



Understanding arsenic dynamics in agronomic systems to predict and prevent uptake by crop plants



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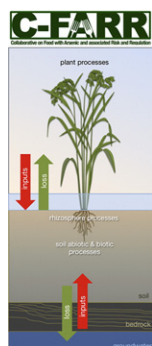
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HIGHLIGHTS

- Consumption of staple foods such as rice, apple juice and vegetables grown in contaminated soil is now recognized as a tangible route of human exposure to arsenic
- Arsenic occurs in food because it is present in the soil and water and is taken up by crop plants.
- Understanding the sources of arsenic to crop plants and influence the dynamics of the agronomic arsenic cycle are key to reducing crop uptake of arsenic now, and preventing exposure in future.
- This review considers natural and anthropogenic sources of arsenic to the soil, biogeochemical cycling, rhizosphere processes, plant processes, and mitigation strategies
- This review recommends: mobilizing existing soil data so that it is readily accessible to commercial and private growers; expanding detailed soil monitoring; reconsideration, unification and enforcement of action levels for agricultural soil arsenic based on updated science, community outreach and education about the potential for arsenic in the soil, as necessary steps to protect valuable soil resources.

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ABSTRACT

This review is on arsenic in agronomic systems, and covers processes that influence the entry of arsenic into the human food supply. The scope is from sources of arsenic (natural and anthropogenic) in soils, biogeochemical

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and rhizosphere processes that control arsenic speciation and availability, through to mechanisms of uptake by crop plants and potential mitigation strategies. This review makes a case for taking steps to prevent or limit crop uptake of arsenic, wherever possible, and to work toward a long-term solution to the presence of arsenic in agronomic systems. The past two decades have seen important advances in our understanding of how biogeochemical and physiological processes influence human exposure to soil arsenic, and this must now prompt an informed reconsideration and unification of regulations to protect the quality of agricultural and residential soils.

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1. Introduction

Consumption of staple foods such as rice, beverages such as apple juice, or vegetables grown in historically arsenic-contaminated soils are now recognized as tangible routes of arsenic exposure. The presence of elevated concentrations of arsenic in the soil is not a pre-requisite for dietary arsenic exposure; seen in the accumulation of arsenic by rice grown in uncontaminated soils (Norton et al., 2012). When drinking-water arsenic concentrations are low, dietary arsenic can be a significant exposure (Carlin et al., 2015). Understanding the sources of arsenic to crop plants and the factors that influence them is key to reducing human exposure now and preventing exposure in future. In addition to the abundant natural sources of arsenic, there are a large number of industrial and agricultural sources of arsenic to the soil; from mining wastes, coal fly ash, glass manufacturing, pesticide application, wastewater sludge, pharmaceutical waste, livestock dips, smelting activities to phosphate fertilizers. Plant uptake of arsenic was previously assumed to be too low to merit setting limits for arsenic in food crops, but given that measurable biological effects occur in at arsenic levels below the current maximum contaminant level (MCL) for drinking water (Bodwell et al., 2004), these low levels can still translate into significant exposures, particularly in children (Davis et al., 2012) and presumably in adults who consume a lot of rice. In response, the World Health Organization (WHO) set an advisory MCL for inorganic arsenic in white (polished) rice of 0.2 mg/kg (WHO, 2016) along with the limit of 10 µg/L in water, and the European Union set similar standards that included a lower MCL (0.1 mg/kg) for rice-containing baby foods (European Union, 2015). Currently, dietary arsenic exposure is suspected to play a role in cardiovascular disease in adults (Moon et al., 2012), and to disrupt the glucocorticoid system (involved in learning and memory) to those exposed in utero (Caldwell et al., 2014). An in depth review of the current findings on the relationship between dietary arsenic exposure and human health is provided by Davis et al. (this issue).

In the United States, regulations on arsenic are distributed to several agencies. The Environmental Protection Agency (EPA) developed the MCL for arsenic in drinking water (10 µg/L) in 2006; a level supported by the World Health Organization, Canada and the European Union. In the state of New Jersey (USA) the limit is 5 µg/L, and in Australia, 7 µg/L. Many other nations still adopt a level of 50 µg/L (Bahrain, Bangladesh, Bolivia, China, Egypt, India, Indonesia, Oman, Philippines, Saudi Arabia, Sri Lanka, Vietnam, Zimbabwe) (Yamamura et al., 2001), with the exception of Mexico (35 µg/L). In the USA, The Food and Drug Administration (FDA) is responsible for setting action levels for arsenic in food, which includes apple and pear juice at 10 µg/L, in line with EPA's drinking water MCL. In Canada, the Canadian Food Inspection Agency issued alerts on excessive arsenic in rice and pear products in 2014. Consistent with the European Commission's limit for arsenic in rice used in food production for infants and young children, the FDA is proposing an action level of 0.1 mg/kg for inorganic arsenic in infant rice cereal (FDA, U., 2016). Foods in Australia and New Zealand may not contain >1 mg/kg dry mass of arsenic, and salt for food use must not contain >0.5 mg/kg. Japan has a limit of 15 mg/kg of arsenic in paddy soils (Japan, 2016). Likewise, Thailand has an agricultural arsenic soil quality standard of 3.9 mg/kg. Within the USA, states differ widely in their action levels for arsenic in soil, for instance New Jersey has a cleanup

criterion of 20 mg/kg and Florida has a cleanup target level of 2.1 mg/kg and 12 mg/kg for industrial sites (Henke, 2009).

Arsenic occurs in food because it is present in soil and water and is taken up by plants. This review article brings together the latest scientific information on arsenic in agronomic systems, describing its sources in soils and the processes that influence the uptake of arsenic by crop plants. The intention of this review is to prompt a reconsideration and unification of government regulations on action levels for arsenic in agricultural soil; raise awareness of how both former and ongoing inputs of arsenic to soil can result in food contamination and impacts to human health and finally, to indicate the way forward for mitigation strategies that safeguard valuable soil resources.

2. Natural sources of arsenic in soil

Below toxic concentrations, the higher the total soil arsenic concentration (the sum of all arsenic species, regardless of bioavailability) the higher the crop uptake of arsenic. This is true of anaerobic cultivation systems such as rice (Adomako et al., 2009; Lu et al., 2009; Williams et al., 2007), aerobic horticultural systems (Norton et al., 2013) as well as conventional (aerobic) agriculture (Williams et al., 2007). The global average total soil arsenic concentration is 5 mg/kg, (equivalent to parts per million), but there is large variation between and within geographical regions (Koljonen et al., 1989). Where soils have formed on arsenic-rich bedrock, or downstream of these bedrocks, very high concentrations of natural arsenic can result. Concentrations of up to 4000 mg/kg arsenic have been measured in soils from the arsenopyrite belt (iron arsenic sulfide, FeAsS) in Styria, Austria (Geiszinger et al., 2002), for instance. There are approximately 568 known minerals that contain arsenic as a critical component (IMA, 2014). Arsenic is present in many rock-forming minerals because it can chemically substitute for phosphorus (V), silicate (IV), aluminum (III), iron (III) and titanium (IV) in mineral structures. Global mapping data of total arsenic concentrations in topsoil is not available, although large-scale regional maps are available for soil arsenic concentrations in Europe (Lado et al., 2008) and the USA (Shacklette and Boerngen, 1984). European data predicts that most soils range <7.5–20 mg/kg arsenic, with a median of 6 mg/kg (Lado et al., 2008). This prediction comes from block regression-kriging; a spatial prediction technique based on regressing soil arsenic concentrations against auxiliary variables, and is useful because it uses a particularly high resolution (block size of 5 km²). On a continental scale, large zones of soils with approximately 30 mg/kg arsenic have been found in southern France, the north-eastern Iberian Peninsula and south-west England, with the two latter being zones of extensive natural mineralization associated with base and precious metal mining activities. The United State Geological Survey (USGS) soil sampling of the contiguous USA reports a mean soil arsenic concentration of approximately 5 mg/kg with 5 and 95 percentile values of approximately 1.3 and 13 mg/kg respectively (Smith et al., 2014). Large regional patterns are apparent in the data, for example the soils of New Hampshire have soil arsenic concentrations of approximately 10 mg/kg arsenic, and Florida, 3.5 mg/kg. The sampling density goal for the USA surface soils and stream sediments database is 1 per 289 km² (USGS, 2016), but is currently at only 1 sample per 1600 km². This contrasts with smaller regional surveys such as the recently published Tellus database for

