AJ ACADEMIC JOURNALS
expand your knowledge

Journal of Toxicology and Environmental Health Sciences

Full Length Research Paper

Potential human risk of dissolved heavy metals in gold mine waters of Gauteng Province, South Africa

C. Kamunda[1*], M. Mathuthu[2] and M. Madhuku[3]

[1]Rusangu University, P.O. Box 660391, Monze, Zambia.
[2]Centre for Applied Radiation Science and Technology, North West University (Mafikeng Campus), P. Bag X2046, Mmabatho, 2735, South Africa.
[3]iThemba LABS (Gauteng), P. Bag X11, Wits, 2050, South Africa.

This paper evaluates the potential health risks from dissolved heavy metals in water sources around a gold mining area in the Gauteng Province of South Africa. In this study, 29 samples of water were collected around a gold mining area and were analyzed for Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd), Chromium (Cr), Copper (Cu), Zinc (Zn), Cobalt (Co) and Nickel (Ni) using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Measured concentrations of these heavy metals were then used to calculate the hazard quotient (HQ) and hazard index (HI) leading to the determination of carcinogenic and non-carcinogenic effects of these heavy metals. The average concentrations of the heavy metals decreased in the order of Ni>Cu> Zn>As> Cr>Co>Pb. In mg.L^{-1} the average concentrations were as follows: Ni (0.39); Cu (0.38); Zn (0.33); As (0.19); Cr (0.14); Co (0.08); Pb (0.01). Hg and Cd were not detectable. For the non-carcinogenic risk assessment, calculated values of HQ showed an HI value of 3.38×10^{-1}, a value less than 1, which is potentially safe according to United States Environmental Protection Agency (USEPA) and South Africa guidelines. When the carcinogenic risk assessment was carried out, the results showed that the total cancer risk due to the heavy metals was 2.94×10^{-6} mainly due to dermal contact. The USEPA considers a cancer risk in the range of 1×10^{-6} to 1×10^{-4} acceptable for regulatory purposes. From the findings presented, it can be concluded that dissolved heavy metal levels in the mine waters were within permissible limits.

Key words: Health risk assessment, heavy metals, hazard index, target hazard quotient, average daily intake, cancer risk.

INTRODUCTION

Human beings have been exposed to heavy metals for an immeasurable amount of time. These heavy metals are found everywhere as a result of both natural and anthropogenic activities such as mining (Gupta and Ali, 2013). Most mining operations use these heavy metals as chemicals to extract valuable minerals. When the

precious mineral has been extracted, the crushed ore and heavy metals become waste that is piled as tailings into large slime dams. These tailings, if not properly managed may produce toxic waters that can potentially destroy aquatic life and poison drinking water supplies for human consumption (MINEO Consortium, 2000). During mining operations, acid drainage may also be produced. This acid drainage produces sulphuric acid which dissolves heavy metals. Once these heavy metals have been dissolved, they can easily be transported from one place to another.

Although all living organisms require varying amounts of heavy metals, they become toxic at higher concentrations (Lane and Morel, 2009). There are also other heavy metals that have no useful role in the human physiology and most other living organisms. Examples of such elements are As, Pb and Hg. They may be toxic even at trace levels of exposure. Arsenic, lead and mercury are the first, second and third hazardous metals, respectively, on the priority list of heavy metal pollutants as designated by the United States Agency for Toxic Substances and Disease Registry (ATSDR, 2007). When heavy metals are ingested, they get absorbed and distributed in tissues and organs. Although excretion occurs through kidneys and the digestive tract, they persist in some storage areas, such as the liver and bones for years or decades causing serious health consequences (Basheer, 2018).

For more than a century now, gold mining has been carried out in South Africa particularly in the Wonderfonteinspruit Catchment Area (WCA) of the Gauteng Province (Winde et al., 2004). The WCA is the world's largest gold and uranium mining basin that has taken place from more than 120 mines. The basin covers an area of 1600 km^2, and has led to a legacy of some 400 km^2 of mine tailings and 6 billion tonnes of pyrite tailings containing low-grade uranium (Liefferink, 2009). These mine tailings, usually 1 to 2 km in diameter, are littered everywhere, posing an environmental threat to local communities. In this study, a potential risk of heavy metals in water to the population around the gold mining area has been carried out, which is a first of its kind. In carrying out this study, the researcher measured the concentration levels of heavy metals in mine water from the study area, and also estimated the health risks associated with these concentrations. Nine heavy metals, namely, As, Pb, Hg, Cd, Cr, Co, Ni, Cu and Zn were included in the measurement.

