



Review

Boron contamination and its risk management in terrestrial and aquatic environmental settings



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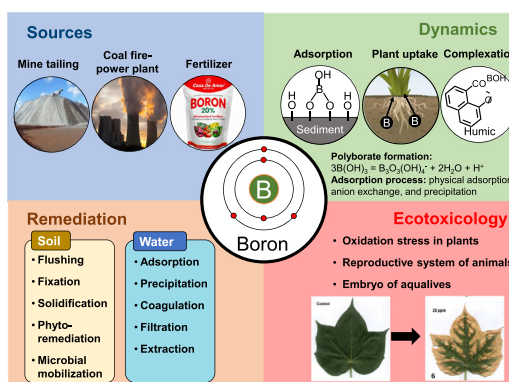
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HIGHLIGHTS

- B is released to environment through irrigation, fertilizer input, and mine wastes.
- B shows a high affinity towards oxygen and exists as borates and oxo-complexes.
- B is the only essential plant nutrient taken up as non-ionic boric acid molecules.
- B in water can be eliminated by adsorption, reverse osmosis, and electro dialysis.
- B toxicity in soil can be mitigated by immobilization and phytoremediation.

GRAPHICAL ABSTRACT



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ABSTRACT

Boron (B) is released to terrestrial and aquatic environments through both natural and anthropogenic sources. This review describes the current knowledge on B contamination in soil and aquatic environments in relation to its geogenic and anthropogenic sources, biogeochemistry, environmental and human health impacts, remediation approaches, and regulatory practices. The common naturally occurring sources of B include borosilicate minerals, volcanic eruptions,

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Mining
 Plant toxicity
 Fertilizers
 Irrigation water
 Animal toxicity
 Human toxicity
 Remediation

geothermal and groundwater streams, and marine water. Boron is extensively used to manufacture fiberglass, thermal-resistant borosilicate glass and porcelain, cleaning detergents, vitreous enamels, weedicides, fertilizers, and B-based steel for nuclear shields. Anthropogenic sources of B released into the environment include wastewater for irrigation, B fertilizer application, and waste from mining and processing industries. Boron is an essential element for plant nutrition and is taken up mainly as boric acid molecules. Although B deficiency in agricultural soils has been observed, B toxicity can inhibit plant growth in soils under arid and semiarid regions. High B intake by humans can be detrimental to the stomach, liver, kidneys and brain, and eventually results in death. Amelioration of soils and water sources enriched with B can be achieved by immobilization, leaching, adsorption, phytoremediation, reverse osmosis, and nanofiltration. The development of cost-effective technologies for B removal from B-rich irrigation water including electro dialysis and electrocoagulation techniques is likely to help control the predominant anthropogenic input of B to the soil. Future research initiatives for the sustainable remediation of B contamination using advanced technologies in soil and water environments are also recommended.

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1. Introduction

Boron (B) displays both metallic and non-metallic characteristics, with the capacity to produce both acids and bases in terrestrial and aquatic ecosystems. Although present in trace levels, B occurs widely in the hydrosphere and lithosphere, and is released to the environment through natural geogenic and anthropogenic inputs. The predominant natural sources of soil B include borosilicate minerals (e.g., tourmaline), volcanic eruptions, geothermal and groundwater streams, and marine water. Global mean seawater B concentration is approximately 4.6 mg B/L, and it often occurs in saline soils derived from marine evaporites (Degryse, 2017; Gmélíng et al., 2007; Helvacı and Palmer, 2017; Pye et al., 2012).

Boron is commercially produced from seawater and minerals, including ulexite, borax, sassolite, colemanite, and kernite. Boron compounds are utilized widely in various industrial products, including borosilicate glass, vitreous enamels, cosmetics, leather, textiles, cleaning detergents, insecticides, and fertilizers (Pye et al., 2012). Although B is an essential trace

element nutrient for plants and is added to the soil as a fertilizer, excessive B accumulation from various anthropogenic inputs is creating an environmental health issue. Major anthropogenic inputs of B include irrigation water, wastewater, fertilizer, and waste derived from mining and processing industries (Brdar-Jokanović, 2020; Park and Schlesinger, 2002; Schlesinger and Vengosh, 2016).

As noted, B is essential for plants, and is absorbed by roots predominantly in the form of boric acid (H_3BO_3) molecules (González-Fontes, 2020). Although B deficiency in agricultural soils has been observed, B toxicity can inhibit plant growth mostly in soils that occur in arid and semiarid regions (Bolaños et al., 2004; Brennan and Adcock, 2004; Nable et al., 1997). High levels of B may arise naturally in soil and groundwater sources of arid and semiarid regions or may be derived from mining, fertilizers, or irrigation water, which can result in B toxicity to plants (Brown et al., 2002; Cervilla et al., 2007). Furthermore, most edible crops are sensitive to B concentrations observed in irrigation water, which is a major source of B input in agricultural soils (Rékási et al., 2021).

When animals and humans ingest B-enriched food or forage, the accumulation of B in their bodies can cause health problems. Excessive B intake may lead to acute toxicity with diarrhea, kidney injury, and, in extreme cases, death resulting from circulatory failure (Goldbach and Wimmer, 2007; Nielsen, 1997, 2014). The World Health Organisation (WHO) guideline for B levels in potable water sources is 0.5 mg B/L, and the threshold daily intake B level for an adult is considered to be 0.16 mg B/kg body weight (WHO, 2009). Amelioration of soils and wastewater containing excess B can be accomplished by immobilization, adsorption, phytoremediation, reverse osmosis, and nanofiltration. The development of cost-effective technologies for B removal from B-enriched irrigation water sources is likely to help control one of the predominant anthropogenic inputs of B in agricultural soil (Cedeño et al., 2015; Hilal et al., 2011).

Large amounts of B are commonly found in rocks of arid regions such as Argentina, Chile, Russia, China, Peru, Turkey and the United States, with last two regions the world's largest B producers (Cahit et al., 2021). Despite the rising application of B in the industry sector and the subsequent release of B to the environment with its ecotoxicity, there are limited published reports on the accumulation, fate, and transport of B in terrestrial and aquatic environments. There were only limited number of reviews on the pollution of B in terrestrial and aquatic environments, and its remediation (Goldberg, 1997; Howe, 1998; Kochkodan et al., 2015; Park and Schlesinger, 2002; Parks and Edwards, 2005; Schlesinger and Vengosh, 2016). Most reviews have focused mostly on B as a nutrient source and managing the deficiency and toxicity of B in agricultural soils (Brown et al., 2002; Padbhushan and Kumar, 2017), and B removal from water sources (Parks and Edwards, 2005). This review aims to describe the current knowledge on B contamination in terrestrial and aquatic environments in relation to its geogenic and anthropogenic sources, biogeochemistry, environmental and human health impacts, remediation approaches, and regulatory practices.

The primary aim of this review is to critically scrutinize the natural and anthropogenic inputs of B in terrestrial and aquatic ecosystems, ecotoxicity risks arising from B input into these environments, and sustainable technologies to manage these risks. The specific objectives of the review include: (i) to identify the origins of B release and pollution in terrestrial and aquatic environments; (ii) to describe the interactions and dynamics of B in the soil–water–plant continuum; (iii) to explain the impacts of B accumulation on ecotoxicity and human health; and (iv) to propose sustainable strategies to ameliorate the risks presented by B accumulation in terrestrial and aquatic environments.

A literature search was conducted in Web of Science Core Collections with the following searching terms: TS = (“boron” OR “borate” OR “boric”) AND TS = (“environment” OR “soil” OR “porous media” OR “terrestrial” OR “aquatic” OR “aqueous” OR “freshwater” OR “lake” OR “river” OR “sediment” OR “marine” OR “ocean”) AND TS = (“contamination” OR “concentration” OR “risk” OR “migration” OR “fate” OR “management” OR “remediation” OR “mitigation”). A total of 5258 results were retrieved (Fig. 1). The results were visualized using the VOSviewer software (version 1.6.19). Major topics include B bioaccumulation in soil, B toxicity, B removal from aqueous system, B adsorption, and phytoremediation (Fig. 1), which will be discussed in this review.

2. Origin and sources of boron contamination

2.1. Geogenic

Boron occurs widely in the lithosphere and is present in rocks and soils, especially in clay-enriched marine sediments (Hilal et al., 2011). The level of B in the earth's crust largely depends on the nature of the rock, with levels ranging from 1 to 500 mg B/kg and with a mean value of B of around 10 mg B/kg. Normally, soils contain about 2 to 100 mg B/kg, with an average level of 30 mg B/kg, depending mainly on the loam parent material. Majority of soils contain a low level of B (<10 mg B/kg), while B-rich soils (10–100 mg B/kg) are commonly linked to volcanic activity (Adriano, 1986). The estimated distribution of the total B content accumulated in the lithosphere includes the following: 10^{18} kg B in continental and oceanic crusts, 10^{10} kg B

in coal resources, 10^{10} kg B in borate reserves, and 10^{10} kg B in biomass (Kochkodan et al., 2015). The relative distribution of B in the environment is summarized in Table 1.

Boron occurs in nature mostly in the form of the oxide (B_2O_3), which combines with other elements to form more or less complex borates. More than 200 B compounds are present in the earth's crust, that include sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) or borax, ulexite ($NaCaB_5O_9 \cdot 8H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) and kernite ($Na_2B_4O_7 \cdot 4H_2O$) (Degryse, 2017; Goldbach, 2020). The presence of concentrated reserves of B minerals is closely linked to volcanic activity, while arid environmental conditions are critical for the preservation of these B reserves.

In the oceans, B is the tenth most abundant element in marine salts, with the concentrations in seawater ranging from 0.52 to 9.57 mg B/L in the Baltic Sea and Mediterranean Sea, respectively. The global mean B level in oceans is between 4.6 and 4.8 mg B/L. It is also present in other hydrological reservoirs including groundwater, surface water, and ice. In groundwater, most B concentrations are highly variable, ranging from 0.017 to 1.9 mg B/L (Parks and Edwards, 2005). There are a variety of other inputs of B in the soil and aquatic environments, and the relevant sources and levels are summarized in Table 2.

2.2. Anthropogenic

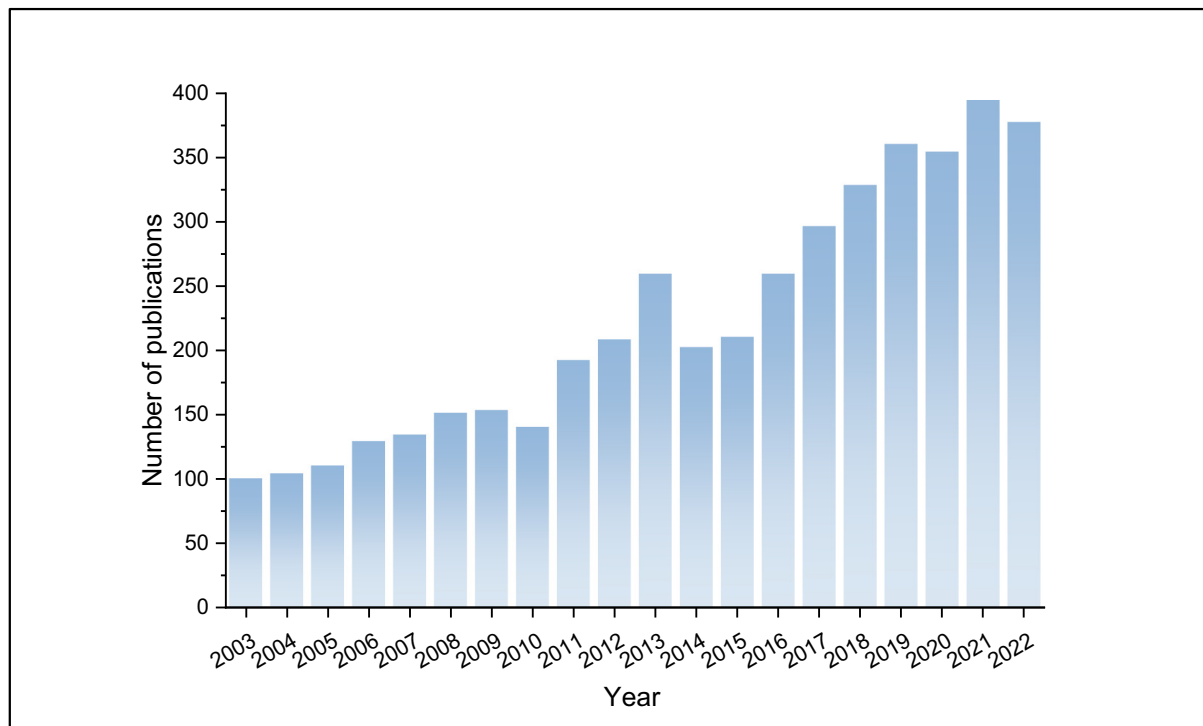
The major anthropogenic industries that produce B-containing wastewater are the glass or ceramic industry (with highest market demand of 56%) and metallurgy (Pye et al., 2012). In addition, sources of environmental contamination from B include discharges from waste minerals and wastewater from mining.

