

1 **Reconnaissance sampling and determination of hexavalent chromium in potentially-contaminated**
2 **agricultural soils in Copperbelt Province, Zambia**

3 Elliott M. Hamilton^{a, b}, Richard M. Lark^b, Scott D. Young^b, Elizabeth H. Bailey^b, Godfrey M. Sakala^c,
4 Kakoma K. Maseka^d, Michael J. Watts^{a,*}

5 ^a*Inorganic Geochemistry, Centre for Environmental Geochemistry, British Geological Survey,*
6 *Environmental Science Centre, Nicker Hill, Keyworth, Nottinghamshire, NG12 5GG, UK*

7 ^b*Centre for Environmental Geochemistry, School of Biosciences, University of Nottingham, Sutton*
8 *Bonington Campus, Loughborough, Leicestershire, LE12 5RD, UK.*

9 ^c*Zambia Agricultural Research Institute, Mount Makulu, Central Research Station, Lusaka, Zambia.*

10 ^d*Copperbelt University, Jambo Drive, Riverside, Kitwe, Zambia.*

11 *Corresponding author: M. J. Watts; email: mwatts@bgs.ac.uk, telephone number: 0115 936 3042

12 **Abstract**

13 The distribution of elemental species of chromium (Cr) in potentially-contaminated soil samples
14 warrants investigation due to the differing mobilities and toxicities of trivalent [Cr(III)] and hexavalent
15 chromium [Cr(VI)]. In addition, the possibility of species interconversions requires the
16 implementation of robust methods that can correct for changes at the point of sampling, extraction
17 and analysis. This work presents the application of speciated isotope dilution mass spectrometry
18 (SIDMS) to accurately quantify Cr(VI) in agricultural soils within close proximity to a mine tailings dam
19 in the Copperbelt Province of Zambia. Interpolated plots of total Cr, produced from data collected
20 through a nested sampling design, were used to optimise the sampling across the spatial domain.
21 Extraction of Cr(VI) was undertaken using a microwave assisted reaction system (80°C for 5 minutes)
22 with 50 mM EDTA, to complex Cr(III) and reduce the likelihood of oxidation during the extraction.
23 Isotopically-enriched ⁵³Cr(VI) was added to each sample prior to extraction to account for species
24 interconversions. The accuracy of the method was confirmed using NIST SRM 2700 and 2701. Cr(VI)

25 concentrations in the soil samples ranged between 0.03 and 0.29 mg kg⁻¹, significantly lower than the
26 residential UK screening value for Cr(VI) of 21 mg kg⁻¹. The data indicate that this site poses a low
27 environmental/human health risk with respect to Cr(VI) exposure.

28 **Keywords**

29 Chromium, hexavalent chromium, SIDMS, speciation, mine tailings

30 **1.0 Introduction**

31 Chromium (Cr) is a naturally-occurring element that exists in the environment primarily as two
32 chemical forms; trivalent chromium (Cr(III)) is considered non-toxic and important for regulation of
33 glucose and lipid metabolism (Krzysik, Grajeta, Prescha, & Weber, 2011), whereas hexavalent
34 chromium (Cr(VI)) is toxic and a known carcinogen through inhalation (Langárd & Costa, 2007).
35 Chromium-containing compounds have a range of uses in industrial applications, including
36 electroplating, steel manufacturing, wood preservation and leather tanning (Dhal, Thatoi, Das, &
37 Pandey, 2013), which has increased both concerns and restrictions over the anthropogenic release of
38 Cr(VI) into the environment (Oh, Song, Shin, Choi, & Kim, 2007).

39 Due to its presence as a positively-charged ion, Cr(III) is less mobile in soil-water systems than Cr(VI)
40 (James & Bartlett, 1983) and is therefore less likely to be transferred into plants grown in
41 contaminated soil (Shanker, Djanaguiraman, & Venkateswarlu, 2009). The majority of Cr(VI) in the
42 environment can be attributed to anthropogenic activity from industrial processes such as leather
43 tanning and metal finishing (Oliveira, 2012). Geogenic Cr(VI) occurs as a result of weathering of
44 ultramafic and serpentinite rocks (Oze, Bird, & Fendorf, 2007); groundwater concentrations in
45 ultramafic areas can range from 0.2 to 180 µg L⁻¹ (Chrysochoou, Theologou, Bompoti, Dermatas, &
46 Panagiotakis, 2016).

