

INTERACTIVE EFFECTS OF CLIMATE VARIABILITY ON HEAVY METAL SPECIATION, BIOAVAILABILITY, AND TROPHIC TRANSFER IN FRESHWATER ECOSYSTEMS

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Abstract

The convergence of climate variability and legacy heavy metal contamination is reshaping the behavior of potentially toxic elements in freshwater ecosystems worldwide. This review synthesizes current scientific understanding of how changing temperature regimes, hydrological extremes, and biogeochemical alterations influence metal speciation, bioavailability, and trophic transfer across multiple ecological scales. At the global scale, climate-driven hydrological variability and permafrost thaw enhance the mobilization of trace metals from terrestrial reservoirs, while at the environmental scale, shifts in pH, dissolved organic matter, and redox conditions modify chemical speciation and toxicity. At the organismal level, physiological stress and climate-induced toxicant sensitivity amplify metal uptake, disrupt metabolic pathways, and increase susceptibility to bioaccumulation and biomagnification through food webs. Emerging evidence indicates that traditional equilibrium-based models such as the biotic ligand model may underestimate exposure risks under rapidly fluctuating environmental conditions associated with climate change. Furthermore, processes such as mercury methylation, brownification, and acid rock drainage amplify ecosystem-level risks and alter contaminant pathways across freshwater and boreal systems. Integrating multi-scale observational studies with advanced modeling approaches, including kinetic and GIS-based frameworks, is essential for improving prediction and management of metal contamination in a changing climate. Overall, the interaction between climate variability and heavy metal dynamics represents a critical challenge for freshwater ecosystem resilience and requires adaptive, bioavailability-based regulatory frameworks.

Introduction

The convergence of anthropogenically induced climate change and legacy chemical pollution represents a critical intersection in modern environmental science, posing a multifaceted threat to the stability and resilience of freshwater ecosystems (Balbus et al., 2013). While the

scientific community has spent decades establishing the foundational principles of trace metal toxicity under stable environmental conditions, the increasing frequency and intensity of climate variability are rendering traditional thermodynamic equilibrium models insufficient for predicting real-world risks (Sinclair et al.,

2024). Freshwater systems are uniquely vulnerable to these changes due to their inherent chemical heterogeneity and their role as the primary recipients of terrestrial runoff, which carries a diverse load of potentially toxic elements (PTEs) such as cadmium, mercury, lead, arsenic, and chromium (Kovacik, 2025). To accurately assess the future of these ecosystems, it is necessary to examine the interactive effects of climate and contaminants across three distinct scales: the global scale of biogeochemical cycling, the environmental scale of water chemistry and metal complexation, and the organismal scale of physiological and transcriptomic response (Coelho et al., 2013).

Evolution of Regulatory Paradigms: From Hardness to Bioavailability

The historical development of water quality criteria (WQC) illustrates a progressive shift toward recognizing the complexity of metal interactions in natural waters. In the mid-twentieth century, early guidance such as the 1968 "Green Book" recognized that the toxicity of metals like copper and zinc depended on the characteristics of the receiving water, yet quantitative understanding remained limited (National Technical Advisory Committee, 1968). Regulatory frameworks initially relied on simple application factors, such as $0.1 \times (96\text{-h LC}_{50})$ for

copper or $0.005 \times (96\text{-h LC}_{50})$ for zinc, to infer chronic effects from acute data (Stephan et al., 1985). By 1980, the United States Environmental Protection Agency (U.S. EPA) transitioned toward hardness-based equations, reflecting the observation that divalent cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}) compete with metal ions for binding sites on aquatic organisms (Mebane et al., 2020). However, hardness-based corrections proved insufficient as they failed to account for the protective role of pH and dissolved organic carbon (DOC) (Playle et al., 1993). This led to the development of the biotic ligand model (BLM), which mechanistically predicts metal toxicity by simulating the competition between the free metal ion and other cations for binding sites on a "biotic ligand," such as a fish gill or a daphnid membrane. The BLM was officially incorporated into the U.S. EPA's 2007 revised aquatic life ambient freshwater quality criteria for copper and has since been expanded to include aluminum, cadmium, cobalt, nickel, lead, and zinc (U.S. EPA, 2007). Despite its advancements, the BLM's reliance on thermodynamic equilibrium poses significant challenges in a climate-driven world where rapid fluctuations in water quality parameters such as "brownification" events or storm-induced pH drops often outpace the kinetics required for equilibrium-based predictions (Gao et al., 2023).

Table 1. Historical Evolution of Regulatory Criteria and Normalization Models for Aquatic Toxicity

sPeriod	Regulatory Milestone	Primary Normalization Factor	Limitations Identified
1968	FWPCA "Green Book"	Narrative/Local Toxicity Tests	Lacked quantitative regional standards
1973-1976	"Blue" and "Red" Books	Application Factors (LC_{50} fractions)	Did not account for water chemistry variability
1980-1985	Explicit Hardness Equations	Total Hardness (CaCO_3 equivalent)	Ignored pH and DOC influences
2007-Present	Biotic Ligand Model (BLM)	Chemical Speciation & Competition	Thermodynamic equilibrium assumptions; data-intensive
Emerging	Multiple Linear Regression (MLR)	Empirical Statistical Relationships	May lack mechanistic depth in novel environments

The Global Scale: Biogeochemical Cycles and Terrestrial Mobilization

At the global scale, climate change acts as a primary driver of the mobilization and transport of trace metals from terrestrial and geological reservoirs into the hydrosphere. The solid-solution partitioning of metals in soils is the fundamental process determining the residence time of these elements and their subsequent release into aquatic environments. Climate variability disrupts this partitioning through altered hydrological cycles, thermal regime shifts, and the degradation of long-term carbon sinks like permafrost and peatlands.

