Arsenic Transfer in Agroecosystems: Soil Processes, Crop Uptake, Predictive Modelling, and Management

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ABSTRACT

Arsenic (As) contamination in agricultural systems poses a persistent risk to food safety and public health, particularly in regions where As-contaminated groundwater is widely used for irrigation. While regulatory efforts have traditionally focused on drinking water, dietary exposure through crops, especially rice, is now recognised as a major pathway of human As intake. This review synthesises current understanding of As behaviour in agroecosystems by integrating soil biogeochemistry, crop uptake mechanisms, predictive modelling, and management strategies. Arsenic sources and transfer pathways across the water-soil-plant continuum are examined; highlighting soils as both sinks and secondary sources of As. Emphasis is placed on As speciation, bioavailability, and mobility, demonstrating why total soil As concentrations alone are poor predictors of crop uptake and exposure risk. Crop-specific uptake mechanisms are reviewed, identifying rice as a high-risk crop due to flooded soil conditions and silicon-mediated arsenite transport, in contrast to lower accumulation in upland cereals. Recent advances in empirical modelling, and machine learning are evaluated as tools for predicting As mobility and soil-plant transfer. These approaches capture non-linear interactions among soil properties and management practices, enabling identification of critical thresholds and safe operating zones. The review argues for risk-informed, crop- and soil-specific guideline values based on bioavailable As fractions and outlines mitigation strategies and key research needs for sustainable As management in agricultural systems.

Keywords : Arsenic, Crop, Bioavailability, Modelling

Introduction

Arsenic (As) contamination in agricultural systems is a persistent global environmental and public health concern. Although exposure through drinking water has been the primary focus of As research

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and regulation for several decades, it is now well established that food-based exposure, particularly through cereal crops, represents an equally important and, in many regions, dominant pathway of human As intake (Meharg and Rahman, 2003; Mondal and Polya, 2008; Mandal *et al.*, 2021). This shift in exposure pathways has significant implications for risk assessment, regulatory frameworks, and mitigation strategies, especially in regions where As-contaminated groundwater is extensively used for irrigation.

Rice-based agroecosystems are uniquely susceptible to As contamination. Flooded paddy soils promote reducing conditions that favour the transformation of arsenate [As(V)] to arsenite [As(III)], a more mobile and bioavailable species that is readily taken up by rice roots through silicon transport pathways (Williams *et al.*, 2007; Meharg and Zhao, 2012). As a consequence, rice accumulates As robustly than most other cereal crops, making it a major dietary source of inorganic As for populations in South and Southeast Asia, parts of East Asia, and increasingly in rice-consuming regions worldwide (Mondal *et al.*, 2010; Mandal *et al.*, 2021). Given that rice constitutes a substantial proportion of daily caloric intake for more than half of the global population, As accumulation in rice grains represents a food safety issue of global significance (Codex, 2017). Regulatory approaches have remained largely drinking-water centric. While guideline values for As in drinking water are well established, comparable standards for agricultural soils and irrigation water are limited, inconsistent, or derived from generic assumptions that do not adequately reflect the biogeochemical conditions of paddy systems (Rahman *et al.*, 2007; Tóth *et al.*, 2016). Existing soil guideline values are typically based on total As concentrations, even though total As is often a poor predictor of plant uptake and dietary exposure. Similarly, irrigation water standards are generally formulated for broad agricultural use and fail to account for cumulative As loading to soils, redox-driven transformations, and soil-plant interactions that ultimately control As transfer to edible plant tissues (Meharg and Rahman, 2003; Mandal *et al.*, 2021). Over the past decade, evidence has increasingly shown that As risk in agricultural systems is governed by a complex interplay of soil physicochemical properties, management practices, and crop-specific uptake mechanisms rather than source concentrations alone. Soil pH, organic carbon content, iron and aluminium oxides, texture, nutrient status, and water management strongly influence As speciation, mobility, and bioavailability (Golui *et al.*, 2017; Mandal *et al.*, 2019a). These controls interact in highly non-linear ways, making it difficult to extrapolate risk from single variables or apply universal threshold values across contrasting soil types and management regimes. As a result, there is growing recognition that As risk assessment must move beyond concentration-centric frameworks toward approaches that explicitly incorporate bioavailability, mobility, and system-specific behaviour (Datta and Young, 2005; Mandal *et al.*, 2023).

In parallel with advances in soil and plant biogeochemistry, data-driven approaches such as machine learning have begun to transform As risk assessment. By capturing non-linear interactions among multiple soil, environmental, and management variables, these approaches provide new opportunities to identify dominant controls, threshold behaviour, and safe operating zones for agricultural production (Mukherjee *et al.*, 2021; Mandal *et al.*, 2021; Mandal, 2025). When combined with field observations, meta-analyses, and mechanistic understanding, machine learning models offer a powerful means of deriving soil- and crop-specific guideline values that are both scientifically robust and practically relevant.

This review synthesises recent advances in understanding As behaviour in agricultural systems, with a particular emphasis on rice-based agroecosystems. It integrates evidence from field studies, experimental investigations, meta-analyses, and predictive modelling to examine As transfer across the water-soil-plant continuum, the controls on As bioavailability and mobility, and the implications for threshold derivation and mitigation strategies. By bringing together biogeochemical insights and machine learning frameworks, this review aims to provide a coherent basis for risk-informed As management in agricultural soils, with direct relevance to food safety, public health, and sustainable land use.

Sources and Pathways of Arsenic in Agricultural Systems

Arsenic enters agricultural systems through a combination of natural geogenic processes and anthropogenic activities, after which it is redistributed within the water-soil-plant continuum. Understanding these sources and pathways is essential for interpreting As accumulation in crops and for designing effective risk management strategies. Unlike point-source contaminants, As contamination in agriculture is typically diffuse, temporally persistent, and strongly mediated by soil and water management practices.

