Trace element accumulation and human health risk assessment of *Labeo capensis* (Smith, 1841) from the Vaal Dam reservoir, South Africa

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ABSTRACT

This paper aimed to determine the trace element concentrations within water, sediment and tissues of the Orange River mudfish *Labeo capensis* (Smith, 1841) collected from the Vaal Dam reservoir, and to assess potential risks associated with the consumption of *L. capensis* muscle tissue. The study was undertaken in March 2013; 22 *L. capensis* were collected with the aid of gill nets. Water and sediment samples were collected on site, and additional water analysis data for the sampling period were received from Rand Water Analytical Facility in Vereeniging. Analysis of water revealed trace elements were present at trace levels. The comparison of trace element concentrations between the water, sediment and fish tissues revealed that the sediment contains the highest concentrations, followed by fish tissues and water. This trend exists as a result of the underlying geology of the Vaal Dam, the physiological and biological characteristics of *L. capensis*, and the physico-chemical state of the water. The risk assessment performed on the muscle tissue revealed that As and Se had total hazard quotient (THQ) values greater than one, and that the levels of As and Se were above the safety threshold values for human consumption.

Keywords: Vaal Dam, *Labeo capensis*, trace element accumulation, bioaccumulation, health risks, target health quotient

INTRODUCTION

Trace elements occur naturally within the environment, entering aquatic ecosystems through various geochemical processes. Anthropogenic activities have increased the rate at which trace elements enter aquatic systems, through urban, industrial and agricultural effluent (Vieira et al., 2011; Copat et al., 2013; Vrhovnik et al., 2013). The persistent nature of trace elements, their toxic characteristics and capability to bio-accumulate within aquatic organisms has brought attention to the problems associated with environmental contamination of trace elements (Castro-González and Méndez-Armenta, 2008; Vieira et al., 2011; Authman et al., 2012). Certain trace elements are considered to be potentially toxic to vertebrates, such as As, Cd and Hg, whilst others are considered essential, such as Cu, Fe and Zn (Authman et al., 2012), but even the essential trace elements may yield toxic effects when exposure levels become elevated (Wood, 2012; Vrhovnik et al., 2013). Aquatic organisms are capable of accumulating trace elements through various uptake routes including adsorption, ingestion and respiration (Vieira et al., 2011; Wood, 2012). The uptake of trace elements is affected by chemical factors such as chemical speciation (Vrhovnik et al., 2013), environmental factors including pH, temperature, turbidity and sediment (Castro-González and Méndez-Armenta, 2008; Wepener et al., 2011), and biological factors including the physiological condition, age, gender, diet and species of organism studied (Castro-González and Méndez-Armenta, 2008; Wood, 2012). The aforementioned factors are all taken into consideration when the biomonitoring of aquatic systems is performed (Wood, 2012).

The biomonitoring of an aquatic system involves the use of biological indicators (Wilson and Baley, 2012), being either effect or accumulation indicators. Fish are often utilized in biomonitoring studies as they possess many characters desired for bioindication (Zhou et al., 2008). These include longevity to assess exposure time, capability to bioaccumulate contaminants to high levels without death, large bodies to supply sufficient tissue for analysis, existence at different trophic levels, abundance, and ease of sampling (Zhou et al., 2008; Wood, 2012). Some trace elements accumulated within fish tissues, including the ones of major concern with regard to pollution, such as Cd, Cu, Pb and Zn, are present at higher concentrations within the liver, kidney and gills in comparison to other tissues (Wepener et al., 2011; Wood, 2012; Squadrone et al., 2013; Vrhovnik et al., 2013; Gilbert and Avenant-Oldewage, 2014). The higher concentrations within the liver and kidney have been attributed to the presence of metallothioneins, and the detoxification role and metabolic activity of these two organs.

Fish are also selected due to their importance for humans as a source of nutrition (Vieira et al., 2011; Authman et al., 2012). Interest in the use of fish has grown substantially due to consumption of fish serving as a potential source of trace element exposure to humans (Castro-González and Méndez-Armenta, 2008; Vieira et al., 2011). This interest increased significantly after the 1956 Minimata Bay incident in Japan, caused by the consumption of mercury-contaminated fish (Castro-González and Méndez-Armenta, 2008). The adverse effects to human health as a result of consumption of contaminated fish are diverse, ranging from neurotoxic to carcinogenic effects (ATSDR, 2003, 2012; Vieira, 2011).

The Vaal River is of great importance to South Africa, supplying water to the largest growing and most industrially active population in the country. The Vaal Dam was constructed upon the Vaal River in 1938 in order to supply water for both

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domestic and industrial use to the Gauteng Province (Wepener et al., 2011), and therefore requires continual monitoring. Studies have previously been performed within the Vaal Dam reservoir assessing the trace element concentrations present within the biota, sediment and water (Retief et al., 2006, 2009; Crafford and Avenant-Oldewage, 2010, 2011; Wepener et al., 2011; Gilbert and Avenant-Oldewage, 2014).

