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Review article

Barium distribution, dynamics and fate in terrestrial and aquatic environments

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ABSTRACT

Barium (Ba) can be found in nature as Ba minerals, such as barite ($BaSO_4$), hollandite ($Ba_2Mn_8O_{16}$), and witherite ($BaCO_3$), and is primarily located in rock-forming minerals, such as potassium-feldspars, micas, apatite, and calcite. Commercial applications for Ba include the production of pesticides, explosives, drilling fluids, and detergents. In addition, Ba is utilized as a pigment in paints, filler in rubber and paper, and as a contrast material for gastrointestinal tract X-ray inspection. In saline soils with high chloride concentrations, Ba forms soluble barium chloride ($BaCl_2$) and becomes more mobile. However, Ba ions are not highly adsorbed in acidic environments, and Ba precipitates become more soluble in acidic soils. Barium is recognized to negatively affect most organisms when it is present in large concentrations. By consuming drinking water and food sources that contain Ba, such as fish and marine life, the general population gets exposed to Ba. Humans with high levels of Ba may experience cardiac arrhythmia, vomiting, diarrhea, hypokalemia, severe hypertension, and even death. While reverse osmosis filtering systems can be used to remove Ba from aqueous media, including drinking water sources, immobilization and phytoremediation methods can help to reduce Ba contamination in soil. The present review provides an insight into the origin, geochemistry, health risks, remediation techniques, and risk management of Ba in complex environmental matrices, such as soil and aquatic ecosystems.

1. Introduction

Barium (Ba) is present as a Group 2 element in the Periodic Table and shares certain chemical characteristics with lead (Pb), strontium (Sr), and calcium (Ca). During the weathering of rocks and minerals, Ba can be released into the environment (Hamidi et al., 2016). Barium is found in Ba-minerals such as hollandite ($Ba_2Mn_8O_{16}$), witherite ($BaCO_3$), and barite ($BaSO_4$). Barium is used to produce pesticides, fire extinguishers, drilling fluids, soaps, and explosives. About 80 % of the Ba is utilized as barite, which is used as a weighing filler to create high-density drilling muds for oil and gas wells. It is also used as filler in paper and rubber, as a pigment in paints, and as a mixture (lithopone) when combined with zinc sulphide. Barium also acts as a "radio-opaque" substance during X-rays of the gastrointestinal tract (Patnaik, 2003; Kaur, 2013). $BaCO_3$is

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used to manufacture ceramic permanent magnets and improve specialty glass products' refractive index. Cement manufacture, especially arc welding, glass manufacturing, electronics, X-ray radiography, cosmetics, medicines, inks, and paints are just a few of the industries that use Ba compounds (Lamb et al., 2013). It is also used to shield against radiation in television and cathode-ray tubes. Certain Ba compounds have also been used as insecticides and rodenticides, such as barium fluorosilicate, barium metaborate, and barium polysulfide (CICAD, 2001). Barium ions usually do not form stable compounds with dissolved organic matter in soil; instead, they are adsorbed onto soil mineral components through ion exchange reactions. Barium is mainly found in inorganic complexes and is stable in a +2 valence state in the natural environment (Du et al., 2023; Lamb et al., 2013). Due to its propensity to create insoluble salts in water and its ability to be weakly complexed by fulvic and humic acids, Ba is typically immobile in most soil systems.

The calcium carbonate ($CaCO_3$) concentration, cation exchange capacity, and pH are the critical soil properties that influence Ba transfer to groundwater (Jeske, 2013; Myrvang et al., 2016a). In the presence of sulphate ions, like in acid sulphate soil, Ba can also precipitate as $BaSO_4$. However, Ba forms soluble barium chloride ($BaCl_2$) and becomes more mobile when there is a high chloride concentration in saline soil. Since Ba precipitates become more soluble and Ba ions are not as firmly adsorbed in acidic environments, Ba may become more mobile in acidic soils (Cappuyns, 2018). Barium is prone to precipitate as insoluble salts like $BaSO_4$ and $BaCO_3$ in aquatic conditions, depending on the concentration of inorganic anions like sulphate and carbonate. The salts of Ba easily soluble in water are chloride, acetate, perchlorate, and nitrate. By forming ion pairs with anions like chloride and bicarbonate, waterborne Ba can also be adsorbed to sediments. A considerable amount of Ba is then removed from surface waters by the sedimentation of suspended solids. Barite precipitation in microorganisms is another method of removing Ba from fresh and marine waters.

The primary source of anthropogenic Ba emission is industrial activities. The atmosphere, soils, surface waters in rural and urban regions, and various foods contain Ba (Tables 1 and 2). For instance, Ba is released into the ecosystem when offshore drilling operations regularly release drilling wastes and mud into the ocean. Although barite is consumed orally under specific conditions, little is known about the possible consequences that environmental exposure may cause to ecological receptors and humans (Viana et al., 2021a). Reverse osmosis systems can be used to remove Ba from aqueous media, including drinking water sources, while immobilization and phytoremediation methods can help to reduce Ba contamination in soil (Brown et al., 2002; Kochkodan et al., 2015).

A handful of studies are available regarding the dynamics and fate of Ba in terrestrial and aquatic ecosystems, despite the growing use of Ba in many industries and its subsequent release into the environment (Kaur and Prakash, 2022; Kojola et al., 1979; Hao et al., 2022). Barium contaminations in aquatic and terrestrial environments, as well as their cleanup, have been discussed by very few researchers (Peana et al., 2021; Schlesinger and Vengosh, 2016; Goldberg, 1997). Most reviews have focused on Ba contamination and toxicity issues (Park and Schlesinger, 2002; Howe, 1998). This review provides a thorough bibliometric analysis of the sources and/or origin, biogeochemistry, removal methods, and risk management of Ba dispersal in complex environmental matrices.

This review aims to critically examine the literature on Ba sources and their reactions, Ba remediation, and possible remediation outcomes of Ba-contaminated soil and aquatic systems. The following keywords were used in the Web of Science core collection/database to search the relevant literature: "barium" OR "barite" AND "environment" OR "soil" OR "lake" OR "river" OR "sediment" OR "marine" OR "ocean" AND TS= ("remediation*" OR "phytoremediation") AND TS= ("soil" OR "terrestrial"). Overall,>1000 results were obtained. VOSviewer (version 1.6.19) was used to visualize the results. Fig. 1 shows the scope of this

Table 1
The different forms of barium in the soil and aquatic environments.

Environment	Forms of Barium	Sources	Description	References
Soil	Barium (Ba)	Mining, industrial activities, and natural weathering	Barium (Ba) naturally occurred as an alkaline earth metal. Typically found in moderate quantities in the environment. Previously recognized minor constituent present in food and potable water. Industrial applications greatly influenced its distribution and prevalence.	Lu et al. (2019)
Soil	Barite ($BaSO_4$)	Geological deposits and mining	Barite primarily found in sedimentary deposits. Serves as a major commercial source of barium, also known as barytes or heavy spar. Widely utilized as a weighting agent in gas wells and drilling muds for oil. Exhibits insolubility in water, enhancing its value in various industrial applications.	(Lamb et al., 2013; Lu et al., 2018)
Soil and aquatic	Witherite ($BaCO_3$)	Natural weathering, industrial activities, and geological deposits	Insoluble minerals ($BaCO_3$) are utilized in the production of bricks, optical glass, rodenticides, and steel. Exhibits low solubility inwater and remain stable in the environment for long periods of time. Can be dangerous if consumed unintentionally.	Ippolito and Barbarick (2006)
Soil and aquatic	Barium ions (Ba^{2+})	Natural weathering, industrial activities, and geological deposits	Barium ions enter soil via precipitation or dust. In water, their concentration is controlled by natural anions.	(Kaur, 2013; Lu et al., 2018; Gjyli and Matta, 2018)
Aquatic	Barium Chloride ($BaCl_2$)	Industrial discharge and urban runoff	This substance plays a crucial role in pigments, aluminium	(Kravchenko et al., 2014)

(continued on next page)

Table 1 (*continued*)

Environment	Forms of Barium	Sources	Description	References
			production, sugar refining, leather tanning and finishing processes, and serves as a key component in pesticides, specifically rodenticides.	
Aquatic	Barium Hydroxide ($Ba(OH)_2$)	Natural weathering and industrial discharge	$Ba(OH)_2$ has higher solubility in water compared to barium sulphate and barium carbonate.	(Gjyli and Matta, 2018)
	Barium Nitrate ($Ba(NO_3)_2$)		Barium nitrate can enter soil and water systems via industrial processes like the production of fireworks, where it serves as a popular green coloring agent.	

review and the article's decision-making process. In addition to helping to promote sustainable solutions for minimizing Ba pollution in the environment, the review aims to bridge knowledge gaps about the growing concerns of Ba accumulation in the soil and aquatic environments (Fig. 2). This information will help develop knowledge on reducing the environmental toxicity of Ba to human and ecosystems. This review has also identified areas where additional research needs to be conducted to effectively address knowledge gaps in studying the dynamics of Ba in environmental matrices.

2. Sources and distribution of barium in the environment

2.1. Sources and distribution of barium in soil

Ba, a potentially toxic element (PTE), is widely dispersed throughout the Earth's crust (mean value: 650 mg kg^{-1}). However, its mass fraction varies greatly depending on the parent material, ranging from 1 mg kg^{-1} for ultrabasic to 830 mg kg^{-1} for acid rocks (Yaroshevsky, 2006). As a result, typical Ba levels in soils worldwide vary widely, ranging from 84 to 960 mg kg^{-1} (Kabata-Pendias and Mukherjee, 2007). As a result, the following Soil Quality Reference Values for Ba represent global natural variations: Brazil (150 mg kg^{-1} – Conselho Nacional de Meio Ambiente (CONAMA), 2009), Canada (500 mg kg^{-1} – Canadian Council of Ministers of the Environment, 2013), the Netherlands (160 mg kg^{-1}– Carlon et al., 2007), Australia (300 mg kg^{-1} – Lia, 2010), and Poland (200 mg kg^{-1}– Carlon et al., 2007). In contrast to loamy and clay soils, which have the highest Ba content, organic soils are considered the most Ba-depleted sources (Kabata-Pendias and Mukherjee, 2007). Barium enrichment can be seen in the soils subjected to intense and prolonged pedogenic processes, even those derived from Ba-deprived parent materials, such as Tertiary sandstones and shales (Magaldi and Arfaioli, 2015). Italian Paleosols under extreme weathering conditions during repeated wet and dry cycles (of the inter-glacial periods in the Pleistocene) showed a similar Ba enrichment. Using various acid digestion processes and instrumental quantification methods, such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Mass

Table 2
Barium concentrations detected in the air, dust, mining zones, soils, and water posed potential environmental contamination.

