Mineral-Phase Controls on Redox Dynamics and Plant-Nutrient Availability in Soils

Abstract. Reactive mineral phases, stable structural components, and microbially mediated redox processes jointly regulate phosphorus, sulfur, metal mobility, and plant-nutrient availability in soils. This article synthesizes a conceptual geochemical interpretation in which Fe and Al phases dominate phosphorus retention and redistribution, sulfur reduction modulates Fe-mediated phosphate release, and structurally persistent Ti- and Zr-bearing phases contribute to long-term soil function. The interpretation emphasizes that fertility emerges from coupled retention, redox transformation, structural stabilization, and biological accessibility rather than from single-element controls.

Keywords: soil redox dynamics; phosphorus availability; iron gels; aluminum gels; sulfate reduction; trace metals; plant nutrition.

1. Introduction and Conceptual Framework

Soil function is governed by interactions between chemically reactive mineral phases and structurally persistent components. In this framework, redox-sensitive Fe gels regulate phosphorus binding, metal retention, and nutrient release under reducing conditions, whereas Al gels provide comparatively redox-stable, long-term phosphorus fixation.

Si-rich gels and amorphous metal silicates are interpreted primarily as structural stabilizers of aggregates and fine fractions. Titanium-bearing phases appear to contribute to aggregation and biologically mediated nutrient availability rather than to direct chemical retention.

Zircon represents the most persistent mineral phase and therefore mainly records long-term soil development. Nevertheless, weak but sustained affinities for sulfate, phosphate, or Fe coatings may generate cumulative effects over extended time scales.

The central premise is that soil fertility reflects a dynamic balance among chemical retention, structural stability, and biological availability. Fe and Al systems dominate chemical storage, whereas Ti- and Zr-associated phases may influence longer-term soil function and vegetation nutrient status.

2. Microbial Regulation of Redox Processes

Microorganisms regulate redox-coupled soil equilibria by mediating transitions between reduced and oxidized forms of key elements. These transformations affect pH, solubility, plant-nutrient availability, and gaseous losses.

Sulfur and nitrogen cycles are particularly sensitive to temperature and moisture, whereas the carbonate–carbonic acid system responds more slowly and contributes to longer-term pH stabilization. Phosphorus is affected mainly indirectly through Fe redox dynamics and pH, because phosphide is generally not a relevant soil phase.

3. Coupled Fe, Al, and P Dynamics

Within this microbial context, Fe and Al phases constitute the principal controls on phosphorus binding, release, and redistribution within the soil profile.

Phosphorus associated with Fe gels derives mainly from dissolved orthophosphate in soil water, phosphate-mineral weathering, and organic-P mineralization. Reduction of older Fe gels releases phosphate, which may subsequently be recaptured by newly formed Fe gels in oxidizing microsites. This Fe–P recycling mechanism governs the spatial redistribution of phosphorus within the profile.

Redox potential may vary substantially during Fe-gel formation and collapse, commonly within 200–400 mV and occasionally above 500 mV. Fe oxidation increases Eh during gel formation, whereas Fe reduction and FeS formation lower Eh during collapse. These cycles make Fe a major redox regulator in podzols and wetlands and strongly influence phosphorus and sulfur mobility.

4. Sulfur Reduction and Phosphorus Mobilization

Sulfur reduction provides a mechanistic link between anaerobic microbial activity, Fe transformation, and phosphorus mobilization.

Sulfate-reducing bacteria convert sulfate to sulfide, which chemically reduces Fe(III) to Fe(II). Consequently, iron reduction in many systems is mediated indirectly by biogenic sulfide rather than solely by direct enzymatic Fe reduction.

Under reducing conditions, sulfide reduces Fe(III) oxides to Fe^{2+}, dissolving phosphorus-binding iron minerals and releasing phosphate into solution. Concurrent iron-sulfide precipitation limits Fe-oxide reformation and thereby further promotes phosphorus release.

Reduced reactive-sulfur availability may increase phosphorus mobility by limiting acidification and weakening Al-bound retention. However, the net effect depends on the balance between reduced Al-associated retention and reduced Fe-mediated phosphorus release.