Northern Ireland that has a sampling density of 2 km² (Young and Donald, 2013) (median total soil arsenic concentration 8.7 mg/kg). At this sampling density, fine-scale data for factors shown to affect soil arsenic, such as bedrock type, altitude and organic matter for instance, can be observed, providing the opportunity to make predictions about arsenic bioavailability and mobility.

Soil or sediment arsenic concentrations are the result of the complex and dynamic interplay between inputs and outputs (Smedley and Kinniburgh, 2002). Natural sources of arsenic to agronomic catchments are dominated by bedrock weathering (mechanical, chemical and biological) and depositional inputs, with the ultimate sinks at the base of catchments often being a significant distance from sources (Saunders et al., 2005). Outputs include leaching into water bodies (vertically and horizontally), soil erosion (Smedley and Kinniburgh, 2002) and biovolatilization (Mestrot et al., 2011). In arid regions surface evaporation of water can lead to arsenic enrichment from the draw up of sub-surface water (Smedley and Kinniburgh, 2002) and from waters used in crop irrigation (Lawgali and Meharg, 2011). Mass-balances (accounting for all inputs and outputs for a particular ecosystem) are rarely conducted for arsenic fluxes within catchment areas, but a good example is from a mining-impacted catchment area (Melegy et al., 2011), where chemical weathering, followed by mechanical weathering dominated arsenic inputs, which were primarily from arsenopyrite. Similarly, in a gold-mining region, weathering contributed an estimated 95% of the arsenic (Drahota et al., 2006). In a forested catchment area, where atmospheric arsenic inputs were the dominant source to highly organic soil (soils with >10% organic matter), inputs of arsenic via precipitation were ~6 g/ha/y (Huang and Matzner, 2007), and organic soils were a net source of arsenic, while mineral soils (<10% organic matter) were a sink. This agrees with depositional inputs of arsenic measured in the UK, which ranged from ~1 to ~10 g arsenic/ha/y (CEH, 2008). UK regional scale maps show that arsenic deposition is highest at altitude and in the west of the country; the least polluted regions with air masses originating in the Atlantic. This suggests a marine source of arsenic. Depositional maps relate well to soil arsenic maps such as in maps of Northern Ireland and England (UKSO, 2016) that show highest arsenic concentrations in peat soils at higher altitude, along with bedrock geological anomalies. Peat soils at higher altitude are sinks for arsenic, and become sources if the peat is mineralized or eroded. The topic of up-land organic soils acting as sinks and sources of arsenic is receiving more research attention (Mikutta and Rothwell, 2016), and could be important on a regional scale as a source of arsenic to downstream sediments.

In large catchment areas of continental importance, such as the deltas that form to the south and east of the Himalayas, plate tectonic-derived mechanical weathering is thought to be the most important source of arsenic. One theory is that the mechanical weathering caused by Pleistocene tectonic uplift in the Himalayas is the key to understanding why arsenic is so elevated in Holocene aquifers, such as those of SE Asia, and in the glacial tills of Europe and North America (Saunders et al., 2005). Mechanical weathering of bedrock exposes previously inaccessible mineral surfaces, and the finer grinding leads to enhanced surface areas for chemical and microbial weathering to take place, causing greater solubilisation of arsenic (Smedley and Kinniburgh, 2002; Saunders et al., 2005; Mailloux et al., 2009). Chemical and microbial weathering can take place at or near the source, or in sediment sinks. For instance, bacteria isolated from Bay of Bengal aquifers can mobilize arsenic from apatite (Mailloux et al., 2009) (see Section 5). Invariably, the arsenic loadings into soil will be dependent on arsenic in the bedrock, and the extent of the weathering of that bedrock-derived material along the route from source to sink. Soils with basalt bedrock had the lowest median arsenic content, while those with psammite, semipelite, and lithic arsenite bedrocks had the highest. Interpretation of such fine-scale mapping can ultimately lead to predictions of soil arsenic concentrations where detailed maps are not available. Combined with an understanding of soil chemistry, this will enhance the ability to predict elevated concentrations of arsenic in crops (Williams et al., 2011).

3. Anthropogenic sources of arsenic to soil

Many anthropogenic activities have increased soil arsenic concentrations above the natural, background levels mentioned in Section 2 above, and they have the potential to increase the arsenic concentration in food. This is especially the case in the USA where the widespread use of arsenic-based herbicides, pesticides and livestock antibiotics throughout the 20th century has ultimately increased the arsenic concentrations of current productive USA agricultural soils (Murphy and Aucott, 1998; Lasky et al., 2004; Nachman et al., 2013).

3.1. Base and precious metal mining

The dominant mineral source of arsenic is thought to be pyrite (iron sulfide, FeS₂) (Fendorf and Kocar, 2009), an economically important ore deposit. High arsenic concentrations are found in many oxide minerals and hydrous metal oxides, either part of their structure or as sorbed and occluded species (Bowell et al., 2014a). Iron oxides accumulate arsenic up to concentrations of several weight percent (1 wt% being equivalent to 10,000 mg/kg), and arsenic tends to bind to iron (III) (hydr)oxides whenever they are present. Arsenic is found predominantly as arsenopyrite but also can occur as orpiment (arsenic trisulphide As₂S₃), realgar (α-As₄S₄) and other arsenic sulfide minerals (Craw and Bowell, 2014; Bowell et al., 2014b). Arsenic is a byproduct of most mining operations and is present at high concentrations in the mine waste, and, because arsenic sulfides are particularly prone to oxidation in surface environments, in mining wastewaters (Craw and Bowell, 2014; Bowell et al., 2014c). Arsenic can constitute 1% or more of the ore and solid waste, and wastewaters and impacted streams often contain dissolved arsenic concentrations ranging from 0.01 to over 10 mg/L. Because mining and smelting operations are localized, arsenic contamination of soils exists around the mine site with the concentration decreasing with distance from the source. Windblown dispersion of fine particulate material is a particular problem, spreading contamination greater distances from the mine site. This fine material - which is not completely removed by washing (Norton et al., 2013) - can directly contaminate plant material; especially leafy material with high surface area. This presents a tangible risk to residents and home gardeners in the vicinity of areas with significant surface soil arsenic contamination. A comparison of arsenic concentrations in vegetables grown in SW England (the site of historic mining activities) with those from a pristine site in NW Scotland found a generally good correlation between total plant arsenic and soil arsenic concentrations. Increased arsenic concentrations were measured in produce from SW England where soil arsenic concentrations ranged from 120 to 1130 mg/kg. Arsenic concentrations were high in leafy greens (kale, spinach, lettuce) and some unpeeled vegetables (potatoes, swedes, carrots) were higher than when peeled, which, in both cases, points to contamination from windblown soil particles and soil adhesion to below ground biomass, rather than from root uptake. In this particular study, the majority of arsenic was present as the inorganic form (Norton et al., 2013). Similar results were obtained from home gardens near the Iron King Mine Superfund Site in Arizona, USA (Ramirez-Andreotta et al., 2013a; Ramirez-Andreotta et al., 2013b). Here the tailings had arsenic concentrations of 3710 mg/kg and residential soil sampled adjacent to the site ranged from 120 to 633 mg/kg. Edible plant tissue concentrations ranged from <0.01 to 1.96 mg/kg (plant concentrations are expressed as dry weight throughout), and were generally positively correlated with soil arsenic concentrations. Leafy and high surface area vegetables such as lettuce, kale, broccoli and cabbage accumulated higher arsenic concentrations than beans, tomatoes, cucumbers and peppers. Arsenic in mine-affected vineyard soils in Italy ranged from 4 to 283 mg/kg and positive correlations were observed between soil concentrations and arsenic levels in vine leaves and grapes, however, levels in wine were low (<1.62 µg/L) (Bertoldi et al., 2013). In the Hunan province, China, the high levels of inorganic arsenic in rice have been traced

