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Opposite Environmental Responses of Arsenic and Cadmium Mediated by Redox Conditions, Sulfur Cycling, and Microorganisms

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Abstract. Arsenic (As) and cadmium (Cd) often coexist in paddy soils and sediments, yet they respond differently to changes in oxygen availability. Under moderately reducing conditions, the dissolution of iron(III) oxides releases sorbed As, whereas increasing pH and stronger surface sorption commonly decrease Cd mobility. Under strongly reducing conditions, microbial sulfate reduction generates sulfide and promotes the precipitation of sparingly soluble CdS. Arsenic may instead be immobilized in sulfide minerals or remain dissolved as thioarsenic species, depending on iron availability, sulfide concentration, pH, and reaction time. Reoxidation can reverse these trends by rebuilding iron oxides that retain As while oxidizing CdS and potentially remobilizing Cd. Iron-reducing bacteria, sulfate-reducing bacteria, sulfur-oxidizing bacteria, cable bacteria, and As-metabolizing microorganisms regulate these linked transformations. The apparent opposite response is therefore conditional rather than universal. Its direction and magnitude depend on Fe-S balance, organic matter, phosphate competition, and wet-dry frequency. Knowing these controls is important for managing As-Cd co-contaminated soils without decreasing the risk of one contaminant while increasing the other.

Keywords: arsenic, cadmium, redox, sulfur cycling, microbial regulation

1. Introduction

Arsenic and cadmium are important contaminants in rice-producing environments because both can move from soil into edible grain. Their environmental risks cannot be evaluated from total concentrations alone. Chemical speciation determines whether an element is dissolved, sorbed, precipitated, or available for root uptake. Recent studies have shown that As mobility is closely linked to iron reduction and sulfur transformation, whereas Cd bioavailability is strongly influenced by pH, sorption, and sulfide precipitation [1, 2]. Root iron plaque can further modify the transfer of both elements at the soil-root interface [3].

The central challenge is that a treatment that immobilizes one element may mobilize the other. Cross-regional field evidence indicates that grain Cd is more closely associated with redox potential, pH, calcium, and microbial composition than with total soil Cd, while grain As is linked to soil As and sulfur-cycling microorganisms [4]. Field measurements also show that extractable Cd and soil

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properties predict crop uptake more effectively than only Cd [5]. These findings demonstrate that As and Cd must be considered as a coupled biogeochemical system rather than as two independent pollutants.

Microorganisms provide the main connection between redox conditions and mineral transformation. Iron-reducing and sulfate-reducing microorganisms can release As from iron oxides or immobilize Cd as CdS [6-9]. During drainage, sulfur oxidation and the formation of new iron oxides may reverse these effects [10, 11]. Other studies have identified links among sulfur transformation, As-bearing minerals, cable-bacteria activity, and cryptic sulfur cycling [12-14]. This paper explains the chemical basis of the opposite As-Cd response, compares the major redox stages, evaluates microbial control, and identifies the environmental conditions that limit simple predictions.

2. Basic differences in the environmental behavior of arsenic and cadmium

2.1. Arsenic forms and main control mechanisms

Arsenic is a redox-active metalloid; therefore, its chemical speciation changes as soil oxygen conditions change. Under oxic conditions, arsenate, As(V), is the dominant inorganic form, generally. Because of its negative charges and strong affinity for iron(III) oxides, As(V) is commonly sorbed onto mineral surfaces or incorporated into newly formed iron minerals. Following flooding, microbial respiration consumes oxygen and promotes iron reduction. The reductive dissolution of iron oxides releases sorbed As into pore water, while microbial processes can reduce As(V) to arsenite, As(III). At near-neutral pH, As(III) occurs mainly as uncharged H3AsO3 and is generally sorbed less strongly by negatively charged soil surfaces [1, 2]. Consequently, flooding often increases dissolved and potentially plant-available As in paddy soils.

The root surface is an important exception to the average soil condition. Oxygen released by rice roots forms an iron plaque around the root. This thin mineral layer can trap As before it enters the plant. Tian et al. found that the plaque worked more like a barrier for As, although the strength of this barrier depended on the amount and form of iron present [3]. A cross-regional soil-to-grain study also showed that grain As was related to soil As and sulfur-cycling microorganisms, not only to total soil concentration [4]. Therefore, As behavior is controlled by both direct changes in oxidation state and indirect changes in iron and sulfur minerals.