Country	Sample types	Barium concentrations	Main findings	References
Southwest China	Soil	518 - 65,760 $mgkg^{-1}$	High quantities of barium (Ba) were found in rice paddy soils, especially around barium salt plant and mining sites.	Lu et al. (2019)
United States	Soil	407 $mgkg^{-1}$	Our study indicated that the utilization of biosolids elevated the overall barium content in soil. However, the resulting barium precipitates were insoluble, posing no significant environmental risk in comparable soil types subjected to similar weather and management practices.	Ippolito and Barbarick (2006)
South Sudan	Water	140 mgL^{-1} (drilling pit) and 0.61–1.2 mgL^{-1} (oil pit)	The utilization of barite as a weighting agent in drilling muds indicated that improperly managed waste from the oil sector was a significant contributor to environmental contamination.	Pragst et al. (2017)
Kupa river drainage basin	Soil	5790 $mgkg^{-1}$	Certain forms of barium compounds readily dissolved in water, leading to their presence in various aquatic habitats such as rivers, streams, and lakes. This resulted in the accumulation of barium in fish and other aquatic organisms.	Frančišković-Bilinski (2006)
Southern Poland	Dust	124–196 ppm	The higher levels of barium detected in antlers indicated elevated air pollution resulting mainly from the combustion of coal for household use, which was exacerbated by geographical features that hindered effective air flow.	Jabłońska et al. (2016)
Southern Poland	Dust	500-1000 μgg^{-1}	Elevated concentrations of barium were detected in airborne dust originating from power plants. Barium levels in the tonsils of children residing near these dust-emitting facilities were notably high. The presence of barium in the tonsils could have potentially served as an indicator of plant pollution in the area.	Nogaj et al. (2011)
Western Australia	Water	7.59 $\mu g\ L^{-1}$- 464.56 $\mu g\ L^{-1}$	The increased exploration of shale gas drilling has notably elevated the potential for barium contamination in groundwater and well systems.	Ridgway and Wajrak (2019)
Netherlands	Water	120 - 10,000 ppm	The increase in death rates among the marine nematode *Rhabditis (Pellioditis) marina* was observed.	Lira et al. (2011)
Southern Brazil	Soil	598 mg kg^{-1}	Due to barium's low solubility, the risks associated with groundwater contamination and its transfer into the food chain is minimal.	(do Amaral Sobrinho et al., 2018)
Southwestern China	Mining zone	6.7–483.1 $\mu g\ L^{-1}$	The heightened levels of Barium found in the water indicated that the contamination of Barium and its dispersion within nearby aquatic ecosystems originated from the mining sites.	Lu et al. (2018)
NA*	Mining zone	700 mg kg^{-1}	Barite-contaminated soils result in various harmful effects on a wide range of organisms, leading to increased Barium movement within the ecosystem.	Lamb et al. (2013)
Gujarat (India)	Soil	266.3–471.7 mg kg^{-1}	Elevated levels of toxic metals in soil diminish fertility; intensify contamination in the food chain, resulting in their accumulation in consumables, posing a risk to human health.	Krishna and Govil (2007)

NA* -Not available.

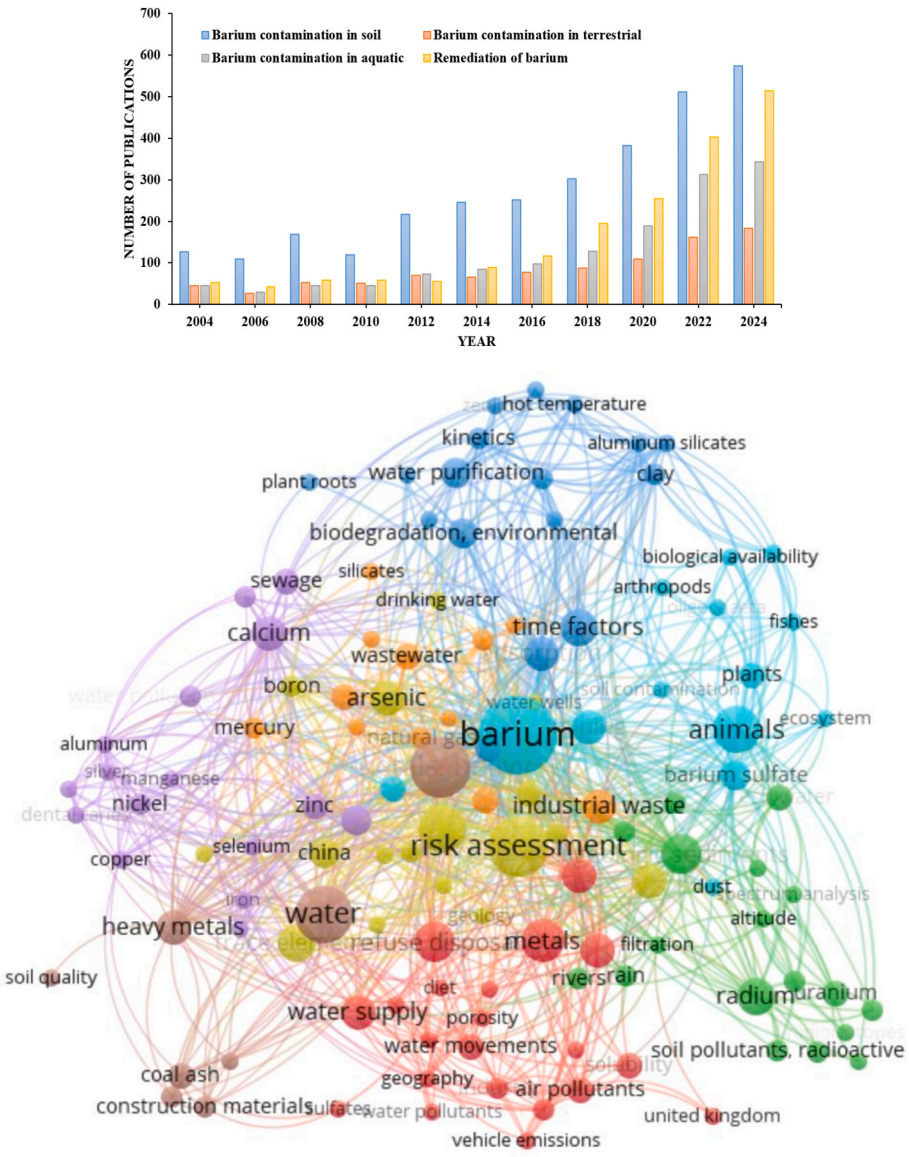

Fig. 1. A. The number of publications on barium over the last 20 years (splitting publications into various categories); Fig. 1 B. Number of publications (2004–2024) covering barium contamination in soil through the keyword co-occurrence network in VOSviewer (version 1.6.19) with node size and label font size; Fig. 1 C. Figures depicting the bibliometric analysis method that results in the selection of literature in a specific database, classifying, and listing them in parallel with in-depth or quantitative analysis.

Spectrometry (ICP-MS), the background levels of Ba in the soil environment across different countries are shown in Table 3.

Compared to other well-studied PTEs like As, Cd, Hg, and Pb, Ba is an overlooked element due to the limited number of studies examining its existence in soils despite its comparatively large abundance in the pedosphere (Cappuyns, 2018). Because of its strong affinity for Mn in soil and its precipitation as carbonate and sulphate, Ba is not readily mobile under the soil ecosystems (Quevauviller, 1998). However, Jeske (2013) found that the potentially bioavailable fractions (F1 and F2 fractions) contain more than 50 % of the total Ba levels when using the five-stage Tessier sequential extraction procedure (Tessier et al., 1979) in Poland forest podzol soils (14.80–38.20 mg kg^{-1} Ba) having no anthropogenic influence. Cappuyns (2018) conducted a thorough fractionation analysis of Ba in 14 alluvial soil samples from Flanders, northern Belgium, utilizing single-phase and three-step sequential extraction procedures. They used the following single-phase extractants for the extraction procedure: 0.01 mol L^{-1} calcium chloride, 0.05 mol L^{-1} ammonium-EDTA, and 0.43 mol L^{-1} acetic acid. The three-step sequential extraction process followed the methods of Rauret et al. (1999). The Standards, Measurements, and Testing Programme guidelines (previously the BCR or Community Bureau of Reference) were also used for the sequential procedures. The results showed that Ba mobility in soils was minimal. Barium was preferentially detected in the residual portion of the BCR sequential extraction process in soil samples that were naturally enriched with Al and Ca. On the other hand, Ba was predominantly present in the reducible fraction in samples with elevated Fe levels, suggesting that Ba was associated with iron (hydro) oxides. While assessing Ba fractionation, the authors emphasized that unexpected side reactions could happen during soil extractions, particularly precipitation of $BaSO_4$ in samples enriched with sulphate.

