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A design of experiments approach to arsenic retention: Interactions between sediment properties and water chemistry

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ABSTRACT

The mobility of arsenic (As) in groundwater is governed by dynamic interactions at the sediment-water interface, where both mineral reactivity and aqueous chemistry play key roles. In the Como aquifer (Northern Italy), As distribution is vertically heterogeneous: shallow horizons remain below the WHO limit of 10 μg/L, whereas deeper zones reach concentrations up to 250 μg/L. Although this variability is well documented, the underlying mechanisms remain only partially understood. To address this gap, we performed batch experiments on shallow and deep aquifer sediments with contrasting composition, systematically varying pH, electrical conductivity, and dissolved organic carbon in a full-factorial design of experiment. Results revealed nonlinear adsorption responses and sediment-specific behaviours. Shallow sediments exhibited stronger and more stable As retention, associated with higher contents of Fe-, Al-, and Mn-(hydr)oxides and greater cation exchange capacity. In contrast, deep-aquifer sediments showed weaker and more variable adsorption, especially under acidic, DOC-enriched, and high-conductivity conditions. Response surface models confirmed that sediment composition governs As retention capacity, while water chemistry modulates its efficiency. This integrative approach links laboratory adsorption patterns with field-scale As distribution, providing a mechanistic explanation for the observed vertical heterogeneity in the Como aquifer and supporting predictive assessment of groundwater vulnerability.

1. Introduction

Arsenic (As) contamination of groundwater poses a major environmental and public health risk due to its toxicity, persistence, and widespread occurrence in natural systems (Patel et al., 2023; Sevak and Pushkar, 2024). Groundwater is a primary source of drinking water and agricultural irrigation in many regions worldwide (Duarte et al., 2024; McCarty et al., 2011; Peña Reyes et al., 2015; Sagar et al., 2023), and large aquifer systems such as the Bengal Basin, Mekong Delta, Red River, and Mississippi Valley have long been recognized as hotspots of chronic As contamination (Ayotte et al., 2015; Fendorf et al., 2010; Postma et al., 2007; Ravenscroft et al., 2009). These systems illustrate that As mobilization is controlled by the interplay between mineralogy, organic matter, and aqueous chemistry operating across diverse geological settings. Developing reliable assessments of groundwater quality and mitigation strategies therefore requires a mechanistic understanding of the processes that govern As partitioning between sediments and porewaters.

Redox conditions are widely regarded as a primary control on As mobility in subsurface environments because they dictate the stability of the mineral phases that sorb As (Stollenwerk, 2003). Adsorption onto iron and manganese (oxyhydr)oxides and organic matter coatings is a dominant mechanism regulating As distribution between solid and aqueous phases (Dixit and Hering, 2003; Goldberg, 2002; Trotta et al., 2025). These reactive coatings provide abundant sorption sites and are highly sensitive to changes in redox potential (Bostick and Fendorf, 2003; Murphy and Strongin, 2009). Under reducing conditions, the dissolution of Fe(III) and Mn(IV) oxides releases previously adsorbed As and can lead to elevated dissolved concentrations (Colombani et al., 2025; Ying et al., 2013). Yet many aquifers exhibit substantial variability in dissolved As under oxic to mildly reducing conditions, where Fe and Mn oxides persist and dissolved Fe^{2+} remains low, indicating that redox transformations alone cannot fully explain As distributions in groundwater (Tufano and Fendorf, 2008; Verbeeck et al., 2020).

Once redox conditions are effectively stable, a wide range of non-redox factors can strongly influence As retention on mineral surfaces.

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Aqueous parameters such as pH, ionic strength, competing anions (e.g., phosphate, silicate), and dissolved organic carbon (DOC) modulate adsorption-desorption reactions by altering surface charge, complexation, and competitive sorption (Tufano and Fendorf, 2008). At the same time, the properties of the sediment matrix, including mineralogical composition, crystallinity, grain size, and the abundance of natural organic coatings, control the density and reactivity of sorption sites (Bostick and Fendorf, 2003; Neidhardt et al., 2018). These coupled mineralogical and aqueous controls are particularly important for the weakly bound, or "exchangeable," As fraction, which constitutes the most reactive pool and is highly sensitive to geochemical perturbations (Bauer and Blodau, 2006; Keon et al., 2001; Liu et al., 2017). Despite this, the influence of non-redox parameters under steady redox conditions remains comparatively poorly constrained, in part because reproducing natural redox gradients in the laboratory is technically challenging, prone to minor oxygen intrusion or microbial activity, and often yields non-reproducible results (Tufano and Fendorf, 2008; Verbeeck et al., 2020).

Most mechanistic insights into As adsorption have been obtained from simplified systems using pure mineral phases or synthetic sorbents such as ferrihydrite or goethite (Dixit and Hering, 2003; Gao and Mucci, 2001). While these studies have been essential for elucidating fundamental sorption mechanisms, they do not capture the compositional heterogeneity and complex surface properties of natural aquifer sediments. Recent investigations have demonstrated that mineralogical variability, reactive surface coatings, and organic matter content exert first-order controls on As adsorption and release under changing hydrogeochemical conditions (Gao et al., 2020; Neidhardt et al., 2018; Rathi et al., 2017; Thi Hoa Mai et al., 2014; Trotta et al., 2025). However, most of these works have examined the influence of individual factors under fixed experimental conditions, rather than quantifying the combined and interactive effects of multiple aqueous parameters in natural sediments. Moreover, studies that simultaneously consider both aqueous chemistry and sediment matrix properties under controlled yet environmentally realistic oxic–sub-oxic conditions are scarce, and the behaviour of the exchangeable As fraction in such settings remains poorly characterized.

