP	**Season**	**Concentration (μgL^{-1})**				**$\alpha_{\text{concentration}}$**	**Removal efficiency**
		Influent	**Primary effluent**	**Secondary effluent**	**Final effluent**		
Athlone	Summer ’10	1189.3 ± 11.1	195.7 ± 9.5	49.3 ± 6.5	20.6 ± 9.5	*	98.27
	Autum ’10	986.9 ± 149.4	108.3 ± 18.0	24.61 ± 2.8	48.1 ± 9.9	*	95.12
	Winter ’10	154.34 ± 10.6	81.15 ± 17.9	36.2 ± 1.9	12.86 ± 0.9		91.67
	Spring ’10	172.4 ± 15.5	81.15 ± 17.9	N/A	40.9 ± 15.1	*	76.29
	α_{season}	*	*				
Bellville old	Summer ’10	267.5 ± 12.3	76.6 ± 6.0	32.8 ± 3.8	55.4 ± 3.6	*	79.29
	Autum ’10	464.9 ± 86.1	31.6 ± 1.5	29.5 ± 8.5	16.9 ± 0.9	*	96.36
	Winter ’10	71.1 ± 10.5	43.6 ± 12.3	41.6 ± 8.7	22.3 ± 7.3	*	68.68
	Spring ’10	55.74 ± 6.7	38.1 ± 10.3	28.7 ± 5.3	35.8 ± 2.9		35.77
	α_{season}	*					
Bellville new	Summer ’10	139.26 ± 7.9	NPST	125.9 ± 11.5	53.9 ± 5.2	*	61.2
	Autum ’10	112.7 ± 10.3	NPST	31.9 ± 6.1	30.8 ± 6.3	*	72.6
	Winter ’10	87.2 ± 15.0	NPST	28.7 ± 9.1	28.7 ± 9.1	*	67.1
	Spring ’10	40.5 ± 5.1	NPST	15.7 ± 1.9	11.6 ± 2.9	*	71.5
	α_{season}	*					
Kraaifontein	Summer ’10	104.4 ± 6.6	61.1 ± 1.7	N/A	17.3 ± 0.3	*	83.4
	Autum ’10	98.3 ± 6.3	73.3 ± 22.9	40.5 ± 8.3	25.16 ± 4.2	*	74.4
	Winter ’10	135.76 ± 4.2	56.8 ± 8.5	31.5 ± 13.6	22.8 ± 9.9	*	83.2
	Spring ’10	96.56 ± 4.5	46.7 ± 5.6	12.8 ± 2.7	7.66 ± 1.9	*	92.1
	α_{season}						
Potsdam	Summer ’10	228.7 ± 11.6	94.6 ± 2.4	22.1 ± 1.0	17.3 ± 4.8	*	92.4
	Autum ’10	1181.9 ± 5.2	567.4 ± 37.5	37.5 ± 11.1	23.0 ± 8.4	*	98.1
	Winter ’10	367.9 ± 11.9	162.7 ± 11.9	34.5 ±12.8	34.9 ± 12.9	*	90.5
	Spring ’10	157.6 ± 75.6	139.7 ± 12.6	41.5 ± 10.8	45.7 ± 10.7	*	70.9
	α_{season}	*	*				
Stellenbosch	Summer ’10	190.0 ± 8.3	101 ± 4.3	25.2 ± 2.9	18.1 ± 0.9	*	90.5
	Autum ’10	244.9 ± 114.1	54.9 ± 1.4	49.0 ± 10.3	33.6 ± 3.8	*	86.3
	Winter ’10	236.7 ± 17.4	218.6 ± 20.2	19.3 ± 5.0	20.6 ± 3.7	*	91.3
	Spring ’10	214.7 ± 17.6	101.9 ± 8.6	22.0 ± 1.9	8.7 ± 0.3	*	95.9
	α_{season}						
Zandvliet	Summer ’10	95.3 ± 4.3	NPST	13.1 ± 0.7	12.7 ± 1.9	*	86.71
	Autum ’10	38.1 ± 3.9	NPST	34.1 ± 3.7	32.1 ± 1.6		15.83
	Winter ’10	62.9 ± 3.2	NPST	24.3 ± 9.1	15.9 ± 7.1	*	74.76
	Spring ’10	21.0 ± 5.7	NPST	19.6 ± 2.0	14.4 ± 1.0		31.75
	α_{season}						

$\alpha_{\text{concentration}}$, Significant difference between the stages of WWTPs; α_{season}, significant difference of seasonal differences; *, difference is significant at α = 0.05; NA, not analysed; NPST, no primary settling tank.

47.07% of total Pb conecntration was removed at the primary settling tank into the primary sludge, while about 22% was trapped into the secondary sludge through the secondary sedimentation tank. The annual mean removal


Concentration (μgL^{-1})
1400
1200
1000
800
600
400
200
0
ARCu
APryCu
ASecCu
AFECu
a
Min Outlier
Max Outlier
Concentration (μgL^{-1})
600
500
400
300
200
100
0
BORCu
BOPryCu
BOSecCu
BOFECu
b
Min Outlier
Max Outlier
Concentration (μgL^{-1})
160
140
120
100
80
60
40
20
0
BNRCu
BNPryCu
BNFECu
c
Min Outlier
Max Outlier
Concentration (μgL^{-1})
160
140
120
100
80
60
40
20
0
KRCu
KPryCu
KSecCu
KFECu
d
Min Outlier
Max Outlier
Concentration (μgL^{-1})
1400
1200
1000
800
600
400
200
0
PRCu
PPryCu
PSecCu
PFECu
e
Min Outlier
Max Outlier
Concentration (μgL^{-1})
400
350
300
250
200
150
100
50
0
SRCu
SPryCu
SSecCu
SFECu
f
Min Outlier
Max Outlier

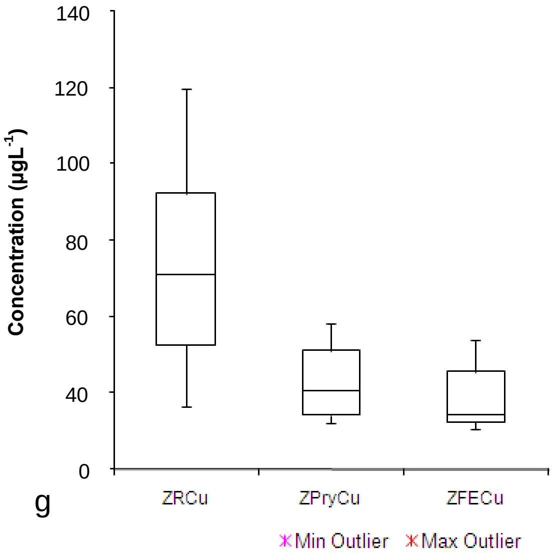


Figure 6. Box and whisker plot for annual Cu concentration in WWTPs. A, Athlone; b, Bellville old; c, Bellville new; d, Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet WWTP.

efficiency of the plant was 57.19% (Figure 2). There was no significant difference due to influent concentration over the study period, but there was significant difference during the summer sampling season due to plant treatment process between the influent and effluent concentration. The lead concentrations into old Bellville plant ranged between 29.88 and 138.35 µgL^{-1} with annual mean of 86.32 µgL^{-1}, while the effluent concentration varied between 15.03 to 37.29 µgL^{-1} with annual mean of 22.84 µgL^{-1} (Table 7). The seasonal removal efficiency ranged from 36.45 to 84.23%. The annual spread of the Pb revealed that 58% of total annual concentration was removed at the primary settling tank and about 20% was removed at the secondary sedimentation tank. The annual removal efficiency of the plant was 67.30% (Figure 2). For the new plant, influent concentration ranged from 23.66 to 282.59 µgL^{-1} with annual mean of 102.20 µgL^{-1} (Table 7). The final effluent concentration ranged between 18.99 and 20.94 µgL^{-1}, while about 77.29% of total influx was trapped into the secondary sludge (Figure 7). The annual mean removal efficiency of the plant was 57% (Figure 2). There was seasonal significant difference due to influent concentration into the two plants. However, significant difference was only observed during summer for old plant and during summer and winter for the new plant due to the plants treatment processes.

Concentrations of Pb into Kraaifontein ranged from 31.5 to 78.6 µgL^{-1} with a final effluent concentration range of 9.49 to 38.66 µgL^{-1} (Table 7). The annual distribution pattern of Pb in the plant is presented in Figure 7d. 42.69% of Pb was removed through the primary sludge, while 23.45% was eliminated in the waste stream through sludge re-circulation. The annual plant removal efficiency was 55% (Figure 2). There was significant difference during the summer due to plant treatment process. There was no significant difference in the influent concentration but there was significant difference between the influent and effluent concentration due to plant treatment processes. The Potsdam WWTP received lead concentration in the range of 36.5 to 77.2 µgL^{-1} and released a concentration range of 7.5 to 27.4 µgL^{-1} (Table 7). The annual mean of influent concentration was 60.58 µgL^{-1}, while the annual mean final effluent concentration was 19.27 µgL^{-1}. The annual distribution in the plant shows that 42.69 and 23.13% of total annual influx was removed at the primary and secondary settling tanks, respectively. There was no significant difference in the influent concentration but there was significant difference between the influent and effluent concentration due to plant treatment processes.

The annual mean concentration into the Stellenbosch and Zandvliet plants was 64.88 and 34.93 µgL^{-1}, respectively. The annual spread pattern for Stellenbosch and Zandvliet (Figure 7) showed that 34.28 and 22.30% of Pb was removed at the primary and secondary tanks of Stellenbosch while 25.02% was trapped into secondary sludge and the un-trapped was retuned in the re-circulated sludge. The annual percentage removals of Pb at the plants were 57.03 and 47% for Stellenbosch and Zandvliet plant (Figure 2). There was significant difference in the influent concentration at Stellenbosch plant but there was no significant difference for Zandvliet over the study period. The two plants had significant difference between the influent and effluent concentration due to plant treatment processes during the summer

Table 7. Mean concentration (±SD) of Pb in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgL^{-1}) with associated total removal efficiency.