2.2. Cadmium forms and main control mechanisms

Cadmium behaves differently because it occurs predominantly as Cd(II) in natural soils and waters, and environmentally relevant redox changes do not usually alter its oxidation state. Instead, flooding modifies the mineral surfaces, ligands, and solution chemistry that control Cd^{2+}. A rise in pH generally increases the negative charge of clay, organic matter, and iron or manganese oxides, thereby strengthening Cd sorption. Cd may also form complexes with organic and inorganic ligands. These processes can reduce dissolved and exchangeable Cd without changing the total Cd concentration. Field evidence from southern China showed that grain Cd was associated with available Cd and with soil pH, calcium, iron, manganese, and sulfur, whereas total soil Cd alone was a poor predictor of crop uptake [5].

Under strongly reducing conditions, sulfate-reducing bacteria generate sulfide. Sulfide reacts with Cd^{2+} to form cadmium sulfide, CdS, a sparingly soluble mineral. Huang et al. observed CdS formation near bacterial cell walls and reported that Fe^{2+} and Zn^{2+} contributed to mixed metal-sulfide

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formation [6]. This process can substantially decrease Cd bioavailability during flooding. However, Cd is immobilized rather than removed: when oxygen returns, CdS may be oxidized and Cd^{2+} may re-enter pore water. Cd behavior therefore depends mainly on sorption and on the dynamic balance between sulfide precipitation and oxidation.

2.3. Chemical basis of the opposite response

The opposite response of As and Cd starts with a basic chemical difference. As it can gain or lose electrons, so redox potential directly changes its oxidation state, charge, and ability to bind to minerals. Cd^{2+} normally does not take part in the same electron-transfer reactions. Redox potential affects Cd indirectly by changing pH and the forms of iron, manganese, and sulfur around it. During early flooding, iron reduction can quickly release As, while higher pH and stronger surface attachment begin to lower Cd mobility. During later sulfate reduction, Cd is strongly fixed as CdS, but As may either form solid arsenic sulfides or remain mobile as thioarsenic compounds [1, 4, 6].

This difference also explains why "fixed in soil" does not always mean "safe for crops." Iron plaque can hold As outside the root, but Cd stored on the plaque may still be related to Cd inside the root [3]. In addition, grain Cd was more strongly linked with higher redox potential and lower pH than grain As in a large international study [4]. Figure 1 summarizes the main controls. As responds through oxidation state and iron-mineral changes, while Cd responds through surface attachment and CdS formation. These two pathways create the basis for opposite behavior during wet-dry cycles.

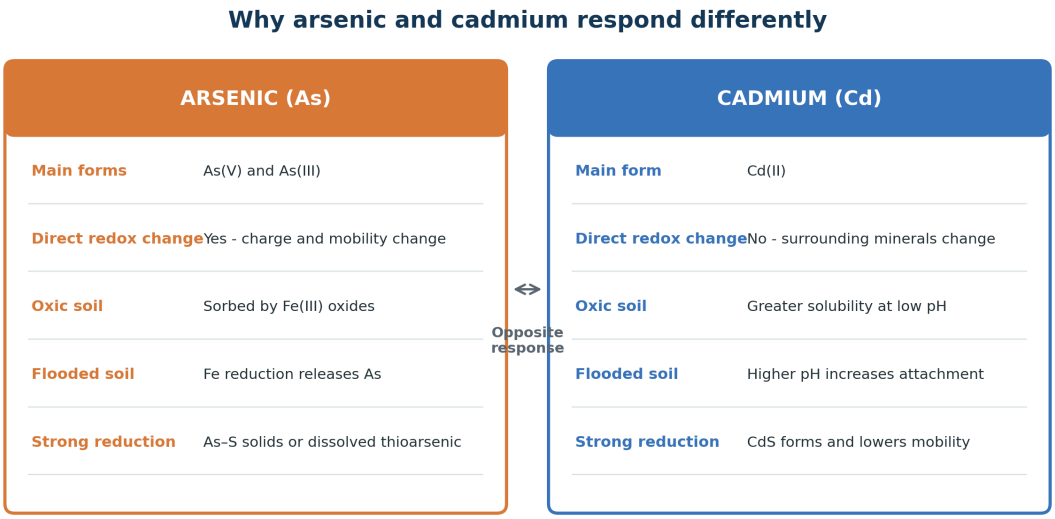


Figure 1. Basic chemical reasons for the different environmental behavior of As and Cd (picture credit: original)

