Risk Assessment of Selenium and Boron Pollutants in Environment

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Review Article

ABSTRACT

According to the literature, there are increasingly more scientific data regarding the environmental pollution of selenium(Se) and the boron(B). The purpose of this review is to give an overview of environmental pollutants for Se andB and the use of plants to alleviate worldwide problems associated with Se and B toxicity. Selenium is an essential element for many species, plant, as well as humans, but it is toxic at higher levels. Boron is relatively soluble in water and commonly causes environmental problems, especially for surface waters where most of the discarded B will end up. Using phytoremediation plants can address this problem. To prevent Se and B toxicity due to excess environmental Se or B, plants may be used to phytoremediate to take up Se and B from soil or water. Research in the past decades had provided a riches ofknowledge regarding the mechanisms by which plants uptake, metabolize, and accumulate Se or B. Moreover, environment studies have revealed the important effects for plantsuptake of Se or B and interactions with herbivores, pollinators, neighbouring vegetation.

Keywords: Selenium; boron; environment; water; soil; plant.

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1. INTRODUCTION

Water is essential to sustain life, and a satisfactory (adequate, safe, and accessible) supply must be available to all. Improving access to safe drinking-water can result in tangible benefits to health World Health Organization [1]. Every effort should be made to achieve a drinking-water quality as safe as practicable. Drinking-water supplies vary from very large urban systems servicing populations with tens of millions to small community systems providing water to very small populations. In most countries, they include community resources as well as piped means of supply. The roles of the water supplier with respect to catchments are to participate in interagency water resource management activities; to understand the risks arising from potentially contaminating activities and incidents; and to use this information in assessing risks to the drinking-water supply and developing and applying appropriate management [2]. Although drinking water suppliers may not undertake catchment surveys and pollution risk assessment alone, their roles include recognizing the need for them and initiating multiagency collaboration for example, with health and environmental authorities. The primary aims with regard to chemical contaminants when a guideline is exceeded or in an emergency is to prevent exposure of the population to toxic concentrations of pollutants particularly trace elements. The purpose of this review is to give an overview of water pollutants selenium and boron. Selenium is an essential element for many species plant, as well as, including humans, but it is toxic at higher levels. The window between Se deficiency and toxicity is very narrow (about one order of magnitude); hence, both Se deficiency and toxicity are problems worldwide [3]. Higher plants do not require Se but readily uptake due to its similarity to sulfur [4]. Although Se accumulation can negatively affect plants, leading to chlorosis and stunted growth, low levels of Se can promote plant growth and stress resistance [5] and [6]. Boron is an essential micronutrient for the normal growth of plants but is usually adsorbed to the soil surface or loaded onto oxides within soils. Boron concentrations in soils are therefore generally controlled by boron adsorption reactions [7] and [8]. Boron is relatively soluble in water and commonly causes environmental problems, especially for surface waters where most of the discarded B will end up [9]. Excess of (B) in the aquatic habitats can cause undesirable B contamination of water, resulting in toxicity of plants, contamination in soil or sediment, and reproductive risks for both animals and human in many semi-arid and arid regions such as Chile, Turkey, China, New Zealand and many parts of USA [10,11,12,13,14]. The high solubility of B minerals in water and its potential to cause teratogenic effects to have raised global concerns about this element for drinking waters reserves where most of them flow through B-enriched areas.

2. SAFE CONCENTRATIONS FOR SELENIUM AND/OR BORON IN DRINKING WATER

Since the whole human population needs drinking water for sustaining life, the saving of a safe water supply is a high priority issue for safeguarding the health and well-being of humans. The production of adequate and safe drinking water is the most important factor contributing to a decrease in death rate and morbidity in developing countries. The World Health Organization reported such nearly half of the population in these countries suffers from health problems correlated with lack of drinking water or/and the presence of microbiologically contaminated water [15].

International Standards for Drinking-water recommended a maximum permissible concentration of 0.01 mgL^{-1} for selenium. Most drinking water contains concentrations of Se that are much lower than 10 µg L^{-1}, except in certain seleniferous areas. Therefore, it would be unusual for drinking water to make a significant contribution to total selenium intake. Even in high selenium areas, the relative contribution of selenium from drinking water is likely to be small in comparison with that from locally produced food [16].

Concentrations of B found in drinking-water from Chile, Germany, the United Kingdom, and the USA ranged from 0.01 to 15.0 mgL^{-1}, with most values clearly below 0.5 mgL^{-1}. These values are harmonious with ranges and means observed for groundwater and surface waters. This consistency is supported by two factors: (i) boron concentrations in water are mainly dependent on the leaching of boron of the surrounding geology, and wastewater discharges, and (ii) boron conventional drinking-water-treatment methods do not remove wastewater discharges.

Concentrations for selenium and/or boron where there are health concerns (maximum

contaminant levels) traditionally, the primary concern in drinking water is microbiological quality. Although this worry has not been reduced in recent years, the attention of the general public and health officials on the importance of chemical quality has increased with the increase of our knowledge on the hazards of exposure to chemical substances. We must assume that there is a potential for all members of the population, including potentially high-risk groups as young children and health-deprived persons, to be exposed to drinking water which might contain possible hazardous contaminants. Accordingly, strict quality requirements must be set to protect public health [15].

There are many sources of contaminations of drinking water which broadly they can be divided into two categories: they are contaminants in ground and surface water; the sources for drinking water production; and contaminants used or generated during the treatment and distribution of drinking water. Contaminants in the ground and surface water will range from natural substances that leaching from the soil, run-off from agricultural activities, controlled discharge from sewage treatment works and industrial plants, and uncontrolled discharges or leakage from landfill sites and chemical accidents or disasters [17].

