

An Integrated Health Risk Evaluation of Toxic Heavy Metals in Water from Richards Bay, South Africa

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Abstract

Heavy metals may affect human health in diverse ways ranging from cancer, reduced growth and development of nervous system damage, organ damage and in extreme cases, death. This study assessed the hazards of heavy metal based on target hazard quotient (THQ), derived from concentrations of heavy metals in water. Eighty-eight (88) water samples were collected from five sources and analyzed for lead (Pb), chromium (Cr), cadmium (Cd), iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) using inductively couple plasma and mass spectrometer (ICP-MS). Their health risks were assessed for oral ingestion and dermal absorption. The non-carcinogenic effects of these metals due to ingestion were found to be in a decreasing order: stream water>effluent water>Indian Ocean>Mzingazi river>Esikhawini tap water. Whereas via dermal absorption, the effects decrease in the order: effluent water>stream water>Mzingazi river>Esikhawini tap water>Indian Ocean. Additionally, carcinogenic risks were found to range from 1.03×10^{-10} - 6.56×10^{-7} in effluent water, 1.14×10^{-8} - 2.22×10^{-7} in stream, 5.15×10^{-11} - 2.61×10^{-7} in Indian ocean, 4.07×10^{-9} - 1.41×10^{-7} in Esikhawini tap water and 5.15×10^{-11} - 2.71×10^{-7} in Mzingazi river. The Hazard indexes of these selected metals in effluent water, river, Indian ocean and Esikhawini tap water were found to be less than a unity, indicating an unlikely health risk to the population using water from these sources.

Keywords: Carcinogenic; Health effects; Heavy metals; Non-carcinogens; Water

Introduction

Anthropogenic activities including industrial processes and mining are the major sources of heavy metals contamination in water [1]. Water is a universal solvent capable of self-decontamination while heavy metals remain the main pollutants of water on an account of accumulation over time [2]. Human exposure to heavy metals is worrisome due to their non-biodegradable nature [3]. Diseases such as abdominal pain, anorexia, cardiovascular diseases, immune dysfunction, hypertension, liver and kidney related disorders, as well as various kinds of cancers could be caused by excessive intake of heavy metals in contaminated water [3,4]. Therefore, contaminated water poses a serious risk to human lives especially in developing countries. In KwaZulu Natal, 14% of population have tap water more than 200 meters away from their houses, while 7.6% do not have access to tap water at all [5]. Hence, they utilize untreated water from other sources including rivers, streams, lakes and Indian Ocean for domestic [5]. Consequently, dermal and oral exposure from heavy metals is the most likely route for human exposure to heavy metals in occupational and residential areas within Richards Bay precinct.

Richards Bay is located on latitude 28.7807° S, 32.0383° E [6] the eastern shores of South Africa (Figure 1), about 180 km north of Durban. It is one of the fastest growing industrial areas in South Africa [7]. Far above 2.0 million metric tonnes of titanium products (titania slag, high purity pig-iron, rutile and zircon) and chemicals products are produced annually in Richards area [7]. These industrial products might introduce toxic heavy metals into the environment which may likely cause adverse health effects to the general public [8]. Susceptibility to diseases and high mortality rate has been associated to living near Industrial areas [8,9].

Studies have been conducted in water samples at Richards Bay but were only limited to vegetation changes due to presence of minerals in water [10], the extent of chemical contaminations [11], saline intrusion

[12] and radiological health risks [13]. The United State Environmental Protection Agency (US EPA) reported that heavy metals enter the human body through several pathways such as food chain, soil ingestion, dermal contact, fume and particles inhalation through mouth and nose [14]. Heavy metals entering the body via ingestion and skin absorption might induce carcinogenic and non-carcinogenic health risks. The present study was design to quantify the concentrations and health risk associated with heavy metals (Pb, Cd, Cr, Fe, Mn, Cu and Zn) in major water sources within Richards's precinct. Internal exposure due to oral ingestion of the aforementioned selected heavy metal is important from the health perspective [15]. Experimental data were used to evaluate the health safety associated with exposure to these heavy metals. The assessment results provided critical environmental health risks to users of water in Richards Bay.

Methods

After a pre-field survey to map out major water sources within Richards Bay, eighty-eight (88) surface water samples were collected from five water sources (Figure 1): Esikhawini tap water, Mzingazi river, effluent water, Indian Ocean and stream water. At each water source, a number of samples were collected from the same calm position except samples from Indian Ocean assuming uniformity of metals in the source owing to the nature of the source which is either continual flow or stagnant. Samples were collected into two litre plastic bottles based

