



International Journal of Research in Agronomy

E-ISSN: 2618-0618
P-ISSN: 2618-060X
© Agronomy
NAAS Rating (2026): 5.20
www.agronomyjournals.com
2026; SP-9(1): 274-279
Received: 13-11-2025
Accepted: 18-12-2025

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Isotherm and thermodynamic insights from desorption-derived arsenic retention in historically contaminated rice soil

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DOI: <https://www.doi.org/10.33545/2618060X.2026.v9.i1Sd.4714>

Abstract

The environmental impact of arsenic contamination in Bengal Delta Plain paddy soils is governed not only by inputs but by the persistence of pre-adsorbed legacy pools, whose equilibrium behaviour remains poorly understood. Whereas adsorption experiments characterize the full spectrum of sorption sites, sequential desorption selectively eliminates weakly bound arsenic, isolating the most persistent and environmentally relevant retention domains. Here, we investigated whether equilibrium relationships derived from sequential desorption can be meaningfully described using conventional isotherm models, and whether such desorption-derived data can serve as a proxy for adsorption behaviour. Five successive desorption cycles were performed at 20 °C and 35 °C on arsenic-loaded paddy soil from West Bengal, and residual pre-adsorbed arsenic (q_r) was related to equilibrium solution concentrations (C_e). Langmuir fitting yielded maximum retention capacity (q_{rmax}) values 8.7–14.2% lower, and affinity constants (K_i) 4.4–6.5 times higher, than equivalent adsorption-derived parameters previously reported for the same soil, indicating selective enrichment of strong binding domains. Freundlich exponents revealed extreme nonlinearity consistent with dominance of high-energy sorption sites. Model performance metrics identified the linear Langmuir form as the best descriptor of desorption-derived equilibria. Thermodynamic analysis indicated spontaneous, endothermic, and entropy-driven retention with increased energetic stability at higher temperature. The post-desorption As retention data qualitatively captured the temperature dependence and energetics pattern of arsenic adsorption behaviour, despite clear quantitative deviations from adsorption-derived parameters. Collectively, the desorption-derived equilibrium data retain the mechanistic signature of arsenic sorption while disproportionately sampling the most persistent retention domains, offering a useful proxy for long-term stability and legacy contamination assessment.

Keywords: Bengal delta plain, Freundlich, Langmuir, pollution, residual, retention

1. Introduction

Arsenic contamination of groundwater represents a major environmental and public health challenge, with an estimated 300–500 million people worldwide exposed through drinking water and irrigated agriculture^[1]. The Bengal Delta Plain (BDP) is one of the most severely affected regions globally, where geogenic mobilization of arsenic has resulted in persistent groundwater contamination across large parts of India and Bangladesh^[2]. Within the Indian segment of the BDP, the state of West Bengal constitutes the major arsenic-impacted agricultural zone. The state is not only the largest rice producer in India, but rice is also the most widely consumed staple crop in the country, which globally ranks second in both production and consumption^[3, 4]. The long-term use of arsenic-contaminated groundwater for irrigation in the region has triggered extensive secondary contamination of agricultural soils, especially paddy soils, facilitating arsenic transfer to rice grains and subsequent entry into the human food chain^[5, 6]. In soil systems, the environmental fate of arsenic is pre-eminently governed by adsorption and desorption processes that regulate solution concentrations, bioavailability, and transport^[7, 8]. In flooded rice agroecosystems, where redox oscillations and repeated irrigation cycles are intrinsic, arsenic desorption plays a critical role in controlling its remobilization to soil solution

and plant uptake^[9]. Despite this relevance, the majority of soil arsenic studies emphasize adsorption behaviour^[10], while desorption has largely been treated as a secondary process rather than a source of equilibrium information.