The world B consumption exceeds 1.5 million tons per year (Özdemir and Kıpçak, 2010). This is mainly due to the wide range of applications for B, which is an active component in the synthesis of ceramics, pharmaceuticals, cosmetics, cleaning detergents, B fertilizers, heat-resistant products, anti-corrosion materials, heavy-duty steel, flame retarding agents, and neutron absorbing materials at nuclear facilities (Hosmane, 2011). Boron effluent may also be present in domestic wastewater in levels ranging from a few hundred mg/L to several mg/L. This is mainly due to the richness of sodium borate in bleach products used in detergents and cleaning agents (Remy et al., 2005).

Other sources of B from human activities are insecticides and fertilizers containing B. Because B is a biologically essential trace element nutrient for plants, it is incorporated in many fertilizers in amounts ranging from 0.01 to 0.06%, with borax being the most common form. An early reference for B allowed in potable water sources was in the document “WHO Guidelines for Drinking-Water Quality” (Gorchev and Ozolins, 1984), which considered the occurrence of B in the aquatic environment as normal and, therefore, not requiring any measures for control. In the aquatic environment, the form in which dissolved B occurs depends on the level of B. At low B levels (≤ 216 mg B/L), soluble B is present mainly as mononuclear B species, $B(OH)_3$ and $B(OH)_4^-$. At higher levels, with increasing pH, B occurs as polynuclear B forms [$B_2O(OH)_6^{2-}$] or species containing B_3O_3 rings [$B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$] (Hilal et al., 2011). Wyness et al. (2003) observed that water ways draining farming areas of south-eastern England with intensive agricultural activities can have mean B levels of up to 387 μ g B/L, which is attributed mainly to the application of B-containing fertilizers and irrigation of B-enriched water.

Boron contains two stable isotopes, ^{10}B and ^{11}B , with their relative abundances of about 20% and 80%, respectively. Boron isotope applications in aquatic investigations are growing because B isotope ratio offers the fingerprint to trace the source of B (natural vs anthropogenic) in natural waters (Nigro et al., 2018a, 2018b; Pennisi et al., 2006), and plant uptake (Dannel et al., 2000, 2002). Boron isotope fractionations are mostly determined by the partitioning between the two predominant soluble B species, $B(OH)_3$ and $B_4BO_4^-$. However, the combination of the isotopic fractionation process and removal of $B_4BO_4^-$ by adsorption, plant uptake and leaching, causes a large isotopic variation of B in natural waters, which can be used to monitor B pollution in aquatic environment (Nigro et al., 2017; Pennisi et al., 2006).

(a)



(b)

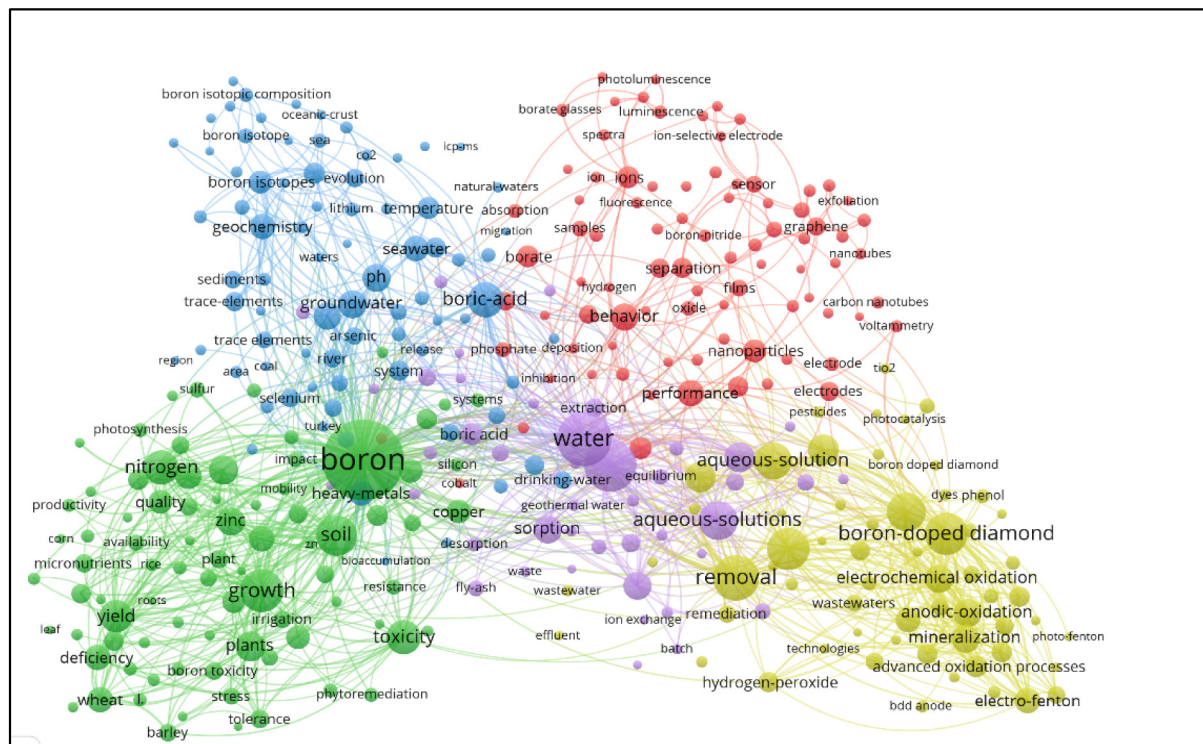


Fig. 1. Systematic literature search results on boron contamination topic. (a) The number of publications related to boron contamination topic in each year following literature screening. (b) Keyword co-occurrence map in this field showing the most frequently investigated topics.

Table 1
Boron distribution in the environment.

The range of existence of Boron	Concentration level of Boron
Continental and oceanic crusts	10 ¹⁸ kg
Commercial borate deposits	10 ¹⁰ kg
Coal deposits	10 ¹⁰ kg
Biomass	10 ¹⁰ kg
Oceans	10 ¹⁵ kg
Groundwater	10 ¹¹ kg
Surface waters	10 ⁸ kg
Ice	10 ¹¹ kg

3. Distribution and speciation of boron in the environment

3.1. Distribution in soil

The distribution of B in the soil in different terrestrial regions of the earth varies, and depends upon the geological (mineralogical), hydrographic, climatic, and soil conditions. Boron-deficient areas are widespread, while high B content is more of a local problem (Gupta et al., 1985). The total B level in soils ranges from 1 to >1000 mg B/kg. The worldwide mean content is 42 mg/kg; most often, values are between 9 and 85 mg/kg (Kabata-Pendias, 2010). Due to its high solubility in aqueous solutions, the distribution of B is also controlled by the movements of groundwater in the lithosphere. Boron-rich waters, such as hydrothermal waters, aquifers, and groundwater, can enrich the soil with B (Gmélung et al., 2007). Rivers can also convey high B content (Cáceres et al., 1992).

Borate deposits are related to volcanic or hydrothermal activities (Ozol, 1978; Ryan and Langmuir, 1993). Volcanic or certain hydrothermal activities create surface deposit areas (Kabata-Pendias, 2010; Ryan and Langmuir, 1993). Because of the ready water solubility of its compounds, B accumulates in the seas and bound in marine sediments, where the B content can be enriched above 100 mg B/L (ppm) (Leeman and Sisson, 1996). Marine sediment with high B content is brought to the surface by the volcanic activity and water movements at the subduction zones of convergent plate boundaries (Ozol, 1978). According to other opinions, the origin of the most significant B deposits is not marine, but continental sediment brought to the surface by acidic volcanism (Helvacı and Palmer, 2017). Main B deposits occur in the United States (in southern California and Nevada), Turkey (in the north-western part of Anatolia), South America (on the high Andean Plateau near the common borders of Argentina, Bolivia, Chile and Peru), China (northeast, middle, and southwest), Russia (southeast, near the Sea of Japan), and Kazakhstan. Carpenter and Kistler (2006) and Helvacı and Palmer (2017) provided detailed information on the formation and geological characteristics of these B deposits. There are significant reserves in the Jammu and Kashmir region in India (Indian Bureau of Mines, 2021). Soil or groundwater sources with a relatively high B

content can be found in the Maremma region of Tuscany in Italy (Pennisi et al., 2006), at Gladstone in South Australia (Cartwright et al., 1984), in Upper Galilee and the Arava Valley of Israel (Ravikovitch et al., 1961), on the west coast of Malaysia (Shorrocks, 1964), and in the Omsk region of West Siberia, Russia (Azarenko, 2007).

Regarding the distribution B in soils, it is critical to remember that there may be a difference between the distribution of deficient or rich areas in the geological sense and from the crop production point of view (Welch et al., 1991). The origin and composition of the soil parent material are the controlling factors in the total level of B in soils. If the soil was formed on sandstone or acid igneous rock parent material that are inherently low in B, then a low total B content in the soil is expected (Mengel and Kirkby, 2001). Boron minerals are relatively insoluble (Goldberg, 1997). Total B content includes strongly bound B, which is not an available fraction. Generally, five different chemical fractions of B are distinguished in soil and sediments: readily soluble, specifically adsorbed, iron and aluminium oxide bound, organically complexed, and residual (occluded) (Datta et al., 2002; Hou et al., 1994). Padbhushan and Kumar (2017) described the effect of various soil characteristics on individual fractions of B. Only less than 2% of the total B content is accessible for absorption by plants, and the fractions taken up are easily soluble and specifically adsorbed B fractions (Datta et al., 2002; Hou et al., 1994; Jin et al., 1987).

The available B content in agricultural soils is optimal in the range of 0.5–5.0 mg B/kg (Gupta, 2007). This fraction is affected by many soil characteristics. An increase in pH in the range above 6.3–6.5 increases B adsorption, so both leaching and crop uptake become limited (Gupta and MacLeod, 1977). Thus, with regard to crop production, B deficiency may develop while total B content remains relatively unchanged (Mengel and Kirkby, 2001). It means that the available fraction of B can show significant variation on different soils with similar total B fraction (Padbhushan and Kumar, 2017; Sidhu and Kumar, 2018). Readily available B content is also influenced by precipitation (Leeman and Sisson, 1996), current soil moisture status, temperature (Goldberg et al., 1993a, 1993b), and the rate of plant uptake. Therefore, attention must be paid to both the spatial and temporal variability of the distribution of the available B fraction.

Soil texture is a major characteristic in controlling the concentration of available B because the quantity and quality of the binding sites greatly influence the binding of B. Aluminium and iron oxides (Goldberg and Glaubig, 1985; Goldberg et al., 1993a, 1993b), magnesium hydroxide, clay minerals (Karahana et al., 2006; Tsadilas et al., 1998), and free calcium carbonate content (Goldberg and Forster, 1991; Majidi et al., 2010) provide adsorption sites for B in soil. In general, fine-textured soils can bind larger amounts of B and, thus, are more resistant to leaching than coarse-textured soils with fewer binding sites (Gupta, 1980). The organic matter level of the soil also greatly influences B accumulation or depletion in the soil (Goli et al., 2019). Yermiyaho et al. (1988) observed that the B sorption capacity of the organic matter is four times more compared to clay because

Table 2
Selected references on the sources of boron contamination in soil (mg/kg) and waterways (mg/L).

Source type	Source region	Estimation	Reference
Hydrothermal activity	Seawater in the oceanic crust	0.08 (mg/L)	(Park and Schlesinger, 2002)
Chemical weathering	Red sandstone and other soil parent rocks	0.026 (mg/kg)	(Klee and Graedel, 2004)
Physical weathering	Red sandstone and other soil parent rocks	0.015 (mg/kg)	(Park and Schlesinger, 2002)
Mine soil	Boron mining	1.36 (mg/kg)	(Klee and Graedel, 2004)
High-temperature hydrothermal vents	Submarine volcano	0.004–0.042 (mg/L)	(You et al., 1995)
Rains	Southern Asia	0.0003–0.009 (mg/L)	(Rose et al., 2000)
Rivers	Great Britain	0.015–0.096 (mg/L)	(Neal and Robson, 2000)
Rhine and Meuse rivers	Netherlands	0.04–0.20 (mg/L)	(Wyness et al., 2003)
Rivers, streams, Pristine	China	0.002–0.51 (mg/L)	(Xu et al., 2010)
Mediterranean basin	Southern Europe	3–13 (mg/kg)	(Kloppmann et al., 2003)
Stagnic fluvisols	Northwest Tunisia	0.63 (mg/kg)	(Tlili et al., 2019)
Surface soil	Cukurova Region of Turkey	0.96–2.69 (mg/kg)	(Irmak and Vapur, 2009)
Sandy clay	Northeast India	30.04 (mg/kg)	(Bhupenandra et al., 2020)
Fluid enrichment of the intraplate volcanic materials	Bakony–Balaton Highland Volcanic Field	6.4–6.9 (mg/kg)	(Gmélung et al., 2007)
Hydrochemical conditions	Groundwater, near Jeddah, Saudi Arabia	3.7–44.98 (mg/L)	(Rehman and Cheema, 2017)
Vicinity of geothermal fields	N. Greece	0.75 (mg/kg)	(Dotsika et al., 2006)

Table 3
Concentrations of boron in fresh surface water.

