Soil Remediation Guidelines for Boron: Environmental and Human Health

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1. Introduction

Boron is an essential micronutrient for plants which occurs in soil and groundwater from a variety of natural or anthropogenic sources. As with most plant nutrients, insufficient amounts may result in deficiency and excess amounts may result in toxicity. The former Alberta soil guideline of 2 mg/kg hot-water soluble ("HWS") boron was not risk-based but was rather based on professional judgment and information available when the guideline was first released in the early 1990s. Various issues have recently been identified with this guideline, including:

- background HWS levels above the existing Tier 1 guideline have been measured in several parts of Alberta in both mineral and organic soils;
- anecdotal evidence from a variety of sites in Alberta and Saskatchewan show apparently healthy growth above the guideline in a variety of plant species;
- the hot-water soluble boron test method may not be most suitable for evaluating plant toxicity for a variety of soil types, and other test methods such as saturated paste boron may be more appropriate;
- some of the literature toxicity data on which the guideline is based is relatively old and has potential methodology issues;
- older toxicity data is generally based on colorimetric detection methods which may result in lower values than the newer, standard ICP detection method; and,
- HWS data is not directly useful for modeling boron transport and risk to various groundwater pathways.

This report compiles and summarizes background information from literature as well as newer toxicological studies from Alberta to derive updated, risk-based soil remediation guidelines for boron. Boron is relatively unique among the metals and metalloids in terms of being highly soluble in water and thus generally more mobile in soil and groundwater. Guideline derivation methodology thus follows the Alberta Tier 1 protocol (AESRD, 2014a), with modifications where appropriate for specific consideration of boron. One such modification is the use of alternative extraction techniques than typically used for metals as discussed in this document.

2. Background Information

Boron is a non-metallic element that occurs naturally in soil and groundwater systems. It is typically classified as a metalloid along with elements such as silicon, arsenic, and antimony, with properties between those of metals and non-metals. Boron is naturally present in the environment due to the decay of plant material and weathering of boron-containing minerals (Butterwick *et al*., 1989). Boron can also be present anthropogenically due to industrial and agricultural uses of boric acid or related salts. Potential anthropogenic sources include the application of fertilizers or herbicides containing boron, application of fly ash or biosolids as soil amendment, the use of waste water for irrigation, or land disposal of industrial wastes containing boron (Agency for Toxic Substances and Disease Registry (ATSDR), 2010). Boron-containing compounds such as borax (a sodium borate salt) are also used in a variety of industrial applications, and have been used in detergents for cleaning tanks, wellheads, or industrial equipment. Boron can also be found in saline produced water and drilling waste, and is thus a common co-contaminant when salinity is introduced from these sources.

2.1 Physical and Chemical Properties

Boron belongs in Group IIIA of the periodic table with an atomic number of 5, atomic weight of 10.81, and oxidation state of +3. Elemental boron has limited industrial uses and is typically not found in nature (US EPA, 2004b). Being a weak acid, boron exists primarily in solution as undissociated boric acid (H_3BO_3) or related salts such as borax ($Na_2B_4O_7$) which has various hydration states with the decahydrate most common.

Physical and chemical properties of boron and selected boron compounds are shown in Table 2.1. Solubility in water of boric acid and borax is relatively high, ranging from approximately 2.5% to 5% at 20^{o}C. Though boron compounds such as boron tribromide, boron trifluoride, and boron trichloride (not shown here) exhibit higher volatility, the typical forms of boron shown here are low in volatility with negligible vapor pressure.

Table 2.1. Physical and Chemical Properties of Boron and Selected Boron Compounds

	Boron	**Boric Acid**	**Borax**	**Anhydrous Borax**	**Boron Oxide**
CAS Registry Number	7440-42-8	10043-35-3	1303-96-4	1330-43-4	1303-86-2
Molecular Formula	B	H_3BO_3	$Na_2B_4O_7.10H_2O$	$Na_2B_4O_7$	B_2O_3
Molecular Weight	10.81	61.83	381.43	201.27	69.62
Boron Content (%)	100	17.48	11.34	21.49	31.06
Physical Form	black crystal or yellow-brown amorphous powder	white or colorless crystalline granules or powder	white or colorless crystalline granules or powder	white or colorless vitreous granules	white or colorless vitreous granules
Specific Gravity (@ 20°C)	2.34	1.51	1.73	2.37	2.46
Melting Point (°C) closed space	2300	171	>62	No data	No data
Melting Point (°C) anhydrous form (crystal)	2300	450	742	742	450
Water Solubility (% w/w)	insoluble	4.72 @ 20°C 27.53 @ 100°C	4.71 @ 20°C 65.63 @ 100°C	2.48 @ 20°C 34.5 @ 100°C	rapidly hydrates to boric acid
Vapor Pressure (mm Hg)	Negligible at 20°C	Negligible at 20°C	Negligible at 20°C	Negligible at 20°C	Negligible at 20°C

Source: US EPA (2004b), ATSDR (2010)

2.2 Analytical Methods

There can exist several different ‘pools’ of boron in soil due to processes such as adsorption (described in more detail in Section 3), and various soil test methods differ in the degree to which these pools are extracted and measured. The three most common extraction methods are described below ranging from most aggressive to least aggressive, and include strong acid-digest boron, HWS boron, and saturated paste boron. Other extraction methods which are less common and less widely available are also briefly discussed, as well as test methodology for vegetation boron.

2.2.1 Strong Acid-Digest Boron

Most Tier 1 soil metals guidelines in Alberta are based on a strong acid-digest procedure. Boron is an exception due to its higher water solubility, with the existing Tier 1 guideline based on the HWS method instead (described in the next section). Regardless, there are cases where it may be useful to evaluate total (acid-digest) boron since it is relevant to certain pathways such as soil ingestion.

The strong acid digest method is typically based on US EPA 3050b, and involves extracting boron from soil with a combination of acid, heat, and oxidizer. A heat source such as a hot-block is typically used with nitric acid (and potentially with hydrochloric acid) used for digestion. Hydrogen peroxide is also used to facilitate breaking up organic matter. The boron content of the resulting extract is then measured, typically with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Older detection methods were typically colorimetric, which potentially could be influenced by or interfered with by other components such as organic matter. The boron concentration is then expressed on a mg B per kg dry soil basis, and generally represents the total amount of boron in a soil sample though large portions are considered environmentally unavailable under most environmental conditions.

2.2.2 HWS Boron

Low boron soils are prevalent globally (Bell, 1997), and thus soil tests to evaluate conditions of potential deficiency are important. The hot water soluble (HWS) boron extraction method is intended to provide a result that correlates with plant deficiency symptoms. Available boron is either adsorbed on soil particles or dissolved in soil solution (USEPA, 2004b, ATSDR, 2010). The test is typically based on Method 9.2.2 (Carter and Gregorich, 2008), and involves combining 2 parts water with one part soil and boiling to extract boron. Extraction ratios may vary somewhat between laboratories (e.g., 4:1 rather than 2:1), as may heating methods, which could include hot-block, hot plate, or microwave. The concentration of boron in the extract water is then measured as described in the previous section, typically using ICP-MS or previously by older colorimetric methods. The boron concentration is then expressed on a dry weight basis, and includes dissolved boron as well as a substantial portion of boron reversibly adsorbed to soil.

2.2.3 Saturated Paste Boron

While the HWS extraction method was designed to test total plant-available boron, it was designed primarily to diagnose deficiency rather than toxicity (Goldberg *et al*, 2002) and may not be representative of ambient environmental concentrations related to plant toxicity. The saturated paste boron methodology is a less aggressive extraction technique than HWS boron, and involves lower temperatures and lower water-to-soil ratios.

The saturated paste boron extraction method takes place at ambient temperature and uses the same methodology as saturated paste extractions used for salinity. The method is described in sources such as Carter and Gregorich (2008) (for ‘Electrical Conductivity and Soluble Ions’), and involves adding incremental amounts of water to dried soil at ambient conditions until a semi-fluid saturated paste is obtained. The saturated paste is vacuum filtered, with the filtrate referred to as the saturated paste extract. The boron concentration in the extract is then measured as previously described, typically by ICP-MS or previously by older colorimetric methods. The boron concentration is originally obtained on a mg/L extract basis, and may also be expressed on a mg/kg soil basis using the saturation percentage (amount of water added to 100 g of dry soil). Since the saturation percentage has environmental relevance and is correlated with soil texture, there are some potential benefits to retaining the measurement on a mg/L basis since it is correlated with soil solution concentrations. Saturated paste boron is typically considered to represent dissolved boron with minimal adsorbed boron, and can be useful to diagnose potential toxicity conditions (Wimmer *et al.*, 2015).

2.2.4 Other Soil Test Methods

Various other soil test methods for boron have also been evaluated for their potential value in helping understand deficiency, toxicity, plant uptake, or transport behavior. These other test methods are typically less common and not readily commercially available, and often include the use of sugar alcohol extractants such as sorbitol or mannitol due to their ability to bond with boron. A variety of such tests is described in Goldberg *et al* (2002), Goldberg *et al* (2005b), Goldberg and Suarez (2014), and includes extractants such as ammonium acetate, calcium chloride-mannitol, diethylene triamine pentaacetic acid (DTPA)-sorbitol, and DTPA-ammonium bicarbonate (Gestring and Solanpour, 1987). In some cases, the sugar-alcohol extraction methods may extract more adsorbed boron from soil than the HWS method, including a method described in Goldberg and Suarez (2014) designed for measuring total sorbed boron for uses such as transport modeling or leaching calculations. In general, no clear benefits of these other tests have been demonstrated in terms of predicting toxicity to plants.

2.2.5 Vegetation Boron

Evaluating boron concentrations in vegetation may be useful for evaluating potential correlations between soil boron, vegetation boron, and deficiency or toxicity symptoms. It is also useful for assessing potential risk to receptors such as livestock or wildlife from ingesting boron which has accumulated into plants. Vegetation boron is typically evaluated using a strong acid digest procedure such as US EPA 3050b whereby vegetation matter is dried and extracted with a mixture of strong acids and oxidizers under heated conditions. Boron content is then evaluated typically by ICP-MS, and normally expressed on a dry weight basis.

2.3 Production and Uses

Boric acid and various borate salts are widely used for a variety of industrial purposes including the manufacture of glass and fiberglass insulation (*e.g.*, borosilicates), porcelain enamel, ceramic glazes, and metal alloys (US EPA, 2004b). Boron-containing compounds are also used as bleaches (*e.g.*, sodium perborates), detergents and laundry additives (*e.g.*, borax), fire retardants for cellulosic products, and wood preservatives and insecticides (Woods, 1994). It was estimated that ceramics and glass (including fiberglass) accounts for more than 50% of the US boron consumption (Woods, 1994).

Boron-containing compounds are also used as both fertilizers and herbicides, with these agricultural uses demonstrating both the nutrition and toxicity aspects of boron interactions with plants. Agricultural uses accounts for 4-6% of the total boron production in the United States, and boron fertilizers have been used for growing beets, sunflower, fruits, and alfalfa in both North America and Europe (Shorrocks, 1997). It is known that different plant species have different boron requirements and tolerances, and variations can be quite significant even between different varieties of the same species (Nable *et al.*, 1997 and Rerkasem and Jamjod, 1997). The range in boron fertilizer requirements partially illustrate this point, as different species can be classified as having “high”, “medium”, or “low” boron requirements as discussed in Gupta (2007). This provides an indicator of minimum requirements, and excessively low or high soil boron levels can lead to either deficiency or toxicity symptoms. The optimum boron range is species-specific and often quite narrow (Gupta *et al*, 1985).

2.4 Levels in the Environment

Boron is a naturally-occurring element that is widespread in nature at relatively low concentrations (Woods, 1994) and occurs naturally in over 80 minerals (CCME, 2009). Boron in the earth’s crust is estimated at an average of approximately 10 mg/kg (WHO, 1998), with rocks and soils typically less than 10 mg/kg although concentrations as high as 100 mg/kg have been reported in shales and some soils (US EPA, 2004b). Some soils in the United States have also been reported up to 300 mg/kg (Shorrocks, 1997 and ATSDR, 2010). It should be noted that these concentrations are for total boron and are not directly comparable to boron concentrations on a HWS or saturated paste basis.

Some data are also available on background boron concentrations in Canadian soils. Total boron concentrations in Alberta tills range from 13 to 70 mg/kg (median 26.5 mg/kg), with concentrations being lowest in the southeast quarter of the province and highest in the northwest. Boron concentrations in northern Alberta increase from east to west (Pawluk and Bayrock, 1969). Mean soil boron concentrations (strong acid digest in aqua regia) for various regions of British Columbia ranged from 4.2 to 30 mg/kg, with minimum and maximum concentrations of 1 and 90 mg/kg (BCMOE, 2005). Total boron concentrations measured by Raza *et al.* (2002) in Saskatchewan ranged from 79 to 138 mg/kg. HWS boron in the same samples ranged from 0.21 to 3.75 mg/kg. The highest concentration was measured in a saline soil.

On an HWS basis, Luther *et al.* (2005) reported background soil boron data from several forested sites from west, northwest, and northern Alberta. In organic soils, background HWS boron averaged 6.1 mg/kg and ranged up to 20.6 mg/kg. This is consistent with results reported in Equilibrium Environmental (2008b) where higher background HWS boron was observed in soils with elevated organic matter, including up to 5.3 mg/kg in a vegetated seasonal drainage channel, up to 9.8 mg/kg in peat soil, and up to 13.3 mg/kg in slough sediment. Mineral soil samples with less organic matter from the same sites tended to have lower background HWS concentrations, averaging 0.5 mg/kg and ranging up to 1.0 mg/kg in several forested sites in Luther *et al.* (2005).

Background HWS boron concentrations up to approximately 3-4 mg/kg HWS in fine-textured soils near Armena, Alberta (Equilibrium Environmental, 2009a).

In fresh water, background boron levels are cited to range from <0.01 to 1.5 mg/L in US EPA (2004b). Moss and Nagpal (2003) report surface waters in Europe generally have low boron concentrations, from 0.001 mg/L up to a maximum of 2.0 mg/L but typically less than 1.0 mg/L (Butterwick *et al*, 1989). Canadian freshwater concentrations are typically less than 0.1 mg/L in all provinces, though some higher ranges have been reported for parts of some provinces such as up to 0.4-0.9 mg/L for the Maritimes, up to 2.6 mg/L for Saskatchewan, up to 0.27 mg/L in Manitoba, and up to 2.3 mg/L in the Northwest Territories (CCME, 2009). Sea water is reported to range from 0.5 to 9.6 mg/L with an average of 4.6 mg/L in US EPA (2004b).

Typical boron concentrations in groundwater are a function of deposit and region, and are typically less than 0.1 mg/L with a 90th percentile of 0.4 mg/L (CCME, 2009). Boron has been observed in deeper Alberta formation waters in concentrations up to 86 mg/L from Mesozoic strata and up to 920 mg/L from Paleozoic strata (Alberta Research Council, 1977). This is consistent with elevated boron often being found along with elevated salinity in produced water.

2.5 Existing Guidelines

Boron has different effects on various types of biological life, and thus a variety of guidelines exist for different receptors. For example, elevated soil boron can negatively affect plant growth and result in the accumulation of excessive boron in plant tissue (Nable *et al.*, 1997, and Hu and Brown, 1997). The existing HWS boron guideline is primarily based on this plant direct soil contact pathway. Humans can be exposed to boron through drinking water from a domestic-use aquifer ("DUA") or direct contact with soil. Toxicological symptoms in humans can include testicular atrophy and spermatogenic arrest (USEPA, 2004a, b), and there is evidence boron is a reproductive toxin in other species as well (USEPA, 2004a,b). Livestock and wildlife can be potentially exposed to boron by ingesting plants grown in areas with elevated boron (Gillespie *et al.*, 2009; Smith and Anders, 1989), though boron is generally not considered to be among the primary trace elements posing toxic concern for livestock (Gupta and Gupta, 1998). Different species can also be exposed to boron through groundwater or surface water, including livestock, wildlife, or aquatic life. Existing Alberta and CCME soil and groundwater guidelines for these receptors are summarized below.

2.5.1 Soil Guidelines

The former Alberta Tier 1 guideline of 2 mg/kg HWS boron was the same as the CCME guideline, and was applied to all land uses and to both fine and coarse soils (Table 2.2). This soil guideline was based on the protection of plants as the most sensitive receptor to boron, which is consistent with irrigation water being among the most restrictive of the water quality guidelines. This guideline was considered an 'interim' guideline from 1991 (CCME, 1991) based on professional judgment and information available at that time.

Table 2.2. CCME and Former Soil Boron Guidelines

Land Use	Guideline (mg/kg HWS)	Soil type	Reference
Agricultural	2	Fine or coarse	AESRD (2014a), CCME (1991)*
Natural Area	2	Fine or coarse	AESRD (2014a)
Residential / Parkland	2	Fine or coarse	AESRD (2014a)
Commercial / Industrial	2	Fine or coarse	AESRD (2014a)

** Also shown in CCME, 2007a and in the CCME Canadian Environmental Quality Guidelines Summary Table as of August 2014 (http://st-ts.ccme.ca/).*

The sources and recommendations for the various 1991 CCME interim guidelines are provided in Angus Environmental (1991) in a report prepared for the CCME Subcommittee on Environmental Quality for Contaminated sites. This report includes a review of guidelines existing at that time from various jurisdictions, including primary sources of British Columbia, Alberta, Ontario, Quebec, California, New Jersey, and other countries such as the Netherlands and the United Kingdom. Most jurisdictions did not have any soil boron guideline at that time, and the adopted interim boron guideline of 2 mg/kg HWS had no documented detailed rationale and appears to have been based primarily on professional judgment from within an older draft set of Alberta Tier 1 guidelines from 1990.

2.5.2 Groundwater and Surface Water guidelines

Existing Alberta and CCME boron guidelines for groundwater and surface water are shown in Table 2.3. Human drinking water has a guideline of 5 mg/L and livestock water also has a guideline of 5 mg/L. Aquatic life can be present in surface water features such as creeks, lakes, or sloughs, with the CCME aquatic life guideline of 1.5 mg/L shown and also adopted by Alberta Environment. The most potentially constraining boron guideline in groundwater is irrigation, with sensitivity varying greatly by plant species and thus a guideline ranging from 0.5 – 6 mg/L is shown in CCME (2005) and AESRD (2014c). Note that the lowest value from this range of 0.5 mg/L is shown in AESRD 2014a. More details regarding the sensitivity of various plant species to boron in irrigation water is provided in Section 5.

Table 2.3. Existing Alberta and CCME Groundwater and Surface Water Boron Guidelines

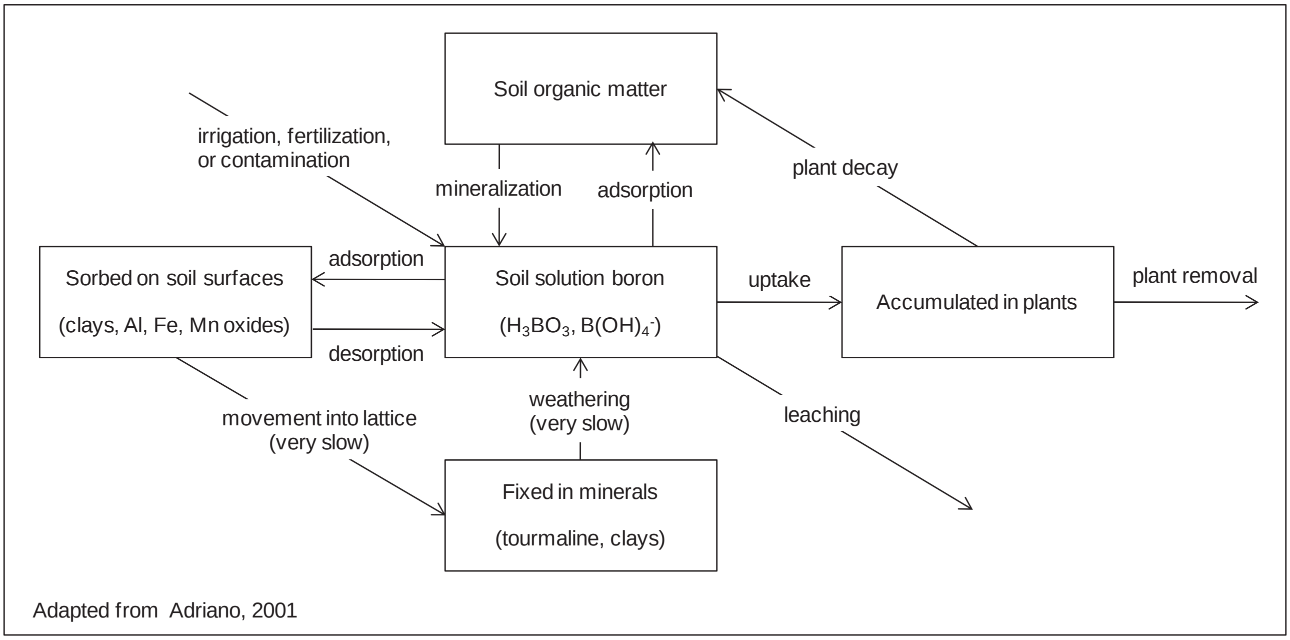
Water Usage	**Guideline (mg/L boron)**	**Reference**
Drinking water	5	AESRD (2014a), Health Canada (2014)
Livestock water	5	AESRD (2014a, 2014c), CCREM (1987), CCME (2005)
Irrigation water	0.5 – 6.0	AESRD (2014c), CCREM (1987), CCME (2005)
Aquatic life	1.5	AESRD (2014a, 2014c), CCME (2009)

3. Analytical Considerations

3.1 Boron Sorption and Soil Pools

Boron undergoes significant binding to the soil matrix, and is highly dependent on specific soil conditions such as pH, texture, clay content, and organic matter (Gupta et al, 1985; Goldberg and Glaubig, 1986; Goldberg and Forster, 1991; Goldberg, 1997). Figure 3.1 shows the main pools where boron can be stored in soil, consisting of soil solution boron, boron sorbed on soil surfaces, boron in soil organic matter, and boron fixed in minerals. Transport and transformation pathways typically relevant for boron are also shown, illustrating the potential for several of these to be occurring simultaneously. Of these pathways, adsorption and desorption onto soil surfaces, upward or downward leaching, uptake by plants, and plant decay to organic matter are likely to be most significant over short or moderate time periods. The release of boron fixed in minerals is a very slow process involving weathering, and this large but typically unavailable boron pool is not measured by standard extraction techniques other than strong acid digestion.

Figure 3.1. Boron Transport and Transformation Pathways



Adapted from Adriano, 2001

Reversible binding of boron to soil is often studied in terms of adsorption isotherms or a partitioning coefficient (Kd), whereby the mass of adsorbed boron (mg/kg) is directly related to the concentration of boron in the pore water (mg/L), also known as ‘soil solution boron’. Unless the soil is extremely coarse (high sand and low clay content), the absolute amount of boron adsorbed to the soil matrix is typically higher than the boron present in soil solution. Other factors potentially influencing boron sorption are other anions (tended to have minimal effect in Goldberg *et al.*, 1996), calcite concentration (Majidi *et al.*, 2010), cation exchange capacity, and surface area (Goldberg *et al.*, 2000). Boron sorption tends to increase with increasing clay content (Goldberg *et al.*, 2005a) and pH (Krishnasamy *et al.*, 2007), reaching a maximum at a pH of approximately 9 (Goldberg, 2004).

3.2 Hot Water Soluble Boron

The HWS method measures soil solution boron as well as sorbed boron and boron in soil organic matter (Goldberg *et al.*, 2002). Soils that have the same HWS boron concentrations can give greatly differing soil solution concentrations depending on the adsorptive capacity of the soil. Fine texture soils bind more boron than coarser soils, with their higher tendency to adsorb boron resulting in lower soil solution boron concentrations for a given soil boron concentration (Gupta *et al.*, 1985).

The HWS procedure is particularly suitable for evaluating soils which are low or marginal in boron content, though soil-solution boron may be a more reliable indicator of potential plant toxicity in soils with higher boron content (Aitken and McCallum, 1988 and Nable *et al.*, 1997). Currently the HWS procedure is routinely performed by most analytical labs in Alberta. The HWS boron procedure displays some inherent variability (particularly at higher boron levels), with variability of 20% or higher often reported by labs. This is potentially due to the high temperatures and variable amounts of time used for the hot-water extraction, and that the HWS extraction draws from more than one soil ‘pool’ of boron.

3.3 Method Sensitivity to Boron Impacts

As was introduced in previous sections, the HWS boron test may not be the best predictor of plant toxicity over a range of soil types due to variations in boron sorption. While the HWS procedure is used for boron deficiency in soil (Nable *et al.*, 1997), soil-solution boron may be a more reliable indicator of potential plant toxicity in soils with higher boron content (Aitken and McCallum, 1988). The USDA (1954) provided an early attempt at correlating plant toxicity with saturated paste soil data (more detail provided in Section 5).

Since historically more HWS boron data has been available than saturated paste boron data, it is useful to examine relationships between these two test methods and how they relate to boron sorption and soil pools as a function of texture. These comparisons between HWS and saturated paste boron have been examined in detail through the Petroleum Technology Alliance of Canada (PTAC) Boron Working Group, with typical preliminary results discussed in presentations such as Equilibrium Environmental (2008a/b, 2009a/b, and 2011).

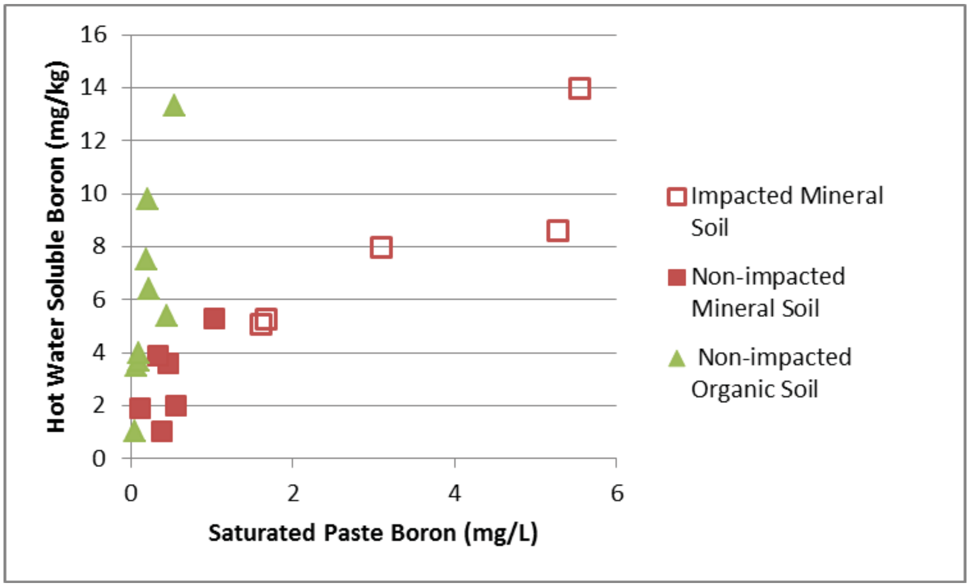
With the goal of providing some initial comparisons, preliminary locations were selected from various Alberta sites in 2007 and tested for saturated paste boron and the standard HWS boron. Saturation percentage was measured for all samples, along with organic matter and clay content for a subset of samples. The saturated paste test initially provides values in mg/L and can also be converted to mg/kg using the saturation percentage for direct comparison with HWS boron results. Acid-digest boron data was also available for four of the mineral soil samples to provide a measure of total boron in soil (relevant for risk-based calculations such as livestock ingesting soil). Table 3.1 summarizes these results, sorted from low to high according to HWS boron levels. Distribution coefficients (Kd values) are also estimated in this table using techniques described further in Section 3.4. The locations were chosen to cover a broad range of HWS boron, ranging from 1 to 14 mg/kg. These included areas low in HWS boron (such as off-site controls), moderate in HWS boron (such as a slough, vegetation scar, or moderately impacted on-site areas), or high in HWS boron (highly impacted on-site locations or the center of a slough). Several peaty soils were also tested for boron (organic matter data not available but likely high), and had HWS boron levels spanning the entire range.

Table 3.1. Preliminary HWS vs Saturated Paste Boron for Various Alberta Sites

Location	HWS Boron (mg/kg)	Acid Digest Boron (mg/kg)	Organic Matter %	Clay %	Saturated Paste Boron			K_d (L/kg)
					Saturation %	Boron (mg/kg)	Boron (mg/L)	
Control A	1.0	54.7			52	0.2	0.38	2.1
Peat A	1.0				196	0.1	0.05	17.6
Veg scar A	1.9		9.7	11.6	77	0.1	0.11	16.2
On-site A	2.0	52.4			72	0.4	0.56	2.9
Peat B	3.5				682	0.5	0.07	40.9
Veg scar B	3.6		5.7	25.2	75	0.3	0.46	7.2
Peat C	3.7				659	0.7	0.10	29.8
Slough edge	3.9		11.8	24.6	86	0.3	0.33	11.1
Peat D	4.0				418	0.4	0.10	37.6
Site impact B	5.1	85.8			75	1.2	1.60	2.4
Site impact C	5.3		4.5	25.6	57	0.9	1.67	2.6
Veg scar C	5.3		7.0	19.2	72	0.7	1.04	4.3
Slough	5.4		23.0	10.6	130	0.6	0.45	10.6
Peat control A	6.4				316	0.7	0.23	24.5
Peat E	7.5				700	1.4	0.20	30.5
Site impact D	8.0		3.9	19.6	55	1.7	3.08	2.1
Site impact E	8.6	91.0			76	4.0	5.26	0.9
Peat control B	9.8				486	1.0	0.21	42.8
Slough center	13.3		29.3	9.2	194	1.1	0.55	22.2
Site impact F	14.0		3.6	33.6	71	3.9	5.54	1.8

Acid-digest levels ranged up to 91 mg/kg, substantially higher than HWS levels as expected. Saturated paste boron (in mg/kg) was lower than HWS boron in all cases, ranging from 0.1 to 4.0 mg/kg. When the saturated paste results are expressed in mg/L, results ranged from 0.05 mg/L in a peat sample to 5.54 mg/L in an impacted mineral soil sample. Based on other site data and proximity to sources of contamination, the vegetation scar locations, the slough locations, On-site A, Control A, and peat controls are all unlikely to be impacted by anthropogenic boron sources and are considered reasonably representative of background conditions. These locations have relatively low saturated paste boron concentrations (ranging from 0.40 mg/L to 1.04 mg/L) despite having HWS boron ranging as high as 13.3 mg/kg for the slough locations, 9.8 mg/kg for the peat controls, and 5.3 mg/kg for the vegetation scar locations. Conversely, the other on-site locations (Site impacts B-F) are likely to be anthropogenically impacted and display saturated paste concentrations ranging from 1.6 mg/L to 5.54 mg/L. Thus, for this dataset, the saturated paste results in mg/L provide a way to distinguish between impacted and unimpacted areas, whereas the HWS results erroneously indicate impacts in the slough, vegetation scar, and some peat soils. This use of saturated paste boron to identify likely site impacts is also shown graphically in Figure 3.2, where organic soils (corresponding to organic matter contents above approximately 20% or saturation percentages above 100%) can be clearly distinguished from the impacted mineral soils despite the elevated HWS boron in each case.

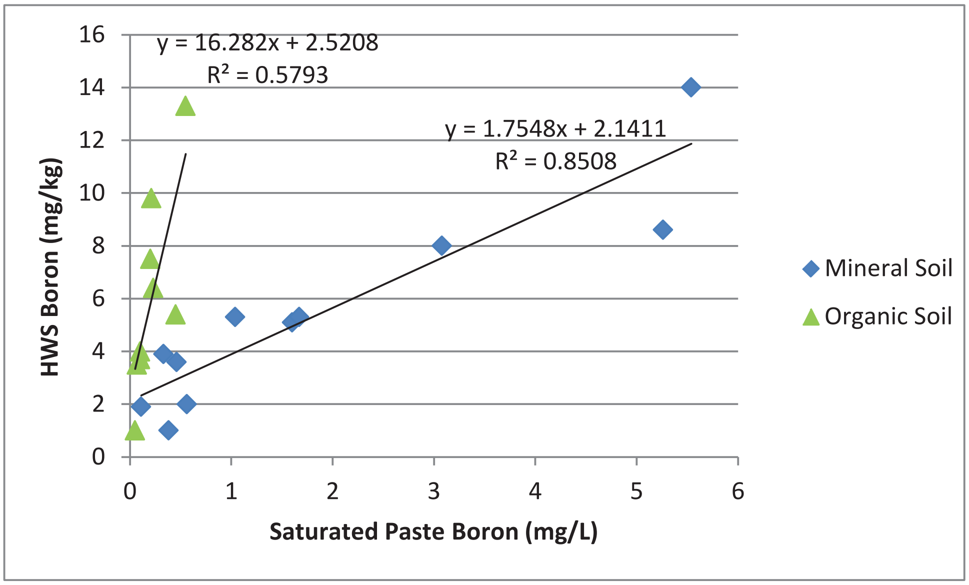
Figure 3.2. Identifying Site Impacts with Saturated Paste Boron



Another use for the above data is to develop correlations to allow an estimation of saturated paste boron (mg/L) from pre-existing HWS boron (mg/kg) data. Figure 3.3 shows the relationship between HWS boron (mg/kg) and saturated paste boron (mg/L) for the above data, separated into organic and mineral soils. Statistically significant ($P<0.01$) positive correlations are apparent, with R^2 values of 0.58 and 0.85 for the organic and mineral soils, respectively. Substantially different slopes are also observed, with a slope of approximately 16 for the organic soils compared to approximately 1.8 for the mineral soils in this dataset.

The difference in slopes is likely due to differences in the boron sorption properties of the organic versus mineral soils. As previously discussed, soils with high clay or organic matter content adsorb boron more strongly, resulting in a lower amount of dissolved boron (from saturated paste boron) relative to the adsorbed boron (from HWS boron). Both clay and organic matter have a high surface area per unit mass, and thus typically increase the saturation percentage of soil containing high amounts of either. This is particularly evident for two of the three slough samples, which have elevated saturation percentages (130%-194%) likely due to the high organic matter content (23.0%-29.3%) relative to other mineral soils. Highly organic peat soils also typically have high saturation percentages, ranging here from 196% up to 700%. In addition, differences in saturation percentage reflect differences in soil porosity. This also adds to the variability when comparing saturated paste extract concentrations with hot water soluble concentrations derived from a uniform soil:water extraction ratio.

Figure 3.3. HWS vs Saturated Paste Boron from Preliminary (2007) Alberta Data



3.4 Estimating K_d Values for Boron

Solid-liquid partition coefficients, or distribution coefficients (K_d) can be used to describe the partitioning of soil boron between solid (adsorbed to soil surface) and liquid (dissolved in soil solution) phases. K_d is expressed as a ratio of the concentration of a compound in surface-bound solid phase to the concentration dissolved in soil solution (USEPA, 1999). This relationship is relevant to guideline derivation since it influences aspects such as mobility and availability. Soil properties which have been shown to influence the boron K_d values include cation exchange capacity, clay and organic matter content, aluminum and iron oxides, and pH (Goldberg, 1997; Janik *et al*. 2015). The following subsections provide an overview of boron adsorption properties and K_d values found in the literature (3.4.1), present the results of a quantitative determination of boron K_d values for two Alberta reference soils (3.4.2), and introduce the concept of estimating boron K_d values from saturated paste and HWS laboratory methods (3.4.3).

3.4.1 Boron Adsorption Isotherms and K_d Parameter

A common way to examine the sorption behavior of chemicals which adsorb to soil is through the use of a distribution coefficient (K_d) which represents the ratio of sorbed boron (C_s, in mg/kg) to dissolved boron (C_w, in mg/L):

$$C_s = K_d * C_w \qquad \textit{Linear}$$

The use of K_d implies a linear adsorption isotherm, which is a special case of the Freundlich isotherm below (Deverel and Fujiji, 1990) where the exponent ‘n’ equals one. The use of Freundlich isotherms is described in Nicholaichuk *et al.*, (1988) for various Saskatchewan soils.

$$C_s = K * {C_w}^{1/n} \qquad \textit{Freundlich}$$

The two-parameter (K and Q) Langmuir isotherm shown below (also used in Shani *et al.*, 1992 for boron transport) is also commonly utilized for partitioning calculations. This isotherm is similar to the linear isotherm with K_d but predicts some reduction in sorption ability at higher concentrations as sorption sites become saturated. Note that the parameter K used in the Langmuir isotherm is not comparable to $K_{d.}$

$$C_s = \frac{K * Q * C_w}{1 + K * C_w} \qquad\qquad Langmuir$$

Where:

C_s = adsorbed boron (mg/kg);
C_w = dissolved boron (mg/L);
Q = Maximum adsorption capacity (mg/kg);
K = Langmuir adsorption equilibrium constant (L/mg)

The linear K_d isotherm is used in Alberta Tier 1 (AESRD, 2014a) for partitioning calculations, though there it is further expressed in terms of organic carbon fraction (f_{oc}) which is more relevant for organic substances than for boron. The partitioning equation is shown below, expressed as a dilution factor ("DF1") which represents the ratio of the concentration of the contaminant (in this case, boron) in soil to the concentration in solution.

$$DF1 = K_d + \frac{\theta_w + (H' * \theta_a)}{\rho_b}$$

Where:

$DF1$ = dilution factor 1 (L/kg);
K_d = distribution coefficient (L/kg);
θ_w = water-filled porosity (dimensionless);
H' = Henry's Law constant (dimensionless);
θ_a = air-filled porosity (dimensionless);
ρ_b = dry soil bulk density (kg/L)

3.4.2 Batch Boron Adsorption Tests for Alberta Reference Soils

Boron adsorption was tested for two Alberta reference soils using batch experiments to generate adsorption isotherms and derive K_d values representative of typical coarse and fine textured soils. Section 5.2 summarizes the characteristics of these reference soils. In brief, coarse (sandy loam) and fine (clay loam) textured reference soils were collected from the A horizon (10 to 20 cm depth) at two locations within Alberta. Table 5.6 summarizes the physical and chemical properties of reference soils including salinity, boron and nutrient levels. Coarse and fine reference soils contained 18% and 32% clay respectively with organic matter ranging from 3% to 4%. Initial HWS boron concentrations were 0.7 mg/kg for the coarse soil and 0.5 mg/kg for the fine soil.

The reference soils were air dried at room temperature and sieved through 2 mm mesh. Residual moisture content was estimated to be approximately 5% by mass. Adsorption properties were tested by a batch procedure (OECD, 2000) typically used to measure adsorption isotherms. The batch procedure involves creating an initial boron solution of known concentration, adding the test soil to the boron solution at a fixed (2:1) water-to-soil ratio, agitating vigorously, and measuring the final dissolved boron concentration after filtering. The difference between the initial and final boron concentrations in solution can be used to calculate the mass of boron which has been sorbed to soil particles by using the water-to-soil ratio. Four concentrations of boron solutions were utilized with nominal concentrations of 1, 2.5, 5, and 10 mg/L boron (sourced from boric acid). Boron concentrations in the initial and final solutions were measured at a commercial laboratory with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

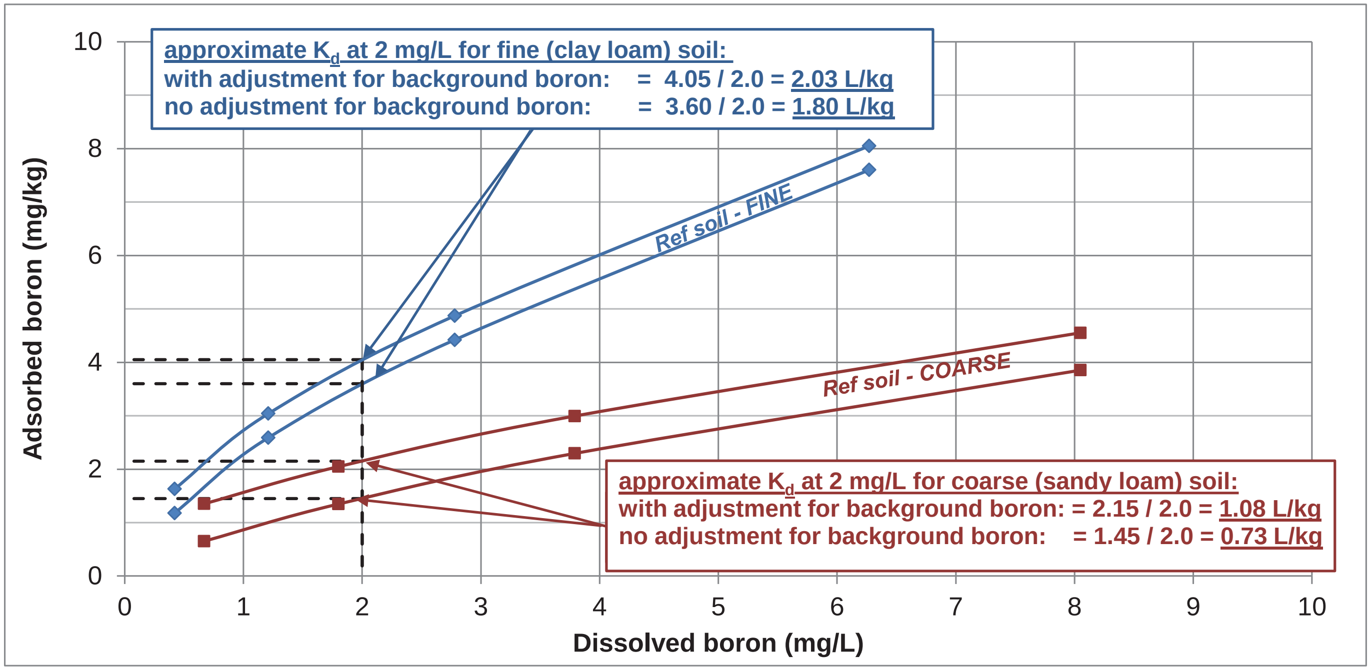
Table 3.2 summarizes the results from these batch experiments, including the initial and final boron concentrations in solution as well as the calculated adsorbed boron which had been adsorbed onto the soil surface from solution. These values of adsorbed boron are initially calculated without any potential adjustments for the initial background boron concentrations in soil, and are denoted as ‘not adjusted’ in Table 3.2 (potential adjustments for background boron are discussed further below). Figure 3.4 shows the resulting adsorption isotherms derived for both the coarse and fine reference soils, with steeper slopes for the fine soil indicating greater adsorption properties and higher K_d values (likely due to the higher clay content). Estimated K_d values are also shown in Table 3.2 using the calculation described below.

Table 3.2. Results for Experimentally Determined K_d for Two Alberta Reference Soils

Initial B concentration		Coarse (sandy loam)					Fine (clay loam)				
Initial nominal solution B	Initial measured solution B (B_i)	Final measured solution B (B_f)	Not adjusted		Adjusted*		Final measured solution B (B_f)	Not adjusted		Adjusted*	
			Adsorbed B	K_d	Adsorbed* B	K_d*		Adsorbed B	K_d	Adsorbed* B	K_d*
mg/L	mg/L	mg/L	mg/kg	L/kg	L/kg	L/kg	mg/L	mg/kg	L/kg	L/kg	L/kg
1	0.98	0.67	0.65	0.97	1.35	2.02	0.42	1.18	2.81	1.63	3.88
2.5	2.44	1.80	1.35	0.75	2.05	1.14	1.21	2.59	2.14	3.04	2.51
5	4.88	3.79	2.30	0.61	3.00	0.79	2.78	4.42	1.59	4.87	1.75
10	9.88	8.05	3.85	0.48	4.55	0.57	6.27	7.60	1.21	8.05	1.28
		Average K_d:		0.70		1.13	Average K_d:		1.94		2.36
		K_d at 2 mg/L:		**0.73**		**1.08**	**K_d at 2 mg/L:**		**1.80**		**2.03**

** Estimate of adsorbed B adjusted upward by initial background boron concentrations in coarse and fine reference soils (0.7 and 0.45 mg/kg HWS B respectively);*

Figure 3.4. Adsorption Isotherms for Boron using Two Alberta Reference Soils



approximate K_d at 2 mg/L for fine (clay loam) soil:
with adjustment for background boron: = 4.05 / 2.0 = 2.03 L/kg
no adjustment for background boron: = 3.60 / 2.0 = 1.80 L/kg

approximate K_d at 2 mg/L for coarse (sandy loam) soil:
with adjustment for background boron: = 2.15 / 2.0 = 1.08 L/kg
no adjustment for background boron: = 1.45 / 2.0 = 0.73 L/kg

Unadjusted K_d values were calculated from the above data based on the ratio of adsorbed to dissolved boron at any particular value of dissolved boron. For instance, at a dissolved boron concentration of 2 mg/L (an arbitrary mid-range concentration), the unadjusted K_d was calculated to be 0.73 and 1.80 L/kg for the coarse and fine reference soils respectively as shown graphically on Figure 3.4.

$$K_d = \frac{adsorbed\ B}{dissolved\ B} = \frac{\left((B_i - B_f) * (w/s)\right)}{B_f}$$

Where:

K_d = distribution coefficient (L/kg);
B_i = initial boron concentration in solution (mg/L);
B_f = final boron concentration in solution (mg/L);
w/s = water to soil ratio (2/0.95, assuming 5% residual soil moisture (L/kg));

Over the concentration range tested, unadjusted K_d values range from 0.48 to 0.97 L/kg for the coarse soil, and from 1.21 to 2.81 L/kg for the fine soil. This results in unadjusted coarse and fine averages of 0.70 and 1.94 L/kg respectively for the concentration range tested, thus similar to the apparent K_d values observed at 2 mg/L. These results show that boron K_d values become lower at higher boron concentrations, thus indicating a non-linear isotherm such as represented by Freundlich or Langmuir isotherms.

Since sorption experiments can be influenced by the initial boron concentrations in soil, some experiments (such as Ryan *et al.*, 1977) pre-rinse soils prior to performing batch adsorption experiments to remove these background effects. To evaluate the potential influence of the measured background boron concentrations of the Alberta reference soils (0.70 and 0.45 mg/kg HWS boron in the coarse and fine soil respectively), an additional experiment was performed whereby the majority of the background boron in the coarse soil was removed by pre-rinsing six times with hot distilled water. The initial background HWS boron concentration in the coarse soil was reduced by approximately 80% with this procedure, at which point the soil was air dried again prior to use in a follow-up sorption experiment at 2.5 mg/L. It was found that the apparent boron sorption of the coarse soil increased due to this pre-rinsing, with the amount sorbed from solution estimated as 1.87 mg/kg based on initial and final boron solution concentrations of 2.54 mg/L and 1.65 mg/L, respectively. This corresponds to an estimated K_d of approximately 1.14 L/kg, higher than the corresponding K_d of 0.75 L/kg estimated without the pre-rinsing step.

This K_d value of 1.14 L/kg from the pre-rinsed coarse experiment matches what is calculated if the amount of adsorbed boron from the non-rinsed coarse experiment was increased by the background HWS boron concentration of 0.7 mg/kg prior to calculating a K_d value (also results in 1.14 L/kg). This ‘adjusted’ K_d value of 1.14 L/kg is also shown in Table 3.2, and suggests that this method may potentially be useful for adjusting for the presence of background boron which is already sorbed to the soil surface. This method essentially assumes that the background HWS concentration in the soil represents sorbed plus dissolved boron, and is available to participate in sorption/desorption processes. By boron mass balance, the total ‘adjusted’ amount of sorbed boron would be the amount sorbed from solution (based on measured initial and final solution concentrations), plus the background boron originally present in the soil.

Results from this potential adjustment technique are also shown in Table 3.2 in the ‘adjusted’ column for adsorbed boron and K_d values for both coarse and fine soil. At a concentration of 2 mg/L, adjusted K_d values of 1.08 L/kg and 2.03 L/kg are obtained for the coarse and fine soils, similar to but somewhat higher than the unadjusted values of 0.73 L/kg and 1.80 L/kg. These adjusted values are also shown on Figure 3.4 for additional context, with the difference between unadjusted and adjusted values providing a potential range for K_d measurements in these reference soils with differing measurement and calculation techniques.

These results from adsorption experiments on the Alberta reference soils were then compared to literature-derived values for context. Gupta *et al.* (1985) provides a summary of several boron adsorption experiments from different researchers performed on a variety of soil types between 1960 and 1982. These experiments provided sorption data according to the two-parameter (K and Q) Langmuir isotherm introduced above (Section 3.4.1). Table 3.3 shows the sorption data including soil texture, soil source, pH, and Langmuir coefficients. The data has been separated into fine and coarse textured soils. Note that this data is taken from several different studies, and thus experimental techniques varied somewhat. For example, the four Arizona soils have the original experiments described in Ryan *et al.* (1977), and involved pre-rinsing the soils to remove background boron prior to performing the batch adsorption experiments.

K_d values were calculated in the same manner (at 2 mg/L dissolved boron) for the various soil types in Table 3.2. For coarser soils, K_d ranged from 0.39 to 2.47 L/kg, with an average of 1.28 L/kg. As expected, values for the clay soils were higher, with K_d ranging from 0.96 to 5.23 L/kg and averaging 2.16 L/kg. Note that these literature averages are similar to the K_d values calculated for the coarse and fine Alberta reference soils at 2 mg/L.

Example data from the coarse ‘Sonoita’ soil and the fine ‘Reagan’ soil are shown in Figure 3.5. K_d values at 2 mg/L are also shown graphically on the figure, and data from the Alberta reference soils (both with and without adjustments for background boron) are also included in Figure 3.5 as dashed lines for comparison purposes. Calculated K_d values at 2 mg/L for the coarse Sonoita and fine Reagan soils were 0.98 and 2.70 L/kg respectively, relatively similar to those observed for the Alberta soils.

The Alberta K_d values for coarse and fine soils also lie within the general broad range found by Janik *et al*. (2015), who found values ranging from 0.36 to 52 L/kg over a wide range of soil types with a median value of 2.15 L/kg. Overall, these literature results from Gupta *et al.* (1985) and Janik *et al.* (2015) thus indicate that the boron sorption properties of these Alberta reference soils are fairly typical of soils found in other regions.