Geogenic and Anthropogenic Sources of Arsenic

In many As-affected regions, particularly in South and Southeast Asia, the dominant source of As is geogenic. Arsenic-bearing minerals such as arsenopyrite (FeAsS), realgar ($As_4 S_4$), orpiment ($As_2 S_3$) in alluvial and deltaic sediments are mobilised through natural biogeochemical processes, most notably reductive dissolution of iron hydroxides under anaerobic conditions (Smedley and Kinniburgh, 2002). Groundwater abstracted from such aquifers often contains elevated As concentrations and serves as both a drinking water source and an irrigation input, thereby linking human exposure and agricultural contamination pathways. In intensively cultivated regions, repeated irrigation with As-contaminated groundwater represents a particularly important mechanism of anthropogenic amplification, effectively recycling geogenic As from aquifers into surface soils over decadal timescales (Meharg and Rahman, 2003; Mandal *et al.*, 2021).

Irrigation Water as a Vector for Soil Arsenic Accumulation

Irrigation water plays a critical but often misunderstood role in As contamination of agricultural soils. While As concentrations in irrigation water alone may not directly predict As levels in crop grains, long-term irrigation with As-contaminated water leads to progressive As accumulation in surface soils, particularly in paddy systems (Panaullah *et al.*, 2008; Mandal *et al.*, 2021) as can be seen in Figure 1. This accumulation transforms soil into a secondary As source, decoupling short-term crop exposure from instantaneous irrigation water concentrations. The apparent weak or non-significant statistical relationship between irrigation water As and grain As observed in several studies should therefore not be interpreted as evidence of negligible irrigation effects (van Geen *et al.*, 2006; Mandal *et al.*, 2021). Instead, it reflects the complexity of As transfer pathways, which are mediated by soil buffering capacity, redox dynamics, irrigation frequency, and water management practices. Once As is incorporated into soil pools, its availability to crops is governed primarily by soil chemical conditions rather than ongoing irrigation water concentrations.

Soil as a Sink, Transformer, and Secondary Source of Arsenic

Soil occupies a central position in the agricultural As cycle, functioning simultaneously as a sink, a transformer, and a secondary source of As to crops. Arsenic introduced via irrigation water is rapidly partitioned among soil solid phases, including adsorption to iron and aluminium oxides, complexation with organic matter, and incorporation into mineral-associated pools (Mandal *et al.*, 2019a). These processes initially limit As mobility but do not eliminate long-term risk. In flooded paddy soils, alternating redox conditions further complicate As behaviour. Reductive dissolution of iron oxides during flooding releases previously sorbed As into soil solution, increasing its bioavailability to rice roots (Meharg and Rahman, 2003; Golui *et al.*, 2017). Conversely, periods of drainage or aerobic management can promote As immobilisation through re-oxidation and re-adsorption. As a result, soil As dynamics are highly sensitive to water management, organic amendments, and nutrient inputs. Importantly, total As concentrations in soil provide limited insight into the fraction that is reactive or bioavailable. Numerous studies have demonstrated that only a small, chemically labile fraction of total soil As governs plant uptake and dietary exposure (Datta and Young, 2005; Mandal *et al.*, 2019b). This distinction underpins the need to focus on bioavailable and mobile As pools rather than total concentrations alone.

Soil-Plant Transfer Pathways and Crop-Specific Behaviour

Arsenic transfer from soil to crops occurs through species-specific uptake pathways that reflect both soil chemistry and plant physiology. In rice, As(III) is taken up predominantly via silicon transporters under anaerobic conditions, whereas As(V) competes with phosphate for uptake under more aerobic conditions (Williams *et al.*, 2007; Meharg and Zhao, 2012). This duality explains the strong sensitivity of rice grain As concentrations to water management, soil redox status, and nutrient interactions. In contrast, upland crops such as wheat and maize, which are typically cultivated under aerobic conditions, exhibit lower As accumulation due to reduced As(III) availability and different uptake mechanisms (Mandal *et al.*, 2019b). Nevertheless, even in these systems, soil properties such as pH, organic carbon, and extractable As remain key determinants of crop uptake, highlighting the universal importance of soil-mediated controls across cropping systems.

Implications for Risk Assessment and Management

The multi-stage nature of As transfer in agricultural systems has important implications for risk assessment. Source-based metrics alone, such as irrigation water As concentrations or total soil As, are insufficient to capture exposure risk. Instead, As risk emerges from cumulative inputs, soil transformation processes, and crop-specific uptake pathways operating over time. This systems perspective underscores the need for integrated assessment frameworks that explicitly consider irrigation history, soil properties, management practices, and crop type. Such an approach provides the conceptual foundation for subsequent sections of this review, which examine As bioavailability, predictive modelling, and threshold derivation in greater detail.

Arsenic Speciation, Bioavailability, and Mobility in Agricultural Soils

Arsenic risk in agricultural systems is fundamentally governed not by total soil As concentrations, but by the fraction that is chemically mobile and biologically accessible to crops. Bioavailability and mobility represent dynamic properties that emerge from interactions among As speciation, soil physicochemical conditions, and management practices. Consequently, understanding these processes is essential for interpreting soil-plant transfer, predicting dietary exposure, and deriving meaningful guideline values.

Arsenic Speciation in Soils

Arsenic occurs in soils primarily as inorganic species, As(V) and As(III), with organic As forms generally contributing a minor fraction in most agricultural systems (Smedley and Kinniburgh, 2002). The dominant species is largely controlled by soil redox conditions. Under aerobic conditions, As(V) predominates and is strongly adsorbed onto iron and aluminium (hydr)oxides, whereas under anaerobic conditions, typical of flooded paddy soils, As(V) is reduced to As(III), which is less strongly sorbed and therefore more mobile (Meharg and Rahman, 2003). Redox-driven transformations are particularly important in rice-growing environments, where periodic flooding and drainage induce repeated cycles of As release and re-immobilisation (Golui *et al.*, 2017). During flooding, reductive dissolution of iron oxides liberates sorbed As into the soil solution, increasing the pool available for plant uptake. Conversely, re-oxidation during drainage promotes As re-adsorption, although this process is often incomplete, leading to net increases in mobile As over time.