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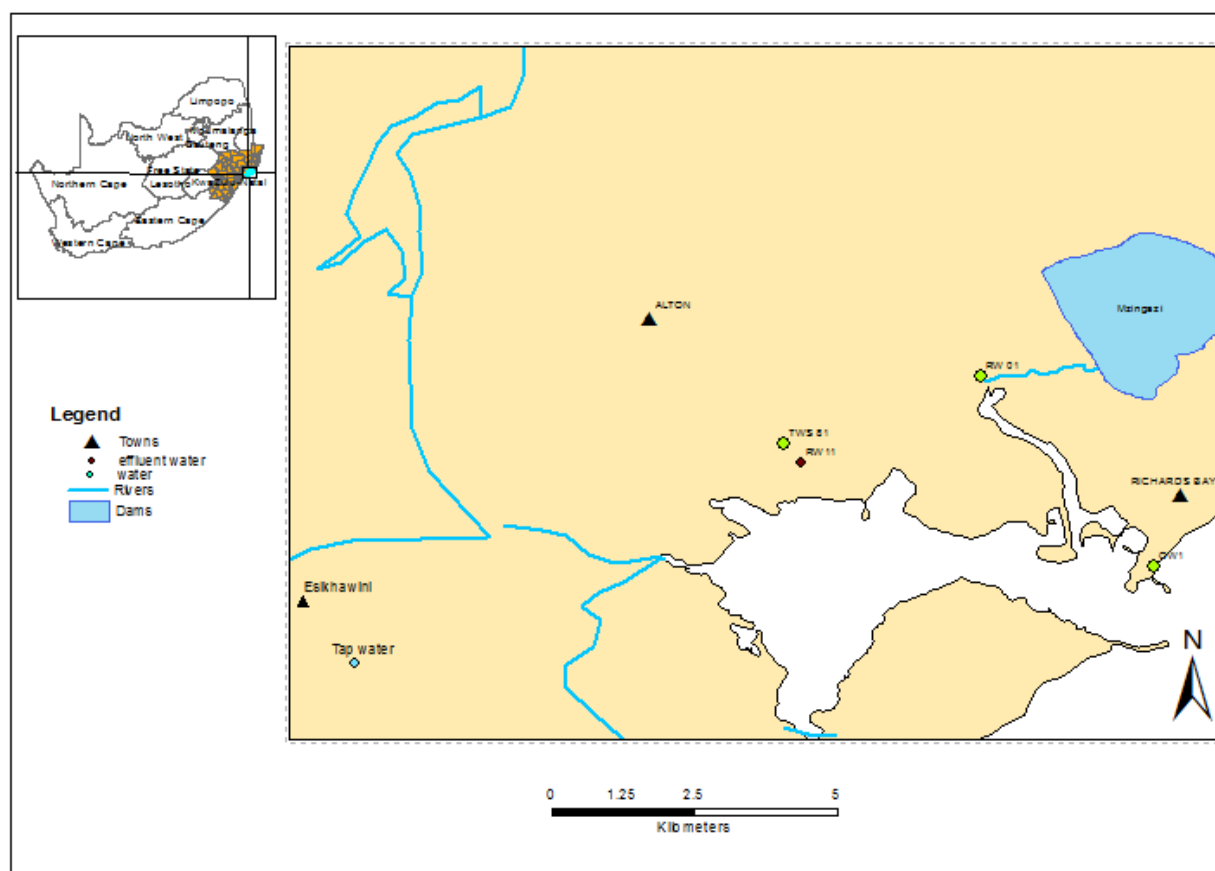


Figure 1: Study map area showing location of Richards Bay and the five water sampling points.

on the South Africa National Standard techniques (SANS) for water quality sampling [16]. Sampling containers were previously washed with tap water and rinsed with distilled water. The collected samples were immediately acidified with ultra-purified 6 M HNO_3 to a $\text{pH} \leq 2$ to keep the metals in solution and prevent them from adhering to the walls of the container [17]. Collected water samples were transported to the University of Johannesburg analytical chemistry laboratory in iceboxes and refrigerated at 4°C until analysis are carried out.

Prior to analysis, samples were filter using a pre-washed $0.45 \mu\text{m}$ pores membrane filter to remove all solid materials. The traced metals were analytically determine using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS: NexION 300D, Perkin Elmer, USA). The spectrometer was carried out by means of the blank solution and four working standard solutions (100, 200, 300 and $400 \mu\text{g.l}^{-1}$) for all the seven elements, starting from a $1000 \mu\text{g.l}^{-1}$ single standard solutions for ICP-MS. All chemicals and reagents used were of analytical grade.

For quality control, quality laboratory methods including standard operating procedure, detector calibration with standards, analysis of a blank sample and replicate analysis, were ensured to guarantee the quality of the analytical data.

Human Health Risk Assessment

The methods proposed for estimation of potential health risks of pollutants were mainly separated into carcinogenic and non-carcinogenic [17]. For carcinogenic contaminants, the observed

exposure concentrations were compared with thresholds for adverse effects or the toxicant reference value (TRV) as determined by dose effect relationships [18].

