New Tier 1 Boron Guideline for Alberta: Boron Soil Ecotoxicity and Methods Development Research

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Summary

Part 1

- Introduction
- Agricultural and Boreal Ecotoxicity Tests
- Boron Soil Analysis
- Chemistry vs Toxicity
- Recommendations

Part 2

- Greg Huber - Equilibrium
- Tier 1 Guideline Development

Acknowledgements

- Petroleum Technology Alliance of Canada (PTAC)
- Environment Canada
- PTAC Boron Working Group

Boron in the Environment

- Naturally present in the environment due to weathering of boron-containing minerals and decay of plant material
- Highly soluble in solution; adsorbed in soil by clay (aluminosilicates) and organic matter
- Background soils generally below current Tier 1 guideline, but in some cases background soils can be above Tier 1 (primarily clayey or organic soils)
- Essential plant micronutrient
  - Difference between plant deficiency and toxicity is small
  - Species-specific, even variant-specific
  - Concentrations which may be toxic to one species may be deficient for another

Anthropogenic Sources

- Fertilizers and herbicides
- Industrial Use/Manufacturing – glass, fiberglass insulation
- Wood Preservative
- Application of fly ash or sewage as soil amendment
- Wastewater irrigation
- Land disposal of industrial wastes
- Use of borax detergent for cleaning tanks, wellheads, equipment
- Saline produced water and drilling waste
  - Common co-contaminant with elevated salinity in Alberta

Why New Research?

- Current Tier 1 boron guideline of 2 mg/kg hot-water soluble (HWS) boron has several problems:

  - Not based on a modern, risk-based approach
  - Based on professional judgement and limited data in 1991
  - HWS test designed to diagnose deficiency, not toxicity
  - Older research often used colorimetric detection methods
  - Background concentrations may exceed guidelines
  - Good growth often observed above Tier 1 guideline
  - Texture (clay and organic matter) influence boron sorption/toxicity
  - Plant available/toxic concentrations not correlated well with HWS B measured across different soil types

Objectives

Narrow range between deficiency and toxicity demands an analytical method capable of measuring plant available B to predict ecotoxicity, regardless of soil characteristics

- ✓ Investigate the saturated paste extraction method for measuring plant available soil boron
- ✓ Conduct plant toxicity tests in a variety of boron spiked soils using agricultural and boreal test species
- ✓ Include a long-term plant growth study and an earthworm reproduction test
- ✓ Compare SatPaste B and HWS B toxicity test dose-responses
- ✓ Compile Species Sensitivity Distributions to derive new soil criteria for agricultural and boreal regions in Alberta

Reference soil collection

- Reference soils required for tox tests (boron spiking)
  - artificial soil as a benchmark
  - Agricultural Region:
    - Fine and Coarse soils
  - Boreal Region:
    - Organic and Mineral
- Soil Collection – Equilibrium: locate and collect four field reference soils using soil maps and field visits.
  - Fine reference soil (clay loam) collected from updated site near Delacour.
  - Coarse reference soil had not yet been sourced in Alberta. Suitable sandy loam reference soil collected near Vulcan.

Reference Soil Collection - Agricultural

Fine reference soil near Delacour (clay loam)

Coarse reference soil near Vulcan (sandy loam)

Reference Soil Collection - Boreal

- organic peat soils and mineral brunisol from location near Whitney Lake Provincial Park

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Soil Properties

	Fine	Coarse	Organic	Mineral	Artificial
Texture	Clay Loam	Sandy Loam		Sand	Sandy Loam
75 um %	32	60	49	96	77
Texture	Fine	Coarse	Fine	Coarse	Coarse
% Sand	33	62		95	68
% Silt	35	20		2	14
% Clay	**32**	**18**		**4**	**18**
% OM	**3.9**	**3.0**	**68**	**5.3**	**10**
Saturation %	**79**	**51**	**552**	**31**	**100**
pH	7.4	5.8	5.5	4.4	6.8

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Test Soils Preparation

- 800 L each of three test soils
- Field Soils air dried to < 10% Moisture, sieved < 2 mm
- Spike with boric acid solution to achieve a target range of total boron concentrations ranging from non-toxic to toxic effects based on range-finding screening tests.
  - nominal total boron concentrations from 2 to 1000 mg/kg dwb (HWS B 0 > 400 mg/kg)
  - Sufficient test concentrations at low end near criteria of 2 mg/kg HWS B to achieve good resolution.
- Bring moisture content to optimal moisture content, 80% WHC
- Age spiked soils 2 weeks

Ecotoxicity Tests

- Plant toxicity tests in soils spiked with a broad range of boron concentrations
  - ➢Six agricultural species in fine, coarse and artificial soil (18 tests)
  - ➢Five boreal species in organic, mineral and artificial soil (11 tests)
- Environment Canada Biological Test Methods:
  - Test for Measuring Emergence and Growth of Terrestrial Plants Exposed to Contaminants in Soil. EPS 1/RM/45 2005.
  - Test for Growth in Contaminated Soil Using Terrestrial Plants Native to the Boreal Region. EPS 1/RM/56
- One long-term growth study with cucumber to flowering stage (3 months)
- Earthworm survival and reproduction test in coarse soil (EPS/1/RM/43)

❖Results from boron toxicity dose-response curves used to generate direct eco-contact guideline based on CCME rank percentile methodology.

Test Design

- 13 treatments including a control; Ten replicates per treatment – 1 L test vessels
- Five to ten seeds per pot
- 2 to 3 week (ag) and 4 to 6 weeks (boreal)
- Controlled environmental conditions

Toxicity Endpoints

- Emergence
- Shoot and Root Length
- Shoot and Root Biomass
- Analytical at Test initiation and Termination
  - pH, EC Moisture, Salinity, Nutrients
  - Total Boron (SAD)
  - HWS B
  - SatPaste B as mg/kg dwb and mg/L
  - Tissue Boron
  - IC_{25} and IC_{50}

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Agricultural Plant Species

Species	Classification	Type	Test Duration	Life Cycle
Alfalfa	Dicot	Agricultural	21 d	Perennial
Barley	Monocot	Agricultural	14 d	Annual
Durum Wheat	Monocot	Agricultural	14 d	Annual
Cucumber	Dicot	Market-garden	14 d	Annual
Carrot	Dicot	Market-garden	21 d	Biennial
Northern Wheatgrass	Monocot	Grasslands	21 d	Annual/perennial

Boreal Plant Species

Species	Classification	Type	Test Duration	Life Cycle
Jack Pine	Gymnosperm	Tree, coniferous	35 d	Perennial
White Spruce	Gymnosperm	Tree, coniferous	42 d	Perennial
Black Spruce	Gymnosperm	Tree, coniferous	42 d	Perennial
Bluejoint Reedgrass	Angiosperm, monocot	Herb, graminoid	28 d	Perennial
Trembling Aspen	Angiosperm, dicot	Tree, deciduous	28 d	Perennial

Boron Analysis

Toxicity data compared to measured boron by Hot Water Soluble (HWS) and Saturated Paste (SP) soil extraction methods to determine best analytical method to predict toxicity.