Country/Region	Source	Concentration (mgB/L)	Remarks	References
USA	Coastal drainage waters	15	B rich deposits	(Deverel and Millard, 1988)
California	Lakes	157–360	B rich deposits	
Argentina	Rio Arenales	<0.3	Near borate plants	(Bundschuh, 1992)
		6.9		
Japan	River Asahi	0.009–0.0117		(Korenaga et al., 1980)
Turkey	Simav River	<0.5	Uncontaminated	(Okay et al., 1985)
		4–7	Contaminated with mine waste	
Canada		0.029–0.086		(Sekerka and Lechner, 1990)
Ontario				
Western Canada	Cold river drainage	0.0627		(Tsul and McCart, 1981)
Pakistan	Degh Nala	<0.01–0.46	Near effluent discharges	(Tehseen et al., 1994)
Chile	Loa River Basin	3.99–26	Soil rich in minerals and natural salts; low rainfall	(Cáceres et al., 1992)
Eastern Austria	Rivers	<0.02	No domestic waste	(Schoeller and Bolzer, 1989)
		0.02–0.05	Domestic discharges	
		0.2–0.3	Heavy waste-water discharges and low water flow	
Central Italy	Thermal Springs	22–20,200	Mount Amiata geothermal activity High B content	(Duchi et al., 1987)
UK	Trent River	0.28–0.87	From 1988 to 1990	(Waggott, 1969)
	Thames River	0.05–0.51		

boric acid easily forms complexes with the polyhydroxy functional groups of the organic matter via ligand exchange mechanism.

Vertical distribution of the available B content is also influenced by the soil parameters already mentioned. It primarily depends on the quality of each soil layer (Tlili et al., 2019). The upper layer of the soil can become poor in B due to leaching, but a high organic matter content can promote B accumulation (Sarkar et al., 2008). Thus, even in the case of vertical distribution, the total and available B concentrations may show opposite trends (Barman et al., 2017).

One can determine which areas will have a higher or lower B content based on soil and climatic conditions. According to Shorrocks (1997), for example, Podzol (Spodosol) is one of the soil groups likely to lead to B deficiency when crops are grown on this soil. However, it is not the only factor. For example, Leeman and Sisson (1996) reported an extremely high B concentration (150 mg B/kg) in podzolic soil. Boron content can also vary significantly within a region. Glacial clays, lacustrine alluvium, and stratified plain reserves in the Amur region of Belarus and Russia contain 35–70 mg B/kg, whereas only 2 mg B/kg can be found in ancient alluvial sands of these regions (Adriano, 1986).

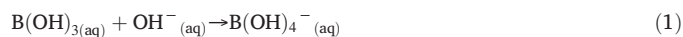
Assessment of the geographical distribution of the bioavailable B fraction found in the surface horizon of the soil, which is critical from crop production point of view, was also carried out. A comprehensive study to map hot water-soluble B in soil involving 30 countries was conducted by Sillanpää (1982). He found that, due to the great variation in B distribution within a country, it is not possible to define the B status precisely for the different countries. However, in general, the soils in Iraq, Mexico, Malta, Turkey, and Syria are rich in B, while the soils in Nepal, Zambia, Nigeria, the Philippines, Malawi, and Sri Lanka typically have a low B content. Shorrocks (1997) reported that there were extensive B-deficient areas in eastern North America, southern Brazil, the Scandinavian Peninsula, mid-western and southern Africa, the eastern coast of China, Korea, and north-eastern India.

Boron distribution is also influenced by human activity. For example, B is taken up by crops and removed from the field, and, at the same time, B is

washed into deeper layers by irrigation, thus decreasing its top layer content. In contrast, B fertilization, the use of B-rich irrigation waters (Kelley and Brown, 1928), organic fertilizers (Purves and Mackenzie, 1973), and certain industrial activities, especially fly ash formation due to coal combustion (Carlson and Adriano, 1993), cause an increase in B in topsoil.

3.2. Distribution in the aquatic environment

Because B occurs naturally in the environment, its residues are expected to remain in water bodies, including surface water (Table 3) and groundwater (Table 4). However, in general, levels of B in surface water are relatively less than the levels toxic to aquatic organisms. Drain waters from irrigation of agricultural lands or from domestic solid waste compost are the anthropogenic sources through which B enters into aquatic environments (Moss et al., 2003). The natural sources of B in aquatic bodies are from seawater encroachment or water-rock interactions (Moneer et al., 2012). The supply of B into aquatic environments differs based on the geology of the surrounding area, rainfall, rate of evaporation, and the type of aquifer (Marine, 1999). Municipal wastewater effluent has a low possibility of becoming a source, and the surrounding geology is usually responsible for high concentrations of B in water (WHO, 2003). On some occasions, sewage sludge is used to fertilize agricultural lands, and wastewater is used for irrigation purposes. Thus, these sources have the potential to add B to the aquatic environment (Moss et al., 2003). Generally, B exists as boric acid and complex poly anions such as $B(OH)_4^-$ in natural water. Various B species' existence is dependent on the levels of B and pH of the solution. Low-pH solutions are dominated by boric acid, while borate ions dominate at high pH conditions (Eq. (1)) (Moneer et al., 2012).



The occurrence and distribution of B in aquatic environments have been extensively studied. The level of B in surface water ranges from $\sim 1 \times 10^{-3}$ to ~ 7 mg B/L, and in seawater, it is ~ 4.4 mg B/L (Moneer et al., 2012). Its

Table 4
Concentrations of boron in groundwater (Solbé et al., 1998).

Country	Region	Concentration (mg/L)	Remarks
United Kingdom	London	0.02–0.54	No. of samples analyzed = 21
	Northumbria	0.31	No. of samples analyzed = 164
Italy	North of Rome	1.0	No. of samples analyzed = 423
Netherlands	Inland areas	0.08–0.6	
Tibet	Tibet autonomous region	>10	Hot springs
India	Delhi	0–3.55	Active floodplain area
Central Italy	Pescara river	>1	Near the coastline
Spain	Valencia	0.64	No. of samples analyzed = 21

value ranges from <0.3 to 100 mg B/L for groundwater sources worldwide (Kochkodan et al., 2015). High B content in shallow groundwater usually originates from upwelling geothermal water or contamination via mining. Additionally, domestic wastewater sources are significantly enriched with varying concentrations of B (Kochkodan et al., 2015).

Several factors control the concentration of B in surface water and groundwater, including the distance to marine coastal regions, industrial and sewage wastewater input, fertilizer input, weathering of parent rock minerals, and dissolution and leaching of salt deposits. For example, in most coastal regions, precipitation containing sea salt spray from oceans is an important source of B input to soil and surface and groundwater (Hilal et al., 2011). A broad range of B levels in surface water and groundwater has been observed (Kuru et al., 2020; Moss and Nagpal, 1981).

According to the International Programme on Chemical Safety (IPCS) report of the WHO in 1998, the mean values for B concentration in water of Russia, Europe, Turkey, and Pakistan were generally lower than 0.6 mg B/L. Specifically in Europe, B in surface water was determined to be between 0.001 and 2 mg B/L with an average value of <0.5 mg B/L. Similar results were recorded in the water bodies in Russia, Turkey, and Pakistan, where the range was 0.01 to 7 mg B/L, and the majority of the values were <0.5 mg B/L. Surface waters in South Africa, Japan, and South America were observed to have B concentrations <0.3 mg B/L. Specifically, in Japan, the level of B in surface water sources had a value of 0.01 mg B/L, and in South Africa, the value for surface water sources was 0.3 mg B/L (Kochkodan et al., 2015). Studies in North America have shown that around 90% of the values for B levels in water sources are <0.4 mg B/L (Moss et al., 2003). The mean concentration of B detected in freshwater in the United States is about 0.1 mg B/L, but it reaches a value of 5–15 mg B/L in the western part of the U.S.A.

A study conducted in British Columbia revealed that the median value of B in surface water sources was around 0.01 mg B/L, and B concentration in the coastal waters of Canada ranged from 3.7 to 4.3 mg B/L (Health Canada, 2020). The B concentration of groundwater in British Columbia was recorded to be within a range of 0.014 to 4.05 mg B/L. In one study area, the minimum detected B concentration had a value of 0.0056 mg/L, and in the same area, B concentrations reached a maximum of 4.15 mg B/L (Moss et al., 2003).

The only distinctive mechanisms that affect the fate of B in aquatic environments are adsorption and desorption with sediments and soil. The majority of the environmentally pertinent B minerals show high solubility in water. Hence, B compounds in water are not efficiently eliminated by natural mechanisms (Butterwick et al., 1989).

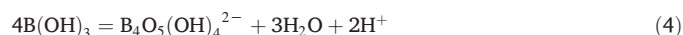
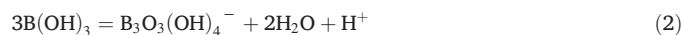
3.3. Chemical forms and speciation

The chemistry of B is governed by its small molecular size and high ionization energy (Woods, 1994). Boron shows a very high affinity towards oxygen, a significant characteristic resulting in forming borates and B oxo-complexes. The most common B compounds (sulphides, oxides, halides, and nitrides) possess the oxidation state of +3. Oxidation states of +1 or 0 are observed in higher boranes, metal borides, sub-valent halides, and compounds with B bonds. The coordination number of natural B compounds is 2 or 4 (Kochkodan et al., 2015).

Boron in the elemental state is inert and insoluble in an aqueous medium (Hawley et al., 1981). Nevertheless, B salts are known to be soluble in water. For example, borax has the highest solubility (25.2 g B/L), and BF_3 has the least solubility (2.4 g B/L) (Kochkodan et al., 2015). Compounds of B are readily transformed into borates once they are exposed to water, and further degradation is not observed (Rai and Zachara, 1984).

Boron released through weathering eventually forms boric acid or borates in aqueous media. Boric acid is a weak acid in an aqueous solution and dissociates as a Lewis acid (Power and Woods, 1997). Thus, inorganic B is dominant in natural water bodies as the mononuclear species, including $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$. The relative distribution of these two B species is determined by the first dissociation constant K_a of boric acid (5.8×10^{-10} mol/L) (Owen, 1934). With a high pK_a value, boric acid

possesses a low rate of dissociation in low or neutral pH values. The pH of the medium is the fundamental factor that predicts the distribution ratio of boric acid molecules:borate ions in an aqueous solution. In seawater, the B species significantly change with pH. Higher pH values are dominated by the monovalent borate anion $\text{B}(\text{OH})_4^-$ and lower pH values by uncharged boric acid molecules (Edzwald and Haarhoff, 2011). Further increase of pH in aqueous solutions favors the formation of polyborate ions including $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^-$, and $\text{B}_4\text{O}_5(\text{OH})_4^-$ (Power and Woods, 1997). Fig. 2 shows the speciation of B with a total concentration of 0.2 M, indicating that the polyborate ions dominate at pH 7–11. The gradual increase of B concentration in aqueous solutions is favored by the formation of tetra borates as follows (Eqs. (2)–(4)) (Fu et al., 2020).



The adsorption of B by soil depends on the pH, organic matter, salinity, clay minerals, and iron and aluminium-hydroxy compounds (Goldberg, 1997). According to WHO (2003), the highest adsorption is observed within the pH range of 7.5–9. Boron fixation in soil occurs via three mechanisms: physical adsorption, anion exchange, and chemical precipitation (Goldberg, 1997; Goldberg et al., 1993a, 1993b). The B fixation process is affected by temperature, moisture level, and wetting and drying cycles (Goldberg, 1997).

4. Biogeochemistry of boron in the environment

4.1. Biogeochemistry of boron in soil

The chemistry and dynamics of B in soil and aquatic environments is relatively less complex compared with other trace-element nutrients (Fig. 3). Boron is unlikely to be subjected to redox or volatilization processes in soil and aquatic environments.

Boron exists in various forms in soil and sediments, including as a solution or in exchangeable or organic-matter complexed forms or primary and secondary minerals. Boron is a micronutrient, and H_3BO_3 is the predominant form of B in soils, under optimum pH conditions, available for plant growth (pH 5–8). The exchangeable B buffers changes in B concentrations of the soil pore water as a result of plant uptake and leaching. Soil organic matter is an important source of plant available B in soil. Boron fertilizer

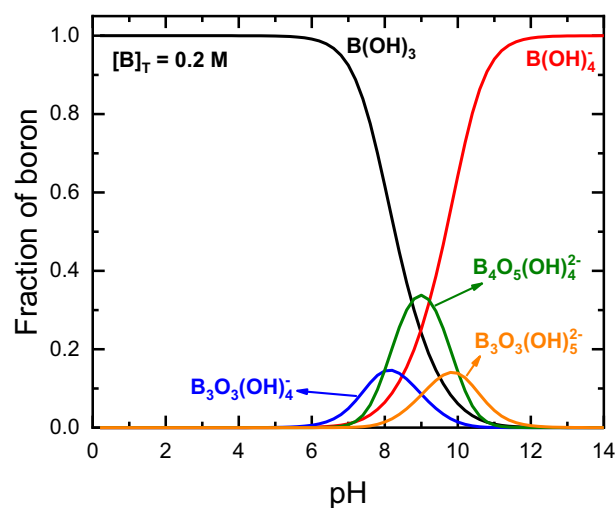


Fig. 2. Speciation of boron in aqueous solution (total boron = 0.2 M). Reproduced from Lin et al. (2021).

