Science of the Total Environment 584–585 (2017) 631–641

Contents lists available at ScienceDirect

Science of the Total Environment

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

Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area

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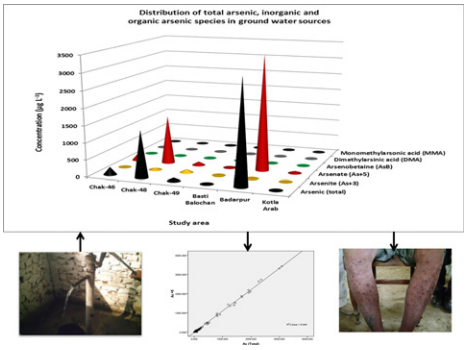
HIGHLIGHTS

- First detailed ground water arsenic speciation profile of Pakistan with highest level of total arsenic up to 3090 μg L^{-1}.
- As^{+5} found to be the major species in groundwater while As^{+3} was dominant at a small number (13) of sources only.
- Mean ratio of As^{+3} to total arsenic slightly higher than found in Bangladesh.
- Highest average daily dose of 236.51 μg kg^{-1} day^{-1} for total arsenic through drinking water ingestion.
- Average daily dose of 15.63 μg kg^{-1} day^{-1} (children) and 15.07 μg kg^{-1} day^{-1} (adults) for As^{+5}.
- Average daily dose of 0.09 μg kg^{-1} day^{-1} (children) and 0.26 μg kg^{-1} day^{-1} (adults) for As^{+3}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 November 2016
Received in revised form 12 January 2017
Accepted 14 January 2017
Available online 26 January 2017

Editor: Jay Gan

Keywords:
Arsenate
Arsenite
Monomethylarsonic acid (MMA)
Dimethylarsinic acid (DMA)
Arsenical pesticides
Provisional tolerable daily intake (PTDI)

ABSTRACT

Understanding arsenic speciation in water is important for managing the potential health risks associated with chronic arsenic exposure. Most arsenic monitoring studies to date have only measured total arsenic, with few looking at arsenic species. This study assessed 228 ground water sources in six unstudied villages in Pakistan for total, inorganic and organic arsenic species using ion chromatography inductively coupled plasma collision reaction cell mass spectrometry. The concentration levels approached 3090 μg L^{-1} (95% CI, 130.31, 253.06) for total arsenic with a median of 57.55 μg L^{-1}, 3430 μg L^{-1} (median = 52) for arsenate (As^{+5}) and 100 μg L^{-1} (median = 0.37) for arsenite (As^{+3}). Exceedance of the WHO provisional guideline value for arsenic in drinking water (10 μg L^{-1}) occurred in 89% of water sources. Arsenic was present mainly as arsenate (As^{+5}). Average daily intake of total arsenic for 398 residents living in the sampled houses was found up to 236.51 μg kg^{-1} day^{-1}. This exposure estimate has indicated that 63% of rural residents exceeded the World Health Organization's provisional tolerable daily intake (PTDI) of 2.1 μg kg^{-1} day^{-1} body weight. Average daily intake of As^{+5} was found to be 15.63 μg kg^{-1} day^{-1} (95% CI, 5.53, 25.73) for children ≤16 and 15.07 μg kg^{-1} day^{-1} (95% CI, 10.33, 18.02) for adults. A mean daily intake of 0.09 μg kg^{-1} day^{-1} was determined for As^{+3} for children and 0.26 μg kg^{-1} day^{-1} for adults. Organic arsenic species such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and Arsenobetaine (AsB) were found to be below their method detection limits (MDLs).

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http://dx.doi.org/10.1016/j.scitotenv.2017.01.089
0048-9697/

1. Introduction

The natural occurrence of arsenic in ground and surface water poses a health risk for approximately 200 million people globally (Naujokas et al., 2013). Epidemiological studies have indicated an association between chronic exposure to inorganic arsenic via drinking water and cancer of the skin, liver, lung, kidney, prostate and bladder (ATSDR, 2007a). The toxicity and carcinogenicity of arsenic is strongly associated with its oxidation states and chemical forms. Arsenic species in water consist of inorganic species such as arsenate ($H_2AsO_4^-$ or As^{+5}), arsenite (H_3AsO_3 or As^{+3}) and organic species like monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AsB). As^{+3} was found to be 10 times more toxic than As^{+5} and 70 times more toxic than MMA^{+5} and DMA^{+5} (Squibb and Fowler, 1983). Higher exposure to inorganic arsenic species is reported to be linked with various toxicities including cardiovascular disorders due to oxidative stress (Singh et al., 2011). Organic arsenic species in the trivalent oxidation state (MMA^{+3} and DMA^{+3}) may induce higher cytotoxic and genotoxic effects than pentavalent species (MMA^{+5} and DMA^{+5}) and inorganic arsenicals due to their higher membrane permeability. This has been exemplified in Chinese hamster ovary cells (Dopp et al., 2004).

