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Use of Boron in Detergents and its Impact on Reclamation

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Use of Boron in Detergents and its Impact on Reclamation

A thesis submitted in partial satisfaction

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in Civil Engineering

by

Maryam Ghavanloughajar

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ABSTRACT OF THE THESIS

Use of Boron in Detergents and its Impact on Reclamation

By

Maryam Ghavanloughajar

Master of Science in Civil Engineering

University of California, Los Angeles, 2015

Professor Michael K. Stenstrom, Chair

Many parts of the world are experiencing severe water drought and it affects societies both economically and environmentally. Therefore, conservation practices are essential to balance water supply and demand. Greywater or wastewaters from showers and luandries, if treated well can be a reliable source for activities such as irrigation, toilet flushing and car washing. Greywaters are not as contaminated as sewage but still may require treatment before reuse. The application of insufficiently treated water for irrigation can cause harm to plants and animals. Pollutant such as boron in greywater is of particular interest because many plants are sensitive to even low concentrations. High concentrations of boron can induce toxicity, reduce growth rate and yield in plants. Therefore, proposed greywater treatment systems need to consider the sensitivity of plant species and boron concentrations and potential removal. This thesis reviews boron chemistry, its effect on plants and currently available boron removal technologies.

The thesis of Maryam Ghavanloughajar is approved.

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University of California, Los Angeles

2015

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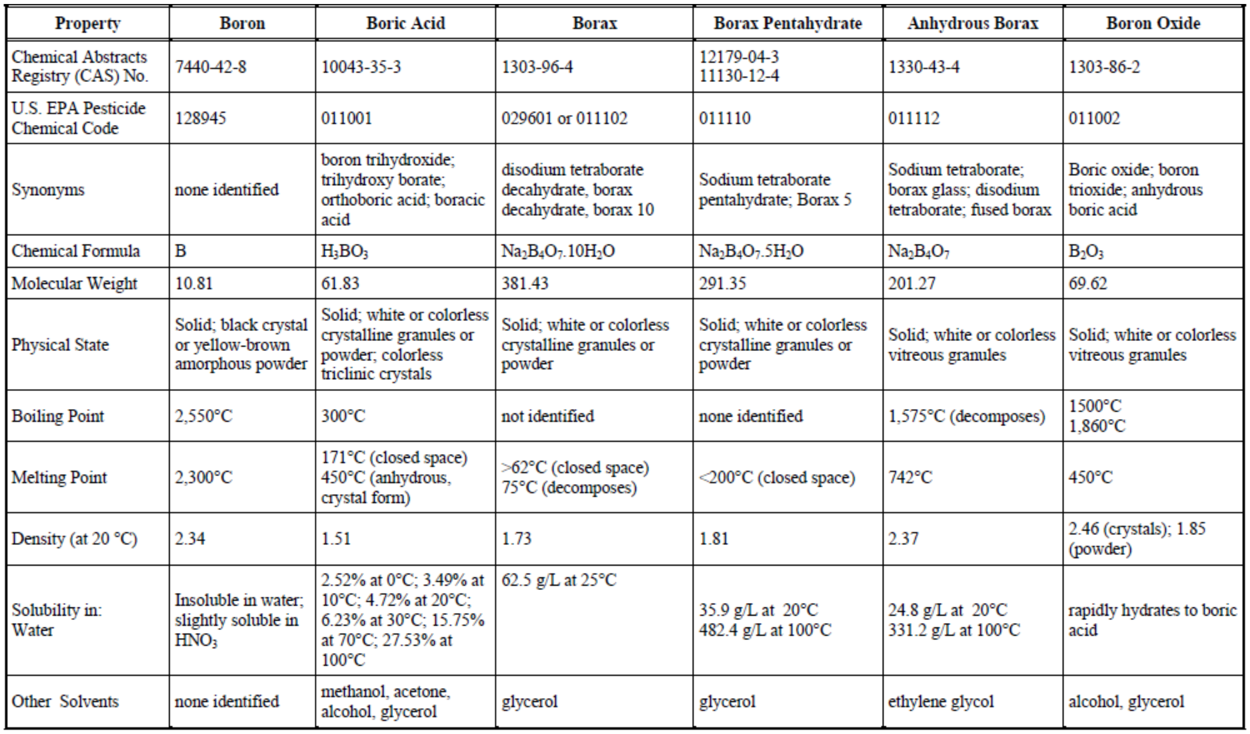
1. Introduction

Development of new reliable local resources is crucial to maintain increasing demand of freshwater. For instance, different available technologies for wastewater treatment enable us to reuse wastewater through reclamation and recycling. Reclaimed wastewater is suitable for a beneficial or controlled use that would not otherwise occur(*1*). Treating greywater for irrigation is one method to conserve water and reduce potable water consumption for landscape purposes. The broad definition of greywater consists of all non-toilet household wastewaters. It includes wastewater from showers, baths, hand basins, washing machines, laundry, dishwashers and kitchen sinks. Separation of greywater from toilets permits more effective, affordable and uncomplicated on-site treatment due to lack of organic matter, nutrients and pathogens. However, a high concentration of surfactants, oils and boron have been observed in greywater as a result of extensive use of detergents(*2*). Eriksson et al (2002) conducted an extensive review on the composition of greywater and they demonstrated that concentration of boron in greywater depends on the types of products used in the household (soaps, detergents), the included appliances (kitchen sinks, dishwashers etc) and treatment methodology. Boron concentrations greater than 0.5 mg/L have not been reported from any greywater sources(*3*). Considering the importance of greywater reuse for arid areas such as Southern California, the aim of this study is to review the environmental fate and effect of boron in greywater reuse. Boron removal methods are also reviewed.

Boron is the first element of Group III, with atomic number of 5 and it is fairly abundant element in the Earth. It shares some similarities with aluminum (which is next element in Group III) due to its related valence and properties; however most of boron properties are analogous to those of

Silicon and in some cases Germanium(*4*). Boron can form compounds with oxygen, fluorine, bromides and chlorine as well as metals. The US Environmental Protection Agency (EPA) provides an extensive list of chemical and physical properties of boron compounds which are shown in Table 1(*5*). Among various boron compounds, boric acid, H3BO3, and borax, Na2B4O7.10H2O, are the most environmentally important compounds since other types of boron compounds are introduced to the environment in such small amounts that their environmental significance is minor. It should be noted that boric acid and borax are also products of the breakdown of other compounds in the natural environment(*6*).

Table 1. Chemical and physical properties of boron and related compounds



Property	Boron	Boric Acid	Borax	Borax Pentahydrate	Anhydrous Borax	Boron Oxide
Chemical Abstracts Registry (CAS) No.	7440-42-8	10043-35-3	1303-96-4	12179-04-3 11130-12-4	1330-43-4	1303-86-2
U.S. EPA Pesticide Chemical Code	128945	011001	029601 or 011102	011110	011112	011002
Synonyms	none identified	boron trihydroxide; trihydroxy borate; orthoboric acid; boracic acid	disodium tetraborate decahydrate, borax decahydrate, borax 10	Sodium tetraborate pentahydrate; Borax 5	Sodium tetraborate; borax glass; disodium tetraborate; fused borax	Boric oxide; boron trioxide; anhydrous boric acid
Chemical Formula	B	H_3BO_3	$Na_2B_4O_7.10H_2O$	$Na_2B_4O_7.5H_2O$	$Na_2B_4O_7$	B_2O_3
Molecular Weight	10.81	61.83	381.43	291.35	201.27	69.62
Physical State	Solid; black crystal or yellow-brown amorphous powder	Solid; white or colorless crystalline granules or powder; colorless triclinic crystals	Solid; white or colorless crystalline granules or powder	Solid; white or colorless crystalline granules or powder	Solid; white or colorless vitreous granules	Solid; white or colorless vitreous granules
Boiling Point	2,550°C	300°C	not identified	none identified	1,575°C (decomposes)	1500°C 1,860°C
Melting Point	2,300°C	171°C (closed space) 450°C (anhydrous, crystal form)	>62°C (closed space) 75°C (decomposes)	<200°C (closed space)	742°C	450°C
Density (at 20 °C)	2.34	1.51	1.73	1.81	2.37	2.46 (crystals); 1.85 (powder)
Solubility in: Water	Insoluble in water; slightly soluble in HNO_3	2.52% at 0°C; 3.49% at 10°C; 4.72% at 20°C; 6.23% at 30°C; 15.75% at 70°C; 27.53% at 100°C	62.5 g/L at 25°C	35.9 g/L at 20°C 482.4 g/L at 100°C	24.8 g/L at 20°C 331.2 g/L at 100°C	rapidly hydrates to boric acid
Other Solvents	none identified	methanol, acetone, alcohol, glycerol	glycerol	glycerol	ethylene glycol	alcohol, glycerol

Boron can be found in surface water and groundwater and the latter is highly affected by wastewater discharges. Based on World Health Organization (WHO) guidelines (2008), boron concentration in groundwater varies from less than 0.3 to more than 100 mg/L throughout the world. These guidelines included a provision to limit boron concentration of 0.5 mg/L for drinking water(*7*). The guidelines (*8*) were changed in 2011 to 2.4 mg/L due to the inability of economically achieving 0.5 mg/L.

