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Review article

The impact of climate change on the flux and fate of metals in freshwater systems: Implications for metal exposure across different scales

Farhan R. Khan[a,*], Nicolas R. Bury[b], Christopher A. Cooper[c], David Boyle[d], Elizabeth Middleton[e], Simon D. Herzog[f]

[a] Department of Climate & Environment, NORCE Norwegian Research Centre AS, Nygårdsporten 112, NO-5008, Bergen, Norway
[b] School of Ocean and Earth Sciences, University of Southampton, Southampton, United Kingdom
[c] International Zinc Association, Brussels, Belgium
[d] Cobalt Institute, London, United Kingdom
[e] NiPERA, Durham, NC, United States
[f] Department of Science and Environment, Roskilde University, 4000, Roskilde, Denmark

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ABSTRACT

Climate change and chemical pollution are two of the gravest environmental concerns, and it is becoming increasingly recognised that climate change and climate variability will alter the environmental distribution and toxicity of chemical pollutants. Trace metals are an established pollutant group where decades of research have been able to determine causal links between environmental concentrations and water chemistry, and accumulation and toxic effects. In the present paper, we assert that to fully comprehend the impact of climate change on metal bioavailability and exposures in freshwaters, three distinct scales need to be understood: (i) the global scale of metal biogeochemical cycling which will alter metal inputs from soil into freshwater; (ii) the environmental scale of fluctuating water chemistry parameters that will change metal complexation dynamics; and (iii) the organismal scale at which climate-induced physiological modifications at the site of uptake may alter the bioaccumulation of metals and climate-induced impairments of cellular function that will change toxicity. At each scale much is already known about the processes and pathways that govern metal input, bioavailability and impacts on biota, but the key impact of climate variability is to alter the frequency, intensity, and rates at which these processes occur with the underlying commonality throughout scales being a shift to a more dynamic system. In an increasingly dynamic environment, it is the kinetics of both chemical and biological reactions that become more important compared to predictions of metal bioavailability from currently utilised thermodynamic equilibrium-based models. Extending such models to include climate variability is not easy, but to begin such a process would ultimately lead to more accurate and realistic applications to policy guidance.

1. Introduction

Climate change and pollution are two of the three environmental problems that constitute a triple planetary crisis (biodiversity loss being the third (UNFCCC, 2022),). In this context, climate change refers to long-term shifts in temperatures and weather patterns with the typical impacts of climate change considered to be global warming, rising sea levels and ocean acidification. For instance, temperature is one of the keystone indicators of climate change and global temperatures have an “80 % likelihood of at least one year temporarily exceeding 1.5 °C between 2024 and 2028” (World Meteorological Organisation, 2024). At current carbon dioxide (CO_2) emission rates, temperature is predicted to increase by 2.7 °C by 2100 (Climate Action Tracker, 2024). The impact of climate change will differ between global regions (polar, temperate, or equatorial) and habitats (forest, tundra, urban, agricultural) causing intense drought or precipitation, increased heat waves and wildfires, and melting glaciers and permafrost. Thus, the consequences of climate change are not unidirectional increases, and are better characterised as climate variability (Thornton et al., 2014). There is also increasing recognition that these global challenges are inter-connected and will influence one another (Deutloff et al., 2025). This is particularly the case for how climate change will alter the environmental distribution and

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* Corresponding author.
E-mail addresses: fakh@norceresearch.no, farhan.khan@gmx.com (F.R. Khan).

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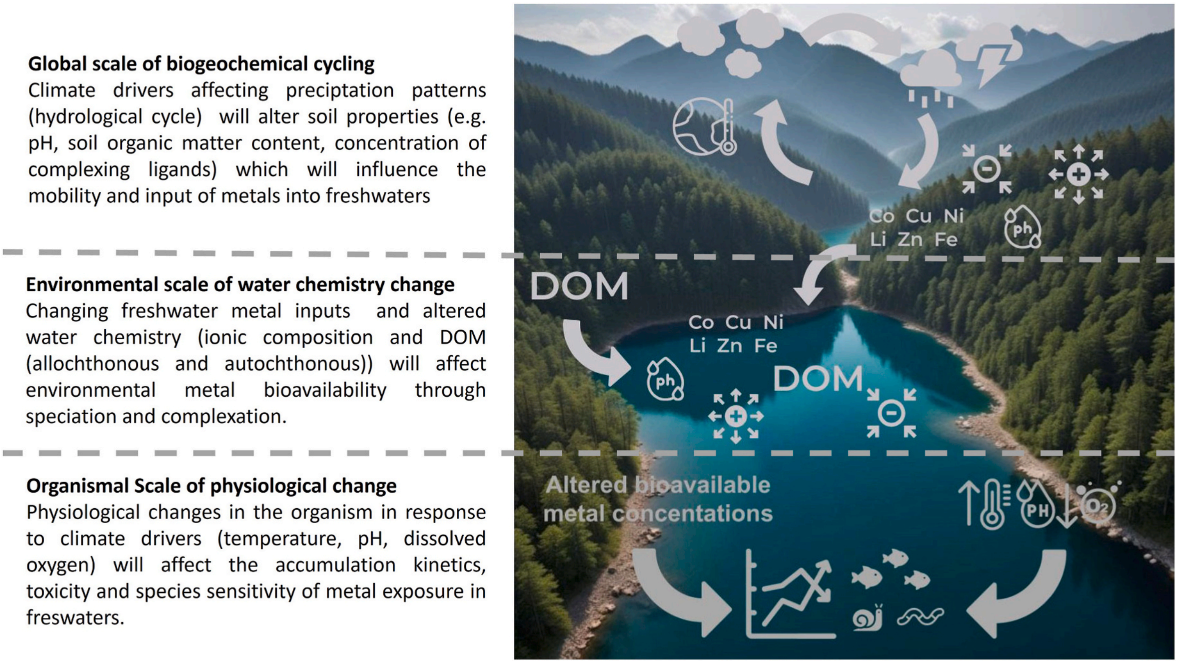
toxicity of chemical pollutants (He et al., 2025; Iordache et al., 2022).

Trace metals are an established pollutant group where decades of research have been able to provide causal links at equilibrium between environmental concentrations and water chemistry, and accumulation and toxic effects (Di Toro et al., 2001; Paquin et al., 2002), but these links may be affected by climate change (Hauser-Davis and Wosnick, 2022). Biogeochemical processes in soils, including sorption/desorption, complexation, and dissolution/precipitation, play a crucial role in determining the residence time of metals and their subsequent release into aquatic environments (Joubert et al., 2007; Violante et al., 2010). Climate change effects, such as changes in temperature, dissolved oxygen (DO) and acidification, as well as other associated parameters, such as fluctuating inputs of Dissolved Organic Matter (DOM), will also alter the carbon composition of water with potential impacts on metal speciation which will either enhance or decrease the environmental bioavailability of metals (Di Toro et al., 2001). Such occurrences in the physical environment may lead to changes in their biotic interactions and toxic responses, leading to climate-induced toxicant sensitivity (CITS). Corollary to CITS is the impact of toxicants on the ability of an organism to respond to climate change, i.e. toxicant-induced climate sensitivity (TICS). Biota will also respond to other facets of climate change that cause physiological stress e.g., changes in temperature, pH, dissolved oxygen, saline water intrusion, DOM, and these will alter organism responses to metals through shared or separate biochemical and physiological pathways (Pinheiro et al., 2021).

