

BIOAVAILABILITY OF METALS IN THE BIOSPHERE

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In some areas, soil, sediment, water, and organic materials may exhibit elevated concentrations of various metals. Under certain conditions, these metals can take on most bioavailable forms. To assess the impacts and potential risks associated with elevated element concentrations, understanding the fraction of whole elements in water, sediment, and soil which are bioavailable is very important. The study aims to examine these conditions to accurately assess potential environmental impacts. For the study, searches were carried out using the keywords "bioavailability", "metal" and "environment" in various combinations in English. The search was limited to articles published open access in NCBI or PubMed, Scopus, and Google Scholar. The language of the manuscript was not restricted. The complex interactions of these diverse factors highlight the difficulty of assessing and understanding the bioavailability of metals in different environmental matrices. The study identified key factors affecting the bioavailability of the metal. These factors can change over time and among different microorganisms, plants, and animals. Research involving field and laboratory studies conducted at specific locations in soil, sediment, and flora using selective chemical extraction techniques is critical to a detailed understanding of the complex ecological processes associated with the bioavailability of metals to organisms.

Keywords: metal bioaccumulation; metal mobility; soil; surface water; plant uptake.

INTRODUCTION

Bioavailability refers to the portion of a metal in a certain environmental component that, during a specific timeframe, is either accessible or can be rendered accessible for absorption by microorganisms in the organism. Numerous researchers acknowledge the crucial metal role speciation in determining the toxic metals bioavailability. Nevertheless, the definite metals types that are decisive for ultimately causing harm to organisms remains unclear. Typically, the toxic effects of heavy metals are attributed to the free metal ion. But, the Biotic Ligand Model revealed that other metal ions significantly affects the uptake of metals by organisms (Paquin et al., 2002). Moreover, in cases where the metal ions penetration into environmental components toward the abiotic faces play a major role in controlling metal uptake, loosely bound metal complexes may play a role in facilitating metal absorption. Consequently, in most instances, the 'bioavailable' species are observed to contain of the available cations (Slaveykova & Wilkinson, 2002) or loosely bound metal species (Mylon et al., 2003).

The ecological fate of some metals such as copper, cadmium, chromium, mercury, nickel, manganese, and lead, along with metalloids like arsenic, antimony, and selenium, is a significant concern. This is especially true near abandoned dumps, mines, tailings ponds and reservoirs, as well as in populated areas and areas with active industrial facilities. Soil, water, sediment, and organic materials of urbanized and industrialized areas may exhibit elevated concentrations of these elements, often stemming from historical mining or industrial activities which result to the realization of other bioavailable species of the metals (Christopher & Rosen, 2009). To gain a comprehensive understanding of elemental abundances, it is essential to acquire data from the lands and watersheds surrounding these sites. Background values, influenced largely due to underlying bedrock and water-rock interface that is established which provide context and perspective to elemental concentrations. This approach aids in assessing the potential environmental impact and understanding whether observed concentrations are within expected or concerning ranges. To assess the properties and impending threats linked to heightened metals level arising as

a result of mineral weathering or mining work, it is crucial to know the quantitative content of bioavailable elements in soil, water, and sediments. It is the quality "bioavailability" that is a key factor in understanding the environmental impact, since it represents that part of the metals that is available for inclusion in the biota (bioaccumulation) (Brit, 2015).

Notably, total metal content per unit volume may not align with metal bioavailability. It is so well known that sulphide minerals, when enclosed in quartz or other chemically inert minerals, can result in significant overall metal concentrations in settled sediments and ground cover. However, the elements are not accessible for assimilation into either plants or animals leading to potentially low environmental effects (Davis et al., 1994). Consequently, the overall environmental impact of mining rocks containing such minerals might be significantly less than mining deposits with more chemically active minerals in less quantity. Associations with sulphide minerals can be formed by metals from mining activities in an aquatic environments with a predominance of chemically reducing states. Whether available in the ore deposit or generated as a result of bacterial sulphate conversion in oxidized tailings most sulphide metal minerals remain relatively immobile in chemically reducing environments.

Given the ever-increasing anthropogenic pressure on the environments. The reason of the research was based on in-depth analysis of the bioavailability of metals to better understand the risks to the population and identify gaps in this area for further research.