47 The speciation of Cr in solid sample matrices has been reviewed in a number of articles (Hamilton,
48 Young, Bailey, & Watts, 2018) (Séby & Vacchina, 2018). The main analytical challenge to address is

49 ensuring accurate determination of Cr(VI) in the sample without causing interconversion of species
50 (Pettine & Capri, 2005), which may lead to under/over-reporting of Cr(VI) (Nagourney, Wilson,
51 Buckley, Kingston, Yang, & Long, 2008) and an insufficient assessment of the associated risk to human
52 health (Novotnik, Zuliani, Ščančar, & Milačič, 2015). Speciated isotope dilution mass spectrometry
53 (SIDMS) was developed to correct for changes in speciation which may occur at sampling, storage
54 and/or analysis (Kingston, Huo, Lu, & Chalk, 1998). This variation on conventional isotope dilution uses
55 species-specific isotopically enriched spikes, added to the sample prior to digestion or extraction, to
56 accurately determine species concentrations in solid matrices and reduce analytical/species
57 conversion errors that may occur through external calibration (Martone, Rahman, Pamuku, &
58 Kingston, 2013).

59 The Copperbelt Province of Zambia has been the site of extensive mining operations for over 100 years
60 (Weissenstein & Sinkala, 2011), which had led to an increase in concentrations of potentially harmful
61 elements (PHEs) such as Cr, arsenic (As), cobalt (Co), lead (Pb) and zinc (Zn) (Bohdan Kříbek, Majer,
62 Veselovský, & Nyambe, 2010) . Numerous studies have evaluated the mobility of these PHEs (Ettler,
63 Mihaljevič, Kříbek, Majer, & Šebek, 2011) (Kaninga, Chishala, Maseka, Sakala, Lark, Tye, et al., 2019)
64 and the risk to human health through consumption of groundwater (von der Heyden & New, 2004)
65 and staple crops grown in contaminated soil (Bohdan. Kříbek, Majer, Knésl, Nyambe, Mihaljevič, Ettler,
66 et al., 2014); outside of the Copperbelt Province, the irrigation of crops with contaminated water and
67 subsequent accumulation of PHEs in soil is well documented (Stasinou & Zabetakis, 2013). However,
68 few studies have investigated the extent of Cr(VI) contamination in tailings-contaminated soil, despite
69 the likelihood of increased preservation of Cr(VI) if the tailings are limed prior to pumping to neutralise
70 and precipitate metals (Tang, Wang, Shuai, & Liu, 2016).

71 The objective of this study was to use previously-reported reconnaissance work to inform more
72 detailed sampling across potentially-contaminated agricultural land within half a kilometre of a large
73 tailings dam in the Copperbelt Province of Zambia. Single-spike speciated isotope dilution mass

74 spectrometry (SIDMS) was then employed to quantify Cr(VI) in 50 soils over this area, to establish
75 whether a human health risk could exist through exposure to Cr(VI) from soil contaminated with
76 tailings material. To the best knowledge of the authors, this work presents the first occasion of SIDMS
77 being used to quantify Cr(VI) in potentially-contaminated soil samples collected from the Copperbelt
78 Province of Zambia.

79 **2.0 Materials and Methods**

80 2.1 Sample Preparation and Analysis

81 Samples were dried at 40°C, disaggregated using a pestle & mortar and sieved to ≤ 2 mm. From this
82 sieved fraction, subsamples were milled to ≤ 53 μm using a planetary ball mill (Retsch GmbH, Germany)
83 for total Cr and Cr(VI) analyses. Samples for measurement of total Cr were prepared using an in-house
84 mixed acid (HF/HNO₃/HClO₄) open vessel hotblock digestion (Watts, Middleton, Marriott, Humphrey,
85 Hamilton, Gardner, et al., 2019). A microwave assisted reaction system (MARS One, CEM Corporation,
86 UK) was used for alkaline extraction of Cr(VI) from soil samples.