The Como aquifer in Northern Italy provides an ideal natural laboratory to address these knowledge gaps. Previous investigations revealed a pronounced vertical heterogeneity in dissolved As, with shallow zones showing concentrations below the WHO limit (10 μg/L) and deeper zones exceeding 250 μg/L (Binda et al., 2022). This strong gradient occurs under oxic to mildly reducing conditions where Fe(III) and Mn(IV) oxides are still present and dissolved Fe^{2+} concentrations remain low (Binda et al., 2022; Trotta et al., 2025). Building on earlier work that highlighted the role of redox-dependent processes in this system (Trotta et al., 2025), the Como aquifer offers an environmentally relevant and experimentally stable window in which to isolate and quantify non-redox controls on As mobility in compositionally heterogeneous sediments.

In this study, we investigate the non-redox mechanisms that regulate As retention under oxic–sub-oxic conditions in the Como aquifer. Specifically, we adopt a Design of Experiments (DoE) approach to systematically vary pH, electrical conductivity (EC), and DOC, allowing us to quantify both linear and interactive effects on As adsorption and on the exchangeable As fraction in natural sediments from both shallow and deep aquifer layers. We then relate these responses to sediment mineralogy, reactive surface coatings, and organic matter content to identify the dominant sorption controls. By combining a multivariate experimental design with detailed sediment characterization under reproducible redox conditions, this work provides mechanistic insight into As partitioning processes across an oxic–sub-oxic boundary and contributes to a more comprehensive understanding of As transport in multi-layered groundwater systems.

2. Materials and methods

This section outlines the field, laboratory procedures, and statistical analysis implemented to investigate the geochemical parameters controlling As adsorption in natural aquifer sediments. To evaluate the synergistic effects of these geochemical parameters, a series of controlled batch adsorption experiments were performed to isolate the influence of selected geochemical variables (pH, electrical conductivity (EC), and dissolved organic carbon (DOC)) on As retention, under reproducible oxic-sub-oxic conditions representative of transition zones in multilayered aquifers. Two sediments with contrasting geochemical and textural properties, collected from the Como aquifer, were used to evaluate how mineralogical composition modulates the response to varying aqueous chemistry. Regarding water composition, the concentrations of selected geochemical parameters were artificially manipulated to replicate realistic environmental conditions within the aquifer.

2.1. *Selection of sediment samples and characterization*

The sediments used in the laboratory batch adsorption experiments were collected from the Como aquifer (Lombardy, Northern Italy) at depth of 50 m ad 70 m, representing the interface between the shallow layer and deep aquifer, respectively. These samples, hereafter referred to as "S" (shallow) and "D" (deep), were selected to capture the vertical heterogeneity in sediment properties that influence As mobility across the aquifer. Previous hydrogeochemical surveys (Binda et al., 2022) have shown that dissolved As concentrations increase markedly with depth, rising from approximately 10 μg/L at shallow depths to values exceeding an order of magnitude higher in the deeper zone, suggesting that sediment reactivity plays a central role in regulating As partitioning. Both samples had been previously characterized in detail (Trotta et al., 2025). In brief, sample S is a non-acidic sediment, while sample D is moderately acidic; both contain organic matter concentrations in the range of 0.3–0.4 %. Major contrasts between the two samples include their cation exchange capacity (CEC), mineralogy, and the abundance of Mn- and Al-(hydr)oxides. Moreover, X-ray diffraction (XRD) analyses revealed differences in the presence of calcite, quartz, feldspars (including albite, amphibole, and orthoclase), and phyllosilicates (predominantly muscovite, antigorite, and chlorite). Calcite was identified as the dominant mineral in sample "S". Conversely, sample D was richer in quartz and feldspars but lacked in the phyllosilicates found in sample "S." This mineralogical composition corresponded with CEC measurements, which were higher for sample S (~40 meq/100 g) and lower for sample D (~20 meq/100 g). Further notable differences include grain size distribution: sample S consists primarily of coarse to medium sand, while sample D is composed of clay and fine sand. Full methodological details and specific sediment characterization results are provided in Supplementary Material, Table S1.

Given the overall lateral homogeneity of the aquifer and the representative mineralogical contrast between these two samples, results derived from S and D sediments can be extrapolated to interpret the broader geochemical behaviour of the Como aquifer.

2.2. *Design of Experiments (DoE)*

2.2.1. *Rationale and selection of experimental parameters*

Batch adsorption experiments were performed to quantify As adsorption onto both sediment types as a function of selected aqueous parameters, under controlled laboratory conditions. A full-factorial design of experiments (DoE) (Leardi, 2009; Callao, 2014) was applied to systematically vary three key groundwater parameters, namely pH, electrical conductivity (EC), and dissolved organic carbon (DOC) content, allowing the structured combination of multiple parameters within single experimental runs, providing a comprehensive evaluation of both their individual and interactive effects on As adsorption. The selected variables were chosen for their representativeness in capturing the key processes governing As-solid interactions in groundwater environments. Although redox potential exerts a primary control on As mobility in reducing aquifers, reproducing fully anoxic conditions in large factorial experiments is technically demanding and often non-reproducible over multi-day equilibration periods (Tufano and Fendorf, 2008; Verbeeck et al., 2020). Therefore, all experiments were conducted under controlled oxic-sub-oxic conditions that correspond to the stable transition domain typically encountered at aquifer interfaces. This setting allows the reliable evaluation of pH, ionic strength, and organic complexation effects while minimizing artefacts caused by unstable redox behaviour.

