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Flashy hydrology, flashier contaminants: redox-driven geogenic contaminant mobilization under increasing hydrologic variability

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ABSTRACT

As precipitation regimes intensify and engineered recharge expands, the vadose zone faces increasingly dynamic wetting–drying cycles that generate redox oscillations and alter geogenic contaminant mobility. Oxygen depletion and microbial respiration can dissolve Fe and Mn (oxyhydr)oxides, key sorption hosts for arsenic (As), chromium (Cr), uranium (U), and related trace elements, producing transient, element-specific, and history-dependent responses. Synthesizing field observations, laboratory experiments, and large-scale monitoring datasets, we identify three management-relevant insights. First, contaminant mobilization under flashy hydrology can occur in short-lived pulses lasting hours to days, faster than typical groundwater-monitoring intervals. Second, single-contaminant frameworks can misrepresent overall geogenic risk because the same wetting event may mobilize arsenic through reductive dissolution while attenuating chromium and uranium through reduction to less mobile forms. Third, repeated wetting–drying cycles may alter or deplete reactive Fe and Mn mineral phases that buffer contaminant release, increasing vulnerability under sustained hydrologic variability. Changing geogenic contaminant concentrations in US municipal groundwater over the past three decades indicate that these processes are already detectable at network scales. Addressing them requires event-scale, multi-element monitoring and process-based models that represent redox hysteresis and mineral transformations from the vadose zone to the aquifer.

KEYWORDS Geogenic contaminants; vadose zone; groundwater quality; arsenic; hydrologic variability

1. Introduction

The vadose zone, the variably saturated region between the land surface and the groundwater table, is a hydrologically and biogeochemically active zone through which recharge and dissolved constituents pass before reaching groundwater [1]. Vadose-zone soil moisture dynamics are increasingly influenced by both climate change and water management [1,2]. Hydrologic variability, defined as changes in the frequency, magnitude, duration, and sequencing of wetting and drying conditions, is increasing globally, with more frequent precipitation extremes and longer dry periods [3]. These shifts alter soil moisture conditions with implications for water storage, plant water availability, and vadose-zone processes [4,5].

Variations in soil moisture directly regulate oxygen dynamics in soils and the vadose zone [2,6]. Soil moisture controls solute and gas diffusivity, microbial

respiration, and the availability of terminal electron acceptors [7]. During dry periods, lower water content increases air-filled pore space and oxygen diffusion, promoting more oxidizing conditions and lower microbial diversity [7]. In contrast, rainfall, irrigation, or recharge events increase soil moisture, reduce gas diffusivity, and generate suboxic and anoxic microsites within pore networks [7]. In this review, oxic conditions refer to environments in which molecular oxygen remains available as the dominant terminal electron acceptor; suboxic conditions describe transitional environments in which oxygen is depleted but strongly reducing processes are not yet dominant; and anoxic conditions refer to environments in which oxygen is effectively absent, and microorganisms rely on alternative terminal electron acceptors [8]. These shifts in oxygen availability drive sequential changes in terminal electron-accepting processes, in which microorganisms progressively use electron acceptors such as O₂, nitrate,

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Mn(IV), Fe(III), and sulfate as reduction-oxidation (redox) conditions become more reducing, thereby altering mineral stability and the aqueous speciation of redox-sensitive elements [9]. As wetting-drying cycles intensify, redox gradients in the vadose zone become increasingly dynamic, with redox potential decreasing during wetting and recovering during drainage [6,10]. Here, redox potential refers to the tendency of an environmental system to accept or donate electrons, commonly represented by Eh or oxidation–reduction potential, whereas redox oscillations refer to repeated shifts between more oxidizing and more reducing conditions during wetting and drying [7]. Soil moisture variability therefore acts not only as a hydrologic signal but also as a key biogeochemical driver in the vadose zone.

In addition to atmospheric hydrologic variability (e.g., precipitation and evaporation), human-engineered water management practices can further amplify biogeochemical dynamics in the vadose zone. Irrigation acts as a recurring pulse that intermittently saturates soils and alters redox conditions in the shallow subsurface [11]. Reactivity is controlled not only by the total volume of water applied, a key driver of vadose-zone processes, but also by the frequency and timing of wetting cycles [12]. Irrigation often creates alternating wetting and drying (AWD) cycles by periodically applying water to otherwise dry soils, then allowing them to drain before the next water application, producing recurring shifts in soil moisture and redox conditions that alter oxygen availability in the root zone [11]. Managed aquifer recharge (MAR) is the intentional replenishment of groundwater with excess water using practices such as surface spreading or injection [13]. MAR methods that infiltrate water through the land surface and vadose zone introduce rapid infiltration pulses that fill pore spaces, restrict oxygen transport, accelerate oxygen consumption, and generate localized reducing environments within the vadose zone [14–17,18]. Because this review focuses on vadose-zone processes, subsequent references to MAR primarily concern surface-based infiltration and flooding practices in which recharge water passes through the unsaturated zone.

Conversely, groundwater extraction and water table fluctuations can enhance vadose-zone aeration and produce highly variable redox conditions [19,20]. Across both natural and engineered soil systems, increasing moisture variability leads to repeated redox fluctuations that influence mineral stability, contaminant partitioning, and aqueous speciation [9]. The vadose zone therefore functions not as a passive conduit for groundwater recharge, but as a reactive domain in which wetting-drying cycles regulate geochemical pathways. In many unconfined aquifers, the vadose zone represents the final reactive boundary before recharge reaches the groundwater table, such that changes in vadose-zone

redox conditions can directly influence contaminant mobility and flux to groundwater [21].

Contaminants whose mobility is oxidation-state dependent and that occur ubiquitously at trace concentrations in soils are particularly sensitive to shifts in redox conditions. Geogenic contaminants are naturally occurring elements or compounds derived from minerals, rocks, sediments, or associated weathering products that can pose risks to human health and ecosystems when mobilized and present at elevated concentrations [22,23]. Among the most prevalent redox-sensitive geogenic elements are arsenic (As), chromium (Cr), and uranium (U), all of which undergo valence-state transformations that strongly influence solubility, sorption behavior, and mineral association in the subsurface [24–26]. These naturally occurring contaminants represent a widespread and persistent groundwater-quality concern globally.

Arsenic contamination alone has exposed hundreds of millions of people worldwide to concentrations exceeding the World Health Organization (WHO) guideline of $10\text{ }\mu\text{g L}^{-1}$, with the majority of affected populations (~94%) located in South and Southeast Asia [23,27]. Uranium similarly poses a widespread groundwater quality concern, including the Indo-Gangetic Basin (India and Pakistan) and parts of the United States (High Plains and Central Valley) [28]. In California's San Joaquin Valley, uranium concentrations exceeding the WHO guideline of $30\text{ }\mu\text{g L}^{-1}$ have been reported in a substantial fraction of groundwater wells [29,30]. Chromium presents additional challenges, as natural and anthropogenic sources are often difficult to distinguish; elevated concentrations have been documented globally, with frequent exceedances of drinking-water standards, with a WHO guideline of $50\text{ }\mu\text{g L}^{-1}$, primarily in geologically enriched regions (Peloponnese, Greece; and Bauru Basin, Brazil) [31].

Importantly, elevated concentrations of geogenic contaminants and associated health risks often disproportionately affect disadvantaged communities. Nationwide geospatial analyses in the United States have identified racial and ethnic disparities in geogenic contaminant concentrations in public drinking water systems [32,33].

Given the widespread occurrence and documented health impacts of redox-sensitive geogenic contaminants such as arsenic, chromium, and uranium, the key question is not only where these elements occur, but how they are mobilized into groundwater [23,28,31]. Fluctuating moisture conditions regulate oxygen availability, microbial metabolism, and mineral stability within the vadose zone, thereby governing the mobilization of these elements [34,35]. As hydrologic variability increases, more frequent wetting–drying or longer-duration flooding of the vadose zone can amplify redox oscillations and mineral transformations [35,36]. These transformations can promote contaminant release or

remobilization or, conversely, stabilize contaminants in less mobile fractions, depending on contaminant speciation, soil mineralogy, organic carbon availability, and the duration and sequence of wetting and drying [37–40]. Consequently, vadose-zone soils are increasingly subject to dynamic biogeochemical transitions under both climate variability and engineered water management [1,36]. This raises a central question: *Does increasing hydrologic variability alter the mobilization of geogenic contaminants in the vadose zone? Does flashier hydrology produce flashier contaminants?*

The objective of this synthesis is to evaluate how increasing hydrologic variability alters the mobility of arsenic, chromium, and uranium through redox-driven changes in mineral stability, contaminant speciation, and transport. By integrating evidence from natural and engineered hydrologic systems, this review identifies three recurring cross-element response patterns. First, the reductive dissolution and oxidative reformation of iron (Fe) (oxyhydr)oxides can produce Fe-coupled contaminant release and retention. Second, differences in transient, element-specific redox thresholds and reaction rates create asynchronous redox windows during wetting–drying transitions. Third, repeated redox oscillations can progressively transform mineral phases and weaken geochemical buffering capacity, increasing the potential for contaminant release over time. Together, these patterns demonstrate that hydrologic variability does not produce a uniform increase in contaminant mobility but instead generates element-specific and history-dependent responses. The following sections examine the mineralogical foundations and hydrologic controls of these behaviors and identify research priorities needed to anticipate vadose-zone biogeochemical responses under increasingly nonstationary conditions.

2. Scope and sources of literature

A targeted critical-review approach was used to synthesize literature on wetting–drying cycles, redox dynamics, mineral transformation, and geogenic contaminant mobility in vadose-zone soils. Peer-reviewed studies were identified through Google Scholar and Scopus using combinations of the terms *vadose zone*, *wetting–drying*, *redox oscillations*, *oxygen dynamics*, *Fe/Mn (oxyhydr)oxides*, *arsenic*, *chromium*, *uranium*, *irrigation*, and *managed aquifer recharge*. The search included publications made publicly available since 2020, but some topics required slightly older papers. Studies were selected based on their relevance to hydrologic forcing, redox transitions, mineral stability, contaminant speciation, and transport. Evidence was drawn from laboratory experiments, soil columns, field studies, wetlands, agricultural systems, groundwater-level fluctuations, and managed aquifer recharge sites. Recent reviews were used to establish broad geochemical behavior,

whereas primary studies were emphasized for transient responses and repeated wetting–drying effects. The objective was mechanistic synthesis rather than exhaustive systematic review or quantitative meta-analysis.

3. Mineralogical and geochemical controls

To evaluate whether increasing hydrologic variability amplifies contaminant mobilization, it is necessary to examine the mineralogical and geochemical controls governing redox-sensitive trace elements in soils. In vadose-zone environments, the distribution and mobility of these elements are controlled by mineral host associations, redox-dependent speciation, and aqueous complexation chemistry. Although lithology governs initial element abundance, environmental behavior is primarily dictated by secondary phases formed during weathering and soil development, particularly Fe and Mn (oxyhydr)oxides, clay minerals, and organic matter [41–46]. Table 1 summarizes the dominant lithologic sources, mineral hosts, and redox controls governing the mobility of redox sensitive trace elements.

A defining feature across geogenic contaminants is their strong association with Fe and Mn (oxyhydr)oxides, including ferrihydrite, goethite, and hematite, which provide high surface area sorption sites for oxyanion-forming species such as arsenate, chromate, and uranyl [24,31,66,67]. Because the stability of these mineral phases is tightly coupled to redox conditions, they exert a dominant control on contaminant mobility. Under reducing conditions, microbial reduction of Fe(III) and Mn(IV) destabilizes these minerals, releasing associated trace elements into porewater [27,68,69]. Conversely, re-oxidation during drying promotes mineral re-precipitation and scavenging of dissolved species, although reformed phases may differ structurally and sorptively from their precursors, introducing hysteresis in contaminant retention.

