Differences in Phytotoxicity and Dissipation Between Ionized & Unionized Oil Sands Naphthenic Acids

Sarah Armstrong

Western Canada Trace Organic Workshop - Calgary

April 24, 2007

John Headley – Environment Canada

Kerry Peru – Environment Canada

Jim Germida – Dept Soil Science, U of S

Environment Canada Environnement Canada

Oil Sands

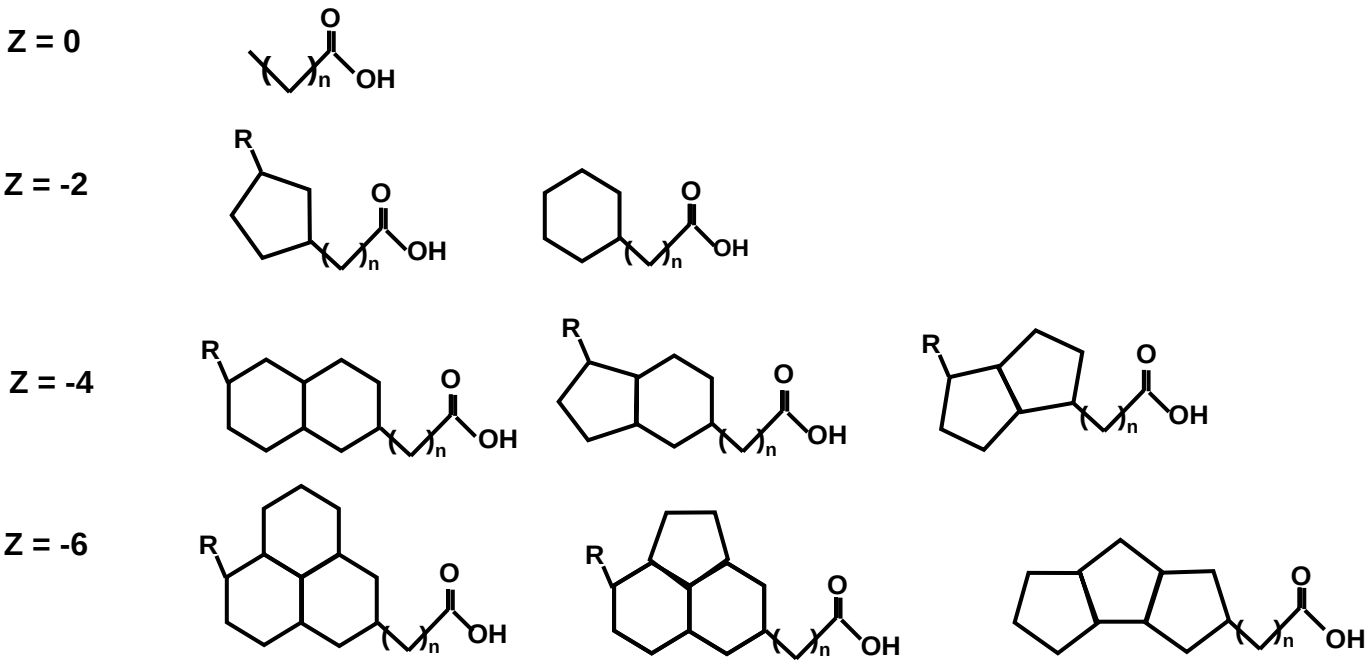
- Alberta's oil sands contains est. 1.7 – 2.5 trillion barrels of oil

- 39% of Canada's crude oil production

- 966,000 barrels/day (2005) and expected to rise to 3 million barrels/day by 2020

Naphthenic Acids

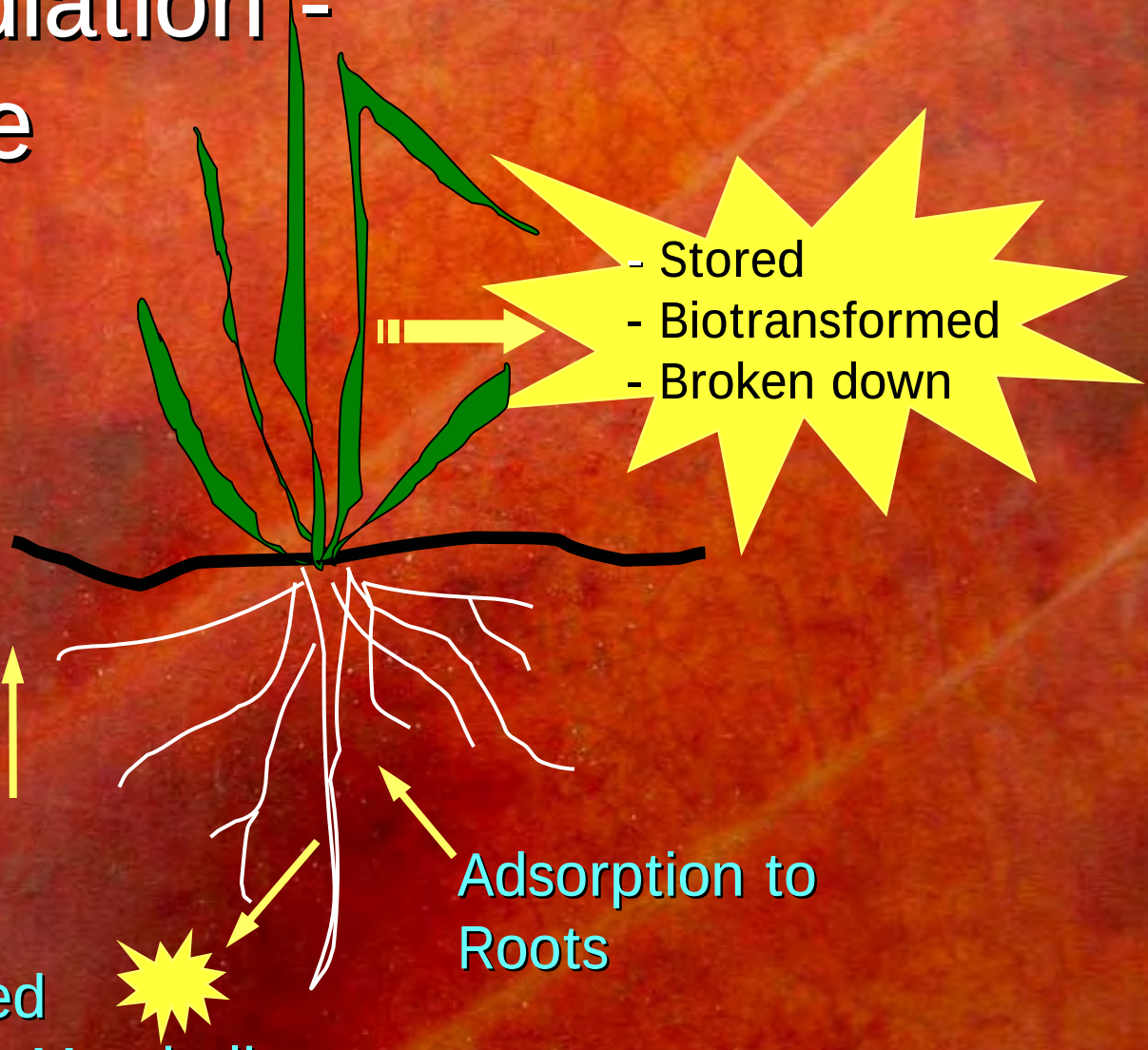
- Mixture of mono- and poly-cycloalkane carboxylic acids with aliphatic side chains of various lengths
- 96 hour LC_{50} 5.6 - 75 mg L^{-1} fish



