



## Bioaccessibility and arsenic speciation in carrots, beets and quinoa from a contaminated area of Chile



Isabel Pizarro<sup>a</sup>, Milagros Gómez-Gómez<sup>b</sup>, Jennifer León<sup>a</sup>, Domingo Román<sup>a</sup>, M. Antonia Palacios<sup>b,\*</sup>

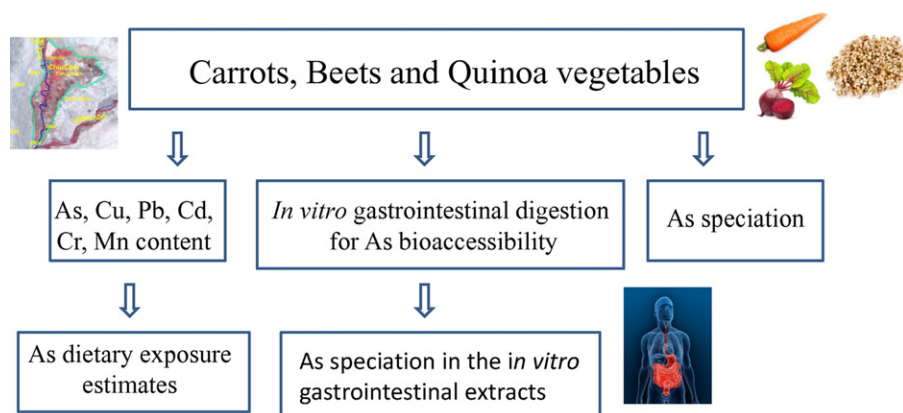
<sup>a</sup> Facultad de Ciencias Básicas, Universidad de Antofagasta, 02800 Antofagasta, Chile

<sup>b</sup> Department of Analytical Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, 28040 Madrid, Spain

### HIGHLIGHTS

- Vegetables from contaminated soils of Chiu Chiu (Chile) present high As levels.
- Only toxic inorganic species of As (III and V) are present in carrots and quinoa.
- No transformations of As species during *in vitro* gastrointestinal digestion.
- Estimated dietary intake and exposure of As have been calculated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Consumption of vegetables grown in arsenic (As)-contaminated soils is an important exposure route to the element for humans. The present study is focused on locally-grown, frequently-consumed vegetables, such as carrots (*Daucus carota*), beets (*Beta vulgaris*) and quinoa (*Chenopodium*) from the As-polluted Chiu Chiu area in Northern Chile. The latter region is affected both by As discharge from copper mining activity and natural As contamination, leading to a high As content in local food and water. For the selected vegetables, the following aspects were investigated: i) Their total As, Cu, Pb, Cr, Cd and Mn content; ii) Arsenic speciation in the edible part of the vegetables by liquid chromatography inductively-coupled plasma mass spectrometry (LC-ICPMS) analysis; iii) Arsenic bioaccessibility in the vegetables during *in vitro* gastrointestinal digestion; iv) Arsenic species present in the extracts obtained from *in vitro* gastrointestinal digestion; and v) Arsenic dietary exposure estimates for the assessment of the risk posed by the vegetables consumption.

A significant degree of As contamination was found in the vegetables under study, their metal content having been compared with that of similar Spanish uncontaminated products. *In vitro* gastrointestinal digestion of the studied vegetables led to quantitative extraction of As from carrots and beets, whereas efficiency was about 40% for quinoa. For carrots, only As(III) and As(V) species were found, being their concentration levels similar. In the case of quinoa, around 85% of the element was present as As(V). For beets, inorganic As(V) and unknown overlapped As species (probably arsenosugars) were found. No significant transformation of the original As

\* Corresponding author.

E-mail address: [palacor@ucm.es](mailto:palacor@ucm.es) (M.A. Palacios).

species was observed during *in vitro* gastrointestinal digestion. Arsenic dietary exposure values obtained for the three vegetables (0.017–0.021  $\mu\text{g As person}^{-1} \text{ day}^{-1}$ ) were much lower than the JFCFA's safety limit of 50  $\mu\text{g As person}^{-1} \text{ day}^{-1}$ . Therefore, no toxicological risk would be expected from the intake of these vegetables.