Additional sorption environments are provided by clay minerals and soil organic matter, which regulate contaminant partitioning through surface complexation, cation exchange, and structural incorporation [70–72]. Organic matter also plays a dual role by complexing trace elements and serving as an electron donor that accelerates microbial redox transformations [10,73]. Despite these multiple retention pathways, the stability of Fe and Mn (oxyhydr)oxides often remains the dominant control under fluctuating redox conditions, effectively linking hydrologic variability to contaminant mobility.

Fluctuations in soil moisture and oxygen availability drive shifts in redox potential that alter both mineral stability and contaminant speciation. As soils become increasingly reduced, terminal electron acceptors are utilized sequentially, leading to dissolution of Fe and

Table 1. Geologic origins and redox-controlled biogeochemical behavior of geogenic trace elements in vadose-zone soils, with key recent references for further reading on their occurrence, speciation, and mobility in soil and aquatic systems.

Element	Geologic origins	Primary mineral hosts	Secondary hosts in soil	Dominant oxidation states	Mobility control	Key references
Arsenic (As)	Sulfide-bearing crustal materials in orogenic belts and sedimentary basins	Arsenopyrite, orpiment, realgar	Fe (oxyhydr)oxides (ferrihydrite, goethite, hematite), Mn oxides, Fe-bearing clays	As(III)* $\rightleftharpoons$ As(V)	Sorption of arsenate (AsO_4^{3-}) to Fe(III) (oxyhydr)oxides; release during reductive dissolution of Fe oxides and competitive ligand exchange with phosphate (PO_4^{3-})	[22,23,27,47,48]
Chromium (Cr)	Mafic and ultramafic rocks (ophiolites, peridotites, serpentinites, basalts)	Chromite, Cr-bearing spinels, pyroxenes, olivine	Serpentine, amphiboles, Fe/Mn (oxyhydr)oxides, clays	Cr(III) $\rightleftharpoons$ Cr(VI)*	Oxidation of Cr(III) to mobile chromate (CrO_4^{2-}), often mediated by Mn oxides	[31,45,49,50,51]
Uranium (U)	Granitic, rhyolitic, and phosphate-bearing rocks; uranium-rich sediments, breccia pipes	Uraninite, pitchblende, coffinite, autunite	Fe/Mn (oxyhydr)oxides, clays, organic matter	U(IV) $\rightleftharpoons$ U(VI)*	Oxidation of U(IV) to uranyl (UO_4^{2+}) followed by formation of mobile Ca-uranyl-carbonate complexes; reduction to U(IV) promotes precipitation and uraninite immobilization	[28,41,52,53]
Antimony (Sb)	Sulfide-bearing ores, hydrothermal deposits	Stibnite, antimony oxides	Fe/Mn (oxyhydr)oxides, clays, organic matter	Sb(III) $\rightleftharpoons$ Sb(V)*	Sorption of antimonate ($\text{Sb}(\text{OH})_6^-$) to Fe/Mn (oxyhydr)oxides; reduction to Sb(III) enhances sorption and complexation with soil organic matter	[54–57]
Manganese (Mn)	Mafic and sedimentary rocks; widely distributed in soils and sediments through weathering	Mn(II)-bearing silicates and carbonates; secondary Mn oxides (birnessite, manganite, hausmannite)	Mn (oxyhydr)oxides, Fe (oxyhydr)oxides, clays, organic matter	Mn(II) $\rightleftharpoons$ Mn(III) $\rightleftharpoons$ Mn(IV)*	Cycling between soluble Mn(II) and insoluble Mn(III/IV) oxides; oxidative precipitation under oxic conditions and reductive dissolution under anoxic conditions; Mn oxides act as strong oxidants	[58,59]
Molybdenum (Mo)	Granitic rocks, porphyry deposits, organic-rich shales	Molybdenite	Fe/Mn/Al (oxyhydr)oxides, clays, organic matter	Mo(IV) $\rightleftharpoons$ Mo(VI)*	Sorption of molybdate (MoO_4^{2-}) to Fe/Mn/Al (oxyhydr)oxides; release during reductive dissolution and immobilization as thiomolybdate species under sulfidic conditions	[60,61]
Selenium (Se)	Black shales, sedimentary rocks, volcanic deposits	Selenides, sulfide minerals	Fe/Al (oxyhydr)oxides, clays, organic matter	Se(0) $\rightleftharpoons$ Se(IV) $\rightleftharpoons$ Se(VI)*	Reduction of mobile selenate (SeO_4^{2-}) to selenite (SeO_3^{2-}) and elemental Se(0); sorption of selenite to Fe/Al (oxyhydr)oxides	[62–64]
Vanadium (V)	Mafic and volcanic rocks, organic-rich shales	Vanadinite, patronite, titanomagnetite	Fe/Al (oxyhydr)oxides, clays	V(IV) $\rightleftharpoons$ V(V)*	Sorption of vanadate (VO_4^{3-}) to Fe/Al (oxyhydr)oxides; redox-controlled reduction to less mobile V(IV)	[24,26,65]

*Indicates the oxidation state that is generally more mobile under circumneutral aqueous conditions.

Mn (oxyhydr)oxides and restructuring of mineral assemblages [6,9]. These changes drive redox-dependent transformations in trace element oxidation state, which directly control solubility, sorption affinity, and aqueous speciation. Eh–pH stability relationships (Figure 1) illustrate that the redox thresholds governing these transformations differ across elements, such that

comparable shifts in redox conditions can mobilize one contaminant while immobilizing another. At the circumneutral pH values (pH 6–8) typical of many soils and groundwaters, the three panels show especially divergent responses to declining Eh. While these diagrams represent equilibrium conditions and do not capture kinetic constraints or microscale heterogeneity, they

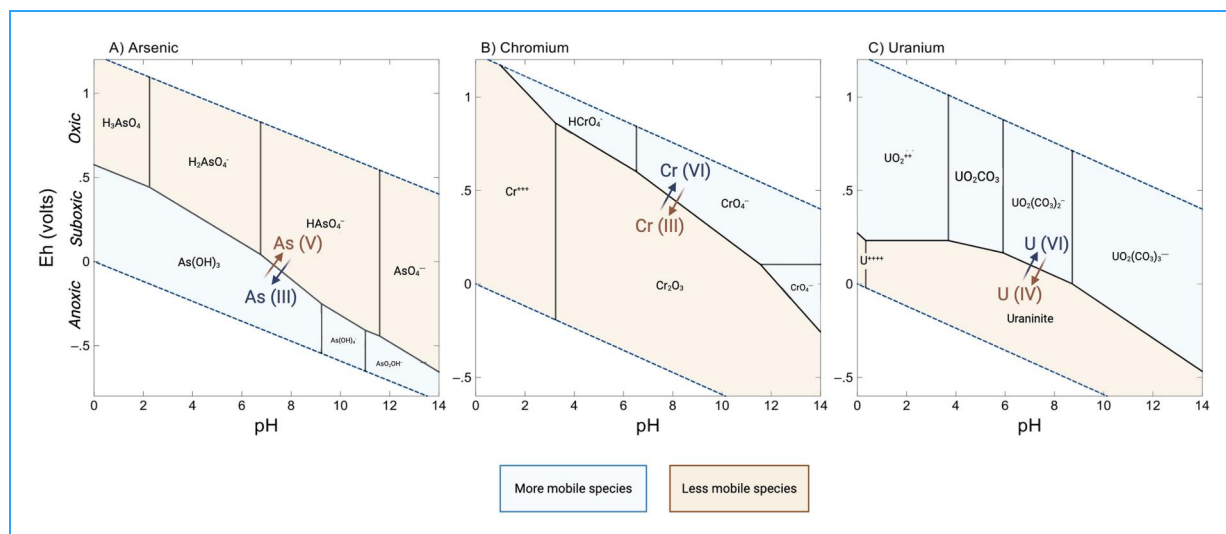


Figure 1. Eh–pH stability diagrams (Pourbaix) showing dominant mobile and less mobile species for (A) arsenic, (B) chromium, and (C) uranium. Blue regions represent more mobile aqueous species, tan regions represent less mobile, often solid phases. Arrows indicate redox transitions between dominant oxidation states in soil. Dashed blue lines denote the stability limits of water ($\text{H}_2/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ boundaries). Diagrams assume 25 °C, 1 atm pressure, and dissolved species activities of 10^{-6} . Generated using Geochemist's Workbench.

provide a useful framework for understanding the divergent redox windows that control arsenic (Figure 1A), chromium (Figure 1B) and uranium (Figure 1C) mobility [24,50,66].

Figure 1A shows that As(V) species dominate under oxic to mildly reducing conditions, whereas As(III) becomes the dominant species under strongly reducing conditions (low Eh). This transition can enhance mobility because As(III) generally sorbs less strongly to Fe (oxyhydr)oxides than As(V), while reductive dissolution of Fe-bearing minerals can simultaneously release previously sorbed arsenic into porewater [27,68]. Figure 1B illustrates the contrasting behavior of chromium: oxidizing conditions favor mobile Cr(VI), primarily as chromate or hydrogen chromate, whereas reducing conditions favor less soluble Cr(III) and Cr-bearing solid phases. Re-oxidation during drying, particularly in the presence of Mn oxides, can therefore remobilize chromium by converting Cr(III) to Cr(VI) [45,50]. Figure 1C shows that oxidizing conditions favor soluble U(VI), including uranyl-carbonate complexes at pH 6.5–9, whereas sufficiently reducing conditions promote conversion to U(IV) and precipitation as uraninite or related sparingly soluble phases [28,66].

Taken together, the Pourbaix diagrams demonstrate that a hydrologically induced decline in Eh can produce contrasting contaminant responses: reducing conditions may mobilize arsenic while promoting the immobilization of chromium and uranium. Subsequent drainage and re-oxidation do not necessarily reverse these responses uniformly. Newly formed Fe oxides can decrease dissolved arsenic concentrations through renewed sorption or co-precipitation [10,43,74]. Chromium may remain immobilized through sorption

or incorporation into reformed Fe phases, but can also be remobilized as Cr(VI) where reactive Mn oxides promote Cr(III) oxidation [49,51,75]. Oxidative shifts can similarly remobilize U(IV) as soluble U(VI), although the net response depends on carbonate chemistry, mineral transformation, and the duration and sequence of wetting and drying [76,77]. These divergent pathways illustrate why redox recovery during drying is not simply the reverse of wetting and why contaminant responses are element-specific and history-dependent.