Total Boron

- Strong acid digest – acid, heat, oxidizer; ICP; mg/kg dwb
- Most Tier 1 metals
- Total pool of soil boron, most largely unavailable
- Soil Ingestion Pathways

Hot Water Soluble Boron

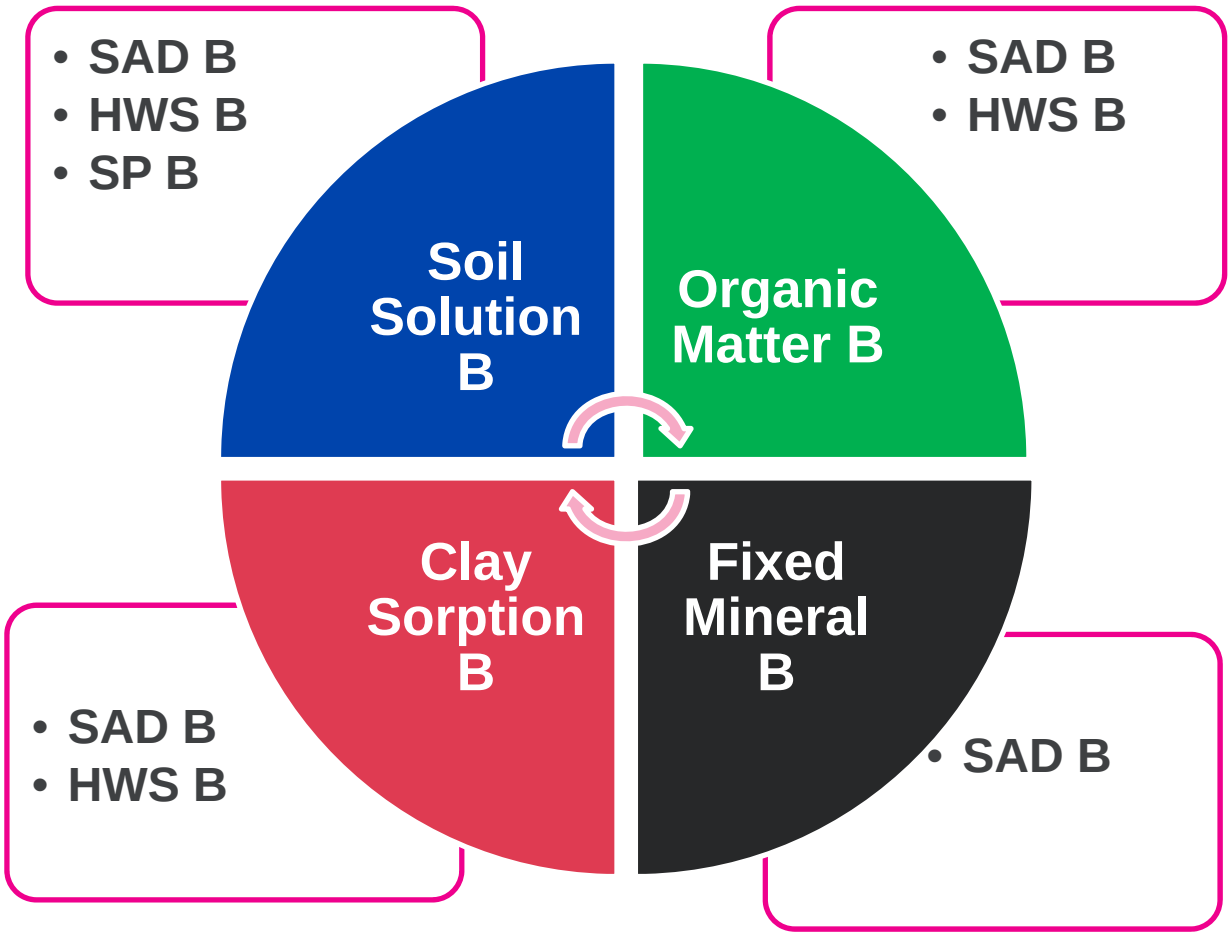
- 2:1 water:Soil with boiling; ICP (historically colorimetric); mg/kg dwb
- Intended to measure total plant-available boron to diagnose deficiency
- Soil solution boron + substantial amount from adsorbed soil pools

Boron Analysis

Saturated Paste Boron

- Less aggressive extraction than HWS B
- Same methodology as saturated paste extractions for salinity
- Incremental water addition to a semi-fluid, saturated paste at ambient temperature.
- Boron measured in the extract (ICP) as mg/L
- May be converted to mg/kg dwb based on saturation %
  - Satn % = amount of water added to 100 g dry soil
  - correlated to soil texture
- mg/L basis advantageous – correlated to soil solution concentration
- Represents dissolved boron in soil solution, minimal adsorbed boron

Boron Soil Pools and Extraction Method



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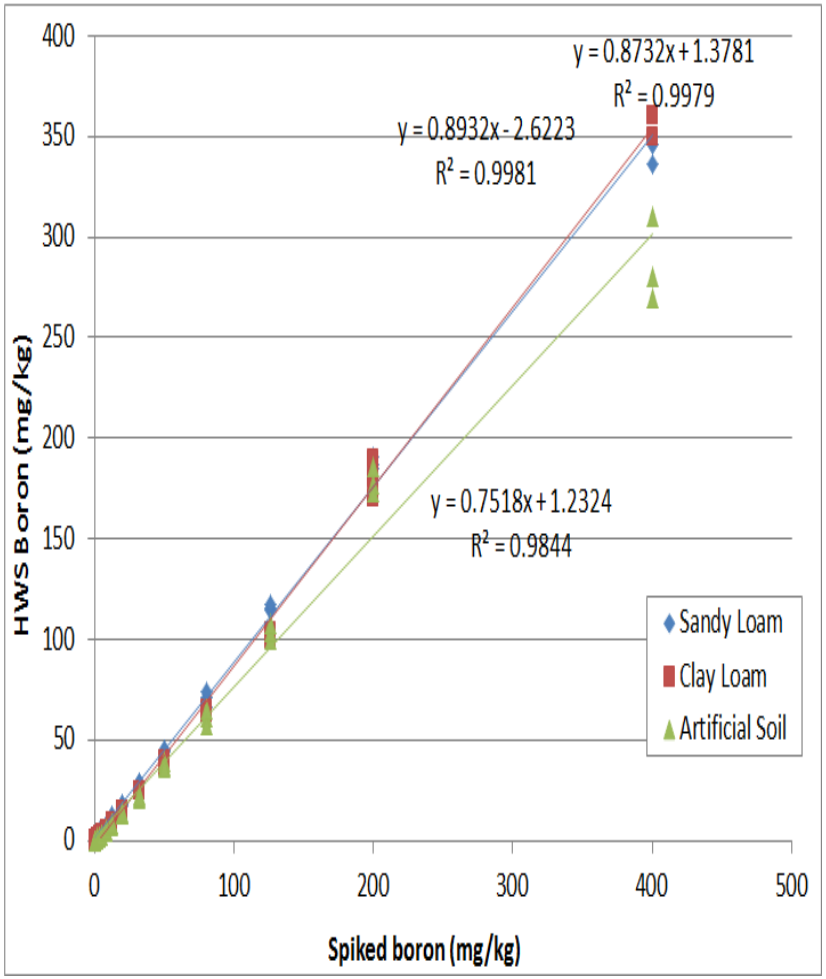
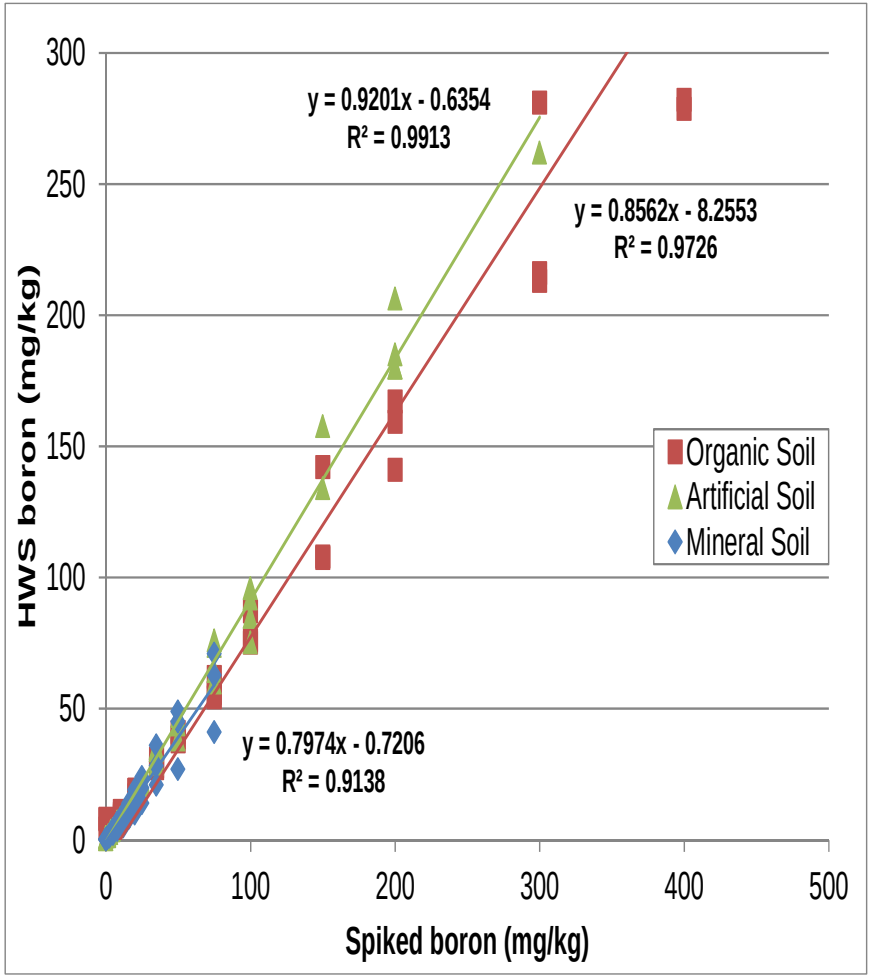
Results: Boron Soil Concentrations - Spiked B vs HWS B