MATERIALS AND METHODS

The study area

The study area is situated near the West Wits line (Far West Rand) in the Gauteng province of South Africa, close to the town of Carletonville and is approximately 70 kilometers southwest of Johannesburg. It lies between 26°18`S - 26°26`S latitude and 27°23`E - 27°31`E longitude. Gold exploration in the area dates back to 1898 and mining started from 1945 to date. Geologically, the area in question, approximately 86 km^2, lies in the lower central part of the Wonderfonteinspruit Catchment Area (WCA). The topography of the area is relatively flat and the vegetation is largely grassland. Livestock farming is also widespread in the surrounding area. The climate is temperate, with temperatures averaging 24°C in summer and 13°C in winter, occasionally dipping below the freezing point. Annual rainfall is about 750 mm (Tyson and Wilcocks 1971). The study area has a worker population of around 14,000 (SGL 2012). There are also some informal settlements residing close to the mine tailings.

Sampling and sample preparation

From the study area, samples of water were collected from different locations using random sampling. All the collected water samples were properly marked and identified by their sampling locations using Global Positioning System (GPS) for later referencing. The sampling procedure was carried out according to methodologies recommended by APHA (1985). Twenty nine (29) water samples, of roughly 100 ml each, were collected in polyethylene bottles using a muslin cloth as a strainer, from each selected location in the gold mining area. All the bottles had to be washed with dilute acid (0.1 M HCl) before use to avoid contamination. The collected samples were then transported to the laboratory and placed in a cold room in readiness for elemental analysis using ICP MS technique (IAEA, 1989).

Microwave digestion

Before ICP-MS was done, all samples were first digested in a Multiwave 3000 microwave system. Digestion is done in order to extract the heavy metals from water samples. 5 ml of each water sample was mixed with 5 ml of nitric acid and 1 ml of hydrochloric acid in a rotor vessel with 1 ml of hydrogen peroxide. The mixture was then digested at a temperature of 120°C for about 45 min. After this, the digested samples were allowed to cool and transferred into 100 mL volumetric flasks with 2% nitric acid. Distilled water was then used to top up to the 100 mL volume (Mathuthu et al., 2016). The digested samples were then allowed to sediment overnight, which was thereafter filtered with No. 40 Whatman filter paper in readiness for ICP-MS.

ICP-MS measurement

The water samples were analyzed for heavy metals using ICP-MS, model PerkinElmer (NexION 300Q) (PerkinElmer 2004-2011). ICP-MS is a powerful tool for analysing heavy metals in environmental samples. The ICP-MS system can quantitatively measure various elements and produce a value of the total concentration of a specific element of interest (Bazilio and Weinrich, 2012). In ICP-MS, the sample components are decomposed into their atomic constituents followed by their ionization in an argon plasma at a temperature of about 6000 to 8000 K (PerkinElmer, 2004-2011). The positively charged ions are extracted from the plasma into a high vacuum of the mass spectrometer where they are separated by mass filters before finally being measured by an ion detector. The instrument runs each sample twice and for about 60 s for each

complete run (USEPA, 2007).

The TotalQuant method was used together with a standard solution in order to improve the analytical accuracy of the results and to be able to detect contamination and drift. The standard used is Perkin Elmer Pure Plus NexION Dual Detector Calibration Solution. TotalQuant calibration was achieved using 200 µg/L of Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U and Zn. For quality control, replicate samples were run together with the standard and blank solutions. The calibration process updates internal response data that correlates measured ion intensities to the concentrations of the elements in the solution. The target heavy metals were As, Pb, Hg, Cd, Cr, Co, Ni, Cu and Zn.