However, carcinogenic method was only applied to quantify the magnitude of health risks of carcinogenic pollutants, but do not quantify the magnitude of health risk of non-carcinogenic pollutants [17]. The non-carcinogenic risks effects are typically based on the target hazard quotient (THQ) [17]. Target hazard quotient is a parameter used to determined exposure dose to pollutant referred to as reference dose (RD). If the quotient is less than 1, there will be no obvious health risk [17]. Conversely, a concern on exposure to these pollutants would be the health risks if THQ is equal to or greater than the RD [17]. Although the THQ-based health risk assessment method does not provide a quantitative estimation of the probability of an exposed population to experience health effect, it provides an indication of the health risk level due to these pollutants [17]. The health risk estimation method has recently been used by Chien et al. [19] and had proven to be effective and worthwhile, hence adopted and utilized in the present study to analyze the health risks associated with pollutants in samples collected from Richards Bay precinct.

Strategies for integrated human health risks assessments

Exposure assessment: Metals arrive inside the human body through several pathways, oral ingestion being the most worrisome pathway [20] hence chronic daily intake (CDI) through drinking water was calculated using equation 1 modified by Muhammad et al. [20] and Shah et al. [21].

$$CDI \left(\frac{\mu\text{g}}{\text{kg}\cdot\text{day}} \right) = \frac{C_{Mw} \times I_R}{B_W} \quad (1)$$

where C_{Mw} is the concentrations of heavy metals in water taken from Table 1, While I_R and B_W are daily water ingestion rate and body weights respectively. The value of these parameters are presented in Table 2.

Similarly, the annual exposure due to ingestion and dermal exposure were also calculated using equations 2 and 3 respectively [17].

$$Exp_{(ing)} = \frac{C_{Mw} \times I_R \times E_F \times E_D}{B_W \times A_T} \quad (2)$$

$$Exp_{(derm)} = \frac{C_{Mw} \times I_R \times E_F \times E_D \times S_A \times P_C \times C_F}{B_W \times A_T} \quad (3)$$

Such that $A_T = E_F \times E_D$

where $Exp_{(ing)}$ and $Exp_{(derm)}$ are the exposure dose rates ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$) through ingestion as well as dermal respectively. E_F , E_D , A_T , S_A , P_C , C_F are exposure frequency, exposure duration, average exposure time, skin area, dermal permeability coefficient and unit conversion factor respectively. The values for these parameters are presented in Table 2 except for P_C which is presented in Table 1.

Non-carcinogenic risk estimations: For non-carcinogenic health risk assessment, Hazard Quotient (HQ) were established for ingestion and dermal exposure routes by means of using equations 4 and 5 respectively adopted from [17,22].

$$HQ_{(ing)} = \frac{Exp_{(ing)}}{RD_{(ing)}} \quad (4)$$

$$HQ_{(derm)} = \frac{Exp_{(derm)}}{RD_{(derm)}} \quad (5)$$

Where $HQ_{(ing)}$ (unit less) and $HQ_{(derm)}$ (unit less) are the hazards quotient via ingestion and dermal contact respectively. $RD_{(ing)}$ and $RD_{(derm)}$ are reference doses (RD) for ingestion (ing) and dermal (derm) exposure in units of ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$).

If the HQ is from n different metals, the non-carcinogenic effects were estimated as a summation of all the HQ due to individual metals which gives the Hazard Index (HI) [17,22]. The HI was calculated using equations 6 and 7 for ingestion and dermal exposure

$$HI_{(ing)} = \sum_{i=1}^n HQ_{(ing)n} = \sum_{i=1}^n \frac{Exp_{(ing)n}}{RD_{(ing)n}} \quad (6)$$

where $HI_{(ing)}$ is the Hazard Index (unit less) via ingestion of the n different metals.

$$HI_{(derm)} = \sum_{i=1}^n HQ_{(derm)n} = \sum_{i=1}^n \frac{Exp_{(derm)n}}{RD_{(derm)n}} \quad (7)$$

$HI_{(derm)}$ is the Hazard Index (unit less) via dermal contact with the n different metals $HI_{(derm)n}$, $Exp_{(derm)n}$, $RD_{(derm)n}$ are the values for individual metals.

Carcinogenic risk calculations: Carcinogenic health risks are expressed by their cancer slope factor (CSF) which converts the estimated exposure via intake of metals into incremental risk of an individual developing cancer over time [17]. Carcinogenic health risks of Richards Bay precinct population using water from these sources were calculated using equation (8) as applied by Iqbal et al. [3] adopted from USEPA 2010.

$$Risk_{(ing)} = \frac{Exp_{(ing)}}{CSF_{(ing)}} \quad (8)$$

where $Risk_{(ing)}$ (unit less) is the carcinogenic risk via ingestion, $CSF_{(ing)}$ is the carcinogenic slope factor via ingestion ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$). The CSF values used in this estimation were adopted from South African Department of Environmental Affairs and the United States Environmental Protection Agency and are presented in Table 1.

Results Presentation

The mean concentrations of heavy metals from various water sampling sources are presented in Table 3. The data were used to estimate the intake and health risks of these metals to the residents of Richards Bay. Chronic daily ingestion (CDI), oral ingestion $Exp_{(ing)}$, dermal exposure $Exp_{(derm)}$, ingestion hazards quotient ($HQ_{(ing)}$) and dermal hazards quotient $HQ_{(derm)}$ were all estimated and presented in Table 4.