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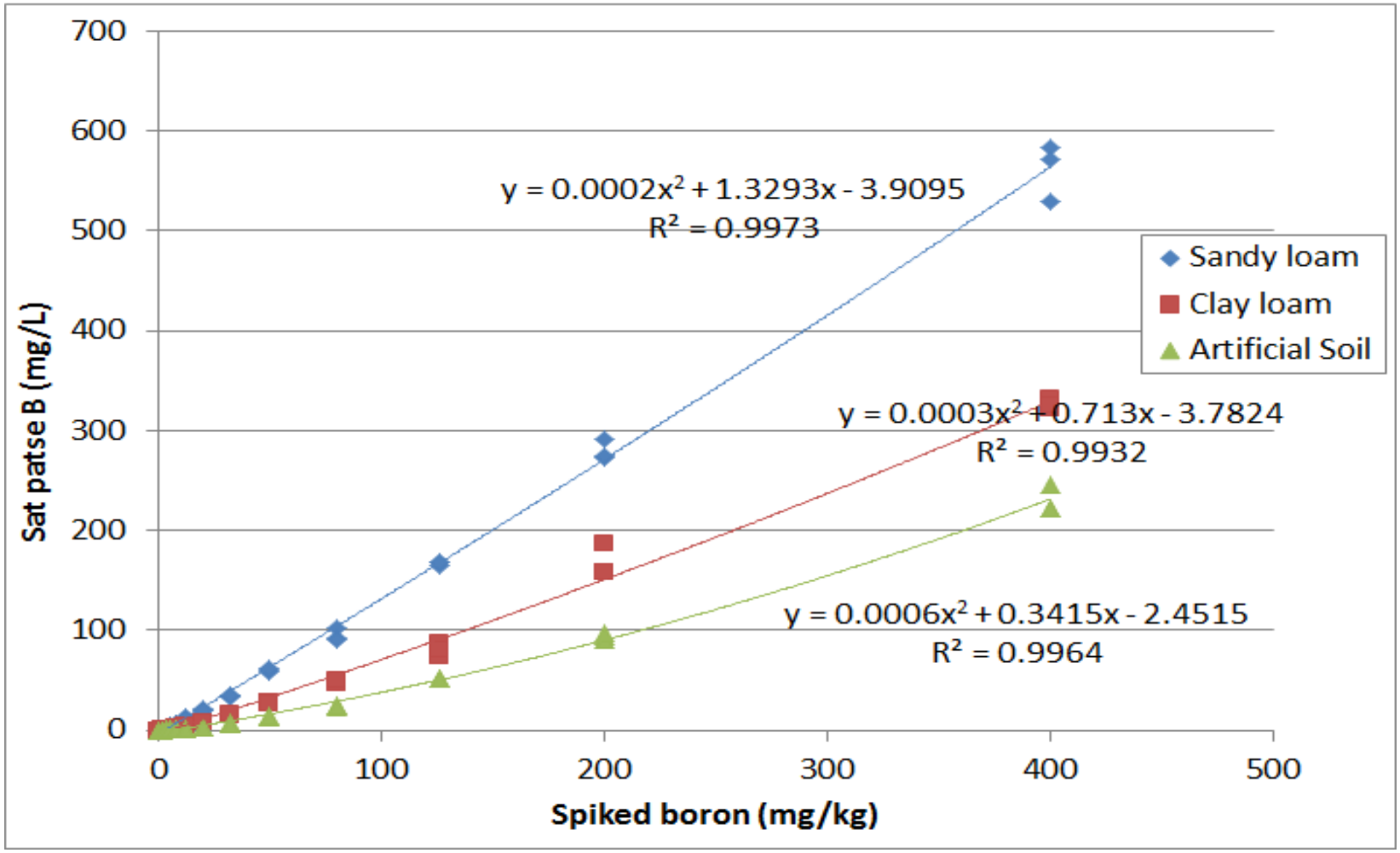
Spiked vs Satpaste B (mg/L) Agricultural Soils



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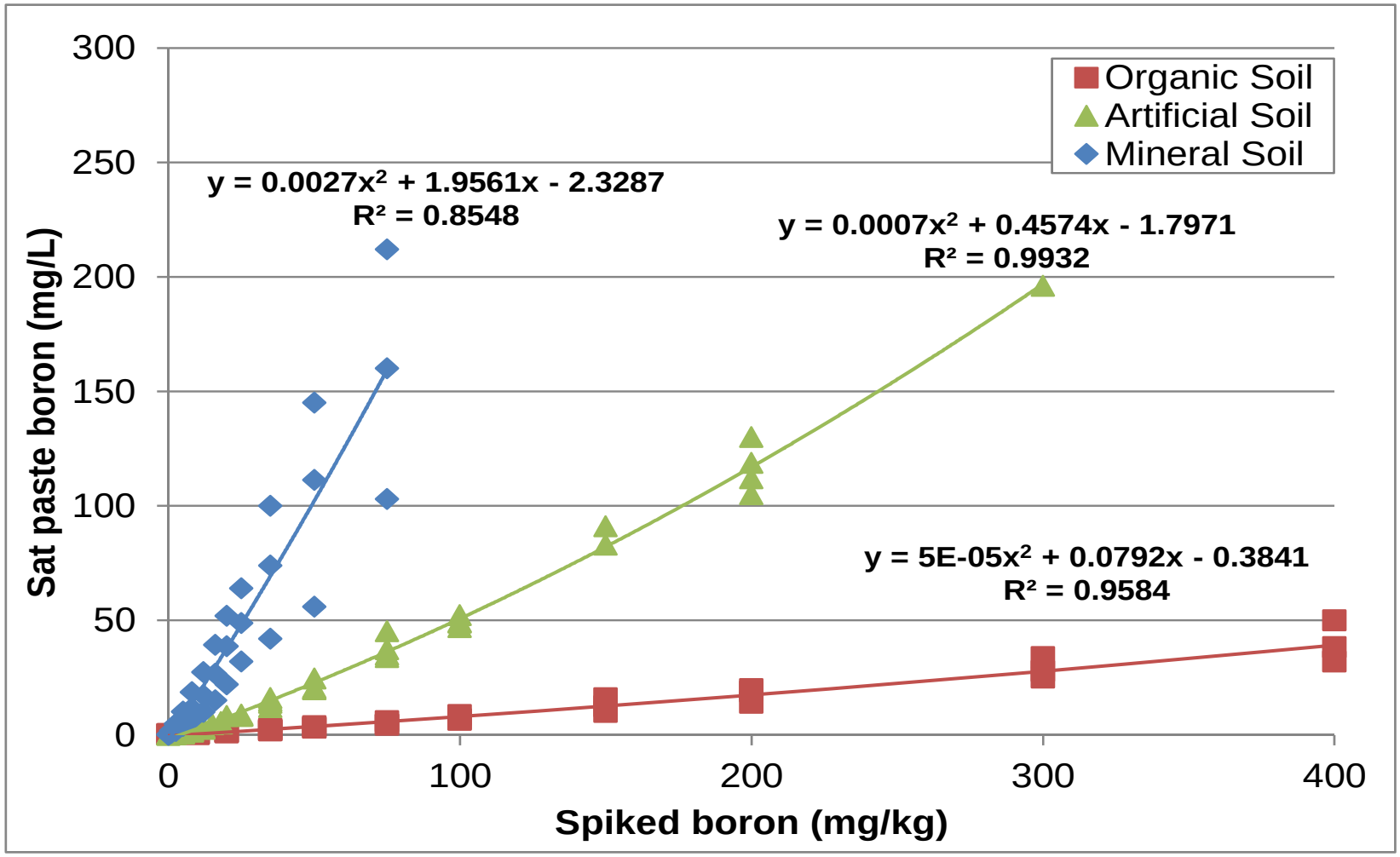
Spiked vs Satpaste B (mg/L) Boreal Soils



