

Review

Aquatic Heavy Metal Speciation and Probabilistic Human Health Risks Under Accelerating Climate Volatility

Anlei Wei ^{1,2}, Xiaodan Ji ², Yifan He ², Xiang Tu ³, Qing Fu ³, Dazhuang Yang ⁴ and Bin Li ^{1,3,*}

¹ College of Water Sciences, Beijing Normal University, Beijing 100875, China; alwei@nwnu.edu.cn

² College of Urban & Environmental Sciences, Northwest University, Xi'an 710127, China; 202533643@stumail.nwu.edu.cn (X.J.); 202533646@stumail.nwu.edu.cn (Y.H.)

³ Chinese Research Academy of Environmental Sciences, Beijing 100012, China; tu.xiang@craes.org.cn (X.T.); fu_qing2023@sina.com (Q.F.)

⁴ Beijing Construction Engineering Group Environmental Remediation Co., Ltd., Beijing 100015, China; yangdazhuang@bceer.com

* Correspondence: libin_2025@163.com

Abstract

Traditional monitoring frameworks heavily rely on static, total heavy metal concentrations and deterministic indices, failing to capture how climate-driven stressors and micro-interface interactions alter the stability, speciation, and bioavailability of toxic metals. This review synthesizes the state-of-the-art literature at the intersection of hydrology, geochemistry, microbial ecology, and toxicology to address this gap. We investigate how shifting redox (*Eh*-pH) gradients and climate-forced hydrological extremes—ranging from drought-induced sediment acidification to flood-driven shear stress—accelerate the reductive dissolution of iron/manganese oxyhydroxides. This process consequently triggers seasonal pulses of bioavailable metals. Furthermore, we evaluate how aged microplastics act as dynamic vector interfaces, altering competitive adsorption kinetics and biological uptake. Crucially, we highlight the heavy metal-microbiome-antibiotic resistance axis, demonstrating how sublethal metal exposure drives the co-selection and proliferation of antibiotic resistance genes (ARGs) via mobile genetic elements, revealing an indirect public health hazard. Finally, we critique deterministic assessments and advocate for probabilistic modeling via Monte Carlo simulations to capture exposure heterogeneity. By bridging macro-scale forcing with microscopic chemical and biological transformations, this review provides a comprehensive synthesis for shifting regulatory frameworks toward dynamic, bioavailability-based ecological governance.

Keywords: heavy metal speciation; climate-driven hydrological extremes; bioavailability and environmental exposure; microplastics–metal interactions; probabilistic risk assessment

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1. Introduction

1.1. Knowledge Gaps and Review Objectives

The contamination of aquatic ecosystems by legacy heavy metals, such as lead (Pb), cadmium (Cd), arsenic (As), and hexavalent chromium (Cr(VI)), remains a cornerstone challenge in environmental geochemistry and public health [1,2]. For decades, regulatory frameworks and monitoring paradigms have leaned heavily on a static metric: total elemental concentrations [3]. While this approach provided the foundational data necessary

for early water quality guidelines, it is increasingly recognized as inadequate for capturing the complex realities of modern aquatic systems. Natural waters and their underlying benthic zones are not inert reservoirs; they are biogeochemically active interfaces governed by fluctuating gradients of pH, redox potential (Eh), dissolved organic matter, and microbial metabolism [4]. Consequently, equating total concentration with ecotoxicological risk overlooks the fundamental principle that a metal's bioavailability and toxicity are dictated almost entirely by its chemical speciation [5]. A heavy metal ion sequestered within a stable crystalline matrix is essentially inert, whereas a bioavailable free ion or a lipophilic organometallic complex can readily partition across biological membranes and induce systemic cellular damage [6].

Despite an extensive corpus of literature detailing heavy metal distribution across global river basins [7], contemporary reviews frequently default to descriptive, spatial-temporal tabulations. These studies typically apply standard, deterministic risk indices to assert localized health hazards, treating the aquatic environment as a stationary system [8]. This static assumption represents a critical scientific blind spot. In an era defined by accelerating hydrological volatility, extreme weather events like prolonged droughts, abrupt rewetting, and severe flooding actively disrupt the physical and chemical equilibria that govern metal stability in water-sediment systems [9]. This volatility is especially evident in transitional ecotones like floodplains and riparian zones. There, seasonal shifts in hydrology and redox potentials not only accelerate metal desorption, but also affect coupled biogeochemical processes, such as microbial denitrification [10].

Furthermore, this conventional perspective frequently isolates heavy metals from the broader exposome. It largely overlooks interfacial interactions with co-occurring anthropogenic pollutants, such as aged microplastics, which act as dynamic transport vectors [11]. As microplastic polymers undergo photo-oxidative and mechanical aging in aquatic environments, the proliferation of oxygen-containing functional groups fundamentally alters competitive adsorption kinetics. This interfacial activity can modify their environmental fate and bioavailability and even facilitate the localized valence transformation of specific redox-sensitive species [12]. This classical view also routinely neglects secondary ecological consequences, such as the selective pressure that sublethal metal concentrations exert on benthic microbial communities, driving the proliferation of environmental antibiotic resistance [13,14].

Recognizing these systemic gaps, this review synthesizes recent developments in the study of aquatic heavy metal pollution. We move from macroscopic forcing (e.g., hydrological extremes) to microscopic interfacial chemistry, and then to probabilistic population-level risk modeling. We first examine how climate-driven hydrological extremes act as macroscopic triggers, altering redox gradients and accelerating the reductive dissolution of sedimentary minerals, thereby driving the seasonal mobilization of legacy metals. We then transition to the micro-scale, evaluating how complexation dynamics and competitive adsorption onto emerging vector surfaces alter chemical speciation and biological uptake. By bridging environmental geochemistry with microbial ecology, we also explore the heavy metal-microbiome-antibiotic resistance axis, elucidating how metal-induced co-selection of antibiotic resistance genes (ARGs) constitutes a profound, indirect public health threat.

Finally, we critique the structural limitations of deterministic health risk assessments (HRAs), advocating for the integration of probabilistic Monte Carlo simulations to accurately quantify multi-pathway exposure heterogeneity [15]. Furthermore, as the dimensionality and frequency of environmental monitoring data increase, this review highlights the emerging necessity of coupling these probabilistic frameworks with advanced, ensemble machine learning models, including Random Forests, Gradient Boosting, and Long Short-Term Memory (LSTM) networks. These computational approaches can capture

highly non-linear environmental dynamics, helping shift risk assessment from retrospective evaluation toward short-term predictive early warning [16]. Ultimately, this review provides a mechanistic synthesis to help transition aquatic pollution governance away from rigid, total-concentration thresholds and toward dynamic, bioavailability-driven regulatory frameworks.

1.2. Literature Search Methodology and Scope

To map the cross-disciplinary boundaries of the climate–metal–resistome axis, this paper follows a structured narrative review methodology that integrates hydrology, environmental geochemistry, microbial ecology, and data science. Relevant literature was retrieved from the Web of Science Core Collection, Scopus, and Google Scholar, focusing primarily on peer-reviewed investigations published between January 1990 and May 2026, and supplemented by foundational texts in chemical speciation modeling. The search strategy employed Boolean operations to intersect keywords across four primary domains. Specifically, terms for geochemical speciation (“heavy metal speciation,” “bioavailability,” “reductive dissolution,” “free ion activity,” and “Biotic Ligand Model”) and hydrological volatility (“climate volatility,” “hydrological extremes,” “sediment resuspension,” and “drought-rewetting”) were combined with phrases targeting microbial and resistome cascades (“antibiotic resistance genes,” “co-selection,” “*nosZ* gene,” “plastisphere,” and “eco-corona”) as well as environmental informatics frameworks (“Monte Carlo simulation,” “probabilistic risk,” “Long Short-Term Memory,” “LSTM,” and “machine learning”).

Papers were selected based on their explicit relevance to legacy heavy metals (Pb, Cd, As, Cr, Cu, and Zn) within freshwater, urban riverine, estuarine, or wastewater-sediment interfaces. To maintain a clear focus on micro-interfacial mechanisms and predictive modeling, baseline spatial monitoring studies that reported total metal concentrations without assessing chemical speciation, microbial dynamics, or probabilistic risk metrics were excluded from this synthesis.

2. Climate-Driven Mobilization Mechanisms in Water-Sediment Systems

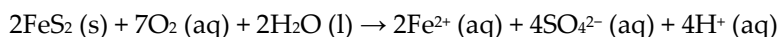
2.1. Hydrological Extremes and Sediment Resuspension

Climate change-induced hydrological volatility has fundamentally altered the physical and hydrodynamic stability of benthic environments [17]. In natural riverine and estuarine networks, bed sediments serve as the primary long-term sink for anthropogenic heavy metals, primarily through entrapment within fine-grained cohesive fractions, organic matter matrices, and mineral precipitates [18]. However, the intensification of extreme hydrometeorological events converts these stable sinks into highly dynamic, diffuse pollution sources [19]. During high-magnitude storms and floods, increased discharge velocity generates shear stress along the sediment–water interface [20]. Once this localized shear stress exceeds the critical shear stress for erosion (τ_c), bulk erosion and resuspension of legacy-contaminated bed sediments occur [21].

This physical displacement instantaneously transfers heavily contaminated particulate matter into the oxygenated water column. The sudden shifting of these solid matrices from anoxic, compacted benthic zones to highly turbulent, oxic fluvial environments triggers rapid shifts in chemical equilibria. Desorption kinetics are sharply accelerated as the high water-to-sediment ratio shifts thermodynamic partition coefficients, prompting a rapid release of weakly bound, exchangeable metal fractions into the dissolved phase [22].

