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Associations between Inorganic Arsenic in Rice and Groundwater Arsenic in the Mekong Delta

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***Highlights (3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Highlights

- 7% of Mekong Delta husked rice exceeded limit for inorganic As
- Grain inorganic As was not related to total soil As
- Grain inorganic As was correlated with local groundwater As
- Links between surface and subsurface soluble As may be due to local aquifer recharge

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Abstract

There is growing concern regarding human dietary exposure to arsenic (As) via consumption of rice. The concentration and speciation of As in rice are highly variable, and models describing rice As speciation as a function of environmental covariates remain elusive. We conducted a survey of paddy rice and soil in the Mekong Delta with the objective of linking patterns in rice As content to soil chemical variables or hydrogeological parameters. The sum of As species (ΣAs) in husked rice averaged 243 μg/kg and the average inorganic As (iAs) content was 84%. There was no relationship found between rice As concentration or speciation and As levels in soil. However, mean As concentrations in groundwater near rice sampling locations were strongly correlated with grain ΣAs and iAs over a large part of the study region, despite the fact that groundwater is not commonly used for rice paddy irrigation in this region. We hypothesize that surficial sediments with high concentrations of soluble and plant-available As also serve as sources of arsenic to downgradient shallow aquifers, explaining the observed associations between rice and groundwater As. This study suggests that shallow groundwater As concentrations may serve as a useful indicator for locations at risk of elevated iAs concentrations in rice.

Introduction

Rice is a food staple for half of the global population and is also a major dietary source of inorganic arsenic (iAs), a non-threshold carcinogen, for humans[1-5]. Rice plants efficiently assimilate arsenic (As) from soils due to growth in flooded conditions in which As is mobilized from the reductive dissolution of iron (Fe) (oxy)hydroxide mineral phases[6-7], and to transporters in rice roots[8-10] which facilitate the inadvertent uptake of As from pore waters. While the processes governing As solubilization in and plant uptake from flooded soils are well-established[3, 11-13], the complexity of these processes has made it a challenge to build models that effectively describe geographic variations in As concentration and speciation in rice as a function of environmental co-variates [14-15].

Interactions between surface environments and shallow aquifers play an important role in the cycling of As in the basins of South and Southeast Asia that are heavily impacted by geogenic As contamination and where rice is a major agricultural crop [16]. In the Bengal Basin, irrigation of dry-season rice with groundwater elevated in As has been linked to increased bioavailable As in paddy soils and consequently high levels of As in rice[1, 17-18]. At the same time, studies in Bangladesh and the Cambodian Mekong Delta have shown that the mobilization of As from river-derived surficial sediments and subsequent hydrological transport to shallow aquifers serves as a control on As distributions in groundwater[19-22]. Surficial environments like rice paddies can thus serve as receptors of subsurface As in irrigation water as well as sources of As to groundwater via aquifer recharge. While the former process is well-recognized as an influence on As bioavailability and plant uptake in rice paddies[17, 23-24], the latter process has received little attention in efforts to describe spatial variations in rice arsenic as a function of environmental variables.

The objective of this investigation was to determine relationships between As speciation in rice and environmental covariates in the Vietnamese Mekong Delta, an important rice-producing region. Recent research in this region has shown that 38% of surveyed rice exceeded the permissible maximum concentration of iAs for children[25], highlighting the need for approaches to identify areas at risk for elevated iAs in rice. Similar to the neighboring Mekong Delta region of Cambodia, rice in this region is primarily irrigated with surface water but there is concern that groundwater – which is elevated in As in much of this region – will increasingly be used for irrigation in the future[14, 26-29]. This study combines original measurements of As speciation in rice collected from the Mekong Delta with analysis of soil-chemical variables and hydrogeochemical parameters gathered from databases to explore associations between As speciation in rice grains and environmental covariates.

