Dust fallout from tailings storage facilities (TSFs) is a major contributor to ambient air pollution 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 μg m⁻³ (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 assessed to be acceptable for a lifetime exposure. The total risk for both exposures (inhalation and the ingestion) was assessed to be below the non-cancer benchmark (hazard indices 1.0) considered to be acceptable for a lifetime exposure. The toxicity of particulate matter is a result of the particle size, which allows the smaller particle to be transported deeper in the respiratory tract (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 ≤ 20 μm) 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.
Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles

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 (CWRD) E 27°57’, S 26°14’; Central Witwatersrand Roodepoort (CWRD) E 27°50’, S 26°12’; Eastern Witwatersrand Springs (ERSP) E 28°16’, 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 ≤ 20 μm fractions were retained for analysis. Each separated sample of ≤ 20 μm 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 ≤ 20 μm), 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 μg/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 Thomas, 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, 1993); however, the health risk posed by quartz in either the micrometre or nanoparticle size ranges is outside the scope of this paper.

\[ \text{FM} = \frac{(M_x \cdot Fe_x)}{(M_0 \cdot Fe_0)} \]

where \(M_x\) and \(Fe_x\) are the concentrations of element \(M\) and Fe in the sample \(x\), and \(M_0\) and \(Fe_0\) 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\(^{-1}\), 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\(^{-1}\). 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® 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 μg 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.
Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles

**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):

\[ EC_{\text{inh}} = C^i \cdot (ET \cdot EF \cdot ED)/AT \]

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

\[ CDI_{\text{ingest}} = (C^i \cdot \text{IngR})/BW \cdot (EF \cdot ED)/AT \cdot CF \]

where \( CDI_{\text{ingest}} \) is the chemical daily intake from soil ingestion (mg kg⁻¹ d⁻¹), \( C \) the chemical concentration in soil (mg kg⁻¹), \( \text{IngR} \) the soil ingestion rate (mg d⁻¹), \( BW \) the body weight (kg); \( CF \) the unit conversion factor \((10^6 \text{ kg mg}^{-1})\), \( EF \) the exposure frequency (350 d⁻¹), \( ED \) the exposure duration (6 years for children and 24 years for adults), \( AT \) the averaging time: for non-carcinogens, \( AT = ED \times 365 \) d × 24 hours; for carcinogens, \( AT = 70 \times 365 \) = 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; Kurt-Karakus, 2012). Although Cr VI is the identified carcinogetic 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).

\[ HQ_{\text{inha}} = EC^i \cdot 0.001/RfC \]

\[ HQ_{\text{ingest}} = CDI/RfD \]

where \( HQ \) is the hazard quotient for COPC, \( HI \) 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).

\[ \text{Total HI} = \sum HI \]

where \( HI_j \) is the hazard index for exposure pathway \( j \). The cancer risk 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).

\[ \text{Total cancer} = CR_{\text{inha}} + CR_{\text{ingest}} \]

**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.
Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles

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)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean concentration in each TSF</th>
<th>Mean concentration across the four TSFs</th>
<th>Concentration in continental crust #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>40.500</td>
<td>42.200</td>
<td>40.200</td>
</tr>
<tr>
<td>K</td>
<td>19.700</td>
<td>21.000</td>
<td>17.000</td>
</tr>
<tr>
<td>Mn</td>
<td>205.220</td>
<td>220.325</td>
<td>220.160</td>
</tr>
<tr>
<td>Cr</td>
<td>410.550</td>
<td>230.120</td>
<td>290.120</td>
</tr>
<tr>
<td>Zn</td>
<td>40.30</td>
<td>70.30</td>
<td>46.65</td>
</tr>
<tr>
<td>Ni</td>
<td>106.60</td>
<td>76.16</td>
<td>56.56</td>
</tr>
<tr>
<td>As</td>
<td>150.140</td>
<td>90.110</td>
<td>1.7</td>
</tr>
<tr>
<td>U</td>
<td>8.7</td>
<td>16.16</td>
<td>1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>16.11</td>
<td>27.24</td>
<td>14.8</td>
</tr>
<tr>
<td>Cd</td>
<td>0.10</td>
<td>1.52</td>
<td>2.42</td>
</tr>
<tr>
<td>Au</td>
<td>0.52</td>
<td>3.91</td>
<td>0.025</td>
</tr>
</tbody>
</table>

# 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 CWJB, ERSP, and CWRD. The enrichment of metals due to the fact that galena (PbS) is one of minerals occurring in tailings could justify these results as long as those elements are dissolved in the solution (España 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).
U fell into the criteria of risk assessment, but naturally occurring U contains three isotopes, 238U, 235U, and 234U 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 Areán, 1999).

