

Simulating Disaster: A Study on the Effects of Heavy Metal Ions on the Flammability of White Spruce Trees

Elise Dimmell, Kara Bjornson, Stefania Mic, Mackenzie Paul, Bronwyn Contini, Sophie Chasse, Jared Assen, Caleb Assen, Tyler Meckelborg, Edward Kosloski, Anna-Maria Boechler, Jay Maillet



Introduction

The devastating 2016 Fort McMurray wildfire prompted our research group to explore possible links between heavy metal ions in the soil and the flammability of white spruce trees, common to the entire boreal forest.

- Heavy metal ions like copper(II), zinc, lead(II), and manganese(II), can affect a plants production of higher energy compounds like terpenoids^{1,2} and are found in oil sands and Fort McMurray area soils and water^{3,4}.
- Leaf litter burn tests have associated higher terpene content with increased fire spread rate and decreased combustion time.⁵

Research Question:

Do heavy metal nitrates affect tree flammability?

The Process

Tree Growth and Storage:

- White spruce (*Picea glauca*) seedlings from Water Valley Forest Nursery (near Cremona, AB) were potted in identical potting soil to grow in an indoor light controlled environment.



Watering Solution / Test Group (all aqueous nitrates)	Stock ion conc. (g/L)
Tap water (Control)	0
Cu ²⁺	0.060
Zn ²⁺	0.170
Pb ²⁺	0.140
Mn ²⁺	8.00

- From toxicological data, 'low' and 'high' concentration trees received 5.0 mL or 10.0 mL respectively of nitrate ion solution diluted to 50.0mL tap water.^{4,6}
- The first spiked trees died due to a combination of an accidental high ambient temperature and lack of water. A second set was restarted and used.

- Trees were grown for six months then cooled from 21°C to 4°C over 4 days. Each was then individually sealed in a plastic bag and frozen at -20°C. This helped dehydrate and preserve the specimens and volatile terpenes.

Sample Preparation:

- After 5 months frozen, each tree was placed on a separate aluminum tray and dried at 40°C over 10 days. The temperature was kept low to reduce volatile terpene loss.