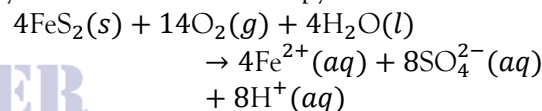
Hydrological Extremes and Sediment Flux

The intensification of the Walker circulation, an ocean-driven pattern of air circulation, has been linked to increasing precipitation and extreme flooding in basins like the Amazon (Barichivich et al., 2018). These hydrological shifts lead to the remobilization of contaminated sediments from floodplains and historical mining areas. During extreme floods, the sheer volume of water generates high stream power, scouring the riverbeds and transporting metal-enriched fine sediments downstream into previously pristine areas. Conversely, prolonged droughts reduce the dilution capacity of rivers, concentrating dissolved pollutants and increasing the contact time between biota and contaminated water (Baker et al., 2022).

In the Amazon basin, climate change is creating a "chaotic" hydrological regime where record-breaking floods alternate with unprecedented droughts. During the 2023 drought, shrinking river levels and extreme heat caused water temperatures to reach 41°C (105.8[°]C), leading to mass mortality events of river dolphins and other aquatic species (Fleischmann et al., 2024). Such events demonstrate that climate change does not merely move pollutants; it creates lethal conditions where elevated toxicant concentrations coincide with extreme thermal stress, a phenomenon that threatens the survival of local communities dependent on these fisheries for subsistence (Baker et al., 2022).

The Permafrost-Sulfide Nexus and Acid Rock Drainage

One of the most alarming manifestations of climate-driven metal mobilization is the "rusting" of Arctic rivers. As the planet warms, the thawing of permafrost soil that has remained frozen for millennia exposes previously sequestered sulfide-rich rocks, such as pyrite (FeS₂), to oxygen and water. This initiates a geochemical chain reaction analogous to acid mine drainage, where the oxidation of sulfide minerals generates sulfuric acid, which then leaches metals such as iron, cadmium, aluminum, and copper from the surrounding bedrock (Skierszkan et al., 2024). In Alaska's Brooks Range, rivers that were once "gin-clear" now run orange and hazy. Research conducted by biogeochemists at the University of California, Riverside, and the University of Alaska indicates that these transformations are occurring across dozens of watersheds (O'Donnell et al., 2024). The process can be chemically represented by the overall oxidation of pyrite:



The resulting acidity (H⁺) can lower the pH of headwater streams to values as low as 3 or 4, further accelerating the weathering of other mineral phases. The released iron eventually precipitates as iron oxides (rust), which stain the streambeds and smother the benthic habitats essential for insect larvae and spawning salmon (Sullivan et al., 2025).

The Environmental Scale: Chemical Speciation and Bioavailability

Once metals enter the aquatic environment, their fate and toxicity are governed by their chemical speciation the specific chemical form in which they exist. Climate change alters the physicochemical parameters that dictate speciation, including pH, temperature, dissolved oxygen, and the composition of dissolved organic matter (DOM) (Di Toro et al., 2001).

Dynamics of Dissolved Organic Matter and "Brownification"

The "brownification" of freshwater lakes, particularly in boreal and temperate regions, is driven by increased terrestrial runoff and the mobilization of soil-derived dissolved organic carbon (DOC) (Kritzberg et al., 2019). Historically, dissolved organic matter (DOM) has been viewed as a protective agent that reduces metal bioavailability by binding free metal ions (M^{2+}) into stable organic complexes, thereby preventing their uptake by aquatic organisms. However, recent research indicates that the quality of DOM its molecular composition and source is just as important as its quantity (Brezonik et al., 2019). Phytoplankton-derived (autochthonous) DOM, characterized by its labile, low-molecular-weight compounds, has a different affinity for metals compared to aromatic, terrestrial (allochthonous) DOM. In some scenarios, DOM can actually increase bioavailability through mechanisms that bypass traditional ion transporters. For example, certain metals can form lipophilic organic complexes that cross plasma membranes via simple passive diffusion. Furthermore, natural organic matter (NOM) can adsorb directly onto the membranes of aquatic organisms, potentially altering membrane permeability and facilitating metal entry (Fortin, 2024).

Ocean and Freshwater Acidification

While Ocean Acidification (OA) is a well-documented global environmental phenomenon, freshwater ecosystems are likewise experiencing climate-driven shifts in pH. Rising atmospheric carbon dioxide (CO_2) concentrations, coupled with changes in watershed and catchment processes, contribute to the acidification of upland streams, rivers, and lakes. A decline in pH generally increases the solubility and bioavailability of toxic heavy metals such as Cadmium and Lead by reducing the availability of carbonate and hydroxide ligands that would otherwise facilitate the formation of insoluble metal precipitates (Peakall & Burger, 2003).

In sedimentary environments, acidification can further enhance metal mobility by promoting the desorption of metal ions from mineral surfaces and organic matter. As pH decreases, previously bound contaminants are released into the pore water and subsequently transported into the overlying water column, increasing the concentration of dissolved metals available for biological uptake. Experimental studies simulating carbon dioxide (CO_2) injection into sediment-seawater systems have demonstrated a direct relationship between declining pH and increased metal mobilization. These findings indicate that acidification can intensify contamination gradients, elevate exposure risks for aquatic organisms, and pose substantial threats to benthic communities and ecosystem health (Molofsky, 2026).