Mobility reflects the interaction among mineral transformations, element-specific redox thresholds, and aqueous ligand chemistry, which together determine whether elements are released, transformed, or retained during wetting–drying cycles. Antimony mobility is strongly controlled by sorption to Fe and Mn (oxyhydr)oxides and organic matter, with reductive mineral dissolution potentially releasing Sb while Sb(III) formation may enhance retention under some conditions [55,57]. Manganese cycles between soluble Mn(II) under reducing conditions and less soluble Mn(III/IV) oxide phases under oxic conditions; these Mn oxides also act as strong oxidants that influence the mobility of other trace elements [59,74,78]. Molybdenum, commonly present as molybdate, may be released during reductive dissolution of Fe, Mn, and Al (oxyhydr)oxides but immobilized through thiomolybdate formation under sulfidic conditions [60,79,80]. Selenium mobility depends on reduction of mobile selenate to more strongly sorbed or solid Se species and on interactions with Fe and Al mineral surfaces [62,81,64]. Vanadium is generally more mobile as V(V) under oxidizing conditions, whereas reduction to V(IV) and sorption to Fe and Al (oxyhydr)oxides decrease mobility [24,26]. These

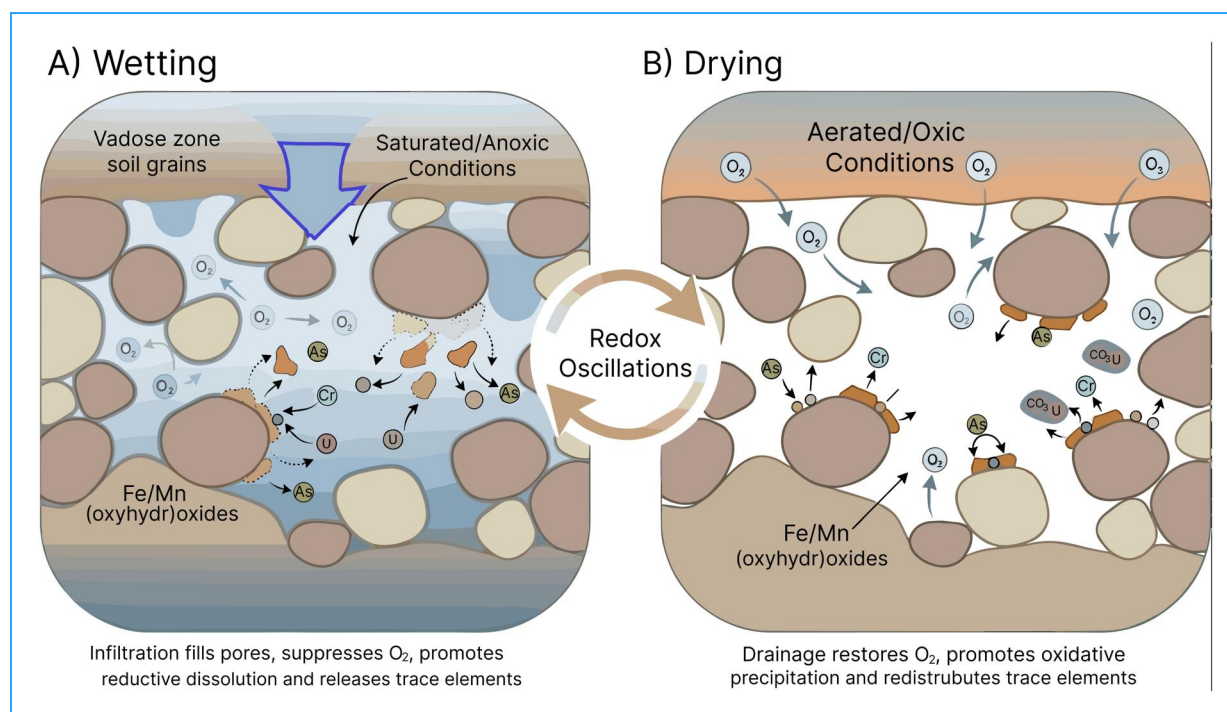


Figure 2. Wetting–drying cycles as a biogeochemical forcing mechanism in vadose-zone soils. (A) Wetting saturates pore spaces, limiting oxygen diffusion and creating anoxic conditions that drive reductive dissolution of Fe and Mn (oxyhydr)oxides and associated shifts in redox-sensitive element speciation. (B) As soils drain, oxygen reenters pore spaces, restoring oxic conditions that promote oxidative precipitation of Fe and Mn (oxyhydr)oxides and redistribution of trace elements between aqueous and solid phases.

element-specific pathways indicate that the redox and mineral controls identified for arsenic, chromium, and uranium extend more broadly across geogenic trace elements.

4. Wetting–drying cycles as a biogeochemical forcing mechanism

Wetting–drying cycles act as a primary hydrologic forcing mechanism in vadose-zone soils by generating redox oscillations that restructure mineral stability and trace-element partitioning between solid and aqueous phases. During wetting, infiltration fills pore spaces and suppresses oxygen diffusion, stimulating microbial respiration and promoting reducing conditions (Figure 2A). The significance of Figure 2A is that wetting initiates a redox cascade: within hours to days, Fe and Mn (oxyhydr)oxides may dissolve, releasing sorbed elements such as arsenic, while changes in oxidation state can simultaneously immobilize other elements, including chromium and uranium. Thus, saturation does not produce a uniform contaminant response but redistributes elements according to their mineral associations and redox sensitivity. As soils subsequently drain and re-aerate, oxygen diffuses back into the pore network, gradually restoring oxidizing conditions (Figure 2B). Figure 2B illustrates that drying is not simply the reverse of wetting. Re-oxidation promotes the

precipitation of new Fe and Mn mineral phases that may re-sorb dissolved contaminants, but it can also remobilize redox-sensitive elements by oxidizing Cr(III) to Cr(VI) or U(IV) to U(VI). Because the reformed minerals and contaminant distributions may differ from their initial states, each cycle can leave a geochemical legacy that influences subsequent wetting events. These alternating states drive repeated cycles of reduction and oxidation that control the dissolution and reformation of Fe and Mn (oxyhydr)oxide minerals and regulate contaminant speciation and mobility [6,9].

Wetting events can rapidly shift vadose-zone redox gradients, although the onset, magnitude, and persistence of reducing conditions vary substantially among systems. During agricultural managed aquifer recharge, Ganot and Dahlke [15] estimated that soil O_2 declined from atmospheric concentrations to 5% over approximately two days across three field sites. Similarly, analysis of high-frequency sensor data from four Central Valley MAR experiments indicated median times of 54 h to zero O_2 and 62 h to minimum Eh, whereas recovery to aerobic conditions required a median of approximately 97 h and a mean of approximately 145 h after flooding ceased [18]. In AWD rice mesocosms, most severely dried paddies did not decline below 0 mV until approximately 36 h after reflooding, and substantial evidence of Fe-oxide reduction generally developed over 72–96 h [82]. These observations indicate that

transitions from oxic to reducing conditions commonly occur over tens of hours to several days rather than according to a universal threshold. The response depends on soil texture, antecedent aeration, temperature, organic carbon availability, flooding duration, and water-filled pore connectivity. Indeed, some wet-dry column systems remained predominantly oxidizing, with leachate Eh ranging from 188 to 329 mV despite cyclic hydrologic forcing [83]. Labile organic carbon can deepen reducing conditions by supporting microbial respiration and electron-acceptor consumption, but its effects depend on physical soil properties and hydrologic residence time [16,73].

These redox oscillations drive repeated transformation of Fe and Mn (oxyhydr)oxides, which function as both major sorbents and redox-active phases in soils. Under reducing conditions, microbial reduction of Fe(III) and Mn(IV) destabilizes these minerals, resulting in their dissolution and the release of associated trace elements into porewater [27,68,69]. Spectroscopic and column studies demonstrate that these phases are not simply dissolved and reformed in a reversible manner; rather, repeated wetting-drying cycles promote restructuring of Fe mineral assemblages, with re-precipitated phases differing in composition, crystallinity, and sorption capacity from their precursors [44,72,73,84]. This hysteretic behavior indicates that mineral transformations accumulate over successive cycles, progressively altering the geochemical framework that governs contaminant retention.

Element-specific responses to these mineral transformations reflect differences in redox sensitivity and aqueous chemistry. Arsenic mobilization is closely coupled to Fe reduction, with declines in redox potential during saturation consistently coinciding with increases in dissolved Fe and arsenic concentrations due to release from Fe (oxyhydr)oxide surfaces [73,85,86]. Under sustained reducing conditions, arsenic commonly shifts toward the more mobile As(III), further enhancing its transport potential. In contrast, chromium exhibits an inverse response, with reduction of mobile Cr(VI) to less soluble Cr(III) during wet phases promoting immobilization, followed by partial re-oxidation to Cr(VI) during drying that increases mobility under oxic conditions [19,20,75,83]. Note that Chen et al. [83], a frequently cited study in this context, used soil artificially amended with chromate rather than soil that was geogenically enriched. Zhang et al. [75], who conducted research in basalt-derived paddy soils with naturally elevated chromium, report qualitatively similar redox-driven behavior but at concentrations reflective of natural geologic enrichment. Uranium displays a distinct but equally redox-sensitive behavior: reducing conditions promote the conversion of soluble U(VI) to sparingly soluble U(IV), often near Fe-reduction fronts, whereas re-oxidation during drainage can remobilize U(VI) [70,87]. However, uranium mobility is also strongly influenced by ligand chemistry; in carbonate-rich

environments, formation of stable Ca-uranyl-carbonate complexes can maintain uranium in solution even under oxidizing conditions, partially decoupling its behavior from Fe cycling [72,88].

Together, these observations demonstrate that wetting-drying cycles act as a coupled hydrologic-bio-geochemical forcing mechanism that drives redox oscillations, mineral transformation, and element-specific mobility responses in the vadose zone. Rather than representing reversible perturbations, repeated cycles progressively reorganize mineral assemblages and geochemical conditions, such that contaminant behavior reflects both instantaneous redox state and cumulative transformation legacy.

5. Cross-element response patterns under increasing hydrologic variability

Repeated wetting-drying cycles do not produce random or purely element-specific behavior. Instead, shared mineral associations and redox dependencies generate recurring and predictable cross-element response patterns that emerge consistently across environmental systems. Three dominant modes can be identified: (1) Fe-coupled mobilization at reductive thresholds, (2) asynchronous redox windows that redistribute contaminant speciation across wet and dry phases, and (3) progressive weakening of geochemical buffering capacity under repeated cycling. These modes are interconnected rather than independent. Figure 3 demonstrates how increasing hydrologic variability drives advancing wetting fronts and redox oscillations, which transform Fe and Mn mineral phases and redistribute geogenic trace elements between solid and aqueous pools. Repeated mineral transformation and contaminant release may, in turn, reduce sorption capacity and redox buffering, increasing the sensitivity of the system to subsequent hydrologic perturbations. The resulting feedback produces contaminant responses that are element-specific, path-dependent, and potentially amplified over successive wetting-drying cycles.

5.1. Fe-coupled co-mobilization

The most consistent cross-element response to wetting-drying forcing arises from the central role of Fe (oxyhydr)oxides, particularly ferrihydrite, goethite, and hematite, as shared mineral hosts for geogenic contaminants. These phases possess abundant surface hydroxyl groups that promote strong adsorption, co-precipitation, and structural incorporation of redox-sensitive trace elements [42,46,67,70,90]. Arsenic (As(V)) forms stable surface complexes or becomes incorporated during Fe mineral formation [46], Cr(III) is readily adsorbed or incorporated into (hydr)oxide matrices [42,83], and U(IV) exhibits strong affinity for Fe phases, with its behavior closely linked to Fe mineral transformations [70].

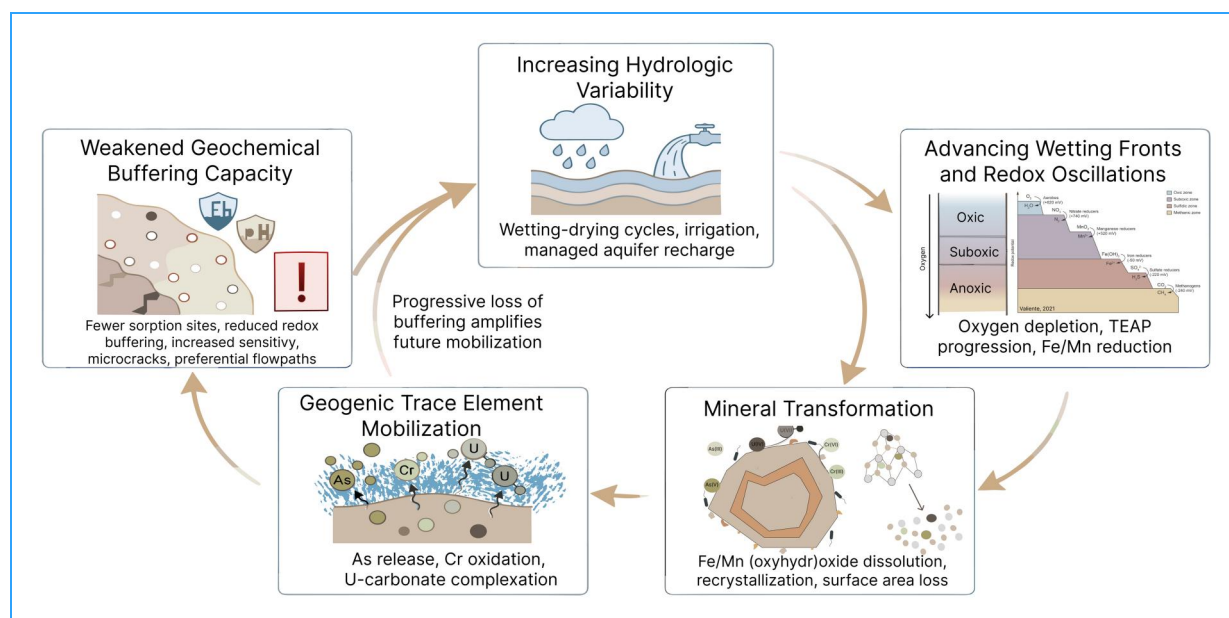


Figure 3. Conceptual framework linking hydrologic variability to recurring cross-element contaminant responses in the vadose zone. Increasing wetting–drying variability generates advancing wetting fronts and redox oscillations that drive Fe and Mn (oxyhydr)oxide dissolution, precipitation, and recrystallization. These mineral transformations regulate element-specific contaminant release, retention, oxidation-state transformation, and aqueous complexation. Repeated cycling may progressively alter geochemical buffering capacity, increasing the sensitivity of vadose-zone soils to subsequent hydrologic perturbations and amplifying future contaminant fluxes. Redox ladder adapted from Valiente et al. [89].