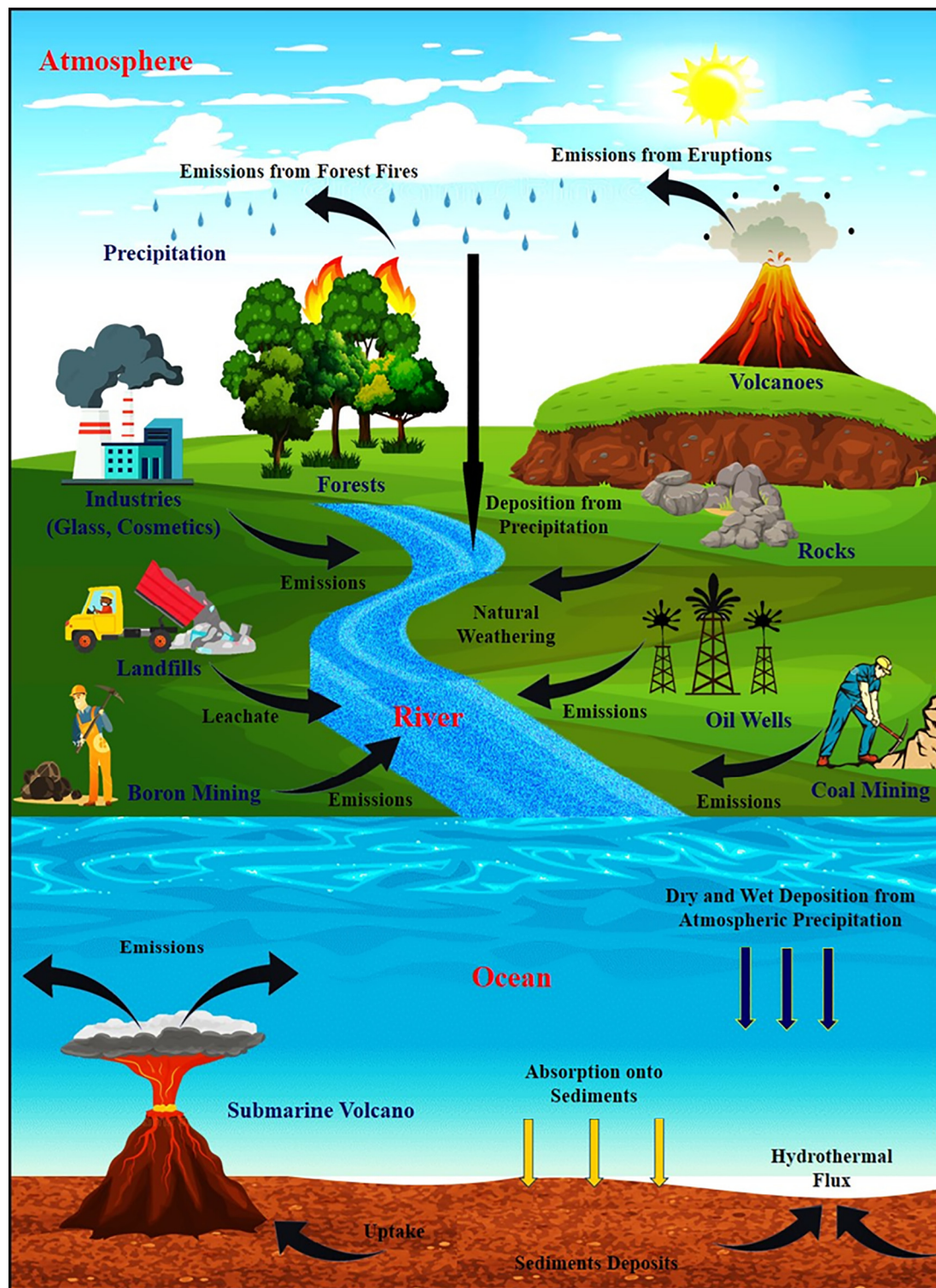


Fig. 3. Interaction of boron in the terrestrial and aquatic environment.

input needs to be carefully managed when applied to soil because the range between B sufficiency and toxicity levels for agricultural crops is relatively narrow. Boron-enriched mineral sources are either insoluble (e.g., tourmaline) or sparingly soluble (e.g., hydrated borate minerals) and are unlikely to determine the supply of B in soil pore water (Goldberg et al., 1993a, 1993b). Boron adsorption reactions with soil and sediment components mainly control the B levels in soil and aqueous solutions, and their bioavailability.

4.2. Biogeochemistry of boron in aquatic environments

The marine system provides most of the earth's B supply, with concentrations ranging from 0.5 to 9.6 mg B/L. For example, B concentration in the Mediterranean Sea is estimated to be high (9.6 mg B/L). The concentration of B in surface water and groundwater sources is normally low and is derived from the dissolution of B from parent rock minerals and soils enriched with borates and borosilicates. Boron levels in groundwater

sources have been shown to vary widely, from <0.3 to >100 mg B/L. For example, B levels in groundwater in southern Europe (e.g., Italy and Spain) were found to range from 0.5 to 1.5 mg B/L and to be 0.6 mg B/L for northern Europe (e.g., Denmark, Germany, and UK).

Boric acid (H_3BO_3) is regarded as a weak acid and does not readily dissociate in an aqueous medium but serves as a Lewis acid by acquiring hydroxyl ions to form the tetrahydroxyborate ion in an aqueous solution. Thus, the predominant inorganic fractions of B in aqueous media are mononuclear species, including H_3BO_3 and the $B(OH)_4^-$ anion. The distribution of B species in marine water depends primarily on the pH of the marine water, with the monovalent $B(OH)_4^-$ anion dominating at higher pH and $B(OH)_3$ acid dominating at lower pH. The distribution of B species in an aqueous system also depends upon B concentrations. At low B levels (<0.02 M), solution B occurs mostly as the mononuclear B species, $B(OH)_3$ and the anion $B(OH)_4^-$, while at higher B levels (0.027–6.48 g B/L) and with increasing pH (6–10), solution polyborate ions, including $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^-$, and $B_5O_6(OH)_4^-$, are likely to occur. The presence of polyborate ions in aqueous solutions is not significant at low B levels (<0.0216 g B/L) in surface and groundwater sources.

4.3. Factors affecting boron biogeochemistry in soil and water

Factors affecting B biogeochemistry, distribution, and availability in soil and water include solution pH, soil texture, soil moisture, and salinity.

As discussed above, pH is one of the dominant factors impacting the speciation and bioavailability of B in soil and aquatic ecosystems. With increasing solution pH, B speciation is likely to transform from the more bioavailable boric acid to the less bioavailable borate anion. Because borate anions are readily adsorbed by soil and sediments, the bioavailability of B decreases with increasing pH. Thus, B adsorption increases with increasing pH; therefore, liming to ameliorate soil acidity can temporarily induce B deficiency in acid soils or decrease B toxicity to plants (Bolan et al., 2001). In addition to ameliorating soil acidity, liming materials, such as calcium carbonate and dolomite, provide surface sites for B adsorption (Goldberg and Forster, 1991). Thus, B adsorption is likely to be greater, especially in calcareous soils with high levels of free calcium carbonate level, thereby resulting in B deficiency (Elrashidi and O'Connor, 1982; Majidi et al., 2010).

Aluminium and iron oxides in soils and sediments have been shown to play a major role in B adsorption (Elrashidi and O'Connor, 1982). Adsorption of B by aluminium and iron oxides increases with rising pH, which is attributed to an increase in the concentration of the borate anion and to the presence of positive charges in these oxides (Su and Suarez, 1995, 1997). Adsorption of B by these oxide minerals involves ligand exchange processes with hydroxyl groups; specific adsorption occurs when the inner-sphere surface complexes with surface functional groups (Su and Suarez, 1995, 2004). Competing inorganic anions, such as silicate, sulphate, phosphate, and oxalate, have been shown to decrease B adsorption by soil and oxides (de Buseti et al., 1995; Lee et al., 2015), and the capacity of these anions to release B from oxides decreases in the order: phosphate > arsenate > sulphate > chloride (Metwally et al., 1974; Goldberg, 1997; Van Eynde et al., 2020). Magnesium hydroxide adsorbs significant quantities of B from the solution (García-Soto and Camacho, 2006; Goldberg, 1997; Rhoades et al., 1970). Thus, the B adsorption capacity of silicate minerals of soils from arid regions has been shown to stem from the surface coatings of magnesium and manganese hydroxide on these minerals (Goldberg, 1997; Rhoades et al., 1970; Tsadilas et al., 1998).

Soil texture is important in B adsorption, which is often found to increase with an increasing clay level of soils and sediments (Elrashidi and O'Connor, 1982; Van Eynde et al., 2020). Boron deficiency is more prevalent in plants grown in sandy soils compared to clay soils, which is attributed to low concentrations of available B in the former soils (Dridi et al., 2019; Fleming, 1980).

Layer silicate clay minerals make a significant contribution to B adsorption in soils and sediments, and B adsorption follows illite > montmorillonite > kaolinite (Goldberg et al., 2000; Keren and Sparks, 1994). Immobilization of B by silicate clay minerals involves two steps; initially,

B is adsorbed through a ligand exchange process with hydroxyl groups on the clay particle edges, which is subsequently incorporated into tetrahedral sites by replacing silicon and aluminium ions (Goldberg, 1997; Goldberg et al., 2000). The B adsorption capacity by silicate minerals is impacted by the nature and amount of exchangeable cations (Goldberg and Suarez, 2011; Mattigod et al., 1985).

Calcium-saturated silicate clays have been shown to adsorb more B compared to sodium and potassium-saturated clays (Goldberg and Suarez, 2011; Mattigod et al., 1985), which is attributed to the fact that Ca-saturated clays remain as tactoids that contain numerous clay particles, while the Na-saturated clays remain in solution as dispersed individual particles (Fatnassi et al., 2022; Keren and Gast, 1981). Because the negative electric potential on the planar surfaces is less extensive in clay tactoids, Ca-saturated clays are more readily accessible to B adsorption than Na-saturated clays (Fatnassi et al., 2022; Keren and Gast, 1981). The ready formation of a calcium-borate ion pair also contributes to increased B adsorption in Ca-saturated clays (Goldberg and Suarez, 2011; Mattigod et al., 1985).

Soil organic matter retains higher amounts of B than mineral soil constituents; hence, soil organic matter is considered an important source of B supply in soil (Gu and Lowe, 1990, 1992; Goldberg and Suarez, 2012). Adsorption of B by mineral soils often increases with increasing inputs of organic amendments, including composts (Yermiyahu et al., 1995; Goldberg and Suarez, 2012). While ligand exchange is an important process for B sorption by organic matter, B–diol complexes also have been shown to form with the hydroxy and carboxylic acid groups of organic matter (Yermiyahu et al., 1988; Goldberg and Suarez, 2012).

5. Bioavailability and toxicity of boron

5.1. Plant-boron interactions

Boron reaches the food chain primarily via plant uptake, and hence bioavailability of B to plants is a major factor in determining B toxicity in human and animals (Brdar-Jokanović, 2020). However, although a century has passed since B was confirmed a biologically essential trace element for higher plants (Warington, 1923), the exact role and the mechanisms of the metabolic functions of this element are still being investigated. Furthermore, it is difficult to determine soil B concentration with toxic effects. For most soils and agricultural plants, 0.5–1.5 mg B/kg (ppm) of hot water extractable B fraction is optimal, which is relatively a narrow range between deficiency and toxicity (Eaton, 1944; Yau et al., 1994). The bioavailability of B is determined by soil pH, moisture and texture, air humidity, and temperature. Vertical distribution in the soil also affects the uptake, i.e. the plant developmental phase in which the toxic effects are manifested. Therefore both disorders of B (i.e., deficiency and toxicity) are likely to occur in the same region, even within the same season (Brennan and Adcock, 2004; Shorrocks, 1997; Yau, 2010; Zhang et al., 2020).