Boron can contaminate water bodies as a result of natural processes or human activities and varies in concentration in surface water, runoff or wastewater(*9*). The most common reason for the presence of boron in the wastewater is the application of boron compounds as a bleaching agent in detergents and cleaning products. Due to the toxicity of a high concentration of boron, different standards limit its concentration in drinking water, irrigation water and wastewater; however those limits vary in different regions. California state guidelines recommended 1 mg boron per liter of drinking water while the EPA suggested that non-regulatory concentrations of boron in drinking water should be about 5 mg/L. The EPA study states that at this concentration adverse health effects are not anticipated to occur in adults over long term exposure, assuming that human daily water consumption is about 2 L/ day(*5*). The California Department of Public Health (CDPH) also regulates boron as a drinking water contaminant. The current Notification Level (NL) for boron, proposed by CDPH, is 1 mg/L (*10*).

Boron is also present in seawater, mainly in the form of boric acid in low concentration. Boron concentration in seawater is estimated to be around 4-5 mg/L which requires it to be removed in desalination processes making irrigation water (*11*, *12*).

Although boron is a necessary element for plant growth at low concentration and must be provided through irrigation or fertilizer, it can become fairly toxic at higher concentrations and the toxicity varies by plant species. Below a threshold concentration, typically less than 5 gram of borax/kilogram of body weight, the effects of boron on mammals, birds and fish are negligible; nonetheless it is toxic to insects which makes boron an ideal choice for a use as insecticides(*6*).

Commercial boron compounds are widely employed in manufacturing industries such as the glass industry for the production of optically and chemically stable glass, enamels, cosmetics, leather, detergents, insecticides and in the preparation of disinfectants and drugs(*4*, *13*).

2. Literature Review

2.1. Chemical properties of boron

Boron chemistry is unique and complex since its chemical and physical properties are significantly different from the other elements in its group. Except for high reducing power, boron shares few similarities with neighboring elements in the periodic table (*12, 14, 15*). Elemental boron is rare and its difficult preparation procedure imposes constraints on experimental and theoretical studies of boron chemistry. Researchers and chemists studying boron are making continuing progress but new results often conflict with previous results, and uncertainties remain.

Boron is a low-abundance element in the Earth's crust that occurs as a trace element in most soils(*16, 17*). Two forms of elementary boron are recognized as 1) fine crystalline (amorphous boron) which is brown in color, and 2) crystalline boron of dark grey color. Two crystalline structures of boron, namely, α-rhombohedral boron (Figure. 1) and β-rhombohedral boron (Figure. 2) exist at atmospheric pressure(*18*). According to Table 2, boron is distributed in various component of the Earth(*4*).

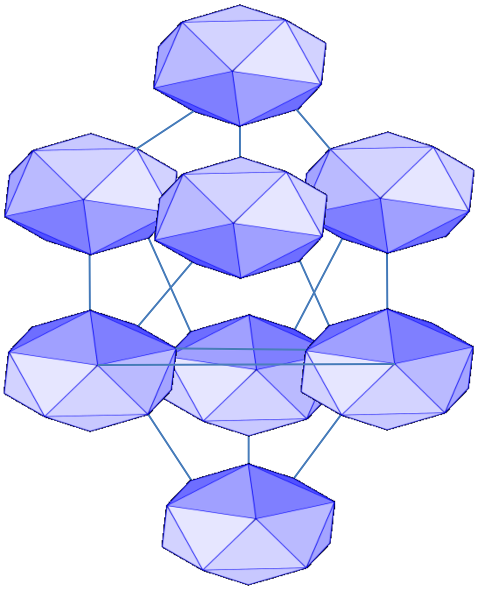


Figure 1. Unit cells of α-boron, rhombohedral setting (Adapted from Albert and Hillebrecht, (*18*))

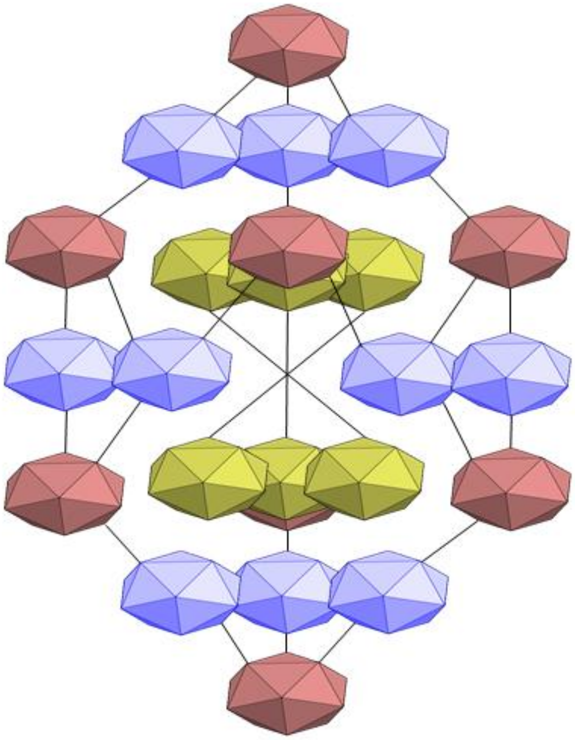


Figure 2. Unit cells of β-boron, rhombohedral setting (Adapted from Albert and Hillebrecht, (*18*))

Table 2. Distribution of Boron in the Earth' components (Adapted from Nemodruk &Karalova, (*4*))

Source	Weight percent of boron
Earth’s crust	$1 * 10^{-3}$
Sedimentary rocks	$1.2 * 10^{-3}$
soils	$1 * 10^{-3}$
Marine clays	$5 * 10^{-3}$
Sea water (dry residue)	$1.5 * 10^{-3}$
Salt springs (dry residue)	$(3\text{-}20) * 10^{-3}$
Marine plants (ash)	$1.5 * 10^{-3}$
Marine animals (ash)	$(3\text{-}100) * 10^{-3}$
Clover, alfalfa (dry matter)	$(7\text{-}57) * 10^{-3}$

Although boron compounds are widespread in nature, naturally occurring minerals containing boron are found in few locations. Boron has accumulated in borate-rich top soil in arid regions such as California as a result of evaporation of water containing boric acid. Large deposits of boron minerals are available in the area of former volcanic activity or thermal activity such as hot springs(*16, 17*). The largest borate deposits are located in the Mojave Desert of the United States, the Alpide belt in southern Asia, and the Andean belt of South America. Table 3 shows the major countries producing boron(*19*). In both 2010 and 2011, California was the only producer of boron in the United States. Boron was California's second most valuable mineral commodity in terms of dollar value, after construction sand and gravel in 2011(*20*).

Table 3. Boron minerals: world production, by country

Country	Production Year (thousand metric tons)				
	2008	2009	2010	2011	2012
Argentina	786	500	623	649	650
Bolivia	56	86	97	135	130
Chile	583	608	504	489	444
China [1]	140	145	150	150	160
Peru	350	187	293	199	104
Russia [2]	400	400	400	400	400
Turkey [3]	2139	1800	2200	2273	2500

1) Boron oxide(B_2O_3) equivalent

2) Blended Russian datolite

3) Concentrates from ore

Four principal commercially valuable boron ores in the United States are: sodium borates tincal, kernite, the calcium borate colemanite, and the sodium-calcium borate ulexite(*21*). Boron products are priced and sold based on boric oxide content (B_2O_3), which varies by ore and compound, and on the absence or presence of sodium and calcium (Table 4) (*19*)

Table 4. Boron minerals of commercial importance

Mineral	Chemical composition	B_2O_3 weight percentage
Boracite	$Mg_3B_7O_{13}Cl$	62.2
Colemantie	$Ca_2B_6O_{11}.5H_2O$	50.8
Datolite	$CaBSiO_4OH$	24.9
Kernite(rasorite)	$Na_2B_4O_7.4H_2O$	51.0
Priceite(pandermite)	$CaB_{10}O_{19}.7H_2O$	49.8
Probertite (kramerite)	$NaCaB_3O_9.5H_2O$	49.6
Sassolite(natural boric acid)	H_3BO_3	56.3
Tincal(natural borax)	$Na_2B_4O_7.10H_2O$	36.5
Tincalconite(mohavite)	$Na_2B_4O_7.5H_2O$	47.8
Ulexite(boronatrocalcite)	$NaCaB_5O_9.8H_2O$	43

As mentioned before, boron is in the Group 13 of periodic table and the ground state configuration is $1S^2\ 2S^2\ 2P^1$. This configuration would be a chemistry of monovalent boron, however the most excited electron configuration of boron is $1S^2\ 2S^1\ 2P^2$. According to latest configuration, boron is trivalent in most cases and the oxidation state is +3(*4*, *17*). Boron is also electron deficient since three single bonds do not support a stable electron configuration. Therefor born has strong tendency to form stable covalent bonds with electronegative atoms such as oxygen. In fact naturally occurring boron is found exclusively bound to oxygen as borates(*22*). Electron deficiency of boron is what accounts for boron being a weak Lewis acid, in that it can accept hydroxide (OH^- ions) in solution(*14*). Boron also uses hydrogen atoms to bridge between two boron atoms and rarely forms boron-boron bounds to compensate electron deficiency(*17*).

Among all boron compounds and minerals, H_3BO_3 (boric acid) and $Na_2B_4O_710H_2O$ (borax) fall within the scope of this research since they are incorporated into laundry detergents, soaps, and other cleaning products.