Table 2. Influence of Environmental Parameter Shifts on Metal Speciation, Bioavailability, and Toxicological Mechanisms

Parameter Shift	Impact on Metal Speciation	Effect on Bioavailability	Mechanism
Temperature Rise	Shifts in complexation equilibrium; increased kinetics	Generally, increases	Higher metabolic demand; faster diffusion
pH Reduction	Decreased carbonate/hydroxide complexation	Increases	Reduced metal precipitation; competition with H^+
DOC Increase	Enhanced complexation with organic ligands	Generally, decreases	Formation of stable organic-metal complexes
Salinity Intrusion	Competition with Ca^{2+} , Mg^{2+} , and Na^+	Decreases	Cation competition for biotic ligand binding sites

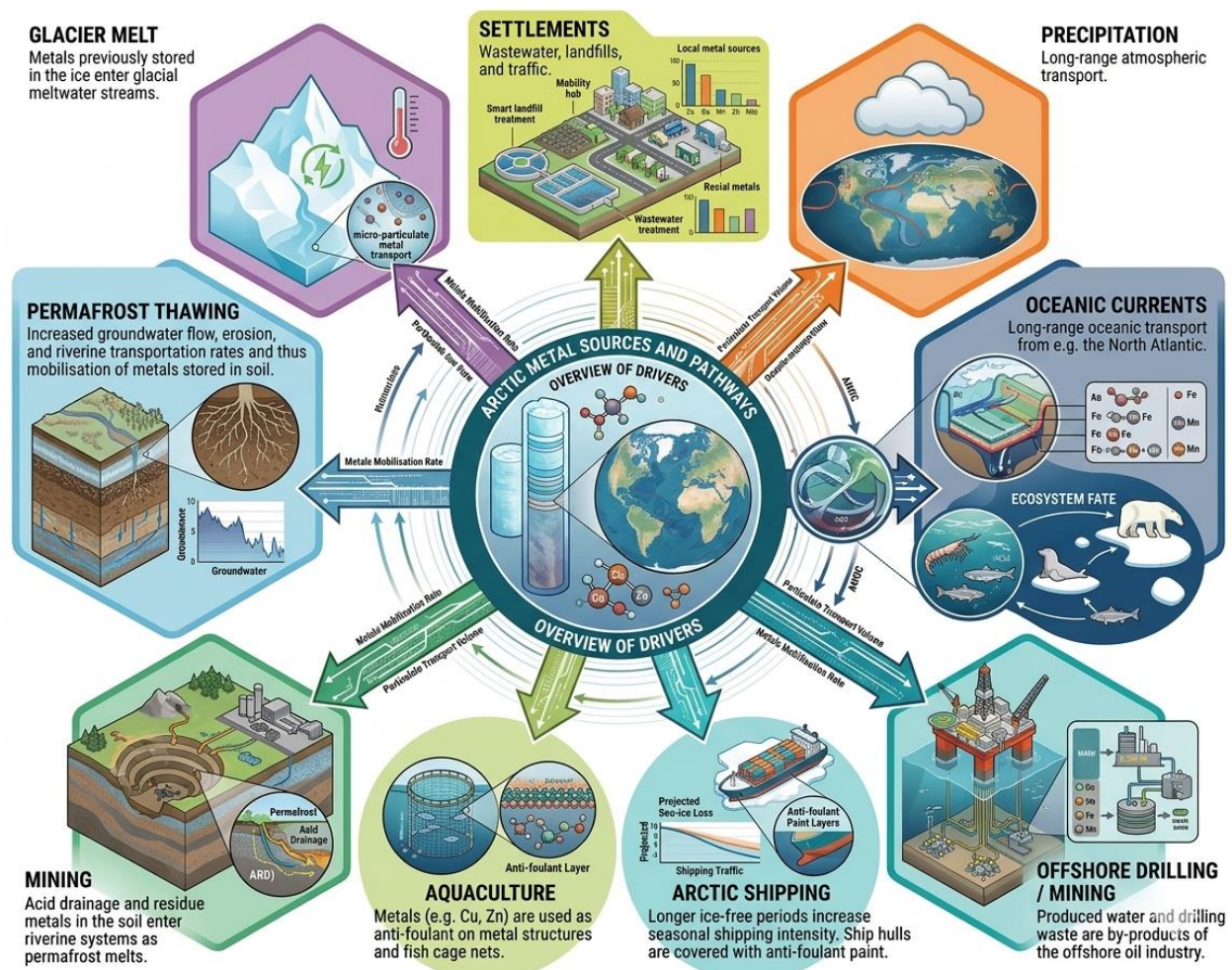
Deoxygenation	Alteration of redox state (e.g., Fe/Mn oxides)	Variable	Release of metals from dissolving oxides in sediments
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The Organismal Scale: Physiology, Transcriptomics, and CITS

At the organismal level, the impact of heavy metals is increasingly viewed through the lens of Climate-Induced Toxicant Sensitivity (CITS). This framework suggests that the physiological stress

caused by climate change such as thermal extremes, hypoxia, and osmotic stress reduces an organism's ability to maintain homeostasis when exposed to chemical contaminants (Angeler et al., 2021).

Figure 1. Conceptual diagram illustrating the major terrestrial, atmospheric, and marine drivers of heavy metal mobilization, transport, and ecosystem exposure pathways in Arctic and boreal watersheds.