The hazard quotient due to ingestion and dermal absorption of Pb, Cr, Cd, Fe, Mn, Cu and Zn are shown in Table 4, columns 2-8. To evaluate the probability of suffering an adverse health effect with time, Hazard Index (HI) which is a summation of the contributions HQs from each metal was obtained for ingestion and dermal exposure and presented in Table 4 column 9.

Table 5 present the carcinogenic health risks were calculated from equation 8 using carcinogenic slope factors (CSF) from Table 1. In Table 6, the metal concentrations in this study were compared with other countries of the world as well as the permissible limits set by South African Department of Water Affairs and Forestry (DWAF) [23], United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) [24].

Discussion of Results

Non-carcinogenic health risk assessment

From Table 4 column 9, the stream is the most contaminated

Elements	P_c (cm.h ⁻¹)	(RD) _(ing) ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$)	(RD) _(derm) ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$)	(CSF) ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$)
Pb	4.0×10^{-3}	1.4	0.42	8.5×10^0
Cr	2.0×10^{-3}	3	0.075	5.0×10^2
Cd	1.0×10^{-3}	0.5	0.025	6.1×10^3
Fe	1.0×10^{-3}	700	140	n/a
Mn	1.0×10^{-3}	24	0.96	n/a
Cu	1.0×10^{-3}	40	8	n/a
Zn	6.0×10^{-4}	300	60	n/a
Tolerance _a	n/a	n/a	n/a	1.0×10^{-6} - 1.0×10^4

^a(US EPA, 2011); n/a: Not available

Table 1: Permeability coefficient (p_c), Reference doses and Carcinogenic Slope Factors (CSF) for various heavy metals and the values are obtained from.

Parameters	Units	EF
Water ingestion rate (I_R)	L/day	2.2
Exposure frequency (E_F)	days/year	365
Exposed skin area (S_A)	cm ²	28,000
Average exposure time (A_T)	H/day	0.52
Exposure duration (E_D)	years	30
Average body (B_W)	kg	70
Exposure time (E_T)	days	10,950
Unit conversion factor (C_F)	L/cm ³	0.001

Table 2: Exposure factors (EF) for heavy metals exposure assessment in water as used in this study.

Sample ID	Sampling locations	No of samples	Concentrations of metals (µg.l ⁻¹)						
			Pb	Cr	Cd	Fe	Mn	Cu	Zn
STRM	Stream	16	0.02 ± 1.47	0.06 ± 0.96	2.21 ± 1.22	3.53 ± 0.99	719.41 ± 2.73	21.73 ± 0.22	0.91 ± 0.84
EFFT	Effluent	18	0.01 ± 0.83	0.01 ± 0.29	0.02 ± 1.46	10.44 ± 2.33	245.64 ± 1.97	10.64 ± 0.61	28.94 ± 0.44
OWN	Indian Ocean	16	0.02 ± 0.31	0.39 ± 0.17	0.01 ± 0.42	4.16 ± 1.48	0.61 ± 0.49	42.13 ± 1.51	7.49 ± 2.01
Tap	Esikhawini Tap water	21	0.01 ± 1.22	0.01 ± 2.01	0.79 ± 1.02	22.38 ± 1.27	5.33 ± 1.84	16.88 ± 2.01	4.24 ± 0.98
RVR	Mzingazi River	17	0.01 ± 0.16	0.27 ± 0.33	0.01 ± 0.51	4.31 ± 0.66	17.67 ± 0.19	2.56 ± 0.74	2.56 ± 0.82

Table 3: Average concentration of heavy metals in water samples collected from five water sources (Esikhawini drinking tap, Indian Ocean, Mzingazi lake, effluent and stream).