to mining activities in the area (Ma et al., 2016; Williams et al., 2009; Zhu et al., 2008).

3.2. Coal combustion for energy

The concentration of arsenic in USA coal ranges from 1 to 71 mg/kg with an average concentration of 24 mg/kg (Kolker et al., 2006). Fly ash, the major byproduct of the coal combustion process, consists of fine particles that are driven out with the flue gases, and is a major source of arsenic to the wider environment. Coal ash is one of the most abundant of industrial wastes; close to 130 million tons (EPA, 2016) of coal fly was generated in the USA in 2014, with 100 million tons estimated from the European Union in 2011 (Feuerborn, 2011). Arsenic concentrates in the fly ash during combustion of coal for energy; the median arsenic concentration in USA fly ash is 71 mg/kg (Yager et al., 2015). Fly ash is often sluiced into settling basins, and because arsenic in fresh ash is quite soluble, wastewater arsenic concentrations can consequently be quite high. Arsenic can build up in the sediments of coal fly ash settling basins and reach concentrations of over 1000 mg/kg. Catastrophic failures of these settling basins have caused severe environmental problems and contaminated surface waters with arsenic (Schmidt, 2010). There is a well-founded concern that arsenic from coal combustion wastes can contaminate soil and enter the food supply. The use of coal fly ash as a soil amendment can lead to elevated arsenic concentrations in crops (as well as boron, selenium and molybdenum), although its lack of soil macronutrients and the potential for arsenic toxicity prevents the sole application of coal fly ash as a soil amendment (Schumann and Sumner, 1999; Jackson et al., 1999). Formulating ash/organic waste mixtures that conform to USEPA regulations for total arsenic application and meet soil and plant fertility requirements has been shown to safe and effective for agronomic use (Schumann and Sumner, 2004).

3.3. Pesticides

Perhaps the largest anthropogenic input of arsenic to agricultural soils in the USA is from the agricultural use of arsenic-based pesticides and herbicides for most of the 20th century. Calcium arsenate and lead arsenate were used extensively up to the 1950s, mostly on orchard soils to combat the codling moth. At peak, 132,000 metric tons of each pesticide compound was applied annually between 1930 and 1940 (Murphy and Aucott, 1998). In addition to apples, inorganic arsenic pesticides were used on a range of crops including essentially all fruit trees, vine berries, sweet potatoes, white potatoes, most vegetables and cotton (Murphy and Aucott, 1998). Both lead and arsenate have long residence times in soils and high concentrations (often >100 mg/kg) of these two elements have been reported in old orchard soils in Washington (Yokel and Delistraty, 2003), North Carolina (Embrick et al., 2005), New Hampshire (Renshaw et al., 2006), New Jersey (Peryea and Creger, 1994) and Virginia (Robinson et al., 2007). There is some evidence of greater mobility for arsenic (than lead) (Renshaw et al., 2006; Peryea and Kammereck, 1997), and retention of both elements depends on soil type and other environmental factors but most of this legacy contaminant remains in the soil (Peryea and Creger, 1994). Use of lead arsenate decreased after 1950s and was finally banned in 1988. The organic arsenic compounds dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) were used as pesticides on cotton and herbicides for golf courses and right-of-ways until they too were withdrawn from use in 2013. High levels of MMA were reported in transient surface waters adjacent to a crop sprayer operation (Bednar et al., 2002). Legacy soil arsenic contamination resulting from organic arsenical pesticides plays a major role in straighthead disease of rice (Rahman et al., 2008) (see Section 6.1). It may be that arsenical pesticides have leached to groundwater, as has been suggested for the Texas High Plains Aquifer (Hudak, 2000), although a study of the Ogallala aquifer in the High Plains in Texas found no evidence of anthropogenic arsenic in

the groundwater (Reedy et al., 2007). Similarly, there was no relationship between groundwater arsenic and past (inorganic) arsenic pesticide usage in a comprehensive study of New Hampshire groundwater sources (Ayotte et al., 2006). About 10%, depending on soil substrate, of monosodium methyl arsenate applied to sandy soils (simulated golf course greens) leached into percolating water. Demethylation and methylation occurred because both inorganic arsenic species and DMA were also detected in the percolating water (Feng et al., 2005). As with mining-impacted soils, plants grown on soils that are high in arsenic from arsenical pesticide contamination take up higher levels of arsenic into their edible tissues, observed for example in potatoes (Codling et al., 2016), carrots (Codling et al., 2015) and leafy green vegetables (McBride et al., 2015; Lim and McBride, 2015).

Former pesticide application has been suggested be a factor in the presence of higher levels of total arsenic found in rice grown in the south-central regions of the USA (Zavala and Duxbury, 2008; Zavala et al., 2008) compared to other areas of the USA and to other countries, such as Bangladesh (Williams et al., 2005a). Evidence on varietal differences in arsenic uptake, speciation and distribution within rice grain (see also Section 6) strongly suggest that soil arsenic concentration is not the sole, nor particularly the main driver of this phenomenon. Factors likely to be influential may also include the differences in the soil microbial community composition between geographical regions that affect arsenic methylation, considering that plants themselves cannot methylate arsenic (Lomax et al., 2012).

3.4. Wood preservatives

Chromated copper arsenate (CCA) is used as a wood preservative and was extensively used on decking and other residential usages until a voluntary manufacturer withdrawal in 2003. The primary health concern is for young children in direct contact with CCA-treated wood, but localized leaching of arsenic (as well as chromium and copper) also occurs to surrounding soil. Soil arsenic concentrations of 37–250 mg/kg have been reported for soils sampled near CCA-treated utility poles (N = 12) (Pouschat and Zagury, 2006) and mean arsenic concentrations for soils collected below decks and footbridges in Florida, USA was reported to be 28.5 mg/kg compared with a control concentration of 1.3 mg/kg (N = 65) (Townsend et al., 2003). Arsenic from CCA contaminated soils appears to be more bioavailable than from other anthropogenic sources to soil (Juhász et al., 2011).