Under saturated conditions, oxygen limitation and carbon-fueled microbial respiration drive reductive dissolution of Fe(III) minerals, destabilizing this shared scaffold and releasing associated arsenic, chromium and uranium [46,70,74,75,91]. Because multiple contaminants partition to the same Fe framework, Fe reduction can generate synchronized pulses of multi-element speciation transformations [24]. Re-oxidation during drying promotes Fe(II) oxidation and precipitation of new Fe phases that may temporarily re-sequester contaminants, although repeated cycling does not necessarily restore equivalent surface area or sorption capacity [46,70,75,92].

This Fe-coupled behavior is especially pronounced in systems dominated by short-range-order Fe minerals, which dissolve rapidly and may recrystallize toward less reactive forms under repeated redox shifts [92,93]. Under increasingly variable hydrologic regimes, this dynamic restructuring can amplify both the frequency and the magnitude of co-mobilization events, particularly where labile carbon inputs enhance microbial Fe reduction. While Mn oxides can function as secondary shared sorbents, observations consistently indicate stronger association of arsenic and many co-occurring trace elements with Fe phases.

5.2. Asynchronous redox windows and ligand decoupling

Despite shared mineral associations, redox-sensitive elements do not respond synchronously to hydrologic

forcing. Wetting–drying cycles instead generate asynchronous redox windows in which elemental mobilization and immobilization occur on distinct thermodynamic and kinetic timelines. During saturation, Mn reduction precedes Fe reduction, and substantial arsenic and uranium transformations typically occur only after redox potentials cross the Fe(III)/Fe(II) threshold, creating a temporal lag between flooding onset and peak release [17,74].

Field and column studies further demonstrate pronounced hysteresis: transition to reducing conditions may occur within hours to days, whereas oxidative recovery can require weeks, extending the residence time of reduced species such as Fe(II) and As(III) in porewater [12,17,44,87,94]. Similar sequencing governs sulfide formation in wetlands and fields, where metals partition into sulfide phases according to solubility constraints, producing staggered immobilization following re-flooding [92,95]. Even at the mineral scale, oxidation of Fe-bearing clays proceeds in two stages, rapid surface oxidation followed by slower structural reorganization, further reinforcing asynchronous redox behavior [67].

In parallel, ligand decoupling can shift contaminant mobility away from Fe-host control. Under reducing conditions, dissolution of Fe (oxyhydr)oxides releases associated U, yet rapid complexation with dissolved organic matter can stabilize uranium independently of the original mineral host [70,91]. Conversely, competitive anions such as phosphate and carbonate may displace arsenate from ferrihydrite surfaces under oxic

conditions, triggering mobilization without Fe reduction [43,46,96]. Chromium provides an additional pathway: association with organic colloids can facilitate transport even where bulk redox conditions favor immobilization [42,97].

Together, these processes demonstrate that moisture variability redistributes contaminant behavior across time and space through both redox sequencing and ligand-driven decoupling. The result is not uniform amplification, but temporally structured and chemically redirected transport pathways under increasingly variable hydrologic regimes.

5.3. Progressive weakening of buffering capacity

The capacity of soils to buffer redox and pH perturbations under repeated wetting–drying is dynamic rather than static. Redox buffering arises from the availability of electron donors and acceptors that moderate changes in redox potential [17,87]. Microbial respiration and oxidation of reduced species consume oxygen, while Fe and Mn (oxyhydr)oxides provide substantial electron-acceptor reserves that can delay large shifts in redox conditions [74,98].

During flooding, reductive dissolution disperses Fe(III) oxide phases and releases structurally associated trace elements; during subsequent drainage, oxidation of Fe(II) produces recrystallized Fe(III) phases that may re-incorporate contaminants at rates differing from their precursors [70,75]. In some systems, initial contaminant pulses are followed by partial stabilization as Fe phases re-precipitate or sulfides form [88,99]. However, this stabilization is conditional. Changes in ligand concentrations (e.g., carbonate intrusion) can disrupt mineral-contaminant associations, producing large increases in porewater concentrations [99]. Similarly, repeated acidic inputs can exhaust alkalinity reserves in engineered soils, leading to a loss of buffering capacity and subsequent contaminant release once thresholds are exceeded [83,100].

Structural changes further influence buffering capacity. Wetting–drying cycles can promote aggregate breakdown, microcrack propagation, and permeability, allowing solutes to bypass reactive zones during repeated cycling [73,75,97,100–102]. In addition, depletion of labile organic carbon may reduce the ability to reestablish strongly reducing conditions in subsequent cycles unless external inputs replenish the system [91]. Taken together, buffering capacity under increasing hydrologic variability is not infinite. Early cycles may exhibit strong resistance to redox and pH perturbations, but repeated threshold crossings can restructure mineralogy, deplete reactive substrates, and weaken geochemical controls. Under increasingly nonstationary hydrologic regimes, this progressive erosion of buffering capacity may shift systems from containment

toward net contaminant flux to groundwater. These dynamics highlight a critical need to move beyond mechanistic understanding toward predictive frameworks that can capture transient, path-dependent behavior under variable hydrologic forcing.

6. Outlook and emerging directions

6.1. From mechanism to prediction under nonstationary hydrology

A central implication of the synthesis presented here is that redox-driven contaminant mobilization in the vadose zone cannot be predicted using frameworks that assume equilibrium behavior or steady-state hydrologic forcing. Mobilization of arsenic, uranium, chromium, and related elements is consistently associated with transient redox perturbations rather than static geochemical conditions [24]. Yet the literature informing predictive frameworks remains dominated by laboratory experiments, short-duration field studies, and single-contaminant conditions that cannot fully resolve multi-element interactions or cumulative responses across repeated hydrologic cycles. As a result, many existing frameworks rely on equilibrium assumptions or simplified redox representations that omit the timing, sequence, and legacy of transient biogeochemical conditions.

Process-based reactive transport models provide a framework for integrating the mechanisms identified in this review by coupling water flow and solute transport with kinetic biogeochemical reactions and evolving mineral properties [103]. For vadose-zone applications, this requires coupling variably saturated flow with gas- and aqueous-phase oxygen transport, microbial consumption of terminal electron acceptors, kinetic dissolution and precipitation of Fe and Mn minerals, and element-specific reactions controlling sorption, aqueous complexation, oxidation state, and secondary-mineral formation. Existing applications demonstrate that these models can explicitly represent organic-matter degradation, sequential redox reactions, Fe and Mn mineral transformations, surface complexation, competitive ligand effects, and contaminant-specific oxidation-state transformations [104–107]. Coupling these reactions with multidimensional hydraulic models can further resolve spatial transport pathways and quantify contaminant inventories and fluxes over longer timescales [108]. Reactive transport models fundamentally couple flow, transport, reaction rates, and evolving porous-medium properties, although their parameterization remains challenging across spatial scales. In particular, uncertainty in reactive surface area, kinetic parameters, and mineral-specific sorption properties can strongly affect model predictions and often requires site-specific experimental data [104].

Contaminant mobilization is governed not only by instantaneous redox state, but also by the sequence, duration, and frequency of wetting–drying cycles, which collectively impose path dependence and hysteresis on geochemical behavior. Wetting-driven redox transitions can occur rapidly. Turkeltaub et al. [18] reported median times of approximately 54 h to zero O_2 and 62 h to minimum Eh across MAR field sites, whereas recovery to aerobic conditions required a median of approximately 97 h and a mean of approximately 145 h. These asymmetric dynamics can prolong nonequilibrium aqueous conditions and produce transient contaminant pulses that models calibrated to average conditions may not capture. Process-based models should therefore retain information about antecedent moisture, mineral state, electron-acceptor inventories, and information on prior events rather than resetting reaction conditions at the beginning of each wetting cycle.

Repeated cycling also restructures the mineral system itself. Fe and Mn (oxyhydr)oxides, which serve as dominant sorption hosts and redox-active phases, do not necessarily dissolve and reform reversibly. Instead, repeated cycling can alter mineral crystallinity, reactive surface area, and sorption-site density, often producing progressively less reactive phases [70]. This creates legacy effects whereby contaminant behavior reflects not only current conditions but also the integrated history of previous redox oscillations. Most studies remain temporally constrained, isolating short-term oscillations rather than capturing the progressive effects of repeated cycling over longer periods [10,17,73]. Predictions based on single-event experiments may therefore underestimate the magnitude or persistence of contaminant mobilization under increasingly variable hydrologic regimes.

Extending process-based models across longer time-scales could reveal whether vadose-zone buffering capacity becomes depleted, renewed, or reorganized. Reactive minerals, sorption sites, electron acceptors, and organic carbon represent finite reservoirs that may be consumed, transformed, replenished, or redistributed through repeated hydrologic forcing. Future models should therefore update inventories of reactive solids and sorption sites alongside dissolved concentrations and account for feedback among mineral dissolution, precipitation, porosity, permeability, and preferential flow [103,104]. Physically based models already demonstrate that fine-textured interlayers can retain a substantial fraction of recharge water for years after surface flooding, decoupling recharge timing from contaminant arrival at the water table [109]. Extending such frameworks could test how climatic history, soil age, weathering intensity, and parent material create regional differences in contaminant vulnerability rather than assuming that equivalent hydrologic forcing produces equivalent responses across landscapes.

Data-driven models provide a complementary means of extending predictions across spatial scales that would be computationally or observationally intensive for fully resolved process-based models [110]. Machine-learning frameworks can identify nonlinear relationships and predict contaminant behavior from soil texture, Fe content, organic carbon, hydrologic history, and other site properties. For example, Tran et al. [111] predicted arsenic remobilization under repeated wetting–drying cycles with high accuracy, while Tran et al. [39] demonstrated substantial site-to-site variation in vadose-zone arsenic attenuation. However, model performance depends on the quality and representativeness of the training data, and predictions may generalize poorly when observations are sparse, spatially biased, or strongly correlated [112]. Purely data-driven models may also reproduce correlations without resolving whether they arise from hydrologic transport, microbial activity, or mineral reactions and, unless conservation constraints are explicitly imposed, do not inherently conserve water, solute, or elemental mass [113].