Research Objective

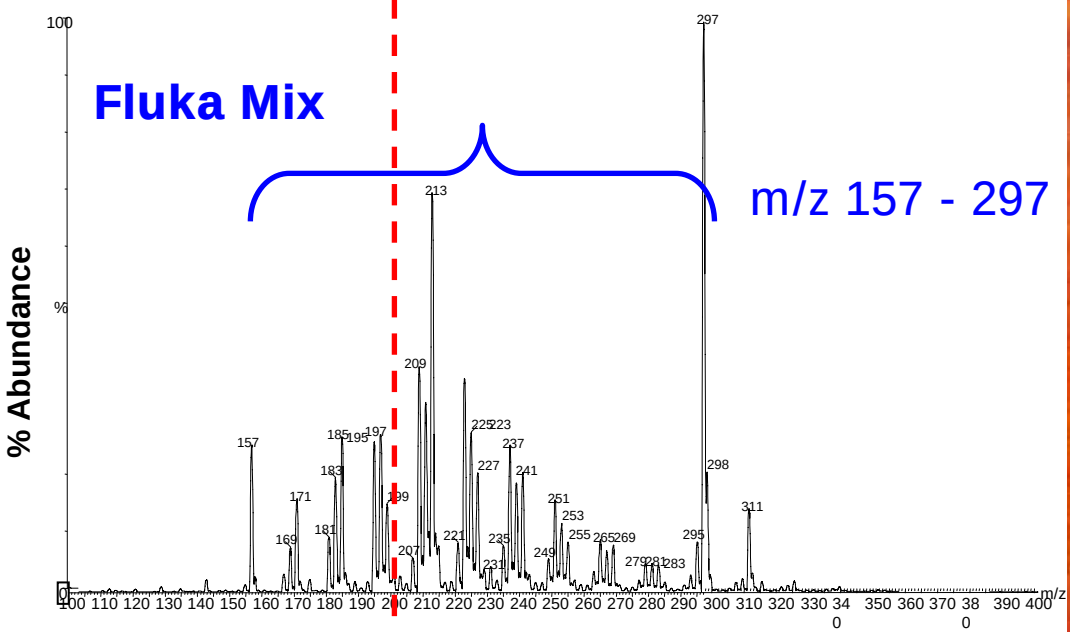
To determine if wetland plants are capable of phytoremediating NAs from contaminated water

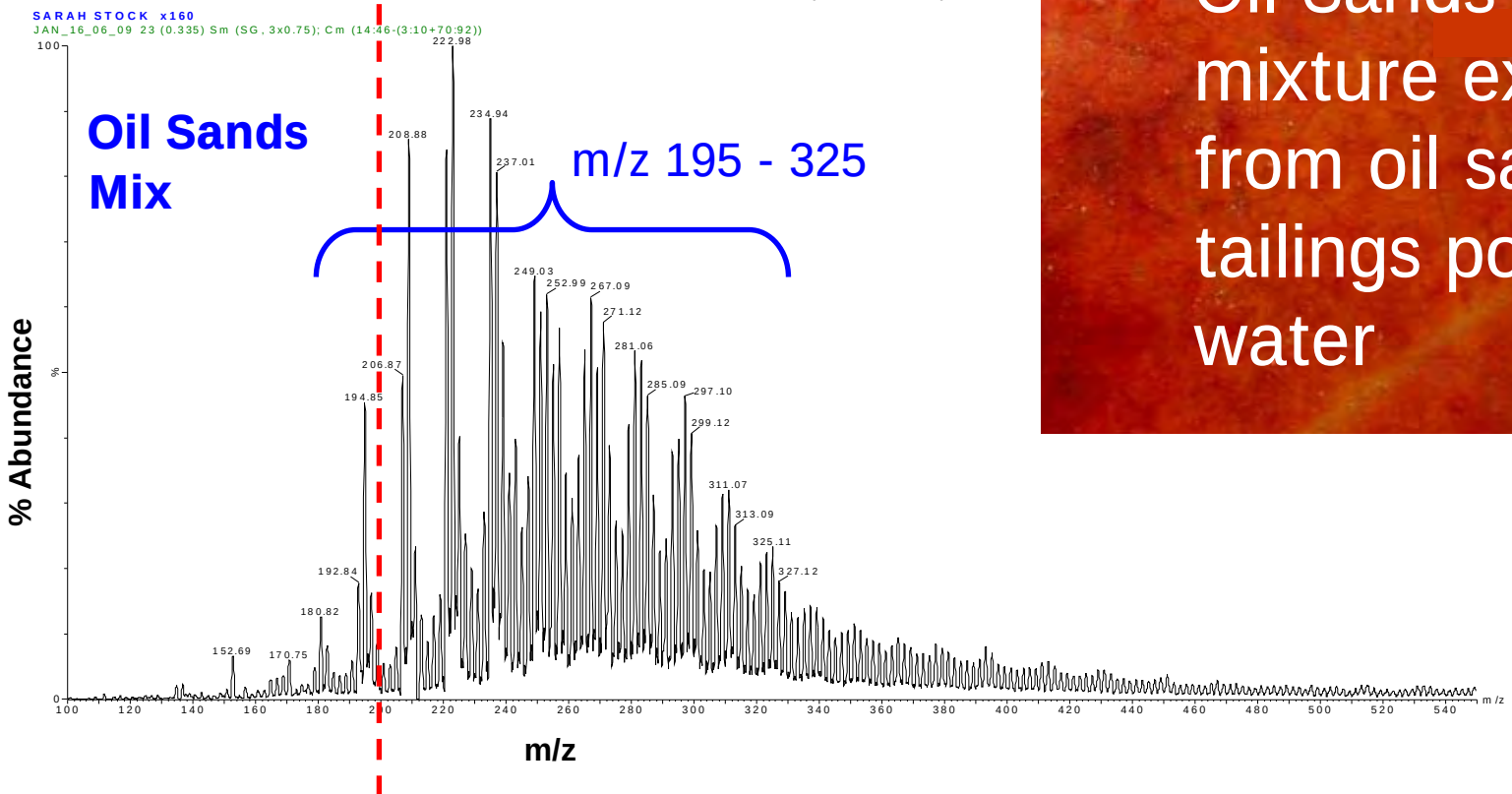
Phytoremediation - Not just one process!