5. Structural Mineral Phases and Long-Term Soil Function

In addition to directly redox-controlled processes, structurally persistent phases may exert slower and more tentative functional effects on nutrient retention and release.

The association between Ti and vegetation may reflect Ti-associated hydrated oxides acting as long-term phosphorus reservoirs. Phosphate may bind to Ti-bearing surfaces and resist leaching, whereas rhizosphere chemistry can mobilize phosphorus for plant uptake. Ti-bearing phases may therefore contribute to ecological nutrient availability rather than only to abiotic retention.

Zircon may function as a long-lived phosphate-buffering phase. Through weak but persistent phosphate affinity, zircon-associated surfaces may stabilize phosphate concentrations in soil solution, with adsorption favored under phosphate surplus and desorption under deficiency, without permanent immobilization in sparingly soluble mineral phases.

6. Trace Metals, Toxicity, and Indirect Redox Effects

Trace metals influence soil processes through toxicity, immobilization, and indirect effects on redox and phosphorus dynamics.

Zn^{2+} is generally more toxic to plants than to bacteria because plant uptake can disrupt metal homeostasis. Pb^{2+} is comparatively more toxic to bacteria, which are directly exposed and may experience inhibition of key enzymes. Ba^{2+} is weakly toxic to both groups and is usually of limited ecological relevance in podzolic soils.

Binding of sulfide and sulfate to Ba, Zn, and Pb generally immobilizes both metals and sulfur as sparingly soluble sulfides and sulfates. This may suppress sulfide oxidation, limit pH decline, and indirectly reduce Fe-controlled phosphate fixation. Ba^{2+}, Zn^{2+}, and Pb^{2+} may also form sparingly soluble phosphate minerals, reducing dissolved and plant-available P. The net outcome is lower metal mobility, a less dynamic P pool, and pH-controlled redistribution of other nutrients.

Zr, Ti, Zn, Pb, and Ba are redox-inert and do not participate directly in microbial electron transfer. They may, however, indirectly affect bacterial redox activity through surface-chemical effects (TiO_2, ZrO_2), adsorption to Fe(III) surfaces (Zn, Pb), or toxicity at elevated concentrations. Ba may weakly suppress sulfate reduction through $BaSO_4$ precipitation, but these effects are negligible in normal soils.

At moderately toxic concentrations (approximately 10^{-4}–10^{-3} M), Zn^{2+} and Pb^{2+} may transiently suppress sulfur-bacterial activity through enzyme inhibition and stress responses, thereby dampening redox fluctuations. This effect ceases after ZnS and PbS precipitation or bacterial adaptation and is negligible under typical soil conditions.

7. Trace Metals as Indicators of Geochemical Processes

Some trace metals are better interpreted as indicators of geochemical state and process intensity than as direct controls on plant nutrition.

Negative associations between plant nutrients and Cr, Ni, and Sr primarily reflect geochemical partitioning rather than toxicity. Cr and Ni occur mainly in stable mineral and oxide fractions weakly coupled to biologically active nutrient pools. Sr correlates negatively with nutrients through competition with Ca and other base cations in the cation-exchange complex. Local Cr and Ni toxicity may occur but does not explain the dominant geochemical relationships.

Because Cr and Ni bind more strongly to Fe oxides than phosphate, they may serve as trace indicators of Fe redox dynamics. Their positive association with P supports the interpretation that phosphorus mobility in acid sulfate soils is controlled mainly by Fe-gel stability rather than by primary mineral formation. Their negative association with Si further distinguishes weathering-related processes from redox-controlled Fe–P–trace-metal dynamics.

8. Conclusion

Soil plant nutrition and fertility are best understood as emergent properties of coupled microbial, mineralogical, and geochemical processes. Fe- and Al-bearing phases regulate phosphorus retention and redistribution; sulfur reduction modulates Fe-mediated phosphate release; and persistent Ti- and Zr-associated phases may contribute to longer-term structural and nutritional buffering. Trace metals can affect nutrient availability through immobilization and toxicity, but they may also provide useful indicators of Fe redox dynamics and broader geochemical partitioning.

Joakim Forssman, JSF-KEMI
Vesslestigen 20 bv
974 53 Luleå
Sweden
Email: Joakim@ekomatte.se