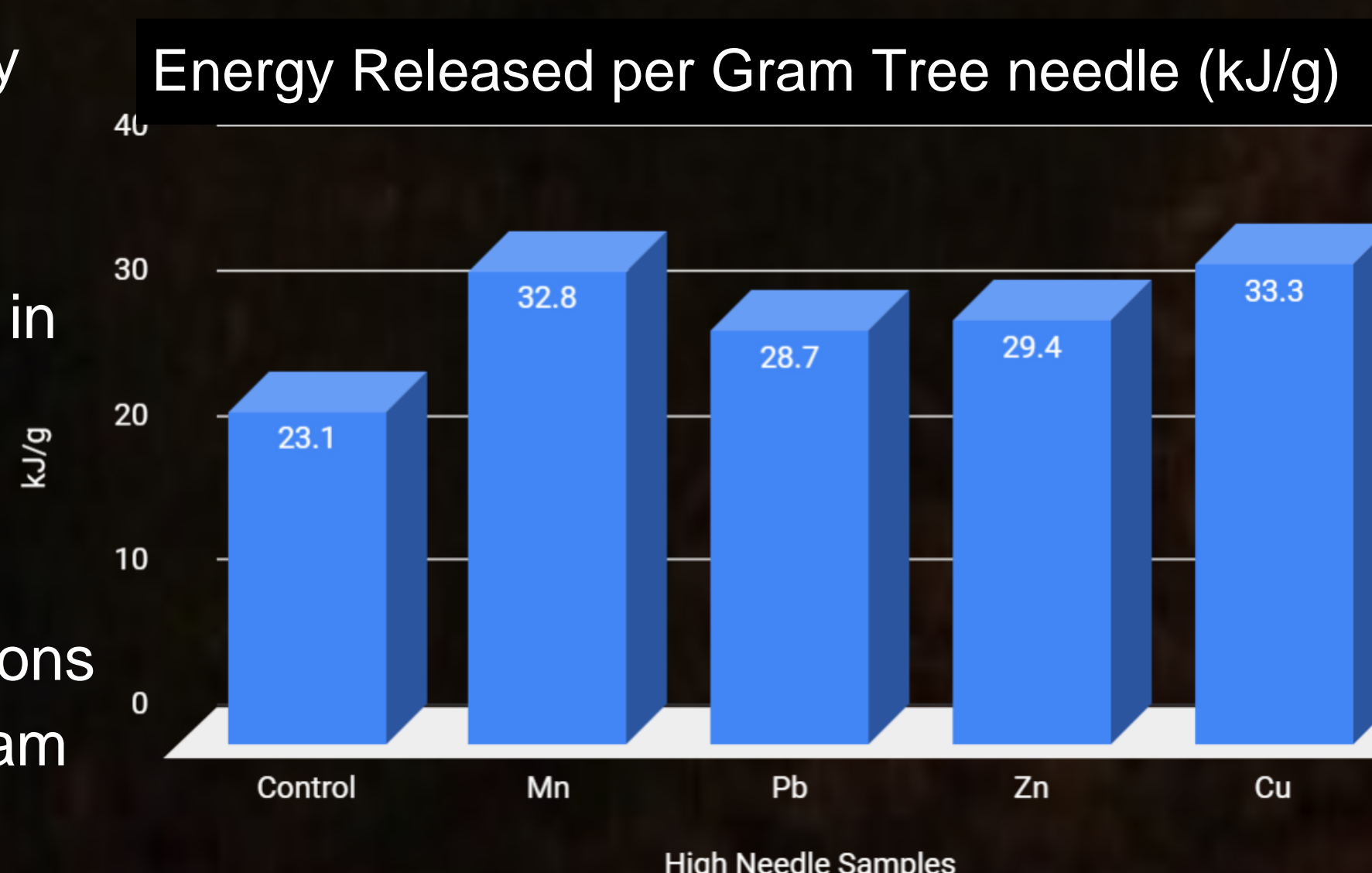


- Each tree's needles, stems and roots were separately bagged.
- Mount Royal University calorimetry samples were ground in a mortar and pestle. Whole pieces were brought to the Canadian Light Source (CLS).

Bomb Calorimetry Findings

In bomb calorimetry, a sample is combusted in a sealed metal vessel filled with O₂(g), the bomb, and