Elements	Pb	Cr	Cd	Fe	Mn	Cu	Zn	HI (ing.derm ⁻¹)
Stream								
CDI	6.69 × 10 ⁻⁴	1.89 × 10 ⁻³	6.95 × 10 ⁻²	1.11 × 10 ⁻¹	2.26 × 10 ¹	6.83 × 10 ⁻¹	2.86 × 10 ⁻²	N/A
(Exp _(ing))	6.29 × 10 ⁻⁴	1.89 × 10 ⁻³	6.95 × 10 ⁻²	1.11 × 10 ⁻¹	2.26 × 10 ¹	6.83 × 10 ⁻¹	2.86 × 10 ⁻²	n/a
(Exp _(derm))	1.60 × 10 ⁻⁵	2.40 × 10 ⁻⁵	4.42 × 10 ⁻⁴	7.06 × 10 ⁻⁴	1.44 × 10 ⁻²	4.35 × 10 ⁻²	1.09 × 10 ⁻⁴	n/a
(HQ _(ing))	4.49 × 10 ⁻⁴	6.29 × 10 ⁻⁴	1.39 × 10 ⁻¹	1.59 × 10 ⁻⁴	9.42 × 10 ⁻¹	1.71 × 10 ⁻²	9.53 × 10 ⁻⁵	1.09 × 10 ⁰
(HQ _(derm))	3.81 × 10 ⁻⁵	3.2 × 10 ⁻⁴	1.77 × 10 ⁻²	5.04 × 10 ⁻⁶	14.90 × 10 ⁻¹	5.4 × 10 ⁻⁴	1.82 × 10 ⁻⁶	1.68 × 10 ⁻²
Effluent								
CDI	3.1 × 10 ⁻⁴	3.10 × 10 ⁻⁴	6.30 × 10 ⁻⁴	3.30 × 10 ⁻¹	77.20 × 10 ⁻¹	3.34 × 10 ⁻¹	9.10 × 10 ⁻¹	n/a
(Exp _(ing))	3.14 × 10 ⁻⁴	3.14 × 10 ⁻⁴	6.28 × 10 ⁻⁴	3.28 × 10 ⁻¹	77.20 × 10 ⁻¹	3.34 × 10 ⁻¹	9.09 × 10 ⁻¹	n/a
(Exp _(derm))	8.00 × 10 ⁻⁶	4.00 × 10 ⁻⁶	4.00 × 10 ⁻⁶	2.08 × 10 ⁻³	4.91 × 10 ⁻²	2.13 × 10 ⁻³	3.47 × 10 ⁻³	n/a
(HQ _(ing))	2.20 × 10 ⁻⁴	1.10 × 10 ⁻⁴	1.3 × 10 ⁻³	4.69 × 10 ⁻⁴	3.2 × 10 ⁻¹	8.36 × 10 ⁻³	3.03 × 10 ⁻³	3.35 × 10 ⁻¹
(HQ _(derm))	1.33 × 10 ⁻⁷	6.67 × 10 ⁻⁸	6.67 × 10 ⁻⁸	1.49 × 10 ⁻⁵	5.12 × 10 ⁻²	2.66 × 10 ⁻⁴	5.79 × 10 ⁻⁵	5.15 × 10 ⁻²
Indian ocean								
CDI	3.14 × 10 ⁻⁴	1.23 × 10 ⁻²	3.14 × 10 ⁻⁴	1.31 × 10 ⁻¹	1.91 × 10 ⁻²	1.32 × 10 ⁰	2.35 × 10 ⁻¹	n/a
(Exp _(ing))	3.14 × 10 ⁻⁴	1.23 × 10 ⁻²	3.13 × 10 ⁻⁴	1.31 × 10 ⁻¹	1.91 × 10 ⁻¹	1.32 × 10 ⁰	2.35 × 10 ⁻¹	n/a
(Exp _(derm))	8.00 × 10 ⁻⁶	1.56 × 10 ⁻⁴	2.00 × 10 ⁻⁶	8.32 × 10 ⁻⁴	1.21 × 10 ⁻⁴	8.43 × 10 ⁻³	8.99 × 10 ⁻⁴	n/a
(HQ _(ing))	1.05 × 10 ⁻⁶	4.09 × 10 ⁻³	1.05 × 10 ⁻⁶	1.87 × 10 ⁻⁴	7.94 × 10 ⁻⁴	3.31 × 10 ⁻²	7.85 × 10 ⁻⁴	3.89 × 10 ⁻²
(HQ _(derm))	1.33 × 10 ⁻⁷	2.60 × 10 ⁻⁶	3.33 × 10 ⁻⁸	5.94 × 10 ⁻⁶	1.26 × 10 ⁻⁴	1.05 × 10 ⁻³	1.49 × 10 ⁻⁵	1.20 × 10 ⁻³
Mzingazi Lake								
CDI	3.14 × 10 ⁻⁴	7.54 × 10 ⁻³	3.14 × 10 ⁻⁴	1.36 × 10 ⁻¹	5.56 × 10 ⁻¹	8.05 × 10 ⁻²	1.41 × 10 ⁻¹	n/a
(Exp _(ing))	3.14 × 10 ⁻⁴	7.54 × 10 ⁻¹	3.14 × 10 ⁻⁴	1.36 × 10 ⁻¹	5.56 × 10 ⁻¹	8.05 × 10 ⁻²	1.41 × 10 ⁻¹	n/a
(Exp _(derm))	8.00 × 10 ⁻⁶	9.60 × 10 ⁻⁵	2.00 × 10 ⁻⁶	8.62 × 10 ⁻⁴	3.54 × 10 ⁻³	5.12 × 10 ⁻⁴	5.39 × 10 ⁻⁴	n/a
(HQ _(ing))	1.05 × 10 ⁻⁶	2.5 × 10 ⁻³	1.05 × 10 ⁻⁶	1.94 × 10 ⁻⁴	2.31 × 10 ⁻²	2.01 × 10 ⁻³	4.70 × 10 ⁻⁴	2.83 × 10 ⁻²
(HQ _(derm))	1.33 × 10 ⁻⁷	1.60 × 10 ⁻⁶	3.33 × 10 ⁻⁸	6.16 × 10 ⁻⁶	3.68 × 10 ⁻³	6.40 × 10 ⁻⁵	8.98 × 10 ⁻⁶	3.76 × 10 ⁻³
Esikhawini Tap water								
CDI	3.14 × 10 ⁻⁵	3.14 × 10 ⁻⁴	2.48 × 10 ⁻²	7.03 × 10 ⁻¹	1.67 × 10 ⁻¹	5.31 × 10 ⁻¹	1.33 × 10 ⁻¹	n/a
(Exp _(ing))	3.14 × 10 ⁻⁵	3.14 × 10 ⁻⁴	2.48 × 10 ⁻²	7.03 × 10 ⁻¹	1.67 × 10 ⁻¹	5.31 × 10 ⁻¹	1.33 × 10 ⁻¹	n/a
(Exp _(derm))	8.00 × 10 ⁻⁷	4.00 × 10 ⁻⁶	1.58 × 10 ⁻⁴	4.48 × 10 ⁻³	1.06 × 10 ⁻³	3.38 × 10 ⁻³	5.09 × 10 ⁻⁴	n/a
(HQ _(ing))	1.05 × 10 ⁻⁷	1.05 × 10 ⁻⁴	8.28 × 10 ⁻⁵	1.01 × 10 ⁻³	6.97 × 10 ⁻³	1.33 × 10 ⁻²	4.44 × 10 ⁻⁴	2.19 × 10 ⁻²
(HQ _(derm))	1.33 × 10 ⁻⁸	6.67 × 10 ⁻⁸	2.63 × 10 ⁻⁶	3.19 × 10 ⁻⁵	1.11	4.22 × 10 ⁻⁴	8.48 × 10 ⁻⁶	1.57 × 10 ⁻³