Desorption studies are conventionally interpreted in terms of the fraction of arsenic released and desorption index^[11]; however, equally important is the fraction that remains retained after repeated desorption events. This residual arsenic represents the most stable and environmentally persistent pool, which governs long-term soil contamination, legacy effects, and delayed remobilization under changing conditions^[12]. Information on this pre-adsorbed strongly retained fraction is not fully conveyed by adsorption experiments alone, because adsorption samples the full spectrum of sorption sites including weak and reversible domains, whereas desorption progressively eliminates these sites and isolates the most energetically dominant interactions. Consequently, desorption-derived retention provides unique insight into the stability, strength, and resilience of soil–arsenic associations that are invisible to adsorption-only approaches. Equilibrium isotherm models such as Langmuir and Freundlich have long been used to quantify adsorption capacity, affinity, and intensity of arsenic in soils^[11, 13–15]. However, the potential of applying these models to equilibrium retention data generated during sequential desorption remains largely unexplored. If desorption-derived retention data can be meaningfully described by isotherm models, they may offer a new perspective on arsenic retention and release dynamics, especially under conditions dominated by strong binding domains.

Thermodynamic analysis has further strengthened mechanistic understanding of arsenic adsorption by elucidating reaction spontaneity, energetic barriers, and temperature sensitivity^[16, 17]. Such analyses have almost exclusively focused on adsorption of arsenic onto fresh soil surfaces. In contrast, the energetics of retaining pre-adsorbed arsenic following desorption events have received little attention, despite being more relevant for long-term contaminated soils subjected to repeated irrigation and equilibration cycles. Assessing the thermodynamics of desorption-derived arsenic retention may therefore reveal whether stabilization of residual arsenic is governed by similar energetic drivers as adsorption, or whether fundamentally different mechanisms operate once it is subject to desorption events. A key unresolved question is whether equilibrium relationships and thermodynamic parameters derived from desorption can serve as meaningful proxies for adsorption behaviour, both in terms of isotherm characteristics and energetic interpretation. Addressing this conceptual and methodological gap is essential for improving predictions of arsenic persistence and remobilization in rice-based agroecosystems. Against this backdrop, the present study systematically compares equilibrium relationships derived from sequential desorption with those obtained from conventional batch adsorption experiments conducted previously on the same paddy soil by Roy *et al.* (2025a)^[15]. The objectives of this study were therefore to: (i) characterise the relationship between residual arsenic retained after sequential desorption and equilibrium solution concentration, (ii) evaluate whether Langmuir and Freundlich models can meaningfully describe this relationship, (iii) compare key isotherm parameters and thermodynamic descriptors derived from desorption-based data with those obtained previously from adsorption experiments on the same soil, and (iv) assess the extent to which desorption-derived equilibrium data can serve as a reliable proxy for adsorption behaviour.

2. Materials and Methods

2.1 Soil sampling and characterization

Surface soil (0–15 cm) was collected from three points within a long-term irrigated rice field at Mitrapur village, Nadia district, West Bengal, India (22.9954° N, 88.6125° E), located in the alluvial zone of the Bengal Delta Plain (BDP). The field has been continuously managed under a rice–rice–fallow rotation for roughly three decades, with extended flooding during rice cultivation^[18]. The soil is classified as a Typic Haplaquepts. After air-drying and sieving (<2 mm), subsamples were homogenized and analyzed for pH, electrical conductivity (EC), texture, soil organic carbon (SOC), total organic carbon (TOC), free CaCO₃, and amorphous and crystalline Fe-oxides in triplicate following established procedures^[15, 19]. The soil had a circumneutral alkaline pH, high SOC, and substantial abundance of free CaCO₃ and amorphous Fe-oxides. The detailed physicochemical properties of the studied soil have been presented in our previous paper^[15].

2.2 Sequential desorption experiment

To generate desorption-derived retention equilibria, 2 g of processed soil was pre-equilibrated with 20 mL of 80 mg L⁻¹ As(V) in 0.01 M KNO₃ for 24 h. Following equilibration, tubes were centrifuged (5000 rpm, 10 min), 10 mL of supernatant was discarded, and an equal volume of arsenic-free 0.01 M KNO₃ was added to initiate desorption. For each desorption cycle, soil suspensions were resuspended and equilibrated for 24 h at either 20 or 35 °C. After equilibration, tubes were centrifuged (5000 rpm, 10 min), and 10 mL of filtered supernatant was collected for arsenic measurement using ICP–MS (Parkin Elmer). This procedure was repeated for a total of five sequential desorption steps, and toluene was added to inhibit microbial activity. Quadruplicate samples were used for each treatment. Residual pre-adsorbed arsenic retained after the n^{th} desorption step ($q_{r,n}$, mg kg⁻¹) was calculated using a mass-balance expression:

$$q_{r,n} = q_{r,n-1} - \frac{(C_{e,n} - C_{i,n})V}{m}$$

where $C_{e,n}$ is the equilibrium arsenic concentration after the n^{th} desorption event, $C_{i,n}$ is the corresponding concentration before desorption, V the solution volume (mL), and m is the soil mass (g).

