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Human bioaccessibility of heavy metals and metalloids naturally occurring at high levels in chestnut grove soils of SW Spain

Juan Carlos Fernández-Caliani[1*], Sandra Fernández-Landero[1], María Inmaculada Giráldez[2]

[1]*Department of Earth Sciences, University of Huelva, Huelva, Spain*
[2]*Department of Chemistry, University of Huelva, Huelva, Spain*
[*]*caliani@uhu.es*

Abstract

In this study, oral bioaccessibility of naturally-occurring trace elements (As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl and Zn) was assessed by *in vitro* simulation of human digestion in order to quantify the fraction of such potentially toxic metal(loid)s that can be dissolved by digestive fluids in the gastrointestinal tract. The results indicated that a considerable portion of the total trace element concentrations could be available for gastrointestinal absorption. Cadmium was the most bioaccessible metal in the gastric fluid, whereas Cu and Tl were the dominant metals solubilised in the gastrointestinal extract. Chemical partitioning of trace elements between gastric and gastrointestinal phases seems to be affected not only by the pH and composition of digestive solutions, but also by the soil properties and constituents.

Keywords: Oral bioaccessibility; geogenic trace elements; soil contamination; human health risk

1. Introduction

Chestnut grove soils of the Sierra de Aracena Natural Park (Huelva, SW Spain) contain elevated levels of geologically-sourced and potentially harmful heavy metal(loid)s, which

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have been accumulated in the surface soil layer by supergene enrichment of carbonate-hosted sulfide mineralizations and subsequent pedogenetic processes (Rivera et al. 2015).

The traditional land use is sweet chestnut cultivation. The harvest method used in the region is to gather the nuts after they fall naturally from the tree, and then pick them up by hand from the ground. Incidental ingestion of topsoil particles via hand-to-mouth contact by hand-harvest workers is a significant pathway of direct trace element exposure.

Thus, the objectives of this study were as follows: 1) to quantify the bioaccessible pools of trace elements that can be solubilized during digestion, and thus become available for absorption through the gastrointestinal epithelium; and 2) to identify the gastrochemical factors and soil parameters influencing the human bioaccessibility.

2. Material and methods

Ten composite surface soil samples (0-20 cm depth) were collected with a bucket auger, air dried, gently crushed and then sieved to <250 µm for bioaccessibility essays.

Oral bioaccessibility was assessed by *in vitro* simulation of human digestion, using the Unified BARGE Method (UBM). A full description of the validated UBM methodology can be found in Wragg et al. (2009) or Denys et al. (2012). *In vitro* bioaccessibility (IVBA) was calculated by dividing the extractable amount of each trace element of concern in the gastric (UBM-G) and gastrointestinal (UBM-GI) phases during the assay by the total trace element concentration in the ingested soil, and expressed on a percentage basis.

Bioaccessible trace element concentrations were measured in the digest extracts by ICP-OES (Cu, Pb and Zn) and ICP-MS (As, Cd, Co, Cr, Ni, Sb and Tl). All measurements were done in triplicate to assess the precision of the digestion procedure, with similar results, and the mean value was taken. The accuracy of the extraction protocol was evaluated by analyzing the SRM NIST 2710a.

3. Results and discussion

The extent of heavy metal(loid) extraction under simulated gastric and intestinal conditions varied largely among samples and elements of concern (Table 1). By far, Zn and Pb were the most abundant metals in the digest extracts, with bioaccessible concentrations as high as 6960 mg $kg^{-1}$of Zn and 4124 mg kg^{-1} of Pb in the UBM-G phase, and 2239 mg $kg^{-1}$of Zn and 1058 mg kg^{-1} of Pb in the UBM-GI phase. The bioaccessible concentrations of the other elements were rather similar and generally below 10 mg kg^{-1}, although the UBM-G level of Cd reached up to 189 mg kg^{-1}(sample 11), and the amount of Cu extracted from the UBM-GI compartment was up to 29.4 mg kg^{-1} (sample 12).

In comparison with the total amounts of trace elements in the studied soil samples (data reported elsewhere by Rivera et al. 2016), the IVBA measurements indicated that Cd and Cu were the most bioaccessible metals in the UBM-G and UBM-GI phases respectively (Fig. 1). Based on the mean values, the relative bioaccessibility of trace elements in the UBM-G phase followed the increasing order of: Cr (0.7%) < Sb (3.0%) ≈ As (3.1%) < Ni (6.8%) < Tl (9.5%) < Zn (13.2%) < Cu (14.1%) ≈ Co (14.2%) << Pb (21.5%) << Cd (37.8 %), whereas in the UBM-GI phase the order was: Cr (0.5%) < As (3.5%) ≈ Zn (3.6%) < Pb (4.5%) < Sb (6.1%) < Ni (6.8%) < Cd (12.1%) < Co (12.8%) < Tl (13.9%) < Cu (17.3%).

