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LAND POLLUTION (G HETTIARACHCHI, SECTION EDITOR)

Soil Pollution Due to Irrigation with Arsenic-Contaminated Groundwater: Current State of Science

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Abstract Food with elevated arsenic concentrations is becoming widely recognized as a global threat to human health. This review describes the current state of knowledge of soil pollution derived from irrigation with arsenic-contaminated groundwater, highlighting processes controlling arsenic cycling in soils and resulting arsenic impacts on crop and human health. Irrigation practices utilized for both flooded and upland crops have the potential to load arsenic to soils, with a host of environmental and anthropogenic factors ultimately determining the fate of arsenic. Continual use of contaminated groundwater for irrigation may result in soils with concentrations sufficient to create dangerous arsenic concentrations in the edible portions of crops. Recent advances in low-cost water and soil management options show promise for mitigating arsenic impacts of polluted soils. Better understanding of arsenic transfer from soil to crops and the controls on long-term soil arsenic accumulation is needed to establish effective arsenic mitigation strategies within vulnerable agronomic systems.

Keywords Arsenic · Soil · Irrigation · Crops · Human health · Mitigation

Introduction

With over 150 million people consuming unsafe amounts of arsenic (As) on a daily basis, chronic arsenic poisoning is major global concern [1]. Adverse human health effects resulting from chronic As consumption include increased risk of cancers, hyperkeratosis, birth defects, cardiovascular disease, neurotoxicity, and diabetes [2–4]. Unlike many pollutants that are strictly anthropogenic in origin, relatively large arsenic concentrations in groundwater stemming from geological sources are common worldwide [5]. Although much of the research concerning the consequences of As in groundwater has focused on understanding the risk of and mitigating exposure to As in drinking water [6], food with elevated As concentrations is also a major exposure route for As [7]. Because the ultimate source of much of this dietary As is soil, As pollution of soils is becoming more widely recognized as a threat to human health.

Use of contaminated groundwater for crop irrigation may result in the accumulation of As in agricultural soils, eventually resulting in decreased crop yields and impaired human health [7]. The threat of As to humans is usually exacerbated in countries that have high population densities, use groundwater as their primary drinking water source, and rely heavily on large quantities of irrigation for agriculture, such as those within South and Southeast Asia. However, contamination of agricultural soils from As in groundwater is truly a global problem, with geographically dispersed countries (e.g., Mexico, Chile, Argentina, Greece, and the USA) experiencing varying degrees of soil contamination [8, 9].

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Arsenic doses that may impact human health are observed in the everyday diets of people around the world, and consumption of high concentrations of As in crops grown in As-contaminated soil is an important exposure pathway. The climate, soils, cropping systems, and agricultural management strategies in regions that utilize As-contaminated water for irrigation vary, affecting the fundamental soil processes that control As accumulation in soil and its uptake by crops. This review paper catalogs the current state of knowledge of soil As contamination from groundwater, highlighting the processes controlling As cycling in soils and their impacts on crop and human health. The specific objectives of this review paper are to (i) identify the major areas of arsenic-contaminated soils from irrigated groundwater; (ii) describe the different mechanistic processes that influence the accumulation of arsenic from irrigated groundwater and how those processes are influenced by anthropogenic management practices; and (iii) evaluate current strategies associated with remediation of As-contaminated soils and mitigation of As uptake by crops. We conclude by identifying major knowledge gaps that may motivate future studies.

Arsenic Pollution of Soils Due to Groundwater Irrigation

The most common means of soil pollution from As-contaminated groundwater arises from irrigation for crop production. Arsenic is ubiquitous in soils, with median background concentrations of ca. 6–7 mg/kg [10]. However, repeated application of contaminated groundwater for irrigation may increase solid-phase concentrations to >10 mg/kg As (Table 1 and Fig. 1) [7]. Although these concentrations may not cause dermal contact or occasional ingestion to be hazardous, elevated As concentrations in rice, maize, wheat, and vegetables have been observed in foods grown in As-contaminated fields (Table 1 and Fig. 1) [45]. The consumption of crops grown on As-polluted soils may pose a health threat from As exposure [45], particularly in areas where the contaminated crops are dietary staples [44]. The specific extent of the risk is partially dictated by factors that control the concentration of As in the food product, such as the soil As concentration, edaphic conditions, and As plant uptake efficacy, each of which will vary for different cropping systems.

