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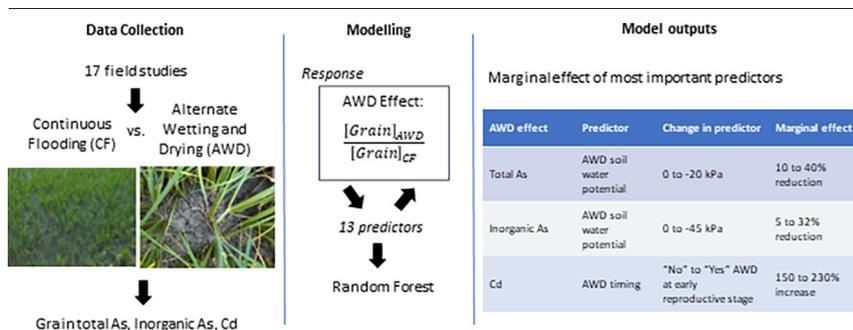
Mitigating the accumulation of arsenic and cadmium in rice grain: A quantitative review of the role of water management

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HIGHLIGHTS

- Compared to CF irrigation, AWD can decrease As in rice grain but Cd may increase.
- Data from 17 field-based articles comparing AWD and CF irrigation were modelled.
- Total and inorganic As decreased with decreasing soil water potential under AWD.
- Cd accumulation was highest when AWD was practiced at the early reproductive stage.
- A minimum trade-off strategy for implementing AWD is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Arsenic exposure through rice consumption is a growing concern. Compared to Continuous Flooding (CF), irrigation practices that dry the soil at least once during the growing season [referred to here as Alternate Wetting and Drying (AWD)] can decrease As accumulation in grain; however, this can simultaneously increase grain Cd to potentially unsafe levels. We modelled grain As and Cd from field studies comparing AWD and CF to identify optimal AWD practices to minimize the accumulation of As and Cd in grain. The severity of soil drying during AWD drying event(s), quantified as soil water potential (SWP), was the main factor leading to a reduction in grain total As and inorganic As, compared to CF. However, lower SWP levels were necessary to decrease grain inorganic As, compared to total As. Therefore, if the goal is to decrease grain inorganic As, the soil needs to be dried further than it would for decreasing total As alone. The main factor driving grain Cd accumulation was when AWD was practiced during the season. Higher grain Cd levels were observed when AWD occurred during the early reproductive stage. Further, higher Cd levels were observed when AWD spanned multiple rice growth stages, compared to one stage. If Cd levels are concerning, the minimum trade-off between total As and Cd accumulation in rice grain occurred when AWD was implemented at a SWP of -47 kPa during one stage other than the early reproductive. While these results are not meant to be comprehensive of all the interactions affecting the As and Cd dynamics in rice systems, they can be used as a first guide for implementing AWD practices with the goal of minimizing the accumulation of As and Cd in rice grain.

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1. Introduction

Arsenic (As) exposure through rice consumption is a growing concern as future climatic conditions are associated with increased accumulation of this metalloid in rice grain (Farhat et al., 2021; Muehe et al., 2019) and rice intake per capita is projected to increase in many countries (FAO, 2021; Gilbert-Diamond et al., 2011). Arsenic toxicity varies with chemical speciation and, among the most common species found in rice grain, arsenite (As^{3+}) is a class one carcinogen and is the most toxic, followed by arsenate (As^{5+}) and lastly, dimethylarsinic acid (DMA), which is generally considered to be of low toxicity (Williams et al., 2005; Zavala et al., 2008). Because it is difficult to separately quantify As^{3+} and As^{5+} and because As^{3+} is predominant, the sum of these two species is often reported as inorganic As (iAs) (Kubachka et al., 2012). In China and the European Union, iAs is regulated at a maximum concentration of $200 \mu\text{g kg}^{-1}$ in polished rice (EU, 2015; USDA, 2018). In the United States, As is currently not regulated in rice grain, but a limit of $100 \mu\text{g kg}^{-1}$ is set for iAs in infant rice cereals (FDA, 2016). With the improvement of chromatography methods, there has been a recent concern with thiolated As species such as dimethylated monothioarsenate (DMMTA), which is even more toxic than iAs and is reportedly widespread in rice grain from different parts of the world (Colina Blanco et al., 2021; Dai et al., 2022).

Rice tends to accumulate more As than other cereal crops largely because it is often cultivated under flooded conditions (Williams et al., 2007). About 75% of the world's rice production comes from lowland systems where fields are flooded for most of the season, an irrigation practice commonly referred to as Continuous Flooding (CF) (Muthayya et al., 2014). Anaerobic soil conditions caused by flooding increase As phytoavailability in the soil because, first, arsenate is reduced to arsenite, which is less strongly adsorbed by soil ferric oxides and more efficiently taken up by rice plants (due to highly active silica transport pathway in rice); second, arsenate adsorption is weaker at the higher soil pH values that are typical of flooded soils, compared to aerobic soils; and third, ferric oxides are reduced to ferrous ions, dissolving As-bearing iron hydro(oxides) and subsequently releasing As into the soil solution (Meharg and Zhao, 2012).

Introducing periods of soil drying during the growing season to aerate the soil is one practice that can substantially decrease As uptake by rice crops compared to CF (Bakhat et al., 2017; Kumarathilaka et al., 2020). Such practices go by a number of names [alternate wetting and drying (AWD), intermittent irrigation, mid-season drain, etc.] depending on the country and variations in type and frequency of drying. For the purposes of this study, we will use the commonly used term AWD to refer to all practices with at least one soil drying event during the growing season. In addition to decreasing grain As, several studies comparing AWD and CF have shown that AWD can maintain yields, reduce water use, and reduce greenhouse gas emissions, although the magnitude of these outcomes vary depending on the severity (soil moisture) and timing (crop stage) of the soil drying event(s) (Carrizo et al., 2017; Jiang et al., 2019).

While AWD can mitigate the accumulation of As, it can promote the accumulation of cadmium (Cd), another toxic element (da Silva et al., 2020). Cd phytoavailability in the soil increases with soil aeration due to many reasons, including: the oxidation of sulfur in Cd sulfide precipitates and the consequent release of Cd^{2+} into soil solution; weaker adsorption of Cd^{2+} to manganese and iron hydroxides at lower pH values that are typical of aerobic soils, compared to anaerobic soils; the oxidation (and subsequent removal from soil solution) of Mn^{2+} , which competes with Cd^{2+} and inhibits its uptake by rice roots (Li et al., 2021; Simmons et al., 2008). The maximum level for Cd in polished rice, currently adopted by FAO/WHO, is $400 \mu\text{g g}^{-1}$ (FAO/WHO, 2006). If background levels of Cd in soil and irrigation water are low, the increase in grain Cd concentration resulting from AWD can still maintain safe Cd levels in rice grain (Honma et al., 2016; Li et al., 2019). However, this may not be true in other circumstances, like in parts of China where As and Cd are elevated co-contaminants (Chi et al., 2018; Yu et al., 2016).

Although there has been considerable research on AWD as a strategy to decrease As accumulation in rice grain compared to CF, the magnitude of

the decrease varies widely (0–90%) across studies (Acharjee et al., 2021; da Silva et al., 2020; Norton et al., 2017). Similarly, there is high variability among studies reporting on the effect of AWD on Cd accumulation in rice grain (from no increase up to 9-fold increase, compared to CF) (da Silva et al., 2020; Xu et al., 2019). This variability is likely due to differences in AWD management, plant genetics and soil characteristics across studies. Here we provide the first quantitative review of the literature of field studies reporting on the effect of AWD on As and Cd accumulation in rice grain. We hypothesized that the severity of soil drying under AWD would be the main factor leading to a decrease in total and inorganic As, and to an increase in Cd levels in rice grain.