Target factors and their respective levels were defined based on in situ measurements of groundwater variability within the study area (Binda et al., 2022) and a review of the most relevant literature (Aiken et al., 2011; Chaudhary et al., 2024; Sun et al., 2022). Although it is impractical to replicate all possible conditions present in natural systems, the chosen parameters and their concentration ranges offer a realistic and representative simplification of the geochemical environment under investigation.

2.2.2. *Artificial groundwater preparation*

Artificial groundwater was prepared to ensure experimental consistency and minimize uncertainties associated with natural groundwater manipulation. Chemical alterations can in fact occur during sampling, transport, and storage due to changes in redox conditions, temperature, and pressure, potentially affecting the stability of geochemical parameters. Such variations may bias the interpretation of adsorption mechanisms, especially in studies focused on the influence of specific water properties on As mobility.

Since the objective of this study was to isolate and evaluate the effects of selected groundwater parameters on As adsorption to sediment, it was essential to create a controlled aqueous matrix in which these variables remained stable throughout the batch experiments, thereby ensuring reliable and reproducible results. Artificial groundwater solutions were prepared using ultra-pure water and amended with appropriate chemical constituents to match the target values for each factor (see detailed information about solution preparation in Supplementary material).

Field measurements in the Como aquifer showed pH values typically ranging from 6 to 8.5, and electrical conductivity between ~200 and ~800 µS/cm. Direct DOC measurements were not available; therefore, the DOC range adopted in the experimental design was derived from values reported in urban aquifer systems in the literature (McDonough et al., 2020; Mladenov et al., 2022). In the experimental design, the ranges of these parameters were intentionally broadened (Fig. 1) to capture not only natural variability but also potential deviations under fluctuating hydrogeochemical conditions. This approach allowed us to evaluate adsorption trends across environmentally relevant conditions as well as possible future scenarios.

These target concentrations were implemented through a full-factorial design of experiments (DoE), encompassing 27 combinations of the three variables (see Table S2 in Supplementary material). Batch adsorption tests were performed for each of the two selected sediment types, resulting in a total of 108 individual experiments (27 water properties combination batches x 2 experimental sediment types x 2 replicates). The experiments were conducted in randomized order to minimize systematic error. Fig. 1 provides a summary of the levels chosen for each factor included in the experimental matrix.

2.2.3. *Adsorption batch experiments*

Arsenic adsorption experiments were conducted by equilibrating 0.5 g of dry sediment with 30 mL of artificially prepared groundwater in LDPE containers (Nalgene, USA). This solid-to-liquid ratio was selected based on previous adsorption study reported in the literature (Miranda et al., 2022). The artificial groundwater solutions were freshly prepared for each experimental run, following the conditions outlined in the experimental illustration in Fig. 1. To each batch, a spike of As standard solution (Merck, Darmstadt, Germany) was then added to achieve a final As concentration of 250 µg/L in suspension. To ensure pH stability throughout the experiment, a buffering agent was introduced. Although not commonly employed in metal(loid) adsorption studies, its use here aimed to reduce variability and avoid potential bias in the interpretation of results. The buffer solution was prepared using a mixture of HEPES, glycine, and succinic acid (Sigma-Aldrich, USA) in a 2:2:1 molar ratio, which provided a broad buffering capacity suitable for the selected pH range (5–9). The pH was adjusted as needed using ultrapure 10 M HNO_3 (Monticelli et al., 2019) or 5 M NaOH (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany). The sample suspensions were then placed onto an orbital shaker, set at 160 rpm, and continuously agitated for 72 h. This equilibration time was determined based on preliminary kinetic tests, which demonstrated that equilibrium between the sediment and solution phases was reliably reached within 72 h across all tested pH conditions (Figure S1, Supplementary material). At the end of the 72-hour period, an aliquot of the suspension was collected, filtered through a 0.22 µm nylon-membrane, and acidified with 2 % v/v HNO_3 for subsequent analysis. Arsenic concentrations in solutions were quantified using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo Scientific iCAP Q, Waltham, MA, USA).

Furthermore, prior to the addition of sediment, the As-spiked solution for each experimental run was sampled and analysed to determine the initial As concentration in solution (C_0). The amount of As adsorbed by sediment was calculated using Eq. (1) (Gunawardana et al., 2015):

$$Q_T = Q_b + v/w(C_0 - C_i) \tag{1}$$

where:

Q_T = total adsorption capacity (mg/kg)

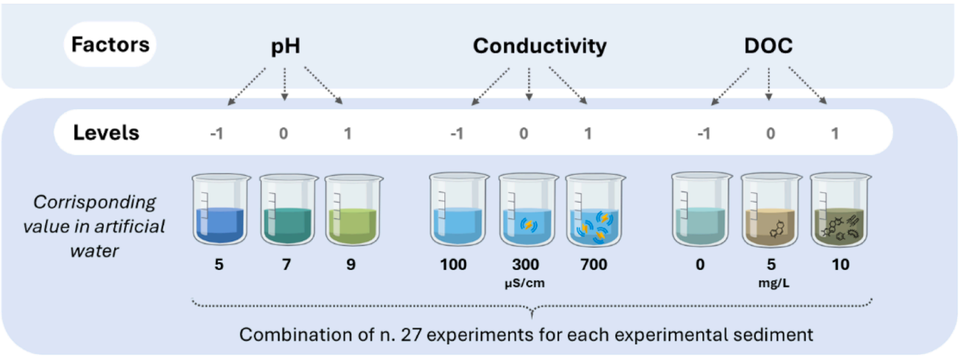

Fig. 1. Schematic representation of the water chemistry factors used in the Design of Experiment (DoE) to model As adsorption onto environmental sediments S and D. The experimental matrix follows a 3^k factorial design, where k represents the number of factors - each tested at three levels (−1, 0, +1). The factors considered include pH, conductivity, and dissolved organic carbon (DOC), with corresponding real values indicated for each level.