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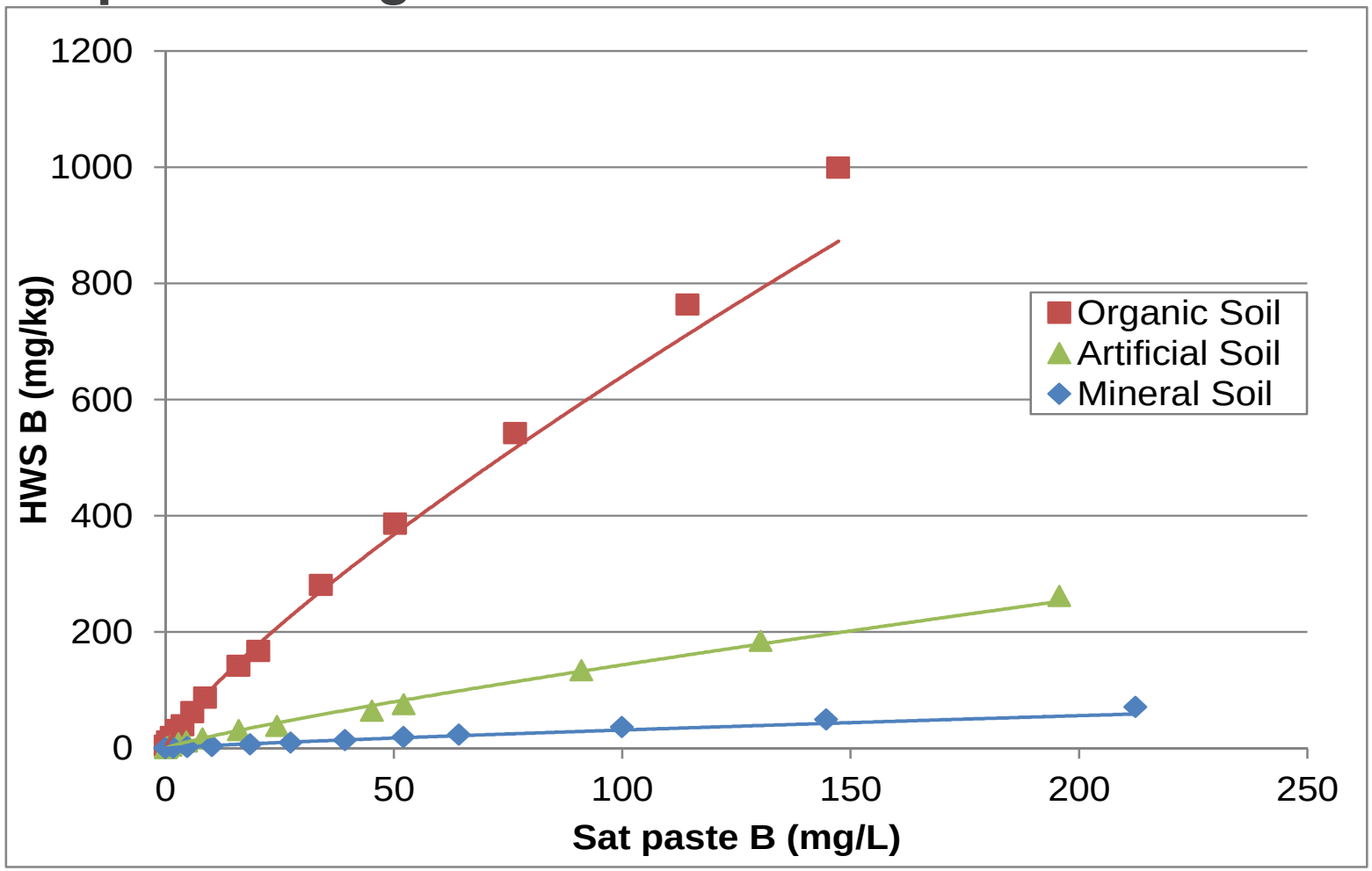
Satpaste B mg/L vs HWS B - Boreal Soils



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Ecotoxicity Test Results

- Cucumber Example – relatively sensitive species

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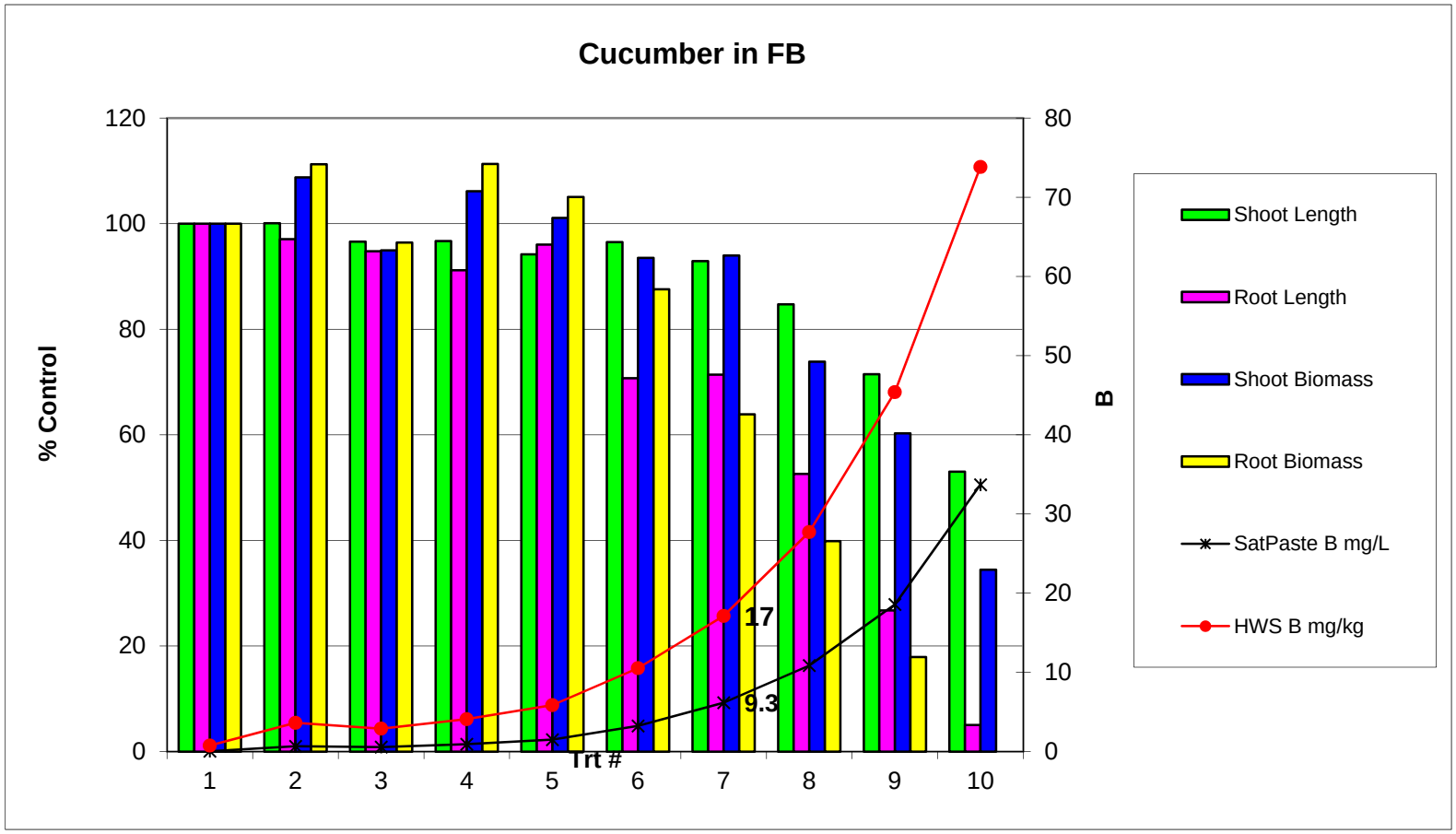
Cucumber in Clay Loam