Hybrid and physics-informed machine-learning approaches offer a path toward combining data-driven flexibility with mechanistic accuracy. Li et al. [114], for example, trained machine-learning surrogates on outputs from a mechanistic surface-complexation model of uranium sorption, reproducing model predictions at substantially lower computational cost. Adhikari et al. [113] extended this approach to reactive transport in heterogeneous porous media by embedding governing flow, transport, and reaction equations directly within a physics-informed neural-network framework. Their model captured mixing-limited reaction fronts while preserving non-negative concentrations, demonstrating how governing equations, boundary conditions, reaction stoichiometry, and conservation constraints can guide predictions in data-scarce subsurface systems [113]. In such hybrid frameworks, process-based models retain the governing hydrologic and geochemical structure, while machine learning can approximate computationally expensive reaction modules, infer unresolved parameters and heterogeneity, assimilate observations, and fill data gaps.

The emerging direction, therefore, is not to choose between process-based and machine-learning approaches, but to develop predictive frameworks that combine mechanistic interpretability with computational adaptability. Future models of nonstationary vadose-zone systems should be able to conserve water and elemental mass, represent evolving mineral and redox states, retain the legacy of prior wetting–drying cycles, and assimilate observations across event to decadal timescales. Achieving this will require multi-cycle, multi-element field datasets that coordinate measurements of hydrology, oxygen, Eh, mineralogy, microbial activity, and dissolved contaminant fluxes. Such integration is essential to move from describing transient

contaminant responses to predicting when, where, and for how long hydrologic variability will threaten groundwater quality.

6.2. Uneven risk, emerging hotspots, and detection gaps

While these limitations constrain our ability to predict contaminant dynamics, emerging evidence also reveals that mobilization risk is not uniformly distributed across landscapes. Evidence synthesized across studies indicates that redox-driven contaminant mobilization is not spatially random, but concentrated within a predictable set of hydrogeologic and land-use contexts where hydrologic variability intersects with reactive geochemical conditions [26,71,72,81]. In agricultural settings, irrigation, fertilizer inputs, and organic carbon loading create conditions conducive to repeated redox cycling, promoting Fe reduction and the mobilization of arsenic, uranium and selenium [72,115,116]. Pulsed irrigation and managed aquifer recharge introduce rapid shifts in soil moisture that drive oxygen depletion within days, creating conditions in which contaminant mobilization is not only possible but recurrent. Vadose zone heterogeneity adds a further complication: fine-grained interlayers can retain substantial fractions of recharged water for years after a flooding event, creating a structural lag between management action and groundwater quality response that current assessment frameworks do not account for [109].

Carbonate-rich systems represent a distinct hotspot for uranium, where Ca–uranyl–carbonate complexes stabilize U(VI) in solution even under conditions that might otherwise favor sorption or reduction, effectively decoupling uranium behavior from Fe cycling and sustaining mobility across a broader range of redox conditions [52,66,71]. Manganese oxide-rich, organic-poor soils present a contrasting pathway for chromium: persistent Mn(III/IV) oxides can oxidize Cr(III) to mobile Cr(VI) even under nominally reducing conditions, enhancing chromium mobility through an oxidative mechanism that is not predicted by bulk redox state alone [49,51]. These element-specific pathways highlight that the same hydrologic forcing can produce fundamentally different contaminant outcomes depending on system mineralogy, an important distinction that single-contaminant monitoring frameworks will consistently miss.

Despite this emerging predictability in hotspot identification, existing groundwater monitoring networks are designed for broad, regulatory coverage rather than geochemical risk, with spatially distributed, low-frequency sampling that prioritizes national representativeness over targeted surveillance of vulnerable settings. The United States Geological Survey (USGS) national network samples on a decadal rotating basis

across 89 distributed networks, providing a valuable baseline, but is structurally ill suited to capturing the episodic, transient concentration pulses that characterize redox-driven mobilization [25]. Risk-based monitoring frameworks that target sampling frequency and site selection to geochemical and hydrologic vulnerability (e.g., reactive mineral assemblages, organic carbon availability, irrigated recharge) would be far better positioned to detect emerging contamination before it reaches regulatory thresholds [23,25].

6.3. Microbial controls on redox dynamics

Microbial processes are central to redox-driven contaminant mobilization yet remain underrepresented in predictive frameworks. Dissimilatory metal-reducing microorganisms drive Fe(III), arsenate, sulfate, and uranium reduction, linking organic carbon availability to contaminant release [22,27,41,73]. However, field data complicate the assumption that organic carbon availability is the primary control on redox timing. At four Central Valley MAR sites, anoxic conditions developed within 2–2.5 days of inundation, governed primarily by physical restriction of oxygen diffusion in water-filled pores (O_2 diffusivity in water is approximately $10,000\times$ lower than in air) with microbial respiration as a contributing rather than sole driver [18]. Clay content and soil temperature were the strongest predictors of the rate of Eh decline, while dissolved organic carbon showed a stronger association with the minimum Eh reached during flooding, suggesting that physical oxygen supply constraints govern the timing of anoxia onset while carbon availability modulates how strongly reducing conditions become.

What this means under a flashier climate is poorly understood. Projected elevated temperatures can accelerate microbial metabolism and accelerate reductive dissolution, while more frequent and intense wetting events promote transient anoxic conditions that favor microbial reduction pathways, but the interaction between these two forcings is rarely resolved [65,84,93,117]. Reactive transport models that parameterize anoxia onset primarily as a function of microbial carbon consumption may therefore misrepresent redox dynamics in physically constrained environments. A hotter, flashier climate does not simply intensify existing microbial dynamics; it alters their timing, amplitude, and recovery trajectory in ways that current models, parameterized under stable temperature and moisture regimes, are not equipped to represent. The temperature sensitivity of microbially mediated reductive dissolution remains particularly poorly constrained, and few studies explicitly link microbial kinetics to hydrologic variability or climate forcing at field scale. Aerobic microbial processes during drying phases, including Mn oxidation and arsenic re-oxidation, are equally

understudied, despite governing whether contaminants released during wet periods are re-immobilized or remain in porewater through subsequent cycles [49,51].

6.4. Toward integrated monitoring, modeling, and management

Addressing these challenges requires interventions across hydrologic, geochemical, and management domains. Current monitoring approaches rely on low-frequency sampling and bulk water chemistry that fail to capture transient redox fluctuations and short-lived contaminant pulses. High-frequency, depth-resolved measurements of redox potential, dissolved oxygen, and contaminant concentrations, as showcased by Turkeltaub et al. [18], are needed to resolve episodic mobilization events before they reach regulatory thresholds. Expanded access to advanced analytical tools, including inductively coupled plasma mass spectrometry (ICP-MS) for trace-element quantification and synchrotron-based spectroscopy (e.g., X-ray absorption spectroscopy [XAS], extended X-ray absorption fine structure [EXAFS]) for oxidation-state and mineral-host identification, can further resolve solid-phase transformations during repeated wetting–drying cycles. Similarly, existing modeling approaches must move beyond equilibrium representations toward coupled reactive transport frameworks that explicitly incorporate microbial processes, mineral transformation, and hydrologic variability.

Water management introduces direct tradeoffs between water quantity objectives and water quality outcomes that current frameworks have not systematically addressed. Soil amendments added to MAR basins to enhance denitrification can simultaneously drive metal mobilization. Column infiltration experiments show average effluent arsenic of $14.7 \mu\text{g L}^{-1}$ in carbon-amended treatments compared to negligible arsenic in unamended controls [16]. This nitrogen–metal tradeoff is a real operational constraint, and designing MAR systems that balance competing objectives requires explicit consideration of redox dynamics rather than treating water quality as a secondary constraint.

In agricultural systems, AWD irrigation consistently reduces cumulative porewater arsenic exposure relative to continuous flooding, by a factor of 8.2 under current (33°C) conditions and by 15.9-fold under a severe warming scenario (38°C , 850 ppmv CO_2), indicating that AWD remains an effective management strategy under future climate projections [12]. Grain arsenic is also reduced by AWD, though more modestly (1.5-fold at 33°C , 1.3-fold at 38°C). Field trials in temperate paddies confirm reductions in grain arsenic alongside methane emission reductions of 40–73% under AWD [11]. However, both studies document a consistent tradeoff: AWD increases cadmium and nickel uptake,

and in Mn oxide-rich soils, the oxidizing phases of AWD cycles may enhance Cr(VI) generation. Mitigation strategies must therefore be evaluated not only for their effectiveness against target contaminants but also for their potential to shift risk to others.

Pre-deployment characterization of vadose zone geochemistry (reactive mineral inventories, redox buffering capacity, organic carbon availability, and depth-resolved texture) should be integrated into standard MAR site assessment wherever geogenic arsenic, chromium and uranium enrichment is indicated by geological mapping of source rock mineralogy, known depositional environments, or background water quality monitoring, rather than treated as optional baseline data. Without this baseline, neither the magnitude of the contaminant mobilization risk nor the timescales over which it operates can be anticipated.

7. Conclusion: flashier hydrology, flashier contaminants

The evidence synthesized here demonstrates that increasing hydrologic variability does not simply perturb vadose-zone geochemistry but reorganizes it through repeated wetting–drying cycles, redox oscillations, and mineral transformation. Across agricultural and environmental systems, fluctuations in moisture and oxygen availability alter microbial respiration and Fe and Mn (oxyhydr)oxide stability, thereby regulating the mobility of redox-sensitive geogenic contaminants. Although arsenic, chromium, uranium, and related elements exhibit distinct redox thresholds and aqueous chemistries, three recurring response patterns emerge: Fe-coupled contaminant release and retention, asynchronous mobilization and immobilization windows, and progressive alteration of geochemical buffering capacity. Increasing hydrologic variability therefore does not produce a uniform increase in contaminant mobility; instead, it produces transient, element-specific, and history-dependent responses.

These responses have direct implications for contaminant fate and environmental exposure. Wetting can transform vadose-zone soils from contaminant sinks into temporary sources by dissolving reactive minerals and releasing previously retained elements into porewater. Subsequent drying may restore retention for some contaminants while remobilizing others favored under oxidizing conditions. As a result, the composition and concentration of recharge reaching groundwater may vary substantially over a single wetting–drying cycle. Fine-textured layers and poorly connected pore domains may further delay contaminant transport, allowing mobilized solutes to persist in the vadose zone and reach groundwater after surface conditions have returned to normal. In agricultural systems, these changes may also alter contaminant availability to

crops, meaning that water-management practices that reduce exposure to one element may increase exposure to another.

Repeated cycling creates an additional long-term concern because contaminant attenuation observed during an initial event may not persist. Dissolution, recrystallization, changes in reactive surface area, and depletion of electron donors or acceptors can progressively reorganize the soil's capacity to buffer redox and pH changes. Consequently, average concentrations or measurements collected between hydrologic events may underestimate episodic releases and cumulative contaminant flux. Field assessment should therefore evaluate both wetting and drainage phases, account for multiple contaminants and exposure pathways, and consider whether repeated hydrologic forcing alters mineral retention over time. Protecting groundwater under increasingly nonstationary hydrology will require site-specific characterization and monitoring strategies that treat the vadose zone as an evolving biogeochemical system rather than a passive pathway for recharge.

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Author contributions

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Data availability statement

No data were generated or analyzed during this study.