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Table 3.3. Boron Adsorption Data from Literature

Coarse soils

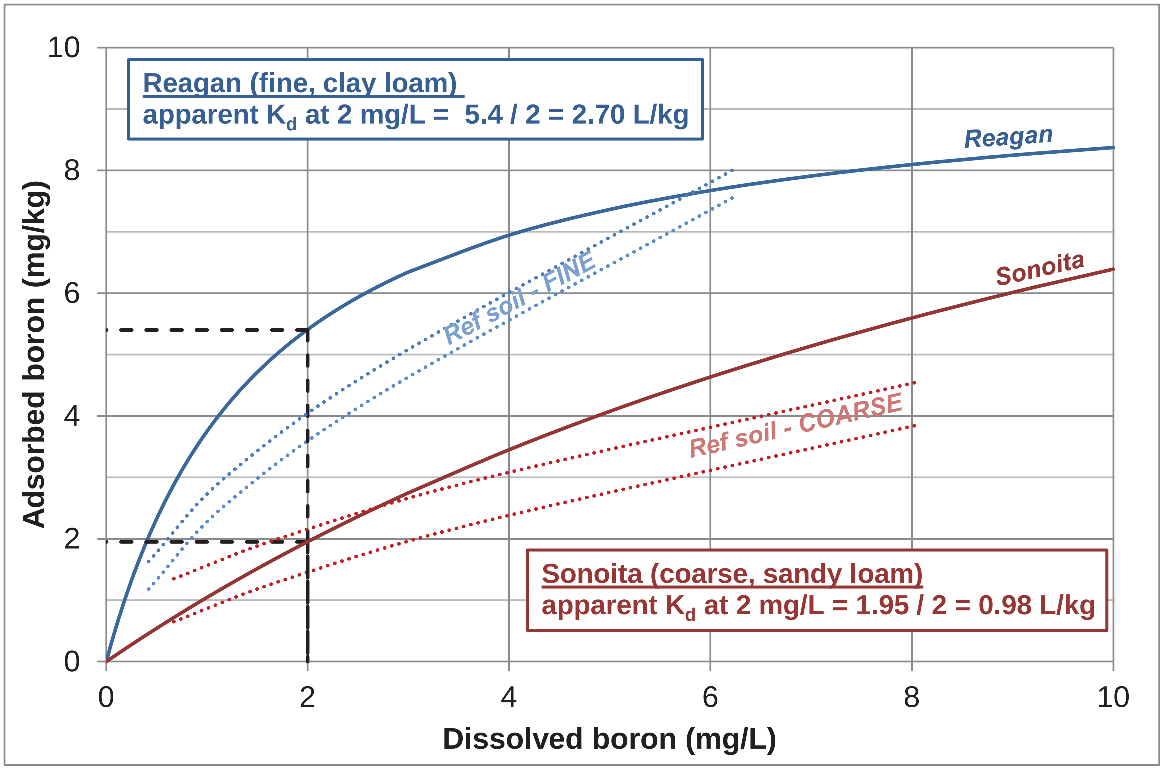
Soil texture	Soil name	Soil source	pH	Langmuir Coefficients Q (mg/kg)	Langmuir Coefficients K (L/mg)	Apparent K_d at 2 mg/L (L/kg)
Sandy loam	Puye	New Mexico	6	2.3	0.26	0.39
Sandy loam	Heperia		7.6	7.3	0.093	0.57
Sandy loam		Punjab	8.2	10	0.071	0.61
Silt loam	Chilcott	California	6.6	12.9	0.064	0.73
Sandy loam	Sonoita	Arizona		14.8	0.076	0.98
Loam	Rincon		7.5	21.3	0.056	1.07
Sandy loam	Anthony	Arizona		20.6	0.086	1.51
Silt loam	Carjo	Arizona	6	7.9	0.37	1.68
Sandy loam	Harvey	New Mexico	7.4	11.7	0.26	2.00
Sandy loam	Lea	New Mexico	7.6	16.3	0.17	2.07
Loam	Laveen	Arizona		22.2	14.3	2.47
				Coarse soils average K_d:		**1.28**

Clay soils

Soil texture	Soil name	Soil source	pH	Langmuir Coefficients Q (mg/kg)	Langmuir Coefficients K (L/mg)	Apparent K_d at 2 mg/L (L/kg)
Clay	Glendale	New Mexico	7.6	33.9	0.03	0.96
Clay loam	Yelo	California	7.7	25	0.059	1.32
Clay	Chino	California	7.6	31.9	0.054	1.55
Clay loam		Punjab	7.8	13.2	31.6	1.57
Clay loam	Gila	Arizona		35.2	0.056	1.77
Clay loam	Reagan	New Mexico	7.5	9.7	0.63	2.70
Clay loam	Aiken		6.7	47.6	0.141	5.23
				Clay soils average K_d:		**2.16**

Data from several studies, summarized in Gupta et al. 1985

Figure 3.5. Typical Literature Isotherms Compared to Alberta Reference Soils



Note: Literature data from Gupta et al, 1985. Soil isotherms established for fine (blue hashed lines) and coarse (red hashed lines) Alberta reference soils (Figure 3.4) are included for comparative purposes. Upper hashed lines use an adjustment for background boron, lower hashed lines are not adjusted.

3.4.3 Boron K_d Values from HWS and Saturated Paste Extraction Methods

For the purposes of these guidelines, K_d has been approximated using boron concentrations measured by hot water soluble and saturated paste methodologies. The concentration of boron in soil is taken to be the total of sorbed plus dissolved boron, and this concentration is assumed to be reasonably represented by HWS boron. Although hot water soluble extraction likely does not capture all sorbed boron, K_d values calculated in this manner are similar to values calculated by standard methods, as shown in the following discussion. Dissolved boron is measured at soil saturation, using the saturated paste extract method, and can be expressed in either mg/L or mg/kg by using saturation percentage as a conversion factor. Acid-digest boron is assumed inaccessible or fixed for these calculations, and is not used. Boron is assumed essentially non-volatile for modeling purposes, and hence H'=0.

Following these assumptions, K_d values can be obtained by subtracting saturated paste soil boron (mg/kg) from the HWS boron (mg/kg) to obtain an estimate of sorbed boron (mg/kg), and dividing the result by saturated paste solution boron (mg/L). These calculations assume that HWS boron represents both adsorbed and dissolved boron, whereas saturated paste boron represents only dissolved boron.

$$K_d = \frac{adsorbed\ B}{dissolved\ B} = \frac{HWS\ B\ \left(\frac{mg}{kg}\right) - Sat\ paste\ B\ \left(\frac{mg}{kg}\right)}{Sat\ paste\ B\ \left(\frac{mg}{L}\right)}$$

$$= \frac{HWS\ B\ (mg/kg)}{Sat\ paste\ B\ (mg/L)} - \frac{Sat\ \%}{100}$$

The final expression utilizing saturation percentage, HWS boron, and saturated paste boron can be rearranged as shown below and was used to generate the estimated K_d values in Table 3.1.

$$\frac{HWS\ boron\ (mg/kg)}{Saturated\ paste\ boron\ (mg/L)} = K_d + \frac{saturation\ \%}{100}$$

The equations above may also be expressed at different moisture contents, such as soil solution concentrations. The form of the equation below is particularly useful for calculating solution boron levels at different field moisture conditions by varying θ_w for a given HWS boron. θ_w/ρ_b is essentially the water content expressed on a L/kg basis, and at the conditions of the saturated paste extraction is equivalent to the saturation percentage divided by 100. Note that this method of using of K_d's for describing the sorption behavior of metals and estimating their partitioning and leaching behavior in soil and groundwater is also consistent with methods described in New Jersey Department of Environmental Protection (2013).

$$\frac{HWS}{C_w} = K_d + \frac{\theta_w}{\rho_b}$$

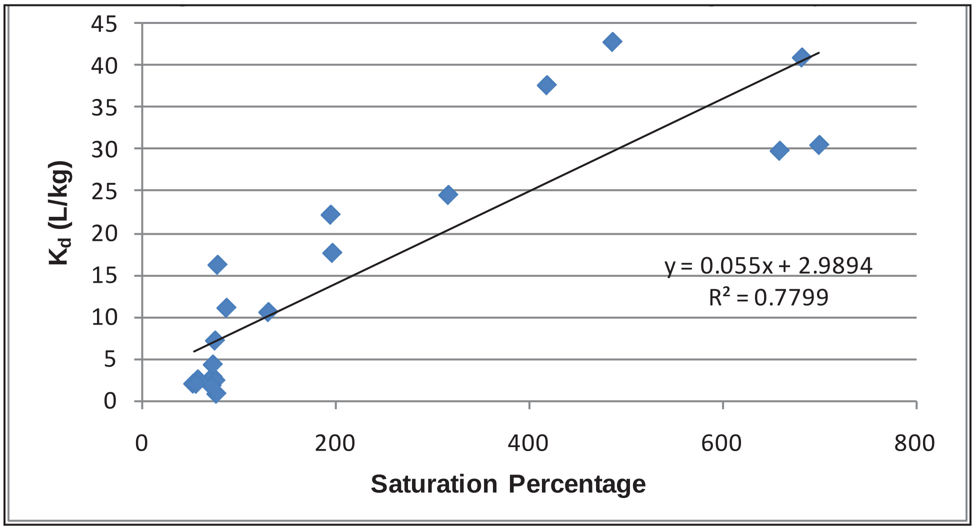
Where:

HWS = hot-water soluble boron (mg/kg);
C_w = dissolved boron (mg/L);
K_d = distribution coefficient (L/kg);
θ_w = water filled porosity (dimensionless)
ρ_b = dry soil bulk density (kg/L)

K_d values in Table 3.1 calculated in this manner range from 0.9 to 42.8 L/kg, with an average of 15.5 L/kg. It should be noted that estimates of K_d have a higher degree of uncertainty for low values of saturated paste boron (in mg/L) due to detection limit issues and high relative errors when dividing by small numbers. K_d is a function of factors such as soil texture and organic matter, with K_d tending to increase with clay content and organic matter content due to the increased surface area for adsorption (Gupta *et al*, 1985).

One way to characterize these soil texture effects in the absence of texture data is to consider saturation percentage instead. Figure 3.6 shows K_d plotted against saturation percentage, which can potentially serve as a proxy for soil surface area and hence clay content and organic matter. A statistically significant ($P<0.001$) positive correlation can be seen between K_d and saturation percentage, with an R^2 value of 0.78 and reduced scatter. This correlation demonstrates the increase in sorbed boron with soil surface area, and can be used in the absence of texture or organic matter data.

Figure 3.6. Effect of Saturation Percentage on K_d from Preliminary Alberta Data

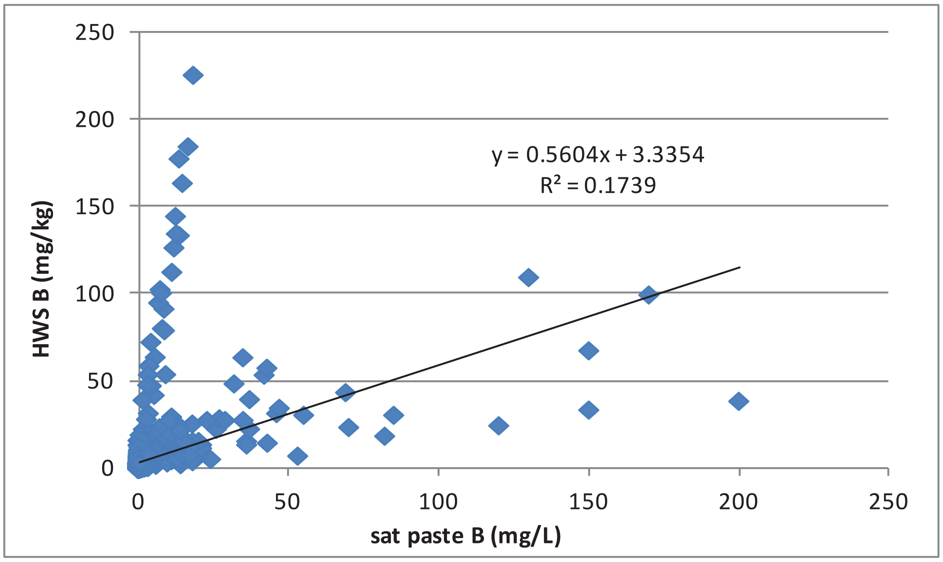


The majority of the K_d values in this dataset are above 2, with most soils either with clay content above 20% or organic matter above 5%. Thus, a preliminary K_d estimate of 2 L/kg for clayey Alberta soils appears reasonable. Lower K_d's of 0.9 and 1.8 were seen at high HWS boron levels (>8 mg/kg), at which point boron binding sites may start to saturate and the use of a linear isotherm involving K_d may be less appropriate. For comparison purposes, substances which do not bind significantly to soil (such as chloride) have a K_d of approximately zero and tend to result in much higher soil solution concentrations and relatively rapid transport.

3.5 Influence of Soil Properties on Analytical Method

As a follow-up to the preliminary 2007 Alberta data discussed above, additional HWS and saturated paste boron data was collected from 2008 through 2014 from a wide range of Alberta sites spanning various soil types and geographical regions. Soils ranged from coarse sandy soils to fine clayey soils and also included highly organic peat soils. Additional HWS and saturated paste data from unspecified locations was also provided in 2008 by various analytical laboratories through the PTAC Boron Working Group including Exova, Maxxam Analytics, AGAT Laboratories, and Access Analytical Laboratories. Figure 3.7 shows the entire dataset plotted as HWS (mg/kg) vs saturated paste boron (mg/L), consisting of approximately 2,300 datapoints from more than 40 sites. A linear regression shows substantial scatter (R^2 of 0.17) and clearly does not describe all data well.

Figure 3.7. Newer Alberta HWS vs Saturated Paste Boron Relationships for All Textures



Assuming these soil relationships are influenced by sorption effects and hence soil texture and organic matter, the same data was grouped according to saturation percentage since it can be used as a good proxy for soil texture and organic matter content. Saturation percentage categories described in Equilibrium Environmental (2014b) were used consisting of >100% (typically heavy clay or organic soils), 43-100% (likely finer clayey soils), and <43% (potentially coarse or silty soils). Results are shown in Figure 3.8, showing distinct relationships for the three soil types with R^2 values ranging from 0.78-0.96 for linear regressions on the left-hand figure. Higher saturation percentages generally correspond with higher slopes and thus higher sorption. The right-hand portion of Figure 3.8 shows the same data but with power-function regressions for two of the series. Power functions are analogous to a Freundlich isotherm, and in some cases improve the overall R^2 value for those saturation percentage classes over particular boron ranges.

These lower boron concentration ranges are shown in Figure 3.9, showing the same data and regressions for HWS boron levels less than 50 mg/kg (left side) and 10 mg/kg (right side). Good fits are apparent, with the power functions showing exponents of less than 1 likely indicating that additional boron sorption is reduced at higher concentrations as sorption sites become saturated. The linear fit with the high saturation percentage (>100%) soils suggests they are not yet approaching maximum sorption capacity of the highly sorptive peat soils.

Figure 3.8. Alberta HWS vs Saturated Paste Boron for Various Saturation Percentage Ranges

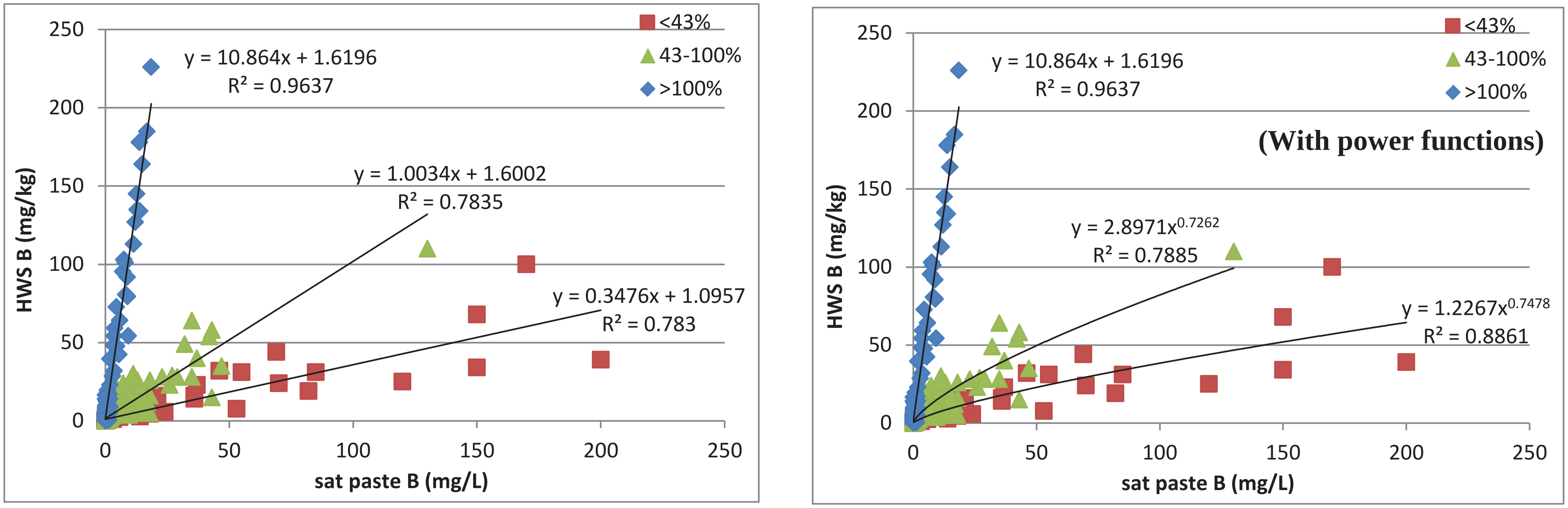
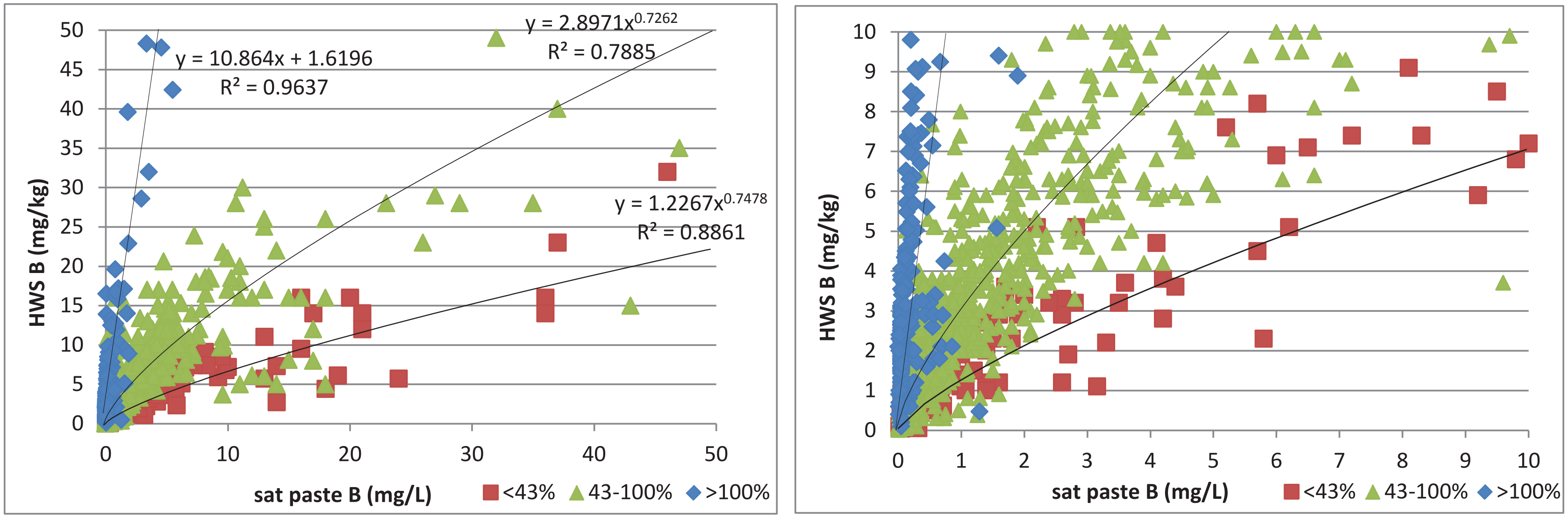


Figure 3.9. Alberta HWS vs Saturated Paste Boron for Various Saturation Percentage Ranges (lower boron concentrations)



For context, this data shows that at a level of 2 mg/kg HWS boron (the existing guideline), saturated paste boron is typically less than 0.5 mg/L for the organic soils, typically less than 1 mg/L for fine soils, and typically less than 2-3 mg/L for coarser soils. As will be discussed later, any potential toxicity at 2 mg/kg HWS could thus vary substantially based on soil type if correlated more strongly with saturated paste boron.

K_d values can then be estimated for these Alberta soils using the above data, excluding data points with low (<0.3 mg/L) saturated paste boron to reduce calculation variability from dividing by small values. The coarse and fine data was further filtered to the 0.5-20 mg/L range for average K_d calculations to maximize relevance to most typical soil concentrations and potential guideline ranges. Average K_d values are shown in Table 3.4, ranging from approximately 0.8 L/kg for the coarser soils with <43% saturation percentage to 2.1 L/kg for finer soils with 43-100% saturation percentage. Heavy clay or organic soils with >100% saturation percentage had the highest average K_d of 8.5 L/kg. The average saturation percentage in each of these ranges is also shown, with 34% for the coarser soils, 61% for fine soils, and 374% for organics.

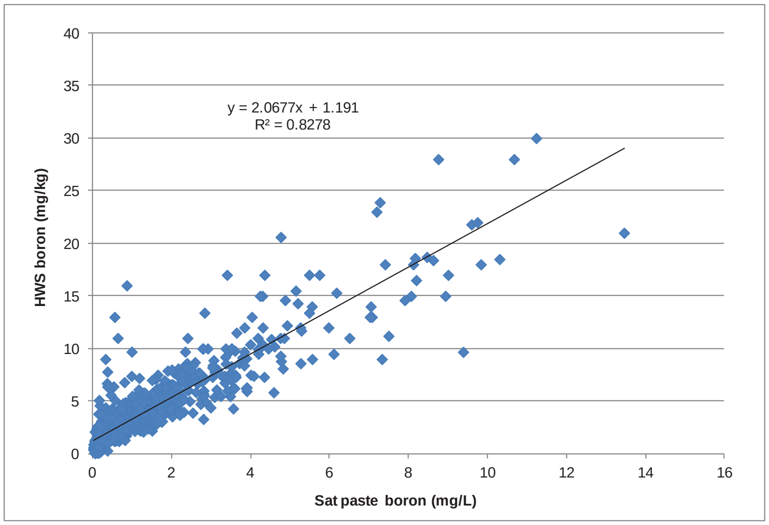
Table 3.4. Estimated K_d values for Typical Alberta Soils

Saturation percentage range	Typical texture	Average K_d (L/kg)	Average saturation percentage
>100%	Heavy clay or organic	8.5	374%
43-100%	Fine textured	2.1	61%
<43%	Coarse textured or silty	0.8	34%

Figure 3.10 shows a subset of this data from the field of sites with fine textured soils near Armena, Alberta. Though some texture variability was present, soils were typically clay loams with an average saturation percentage of approximately 60%. A good linear regression is observed with an R^2 of 0.83, with 5 mg/kg HWS boron corresponding to approximately 1.85 mg/L saturated paste boron. At a saturated paste B of 2 mg/L, this represents an estimated K_d value of 2.1 L/kg, and is generally consistent with the fine soil range shown in the above table.

Kd values shown for fine and coarse textured soils in Table 3.4 are used below for soil guideline development.

Figure 3.10. HWS vs Saturated Paste Boron for Fine Textured Soils Near Armena, Alberta



4. Receptors, Pathways, and Boron Transport

4.1 Receptors of Concern and Pathways of Exposure

Receptors of concern are humans and ecological organisms (e.g., plants, wildlife, *etc*.) that could potentially be exposed to chemicals of concern and/or may be sensitive to the development of chemical-related adverse effects. Ecological receptors are selected based on their importance to society and property owners, the maintenance of a healthy and functioning food web, and species diversity. In addition, these receptors are selected based on their sensitivity to developing chemically related adverse effects as well as on their potential for being exposed. Receptors of concern for boron and the various pathways by which they may be exposed are described in the sections below for the various land uses described in Alberta Tier 1 protocol (AESRD, 2014a). In particular, boron is relatively unique of the metals/metalloids listed in the Tier 1 guidelines in that its higher water solubility results in increased importance of various groundwater-related pathways. Boron present in shallow soil could leach downward toward a potential domestic use aquifer (DUA), and laterally through groundwater toward a nearby surface water body. Consequently, groundwater pathways such as protection of the DUA for human drinking water, protection of livestock water and irrigation water for agricultural use, and protection of surface water for both aquatic life and wildlife watering will be considered for boron. These pathways are in addition to the direct soil contact and ingestion pathways which are typically considered for other metals/metalloids.

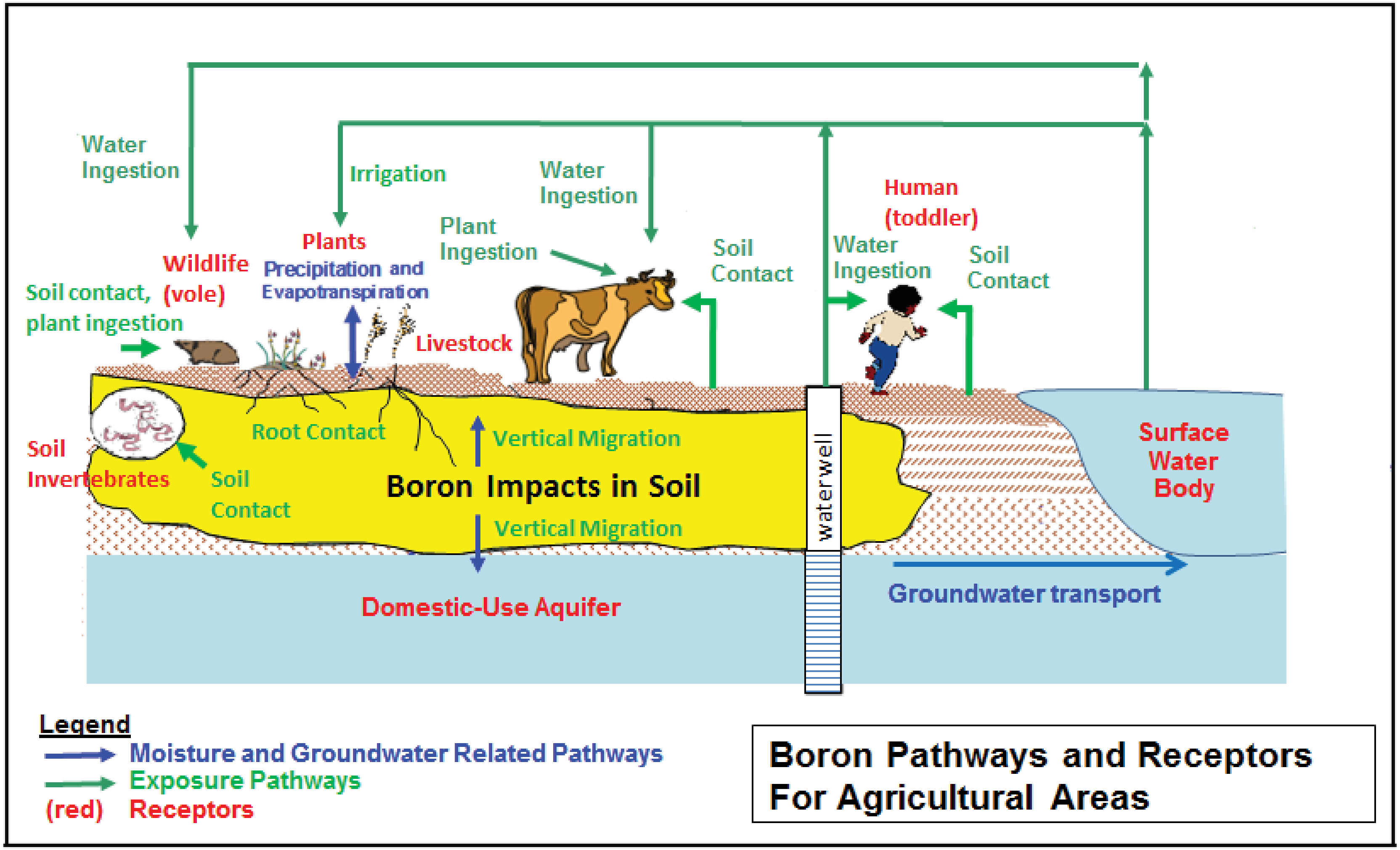
4.1.1 Agricultural Areas

Alberta Tier 1 protocol states that on agricultural land the primary land use is growing crops or tending livestock as well as human residence. This also includes agricultural lands that provide habitat for resident and transitory wildlife and native flora (AESRD, 2014a). Human and ecological receptors and pathways relevant to boron are listed below and shown schematically in Figure 4.1, followed by additional detail on key receptors.

Human receptors and exposure pathways:

- Direct contact with contaminated soil (soil ingestion, dermal contact with soil, inhalation of soil and soil-derived particulate)
- Ingestion of groundwater (potable water scenario)
- Ecological receptors and exposure pathways
- Soil contact with plants and invertebrates
- Soil and food ingestion by livestock and wildlife
- Soil nutrient cycling processes
- Protection of surface water sustaining aquatic life
- Protection of groundwater and surface water used for livestock watering
- Protection of groundwater and surface water used for irrigation
- Protection of surface water used for wildlife watering

Figure 4.1. Boron Receptors and Pathways for Agricultural Areas



Humans can be exposed to boron through consumption of drinking water sourced from a DUA. A toddler is used as the human receptor for agricultural areas, and incidental ingestion of soil can occur for children that might play or spend time in vegetated or exposed soil areas. Dermal exposure can occur when soil comes into contact with skin, and dust from soil may potentially be inhaled.

Plants and soil invertebrates (collectively known as ‘soil dependent biota’) can be directly exposed to boron in shallow soils. These plants can include cultivated crops, as well as native flora. Available literature data indicates that the bulk of root mass for many crop species will be located within the 0 to 1.5 m soil depth interval, though some crop species have root systems that could potentially extend to deeper soil depths (*e.g.*, alfalfa up to 3 m). For metals and metalloids, on a Tier 1 basis it is typically considered that plants roots may potentially come in contact with the chemicals of concern regardless of what depth the impacts are located at. Plants can also be irrigated with water sourced from surface water or groundwater in agricultural areas.

Livestock is assumed to be present in agricultural areas, with a cow used as the representative livestock species. Livestock can be potentially exposed to boron through direct soil ingestion or consumption of plants that have bioconcentrated boron. Livestock can also be exposed to boron in groundwater or surface water that is used as a source of drinking water.

Wildlife is assumed to be potentially present in agricultural areas, with the meadow vole used as a surrogate wildlife species due to their small size and subsequent increased relative exposure to soil contaminants. Wildlife such as voles can be potentially exposed to boron through direct soil ingestion or consumption of plants or seeds that have bioconcentrated boron from soil. Wildlife may also potentially be exposed to boron through ingestion of surface water.

Aquatic life could potentially be exposed to boron in groundwater if a surface water feature such as a creek or slough containing various aquatic life species is located down gradient of groundwater flow. Potential aquatic species include various vertebrates (*e.g.*, amphibians, fish), invertebrates (*e.g.*, insects, crustaceans) and aquatic plants and algae (CCME, 2009).

4.1.2 Natural Areas

Alberta Tier 1 protocol defines natural areas as being away from human habitation and activities, where the primary concern is the protection of ecological receptors. Accordingly, human exposure pathways are not considered, with the exception of the DUA pathway which applies to all land uses. Much of Alberta’s forested land is considered natural area land use, including boreal forest areas. Thus, different vegetation species may be present than in agricultural areas, and soil types may also differ and could include organic soils such as peat or muskeg. Livestock is not normally considered present in natural areas, with the exception of specified grazing leases where the livestock soil and groundwater pathways must also be considered. Wildlife and aquatic life are also both considered receptors in natural areas.

4.1.3 Residential / Parkland Areas

The primary activity in residential/parkland areas is human residence and recreational activity, and includes campgrounds and urban parks. The same human and ecological exposure pathways as for agricultural land are considered for residential / parkland areas, with the exception of livestock, irrigation, and wildlife pathways which are excluded.

4.1.4 Commercial / Industrial Areas

On commercial land, the primary activity is commercial (e.g., shopping mall) and all members of the public, including children, have unrestricted access. On industrial land, children are not permitted continuous access and the primary activity is the production, manufacture, or construction of goods. The same pathways as residential / parkland areas apply to commercial / industrial areas, though with some adjustments to assumed human exposure times. A toddler is the representative human receptor for commercial land and an adult for industrial land. For boron, the main receptor exposure pathways for these areas are thus considered human and ecological direct soil contact, DUA, and aquatic life. The potential for off-site migration of soils via wind erosion to more sensitive adjacent land uses is also considered for commercial / industrial areas.

4.2 Boron Transport

The groundwater model used in Alberta Tier 1 protocol can be used to predict the transport of boron through groundwater toward receptors such as the DUA or a surface water body and derive soil guidelines protective of these receptors. This model is based on protocol described in CCME (2006), and considers four processes as described in AESRD (2014a):

1. Partitioning of the substance from soil to pore water (soil solution, or leachate);
2. Transport of the leachate from the base of the contamination to the groundwater table;
3. Mixing of the leachate with groundwater; and,
4. Transport of the substance in groundwater down-gradient to a discharge point.

Each of these four processes is associated with a dilution factor (DF1 through DF4), with details relevant to boron described in the sections below.

4.2.1 Partitioning and Soil Solution Boron (DF1)

Partitioning describes the tendency for a compound in soil to be distributed between soil pore water and the solid phase. The degree to which a compound partitions on to the solid phase or into pore water is described by its K_d value. The smaller the K_d the greater the tendency for a compound to remain in soil pore water rather than sorb on to the solid phase. Like most inorganic compounds, K_d for boron is strongly influenced by soil texture (particularly clay content) although organic matter can control sorption in organic soils.

The prediction of pore water boron concentrations (also referred to here as leachate concentrations or soil solution boron) is based on measured soil data. Calculations may be performed starting with HWS boron as a metric for total mobile (dissolved plus adsorbed) boron, but it is more useful in this case to start with measured saturated paste boron data which represents dissolved boron at soil saturated paste extract conditions. Saturated paste boron data (in mg/L) can be used to estimate soil solution boron for transport purposes. Using the K_d relationships developed in Section 3, soil solution boron can be estimated at various soil moisture contents, ranging from fully saturated soils (similar to groundwater concentrations as would be measured in monitoring wells) to partially saturated soils in the vadose zone at field moisture conditions.

Moisture contents for unsaturated soils are less than the moisture contents in saturated pastes, and boron concentrations on a soil solution (mg/L) basis thus tend to be higher than on a saturated paste (mg/L) basis. However, the relative decrease in boron concentration from soil solution to saturated paste is less than what would be predicted for a non-sorptive species such as chloride.

Based on previous assumptions regarding K_d and adsorption, the concentration decrease from soil solution boron to saturated paste boron is derived from the DF1 equation as shown below. The DF1 equation below has been modified from the Tier 1 protocol to express the ratio between saturated paste boron and soil solution boron at a given soil moisture content.

$$DF1 = \frac{Saturated\ paste\ B\ (mg/L)}{Soil\ solution\ B\ (mg/L)} = \frac{K_d + \frac{\theta_w}{\rho_b}}{K_d + \frac{saturation\ \%}{100}}$$

Where:

DF1 = modified dilution factor 1 (dimensionless)
Kd = distribution coefficient (L/kg)
θw = water-filled porosity (dimensionless);
ρb = dry soil bulk density (kg/L);

As an example, water content is typically reduced by several-fold when adjusting from saturated paste to unsaturated moisture content for typical soil textures and saturation percentages. Assuming a K_d of 2.1 and saturation percentage of 61% for fine soils with a Tier 1 default bulk density of 1.4 kg/L and moisture-filled porosity of 0.168, the modified DF1 is calculated to be 0.82. This represents an approximate 1.22-fold decrease (*i.e.*, the inverse of 0.82) in boron concentration from soil solution to saturated paste, whereas a non-sorptive species such as chloride would decrease by approximately 4-fold under the same conditions. Similarly, using a K_d of 0.8, a bulk density of 1.7 kg/L, and saturation percentage of 34% results in a modified DF1 of approximately 0.76 for coarse soils, and represents an approximate 1.31-fold decrease in boron concentration from soil solution to saturated paste. This demonstrates the buffering provided by soil boron sorption (Jame *et al.*, 1982, Keren, 1990), and indicates that saturated paste boron can be a good predictor for soil solution boron.

4.2.2 Leaching Toward a DUA (DF2)

Dilution Factor 2 (DF2) represents the ratio of the concentration of leachate in contact with contaminated soil to the predicted leachate concentration directly above the groundwater table. DF2 is taken to be 1 (*i.e.*, no dilution) on a Tier 1 basis since it is assumed the contaminated soil extends down to the water table.

$$DF2 = 1\ \ (no\ dilution\ on\ Tier\ 1\ basis)$$

If a value for DF2 is calculated on a Tier 2 basis using techniques in AESRD (2014b), the resulting dilution factor is a function of parameters such as infiltration rate, distance between the bottom of impacts and the water table, and the retardation (slowing) of boron transport relative to water due to sorption processes.

4.2.3 Dilution into DUA (DF3)

Once the water table (assumed to be a DUA on a Tier 1 basis) is reached, the boron is then diluted as it enters the laterally-moving groundwater as per the ‘Dilution Factor 3’ calculation (AESRD, 2014a,b):

$$DF3 = 1 + \frac{Z * V}{I * X}$$

Where:

$DF3$ = dilution factor 3 (unitless)
Z = mixing depth (m)
V = Darcy velocity (flux) in DUA (m/yr)
I = infiltration (drainage) rate (m/yr)
X = length of contaminated soil (m)

Default parameters are provided in AESRD (2014a), with the DUA Darcy velocity (V) being a function of DUA hydraulic gradient and hydraulic conductivity (varies for fine and coarse soils). Infiltration (drainage) rate also varies for fine and coarse soils, with a default drainage rate (flux) of 12 mm/year for fine soils and 60 mm/year for coarse soils. Source length is assumed to be 10 m on a Tier 1 basis, with mixing depth either set as 2 m for the drinking water pathway, or calculated as a function of vertical dispersion, drainage rate, DUA velocity, aquifer thickness, and source length for other pathways.

4.2.4 Lateral Transport (DF4)

Once diluted into groundwater, boron may potentially be transported laterally toward an aquatic life receptor assumed to be 10 m away on a Tier 1 basis (relevant to the aquatic life and wildlife watering pathways). For sorptive solutes such as boron, a ‘retardation factor’ is used to describe the slowed transport of the solute relative to the moving water. The retardation factor is calculated below based on K_d and soil properties (AESRD, 2014a):

$$R = 1 + \frac{\rho_b * K_d}{\theta_t}$$

Where:

R = retardation factor (unitless)
ρ_b = dry soil bulk density (kg/L)
K_d = distribution coefficient (L/kg)
θ_t = total soil porosity (dimensionless)

Using default Alberta Environment parameters for fine soil (ρ_b = 1.4 kg/L and θ_t = 0.47), a retardation factor of approximately 7.3 is calculated assuming a K_d of 2.1. Similarly, a retardation factor of approximately 4.8 is calculated for coarse soil (ρ_b = 1.7 kg/L and θ_t = 0.36) assuming a K_d of 0.8.

DF4 is then calculated as per AESRD (2014a) as a function of retardation factor, transport distance, groundwater velocity, dispersivity, and decay. Though boron may change specific form based on conditions such as pH or moisture level, boron is generally not transformed or degraded in the environment (US EPA, 2004b) and thus decay is assumed negligible. In the absence of decay, the short transport distance to a surface water receptor (assumed at 10 m) results in minimal dispersion and a DF4 of approximately 1 on a Tier 1 basis.

$$DF4 = 1 \ \ (effectively\ no\ dilution\ on\ a\ Tier\ 1\ basis)$$

5. Toxicity to Plants

Boron toxicity to plants is discussed in this section and is considered one of the main constraining pathways. This section is grouped into three subsections, first describing literature results for plant boron uptake and toxicity in Section 5.1. This is then followed by results of more recent Alberta boron toxicity testing with agricultural plants in Section 5.2 and boreal / natural area plants in Section 5.3.

5.1 Plant Toxicity Data from Literature

Substantial literature data is available discussing various aspects of boron plant toxicity. This section describes literature results boron uptake into plants and its relationship to toxicity (Section 5.1.1), followed by a more detailed review of literature toxicity results from sand culture experiments (Section 5.1.2 and 5.1.3) and in soil (Section 5.1.4).

5.1.1 Uptake of Boron into Plants

Boron is an essential micronutrient, and boron deficiency can cause adverse effects such as inhibited growth and reduced seed production (Dell and Huang, 1997), as well as reduced shoot and root growth, vessel formation, and photosynthesis (Çetinkaya *et al.*, 2014). Various theories have been proposed and experiments conducted to determine the principle mechanisms through which boron is accumulated. There is evidence for both active and passive mechanisms of uptake (Hu and Brown, 1997). Boron is absorbed from soil solution by roots mainly as undissociated boric acid (Goldberg, 1997). Boron is typically transported to upper plant parts and does not accumulate substantially in roots.

Certain plants have mechanisms for a tolerance of elevated boron concentrations in solution and soil (Nable, 1988). Of interest is that decreased uptake was associated with increased tolerance between six genetic varieties of wheat. In general, a linear uptake of boron into plants with increasing soluble boron concentrations in soil can be expected, although the slope may differ between species and genotypes (Nable *et al.*, 1997). In other words, a 1:1 ratio of increased plant uptake with increased boron solution concentrations cannot be expected for all plant species (Banuelos *et al*, 1990).

Various publications have studied the uptake of boron into plants. Hydroponic studies are frequently used to examine the uptake of boron into plants from solutions containing boron (examples include Eaton, 1944; Nable *et al.*, 1997; Hu and Brown, 1997; Goldberg, 1997). It should be noted that uncertainties exist regarding the interpretation of plant uptake data based on hydroponic solution studies compared to plant uptake of boron in a soil environment. For example, sand culture experiments have different sorption properties compared to those performed in soil, and thus care must be taken when comparing soil concentrations versus solution concentrations for different media types. Laboratory conditions may overestimate or underestimate field transpiration rates, which have been shown to correlate with boron uptake (Hu and Brown, 1997).

Bioconcentration factors (BCFs) are one way to measure plant boron uptake and attempt to predict vegetation concentrations based on soil boron concentrations. BCF’s are defined as vegetation boron concentrations (mg/kg dry basis) divided by soil boron concentrations (mg/kg), with different soil boron tests thus resulting in different BCF ranges. If using the HWS method, BCF’s could be calculated as BCF = vegetation boron / HWS boron; both in mg/kg dry basis. The weight of available data suggests that greater BCFs may occur at relatively low HWS boron concentrations (*e.g.*, less than 2 mg/kg). For example, Mellbye *et al.* (1999) measured the uptake of boron into tall fescue and a perennial ryegrass in silt loam and silty clay soils. Vegetation boron concentrations ranging from 22 to 38 mg/kg were observed at HWS boron ranging from 0.6 to 1.1 mg/kg resulting in a geometric mean BCF of 38. Note that these HWS boron concentrations are relatively low, and BCFs are likely higher at low HWS boron concentrations since active boron uptake may play a larger role to meet the plants minimum boron requirements in low-boron soils.

For comparison purposes, vegetation boron levels and BCFs were evaluated for several sites with fine textured soils (typically clay, clay loam, sandy clay) near Armena, Alberta (Equilibrium Environmental, 2009a). A variety of annual crops and forages were tested in soils ranging up to 6.5 mg/kg HWS boron (averaged over the top 30 cm). Vegetation boron ranged up to 36 mg/kg in annual crops and 75 mg/kg in forages. BCF's were calculated for each site by dividing vegetation boron by the depth weighted HWS boron concentrations from 0-30 cm sampling depths and averaging over all sampling locations (results shown in Figure 5.1 along with vegetation boron and soil boron). BCFs ranged from 2.2 to 22 for annual crops, with canola exhibiting the highest cultivar BCF. Peas exhibited the second highest cultivar BCF of 12.8 with wheat and barley showing the lowest annual crop BCFs of 2-4. It is noteworthy that wheat is considered a 'sensitive' species toward boron in irrigation guidelines, and it displayed lower BCFs than other species such as corn, considered to be 'moderately tolerant'. BCF's for the forage sites ranged from 2.9 to 18.3, with the maximum occurring at Pasture C. Forages generally showed greater variability than the annual crops, potentially due to the large variation in individual species comprising the pasture mixtures. The maximum BCF observed for this set of Armena sites was 22 (canola), whereas the overall average was 7.6.

An additional boron toxicity study including soil boron, vegetation boron, and resulting BCFs was carried out in outdoor tub experiments in Alberta (Equilibrium Environmental, 2008a, 2009b). A variety of common agricultural and natural area plant species as well as some garden fruit and vegetable species were grown in sandy loam to loamy soils with varying HWS boron concentrations of <2 mg/kg to 50 mg/kg. Kentucky bluegrass, carrot, blue grama grass, strawberry, red fescue, red clover and durum wheat were all grown in each of five separate tubs, each tub with different soil boron concentrations. Good growth was observed up to and including tub 4 (with approximately 10 mg/kg HWS boron in soil), with poor or no growth observed in tub 5. Vegetation boron levels were also measured, and BCFs calculated for each species by dividing vegetation boron by HWS soil boron (both on a mg/kg basis). Figure 5.2 shows the soil boron and vegetation boron for each of the species tested, with BCFs of 4, 10, 15, and 50 also plotted for visual context. Over the soil range with good plant growth (up to and including tub 4), measured BCFs ranged from 5 to 47 for all species, with an average of 20.1. Minimum BCF's were observed for wheat, bluegrass, and red fescue, and the maximum for strawberries and carrots.

Figure 5.1. Vegetation Boron and Bioconcentration Factors for Field of Sites near Armena, Alberta (2006-2009)

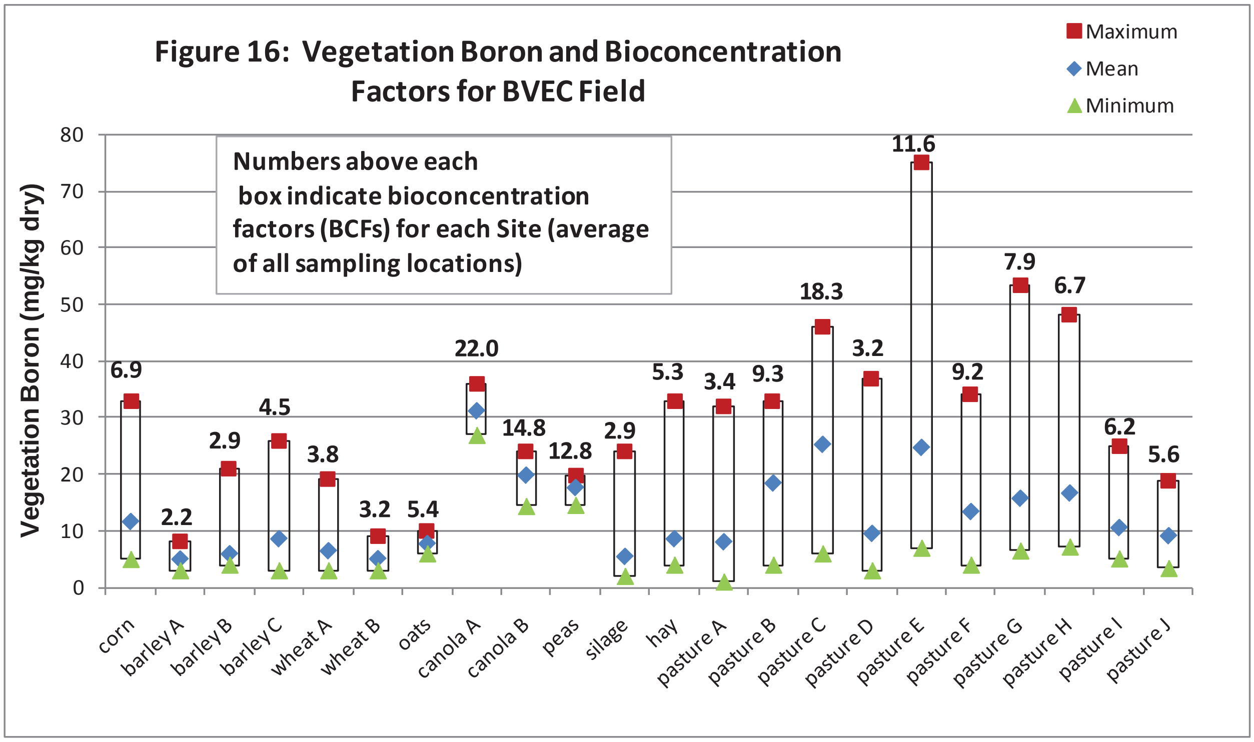
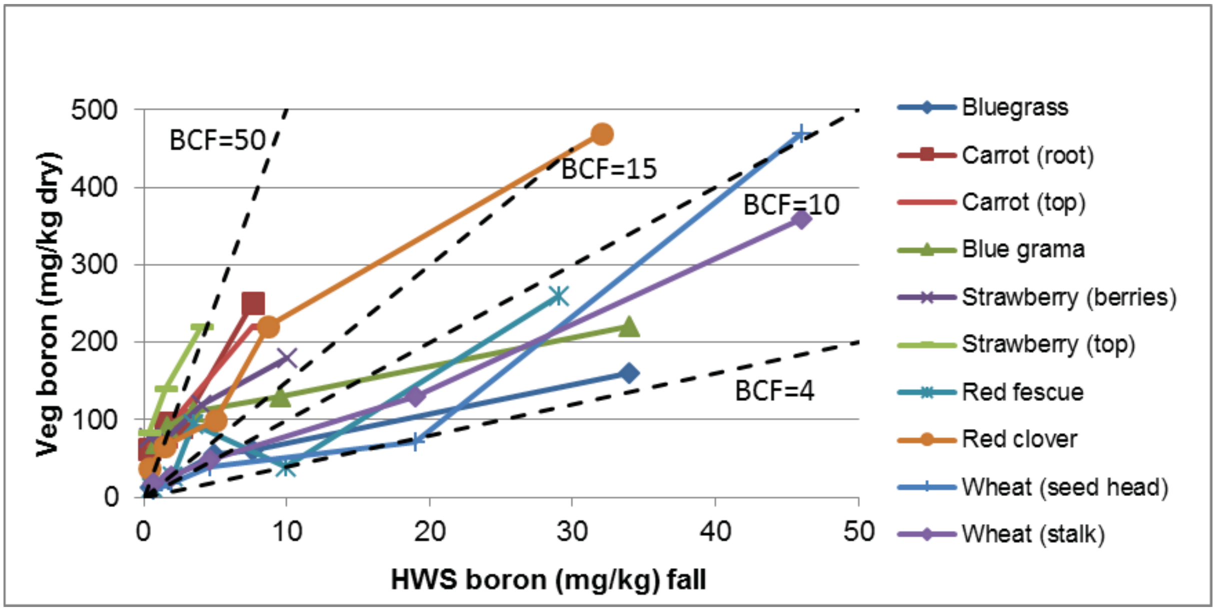


Figure 5.2. Boron Bioconcentration in Alberta Tub Experiments



In addition to potentially being of value in diagnosing deficiency and/or toxicity to plants (each discussed further below), this vegetation boron and BCF data is also useful for predicting potential boron concentrations consumed by livestock and/or wildlife from grazing on plants. In this context of risk to livestock and wildlife, the garden species tested here including carrots and strawberries are of less relevance, with wheat, clover, and the other grasses of more relevance. If carrots and strawberries are excluded, the range of BCF's is 5 to 24.1 with an average of 12. This range of plant species and BCF's is considered more relevant to livestock and wildlife food consumption, and is considered further in Section 9.3.