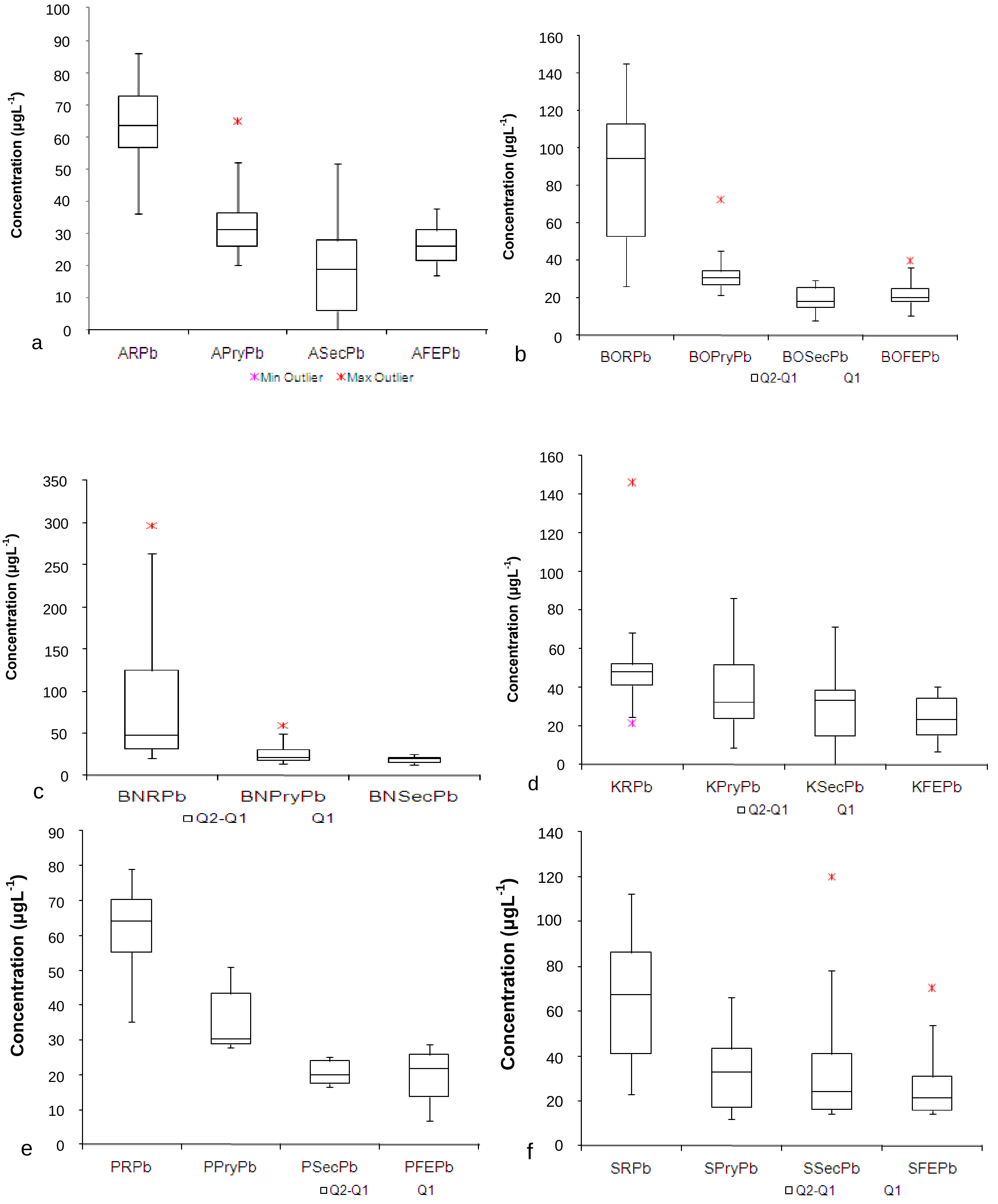
WWTP	Season	Concentration (µgL^{-1})				α concentration	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	81.89 ± 4.2	22.7 ± 3.7	10.3 ± 4.0	28.9 ± 5.9	*	64.75
	Autum ’10	61.5 ± 8.8	28.9 ± 4.8	23.9 ± 1.1	26.7 ± 9.2		56.58
	Winter ’10	64.8 ± 5.4	52.2 ± 15.0	43.2 ± 7.6	20.4 ± 1.4		68.52
	Spring ’10	49.6 ± 11.6	32.6 ± 5.9	N/A	30.3 ± 7.2		38.89
	α season						
Bellville old	Summer ’10	138.35 ± 5.8	30.0 ± 1.6	14.9 ± 6.7	37.29 ± 2.4	*	73.1
	Autum ’10	81.8 ± 23.4	57.9 ± 16.4	21.3 ± 5.1	20.0 ± 1.9		75.5
	Winter ’10	95.3 ± 2.2	26.1 ± 5.1	19.2 ± 8.9	15.03 ± 5.0		84.2
	Spring ’10	29.88 ± 4.3	27.9 ± 4.3	23.5 ± 7.4	18.9 ± 1.4		36.5
	α season		*				
Bellville new	Summer ’10	65.9 ± 12.7	NPST	48.1 ± 13.2	20.7 ± 4.7	*	68.7
	Autum ’10	282.59 ± 21.6	NPST	21.4 ± 7.8	20.9 ± 0.2	*	92.6
	Winter ’10	36.7 ± 3.2	NPST	12.6 ± 4.6	20.2 ± 0.4		44.9
	Spring ’10	23.66 ± 2.7	NPST	18.9 ± 2.3	18.9 ±1.4		19.7
	α season		*				
Kraaifontein	Summer ’10	31.5 ± 15.2	12.0 ± 2.6	N/A	9.49 ± 2.5	*	69.8
	Autum ’10	78.6 ± 59.0	73.4 ± 15.0	51.1 ± 17.9	38.66 ± 2.9		50.8
	Winter ’10	52.8 ± 4.6	36.3 ± 12.3	35.1 ± 3.4	29.2 ± 5.3		44.7
	Spring ’10	44.5 ± 3.8	32.8 ± 4.3	25.9 ± 9.3	19.6 ± 2.9		55.9
	α season						
Potsdam	Summer ’10	62.9 ± 1.7	28.8 ± 0.5	17.7 ± 1.6	7.5 ± 0.6	*	88.1
	Autum ’10	77.2 ± 1.8	46.2 ± 4.3	24.4 ± 0.4	27.4 ± 2.2		64.5
	Winter ’10	65.6 ± 2.6	37.8 ± 7.7	21.5 ± 3.9	17.2 ± 2.7		73.8
	Spring ’10	36.5 ± 1.2	26.1 ± 0.8	19.2 ± 1.4	24.9 ± 1.5		31.8
	α season						
Stellenbosch	Summer ’10	72.5 ± 8.9	13.7 ± 1.7	14.6 ± 0.4	14.3 ± 0.1	*	80.3
	Autum ’10	102.9 ± 8.2	83.4 ± 4.5	49.5 ± 32.4	40.8 ± 18.2		60.4
	Winter ’10	56.8 ± 15.6	51.5 ± 12.8	29.9 ± 4.8	25.5 ± 4.7		55.2
	Spring ’10	27.2 ± 4.8	21.9 ± 5.4	18.7 ± 2.6	18.5 ± 3.6		32.2
	α season		*				
Zandvliet	Summer ’10	45.7 ± 2.3	NPST	33.9 ± 6.2	15.4 ± 3.0	*	66.4
	Autum ’10	42.7 ± 1.6	NPST	31.3 ± 19.1	25.7 ± 4.9		39.9
	Winter ’10	18.3 ± 2.0	NPST	13.9 ± 1.3	11.5 ± 3.9		37.1
	Spring ’10	32.9 ± 16.9	NPST	11.5 ± 3.9	17.9 ± 3.3		45.5
	α season						

α concentration, Significant difference between the stages of WWTPs; α season, significant difference of seasonal differences; *, difference is significant at α = 0.05.

season.

Mercury

Mercury concentrations in raw water into Athlone ranged from 2.20 to 3.34 µgL^{-1}, while in final effluent, its concentration ranged from 0.19 to 2.57 µgL^{-1} (Table 8). Percentage removal of mercury in the treatment plant ranged from 23.01 to 91.46%, while the annual mean influent, annual mean effluent and percentage removal


a
Concentration (µgL^{-1})
100
90
80
70
60
50
40
30
20
10
0
ARPb
APryPb
ASecPb
AFEPb
Min Outlier
Max Outlier
b
Concentration (µgL^{-1})
160
140
120
100
80
60
40
20
0
BORPb
BOPryPb
BOSecPb
BOFEPb
Q2-Q1
Q1
c
Concentration (µgL^{-1})
350
300
250
200
150
100
50
0
BNRPb
BNPryPb
BNSecPb
Q2-Q1
Q1
d
Concentration (µgL^{-1})
160
140
120
100
80
60
40
20
0
KRPb
KPryPb
KSecPb
KFEPb
Q2-Q1
Q1
e
Concentration (µgL^{-1})
90
80
70
60
50
40
30
20
10
0
PRPb
PPryPb
PSecPb
PFEPb
Q2-Q1
Q1
f
Concentration (µgL^{-1})
140
120
100
80
60
40
20
0
SRPb
SPryPb
SSecPb
SFEPb
Q2-Q1
Q1

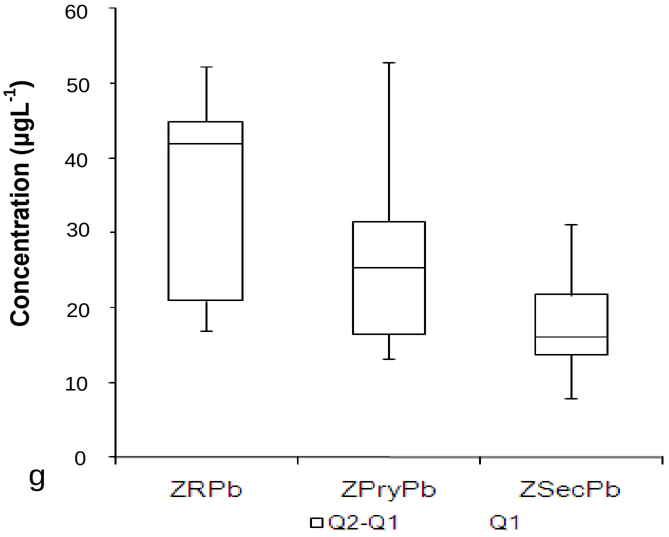


Figure 7. Box and whisker plot for annual spread of Pb concentration in WWTPs. a, Athlone; b, Bellville old; c, Bellville new; d, Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet.

were 2.82 µgL^{-1}, 1.74 µgL^{-1} and 41.93%, respectively. 19.86 and 34.04% of Hg was removed at the plant during the primary and secondary settling tank (Figure 8a) with annual removal efficiency of 41.93% (Figure 2). There was no significant at the plant either due to seasonal difference or due to plant treatment process. Concentration into the Bellville treatment plants ranged from 1.77 to 3.74 µgL^{-1} for the old plant and 0.84 to 2.92 µgL^{-1} for the new plant. The effluent concentration varied between 0.38 and 1.90 µgL^{-1} in old plant and from 0.17 to 2.61 µgL^{-1} in the new plant. The annual mean influent concentration was 2.69 and 2.01 µgL^{-1}, while mean annual effluent concentration was 1.22 and 1.40 µgL^{-1} for the old and new plants, respectively (Table 8). The annual distribution pattern and removal efficiency are presented in Figures 8b and c. 17.91% of the total Hg concentration was removed at the secondary settling tank into secondary sludge in the new plant while 59.65 and 16.72% were trapped into primary and secondary sludge of the old treatment plant. Significant difference observed was due to concentration change arising from the treatment process.