Where to Begin?

- What happens to NAs and plants in a hydroponic system?
  - Monitor concentration in the hydroponic nutrient medium over time
  - Determine phytotoxic effects in the plants by monitoring transpiration and growth over time

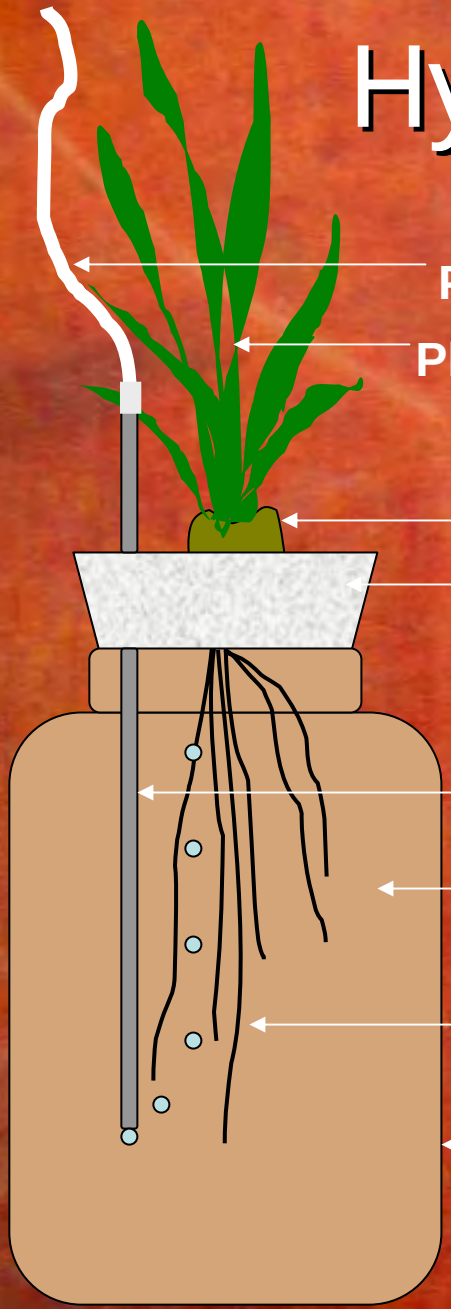




Not all NA mixes are the same!

- Fluka NA mixture commercially available
- Oil Sands NA mixture extracted from oil sands tailings pond water

Hydroponic Test Systems



Plastic Aeration Tube

Plant Shoot

Plant Rhizome

Foam plug to support plant rhizome and aeration tube

Glass Aeration Tube

¼ Strength Hoagland's Nutrient Medium (2.5 L)

Plant Roots

2.5 L Amber Glass Bottle (covered with aluminum foil)

Wetland Species

Cattail (*Typha latifolia*)

- Emergent native macrophyte
- Common, prolific, easy to grow and transplant
- Extensive root system
- Can cover large areas
- High transpiration rate

Common Reed Grass
(*Phragmites australis*)

Hard-stem Bulrush
(*Scirpus lacustris*)

Experimental Design

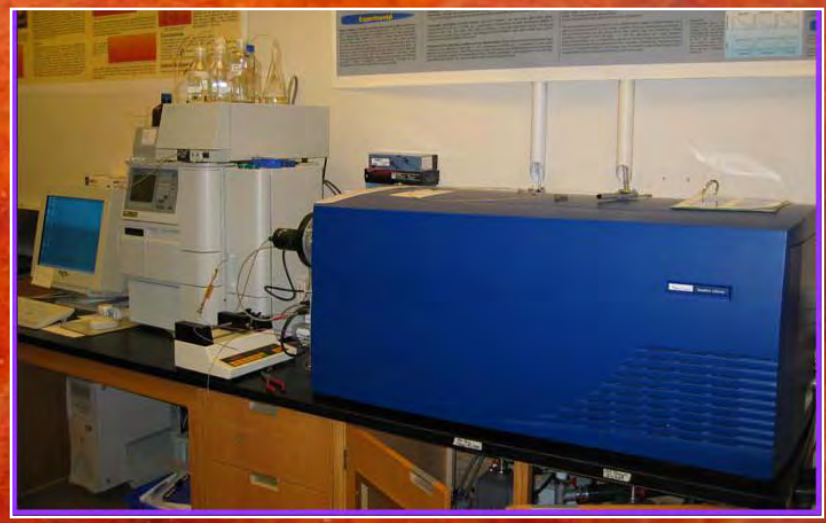
Treatment	Nominal Dose	Purpose
Abiotic Unplanted Control	Unplanted + 60 mg L^{-1} + sodium azide	NA losses due to the experimental set up
Biotic Unplanted Control	Unplanted + 60 mg L^{-1}	NA losses due to natural establishment of microorganisms
Planted Control	Planted + 0 mg L^{-1}	Background MS signal produced by media and plants and toxicity control
Planted Low Dose	Planted + 30 mg L^{-1}	NA uptake and toxicity under low exposures
Planted High Dose	Planted + 60 mg L^{-1}	NA uptake and toxicity under high exposures

Experimental Details

- Collected media samples Day 0, 5, 10, 20, 30
- Adjusted pH every 5 days and recorded media loss (transpiration)
- Plant fresh weight (Day 0 and Day 30)

Analytical Analysis

- Mass spectrometry with electrospray operating in negative ion mode
- Loop injection
- External standard method