The Orange River mudfish *Labeo capensis* (Smith, 1841), is a benthic cyprinid which thrives in large impoundments (Skelton, 2001). This species is utilized in physiological and ecological research, and shows potential as a commercial species within large impoundments (Skelton, 2001), such as the Vaal Dam reservoir. Wepener et al. (2011) assessed the effects of various stressors within the Vaal River System, below the dam wall, on this species, which indicated that it is sensitive to alterations within its environment at subcellular, tissue, whole organism and population levels. Trace element concentrations were assessed for the muscle tissue of *L. capensis*, with Cu having the highest concentration, in comparison to Cd, Cr, Ni, Pb and Zn, for the specimens sampled from the Vaal Dam (Wepener et al., 2011). The distribution of trace elements in fish is highly dependent on the physic-chemical properties of the trace elements as well as the properties of the tissues; analysing different tissues allows for a more detailed insight into the source of the element and the kind of exposure to it.

The present study aimed at determining the trace element concentrations within blood, gill arch, gill filament, kidney, liver, muscle and skin of *L. capensis* from the Vaal Dam, providing a more comprehensive view of *L. capensis* and its possible role as a sentinel organism as well as to determine the potential risk associated with the consumption of the muscle tissue.

MATERIALS AND METHODS

Sampling

Surface water, sediment and fish were collected in March 2013 at the Vaal Dam reservoir (26°52.249′ S; 28° 10.249′ E). Water and sediment samples were collected and stored in acid-washed polyethylene tubes. Rand Water Analytical Facility provided water quality data and trace element concentrations for filtered (0.45 µm) water samples for the Vaal Dam reservoir for a 7-month period ($n = 7$) up to the sampling date. Twenty-two (22) *L. capensis* specimens were collected with the aid of gill nets with mesh sizes of 70–120 mm, in order to catch fish of similar size. Fish were removed from the net, placed in a live well and transported back to shore. Fish were weighed, measured and blood was drawn from the dorsal aorta utilizing Lithium-Heparin Vacutainer tubes (Vaccuette, Greiner Bio-one). Thereafter the fish were euthanized by severing the spinal cord posterior to the head. Tissue samples (gill arch, gill filament, kidney, liver, muscle and skin) were collected from each fish utilizing stainless steel dissection instruments. Each tissue was separately stored in sterile 50 mL falcon tubes (Cellstar Tubes, Greiner Bio-one) and frozen at –21°C prior to analysis.

Tissue digestion and ICP analysis

Sub-samples of 100 mL water were filtered through 0.45 µm nitrocellulose filter paper (Merck Millipore) and acidified with 1.54 mL 65% Suprapur nitric acid (Merck, South Africa) and transferred into 15 mL falcon tubes (Cellstar Tubes, Greiner Bio-one). Sediment samples were removed from the freezer and allowed to thaw. Approximately 1 g ww (wet weight) of sediment was weighed out into acid-washed glass Petri dishes utilizing a Sartorius CP225D scale (readability: 0.01/0.1 mg). Frozen fish tissue samples were thawed, gills were separated into gill arches and gill filaments and approximately 1 g ww of each tissue, except blood, was weighed out with the Sartorius scale and placed on acid-washed Petri dishes. Tissue and sediment samples were placed in a drying oven at 100°C, and dried to the point where weights remained constant. Dry weights were recorded and dried samples were stored in a desiccator cabinet until digestion. Blood samples were thawed and approximately 2 mL of blood was directly utilized for digestion.

Approximately 2 mL of blood and 0.5 g of each dried sample was placed in acid-washed Teflon microwave digestion tubes and the required quantities of 65% Suprapur nitric acid (Merck, South Africa), 30% Suprapur hydrochloric acid (Merck, South Africa) and 30% hydrogen peroxide (Merck, South Africa) were added as per Table 1. The digestions were performed utilizing a CEM Mars6 digestion microwave. Post-digestion, the samples were decanted into acid-washed 50 mL volumetric flasks and diluted to 50 mL with Milli-Q water. The digested samples were transferred into 50 mL falcon tubes and stored at 4°C prior to analysis. Certified reference materials utilized include SRM 1643e Trace Elements in Water, SRM 2976 Mussel Tissue, DOLT-4 and LGC6187 River Sediment.

The analysis of Cu, Fe and Zn was performed utilizing an inductively coupled plasma optical emission spectrometer (Spectro Arcos ICP-OES FSH122), whilst the rest of the elements were analysed utilising an inductively coupled plasma mass spectrometer (Perkin Elmer NexION X series). Yttrium (100 µL) was used as an internal standard, added on-line to each sample using an internal standard mixing kit.

Statistical analysis

Statistical analysis was performed using IBP SPSS V.21 (Statistical Package for Social Sciences, SPSS Inc.) for Windows. The Pearson correlation test was performed to determine if correlations exist between the trace element concentrations for each tissue analysed. Significance in differences was identified if $P < 0.05$.