Conceptualising Bioavailable and Mobile Arsenic

Bioavailable As refers to the fraction of total soil As that can interact with plant roots over relevant timescales, whereas mobile As denotes the fraction capable of migrating within the soil profile or entering soil solution. These fractions are operationally defined rather than absolute and are commonly approximated using chemical extraction techniques that target labile As pools (Datta and Young, 2005). Sequential extraction schemes and singleextractant methods, such as phosphate, bicarbonate, or weak acid extractions, have been widely used to estimate reactive As pools (Wenzel *et al.*, 2001; Golui *et al.*, 2017). Although no single extraction perfectly represents plant-available As, these approaches consistently demonstrate that only a small proportion of total soil As governs uptake by crops (Mandal *et al.*, 2019a). This distinction explains why soils with comparable total As concentrations can exhibit vastly different risks in terms of crop contamination. Recent studies have further refined this concept by focusing on the most mobile As fraction, often referred to as the water and acid-soluble pool (PF_1), which is closely linked to environmental risk and bio-accessibility (Qi *et al.*, 2025; Mandal, 2025). These approaches reinforce the need to move beyond total As metrics when assessing agricultural risk.

Soil Chemical Controls on Arsenic Bioavailability

Soil pH is one of the most influential controls on As mobility and bioavailability. Arsenate adsorption onto oxide surfaces is strongest under slightly acidic to neutral conditions and decreases under alkaline pH, where surface charge becomes increasingly negative and repels As(V) anions (Smedley and Kinniburgh, 2002). Arsenite, in contrast, exhibits weaker pH-dependent sorption, contributing to its greater mobility in flooded soils. Organic carbon plays a dual and often contradictory role in As behaviour. Organic matter can immobilise As through complexation and co-precipitation with iron oxides, reducing its availability to plants (Buschmann *et al.*, 2006; Mandal *et al.*, 2019b). Conversely, dissolved organic carbon may enhance As mobility by competing for sorption sites, forming soluble organo-As complexes, or stimulating microbial reduction of iron oxides under anaerobic conditions (Sengupta *et al.*, 2023). Iron availability is another critical regulator of As mobility. Iron oxides act as major sinks for As in soils, but their stability is strongly redox-sensitive. The breakdown of iron plaques on rice roots and iron oxides in soil during flooding releases As into soil solution, directly increasing bioavailability (Meharg and Rahman, 2003; Bhattacharyya *et al.*, 2021). Nutrient interactions, particularly with phosphate and silicon, further modulate As behaviour through competitive sorption and uptake processes (Meharg and Zhao, 2012; Mandal *et al.*, 2021).

Role of Soil Texture and Mineralogy

Soil texture exerts a strong indirect influence on As mobility by controlling the abundance of reactive mineral surfaces and the soil's capacity to buffer chemical perturbations. Fine-textured, clay-rich soils typically possess higher iron oxide content and greater sorptive capacity, often resulting in lower As mobility under comparable conditions (Mandal, 2025). However, this relationship is not linear. Extremely fine textures can promote colloidal transport or amplify sensitivity to pH and organic carbon fluctuations, leading to episodic increases in mobile As. Recent global-scale modelling efforts have demonstrated that texture-specific interactions between pH and organic carbon generate distinct "mobility control zones" across soil classes (Mandal, 2025). These findings highlight the inadequacy of uniform threshold values and emphasise the importance of texture-aware risk assessment frameworks.

Implications for Soil-Plant Transfer

The combined effects of speciation, chemical controls, and texture determine the pool of As accessible to plant roots. In rice systems, elevated As(III) concentrations in flooded soils enhance uptake through silicon transporters, while in aerobic systems As(V) uptake is constrained by stronger sorption and competition with phosphate (Williams *et al.*, 2007; Meharg and Zhao, 2012). Importantly, management practices that modify redox conditions, organic carbon inputs, or nutrient availability can shift As from relatively inert pools into bioavailable forms without altering total soil As concentrations. These processes explain why As risk cannot be reliably inferred from total soil As alone and underscore the need for bioavailability-informed thresholds. The mechanistic understanding presented in this section provides the foundation for subsequent sections, which examine how these controls are captured using predictive models and translated into guideline values for agricultural soils.

Soil-Plant Transfer of Arsenic: Crop-Specific Pathways and Controls

Transfer of As from soil to crops represents the critical link between environmental contamination and human exposure. While soil As bioavailability governs the pool accessible to roots, plant uptake, translocation, and sequestration processes ultimately determine As accumulation in edible tissues. These processes vary markedly among crops and are strongly modulated by soil conditions and agronomic management, resulting in substantial variability in dietary risk even under similar soil As loads.

Uptake Mechanisms of Arsenic in Plants

Arsenic enters plant roots primarily in its inorganic forms, As(V) and As(III), via distinct uptake pathways. Arsenate, being a chemical analogue of phosphate, is taken up through phosphate transporters under aerobic soil conditions, whereas As(III), a neutral molecule at circumneutral pH, enters roots predominantly through aquaglyceroporins and silicon transporters (Williams *et al.*, 2007; Meharg and Zhao, 2012). The relative importance of these pathways is controlled by soil redox status, pH, and nutrient availability. Once inside the plant, As may be translocated to above-ground tissues or detoxified through reduction, complexation with thiol-rich compounds such as phytochelatins, and sequestration into vacuoles (Song *et al.*, 2014). The efficiency of these internal detoxification mechanisms differs among plant species and genotypes, contributing to large variations in grain As concentrations.