Human health risk assessment

Human health risk assessment is the process of estimating the nature and probability of adverse health effects in humans who may be exposed to environmental contaminants (NRC, 1999). It is also a process used to estimate health effects that might result from exposure to carcinogenic and non-carcinogenic contaminants (USEPA, 2001). This provides information to decision-makers about the possible consequences of actions, source treatment, disposal and remediation options, as well as clean-up standards of contaminated sites. The risk assessment process is made up of four basic steps: hazard identification, exposure assessment, toxicity (dose-response) assessment, and risk characterization (USEPA, 2001). Risk is defined as the probability of suffering harm while hazard is the source of risk (USEPA, 2001). Contaminants such as heavy metals do not cause a risk unless exposure has occurred.

Hazard Identification basically aims to investigate what contaminants are present at a site, their concentrations, and their spatial distribution (Kamunda et al., 2016). In the study area heavy metals such as As, Pb, Hg, Cd, Cr, Co, Ni, Cu and Zn were identified as possible hazards for the community.

The purpose of exposure assessment is to measure or estimate the intensity, frequency, and duration of human exposures to an environmental contaminant. In this study, exposure assessment was carried out by measuring the concentrations and the Average Daily Intake (ADI) of heavy metals through ingestion, and dermal contact by individuals from the study area.

Dose-response assessment estimates the toxicity, considering adverse effects and exposure levels of carcinogenic and non-carcinogenic contaminants. The carcinogen slope factor (CSF) and the reference dose (RfD), are two principal toxicity indices used. RfD values are derived from animal studies using the "No observable effect level" principle. For humans, RfD values are multiplied 10-fold to account for uncertainties (Kamunda et al., 2016).

Risk characterization predicts the potential cancerous and non-cancerous health risk of the population by integrating all the information gathered from hazard identification, exposure assessment, and toxicity assessment to arrive at quantitative estimates of cancer risk and hazard indices (Liang et al., 2011).

Risk assessment of heavy metals in water samples

The potential risk from heavy metals in contaminated water is calculated based on recommendations by several USEPA publications (USEPA 1989). The Average Daily Intake (ADI) (mg/kg-day) ingestion and dermal contact were calculated using the following exposure equations 1 to 3 as prescribed by USEPA (1989):

Ingestion of heavy metals through water samples

$$ADI_{ing} = \frac{C \times IR_{ing} \times EF \times ED}{BW \times AT \times 10^6}$$

(1)

where ADI_{ing} (mg/kg-day), is the average daily intake of heavy metals ingested from water, C = concentration of heavy metals in mg/L. IR_{ing} (mg/day) is the ingestion rate, EF (days/year) is the exposure frequency, ED (years) is the exposure duration, BW (kg) is the body weight of the exposed individual, and AT (days) is the time period over which the dose is averaged and 10^6 is the conversion factor in kg/mg.

Dermal contact with water

$$ADI_{dem} = \frac{C \times SA \times PC \times ET \times EF \times ED \times CF}{BW \times AT}$$

(2)

where ADI_{dem} (mg/kg-day) is average daily intake of heavy metals via dermal contact from water. C (mg/L) is the concentration of heavy metal in water, SA (cm^2) is the exposed skin area, PC (cm/h) is the dermal permeability coefficient, ET (h/day) is the exposure time during bathing and shower, and CF (L/cm^{-3}), the unit conversion factor. EF, ED, BW and AT are as defined earlier in Equation 1 (Table 1).

Non-carcinogenic risk assessment of heavy metals

Non-carcinogenic hazards are characterized by the hazard quotient (HQ). HQ is a unitless number that is expressed as the probability of an individual suffering an adverse effect. The hazard quotient is defined as the quotient of the average daily intake or dose divided by the toxicity threshold value, which is referred to as the reference dose (RfD) of a specific chemical (USEPA, 1989):

$$HQ = \frac{ADI}{RfD}$$

(3)

where RfD is the chronic reference dose for the heavy metal (mg/kg-day). For n number of heavy metals, the non-carcinogenic effect to the population is a result of the summation of all the HQs due to individual heavy metals. This is considered to be another term called the Hazard Index (HI) as described by USEPA (1989). Equation 4 shows the mathematical representation of this parameter:

$$HI = \sum_{k=1}^{n} HQ_k = \sum_{k=1}^{n} \frac{ADI_k}{RfD_k}$$

(4)

where HQ_k ADI_k is RfD_k are values of heavy metal k. If the HI value is less than one, the exposed population is unlikely to experience adverse health problems. If the HI value exceeds one, then there may be concern for potential non-carcinogenic effects (USEPA, 1989).

