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

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Abstract

The distribution of elemental species of chromium (Cr) in potentially-contaminated soil samples warrants investigation due to the differing mobilities and toxicities of trivalent [Cr(III)] and hexavalent chromium [(Cr(VI)]. In addition, the possibility of species interconversions requires the implementation of robust methods that can correct for changes at the point of sampling, extraction and analysis. This work presents the application of speciated isotope dilution mass spectrometry (SIDMS) to accurately quantify Cr(VI) in agricultural soils within close proximity to a mine tailings dam in the Copperbelt Province of Zambia. Interpolated plots of total Cr, produced from data collected through a nested sampling design, were used to optimise the sampling across the spatial domain. Extraction of Cr(VI) was undertaken using a microwave assisted reaction system (80°C for 5 minutes) with 50 mM EDTA, to complex Cr(III) and reduce the likelihood of oxidation during the extraction. Isotopically-enriched ^{53}Cr(VI) was added to each sample prior to extraction to account for species interconversions. The accuracy of the method was confirmed using NIST SRM 2700 and 2701. Cr(VI) concentrations in the soil samples ranged between 0.03 and 0.29 mg kg^{-1}, significantly lower than the residential UK screening value for Cr(VI) of 21 mg kg^{-1}. The data indicate that this site poses a low environmental/human health risk with respect to Cr(VI) exposure.

Keywords

Chromium, hexavalent chromium, SIDMS, speciation, mine tailings

1.0 Introduction

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

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

The speciation of Cr in solid sample matrices has been reviewed in a number of articles (Hamilton, Young, Bailey, & Watts, 2018) (Séby & Vacchina, 2018). The main analytical challenge to address is ensuring accurate determination of Cr(VI) in the sample without causing interconversion of species (Pettine & Capri, 2005), which may lead to under/over-reporting of Cr(VI) (Nagourney, Wilson, Buckley, Kingston, Yang, & Long, 2008) and an insufficient assessment of the associated risk to human health (Novotnik, Zuliani, Ščančar, & Milačič, 2015). Speciated isotope dilution mass spectrometry (SIDMS) was developed to correct for changes in speciation which may occur at sampling, storage and/or analysis (“Skip” Kingston, Huo, Lu, & Chalk, 1998). This variation on conventional isotope dilution uses species-specific isotopically enriched spikes, added to the sample prior to digestion or extraction, to accurately determine species concentrations in solid matrices and reduce analytical/species conversion errors that may occur through external calibration (Martone, Rahman, Pamuku, & Kingston, 2013).

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

The objective of this study was to use previously-reported reconnaissance work to inform more detailed sampling across potentially-contaminated agricultural land within half a kilometre of a large tailings dam in the Copperbelt Province of Zambia. Single-spike speciated isotope dilution mass spectrometry (SIDMS) was then employed to quantify Cr(VI) in 50 soils over this area, with total Cr ranging from 37-107 mg kg^{-1}, to establish whether a human health risk could exist through exposure to Cr(VI) from soil contaminated with tailings material. To the best knowledge of the authors, this work presents the first occasion of SIDMS being used to quantify Cr(VI) in potentially-contaminated soil samples collected from the Copperbelt Province of Zambia.

2.0 Materials and Methods

2.1 Sample Preparation and Analysis

Samples were dried at 40°C, disaggregated using a pestle & mortar and sieved to ≤2 mm. From this sieved fraction, subsamples were milled to ≤53 µm using a planetary ball mill (Retsch GmbH, Germany) for total Cr and Cr(VI) analyses. Samples for measurement of total Cr were prepared using an in-house mixed acid ($HF/HNO_3/HClO_4$) open vessel hotblock digestion (Watts, Middleton, Marriott, Humphrey, Hamilton, Gardner, et al., 2019). A microwave assisted reaction system (MARS One, CEM Corporation, UK) was used for alkaline extraction of Cr(VI) from soil samples.