The dominant function of B is in the synthesis of the cell wall, as well as in maintaining its structure and function. Boric acid and the borate anion both form ester bonds with molecules containing hydroxyl groups (e.g., ribose, apiose, and sorbitol). By forming complexes with apiose residues of rhamnogalacturonan II (RGII) monomers, the element contributes to the stability of the cell wall (Matoh, 1997; Matoh et al., 1996; O'Neill et al., 2004). It also complexes with glycosyl inositol phosphoryl ceramides that bind the plasma membrane with the wall. Furthermore, B forms complexes with amino acids and phenolics. It has been proposed that the predominant function of B in plants is to stabilize molecules with *cis*-diol groups regardless of their biological function (Chormova and Fry, 2016; Chormova et al., 2014). Because B is related to plasma membrane functions, the element is involved in various enzymatic processes, along with the transport of hormones and metabolites (Seth and Aery, 2017). Boron is involved in both vegetative (root elongation, leaf expansion) and generative (flower, fertilization, fruit, seed) growth and development at the plant organ level. Boron is necessary for pollen-tube growth (Obermeyer

et al., 1996). Boron deprivation leads to the impairment of leaf structure and function, resulting in reduced CO₂ assimilation and photosynthesis (Camacho-Cristóbal et al., 2018; Goldbach and Wimmer, 2007; Landi et al., 2019; Li et al., 2017; Shireen et al., 2018).

Unlike other nutrient elements that are absorbed by plant roots mostly in the charged ionic forms, B is predominately (96–98%) taken up as a small un-dissociated molecule of boric acid, for which plant cell membranes are highly permeable (Raven, 1980). Merely 2–4% of B is absorbed up in the form of borate anions (Bolaños et al., 2004). The molecule easily enters the cell through the lipid bilayer and Hg-sensitive channels such as aquaporins and protein channels (Dordas et al., 2000; Marschner, 1995). In conditions of B sufficiency, the uptake from the soil and further transport is principally by passive diffusion, which has long been hypothesized as being the exclusive transport mechanism (Hu and Brown, 1997; Nable, 1988; Nable et al., 1990). It was eventually established that the mechanism of uptake and translocation depends on external B availability. In deficiency, active mechanisms have to be engaged to act against the concentration gradient and maintain homeostasis. Active transport involves boric acid channels, i.e., nodulin 26-like intrinsic proteins (NIPs) and borate transporters (BORs) (Fig. 4), both first identified in *Arabidopsis* and later confirmed in various plants, mainly agricultural plants. Additionally, the borate transporter BOR4 participates in the exclusion of excessive B from plant tissues (Huang et al., 2022; Miwa et al., 2013; Reid, 2014; Shao et al., 2017). The mobility of B in a plant species largely depends on the primary product of photosynthesis (Gauch and Dugger Jr., 1953). Most species produce sucrose, which results in restricted B phloem mobility. However, the element builds complexes with polyols and is, therefore, highly mobile in the phloem of species in which they are the primary photosynthesis products. Hence, differences in B concentration pattern occur across the leaves of species with rapid or limited phloem mobility. The concentration is uniform in phloem-mobile species. The element accumulates in young leaves and fruits. In species with mobility being limited to the xylem, B is transported via the transpiration stream and accumulates in leaf tips and margins, and the level is higher in older leaves than in younger leaves (Stangoulis et al., 2010).

According to Lovatt (1985), at the beginning of the evolution of higher plants, B was not sufficiently represented in the environment and, therefore, was not an essential nutritional element. Xylem evolution and passive transport by the transpiration flow allowed the accumulation of B in the shoot tips of primitive higher plants in a concentration sufficient to be included in their metabolism and to become an essential nutrient. Lewis (2019) hypothesized against the essentiality of the element and made arguments about its potential toxicity. He discussed the mechanisms that plants

have developed during evolution to overcome toxicity. The hypothesis sparked a debate, pointing again to the uniqueness of B and the need for further research on its roles in plant metabolism (González-Fontes, 2020; McGrath, 2020; Wimmer et al., 2020).

5.2. Toxicity of boron to plants, animals, and humans

When excessive, soil-bioavailable B can exert toxicity on plants. The symptoms of the disorder were described as early as Christensen (1934) and Eaton (1944). However, B toxicity as a potentially serious problem in agricultural production was first recognized in the eighties of the last century in Australia, on field-grown barley cv. Clipper (Cartwright et al., 1984). Brown necrotic spots noticed on leaves which are a symptom of the toxicity were previously thought to be due to *Pyrenophora teres* f. ssp. *maculata* infestation. The barley yield loss was approximately 17%, and the dry shoot B concentration was 96 mg/kg. Boron toxicity is generally associated to warm arid and semiarid regions, although it can be found in arid environments at low temperatures (Mahalakshmi et al., 1995; Nable et al., 1997; Paull et al., 1991; Thili et al., 2019; Ye et al., 2003; Yermiyahu and Ben-gal, 2017).

As a consequence of detrimental effects on protein biosynthesis, cell division and development, and reactions involving ATP and NADPH, B toxicity may operate at a level of virtually all plant organs. The symptoms and their severity vary among species and include necrosis, chlorosis, and lesions on leaves, decreased root elongation, delayed developmental phases, and consequently reduced yield (Landi et al., 2019; Paull et al., 1990; Reid et al., 2004).

Boron requirements and toxicity tolerance differ among species, as well as within plant species (Table SI 1). Monocotyledons contain less B than dicotyledons (Gupta et al., 1985). Therefore, cereals, which are monocotyledons, generally require the least amount of B, while vegetables and fruit trees require a moderate amount. Legumes and tuber species require considerably higher B amounts. But the classification is not rigorous. In addition, in spite of the fact that plants that grow on B-laden soils take up comparatively higher B quantities, the tissue concentration is not an indicator of toxicity. Accordingly, critical B concentrations are difficult to determine even within a species. For barley and wheat, an extremely wide range, from as low as 10 to even >300 mg B/kg, has been reported. In addition to inter and intra-specific variability, critical plant B concentration depends on several factors, including plant organ, developmental phase, experimental conditions (field, pot, hydroponic, or in vitro), treatment intensity, and application time. Therefore, B tolerant varieties are not necessarily characterized by low tissue B concentrations (Blevins and Lukaszewski,

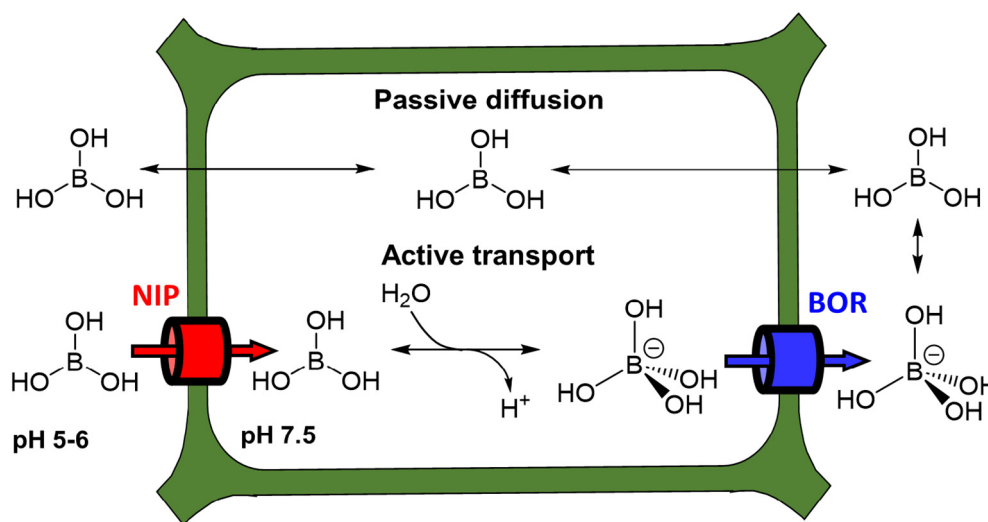


Fig. 4. Scheme of passive diffusion and active transport mechanisms of boron into plant cell. (NIP: nodulin 26-like intrinsic protein, BOR: borate transporter). Reproduced based on Yoshinari and Takano (2017a, 2017b).

1998; Cervilla et al., 2007; Furlani et al., 2003; García-Sánchez et al., 2020; Landi et al., 2013; Marschner, 2012; Nable et al., 1997; Torun et al., 2006; Zhao et al., 2019a). Reduced uptake (Huang and Graham, 1990), redistribution among organs (Nable, 1989), efflux from plant roots (Reid, 2007), chelating with organic compounds (Landi et al., 2015; Papadakis et al., 2018), separation in vacuoles and cell walls (Wakuta et al., 2016), and strong antioxidant response (Landi et al., 2012) are proposed as possible mechanisms of B tolerance. Nevertheless, the widely documented intraspecific differences in tolerance are used by breeders to improve the productivity of agricultural plants in B-toxicity-prone areas.

Borax and boric acid were used for the preservation of all kinds of food except milk, and B was been considered to be a useful and harmless element for human nutrition (Nielsen, 1997). However, when ingested in doses higher than 4 mg/day, B disturbs the appetite, digestion, and health (Wiley, 1904). Therefore, its use as a preservative has been prohibited since the mid-1950s.

Boron exhibits beneficial effects on plants, animals and humans. The element is not considered essential in animal and human nutrition because its specific biochemical function has not yet been reported, and deficiency does not interrupt the mammal life cycle (WHO, 1996). Boron affects the metabolism of macro- and secondary-nutrients (e.g., P, S, Ca, and Mg), triglycerides, glucose, amino acids, proteins, reactive oxygen compounds, and estrogens. Thus, it influences the function of a range of organs, that include the brain, skeleton, and immune system. Positive effects of B in the prevention of arthritis, osteoporosis, and yeast infection have been reported. In addition, central nervous system functioning, certain cancer-cell-growth retardation, and improved hormone (thyroid, insulin, estrogen, progesterone) functioning have been reported as a result of B treatment (Nielsen, 2014 and references therein).

Boron is ingested primarily from food sources, and is absorbed from the gastrointestinal tract and excreted in the urine. The suggested daily intake ranges from 1 to 28 mg (EFSA, 2004; FNB, 2001; WHO, 1996). Toxicity in humans is rare, even in regions where the drinking water has high concentrations and where people work in B mines and industry (Sayli et al., 1998, 2003). However, acute ingestion of high doses can cause diarrhea, dermatitis, and lethargy (Linden et al., 1986). Chronic B toxicity includes neurological effects, kidney damage, and reduced appetite, body weight, and reproduction activity (Hunt, 1993; Nielsen, 1997; Uluşik et al., 2018).

6. Risk management of boron in contaminated environment

6.1. Remediation of boron-contaminated soil

Several remediation technologies can be applied to mitigate or eliminate B contamination in soils. These remediation approaches can be categorized as in-situ or ex-situ techniques. However, the procedures used within the two remediation approaches can be grouped into physicochemical and biological methods (Derakhshan Nejad et al., 2018) (Table 5; Fig. 5).

6.1.1. Physicochemical remediation

In the case of B, the most common treatment process is leaching, which means watering with excessive water. The method can be used on moderately B-polluted soils so that the amount of water applied does not cause nutrient loss (Moraga et al., 2014; Rámila et al., 2016b). The volume of water required for the intervention can be significant. In soil with a maximum content of 10 mg B/kg in the saturation extract, 3000 mm of water is required to reach the 1 mg B/kg value for the 0–1.5 m soil layer (Bingham et al., 1972).

Physicochemical remediation of soils with high B content can also mean adding different amendments to the soil, which can reduce the leaching and bioavailability of B. On acidic soils, by raising the pH with the use of lime or calcium phosphate, the absorption of B by plants can be reduced, while on saline soils, a similar effect can be achieved with gypsum (Bartlett and Picarelli, 1973; Nable et al., 1997). Organic materials like compost can efficiently moderate the harmful impact of B in soil (Esteban et al., 2016a, 2016b). The application of nanoparticles for binding soil contaminants is

a new method. Mahdavi et al. (2020) observed that MgO nanoparticles were effective in the remediation of B in moderately contaminated soil.

6.1.2. Phytoremediation

In the process of phytoremediation, plants are used to ameliorate the risk of pollution. In the case of B pollution, several subtypes of phytoremediation can be used (Rámila et al., 2016b). The most widely researched technique is phytoextraction, during which B-tolerant plants are used to accumulate B in their aboveground parts. Excess B can thus be removed by harvesting the plants. Among herbaceous dicotyledons, most information is available on *Brassica napus* (rapeseed), *Brassica juncea* (brown mustard), and *Gypsophila* (baby's breath) species (Diehn et al., 2019; Dinh et al., 2021; Rámila et al., 2016b). Among the monocotyledons, *Puccinellia* (alkali grass) and *Festuca* (fescue) species have been studied most widely for B uptake (Rámila et al., 2016b; Zhao et al., 2019b). In relation to phytomanagement solutions for inhibiting B pollution in soil, *Populus* (poplar) species have been investigated most often and proved to be an effective tool by reducing B leaching and accumulating B in plant tissue (Chen et al., 2017; Rámila et al., 2016b; Yıldırım and Kasım, 2018).

