Chemosphere 182 (2017) 433–440

Contents lists available at ScienceDirect

Chemosphere

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

Comparative analysis of speciation and bioaccessibility of arsenic in rice grains and complementary medicines

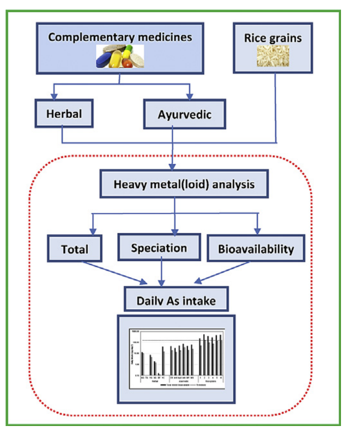
S. Bolan [a, b], A. Kunhikrishnan [c], S. Chowdhury [d], B. Seshadri [a, b, *], R. Naidu [a, b], Y.S. Ok [e]

[a] Global Centre for Environmental Remediation, University of Newcastle, NSW 2308, Australia
[b] Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), University of Newcastle, NSW 2308, Australia
[c] Department of Agro-Food Safety, National Institute of Agricultural Science, Wanju, Jeollabuk-do 55365, Republic of Korea
[d] Department of Soil Science, Sher-e-Bangla Agricultural University, Dhaka 1207, Bangladesh
[e] Korea Biochar Research Center & Department of Biological Environment, Kangwon National University, Chuncheon 200-701, Republic of Korea

HIGHLIGHTS

- As species in rice and complementary medicines was examined by fractionation and EXAFS.
- As bioavailability in rice and complementary medicines was examined using PBET.
- PBET showed difference in As bioavailability amongst rice and complementary medicines.
- Daily As intake values may exceed safe levels in rice but not in complementary medicines.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 February 2017
Received in revised form
7 April 2017
Accepted 24 April 2017
Available online 3 May 2017

Keywords:
Heavy metal(loid)s
Ayurvedic medicines
Chinese medicines
Complementary medicines
Rice grains
Toxicity

ABSTRACT

In many countries, rice grains and complementary medicines are important sources of arsenic (As) consumption. The objective of this study was to compare the speciation and bioaccessibility of As in selected rice grains and complementary medicines. A number of rice grain samples, and a range of herbal and ayurvedic medicines were analyzed for total As, speciation of As using sequential fractionation and extended x-ray absorption fine structure (EXAFS) techniques, and bioaccessibility of As using an *in vitro* extraction test. The daily intake of As through the uptake of these As sources was compared with the safety guidelines for As. The results demonstrated higher levels of As in ayurvedic medicines compared to herbal medicines and rice grains. The sequential fractionation showed the dominance of organic-bound As species in rice grains and herbal medicines, however, inorganic-bound As species dominated the ayurvedic medicines. This implies that As is derived from plant uptake in herbal medicines and rice grains, and from inorganic mineral input in ayurvedic medicines. Arsenic bioaccessibility was higher in ayurvedic than herbal medicines and rice grains, suggesting that inorganic As added as a mineral

* Corresponding author. Global Centre for Environmental Remediation, University of Newcastle, NSW 2308, Australia.
E-mail address: balaji.seshadri@newcastle.edu.au (B. Seshadri).

http://dx.doi.org/10.1016/j.chemosphere.2017.04.126

therapeutic input is more bioaccessible than organic As species derived from plant uptake. This study also showed a positive relationship between soluble As fractions and bioaccessibility indicating that solubility is an important factor controlling bioaccessibility. The daily intake values for As as estimated by total As content are likely to exceed the safe threshold level in rice grains that are enriched with As.

1. Introduction

Arsenic (As), which occurs naturally in a number of forms (or species), is classified as a class one carcinogen by the World Health Organisation's International Agency for Research on Cancer (IARC, 2004). High levels of As intake can raise the risk of developing lung, bladder and skin cancer, cardiovascular disease, diabetes, skin lesions, gastrointestinal illness and other serious health problems, eventually leading to death (WHO, 2010; Zhang et al., 2016). Significant detrimental impacts of As on human health have been reported in some endemic areas of Bangladesh, India, Chile, and China, and millions of people are potentially at risk from As poisoning (Bhattacharya et al., 2012; Hojsak et al., 2015; Mahimairaja et al., 2005). In these countries, As reaches food chain mainly through the use of potable water and plant uptake resulting from the irrigation of As-rich water. Regular rice consumption has been considered as a major source of As intake in human in many countries including Bangladesh and Vietnam where As-rich groundwater is used to irrigate rice crop (Meharg and Zhao, 2012; Williams et al., 2006). Also, rice is more efficient than other grain crops like barley and wheat at taking up As from soils (Williams et al., 2007). However, the concentration of As in rice grains depends on a number of factors including rice cultivars, As concentration in the irrigation water and irrigation management practices (Halder et al., 2012; Hojsak et al., 2015; Hu et al., 2013; Kuramata et al., 2011; Linquist et al., 2015; Mandal and Suzuki, 2002; Rahman and Hasegawa, 2011; Williams et al., 2005).

