

# Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles from Witwatersrand gold tailings

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## Synopsis

Severe episodes of windblown dust from mine tailings storage facilities (TSFs) are a common phenomenon on the Witwatersrand, especially during the spring windy season. For communities around TSFs, such events pose health and environmental challenges. This paper reports on health risk assessment using US Environmental Protection Agency (US EPA) risk assessment methods for heavy metal elements in windblown dust from TSFs on the central and east Witwatersrand. Samples of surface material from these TSFs were analysed for heavy metal content using inductively coupled plasma-mass spectrometry (ICP-MS). From a range of 30 heavy metals analysed, only As, Cd, Cr, Pb, and U were enriched by a factor of two or more above the average crustal composition and at concentrations that could be of possible health concern-elements present in the range of a few parts per billion (ppb) or lower were ignored. As, Cd, Cr, Pb and U were selected for a comprehensive risk assessment from exposure through airborne routes, mainly considering inhalation and ingestion. Ambient exposures were based on a worst-case measured episode of 540  $\mu$ g m<sup>-3</sup> (24-hour average), which was projected over each day of an annual exposure for the hours for which the wind speed was above the threshold for dust generation.

US EPA risk assessment methods were used to determine the inhalation and ingestion hazard quotients and hazard indices for adults and children. The sum of the hazard indices was assessed to be below the non-cancer benchmark (hazard indices 1.0) considered to be acceptable for a lifetime exposure. The total risk for both exposures (inhalation and the ingestion) was within the range of 1 per 1 000 000 to 100 per 1 000 000 taken as 'acceptable risk' by the US EPA for adults and children. These results represent the first quantitative health risk assessment of the hazard posed by heavy metals in windblown mine tailings dust on the Witwatersrand goldfield.

#### Keywords

mine tailings, dust, airborne particles, health risk, inhalation, ingestion heavy metals, arsenic, cadmium, chromium.

#### Introduction

Dust fallout from tailings storage facilities (TSFs) is a major contributor to ambient air pollution on the Witwatersrand, especially during dust storm episodes in the spring season when ambient PM10 aerosol concentrations (particles smaller than 10  $\mu$ m) can reach 2 000  $\mu$ g m<sup>-3</sup> (24-hour average) (Annegarn, Scorgie, and Sithole, 2002; Annegarn *et al.*, 1990; Blight and Caldwell, 1984; Ojelede, Annegarn, and Kneen, 2012). Numerous public statements and claims have been made by individuals and organizations about the dust fallout from tailings affecting public health through several routes of

exposure (Bega, 2011a, 2011b; Federation for a Sustainable Environment, 2010). Inhalation or ingestion of particulate matter (PM) has been shown to have adverse impacts on human health (Valavanidis, Fiotakis, and Vlachogianni, 2008; Wilson and Suh, 1997). Furthermore, several studies have confirmed a strong link between the inhalation of fine aerosols in ambient environments and the occurrence of cardiopulmonary mortality and respiratory diseases (Berico, Luciani, and Formignani, 1997; Dockery, 2001; Harrison and Yin, 2000; Fubini and Fenoglio, 2007; Griffin, Kellogg, and Shinn, 2001; Park et al., 2004; Pope and Dockery, 2006; Schwartz, 1994; Wilson and Suh, 1997). According to Schwartz (1992) and the World Health Organization (2006), for human health, there is 'no safe threshold' level of PM exposure. The toxicity of particulate matter is a result of on the particle size, which allows the smaller particle to be transported deeper in the respiratory track (Bakand and Hayes, 2010; Harrison and Yin, 2000) and is exacerbated by metals and metalloids that adhere to the surfaces of such particles (Berico, Luciani, and Formignani, 1997; Ghio and Devlin, 2001; Soukup, Ghio, and Becker, 2000; World Health Organization, 2003).

This study comprises a health risk assessment on the inhalation and ingestion of heavy-metals enriched particles generated by wind erosion (dust fractions  $\leq 20 \ \mu$ m) from gold tailings storage facilities in the central Witwatersrand Basin. Despite the known hazards of inhaled fine particle and public concern, we could find no prior quantitative health risk assessment of windblown dust from gold mine tailings of the Witwatersrand.

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The key objectives are as follows:

- To sample and separate the inhalable fraction of a representative suite of source materials from gold mine TSFs
- ► To determine the elemental compositions of the separated inhalable fractions of the samples
- To identify dominant heavy metals that are present at concentrations above crustal averages
- To calculate the non-cancer and the cancer risks for adults and children, considering the inhalation and ingestion exposures associated with seasonal wind storms on the Witwatersrand.

## Materials and methods

## Study area, sample collection, and sample treatment

The study area and sampling sites extended over the central and eastern Witwatersrand Basin. The sampling sites included the following tailings storage facilities (coordinates are for the centre points of the facilities): Central Witwatersrand (CWJH) E 27°57′, S 26°14′; Central Witwatersrand Roodepoort (CWRD) E 27°50′ S 26°12′; Eastern Witwatersrand Springs (ERSP) E 28°18′, S 26°21′, and Eastern Witwatersrand Boksburg (ERBK) E 28°12′, S 26°14′.