1	2	3	4	5	6	7	8	9	10	Trt #
0.8	3.6	2.9	4.1	5.9	11	17	28	45	74	HWS B mg/kg
0.08	1.0	0.9	1.4	2.3	4.9	9.3	16	28	51	Satpaste B mg/L

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Barley in Clay Loam

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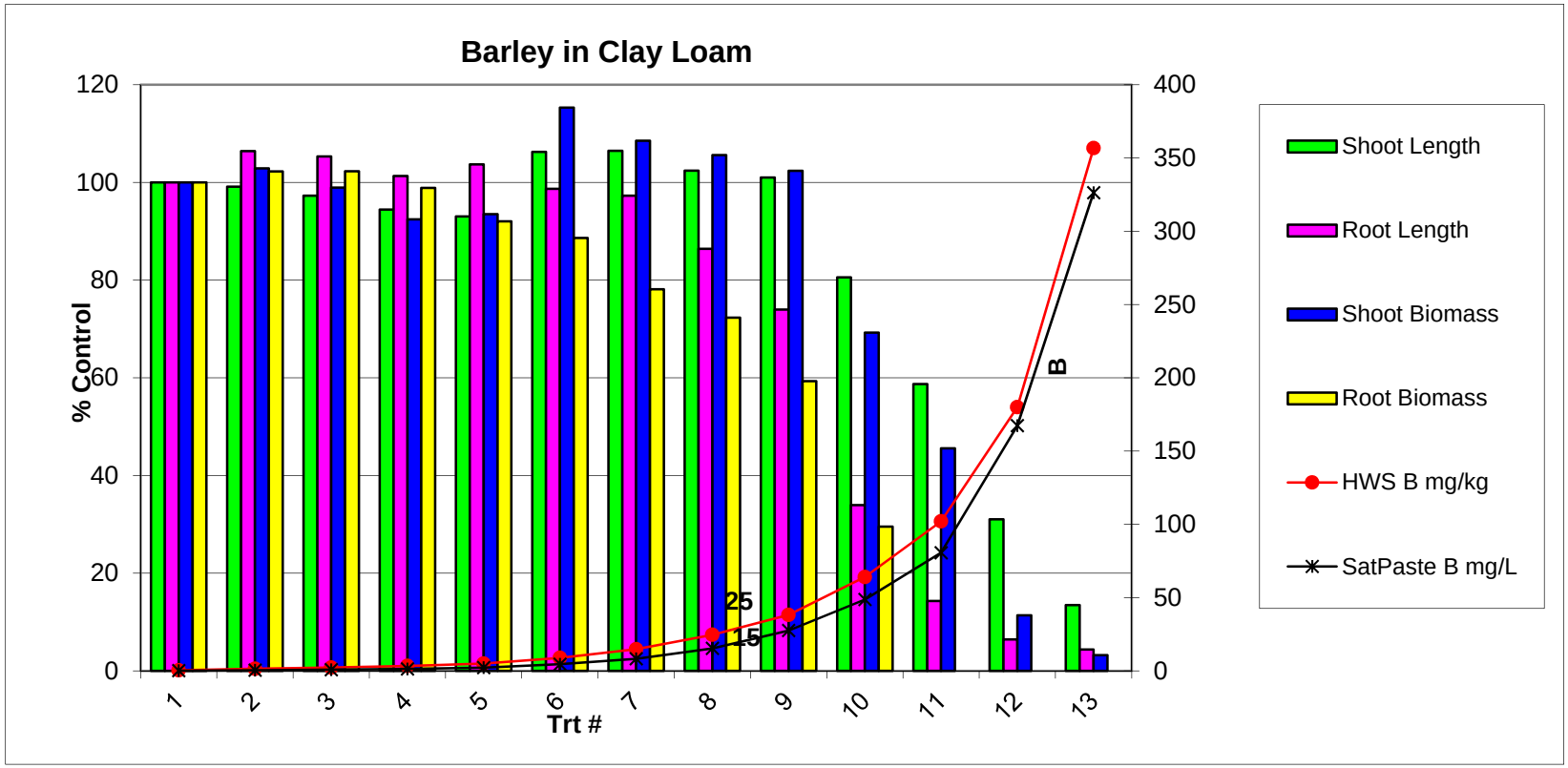
Barley in Clay Loam - Summary



1	2	3	4	5	6	7	**8**	9	10	11	12	13	
0.4	1.5	2.3	3.4	5.0	9	15	**25**	38	64	102	180	357	HWS B mg/kg
0.2	0.5	0.8	1.4	2.3	4.6	8.2	**15**	28	49	81	167	326	Satpaste B mg/L

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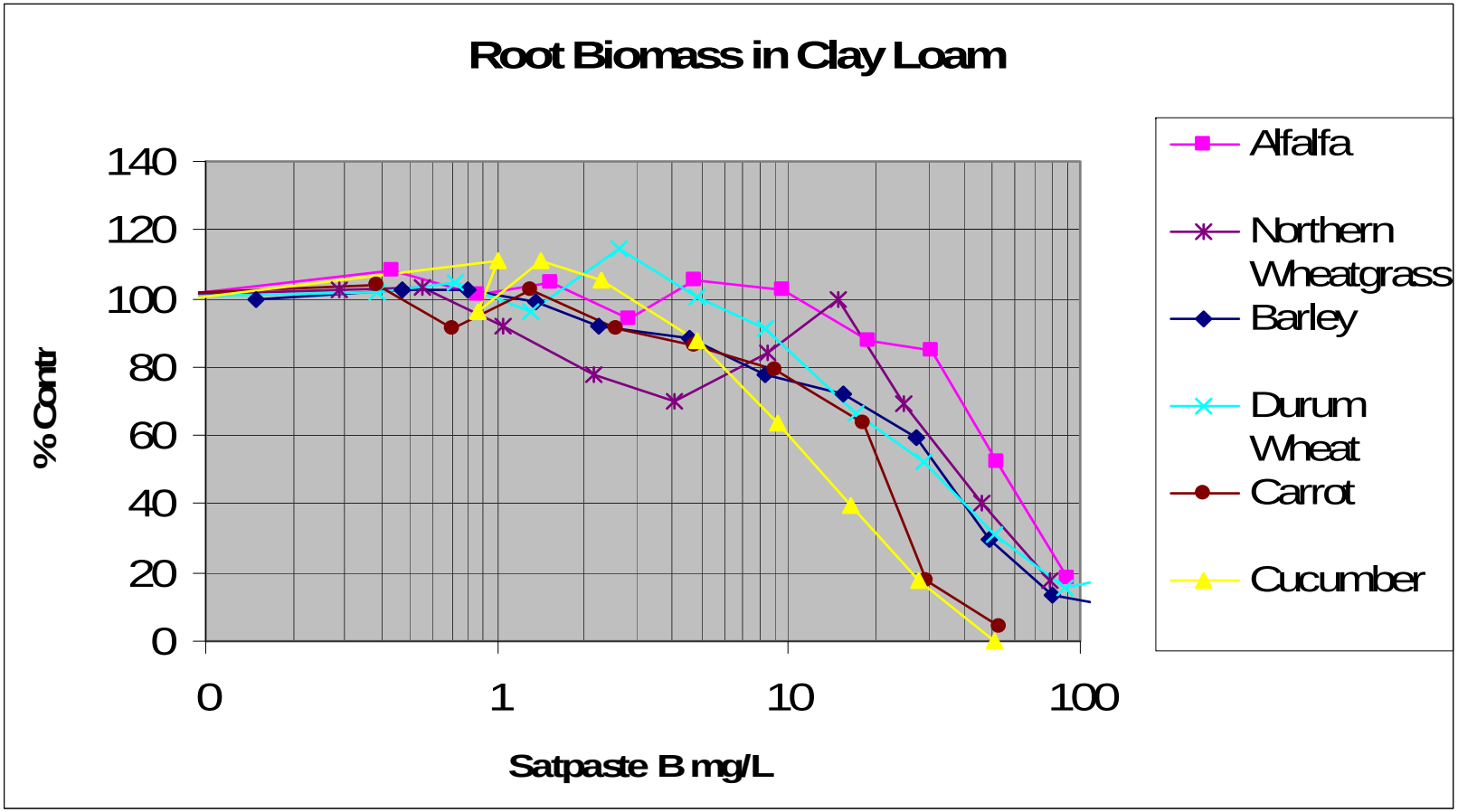
Species Sensitivity Comparison in Clay Loam