87 Determination of total Cr was performed by ICP-MS using an Agilent 7500cx instrument (Agilent
88 Technologies, Tokyo, Japan) using previously reported operating conditions (Hamilton, Barlow,
89 Gowing, & Watts, 2015); measurement of Cr(VI) in alkaline extractions was undertaken using an
90 Agilent 8900 ICP-QQQ instrument. Chromatographic separation employed an Agilent 1260 Infinity II
91 Bio-Inert Liquid Chromatography (HPLC) System equipped with a 100 μL injection loop and a PRP-X100
92 anion exchange column (PEEK, 250 mm x 4.6 mm x 5 μm) (Hamilton Company, USA) connected to the
93 nebuliser of the ICP-QQQ using a single piece of 1/16" OD PEEK tubing. The ICP-QQQ instrument was
94 optimised prior to connection of the LC system using a 1 $\mu\text{g L}^{-1}$ tuning solution and operated in helium
95 (He) collision mode at a flow rate of 5.5 mL min⁻¹ to minimise the impact of polyatomic interferences
96 such as ⁴⁰Ar¹²C⁺. Cr was monitored at m/z 52 for total Cr analysis and m/z 50, 52, 53 and 54 for HPLC
97 analysis. Soil pH measurements were undertaken on ≤ 2 mm subsamples using a solid body combined

98 pH electrode in a 0.01 M CaCl₂ slurry (solid to solution ratio of 1:2.5). Loss-on-ignition (LOI) was
99 measured on a 1 g subsample of milled material.

100 2.2 Study Area and Sampling

101 The study area comprises a village within 1 km of a tailings dam used by Mopani Copper Mines in
102 Kitwe, Zambia (-12.800346, 28.118721, Figure 1); the mine has been in operation for 28 years. Initially,
103 reconnaissance sampling of agricultural land was undertaken; this process has been outlined by Lark
104 *et al.* (Lark, Hamilton, Kaninga, Maseka, Mutondo, Sakala, et al., 2017). Briefly, a nested sampling
105 design was implemented to assess the spatial variation of chromium across the agricultural land within
106 the village, which involved collecting samples along transects with sample main stations at loose
107 intervals between 100 m and 200 m with substations in random directions a further 100 m, 10 m and
108 1 m from the initial main stations (Figure 1i). At each main station and substation, a topsoil sample (0–
109 15 cm depth) was collected from a composite of 5 sub-samples using a Dutch auger. The data on total
110 Cr (section 2.1) were then used to produce interpolated values at locations on a fine grid across the
111 study area by the method of ordinary kriging as implemented in the gstat package for the R platform
112 (Pebesma, 2004; R Core Team, 2014). The interpolated values were then used to produce a map of
113 total Cr with the visualization tools of the ESRI ArcGIS® software (Figure 1ii). The same method was
114 used to interpolate values of soil pH and LOI at the same grid nodes.

135 The selection of sample points for this study was done with the cube algorithm of Deville and Tillé
136 (2004) as implemented in the BalancedSampling library for the R platform (Grafström & Lisic, 2016).
137 The objective of this method is to draw a sample by random sampling according to pre-determined
138 set of inclusion probabilities, in this case for the nodes of the fine grid for which interpolated values
139 of Cr, pH and LOI were available, the sample was therefore unbiased. At the same time the algorithm
140 achieved spatial balance; the mean coordinate values of the sample points are close to the mean
141 coordinate values of all points on the sample site, and are also spread in the feature space defined by
142 the interpolated values of Cr, LOI and pH. The sample therefore covers the range of these values. A
143 total of 50 sample locations were selected in this way, and their coordinates were exported to the
144 open source application "maps.me" for subsequent location and sampling. The same field sample
145 protocol was followed as described above for the initial reconnaissance survey of the site.