MATERIALS AND METHODS

The current review study uses 20 years of peer-reviewed papers published between January 2004 and December 2023. The search was carried out using the keywords "bioavailability", "metal" and "environment" in various combinations in English. The search was limited to articles published in the public domain. The language of the manuscript was not restricted. The publication or study was not limited to a specific geographic location. Searches were conducted in NCBI or PubMed, Scopus and Google Scholar. The methodology was based on recommendations (Page et al., 2020).

At the first stage, manuscript abstracts were examined. The purpose of this stage was to exclude erroneous manuscripts that are not related to the topic under study.

Articles were in demand that were aimed at studying the phenomenon of bioavailability of metals common in various environmental environments, namely:

- identifying the features of this phenomenon;
- study of factors promoting and inhibiting the bioavailability of metals;
- improved understanding of metal uptake by organisms in different environments;
- study of bioavailability by selective chemical extraction.

Only studies that addressed at least one of the areas listed above were selected. Next, the selected manuscripts were subjected to detailed reading and critical assessment of their informativeness for the stated purpose of the current study. Methods of analysis and synthesis were used to systematize the information identified, methods of logical thinking and comparison were used to understand risks and identify gaps. Cross-references were also taken into account if they provided useful information in accordance with the objectives of the current study.

It is expected that the results of the current study will help interested scientists discover new directions of research and progress in this field of knowledge, and will also help practitioners and decision makers act with greater caution, taking into account all the risks to humanity.

RESULTS AND DISCUSSIONS

In total, the search identified 1369 literature references matched from January 2004 to December 2023. The distribution of the number by database was as follows: NCBI or PubMed – 315 papers, Scopus – 741 and Google Scholar – 313. The

distribution of publications by year in different databases is presented in Figure 1.

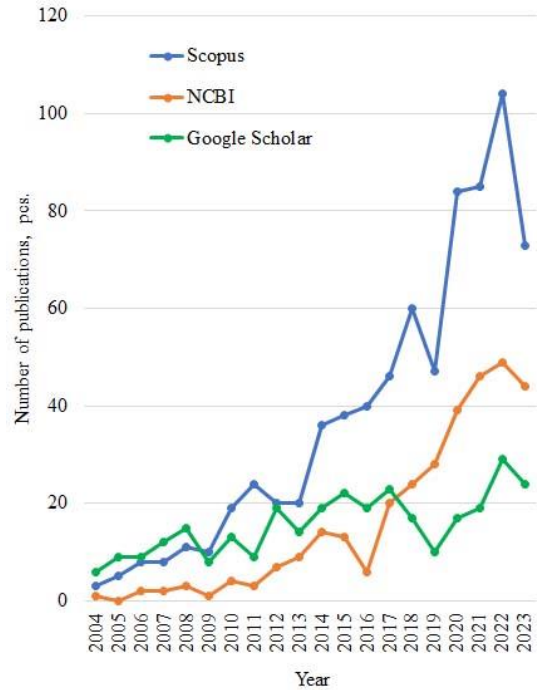


Figure 1. Number of scientific articles on the query topic from January 2004 to December 2023 for Scopus, Google Scholar, NCBI or PubMed

As a result of the search, 521 literature sources were rejected as duplicates; 259 scientific studies were rejected as not relevant to the query topic and only 589 articles had their full text reviewed (Figure 2).

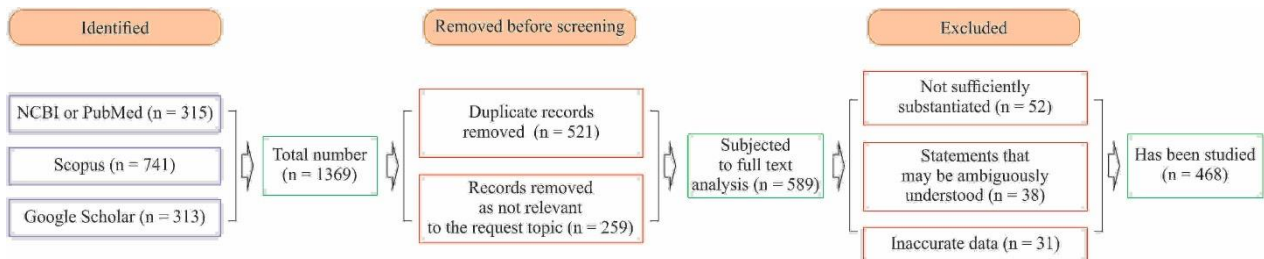


Figure 2. Systematic selection of sources according to the study purpose

After peer review of the full text, 52 studies were identified as having insufficient evidence, 38 studies had findings that were unclear, and 29 studies had inaccurate data. For these reasons, these sources were also excluded. Thus, 486 studies were most suitable for identifying information in accordance with the purpose of the current study.