Arsenic Pollution of Rice-Field Soils

Rice is one of the most impacted crops from As-polluted irrigation water and soil [7, 43], making it a common vehicle for dietary intake of As. The natural ability of the plant to take up As, in combination with many agronomic, geochemical, and hydrological factors, leads to As accumulation in rice [46]. For example, management of the rice plant frequently consists of controlled flooding in order to eliminate competition from weeds, reduce herbicide needs, and increase yields [47]. To create flooded conditions, large quantities of irrigation water may be used in both dry and wet seasons, depending on the ability of a rice paddy to receive adequate natural saturation. Flooding changes natural soil hydrodynamics, results in high loadings of As in soil if contaminated groundwater is utilized for irrigation (Table 1), and can also change soil geochemical conditions to promote As solubilization and plant uptake (Fig. 2 and "Processes Impacting Arsenic Partitioning in Flooded Cropping Systems"). Where contaminated groundwater is extensively used for irrigation of rice-field soils, As can be transferred from soil into rice at levels sufficient to decrease yields and create dangerous grain concentrations [1, 11, 12, 28•, 48, 49, 50•, 51]. Routine consumption of rice with grain As concentrations above 200 μg/kg has been linked to genotoxic effects in humans [44], and polluted soils may yield rice with grain As concentrations that are nearly an order of magnitude higher than this threshold level (Table 1).

The extent of As loading onto rice-paddy soils can be quantified using previously defined irrigation rates and measured As groundwater concentrations [34]. If 1 m of groundwater [1, 7] containing 500 μg/L As (Table 1) is applied over a hectare of rice-paddy fields throughout a growing season, roughly 5.0 kg of As would be loaded annually onto the soils. Assuming this amount of As is evenly distributed within the top 20 cm of soil with a density of 0.89 g/cm^3 [13], soil As concentrations could increase by up to 2.8 mg/kg/year of irrigation. Within several years, soil As concentrations could increase from background levels (e.g. 6 mg/kg [13]) to greater than 10 mg/kg, a value that has been shown to lead to crop As concentrations that have harmful impacts on human health (Fig. 1) [44]. This calculation roughly agrees with field studies from Bangladesh and India, where irrigation with As-contaminated groundwater over periods of 7 to 18 years raised topsoil As concentrations from baseline concentrations of 6.6 to >10 mg/kg [28•]. Overall As accumulation depends on a range of environmental and agronomic factors [13, 52] (see "Arsenic Cycling in Soils Following Irrigation With Contaminated Groundwater"), and for a field site in Bangladesh, models predict that soil As accumulation of ~20–60 mg/kg is likely to occur between 1990 and 2050, given current irrigation rates [13].

Rice grain concentrations trend with soil As concentrations (Fig. 1) [53], highlighting the direct relationship between soil concentrations and dietary As exposure. Specific soil-to-grain As transfer varies with crop type and location [28•, 54], and a number of factors may also impact As transfer within the rice plant itself [25•, 54]. However, higher soil As concentrations generally correspond to higher As transfer rates from soil to rice grains [54, 55], and in areas with homogeneous soils and crop management practices, strong positive correlations exist between soil and rice-grain As concentrations [14, 53].

Table 1 Variability of As concentrations in groundwater, soil, and crops from a range of locations where soils are polluted due to irrigation with contaminated groundwater. Selected studies are grouped by crop type and country to highlight key areas of focus within previous research

Country	Groundwater As (μg/L)	Soil As (mg/kg)	Crop As (μg/kg)	References
Rice				
Bangladesh	38–>1800	11–32	58–1835	[7, 11–15, 16•, 17–24]
Cambodia	1–1610	0.07–33	8.0–650	[25•, 26•, 27]
India	5.3–>1800	3.34–95.3	ND–1238	[28•, 29, 30•, 31, 32]
Korea	ND–109	3.9–9.9	30–220	[33]
Nepal	ND–1014	7.4–12.5	60–330	[34]
Taiwan	32–881	11.8–112	290–660	[35•, 36, 37]
Other cereals[a]				
Cambodia	247–1842	12.86	–	[26•]
China	43–1326	7.4–22.8	22.8–365	[38•]
Greece	ND–>1000	5–513	–	[39]
India	0–>50	8.9–13.12	0.01–1.14	[40]
Mexico	ND–>1000	0.046–1.89	3.8–48.47	[41]
Vegetables[b]				
Bangladesh	38–50	2.3–14.37	50–910	[7, 12, 15, 42]
Greece	ND–>1000	20–513	0.3–25	[39]
India	0–>50	8.9–13.12	0.05–1.08	[40]
Nepal	5–>2000	6.1–16.7	6–1020	[7, 34]

ND no detection

[a] Wheat and maize

[b] Potatoes, cauliflower, onion, and brinjal; note that vegetable washing procedures were not specified for all studies