Bioconcentration factor

Bioconcentration factors (BCF) indicate the ratio in element concentrations between the environment and fish and allow for the determination of elemental partitioning between samples. The BCF values were calculated according to Abel (1989), using the mean concentration values of each element present in the water, sediment and fish tissues. The BCF values were calculated as below, with *C* representing the median concentration of the sample type.

TABLE 1
Quantities of the required chemicals for the digestion of each sample type

Sample Type	30% HCL	65% HNO_3	H_2O_2
Blood	–	10 mL	5 mL
Dry Tissue	–	10 mL	5 mL
Sediment	9 mL	3 mL	–
Filter Paper	9 mL	3 mL	–

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$$BCF = C_{Fish\ tissue}/C_{Water} \quad (1)$$

$$BCF = C_{Fish\ tissue}/C_{Sediment} \quad (2)$$

Target hazard quotient and risk assessment

The target hazard quotient (THQ) values were determined in order to assess possible risk associated with consumption of *L. capensis* muscle tissue, with regard to the trace element concentrations. The THQ values serve as an integrated risk index, comparing the ingested dose of a contaminant with the reference dose thereof; thus providing an integral parameter for risk assessment of the intake of trace elements within food (Storelli, 2008). The THQ for each element was determined utilizing standardized parameters as set by the US Environmental Protection Agency (USEPA, 2014). The THQ values were calculated using the parameters presented in Table 3. The element concentrations presented in Table 5 as µg/g dw were converted into µg/g ww using the factor which was recorded for each tissue during dry weight determination; these concentrations are presented in Table 6.

$$THQ = (EF_r \times ED_r \times IRF \times C)/(RfD_o \times BW \times AT) \quad (3)$$

THQ values obtained with the formula and standardized parameters presented in Table 3 provide a theoretical risk assessment for individual trace elements. Total hazard index (HI) was calculated to indicate the potential risk associated with the consumption of a combination of trace elements. The HI value was calculated from the sum of all of the THQ values for all of the elements analysed to produce a risk value (Bogdanović et al., 2014). The HI provides the total hazard index for all of the elements studied, utilizing the formula below with elements $n = 12$.

$$HI = \Sigma^n THQ \quad (4)$$

TABLE 2
Parameters utilized for calculation of THQ in accordance with USEPA (2014)

Variable		Symbol	Value
Average time of exposure (days)		AT	365
Body weight (kg)		BW	70
Elemental concentration (mg/kg)		C	*
Exposure duration (years)		EDr	30
Exposure frequency (days/year)		EFr	365
Fish consumption rate (kg/day)		IRF	0.054
Oral reference dose (mg/kg-day)		RfD0	
Trace element	**RfD0**	**Trace element**	**RfD0**
As	0.0003	Mn	0.14
Cd	0.001	Ni	0.02
Co	0.0003	Pb	**
Cr	1.5	Se	0.005
Cu	0.04	V	0.003
Fe	0.7	Zn	0.3

** Metal concentrations provided in Table 6*
*** No RfD0 for Pb has been set by the US EPA*

RESULTS

Water and sediment

Table 3 presents the concentrations of elements within the water and sediment from the Vaal Dam. Iron was present at the highest concentrations for both water and sediment. Se was the only trace element below the detection limits for the water analysed with ICP OES at the University of Johannesburg. The order of trace element concentrations for the sampled water, in descending order, was: Fe > Cu > Mn > Co > Ni > Zn > Pb > As > V > Cr > Cd , and for the sediment was: Fe > Mn > Cr > V > Zn > Ni > Cu > Pb > Co > As > Se > Cd.

Trace element concentrations within *L. capensis* tissues

Sampled fish were all of similar size, with mean standard length of 25.8 ± 4.5 cm and mean weight of 0.41 ± 0.17 kg. The trace element concentrations for the blood, gill arch, gill filament, kidney, liver, muscle and skin of *L. capensis* from the Vaal Dam reservoir are presented in Table 4. Elements which accumulated to the greatest extent within the fish tissues, in comparison to the water and sediment, included As in the gill arches, Mn in the gill filaments, Cd and Co in the kidneys and Cu, Se and Zn within the liver. The sediment recorded the highest concentrations for Cr, Fe and V and the water data received from Rand Water Analytical Facility indicated the highest concentration for Pb. The liver and

TABLE 3
Mean water quality parameters and element concentrations and standard deviation (SD) of the surface water from the Vaal Dam reservoir, obtained from Rand Water Analytical Facility for a seven month period prior to sampling ($n = 7$) and from water and sediment samples collected in March 2013, with the detection limits (LOD) for water and sediment; EC: electrical conductivity, DO: dissolved oxygen