Rice as a High-Risk Crop for Arsenic Accumulation

Rice is uniquely susceptible to As accumulation due to the flooded conditions under which it is typically cultivated (Devi *et al.*, 2023). Anaerobic paddy soils promote the dominance of As(III), which is readily taken up through silicon transport pathways (OsLSi1 and OsLSi2) that are highly expressed in rice roots (Meharg and Rahman, 2003; Williams *et al.*, 2007). This physiological trait, combined with elevated As mobility under reducing conditions, explains why rice accumulates substantially higher As concentrations than most other cereals grown on the same soils. Numerous field studies have demonstrated strong soil-to-grain As transfer in rice systems, particularly where long-term irrigation with As-contaminated groundwater has elevated soil As levels (Panaullah *et al.*, 2009; Mandal *et al.*, 2021). Importantly, rice grain As concentrations often show weak or inconsistent relationships with irrigation water As alone, reinforcing the central role of soil-mediated processes in governing uptake (Mandal *et al.*, 2021). Water management practices such as continuous flooding, alternate wetting and drying, and intermittent irrigation further influence As availability and uptake by altering soil redox dynamics and iron plaque formation on roots (Bhattacharyya *et al.*, 2021; Mandal *et al.*, 2021).

Upland Crops: Wheat and Maize

In contrast to rice, upland crops such as wheat and maize are generally cultivated under aerobic soil conditions, where As(V) predominates and As is more strongly retained by soil minerals. Consequently, these crops typically accumulate lower As concentrations in edible tissues compared to rice grown on the same soils (Mandal *et al.*, 2019a; Golui *et al.*, 2019). However, reduced accumulation does not imply negligible risk. Field and pot studies have shown that As uptake by wheat and maize remains sensitive to soil pH, organic carbon content, and extractable As pools, particularly in soils receiving organic amendments or irrigated with As-contaminated water over long periods (Mandal *et al.*, 2019a; Mandal *et al.*, 2019b). Predictive approaches based on bioavailable As rather than total soil As have been shown to explain a large proportion of variability in grain As concentrations in these crops, underscoring the general applicability of bioavailability-driven frameworks across cropping systems (Datta and Young, 2005; Mandal *et al.*, 2019a).

Role of Agronomic Management in Modulating Soil-Plant Transfer

Agronomic practices exert strong control over As transfer from soil to plants by modifying both soil chemistry and plant physiology. Water management is particularly influential in rice systems, where shifting from continuous flooding to alternate wetting and drying can substantially reduce grain As concentrations by limiting As(III) formation and promoting As immobilisation (Bhattacharyya *et al.*, 2021; Mandal *et al.*, 2021b). Similarly, soil amendments such as organic matter, biochar, and iron-based materials can alter As bioavailability through complexation, sorption enhancement, or competition with nutrients such as phosphate and silicon (Mandal *et al.*, 2019b; Khanam *et al.*, 2024). Nutrient management also plays a critical role. Phosphorus additions can either suppress or enhance As uptake depending on soil conditions, while silicon fertilisation has been shown to reduce As uptake in rice by competitively inhibiting arsenite transporters (Meharg and Zhao, 2012). These interactions highlight the importance of integrated soil-plant management strategies that account for both chemical and physiological controls on As uptake.

Implications for Dietary Exposure and Risk Assessment

The crop-specific nature of As uptake has direct implications for dietary exposure and risk assessment. Rice-based diets are inherently more vulnerable to As exposure due to the high accumulation potential of rice grains, whereas diversification toward upland cereals can reduce dietary risk under comparable soil As levels. However, such shifts are not always feasible due to agroecological, cultural, and economic constraints. These complexities reinforce the need for risk assessment frameworks that explicitly incorporate crop type, management practices, and soil bioavailability rather than relying on uniform soil As thresholds.

Modelling Arsenic Risk in Agricultural Systems: From Empirical Relationships to Machine Learning Frameworks

The complexity of As behaviour in agricultural systems poses a major challenge for conventional risk assessment approaches. Non-linear interactions among soil properties, redox dynamics, management practices, and crop-specific uptake mechanisms limit the predictive power of simple concentration-based or single-factor models. As a result, modelling frameworks have evolved from empirical regressions toward integrative and data-driven approaches capable of capturing system-level behaviour across spatial and temporal scales.

Empirical and Mechanistic Modelling Approaches

Early attempts to model As transfer in agricultural systems relied primarily on empirical relationships between As concentrations in irrigation water, soil, and crop tissues. Linear and generalized linear regression models were widely used to identify dominant predictors of grain As concentrations, often highlighting soil As as a stronger determinant than irrigation water As (Meharg and Rahman, 2003; Mandal and Mondal, 2025). While such models provided important first-order insights, their applicability was often constrained by site specificity and limited ability to capture non-linear interactions. Mechanistic approaches, including solubility-based models and free ion activity models (FIAM), sought to improve prediction by explicitly linking soil chemical properties to metal(loid) availability and plant uptake (Datta and Young, 2005). These models have been successfully applied to predict As uptake by crops such as wheat and rice using extractable As, soil pH, and organic carbon as key inputs (Golui *et al.*, 2017; Mandal *et al.*, 2019a). However, mechanistic models typically require detailed input data and simplifying assumptions that limit their scalability across diverse soil types and management regimes.

Meta-Analysis as a Tool for Threshold Identification

Meta-analytical approaches represent an important intermediate step between site-specific models and large-scale prediction. By synthesising data across multiple field studies, meta-analyses enable identification of statistically robust relationships and critical breakpoints that are not evident in individual experiments. Applications of meta-analysis in As research have demonstrated that soil As concentration is often a stronger predictor of rice grain As than irrigation water As, particularly when evaluated across heterogeneous field conditions (Mandal *et al.*, 2021). Decision tree and logistic regression models applied to meta-data have further revealed threshold-type behaviour, where grain As concentrations increase sharply beyond specific soil As levels rather than following linear trends (Mukherjee *et al.*, 2021; Mandal and Mondal, 2025). These findings challenge the validity of generic guideline values and highlight the need for crop- and system-specific thresholds informed by probabilistic risk rather than mean responses.