In this paper, we provide an overview of the impacts of climate change stressors on trace metal exposure in freshwaters. We limit the scope of our paper to freshwaters because of the inherent chemical heterogeneity of freshwaters and decades of research that have focused on how water chemistry alters metals bioavailabilities and utilisation of these relationships in chemical equilibrium-based models such as the Biotic Ligand Model (BLM, Di Toro et al., 2001; Paquin et al., 2002). We assert that to fully comprehend the impact of climate change on metal bioavailabilities and impacts in freshwaters, three distinct scales need to be understood (Fig. 1): (i) the global scale of metal biogeochemical cycling which will alter metal inputs from soil into freshwater; (ii) the environmental scale of fluctuating water chemistry parameters that will change metal complexation dynamics; and (iii) the organismal scale at which climate-induced physiological modifications at the site of uptake may alter the bioaccumulation of metals and climate-induced impairments of cellular function that will change toxicity. Although much is already known about the underlying processes and pathways that govern metal input, bioavailability, and impacts on biota, there is a need to recognise complexity and the increased variability of the effects of climate change on each of the three scales we highlight. To protect biota and ecosystem health during climate change and increased exposure to chemical contaminants, it is necessary to establish the conditions and drivers that result in systems reaching a threshold or ‘tipping point’ (Dakos et al., 2019). This is defined as a change in conditions, whether abiotic and/or biotic, that reaches a threshold beyond which there is irreversible change in organismal homeostasis, population viability, or ecosystem integrity (Dakos et al., 2019).

2. The global scale – soil to water dynamics

Metals in soil originate from a variety of natural (geogenic) and human-induced (anthropogenic) sources. Natural sources include weathering of rock and volcanic activity (Garnier et al., 2009; Sun et al., 2022). Typical background soil concentrations of key metals are approximately 52 mg/kg soil for zinc (Zn), 15.7 mg/kg soil for lead (Pb), 13 mg/kg soil for copper (Cu), and 14.4 mg/kg soil for nickel (Ni) (Kabata-Pendias, 2000; Tóth et al., 2016). In contrast, anthropogenic sources, such as industrial activities including mining, manufacturing, and waste incineration, substantially increase metal inputs into the environment (Niu et al., 2021). Moreover, agricultural practices, urban runoff, wastewater discharge, and atmospheric deposition add further to metal contamination (Barth et al., 2009; J. Scott et al., 2005; Tóth et al., 2016). Common values in impacted areas can reach 89–128, 19–31, 21–29, and 8–16 mg/kg soil for Zn, Pb, Cu, and Ni, respectively (Alloway, 2012; Wei and Yang, 2010). Extreme levels of Zn, Pb, and Cu are found near heavily polluted areas, where these metals can exceed natural background levels by two to three times or more. Globally, Zn, Pb, and Cu levels in industrial or urban soils often rise above 115, 25, and 23 mg/kg soil, respectively (Binner et al., 2023; Hou et al., 2025). Many of the anthropogenic activities have historically been located near rivers and lakes, potentially contributing to freshwater and sediment



Global scale of biogeochemical cycling
Climate drivers affecting preciptation patterns (hydrological cycle) will alter soil properties (e.g. pH, soil organic matter content, concentration of complexing ligands) which will influence the mobility and input of metals into freshwaters

Environmental scale of water chemistry change
Changing freshwater metal inputs and altered water chemistry (ionic composition and DOM (allochthonous and autochthonous)) will affect environmental metal bioavailability through speciation and complexation.

Organismal Scale of physiological change
Physiological changes in the organism in response to climate drivers (temperature, pH, dissolved oxygen) will affect the accumulation kinetics, toxicity and species sensitivity of metal exposure in freswaters.

Fig. 1. Overview of climate change impacts on metal bioavailabilities at different scales (i) the global scale of metal biogeochemical cycling, (ii) the environmental scale of fluctuating water chemistry parameters, and (iii) the organismal scale of physiological adaptation.

Table 1
Factors influencing the mobility of metals in soil: chemical processes, soil interactions, and climate drivers.

Metal Element	Key Mobility Factors	Major Climate Drivers	References
Iron (Fe)	Redox-sensitive; binds to organics; forms oxides	Precipitation, hydrology, land use	(Björnerås et al., 2017; Sarkkola et al., 2013)
Manganese (Mn)	Redox-sensitive; pH; microbial activity	Precipitation, drought, flooding, temperature	(Søndergaard et al., 2007; Sparrow and Uren, 2014; Stahl and James, 1991; Hardie et al., 2007; Khoshru et al., 2023)
Aluminum (Al)	pH-sensitive (acidic); complexes with organics	Temperature, precipitation, salinization,	(Hagvall et al., 2015; Langer et al., 2023; K. Li et al., 2024)
Chromium (Cr)	Redox and pH-sensitive; binds to oxides	Climate zone shifts, precipitation, topography	((Bai et al., 2024; Chrysochoou et al., 2016; Schulz-Zunkel et al., 2015)
Zinc (Zn)	pH-sensitive; organic matter	Temperature, drought	(Azouzi et al., 2015; Padoan et al., 2020; Rennert and Rinklebe, 2017)
Arsenic (As)	Redox-sensitive; binds to oxides	Drought, groundwater fluctuation	(Aribam et al., 2021; Ponting et al., 2021; Schulz-Zunkel et al., 2015)
Nickel (Ni)	Redox and pH-sensitive; binds to oxides	Flooding, waterlogging (redox), drought	(Bearup et al., 2014; Rennert and Rinklebe, 2017; Shakesby et al., 1993; Søndergaard et al., 2007)
Cobalt (Co)	Redox and pH-sensitive; binds to oxides	Drought, flooding, Mn cycling	(Rennert and Rinklebe, 2017; Sricharoenvech et al., 2024)
Lead (Pb)	Low mobility; pH; strong soil binding; binds to oxides	Minor climate effects, land use change	(Jardine et al., 2006; Kylander et al., 2008; Turpeinen et al., 2000)
Copper (Cu)	pH and redox-sensitive; complexes with organics	Precipitation, temperature, soil moisture	(Borch et al., 2010; Sereni et al., 2024)
Cadmium (Cd)	pH and redox-sensitive; complexes with organics	Temperature, precipitation, salinization	(Acosta et al., 2011; Kubier et al., 2019; Padoan et al., 2020; Wijngaard et al., 2017))

contamination (Arnell et al., 2015; Zhao et al., 1999).

Climate-driven changes such as increased precipitation intensity and altered hydrological regimes can enhance erosion and leaching, thereby increasing the flux of metal-bound particles and dissolved metal complexes from soils into freshwater systems.

2.1. Factors controlling the mobility of metals in soils

When metals are introduced into the terrestrial environment, it is the solid-solution partitioning in soils that mainly determines metal mobility and transfer to the aquatic environment (Chowdhury and Singer, 2022; Domergue and Védy, 1992). This is controlled via various physical and chemical properties of soil, such as soil texture and composition, soil pH and redox potential, and DOM, which is defined as mainly carbon-based material that can pass through a 0.45 μm filter.

Soils can be classified based on particle size, ranging from large boulders to sand (0.06–2 mm), silt (0.002–0.06 mm), and clay (<0.0002 mm), including colloid clay particles that remain in solution. Soils with a high clay and mineral oxide content tend to retain more metals due to adsorption, precipitation, or complexation (Cavallaro and McBride, 1984; Elliott et al., 1986; Spark K M et al., 1995) compared to sandy soils, which are more susceptible to leaching due to the porous nature of the substrate (Zhao et al., 1999). Humic substances, as key components of soil organic matter, play a central role in metal complexation and mobility (Tipping, 2002). Soil organic matter can form both stable and water-soluble complexes with metals in pore water (Li et al., 2024; Wagai and Mayer, 2007; Yang et al., 2024). These complexes serve as significant vectors, especially in the uppermost soil layer (Neagoe et al., 2012) through which metals can be leached from soils and transferred to ground and surface waters (Chen et al., 2010), while deep soil organic matter is crucial for metal retention due to its long residence time (Jardine et al., 2006).