Using a sequential extraction process designed for tropical soils, Corrêa Nogueirol and Ferracciú Alleoni (2013) studied the possible mobility of Ba, Cu, Ni, Pb, and Zn in the disturbed soils of anthropogenically impacted sites contaminated with waste from the automotive

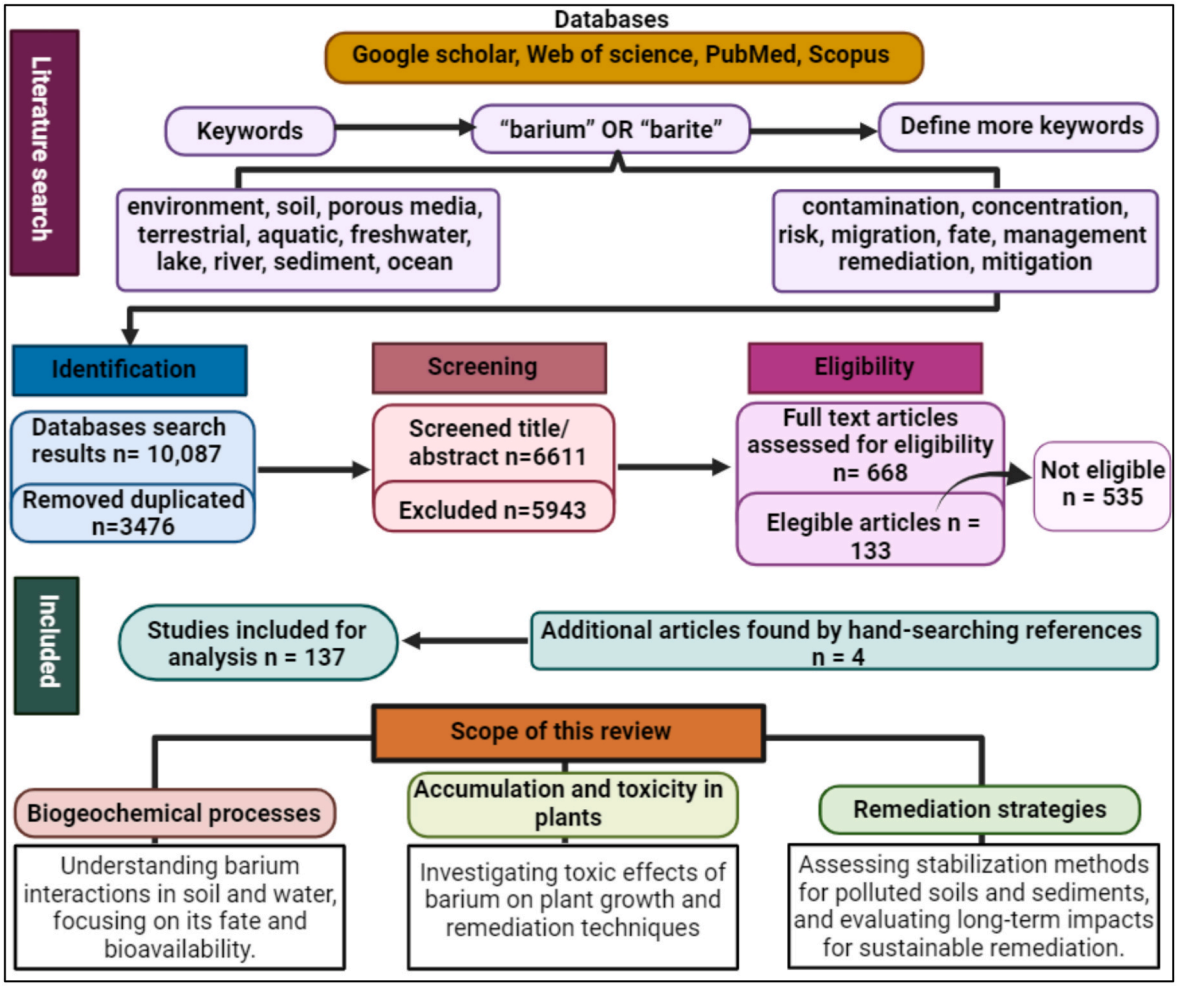

Fig. 1. (*continued*).

industry (Silveira et al., 2006). Total metal levels at the contaminated site exceeded the European Community's intervention limits. The possible application of Ba isotopes as a tracer in soils was investigated by Gong et al. (2020). An analysis of a deep (about 6 m depth) Chinese latosol profile revealed Ba mass percentages along the weathering layers that ranged from 53.8 to 547 mg kg^{-1}. This study assessed three fractions of a sequential extraction scheme: residual Ba, Fe-Mn (oxyhydr) oxides linked with Ba, and exchangeable Ba. A multi-collector ICP-MS was used to measure the Ba isotope ratios. They have attained the following significant conclusions: i) Ba retention was primarily dependent on the exchangeable and reducible fractions, and the $\delta^{137/134}$Bain these fractions showed that the soil was enriched by Ba isotopes with smaller atomic masses when compared to the parent material; and ii) in highly weathered soils, leaching was facilitated by soil/water moving downward to the soil profile, which dominates the transport of exchangeable Ba.

2.2. Sources and distribution of barium in the aquatic environment

The distribution of Ba in aquatic bodies is often also controlled by natural processes. Barium salts of acetate, nitrate, and halides dissolve in water, whereas their carbonate, chromate, fluoride, oxalate, phosphate, and sulphate counterparts show low solubility. Low pH groundwater in contact with granite-like igneous rocks, alkaline igneous and volcanic rocks, and sedimentary rocks enriched with Mn usually shows the highest amounts of Ba in drinking water (WHO, 2004). A comprehensive groundwater chemical database (n = 2369 water samples) covering approximately 100,000 km^2 in southern Quebec, Canada, was compiled by Bondu et al. (2020). The amounts of Ba in groundwater varied greatly, ranging from below the detection limit (0.002 mg L^{-1}) to exceptionally high values (90 mg L^{-1}), far greater than the 1 mg L^{-1} Ba recommended for drinking water in Canada. Researchers have found groundwater enriched with Ba generally had a significant amount of K and Sr at % (w/w) (Kaur and Prakash, 2022; Hao et al., 2022). This PTE can encourage environmental pollution through anthropogenic activities such as Ba mining and the production of goods containing Ba (Lu et al., 2018). The estimated 178 million tons of barite reserves in Tianzhu County, Guizhou Province, southern China, constitute over 70 % of Chinese Ba deposits. To determine the levels of total barium (TBa) and dissolved barium (DBa), Lu et al. (2018) gathered 63 water samples from Tianzhu County, China. Mass fractions of Ba for TBa and DBa ranged from 7.5 to 222.7 μg L^{-1} and up to 483.1 μg L^{-1}, respectively. They have hypothesized that the primary cause of Ba enrichment in surface and groundwater samples might be due to intense Ba mining.

Nevertheless, every reading was below the WHO's threshold level, *i.e.,* 700 μg L^{-1} Ba (WHO, 2011). Furthermore, the PHREEQC software, a geochemical speciation model, identified five primary Ba species in the water samples during analysis: $Ba^{2+,}$ $BaSO_4$, $Ba(HCO_3)_2$, $BaCO_3$, and $BaOH^+$. Nonetheless, over 89 % of all Ba chemical species were Ba^{2+}. The drop in water quality in urban areas is primarily due to the rising saline levels, and the over-exploitation of drinking water reservoirs is a matter of concern nowadays. In this regard, the hydrogeochemical behaviour of Ba, B, Rb, and Sr was studied in the Metropolitan Zone of Mexico City Aquifer, the main drinkable water supply for over 8.9

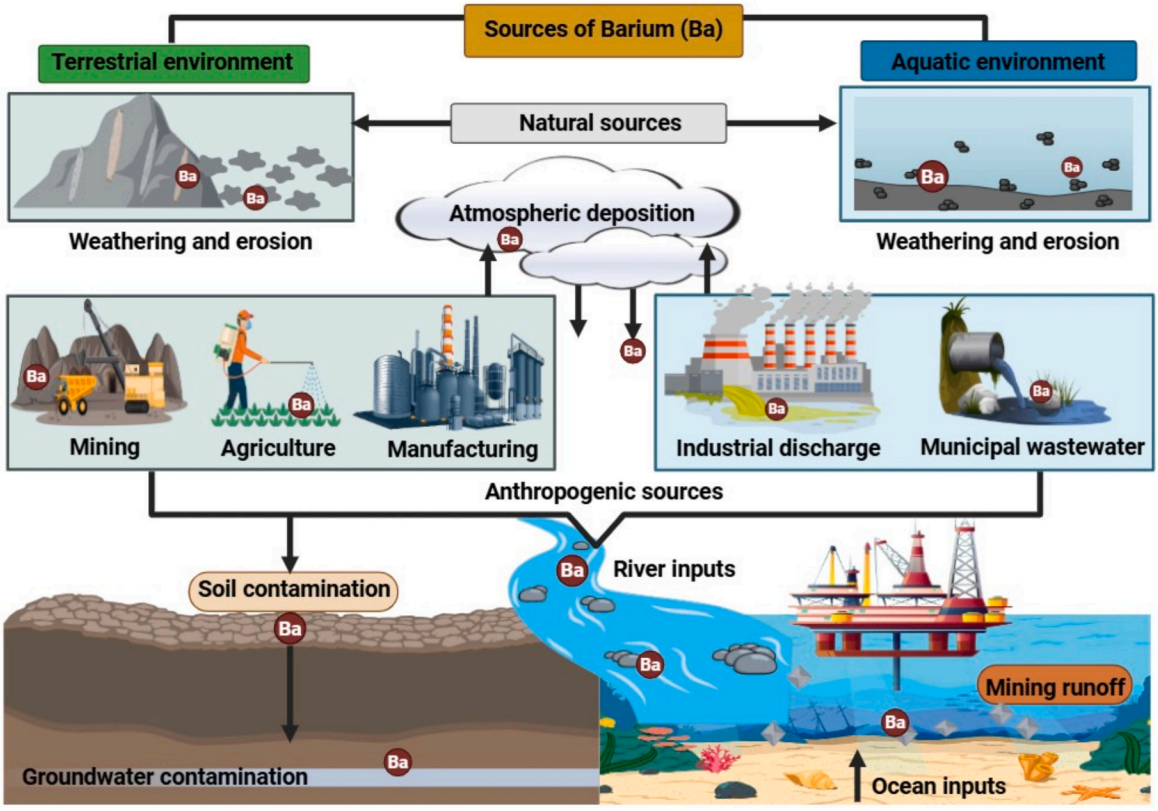

Fig. 2. Schematic showing sources of barium in terrestrial and aquatic environments.

Table 3
Barium background levels in worldwide soils.

