Food Chemistry 246 (2018) 258–265

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Effect of food preparation using naturally-contaminated groundwater from La Pampa, Argentina: Estimation of elemental dietary intake from rice and drinking water

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ARTICLE INFO

Keywords:
Arsenic
Vanadium
Molybdenum
Rice
Drinking Water
Washing
Cooking
Dietary intake

ABSTRACT

Water from La Pampa, Argentina, was used for washing and cooking rice to examine the *in-situ* impact of using naturally-contaminated water for food preparation on the elemental dietary intake. Whilst washing with the control tap water (28 μg/L As) reduced the concentration of As in rice by 23%, the use of different well waters (281–1144 μg/L) increased As levels significantly (48–227%) in comparison with the original concentration in the rice (0.056 μg/g). Cooking the rice at a low water-to-rice ratio (2:1) using modern methods increased the levels of As in the cooked samples by 2–3 orders of magnitude for both pre-washed and un-washed rice. Similar trends were observed for vanadium. Although the levels of manganese, iron, copper, zinc and molybdenum in rice were reduced during washing and cooking for most water samples, the molybdenum concentration in the cooked rice doubled (2.2–2.9 μg/g) when using water containing > 1 mg/L Mo.

1. Introduction

Argentina has long been documented as one of the regions of Latin America most affected by arsenic (As) contamination of natural origin (Bundschuh et al., 2012). Much of the research has focused on As in drinking water originating from surface and/or groundwater (Bundschuh et al., 2012; Nicolli et al., 2012), however less attention has been paid to the potential exposure of As to humans via the food chain (Bundschuh et al., 2012). Although some major urban communities of Argentina have commercial sources of treated drinking water, As-contaminated well water is primarily used for the irrigation of agricultural land and the watering of livestock. Moreover, untreated well waters are still used in many rural communities as sources of drinking water (O'Reilly, Watts, Shaw, Marcilla, & Ward, 2010; Watts, O'Reilly, Marcilla, Shaw, & Ward, 2010) and for the preparation of foodstuffs. One of the affected provinces, namely La Pampa, has been reported to have high levels of As in the groundwater of up to 5.3 mg/L. These levels have been linked to volcanic activity, hydrothermal reservoirs and Quaternary loess sediments (Nicolli, Bundschuh, García, Falcón, & Jean, 2010; Smedley, Nicolli, Macdonald, Barros, & Tullio, 2002; Smedley et al., 2005). Other elements, such as V, Mo, Fe, Mn, Cu and Zn, may also be found in local groundwater associated with high levels of As, due to the geochemistry of the region (Nicolli et al., 2012; Smedley et al., 2002). Long term exposure to As in groundwater has been linked to health problems in the local population, such as skin cancer, diabetes and stress-related disorders (Farnfield, 2012; Lord, 2014; McClintock et al., 2012). Although some studies have examined the As levels of local foodstuffs in Argentina (Cabanillas-Vidosa, Rosso, Bassani, Corelli, & Sandrini, 2014; Sigrist, Hilbe, Brusa, Campagnoli, & Beldoménico, 2016), the effect of the chemical characteristics of the water used in food preparation on the total elemental dietary intake has not been fully evaluated (Ward et al., 2014). Rice has been chosen in this study because it provides a good model to show how preparation methods may affect the chemical composition of food as consumed. Moreover, the obtained data can be compared with analogous studies in Asian countries with As-related contamination problems (India, Bangladesh, Cambodia, Pakistan, Myanmar, Thailand, Vietnam and China), where rice is the main staple food. Thus, the aim of this work was to determine how the preparation of Argentine rice using local water samples from the La Pampa province may influence the dietary intake of As and other trace elements (V, Mo, Fe, Mn, Cu and Zn). Furthermore, the effect of diverse methods of preparation of the foodstuffs, such as the pre-washing of the rice, was also assessed. While most studies that evaluate the dietary intake of toxic elements base their

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https://doi.org/10.1016/j.foodchem.2017.11.019
Received 25 July 2017; Received in revised form 3 November 2017; Accepted 6 November 2017
Available online 07 November 2017
0308-8146/

Table 1
Samples collected from urban and rural wells of communities in La Pampa, Argentina that were used as washing and cooking water in this study.

Sample ID	GPS coordinates	Description	Water type
Tap water	37°58′57″ S 63°36′17″ W	Urban supply in General San Martín	Urban water from a treatment plant that processes piped surface water from the Colorado river in southern La Pampa.
Well 1	37°56′11″ S 63°35′50″ W	Rural farm well near General San Martín	Untreated groundwater
Well 2	35°58′44″ S 64°15′30″ W	Rural farm well 6 km south of Eduardo Castex	Untreated groundwater
Well 3	35°59′53″ S 64°14′58″ W	Rural farm well 7.5 km south of Eduardo Castex	Untreated groundwater

calculations on the elemental content of raw foodstuffs, this study aims to provide a more comprehensive estimation of the intake by assessing the changes in food composition during the washing and cooking processes.

2. Materials and methodology

2.1. Field study

The province of La Pampa is located in the central zone of Argentina, an area that covers approximately 140,000 km^2 within the Chaco-Pampean Plain (Smedley et al., 2002). This province has a semi-arid climate with an annual rainfall between 650 and 700 mm (O'Reilly et al., 2010), which influences the mobilisation and accumulation of As in different environmental compartments (water and/or soils) (Nicolli et al., 2012). The water samples in this study were collected from General San Martín and Eduardo Castex in May 2016 (Table 1). Three different rural wells (naturally contaminated water) and one reverse osmosis treated municipal tap water (control) were used for the *in-situ* preparation of rice throughout this study.