Conversely, prolonged drought periods induce severe low-flow conditions, leading to the aerial exposure and desiccation of shallow littoral sediments and critical riparian

buffer zones [23]. Under these prolonged subaerial conditions, oxygen penetrates deep into previously anoxic mudflats, initiating macro-oxidation of sedimentary matrix minerals [24]. This exposure triggers the oxidative dissolution of authigenic metal sulfides (such as pyrite, FeS_2), a process that generates substantial hydrogen ions and drastically depresses localized pH values [25]:



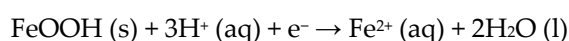
When subsequent intense precipitation events abruptly terminate these droughts, the sudden rewetting flushes highly soluble, liberated heavy metal ions (Pb^{2+} , Cd^{2+} , Zn^{2+}) directly into the receiving water body as a concentrated toxic pulse [26]. While the exact magnitude of this chemical release is highly contingent upon localized mineral matrices and organic fractions, specific empirical investigations underscore its potential scale. For instance, controlled laboratory simulations of hyposulfidic littoral sediments by [25] demonstrated that severe desiccation can induce a localized pH drop of 1–2 units and an 87% reduction in acid volatile sulfides (AVS). Under these discrete experimental conditions, dissolved iron (Fe) reached transient peak porewater concentrations of approximately 60 mg L^{-1} prior to subsequent dispersion and loss via flushing and precipitation [25]. Crucially, this volatility is not confined to the main river channel; it profoundly impacts transitional ecotones. When extreme precipitation forces rivers to breach their banks and reconnect with adjacent floodplains, the sudden inundation drastically alters hydrological connectivity and soil carbon thresholds [27]. This rapid shift effectively uncouples vital biogeochemical cycles. The resultant pulse of liberated heavy metals exerts acute toxicity on benthic microbial communities, significantly suppressing seasonal denitrification enzyme activity and actively inhibiting the expression of critical functional genes, such as the *nosZ* gene [28]. In legacy mine systems, episodic shifts in subsurface connectivity can occur within hours to trigger “hot moments” of metal mobilization. Field observations from a legacy mining catchment highlight how heavily skewed transport kinetics could become. In one case study, a single two- to three-month window delivered 50% to 56% of the total annual zinc export [27]. These transient pulses generated daily fluxes up to 8.4 kg d^{-1} and pushed the local Pollution Load Index (PLI) past 500 at an isolated subsurface monitoring hotspot [27], an extreme departure from the standardized environmental baseline where a PLI value of 1.0 separates unpolluted conditions from progressive contamination. Crucially, this extreme value is a highly localized anomaly restricted to deep underground storage zones (191 m below surface) governed by a stagnant “fill-and-spill” mechanism; prolonged residence times within sulfide-rich waste deposits allow for massive, threshold-driven solute accumulation before export, and it does not reflect baseline surface-water quality. Although the absolute quantities are strictly bound to local conditions like mineralization type, tailing volumes, and rainfall patterns, this tendency for a fraction of the year to dominate contaminant export is typical across altered watersheds. Consequently, climate-driven metal mobilization can functionally transform floodplains from essential ecological nitrogen sinks into impaired, toxic environments.

2.2. Shifting Redox (Eh) and pH Gradients

The chemical mobility of heavy metals within transitional water-sediment systems is inextricably linked to localized vertical and horizontal redox gradients, which are increasingly modulated by rising global temperatures [29]. Elevated seasonal temperatures ranging from 17.2°C to 28.5°C accelerate microbial respiration rates within the benthic boundary layer, rapidly depleting overlying dissolved oxygen (DO) and driving a transition to more sulfidic conditions [30]. In the absence of counteracting macrobenthic bioturbation, this shift can increase integrated porewater sulfide concentrations by 3.0- to 6.1-fold, significantly accelerating highly temperature-dependent microbial sulfate reduction [29]. As

the sediment profile shifts downward into this deeply reducing state ($Eh < 0$ mV), microbial metabolic pathways sequentially utilize these alternative terminal electron acceptors to drive subsequent heavy metal transformations [31].

The most critical geochemical consequence of this climate-forced anoxia is the reductive dissolution of amorphous and crystalline iron and manganese (Fe/Mn) oxyhydroxides (γ -FeOOH and MnO_2) driven by iron-reducing bacteria [32]. Under normal oxic conditions, these reactive mineral phases act as incredibly efficient scavenging matrices, immobilizing heavy metals and metalloids via co-precipitation and strong inner-sphere surface complexation [33]. However, under strongly reducing conditions, Fe(III) is microbially reduced to highly soluble Fe(II), causing the complete collapse of the host mineral matrix [34]:



This structural dissolution instantaneously liberates co-precipitated metals, allowing them to freely diffuse across the sediment–water interface [35]. Beyond passive liberation, specific highly reactive oxyanions behave as active participants within these transient redox ladders. For example, hexavalent chromium (Cr(VI)), a highly mobile and carcinogenic species, is profoundly sensitive to these localized shifts. Under climate-induced hypoxia, Cr(VI) can be reduced to the less toxic and highly insoluble Cr(III) via electron transfer from microbially generated Fe(II) and labile dissolved organic matter [36]. However, this natural attenuation is highly fragile. In agricultural watersheds, the influx of nitrate-rich runoff introduces a preferential terminal electron acceptor that competitively suppresses this natural reduction pathway, inadvertently stabilizing and maintaining Cr(VI) in its most toxic state despite the onset of sediment anoxia [37]. Shifting redox states and localized pH gradients can alter the thermodynamic speciation and biological exposure thresholds of metals released from sediments. To quantify these effects, various modeling frameworks (Table 1) have been used.

Table 1. Comparative analysis of primary geochemical speciation and bioavailability frameworks.

Model Architecture	Core Thermodynamic Assumptions	Operational and Data Limitations	Regulatory and Field Applicability
Free Ion Activity Model (FIAM)	- Biological uptake and toxicity are directly proportional to the activity of the uncomplexed free metal ion. - Hydrophilic metal complexes are non-bioavailable.	- Ignores competitive binding dynamics from protective background cations (e.g., Ca, Mg) at the cell membrane. - Assumes rapid thermodynamic equilibrium.	- Baseline testing in simplified, low-organic synthetic laboratory matrices. - Poor performance in dynamic natural waters.
Biotic Ligand Model (BLM)	- Integrates chemical speciation with toxicological interaction. - Toxic responses are driven by competitive binding between the free metal cation and protective ions (Ca, Mg, H) at a specific biological binding site (the biotic ligand).	- Requires exhaustive, high-frequency water chemistry inputs (pH, DOC, alkalinity, major dissolved ions) to achieve model convergence. - Structurally limited under non-equilibrium conditions.	- Modern site-specific regulatory water quality criteria (WQC) development. - Predicting acute and chronic metal toxicity thresholds across dynamic river basins.
WHAM / NICA-Donnan	Models competitive binding and electrostatic interactions onto highly heterogeneous natural organic matter (humic and fulvic acids).	- High computational overhead. - Model parameterization varies significantly based on regional and seasonal dissolved organic matter (DOM) sources.	- Characterizing deep benthic sediment porewaters and organic-rich urban wastewater interfaces. - Advanced speciation modeling in complex ecotones.

2.3. Dissolved Organic Matter (DOM) Dynamics

Climate change-induced alterations in terrestrial precipitation patterns and rising temperatures have profoundly modified the flux, molecular weight, and structural composition of dissolved organic matter (DOM) entering aquatic networks [38]. Intensive storm runoffs accelerate the leaching of humic and fulvic acids from riparian soils into river systems, shifting the ambient DOM pool toward highly aromatic, high-molecular-weight compounds rich in oxygenated functional groups [39]. These functional groups serve as powerful polydentate ligands capable of forming highly stable coordination complexes with heavy metal cations [40]. In particular, humic acids are characterized by molecular weights ranging from several thousand to approximately 100,000 Da and are dominated by aromatic carbon structures bearing abundant carboxyl and phenolic hydroxyl groups. Such high-molecular-weight humic substances can form multidentate metal–organic complexes, especially with transition metals such as Cu^{2+} , thereby substantially reducing metal solubility, mobility, and bioavailability in aquatic systems [40].

Strong complexation with high-molecular-weight humic substances effectively “shields” the metal cations, preventing their natural adsorption onto mineral surfaces and extending their downstream transport distances [41]. However, when these dissolved complexes transition into clearer, low-flow water bodies, they undergo intensive photolytic degradation and microbial processing [42]. For example, more than 99% of the dissolved iron pool in marine waters is bound by strong natural organic ligands [42], demonstrating that organic complexation plays a dominant role in controlling metal solubility, speciation, and transport across saline gradients. Under sunlit surface-water conditions, these Fe^{3+} –DOM complexes become important substrates for ligand-to-metal charge-transfer reactions and photo-Fenton processes, which accelerate DOM degradation and alter the stability of metal–organic associations [42]. This degradation-induced destabilization of metal–organic complexes frequently results in the cleavage of protective ligand bonds, abruptly releasing free, uncomplexed hydrated metal ions back into the aquatic matrix [43]. Free uncomplexed forms have the highest biological permeability. Thus, climate-driven DOM cycling can alternate between sequestering metals for transport and suddenly releasing them as bioavailable species. This creates considerable variability in metal exposure [44]. Notably, climate-induced reductions in freshwater and organic matter inputs can reorganize DOM–metal interactions, while a large proportion of both DOM and associated trace metals may reside in the truly dissolved fraction (<1 kDa), which exhibits exceptionally high mobility. Consequently, relatively small shifts in DOM composition can alter the partitioning and biological accessibility of highly toxic metals such as Cu and Cr, transforming previously stabilized metal pools into bioavailable contaminant pulses [44].

2.4. Capturing Transient Pulses: The Shift to Water Environment Informatics

The classical paradigm of relying on low-frequency, monthly grab-sampling protocols is inherently ill-equipped to capture the highly transient, stochastic transitions that characterize climate-driven metal mobilization [45]. Heavy metal fluxes during “first flush” events or sudden DOM photolysis occur on the scale of hours to days, rendering traditional monitoring structurally blind to peak toxicological exposures [46]. Indeed, the inability of low-frequency monitoring to resolve within-event dynamics is highlighted by recommendations that several samples be collected during each rainfall event rather than a single sample obtained within the first 30 min of discharge. Even under such limited monitoring coverage, benchmark exceedance frequencies reached 93.1% for Al, 100% for Mg, 86.2% for Cu, and 48.3% for Fe, underscoring the likelihood that conventional sampling strategies substantially underestimate the magnitude and timing of short-lived toxic exposure events [46].