Table 1. Exposure parameters used for risk assessment through ingestion and dermal pathways in water samples (Kamunda et al. 2016).

Parameter	Unit	Individual	References
Body weight (BW)	kg	70	DEA (2010)
Exposure frequency (EF)	days/year	350	DEA (2010)
Exposure duration (ED)	years	30	DEA (2010)
Ingestion rate (IR_{ing})	L/day	2	DEA (2010)
Skin surface area (SA)	cm^2	5800	DEA 2010)
Average time (AT)	**days**		
For carcinogens		365×70	DEA (2010)
For non-carcinogens		$365 \times ED$	DEA (2010)
Exposure time during bathing and shower (*ET*)	h/day	0.3	Liang et al. (2011)
*D*ermal permeability coefficient (PC)	cm/h	1.0×10^{-3}	Liang et al. (2011)
Unit conversion factor (CF)	L/cm^{-3}	1.0×10^{-3}	Liang et al. (2011)

Table 2. Reference doses (RfD) in (mg/kg-day) and Cancer slope factors (CSF) for the different heavy metals (Kamunda et al., 2016).

Heavy metal	Ingestion RfD	Dermal RfD	Ingestion CSF	Dermal CSF	References
As	3.00E-04	3.00E-04	1.50E+00	1.50E+00	USEPA (2011a)
Pb	3.60E-03	-	8.50E-03	-	Luo et al. (2012)
Hg	3.00E-04	3.00E-04	-	-	DEA (2010)
Cd	5.00E-04	5.00E-04	-	-	DEA (2010)
Cr (VI)	3.00E-03	-	5.00E-01	-	USEPA (2011a)
Co	2.00E-02	5.70E-06	-	-	USEPA (2011a)
Ni	2.00E-02	5.60E-3	-	-	IRIS (2007)
Cu	3.7.00E-02	2.40E-2	-	-	USEPA (2011a)
Zn	3.00E-01	7.50E-02	-	-	USEPA (2011a)

Carcinogenic risk assessment of heavy metals

For carcinogens, the risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen. The basic equation for calculating the lifetime cancer risk is:

$$Risk = ADI \times CSF$$

(5)

where "Risk" is a unitless probability of an individual developing cancer over a lifetime; ADI is the average daily intake or dose as highlighted earlier. CSF is the cancer slope factor, expressed in $(mg/kg/day)^{-1}$. It converts the estimated daily intake of the heavy metal averaged over a lifetime of exposure directly to incremental risk of an individual developing cancer (USEPA, 1989).

The total lifetime cancer risks for an individual is calculated from the average contribution of the individual heavy metals in the different media for all the pathways using the following equations:

$$Risk_{(total)} = Risk_{(ing)} + Risk_{(dermal)}$$

(6)

where Risk $_{(ing)}$, Risk $_{(inh)}$, and Risk $_{(dermal)}$ are risks contributions through different media, that is, soil, water and plants. For n number of heavy metals, the risk for the given pathway is given by Equation 7 as follows:

$$Risk_{pathway} = \sum_{k=1}^{n} ADI_k CSF_K$$

(7)

where ADI_k and CSF_k are the ADI and CSF, for the kth heavy metal. Both non-carcinogenic and carcinogenic risk assessment of heavy metals are estimated from RfD and CSF values largely derived from DEA (2010) and USEPA guidelines as shown in Table 2.

RESULTS AND DISCUSSION

Concentrations of heavy metals in water samples

The average concentrations of heavy metals in water samples $(mg.L^{-1})$ from the different locations of the gold mining area are presented in Table 3. These average concentrations were then used to calculate the average

Table 3. Concentrations of heavy metals in water from the mining area.