2.2. Sampling and analysis of water

For total trace element analysis, 15-mL aliquots of water were collected and filtered through a 0.45 µm syringe-driven unit (Millex®-GP, Millipore, UK) at each sampling location and transferred into pre-acidified (5% v/v nitric acid, trace element grade from Aristar®, Fisher Scientific, UK) polypropylene tubes (Fisher Scientific Ltd, UK). As speciation was undertaken using a field-based solid phase extraction (SPE) kit developed by Watts et al. (2010). The kits contained pre-conditioned 500 mg Bond Elut® strong cation exchange (SCX) and strong anion exchange (SAX) cartridges (Agilent Technologies, UK). Each cartridge was pre-conditioned using 15 mL of 50% v/v methanol (Sigma-Aldrich, Dorset, UK) and 10 mL of distilled deionised water (DDW, 18.2 MΩ), an additional aliquot of 15 mL 1 M phosphoric acid (BDH, Aristar®, UK) was used in the case of the SCX. Any residual liquid that may still impregnate the ion exchange resins was completely removed by flashing air through the cartridges repeated times just before sampling. As such, a 30 mL volume of water sample was passed through the SPE cartridges using a 20 mL syringe (BD Plastipak™, UK). Arsenite, As(III) does not interact with either cartridge and therefore passes through to the effluent. The SCX cartridge retains the dimethylarsinic acid (DMA), whilst the SAX cartridge retains the monomethylarsonic acid (MA) and arsenate As(V) species. All collected water samples and SPE kits were then fully labelled, packed and stored in a fridge at 4 °C before transportation to the University of Surrey for elution processing and further analysis. All analyses were carried out in quintuplicate.

The trace element levels in the cooking (tap and well) and washing water samples were determined using an Agilent 7700x Series inductively coupled plasma-mass spectrometer, ICP-MS (Agilent Technologies, UK) using a collision/reaction cell pressurised with helium for the removal of interfering polyatomic ions (3rd generation Octopole Reaction System, Agilent Technologies). The use of 4.8 mL/min He flow in the octopole cell ensured the satisfactory elimination of the $^{40}Ar^{35}Cl^{+}$ interference on ^{75}As determination (Yamanaka and Willbur, 2013). The ICP-MS instrument was tuned using a 1 µg/L solution containing Li, Co, Y, Ce and Tl in 2% HNO_3 (v/v) (Agilent Technologies) and calibrated on a daily basis with V, Mn, Fe, Cu, Zn, As and Mo traceable standards (1000 mg/L of stock solution, BDH, Aristar®, UK), using 100 µg/L Sc, Ge and Rh as internal standards (100 µg/L, Agilent Technologies, UK). The ^{45}Sc signal was used to correct for ^{51}V, ^{55}Mn, ^{56}Fe and ^{63}Cu counts; ^{72}Ge for ^{66}Zn and ^{75}As; and finally ^{103}Rh for ^{95}Mo. Two water certified reference materials (CRMs), namely, NIST SRM 1640a (National Institute of Standards and Technology, USA) and TMDA-51.4 (National Water Research Institute, Canada) (n = 6) were used to evaluate the levels of accuracy and precision for the measurements by ICP-MS. The measured values for each element were in good agreement with the certified values for both CRMs and the range of calculated analyte recoveries (%) were; ^{75}As (97–99%), ^{51}V (100–102%), ^{55}Mn (96–99%), ^{56}Fe (97–101%), ^{63}Cu (100–103%), ^{66}Zn (95–102%) and ^{95}Mo (98–103%). The levels of precision (between-batch) were found to be very good with relative standard deviations RSD < ± 1%. The limits of detection [mean + (3 × SD)] for all measured elements in water were; 0.02 µg/L As, 0.02 µg/L V, 0.03 µg/L Mn, 0.50 µg/L Fe, 0.05 µg/L Cu, 0.10 µg/L Zn and 0.06 µg/L Mo.

2.3. Preparation and analysis of rice

A polished long thin grain variety of locally produced rice was purchased from supermarkets in Argentina. Two procedures were evaluated for the preparation of rice; method A involved washing of the rice prior cooking, whilst for method B the rice samples were cooked directly. The rice samples were washed by mixing 1 cup of raw rice (~75 g dry weight) with the same volume of water (~90 mL) and stirring using a plastic spoon for 2 min. The resultant washing water was then decanted and an aliquot (ca. 15 mL) was passed through a 0.45 µm syringe-top filter and acidified by addition of 2 drops of 5% nitric acid, whilst the remaining water was discarded. This step was repeated twice using fresh water (total washing volume 270 mL, 6 min). The three samples of the sequential washing steps and the resulting washed rice were stored in a fridge at 4 °C until further analysis.

All samples of rice (pre- or un-washed) were cooked *in-situ* using an electric rice cooker (Guangdong Oushiba Car Appliance Co., Ltd. China), at a ratio of 1 vol of rice to 2 volumes of freshly collected water (tap or well), according to manufacturer's recommendations. After ~15 min the cooker automatically turned-off and it was left to stand for about 5 min to ensure complete evaporation of the cooking water. Then, the cooked rice was removed from the cooker and air-dried before being transferred to a polypropylene bag, sealed and stored in a fridge at 4 °C until further analysis. Cooking experiment were performed in duplicate.

Before analysis, the rice samples (raw, washed or cooked) were kept in a drying cabinet (LTE Scientific Ltd, UK) at 60 °C for 72 h or until constant dry weight. Approximately, 0.5000 ± 0.0001 g of dried rice were subjected to ashing using a muffle furnace (Carbolite AAF1100) at 500 °C for 12 h; the resulting ash was homogenised and dissolved with 1 mL of concentrated HNO_3 (Primar plus 68% (v/v), Fisher Scientific).