Undisturbed bulk samples (approx. 5 kg) were collected at source from a depth of 15 cm to avoid material already exposed to water and aeolian erosion. Samples taken from the top level of the TSFs represented the core deposited material as original material. Samples from the side slopes and bottom represented material eroded from the top layers by wind or water, and redeposited. After drying at room temperature, bulk material was separated by particle size using an AS 200 Jet Sieve Shaker® and the  $\leq$  20 µm fractions were retained for analysis. Each separated sample of  $\leq$  20 m dust obtained from the shaker, comprising 5 g or less, was labelled and stored in a clean glass bottle. All the separated sub-samples were stored at room temperature until needed for further analysis.

## Sample preparation and analysis

For each sample, 0.2 g of sieved tailings material (diameter  $\leq$  20  $\mu m$ ), the digestion procedure was as follows

- Step 1: 10 ml of 10:1 HF:HCl was added to the sample, which was then heated to 110°C for 210 minutes until dry (this step repeated three times to ensure dissolution of quartz and oxides)
- Step 2: 7.5 ml HCl + 7.5 ml HNO3 were added to the dry residue, followed by heating to 110°C for 230 minutes—until dry
- Step 3: 0.5 ml HF, 2 ml HCL, and 10 mL HNO3 were added to the sample residue, which was then heated to 110°C for 60 minutes—not dry
- Step 4: The sample was diluted to 50 ml with deionized water.

Over 30 elements were measured using inductively coupled plasma-mass spectrometry (ICP-MS, using a Varian 810 instrument in standard resolution mode). A solution of Ru, Re was used as a constant bleed into the uptake stream as an internal standard. To correct for mass bias and calibration drift during sample analysis by ICP-MS, an internal standard solution containing 10  $\mu$ g/L of Be, Re, Ru, was bled into the sample uptake line using a glass T-shaped mixing chamber (Glass Expansion TM). As part of the quality assurance procedures, a series of certified reference materials (CRMs), reagents, procedural blanks, and many duplicates (both procedural and analytical) were analysed with every batch of 20 samples.

## Heavy metal identification and enrichment factors

From the range of 30 elements analysed, a selection was made of elements in the parts per million (ppm) and higher concentration range. This sub-set included the heavy metals As, Pb, U, Zn, Ni, Au, Cr, Cd, K, Fe, and Mn. Of these, only metals that were enriched in the tailings with respect to average crustal composition were selected for the health risk assessment. For the purposes of this study, *enriched* was taken as any element with an enrichment factor (EF) greater than 2. Elements with concentrations less than 1 ppm were not considered, as these are unlikely to constitute a health hazard, even if they were enriched relative to average crustal composition.

Si (the major metal present in the tailings) in the form of quartz is known to constitute a health hazard greater than when present in silicon-aluminium-potassium minerals (Hnizdo, 1995, 1994; Hnizdo, Sluis-Cremer, and Thomass, 1993); however, the health risk posed by quartz in either the micrometre or nanoparticle size ranges is outside the scope of this paper.

For the calculation of the EF, iron was used as the reference element (Taylor and McLennan, 1995). The average crustal abundance of Fe is 43 200 ppm (Rudnick and Presper, 1990; Shaw, Dostal, and Keays, 1976). Equation [1] was used for the EF enrichment factor calculation.

[1]

$$FM = (M_x * Fe_b) / (M_b * Fe_x)$$

where  $M_x$  and  $Fe_x$  are the concentrations of element M and Fe in the sample *x*, and  $M_b$  and  $Fe_b$  are the mean concentrations of element M and Fe in the continental crust (Wedepohl, 1995). All concentrations are in ppm. Although it would be preferable to use the most abundant element, silicon, as the reference element, silicon cannot be determined by ICP-MS.

#### Aerosol concentration determination

Onset of saltation (movement of sand grains) occurs at a wind speed of approximately 4 m s<sup>-1</sup>, and increases with wind speed proportional to the square of the velocity. Significant generation of dust resulting in visible plumes begins only above about 6 m s<sup>-1</sup>. Dust generation is dependent further on the exposure of dry. unvegetated soil or sand surfaces. The frequency of such winds is seasonally dependent; on the South African highveld the dusty season is from the onset of spring winds at the beginning of August through mid-October, by which time, spring rainfall suppresses further windblown dust generation. Measurements of ambient aerosol (dust) concentrations were made with Grimm<sup>®</sup> aerosol monitor during three weeks in September 2010. During this monitoring period, high-dust episodes occurred, associated with short-duration convective thunderstorms. These episodes were selected as worst-case scenarios of extreme dust storm days. The worst-case scenario assumed that the highest 24-hour concentration  $(540 \ \mu g \ m^{-3})$  (Ojelede, Annegarn, and Kneen, 2012) persisted for the entire three-month windy season (August, September, and October). This scenario was used in the calculation of the exposure concentration of airborne aerosol for the risk assessment.

## Exposure assessment

#### Inhalation and ingestion exposure

Two routes of exposure, inhalation and ingestion, were considered for the potential health risk posed by heavy metals in airborne particles to the population living around the TSFs. Intake of each element was calculated according the current standard risk assessment procedures of the US EPA (2011a, b). For the risk calculation formula, the exposure duration is required to be expressed as the average exposure in units of hours per day. Mean exposure duration (time) (ET) to the windblown dust from the TSFs was derived using the wind speed and direction record from the meteorological station at OR Tambo International Airport (courtesy of the South African Weather Service). A ten-year record from 2000 to 2009 was used to extract the number of hourly wind speeds above the threshold of 6 m  $s^{-1}$  for the onset of dust generation. This process yielded an annual average exposure time ET = 2.5 h  $d^{-1}$ .