placed in a thermally insulated vessel containing water. The energy transferred to heat the components is calculated.

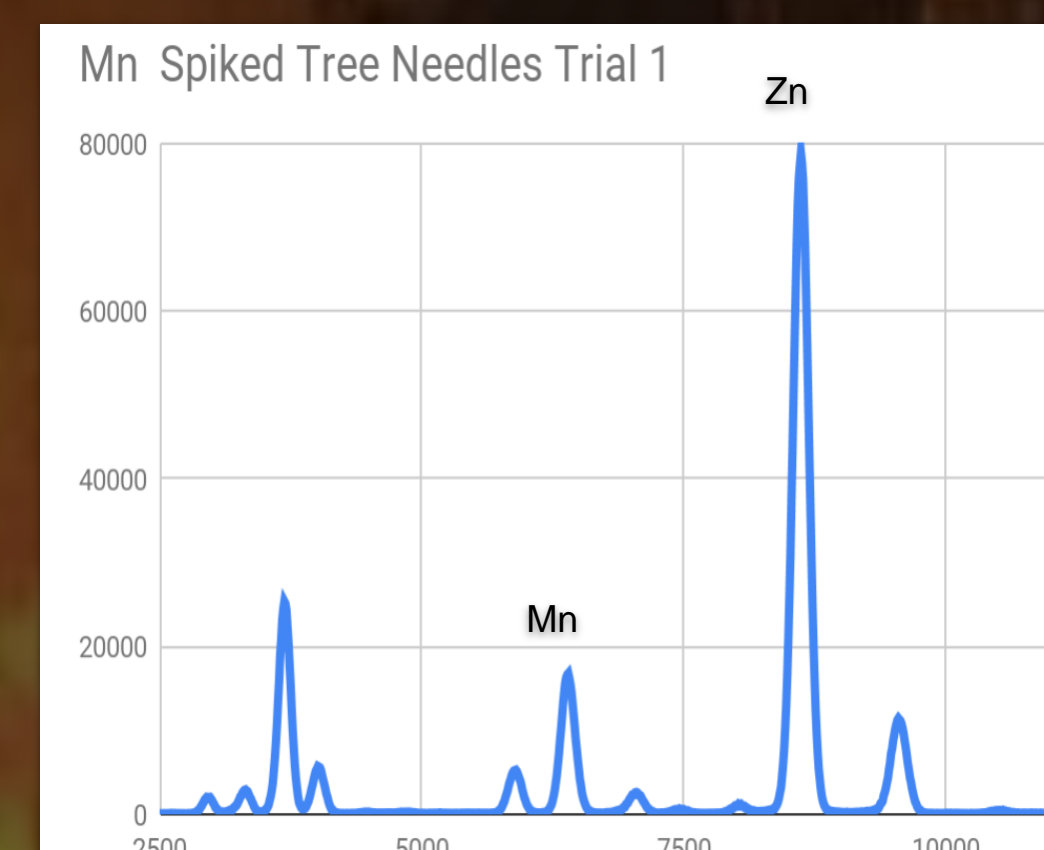
- At Mount Royal University (Calgary, AB), needle samples were put into capsules and combusted in the calorimeter.
- Samples from all trees spiked with heavy metal ions released more energy/gram than the control.