Mercury concentration at the Kraaifontein plant ranged from 0.64 to 4.07 µgL^{-1} with annual mean of 2.22 µgL^{-1} while the final effluent concentration ranged from 0.08 to 3.17 µgL^{-1} with annual mean of 1.80 µgL^{-1} (Table 8). The seasonal removal efficiency of the plant ranged between 20.96 and 88.05%. Annual spread (Figure 8d) shows that 14.65% was removed at the primary settling tank, while about 26% was taken off at the secondary sedimentation tank. The annual mean removal efficiency of the plant was 48.13% (Figure 2). There was significant difference due to seasonal change in influent concentration and due to concentration change from plant treatment process. Potsdam received the highest mercury concentration. The annual mean concentration was 5.53 µgL^{-1} with corresponding effluent concentration of 1.80 µgL^{-1}. The percentage removal varied from 7.87 to 90.04% (Table 8). The plant distribution trend shows that 13.56 and 44.3% was removed at the primary and secondary sedimentation, respectively (Figure 8e). The annual mean removal efficiency was 53.38%. There was significant difference due to seasonal change in influent concentration into the plant. Stellenbosch and Zandvleit received Hg concentration range of 0.64 to 4.26 µgL^{-1} and 0.69 to 3.99 µgL^{-1} respectively (Table 8).

The final effluent in the two plants ranged from 0.25 to 3.59 µgL^{-1} for Stellenbosch and 0.15 to 2.99 µgL^{-1} for Zandvliet, 31.06 and 8.87% of total mercury in the waste influent was removed at the primary and secondary tanks of Stellenbosch, while 22.39% was removed at the secondary tank of Zandvliet plant (Figure 8f and g). The annual removal efficiency of the plant was 51.38% for Stellenbosch and 33.41% for Zandvliet (Figure 2). There was significant difference due to influent concentration and treatment process at Stellenbosch; however, Zandvliet plant showed only significant difference in mercury influent over the study period.

Nickel

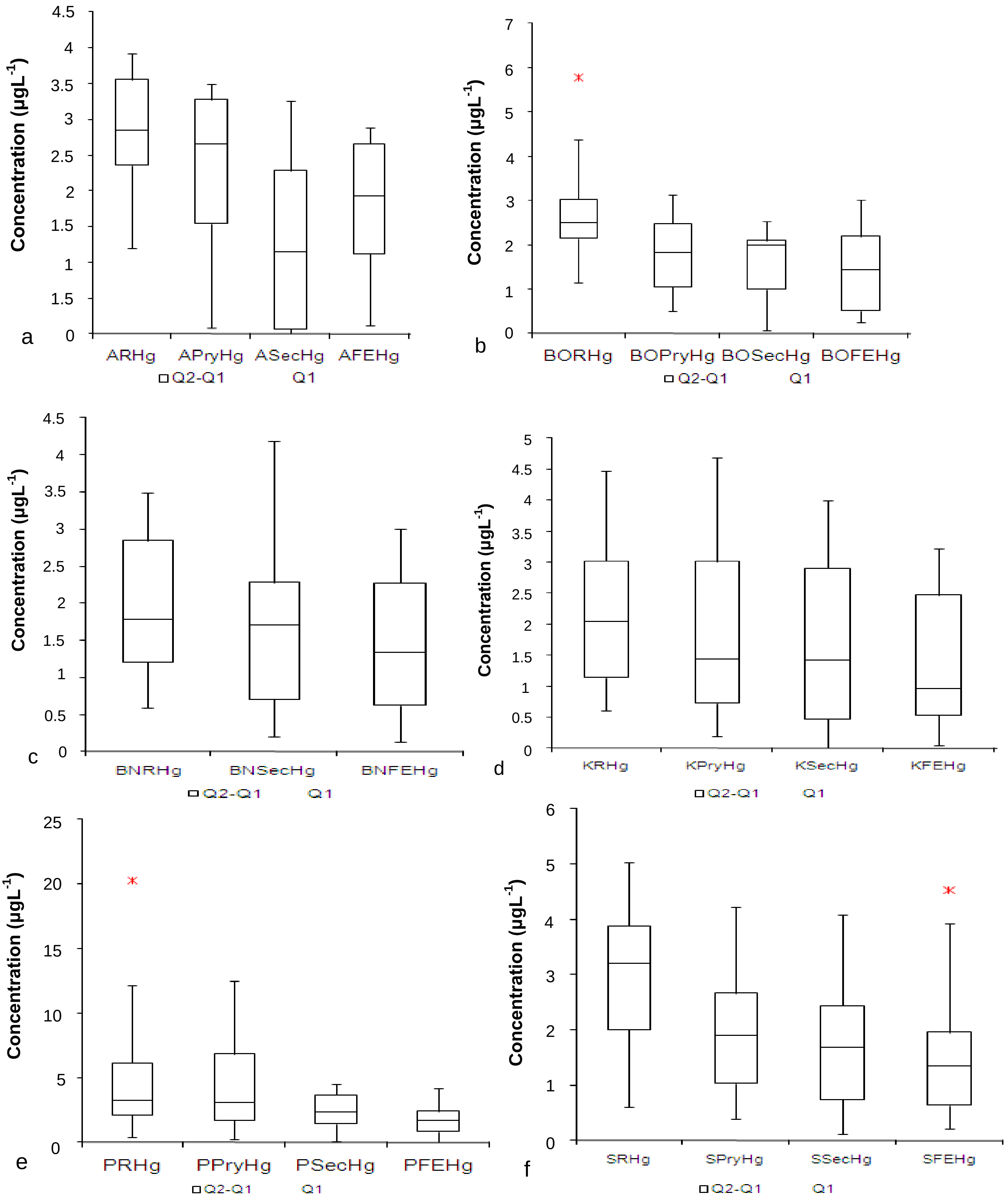
Athlone nickel concentration ranged from 50.32 to 118.72 µgL^{-1} in the raw influent. The effluent concentration varied between 30.42 and 91.68 µgl^{-1} (Table 9). The annual mean influent for the plant was 74.57 µgL^{-1} while the

Table 8. Mean concentration (±SD) of Hg in the influent, primary, secondary and final effluent of WWTPs during the different seasons (μgL^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (μgL^{-1})				α concentration	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	2.2 ± 1.2	0.4 ± 0.3	0.3 ± 0.2	0.19 ± 0.1		91.5
	Autum ’10	3.2 ± 0.7	3.2 ± 0.3	2.9 ± 0.4	2.3 ± 0.8		26.5
	Winter ’10	2.6 ± 0.4	2.2 ± 0.4	1.9 ± 0.2	1.9 ± 0.1		26.7
	Spring ’10	3.3 ± 0.5	3.3± 0.3	N/A	2.27 ± 0.2		23.0
	α season						
Bellville old	Summer ’10	1.77 ± 0.9	0.8 ± 0.3	0.1 ± 0.1	0.38 ± 0.1		78.9
	Autum ’10	3.74 ± 2.0	1.4 ± 0.3	1.1 ± 0.1	0.7 ± 0.3		81.5
	Winter ’10	2.6 ± 0.2	2.5 ± 0.3	2.2 ± 0.2	1.9 ± 0.1		25.4
	Spring ’10	2.7 ± 0.6	2.7 ± 0.6	2.5 ± 0.3	2.2 ± 0.1		29.9
	α season			*			
Bellville new	Summer ’10	0.84 ± 0.3	NPST	0.3 ± 0.2	0.17		80.05
	Autum ’10	1.5 ± 0.4	NPST	1.4 ± 0.6	0.8		47.8
	Winter ’10	2.7 ± 0.3	NPST	2.2 ± 0.3	2.0 ± 0.2		26.3
	Spring ’10	2.92 ± 0.9	NPST	2.6 ± 1.4	2.6 ± 0.1		10.6
	α season	*					
Kraaifontein	Summer ’10	0.6± 0.03	0.3± 0.1	N/A	0.1± 0.03		88.1
	Autum ’10	1.5± 0.2	0.9± 0.1	0.8± 0.2	0.7± 0.1		50.4
	Winter ’10	2.7± 0.3	2.4± 0.5	2.2± 0.7	1.8± 0.6		33.1
	Spring ’10	4.0± 0.7	3.9± 0.7	3.9± 0.7	3.2± 0.1		20.9
	α season	*	*	*		*	
Potsdam	Summer ’10	0.8 ± 0.3	0.3 ± 0.1	0.1 ± 0.04	0.1 ± 0.1		87.3
	Autum ’10	14.5 ± 5.1	12.1 ± 0.4	3.1 ± 1.2	1.5 ± 0.5		90.0
	Winter ’10	2.6 ± 0.1	2.2 ± 0.1	2.1 ± 0.3	1.8 ± 0.2		30.7
	Spring ’10	4.2 ± 0.5	4.4 ± 0.7	4.1 ± 0.6	3.9 ± 0.3		7.9
	α season	*	*	*		*	
Stellenbosch	Summer ’10	0.6 ± 0.02	0.5 ± 0.1	0.1 ± 0.03	0.3 ± 0.03		61.3
	Autum ’10	3.0 ± 0.7	1.4 ± 0.2	1.4 ± 0.5	1.0 ± 0.5		65.2
	Winter ’10	3.8 ± 1.1	2.2 ± 0.1	1.8 ± 0.3	1.4 ± 0.1		63.3
	Spring ’10	4.3 ± 0.7	4.0 ± 0.2	3.7 ± 0.3	3.6 ± 0.8		15.7
	α season						
Zandvliet	Summer ’10	0.7 ± 0.1	NPST	0.3 ± 0.1	0.2 ± 0.02		77.60
	Autum ’10	1.8 ± 0.3	NPST	1.4 ± 0.03	1.3 ± 0.2		29.48
	Winter ’10	1.57 ± 0.1	NPST	1.56 ± 0.1	1.55 ± 0.03		1.5
	Spring ’10	3.9 ± 1.2	NPST	3.0 ± 0.4	2.9 ± 0.7		25.1
	α season	*		*		*	