Changes in pH levels can affect the binding capacity of metal complexes and their solubility (Kicińska et al., 2022). Acidic pH can increase the mobility of metals due to the dissolution of metal minerals and hydrous oxides, while higher pH levels favour the sorption of hydrolysed metals (Borch et al., 2010; Rieuwerts et al., 2006). Closely linked to pH is the redox potential, with reducing conditions promoting the release of metals through reductive dissolution of iron (Fe) and manganese (Mn) oxide binding phases e.g., in waterlogged soils (Schulz-Zunkel et al., 2015; Smedley and Kinniburgh, 2002). The soil redox potential is influenced by factors such as pH, soil moisture, oxygen availability, organic matter content, microbial activity, and the presence of redox-sensitive elements like Fe and Mn (Hesterberg, 1998; Violante et al., 2010). Climate change drivers will affect metal mobility from catchments into aquatic systems in various ways (Table 1), which will differ by geographic location, as each region experiences distinct climate-related changes (Calvin et al., 2023).

2.2. Increased temperature and drying conditions

Higher temperatures can also accelerate the release of metals (Azouzi et al., 2015; Kubier et al., 2019; Sparrow and Uren, 2014) from soil particles into the soil solution by enhancing weathering and the kinetics of geochemical processes (Biswas et al., 2018; Brown, 1970). Further, temperature shifts and changes in soil moisture alter microbial community composition, with higher temperatures enhancing microbial activity and accelerating organic matter decomposition (Bach and Hofmockel, 2016; Tisdall and Oades, 1982). This process lowers cation exchange capacity (CEC) and increases soil erosion during heavy rain, thus reducing the soil's ability to retain metals even further (Rajkumar et al., 2013).

Directly related to warmer temperatures due to climate change is the degradation of permafrost, which poses significant risks, particularly in the Arctic and in high-altitude areas with fragile ecosystems susceptible to climate change (Post et al., 2009). Thawing permafrost can release metals from un-contaminated, as well as industrial and contaminated sites (Langer et al., 2023) and can affect metal mobility by creating new hydrological pathways and increasing erosion due to reduced ground stability (Miner et al., 2021; Zaharescu et al., 2016). For example, a study on seasonal trends in acid mine drainage from a sulphide-rich coal mine waste rock in the high Arctic of Svalbard found that key processes such as sulphide oxidation, ion exchange, and silicate weathering contributed to the release of metals such as Fe, aluminium (Al), Mn, Zn, and Ni in runoff during thaw and heavy rain events (Søndergaard et al., 2007). Thus, the combined effects of rising temperatures and shifting precipitation patterns not only reduce the soil's capacity to retain metals but also often enhance their mobility, particularly during dry-wet cycles that facilitate the transport of these accumulated metals.

2.3. Wetting-drying cycles

Fluctuations between flooding and drying can affect the mobility of many metals like cadmium (Cd), Cu, chromium (Cr), Ni, and Zn by altering redox-sensitive metal speciation and causing the transformation or dissolution of metal oxides, hydroxides, sulphides, and organic complexes (Ponting et al., 2021; Schulz-Zunkel et al., 2015). This was seen at mine sites in the wet-dry tropics of northern Australia, where acid rock drainage with lower pH and higher metal concentrations during a prolonged dry period, resulting in the oxidation of pyrite and sulphidic minerals and the production of acid and the release of metals (Nordstrom, 2009; Streten-Joyce et al., 2013). When the first rains arrived, accumulated salts were washed away, causing a spike in metal concentrations (Nordstrom, 2009). Similar trends have also been observed in acid sulphate soils in southern Australia (Mosley et al., 2014) as well as watersheds in the Colorado Rockies (Manning et al., 2024). In this region, the increase in mean annual temperature caused a shift in the hydrologic regime, resulting in an increase of about 2 % per year in the dissolved concentrations of metals. This has doubled the concentrations of sulphate, Zn, and Cu in streams over the past 30 years. Furthermore, in agricultural regions in Spain, rising temperatures have led to increased evapotranspiration, which reduces soil moisture and contributes to salinization. When irrigation is used to compensate for water loss, especially with salty water or poor drainage, salts accumulate in the soil because there is insufficient rainfall to wash them away. Higher salinity is linked to an increase in major cations, which compete with metals for sorption sites in the soil. As a result, this reduces the soil's ability to retain metals and increases the mobility as seen for Pb, Cu, and Cd (Acosta et al., 2011).

2.4. Extreme rainfall events

Mean annual precipitation is projected to increase in many temperate regions and the Arctic (Olsson and Foster, 2013), along with predictions of more intense precipitation leading to increased surface runoff and flooding (Bronstert, 2003; Kharin et al., 2007; Kundzewicz et al., 2014). Altered precipitation patterns, like extreme rainfall events, affect redox conditions, soil pH, organic matter decomposition, and soil particle mobility (Buytaert et al., 2011; Whitehead et al., 2009). These changes can enhance the mobilisation of metals by increasing the release of metal-binding organic matter and colloids, and by facilitating the transport of organo-mineral complexes into freshwater systems (Gao et al., 2025; Herzog et al., 2019; Valencia-Avellan et al., 2017). With respect to DOM, climatic factors influence both short-term variability and long-term trends in concentrations, with future projections indicating significant increases and seasonal variations in northern catchments (Jennings et al., 2010; Naden et al., 2010). In addition, dissolved Fe, which can influence metal mobility via immobilisation and complexation, has experienced significant increases in concentration in freshwater systems throughout North America and Europe, associated with changes in hydrology and precipitation patterns (Björnerås et al., 2017). The relationship between climate change and hydrological alterations highlights the need for comprehensive studies on DOM, clay, and Fe dynamics to accurately predict future metal fluxes from catchments in those regions.

In addition, extreme weather events associated with precipitation can lead to soil erosion (Eekhout and de Vente, 2022; Ströberg et al., 2017). Erosion serves as a significant diffuse source of metals to water bodies, primarily from agricultural and forestry lands that expose soil, making it more vulnerable to surface runoff and flash flooding during extreme rainfall events (Comber et al., 2023). This erosion process is intensified by agricultural expansion and deforestation, both of which significantly increase soil loss (Borrelli et al., 2020). In the case of contaminated soils, this can have a direct impact on adjacent freshwater systems through the transfer of pollutants (Ströberg et al., 2017). Further, extreme events such as heavy rainfall and flooding can trigger landslides and compromise hydraulic structures such as dams and spillways, which in turn can lead to increased metal releases from mineral deposits and mining waste (Anawar, 2013). A prominent example is the 2019 Brumadinho dam collapse in Brazil, which resulted in the release of 12 million cubic meters of tailings (Pacheco et al., 2022).

2.5. Shifts in vegetation cover

Shifts in vegetation cover induced by climate change also influence soil stability and organic matter content, and therefore impact metal binding and mobilisation (Borrelli et al., 2020). One example is wildfires, which are a natural process, but are becoming more frequent and severe due to climate change, creating a positive feedback loop in many regions (Bowring et al., 2022). The combustion of vegetation releases metals into the atmosphere, and ash from burned vegetation, which contains elevated metal levels, can leach into water bodies through runoff (Abraham et al., 2017). Intense heat from fires also alters soil properties, making it more prone to erosion, which further contributes to the transfer of these metals into aquatic systems (Shakesby et al., 1993). Wildfires can both directly and indirectly affect aquatic fauna (Gomez Isaza et al., 2022), and the impact of black carbon produced during combustion on metal bioavailability in freshwaters is further discussed in the section Environmental Scale.