2.3 Isotherm modelling of residual arsenic

The equilibrium relationship between retained arsenic (q_r) and its solution concentration (C_e) was evaluated using linear and nonlinear forms of the modified Langmuir and Freundlich isotherms. The modified Langmuir model is written as:

$$q_r = \frac{q_{r,\max} K_l C_e}{1 + K_l C_e}$$

and linearized as:

$$\frac{C_e}{q_r} = \frac{C_e}{q_{r,\max}} + \frac{1}{q_{r,\max} K_l}$$

The modified Freundlich model is expressed as:

$$q_r = K_f C_e^{\frac{1}{n}}$$

with its linear form:

$$\log q_r = \log K_f + \frac{1}{n} \log C_e$$

where $q_{r_{max}}$ (mg kg⁻¹) represents maximum retention capacity, K_f (L mg⁻¹) denotes affinity, K_f (L kg⁻¹) indicates retention strength, and $\frac{1}{n}$ describes retention intensity. Isotherm fitting was performed in R using *AdIsMF* version 0.1.0 [20], and q_r - C_e plots were visualized in Microsoft Excel.

2.4 Model performance evaluation

Model selection criteria and goodness-of-fit were assessed using Akaike Information Criterion (AIC), corrected AIC (AICc), Bayesian Information Criterion (BIC), and accuracy metrics including RMSE, MAE, MAPE, and χ^2 [21, 22]. All metrics were computed in *AdIsMF* version 0.1.0 [20].

2.5 Thermodynamic analysis

Energetic descriptors of arsenic retention were assessed by estimating changes in the standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) using procedures outlined by Roy *et al.* (2025a) [15]. Thermodynamic calculations were executed using the R package *SHAKTI* version 0.1.0 [23].

2.6 Statistical analysis

Significance testing and post-hoc comparisons were performed in RStudio (version 1.3.1093) using the *doebioresearch* package version 0.1.0 [24].

3. Results and Discussion

3.1 Residual arsenic behaviour following sequential desorption

Figure 1 depicts the relationship between residual pre-adsorbed arsenic retained on the soil after sequential desorption (q_r), or retained arsenic, and the corresponding equilibrium solution concentration (C_e) at 20 °C and 35 °C. Across both temperatures, q_r increased systematically with increasing C_e , producing smooth, monotonic relationships that indicate the persistence of a well-defined equilibrium between solid and solution phases, while the progressive removal of weakly bound arsenic during earlier desorption steps constrains these equilibria to arsenic associated with energetically stronger sorption domains. A clear temperature effect was evident throughout the measured C_e range. At 20 °C, q_r increased from approximately 572 to 611 mg kg⁻¹ as C_e rose from 1.90 to 5.54 mg L⁻¹, whereas at 35 °C, q_r ranged from about 640 to 675 mg kg⁻¹ over a slightly narrower C_e window of 1.74–4.65 mg L⁻¹. The nearly constant difference in residual arsenic between the two temperatures, around 64–68 mg kg⁻¹, indicates that higher temperature consistently enhanced arsenic retention irrespective of equilibrium concentration. Although the residual arsenic difference between 20 °C and 35 °C remained nearly constant across concentrations, the slightly higher slope at 35 °C indicates a modest increase in retention sensitivity to solution concentration at elevated temperature. Notably, even the lowest residual arsenic concentrations measured after five sequential desorption events correspond to approximately 79–82% of the maximum adsorption capacities previously reported for this soil by Roy *et al.* (2025a) [15], demonstrating that the majority of arsenic remained strongly retained despite repeated desorption. Such persistence indicates dominance of high-energy sorption

domains, most plausibly inner-sphere arsenate complexes associated with amorphous and short-range ordered Fe(III) oxides [25]. The close correspondence in temperature response and concentration dependence between desorption-derived retention and adsorption behaviour indicates that desorption-derived equilibrium data preserve essential features of arsenic sorption while disproportionately representing the most stable, high-affinity binding domains that are critical for long-term arsenic retention and environmental risk assessment.