Default exposure parameter values used for the dose calculation for inhalation and ingestion pathways are taken from the US EPA (2011b). Equations [2] and [3] were used for calculation of the exposure concentration for inhalation and chemical daily intake for the ingestion as developed by the US EPA (2011b):

$$EC_{inh} = C^* (ET^*EF^*ED) / ATn$$
[2]

where  $EC_{inh}$  is the exposure concentration for inhalation, C the metal concentrations in 24 hours for worst-day dust concentration (540 mg kg<sup>-1</sup> or µg m<sup>-3</sup>), ET the exposure time (2.5 h d<sup>-1</sup>), EF the exposure frequency (350 d a<sup>-1</sup>), ED theexposure duration (6 years for children and 24 years for adults), AT*n* the averaging time: for non-carcinogens, AT = ED × 365 d × 24 hours; for carcinogens, AT = 70 × 365 d × 24 hours).

 $CDI_{ingest} = (C^*IngR)/BW^*(EF^*ED)/AT^*CF$ 

[3]

where  $\text{CDI}_{ingest}$  is the chemical daily intake from soil ingestion (mg kg<sup>-1</sup> d<sup>-1</sup>), C the chemical concentration in soil (mg kg<sup>-1</sup>), IngR the soil ingestion rate (mg d<sup>-1</sup>), BW the body weight (kg); CF the unit conversion factor (10<sup>-6</sup> kg mg<sup>-1</sup>), EF the exposure frequency (350 d<sup>-1</sup>), ED the exposure duration (6 years for children and 24 years for adults), AT the averaging time (for non-carcinogens, AT= ED × 365 d; for carcinogens, AT = 70 × 365 = 25 550 d).

#### **Risk characterization**

Risk characterization for selected heavy metals was assessed for adults and children in calculating the non-cancer and cancer risk adopting the equations described in the EPA Methods (US EPA, 2011a, b, 2005a, b, c). The non-cancer risk was calculated by assessing the hazard quotient and hazard indices only for the selected enriched elements. The hazard quotient was derived by assessing each heavy element encountered and computing the results for the concentration inhaled or dose ingested using exposure duration (Equations [4] and [5]).

The reference dose (RfD) is 'an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime' (US EPA, 2011a). Reference concentration is 'an estimated daily concentration of a chemical in air, the exposure to which over a specific exposure duration poses no appreciable risk of adverse health effects, even to sensitive populations' (US EPA, 2011a).

RfC and RfD were from the US EPA (2012). An assumption on the toxic values (RfC and RfD) of Cr VI as total Cr was made in the risk assessment based on previous risk assessment studies on dust (Hu *et al.*, 2011, 2012; Kurt-Karakus, 2012). Although Cr VI is the identified carcinogenic chemical form of Cr, for screening purposes in this study the risk factor was calculated as though all Cr present was in the form of Cr VI. If the calculated risk for the total amount of Cr was within the acceptable limit, then any lesser fraction of Cr VI would similarly be within the limits, and the need for separate chemical speciation of the Cr components could be avoided.

A hazard index (HI) was obtained by summing the results from hazard quotient (Equation [6]) taking into account both routes of exposure (US EPA, 2011b).

HQ inhalation=EC*0.001/RfC	[4]

HQ <i>ingestion</i> = CDI/RfD	[5]
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CDI is the daily intake (mg kg<sup>-1</sup>d<sup>-1</sup>); RfC is the reference concentration inhaled material (mg m<sup>-3</sup> per day).

RfD is the reference dose of ingested material  $(mg kg^{-1} d^{-1})$ .

HI =	ΣΗΟί		

where  $HQ_i$  is the hazard quotient for  $COPC_i$ 

 $HI_{ingestion} = \sum_{I} \{ DI_{I} / RfD_{I} + DI_{2} / RfD_{2} \dots DI_{I} / RfD_{i} \}$ [7]

[6]

where  $DI_i$  is the daily intake for *i*<sup>th</sup> toxicant in (mg kg<sup>-1</sup> d<sup>-1</sup>) and RfD<sub>i</sub> is the reference dose for *i*<sup>th</sup> toxicant in mg kg<sup>-1</sup> d<sup>-1</sup>.

Total HI = 
$$\Sigma_j$$
 HI<sub>j</sub> [8]

where HIj is the hazard index for exposure pathway j.

The cancer risk was computed for both routes of exposure (inhalation and ingestion). To calculate the excess lifetime cancer risk due to inhalation and ingestion of particulate matter, Equations [9] and [10] were used (US EPA, 2011b). The cancer inhalation unit risk factor (IURF) [(mg m<sup>-3</sup>)<sup>-1</sup>] and slope factor (SF) [mg<sup>-1</sup> kg d] values were taken from US EPA (2012) for As and Cr, while the SF for Cd was from the Agency for Toxic Substances and Disease Registry (2008).

$$CR_{inhalation} = EC \times IURF$$
 [9]

where CR is the cancer risk, EC is the chronic daily exposure concentration (averaged over a 70-year lifetime) for inhalation of particulate matter [mg kg<sup>-1</sup>], and IURF is the inhalation unit risk factor [(mg m<sup>-3</sup>)<sup>-1</sup>].

$$CR_{ingestion} = CDI \times SF$$
 [10]

where CDI is chemical daily intake, and SF is the slope factor. Total risks were calculated by summing the CR values for both routes of exposure, for the inhalation and ingestion risks (Equation [11]) (US EPA, 2011b):

Total cancer =  $CR_{inhalation} + CR_{ingestion}$  [11]

#### Statistical analysis

Descriptive statistics (means and standard deviations) of the elemental concentrations for samples from each TSF were calculated using the Statistical Package for the Social Sciences (SPSS®) software.