Bioavailability

The bioavailability of a metal is directly associated with its species or form. In this context, bioavailability is understood like metal' ability (or of a elementary type) to be assimilated by an organism and impact its stages of development (Singh & Prasad, 2023). This term encompasses both harmful toxins and essential nutrients, signifying substances that can be detrimental or beneficial and necessary. The bioavailability of pollutants is an important scientific reference that helps in environmental risk assessment (Jin et al., 2023). Crucially, for a substance to be considered bioavailable, it must upset the lifespan of an organism (Nnaji et al., 2023). If a metal is taken

into an organism but does not significantly impact it, it is not deemed bioavailable.

Certain bacteria and fungi have developed resistance mechanisms that allow them to continue to exist at elevated metal levels by complexing metal ions with proteins to generate insoluble metal sulphides, which actually reduces metal absorption. Direct or in situ measurement of metal speciation is a complex process. Frequently, laboratories attempt to simulate natural environments to create an approximation. However, as metal phases are in persistent change, determination of metallic content per unit volume in the environment is possible only from a snapshot at a certain moment. The environment is variable over time, and species undergo constant changes under the influence of environmental factors. For example, a study (Zhao et al., 2021) found through fractional analysis that potential bioavailability in surface soils declines in the direction Cd > As > Cu > Ni > Zn > Cr > Pb > Hg. Sorption methods play a significant part in determining metals bioavailability. Sorption encompasses various processes that remove a metal ion from a solution,

including absorption, adsorption, diffusion into a solid, and precipitation. The reverse process, where metals dissolve back into a solution, is known as desorption. Understanding these processes is crucial for comprehending the dynamic interplay of metal bioavailability in the environment (Robert et al., 2005; Cai et al., 2021; Dietrich et al., 2021).

The United State Environmental Protection Agency (USEPA) identifies certain metals as of primary concern in bioavailability studies: Arsenic, Antimony, Aluminium, Beryllium, Copper, Chromium, Cadmium, Lead, Nickel, Selenium, Mercury. These metals are of great concern as a result of their contact with organisms which may lead to high risks. Studying the bioavailability of these metals is crucial for understanding their environmental impact and potential implications for ecosystems and human health (McKinney & Rogers, 1992; Abbas et al., 2023). Metals exhibit dispersion in soil, water, and air, and geoscientists primarily interested in metals dissolved in natural surface and ground waters, diffused in soil and sediments, and suspended as particles in surface waters. Mineralogy control the availability and movement of metals during precipitation, but other associations may be observed for bioavailable fractions (Cánovas et al., 2023). In addition, metals present in the pore fluid in sediments are also of interest (Figure 3) (Mitra et al., 2022).

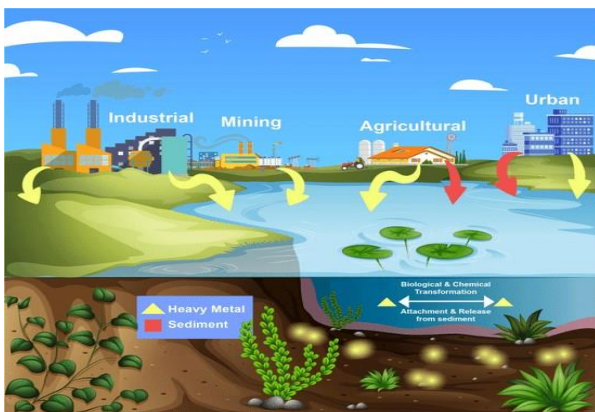


Figure 3. Interrelationships of human activities, metals, and the environment (Mitra et al., 2022, Creative Commons Attribution License International CC-BY 4.0)