Study area	Ba (mg kg^{-1}) mean or median	Number of soil samples	Digestion and/or quantification method	References
Near McMurdo Station, Antarctica	109 (grey soil); 145 (red soil)	12	USEPA 3050 digestion method and ICP OES	Crockett (1998)
Eastern Amazon, Brazil	16.7 (mean); 20.9 (median)	504	Aqua regia and ICP OES	Gonçalves et al. (2022)
Minas Gerais State (Southeast Brazil)	51.6 (median)	697	USEPA 3051A digestion method and ICP OES	de Souza et al. (2015)
4095 sites throughout mainland China	450 (mean)	12,400	HNO_3, HF, and $HClO_4$ digestion and ICP OES	Chen et al. (1991)
Samples from 13 out of 15 Cuban provinces	128.7 (mean)	33	USEPA 3051A digestion method and ICP OES	Alfaro et al. (2015)
33 European countries	62 (median)	2108	Modified aqua regia and ICP-MS	Reimann et al. (2018)
Northwest Siberia	224 (O horizon); 379 (B horizon-coarse); 473 (B horizon-heavy); 65.1 (peat lands)	344 soil horizons	ICP-MS*	Opekunova et al. (2019)
The main Hawaiian islands	175.15 (mean); 93.59 (median)	125	Not mentioned	Hawaii Department of Health (2012)
Northern Belgium	328 (mean); 380 (median)	749	HCl, HNO_3 and HF digestion and ICP-MS	Cappuyns (2022)
81 % of the Australian territory	66.8 (median)	1313	Aqua regia and ICP-MS	Reimann and de Caritat (2017)
British Columbia, Canada	184 (mean)	37	Digestion with 1:1 v v^{-1} HNO_3 and HCl and ICP-MS	Sanei et al. (2007)
Six cities in the State of Florida, USA	23.4 (Clay County); 119 (Ocala); 20.3 (Orlando); 48.1 (Penascola); 23.7 (Tampa); 29.1 (West Palm Beach)	214	USEPA 3050B Method and ICP-MS	da Silva et al. (2020)

million people (Morales-Arredondo et al., 2022). The acquired data on Ba allowed for essential discussions on the Ba vs. SO_4^{2-}behaviour. While sulphate can be transformed into hydrogen sulphide, the existing redox conditions determine Ba high solubility, which can lead to lower SO_4^{2-} levels. Table 4 lists the Ba mass fractions in drinking water samples collected from various countries, *i.e.,* primarily bottled mineral water. Most samples (with few exceptions) have Ba levels far below the WHO standard (700 μg L^{-1}).

3. Biogeochemistry of Ba in the environment

3.1. Anthropogenic impact on soil barium

As discussed in the present review, increased concentrations of Ba in soil and groundwater can result from mining, industrial operations, and anthropogenic impacts on agroecosystems. These factors affect the Ba biogeochemical processes. Ippolito and Barbarick (2006) investigated

Table 4
Barium mass fractions in worldwide drinking waters.

Country	Sample type	Ba (μg L^{-1}) range (mean or median)	Number of water samples	Quantification method	References
38 European countries	Bottled mineral water	0.05–26800 (29)	884	ICP-MS	Demetriades et al. (2015)
Italy	Bottled mineral water	<7–660 (80)	60	GFAAS	Fagioli et al. (1988)
Poland	Bottled mineral water	13.6–1120	23	ICP OES	Garbos and Swiecicka (2013)
Poland	Bottled spring water	4.4–430	15	ICP OES	Garbos and Swiecicka (2013)
Egypt	Bottled potable water	3.15–293	11	ICP-MS	Bekhet (2010)
Brazil	Bottled mineral water	<1–386	27	ICP OES	Santos et al. (2016)
Canada	Bottled mineral water	10–662 (211)	42	ICP-MS	Dabeka et al. (2002)
Canada	Bottled spring water	0.54–548 (65)	102	ICP-MS	Dabeka et al. (2002)
Bulgaria	Bottled mineral water	<0.018–55.3 (5.49)	17	ICP-MS	Lyubomirova et al. (2020)
Croatia	Bottled mineral water	9.33–50.3	6	ICP-MS	Kljaković-Gašpić et al. (2024)
Kosovo	Artesian, well, and tap water	0.41–590.5 (48.3)	951	ICP-MS	Berisha and Goessler (2013)
28 countries[a]	Bottled mineral water	0.02–557 (21.0)	132	ICP-MS	Krachlerk and Shotyk (2009)

[a] Australia, Belgium, Brazil, Canada, Czech Republic, Denark, Dominican Republic, England, Finland, France, Germany, Hong Kong, Iceland, Israel, Italy, Japan, Kenya, Mexico, The Netherlands, Peru, Poland, Slovenia, Spain, Sweden, Switzerland, Trinidad, the U.S., and Yugoslavia.

Ba accumulation in Platner loam soil treated with biosolids (sewage sludges) in a dryland wheat agroecosystem close to Brighton, Colorado, USA. Barium accumulation in the topsoil layer rose with the addition of biosolids. In contrast, DTPA-extractable Ba decreased with time, confirming the theory that adding biosolids to soils causes the formation of insoluble Ba precipitates. According to Thouin et al. (2019), adding ochre and cow manure to percolated soil of mine tailings from Pontgibaud, France, raised the concentration of Ba in leaching water up to 65 $\mu g L^{-1}$. Extremely high Ba concentrations in paddy soils and Ba accumulation in rice up to 3.50 mg kg^{-1} in rice grain were found in a study in Ba mining sites in China that showed the high Ba concentrations and Ba bioavailability in crops (Lu et al., 2019).

3.2. Dynamics of barium in mineral exploration

In mineral exploration within intensely weathered areas and where environmental contamination is not a major issue, the focus shifts to the geological and geochemical understanding of the mineral deposit itself, especially for detecting potential mineral ore bodies (Arndt et al., 2017; Gandhi and Sarkar, 2016). The primary goals of such exploration are to identify economically explorable mineral deposits containing the element(s) of interest, considering their geological distribution and concentration, often using geochemical and hydrogeological data to understand their mobility and behavior in a weathered environment (Blake et al., 2022). By analysing indicator minerals and understanding soil and rock geochemistry, it is possible to predict and locate mineral deposits hidden beneath the deeply weathered surface (Balaram and Sawant, 2022). In the case of Ba, in such areas with strong weathering, Ba is primarily released from mineralized black shales and associated rock-forming minerals during weathering processes and anthropogenic disturbance activities such as excavation and drilling, and breaks down crushing of rocks (Parviainen and Loukola-Ruskeeniemi, 2019; Charbonnier et al., 2022). In remote sites with less concern for environmental contamination, the released Ba can then become mobile, potentially contaminating groundwater, surface water, and soil, presenting a risk of exposure to wildlife ecosystems. For example, a significant influence of black shale weathering on riverine dissolved Ba fluxes has been demonstrated by positive relationships between dissolved Ba and associated ions such as sulphate ions and the trace element, rhenium (Re) in the Yamuna Basin rivers (Dalai et al., 2002). However, in the presence of excess sulphate concentration resulting from the weathering of black shale, Ba is expected to be precipitated as barite, thereby reducing Ba toxicity (Renock et al., 2016).

3.3. Biogeochemistry of barium in soil

The biogeochemical fate of Ba in soil depends on its speciation, which in turn is controlled by mineral weathering, nutrient cycling, microbial activity, pH, redox conditions, and anthropogenic impact (Fig. 3). Barium does not appear as a divalent cation (Ba^{2+}) in most natural waters as its quickly immobilized by SO_4^{2-} as barite ($BaSO_4$, 0.2–0.3 mg L^{-1}) and by CO_3^{2-} as whiterite ($BaCO_3$, <2 mg L^{-1}) (Cappuyns, 2018; Kabata-Pendias, 2011). Labile Ba generally has a strong affinity for exchangeable sites for clay minerals (Lee et al., 2007) and soil organic matter (SOM) (Myrvang et al., 2016a). Barium is also preferentially associated with Mn oxides (primarily as *Ba-birnessite)* and, to a lesser extent, with Fe oxides (Manceau et al., 2007).

Besides barite, all Ba salts become more soluble in the soil as pH decreases (Madejón, 2013; Cappuyns, 2018). However, the solubility of barite increases at low pH under strongly reducing conditions where the sulphate is reduced (Kravchenko et al., 2014; Madejón, 2013; Magalhães et al., 2012, 2014). The solubility of barite also increases at increasing pressure and temperature (highest at 90 °C) and by high NaCl concentrations and high temperatures in combination (Corrêa et al., 2022). High electric conductivity has also been found to reduce the Ba sorption to soil colloids such as FeO(OH) (Ye and Prigiobbe, 2018).

3.3.1. Redox reactions and soil biology

Geological, biological, and human factors can affect Ba concentration and existence, and this has a direct impact on the soil and aquatic species (Fig. 4). Magalhães et al. (2012) reported a significant increase in Ba solubilization from a Glei soil under low Eh conditions. Magalhães et al. (2014) conducted a pot experiment on barite-enriched soil under reducing conditions. They found increased concentrations of labile Ba with a reduction of the more non-labile forms. The findings demonstrated how low Eh conditions in soil increased the bioavailability and consequently promoted the uptake of Ba in rice plants. Frohne et al. (2015) found a positive correlation of Eh, Ba, and Sr in Ba-contaminated floodplain soil suspension originating from the Wupper River in Germany. About 55 % of the dynamics of Ba in their investigation could be attributed to both low Eh and DOM, although the direct influence of DOM on Ba was unclear. In a tropical histosol, peatland in Malaysia representing forest and different cropping systems, soil Ba and other trace metals were measured in dry and wet seasons (Dhandapani et al., 2020). Methane emission from soil correlated positively with OM content and Ba, Mn, Cu, Co, and Al, implying the importance of understanding the role of trace metals in the biogeochemical functions of peatlands under dry and wet seasons (Dhandapani et al., 2020). In a study on mild acidic (pH ~5.4) tropical topsoil consisting of loam and