Materials and Methods

Rice and Soil Collection and Processing. Rice (n=45) and soil (n=16) samples were collected at harvest in November 2014, March 2015, and March 2018 along a ca. 60 km stretch of the Bassac and Mekong Rivers in Vietnam. Most samples were collected from districts in An Giang (AG) Province: An Phu (AG-AP), Chau Doc (AG-CD), Chau Phu (AG-CP), Phu Tan (AG-PT), Choi Moi (AG-CM), and Tan Chau (AG-TC) (Figure 1). A limited number of additional samples were collected in Long An (LA) and Dong Thap (DT) Provinces. Because the sample size is relatively small and involves analysis of husked instead of white rice, this work should not be interpreted as a comprehensive survey or as a food safety risk assessment, but rather as an examination of associations between As speciation in rice and environmental variables. All but one farmer reported using surface and not groundwater for irrigation (Sample AP-15, see Supplementary Information (SI)). Additional sampling details and procedures for As extraction from rice grains are described in SI. Extraction efficiency and analytical precision were evaluated using NIST Standard Reference Material (SRM) 1568b.

Hydrogeochemical Data. Arsenic concentrations and well depths from > 50,000 groundwater wells, previously published in Erban, et al. [26], were used to examine relationships between grain As and local groundwater As concentrations. Arsenic concentrations (Fig. 1A) from wells within 1.5 km of each rice sampling location were aggregated due to well-documented spatial variability in As concentrations in deltaic aquifers[16, 30-31]. 336 groundwater samples were included in this analysis, with more than two-thirds of the groundwater samples drawn from wells within 1 km of the rice sampling location (Fig. S1). Additional details regarding selection of groundwater data are available in SI. Information on the thickness of the clay layer between the surface and the aquifer sediments was gathered from borehole logs from the Department of Water Resources Planning and Investigation for the South (DWRPIS) of Vietnam. DWRPIS borehole data were supplemented with a limited number of original sediment cores[32]. Porewater was extracted from sediment cores using the anoxic squeezing technique[33]. Further details on sediment cores and the interpretation of borehole logs are available in SI.

Chemical Analyses. Filtered rice flour extracts, porewater, and groundwater samples were analyzed via HPLC-ICP-MS (Perkin-Elmer Series 200 HPLC hyphenated to an Elan ICP-MS) using a PRP X-100 column (Hamilton). The sum of As(III) and As(V) is reported as iAs. Additional details of the speciation analysis are available in SI. Elemental concentrations in soil were determined with X-ray fluorescence (PANalytical Axios mAX).

3. Results and Discussion

3.1 Arsenic in Rice Grains and Soil. Analysis of As speciation in the NIST 1568b SRM extract agreed to within 10% of certified values (Table S1). The sum of As species (ΣAs) in the husked rice samples ranged from 63 to 528 µg As/kg rice, with a mean of 243 (±119) µg/kg (Fig. 1B and S2). The dimethylarsinic acid (DMAs(V)) fraction varied from 0% to 48% (mean: 16%). Monomethylarsonic acid (MMAs(V)) was a minor component of grain As, representing at most 1.6% of ΣAs. ΣAs concentrations are similar to earlier total As data collected in the Mekong Delta[14, 25], though prior studies did not report As speciation. Three samples had concentrations in excess of the Codex Alimentarius limit of 350 µg/kg for iAs in husked rice. Total As (tAs) in paddy soil ranged from 6 to 20 mg/kg (Fig. S3 and Table S2), with 6 mg/kg typically considered the cutoff between uncontaminated and contaminated soil[34]. There was no significant correlation between tAs and grain As content (See Figs. S4-S5 for a correlation analysis of grain As with soil elemental concentrations). Prior investigations in sites where irrigation water is not elevated in As have also found that total and extractable concentrations of soil As are poor predictors of grain As content[14-15, 25, 35], underscoring the challenge of predicting spatial variability in the As content of rice.