To accurately model these dynamic thresholds, modern environmental governance must pivot toward advanced water environment informatics. The deployment of high-frequency, in situ multi-parameter sensor arrays generates the multidimensional time-series datasets required to observe these micro-interfacial shifts in real time [47]. While these electronic sensor streams provide unparalleled temporal resolution for capturing acute, transient pulses, they are optimally complemented by established active and passive bio-monitoring approaches. Leveraging the natural biosorption capabilities of aquatic organisms—such as macroalgae, bryophytes (mosses), and rooted macrophytes—acts as a robust, time-integrating sampling mechanism. These biological matrices effectively smooth out short-term stochastic noise, yielding a reliable, integrated metric of cumulative bio-available heavy metal exposure over extended environmental windows [47]. Furthermore, decoding the complex, non-linear relationships hidden within these vast datasets necessitates a departure from deterministic statistics. As detailed comprehensively in Section 5.4, the integration of advanced ensemble deep learning algorithms allows for the extraction of these temporal dependencies and stochastic transition states within the water-sediment system [48]. By coupling high-resolution sensor data with these downstream predictive pipelines, researchers can establish robust, short-term early warning systems for toxic metal outputs, fundamentally shifting aquatic risk management from a reactive framework to a proactive, predictive science [49].

3. Micro-Interface Speciation and Bioavailability

3.1. Chemical Speciation and the Biotic Ligand Model (BLM)

The ecotoxicological impact of heavy metals in aquatic environments is fundamentally governed by their thermodynamic speciation rather than their total environmental burden [50]. Classical regulatory approaches rely heavily on the Free Ion Activity Model (FIAM), which postulates that the biological response to a metal is directly proportional to the activity of the free, uncomplexed aqueous metal ion (e.g., Cd^{2+} , Pb^{2+}) in the bulk solution [51]. However, the FIAM falls short in highly dynamic transitional waters where the influx of dissolved organic carbon and competing basic cations (Ca^{2+} , Mg^{2+}) rapidly shift equilibrium states [52]. For example, copper in open-ocean systems is predominantly (>99%) bound to organic ligands, including terrestrially derived humic substances. Under Cu-limiting conditions, phytoplankton growth responds not only to the free Cu^{2+} concentration but also to the concentration of Cu–organic complexes ($[\text{Cu-L}]$), which can be assimilated via high-affinity transport systems. This demonstrates that organically complexed metals, previously assumed inert under the FIAM, can represent a substantial bioavailable fraction, particularly in environments with fluctuating DOM inputs [52].

To resolve this, modern environmental risk assessments increasingly employ the Biotic Ligand Model (BLM), which establishes a competitive, thermodynamic framework for metal-organism interactions [53–55]. The BLM mathematically treats the biological receptor, such as the gill epithelium of benthic macroinvertebrates or fish, as a distinct thermodynamic ligand that actively competes with both inorganic cations and dissolved organic matter for heavy metal binding [56]. For example, competing basic cations act as strong suppressors of heavy metal uptake at these binding sites. In representative ecotoxicological frameworks—such as an acute Gadolinium (Gd^{3+}) exposure model calibrated for the freshwater crustacean *Daphnia magna*—the conditional stability constant for Calcium ($\log K_{\text{CaBL}} = 6.04$) serves as a representative parameter optimized via Markov chain Monte Carlo fitting [56]. This calibrated value quantifies the thermodynamic affinity of Ca^{2+} for the biotic ligand to suppress toxic metal accumulation, providing a self-consistent parameter set useful for predictive environmental risk assessment. However, the operational accuracy of such values remains fundamentally sensitive to the structural bounda-

ries of the chosen chemical speciation model and the resolution of dissolved metal measurements. Humic substances, particularly humic acids, further sequester free metal ions, reducing their availability to the biotic ligand [57]. The BLM framework has been successfully applied to organisms ranging from *Daphnia magna* to fish species such as *Oncorhynchus mykiss* and *Pimephales promelas*, with model-predicted survival rates showing strong agreement with observations in both synthetic and natural waters [56]. While the BLM represents a major conceptual leap by integrating water chemistry with biological uptake, its traditional application assumes a relatively homogeneous distribution of dissolved species. This assumption becomes increasingly problematic in heavily contaminated water–sediment systems, where emerging anthropogenic particles create highly reactive micro-environments that can significantly alter localized metal partitioning [58]. In mining- and smelting-impacted catchments, contaminated dust, slag-derived particulates, tailings, and metal-bearing soil colloids act as mobile carriers that transport contaminants across sharp geochemical gradients. These systems commonly exhibit highly heterogeneous contaminant distributions and complex mixing zones, causing localized shifts in metal speciation, mobility, and bioavailability that are often poorly represented by conventional equilibrium-based risk assessment frameworks [58].

3.2. Emerging Vector Interfaces: Microplastics and the “Eco-Corona”

The pervasive accumulation of microplastics within benthic sediment matrices has introduced a novel, highly dynamic transport vector for heavy metal pollutants [58]. In some riverine sediments, microplastic concentrations exceed 10^3 particles kg^{-1} dry weight, providing extensive surfaces for contaminant sorption and transformation processes. Environmental weathering transforms microplastics from passive debris into dynamic, mobile transport vectors for heavy metals [59]. While pristine microplastics possess hydrophobic surfaces with minimal binding affinity for cationic metals, photo-oxidative and mechanical aging in aquatic systems fundamentally alter this baseline. The progressive accumulation of oxygen-containing surface functional groups—such as carbonyl, carboxyl, and hydroxyl moieties—shifts metal binding from weak electrostatic attraction to stable, inner-sphere chemisorption [60]. This transformation is particularly evident for common polymers such as polyethylene (PE) and polypropylene (PP), whose initially nonpolar surfaces acquire reactive coordination sites during environmental weathering. These oxygenated functional groups facilitate the formation of partially covalent metal–oxygen bonds with contaminants, typically displaying a selective affinity hierarchy of $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ governed by differences in ionic radius and electronegativity. This preferential coordination shifts metal retention from weak electrostatic sorption to stable inner-sphere chemisorption, thereby increasing the persistence of metal–microplastic associations in aquatic environments [60].

In real-world aquatic systems, however, microplastics rarely exist as “bare” or purely oxidized particles. Upon entering the water column and settling into benthic sediments, these synthetic polymers immediately interact with dissolved organic matter (DOM) and microbial communities. Within minutes, a conditioning film develops, facilitating rapid biofilm colonization to form a complex biological “eco-corona” [61]. Experimental evidence shows significant microbial attachment on common polymers—including PE, PP, PET, and PVC—within just 10 min of exposure. The initial adsorption of dissolved organic matter (DOM) forms a primary conditioning film that facilitates subsequent microbial adhesion and succession, ultimately producing a three-dimensional heterogeneous plastsphere embedded in extracellular polymeric substances (EPS). This transformation fundamentally alters the surface properties of microplastics, enhancing their chemical reactivity, sorptive capacity for trace metals, and ecological interactions compared with pristine or oxidized laboratory analogs [61].

Within this hierarchical structure, the EPS-rich biofilm represents the primary reactive interfacial layer governing contaminant partitioning. The extracellular polymeric substances (EPS) secreted by the biofilm are densely enriched with carboxyl, hydroxyl, and amine groups, which can substantially enhance the chemisorption capacity for heavy metals far beyond the binding potential of the underlying plastic vector itself [62]. Furthermore, this metabolically active interfacial layer can potentially facilitate valence transformations, such as mediating the localized reduction of Cr(VI) to Cr(III) within the micro-environment of the biofilm [63].

The EPS matrix of the biofilm provides a highly reactive, high-energy sorption surface, enriched with carboxyl, hydroxyl, and nitrogen-containing functional groups derived from polysaccharides, proteins, and lipids. This functional complexity dramatically increases the available binding sites compared with pristine microplastics. The eco-corona modification enhances the vector interface's ability to adsorb coexisting organic pollutants, for instance, tetracycline adsorption increased by about 3.8-fold in lab experiments [63]. However, this quantitative multiplier cannot be directly applied to inorganic species due to fundamental differences in binding mechanisms. While organic pollutants typically utilize hydrophobic or π - π interactions, heavy metal cations rely on electrostatic attraction and inner-sphere coordination; thus, while biofilm formation still significantly enhances heavy metal retention (such as Pb(II)), its exact magnitude is governed by distinct thermodynamic boundaries [63]. While direct measurements for heavy metals are fewer, prior research indicates that biofilm formation also enhances metal adsorption, including Pb(II), by providing chemically diverse and spatially heterogeneous coordination environments. The combined effect of surface functionalization and increased porosity transforms the biofilm-coated microplastic into a dynamic, metabolically active interface that not only sequesters metals but also locally modulates their chemical speciation and redox state, consistent with mechanisms such as potential Cr(VI) reduction [63].

3.3. Mechanistic Insights: Bridging DFT with In Situ Spatial Gradients

Understanding the precise, orbital-level interactions between heavy metal cations and weathered microplastic surfaces requires analytical approaches that extend beyond macroscopic batch adsorption experiments. To decode these micro-interfacial mechanisms, contemporary environmental physical chemistry increasingly relies on Density Functional Theory (DFT) simulations [64]. For example, DFT calculations can quantify metal-polymer interaction energies at the quantum-chemical level, revealing adsorption energies on the order of -2.26 eV for Cu-polyethylene complexes. These values were obtained via geometric optimization using the B3LYP functional with the LanL2dz basis set, followed by high-resolution single-point energy calculations at the def2-TZVP level that incorporate an implicit SMD solvation model. This computational approach enables us to distinguish weak van der Waals interactions from stronger electrostatic or coordination-type bonding [64]. In combination with wave-function and electron-density analyses, DFT further enables visualization of charge redistribution and interfacial electron-density accumulation, while Reduced Density Gradient (RDG) diagnostics allow discrimination between noncovalent interactions and directional metal-surface coordination. This multi-level electronic-structure information provides a mechanistic bridge between experimentally observed adsorption behavior and the underlying orbital-scale processes governing metal retention on microplastic surfaces [64].