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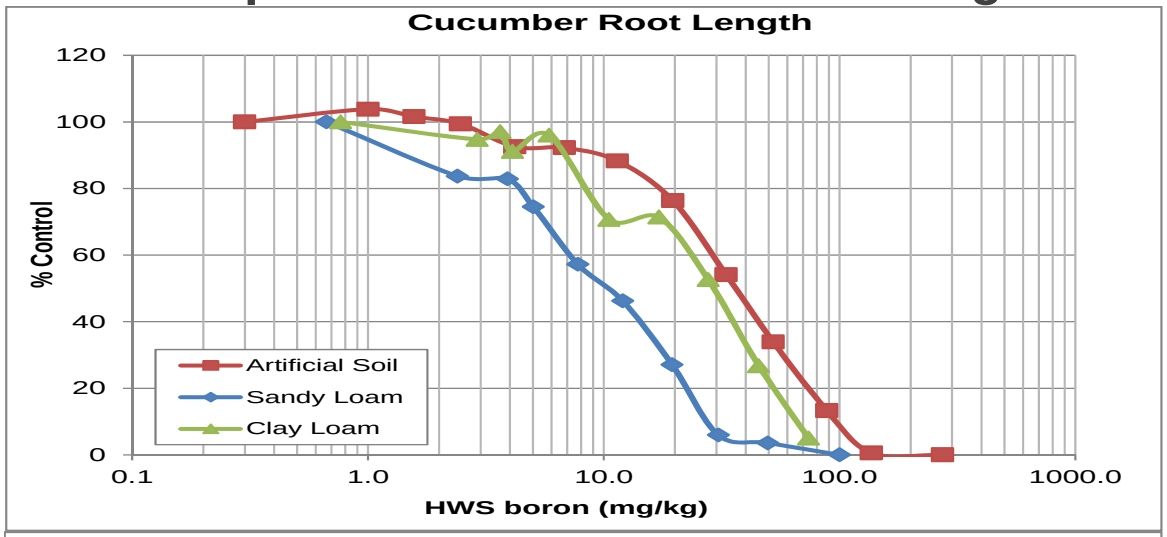
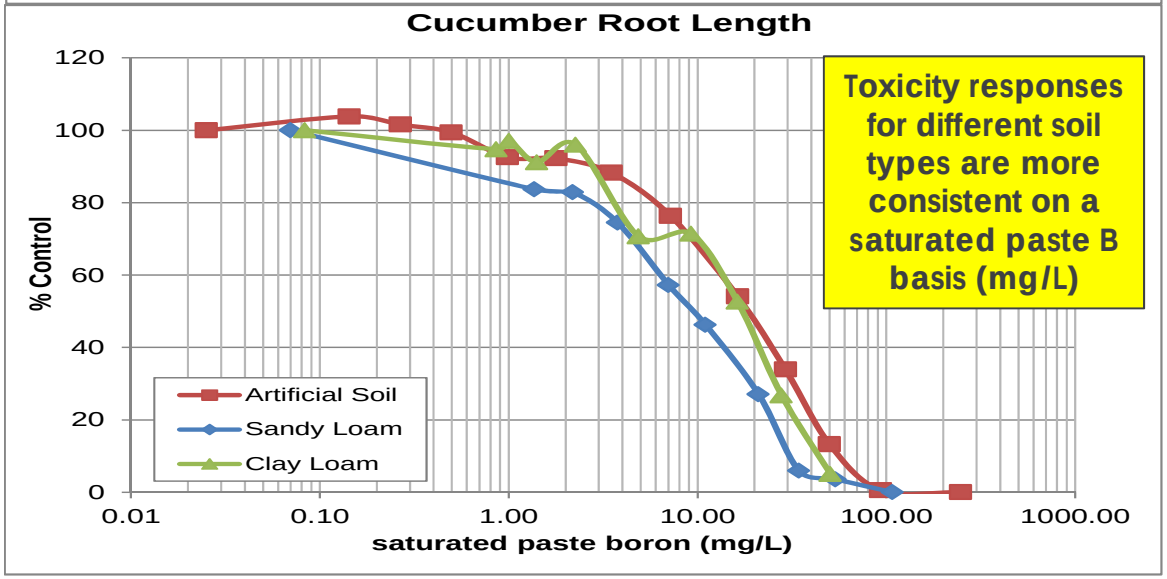
Example Dose Response – Cucumber Root Length





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Boreal Species Toxicity Tests

- Similar dose response patterns and IC_{25} concentrations for satpaste B mg/L
- IC_{25} range from 1.42 mg/L jack pine root biomass in organic soil to 67.6 mg/L for white spruce shoot length in organic soil
- Stimulation effects at low concentrations
- Higher variability in boreal species (smaller plants, delicate roots, longer tests)

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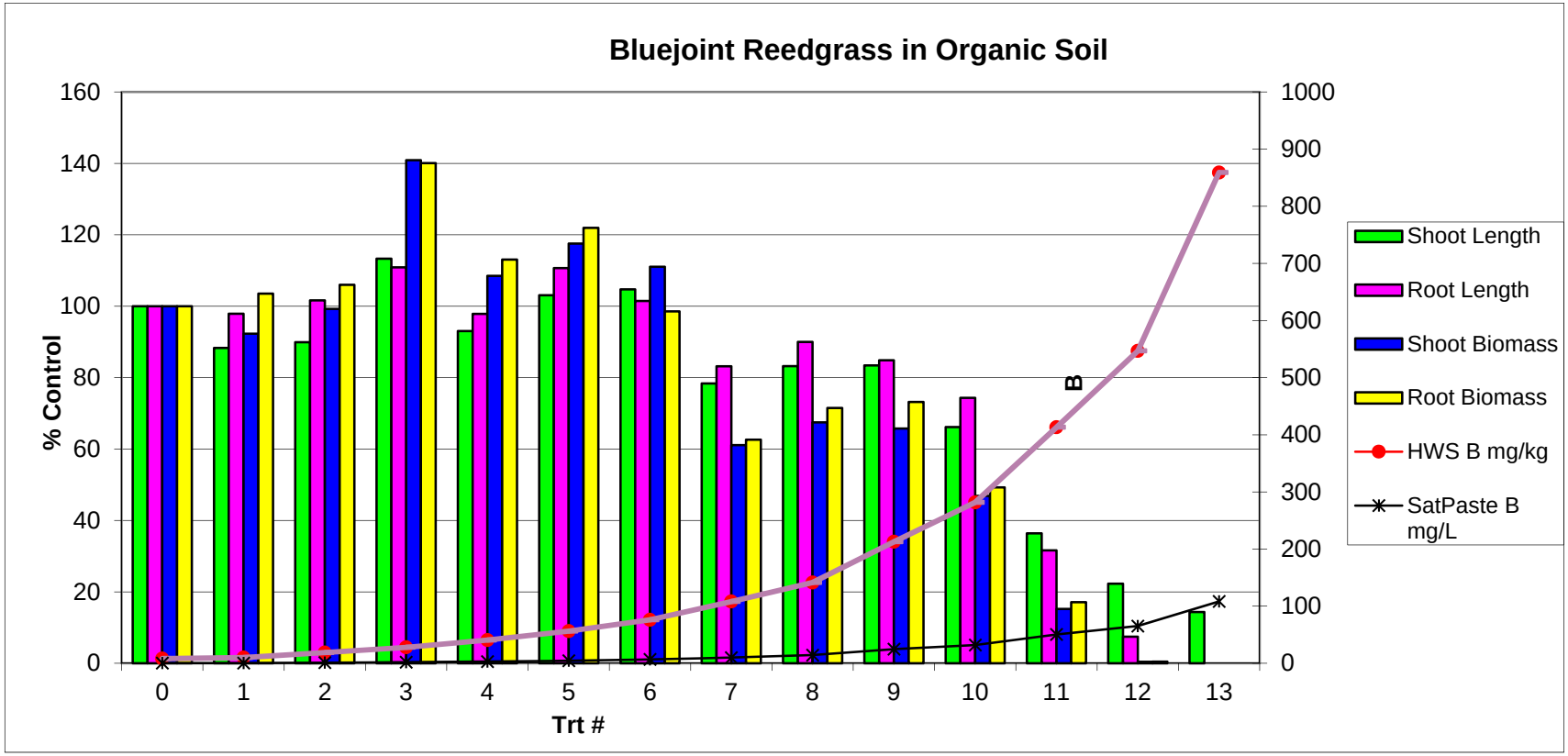
Bluejoint Reedgrass in Organic Soil