2.1 Selenium

The levels of selenium in surface water and groundwater range from 0.06 μgL^{-1} to about 400 μgL^{-1} [18] reported that in some areas selenium levels in groundwater might approach 6000 $\mu g\ L^{-1}$. Concentrations increase at high and low pH such a result of transformation into compounds of greater solubility in water. The standard of selenium in tap water samples from public water supplies around the world are ordinarily much less than 10 $\mu g\ L^{-1}$ however, may exceed 50 $\mu g\ L^{-1}$ [19;20] and [21]. Drinking water from a high soil selenium area in China was reported to contain 50–160 $\mu g\ L^{-1}$ [22].

WHO [16] International Standards for Drinking-water recommended a maximum permissible concentration of 0.05 mg L^{-1} for selenium, based on health concerns. That in the 1963 International Standards, such value was reduced to 0.01 mg L^{-1}, in which was retained in 1971 as International Standards as a temporary upper concentration limit, while recognizing in which

selenium is an essential trace element for some species. In the first edition of the Guidelines for Drinking-water Quality, published in 1984, the guideline value of 0.01 mg L^{-1} was again held, though it was noted that in areas of relatively lower or higher selenium dietary intake, the guideline value might have to be modified accordingly [18]. The 1993 Guidelines suggested a health-based guideline value of 0.01 mg L^{-1} human studies. A Kansas surface water quality standard for aquatic life is 20 $\mu g\ L^{-1}$ Se (acute), and 5 $\mu g\ L^{-1}$ Se (chronic) [23]. And for agricultural purposes, Se concentration of livestock is 50 $\mu g\ L^{-1}$, and that of irrigation water is 20 $\mu g\ L^{-1}$. Also, Se concentration for livestock is 50 $\mu g\ L^{-1}$, and that of irrigation water is 20 $\mu g\ L^{-1}$. The daily dietary need of Se for adult's ranges between 50 to 200$\mu g\ day^{-1}$ as recommended by the U.S. National Research Council [24], but this range depends on physiological status [25]. The recommended daily allowances of dietary Se in women, men, and infants are approximately 55$\mu g\ day^{-1}$, 75$\mu g\ day^{-1}$, and 8.7–10$\mu g\ day^{-1}$, respectively [25].

2.2 Boron

The majority of the Earth's boron occurs in the oceans, with an average concentration of 4.5 mg L^{-1} [26]. Butterwick et al. [27] reported that amount of boron in fresh water depends on factors such as the geochemical nature of the drainage area, inputs from industrial and municipal effluents, and also proximity to marine coastal regions. There is a good recent review of boron in drinking water with consideration of human health [28]. EPA [29] EPA has released a recent review on boron also. The natural borate content of surface water and groundwater is usually small. The borate content of surface water may be significantly increased as a result of wastewater discharges because borate compounds are ingredients of domestic washing agents [30]. Usually, occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicates. The concentrations of boron in groundwater throughout the world range widely, from <0.3 to >100 mg L^{-1}. In general, concentrations of boron in Europe were biggest in southern Europe like Italy, Spain and least in northern Europe like Denmark, France, Germany, the Netherlands, and the United Kingdom. For Italy and Spain, the mean boron concentrations ranged from 0.5 to 1.5 mg L^{-1}. The value rangedup to approximately 0.6 mg L^{-1} in the Netherlands and the United Kingdom, and

around 90% of samples in France, Denmark, and Germany found to contain boron with concentrations below 0.3, 0.3, and 0.1 mg L^{-1}, respectively [1]. Haberer, [31] reported that monthly mean values of boron in the Ruhr River, Germany, ranged from 0.31 to 0.37 mg L^{-1} in a survey conducted during 1992-1995.

For the fresh surface water, Boron concentrations range from <0.001 to 2 mg L^{-1} in Europe, so with mean values typically below 0.6 mg L^{-1}. Similar concentration ranges have been reported for water bodies within Pakistan, Russia, and Turkey, from 0.01 to 7 mg L^{-1}, with most values below 0.5 mg L^{-1}. Concentrations ranged up to 0.01 mg L^{-1} in Japan and up to 0.3 mg L^{-1} in South African surface waters. Samples taken in surface water from two South American rivers Rio Arenales, Argentina, and Loa River, Chile showed boron at concentrations ranging between 4 and 26 mg L^{-1} in areas rich in boron-containing soils. In other regions, the Rio Arenales contained less than 0.3 mg L^{-1} (B). Concentrations of boron in surface waters of North America (Canada, USA) ranged from 0.02 mg L^{-1} to as far as 360 mg L^{-1}, indicative of boron-rich deposits. However, typical boron concentrations were less than 0.1 mg L^{-1}, with a 90th percentile boron concentration of approximately 0.4 mg L^{-1} [32].

Anderson [33] reported that the mean daily intake of boron in the diet is arbitrated to be near 1.2 mg day^{-1}. Concentrations of boron in drinking-water have wide ranges, which depending on the source of the drinking water, but for most of the world, the range is judged to be among 0.1 and 0.3 mg L^{-1}. Based on usage data, the consumer products have been estimated to contribute a geometric mean of 0.1 mg day^{-1} to the estimation of total boron exposure [1]. The contribution of boron intake from the air is negligible. Therefore, the total daily intake can be estimated from mean concentrations and concentration ranges to be between 1.5 and 2 mg L^{-1}. The general conclusion from recent studies is that boron is available in sufficient quantities in human diets. Boron in drinking water is not a health concern at this time. The recommended allowable concentration for boron in drinking water is about 1 mg L^{-1} and higher [28] with EPA [29] reporting that, a Health Reference Level of 1.4 mg L^{-1} in drinking water, and a reference dose value of 0.2 mg kg^{-1} body weight day^{-1}.