Emergence of Machine Learning in Arsenic Risk Modelling

Machine learning (ML) approaches have gained increasing prominence in As risk assessment due to their ability to model complex, non-linear relationships without requiring explicit mechanistic specification. Algorithms such as random forest, gradient boosting machines, and generalized additive models have been applied to predict As mobility, bioavailability, and soil-plant transfer across large and diverse datasets (Qi *et al.*, 2025; Mandal, 2025). Unlike traditional regression models, ML approaches can simultaneously account for interactions among soil pH, organic carbon, texture, cation exchange capacity, total As, and management-related variables. This capacity is particularly valuable in As-contaminated agricultural systems, where multiple controls operate concurrently and often in opposing directions. Comparative studies have consistently shown ensemble methods such as random forest to outperform linear and semi-parametric models in predicting mobile As fractions and crop uptake metrics (Sengupta *et al.*, 2023; Mandal, 2025).

Predicting Arsenic Mobility and Bioavailability Using Machine Lerning

Recent modelling efforts have shifted focus from predicting total As concentrations to predicting operationally defined mobile or bioavailable As fractions. Metrics such as the water-and acid-soluble As fraction (PF_1) have emerged as meaningful indicators of environmental and agronomic risk, capturing the As pool most likely to enter soil solution and plant roots (Qi *et al.*, 2025). Machine learning models trained on globally harmonised soil datasets have demonstrated that soil pH and organic carbon exert strong, non-linear controls on As mobility, with these effects further modulated by soil texture (Mandal, 2025). Simulation studies have revealed the existence of "mobility control zones" in pH-organic carbon space, within which As mobility remains below defined risk thresholds. These zones vary systematically across USDA soil texture classes, reinforcing the inadequacy of uniform guideline values and the importance of texture-aware risk assessment.

Beyond prediction, ML models enable scenario-based simulations that support practical decision-making. By systematically varying soil properties within realistic ranges, it is possible to identify conditions under which As mobility and crop uptake are minimized, even in soils with elevated total As concentrations. Such simulations provide a powerful tool for evaluating management options, including pH adjustment, organic amendment strategies, and crop selection, without the need for extensive field trials. Importantly, ML-derived predictions can be translated into probabilistic risk metrics rather than deterministic outcomes. This shift allows risk to be expressed in terms of likelihood of exceeding food safety thresholds, aligning more closely with regulatory and public health decision-making frameworks (Mukherjee *et al.*, 2021; Mandal *et al.*, 2021).

Limitations and Integration with Mechanistic Understanding

Despite their strengths, machine learning approaches are not without limitations. ML models are inherently data-driven and may lack interpretability if not carefully designed and validated. Moreover, they do not explicitly simulate chemical speciation or microbial processes, instead capturing their net effects through correlated predictors such as pH, organic carbon, and texture. Consequently, ML outputs should be interpreted in conjunction with mechanistic understanding rather than as standalone representations of As behaviour. The most robust modelling frameworks therefore integrate mechanistic insight, empirical data, and machine learning prediction. Such hybrid approaches leverage the explanatory power of soil chemistry while exploiting the predictive strength of ML, providing a coherent pathway from process understanding to actionable risk thresholds.

Deriving Thresholds and Guideline Values for Arsenic in Agricultural Systems

Establishing threshold and guideline values for As in agricultural soils and irrigation water is essential for protecting food safety and public health. However, unlike drinking water standards, which are relatively well defined, As thresholds for agricultural systems remain fragmented and often poorly aligned with soil-plant processes. The complexity of As behaviour in soils, coupled with crop-specific uptake mechanisms, necessitates a shift from generic concentration-based limits toward risk-informed, system-specific thresholds.

Most existing soil guideline values for As are based on total As concentrations and are intended for generic agricultural or environmental protection purposes. Such values typically range from 10 to 50 mg kg^{-1}, depending on jurisdiction, and are not tailored to specific cropping systems or management conditions (Rahman *et al.*, 2007; Tóth *et al.*, 2016). These thresholds implicitly assume uniform bioavailability across soils, an assumption that is inconsistent with the strong influence of pH, redox conditions, organic carbon, and mineralogy on As mobility. Similarly, irrigation water standards for As are largely derived from broad agricultural considerations rather than crop-specific exposure pathways. The commonly cited limit of 100 µg L^{-1} for irrigation water does not explicitly account for cumulative As loading to soils, nor does it reflect the indirect but persistent role of irrigation water in elevating soil As over time (Meharg and Rahman, 2003; Mandal *et al.*, 2021). As a result, compliance with irrigation water guidelines does not necessarily ensure protection against crop contamination, particularly in long-established paddy systems.

Soil Arsenic Thresholds Based on Crop Safety

Recent evidence indicates that soil As concentration is a stronger and more consistent predictor of crop As accumulation than irrigation water concentration, particularly for rice (Mandal *et al.*, 2021). Meta-analytical and decision tree approaches have revealed threshold-type behaviour, where the probability of rice grain As exceeding food safety limits increases sharply beyond specific soil As concentrations rather than following a linear trend. These findings support the derivation of soil As thresholds explicitly linked to crop safety outcomes. For Asian paddy soils, soil total As concentration of 14 mg kg^{-1} and bioavailable As of 5.70 mg kg^{-1} have been shown to correspond to a marked increase in the likelihood of rice grain As exceeding Codex maximum allowable concentrations (Mandal *et al.*, 2023). Importantly, these thresholds are probabilistic rather than absolute, reflecting variability in soil properties, management practices, and rice genotypes.