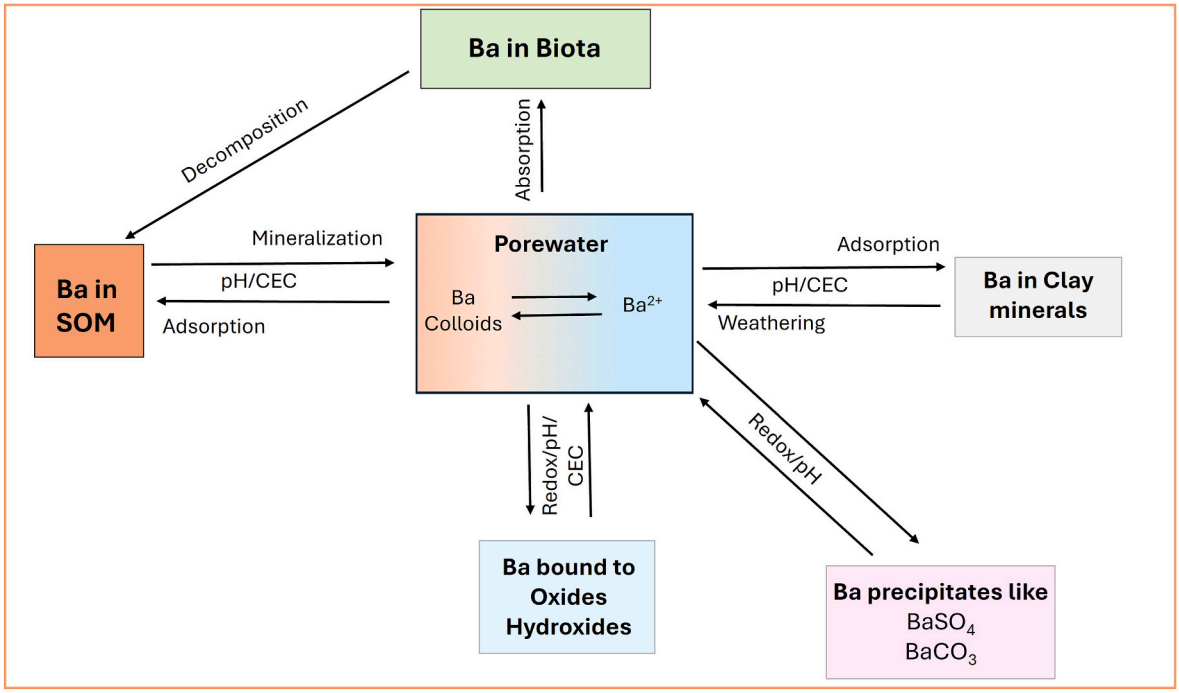

Fig. 3. Schematic showing barium biogeochemistry in soil (SOM: Soil organic matter).

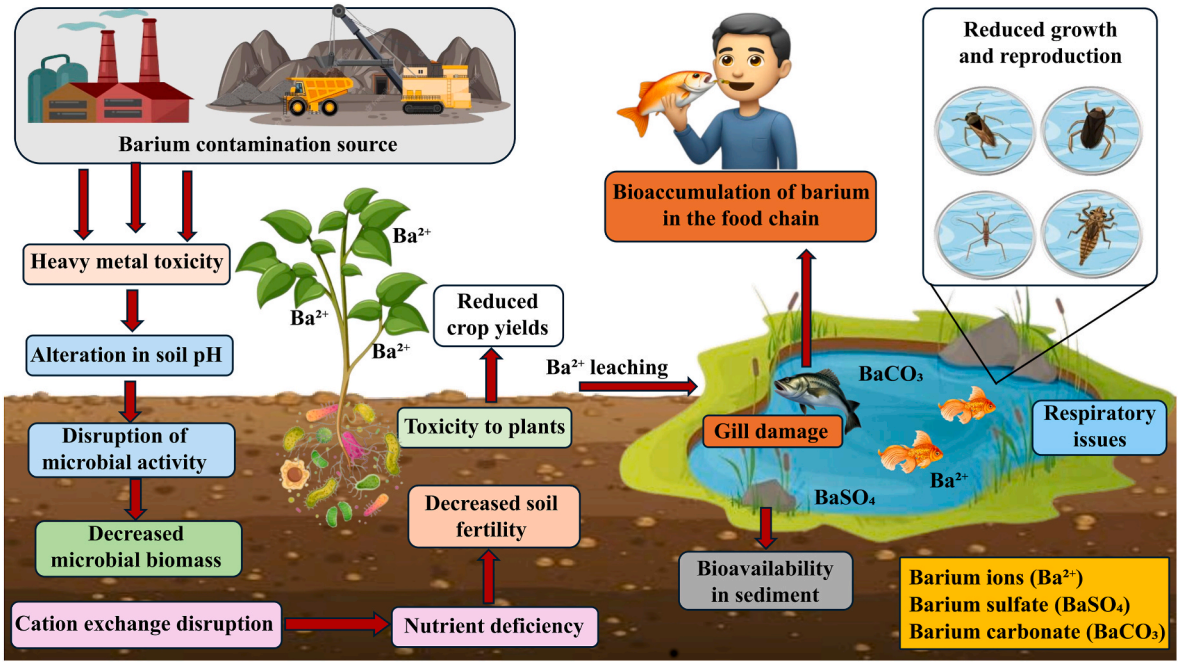

Fig. 4. Schematic highlighting the overall impacts of barium contamination on soil and aquatic organisms.

sandy loam in Malaysia; Sultan and Shazili (2009) reported that alkali and earth alkali metals (including Ba) were significantly depleted by preferential leaching and/or plant uptake process. Sanchez-Moral et al. (2004) reported that barite precipitates in bacterial biofilms on volcanic rocks in Roman catacombs of Italy. This was explained by the bacterial weathering of the rocks, which mobilized the mineral Ba. Another interesting feature of the study was that bacteria isolates later resulted in witherite precipitation, which could not have happened in the catacombs due to the presence of sulphates and gypsum.

Microbial mobilization of Ba from barite by sulphate-reducing bacteria is a relevant natural process. Both Baldi et al. (1996) and Bolze et al. (1974) reported that this takes place at strongly reducing conditions (Eh −220 mV). The study by Baldi et al. (1996) reported high concentrations of Ba in suspended particulate matter (0.42–1.58 Ba mg g^{-1}) in a Ba-rich anoxic sewage sludge from Florence, Italy. This suspended Ba was, however, effectively removed by 30 % upon aeration, increasing the Eh from −110 to 250 mV. The initial solubilization of Ba during the reducing conditions was attributed to sulphate-reducing bacteria. A laboratory study used the sulphate-reducing bacteria *Desulfovibrio desulfuricans* using barite as the only sulphate source. The bacteria solubilized three times more Ba from barite than the uninoculated control medium. Sulphate-reducing bacteria have been demonstrated to

utilize barite under sulphate-limited environments as electron acceptors for their metabolic activities in aquatic environments (Bolze et al., 1974; Báez-Cazull et al., 2008).

3.3.2. Exchangeable barium

Barium is a strong cation exchanger; hence, $BaCl_2$ is commonly used to displace soil exchangeable cations quantitatively. At soil pH below 4, Ba can be substantially released but tends to precipitate rapidly as barite in the presence of sulphate (Cappuyns, 2022). Lu et al. (2019) reported a significant increase in Ba uptake in rice at low pH (presumably at reducing conditions), indicating an increase in Ba biomobilization in paddy soil as pH decreases. As pH increases, Ba is immobilized by precipitation onto oxides and hydroxides (Lu et al., 2019; Ye and Prigiobbe, 2018). The divalent cation Ba^{2+} has nearly the same ionic radius as K^+ in natural soils (Kabata-Pendias, 2011), and Ba^{2+}can effectively substitute K^+ in the sheet interlayers of micas and negatively charged surface sites of clay minerals. Moreover, Ba can also isomorphically replace Sr and Ca in soil constituents (Alloway, 2013). Barium ions adsorbed to clay particles may be (re)mobilized by supplying K^+ and NH_4^+-rich fertilizers (Peana et al., 2021). A study by da Silva Junior et al. (2022) on nine selected soil sites in Brazil's Amazon rainforest reported a strong positive correlation between soil cation exchange capacity (CEC) and Ba retention, which was attributed to the negatively charged clay and silt colloids.

Lamb et al. (2013) found a strong relationship between Ba concentrations of pore water derived from a barite-contaminated soil (in Australia) and exchangeable Ba, indicating that ion exchange processes influence Ba solubility. Lee et al. (2007) reported a strong sorption capacity of Ba on muscovite, particularly when coated with dissolved organic matter (DOM). A study by Myrvang et al. (2016a) in Norway on Ba speciation in soil pore water of sandy soil amended with peat OM and Ba-enriched carbonatite rock powder showed that Ba^{2+} in pore water mainly originated from exchange sites on colloids associated with biotite. Immobilization of Ba^{2+} was controlled primarily by the fraction of DOM of pore water (Fig. 3). The strong relationship between pore water Ba^{2+} and Ca^{2+} ($r = 0.81$) suggests that Ba may follow the geochemistry of Ca and possibly compete for the same functional groups on SOM. Reducible Ba in peat samples collected from a minerotrophic fen in Kalamazoo, Michigan, USA, demonstrated to be primarily associated with Mn oxides and soil organic matter (SOM) (Koretsky et al., 2007).

3.4. Biogeochemistry of barium in aquatic environments

Water bodies have different concentrations of the naturally found Ba. The typical concentration of Ba in natural water, such as lakes, rivers, and seas, ranges from 29 to <0.001 μg kg^{-1} (Liguori et al., 2016). Typical values for Ba concentrations usually found in surface waters impacted by mining activities can range from 6.7 to 483.1 μg L^{-1}(total Ba) and 7.5–222.7 μg L^{-1}(dissolved Ba), which exceed the 10 μg L^{-1} Ba in surface water set by the Ministry of Environment Protection of China guidelines (Lu et al., 2018). Barium is primarily found in marine environments as the mineral barite ($BaSO_4$), which is also linked to organic carbon flux and marine biological waste, suggesting that it plays a role in the biological cycling of the marine environment (Ford et al., 2011; Liguori et al., 2016). Variable concentrations of Ba are found in marine sediments in connection with carbonates, organic matter, opal, ferromanganese oxyhydroxides, terrestrial silicates, detrital materials, and barite (Ford et al., 2011; Kojola et al., 1979). Leaching from sedimentary rocks into aquifers, as seen in some parts of the United States (Marandi et al., 2004), and the dissolution of carbonate cement in sandstones, the responsible factor for the Marília Formation in São Paulo, Brazil (Tavares et al., 2015), are the two natural sources of Ba in groundwater. Generally speaking, the geological composition, including the crystalline basement and its weathering zone, is responsible for Ba anomalies in aquifer systems and can affect the amount of Ba in drinking water reservoirs (Marandi et al., 2004). Moreover, isomorphic substitutions of Ba in clay minerals and the dissolution of soil minerals, including carbonates, sulphates, and silicates containing Ba, can both raise the amount of Ba in water through soil leaching processes (Gonneea and Paytan, 2006). The concentration of Ba in aquatic environments is directly influenced by pH, redox potential, and the presence of other solutes, such as bicarbonates. The solubility of Ba in natural fluids is influenced by pH, both acidic and alkaline environments affecting the stability and mobilization of Ba species. Barium compounds, such as $BaCO_3$, exhibit pH-dependent solubility behaviour, increasing their solubility in alkaline circumstances and reaching a plateau in acidic to neutral pH ranges. While higher pH levels can impact the stability and solubility of barium arsenate and barium hydrogen arsenate, lower pH values can increase the solubility of $BaCO_3$ (Zhu et al., 2005). Barium is released into the sediment solution under low pH and strongly anaerobic circumstances, which may impact its solubility (Carbonell et al., 1999). Carbonate precipitation may regulate the chemistry of Ba in water because Ba solubility decreases when bicarbonate species activity increases in relation to other solute concentrations in water (Fuerstenau and Herrera-Urbina, 1992; Chen et al., 2005). Redox reactions can also impact the biogeochemistry of Ba in aquatic environments. As an example, barite dissolution in anoxic marine waters can raise the Ba activity and dissolved Ba levels can rise with depth, with concentrations in surface and bottom waters across various basins ranging from 45 to 85, 64–280, and 180–460 $nmolL^{-1}$(Falkner et al., 1993).