3. CONCENTRATION AND DESIRED RANGES FOR SELENIUM AND/OR BORON IN THE SOIL

3.1 Selenium

Selenium (Se) is already present in the earth's crust often in association with sulfur-containing minerals. Selenium (Se) has an atomic number of 34 and atomic weight of 78.96. It appears just below sulfur in the periodic table of elements. It is usually found in concentrations of 50–90 µg kg^{-1}, but higher levels can be associated with some volcanic, sedimentary, and carbonate rocks. Se concentrations in soils vary widely, from 5 to 1 200,000 µg kg^{-1}, being higher in soils of more recent volcanic origin. Selenium happens in soils in several forms, according to its possible oxidation states: selenides (Se^{2-}), amorphous or polymeric elemental selenium (Se^0), selenites (Se^{4+}) and selenates (Se^{6+}) [22]; and UK [34] The Se speciation in soil is basically controlled by three mechanisms: oxidation vs. reduction, mineralization vs. immobilization, and volatilization.

Selenium and several other trace elements can act either as essential micronutrient at low concentrations or as toxins at elevated concentrations. Gough [35] provided summaries of element concentrations, both bioessential and toxic to plants, animals, and man. Specifically, safe and adequate Se concentrations in animal forage diets are 0.1-0.3 mg kg^{-1}, dry mass [36], with a critical or limit threshold value of Se 5 mg kg^{-1} [24]. The criterion or limit of B has been set at 2.5–8.0 mg L^{-1}.

Acidic and reducing conditions decrease inorganic selenites for elemental selenium, while alkaline and oxidizing conditions favor the formation of selenates. Because selenites and selenates are considered soluble in water, selenium is leached from well-aerated alkaline soils that favor its oxidation. Elemental selenium and selenides are insoluble in water; consequently, selenium tends to be retained in wet poorly aerated soils the reducing conditions of which favor those forms. Therefore, in alkaline soils selenium is available for uptake by plants, whereas in acidic soils, the availability of selenium is limited due to the adsorption of selenites and selenates to iron and aluminium oxide sols [24]. Selenate and selenite are the dominant forms (species) of selenium in most soils and waters; elemental selenium and selenide are found in only small concentrations.

Of the two dominant forms. The mobility of selenium depends on many soil properties including pH, oxidation potential, organic carbon, calcium carbonate, and cation exchange capacity. Elemental selenium is relatively unstable. It can be reduced to selenide forms or oxidized to selenite forms. Selenide can occur in solid, aqueous, and gaseous forms.

3.2 Boron

Elemental boron exists as a solid at room temperature either as black monoclinic crystals or a yellow or brown amorphous powder when polluted. The crystalline and the amorphous forms of boron have specific gravities of 2.37 and 2.34, respectively. Boron is a relatively inert metalloid except where in contact with strong oxidizing factors. WHO [37] that Sodium perborate are per-salts which are hydrolytically unstable because they contain characteristic boron oxygen-oxygen bonds that react with water to form hydrogen peroxide and stable sodium metaborate ($NaBO_2 \cdot nH_2O$). According to Weast et al., [26] mentioned that the majority of the Earth's boron occurs in the oceans with an average concentration of 4.5 mgL^{-1}. The amount of boron in fresh water depends on factors such as the geochemical nature of the drainage area, marine coastal regions, and inputs from industrial and municipal effluents [27]. According to Budavari et al. [38] report that Boron (CAS no. 7440-42-8) is not found in elemental form in nature. It exists as a mixture of the ^{10}B (19.78%) and ^{11}B (80.22%) isotopes. Boron's chemistry is complex and resembles silicon [39].

Soils and sediments may adsorb waterborne boron. Adsorption-desorption reactions are predictable to be the only significant mechanism influencing the fate of boron in water [40]. Boron adsorption depends on the pH of the water and the concentration of boron in solution. The greatest adsorption is observed at pH 7.5-9.0 [41,42,43].

4. APPLICATION OF PLANTS FOR PHYTOREMEDIATION

In the case of phytoremediation, there are two types of approaches that are utilized. These types are: (1) where total uptake of elements is comparable to that of other similar hyperaccumulators due to the high yield of the above-ground biomass, then the application of high biomass producing plants is characterized by the lower ability to accumulate the target

elements, and (2) the application of hyperaccumulators, such as alpine pennycress or alpine pennygrass *(Thlaspicaerulescens)* or a species of flowering plants native to Europe, Asia and North Africa *(Alyssum bertolonii)* will produce a relatively low amount of above-ground biomass. However, the plants will accumulate high amounts of one or more heavy metals or toxic elements.

According to Barcelo and Poschenrieder [44] have found that these plants will accumulate (≥ 100 times) more heavy metals or toxic elements in above ground conditions than do non-hyperaccumulators growing in the same conditions. This is accomplished without any apparent or observable symptoms in the plant's tissues. According to Jabeen et al., [45] did a study that showed heavy metal or toxic element concentrations in the plant's shoots should be approximately from 50 to 100 times greater than what would be considered 'normal' plants. According to McGrath and Zhao [46] have noted that the ratio of a plant's toxic substance accumulation in its tissues compared to its concentration in the living environment of that organism, or its bioaccumulation coefficient, must have a value greater than 1. Also, they have shown in another study that heavy metal or toxic element concentrations in the plant's shoots should be higher than in the plant's roots showing fast growth and a high accumulating biomass. According to Marchiol et al., [47] has shown that these plants can be easily grown as an agricultural crop and are fully harvestable.