### Table II
Summary of Hi values via inhalation and ingestion for children and adults

<table>
<thead>
<tr>
<th>Tailings</th>
<th>Element</th>
<th>HQ inhalation</th>
<th>HI inhalation</th>
<th>HQ ingestion</th>
<th>HI ingestion</th>
<th>HI ingestion + inhalation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Children</td>
<td>Adults</td>
<td>Children</td>
<td>Adults</td>
<td>Children</td>
</tr>
<tr>
<td>ERSP</td>
<td>Cr</td>
<td>2.34E-01</td>
<td>2.34E-01</td>
<td>0.85</td>
<td>0.85</td>
<td>1.85E-03</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>6.17E-01</td>
<td>6.17E-01</td>
<td></td>
<td></td>
<td>7.31E-03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>3.38E-04</td>
<td>3.38E-04</td>
<td></td>
<td></td>
<td>1.60E-06</td>
</tr>
<tr>
<td>ERBK</td>
<td>Cr</td>
<td>2.98E-01</td>
<td>2.98E-01</td>
<td>0.79</td>
<td>0.79</td>
<td>2.35E-03</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>4.97E-01</td>
<td>4.97E-01</td>
<td></td>
<td></td>
<td>5.89E-03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>1.41E-04</td>
<td>1.41E-04</td>
<td></td>
<td></td>
<td>2.07E-05</td>
</tr>
<tr>
<td>CWJB</td>
<td>Cr</td>
<td>1.15E-01</td>
<td>1.15E-01</td>
<td>0.45</td>
<td>0.45</td>
<td>9.11E-04</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>3.35E-01</td>
<td>3.35E-01</td>
<td></td>
<td></td>
<td>3.96E-03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>4.36E-03</td>
<td>4.36E-03</td>
<td></td>
<td></td>
<td>2.07E-05</td>
</tr>
<tr>
<td>CWRD</td>
<td>Cr</td>
<td>7.05E-02</td>
<td>7.05E-02</td>
<td>0.58</td>
<td>0.58</td>
<td>5.57E-04</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>4.95E-01</td>
<td>4.95E-01</td>
<td></td>
<td></td>
<td>5.87E-03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>1.49E-02</td>
<td>1.49E-02</td>
<td></td>
<td></td>
<td>7.05E-05</td>
</tr>
</tbody>
</table>

### Table III
Total risk of selected heavy metals Cr, Cd, and As via inhalation and ingestion exposure routes

<table>
<thead>
<tr>
<th>Tailings</th>
<th>Element</th>
<th>CR inhalation</th>
<th>CR ingestion</th>
<th>CR ingestion + inhalation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Children</td>
<td>Adults</td>
<td>Children</td>
</tr>
<tr>
<td>ERSP</td>
<td>Cr</td>
<td>3.46E-06</td>
<td>6.01E-07</td>
<td>6.24E-05</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>5.89E-05</td>
<td>1.36E-05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>2.00E-10</td>
<td>4.63E-11</td>
<td></td>
</tr>
<tr>
<td>ERBK</td>
<td>Cr</td>
<td>4.41E-06</td>
<td>1.02E-06</td>
<td>5.19E-05</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>4.75E-05</td>
<td>1.10E-05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>8.33E-11</td>
<td>1.93E-11</td>
<td></td>
</tr>
<tr>
<td>CWJB</td>
<td>Cr</td>
<td>1.71E-06</td>
<td>3.85E-07</td>
<td>3.37E-05</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>3.20E-05</td>
<td>7.40E-06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>2.58E-09</td>
<td>5.89E-10</td>
<td></td>
</tr>
<tr>
<td>CWRD</td>
<td>Cr</td>
<td>1.04E-06</td>
<td>2.42E-07</td>
<td>4.84E-05</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>4.73E-05</td>
<td>1.10E-05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>8.82E-09</td>
<td>2.04E-09</td>
<td></td>
</tr>
</tbody>
</table>
Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles

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.

Acknowledgements
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References


Health risk posed by enriched heavy metals (As, Cd, and Cr) in airborne particles