2. Materials and methods

2.1. Data collection

We searched Google Scholar for research articles published any time before September 2021 that reported rice grain total As (tAs), inorganic As (iAs) and/or Cd under AWD irrigation compared to CF (control treatment) in field experiments. We searched for articles containing the words “rice” and (“irrigation” or “water management”) and (“arsenic” or “cadmium”) and “grain” occurring anywhere in the article. Here, we refer to CF as an irrigation practice where the soil is kept submerged from the initial flood (i.e., transplanting in transplanted systems, sowing in water seeded systems, or 3–4 leaf stage in drill seeded systems) until the pre-harvest drainage. In AWD, at least once between the initial flood and the pre-harvest drainage, the soil is allowed to dry and is subsequently reflooded.

We only selected studies that included information on a set of 13 predictor variables, which were chosen for modelling because they were frequently reported and/or are known to affect As and Cd accumulation under AWD. A detailed description of all variables is presented in Table 1. The following variables are related to general study conditions: soil organic matter (SOM), soil pH, soil clay content, soil total As or Cd concentration,

Table 1
Description of the 13 predictor variables evaluated in the models.

Variable name	Description	Range of values or categories
SOM (%)	Soil organic matter.	0.95–4.15
pH	Soil pH, measured pre-flooding.	4.4–8.3
Clay (%)	Soil clay content.	9.4–60.4
Soil total As or Cd (mg kg^{-1})	Soil background total As or Cd concentration.	Soil As: 0.252–26.2 Soil Cd: 0.009–6.4
Organic fertilizer	Whether any organic fertilizer was applied pre-plant or during the growing season.	Yes; no.
Rice cultivar group	Group (or subspecies) comprising the rice cultivar (genotype).	<i>Japonica</i> ; <i>indica</i> ; aus; aus-admix.
Rice hybrid	Whether the cultivar used is a hybrid.	Yes; no.
Grain type	Grain type used for tAs, iAs and/or Cd measurement.	White (i.e., polished); brown (i.e., unpolished); hulled.
AWD SWP (kPa)	Soil water potential in the rooting zone immediately before reflooding.	0 – (–162)
AWD vegetative stage	Related to when in the growing season AWD was implemented, from the start of the first drying period thru the reflooding of the last drying period, including flooding periods in between.	Yes; no. Yes if AWD treatment spanned any period before panicle initiation (i.e., from initial flood to maximum tillering).
AWD early reproductive stage		Yes; no. Yes if AWD treatment spanned any period between (and including) panicle initiation and booting.
AWD late reproductive stage		Yes; no. Yes if AWD treatment spanned any period after booting (i.e., heading and later).
AWD seasonal span	The span of the AWD treatment in relation to the three growth stages above.	1; 2; 3.

use of organic fertilizers, rice cultivar group, rice hybrid and grain type. When SOM was not reported, it was estimated by multiplying soil organic carbon by 1.72 (Nelson and Sommers, 1982). The percent clay in the soil was considered to be representative of soil texture because in some studies it was the only particle size fraction reported. The remaining five variables are related to AWD management, as described below.

The severity of the soil drying event(s) in AWD is represented by the soil water potential (SWP) measured in the root zone immediately before reflooding. SWP is a measurement of how tightly the soil water is bound to soil particles and is a good indicator of plant available water. It is given in units of pressure, which is often negative in the soil, indicating tension of the water to the soil particles, and more negative SWP values generally indicate less plant available water. We chose SWP as a measure of soil moisture because it was the most frequently reported, although we identified some studies [e.g., Das et al., 2016; Linquist et al., 2015] where a different soil moisture measurement was reported and therefore were not included in our study. When multiple drying events were imposed and slightly different SWP values were reported for each event, we averaged SWP across events. SWP was measured in various ways across the studies, either directly (e.g., tensiometers or resistance-based sensors) or indirectly (e.g., soil moisture release curves constructed from tempe cells), and the rooting zone where the measurements were taken varied slightly (10–25 cm depth, Electronic Supplementary Materials). Further, based on results from a summary of experiments in Asia, we assumed SWP to be -10 kPa when Safe AWD (perched water level of 15 cm below the soil surface) was conducted (Lampayan et al., 2015) and in one case (Fernández-Baca et al., 2021) we assumed SWP to be zero because, according to the authors, the soil dried to near saturation in the given AWD treatment.

The other variables related to AWD management were selected in the process of feature engineering during model development and, in combination, are related to when AWD was practiced in the season. As an example, consider an AWD treatment where the first drying event started at the tillering stage and was followed by two drying events, the last one being reflooded at the booting stage and followed by CF thereafter, until the pre-harvest drain. This AWD treatment would be classified as “yes” for AWD vegetative stage, “yes” for AWD early reproductive stage, “no” for AWD late reproductive stage, and the AWD seasonal span would be two stages (vegetative + early reproductive). An additional reason for including AWD seasonal span in our models, was that this variable was correlated with the number of AWD drying events conducted (see Results), which was not reported by several studies.

In addition to the data collected from the literature, our database comprises new data on Cd concentration that was measured on grain samples obtained from two published studies that reported on As concentration only (Carrijo et al., 2019; LaHue et al., 2016). Brown and white rice samples from all experimental units ($n = 36$) from the LaHue et al. (2016) study and the “CF” and “High Severity-Panicke Initiation” treatments ($n = 16$) from the Carrijo et al. (2019) study were analyzed for Cd. Grain (0.5 g) was digested with 5 mL of 65% HNO_3 and 3 mL of 30% H_2O_2 in a block digestion system and Cd was quantified using Inductively Coupled Plasma Mass Spectrometry [ICP-MS 7900 Agilent Technologies, (Carrijo et al., 2019) and ICP-MS Perkin-Elmer Elan DRC (LaHue et al., 2016)]. All samples were analyzed in duplicates and for each batch, two blanks and one certified reference material (NIST 1568b, National Institute of Standards and Technology, Gaithersburg, MD, USA) were included for quality control.

2.2. Dataset groups

We grouped the data into three datasets corresponding to the elements of interest (tAs, iAs and Cd). Within each dataset and for each observation (side-by-side comparison between AWD and CF), we calculated the response variable, AWD effect:

$$\text{AWD effect} = \frac{\text{Conc}_{\text{AWD}}}{\text{Conc}_{\text{CF}}} \quad (1)$$

where $\text{Conc} (\mu\text{g kg}^{-1})$ = concentration of tAs, iAs or Cd measured in rice grain.

Cd data from one year of one study [year 2015 in Li et al., 2019] were identified as outliers and were removed after a thorough evaluation of the study revealed that seasonal fluctuation of Cd levels in the irrigation water may have led to elevated grain Cd concentration in the AWD treatment [Table S4 in Li et al., 2019]. Prior to modelling, we took the natural logarithm of the AWD effect to linearize the metric and increase normality of sample distribution (Hedges et al., 1999). For ease of interpretation, all the graphs herein showing the AWD effect were backtransformed, so that an AWD effect of 1.0 means that the element concentration in rice grain is the same under AWD and CF irrigation.

2.3. Random forest regression modelling

Random forest is a non-parametric modelling method that can account for non-linear relationships between multiple variables (Breiman, 2001) and has been widely used to predict the fate of contaminants in agroecosystems (Hu et al., 2020; Sengupta et al., 2021; Wang et al., 2020). We used the ‘caret’ package in R software (Kuhn, 2008; Team, 2021) to develop all random forest regression models herein. First, each dataset was split into training (75%) and testing (25%) data, and the former was fit to the full random forest model containing all 13 predictors and the natural log of the response variable (AWD effect). We used the “train” function to fit the model over different tuning parameters (mtry) and automatically select the model with the least mean squared error (MSE). Weights (w) were given to observations based on the sample size method proposed by Schmidt and Hunter (2015) and modified to include the term “grain types”, which accounts for situations where element concentration was measured in different grain types from the same sample (e.g., tAs concentration measured in both white and brown rice, resulting in two observations representing one experimental unit):

$$w = \frac{\text{rep} \times \text{experiment}}{\text{grain types}} \quad (2)$$

where rep = number of treatment replications, experiment = number of site-years, grain types = number of grain types analyzed per experimental unit. Study bias was assessed visually using funnel plots (package ‘metafor’) and using the inverse of the weight as the estimator of variance (Borenstein et al., 2021).