Element	Water (µg/L)	SD	Sediment (µg/g dw)	SD	LOD (µg/L)
As	2.00 *	0.24	0.65	0.08	1.00*
Cd	0.47	0.36	0.002	0.0003	0.001
Co	21.9	53.16	1.32	0.17	0.002
Cr	1.22	2.16	24.85	3.04	0.003
Cu	32.6	25.8	4.52 *	0.57	2.50 *
Fe	158.3	69.9	4 280 *	533	2.00 *
Mn	31.7	36.4	35.89	4.34	0.004
Ni	6.07	5.12	4.55	0.576	0.002
Pb	2.5	3.23	1.61	0.19	0.001
Se	**	**	0.41	0.051	0.001
V	1.33	3.49	12.95	1.48	0.003
Zn	3.61	3.17	5.80 *	0.68	1.00 *
Parameter					
EC	21.5 mS/cm	1.25			
DO	7.46 mg/L	1.03			
pH	7.9	0.2			

** Analysis performed on ICP-OES*
*** Below detection limits*

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kidney accumulated most elements at higher concentrations in comparison to the other tissues. The liver accumulated the highest concentrations for Cu, Fe, Se and Zn whilst the kidney accumulated the highest concentrations for Cd, Co, Ni and Cu. The gill arch yielded the highest concentrations for As, Cr and V. The highest concentrations of Mn and Pb were present within the gill filament. The muscle and skin had lower concentrations with blood yielding the lowest concentrations of all of the analysed tissues.

The BCF values for each element were calculated for the trace elements in water and sediment compared with concentrations in the tissues of *L. capensis* (Table 5). The values from Table 5 indicate that As was present at higher levels in the gill arch, kidney and liver than in both the water and sediment. Cd was present at higher levels in the fish tissues than in sediment, but was only recorded at higher concentrations in kidney and liver than in the water. Co was present at higher levels within kidney than water and sediment. Cr, Ni and Pb possessed BCF

TABLE 4
Results of trace element concentrations (µg/g dw) present within the tissues of the *Labeo capensis*, *n* = 22, collected from the Vaal Dam reservoir in April 2013, with the highest median concentrations bolded

Element		Blood	Gill a	Gill	Kidney	Liver	Muscle	Skin
As	Mean	0.14	5.24	1.96	4.11	4.12	1.47	0.63
	Median	0.08	**3.87**	1.55	2.47	3.01	0.91	0.34
	SD	0.19	3.75	1.34	3.53	2.62	1.64	0.77
Cd	Mean	0.03	0.16	0.23	4.32	1.03	0.08	0.10
	Median	0.03	0.13	0.17	4.11	0.98	0.08	0.09
	SD	0.02	0.12	0.16	2.72	0.61	0.01	0.02
Co	Mean	0.03	0.17	0.25	6.818	0.44	0.03	0.09
	Median	0.01	0.15	0.22	**6.185**	0.42	0.03	0.09
	SD	0.05	0.05	0.08	3.414	0.13	0.01	0.03
Cr	Mean	0.16	1.37	1.42	0.3	0.41	0.22	0.31
	Median	0.17	**1.08**	0.97	0.17	0.27	0.18	0.22
	SD	0.1	0.95	1.09	0.34	0.46	0.17	0.25
Cu	Mean	0.48	2.43	3.33	25.44	782.6	1.55	7.99
	Median	0.4	2.35	2.89	13.87	**616.2**	1.59	1.56
	SD	0.27	0.96	1.19	36.31	540.6	0.86	24.92
Fe	Mean	127.5	23.69	229.3	356.5	1113	16.62	29
	Median	127.8	1.17	216.7	372.8	**798**	16.49	17.53
	SD	52.73	53.19	70.51	123.5	1405	10.25	31.67
Mn	Mean	0.31	54.63	65.25	6.38	9.8	1.5	1.87
	Median	0.16	34.45	**47.27**	5.78	9.68	1.44	1.4
	SD	0.68	37.03	42.1	2.92	3.23	0.83	1.52
Ni	Mean	0.21	0.39	0.31	2.2	0.83	0.13	0.27
	Median	0.02	0.28	0.28	**1.96**	0.46	0.11	0.21
	SD	0.28	0.33	0.11	1.01	1.24	0.08	0.18
Pb	Mean	0.02	1.91	2.14	0.47	0.26	0.04	0.24
	Median	0.01	0.54	**0.66**	0.46	0.19	0.02	0.08
	SD	0.04	3.05	3.58	0.22	0.31	0.04	0.41
Se	Mean	0.47	2.17	3.69	9.45	46.29	2.39	2.19
	Median	0.42	2.19	3.82	8.67	**42.32**	2.58	2.11
	SD	0.20	0.48	0.61	3.29	20.46	0.85	0.39
V	Mean	0.10	3.29	1.18	3.15	2.64	0.11	0.19
	Median	0.02	**3.29**	1.07	3	2.53	0.08	0.16
	SD	0.12	0.85	0.29	1.19	0.88	0.08	0.11
Zn	Mean	4.38	88.19	80.2	119.8	179.3	29.4	83.93
	Median	4.02	78.80	71.13	115.9	**156.0**	28.5	80.79
	SD	1.80	29.05	23.12	50.76	62.18	13.57	19.68

** Blood concentrations expressed in µg/g ww*

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TABLE 5
BCF values calculated between the median trace element concentrations of each *Labeo capensis* tissue compared to the water and sediment trace element concentrations. BCF values greater than 1 indicated in bold.