VOLUME 117

Table I

Measured mean concentration of heavy metals in the gold mine tailings storage facilities (TSFs) compared to Earth crustal averages (bold indicates above crustal average) (ppm)

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Element		Mean concentra	tion in each TSF	:	Mean concentration	Concentration in	
	ERSP	ERBK	CWJB	CWRD	across the four TSFs	continental crust #	
Fe	40 500	42 200	44 800	21 300	37 100	43 200	
К	19 700	21 000	10 670	22 00	11 700	21 400	
Mn	205	220	325	160	240	716	
Cr	410	550	230	120	290	126	
Zn	40	30	70	30	46	65	
Ni	106	60	76	16	60	56	
As	150	140	90	110	116	1.7	
U	8	7	16	16	13	1.7	
Pb	16	11	27	24	21	14.8	
Cd	0.10	0.08	1.52	5.67	2.42	0.10	
Au	0.52	0.72	3.91	1.30	2.09	0.0025	

# Adopted from Wedepohl, 1995

#### **Results and discussion**

Mean concentrations of elements around TSFs are presented in Table I and are compared to average concentrations in the continental crust as proposed by Wedepohl (1995).

Mean concentrations of As, Au, and U were above the Earth crustal average in the four tailings; Pb concentration was higher at CWRD, CWJB, and ERSP. Cr and Ni concentrations were above the crustal average at CWJB, ERBK, and ERSP. Mean concentrations across the four TSF complexes showed that As, Au, U, Pb, Cd, Cr, and Ni were all above the crustal average.

The elevated concentration of these metals may be explained by the mineralogical features of the Witwatersrand Basin gold deposits. Concentrations of elements below the Earth crustal average, including K, Mn, Zn, Fe, are not surprising for the gold tailings material (a silica-rich mineral matrix) (Frimmel and Minter, 2002; Robb and Meyer, 1995).

Results on the elemental enrichment with respect to average crustal composition in the sub-20  $\mu$ m tailings fraction were derived using Equation [1] and were broken down into two ranges. The first range included elements with EF >2, which were Au (78 500), Cd (18 800), As (64), U (8), Cr (2), and Pb (2); while in the second range K (0.90), Ni (0.80), Zn (0.70), Fe (1), and Mn (0.25) presented an EF <2. The EF of elements in the tailings occurs in the order: Au>Cd>As>U>Cr>Pb>Fe>K>Ni>Zn>Mn.

Cd, Au, and As had the highest enrichment factors, falling in the class of extremely high enrichment (EF >40). Similar results on Au enrichment factors (20–400) in the sediments have been documented by Roychoudhury and Starke (2006), and the presence of arsernopyrite has been previously demonstrated (Genkin *et al.*, 1998). The enrichment of metals (*e.g.* As and Cd) in pyrite tailings is explained by adsorption onto the pyrite or by Feoxyhydroxides generated by the oxidation of pyrite (Öhlander *et al.*, 2007). Cd is found in sulphide minerals such as greenockite (CdS) which are among the minerals associated with gold in the Witwatersrand. The enrichment of Cr is due to the fact that its composition is made up of 30% of phyllosilicates (Feather and Koen, 1975). Cr is hosted in phyllosilicates, and a similar moderate enrichment has been recorded by Craw, Windle, and Angus (1999). U enrichment in tailings dumps may be explained by the enhanced uranium content of the Dominion Reef (one of the gold-bearing horizons mined on the Witwatersrand) (Robb and Meyer, 1995). Pb indicates a moderate enrichment, which can be explained by the fact that galena (PbS) is one of minerals associated with gold ore. Pb occurs also as the end-member of the uranium radioactive decay series. Fe, K, Mn, Zn, and Ni are not enriched, with values EF < 2. The acidification occurring in tailings could justify these results as long as those elements are dissolved in the solution (Espana et al., 2005; Tutu, McCarthy, and Cukrowska, 2008). Tutu, McCarthy, and Cukrowska (2008) reported the occurrence of acidification in tailings in which oxidation reactions contribute to the dissolution of elements such as U. As. Cu. Ni, Co, and Zn.

The risk assessment includes non-cancer and cancer risk. Enriched elements (Cr, Cd, and As) with EF >2 were used for risk assessment. However, Pb was not assessed due to the lack of data on the exposure concentration for inhalation or reference dose (Integrated Risk Information System, 2005) and might require a particular method of risk assessment which considers several sources of intake (US EPA, 2002). Although Au was enriched, it was not considered for further analysis because it is biologically inert (Walker, 2007).

Results on non-cancer risk are summarized in Table II, indicating the hazard quotient and hazard indices via inhalation and ingestion for the adults and children. HI shows values of less than unity, which is considered as a threshold. The interpretation of risk assessment (extrapolated from recorded values for the inhalation or ingestion of enriched elements of critical concern (*i.e.* As, Cr, and Cd) revealed that there was no evidence of negative health impacts for either children or adults according to benchmarks established by the US EPA (1986).