After fitting the training data to the full model, we performed cross validation to calibrate the model and avoid overfitting. We determined the optimum cross validation parameters (number of folds and repetitions) by selecting the calibrated model with closest MSE to that obtained between the uncalibrated model's predictions and the testing data. We then performed feature engineering on the training data, starting with the calibrated, full model. The final model was selected based on the least out-of-bag MSE. Finally, the final model was applied to the testing data and the model's performance was assessed by computing the MSE and the coefficient of determination (R^2) between the observed (i.e., test data) and the model predicted values.

Using the final model, variable importance was assessed using the Gini index (mean decrease in node impurity) and is presented here as a percentage relative to the importance of all variables. Partial dependence plots (PDPs) were also created based on the final model to visualize how a single variable impacts the outcome of the prediction (i.e., marginal effect of one variable). To reduce the likelihood of presenting results that are unconstrained by data, we restricted each predictor variable in the PDP to the 5th and 95th percentiles for continuous variables and, for categorical variables, we ensured that each category present in the PDP was represented by more than one study (all categories met this requirement). To facilitate visualization of general trends observed in PDPs from continuous variables, the marginalized predictions were fit to a locally weighted polynomial (LOESS) regression curve and a 95% confidence interval for the regression fit was calculated. PDPs of the most important variables (relative

importance >20% based on the Gini index) are presented in the main article, while PDPs of less important variables are presented in the Supplementary Materials.

2.4. Relationship between total and inorganic As under AWD

Because the iAs dataset included measurements of tAs taken on the same sample, we used this dataset to determine how AWD affects the relationship between tAs and iAs. Thus, in addition to the iAs model, we developed two random forest models (as described above) using the iAs dataset: one on the paired tAs data (response variable = AWD effect on tAs) and the other with the response variable being iAs as a percentage of tAs [iAs, % of tAs]:

$$iAs, \% \text{ of } tAs = \left(\frac{Conc_{iAs}}{Conc_{tAs}} \right) \times 100 \quad (4)$$

where Conc ($\mu\text{g kg}^{-1}$) = concentration in rice grain from plants grown under AWD irrigation.

Finally, marginal effects of the most important variable in the iAs, tAs and [iAs, % of tAs] models were extracted and combined into one PDP.

2.5. Concomitant effect of AWD on total As and Cd

The Cd dataset also included paired tAs data, thus we used this dataset to investigate the dual effect of AWD on Cd and tAs. We first developed a random forest model (as described above) for the paired tAs data (response variable = AWD effect on tAs). We then extracted the marginal effects of the interaction of the most important variables in the tAs and Cd models and combined them into one PDP. We also calculated the trade-off value, modified from Honma et al. (2016):

$$\text{Trade-off value} = \frac{\text{Pred AWD effect}_{iAs}}{\max(\text{Pred AWD effect}_{iAs})} + \frac{\text{Pred AWD effect}_{Cd}}{\max(\text{Pred AWD effect}_{Cd})} \quad (3)$$

where Pred AWD effect = predicted AWD effect marginalized over the interaction of the most important variables.

3. Results

3.1. Overview of datasets

The literature search returned 30,800 articles, of which we reviewed the most relevant 1000 because the articles became increasingly off-topic as the relevancy decreased. Seventeen studies met our criteria and a total of 321, 124 and 181 observations were included in the tAs, iAs and Cd

datasets, respectively (Table S1). Importantly, many studies were excluded for not reporting the severity of soil drying imposed with AWD. The Cd dataset includes 36 observations that have not been published before and are synthesized in Table S2. The complete database with information on individual studies and observations is available in the Electronic Supplementary Material.

While the tAs and Cd datasets include studies from different countries, the iAs dataset comprises USA studies only (Table S1) and models derived from this dataset had generally lower predictive power (Table S3). Funnel plots created for each weighted mean AWD effect (one per model) did not indicate the presence of study bias (Fig. S1). Across all datasets and treatments (AWD and CF), rice grain concentration of tAs, iAs and Cd ranged from 25 to 750 (mean = 150), 19–96 (mean = 47) and 0–257 (mean = 34) $\mu\text{g kg}^{-1}$, respectively (Electronic Supplementary Material).

Overall, based on unweighted observations, AWD decreased tAs by 32% (median AWD effect = 0.68), decreased iAs by 22% (median AWD effect = 0.78) and increased Cd by 58% (median AWD effect = 0.42), compared to CF (Fig. 1). Median AWD effects for paired tAs data from the iAs (0.58) and Cd (0.75) datasets were similar to that observed in the tAs dataset (0.68).

Based on partial data available (87% of all observations in our database), AWD seasonal span was correlated with the number of AWD drying events (Kruskal-Wallis test $p < 0.001$). The average number of AWD drying events followed by the standard error of the mean for an AWD seasonal span of one, two and three stages were 1.1 (0.06), 3.5 (0.27), 4.8 (0.38).

3.2. Soil water potential is the main driver of tAs and iAs in rice grain under AWD

Across the 13 variables evaluated as potential predictors of the AWD effect on tAs, SWP was by far the most important variable, with a relative importance of 52% (Fig. 2). AWD timing (i.e., AWD vegetative stage, early reproductive stage, late reproductive stage), AWD seasonal span, soil texture (i.e., clay) and SOM provided small contributions to the model. SWP was also the most important variable in the iAs model (relative importance of 89%, Fig. 2). Unlike the tAs model, only one variable representing AWD timing (AWD vegetative stage) contributed to the iAs model, with a relative importance of 11%. Further, none of the variables representing study conditions (e.g., soil properties, rice cultivar group) contributed to the iAs model, although we could not evaluate the impact of organic fertilizers and hybrids because all studies in the iAs dataset involved conventional fertilizers and non-hybrid rice cultivars.

PDPs for SWP illustrate how predictions are affected by changes in SWP alone (Fig. 2). They predict a steep drop in the AWD effect on grain tAs (10% to 40% reduction, compared to CF) as SWP decreases from zero (soil saturation) to approximately -20 kPa, after which there is only a minor decrease in AWD effect with decreasing SWP. Compared to CF, drying the soil to -20 kPa can decrease tAs in rice grain by 40% on average and by 52% if all other (less important) variables are simulated to minimize

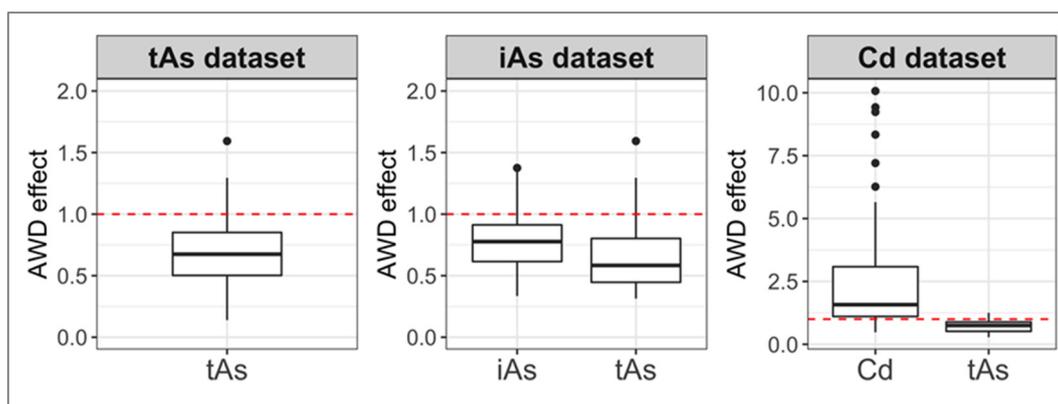


Fig. 1. Boxplots of unweighted observations in the total As (tAs), inorganic As (iAs) and Cd datasets. The bold horizontal line indicates the median. The iAs and Cd datasets include paired tAs data. AWD effect = grain concentration in AWD relative to that in CF. The red dotted line indicates an AWD effect of 1 (i.e., grain concentration in AWD is the same as that in CF).