3. Opposite transformations along a redox gradient

3.1. Moderate reduction: the typical opposite-response stage

At the onset of flooding, microorganisms first consume dissolved oxygen and nitrate. As these electron acceptors become depleted, iron(III) reduction becomes increasingly important. Chi et al. reported that vertical gradients in redox potential and pH produced marked differences in As and Cd

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bioavailability in paddy soil. Iron-reducing bacteria promoted iron-oxide dissolution, whereas sulfate-reducing bacteria became more important at greater soil depth [7]. Released Fe and As enter pore water, and microbial As(V) reduction can increase the proportion of As(III). As mobility therefore generally increases during this stage, although the magnitude of the increase is soil dependent.

Cd often moves in the opposite direction. Flooding commonly raises pH, increases the number of negative binding sites, and starts the formation of small amounts of sulfide. These changes increase Cd attachment and reduce dissolved Cd. Yin et al. showed that iron and sulfur cycles together controlled the bioavailability of both elements in co-contaminated paddy soil [8]. Yan et al. also found that sulfate treatment could lower exchangeable Cd and, in some soils, lower pore-water As [9]. The moderate-reduction stage therefore shows the common pattern of As activation and Cd passivation, although the size of each response depends on the soil.

3.2. Strong reduction: stable Cd but two possible arsenic pathways

When redox potential falls further, sulfate reduction becomes a major process. Sulfate-reducing bacteria produce HS^- and S^{2-}, and CdS precipitation becomes a strong sink for Cd [6, 8]. Because CdS dissolves very slowly, Cd can remain at low bioavailability even when total Cd is high. Added sulfate can strengthen this effect, but enough organic carbon or another electron donor is needed to support microbial sulfate reduction. Soil pH and competition from Fe^{2+} and Zn^{2+} also affect the type and stability of the sulfide minerals that form [6, 9].

Arsenic does not follow one simple path in this stage. High sulfide may lead to solid As_2S_3 or As attached to FeS, which lowers mobility. However, sulfide can also produce dissolved thioarsenic compounds. These compounds may stay in pore water and can be available to rice. Yin et al. found that the ability of sulfate reduction to limit As movement depended strongly on active iron and the starting pollution condition [8]. Yan et al. reported different results among three co-contaminated soils [9]. Therefore, strong reduction gives a stable direction for Cd but a split direction for As. The balance among Fe^{2+}, sulfide, pH, and reaction time decides the final result.

3.3. Reoxidation: reversal of the response pattern

Drainage or radial oxygen loss from rice roots raises soil redox potential. Fe^{2+} is oxidized to form new iron(III) oxides with abundant reactive surface sites that can sorb dissolved As. Oxidation can also convert As(III) to As(V), which is generally retained more strongly by iron oxides. Cd may respond in the opposite direction because CdS can be oxidized and release Cd^{2+}. The rate and extent of this release depend on pH, residual sulfide, and the incorporation of Cd into FeS or ZnS phases [6]. Reoxidation may therefore decrease As mobility while increasing the potential for Cd remobilization; however, neither response should be assumed to be complete or universal.

Field research shows that this trade-off is difficult to avoid through irrigation alone. In a two-year study, drier water management lowered plant As but increased Cd uptake. None of the six irrigation methods lowered both grain As and Cd in the tested soil [10]. Fang et al. combined intermittent flooding with sulfate and limestone and obtained better control of both elements [11]. Sulfate supported CdS formation during reducing periods, while limestone raised pH and lowered Cd activity. The result shows that water management should be combined with sulfur and pH control instead of being used alone. Figure 2 shows the three redox stages and the sulfur-cycle switch.