References

1. Stewart RD, Flury M, Ajami H, et al. Emerging issues and research opportunities in vadose zone processes. *Vadose Zone Journal*. 2025;24:e70030. doi: [10.1002/vzj2.70030](https://doi.org/10.1002/vzj2.70030)
2. Oishy MN, Shemonty NA, Fatema SI, et al. Unravelling the effects of climate change on the soil-plant-atmosphere interactions: a critical review. *Soil Environ Health*. 2025; 3(1):100130. doi: [10.1016/j.seh.2025.100130](https://doi.org/10.1016/j.seh.2025.100130)
3. Swain DL, Langenbrunner B, Neelin JD, et al. Increasing precipitation volatility in twenty-first-century California. *Nature Clim Change*. 2018;8(5):427–433. doi: [10.1038/s41558-018-0140-y](https://doi.org/10.1038/s41558-018-0140-y)
4. Berg A, Sheffield J. Climate change and drought: the soil moisture perspective. *Curr Clim Change Rep*. 2018;4(2): 180–191. doi: [10.1007/s40641-018-0095-0](https://doi.org/10.1007/s40641-018-0095-0)
5. Zaitchik BF, Rodell M, Biasutti M, et al. Wetting and drying trends under climate change. *Nat Water*. 2023;1(6):502–513. doi: [10.1038/s44221-023-00073-w](https://doi.org/10.1038/s44221-023-00073-w)
6. Furtak K, Wolińska A. The impact of extreme weather events as a consequence of climate change on the soil moisture and on the quality of the soil environment and agriculture – a review. *Catena (Amst)*. 2023;231:107378. doi: [10.1016/j.catena.2023.107378](https://doi.org/10.1016/j.catena.2023.107378)
7. Zhang Z, Furman A. Soil redox dynamics under dynamic hydrologic regimes—a review. *Sci Total Environ*. 2021;763: 143026. doi: [10.1016/j.scitotenv.2020.143026](https://doi.org/10.1016/j.scitotenv.2020.143026)
8. Reineke W, Schlömann M. 2023 *Environmental microbiology*. Berlin (Germany): Springer. doi: [10.1007/978-3-662-66547-3](https://doi.org/10.1007/978-3-662-66547-3)
9. Xu Z, Tsang DCW. Redox-induced transformation of potentially toxic elements with organic carbon in soil. *Carbon Res*. 2022;1(1):9. doi: [10.1007/s44246-022-00010-8](https://doi.org/10.1007/s44246-022-00010-8)
10. Tran THH, Kim SH, Jo HY, et al. Transient behavior of arsenic in vadose zone under alternating wet and dry conditions: a comparative soil column study. *J Hazard Mater*. 2022;422:126957. doi: [10.1016/j.jhazmat.2021.126957](https://doi.org/10.1016/j.jhazmat.2021.126957)
11. Vitali A, Moretti B, Bertora C, et al. The environmental and agronomic benefits and trade-offs linked with the adoption alternate wetting and drying in temperate rice paddies. *Field Crops Res*. 2024;317:109550. doi: [10.1016/j.fcr.2024.109550](https://doi.org/10.1016/j.fcr.2024.109550)
12. Duncan AH, Armenta N, Garcia-Ledezma F, et al. Alternate wetting and drying limits arsenic in porewater and rice grain under severe future climate conditions. *Environ Sci Technol*. 2025;59(42):22796–22806. doi: [10.1021/acs.est.5c03552](https://doi.org/10.1021/acs.est.5c03552)
13. Dillon P, Stuyfzand P, Grischek T, et al. Sixty years of global progress in managed aquifer recharge. *Hydrogeol J*. 2019;27(1):1–30. doi: [10.1007/s10040-018-1841-z](https://doi.org/10.1007/s10040-018-1841-z)
14. Dutta T, Carles-Brangarí A, Fernández-García D, et al. Vadose zone oxygen (O₂) dynamics during drying and wetting cycles: an artificial recharge laboratory experiment. *J Hydrol*. 2015;527:151–159. doi: [10.1016/j.jhydrol.2015.04.048](https://doi.org/10.1016/j.jhydrol.2015.04.048)
15. Ganot Y, Dahlke HE. Natural and forced soil aeration during agricultural managed aquifer recharge. *Vadose Zone J*. 2021;20(3):e20128. doi: [10.1002/vzj2.20128](https://doi.org/10.1002/vzj2.20128)
16. Pensky J, Fisher AT, Gorski G, et al. Linking nitrate removal, carbon cycling, and mobilization of geogenic trace metals during infiltration for managed recharge. *Water Res*. 2023; 239:120045. doi: [10.1016/j.watres.2023.120045](https://doi.org/10.1016/j.watres.2023.120045)

17. Pensky J, Fisher AT, Gorski G, et al. Enhanced cycling of nitrogen and metals during rapid infiltration: implications for managed recharge. *Sci Total Environ.* 2022;838(Pt 4): 156439. doi: [10.1016/j.scitotenv.2022.156439](https://doi.org/10.1016/j.scitotenv.2022.156439)
18. Turkeltaub T, Prieto García C, Dahlke HE, et al. Predictability of redox potential and oxygen status in managed aquifer recharge sites based on sensor data and regression techniques. *J Hydrol.* 2025;660:133486. doi: [10.1016/j.jhydrol.2025.133486](https://doi.org/10.1016/j.jhydrol.2025.133486)
19. Liu M, Fu Q, Li T, et al. Effects of mulch drip irrigation on the coupled heat-Fe drive in root zone soils and analysis of soil Cr(VI) remediation mechanism. *Soil Tillage Res.* 2026;256:106884. doi: [10.1016/j.still.2025.106884](https://doi.org/10.1016/j.still.2025.106884)
20. Xiao W, Ye X, Zhu Z, et al. Combined effects of rice straw-derived biochar and water management on transformation of chromium and its uptake by rice in contaminated soils. *Ecotoxicol Environ Saf.* 2021;208:111506. doi: [10.1016/j.ecoenv.2020.111506](https://doi.org/10.1016/j.ecoenv.2020.111506)
21. Dahan O. Vadose zone monitoring as a key to groundwater protection. *Front Water.* 2020;2:599569:1-9. doi: [10.3389/frwa.2020.599569](https://doi.org/10.3389/frwa.2020.599569)
22. Fakhreddine S, Prommer H, Scanlon BR, et al. Mobilization of arsenic and other naturally occurring contaminants during managed aquifer recharge: a critical review. *Environ Sci Technol.* 2021;55(4):2208–2223. doi: [10.1021/acs.est.0c07492](https://doi.org/10.1021/acs.est.0c07492)
23. Mukherjee A, Coomar P, Sarkar S, et al. Arsenic and other geogenic contaminants in global groundwater. *Nat Rev Earth Environ.* 2024;5(4):312–328. doi: [10.1038/s43017-024-00519-z](https://doi.org/10.1038/s43017-024-00519-z)
24. Coyte RM, Vengosh A. Factors controlling the risks of co-occurrence of the redox-sensitive elements of arsenic, chromium, vanadium, and uranium in groundwater from the Eastern United States. *Environ Sci Technol.* 2020;54(7): 4367–4375. doi: [10.1021/acs.est.9b06471](https://doi.org/10.1021/acs.est.9b06471)
25. Erickson ML, Elliott SM, Musgrove M, et al. Decadal trends and occurrence of geogenic constituents and mixtures in groundwater across the continental United States. *ACS ES&T Water.* 2026;6(2):664–678. doi: [10.1021/acsestwater.5c00756](https://doi.org/10.1021/acsestwater.5c00756)
26. Peel HR, Balogun FO, Bowers CA, et al. Towards understanding factors affecting arsenic, chromium, and vanadium mobility in the subsurface. *Water (Basel).* 2022; 14(22):3687. doi: [10.3390/w14223687](https://doi.org/10.3390/w14223687)
27. van Genuchten CM, Wang K, Jakobsen R. Vadose zone perspectives in global arsenic research: a review and future opportunities. *Vadose Zone J.* 2024;23(4):e20313. doi: [10.1002/vzj2.20313](https://doi.org/10.1002/vzj2.20313)
28. Smedley PL, Kinniburgh DG. Uranium in natural waters and the environment: distribution, speciation and impact. *Appl Geochem.* 2023;148:105534. doi: [10.1016/j.apgeochem.2022.105534](https://doi.org/10.1016/j.apgeochem.2022.105534)
29. Levy ZF, Balkan M, Shelton JL. Quality of groundwater used for domestic supply in the modesto, turlock, and merced subbasins of the San Joaquin Valley, California. In *Open-File Report (Nos. 2022–1116)*. U.S. Geological Survey; 2023. doi: [10.3133/ofr20221116](https://doi.org/10.3133/ofr20221116)
30. Rosen MR, Burow KR, Fram MS. Anthropogenic and geologic causes of anomalously high uranium concentrations in groundwater used for drinking water supply in the southeastern San Joaquin Valley, CA. *J Hydrol.* 2019;577: 124009. doi: [10.1016/j.jhydrol.2019.124009](https://doi.org/10.1016/j.jhydrol.2019.124009)
31. Guo H, Liu C, Yan S, et al. Source, distribution, and geochemical processes of geogenic high chromium groundwater around the world: a critical review. *J Hydrol.* 2024; 638:131480. doi: [10.1016/j.jhydrol.2024.131480](https://doi.org/10.1016/j.jhydrol.2024.131480)
32. Martinez-Morata I, Bostick BC, Conroy-Ben O, et al. Nationwide geospatial analysis of county racial and ethnic composition and public drinking water arsenic and uranium. *Nat Commun.* 2022;13(1):7461. doi: [10.1038/s41467-022-35185-6](https://doi.org/10.1038/s41467-022-35185-6)
33. Smalling KL, Romanok KM, Bradley PM, et al. Mixed contaminant exposure in tapwater and the potential implications for human-health in disadvantaged communities in California. *Water Res.* 2024;267:122485. doi: [10.1016/j.watres.2024.122485](https://doi.org/10.1016/j.watres.2024.122485)
34. Cooper P, Olafuyi L, Ibrahim N, et al. A laboratory simulation to investigate effects of moistures on U distribution among solid phase components in army range soils. *MethodsX.* 2022;9:101678. doi: [10.1016/j.mex.2022.101678](https://doi.org/10.1016/j.mex.2022.101678)
35. Miele F, Benettin P, Wang S, et al. Spatially explicit linkages between redox potential cycles and soil moisture fluctuations. *Water Resour Res.* 2023;59(3):e2022WR032328. doi: [10.1029/2022WR032328](https://doi.org/10.1029/2022WR032328)
36. Machado-Silva F, Weintraub MN, Ward ND, et al. Short-term groundwater level fluctuations drive subsurface redox variability. *Environ Sci Technol.* 2024;58(33):14687–14697. doi: [10.1021/acs.est.4c01115](https://doi.org/10.1021/acs.est.4c01115)
37. Liu H, Yuan R, Sarkodie EK, et al. Insight into functional microorganisms in wet-dry conversion to alleviate the toxicity of chromium fractions in red soil. *Front Microbiol.* 2022;13:977171. doi: [10.3389/fmicb.2022.977171](https://doi.org/10.3389/fmicb.2022.977171)
38. Meng L, Zuo R, Wang J, et al. Response of the redox species and indigenous microbial community to seasonal groundwater fluctuation from a typical riverbank filtration site in Northeast China. *Ecol Eng.* 2021;159:106099. doi: [10.1016/j.ecoleng.2020.106099](https://doi.org/10.1016/j.ecoleng.2020.106099)
39. Tran THH, Chung J, Kwon MJ, et al. Data-driven framework for determining site-specific attenuation factors of arsenic in the vadose zone. *Environ Sci Technol.* 2026;60(4):3427–3437. doi: [10.1021/acs.est.5c09358](https://doi.org/10.1021/acs.est.5c09358)
40. Zhai H, Kleawsampanjai P, Wang R, et al. Effect of alternating wetting and drying cycles on selenium aging in three soils amended with selenate/selenite. *J Soils Sediments.* 2025;25(5):1532–1543. doi: [10.1007/s11368-025-04025-7](https://doi.org/10.1007/s11368-025-04025-7)
41. Banala UK, Das NPI, Toleti SR. Microbial interactions with uranium: towards an effective bioremediation approach. *Environ Technol Innov.* 2021;21:101254. doi: [10.1016/j.eti.2020.101254](https://doi.org/10.1016/j.eti.2020.101254)
42. Boschetti T, Segadelli S, Gori F, et al. A preliminary study on the effects of rainfall-related conditions on chromium increase in ultramafic-hosted springs: a possible climate change concern? *Sci Total Environ.* 2025;958:177826. doi: [10.1016/j.scitotenv.2024.177826](https://doi.org/10.1016/j.scitotenv.2024.177826)
43. Cai D, Kong S, Shao Y, et al. Mobilization of arsenic from As-containing iron minerals under irrigation: effects of exogenous substances, redox condition, and intermittent flow. *J Hazard Mater.* 2022;440:129736. doi: [10.1016/j.jhazmat.2022.129736](https://doi.org/10.1016/j.jhazmat.2022.129736)
44. Majumdar A, Upadhyay MK, Giri B, et al. Arsenic dynamics and flux assessment under drying-wetting irrigation and enhanced microbial diversity in paddy soils: a four year study in Bengal delta plain. *J Hazard Mater.* 2021;409: 124443. doi: [10.1016/j.jhazmat.2020.124443](https://doi.org/10.1016/j.jhazmat.2020.124443)
45. Perraki M, Vasileiou E, Bartzas G. Tracing the origin of chromium in groundwater: current and new perspectives. *Curr Opin Environ Sci Health.* 2021;22:100267. doi: [10.1016/j.coesh.2021.100267](https://doi.org/10.1016/j.coesh.2021.100267)
46. Yang P-T, Hashimoto Y, Wu W-J, et al. Effects of long-term paddy rice cultivation on soil arsenic speciation. *J Environ Manage.* 2020;254:109768. doi: [10.1016/j.jenvman.2019.109768](https://doi.org/10.1016/j.jenvman.2019.109768)
47. Hug SJ, Winkel LHE, Voegelin A, et al. Arsenic and other geogenic contaminants in groundwater – a global challenge. *Chimia (Aarau).* 2020;74(7-8):524–537. doi: [10.2533/chimia.2020.524](https://doi.org/10.2533/chimia.2020.524)