α concentration, Significant difference between the stages of WWTPs; α season, significant difference of seasonal differences; *, difference is significant at α = 0.05; NA, not analysed; NPST, no primary settling tank.

annual effluent mean was 55.49 μgL^{-1}. The distribution pattern of nickel in the plant is presented in Figure 9a. 16.54 and 27.17% of total nickel concentration into the plant was removed at the primary and secondary


a
Concentration (μgL-1)
4.5
4
3.5
3
2.5
2
1.5
1
1.5
0
ARHg
APryHg
ASecHg
AFEHg
□Q2-Q1
Q1
b
Concentration (μgL-1)
7
6
5
4
3
2
1
0
BORHg
BOPryHg
BOSecHg
BOFEHg
□Q2-Q1
Q1
c
Concentration (μgL-1)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
BNRHg
BNSecHg
BNFEHg
□Q2-Q1
Q1
d
Concentration (μgL-1)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
KRHg
KPryHg
KSecHg
KFEHg
□Q2-Q1
Q1
e
Concentration (μgL-1)
25
20
15
10
5
0
PRHg
PPryHg
PSecHg
PFEHg
□Q2-Q1
Q1
f
Concentration (μgL-1)
6
5
4
3
2
1
0
SRHg
SPryHg
SSecHg
SFEHg
□Q2-Q1
Q1

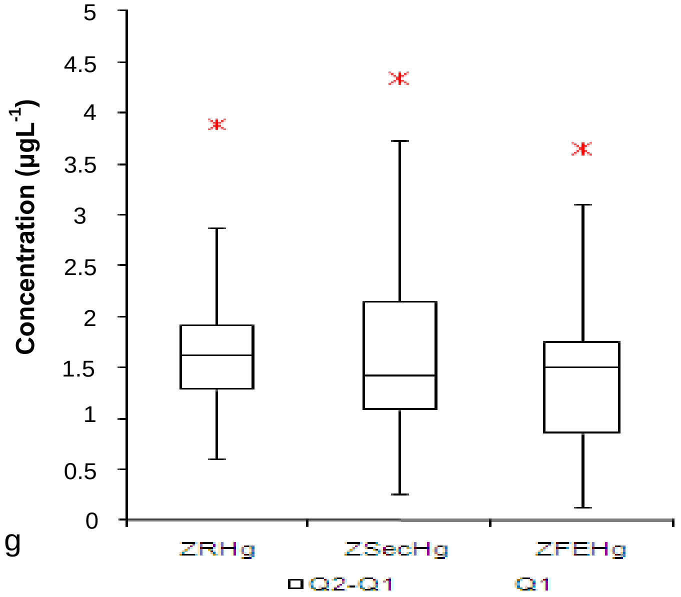


Figure 8. Box and whisker plot for annual Hg concentration in WWTP. a, Athlone; b, Bellville old; c, Bellville new; d, Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet.

sedimentation tanks respectively for the study period. The removal efficiency of the plant ranged from 10.89 to 40.52% with annual mean of 28.43% (Figure 9). Concentration difference was significant due to seasonal influent concentration during winter. The old and new Bellville plants concentrations ranged from 59.59 to 176.76 µgL^{-1} and 42.76 to 95.16 µgL^{-1}, respectively, while their final effluent ranged from 19.21 to 91.91 µgL^{-1} and 25.51 to 85.47 µgL^{-1} (Table 9). The seasonal removal efficiency varied between 7.54 and 67.77% for the old and between 9.35 to 40.35% for the new plant. The annual influent mean was 104.56 and 74.26 µgL^{-1} for the old and for the new plant while the corresponding annual effluent mean concentration was 54.43 and 62.60 µgl^{-1}. The annual distribution spread for nickel is presented in Figure 9b and c. The annual removal efficiency for the plants was 47.72 and 18.69% for old and new plant, respectively (Figure 2). There was significant difference in the old plant due to seasonal and treatment process while in the new plant, significant difference was solely due to seasonal variation in the influent concentration.

The annual mean influent into Kraaifontein plant was 47.59 ± 31.17 µgL^{-1} with corresponding effluent concentration of 37.55 ± 26.51 µgL^{-1} (Table 9). The seasonal removal efficiency of the plant varied between 13.79 and 28.25% (Table 9). The distribution pattern in the plant shows that 11.3 and 35.5% nickel was removed at the primary and secondary tanks. The mean annual removal efficinecy of the plant was 23.64% (Figure 2). There was significant difference due to influent concentration change and concentration change as a result of the treatment process. Postdam received the highest annual mean concentration of 429.01 µgL^{-1} among all the plants investigated. The corresponding annual mean effluent cocnetration was 107.02 µgL^{-1}. The annual removal efficiency was 60.42% (Figure 9). 48.4 and 25.12% of total nickel concentration was removed at the primary and secondary sedimentation tanks over the study period (Figure 2). There was significant difference in the plant due to seasonal and treatment process during summer, winter and spring. Stellenbosch and Zandvliet plant received annual influent concentration of 49.23 and 37.57 µgL^{-1} (Table 9). Zandvliet raw influent cocentration was the least of all the investigated plants. The annual effluent mean were 33.56 and 30.76 µgL^{-1} for Stellenbosch and Zandvliet, respectively. The distribution pattern revealed that 16.47 and 7.58% was removed at the primary and secondary sedimentation tanks of Stellenbosch, while 11.45% was removed at the secondary settling tanks of Zandvliet plant.

The annual mean of plant removal efficiency was 33.25 and 16.39% for Stellenbosch and Zandvliet, respectively (Figure 2). There was significant difference in the plant due to seasonal variation and treatment process.

Zinc

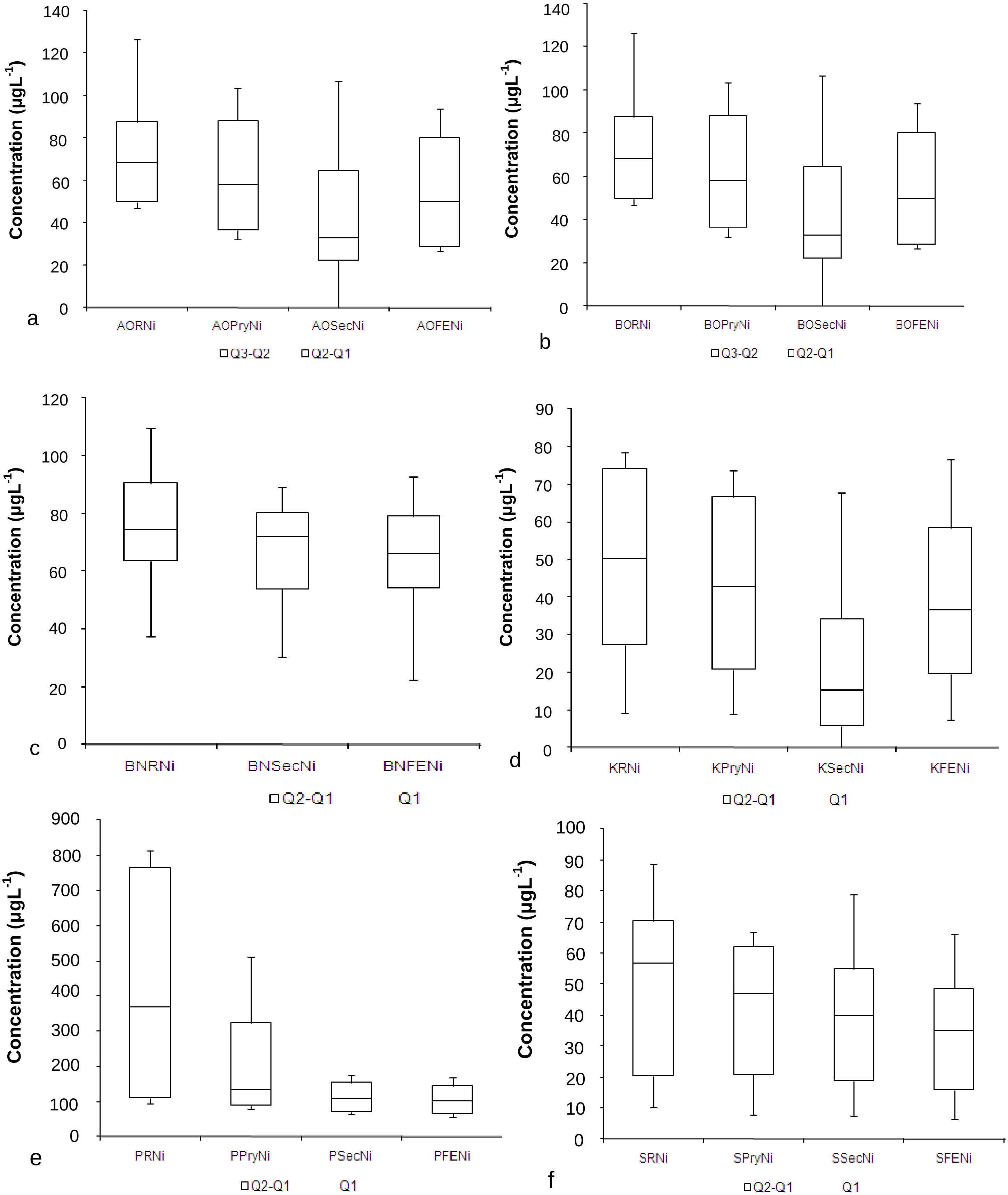
Zinc was generally the highest trace metals in all the WWTPs investigated. The Athlone influent concentration ranged from 961.367 to 1431.95 µgL^{-1} with annual mean of 1236.71 µgL^{-1} (Table 10). The final effluent