3.5. Organic manures

Land application of sewage sludge (biosolids) in the USA is regulated by Environmental Protection Agency Part 503 Biosolids rule; which set the maximum arsenic concentration of the sludge at 75 mg/kg, an annual pollutant-loading rate of 2.0 kg arsenic/ha (kg/ha) and a cumulative pollution-loading rate of 41 kg/ha over the lifetime of applications. Assuming a plow layer of 17 cm, application at the maximum annual rate implies an approximate 1.2 mg/kg maximum increase in soil arsenic, while the cumulative maximum loading rate could increase soil arsenic concentrations by approximately 24 mg/kg over the lifetime of application and assuming no loss from the soil profile. This cumulative loading rate of 24 mg/kg is significant when considered against an average soil arsenic concentration of 5 mg/kg (see Section 2), however, relative to mine-impacted or inorganic arsenic pesticide impacted soils where arsenic concentrations are frequently >100 mg/kg, it is of lesser concern. Also, sewage sludge is often high in aluminum and iron oxide phases, used in the flocculation process, which are efficient scavengers of inorganic arsenic thus lowering the arsenic bioavailability (Carbonell-Barrachina et al., 2000).

Arsenic occurs in animal wastes primarily because of the former use of arsenic antibiotics in poultry and turkey feed; until 2015 four drugs, roxarsone, p-arsanilic acid, carbarsone and nitroson, were regulated for use, with roxarsone being the most prevalent. As of 2016 all four of

these compounds have all been withdrawn from use (USFDA, n.d.). All four are organic arsenic compounds with an arsenate functional group attached to a benzene ring, and differ by other substituents on the ring. The compounds are not readily adsorbed or metabolized and so occur at concentrations up to 40 mg/kg in animal manures. This provides three points of entry to the human food chain; directly through arsenic in chicken and turkey meat (Lasky et al., 2004; Nachman et al., 2013; Taylor, 2004), from plant uptake after land application of manure, and runoff to surface water or groundwater. A number of studies have shown that these organic arsenic compounds can be degraded by both photolytic (Bednar et al., 2003) and microbial (Stolz et al., 2007) processes and that this degradation happens both during composting of stockpiled litter (Garbarino et al., 2003; Jackson et al., 2003) and after land application (Jackson et al., 2006; Rutherford et al., 2003). Long term application of poultry litter to Upper Coastal Plain soils increased soil arsenic concentrations from 2.7 to 8.4 mg/kg after 25 years of application (Han et al., 2004). Similar increases have been reported for other southern states of the USA (Fisher et al., 2015). There is evidence to suggest that other soluble constituents of the litter, for example phosphate and dissolved organic carbon compounds, facilitate arsenic solubility and leaching (Jackson et al., 2006; Fisher et al., 2015; Shah et al., 2009).

3.6. Seaweed fertilizers

Seaweeds can contain far higher concentrations of arsenic than crop plants: up to 100 mg/kg (Taylor et al., this issue). In most cases the arsenic is present as arsenosugars, which are of low toxicity to humans (Taylor et al., this issue). However, as in the case of poultry litter, these compounds degrade (ultimately) to inorganic arsenic after land application (Castlehouse et al., 2003). Although seaweeds are a 'niche' soil amendment, their use agriculture is increasing and has been adopted by many organic farms as a soil fertilizer as well as a feed additive in organic dairy farming (Antaya et al., 2015).

4. Biogeochemical cycling within terrestrial agronomic ecosystems

Arsenic cycles within the soil surface and near-surface environment (Bowell, 1994), influenced by mineralogy, abiotic factors such as pH and redox potential (E_H), and biotic factors such as microbially-mediated biomethylation.

4.1. Redox regulation

The most important biogeochemical step in the exposure of humans to arsenic is its release from soils and sediments into pore water; the water contained within soil pores and/or rock (Fendorf and Kocar, 2009). With the exception of extreme pH conditions (<4 or >9), or high concentrations of competing ions (e.g. phosphate, silicic acid or silicate (Luxton et al., 2006)) the release of arsenic from its strong bonds with soil particles depends upon redox potential (E_H); the extent of aeration of the soil (Fendorf and Kocar, 2009). As E_H falls, electron acceptors are depleted and anoxic conditions develop, causing iron oxides and oxyhydroxides to be reduced and dissolve, releasing sorbed arsenic into the soil solution (Meharg and Zhao, 2012) where it can be taken up by plant roots, or leached into groundwater.

Agronomic cropping systems can be divided with respect to arsenic mobilization on the basis of their redox status. Dominant biogeochemical processes influencing aerobic systems, specifically cereals, upland rice, fruit tree orchards, and community gardens, differ from those that dominate in anaerobic systems, predominantly in flooded rice paddies. In aerobic soils, arsenic speciation is predominantly arsenate (arsenic (V)), and is tightly bound to soil particles. Under anaerobic or flooded conditions, arsenic is reduced, and arsenite (arsenic (III)) is the dominant species (Fendorf and Kocar, 2009). Arsenite is less stably bound to aluminum hydroxides and aluminosilicate clay minerals in

the soil than arsenate, for which they exhibit a much stronger binding preference (Fendorf and Kocar, 2009). With few exceptions (such as under conditions of sulfur release), transition of arsenic speciation from arsenate to arsenite is the most influential factor to arsenic bio-availability; and it is under anaerobic conditions where arsenic becomes an imminent human health concern. Influential biogeochemical processes in aerobic systems are ageing and accumulation of arsenic in soil, and in anaerobic systems reductive dissolution of iron-bearing minerals is the dominant process.

4.2. Biotransformation to methylated and volatile species

Volatile arsenicals are arsenic species with a boiling point below 150 °C; the most volatile of which is arsine gas (AsH_3), followed by monomethylarsine ($MeAsH_2$), dimethylarsine (Me_2AsH_2) and finally completely methylated trimethylarsine (TMA).

Volatile arsenic species can be formed either biotically – by fungi, bacteria and algae (Mestrot et al., 2011; Wang et al., 2014; Turpeinen et al., 2002) or abiotically (Wang et al., 2014). In natural systems arsines readily react with oxygen to form non-volatile oxidation products, with AsH_3 most rapidly oxidized and challenging to detect in environmental samples. Oxidation of the arsine gases to inorganic arsenic species completes the arsenic cycle, with arsenic returned to the soil by rain or dry deposition (Pongratz, 1998).

Arsenic methylation in soils increases with decreasing redox potential (Frohne et al., 2011), and addition of organic matter. Increased arsenic volatilization was measured in soil after the addition of rice straw (Jia et al., 2013a), and animal waste products (Mestrot et al., 2013). Inoculation of fungi (*Penicillium* and *Ulocladium* spp.) increased arsenic volatilization up to 8 fold in heavily contaminated and spiked soils (Edvantoro et al., 2004). Microbially mediated arsenic volatilization remains very inefficient, which hinders attempts to use it in soil remediation. Gaseous arsines are volatilized from arsenic contaminated soils into the atmosphere at very low rates: a microcosm study found 0.5–70 μg of arsenic kg^{-1} soil $year^{-1}$ was volatilized from a range of soils and a range of arsenic levels (Mestrot et al., 2011), and field measurements of arsenic volatilization are 1–2 orders of magnitude lower than those made in laboratory mesocosms (Meharg and Zhao, 2012). Genetic transformation of bacteria, using genes encoding for the protein product arsenite S-adenosyl methyltransferase (*arsM*) is an attempt to enhance arsenic methylation and volatilization. The *arsM* from *Rhodopseudomonas palustris* was expressed in *Sphingomonas desiccabilis* and *Bacillus idriensis* grown in an aqueous system, resulting in a 10-fold increase in arsenic volatilization compared to the wild type strains. In a soil-based system, 2.2–4.5% of arsenic was removed via microbially-mediated volatilization over an incubation period of 30 days (Liu et al., 2011) (see also Section 5.1).