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## 1. Introduction

Since 1915, the Northern Chilean economy has been mainly supported by the exploitation of copper mining resources and mineral smelting plants. Arsenic can be present in minerals, associated with copper and other heavy metals, e.g. being present in enargite ( $\text{Cu}_3\text{AsS}_4$ ). During the pyrometallurgical process, As is released as  $\text{As}_2\text{O}_3$  both in the form of gas phase and as fine particles (Soriano et al., 2012). In addition, the Loa river water is also naturally contaminated by As. The concentration of As in the water of the Loa hydrographic basin changes dramatically over the course of the river. This can vary from no contamination in the Copiapó river (snow melting, concentration  $<0.005 \text{ mg L}^{-1}$ ) to extreme contamination in the San Salvador river ( $2.0\text{--}2.5 \text{ mg L}^{-1}$ ) (Sträter et al., 2010; Pizarro et al., 2010). Between 1958 and 1970, the Antofagasta population was drinking water from the Loa river with an As concentration of about  $1000 \mu\text{g L}^{-1}$  (most probably in the form of As(V)). Successive improvements in the water treatment resulted in an annual average value of  $50 \mu\text{g As L}^{-1}$ , unfortunately with some areas still presenting levels well above the average. These As levels are still far from the World Health Organization (WHO) maximum recommended levels of  $10 \mu\text{g L}^{-1}$  (WHO, 1996). Therefore, natural geological As contamination of water, anthropological action, the area desert climate, and the exposure of organisms to this high As contamination, result in very extreme conditions for life. This is similar to other situations in well-known parts of the world contaminated with As such as India, China or New Zealand (Ahsan and Del Valls, 2011; Huang et al., 2014; Shakoor et al., 2015; Rahman et al., 2014a, 2014b). Contamination of As and other heavy metals has been reported in soil, water and vegetables growing in the Chilean II Region (Pizarro et al., 2003b; Flynn et al., 2002).

Cancer and other diseases associated with As exposure reach alarming levels in this Chilean area. Recent studies have shown the presence of As(III) in the auricle and saphena of the people living in the Chiu Chiu area, suggesting that As could be involved in cardiovascular disease development (Roman et al., 2011). Bronchial, lung, bladder diseases and renal cancer have an alarmingly unusual high incidence in this region (Steinmaus et al., 2013; Ferreccio et al., 2013). Assessment of the contribution to human diet of As and other contaminant elements in food requires studying not only their total element content but also their absorption rates in the gastrointestinal tract. A way to evaluate the absorbable fraction in trace element bioaccessibility studies is the "*in vitro*" simulation of the digestion process. In the case of As, it is also important to discern its species present in food and their possible transformation during the digestion process (Hur et al., 2011; Khouzam et al., 2011; Calatayud et al., 2013).

Inorganic arsenic species are the most dangerous forms of the element in food, being As(III) more toxic than As(V). The formation of As(III) from As(V) species present in natural environmental conditions, can be attributed in most of the cases to a detoxification mechanism taking place in microorganisms but also in more complex organisms, where reduction occurs prior to methylation. The methylation process first generates monomethylarsonic acid (MMA) and then dimethylarsinic acid (DMA), both being less toxic than inorganic species (Cullen, 2014).

Vegetables, and in particular rice, growing in natural or contaminated soils are one of the most interesting food samples, from the toxicological point of view, for As bioaccessibility and speciation studies. Rice presents the highest concentrations of inorganic arsenic species as compared to other tested products (Tyson, 2013; Rahman et al.,

2014a, 2014b; He et al., 2012). Broccoli, lettuce, potatoes or carrots, can also accumulate As when the soil or the irrigation water contains As(V) (Johnson et al., 2010).