South and Southeast Asia are the areas of greatest concern for As accumulation in rice-paddy soils following irrigation with contaminated groundwater. Throughout the densely populated river basins that drain the Himalayas, rice is a staple crop, and natural As contamination of groundwater [6] has been used extensively for irrigation of dry-season rice for the past 40 years. For instance, in the Bengal Delta of Bangladesh and India, one of the most severely impacted and extensively studied areas, As concentrations in irrigation water applied to rice-paddy fields frequently exceed 50 μg/L [11, 12, 15, 16•, 51, 52, 56••], reaching as high as 1800 μg/L [15]. As a consequence, soil As concentrations in polluted fields can reach up to 95 mg/kg, and rice grains may have As concentrations of up to 1835 μg/kg [11, 12, 43] (Table 1). Rice constitutes approximately 66 % of the caloric intake in the region and up to 50 % of the daily As consumption for some people [57]. Assuming 0.47 kg/day of rice [58] with a As concentration of 400 μg/kg is consumed by people in the region, with average body weights of 60 and 40 kg for males and females, then ~3.1–4.7 μg of As/kg body weight is consumed through rice per day, values that are just above 3.0 μg of As/kg body weight per day, the WHO lower limit on the benchmark dose for a 0.5 % increased incidence of lung cancer ($BDML_{0.5}$) associated with dietary exposure to inorganic

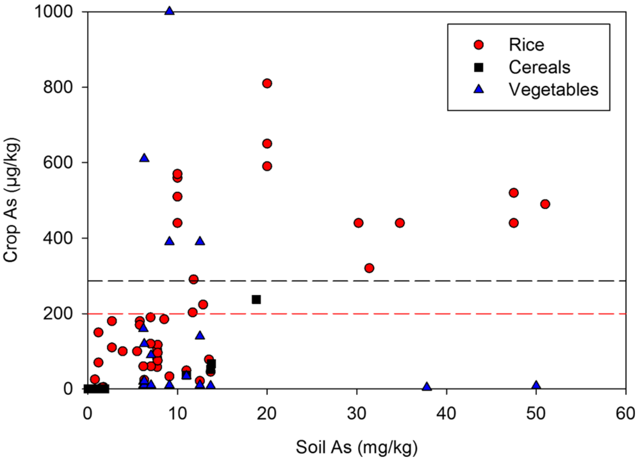

Fig. 1 Measured soil As concentrations with corresponding crop As concentrations for rice (grain) [11, 12, 26•, 31, 33, 34, 35•, 40, 43], other cereals (wheat and maize) [38•, 40, 41], and vegetables (potatoes, cauliflower, onion, and brinjal) [34, 39, 40]. Soil and crop As concentrations represent total concentrations, and selected data represent studies for which corresponding soil and crop concentrations were specifically tabulated. Crop As is shown for only the edible portion of each crop: rice grain, bulb (onion), fruit (cauliflower), and tuber (potato). The *red* and *black dashed lines* represent the estimated concentration of As observed in rice and maize (200 and 286 μg/kg), respectively, for which genotoxic effects could occur following routine dietary consumption ("Arsenic Pollution of Soils Due to Groundwater Irrigation") [44]

arsenic [59]. People in households who consume rice with higher As concentrations (e.g., the upper range in Fig. 1) could be more than doubling their $BMDL_{0.5}$ on a daily basis. In addition to human health effects, As contamination in this region may also affect crop yields. Recent laboratory experiments have shown a 6–100 % yield loss in rice due to arsenic-induced straighthead [50•], and further widespread decreases in rice yields would have a devastating effect on the region's economies, which rely heavily on rice production.

The Mekong River basin of Cambodia also contains highly As-contaminated rice-paddy soils [25•, 26•, 27]. Paddy topsoil is irrigated with groundwater containing concentrations of As as large as 1610 μg/L [60], ultimately resulting in rice-grain As concentrations up to 400 μg/kg, depending on the province (Table 1) [26•]. Cambodia also provides an example of a location where the extent of contamination is highly spatially dependent. Within the Kandal Province, mean concentrations of As in paddy soils were 12.9±10.4 mg/kg, mean rice-grain concentrations were 0.25±0.19 μg/g, and residents were consuming on average 1.839±2.423 μg inorganic As/kg/day [26•]. Although this average daily As intake is below the FAO/WHO guidelines (3.0 μg of As body weight/day) [59], some residents in the study were consuming as much as 4.262 μg inorganic As/kg/day.

Studies from Korea, Nepal, and Taiwan have also shown that elevated concentrations of As in rice grains (up to 660 μg/kg) are generally associated with use of As-contaminated groundwater for irrigation and elevated As concentrations in paddy soils [8, 34, 35•, 36, 37]. Studies have shown that As concentrations in soil are spatially variable from field to regional scales [e.g., India (1–95 mg/kg), Korea (3.9–9.9 mg/kg), Nepal (7–12.5 mg/kg), and Taiwan (11.8–112 mg/kg)], but, in general, increasing soil As concentrations tended to trend with increasing rice-grain As concentrations (Table 1).