The results in Table II on the total of hazard indices show values less than unity for all four TSFs, indicating that the concentrations are within acceptable limits.

The cancer risk was assessed on the enriched elements (As, Cd, and Cr) classified as carcinogenic (Fishbein, 1984; Kyle *et al.*, 2011; US EPA, 1998; Smith and Steinmaus, 2009; Wang *et al.*, 2011).

Table II	Table II										
Summary of HI values via inhalation and ingestion for children and adults											
Tailings	Element	nent HQ inhalation		HI inhalation		HQ ingestion		HI ingestion		HI ingestion + inhalation	
		Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
	Cr	2.34E-01	2.34E-01			1.85E-03	1.98E-04				
ERSP	As	6.17E-01	6.17E-01	0.85	0.85	7.31E-03	7.83E-04	9.2E-03	2.0E-04	0.86	0.86
	Cd	3.38E-04	3.38E-04			1.60E-06	1.71E-07				
	Cr	2.98E-01	2.98E-01			2.35E-03	2.52E-04				
ERBK	As	4.97E-01	4.97E-01	0.79	0.79	5.89E-03	6.31E-04	8.2E-03	8.8E-04	0.80	0.80
	Cd	1.41E-04	1.41E-04			6.67E-07	7.14E-08				
	Cr	1.15E-01	1.15E-01			9.11E-04	9.76E-05				
CWJB	As	3.35E-01	3.35E-01	0.45	0.45	3.96E-03	4.25E-04	4.9E-03	9.8E-05	0.46	0.45
	Cd	4.36E-03	4.36E-03			2.07E-05	2.21E-06				
	Cr	7.05E-02	7.05E-02			5.57E-04	5.97E-05				
CWRD				0.58	0.58			6.5E-03	7.0E-04	0.59	0.58
	As	4.95E-01	4.95E-01			5.87E-03	6.29E-04				
	Cd	1.49E-02	1.49E-02			7.05E-05	7.56E-06				

Tailings	Element	Element CR inhalation		CR inhalation		CR ingestion		CR ingestion		CR ingestion + inhalation	
		Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
	Cr	3.46E-06	8.01E-07	6.24E-05	1.44E-05	2.69E-07	1.15E-07	5.9E-07	2.5E-07	6.30E-05	1.47E-05
ERSP	As	5.89E-05	1.36E-05			3.20E-07	1.37E-07				
	Cd	2.00E-10	4.63E-11			9.48E-10	4.06E-10				
	Cr	4.41E-06	1.02E-06	5.19E-05	1.20E-05	3.43E-07	1.47E-07	6.0E-07	2.6E-07	5.25E-05	1.23E-05
ERBK	As	4.75E-05	1.10E-05			2.57E-07	1.10E-07				
	Cd	8.33E-11	1.93E-11			3.95E-10	1.69E-10				
	Cr	1.71E-06	3.95E-07	3.37E-05	7.79E-06	1.33E-07	5.69E-08	3.2E-07	1.4E-07	3.40E-05	7.93E-06
CWJB	As	3.20E-05	7.40E-06			1.73E-07	7.43E-08				
	Cd	2.58E-09	5.98E-10			1.22E-08	5.25E-09				
CWRD	Cr	1.04E-06	2.42E-07	4.84E-05	1.12E-05	8.11E-08	3.48E-08	3.8E-07	1.6E-07	4.88E-05	1.14E-05
	As	4.73E-05	1.10E-05			2.57E-07	1.10E-07				
	Cd	8.82E-09	2.04E-09			4.18E-08	1.79E-08				

U fell into the criteria of risk assessment, but naturally occurring U contains three isotopes, <sup>238</sup>U, <sup>235</sup>U, and <sup>234</sup>U so the carcinogenic risk depends on the different radiological properties of these isotopes (Eisenbud and Gesell, 1997). It was outside the scope of this work to assess the excess lifetime cancer risk for uranium.

Equations [9] and [10] were applied for calculating the cancer risk via inhalation and ingestion, respectively. The total cancer risk for Cd, Cr (VI), and As via inhalation and ingestion (Equation [11]) showed values between 1.0E-05 and 1.0E-06 for adults, and from 3.0E-05 to 6.0E-05 among children (Table III). The total cancer risk fell within the tolerable risk range of  $10^{-4}$  to  $10^{-6}$  (US EPA, 1991).

However, the full health effects of inhaled mineral dust need to include factors other than the heavy metal content dealt with in this contribution—the crystalline habit of minerals such as quartz and the possible aggravating effects of particles in the nanoparticle size range present additional hazards (Bakand, Hayes, and Dechsakulthorn, 2012, Davies and Mundalamo, 2010; Oberdörster, 2005, Hoet *et al.*, 2004). Within mixed dust, mineral particles can interact synergistically to increase or attenuate the toxicity (Fubini and Otero Areàn, 1999).

## Conclusions

Chemical analysis of sub-20  $\mu$ m dust fractions collected from four gold TSFs at Witwatersrand basin revealed elements such As, U, Cd, Pb, and Cr with EF>2. This enrichment is due to the fact that those elements occur in the gold-bearing ores.