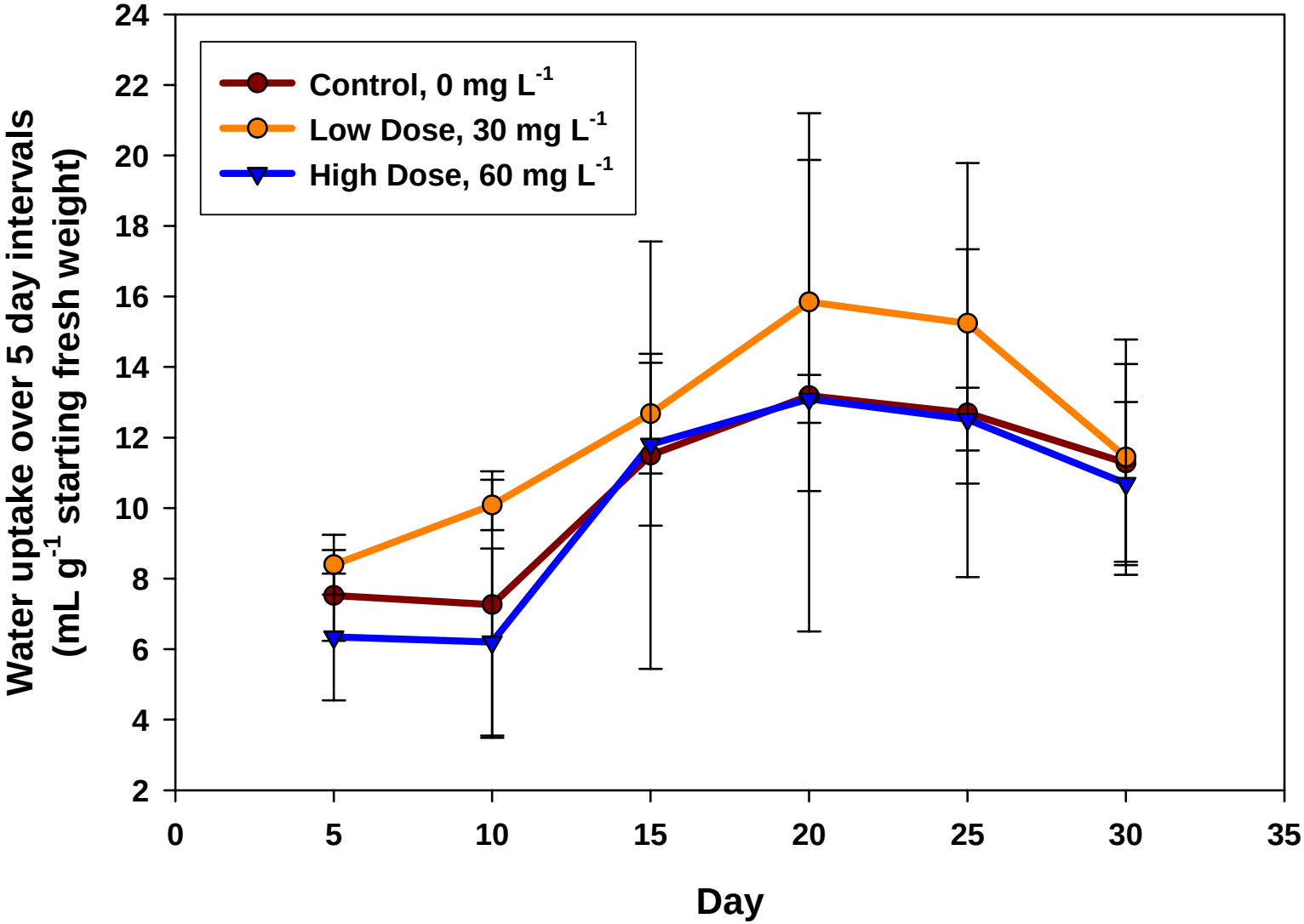


- Prior to analysis all samples were cleaned up using solid phase extraction (SPE)
- Removes background ions for better analysis

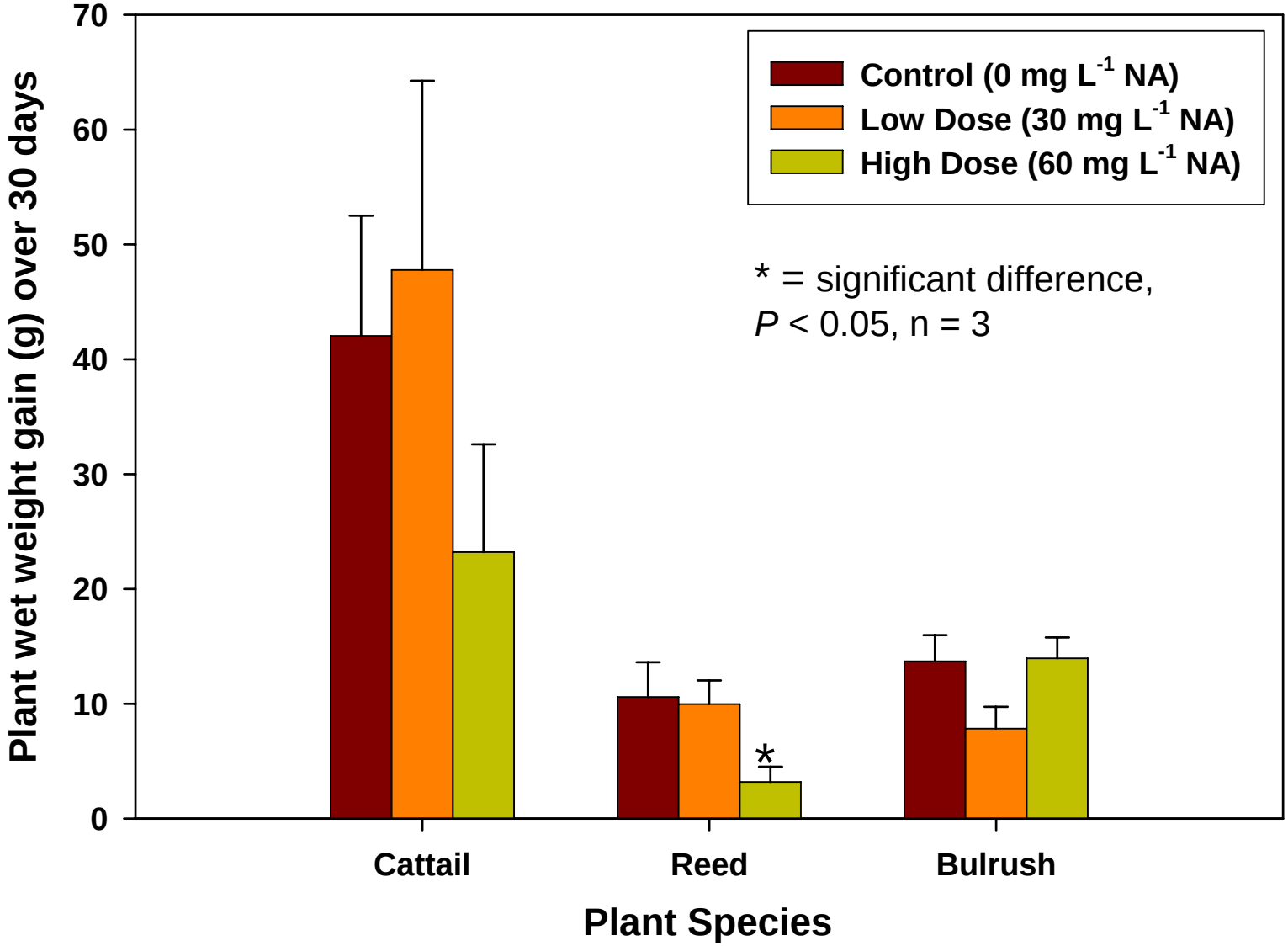
Hydroponic Experiments

1. Medium at pH = 7.8	**2. Medium at pH = 5.0**
-NAs ionized (polar) -Water soluble -Alkaline conditions similar to tailings ponds	-NAs unionized (non-polar, lipid soluble) -Acidic aquatic environments (bogs)