Moreover, metals can be released into the atmospheric space through natural geochemical processes, various anthropogenic activities (in particular, lead containing gasoline and coal combustion, smelting), and bacterial activities. These atmospheric metallic instability are of crucial considerations in the comprehensive research of such metal quality as bioavailability. Bioaccumulation of metals by naturally occurring organisms of various classes in surface waters and terrestrial environments is likely to have a negative impact on human health. In every environment, such as air, sediments and natural waters, bioavailability is a multifaceted function that is predisposed through numerous causes. Whatever the factors, they take into account the total content of metals per unit volume and their physicochemical forms (speciation). In addition, factors also take into account the content of suspended particles, redox potential, pH, heat/cold, mineralogy, carbon-based matter content of solid and dissolved solids, water velocity, volume and its availability over time, which is especially important for arid and semi-arid regions. Additionally, factors such as windblown and recovery metals by precipitation from the atmosphere (with the regularity being more significant than quantity) should be taken into account (Miranda et al., 2021). More factors discussed are interconnected and exhibit seasonal and temporal variations

(Cánovas et al., 2023). Research has even found that such factors also include chloride complexes, which has a direct consequence on metals bioavailability, although the process itself and its effectiveness depend on a number of features, such as type of flora or the species, initial concentrations, nature of habitat (Dołęgowska et al., 2022). Also, the concentrations of bioavailable metals depend significantly on the types of chemical extractants (Wang et al., 2021). Altering one factor may have cascading effects on several others. Furthermore, the influence of generally poorly understood biological factors appears to be significant in the bioaccumulation of metals, posing challenges for accurately predicting metal bioavailability. The intricate interplay of these diverse factors underscores the complexity of assessing and understanding the bioavailability of metals in various environmental matrices. Understanding the metals bioavailability in natural surface waters and soil involves considering several major controls and employing specific analytical methods. Redox potential, organic matter content, pH, temperature can be highlighted as key factors and actions to comprehend bioavailability (Guarino et al., 2022).

An accurate assessment of the elements bioavailability and mobility can be obtained after understanding soil acidity, organic matter, sulphur, and carbonate content. Soil scientists specializing in agriculture have dedicated over a century to investigation of nutrient chemistry which are present in the soil. Various soil testing procedures have been established to determine the occurrence and availability of fundamental elements crucial for high-quality plant growth (Hu et al., 2015; Ding et al., 2017; Wanget et al., 2021). Among these elements, potassium, phosphorus, and nitrogen, together with assessments of acidity index and salinity, stand out as the utmost frequently determined elemental properties (Peck & Soltanpour, 1990). The study of the physical-chemical aspects of nutrient availability in soil is a topic addressed by Corey (1990), shedding light on the complex interactions that influence the accessibility of nutrients to plants. In addition, the studies provide comprehensive review of soil testing correlations, offering insights into the interactions of different soil characteristics and the concentration of essential nutrients (Dahnke & Olson, 1990; Havlin, 2020; Liu et al., 2021). These studies and correlations play a pivotal role in guiding agricultural practices, ensuring optimal conditions for plant growth, and maximizing crop yield (Guan et al., 2023).

Conditions promoting bioavailability in soil

Metals enter the food chain through agricultural products through absorption by plants (González-Valoys et al., 2021; Hu et al., 2015; Guérin et al., 2022). However, key stages for a successful uptake are:

- elements supply to the plant root from the soil;
- elements penetration through the membrane of root epidermal cells;
- elements transport to the xylem from epidermal cells, which is required for transporting an elements' solution to shoots;
- possible movement from the leaves of plants to storage tissues that are suitable for consumption (fruits, seeds, roots) in the phloem transport system.

Once metals have passed through these stages and accumulated in plants, they become available to the local population and herbivores immediately or through the food pyramid. The entry of food pyramid elements is often limited by the movement from the soil to the plant root (Hussain et al., 2021; Vasile et al., 2021; Chen et al., 2022). This crucial step stands heavily influenced by the elements levels in earth orifice mixture that, in turn, are measured by several confined ground properties, including acidity index, water content, humidity, redox potential, and other criteria.

Climate makes a significant contribution to the formation of soil types, and these two factors, climate and soil type, largely dictate the mobility and availability of elements, including metals and metalloids (Nedrich & Burton, 2017; Koptsik & Koptsik, 2022). Arid climates, such as those in the western United States, tend to a low content of organic matter and high carbonate and salt abundances. These steps generally contain the metals under investigation, contributing to their presence in the soil. In humid climates, like those in the eastern United States, high organic matter content dictates the need to assess the hazards of organic matter-associated metals and the residence time of such metals. With time, as abundant of the organic component oxidizes, adsorbed metals may be free or become accessible. In equatorial climates, the build-up of aluminium and manganese, as well as of iron oxide minerals in the soil, contributes to limiting the movement and availability of metals and metalloids (Idowu, 2022).