146 2.3 Reagents and Materials

147 All solutions were prepared in 18.2 MΩ cm ultrapure water. The natural abundance standard of
148 ⁵²Cr(VI) was purchased as a 1000 mg L⁻¹ solution in water (High Purity Standards, SC, USA), no further
149 preparation was required. ⁵³Cr(VI) solution was prepared from the isotopically-enriched oxide
150 (ISOFLEX, CA, USA) according to instructions outlined in EPA Method 6800 ("EPA Method 6800:
151 Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry," 2014). The concentration of
152 ⁵³Cr(VI) in the stock and spiking solutions were verified before analysis using reverse isotope dilution;
153 the isotopic composition of the spike solution is given in Table 1.

154 **Table 1. Isotopic composition of ⁵³Cr(VI) used throughout study.**

Isotope	Abundance (%)
50	Not detected
52	2.8 ± 0.3
53	97.2 ± 0.4

54	Not detected
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155

156 Ethylenediaminetetraacetic acid (di-ammonium salt, $\text{NH}_4\text{-EDTA}$), trisaminomethane (TRIS) and
157 ammonium nitrate (NH_4NO_3) (Sigma Aldrich, UK) were used for the preparation of the
158 chromatographic mobile phase. The certified reference materials (CRMs) SRM 2700 Hexavalent
159 Chromium in Contaminated Soil (Low Level) and SRM 2701 Hexavalent Chromium in Contaminated
160 Soil (High Level) (NIST, USA) were used to verify the accuracy of the extraction procedure.

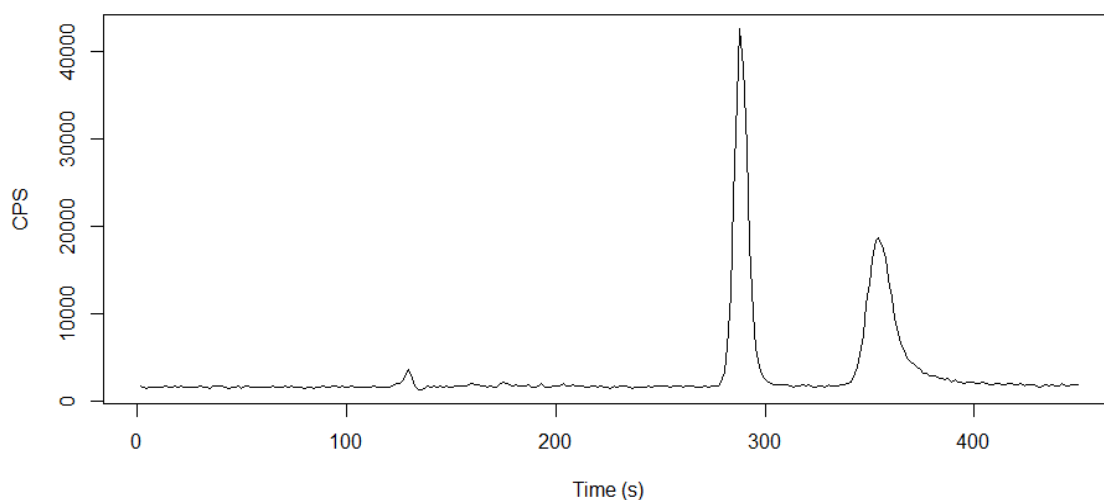
161 2.4 Determination of Cr(VI)