Sample ID	Latitude	Longitude	Heavy metals concentration (mg.L^{-1})						
			As	Pb	Cr	Cu	Zn	Co	Ni
DSW451	26°26'19.74"S	27°29'54.84"E	0.25	0.04	0.36	0.12	0.24	0.08	0.26
DSW112	26°25'28.02"S	27°29'31.50"E	0.20	0.00	0.30	0.08	0.38	0.04	0.18
DSW183	26°23'0.12"S	27°30'14.10"E	0.31	0.00	0.00	0.08	0.28	0.02	0.18
DSW204	26°22'45.12"S	27°29'52.44"E	0.02	0.00	0.00	0.02	0.12	0.04	0.24
DSW405	26°21'43.08"S	27°29'58.86"E	0.99	0.00	0.24	3.72	0.34	0.36	2.26
DSW406	26°21'43.26"S	27°30'5.28"E	0.74	0.00	0.00	0.04	0.10	0.02	0.24
DSW407	26°21'53.28"S	27°29'54.54"E	0.86	0.00	0.00	1.40	0.24	0.20	0.94
DSW358	26°21'49.56"S	27°27'39.90"E	0.74	0.00	0.00	2.42	0.48	0.14	2.68
DSW179	26°23'22.74"S	27°28'13.92"E	0.00	0.00	0.00	0.04	0.30	0.02	0.14
DSW4210	26°20'36.24"S	27°26'1.02"E	0.00	0.00	0.00	0.04	0.00	0.02	0.12
DSW2111	26°21'25.14"S	27°26'10.32"E	0.11	0.00	0.00	0.06	0.40	0.04	0.16
DSW712	26°21'27.42"S	27°25'59.22"E	0.33	0.00	0.20	0.02	0.22	0.04	0.14
DAM313	26°21'19.32"S	27°25'52.44"E	0.21	0.00	0.32	0.04	0.32	0.06	0.34
DSW914	26°20'59.34"S	27°25'52.44"E	0.00	0.00	0.00	0.08	0.18	0.06	0.30
DSW3615	26°20'28.44"S	27°25'42.06"E	0.00	0.00	0.00	0.04	0.12	0.04	0.26
DSW3816	26°19'38.10"S	27°24'15.42"E	0.00	0.00	0.00	0.06	0.00	0.04	0.20
DSW3917	26°18'57.96"S	27°23'3.36"E	0.00	0.00	0.00	0.06	0.16	0.02	0.16
DSW1618	26°23'44.76"S	27°25'57.84"E	0.14	0.02	0.40	0.10	0.18	0.04	0.22
DSW4319	26°21'57.30"S	27°26'34.98"E	0.06	0.04	0.24	0.22	0.26	0.08	0.26
DSW2920	26°20'32.40"S	27°26'40.86"E	0.34	0.00	0.18	0.06	0.26	0.02	0.14
WV2	26°23'45.90"S	27°28'43.26"E	0.12	0.02	0.28	1.84	0.28	0.66	1.04
WV3	26°23'44.10"S	27°29'2.04"E	0.00	0.02	0.30	0.08	0.48	0.02	0.14
WV4	26°23'38.88"	27°29'5.16"E	0.00	0.00	0.24	0.08	0.76	0.04	0.12
WV5	26°23'40.20"S	27°29'5.52"E	0.00	0.02	0.00	0.02	2.12	0.02	0.14
WV9	26°23'13.80"S	27°30'59.76"E	0.00	0.02	0.00	0.08	0.34	0.04	0.08
WV13	26°23'21.24"S	27°31'20.04"E	0.00	0.00	0.18	0.06	0.30	0.00	0.08
WV14	26°23'23.46"S	27°31'11.70"E	0.00	0.00	0.24	0.02	0.24	0.02	0.12
WV15	26°23'16.68"S	27°30'44.10"E	0.00	0.02	0.26	0.02	0.20	0.02	0.12
WV16	26°22'60.00"S	27°30'36.12"E	0.00	0.02	0.28	0.06	0.24	0.02	0.14
-	-	Average	0.19	0.01	0.14	0.38	0.33	0.08	0.39
-	-	Minimum	0.00	0.00	0.00	0.02	0.00	0.00	0.08
-	-	Maximum	0.99	0.04	0.40	3.72	2.12	0.66	2.68

daily intakes for residents leading to non-carcinogenic and carcinogenic risk assessment for individual members of the public. The results presented show that the average concentration of heavy metals in water from the gold mining area decreased in the order of Ni>Cu> Zn>As> Cr>Co>Pb. The ranges in mg.L^{-1} were as follows: Ni (0.08 to 2.68 with an average of 0.39); Cu (0.02 to 3.72 with an average of 0.38); Zn (0.00 to 2.12 with an average 0.33); As (0.00 to 0.99 with an average 0.19); Cr (0.00 to 0.40 with an average 0.14); Co (0.00 to 0.66 with an average 0.08); Pb (0.00 to 0.04 with an average 0.01). Although Hg and Cd were measured, their concentrations were not detectable.