Health risk assessment, including non-carcinogenic risk estimation via inhalation and ingestion of As, Cd, and Cr (VI) presented hazard indices of less than unity for children and adults. The total cancer risk level fell within the range of acceptable risk  $(10^{-4} \text{ to } 10^{-6})$  suggested by US EPA. Non-

667 <

carcinogenic and carcinogenic risks were found to be below the thresholds for public health and permissible for ambient exposures.

However, continued mitigation of airborne dust emissions and enforcement of current national dust fallout standards are important to maintain ambient dust levels within the risk levels reported in this work.

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#### References

- Agency for toxic substances and disease registry. 2008. Draft toxicological profile for cadmium. http://www.atsdr.cdc.gov./toxprofiles/tp5.pdf [Accessed 5 September 2011].
- ANNEGARN, H.J., SCORGIE, Y., and SITHOLE. J. 2002. Dust monitoring and mitigation on surface gold tailings reclamation. *Proceedings of Surface Mining 2002 – Modern Developments for the New Millennium*. South African Institute for Mining and Metallurgy, Johannesburg. pp. 103–109.
- ANNEGARN, H., ZUCCHIATTI, A., SELLSCHOP, J.P.F., and BOOTH-JONES, P.A. 1990. Time variations of dust concentration and elemental composition in a gold mine. *Mining Science and Technology*. vol. 10. pp. 1–14.
- BAKAND, S., HAYES, A., and DECHSAKULTHORN, F. 2012. Nanoparticles: a review of particle toxicology following inhalation exposure. *Inhalation Toxicology*, vol. 24, no. 2. pp. 125–135.
- BAKAND, S. and HAYES, A. 2010. Troubleshooting methods for toxicity testing of airborne chemicals in vitro. *Journal of Pharmacological and Toxicological Methods*, vol. 61. pp.76–85.
- BEGA, S. 2011a. Living in S.A.'s own Chernobyl. Saturday Star, 8 January 2011. p. 13.
- BEGA, S. 2011b. Toxic mine dump time bomb threatens. Saturday Star, 5 November 2011. p. 15.
- BERICO, M., LUCIANI, A., and FORMIGNANI, M. 1997. Atmospheric aerosol in an urban area – measurements of TSP and PM10 standards and pulmonary deposition assessments. *Atmospheric Environment*, vol. 31. pp. 3659–3665.
- BLIGHT, G.E. and CALDWELL, J.A. 1984. The abatement of pollution from abandoned gold residue dams. *Journal of the South African Institute of Mining and Metallurgy*, vol.84, no. 1. pp.1–9.
- CRAW, D., WINDLE, S.J., and ANGUS, P.V. 1999. Gold mineralization without quartz veins in a ductile – brittle shear zone, Macraes Mine, Otago Schist, New Zealand. *Mineralium Deposita*, vol. 34. pp. 382–394.
- DAVIES, T.C. and MUNDALAMO, H.R. 2010. Environmental health impacts of dispersed mineralization in South Africa. *Journal of African Earth Sciences*, vol. 58. pp. 652–666.
- DOCKERY, D.W. 2001. Epidemiological evidence of cardiovascular effects of particulate air pollution. *Environmental Health Perspective*, vol. 109. pp. 483–486.
- EISENBUD, M. and GESELL, T. 1997. Environmental Radioactivity; from Natural Industrial, and Military Sources. 4th edn. Academic Press Elsevier, San Diego.
- 668 JULY 2017