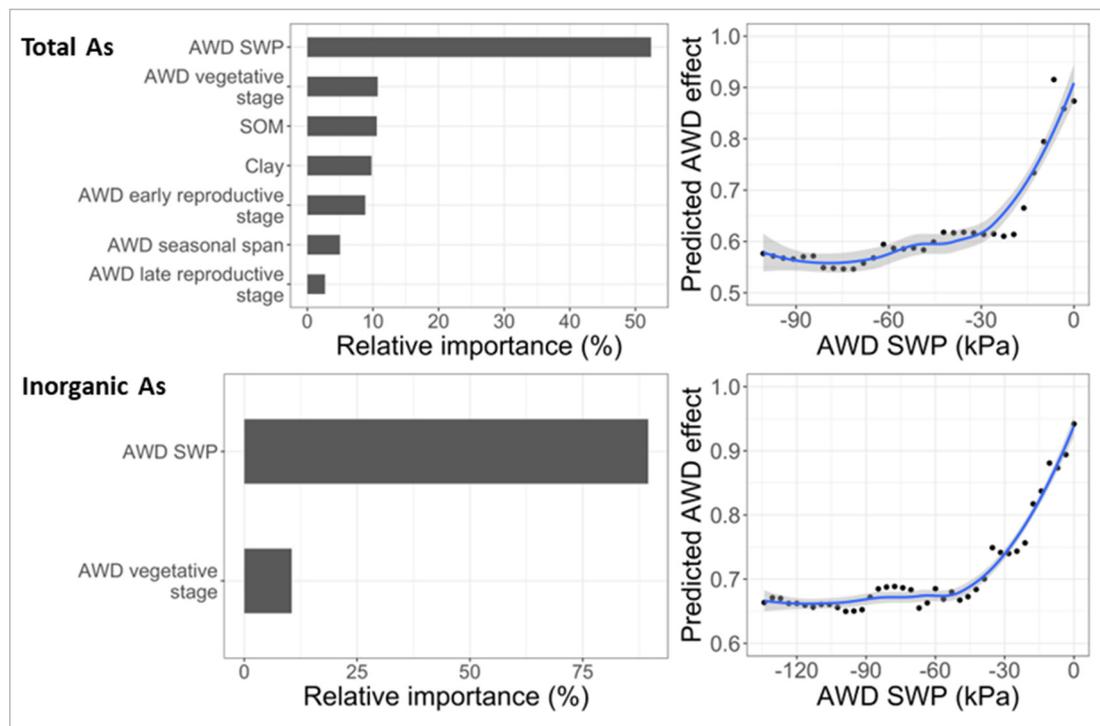


Fig. 2. AWD effect (grain concentration in AWD relative to that in CF) on total As and inorganic As. Variable importance plots (left) are based on the Gini index. Partial dependence plots (right) are presented for the most important variable. For visualization purposes, predictions (points) were fitted to a LOESS regression (lines) and shades represent the 95% confidence interval of the regression. It should be noted that the LOESS fit was poor for total As around SWP -15 to -30 kPa (upper right). SWP = soil water potential, SOM = soil organic matter. AWD vegetative, AWD early reproductive and AWD late reproductive stages, and AWD seasonal span are described in the Materials and Methods. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

the AWD effect (PDPs are presented in Fig. S2). The iAs model predicts a similar trend of decreasing AWD effect with decreasing SWP, but the curve levels off at a lower SWP (approximately -45 kPa) compared to the tAs model (-20 kPa). Compared to CF, drying the soil to -45 kPa can decrease iAs in rice grain by 32% on average and by 36% if AWD is implemented after the vegetative stage (PDP is presented in Fig. S3 of the Supporting Information).

3.3. Under AWD tAs decreases more than iAs

To determine the relationship between tAs and iAs under AWD, we used paired tAs and iAs data to model the proportion of iAs relative to tAs in grain [iAs, % of tAs]. The model indicated that the [iAs, % of tAs] depends on the severity of soil drying implemented with AWD and is higher with increased soil drying (Fig. 3). As a result, while decreasing SWP is effective at decreasing both tAs and iAs, the decrease in iAs is smaller. For example, if SWP is decreased from -10 to -45 kPa, is more impactful at decreasing tAs (18% decrease at -10 kPa and 50% decrease at -45 kPa, compared to CF), than at decreasing iAs (10% decrease at -10 kPa and 34% decrease at -45 kPa, compared to CF) because iAs makes up a larger proportion of tAs at -45 kPa (75%) than at -10 kPa (65%).

3.4. Timing is the main driver of Cd in rice grain under AWD

Contrary to our hypothesis, the most important variable (relative importance = 29%) in the Cd model was related to AWD timing, specifically, whether AWD occurred during the early reproductive stage (i.e., panicle initiation thru booting) (Fig. 4A). The AWD SWP and AWD seasonal span were also important, with relative importances of 24 and 21%, respectively. Less important (relative importance < 20%) variables that contributed to the model include the background concentration of Cd in the soil and the two other variables related to AWD timing (AWD vegetative stage and AWD late reproductive stage). We could not evaluate the impact of organic

fertilizer use because none of the studies in this dataset involved the addition of organic fertilizers.

PDPs for the most important variables in the Cd model are presented in Fig. 4B. It is helpful to interpret the results for AWD early reproductive stage and AWD seasonal span together because both variables are related to when AWD was practiced in the season. Based on the model, more Cd is accumulated in rice grain if AWD occurs during the early reproductive stage. In addition, more Cd is accumulated when AWD spans more than one stage,

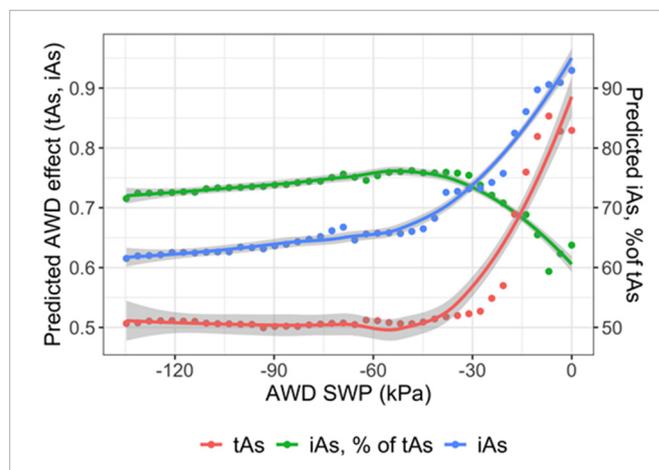


Fig. 3. Partial dependence plot for soil water potential (SWP), based on iAs, tAs and [iAs, % of tAs] models developed from paired total As (tAs) and inorganic As (iAs) data. For visualization purposes, predictions (points) were fitted to a LOESS regression (lines) and shades represent the 95% confidence interval of the regression. It should be noted that the LOESS fit was poor for tAs around SWP -15 to -30 kPa. AWD effect = grain concentration in AWD relative to that in CF. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