In a study performed by Lasat [48], it was found that phytoremediation will consist of technologies that either reduce or completely remove pollutants or contamination in soil by using naturally occurring or genetically modified plants. According to Khan et al., [49] have determined that this situation is due to greatly reduced costs when compared with conventional remediation technologies.In contrast to phytoremediation, conventional remediation technologies or processes will often employ neutralizing agents or substances or physiochemical agents that will have a detrimental effect on the environment.

In multiple studies done by Cunningham et al., [50]; Greenberg et al., [51]; Abhilash [52] and Doty et al., [53], it was discovered plants can serve as natural, cost-effective, solar-driven pumping and filtering systems to process contaminants. These plants can absorb mostly water-soluble contaminants through their roots.

These contaminants are extracted and translocated into plant tissues and plant roots. Then they can be sequestered, volatilized or metabolized. In three other studies conducted by Wu et al., [54] and Ghosh and Singh [55], they reported that there are over 400 plant genera or species in 45 plant families have been discovered to date that can act as hyperaccumulators of metals like alpine pennycress, hemp, mustard plants and pigweed.

In studies conducted by Salt et al., [56] and Dushenkov [57], they have reported that among these plant families will include such species as *Asteraceae, Brassicaceae, Euphorbiaceae, Lamiaceae and Scrophulariaceae.* Lasat [58] conducted a study on plants that have shown a very high bioaccumulation potential for Cd, Co, Cu, Ni, Se and Zn. Vijayarengan [59] has reported that certain cereal crops, including alfalfa *(Medicagosativa L.),* sorghum *(Sorghum bicolor)* and maize *(Zea mays L.),* have demonstrated an ability to accumulate high amounts of heavy metals. Ebbs and Kochian [60] have determined that if these plants possess a large enough capacity and biomass to complete remediation within a reasonable period from polluted soils, then these plants can be successfully utilized to accumulate heavy metals or toxic elements. To ensure successful phytoremediation of soil, it will obviously depend on the plant's capacity to hyperaccumulate large amounts of heavy metals or elements.

Nyberg, [61] reported plants that have been used for phytoremediation of Selenium (Se) might generate other useful by-products depending on their structural, chemical, and energetical characteristics, such as fibers to produce paper and building materials. Plants might also be used as a source of energy for heat production by the combustion of the dried plant material or by fermentation of methane or ethanol. Also, a large variety of chemical compounds (e.g., oil, sugars, fatty acids, proteins, pharmacological substances, vitamins, and detergents) are naturally produced by plants and may be useful byproducts of the phytoremediation process.

Selenium accumulation in leaves was greatest when Se was supplied as selenate followed by selenomethionine and then selenite. Terry andBanuelos, [62] reported in roots, selenomethionine was accumulated the most, followed by selenite and selenate. It seems, therefore, that selenate is more mobile inside plant tissues than selenite and selenomethionine.

Selenate is the highly bioavailable form of soluble Se that is most commonly found in soils and subsurface drainage waters. Selenate is believed to be taken up and assimilated by the enzymes of the sulfate assimilation pathway. Metabolism of Se through this pathway leads to the formation of Se analogs of the S-containing amino acids (e.g., selenocysteine, selenocystathionine, selenohomocysteine, and selenomethionine). There is evidence that Se analogs of S compounds compete for various enzymes in the S assimilation pathway. Selenium and several other trace elements can act either as essential micronutrients at low concentrations or as toxins at elevated concentrations. Gough [35] provided summaries of element concentrations, both bioessential and toxic to plants, animals, and man. Specifically, safe and adequate Se concentrations in animal forage diets are 0.1-0.3 mg kg^{-1}, dry mass [36], with a critical or limit threshold value of Se 5 mg kg^{-1} [37]. The criterion or limit of B has been set at 2.5–8.0 mg L^{-1}.

Treatment wetland:

A very cost-effective way to treat wastewater is through a process called Constructed Wetlands (CW). Badejo et al., [63] and Kouawa et al., [64] have stated that this process offers a very promising alternative for treating industrial, domestic and agricultural wastewater. Kadlecand Wallace [65] and Brix [66] have explained that CWs can remove pathogenic microorganisms are persistent organic pollutants, nutrients, and trace elements from domestic and industrial wastewater by acting as a bio-filter. Additionally, Kadlec and Wallace [65] and Brix [66] also found that CWs operate as engineered ecosystems that operate a controlled environment. The CWs use natural processes that are aimed at improving water quality by using microbial assemblages and wetland soils and vegetation.