3.5. Factors affecting barium biogeochemistry in soil and water

Generally, plant uptake of Ba from the soil is considered low (Myrvang et al., 2016b, 2017). Yet, high concentrations of Ba are found in certain plant species, *e.g.,* the Brazilian Nut tree (Peana et al., 2021), *Vicia cracca* (Myrvang et al., 2016b), *Indigofera cordifolia* (Raghu, 2001), twigs of *Cassia auriculata* (Nagaraju and Karimulla, 2002), and in mushrooms (Agaricales) demonstrating that certain plant species can accumulate Ba. Plant species with higher affinity for Ca, such as dicots (*e.g.,* legumes), have been reported to take up more Ba and Sr compared to monocots (*e.g.,* grasses), and perhaps due to isomorphic substitution of Ba, Sr and Ca in the biogeochemical cycle (Myrvang et al., 2016b, 2017).

4. Bioavailability and toxicity of Ba

4.1. Plant-barium interactions

Despite being present in tissues, Ba is not essential for life, including plants. Plants typically contain 2–13 mg kg^{-1} of Ba (Kabata-Pendias and Mukherjee, 2007). Moreover, Ba has been described as an essential plant-biophilic component (Padilla and Anderson, 2002). Barium was mostly taken up by plants as Ba^{2+}, a divalent cationic form (de Souza Cardoso et al., 2023). As with other plant nutritional elements, this element must be absorbed via active transport in the plant roots (Peana et al., 2021). According to Kabata-Pendias and Mukherjee (2007), the toxicity of Ba to plants has been associated with a reduction in some plant nutrients like Ca, Mg, and S because of the production of low-solubility products (*e.g.*, $BaCO_3$ and $BaSO_4$). Studies using soybean nutrient solutions showed reduced leaf area and yield, as well as signs of Ba toxicity (such as interveinal chlorosis and marginal necrotic spots) in Tanzania Guinea grass leaf laminae at dosages ranging from 0.5 to 20 mmol L^{-1} (Monteiro et al., 2011) (Supplementary information (SI) Table 1)). Low dosages (*e.g.*, 500 and 2000 μmol L^{-1}) stimulated cucumber seed germination (Sleimi et al., 2021), whereas high doses (*e.g.*, 100, 1000, and 5000 μmol L^{-1}) inhibited growth and leaf photosynthetic activity and shut down stomatal opening due to the reduced K absorption (Suwa et al., 2008) (SI Table 1). In contrast, the antioxidant enzymes ascorbate peroxidase, guaiacol peroxidase, and catalase showed increased activity in the various plant tissues when cucumbers were exposed to doses ranging from 100 to 500 μmol L^{-1} in the same

study. This suggests that Ba is toxic (Sleimi et al., 2021) (SI Table 1). Researchers have shown that the antioxidant enzymes catalase and ascorbate peroxidase were more active in the European sea rocket (a halophyte) and brown mustard (a glycophyte) (Bouslimi et al., 2021). However, they have found that after being exposed to Ba, the glutathione peroxidase activity of brown mustard increased.

Although the physiology of Ba appears to follow the hormesis effect (*i.e.*, with a biphasic dose-response impact, having a low-dose stimulation and high-dose inhibition), the effects of this element differ depending on the species of plant (Agathokleous et al., 2019). Regarding the antagonistic relationship between Ba and K, Peana et al. (2021) found that plant roots prefer K over Ba in certain circumstances. Nevertheless, according to the depth of the plant root system and the biogeochemical cycling process that determines the Ba/K concentration ratio of the topsoil, it was found that plants carry both elements upward to their leaves from deeper soil layers (Peana et al., 2021). Plant tissue concentrations of Ba and Ca were correlated with soil conditions and various species, including barley, tall fescue, great mullein, carrot, radish, spinach, grey pea, white clover, and bird vetch that can absorb Ba in a range of 100–700 mg kg^{-1} in shoots and 100–600 mg kg^{-1} in roots (Myrvang et al., 2016a; SI Table 1). Due to low barite solubility, barite formation may occur as a biomineralization processes or may form following cell disintegration (Abbasi et al., 2016). Researchers have found that lettuce exposure to Ba decreased their roots and shoot growth (de Souza Cardoso et al., 2023).

Additionally, different soil types affect how well different plant species absorb Ba. Melo et al. (2014) studied pea, sorghum, soybean, and maize exposure to high Ba concentrations in two soils (Oxisol and Entisol) and found that only pea was impacted in the Oxisol. In contrast, pea, sorghum, and soybean were impacted (with a decrease in biomass production) in the Entisol. de Souza Cardoso et al. (2023) and Melo et al. (2014) have found leaf chlorosis in lettuce, soybeans, and peas as a common indication of Ba toxicity. SI Table 1 summarizes Ba impacts on plants from contemporary literature.

Cyperus papyrus and *Typha domingensis* were chosen as potential phytoremediation species to remove Ba from flooded soils. In contrast, *Typha domingensis* and *Eleocharis acutangular* were selected to remove Ba from non-flooded soils. Plant tissues with high biomass production had higher Ba concentrations (de Castro Ribeiro et al., 2018; Ferreira et al., 2019; Viana et al., 2019) (SI Table 2). In uranium tailings containing Ba, the *Miscanthus floridulus* and *Phragmites australis* were successfully tested as Ba phytoremediation species. *Miscanthus floridulus* exhibited the highest rate of Ba absorption, while *Phragmites australis* had the greatest phytoremediation factor (Li et al., 2011). Researchers have found that compared to other metals (like Pb or Cd), vegetable samples gathered from community gardens in the USA were significantly more capable of accumulating Ba (McBride et al., 2014; Ferreira et al., 2019; da Silva Junior et al., 2022). However, because of the contribution of particulate material deposition in shoot tissues, soil Ba content was lower than soil Pb (McBride et al., 2014). da Silva Junior et al. (2022) reported that the outer parenchyma tissue of Brazil nuts seeds formed the "ring shape" when there was an accumulation of selenium, Ba, and sulphur in the epidermal tissues (SI Table 2). They mapped Ba distribution and found the elemental association of Ba with sulphur and selenium, *i.e.,* the low solubility compounds (*e.g.*, $BaSeO_4$ and $BaSO_4$) were formed.

4.2. Human/animal-barium interactions

People living near Ba mining or processing facilities may be exposed to high concentrations of Ba, mainly through the inhalation of fugitive Ba-enriched dust particles (de Castro Ribeiro et al., 2018; Padbhushan and Kumar, 2017). The main exposure routes of Ba to the public are food and drinking water. Many organisms may have adverse effects from high Ba concentrations. Since Ba is not a necessary nutrient for plants or animals, high amounts of it can negatively impact different organisms. Ba entry into the food chain is also facilitated by its accumulation in fish and marine species. Excessive ingestion of Ba in humans can cause cardiac arrhythmia, vomiting, diarrhea, hypokalemia, and severe hypertension and can also be lethal if proper treatments are not provided.

While soluble species are frequently regarded as hazardous, insoluble Ba salts, like $BaSO_4$, are usually harmless or only mildly poisonous to humans. For diagnosing colorectal and upper gastrointestinal disorders using X-rays, $BaSO_4$ is frequently utilized as a contrast agent, as it has no adverse effect on humans and remains unabsorbed. However, consuming soluble Ba salts causes harmful effects on regular cell processes, such as hypokalemic paralysis, which can lead to cardiac and respiratory arrest (Abbasi et al., 2016; Bhoelan et al., 2014). There has been a single report of suicide caused by ingesting large amounts of soluble Ba acetate (Fenu et al., 2021). The most common cause of Ba poisoning is ingesting Ba-containing foods, especially carbonate. $BaCO_3$ is a potent toxin because it dissolves readily in the stomach's acidic environment. So, $BaCO_3$ was employed as a rodenticide in the past. Inhalation and skin contact can also result in Ba contamination, particularly in the workplace.

However, long-term exposure can be harmful, particularly for kids and teens, as it can impact their health in the long term. Furthermore, the US Environmental Protection Agency's (EPA) found that Ba carcinogenic potential could not be ascertained after inhalation, and it is unlikely to cause cancer in humans even after oral consumption (Wang et al., 2021). Given the paucity of evidence on barium carcinogenicity, more research is required to elucidate this aspect. Although Ba does not bioaccumulate in human tissues, insoluble chemicals can accumulate in the lungs, resulting in "Baritosis," a benign illness. Muscle weakness and gastrointestinal problems can result from consuming drinking water with Ba levels significantly higher than the EPA recommended levels for more extended periods.