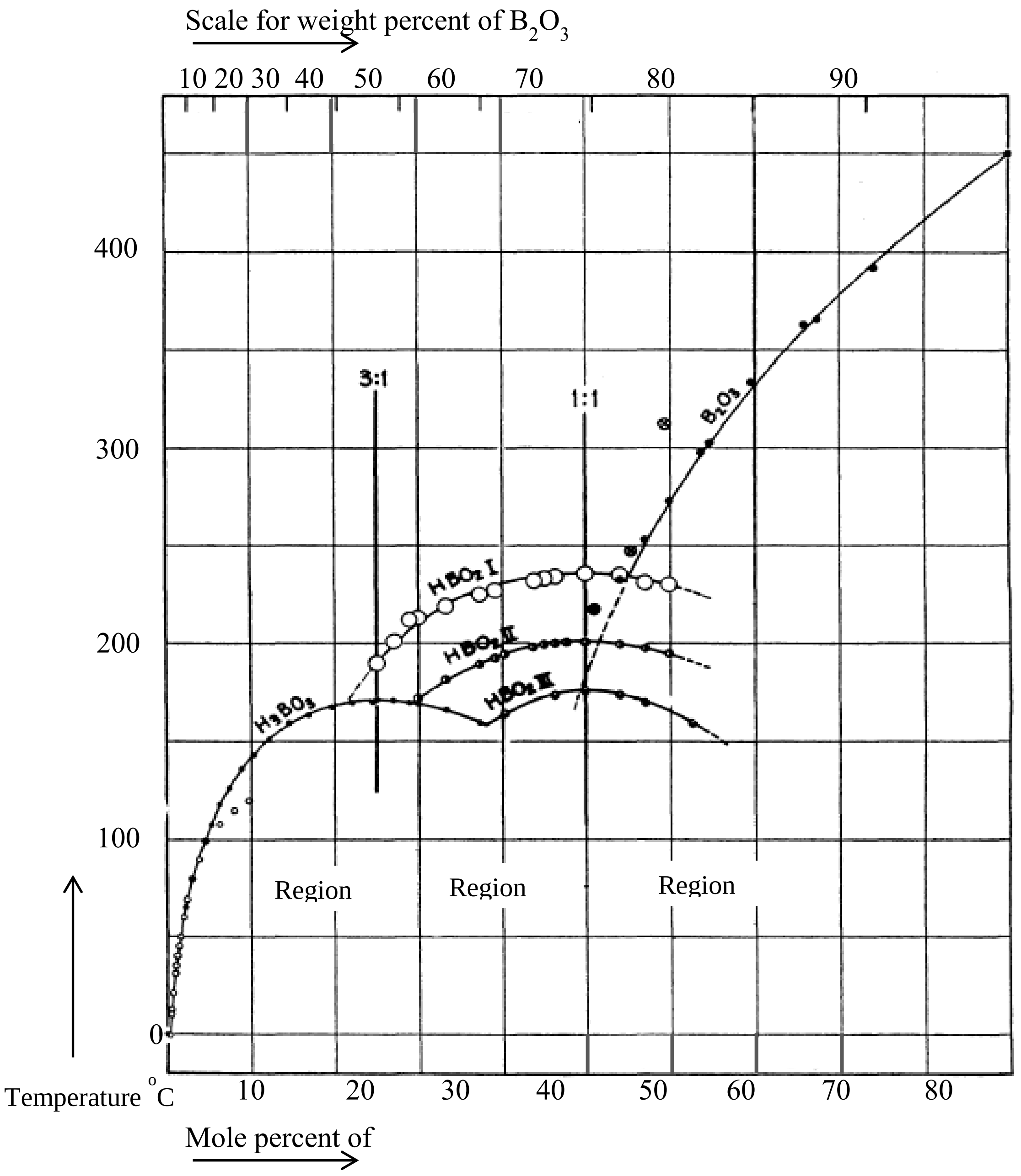
2.1.1. Boric acid

Two forms of boric acid in free state are: metaboric acid, HBO_2, and orthoboric acid H_3BO_3. Orthoboric acid, or simply boric acid is obtained from mineral sassolite and crystallizes in the form of fine, waxy and white flakes. Crystalline boric acid is essentially layers of H_3BO_3 molecules held together by hydrogen bonds(*23*). Some of important physicochemical properties of boric acid are given in Table 5(*4*, *24*).

Table 5. Physicochemical properties of boric acid

Property	Unit	Numerical value
Density	g/cm^3	1.48-1.51
Heat of dehydration (to form crystalline orthoboric acid)	kcal/mole of boric acid	-9.3(25^o)
Heat of vaporization	kcal/mole of boric acid	23.43
Heat of solution (to form a 0.05M solution)	kcal/mole of boric acid	-5.166

When boric acid is heated, it loses water, changing to three different crystal forms of metaboric acid. Upon more heatin0 at high temperature, composition of a viscous liquid containing HBO_2 and B_2O_3 has been observed(*24, 25*). Figure 3 shows the dehydration diagram and melting point for the H_2O-B_2O_3 system.



Dominant component in region A: H_3BO_3

Dominant component in region B: HBO_2

Dominant component in region C: B_2O_3

Figure 3. Dehydration diagram for the H_2O-B_2O_3 system (Adapted from Kracek et al, (*25*))

The following equations describe dehydration process of boric acid(*23*):

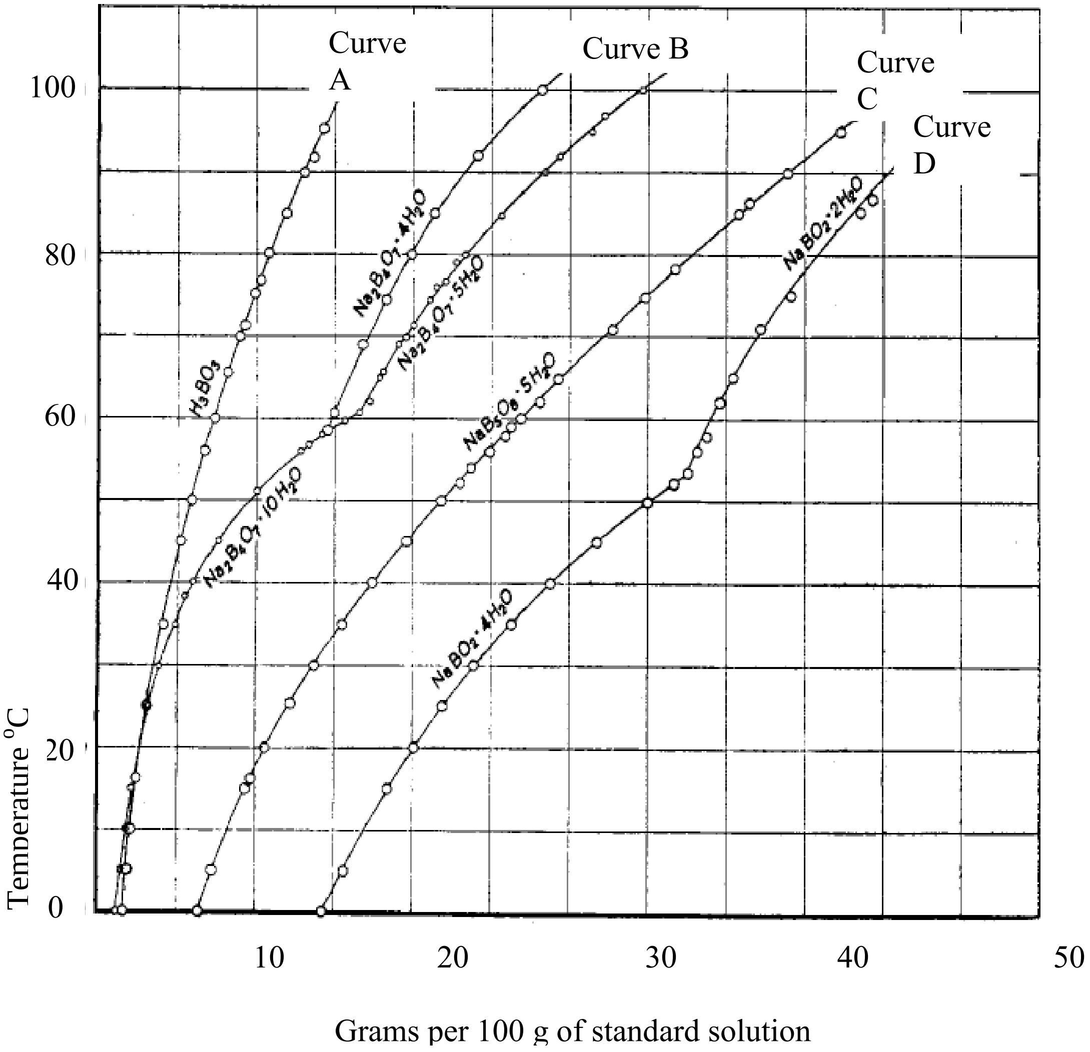
Orthoboric acid gradually loses water, and changes to metaboric acid

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

At higher temperatures, all the water is lost, and anhydrous boric oxide is formed

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

In water, boric acid exists in monomeric form of $B(OH)_3$ in which boron and oxygen atoms form a planner arrangement. Therefor the aqueous boric acid molecules formula can be described as $B(OH)_3(^{+}OH_2)$ that explains that it is monomeric, uncharged and a weak Lewis acid nature(*4*, *24*, *26*). The solubility of boric acid as well as other boron compounds is illustrated in Figure 4(27). Borate arrangement in borax, including more bonds between ions, accounts for greater stability of borax against dehydration(*28*).