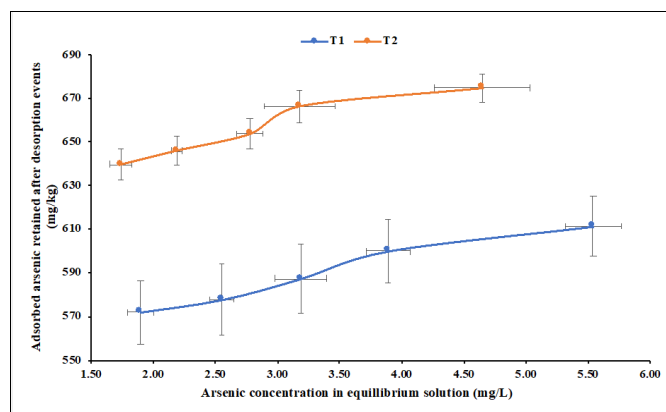


Fig 1: Plot of pre-adsorbed arsenic retained after desorption events vs arsenic concentration in equilibrium solution at different temperatures (T₁ = 20 °C; T₂ = 35 °C)

3.2 Isotherm parameters characterising residual arsenic retained after desorption

Isotherm fitting of the post-desorption retention data (Table 1) yielded Langmuir $q_{r_{max}}$ values of 631–637 mg kg⁻¹ at 20 °C and 697–700 mg kg⁻¹ at 35 °C. These $q_{r_{max}}$ values are 8.7–14.2% lower than, but still comparable to, the adsorption-derived monolayer adsorption maxima (q_{max}) values previously reported for the same soil [15]. This systematic reduction reflects the fact that sequential desorption removes weakly bound arsenic [26], so the fitted retention capacity represents the residual population of high-affinity sorption sites rather than the total sorption inventory. In this sense, $q_{r_{max}}$ from desorption-derived isotherms should be interpreted as an *effective retention capacity of the strongest binding domains*, not as a true monolayer adsorption maximum. In contrast, the Langmuir affinity constant (K_f) was 4.43–6.53 times higher than values obtained from batch adsorption on the same soil [15], increasing from 4.2–4.8 L mg⁻¹ at 20 °C to 5.7–6.1 L mg⁻¹ at 35 °C (Table 1). Elevated K_f values indicate that the retained arsenic is associated with energetically dominant sorption sites, consistent with the selective survival of inner-sphere complexes during repeated desorption [27]. Sequential desorption is known to preferentially deplete outer-sphere or weakly coordinated arsenic, leaving behind complexes that exhibit high apparent affinity when refitted using equilibrium models. Thus, the desorption-derived K_f does not exaggerate affinity artefactually, but rather reflects site-strength weighting imposed by the experimental pathway.

Freundlich parameters provide complementary insight into surface energy distribution. The Freundlich exponent ($1/n$) remained invariant around 0.06 across temperatures and fitting approaches (Table 1), indicating an extremely nonlinear isotherm [28], and a pronounced skew toward high-energy binding domains. Values of $1/n$ approaching zero indicate that retention is dominated by a small population of very high-energy sorption sites with strong binding affinities, such that incremental increases in equilibrium concentration yield