Density Functional Theory (DFT) simulations provide unparalleled spatial and energetic resolution, calculating binding energies, electron density distributions, and the thermodynamic stability of metal-polymer complexes at the quantum mechanical level [65]. For instance, first-principles calculations using RKS/UKS frameworks with stringent con-

vergence criteria (down to $\sim 10^{-8}$ au) enable the accurate determination of adsorption energies, where negative values explicitly indicate thermodynamically favorable metal–polymer interactions. Such simulations further resolve stability differences between oxidation states, showing that Cr(III) complexes (modeled as $\text{Cr}(\text{OH})_2^+$) can reach adsorption energies as low as -3.67 eV, reflecting significantly stronger and more stable binding than Cr(VI) species. This value is resolved using an Unrestricted Kohn-Sham (UKS) framework to describe the open-shell $[\text{Ar}]3d^3$ electronic configuration of Cr^{3+} , with geometry optimization carried out at the B3LYP-D3/def2-TZVP(-f) level under SMD solvation, further refined by the $\omega\text{B97M-V}$ functional. The final electronic energies are determined using the PWPB95-D3 functional and a def2-TZVPP basis set, using a strict energy convergence threshold of 1.0×10^{-8} au and counterpoise corrections to eliminate basis set superposition error (BSSE) [65].

Furthermore, charge density difference (CDD) mapping and interaction region indicator (IRI) analyses allow direct visualization of electron accumulation and depletion zones at adsorption sites, distinguishing covalent bonding regions from weaker van der Waals interactions. Complementary density-of-states (DOS) and orbital hybridization analyses further reveal how electronic restructuring at the interface governs the stability and selectivity of these complexes [65].

By modeling specific geometries, these DFT analyses reveal whether adsorption is governed by cation– π interactions or covalent-like coordination with oxygenated defects [66]. For example, geometry-optimized structures calculated using B3LYP/DFT (Gaussian 16) demonstrate that polycation–nanoplastic systems can stabilize either through electrostatic cation– π attraction between highly charged metal species and the quadrupole moment of aromatic rings, or through the formation of C–O–M coordination bonds associated with surface oxygen functionalities. Comparative binding energy calculations further distinguish these mechanisms, showing that coordination complexes involving oxygen-containing sites exhibit distinct thermodynamic signatures relative to purely cation– π -driven assemblies. In systems containing polymeric coagulants with higher charge density, DFT results additionally indicate enhanced stabilization via stronger cation– π interactions, highlighting the extreme sensitivity of adsorption pathways to both molecular geometry and electronic structure [66].

However, pure DFT operates in idealized quantum-mechanical vacuums or implicit solvent models. To translate these theoretical mechanisms into practical environmental risk assessments, computational simulations must be strictly coupled with rigorous in situ benthic sediment sampling and empirical validation [67]. This empirical pairing is critical because idealized vacuum or implicit-solvent models inevitably simplify or omit multi-component aquatic dynamics. Specifically, static electronic structure calculations fail to capture competitive hydration (where hydrogen bonding between water molecules and polymer surfaces systematically occupies potential binding sites), and they overlook ionic background interference—where coexisting salinity matrices (Na^+ , Mg^{2+}) actively outcompete trace metals for active monolayer sorption sites. Furthermore, implicit-solvent dielectric fields cannot dynamically resolve how shifting ambient pH alters the protonation states of primary hydrogen-bond-donating groups (such as RCOOH), nor do they reflect the highly heterogeneous physical cracks and oxygenated variations generated by natural, seasonal solar weathering of microplastic surfaces. Validating DFT-predicted binding models requires observing how they hold up across real-world spatial gradients. For instance, designing longitudinal river transects that track microplastic and metal co-occurrence from heavily industrialized urban origins down through transitional agricultural zones allows researchers to empirically quantify how shifting ambient pH, DOM fluxes, and competitive mineral matrices either confirm or disrupt theoretical competitive adsorption hierarchies in the field [68].

3.4. Bioavailability, Gut Microbiome Toxicity, and the “Trojan Horse”

The convergence of heavy metals and eco-corona-coated microplastics at the sediment–water interface carries profound toxicological implications for benthic ecology. Benthic macroinvertebrates, which serve as the foundational trophic layer in many aquatic food webs, indiscriminately ingest contaminant-bearing microplastics alongside natural sediment and detritus [69]. Because the seabed acts as the primary sink for weathered microplastics, benthic deposit feeders and scavengers routinely mistake these contaminant-laden particles for natural detritus [68]. This indiscriminate ingestion bypasses environmental barriers, routing bound heavy metals directly into the foundational layer of the aquatic food web. This sustained physiological stress inflicts severe metabolic costs; for example, *Hexaplex trunculus* exhibited a 21% reduction in biochemical energy content following microplastic exposure, underscoring the heightened vulnerability of benthic organisms to sustained environmental stress [69].

Once ingested, the microplastic vector transports the concentrated heavy-metal payload directly into the organism’s digestive tract. The highly acidic, enzyme-rich environment of the gut presents a radically different chemical milieu compared to the surrounding ambient water [70]. Microplastics function not only as transport vectors but also as delivery platforms that release associated contaminants within the gastrointestinal tract. Experimental studies have shown that pollutant desorption rates under simulated intestinal conditions can be up to 30 times greater than those observed in seawater, reflecting the profound influence of digestive chemistry on contaminant mobilization. Consequently, metals associated with microplastic surfaces may become substantially more bioaccessible following ingestion, enhancing intestinal exposure and toxicological risk compared with equivalent metal concentrations dispersed in the surrounding aquatic environment [70]. Under these physiological conditions, the adsorption–desorption equilibrium established on the microplastic surface can shift markedly. Metals previously associated with the polymer matrix or its EPS-rich eco-corona through adsorption, complexation, or chemisorption may undergo substantially enhanced release within the gut, increasing the local concentration of bioavailable metal species at sites of uptake and absorption [71].

The immediate ecotoxicological consequence of this “Trojan Horse” effect is intensely localized. Long before these metals bioaccumulate in host tissues or biomagnify up the broader trophic ladder, the acute localized pulse of free metal ions induces severe oxidative stress and profound dysbiosis within the organism’s intestinal microbiome [72]. This disruption of the gut flora impairs digestive enzyme activity, compromises immune responses, and weakens the organism’s baseline physiological resilience, representing a critical but historically overlooked pathway of heavy metal toxicity in benthic ecosystems [73]. Experimental evidence indicates that heavy metal–microplastic complexes can amplify toxicity beyond that caused by either stressor alone, aggravating oxidative damage and producing deeper alterations in gut microbial diversity. Such combined exposures have been associated with destabilization of intestinal microbial communities, shifts in the balance between beneficial and pathogenic taxa, and disruption of key digestive enzymes, including reductions in amylase activity and alterations in trypsin function. These physiological disturbances can weaken intestinal immune defenses, interfere with normal cellular metabolism, and ultimately impair growth, reproduction, and survival. Because many benthic organisms continuously ingest sediment-associated microplastics, this contaminant delivery pathway may represent a persistent source of sublethal stress capable of reshaping both host health and sediment-associated microbial processes at the ecosystem scale [72,73]. To integrate these micro-interfacial mechanisms with their cascading ecological consequences across organismal, community, and biogeochemical levels, a comprehensive framework of the climate–metal–resistome axis is presented in Figure 1.

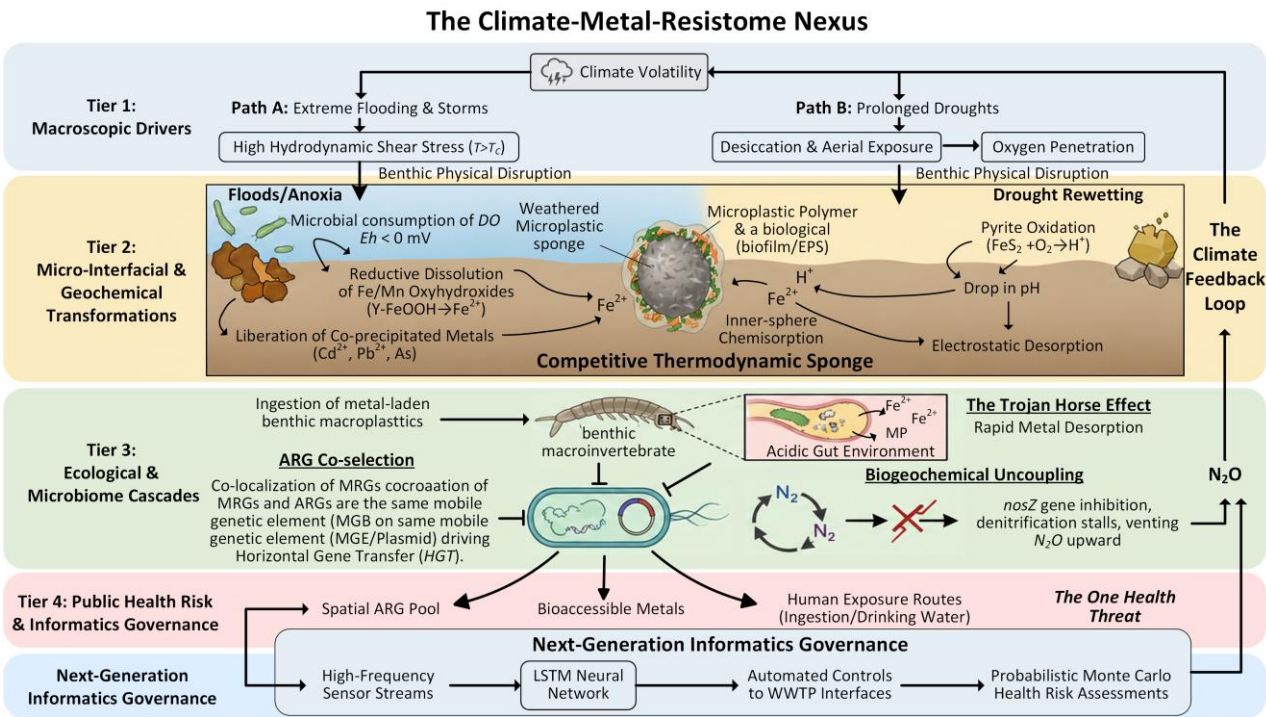


Figure 1. Conceptual architecture of the Climate–Metal–Resistome Nexus across aquatic water–sediment systems. The framework traces the cascade from macroscopic climate forcing down to micro-interfacial speciation, microbial evolutionary cascades (*nosZ* suppression and ARG co-selection), and the ultimate scaling up to machine learning-coupled human health risk assessments. Abbreviations: *nosZ*, nitrous oxide reductase functional gene; ARG, antibiotic resistance gene; MGE, mobile genetic element; EPS, extracellular polymeric substances.