Q_b = As background concentration (mg/kg)
v = volume of the suspension (L)
w = mass of sediment (kg)
C_o = initial As concentration before sediment contact (mg/L)
C_i = equilibrium As concentration after 72 h (mg/L)

Control (blank) experiments were conducted in parallel with the actual tests to determine any natural release of As from the sediment into the artificial groundwater. These controls were prepared using identical combinations of pH, conductivity, and DOC as in the corresponding experiments, lacking in the addition of As standard solution. After 72 h, an aliquot of each control was filtered and analysed to determine the background concentration of As leached from the sediment (Table S3). These values were incorporated into Eq. (1) as factor (Q_b) to account for any sediment As release and incorporate it to the total (maximum) adsorption capacity.

2.3. Data analysis

To evaluate the results of the adsorption experiments, the response variable Q_T, obtained from the full-factorial experimental design, was statistically analysed using the Chemometric Agile Tool (CAT) software (Leardi., 2019). The full model included three factors (pH, conductivity, and dissolved organic carbon (DOC)) each tested at three levels. The model is described by Eq. (2):

$$y = b_0 + b_{Conductivity}x_{Conductivity} + b_{pH}x_{pH} + b_{DOC}x_{DOC} + bx_{Conductivity}x_{pH} + bx_{Conductivity}x_{DOC} + bx_{pH}x_{DOC} + bx_{Conductivity}{}^2 + bx_{pH}{}^2 + bx_{DOC}{}^2 \quad (2)$$

The equation incorporated main effects (linear terms), interactions between factors, and second order (quadratic) terms to account for curvature in the response. An analysis of variance (ANOVA) was conducted with a significance level of p-value < 0.05 to determine the statistical relevance of each individual factor, as well as their interactions. This procedure allowed for the validation of experimental outcomes and the identification of non-significant factors, ensuring the robustness and interpretability of the results. A multiple linear regression (MLR) model was used to represent the response surfaces.

2.4. QA/QC

Throughout all experimental process, rigorous quality assurance and quality control procedures were applied to ensure the reliability and reproducibility of the analytical results. Procedural blanks were prepared using ultrapure water (18.2 MΩ·cm resistivity) generated by a Sartorius Arium Mini system (Göttingen, Germany) and processed in the same manner as for each batch experiment. Ultrapure nitric acid (HNO_3) used for sample acidification and cleaning procedures was obtained by sub-boiling distillation of analytical-grade HNO_3 (65 % w/w, Carlo Erba Reagenti, Milan, Italy) using a Milestone DuoPUR system (Shelton, CT, USA), following the protocol described in (Monticelli et al., 2019). A 100 mg/L As ICP-MS standard stock solution (Carlo Erba, Milan, Italy)was used to prepare the ICP-MS calibration standards for quantifying As concentrations. To account for instrumental drift and matrix effects, a rhodium (Rh) standard solution (Merck, Darmstadt, Germany) was spiked into all samples as an internal standard prior to analysis. All experimental work was conducted using low-density polyethylene (LDPE) bottles (Nalgene, USA) that had been thoroughly cleaned. The cleaning protocol included a 48-hour soak in a detergent solution (4 mL/L Nalgene L900), followed by sequential rinsing with 2 % HNO_3 (w/w) and 0.01 M HCl. Bottles were subsequently rinsed three times with ultrapure water and allowed to dry under a laminar flow hood. Test tubes used for ICP-MS analysis were cleaned following the same procedure to ensure consistency and prevent cross-contamination. All analytical procedures, including instrumental calibration, blank corrections, and replicate measurements, were conducted following standardized QA/QC protocols previously published elsewhere (Binda et al., 2018). Replicate analyses of experimental samples yielded relative standard deviations (RSDs) below 10 %, confirming the precision and reproducibility of the measurements.

3. Results and discussion

3.1. Influence of the aquatic variables on As adsorption

The experimental adsorption data obtained from the full-factorial design are summarized in Table S4 (Supplementary material), which reports the range of pH, EC, and DOC values explored and the corresponding total adsorption capacities (Q_T) measured for both sediment types. In both sediments, QT values spanned approximately one order of magnitude across the tested conditions, confirming the strong dependence of As adsorption on the combined effects of the parameters tested. In accordance with the model described in Eq. (2) of the *Materials and Methods* section, each sediment sample was modelled using three linear terms (one per factor), three interaction terms, and three quadratic terms. Coefficients derived from the model are presented in Fig. 2 for sediment S (panel a) and sediment D (panel b). The percentage of variance explained by the model was approximately 66 % for sediment S and 76 % for sediment D.

In detail, for sediment S, only a subset of variables and their interactions were found to be statistically significant (factor-specific p-values are reported in Table S5). The linear terms for conductivity, pH, and DOC generally showed no significant impact on As adsorption. However, interaction terms such as conductivity*DOC, conductivity*pH, and the quadratic terms of conductivity and pH were statistically relevant. All significant interactions and quadratic terms were negative, suggesting an overall inhibitory effect on As adsorption.

Distinct results were observed for sediment D (Fig. 2b). In this case, significant variables included the linear term for pH, the interaction conductivity*DOC, and the quadratic terms for pH and DOC, resulting having the highest influence on As sequestration. The negative coefficient of the linear pH term indicated a decreasing adsorption efficiency with increasing pH. However, the significance of the quadratic pH term distorted the response surface across the experimental domain, suggesting that a linear interpretation would be misleading.