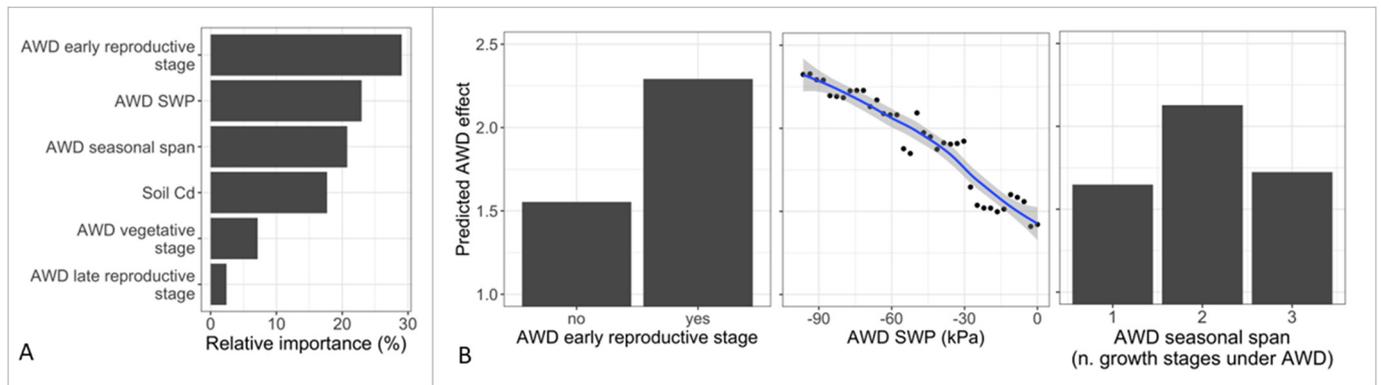


Fig. 4. AWD effect (grain concentration in AWD relative to that in CF) on Cd. A) Variable importance plot based on the Gini index. B) Partial dependence plots for the most important variables. For visualization purposes, predictions (points) were fitted to a LOESS regression (lines) and shades represent the 95% confidence interval of the regression. SWP = soil water potential. AWD vegetative stage, AWD early reproductive stage, AWD late reproductive stage and AWD seasonal span are described in the Methods. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

compared to a single stage. Together, these results indicate that implementing AWD during the early reproductive stage leads to a substantial increase in grain Cd, compared to CF, and a further increase is expected if AWD also occurs during the vegetative and/or late reproductive stages. In addition, the model predicts an approximately linear increase in the AWD effect on Cd (from 150% to 230%, compared to CF) as the AWD SWP decreases from near zero to -90 kPa. When all variables in the model are simulated to enhance Cd accumulation, grain Cd concentration is more than 4 times higher in AWD compared to CF (Fig. 4B and Fig. S4).

It is worth noting that despite the predicted decrease in AWD effect when AWD span increases from two to three stages (Fig. 4B), this is likely an artifact of all the observations with an AWD span of three in this dataset being associated with high SWP values (≥ -15 kPa). When we repeated this analysis accounting for six growth stages (early tillering, late tillering, panicle initiation, booting, heading and ripening), there was a trend of increasing AWD effect with increasing number of growth stages (Fig. S5). We therefore expect that longer AWD seasonal span is associated with higher Cd accumulation.

3.5. Water management when both Cd and As are important

To determine the concomitant effect of AWD on Cd and As, we modelled paired tAs data ($n = 181$) from the Cd dataset. In agreement with the tAs model ($n = 321$, Fig. 2), the most important variable in the paired tAs model was AWD SWP (relative importance = 43%, data not shown). Interaction PDPs were obtained for the most important variables affecting tAs and Cd (AWD SWP, AWD early reproductive stage and AWD seasonal span) (Fig. 5). Overall, AWD had a larger impact on grain Cd than grain tAs. For example, depending on how AWD is managed, grain Cd concentration may increase more than 4 times, while tAs concentration may decrease only by half, relative to CF. In agreement with the unpaired tAs model ($n = 321$), AWD timing (i.e., rice growth stage(s) when AWD occurred) did not impact tAs as much as Cd, although tAs predictions are lower when AWD occurs in the early reproductive stage and/or spans more than one stage, which is the opposite trend of that observed for Cd. The minimum trade-off value was observed when the soil was dried to -47 kPa either during the vegetative (before panicle initiation) or late reproductive (heading and after) stage. This resulted in an average 41% increase in grain Cd and 35% decrease in grain tAs under AWD, compared to CF.

4. Discussion

The major drivers of all (tAs, iAs and Cd) models in our study were related to how AWD irrigation was practiced, which was expected because model predictions (i.e., AWD effect) were relative to a control irrigation

practice (CF). It is worth noting, however, that other management practices and site-specific characteristics such as soil properties, including the total concentrations of As and Cd in the soil, can have a large impact on actual As and Cd concentrations in rice grain (Hu et al., 2020).

It was somewhat unexpected that soil pH was not an important driver of the AWD effect on Cd, despite the relatively wide range of soil pH represented in the Cd dataset (4.3–7.0, Electronic Supplementary Material). Soil pH is the primary driver of Cd solubility in soils and because flooding tends to bring soil pH near neutrality, CF is generally more effective at decreasing Cd solubility in acidic soils, compared to neutral soils (Chen et al., 2016; Huang et al., 2021). It is likely that interactions between soil pH and SWP influenced the AWD effect on Cd but were purged from the model due to the larger main effect of SWP and the relatively small dataset, which limited the exploration of interactions. Similarly, interactions between SWP and other soil properties were possible but not detected due to lack of data; for example, the increase in grain Cd due to AWD could be higher in soils that are richer in iron and manganese (oxy)hydroxides, which after oxidation caused by soil drying, release Cd in the porewater (Huang et al., 2021).

4.1. Rice grain total and inorganic As under AWD

Arsenic phytoavailability in soil is largely determined by soil redox potential (Eh) (Tufano et al., 2008) and because Eh is positively correlated with soil moisture, and thus inversely correlated with oxygen content, it is not surprising that SWP was the major driver of grain tAs and iAs concentrations under AWD (Fig. 2). Importantly, the SWP values (< -20 kPa) required here for minimum tAs and iAs concentrations are often associated with reduced yields (Carrijo et al., 2017; Monaco et al., 2021; Song et al., 2018), although there are exceptions (Carrijo et al., 2018; Chlapecka et al., 2021; Kumar et al., 2017). Still, substantial reductions in grain tAs (up to 52%) and iAs (up to 27%) can be achieved if the soil is dried to -20 kPa (Fig. 2).

Both the tAs and the iAs PDPs show an abrupt change in slope at a critical SWP, where further soil drying translates to little or no decrease in As in rice grain (Fig. 2). This was also observed in studies comparing AWD treatments differing solely in the severity of soil drying (similar AWD timing, span, number of drying events) (Carrijo et al., 2018; Linguist et al., 2015). One possible explanation for this sudden lack of response to soil drying is that, when the soil is dried to this critical SWP (approximately -20 kPa for tAs and -55 kPa for iAs), As phytoavailability remains low beyond the drying period and thru the subsequent drying event (assuming multiple drying events, which represents the majority of our database). As a result, the total number of days in which As uptake is prevented/lowered is the same whether the soil is dried to that critical SWP or beyond it. Arsenic phytoavailability can remain low beyond the drying period because As is