In two studies conducted by Maine et al., [67] and Vymazal [68], they found that CWs are complex matrixes of distinct anaerobic and aerobic treatment zones. These CWs process wastewater in the same manner as do natural wetlands. CWs are classified by either the water flow regime (horizontal or vertical flow, surface or sub-surface flow) or by the type of macrophylic, or aquatic plant, growth (rooted with either floating leaves, free-floating, emergent or submerged). According to the studies done by the U.S. EPA [69] and Arias and Brown [70], CWs have been broadly classified into Sub-

Surface Flow (SSF) or Vegetated Submerged Bed (VSB) and Surface Flow (SF) or Free-water Surface (FWS) categories. According to Ayaz and Akca [71] have found that for developing countries CW is reportedly better suited in offering lower maintenance and construction costs for domestic wastewater treatment. According to Chen et al., [72] and Chung et al., [73] have completed studies, along with other on-going studies, that have discussed the possibility of using the natural environment to purify wastewater or complete wastewater purification. Researchers have pointed out, for an extended period, that within the natural environment (wetlands, soils, etc.) there is a high capacity for pollution remediation or removal. Kadlec and Wallace [65] have found that a wide range or variety of pollutants, including nutrients, heavy metals, pathogens suspended solids and organic compounds, have been removed using CWs. Additionally, CWs improve water quality by utilizing natural processes. These processes include associated microbial assemblages, wetland vegetation and soils. They detailed how pollutants in CWs are removed or reduced through the wetland processes. These processes include the use of chemical networks (that create products that are contaminants of interest by themselves); microbial mediated processes (the removal of pollutants as a result of the activity of microorganisms and other bacteria); sorption (either Langmuir, linear or Fruendlich); volatilization (that results in the formation of gases that are released into the atmosphere); sedimentation (mainly involving suspended solids); seasonal cycle; photodegradation (its effectiveness is determined by the radiation dose rate and the concentration of organisms); accretions (creation of new soils and sediments), transpiration flux; vertical diffusion in soils and sediments; and plant uptakes (where plants take up trace chemicals and nutrients to sustain their metabolism and for storage respectively).

According to Vymazal and Kropfelova [74] reported that macrophytes have rich rhizomes and roots that can provide substrates for attached bacteria. Plus, macrophytes that are used in CWs are usually quite tolerant of high nutrient and organic uploading from the wastewater. In a study performed by Truong [75] in 1996 it was found that secondary-treated effluent was used for lawn irrigation by using vetiver. The plant (*VetiveriaZizanioides)* easily accessible, commercially affordable and publicly available in local South Africa marketplaces. The re-use of wastewater in primarily semi-arid South Africa represents a very valuable source of water. For example, the city of Tshwane, Gauteng Province, South Africa has ten wastewater treatment plants. These plants include Dasport, Rooiwal, Zeekoegat, Klipgat, Babelegi, Sandspruit, Temba, Baviaanspoort, Rietgat, and Sunderland Ridge. For example, a certain percentage of indirect re-use of treated effluent is currently being processed at the Daspoort Wastewater Treatment Works (DWWTW). This treated wastewater effluent is released into the Apies River. From there it flows in to dammed reservoirs. Then the treated effluent is withdrawn and further treated at other water treatment plants where it is utilized. However, due to some algae growing in the dams' reservoirs, the initially treated effluent has a deteriorated quality.

In recent years, constructed wetlands (CWs) have been received the most attention in the urban wastewater treatment, particularly in decentralized sanitation, for the reason that they are affordable, reliable, simple in design and operation, and offer environmentally sound approach [54]. These ecologically engineered systems are known to be effective at removing many pollutants such as organic compounds, suspended solids, pathogens, nutrients, and emergent pollutants [76]. They are designed to get the advantage of the same processes occurring in natural wetlands, however, within a more controlled environment. Gaining a better understanding of the mechanisms associated with CWs has driven to a wide variety of designs and configurations to achieve a more efficient domestic sewage treatment, for example, single-staged modification [77] and [78], multi-staged in series [79], and/or combination with other treatment technologies [80].

5. THE WETLAND TREATMENT SYSTEM FOR TRACE ELEMENT SEQUESTRATION

Galkaduwa et al. [81] reported that the constructed wetland treatment systems are effective in removing Se from flue-gas desulfurization wastewater, leading to the complete Se retention by the soil columns. As for Boron, retention was weak, appropriate with field observations. Changing redox conditions in the soil led to mobilization of the initially retained Se (~ 4 to 5%). They used micro-XANES analyses that indicated the retention mechanism of Se from the FGD wastewater was via the transformation of Se into reduced/stable forms

[Se(IV), organic Se, and Se (0)]. These studies present useful information to improve the performance and longevity of a full-scale CWTS for FGD wastewaters. Pilon-Smits et al. [82] reported that phytoextraction of selenite in contaminated water from wetland species is five times greater than selenite in contaminated water. Factors such as salinity, pH, temperature, levels of other pollutants, and competitive strength affect the performance of the wetland plant species. It is important to mention that high Se accumulation in plant tissues (shoot and root) is a threat to wildlife, and their disposal in an appropriate way is important [82]. Operating halophytes as a plant bio-filter making use of living material to capture and biologically degrade pollutants of marine aquaculture effluent is a low-cost opportunity to mitigate potential negative impacts on the environment [83].

According to Diaz et al. [84] found that a number of halophytic species (*Salicorniabigelovii, Distichlisspicata*, *Spartinagracilis*, *Atriplexlentiformis, Allenrolfeaoccidentalis, and Bassiahyssopifolia*), which were grown under irrigation with saline drainage water over a 4-6-year period in the San Joaquin Valley of California grew very successfully and also can effectively reduce saline drainage effluent. Halophyte tissues contained high levels of salts that total ash content ranged between 6 and 52% and accumulated in Na^+, Cl^-, SO_4^{2-}, NO^{3-}, B and Se to levels close or above the maximum tolerable levels (MTL). The halophyte species that accumulated Se at highest rate was *Salicorniabigelovii* with an average concentration of 16.3 mg kg^{-1}, and B concentration ranged to 1680 mg kg^{-1}.