Curve A: Solubility of H_3BO_3

Curve B: Solubility of $Na_2B_4O_7$

Curve C: Solubility of NaB_5O_8

Curve D: Solubility of $NaBO_2$

Figure 4. Solubility diagram of boric acid and other boron compounds (Adapted from Blasdale & Slansky, (*27*))

Boric acid is a weak acid with the first dissociation constant of $5*10^{-5}$. However, the acidic properties of boric acid increase in presence of some natural salts.

The boric acid ion is hydrated in aqueous solution according to following reaction(*4*, *26*):

$$H_3BO_3 + 2H_2O \longleftrightarrow H_3O^+ + B(OH)^-{}_4$$

Based on this equation boric acid accepts hydroxide ion from water and releases a proton into solution. Boric acid dissociates as a function of pH. At higher pH, the anion, $B(OH)_4{}^-$, is predominant, while at lower pH the uncharged species are predominant. At low concentrations ($\leq$0.02M), only the mononuclear species $B(OH)_3$ and $B(OH)^-{}_4$ are present. At higher concentrations and with increasing pH, polynuclear ions such as $B_2O(OH)_6{}^{2-}$ or those incorporating B_3O_3 rings such as $B_3O_3(OH)^-{}_4$ are formed. Thus, at the higher concentrations, the interaction between $B(OH)_3$ and $B(OH)^-{}_4$ may occur based on following equation(*22*):

$$B(OH)_3 + 2B(OH)_4^- \longleftrightarrow [B_3O_3\,(OH)_5]^{2-} + 3H_2O$$

Formation of other polymeric species is feasible based on following equation(*29*):

$3\ B(OH)_3 = B_3O_3(OH)_4^- + H^+ + 2H_2O$ pK=6.84

2.1.2. Borax

Sodium borates as shown in Table 6, in their 5- and 10- hydrate and anhydrous forms, are commercially the most important compounds of borate(*24*). The 10-hydrate form of sodium borate is incorporated in many cleaning and personal care products, metallurgical fluxes, corrosion inhibition, adhesives, wire drawing and stabilizers.

Table 6. Molecular formula of sodium borate compounds (Adapted from Duydu et al, (*30*))

Name of compound Property	Anhydrous borax	Borax pentahydrate	Borax (Sodium tetraborate decahydrate)
Molecular formula	$Na_2B_4O_7$	$Na_2B_4O_7.5H_2O$	$Na_2B_4O_7.10\ H_2O$
Molecular weight	201.27	291.35	381.43
Boron content (%)	21.49	14.85	11.34

The early use of sodium tetraborate decahydrate, $Na_2BO_4.10H_2O$, or borax was to make perborate, the bleaching agent used in household detergent(*30*). It can contribute to the softening of hard water by tying up calcium ions, as well as acting as a buffer agent. Sodium perborates such as $NaBO_3\ .1H_2O$ or $4H_2O$ have been added into powdered detergents. Perborates release hydroperoxide ion upon their dilution in alkaline wash water based on following equation(*21*) :

$$Na_2\,[(HO)_2B(OO)_2B(OH)_2\,] * 6H_2O + 2OH^- \longrightarrow 2NaB(OH)_4 + 2OOH^- + 4H_2O$$

Borax also can be converted to boric acid by the action of hydrochloric acid(*31*):

$$Na_2B_4O_7 * 10H_2O + 2\ HCl \longrightarrow 4\ H_3BO_3\,[\text{or } B(OH)_3] + 2\ NaCl + 5\ H_2O$$

2.2. Boron impact on plants

Boron is an essential element for plant growth and it can be added directly to the soil as fertilizer(*13*), however, at high boron concentrations of are toxic to plants. Therefore for proper growth of plants, it is important to quantify the minimum and maximum concentrations of boron.

Boron can support the growth of plants and crops in different processes. One such process is the ability of boron to facilitate sugar movement from leaves to stems. Gauch and Dugger ‘s 1953 study demonstrated that boron deficiency symptoms correlate with sugar deficiency, as sugar accumulates in leaves and cannot move towards other parts of the plant(*32*). Moreover, boron plays a role in the growth of cell walld. Brown et al. reported the importance of sufficient boron in the stabilization of cell wall structure and the regulation of pore sizes of cell walls(*33*). Sprague summarized that boron is involved in other aspects of plant growth such as enzymatic reactions, nucleic acid metabolism along with cell structure(*6*).

While the boron requirement in plants is well established, high concentrations of boron in irrigation water can lead to damage of some plants and crops. Boron accumulation in plant leaves and roots due to transpiration induces boron toxicity. Toxicity symptoms appear on older leaves as a yellowing, spotting, or drying of leaf tissue at the tips and edges.

Plant tolerances to boron are one of the most important criteria for greywater treatment and it is critical to adjust and develop greywater treatment processes in order to avoid generating plant toxicity. One must take into account that soil structure, pH, rainfall and humidity also play a role in overall boron uptake by plants.

Not all crops are equally sensitive to boron; some plants can show boron deficiency at a concentration that would be toxic to a different plant. The first extensive, quantitative comparison of the effect of boron on fifty species of plants was that of Eaton (*34*) who used sand culture for plant growth and irrigated them with different boron concentrations in standard nutrient solution. Table 7, which is developed based on Eaton's measurements, contains boron concentrations for optimal growth and the lowest concentration for toxicity. According to Table 7, plants are classified as sensitive if they have a tolerance index of less than 50, a semi tolerant index of 50-100, or a tolerant index greater than 100. The tolerant index is defined as 100 times the ratio of the average weight of plants grown in 5, 10, and 15 ppm boron to the largest weight of plants grown in either trace or 1 ppm boron in solution(*34*).

Table 7. Plants growth as affected by Boron (Adapted from Eaton, (*34*))

Plant	Boron concentration for best growth (ppm)	Lowest concentration for injury (ppm)	Relative tolerance
Sensitive			
Violets	Trace	5	20
Grapes	1	5	9
Pansies	Trace	5	24
Semi tolerant			
Peas	1	5	55
Sweet potatos	Trace	5	63
Celery	15	25	89
Alfa alfa	15	15	98
Tolerant			
Turnips	5	25	115
Cotton	10	10	130
Asparagus	15	25	217

Crop sensitivity is the limiting factor for boron concentration in irrigation water. Rowe and Abdel-Magid summarized detailed guidelines for allowable concentrations of boron in reclaimed water intended for agricultural reuse, as presented in Table 8(*1*).

Table 8. Limits of boron in irrigation water(Parts per million)(Adapted from Rowe & Abdel-Magid, (*1*))

Class of water	Plant sensitivity		
	Sensitive	Semi tolerant	Tolerant
Excellent	<0.33	<0.67	<1.00
Good	0.33-0.67	0.67-1.33	1-2
Permissible	0.67-1	1.33-2	2-3
Doubtful	1-1.25	2-2.5	3-3.75
Unsuitable	>1.25	>2.5	>3.75

2.3. Survey of boron in commercial products

Boron compounds have many applications worldwide. For example, the principal industrial uses of borax and boric acid are in the production of glass, ceramics, soaps, detergents, and bleaches. Figure 5 illustrates the U. S. consumption of boron compounds by end use.

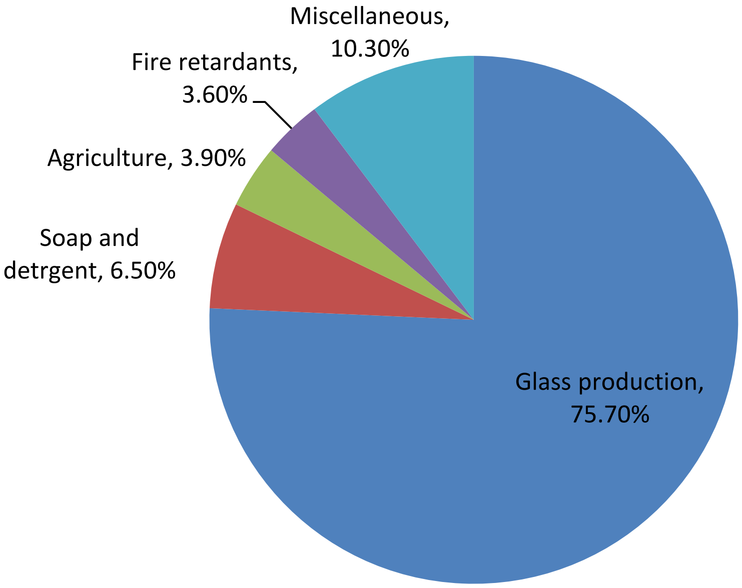


Figure 5. Year 2000 U.S. consumption of boron by end use(Adapted from Parks & Edwards, (*14*))

Boron is mainly used as an additive in glass production because of its mechanical properties. Boron can reduce the thermal expansion of glass, therefore improving its strength, chemical resistance, and durability. It also can provide resistance against vibration, high temperature, and thermal shock. Boron can improve glass manufacturing by reducing the viscosity of glass during production (*14, 19*). Depending on the application and quality of the glass, either borax, boric acid, colemanite, ulexite, or sodium borates can be used(*19*).