Table 9. Mean concentration (±SD) of Ni in the influent, primary, secondary and final effluent of WWTPs during the different seasons (μgL^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (μgL^{-1})				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	50.3 ± 2.9	33.4 ± 1.2	32.8 ± 1.5	30.4 ± 2.5		39.5
	Autum ’10	51.6 ± 7.8	41.4 ± 6.7	41.6 ± 17.7	30.7 ± 7.1		40.5
	Winter ’10	118.7 ± 8.0	99.9 ± 3.9	93.5 ± 17.6	91.7 ± 2.2		22.8
	Spring ’10	77.6 ± 2.2	74.2 ± 10.2	N/A	69.1 ± 7.9		10.9
	α_{season}	*	*		*		
Bellville old	Summer ’10	99.5 ± 8.9	87.7 ± 3.0	62.7 ± 2.4	32.3 ± 10.1	*	67.6
	Autum ’10	59.6 ± 3.3	29.4 ± 5.4	23.3 ± 5.1	19.2 ± 1.0		67.8
	Winter ’10	176.8 ± 17.1	98.8 ± 2.9	97.2 ± 8.4	91.9 ± 6.9	*	48.0
	Spring ’10	80.4 ± 19.0	77.0 ± 4.8	68.1 ± 1.7	74.3 ± 11		7.5
	α_{season}	*	*	*	*		
Bellville new	Summer ’10	71.8 ± 3.8	NPST	66.9 ± 5.4	65.1 ± 2.0		9.4
	Autum ’10	42.8 ± 8.3	NPST	31.0 ± 0.5	25.5 ± 3.4		40.4
	Winter ’10	95.2 ± 6.1	NPST	87.1 ± 3.6	85.5 ± 8.3		10.2
	Spring ’10	87.3 ± 19.6	NPST	76.2 ± 3.9	74.3 ± 11.4		14.9
	α_{season}	*		*	*		
Kraaifontein	Summer ’10	70.2 ± 4.5	61.7 ± 3.8	N/A	52.7 ± 4.9	*	24.9
	Autum ’10	33.2 ± 1.5	25.7± 1.8	24.1 ± 1.3	24.1 ± 0.4		27.6
	Winter ’10	10.6 ± 2.2	9.8± 0.9	7.7 ± 0.1	7.6 ± 0.1		28.3
	Spring ’10	76.3 ± 2.2	71.6± 2.0	65.5 ± 3.6	65.8 ± 9.4		13.8
	α_{season}	*	*	*	*		
Potsdam	Summer ’10	116.9 ± 12.2	83.9 ± 6.2	71.7 ± 0.9	67.9 ± 2.4	*	41.9
	Autum ’10	102.6 ± 9.9	89.3 ± 0.8	72.1 ± 7.5	61.8 ± 5.4		39.8
	Winter ’10	719.8 ± 91.6	490.6 ± 26.6	166.4 ± 9	159.1 ± 7.4	*	77.9
	Spring ’10	776.7 ± 35.9	220.0 ± 51.4	142.6 ± 9	139.3 ± 4.1	*	82.1
	α_{season}	*					
Stellenbosch	Summer ’10	65.1 ± 3.5	61.5 ± 1.0	45.6 ± 1.4	45.6 ± 1.4	*	30.0
	Autum ’10	36.7 ± 14.3	30.1 ± 4.4	25.1 ± 3.6	22.9 ± 3.8		37.4
	Winter ’10	10.9 ± 0.8	8.1 ± 0.3	7.5 ± 0.1	7.1 ± 0.5	*	35.2
	Spring ’10	84.2 ± 7.7	64.8 ± 12.6	64.5 ± 12.6	58.6 ± 6.6		30.4
	α_{season}	*	*	*	*		
Zandvliet	Summer ’10	46.2 ± 0.6	NPST	31.5 ± 3.4	24.4 ± 1.4	*	47.2
	Autum ’10	25.0 ± 0.9	NPST	23.9 ± 0.5	22.1 ± 0.6		11.9
	Winter ’10	7.9 ± 0.3	NPST	7.8 ± 0.1	7.7 ± 0.5		3.3
	Spring ’10	71.1 ± 14.0	NPST	69.9 ± 4.4	68.9 ± 7.6		3.1
	α_{season}	*		*	*		

$\alpha_{concentration}$, Significant difference between the stages of WWTPs; α_{season}, significant difference of seasonal differences; *, difference is significant at α = 0.05; NA, not analysed; NPST, no primary settling tank.

concentration varied between 222.68 and 298.44 μgL^{-1} with annual mean concentration of 251.47 μgL^{-1}. The seasonal percentage removal of the plant varied from 68.96 to 84.45%. The annual distribution pattern in the


Concentration (µgL^{-1})
140
120
100
80
60
40
20
0
a
AORNi
AOPryNi
AOSecNi
AOFENi
□Q3-Q2
□Q2-Q1
Concentration (µgL^{-1})
140
120
100
80
60
40
20
0
b
BORNi
BOPryNi
BOSecNi
BOFENi
□Q3-Q2
□Q2-Q1
Concentration (µgL^{-1})
120
100
80
60
40
20
0
c
BNRNi
BNSecNi
BNFENi
□Q2-Q1
Q1
Concentration (µgL^{-1})
90
80
70
60
50
40
30
20
10
0
d
KRNi
KPryNi
KSecNi
KFENi
□Q2-Q1
Q1
Concentration (µgL^{-1})
900
800
700
600
500
400
300
200
100
0
e
PRNi
PPryNi
PSecNi
PFENi
□Q2-Q1
Q1
Concentration (µgL^{-1})
100
90
80
70
60
50
40
30
20
10
0
f
SRNi
SPryNi
SSecNi
SFENi
□Q2-Q1
Q1

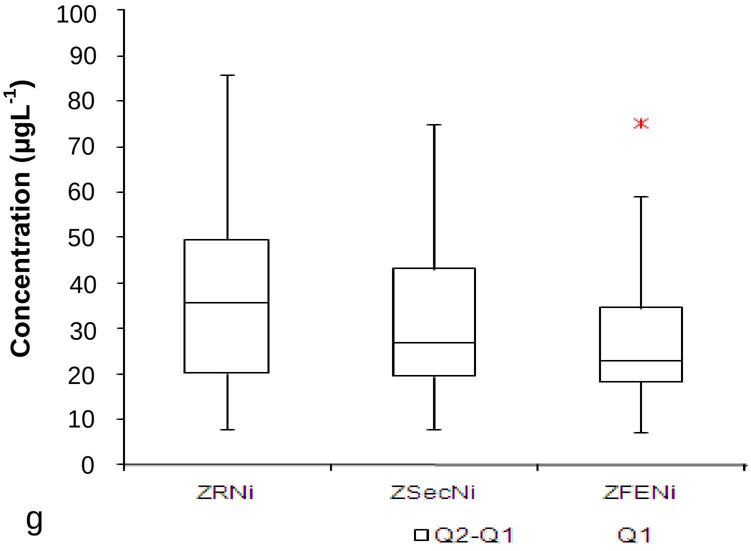


Figure 9. Box and whisker plot for annual Ni concentration in WWTP. a, Athlone; b, Bellville old; c, Bellville new; d; Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet.

plants showed that 44.99 and 31.24% of total annual concentration was removed through primary and secondary sedimentation tanks (Figure 10a). The annual mean removal efficiency of the plant was 78.78% (Figure 2). There was significant difference in the plant due to seasonal variation and treatment process. The old Bellville plant influent concentration ranged from 766.6 to 2079.12 µgL^{-1} while the final effluent varied between 332.53 to 533.77 µgL^{-1} (Table 10). The annual spread is presented in Figure 10b. For the period investigated, 44.67% of Zn concentration into the plant was removed at the primary and 18.51% was taken off at the secondary sedimentation tank. The seasonal removal efficiency ranged from 46.88 to 84.01%, while the annual mean removal efficiency was 65.45% (Figure 2). There was significant difference in the plant due to seasonal variation and treatment process. However, the new Bellville plant influent concentration ranged from 400.94 to 1472.70 µgL^{-1} with annual mean concentration of948.19 µgL^{-1} and the effluent concentration varied from 248.33 to 468.05 µgL^{-1} with annual mean of 351.86 µgL^{-1}. Seasonal plant removal efficiency ranged from 6.69 to 72.40%. 34.16% was trapped into the secondary sludge while the balance was returned in the activated sludge (Figure 2). There was significant difference in the plant due to seasonal variation and treatment process. The influent concentration at Kraaifontein ranged from 638.43 to 1206 µgL^{-1} with annual mean of 933.21 µgL^{-1} and effluent concentration varied from 208.29 to 24.30 µgL^{-1} with annual mean of 222.80 µgL^{-1} (Table 10). The plant shows that 37.59 and 36.89% of Zn influx into the plant was removed at the primary and secondary sedimentation tanks (Figure 10d) for the studied period. The seasonal removal efficiency varied between 67.17 and 82.74% while the annual mean removal efficiency was 74.47% (Figure 2).

Potsdam influent concentration ranged from 822.99 to 1065.72 µgL^{-1} with annual influent mean of 887.14 µgL^{-1} while effluent concentration ranged from 183.79 to 410.82 µgL^{-1} with annual mean of 310.56 µgL^{-1} (Table 10). The distribution of Zn in the plants shows that 21.29 and 39.42% was removed into primary and secondary sludge, respectively. The seasonal removal efficiency ranged from 50.54 to 82.74% with annual mean of 63.74% (Figure 2). There was significant difference in the plant due to seasonal variation and treatment process. Stellenbosch and Zandvliet plants received concentration range of 582.09 to 925.48 µgL^{-1} and 380.19 to 521.8 µgL^{-1}, respectively (Tables 10).

39.57 and 27.14% of total zinc concentration into Stellenbosch plant was removed at the primary and settling tanks while 56.89% was removed at the secondary tank of Zandvliet (Figure 10f and g). Removal efficiency was 70.1% for Stellenbosch and 62.83% for Zandvliet. In the two plants, there was significant difference in the plant due to seasonal variation and treatment process.