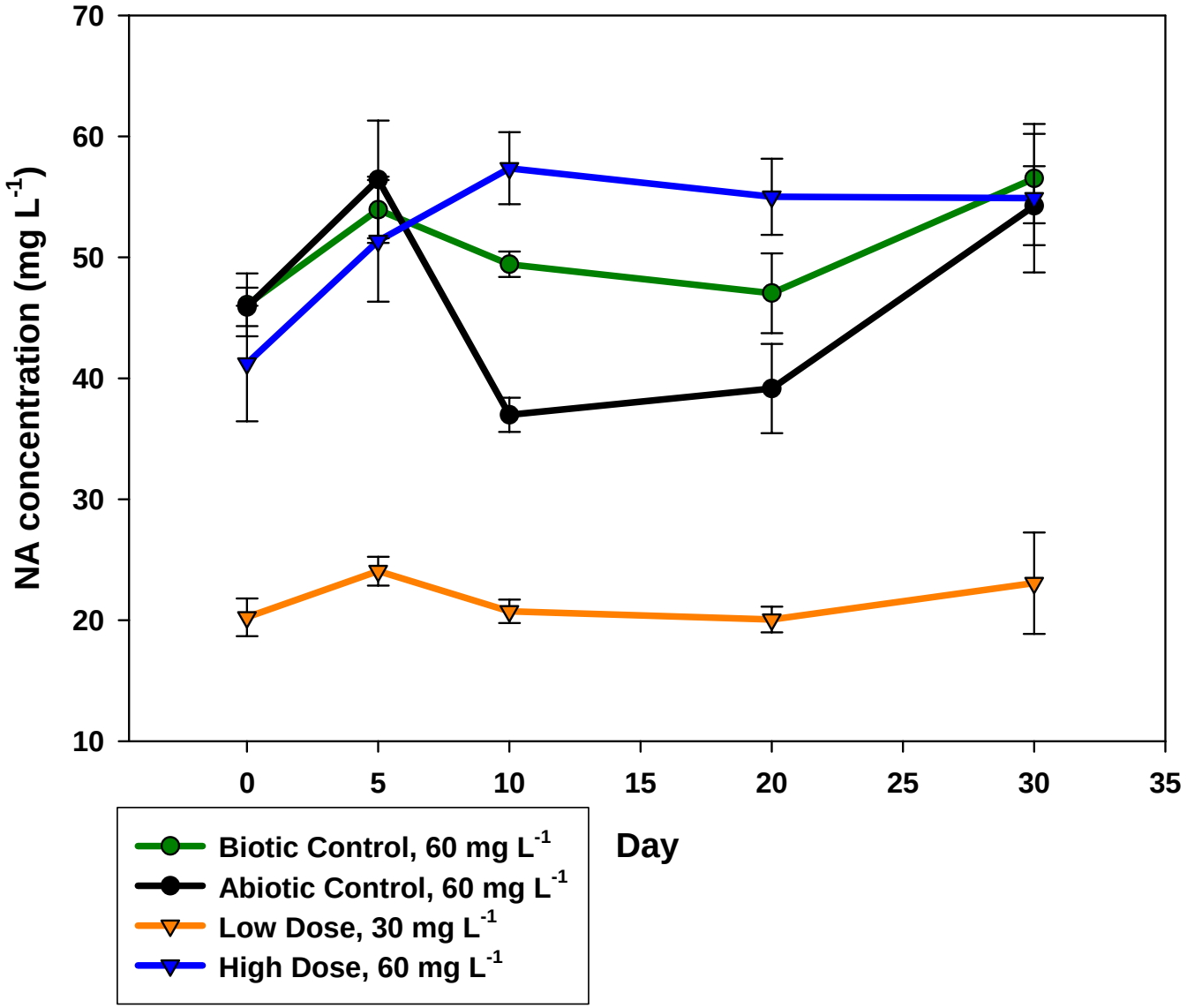
Toxicity: Transpiration (pH = 7.8)



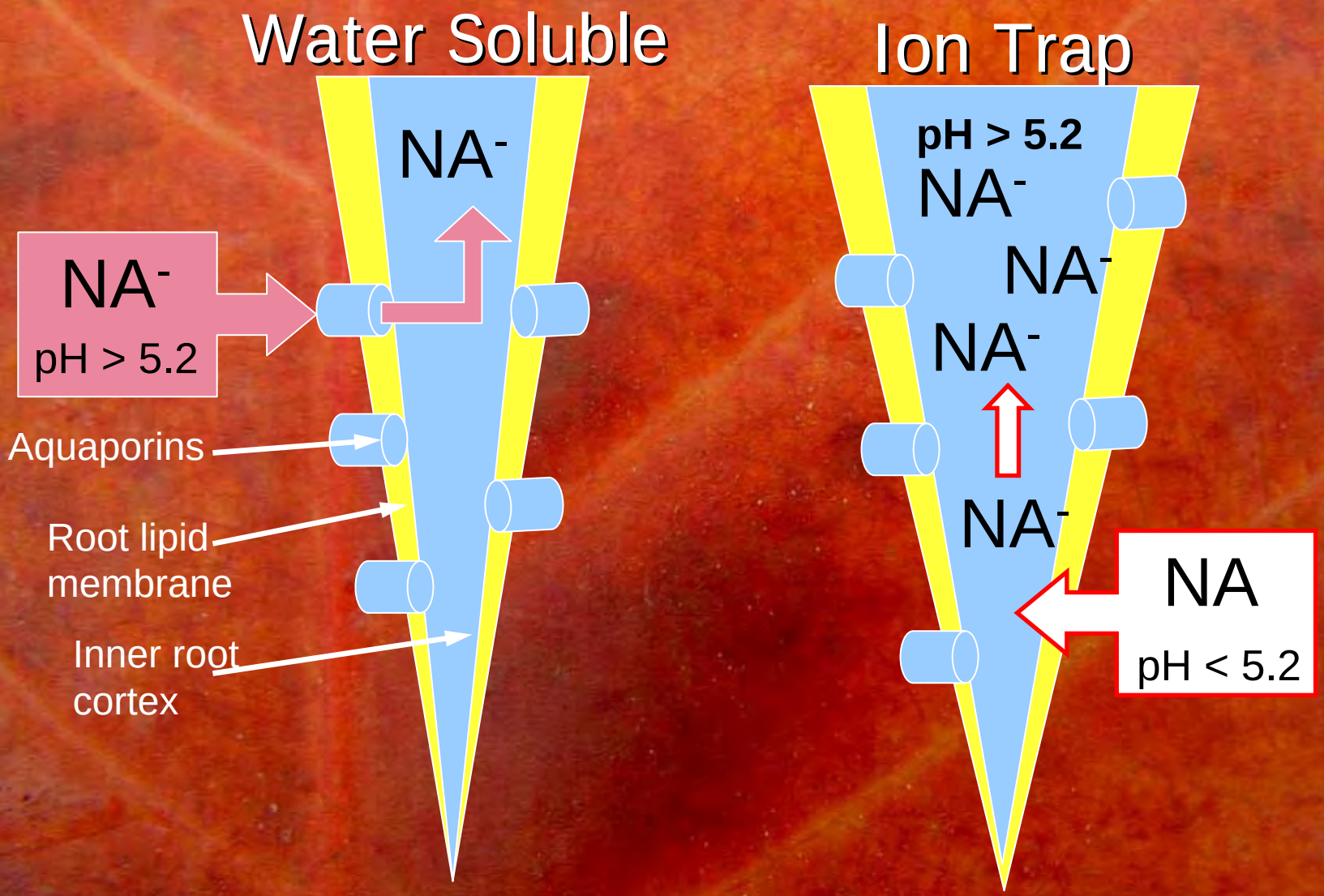
Toxicity: Growth (pH = 7.8)