Metabolic and Transcriptomic Response Failures

Recent advances in Transcriptomics have provided a molecular-level perspective on the synergistic effects of climate stressors and heavy metal toxicity. In studies involving the freshwater hydrozoan *Craspedacusta sowerbii*, exposure to cadmium sulfate (CdSO_4) induced rapid immobilization followed by complete mortality within 24 hours. Transcriptomic (RNA sequencing) analyses revealed that this lethal response was preceded by a broad and coordinated down-regulation of genes associated with central metabolic pathways, including fatty acid metabolism, cell cycle regulation, and anti-aging mechanisms (Singh et al., 2016).

This pattern, often described as a “metabolic collapse,” contrasts sharply with organismal responses to other environmental stressors such as antibiotics, where adaptive defense mechanisms are typically activated through the up-regulation of stress-response genes. In the case of heavy metal exposure, however, the organism appears unable to initiate an effective compensatory transcriptional response, leading to systemic physiological failure.

This vulnerability is further intensified under elevated temperature conditions. Increased temperatures elevate metabolic rates, thereby increasing oxygen demand and nutrient consumption. When such physiological acceleration occurs in contaminated environments, it can enhance the uptake and internal accumulation of toxic substances, amplifying bioaccumulation effects and reducing overall organismal resilience (Xiao et al., 2024; Yan, 2026).

Biological Feedback and Transporter Regulation

A sophisticated mechanism through which climate change affects metal toxicity is biological feedback. Aquatic organisms possess specific acquisition strategies for essential metals such as zinc (Zn) and copper (Cu), which are necessary for enzyme function and growth. Toxic metals like cadmium (Cd) can “hijack” these transporters due to their chemical similarity (Lange & Segner, 2023). When environmental conditions alter the

availability of essential metals, an organism may up-regulate its transporters to compensate for a perceived deficiency. This increase in the number of binding sites on the membrane inadvertently increases the uptake rate of nonessential, toxic metals. This biological feedback mechanism represents a knowledge gap in current models such as the biotic ligand model (BLM), which assume that the number of binding sites (the biotic ligand density) remains constant (Lavoie, 2013).

Mercury Methylation: Boreal Lakes and Arctic Systems

Mercury (Hg) is a unique heavy metal due to its global atmospheric transport and its transformation into methylmercury (MeHg), a potent neurotoxin that biomagnifies through food webs. Boreal and Arctic ecosystems are particularly sensitive to mercury because they contain large reservoirs of legacy mercury in peatlands and permafrost (Niyogi & Wood, 2004).

The Oxidic Methylation Paradigm Shift

Traditionally, mercury methylation was understood as a strictly anaerobic process occurring in the anoxic layers of sediments and stratified water columns, mediated by microbes carrying the *hgcAB* gene pair (Paranjape & Hall, 2017). However, climate change is shifting this paradigm. Increasing terrestrial runoff of dissolved organic matter (DOM) provides a substrate for alternative methylation pathways that may occur under oxic conditions in pelagic waters. Prokaryotes such as bacteria in the genus *Nitrospina* have been identified as carrying *hgcAB*-like genes and potentially contributing to methylmercury (MeHg) formation in oxic environments (Tada et al., 2020). This shift has profound implications: as lakes experience longer periods of thermal stratification and increased DOM inputs, the spatial and temporal “hotspots” for mercury methylation are expanding potentially undoing the benefits of global industrial mercury emission reductions (Rodriguez et al., 2022).

The Bell-Shaped Response to Organic Matter

The relationship between dissolved organic matter (DOM) and mercury bioavailability is not linear. In Swedish boreal lakes, research has identified a "bell-shaped" pattern where methylmercury (MeHg) bioaccumulation initially increases with increasing DOM concentration up to a threshold of approximately 8.5 mg/L of carbon (Gallorini &

Loizeau, 2021). Below this threshold, DOM facilitates the transport and microbial transformation of mercury. Above this threshold, the strong binding affinity of refractory organic compounds reduces the concentration of bioavailable Hg^{2+} , leading to a progressive decrease in methylation rates (Rodríguez, 2023).

Table 3. Climate-Driven Impacts on Boreal Ecosystem Components and Their Influence on Mercury Cycling Dynamics

Boreal Component	Impact of Climate Warming	Effect on Mercury Cycle
Peatlands/Bogs	Increased decomposition; water table fluctuation	Shift from mercury sink to mercury source
Lake Stratification	Stronger/longer thermal layering	Enhanced anoxic methylation zones
Plankton Blooms	Increased labile autochthonous DOM	Accelerated methylation rates in sediments
Terrestrial Runoff	Increased "brownification" (allochthonous DOM)	Enhanced Hg transport; variable methylation

Trophic Transfer and Biomagnification

The movement of metals through the food web determines the ultimate risk to top predators and human health. Biomagnification is the process where a substance's concentration increases at successively higher trophic levels, whereas bioaccumulation refers to the increase within an individual organism over time (Adams et al., 2020).

The efficiency of contaminant transfer through trophic levels is commonly quantified using indices such as the Biomagnification Factor (BMF) and the Trophic Transfer Factor (TTF). Values greater than 1.0 indicate net biomagnification, meaning that contaminant concentrations increase with each successive trophic level. In such cases, the contaminant is effectively amplified through the food web rather than being diluted. Climate change further modifies these transfer dynamics by restructuring aquatic food webs and altering species composition. Thermal stress, acidification, and habitat degradation can lead to the loss of sensitive zooplankton populations, thereby shortening food chain length or forcing higher trophic organisms to rely on alternative prey sources. This alternative prey may be more benthic in nature and potentially more contaminated, resulting in increased exposure and higher toxicant burdens in predators (Hama Aziz et al., 2023).