The rate of metal uptake also depends on the relative abundance and availability of certain elements, and on plant types. The absorption of minor elements such as arsenic and cadmium can be significantly reduced if the bioavailability of essential nutrients such as phosphorus and calcium, respectively, is sufficient, due to their chemical proximity. Researchers have identified complicated interactions between elements and the objects of their accumulation, if bioavailability depends on the amount or ratio of several elements (Gong et al., 2020). Such cases may include copper toxicity, which is associated with low levels of zinc, iron, molybdenum and sulphate (Chaney, 1988).

This scientific literature is rich in studies describing the anthropogenic contributions of industrial and mining industries to the elements' presence in the natural components, as well as their impact on bioavailability to biological entities (Ippolito et al., 2017; García-Lorenzo et al., 2019; Gauthier-Manuel et al., 2021). Options for examples may vary depending on the toxic metals' presence on soil close and distant from anthropogenic sources of contamination (Pouyat & McDonnell, 1991), on the generation of acid mine drainage (Filipek et al., 1987) on metal absorption by vertebrate organisms during laboratory tests (Brown et al., 1995), and on metal absorption by vertebrate animals near industrial enterprises (Storm et al., 1994).

Metal distribution in sediments and surface waters

In aquatic environments, after being discharged but before being taken up by biological objects, metals undergo partitioning between phases: liquid and solid. In each of the phases, under the influence of the strength of metal-ligand bonds and the concentration of ligands, further distribution between ligands occurs. Metals can be distributed into six fractions in solid phases, that is, in particles of natural water bodies, in sediments and in soils: (a) dissolved – metals that are present in a dissolved form in the water; (b) exchangeable – metals that are readily exchangeable with other ions in the environment; (c) carbonate – metals associated with carbonate minerals; (d) iron-manganese oxide – metals associated to Fe-Mn oxides; (e) organic – metals bound to organic component; (f) crystalline – metals present in crystalline structures. Sequential partial extraction procedures reveal how different metals partition within these phases. The apportioning processes are significantly influenced by disparities on environmental factors such as acidity, redox state, organic content, and other conditions. This complex interplay of factors affects the metals distribution in a liquid environments and is decisive in determining their bioavailability and potential impact on ecosystems. Studies by Elder (1989) and Salomons (1995) have contributed to our understanding of these partitioning dynamics in aquatic systems.

The carbonate fraction can precipitate and accumulate in the ground cover. This fraction consists of metals chemically associated with carbonate minerals contained in soil and sedimentary rocks. Metals adsorbed on coatings or on particles of Fe-Mn oxides constitute the iron and manganese oxide fraction. The crystalline fraction includes metals found in crystalline arrangement of metals that are usually inaccessible to biota. The organic fraction includes metals associated with different organic matter forms (Sarkar, 2021).

Hydrogen ion activity, commonly expressed as acidity index, stands out as arguably the most influential and significant criterion in the speciation of metals, in their potential bioavailability in aqueous solutions, transfer into living organisms, solubility from mineral surfaces. The acidity indicator plays a pivotal role in the processes of assimilation, removal and transition into metal hydroxide solution. In natural water conditions, most metal hydroxide minerals exhibit extremely low solubility. As the acidity indicator decreases, the hydroxide ion activity increases, leading to an increase in the solubility of metal hydroxide minerals. Consequently, metals that go into solution will potentially be more available for absorption by organisms and involved in biological cycles as the acidity level decreases. In an ionic structure, often pose a greater danger to aquatic organisms due to their high toxicity, highlighting the crucial role of pH in determining the environmental impact of metals in aquatic ecosystems (Salomons, 1995).