To complement this conceptual framework, Table 2 provides a compiled meta-summary of the key quantitative empirical endpoints, system contexts, and operational boundaries across these interconnected micro-interfacial and biogeochemical processes.

Table 2. Quantitative meta-summary of key empirical findings and system contexts.

Target Inter-facial Process	Measured Quantitative Endpoint	Reported System Conditions	Context-Specific Constraints	Source
Plastisphere vector sorption	Approximately 3.8-fold increase in adsorption capacity compared to pristine microplastics.	- Model organic antibiotic: Tetracycline. - Controlled bench-scale laboratory experiments.	Driven by complex multi-functional organic mechanics (π – π electron interactions, hydrogen bonding). Cannot be directly extrapolated as a uniform scaling multiplier for simple heavy metal cations.	[63]
Biogeochemical nitrogen uncoupling	Nearly 10-fold accumulation of nitrous oxide (N_2O); relative enzyme activity dropped from 97.25% down to 43.05%.	- Model heavy metal: Cadmium (Cd(II)) at 5–10 mg/L. - Enriched denitrifying benthic sediments.	Represents a post-translational biochemical enzyme repression specific to the multicopper coordination centers of nitrous oxide reductase; preceding reduction steps (nitrate/nitrite) remain unhindered.	[74]
Hydrological event exposure	48.3% to 100% benchmark exceedance frequencies across targeted trace metals (Al, Mg, Cu, Fe).	- Dynamic storm-driven “first flush” hydrology. - Within-event high-frequency stormwater sampling.	Quantifications are strictly bound to short-lived, transient hydrologic event windows; traditional low-frequency monthly grab-sampling protocols completely miss these peak toxic exposures.	[46]

4. The Heavy Metal-Microbiome-Antibiotic Resistance Axis

4.1. Alteration of Benthic Microbial Architecture and Bioenergetic Trade-Offs

Traditional toxicological frameworks assess heavy metal risk primarily through the lens of direct organ damage in higher vertebrates or acute mortality in indicator species. However, an increasingly critical, and largely invisible, ecological casualty is the foundational aquatic microbiome [75–77]. In benthic sediments, heavy metals rarely exist at concentrations that cause immediate, widespread bacterial sterilization. Instead, elements like copper (Cu^{2+}), zinc (Zn^{2+}), and hexavalent chromium (Cr(VI)) persist at sublethal concentrations, exerting a chronic, highly targeted selective pressure on microbial community architecture [78].

Prolonged exposure to these metallic stressors induces severe oxidative stress, disrupting cellular respiration and denaturing critical enzymes within susceptible bacterial taxa [79]. This drives a deterministic shift in community composition; sensitive species are rapidly outcompeted, resulting in a profound loss of alpha diversity and a structural restructuring of the microbiome toward metal-tolerant phenotypes [80,81]. However, survival carries a steep bioenergetic “fitness cost” [14]. Continuously operating transmembrane efflux pumps and synthesizing heavy intracellular metallothioneins drain precious ATP. By diverting cellular energy away from primary metabolism and growth, these strategies reduce the overall ecological competitiveness of the bacterial population when metal levels fluctuate. This trade-off significantly diminishes the carbon-processing efficiency and metabolic versatility of the benthic zone, permanently altering the ecosystem’s service functions [82].

4.2. Genetic Linkage: Mechanisms of ARG Co-Selection and Evidence

The most alarming consequence of this heavy-metal-induced microbial restructuring is the phenomenon of co-selection for antibiotic resistance [83]. Aquatic environments serving as sinks for heavy metals, particularly downstream of wastewater treatment plant (WWTP) effluent discharges and industrial urban rivers, frequently exhibit a paradoxical surge in antibiotic resistance genes (ARGs), even in the complete absence of pharmaceutical antibiotics [84]. This synergistic proliferation is fundamentally driven by two primary modes of genetic linkage. Cross-resistance emerges through non-specific cellular defense mechanisms, such as multi-drug efflux pumps, which simultaneously eject both toxic heavy metal cations and clinical antibiotics from the cytosol. Simultaneously, co-resistance establishes a more persistent genetic hazard, where metal resistance genes (MRGs) and ARGs are frequently co-localized on the same mobile genetic elements (MGEs), including broad-host-range plasmids, transposons, and Class 1 integrons [14].

Crucially, climate-driven hydrological volatility functions as a primary driver of resistome dynamics rather than acting as a passive background variable. Shifting hydrologic regimes alternate between extended low-flow droughts and intense scouring floods, generating sharp, episodic fluctuations in sediment redox potentials and porewater chemistry. These localized transitions cause transient, sublethal pulses of bioavailable trace metals to desorb from mineral matrices into the surrounding active biofilm interface [85]. Because these concentration spikes occur rapidly, they exert a pronounced ‘pulse–press’ selective pressure on the benthic microbiome [86]. To survive these chemical inputs, microbial communities leverage co-selection pathways, wherein genes conferring heavy metal tolerance (MRGs) and ARGs are co-localized on the same mobile genetic elements, such as plasmids or integrons [87]. Consequently, climate-induced physical disruptions directly accelerate horizontal gene transfer within the plastosphere and benthic sediment matrices, transforming climate-impacted urban freshwater ecotones into localized hotspots for resistome proliferation.

To move beyond speculative correlation, recent research has pivoted toward Metagenomic Shotgun Sequencing as the definitive tool for characterizing this resistome [88]. Unlike traditional qPCR methods, which only quantify known genes, metagenomic assembly allows researchers to reconstruct complete genomic contigs. This provides direct physical evidence by revealing that MRGs and ARGs are indeed physically linked on the same DNA fragments within the same bacterial genome, confirming their potential for horizontal gene transfer (HGT) [74]. Consequently, the environmental persistence of heavy metals maintains a constant evolutionary pressure that stabilizes these resistance markers, effectively accelerating the selection and enrichment of multidrug-resistant (MDR) phenotypes in natural waters [89].

4.3. The “One Health” Perspective: Environmental Reservoirs

The sediment resistome is not merely a localized ecological issue; it represents a critical One Health challenge. Urban river networks act as regional conduits that flush metal- and antibiotic-resistant bacteria from upstream waste directly into human interfaces [90]. Fueled by hydrological transport and reclaimed-water irrigation, these resistance reservoirs breach ecological boundaries—contaminating agricultural soils, food crops, and drinking-water intakes. This widespread environmental network effectively shorts out traditional clinical containment, linking downstream ecosystems directly to human and animal health systems.

Consequently, metal-contaminated sediments function as expansive and persistent evolutionary reservoirs in which resistance determinants are maintained, exchanged, and amplified before re-entering human and animal populations. By actively feeding the clinical resistome, these environments complicate the management of infectious diseases and contribute to the broader global burden of antimicrobial resistance [91]. This bidirectional exchange directly threatens modern medicine. As environmental resistance determinants spill over into clinical settings, they actively drive treatment failures, force reliance on toxic second-line therapies, and compromise standard surgical prophylaxis. The magnitude of this challenge is reflected in the global disease burden attributable to antimicrobial resistance: approximately 5 million deaths were associated with AMR in 2019, including 1.27 million deaths directly attributable to drug-resistant bacterial infections [92]. Under unmitigated baseline scenarios, annual mortality has been projected to approach 10 million by 2050 [93]. However, it is critical to note that this 2050 projection has been methodologically contested by epidemiological experts who caution that such long-term forecasting relies on linear economic extrapolations that may overestimate future resistance-attributable mortality trajectories [94].

Modern regulatory frameworks must therefore recognize such zones not only as sites of chemical contamination but also as biological catalysts capable of undermining the long-term efficacy of antimicrobial therapies.

4.4. Biogeochemical Uncoupling: The Disruption of the *nosZ* Gene

Beyond the proliferation of resistance, heavy metal accumulation actively uncouples key biogeochemical cycles, particularly the nitrogen cycle. In both engineered systems such as wastewater treatment bioreactors and natural environments such as restored floodplains, denitrification represents a critical ecological service responsible for removing excess reactive nitrogen from aquatic systems. However, the metalloenzymes that mediate this pathway are highly sensitive to heavy metal stress, which can disrupt microbial activity and impair nitrogen transformation processes [95].

The sequential respiratory pathway of biological denitrification relies on a tightly coupled cascade of four specialized metalloenzymes: nitrate, nitrite, nitric oxide, and nitrous oxide reductases ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$). In highly volatile settings like restored floodplains or wastewater bioreactors, legacy heavy metals act as severe chemical stressors that disrupt this enzymatic chain through immediate cofactor inactivation, structural denaturation, and competitive ion substitution. Specifically, divalent metal spikes actively corrupt the catalytic cores of these reductases. For example, excess ambient Zn^{2+} or Cd^{2+} ions directly displace essential native cofactors like Mg^{2+} from enzyme binding sites, collapsing catalytic efficiency. Simultaneously, non-target metal binding to heme-containing proteins blocks electron transport pathways, arresting the reduction cascade before it can reach completion.