4.3. Changes in soil arsenic bioavailability due to ageing

Although arsenic in aerobic soils has a lower bioavailability and presents less of an immediate concern for crop uptake, aerobic soil can accumulate arsenic from human inputs, retain them for long periods of time, and release them when redox conditions change (see Section 3.3). Human inputs of arsenic, as discussed in Section 3, are diverse; biosolids, sewage sludge, coal fly ash, poultry litter, industrial waste, arsenical pesticides and from irrigation with naturally arsenic-enriched groundwater. For aerobic soils, ageing – where binding stability of arsenic to soil particles increases over time, is a particularly important part of arsenic cycling. Factors controlling ageing of arsenic include soil type, organic matter content and arsenic species. Both inorganic and organic arsenic species are subject to ageing, with studies indicating a slow oxidation process from arsenite to arsenate over time (Yang et al., 2005).

5. Rhizosphere processes

Processes occurring in the rhizosphere (the boundary layer of soil under the influence of plant roots) dramatically influence arsenic concentrations and bioavailability because they involve local alterations in redox potential, pH and organic matter content. Rhizosphere acidification occurs during iron uptake by all plant species during cation uptake and charge balance, when protons are released into the rhizosphere. Plants release anywhere from 10 to 250 mg of carbon per gram of root tissue into the rhizosphere; about 10–40% of their total photosynthetically fixed carbon (Newman, 1985), making the rhizosphere particularly rich in organic carbon compared to bulk soil, which in turn exerts an influence on arsenic solubility by stimulating microbially-mediated reductive dissolution of soil minerals. Large differences have been found in the arsenic concentration of rhizosphere soils compared with bulk soils in highly arsenic-contaminated areas, with higher concentrations of arsenic in rhizosphere soils compared to bulk soils (Acosta et al., 2015).

In anaerobic soils, the iron plaque that develops on the submerged stem and roots of rice plants dominates rhizosphere dynamics of arsenic. In flooded environments such as paddy fields, plants oxygenate the rhizosphere through specialized tissues called aerenchyma, which are found in many aquatic plants and emergent macrophytes such as rice. This radial oxygen loss creates an oxidized layer around plant tissue that stimulates aerobic microbial activity and the oxidation of iron, which precipitates and forms a visible iron plaque on the root surface (Wu et al., 2016; Seyfferth, 2015; Yamaguchi et al., 2014; Lee et al., 2013; Hossain et al., 2009). Formation of an iron (oxyhydr)oxide plaque on root surfaces can alter the uptake of arsenic by rice, acting as a sorbent for excess nutrients such as ferrous iron (reduced iron) as well as arsenic and aluminum (Wu et al., 2012). Rates of oxygen loss influence iron plaque formation (Wu et al., 2012), and vary between rice cultivars (Li et al., 2015; Mei et al., 2012). Studies conducted over the last forty years are inconsistent on whether iron plaque prevents or enhances arsenic uptake by plants (Seyfferth, 2015), and the hypothesis that arsenic influences the quality and amount of the iron plaque (Lee et al., 2013). Profound differences in mineral composition and quantity of laboratory-created iron plaques has been demonstrated experimentally (Seyfferth, 2015), which may have contributed to these inconsistencies.

5.1. Microbial activity

Microbes directly and indirectly influence arsenic speciation in rhizosphere soil, and are widely considered to play a key role in arsenic biogeochemistry (Gadd, 2010). Under certain nutrient-limited conditions, microbes actively weather minerals to access nutrients for cellular growth, which releases arsenic (Mailloux et al., 2009), as well as creating abiotic conditions that induce changes in arsenic speciation via production of organic acids, polysaccharides and ligands. Soil microorganisms can strongly affect soil redox, regulating arsenic release into pore water (Wang et al., 2016a). A number of strains of bacteria have also been shown to contribute to the formation of arsenic minerals by using arsenic as a terminal electron acceptor, such as *Desulfosporosinus auripigmentum* (Newman et al., 1997), *Desulfovibrio* strain Ben-RB (Macy et al., 2000), *Shewanella oneidensis* (Wang et al., 2016b) and *S. putrefaciens* CN32 (Smeaton et al., 2012). These microorganisms also differ in their capabilities for liberating arsenic from specific arsenate-bearing minerals (Wang et al., 2016a).

Microbial transformation can mobilize arsenic by converting inorganic to organic forms, including MMA and DMA (Jia et al., 2013b; Xu et al., 2016). Plants translocate organic arsenicals from roots to the (frequently edible) above-ground parts more efficiently than inorganic arsenic (Carey et al., 2011a; Carey et al., 2011b; Carey et al., 2010) (see Section 6), therefore microbial transformation to organic arsenicals can increase human dietary exposure.

Plants, green algae and microbes can all enzymatically transform arsenic species (Jia et al., 2013b; Baker et al., 1983), but methylated forms of arsenic detected in plants are a product of rhizosphere bacteria; plants cannot methylate arsenic (Lomax et al., 2012; Jia et al., 2013b; Hansen et al., 2011; Arao et al., 2011). The genomes of >85 arsenic-metabolizing archaea and bacteria have been sequenced for genes involved in arsenic metabolism (Andres and Bertin, 2016). In bacteria, archaea and fungi, arsenic methylation is catalyzed by homologs of *arsM*, (see Section 4) (Jia et al., 2013b). Resistance to arsenite and arsenate exists in nearly all microbes, which also confers the ability to transform arsenate into volatile arsine gases (Zhang et al., 2011), a particularly effective way of removing arsenic.

Profiling the transcriptome, proteome and metabolome of arsenic contaminated soils offers way of understanding microbially-mediated rhizosphere arsenic processes (Andres and Bertin, 2016). This approach measures the presence and expression of specific genes, rather than attempting to isolate and study the microbes that carry them, 98% of which – it is estimated – do not grow in culture (Stewart, 2012). Microbially mediated arsenic metabolic processes that play a major role in arsenic cycling in agronomic systems include arsenite oxidation (via the *aii* genes), arsenate respiration (via the *arr* genes), arsenate reduction (via the *ars* genes) and arsenite methylation (via the *arsM* genes) (Xiao et al., 2016). Interested readers are referred to the recent excellent work of Andres and Bertin (Andres and Bertin, 2016) for a comprehensive review of this subject. Microbially mediated redox processes strongly influence arsenic uptake in rice, involving *aioA*, *arsC* and *arrA* (Jia et al., 2013b), with pH emerging as an important factor in the distribution of microbes in paddy soils. Testing a variety of soils has shown that bacteria possessing the *arsM* gene for methylating arsenic are widespread and phylogenetically diverse, and even in paddy soils with low concentrations of arsenic, genes for arsenic metabolism are abundant (Jia et al., 2013b).

6. Arsenic and crop plants

Much of our understanding about the physiological mechanisms of arsenic uptake in plants comes from the study of a limited number of species. Called *model plant* species, they are extensively studied, well described, easy to grow, and the results can be compared between studies. The understanding is that the information gained from studying model plants is applicable to other plant species. From a genetic perspective, orthologous genes exist in different plant species that have evolved from a common ancestral gene, and they usually retain the same function. Characterization of arsenic-related genes in a model plant strongly suggests that they exist and perform similar functions in other species. Caveats to this are their levels of expression, which makes some plants more adept at accumulating arsenic than others. In this section, much of the knowledge gained on arsenic uptake and metabolism of plants comes from the study of mouse-eared pennycress (also called thale cress or rockcress) (*Arabidopsis thaliana* Heynh.) and rice (*Oryza sativa* L.); model plants with fully sequenced genomes. These species represent dicotyledonous (e.g. flowers, vegetables, deciduous trees) and monocotyledonous plant species (e.g. grasses, palm trees) respectively, thereby representing much of the edible crop species. An exception to this is the study of the arsenic hyperaccumulating fern (Chinese Brake fern, *Pteris vittata*), a seedless plant that is able to accumulate up to 22,630 mg/kg (dry weight) arsenic in its fronds (Ma et al., 2001).