Water							
Element	**Blood**	**Gill a**	**Gill**	**Kidney**	**Liver**	**Muscle**	**Skin**
As	0.041	**1.93**	0.776	**1.24**	**1.50**	0.456	0.171
Cd	0.175	0.269	0.361	**8.78**	**2.09**	0.169	0.199
Co	0.004	0.007	0.010	0.282	0.019	0.001	0.004
Cr	0.067	0.886	0.796	0.14	0.219	0.145	0.182
Cu	0.003	0.072	0.089	0.426	**18.9**	0.049	0.048
Fe	0.001	0.007	**1.37**	**2.36**	**5.05**	0.104	0.111
Mn	0.003	1.09	**1.49**	0.182	0.305	0.045	0.044
Ni	0.014	0.046	0.046	0.323	0.075	0.019	0.035
Pb	0.033	0.216	0.264	0.185	0.076	0.009	0.033
Se	*	*	*	*	*	*	*
V	0.062	**2.47**	0.804	**2.26**	**1.9**	0.062	0.121
Zn	0.023	**21.8**	**19.8**	**32.1**	**43.2**	**7.9**	**22.4**
Sediment							
Element	**Blood**	**Gill a**	**Gill**	**Kidney**	**Liver**	**Muscle**	**Skin**
As	0.13	**5.92**	**2.37**	**3.78**	**4.61**	**1.4**	0.52
Cd	**13**	**63**	**84.5**	**2 054**	**488**	**39.5**	**46.5**
Co	0.01	0.11	0.17	**4.7**	0.32	0.02	0.07
Cr	0.01	0.04	0.039	0.007	0.01	0.007	0.01
Cu	0.09	0.52	0.64	**3.07**	**136.4**	0.35	0.34
Fe	0.03	0	0.05	0.09	0.19	0.004	0.004
Mn	0.004	0.96	**1.32**	0.16	0.27	0.04	0.04
Ni	0.003	0.06	0.06	0.43	0.10	0.03	0.05
Pb	0.008	0.34	0.41	0.29	0.12	0.01	0.05
Se	**1.03**	**5.37**	**9.36**	**21.26**	**103.7**	**6.32**	**5.17**
V	0.001	0.25	0.08	0.23	0.2	0.006	0.01
Zn	0.69	**13.59**	**12.27**	19.98	26.9	4.92	13.93

** BCF value could not be determined as elemental concentration was below detection in water samples*

values of less than 1, indicating that these elements occurred at higher concentrations within the environment than within the fish tissues. Fe had BCF values greater than 1 for kidney and gill filament when compared to the water, but compared to sediment this BCF was less than 1 for all fish tissues. The BCF (muscle/water) was greater than 1 only for Zn, whilst for the other elements these BCF values were less than 1. The BCF (muscle/sediment) was higher than 1 for As, Cd, Se and Zn while for all other measured elements the BCF was below 1 (see Table 5)

THQ values

The THQ values were determined for each trace element based on the parameters listed in Table 2 as set out by the US EPA (2014). The THQ values are presented within Table 6. The data presented in Table 6 reveal that As and Se had THQ values greater than 1 whilst all other elements under investigation had THQ values below 1. THQ values greater than 1 indicate potential risk to humans (Bogdanović et al., 2014). The HI value from the THQ values was 18.491, revealing that a potential risk exists with the consumption of *L. capensis* muscle tissue.

TABLE 6
Target Hazard Quotients (THQ) values for elemental concentrations present within the muscle tissue of L. capensis collected from the Vaal Dam reservoir

Element	Median conc.(µg/g	THQ Value
As	0.185	14.29
Cd	0.016	0.37
Co	0.006	0.45
Cr	0.036	0.001
Cu	0.323	0.19
Fe	3.35	0.11
Mn	0.292	0.05
Ni	0.023	0.03
Pb	0.005	*
Se	0.523	2.42
V	0.017	0.13
Zn	5.797	0.45