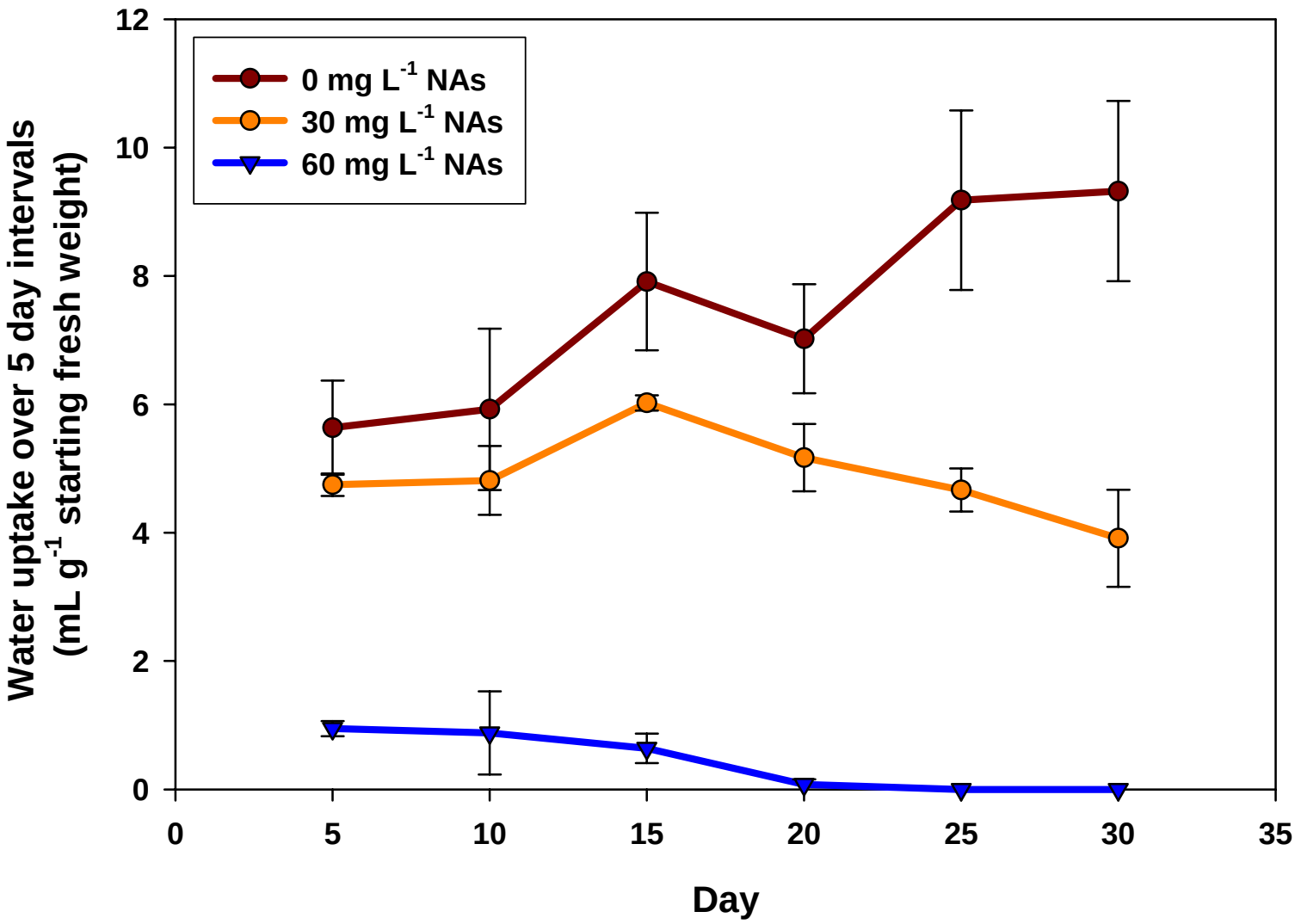
Dissipation: Cattail (pH = 7.8)