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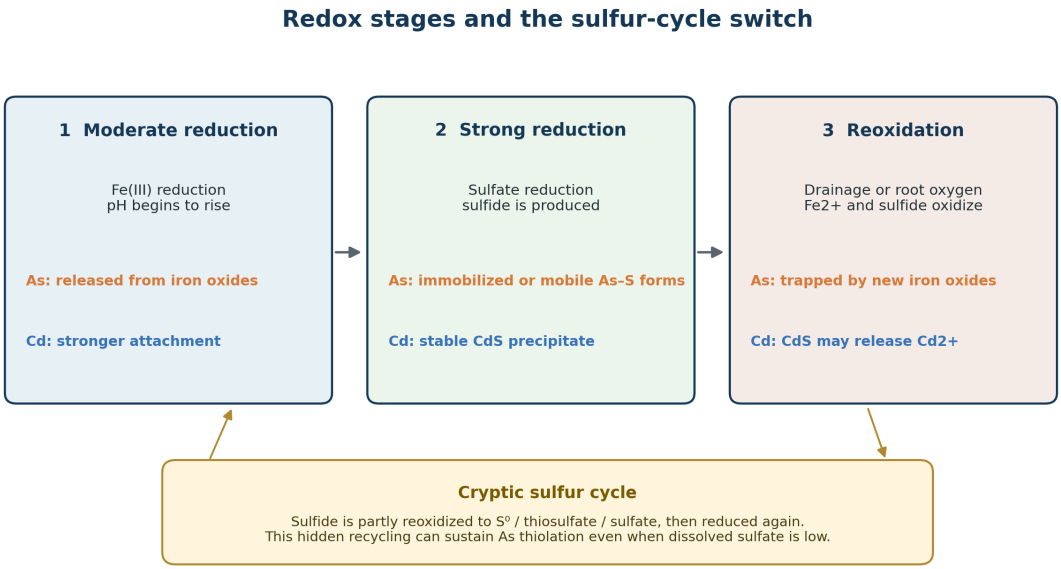


Figure 2. Three redox stages, the opposite response of As and Cd, and the hidden recycling of sulfur (picture credit: original)

4. Effects of key sulfur-cycle processes

4.1. Sulfate reduction: consistent Cd passivation and a variable As response

Sulfate reduction is the main biological source of sulfide in strongly reducing paddy soil. Sulfate-reducing bacteria use sulfate as an electron acceptor and produce reduced sulfur through enzymes such as DsrAB. Cd^{2+} reacts quickly with the sulfide and forms CdS, so the direction for Cd is usually clear: dissolved and exchangeable Cd fall [6, 8]. This one-way passivation is strong because CdS has low solubility. However, it can be weaker when sulfide production is slow, when pH is low, or when other metals use much of the available sulfide.

For As, sulfate reduction can cause either fixation or continued movement. Chen et al. found that sulfur transformation in acid-mine-affected paddy fields changed iron-oxide-bound As into more stable sulfide minerals [12]. In other soils, however, dissolved thioarsenic compounds can form. Yan et al. found that sulfate lowered As in some soils but not in all soils [9]. The main reason is competition among As, iron, and sulfide. If active iron is available, FeS and As-S solids can trap As. If sulfide is present in a form that supports soluble thioarsenic, As may remain mobile. Sulfate concentration alone is therefore not enough to predict As bioavailability.

4.2. Sulfide oxidation: a major driver of response reversal

Sulfide oxidation begins when oxygen or nitrate reaches reduced soil. Sulfur-oxidizing bacteria change sulfide into elemental sulfur, thiosulfate, or sulfate. This removes the sulfide that keeps Cd in CdS and can allow Cd^{2+} to return to pore water. Acid made during sulfide oxidation may further increase Cd solubility. At the same time, oxidation of Fe^{2+} produces new iron oxides that trap As. Thus, one oxidation process can reactivate Cd while immobilizing As. This is the chemical center of the phase reversal described in Section 3.3 [6, 10, 11].

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Some sulfur-oxidizing bacteria can move electrons over long distances. Cable bacteria oxidize sulfide in deeper, oxygen-free sediment and pass electrons to oxygen or nitrate near the surface. A field and core-incubation study found that cable-bacteria activity built an iron-oxide layer that trapped As during oxygen-rich periods. When anoxia later destroyed this layer, As was released in a strong pulse [13]. Although this study was carried out in marine sediment, it shows an important general mechanism: sulfur oxidation can rebuild an iron trap for As while changing sulfide stability. Similar microscale separation can occur near rice roots, where oxygen enters only a thin surface zone.