Complementary medicines refer to a broad group of natural or alternative medicines, and include herbal, ayurvedic, Chinese traditional and homeopathic medicines, and vitamin and dietary health supplements (WHO, 2005). Most risks associated with complementary medicines result from contaminants that include pesticide residues and heavy metal(loid)s (Bolan et al., 2016; Denholm, 2010). The presence of heavy metal(loid)s including As in complementary medicines is attributed to contamination during cultivation of plants used for complementary medicines, accidental cross-contamination occurring during processing, and the introduction of metal(loid)s as a therapeutic ingredient (Mathews et al., 2012; Saper et al., 2004; Sarma et al., 2011; Tripathi et al., 2012). Cooper et al. (2007) observed the presence of As as realgar in two Chinese medicines (Liu Shen Wan and Niu Huang Chieh Tu Pien) through X-ray diffraction studies. When complementary medicines that are enriched with metal(loid)s including As, as a part of their preparation to treat diseases including tumors are taken regularly, increasing incidences of As poisoning, both acute and chronic cases, have been reported (Cooper et al., 2007; Pinto et al., 2014; Saper et al., 2004; Zhou et al., 2015).

Bioaccessible metal(loid) concentrations are more important for risk assessment than total metal(loid) contents, and therefore studies on As bioaccessibility are required for determining human As intake from rice and complementary medicines for use in accurate risk assessments to establish maximum levels of As in food and medicines. Studies on As bioaccessibility are often conducted using simple, fast, reproducible, and cost-affordable *in vitro* digestive methods that aim to mimic the physicochemical and enzymatic processes of the human digestive system (Laird et al., 2007; Van de Wiele et al., 2010).

Although there have been a number of reports on the speciation and bioaccessibility of As in rice grains (He et al., 2012; Juhasz et al., 2006; Signes-Pastor et al., 2012; Williams et al., 2005), only very few studies have been reported in complementary medicines (Jayawardene et al., 2010; Koch et al., 2011; Ventola, 2010). Effective strategies to minimise or eliminate heavy metal(loid) risk from these sources are challenging for policy makers, but critical for optimising health benefits. The objectives of this study were to: (i) measure As content in selected complementary medicines and rice grains; (ii) examine the speciation and bioaccessibility of As in these complementary medicines and rice grains; and (iii) quantify the daily intake of As through the consumption of these medicines and rice grains.

2. Materials and methods

2.1. Rice grains and complementary medicines

The rice grains were obtained from grains collection centres maintained by various research groups in Bangladesh, Korea, and India (Table 1). The rice crops were grown either under greenhouse or field conditions with irrigation water containing various levels of As supplied as $Na_2HAsO_4{\cdot}7H_2O$. The herbal and ayurvedic medicines were purchased in 2014 from Indian and Chinese shops (Table 1). The complementary medicine products included in this study are based on their heavy metal(loid) content derived from literature data. An additional four (two herbal and two ayurvedic) complementary medicines were sourced and analyzed to test the regression relationships derived between bioaccessibility and speciation of As. These included two herbal [Obeslim (OS) and Rumarid (RR)] and two ayurvedic [Trivang Bhasma (TB) and Hing Wastika (HW)] medicines. The results reported for As were part of a study on the bioavailability of major heavy metal(loids) including As, Pb, Cd, and Hg in complementary medicines (Bolan et al., 2016).

2.2. Total As analysis

For total As analysis, the rice grains and complementary medicines (0.5 g, <0.2 mm) were taken in a digestion vessel with 5 ml of *aqua regia* (1:3 HNO_3: HCl). The *aqua regia* suspension was digested in a micro-wave oven as outlined in Method 3051H (USEPA, 1997). For quality assurance, the appropriate number of blank and standard reference material samples [certified reference material (CRM) - Montana Soil (SRM 271) and Rowe Scientific (NCS-DC73349)] were included in the digestion procedure and sample analysis. All digested solutions were diluted with MQ water and spiked with an internal standard solution. The As concentration was measured using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent) with a combination of internal standardisation and external calibration.