The results of the measurements were also compared with national and international guidelines for permissible limits of heavy metals in drinking water presented in Table 4. The results revealed that the average concentrations of As, Ni, Cr, and Zn in drinking water were higher than permissible limits whilst those of the remaining heavy metals were within permissible limits. The high concentrations of these metal elements could be attributed to high levels of acid mine drainage as

Table 4. Permissible limits of heavy metals in drinking water.

Country	Heavy metals concentration limit (mg.L^{-1})									References
	As	Pb	Hg	Cd	Cr	Cu	Zn	Co	Ni	
USEPA	0.01	0.015	0.002	0.005	0.1	1.3	0.5	0.1	n.a	USEPA (2011b)
WHO	0.01	0.01	0.006	0.003	0.05	2.0	n.a	n.a	0.07	WHO (2008)
South Africa	0.01	0.01	0.001	0.003	n.a	1.0	n.a	n.a	n.a	DOH (2004)

n.a: Not available.

Table 5. Average Daily Intake (ADI) and their corresponding Hazard Quotient (HQ) values due to ingestion and dermal contact with water for heavy metals from mining area.

Parameter	ADI and HQ Values							Total (HI)
	As	Pb	Cr	Cu	Zn	Co	Ni	
ADIing	5.25E-09	2.08E-10	3.80E-09	1.04E-08	9.01E-09	2.10E-09	1.08E-08	4.15E-08
ADIder	4.57E-06	1.81E-07	3.30E-06	9.01E-06	7.84E-06	1.82E-06	9.37E-06	3.61E-05
Total ADI	4.58E-06	1.81E-07	3.31E-06	9.02E-06	7.85E-06	1.83E-06	9.38E-06	3.61E-05
RfDing	3.00E-04	3.60E-03	3.00E-03	3.70E-02	3.00E-01	2.00E-02	2.00E-02	
HQing	1.75E-05	5.77E-08	1.27E-06	2.80E-07	3.00E-08	1.05E-07	5.38E-07	1.98E-05
RfDder	3.00E-04	n.a	n.a	2.40E-02	7.50E-02	5.70E-06	5.60E-03	
HQder	1.52E-02	n.a	n.a	3.75E-04	1.05E-04	3.20E-01	1.67E-03	3.38E-01
Total HQ	1.53E-02	5.77E-08	1.27E-06	3.76E-04	1.05E-04	3.20E-01	1.67E-03	3.38E-01

n.a: Indicates that reference doses were not available for calculation.

reported by Winde et al. (2004) in the area, which is catalytic to the solubility and leaching of these heavy metals.

Non-carcinogenic risk assessment of heavy metals through water samples

Non-carcinogenic risk of heavy metals for individual members of the public were calculated based on reference doses (RfD) presented in Table 2 and on the results of Average Daily Intake (ADI) values calculated for the water samples. The results were then presented in terms of the Hazard Quotient (HQ) and Hazard Index (HI) for ingestion and dermal pathways. Ingestion and dermal pathways were considered in the non-carcinogenic risk assessment. Table 5 tabulates results of ADI values used together with their corresponding HQ values. In this situation, Equations 1 and 2 described earlier were used to calculate ADI values for water samples. Calculated values of HQ showed an HI value of 3.38×10^{-1}. This is less than 1 and potentially safe according to USEPA (1989) and South Africa guidelines (DEA, 2010). In this scenario, the dermal pathway contributed more than the ingestion pathway.