3.2. Water and sediment properties interaction

The adsorption response of the two sediments exhibited marked differences. To move beyond the limitations of a water-eantered perspective, which may overlook key controlling factors, interpretation of the results is here contextualized by considering the influence of solid-phase properties. This approach is particularly relevant given that the exchangeable geochemical fraction of As, which is the focus of this study, is strongly governed by sediment characteristics and the continuous geochemical interactions occurring at the solid-liquid interface. The specific effects contributing to the observed trends are outlined below:

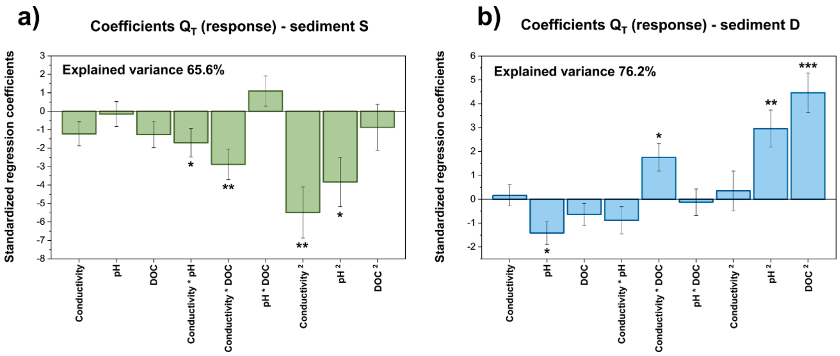

Fig. 2. Pareto charts showing the effects of linear, interaction, and quadratic model terms on the adsorption capacity (Q_T) of As onto sediment S (panel a, green) and sediment D (panel b, blue), as derived from the regression model described in Eq. (2). Bars represent the absolute magnitude of each coefficient, with confidence intervals indicated. Asterisks denote the level of statistical significance of each term ($* = p < 0.05$; $** = p < 0.01$; $*** = p < 0.001$).

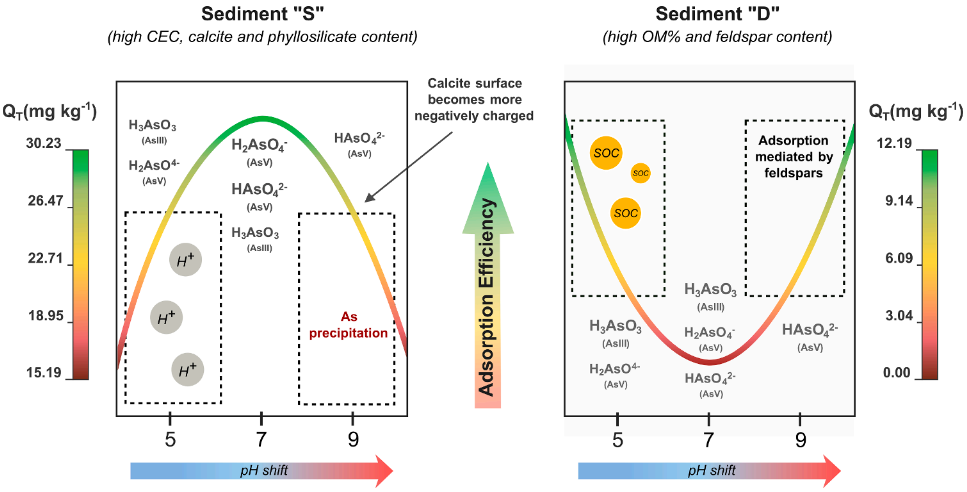

Fig. 3. Schematic representation of the pH-dependent As adsorption efficiency in sediments “S” and “D” and linked mechanisms. The coloured parabolic lines indicate the relative adsorption capacities (Q_T) across the tested pH range. Arsenic species shown in each panel represent the dominant aqueous forms at the corresponding pH conditions.

3.2.1. pH

The influence of pH on As adsorption was statistically significant and differed markedly between the two tested sediments (Fig. 3). Sediment D contained slightly more organic matter than sediment S (Table S1), which could, in principle, have enhanced As adsorption under reducing conditions (Verbeeck et al., 2020). However, this difference in composition was too small to account for the contrasting behaviours observed. Instead, the divergences are more plausibly explained by differences in mineralogical composition, which exerted a much stronger control on As adsorption capacity than the limited variation in organic content. For instance, although sediment S contained a higher abundance of clay minerals (e.g., *muscovite*; Table S1), these phases did not substantially enhance As retention within the exchangeable fraction examined here. This proves that finer-grained or clay-rich textures alone are not sufficient to increase As adsorption, as mineralogical composition and surface reactivity exert a stronger control on sorption efficiency. This is consistent with previous findings that clay minerals mainly stabilize metalloids in more recalcitrant, non-labile geochemical fractions (Miranda et al., 2022), and thus contributed little to the reversible sorption processes dominating As behaviour in this study. Instead, the observed differences likely arose from the greater abundance of Fe-, Al-, and Mn-oxides and hydroxides in sediment S, which are known to facilitate strong surface complexation with As. Furthermore, pH-dependent processes may have amplified these contrasts: at acidic pH, proton influx may have neutralized surface charges on phyllosilicates in sediment S via protonation of surface hydroxyl groups (-OH), thereby reducing the number of available sorption sites (Li et al., 2023). At neutral pH, sediment D exhibited negligible adsorption, likely due to As predominantly existing in the form of As(III), which generally exhibits lower adsorption affinity to the solid phase (Trotta et al., 2025). Sediment S, conversely, showed maximum adsorption at neutral pH, likely due to the higher presence of Fe-, Al-, and Mn-oxides and hydroxides that facilitate surface complexes with As (Giles et al., 2011; Jeong et al., 2007).