Adsorption, the process wherein dissolved metals bind to solid particle surfaces, particularly organic matter, aluminium oxide minerals, iron oxide mineral, manganese oxide minerals, clay, is highly dependent on the acidity indicator. Additionally, the active surfaces' availability and the dissolved metal component in the environment also play crucial roles in the adsorption process. The pH of the environment influences the charge on these surfaces and, consequently, the affinity of metals for adsorption. The interaction between pH, particulate surfaces, and dissolved metal content is integral to understanding the fate and bioavailability of metals in marine schemes (Elhaj Baddar et al., 2023; Liao et al., 2023; Stauber et al., 2023). Metals exhibit varying tendencies to be adsorbed for various values of acidity indicator, and the sorption ability of oxide surfaces typically changes from nearly 0% to close to 100% approximately in the range of 2 pH units. For different metals, the adsorption edge, which represents the pH range in which a rapid change in sorption capacity occurs, differs. This feature promotes the precipitation of various metals over a wide range of acidity index' values (Rieuwerts, 1998).

As a consequence, mixing metal-rich, acidic water through higher pH value, metal-poor water can lead to the spreading and parting of metals. Altered metals are adhered onto several media transversely a variety of pH values. Cadmium and zinc normally take adsorption limits at higher pH matched to iron and copper resulting in much mobile and possibly to be more broadly detached. Adsorption limits also differ with the levels of the complexing agent; thus, higher levels of the complexing agent upsurge the pH of the adsorption limit. The interplay between different cations in aquatic environments is indeed complex and crucial for understanding metal adsorption dynamics (Bourg, 1988). The competition between major cations like magnesium (Mg^{2+}) and calcium (Ca^{2+}) with other metal cations for adsorption sites significantly influences the fate and mobility of metals in such environments. Let's delve deeper into these interactions and their implications (Salomons, 1995).

The size of particles and the resultant total surface area accessible for adsorption are vital features in adsorption practises that can influence metal bioavailability (Luoma, 1983). Minor units with large surface-area-to-mass ratios allow for further adsorption likened to an equal mass of large units with

small surface-area-to-mass ratios. Decreased adsorption can increase metal bioavailability by uplifting levels of dissolved elements in the nearby water.

The size of particles released during mining activities hinge on the exact mining and beneficiation methods employed. Finely milled ore has the latent to discharge abundant lesser particles. These lesser particles can be more broadly disseminated by water and wind and can also serve as sites of improved adsorption. Subsequently, the environmental influence of mine tailings discharge into fine-grained sediment, such as silty clays normally originate in many plays, may be significantly lesser than that of tailings discharged into sand or coarse-grained sediment with lesser surface area and adsorption capability. Understanding the particle size distribution is crucial for assessing and mitigating the environmental impact of mining activities (Phelelani, 2007).

Temperature plays a significant role in metal speciation as utmost chemical response degrees are extremely subtle to temperature variations (Elder, 1989). A temperature rise of 10 °C can dual biochemical response degrees, which are often the dynamic force for kinetically slow responses in Earth's surface conditions, enhancing the trend of a co-ordination to reach stability. Temperature can influence the extents of metal assimilation by organisms because biological route degrees, as mentioned earlier, classically paired at every 10 °C temperature increase (Luoma, 1983; Prosi, 1989). The high temperature may disturb both the inflow and efflux degrees of metals, leading to variations in net bioaccumulation. Understanding the temperature dependence of these processes is crucial for assessing the impact of temperature changes on metal cycling in aquatic environments (Luoma, 1983).

Today, organic carbon-rich soil, stuck interstitial solutions frequently generate a sturdily sinking (anoxic) condition. The low redox potential in the surroundings would be able to facilitate sulphate decrease and the removal of sulphide minerals. Throughout diagenesis, an important quota of the non-silicate-bound portion of possibly lethal metals such as arsenic, cadmium, copper, mercury, lead, and zinc can experience co-precipitation using pyrite, making unsolvable sulphides thereby rendering them unattainable to biota. Seasonal variations in flow rates or storms that introduce oxygenated (sea) water can trigger rapid reactions in this anoxic sediment, leading to the release of substantial proportions of these metals. The processes of pyritization and de-pyritization likely play a crucial role in controlling the bioavailability of many trace metals, particularly in marine environments (Morse, 1994).

Metal uptake paths into aquatic organisms

Metal absorption of metals by plants and apportioning in the soil are pooled in the marine system. Two major pathways or absorption routes are accessible for metal assimilation in bond- and (or) detritus-feeding marine species: (i) incorporation of metal-enriched dregs and deferred particles during nurturing, and (ii) uptake from solution. Subsequently, information on geochemical responses of metals in water and dregs are essential to comprehend panels on metal bioavailability in regular water. Inappropriately, numerous organic influences regulating metal bioaccumulation in marine organisms are ambiguous; this point strictly bounds our attentive of metal bioavailability (Luoma, 1983).

