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Contents

Abbreviations

As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
CRM	Certified reference material
DMA	Dimethylarsinic acid
DMA(III)	DMA with trivalent arsenic
DOM	Dissolved organic matter
EFSA	European Food Safety Authority
FAO	Food and Agriculture Organization
GF-AAS	Graphite furnace – atomic absorption spectroscopy
GSH	Glutathionine
HG-AAS	Hydride generation – atomic absorption spectroscopy
HG-AFS	Hydride generation – atomic fluorescence spectroscopy
HPLC	High-performance liquid chromatography
ICP-MS	Inductively-coupled plasma mass spectrometry
ICP-OES	Inductively-coupled optical emission spectroscopy
LOD	Limit of detection
MMA	Monomethylarsonic acid
MMA(III)	MMA with trivalent arsenic
NAA	Neutron activation analysis
NIP	Nodulin 26-like intrinsic protein
OVT	Ovular vascular trace
PC	Phytochelatin
QTL	Quantitative trait locus
SIMS	Secondary ion mass spectrometry
TMA	Tetramethylarsonium ion
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectrometry
XRF	X-ray fluorescence

Chapter 1
Introduction

1.1 Arsenic Exposure from Rice

The first solid food that most humans eat as weaning babies is rice, because of its blandness, lack of allergen reactions and material properties that give rise to a palatable porridge (Meharg et al. 2008). It is also the dietary staple for half the world's population (Meharg et al. 2009). Rice is approximately tenfold elevated in arsenic concentration compared to all other dietary grain staples (Williams et al. 2007a, b). The major component species of total arsenic in rice grain is inorganic arsenic (arsenate and arsenite), a class 1, non-threshold carcinogen (Meharg et al. 2009). Inorganic arsenic gives rise to a range of cancers: lung bladder and skin being the most prominent (NRC 2001; WHO 2004). Chronic exposure to inorganic arsenic species is also implicated in a range of other negative health impacts such as hypertension, diabetes, and premature births (NRC 2001; WHO 2004).

While there is rightful concern regarding high levels of inorganic arsenic exposure to ~100 million people around the world through elevated drinking water supplies (Ravenscroft et al. 2009; Smedley and Kinniburgh 2002), arsenic from rice is the largest dietary source of arsenic to the world's population with no elevated arsenic in their drinking water (EFSA 2009; Meacher et al. 2002; Meharg et al. 2009; Meliker et al. 2006; Tsuji et al. 2007; Yost et al. 2004). Even in many of the countries with highly elevated arsenic in drinking waters, because those countries at the heart of the arsenic drinking water crisis in southeast (SE) Asia and the Indian subcontinent have subsistence rice diets, rice is still a major dietary contributor to arsenic intake, and indeed may be the dominant source, particularly when drinking water sources have been reduced through mitigation (Kile et al. 2007; Mondal and Polya 2008; Ohno et al. 2007).

Even at baseline (i.e. not further elevated through anthropogenic activity), arsenic in rice is problematic (Lu et al. 2010; Meharg et al. 2009); at its worst it is predicted that 22 in 10,000 Bangladeshi population will suffer bladder and lung cancers from lifetime exposures to "natural" levels of arsenic in rice (Meharg et al. 2009). If rice is grown on geogenically, naturally, arsenic enriched soils, rice arsenic level

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further elevated from average baseline may be expected (Lu et al. 2010). Anthropogenic elevation of arsenic in rice grain occurs from three major pollution scenarios:

(a) Irrigation of rice paddies with groundwater elevated in arsenic, as occurs in Bangladesh and West Bengal India (Duxbury et al. 2003; Meharg and Rahaman 2003; Pal et al. 2009; Williams et al. 2006);
(b) Contamination of paddy soils from industrial and mining activity, with this problem being extensive over SE Asia (Liao et al. 2005; Williams et al. 2009; Zhu et al. 2008);
(c) Growing paddy rice on soil previously treated with arsenical pesticides, as occurs in South Central USA (Williams et al. 2007).

In the areas of the Indian sub-continent impacted by groundwater arsenic, not only does the irrigation with contaminated groundwater lead to elevation of arsenic in rice, rice also effectively scavenges arsenic from its cooking water (Bae et al. 2002; Pal et al. 2009) further elevating dietary exposure, remembering that the populace affected by this elevated arsenic in rice are also exposed to elevated arsenic in drinking water. This entwining of groundwater and rice exposure pathways creates many logistical problems with respect to the management of water resources in the affected regions (Meharg and Raab 2010).