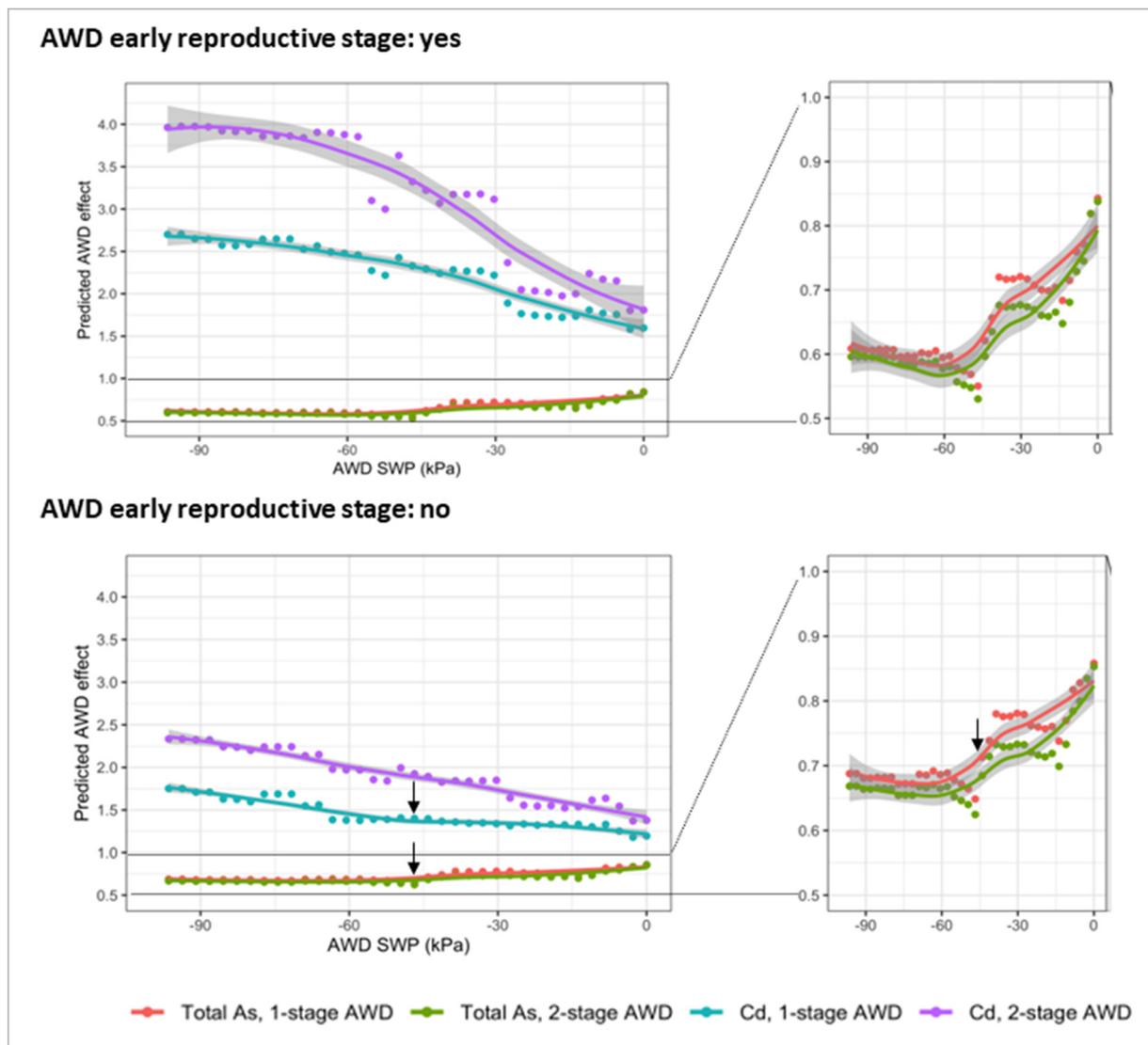


Fig. 5. Concomitant AWD effect (grain concentration in AWD relative to that in CF) on Cd and total As based on paired data. Interaction partial dependence plots were obtained for the most important variables affecting total As and Cd [AWD SWP, AWD early reproductive stage and AWD seasonal span (only one and two stages are shown for simplicity)]. For visualization purposes, predictions (points) were fitted to a LOESS regression (lines) and shades represent the 95% confidence interval of the regression. Dotted sections were amplified (right). Arrows indicate the scenario of minimum trade-off, which occurred when AWD was implemented at a SWP of -47 kPa during one stage other than the early reproductive. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

often immobilized (upon soil drying) faster than it is mobilized (upon reflooding), due to the faster kinetics of arsenate reduction compared to arsenite oxidation (Couture et al., 2015; Onken and Hossner, 1996; Takamatsu et al., 1982). Alternatively, it is possible that severe drying causes soil Eh to remain high (and, as a consequence, As phytoavailability to remain low) beyond the drying period, as this lack of response to increased soil drying was also observed for methane emissions (Balaine et al., 2019).

Paired tAs and iAs data from AWD plots indicated that the proportion of iAs relative to tAs in rice grain [iAs,% of tAs] increases with soil drying (Fig. 3). Higher [iAs,% of tAs] was also observed in upland rice when compared to flooded rice (Moreno-Jiménez et al., 2014; Xu et al., 2008). This is likely a result of aerobic soil conditions favoring demethylation over methylation reactions promoted by soil biota, resulting in a higher proportion of iAs relative to tAs in the soil solution which is subsequently reflected in the rice grain (Reid et al., 2017). In practice, AWD is less effective in mitigating the accumulation of iAs (up to 36% at -45 kPa) than tAs (up to 52% at -20 kPa) and, if the goal is to decrease grain iAs, the soil should be dried further than it would for decreasing tAs alone.

4.2. Rice grain Cd under AWD

In contrast to As, Cd phytoavailability in soil increases under aerobic conditions (Simmons et al., 2008), thus it was not surprising that Cd concentration in rice grain increased with decreasing SWP (Fig. 4B). Also, unlike As, both mobilization (upon soil drying) and immobilization (upon flooding) of soil Cd are rapid processes, with almost complete mobilization/immobilization occurring within 2 days after aerobic/anaerobic conditions develop (Yang et al., 2021). This could explain the near linear relationship between Cd predictions and SWP (Fig. 4B). Alternatively, if severe soil drying causes the soil Eh to remain high (or soil pH to remain low) beyond the drying period, as previously discussed, this higher Eh range may still allow for fluctuations in Cd (but not As) phytoavailability, because Cd reduction-oxidation reactions occur at a higher Eh range compared to As (Honma et al., 2016). Therefore, within the range of SWP values observed here (0–95 kPa), decreasing SWP always translated into increased Cd accumulation. Further, if Cd uptake under AWD occurs almost exclusively during the soil drying (aerobic) periods, then total Cd uptake must be

correlated with the cumulative amount of time in the season during which the soil was unflooded. This may explain why AWD seasonal span, which was correlated with the number of AWD cycles, was important for Cd (Fig. 4A) but not As (Fig. 2).

Grain Cd accumulation under AWD was highest when AWD occurred during the early reproductive stage (Fig. 4). Assuming that phytoavailability of soil Cd is low throughout the season in CF systems (due to flooding effects on soil chemistry), the effect of AWD timing on grain Cd must be based primarily on seasonal patterns of Cd uptake and allocation to the grain, driven by plant physiology alone. In a hydroponic study where a constant rate of Cd was supplied to rice plants either before or after flowering, the majority (60%) of Cd in mature grains was taken up before flowering (vegetative + early reproductive stages) and was remobilized to the grain during grain filling (Rodda et al., 2011). It is unclear how much of that 60% was taken up specifically at the early reproductive stage. However, in field rice grown under CF, manganese uptake was highest during the early reproductive stage (Beyrouthy et al., 1994); thus, the potential for Cd uptake could also be highest at this time, because the manganese transporter OsNramp5 (Natural Resistance-Associated Macrophage Protein 5) is the principal mediator of Cd uptake into rice roots (Ishikawa et al., 2012; Sasaki et al., 2016; Sasaki et al., 2012). This would explain why Cd accumulation was highest when AWD occurred during the early reproductive stage.