disproportionately small increases in sorbed mass, reflecting a narrow, energetically focused very strong sorption regime rather than a broad continuum of heterogeneous site energies [29]. Such extreme nonlinearity is far more pronounced than that observed in adsorption experiments on the same soil with $1/n$ values ranging from 0.4–0.6 [15], highlighting the strong filtering effect imposed by sequential desorption. Mechanistically, these very low $1/n$ values indicate that arsenic retention after desorption is governed almost exclusively by inner-sphere complexation on amorphous and short-range-ordered Fe(III) oxides [30], which form bidentate-binuclear or monodentate-mononuclear complexes of high stability [27]. Such complexes are known to resist displacement during repeated equilibration and dominate the residual sorbed pool once weaker interactions are exhausted. The invariance of $1/n$ with temperature, despite increasing q_{rmax} and K_f , further suggests that warming strengthened retention on already dominant high-energy sites, rather than activating new classes of sorption sites or redistributing site energies [28]. Consequently, the desorption-derived Freundlich parameters do not imply an intrinsically homogeneous soil surface, but rather reflect a selectively retained energetic domain that governs long-term arsenic stability. Taken together, the Langmuir and Freundlich parameters demonstrate both convergence and divergence between desorption-derived and adsorption-derived isotherms. Convergence is evident in the preservation of concentration dependence and temperature sensitivity, indicating that desorption-derived data retain the fundamental equilibrium structure of arsenic–soil interactions. Divergence arises in parameter magnitudes: desorption-derived q_{max} values are lower, K_f values are higher, and $1/n$ values are an order of magnitude smaller than those from adsorption experiments. These differences reflect pathway-dependent weighting of sorption sites. Accordingly, desorption-derived isotherms can serve as robust proxies for high-affinity adsorption behaviour, but they should not be used interchangeably with adsorption isotherms to infer total sorption capacity or surface heterogeneity. Instead, they provide a targeted representation of the most stable arsenic retention domains, which are particularly relevant for long-term mobility and legacy contamination assessments.

Table 1: Parameters of linear and nonlinear isotherm models for arsenic retained on soil after desorption events*

Sorption Model	Adsorption Parameter	Temperature			
		Linear		Non-linear	
		20 °C	35 °C	20 °C	35 °C
Langmuir model	q_{rmax} (mg kg ⁻¹)	637 ^b	700 ^a	631 ^b	697 ^a
	K_l (L mg ⁻¹)	4.17 ^b	5.70 ^a	4.75 ^b	6.07 ^a
Freundlich model	$1/n$	0.06 ^a	0.06 ^a	0.06 ^a	0.06 ^a
	K_f (L kg ⁻¹)	547 ^b	619 ^a	547 ^b	619 ^a

*Values within a row that share the same letter are not significantly different from each other.

3.3 Performance of linear and nonlinear isotherm models for desorption-derived retention data

Model performance statistics (Table 2) demonstrate that conventional adsorption isotherm models, with slight modifications, can describe the equilibrium relationship between residual arsenic retained after sequential desorption and solution concentration with high fidelity. Among all tested models, the linear Langmuir model showed the strongest overall performance, exhibiting the lowest information criteria values (AIC = −85.3, AICc = −61.3, BIC = −86.5) and the highest coefficient of determination (R^2 = 0.998). The superior performance of the linear Langmuir model reflects the fact that sequential desorption isolates a restricted population of energetically similar, high-affinity sorption sites, resulting in retention equilibria that are effectively constrained to a narrow, near-linear sorption domain. In contrast, nonlinear formulations of both models showed substantially poorer performance based on information criteria (AIC > 30), indicating over-parameterization relative to the limited number of equilibrium points generated by sequential desorption. The strong performance of the linear Langmuir model mirrors trends reported for batch adsorption on the same soil, despite the fundamentally different experimental pathway. This similarity suggests that desorption-derived equilibrium data preserve the dominant monolayer-type, high-affinity retention behaviour characteristic of Fe-oxide-controlled arsenic sorption on BDP soil [11].

Table 2: Performance of linear and nonlinear forms of isotherm (modified Freundlich and Langmuir) models for fitting the desorption-derived arsenic retention data*

Model	Model selection criteria			Model accuracy measures				
	AIC	AICc	BIC	RMSE	MAE	MAPE	χ^2	R^2
Freundlich linear	−41.1 ^b	−17.4 ^b	−42.6 ^b	3.12 ^a	2.78 ^a	0.45 ^a	0.09 ^a	0.946 ^b
Freundlich nonlinear	31.2 ^a	55.2 ^a	30.1 ^a	3.12 ^a	2.77 ^a	0.45 ^a	0.08 ^a	—
Langmuir linear	−85.3 ^c	−61.3 ^c	−86.5 ^c	4.15 ^a	3.4 ^a	0.56 ^a	0.17 ^a	0.998 ^a
Langmuir nonlinear	32.9 ^a	56.9 ^a	31.7 ^a	3.82 ^a	3.45 ^a	0.56 ^a	0.14 ^a	—