162 Samples for measurement of Cr(VI) were prepared using microwave-assisted single-spike speciated
163 isotope dilution mass spectrometry (SIDMS) according to the method outlined by Guidotti *et al.* with
164 minor modifications (Guidotti, Abad, Rodríguez-González, Alonso, & Beone, 2015). Briefly, a 0.2 g
165 subsample of the dried milled material was added to the microwave vessel, followed by 10 ml of 50
166 mM $\text{NH}_4\text{-EDTA}$ (pH 10.0). The vessel was then spiked with 0.4 ml of $^{53}\text{Cr(VI)}$ at a concentration
167 sufficient to double the natural $^{53}\text{Cr(VI)}$ present in the sample. The use of a single isotopically-enriched
168 spike was considered appropriate due to the reducing capacity of the soils (low pH, high
169 concentrations of iron and aluminium), minimising the risk of conversion of Cr(III) to Cr(VI) during the
170 extraction procedure. The use of $\text{NH}_4\text{-EDTA}$ as an extractant has also been shown to complex
171 solubilised forms of Cr(III), further reducing the likelihood of oxidation (Fabregat-Cabello, Rodríguez-
172 González, Castillo, Malherbe, Roig-Navarro, Long, et al., 2012). The sample was then subjected to a 5
173 minute heating programme at 80°C (8 minute ramp time), cooled and centrifuged at 4000 min^{-1} for 20
174 minutes to separate the supernatant from the extracted solid material. Prior to chromatographic
175 separation, the sample was diluted with ultrapure water (2-fold for samples, 10- or 100-fold for CRMs)
176 to ensure all analyses were within the pulse-counting mode of the electron multiplier (EM). In addition
177 to the samples, at least two CRM replicates (either NIST SRM 2700 or 2701), three reagent blanks and
178 two duplicate samples were extracted in each microwave batch.

179 **3.0 Results and Discussion**

180 **3.1 Analytical Figures of Merit for HPLC-ICP-QQQ Speciation of Chromium**

181 Speciation of Cr(VI) and Cr(III) in alkaline extractions was achieved in 7.5 minutes using an isocratic
182 elution programme (100% 40 mM NH₄NO₃/50 mM TRIS Buffer/5 mM NH₄-EDTA, pH 7.0) at a flow rate
183 of 1.2 mL min⁻¹. An example chromatogram at m/z 52 is shown in Figure 2.



184
185 **Figure 2. Speciation of Cr(VI) and Cr(III) in a natural isotopic abundance standard (10 µg L⁻¹).**

186 The Cr(III) determined in the alkaline extractions is considered “soluble” Cr(III) as the alkaline
187 extraction procedure does not mobilise all forms of Cr(III); aged Cr(OH)₃ and Cr₂O₃ remain in the solid
188 phase (Wolle, Rahman, Skip Kingston, & Pamuku, 2014). The small peak at 130 s could be attributed
189 to the formation of Cr(OH)₄⁻, a complex of Cr(III) which is soluble in alkaline solutions (Drinčić, Zuliani,
190 Ščančar, & Milačič, 2018).

191 The method limit of detection (LOD), calculated as three times the standard deviation of the ⁵²Cr(VI)
192 concentration measured in ten reagent blanks spiked with ⁵³Cr(VI), was 0.03 mg kg⁻¹.

193 NIST SRM 2700 (Hexavalent Chromium in Contaminated Soil Low Level, certified value 14.9 ± 1.2 mg
194 kg⁻¹) demonstrated good accuracy with an average recovery of 109 ± 3 % across four replicates; SRM
195 2701 (Hexavalent Chromium in Contaminated Soil High Level, certified value 551.2 ± 34.5 mg kg⁻¹)
196 indicated negative bias with an average recovery of 86 ± 6 % across the same number of replicates.

197 The higher concentration of Cr(VI) in SRM 2701 made it difficult to achieve a 1:1 spiking ratio with the
198 ⁵³Cr(VI) isotopically-enriched spike used in this work, which could have resulted in poorer isotopic
199 mixing and equilibration for this reference material (Vogl, 2007); the lower Cr(VI) concentration in
200 SRM 2700 is more representative of the samples analysed in this study.