- ESPANA, S.J., PAMO, E.L., SANTOFIMIA, E., ADUVIRE, O., REYES, J., and BARETTINO, D. 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel River Watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications. *Applied Geochemistry*, vol. 20. pp. 1320–1356.
- FEATHER, C.E., and KOEN, G.M. 1975. The mineralogy of the Witwatersrand reefs. *Mineral Science and Engineering*, vol. 7, pp. 89–224.
- FEDERATION FOR A SUSTAINABLE ENVIRONMENT. 2010. Annual report on the past year's activities. Rivonia, Johannesburg. 51 pp.
- FISHBEIN, L. 1984. Overview of analysis of carcinogenic and/or mutagenic metals in biological and environmental samples – arsenic, beryllium, cadmium, chromium and selenium. *International Journal of Environmental Analytical Chemistry*, vol. 17. pp. 113–170.
- FRIMMEL, H.E. and MINTER W.E.L. 2002. Recent developments concerning the geological history and genesis of the Witwatersrand gold deposits, South Africa. *Integrated Methods for Discovery: Global Exploration in the Twenty-First Century*. Goldfarb, R.J. and Nielsen, R.L. (eds). *Special Publication*, vol. 9. Society of Economic Geologists. pp. 17–45.
- FUBINI, B. and FENOGLIO, I. 2007. Toxic potential of mineral dusts. *Elements*, vol. 3. pp. 407–414.
- FUBINI, B. and OTERO AREAN, C. 1999. Chemical aspects of the toxicity of inhaled mineral dust. *Chemical Society Reviews*, vol.28. pp. 373–381.
- GENKIN, A.D., BORTNIKOV, N.S., CABRI, L.J., WAGNER, F.E., STANLEY, C.J., SAFONOV, Y.G., MCMAHON, G., FREIDL, J., KERZIN, A.L., and GAMYANIN, G.N. 1998. A multidisciplinary study of invisible gold in arsenopyrite from four deposits in Siberia, Russian Federation. *Economic Geology*, vol. 93. pp. 463–487.
- GHIO A. J. and DEVLIN, R.B. 2001. Inflammatory lung injury after bronchial instillation of air pollution particles. *American Journal of Respiratory and Critical Care Medicine*, vol. 164. pp. 704–708.
- GRIFFIN, D., KELLOGG, C. and SHINN, E. 2001. Dust in the wind: long-range transport of dust in the atmosphere and its implications for global public and ecosystem health. *Global Change and Human Health*, vol. 2. pp. 20–33.
- HARRISON, R.M. and YIN, J. 2000. Particle matter in the atmosphere: which particle properties are important for its effects on health? *Science of the Total Environment*, vol. 249. pp. 85–101.
- HOET, P.H.M., BRÜSKE-HOHLFELD, I., and SALATA, O.V. 2004. Nanoparticles known and unknown health risks. *Journal of Nanobiotechnology*, vol. 2, no. 12. 15 pp. DOI:10.1186/1477-3155-2-12
- HNIZDO, E. 1995. Risk of silicosis in relation to fraction of respirable quartz. American Journal of Industrial Medicine, vol. 27. pp. 619–622.
- HNIZDO, E. 1994. Risk of silicosis: Comparison of South African and Canadian miners. American Journal of Industrial Medicine, vol. 25. pp. 771–772.
- HNIZDO, E., Sluis-Cremer, G., and Thomas, G.K. 1993. Correlation between radiological and pathological diagnosis of silicosis: An autopsy population based study. *American Journal of Industrial Medicine*, vol. 24. pp. 427–445.
- HU, X., ZHANG, Y., LUO, J.U., WANG, T., LIAN, H., and DING, Z. 2011. Bioaccessibility and health risk of arsenic, mercury and other metals in urban street dusts from a mega-city, Nanjing, China. *Environmental Pollution*, vol. 159. pp. 1215–1221.
- HU, X., ZHANG, Y., DING, Z., WANG, T., LIAN, H., SUN, Y. and WU, J. 2012. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China. *Atmospheric Environment*, vol. 57. pp. 146–152.
- INTEGRATED RISK INFORMATION SYSTEM, 2005. Lead and compounds (inorganic) (CASRN 7439-92-1) | IRIS | USEPA. https://cfpub.epa.gov/ncea/iris/iris\_documents/documents/subst/0277\_su mmary.pdf [Accessed 10 August 2016].
  - The Journal of the Southern African Institute of Mining and Metallurgy

KURT-KARAKUS, P.B. 2012. Determination of heavy metals in indoor dust from Istanbul, Turkey: estimation of the health risk. *Environment International*, vol. 50. pp.47–55.

KYLE, J.H., BREUER, P.L., BUNNEY, K.G., PLEYSIER R., and MAY, P.M. 2011. Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their deportment in gold processing. Part 1: Mineralogy, aqueous chemistry and toxicity. *Hydrometallurgy*, vol. 107. pp. 91–100.

OBERDÖRSTER, G. 2005. Inhaled nano-sized particles: potential effects and mechanisms. *Proceedings of the First International Symposium on Occupational Health Implications of Nanomaterials*, Buxton, UK. Health and Safety Executive, Great Britain and the National Institute for Occupational Safety and Health, United States.

ÖHLANDER, B., MÜLLER, B., AXELSSON, M., and ALAKANGAS, L. 2007. An attempt to use LA-ICP-SMS to quantify enrichment of trace elements on pyrite surfaces in oxidizing mine tailings. *Journal of Geochemical Exploration*, vol. 92. pp. 1–12.

OJELEDE M.E., ANNEGARN, H.J., and KNEEN, M.A. 2012. Evaluation of aeolian emissions from gold mine tailings on the Witwatersrand. *Aeolian Research*, vol. 3. pp. 477–486.

OJELEDE, M.E. 2012. Risk assessment of atmospheric emissions from gold mine tailings on the Witwatersrand. PhD thesis, University of Johannesburg, South Africa.

PARK, R.J., JACOB, D.J., FIELD, B.D., YANTOSCA, R.M., and CHIN, M. 2004. Natural and transboundary pollution influences on sulfate–nitrate–ammonium aerosols in the United States: implications for policy. *Journal of Geophysical Research*, vol. 109, D15204. DOI:10.1029/2003JD004473

POPE III, C.A. and Dockery, D. W. 2006. Health effects of fine particulate air pollution: lines that connect. Journal of Air and Waste Management Association, vol. 56. pp. 709–742.

ROBB, L.J. and MEYER, F.M. 1995. The Witwatersrand basin, South Africa, geological framework and mineralization processes. *Ore Geology Reviews*, vol. 10, no. 2. pp. 67–94.

ROYCHOUDHURY, A.N. and STARKE, M.F. 2006. Partitioning and mobility of trace metals in the Blesbokspruit: Impact assessment of dewatering of mine waters in the East Rand, South Africa. *Applied Geochemistry*, vol. 21. pp. 1044–1063.

RUDNICK, R.L. and PRESPER, T. 1990. Geochemistry of intermediate/- to highpressure granulites. *Granulites and Crustal Evolution*. Vielzeuf, D. and Vidal, P. (eds). Kluwer, Dordrecht. pp. 523–550,

Schwartz, J. 1994. Particulate air pollution and respiratory disease. Environmental Research, vol. 62. pp. 7–13.

SCHWARTZ, J. 1992. Particulate air pollution and daily mortality: a synthesis. *Public Health Reviews*, vol. 19. pp. 39–60.