*Values in a single column that share the same letter are not significantly different from each other

3.4 Thermodynamic interpretation of desorption-derived arsenic retention

Thermodynamic parameters derived from desorption-based equilibrium data (Table 3) provide insight into the energetics governing residual arsenic retention on the Mitrapur soil. The negative ΔG° values at both temperatures confirm that retention of pre-adsorbed arsenic after sequential desorption remains thermodynamically spontaneous. The more negative ΔG° at 35 °C (−17.5 kJ mol⁻¹) relative to 20 °C (−16.1 kJ mol⁻¹) indicates enhanced spontaneity with increasing temperature. This temperature response parallels adsorption thermodynamics previously reported for the same soil, although absolute magnitudes are lower. The positive enthalpy change (ΔH° = 11.6

kJ mol⁻¹) indicates that residual arsenic retention is endothermic. Unlike adsorption on fresh surfaces, this endothermicity reflects post-adsorption stabilization processes, including partial dehydration of arsenate and reorganization of Fe–O coordination environments around already bound arsenic, rather than the occupation of new sorption sites [31, 32]. The positive entropy change (ΔS° = 0.095 kJ K⁻¹ mol⁻¹) further indicates that retention after desorption is entropy-driven. In a sequential desorption context, this entropy gain is best explained by displacement of structured interfacial water and continued reorganization of hydration shells surrounding strongly bound arsenic, rather than by arsenic release into solution [33, 34]. The persistence of positive ΔS° despite repeated desorption

underscores the thermodynamic stability of the retained arsenic pool. Desorption-derived thermodynamic parameters converge with adsorption results in sign and temperature response, confirming spontaneous, endothermic, and entropy-driven arsenic retention. However, their lower magnitudes indicate that they represent stabilization of an already selected high-affinity sorption pool rather than total adsorption energetics. Thus, desorption-based thermodynamics are unsuitable for estimating absolute adsorption energies but provide a robust proxy for assessing the stability, persistence, and resistance to release of soil-retained arsenic, particularly under long-term or legacy contamination scenarios.

Table 3: Thermodynamic parameters for retention of pre-adsorbed arsenic on Mitrapur soil after desorption events*

ΔG° (KJ mol ⁻¹)		ΔH° (kJ mol ⁻¹)	ΔS° (kJ K ⁻¹ mol ⁻¹)
20 °C	35 °C		
-16.1 ^a	-17.5 ^b	11.6	0.095

*Different superscript letters on the ΔG° values at different temperatures indicate statistically significant differences

4. Conclusion

This study demonstrates that equilibrium relationships derived from sequential desorption can be effectively interpreted using conventional adsorption isotherm frameworks, with slight modifications, providing a robust means to characterise the stability of soil-retained arsenic. Residual arsenic exhibited smooth, concentration-dependent equilibrium behaviour that closely resembled classical adsorption isotherms, despite being generated through progressive desorption. The persistence of high residual arsenic loadings—only moderately lower than adsorption maxima from fresh batch experiments on the same soil—highlights the dominance of strong, high-energy sorption domains controlling long-term arsenic retention. Desorption-derived isotherm parameters showed consistent and interpretable trends. Langmuir capacities reflected the *effective retention capacity of the strongest sorption sites*, while elevated affinity constants and extremely low Freundlich $1/n$ values indicated preferential stabilization of energetically dominant inner-sphere complexes following depletion of weakly bound fractions. Among tested models, the linear Langmuir formulation provided the most parsimonious description of desorption-derived equilibrium data. Thermodynamic analysis further confirmed that retention of already adsorbed arsenic after desorption remains spontaneous, endothermic, and entropy-driven, with higher temperature enhancing stabilization rather than promoting new adsorption. Overall, the findings establish that desorption-derived equilibrium data converge with adsorption data in mechanism and temperature response, but diverge quantitatively due to pathway-dependent site weighting. Sequential desorption thus offers an environmentally relevant proxy for assessing the persistence and stability of strongly retained arsenic. Future studies should test the generality of this approach across soils differing in mineralogy, redox status, and ageing history.