Depending on the experimental conditions, the level of B accumulated in plants can vary over a wide range, even in the case of the same plant species. In addition, B can be enriched to a different extent in individual plant parts (Rékási et al., 2021). The shoot of *Brassica juncea* contained 1800–2911 mg B/kg when grown with a river sediment containing of 77 mg B/kg (Tassi et al., 2011). But when planted on soil with a B level of 58 mg/kg, B content in the plant shoot was 112 mg B/kg (Bañuelos et al., 1993a, 1993b). Boron content reached 845 mg B/kg in the leaves of *Populus* sp., while under the same conditions, the B content in the stem was only 21 mg B/kg. The highest recorded value was measured in *Puccinellia frigida*, where B content reached over 5000 mg B/kg in the dry matter (Rámila et al., 2016a).

Despite high plant B concentrations, phytoremediation is a slow process, but it can be accelerated in several ways. Induced or enhanced phytoremediation is a process in which additives are used to increase the bioavailability or reduce the stress caused by the pollutant, thus improving the efficiency of phytoremediation (Barbafieri, 2016). The application of humic acids as chelating agents enhances the release of B from soil constituents and its uptake in different crops (Angin et al., 2008; Turan and Angin, 2004). Jasmonic acid was found to be effective in ameliorating the toxicity of high B concentration on *Puccinellia tenuiflora*, thus promoting its effectiveness in soil remediation (Zhao et al., 2019b). The combined input of urea and cytokinin enhanced sixfold the amount of B extracted by *Helianthus annuus* (sunflower) on contaminated sediment (Barbafieri, 2016). Regarding the biological enhancement methods, according to the results of Estringü et al. (2014), *Bacillus megaterium* compensated for the negative effect of B pollution on the biomass of *Brassica napus*, thus increasing the level of B taken up from the soil. Promoting plant growth with fertilizer increases the effectiveness of phytoremediation (Giansoldati et al., 2012).

Most experimental results refer to a period of one or two years. Depending on the tested plant and the experimental setup, the initially available B concentration can be reduced by 30–50% during such a time interval (Rámila et al., 2016b). Based on these short-term investigations, the time required to reach the target B concentration cannot be accurately estimated because the efficiency of phytoextraction shows a gradually decreasing trend over the years (Bañuelos et al., 1995).

6.2. Remediation of boron-contaminated water sources

Boron-enriched water is an important source of B input to soil and aquatic environments. As described above, in aqueous environments, solution B occurs in various forms, depending on the solution pH and B level. At low B level (≤ 216 mg B/L), solution B mostly occurs as the mononuclear B species, $B(OH)_3$ and $B(OH)_4^-$. At high B levels with the increase in pH, polynuclear B species, including $B_2O(OH)_6^{2-}$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$, are formed. Because B concentration in marine water is around 4.8 mg B/L, it is expected that mostly mononuclear species $B(OH)$

Table 5
Selected references on the remediation of boron contamination in soil and waterways.

Environmental matrix	Initial concentration (I.C.) and/or degree of contamination	Test plant and/or amendment	Efficiency	References
Physicochemical remediation				
Soil with naturally high boron content	Water-extractable B 0.6–10.3 mg/L	Leaching by irrigation for 7 months, applying ~14 ft of water.	Water-extractable B removal: 33.3–94.4%	(Bingham et al., 1972)
Contaminated soil	2 and 10 mg/L solution treatment	2% nano-MgO, 1% biochar, 1% humic acid	MgO nanoparticles increased the ratio of residual B fraction in soil from ~50% to ~70%, while humic acid and biochar decreased adsorption	(Mahdavi et al., 2020)
Soil with naturally high boron content	Water-extractable B: 38 mg/L	Modifying acid titratable basicity using H ₂ SO ₄ (96%) and leaching with water: Acidified-extracted Acidified-extracted-alkalized Acidified-alkalized-extracted	B concentration in leachate (mg/L) 12.3–32.4 12.3–26.0 8.5–13.0	(Prather, 1977)
Soil	Boron	Liming	na.	(Bartlett and Picarelli, 1973)
Seawater and desalinated seawater	Mg depletion and Ca enrichment in residual seawater	Coal and fly ash	95.0%	(Polat et al., 2004)
Water	Boron	Ceramic foam supported active materials (CF-mesoporous silica)	na.	(Sanfeliu et al., 2015)
Wastewater	Boric acid (H ₃ BO ₃) and perborate (NaBO ₃)	Chemical oxo-precipitation (COP)	98.5%	(Shih et al., 2014)
Water	Boron as barium perborate salts	Hydrogen peroxide (H ₂ O ₂) (COP)	99.70%	(Lin et al., 2016)
Water	Boron	Eggshell	96.30%	(Al-Ghouti and Salih, 2018)
Desalinated water	Boron	Eggshell membrane (ESM) and modified eggshell membrane (MESM)	ESM 97.0% & MESM 95.0%	(Al-Ghouti and Salih, 2018)
Wastewater	Poplar plants and Boron	Hybrid poplar clones (phytoremediation)	na.	(Chen et al., 2017)
Water	Boron	Activated carbon and Sawdust	na.	(Jaouadi, 2021)
Saline groundwater	Low concentration B in saline groundwater under pH 7–10, 25 °C to 70 °C	Ion exchange resin	na.	(Hussain et al., 2019)
Aqueous solutions	Boric in aqueous solutions	<i>N,N</i> -bis(2,3-dihydroxypropyl) octadecylamine (BPO)	na.	(Bicak et al., 2003)
Aqueous solutions	Boric acid under ionic form and high pH condition	Reverse osmosis	69.0%	(Öztürk et al., 2008)
Aqueous solutions	B in aqueous solution under suitable conditions	Electrodialysis (ED) with anion-exchange membranes (AHA, ACM, AMH)	na.	(Yazicigil and Oztekin, 2006)
Water	B in river water and B in produced water	Electrocoagulation (EC)	Up to 80.0%	(Chen et al., 2020)
Bioremediation				
Minimal and soil extract liquid media	Boric acid: 20 mM (1.22 mg/L) 40 mM (2.78 mg/L)	Selected actinobacteria: <i>Streptomyces</i> sp. 053 <i>Streptomyces</i> sp. 128	Boric acid removed: 36.7–59.0% 59.1–72.7%	(Moraga et al., 2017)
Bioremediation combined with phytoremediation				
Contaminated soil	Treatment: 15 mg/kg B	Test plant: <i>Brassica napus</i> with or without <i>Bacillus megaterium</i>	<i>B. napus</i> extracted 178 g B/ha without and 636 g B/ha with <i>B. megaterium</i> .	(Esringü et al., 2014)
Contaminated soil	Total B: 58.1 mg/kg; Available B: 3.75 mg/kg ³	Natural meadow vegetation with <i>Bacillus megaterium</i> var. <i>phosphaticum</i> PGPR	B removal was increased by PGPR together with P fertilization by a maximum of 57%	(Gullap et al., 2014)
Phytoremediation combined with physicochemical remediation				
Contaminated soil	24 mg/L soluble B	Test plant: <i>Solanum lycopersicum</i> , amendment: compost 4 and 6%	6% compost amendment significantly reduced B concentration in plant leaves	(Esteban et al., 2016a, 2016b)
Phytoremediation				
Contaminated soil	Total B: 62 mg/kg; water-extractable B: 8.5 mg/L	Test plant: castor oil (<i>Ricinus communis</i> L.)	Time required for 50% removal: control: 14.9 yrs., filter cake addition: 16.3 yrs., peat addition: 12.2 yrs.	(Abreu et al., 2012)
Contaminated soil	I.C.: 0.2 mg/kg Contamination: 0–180 B (as H ₃ BO ₃)	Test plant: vetiver grass (<i>Vetiveria zizanioides</i>) + 0–400 kg/ha humic acid solution	B removal was proportional with B contamination and enhanced by humic acid up to 73 µg/pot (4.8 fold compared to control)	(Angin et al., 2008)
Soil with naturally high B content	Water-extractable B: 3 mg/L in greenhouse and up to 10 mg/L in field experiment	Test plants: Indian mustard, canola, tall fescue, kenaf, birdsfoot trefoil	Extractable B removal: control: 10–14%, Indian mustard: 37–40%, canola: 33%, tall fescue and kenaf: 37%, birdsfoot trefoil: 41%	(Bañuelos, 1996)
Soil with naturally high B content	Water-extractable B: 1–10 mg/kg	Test plants: Indian mustard, tall fescue, birdsfoot trefoil, kenaf	Extractable B removal: control: 3–11%, Indian mustard: 32–57%, tall fescue: 26–54%, birdsfoot trefoil: 28–56%, kenaf: 26%	(Bañuelos et al., 1993a)
Soil with naturally high B content	Water-extractable B: 3.00 mg/kg	Test plants: brown mustard, tall fescue	Extractable B removal: control: 21%, brown mustard and tall fescue: 37%	(Bañuelos et al., 1993b)
Soil with naturally high B content	Water-extractable B: >5 mg/L	Test plant: tall fescue (3 harvests/year)	yr1: –201 mg/m yr2: –492 mg/m	(Bañuelos et al., 1995)
Open B mine sites	12–45 mg/kg B	Test plants: <i>Puccinella distans</i> , <i>Gypsophila perfoliata</i> , <i>Isatis glauca</i> , <i>Elymus elongatus</i> , <i>Glaucium corniculatum</i> , <i>Alyssum sibiricum</i> , <i>Polygonum equisetiforme</i> , <i>Chenopodium album</i> , <i>Tamarix tetrandra</i>	All of the test plants were B accumulators. The highest B content of 270 mg/kg was found in <i>P. distans</i>	(Böcük and Türe, 2014)
Soil with naturally high B content	Water-extractable B: 0.12 and 10.45 mg/L	Test plant: “agretti” (<i>Salsola soda</i>), irrigation water contained 4 mg/L B	<i>S. soda</i> tolerated 10.45 mg/L B soil with additional irrigation of 4 mg/L B water and accumulated up to 110 mg/kg B without toxicity symptoms.	(Centofanti and Bañuelos, 2015)

Table 5 (continued)

Environmental matrix	Initial concentration (I.C.) and/or degree of contamination	Test plant and/or amendment	Efficiency	References
Contaminated soil	B treatment: 0–240 mg/L	Test plant: <i>Stizolobium aterrimum</i>	<i>S. aterrimum</i> extracted 150–379 g/ha B	(Costa et al., 2018)
Contaminated soil	30, 60, 120, 240, and 480 mg/L B soil	Test plant: <i>Calopogonium mucunoides</i>	<i>C. mucunoides</i> tolerated B doses up to 480 mg/L B and removes B contamination in 1–2 years.	(da Silva et al., 2021)
Contaminated soil	Water-extractable B: 3.8 mg/kg, total B: 6.4 mg/kg	Test plants: mustard, turnip, amaranth, kenaf	Removal factor of the plants were kenaf: 52.8, mustard: 25.0, amaranth: 22.0, turnip: 18.2	(dos Santos et al., 2010)
Contaminated river sediment	77.1 mg/kg total and 40.1 mg/kg available fraction	Test plant: <i>Brassica juncea</i> , nitrogen fertilization: 0–200 kg/ha urea	Phytoextracted B increased from 5 to 45 mg lysimeter ⁻¹ in parallel with increasing N fertilization	(Giansoldati et al., 2012)
Soil with naturally high B content	Total B: 4630–9310 mg/kg, available B: 2480–5740 mg/kg in 0–5 cm layer	Test plant: <i>Puccinellia frigida</i>	<i>P. frigida</i> tolerates extremely high >4000 mg/kg available B and high concentrations in shoots (>4900 mg/kg DW). Concentrations in plant tissue were 0.9–2.8 times higher than available B in soil.	(Rámila et al., 2015)
Perlite	500 mg/L B in Hoagland solution	Test plant: <i>Puccinellia frigida</i>	The B concentration in <i>P. frigida</i> reached a value 10 times higher (5000 mg/kg DM) than in the medium.	(Rámila et al., 2016)
Wood-waste	30 mg/kg total B	Test plant: <i>Populus sp.</i>	During 3 years, the poplars extracted into their leaves up to 42% of the B present in the wood-waste	(Robinson et al., 2007)
Contaminated river sediment	77.1 mg/kg total and 40.1 mg/kg available fraction	Test plants: <i>Brassica juncea</i> , <i>Zea mays</i> , <i>Helianthus annuus</i>	After two 35 days growing cycles, the residual B available fraction decreased by ~50% for each plant.	(Tassi et al., 2011)
Soil amended with nano-CeO ₂ at 0–800 mg/kg	25 mg/kg available and 60 mg/kg total B	Test plant: <i>Helianthus annuus</i>	B concentration in <i>H. annuus</i> stem and leaves reached 1.8 and 28 times higher B content than the available B in soil, respectively.	(Tassi et al., 2017)
Contaminated soil	Treated with 100 mg/kg B (H ₃ BO ₃)	Test plants: <i>Zea mays</i> , <i>Helianthus annuus</i> Organic complexifying agents: 0–10.0 m mol/kg: citric acid, DTPA, EDTA, humic acid	Humic acid was the most effective in enhancing B uptake in both species. Sunflower was more effective in uptake.	(Turan and Angin, 2004)
Soil	Boron	Kenaf (<i>Hybiscus canabinnus</i>), mustard (<i>Brassica juncea</i>), turnip (<i>Raphanus sativus</i>) and amaranth (<i>Amaranthus crentus</i>) (Phytoremediation)	18.2%–52.8%	(Santos et al., 2010)
Nutrient solution	0.25 (control), 1, 5, 10, 50, 100, 250, 500, 750, and 1000 mg/L B for 15 d	Test plants: reed (<i>Phragmites australis</i> L.), cattail (<i>Typha latifolia</i> L.) and vetiver (<i>Chrysopogon zizanioides</i> L.)	Reed, cattail and vetiver survived at up to 250, 500 and 750 mg/L B, and their biomass decreased significantly at 1, 50 and 500 mg/L, respectively. Reed had a higher ability to uptake B at B < 250 mg/L, whereas cattail at B > 250 mg/L.	(Xin and Huang, 2017)
Hydroponic/Hoagland solution	Maximum B doses by plants were: <i>T. pannonicum</i> (40 mg/L), <i>S. glauca</i> (250 mg/L), <i>I. wilsonii</i> (700 mg/L), and <i>P. tenuiflora</i> (300 mg/L)	Test plants: <i>Tripolium pannonicum</i> , <i>Suaeda glauca</i> , <i>Iris wilsonii</i> , and <i>Puccinellia tenuiflora</i>	Maximum B concentrations in shoot tissues were: <i>T. pannonicum</i> (0.45 mg/g DW), <i>S. glauca</i> (2.48 mg/g DW), <i>I. wilsonii</i> (15.21 mg/g DW), and <i>P. tenuiflora</i> (8.03 mg/g DW).	(Zhao et al., 2019a)
Hydroponic/Hoagland solution	300 mg/L B + different jasmonic acid	Test plant: <i>Puccinellia tenuiflora</i>	0.1 mM jasmonic acid decreased the bioconcentration factor of B in the shoot from 70 to 20 but doubled the dry biomass.	(Zhao et al., 2019b)
Water	B contamination	Poplar and willow (constructed wetland)	35.0–54.0%	(Yıldırım and Kasım, 2018)