** THQ value could not be calculated for Pb as no RfD_o value has been set by the US EPA*

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DISCUSSION

Water and sediment

Analysis of the water samples indicated that most element concentrations were lower in the water than in sediment and fish tissues, but As, Cd, Co, Cu, Ni, Pb and Zn concentrations were higher in water than sediment. The underlying geology of the Vaal catchment area, comprised of pyrite, chalcopyrite and sphalerite deposits, may be the cause of the elevated levels of Cu, Fe and Zn within the water (DWAF, 1996). Gilbert and Avenant-Oldewage (2014) found similar trends for trace element concentrations but obtained higher values for Cu, Mn and Fe within the water. Retief et al. (2009) similarly found that the dominant trace elements within the water were Fe, Cu and Mn, and compared to the current study observed higher concentrations for all trace elements. The values for electrical conductivity (EC), dissolved oxygen (DO) and pH indicate quite stable conditions, at least for the 7-month period of investigations. The present conditions favour hydrolyses of the aquo complexes of most metal ions followed by the formation of hardly soluble oxides and hydroxides, which get sequestered into the sediment. Most metals present at the pH prevailing in the investigated water body exist as hydroxo complexes, which are far less bioavailavble than the 'pure' cation, explaining the relatively low BCF observed in our study (Sigg and Stumm, 1996).The sediment concentrations within this study reveal similar trends to those observed by Gilbert and Avenant-Oldewage (2014), Retief et al. (2009), and Gouws and Coetzee (1997), in which Fe, Mn, Cr, Cu and Zn were the dominant trace elements, but were present at higher concentrations than in the present study. Fe has remained the most dominant element, present at the highest concentrations in comparison to the other elements investigated within the sediment of the Vaal Dam reservoir over the past 16 years. Aprile and Bouvy (2008) similarly found Fe to be present at the highest concentration within the sediments of the Tapacurá River basin, occurring at concentrations of 19830 µg/g dw, greatly exceeding that found in the present study (4 280 µg/g dw).

Fish tissue concentrations

There is great variation in the accumulation of trace elements in the tissues of *L. capensis*, differing between each tissue type and trace element. The data presented in Table 4 indicate that the liver, kidney and gill tissues (both arch and filaments) had accumulated the trace elements to higher concentrations than the muscle, skin and blood of *L. capensis*. This is further evident in the BCF values determined in Table 5, as the liver, kidney and gill tissues had many BCF values greater than 1. Similar trends have been observed in previous studies conducted on fishes from the Vaal Dam reservoir, in which the gills, kidney and liver possess the highest element concentrations of the tissues studied (Retief et al., 2006; 2009; Crafford and Avenant-Oldewage, 2010; 2011; Gilbert and Avenant-Oldewage, 2014).

Functioning as the primary detoxification organ, the liver performs crucial roles in blood filtration and toxicant removal (Wood, 2012). It possesses high levels of metallothioneins which have high affinities for binding trace elements, which accounts for the higher element levels in this organ (Wood, 2012). In the present study, the liver had accumulated the highest concentrations of Cu, Fe, Se and Zn. Gilbert and Avenant-Oldewage (2014) found that the liver of *Labeobarbus kimberleyensis* (Gilchrist and Thompson, 1913) had accumulated the highest concentrations of Cu (11.68 µg/g dw), Fe (113.22 µg/g dw), Se (2.57 µg/g dw) and Zn (32.6 µg/g dw), whilst Crafford and Avenant-Oldewage (2011) found that livers of *Clarias gariepinus* Burchell, 1822 had accumulated higher Cu (40.22 µg/g dw), Fe (2041.79 µg/g dw) and Zn (76.61 µg/g dw) levels than other tissues. In comparison to the these studies, *L. capensis* liver tissue possessed higher concentrations of Cu, Fe, Se and Zn. Trace elements associated with the blood of fish, such as Cu, Fe and Zn, are expected to occur at higher concentrations within the liver (Carvalho and Fernandes, 2006). High levels of Se within the liver have similarly been shown by Gilbert and Avenant-Oldewage (2014) for *L. kimberleyensis* and by Jarić et al. (2011) for *Acipenser ruthenus*.

The kidney also functions in detoxification, but serves as the primary excretory organ of fish (Wood, 2012). Amiard et al. (2006) associated the high detoxification role and trace element sequestration potential of kidney tissue to the presence of metallothioneins within this organ. In the current study, Cd (4.11 µg/g dw), Co (6.185 µg/g dw) and Ni (1.96 µg/g dw) were present at their highest concentrations within the kidney. Both Cd (Ashraf, 2005) and Ni (De Boek et al., 2010) have been associated with the kidneys of fish, and Gilbert and Avenant-Oldewage (2014) found Ni (0.251 µg/g dw) to be present at high concentrations within kidney, second only to liver. The presence of high Co concentrations in the kidney may be attributed to its role in blood pressure regulation (Fallah et al., 2011). Cadmium possesses low trophic transfer rates, and occurs at higher concentrations in organisms of lower trophic levels (Simon and Garnier-Lapace, 2005).