In conditions of deficiency, the addition of boron-containing fertilizer can increase boron uptake and improve yield. For example, clover yield increased when additional boron was added to Punjabi soils, which initially had HWS boron concentrations from 0.36 to 1.85 mg/kg (Arora and Chahald, 2007). Shaaban (2014) also cites several studies where yield and growth improved when crops were supplied with boron. Brennan *et al.* (2014) examined the response of canola and lupin to different forms of boron-containing fertilizer in acidic, sandy soils in Australia and concluded that care is required with boron form and application rates to avoid potentially inducing toxicity effects. Sprague (1972) also noted that soil boron levels which may cause toxicity symptoms in one species may cause deficiency in others

When excess boron is present in soil, plants can sometimes be used to remediate (bio-extract) boron via plant uptake (Banuelos *et al*, 1993a). For example, Banuelos *et al* (1993b, 1995) discuss the extraction of boron from soil using boron-tolerant plant species such as tall fescue, Indian mustard, birdsfoot trefoil, and kenaf. Soil boron concentrations were generally between 4-6 mg/L saturated paste boron, with these boron concentrations in these experiments not observed to affect growth (Banuelos *et al.*, 1993b) or show visual toxicities (Banuelos, *et al* 1995). Vegetation boron concentrations averaged approximately 100-120 mg/kg in tall fescue and birdsfoot trefoil, approximately 224 mg/kg in Indian mustard, and 685 mg/kg in kenaf. Based on mass balance calculations, the overall conclusions were that boron removal by such plants could be useful under some circumstances. The use of poplar trees to phytoextract boron from soil was also evaluated in sand culture experiments (Banuelos *et al*, 1999), with leaf boron concentrations ranging up to approximately 500 mg/kg and no negative effects on growth observed at solution boron concentrations of 1-5 mg/L (Shannon *et al.*, 1999). Other plant species which have been examined for their ability to tolerate and phytoremediate relatively high boron concentrations include castor oil plants (Abreu *et al.*, 2012) and *Puccinellia frigida*- a South American plant which colonizes hydrothermal springs and has been observed growing in conditions with boron concentrations above 400 mg/L (Rámila *et al.*, 2015).

Increased plant uptake beyond a certain threshold can lead to plant tissue concentrations that are associated with symptoms of toxicity (Nable *et al.*, 1997; Hu and Brown, 1997). For example, boron toxicity has been observed in plants growing in soils which have inherently high natural concentrations, have been over-fertilized with minerals high in boron, have received combustion residues, or have been irrigated with water high in boron content (Sotiropoulos *et al.*, 2002). Visual toxicity symptoms can often include yellowing, chlorosis, or necrosis of leaf margins or tips (Camacho-Cristobal *et al.*, 2008), as well as growth reduction as described in later sections.

Many studies attempt to correlate toxicity symptoms with vegetation boron concentrations (Gupta, 2007). For example, Gestring and Soltanpour (1987) grew alfalfa (*Medicago sativa*) in three soils of differing textures and different boron levels and found that plant yields were significantly reduced in sandy loam and loam soils, but not in silty loam soils. The authors concluded that the soil boron extraction methods used in the study did not adequately assess the potential for boron toxicity towards plants, whereas plant tissue boron concentrations were a more reliable indicator. The critical range of plant tissue boron concentration in alfalfa resulting in significant yield reduction in this experiment was found to be 850 to 975 mg boron/kg plant tissue. However, Nable *et al.,* (1997) cautioned that there are serious problems with the use of foliar analysis for diagnosing boron toxicity in plants. There is often a wide range of critical values reported for the same species depending on other factors such as growing conditions and which part of the plant is sampled. For example, Gupta (2007) list toxic boron levels in wheat ranging from 16 to 400 mg/kg depending on the plant part sampled and growing conditions. Kluge and Podlesak (1985) found that symptoms of boron toxicity occurred in pot-grown spring barley (*Hordeum vulgare*) at boron leaf tissue concentrations of 60 to 80 mg/kg dry weight, whereas Gupta (2007) summarizes data showing toxicity symptoms appearing over the wide range of 50-420 mg/kg dry weight for whole barley shoots. As an example of variations due to growing conditions, Nable *et al.,* (1997) reports that the use of vegetation boron thresholds established from greenhouse experiments may overestimate field toxicity thresholds due to various factors including a loss of boron in plant tissue from field experiments due to rainfall. Overall, Nable recommends that foliar analysis (vegetation boron) of field-grown plants be considered only a crude tool for assessing plant toxicity, and to interpret results from this method with caution. The alternative of predicting plant toxicity from soil data is discussed in the sections below.

5.1.2 Plant Toxicity and Soil Test Methods

Older literature toxicity data of varying quality and relevance based on soil HWS boron is available for a selection of plant species including Norway Maple and other trees in Ontario (Palmer and Linzon, 1981, Temple *et al*., 1978), field beans (Gupta and Cutcliffe, 1984), strawberry (Haydon, 1981), and other crops such as spinach, lettuce, onion, potato, bean, oat, tomato, and cabbage (MacKay *et al*., 1962). Some of these studies reported the onset of toxicity symptoms at below 2 mg/kg HWS for certain potentially sensitive species, including reported values of 1.4 mg/kg for Norway Maple, 1.5 mg/kg for field beans, and 1.9 mg/kg for strawberry. These studies were among those considered when developing the Ontario soil quality guideline of 1.5 – 2 mg/kg HWS boron (Ontario Ministry of Environment and Energy, 1996, 1997). There are many difficulties and uncertainties involved with the use of this data. For instance, these studies are typically 20-45 years old and used colorimetric detection methods, which measure dissolved $B(OH)_3$ in the extract (Keren, 1996) rather than the newer ICP method, which measures total boron in solution. This may lead to differences in boron quantification when other forms of boron, such as boron associated with dissolved organic matter, are present in the extract. Some studies may have sampling issues, such as Gupta and Cutcliffe (1984) which reports HWS boron concentrations in soil after harvest. The results reflect loss of boron due to plant uptake and potential leaching from the sandy soils over the growing season. Consequently, boron concentrations in soil were higher after the pre-planting boron application in spring and for some period during the growing season. Beans grown in the same soil one year later showed no toxicity symptoms. Most of these studies also reported the apparent onset of potential toxicity rather than the less subjective endpoints preferred by CCME (2006) such as concentrations causing 25% yield reductions (IC_{25}'s). The measurement units are also somewhat uncertain in some of these studies, such as HWS boron being shown in mg/L in Temple *et al.* (1978). Texture is also uncertain in some of these studies, and there are inherent difficulties involved in applying HWS toxicity data to soils with different textures as described below.

The HWS test was primarily designed to diagnose deficiency rather than toxicity (Goldberg et al, 2002 and Bingham 1973), and the substantial amount of adsorbed boron measured by this method does not reflect the concentration of dissolved boron directly in contact with plant roots. Boron concentrations in soil solution have been shown to be a better predictor of plant toxicity based on several soil and sand culture experiments where variable boron concentrations were applied and plant toxicity measured (Ryan *et al.*, 1977, Aitken and McCallum, 1988, and Keren *et al.*, 1985a). This soil solution boron is often approximated from a saturated paste extract (Nable *et al.*, 1997 and Bingham, 1973), and typically gives results lower than the HWS procedure if both are expressed in mg/kg of soil (Elseewi and Elmalky, 1979). This indicates that the mass of sorbed boron tends to be higher than the mass of dissolved boron for many soil conditions. Different extraction techniques were examined in Xu *et al.* (2001), where a technique similar to a saturated paste extract also resulted in substantially lower soil boron concentrations than the HWS technique. Saturated paste boron results are most commonly expressed in mg/L to allow comparison with plant toxicity data from literature.

Early attempts to estimate sensitivity of plants to saturated paste boron have been reported in USDA (1954). These ranges appear to be based on sand culture plant toxicology data (Eaton, 1935; Eaton, 1944) and related irrigation guidelines (Scofield, 1935), and are explicitly stated as ‘tentative’ limits based on existing information. Boron concentrations <0.7 mg/L are listed as ‘probably safe for sensitive plants’, concentrations from 0.7-1.5 mg/L listed as ‘marginal’, and concentrations >1.5 mg/L ‘appear to be unsafe’ but that ‘more tolerant plants can withstand higher concentrations, but limits cannot be set on the basis of present information’ (USDA, 1954). A more detailed analysis of this older toxicity data from literature sand culture experiments is provided below.

5.1.3 Initial Sand Culture Experiments

Between 1929 and 1934, boron toxicity tests were performed in Riverside, California on fifty plant species (58 varieties) in outdoor coarse sand cultures (Eaton, 1935; Eaton 1944) to provide a basis for irrigation guidelines. The sand was fully saturated with a boron/nutrient solution once or twice each day, with boron concentrations (treatment levels) of 0.03-0.04 (trace), 1.0, 5.0, 10, 15, and 25 mg/L. Excess solution was drained into auxiliary reservoirs, and thus the plant roots were in contact with the boron concentrations of the irrigation water which is considered representative of approximate soil solution levels in this experimental setup (Gupta *et al*, 1985). Plant response was measured by total dry weight as well as leaf, root, laminae or ‘other’ masses in some cases. Though boron toxicity was assessed via plant mass, a particular focus was also placed on visual indicators such as leaf damage which is more challenging and subjective to quantify. Plants were then placed into categories of either “Sensitive”, “Semi-Tolerant”, or “Tolerant” based these results, with blackberry and lemon listed as among the most sensitive species and asparagus as one of the least sensitive species.

Based primarily on these sand culture experiments by Eaton, various supplementary rankings were created in later years (e.g., Maas, 1987) which formed the basis for irrigation guidelines such as those used by CCME (CCREM, 1987 and CCME, 2005) and Alberta (AESRD, 2014c). These are expressed in Table 5.1 as ranges of soil solution boron that are safe for crop species of varying sensitivities. The ranges used by CCME are also similar to those published in Keren and Bingham (1985c), Chen *et al*., (2011), and Wilcox (1960). The ranges of boron are presented as soil solution boron at field moisture conditions, and thus represent the concentration of boron directly in contact with plant roots.

The crops in the table below are grouped by sensitivity, with the crops within each group additionally ordered from most sensitive to least sensitive. This table forms the basis of irrigation guidelines for CCME (2005), British Columbia (BCMOE, 2003), and Alberta (AESRD 2014c). The irrigation guidelines range from 0.5 to 6 mg/L depending on the species irrigated, wherein the maximum concentrations tolerated in irrigation water without yield reductions are equal to soil solution concentrations or slightly less (CCREM, 1987). Note that the 0.5 mg/L irrigation guideline shown in AESRD (2014a) lists solely the lowest end of this range (i.e., does not consider species sensitivity), but the Environmental Quality Guidelines for Alberta Surface Waters (AESRD, 2014c) show the 0.5 to 6 mg/L range directly as per CCME.

Though the most sensitive species listed (blackberries) is less frequently seen in Alberta, the second-most sensitive category (thresholds up to 1 mg/L) contains several Alberta-relevant species such as wheat and barley. Note that these ranges are based on threshold effects, whereas other responses to other contaminants such as hydrocarbons are typically based on acceptable effect levels above thresholds.

Table 5.1. Relative Tolerance of Agricultural Crops to Boron for Irrigation Guidelines

Tolerance	**Maximum Concentration in Soil Solution Without Yield Reduction (mg/L)**	**Agricultural Crop**
Very sensitive	< 0.5	Blackberry
Sensitive	0.5 - 1.0	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet potato, ***wheat, barley***, sunflower, mung bean, sesame, lupin, strawberry, Jerusalem artichoke, kidney bean, lima bean
Moderately sensitive	1.0 - 2.0	Red pepper, pea, ***carrot, radish***, potato, ***cucumber***
Moderately tolerant	2.0 - 4.0	***Lettuce***, cabbage, celery, turnip, Kentucky bluegrass, oat, corn, artichoke, tobacco, mustard, ***clover***, squash, muskmelon
Tolerant	4.0 - 6.0	Sorghum, ***tomato***, ***alfalfa***, purple vetch, parsley, red beet, sugar beet
Very tolerant	6.0 - 15.0	Asparagus

*Species in **bold** are Environment Canada test species which have been chosen as useful benchmarks for performing laboratory toxicity testing (Environment Canada, 2007a).*

Source: CCREM (1987), Westcot and Ayers (1984), and Maas (1987). Used directly as irrigation guidelines in CCME (2005), and AESRD (2014c).

As an example of estimating acceptable effect levels from this older sand culture data, IC_{25} values for ten of the most sensitive agricultural fruit, flower, and tree species relevant to Canada from Eaton (1944) were generated and are shown in Table 5.2 below. The species are ranked in the same order as Eaton (1944) based on the average reduction in total dry weight at 5, 10, and 15 mg/L B plus visual observations, with blackberry (#1) ranked as most sensitive. Other sensitive species less relevant to Canada such as lemon (#2), fig (#7), and persimmon (#6) are not shown here. These estimated IC_{25}'s are based on a 25% reduction in total dry weight relative to the maximum growth, and should be considered approximate since the datasets are relatively small with coarse spacing between treatment levels. Estimated IC_{25} values ranged from 0.7-2.8- mg/L with blackberry and pansy having the lowest estimated IC_{25} values.

Since blackberries were ranked by Eaton as the most sensitive of all 58 species tested, the blackberry yield-response data are shown in Figure 5.3 along with the estimated IC_{25} value.

Negligible loss of baseline mass was observed at 1 mg/L, with an IC_{25} (25% loss of baseline mass) estimated at approximately 1.9 mg/L by interpolation. Observations of the blackberry symptoms during the test indicated that the mesophyll of the leaves was mildly buckled in the 0.03 mg/L boron dosage, likely due to boron deficiency. In the 1 mg/L dosage, older leaves on the blackberry plants showed marginal burning at the tips but were otherwise normal. In the 5 mg/L dosage, little growth occurred, and at boron concentrations >5 mg/L plants died early in the season (hence no data above 5 mg/L and an estimated IC_{25} between 1 and 5 mg/L).

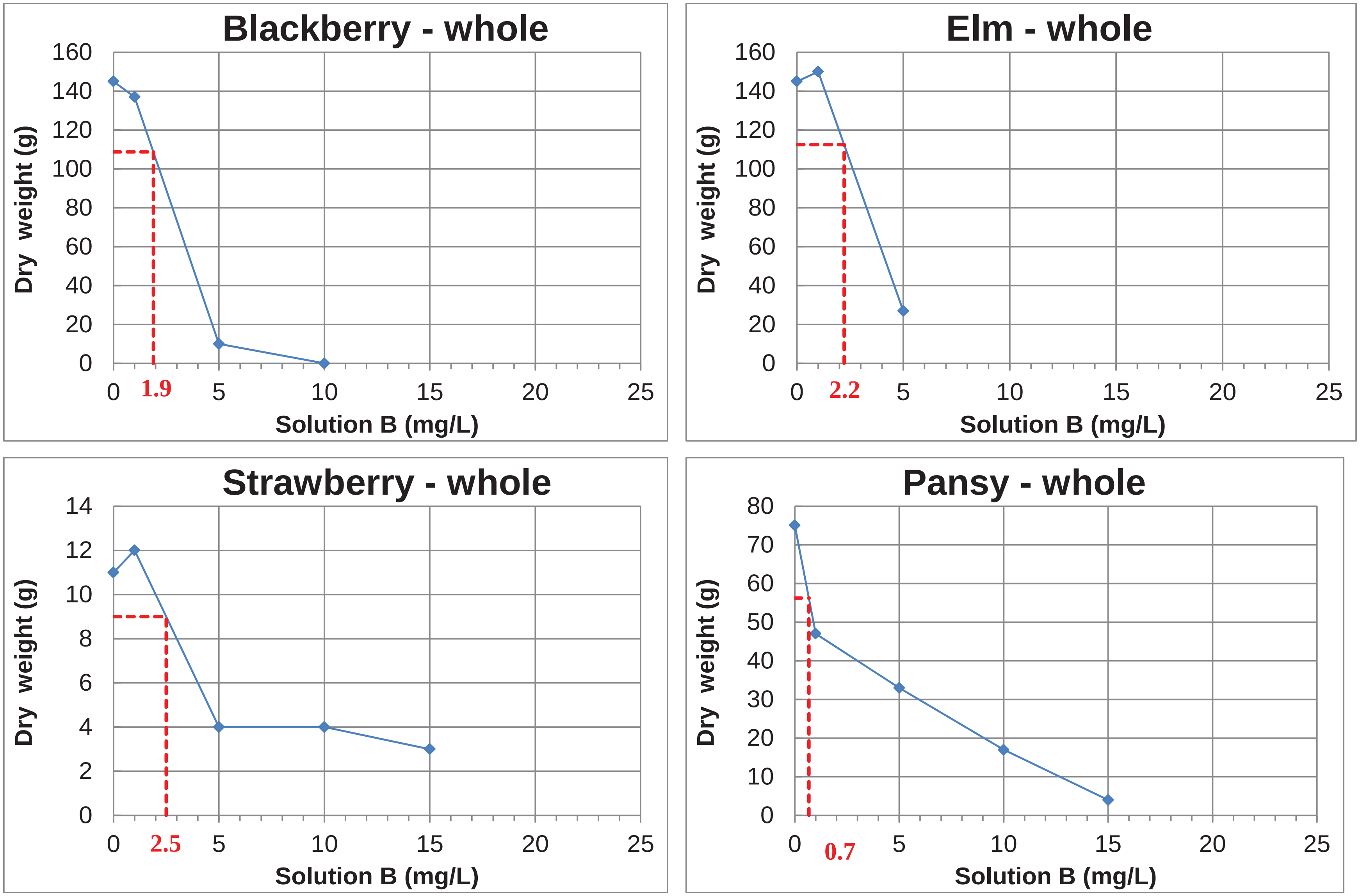
Table 5.2. Summary of Estimated IC_{25}s from Sensitive Fruit, Flower, and Tree Species

Ranking (Eaton)	Common Name	*Botanical Name*	Calculated IC_{25} (mg/L)	Test Duration
1	Blackberry	*Rubus* sp Mammoth Thornless	1.9	8 months
3	Elm	*Ulmus americana* L.	2.2	8 months
4	Cherry	*Prunus avium* L. Mazzard	2.3	8 months
5	Peach	*Prunus persica* L. Batsch	2.8	8 months
8	Strawberry	*Fragaria* sp Klondike	2.5	5 months
9	Lupine	*Lupinus hartwegii* Lindl.	2.2	7 months
10	Grape	*Vitis vinifera* L. Malaga	2.2	8 months
11	Grape	*Vitis vinifera* L. Sultanina	2.2	5 months
12	Violet	*Viola odorata* L Princess of Wales	2.6	6 months
13	Pansy	*Viola tricolor* L.	0.7	6 months

Note: analysis performed on raw data from Eaton 1944. Rankings as per Eaton (1944)

Similar approximate yield-response curves were created for the other reportedly sensitive species to estimate the IC_{25} values summarized above. For example, Figure 5.3 also shows additional dose-response curves for pansy, elm, and strawberry with IC_{25} values estimated by interpolation to be 0.7, 2.2, and 2.5 mg/L respectively. Pansy shows the lowest IC_{25} calculated in this manner, but is ranked as #13 by Eaton due to the more gradual reduction in growth from 5-15 mg/L compared to blackberry, and the lack of visual injury at 1 mg/L. The vegetation boron concentration of pansy at 1 mg/L was also not highly elevated, suggesting the reported reduction in growth at 1 mg/L may be anomalous and/or due to experimental variability. Pansies are also reported in horticultural publications to be prone to boron deficiency (*e.g.*, Krug *et al.*, 2011), suggesting that the estimated IC_{25} shown in Table 5.2 is likely conservative. This and additional Eaton data are summarized in (AEP, 2015).

Figure 5.3. Yield Response and Estimated IC_{25} for Sensitive Species Exposed to Boron in Soil Solution



Note: analysis performed on raw data from Eaton 1944

5.1.4 More Recent Sand Culture Experiments

More recent sand culture studies have provided supplementary information on additional food-crops, and also refined the sensitivity thresholds of crops. In some cases this has resulted in differing sensitivity classifications for various plant species. For example, wheat is often listed as a sensitive crop in irrigation tables such as Table 5.1. Barley is also shown as ‘sensitive’ in this table, based on limited results from a hydroponic study from Iraq which reported identical toxicity thresholds of 0.8 mg/L for wheat, barley, mung bean, and sesame (Khudairi, 1961). Other references list barley as ‘moderately tolerant’ instead, such as Eaton (1944) where barley was unaffected by boron at 1 mg/L but showed signs of reduced yield at 5 mg/L, resulting in a ‘moderately tolerant’ classification.

Two boron toxicity reviews (Maas, 1986; Maas and Tanji, 1990) cite a more recent sand culture experiment performed by Bingham *et al* (1985) whereby barley yield was evaluated for a range of boron levels in irrigation water. The irrigation water was percolated through the sand cultures several times daily, thus representing approximate soil solution concentrations. Barley shoot and grain yield were not negatively affected up to boron thresholds of 2.5 and 3.4 mg/L respectively, resulting in a ‘moderately tolerant’ rather than ‘sensitive’ classification. Above these thresholds, yield started to decline at a relatively constant slope.

This threshold and slope approach described above is known as the ‘Maas-Hoffman Salinity Response Model’, and can be used to model the effects of elevated salt or boron on yield. It can be described by the equation:

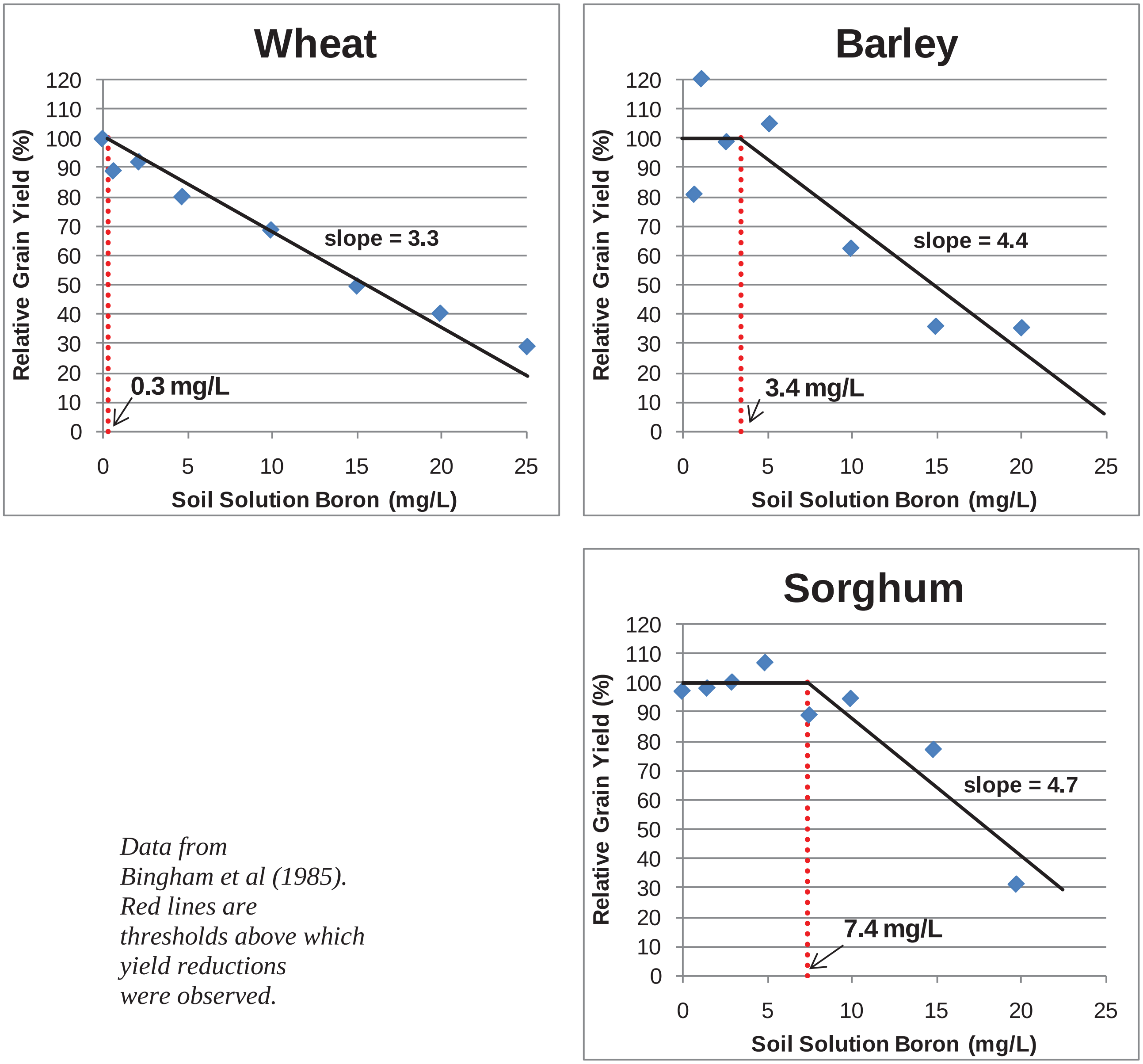
$$Y = 100 - m(X - A)$$

Where:

Y = Relative yield (%);
X = Concentration of boron in soil solution (mg/L);
A = Threshold boron concentration (mg/L);
m = Decrease in relative yield per unit increase in boron concentration (%);

The sand-culture experiment described above for barley (Bingham *et al*, 1985) also evaluated wheat (classified as ‘sensitive’) and sorghum (classified as ‘tolerant’). Grain yield responses to different irrigation water concentrations (approximately equal to soil solution concentrations in this case) are shown in Figure 5.4 for each of the three crops tested in this study.

Figure 5.4. Grain Yield Responses for Barley, Wheat, and Sorghum



Data from Bingham et al (1985). Red lines are thresholds above which yield reductions were observed.

The experimenters identified threshold values of 0.3 mg/L for wheat, 3.4 mg/L for barley, and 7.4 mg/L for sorghum. Note that the threshold for wheat is approximate due to the low number of datapoints below 1 mg/L. Khudairi (1961) reported a wheat threshold of 0.8 mg/L which falls generally within the range reported by Bingham et *al* (1985). Above these thresholds, wheat grain yield declined at 3.3% for each additional 1 mg/L boron in irrigation water, whereas barley and sorghum grain yield declined at 4.4% and 4.7% respectively. It is noteworthy that for these three species a larger toxicity threshold corresponded to a steeper yield response slope. This data predicts that wheat grain yield could be reduced by approximately 3-6% for soil solution boron between 1-2 mg/L. It also shows that boron levels that are protective for a sensitive species such as wheat could potentially be deficient for a more tolerant species such as sorghum which shows increasing yield with increasing boron concentrations up to 5 mg/L. Table 5.3 below shows predicted soil solution boron corresponding to 25% yield reduction, thus representing IC_{25} values.

Table 5.3. Estimated Soil Solution Boron for 25% Yield Reductions

Species	Solution Boron (mg/L)		
	Threshold	Slope % per mg/L soil solution	IC_{25}
Wheat	0.3	3.3	7.9
Barley	3.4	4.4	9.1
Sorghum	7.4	4.7	12.7

The threshold for barley obtained in the above study of (3.4 mg/L) is similar to that observed in Chauhan and Asthana (1981), which studied the effects of boron in irrigation water on barley growth in a sandy loam soil. Saturated paste soil boron was also evaluated (after irrigation), and barley yield and vegetation boron was measured. The researchers concluded that visual toxicity symptoms appeared above 4 mg/L saturated paste boron, and that higher concentrations were required to cause measurable yield reductions.

There are also other examples of literature sources reporting different threshold values for some of the crops listed in Table 5.1. For instance, Aitken and McCallum (1988) reported sunflower yield was not negatively affected until soil solution boron reached approximately 1.9 mg/L at which point yield started to decrease. This would result in a ‘moderately sensitive’ classification in Table 5.1 rather than ‘sensitive’. Similarly, El-Sheik *et al.*, (1971) studied squash, melon, cucumber, and corn in a sand culture experiment, with corn and cucumber showing some yield reductions at 4 mg/L (‘moderately tolerant’) whereas squash and melon did not.

Some of these plant species shown as sensitive in Table 5.1 (such as cowpea, onion, and garlic) have been re-examined in literature and in some cases found to be less sensitive. For example, several newer sand culture experiments were also performed in Riverside, California at the U.S. Salinity Laboratory by Francois from 1984 to 1992 and provided updated boron thresholds from the original Eaton (1944) dataset. Francois (1988) stated that these older Eaton studies were obtained from a small plant population, contained no treatment replication, and were often based on visual occurrence of leaf injury rather than yield reduction. Some of these updated studies have shown that the B concentration in soil water that produced the highest yield also exhibited leaf injury in some cases. Thus, leaf injury is not a reliable indicator of yield reduction, and the classifications from Eaton (1944), “which have continued to be perpetuated for lack of other data, have the tendency to lower the tolerance threshold” (Francois, 1989).

Table 5.4. Summary of Plant Species Thresholds, Slopes and Calculated IC_{25}s from Newer Sand Culture Experiments

Common Name	*Botanical Name*	Tolerance Based on	Threshold B (mg/L)	Slope (%/mg·L^{-1})	Calculated IC_{25} (mg/L)	Sensitivity Rating	Reference	Test Duration
Barley	*Hordeum vulgare*	Grain yield	3.4	4.4	9.1	moderately tolerant	Bingham *et al*., 1985	6 months
Bean, snap	*Phaseolous vulgaris*	Pod yield	1	12	3.1	sensitive	Francois, 1989	2.5 months
Broccoli	*Brassica oloracea* (Botrytis group)	Head fresh weight	1	1.8	14.9	moderately sensitive	Francois, 1986	3.5 months
Cauliflower	*Brassica oloracea* (Botrytis group)	Curd fresh weight	4	1.9	17.2	moderately tolerant	Francois, 1986	3.5 months
Celery	*Apium graveolens var. dulce* (Mill.) Pers	Petiole fresh weight	9.8	3.2	17.6	very tolerant	Francois, 1988	4.5 months
Cowpea	*Vigna unguiculata* Walp.	Seed yield	2.5	12	4.6	moderately tolerant	Francois, 1989	2-3 months
Garlic	*Allium sativum*	Bulb yield	4.3	2.7	13.6	tolerant	Francois, 1991	7.5 months
Lettuce	*Lactuca sativa*	Head fresh weight	1.3	1.7	16.0	moderately sensitive	Francois, 1988	3.5 months
Onion	*Allium cepa*	Bulb yield	8.9	1.9	22.1	very tolerant	Francois, 1991	7.5 months
Radish	*Raphanus sativus*	Root fresh weight	1	1.4	18.9	moderately sensitive	Francois, 1986	1.5 months
Sorghum	*Sorghum bicolor* Moench	Grain yield	7.4	4.7	12.7	very tolerant	Bingham *et al*., 1985	4 months
Squash, Scallop	*Cucurbita pepo* var melopepo Alef	Fruit yield	4.9	9.8	7.5	tolerant	Francois, 1992	1.5 months
Squash, Winter	*Cucurbita moschata* Poir	Fruit yield	1	4.3	6.8	moderately sensitive	Francois, 1992	3 months
Squash, zucchini	*Cucurbita pepo* var melopepo Alef	Fruit yield	2.7	5.2	7.5	moderately tolerant	Francois, 1992	1.5 months
Sugar beet	*Beta vulgaris*	Storage Root fresh weight	4.9	4.1	11.0	tolerant	Vlamis & Ulrich, 1973	1.5 months
Tomato	*Lycopersicon lycopersicum* Karst. Ex Farw.	Fruit yield	5.7	3.4	13.1	tolerant	Francois, 1984	3-4 months
Wheat	*Triticum aestivum*	Grain yield	0.75-1.0 [1]	3.3	8.3	sensitive	Bingham *et al*., 1985; Khudairi, 1961	6 months

Adapted from Maas and Grattan (1999)

[1] *Threshold from Khudairi 1961, slope from Bingham 1985*

From these updated experiments, three types of squash (Francois, 1992), garlic & onions (Francois, 1991), snap beans & cowpeas (Francois, 1989), lettuce & celery (Francois, 1988), broccoli, radish & cauliflower (Francois, 1986), and tomato (Francois, 1984) were all reported with boron thresholds and slopes. A summary of thresholds, slopes, and calculated IC_{25}s from these experiments are summarized in Table 5.4. IC_{25}s for these food-crops range from 3.1 mg/L for snap beans to 22.1 mg/L for onions. Note that this onion sensitivity is notably lower than was reported in Table 5.1. This table also includes various other updated sand culture experiments from other researchers, as shown in and adapted from sources such as Maas and Grattan, 1999 and Grieve *et al*, 2011.

Ornamental shrubs were also studied in Francois and Clark (1979), where young shrubs from a nursery were transplanted from their original containers to sand cultures and tested with irrigation boron concentrations of 0.5 mg/L (‘control’), 2.5 mg/L (‘low boron’), and 7.5 mg/L (‘high boron’). The experiment continued for approximately 3 years, with visual observations and growth evaluated at various times. A particular emphasis was placed on visual observations since appearance is particularly important for ornamentals. Species were classified as either ‘tolerant’, ‘semi-tolerant’, or ‘sensitive’, with the most sensitive species reported to be Oregon grape, photinia, xylosma, thorny elaeagnus, and others. These sensitive species showed varying degrees of visual effects at the 2.5 mg/L boron treatment, with more severe effects at 7.5 mg/L. In contrast, most of the ‘tolerant’ species (such as Japanese boxwood, oleander, Chinese hibiscus, Indian hawthorn, and natal plum) showed no effect at 2.5 mg/L and in some cases no effect at 7.5 mg/L. The ‘sensitive’ species from this study were later classified in Maas (1987) as ‘very sensitive’ with a threshold of <0.5 mg/L, though again this appears to be a conservative threshold likely to be safe. The actual thresholds are likely between 0.5 mg/L and 2.5 mg/L based on the raw data above, since no effects were reported in any of the control shrubs with 0.5 mg/L boron. It was also noted in this study that climatic conditions play an important role in boron tolerance, since the movement of boron into plant leaves is governed by transpiration. Thus, injury to plants would likely be reduced in cooler, wetter climates compared to the hot, dry climate in California where these tests were performed.

Results from several of the above studies for trees and other ornamental landscape plants are summarized in Wu and Dodge (1995). The study used a classification system for boron in irrigation water ranging from ‘sensitive’ (effects at 1-2 mg/L) to ‘highly tolerant’ (no effects at 6-10 mg/L). As reported in the original studies, fruit trees and certain ornamental shrubs were listed as most sensitive. Brown *et al.* (1998) performed boron toxicity tests on more than twenty ornamental species, primarily to evaluate visual toxicity symptoms in plants which produce polyols (sugar alcohols) compared to those which do not. Boron treatments of 0.5, 5, and 25 mg/L were applied once a week to plants growing in a potting mix, and clean irrigation water applied during the other days. The observed toxicity symptoms were useful for understanding the variability in symptoms between plant types and polyol effects; though no clear conclusions can be drawn regarding toxic thresholds due to unknown solution concentrations in the soil once adsorption, evaporation, and plant uptake are considered.

5.1.5 Plant Toxicity Studies in Soil

While sand culture experiments are generally based on solution concentrations in mg/L, toxicity tests are also frequently performed in soil with concentrations measured in mg/kg. For example, barley appeared sensitive in sandy soil in Gupta (1971), and was studied further in Riley (1987). Here, yield reductions of approximately 15-25% for shoots and roots were observed when 2 mg/kg B was added to soil (sand with 3.5% clay). Due to low sorption, this likely represents more than 5 mg/L soil solution boron based on regressions for sand such as in Section 5.3.2.

Since soil solution boron is difficult to directly measure, one option is to measure saturated paste boron as a proxy (potentially with corrections) for soil solution boron at field moisture conditions. As soil moisture is reduced to field conditions via evaporation, the equilibrium between dissolved boron and adsorbed boron serves as a type of buffer, and the increase in solution boron concentration is not as substantial as it would be for substances such as salts (eg, chloride) where adsorption processes are proportionally less significant (Jame *et al.*, 1982 and Gupta *et al.*, 1985). Soil solution boron at field moisture conditions is estimated to be approximately 15-30% higher than the saturated paste concentration for typical clay soils, a correction which is useful when comparing toxicity data from irrigation water to toxicity data from soil.

As an example of a toxicity study in soil, Keren *et al.* (1985a) evaluated the relative yield of wheat grown in soils of different clay contents with varying amounts of boron added to the soil. Figure 5.5 shows that the relationship between the total amount of available boron added to soil and plant toxicity and yield response is related to the soil clay content. Soils with higher clay content displayed less yield reduction than soils with lower clay content at equivalent soil boron additions, likely related to the increased boron adsorption capacity of clay soils.

Figure 5.6 shows the same % yield data, but relative to soil solution boron as measured by the saturated paste test and corrected to field moisture conditions. It can be seen that the yield responses are more consistent for the different soil types when expressed by soil solution boron (in mg/L) rather than total boron added to soil (in mg/kg). This supports the previously discussed tendency for plant toxicity to be determined largely by soil solution boron. This data is also consistent with Figure 5.4 in that it shows a similar slope for wheat yield of 3.5% per 1 mg/L compared to 3.3% per 1 mg/L. Thus, this data predicts a soil solution boron concentration of 2 mg/L could result in an approximate 7% reduction in wheat yield, assuming a negligible threshold value and uniform concentration over the root zone.

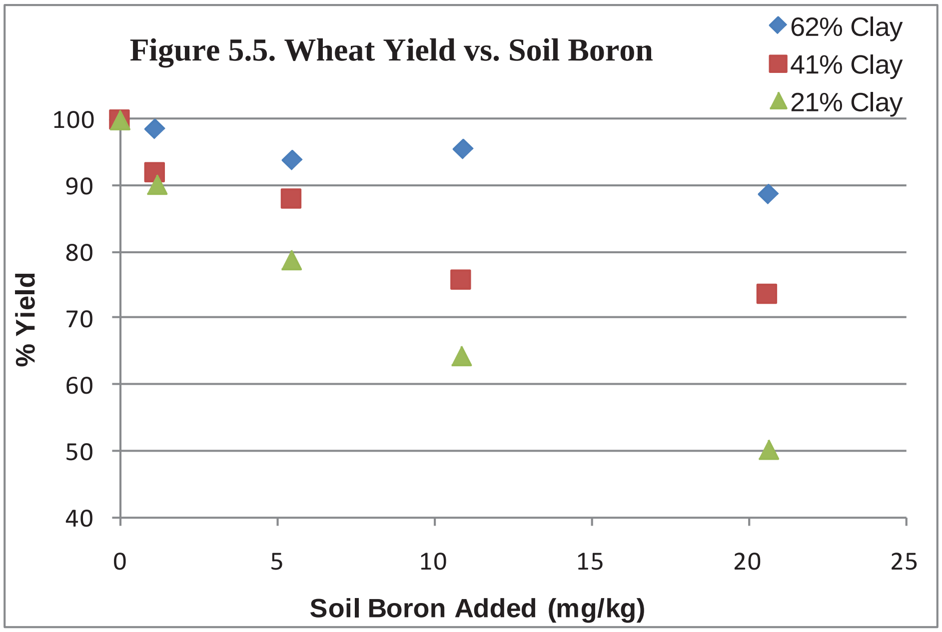


Figure 5.5. Wheat Yield vs. Soil Boron

Source: Keren et al., 1985a

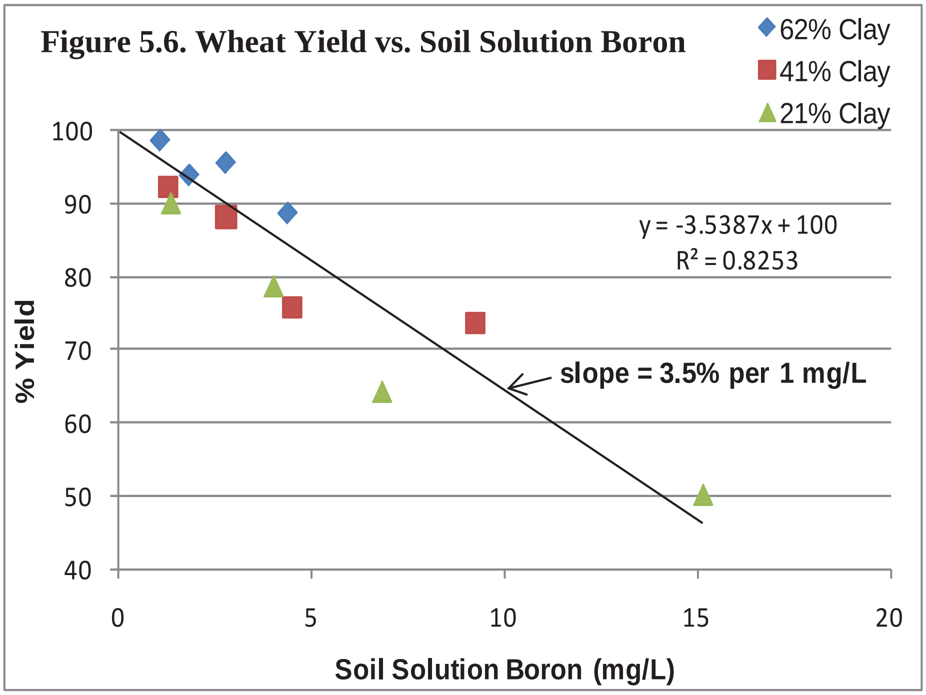


Figure 5.6. Wheat Yield vs. Soil Solution Boron

Source: Keren et al., 1985a

This finding that boron toxicity is affected by soil properties was also reported in John *et al.* (1977) where HWS boron concentrations alone were not sufficient to predict boron toxicity to spinach in different soil types, and soil properties also needed to be considered. Soil properties such as clay content and organic matter affect boron adsorption, with Hatcher *et al.*, (1959) studying beans in three different soil types and also demonstrating that plant toxicity is related primarily to dissolved boron and is not substantially influenced by sorbed boron. Thus, it has been concluded by a variety of sources that boron in soil solution, rather than adsorbed boron, primarily influences boron uptake and toxicity in plants (Keren *et al.*, 1985b).

For other possible influences on plant boron toxicity, Yermiyahu *et al.* (2008) reviewed the available literature regarding potential interactions of salinity and boron on plant growth. Different studies report conflicting results, such as Bingham *et al* (1987) showing salinity and boron to be independent stressors on wheat, whereas Ben-Gal and Shani (2002) showed a reduction in boron toxicity to tomato in the presence of additional salinity stress. Overall, Yermiyahu *et al.* (2008) concludes there appears to be a general trend of toxic effects being somewhat less severe for the combined boron and salinity than would be expected if these two factors were additive. One potential explanation is reduced boron uptake in the presence of chloride. For other interactions, Khan *et al.*, (2014) reported an increase in B toxicity at high sodium concentrations in maize, whereas N application alleviated B toxicity in rice (Koohkan and Maftoun, 2014).

5.2 Toxicity Data From Recent Alberta Research: Agricultural Species

To supplement this literature toxicity data, updated toxicity testing for plants was performed using standardized Environment Canada testing protocols. This involved using relevant Alberta reference soils and simultaneous measurements of HWS and saturated paste boron to further evaluate which test method provides better correlation with plant toxicity over a range of soil types. Methodology is described in Section 5.2.1, followed by test soil properties and spiking in Section 5.2.2, results and dose-response curves in Section 5.2.3, generation of IC_{25} values in Section 5.2.4, and a discussion of long-term growth in Section 5.2.5.

5.2.1 Methodology

The updated boron toxicity tests for agricultural plants were performed from 2011-2013 based on standard Environment Canada toxicity testing protocols (Environment Canada 2005, 2013). Tests were conducted on six Environment Canada standard agricultural plant test species including alfalfa, barley, carrot, durum wheat, northern wheatgrass and cucumber to provide a good cross-section of plant types and likely sensitivities. Tests were conducted on two field-collected reference soils from Alberta: a sandy loam and a clay loam to be representative of typical coarse and fine soils, respectively. Soils were spiked with boric acid (typically eleven to thirteen treatment levels), with resulting concentrations ranging from 0 to >400 mg/kg HWS B and corresponding saturated paste B from 0 to >300 mg/L depending on soil type. Ten replicates (test vessels) were typically used for each treatment level, with multiple seeds per vessel. Temperature, lighting, humidity, and soil moisture were also controlled. The test duration was typically two to three weeks depending on plant species. Table 5.5 provides a summary of the plant species and descriptions, including type of plant and life cycle as well as test duration. For context and method validation, tests were also conducted on artificial soils. Boron concentrations were measured in the soil and plant tissue, and the toxicological effect measured via four standard endpoints: shoot biomass, shoot length, root biomass, and root length. Further details of testing protocol are described in Environment Canada (2013).

Table 5.5. Agricultural Test Plant Species Properties

Species	Classification	Type	Test Duration	Life Cycle
Alfalfa	dicot	agricultural	21 days	perennial
Barley	monocot	agricultural	14 days	annual
Durum Wheat	monocot	agricultural	14 days	annual
Cucumber	dicot	market-garden	14 days	annual
Carrot	dicot	market-garden	21 days	biennial
Northern Wheatgrass	monocot	grasslands	21 days	annual/perennial

5.2.2 Test Soil Properties and Spiking

Table 5.6 summarizes soil textural and chemical properties of the agricultural reference soils including salinity, boron and nutrient levels (Exova, 2012). Test soils consist of a clay loam (32% clay), a sandy loam (18% clay) and an artificial soil (17.7% clay), with organic matter contents ranging from 3 % (sandy loam) to 10% (artificial soil). Salinity was low in all samples (maximum electrical conductivity (EC) of 0.89 dS/m and maximum sodium adsorption ratio (SAR) of 0.2), as well as low chloride and low sulfate (particularly in the field soils). Initial HWS boron concentrations ranged from 0.2 to 0.6 mg/kg HWS for the three soil types.

The artificial soil was formulated using standard methodology from Environment Canada (2007a), and consists of 70% sand, 20% clay, and 10% peat with pH adjusted to neutral by calcium carbonate. Though it is classified as a coarse ‘sandy loam’ via textural analysis, the presence of peat results in increased boron sorption and some behaviors more similar to a fine soil. This includes a relatively high saturation percentage, and corresponding high sorption when spiked with boron as described below.

The test soils were spiked with varying concentrations of boron (as boric acid) and analyzed using different extraction methods. Figure 5.7 shows resulting HWS (mg/kg) and saturated paste (mg/L) boron concentrations for the three soil types based on spiked B concentrations (mg/kg). The top part of Figure 5.7 shows HWS versus spiked B, with slopes of 0.75 to 0.89 indicating that the recovery of spiked B using the HWS extraction method is relatively high and consistent between the soil types. This is consistent with the HWS B extraction method measuring both the sorbed and dissolved boron fractions in soil, and indicates 75 to 89% of the spiked boron is recovered in these cases.

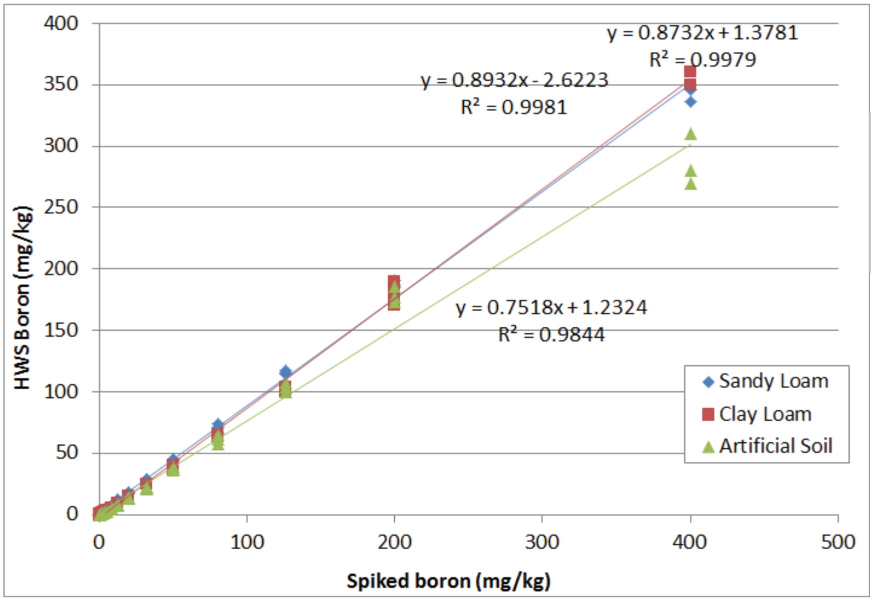
Table 5.6. Agricultural Reference Soil Properties

		Agricultural Reference Soils		
Test	**Parameter**	**Fine**	**Coarse**	**Artificial**
Hydrometer Analysis	Texture	Clay loam	Sandy loam	Sandy loam
	% sand	33.0	61.6	68.3
	% silt	35.0	20.4	14
	% clay	**32.0**	**18.0**	**17.7**
Sieve Analysis	% retained 75 um	32.0	60.1	77.4
	Coarse vs fine	**Fine**	**Coarse**	**Coarse**
Other texture related parameters	CEC (meq/100g)	19	16	18
	Organic matter (%)	**3.9**	**3.02**	**10.1**
	Saturation (%)	79	51	~100
Soil Chemistry	EC (dS/m)	0.51	0.26	0.89
	SAR	<0.1	<0.1	0.2
	Chloride (mg/kg)	7	7	21
	Sulfate (mg/kg)	12	11.4	354
	pH	7.4	5.8	7.2
	*SAE Boron (mg/kg)	10	4.0	1.0
	HWS Boron (mg/kg)	0.45	0.7	0.15
	Sat paste Boron (mg/L)	0.09	0.11	0.03
Soil Nutrients	Nitrate-N (mg/kg)	9	4	2
	Phosphorous (mg/kg)	<5	13	43
	Potassium (mg/kg)	287	364	46
	Ammonium-N (mg/kg)	0.4	0.6	34.8

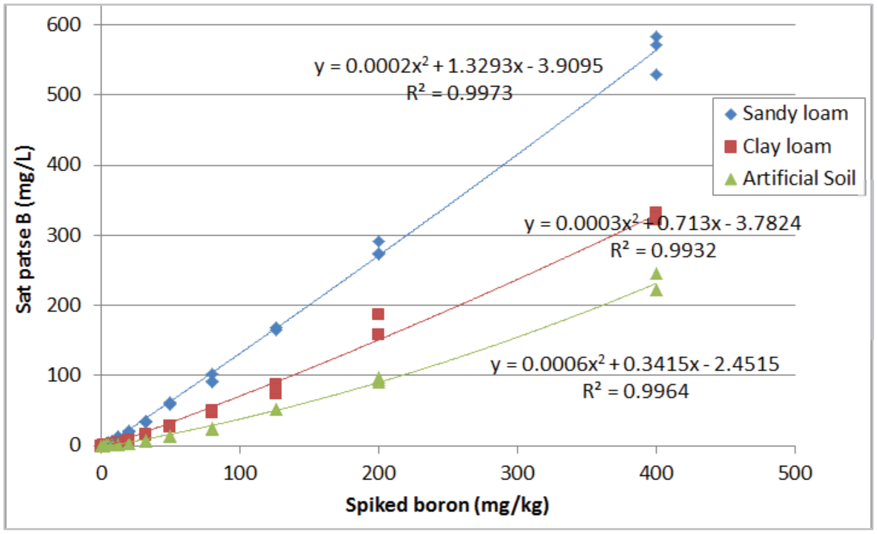
*__*SAE:*__ *Strong acid extractable*

The bottom part of Figure 5.7 shows saturated paste B (mg/L) versus spiked B, and illustrates a wider variability across the three soil types. The saturated paste extraction method measures the dissolved fraction of the boron pool, and results in lower recovery of the original spiked concentrations if expressed on a mg/kg basis. The different sorption properties of the three soil types thus results in different saturated paste boron on a mg/L basis, with the sandy loam showing the highest saturated paste boron (mg/L) for a given spiked B level. The clay loam and the artificial soil show increasing boron sorption, and resulting lower saturated paste concentrations in mg/L for a given spiked B level. On a mg/kg basis, the saturated paste boron test recovered between 59-65% of the spiked boron for the sandy loam, 41-56% for the clay loam, and 38-55% for artificial soil. Lowest recoveries were observed at the lowest spike levels.