At basic pH, the adsorption behaviour of the two sediments diverged further. Sediment S exhibited a decrease in As adsorption, likely due to electrostatic repulsion arising from negatively charged, calcite-dominated mineral surfaces (Al Mahrouqi et al., 2017). In contrast, sediment D showed increased adsorption, which can be attributed to the presence of feldspars, known for their affinity for As(V) through electrostatic interactions (Yazdani et al., 2016). Under these alkaline conditions, the formation of secondary calcium arsenate or carbonate-arsenate phases (e.g., $Ca_3(AsO_4)_2$, $CaCO_3 \cdot AsO_4$) may also have contributed to the observed decrease in dissolved As concentration. Such precipitation processes, while removing As from solution, may do not represent true surface adsorption and could therefore leaf to a slight overestimation of the calculated adsorption capacity.

3.2.2. Electrical Conductivity

Conductivity, experimentally modulated through $CaCl_2$ addition, significantly affected only sediment S (Fig. 2), which is characterized by a higher CEC (Table S1). At high ionic strength, the saturation of available sorption sites likely inhibited As uptake by intensifying competitive interactions between As species and strong divalent ions (e.g., Ca^{2+}) (John et al., 2018).

Interestingly, maximum As adsorption was observed at intermediate conductivity levels, indicating a non-linear response. At these conditions, Ca^{2+} may have transiently promoted adsorption by forming weak outer-sphere bridges between negatively charged sediment surfaces and arsenate species, thereby offsetting electrostatic repulsion. Although this mechanism is generally more effective for cationic metals (Miranda et al., 2022) (Miranda et al., 2022), it can still contribute modestly to oxyanion retention under moderate ionic strength (Fakhreddine and Fendorf, 2021).

At higher conductivity, however, this effect was overwhelmed by reduced electrostatic attraction and increased competition from background electrolytes, leading to suppression of arsenate adsorption (Antelo et al., 2005). Thus, the observed non-linear pattern reflects a balance between a limited Ca^{2+}-bridging effect at moderate ionic strength and dominant competitive and electrostatic processes at elevated conductivity. Furthermore, a significant interaction between pH and conductivity was observed, whereby their simultaneous increase result in a significant decrease in As adsorption (Fig. 2). This trend can be attributed to two complementary mechanisms- First, at high pH, sediment surfaces became more negatively charged (Fig. 3), reducing their affinity for anionic arsenate species. Second, elevated conductivity increased solution ionic strength, compressing the electrical double layer and intensifying competition for surface sites. Pareto charts (Fig. 2) further emphasized the importance of this interaction in sediment S, suggesting a competitive binding effect between Ca^{2+} and H^{+} ions for reactive sites. This interpretation is consistent with Hanif et al. (2024), who reported that metal adsorption onto clay minerals and organic matter significantly decreased under saline and mildly neutral pH conditions, as a result of stronger ionic competition and weaker surface complexation due to increased ionic competition and weaker surface complexation.

3.2.3. Dissolved Organic Carbon

Pareto analysis identified DOC as the dominant factor governing As partitioning at the sediment-water interface for sediment D (Fig. 2). Experimental results revealed a non-monotonic relationship between DOC concentration and As adsorption: the highest efficiency occurred at the extremes of the tested range (0 and 10 mg/L), while lowest adsorption was observed at 5 mg/L.

In the absence of DOC, adsorption was maximized, likely due to the lack of competition from organic ligands and the deficiency of soluble organo-As complexes (Lin and Chen, 1998), which allowed unrestricted interaction between As species and sediment sorption sites. At the intermediate DOC level (5 mg/L), adsorption decreased markedly, consistent with competitive binding of humic substances and arsenate species to mineral surfaces (Liu and Cai, 2010).

At higher DOC concentrations, surprising, adsorption increased again. This reversal likely reflected the formation of ternary DOC-Fe-As complexes or co-flocculation of DOC with Fe- and Al-(hydr)oxides (Asmala et al., 2014), processes that can enhance As immobilization through bridging or precipitation pathways (Aiken et al., 2011),

Similar non-linear responses have been previously observed in metal (loid)s-humic substances interactions, where adsorption is controlled by the balance among competition, complexation, and surface-bridging mechanisms (Tomczak et al., 2019). Although elevated DOC concentrations are commonly associated with increased metalloid solubility, primarily due to the formation of organo-As complexes in solution (Jin et al., 2019), in this study that trend was observed only at moderate DOC levels, while higher DOC concentration appeared to promote solid-phase retention instead.