Arsenic Pollution of Soils Used for Growing Other Cereals and Vegetables

Although rice production has been the focus of the majority of recent research concerning As uptake by crops, As pollution of soils from groundwater irrigation has also been observed for other cereal and vegetable cropping systems (Table 1). Even though such systems do not require flooded conditions for maximizing yields, irrigation and agronomic practices may result in soil As concentrations that are sufficient to create crop As concentrations that threaten human health. For example, maize is commonly grown on well-drained soil, but adequate water (approximately 0.65 m [61]) is critical to its cultivation. In areas where rainfall is insufficient, the use of As-contaminated groundwater for irrigation can contribute to soil loading of As. If 0.65 m of groundwater containing an average of 500 μg/L As (Table 1) is applied over an hectare of maize fields, then roughly 3.25 kg of As would be loaded annually onto the soils. Assuming this amount of As is added into the top 20 cm of the irrigated surface of a 1-ha maize field with a soil density of 1.3 g/cm^3 [62], soil As concentrations would increase by 1.25 mg/kg annually. As with rice fields, elevated soil As in upland systems could lead to As accumulation in food crops, with possible adverse health implications.

Currently, there are few field-verified models that quantify As transfer to crops within groundwater-polluted upland soils. Based on (1) the threshold rice-grain As concentration of 200 μg/kg for genotoxic effects associated with rice consumption [44], (2) typical rice consumption rates of 0.47 kg/person/day in Bangladesh [58], and (3) typical maize consumption rates of 0.33 kg/person/day in Mexico [41], a threshold As maize concentration of 286 μg/kg can be estimated for areas where maize is a staple crop. Cereal crops may have As concentrations that approach this threshold level; however, data from previous research suggest that in most cases, such concentrations are not common (Table 1, Fig. 1). Nonetheless, repeated seasonal irrigation with As-contaminated groundwater may cause soil pollution and create future threats to human health in upland cropping systems. Further research is needed to better understand the controls on As uptake by plants in upland systems, quantify specific As bioavailability for different upland crops, and assess the human health risks imposed by excessive loading of As to upland cropping system soils.

Differences in cropping system management may impact the accumulation, cycling, and plant uptake of As in agricultural fields ("Processes Impacting Arsenic Partitioning in Upland Cropping Systems"). Within upland systems, concentrations in vegetables and cereals tend to vary more than those found in rice grains (Fig. 1), likely due to the decreased mobility of As in aerobic soils and varying plant uptake capabilities. In the Nawalparasi District of Nepal, crop As concentrations of four different vegetables showed variable dependence on soil As concentration [34]. Soil concentration had little to no effect on As concentrations found in the tuber of the potatoes, whereas crop As concentrations were proportional to soil As concentrations for cauliflower, onion, and brinjal. Moreover, As concentrations from crop to crop also varied, and As concentrations in onion bulbs (range 10–1020 μg/kg) tended to be higher than those in cauliflower (90–610 μg/kg) and brinjal (10–140 μg/kg) [34].

Although many known cases of As-contaminated soils are found in Asia, irrigation with As-contaminated groundwater has also led to As accumulation in soils and crops within other parts of the world. High As concentrations have been recorded in groundwater throughout the southwest USA in areas such as the southern Carson Desert in Nevada, San Joaquin Valley in California, and the Basin and Range Province in Arizona [63]. Additionally, the Zimapan Valley, Baja California, Comarca Lagunera, and San Luis Potosi are a few agriculturally productive areas of Mexico where groundwater also may exhibit high concentrations of As [41, 63]. Although some irrigation with surface water is common in these regions, areas where groundwater irrigation is extensive, such as the High Plains and California Central Valley in the USA [64] and Sonora State and Baja California Sur in Mexico [65], are susceptible to soil As accumulation.

In San Luis Potosi, irrigation of maize with As-contaminated groundwater with concentrations exceeding 1000 μg/L has caused soil As concentrations up to 1932 mg/kg (Table 1) [41, 66•]. In this study, arsenic mobility in soils was enhanced by maize organic acid exudation, but As uptake by plants was moderated by the high Fe and Mn contents of the soil (as discussed in "Processes Impacting Arsenic Partitioning in Upland Cropping Systems"). Within the Chalkidiki Prefecture in Northern Greece, geothermal conditions have created groundwater As concentrations that exceed 1000 μg/L [39]. Measured soil As concentrations in irrigated agricultural fields ranged from 5 to 513 mg/kg, and As contamination reached soil depths of 50 cm in some areas. Despite soil contamination, only small concentrations (0.3–25 μg/kg) of As were found in the flesh of olives [39].

Arsenic Cycling in Soils Following Irrigation with Contaminated Groundwater

Upon introduction of As-contaminated irrigation water into a soil system, a multitude of physical, biogeochemical, edaphic, climatic, and anthropogenic factors ultimately determine the extent to which As accumulates in soil, leaches to groundwater, or is taken up by plants. In terms of edaphic factors, mineralogy, soil texture, pH, and redox status interplay to control the speciation and fate of As in agricultural fields. In most irrigated soils, metal oxides are the primary As sinks, although clay, sulfide, and carbonate minerals may also sequester As, depending on the soil pH [14, 17, 67–69]. In particular, As sorption to iron (Fe) and aluminum (Al) oxides immobilizes As within irrigated topsoil, thereby decreasing As leaching and plant uptake, unless conditions become favorable for As remobilization. Desorption of As from soil minerals may be promoted by competitive ion displacement by phosphate, silica, carbonate, and organic matter, each of which may be native to the soil, added via irrigation water application, or introduced through other agricultural management practices (e.g., fertilizer application) [25•, 26•, 29, 33, 35•, 67].