An evaluation to determine the pathway that contributed

the most to non-carcinogenic risk was done. Results showed that the dermal pathway contributed more to non-carcinogenic risk with an HQ value of 3.38 ×10^{-1} with the ingestion pathway contributing a negligible amount of only 1.98 ×10^{-5}. Results also showed that Co contributed the most to the non-cancer risk, followed by As and then Ni. This was primarily because As is a non-essential element in plants and animals. Although Co plays a vital role in nitrogen fixing and Cr in the metabolism of fats and cholesterol, their ADI values for soil were closer to the toxicity threshold doses for the dermal pathway and ingestion pathway, thereby becoming more hazardous than the other heavy metals.

Carcinogenic risk assessment of heavy metals through water samples

As, Pb, and Cr were considered as metals that have the potential to cause carcinogenic risk. The cancer risks for individual members of the public were calculated from the average contribution of the individual heavy metals in water samples. In order to calculate the ADI values, Equations 1 and 2 described earlier were used. On the other hand, Equations 5, 6 and 7, also earlier mentioned were used to determine the cancer risk. The ingestion

Table 6. ADI values and the cancer risk values through ingestion and dermal contact of heavy metals for individual members of the public for water from mining area.

Parameter	ADI and cancer risk values			Total risk
	As	**Pb**	**Cr**	
ADIing	2.25E-09	8.91E-11	1.63E-09	1.78E-08
ADIder	1.96E-06	7.75E-08	1.42E-06	1.55E-05
Total ADI	1.96E-06	7.76E-08	1.42E-06	1.55E-05
CSFing	1.50E+00	8.50E-03	5.00E-01	-
Risking	3.38E-09	7.57E-13	8.14E-10	4.19E-09
CSFder	1.50E+00	n.a	n.a	
Riskder	2.94E-06	n.a	n.a	2.94E-06
Total Risk	2.94E-06	7.57E-13	8.14E-10	2.94E-06

n.a: Indicates that cancer slope factors were not available for risk calculation.

and dermal pathways were considered for estimating the cancer risk of heavy metals for water. The results for individual cancer risk are presented in Table 6. The same table also presents ADI values used in the calculation of the cancer risk. For those metals without known cancer slope factors, the risk was not calculated. The results shown indicate that the total cancer risk was 2.94×10^{-6} mainly due to dermal contact.

Conclusion

The main objective of this study was to evaluate potential health risks as a result of heavy metals in water samples collected from different locations around the gold mining area in the Gauteng Province of South Africa. The average concentrations of heavy metals in water samples from the different locations decreased in the order of Ni>Cu>Zn>As>Cr>Co>Pb. The ranges in $mg.L^{-1}$ were as follows: Ni (0.08 to 2.68 with an average of 0.39); Cu (0.02 to 3.72 with an average of 0.38); Zn (0.00 to 2.12 with an average 0.33); As (0.00 to 0.99 with an average 0.19); Cr (0.00 to 0.40 with an average 0.14); Co (0.00 to 0.66 with an average 0.08); Pb (0.00 to 0.04 with an average 0.01). Compared with national and international guidelines for permissible limits, the average concentrations of As, Ni, Cr, and Zn in drinking water were higher than permissible limits.

When non-carcinogenic risk assessment was carried out, calculated values of HQ showed an HI value of 3.38×10^{-1}, a value less than 1, which is potentially safe according to USEPA and South Africa guidelines. On the other hand, carcinogenic risk assessment carried out showed that the total cancer risk due to the heavy metals of 2.94×10^{-6}, is mainly due to dermal contact. The US Environmental Protection Agency considers a cancer risk in the range of 1×10^{-6} to 1×10^{-4} acceptable for

regulatory purposes. From the findings presented, it was concluded that dissolved heavy metal levels in mine water were within permissible limits in the mining area.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

American Public Health Association (APHA) (1985). Standard methods for the examination of water and wastewater. Washington, New York, USA.

Agency for Toxic Substances and Disease Registry (ATSDR) (2007). Guidance for the Preparation of a Twenty First Set Toxicological Profile. http://www.atsdr.cdc.gov/toxprofiles/guidance/set_21_guidance.pdf . Accessed 10 May 2017.

Basheer AA (2018). Chemical chiral pollution: Impact on the society and science and need of the regulations in the 21st century, Chirality, 30:402-406.

Bazilio A, Weinric J (2012). The Easy Guide to: Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). http://www.ecs.umass.edu/eve/facilities/equipment/ICPMS/ICPMS%20quick%20guide.pdf. Accessed 12 May 2016.