Figure 5.7. HWS and Sat Paste Boron vs Spiked Boron in Agricultural Reference Soils



Approximate
% recovery
on a mass basis
(89% recovery)
(87% recovery)
(75% recovery)



Approximate
% recovery
on a mass basis
(59-65% recovery)
(41-56% recovery)
(38-55% recovery)

Figure 5.8 shows HWS B regressed with saturated paste B (mg/L) for the full range of boron spike levels. Differences in sorption properties between the three soil types are apparent, with artificial soil and clay loam showing the highest sorption (higher HWS B for given saturated paste B), and sandy loam showing the lowest sorption. The artificial soil shows more sorption than the fine clay loam here, likely due to the high boron sorption properties of the peat. The bottom part of the Figure shows a truncated set of the HWS B vs saturated paste B regression, focusing on the range of concentrations commonly seen in boron-impacted soils. The existing guideline of 2 mg/kg HWS boron corresponds to less than 0.5-1 mg/L saturated paste boron for all three soil types.

Figure 5.8. HWS vs Saturated Paste Boron for Spiked Agricultural Reference Soils

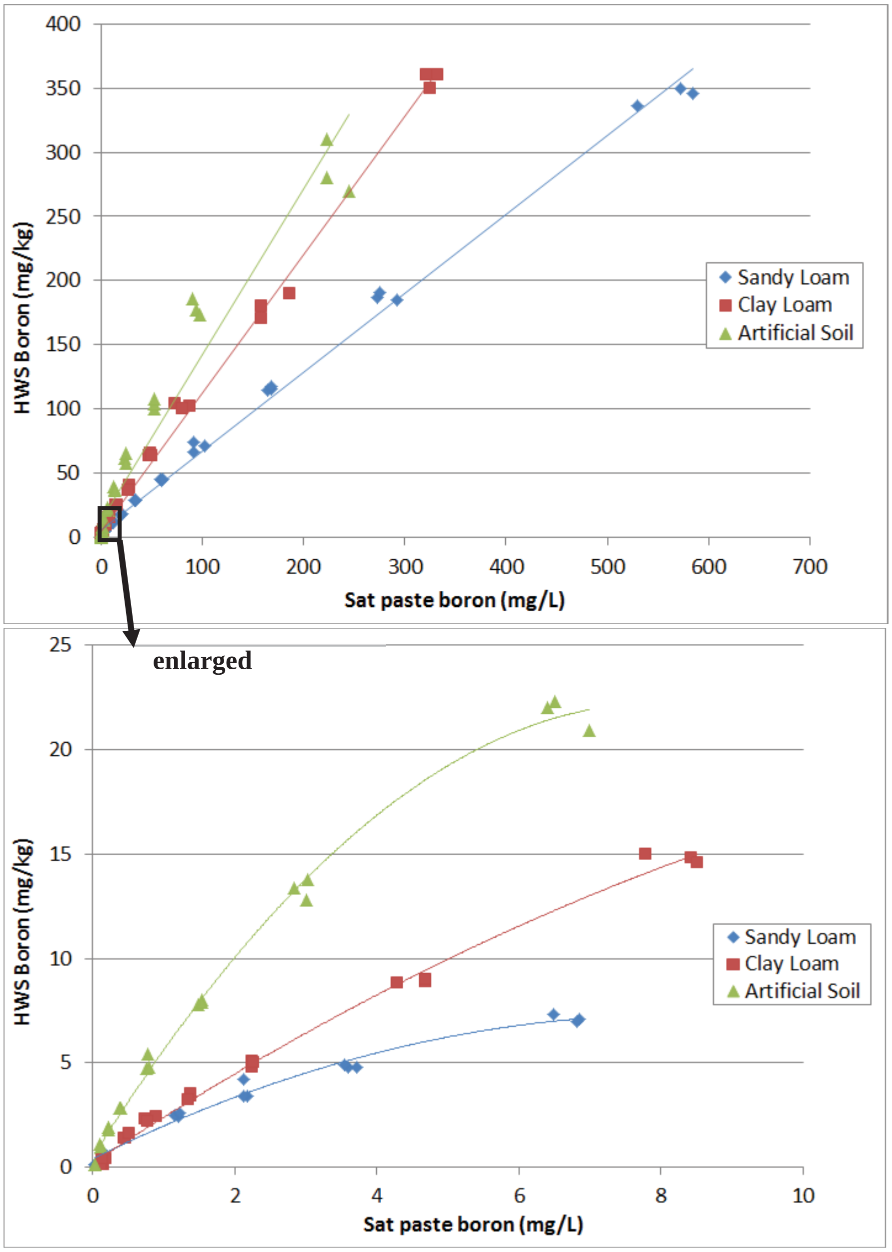
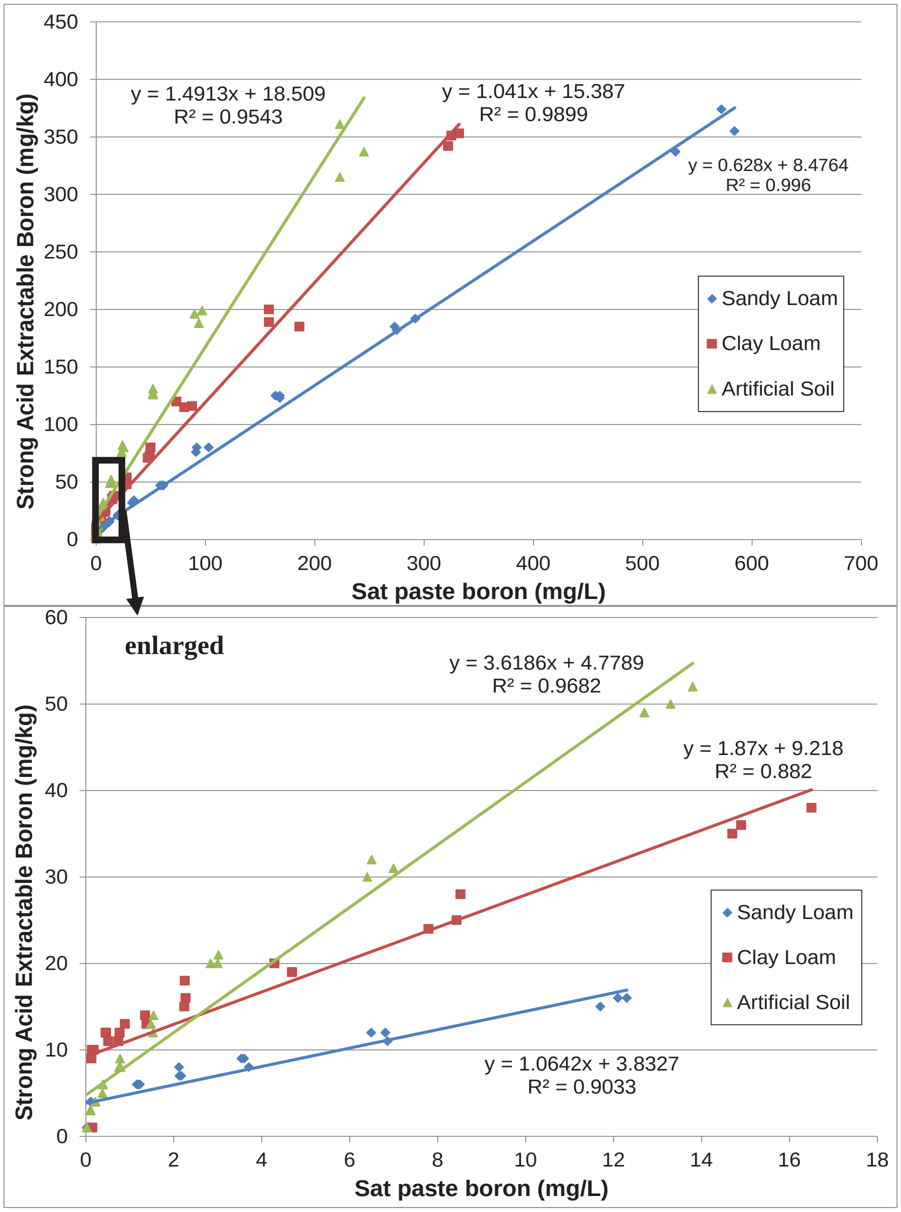


Figure 5.9 shows the regression of strong acid extractable boron (mg/kg) with saturated paste boron (mg/L) for the three soil types used for the agricultural experiments. Differences in sorption properties between the three soil types are again apparent, with artificial and clay loam soils more sorptive than the sandy loam (higher strong acid extractable B for given saturated paste B). This relationship is relevant to the soil ingestion pathways for humans, livestock, and wildlife due to the strong acidity of the gut. The bottom part of the figure shows a truncated dataset focussed on the practical range of concentrations more relevant to guideline derivation. Here, data corresponding to higher boron concentrations has been excluded and a new regression established. Of the two natural soil types, clay loam shows a higher strong acid extractable B for a given saturated paste B concentration (steeper slope and higher y-intercept), and is thus used as a basis for soil ingestion calculations in Section 9 and 10.

Figure 5.9. Strong Acid Digest vs Sat Paste Boron for Spiked Agricultural Reference Soils



5.2.3 Dose-Response Curves

The plant species were grown from seed in the spiked soils, with the various plant growth endpoints measured at test termination. Figures 5.10 and 5.11 show two typical endpoints, root length (left) and shoot biomass (right), for cucumber, which is a relatively sensitive species. Both HWS (top) and sat paste (bottom) data are plotted for all three test soils. The error bars represent the standard deviation and illustrate the inherent variability of plant toxicity tests, with these tests employing a high level of replication (n up to 10 in many cases). Figures 5.12 and 5.13 show the same endpoints with the responses (averaged by replicates) normalized to be a percentage relative to the control (baseline). Expressing the data as a percentage of the control allows for comparison between tests since other non-contaminant factors such as soil texture can affect growth differently for different plant species. Cucumber responses differ in magnitude between the three soil types when measured in terms of HWS B (top), with less difference between soil types observed on a saturated paste basis in mg/L (bottom). This suggests saturated paste boron is less influenced by soil texture than HWS boron when predicting plant toxicity, a result consistent with previous literature results.

As examples of other species and endpoints, barley root length data and carrot shoot length are shown in Figures 5.14 and 5.15 respectively. Carrot appears more sensitive than barley based on these figures, both in terms of HWS and saturated paste B. Similar general trends are seen in these two species as is observed for cucumber in that toxicity is similar across soil textures when boron is measured by saturated paste than as HWS B.

Figures 5.16 through 5.19 present the normalized response curves for the two field reference soils for all four endpoints (shoot biomass, root biomass, shoot length, and root length), respectively. All six plant species are shown on each figure, with clay loam responses on the left and sandy loam responses on the right. HWS B data are presented on the top, and saturated paste B results on the bottom for each given endpoint. Of the six species tested, carrot and cucumber are generally the most sensitive while barley and alfalfa are generally the least sensitive. Root endpoints are generally more sensitive than shoot endpoints across all species tested. Normalized plant responses (% control) rarely fall below 75% (IC_{25}) at HWS B concentrations lower than approximately 10 mg/kg or saturated paste concentrations below 4 mg/L. Tabulated response data is shown in more detail in (AEP, 2015), and IC_{25}s are further discussed in Section 5.2.4 below.

In some cases, an increase in boron concentration is correlated with increased plant biomass or length relative to the control, deemed a stimulation or hormetic effect. Examples of apparent stimulation effects can be seen in Figure 5.16 in which shoot biomass increases for species such as barley and alfalfa in sandy loam as boron concentration increases up to approximately 2 to 3 mg/L saturated paste B. Barley shoot biomass also shows apparent stimulation in clay loam in Figure 5.16, with maximum growth observed at approximately 4 mg/L saturated paste boron. Other examples are visible in Figure 5.19 in which root length indicates a stimulation effect for durum wheat in clay loam and alfalfa and carrot in sandy loam. The presence of potential stimulation effects suggests boron deficiency is possible for some plants in these typical reference soils.

Figure 5.10. Example Response: Cucumber Root Length

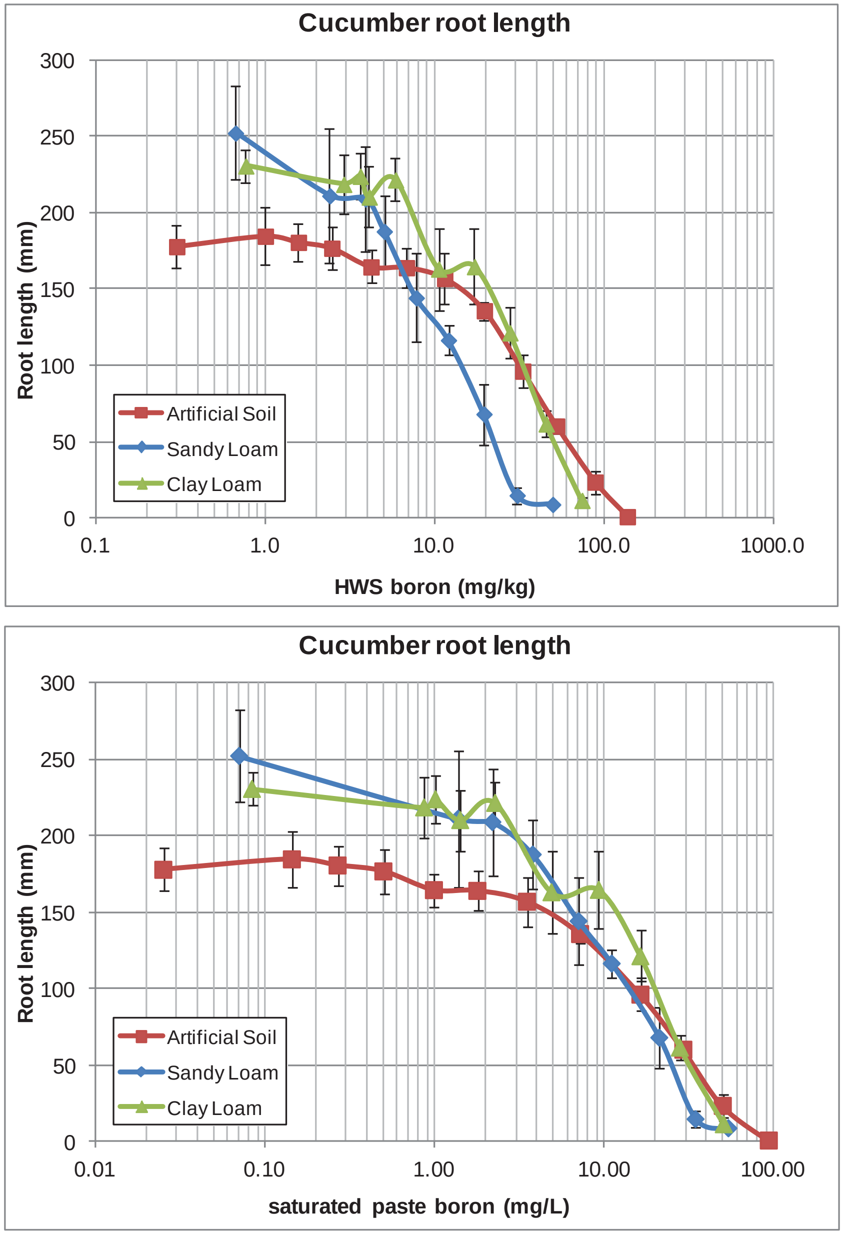


Figure 5.11. Example Response: Cucumber Shoot Biomass

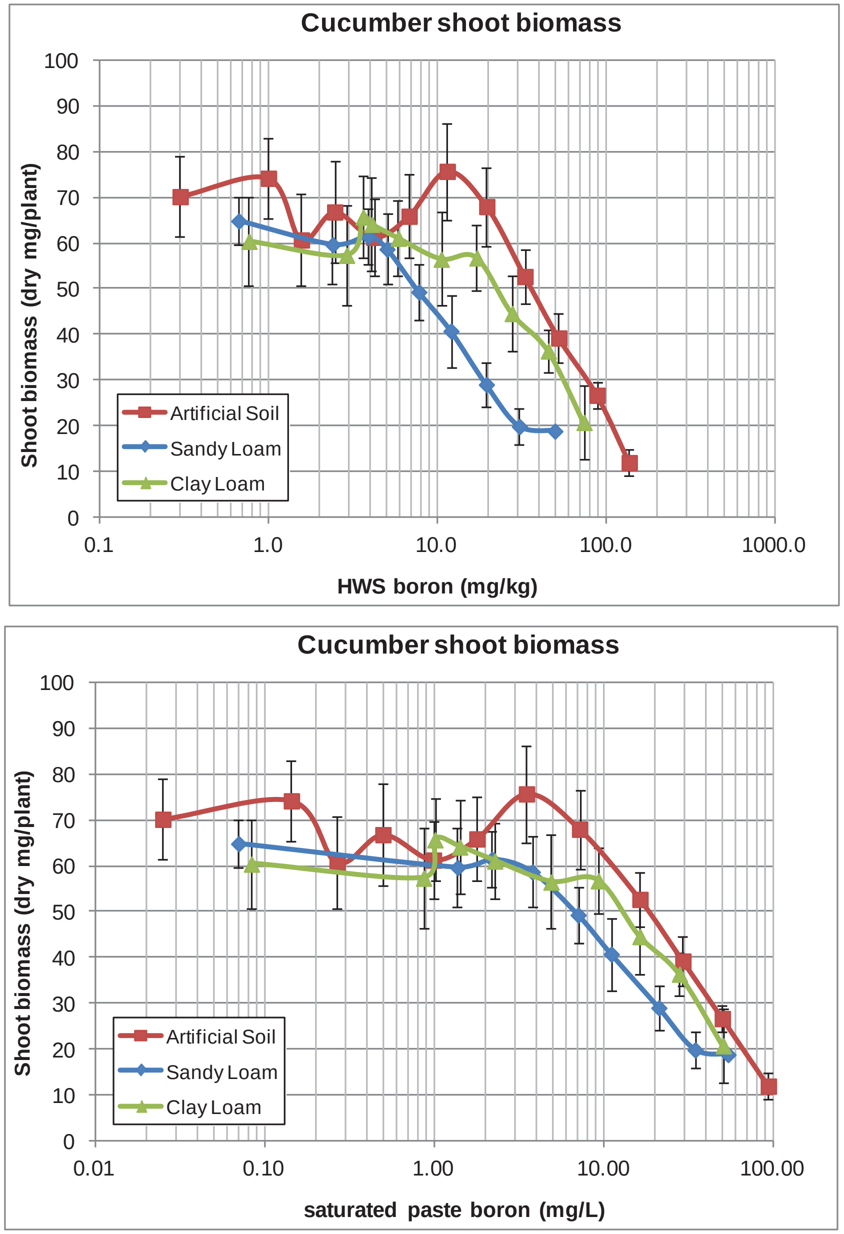


Figure 5.12. Normalized Cucumber Root Length

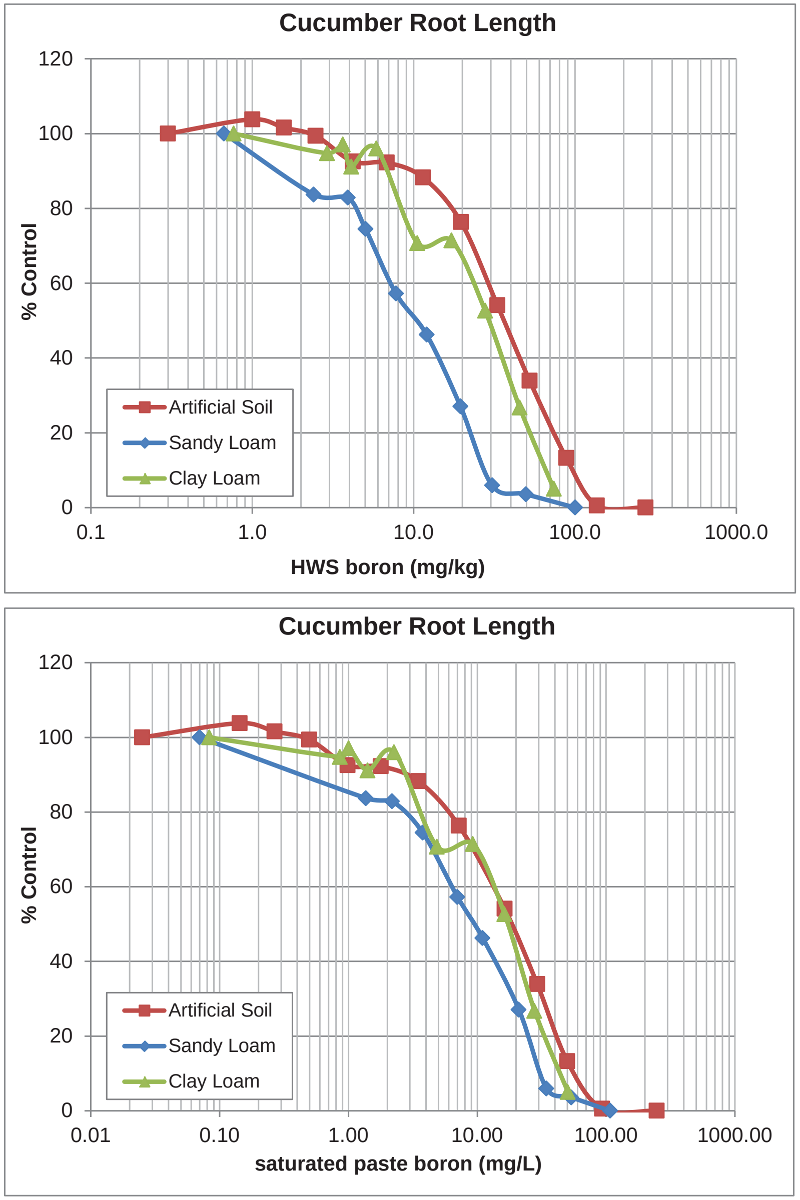


Figure 5.13. Normalized Cucumber Shoot Biomass

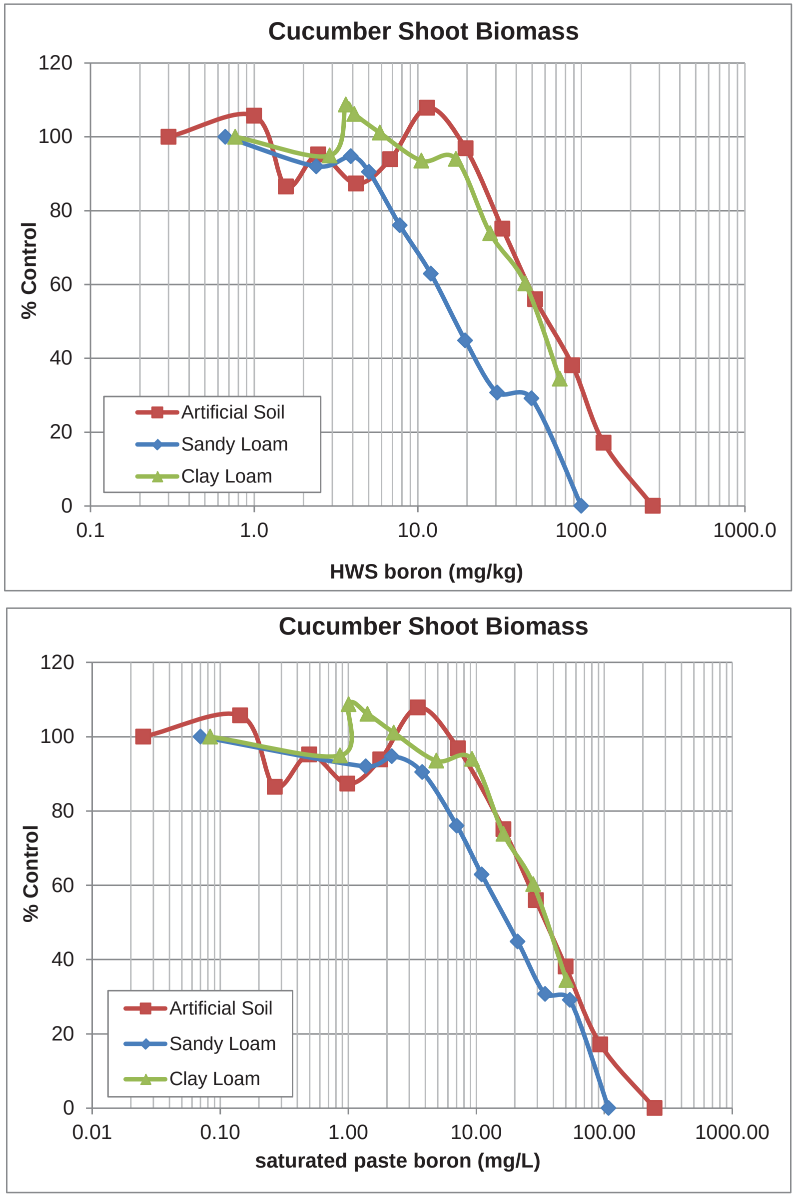


Figure 5.14. Normalized Barley Root Length

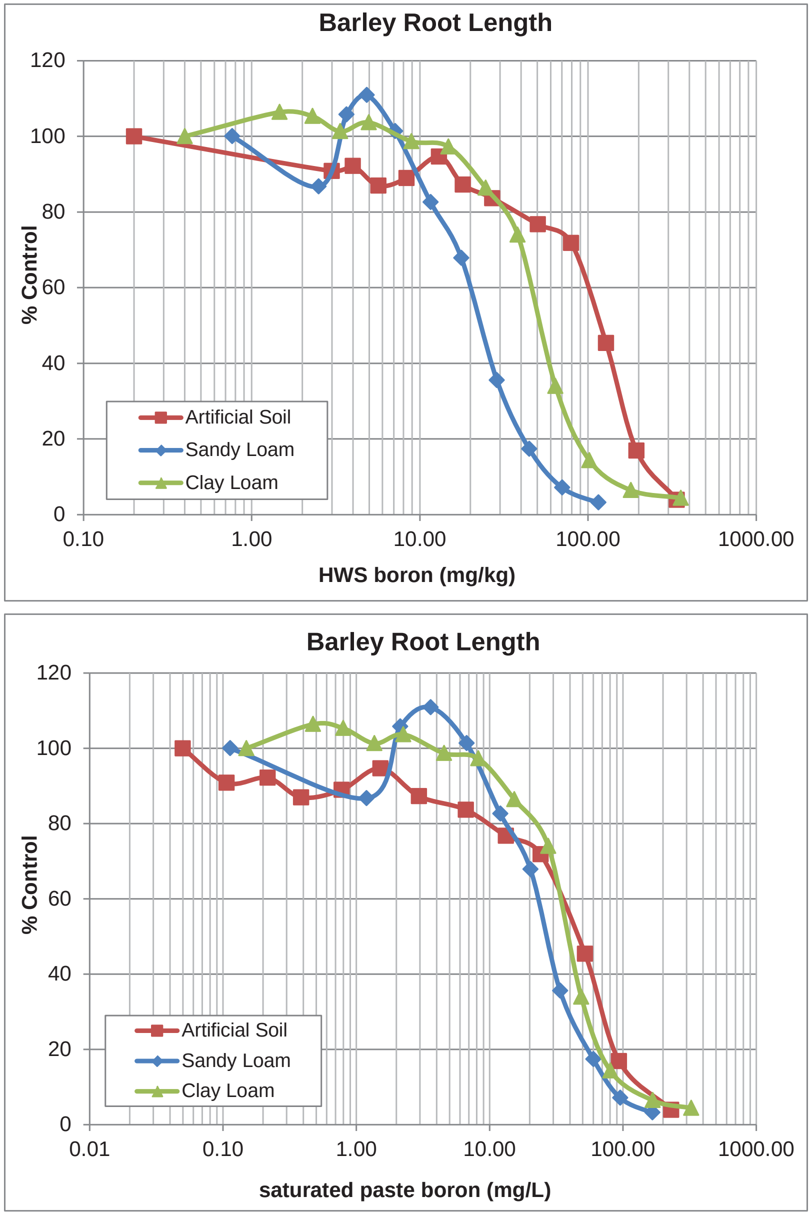


Figure 5.15. Normalized Carrot Shoot Length

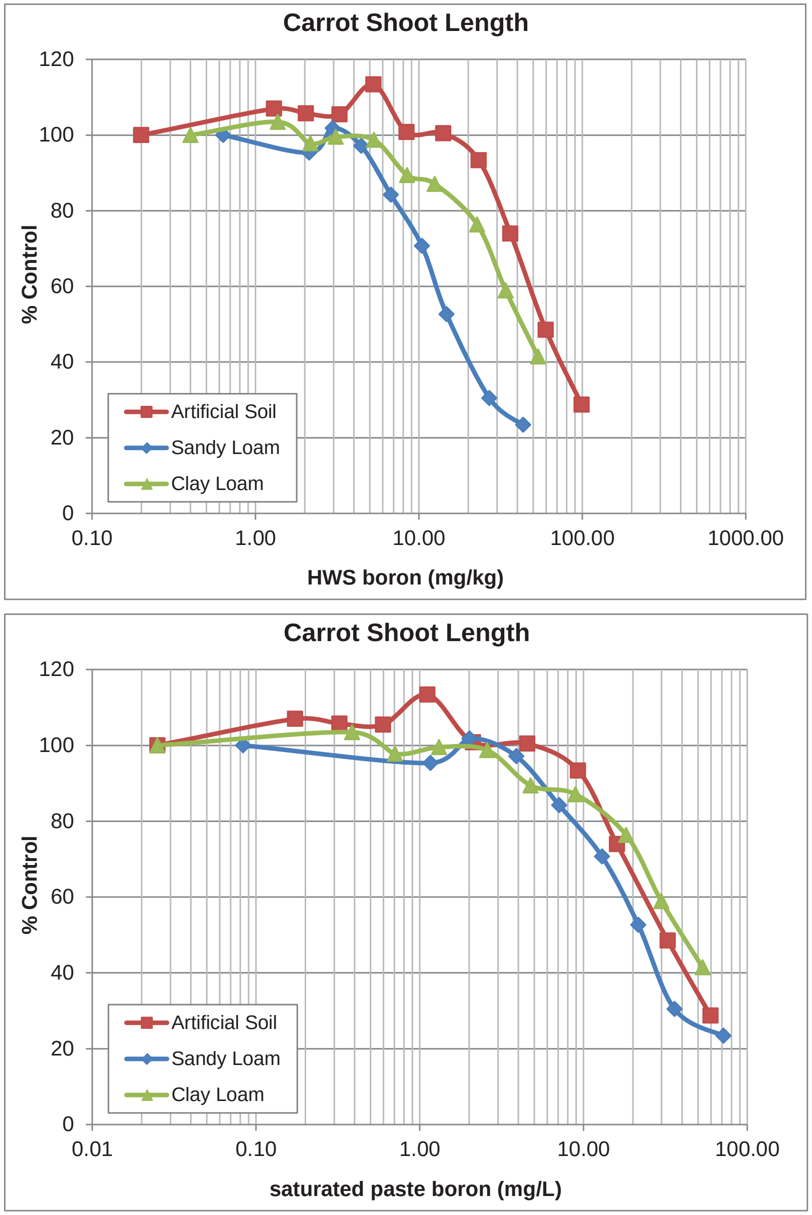


Figure 5.16. Six Agricultural Species in Clay Loam and Sandy Loam: Shoot Biomass

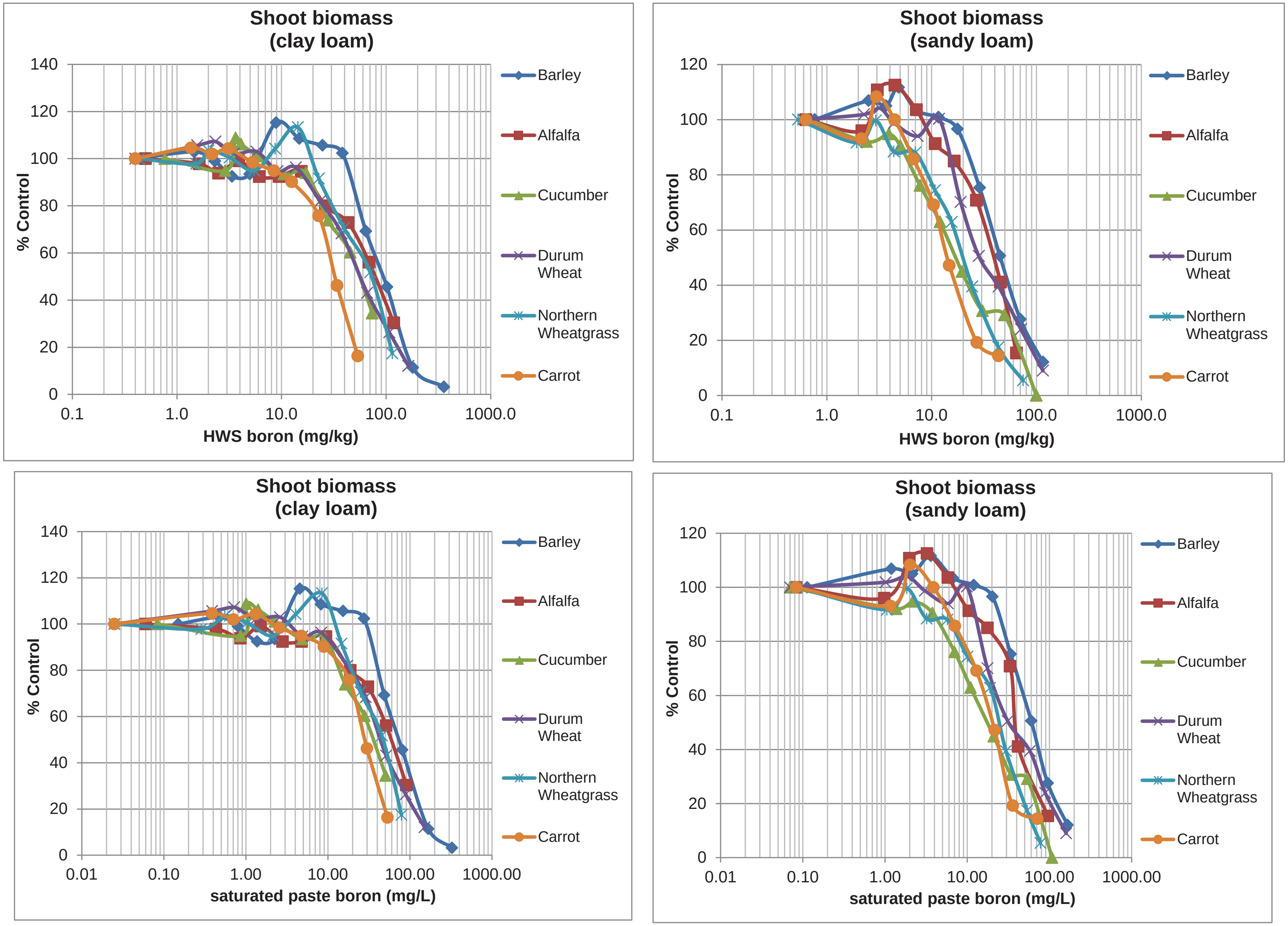


Figure 5.17. Six Agricultural Species in Clay Loam and Sandy Loam: Root Biomass

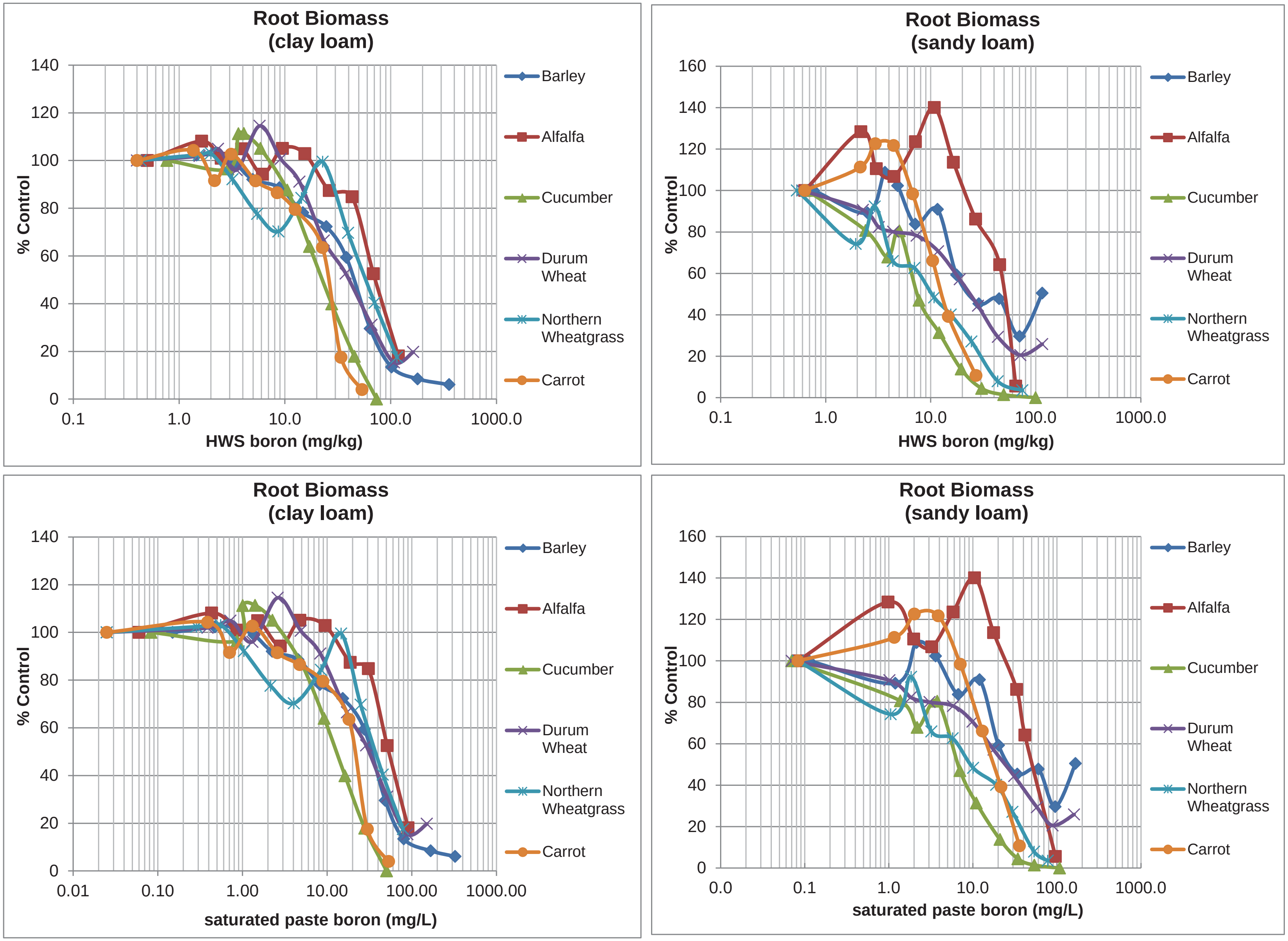


Figure 5.18. Six Agricultural Species in Clay Loam and Sandy Loam: Shoot Length

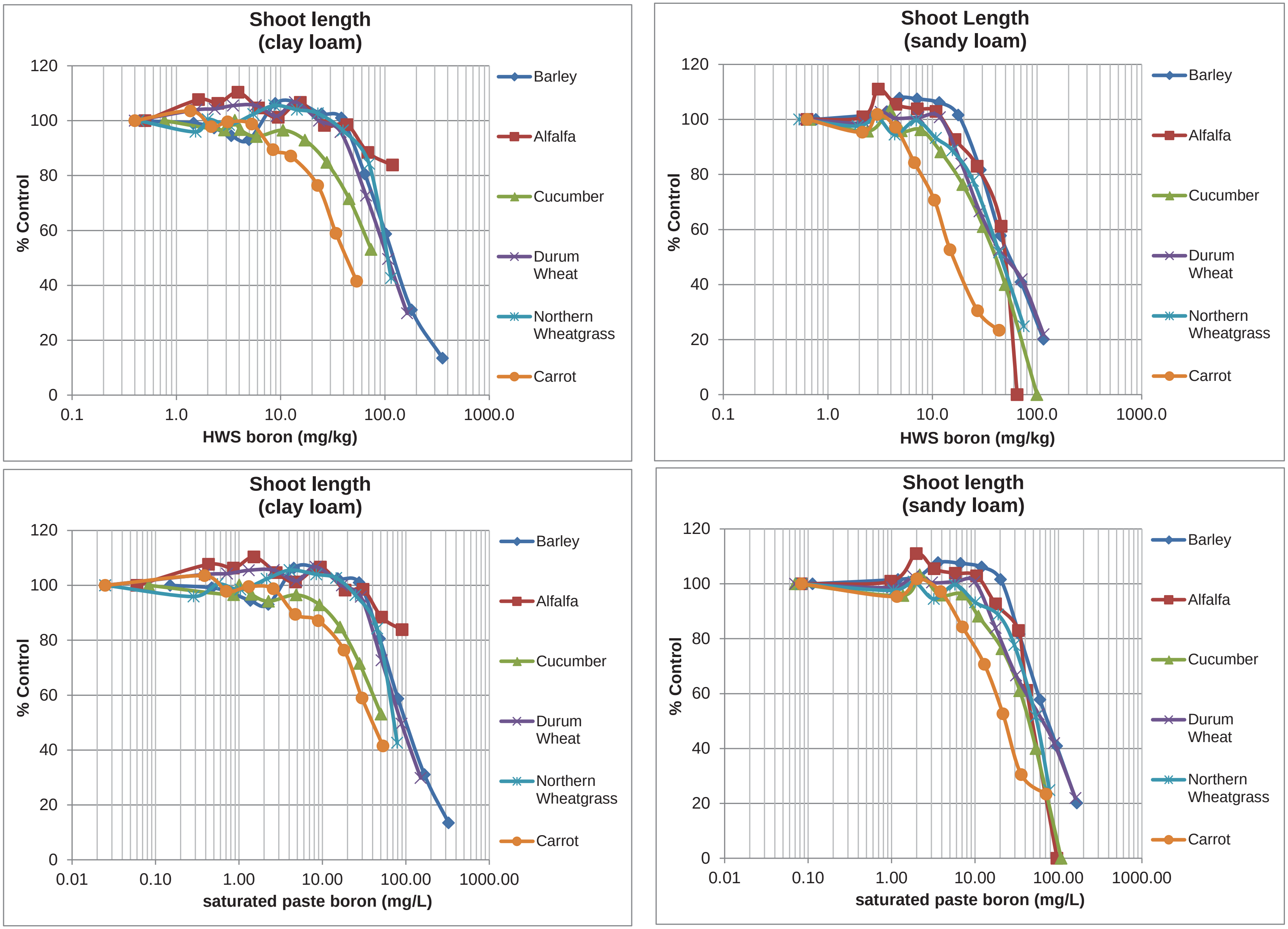
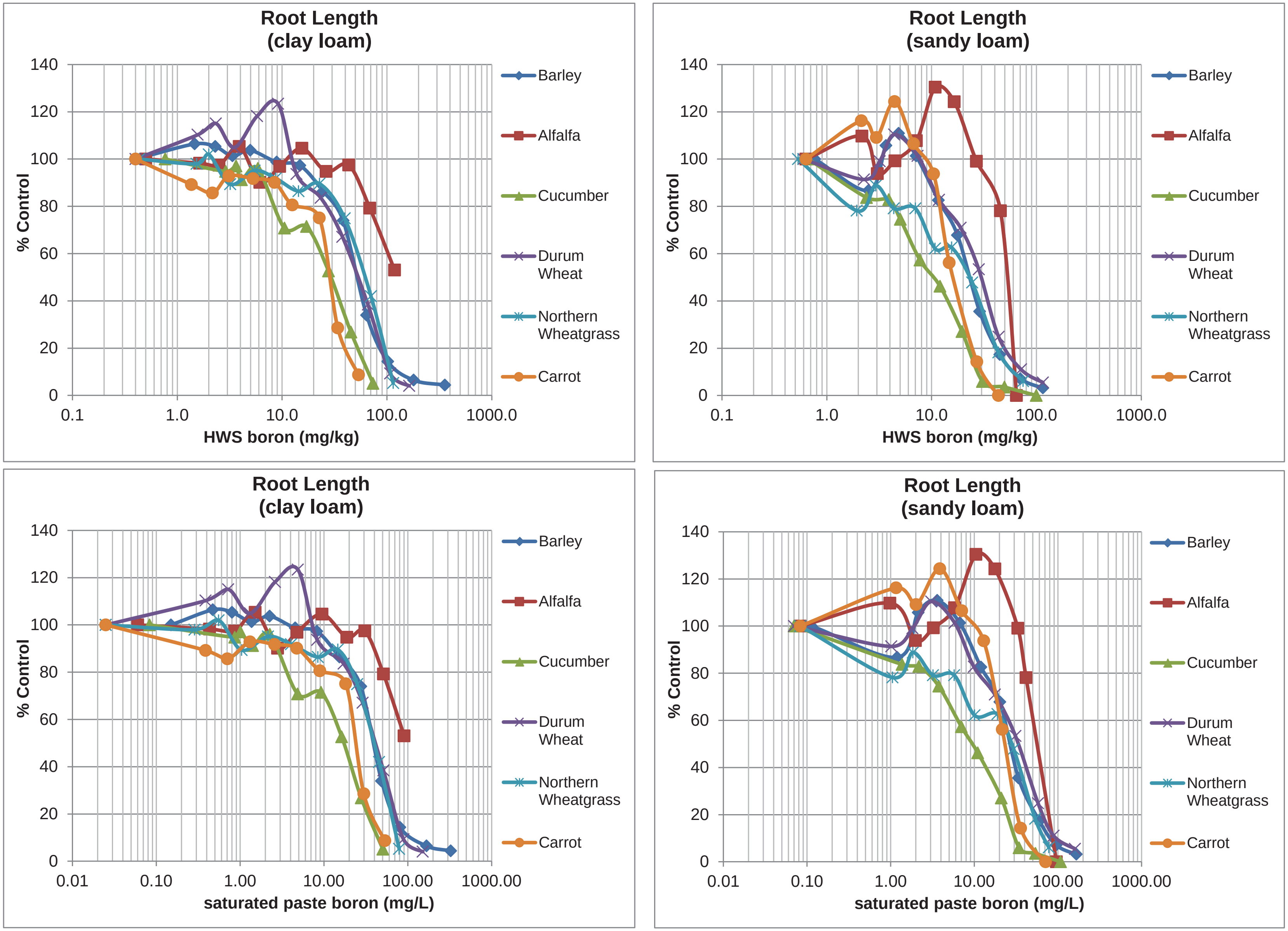


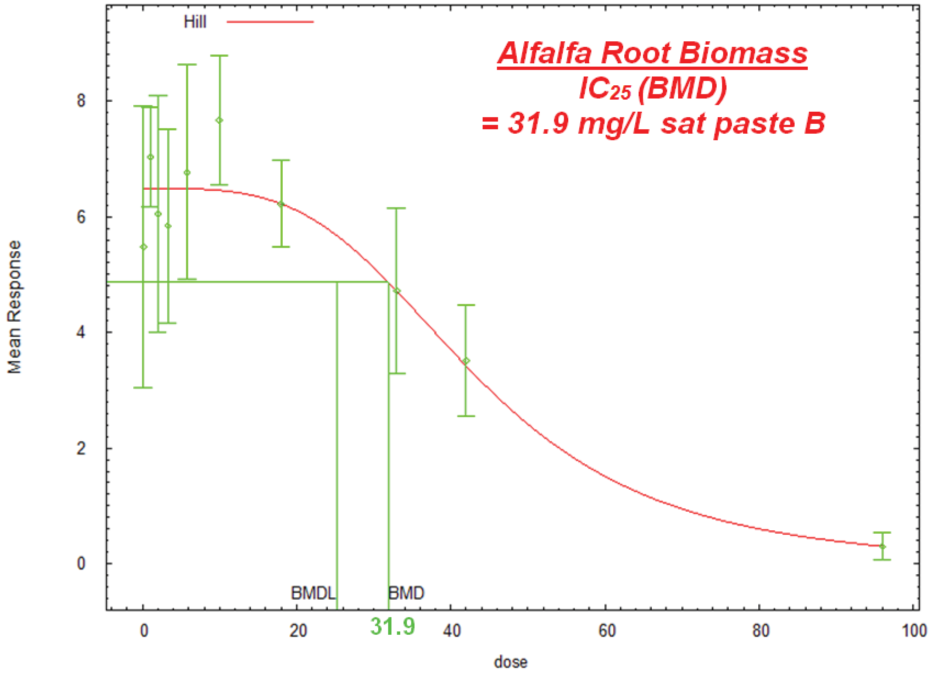
Figure 5.19. Six Agricultural Species in Clay Loam and Sandy Loam: Root Length



5.2.4 IC_{25} Estimation

The soil concentration (expressed on a mg boron /L saturated paste extract basis) at which a 25% reduction in measurable plant endpoints is observed (compared to controls) was estimated using Benchmark Dose Software (BMDS) (US EPA, 2014). This is referred to as an IC_{25}, and is a typical endpoint used for deriving soil guidelines (CCME, 2006). The continuous Hill model was used to plot the data and derive IC_{25} values, a model which fits data to a dose-response curve which typically involves an initial threshold below which toxic effects are not seen, and then a reduction in growth as concentrations increase further. An example is shown in Figure 5.20 for alfalfa root biomass. The raw data (green) is shown as averages with error bars, and the best fit Hill model shown as a red line. The IC_{25} is derived at 75% of the modeled baseline response, with the benchmark dose (BMD, or IC_{25}) shown here as 31.9 mg/L saturated paste boron.