Determination of total Cr was performed by ICP-MS using an Agilent 7500cx instrument (Agilent Technologies, Tokyo, Japan) using previously reported operating conditions (Hamilton, Barlow, Gowing, & Watts, 2015); measurement of Cr(VI) in alkaline extractions was undertaken using an Agilent 8900 ICP-QQQ instrument. Chromatographic separation employed an Agilent 1260 Infinity II Bio-Inert Liquid Chromatography (HPLC) System equipped with a 100 µl injection loop and a PRP-X100 anion exchange column (PEEK, 250 mm x 4.6 mm x 5 µm) (Hamilton Company, USA) connected to the nebuliser of the ICP-QQQ using a single piece of 1/16" OD PEEK tubing. The ICP-QQQ instrument was optimised prior to connection of the LC system using a 1 µg L^{-1} tuning solution and operated in helium (He) collision mode at a flow rate of 5.5 ml min^{-1} to minimise the impact of polyatomic interferences such as $^{40}Ar^{12}C^{+}$. Cr was monitored at *m/z* 52 for total Cr analysis and *m/z* 50, 52, 53 and 54 for HPLC analysis. Soil pH measurements were undertaken on ≤2 mm subsamples using a solid body combined pH electrode in a 0.01 M $CaCl_2$ slurry (solid to solution ratio of 1:2.5). Loss-on-ignition (LOI) was measured on a 1 g subsample of milled material.