The molecular aspects of Ba toxicity in animals and human involve the blockage of potassium (K) channels, in particular the K inward rectifier channels (K-IRCs) of the KCNJx gene family, which belongs to a large family of genes that produce K channels (Bhoelan et al., 2014). These channels, which control the influx and efflux of K^+ in cells, play a critical in the ability of cells to generate and transmit electrical signals. Extracellular Ba enters and strongly binds the K selectivity filter region resulting in blockade of the K conducting pore and inhibiting K transport out of cells, thereby leading to a decrease in serum K concentration (i.e., hypokalemia) (Zaydman et al., 2012). This disrupts electrical excitability in muscles and nerves, causing muscle stimulation followed by weakness, tremors, and potential paralysis. Barium also acts as a physiological antagonist to K, and at high doses can cause cardiovascular collapse or respiratory failure due to its effects on cardiac and skeletal muscle function (Restrepo-Angulo et al., 2010; Oskarsson, 2015; Krishna et al., 2020).

Plants can mobilize insoluble Ba salts, resulting in the rise of Ba in the body when people take plant-based foods. Long-term high Ba consumption is linked to cardiovascular dysfunction and kidney impairment (Choudhary and Kumar, 2024; Dallas et al., 2001). Numerous studies have linked Ba contamination to congenital abnormalities in newborns, an emerging problem (Krishna et al., 2020; Abbasi et al., 2016; Fenu et al., 2021). Prenatal exposure, as indicated by Ba levels in pregnant women's hair, was found to be strongly associated with an elevated risk of heart problems, neural tube malformations, and orofacial clefts in the offspring (Zhang et al., 2018; Lv et al., 2021). Therefore, it is essential to carefully examine the water that pregnant and fertile women usually drink. Given that Ba appears to exacerbate depression, another risk factor was identified for older women, though this phenomenon was not observed in men (Lv et al., 2021).

5. Risk management of barium in the environment

Risk management of soil and groundwater contamination can be accomplished by defining intervention values for Ba in soils, sediments, surface water, and groundwater and adopting regulatory measures that

prevent the anthropogenic dispersal of Ba in the environment. However, ecological engineering approaches are needed to ensure that Ba removal is performed or its concentration is reduced to a level permissible in contaminated soil and water, which would otherwise endanger ecosystems and human health.

5.1. Intervention values for barium in soil and water

Many nations worldwide have established threshold, intervention, and/or guideline values for Ba, although these values can vary greatly (SI Table 3) by many orders of magnitude. These figures are typically derived from the total Ba concentrations in the soils. The differentiations are based on land use, such as residential versus non-residential, which is further related to Ba different intervention/cleanup values for a particular country. The mobile or "available" fraction of an element is sometimes ascertained through extraction/leaching tests, or regulations employ adjustments of threshold values based on the pH, organic matter content, and/or clay content of the soil because it can be challenging to correlate the total concentrations of elements in soil with their potential risks. In Alberta, Canadian researchers have extracted Ba from soil (as a part of a tiered approach) using a diluted $CaCl_2$ solution (0.1 mol L^{-1}), where strong acid digestion was utilized to quantify non-barite Ba in the first phase (Kaur and Prakash, 2022; Hao et al., 2022). The total amount of Ba-compounds in soil, as well as their leachability based on groundwater criterion (1600 $mgkg^{-1}$), is known as Soil Cleanup Target Levels in Florida (USA) (Florida Department of Environmental Protection, 2005). A leaching test like the Synthetic Precipitation Leaching Procedure (SPLP) can be used to evaluate the leaching potential (US EPA, 1994). The Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1992) or SPLP is used to evaluate the Mobility Criteria in Connecticut, USA. Compared to soil clean-up values, the recommended values for Ba in drinking water or groundwater are substantially different (SI Table 3). Florida is one noteworthy example, where groundwater with poor quality has been shown to have a value of 20,000 μg L^{-1} Ba (Florida Department of Environmental Protection, 2005). The World Health Organization set a Ba drinking water quality standard of 1300 μg L^{-1}. The Australian National Health, Medical Research Council and the US -EPA set a threshold of 2000 μg L^{-1}. According to Sharma and Bhattacharya (2017), drinking water that satisfies US-EPA standards is safe and carries little to no risk. Excessive Ba concentrations in soil and water are deemed polluted and need to be cleaned up. Even though groundwater contamination frequently co-exists with soil pollution, we will discuss the remedial strategies for Ba from soil and water.

5.2. Remediation of barium-contaminated soil

Because Ba is less dangerous than other metals like Zn, Cd, Pb, etc., remediation of Ba-contaminated soils has not received much attention in the literature. The most researched method is phytoremediation, a plant-based strategy that uses plants to remove toxic contaminants from soil or reduce their bioavailability (Berti and Cunningham, 2000). The effectiveness of several plant species in extracting Ba from soil has been discussed in many studies (SI Table 2; Fig. 5). A case study on Ba remediation in soil is provided in Section 6. Barium could be immobilized using sunflower (*Helianthus giganteus*) (Zargan and Fakharyfar, 2016). Chelating compounds are occasionally utilized to improve the effectiveness of metal phytoremediation. However, neither the distribution of Ba in the soil's geochemical fractions nor the uptake of Ba by plants changed when EDTA was added to the soil contaminated by oil exploration drilling waste (Andrade et al., 2014). Numerous research (Raghu, 2001; Nogueira et al., 2010; Kujawska and Pawłowsk, 2019) have examined the transfer of Ba from soil to plants to assess the possible dangers for intake by humans and animals.

Sulphates, phosphates, and carbonates can also stabilize Ba in soils. No real-world applications that particularly target the immobilization of Ba in soil have been published in the literature (Harle et al., 2003). Only one published study examined flotation as a remediation method for Ba-contaminated soil (Labidi, 2018). They have found that it was possible to recover up to 85 % of $BaSO_4$ from soil artificially polluted with the Ba. Nevertheless, no further tests were carried out about the flotation method for field Ba-contaminated soils.

5.3. Removal of barium from aquatic environments

Ba should be removed from the wide range of aquatic systems (Fig. 5). A case study on Ba removal from waste water is provided in Section 6. Among other things, oil-field-generated waters have significant levels of hydrocarbons and Ba (up to 850 mg L^{-1}) (Abbas et al.,

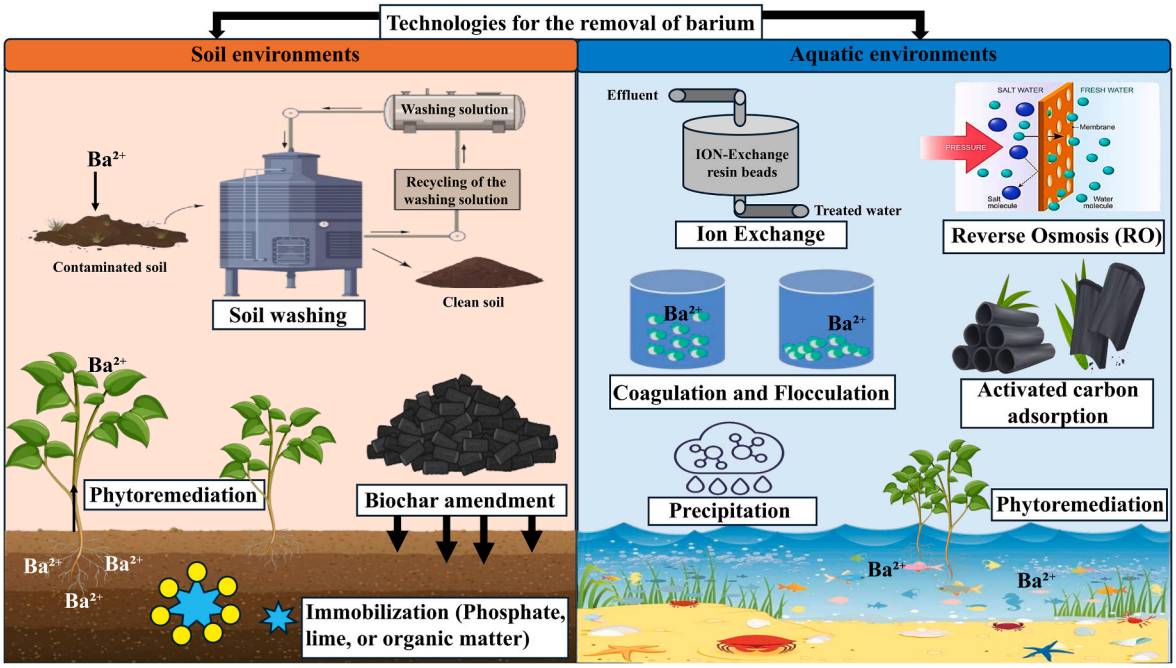

Fig. 5. Schematic showing the removal of barium from aquatic and soil environments.

2021). Elevated Ba concentrations (up to 467 mg L^{-1}) may also be present in flow back water produced during hydraulic fracturing, which is used to produce shale gas (Owen et al., 2020). Shale gas flow back water must be treated by reverse osmosis desalination before it is released into the environment. High Ba^{2+} concentrations in flow back water must be eliminated because they significantly increase $BaSO_4$ scaling (Liu et al., 2020). Barium can be found naturally in some aquifers in addition to the contribution of artificial sources. It dissolves from naturally occurring minerals in the subsurface that come into contact with groundwater and enters the sources of drinking water (US EPA, 2006). Depending on the type of water to be treated and to get the desired water quality, sorption, ion exchange, chemical precipitation, lime softening, reverse osmosis, and electro-dialysis can be used to remove Ba from water (Graça et al., 2022). Most experiments reported in the literature employ sorbents to extract Ba from water with concentrations up to 600 mg L^{-1} of Ba (SI Table 4). The treated fluids range from "real" samples like well or groundwater, river water, water treatment plant effluents, industrial effluents, and simulated saline oilfield wastewater to test solutions that contain $BaCl_2$ in deionized water (SI Table 4). The removal of Ba from water has been studied using a wide range of sorbents, including hydrotalcite-like compounds based on Mg-Fe complex (Kato et al., 2013), metal-organic frameworks functionalized with sulphate/sulphonic (Peng et al., 2016), natural and Iron (III) oxide-modified allophane, Beidellite and Zeolite (Baldermann et al., 2020), biochar made from straw (Younis et al., 2020), or biosorbents made locally from *Monotheca buxifolia* seeds (Khan et al., 2022) (Fig. 5). Adsorption was controlled by physical processes in addition to ion exchange, precipitation, intercalation and surface complexation depending on the types of absorbent and operating conditions (Baldermann et al., 2020). As $BaCO_3$ is poorly soluble, Ba precipitates as $BaCO_3$ at pH 8–9.