Figure 5.20. Example BMDS IC_{25} Plot – Alfalfa (Root Biomass) in Sandy Loam Soil



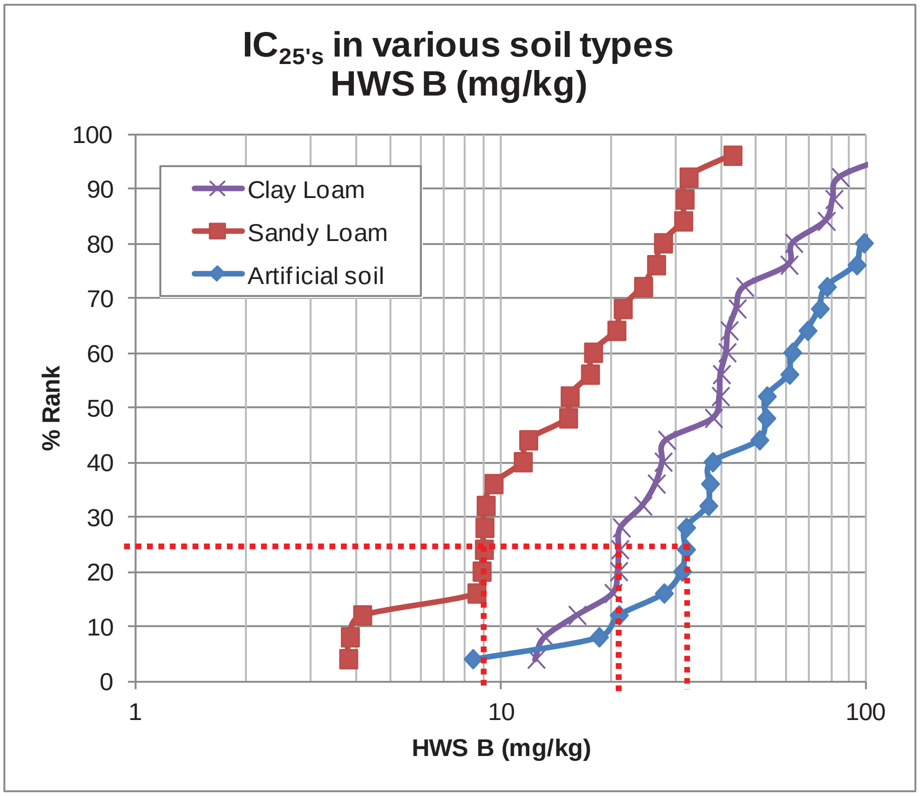
BMDS curves and IC_{25}'s for all agricultural species, endpoints, and soil types are provided in AEP (2015), including lower 95% confidence intervals. Table 5.7 summarizes the IC_{25} results for the four endpoints, six plant species, and three soil types tested. The saturated paste B IC_{25} values range from 2.61 mg/L (cucumber root biomass – sandy loam) to 92.76 mg/L (alfalfa shoot length – clay loam). Root endpoints were generally more sensitive than their shoot counterparts within each given plant species. The geometric mean of the resulting IC_{25} values of the two shoot and two root endpoints for each test are also shown since these pairs of endpoints (e.g., shoot biomass and shoot length) are often highly correlated.

As noted in Section 5.2.3 above, a stimulation / hormetic effect is apparent in some endpoints/species. Though hormetic models can be used to model such effects, the Hill model (which does not include hormesis) was used exclusively during this analysis for consistency. Hormetic models fit the data to a lower baseline followed by an increase due to stimulation followed by a decrease due to toxicity (baseline defined by the lowest dose response as per Schwarz (2013)). By comparison, the Hill model places the baseline within the range of responses measured along the first few boron doses, which typically results in a higher baseline in datasets which have hormesis. This results in the IC_{25} occurring at higher growth levels, and thus a reduced IC_{25} boron concentration. Thus, the use of the Hill model is considered conservative for datasets which have hormesis and was thus used for all datasets.

Table 5.7. Agricultural Plant Saturated Paste Boron IC_{25}s (Exova, 2011-2013)

Species	Endpoint	saturated paste B (mg/L) IC_{25}		
		sandy loam	**clay loam**	**artificial soil**
Alfalfa	Shoot biomass	23.88	29.52	69.41
Alfalfa	Root biomass	31.9	33.6	25.48
Alfalfa	Shoot length	32.55	92.76	40.25
Alfalfa	Root length	40.4	63.3	51.22
geometric mean shoots		**27.9**	**52.3**	**52.9**
geometric mean roots		**35.9**	**46.1**	**36.1**
Barley	Shoot biomass	32.8	47.1	34.07
Barley	Root biomass	15.99	12.35	8.88
Barley	Shoot length	39.61	59.64	69.63
Barley	Root length	15.52	25.1	23.82
geometric mean shoots		**36.0**	**53.0**	**48.7**
geometric mean roots		**15.8**	**17.6**	**14.5**
Carrot	Shoot biomass	11.14	16.09	13.46
Carrot	Root biomass	11.64	11.65	11.57
Carrot	Shoot length	11.3	16.59	13.88
Carrot	Root length	15.35	19.6	16.91
geometric mean shoots		**11.2**	**16.3**	**13.7**
geometric mean roots		**13.4**	**15.1**	**14.0**
Durum Wheat	Shoot biomass	15.2	20.12	32.28
Durum Wheat	Root biomass	7.84	13.99	8.45
Durum Wheat	Shoot length	25.91	47.4	50.42
Durum Wheat	Root length	16.5	22.3	15.93
geometric mean shoots		**19.8**	**30.9**	**40.3**
geometric mean roots		**11.4**	**17.7**	**11.6**
Northern Wheatgrass	Shoot biomass	11.55	26.12	39.62
Northern Wheatgrass	Root biomass	4.15	28.3	26.16
Northern Wheatgrass	Shoot length	33.59	53.18	59.62
Northern Wheatgrass	Root length	12.34	27.1	24.88
geometric mean shoots		**19.7**	**37.3**	**48.6**
geometric mean roots		**7.2**	**27.7**	**25.5**
cucumber	Shoot biomass	7.81	16.23	18.39
cucumber	Root biomass	2.61	6.43	3.85
cucumber	Shoot length	21.71	25.85	34.36
cucumber	Root length	3.89	6.64	7.11
geometric mean shoots		**13.0**	**20.5**	**25.1**
geometric mean roots		**3.2**	**6.5**	**5.2**

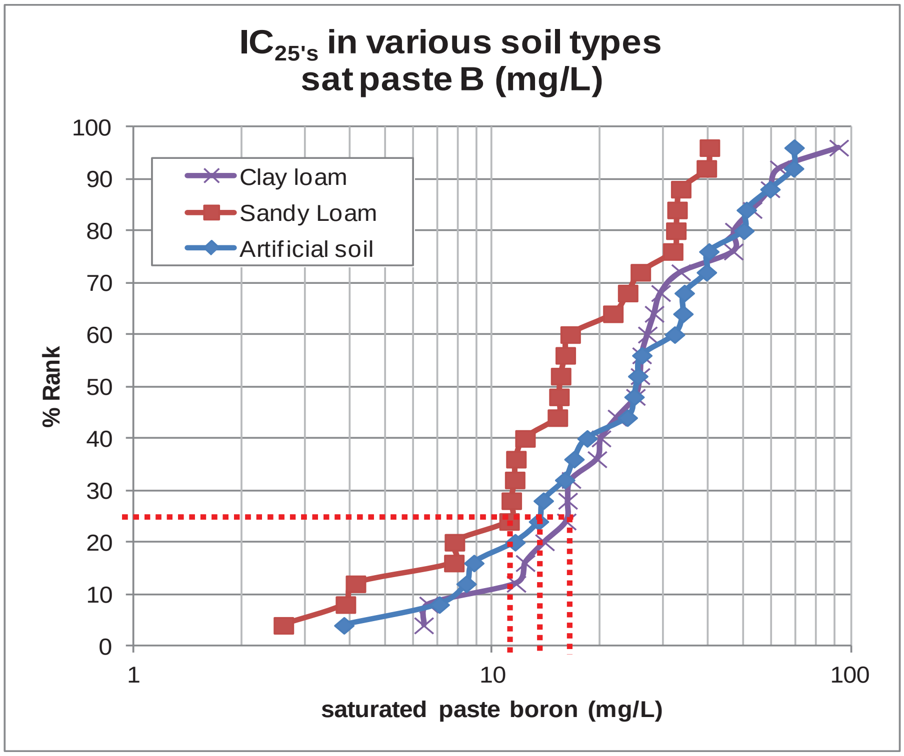
Figure 5.21. Agricultural Plant SSD’s (HWS Boron) from Exova Tests



Each datapoint represents one of 4 endpoints for one of 6 plant species plotted in rank order (*e.g.*, cucumber root biomass is most sensitive datapoint for each soil type)

<u>25th percentile:</u>
8.9 - 32
mg/kg HWS

Figure 5.22. Agricultural Plant SSD’s (sat paste boron) from Exova Tests



Each datapoint represents one of 4 endpoints for one of 6 plant species plotted in rank order (*e.g.*, cucumber root biomass is most sensitive datapoint for each soil type)

<u>25th percentile:</u>
11.2 - 16.1
mg/L sat paste

The IC_{25} values are plotted as Species Sensitivity Distributions (SSD's) to illustrate their range across clay loam, sandy loam and artificial soils in terms of HWS boron (Figure 5.21) and saturated paste boron (Figure 5.22). Each curve thus has 24 datapoints based on four plant endpoints for each of the six species. The HWS dataset illustrates a wider IC_{25} range across the three soil types, while the saturated paste data (in mg/L) shows more consistency across the three soils (Equilibrium Environmental, 2014a).

25th percentiles from SSD's are used for agricultural guideline development and are also shown on Figures 5.21 and 5.22 for initial context. On an HWS basis, they range from 8.9 to 32 mg/kg HWS for the three soil types (a 3.6-fold range), with the lowest value for sandy loam and the highest value for artificial soil. On a saturated paste boron basis, the 25th percentiles range from 11.2 to 16.1 mg/L, representing a 1.4-fold range and thus demonstrating improved toxicity correlation across soil types for the saturated paste boron test. Data for invertebrates and additional literature data for plants are also added to these SSD's in Section 9 where overall guidelines for soil dependent biota are derived.

5.2.5 Long-Term Growth Experiments

For some additional insight into long-term growth, an 11-week long-term cucumber toxicity test was conducted by Exova in clay loam soil since cucumber appeared to be the most sensitive of the six agricultural species. The Environment Canada standard toxicity tests are of shorter duration (2 – 3 weeks), and thus this longer-term test involved non-standard, non-validated experimental protocol due to additional new factors such as larger plant shoot size, nutrient requirement issues, and root restriction issues. Results are thus not considered directly comparable to the short-term tests, and primarily provide some additional context for long term growth. Though these values are considered to have substantial uncertainty due to methodology issues in the long-term test, the resulting cucumber shoot biomass IC_{25} for saturated paste boron was estimated to be 4.53 mg/L using BMDS, and the shoot length IC_{25} was estimated to be 3.79 mg/L with a geometric mean of 4.14 mg/L for the overall cucumber shoot endpoint. The root endpoints did not yield conclusive results due to substantial root-balling and issues related to separating the fine roots from soil. Visually, cucumber growth was generally good and flowering was observed except at high doses (Equilibrium, 2013a). In order to include these long term cucumber toxicity results into the cumulative dataset without over-weighting cucumbers relative to other species, a geometric mean was calculated for the non-standard long-term shoot IC_{25} from this test combined with the standard shorter-term cucumber shoot results when deriving an overall soil-dependent biota guideline in Section 9.

Long term boron toxicity demonstrations have also previously been carried out in Alberta in separate studies over 6 weeks in greenhouse experiments and 13 weeks in field experiments (Equilibrium, 2009b). Durum wheat, carrot, red clover, red fescue, blue gramma grass, Kentucky bluegrass and strawberry were tested in field soils at five HWS boron levels of approximately 0.2, 2.5, 5.8, 12.8 and 56.8 mg/kg. Of the five boron levels, the maximum growth was observed at 5.8 mg/kg and 12.8 mg/kg HWS B (treatments 3 and 4). At lower concentrations (treatments 1 and 2), growth was somewhat lower potentially due to boron deficiency. At the highest dose (treatment 5), growth was substantially reduced or non-existent indicating substantial toxicity. These HWS B doses associated with maximum growth were associated with saturated paste B concentrations of 3.8 mg/L and 9.2 mg/L. Good growth through the entire plant life-cycle was observed during these long-term tests, including the generation of full strawberries, carrots, and wheat seeds. Overall, these long-term field and greenhouse tests are consistent with the Exova long-term cucumber test in terms of showing good growth being possible through the entire plant life cycle at concentrations substantially above the existing Tier 1 guideline.

5.2.6 Vegetation Boron

As primary producers, plants take up boron from soil solution through their roots and transfer it into vegetation tissue. Animals consuming plant tissue may thus be exposed to concentrations of boron which are higher than soil concentrations through a process of bio-concentration. As such, understanding how boron is concentrated in plant tissues is important in establishing guidelines for wildlife and livestock exposure to food.

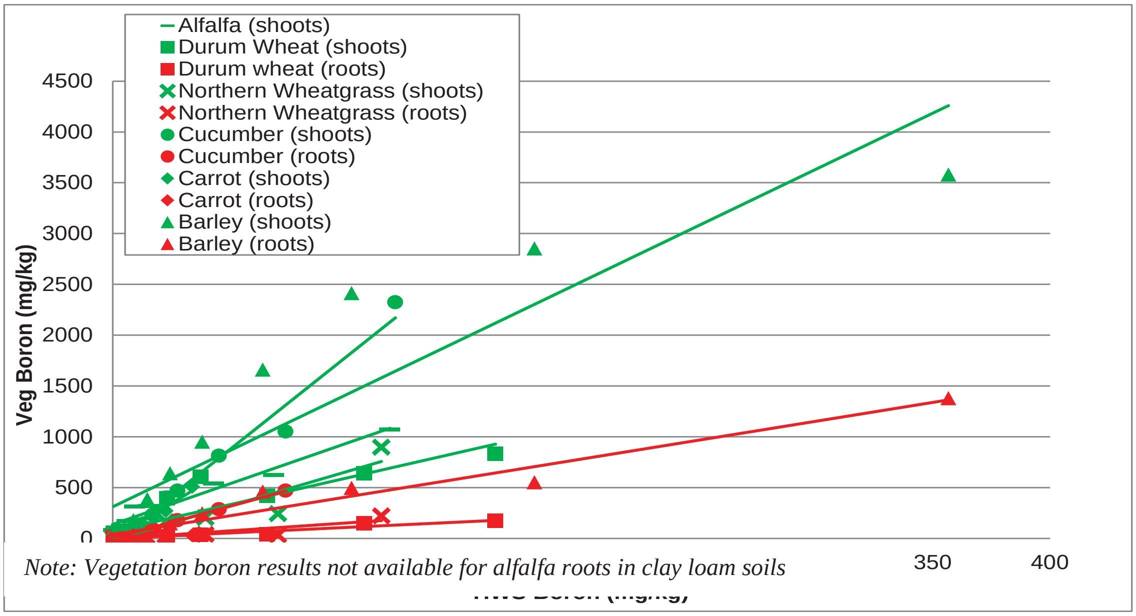
The relationship between soil boron concentrations and the concentration of boron in plant tissue was examined in both coarse (sandy loam) and fine (clay loam) soils for each of the six agricultural test species discussed in previous sections. Vegetation boron concentrations were measured for both shoot and root tissue using strong acid digestion techniques described in Section 2.5.5.

Bioconcentration factors (BCF's) are typically expressed as vegetation concentrations divided by soil concentrations, with both typically on a mg/kg basis (CCME, 2006). As such, bioconcentration relationships between soil boron in HWS (mg/kg) and vegetation boron (mg/kg) are shown in Figures 5.23 and 5.24 from the previously described toxicity testing on agricultural species. Six plant species were tested including alfalfa, durum wheat, northern wheatgrass, cucumber, carrot and barley in both root and shoot tissue. These figures show the full HWS B range tested, ranging up to 200-350 mg/kg HWS B and show corresponding vegetation boron concentrations ranging up to several thousand mg/kg (with substantial toxicity noted at these high levels). To refine the dataset to a range of boron levels more relevant to typical soil concentrations and potential guideline ranges, Figures 5.25 and 5.26 show these bioconcentration relationships in fine and coarse soils focused on HWS boron levels ranging from 0 to 35 mg/kg.

In Figures 5.25 and 5.26, rates of boron accumulation representing BCF's were estimated from linear regression lines, with best fits obtained by using intercepts (mg/kg vegetation boron) as well as slopes (mg/kg vegetation boron / mg/kg soil boron). From fine textured soils, regression line slopes (similar to BCF's) for the six test species ranged from 6.8-24.8 for shoots and 0.4-4.8 for roots, whereas in coarse soils wider ranges were observed (shoot slopes ranging from 10.4-61.4 and root slopes from 0.3-9.2). Intercepts were generally less than 10 mg/kg vegetation boron, ranging up to 49.3 mg/kg. In general, alfalfa, cumber, and barley tended to have highest overall vegetation shoot boron concentrations, with northern wheatgrass and carrot having generally lower concentrations. Irrespective of soil texture, roots were found to accumulate boron at a lower rate compared to shoot tissue for all species examined.

Note that these bioconcentration relationships have less variability related to textural differences when expressed relative to saturated paste B (mg/L) rather than HWS B. However, since BCFs are typically calculated using mg/kg units for soil, HWS boron has been chosen to express BCFs herein.

Figure 5.23. Bioconcentration Relationships in Clay Loam – full HWS B range



Note: Vegetation boron results not available for alfalfa roots in clay loam soils

Figure 5.24. Bioconcentration Relationships in Sandy Loam for – full HWS B range

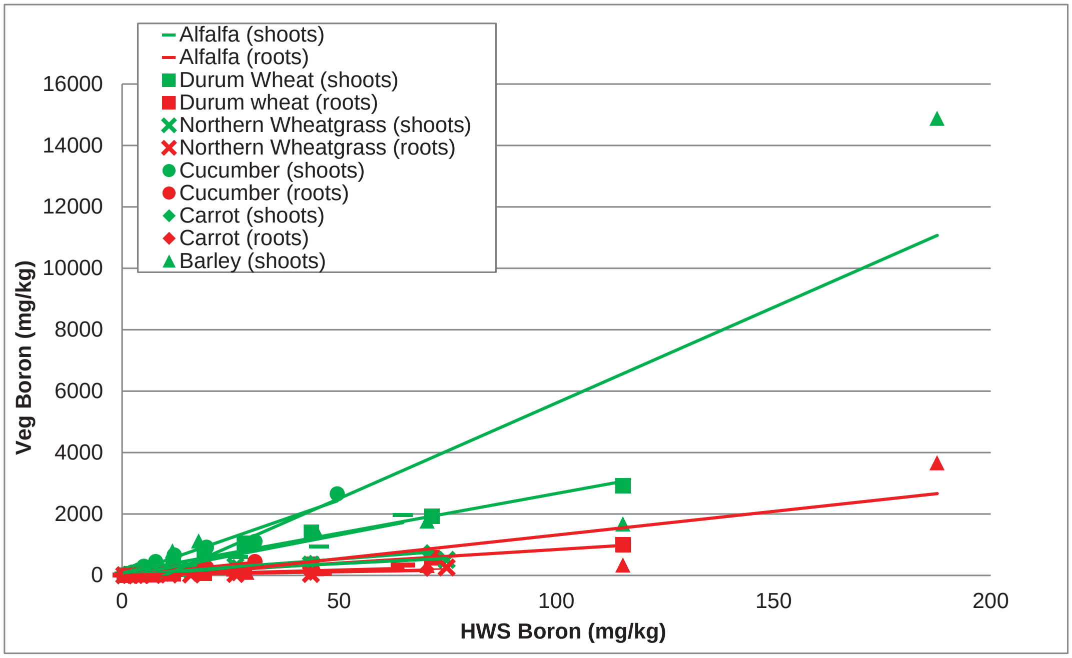
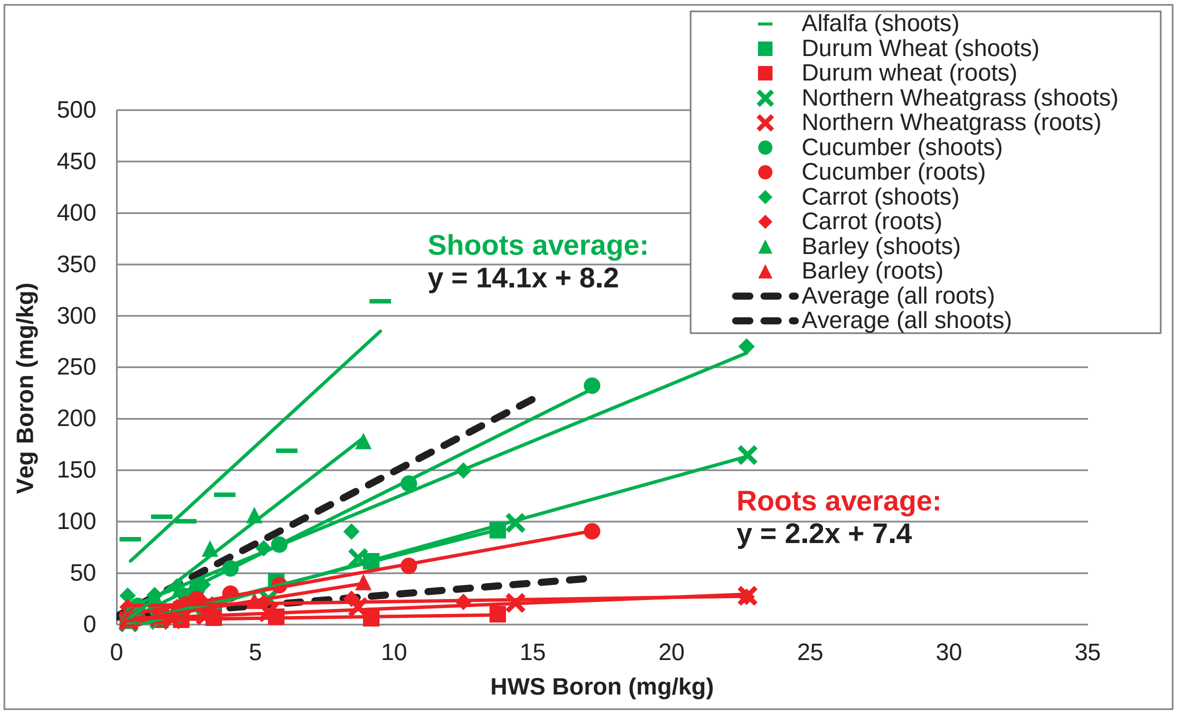


Figure 5.25. Bioconcentration Relationships in Clay Loam (Soil HWS B 0 to 35 mg/kg)



Note: Vegetation boron results not available for alfalfa roots in clay loam soils

Figure 5.26. Bioconcentration Relationships in Sandy Loam (Soil HWS B 0 to 35 mg/kg)

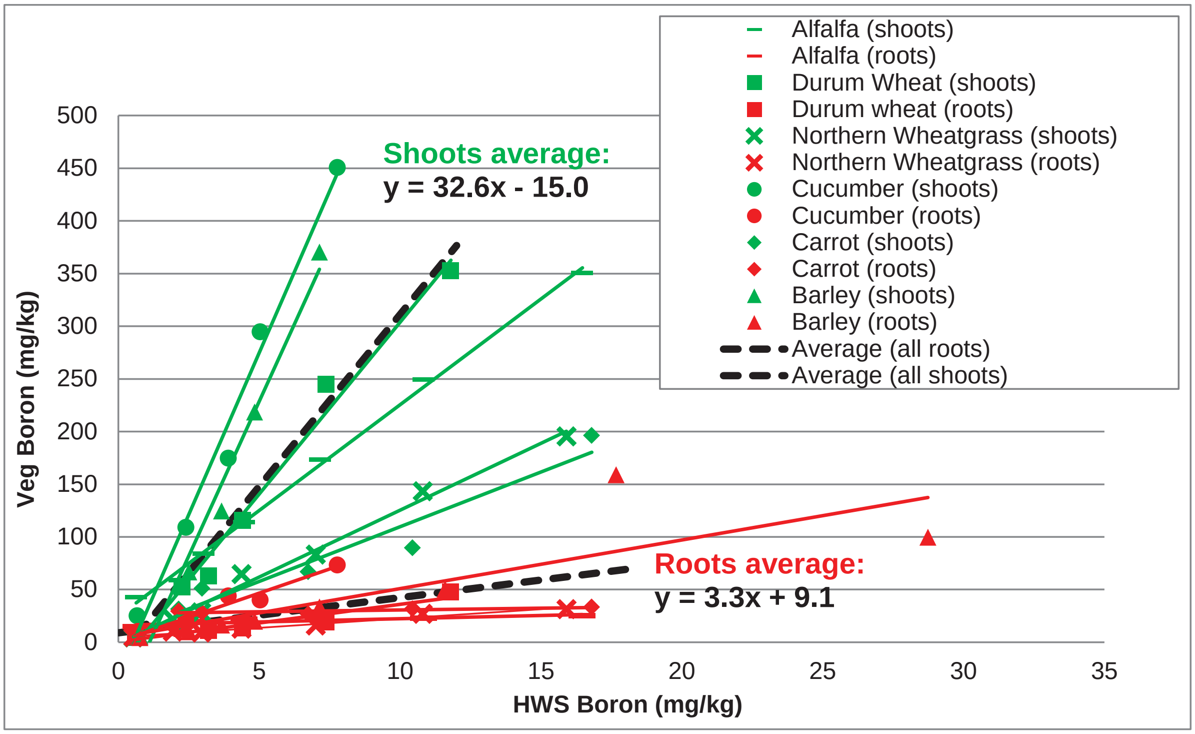


Table 5.8 summarizes these regression results from the shoot and root tissue of each of the test species in fine and coarse soils for HWS B (mg/kg). Average regression lines for shoot tissue in clay loam and sandy loam soils expressed on a HWS B (mg/kg) basis were y=14.1(x)+8.2 and y=32.6(x)-15.0, respectively, while for roots, these average regression equations were y=2.2(x)+7.4 and y=3.3(x)+9.1 for clay loam and sandy loam soils respectively. For shoots, the average slopes were 14.1 in clay loam and 32.6 in sandy loam, whereas for roots the average slopes were 2.2 in clay loam and 3.3 in sandy loam. For shoots and roots combined, the average slope is approximately 8.7 for fine soils and 18.0 for coarse soils. These slopes are similar to bioconcentration factors, and are used further in Section 9 for evaluating potential livestock and wildlife exposure to boron ingested from vegetation.

Table 5.8. Summary of Agricultural Bioconcentration Regression Data for HWS B (mg/kg)

Species/Soil	Clay loam		Sandy loam	
	y-intercept (b)	**slope (m)**	**y-intercept (b)**	**slope (m)**
SHOOT TISSUE				
Alfalfa	49.3	24.8	24.7	20.1
Barley	-3.5	20.8	-64.8	58.7
Cucumber	-0.9	13.4	-31.8	61.4
Carrot	11.8	11.1	5.9	10.4
Durum Wheat	-1.5	6.8	-22.4	32.6
Northern Wheatgrass	-6.2	7.5	-1.5	12.7
Average shoots:	8.2	14.1	-15.0	32.6
ROOT TISSUE				
Alfalfa	-	-	16.2	0.61
Barley	2.0	4.3	4.6	4.6
Cucumber	7.4	4.9	0.8	9.2
Carrot	18.2	0.4	27.2	0.3
Durum Wheat	4.3	0.4	0.7	3.5
Northern Wheat Grass	4.9	1.1	5.0	1.8
Average roots:	7.4	2.2	9.1	3.3
Shoots and Roots Combined	**7.8**	**8.7**	**-3.0**	**18.0**

Linear regression equation y = m(x)+b, where y = vegetation boron (mg/kg) and x = soil HWS boron (mg/kg)

5.3 Toxicity Data From Recent Alberta Research: Boreal and Natural Area Species

More than 50% of Canada's total land mass is comprised of the boreal and taiga ecozones (Environment Canada 2013), with boreal species thus an important part of the natural areas of Alberta. This section describes the boreal plant toxicity testing performed in Alberta for boron, involving a different set of test species and reference soils relevant to boreal/natural areas. Methodology is described in Section 5.3.1, followed by test soil properties and spiking in Section 5.3.2, results and dose-response curves in Section 5.3.3, and IC_{25} values in Section 5.3.4.

5.3.1 Methodology

Boreal / natural area boron toxicity tests for plants were performed by Exova in 2013-2014 using Environment Canada testing protocol developed for the boreal region (Environment Canada 2013). Tests were conducted on five Environment Canada standard boreal plant test species including jack pine (*Pinus banksiana*), white spruce (*Picea glauca*), black spruce (*Picea mariana*), bluejoint reedgrass (*Calamagrostis canadensis*), and trembling aspen (*Populous tremuloides*) to provide a range of plant types and likely sensitivities. The test duration was typically four to six weeks depending on plant species, with durations longer than the agricultural species due to the slower growth rates. Table 5.9 provides a summary of the boreal plant species and descriptions, including type of plant and life cycle as well as test duration.

Table 5.9. Boreal Test Plant Species Properties

Species	Classification	Growth form	Test Duration	Life Cycle
Jack pine	gymnosperm	tree, coniferous	35 days	perennial
White spruce	gymnosperm	tree, coniferous	42 days	perennial
Black spruce	gymnosperm	tree, coniferous	42 days	perennial
Bluejoint reedgrass	angiosperm, monocot	herb, graminoid	28 days	perennial
Trembling aspen	angiosperm, dicot	tree, deciduous	28 days	perennial

Two field-collected forest reference soils from Alberta were used: an organic peat soil and a coarse mineral soil, both selected to be representative of soil conditions typical for boreal / natural areas. An artificial soil similar to that used for agricultural plants was also used (comprised of sand, clay, and peat), but adjusted to have a lower pH more typical of boreal / natural areas. Soils were spiked with varying levels of boric acid (typically twelve treatment levels), with resulting concentrations ranging from 0 to >250 mg/kg HWS B and corresponding saturated paste B from 0 to >150 mg/L depending on soil type. Eight replicates (test vessels) were typically used for each treatment level, with multiple seeds per vessel. Temperature, lighting, humidity, and soil moisture were also controlled. Toxicological effects were measured via the same four standard endpoints used for the agricultural species, including shoot biomass, shoot length, root biomass, and root length. Further details of boreal plant test protocol are provided in Environment Canada 2013, with other details of the boreal method development process shown in Saskatchewan Research Council (2006) and Environment Canada / Saskatchewan Research Council (2007).

5.3.2 Test Soil Properties and Spiking

Table 5.10 summarizes soil textural and chemical properties of the boreal / natural area reference soils including salinity, boron and nutrient levels. Test soils consist of an organic peat soil (68.4% organic matter), a coarse sandy mineral soil (3.5% clay) and an artificial soil (17.7% clay). Salinity was low in all samples (maximum EC of 0.89 dS/m and maximum SAR of 0.4), with chloride and sulfate also low (generally less than 100 mg/kg). Initial HWS boron concentrations ranged from <0.2 to 0.76 mg/kg HWS for the three soil types.

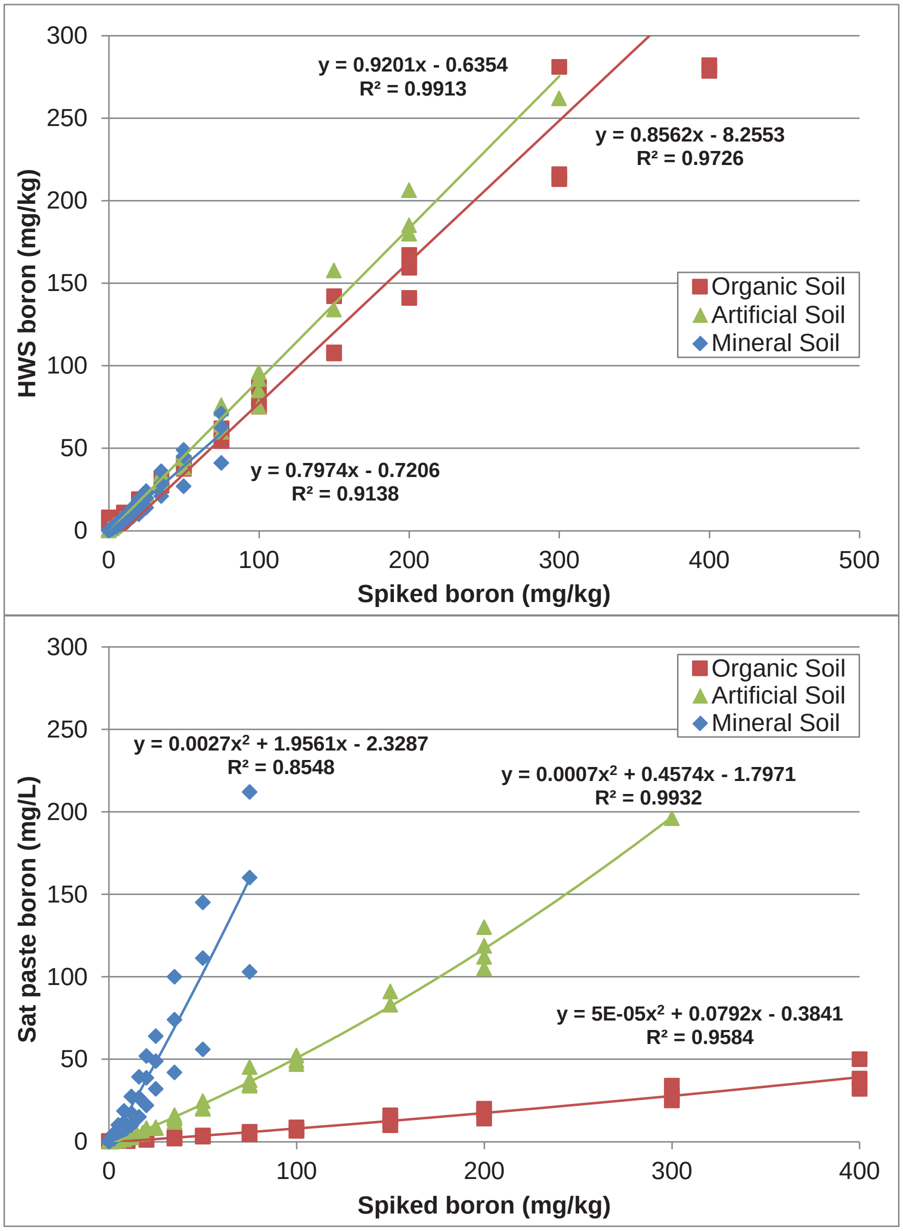
Table 5.10. Boreal Reference Soil Properties

		Reference Soils		
Test	**Parameter**	**Organic**	**Mineral**	**Artificial**
Hydrometer Analysis	Texture	N/A	Sand	Sandy loam
	% sand	--	94.5	68.3
	% silt	--	2	14
	% clay	**--**	**3.5**	**17.7**
Sieve Analysis	% retained 75 um	--	96.1	77.4
	Coarse vs fine	**--**	**Coarse**	**Coarse**
Other parameters	Organic matter (%)	**68.4**	**5.3**	**10.1**
	Saturation (%)	552	31	~100
Soil Chemistry	EC (dS/m)	0.23	0.07	0.70
	SAR	0.4	0.3	0.21
	Chloride (mg/kg)	88	2	16.9
	Sulfate (mg/kg)	96	1.9	157
	pH	5.5	4.4	6.6
	*SAE Boron (mg/kg)	14.1	<2	<2
	HWS Boron (mg/kg)	0.76	<0.2	<0.2
	Sat paste Boron (mg/L)	0.12	<0.05	<0.05
Soil Nutrients	Nitrate-N (mg/kg)	20	<2	2
	Phosphorous (mg/kg)	<20	38	43
	Potassium (mg/kg)	<120	<25	46
	Ammonium-N (mg/kg)	6.1	<0.3	34.8

*__SAE:__ _Strong acid extractable_

The boreal artificial soil was formulated using standard methodology from Environment Canada (2013), and consists of 70% sand, 20% clay, and 10% peat (as per the agricultural tests) with pH adjusted to approximately 6.6 for these boreal tests. This is more acidic compared to the artificial soil formulated for agricultural plants (pH of approximately 7.2) to correspond to naturally acidic forest soils. As noted previously, although the artificial soil is classified as coarse, the presence of peat and 20% clay results in increased boron sorption and some behaviors more similar to a fine soil.

Figure 5.27. HWS and Sat Paste Boron vs Spiked Boron in Boreal Reference Soils



Approximate
% recovery
<u>on a mass basis</u>
(89% recovery)
(86% recovery)
(92% recovery)

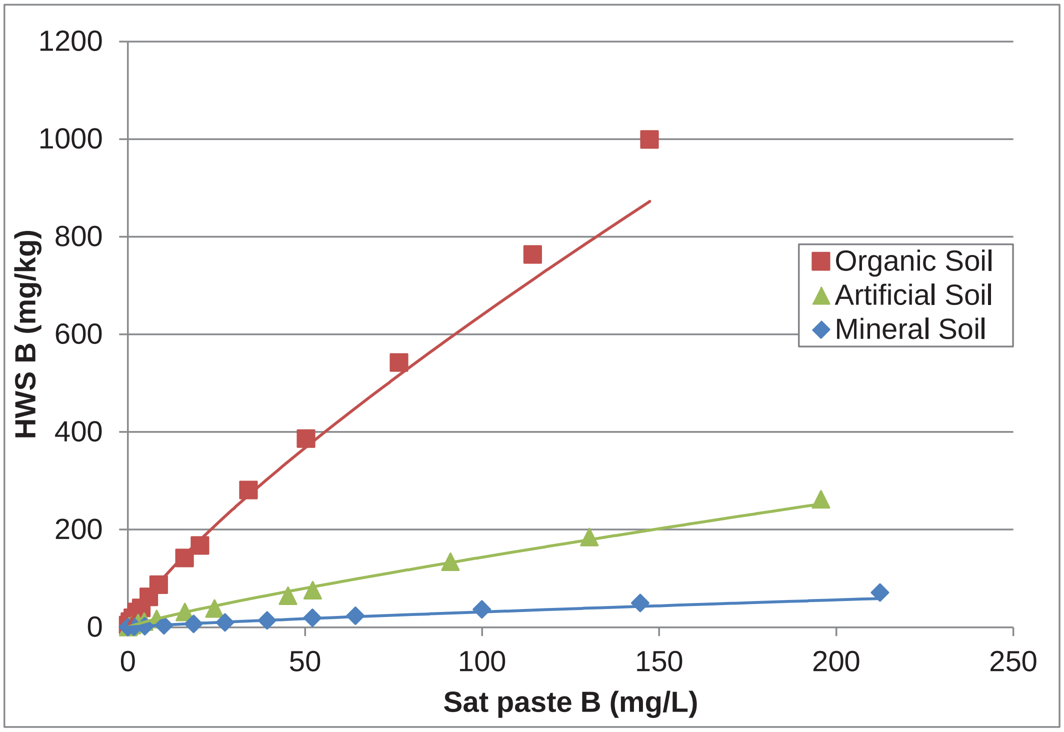
Approximate
% recovery
<u>on a mass basis</u>
(30-57% recovery)
(38-55% recovery)
(64-89% recovery)

The test soils were spiked with varying concentrations of boron (as boric acid) and analyzed using different extraction methods. Figure 5.27 shows resulting HWS (mg/kg) and saturated paste (mg/L) boron concentrations for the three soil types based on spiked B concentrations (mg/kg). The top part of Figure 5.27 shows HWS versus spiked B, with slopes of 0.80 to 0.92 indicating that the recovery of spiked B using the HWS extraction method is relatively complete and consistent between the soil types. This is consistent with the HWS B extraction method measuring both the sorbed and dissolved boron fractions in soil (thus not strongly influenced by sorption differences), and indicates 86 to 92% of the spiked boron is recovered in these cases.

The bottom part of Figure 5.27 shows saturated paste B (mg/L) versus spiked B, and illustrates the different sorption properties of the three soil types. The differences between these different soil types is greater than was seen for the agricultural soils, with the coarse mineral soil showing the highest saturated paste boron (mg/L) for a given spiked B level (consistent with low boron sorption). The artificial and organic soils show increasing boron sorption, resulting in lower saturated paste concentrations in mg/L for a given spiked B level. On a mg/kg basis, the saturated paste boron test recovered between 64-89% of the spiked boron for the sandy mineral soil, 38-55% for the artificial soil, and 30-57% for the organic soil

Figure 5.28 shows HWS B regressed with saturated paste B (mg/L) for the full range of boron spike levels. Differences in sorption properties between the three soil types are apparent, with organic and artificial soils showing the highest sorption (higher HWS B for given saturated paste B), and the coarse mineral soil showing the lowest sorption. For example, 2 mg/kg HWS in the sandy mineral soil is approximately 4.8 mg/L saturated paste, and less than 0.1 mg/L in the organic soil. The organic soil shows substantially more sorption than the artificial soil, likely due to the high boron sorption properties of the peat. This figure implies a high K_d value for organic soil and a low K_d value for the coarse mineral soil, consistent with observations in Section 3.

Figure 5.28. HWS vs Sat Paste Boron for Spiked Boreal Reference Soils



5.3.3 Dose-Response Curves

Dose response curves were established for each of the five boreal species tested using techniques similar to the agricultural soils. As with the agricultural species, boreal plants were grown from seed in the spiked soils with plant growth endpoints measured at test termination. The figures below show the growth responses (averaged over replicates and measured as percentage relative to the control) of shoot biomass, shoot length, root biomass, and root length for jack pine (Figure 5.29), white spruce (Figure 5.30), and bluejoint reedgrass (Figure 5.31). Both HWS (top) and sat paste (bottom) data are plotted for organic (blue), mineral (green), and artificial (red) test soils to provide texture comparisons. For all species, responses vary more between soil types when measured as HWS boron (top), with toxicity responses for the different soils becoming more similar when boron is measured on a saturated paste basis in mg/L (bottom). As with agricultural plants, saturated paste boron is thus a more appropriate test for predicting toxicity across a range of soil types. Note that toxicity tests on black spruce and trembling aspen were conducted solely in artificial soils, thus comparisons based on soil type were not possible. Other dose-response relationships for these species are outlined below.

Figure 5.32 through 5.35 show dose-response curves for all fives species for shoot biomass, root biomass, shoot length, and root length respectively. In each Figure, responses are shown for the three test soils (organic, mineral or artificial), where available. Organic soil responses are shown on the left, mineral soil responses on the right, and artificial soil responses on the bottom. All results are presented as saturated paste boron (in mg/L) since toxicity responses are more consistent across soil types as discussed above. Though variability is observed between species, endpoints, and soil types, bluejoint reedgrass appears to be one of the more sensitive species to boron exposure in organic and mineral soils, whereas white spruce appears to be one of the more sensitive species in artificial soil. Root endpoints are generally more sensitive than shoot endpoints across all species tested. Normalized plant responses (% of control) rarely fall below 75% (similar to an IC_{25}) at saturated paste concentrations below 5 mg/L. Tabulated response data is shown in more detail in AEP (2015), and IC_{25}s are further discussed in Section 5.2.4 below.

A stimulation (hormetic) response to initial boron concentrations was observed in some cases, though this effect was least apparent for black spruce. The presence of potential stimulation effects suggests boron deficiency is possible for some plants in these typical reference soils. Trembling aspen and bluejoint reedgrass demonstrated the greatest stimulatory responses where increases to more than 200% of control levels were observed in some cases. In artificial soils, unusual dose-response relationships were observed for bluejoint reedgrass where a stimulatory-inhibitory-stimulatory pattern preceded the more significant reductions in plant growth.

Figure 5.29. Jack Pine Dose-Response Curves

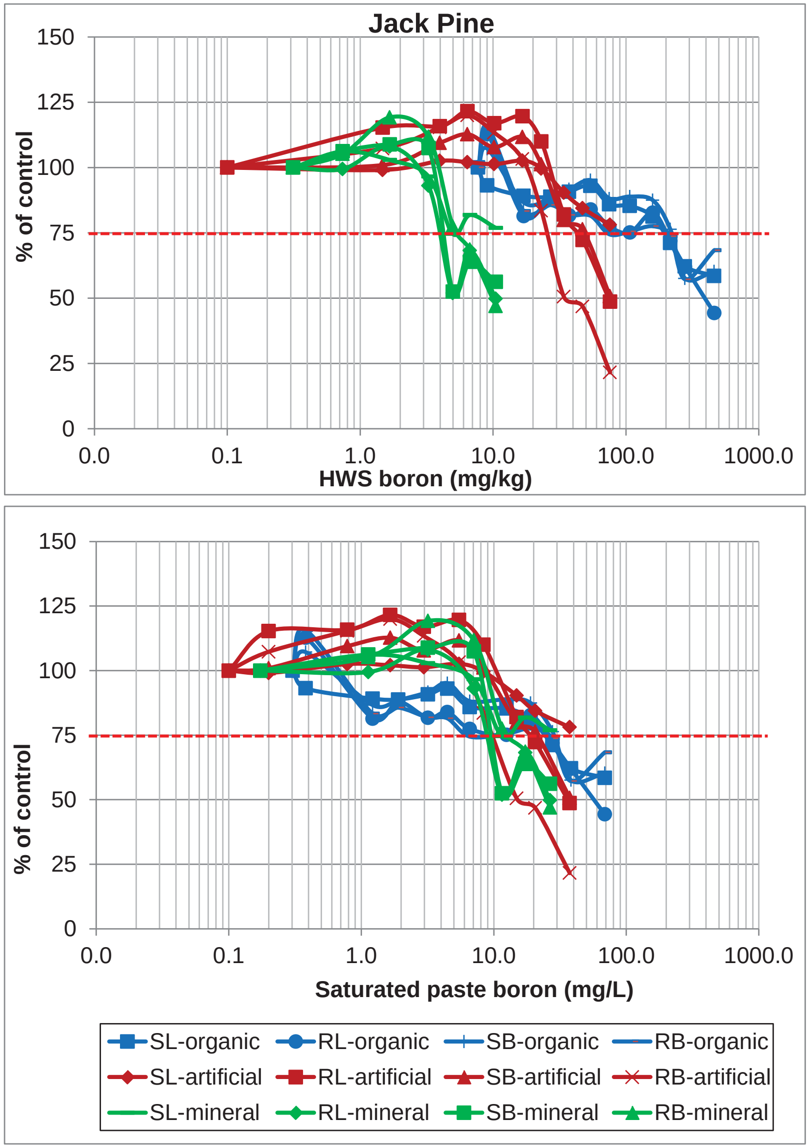
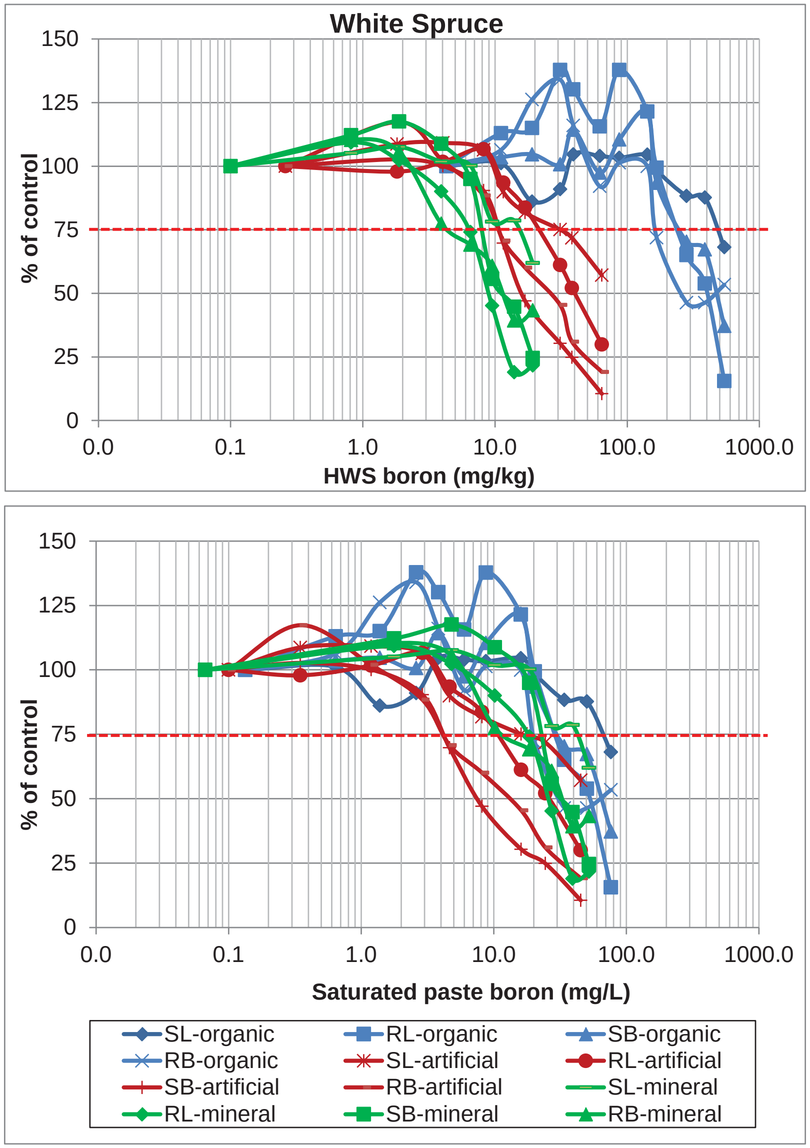


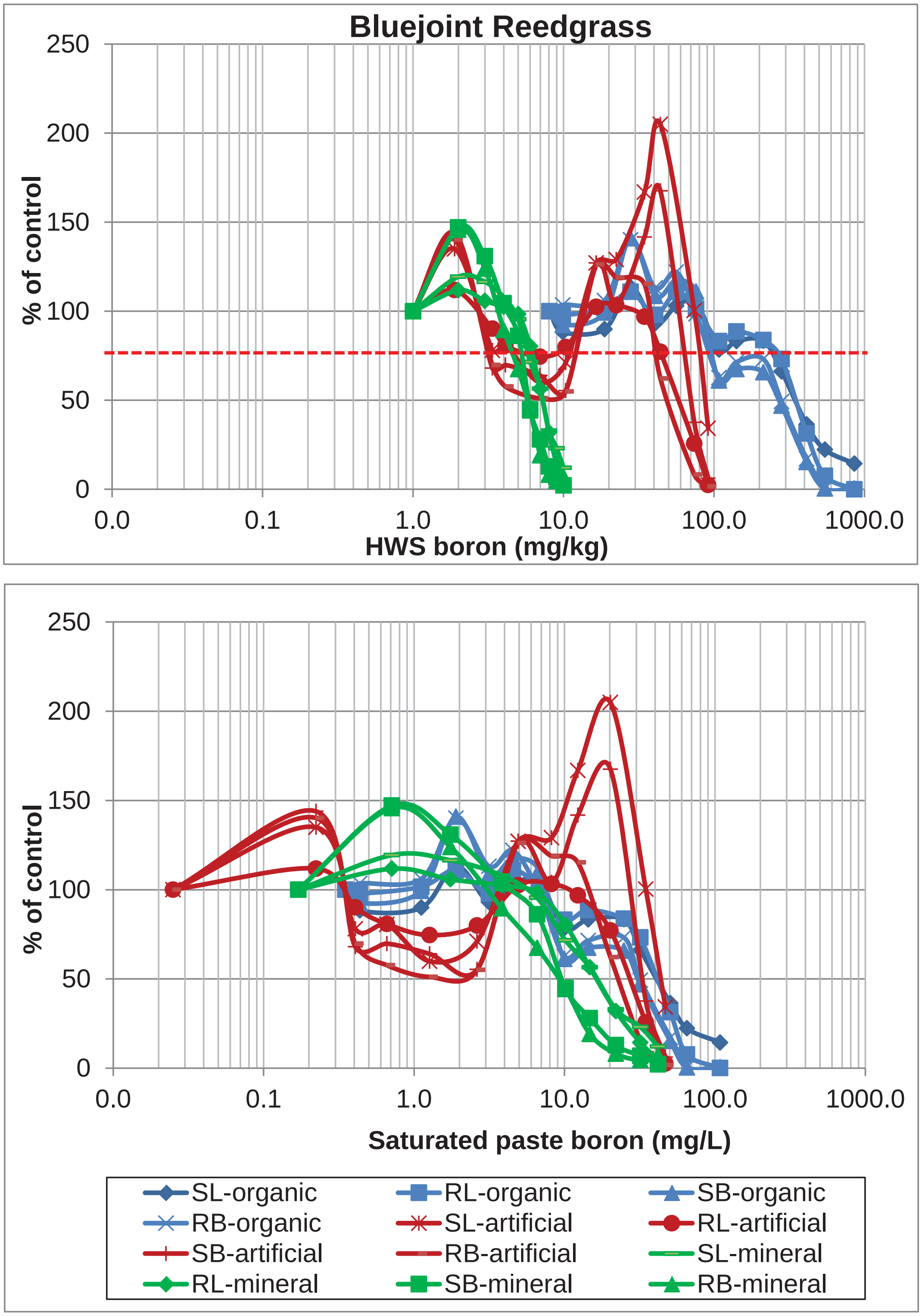
Figure 5.30. White Spruce Dose-Response Curves



Notes:

1) *Red hashed line indicates response that represents a 25% reduction based on controls;*
2) *plant tissues measure: SL = shoot length, RL = root length, SB = shoot biomass, RB = root biomass;*
3) *test soils: organic = blue, mineral = green, artificial = red.*

Figure 5.31. Bluejoint Reedgrass Dose-Response Curves



Notes:

1) Red hashed line indicates response that represents a 25% reduction based on controls;
2) plant tissues measure: SL = shoot length, RL = root length, SB = shoot biomass, RB = root biomass;
3) test soils: organic = blue, mineral = green, artificial = red.