Role of Bioavailable and Mobile Arsenic in Threshold Definition

Thresholds based solely on total soil As fail to capture the fraction that is relevant for plant uptake and human exposure. Incorporating measures of bioavailable or mobile As provides a more mechanistically meaningful basis for risk assessment. Operationally defined pools, such as extractable As fractions or the water- and acid-soluble fraction (PF_1), have been shown to correlate more strongly with crop uptake than total As concentrations (Datta and Young, 2005; Golui *et al.*, 2017). Machine learning analyses of large soil datasets have further demonstrated that mobile As fractions respond non-linearly to soil pH, organic carbon, and texture, leading to distinct risk profiles across soil types (Qi *et al.*, 2025; Mandal, 2025). Thresholds defined in terms of mobile As therefore inherently account for soil buffering capacity and chemical controls, offering greater transferability across regions than fixed total a limits.

Irrigation Water Thresholds: Indirect but Cumulative Risk

Unlike soil thresholds, irrigation water As limits cannot be reliably derived solely from direct relationships with crop As concentrations. While short-term correlations between irrigation water and grain As are often weak, long-term irrigation with As-contaminated water leads to progressive soil accumulation and increased risk over time (Panaullah *et al.*, 2008; Mandal *et al.*, 2021). Consequently, irrigation water thresholds should be viewed as preventive rather than predictive, aimed at limiting soil loading rather than guaranteeing immediate crop safety. Recent evidence has enabled the derivation of a rice-specific irrigation water guideline value of 190 µg L^{-1}, based on probabilistic machine learning modelling of soil-water-rice transfer and food safety outcomes, rather than direct water-grain correlations (Mandal *et al.*, 2025). This value reflects the indirect but time-integrated role of irrigation water in elevating soil As to levels that increase the likelihood of rice grain As exceeding food safety limits.

Management and Mitigation Strategies for Arsenic in Agricultural Systems

Effective management of As in agricultural systems requires strategies that address not only As sources but also the soil and plant processes that control As mobility, uptake, and accumulation in edible tissues. Given the strong influence of soil chemistry, crop type, and agronomic practices on As behaviour, mitigation approaches must be context-specific and informed by an understanding of system-level controls rather than relying on universal interventions.

Water Management as a Primary Control Lever

Water management is one of the most influential tools for controlling As availability in rice-based systems. Continuous flooding promotes anaerobic soil conditions, leading to reductive dissolution of iron oxides and increased mobilisation of As into soil solution (Meharg and Rahman, 2003). In contrast, alternate wetting and drying (AWD) introduces periodic aerobic phases that suppress As(III) formation and enhance As immobilisation through re-oxidation processes. Numerous studies have demonstrated that AWD can substantially reduce grain As concentrations without compromising yield when implemented appropriately (Bhattacharyya *et al.*, 2021; Sengupta *et al.*, 2021). However, the effectiveness of AWD depends on soil texture, organic carbon content, and irrigation history. In soils with limited buffering capacity or high organic matter, intermittent drying may not fully suppress As mobilisation, highlighting the need for site-specific evaluation rather than blanket recommendations.

Soil Amendments and Chemical Stabilisation

Soil amendments offer a second major avenue for As mitigation by modifying sorption capacity, redox behaviour, and nutrient interactions. Organic amendments such as farmyard manure, compost, and crop residues can reduce As bioavailability through complexation and co-precipitation with iron oxides, although their effects are often dose- and context-dependent (Mandal *et al.*, 2019b; Golui *et al.*, 2019). In some cases, dissolved organic carbon released from amendments may enhance As mobility by competing for sorption sites or stimulating microbial reduction processes. Biochar has attracted particular attention as a mitigation amendment due to its capacity to increase soil pH, enhance sorption surfaces, and modify nutrient dynamics. Experimental studies have shown that biochar application, especially when combined with AWD, can significantly reduce As accumulation in rice grains by altering competitive interactions among As, silicon, phosphorus, and sulfur, as well as by influencing the expression of As transporters (Khanam *et al.*, 2024). Nevertheless, contradictory findings across studies indicate that biochar effects are highly dependent on feedstock, pyrolysis conditions, application rate, and soil properties, underscoring the need for cautious, evidence-based deployment. Iron-based amendments, including iron oxides and iron-rich vermicompost, can enhance As immobilisation by increasing the abundance of sorptive surfaces (Sengupta *et al.*, 2023). While effective under controlled conditions, their long-term performance in flooded soils may be limited by redox instability, necessitating integration with water management strategies to sustain As retention (Sengupta *et al.*, 2021).

Crop Selection and Diversification

Crop choice represents a structural mitigation strategy that can substantially reduce dietary As exposure. Upland crops such as wheat and maize generally accumulate lower As concentrations than rice when grown on the same soils, owing to aerobic cultivation conditions and different uptake pathways (Mandal *et al.*, 2019a). Whereas agroecologically and socioeconomically feasible, diversification away from continuous rice cultivation can therefore reduce risk. Within rice systems, varietal selection offers additional mitigation potential. Genotypic differences in As uptake, translocation, and sequestration have been widely documented, and cultivars with lower grain As accumulation have been identified (Williams *et al.*, 2007; Khanam *et al.*, 2021). However, trade-offs with yield, nutrient use efficiency, and farmer preference often limit large-scale adoption, reinforcing the need to integrate varietal selection with soil and water management.

Toward Adaptive and Context-Specific Mitigation Strategies

No single management practice can universally mitigate As risk across all agricultural systems. Effective mitigation requires adaptive strategies that combine water management, soil amendments, nutrient optimisation, and crop selection in ways that are tailored to local soil properties, cropping systems, and socio-economic constraints. Importantly, mitigation efforts should be evaluated not only in terms of reducing total soil As but also in terms of their impact on bioavailable and mobile As fractions, which ultimately govern plant uptake and dietary exposure. Framing mitigation success through this lens aligns management objectives with the risk-based threshold frameworks discussed earlier in this review and provides a coherent pathway toward sustainable As management in agriculture.