Evidence of Cadmium and Mercury Biomagnification

While many trace metals such as copper and zinc are actively regulated by biological systems and therefore do not typically exhibit biomagnification, certain elements—including cadmium (Cd) and methylmercury (MeHg)—represent important exceptions. In discrete freshwater food-web studies, cadmium has been observed to biomagnify by up to 15-fold within only two trophic transfers. This elevated enrichment is particularly evident in food chains involving macrophyte-associated invertebrates and benthic fish species, where sediment-water interactions enhance contaminant availability and uptake (Xiao et al., 2024).

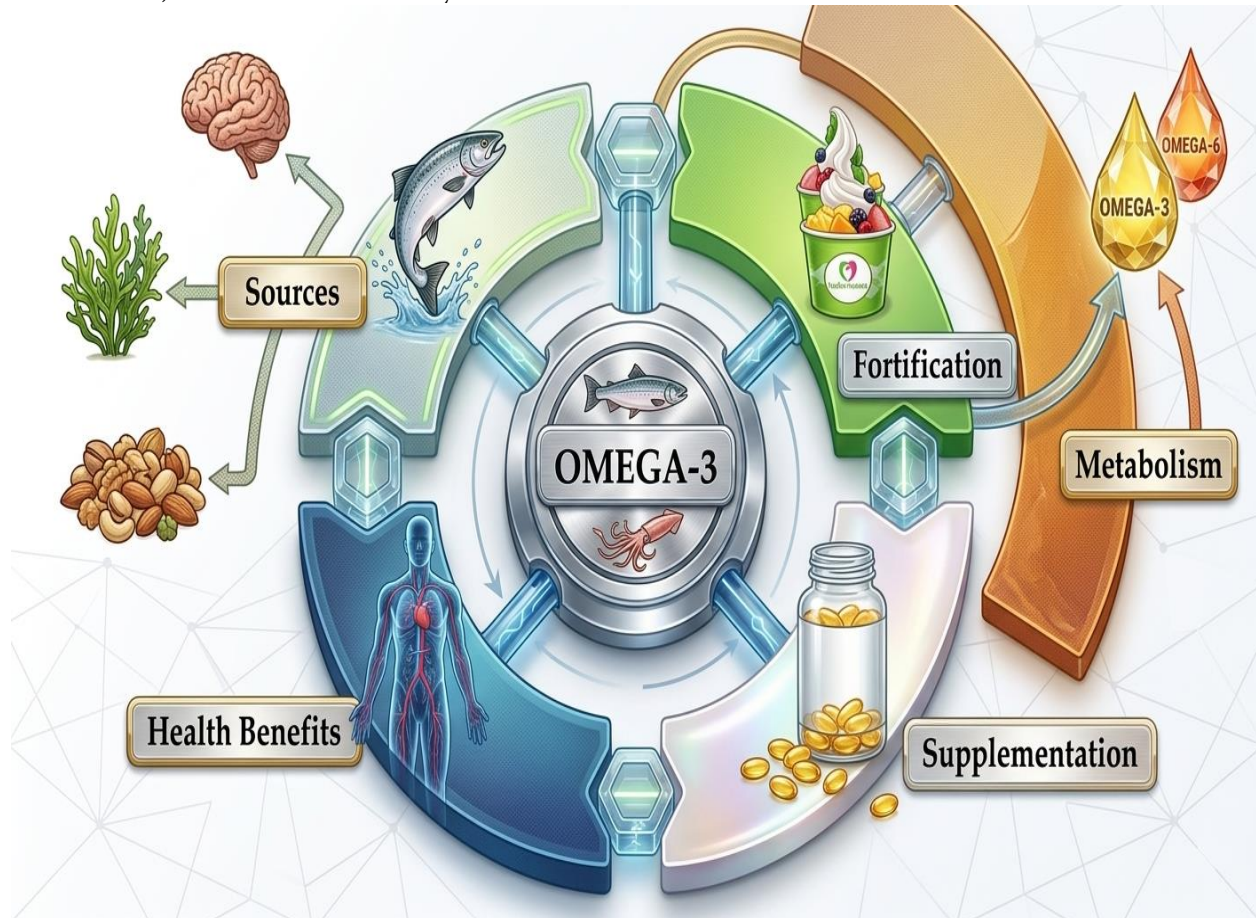
Nutritional Deterioration: PUFA vs. MeHg

A critical emerging insight is the trade-off between essential nutrients and contaminants. Polyunsaturated fatty acids (PUFAs), such as

omega-3s, are crucial for the health and survival of aquatic organisms and their human consumers. Climate warming and "browning" have been shown to decrease the production of essential fatty acids at the base of the food web while simultaneously increasing the supply of toxic

methylmercury (Khan et al., 2025). This dual pressure reduced dietary quality combined with increased toxicant exposure destabilizes trophic interactions and reinforces the turbid, degraded states of freshwater systems (Noyes & Lema, 2015).

Figure:1 Comprehensive Overview of Omega-3 Fatty Acids: Sources, Health Benefits, Supplementation, Fortification, and Metabolic Pathways



Region-Specific Case Studies and Vulnerabilities

The impacts of climate-metal interactions are highly region-specific, dictated by local geology, socioeconomic factors, and the nature of the climatic shifts (Campbell, 2004).

Colorado Rocky Mountains: Acid Rock Drainage Trends

In the mineralized watersheds of the Colorado Rockies, concentrations of zinc, copper, and sulfate have doubled over the past 30 years. A

comprehensive analysis of 22 headwater streams across 17 watersheds revealed that these trends are regional and statistically significant. The greatest increases have been observed in the highest, coldest mountain streams, which have warmed past the freezing threshold since 1980 (Grasby, 2026).