In most environments, arsenic is found as oxyanions in the + III or + V state. In general, As(V) is considered to be less mobile than the As(III) species [68]; however, both As(V) and As(III) may be readily taken up by plants via phosphate and silicon transport pathways in roots, respectively [46]. Because irrigation practices may directly affect the redox conditions of soils (and thus the relative proportion of As(III) and As(V) and the stability of host mineral phases), the predominant redox state of As may vary with cropping system or water management regime (Fig. 2) [70]. The relative importance of redox and sorption processes, as well as their net effect on As mobility and bioavailability, varies with cropping system, agricultural management practices, and other environmental factors.

Processes Impacting Arsenic Partitioning in Flooded Cropping Systems

In addition to introduction of As in soils by irrigation, the specific hydrologic regime and edaphic conditions associated with rice paddies also affect the cycling and uptake of As (Fig. 2a). Flooded conditions during typical stages of rice cultivation induce Eh values as low as −120 mV [67], and flooding of rice paddies during both the wet and dry seasons causes considerable As(III) release from soil to porewater [12, 30•]. Reductive dissolution of Fe(III) (oxyhydr)oxides is the primary mechanism for release of As during soil saturation and is recognized as a major route of As solubilization in areas such as Bangladesh, Cambodia, India, Korea, and Taiwan [12, 25•, 26•, 29, 33, 35•, 40]. Reduction of As(V) to As(III) within the soil-rice system may also enhance As mobility [12]. Rice roots readily absorb As, which can translocate through the plant and create elevated As concentrations within rice grains [46, 71]. Arsenic mobilized to porewater can also leach through the soil/sediment profile, furthering groundwater contamination [68], or be carried away from the system with receding floodwater [17, 72]. Research quantifying As mass balance indicates that groundwater-irrigated rice-field soils are net sinks for As [56••], but long-term As mobility and mechanisms of plant uptake are open areas of study.

Although rice is grown in saturated, reducing conditions, Fe(III) mineral accumulation around roots is facilitated due to the oxygenation of the rhizosphere by *aerenchyma* within the rice plant, resulting in the oxidation of soil Fe(II) to Fe(III). Fe(III) plaques surrounding rice roots have been found in As-contaminated areas such as West Bengal, India, and southwestern Taiwan [35•, 73], and these plaques may sequester As, decreasing the total As available for plant uptake, or potentially enhance As(III) uptake [74•, 75, 76]. Arsenic may be released from plaques due to rice root necrosis and changing redox conditions associated with seasonal wetting and drying of paddy soils [35•, 69, 74•]. Arsenic speciation and cycling within root plaques remain active areas of investigation.

In concert with irrigation water flow, soil biogeochemical processes can act to create spatial variability in soil As concentrations within rice fields. In Bangladesh, for example, rice fields are typically irrigated by distributing water across the field from an inlet on the perimeter [17]. As water flows across the field, co-precipitation with Fe(III) oxides formed in the water column and sorption to soil minerals remove As from solution [14, 16•, 17, 28•, 77]. Based on the rate of reactions relative to flow velocities, As may preferentially accumulate in soils near the irrigation inlet, and soil As concentrations can decrease by up to ~50 % over 20 m of flow path across a field [14, 16•, 17, 28•]—a field-scale phenomenon that can impact As concentrations within rice plants [14, 16•, 17, 28•]. Additionally, downward water percolation at field boundaries facilitates vertical transport of water from irrigated fields [78, 79], but As may remain in the soil planting zone due to sorption to soil minerals [33•, 69].

Rice-field soil As concentrations may also vary seasonally [30•]. Arsenic accumulated in soils through irrigation with contaminated groundwater in the dry season [17] may be reductively re-mobilized and removed from fields during wet-season monsoonal flooding [17, 72]. The time period at which rice paddies are subjected to flooding conditions also affects As mobility, potentially impacting temporal variability in As uptake by rice plants [74•] and seasonal dietary As consumption [80]. Despite observed temporal variability in soil As concentrations, the net effect of dry-season groundwater irrigation is generally As accumulation in soil over time [13, 17, 18, 72].

Processes Impacting Arsenic Partitioning in Upland Cropping Systems

In most upland cropping systems (such as for maize and wheat), soils are managed to avoid waterlogging, and crops tend to be grown in aerobic soils. The aerobic redox state favors the presence (and formation) of As(V), resulting in less As movement via water flow than in rice paddies. However, mobilization and plant incorporation of As can still occur within upland systems [46] (Fig. 2b).