Figure 5.32. Boreal Species Responses in Various Soil Types: Shoot Biomass

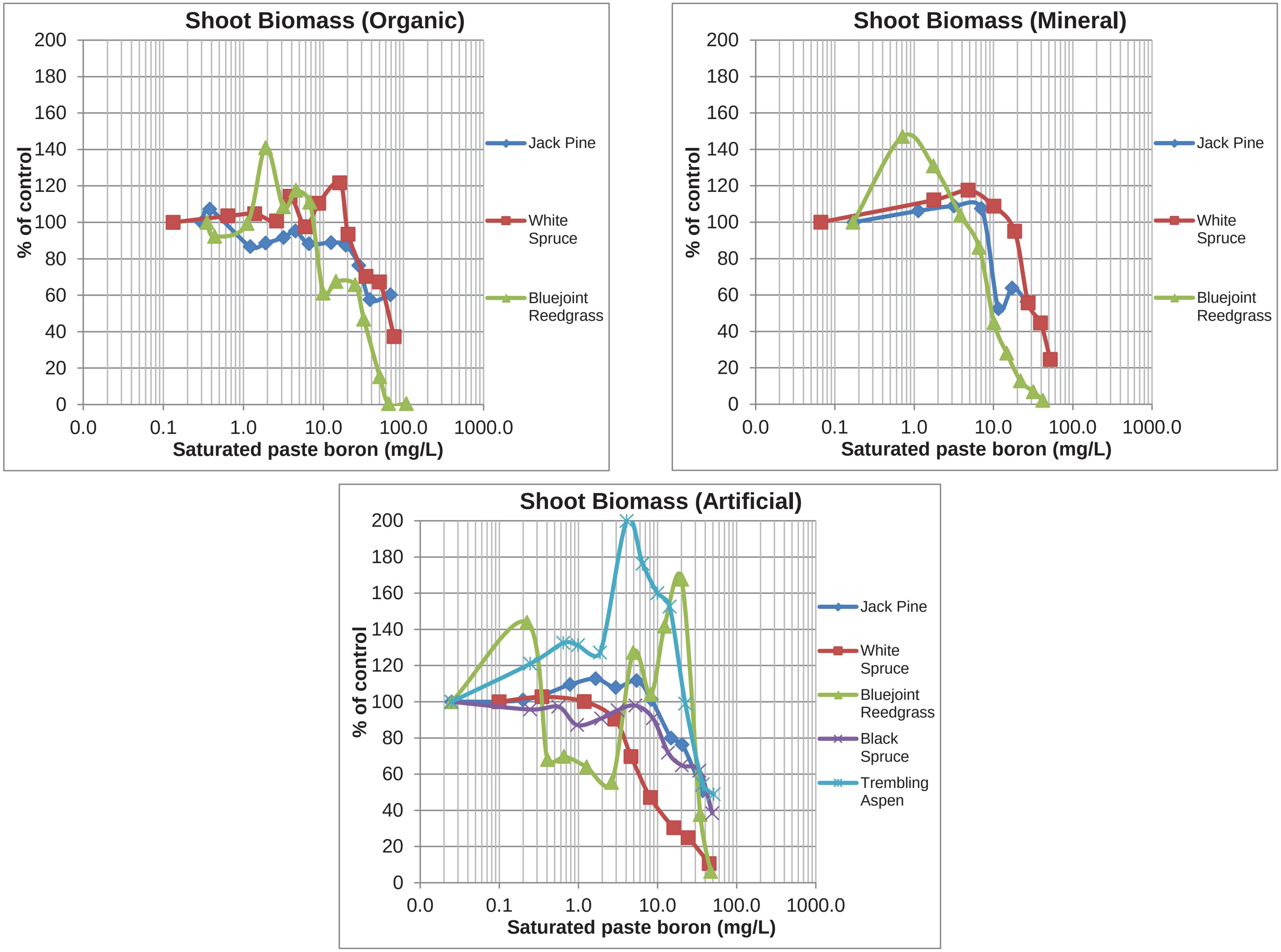


Figure 5.33. Boreal Species Responses in Various Soil Types: Root Biomass

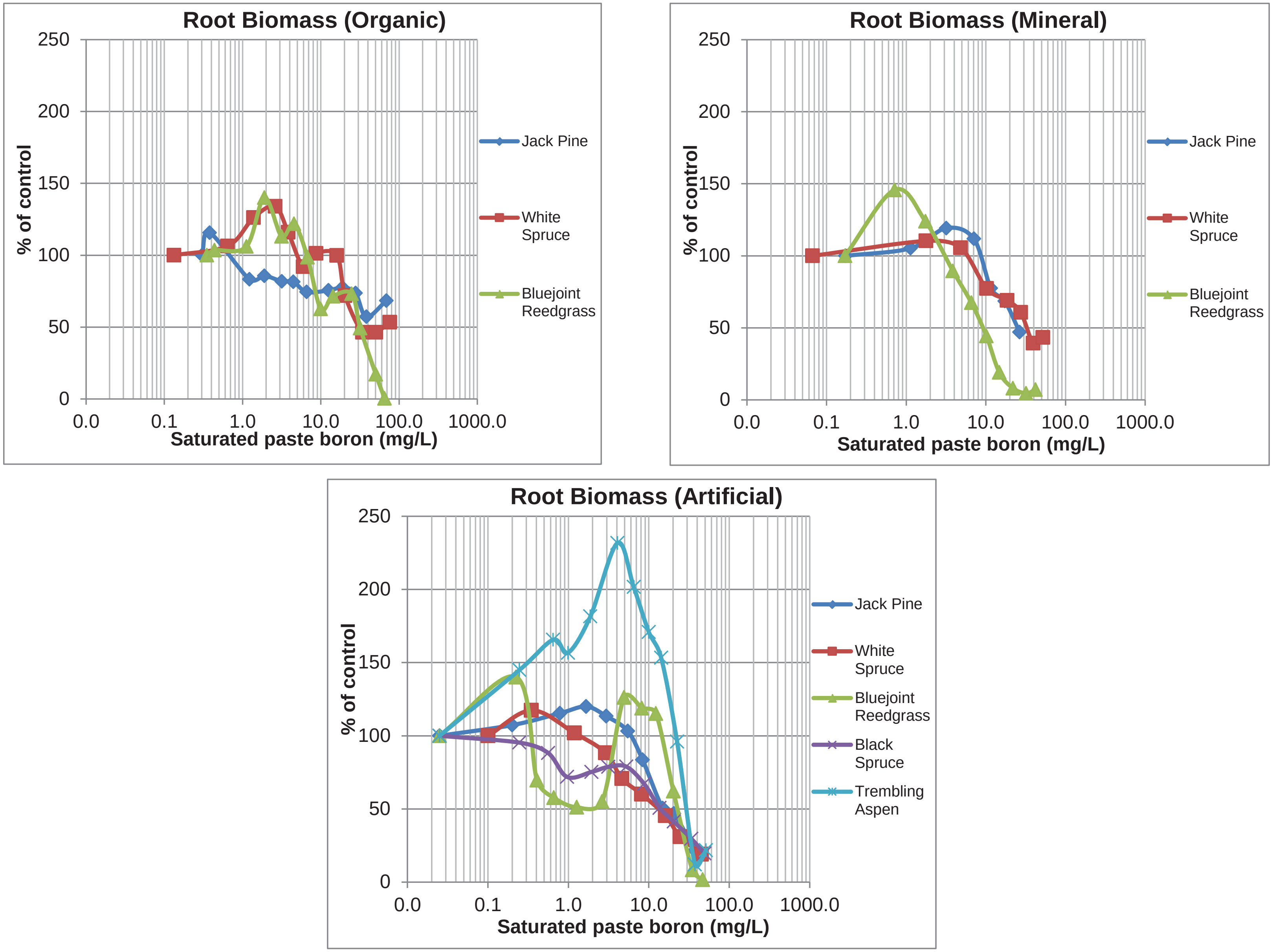


Figure 5.34. Boreal Species Responses in Various Soil Types: Shoot Length

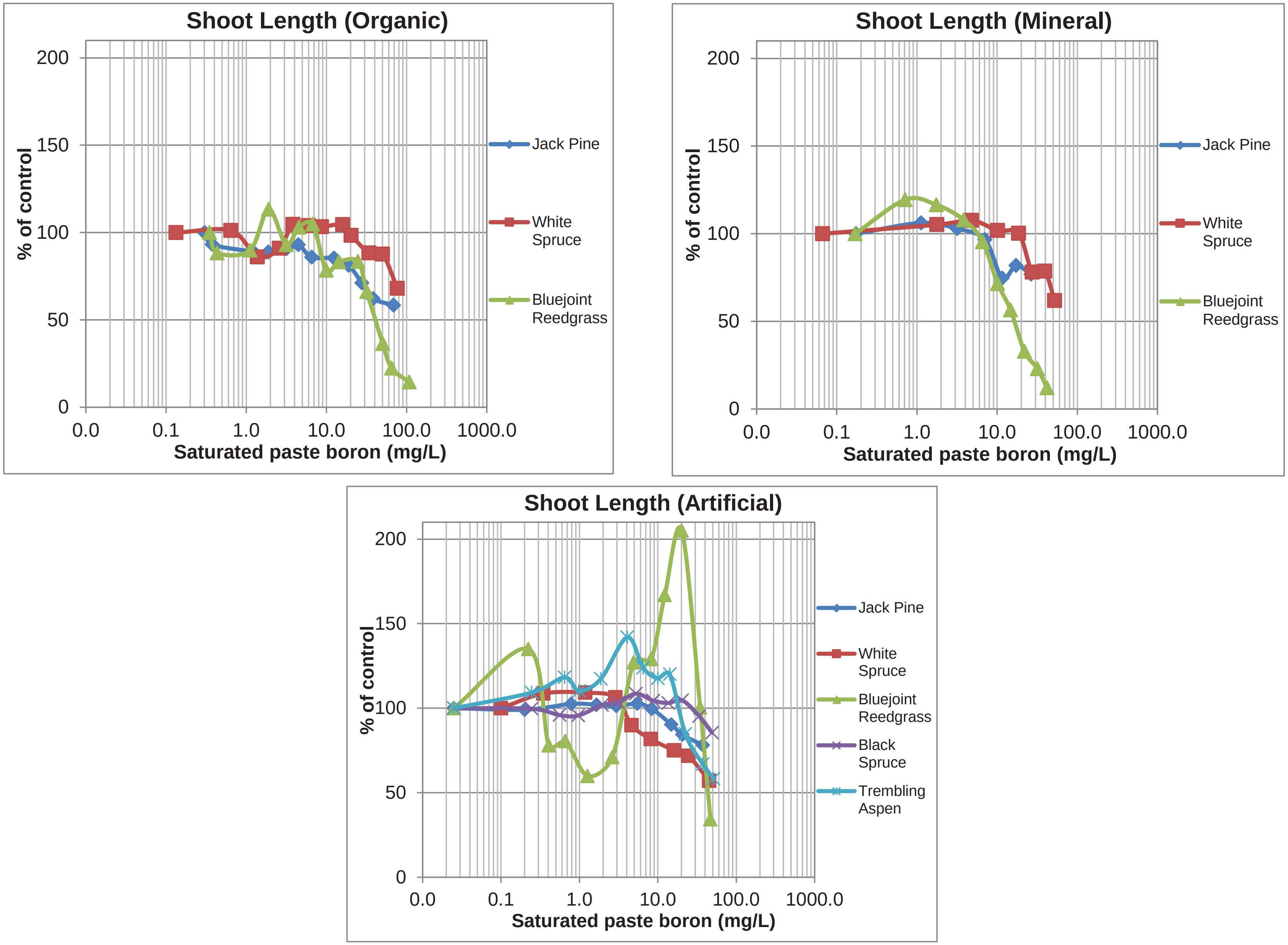
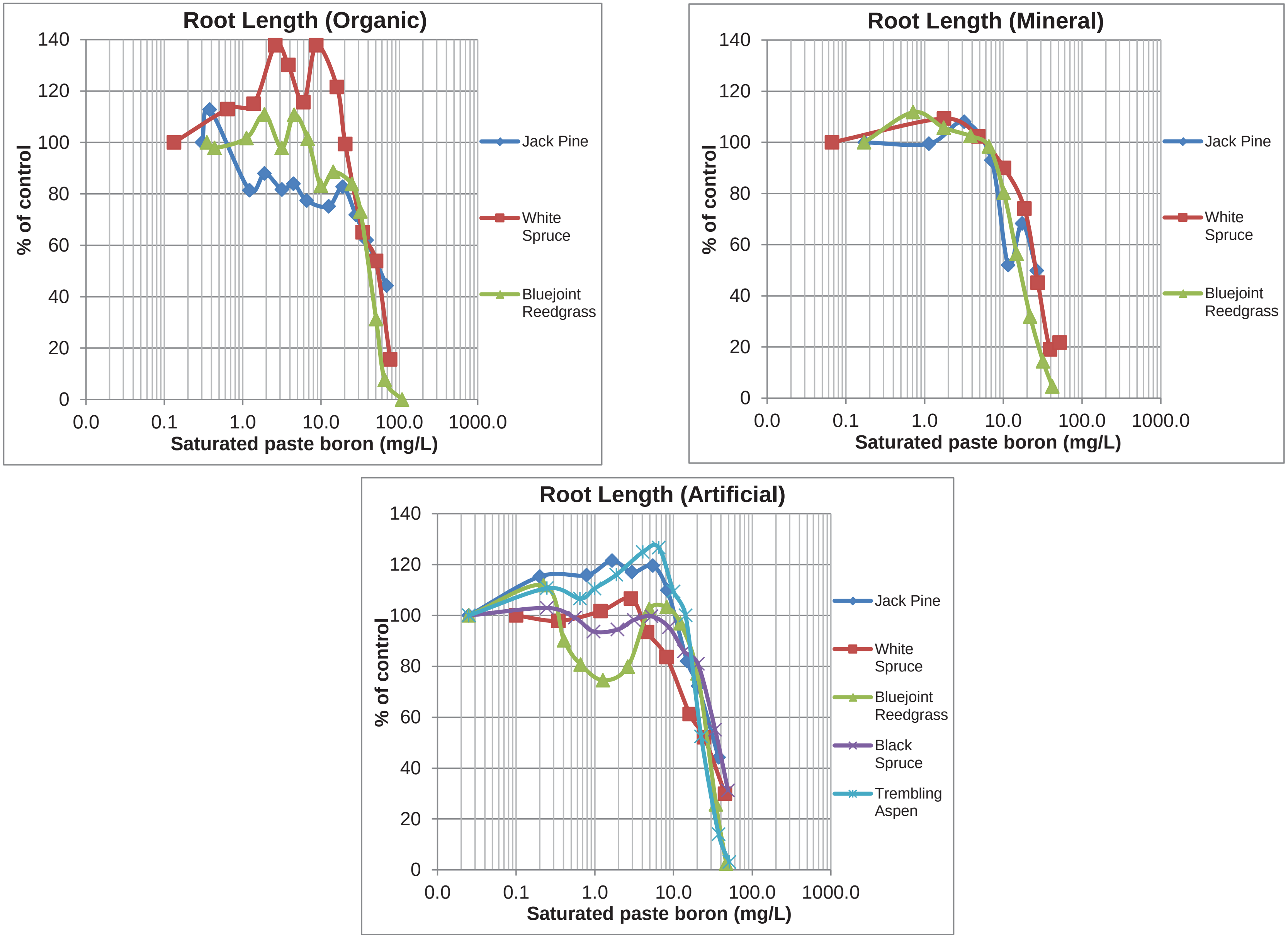


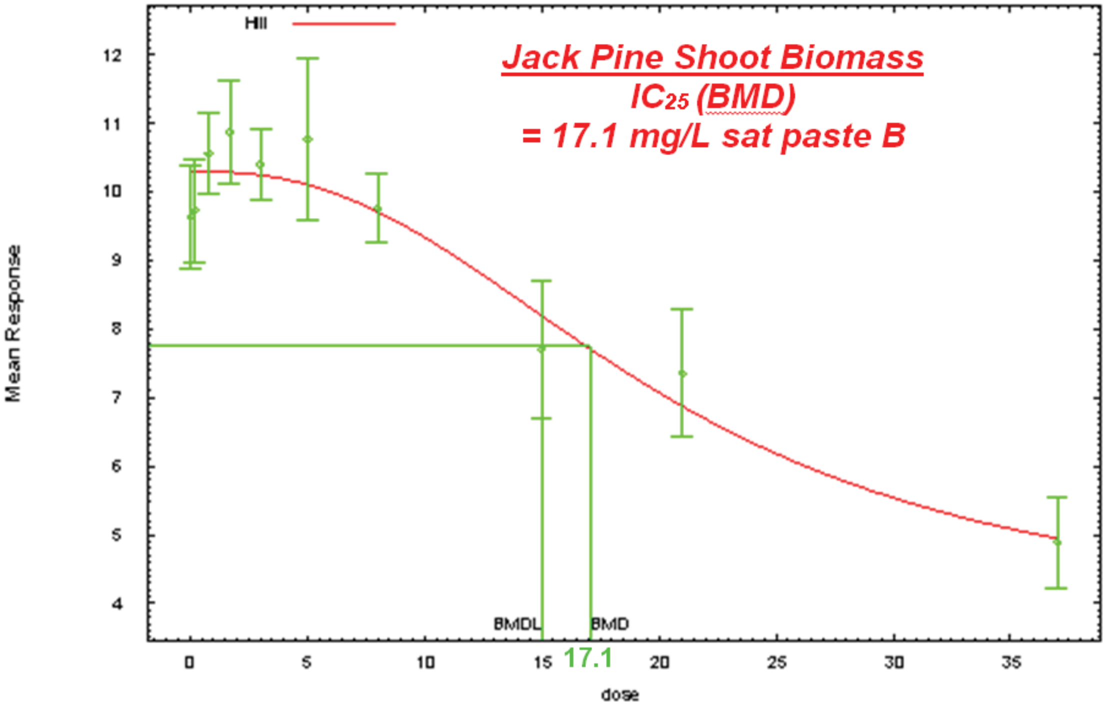
Figure 5.35. Boreal Species Responses in Various Soil Types: Root Length



5.3.4 IC_{25} Estimation

As with agricultural plants, IC_{25}s were calculated for four boreal species using the continuous Hill model routine within BMDS (US EPA, 2014). Separate IC_{25}s were derived from toxicity results from the three test soils (organic, mineral, and artificial soil) for each species and each endpoint (shoot biomass, shoot length, root biomass, and root length). An example plot is shown in Figure 5.36 below for jack pine shoot biomass. The raw data (green) is shown as averages with error bars, and the best fit Hill model shown as a red line. The IC_{25} is derived at 75% of the modeled baseline response, with the benchmark dose (BMD, or IC_{25}) shown here as 17.1 mg/L saturated paste boron.

Figure 5.36. Example BMDS IC_{25} Plot – Jack Pine (Shoot Biomass) in Artificial Soil



In total, forty-four IC_{25} values were calculated for all species, endpoints, and soil types with results summarized in Table 5.11 and details presented in AEP (2015) (including lower 95% confidence intervals). The geometric mean of the resulting IC_{25}s of the two shoot endpoints and the two root endpoints for each test are also shown since these pairs of endpoints (e.g., shoot biomass and shoot length) are often highly correlated. Note that black spruce shoot length in artificial soil showed less than a 25% reduction over the entire dose range, and thus the maximum response (IC_{16}) was conservatively used instead of an IC_{25} in that instance. Overall, the saturated paste B IC_{25}s range from 1.42 mg/L (jack pine root biomass in organic soil) to 67.59 mg/L (white spruce shoot length in organic soil). As with the agricultural species, root endpoints tended to be more sensitive than shoot endpoints within each plant species. Note that the jack pine root biomass in organic soil endpoint appears potentially anomalous based on the corresponding shoot data for the same test (substantially higher tolerance) and root data for other tests and species.

Table 5.11. Boreal Plant Saturated Paste Boron IC_{25}s (Exova, 2013-2014)

Species	Endpoint	Saturated paste B (mg/L) IC_{25}		
		Organic soil	Mineral soil	Artificial soil
Jack Pine	Shoot biomass	42.60	9.15	17.06
Jack Pine	Root biomass	1.42	13.50	8.52
Jack Pine	Shoot length	29.55	10.01	34.62
Jack Pine	Root length	1.71	7.78	15.06
	geomean shoots	**35.48**	**9.57**	**24.30**
	geomean roots	**1.56**	**10.25**	**11.33**
White Spruce	Shoot biomass	33.15	21.61	4.07
White Spruce	Root biomass	18.48	12.46	5.04
White Spruce	Shoot length	67.59	28.07	8.19
White Spruce	Root length	26.33	17.77	12.96
	geomean shoots	**47.34**	**24.63**	**5.77**
	geomean roots	**22.06**	**14.88**	**8.08**
Bluejoint Reedgrass	Shoot biomass	17.20	4.79	31.62
Bluejoint Reedgrass	Root biomass	12.28	5.50	18.06
Bluejoint Reedgrass	Shoot length	29.14	8.27	40.68
Bluejoint Reedgrass	Root length	29.57	10.39	22.86
	geomean shoots	**22.39**	**6.29**	**35.87**
	geomean roots	**19.06**	**7.56**	**20.32**
Black Spruce	Shoot biomass	-	-	16.68
Black Spruce	Root biomass	-	-	6.68
Black Spruce	Shoot length	-	-	49.3*
Black Spruce	Root length	-	-	23.41
	geomean shoots	**-**	**-**	**16.68**
	geomean roots	**-**	**-**	**12.51**
Trembling Aspen	Shoot biomass	-	-	20.90
Trembling Aspen	Root biomass	-	-	22.98
Trembling Aspen	Shoot length	-	-	21.92
Trembling Aspen	Root length	-	-	16.06
	geomean shoots	**-**	**-**	**21.41**
	geomean roots	**-**	**-**	**19.21**

Note: Toxicity testing was conducted solely in artificial soil for black spruce and trembling aspen.
** Maximum response (IC_{16}) used for black spruce shoot length in artificial soil*

As with the agricultural species, a stimulation / hormetic effect is apparent in some boreal endpoints/species. Though hormetic models can be used to model such effects, the Hill model (which does not include hormesis) was used exclusively during this analysis for consistency and since it incorporates a degree of conservatism compared to hormetic models (discussed previously for the agricultural species in Section 5.2.4).

In comparison, the above IC_{25} results (on a spiked boric acid basis) are in a similar general range as in previous boreal method-development work conducted by Environment Canada and the Saskatchewan Research (Saskatchewan Research Council, 2006 and Environment Canada, 2010). There, toxicity testing using boric acid was conducted in similar artificial soil for the five species tested here plus two additional species (goldenrod and paper birch). IC_{25} results for shoot and root endpoints ranged from approximately 150 to 800 mg/kg spiked boric acid in artificial soil (saturated paste boron not directly measured), with trembling aspen, bluejoint reedgrass, goldenrod, and paper birch generally appearing most sensitive. In comparison, the IC_{25} results for artificial soil presented in Table 5.11 correspond to spiked boric acid levels ranging from approximately 75 to 555 mg/kg for shoots (4.1 to 49.3 mg/L saturated paste B) and 85 to 295 mg/kg for roots (5.0 to 23.4 mg/L saturated paste B) using a saturated paste versus spike level regression such as Figure 5.27. This suggests a reproducibility of the results within the same soil type (such artificial soil), with the saturated paste boron methodology helping extend this across a range of soil types.

6. Toxicity to Soil Invertebrates

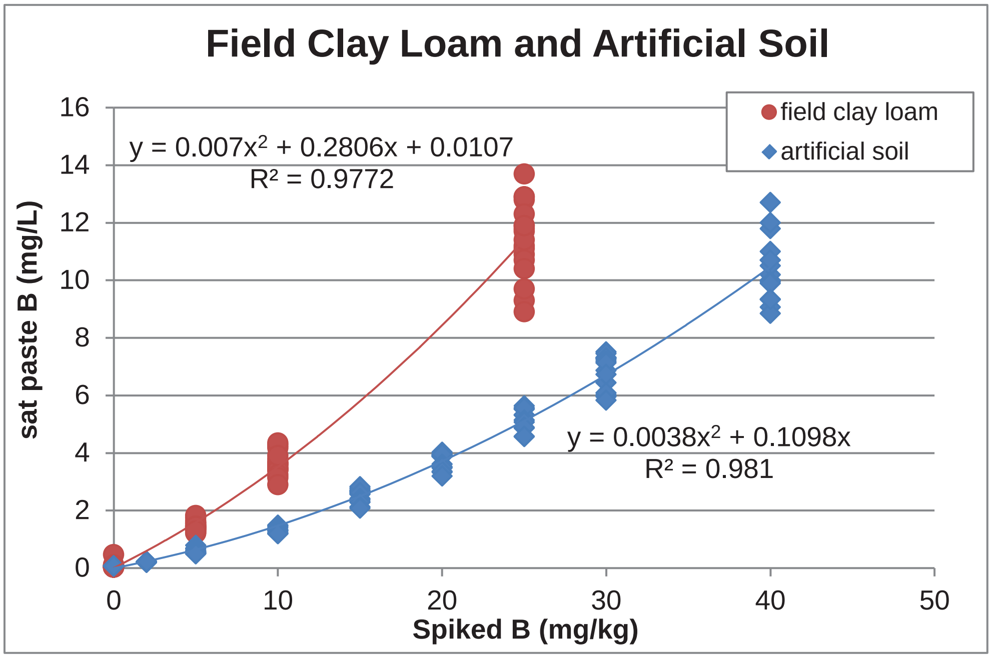
Soil invertebrates are crucial components of the soil ecosystem because they aid in the decomposition, nutrient cycling, mixing, and overall health of the soil. Various invertebrate groups such as earthworms, collembola (springtails), and mites of various sub species have been used extensively by Environment Canada in eco-toxicological method development studies with boric acid often used as a reference toxicant. The typical approach to assess boron toxicity has been to add boron-containing compounds such as boric acid (H_3BO_3) in varying concentrations to soil followed by assessing the effects on specific invertebrate endpoints such as lethality or reproduction. The concentration at which 50% or 25% effect levels are observed for these endpoints (e.g.,LC_{50}, LC_{25}, EC_{25}, IC_{25}) is often used as a basis for further interpretation or guideline development. For guideline development purposes, more sensitive endpoints such as reproduction are more relevant than lethality endpoints, thus the focus below is on reproductive IC_{25}s for guideline development. AEP (2015) presents the raw data and details of the analyses conducted in guideline development.

6.1 Soil Test Methods and Regressions

Most of the invertebrate data from literature is based on spiked B (from boric acid) concentrations, and typically does not have soil concentrations such as HWS or saturated paste boron directly measured. These literature experiments were typically performed with artificial soil or field clay loam, and appropriate soil regressions from the recent Alberta plant toxicity testing can be used to estimate soil concentrations based on spiked B levels. Estimated soil concentrations will generally be expressed on a saturated paste boron basis (in mg/L) to be consistent with the plant toxicity data where it was a more consistent predictor of toxicity across a range of soil textures.

Figure 5.7 previously showed a regression of ‘spiked’ B (mg/kg, from H_3BO_3) with saturated paste B (mg/L) for artificial and clay loam soils over a wide spiked boron range up to 400 mg/kg. The majority of this range tends to be relevant to less sensitive endpoints (such as lethality), whereas a regression obtained from the lower range is relevant to more sensitive endpoints such as reproduction. The soil regressions in Figure 6.1 show the low range data (up to 40 mg/kg spiked B) to optimize accuracy across the lower range of boron concentrations. The equations for each regression indicate the difference between soil types when predicting saturated paste B concentrations. For example, a spiked B of 25 mg/kg is associated with a saturated paste B of approximately 5 mg/L in artificial soil or 11 mg/L in field clay loam using the low range regression. All spiked B data from the literature data presented below will also be converted to a predicted saturated paste B based on these regressions for the appropriate soil type. The low range regression is used for spiked values up to approximately 50 mg/kg, and the high range regression is used for spiked values above 50 mg/kg (the two ranges give equivalent values at approximately 55-60 mg/kg). Note that new earthworm data generated by Exova in 2013 (AEP, 2015) includes directly measured saturated paste boron from soils and thus no prediction from regressions was necessary for this experiment.

Figure 6.1. Low-Range Saturated Paste B Regressions for Clay Loam and Artificial Soils



6.2 Invertebrate Toxicity Data from Literature

The following section provides an overview of the available literature on boric acid as a reference toxicant for evaluating toxicity to termites, earthworms (*Eisenia andrei and Dendrodrilus rubidus*), springtails (*Folsomia candida, Folsomia fimetaria and Proisotoma minuta*) and Oribatid mites (*Oppia nitens*) in soil. Relevant results are summarized in Table 6.1 for 50% effect levels for all non-reproductive endpoints (eg, lethality and avoidance), and in Table 6.2 for 25% effect levels for the non-reproductive and reproductive endpoints. Further details of how similar studies or endpoints were combined and used to generate IC_{25} values on a saturated paste basis are shown in AEP (2015).

Termites

Grace, 1991

Boric acid and other boron-containing compounds are often used as “environmentally-friendly” insecticides and wood-preservatives (Gentz and Grace, 2006). Consequently, some boron toxicity data is available for insects such as termites. For instance, Grace (1991) evaluated the effects of adding varying levels of disodium octaborate tetrahydrate (containing 21.0% B) or zinc borate (containing 14.9% B) to sand into which two types of subterranean termite tunneled (*R. flavipes and C. formosanus*) for 10 days. Addition levels of the borates were 5,000 ppm, 10,000 ppm, or 15,000 ppm. On a boron basis, these levels correspond to 1,050 – 3,150 mg/kg boron for sodium octaborate and 745 – 2,235 mg/kg boron for zinc borate. Results varied between termite species, borate type, and addition level, with increased mortality observed for all treatment levels (% mortality ranged from 20% to 94% compared to less than 10% in controls). Though results were variable, estimated 50% effect levels (LC_{50}’s) ranged from approximately 745 mg B/kg in *R. flavipes* to approximately 1,000-2,000 mg B/kg in *C. formosanus* depending on the type of borate salt. This lowest approximate LC_{50} of 745 mg B/kg is shown in Table 6.1, with the generally high doses not allowing reliable LC_{25} estimates to be generated. Sorption of boron would likely be minimal in these experiments due to sand rather than soil being the treated medium, potentially resulting in increased toxicity compared to soil (all other invertebrate data described below used soil as a medium).

Earthworms

Ingraldi, 2004

In 2004, Environment Canada commissioned a study to compare the response of two species of earthworm, *Eisenia andrei* and *Eisena fetida*, to boron-contaminated clay loam and artificial soils. The study evaluated avoidance behavior, lethality, and reproductive success. For the lethality endpoint for *Eisenia andrei*, a 14 day study found a boric acid concentration of 4,621 mg/kg as the LC_{50} in clay loam (Table 6.1). In artificial soils, the *Eisenia andrei* LC_{50} was lower than it was in clay loam soils with a concentration of 3,236 mg boric acid/kg. *Eisenia fetida* showed a similar LC_{50} in clay loam of 4,365 mg boric acid/kg. These lethality values represent some of the highest LC_{50}'s shown in Table 6.1, and are also referred to in a 2007 Environment Canada Report (Environment Canada, 2007c). LC_{25}'s were not directly calculated for this study, but would be above 3,000 mg boric acid/kg in all three cases and substantially above the range of other LC_{25}/IC_{25} datapoints in Table 6.2. For the acute avoidance endpoint, a non-lethal endpoint which is sometimes used as an alternative to reproductive tests, *Eisenia andrei* were observed to avoid boron-contaminated clay loam at an IC_{50} of 661 mg boric acid/kg.

Reproductive toxicity tests for *Eisenia andrei* were assessed in an 84 day study by both the number of juveniles and the mass of juveniles in clay loam soil. The IC_{25} for the number of juveniles was 158 mg boric acid/kg, and for the mass of juveniles the IC_{25} was 69 mg boric acid/kg. The geometric mean of these related endpoints is 104 mg boric acid/kg, and corresponds to a predicted saturated paste B of 7.5 mg/L in Table 6.2 and Appendix E.

Environment Canada, 2004 and 2007b

Toxicity tests on the earthworm *Eisenia andrei* (Environment Canada 2004, 2007b) involved additions of boric acid to natural or artificial soil and testing either lethality or avoidance responses. 14-day and 7-day acute lethality (LC_{50}) values of approximately 3,500 and 3,800 mg boric acid/kg respectively were obtained in artificial soil. LC_{25} values were not calculated, but would likely be approximately 2,500 – 3,500 mg boric acid/kg for 14 and 7 days, and substantially above the range of the data in Figure 6.2. 48-hour acute avoidance tests were also performed by adding boric acid to natural (clay loam) soil, giving a 50% effect concentration (EC_{50}) of 873 mg boric acid/kg based on the geometric mean of data from four labs. A 25% effect concentration (EC_{25}) was also generated for the avoidance endpoint, yielding a geometric mean value of 406 mg boric acid/kg (Table 6.1).

Environment Canada, 2008-2010

Various studies were carried out between 2008 and 2010 on *Dendrodrilus rubidus* in artificially formulated soil to test for lethality and reproduction endpoints. Four 28 day studies (2008-2010) yielded an average LC_{50} value for lethality of 1,041 mg boric acid/kg (1966 mg/kg, >800 mg/kg, >600 mg/kg and >800 mg/kg) (Table 6.1). LC_{25} values were not reported.

IC_{25}'s were also reported for the juvenile reproduction endpoint and are shown as a geometric mean of the four studies between 2008-2010 in Table 6.2. Boric acid IC_{25}s of 301 mg/kg (2008), 375 mg/kg (2009), 174 mg/kg (2010) and 262 mg/kg (2010) yielded a geometric mean of 268 mg/kg. This corresponds with a geometric mean saturated paste IC_{25} of 13.5 mg/L which is one of the highest reproduction values reported in Table 6.2.

Collembola (Springtails)

Environment Canada, 2010-2012

From springtail toxicity tests in 2010, 7-day and 21-day LC_{50} concentrations for lethality in artificial soil for *Proisotoma minuta* were 687 mg/kg (one test) and 296 mg/kg (average of two tests, one yielding 360 mg/kg and the other 232 mg/kg) as boric acid, respectively. The two 21-day 2010 trials plus an additional 21-day trial in 2012 yielded LC_{25}'s ranging from 292 to 337 mg boric acid/kg, with a geometric mean of 308 mg/kg.

Juvenile reproduction tests were also conducted in the three trials over 21 days in 2010 and 2012. IC_{25} values were generated for each of the three trials between 2010 and 2012 (155, 235 and 264 mg boric acid/kg) and are reported in Table 6.2 as the geometric mean of 213 mg boric acid/kg and a corresponding saturated paste IC_{25} of 9.4 mg/L.

CECOTOX, 2005

Toxicity data using lethality and reproduction as endpoints were obtained for boric acid in artificial and clay loam soils for two springtail species, namely, *Folsomia fimetaria* and *Folsomia candida* (CECOTOX, 2005). 7 and 14-day acute lethality trials for *Folsomia fimetaria* were carried out in artificial soils, resulting in LC_{50} values of 958 and 641 mg boric acid/kg, respectively. In clay loam, the resulting LC_{50}'s for the 7 day time period was 905 mg boric acid/kg, and for 14 days was 282 mg boric acid/kg (Table 6.1). The *Folsomia fimetaria* data were analyzed using BMDS and the Hill model to yield LC/IC_{25} values. In artificial soils, the LC_{25} were 693 and 450 mg boric acid/kg for 7 and 14 day trials, respectively, with a geometric mean of 558 mg/kg. In clay loam soils, 7 and 14 day LC_{25}'s were 399 and 155 mg boric acid/kg respectively, with a geometric mean of 249 mg/kg. These data indicate that boric acid had a more toxic effect in clay loam soils compared to artificial soils.

For the reproductive endpoint, a 28 day trial was conducted in artificial and clay loam soils. Reproductive IC_{25} values for *Folsomia fimetaria* in both artificial and clay loam soils were obtained over two trials (October and December 2004). The artificial soils IC_{25}'s were 90 and 79.3 mg boric acid/kg, reported in Table 6.2 as a geometric mean of 84 mg/kg and represents the lowest estimated saturated paste IC_{25} of 2.4 mg/L for invertebrates. For clay loam, IC_{25}'s of 114.5 mg/kg (October 2004) and 45.4 mg/kg (December 2004) as boric acid were estimated, and was reported in Table 6.2 as a geometric mean of 72 mg boric acid/kg which corresponds with an estimated saturated paste B IC_{25} of 4.7 mg/L. It is important to note that these two trials varied considerably from each other, with the 45 mg boric acid/kg value from December 2004 having exhibited anomalously high control values. This demonstrates the large influence that variable control data can have on the result of individual studies, and that evaluating numerous studies is necessary to reduce this overall variability and sensitivity.

LC_{50} and IC_{50} data were also provided for *Folsomia candida*, though raw data was not provided and thus LC/IC_{25}'s could not be derived. The authors stated that *Folsomia fimetaria* were generally more sensitive than *F. candida*, thus the *F. fimeteria* dataset presents the bulk of information from the species which will likely yield more conservative EC/IC values. 7-day and 14-day acute lethality trials for *Folsomia candida* were carried out in artificial soils, resulting in LC_{50}'s of 1,521 mg/kg and 800 mg/kg as boric acid, respectively. In clay loam, the resulting LC_{50}'s for the 7 and 14 day time periods were 1,590 mg/kg and 663 mg/kg.

For the *Folsomia candida* reproductive endpoint, a 28 day trial was conducted in artificial and clay loam soils. The artificial soil IC_{50} reported was 147 mg boric acid/kg, and the clay loam was 169 mg/kg. As with the lethality data for *Folsomia candida*, raw data were not included, and thus IC_{25}s have not been derived from this study. Overall, the comparison of artificial versus clay loam soils indicated that the toxicity of boron is relatively similar between these soil types for *Folsomia candida*.

Environment Canada, 2007c

Additional tests on the springtail *Folsomia candida* (Environment Canada, 2007c) also involved boric acid additions to artificial soil, followed by evaluating lethality and reproductive effects. A mean 14-day acute lethality (LC_{50}) value of 1,128 mg boric acid/kg was obtained. LC_{25}'s were not calculated, though they appear likely to be near 700 mg boric acid/kg on average.

Longer-term (28-day) reproduction tests yielded IC_{25} values for juvenile production of 146 or 290 mg boric acid/kg, depending on the springtail extraction method used. The geometric mean of these two extraction methods (152 mg boric acid/kg) is shown in Table 6.2, and corresponds to an estimated saturated paste B IC_{25} of 5.6 mg/L.

Oribatid Mites

Environment Canada, 2006-2010

The effect of boric acid on the oribatid mite, *Oppia nitens*, was evaluated with lethality and reproduction as endpoints over a period of 28 and 35 days. The average LC_{50} value of 1,061 mg boric acid/kg was obtained for the 28-day trials in artificial soil (average of two trials) (2006-2007), while the 35-day trials indicated an average LC_{50} of 628 mg boric acid/kg (2010). An LC_{25} of 730 mg boric acid/kg was obtained for the 2006 28-day trial, though LC_{25}s were not calculable for the other trials.

IC_{25}s were generated for reproductive endpoints for the four artificial soil trials between 2006 and 2010. The geometric mean of the four trials (two 28 days and two 35 days) was 249 mg boric acid/kg which corresponds to an estimated saturated paste IC_{25} of 12.0 mg/L (Table 6.2).

Princz, 2010

Toxicity testing for lethality and reproduction on *Oppia nitens* (oribatid mite) was conducted by Princz *et al.*using field-collected forest soil from Saskatchewan which was either used unamended as-is (2% organic matter) or amended with 8% peat (to 7% organic matter) (Princz *et al.*, 2010). Hydrometer analysis (43% sand, 49% silt, 8% clay) placed the forest soil at the bottom boundary of the 'loam' category within the soil texture triangle indicating a relatively coarse soil with low clay content and likely low boron sorption. Three trials with boric acid were performed in total: 1) unamended, age-unsynchronized; 2) amended, age-unsynchronized; 3) amended, age-synchronized. The study reported that age synchronized data was less variable than age unsynchronized data, and that the peat amendment generally increased reproduction and reduced variability.

28-day LC_{50} values were obtained of 250 mg boric acid/kg for the unamended, unsynchronized soil and an average of mg boric acid/kg for the amended soil (530 and 847 mg/kg for unsynchronized and synchronized trials, respectively). LC_{25} data was also independently derived from the original dataset, resulting in LC_{25} values ranging from 180 mg/kg (unamended) to 300-610 mg boric acid/kg (amended) for the lethality endpoint, with an overall geometric mean of 277 mg/kg.

28-day reproduction IC_{25} values were also derived from the 28-day reproduction tests. IC_{25}s ranged between 74 to 80 mg boric acid/kg for the unamended and amended treatments respectively, with a geometric mean of 77 mg/kg. This corresponds with an estimated saturated paste boron IC_{25} of 5.1 mg/L based on the field clay loam regression (Figure 6.1). As with the lethal endpoints, the presence of peat reduced boron toxicity for the reproductive endpoints.

6.3 Updated Earthworm Toxicity Testing in Alberta Reference Soil

Exova, 2013

Earthworm (Eisenia andrei) reproductive endpoint tests were carried out by Exova in 2013 on field sandy loam soils for the number of juveniles and the mass of juveniles (AEP, 2015). Saturated paste boron was measured directly in this study and thus there were no estimates of sat paste B from the regression (as was the case with the literature data). The number of juveniles varied from 0 to 37 survivors between the 12 replicates within each dose, indicating a high level of natural variability with juvenile earthworms. Likewise, the mass of the juveniles ranged from 4 mg to 54 mg per individual. Thirteen dosages were tested over 63 days, ranging from 0.2 mg/L to 130 mg/L saturated paste boron yielded a number of juvenile IC_{25} of 5.4 mg/L saturated paste boron, and a juvenile mass IC_{25} of 26.4 mg boron /L saturated paste extract (Table 6.2). This juvenile mass IC_{25} is the highest reproduction value reported in Table 6.2. The raw data and BMDS curves with generated IC_{25}s are shown in AEP (2015).

6.4 Summary of Invertebrate Toxicity Data

Data from the above mentioned invertebrate studies are summarized in Table 6.1 for 50% effect levels for non-reproductive endpoints, generally showing LC_{50} values with minimal combining of related or redundant endpoints. Table 6.2 shows 25% effect levels for reproductive endpoints and non-reproductive endpoints, where related or redundant endpoints have been combined via geometric means to generally have one IC_{25} and/or LC_{25} for a given species and soil type (further details provided in AEP (2015)). In both tables, spiked boric acid concentrations are shown as well as the equivalent spiked boron concentrations (both on a mg/kg basis). In Table 6.2, which consists of a combination of data gathered from the literature and from recent (2013) Exova earthworm experiments, estimated saturated paste boron concentrations are also shown based on the soil regressions discussed in Section 6.1. The Exova 2013 experiments directly measured saturated paste boron concentrations from soils and thus do not show spiked boron levels since regressions were not needed.

Lethality LC_{25} endpoints range from 17.7 mg/L to 51.1 mg/L, and reproductive IC_{25} endpoints range from 2.4 mg/L to 26.4 mg/L. The two lowest invertebrate IC_{25} in Table 6.2 are estimated at 2.4 mg/L and 4.7 mg/L in artificial soil and clay loam respectively for reproductive endpoints in one species of springtail (*Folsomia fimeteria*). For context, the 25th percentile of the data shown in Table 6.2, (ten values for reproductive endpoints and six values for non-reproductive endpoints) is approximately 6.6 mg/L which has relevance for guideline development.

Table 6.1. Invertebrate Boron Toxicity – 50% Effect Data on All Non-Reproductive Endpoints

Common Name	Species	Test	Duration	Soil	Measure	Boric acid added (mg/kg)	Boron (B) added (mg/kg)	Reference	Notes
LC/IC50s									
Earthworm	*Eisenia andrei*	Lethality	14 days	clay loam	LC50	4621	808	Ingraldi, 2004	
Termites	*R.flavipes, C.formosanus*	Lethality	10 days	sand	LC50	n/a	745	Grace, 1991	lowest approximate LC50 shown
Earthworm	*Eisenia fetida*	Lethality	14 days	artificial	LC50	4365	763	Ingraldi, 2004	
Earthworm	*Eisenia andrei*	Lethality	7 days	artificial	LC50	3800	664	Environment Canada, 2004	
Earthworm	*Eisenia andrei*	Lethality	14 days	artificial	LC50	3500	612	Environment Canada, 2004	
Earthworm	*Eisenia andrei*	Lethality	14 days	artificial	LC50	3236	566	Ingraldi, 2004	
Springtail	*Folsomia candida*	Lethality	7 days	field clay loam	LC50	1590	278	CECOTOX, 2005	
Springtail	*Folsomia candida*	Lethality	7 days	artificial	LC50	1521	266	CECOTOX, 2005	
Springtail	*Folsomia fimetaria*	Lethality	7 days	field clay loam	LC50	905	158	CECOTOX, 2005	
Earthworm	*Eisenia andrei*	Avoidance	2 days	field clay loam	EC50	873	153	Environment Canada, 2004	average of 4 labs
Springtail	*Folsomia candida*	Lethality	14 days	artificial	LC50	1128	197	Environment Canada, 2007c	
Oribatid mite	*Oppia nitens*	Lethality	28 days	artificial	LC50	1061	185	Environment Canada, 2006-2010	average of two trials (2006-2007)
Earthworm	*Dendrodrilus rubidus*	Lethality	28 days	artificial	LC50	1041	182	Environment Canada, 2008-2010	avg. of 4 separate 28 day studies in 2008-‘10
Springtail	*Folsomia fimetaria*	Lethality	7 days	artificial	LC50	958	167	CECOTOX, 2005	
Oribatid mite	*Oppia nitens*	Lethality	28 days	field loam with 7% OM	LC50	689	120	Princz *et al.*, 2010	amended, avg. of unsync. and sync trials
Springtail	*Folsomia candida*	Lethality	14 days	field clay loam	LC50	663	116	CECOTOX, 2005	
Earthworm	*Eisenia andrei*	Avoidance	2 days	clay loam	EC50	661	116	Ingraldi, 2004	
Springtail	*Folsomia candida*	Lethality	14 days	artificial	LC50	800	140	CECOTOX, 2005	
Springtail	*Proisotoma minuta*	Lethality	7 days	artificial	LC50	687	120	Environment Canada, 2010-2012	
Springtail	*Folsomia fimetaria*	Lethality	14 days	artificial	LC50	641	112	CECOTOX, 2005	
Oribatid mite	*Oppia nitens*	Lethality	35 days	artificial	LC50	628	110	Environment Canada, 2006-2010	average of two trials (2010)
Springtail	*Folsomia fimetaria*	Lethality	14 days	field clay loam	LC50	282	49	CECOTOX, 2005	
Oribatid mite	*Oppia nitens*	Lethality	28 days	field loam with 2% OM	LC50	250	44	Princz *et al.*, 2010	unamended, unsynchronized soil
Springtail	*Proisotoma minuta*	Lethality	21 days	artificial	LC50	296	52	Environment Canada, 2010-2012	average of two trials in 2010

Table 6.2. Invertebrate Boron Toxicity – 25% Effect Data on Reproductive and Non-Reproductive Endpoints

Common Name	Species	Test	Duration	Soil	Measure	Boric acid added (mg/kg)	Boron (B) added (mg/kg)	sat paste Boron (mg/L)	Reference	Notes
Oribatid mite	*Oppia nitens*	Lethality	28 days	artificial	LC25	730	128	**51.1**	Environment Canada, 2006-2010	single trial from 2006
Earthworm	*Eisenia andrei*	Avoidance	2 days	field clay loam	EC25	406	71	**48.4**	Environment Canada, 2004	geomean from 4 laboratories
Springtail	*Folsomia fimetaria*	Lethality	7-14 days	artificial	LC25	558	98	**36.6**	CECOTOX, 2005	geomean of 7 and 14 days
Oribatid mite	*Oppia nitens*	Lethality	28 days	loam with 2-7% OM	LC25	277	48	**30.1**	Princz *et al.*, 2010	geomean of amended and unamended soils
Earthworm	*Eisenia andrei*	Reproduction	63 days	sandy loam	EC25	*	*	**26.4**	* Exova, 2013	mass of juveniles
Springtail	*Folsomia fimetaria*	Lethality	7-14 days	field clay loam	LC25	249	43	**25.4**	CECOTOX, 2005	geomean of 7 and 14 days
Springtail	*Proisotoma minuta*	Lethality	21 days	artificial	LC25	308	54	**17.7**	Environment Canada, 2010-2012	geomean of 3 separate studies (2010-2012)
Earthworm	*Dendrodrilus rubidus*	Reproduction	56 days	artificial	EC25	268	47	**13.5**	Environment Canada, 2008-2010	geomean of four 56 day studies in 2008-2010
Oribatid mite	*Oppia nitens*	Reproduction	28 days	artificial	EC25	249	44	**12.0**	Environment Canada, 2006-2010	geomean of all four trials (2006-2007, 2010)
Springtail	*Proisotoma minuta*	Reproduction	21 days	artificial	EC25	213	37	**9.4**	Environment Canada, 2010-2012	geomean of 3 separate studies (2010-2012)
Earthworm	*Eisenia andrei*	Reproduction	84 days	clay loam	EC25	104	18	**7.5**	Ingraldi, 2004	geomean of number and mass of juveniles
Springtail	*Folsomia candida*	Reproduction	28 days	artificial	EC25	152	27	**5.6**	Environment Canada, 2007c	geomean of 2 extraction methods
Earthworm	*Eisenia andrei*	Reproduction	63 days	sandy loam	EC25	*	*	**5.4**	* Exova, 2013	number of juveniles
Oribatid mite	*Oppia nitens*	Reproduction	28 days	loam with 2-7% OM	EC25	77	13	**5.1**	Princz *et al.*, 2010	geomean of amended and unamended soils
Springtail	*Folsomia fimetaria*	Reproduction	28 days	clay loam	EC25	72	13	**4.7**	CECOTOX, 2005	number of juveniles (geomean of two 28 day trials)
Springtail	*Folsomia fimetaria*	Reproduction	28 days	artificial	EC25	84	15	**2.4**	CECOTOX, 2005	number of juveniles (geomean of two 28 day trials)

*Note: 2013 Exova study directly measured saturated paste B, thus estimations from spiked boron levels are not required. All other studies had saturated paste boron estimated from spiked boron levels using soil regressions

7. Toxicity to Humans

7.1 Human and Mammalian Toxicity Data

Though at present no biochemical function has been clearly identified in humans, boron is a trace element for which essentiality is suspected but has not been directly proven (USEPA, 2004a,b). For example, boron deficiency may affect calcium and magnesium metabolism in bone, leading to changes similar to those seen in osteoporosis (Nielsen, 1994 cited in US EPA 2004b). There is also evidence that boron deficiency may have an effect on brain function as demonstrated by electroencephalogram changes suggestive of behavioral activation (*e.g*. drowsiness) and mental alertness (Nielsen, 1997).