The present study is focused on the determination of As (and its implications for human health) in carrots, beets and quinoa from the polluted Chiu Chiu area located in Northern Chile (about 10 km from Calama and 235 km from Antofagasta city). The following issues were investigated: i) Determination of total content of As and other metals from mining activities (Cr, Cu, Pb, Mn and Cd) in the edible parts of carrots, beets and quinoa grown in the area where the indigenous population live; ii) As species present in the edible part of these vegetables; iii) Arsenic bioaccessibility in the vegetables under *in vitro* gastrointestinal digestion; iv) Arsenic species present in the *in vitro* gastrointestinal extracts; and vi) Evaluation of the health risk posed by the As dietary exposure estimates.

## 2. Materials and methods

### 2.1. Instrumentation

An ICPMS, (HP-4500, Agilent Technologies, Analytical System, Tokyo, Japan) operating under normal multi-element tuning conditions was used for total arsenic and other metals analysis. The main analytical parameters of the ICPMS were the following: R.F. forward power, 1350 W; reflected power, 2.2 W; plasma argon flow rate,  $14 \text{ L min}^{-1}$ ; auxiliary argon flow rate,  $0.9 \text{ L min}^{-1}$ ; nebulizer argon flow rate  $0.85 \text{ L min}^{-1}$ , integration time, 0.1 s per point; points per peak, 3.

For arsenic speciation, an ICPMS has been used as detector system after LC species separation. The column effluent was directly introduced into a Meinhard-type concentric glass nebulizer and a double-pass Scott-type spray chamber with a Peltier cooling system set at  $5^\circ\text{C}$ . Data was collected by single ion monitoring at  $m/z$  75. For chromatographic separation, a high-pressure pump (LDC Division, Riviera Beach, Florida, USA) was used as a sample delivery system. Samples of  $100 \mu\text{L}$  were introduced through a  $0.45\text{-}\mu\text{m}$  nylon syringe filter into an injection valve (Rheodyne 9125, USA). Polytetrafluoroethylene tubing (i.d.  $0.5 \text{ mm}$ ) connections were used for coupling the LC system to ICP-MS. A Hamilton PRP- $\times$  100 LC column ( $10 \mu\text{m}$ ,  $250 \text{ mm} \times 4.1 \text{ mm}$ ) Torrance, CA, USA) with a Phenomenex precolumn ( $25 \times 2.3 \text{ mm}$   $12\text{--}20 \mu\text{m}$ ) was used.

All signal quantification was performed in the peak area mode. Peaks were integrated using either ICPMS Chemstation software (Agilent Technologies) or Grams/32 software (Galactic Industries, Salem, NY, USA).

A Sonopuls Ultrasonic Homogenizer (HD 2200, Bandelin Electronic, Berlin, Germany), a Vibromatic rocking mixer (Selecta, Barcelona, Spain) and a Gyrozen 416 Centrifuge (Controltecnia Instruments, Barcelona, Spain) were also used in the sample extraction process.

### 2.2. Reagents

A standard solutions of As(III) of  $1000 \text{ mg L}^{-1}$  TraceCERT™ Ultra (Fluka, Sigma-Aldrich, Steinheim, Germany) and As(V)  $1000 \text{ mg L}^{-1}$  CertiPUR (Merck, Darmstadt, Germany), both prepared in  $\text{HNO}_3$  (2% v/v), were used. Dimethylarsinic acid (DMA) and methylarsonic acid (MMA) standard solutions of  $1000 \text{ mg L}^{-1}$ , were prepared from methyl disodium arsenate ( $\text{Na}_2\text{CH}_3\text{AsO}_3$ , 99% Supelco, Bellefonte, PA, USA) and cacodylic sodium trihydro (( $\text{CH}_3$ ) $_2\text{AsNaO}_2 \cdot 3\text{H}_2\text{O}$ ) 98% Fluka) TraceCERT™. Arsenobetaine (AsB) and arsenocholine (AsC) were obtained from Tri Chemical Laboratory Inc. (Japan). Cd (Fluka), Cu (Fluka), Mn

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