2.2 Study Area and Sampling

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

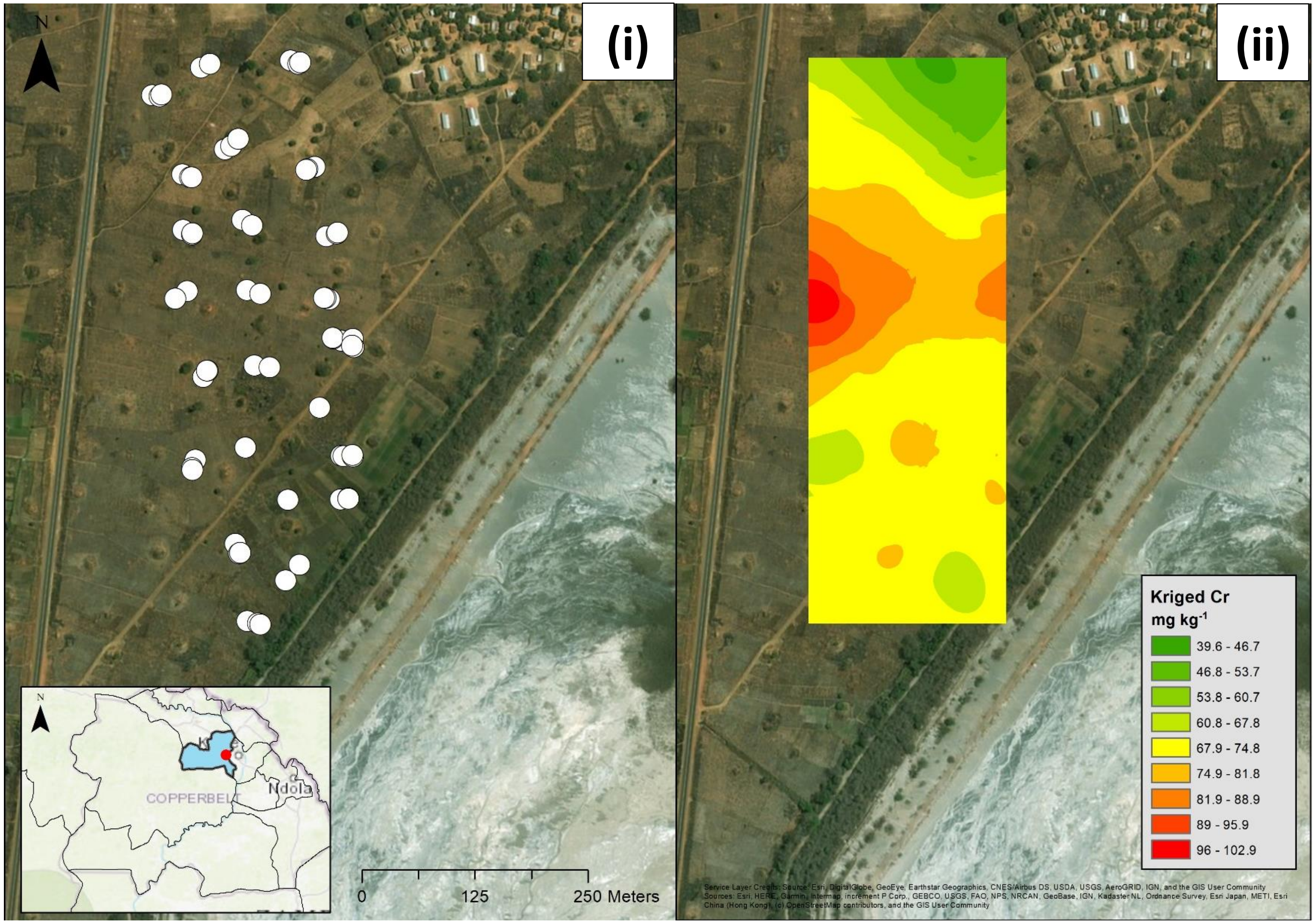

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Figure 1. Study site with (i) sample points for nested sampling design (white circles) and (ii) kriging output created from total Cr data. Maps created using ArcGIS® software by Esri. ArcGIS® and ArcMap™ are the intellectual property of Esri and are used herein under license. Copyright © Esri. All rights reserved.

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

2.3 Reagents and Materials

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

Table 1. Isotopic composition of ^{53}Cr(VI) used throughout study.

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

Ethylenediaminetetraacetic acid (di-ammonium salt, NH_4-EDTA), trisaminomethane (TRIS) and ammonium nitrate (NH_4NO_3) (Sigma Aldrich, UK) were used for the preparation of the chromatographic mobile phase. The certified reference materials (CRMs) SRM 2700 Hexavalent Chromium in Contaminated Soil (Low Level) and SRM 2701 Hexavalent Chromium in Contaminated Soil (High Level) (NIST, USA) were used to verify the accuracy of the extraction procedure.

2.4 Determination of Cr(VI)

Samples for measurement of Cr(VI) were prepared using microwave-assisted single-spike speciated isotope dilution mass spectrometry (SIDMS) according to the method outlined by Guidotti *et al*. with minor modifications (Guidotti, Abad, Rodríguez-González, Alonso, & Beone, 2015). Briefly, a 0.2 g subsample of the dried milled material was added to the microwave vessel, followed by 10 ml of 50 mM NH_4-EDTA (pH 10.0). The vessel was then spiked with 0.4 ml of ^{53}Cr(VI) at a concentration sufficient to double the natural ^{53}Cr(VI) present in the sample. The use of a single isotopically-enriched spike was considered appropriate due to the reducing capacity of the soils (low pH, high concentrations of iron and aluminium), minimising the risk of conversion of Cr(III) to Cr(VI) during the extraction procedure. The use of NH_4-EDTA as an extractant has also been shown to complex solubilised forms of Cr(III), further reducing the likelihood of oxidation (Fabregat-Cabello, Rodríguez-González, Castillo, Malherbe, Roig-Navarro, Long, et al., 2012). The sample was then subjected to a 5 minute heating programme at 80°C (8 minute ramp time), cooled and centrifuged at 4000 min^{-1} for 20 minutes to separate the supernatant from the extracted solid material. Prior to chromatographic separation, the sample was diluted with ultrapure water (2-fold for samples, 10- or 100-fold for CRMs) to ensure all analyses were within the pulse-counting mode of the electron multiplier (EM). In addition to the samples, at least two CRM replicates (either NIST SRM 2700 or 2701), three reagent blanks and two duplicate samples were extracted in each microwave batch.