Researchers have concluded that declining streamflows (reduced dilution) account for only about half of the observed increase in concentrations. The remainder is driven by

increased mass export of metals from the mountains, likely due to the melting of underground ice and permafrost which exposes fresh rock to oxygen and water. These rising "background" metal levels complicate the remediation of historical mine sites, as attaining water quality standards becomes increasingly difficult when the natural baseline is shifting upward (Burn et al., 2024).

South Asian Rivers: Transboundary Pollution Risks

South Asia faces a severe water management crisis, with rivers like the Indus, Ganges, and Brahmaputra being among the most heavily polluted in the world. The lack of adequate freshwater management, combined with the transboundary nature of these rivers, makes the derivation of water quality criteria (WQC) a high priority. Risk assessments using species sensitivity distribution (SSD) models indicate that these rivers are highly polluted with transition metals like manganese, iron, cadmium, and zinc, posing significant ecological risks to a large number of aquatic species (Balbus et al., 2013).

Climate change exacerbates these risks by altering the timing of snowmelt in the Himalayas, which controls the peak runoff and flow regimes of these basins. Changes in flow volume directly impact the concentration and transport of pollutants across international borders, necessitating integrated watershed management strategies (Sinclair et al., 2024).

Advanced Predictive Modeling and Future Directions

The limitations of traditional models in the face of climate change have triggered the development of more robust, multi-stressor approaches to ecological risk assessment (ERA) (Kovacik, 2025).

Integrating Statistical and GIS-Based Models

To move beyond the "one metal, one organism" paradigm, researchers are increasingly employing statistical methods such as:

Positive Matrix Factorization (PMF): Used for source apportionment to identify specific

industrial or natural origins of heavy metal pollution (Angeler et al., 2021).

- **Nemerow Index Method:** An integrated approach to evaluate the overall degree of heavy metal contamination in complex systems.
- **Monte Carlo Simulations:** Probabilistic assessments that incorporate uncertainty in exposure and toxicity estimates.
- **Geographic Information Systems (GIS):** Enhancing spatial analysis to map risk distributions and inform public health interventions (Gao et al., 2023).

The Need for Kinetic and Multi-Stressor Frameworks

The future of metal risk assessment lies in the integration of chemical kinetics and biological feedback mechanisms into regulatory models. While the BLM provides a mechanistic basis for bioavailability, it must be extended to include variables like fluctuating water temperatures and non-equilibrium DOC dynamics. Furthermore, the "nutritional status" of the ecosystem incorporating factors like PUFA availability should be considered alongside contaminant concentrations to provide a holistic view of ecosystem health (Baker et al., 2022).

Conclusions

The interactive effects of climate variability on heavy metal speciation, bioavailability, and trophic transfer in freshwater ecosystems represent a paradigm-shifting challenge for environmental science. The traditional focus on thermodynamic equilibrium and static water quality criteria is no longer sufficient to protect biodiversity and public health in a rapidly changing world.

The mobilization of metals through permafrost thaw and acid rock drainage indicates that the "geological clock" has been accelerated by anthropogenic warming, turning pristine headwaters into sources of toxic contamination. The "brownification" of lakes and the shift toward oxic mercury methylation underscore the importance of understanding the molecular quality of organic matter in governing chemical transformations. At the organismal level, the

framework of Climate-Induced Toxicant Sensitivity (CITS) highlights the vulnerability of species struggling to acclimate to simultaneous thermal and chemical stressors. To mitigate these risks, stakeholders must adopt adaptation strategies such as Integrated Water Resource Management (IWRM) and Ecosystem-based Adaptation (EbA). Regulatory frameworks must transition toward more flexible, bioavailability-based systems that account for the full complement of water chemistry parameters. Ultimately, the resilience of our global freshwater resources will depend on our ability to integrate climate projections into pollution control strategies, ensuring that the water systems of the future remain capable of sustaining both ecosystem integrity and human well-being.

REFERENCES

- Balbus, J. M., Boxall, A. B. A., Fenske, R. A., McKone, T. E., & Zeise, L. (2013). Implications of global climate change for the assessment and management of human health risks of chemicals in the natural environment. *Environmental Toxicology and Chemistry*, 32(1), 62-78. <https://doi.org/10.1002/etc.2046>
- Coelho, F. J. R. C., Santos, A. L., Coimbra, J., Almeida, A., Cunha, Â., Cleary, D. F. R., Calado, R., & Gomes, N. C. M. (2013). Interactive effects of global climate change and pollution on marine microbes: the way ahead. *Ecology and Evolution*, 3(6), 1808-1818. <https://doi.org/10.1002/ece3.565>
- Hama Aziz, K. H., Mustafa, F. S., Omer, K. M., Hama, S., Hamarawf, R. F., & Rahman, K. O. (2023). Heavy metal pollution in the aquatic environment: efficient and low-cost removal approaches to eliminate their toxicity: a review. *RSC Advances*, 13(25), 17595-17510. <https://doi.org/10.1039/d3ra00723e>
- Khan, F. R., Bury, N. R., Cooper, C. A., Boyle, D., Middleton, E., & Herzog, S. D. (2025). The impact of climate change on the flux and fate of metals in freshwater systems: Implications for metal exposure across different scales. *Environmental Research*, 287, Article 123057. <https://doi.org/10.1016/j.envres.2025.123057>
- Kovacik, A. (2025). The biological relevance of potentially toxic metals in freshwater fish. *Frontiers in Physiology*, 16, Article 1609555. <https://doi.org/10.3389/fphys.2025.1609555> Cited by: 4
- Noyes, P. D., & Lema, S. C. (2015). Forecasting the impacts of chemical pollution and climate change interactions on the health of wildlife. *Current Zoology*, 61(4), 666-689. <https://doi.org/10.1093/czoolo/61.4.669>
- Sinclair, T., Craig, P., & Maltby, L. L. (2024). Climate warming shifts riverine macroinvertebrate communities to be more sensitive to chemical pollutants. *Global Change Biology*, 30(1), e17254. <https://doi.org/10.1111/gcb.17254>
- Xiao, W., Zhang, Y., Chen, X., Sha, A., Xiong, Z., Luo, Y., Peng, L., Zou, L., Zhao, C., & Li, Q. (2024). The easily overlooked effect of global warming: Diffusion of heavy metals. *Toxics*, 12(6), 400. <https://doi.org/10.3390/toxics12060400>
- Adams, W., Blust, R., Dwyer, R., Mount, D., Nordheim, E., Rodriguez, P. H., & Spry, D. (2020). Bioavailability assessment of metals in freshwater environments: A historical review. *Environmental Toxicology and Chemistry*, 39(1), 48-59. <https://doi.org/10.1002/etc.4558>