Study on bioavailability propose that marine organisms proficiently assimilate free metal ions, precisely metal hydroxides, from solution. Likewise, surface-dwelling animals show a complex effectiveness in enthralling metals from solutions associated to straight digestion of particulate matter. Accordingly, geological and ecological situations that upsurge

dissolved metal loads, such as lesser pH, lead to larger metal bioavailability. Unintended influences, such as higher particle or sediment size, can also contribute to improved metal bioavailability by reducing adsorption and elevating dissolved metal contents. Although metal assimilation from ingested particulate matter is crucial, especially considering the high metal concentrations in this form, the availability of metals in solution vestiges an important influence in bioaccumulation (Luoma, 1983).

The effectiveness of bioaccumulation through dregs absorption is influenced by the geochemical possessions of the sediment. Luoma (1983) illustrates the difference in cadmium assimilation from sediment iron content. In sediment rich in iron oxides, cadmium uptake was not observed, while a notable portion of total cadmium uptake occurred when clams ingested iron-poor sediment. This point out the significance of sediment alignment in inducing the bioaccumulation of metals by marine organisms.

Transfer of heavy metals from soil to plants

Bioavailability of heavy metals is a practise that depends on a mixture of chemical, biological and environmental factors (Guala et al., 2010). The heavy metals build-up in plants extremely depends on the accessibility in the soil (Annan et al., 2013). The greater the extent of the heavy metals in the soil, the greater the predisposition of build-up in plants matters (Vaikosen & Alade, 2011). Heavy metals are not normally impassive even after the conduct of waste and thus upsurge risk of soil pollution, border with plants and roots, and consequently to the food chain when eaten by animals and humans. Plants absorb metals from soil and water, they mainly accumulate in the roots, and then some quotas are transfer to parts of plant. Plant can stop heavy metals through preoccupation and build-up by roots, adsorption onto roots, or precipitation within rhizosphere (Yoon et al., 2006).

Geochemical and ecological procedures that upset bioavailability

Indeed, the availability and impact of metals in aquatic environments are influenced by a complex interaction of geochemical and biological factors. Understanding how these factors work together is crucial for assessing ecological risks and managing ecosystems efficiently. These are the most important factors affecting metal availability: (i) metal levels of solutions; (ii) solute metal speciation; (iii) metal levels in food; (iv) metal apportioning among ligands within food; (v) effect of other cations; (vi) temperature; (vii) pH value; (viii) redox potential. Assimilation happens when absorption of one metal brings some mixtures that disturb build-up of both metals. Absorption of Zn by Cd exposure have been experimented. Differences are usually noticed in concurrent disclosure to some metals. Desorption of zinc uptake occurs during exposure to cobalt and to copper in phytoplankton and microalgae. Differences between cadmium and zinc may be observed in phytoplankton and microalgae. Some studies report differences in other metals, such as between mercury and cadmium or between lead and copper in other organisms. In addition, common metals, including magnesium and potassium, are capable of inhibiting some organometallic interactions. This phenomenon facilitates the entry of zinc into the fish's body, but at the same time it does not affect the absorption of cadmium and copper. Observational research suggests that the ability of some potentially toxic cationic metals to be absorbed by organisms, such as cadmium, cobalt, copper, nickel, and zinc, in anaerobic sediment is linked to the overall concentration of the indicated metals in pore fluids (Ankley et al., 1994). It has been proposed that measuring control of acid volatile sulphide (AVS) and at the same time extract the metal (SEM) contents of sediment can predict these metals bioavailability. AVS represents the sulphide fraction extracted by cold HCl, primarily

consisting of iron-sulphide complexes, while SEM is the sum of metal concentrations simultaneously extracted with AVS. Elevated toxicity degree in benthic fauna, typically invertebrates, and supposedly increased bioavailability of the indicated metals occur when the SEM-AVS ratio exceeds one. As mentioned earlier, temperature parameter can have a significant impact the speed of metabolic processes, with rates doubling for each interval of temperature increase by 10 °C. However, this upsurge in biological process rates does not necessarily lead to complex metal bioaccumulation, as both inflow and efflux rates of metals may be higher. The transport of metals can vary between relatively unpolluted systems and concerned or contaminated systems (Lee et al., 2000).