Boron compounds offer benefits in detergents so they can be used in the manufacturing of detergents and bleaches as well. Some of those benefits are as follows:

- Alkaline buffering and pH control of solution
- Borate and perborates form soluble complexes with calcium ions. As a result, water hardness is reduced upon removal of calcium ions.
- Improvement of surfactant performance. Negatively charged surfactants can form complexes with calcium ion in water prior to delivering their detergency function. Borates compete successfully with the surfactant for the calcium ions and formation of complexes between them improves surfactant performance.
- The borate component aids overall detergency

Boron is added to detergents in the form of sodium perborates or perborate tetrahydrate since they have a peroxygen bond that can deliver oxidizing bleaching agent to the solution. Sodium perborate, however, requires hot water ($60^{o}C$) to undergo hydrolysis, unless an activator is present. Concerns have emerged over excessive boron levels in wastwater due to sodium perborate in detergents. Therefore, sodium percarbonate has been used as a substitute, primarily in Europe, because it produces hydrogen peroxide at lower temperatures. Whit this substitution boron consumption has been affected (*14, 19*).

The U. S. department of health and human services provides a database on chemical ingredients of over 14000 consumer brands. Available information is from brand-specific labels and Material Safety Data Sheets provided by manufacturers.

The following table is adapted from the U. S. department of health and human services website and indicates the percentage of different boron compounds in various household products(*35*).

Table 9. Percentage of boron compounds in different cleaning products

Brand	Form	Percent
Sodium tetraborate anhydrous **$Na_2B_4O_7$**		
Cheer Liquid Laundry Detergent-01/08/2004-Old Product	Liquid	1-5
Tide Ultra Liquid-03/24/2006	Liquid	1-5
Tide Free Ultra Liquid-03/24/2006	Liquid	1-5
Gain Liquid Detergent, Original	Liquid	0.5-5
Era Liquid Laundry Detergent-01/11/2008	Liquid	1-5
Sodium tetraborate pentahydrate **$Na_2B_4O_7. 5H_2O$**		
Whink Wash Away Pre-Treatment & Stain Remover	Liquid	1-4
Whink Uniform Wash, Laundry Stain Remover	Liquid	0.5-1.5
Sodium borate decahydrate **$Na_2B_4O_7. 10H_2O$**		
Ivory Snow Liquid Laundry Detergent-Old Product	Liquid	1-5

Table 9. (Continued)

Brand	Form	Percent
Spray N Wash Stain Stick-04/11/2002-Old Product	Solid	1-2
Seventh Generation, Natural Lavender Laundry Liquid	Liquid	0.03-3
Seventh Generation, Sensitive Care Laundry Liquid	Liquid	1-10
DIP-IT Food & Beverage Stain Cleaner Powder-01/08/2010	Powder	2.5-10
OxiClean Max Force 4 In 1 Stain Fighting Power Pre-Treater Gel Stick	Solid	1-2
Boraxo Powdered Hand Soap-08/30/2007-Old Product	Powder	60-100
Twenty Mule Team Powdered Hand Soap-08/30/2007-Old Product	Powder	60-100
Boric acid (H_3BO_3)		
Hot Shot Maxattrax Ultra Brand Ant Killing Gel	Gel	5
Cascade Automatic Dishwashing Liquigel-09/07/2006	Gel	1-5

Table 9. (Continued)

Brand	Form	Percent
Seventh Generation Baby Natural 4X Laundry Detergent, Fresh & Clean	Liquid	1-3
Green Works Natural Laundry Stain Remover	Liquid	1-5

3. Boron removal technologies

Numerous technologies have been proposed for boron removal. This paper reviews conventional and advanced methods for boron removal. Most boron removal processes developed around the idea of using seawater or contaminated water as a source of potable or irrigation water since nearly all of those water sources have concentrations of boron which usually exceed allowable limits.

3.1. Chemical precipitation

Among different technologies, chemical precipitation is well-adapted for removal of boron at high concentrations. Some chemical precipitation reactions have the ability to utilize different precipitants to remove boron. Xu and Jiang (*13*) mentioned the potential of organic and inorganic compounds to precipitate boron from a solution through the coagulation-precipitation processes(*13*). They also extensively reviewed application and effectiveness of those compounds. Table 10 is adapted from their review and shows chemical precipitants for boron removal.

Table 10. Common chemical precipitant for boron removal(Adapted from Xu and Jiang, (*13*))

Precipitant	Sample	Initial concentration	Final concentration	Favorable conditions	Limitation
Inorganic precipitant					
Lime	2.65:1 as mole ratio of B:Ca, in boric acid solution	6200 mg/L (B) .	450 mg/L (B) 400-600 mg/L (Ca)	pH=10 1-4 days 25 °C	Dependent on pH, reaction time, relative concentration More removal(400 mg/L) is possible by adding more lime (high pH and significant quantity of lime)
Powdered lime	50 g/L of powdered lime	700 mg/L (B)	50 mg/ (B)	90 °C 2 h	
aluminum sulfate	1125 mg/L with lime for incinerator quench water	1.2 mg/L	0.16 mg/L(87%)	pH =12.0	

Table 10. (Continued)

Precipitant	Sample	Initial concentration	Final concentration	Favorable conditions	Limitation
Inorganic precipitant					
Iron salts	Sequential addition of reagent.		10 mg/L	pH 8-9	Iron(III) is better since iron(II) precipitates were difficult to filter
Magnesium oxide			95% removal	10 h at 20 °C possible to use water to remove B2O3 from the metal oxide after heat treatment	Dependent on quality of reagent and contact time
Alumina-Lime-Soda Process	Raw water	1.7 mg/L	0.2 mg/L	Method for softening brackish water	

Table 10. (Continued)

Precipitant	Sample	Initial concentration	Final concentration	Favorable conditions	Limitation
Organic precipitant					
Polyvinyl Alcohol (PVA).		150 mg/L	60% removal	room temperatur, additional calcium hydroxide improves removal	
Hydroxycarboxylic Acid				Formation of complex	Dependent on number of groups (hydrous or carboxylic), pH,concentration and precipitation mode
Organic Dioxime	1,2-cyclohexanedione dioxime (nioxime)	1000 mg/L			High cost

Remy et al, 2005 (*9*), indicated the difficulty of quantifying boron precipitation from dilute solution and expensive process of drying final solution to acquire final product. They proposed the novel method by using calcium hydroxide in powder form and they successfully reduced the concentration of boron from 700 to less than 50 mg L^{-1} by maintaining high temperature about 90^{o} C for about 2 hours(*9*).

Although different precipitants are capable of removing boron from water, effective chemical precipitation requires adjusting water pH and high chemical doses and other coagulation aids are required for removing boron from low concentration solution. Voluminous amounts of sludge are produced. Sludge chemical reaction is another issue associated with this method(*13*).

3.2. Ion exchange

In the study done by Aly et al, 2014 (*36*), boron was found in olive mill waste water with a concentration of 9.8 mg L^{-1}, using the azomethine-H analytical method. This proposed method is based on three successive column treatment including columns of gravel, sand and natural zeolite as an ion exchanger. They found that the zeolite is an efficient treatment and can decrease concentration of boron by 92.4% to 0.74 mg L^{-1}. Figure 6 illustrates effectiveness of zeolite in reducing boron from olive mill wastewater and also indicates that latter processes are not capable of reducing more boron from solution(*36*).

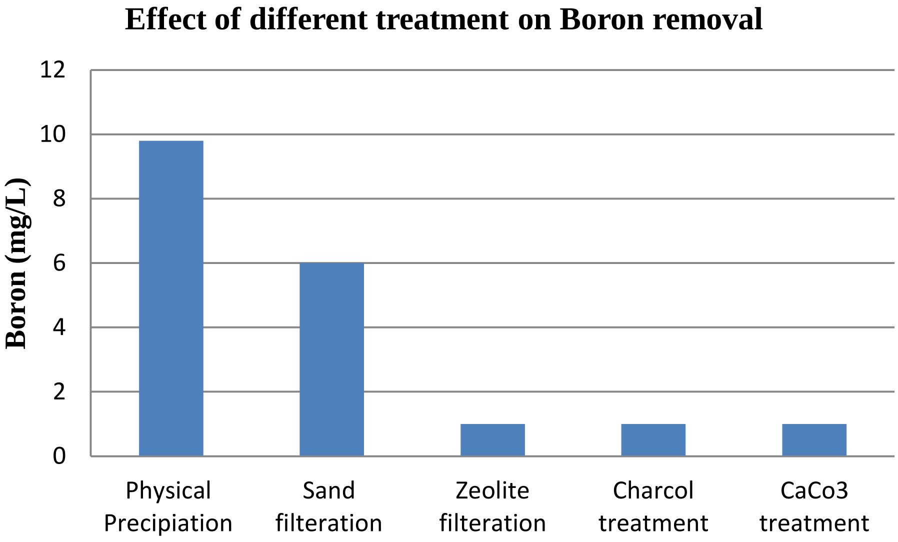


Figure 6. Impact of different treatment steps on boron removal from olive mill wastewater (Adapted from Aly et al (*36*))

3.3. Adsorption

A general sorption process is one of the most promising methods to remove contaminants from water due to low waste generation, moderate cost and possibility of using natural material as adsorbent. Adsorption processes are frequently used in water treatment to remove synthetic organic chemicals, disinfection by products as well as taste and odor(*37*), while adsorption treatment of wastewater is supplementary process in addition to conventional biological processes for the removal of refractory constituents and heavy metals(*38*).