201 3.2 Processing of SIDMS Data

202 The microwave-assisted extraction described in section 2.4 was applied to the 50 agricultural soil
203 samples collected from Mugala Village in the Copperbelt Province of Zambia, followed by LC analysis
204 to separate the extracted forms of Cr(VI) and Cr(III). Integrated peak areas for *m/z* 50, 52, 53 and 54
205 were extracted from the instrument data processing software and used to calculate abundances and
206 the ⁵³Cr(VI)/⁵²Cr(VI) isotope ratio. Mass bias correction factors were calculated from a natural standard
207 analysed over the course of the analytical run at regularly bracketed intervals (Rousseau, Sonke,
208 Chmeleff, Candaudap, Lacan, Boaventura, et al., 2013). Following data processing, Eq. (1) (Huang,
209 Yang, Zhuang, Wang, & Lee, 2004) was used to calculate Cr(VI) concentrations in the soil samples:

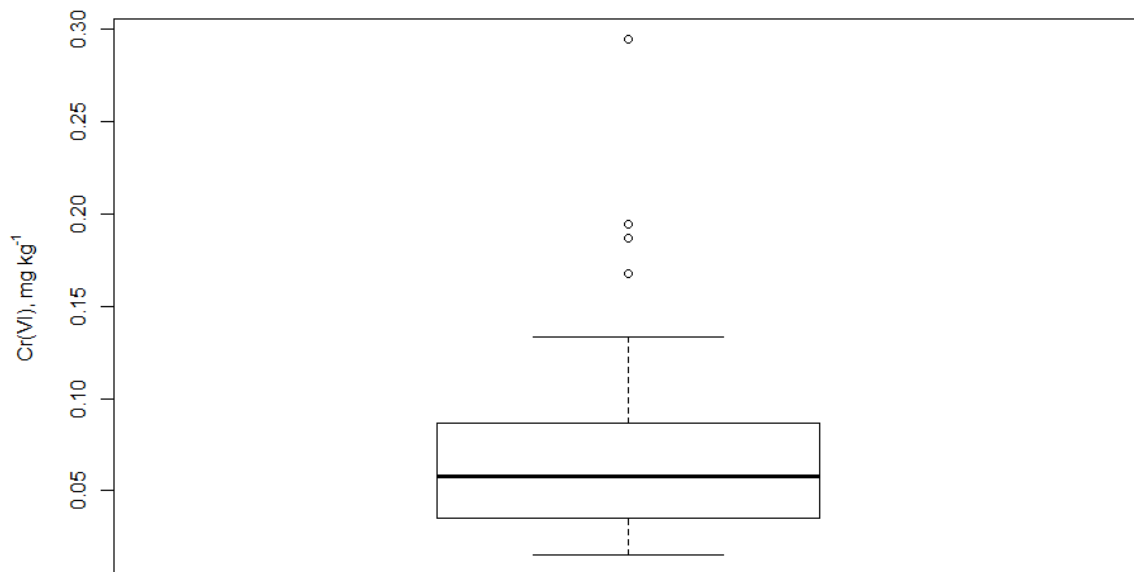
$$210 \quad C_x = C_s \frac{M_x W_s A_s - R B_s}{M_s W_x R B_x - A_x} \quad (1)$$

211 where C_x is the concentration of Cr(VI) in the sample, C_s is the concentration of Cr(VI) in the ⁵³Cr(VI)
212 spike solution (in $\mu\text{g l}^{-1}$), M_x is the natural relative atomic mass (⁵²Cr), M_s is the isotopically-enriched
213 relative atomic mass (⁵³Cr), W_s is the mass of the spike solution (in g), W_x is the mass of the soil sample
214 (in g), A_s is the abundance of ⁵²Cr in the spike solution, R is the ⁵²Cr(VI)/⁵³Cr(VI) isotope ratio, B_s is the
215 abundance of ⁵³Cr in the spike solution, B_x is the abundance of ⁵³Cr in the unspiked sample and A_x is
216 the abundance of ⁵²Cr in the unspiked sample.

217 3.3 Total Cr and Cr(VI) in Mugala Village Soil Samples

218 Total Cr, Cr(VI), soil pH and selected element concentrations for the 50 agricultural soil samples are
219 presented in Table S1 of the Supplementary Material. The total Cr ranged from 53 to 82 mg kg⁻¹, with

220 a median concentration of 70 mg kg⁻¹. Although these concentrations are higher than previously
221 reported data for topsoil Cr in this region (Bohdan Křibek, Majer, Veselovský, & Nyambe, 2010), the
222 study site is within close proximity to a large tailings dam and is therefore more likely to have elevated
223 topsoil concentrations through the deposition of wind-blown dust (Middleton, Watts, Beriro,
224 Hamilton, Leonardi, Fletcher, et al., 2017; Nakaona, Maseka, Hamilton, & Watts, 2019).