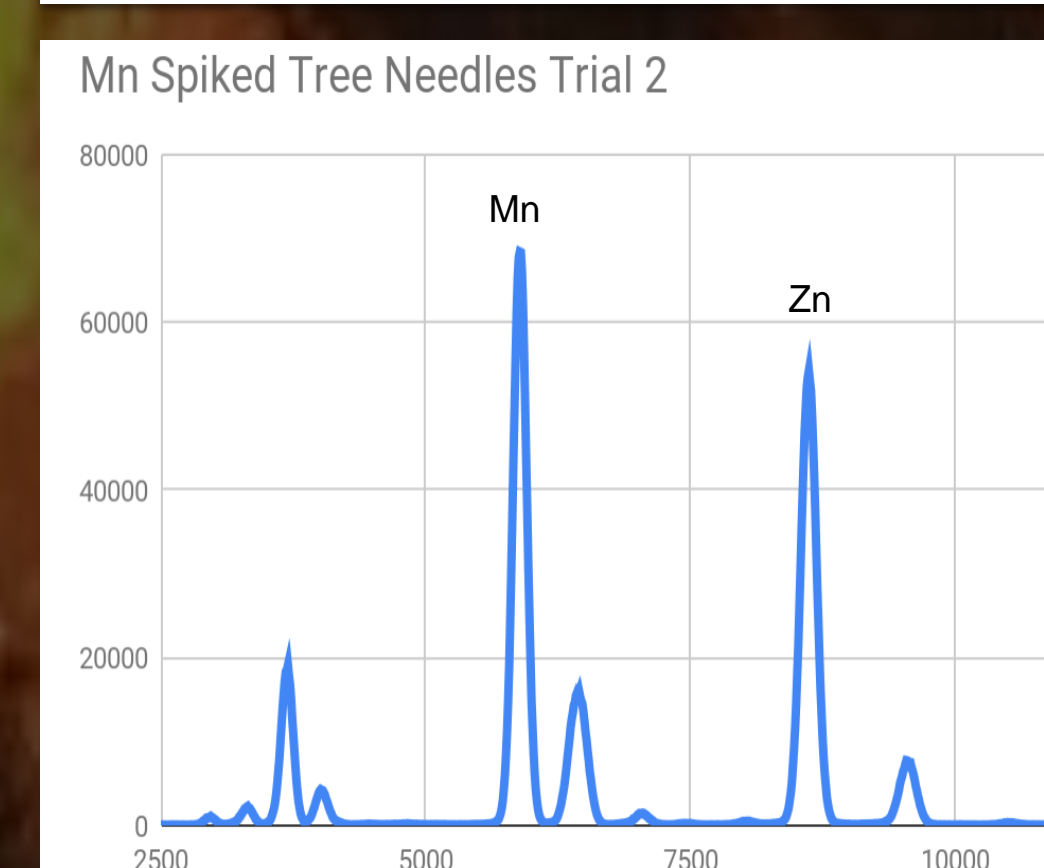
X-Ray Fluorescence (XRF) Findings

XRF on the CLS IDEAS beamline was used to determine metal ion composition in the samples. In XRF, x-rays strike the sample, exciting and dislodging low energy level electrons. To fill the space created, an electron in a higher energy level drops down, releasing energy in the form of a photon, unique to each metal, which is detected.

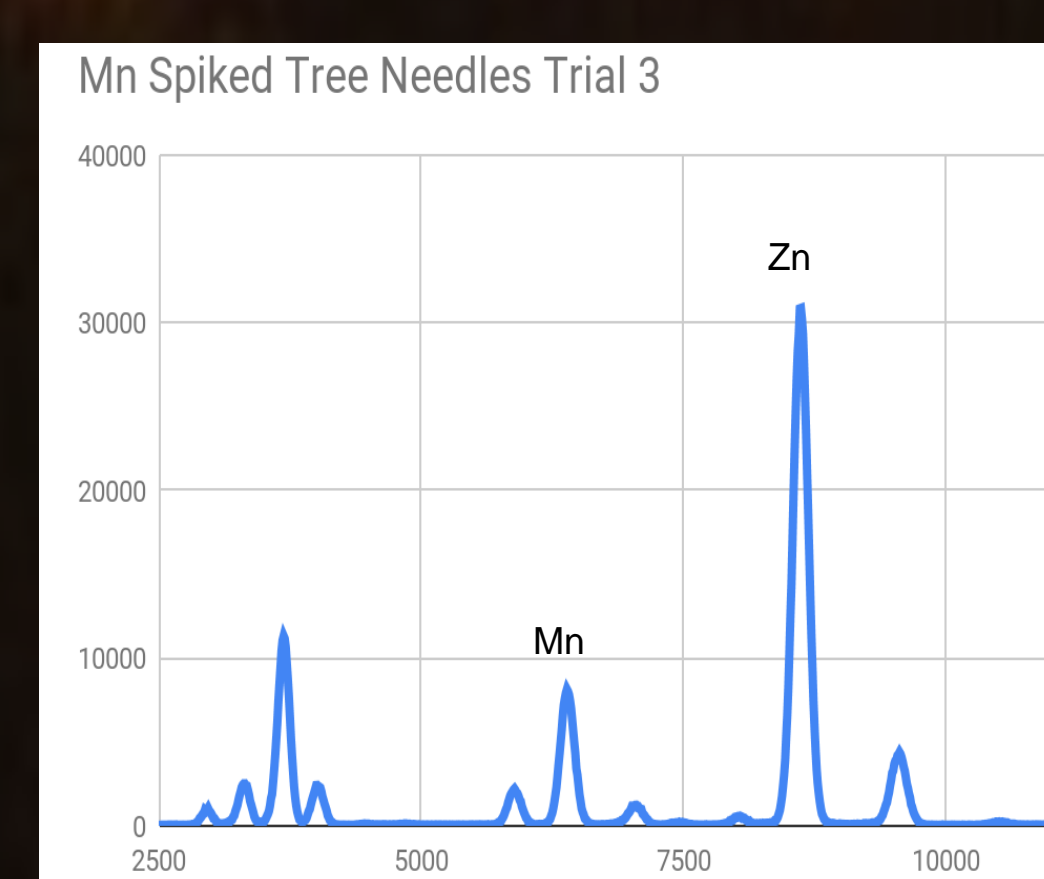
1. Mn spiked tree needles were found to contain a high presence of Zn.



- The first trial found a relatively high presence of Zn in the sample of tree spiked with Mn.
- To confirm the unexpected result, a test of a second new sample was run.