n/a: Not applicable

Table 4: Chronic daily ingestion (CDI), exposure via ingestion (Exp_(ing)), dermal exposure (Exp_(derm)), ingestion hazards quotient (HQ_(ing)) and dermal hazards quotient (HQ_(derm)) within the study area.

source and has ingestion Hazard Index greater than unity (Figure 2). Manganese (Mn) is the most concentrated metal (Table 3) in this water source. This result agreed with the report of the city of Mhlathuze municipality which necessitated the warning recently issued to the residents of Richards Bay not to use water supply to their taps until it's cleared of manganese [25]. Water from this stream if continually used for drinking purpose without preceding treatment for Mn and Zn may cause diseases such as Alzheimer's as well as upsets the intellectual functions of younger children [26]. The high contamination of Mn observed in these streams may be attributed to either contaminant from industrial processes, leaching from industrial dust settling on land as well as pollution from human activities within Richards Bay. Alternatively, it might be from the natural content of the soil within Richards Bay.

Conversely, hazard indexes for effluent water were found to be 3.35 × 10⁻¹ and 5.15 × 10⁻² (Table 4 column 9) respectively hence there is no anxiety for possible non-carcinogenic risk from this source. This may be ascribed to the treatment completed on the effluent water by company prior disposal.

Hazard Indexes via ingestion were obtained to be 3.89 × 10⁻², 2.83 × 10⁻² and 2.19 × 10⁻² for Indian Ocean, Mzingazi lake and Esikhawini tap water respectively (Table 4 column 9). Furthermore, indexes via dermal absorptions were 1.20 × 10⁻³, 3.76 × 10⁻³ and 1.57 × 10⁻³ for Indian Ocean, Mzingazi lake and Esikhawini tap water respectively (Table 4 column 9). The hazard indexes for ingestion and dermal were both less than unity hence there is no concern for potential non-carcinogenic health effects at present. Therefore, these water sources may be consider as suitable alternative in times of water paucity.

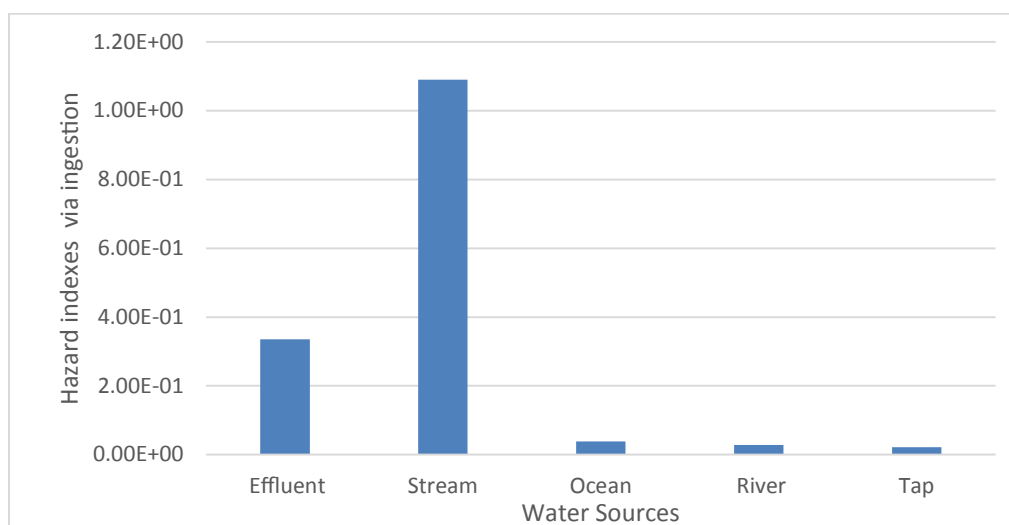


Figure 2: Hazard indexes of heavy metals in water via ingestions.