Table 1. Average trace element concentrations in the gastric and gastrointestinal phases (mg kg^{-1})

Sample	4	5	7	8	9	11	12	13	14	16
Gastric phase (UBM-G)										
Cd	11.3±1.8	8.6±2.1	9.0±1.8	8.8±0.8	1.8±0.4	189±29	39.9±4.5	2.3±0.6	9.9±1.2	4.3±1.0
Cr	0.3±0.1	0.2±0.1	0.3±0.1	0.7±0.1	0.7±0.1	0.4±0.1	0.4±0.1	0.3±0.1	0.3±0.1	0.4±0.1
Ni	1.3±0.2	2.0±0.6	1.2±0.3	0.6±0.1	0.9±0.1	5.0±1.0	4.6±0.6	1.1±0.3	0.9±0.1	1.6±0.4
Co	1.0±0.2	1.3±0.4	1.8±0.4	2.7±0.2	2.8±0.4	1.2±0.2	1.9±0.2	2.2±0.5	5.9±0.9	1.6±0.4
Zn	555±1	717±4	646±1	1359±7	477±2	2562±20	6960±95	231±1	4024±9	39.4±0.2
As	8.8±1.5	2.5±0.7	2.0±0.5	2.0±0.1	2.3±0.3	3.7±0.7	2.8±0.4	2.9±0.7	6.3±0.9	3.5±0.9
Sb	0.6±0.1	0.4±0.1	0.4±0.1	1.8±0.1	0.3±0.1	0.4±0.1	0.5±0.1	0.3±0.1	0.4±0.1	0.3±0.1
Cu	5.3±1.0	6.9±2.2	7.2±1.8	5.0±0.4	5.6±0.9	8.2±1.6	19.2±2.6	5.1±1.3	3.9±0.7	4.8±1.4
Tl	1.0±0.2	0.2±0.1	0.3±0.1	0.2±0.1	0.3±0.1	0.2±0.1	0.3±0.1	0.3±0.1	9.0±1.3	0.1±0.1
Pb	233±1	101±1	749±5	3218±9	935±5	74.2±2.1	588±1	377±2	4124±7	47.0±0.8
Gastrointestinal phase (UBM-GI)										
Cd	3.4±0.6	2.5±0.5	2.6±0.5	3.5±0.5	0.2±0.1	87.6±9.0	14.8±2.6	0.5±0.2	3.8±0.6	1.1±0.4
Cr	0.2±0.1	0.2±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.2±0.1	0.3±0.1	0.2±0.1	0.2±0.1	0.3±0.1
Ni	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.2	0.2±0.2	0.1±0.1	0.2±0.2	0.1±0.1	0.1±0.2	0.2±0.2
Co	0.8±0.1	1.4±0.2	1.5±0.2	2.7±0.2	1.7±0.1	1.3±0.1	1.6±0.2	1.9±0.2	5.8±0.6	1.5±0.2
Zn	118±1	131±1	154±1	220±1	119±1	1077±4	2239±8	48.5±0.1	926±5	20.4±0.2
As	9.7±0.8	2.9±0.3	2.4±0.2	2.4±0.2	2.3±0.2	3.9±0.3	2.8±0.2	3.2±0.3	7.5±0.7	4.1±0.4
Sb	0.8±0.1	0.4±0.1	0.7±0.1	2.2±0.1	0.5±0.1	0.6±0.1	0.9±0.1	0.5±0.1	1.0±0.1	0.5±0.1
Cu	6.3±0.6	8.9±1.0	7.8±0.9	6.6±0.5	6.2±0.6	11.5±1.0	29.4±2.5	5.9±0.6	4.7±0.6	5.4±0.8
Tl	1.1±0.1	0.4±0.1	0.4±0.1	0.4±0.1	0.4±0.1	0.3±0.1	0.4±0.1	0.4±0.1	9.0±0.8	0.3±0.1
Pb	43.7±3.4	17.1±1.7	177±15	388±22	217±14	16.0±1.3	235±16	57.9±4.4	1058±85	13.1±1.6