As rice is traded locally, nationally and internationally, rice elevated in arsenic in one region may become the food staple of populations geographical remote from the food production source (Meharg et al. 2009; Meharg and Raab 2010). This makes arsenic in rice a trans-boundary concern of global consequence. The European Food Safety Authority (EFSA 2009) has recently evaluated dietary sources of arsenic to the European populace, and concluded that grain staples contributed ~60% of dietary exposure to inorganic arsenic, the species of most concern (EFSA 2009), with rice dominating this grain exposure as rice has typically ~10-fold higher concentration of inorganic arsenic in grain than other crops such as wheat or barley. To put these exposures into context, tap water contributed <5% inorganic arsenic to the European diet. Average rice consumption in the United Kingdom (UK), for example, is only 10 g/day (Meharg 2007), which is not untypical for a Western European diet (Meharg et al. 2009). For specific subgroups in Europe, such as those who follow SE Asian and Indian sub-continent dietary patterns, exposure to inorganic arsenic from rice is much higher. On average a UK Bangladeshi consumes 250 g of rice per day, with the Bangladeshi community in the UK constituting 5% of the population (Meharg 2007). The population of countries such as Bangladesh, Laos and Myanmar typically consume 400–500 g of rice per day (Meharg et al. 2009).

Besides rice subsistence diets, rice is the mainstay of restricted diets such as vegan, macrobiotic and dietary item avoidance regimens, due to the origin of these diets on Eastern cuisine (vegan and macrobiotic) and to its low gluten (wheat intolerance). For breast cancer patients avoiding animal milks (due to their hormone content) and for lactose intolerance patients, rice milk may be consumed to replace animal milks in the diet (Kushi 2004).

1.2 Historical Context

Initial studies regarding arsenic concentration of rice grain were first published for Taiwan (Schoof et al. 1998), the US (Schoof et al. 1999; Tao and Bolger 1998), and Vietnam (Phuong et al. 1999), identifying rice as high in total and inorganic arsenic, stating that it may be an important dietary input. These formative studies had little context in which to place their findings and did not show whether the rice they analysed was anthropogenically contaminated or not. They also could not extrapolate their findings more generically because of the limited number of samples analysed.

The role of plant and soil factors responsible for arsenic accumulation in rice started to be unravelled in the first decade of the twentieth century. Abedin et al. (2002a, b) identified that the irrigation of paddy rice with arsenic elevated water to the levels commonly found in the groundwater in Bangladesh and West Bengal, India, may be of concern, placing their physiological studies into arsenic assimilation by rice into this context. This was shortly followed by the first field surveys of arsenic in rice, identifying that there was indeed extensive arsenic contamination of rice, and paddy soil, in Bangladesh (Duxbury et al. 2003; Meharg and Rahman 2003).

These findings provided impetus to further study, resulting in the first paper to place arsenic in rice in a global context, leading to a realization that EU, US and Bangladeshi rice was elevated above “natural”, and the first to realise that arsenic speciation in rice varied between different rice producing regions (Williams et al. 2005). The findings for Bangladesh were further clarified by a detailed rice grain survey (Williams et al. 2006), while concerns regarding US (Williams et al. 2007a), EU (Williams et al. 2007b) and Chinese (Zhu et al. 2008) rice were also characterized. Note that rice is widely exported, globalizing problems regarding arsenic in rice from specific elevated locations (Meharg et al. 2009; Williams et al. 2005; Zavala and Duxbury 2008). The most detailed global assessment of total and inorganic arsenic concentration of rice grain to date was published by Meharg et al. (2009), enabling potential cancer risks from rice to be calculated on a regional basis. This study shows an elevated risk of bladder and lung cancers from rice, based on the most up to date US Environmental Protection Agency (EPA) modelling of inorganic arsenic cancer risks, and that those risks are highest for countries such as Bangladesh that have very high rice consumption rates and highly contaminated rice from anthropogenic activity.

1.3 Biogeochemistry of Paddy Soils

Arsenic is problematic in rice due to the fact that rice is the only major crop grown anaerobically (i.e. under flooded conditions), and that rice is particularly efficient at assimilating some forms of arsenic, particularly those generated under anaerobic conditions, and exporting them to grain (Williams et al. 2007; Xu et al. 2008).