48. Wang J, Li Z, Zhu Q, et al. Review on arsenic environment behaviors in aqueous solution and soil. *Chemosphere*. 2023;333:138869. doi: [10.1016/j.chemosphere.2023.138869](https://doi.org/10.1016/j.chemosphere.2023.138869)
49. Ao M, Sun S, Deng T, et al. Natural source of Cr(VI) in soil: the anoxic oxidation of Cr(III) by Mn oxides. *J Hazard Mater*. 2022;433:128805. doi: [10.1016/j.jhazmat.2022.128805](https://doi.org/10.1016/j.jhazmat.2022.128805)
50. Janssen DJ, Bauer KW, Bruggmann S, et al. The global biogeochemical cycle of chromium at the Earth's surface. *Global Biogeochem Cycles*. 2025;39(6):e2025GB008525. doi: [10.1029/2025GB008525](https://doi.org/10.1029/2025GB008525)
51. Liang J, Huang X, Yan J, et al. A review of the formation of Cr(VI) via Cr(III) oxidation in soils and groundwater. *Sci Total Environ*. 2021;774:145762. doi: [10.1016/j.scitotenv.2021.145762](https://doi.org/10.1016/j.scitotenv.2021.145762)
52. Liu Z, Liang Y, Zhu P, et al. Uranium contamination in groundwater: sources, speciation, transformations, migration, and remediation strategies. *ACS EST Water*. 2025;5(8):4301–4321. doi: [10.1021/acsestwater.5c00274](https://doi.org/10.1021/acsestwater.5c00274)
53. Westrop JP, Snow DD, Weber KA. 2022 Mobilization of naturally occurring uranium in groundwater under intensely managed farmland. In: Ray C, Muddu S, Sharma S, editors. *Food, energy, and water nexus*. Cham (Switzerland): Springer International Publishing. p. 215–231. doi: [10.1007/978-3-030-85728-8_12](https://doi.org/10.1007/978-3-030-85728-8_12)
54. Bolan N, Kumar M, Singh E, et al. Antimony contamination and its risk management in complex environmental settings: a review. *Environ Int*. 2022;158:106908. doi: [10.1016/j.envint.2021.106908](https://doi.org/10.1016/j.envint.2021.106908)
55. Da Costa L, Zopfi J, Alewell C, et al. Antimony mobility in soils: current understanding and future research directions. *Environ Sci Process Impacts*. 2025;27(4):833–848. doi: [10.1039/D4EM00743C](https://doi.org/10.1039/D4EM00743C)
56. Majzlan J, Filella M. What do we know about the natural sources, transport and sinks of antimony in the environment? *Geochemistry*. 2024;84(1):126072. doi: [10.1016/j.chemer.2023.126072](https://doi.org/10.1016/j.chemer.2023.126072)
57. Verbeeck M, Thiry Y, Smolders E. Soil organic matter affects arsenic and antimony sorption in anaerobic soils. *Environ Pollut*. 2020;257:113566. doi: [10.1016/j.envpol.2019.113566](https://doi.org/10.1016/j.envpol.2019.113566)
58. Akil Prasath RV, Dewangan C, Kumar T, et al. Critical review of manganese sources, pollution, ecotoxicological risks, and mine remediation: synthesis of a site-specific restoration framework. *J Environ Manage*. 2026;404:129500. doi: [10.1016/j.jenvman.2026.129500](https://doi.org/10.1016/j.jenvman.2026.129500)
59. Podgorski J, Berg M. Manganese, a hidden threat to global water quality and health. *Nat Water*. 2026;4(8):954–964. doi: [10.1038/s44221-026-00676-z](https://doi.org/10.1038/s44221-026-00676-z)
60. Smedley PL, Kinniburgh DG. Molybdenum in natural waters: a review of occurrence, distributions and controls. *Appl Geochem*. 2017;84:387–432. doi: [10.1016/j.apgeochem.2017.05.008](https://doi.org/10.1016/j.apgeochem.2017.05.008)
61. Wang D. Redox chemistry of molybdenum in natural waters and its involvement in biological evolution. *Front Microbiol*. 2012;3:427. doi: [10.3389/fmicb.2012.00427](https://doi.org/10.3389/fmicb.2012.00427)
62. Ascencio-Damian JE, Inoue D, Ike M. A structured review of selenium pollution in global aquatic environments: sources, levels, and co-pollutants. *Environ Qual Mgmt*. 2026;35(4):e70366. doi: [10.1002/tqem.70366](https://doi.org/10.1002/tqem.70366)
63. Khanna K, Kumar P, Ohri P, et al. Harnessing the role of selenium in soil–plant–microbe ecosystem: ecophysiological mechanisms and future prospects. *Plant Growth Regul*. 2023;100(2):197–217. doi: [10.1007/s10725-022-00830-z](https://doi.org/10.1007/s10725-022-00830-z)
64. Wang Z, Huang W, Pang F. Selenium in soil–plant–microbe: a review. *Bull Environ Contam Toxicol*. 2022;108(2):167–181. doi: [10.1007/s00128-021-03386-2](https://doi.org/10.1007/s00128-021-03386-2)
65. Wnuk E. Mobility, bioavailability, and toxicity of vanadium regulated by physicochemical and biological properties of the soil. *J Soil Sci Plant Nutr*. 2023;23(1):1386–1396. doi: [10.1007/s42729-023-01130-9](https://doi.org/10.1007/s42729-023-01130-9)
66. Dewey C, Sokaras D, Kroll T, et al. Calcium-uranyl-carbonate species kinetically limit U(VI) reduction by Fe(II) and lead to U(V)-bearing ferrihydrite. *Environ Sci Technol*. 2020;54(10):6021–6030. doi: [10.1021/acs.est.9b05870](https://doi.org/10.1021/acs.est.9b05870)
67. Zhao Z, Yuan Q, Meng Y, et al. Oxidation of bioreduced iron-bearing clay mineral triggers arsenic immobilization. *Environ Sci Pollut Res Int*. 2022;29(29):44874–44882. doi: [10.1007/s11356-022-19028-x](https://doi.org/10.1007/s11356-022-19028-x)
68. Fakhreddine S, Prommer H, Gorelick SM, et al. Controlling arsenic mobilization during managed aquifer recharge: the role of sediment heterogeneity. *Environ Sci Technol*. 2020;54(14):8728–8738. doi: [10.1021/acs.est.0c00794](https://doi.org/10.1021/acs.est.0c00794)
69. Wang Y, Li J, Ma T, et al. Genesis of geogenic contaminated groundwater: As, F and I. *Crit Rev Environ Sci Technol*. 2021;51(24):2895–2933. doi: [10.1080/10643389.2020.1807452](https://doi.org/10.1080/10643389.2020.1807452)
70. Ding B, Liang J, Dong Y, et al. The effects of water-flooding and wet-to-dry transition on phase transformation of schwertmannite chemically formed in constant pH condition. *Chem Geol*. 2024;656:122094. doi: [10.1016/j.chemgeo.2024.122094](https://doi.org/10.1016/j.chemgeo.2024.122094)
71. Lopez AM, Wells A, Fendorf S. Soil and aquifer properties combine as predictors of groundwater uranium concentrations within the Central Valley, California. *Environ Sci Technol*. 2021;55(1):352–361. doi: [10.1021/acs.est.0c05591](https://doi.org/10.1021/acs.est.0c05591)
72. Malakar A, Ray C, D'Alessio M, et al. Interplay of legacy irrigation and nitrogen fertilizer inputs to spatial variability of arsenic and uranium within the deep vadose zone. *Sci Total Environ*. 2023;897:165299. doi: [10.1016/j.scitotenv.2023.165299](https://doi.org/10.1016/j.scitotenv.2023.165299)
73. Tran THH, Kim SH, Lee H, et al. Variable effects of soil organic matter on arsenic behavior in the vadose zone under different bulk densities. *J Hazard Mater*. 2023;447:130826. doi: [10.1016/j.jhazmat.2023.130826](https://doi.org/10.1016/j.jhazmat.2023.130826)
74. Maguffin SC, Abu-Ali L, Tappero RV, et al. Influence of manganese abundances on iron and arsenic solubility in rice paddy soils. *Geochim Cosmochim Acta*. 2020;276:50–69. doi: [10.1016/j.gca.2020.02.012](https://doi.org/10.1016/j.gca.2020.02.012)
75. Zhang K, Yang Y, Chi W, et al. Chromium transformation driven by iron redox cycling in basalt-derived paddy soil with high geological background values. *J Environ Sci (China)*. 2023;125:470–479. doi: [10.1016/j.jes.2021.12.013](https://doi.org/10.1016/j.jes.2021.12.013)
76. Ding Y, Yuan Y, Zeng T, et al. Water content-driven uranium fraction transformation and stability dynamics in contaminated soils. *J Hazard Mater*. 2026;501:140832. doi: [10.1016/j.jhazmat.2025.140832](https://doi.org/10.1016/j.jhazmat.2025.140832)
77. Van Berk W, Fu Y. Redox roll-front mobilization of geogenic uranium by nitrate input into aquifers: risks for groundwater resources. *Environ Sci Technol*. 2017;51(1):337–345. doi: [10.1021/acs.est.6b01569](https://doi.org/10.1021/acs.est.6b01569)
78. Li H, Santos F, Butler K, et al. A critical review on the multiple roles of manganese in stabilizing and destabilizing soil organic matter. *Environ Sci Technol*. 2021;55(18):12136–12152. doi: [10.1021/acs.est.1c00299](https://doi.org/10.1021/acs.est.1c00299)
79. Lin K, Yang Z, Yu T, et al. Enrichment mechanisms of Mo in soil in the karst region Guangxi, China. *Ecotoxicol Environ Saf*. 2023;255:114808. doi: [10.1016/j.ecoenv.2023.114808](https://doi.org/10.1016/j.ecoenv.2023.114808)
80. Wu Z, Hou Q, Yang Z, et al. Identification of factors driving the spatial distribution of molybdenum (Mo) in topsoil in the Longitudinal Range-Gorge Region of Southwestern China using the Geodetector model. *Ecotoxicol Environ Saf*. 2024;271:115846. doi: [10.1016/j.ecoenv.2023.115846](https://doi.org/10.1016/j.ecoenv.2023.115846)