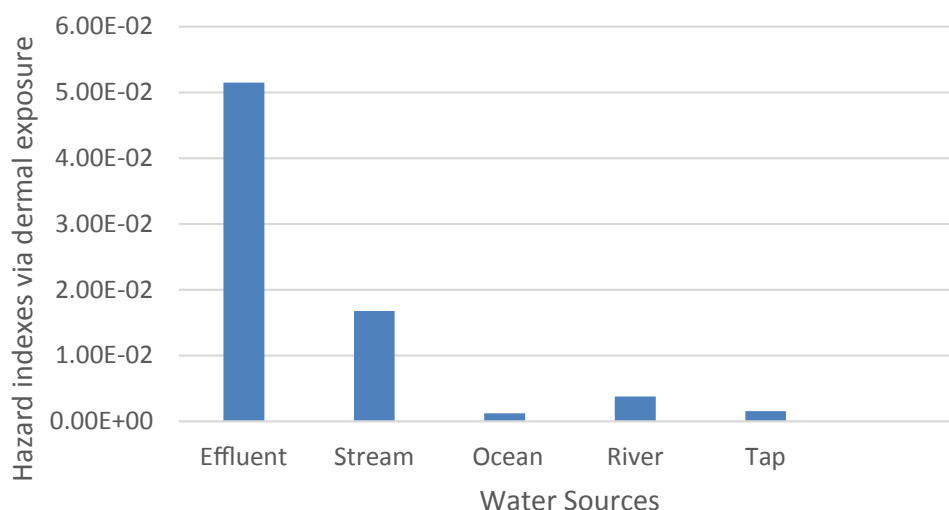


Figure 3: Hazard indexes of heavy metals in water via dermal absorptions.

The low Hazard indexes observed in untreated water sources (ocean and river) resulted from the low concentrations of these metals in the samples. This in turn can be linked to the ability of water to purify itself over time through natural processes of dilution and sedimentation. While the low concentrations in drinking taps water may be linked to foregoing treatment before supply.

In this study, the non-carcinogenic effects of metals due to ingestion were generally found to be in the order; stream>effluent water>Indian Ocean>Mzingazi river>Esikhawini tap water (Figure 2). Whereas via dermal absorption decreases in the order effluent water>stream>Mzingazi river>Esikhawini tap water>Indian Ocean (Figure 3).

Carcinogenic health risk assessment

The carcinogenic risks were calculated for Lead (Pb), Chromium (Cr) and cadmium (Cd) based on recommendation of the United States environmental protection Agency. The risk ranges from $1.03 \times$

10^{-10} - 6.56×10^{-7} in effluent water and 1.14×10^{-8} - 2.22×10^{-7} in stream (Table 5 columns 4 and 3 respectively). Similarly, risk obtained was ranging from 5.15×10^{-11} to 2.61×10^{-7} in Indian ocean, 4.07×10^{-9} - 1.41×10^{-7} in drinking tap water and 5.15×10^{-11} - 2.71×10^{-7} in Mzingazi Lake (Table 5 columns 4 and 3 respectively).

Although United States Environmental Protection Agency accept a range of 1.00×10^{-6} - 1.00×10^{-4} (USEPA 2015) for monitoring purposes, South African Department of Environmental Affairs tolerate only 5.00×10^{-6} as the frontier for individual cancer jeopardy [27]. Therefore, the cancer risk owing to Pb, Cr and Cd concentrations in water samples obtained from Richards Bay effluent water, stream, Indian Ocean, Esikhawini tap water and Mzingazi Lake are inconsequential at present.

Generally, using constant parameters such as (body weight, water consumption rate, age, slope factors and exposure duration) constant, Carcinogenic and non-carcinogenic risks are directly proportional to the concentrations of heavy metals in the water sample.

Comparison of data from the present study with other results obtained across the globe revealed the concentration of Pb ($0.01 \mu\text{g.l}^{-1}$) in Mzingazi river (South Africa) is lower than what was obtained in rivers of Warri, Tigris, Odiel, Hindo, Yangt and steam rivers in Nigeria, Turkey Spain, India and China respectively but slightly higher than what was reported from siling watershed in China. Conversely Mn concentration in Richards Bay stream was higher than of Simly and Khanpur streams in Pakistan [15] as well as Zulfi district stream in Saudi Arabia. Though Mn concentration in Richards Bay stream is lower compared to that reported in the Witwatersrand goldfields of South Africa the concentration is still higher than the South African Target Water Quality Range [23].