SHAW, D.M., DOSTAL, J., and KEAYS, R.R. 1976. Additional estimates of continental surface Precambrian shield composition in Canada. *Geochimica et Cosmochimica Acta*, vol. 40. pp. 73–84.

SMITH, A.H. and STEINMAUS, C.M. 2009. Health effects of arsenic and chromium in drinking water: recent human findings. *Annual Review of Public Health*, vol. 30. pp. 107–120.

SOUKUP, J.M., GHIO, A.J., and BECKER, S. 2000. Soluble components of Utah Valley particulate pollution alter alveolar macrophage function in vivo and in vitro. *Inhalation Toxicology*, vol. 12. pp. 401–414.

TAYLOR, S.R. and MCLENNAN, S. M. 1995. The geochemical evolution of the continental crust. *Reviews in Geophysics*, vol. 33. pp. 241–265.

TUTU, H., MCCARTHY, T.S., and CUKROWSKA, E. 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. *Applied Geochemistry*, vol. 23. pp. 3666–3684.

Us Epa. 2012. Regional screening levels (RSL) tables (Last updated November 2012). United States Environmental Protection Agency, Washington DC http://www.epa.gov/PacificSouthwest/Superfund [Accessed 9 August 2016].

Us Epa. 2011a. Exposure factors handbook (final edition). United States Environmental Protection Agency, Washington, DC. EPA/600/R-09/052F. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252 [Accessed 29 October 2016]. Us Epa. 2011b. Risk assessment guidance for superfund. Part A: Human health evaluation manual; Part F, Supplemental guidance for inhalation risk assessment, vol. I. United States Environmental Protection Agency, Washington, DC. https://www.epa.gov/risk/risk-assessment-guidancesuperfund-rags-part-f [Accessed 9 August 2016].

Us Epa. 2005a. Guidelines for carcinogen risk assessment. Risk Assessment Forum, United States Environmental Protection Agency, Washington, DC. EPA/630/P-03/001F. https://www.epa.gov/risk/guidelines-carcinogenrisk-assessment [Accessed 10 August. 2016].

Us Epa. 2005b. Human health risk assessment protocol. Appendix C. Risk characterization equations. United States Environmental Protection Agency, Washington, DC. https://archive.epa.gov/epawaste/hazard/tsd/td/web/pdf/05hhrapapc.pdf [Accessed 10 August 2016].

Us Epa. 2005c. Human health risk assessment protocol hazardous waste combustion facilities. United States Environmental Protection Agency, Washington, DC. http:// https://nepis.epa.gov/Exe/ [Accessed 10 August 2016].

Us Epa. 2002. A review of the reference dose and reference concentration processes EPA/630/P-02/002F. United States Environmental Protection Agency, Washington, DC. https://www.epa.gov/sites/production/files/2014-12/documents/rfdfinal.pdf [Accessed 10 August 2016].

Us Epa. 1991. Guidelines for developmental toxicity risk assessment. 56 FR 63798-63826. United States Environmental Protection Agency, Washington, DC. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=23162 [Accessed 10 August 2016].

Us Epa. 1998. Toxicological review of hexavalent chromium. https://ofmpub.epa.gov/eims/eimscomm.getfile?p\_download\_id=498828 [Accessed 24 August 2016].

Us Epa. 1986. Guidelines for the health risk assessment of chemical mixtures. 51 Federal Register 34014. United States Environmental Protection Agency, Washington, DC. https://ofmpub.epa.gov/eims/eimscomm.getfile?p\_download\_id=4487 [Accessed 10 August 2016].

VALAVANIDIS, A., FIOTAKIS, K., and VLACHOGIANNI, T. 2008. Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. *Journal of Environmental Science and Health, Part C, Environmental Carcinogenesis and Ecotoxicology Reviews*, vol. 26, no. 4. pp. 339–362.

WALKER, N. 2007. Research concept: Nano-scale gold. http//ntp.niehs.nih.gov/ntp/.../6\_walker\_Nanogold\_for\_BSC\_120607.pdf [Accessed 23 June 2012].

WANG, Z.X., CHEN, J.Q., CHAI, L.Y., YANG, Z.H., HUANG, S.H., and ZHENG, Y. 2011. Environmental impact and site-specific human health risks of chromium in the vicinity of a ferro-alloy manufactory, China. *Journal of Hazardous Materials*, vol. 190. pp. 980–985.

WEDEPOHL, K.H. 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta*, vol. 59, no. 7. pp. 1217–1232.

WILSON, W.E. and SUH, H.H. 1997. Fine particles and coarse particles: concentration relationships relevant to epidemiologic studies. *Journal of Air and Waste Management Association*, vol. 47. pp. 1238–1249.

WORLD HEALTH ORGANIZATION. 2006. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide: Global update 2005. Summary of risk assessment. WHO/SDE/PHE/OEH/06.02. Geneva http://whqlibdoc.who.int/hq/2006/WHO\_SDE\_PHE\_OEH\_06.02\_eng.pdf [Accessed 10 March 2013].

WORLD HEALTH ORGANIZATION. 2003. Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide. Report on a WHO working group, Bonn, EUR/03/5042688, Geneva. http://ec.europa.eu/environment/archives/cafe/activities/pdf/1st\_report. pdf [Accessed 30 August 2012]. ◆

The Journal of the Southern African Institute of Mining and Metallurgy

VOLUME 117