Activated carbon which has porous structure on its surface is formed by thermochemical decomposition of organic materials followed with exposure to oxidizing gases(*38*). Although activated carbon is one of the principal types of adsorbents, it does not demonstrate a high ability for boron removal*(13), (39)*. In the experiment that was originally designed for investigating effectiveness of different adsorbents within static and dynamic flow, the effect of different impregnantes was also reported. It was found that the application of different impregnantes can increase boron adsorption by activated carbon. Among those experiments, removal of boron using activated carbon impregnated with mannitol exhibited more efficiency(*39*).

In another experiment, boron removal from high and low concentrated aqueous solutions was investigated by using activated alumina. Bouguerra et al demonstrated that 0.8 and 5 g of activated alumina are capable of up taking 40% and 65% of boron from low and high boron concentration solutions, respectively. According to their batch experiment, the optimal stirring time is about 30 minute and pH should be kept around 8.5 for both concentrations of 5 and 50 mg/L of boron in solution(*40*).

Fly ash is also reported to have the potential of being adsorbent for removal of contaminants. One advantages of fly ash over activated carbon is the fact that fly ash is a waste product of combustion, therefore it is less expensive and there is no need of regeneration after utilization which again can reduce the total cost. Ozturk and Kavak, 2005 (*41*), examined the effectiveness of fine particle size of fly ash (250-400μm) for removing boron at the concentration of 600 mg/L from H_3BO_3 solution in batch and column adsorption experiments. They also investigated the effect of pH, agitation time, initial boron concentration, temperature and adsorbent dosage in the final boron removal. In all experiments, boron removal tended to decline with increasing temperature, and the 90% removal were observed at 25^o C and pH of 2 by using 4-5 grams of fly ash in a 50 mL solution (Figure 7). A column experiment revealed a higher capacity for adsorption at about 46.2 mg /g, compared to adsorption capacity of 20.9 mg/g for batch experiment(*41*).

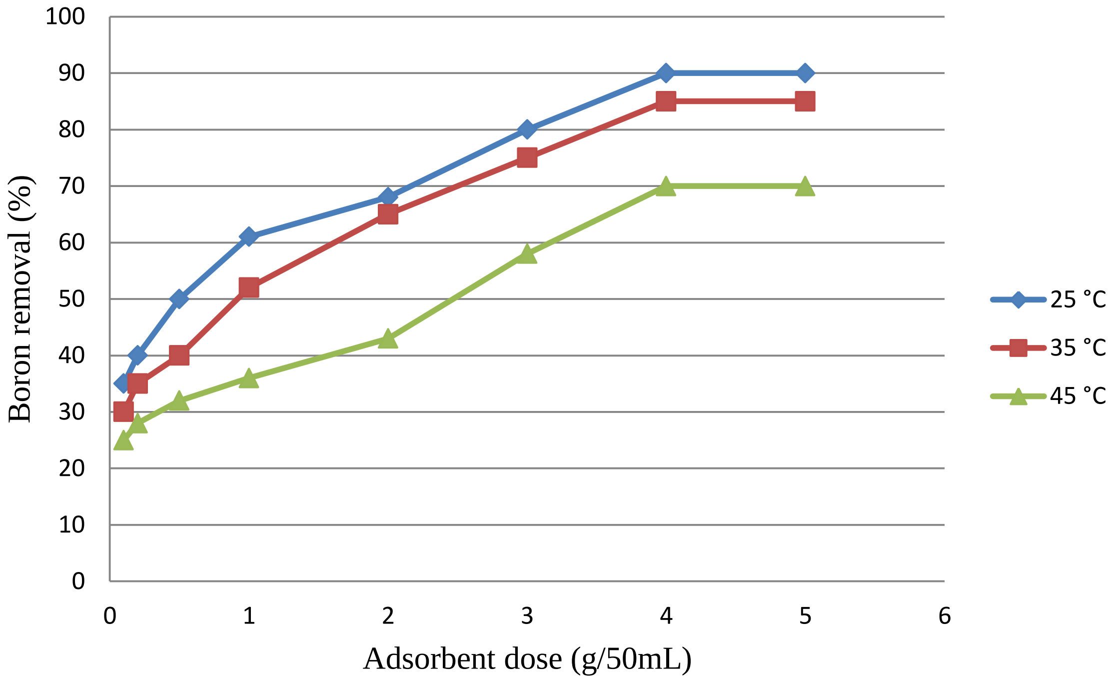


Figure 7. Effect of adsorbent dose on the removal of boron at pH=2 (Adapted from Ozturk & Kavak (*41*))

The ability of crushed coal and three different fly ash samples obtained from different power plants for boron removal from sea water and desalinized seawater were examined. Polat et al, 2004 (*42*), demonstrated that one type of fly ash is able to reduce boron level from sea water by 97% while lowest removal was observed to be 60%, using crushed coal. However, coal is a better candidate for continuous treatment since it can maintain its adsorption ability after several regeneration cycles. They also conducted various batch and column experiments and found that boron removal efficiency depends to some extent on reaction time and liquid to solid ratio(*42*).

Other unconventional adsorbents also acquire the ability of adsorbing boron. Red mud is an example of such a low cost material, which is a waste product from alumina refineries. It can be used as a mixed adsorbent with different metal oxides. Cengeloglu et al found that neutralized red mud can remove about 93% of boron from solutions which initial concentration of boron is

43 mg/L. They also observed that in batch equilibration technique the equilibrium time needed for adsorption is about 20 minutes which is relatively shorter compare to other adsorbents(*43*).

3.4. Reserve osmosis

Reserve osmosis (RO) utilizes a membrane to separate dissolved solutes from water. Water has to be pressurized towards semipermeable membrane to overcome natural osmotic pressure(*37*). RO is widely used for desalination of seawater or brackish water especially for irrigation purposes in area where the shortage of water is a concern. In wastewater treatment, RO is considered a highly effective treatment to remove remaining dissolved constituents after advance treatment. However, high efficiency is achieved only if a high quality of feed water is introduced to RO unit(*38*).

Boron is present in seawater at the concentration of 4 to 5 ppm(*11*). Boron in seawater is found in form of boric acid, H_3BO_3, weak acid that has poor rejection in its neutral form. Higher rejection is attainable by elevating pH above the pKa value, where borate ion is formed(*11, 37*). The rejection of boron by RO is better for the borate ion due to its charge. Therefore adjusting pH is a key feature for removing boron by using RO. Bouguerra et al studied boron rejection vs. feed water pH at different recovery rates (*Y*). Their results are plotted in Figure 8 (*40*).

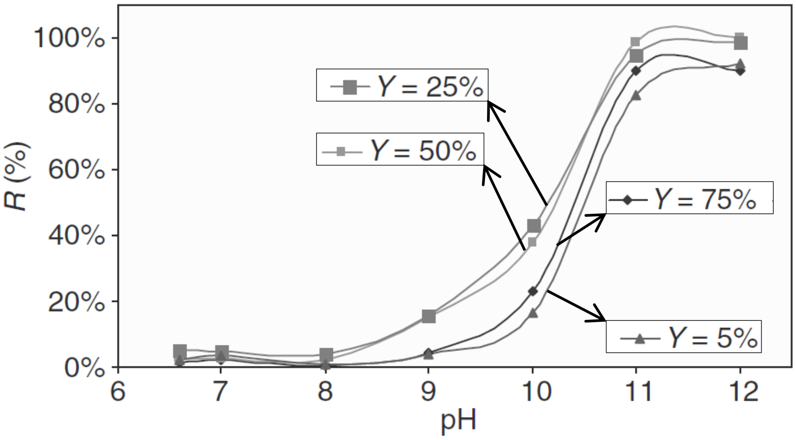


Figure 8. Effect of pH on boron removal (Adapted from Bouguerra et al (*40*))

Their results show that a single stage reserve osmosis process is not sufficient or cost effective for removing boron to irrigation concentrations, and additional steps such as pH adjustment, ion exchange or multistage RO must be used to achieve acceptable boron concentration.

Tu et al, 2010 (*44*), reviewed process for boron removal and compared rejection efficiencies for eight commercial membranes at standard test conditions. The results are shown in Figure 9(*44*). Membrane type A and B are nano filtration membranes, while type C and D are suitable for brackish reverse osmosis and type E, F, G and H are applicable for seawater reverse osmosis.