Nevertheless, $Ba(OH)_2$ is produced if the pH rises further and dissolves in water (Krause and Stover, 1982). Thus, Ba can be extracted from water by precipitation under regulated circumstances. Barium concentrations below the detection limit were obtained when 12 mmolL^{-1}sodium carbonate was added to well and groundwater samples (Parks and Edwards, 2006). This was most likely caused by the precipitation of $BaCO_3$ (average water pH = 10.3; pH range 9.6–11.1). Adding limewater (calcium hydroxide) to water raises its pH, which is known as "lime softening." Usually, water is softened with lime to eliminate calcium and magnesium. Barium is also eliminated when it precipitates. According to Ronquim et al. (2018), Ba is extracted from synthetic solutions, *i.e.,* representing typical industrial wastewater, through membrane treatment by adding excess sulphate in batches. The ion exchange method makes use of strong-acid ion exchangers with sulphonic acid functional groups or weak-acid cation exchangers with carboxylic acid functional groups that are used in the ion exchange technique (Krause and Stover, 1982; Snoeyink et al., 1987). Krause and Stover (1982) studied various resin types to treat raw water, where Ba concentrations ranged between 5.5 and 5.7 mg L^{-1}. They found that all three resins had a Ba removal efficiency of 95 % or higher. Barragan et al. (2022) used electrodialysis to extract Ba^{2+} and Mg^{2+} from artificial brine solutions selectively. The use of novel reverse osmosis (RO) and hydrophilic nanofiltration (NF) membranes for the reuse of rejected water was studied by Alzahrani et al. (2013). Hard salts were more successfully rejected by the reverse osmosis membrane, which rejected 85.4 % of $BaCl_2$, producing Ba concentrations much below the allowable WHO and US EPA limits (Wadekar and Vidic (2018). Distillation is also advised by commercial water treatment system suppliers for the removal of Ba from water. Nevertheless, there aren't many published scientific investigations that concentrate exclusively on Ba removal. Lastly, oilfield-produced water is desalinated using a process called freeze-thaw/evaporation (FTE), which first forms ice crystals by freezing and then melts the ice to produce fresh water (Amakiri et al., 2022).

5.4. Case studies of remediation of barium contamination

Case study 1: Phytoremediation of barium in flooded soils.

Phytoremediation is considered a low-cost, green technology using plants to absorb and extract Ba and other elements from contaminated soil. This field study was conducted in Brasil, in an area with an historical Ba contamination using *Typha domingensis* and *Eleocharis acutangular* macrophytes. Key factors influencing Ba removal include plant species selection, cutting frequency (Viana et al., 2019), planting densities (Viana et al., 2021a, 2021b), and the use of techniques like intercropping to increase plant biomass and Ba uptake (de Carvalho et al., 2019).

The greatest Ba phytoextraction (aerial part and root) was achieved by a low-density treatment, which removed approximately 3 kg of Ba/ha (Viana et al., 2021b). *T. domingensis* and *C. papyrus* showed high Ba concentration in plant tissues, as well as with high biomass production, making them potential candidates for phytoremediation schemes to remove Ba from flooded soils (de Castro Ribeiro et al., 2018). In spiked soils, *T. domingensis* achieved 100 % removal at 2.5 mg kg^{-1} Ba and more than 20 % at higher Ba doses. In field-contaminated soils, the translocation of Ba to plants is usually lower than 100 % (*e.g.*, 32–48 %, Viana et al. (2019). Besides the type of contamination (anthropogenic versus spiked) and the plant species, the removal efficiency is also influenced by other parameters such as cutting frequency of the plants and the application of fertilizers. Viana et al. (2019) found that cuts of *T. domingensis* and *E. acutangula* at intervals of 120 days or more were associated with elevated levels of Ba in the plant tissue and a decrease of soil Ba.

Case study 2: Photocatalytic removal of barium from wastewater: Photocatalysis is gaining increasing attention as a means of removing organic and inorganic pollutants from wastewater (*e.g.* Friedmann, 2022; Tiwari et al., 2025). Fontana et al. (2018) investigated the effect of different additives and catalysts on the Ba(II) removal process by photocatalysis. As catalysts, different types of TiO_2 (anatase, P25, commercial TiO_2), ZnO and Nb_2O_5 were investigated. Different experimental conditions (pH, type and concentration of additives), concentration of catalyst and presence of interfering ions were analysed, in order to optimize the removal of Ba from wastewater.

- Additives: the presence of additives (formic acid, isopropanol and methanol in this case) influences the rate of the photocatalytic reaction (Li et al., 2023). Only formic acid showed a positive effect on the removal of Ba(II) from the solution (Fontana et al., 2018)
- pH: the reduction of Ba(II) concentrations in solution was only significant at pH values higher than 5.5 (Fontana et al., 2018)
- Catalyst concentration: High amounts can hinder the photocatalysis process (Carp et al., 2004). An increase in photocatalytic activity was observed when the catalyst concentration increased from 0.05 to 0.1 g/L. At concentration >0.5 g/L, no significant improvement in photocatalytic activity was noticed (Fontana et al., 2018).
- Initial concentration of Ba(II): The decrease of the metal ion concentrations in solution generally leads to a decrease in the photocatalytic reduction potential, and thus to slower removal (Carp et al., 2004). With a Ba(II) concentration of 10 mg L^{-1}, the photocatalytic reduction process was delayed by ±80 min (Fontana et al., 2018).
- Chloride ions: Depending on the specific conditions, dissolved chlorides can either inhibit or enhance photocatalytic degradation of pollutants in wastewater (Delarmelina et al., 2023). In the case study of Fontana et al. (2018), Ba(II) removal kinetics, were significantly slower at higher chloride concentrations.
- Contact time: Contact time between the additive (formic acid) and the catalyst before the photocatalytic process was also significantly improving the catalytic activity, with anatase, P25 and ZnO being the best catalysts.

6. Future research needs

While the primary natural source of Ba is barite mineral present in shale and coal, Ba reaches the environment through anthropogenic emissions including industrial activities such as onshore and offshore gas and oil drilling operations. Although barite is consumed orally under specific conditions, little is known about the possible consequences that environmental exposure may cause to ecological receptors and humans. Given the increasing release of Ba to the environment through both geological and anthropogenic sources, and existing knowledge gaps regarding the long-term environmental fate of Ba, the following research directions are suggested:

Speciation of Ba: Cutting-edge spectroscopic techniques are crucial to comprehending the geochemical mechanisms of multiple Ba species in diverse soil and aquatic circumstances. Speciation of Ba is critical for understanding the mobility and bioavailability of Ba and also developing techniques for remediation of Ba contamination.

Factors affecting Ba distribution: Barium can be found in soil and water in various forms, such as free cations, carbonate and sulphate precipitates, and inorganic and organic complex species. Environmental, i.e., aquatic and soil factors, affect Ba interactions, fate, and bioavailability. For example, oxic environments with high levels of sulphur and carbonate facilitate Ba precipitation, inhibiting its bioavailability. In contrast, high saline conditions promote the solubility and mobility of Ba. It is important to examine the soil, water and environmental factors affecting the distribution of Ba, which will facilitate the development of models to predict the fate and behaviour of Ba in terrestrial and aquatic systems.

Risk assessment of Ba: Risk assessment of Ba in terrestrial and aquatic ecosystems requires ecotoxicological assessment utilizing in-situ biomonitoring approaches involving techniques such as bioaccumulation and biomarker analysis (i.e., biochemical, morphological, or molecular) in terrestrial and aquatic organisms.

Remediation of Ba contamination: While ion exchange and reverse osmosis techniques are applied to remove Ba from aquatic systems, precipitation of Ba as barium sulphate reduces the bioavailability of Ba in soil. It is crucial to assess in-situ Ba stabilizing procedures in contaminated soils, sediments, and aquatic systems employing cutting-edge adsorbents like biochar and nanomaterials to achieve risk-based remediation. Furthermore, monitoring long-term release and remobilization of Ba from the immobilized medium is also crucial.

7. Conclusions

The extensive industrial use of Ba and the resulting environmental discharge of Ba, as well as the current lack of knowledge regarding the behaviour and dynamics study of Ba in the soil and aquatic ecosystems, drive the quest of the present review. Barium is primarily found in nature as barite minerals, shale, and coal. Still, it can also accumulate in terrestrial and aquatic ecosystems due to human activities like oil and gas drilling. Barium can be found in soil and water in various forms, such as free cations, carbonate and sulphate precipitates, and inorganic and organic complex species. By consuming Ba-contaminated food and drinking water, Ba levels in the general population rise to dangerous levels. High levels of Ba absorption are likely to impair gastrointestinal function. They can have an impact on the brain and nervous system, leading to heart abnormalities, respiratory disorders, and paralysis, even though Ba is not considered a human carcinogen. Immobilization and phytoremediation methods can reduce soil contamination, while precipitation, reverse osmosis, and electrodialysis methods can eliminate Ba from water.

CRediT authorship contribution statement

Shailja Sharma: Writing – original draft, Visualization, Validation, Funding acquisition, Formal analysis, Data curation. **Shiv Bolan:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Santanu Mukherjee:** Writing – original draft, Formal analysis, Data curation, Conceptualization. **Luiz Roberto Guimarães Guilherme:** Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation. **Douglas Gomes Viana:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Amanda Duim Ferreira:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Mona Bakke Myrvang:** Validation, Supervision, Software, Formal analysis, Data curation, Conceptualization. **Åsgeir R. Almås:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Elin Lovise Folven Gjengedal:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Valérie Cappuyns:** Writing – review & editing, Visualization, Investigation, Funding acquisition, Formal analysis, Data curation. **Marcelo Braga Bueno Guerra:** Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Cynthia de Oliveira:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Dane Lamb:** Visualization, Validation, Investigation, Funding acquisition, Formal analysis, Data curation. **Kadambot H.M. Siddique:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Nanthi Bolan:** Writing – review & editing, Formal analysis, Data curation, Conceptualization.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2025.123059.

Data availability

No data was used for the research described in the article.

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