The toxicity of boron has been studied in laboratory animals and episodes of human poisoning. Comprehensive toxicological profiles have been developed by several agencies including the World Health Organization (WHO, 1998), the Agency for Toxic Substances and Disease Registry (ATSDR, 2010), and the US Environmental Protection Agency (US EPA, 2004a,b). Boric acid and borax were widely used in medicine at the beginning of the century for therapeutic purposes to treat certain diseases such as epilepsy and infections (WHO, 1998). This practice resulted in adverse effects in some patients and was discontinued.

A compilation of boron toxicity data from literature relevant to human exposure to boron is presented in Table 7.1 with data primarily sourced from WHO (1998), US EPA (2004a,b), and ATSDR (2010). Acute exposure to boron has been documented in cases of both adults and infants. US EPA (2004a,b) reported minimum lethal doses ranging from 15 to 20 g in adults, to 2 to 3 g in infants. Adult patients undergoing boron neutron capture therapy for brain tumors received a dose of 25 to 35 mg B/kg body weight and exhibited nausea, vomiting, and flushed skin. A single dose of 70 mg/kg body weight to a patient recovering from a surgery via a subcutaneous fluid infusion caused severe cutaneous and gastrointestinal symptoms (Culver and Hubbard, 1996; USEPA 2004a,b). In all cases reported in Culver and Hubbard (1996) in which the dose was below 3.68 mg B/kg body weight, patients did not indicate any adverse effects. Baker *et al*. (1986) which was summarized in USEPA (2004a,b) reported that infants accidentally exposed to boric acid in formula exhibited a rash at a dose of 30.4 mg B/kg-day. At a higher dose of 94.7 mg B/kg-day, an infant exhibited symptoms of diarrhea and vomiting. In general, reviews of the available literature such as that of Culver and Hubbard (1996) and WHO (1998) suggest that the most common symptoms of accidental boron poisoning are diarrhea, vomiting, abdominal pain, lethargy, skin rash, headaches, and lightheadedness (US EPA, 2004a,b). From the available data, Culver and Hubbard (1996) reported a NOAEL for humans of 2.5 mg B/kg-day and suggested that infants were no more sensitive to boron than adults.

Longer-term human exposure to boron with unintended side effects has also been documented in the literature. When boron-containing epilepsy medication was taken orally at doses of 2.5 to 24.8 mg B/kg-day over several years, no symptoms were observed at the lowest dose (2.5 mg B/kg-day), whereas indigestion, dermatitis, alopecia, and anorexia were observed at 5 mg/kg-day and higher (Culver and Hubbard, 1996; US EPA 2004a,b). Over a duration of 4 to 10 weeks, infants orally exposed to a borax and honey mixture on pacifiers exhibited seizures and other milder effects (O'Sullivan and Taylor, 1983) with a LOAEL of 3.2 mg/kg-day estimated by the USEPA (2004a,b). Male workers inhaling boron salts during the production of boric acid over 10 years or more (>3,650 days) were reported on by Tarasenko *et al*. (1972). The men were exposed to 22 to 80 mg of boron salts/m^3 as vapour and aerosols, and exhibited decreased sexual function, sperm count and motility.

Various mammalian species such as dogs, rats, rabbits, and mice are also shown and often used to supplement toxicity data when human data are limited (also relevant to wildlife as discussed in Section 8). Boron toxicity estimates for humans were initially based on research conducted on dogs (Weir and Fisher, 1972), but have been updated to be based on newer research on rats, mice, and rabbits in light of some limitations of the dog toxicity results (US EPA, 2004a,b). A summary of the research on rats, mice and rabbits are provided below and also in Table 7.1.

Rats are considered the most sensitive of mice, rats and rabbits (US EPA, 2004 a,b; Heindel *et al.*, 2004), with the associated toxicity data of relevance to both humans and wildlife. Pregnant rats were exposed to 0, 163, 330, and 539 mg boric acid/kg-day (0, 29, 58 and 95 mg B/kg-day, respectively) in Heindel *et al.* (2002, 2004). Pregnant rats exhibited increased liver and kidney weight at boric acid doses above 163 mg/kg-day, decreased weight gain at doses above 330 mg/kg-day, and altered food and water intake at doses above 539 mg/kg-day (Heindel *et al.*, 2002, 2004). The embryonic mortality rate was significantly greater than controls at 539 mg/kg-day boric acid (fed to pregnant mothers) and the live-litter size was lower. Offspring exhibited decreased weight gain at all dose levels (78, 163 and 330 mg boric acid/kg-day), ranging from a 6-7% decrease in the low doses to a 50% decrease at the highest dose. Fetal malformations, including rib and brain deformities were also observed in fetuses at doses above 163 mg boric acid/kg-day (Heindel *et al.*, 2002, 2004). A LOAEL of 78 mg boric acid/kg-day (13.6 mg B/kg-day) and NOAEL of <78 mg boric acid/kg-day were derived for rats within the Heindel *et al.* studies. In a similar study, Price *et al.* (1996a) reported similar results to Heindel *et al.* (2002), and drew comparisons between the two. A pre-natal NOAEL of 55 mg boric acid/kg-day (9.6 mg B/kg-day) was derived for maternal and fetal endpoints (fetal being the more sensitive). A post-natal NOAEL of 74 mg boric acid/kg-day (12.9 mg B/kg-day) was also reported based on offspring endpoints. Due to their sensitivity and direct correlation with boron dose levels in the Price *et al.* (1996a) dataset, a review report by Allen *et al.* (1996) proposed that fetal weight was the most effective endpoint for analysis of dose estimations. The US EPA (2004a,b) reviewed, combined and summarized the Heindel *et al.* and Price *et al.* studies and determined a LOAEL of 13.3 mg B/kg-day and a benchmark dose lower limit ($BMDL_{05}$) of 10.3 mg/kg-day based on the decreased fetal weight endpoint. This $BMDL_{05}$ of 10.3 mg/kg-day was subsequently used to derive human reference doses with the application of uncertainty factors.

For mice, Heindel *et al.* (1992, 1994) dosed pregnant mice with 0, 248, 452 and 1003 mg boric acid/kg-day. Decreased weight gain was observed at the 1003 mg boric acid/kg-day dose (175 mg B/kg-day). Maternal kidney weight and water intake were increased at the 452 mg boric acid/kg-day dose. Mild renal lesions were also observed at the lower dose of 248 mg boric acid/kg-day. Fetal body weight and fetal success (based on number of resorptions per litter) were both decreased, and malformations increased at 452 mg boric acid/kg-day. The NOAEL reported for these studies for mice was 248 mg boric acid/kg-day, equivalent to 43.3 mg B/kg-day (US EPA, 2004a,b).

For rabbits, boron toxicity in pregnant rabbits was evaluated with doses of 0, 62.5, 125 and 250 mg boric acid/kg-day (Heindel *et al.*, 1994 and Price *et al.*, 1996b). At 250 mg/kg-day (43.7 mg B/kg-day), fetal survival was decreased, as measured by the specific endpoints of prenatal mortality, litter size, and non-live fetuses. Fetal malformations were also increased at 250 mg/kg-day. However, fetal body weight at this 250 mg/kg-day dose level was not statistically different than the control group, and only mild maternal effects were observed. No definitive adverse effects were measured at the two lowest doses of 62.5 and 125 mg boric acid/kg-day. Kidney weight, uterine weight and body weight endpoints indicated comparable toxicity dose levels as mice (Heindel *et al.*, 1994; Price *et al.*, 1996b), both of which were less sensitive than rats as noted above. LOAELs of 250 mg boric acid/kg-day (43.7 mg B/kg-day) were reported for both studies. A NOAEL for rabbits was also reported in Heindel *et al.* (1994) as 125 mg boric acid/kg-day, which corresponds to 21.9 mg B/kg-day (US EPA, 2004a,b).

This data suggests a threshold exists for boron toxicity below which a relatively low probability is expected for the occurrence of adverse effects in a human population. A human health oral reference dose of 0.2 mg/kg-day has been developed by the US EPA, providing an estimate of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2004a,b). This human oral reference dose of 0.2 mg/kg-day was derived from an interpolated 5% decreased fetal weight in rats, and was based on a $BMDL_{05}$ of 10.3 mg B/kg-day. This $BMDL_{05}$ was generated from the combined results described above from Price *et al.* (1996a) and Heindel *et al.* (1992 and 1994) and summarized by Allen *et al.* (1996). Rats were the species of greatest relevance from which to derive the BMDL because they were found to be more sensitive than mice and rabbits. The derived human reference dose also included the application of a derived 66-fold uncertainty factor to account for animal-to-human and sensitive-human variability (US EPA, 2004a,b). This oral reference dose is considered the Tolerable Daily Intake (TDI) in further calculations. Note that the US EPA (2004) TDI of 0.20 mg/kg-day was used to develop the human health related Alberta Tier 1 soil remediation guidelines for boron rather than the comparable Health Canada ‘acceptable daily intake’ (ADI) value of 0.035 mg B/kg-day (Health Canada, 1990). The US EPA TDI is more recent and based on toxicity research that was not available when the Health Canada ADI was developed. It also incorporates a more recent protocol for deriving uncertainty factors for applying animal toxicity data to humans.

It should be noted that this reference value is applicable to all sources of boron exposure including soil, drinking water, and the ingestion of boron in various foods. Humans are exposed daily to boron present in food. Fruits, vegetables, pulses, legumes, and nuts contain relatively high concentrations of boron, whereas, dairy products, fish, meats, and grains contain relatively low concentrations. Rainey *et al*. (1996) estimated that the median, mean, and 95th percentile daily intakes of boron for all sexes and age groups in the United States to be 0.76, 0.93, and 2.16 mg/day, respectively. The World Health Organization (WHO 1998) calculated a mean daily intake for boron of 1.2 mg/day. A substantial increase in these uptake rates could occur for individuals with unique and consistent dietary preferences due to the relatively high content of boron in certain foods and beverages. For example, one serving of wine or the consumption of a single avocado provides a boron dose of 0.42 or 1.11 mg respectively (Anderson *et al*., 1994).

More recent work by Rainey *et al*. (2002) (cited by ATSDR 2010) estimates the mean boron intakes for various population subgroups as: 0.80 mg/day for 4-8 year olds, 1.02 mg/day for 14-18 year old males, 1.00 mg/day for adult females, and 1.28 mg/day for adult males. Based on this data, the mean daily intake of boron in the diet of a toddler and adult was assumed to be 0.80 and 1.28 mg/day respectively. This results in an estimated daily intake (EDI) on a per kilogram body weight basis for a 16.5 kg toddler of 0.048 mg/kg-day. Subtracting this EDI from the TDI results in a residual tolerable daily intake (rTDI) of 0.20 – 0.048 = 0.152 mg/kg-day for a toddler. Similarly, the EDI for a 70.7 kg adult is calculated to be 0.018 mg/kg-day, resulting in a higher rTDI of 0.182 mg/kg-day for an adult.

Table 7.1. Human and Mammalian Boron Toxicity Data

Species	Route of Exposure	Dose	Duration (days)	Results Details	Reference
Humans	Inhalation	22 to 80 mg/m^3	>3650	Decreased sperm count, sperm motility.	Tarasenko *et al*. 1972
Humans	Oral	30.4, 94.7 mg/kg	Single dose	Rash at lower dose, diarrhea and vomiting at higher dose	Baker *et al*. 1986 in US EPA, 2004a,b
Humans	Oral	1.4 – 70 mg/kg	Single dose	No effects less than 3.68 mg B/kg. Nausea, vomiting, skin flush at 25-35 mg B/kg. Severe cutaneous and gastrointestinal symptoms at 70 mg B/kg.	Culver and Hubbard, 1996 in US EPA, 2004a,b
Humans	Oral	2.5 – 24.8 mg/kg-day	Several years	Indigestion, dermatitis, alopecia, anorexia at 5 mg B/kg-day. No symptoms at 2.5 mg B/kg-day.	Culver and Hubbard, 1996 in US EPA, 2004a,b
Humans	Oral	9.6-33 mg/kg-day	4-10 weeks	Seizures and other milder effects from infants consuming honey-borax mixture on pacifier. LOAEL estimated as 3.2 mg/kg-day	O'Sullivan and Taylor, 1983; Taylor 1997; both in US EPA, 2004a,b
Dogs	Oral	6, 60.5 mg B/kg-d	90	Severe testicular atrophy.	Weir and Fischer, 1972
Dogs	Oral	6.8, 22.8 mg B/kg-d	90	Testicular atrophy, spermatogenic arrest.	Weir and Fischer, 1972
Mice	Oral	0, 21, 70, 210 mg B/kg-d	5 + 5 + 11	Decreased testes weight; At 210 mg/kg-d exfoliation/disruption of seminiferous tubules, inhibited spermiation noted.	Harris *et al*. 1992
Mice	Oral	0, 21, 70, 210 mg B/kg-d	7	All dams failed to produce litters.	Harris *et al*. 1992
Mice	Oral	288 mg B/kg-d	91	Degeneration of seminiferous tubules.	Dieter *et al*. 1994
Mice	Oral	201 mg/kg-d	721	Degeneration of seminiferous tubules, testicular atrophy, interstitial hyperplasia.	NTP, 1987
Mice	Oral	0, 26.6, 111, 220 mg B/kg-d	189	Reduced sperm motility; At 111 mg/kg-d decreased fertility and mating index, decreased testes, epididymis weight, decreased sperm count, increased sperm abnormalities, atrophy of seminiferous tubules; infertility at 220 mg/kg-d.	Fail *et al*. 1991
Mice	Oral	0, 31.8, 152, 257 mg B/kg-d	189	Decreased litter adjusted F2 pup weight, shorter estrous cycle (F1); At 152 mg/kg-d longer gestational period (F0), decreased litter adjusted F1 pup weight; Complete infertility at 257 mg/kg-d.	Fail *et al*. 1991
Mice	Oral	0, 43, 79, 175 mg B/kg-d	17	Reduced fetal body weight, increased incidence of resorptions.	Heindel *et al*. 1992, 1994
Mice	Oral	0, 43, 79, 175 mg B/kg-d	17	Malformations including increased incidence of short rib XIII, decreased incidence of rudimentary or full ribs(s) at lumbar I.	Heindel *et al*. 1992, 1994
Mice	Oral	0, 43, 79, 175 mg B/kg-d	17	Mild renal lesions (2/10) noted at 43.4 mg/kg-d; At 79 mg/kg-d increased water intake, increased kidney weight, decreased weight gain noted. NOAEL was reported as 43 mg B/kg-day	Heindel *et al*. 1992, 1994
Mice	Oral	70 mg B/kg-d	1	Decreased fetal body weight for all days of exposure; Increased incidence of fetuses with cervical rib and rib agenesis when treated on G8 (not other days).	Cherrington and Chernoff, 2002
Mice	Oral	0, 131 mg B/kg-d	1	Increased incidence of fetuses with cervical ossification (unilateral thoracic vertebrae and cercival rib formation/ossification differences).	Cherrington and Chernoff, 2002
Mice	Oral	0, 131 mg B/kg-d	1	Multiple thoracic skeletal malformations (11 forms) noted, in particular rib development.	Cherrington and Chernoff, 2002
Mice	Oral	88 mg B/kg-d	5	Reduction in length of fetal rib XIII	Cherrington and Chernoff, 2002
Rabbits	Oral	0, 11, 22, 44 mg B/kg-d	14	Decreased maternal body weight gain, food intake, uterine weight, number of ovarian corpora lutea. Increased relative kidney weight.	Price *et al*. 1996b
Rabbits	Oral	0, 11, 22, 44 mg B/kg-d	14	Increased resorptions (90% versus 6% in controls), increased percentage of pregnant females with no live fetuses (73% versus 0% in controls), decreased litter size (2.3 versus 8.8 in controls). NOAEL was reported as 22 mg B/kg-day	Price *et al*. 1996b

Table 7.1. Human and Mammalian Boron Toxicity Data

Species	Route of Exposure	Dose	Duration (days)	Results Details	Reference
Rabbits	Oral	0, 11, 22, 44 mg B/kg-d	14	Cardiovascular malformations (interventricular septal defect in 57% versus 0.6% in controls).	Price *et al.*, 1996b
Rats	Inhalation	12 to 73 mg B/m^3	70 to 168	No effects on ovaries or testes of exposed rats.	Wilding *et al.*, 1959
Rats	Oral	44, 53, 88 mg B/kg-d	14	Significant damage to male reproductive tissues.	Fukuda *et al.*, 2000; Kudo *et al.*, 2000; Ku *et al.*, 1993
Rats	Oral	0, 300, 500 mg/kg	14	Decreased testis and epididymis weight, histopathological changes to reproductive tissues, mild inhibition of spermiation, necrosis/degeneration of germ cells.	Fukuda *et al.*, 2000
Rats	Oral	0, 125, 250, 500 mg/kg	28	Decreased sperm count and sperm motility; Histological changes (500 mg/kg-d); Necrosis or degeneration of germ cells and decreased spermatogonia (dose of effect no reported).	Kudo *et al.*, 2000
Rats	Oral	0, 26, 38, 52, 78 mg B/kg-d	63	Inhibited spermiation; Decreased epididymal sperm counts (dose of effect not reported); testicular atrophy (52 mg/kg-d); areas of focal atrophy (38 mg/kg-d.	Ku *et al.*, 1993
Rats	Oral	0, 50, 150, 500 mg/kg-d	21	Decreased fertility index, increased pre-implantation loss when mated with unexposed females, effect on sperm; Complete lack of fertility, atrophy of seminiferous tubules, multinucleated giant cells in the testes at 500 mg/kg-d.	Yoshizaki *et al.*, 1999
Rats	Oral	0, 25, 50, 100 mg B/kg-d	60	Testicular atrophy, decrease in testes and epididymis weights, loss of germinal cell elements, reduced fertility; Decrease in seminiferous tubule diameter in all groups (dose-related manner).	Lee *et al.*, 1978
Rats	Oral	0, 43, 86, 172 mg B/kg-d	60	Infertile for 5 weeks after exposure; Completely infertile (172 mg/kg-d or 2000 ppm). No decrease in litter size or fetal death therefore infertility appears to be due to germinal aplasia.	Dixon *et al.*, 1979
Rats	Oral	136 mg B/kg-d	60	Decreased weights of testis, epididymis, seminal vesicles, prostate, vas deferens, decreased sperm motility, number of spermatocytes, spermatid and Leydig cells. Decreased testosterone levels.	Nusier and Bataineh, 2005
Rats	Oral	0, 23.7, 44.7 mg B/kg-d	70	Impaired spermatogenesis; At lower dose decreased weight of testes, seminal vesicles.	Seal and Weeth, 1980
Rats	Oral	0, 5.9, 17.5, 58.5mg B/kg-d	14	Complete lack of fertility associated with lack of viable sperm in atrophied testes.	Weir and Fischer, 1972
Rats	Oral	0, 5.9, 17.5, 58.5mg B/kg-d	14	Lack of fertility and decreased ovulation in females when mated with unexposed males.	Weir and Fischer, 1972
Rats	Oral	0, 3, 6, 10, 13, 25 mg B/kg-d	20	Decreased fetal body weight, skeletal abnormalities evident on G0. When examined until PND21, these effects were not observed. Developmental effects persisted postnatally only at 25 mg/kg-d.	Price *et al.*, 1998
Rats	Oral	0, 44, 87, 175, 350 mg B/kg-d	1	Effects on spermiation, epididymal sperm morphology.	Linder *et al.*, 1990
Rats	Oral	0, 60.9 mg B/kg-d	28	Inhibited spermiation; degeneration of seminiferous tubules; decreased serum testosterone.	Treinen and Chapin, 1991
Rats	Oral	500 mg/kg	1	Decreased fetal body weight when exposed on GD 7, 9, 10, 11; Altered cephalo-caudal gene expression pattern when exposed on GD9; Disrupted axial development when exposed on GD8, 9 or 10; Cervical rib or vertebral malformations when exposed on GD8; Dramatic alterations in number of vertebrae, ribs or sternebrae when exposed on GD9.	Narotsky and Kavlock, 2003
Rats	Oral	0, 14, 29, 58, 94 mg B/kg-d	20	Reduced fetal body weight; At 29 mg B/kg-d increased incidence of malformations noted including enlarged lateral ventricles of the brain and	Heindel *et al.*, 1992, 1994

Table 7.1. Human and Mammalian Boron Toxicity Data

Species	Route of Exposure	Dose	Duration (days)	Results Details	Reference
				agenesis or shortening of the rib XIII.	
Rats	Oral	0, 14, 29, 58, 94 mg B/kg-d	20	Increased liver and kidney weights, altered water and/or food intake; At 58 mg B/kg-d decreased weight gain noted. NOAEL was reported as <13.6 mg B/kg-day	Heindel *et al.*, 1992, 1994
Rats	Oral	0, 3, 6, 10, 13, 25 mg B/kg-d	20	Increased incidence of short rib XIII, wavy ribs at 13 mg B/kg-d. When pups examined until PND21, effects only significant at 25 mg B/kg-d. A prenatal NOAEL of 9.6 mg B/kg-day and postnatal NOAEL of 12.9 mg B/kg-day were reported.	Price *et al.*, 1996a
Rats	Oral	0, 3.3, 6.3, 9.6, 13, or 25 mg B/kg-d	20	Increased relative kidney weight.	Price *et al.*, 1996a

7.2 Exposure Equation for Humans

The equation from AESRD (2014a) to calculate exposure and soil remediation guidelines for human direct soil contact (soil ingestion, dermal contact, and particulate inhalation) is shown below. This equation is taken directly from CCME (2006), and applies to threshold chemicals such as boron where a threshold exists below which adverse effects are not expected (*i.e.*, a non-carcinogenic substance). Since the soil ingestion pathway is expected to predominate, the guideline calculated is based on total acid digest boron due to the high acidity of the human gut. Parameter values are shown for both adults and toddlers depending on land use. This equation is used further in Section 10 along with an additional conversion factor between acid digest boron and saturated paste boron to derive a human direct soil contact guideline for boron.

$$SRG_{HH-DC} = \frac{(TDI - EDI) \times SAF \times BW}{[(AF_G \times SIR) + (AF_L \times IR_S \times ET_2) + (AF_S \times SR)] \times ET_1} + BSC$$

Where:

SRG_{HH-DC} = Human direct contact guideline mg/kg acid digest boron

TDI	=	Tolerable daily intake	0.200 mg/(kg-day)	US EPA 2004a
EDI	=	Estimated background daily intake	0.048 mg/(kg-day) (toddler) 0.018 mg/(kg-day) (adult)	ATSDR 2010 ATSDR 2010
SAF	=	Soil allocation factor (non-volatile, allocated between soil, water, food, consumer products)	0.25 (four compartments);	AESRD 2014a
BW	=	Body weight of human receptor:	16.5 kg (toddler) 70.7 kg (adult)	AESRD 2014a AESRD 2014a
AF_G	=	Absorption factor for gut	1.0 (100% absorbed)	assumed
SIR	=	Soil ingestion rate:	8.0×10^{-5} kg/day (toddler) 2.0×10^{-5} kg/day (adult)	AESRD 2014a AESRD 2014a
AF_L	=	Absorption factor for lungs	1.0 (100% absorbed)	assumed
IR_S	=	Inhalation of soil particles	7.1×10^{-9} kg/day (toddler) 1.2×10^{-8} kg/day (adult)	AESRD 2014a AESRD 2014a
ET_2	=	Exposure term 2	1 (agricultural) 0.4167 (industrial)	AESRD 2014a AESRD 2014a
AF_S	=	Absorption factor for skin	0 (not absorbed)	US EPA 2004
SR	=	Soil dermal contact rate	N/A (since not absorbed)	N/A
ET_1	=	Exposure term 1	1 (agricultural) 0.6593 (industrial)	AESRD 2014a AESRD 2014a
BSC	=	background soil concentration	mg/kg acid digest boron	

8. Toxicity to Livestock, Wildlife, and Aquatic Life

Livestock, wildlife, and aquatic life may all be exposed to boron in soil, food, or water, and thus an understanding of potential boron toxicity to these classes of organisms is important for deriving guidelines. Livestock and wildlife are first considered in Section 8.1 due to similarities in their guideline derivation process, followed by aquatic life in Section 8.2.

8.1 Livestock and Wildlife

Livestock and wildlife are both considered to be potentially present on agricultural land, and may be exposed to boron from ingested soil and food as well as from drinking water. This also applies to wildlife in natural areas, and to livestock present on grazing leases in natural areas.

8.1.1 Livestock Toxicity Data

A number of studies have examined the adverse effects of boron on livestock health and are summarized in Table 8.1 below. These include primarily chickens and cattle as well as limited information for sheep, lambs, and goats.

For chickens, boric acid is often added to chicken litter to control beetle populations in poultry-houses and was studied in Dufour *et al.* (1992). Here, chicks exposed for 15 days to litter with higher-than-recommended boric acid treatments (3.6 and 7.2 kg boric acid/9.3 m^2) showed reduced growth and feather abnormalities. In contrast, those exposed to the upper end of the manufacturer-recommended range of boric acid treatment (0.4-0.9 kg/9.3 m^2) showed no apparent adverse effects. In a separate part of this study, chicks ingested feed treated with boric acid concentrations of up to 5,000 mg/kg for two weeks. Chicks had significantly lower body weight at feed levels of 2,500 or 5,000 mg boric acid/kg (437 and 873 mg B /kg, respectively), but no apparent effects on body weight or feed consumption at lower levels of 0, 500, or 1,250 mg boric acid/kg (0, 87, and 218 mg B /kg, respectively) in feed. A dose-related feather abnormality was also observed at the 5,000 mg boric acid/kg level. From this study, the feed treatment level of 1,250 mg boric acid/kg (218 mg B/kg) can be considered an approximate 'no observed adverse effect level' (NOAEL) for chicks, corresponding to an approximate daily B dose of 20 mg/kg-day based on estimates of the average daily feed consumption rate and average body weight over the duration of the study. For adult chickens, Puls (1994) stated that egg production ceased at 5,000 mg boric acid/kg in feed (875 mg B/kg), along with an increase in chick mortality rate. Rossi (1993a) evaluated effects on adults at 250 mg B/kg feed, with no effect on adult mortality, body weight, or egg production. Females showed a 20% decrease in hatchability in 12 weeks, and males showed no effect on hatchability or fertility but showed some increase in damaged sperm cells. These low-level reproductive effects correspond to a daily dose of approximately 10.9 mg B/kg-day based on the reported 3.73 kg body weight and final food intake rate of 163 g/day.

The effects of boron on cattle have also been studied, often in the context of determining safe levels for drinking water in areas where water sources may have naturally elevated boron such as in parts of California and Nevada (Green and Weeth, 1977). The Alberta livestock watering guideline for boron is 5 mg/L, which is equivalent to a dose of approximately 1 mg/kg-day. This guideline is sourced from CCME (CCREM, 1987), which notes there is no evidence that relatively high boron concentrations are toxic to livestock and therefore little work has been done to establish safe levels for boron. CCREM (1987) also notes that concentrations several times higher than 5 mg/L are likely safe. This guideline was based on water quality criteria developed by the National Academy of Sciences and the National Association of Engineering (NAS/NAE, 1972) which were set at the maximum boron concentration measured in U.S. rivers and lakes. Canadian Drinking Water Guidelines (Health Canada, 2014) also support the position that concentrations several times higher than 5 mg/L are likely safe, as do other reviews such as Eisler

(1990), Puls (1994), and Moss and Nagpal (2003). For example, Weeth *et al.* (1981) did not observe adverse effects (such as differences in weight, food, or water consumption) when cattle consumed water with up to 120 mg/L boron over a period of 10 days. However, increased phosphate excretion was observed at levels starting at approximately 60 mg/L (7.65 mg B/kg-day), with no effects observed at 30 mg/L (approximately 4.6 mg B/kg-day). Conversely, various effects including lethargy, inflammation of legs, and decreased food and water consumption were observed when cattle were exposed to boron concentrations of 150-300 mg/L in drinking water for 30 days (Green and Weeth, 1977). This is consistent with a related experiment where 150-300 mg boron/L in drinking water also showed adverse effects in rats over a 70 day exposure in Seal and Weeth (1980).

Significant adverse effects have been observed in cattle at dietary doses of 15 mg/kg-day and greater. For example, the above Green and Weeth (1977) study presents daily doses of approximately 15-25 mg/kg-day (for 150-300 mg/L in water) based on the specific cattle weights and water intake rates cited in the original paper (yearling heifers with an average weight of 288 kg and baseline water intake of approximately 27 L/day). This study (frequently cited in various reviews including Eisler (1990) and Moss and Nagpal (2003) speculated that boron concentrations in water of 40 to 150 mg/L appear “safe” for livestock, based in part on a taste/rejection experiment within the same study whereby cattle preferred tap-water over boron-containing water at boron concentrations of 29-95 mg/L but no adverse effects were noted. Previous studies with rats such as Green *et al.* (1973) (cited in Nielsen (1986) and Seal and Weeth (1980)) where 75 mg/L in water did not show adverse reproductive effects in rats were also cited in Green and Weeth (1977) as supporting a minimum tolerated concentration of 40 mg/L for livestock. The lower concentration of 40 mg/L recommended in Green and Weeth (1977) was also listed as “safe” or “maximum tolerated” in Eisler (1990). Puls (1994) recommended a similar but somewhat lower safe level up to 30 mg/L in livestock drinking water, likely based on the phosphate excretion observations from Weeth *et al.* (1981).

Boron concentrations in cattle feed of 150 mg/kg are considered safe (NAS, 1980; Eisler, 1990; Moss and Nagpal, 2003) based on studies where borax is added to feed. For example, Owen (1944) added 16-20 g of borax daily (approximately 1,800 to 2,300 mg B daily) for 42 days to the feed of Ayrshire dairy cows. This results in a reported feed concentration 283 mg/kg boron, and a reported daily borax intake of 18-23 g (equivalent to approximately 2.0 – 2.6 g B daily). Based on the reported average cattle weight of 370 kg, this results in boron doses of 5.6-7.0 mg/kg-day with no adverse effects observed. It should be noted that the boron concentration in feed from this 1944 study has been inconsistently reported as 157 mg/kg in NAS (1980) and several other reviews such as Eisler (1990) and Moss and Nagpal (2003), potentially due to using assumed cattle weights and food intake rates rather than the specific values reported in the study. Overall, this study suggests that feed boron concentrations up to approximately 280 mg/kg can be tolerated without apparent adverse effects. This is also consistent with the Puls (1988, 1994) reviews which state that adverse effects have not been reported below levels of 4.5 mg/kg-day boron, or approximately 200 mg B/kg in feed.

Overall, the weight of available evidence from toxicology studies with cattle suggests that daily doses of 5.5 mg/kg-day (based on 30 mg/L in cattle drinking water with default cattle assumptions, and consistent with Owen (1944)) are likely safe with a low probability for significant deleterious effects.

Detailed quantitative toxicity data for other types of livestock are more limited, and primarily useful for additional context. For example, goat data cited in Puls (1994) is primarily limited to acute toxicity from single doses, such as lethality being observed at a single dose of 3,600 mg B/kg body weight from accidental fertilizer poisoning. In rare cases, excessive boron intake from grazing animals has also been reported, though intakes would be highly variable depending on soil type, boron status of the soil, and plant species consumed (Gough *et al.*, 1979). For example, there have been reports of lambs and sheep developing symptoms such as enteritis when grazing on soils with naturally-elevated boron in parts of the Kulundinsk Steppe in Russia (Plotnikov, 1960, cited in Gough *et al.* (1979)) and Kazakhstan (Koval'skii, 1965, cited in Butterwick *et al.* (1989)). Naturally-occurring concentrations in soil of 30-300 mg B/kg and in water of 1-20 mg B/L were reported, though evaluating the reported soil concentrations is difficult due to apparent differences in soil test methodologies. Plotnikov (1960) also performed a feeding trial where 5 mg B/kg in feed was supplied to lambs followed by an increase to 12.4 mg B/kg in feed, with molybdenum and other salts also supplied for some treatments. Some pulmonary and gastro-intestinal symptoms were observed for the boron treatment, though it was reported that the largest effects were from the combination of boron and molybdenum.

Table 8.1. Livestock Boron Toxicity Data

Species	Boron form	Route of Exposure	'B' Dose or concentration	Duration (days)	Measured or Estimated Dose in mg B/kg-day	Results Details	Reference
chickens (adult)	Boric acid and borax	diet	250 mg B/kg feed	84-112	10.9[a]	No effect on adult mortality, body weight, or egg production. Females showed 20% decreased hatchability. Males showed no effect on fertility or hatchability, but some increase in damaged sperm cells. 10.9 mg B/kg-day considered approximate NOAEL/LOAEL	Rossi (1993a), Puls (1994), Moss and Nagpal (2003)
chickens (adult)	boric acid	diet	873 mg B/kg feed (5,000 mg boric acid/kg feed)	6	37.5	Egg production ceased, 10% mortality rate in chicks	Puls (1994), Moss and Nagpal (2003)
chickens (chicks)	boric acid	contact with treated litter	Up to 1.3 kg B/ 9.3 m^2 (=7.2 kg boric acid/9.3 m^2)	14	--	Feather abnormality and weight loss at 3.6 and 7.2 kg boric acid/9.3 m^2. No effect at recommended 0.9 kg boric acid/9.3 m^2	Dufour *et al.,* (1992)
chickens (chicks)	boric acid	diet	0-873 mg B/kg feed (=0-5,000 mg boric acid/kg feed)	15	0-56[b]	Weight decreased significantly with 2,500 mg boric acid/kg (437 mg B/kg) or more in feed). No apparent effects at 1,250 mg/kg boric acid in feed (218 mg B/kg feed, or 20 mg B/kg-day body wt)[b]	Dufour *et al*., (1992)
chickens (chicks)	boric acid	diet	0-300 mg B/kg feed	21	--	Reduced body weight at 300 mg B/kg in feed. Up to 240 mg B/kg in feed was not detrimental	Rossi (1993b)
sheep	boron	diet and drinking water	--	--	--	Developed enteritis when grazing on soils naturally with 30-300 mg B/kg and water with 1-20 mg B/L	Koval'skii (1965) *in Butterwick et al., (1989)*
lambs	--	diet	--	>18	5 then 12.4 mg B/kg-day, some combined with molybdenum	Rhinitis, conjunctivitis, bronchitis, pneumonia, gastro-enteritis, with largest effects from 12.4 mg B/kg-day combined with 45 mg molybdenum/kg-day	Plotnikov (1960) *in Gough et al., (1979)*
goats	--	ingestion	400-3,600 mg B kg body wt	Single dose	--	Fatal at 3,600 mg B/kg body wt. Toxic at 1,800 mg B/kg body wt. Toxic at 400 mg B/kg body wt.	Puls (1994)
cattle	borax	ingestion	~500 mg B/kg body wt	Single dose	--	Death (effect observed from a single accidental ingestion)	Brockman *et al*. (1985)
cattle	borax	ingestion	200-600 mg B/kg body wt	Single dose	--	Typical lethal dose in animals	Brockman *et al*. (1985), Puls (1994)
cattle	borax	diet	2,000-2,600 mg B/day (via 283 mg B/kg feed)	42	5.6 - 7.0[c]	No adverse effects observed; all boron excreted primarily in the urine	Owen (1944)
cattle	borax	drinking water	29-95 mg B/L	--	2.7 – 8.8[d]	Aesthetic – above 29 mg/L preferred tap-water to boron water. No toxic effects reported in this range	Green and Weeth (1977)
cattle	borax	drinking water	up to 120 mg B/L	10	Up to 13.8[e]	No effect on feed or water consumption for all levels; no overt signs of toxicosis. Increased phosphate excretion above 30 mg/L (4.6 mg/kg-day), starting at 60 mg/L (7.65 mg/kg-day)	Weeth *et al*., (1981)

Table 8.1. Livestock Boron Toxicity Data

Species	Boron form	Route of Exposure	'B' Dose or concentration	Duration (days)	Measured or Estimated Dose in mg B/kg-day	Results Details	Reference
cattle	borax	drinking water	150-300 mg B/L	30	15 – 25[d]	Decreased feed and water consumption, weight loss, edema, inflammation of legs, abnormal blood chemistry	Green and Weeth (1977)
Summaries / recommendations from review documents							
cattle	borax	diet	150 mg B/kg feed	chronic	3.4	maximum tolerable level, as borax	NAS (1980), Eisler (1990), Moss and Nagpal (2003)
cattle	borax	diet	>200 mg B/kg feed	chronic	>4.5	No observed toxic effects have been recorded at less than 4.5 mg/kg-day	Puls (1988), Puls (1994)
cattle	borax	drinking water	40 mg B/L	chronic	7.3	Maximum tolerated	Eisler (1990)
cattle	borax	drinking water	up to 30 mg B/L	chronic	5.5	Safe level	Puls (1994), Moss and Nagpal (2003)

Notes:

-- *Not known or not able to be calculated with information provided*

[a] *based on reported chicken 3.73 kg body weight and final food intake rate of 0.163 kg/day*

[b] *based on estimated average body weight and average food intake rate over duration of study for specific treatment group (e.g., for the 1250 mg boric acid/kg group, based on average 18.6 g/day feed rate and estimated average 203.4 g body weight)*

[c] *based on reported borax added to food (approximately 283 mg/kg B in food) of cows with average 370 kg weight, at 6.3-8.2 kg/day food intake*

[d] *based on reported borax added to water for yearling heifers (288 kg average), approximately 27 L/day water at lower doses*

[e] *based on reported borax added to water for yearling heifers (298 kg average), approximately 33 L/day water. Also 40 mg/kg B in hay*

Unless noted otherwise, daily doses based on default body weights and intakes shown below:

-chicken: 2.8 kg body weight (Moss and Nagpal, 2003), 0.11 kg/day food intake (CCME, 2006)

-cow: 550 kg body weight, 12.3 kg/day food intake, 100 L/day water intake (CCME, 2006 and AESRD, 2014a)

8.1.2 Wildlife Toxicity Data

Wildlife is assumed to be potentially present in both natural areas and agricultural areas, with Alberta Environment using the meadow vole as a representative wildlife species (AESRD, 2014a) since small animals are typically maximally exposed to soil contaminants. Since boron toxicity data specifically for the meadow vole is not available, data for other relevant species such as rats, mice, and rabbits will considered as well as other forms of wildlife such as mallards.

Boron toxicity data indicates that boron can be a reproductive toxin at sufficiently high exposures (USEPA, 2004a,b). Examples of toxicity endpoints for rats, mice and rabbits are summarized in detail in Section 7.1 above (since they have been studied as proxy species to assess human toxicity) and are briefly described below in reference to wildlife. Mallard duck toxicity is also discussed in further detail below and summarized in Table 8.1.

Rats are considered the most sensitive of mice, rats and rabbits (US EPA, 2004 a,b; Heindel *et al.*, 2004) and are thus of relevance to other forms of wildlife. A LOAEL of 78 mg boric acid/kg-day (13.6 mg B/kg-day) and a NOAEL of <78 mg boric acid/kg-day were derived for rats within the Heindel *et al*. studies. In a similar study, Price *et al.* (1996a) reported a pre-natal NOAEL of 55 mg boric acid/kg-day (9.6 mg B/kg-day) for maternal and fetal endpoints (fetal being the more sensitive), and a post-natal NOAEL of 74 mg boric acid/kg-day (12.9 mg B/kg-day) was reported based on baby rat endpoints. The USEPA (2004a,b) reviewed, combined and summarized the Heindel *et al.* and Price *et al.* studies and determined a LOAEL of 13.3 mg B/kg-day and a $BMDL_{05}$ of 10.3 mg/kg-day based on the decreased fetal weight endpoint. For mice, Heindel *et al*. (1992, 1994) reported a NOAEL of 248 mg boric acid/kg-day, which is summarized by the USEPA and expressed as 43.3 mg B/kg-day (USEPA, 2004a,b). They also reported a LOAEL of 452 mg boric acid/kg-day for mice. Rabbits were more sensitive than mice but less so than rats, with a NOAEL of 125 mg boric acid/kg-day (22 mg B/kg-day), and a LOAEL of 250 mg boric acid/kg-day (43.7 mg B/kg-day) (Heindel *et al.*, 1994; Price *et al.*, 1996b; USEPA, 2004a,b).

NRC (2005) states it is unlikely that boron toxicity under normal environmental conditions is a concern for animals, other than waterfowl in specific habitats. For example, mallards have been evaluated for boron toxicity based on observed instances of toxicity in the field. In particular, irrigation drainage water in the San Joaquin Valley in California had resulted in highly elevated boron concentrations in surface water (such as the Kesterson Reservoir) and consequently high boron concentrations (up to 1,860 mg/kg) in wetland plants consumed by waterfowl (NRC, 2005). Toxicity of boron to mallard ducks was studied by Smith and Anders (1989) in terms of reproductive success and effects on adults and ducklings, and Hoffman *et al.* (1990) in terms of effects on ducklings. In the Smith and Anders (1989) study, boron was dosed to the parents before conception, during pregnancy, and to the ducklings directly after hatching for three weeks. There were no significant effects on adult weight at any of the dose levels. However, hatching success, hatching weight, duckling survival and duckling weight in the first three weeks after hatching were found to be significantly impaired by 1,000 mg B/kg in feed (Smith and Anders, 1989). Duckling weight was also 10% lower in the 30 mg B/kg group compared to the control group after three weeks, however, the reliability of this 30 mg B/kg dose effect is unclear since there was no further difference with the 300 mg B/kg dose. The Hoffman *et al.* (1990) study also noted that there was a decrease in food consumption and an approximate 10% decrease in weight gain in the first three weeks of duckling life for 100 and 400 mg B/kg in feed. However, these differences were transient and were not observed with a full 10 week treatment period. Solely the 1,600 mg B/kg group had statistically significant reduced weight at the end of the full 10-week period (particularly for females), along with a 10% decreased survival rate. The most sensitive endpoint appeared to be decreases in brain ATP levels and corresponding reductions in activity level, with statistically significant effects observed at 400 mg B/kg in feed. Overall, no significant effects were noted at 100 mg B/kg in feed, with the authors stating that concentrations above 100 mg B/kg in feed could potentially adversely affect duckling development. These findings appear generally consistent with a newer study by Stanley *et al.* (1996), where adults and the produced ducklings were fed with treatments of 0, 450, or 900 mg B/kg in feed. Significant effects were noted on adult weight, egg weight, fertility, and hatching success at 900 mg/kg, along with significant reductions in duckling growth and survival. Duckling growth appeared marginally (10%) reduced at 14 days at 450 mg/kg, but was not statistically significant.

Overall, the data from these mallard studies is useful for providing context for typical feed boron concentrations which may cause toxic effects in mallards, with it appearing that feed concentrations above 100-400 mg B/kg (Puls, 1994) have the potential to cause toxic effects. Feed at 100 mg B/kg appears unlikely to cause significant adverse effects, equivalent to approximately 14.6 mg B/kg-day based on reported body weights and feed intake rates from Hoffman *et al.* (1990).

Table 8.2. Wildlife Boron Toxicity Data

Species	Boron form	Route of Exposure	'B' Dose or concentration	Duration (days)	Measured or Estimated Dose in mg B/kg-day	Results Details	Reference
mallards (adults)	boric acid	diet	0, 30, 300, 1000 mg B/kg feed	>60	--	No signs of toxicosis or significant decreases in adult weight. Hatching success and embryo survival significantly deceased at 1,000 mg B/kg feed	Smith and Anders (1989)
mallards (ducklings)	boric acid	diet	0, 30, 300, 1000 mg B/kg feed, (same as parents)	21 (after hatching)	--	Significantly deduced growth, weight, and higher hatchling mortality at 1,000 mg/kg. Duckling weight reduced by 10% at 21 days for 30 and 300 mg B/kg feed,	Smith and Anders (1989)
mallards (ducklings)	boric acid	diet	0, 100, 400, 1600 mg B/kg feed	70	0, 14.6, 60.9, 257 mg B/kg-day	Increased mortality, reduced overall growth, and delayed growth at 1,600 mg/kg (particularly females). Some delayed growth at 100 and 400 mg/kg in females though effects were transient. Altered brain chemistry at 400 mg/kg. No significant effects at 100 mg B/kg in feed (14.6 mg B/kg-day)	Hoffman *et al*., (1990)
mallards (adults)	boric acid	diet	0, 450, 900 mg B/kg feed	120	--	Significant reductions in adult weight, egg weight, egg fertility, and hatching success at 900 mg B/kg feed. No consistent significant effects at 450 mg B/kg feed	Stanley *et al*., (1996)
mallards (ducklings)	boric acid	diet	0, 450, 900 mg B/kg feed	14	--	Significant reductions in weight, growth, survival at 900 mg B/kg feed. 10% weight and growth reduction at 14 days at 450 mg B/kg feed, but not statistically significant. No other effects at 450 mg B/kg feed	Stanley *et al*., (1996)

Notes:

-- *Not known or not able to be calculated with information provided*

8.1.3 Exposure Equations for Livestock and Wildlife

The Alberta Environment Tier 1 equation for estimating ingestion exposure of livestock or wildlife primarily considers soil ingestion due to the low potential for certain chemicals such as petroleum hydrocarbons to accumulate in plants (AESRD, 2014a). Since boron is known to bioconcentrate into plants, the comparable CCME (2006) equation was used since it considers plant (food) ingestion as well as soil ingestion. This equation is shown below, and calculates a soil-and-food ingestion guideline based on factors such as the daily threshold effect dose (DTED) as well as the body weight, food ingestion rate, and soil ingestion rate for livestock or wildlife. It also uses a bioconcentration factor describing the uptake from soil into plants.

$$SRG_{SFI-L/W} = \frac{0.75 \times DTED \times BW_{L/W}}{\left(SIR_{L/W} \times BF\right) + \left(FIR_{L/W} \times BCF\right)}$$

Where:

$SRG_{SFI\text{-}L/W}$ = soil guideline for protection of livestock/wildlife from soil and food ingestion (mg/kg)
0.75 = allocation factor to prevent 75% of DTED from being exceeded by soil and food
$DTED$ = daily threshold effect dose (mg/kg-bw/day)
$BW_{L/W}$ = body weight (kg)
$SIR_{L/W}$ = soil ingestion rate (kg/day)
$FIR_{L/W}$ = food ingestion rate (kg/day)
BF = bioavailability factor (unitless)
BCF = bioconcentration factor (unitless)

The food ingestion rates (FIR) for livestock and wildlife can be estimated using the allometric equation below for mammals (AESRD, 2014a; CCME, 2006) and are consistent with default values shown in AESRD, 2014a for proxy species such as cattle and meadow voles.

$$FIR_M = 0.0687 \times (BW)^{0.822}$$

Where:

FIR_M = Food ingestion rate for mammalian species (kg/day)
BW = Body weight (kg)

An additional allometric equation is provided in CCME (2006) for avian species:

$$FIR_A = 0.0582 \times (BW)^{0.651}$$

Where:

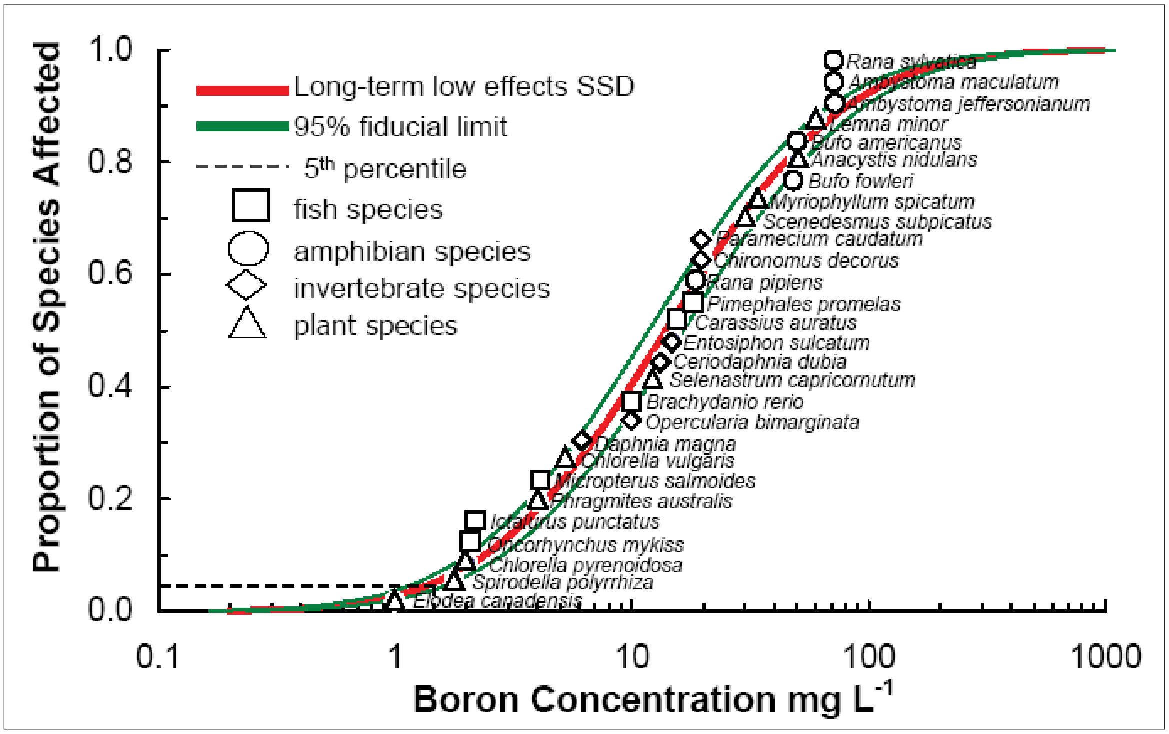
FIR_A = Food ingestion rate for avian species (kg/day)
BW = Body weight (kg)

The above equation for developing guidelines for livestock and wildlife soil and food ingestion can also be used to calculate exposure based on soil and food intake rates and bioconcentration factors, with exposure calculations for this pathway discussed in more detail in Section 9.