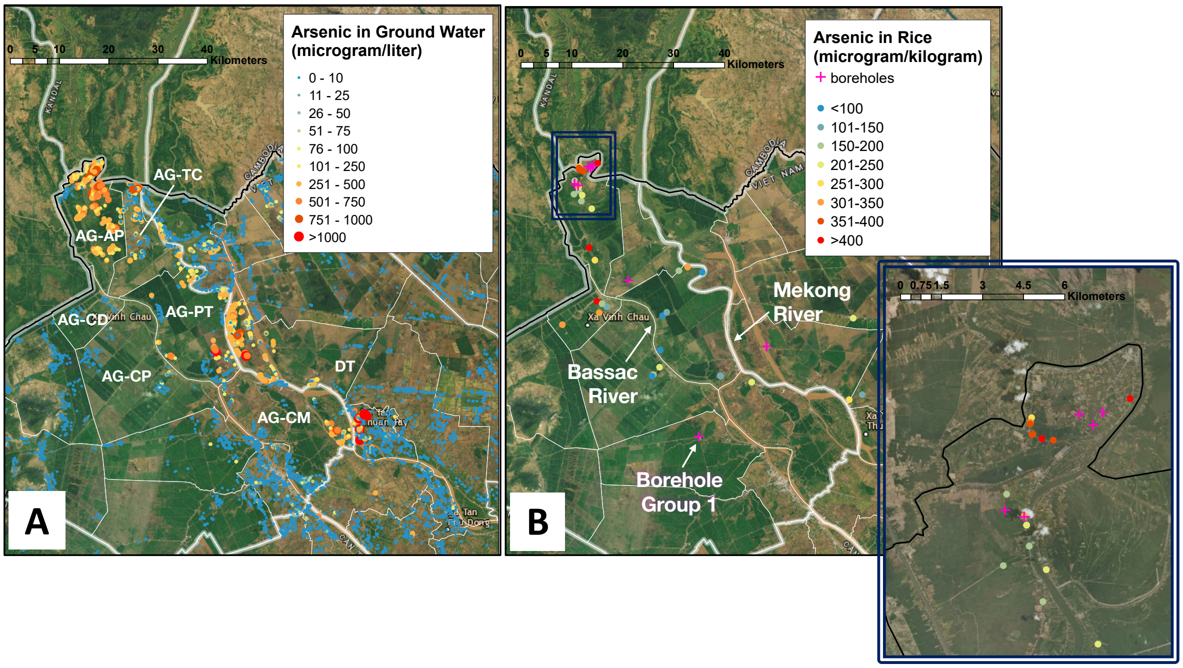

Figure 1. (A) Arsenic in groundwater in the Mekong Delta of Vietnam[26]. Sampling regions are identified by their two or four-letter code. Sample region LA is not shown. **(B)** ΣAs in rice (circles) and borehole locations (crosses). Two samples (LA-1 and LA-2) were collected from an area outside of this map. The inset shows a zoomed-in view of sample region AG-AP.

3.2 Associations between Arsenic in Local Groundwater and Rice Grains. Groundwater wells near rice sampling locations had As concentrations between 0 and 751 µg/L (mean: 109 µg/L) (Fig. S6). Correlation analysis between ΣAs, iAs, and DMAs(V) in rice grain and As concentrations in local groundwater revealed two groups of rice samples with different patterns in the relationship between rice and groundwater As (Fig. 2). In the first group of 35 samples, there was a significant correlation between groundwater As and rice ΣAs, iAs, and DMAs(V)