Acknowledgements

The first author acknowledge the financial support provided through the IARI PhD Scholarship provided by the Graduate School, ICAR-Indian Agricultural Research Institute, New Delhi.

Conflict of Interest

Authors do not have any conflict of interests to declare.

Ethical issues

None

References

1. Mukherjee A, Coomar P, Sarkar S, Johannesson KH, Fryar AE, Schreiber ME, *et al.* Arsenic and other geogenic contaminants in global groundwater. *Nat Rev Earth Environ.* 2024;5(4):312-328.
2. Chakraborty M, Mukherjee A, Ahmed KM. Regional-scale hydrogeochemical evolution across the arsenic-enriched transboundary aquifers of the Ganges River Delta system, India and Bangladesh. *Sci Total Environ.* 2022;823:153490.
3. Roy A, Datta SP, Barman M, Bhattacharyya S, Meena MC, Golui D, *et al.* Biomass yield of rice (*Oryza sativa*) cultivars as affected by applied silicate in an Inceptisol. *Indian J Agric Sci.* 2020;90(9):1796-1799.
4. Roy A, Datta SP, Barman M, Bhattacharyya S, Meena MC, Golui D, *et al.* Partitioning of arsenic in low and high arsenic accumulating rice (*Oryza sativa*) cultivars. *Indian J Agric Sci.* 2020;90(9):1776-1779.
5. Golui D, Raza MB, Roy A, Mandal J, Sahu AK, Ray P, *et al.* Arsenic in the soil–plant–human continuum in regions of Asia: exposure and risk assessment. *Curr Pollut Rep.* 2023;9(4):760-783.
6. Roy A, Datta SP, Barman M, Golui D, Bhattacharyya S, Meena MC, *et al.* Co-application of silicate and low-arsenic-accumulating rice cultivars efficiently reduces human exposure to arsenic: a case study from West Bengal, India. *Toxics.* 2023;11(1):64.
7. Zhang X, Zhang P, Wei X, Peng H, Hu L, Zhu X. Migration, transformation of arsenic, and pollution controlling strategies in paddy soil–rice system: a comprehensive review. *Sci Total Environ.* 2024;951:175500.
8. Chen W, Huang Q, Gao J, Cai Y, Xiao L, Wang Y, *et al.* Influence of low-molecular-weight organic acids on arsenic adsorption–desorption behavior in soil: implications for biochar amendments. *Water Air Soil Pollut.* 2024;235(6):383.
9. Yamaguchi N. Mechanisms underlying abiotic immobilization of inorganic arsenic in flooded paddy soils: a review. *Soil Sci Plant Nutr.* 2025;71(6):659-669.
10. Meena S, Chobhe KA, Golui D, Bana RS, Gawdiya S, Roy A. Assessing the impact of altered clay mineral and red mud derivatives on the characteristics of mustard (*Brassica juncea*) and the soil arsenic content. *Int J Plant Soil Sci.* 2023;35(19):200-206.
11. Raza MB, Datta SP, Golui D, Barman M, Ray P, Upadhyay D, *et al.* Enhancing soil arsenic immobilization with organic and inorganic amendments: insights from sorption–desorption study. *Environ Monit Assess.* 2025;197(1):76.
12. Pati R, Mukhopadhyay D. Arsenic sorption/desorption kinetics in some soils of West Bengal. *J Agric Technol.* 2016;3(2):19-27.
13. Feng Q, Zhang Z, Chen Y, Liu L, Zhang Z, Chen C. Adsorption and desorption characteristics of arsenic on soils: kinetics, equilibrium, and effect of Fe(OH)₃ colloid, H₂SiO₃ colloid and phosphate. *Procedia Environ Sci.* 2013;18:26-36.