By contrast, DOC had no significant effect on As adsorption in

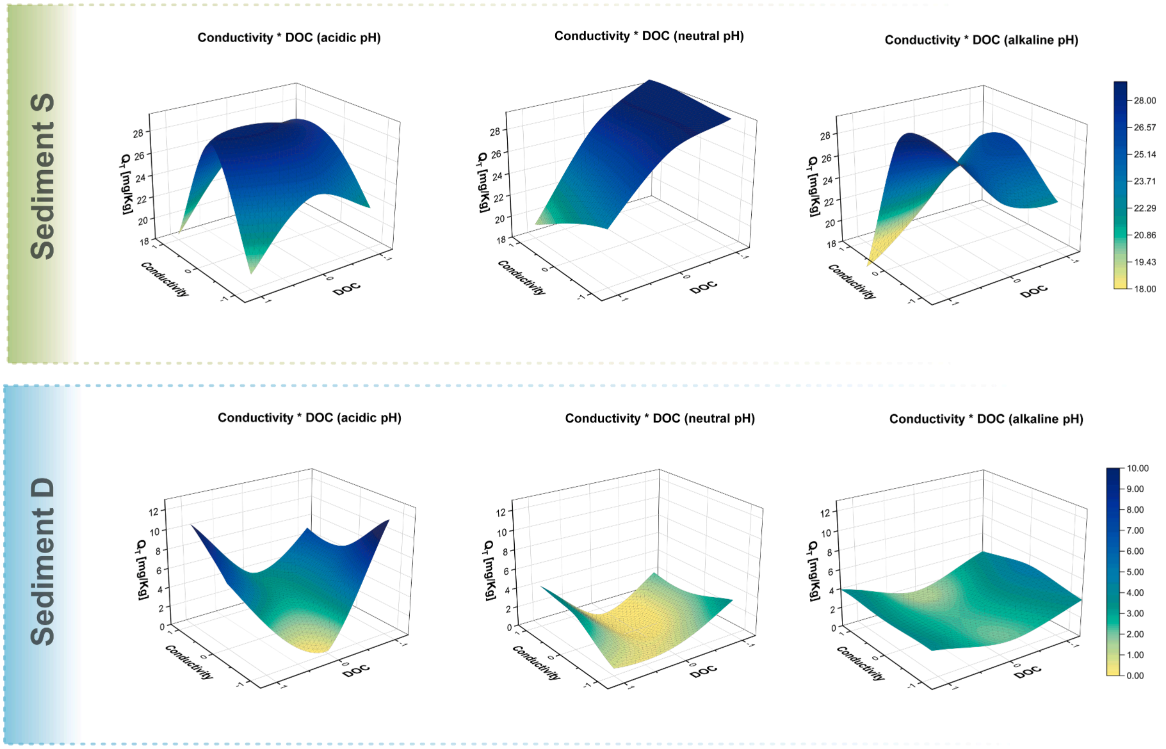

Fig. 4. Response surface plots illustrating the interaction effects of conductivity and dissolved organic carbon (DOC) on As adsorption (Q_T) under varying pH conditions (acidic, neutral, alkaline) for sediments S (top row) and D (bottom row). Each surface represents the modelled Q_T response derived from factorial experiments. Colour gradients indicate adsorption capacity, ranging from yellow (low Q_T) to dark blue (high Q_T). Sediment-specific colour scales are shown to the right of each row, highlighting distinct adsorption behaviours and interaction effects across the pH spectrum.

sediment S. This outcome can be explained by the abundance of geogenic metal cations in this sample (Table S1), which likely bound strongly to DOC, reducing the pool of free organic ligands available to compete with As for surface sites or to form soluble organo-As complexes (Fisher-Power et al., 2016). As a result, DOC exerted only a limited influence on As mobility in this more mineralogically reactive sediment type. is a diminished influence of DOC on As mobility in this more mineralogically reactive sediment.

3.3. *Adsorption response surfaces*

The results of the factorial experiments, which quantified the effects of the tested variables on As adsorption, were used to generate response surface models (Fig. 4). These visualizations effectively illustrated how sediment properties and water chemistry interacted to control adsorption processes. Overall, sediment properties played the primary role in determining As adsorption efficiency, while water chemistry acted as a secondary factor that modulated sorption mechanisms at the solid–liquid interface. The response surfaces derived from sediment S exhibited substantially greater complexity than those of sediment D, reflecting the more intricate interactions associated with the surface aquifer material and consistent with the characteristics described in the previous section. By contrast, sediment D showed more stable and less responsive adsorption behaviour across the same experimental domain. This supports the interpretation that its lower surface reactivity, finer texture, and reduced CEC constrained its ability to interact dynamically with aqueous conditions, resulting in comparatively lower geochemical sensitivity.

3.4. *Modelling As behaviour in the Como aquifer*

Overall, sediment S exhibited a stronger affinity for arsenic (As) than sediment D, as indicated by both adsorption efficiency and Qt values across the experimental matrix (Fig. 5, panel a). Furthermore, As adsorption in sediment S responded consistently to variations in water chemistry, whereas sediment D showed a generally weaker and less dynamic response under comparable conditions. These contrasting patterns suggest that sediment S had a greater capacity to buffer in situ As concentrations, while sediment D was less effective in retaining As. Such differences in adsorption affinity may substantially influence the vertical distribution of As within the aquifer system.

Field data from the previous study by Binda et al. (2022) reported elevated As concentrations in the groundwater extracted from deeper aquifer horizons (Fig. 5b). This vertical enrichment aligns with the weaker adsorption capacity observed in the present study for sediment D, which immobilized, on average, only ~20 % of dissolved As under simulated aquifer conditions (Fig. 5b). In contrast, sediment S demonstrated significantly higher adsorption potential, indicating a greater capacity to retain As at shallower depths and thereby mitigate its migration into groundwater. At the basin scale, sediment S occurs at depths consistent with the presence of low-permeability layers, whereas sediment D is located at more permeable horizons where wider water circulation is expected.

The present experimental results also support the geochemical hypothesis previously proposed by Binda et al. (2022), namely that As enrichment in the deep aquifer originates from the upwelling of solute-rich fluids along the backthrust of the *Gonfolite Lombarda*, a paleo-seismic fault structure intersecting the aquifer at depth (Ferrario et al., 2015). Such fluids have been hypothesized to carry high solutes loads, elevated concentrations of dissolved CO_2 (resulting in slightly acidic pH), and potentially increased DOC due to the interaction with organic-rich lenses encountered during upward migration (Rotiroti et al., 2015, 2014).