Metabolism of inorganic arsenic to trivalent methylated arsenic species plays an important role in increasing the toxic effects as MMA^{+3} has shown higher toxicities than As^{+3} (Petrick et al., 2001; Petrick et al., 2000). Based on these studies, the International Agency for Research on Cancer considers DMA and MMA as possible carcinogens to humans (International Agency for Research on Cancer, IARC, 2012). Despite this, there is no definitive understanding of the mechanism for carcinogenic effects of arsenic species. It is important to measure their concentrations in the environment and biological systems after ingestion to help understand their roles in the development of cancer (Hughes, 2009).

Organic forms of arsenic such as DMA have been used as ingredients in some pesticides such as monosodium methanearsonate (MSMA) or disodium methanearsonate (Ahuja, 2008; Hughes et al., 2011). Following the identification of organic arsenic species in surface waters or aquifers and associated carcinogenic effects, policy has been developed to limit exposure. For example, the US EPA produced the organic arsenical product cancellation order (US Environmental Protection Agency, USEPA, 2009) and EU pesticide legislation was developed i.e. Commission Directive 2003/3/EC: Regulation (EC) No 304/2003 (Official Journal of the European Union, 2003). Nevertheless, few studies, particularly in arsenic affected regions, exist on inorganic arsenic speciation in water (Chen et al., 1994; Bhattacharya et al., 2006). In such regions, exposure assessments of inorganic and organic arsenic species may assist in identifying the likely sources associated with cancer clusters. These may include arsenic contaminated ground water used for drinking, food preparation, cooking and irrigation purpose. Previous studies undertaken in Pakistan have only determined inorganic arsenic using commercial field testing kits (Mahar et al., 2015; Uqaili et al., 2012; Ahmad et al., 2004) or validated a small percentage of samples in the laboratory for inorganic arsenic (Haque et al., 2008; Farooqi et al., 2007). Whereas, arsenic speciation studies (Zahir et al., 2015; Brahman et al., 2013 and Baig et al., 2016) have only analysed As^{+3} using simple spectrophotometry or Graphite Furnace Atomic Absorption Spectrometry (GFAAS). As^{+5} has been determined only as the difference between total inorganic arsenic and As^{+3}, whilst organic arsenic species (DMA, MMA and AsB) have not been analysed in water.

Considering the unknown extent of arsenic species in ground water and uncertainties regarding the species dependent arsenic toxicity, the aim of this study was to conduct an exposure assessment for different arsenic species in the groundwater of six previously unexplored rural settings. The specific objectives were to; 1) assess the spatial distribution of total arsenic, inorganic (As^{+3} and As^{+5}) and organic arsenic species (DMA, MMA and AsB) in ground water aquifers; 2) determine the magnitude of arsenic exposure from domestic ground water and associated health implications.

Table 1
Summary of Quality Control Data of six analytical batches.

Parameter	Method Detection Limits (MDLs)			Calibration Standard (CAL)		Initial Calibration Verification (ICV)		Duplicate (DUP)		Matrix Spike (MS)		Certified Reference Material (CRMs) NIST 1640a		Laboratory Fortified Blank (BS)	
	% Rec.	Results	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	Results	SD
Total As	84	0.31	0.28	100	3.16	98	8.01	117	2.46	98	10.57	96	6.91	86%	0.62	0.56
As^{+3}	97	0.36	0.05	104	7.28	108	4.08	106	3.83	103	4.89	–	–	89%	0.78	0.37
As^{+5}	109	0.12	0.03	101	9.5	98	1.63	102	7.66	107	7.72	–	–	98%	1.07	0.16
MMA	90	0.18	0.04	97	7.21	75	14.29	109	4.4	109	7.35	–	–	97%	1.24	0.21
DMA	96	0.27	0.04	103	6.47	113	1.63	106	4.69	106	6.93	–	–	97%	1.1	0.17
AsB	100	0.37	0.03	–	–	107	8.57	–	–	–	–	–	–	99%	1.08	0.09

Expected percent recovery: 75–125%.