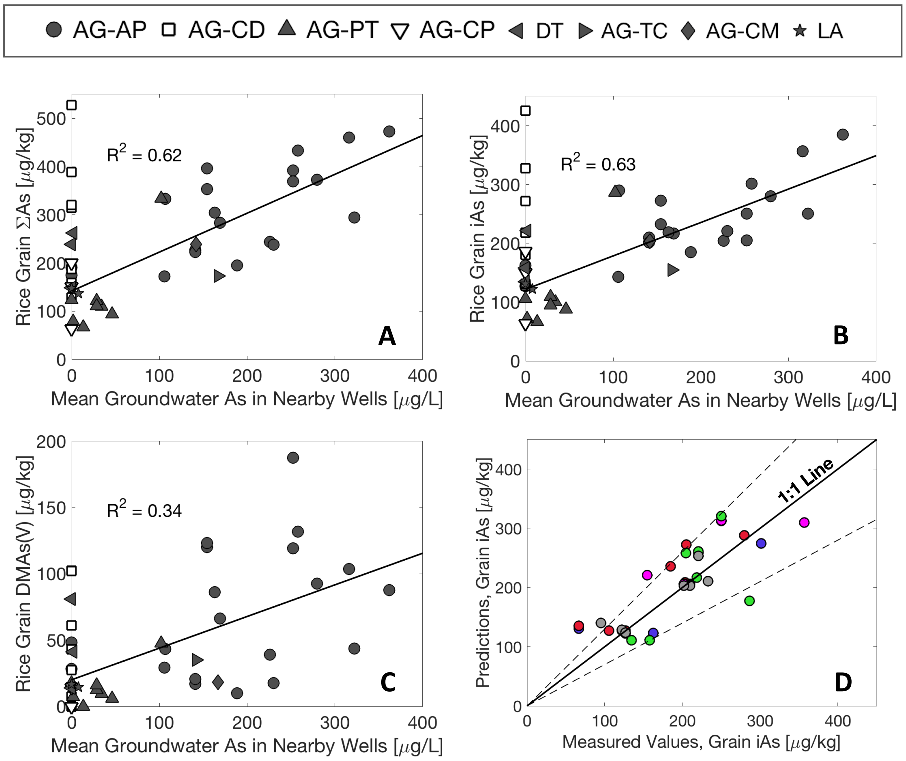

Figure 2: Concentrations of **(A)** ΣAs species, **(B)** iAs, and **(C)** DMAs(V) in rice grains as a function of mean groundwater As concentrations in wells nearby rice sampling locations. Unfilled points are samples from districts AG-CD and AG-CP and are excluded from the linear model analysis. Solid lines show least-squares linear model fits. **(D)** Comparison of predicted grain iAs concentrations with measured grain iAs concentrations, in n=7 samples held out as a testing set. The solid line shows the 1:1 line and dashed lines show 30% error bounds. Colors represent predictions from five representative hold-out tests. Samples from all districts except AG-CD and AG-CP were included in hold-out tests.

(Table 1). ΣAs and iAs in this group were well-described by a linear model, while DMAs(V) was described less well. The prediction accuracy of the model was validated by randomly holding out

7 samples (~20% of the dataset) as a testing set during model parameterization and then determining the root mean square error (RMSE) of the predictions of the testing set. This procedure was repeated 100 times. The median RMSE was 46.6 and 36.9 for iAs and DMAs(V), respectively (Fig. S7). Figure 2(D) compares predicted vs. measured grain iAs concentrations in a representative set of hold-out samples. The model predicted grain iAs concentrations reasonably well, with most predictions falling within 30% of the measurement. While the model is fairly robust for iAs, the prediction accuracy for DMAs(V) is poor given that the RMSE is large relative to the mean and median DMAs(V) concentrations of 49.0 and 28.8 μg/kg, respectively. Modeling iAs is more important than DMAs(V) since iAs is the more toxic and the only regulated form of As in rice.