Another example is bark beetle infestations, exacerbated by climate change in regions such as Asia, Europe, and North America. These can significantly accelerate the release of metals from soil into water bodies (Su et al., 2017). As dead trees decay, they release organic matter into the soil, which increases microbial activity and lowers soil pH. This decrease in pH can increase the leaching of metals such as Cd, Cu, Ni, and Zn that are bound to organic matter (Bearup et al., 2014). In addition, beetle infestations disturb the soil surface, exposing bare soil to erosion by wind and water, which further transports particles containing adsorbed metals into water bodies (Su et al., 2017).

The dynamics of metals in soils vary significantly between regions, depending on climate scenarios and soil properties. These factors ultimately determine the terrestrial input of metals into aquatic systems. The biogeochemical behaviour of Cu in European soils is a good example of this complexity (Ballabio et al., 2018). Projected changes in rainfall patterns due to climate change are expected to directly impact Cu accumulation and export in soils (Sereni et al., 2024). Increased rainfall intensity and frequency can enhance Cu transport during heavy precipitation events through greater runoff and soil erosion, while lighter rains may result in reduced transport (Frogner-Kockum et al., 2020). Given these complexities, further studies are essential to accurately predict patterns of metal accumulation in soils and subsequent mobility into aquatic ecosystems.

3. The environmental scale - changes in aquatic metal bioavailability

Climate change alters the soil/water metal dynamics and input, dependent on regional factors (section The Global Scale). It will also alter the chemical composition of water with impacts on metal speciation in freshwater systems, enhancing or decreasing bioavailability of metal inputs from soil. Metal mobility between water and river sediments and availability to biota is influenced by similar factors as those in soil such as pH, redox potential, and inorganic and organic content that control processes such as sorption, complexation, and dissolution (Osadchyy et al., 2016). These factors also influence whether metals in the aquatic environment remain in suspension or form aggregates and precipitate into sediments (Herzog et al., 2024; Warren and Haack, 2001).

3.1. Increased drying conditions or rainfall events

Changes in land-riverine interconnectivity due to climate change alter inorganic and organic molecule composition in aquatic environments (Li et al., 2024; van Vliet et al., 2023). It is well established that water chemistry is pertinent to metal bioavailability and toxicity (Adams et al., 2020). Under low-precipitation conditions, river water is predominantly fed from groundwater that is enriched in calcium (Ca) and silicon (Si) due to the percolation of water through the bedrock (Li

Table 2
Metal binding properties of dissolved organic matter.

Metal Element	Binding Moiety	Predominant DOM type	Climate change scenario	References
Lead (Pb)	Carboxylic > phenolic	allochthonous	Browning, Flooding	(Guo et al., 2019; Habibul and Chen, 2018)
Chromium (Cr (VI))	Carboxyl > phenol > polysaccharide > methyl	allochthonous	Browning, Flooding	(Liu et al., 2021; Zhang et al., 2018)
Copper (Cu)	Carboxylic acid, polysaccharides, phenol, amide alcohol, benzylic C=O of amide and O-H of Phenols	allochthonous	Browning, Flooding	(Chen et al., 2019; Guo et al., 2019; Liu et al., 2021; Manceau and Matynia, 2010)
Cadmium (Cd)	C=O of amides > O-H of phenols			Liu et al. (2021)
Zinc (Zn)	Carboxyl and hydroxyl groups (C-O of carbohydrates > C-O of amide > C=O of amide > C-O of ether and alcohols > c = C aromatic ring > O-H carboxylic acid	autochthonous	Eutrophication, Wildfires, Permafrost	Liu et al. (2021)
Molybdenum (Mo)	Amines	anthropogenic allochthonous	Glacial melt, urban run-off, Wildfires	Chen et al. (2019)
Cobalt (Co)	Amines	anthropogenic allochthonous	Glacial melt, urban run-off, Wildfires	Chen et al. (2019)
Nickel (Ni)	Hydroxyl and amino groups	anthropogenic allochthonous	Glacial melt, urban run-off, Wildfires	Li et al. (2017)

et al., 2024; Stewart et al., 2022). In some regions, sea level rise due to the combined effect of the melting of ice sheets at both poles and ocean temperature rise will result in saltwater intrusion into coastal groundwater, thereby altering the ion content (increase in salinity) of freshwater streams (Zamrsky et al., 2024). Under these drought scenarios, it is predicted that freshwater will become more ion-rich; where such conditions are known to reduce metal toxicity via complexation or competition between cations and metals at sites of uptake (Pagenkopf, 1983).

Rainwater is generally ion-poor and acidic, but its chemical composition is influenced by anthropogenic activity (Keresztesi et al., 2020). During intense precipitation events, the quantity of rainwater falling on the ground far exceeds that directly entering freshwater systems based purely on the surface area of the catchment and water bodies. This rainwater will bring surface-derived constituents and, due to the intensity and volume of precipitation, also resuspend riverbed sediments, releasing bound metals into the water, and resulting in dissolved metals under dissolution conditions (Clemente and Huntsman, 2019).

Table 3
Climate change effects on dissolved organic matter composition in freshwater systems.

Climate change effect	Impact on Dissolved organic matter composition	References
Glacial Melt	Export of protein-like DOM Increase in aged DOM	Hood et al. (2015)
Flooding/ increase run-off	Increase in bioreactive DOM (amine and sulphur DOM from urban areas) Increase in export of aromatic DOM	van Vliet et al. (2023)
Permafrost loss	Increase in aliphatic content in DOM Increase in labile DOM (soil degradation)	(Schuur et al., 2008)
Drought	Increase in protein-like DOM Increase in labile DOM	van Vliet et al. (2023)
Wildfires	Increase in black carbon Lipid/aliphatic/peptide-like compounds → tannin-like compounds → condensed aromatic compounds Decrease in aromaticity Increase in nitrogen in DOM pool	(Bowring et al., 2022; Coppola et al., 2022; Jones et al., 2020)
Browning	Increase in humic-like DOM Increase in higher molecular weight DOM	Williamson et al. (2015)
Eutrophication	Increase in labile DOM Decrease in aromaticity	(van Vliet et al., 2023; Wiley and McPherson, 2024))

Sources of freshwater DOM are either allochthonous i.e., those derived from the breakdown of terrestrial material, including anthropogenic allochthonous DOM in urban environments, from road runoff and stormwater overflow, or autochthonous, being produced by benthic algae, phytoplankton, and eukaryotic organisms within the water body (Wood et al., 2011). There is also an estimated 6 peta-grams (e.g., gigatonnes) of organic carbon stored in glacial ice from both allochthonous and autochthonous sources, that will enter freshwater due to the loss of ice as temperatures rise (Hood et al., 2015). Dissolved organic matter, possesses a variety of aromatic and aliphatic functional groups including carboxyl, phenol, quinonyl, aldehyde, ester, ketone, hydroxyl, amino, and glycosol side chains, depending on its source. The proportion of these functional groups determines the hydrophobic and hydrophilic properties of the DOM which contributes to electron transfer capabilities, as well as adsorption and chelation of metals (Table 2) (Benner and Amon, 2015; Chen et al., 2019; Guo et al., 2019; Habibul and Chen, 2018; Kellerman et al., 2014; Liu et al., 2021; Zhang et al., 2018). For example, aliphatic carboxylic acids that have hydroxyl or carboxyl substitution have a far greater affinity for metals than unsubstituted forms (Manceau and Matynia, 2010). Terrestrial-derived DOM is characterised by an increase in Chromophoric DOM (CDOM), which more readily undergoes photolysis or indirect photochemistry following sunlight absorption. This can release metals bound to DOM (Kneer et al., 2021; Li et al., 2017; Liu et al., 2021) and the photochemical reaction enhances electron transfer potential reducing metal ions and increasing metal bioavailability (Vione and Scozzaro, 2019). Autochthonous DOM has more aliphatic and less oxidised with carboxyl side chains that bind metals like Zn and the sulphide-based side chains (e.g. reduced thiols and thioesters or oxidised sulphoxides and sulphonates) which are more likely to sequester intermediate and soft Lewis' acid metals and those metals described as chalcophile elements, such as Ni, Cu, selenium (Se), As, and Cd (Kneer et al., 2021; Li et al., 2017; Liu et al., 2020, 2021).