6.1. Phytotoxicity of arsenicals

Arsenic is toxic to plants (Sharma, 2012). Despite lower acute human toxicity of the organic arsenicals (median lethal dose is 700–1600 mg/kg and 700–2600 mg/kg for MMA and DMA respectively compared to 10–20 mg/kg for inorganic forms) (Le et al., 2000) no one form of arsenic is consistently more toxic to plants (Finnegan and Chen,

2012a). Soybean yields are affected when tissue arsenic levels exceed 1 mg/kg, and 4 mg/kg limits cotton yields (Deuel and Swoboda, 1972), whereas in barley tissue concentrations of 20 mg/kg inhibited growth (Davis et al., 1978). Higher yield-limiting arsenic levels have been recorded in rice: 20–100 mg/kg in above ground biomass, and 1000 mg/kg in root tissue (Adriano, 2001). By contrast, potatoes (*Solanum tuberosum* L.) suffered no growth inhibition in soils containing 290 mg/kg arsenic (Codling et al., 2016). In some plants species, organic forms are more toxic than inorganic, for example in rice (order of toxicity: MMA > arsenite > arsenate = DMA) (Marin et al., 1992a), and in smooth cordgrass (*Spartina alterniflora* Loisel) (DMA = MMA > arsenite > arsenate) (Carbonell-Barrachina et al., 1998).

Plants vary in their tolerance to arsenic, and the stress response differs for each arsenic species (Choudhury et al., 2011; Shri et al., 2009; Chakrabarty et al., 2009). The chemical similarities between arsenate and phosphate means that arsenic can replace phosphate in biomolecules like ATP (adenosine triphosphate, a molecule used for intercellular energy transfer), with negative impacts on growth and metabolism (Ullrich-Eberius et al., 1989). In rice in particular, DMA and MMA induce straighthead disease (arsenic-associated straighthead disease), significantly lowering yield of certain rice varieties (Rahman et al., 2008). Straighthead is a physiological disorder of rice characterized by sterile florets, which remain upright at maturity instead of bending over under the weight of the filled grain. The exact cause of straighthead is unknown, but consistent flooding, low soil pH, high iron availability and high organic matter content have all been implicated in naturally-occurring straighthead disease (Rahman et al., 2008). Arsenic's suspected role in straighthead comes from observations of more frequent outbreaks in rice grown in soil where arsenical herbicides such as monosodium methanearsonate (MSMA) – used in cotton production in the USA – have been historically applied.

6.2. Arsenic uptake mechanisms

In magnitude, plants take up arsenicals from the soil in the order arsenite > arsenate > DMA > MMA (Raab et al., 2007; Finnegan and Chen, 2012b), with the various arsenic species entering via different root membrane transport proteins in the root plasma membrane that allow ions and molecules to cross with varying levels of selectivity, or target specificity. Similarities in chemical structure between arsenate and phosphate, and between arsenite and silicic acid, govern their entry into root cells. Arsenate enters root cells through phosphate transporters (the Phosphate Transporter 1 family of proteins; PHT1) in both the model plant *Arabidopsis thaliana* (Shin et al., 2004; Remy et al., 2012) and in rice (Jia et al., 2011; Ye et al., 2015; Sun et al., 2012) (Fig. 1). In rice, Low Silicon 1 (OsLsi1) and OsLsi2 are silicic acid transporters and arsenite, MMA^V, and DMA^V are among their unintended targets (Li et al., 2009a; Ma et al., 2008). These Nodulin 26-like Intrinsic Proteins (NIPs) (Abedin et al., 2002), which are members of the aquaporin water channel superfamily of proteins (Pommerrenig et al., 2015) embedded in the exodermal cell membranes of rice roots, move arsenic from the soil into the vascular system for distribution to the stem and leaves. OsLsi2 works in tandem with OsLsi1 to transport arsenite inward toward the xylem (Mitani et al., 2009; Ma et al., 2007a) (vascular tissue that conducts water and dissolved nutrients up from the roots). The arsenic uptake specificity of OsLsi1 is arsenite >> MMA > DMA (Abedin et al., 2002). These bidirectional NIP transport proteins also efflux arsenite back in to the soil, but since OsLsi1 effluxes only 15–20% of the arsenite in roots cells (Zhao et al., 2010), there may be other unidentified arsenite efflux transporters contributing to this process.

6.3. Arsenic transport and metabolism in plants

Transport of arsenite into the xylem for delivery to the shoot is less well characterized than its uptake from the soil. Arsenic is transported to the grain mainly via the phloem (Carey et al., 2011a; Carey et al.,

2011b; Carey et al., 2010) (vascular tissue that conducts sugars and metabolic products from the leaves), by transporters in the nodes (Song et al., 2014a), but their characterization is still in the early stages. Transporters for myo-inositol (Inositol Transporter 2 and 4); an important sugar for developing rice grains, also transport arsenite into the phloem companion cells (Schneider et al., 2006; Schneider et al., 2007). In *Arabidopsis*, INT2 or AtINT4 load about 45–64% arsenite into the grain (Duan et al., 2015). The identity of transporters that move arsenite out of the phloem and into the grain are also unknown, but manipulating the target specificity of the INT genes might show promise in molecular genetic or plant breeding mitigation efforts as a way to prevent arsenite from reaching the grain.

Despite having a lower affinity for transporters into the plant than the inorganic forms, organic arsenic species are more efficiently transported toward the shoot than inorganic forms (Raab et al., 2007; Finnegan and Chen, 2012b) because they are not complexed by phytochelatin (PCs); sulphhydryl-rich glutathione (GSH) polymers (Zenk, 1996; Schmoger et al., 2000). Likewise, in broad beans (*Vicia faba* L.) grown in a soil containing 90% inorganic arsenic, DMA and MMA were the dominant arsenic forms in the bean (68%) (Sadegh et al., 2016). In root vegetables, carrot (*Daucus carota* L.) and beet (*Beta vulgaris* L.) grown on arsenic-contaminated soils, arsenic forms were predominantly inorganic, but for beets in particular were not readily identified using the typical standards (arsenate, arsenite, MMA and DMA) (Pizarro et al., 2016).

The arsenic species composition of rice grain is influenced by the arsenic transport rate of the particular cultivar (Seyfferth et al., 2011; Williams et al., 2005b). Rice cultivars currently grown in the USA have an arsenic speciation split approximately equally between inorganic arsenic and DMA, while cultivars grown in Bangladesh contain mostly inorganic arsenic (Williams et al., 2005b). While lower inorganic arsenic in rice grain seems favorable for avoiding human health effects, the assumed safety of DMA is contentious (Hughes, 2002), being based on acute toxicity data, and not on genotoxicity or carcinogenicity, which are equally relevant in long term safety considerations.