225
226 **Figure 3. Distribution of Cr(VI) concentrations in agricultural soil samples.**

227 Cr(VI) concentrations in the soil samples ranged from 0.03 to 0.29 mg kg⁻¹ (Figure 3), corresponding to
228 between 0.04 and 0.44% of the total Cr in the soil samples. At the time of writing, there is no screening
229 or guidance value for Cr(VI) in agricultural soil for Zambia. Therefore, the UK's provisional category 4
230 screening level (C4SL) for Cr(VI) was used to assess the significance of these concentrations. Based on
231 the land-use of the study site (residential with consumption of homegrown produce), none of the soil
232 samples exceeded the C4SL of 21 mg kg⁻¹ Cr(VI). This is likely due to the lateritic nature of the soils,
233 with the presence of high concentrations of reducing components such as Fe and Al. In addition, the
234 agricultural management strategies in place at the site, including reincorporation of crop residues
235 following cultivation, are likely to increase soil organic carbon (SOC) (Zhang, Li, Gregorich, McLaughlin,
236 Zhang, Guo, et al., 2019) leading to greater reduction of Cr(VI).

237 From the measured speciation data, it can be concluded that Cr(VI) poses a relatively low
238 environmental and/or human health risk at this site, either through direct soil-to-mouth transfer or
239 from indirect exposure through wind-blown dust deposition onto staple crops.

240 **4.0 Conclusions**

241 The analysis of the agricultural soil samples indicate that a Cr(VI) exposure risk is relatively low in this
242 area of the Copperbelt Province. Through the implementation of robust extraction and analytical
243 methods, Cr(VI) was accurately quantified in the soil samples. Taking into consideration the total Cr
244 concentrations in the samples, this study has once again highlighted the importance of speciation
245 analysis to fully understand and evaluate the risk to environment and human health.

246 Although none of the analysed soil samples exceeded either the European total Cr threshold value
247 (100 mg kg^{-1}) (Tóth, Hermann, Da Silva, & Montanarella, 2016) or the UK Cr(VI) C4SL (21 mg kg^{-1}), there
248 may still be an exposure risk from compounding factors not investigated in this study. The dietary
249 intake for the inhabitants of the village is dependent on subsistence agriculture, resulting in a much
250 lower diversity of source. Due to the proximity of the mine tailings, there may be increased exposure
251 to potentially harmful elements (PHEs) at concentrations close to threshold values, which themselves
252 may have been derived without taking into account different pathways of exposure (oral ingestion,
253 inhalation, crop consumption) and differences in bioaccessibility depending on source (Ljung, Oomen,
254 Duits, Selinus, & Berglund, 2007). Therefore, wider health studies are required to address the
255 significance of chronic sub-threshold PHE exposure on the health of people living within close
256 proximity to mine tailings, which could feed into refinement of threshold value derivation and
257 improvement of soil management and/or remediation strategies on a site-specific basis.

258 Future work involves understanding the availability of Cr(VI) in contaminated soils to both plants and
259 humans, which could better inform remediation strategies. The use of microdialysis as a soil sampling
260 technique is an emerging field with great potential for minimally-invasive assessment of inorganic
261 fluxes and diffusion through soil systems (Humphrey, Young, Bailey, Crout, Ander, Hamilton, et al.,

262 2019). Coupling this technique to an analytical detector such as ICP-MS, or even a separation
263 technique such as HPLC prior to detection, could allow for near real-time monitoring of the fate and
264 stability of inorganic soil components across shorter time scales than conventional techniques (e.g.
265 diffusive gradients in thin films (DGTs), isotope dilution assays) can capture.

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271

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