- Di Toro, D. M., Allen, H. E., Bergman, H. L., Meyer, J. S., Paquin, P. R., & Santore, R. C. (2001). Biotic ligand model of the acute toxicity of metals. 1. Technical basis. *Environmental Toxicology and Chemistry*, 20(10), 2383–2396. <https://doi.org/10.1002/etc.5620201034>
- Gao, Y., De Schampelaere, K. A., & Smolders, E. (2023). Dynamic exposure and kinetics in modeling metal bioavailability to aquatic organisms: A review. *Environmental Science & Technology*, 57(14), 5512–5525. <https://doi.org/10.1021/acs.est.2c08910>
- Mebane, C. A., Sumpter, J. P., Fairbrother, A., Adams, W. J., Augspurger, T., de Schampelaere, K. A., ... & Schlekot, C. E. (2020). Scientific advancement and the conversion of science into water quality regulation: A perspective on challenges and opportunities. *Environmental Toxicology and Chemistry*, 39(1), 60–73. <https://doi.org/10.1002/etc.4593>
- National Technical Advisory Committee. (1968). *Water quality criteria: Report of the National Technical Advisory Committee to the Secretary of the Interior ("Green Book")*. Federal Water Pollution Control Administration.
- Playle, R. C., Dixon, D. G., & Burnison, K. (1993). Copper and cadmium binding to fish gills: Estimates of cofactor binding constants and modeling of copper and cadmium accumulation on gills. *Canadian Journal of Fisheries and Aquatic Sciences*, 50(12), 2678–2687. <https://doi.org/10.1139/f93-291>
- Stephan, C. E., Mount, D. I., Hansen, D. J., Gentile, J. H., Chapman, G. A., & Brungs, W. A. (1985). *Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses*. U.S. Environmental Protection Agency, Office of Research and Development. PB85-227049.
- U.S. Environmental Protection Agency. (2007). *Aquatic life ambient freshwater quality criteria for copper – 2007 revision*. Office of Water. EPA-822-R-07-001.
- Baker, J. C. A., Cintra, B. B. L., Gloor, M., Boom, A., Neill, D., Clerici, S., Leng, M. J., Helle, G., & Brienen, R. J. W. (2022). The changing Amazon hydrological cycle Inferences from over 200 years of tree-ring oxygen isotope data. *Journal of Geophysical Research: Biogeosciences*, 127(11). <https://doi.org/10.1029/2022jg006955>
- Barichivich, J., Gloor, E., Peylin, P., Brienen, R. J. W., Schöngart, J., Espinoza, J. C., & Pattanyak, K. C. (2018). Recent intensification of Amazon flooding extremes driven by strengthened Walker circulation. *Science Advances*, 4(9). <https://doi.org/10.1126/sciadv.aat8785>
- Fleischmann, A., Papa, F., Hamilton, S., Melack, J., Forsberg, B., Val, A., Collischonn, W., Laipelt, L., Rossi, J., Comini de Andrade, B., Mendel, B., Alves, P., Glorize, M., Custodio, L., Gomes, M. C., Hymans, D., Keppe, I., Mendes, R., Gomes, R., Silva, P., Vieira, C., Xavier, R., Zumak, A., Ruhoff, A., & Zhou, W. (2024). Extreme warming of Amazon waters in a changing climate. *EarthArXiv*. <https://doi.org/10.31223/x56d9t>
- Burn, C. R., Bartsch, A., Chakraborty, E., Das, S., Frauenfelder, R., Gärtner-Roer, I., Gislén, K. G., Herring, T., Jones, B. M., Kokelj, S. V., Langer, M., Lathrop, E., Murton, J. B., Nielsen, D. M., Niu, F., Olson, C., O'Neill, H. B., Opfergelt, S., Overduin, P. P., ... Tank, S. E. (2024). Developments in permafrost science and engineering in response to climate warming in circumpolar and high mountain regions, 2019–2024. *Permafrost and Periglacial Processes*. <https://doi.org/10.1002/ppp.2261>