Arsenic detoxification inside cells uses a multi-step process beginning with reduction of arsenate to arsenite using an arsenate reductase enzyme (Sanchez-Bermejo et al., 2014; Chao et al., 2014). In *Arabidopsis*, the protein High Arsenic Content1 (HAC1; also called Arsenate Reductase QTL1; ARQ1) reduces arsenate (Chao et al., 2014). Even though arsenite is more toxic than arsenate (Abedin et al., 2002; Styblo et al., 2000; Marin et al., 1992b), it is hypothesized that ancestral organisms to plants were exposed almost exclusively to arsenite before atmospheric oxygen enabled arsenate formation (Rosen, 1999), and this mechanism persisted through natural selection. Arsenite is then complexed by PCs, and transported in to the vacuole (Zenk, 1996) via ATP Binding Cassette (ABC-type) transporters (Song et al., 2014b; Song et al., 2010a). This process depletes glutathione availability, rendering the plant more susceptible to other oxidative stresses, which inhibits photosynthesis, pigment production, and the integrity of cell membranes (Hartley-Whitaker et al., 2001; Lee et al., 2012; Mascher et al., 2002; Stoeva et al., 2003).

7. Limiting arsenic uptake by crops

7.1. Water management

Although the traditional method for cultivating rice involves flooding leveled, tilled fields before or shortly after planting germinated seedlings, flooded soil is not a biological requirement of rice plants. Flooding is used for weed and vermin control, for mobilization of key nutrients such as iron, phosphate and zinc, and importantly, flooding discourages the buildup of root nematodes over multiple years of rice growth. As mentioned earlier, flooded conditions mobilize soil-bound arsenic through reductive dissolution of Fe (oxyhydr)oxides, and the reduction of arsenate to the more mobile arsenite (Dixit and Hering,

2003). Water management strategies that involve periods of oxic soil conditions can decrease arsenic uptake in rice by limiting dissolution of arsenic. Rice grown in non-flooded or aerobic conditions has a lower yield than intermittently or constantly flooded rice (Li et al., 2009b; Grassi et al., 2009; Arao et al., 2009). Intermittent flooding (flooding maintained until full tillering, followed by intermittent irrigation) is a promising management technique to reduce arsenic levels, and can potentially produce higher grain yields than either non-flooded or constantly flooded conditions (Hu et al., 2013a). However, oxic conditions increase cadmium concentrations in the grain when grown in acidic soils (Hu et al., 2013a; Hu et al., 2013b; Honma et al., 2016), and cadmium is also a highly toxic metal. The observed increases in cadmium were also a cultivar-specific trait, but the increase in cadmium uptake between rice grown under aerobic conditions were approximately an order of magnitude greater than their flooded counterparts. Pot experiments suggest that water management strategies implemented during the heading period of rice growth (when the rice panicle has emerged from the stem and is fully visible, just before flowering) can

regulate both arsenic and cadmium concentration in the grain (Arao et al., 2009; Hu et al., 2013b).

7.2. Amendment and fertilization practices

Soil amendment involves incorporating substances into the plow layer that either add missing nutrients, reduce the bioavailability of existing potentially toxic substances (to prevent crop uptake), or both. Soil amendments that have shown potential in reducing arsenic uptake by plants include iron-, and silica-based additives. The use of iron-based amendments increases in the concentration of free iron oxide in the soil, retarding the release of arsenite from the solid phase into soil solution, (mentioned in Section 4.1 and discussed in Section 5), whereas silica fertilization inhibits arsenic uptake by competitive inhibition at the plant root surface while adding an essential nutrient.

Zero valent iron powder (90% iron) and iron oxide (56% iron) incorporation prevented uptake of arsenic in to the grain of rice grown on soil containing 39.5 mg/kg total arsenic by approximately 45%, and

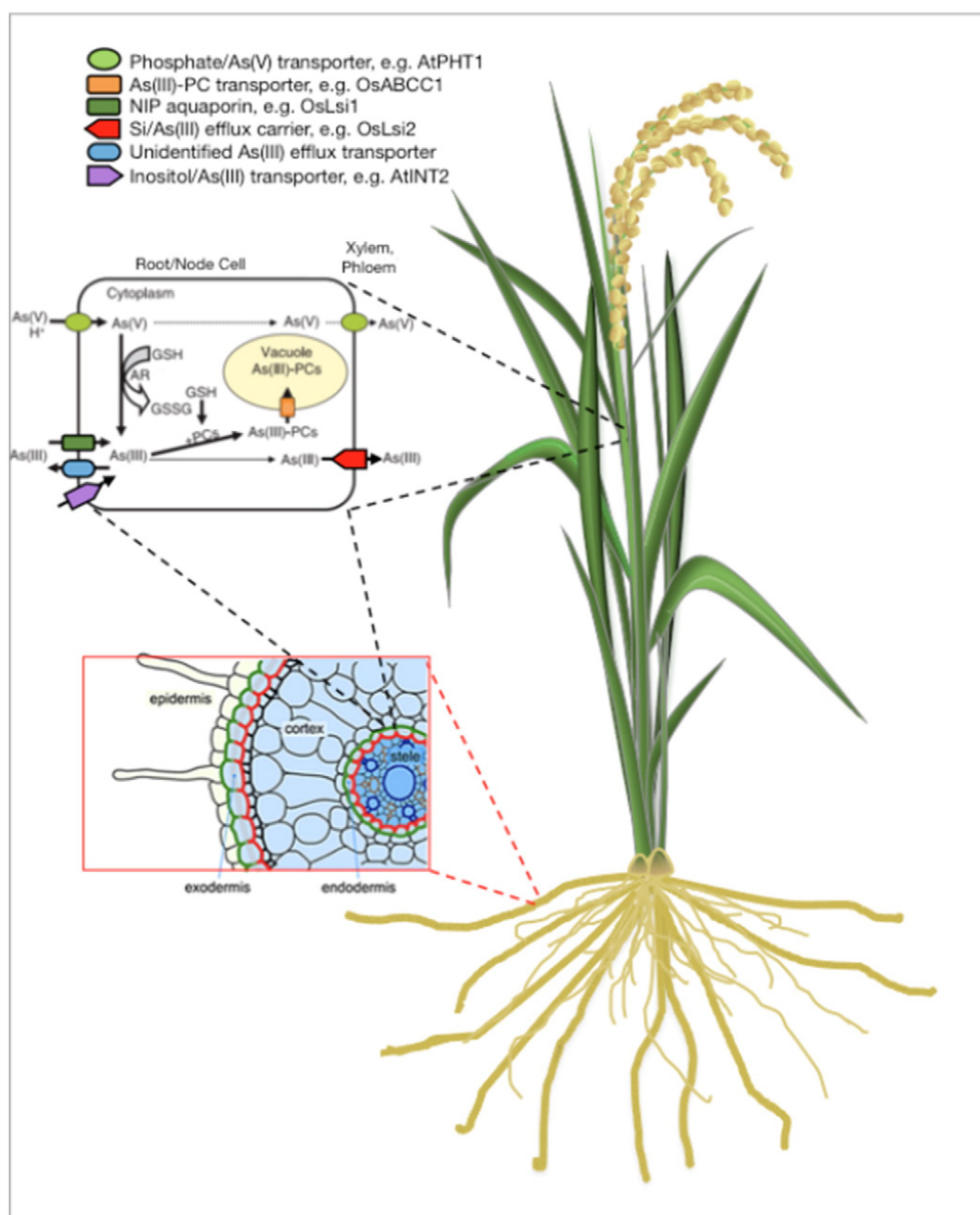


Fig. 1. Generalized diagram of arsenic uptake, transport and metabolism in plants. GSH, glutathione; AR, arsenate reductase; GSSG, oxidized glutathione; PC, phytochelatins. Modified from Zhao et al. (2009) and Ma et al. (2007b).

corresponded with a reduction in bioavailable arsenic in the soil (Matsumoto et al., 2016). Amendment with iron oxides (at a rate of 2%) was also more effective at reducing grain arsenic than phosphate amendment (Farrow et al., 2015). Amendments have also been used in combination with water management strategies to try and reduce both arsenic and cadmium concentrations in rice simultaneously (Honma et al., 2016), without success. Reduction of arsenic in the grain was achieved with iron oxide addition and constant flooding, whereas cadmium reduction was achieved with converter furnace slag addition and rain water management (no irrigation after midseason drainage until harvest).