Arsenic sequestration in upland soils is governed by soil mineralogy, organic matter content, and plant activity. Similar to rice paddies, metal oxides (mainly Fe), clay minerals, and carbonates are the primary As sinks in oxic cropping systems. However, compared to submerged rice cultivation systems, oxic, upland soils experience less As mobilization via reductive dissolution because the systems do not experience widespread reducing conditions from waterlogging. Instead, As mobilization in oxic cropping systems is primarily a consequence of the competitive effects of phosphate, silica, carbonate, and organic matter (including root exudates) for sorption sites on soil minerals [81–85]. Phosphate is thought to be most important competitor of As in upland systems due to its chemical similarity with As(V) and high affinity for mineral surfaces. However, organic matter also has a significant impact on As accumulation in soils, as As may complex with organic matter that is bound to metal oxides via metal-bridging processes [86], thereby increasing the As sorption capacity of soils. Silica impacts As(III) uptake by plants due to their similar modes of sorption to plant roots and transport pathways [46]. Finally, Fe(III) plaques have been found to form in oxic cropping systems, such as maize, and have a similar impact on accumulation and plant uptake as they do within suboxic rice cultivation systems [41].

Due to the relatively low mobility of As(V) in aerobic soils [68], loading of As-contaminated groundwater to maize fields concentrates As within shallow soil depths [25•, 67]. However, as compared with rice, little research has been conducted to assess the spatial and temporal variability of As concentrations in upland cropping systems, and the effects of long-term application of As-contaminated irrigation water are not well established.

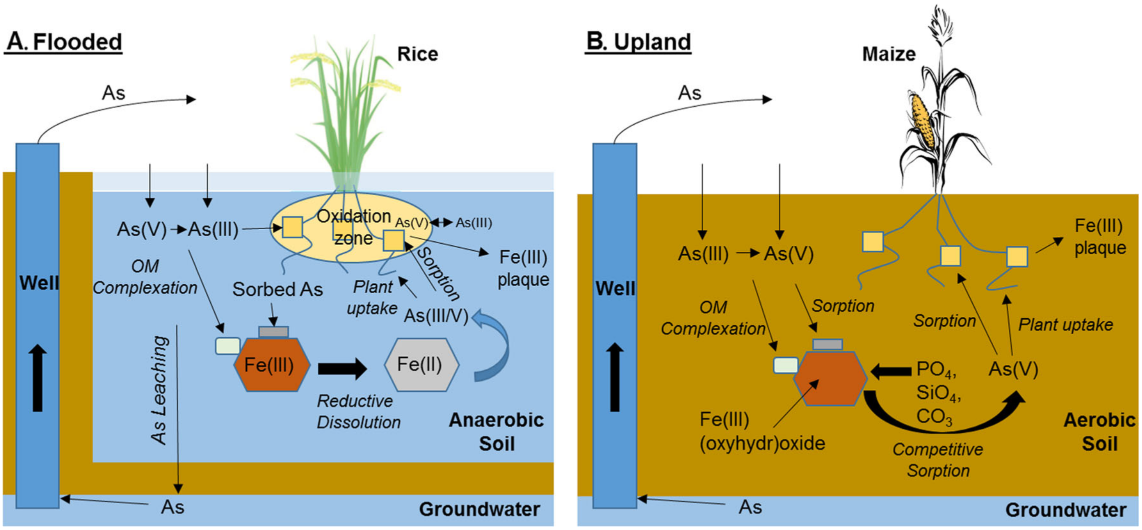

Fig. 2 Dominant processes controlling arsenic cycling in soils polluted by irrigation with contaminated groundwater. **a** In flooded cropping systems, such as rice, reducing conditions enhance As mobility and release from Fe(III) (oxyhydr)oxides, facilitating As plant uptake and leaching to groundwater. **b** In upland cropping systems, such as maize, oxic conditions promote As accumulation and sequestration by Fe(III) (oxyhydr)oxides, but competitive sorption of PO_4, SiO_4, and CO_3 species may lead to increased As availability for plant uptake

Arsenic Management and Remediation

Innovative remediation practices are required to address soil As contamination in a variety of agricultural landscapes, each with unique geologic, hydrologic, agricultural, and economic characteristics. Although a number of potential strategies may be utilized for treating As-contaminated water and remediating As-contaminated soils—including filtration, stabilization, phytoremediation, soil washing, vitrification, and geomicrobial processing [1, 7, 69]—such strategies may be impractical for extensive use within agronomic systems due to the volumes of irrigation water required, the areal extent of soil pollution, and the costs of highly technical treatments. In practice, strategies for mitigating the impact of soil As pollution of groundwater-irrigated fields have relied on decreasing As application to fields through water, soil, and crop management, or on remediating soil and altering crop choices to decrease plant As uptake. Here, we describe recent advances in low-cost water and soil management options for mitigating As impacts of soils polluted through irrigation with contaminated groundwater. Additional insights not covered here may be obtained from prior reviews that summarize common strategies for mitigating high As concentrations in South Asian rice [1, 87].