4.3. Concomitant effect of AWD on total As and Cd

Paired Cd and tAs data revealed that AWD has a stronger impact on grain Cd than tAs concentrations (Fig. 5). Therefore, if Cd levels under CF are already high, implementing AWD to mitigate As accumulation is likely not a good practice unless it is combined with another strategy to decrease Cd accumulation. For example, AWD can be combined with soil amendments (e.g., lime) to decrease Cd uptake during the aerobic periods (Fang et al., 2021; Shi et al., 2019). AWD can also be combined with genotypes that overexpress OsHMA3, a tonoplast transporter that sequesters Cd into root vacuoles, resulting in near zero Cd levels in grain (Sasaki et al., 2014; Ueno et al., 2010) and no negative impact on yield (Lu et al., 2019). If Cd levels are not high under CF, the models developed here (Fig. 5) can be used to estimate the increase in Cd concentration with AWD and prevent grain Cd from increasing above unsafe levels. Importantly, the best tAs and Cd trade-off scenario, which resulted in a comparable increase in Cd and decrease in tAs, could result in yield losses due to the severity of soil drying required (-47 kPa) (Carrijo et al., 2017).

4.4. Considerations and future directions

In this study, we provide the first quantitative analysis of the field literature on AWD and its impact on As and Cd accumulation in rice grain. We found that AWD management strongly affects grain As and Cd concentrations and the models developed here can serve as guidance for AWD implementation. That said, it is important to recognize that the predictors evaluated in our models were constricted to variables often reported in the literature. It was not possible to evaluate the impact of several potentially important variables, such as the As and Cd levels in irrigation water and soil mineralogy, especially Fe and Mn oxides. Further, although we did not observe an effect of cultivar group (e.g., *japonica*, *indica*) or the use of hybrids (versus conventional cultivars), there is ample evidence that plant genetics affect As and Cd accumulation in rice grain (Cao et al., 2017; Chi et al., 2018; Ishikawa et al., 2012; Kumarathilaka et al., 2018; Lu et al., 2019). Lastly, our database could have been substantially larger if more studies had reported the severity of soil drying, which was identified as a main driver of As and Cd accumulation under AWD. Future AWD studies should report at least one measurement of soil moisture. Our analysis could also have been more comprehensive if more studies reported iAs, rather than tAs only. Inorganic As should be quantified separately, as it is highly toxic, is becoming more prevalent with climate

change, and as exemplified in this study, there is not a fixed relationship between tAs and iAs.

CRediT authorship contribution statement

Daniela R. Carrijo: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing – original draft. **Gabriel T. LaHue:** Investigation, Writing – review & editing. **Sanjai J. Parikh:** Writing – review & editing. **Rufus L. Chaney:** Investigation, Writing – review & editing. **Bruce A. Linquist:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.156245>.

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Supplementary material for manuscript “Mitigating the accumulation of arsenic and cadmium in rice grain: a quantitative review of the role of water management”

Table S1. Overview of the total As (tAs), inorganic As (iAs) and Cd datasets. The contribution of a study to a dataset was calculated as the percentage of observations provided by the study and weighted by Equation (2). One observation represents a side-by-side comparison between AWD and CF in the field.

Study	Field location(s)	Contribution to dataset (%)		
		tAs	iAs ^a	Cd ^a
Acharjee et al., 2022	West Bengal, India	3	-	-
Aguilera et al., 2022	California, USA	2	16	6
Carrijo et al., 2019	California, USA	5	44	1
Li et al., 2019; Carrijo et al., 2018	California, USA	2	21	3
Da Silva et al., 2020	Rio Grande do Sul, Brazil	16	-	38
Fernández-Baca et al., 2021	Arkansas, USA	-	16	-
Islam et al., 2017	Faridpur/Rajshahi/ Mymensingh, Bangladesh	18	-	-
LaHue et al., 2016	California, USA	2	-	4
Martínez-Eixarch et al., 2021	Catalonia, Spain	11	-	-
Monaco et al., 2021	Vercelli, Italy	14	-	-
Norton et al., 2017a	Mymensingh, Bangladesh	1	-	3
Norton et al., 2017b	Madhupur/Rajshahi/ Mymensingh, Bangladesh	13	-	31
Perry et al., 2022	California, USA	4	3	10
Sarkar et al., 2012	West Bengal, India	2	-	-
Sengupta et al., 2021	West Bengal, India	4	-	-
Xu et al., 2019	Yangzhou, China	2	-	4
Total number of observations		321	124	181

^aIncludes paired tAs data, except for one study ⁷.

^bIncludes new Cd data reported in this study.

Table S2. Grain Cd concentration measured in one AWD treatment from study ³, in addition to the control, and all the treatments from study ⁹. Treatment means are followed by standard error of means (n=4 ³ and n=3 ⁹). Recoveries of the reference material (NIST 1568b) are also presented. Duplicate samples of each experimental unit were within 10% of each other and blanks were always below the detection limit.

Study reference	Year	Treatment	Cd (ppb)		Recovery of NIST 1568b
			White	Brown	
LaHue et al., 2016	2016	Continuously flooded (control)	4 (0.3)	4 (0.2)	97%
		High severity, panicle initiation	9 (1.3)	11 (1.4)	
Carrijo et al., 2019	2013	Water seeded (control)	15 (4)	21 (3)	85%
		Water seeded AWD	64 (9)	67 (9)	
		Drill seeded AWD	46 (6)	49 (10)	
	2014	Water seeded (control)	14 (8)	14 (1)	
		Water seeded AWD	43 (11)	67 (7)	
		Drill seeded AWD	46 (13)	61 (8)	

Table S3. Models developed from each dataset. Model tuning parameters (cross validation and mtry) and the resulting mean squared error (MSE, units of the response variable, Eq. 1 and Eq. 4) and coefficient of determination (R^2) between predicted values and new (untrained) values are shown.

Dataset	Model	Response variable	Cross validation (folds, replicates)	mtry	MSE	R^2
Total As	tAs	tAs_{AWD}/tAs_{CF}	5, 10	4	0.020	0.70
Inorganic As	iAs	iAs_{AWD}/iAs_{CF}	10, 10	1	0.018	0.46
	tAs	tAs_{AWD}/tAs_{CF}	10, 10	2	0.031	0.70
	iAs, % of tAs	iAs_{AWD}/tAs_{AWD}	10, 10	2	0.026	0.35
Cd	Cd	Cd_{AWD}/Cd_{CF}	30, 3	4	0.706	0.68
	tAs	tAs_{AWD}/tAs_{CF}	10, 10	5	0.016	0.73

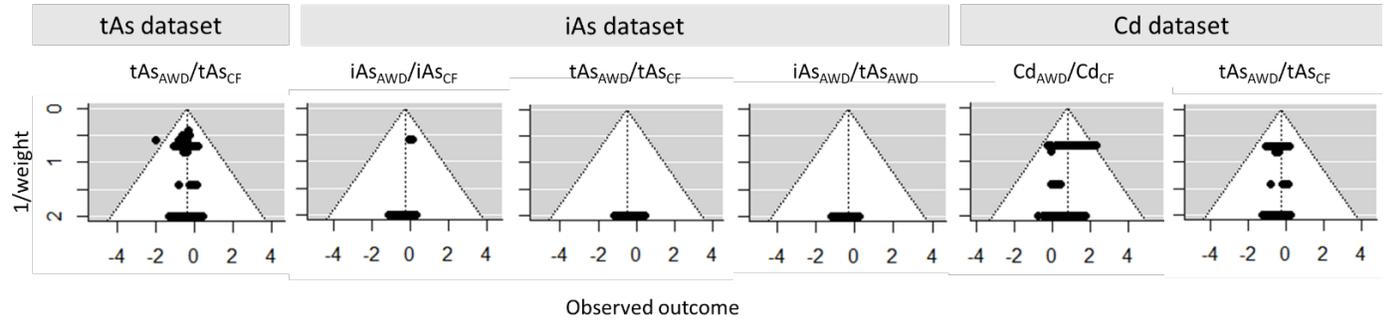


Figure S1. Funnel plots showing study bias for each model. Ideally, data points should fit within the triangle, as it is expected that the range of observed outcomes among studies with large samples sizes (tip of the triangle) should be smaller than that among studies with small sample sizes (bottom of triangle).