Seasonal variability and percentage removal of metals from wastewater treatment plants investigated

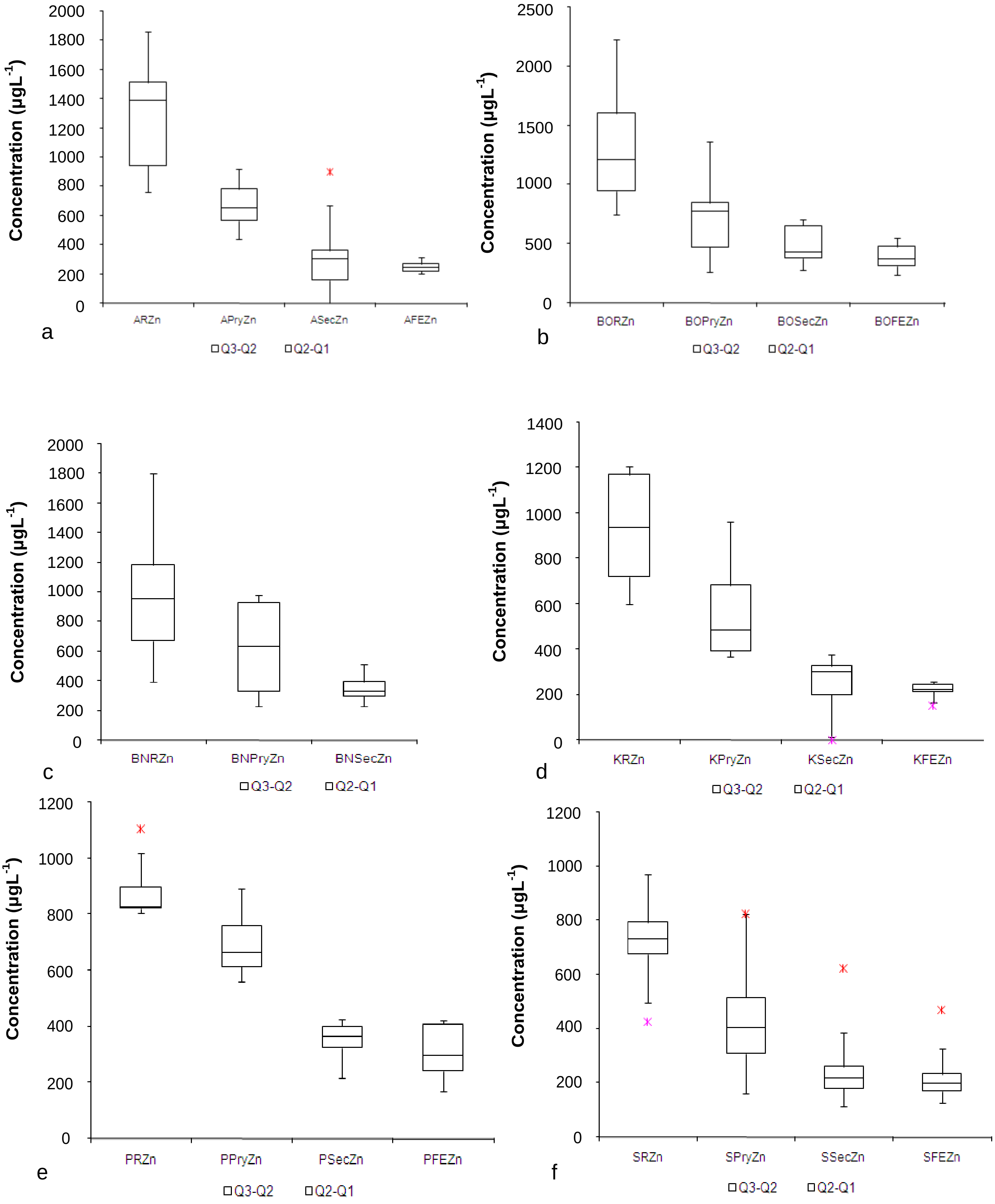
The activated sludge process are generally designed for organic matter removal by microorganisms, while heavy

Table 10. Mean concentration (±SD) of Zn in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgL^{-1}) with associated total removal efficiency.

WWTP	Season	Concentration (µgL^{-1})				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary effluent	Secondary effluent	Final effluent		
Athlone	Summer ’10	1431.9 ± 16.8	912.5 ± 9.6	527.1 ± 324	222.7 ± 22	*	84.5
	Autum ’10	1411.9 ± 252.3	517.0 ± 69	303.6 ± 121.8	255.1 ± 14	*	82.2
	Winter ’10	1121.6 ± 611.1	644.5 ± 124	344.9 ± 74.6	229.7 ± 18	*	79.5
	Spring ’10	961.4 ± 24.9	647.2 ± 12.1	N/A	298.4 ± 13.5	*	68.9
	α_{season}	*					
Bellville old	Summer ’10	1004.8 ± 0.8	883.5 ± 124.6	699.6 ± 8.5	533.8 ± 15.2	*	46.9
	Autum ’10	2079.1 ± 134.4	832.3 ± 548.8	540.5 ± 115.2	332.5 ± 117	*	84.0
	Winter ’10	766.7 ± 17.6	460.9 ± 18.7	295.6 ± 16.9	332.7 ± 36	*	56.61
	Spring ’10	1455.5 ± 32.9	758.8 ± 37.1	417.7 ± 25.7	374.1 ± 22	*	74.3
	α_{season}	*					
Bellville new	Summer ’10	1148.2 ± 10.7	NPST	932 ± 10.2	316.9±3.6	*	72.4
	Autum ’10	1472.7 ± 288	NPST	929 ± 55	468 ± 53.9	*	68.2
	Winter ’10	770.9 ± 9.3	NPST	253 ± 22.5	248 ± 16.9	*	67.8
	Spring ’10	400.9 ± 5.1^{fij}	NPST	383 ± 23.1	374 ± 22.4	*	6.7
	α_{season}	*					
Kraaifontein	Summer ’10	1206.9 ±1.2	391.5 ± 4.6	N/A	208.3 ± 17.3	*	82.7
	Autum ’10	638.4 ± 47.5	425.0 ± 51	356.5 ± 27.6	209.6 ± 53.6	*	67.2
	Winter ’10	756.1 ± 35.9	560.1 ± 47	319.1 ±13.0	232.0 ± 13.3	*	69.3
	Spring ’10	1131.5 ± 46.1	952.9 ±12	277.1 ± 10.0	241.3 ± 20.1	*	78.7
	α_{season}	*	*				
Potsdam	Summer ’10	822.9 ± 1.5	626.3 ± 10.3	341.3 ± 7.6	260.1 ± 1.6	*	68.4
	Autum ’10	1065.7 ± 47.8	846.3 ±45.9	250.1 ± 39.9	183.8 ± 10.8	*	82.8
	Winter ’10	829.3 ± 29.2	727.8 ± 29.6	384.2 ± 11.0	387.6 ± 48.4	*	53.3
	Spring ’10	830.6 ±13.9	592.8 ± 28.8	418.6 ± 5.9	410.8 ± 10.3	*	50.5
	α_{season}						
Stellenbosch	Summer ’10	684.9 ± 16.6	351.2 ± 22.4	128.5 ± 13.9	133.7 ± 13.4	*	80.5
	Autum ’10	581.1 ± 167.2	209.7 ± 43.2	247.9 ± 8.4	215.2 ± 2.9	*	62.9
	Winter ’10	925.5 ± 39.1	754.2 ± 78.2	402.4 ± 191.8	353.8 ± 100.5	*	61.8
	Spring ’10	734.2 ± 3.8	452.9 ± 15.1	195.2 ± 3.2	182.1 ± 4.8	*	75.2
	α_{season}						
Zandvliet	Summer ’10	5128.3 ± 10.2	NPST	2119.9 ± 11.8	909.4 ± 23.1	*	82.3
	Autum ’10	395.2 ± 19.8	NPST	277.2 ± 18.2	191.8 ± 10.9	*	51.5
	Winter ’10	380.2 ± 14.8	NPST	223.9 ± 17.6	190.0 ± 5.2	*	50.0
	Spring ’10	965.8 ± 19.8	NPST	340.6 ± 5.2	313.2 ± 1.5	*	67.6
	α_{season}						

$\alpha_{concentration}$, Significant difference between the stages of WWTPs; α_{season}, significant difference of seasonal differences; *, difference is significant at $\alpha = 0.05$; NA, not analysed; NPST, no primary settling tank.

metals removal is considered as side benefit, and has been quite variable (Busetti et al., 2005; Ustun, 2009; Chanpiwat et al., 2010). Metal removal efficiency is not only affected by metal influent concentration, but also by


a
Concentration (μgL-1)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
ARZn
APryZn
ASecZn
AFEZn
□Q3-Q2
□Q2-Q1
b
Concentration (μgL-1)
0
500
1000
1500
2000
2500
BORZn
BOPryZn
BOSecZn
BOFEZn
□Q3-Q2
□Q2-Q1
c
Concentration (μgL-1)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
BNRZn
BNPryZn
BNSecZn
□Q3-Q2
□Q2-Q1
d
Concentration (μgL-1)
0
200
400
600
800
1000
1200
1400
KRZn
KPryZn
KSecZn
KFEZn
□Q3-Q2
□Q2-Q1
e
Concentration (μgL-1)
0
200
400
600
800
1000
1200
PRZn
PPryZn
PSecZn
PFEZn
□Q3-Q2
□Q2-Q1
f
Concentration (μgL-1)
0
200
400
600
800
1000
1200
SRZn
SPryZn
SSecZn
SFEZn
□Q3-Q2
□Q2-Q1