Studies had also been conducted on the suitability of Salicornia spp. as a wastewater biofilter. According to Shpigel et al. [85] reported that a constructed wetland (CW) planted with *Salicornia persica* was effective in the removal of N, P, and total suspended solids (TSS) from a 1,000m^3 commercial, intensive, semi-recirculated aquaculture system growing 100 tonnes of gilt-head seabream 1-500 g in size. It was estimated which about 10,000m^2 of wetland planted with *S. persica* would be required to remove nitrogen and TSS in wastewater during one year. *Salicornia europaea* has also been shown to have significant potential in the treatment of aquaculture effluent. According toWebb et al., [86] described a wetland filter bed planted with marsh samphire to evaluate its ability to treat the wastewater from a commercially operated marine

fish and shrimp farm. The results demonstrated the effectiveness of a marsh samphire wetland in removing N and P from the wastewater, with 91-99% of influent dissolved inorganic nitrogen and 41-88% of influent dissolved inorganic phosphorus removed.

According to Saeed at al., [87] reported when treating wastewaters with high loads and unstable concentrations, that CWs provide an excellent alternative while contains abundant toxic contaminants. In a study done by Maine et al., [88], it was found that for treating various types of effluents or wastewaters with major contaminants that originated from the metallurgical and tannery industries that different scales of CWs have been tested and used. These major contaminants have included N, P, biological oxygen demand (BOD), chemical oxygen demand (COD) and metals. In two other studies done by Türker et al., [14], they determined that the use of CWs to remove B saw some successful attempts. Respectively, Huang et al., [89] and Lin and Terry [90] reported similar results with removing Se.

However, Zhang et al., [91] and Türker et al., [92] reported only rarely successful attempts have occurred in treating wastewater high in B, salts and Se by using CW. This is due to both the high B and salt toxicities that the remediating plants experience. According to Bonilla et al. [93] has found that complicated eco-physiological responses in plants occurred that were caused by the interactions of B and salt. It affected their ability to absorb various elements. CWs were found to offer the possibility for treating saline drainage effluent that is high in B and Se under challengeable conditions. This can be provided if the wetland plants possess superior growth rates, the ability to accumulate B, Cl, Na and Se in their shoots and exhibit high B and salt tolerances. Kadlecand Wallace [65] review the removal of boron in treatment wetlands; however, they point out that most treatment wetlands are not designed to remove boron because boron is not generally the important contaminant. For the proposed Westar treatment wetland, it is anticipated that successful reduction in the concentration of other contaminants will result in sufficient reduction in the concentration of boron, also Talley, [94] conducted research at pilot-scale CWTS at the Westar Energy's the Jeffrey Energy Center (JEC). This provided an opportunity to assess the behavior of Flue Gas Desulfurization water(FGD) wastewater constituents under real

field conditions. Galkaduwa et al. [81] compared the removal efficiency of each constituent by the saturated soil column system and the pilot-scale CWTS. The removal efficiencies of the flushed columns were used to compare the performance efficacy of the pilot-scale CWTS as those were more realistic for the field situation. The effectiveness of removing Se from the FGD wastewater by the soil columns was 100% whereas that of by the pilot-scale CWTS was 80%, it was assumed that the variation of field conditions (e.g. occasional drying) might have influenced the Se removal by the pilot-scale CWTS.

The information on the removal of B in various types of CWs is limited. Also, the removal processes in CWs that are responsible for B removal have not been understood clearly. The chemistry of B differs from that of other trace elements, and the overall B removal process in CWs is very complex, making the identification of specific removal pathways more difficult. Nevertheless, several experiments have been carried out to determine B removal path-ways in CW systems [11,95,13,14]. So far, the studies have been indicated which the processes responsible for the removal of B from CWs are sorption and plant uptake. However, environmental factors such as temperature, pH, transpiration rate, solution composition and competing species, hydraulic retention time, filtration media and operational factors are also important factors in B removal process in CWs.

Despite the fact that several studies have reported information about the use of CWs for B removal, detail information on removal processes can be lacking direct evidence for specific B removal rate in CWs [96] and [97]. The majority of data about B removal rate in CWs were obtained from microcosms [11,98,13] andmesocosms (Mesocosms are artificially constructed model ecosystems used for experimental study of analogous natural ecosystems) [95] and [14] but some data are also available from the full-scale CWs [99] and [100]. In CWs, regardless of system size that B removal rates ranged from 0% to 65% according to the selection of design factor, also the initial B concentrations the presence of biologically absorbable B form as boric acid in wastewater, and natural climatic conditions.

The researchers [101] conducted a six-year field trial that demonstrated that these two clones had acceptable B and salt tolerances after the two

clones were irrigated with poor quality water. The water contained a salinity content that ranged from 10 to 30 mS cm^{-1} and B at 10 mg L^{-1}. In a very recent study conducted by HuiandBañuelos [101], they reported these two hybrid poplar clones removed B with 26.7-45.6 percentages and Se with 50-69.4 percentages by clone 345-1 and from B with 22.9-29.4 percentages and Se with 31.7-43.8 percentages by clone 347-1, respectively. According toParker and Page [102] have detailed a recently proposed strategy for reducing Se levels in the soil of phytoremediation of vegetation management of Se. However, Chaney [103], and Chaney et al. [104], McGrath et al. [105] and Kumar et al., [106] have earlier reported on phytoremediation for other trace elements.