Gills consist of the gill arch and gill filaments, and function as the primary respiratory organs (Wood, 2012). The arch and filament are often studied together as whole gills (Jirsa et al., 2008; Squadrone et al., 2013; Subotić et al., 2013; Gilbert and Avenant-Oldewage, 2014), but are also investigated separately (Crafford and Avenant-Oldewage, 2010; 2011). The present study found As (3.87 µg/g dw), Cr (1.08 µg/g dw) and V (3.29 µg/g dw) accumulated to the greatest extent in the gill arch, with Mn (47.27 µg/g dw) and Pb (0.66 µg/g dw) found at the highest concentrations in the gill filaments. In comparison to studies by Crafford and Avenant-Oldewage (2010; 2011), Pb (13.07 µg/g dw) accumulated to the greatest extent in the gill filament, while Mn (34.06 µg/g dw) accumulated to the greatest extent in the gill arch, with the gill filament displaying the next highest concentration of Mn (25.75 µg/g dw). The high Mn concentrations corroborate trends observed in studies on *Silurus glanis* (Squadrone et al., 2013) and *Lota lota* (Subotić et al., 2013) in which the gill tissues possessed the highest Mn concentrations in relation to all tissues studied. Squadrone et al. (2013) concluded that increased Pb concentrations in gill tissue may be attributed to the lower pH values resulting from increased carbon dioxide levels within the gill chamber, but also indicate an at least temporary pollution of the water phase, as they serve as the main uptake route for this element. Squadrone et al. (2013) found that Cr (0.15 µg/g dw) had accumulated to the highest levels in gill tissue, but this value was lower than that obtained for the gill arches and filaments within the present study. Chen and Folt (2000) described that As did not biomagnify, but rather biodiminished, decreasing in concentration through increasing trophic levels.

Trace elements taken up by fish are transported throughout the body by the blood (Wood, 2012). Blood is seldom investigated; Sturrock et al. (2013) summarized previous studies involving fish blood, which showed that only Cu, Mn, Se and Zn have been studied for blood. Trace elements found to be

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present within *L. capensis* blood were all present at the lowest concentrations compared to the other tissues. Cu (0.4 µg/g ww), Fe (127.8 µg/g ww) and Zn (4.02 µg/g ww) were found to be the elements present at relatively high concentrations within the blood of *L. capensis*, which is understandable as these four elements are commonly associated with fish blood (DWAF, 1996). Sturrock et al. (2013) found greater Cu (0.84 µg/g) and lower Zn (0.7 µg/g) values for *C. carpio* in comparison to the earlier studies cited in their paper; however the specimens utilized in Sturrock et al.'s study underwent laboratory exposure unlike the *L. capensis* utilised in the present study which was collected from an impoundment.

The dominant elements within *L. capensis* muscle tissue were As, Cu, Fe, Mn, Se and Zn, which were present at higher concentrations than Cd, Co, Cr, Ni, Pb and V. High concentrations of Cu (1.59 µg/g dw), Fe (16.49 µg/g dw) and Zn (29.4 µg/g dw) in muscle are not surprising in this tissue and these findings corroborate previous studies (Wepener et al., 2011; Subotić et al., 2013; Gilbert and Avenant-Oldewage, 2014). Furthermore, in comparison to other elements within muscle tissue, previous studies have reported high As, Mn and Se concentrations. Subotić et al. (2013) found that As (0.93 µg/g dw), Mn (0.65 µg/g dw) and Se (0.05 µg/g dw) were present at higher concentrations than other elements studied for *C. carpio*, and Gilbert and Avenant-Oldewage (2014) found Se (0.653 µg/g dw) to be present at higher levels within muscle tissue than gills of *L. kimberleyensis*. The present study found *L. capensis* to have a slightly lower concentration of As (0.91 µg/g dw) and higher concentrations of Mn (1.44 µg/g dw) and Se (2.58 µg/g dw) in comparison to the aforementioned studies. Elevated Se concentrations may also be attributed to As concentrations, as Se functions in As detoxification (Sah et al., 2013). Otachi et al. (2014) found higher concentrations of Mn (2.43 µg/g dw) and Zn (604 µg/g dw) and lower concentrations of Cu (0.54 µg/g dw), Fe (14.3 µg/g dw) and Pb (0.024 µg/g dw) in the muscle tissue of *Oreochromis leucostictus* from Lake Naivasha in comparison to that of *L. capensis*. The increased levels of Zn in *O. leucostictus* muscle tissue may be associated with the increased Zn concentrations within the sediment of Lake Naivasha, 229.6 µg/g dw in comparison to 5.8 µg/g dw for the sediment of the Vaal Dam.