14. Rawat AP, Kumar V, Singh P, Shukla AC, Singh DP. Kinetic behavior and mechanism of arsenate adsorption by loam and sandy loam soil. *Soil Sediment Contam.* 2022;31(1):15-39.
15. Roy A, Manjaiah KM, Datta SP, Rakshit D, Barman M, Ray P, *et al.* Effect of low-molecular-weight organic acids and silicon on arsenic adsorption and desorption in a paddy soil of Bengal Delta Plain: insights from thermodynamics and equilibrium modeling. *Water Air Soil Pollut.* 2025;236(6):344.
16. Maji SK, Pal A, Pal T, Adak A. Adsorption thermodynamics of arsenic on laterite soil. *J Surf Sci Technol.* 2007;23(3-4):161-170.
17. Mohd Fairuz FS, Md Muslim NZ, Wan Abdullah WN, Mohd Shohaimi NA, Abdullah NH, Ab Halim AZ, *et al.* Kinetics, thermodynamics, and mechanistic studies of arsenic removal utilizing natural soil as adsorbent. *Langmuir.* 2024;40(38):20101-20112.
18. Roy A, Datta SP, Manjaiah KM, Barman M, Ray P, Golui D, *et al.* Arsenic budgeting in a long-term irrigation-contaminated rice field of Bengal Delta Plain. *Plant Sci Today.* In press.
19. Singh SK, Biswas DR, Srinivasamurthy CA, Datta SP, Jayasree G, Jha P, editors. *Soil analysis*. 1st ed. New Delhi: Indian Society of Soil Science; 2019. p. 1-600.
20. Rakshit D, Roy A, Manjaiah KM, Datta SP, Das R. *AdIsMF*. R package. 2024.
21. Rakshit D, Roy A, Atta K, Adhikary S, Vishwanath. Modeling temporal variation of particulate matter concentration at three different locations of Delhi. *Int J Environ Clim Change.* 2022;12(11):1831-1839.
22. Rakshit D, Paul RK, Yeasin M, Emam W, Tashkandy Y, Chesneau C. Modeling asymmetric volatility: a news impact curve approach. *Mathematics.* 2023;11(13):2793.
23. Roy A, Rakshit D, Datta S, Manjaiah KM, Barman M, Mandal D. *SHAKTI*. R package. 2025.
24. Popat R, Banakara K. *Doebioresearch*: analysis of design of experiments for biological research. R package. 2020.
25. Chang Y, Wang S, Che F, Dong X, Yang X, Chen H, *et al.* Arsenic source-sink dynamics under phosphorus competition in sediments from river-lake connected systems. *Environ Sci Process Impacts.* 2025;27(3):706-717.
26. Zhang H, Selim HM. Kinetics of arsenate adsorption-desorption in soils. *Environ Sci Technol.* 2005;39(16):6101-6108.
27. Gao X, Root RA, Farrell J, Ela W, Chorover J. Effect of silicic acid on arsenate and arsenite retention mechanisms on 6-L ferrihydrite: a spectroscopic and batch adsorption approach. *Appl Geochem.* 2013;38:110-120.
28. Kumar R, Kumar R, Mittal S, Arora M, Babu JN. Role of soil physicochemical characteristics on the present state of arsenic and its adsorption in alluvial soils of two agri-intensive regions of Bathinda, Punjab, India. *J Soils Sediments.* 2016;16(2):605-620.
29. Shikuku VO, Mishra T. Adsorption isotherm modeling for methylene blue removal onto magnetic kaolinite clay: a comparison of two-parameter isotherms. *Appl Water Sci.* 2021;11(6):103.
30. Hou L, Liang Q, Wang F. Mechanisms that control the adsorption-desorption behavior of phosphate on magnetite nanoparticles: the role of particle size and surface chemistry characteristics. *RSC Adv.* 2020;10(4):2378-2388.
31. Mähler J, Persson I, Herbert RB. Hydration of arsenic oxyacid species. *Dalton Trans.* 2013;42(5):1364-1377.
32. Maslova MV, Ivanenko VI, Yanicheva NY, Mudruk NV. Comparison of the sorption kinetics of lead (II) and zinc (II) on titanium phosphate ion-exchanger. *Int J Mol Sci.* 2020;21(2):447.
33. Aremu JO, Lay M, Glasgow G. Kinetic and isotherm studies on adsorption of arsenic using silica based catalytic media. *J Water Process Eng.* 2019;32:100939.
34. Carneiro MA, Pintor AM, Boaventura RA, Botelho CM. Efficient removal of arsenic from aqueous solution by continuous adsorption onto iron-coated cork granulates. *J Hazard Mater.* 2022;432:128657.