4.3. The cryptic sulfur cycle: a hidden source of long-term instability

A cryptic sulfur cycle occurs when sulfide is partly oxidized and the oxidized sulfur is reduced again so quickly that sulfate or sulfide does not build up to a high measured concentration. The cycle can involve elemental sulfur, thiosulfate, iron sulfides, sulfate-reducing bacteria, and sulfur-oxidizing bacteria. Because the intermediate products are short-lived, a single pore-water sample may suggest that little sulfur cycling is occurring even when the real turnover rate is high. Chen et al. showed close links among sulfur transformation, iron minerals, and As stabilization in paddy soil [12], while the cable-bacteria study showed that spatially separated sulfur oxidation can strongly change the iron-As trap [13].

A 2025 paddy-soil experiment gave direct evidence that repeated redox cycles can uncover this hidden process. After the main sulfate pool was reduced, partly oxidized sulfur supplied a small secondary sulfate pool. Its repeated reduction supported the formation of methylated thioarsenic compounds even under sulfur-limited conditions [14]. This finding is important because mobile As-S forms may continue to appear after dissolved sulfate seems exhausted. For Cd, the same recycling can repeatedly form and oxidize CdS, causing short periods of fixation followed by release. The cryptic sulfur cycle therefore explains why long-term field behavior may be less stable than short laboratory tests suggest. Time-series measurements of sulfate, sulfide, intermediate sulfur, As forms, and Cd forms are needed to detect it.

5. Microbial functional groups driving the opposite response

5.1. Iron-reducing bacteria: initiation of the response

Iron-reducing bacteria become active after oxygen and nitrate are depleted. They use iron(III) minerals as electron acceptors and convert solid Fe(III) to dissolved Fe^{2+}. This process weakens or dissolves As-bearing iron oxides and releases previously sorbed As into pore water [1, 7]. The same flooding period frequently raises soil pH and increases Cd sorption, producing the early pattern of As mobilization and Cd immobilization. However, the effect depends on the mineral composition of the soil. Highly reactive iron oxides can release As rapidly, while later FeS formation may create new surfaces that retain part of the released As [8, 12]. Iron-reducing bacteria should therefore be viewed as initiators of a sequence rather than as the sole cause of the final contaminant distribution.

5.2. Sulfate-reducing bacteria: separation of As and Cd pathways

Sulfate-reducing bacteria use sulfate as an electron acceptor and generate reduced sulfur. Their activity strongly favors CdS precipitation and commonly decreases dissolved and exchangeable Cd [6, 8, 9]. The As response is more variable. Sulfide may promote As-bearing sulfide minerals or As

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sorption onto FeS, but it may also produce dissolved thioarsenic species [8, 9, 12]. Carbon availability, pH, active iron, and the ratio of sulfide to As determine which pathway dominates. Consequently, the abundance of sulfate-reducing bacteria alone cannot predict As mobility; measurements of functional activity, sulfur intermediates, and As speciation are also required.

5.3. Sulfur-oxidizing bacteria and cable bacteria: control during reoxidation

Sulfur-oxidizing bacteria become important when oxygen or nitrate enters reduced soil. By oxidizing sulfide, they weaken the chemical conditions that stabilize CdS and may increase Cd remobilization. At the same time, Fe^{2+} oxidation produces fresh iron(III) oxides that can sorb As [10-12]. Cable bacteria provide a special example because they connect sulfide oxidation at depth with oxygen or nitrate reduction near the surface through long-distance electron transport. Their activity can build an iron-oxide barrier that retains As, but the later dissolution of this barrier under anoxia can produce a short As-release pulse [13]. It should be noted that most mechanistic evidence for cable-bacteria-driven geochemical transformation originates from marine sediment systems; direct in situ field evidence in paddy soils remains limited. Therefore, an equivalent effect should not be assumed to occur widely in paddy soils without direct field verification.

5.4. Arsenic-metabolizing microorganisms: an independent control on As

Arsenic-metabolizing microorganisms directly change As oxidation state through arsenate reduction and arsenite oxidation. Reduction of As(V) to As(III) generally increases mobility near neutral pH because uncharged As(III) is retained less strongly by many soil surfaces. In contrast, microbial As(III) oxidation can support As(V) formation and stronger sorption onto iron oxides [1, 2]. These reactions may occur at the same time as iron and sulfur cycling, so As can depart from the simple response expected from redox potential alone. The As-specific pathway has no direct equivalent for Cd, whose oxidation state normally remains Cd(II). It is therefore an important source of asymmetry between the two contaminants.