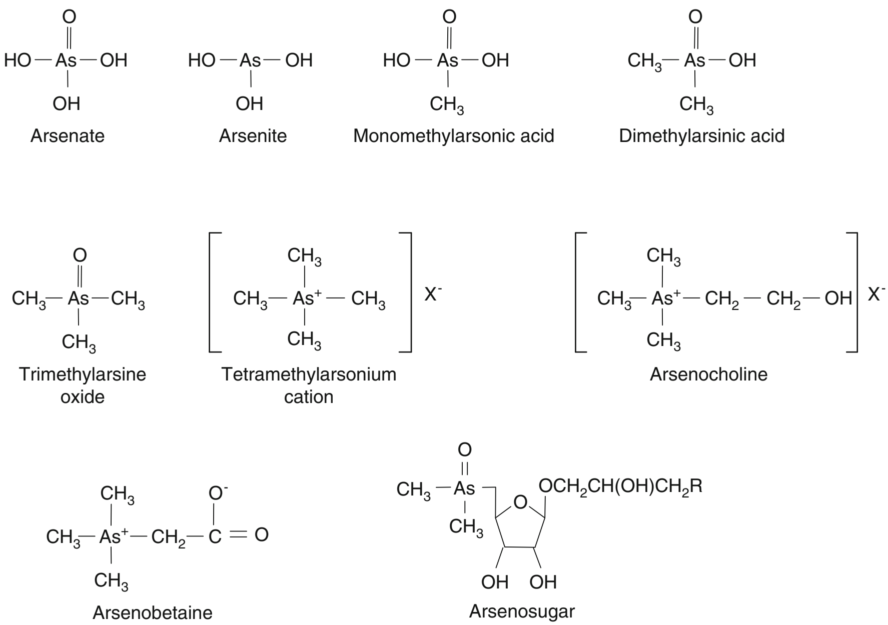

Fig. 1.1 Structural formulae of arsenic species

The element arsenic exists in a multitude of different chemical species in biological tissues, soils, waters and minerals, many of which are biotically and abiotically inter-convertible under a range of conditions observed in terrestrial and marine environments (Cullen and Reimer 1989). A list of the "free", that is not ligand co-ordinated, arsenic species routinely observed are given in Fig. 1.1. These can be considered as inorganic (arsenate and arsenite) or organic (including monomethylarsonic acid [MMA], dimethylarsinic acid [DMA], tetramethylarsonium [TMA], asenobetaine (AB) and arsenosugars). The inorganic species are generally more acutely toxic than organic species (Aposhian et al. 2004), with the exception of trivalent MMA(III) and DMA(III), which are intermediates of the arsenic methylation pathway, and organic species developed for chemical warfare, but these chemical agents are not found naturally, and only exist in nature highly localized around a small number of munition manufacture and testing sites (Arao et al. 2009; Baba et al. 2008).

The inorganic species arsenate [As(V)] and arsenite [As(III)] are redox sensitive, arsenite predominating under reduced and arsenate under oxidized conditions (Zhao et al. 2010). This interchange of species can be driven chemically through changing Eh and pH, as well as the presence of chemical oxidants and reductants, or enzymatically. Arsenate reductases, which are widespread in biota, can reduce arsenate to arsenite. Arsenate can be used as a terminal electron acceptor (Heimann et al. 2007), while arsenite may be oxidized by certain microbes to produce energy (lithotrophy) (Rhine et al. 2006). Arsenite can be methylated aerobically or anaerobically

(Cullen and Reimer 1989). In soils methylated arsenic species can be either partially demethylated or totally mineralized (Gao and Burau 1997; Huang et al. 2007).

With respect to plant uptake and transport, protonated arsenic species (arsenite, MMA and DMA) can behave like silicic acid analogues (Li et al. 2009a, b) and arsenate, and potentially deprotonated DMA, as phosphate analogues (Karim et al. 2009). These species have varying affinities for minerals present in the soil. Under oxidized conditions arsenate has a high affinity for iron oxyhydroxides (FeOOH) and manganese oxides (Chen et al. 2005), which makes it relatively immobile in soils, while arsenite has a lower affinity for these solid phases, making it more mobile. Under strongly reduced conditions arsenic can be precipitated as sulphide minerals such as arsenopyrite (Smedley and Kinniburgh 2002). The humic and fulvic acids that constitute dissolved organic matter in soil pore waters compete with arsenate for anion exchange sites.

Arsenic speciation is highly dynamic over the range of redox potential found in paddy fields, and those redox conditions vary spatially and temporally throughout the growing season (Dittmar et al. 2007; Takahashi et al. 2004). The flooding regimen is an obvious driver for redox, as is the vertical gradient with atmospheric oxygen perfusing down the soil profile. Rice roots aerate their rhizosphere to enable roots to survive in reduced conditions, creating redox gradients from the root surface to the bulk soil, leading to the formation of iron plaque on the root surface and in the rhizosphere (Chen et al. 2005; Liu et al. 2006).

1.4 Plant Physiology

The complexity of arsenic dynamics in soil is mirrored by that in the rice plant. Plant roots assimilate arsenic species through both silicic acid pathways (arsenite, protonated MMA and DMA) (Ma et al. 2008; Li et al. 2009a) and through phosphate transport pathways (Abedin et al. 2002b; Wu et al. 2011). Phosphate is an essential, and usually limiting, macronutrient, while rice is a silicon accumulator, thus rice is efficient at acquiring silicic acid and phosphate from the soil, making it efficient at assimilating arsenic analogues of these moieties. It is this efficiency at silicic acid/arsenite assimilation, combined with the mobilization of arsenite under reduced conditions that sets rice apart with respect to high grain arsenic burdens, as compared to crops grown under aerobic soil conditions (Zhao et al. 2010).

Once within the plant the arsenic species undergo metabolism, complexation, symplastic transport, sub-cellular localization, xylem transport to shoots and grain, with potential remobilization from shoot to grain via phloem during grain fill. Unravelling the molecular regulation of these processes is complicated as the arsenic species also exert toxicological action through inhibition of ATP formation and other phosphorylation processes, oxidative stress and binding to protein sulphylhydryl groups amongst others (Meharg and Hartley-Whitaker 2002). This toxicological action leads to grain yield reduction, further exacerbating agronomic concerns regarding arsenic in paddy rice cultivation (Panaullah et al. 2009).