Water Management

Irrigation source selection and components of irrigation delivery are key practices that influence soil As contamination. However, the use of cheap and accessible irrigation sources, such as shallow wells, may be the only affordable agricultural water option given agronomic water demands [1, 7]. Land-based treatment schemes that induce arsenic removal from flowing irrigation water have been suggested as low-cost strategies to minimize As loading to rice-field soils. In general, due to sorption and oxidative co-precipitation reactions, As concentrations in flowing water decrease with flow distance ("Processes Impacting Arsenic Partitioning in Flooded Cropping Systems"), although removal rates are variable depending on the specific system hydraulics [16•]. Measurements of As in rapidly flowing, channelized water demonstrate varying degrees of As removal from solution [14, 18, 77, 88]; removal is greatest in shallow slow-flowing water across fields [14, 16•, 18, 28•, 29]. These observations indicate that As removal from solution via pre-field hydraulic management of irrigation water may be a practical strategy for decreasing soil As pollution, given the technical, financial, and land limitations of many agronomic systems. Although such strategies have been examined within the context of rice production, they also have potential utility for management of upland cropping systems.

Within irrigation distribution channels, dissolved As concentrations in flowing irrigation water vary over space and time, and removal capacities are governed by flow dynamics and input water chemistries. Although As removal may be limited in some channels [18], As concentrations have been observed to decrease by up to 50 % within a 100-m irrigation channel [14]. Modifications to channel geometries that increase channel residence times and soil water contact may enhance As removal from irrigation water within channels, and dissolved As concentrations have decreased by up to 80 % along the shallow wetting front in 200-m long channels [77] (although such flow conditions may be challenging to maintain over long irrigation events). Additionally, removal of dissolved and total As within irrigation water was more than doubled when channels were amended with jute-based structures that increased channel residence times and trapped suspended particles [88]. Importantly, tests of channel design and amendments for minimizing As loading to fields remain in pilot stages, and mitigation of soil pollution requires field verification.

Water management within open or vegetated fields may also be used to mitigate soil pollution from contaminated groundwater. Arsenic concentrations in irrigation water can vary throughout a field by as much as 66.7 % based on distance from the field inlet, suggesting that open fields could be utilized to treat water flowing toward adjacent crop areas [18]. The specific degree of As removal from irrigation water within open fields is controlled by the height and velocity of the flowing water, and the utility of field treatment strategies must be balanced with the potential for water loss [16•]. Finally, intermittent flooding and sprinkler irrigation of rice paddies may also decrease As uptake by rice due to oxidative As immobilization in the rice rhizosphere [74•, 89]. However, such strategies require further investigation to quantify their long-term utility, impacts on rice yields, and potential for enhancing plant uptake of co-contaminants, such as cadmium [89–91].

Soil Management

Soil management may be another effective means for minimizing, or slowing, As accumulation in fields irrigated with contaminated groundwater. In rice fields in the Bengal Delta, raised field boundaries (bunds) are not commonly plowed, in contrast with field interiors, which develop a firm plow pan. A substantial amount of irrigation water is lost through bund infiltration, though much of the As derived from the water accumulates in the paddy soils [33•, 85]. Sealing bunds, either through plowing or adding plastic barriers, can decrease bund water loss by roughly 50 % [78, 79, 92], decreasing irrigation water application needs for fields and decreasing seasonal As loading to soils by approximately 15 % [78].

Within upland cropping systems, several approaches may help mitigate As loading to soils and uptake by crops. Agronomic practices that increase soil water retention—such as no-till farming, construction of raised beds, maintenance of topsoil vegetation, and organic matter amendment—can reduce irrigation water requirements [1, 93] and therefore decrease As loading rates to soils. Additionally, because phosphate competes with As for sorption sites and can mobilize As within aerobic soils ("Processes Impacting Arsenic Partitioning in Upland Cropping Systems"), decreasing the use of high-phosphorus fertilizers, if possible given agronomic demands, may help limit As release from soil and uptake by crops. Finally, amending soils with Fe(III) (oxyhydr)oxides can help sequester soil As in aerobic, upland systems, where the potential for Fe(III) reductive dissolution and concomitant As release is minimal [1].

Knowledge Gaps

Arsenic contamination of food crops represents a significant threat to global food security and human health. Irrigation with As-contaminated groundwater is the major route by which soils become polluted and As transfers to crops. Mitigating the threat to crops posed by As accumulation in soils from irrigation requires evaluation of the diverse physical, chemical, and biological factors that govern As distributions in the environment. Furthermore, application of this knowledge for the betterment of human health requires evaluation of socioeconomic and demographic constraints on food production needs and As mitigation strategies. Several areas that are ripe for future research may provide invaluable insights into As dynamics in soils, increase our ability to assess human health risks from soil conditions, and speed development of novel strategies to minimize human As exposure from crop consumption.