3.0 Results and Discussion

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

Speciation of Cr(VI) and Cr(III) in alkaline extractions was achieved in 7.5 minutes using an isocratic elution programme (100% 40 mM NH_4NO_3/50 mM TRIS Buffer/5 mM NH_4-EDTA, pH 7.0) at a flow rate of 1.2 ml/min.

The Cr(III) determined in the alkaline extractions is considered “soluble” Cr(III) as the alkaline extraction procedure does not mobilise all forms of Cr(III); aged $Cr(OH)_3$ and Cr_2O_3 remain in the solid phase (Wolle, Rahman, Skip Kingston, & Pamuku, 2014). The small peak at 130 s could be attributed to the formation of $Cr(OH)_4^-$, a complex of Cr(III) which is soluble in alkaline solutions (Drinčić, Zuliani, Ščančar, & Milačič, 2018).

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

NIST SRM 2700 (Hexavalent Chromium in Contaminated Soil Low Level, certified value 14.9 ± 1.2 mg kg^{-1}) demonstrated good accuracy with an average recovery of 109 ± 3 % across four replicates; SRM 2701 (Hexavalent Chromium in Contaminated Soil High Level, certified value 551.2 ± 34.5 mg kg^{-1}) indicated negative bias with an average recovery of 86 ± 6 % across the same number of replicates. The higher concentration of Cr(VI) in SRM 2701 made it difficult to achieve a 1:1 spiking ratio with the ^{53}Cr(VI) isotopically-enriched spike used in this work, which could have resulted in poorer isotopic mixing and equilibration for this reference material (Vogl, 2007); the lower Cr(VI) concentration in SRM 2700 is more representative of the samples analysed in this study.

3.2 Processing of SIDMS Data

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

$$Cx = Cs \frac{Mx}{Ms} \frac{Ws}{Wx} \frac{As - RBs}{RBx - Ax} \tag{1}$$

where Cx is the concentration of Cr(VI) in the sample, Cs is the concentration of Cr(VI) in the ^{53}Cr(VI) spike solution (in µg l^{-1}), Mx is the natural relative atomic mass (^{52}Cr), Ms is the isotopically-enriched relative atomic mass (^{53}Cr), Ws is the mass of the spike solution (in g), Wx is the mass of the soil sample (in g), As is the abundance of ^{52}Cr in the spike solution, R is the ^{52}Cr(VI)/^{53}Cr(VI) isotope ratio, Bs is the abundance of ^{53}Cr in the spike solution, Bx is the abundance of ^{53}Cr in the unspiked sample and Ax is the abundance of ^{52}Cr in the unspiked sample.

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

Total Cr, Cr(VI), soil pH and selected element concentrations for the 50 agricultural soil samples are presented in Table S1 of the Supplementary Material. The total Cr ranged from 53 to 82 mg kg^{-1}, with a median concentration of 70 mg kg^{-1}. Although these concentrations are higher than previously reported data for topsoil Cr in this region (Bohdan Kříbek, Majer, Veselovský, & Nyambe, 2010), the study site is within close proximity to a large tailings dam and is therefore more likely to have elevated topsoil concentrations through the deposition of wind-blown dust (Middleton, Watts, Beriro, Hamilton, Leonardi, Fletcher, et al., 2017; Nakaona, Maseka, Hamilton, & Watts, 2019).