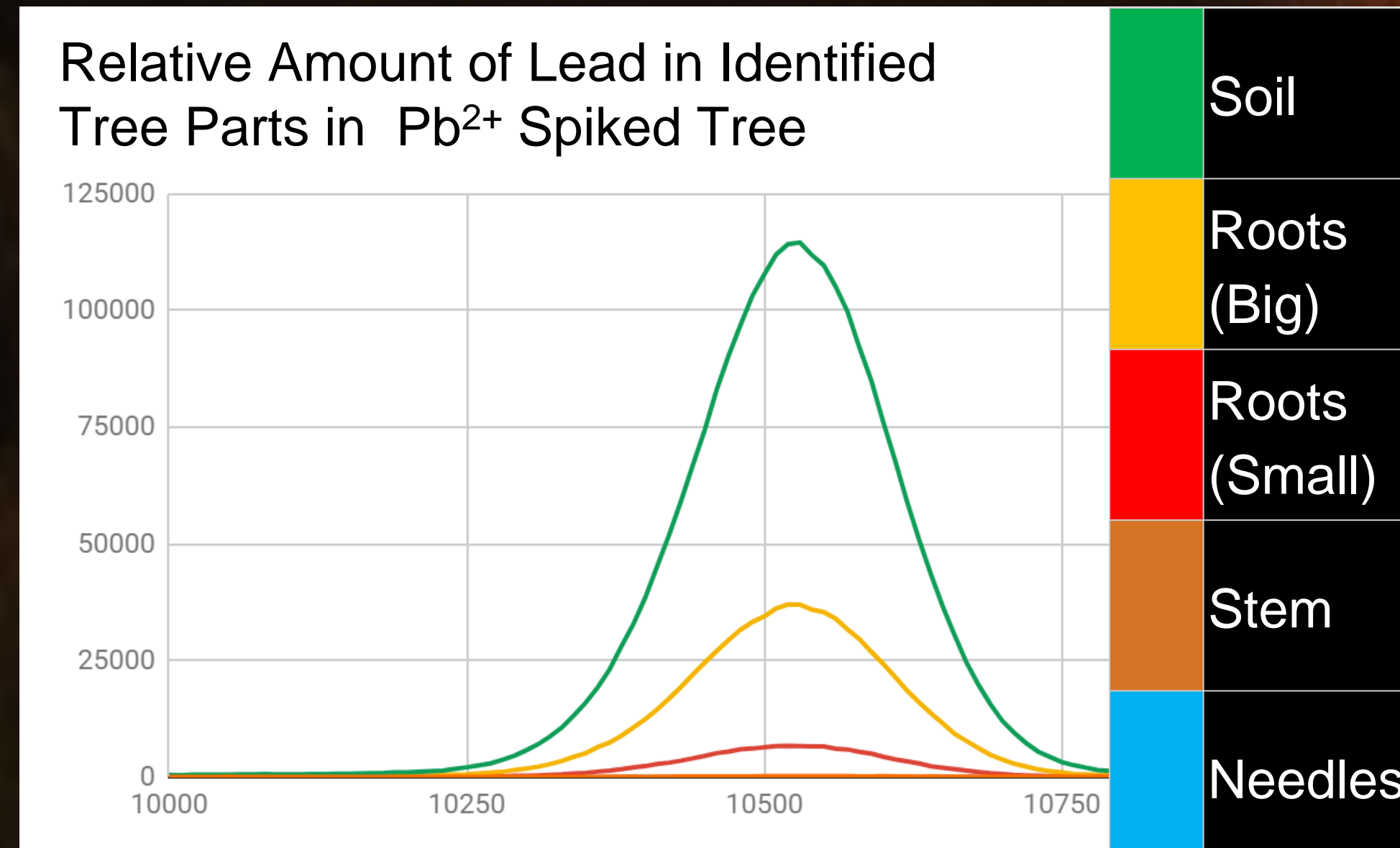


- A new sample found high Mn and Zn.
- Due to the discrepancies, multiple scans on the new sample were done.