₃ and B(OH)₄⁻ occur in ocean water. This section covers the various traditional and advanced remediation technologies used for B elimination from aqueous systems that involve adsorption and precipitation, anion exchange, reverse osmosis, liquid-liquid extraction, electrodialysis and phytoremediation processes (Tables 6).

6.2.1. Adsorption and chemical precipitation

Various adsorbents, including metal oxides, are used to remove B from water (Lin et al., 2021; Mahasti et al., 2022). Recently, synthetic anionic clays including double-layered hydroxides (DLHs) or hydrotalcites [e.g., hydrocalumite (Ca₄Al₂(OH)₁₂(OH)₂·6H₂O) and ettringite (Ca₆Al₂(OH)₁₂(SO₄)₃·26H₂O) DHLs] were found to be suitable for the adsorption of various oxyanions including B from high pH wastewater sources (Gao et al., 2017; Chrysochoou and Dermatas, 2006). However, maintenance of high pH levels in the treatment process is required because of the chemical instability of both of these DLHs at low pH conditions.

The removal of B from aqueous systems by various metal hydroxides, including Ti(IV), Zr(IV), Fe(III), La(III), Al(III), and Zn(II), has been investigated, and the capacity of hydroxides for B removal had the following

ranking: Al(OH)₃ < Fe(OH)₃ < Ti(OH)₄ < La(OH)₃ < Zr(OH)₃. However, their low mechanical stability renders them unsuitable for large-scale applications. Mixed Zr-Fe hydroxides with good mechanical strength have been found to be chemically stable, with high B adsorption capacity (Bhagyaraj et al., 2021; Kydd, 1983; Xu and Jiang, 2008).

Aluminium hydroxides (Al(OH)₃) were examined for the adsorption of B from aqueous systems. Boron adsorption by Al(OH)₃ decreased with increasing degree of crystallinity of Al(OH)₃ (Dubey and Mehrotra, 1964; Prodromou, 2003).

Activated carbon (AC) is used widely for the removal of pollutants including B in wastewater and groundwater sources (Melliti et al., 2020; Yagmur Goren et al., 2022). The impregnation of AC with citric or tartaric acid has been shown to enhance B adsorption capacity. Granulated AC treated with mannitol was demonstrated to be effective in the removal of B from industrial wastewater with B levels of 25–70 mg/L B (Kluczkwa et al., 2007a, 2007b).

There are several inorganic and organic chemicals that can be used to precipitate B in wastewater streams. Lime precipitation can reduce B concentration from >1000 mg B/L to around 400 mg B/L in wastewater, and

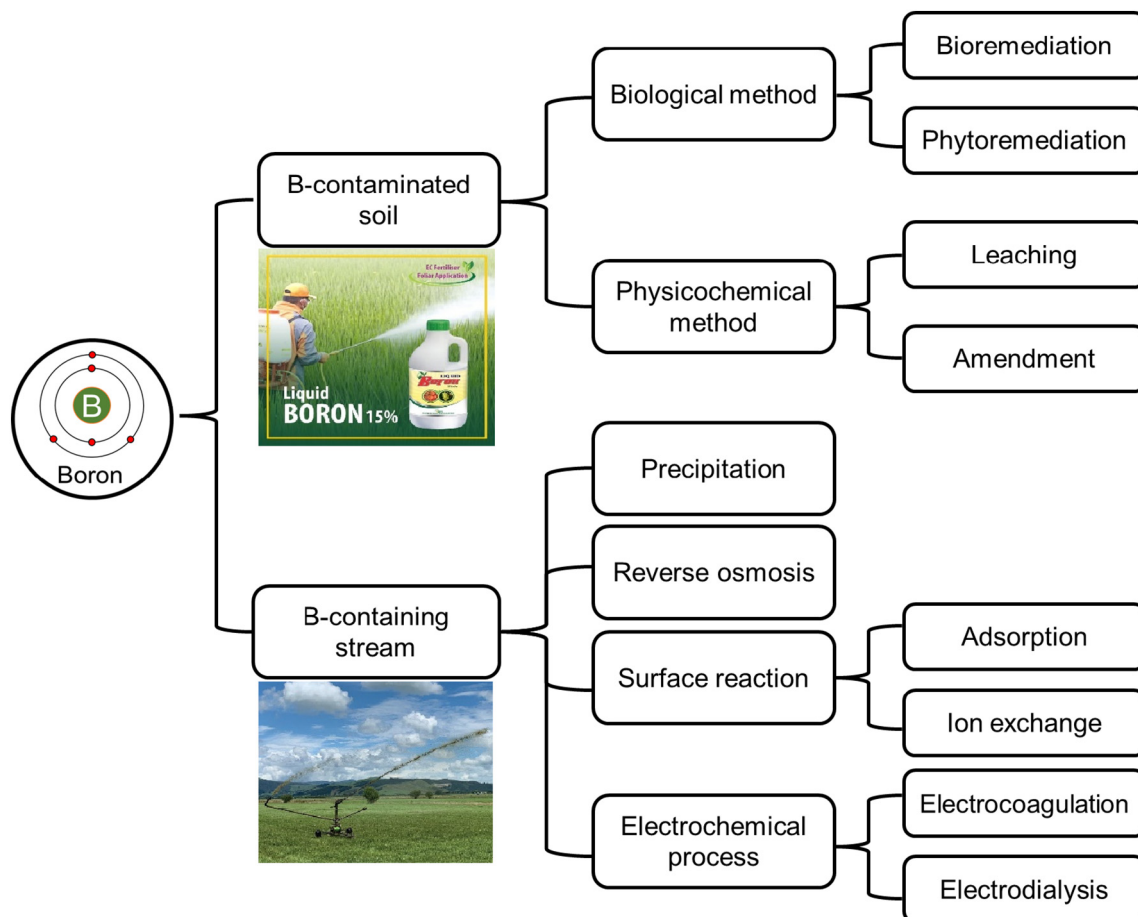


Fig. 5. Technologies for the removal of boron from aquatic and soil environments.

subsequent application of metallic compounds or organic polyelectrolytes used for the coagulation can decrease B levels to <400 mg/L (Remy et al., 2005). However, because extreme solution pH levels are likely to decrease B removal efficiency, the requirement of a large volume of chemicals to buffer pH is likely to lead to issues with salinity. Although zirconyl chloride, chromium(III) nitrate, and nickel-(II) compounds have been found to be effective in the removal of B from solution through precipitation reactions, their cost hinders their application in commercial operations (Kydd, 1983). The precipitability of B was found to be enhanced with the addition of hydrogen peroxide (Lin et al., 2017). In the presence of hydrogen peroxide, perborate anions would form in alkaline conditions, which could be easily precipitated with base earth metal ions, such as Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , in ambient condition (Shih et al., 2014).

6.2.2. Ion-exchange resin and liquid-liquid extraction

An anion-exchange resin material, Amberlite with *N*-methylglucamine functional groups, has been found to be B-specific, and offers an effective ion exchange efficiency for B. Although the selectivity of this resin for B is relatively high, the anion exchange capacity decreases with increasing flow rate (Simonnot et al., 2000). Some polymer-supported resins, including iminodipropylene glycol, were found to be effective in chelating B and removing it at high levels. For example, glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-divinyl benzene (DVB) terpolymer beads possess high B loading capacity with reasonably rapid ion exchange capability (Senkal and Bicak, 2003). A continuous polymer-enhanced ultra-filtration (PEUF) system was demonstrated to be effective for eliminating B from water sources via the complexation of B with polyvinyl alcohol (PVA) (Dilek et al., 2002).

The liquid-liquid extraction process involves dispersing water-insoluble poly-hydroxy compounds in appropriate water-immiscible solvent

solutions, which have specific complexation capacity with B. This technology was originally proposed exclusively for recovering B to produce boric acid from weak-brine liquors with high B concentrations (>1.0%). For example, *N,N*-Bis(2,3-dihydroxypropyl) octadecylamine (BPO) in 2-ethyl hexanol was found to be effective in the removal of B in aqueous media containing 1.2% (w/w) boric acid, and the complexed B can be recovered readily by extracting with dilute sulphuric acid (Bicak et al., 2003; Kluczka et al., 2007a, 2007b).

6.2.3. Reverse osmosis (RO)

Applying a multistage reverse osmosis (RO) system is effective in reducing B concentration to the WHO drinking water guideline standard value (i.e., 0.5 mg/L) (WHO, 2009). However, about 2–20 L of wastewater are produced for every 1 L of B-free water. Furthermore, the low-energy efficiency of RO also restricts its application for the removal of B from water sources. Nevertheless, a multistage RO system with low-pressure membranes is applicable for B removal during seawater desalination. It maintains a high B removal efficiency with relatively low energy consumption.

In order to increase B recovery, feed-water pH needs to be raised to >9, which can accelerate the scaling potential of the membrane. An emerging method using a cellulose acetate butyrate membrane has been found to achieve greater removal of boric acid compared to the traditional cellulose-acetate membrane. However, for water with low B concentrations (< 500 mg B/L), RO treatment was found to be energy intensive compared to anion-exchange technology (Abdellah et al., 2020; Sorg, 1980).

6.2.4. Electrodialysis (ED) and electrocoagulation (EC)

Treatment of wastewaters containing B by electrodialysis (ED), which involves using various dialysis membranes including the heterogeneous, homogeneous, and ionic ion-exchange resin membranes, was examined

Table 6
Adsorption of boron from aqueous solution.
Adopted from Bhagyaraj et al. (2021).