In unpolluted systems where metal contributions primarily result from the erosion of watershed substrates, particulate transport predominate (Elder, 1989). In contrast, in disturbed or polluted systems, such as those affected by acid-mine drainage, point sources often deliver metals in a soluble phase or related to organic matter, leading to a higher amount of dissolved metals and increased bioavailability (Salomons & Forstner, 1984).

Bioavailability assessment by selective chemical abstraction

Bioavailability assessment is significantly influenced by the choice of chemicals and methods for the extraction of certain elements in soil, as it determines their solubility. Various soil testing procedures and fractional or sequential chemical extraction techniques are mostly used to study metal behaviour. Some of these extraction techniques are:

- water or MgCl₂ at neutral or ambient soil pH – used for easily soluble metals;
- solubility in a weak base (acidity index 9) – applied for humic substances;
- a weak acid or an acid with excess water in a buffer solution, where the acidity index takes values in the range of 2...5 – remove metals linked with carbonate segments;
- chelating agent such as EDTA or DPTA buffered (to acidity index 7) – used for complexation;
- hydroxylamine hydrochloride – targets the "reducible" phase linked with iron and manganese oxides/hydroxides;
- strong acid (HCl, acidity index 1) – identifies the maximum motion of most metals;
- oxidation by hydrogen peroxide – remove metals that are connected to organic matter and/or sulphide minerals;
- strong oxidizing acid (HNO₃) – executes the previous two steps simultaneously;
- combined action of strong acid and HF – dissolves residual silicate minerals.

The nature of the extractants depends on factors such as sediment/soil type, environmental conditions, and the specific metals of curiosity. But, it's vital to note that these sequential/fractional extractions are "operational," meaning they are not completely explicit to metals or chemical stages. Therefore, any determination of bioavailability should be carefully calibrated with direct measurements of the actual behaviour of metals in soil and plants. For example, O'Connor (1988) increases alarms about the use of the DPTA technique, showing that its consequences are occasionally similar to plant uptake and sometimes not. Subsequently, he commends direct analysis of the total plant and/or its constituent parts, in addition to chemical leaks, to precisely determine bioavailability (Chao, 1984).

CONCLUSION

The bioavailability of metals free from mineral deposits is a multifaceted and dynamic route, predisposed by numerous unified chemical, biological, and ecological features. These factors can differ over time and among diverse microorganisms, plants, and animals. In the context of topsoil and shallow water, several key factors come into play, as outlined below.

Mining Method: The method used for mining can significantly affect the release of metals. Different mining techniques may expose minerals to varying degrees, influencing subsequent metal release.

Presence or Absence of Sulphide Minerals: Sulphide minerals, when present, can have a substantial impact on metal release. For instance, metals associated with sulphide minerals may become more bioavailable under certain conditions.

Water Quantity: The amount of water present in the environment plays a crucial role. The quantity of water can influence the transport and dispersion of metals, affecting their bioavailability.

Acid-Buffering Capacity: The ability of the environment to buffer against acidity is important. Acidic conditions can enhance the release of metals, impacting their bioavailability.

Existence of Organic Substance and Fe/Me Oxide Minerals: Organic matter and minerals like iron and manganese oxides can interact with metals, affecting their speciation and bioavailability.

Element Speciation: The chemical phase in which metal constituent occurs (speciation) is a key determinant of its bioavailability. Different species of a metal may have varying degrees of mobility and toxicity.

Concentrations of other Constituents: The presence of other constituents in water, such as ions or complexing agents, can influence the behaviour of metals. Competition for binding sites or formation of complexes can affect bioavailability.

Field and laboratory studies conducted at specific locations, by means of soil, sediment, plants, and careful choice of chemicals for extraction are crucial for a detailed understanding of these complex environmental processes. Such studies provide insights into the interactions between minerals, metals, and the surrounding ecosystem, helping to assess and manage the potential environmental impacts associated with metal release from mineral deposits. These studies contribute significantly to our understanding of the complex dynamics governing the availability and uptake of metallic and non-metallic element in various environmental settings.

Author's statements

Contributions

The authors declare that they have made equal contributions to the current research, namely: Conceptualization, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing were performed by B.N.H. and G.G.Y.

Declaration of conflicting interest

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No data were used for the current study.

AI Disclosure

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