These disruptions are particularly critical in the final step of the pathway, where nitrous oxide reductase catalyzes the reduction of N_2O to N_2 . This multicopper enzyme depends on precisely coordinated copper centers, making it especially sensitive to disruption by competing or toxic metal species [96]. As a result, heavy metal exposure can create a functional bottleneck at this terminal step, suppressing complete denitrification and limiting the removal of reactive nitrogen from aquatic ecosystems [95].

A vital toxicological endpoint often overlooked in traditional HRAs is the specific inhibition of nitrous oxide reductase, the enzyme responsible for this terminal step [97]. This stage represents a critical ecological safeguard, particularly in coastal and estuarine networks where biological denitrification accounts for roughly 90% of total nitrogen removal under optimal conditions [97]. However, this upper-bound estimate is highly context-dependent; its actual dominance is continuously shaped by competing processes, such as anaerobic ammonium oxidation (anammox), dissimilatory nitrate reduction to ammonium (DNRA), and physical burial, and it remains highly vulnerable to suppression by trace-metal pollution. While conventional risk models focus heavily on generalized microbial growth inhibition, they consistently fail to account for the highly selective, biochemically driven toxicity that specific heavy metals exert on this endpoint. For instance, controlled laboratory trials within a single microbial culture system demonstrate that cadmium (Cd(II)) exposure at high operational concentrations between 5 and 10 mg/L induces a nearly ten-fold accumulation of N_2O without significantly impeding the preceding reduction steps of nitrate (NO_3^-) or nitrite (NO_2^-) [97]. This targeted suppression manifested as a clear reduction in relative enzyme activity, decreasing from 97.25% down to 43.05% of control levels under these specific experimental conditions.

Intriguingly, molecular investigations reveal that this metal-induced disruption can operate via distinct, multi-tiered pathways [98,99]. At the post-translational level, the toxicity is purely biochemical rather than genetic; even when environmental stress up-regulates the transcription of the *nosZ* gene encoding the enzyme, the actual catalytic activity of the folded protein is severely repressed [100]. Conversely, broader suites of trace metals, particularly when mobilized during sudden climate-driven redox shifts or carried via microplastic vectors, can act upstream to actively suppress the expression and transcription of the *nosZ* gene itself [101].

Whether operating through direct enzymatic inhibition or transcriptional silencing, this toxicological suppression structurally uncouples the denitrification pathway. As a result, heavy metal-impaired sediments and water treatment interfaces fail to complete the nitrogen cycle, leading to the massive accumulation and emission of nitrous oxide (N_2O), a potent greenhouse gas with a 100-year global warming potential (GWP_{100}) 273 times that of carbon dioxide, according to the IPCC Sixth Assessment Report (AR6) [102]. This establishes a previously neglected, critical feedback loop where localized heavy metal toxicity actively accelerates macro-scale climate change emissions.

5. Evolution of Human Health Risk Assessment: From Deterministic to Probabilistic Frameworks

5.1. The Structural Limitations of Deterministic Models

The foundational framework for evaluating the human health implications of aquatic heavy metal exposure relies on the standard deterministic risk assessment paradigm established by global regulatory bodies such as the United States Environmental Protection Agency [103]. This classical approach calculates the Chronic Daily Intake (CDI) across multiple exposure pathways, predominantly direct ingestion, dermal contact, and the consumption of contaminated aquatic biota, to estimate non-carcinogenic risk via the Hazard Quotient (HQ) and carcinogenic threat via the Incremental Lifetime Cancer Risk (ILCR) [104]. To quantify these risk metrics, the paradigm integrates environmental monitoring data with established toxicological parameters, utilizing oral reference doses (RfD) and cancer slope factors (CSF) derived from standardized databases such as the USEPA Integrated Risk Information System (IRIS). The calculated CDI serves as a lifetime exposure baseline, incorporating fixed physiological variables including standard ingestion rates, body weight, exposure frequency, and duration. For non-carcinogenic endpoints, individual contaminant risk is evaluated by calculating the ratio of the CDI to its corresponding RfD , where an $\text{HQ} > 1$ denotes an unacceptable non-cancer hazard. To address real-world exposure to complex chemical mixtures, these individual quotients are aggregated into a cumulative Hazard Index ($\text{HI} = \sum \text{HQ}$), which accounts for the additive systemic toxicity of co-occurring metals. Conversely, carcinogenic risks are modeled by multiplying the pathway-specific CDI by the CSF to yield the ILCR, which represents the excess probability of an individual developing cancer over a nominal 70-year lifetime. These numerical outputs are subsequently benchmarked against international safety thresholds, such as the USEPA acceptable target cancer risk range of 1×10^{-6} to 1×10^{-4} , providing regulatory agencies with a binary tool to distinguish tolerable baselines from severe public health hazards requiring urgent intervention.

While this deterministic architecture provided the necessary baseline for early environmental governance, it is inherently static. The methodology relies exclusively on single-point estimates, typically utilizing the arithmetic mean or the 95% upper confidence limit of the contaminant concentration, coupled with fixed physiological parameters, such as a standardized adult body weight or a uniform daily ingestion rate [105]. This mathematical rigidity flattens real-world demographic diversity into a fictional average. By multiplying worst-case, conservative assumptions at every step, these models compound safety margins into hyper-inflated risk values that distort actual public health priorities. Paradoxically, this one-size-fits-all averaging erases the very populations most at risk—such as subsistence fishing communities or children—whose unique dietary intake and developmental vulnerabilities are excluded from standard statistical baselines [106].

5.2. Capturing Population Heterogeneity and Data Sparsity

To resolve the structural limitations of point-estimate methodologies, contemporary environmental toxicology has increasingly adopted advanced probabilistic modeling architectures, most notably Monte Carlo simulations [107]. Rather than assigning a singular, deterministic value to an exposure parameter, probabilistic frameworks assign specific probability density functions, such as lognormal distributions for environmental contaminant concentrations or uniform distributions for exposure durations, to every variable within the fundamental risk equation [108]. Through tens of thousands of iterative computational permutations, the Monte Carlo algorithm randomly samples from these input distributions to generate a comprehensive, continuous probability distribution of the potential human health risk [109]. This stochastic output allows risk assessors to precisely quantify specific exposure percentiles, reliably isolating the 90th or 95th percentile risk thresholds to protect highly sensitive demographic groups without grossly overestimating the baseline risk to the general population [110]. The core structural and methodological distinctions between these conventional point-estimate paradigms and advanced probabilistic exposure frameworks are synthesized comprehensively in Table 3.

Table 3. Methodological comparison of human health risk assessment (HRA) frameworks.

Evaluation Attribute	Deterministic Approach	Probabilistic Approach
Input Data Treatment	Uses rigid, single-point metrics (typically the arithmetic mean or the 95% Upper Confidence Limit) for environmental concentrations and exposure factors.	Assigns continuous probability density functions (e.g., lognormal, beta, or uniform distributions) to every exposure variable.
Population Heterogeneity	Compounds multiple conservative assumptions, completely masking natural behavioral and physiological variations.	Captures full population variance through tens of thousands of random iterative computational permutations.
Risk Characterization	Yields a single, binary numerical risk value (e.g., Hazard Index > 1 or <1), which can obscure public health priorities.	Outputs a continuous risk probability distribution curve, enabling targeted isolation of the 90th or 95th percentile exposure risks.
Subpopulation Safeguards	Tends to protect the generic “average adult,” frequently overlooking highly vulnerable groups (e.g., children, subsistence fishers).	Effectively isolates and quantifies risk boundaries for highly exposed or sensitive demographic cohorts.
Primary Limitation	Prone to severe mathematical overestimation of chronic risk due to the compounding of maximum conservative parameters.	Heavily dependent on intensive, high-quality data monitoring; vulnerable to geographical biases if input data is sparse.

However, executing a statistically robust probabilistic simulation is heavily dependent on the density and quality of the input monitoring data. In many regions, environmental monitoring data is plagued by spatial data gaps, missing observations, or uneven reporting across yearbooks and monitoring networks [111]. To resolve this data sparsity without introducing geographical bias, contemporary risk assessments must deploy advanced spatial data science techniques prior to running Monte Carlo simulations. Integrating geographic information systems (GIS) with multilevel imputation frameworks or predictive mean matching allows researchers to reconstruct missing data structures within environmental datasets [112]. This preprocessing step ensures that the input probability density functions reflect true regional variations rather than localized reporting gaps, making the downstream risk distributions highly reliable.

5.3. Integrating Bioaccessibility and Mixture Toxicity

Despite the immense mathematical sophistication of probabilistic frameworks, their ultimate predictive accuracy remains heavily constrained by the chemical assumptions embedded within the input variables. Classical human health risk assessments universally assume a relative bioavailability of 100%, implicitly asserting that every ingested heavy metal molecule is entirely absorbed across the human gastrointestinal epithelium into systemic circulation [113]. This assumption is geochemically invalid. To generate truly accurate probabilistic risk trajectories, modern Monte Carlo simulations must move beyond total elemental concentrations and integrate empirical bioaccessibility factors derived from rigorous *in vitro* simulated gastrointestinal digestion models [114].

Furthermore, this approach must account for the reality that human populations are rarely exposed to single, isolated heavy metals. Aquatic ecosystems routinely present complex chemical “cocktails” where multiple contaminants co-occur [115]. Traditional assessments frequently rely on a linear summation of risk values, known as the Hazard Index, which assumes that the toxic effects of distinct metals are merely additive. However, heavy metals often exhibit significant synergistic toxicological interactions when co-ingested. For instance, concurrent exposure to Cr(VI) and arsenic can saturate cellular detoxification pathways and accelerate oxidative stress at rates far exceeding the predictions of independent, linear models [116]. This non-linear metabolic acceleration is hypothesized to arise from a localized conflict within the intracellular environment.