3.2. Variables influencing DOM composition and metal bioavailability

3.2.1. Eutrophication

Climate change has seen a rise in global DOM concentration in both lentic and lotic environments over the last 40 years (Table 3) (Meyer-Jacob et al., 2019; Monteith et al., 2007; Porcal et al., 2009; Rose et al., 2023). In regions with increased rainfall, greater run-off from agricultural land brings increased nutrient (N and P) load, coupled with an increase in water temperature, resulting in an increase in the frequency and extent of planktonic or benthic algal blooms, altering the ratio of allochthonous:autochthonous DOM in rivers and lakes. Algae require metals for growth, and it is well established in marine environments that Fe, and in some instances Zn, is a limiting nutrient for phytoplankton proliferation (Moore et al., 2001). Seldom have metal concentrations been considered as a limiting factor in algal growth in freshwaters due to the input from rock weathering. On senescence, the algal bloom releases large quantities of autochthonous DOM, which is associated with greater aromatic side chains that may sequester certain metals (Table 2).

Senescence of the algal bloom also results in reduced DOM concentrations leading to hypoxia. Globally, hypoxic zones in coastal waters (Rabalais et al., 2009) and lacustrine environments (Jenny et al., 2016) are on the rise. In aquatic systems, this will alter the dynamics of the oxycline, reducing the oxygenation and increasing the reducing zones. The changes in the redox potential associated with different O_2 concentrations is a vital component of redox-metal geochemical cycling. Under hypoxia, reduction occurs, resulting in reduced forms of redox metals, such as Fe^{2+} and Cu^{+} and altering the acid volatile sulphide/simultaneously extracted metal (AVS/SEM) ratio (Allen et al., 1993). In stratified lakes, the turnover of the oxycline also brings other nutrients to the surface such as phosphate that enhance phytoplankton growth.

3.2.2. pH

Changes in DOM input also introduces organic acids into freshwaters, however the relationship between DOM and pH is not straightforward (Lawrence and Roy, 2021). Adding carbon may only result in weak acidification from carbonic acid and a drop of ~0.3 pH units has been measured over the last 35 years in a number of German lakes (Weiss et al., 2018) and is predicted to drop by between 0.3 and 0.5 pH units by 2100 in Laurentian Great lakes (Phillips et al., 2015). The presence of strong acids such as nitric acid (HNO_3) and sulphuric acid (H_2SO_4) through, for instance, acid rain, is expected to decrease pH substantially by a few pH units (Hasler et al., 2018). The impact on the aquatic environment will depend on the underlying geology of the catchment which determines the water body's buffering capacity, with waters in limestone regions being affected less due to their high carbonate content. Too low pH is, in itself, toxic to the majority of freshwater species (Khan et al., 2012b). There are, however, regions around the globe where freshwaters are naturally acidic due to the large quantities of DOM, such as the Rio Negro in the Amazon River basin where pH ranges from 3 to 5 and organisms have adapted (Val et al., 1998). Metal bioavailability may be reduced at lower pH values due to the higher concentration of H^{+} ions competing with metal cations on the sites of metal uptake as well as effects on enzymatic processes (Campbell et al., 1985). On the other hand, low pH impacts the proton gradient across the epithelium that drives some ion transport processes and ammonia excretion, perturbation which will affect animal health in other ways (Liu et al., 2013). Lower pH favours the dissolution of metals from metal inorganic and organic complexes (Campbell et al., 1985). But the modulating effect of pH on metal solubility may be metal specific and is perhaps best exemplified with aluminium (Al) where Al is relatively insoluble at pH 6.0–8.0, but the solubility, bioavailability, and toxicity increases under more acidic or alkaline conditions (Poléo and Hytterød, 2003).

Catchment geology may result in waters with naturally high pH and an increase in weathering due to alterations in precipitation patterns will likely increase the input of alkaline material. pH may also fluctuate widely during increased eutrophication, for example a pH of 10.54 was measured in Slapton Lea, UK during a blue-green algal bloom (D. M. , Scott et al., 2005). Higher pH is more often associated with a decrease in metal toxicity due to the formation of metal hydroxide complexes. However, for certain metals, these hydroxides are readily available, and, for example, an increase in Cu toxicity as pH rises has been observed in several freshwater invertebrates (de Schamphelaere and Janssen, 2002; Markich et al., 2003; Nys et al., 2016).

3.2.3. Wildfires

Wildfires produce large quantities of pyrogenic organic material, black carbon (BC), and incomplete combustion of carbon which leads to polyaromatic products that may remain for millennia in soil (Coppola et al., 2022). Soil microbes oxidise BC rendering it more hydrophobic and soluble, and BC in surface soils following fires enter rivers following rain. This alters the allochthonous dissolved organic carbon (DOC): allochthonous dissolved black carbon (DBC) ratio, with between 2 and 15 % of total DOC being derived from DBC (Coppola et al., 2022; Jones et al., 2020), and annually 43±15 Tg of DBC is transported by rivers to the ocean (Jones et al., 2020; Hameed et al., 2023). DBC derived from wildfires possesses more carboxylic and amide groups due to low temperature combustion leading to greater aromaticity and formation of pyridinic structures as the fire temperature increases (Lopez et al., 2024) when compared to natural DOM. This property of DBC has been demonstrated to bind more metals like Cu, Ni, Cd, Cr, As and Pb (Campos et al., 2016; Hameed et al., 2023; Lopez et al., 2024; Song et al., 2021; Stein et al., 2012).

3.2.4. Browning

Lake browning, the term used to describe the colour of inland waters from an increase in predominantly terrestrially-derived DOM from runoff over the last 50 years, reduces the photic zone, impacting primary production and food webs (Vione and Scozzaro, 2019; Williamson et al., 2015). This, in turn, limits algal growth, a source of allochthonous DOM, thus resulting in a trade-off between nutrient input and light penetration to determine freshwater algal biomass. For example, in some cyanobacteria, photochemistry rather than biological factors is responsible for facilitated uptake of Fe (Fujii et al., 2011). This is due to the light-induced photochemical reduction of ferric iron (Fe^{3+}) to the more readily available ferrous iron (Fe^{2+}) by direct ligand-to-metal charge transfer (Barbeau et al., 2001). In the euphotic zone of lakes, DOM-metal complexes will potentially reduce metal bioavailability, but if these complexes aggregate and precipitate, they provide a source of organic carbon and metals for sediment dwelling organisms.

Overall, climate change will increase freshwater DOM. Increases in DOM, irrespective of source, are known to bind metals and thus reduce bioavailability to aquatic organisms. On the one hand, this may reduce metal toxicity with fewer toxic metal ions being present, though the degree of specific metal binding will depend on the side chain characteristics of the DOM, which in turn depend on the source. On the other hand, there will also be a reduction in metal bioavailability to organisms that are dependent on an aquatic source of dissolved essential metals. This is evident in primary producers, which are reliant on this source of micronutrients, and where aquatic metals are also an important source for other aquatic organisms, including fish (Bury and Grosell, 2003). Whether the increase in DOM can counterbalance the predicted increase in metal inputs in freshwaters is currently unknown, and alterations in the carbon and micronutrient biogeochemical cycling due to climate change are still being unravelled.