Table 1: Summary of Linear Model Coefficients and Uncertainty Estimates

Linear Regression Model* *Error terms show 95% confidence intervals of the parameter estimates. Units for rice grain As concentrations are μg/kg. Units for groundwater As concentrations are μg/L.	R^2	**Spearman's ρ**
Grain ΣAs = 0.81(±0.23) x Groundwater As + 142.9(±37.5)	0.62	0.70 ($p < 0.001$)
Grain iAs = 0.57(±0.15) x Groundwater As + 121.9(±25.7)	0.63	0.70 ($p<0.001$)
Grain DMAs(V) = 0.24(±0.12) x Groundwater As + 20.1(±19.8)	0.34	0.44 ($p=0.002$)

In the second group of 10 rice samples, As concentrations were decoupled from nearby groundwater concentrations. These samples were exclusively drawn from districts AG-CD and AG-CP, located west of the Bassac River. Arsenic was undetected in all local groundwater, while rice grain ΣAs in this region ranged from 64 to 528 μg/kg. Soil tAs in these districts ranged from

7 to 16 mg/kg, similar to concentrations measured throughout the broader region (Fig. S3). In their modeling study of groundwater As in Mekong Delta aquifers, Erban, et al. [26] found that explanatory variables that predicted occurrence of elevated groundwater As throughout most of the Mekong Delta were unable to describe variations in groundwater As within this zone west of the Bassac.

3.3 Links Between Near-Surface Arsenic Release and Arsenic in Shallow Aquifers. The significant correlation between rice iAs and local groundwater As over much of the study region raises two questions. First, why is groundwater from up to 1.5 km away and tens of meters below the land surface a good predictor of As uptake into rice, given that the latter depends on As solubility in the immediate vicinity of roots? Second, why does this association hold over a large part of the study region but break down for a subset of rice samples?

An explanation for the first question is that near-surface sediments in deltaic systems in South and Southeast Asia act as a source of As to downgradient aquifers via recharge, so As solubilization in surficial environments, including rice paddies, can be linked to elevated As in local groundwater[20]. A prior investigation in the Cambodian Mekong Delta, ~80 km upstream of our study area, showed that groundwater with elevated As was downgradient of landscape features with hydro-biogeochemical conditions favorable to As mobilization (e.g., long-term inundation; reactive As-bearing mineral deposits; labile carbon to fuel microbial activity[20-21, 36-37]). We propose that in our study region, biogeochemical conditions controlling the solubility and plant-availability of As in surface environments also regulate As mobilization to groundwater via recharge, resulting in strong correlations among As solubilization in surficial sediments, uptake into rice, and transport to local groundwater.

This conceptual model linking As solubilization in near-surface and aquifer sediments via recharge depends on hydrologic connectivity between surficial and aquifer sediments. A lack of hydrologic communication could explain the decoupling between rice and groundwater As in districts AG-