When Cr(VI) crosses the cell membrane via non-specific anion transporters, it undergoes rapid step-by-step reduction to trivalent chromium (Cr(III)) via highly reactive intermediate states (Cr(V) and Cr(IV)). This pathway typically relies on intracellular non-enzymatic reducing agents, primarily reduced glutathione (GSH) and NADPH-dependent cellular reductases [116]. The simultaneous presence of trivalent arsenite (As(III)) may place a competing strain on these exact same detoxification networks. Because As(III) exhibits a high binding affinity for sulfhydryl groups, it can systematically deplete the intracellular GSH pool and inactivate glutathione-dependent antioxidant enzymes. Where these two pathways overlap, the literature suggests that co-exposure can induce a compounding depletion of the cell's primary thiol-based defenses [116].

Under conditions of severe GSH depletion, transient Cr(V) and Cr(IV) intermediates may persist longer, potentially accelerating the generation of hydroxyl radicals ($\bullet\text{OH}$) and secondary reactive oxygen species (ROS) via Fenton-like cyclic reactions. By impairing xenobiotic detoxification systems and compounding reactive oxygen species (ROS) generation through shared metabolic constraints, this combined exposure shifts cellular damage from an additive trend into a pronounced, synergistic escalation. Traditional linear risk assumptions, such as the simple summation of Hazard Indices, fundamentally fail to model this mechanistic cascade, masking severe, synergistic toxicological outcomes. Developing advanced mixture toxicity indices and coupling them with biokinetic modeling within the Monte Carlo framework represents a critical frontier in capturing the true cumulative burden of the environmental exposome.

5.4. Next-Generation Risk Forecasting via Machine Learning Integration

The final frontier in human health risk modeling involves bridging the gap between probabilistic calculations and advanced water environment informatics. While Monte Carlo simulations excel at quantifying parameter uncertainty, they remain structurally bound to static, steady-state exposure equations that treat environmental data as stationary [117]. To transition risk assessment from a retrospective calculation to a dynamic forecasting discipline, contemporary researchers are beginning to couple probabilistic frameworks with ensemble machine learning models, such as Random Forest, Gradient Boosting, or Long Short-Term Memory (LSTM) networks [118].

The core limitation of classical human health risk assessment frameworks lies in their foundational assumption of environmental stationarity. Traditional regulatory paradigms model human exposure by treating heavy metal concentrations as stable, mean baselines over multi-decadal timelines. Accelerating climate volatility fundamentally invalidates these stationary models, as extreme hydrometeorological events inject severe, non-linear stochastic variance into surface water qualities [119]. A population’s true exposure profile under a volatile climate shifting between prolonged desiccation and concentrated toxic flushes is characterized by acute, transient risk peaks rather than chronic, uniform averages. Consequently, transitioning to probabilistic Monte Carlo frameworks becomes a mathematical necessity to capture this climate-induced exposure heterogeneity. By integration of high-frequency time-series datasets into ensemble machine learning models—such as Long Short-Term Memory networks—environmental informatics can successfully map these climate-driven, non-stationary contamination waves, shifting risk assessment from a static, retrospective calculation to an adaptive, predictive early-warning architecture [120].

This integration marks a major transformation from reactive, lab-based monitoring to proactive, large-scale predictive modeling capable of handling high-dimensional environmental data and complex, non-linear associations. Traditional analytical frameworks, while reliable, are severely constrained by high operational costs and time delays that preclude real-time intervention. Integrating machine learning and deep learning methodologies addresses these limitations by decoding temporal and spatial toxic metal fluctuations across dynamic aquatic systems. For instance, robust ensemble algorithms like Random Forest (RF) effectively mitigate overfitting when evaluating expansive ecological risk datasets and spatial contamination profiles. Concurrently, high-accuracy frameworks such as Gradient Boosting Machines (GBM) deliver exceptional precision, often operating within a 92% to 97% accuracy threshold, making them uniquely suited for short-term temporal forecasting.

To capture the continuous-time-series dependencies inherent to climate-driven hydrological shifts, deep learning architectures like LSTM networks are utilized to model cyclical and irregular heavy-metal pulses over extended periods. By feeding real-time, high-frequency water-quality data into these neural networks, researchers can predict the highly non-linear, transient heavy-metal pulses driven by extreme climate events, as outlined in earlier sections. These machine learning-driven concentration forecasts can then be dynamically channeled directly into Monte Carlo simulation engines [121]. The computational strengths, target metrics, and operational data constraints of these respective machine learning frameworks are compared and synthesized in Table 4.

Table 4. Technical synthesis of machine learning architectures in environmental informatics.

Algorithmic Architecture	Core Computational Strengths	Target Water Quality Metrics	Primary Vulnerabilities and Data Constraints
Random Forest (RF)	• Exceptional resistance to overfitting when processing high-dimensional environmental datasets. • Handles non-linear variables efficiently.	• Mapping spatial contamination profiles. • Regional ecological risk classification. • Heavy metal source allocation.	• Struggles to accurately capture continuous temporal time-series dependencies. • Sub-optimal performance for real-time trend forecasting.
Gradient Boosting Machines (GBM)	• Extremely high accuracy thresholds (typically 92% to 97%).	• Short-term temporal metal concentration forecasting.	• Highly sensitive to noisy data and outlier observations.

	Optimizes loss functions through iterative weak learners.	High-precision water quality anomaly detection.	Demands meticulous, clean data preprocessing pipelines.
Long Short-Term Memory (LSTM)	- Deep recurrent architecture explicitly engineered to retain long-term dependencies in sequential time-series data. - Decodes cyclic and irregular trends.	- High-frequency, real-time prediction of transient toxic metal pulses. - Forecasting stochastic climate-driven contaminant waves.	- Requires massive, continuous high-frequency datasets to prevent model drift. - High computational overhead during the model training phase.

When these predictive models are integrated into hybrid pipelines and enhanced with Bayesian optimization, the resulting frameworks can formulate explicit prediction intervals. This probabilistic coupling allows risk models to account for the inherent stochasticity and uncertainty of the environmental exposome. Ultimately, this integration allows public health officials to dynamically model population-level risk shifts days or weeks before an environmental contamination pulse reaches downstream drinking water treatment infrastructures or agricultural irrigation zones [122]. By shifting from isolated retrospective equations to adaptive, hybrid informatics pipelines, modern frameworks can detect real-time contamination anomalies and issue automated early warnings, establishing an invaluable computational tool for proactive health protection and dynamic, bioavailability-based ecological governance.

6. Future Perspectives: Ecological Governance and Engineering Resilience

By crossing the boundaries of hydrology, micro-interfacial geochemistry, microbial genomics, and advanced environmental informatics, this review reveals a clear imperative for systemic change. While individual technical components rely on established baseline methodologies [123–135], the integrated multi-tier management frameworks and strategic roadmaps detailed below constitute our original conceptual contributions toward shifting environmental governance from a reactive paradigm into a dynamic, predictive reality. To provide a high-level, interdisciplinary matrix of the foundational climate stressors and cross-disciplinary impacts guiding these solutions, the overarching relationships are synthesized in Table 5.

Table 5. Interdisciplinary synthesis matrix of the climate–metal–resistome nexus across aquatic systems.

Climate Volatility Stressor	Micro-Interfacial Geochemical Shift	Microbial Ecology Cascade	Ecotoxicological and Human Health Consequences	Core Interdisciplinary Intersection and Takeaway
Accelerated Storms and Extreme Run-off Events	Rapid desorption of bed-sediment heavy metals due to shifting ionic strength; intense particulate-bound transport vectors.	Transient influx of mobile genetic elements (MGEs) and exogenous ARGs into urban waterways.	Acute spikes in bioavailable dissolved metal fractions; sudden elevation in cumulative Hazard Index (HI) values for downstream populations.	Hydrology → Geochemistry → Public Health: Mechanical hydrological flushing resets chemical equilibria at the water-sediment interface, converting legacy sinks into acute exposure pathways.
Prolonged Drought and Extended	Evaporative solute concentration; severe	Shifts in benthic community structure to-	Chronic exposure to highly stable organo-metal	Climate Forcing → Microbial Ecology → Toxicology: Reduced dilution capacity

Low-Flow States	drops in dissolved oxygen driving sediment reductive dissolution.	ward anaerobic pathways; metabolic enrichment of highly metal-tolerant strains.	complexes; elevated probabilistic risk profiles via food-chain bioaccumulation.	drives a drop in redox potential, restructuring the microbiome and compounding long-term toxicological stress.
Thermal Stratification and Ambient Warming	Accelerated heavy metal speciation kinetics; increased diffusion flux of hazardous ions from benthic layers into the water column.	Accelerated microbial metabolic rates coupled with selective thermodynamic inhibition of terminal reduction enzymes (e.g., nitrous oxide reductase, N ₂ OR).	Metabolic amplification of intracellular metal uptake; elevated cellular generation of destructive ROS.	Geochemistry → Microbial Genomics → Climate Feedbacks: Thermal stress alters metal speciation while simultaneously blocking the <i>nosZ</i> gene pathway, turning impaired ecosystems into active N ₂ O greenhouse gas sources.

6.1. Optimizing the WWTP Interface and the “Resilience Premium”

As the primary convergence points between urban anthropogenic pollution and natural aquatic networks, wastewater treatment plants (WWTPs) represent the most critical intervention interface for heavy metal management [123]. Historically, WWTP operations have prioritized meeting static effluent discharge limits for carbon and nitrogen. However, as extreme weather events drive sudden influent heavy metal shock loads, the biological nutrient removal processes within these engineered systems become acutely vulnerable [124]. The toxicological suppression of the *nosZ* gene by sublethal metal concentrations not only degrades effluent quality but triggers massive, unintended emissions of nitrous oxide (N₂O) from the bioreactors [125].