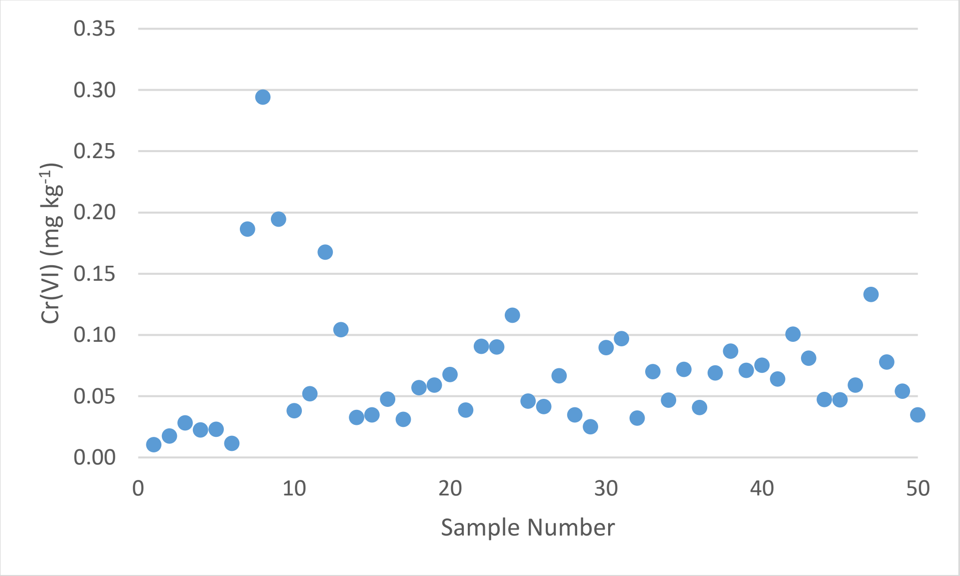

Figure 3. Distribution of Cr(VI) concentrations in agricultural soil samples.

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

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

4.0 Conclusions

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

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

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References

"Skip" Kingston, H. M., Huo, D., Lu, Y., & Chalk, S. (1998). Accuracy in species analysis: speciated isotope dilution mass spectrometry (SIDMS) exemplified by the evaluation of chromium species. *Spectrochimica Acta Part B: Atomic Spectroscopy, 53*(2), 299-309.

Chrysochoou, M., Theologou, E., Bompoti, N., Dermatas, D., & Panagiotakis, I. (2016). Occurrence, Origin and Transformation Processes of Geogenic Chromium in Soils and Sediments. *Current Pollution Reports, 2*(4), 224-235.

Dhal, B., Thatoi, H. N., Das, N. N., & Pandey, B. D. (2013). Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. *Journal of Hazardous Materials, 250-251*, 272-291.

Drinčić, A., Zuliani, T., Ščančar, J., & Milačič, R. (2018). Determination of hexavalent Cr in river sediments by speciated isotope dilution inductively coupled plasma mass spectrometry. *Science of The Total Environment, 637-638*, 1286-1294.

. EPA Method 6800: Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry. In. (2014)).

Ettler, V., Mihaljevič, M., Kříbek, B., Majer, V., & Šebek, O. (2011). Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia. *Geoderma, 164*(1), 73-84.

Fabregat-Cabello, N., Rodríguez-González, P., Castillo, Á., Malherbe, J., Roig-Navarro, A. F., Long, S. E., & Alonso, J. I. G. (2012). Fast and Accurate Procedure for the Determination of Cr(VI) in Solid Samples by Isotope Dilution Mass Spectrometry. *Environmental Science & Technology, 46*(22), 12542-12549.

Grafström, A., & Lisic, J. (2016). Balanced and Spatially Balanced Sampling,. In): R package version 1. 5. 2.

Guidotti, L., Abad, S. Q., Rodríguez-González, P., Alonso, J. I. G., & Beone, G. M. (2015). Quantification of Cr(VI) in soil samples from a contaminated area in northern Italy by isotope dilution mass spectrometry. *Environmental Science and Pollution Research, 22*(22), 17569-17576.

Hamilton, E. M., Barlow, T. S., Gowing, C. J. B., & Watts, M. J. (2015). Bioaccessibility performance data for fifty-seven elements in guidance material BGS 102. *Microchemical Journal, 123*, 131-138.

Hamilton, E. M., Young, S. D., Bailey, E. H., & Watts, M. J. (2018). Chromium speciation in foodstuffs: A review. *Food Chemistry, 250*, 105-112.