6. Environmental factors that disturb the opposite response

6.1. Fe-S balance and pH thresholds

The balance between reactive iron and reduced sulfur determines whether As is released, resorbed, or incorporated into sulfide phases. When reactive iron is abundant, newly formed FeS or iron oxides may provide binding sites for As. When sulfide is excessive relative to iron, dissolved thioarsenic species may become more important [8, 9, 12]. Soil pH simultaneously influences mineral surface charge, Cd sorption, sulfide speciation, and the stability of metal sulfides. Higher pH commonly lowers Cd activity, while acidic conditions can weaken Cd sorption and increase the consequences of CdS oxidation [5, 6, 11]. No single Fe: S ratio or pH threshold is expected to apply to every soil because mineralogy and organic matter alter the relevant reactions.

6.2. Phosphate and organic matter competition

Phosphate can compete with arsenate for sorption sites on iron oxides and may increase As mobility even under otherwise favorable retention conditions [1, 2]. Organic matter has several, sometimes opposing, effects. It supplies electron donors for microbial iron and sulfate reduction, complexes dissolved metals, changes pH, and may block mineral sorption sites. Chi et al. showed that organic

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matter and redox processes jointly controlled vertical differences in As and Cd bioavailability [7]. Therefore, adding organic amendments cannot be assumed to immobilize both contaminants. The chemical composition and degradability of the amendment must be considered together with iron and sulfur availability.

6.3. Dynamic effects of wet-dry frequency

Wet-dry cycles repeatedly switch the system between iron reduction, sulfate reduction, and reoxidation. Short drainage periods may rebuild iron oxides and reduce As mobility, but they may also oxidize CdS and increase Cd availability. Longer flooding can restore Cd immobilization while increasing the risk of As release [10, 11]. Repeated cycling also creates short-lived sulfur intermediates that sustain the cryptic sulfur cycle and thioarsenic formation [14]. Thus, sampling only before and after an experiment may miss concentration pulses that control plant exposure. Time-resolved measurements are needed to connect irrigation frequency with actual uptake by rice.

7. Research uncertainties and priority questions

7.1. In situ occurrence and bioavailability of thioarsenic

Thioarsenic compounds are central to the variable As response under sulfide-rich conditions, but their field importance remains difficult to quantify. These species can be short-lived and may transform during sampling, storage, or analysis. Their presence does not automatically prove high plant availability because uptake depends on the exact molecular form and on competing solutes [8, 9, 14]. Future studies should combine rapid field preservation, As-speciation analysis, and plant-uptake measurements instead of inferring bioavailability from total dissolved As.

7.2. Oxidation and remobilization of CdS

CdS is often treated as a stable endpoint of Cd immobilization, but its persistence during drainage is not fully predictable. Oxidation rates depend on crystal form, particle size, pH, oxygen transport, microbial activity, and the incorporation of Fe or Zn into sulfide minerals [6]. Field irrigation studies show that Cd uptake can rise under more aerobic management [10, 11], yet the relative contributions of CdS oxidation, decreasing pH, and changing sorption surfaces are not always separated. Controlled experiments that follow solid Cd phases and pore-water Cd through several redox cycles are needed to resolve this mechanism.

7.3. Processes at the root-soil interface

The rice rhizosphere contains steep microscale gradients that differ from bulk soil. Oxygen released by roots promotes iron-plaque formation and localized sulfur oxidation, while nearby anoxic zones support iron and sulfate reduction. Iron plaque can limit As entry into roots, but its relationship with Cd accumulation is more complex [3]. Regional studies also show that crop transfer depends on microbial communities and soil chemistry at the same time [4, 5]. Future work should combine microsensors, mineral mapping, microbial functional genes, and root-uptake measurements to determine when the rhizosphere protects the plant and when it creates short contaminant pulses.

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8. Conclusion

The opposite environmental responses of As and Cd arise from different chemical properties. Redox potential directly changes As speciation and controls the stability of As-bearing iron minerals. Cd remains mainly as Cd(II) and responds indirectly through pH, sorption, and sulfide precipitation. Moderate reduction commonly mobilizes As while decreasing Cd mobility. Strong sulfate reduction consistently favors CdS formation, whereas As may be immobilized or remain mobile as thioarsenic. Reoxidation can rebuild an iron sink for As while creating conditions for Cd remobilization. Microbial iron and sulfur cycling drives these phase changes, but the observed response is modified by Fe-S balance, pH, organic matter, phosphate, and wet-dry frequency.

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