Under experimental conditions simulating acidic, mild to high-conductivity, and DOC-enriched scenarios, the adsorption efficiency of sediment D significantly declined. At low pH, negatively charged As species experienced reduced electrostatic attraction to mineral surfaces, particularly those depleted in (hydr)oxides or rich in feldspars. Increased ionic strength further compresses the sediment surfaces electrical double layer and enhances competition from Ca^{2+} ions, while moderate DOC levels can either compete with As for sorption sites or promote the formation of soluble organo-As complexes. Although at higher DOC concentrations some As may be removed from solution via co-flocculation or ternary complex formation, this mechanism is not equivalent to stable adsorption onto mineral surfaces and may not ensure long-term immobilization.

In contrast, sediment S, displayed a more robust response under the same conditions, owing to its higher content of Fe-, Al-, and Mn-oxyhydroxides and phyllosilicates, which provide abundant reactive surfaces for As binding. Even when DOC and conductivity were elevated, sediment S kept a moderate to high capacity for As adsorption, particularly at neutral pH.

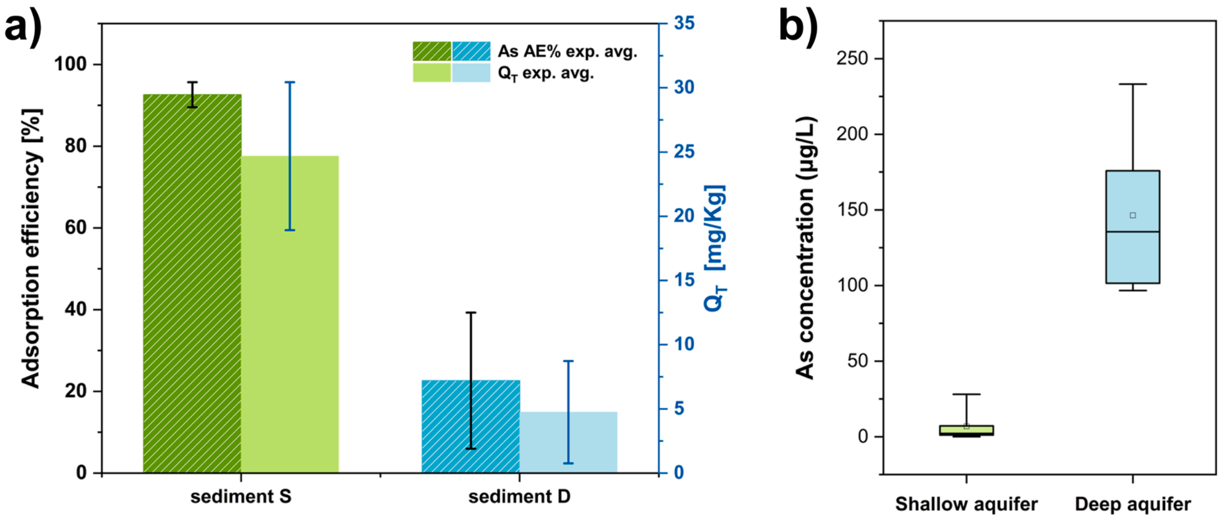

Fig. 5. a) Experimental average adsorption efficiency (AE %) and adsorption capacity (Q_T) of As for sediments S (green) and D (blue). Sediment S demonstrates significantly higher As retention capacity across both metrics, with lower variability (error bars are also presented), indicating a more consistent adsorption behaviour under variable geochemical conditions. b) Arsenic concentrations measured in groundwater from shallow layer and deep aquifer (modified from Binda et al., 2022). Higher As levels in the deep aquifer align with the lower adsorption capacity of sediment D, suggesting reduced buffering potential at depth.

These characteristics suggest that sediment S functions as an effective geochemical barrier, contributing to the lower As concentrations typically observed in shallow aquifer zones.

4. Conclusions

This study systematically examined the adsorption behaviour of As onto natural sediments under controlled geochemical conditions, emphasizing the exchangeable fraction that governs its mobility in groundwater. Results highlighted the critical role of both sediment characteristics and groundwater chemistry in governing As partitioning at the sediment-water interface. Adsorption batch experiments demonstrate that As mobility cannot be attributed to a single factor, but rather emerges from the interplay between sediment properties (such as mineralogy, cation exchange capacity, and grain size) and aqueous parameters, including pH, conductivity, and dissolved organic carbon (DOC).

The interaction between these factors revealed non-linear, sediment-specific effects, particularly in systems with high surface reactivity. Importantly, sediment properties emerged as the primary control over As retention, while water chemistry acted as a modulating influence rather than a sole determinant. These findings confirm that As retention results from a coupled control, where solid-phase properties set the framework for adsorption, and aqueous parameters determine the extent and variability of the process. Misinterpretations may arise when either component is considered in isolation.

Moreover, the study provides support for the conceptual model of As migration in the Como aquifer: the deep aquifer receives As-rich fluids from depth, which are insufficiently attenuated by the low-reactivity sediments encountered along the flow path. Conversely, overlying strata composed of more reactive mineral assemblages are capable of adsorbing and immobilizing As, thus preventing its upward migration into shallower potable water sources.

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CRediT authorship contribution statement

S. Trotta: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **G. Binda:** Writing – review & editing, Supervision, Resources. **M.F. Ferrario:** Writing – review & editing, Resources. **A. Pozzi:** Writing – review & editing. **A.M. Michetti:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sara Trotta reports financial support was provided by European Union. If there are other authors, they 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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100977.

Data availability

Data will be made available on request.

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