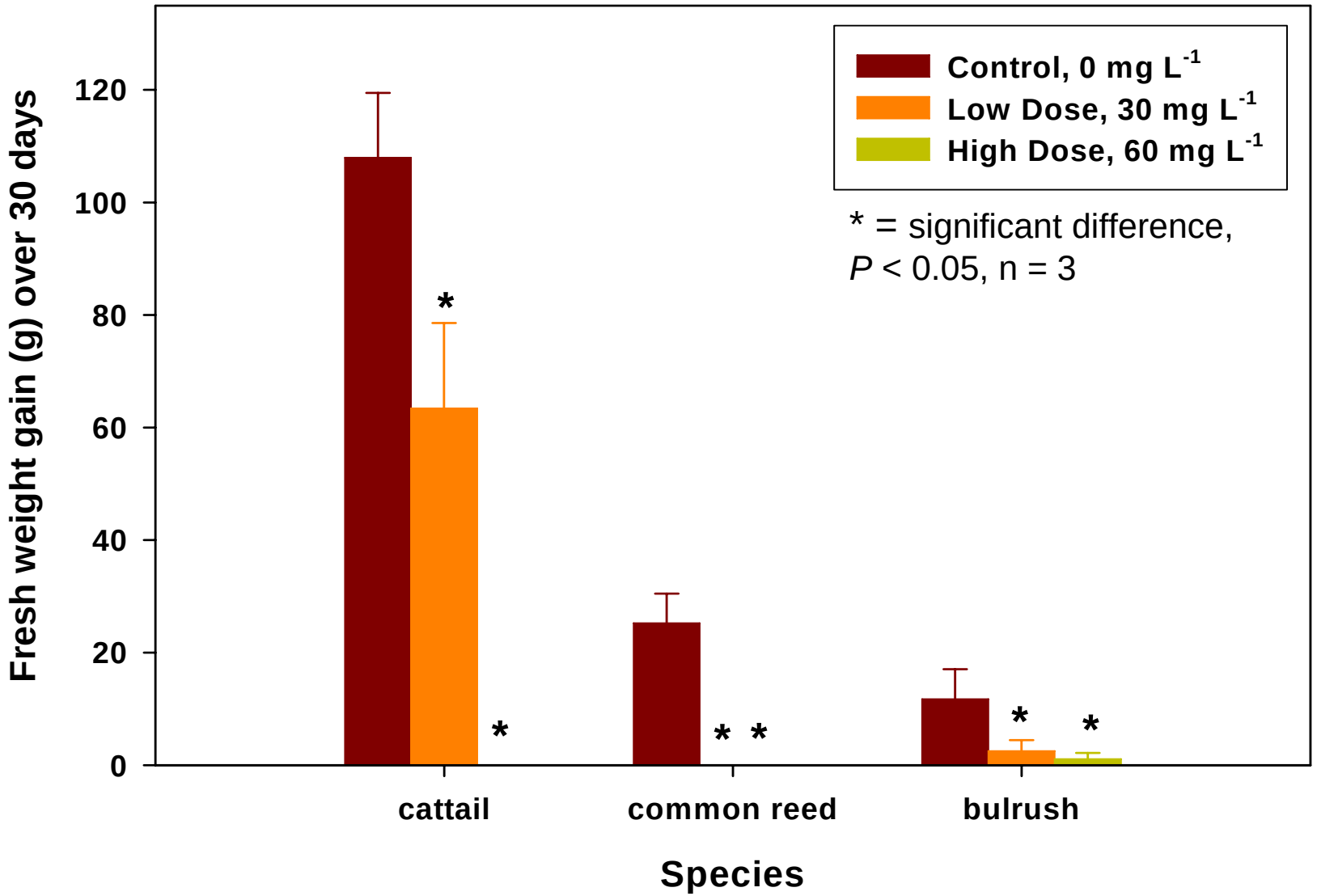
Two Uptake Mechanisms



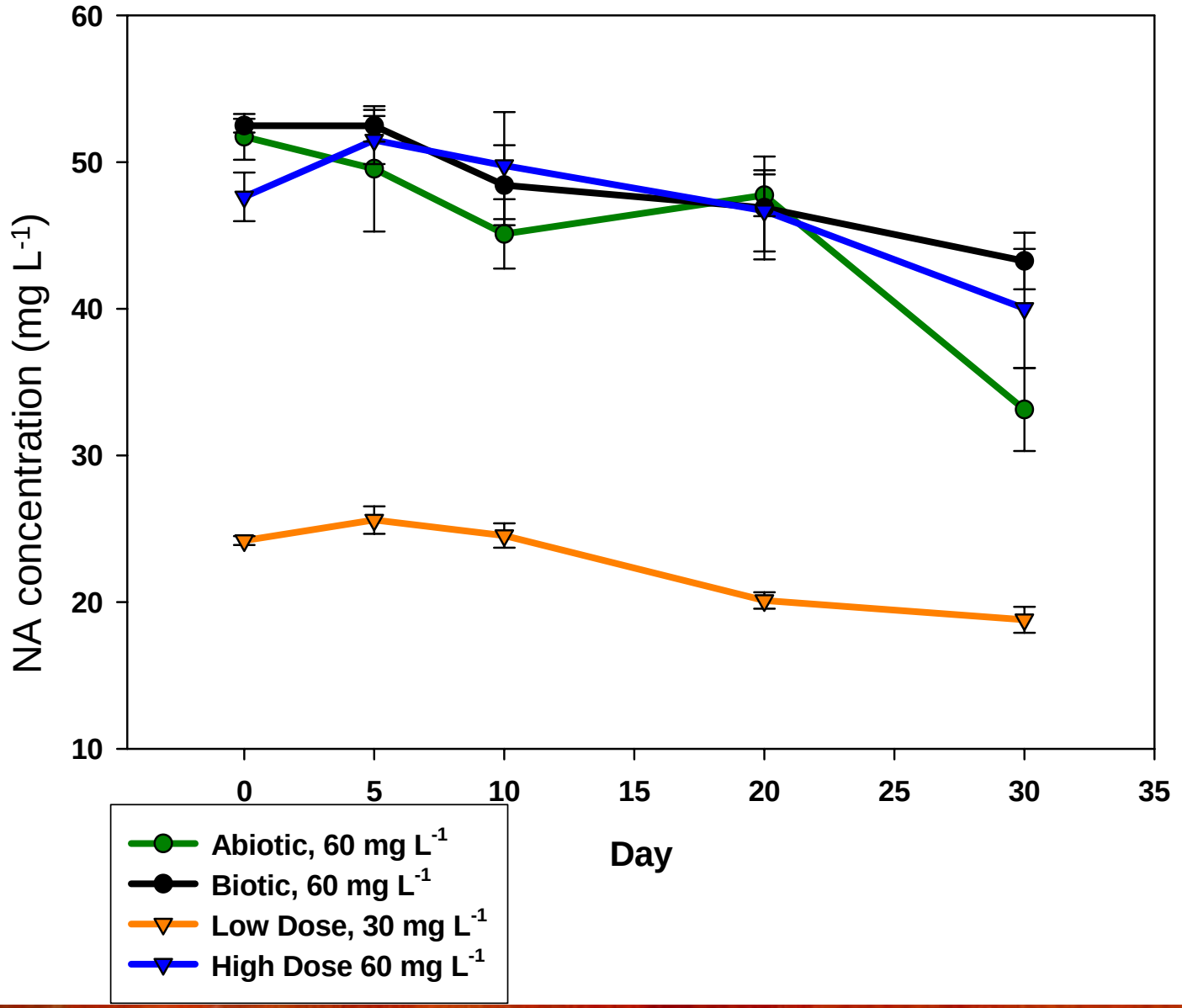
Toxicity: Transpiration (pH = 5.0)



Toxicity: Growth (pH = 5.0)