- Inspecting the specimens, compared to the first sample which had old needles, we could also see new growth needles on the second sample.
- Interestingly, new growth needles may have been scanned and the source of the relatively high Mn.

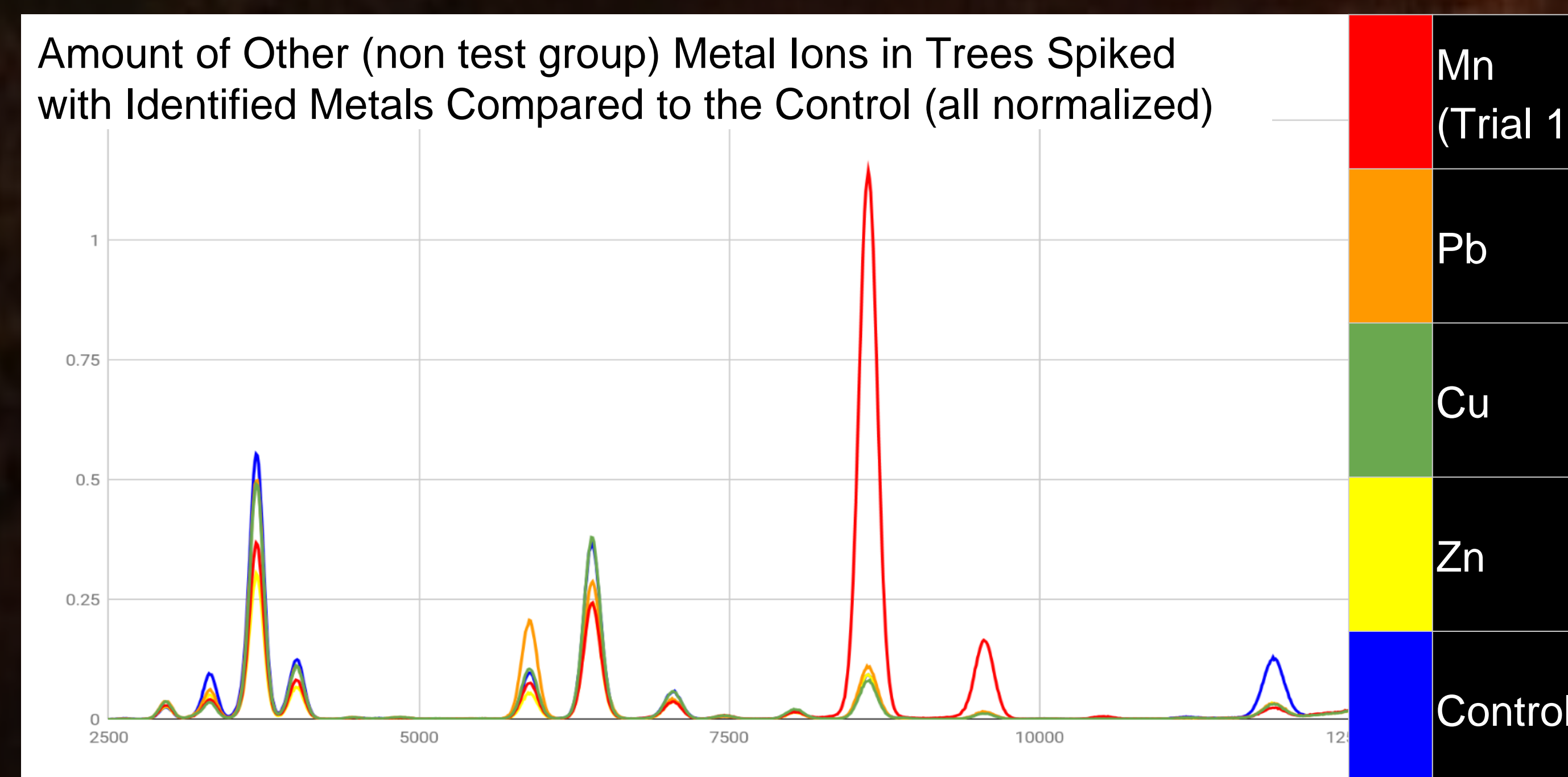
2. Most metals were uptaken into the roots but did not go further into the tree.