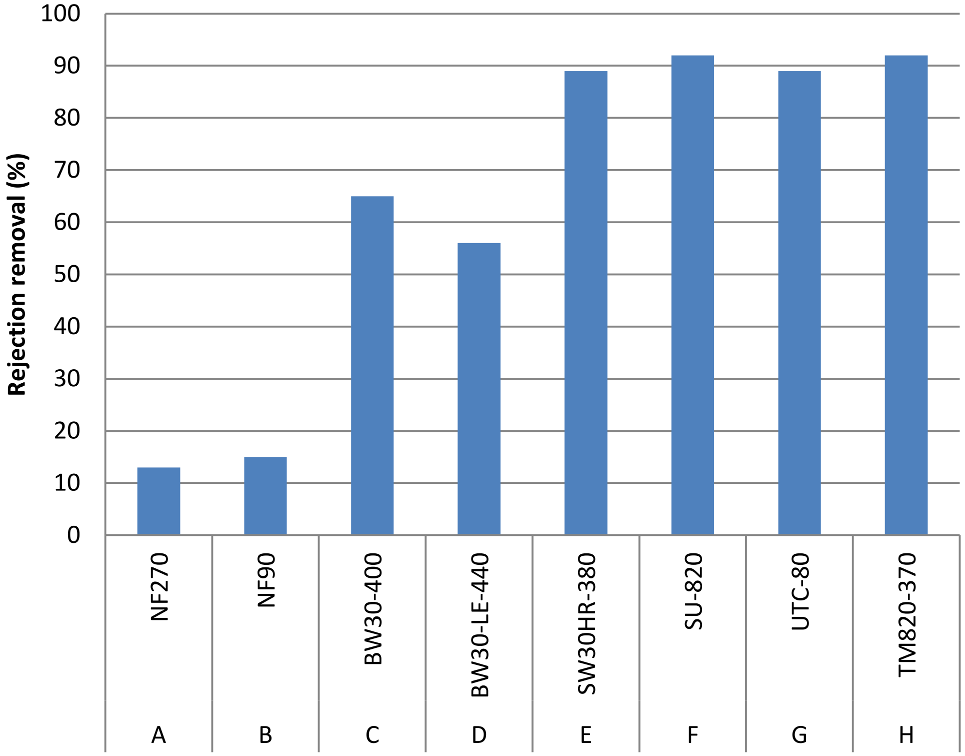


Figure 9. Boron rejection efficiencies of eight commercial membranes at standard test conditions (Adapted from Tu et al (*44*))

In another study, Cengeloglu et al, 2008 (*45*), investigated the removal of boron, using reverse osmosis technique and they compared three different membrane type: BW-30 (FILMTEC) and AG (GE Osmonics) and SWHR. They demonstrated that although, the initial concentration of boron in solution affects boron concentration in the permeate stream, it is not influential to the rejection rate. Based on their experiments, the rejection of boron mainly depends on membrane type, pressure and pH of feed water, which is in agreement with previous studies. The maximum removal was observed using an SWHR membrane at pH of 11 at 30 bar pressure(*45*) .

3.5. Constructed wetland

As mentioned earlier, boron is present in domestic greywater due to everyday usage of detergents. Therefore the problem of removing boron from greywater becomes a concern due to its toxicity on plants, and consequently it is necessary to reduce the boron concentration prior to any further application of treated greywater. The majority of removal processes, as discussed previously, were developed to remove boron from industrial wastewater or seawater at large scale, while constructed wetlands provide an opportunity for wastewater treatment for small communities. Aided by their complex biological and physical environments, constructed wetlands are able to detoxify wastewater by immobilizing and /or transforming contaminants to less toxic forms(*46*) . Based on most recent EPA design manual of constructed wetlands, they are categorized in two types: surface flow wetlands in which water flows above ground and through the leaves and stems of plants, and subsurface flow wetlands where the water level is below the ground surface and water flows through a media such as sand or gravel bed and roots of plants(*47*) . Figure 10 and 11 illustrate the schematic of each of those types.

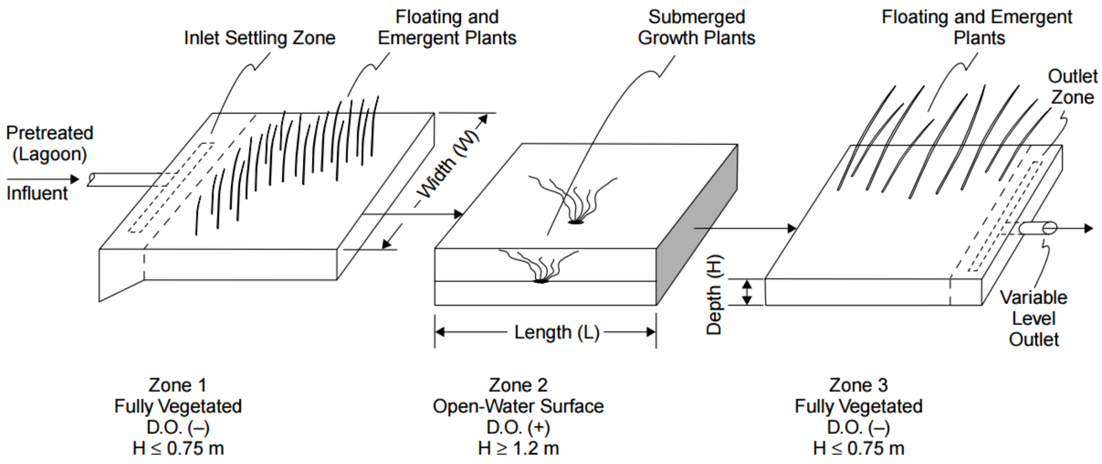


Figure 10. Elements of a free water surface (FWS) constructed wetland

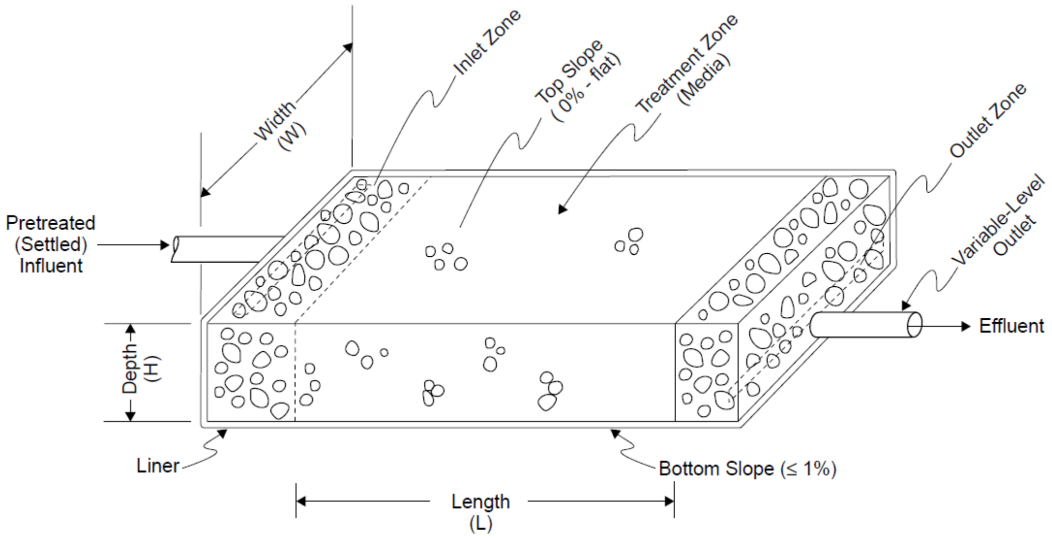


Figure 11. Elements of a vegetated submerged bed (VSB) system

Figure 12 represents the most common configuration of vertical flow constructed wetlands which are essentially vegetated filter beds. The water flows vertically down through the filter matrix to the bottom of the basin where it is collected. Examining vertical flow wetland revealed that it is capable of removing organic load up to 90% as well as removing major nutrients such as nitrogen and phosphorous if an effective pretreatment procedure be applied(*48*).

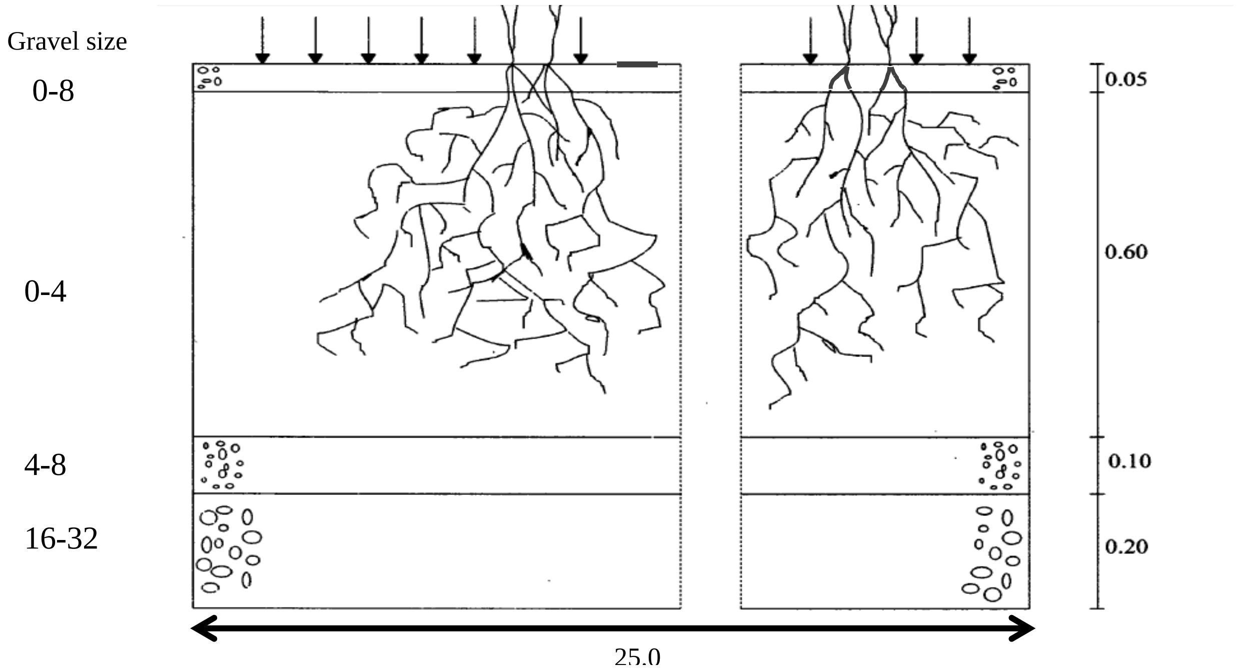


Figure 12. Cross sections of the constructed wetlands(Adapted from Luederitz et al(*48*))

In an extensive wetland microcosm study, the ability of fourteen plants common to wetland environments in the mid-western United States to accumulate selenocyanate, arsenic and boron from electric utility wastewater were tested. Microcosms were filled with coarse Colma and organic based potting medium and irrigated with nutrient solution for three months in order to promoting plant growth. It was calculated that residence time of water in each microcosm is about 12 days. Utility wastewater with boron concentration about 50 mg L-1 was introduced, after plant development. Figure 13 illustrates the concentration of boron inlet water (solid circles) and outlet water (solid triangles) of the treatment microcosms for next 42 days(*46*). The wetland microcosms reduced the concentration of boron by 31%.