Conclusion

Arsenic contamination in agricultural systems represents a complex and persistent challenge that extends beyond traditional drinking-water-focused paradigms of exposure. This review highlights that As risk in agroecosystems is fundamentally governed by the interactions among water sources, soil physicochemical properties, crop-specific uptake mechanisms, and agronomic management practices. As such, reliance on total As concentrations or generic guideline values provides an incomplete and often misleading basis for risk assessment and mitigation. Evidence synthesised here demonstrates that soil acts as the central regulator of As transfer to crops, integrating cumulative inputs from irrigation water and modulating As bioavailability through redox processes, mineral interactions, and organic matter dynamics. Rice-based systems are particularly vulnerable due to flooded conditions and silicon-mediated uptake pathways, whereas upland crops generally exhibit lower accumulation under aerobic conditions. These crop-specific behaviours underscore the need for differentiated risk frameworks rather than uniform thresholds across agricultural systems. Advances in empirical modelling, meta-analysis, and machine learning have substantially improved the ability to predict As mobility and crop uptake across diverse soils and management contexts. By capturing non-linear interactions among key soil variables, these approaches enable the identification of critical thresholds, safe operating zones, and management-sensitive risk profiles. Importantly, they provide a pathway for translating mechanistic understanding into probabilistic, risk-informed guideline values that are more aligned with food safety outcomes than traditional concentration-based limits. Effective mitigation of As in agriculture requires integrated strategies that combine water management, soil amendments, nutrient optimisation, and crop or cultivar selection. No single intervention is universally effective, and management success depends on local soil properties, cropping systems, and socio-economic constraints. Predictive frameworks that link soil chemistry with management scenarios offer a promising route toward targeted, evidence-based interventions. Looking ahead, sustainable As risk management will depend on adaptive frameworks that incorporate bioavailability, crop specificity, and environmental change. Integrating mechanistic insight with data-driven prediction, and embedding these advances within decision-support tools, will be essential for safeguarding food systems and public health in As-affected regions. This review provides a foundation for such efforts by synthesising current knowledge and outlining pathways toward more robust, context-aware As management in agricultural landscapes.

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Table 1. Amount of arsenic in soil, irrigation water and rice as reported in different studies conducted in Asian countries (adapted from Mandal *et al.*, 2021)

Sl. No	Author and year of publication	Location	No. of sites	Parameters Analyzed (Range or mean)												Correlation (grain As vs soil As)
				t-As in grain (mg kg^{-1}) (dry mass)	SE(m)	As in Irrigation water ($\mu g\ L^{-1}$) (filtered)	As in soil (mg kg^{-1}) (dry mass)	pH	OC (%)	Texture	Redox (mv)	Fe (mg kg^{-1})	P (mg kg^{-1})	S (mg kg^{-1})		
1	Roychowdhury, 2008a	India	23	0.043-0.662	---	18-200	3.34-31.6	---	---	---	---	---	---	---		---
		India	18	0.045-0.386	---	4-82	5-95.3	---	---	---	---	---	---	---		---
2	Chowdhury *et al.*, 2018	India	10	0.036-1.56	---	74-301	12.75-37.23	---	---	---	---	---	---	---		---
3	Roychowdhury *et al.*, 2008b	India	8	0.045-0.386	---	2-82	5-95.3	---	---	---	---	---	---	---		---
4	Chowdhury *et al.*, 2020	India	3	0.224-0.389	---	10-493	1.53-30.17	7.39 - 7.74	1.86 - 2.14	---	153-163	---	---	---		---
5	*Biswas *et al.*, 2018	India	24	0.550	---	410	7.06	8.1	3.97	Silty Clay	---	14.99	6.24	---		---
6	*Bhattacharya *et al.*, 2010a	India	18	0.160-0.230	---	530	3.34-4.6				---	---	---	---		---
		India	12	0.160-0.300	---	400	5.26-7.10	7.66	0.72	Clay Loam	---	---	---	---		---
		India	12	0.230-0.400	---	420	7.03-9.72				---	---	---	---		---
		India	12	0.240-0.580	---	400	5.31-5.82				---	---	---	---		---
		India	9	0.290-0.540	---	440	4.01-5.52				---	---	---	---		---
7	*Bhattacharya *et al.*, 2010b	India		0.140-0.310	---	360-470	4.26-5.85	---	---	---	---	---	---	---		---
8	*Biswas *et al.*, 2014	India	94	0.330	---	420	8.35	---	---	---	---	---	---	---		---
		India	78	0.230	---	350	6.17	---	---	---	---	---	---	---		---
9	Golui *et al.*, 2017	India	13	0.002-1.26	---	180-570	0.196-2.33	8.06	0.45	---	---	---	---	---		0.76
10	Mukherjee *et al.*, 2017	India	22	0.210-0.720	---	56-585	9.05-25.80	---	---	---	---	---	---	---		0.85
11	*Rahaman and Sinha, 2013	India	2	0.390-0.670	---	430-540	9.8-10.7	7.91 - 8.30	---	Silty Clay-Silty Loam	---	2.79-3.11	13-19	---		0.673
12	Sarkar *et al.*, 2012	India	1	0.420-0.560	---	106-573	16.22-18.74	7.22	0.99	Silty Clay	---	---	32.85	---		---
13	Sinha and Bhattacharyya, 2014	India	1	0.103-0.141	---	320	2.38-3.03	---	---	---	---	---	25.23-37.04	---		---
14	Srivastava *et al.*, 2015	India	58	0.179-0.932	---	0-312	3-35	---	2.52	Clay Loam-Clay	---	---	25.6	6.84		---
15	Talukder *et al.*, 2011	Bangladesh	1	0.470	---	100	8.12	6.1	0.95	Sandy Clay Loam	---	68.36	5.47	2.36		---