Bañuelos et al., [107,108] and Bañuelos and Meek [109] have shown that planting certain plant species, especially the *Brassica* species, have led to total soil Se reductions up to 20 percent under field conditions and 40 percent under greenhouse conditions after one growing season and study was long-term goal is to improvea phytoremediation scheme for Se using plant species, e.g., *Brassica*, as a means of attenuating Se buildup in soils irrigated with Se-laden agricultural effluent. Researchers, Lewis [110]; Frankenberger and Karlson [111] and Terry and Zayed [112,113] found that most Se was removed by plants although there may have been biological volatilization of Se. Bañuelos et al. [108] reported that plant accumulation of Se accounted for at least 50 percent of the Se removed in soils planted with *Brassica* and up to 20 percent in soils planted with barley. Although additional plantings were necessary to further decrease the Se content in the soil, results have shown the tested *Brassica* species led to a significant reduction in Se when added to soil using Se-laden effluent.

Constructed wetlands have also been shown to remove significant amounts of Se from waters contaminated with agricultural irrigation drainage water [114,115].The principal mechanisms of Se removal by wetlands are (1) the dissimilatory anaerobic reduction of Se oxyanions (selenate and selenite) to less soluble or insoluble forms (e.g., Se^{2-}, Se^0) [116], and (2) biological volatilization of Se to the atmosphere through assimilatory reduction and methylation by plants [117] and microbes [118], a process that is particularly desirable because it leads to a net loss of Se from the local ecosystem, thereby preventing its entry into the food chain. In

designing constructed wetlands, there are a number of treatment options for altering the distribution of Se removal between the two pathways. One of the potions is by plant species selection. According to Lin and Terry [90] reported that the vegetated wetlands were able of significantly reducing Se from the inflow drainage water, and an average of 69.2 percentage of the total Se mass in the inflow was removed. Most of the Se was retained in sediment, and <5% of the Se was accumulated in plant tissues, [116], upon the addition of organic amendments [111], artificially varying levels of aeration, [119] and manipulation of plant−substrate arrangement, composition, and structure [120].

CWs are complex biological and physical environments that collectively change the chemical nature of contaminants. They are used to detoxify wastewater by immobilizing and/or transforming pollutants to less-toxic forms. This is particularly important in the case of metalloids like selenium (Se) and arsenic (As), which can be transformed by both biological and chemical processes to a variety of forms that differ in mobility and toxicity [118]. The growth and adaptation of plants to the anoxic conditions in wetland sediments drive many of these processes [121]. For example, the activity of the plant roots alters the chemical conditions of the surrounding sediment, enhancing the rate of transformation and fixation of metals [122]. Alternatively, the pollutants may be taken up into the plant tissues, where they are accumulated [123] and [124], biotransformed to less toxic or immobile states, and/or volatilized to the atmosphere [125] and [90]. Plants are also important because they supply fixed-carbon to the sediments, which is an energy source for bacterial transformation of contaminants [121].

Constructed wetland technology has been applied successfully as a low-cost treatment for effluents produced by many electricity generating facilities and oil refineries that are contaminated with a number of different metals and metalloids [125] and [126,127].

The complex biogeochemical mechanisms in CWTSs influence the efficiency of Se removal from contaminated wastewater streams. Eggert et al. [128] suggested that the mechanism of Se removal from FGD wastewater was rapid complexation of selenite with Fe oxy(hydr)oxides or direct adsorption of selenate to Fe oxy(hydr)oxides. These wastewaters typically contained relatively low concentrations of the metalloids Se, As, and boron (B) [125] and [126]. The wastewater in the present study, however, was produced by the sour water stripper of a coal gasification plant at a power generating facility and contained Se at a concentration which was several orders of magnitude higher (1.4 mg L^{-1}) than those used in previous studies [125]. Furthermore, this wastewater contained Se as the more toxic anion selenocyanate (SeCN$^-$) instead of selenate or selenite, which are present in other electric utility effluents [126] oil refinery effluent [125] or in agricultural drainage water [90].

Wetland microcosms may be used to evaluate whether constructed wetlands would potentially be effective in treating wastewater contaminated with a specific suite of toxicants. Microcosm experiments have distinct advantages over field trials [129], because they are substantially cheaper to construct and because the fate of extremely toxic contaminants such as SeCN$^-$ can be tested without risking damage to a field environment. Microcosms also permit mass balances to be calculated for the contaminants, which may enable determination of full-size wetland design criteria. If the initial tests with microcosms show that wetlands might be a satisfactory approach to wastewater treatment.

5.1 Selenium and Health

The essentiality of Se as a trace element was identified in the late 1950s and early 1960s [25]. Around 35 selenoproteins have been identified, and some of selenoproteins perform important enzymatic functions for human biology [130]. Selenium enters to the food chain via plant uptake from soils. The Se deficiency is commonly seen in regions where soils are low in Se concentration [130]. Soil chemical properties such as acidity, and complexation with Fe and Al reduces Se uptake by plants. Selenium has been identified as an essential component of enzyme glutathione peroxidase (GSH-Px), which helps protecting tissues against oxidative damage [25]. A deficiency of Se affects oxidative damage to red blood cells and reduces the activity of glutathione peroxidase enzyme [131]. Due to the interaction of Se with Vitamin E and fatty acids, all Se deficiency diseases in animals might be associated with vitamin E deficiency. Selenium causes white muscle diseases of animals. Those diseases include reduced appetite, growth, production and reproductive fertility, unthriftyness, and muscle weakness [25].

Selenium deficiency in animals is prevalent around the world and commonly found in South America, North America, Africa, Europe, Asia, Australia, and New Zealand.