Skin is a seldom-studied tissue for element analysis, but is often consumed along with muscle tissue (Zeng et al., 2012). Serving as a protective layer, skin is in direct contact with the ambient environment, similarly to the gills, and trace elements may accumulate within skin (Uysal et al., 2008). Trace elements studied all occurred at low concentrations within skin, and the trend observed corroborates that of previous studies (Uysal et al., 2008; Zeng et al., 2012). The values obtained for *Chelon labrosus* skin by Uysal et al. (2008) were as follows: Cu (1.47 µg/g dw), Co (0.56 µg/g dw), Cr (0.32 µg/g dw), Fe (14.69 µg/g dw), Mn (0.51 µg/g dw) and Zn (20.51 µg/g dw). Those obtained by Zeng et al. (2012) for *Cyprinus carpio* skin were as follows: Cd (0.03 µg/g dw), Cr (1.10 µg/g dw), Cu (2.03 µg/g dw), Mn (0.74 µg/g dw), Ni (0.34 µg/g dw), Pb (0.16 µg/g dw) and Zn (245.67 µg/g dw). In comparison to these studies, *L. capensis* skin possessed lower values for Zn (80.79 µg/g dw), Ni (0.21 µg/g dw) and Pb (0.08 µg/g dw) and higher values for Fe (17.53 µg/g dw) and Mn (1.4 µg/g dw). The Cr (0.22 µg/g dw) and Co (0.09 µg/g dw) values obtained for *L. capensis* were lower than those obtained by Uysal et al. (2008), probably due to the differing physiological roles of skin for estuarine fish vs. freshwater fish, which affects the transcutaneous uptake of metals (Uysal et al., 2008). The skin Cd concentration (0.093 µg/g dw) for *L. capensis* was higher than that obtained by Zeng et al. (2012), possibly due to increased transcutaneous uptake of Cd from the water.

Target health quotients and risk assessment

The calculated THQ values for *L. capensis* provide a hypothetical risk assessment based on the standardized parameters (Table 2), as no data were collected through surveys to determine the average weight of adults within the area, nor the average fish meal size or consumption frequency.

The calculated THQ values presented in Table 6 indicate that only As (14.29) and Se (2.42) had THQ values greater than 1, indicating a potential risk for fish consumers. The risk is further reinforced by the median As wet weight concentration of 0.185 µg/g, which is greater than the provisional maximum tolerable daily intake value of 0.1 µg/g as set by the FAO/WHO (2011) (Table 7). A similar study performed by Gilbert and Avenant-Oldewage (2014) on *L. kimberleyensis* obtained a THQ value of 0.962 for As; however, this value was obtained utilizing the dry weight concentrations for the specimens. Similarly, the median wet weight Se concentration of 0.523 µg/g surpasses the provisional maximum tolerable daily intake values of FAO/WHO (0.3 µg/g). All other investigated elements gave THQ values below 1, revealing that, individually, they did not pose a risk to humans. However, the HI value of 18.491 reveals that a potential risk exists for humans consuming these fish,

TABLE 7
Summary of provisional maximum tolerable daily intake values for human consumption of contaminated fish muscle for the trace elements (µg/g) under investigation from literature in comparison to the median wet weight concentrations obtained for *Labeo capensis* muscle tissue

Permissible daily element concentration limit (µg/g)												Source
As	Cd	Co*	Cr	Cu	Fe*	Mn	Ni	Pb	Se	V*	Zn	
1.2	4											USEPA, 2000
1.4	0.3		1	20			80	1.5			5	FAO/WHO, 1984
			0.15	30								FEPA, 2003
	0.5							2				WHO, 1993
	10			50				5-30			200–500	WHO, 1982
0.1				10				0.5	0.3		40	FAO/WHO, 2011
	0.05							0.3				EU, 2006
0.185	0.016	0.006	0.036	0.323	3.35	0.292	0.023	0.005	0.523	0.017	5.79	Results of present study

** Permissible daily limit not available yet*

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based on the combination of elements investigated. Otachi et al. (2014) had obtained THQ values which exceed that of the current study for Cd (0.98), Cu (0.018), Mn (0.023) and Zn (2.67), but not for Cu (0.019), in the muscle of *O. leucostictus* ,. Similarly, *O. leucostictus* presented a health risk to fish consumers within Lake Naivasha, Kenya, as THQ values for Li and Zn were greater than 1, and the concentrations of Li and Cd had surpassed the respective provisional maximum tolerable daily intake concentrations.

CONCLUSION

The study indicates that *L. capensis* effectively accumulates trace elements, some to higher concentrations than that present in the water, but to lower levels than is present in the sediment of the Vaal Dam reservoir. Trace element concentrations accumulated by *L. capensis* exceed that of *L. kimberleyensis*, but are lower than those recorded for *C. gariepinus* from the Vaal Dam reservoir. The liver, kidney and gills (arch and filaments) accumulated trace elements to the highest concentrations in comparison to skin, muscle and blood, a trend often noted in previous studies. A health risk is also associated with the consumption of *L. capensis* muscle tissue as As and Se recorded THQ values greater than 1. The risk to humans is further inferred by the HI value of 18.491. However, this should be confirmed in follow-up surveys of the local population in the Vaal Dam area. Furthermore, the mean muscle concentrations for As and Se are above the recommended provisional maximum tolerable daily intake values outlined by various global institutions, reinforcing the risk of exposure through consumption of *L. capensis* muscle tissue. It is recommended that trace element concentrations within *L. capensis* be monitored to determine if the trend identified above is maintained, and that future studies performed within the Vaal Dam reservoir should be accompanied by accurate determination of health risk factors for the local population relying on fish from this system as a regular food source.

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