16	*Dahal *et al.*, 2008	Nepal	10	0.60-0.330	0.01	5-1014	6.1-16.7	8.0	---	---	---	---	---	---	0.68
17	*Hsu *et al.*, 2012	Taiwan	1	0.290-0.660	---	26-67	11.8-112	5.6-6.5	---	Silty Clay Loam	---	5.85-13.1	---	---	---
18	Rahman *et al.*, 2014	Bangladesh	2	0.290-0.650	---	25-419	9.12-11.23	6.8		---	---	---	---	---	---
19	Rahman *et al.*, 2007	Bangladesh	6	0.600-0.700	---	70	14.5	7.1		Clay loam	---	---	6.8	---	---
20	Rahman *et al.*, 2010	Bangladesh	44	0.230	---	87.30	13.0	---	---	---	---	---	---	---	---
21	*van Geen *et al.*, 2006	Bangladesh	6	0.280-0.440	---	0-185	2.9-29	---	---	---	---	---	---	---	---
22	*Islam *et al.*, 2017	Bangladesh	3	0.288-0.320	---	2.4-255.4	2.7-15.7	6.1-7.6	2.0-2.4	Clay-Silty Clay Loam	---	---	---	---	---
23	*Ahmed *et al.*, 2011	Bangladesh	10	0.101-0.338	0.012 - 0.024	0-234	0.9-8.7	5.0-7.5	0.74 - 1.62	---	---	9.1-17.5	---	---	---
24	Sharma *et al.*,2017	India	12	0.03-0.33	---	2.31-15.91	0.06-0.11	---	---	---	---	---	---	---	---
25	Reid *et al.*, 2021	Vietnam	16	0.063-0.528	---	0-751	6-20	---	---	---	---	---	---	---	---
26	*Wang *et al.*, 2019	China	5	0.039–0.084		5.5–9.1	---	---	---	---	---	---	---	---	---

* Reported Arsenic concentration for polished rice

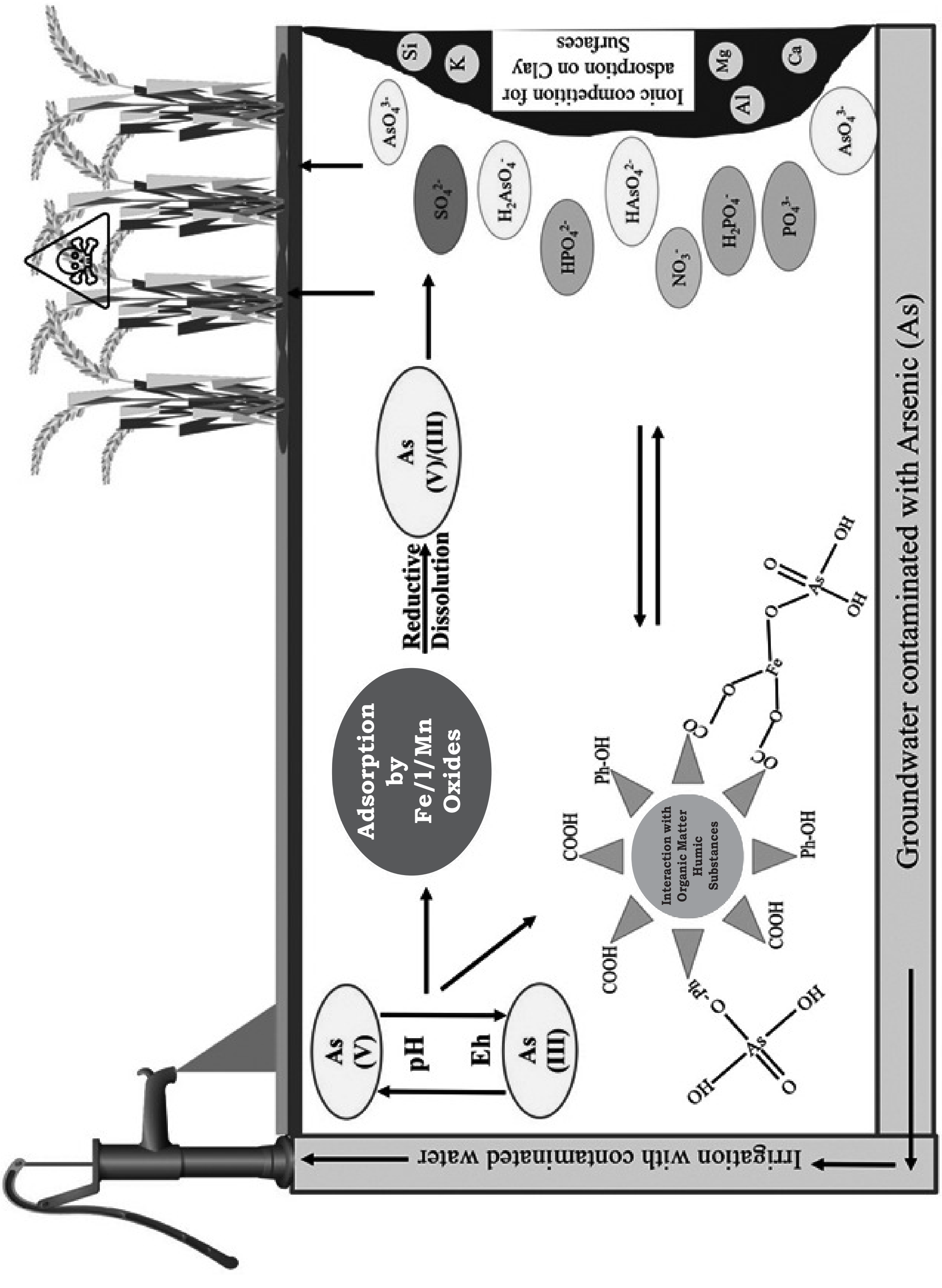

Figure 1. The arsenic (As) pathway in rice field (adapted from Sengupta *et al.*, 2022)