4. The organismal scale - physiological impact of climate change on metal exposure

In freshwater systems, increasing temperature, decreasing DOM and increasing acidity (lower pH) are considered to be the most important climate stressors that may lead to a decrease in the overall fitness of an organism (Table 4) (Pinheiro et al., 2021). Other climate-related stressors may also affect baseline physiology; for instance, high levels of DOM or saltwater intrusion into freshwaters may affect ionic regulation and membrane permeability (Griffith, 2017), but in these cases, the reduction in metal bioavailability from complexation would outweigh the physiological adaptation. Maintaining biological function when environmental temperature, DO and pH are forcing organisms into physiological stress will impact their sensitivity to metal exposure.

Table 4
Summary of the effects of climatic stressors (increasing temperature, reduced dissolved oxygen and lowered pH) on the physiology of freshwater organisms and potential implication of metal uptake, accumulation and toxicity.

Climatic stressor	Physiological change	Implication for metal-biota interaction	References
Increased temperature	Ectotherm's body temperature is based on the ambient environment. All aspects of physiology are temperature sensitivity. Reaction rates increase with temperature (i.e. Q10). Warming is also associated with hypoxia resulting in increased ventilation rate.	Increase in metal uptake rate constants with temperature rise seen across metal and aquatic species - Q10 for metal uptake in range of 3–12. Metal elimination is not as commonly affected by temperature. Uptake > Efflux leads to increased metal accumulation with temperature and potential increases in metabolically active metals.	(Bervoets et al., 1996; Blust et al., 1994; Nichols, and Playle, 2004; Sokolova and Lannig, 2008)
Reduction in dissolved oxygen	Lower biological oxygen demand. Increase ventilation rate. Increase the blood volume in the gills by perfusing a larger gill area with blood.	Earlier onset of toxicity when fish were exposed to metals under hypoxia. Proposed mechanism of increased uptake as a result of increased uptake rate was not strongly supported. Hypoxia generates reactive oxygen species (ROS) as do some metals. Explanation for lethality resulting from synergism and/or additivity between stressors acting on to generate ROS and invoke ROS-scavenging enzymes.	(Ficke et al., 2007; Garcia Sampaio et al., 2008; Hattink et al., 2006; Lloyd, 1961; Ransberry et al., 2016)
Acidification of freshwaters	Great overlap with environmental changes in metal bioavailability and solubility: toxicity of pH, competition with H$^+$, solubility of metals at acid and alkaline pHs promotes bioavailability and toxicity. Physiologically, low pH increases gill mucus, affects cell membrane permeability and trans-epithelial electrical potential.	Implications of physiological changes on metal uptake and toxicity are purely defined since pH has a controlling effect on waterborne metal bioavailability. Reduction in metal uptake from protective function of increased mucus production. Possible increases in uptake from changes in membrane permeability and electrical potential.	(Hauser-Davis and Wosnick, 2022; Pinheiro et al., 2019, 2021; Wang et al., 2016))

4.1. *Influence of temperature on the physiology of metal accumulation*

Since ectotherms (including freshwater fish and invertebrates) cannot physiologically regulate internal temperature, even small changes in the ambient temperature will be reflected in their body temperature (Ficke et al., 2007; (Pörtner and Farrell., 2008); Sokolova and Lannig, 2008). Temperature tolerance ranges are largely species-specific, and species may be stenothermal (narrow range) or eurythermal (wide range), thus not all species will be affected similarly, which may lead to changes in species composition or abundances in different locations (Pörtner and Knust., 2007). However, behavioural thermoregulation is possible through the movement to more optimal conditions, organisms are limited by the available temperature range (Ficke et al., 2007). On the physiological level, all aspects of physiology are affected by increases in temperature since biochemical processes vary as a function of body temperature in accordance with the principles of Arrhenius Law, which describes the thermal dependency of reaction rates (Ficke et al., 2007; Schulte et al., 2011). Thus, an ectotherm's performance in growth, reproduction, immune competence and overall fitness and competitiveness is affected by temperature (Pörtner and Farrell, 2008). An added dimension to this is the inverse relationship between increased water temperature and a reduction in oxygen solubility, which leads to an increase in biological oxygen demand (Kalff, 2000). Therefore, at elevated temperatures, organisms may face the additional pressure of an "oxygen squeeze" where decreased levels of DO cannot meet increased demand. Nonetheless, the effects of temperature alone on the accumulation and toxicity of several metals have been studied in an array of species.

The increase in metal-associated effects is often attributed to an increase in the metal uptake rate constant (k_u). Increasing the temperature from 10 °C to 20 °C increased the Cd k_u in *Daphnia magna*, but a further increase to 26 °C did not correspondingly increase k_u (Heugens et al., 2003). Similar temperature-dependent increases in uptake were seen with rainbow trout (*Oncorhynchus mykiss*) exposed to silver (Ag) (Nichols, and Playle, 2004), in midge larvae *Chironomus riparius* exposed to Cd or Zn (Bervoets et al., 1996), and in *Artemia* spp. Exposed to Cu (Blust et al., 1994). In a 2008 review, Sokolova and Lannig (2008) found that 85 % of reviewed studies showed that an increase in temperature resulted in an increased metal uptake (or accumulation), however, the elimination rate constant (k_e) was not similarly affected as only a quarter of studies showed elevated temperature increased k_e. Generalisations across metals and across species should be made with care, as the accumulation of the non-essential Cd was higher at 20 °C compared to at 10 °C in European carp (*Cyprinus carpio*), while temperature had no effect on the accumulation of essential metals Zn and Cu (Castaldo et al., 2021).

The mechanistic understanding of the positive effect of temperature on trace metal uptake is increased gill ventilation, though this is also in response to increased physiological oxygen demand. At the cellular level, metal transport pathways include passive diffusion across cell membranes, facilitated transport and active transport by ion channels. The Q10 for metal uptake, which is the increase in uptake rate for every 10 °C rise in temperature, is in the range of 3–12 (i.e. a 3-12-fold increase) for active uptake (Hutchins et al., 1996), but the Q10 values for passive diffusion is at most 1.4 (Willmer et al., 2000). The active transport via ion pumps thus offers a more compelling case as the main routes of metal entry (Balamurugan and Schaffner, 2006) and are known in ectotherms to be strongly affected by environmental temperature. Moreover, temperature may result in changes to membrane permeability and integrity, which may affect the mobility and function of membrane-associated receptors, transport and channel-proteins (Sokolova and Lannig, 2008). The consequence of the disparity between uptake and elimination is that, in general, temperature increases lead to greater levels of metal accumulation across metals and species. This means a greater internal concentration that is metabolically available to cause a toxic response, and whilst internalised metals may