81. Pang Y, Cheng X, He J, et al. Influences of hydrological and agricultural conditions on selenium distribution in groundwater: a case study in Sanjiang plain, Northeast China. *J Contam Hydrol.* 2025;275:104700. doi: [10.1016/j.jconhyd.2025.104700](https://doi.org/10.1016/j.jconhyd.2025.104700)
82. Evans AE, Limmer MA, Seyfferth AL. Indicator of redox in soil (IRIS) films as a water management tool for rice farmers. *J Environ Manage.* 2021;294:112920. doi: [10.1016/j.jenvman.2021.112920](https://doi.org/10.1016/j.jenvman.2021.112920)
83. Chen Z, Chen Y, Liang J, et al. The release and migration of Cr in the soil under alternating wet-dry conditions. *Toxics.* 2024;12(2):140. doi: [10.3390/toxics12020140](https://doi.org/10.3390/toxics12020140)
84. Yuan C, Qiao J, Li F, et al. Community dynamics of As(V)-reducing and As(III)-oxidizing genes during a wet-dry cycle in paddy soil amended with organic matter, gypsum, or iron oxide. *J Hazard Mater.* 2020;393:122485. doi: [10.1016/j.jhazmat.2020.122485](https://doi.org/10.1016/j.jhazmat.2020.122485)
85. Chen H, Chen M, Zhang W, et al. Dual regulation mechanisms of LDHs on cadmium and arsenic availability in paddy soils under alternating wet-dry conditions: chemical immobilization and microbial responses. *Chem Eng J.* 2025;523:168484. doi: [10.1016/j.ccej.2025.168484](https://doi.org/10.1016/j.ccej.2025.168484)
86. Fang X, Colina Blanco AE, Christl I, et al. Simultaneously decreasing arsenic and cadmium in rice by soil sulfate and limestone amendment under intermittent flooding. *Environ Pollut.* 2024;347:123786. doi: [10.1016/j.envpol.2024.123786](https://doi.org/10.1016/j.envpol.2024.123786)
87. Tolar BB, Boye K, Bobb C, et al. Stability of floodplain subsurface microbial communities through seasonal hydrological and geochemical cycles. *Front Earth Sci.* 2020;8:338. doi: [10.3389/feart.2020.00338](https://doi.org/10.3389/feart.2020.00338)
88. Peña J, Straub M, Flury V, et al. Origin and stability of uranium accumulation-layers in an Alpine histosol. *Sci Total Environ.* 2020;727:138368. doi: [10.1016/j.scitotenv.2020.138368](https://doi.org/10.1016/j.scitotenv.2020.138368)
89. Valiente N, Jirsa F, Gómez-Alday JJ. Saline Lakes as barriers against pollution: a multidisciplinary overview. *Limnetica.* 2022;41(2):1. doi: [10.23818/limn.41.17](https://doi.org/10.23818/limn.41.17)
90. Mlangeni AT, Perez M, Raab A, et al. Simultaneous stimulation of arsenic methylation and inhibition of cadmium bioaccumulation in rice grain using zero valent iron and alternate wetting and drying water management. *Sci Total Environ.* 2020;711:134696. doi: [10.1016/j.scitotenv.2019.134696](https://doi.org/10.1016/j.scitotenv.2019.134696)
91. Chen C, Qu W, Gao Z-Y, et al. Soil redox status and dissolved organic matter control the biogeochemical transformations of arsenic in paddy soils. *J Hazard Mater.* 2026;501:140737. doi: [10.1016/j.jhazmat.2025.140737](https://doi.org/10.1016/j.jhazmat.2025.140737)
92. Zhang P, Xiao J, Yu Z, et al. Release and immobilization of arsenic and antimony in contaminated soil system during sulfidation and reoxidation cycling. *J Hazard Mater.* 2025;498:139979. doi: [10.1016/j.jhazmat.2025.139979](https://doi.org/10.1016/j.jhazmat.2025.139979)
93. Chen MA, Mehta N, Kocar BD. Semiconducting hematite facilitates microbial and abiotic reduction of chromium. *Sci Rep.* 2022;12(1):9032. doi: [10.1038/s41598-022-12824-y](https://doi.org/10.1038/s41598-022-12824-y)
94. Zeng S, Chen Y, Zhang N, et al. Tetracycline effects on arsenate reduction in agricultural soils under different soil water contents. *Environ Pollut.* 2026;389:127398. doi: [10.1016/j.envpol.2025.127398](https://doi.org/10.1016/j.envpol.2025.127398)
95. Hansen DJ, Horne AJ. The effect of drying/re-flooding on trace metal, As and Se fluxes in a treatment wetland: addressing growing environmental concerns. *Biology (Basel).* 2022;11(2):188. doi: [10.3390/biology11020188](https://doi.org/10.3390/biology11020188)
96. Rahman KMA, Kibria MG, Hosenuzzaman M, et al. Alternate wetting and drying decreases arsenic content and increases yield of rice grown in organic matter amended soil. *EJSS.* 2024;13(2):139–144. doi: [10.18393/ejss.1418487](https://doi.org/10.18393/ejss.1418487)
97. Wang Q, Li J, Wang F, et al. Effective immobilization of geogenic As and Pb in excavated marine sedimentary material by magnesite under wet-dry cycle, freeze-thaw cycle, and anaerobic exposure scenarios. *Sci Total Environ.* 2022;848:157734. doi: [10.1016/j.scitotenv.2022.157734](https://doi.org/10.1016/j.scitotenv.2022.157734)
98. Mabagala FS, Wang T, Feng Q, et al. Application of iron-bimetal biochar for As and Cd reduction and soil organic carbon preservation under varying moisture. *Agriculture.* 2025;15(11):1114. doi: [10.3390/agriculture15111114](https://doi.org/10.3390/agriculture15111114)
99. Straub M, Peña J, Flury V, et al. Uranium stability in a large wetland soil core probed by electron acceptors, carbonate amendments and wet-dry cycling in a long-term lysimeter experiment. *Sci Total Environ.* 2022;803:149783. doi: [10.1016/j.scitotenv.2021.149783](https://doi.org/10.1016/j.scitotenv.2021.149783)
100. Zhang W, Jin D, Yuan J. Speciation transformation and release of Cr(VI) in a GGBS-NaOH treated soil under acidic wet-dry cycle: leaching characteristics and microscopic mechanisms. *J Cleaner Prod.* 2024;456:142424. doi: [10.1016/j.jclepro.2024.142424](https://doi.org/10.1016/j.jclepro.2024.142424)
101. Li X, Yu X, Liu L, et al. Cyclic drying and wetting tests on combined remediation of chromium-contaminated soil by calcium polysulfide, synthetic zeolite and cement. *Sci Rep.* 2021;11(1):11643. doi: [10.1038/s41598-021-91282-4](https://doi.org/10.1038/s41598-021-91282-4)
102. Liang K, Hong C, Luo J, et al. Radon attenuation characteristics of compacted soil layer for uranium mill tailings pond subjected to drying-wetting cycles. *Sci Total Environ.* 2022;851(Pt 2):158184. doi: [10.1016/j.scitotenv.2022.158184](https://doi.org/10.1016/j.scitotenv.2022.158184)
103. Ladd AJC, Szymczak P. Reactive flows in porous media: challenges in theoretical and numerical methods. *Annu Rev Chem Biomol Eng.* 2021;12(1):543–571. doi: [10.1146/annurev-chembioeng-092920-102703](https://doi.org/10.1146/annurev-chembioeng-092920-102703)
104. Baqer Y, Thornton S, Stewart DI, et al. Analysis of uranium sorption in a laboratory column experiment using a reactive transport and surface complexation model. *Transp Porous Med.* 2023;149(2):423–452. doi: [10.1007/s11242-023-01956-y](https://doi.org/10.1007/s11242-023-01956-y)
105. Gao ZP, Jia YF, Guo HM, et al. Quantifying geochemical processes of arsenic mobility in groundwater from an inland basin using a reactive transport model. *Water Resour Res.* 2020;56(2):e2019WR025492. doi: [10.1029/2019WR025492](https://doi.org/10.1029/2019WR025492)
106. Pan C, Giammar D. Interplay of transport processes and interfacial chemistry affecting chromium reduction and reoxidation with iron and manganese. *Front Environ Sci Eng.* 2020;14(5):81. doi: [10.1007/s11783-020-1260-y](https://doi.org/10.1007/s11783-020-1260-y)
107. Ying R, Yang B, Chen M, et al. Characteristics and numerical simulation of chromium transportation, migration and transformation in soil-groundwater system. *J Hazard Mater.* 2024;471:134414. doi: [10.1016/j.jhazmat.2024.134414](https://doi.org/10.1016/j.jhazmat.2024.134414)
108. Kim B-J, Ko M-S. Two-dimensional reactive transport model as a new approach for identifying the origins and contribution of arsenic in a soil and water system. *Sci Total Environ.* 2023;898:165468. doi: [10.1016/j.scitotenv.2023.165468](https://doi.org/10.1016/j.scitotenv.2023.165468)
109. Perzan Z, Osterman G, Maher K. Controls on flood managed aquifer recharge through a heterogeneous vadose zone: hydrologic modeling at a site characterized with surface geophysics. *Hydrol Earth Syst Sci.* 2023;27(5):969–990. doi: [10.5194/hess-27-969-2023](https://doi.org/10.5194/hess-27-969-2023)
110. Tesoriero AJ, Wherry SA, Dupuy DI, et al. Predicting redox conditions in groundwater at a national scale using random forest classification. *Environ Sci Technol.* 2024;58(11):5079–5092. doi: [10.1021/acs.est.3c07576](https://doi.org/10.1021/acs.est.3c07576)
111. Tran THH, Kim SH, Nguyen QHN, et al. Explainable machine learning for arsenic remobilization potential in the vadose zone: leveraging readily available soil properties. *J Hazard Mater.* 2025;493:138400. doi: [10.1016/j.jhazmat.2025.138400](https://doi.org/10.1016/j.jhazmat.2025.138400)



112. Friedel MJ, Wilson SR, Close ME, et al. Comparison of four learning-based methods for predicting groundwater redox status. *J Hydrol.* 2020;580:124200. doi: [10.1016/j.jhydrol.2019.124200](https://doi.org/10.1016/j.jhydrol.2019.124200)
113. Adhikari K, Mamud ML, Mudunuru MK, et al. Reactive transport modeling with physics-informed machine learning for critical minerals applications. *Transp Porous Med.* 2026;153(4):45. doi: [10.1007/s11242-026-02301-9](https://doi.org/10.1007/s11242-026-02301-9)
114. Li C, Adeniyi EO, Zarzycki P. Machine learning surrogates for surface complexation model of uranium sorption to oxides. *Sci Rep.* 2024;14(1):6603. doi: [10.1038/s41598-024-57026-w](https://doi.org/10.1038/s41598-024-57026-w)
115. Xiao Z, Xie X, Pi K, et al. Impact of organic matter on arsenic mobilization induced by irrigation in the unsaturated and saturated zones. *J Hydrol.* 2021;602:126821. doi: [10.1016/j.jhydrol.2021.126821](https://doi.org/10.1016/j.jhydrol.2021.126821)
116. Zhou T, Ruud N, Šimůnek J, et al. The impact of managed aquifer recharge on the fate and transport of pesticides in agricultural soils. *Water Res.* 2024;267:122442. doi: [10.1016/j.watres.2024.122442](https://doi.org/10.1016/j.watres.2024.122442)
117. Liu N, Wang X, Chen M, et al. Migration and transformation of Pb and Cd in the unsaturated zone induced by water table fluctuations. *J Hazard Mater.* 2025;492:138188. doi: [10.1016/j.jhazmat.2025.138188](https://doi.org/10.1016/j.jhazmat.2025.138188)