- Tracking the presence of a metal through an entire tree of that group shows a relatively high amount in the soil (green) then less in the roots and almost none, at this scale, in the stem and needles.

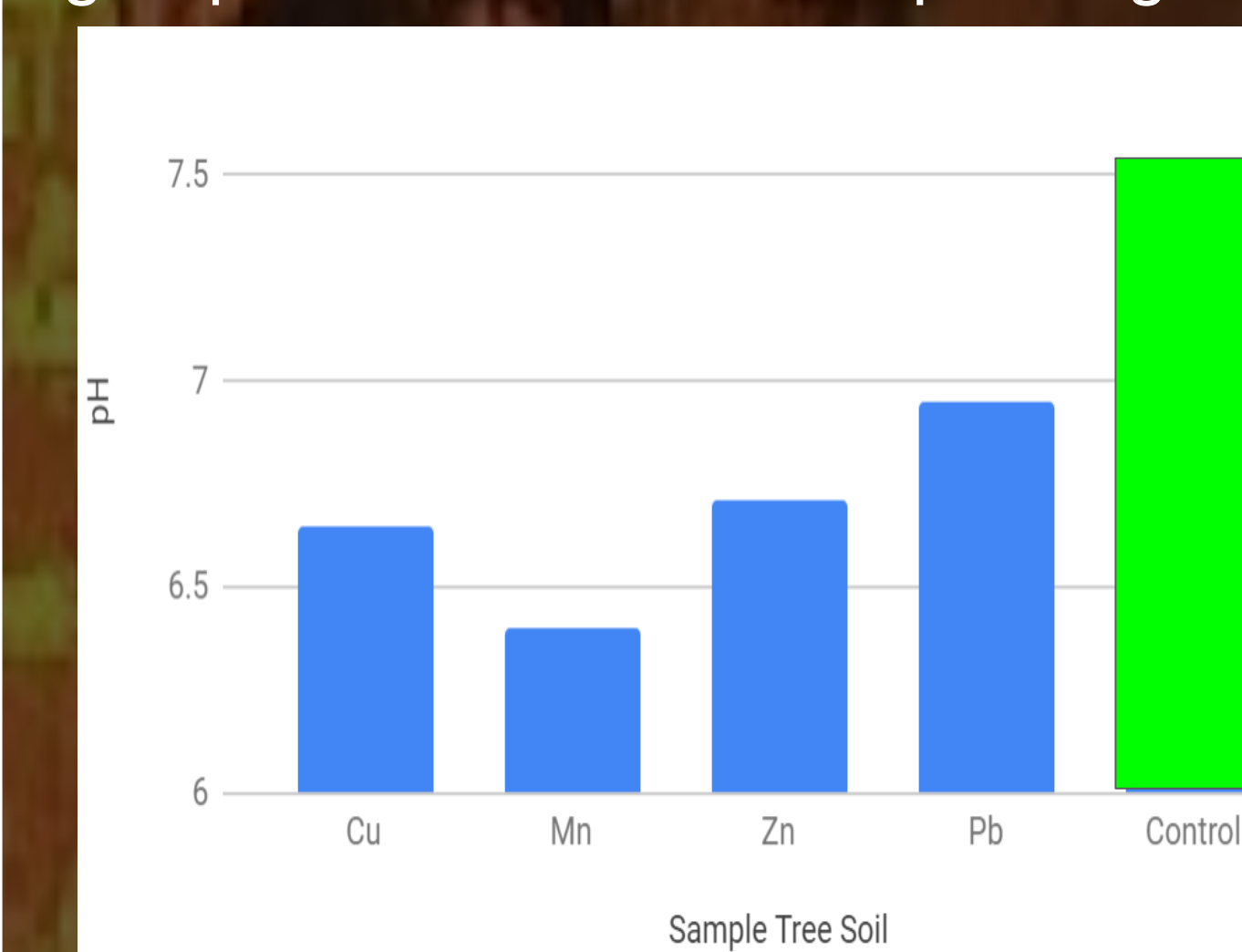
3. Trees spiked with test metal ions had, in their needles, a change in the amounts of other, non-test, metal ions. Compared to the control, needles of spiked trees had:

- a relative decrease of calcium, iron, and bromine.
- an increase in the relative amount of zinc.
- no noticeable change in the relative amount copper.
- a decrease in manganese in half the samples.