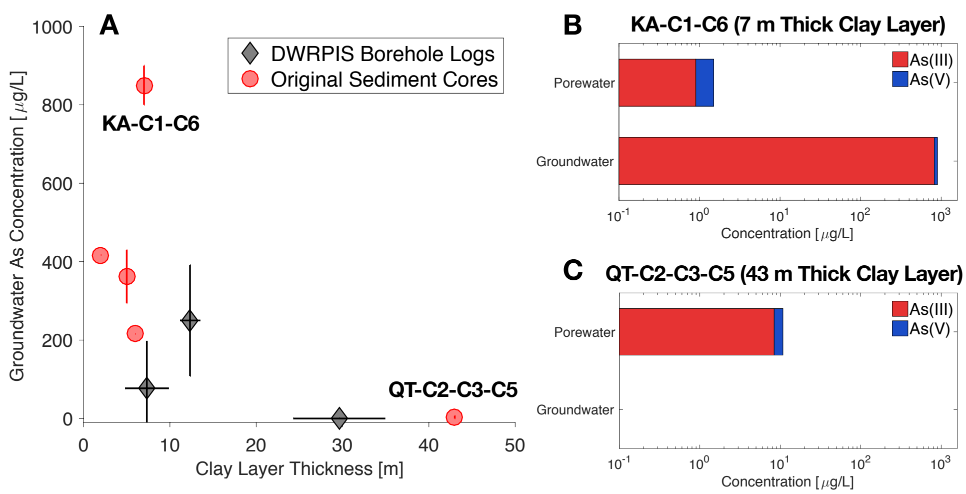

Figure 3: (**A**) Relationship between clay layer thickness and As concentrations in underlying groundwater, collected from DWRPIS boreholes logs (◊) and original sediment cores (o). Horizontal error bars indicate the standard deviation of the clay layer thickness inferred from n=3 borehole logs, and vertical error bars indicate the standard deviation of groundwater As concentrations in the n=5 groundwater wells closest to each borehole. For original sediment cores, groundwater As was measured in a well directly adjacent to the coring location. (**B-C**) As(III) and As(V) concentrations in porewater and groundwater in sediment core KA-C1-C6, with a 7m thick clay layer (B), and QT-C2-C3-C5, with a 43m thick clay layer (C). No As was detected in the groundwater at the QT-C2-C3-C5 location.

CD and AG-CP. The thickness of the confining clay layer separating these strata can be an important control on hydrologic connectivity[26, 38]. We used borehole logs, original sediment cores, and well depth distributions to explore the role of the clay layer in controlling surface-subsurface connectivity. Groundwater As was inversely related to clay layer thickness, with clay layers > 25 m thick characterized by undetectable As in nearby groundwater while clay layers between 5-15 m thick were associated with highly variable groundwater As levels (Fig. 3A). Original analysis of sediment cores found that As concentrations in groundwater beneath a 43 m thick clay layer

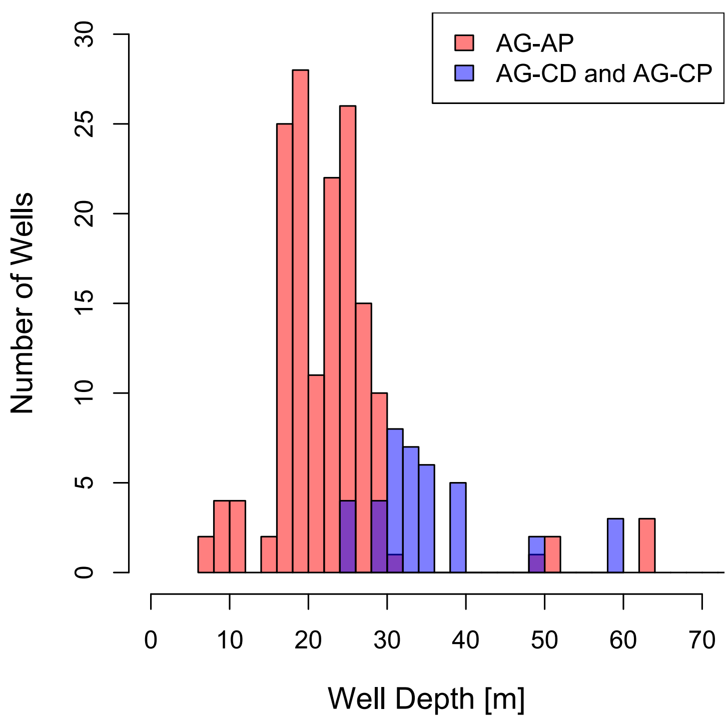

Figure 4: Distribution of well depths in study sub-regions AG-CD and AG-CP, where rice and groundwater As were decoupled, compared to well depths in AG-AP, where rice grain iAs was correlated with groundwater As concentrations.

were undetectable, while beneath a 7m thick clay layer the As concentration was 865 μg/L. Arsenic concentrations in the overlying porewater of these cores were 10.8 and 1.5 μg/L, respectively (Fig. 3B-C).