1	2	3	4	5	6	7	**8**	9	10	11	12	13	
9.9	19	28	41	56	76	108	**141**	213	282	413	547	859	HWS B mg/kg
0.2	0.5	0.8	1.4	2.3	4.6	8.2	**15**	28	32	50	65	108	Satpaste B mg/L

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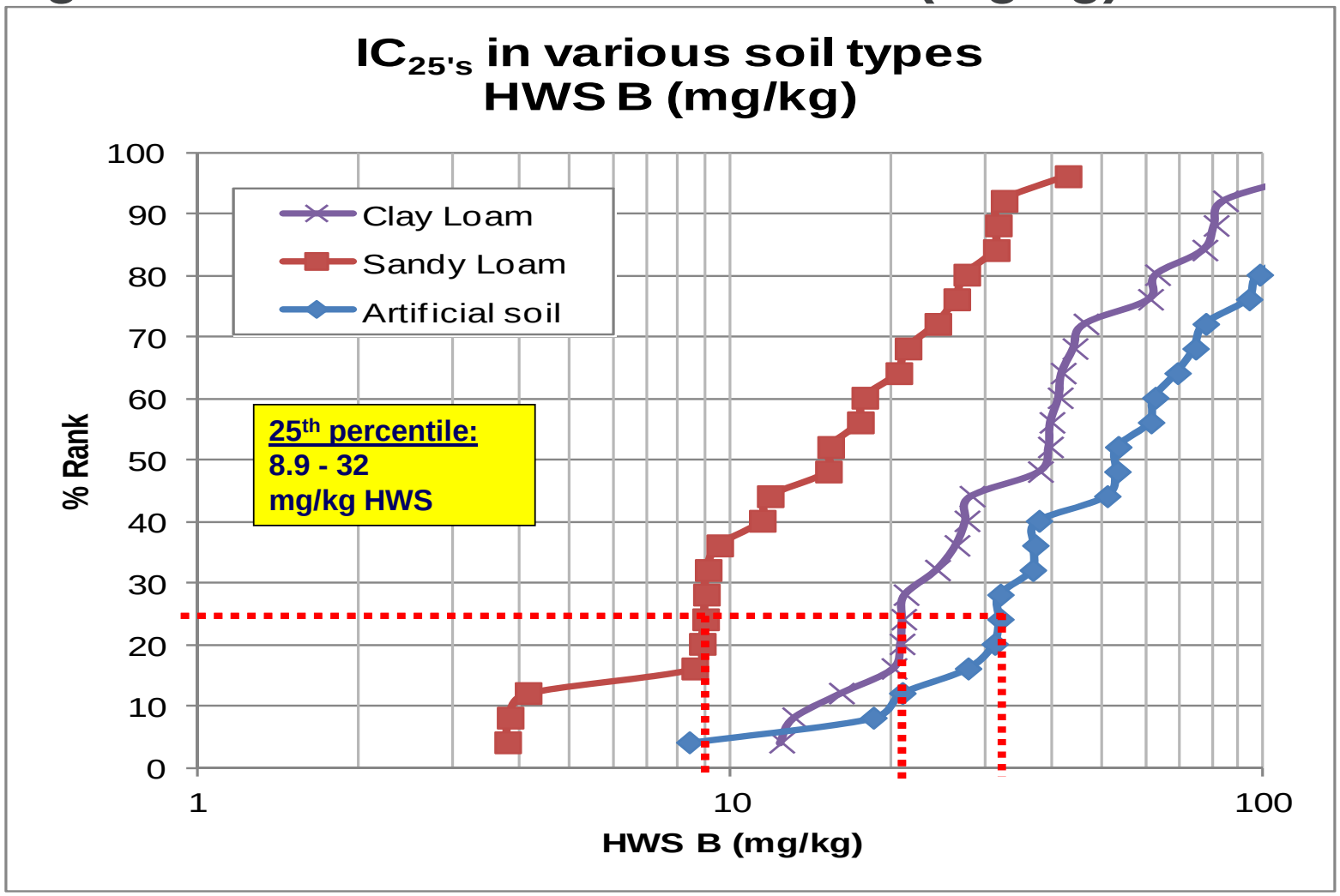
Agricultural Plant SSDs – HWS B (mg/kg)



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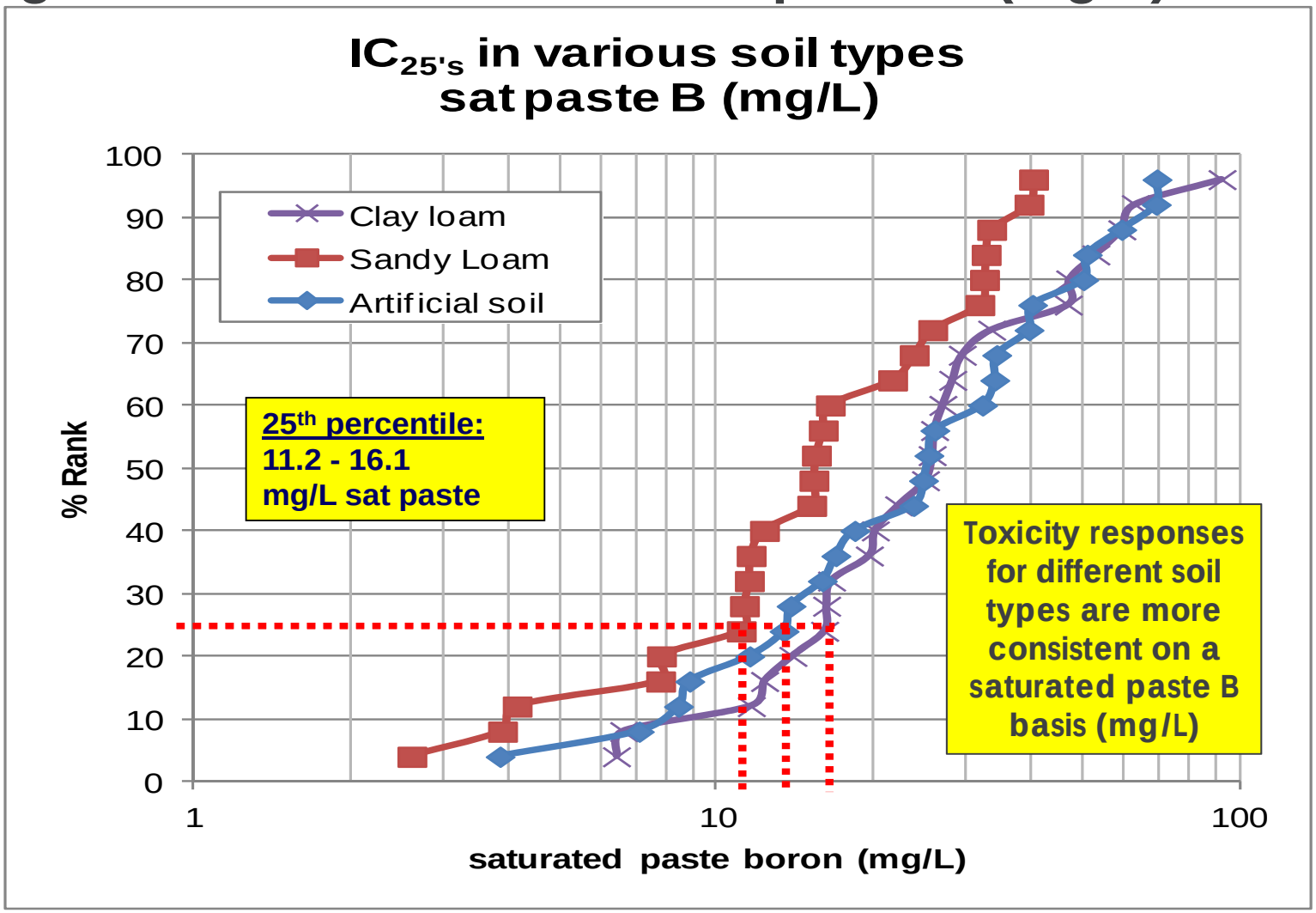
Agricultural Plant SSDs – Satpaste B (mg/L)