Huang, Z.-Y., Yang, C.-Y., Zhuang, Z.-X., Wang, X.-R., & Lee, F. S. C. (2004). Determination of trace lead in the high salt matrix of comestible CaCO3 by an isotope dilution method with detection by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta, 509*(1), 77-82.

James, B. R., & Bartlett, R. J. (1983). Behavior of Chromium in Soils: V. Fate of Organically Complexed Cr(III) Added to Soil. *Journal of Environmental Quality, 12*(2), 169-172.

Kaninga, B. K., Chishala, B. H., Maseka, K. K., Sakala, G. M., Lark, M. R., Tye, A., & Watts, M. J. (2019). Review: mine tailings in an African tropical environment—mechanisms for the bioavailability of heavy metals in soils. *Environmental Geochemistry and Health*.

Kříbek, B., Majer, V., Knésl, I., Nyambe, I., Mihaljevič, M., Ettler, V., & Sracek, O. (2014). Concentrations of arsenic, copper, cobalt, lead and zinc in cassava (Manihot esculenta Crantz) growing on uncontaminated and contaminated soils of the Zambian Copperbelt. *Journal of African Earth Sciences, 99*, 713-723.

Kříbek, B., Majer, V., Veselovský, F., & Nyambe, I. (2010). Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: A topsoil vs. subsurface soil concept. *Journal of Geochemical Exploration, 104*(3), 69-86.

Krzysik, M., Grajeta, H., Prescha, A., & Weber, R. (2011). Effect of cellulose, pectin and chromium(III) on lipid and carbohydrate metabolism in rats. *Journal of Trace Elements in Medicine and Biology, 25*(2), 97-102.

Langárd, S., & Costa, M. A. X. (2007). CHAPTER 24 - Chromium. In G. F. Nordberg, B. A. Fowler, M. Nordberg & L. T. Friberg (Eds.), *Handbook on the Toxicology of Metals (Third Edition)*, (pp. 487-510). Burlington: Academic Press.

Lark, R. M., Hamilton, E. M., Kaninga, B., Maseka, K. K., Mutondo, M., Sakala, G. M., & Watts, M. J. (2017). Nested sampling and spatial analysis for reconnaissance investigations of soil: an example from agricultural land near mine tailings in Zambia. *European Journal of Soil Science, 68*(5), 605-620.

Ljung, K., Oomen, A., Duits, M., Selinus, O., & Berglund, M. (2007). Bioaccessibility of metals in urban playground soils. *Journal of Environmental Science and Health, Part A, 42*(9), 1241-1250.

Martone, N., Rahman, G. M. M., Pamuku, M., & Kingston, H. M. S. (2013). Determination of Chromium Species in Dietary Supplements Using Speciated Isotope Dilution Mass Spectrometry with Mass Balance. *Journal of Agricultural and Food Chemistry, 61*(41), 9966-9976.

Middleton, D. R. S., Watts, M. J., Beriro, D. J., Hamilton, E. M., Leonardi, G. S., Fletcher, T., Close, R. M., & Polya, D. A. (2017). Arsenic in residential soil and household dust in Cornwall, south west England: potential human exposure and the influence of historical mining. *Environmental Science: Processes & Impacts, 19*(4), 517-527.

Nagourney, S. J., Wilson, S. A., Buckley, B., Kingston, H. M. S., Yang, S.-Y., & Long, S. E. (2008). Development of a standard reference material for Cr(vi) in contaminated soil. *Journal of Analytical Atomic Spectrometry, 23*(11), 1550-1554.

Nakaona, L., Maseka, K. K., Hamilton, E. M., & Watts, M. J. (2019). Using human hair and nails as biomarkers to assess exposure of potentially harmful elements to populations living near mine waste dumps. *Environmental Geochemistry and Health*.