8.2 Aquatic Life

Boron can be toxic to a variety of freshwater fish, amphibians, plants and invertebrates. Based on a review of existing toxicity data and guideline protocols at the time, British Columbia developed a guideline of 1.2 mg/L in 2003 (BCMOE, 2003). Ontario Ministry of Environment and CCME more recently developed a freshwater aquatic life guideline (CCME, 2009) based on a similar toxicity dataset and interpreted using the rank percentile techniques outlined in CCME (2007b). A species-sensitivity distribution (SSD) developed from this data is shown in Figure 8.1 (CCME, 2009) whereby species are ranked from most-sensitive to least-sensitive based on boron concentrations in mg/L. Three types of plant and algae species are shown as most sensitive, followed by rainbow trout (*O. mykiss*) and channel catfish (*I. punctatus*). Amphibians and invertebrates generally appear less sensitive to boron. The 5th percentile of this SSD distribution was taken as the guideline value, shown here as 1.5 mg/L (marginally higher than the 2003 BC guideline). This 1.5 mg/L aquatic life guideline was used to develop Tier 1 guidelines by Alberta Environment in 2010 and was adopted by in AESRD (2014c).

Figure 8.1. Species-Sensitivity Distribution for Freshwater Aquatic Life



Source: CCME, 2009

9. Derivation of Environmental Soil Remediation Guidelines

9.1 Guidelines for Ecological Direct Soil Contact for Soil Dependent Biota

In this section, literature data for plants and invertebrates are combined with the more recent laboratory toxicity data to generate species sensitivity distributions (SSDs) for a wide range of soil-dependent biota. These include agricultural species, boreal species, fruit species, flower species, vegetable species, grass species, and a number of soil invertebrate species. A summary of how the data for each of these categories was compiled and combined is provided below.

Agricultural plant data from the 2011-2013 Exova study (summarized in Section 5.2) were used for each of the six agricultural species in clay loam and sandy loam. Since length and biomass are highly correlated for each of shoots and roots, geometric means were calculated for shoot length and shoot biomass (to yield one shoot endpoint) and for root length and root biomass (to yield one root endpoint). Since the saturated paste methodology minimized the differences between textures for plants, a geometric mean was also taken for the two textures for each endpoint. This results in one shoot endpoint and one root endpoint for each of the six agricultural species to be used in the final SSD. Further details of the IC_{25} data and methods used for combining endpoints from these agricultural experiments are found in AEP (2015).

For the boreal species from the 2013-2014 Exova study (summarized in Section 5.3), the data for the three species which were tested for all three soil types (sandy mineral soil, organic soil, and artificial soil) showed relative consistency between the soil types by expressing toxicity results on a mg/L saturated paste basis. In general, the sandy mineral soil showed the more conservative and less variable results of the two field soils (sandy mineral soil and organic peat soil), and thus the mineral soil results were used for inclusion in the final SSD. In the same manner as the agricultural soils, the related length and biomass endpoints were combined in a geometric mean for shoots and roots separately. Further details of the IC_{25} data and methods used for combining endpoints from these boreal experiments are found in AEP (2015).

Plant data from literature was used to supplement the recent Exova plant studies, consisting primarily of the sand culture experiments described in Sections 5. Eaton (1944) data described in Section 5.1.3 for sensitive fruit, tree, and flower species were used, along with other less sensitive species tested by Eaton and shown in more detail in AEP (2015). More recent sand culture data described in Section 5.1.4 was also included and shown in AEP (2015). For these sand culture experiments, IC_{25} values were originally based on soil solution boron, and were converted to a saturated paste B basis using a conversion factor of approximately 1.27 which is an average of the coarse (1.31) and fine (1.22) soil estimates using DF1 calculation techniques from Section 4.2.1. With this conversion, these estimates of IC_{25} on a saturated paste basis are estimated to result in similar soil solution concentrations as experienced by plants in the sand culture experiments. The geometric mean of the IC_{25} values was taken when multiple entries (distinct tests or studies) existed for the same species. In addition, to reduce bias towards any one study with multiple endpoints, the minimum endpoint was used to represent multiple comparable endpoints for the same species reported from a single study. Further details of the methods used for combining endpoints and studies from these sand culture experiments are shown in AEP (2015).

Invertebrate data from literature and the more recent Exova earthworm study were also incorporated into the final soil-dependent biota SSD. Both non-reproductive and reproductive endpoints were used, based primarily on estimated or measured LC_{25}/IC_{25} values. Since they are based on estimated saturated paste concentrations from spiked boron regressions, literature data for a particular endpoint were generally combined via geometric means such that there was a single LC_{25} and/or IC_{25} for a given invertebrate species for a given soil type. Since saturated paste boron was measured directly, the endpoints for the Exova earthworm study were retained as distinct endpoints. Further details of the soil invertebrate data are provided in AEP (2015).

The combined dataset described above results in a single dataset for soil dependent biota on a mg/L saturated paste basis which is applicable to all land uses for both fine and coarse soil types. The combined soil-dependent biota dataset is shown in Table 9.1, shown in order of least sensitive to most sensitive. The species, endpoint (if applicable), and soil type are indicated for each datapoint with its IC_{25} and rank. The ranking method utilized was that recommended by the CCME (2006).

Two invertebrates were found to be the least sensitive soil dependent biota, the orbatid mite *Oppia nitens* and the earthworm *Eisenia andrei* with IC_{25} values of 51 (lethality) and 48 (avoidance) mg/L saturated paste B. Barley and alfalfa were the least sensitive plant species with IC_{25} values of 38-44 mg/L saturated paste B, while the most sensitive plant species included the pansy and blackberry with estimated IC_{25} values of 0.53 and 1.5 mg/L saturated paste B respectively. Note that the ten most sensitive endpoints are derived from the older Eaton sand culture experiments described in Section 5.1.3.

The data summarized in Table 9.1 is shown graphically in a species sensitivity distribution (SSD) in Figure 9.1. The soil dependent biota species names are shown on the right hand side, listed in order of IC_{25} sensitivity. The data fits a log-linear regression closely, with an R^2 of 0.97. The sole datapoint which is substantially outside the 95% confidence limits for the line of best fit is pansy, which is ranked here as the most sensitive species based on the estimated IC_{25} from Eaton (1944) data. As previously discussed in Section 5.1.3, this estimated IC_{25} datapoint is potentially anomalous and/or due to experimental variability based on visual toxicity symptoms and the overall dose-response curve, in conjunction with pansy being known to be prone to boron deficiency and ranked as #13 in sensitivity by Eaton.

Table 9.1. Combined Saturated Paste Boron IC_{25}s for Soil Dependent Biota

Rank	Description	IC_{25} (mg/L sat paste B)	rank percentile [1]
78	*Oppia nitens* – lth (A)	51.14	0.987
77	*Eisenia andrei* – avd (CL)	48.36	0.975
76	Barley - shoots (CL, SL)	43.68	0.962
75	Alfalfa - roots (CL, SL)	40.69	0.949
74	Alfalfa - shoots (CL, SL)	38.21	0.937
73	*Folsomia fimetaria* – lth (A)	36.64	0.924
72	*Oppia nitens* – rep (L)	30.08	0.911
71	N. Wheatgrass - shoots (CL, SL)	27.10	0.899
70	*Eisenia andrei* – rep (SL)	26.40	0.886
69	*Folsomia fimetaria* – lth (CL)	25.43	0.873
68	Durum wheat - shoots (CL, SL)	24.73	0.861
67	White spruce - shoots (MIN)	24.63	0.848
66	*Prosomia Minuta* – lth (A)	17.71	0.835
65	Onion (S Cul)	17.47	0.823
64	Mustard (S Cul)	17.26	0.810
63	Vetch (S Cul)	16.70	0.797
62	Barley - roots (CL, SL)	16.68	0.785
61	Oxalis (S Cul)	16.29	0.772
60	Celery (S Cul)	14.94	0.759
59	White spruce - roots (MIN)	14.88	0.747
58	Carrot - roots (CL, SL)	14.23	0.734
57	Durum wheat - roots (CL, SL)	14.19	0.722
56	N. Wheatgrass - roots (CL, SL)	14.08	0.709
55	Cauliflower (S Cul)	13.60	0.696
54	Carrot - shoots (CL, SL)	13.53	0.684
53	*Dendrodrilus rubidus* – rep (A)	13.48	0.671
52	Cabbage (S Cul)	13.15	0.658
51	Lettuce (S Cul)	11.99	0.646
50	*Oppia nitens* – rep (A)	11.97	0.633
49	Broccoli (S Cul)	11.78	0.620
48	Beet (S Cul)	10.87	0.608
47	Garlic (S Cul)	10.75	0.595
46	Radish (S Cul)	10.44	0.582
45	Jack pine - roots (MIN)	10.30	0.570
44	Sorghum (S Cul)	10.04	0.557
43	Tomato (S Cul)	10.02	0.544
42	Jack pine - shoots (MIN)	9.57	0.532
41	Parsley (S Cul)	9.53	0.519
40	California poppy (S Cul)	9.51	0.506
39	*Proisotoma minuta* – rep (A)	9.35	0.494
38	Kentucky bluegrass (S Cul)	9.10	0.481
37	Sugar beet (S Cul)	8.70	0.468
36	Cucumber - shoots (CL, SL)	8.20	0.456
35	Potato (S Cul)	7.98	0.443
34	Bluejoint Reedgrass - roots (MIN)	7.56	0.430
33	*Eisenia andrei* – rep (CL)	7.46	0.418
32	Common wheat (S Cul)	6.56	0.405
31	Bluejoint Reedgrass - shoots (MIN)	6.29	0.392
30	Oats (S Cul)	6.13	0.380
29	*Folsomia candida* – rep (A)	5.60	0.367
28	Alfalfa (S Cul)	5.56	0.354
27	*Eisenia andrei* – rep (SL)	5.39	0.342

Rank	Description	IC_{25} (mg/L sat paste B)	rank percentile [1]
26	Squash (S Cul)	5.38	0.329
25	*Oppia nitens* – rep (L)	5.05	0.316
24	*Folsomia fimetaria* – rep (CL)	4.66	0.304
23	Cucumber - roots (CL, SL)	4.57	0.291
22	Barley (S Cul)	3.77	0.278
21	Carrot (S Cul)	3.74	0.266
20	Corn (S Cul)	3.35	0.253
19	Larkspur (S Cul)	3.25	0.241
18	Pea (S Cul)	3.16	0.228
17	Sweet pea (S Cul)	2.90	0.215
16	Lima bean (S Cul)	2.82	0.203
15	Zinnia (S Cul)	2.73	0.190
14	Jeruselum Artich (S Cul)	2.68	0.177
13	Kidney bean (S Cul)	2.48	0.165
12	Snap bean (S Cul)	2.45	0.152
11	*Folsomia fimetaria* – rep (A)	2.43	0.139
10	Cow pea (S Cul)	2.31	0.127
9	Peach (S Cul)	2.19	0.114
8	Violet (S Cul)	2.02	0.101
7	Strawberry (S Cul)	1.98	0.089
6	Cherry (S Cul)	1.85	0.076
5	Grape (S Cul)	1.78	0.063
4	Elm (S Cul)	1.75	0.051
3	Lupine (S Cul)	1.71	0.038
2	Blackberry (S Cul)	1.49	0.025
1	Pansy (S Cul)	0.53	0.013
	25th percentile (from SSD)	**3.3**	**--**
	50th percentile (from SSD)	**7.9**	**--**

Notes:

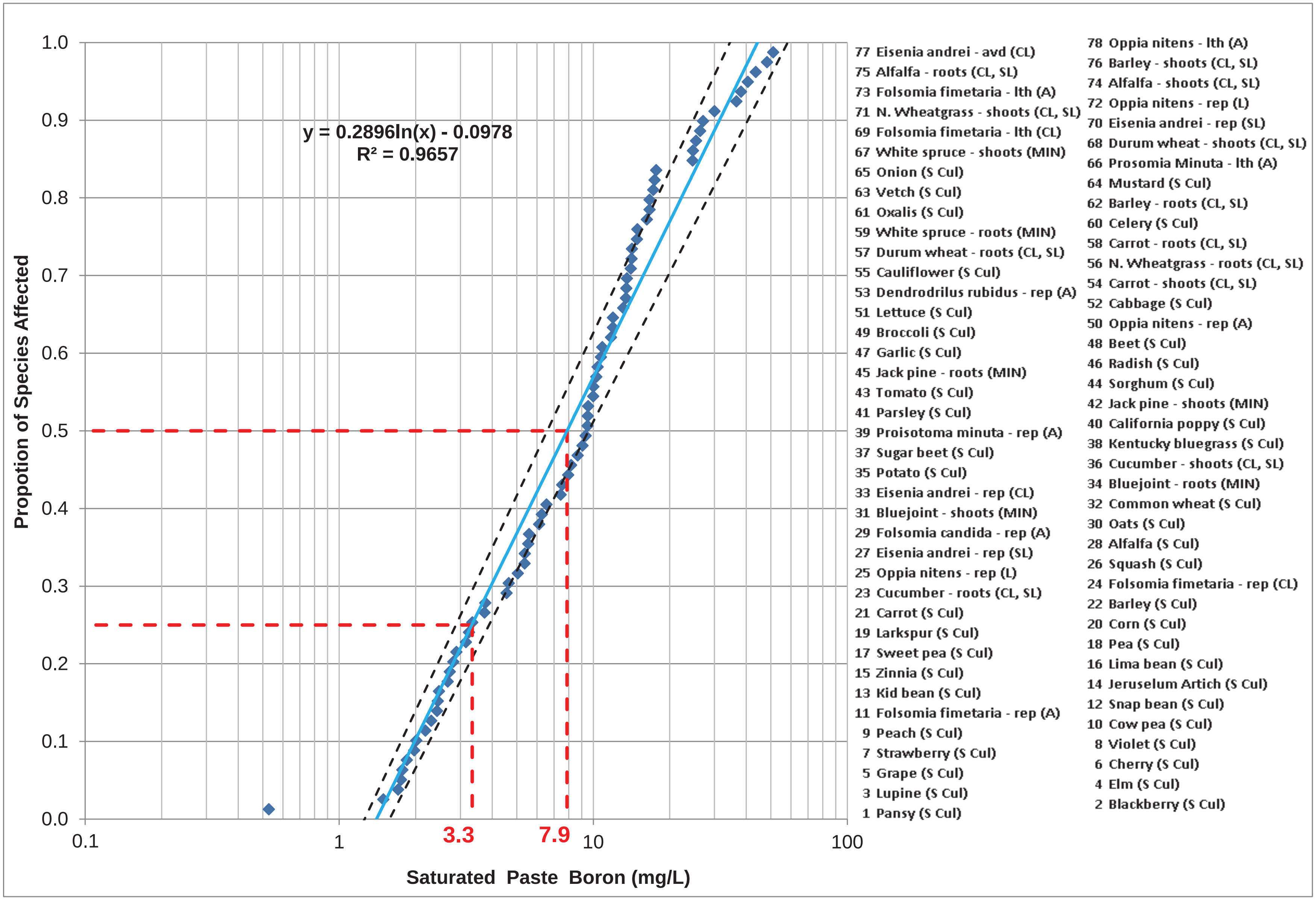
1) IC25s ranked using the CCME recommended ranking method (CCME, 2006);
*2) texture abbreviations: artificial soil (**A**), clay loam (**CL**), loam (**L**), coarse mineral soil (**MIN**), sand culture (**S Cul**), sandy loam (**SL**);*
*3) invertebrate endpoint abbreviations: avoidance (**avd**), lethality (**lth**), reproduction (**rep**)*

The 25th percentile of the derived SSD is 3.3 mg/L saturated paste boron representing the ecological direct soil contact guideline for residential/parkland, agricultural and natural area lands. The 50th percentile of the derived SSD is 7.9 mg/L saturated paste boron representing the ecological direct soil contact guideline for commercial and industrial lands.

Agricultural, Natural Area, Residential, Parkland: $SRG_{ECO\text{-}DC}$ **= 3.3 mg/L**

Commercial, Industrial: $SRG_{ECO\text{-}DC}$ **= 7.9 mg/L**

Figure 9.1. Soil Dependent Biota Boron Species Sensitivity Distribution (SSD)



Note: dashed lines represent the upper and lower 95% confidence limits of the line of best fit

9.2 Livestock and Wildlife Soil and Food Ingestion

Livestock and wildlife may be exposed to boron in feed via grazing, or for livestock via harvested feed such as hay, silage, or grains. Though boron is generally considered to be of relatively lower toxicity to grazing animals compared to several other metals (Gupta and Gupta, 1998), the potential exposure of livestock and wildlife to excessive boron intake from food can be evaluated using CCME (2006) equations and protocol. To generate quantitative guidelines for these pathways, this protocol states that at least three studies must be considered, with at least two of them oral mammalian studies and one oral avian study. A maximum of one laboratory rodent study may be used to fulfill the data requirements for mammalian species if required. A grazing herbivore with a high food ingestion rate to body weight ratio should also be considered, since small species with higher relative food ingestion rates (such as the meadow vole, the surrogate wildlife species) tend to be more highly exposed than larger species with relatively lower food ingestion rates (such as cattle, the surrogate livestock species). Sufficient quantitative data is required to generate a 'daily threshold effect dose' (DTED), preferably based on 25% effect levels (*i.e.*, EC_{25}) for the most relevant/sensitive endpoints for the most exposed species (CCME, 2006). Depending on data quality, the lowest observed adverse effects level (LOAEL) may also be used in some cases.

The literature available pertaining to boron toxicity to livestock and wildlife is described in Sections 8.1.1 and 8.1.2, with additional data on laboratory rodents such as rats and mice in Section 7.1. Though many of these studies provide useful results and general effect ranges, data quantity and quality varies greatly between these studies. For example, several studies have various data limitations such as limited dose ranges (Rossi 1993a for chickens, Green and Weeth 1977 for cattle), short duration (Weeth *et al.*, 1981 for cattle), sparse or unavailable information (Koval'skii 1965 and Plotnikov 1960 for sheep and lambs), changing body weights and insufficient feed intake rate data (Smith and Anders, 1989 and Stanley, 1996 for mallards), and lack of reproductive data for various species (such as cattle). In some cases, quantitative data providing clear dose-response relationships is available for some endpoints (such as rat fetal weight as described in US EPA 2004a,b) but other potentially sensitive endpoints (such as the prevalence or severity of rat fetal malformations) were highly variable with a general absence of a clear dose-response curve. Overall, the toxicity dataset is deemed to be more appropriate for identifying general ranges or the absence/onset/presence of effects, but is insufficient for identifying quantitative EC_{25} levels for a sufficient range of sensitive endpoints and relevant species as per CCME (2006) protocol.

As an alternative to deriving numerical guidelines for livestock and wildlife soil and food ingestion, a weight-of-evidence approach is used here to evaluate potential boron intake rates and risk to a range of livestock and wildlife species for which sufficient data is present. In practice, boron intakes from vegetation are expected to be highly variable depending on factors such as soil type, boron status of the soil, and plant species consumed (Gough *et al.*, 1979). The analysis here assumes soil boron concentrations at the ecological direct soil contact guideline previously derived, and estimates typical vegetation boron concentrations based on observed bioconcentration factors. This approach also conservatively assumes that all boron which is in vegetation is 100% bioavailable.

For this analysis, it is assumed that soils are uniformly at the ecological direct soil contact guideline of 3.3 mg/L saturated paste boron for protection of plants and soil invertebrates. This corresponds to approximately 4.8 and 7.0 mg HWS boron/kg for typical coarse and fine soils using the regressions in Section 5.2 (Figure 5.8). It is assumed that livestock and wildlife consume a mixture of shoot, root, grain, and seed tissue of plants, referred to as 'vegetation'.

Grains and seeds tend to have lower vegetation boron than shoots, and are assumed to be reasonably represented by the bioconcentration factors for roots. Based on vegetation boron versus HWS soil boron regressions shown in Section 5.2.6, average bioconcentration factors for shoots and roots combined are estimated as 9.7 for fine soils and 17.4 for coarse soils over the relevant HWS boron range. These average bioconcentration factors also appear reasonable based on the longer-term Alberta field and test plot data described in Section 5.1.1. Combining these bioconcentration factors with the estimated HWS soil concentrations results in estimated average vegetation boron concentrations of 68 mg/kg for fine soils and 84 mg/kg for coarse soils. For initial context, these estimated vegetation concentrations are below levels considered potentially toxic in summaries such as Puls (1994) and Eisler (1990).

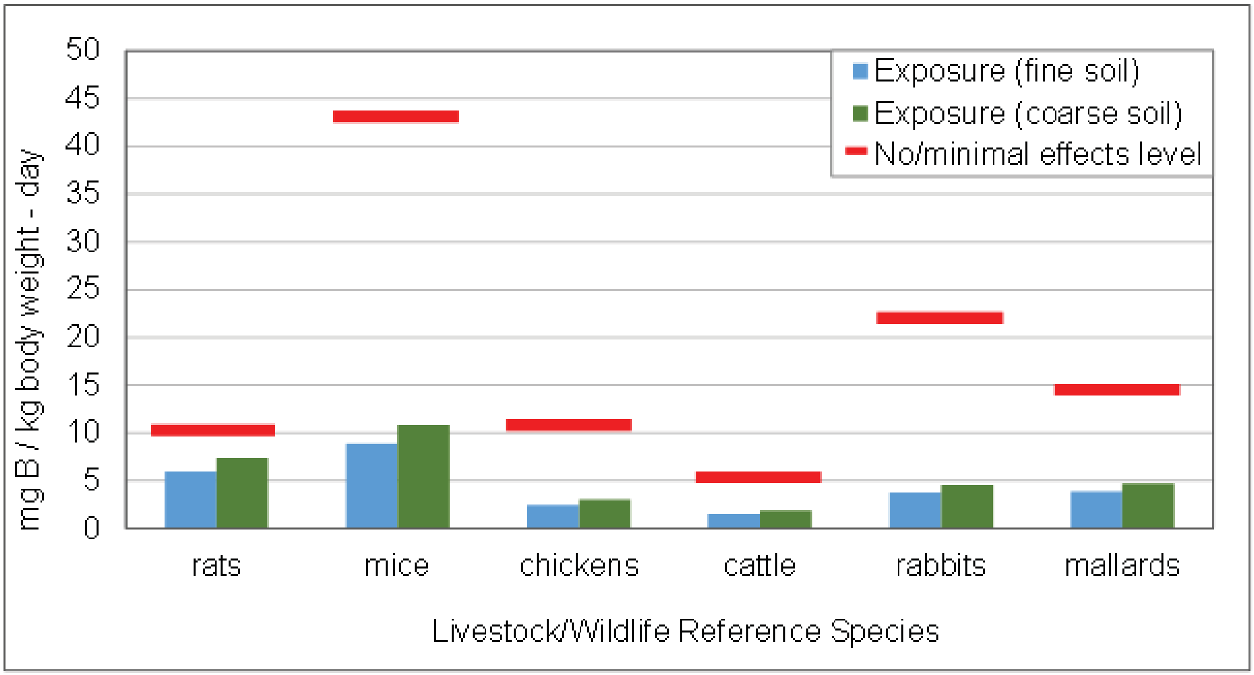
To determine potential exposure from these levels of vegetation boron for various reference livestock/wildlife species (rats, mice, chickens, cattle, rabbits, and mallards), body weights and food ingestion rates were estimated. Body weights were based on the default body weight for cattle, and the actual body weights cited in the relevant studies for other species. Food ingestion rates were calculated using the mammalian and avian allometric equations from Section 8.1.3 based on body weight. By combining the food ingestion rate with the estimated vegetation boron concentration and body weight, daily exposures to boron are derived and shown in Table 9.2 for fine and coarse soils.

From the toxicity literature described in Sections 7.1, 8.1.1, and 8.1.2, levels which are estimated to result in no effects or minimal effects for the most sensitive endpoints are also shown for each of these species. For rats, the $BMDL_{05}$ for decreased fetal weight was used (US EPA 2004a,b). For mice, the NOAEL for reduced fetal success, body weight, and fetal malformations was used (Heindel *et al.*, 1992, 1994). For chickens, the NOAEL/LOAEL for reduced hatchability and damaged sperm cells was used (Rossi, 1993a). For cattle, the NOAEL for increased phosphate excretion was used (Weeth *et al.*, 1981). For rabbits, the NOAEL for reduced fetal success and malformations was used (Heindel *et al.*, 1994). For mallards, the NOAEL for reduced brain ATP and activity levels was used (Hoffman *et al.*, 1990).

Exposure ratios can then be calculated as the estimated daily exposures divided by the no/minimal effects levels. These exposure ratios are all less than unity, indicating a low probability for the occurrence of significant negative effects from livestock/wildlife food ingestion. Rats appear to be the most highly-exposed species, with exposure ratios of 0.58 and 0.72 for fine and coarse soil respectively. The other reference species' exposure ratios ranged from 0.17 to 0.34, with chickens, cattle and mallards being the species with the next-highest estimated exposure ratios. Though cattle have the lowest estimated no/minimal effects threshold on a body-weight basis (5.5 mg/kg-day), the smaller body weight and relatively higher food intake of rats results in them being more highly exposed than cattle. Mice had the lowest body weight (28 g), most similar to the body weight of the default wildlife species (meadow vole, 17 g) and show a relatively low estimated exposure ratio of approximately 0.20-0.25.

The data from Table 9.2 is shown visually in Figure 9.2 below, where the estimated daily exposure from boron in vegetation is expressed as blue bars for fine soil and green bars for coarse soil. The daily doses estimated to result in no or minimal effects are also shown as red lines for each of the five species. In each case, the estimated exposures are less than the no/minimal effects level, consistent with exposure ratios less than unity.

Figure 9.2. Estimated Exposures from Livestock and Wildlife Food Ingestion



Exposures estimated based on soil saturated paste B of 3.3 mg/L, estimated to correspond to approximately 4.8 mg/kg HWS (coarse soil) and 7.0 mg/kg HWS (fine soil) for use in bioconcentration factors

Livestock and wildlife's exposure to boron from food is calculated to be substantially higher than from incidentally consumed soil using AESRD (2014) and CCME (2006) equations, and thus the food exposures discussed above are sufficiently representative of both soil and food ingestion. These exposure ratios are also less than 0.75, thus allowing a 25% allocation of total exposure to come from drinking water as per AESRD (2014) and CCME (2006) protocol. Thus, the soil guideline derived herein for ecological direct soil contact (protection of plants and soil invertebrates) is also considered sufficiently protective of livestock and wildlife soil and food ingestion.

Table 9.2. Estimated Exposures from Livestock and Wildlife Food Ingestion

Species	Body Weight	Food Ingestion Rate	Exposure		Daily dose for no/minimal effects	Toxicity endpoint	Primary reference	Exposure ratio	
			fine	coarse				fine	coarse
	kg	kg/day	mg/kg-day	mg/kg-day	mg/kg-day			-	-
rats	0.24	0.021	6.0	7.4	10.3	BMDL$_{05}$ (reduced fetal weight)	US EPA (2004a,b)	**0.58**	**0.72**
mice	0.028	0.0036	8.8	10.9	43	NOAEL (reduced fetal success, body weight, malformations)	Heindel *et al.* (1992, 1994)	**0.20**	**0.25**
chickens	3.7	0.14	2.5	3.1	10.9	NOAEL/LOAEL (reduced hatchability, damaged sperm cells)	Rossi (1993a)	**0.23**	**0.28**
cattle	550	12.3	1.5	1.9	5.5	NOAEL (increased phosphate excretion)	Weeth *et al.* (1981)	**0.28**	**0.34**
rabbits	3.5	0.19	3.7	4.6	22	NOAEL (reduced fetal success, malformations)	Heindel *et al.* (1994)	**0.17**	**0.21**
mallards	1.1	0.062	3.8	4.7	14.6	NOAEL (reduced brain ATP levels and activity levels)	Hoffman *et al.* (1990)	**0.26**	**0.32**

Note: Body weights based on Alberta Environment / CCME default for cattle, and typical weights for other species based on the relevant toxicity studies. Food ingestion rates based on the mammalian or avian allometric equations (Section 8.1.3).

9.3 Guideline for Irrigation Water

Groundwater can potentially be used for irrigation, with an irrigation water guideline for boron ranging from 0.5-6 mg/L in AESRD (2014c) as discussed in Section 2.5.2. This range has been derived from plant sensitivity rankings discussed in Section 5.1.3 and Table 5.1, most of which were derived from no-effect thresholds from older sand culture experiments such as Eaton 1935 and 1944. As discussed in Sprague (1972), such thresholds do not consider differences in soils, climate, or irrigation water use, and thus tend toward minimum limits for most adverse conditions. Based on the responses of sensitive species such as blackberry shown in Figure 5.3 and Table 5.2, irrigation water concentrations below 1 mg/L appear to pose minimal risk and will be used as a basis for deriving soil irrigation guidelines below.

Assuming a groundwater boron irrigation guideline of 1 mg/L, a corresponding soil remediation guideline (on a mg/L saturated paste basis) was established using Tier 1 groundwater calculations described in Section 4.2. The derived guidelines are presented in Table 9.3 along with the dilution factors (DF1-3) utilized in their derivation (DF4 not used here since it relates to lateral transport toward an aquatic life receptor). For fine and coarse soils, the overall soil remediation guideline for irrigation water (SRG_{IW}, on a mg/L saturated paste boron basis) is calculated as:

$$SRG_{IW} = \text{GW guideline} \times DF1 \times DF2 \times DF3$$

Table 9.3. Soil Remediation Guidelines for Irrigation Water

Irrigation water pathway	Fine texture	Coarse texture
Groundwater guideline	1 mg/L	1 mg/L
DF1	0.823	0.767
DF2	1	1
DF3	3.86	4.64
Soil guideline (saturated paste boron)	**3.18 mg/L**	**3.56 mg/L**

DF1 in this context represents the ratio between boron in soil water and boron in saturated paste, both on a mg/L basis. As discussed in Section 4.2.1, this ratio is based on estimated K_d data from Section 3.4 and was estimated to be 0.823 for fine soil and 0.767 for coarse soil. These are based on estimated K_d values of approximately 2.1 and 0.8 L/kg for fine and coarse soils, and are consistent with the conversion factors of 1.22 and 1.31 used in Section 4.2.1.

As outlined in Section 4.2, DF2 is considered equivalent to 1 on a Tier 1 basis due to the assumed proximity of the impacts to the water table.

DF3, representing the mixing of leached boron with groundwater, was calculated to be 3.86 for fine soils using Tier 1 defaults (AESRD, 2014c) and the equation presented in Section 4.2.3. Parameter values for fine soil include 0.38 m, 0.896 m/year, 0.012 m/year, and 10 m/year for calculated mixing depth (Z), Darcy velocity in groundwater (V), infiltration rate (I), and length of contaminated soil (X) respectively. These variables are texture dependent, and result in a corresponding DF3 of 4.64 for coarse soil based on the higher default drainage rates and Darcy velocity in groundwater based on Tier 1 defaults.

For fine and coarse soils, guidelines were calculated to be 3.18 and 3.56 mg/L saturated paste boron, respectively. Since the guidelines derived for fine and coarse soils are relatively similar to each other, it is reasonable to use an average guideline to represent both soil textures. This results in an overall soil guideline of 3.4 mg/L saturated paste boron for the protection of irrigation water.

$$\boldsymbol{SRG_{IW}} \mathbf{= 3.4\ mg/L}$$

9.4 Guideline for Freshwater Aquatic Life

The Tier 1 surface water guideline for aquatic life is 1.5 mg/L as discussed in Section 8.2. To derive a soil guideline which is protective of this receptor, Tier 1 dilution factor calculations were performed in a manner similar to the irrigation water pathway. The derived aquatic life guidelines are presented in Table 9.4 along with the dilution factors (DF1-4) utilized in their derivation. Note that DF4 is included in this calculation due to the lateral transport toward the aquatic life receptor.

$$\mathrm{SRG_{FWAL}} = \text{GW guideline x DF1 x DF2 x DF3 x DF4}$$

For both soil types, DF1, DF2, and DF3 are the same as those derived for irrigation water. DF4 was also calculated to be essentially 1 due to the short transport distance (assumed 10 m) and lack of biodegradation for boron.

Table 9.4. Soil Remediation Guidelines for Aquatic Life

Aquatic life pathway	Fine texture	Coarse texture
Groundwater guideline	1.5 mg/L	1.5 mg/L
DF1	0.823	0.767
DF2	1	1
DF3	3.86	4.64
DF4	1	1
Soil guideline (saturated paste)	**4.76 mg/L**	**5.34 mg/L**

For fine and coarse soils, guidelines were calculated to be 4.76 and 5.34 mg/L saturated paste boron, respectively. Since the guidelines derived for fine and coarse soils are relatively similar to each other, it is reasonable to use an average guideline to represent both soil textures. This results in an overall soil guideline of 5.0 mg/L saturated paste boron for the protection of freshwater aquatic life.

$$\boldsymbol{SRG_{FWAL}} \mathbf{= 5.0\ mg/L}$$

9.5 Guideline for Livestock Watering

The Tier 1 boron guideline for livestock drinking watering is 5 mg/L. To derive a soil guideline which is protective of this receptor, Tier 1 dilution factor calculations were performed in a manner similar to previous sections. The derived guidelines are presented in Table 9.5 along with the dilution factors (DF1-3) utilized in their derivation. DF1 is modified for use with the saturated paste extract method, as described in Section 4.2.1. For fine and coarse soils, guidelines were calculated to be 15.88 and 17.78 mg/L saturated paste boron respectively.

Table 9.5. Soil Remediation Guidelines for Livestock Watering

Livestock watering pathway	Fine texture	Coarse texture
Groundwater guideline	5 mg/L	5 mg/L
DF1	0.823	0.767
DF2	1	1
DF3	3.86	4.64
DF4	1	1
Soil guideline (saturated paste)	**15.88 mg/L**	**17.78 mg/L**

Since the guidelines derived for fine and coarse soils are relatively similar to each other, it is reasonable to use an average guideline to represent both soil textures. This results in an overall soil guideline of 16.8 mg/L saturated paste boron for the protection of livestock watering.

$$SRG_{LW} = 16.8 \text{ mg/L}$$

9.6 Guideline for Wildlife Watering

There are currently no Alberta Tier 1 groundwater boron guidelines for wildlife watering. If the livestock watering guideline of 5 mg/L is also used for wildlife watering as recommended in Eisler (1990), a wildlife watering guideline can be calculated using the Tier 1 dilution factors. Unlike the livestock watering exposure pathway, the wildlife watering pathway assumes a 10 m transport distance to the nearest surface water source. However, as noted for the aquatic life pathway, the short transport distance and lack of biodegradation results in a DF4 of approximately 1. As a result, the soil guideline for the protection of wildlife watering is the same as for livestock.

$$SRG_{WW} = 16.8 \text{ mg/L}$$

9.7 Guideline for Offsite Migration

Tier 1 guidelines consider the potential for contaminants to migrate between areas of distinct land use. In particular, the offsite migration pathway is considered to ensure that guidelines set for commercial and industrial land (less sensitive) do not result in adjacent, more sensitive land being contaminated at levels above applicable ecological guidelines through wind and/or water transport. The ecological guideline for protecting adjacent land from wind and water erosion of soil is calculated from the equation below (AESRD 2014a). As described in CCME (2006), the model essentially assumes 0.14 cm of contaminated soil from the site is eroded and transported onto an equal area offsite and mixed into 2 cm of soil at background conditions. This equation is typically expressed in mg/kg, but will be applied here on a mg/L saturated paste boron basis.

$$SRG_{EC\text{-}OM} \quad = \quad (14.3 \text{ x } SRG_A) - (13.3 \text{ x } BSC)$$

Where:

$SRG_{EC\text{-}OM}$ = ecological soil remediation guideline for offsite migration via wind and water erosion
SRG_A = ecological direct soil contact guideline for agricultural land use
BSC = background soil concentration

Background soil concentrations ('BSC' in the above equation) were estimated at approximately 0.1 mg/L saturated paste boron based on ambient boron concentrations in the fine (clay loam) and coarse (sandy loam) agricultural reference soils.

The agricultural direct soil contact guideline for soil dependent biota ('SRG_A' in the above equation) was derived in Section 9.1 to be 3.3 mg/L saturated paste boron for fine and coarse soils. Using the above equation the derived ecological offsite migration guideline was calculated to be 45.9 mg/L saturated paste boron, and is to be applied to commercial and industrial lands.

$$\boldsymbol{SRG_{EC\text{-}OM} = 45.9 \text{ mg/L}}$$

9.8 Nutrient Cycling

Maintaining healthy nutrient cycling through soil microbial and enzymatic activities is important to the overall health of the soil ecosystem. Though the majority of research on boron toxicity in soil has been related to plants and invertebrates, boron is also potentially toxic to bacteria and other micro-organisms. Boric acid or related salts are sometimes used as a wood preservative (Butterwick *et al.*, 1989), food preservative (Ahmed and Fujiwara, 2010b), or antiseptic (Sprague, 1972), though relatively high concentrations are typically required. This is consistent with Butterwick *et al.* (1989) stating that bacteria and fungi are generally far less sensitive to boron than plants. In some cases, highly boron-tolerant bacteria have been studied with tolerances in the 100's or 1,000's of mg/L (Ahmed and Fujiwara, 2010a; Yoon *et al.*, 2010). Certain bacteria also appear to require boron for growth and activities such as nitrogen fixation (Yoon *et al.*, 2010).

Various studies (some tabulated in Crommentuijn *et al.*, 1995 and referenced in RIVM, 2010) have evaluated the effects of boron on soil bacteria and soil enzymes. In some studies such as Bilen *et al.* (2011), some beneficial ranges have been observed where moderately increased boron concentrations in soil result in increased microbial and enzymatic activity prior to reductions at higher doses. At higher concentrations, studies by Liang and Tabatabai (1977, 1978) examined the effects of numerous trace elements including boron on microbial nitrification and nitrogen mineralization in soils via bacteria such as *Nitrobacter*. At the sole dose tested (5 mmol spiked B/kg, equivalent to 54 mg/kg), inhibition of nitrification and nitrogen mineralization was observed at levels ranging from 7% to 92% over a range of soil types, with an average inhibition of 36% over these two studies at this dose. Other studies also examined the effects of boron on various soil enzymatic activities, including nitrate reductase (Fu and Tabatabai, 1989), dehydrogenase (Rogers and Li, 1985), urease (Tabatabai, 1977), arylsulfatase (Al-Khafaji *et al.*, 1979), and ß-glucosaminidase (Ekenler and Tabatabai, 2002). In one example (Tabatabai, 1977), inhibition of urease activity ranged from 13% to 98% depending on soil type at 54 mg spiked B/kg, with an average of 30.8% inhibition and most typically below 30%. Soil dehydrogenase activity was tested in Rogers and Li (1985), with minor (<25%) inhibition observed up to 91 mg spiked B/kg and 50% inhibition occurring at approximately 140-350 mg spiked B/kg. Nitrate reductase was observed in Fu and Tabatabai (1989) to range from 29% stimulation to 33% inhibition at 27 mg spiked B/kg in a range of soil types, with an average effect near zero. ß-glucosaminidase was observed to be inhibited by 4%-46% at 54 mg/kg spiked B, with an average of 27% inhibition (Ekenler and Tabatabai, 2002). Arylsulfatase was found to be inhibited by 60-72% at 270 mg spiked B/kg, with inhibition dropping to an average of 20% at 27 mg spiked B/kg. In all cases, boron was found to be less inhibitory on microbial and enzymatic activities than more toxic elements such as mercury and silver.

Based on the above studies, inhibitory effects generally appear to be occurring at soil boron levels substantially above the previously derived ecological direct soil contact guideline of 3.3 mg boron/L saturated paste extract. This corresponds to HWS boron levels of approximately 4.8-7 mg/kg for typical fine and coarse soils based on soil regressions in Section 5.2.2, which are comparable to spiked B concentrations due to the high recovery of the HWS test. Due to the relative lack of detailed microbial dose-response data, especially at lower soil concentrations, deriving a numerical guideline on a mg/L saturated paste boron basis for nutrient cycling is not practical. However, it appears that the ecological direct soil contact guideline derived herein for plants and invertebrates is sufficiently protective of nutrient cycling as well.

10. Derivation of Human Health Soil Remediation Guidelines

This section derives guidelines for protection of human health, including guidelines for direct soil contact in Section 10.1 and for human drinking water in Section 10.2.

10.1 Guideline for Direct Soil Contact

Guidelines to protect humans from direct soil contact to boron were established based on the equations presented in Section 7.2. The numerator variables ((TDI-EDI) x SAF x BW) represent the tolerance of a human to boron exposure, and incorporate a soil allocation factor (SAF) which is the proportion of total boron exposure which will come from soil. Since boron is essentially non-volatile, the SAF was adjusted to 0.25 from the default of 0.20 as per Tier 1 procedures (AESRD, 2014a) based on the five environmental compartments (soil, water, air, food, and consumer products). The soil contact guideline also incorporates three major routes by which contaminants in soil may enter the human body. These routes include soil ingestion, inhalation of contaminants bound to dust, and absorption through the skin, and are represented by the denominator variables (AF_G x SIR), (AF_L x IR_S x ET_2), and (AF_S x SR) respectively. Because boron absorption through skin is considered negligible (US EPA, 2004b), the skin absorption route is assumed to be equivalent to zero.

Agricultural and residential / parkland areas are considered sensitive land uses for human direct soil contact, with the pathway not considered for natural areas due to minimum exposure time. Here, the modeled individual is a toddler with an overall exposure term of 1 (ET_1 and ET_2 both equal to 1), which assumes the individual is potentially exposed 24 hours per day, 365 days per year. For these land uses the numerator variable ((TDI-EDI) x SAF x BW)) was calculated to be 0.625 mg/day. TDI and SAF are constants (Section 7), while EDI and BW were set to 0.048 mg/kg-day (Section 7.1) and 16.5 kg (Tier 1 default) to represent characteristics of a toddler. The denominator variable representing soil ingestion was equivalent to the toddler SIR of 8.0×10^{-5} kg/day ($AF_G = 1$), while the denominator variable representing the inhalation route was calculated to be equivalent to the toddler IR_S of 7.1×10^{-9} kg/day ($AF_L = 1$). The BSC was assumed to be 10 mg/kg strong acid extractable boron based on the clay loam reference soil. The derived guideline for the human health direct soil contact pathway under agricultural and residential / parkland land uses was calculated to be 7,822 mg/kg strong acid extractable boron. The corresponding saturated paste boron is estimated to be approximately 7,500 mg/L based on extrapolating the clay loam regression shown in Figure 5.9 (slope = 1.041, intercept = 15.387). This guideline and associated variables are presented in Table 10.1.

Agricultural and Residential / Parkland $SRG_{HH\text{-}DC}$ **= 7,500 mg/L**

Table 10.1. Soil Remediation Guidelines for Human Direct Soil Contact

Direct soil contact parameters	Agricultural & Residential / Parkland	Commercial	Industrial
Boron tolerance term (mg/day) ((TDI-EDI) x SAF x BW))	0.625	0.625	3.215
Soil ingestion term (kg/day) (AF_G x SIR)	$8.0x10^{-5}$	$8.0x10^{-5}$	$2.0x10^{-5}$
Inhalation term (kg/day) (AF_L x IR_S x ET_2)	$7.1x10^{-9}$	$3.0x10^{-9}$	$5.0x10^{-9}$
Dermal contact term (kg/day) (AF_S x SR)	0	0	0
ET_1	1	0.6593	0.6593
BSC (mg/kg – ^{A}SAE boron)	10	10	10
SRG_{HH-DC} (mg/kg – ^{A}SAE boron)	7,822	11,887	243,768
SRG_{HH-DC} (mg/L – Sat paste boron)	**7,500**	**11,000**	**234,000**

Notes:

1) Variable abbreviations are referenced from Section 7;

2) Guidelines derived for agricultural and residential / parkland areas are based on a toddler with full exposure (ET_1=1, ET_2=1). Commercial areas are based on a toddler and Industrial areas are based on an adult with limited exposure (ET_1=0.6593, ET_2=0.4167).

^{A} *SAE: Strong acid extractable boron*

Commercial lands are modeled with a child receptor using an overall exposure term of 0.275 (ET_1 of 0.6593 and ET_2 of 0.4167) which assumes the individual is exposed approximately 10 hours per day, 4.6 days per week. For these land uses the numerator variable ((TDI-EDI) x SAF x BW)) was calculated to be 0.625 mg/day. TDI and SAF are constants (Section 7), while EDI and BW were set to 0.048 mg/kg-day (Section 7.1) and 16.5 kg (Tier 1 default) to represent characteristics of a toddler. The denominator variable representing soil ingestion was equivalent to the toddler SIR of $8.0x10^{-5}$ kg/day (AF_G = 1), while the denominator variable representing the inhalation route was calculated to be $3.0x10^{-9}$ kg/day, representing the toddler IR_S ($7.1x10^{-9}$ kg/day) multiplied by ET_2 (0.4167) and AF_L equal to 1. The BSC was assumed to be 10 mg/kg strong acid extractable boron based on the clay loam reference soil. The derived guideline for the human health direct soil contact pathway under commercial land use was calculated to be 11,887 mg/kg strong acid extractable boron. The corresponding saturated paste boron is estimated to be approximately 11,000 mg/L based on extrapolating the clay loam regression shown in Figure 5.9 (slope = 1.041, intercept = 15.387). This guideline and associated variables are presented in Table 10.1.

***Commercial SRG_{HH-DC}* = 11,000 mg/L**

Industrial lands are considered less sensitive for human direct soil contact. Here, the modeled individual is an adult with an overall exposure term of 0.275 (ET_1 of 0.6593 and ET_2 of 0.4167) which assumes the individual is exposed approximately 10 hours per day, 4.6 days per week. For these land uses the numerator variable ((TDI-EDI) x SAF x BW)) was calculated to be 3.215 mg/day. TDI and SAF are constants (Section 7), while EDI and BW were set to 0.018 mg/kg-day (Section 7.1) and 70.7 kg (Tier 1 default) to represent characteristics of an adult. The denominator variable representing soil ingestion was equivalent to the adult SIR of $2.0\text{x}10^{-5}$ kg/day ($AF_G = 1$), while the denominator variable representing the inhalation route was calculated to be $5.0\text{x}10^{-9}$ kg/day, representing the adult IR_S ($1.2\text{x}10^{-8}$ kg/day) multiplied by ET_2 (0.4167), with AF_L equal to 1. The BSC was assumed to be 10 mg/kg (strong acid extractable boron) representing observed background boron concentrations in clay loam reference soils. The derived guideline for the human health direct soil contact pathway under commercial and industrial land uses was calculated to be 243,768 mg/kg strong acid extractable boron. The corresponding saturated paste boron is estimated to be approximately 230,000 mg/L based on extrapolating the clay loam regression shown in Figure 5.9 (slope = 1.041, intercept = 15.387). This guideline and associated variables are presented in Table 10.1.

$$\textit{Industrial } SRG_{HH\text{-}DC} = \mathbf{230{,}000\ mg/L}$$

10.2 Guideline for Human Drinking Water (DUA)

The Tier 1 guideline for human drinking water (DUA) is 5 mg/L (Section 2.5.2). In order to derive a soil guideline which is protective of this receptor, Tier 1 dilution factor calculations were used as in previous sections. The derived guidelines are presented in Table 10.2 along with the dilution factors (DF1-3) utilized in their derivation. DF1 is modified for use with the saturated paste extract method, as described in Section 4.2.1. Note that DF4 is not used since it is assumed a potential DUA is directly below the impacts, without any lateral offset distance. One difference between guidelines calculated for the human drinking water pathway compared to other groundwater pathways is that the mixing depth is assumed to be a fixed 2 m regardless of source length or other soil or groundwater properties. This results in larger calculated DF3 values than for the other pathways, with a DF3 of 15.9 calculated for fine soil and 30.87 for coarse soil. For fine and coarse soils, this results in calculated guidelines of 65.5 and 118.3 mg/L saturated paste boron, respectively. Since these guidelines differ by approximately 2-fold, distinct guidelines are retained for each texture for this pathway.

$$SRG_{DUA} = 65.5 \text{ mg/L (fine)}$$

$$SRG_{DUA} = 118.3 \text{ mg/L (coarse)}$$

Table 10.2. Soil Remediation Guidelines for Human Drinking Water

Human drinking water pathway	Fine texture	Coarse texture
Groundwater guideline	5 mg/L	5 mg/L
DF1	0.823	0.767
DF2	1	1
DF3	15.93	30.87
Source concentration (saturated paste)	**65.5 mg/L**	**118.3 mg/L**

10.3 Guideline for Offsite Migration

Similar to the ecological offsite migration guideline derived in Section 9.7 to protect soil dependent biota, an offsite migration guideline can also be calculated to protect the human direct soil contact pathway on sensitive land (agricultural or residential / parkland) adjacent to commercial / industrial land. Using the agricultural human direct soil contact guideline of 7,500 mg/L saturated paste boron (Section 10.1), an offsite migration guideline for human direct soil contact to be applied to commercial / industrial land is derived as approximately 107,000 mg/L saturated paste boron using techniques from Section 9.7.

$$\boldsymbol{SRG_{HH\text{-}OM} = 107{,}000\ \mathrm{mg/L}}$$

11. Summary of Derived Guidelines

Table 11.1 summarizes all of the Tier 1 guidelines derived for boron in Sections 9 and 10. All guidelines are shown on a mg/L saturated paste boron basis. For agricultural, natural area, and residential / parkland land-uses, the most constraining guideline is 3.3 mg/L saturated paste boron based on the ecological direct soil contact pathway. This is slightly lower than the irrigation guideline of 3.4 mg/L for agricultural land. For commercial and industrial land, protection of aquatic life is the most constraining pathway with a guideline of 5.0 mg/L. Numerical guidelines have not been derived for livestock and wildlife soil and food ingestion exposure pathway, because it was shown to be less sensitive than the ecological direct soil contact exposure pathway. In general, the guidelines for human pathways are less constraining than the guidelines for ecological pathways.

Table 11.1. Summary of Tier 1 Boron Soil Remediation Guidelines – All Land Uses and Exposure Pathways

Receptor	**Overall Guideline**		**Human**				**Ecological**													
Pathway			**Direct Soil Contact**	**Protection of Domestic Use Aquifer**		**Off-Site Migration**	**Direct Soil Contact**		**Livestock Soil and Food Ingestion**	**Wildlife Soil and Food Ingestion**	**Protection of Freshwater Aquatic Life**		**Protection of Livestock Water**		**Protection of Wildlife Water**		**Protection of Irrigation Water**		**Off-Site Migration**
Soil Type	**Fine**	**Coarse**		**Fine**	**Coarse**		**Fine**	**Coarse**			**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**	
Unit	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Natural	**3.3**	**3.3**	-	65	118	-	3.3	3.3	-	-	5.0	5.0	-	-	17	17	-	-	-
Agricultural	**3.3**	**3.3**	7,500	65	118	-	3.3	3.3	-	-	5.0	5.0	17	17	17	17	3.4	3.4	-
Residential/ Parkland	**3.3**	**3.3**	7,500	65	118	-	3.3	3.3	-	-	5.0	5.0	-	-	-	-	-	-	-
Commercial	**5.0**	**5.0**	11,000	65	118	110,000	7.9	7.9	-	-	5.0	5.0	-	-	-	-	-	-	46
Industrial	**5.0**	**5.0**	230,000	65	118	110,000	7.9	7.9	-	-	5.0	5.0	-	-	-	-	-	-	46

Note: all boron guidelines expressed on a mg/L saturated paste boron basis

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