Coupled Reactive Transport Modeling and Isotopic Tracer Integration for Quantifying Heavy Metal Attenuation Kinetics in Riparian Vadose Zone Sediments

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Abstract. Anthropogenic heavy metal contamination of riparian vadose zone sediments represents a persistent threat to groundwater quality and fluvial ecosystem integrity. This study presents a coupled reactive transport modeling (RTM) framework integrating stable isotopic tracers (δ66Zn, δ114Cd) with multi-phase geochemical partitioning algorithms to quantify attenuation kinetics of zinc, cadmium, and lead in heterogeneous alluvial sediment profiles. Column leaching experiments were conducted under controlled redox gradients, and outputs were calibrated against PHREEQC-3 geochemical simulations. Results demonstrate that organo-mineral co-precipitation at redox transition zones accounts for 61–74% of total metal immobilization, with kinetic rate constants exhibiting a strong pH dependency ($R^2 = 0.94$). The proposed framework improves predictive accuracy for contaminant breakthrough modeling by 38% over conventional Kd-based approaches, providing a robust tool for vadose zone remediation design.

Keywords: reactive transport modeling, vadose zone geochemistry, heavy metal attenuation kinetics, stable isotope fractionation, organo-mineral co-precipitation, riparian sediment contamination, redox-driven partitioning, PHREEQC geochemical simulation, contaminant breakthrough modeling

Introduction

Escalating industrialization and intensified agricultural activity have precipitated widespread heavy metal accumulation in riparian corridor sediments, posing critical risks to both subsurface water resources and dependent ecological systems. As of 2024–2026, the World Health Organization and European Environment Agency have identified cadmium, lead, and zinc as priority contaminants in alluvial and floodplain environments, with documented exceedances of regulatory threshold concentrations in over 34% of monitored riparian catchments across Europe and East Asia. The migration of these metals through the unsaturated, or vadose, zone constitutes a principal pathway for groundwater deterioration, yet the governing attenuation mechanisms remain incompletely characterized in heterogeneous sediment matrices subject to fluctuating hydrological and redox conditions. Conventional contaminant fate assessments have historically relied upon linear distribution coefficient (Kd) approaches, which systematically underestimate metal mobility under dynamic redox and pH regimes. The inadequacy of static partitioning models has been increasingly acknowledged in the peer-reviewed literature, driving demand for mechanistically explicit reactive transport frameworks capable of resolving coupled geochemical processes—including surface complexation, competitive adsorption, reductive dissolution of iron and manganese oxyhydroxides, and organo-mineral co-precipitation—at fine spatial and temporal resolutions. Recent advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have concurrently expanded the utility of stable metal isotope systems (δ66Zn, δ114Cd, δ208Pb) as in-situ process tracers, enabling discrimination between abiotic and biologically mediated attenuation pathways in complex porous media. Despite these technical developments, the integration of isotopic tracer data directly into calibrated reactive transport model architectures remains methodologically underdeveloped, particularly for riparian vadose systems characterized by pronounced lithological heterogeneity and episodic recharge dynamics. Existing coupled modeling studies have largely been confined to saturated zone applications or simplified homogeneous column analogues, leaving a substantive gap in predictive capability for real-world unsaturated sediment profiles with transient moisture content and temporally variable geochemical boundary conditions. The present study addresses this knowledge gap by developing and validating a novel coupled RTM–isotope integration framework, benchmarked against PHREEQC-3 multi-component equilibrium-kinetic simulations and experimental column leaching datasets derived from riparian sediment profiles collected along a zinc–cadmium-impacted fluvial corridor. The paper proceeds as follows: Section 2 describes the field sampling methodology and experimental column design; Section 3 presents the theoretical basis and parametrization of the coupled RTM framework; Section 4 details the isotopic tracer calibration procedure and uncertainty quantification protocol; Section 5 reports primary simulation outputs and validation metrics against observed breakthrough curves; and Section 6 synthesizes findings into practical implications for vadose zone contaminant management and remediation engineering.

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