However, the concentrations of Pb, Cr, Cd, Fe, Cu, Zn in this study were within limits set out by DWAF, WHO and US EPA for regulatory purposes (Table 6).

Results in Table 6 of the present research study has showed that manganese (Mn) was the most abundant heavy metal within Richards Bay precinct with the measured results of 0.72 mg.l^{-1} , 0.22 mg.l^{-1} higher than recommended human health risk dose of 0.5 mg.l^{-1} , but lower than i.e., 0.86 mg.l^{-1} in Hindo River, Turkey and 6 mg.l^{-1} in Goldfield water, South Africa.

Conclusion

The concentrations of Pb, Cr, Cd, Fe, Cu and Zn within all the water sources investigated were lower while Mn was slightly higher than the South African Target Water Quality Range (TWQR) as well as the permissible limits set out for regulatory purposes by the World Health Organization. Hence the carcinogenic and non-carcinogenic health risk owing to ingestion and dermal exposure to these metals are improbable. The results further demonstrated that industrial activities within the Richards Bay precinct contributes minimally to the health risk to the population in terms of heavy metals contamination in water.

However, deliberated efforts must be taken to sustain and where possible improve on the environmental safety methods being practiced by government and managements of companies within Richards in order to avoid accumulation of heavy metal concentration in water bodies within its immediate neighborhood. Furthermore, the stream within the facility should be sanitized by clearing the bushes, leafy vegetables and rotten grasses which are natural source of manganese which also is a contributing factor to the high level of Mn in these streams.

Sampling site/Elements	Pb	Cr	Cd
Effluent	3.69×10^{-8}	6.56×10^{-7}	1.03×10^{-10}
Stream	7.39×10^{-8}	2.22×10^{-7}	1.14×10^{-8}
Average	5.54×10^{-8}	4.39×10^{-8}	5.75×10^{-9}
Indian Ocean	3.69×10^{-8}	2.61×10^{-7}	5.15×10^{-11}
Esikhawini tap water	3.69×10^{-9}	1.41×10^{-7}	4.07×10^{-9}
Mzingazi Lake	3.69×10^{-8}	2.71×10^{-7}	5.15×10^{-11}
Average	2.58×10^{-8}	6.47×10^{-7}	1.39×10^{-9}
Permissible ranges			
SA. Reg. Gazt., 2006	5.00×10^{-6}	5.00×10^{-6}	5.00×10^{-6}
USEPA 2004	1.0×10^{-6} - 1.0×10^{-4}	1.0×10^{-6} - 1.0×10^{-4}	1.0×10^{-6} - 1.0×10^{-4}

Table 5: Carcinogenic health risk (unit less) of metals in water samples due to ingestion of lead (Pb), Chromium (Cr) and cadmium (Cd).

Sampling sites	Country	Concentration of metals ($\mu\text{g.l}^{-1}$)						
		Pb	Cr	Cd	Fe	Mn	Cu	Zn
Richards bay stream	South Africa	0.02	0.06	2.21	3.53	719.41	21.73	0.91
Effluent	South Africa	0.01	0.01	0.02	10.44	245.64	10.64	28.94
Indian ocean	South Africa	0.01	0.39	0.01	4.16	0.61	42.13	7.49
Esikhawini taps	South Africa	0.01	0.01	0.79	22.38	5.32	16.88	4.24
Mzingazi river	South Africa	0.01	0.24	0.01	4.31	17.67	2.56	4.49
Warri River	Nigeria	0.85	0.52	0.04	N/a	682.00	2.65	138.00
Tigris River	Turkey	0.34	5.00	1.37	388.00	467.00	165.00	37.00
Hindon River	India	901.2	332.10	24.00	1229.2	857.90	4290.20	833.20
Yangtz River	China	55.10	20.90	4.70	239.80	5.40	10.70	9.40
Goldfields water	South Africa	7.50	23.00	6.80	20100.00	6000.0	280.00	1930
Siling watershed	China	BDL	44.71	1.18	41.00	37.32	BDL	37.00
Simly river	Pakistan	200.00	75.00	17.00	60.00	14.00	22.00	25.00
Khanpur river	Pakistan	221.00	46.00	20.00	51.00	11.00	9.00	15.00
Han River	China	11.02	10.32	1.38	20.63	18.79	18.97	N/A
Zulfi District	Saudi Arabia	0.16	3.69	0.03	5290.81	64.75	N/A	12.12
Irrigation used	South Africa	0-200	0-100	0-10	0-500	0-20	0-200	1000
Potable limit	WHO	0-10	0-50	0-3	0-100	0-50	0-1000	0-500
Drinking water	US	15.00	100.00	5.00	300.00	50.00	1300.00	5000.0

N/A: Not applicable; BDL: Below detection limits

Table 6: Comparison of average concentrations of heavy metals in water samples from Richards Bay with other countries of the world.

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