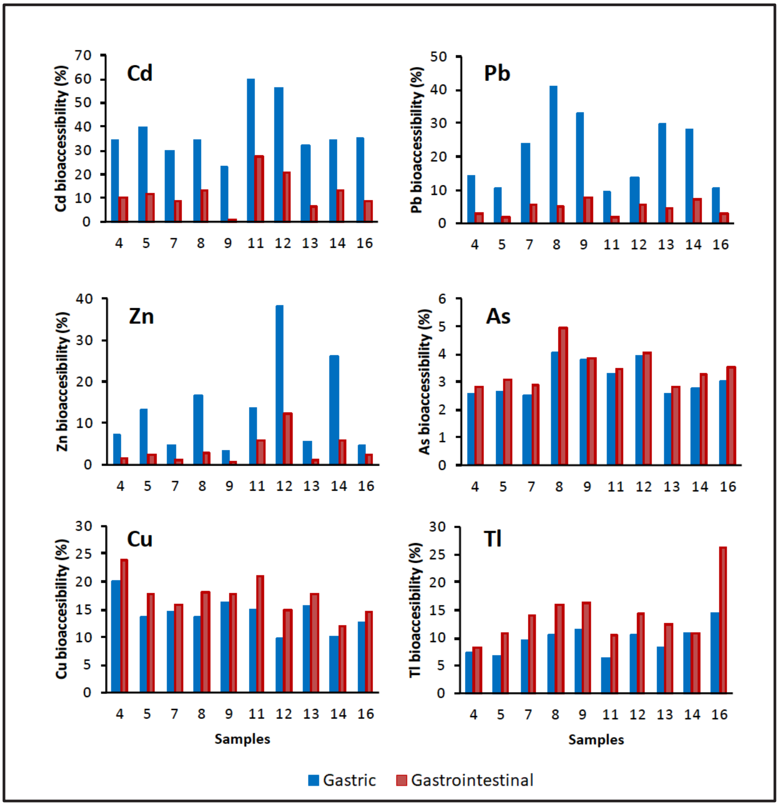

Fig. 1. Bioaccessible fraction of the most concerned trace elements in the gastric and gastrointestinal phases

A plausible explanation for the chemical partitioning pattern between the UBM-G and UBM-GI phases of the sequential *in vitro* extraction is based on the strongly pH-dependent behavior of metallic cations in the gastric and intestinal model solutions (e.g. Fernández-Caliani et al., 2019).

The highly acidic environment of the stomach compartment increased the solubility of Cd, Pb and Zn in the gastric extracts. The decrease of bioaccessibility of such divalent heavy metals observed in the UBM-GI phase may be attributed to chemical precipitation from solution under the slightly alkaline conditions prevailing in the small intestine and/or re-adsorption onto remaining soil particles. Bioaccessibility of Cu and Tl was significantly increased ($p<0.04$) after gastrointestinal digestion, probably due to the use of certain organic reagents that can form complexes with ions of these metals at the near-neutral pH of the gut (Cai et al. 2016), thus enhancing their bioaccessibility. Oxyanion-forming elements, like As, Sb and Cr, appear to be evenly distributed among the UBM-G and UBM-GI phases, suggesting that their solubilities were similar in both compartments.

Statistically significant ($p<0.05$) high correlations were obtained between the bioaccessibility of trace elements and certain soil parameters (soil data reported by Rivera et al. 2016). It was found high good correlation among the bioaccessible fractions of Zn, As, Tl and the content of Fe oxides in the ingested soil, as well as between the Cr bioaccessible fraction and the clay content of soil (Fig. 2), which may indicate that this metal is mostly concentrated in the residual silicate fraction. On the other hand, the bioaccessible amounts of the total concentrations of Pb, Co and Tl were highly negative correlated with the cation exchange capacity (CEC) of soils, indicating that they occur in non-exchangeable forms. This suggests that bioaccessibility is affected not only by the pH and composition of digestive solutions but also, to some extent, by the physicochemical properties and constituents of the soil.

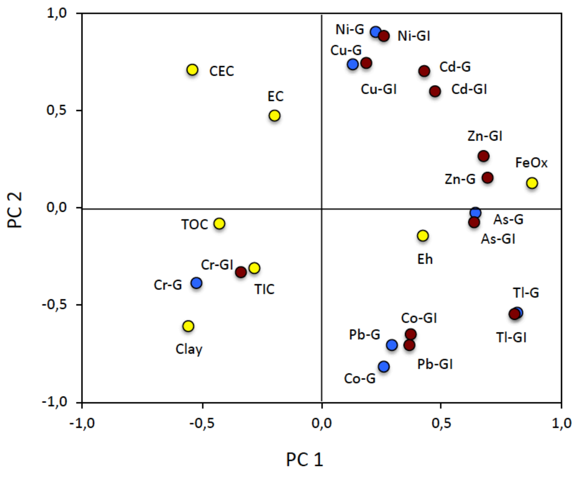

Fig. 2. PCA diagram showing the relationships between bioaccessibility of trace elements and soil properties. G (gastric phase); GI (gastrointestinal phase); Clay (clay content); FeOx (iron oxides content); CEC(cation exchange capacity); EC (electrical conductivity); Eh (redox potential); TOC (total organic carbon content); TIC (total inorganic carbon content)

4. Conclusions

There are several conclusions that can be drawn from this study:

- Bioaccessibility of trace elements varied within a range of values in both digest extracts. Cadmium was the most bioaccessible metal in the gastric fluid, whereas Cu and Tl were the dominant metals dissolved in the gastrointestinal extract.
- Chemical partitioning pattern between gastric and gastrointestinal phases of the sequential *in vitro* extraction is based mainly on the strongly pH-dependent behavior of heavy metals.
- Bioaccessibility seems to be controlled not only by the gastrochemical behavior of trace elements but also by soil properties and constituents.
- The IVBA measurements can help in assessing the human health risks posed to the hand-harvest workers that are being exposed to harmful trace elements via incidental ingestion of soil.

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