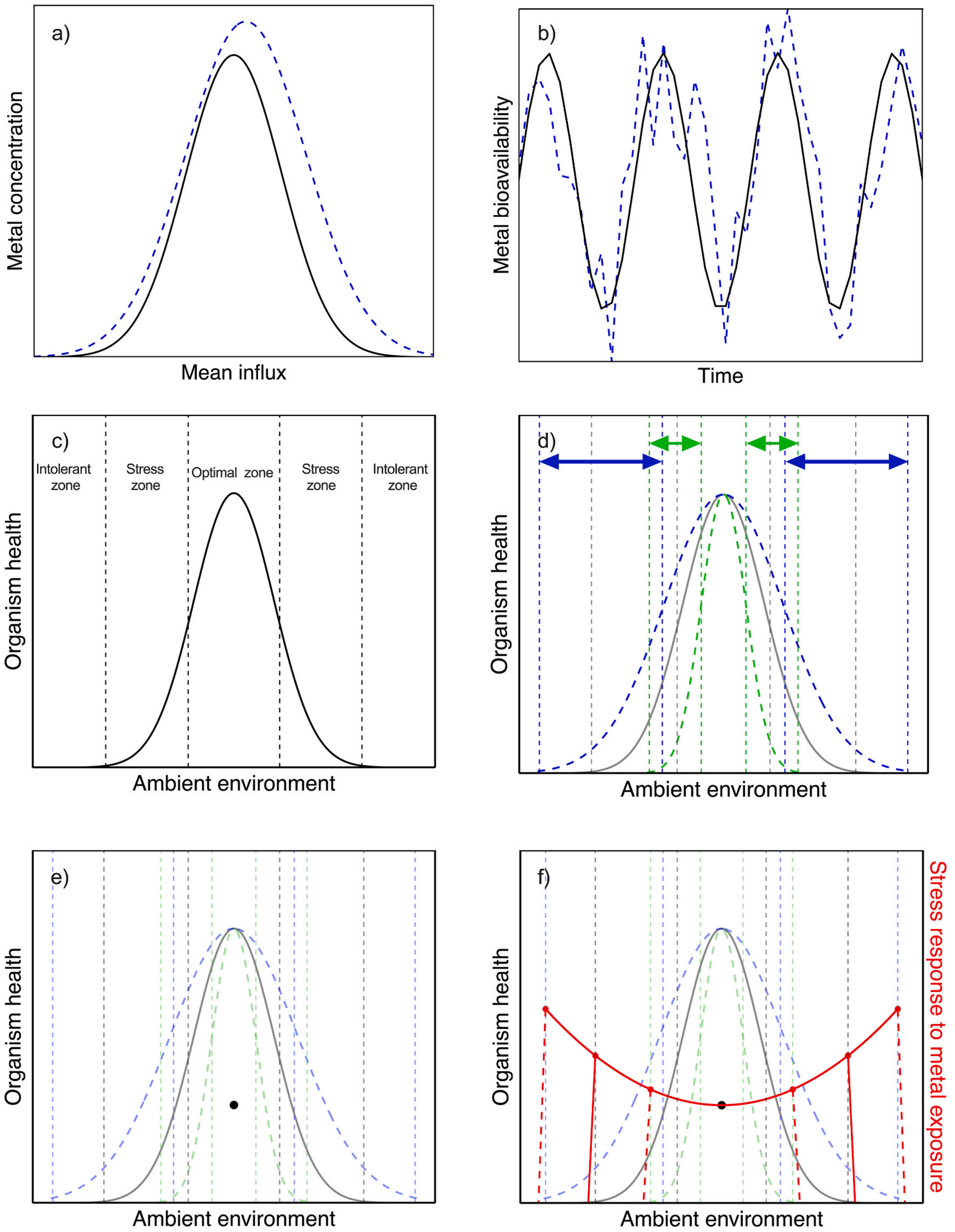


Fig. 2. Impact of climate change on metal mobility and exposure across scales. The Global scale (a) depicts longer-term shifts in mean and intensity of metal fluxes from catchments to freshwater systems (black line denotes the current climate and the blue dotted line the expected shift under new climatic conditions). Although generally promoting the mobilisation of metals into aquatic environments, the overall impact can vary regionally. At the Environmental scale (b) there will be increased variability in intensity and frequency of metal concentrations and bioavailability in freshwater (black and blue lines as in panel a). The Organismal scale (c–f) first shows the normal distribution of organism health over the ambient environmental conditions described by optimal, stressed and intolerant zones (i.e. Shelford's law of tolerance, c). The impact of climate change (d) is described as a widening (blue dotted lines) or narrowing (green dotted lines) of an organisms' tolerance range with associated shifts in the boundaries of optimal, stressed and intolerant zones (blue and green arrows). The introduction of a metal stressor under optimal conditions will cause a reduction in organism health (black dot, e) understanding that this reduction is based on the metal (essentiality, toxicity) and exposure (concentration, duration). The stress response to metal exposure (red line, right x-axis, f) will increase as the organism is exposed under increasingly stressed environmental conditions until the organism becomes intolerant of the ambient environment, accounting for the revised boundaries of the optimal, stressed and intolerant zones, reaching a tipping point whereby metal exposure is no longer the most relevant concern (i.e. the stress response to metal exposure falls as the organism is no longer able to survive). See Discussion for further details. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

be subject to detoxification (Khan et al., 2012a; Rainbow, 2002), the effect of climate stressors on detoxification has yet to be studied. Thus, the same principles of thermal dependence of reaction rates that applies to the uptake of metals may also apply to chemical reactions that, for instance, lead to the production of free radicals, commencement of oxidative stress, and biomarker responses (Ficke et al., 2007; Pinheiro et al., 2019; Silva et al., 2018). Importantly, it should be noted that laboratory experiments in which temperature increases are coupled with metal exposure often exceed the range of increase predicted by global warming, and there is a need for environmental realism within study design.

4.2. *Effects of oxygen availability on metal stress responses*

Oxygen solubility in water has an inverse relationship with water temperature, where water at 0 °C hold 14.6 mg O_2 L^{-1} whereas water at 25 °C holds about 8.3 mg O_2 L^{-1} (Kalff, 2000). Factors other than temperature, such as eutrophication, and oxygen demands from plant, animal and microbial aerobic respiration can also decrease DO in the water column (Ficke et al., 2007). A DO concentration of ≥ 5 mg O_2 L^{-1} is acceptable for most aquatic organisms, but around 2–3 mg O_2 L^{-1} is considered hypoxic (Kalff, 2000). The physiological effects of hypoxia are, in part, similar to those of elevated temperature, given the relationship between these two environmental stressors. As with elevated temperature, the effects of hypoxia are not equal amongst species, but in the short-term (up to 96 h), the challenge is to obtain enough oxygen to meet basic metabolic demands (Gilmore et al., 2018).

Fish may counter hypoxia by breathing air at the water's surface (aquatic surface respiration) and decreasing activity to lower oxygen demand (Gilmore et al., 2018). To increase oxygen supply, fish will increase their ventilation rate at the gills and increase the blood volume in the gills by perfusing a larger gill area with blood (Ficke et al., 2007). This will increase the volume of water that passes over the gills, increasing the surface area of the gills, and increasing the extraction of oxygen from the water. The effort to increase oxygen uptake thus opens the possibility of increased metal uptake via the gills in metal-contaminated hypoxic locations. In early laboratory experiments, rainbow trout experienced the onset of lethal effects earlier when exposed to Zn under hypoxia compared to normoxia (Lloyd, 1961), with the explanation of increasing uptake due to greater gill ventilation thought to be the likely mechanism. However, more recent studies testing the relationship between gill ventilation and metal accumulation have shown that this is not a likely mechanism. For instance, Zn uptake rates were much lower than predicted from a ventilation-and-diffusion–regulated uptake mechanism in carp (*Cyprinus carpio* (L.)) (Hattink et al., 2006). Yet there remains continuing evidence that a combination of hypoxia and metal exposure results in adverse effects that are greater than the individual effect of either stressor alone (Garcia Sampaio et al., 2008; Ransberry et al., 2016). In particular, the markers of oxidative stress-induced damage and defence are both affected by hypoxia and metal exposure.