There were no complete borehole logs near rice sampling locations in AG-CD and AG-CP, where rice and groundwater As were decoupled, so we instead examined well depth distributions to infer clay layer thicknesses. Shallower wells can indicate thin clay layers while deeper wells indicate a need to drill through thicker clay layers before reaching sandy aquifers suitable for groundwater extraction. The mean well depth in AG-AP was shallower than in AG-CD/AG-CP (Figure 4). A significant fraction of wells in AG-AP were shallower than 20 m, while all of the wells in AG-CD and AG-CP were deeper than 25m, with most, deeper than 30 m. The borehole analysis indicated that clay layers < 20 m thick were characterized by elevated As concentrations, while in locations with clay layers > 25 m thick groundwater As was negligible. The deeper wells in AG-CD and AG-CP thus suggest a thick clay layer that could impede As transport from near-surface to aquifer sediments, and provide a potential explanation for the lack of correlation between rice and groundwater As in this subset of samples.

3.4 Limitations of the Study and Implications for Assessing Spatial Variability of Inorganic As in Rice. This study reports arsenic speciation in rice collected in the Vietnamese Mekong Delta and presents a parsimonious model describing iAs concentrations in rice as a function of local groundwater As levels. This finding is novel in the context of rice paddies that are irrigated with surface waters that are low in As. We caution that this study lacks the detailed hydrogeochemical measurements and modeling needed to provide a mechanistic explanation for this linkage between As uptake by plants at the surface and As concentrations in shallow groundwater. However, insights gained from prior investigations in similar deltaic aquifer systems[20-21, 36, 39] provide a basis for a conceptual model in which surficial sediments with soluble and plant-available As

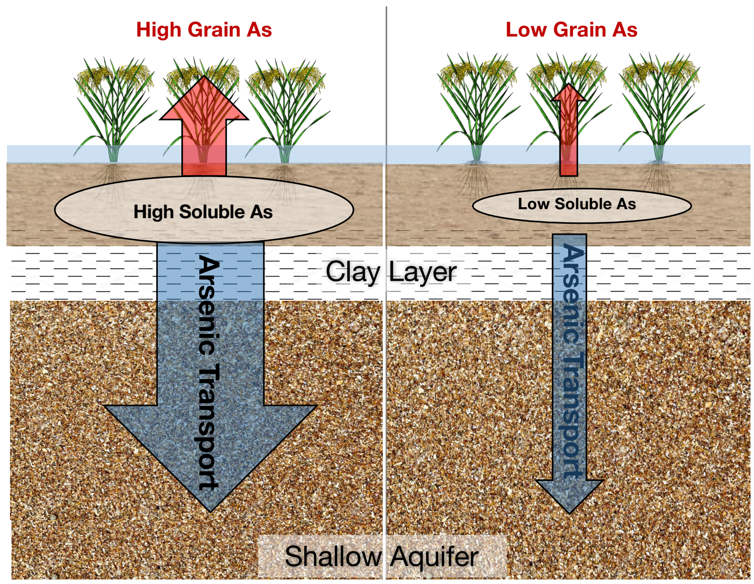

Figure 5: Conceptual model linking rice grain As concentrations with As concentrations in local groundwater, highlighting the role of surficial alluvial sediments as a source of As to both rice plants and downgradient aquifers. The size of ovals and arrows arrows represents the magnitude of As pools and fluxes. This model relies on the existence of significant hydrologic connectivity between surficial and shallow aquifer sediments.

lead to high levels of As uptake into rice and also act as a source of As to local groundwater (Fig. 5). A key limitation to this model is that it fails to describe variations in rice iAs in a subset of the study region. While the reason for this requires further study, there is evidence for a thick clay layer in this sub-region which could sever the surface-subsurface connectivity underlying this model. We suggest that this model can assess spatial variations in the iAs content of Mekong Delta rice so long as there is hydrologic connectivity between near-surface and aquifer sediments. Locations with negligible groundwater As, like AG-CD and AG-CP, will require further investigation since this may be an indication of limited local aquifer recharge rather than low plant-available As in surficial sediments.

ASSOCIATED CONTENT

Supporting Information. Additional data and all experimental details are presented in the Supplementary Information section.

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Notes: The authors declare no competing financial interest.

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***Declaration of Interest Statement**

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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