The Se dietary intake of humans varies from region to region depending on the Se concentration of soil. The most common Se deficiency diseases reported in humans are keshan disease, an endemic cardiomyopathy (heart disease) that mainly affects children and women; kashin-beck disease, an endemic osteoarthropathy causing deformity of the affected joints; iodine deficiency disorders, role of seleno-enzymes in thyroid function; and cancer [25]. Selenium deficiency can link to other diseases such as immune function, viral infection, reproduction, depressed mood and more hostile behavior, thyroid function, cardiovascular disease, oxidative-stress or inflammatory conditions [130].

Fordyce [25] has reviewed the effect of Se toxicity in animals. Experiments carried out with laboratory animals have found that hydrogen selenide can cause lovertumors in rats. Selenium sulfide was proven to be carcinogenic for rats. Selenosis was reported in aquatic species and birds. For example, birds at the Kesterson Reservoir in California, US, were affected by high Se concentration (300 mg Se L^{-1}) of agricultural drainage water [25]. Methylation of Se is a detoxification mechanism performed by animals. Mono-, di-, or trimethylated Se are formed by metabolizing organic and inorganic Se. Among these, monomethylated forms are more toxic. Selenium toxicity to humans is less common than Se deficiency. An endemic human selenosis was reported in seleniferous areas of China in 1960s [132]. The reason for Se toxicity in this case was the consumption of high-Se crops grown on soils derived from coal. Selenium concentration of soil in these regions was reported up to 6000 mg kg^{-1}. The primary symptoms of selenosis are hair and nail loss [25]. Disorders of the nervous system, skin, poor dental heath, garlic breath, and paralysis are also the symptoms of selenosis [25,132].

Selenium and sulfur share, very similar chemical properties. Selenium has an important role in biochemical systems. At low levels of nutritional supply, it is essential to the health of animals and humans. At high levels, it is poisonous. The concentration range from trace element requirement to lethality is quite narrow [133]. While the minimum nutritional level for animals is about 0.05 to 0.1 mg Se kg^{-1} dry forage feed, exposure to levels of 2 to 5 mg Se kg^{-1} dry forage will lead to toxic problems in animals [134,133].

5.2 Boron and Health

Boron, in the earth's crust, can be found in most soil types as well as in alkaline soil. While most of the earth's soils have <10 ppm boron the range is from 2 to 100 ppm with the average soil boron concentration reported to be 10 to 20 ppm [28]. Whilst large areas of the world can be boron deficient, high concentrations are found, for example, in parts of the western United States, throughout China, Brazil and Russia. The world's richest deposits of boron are located in a geographic region that stretches from the Mediterranean countries inland to Kazakhstan. Boron concentrations in rocks range from 5 ppm in basalts to 100 ppm in shales [135]. Most essential elements that make their way into the human food and water supply are directly derived only from soil minerals. While most environmental sources of boron are geogenic in nature, some trace elements such as boron, iodine, and selenium are supplied in significant amounts to soils by atmospheric transport from the marine environment. Deficiency problems associated with these elements are therefore generally less common in coastal areas than farther inland [136].

The negative effects mainly refer to its toxicity, the 50% lethal dose of boron as boric acid for one-time administration is 2.6 g Kg^{-1} body weight, relatively close to that of the table salt (3 g Kg^{-1} body weight) [137]. Nevertheless, several case reports deal with boron intoxication in humans. When boric acid is ingested at daily dose levels of 0.14-0.43 g boric acid Kg body weight (equivalent to about 25-76 mg-boron Kg^{-} body weight) for days and even weeks, a variety of symptoms appear [138] and [29]. The most common are the gastrointestinal ones, such as vomiting, diarrhea and abdominal pain. Besides these, there are others like headache, light headedness, and rash [139,140]. An ingestion of the equivalent of 0.2 g Kg^{-1} boron [141] or an exposure to boron oxide and boric acid dust at 4.1 mg m^3 will lead to poisoning [142]. When boron has been used in patients with renal function impairment or in infants and young adults in excessive amounts for more than 3–4 days, safety precautions have been raised [143] and [144]. It was observed that within the first 24 to 48 hours after boric acid ingestion, it increases the urinary riboflavin excretion in approximately

two thirds of the patients. These data provide evidence of a previously unrecognized hazard of boric acid ingestion in patients. According to Dinca and Scorei [138] repoted Boric acid complexes with polyhydroxylribitol side chain of riboflavin will increase the water solubility of boric acid. The free boric acid that diffuses freely through the cellular membrane gives the toxicity of boric acid/borate salts. Being in excess, it could also block the cellular metabolic activity, eventually giving apoptosis [28,145,146].

Other occupation studies have reported on the relation of respiratory symptoms, pulmonary function, and abnormalities of chest radiographs to estimate exposures of borax dust. In a cross-sectional study of 629 actively employed borax workers, 93% of eligible workers, participant exposures ranged from 1.1 mg B/m^3 to 14.6 mg B/m^3. Symptoms of acute respiratory irritation such as dryness of mouth, nose, or throat, dry cough, nose bleeds, sore throat, productive cough, shortness of breath, and chest tightness were related to exposures of 4.0 mg B/m^3 or more. They were infrequent at exposures of 1.1 mg B/m^3. Symptoms of persistent respiratory irritation were related to exposure among non-smokers. Radiographic abnormalities were uncommon and were not associated with dust exposure [147].

6. CONCLUSION

The environmental pollution of Se and B are significantly spread the world. In this review, we have addressed the mechanism of uptake and toxicity of Se and B in plant including phytoremediation aspect. However, still there are many faces of Se and B which need to be uncovered. In addition, how different plants have different Se and B tolerance and detoxification mechanisms, and exploitation of these mechanisms to improve phytoremediation of Se and B, also needs to be uncovered by integrating both the approaches.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Author has declared that no competing interests exist.

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