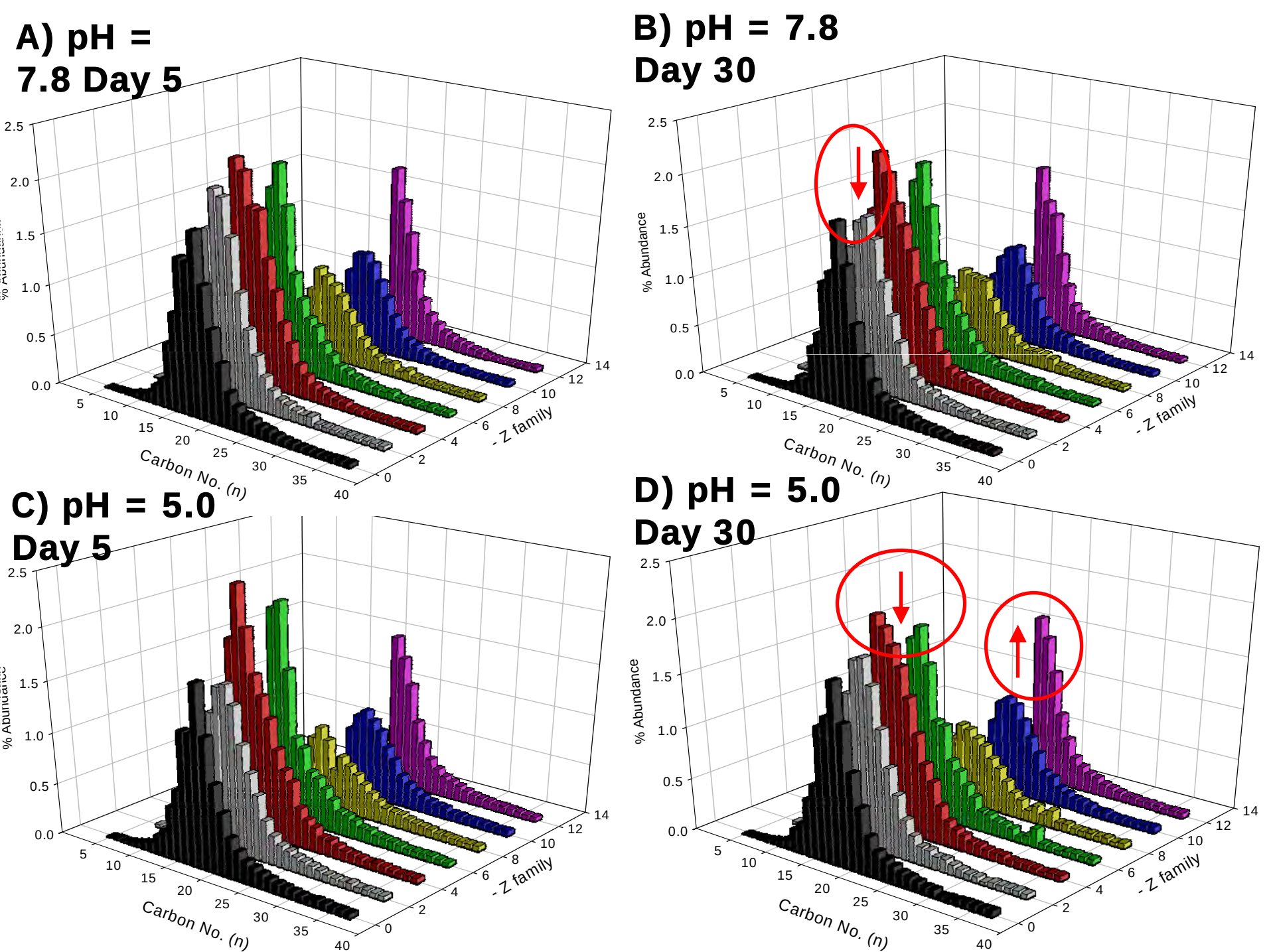
Dissipation: Cattail (pH = 5.0)



Total Naphthenic Acid Dissipation

- No significant difference in dissipation of NA in both planted and unplanted treatments

- Is there selective ion uptake?


A) pH = 7.8 Day 5
B) pH = 7.8 Day 30
C) pH = 5.0 Day 5
D) pH = 5.0 Day 30
% Abundance
Carbon No. (n)
- Z family

Discussion & Conclusions

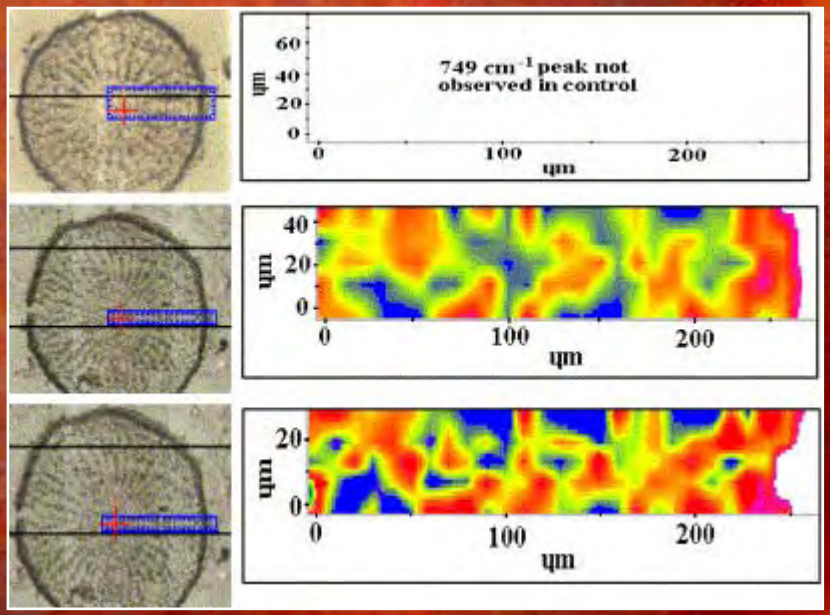
- NAs are more toxic in their unionized form
- Although no dissipation was noted in total NA concentration, changes observed when looking at specific NA ions
- Amount and size of selective ion uptake is too small relative to higher molecular weight compounds within natural variability
- NAs may be taken up by an “Ion Trap” mechanism

NA Fate in Plant Tissue

- Analyzing NAs in plant tissue – tricky because plants contain a lot of endogenous carboxylic acid compounds
  - Traditional methods destructive (no spatial information). Accelerated Solvent Extraction (ASE) was not successful
  - Now trying Synchrotron Fourier Transform Infrared (FTIR) microspectroscopy

Synchrotron FTIR Microspectroscopy

- Mid-IR beamline (λ =2.5 – 13 um) – provides highly specific chemical characterization including type, distribution and relative abundance
- Observe structural changes in plant tissue
- Microscopic analysis of root cross section



Dokken et al.
Microchemical Journal
(2005) 81:86-91

Acknowledgements

- Committee: Drs. Monique Dubé, Dr. Dena McMartin (U of R), Dr. Hans Peterson, Dr. Barry Blakley
- Dr. Susan Kaminskyj (U of S, Biology) , Dr. Kathy Gough (U of M) , Tim May (CLS) and Dr. Stephen Urquhart (U of S, Chemistry)
- Lori Philips (U of S, Soil Science)

Funding:

- NSERC
- Program of Energy Research & Development
- Technology & Innovation Heavy Oil & Bitumen Climate Change Program