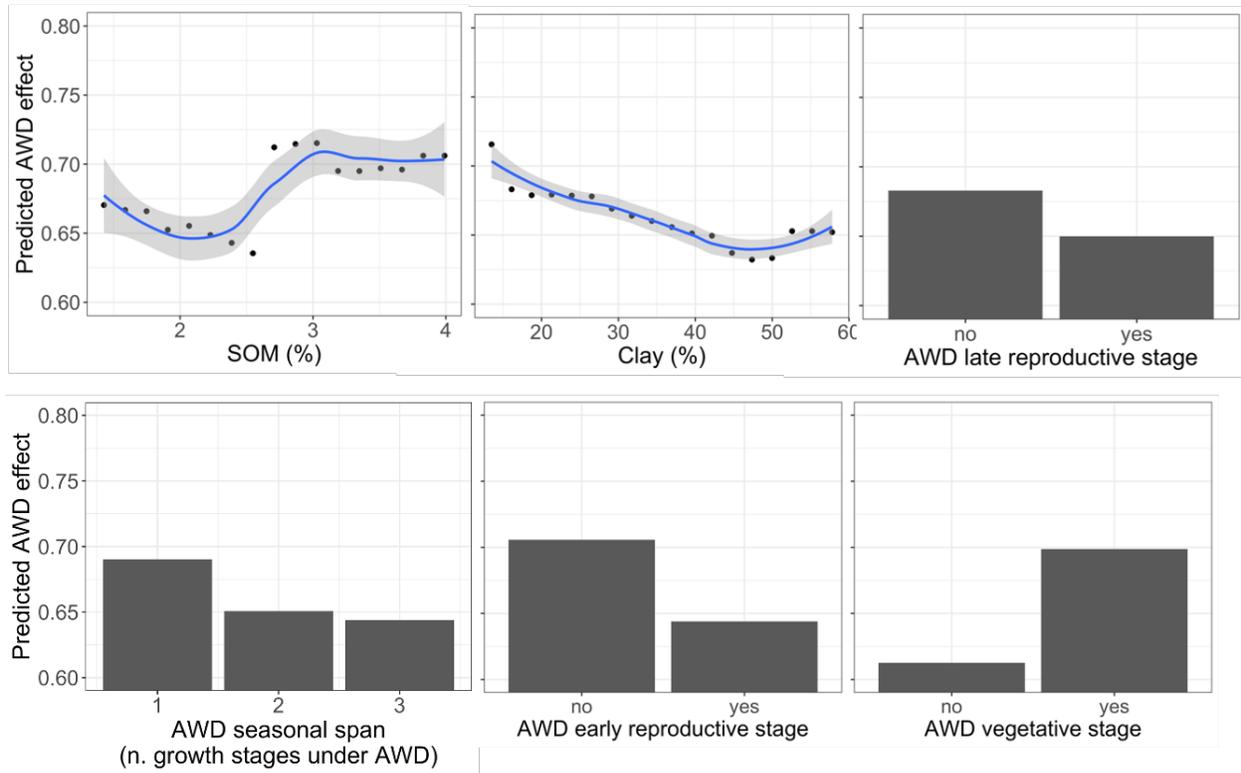


Figure S2. Partial dependence plots for the less important variables (variable importance <20% based on the Gini index) of the total As model. Predicted values (points) were fitted to a LOESS curve (blue lines) and shades represent the 95% confidence interval of the regression. SWT=soil water tension, SOM=soil organic matter. AWD vegetative stage, AWD early reproductive stage, AWD late reproductive stage and AWD seasonal span are described in the Methods. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

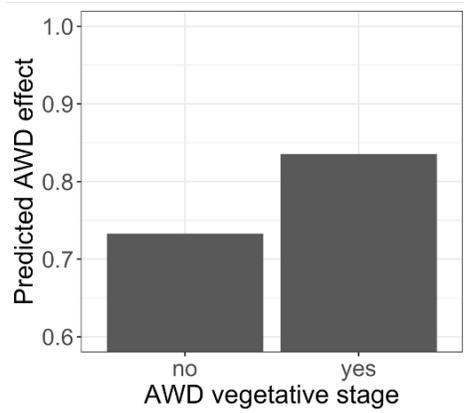


Figure S3. Partial dependence plot for the less important variable (variable importance <20% based on the Gini index) of the inorganic As model. AWD vegetative stage is described in the Methods. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

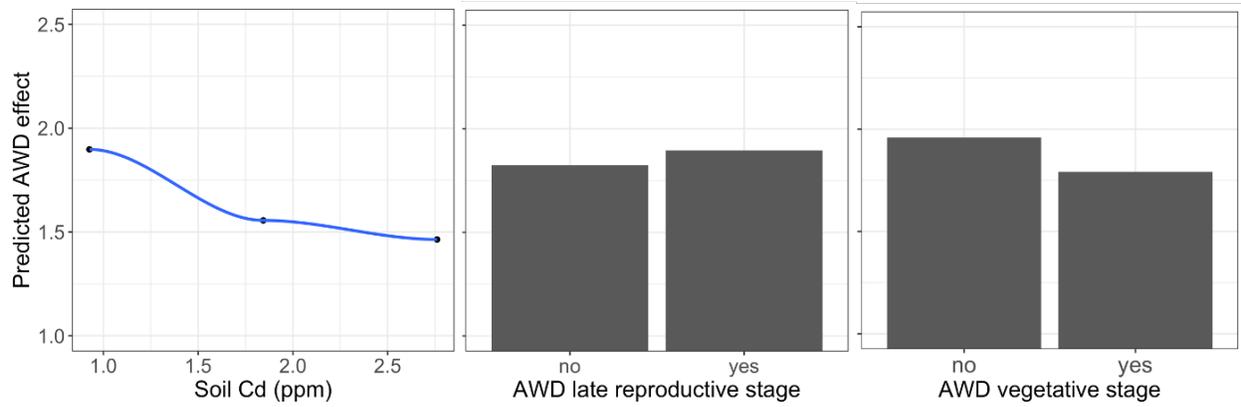


Figure S4. Partial dependence plots for the less important variables (variable importance <20% based on the Gini index) of the Cd model. Predicted values (points) were fitted to a LOESS curve (blue line). AWD vegetative stage and AWD late reproductive stage are described in the Methods. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

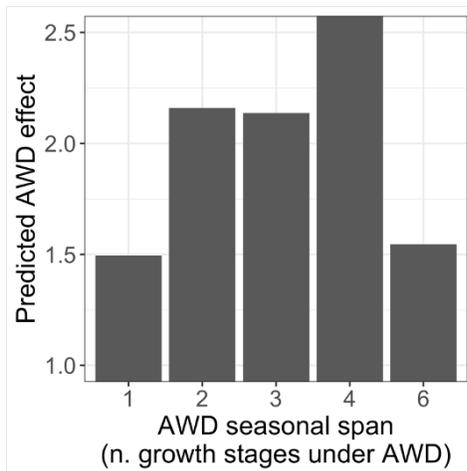


Figure S5. Partial dependence plot for the effect of AWD seasonal span, based on six instead of three rice stages, on the Cd model. The six stages considered were: early tillering, late tillering, panicle initiation, booting, heading and grain filling. All observations from category “6” were associated with high (≥ -15 kPa) soil water potential values. AWD effect = 1 indicates that grain concentration in AWD is the same as that in CF.

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