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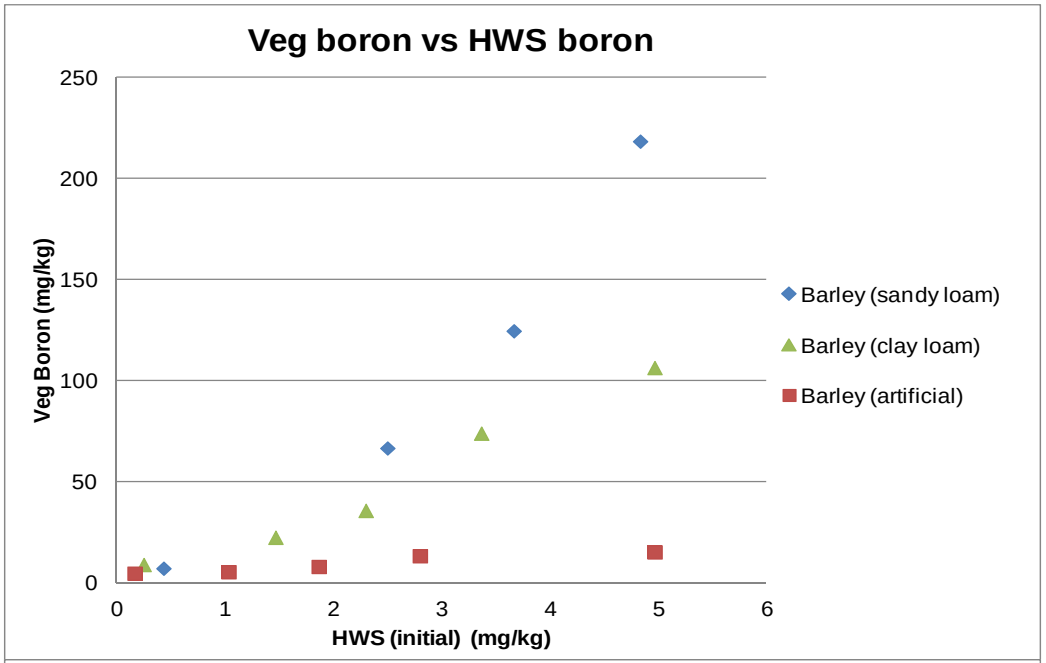
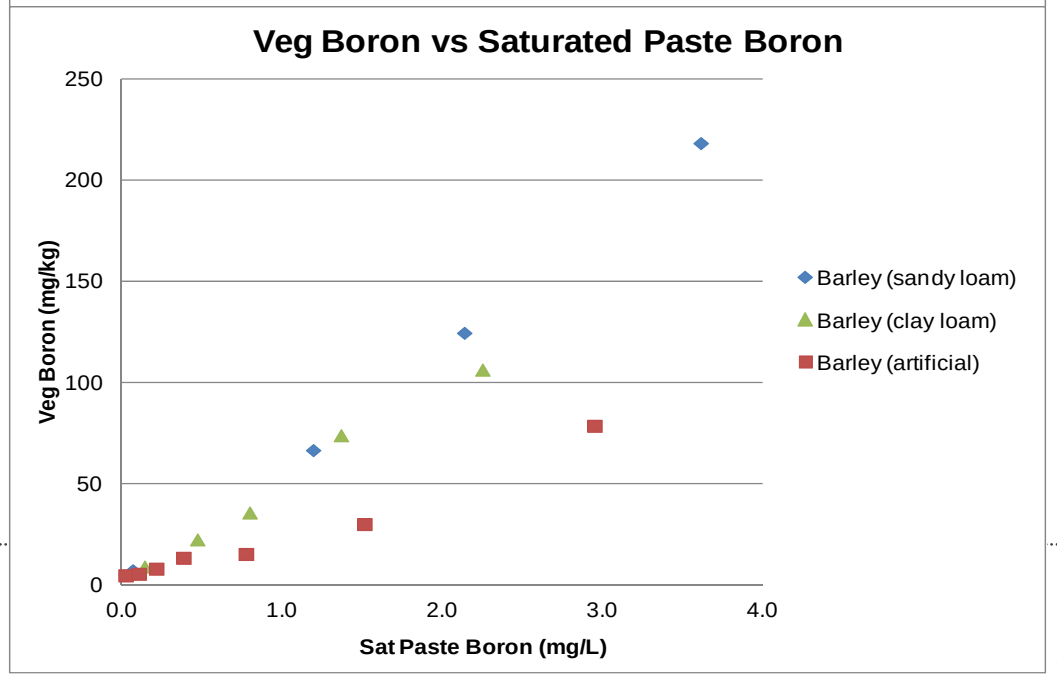
Vegetation boron

- Soil texture also influences plant boron uptake
- For a given HWS, most boron taken up by plants in sandy loam, least taken up in artificial soil
- Differences in soil type reduced when using saturated paste boron (mg/L)
- Lower BCFs (bioconcentration factors) in roots than shoots





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Cucumber Long-Term Growth Test

- 3 month test in clay loam
- Non-Standardized methodology
- Good growth and flowering in all treatments except high doses
- No root data obtainable
- Shoot biomass IC_{25} = 4.53 mg/L SP B
- Shoot length IC_{25} = 3.79 mg/L SP B
- Similar range of toxicity results to short-term test

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Earthworm Survival and Reproduction

- Earthworms exposed to boron in coarse sandy loam (13 treatments, 12 reps)
- 63 days exposure, measure adult survival, number of juveniles per adult and juvenile mass (growth).
- Juvenile # IC_{25} = 5.4 mg/L satpaste B
- Juvenile mass IC_{25} = 26.4 mg/L satpaste B
- High natural variability in reproductive endpoints; responsive to soil texture.

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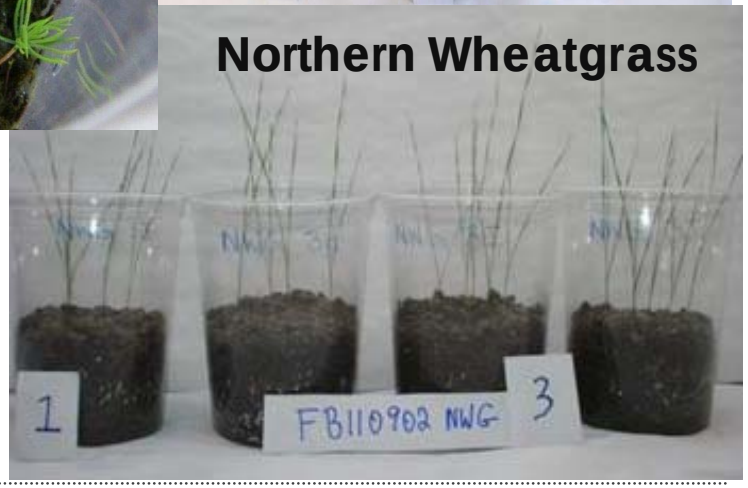
Summary

- HWS B not a good predictor of plant toxicity over different soil types
- HWS B measures primarily sorbed boron, with boron sorbed on clay and organic matter not directly toxic to plants
- Saturated paste B (mg/L) better correlated to soil solution B, plant toxicity response, and boron tissue uptake, regardless of soil characteristics
- Boreal species similar sensitivity to agricultural species;
  - cucumber, carrot, jack pine: sensitive
  - barley, alfalfa, white spruce: least sensitive
- Good growth often observed well above the current Tier 1 guideline of 2 mg/kg HWS boron, often into 4-10 mg/kg range or higher
- Growth stimulation for some species (2 to 4 mg/L SP B)
- IC_{25}s Agricultural: 3.2 – 53.0 mg/L; boreal: 1.6 – 29.4 mg/L
- This plant toxicity data can be combined with literature data and invert data to create overall eco-contact guideline (presentation #2)



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