Soil pH Findings

The pH of the soil decreased in the heavy metal nitrate spiked watering groups but still fell within optimal guidelines for soil pH.⁷



- Other research has found that a slightly acidic soil pH results in an increase in the production higher energy compounds, such as terpenes, within the trees.²
- This may explain why the spiked needle samples had a greater energy per gram than the control needles.

Overall Findings

Our data suggests that the introduction into the soil of some heavy metal nitrates, such as Cu²⁺, Zn²⁺, Pb²⁺, and Mn²⁺, increases the calorimetric energy content of white spruce trees. This may, in turn, intensify tree and associated forest flammability.

The presence of some metal ion nitrates in the soil are associated with a reduction in soil pH and a reduction in the relative amount of some metabolically important metals such as calcium, iron, and bromine, and an increase in zinc in the tree. These changes in turn could be linked to the differences in energy content within the needles of the trees.

Future Research

We would like to examine how soil pH influences the uptake of micronutrients and macronutrients and how this affects the degree of uptake of heavy metals in the tree as tissues age. We would also like to investigate the relationship between manganese and zinc in the needles. Researching the effect of high energy terpenes on the uptake of heavy metals in the tree would also be interesting in order to further examine the effect of terpenes on live tree flammability.

References

- 1 Werner, A., Napierala-Filipiak, A., Mardarowicz, M., Gawdzik, J.. (2004). The effects of heavy metals, content of nutrients and inoculation with mycorrhizal fungi on the level of terpenoids in roots of *Pinus sylvestris* seedlings. *ACTA PHYSIOLOGIAE PLANTARUM*, Vol. 26. No. 2.: 187-196
- 2 Khan, M.T.H.. (2007). *Bioactive Heterocycles III, vol.9*. Springer-Verlag. 1861-9282, doi: 10.1007/978-3-540-73402-4
- 3 J. V. Headley , B. Crosley , F. M. Conly & E. K. Quagraine. (2005). The Characterization and Distribution of Inorganic Chemicals in Tributary Waters of the Lower Athabasca River, Oil Sands Region, Canada, *Journal of Environmental Science and Health*, 40:1, 1-27, DOI: 10.1081/ESE-200033418
- 4 Alberta Government. (2016). Burned and Unburned Soil Samples Metals Result; 16-00222; July 28, 2016. *Alberta Health Horse River Fire Response – Fort McMurray and Anzac, RMWB*.
- 5 Ormen, E., Cespedes, B., Sanchez, I.A., Velasco-Garcia, A., Moreno, J.M., Fernandez, C., Baldy, V.. (2009). The relationship between terpenes and flammability of leaf litter. *Forest Ecology and Management*. Elsevier. 257, 471–482
- 6 Reichman, S.M.. (2002). The Responses of Plants to Metal Toxicity: A review focusing on Copper, Manganese and Zinc. *Australian Minerals & Energy Environment Foundation*. Paper No.14. 1-876205-13-X
- 7 Australian Society of Plant Scientists, New Zealand Society of Plant Biologists, and New Zealand Institute of Agricultural and Horticultural Science. (2018). *Plants in Action - Adaptation in Nature, Performance in Cultivation, Edition 2*. <http://plantsinaction.science.uq.edu.au>.

Acknowledgements

A special thank you to the following for their support during this research:

- Water Valley Forest Nursery and Greenhouses
- Anna-Maria Boechler (CSL)
- Jay Maillet (U of S)
- Dr. Chris Lovallo (MRU)
- Dr. David Muir (CLS)
- Edward Kosloski
- Shannon Dougall