A combination of ethylenediaminetetraacetic acid ferric sodium salt (iron EDTA) and calcium peroxide was effective for reducing arsenic uptake by vegetable crops (lettuce, Chinese cabbage and radish) from soils containing 14 mg/kg total arsenic (Chou et al., 2016), again by increasing amorphous aluminum and iron oxides. It is likely that this level of arsenic contamination would be deemed too high for commercial vegetable production, so these amendments may only be feasible for use in private vegetable gardens. Questions remain about whether iron oxide amendment application only temporarily reduces arsenic bioavailability (Tiberg et al., 2016). In addition, the suitability for arsenic immobilization is highest at the lower soil pH range, and is strongly affected by soil phosphorus concentration, which strongly competes with arsenic.

Rice plants take up high concentrations of silica, constituting up to 10% of dry matter in the straw and husk of the plant (Penido et al., 2016). As mentioned earlier (Section 6) the silicon membrane transporter (Lsi1) is the main route of arsenite entry in to rice root cells, and provision of silicon causes competitive inhibition of arsenite uptake. Increasing silicon availability in the soil also reduces the expression of the Lsi1 transporter in the plant, which further decreases the potential for arsenic uptake. Fertilization of rice paddy soils with silicon is a potential mitigation strategy for preventing or reducing arsenic uptake by rice through competitive inhibition of arsenite uptake (Meharg and Meharg, 2015). The use of synthetic silicon fertilizers, such as calcium silicate or silica gel is prohibitively expensive for smallholder farmers in developing countries, however reusing the silicon-rich parts of the rice plant that remain after harvesting and grain processing may provide a sustainable solution that also addresses the ongoing issue of silicon depletion of the soil (Penido et al., 2016). Soil incorporation of fresh rice husks, or the ash that remains after burning the husk and straw for energy (which is a common practice for smallholder farmers), can provide silicon without increasing methane production and decreases either total or inorganic arsenic in rice grain (Seyfferth et al., 2016).

Despite the potential of soil amendment with iron oxides or silica to reduce arsenic bioavailability or prevent plant uptake of arsenic, the high cost of these amendments inevitably prevents their use, especially by smallholder farmers. Large rice producers in the US or Europe have not so far adopted widespread use of these soil amendments to reduce rice grain arsenic concentrations. It is also reasonable to assume that use of expensive soil amendments would drive up the cost of rice. Their lack of use may also be attributable to the fact that iron amendments are essentially untested in a diverse range of large-scale agricultural settings and their performance will vary between soil types. In non-rice agricultural systems arsenic is tightly bound to the solid phase; significant crop uptake from oxidized soil is likely to be a result of extreme contamination, in which case effective mitigation is restricted to redirecting land use away from edible crops. In systems subject to periodic flooding, improving drainage remains the best mitigation strategy.

7.3. Mitigation using plant breeding approaches

The development of crops that accumulate high levels of arsenic and yet remain healthy, while preventing arsenic from reaching the edible grain is thought to hold great potential as a strategy for reducing human exposure to dietary arsenic. The use of molecular genetics

techniques such as alterations in gene expression characteristics, gene editing to alter target specificity, or alternately, using traditional plant breeding techniques are both tangible approaches. Both use knowledge of the arsenic uptake and tolerance characteristics of plants to develop varieties with desired characteristics. These characteristics include lower arsenic uptake (Norton et al., 2009), higher arsenite efflux (Duan et al., 2012) and increased vacuolar arsenic sequestration (Song et al., 2010b). For instance, many rice cultivars have now been screened to identify those that accumulate lower levels of arsenic in their grain and efforts are underway to identify the genes underlying this trait (Norton et al., 2009; Norton et al., 2014). Overexpressing Arabidopsis ABC-type transporters that sequester arsenite-PC complexes in the cell vacuole results in plants able to grow in otherwise toxic concentrations of arsenic (Song et al., 2010a). Conversely, knocking out the function of the related rice ABC transporter OsABCC1 results in higher levels of grain arsenic. The OsABCC1 transporter limits arsenic transport to grains by sequestering arsenic in the vacuoles of the phloem companion cells directly connected to the grain. By combining what we have learned from the overexpression studies in Arabidopsis and the loss-of-function study in rice, overexpression of OsABCC1 can be used as a strategy to breed arsenic tolerance and low-arsenic accumulating rice cultivars. Another promising strategy is based on expressing the arsenate efflux transporter from yeast (*Saccharomyces cerevisiae*) in rice, which can reduce arsenic accumulation in brown rice by 20%. A less successful idea to methylate sodium arsenite to DMA by expressing an algal arsM gene in Arabidopsis resulted in lethal phytotoxicity (Tang et al., 2016), suggesting that arsenic methylation in plants can only be an effective detoxification strategy if volatile arsines are the end point of the methylation.

8. Conclusions

The discovery of arsenic in staple foods, beverages and other products has increased awareness and stimulated research on the sources and the processes involved. The information brought together here illustrates the numerous geochemical and biological processes that influence the movement of arsenic into the food supply.

It is clear there must be strategies for preventing arsenic exposure, that operate in both the short term – to protect consumers from existing contamination – and in the long term, to prevent further contamination. This requires government regulation on the permissible levels of arsenic food, with lower levels for infant foods (see Nachman et al., this issue), which must work in tandem with long term goals to address arsenic in agricultural soils, actively prevent further inputs and identify contaminated areas for mitigation. Our recommendations are that the information in this review is used to inform a reconsideration and a unification of regulations on the action levels of agricultural soil arsenic, which in the USA for example, exist only at the state level, vary widely from state to state, and have no formal channels of enforcement. We recommend that educating the community and garnering their support and involvement for lowering exposure to arsenic through food is an approach already shown to hold enormous potential. Direct involvement of the commercial rice growing community in research and development of arsenic mitigation strategies and amendments is needed. Much effort has been given to short-term, greenhouse-scale testing of amendment formulations that will ultimately be too expensive, impractical, or ineffective in the long term. Community-based participatory research should extend to the agricultural community, leading to partnerships that will make longer-term field-scale testing of mitigation strategies accessible. Feasibility should be a primary consideration in arsenic mitigation research. Community outreach efforts targeted to commercial growers or the home gardener specifically must raise awareness of the significance and potential impacts of former land uses, encouraging testing for the presence of arsenic in the soil and educating growers on crops shown to accumulate arsenic in their edible parts. Information gathering on former arsenic input into the soil from pesticides and from proximity to various waste sites is of paramount

importance, and will allow monitoring and mitigation to be targeted to where it is needed most. Currently there is no readily available source of soil arsenic concentration information at a sufficient resolution to inform commercial producers or homeowners: this information needs to be accessible to everyone, everywhere. Going forward, management and remediation of arsenic contaminated soils is essential both for human health and food security, and innovative technologies are urgently needed that will expedite this process. Innovative solutions such as the use of rice husks to add silicon to the soil to offset arsenic uptake, and the use of cultivars with low-arsenic accumulating characteristics point the way forward for sustainable solutions.

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