Controls on As Transfer from Soil to Crops. Although a rough correlation exists between As concentrations in soils and edible parts of crops (Fig. 1), in practice, our inability to predict crop As concentrations from soil concentrations, environmental conditions, and management practices limits our capacity to assess risks associated with cultivating crops in As-contaminated areas. This issue is exacerbated by uncertainties in As translocation factors within plants [36] and health impacts associated with As consumption rates through food [25•, 42, 45, 80, 94]. Future research should systematically evaluate the mechanistic drivers on As partitioning and transfer among soil solid phases, soil porewater, and plants. In addition, As transfer relationships are needed for cropping systems other than rice, which to date has been the primary focus of such research [13, 28•, 95]. Better quantitative models for soil-plant As transfer would enable growers and policy makers to balance risks associated with threatened food safety, crop yields, and economic sustainability.

Factors Controlling Long-Term As Accumulation in Soils. - Myriad interdependent processes control the accumulation and distribution of As applied to fields with irrigation water (Fig. 2). To date, limited research has sought to define how these processes vary over space and time [6, 13, 14, 17]. Within both flooded and upland fields, specific As sinks, such as soil Fe oxide minerals and root plaques, need to be better evaluated because their ability to sequester As may be sensitive to temporal environmental and management changes, potentially providing as yet-underappreciated sources of As to porewater and plants. At a large scale, detailed evaluation of seasonal and management factors that control As fluxes out of fields is required to quantify net annual As accumulation rates and define the lengths of time over which irrigated fields remain viable. Research that elucidates different As cycling pathways within agronomic systems will enable a more complete assessment of cropping system vulnerabilities to long-term As loading and soil pollution.

Sustainable As Mitigation Strategies and Remediation Technologies. Currently, there are no widely applicable approaches for mitigating soil As pollution in fields where contaminated groundwater is relied upon as the predominant irrigation source. Recent advances in management strategies include altering cropping conditions to induce biogeochemical conditions that minimize As release from soils and plant uptake, fertilizing fields to stabilize As in soils, and utilizing As-tolerant crop varieties [87]. However, such methods may be challenging to implement broadly due to cost, tradition, and information access limitations. Agricultural engineering approaches that optimize hydrogeochemical conditions and promote As removal from irrigation water prior to field application [16•, 18, 77, 88] have the benefit of being low cost and relatively easy to implement, but the overall effectiveness and long-term sustainability of such strategies need to be determined. Similarly, strategies that minimize application rates of contaminated groundwater need to be put into the context of overall water budgets that link crop evapotranspiration and soil infiltration [78, 96]. Novel feasible and efficient As mitigation strategies are needed to ensure that food security is not compromised in regions where As-contaminated groundwater is necessary for irrigation of staple crops.

Conclusions

Pollution of agricultural soils from irrigation with As-contaminated groundwater is an issue of growing concern, threatening food security and human health. Within both flooded and upland cropping systems, repeated applications of As via irrigation water can cause soil As concentrations to rise significantly above background concentrations (>10 mg/kg) and enhance As transfer into plants. Globally, rice represents one of the most impacted crops from As-polluted irrigation water and soil, but elevated concentrations of As have also been observed in maize, wheat, and several vegetables. Although daily As dietary guidelines are evolving, studies have shown that As in crops at certain concentrations could lead to decreases in crop yields and adverse health effects in humans. Therefore, future research that combines an understanding of fundamental processes impacting As distributions in groundwater-soil-crop systems with toxicological studies will be vital.

Following application of As-contaminated irrigation water to soils, a complex combination of environmental and agronomic factors governs the ultimate fate of As. Within flooded systems, reductive dissolution of Fe oxides is the dominant mechanism by which As is mobilized from soil solid phases and made available for plant uptake. In upland cropping systems, As availability is generally controlled by its desorption from soil mineral surfaces due to competitive ligand exchange or mobilization by plant organic acid exudates. These processes can lead to variable As concentrations in soil and crops across a field and over time, depending on water management and climatic effects, and research is needed to better quantify the controls on As accumulation following application of contaminated groundwater to fields. Moreover, although crop As concentrations generally trend with soil concentrations, variability exists across crop systems, management schemes, and locations, and specific factors governing soil-plant As transfer remain to be elucidated, particularly for agronomic systems beyond Asian rice.

Despite the scale and consequences of soil As pollution, there are few broadly applied strategies for mitigating the issue. Many existing methods for soil As remediation are impractical for agricultural systems, where pollution may be widely dispersed and alternate water and land resources are unavailable. Recent advances in low-cost soil and water management strategies show promise for helping to mitigate As loading to soils and plant uptake, but most remain in proof-of-concept phases. Likely, a site-specific combination of approaches would be needed for effectively preventing the adverse impacts to crop and human health associated with soil As pollution, but rapid research and implementation of field-appropriate innovations are needed to ensure the sustainability of As-polluted agroecosystems.

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Conflict of Interest The authors declare no conflicts of interest.

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- •• Of major importance

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