Adsorbent	Size (μm)	pH	T ($^{\circ}\text{C}$)	q_{max}	Regenerating agent	Reusability (cycles)	Ref
Clays							
Bentonite	50–250	9.3	na.	0.51 mg/kg	na.	na.	(Jalali et al., 2016)
Kaolinite	100–200	9.0	na.	0.60 mg/kg	na.	na.	(Jalali et al., 2016)
Zeolite	50–250	8.0	na.	0.53 mg/kg	na.	na.	(Jalali et al., 2016)
Fe-Bentonite	na.	na.	na.	0.83 mg/kg	na.	na.	(Jalali et al., 2016)
Fe-Kaolinite	na.	na.	na.	0.80 mg/kg	na.	na.	(Jalali et al., 2016)
Fe-Zeolite	na.	na.	na.	0.76 mg/kg	na.	na.	(Jalali et al., 2016)
Waste calcite	10–100	9.4	na.	1.05 mg/kg	na.	na.	(Jalali et al., 2016)
Waste calcite-Fe	na.	na.	na.	1.60 mg/kg	na.	na.	(Jalali et al., 2016)
Vermiculite	na.	11.0	56.5	217.4 mg/kg	na.	na.	(Demirçivi and Saygılı, 2017)
Vermiculite-GA	na.	8.48	40.79	303.0 mg/kg	na.	na.	(Demirçivi and Saygılı, 2017)
Mg-Al-LDH nanosheets	I-LDH 0.1, U-LDH 1–2	na.	na.	21.6 mg/kg	na.	na.	(Gao et al., 2017)
Mg-Al-CLDH nanosheets	I-CLDH 10–40 nm, U-CLDH 1–2	7	25	77.8 mg/kg	na.	na.	(Gao et al., 2017)
CQDs-LDH	4–10 nm	8.5		20.61 mg/kg	na.	na.	(Meng et al., 2018)
Polymers							
NMDG@PAF1	na.	na.	25	18.4 mg/kg	1 M HCl, 1 M NaOH	99% (10)	(Kamcev et al., 2019)
NMDG@PAF2	na.	na.	25	16.9 mg/kg	1 M HCl, 1 M NaOH	99% (10)	(Kamcev et al., 2019)
NzMDG@PS-DVB	355	8.3	25	13.2 mg/kg	5% H ₂ SO ₄	99%	(Recepoğlu et al., 2017)
NMDG@cellulose fiber	175	8.3	25	18.5 mg/kg	5% H ₂ SO ₄	–	(Recepoğlu et al., 2017)
NMDG@cellulose spheres	100	na.	25	12.4 mg/kg	na.	na.	(Liu et al., 2017)
NMDG@chitosan	2500	7	25	19.9 mg/kg	0.5 M HCl, 0.5 M NaOH	94% (5)	(Ting et al., 2016; Wu et al., 2019)
NMDG@nylon fiber	30	7	30	17.2 mg/kg	na.	na.	(Ting et al., 2016)
NMDG@PAN nanofiber	200	7	na.	5.5 mg/kg	0.001 M HCl	na.	(Wang et al., 2014)
NMDG@aerogel	na.	9.5	25	31.8 mg/kg	3% HCl, 3% NH ₄ OH	85% (5)	(Sun et al., 2018)
Diaion CRB 02	118–300	8.2	25	6.27 mg/kg	na.	na.	(Kabay et al., 2007)
Dowex-XUS 43594.00	550	8.2	25	6.69 mg/kg	na.	na.	(Kabay et al., 2007)
Chitosan	100–300	6.5	na.	2.1 mmol/g	na.	na.	(Sabarudin et al., 2005)
GMA–MMA–DVB	110–120	na.	na.	2.15 mmol/g	na.	na.	(Biçak et al., 2001)
Styrene-DVB	74–149	9	25	3.4 mmol/g	na.	na.	(Köse and Öztürk, 2008)
Activated carbon							
Activated carbon CWZ-30 (AC)	na.	6	20	0.434 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with calcium chloride (ACpCa)	na.	6	20	0.774 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with orthophosphoric (V) acid (ACpPA)	na.	6	20	1.049 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with citric acid (ACpCA)	na.	6	20	1.002 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with tartaric acid (ACpTA)	na.	6	20	2.197 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with glucose (ACpG)	na.	6	20	0.500 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated carbon impregnated with mannitol (ACpM)	na.	6	20	2.027 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Activated alumina (Al ₂ O ₃)	na.	6	20	1.965 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
Zirconium dioxide (ZrO ₂)	na.	6	20	0.428 mg/kg	na.	na.	(Kluczka et al., 2007a, 2007b)
AC-Sawdust	na.	9.6	25	1.42 mg/kg	na.	na.	(Jaouadi, 2021)
Fe-impregnated	na.	8.3	na.	55.8 mg/g	NaOH solution	95–98%	(Zelmanov and Semiat, 2014)
Cur-AC					pH 11–12.5		
GAC							
ACISA	na.	4.68	30	na.	na.	na.	(Çelik et al., 2008)
AC-olive bagasse	na.	5.5	25	3.5 mg/kg	na.	na.	(Köse et al., 2011)
ACISA	na.	4.68	25	1.777 mg/kg	na.	na.	(Can et al., 2012)
AC-commercial from Chemviron Carbon	na.	7	25	0.85 mg/kg	na.	na.	(Kluczka et al., 2019)
AC-xylitol	na.	8.5	25	1.5 mg/kg	na.	na.	(Kluczka et al., 2019)
AC-mannitol	na.	8.5	25	1.45 mg/kg	na.	na.	(Kluczka et al., 2019)
AC-sodium gluconate	na.	8.5	25	1.04 mg/kg	na.	na.	(Kluczka et al., 2019)
Biochar							
Lantana300	na.	2.5	25	4.863 mmol/kg	0.1 M NaNO ₃	37.52%	(Labanya et al., 2022)
Lantana450	na.	2.5	25	5.704 mmol/kg	0.1 M NaNO ₃	28.56%	(Labanya et al., 2022)
Pine needle 300	na.	2.5	25	3.964 mmol/kg	0.1 M NaNO ₃	52.82%	(Labanya et al., 2022)
Pine needle 450	na.	2.5	25	5.319 mmol/kg	0.1 M NaNO ₃	46.04%	(Labanya et al., 2022)
Wheat straw 300	na.	2.5	25	3.375 mmol/kg	0.1 M NaNO ₃	53.74%	(Labanya et al., 2022)
Wheat straw 450	na.	2.5	25	3.204 mmol/kg	0.1 M NaNO ₃	44.22%	(Labanya et al., 2022)
Fly ash							
Soma ash	na.	6.5	na.	Boron removal 81%	na.	na.	(Polat et al., 2004)
Yatagan ash	na.	6.5	na.	Boron removal 79%	na.	na.	(Polat et al., 2004)
Yenikoy ash	na.	6.5	na.	Boron removal 83%	na.	na.	(Polat et al., 2004)
South African ash	na.	6.5	na.	Boron removal 76%	na.	na.	(Polat et al., 2004)
Fly ash (“Boruta” power plant in Zgierz, Poland)	105.5	10.5	24.85	0.488 mg/kg	na.	na.	(Ulatowska et al., 2020)
Fly ash (“Boruta” power plant in Zgierz, Poland)	105.5	10.5	34.85	0.492 mg/kg	na.	na.	(Ulatowska et al., 2020)
Fly ash (“Boruta” power plant in Zgierz, Poland)	105.5	10.5	44.85	0.495	na.	na.	(Ulatowska et al., 2020)
Fly ash (Kemerko’ y thermal power plant, Milas, Mugla, Turkey)	na.	10	25	0.0025 mg/kg	na.	na.	(Yüksel and Yürüm, 2009)

by Melnik et al. (1999). The results have indicated that when the influent water B level was >4.5 mg B/L, B level in the dialyate is unlikely to be decreased to the potable water standard (i.e., 0.3–0.5 mg B/L). At high B concentration (>4.5 mg B/L), a supplementary polishing of the dialyate by ion-exchange resin was necessary to reduce B concentration to the drinking-water standard.

The electrocoagulation (EC) technique encompasses an electrolytic reaction chamber with aluminium (or iron) electrodes and a separation vessel. The feed aqueous solution is passed through the reaction chamber and is subjected to flocculation by Al or Fe ions released from the electrodes, with the resultant floccules containing B trapped by hydrogen gas formed at the cathode. In treating an industry effluent, EC with Al anodes was shown to remove 15–20% more B compared to the application of alum coagulation alone, and the cost of operating EC was projected to be 6.2 times less compared to that of simple flocculation (Chen et al., 2020).

6.2.5. Phytoremediation

Phytoremediation is considered as a green remediation technology to remove potentially toxic elements including B, especially in wastewater streams. The application of phytoremediation technology to ameliorate soil contaminated with B is discussed in the earlier section. Constructed wetlands including vertical flow constructed wetlands (VFCW) are used to eliminate B from various wastewater streams. For example, Xia et al. (2021) noticed that *Myriophyllum elatinoides*, a widespread submerged/floating macrophyte, which tolerates high concentrations of B in wastewater (40 mg B/L) was found to effectively remove of B from B-enriched wastewater streams. Similarly, Correia et al. (2022) monitored the removal of B from wastewater using a VFCW system with *Vetiveria zizanioides* plant species, and noticed 60 and 26% removal efficiency at 15 and 30 mg B/L concentrations, respectively. Yıldırım and Kasım (2018) examined the removal of B using a number of poplar (*Poplar* sp.) willow (*Salix* sp.) species and concluded that fast growing, coppicing and deep rooting capacity of these species with their relatively high phytostabilization and phytoextraction efficiency enable these plants ideal in removing B from the contaminated water streams. Similarly, Chen et al. (2017), and Zhu and Bañuelos (2017) noticed that hybrid clones of poplar species were effective in the removal of B from constructed wetlands.

In conclusion, B from water can be eliminated by a number of technologies. However, most of these technologies have some limitations and are applicable only under specific conditions. Precipitation process can efficiently eliminate B, but it involves maintaining pH at a high level, resulting in high salinity and the production of a large volume of sludge for disposal. Activated carbon and clay adsorbents have relatively low B removal capacity and are not readily applicable to the industry-scale treatment of B-containing water sources. Mg-Al double-layered hydroxide compounds have been found to possess high B removal capacity. Liquid-liquid extraction can be suitable for the recovery of B from B-enriched effluents, but it is economically effective only when the original B concentration is high (>3 g B/L). Although a B-specific anion-exchange resin can offer an effective solution for B removal, the high costs of installation and treatment of a large volume of regeneration wastes hinder its application. Reverse osmosis and electro dialysis technologies may be considered efficient in eliminating B, but the relatively high possibility for scaling and fouling limit the large-scale application of these technologies for B removal. Electrocoagulation is an economical and environmentally-friendly option for B removal from industrial and sewage wastewater sources. The method also generates metal hydroxides that can be used as adsorbents for contaminants. Phytoremediation can be used as a green technology to manage B pollution in soil, sediments and water.

7. Summary and future research needs

Although B occurs naturally including borosilicate minerals, volcanic eruptions, geothermal streams, and marine water, B accumulation in terrestrial and aquatic environments occurs mostly through anthropogenic

sources including fertilizer application, wastewater irrigation, and waste from mining and processing industries. However, the mobility of B in soil and groundwater sources is inhibited by its ability to get adsorbed onto soils and sediments, while complexing of B with inorganic and organic anions increases the solubility and bioavailability of B. Boron is the only essential nutrient taken up mostly as non-ionic boric acid molecules, and both deficiency and toxicity of B in soils can impact plant growth (Cakmak and Römheld, 1997). The general population is exposed to B intake through the ingestion of food and drinking water, and it becomes toxic when consumed in large amounts. Boron toxicity in soil can be mitigated by immobilization and phytoremediation techniques, and B in water can be eliminated by adsorption, reverse osmosis, electro dialysis, and phytoremediation techniques.

With the large-scale industrial application of B and the subsequent release of B into the environment, and also the present state of limited understanding of the biogeochemical interactions, transformation, mobility, and ecotoxicity of B in terrestrial and aquatic environments, the following research needs exist:

Biogeochemical processes: In soil and aquatic environments, B occurs in different forms including free anion, non-ionic molecular species, and inorganic and organic complexes species. The interactions of B in soil and aquatic systems, and the fate and bioavailability of B are controlled by a spectrum of soil (e.g., pH, organic matter, clay), aquatic (e.g., salinity, DOC), and environmental (moisture content, temperature) factors. It is important to understand the transformation, chemical speciation, and redistribution of various species of B in soil and aquatic environments using modern spectroscopic techniques.

Accumulation and toxicity of B in plants: Boron is absorbed by plant roots mostly as a non-ionic molecular boric acid molecule. The biochemical processes contributing to the formation of boric acid molecule in porewater and the subsequent accumulation of B in various components of plants in relation B toxicity need to be examined by monitoring B isotope redistribution at the soil-plant interface, within plant metabolic processes, and its influence on biogeochemical transformation processes of B in soils. Furthermore, it is critical to monitor B deficiency and toxicity of arable crops under field conditions, and plant rhizosphere B transformation processes underlying cost-effective phytoremediation techniques for B-contaminated sites.

Remediation of boon contaminated soil and aquatic systems: It is critical to evaluate in-situ B stabilization approaches in polluted soils and sediments using waste by-products and emerging adsorbents including biochar and nanomaterials. Furthermore, the long-term examination of the release and remobilization of B from immobilized media is critical to achieve risk-based remediation. Ecotoxicological assessment of terrestrial and aquatic environments polluted with the accumulation of B using biomonitoring techniques is necessary for risk evaluation and sustainable remediation.

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Credit authorship contribution statement

Shiv Bolan, Hasintha Wijesekara, Nanthi Bolan - Conceptualization, Writing – original skeleton of the entire draft, prepared Sections 1 and 7.

Tao Zhang – Covered Section 2.

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Liuwei Wang – Covered Section 1 with literature data on publications and co-occurrence.

Kadambot H.M. Siddique, M.B. Kirkham - contributed to the interpretation of the discussion of various sections and provided critical revision and editing of the article.

Data availability

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

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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