We argue that future engineering strategies must pivot toward dynamic, data-driven operational management to mitigate these secondary environmental impacts. In our framework, by deploying the real-time machine learning forecasting frameworks described in Section 5.4, facility managers can generate short-term early warnings of stochastic transitions in influent metal loads and impending N₂O emission spikes [126]. This predictive capability enables the real-time optimization of aeration strategies and energy consumption, allowing the facility to absorb transient toxic shocks without compromising biological integrity. Achieving this operational agility yields a quantifiable multi-objective operational equilibrium, a systemic co-benefit where the WWTP simultaneously minimizes its greenhouse gas footprint, maximizes energy efficiency, and prevents the downstream discharge of bioavailable metal fractions [127]. Operationally, this state represents the optimization threshold where trade-offs between biological treatment stability, energy expenditure, and effluent ecotoxicity are dynamically balanced under volatile influent conditions.

6.2. Ecological Restoration of Transitional Floodplains

While engineered interventions at the WWTP interface are vital, systemic heavy metal governance must also incorporate the ecological restoration of natural transitional ecotones. Riparian floodplains function as the primary biogeochemical buffers for riverine networks, natively supporting the mechanistic controls of denitrification [128]. However, decades of artificial channelization, coupled with legacy metal contamination, have severely impaired their ecological service functions.

We propose that future restoration initiatives must move beyond simple geomorphological reshaping and focus directly on rehabilitating the fundamental biogeochemical pathways of the benthic zone. Re-establishing natural hydrological connectivity across these floodplains is essential to stabilizing seasonal soil redox potentials and carbon thresholds, which in turn dictate the chemical speciation and sequestration of legacy heavy metals [129]. By carefully managing these soil properties, restoration projects can

actively reverse the metal-induced dysbiosis of the benthic microbiome, promoting the seasonal recovery of denitrification enzyme activity. To practically maintain this functional expression of the *nosZ* gene under field conditions, restoration frameworks must deploy a triad of targeted eco-engineering interventions.

First, the in situ application of surface-modified biochar or functionalized clay amendments into contaminated benthic zones can dynamically immobilize free divalent metal fractions (such as Cd^{2+} or Pb^{2+}) via surface complexation. This drastically lowers their bioavailability, thereby lifting the chemical inhibition on the terminal nitrous oxide reductase (N_2OR) enzyme. Second, engineers can optimize the hydrological regime by utilizing controlled sluice-gate systems to regulate seasonal wetting/drying cycles. Maintaining precise sediment redox potential (E_h) and neutral pH levels drives the precipitation of mobile heavy metals into highly stable, insoluble mineral phases, such as metal sulfides, during critical denitrification windows. Finally, the integration of nature-based solutions (NBS)—specifically the deployment of rhizosphere-engineered riparian wetlands using metal-tolerant macrophytes—can physically intercept upstream dissolved metal loads. Simultaneously, these plant roots release specific organic carbon exudates (such as low-molecular-weight organic acids) that support the metabolic proliferation of indigenous, metal-resilient denitrifying strains harboring Clade II *nosZ* pathways. Restoring and maintaining these genetic cascades ensures that floodplains act as robust, natural nitrogen sinks rather than secondary sources of potent greenhouse gases and mobile toxic metals [130].

6.3. Macroscopic Ecological Governance and Environmental Informatics

Scaling these micro-interfacial and facility-level insights up to regional and national policy requires a paradigm shift in macroscopic ecological governance. Policymakers increasingly rely on massive, longitudinal databases, such as national urban water statistics yearbooks, to track pollution trends and allocate infrastructure funding [131]. However, deriving actionable governance strategies from these extensive datasets is frequently hindered by profound spatial data gaps and inconsistent reporting metrics across diverse regional jurisdictions [132].

To extract reliable, structural insights for national policy, we advocate a paradigm shift where the next generation of environmental governance must heavily leverage advanced informatics. The deployment of multilevel imputation techniques is strictly necessary to resolve missing data structures without introducing geographical bias, ensuring that datasets from highly developed coastal regions and remote, sparsely monitored provinces can be evaluated simultaneously [133]. Furthermore, applying advanced multivariate statistical tools, such as Kernel Density Estimation and high-dimensional clustering, to these imputed longitudinal datasets allows regulatory bodies to identify hidden stochastic transitions in regional water quality over multi-year periods [134]. To ensure these digital twin architectures reflect true environmental endpoints, macroscopic governance frameworks should actively cross-validate computational outputs with regional biological monitoring networks. Incorporating large-scale biomonitoring maps—such as standardized moss-bag deployments or macrophyte tissue analysis protocols—provides a tangible, ecological ground-truth layer. This integration anchors the spatial risk predictions generated by machine learning pipelines within verified, long-term biological realities [134]. By fusing probabilistic exposure modeling, predictive machine learning, regional biomonitoring datasets, and rigorous data imputation, environmental agencies can transition from reactive, localized pollution control toward holistic, predictive ecological governance across entire watersheds [135].

7. Conclusions and Paradigmatic Shifts in Aquatic Ecotoxicology

By synthesizing ecotoxicological data spanning the past three decades (1995–2026), this review charts a clear evolutionary shift away from traditional 20th-century frameworks—which treated benthic sediments as static, isolated sinks evaluated purely through bulk chemical extraction—toward a dynamic, interdisciplinary paradigm. Historically, regulatory frameworks assumed stable water-sediment interfaces where contaminants remained safely sequestered under equilibrium conditions. Today, accelerating climate volatility fundamentally invalidates this isolationist view. Climate-driven hydro-meteorological extremes, manifesting as alternating cycles of severe drought-induced sediment oxidation and high-magnitude flooding, actively convert benthic zones into volatile sources of diffuse pollution. These physical displacements do not merely redistribute particulate matter; they alter localized redox and pH gradients, causing the physical and biological uncoupling of vital riverine and floodplain ecotones.

This shifting baseline is further complicated by microplastic matrices, which have rewritten the rules of chemical speciation and bioavailability in benthic environments. Pristine polymer behaviors have been eclipsed by the real-world complexities of environmental weathering and the rapid formation of the biological eco-corona, which exponentially magnifies heavy-metal chemisorption and alters local valence states. As demonstrated by the integration of molecular-scale DFT simulations with field-scale spatial gradients, these micro-interfaces act as transport vectors that bypass traditional ecotoxicological models. Once ingested, these metal-laden particles trigger a “Trojan Horse” effect, inducing severe, localized oxidative stress and dysbiosis within the gut microbiome long before traditional biomagnification risks manifest in higher trophic levels. This biological interface extends into a critical evolutionary hazard: sublethal heavy metal concentrations serve as a persistent selective pressure that drives the co-selection and horizontal transmission of antibiotic resistance genes, stabilizing an environmental reservoir of multi-drug-resistant pathogens. Furthermore, the toxicological suppression of the microbial *nosZ* gene uncouples the denitrification pathway. This specific enzymatic disruption transforms heavy metal-impaired sediments from critical nitrogen sinks into direct sources of the potent greenhouse gas N_2O , establishing a localized chemical feedback loop that actively drives macro-scale global warming.

Managing these multi-tiered ecological cascades requires a parallel shift in human health risk assessment and environmental governance. The field must move beyond the conservative overestimations of static, deterministic point-estimate frameworks. By evolving toward probabilistic Monte Carlo simulations that explicitly integrate empirical bioaccessibility factors, mixture toxicity synergies, and multilevel spatial data imputation, risk modeling can accurately capture population-level heterogeneities without succumbing to regional data sparsity. The next operational phase merges these advanced probabilistic frameworks with next-generation water environment informatics. Coupling high-frequency, in situ multi-parameter sensor arrays with ensemble deep learning algorithms like LSTM networks allows for the real-time prediction of non-linear toxic pulses. Whether applied to achieve a “Resilience Premium” via automated wastewater treatment plant optimization, to monitor the biogeochemical recovery of restored floodplains, or to drive macro-scale watershed policies, this convergence of data science and molecular geochemistry provides the predictive toolkit required to safeguard global water security and public health in an era of unprecedented planetary change.

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Abbreviations

AMR	Antimicrobial Resistance
Anammox	Anaerobic Ammonium Oxidation
AR6	IPCC Sixth Assessment Report
ARG	Antibiotic Resistance Gene
As(III)	Trivalent Arsenite
AVS	Acid Volatile Sulfides
BLM	Biotic Ligand Model
BSSE	Basis Set Superposition Error
CDI	Chronic Daily Intake
CDD	Charge Density Difference
Cd(II)	Divalent Cadmium Ion
CSF	Cancer Slope Factor
Cr(VI)	Hexavalent Chromium
DOS	Density of States
DFT	Density Functional Theory
DNRA	Dissimilatory Nitrate Reduction to Ammonium
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
EPS	Extracellular Polymeric Substances
FIAM	Free Ion Activity Model
GBM	Gradient Boosting Machines
GIS	Geographic Information Systems
GSH	Reduced Glutathione
GWP100	100-Year Global Warming Potential
HGT	Horizontal Gene Transfer
HI	Hazard Index
HQ	Hazard Quotient
HRA	Human Health Risk Assessment
HSAB	Hard-Soft Acids and Bases
ILCR	Incremental Lifetime Cancer Risk
IRIS	Integrated Risk Information System
IRI	Interaction Region Indicator
LSTM	Long Short-Term Memory
MDR	Multidrug-Resistant
MGE	Mobile Genetic Element
MP	Microplastic
MRG	Metal Resistance Gene
N2OR	Nitrous Oxide Reductase Enzyme
NBS	Nature-based Solution
<i>nosZ</i>	Nitrous Oxide Reductase Functional Gene

PE	Polyethylene
PET	Polyethylene Terephthalate
PLI	Pollution Load Index
PP	Polypropylene
PVC	Polyvinyl Chloride
qPCR	Quantitative Polymerase Chain Reaction
RF	Random Forest
RfD	Oral Reference Dose
RKS	Restricted Kohn-Sham
ROS	Reactive Oxygen Species
SMD	Solvation Model based on Density
UKS	Unrestricted Kohn-Sham
USEPA	United States Environmental Protection Agency
WWTP	Wastewater Treatment Plant

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