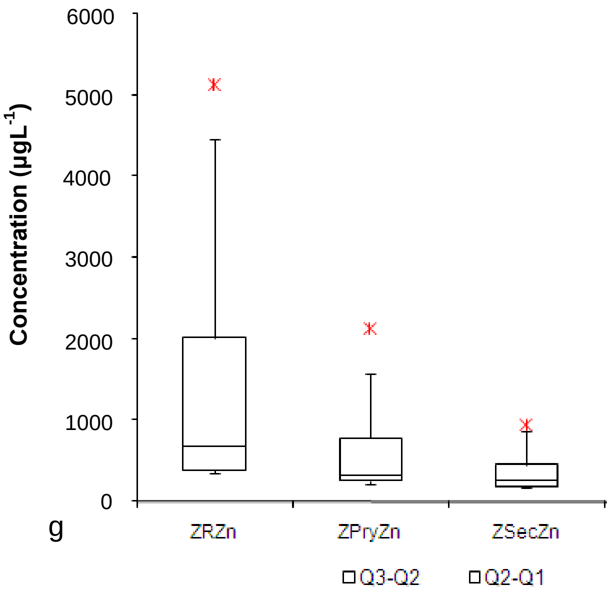


Figure 10. Box and whisker plot for annual Zn concentration in WWTPs. a, Athlone; b, Bellville old; c, Bellville new; d, Kraaifontein; e, Potsdam; f, Stellenbosch; g, Zandvliet.

other conditions such as the operating parameters, for example, the retention time in the treatment plants, flow rate, physical, chemical and biological factors (Wang et al., 1999). Metals removal is known to be dependent on dissolved organic matter (Oliveira et al., 2007) and pH (Cheng et al., 1975; Wang et al., 1999), as removal efficiency increases with pH until they precipitate as hydroxides. Wastewater treatment plants are usually operated at pH 7 to 9. Thus, because of differing metal solubilities at these pH values, retention time, flow rate, and since wastewater composition is always complex, removal is attributed to these factors (Wang et al., 1999). In this study, the pH values for untreated influent and treated effluent ranged from 6.5 to 7.7 at a temperature range of 17 to 19°C. This caused variation in removal efficiency for metals in the WWTPs investigated. Generally, the level of metal removal from the treatment plants remained unpredictable for the period investigated (Figure 2).

The long-term dataset obtained from the WWTPs showed that the investigated WWTPs received varying concentrations of heavy metals in the raw wastewater, of which Cu and Zn were the most abundant. The seasonal variations in the metals analyzed from all the treatment plants are presented in Tables 1 to 9. The results illustrated that the wastewater metals composition is complex and quite variable. The concentrations of heavy metals in the raw wastewater were generally similar in WWTPs under study. This could be attributed to the fact that all the WWTPs received a mixture of domestic wastewater, storm water and industrial effluent. Generally, the abundance distribution pattern of heavy metals in terms of concentration is Zn > Cu > Pb > Cr > Ni > As > Co > Cd > Hg. The variation in wastewater metal content can further be attributed to diversity in economic activities and the living pattern in the province. The Athlone, Potsdam, Bellville, Stellenbosch and Zandvliet plants are known to receive high industrial waste when compared to Kraaifontein (Moeletsi et al., 2004). There are many catering, restaurants, sawmills, Ni-Cd and carwash industries in the Western Cape Province that release their waste for further treatment by the municipality. Generally, the influent values are higher than effluent values. The average removal efficiency for the plants could be rated effective on an annual basis as the effluent values are always lower than the influent values for all the metals in all the measurement. As shown in Figure 2, metals removal occurs both in the primary (where portion of metals adsorb to the particles) and in the secondary biological treatment (where metals are removed by biosorption) (Ustun, 2009). The relationship between influent and removal efficiency agreed with previous research findings (Kulbat et al., 2003; Shomar et al., 2004; Oliveira et al., 2007) where it was observed that the removal of heavy metals in the wastewater is directly proportional to the metal concentration in the influent.

From this study, the Potsdam treatment plant was the most effective at heavy metal removal (Figure 2). On average, the Potsdam treatment plant like every plant, received industrial, domestic and storm water except for Kraaifontein with about 90% domestic influent, the plant effectiveness at metal removal can be attributed to the living pattern and the installation of new treatment plant at Potsdam to complement the old plant. The annual abundance pattern for arsenic in all treatment plants can be rated as new Bellville > Stellenbosch > old Bellville > Athlone > Kraaifontein ≥ Potsdam > Zandvliet. The removal efficiency for arsenic was best at Potsdam plant for all the seasons except during the spring. Arsenic compounds are extensively used in the wood processing industries to protect the timbers. Two wood processing industries are functioning in the vicinity of the Stellenbosch WWTP. These industries may use arsenic compounds to protect timbers, the uses of which are subsequently released in their waste. Generally, arsenic concentration in effluent from all the treatment plants investigated fell below the South African water quality guideline of 10 μgL^{-1} (DWAF, 1996). However, it was above the CCME (1999) recommendation. All the treatment plants could be rated high except for Athlone during the Autum and Spring due to malfunctioning of the plants. The cadmium annual abundance pattern by plant could be rated as Potsdam > Kraaifontein > Athone ≥ old Bellville > Stellenbosch ≥ Zandvliet ≥ new Bellville. The possible sources of cadmium into water ways are launderettes, electroplating workshops, plastic manufacturing, pigments, enamels, paints among others. Cadmium was well removed from Athlone, Bellville old, Kraaifontein and Potsdam, while the Bellville new and Stellenbosch plants were not very effective.

The influent and effluent concentrations were within the reported values elsewhere (Table 11). No significant difference was observed for raw effluent except for Kraaifontein and Potsdam during the winter season. The reported concentration fell below SWQG of 10 ugl^{-1} limit for irrigation and livestock (DWAF, 1996; CCME, 1999) but higher than 0.017 and 0.02 μgL^{-1} for human consumption (CCME, 1999). The general abundance pattern for cobalt for the treatment plants could be rated as Potsdam > Kraaifontein > Athlone ≥ old Bellville > Stellenbosch ≥ Zandvliet ≥ new Bellville. The removal efficiency is presented in Figure 2. Cobalt was well removed from all the plants in this study except at Potsdam during the spring season (Table 4). Statistical analysis showed no significant difference ($P<0.05$) in the influent concentration during the sample period except for Kraaifontein and Potsdam during the winter season. Cobalt concentrations in the final effluent were within the Department of Water Affairs recommended values for freshwater (DWAF, 1996). In terms of abundance in the WWTPs, all the investigated plants could be rated as Potsdam > Athlone > old Bellville > new Bellville > Stellenbosch > Kraaifontein > Zandvliet. When compared the influent and effluent concentration with other plants in the developed countries, the range fit within the limits was reported (Table 11). However, Kraaifontein treatment plants perfomed poorly at total chromium removal from waste stream as less than 20%. This is similar to the finding in countries like Greece, Brazil and Poland (Kulbat et al., 2003; Firfilionis et al., 2004; Oliveira et al., 2007). No significant difference ($P < 0.05$) was observed between the influent and effluent concentration of the investigated plants.

Copper was the second dominant metal as zinc in the treatment plant investigated. The abundance pattern revealed that Athlone > Potsdam > Stellenbosch > Bellville old > Kraaifontein > Bellville new > Zandvliet. Athlone, Potsdam, Bellville old, and Stellenbosch received the high concentrations of copper in the influent waste; this could be attributed high industrial influx to these treatment plants (Moeletsi et al., 2004). Other possible sources of heavy metals into these plants are the leachate from landfill sites that are often pumped into the plants for treatment especially at Bellville and Stellenbosch. Generally, copper was well removed from all the treatment plants except at Zandvliet during Autum where less than 20% was removed. This is similar to the finding of Firfilins et al. (2004).

The range of copper concentration reported in this study was also within the studies reported in most countries and was within the freshwater limit set by the department of water affairs for irrigation, aquatic life and livestock management (DWAF, 1996). Pb removal efficiency in the plants could be rated effective as between 40 to 95% of the total influx was removed from the waste stream. The reported concentration range for the investigated treatment plants were collaborated by previous studies elsewhere (Table 11), while the plants abundance patter could be rated as new Bellville > old Bellville > Stellenbosch ≥ Athlone > Potsdam > Kraaifontein > Zandvliet. This abundance distribution pattern can largely be attributed to the industrial effluent being received at each of the treatment plant and the living pattern of the residents in the study area. There was significant difference between the influent and effluent concentration for most of the plants as the final effluent concentration was generally lower than the influent. The final effluent concentration fell below the SA waste quality guidelines for aquatic life, irrigation and livestock production purposes. However, the concentration was far above the CCME guidelines (1999).

Sources of mercury to the environment include dental practices, clinical thermometers, glass mirrors among others. Mercury is known to be highly toxic and can affect human health at the lowest concentration of possible exposure. For the WWTPs, no significant difference was noticeable between the influent and effluent concentration. However, all the wastewater treatment plants could be rated effective with the exception of Athlone and Zandvliet where percentage removal fell below 30% over the study period. Potsdam was highly

Table 11. Heavy metal concentrations in influent and effluents from other countries and investigated treatment plants in Cape Town.

Metal	Country	Untreated influent (μgL^{-1})	Treated effluent (μgL^{-1})	References
As	Spain	2.2	-	European Communities (2001)
	Italy	0.3-31	0.5-9.2	Busetti et al. (2005)
	Israel	5.6	5.1	Shomar et al. (2004)
	South Africa	5-43.76	1.12-5.69	Present study
Cd	Austria	<20-60	<20-60	European Communities (2001)
	Poland	<0.01	<0.01	Kulbat et al. (2003)
	France	6-85	-	European Communities (2001)
	Germany	0.4	-	European Communities (2001)
	Greece	<1-44	<1	Karvelas et al. (2003)
	Greece	0.56	0.34	Firfilionis et al. (2004)
	Israel	0.6	0.8	Shomar et al. (2004)
	Italy	0.2-1.8	0.1-1.6	Busetti et al. (2005)
	Spain	0.06 – 1.19	0.04 – 0.11	Oliveira et al. (2007)
	Turkey	0-137	4-5	Ustun (2009)
	South Africa	1.07-17.39	0.52-2.58	Present study
Hg	Austria	<10	<10	European Communities (2001)
	Spain	0-0.5	0-0.24	Oliveira et al. (2007)
	France	1-8	-	European Communities (2001)
	Italy	<1	-	European Communities (2001)
	Germany	0.6	0.1	European Communities (2001)
	Italy	0.2-147	0.1-9.5	Busetti et al. (2005)
	South Africa	0.6-14.5	0.1-3.2	Present study
Zn	Poland	270-800	-	Chipasa (2003)
	Poland	270-300	90-120	Kulbat et al. (2003)
	Austria	<20-3700	20-500	European Communities (2001)
	Greece	330-3200	20-900	Karvelas et al. (2003)
	Greece	456	268	Firfilionis et al. (2004)
	Israel	75	54	Shomar et al. (2004)
	Italy	100-900	-	European Communities (2001)
	Italy	61-833	24-238	Busetti et al. (2005)
	South Africa	400.9-5128.3		Present study
Cr	Greece	102.1	56.9	Firfilionis et al. (2004)
	Austria	6200-7900	<900-5600	Firfilionis et al. (2004)
	Italy	0.5-18.4	0.4-8.2	Busetti et al. (2005)
	Greece	28-52	0.1-16	Karvelas et al. (2003)
	Turkey	174-2120	132-423	Ustun (2009)
	Poland	20	10	Kulbat et al. (2003)
	Spain	6.87	5.74	Oliveira et al. (2007)
	South Africa	31.2-223.62	23.8-153.4	Present study
Co	South Africa	0.34-11.65	0.17-4.73	Present study
Cu	Poland	52.2	26.0	Firfilionis et al. (2004)
	Spain	17.31	9.66	Oliveira et al. (2007)

Table 11. Contd.