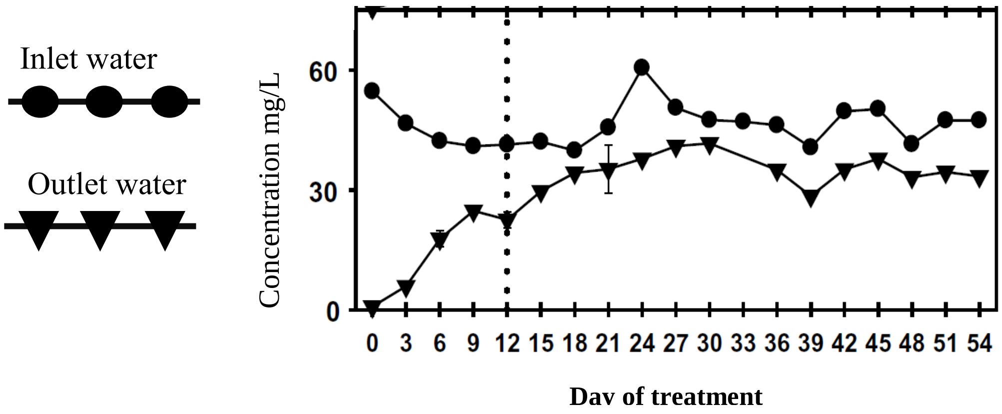


Figure 13. Concentration of boron in inlet and outlet water(Adapted from Ye et al(*46*))

It was also demonstrated that not all plants have same capability for boron accumulation which is in agreement with previous studies. Experimental results showed that seven out of fourteen species survived and could accumulate boron in their structure; however they were only responsible for 3% of boron removal. Figure 14 represents the mass balance on boron removal. Based on this figure absorption to soil layer is the significant pathway for boron removal.

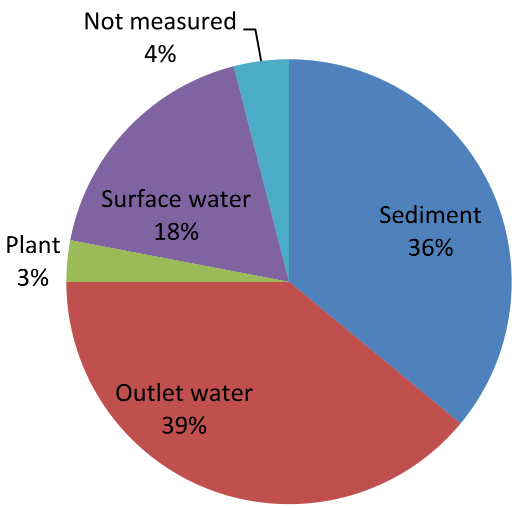


Figure 14. Mass balance of boron(Adapted from Ye et al (*46*))

Another novel configuration that utilizes both tricking filter concept and constructed wetland is introduced by Gross et al. This system combines operational principles of trickling filter and vertical flow to treat greywater(*2*). A trickling filter in general is a fixed-bed, biological reactor that operates under aerobic conditions. Continuous distribution of pre-settled wastewater over attached biofilm is a principal process considered for trickling filter. As the water migrates through the pores of the media, organics are aerobically degraded by the biofilm covering the filter material. Trickling filters can provides a simple, cost effective treatment for removing BOD in wastewater treatment(*38*).

Gross et al, 2007 (*49*), improved boron removal of a vertical flow constructed wetland by collecting effluent and recycling it by the rate of 390 L h^{-1}. The pilot system was composed of two containers. The upper container consists of three layers of media which operate as infiltration, biological active or drainage layer. The lower container is designed for collecting water from the upper one. The plants in this study were papyrus (*Cyperus haspan*) and pennyworth (*Hydrocotylr leucocephala*). About 65% of boron was removed from introduced greywater during the short term study (Figure 15), however final concentration of 0.6 mg B L^{-1} in effluent was twice the amount of boron concentration in freshwater. Lettuce irrigated with treated grey water developed brown patches indicating the concentration of total boron was excessive. It was been observed that boron mainly accumulated on soil layer rather than other layers or plants, therefore it was suggested that increasing soil volume or introducing more tolerant plants can increase boron removal from water (*49*).

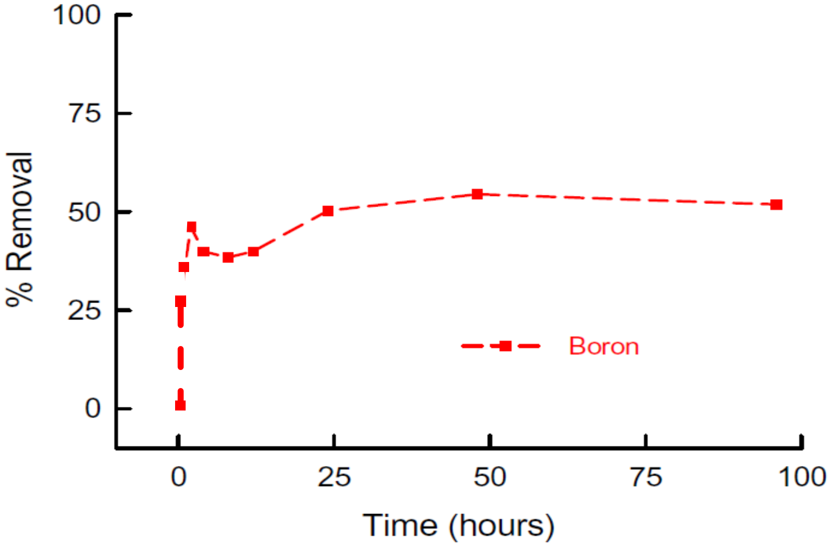


Figure 15. Percent removal of boron by a recycled vertical flow constructed wetland(Adapted from Gross et al (*49*))

4. Discussion

4.1. Summary

In order to expand greywater application it is necessary to introduce safe, well treated greywater to environment. It is especially important to protect plants and animals from the toxicity that can be caused by high concentrations of boron. The complex chemistry of boron and its dependence to pH impose challenge for developing effective boron removal techniques. However, as discussed throughout this paper, boron can be removed from water and wastewater by various technologies. A comparative study revealed that each of those techniques has their own limitation and preferences. Although some techniques have a high potential for removing boron from water or wastewater, it should be noted that feasibility and practicality of those technologies are of a great concern for on-site greywater treatment. Table 11 summarizes advantages and disadvantages of previously reviewed techniques.

Table 11. Comparison of different boron removal technologies

Method	Advantages	Disadvantages
Chemical precipitation	Simple Well tested in laboratories	High pH or high temperature Voluminous amount of sludge Low concentration of boron
Adsorption	Less waste generation Moderate cost	Regenerating
Ion exchange	Utilize natural material Cost effective Durable	Competition between ions
Reverse osmosis	Continuous stream	Single reverse osmosis procedure is not sufficient Pretreatment requirement
Constructed wetland	Affordable Simple operation Reliability	10-65% removal Time consuming process Impact of climate change affect long term sustainability of wetland media

5. Conclusions and Recommendations

Based on an extensive review on greywater applications and consequently boron removal techniques, following suggestions are proposed:

- Introducing of boron to greywater should be avoided or at least limited. This can be achieved by using more environmentally friendly detergents and soaps.
- On-site treatments that adopt constructed wetlands can select plants that are more capable of boron accumulation.
- Landscape gardening can be modified by growing plants that are more tolerant toward boron. Table 12 shows boron tolerance of some of Southern California's plants.

Table12. Boron tolerance of Southern California's plants

Plants	Boron tolerance	Reference
Oxlis	Tolerant	*34*
Cotton	Tolerant	*34*
cattail	Tolerant	*46*
Rabittfoot grass	Tolerant	*46*
Grapefruit	Sensitive	*50*
Orange	Sensitive	*50*
lemon	Very sensitive	*50*

- Natural ion exchange is a promising and affordable method that can be used in conjunction with other treatments (more experiments are needed).
- Potential of using different types of soil for boron adsorption should be investigated.

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