Department of Environmental Affairs (DEA) (2010). The Framework for the Management of Contaminated Land, South Africa. http://sawic.environment.gov.za/documents/562.pdf.

Department of Health (DOH) (2004). Regulation Relating to Maximum levels for Metals in Foodstuffs, South Africa.http://web.capetown.gov.za/eDocuments/Regulations_Relating_to_Maximum_Levels_for_Metals_in_Foodstuffs_-_R_500_of_2004_95200519507_245.pdf.

Gupta VK, Ali I (2013). Environmental water: Advances in treatment, remediation and recycling, Elsevier, The Netherlands.

International Atomic Energy Agency (IAEA) (1989). Measurement of Radionuclides in Food and the Environment. Technical Report Series No. 295, Vienna, Austria.

Kamunda C, Mathuthu M, Madhuku M (2016). Health Risk Assessment of Heavy Metals in Soils from Witwatersrand Gold Mining Basin, South Africa. International Journal of Environmental Research and Public Health 13:663.

Lane TW, Morel FM (2009). A biological function for cadmium in marine diatoms. Proceedings of the National Academy of Sciences 200:462-431. http://www.pnas.org/cgi/pmidlookup?view=lon&andpmid=10781068.

Liang F, Yang SG, Sun C (2011).Primary Health Risk analysis of metals in surface water of Taihu Lake China. Bulletin of Environmental Contamination and Toxicology 87(4):404.

Liefferink M (2009). A South African Perspective: Radioactive Contamination and Acid Mine Drainage (AMD). Discussing pollution risks within the gold mining sector. Federation for a Sustainable Environment.

Luo XS, Ding J, Xu B (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. Science of the Total Environment 424:88-96.

Mathuthu M, Kamunda C, Madhuku M (2016). Modeling of Radiological Health Risks from Gold Mine Tailings in Wonderfonteinspruit Catchment Area, South Africa. International Journal of Environmental Research and Public Health 13:570.

MINEO Consortium (2000). Review of potential environmental and social impact of mining. User need document Part 2, IST-1999-10337. http://www2.brgm.fr/mineo/UserNeed/IMPACTS.pdf.

National Research Council (NRC) (1999) Arsenic in drinking water. Washington, DC: 251-257.

Perkin E (2004-2011). ICP-Mass Spectrometry, Tehnical Note.USA. www.perkinelmer.com. Accessed 14 December 2016.

Sibanye Gold Limited (SGL) (2012). Competent person's report on the material assets of Driefontein Gold Mine.

Tyson PD, Wilcocks JRN (1971). Rainfall variation over Johannesburg – the local climate over Johannesburg. Department of Geography and Environmental Studies, Universtiy of Witwatersrand, Johannesburg. Occasional paper 428.

United States Environmental Protection Agency (USEPA) (1989). Risk assessment guidance for Superfund. Human health evaluation manual, (part A) [R], vol. 1. Washington, DC: Office of emergency and remedial response; EPA/540/1-89/002, USA.

United States Environmental Protection Agency (USEPA) (2001). Toxics Release Inventory. Public Data Release Report, USA. www.epa.gov/tri/tridata/tri01. Accessed 14 November 2017.

United States Environmental Protection Agency (USEPA) (2011a). Recommended Use of BW3/4 as the Default Method in Derivation of the Oral Reference Dose. EPA/100/R11/001. Office of the Science Advisor, USA. http://www.epa.gov/raf/publications/pdfs/recommended-use-of-bw34.pdf.

United States Environmental Protection Agency (USEPA) (2011b). National Primary Drinking Water Regulations. Retrieved from http://water.epa.gov/drink/contaminants/index.cfm#List.

World Health Organisation (WHO) (2008). Guidelines for drinking water quality, 3rd Edition, Incorporating 1st and 2nd addenda, Recommendations, World Health Organisation, Geneva Vol. 1.

Winde F, Wade P, Van der Walt IJ (2004). Gold tailings as a source of waterborne uranium contamination of streams — the Koekemoerspruit (Klerksdorp goldfield, South Africa) as a case study. Part I: Uranium migration along the aqueous pathway. *Water SA, 30*, 219–226.