	Poland	70	10	Kulbat et al. (2003)
	Turkey	0-137	4-5	Ustun (2009)
	Germany	-	-	European Communities (2001)
	Italy	-	-	Busetti et al. (2005)
	South Africa	21.0-1189.3	7.7-55.4	Present study
Pb	Poland	37-148	-	Chipasa (2003)
	Poland	15	<10	Kulbat et al. (2003)
	Austria	<20-60	<20-60	European Communities (2001)
	Greece	28.6	13.1	Firfilionis et al. (2004)
	Republic of Korea	2.93-79.33	0.70-17.45	Chanpiwat et al. (2010)
	Spain	37.42	22.57	Oliveira et al. (2007)
	Turkey	6-358	22-30	Ustun (2009)
	Italy	10-61	1.0-11	Busetti et al. (2005)
	South Africa	10-61	1.0-11	Present study
Ni	Greece	32.2	32.2	Firfilionis et al. (2004)
	Poland	30	10	Kulbat et al. (2003)
	Republic of Korea	4.88-116.6	3.36-51.53	Chanpiwat et al. (2010)
	Turkey	59-202	24-53	Ustun (2009)
	South Africa	7.9-776.7	7.6-159.1	Present study

effective at Hg removal as for other metals except for the spring season. The poor performance of the plant for Hg removal could be attributed to plant overload which subsequently affected the retention time of water in the plant. The concentration reported in this study for mercury was higher than values reported in Austria, France, Spain and Germany (Oliveira et al., 2007; European Communities, 2001); however, it was lower than the finding of Busetti et al. (2005). The possible sources of nickel into wastewater or other environmental components includes alloys, electroplating, nickel-cadmium batteries, launderettes and paints productions. Ni was not well removed from all the investigated plants except for Potsdam during the winter and spring seasons. Nickel removal in Bellville new and Kraaifontein WWTPs were least as annual removal for these plants were less than 30% (Figure 2). Findings from this study were similar to values reported in influent and effluent waste from other studies as presented in Table 11. No significant difference was noticeable between the influent and effluent water; however, WWTPs like Athlone, Potsdam and Stellenbosch show some seasonal variation in the influent Ni concentration.

Sources of zinc include domestic wastes, galvanizing, batteries, paints, fungicides, textiles, cosmetics, pulp, paper mills and pharmaceutics. In this study, Zn was the most dominant metal in all the WWTPs investigated. The annual plant rating can be rated as Zandvliet > Bellville old > Athlone > Bellville new ≥ Kraaifontein > Potsdam > Stellenbosch. The range of zinc in this study was generally higher than findings in other studies (Table 11). In terms of removal efficiency, Athlone treatment plant had the highest and can be rated above other plants. There was significant difference between the influent and effluent concentration over the study period. Considering the high concentration of Zn received at these plants, the final effluent concentration was within the national water act waste discharge standards (DWAF, 2010).

Conclusion

The results revealed that differences in metal concentrations in the influent were site-specific and varied by the period of sample collection. Metal variations could be related to the diversified industrial activities, especially from a multitude of smaller sized companies. A significant difference in metal concentrations between influent and effluent was found, except for Hg. Metal concentrations in the influent to the biological treatment of the WWTP's and the removal efficiencies that have been found in this study are within the ranges reported in the current literature. However, using the final effluent for irrigation purposes as it were found for some treatment plants could pose serious health risks in the future considering plant overload and intermittent breakdown of some these treatment plants.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGEMENTS

The authors want to thank the Department of Geology, University of Stellenbosch for sample analysis. This study was financially supported by NRF and Cape Peninsula University of Technology grant given to Mr. O. O. Olujimi for part of his doctoral studies.

Abbreviations

EDMs, Endocrine disrupting metals; **WWTPs,** wastewater treatment plants; **ICP-MS,** inductively coupled plasma mass spectrometry.

REFERENCES

Akan JC, Abdulrahaman FI, Dimari GA, Ogugbuaja VO (2008). Physicochemical determination of pollutants in wastewater and vegetables samples along the Jakara wastewater channel in kano metropolis Kano State, Nigeria. Eur. J. Sci. Res. 23(1):122-133.

Ayeni OO, Ndakidemi PA, Snyman RG, Odendaal JP (2010). Metal contamination of soils collected from four different sites along the lower Diep River, Cape Town, South Africa. Int. J. Phys. Sci. 5(12):2045-2051.

Busetti F, Badoer S, Cuomo M, Rubino B, Traverso P (2005). Occurrence and removal of potentially toxic metals and heavy metals in the wastewater treatment plant of Fusina (Venice, Italy). Ind. Eng. Chem. Res. 44:9264-9272.

CCME-Canadian Council of Ministers of the Environment (1999). Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg.

Chanpiwat P, Kim K, Sthiannopkao S (2008). Heavy metals in wastewater Treatment Plant. Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes (GREAT 2008), 4th IGCP 516, and 5th APSEG; November 24-26, 2008, Bangkok, Thailand.

Chanpiwat P, Sthiannopkao S, Kim K-W (2010). Metal content variation in wastewater and biosludge from Bangkok's central wastewater treatment plants. Microchem. J. 95:326-332.

Cheng MH, Patterson ER, Minear RA (1975). Heavy metals uptake by activated sludge. Water Pollut. Control Fed. J. 47:362-376.

Chipasa KB (2003). Accumulation and fate of selected heavy metals in a biological wastewater treatment systems. Waste Manage. 23:135-143.

DWAF (1996). Water Quality Guidelines, Field Guide (1st edition). Pretoria.

DWAF (2010). National Water act waste discharge standards. www.urbanwater.co.za 27 May 2011

European Communities (2001). Pollutants in urban wastewater and sewage sludge. Final Report, ISBN 92-894-1735-8; Office for Official Publications of the European Communities: Luxembourg.

Firfilionis G, Paraskevopoulou V, Vilioti G, Dassenakis M (2004). The removal of trace metals at the wastewater treatment plant of Psyttalia. Mediterr. Mar. Sci. 5(1):71-81.

Jackson VA, Paulse AN, Stormbroek T, Odendaal JP, Khan W (2007). Investigation into metal contamination of the Berg River, Western Cape, South Africa. Water SA 33(2):175-182.

Jackson VA, Paulse AN, Odendaal JP, Khan W (2009). Investigation into the metal contamination of the Plankenburg and Diep Rivers, Western Cape, South Africa. Water SA 35(3):289-299.

Jaganyi D, Tesfai FK, Southway C, Mamabolo M (2005). Determination of inorganic pollutants and assessment of the current South African guidelines on permissible utilisation of sewage sludges. Water SA 31(3):359-368.

Karvelas M, Katsoyiannis A, Samara C (2003). Occurrence and fate of heavy metals in the wastewater treatment process. Chemosphere 53:1201-1210.

Kulbat E, Olanczuk-Neyman K, Quant B, Geneja M, Haustein E (2003). Heavy metals removal in the mechanical-biological wastewater treatment plant "Wschod" in Gdansk. Pol. J. Environ. Stud. 12(5):635-641.

Moeletsi M, Mazema H, Halday I (2004). Strategy for mitigating the impacts of heavy metals in wastewater and the economic and environmental implications for the city of Cape Town. Proceedings of the 2004 Water Institute of Southern Africa (WISA) Biennial Conference 2-6 May 2004 ISBN: 1-920-01728-3 Cape Town, South Africa.

Ogunfowokan AO, Torto N, Adenuga AA, Okoh EK (2006). Survey of levels of phthalate ester pasticizers in a sewage lagoon effluent and a receing stream. Environ. Monit. Assess. 118:457-480.

Oliveira AD, Bocio A, Trevilato TMB, Takayanagui AMM, Domingo JL, Segura-Muniz SI (2007). Heavy metals in untreated/treated urban effluent and sludge from biological wastewater treatment plant. Environ. Sci. Pollut. Res. 14(7):483-489.

Olujimi OO, Fatoki OS, Odendaal JP, Daso AP, Oputu OU (2012). Preliminary Investigation into Occurrence and Removal of Arsenic, Cadmium, Mercury, and Zinc in Wastewater Treatment Plants in Cape Town and Stellenbosch. Pol. J. Environ. Stud. 21(6):1755-1765.

Rajbanshi A (2008). Study on Heavy Metal Resistant Bacteria in Guheswori Sewage Treatment Plant. Our Nat. 6:52-57.

Shomar BH, Muller G, Yahya A (2004). Potential use of treated wastewater sludge in the agricultural section of the Gaza Strip. Clean Technol. Environ. Policy 6:128-137.

Shuping LS (2008). Biomonitoring of metal contamination in the lower Diep River, Milnerton, Western Cape. (MTech Dissertation, Cape Peninsula University of Technology). pp. 60-64.

Sorme L, Lagerkvist R (2002). Source of heavy metals in urban wastewater in Stockholm. Sci. Total Environ. 298:131-145.

Wang J, Huang CP, Herber EA, Poesponegoro I, Poesponegoro H, Takiyama LR (1999). Effects of dissolved organic matter and pH on heavy metal uptake by sludge particulates exemplified by copper(II) and nickel(II): Three-variable model. Water Environ. Res. 71:139-147.

Ustun GE (2009). Occurrence and removal of metals in urban wastewater treatment plants. J. Hazard. Mater. 172:833-838.