Changes in DO availability can alter the generation of reactive oxygen species (ROS) and hypoxia, as well as hyperoxia, resulting in increased oxidative stress (Lushchak, 2011). Thus, both redox active metals (e.g. Cu) and hypoxia act upon the ROS-scavenging enzymes, superoxide dismutase (SOD) and catalase (CAT), amongst other biomarker responses (Garcia Sampaio et al., 2008; Ransberry et al., 2016). Prolonged exposure to hypoxic conditions may result in reduced growth, fecundity and mortality (Pörtner and Lannig, 2009), which, as general signs of reduced fitness would increase susceptibility to pollutants, including metals. However, prolonged hypoxia activates alternative metabolic pathways to increase oxygen extraction (Zhou et al., 2000). Furthermore, liver glycogen is subject to glycolysis producing lactic acid, which may result in lactic acidosis, a drop in pH in blood and tissue (Hattink et al., 2006; Zhou et al., 2000). This ties the climate stressors of temperature and reduced DO to the third factor of pH as either external or internal acidic conditions increase.

4.3. *Role of pH in mediating metal dynamics and responses to metal exposure*

As discussed in the previous section (see 'Variables influencing DOM composition and metal bioavailability') pH plays a critical role in the environmental bioavailability of metals through complexation and competition with metal cations but also has the potential to perturb physiological processes that impact metal uptake, accumulation and toxicity. At the gill surface, both the pH of the gill microenvironment and mucus secretions respond to ambient pH. Mucus secretions increase at lower pH values and have been shown to be protective by reducing metal uptake. The mucus-copper complex accounted for almost 20 % of the total Cu concentration when Carp (*Cyprinus carpio*) were exposed at pH 6.12, but decreased as pH was increased (Tao et al., 2002). A similar barrier has been shown in the rainbow trout gut (Kamunde and MacPhail, 2011; Khan and McGeer, 2013). pH also has a vital function in maintaining cell membrane permeability with deviations from the optimal condition resulting in structural changes which may result in increased uptake of metals (Hauser-Davis and Wosnick, 2022). pH also exerts a lesser-known effect directly on the trans-epithelial electrical potential (TEP) across the outer surface of aquatic animals (Wood et al., 1998), which can potentially influence the electrochemical gradient of any charged molecules, including metal ions, and thus uptake via the gills (Pinheiro et al., 2021).

Overall, climate change factors (temperature, DO and pH) will impact the physiology of freshwater organisms exposed to metals. Whilst there have been some efforts made to understand these impacts experimentally, most studies employ a multiple-stressor approach combining metal exposure with temperature or pH, for instance, and the impact on toxicological endpoints often results from changes in water chemistry or short-term physiological changes to laboratory conditions (e.g., Garcia Sampaio et al., 2008; Mattsson and Crémazy, 2023; Pinheiro et al., 2019; Ransberry et al., 2016; Silva et al., 2018). However, such simulations only seek to mimic a small portion of real-world complexities. To move forward, there needs to be a greater recognition of climate variability and the effect on an organism's tolerance range, response magnitudes, and tipping points, as discussed in the next section.

5. Discussion

Climatic impacts will not be equal across different regions, individual metals will react differently within the environment, and generalisations for the impact of climate change on the fluxes and fates of metals in freshwaters are challenging. However, based on the available literature, we suggest the following overarching considerations: (a) increased metal fluxes from catchments into freshwater systems, (b) increased variability of the bioavailable fraction, and (c) metal exposure to organisms that are increasingly physiologically stressed by climate change (Fig. 2). On a Global scale, climate change is expected to alter soil properties and hydrological connectivity, which affects metal fluxes from catchments to freshwater systems (Osadchyy et al., 2016). While increased precipitation and runoff generally promote the mobilisation of metals into aquatic environments, the overall impact can vary (Fig. 2a (Dakos et al., 2019),). In some regions, reduced runoff or altered land use may decrease metal transport to freshwater systems instead (Visser et al., 2012). At the Environmental Scale, although greater metal inputs will occur, there will also be greater inputs of factors that modify bioavailability, most notably the sources and properties of organic carbon that alter metal complexation. Complexation decreases the free metal ion concentrations in the pelagic zone, but conversely, increases input into sediments due to sedimentation processes. The inputs of DOM, driven by the occurrence of extreme weather events will result in more variable and less predictable metal bioavailability (Fig. 2b).

At the Organismal Scale, the health of an organism within its environment is described by Shelford's Law of Tolerance within which an organism can experience optimal conditions at which it reaches maximum performance and increasing sub-optimal conditions at which the organisms survives but experiences increasing levels of stress (stress zone) until a critical point in which the organism can no longer survive (intolerant zone) (Fig. 2c) (Franke et al., 2024). Short-term acclimation and long-term adaptation can lead to a shift in these tolerance ranges - climate change may narrow a tolerance range if more of the environment becomes inhospitable or widen the range if an organism can adapt to a wider range of conditions. In either case, the organism will experience a change in position of the stress boundary, and organisms within more variable climates spend more time in the stress zone (Fig. 2d). When a metal stressor is introduced under optimal conditions, the exposure causes a reduction in organism health that is based both on the metal (essentiality, toxicity) and on the exposure (concentration, duration) (Fig. 2e). The stress response to metal exposure will increase as the organism is exposed under increasingly stressed environmental conditions (i.e., multiple stressors) (Fig. 2f). When the organism becomes intolerant of the ambient environment, accounting for the revised boundary of stress and intolerant zone, a critical tipping point is reached whereby metal exposure is no longer the most relevant concern, and the stress response to metal exposure falls as the organism fails to survive (Fig. 2f).

At each scale, much is already known about the processes and pathways that govern metal input, bioavailability, and impacts on biota (Luoma and Rainbow, 2008). These processes are defined as the underlying connectivity of metal fluxes/fates, environmental bioavailability, metal uptake, and ultimately toxicity (Pagenkopf, 1983). Climate variability will alter the frequency, intensity, and rates at which these processes occur, with the underlying commonality throughout scales being a shift to a more dynamic system (Thornton et al., 2014), whether globally, environmentally, or organismally. Current exposure and bioavailability models are equilibrium-based and take into account toxicity modifying factors (Di Toro et al., 2001; Paquin et al., 2002), but they do not yet capture the non-equilibrium conditions caused by climate-induced perturbations in freshwaters (Pinheiro et al., 2021). In a much more dynamic environment, it is the kinetics of reactions (e.g., at the organismal scale, altered metal uptake patterns and toxicodynamics due to altered metabolic processes) in response to climate variability (Sokolova and Lannig, 2008) that become more important compared to predictions of metal bioavailability from thermodynamic equilibrium models. These models will need to be modified to guide policymakers on potential metal toxicology scenarios based on more variable climatic conditions. However, the challenge lies in trying to capture the complexity of climatic variability within experimental designs rather than selecting one or two stressors in addition to metal exposure, whilst also recognising that these combined stressors are long-term conditions subject to variability, rather than a fixed acute exposure scenario. Extending predictive models to include climate variability is clearly no easy task, but to begin such a process would ultimately lead to more accurate and realistic applications to policy guidance.

6. Conclusion

To understand the impact of metals during climate change, a number of factors are required. Climate change scenarios are routinely being updated and regional impacts refined as more data are acquired. What is clear is that climate change parameters do not often follow simple linear patterns, and increasingly variable and/or extreme events are likely to be the norm (Thornton et al., 2014). If we are to better understand the impacts, we need to accept this unpredictability and provide advice based on the predicted scenarios at a regional scale. Existing frameworks for models to predict acute and chronic toxicity (Paquin et al., 2002) will need to be adapted to more dynamic processes and will require an acceptance of decisions based on climate predictions. If the aim is to protect wildlife, then we need to identify the tipping points (e.g., Fig. 2f) where the environmental metal inputs, speciation, and physiological adaptations push organisms outside of their tolerance window.

CRediT authorship contribution statement

Farhan R. Khan: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Nicolas R. Bury:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition. **Christopher A. Cooper:** Writing – review & editing, Project administration. **David Boyle:** Writing – review & editing. **Elizabeth Middleton:** Writing – review & editing. **Simon D. Herzog:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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