Novotnik, B., Zuliani, T., Ščančar, J., & Milačič, R. (2015). Content of trace elements and chromium speciation in Neem powder and tea infusions. *Journal of Trace Elements in Medicine and Biology, 31*, 98-106.

Oh, Y. J., Song, H., Shin, W. S., Choi, S. J., & Kim, Y.-H. (2007). Effect of amorphous silica and silica sand on removal of chromium(VI) by zero-valent iron. *Chemosphere, 66*(5), 858-865.

Oliveira, H. (2012). Chromium as an Environmental Pollutant: Insights on Induced Plant Toxicity. *Journal of Botany, 2012*, 8.

Oze, C., Bird, D. K., & Fendorf, S. (2007). Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proceedings of the National Academy of Sciences, 104*(16), 6544.

Pebesma, E. J. (2004). Multivariable geostatistics in S: the gstat package. In): The R Journal 8(1) 204-218.

Pettine, M., & Capri, S. (2005). Digestion treatments and risks of Cr(III)–Cr(VI) interconversions during Cr(VI) determination in soils and sediments—a review. *Analytica Chimica Acta, 540*(2), 231-238.

R Core Team. (2014). R: A language and environment for statistical computing. In). Vienna, Austria: R Foundation for Statistical Computing.

Rousseau, T. C. C., Sonke, J. E., Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Seyler, P., & Jeandel, C. (2013). Rare earth element analysis in natural waters by multiple isotope dilution – sector field ICP-MS. *Journal of Analytical Atomic Spectrometry, 28*(4), 573-584.

Séby, F., & Vacchina, V. (2018). Critical assessment of hexavalent chromium species from different solid environmental, industrial and food matrices. *TrAC Trends in Analytical Chemistry, 104*, 54-68.

Shanker, A. K., Djanaguiraman, M., & Venkateswarlu, B. (2009). Chromium interactions in plants: current status and future strategies. *Metallomics, 1*(5), 375-383.

Stasinos, S., & Zabetakis, I. (2013). The uptake of nickel and chromium from irrigation water by potatoes, carrots and onions. *Ecotoxicology and Environmental Safety, 91*, 122-128.

Tang, H., Wang, X., Shuai, W., & Liu, Y. (2016). Immobilization of Rare Earth Elements of the Mine Tailings Using Phosphates and Lime. *Procedia Environmental Sciences, 31*, 255-263.

Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International, 88*, 299-309.

Vogl, J. (2007). Characterisation of reference materials by isotope dilution mass spectrometry. *Journal of Analytical Atomic Spectrometry, 22*(5), 475-492.

von der Heyden, C. J., & New, M. G. (2004). Groundwater pollution on the Zambian Copperbelt: deciphering the source and the risk. *Science of The Total Environment, 327*(1), 17-30.

Watts, M. J., Middleton, D., Marriott, A., Humphrey, O., Hamilton, E., Gardner, A., Smith, M., McCormack, V. A., Menya, D., Munishi, M., Mmbaga, B., & Osano, O. (2019). Source apportionment of micronutrients in the diets of Kilimanjaro,Tanzania and Counties of Western Kenya. *Scientific Reports*.

Weissenstein, K., & Sinkala, T. (2011). Soil pollution with heavy metals in mine environments, impact areas of mine dumps particularly of gold- and copper mining industries in Southern Africa. *Arid Ecosystems, 1*(1), 53.

Wolle, M. M., Rahman, G. M. M., Skip Kingston, H. M., & Pamuku, M. (2014). Optimization and validation of strategies for quantifying chromium species in soil based on speciated isotope dilution mass spectrometry with mass balance. *Journal of Analytical Atomic Spectrometry, 29*(9), 1640-1647.

Zhang, Y., Li, X., Gregorich, E. G., McLaughlin, N. B., Zhang, X., Guo, Y., Gao, Y., & Liang, A. (2019). Evaluating storage and pool size of soil organic carbon in degraded soils: Tillage effects when crop residue is returned. *Soil and Tillage Research, 192*, 215-221.