- Grasby, S. E. (2026). Release of toxic-metal acid brines related to slumping of Cretaceous mudstones Smoking Hills (Ingniryuat), Arctic Canada. *Geology*, 54(4), 296–300. <https://doi.org/10.1130/G53747.1>
- O'Donnell, J. A., Carey, M. P., Koch, J. C., Baughman, C. A., Hill, K., Evinger, T., Frei, R. J., Poulin, B. A., & Sullivan, P. F. (2024). *Rusting rivers: Assessing the causes and consequences in Alaska and across the Arctic* (Technical Report No. OAR-ARC-25-14). National Oceanic and Atmospheric Administration.
- Skierszkan, E. K., Dockrey, J. W., & Lindsay, M. B. J. (2024). Metal mobilization from thawing permafrost is an emergent risk to water resources. *ACS ES&T Water*, 5(1), 20–32. <https://doi.org/10.1021/acsestwater.4c00789>
- Sullivan, P. F., Carey, M. P., Koch, J. C., Baughman, C. A., Hill, K., Evinger, T., Frei, R. J., Poulin, B. A., & O'Donnell, J. A. (2025). Wild, scenic, and toxic: Recent degradation of an iconic Arctic watershed with permafrost thaw. *Proceedings of the National Academy of Sciences*, 122(37), e2425644122. <https://doi.org/10.1073/pnas.2425644122>
- Brezonik, P. L., Finlay, J. C., Griffin, C. G., Arnold, W. A., Boardman, E. H., Germolus, N., Hozalski, R. M., & Olmanson, L. G. (2019). Iron influence on dissolved color in lakes of the Upper Great Lakes States. *PLOS ONE*, 14(2), e0211979. <https://doi.org/10.1371/journal.pone.0211979>
- Campbell, P. G. C. (2004). Predicting metal bioavailability – applicability of the Biotic Ligand Model. *CIESM Workshop Monographs*, 19, 25-28.
- Fortin, C. (2024). Metal bioavailability in aquatic systems beyond complexation and competition. *Frontiers in Environmental Chemistry*, 5, 1345484. <https://doi.org/10.3389/fenvc.2024.1345484>
- Kritzberg, E. S., Hasselquist, E. M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., Valinia, S., Hansson, L.-A., & Laudon, H. (2019). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, 49(2), 375–390. <https://doi.org/10.1007/s13280-019-01227-5>
- Angeler, D. G., Allen, C. R., Garmestani, A., Gunderson, L., & Johnson, R. K. (2021). Panarchy and management of lake ecosystems. *Ecology and Society*, 26(4). <https://doi.org/10.5751/es-12690-260407>
- Molofsky, L. J. (2026). Biotransformation processes relevant to geologic carbon sequestration: Potential implications for environmental fate. *PubMed Central*.
- Peakall, D., & Burger, J. (2003). Methodologies for assessing exposure to metals: Speciation, bioavailability of metals, and ecological host factors. *Ecotoxicology and Environmental Safety*, 56(1), 110–121. [https://doi.org/10.1016/s0147-6513\(03\)00055-1](https://doi.org/10.1016/s0147-6513(03)00055-1)
- Singh, S., Parihar, P., Singh, R., Singh, V. P., & Prasad, S. M. (2016). Heavy metal tolerance in plants: Role of transcriptomics, proteomics, metabolomics, and ionomics. *Frontiers in Plant Science*, 6. <https://doi.org/10.3389/fpls.2015.01143>
- Xiao, W., Zhang, Y., Chen, X., Sha, A., Xiong, Z., Luo, Y., Peng, L., Zou, L., Zhao, C., & Li, Q. (2024). The easily overlooked effect of global warming: Diffusion of heavy metals. *Toxics*, 12(6), 400. <https://doi.org/10.3390/toxics12060400>

- Yan, H. (2026). Physiological and transcriptomic responses of the freshwater hydrozoan *Craspedacusta sowerbii* to acute antibiotic and cadmium exposure. *Biology*.
- Lange, A., & Segner, H. (2023). The role of glutathione and sulfhydryl groups in cadmium uptake by cultures of the rainbow trout RTG-2 cell line. *Cells*, 12(23), 2720. <https://doi.org/10.3390/cells12232720>
- Lavoie, M. (2013). Predicting cadmium accumulation and toxicity in a green alga in the presence of varying essential element concentrations using a Biotic Ligand Model. *Environmental Science & Technology*, 47(21), 12253–12260. <https://doi.org/10.1021/es402630z>
- Niyogi, S., & Wood, C. M. (2004). Biotic Ligand Model, a flexible tool for developing site-specific water quality guidelines for metals. *Environmental Science & Technology*, 38(23), 6177–6192. <https://doi.org/10.1021/es0496524>
- Gallorini, A., & Loizeau, J.-L. (2021). Mercury methylation in oxic aquatic macro-environments: a review. *Journal of Limnology*, 80(2). <https://doi.org/10.4081/jlimnol.2021.2007>
- Paranjape, A. R., & Hall, B. D. (2017). Recent advances in the study of mercury methylation in aquatic systems. *FACETS*, 2(1), 85–119. <https://doi.org/10.1139/facets-2016-0027>
- Rodríguez, J. (2023). Mercury methylation in boreal aquatic ecosystems under oxic conditions and climate change: a review. *Frontiers in Marine Science*, 10. <https://doi.org/10.3389/fmars.2023.1198263>
- Rodríguez, J., Andersson, A., Björn, E., Timonen, S., Brugel, S., Skrobonja, A., & Rowe, O. (2022). Inputs of terrestrial dissolved organic matter enhance bacterial production and methylmercury formation in oxic coastal water. *Frontiers in Microbiology*, 13. <https://doi.org/10.3389/fmicb.2022.809166>