Plant Uptake of Metals and PHCs: Advancing ERA

RemTech East 2023

Erik J. Martin, Ph.D., D.A.B.T., P.Biol.

Discipline Leader, Risk Assessment & Toxicology
Vertex Resource Group Limited

June 1, 2023

VERTEX

Outline

1. Project Background
2. Workplan and Methods
3. Findings
4. Conclusions
5. Future Research Plans

Project Team

Dr. Gwen O'Sullivan, Ph.D., M.R.S.C.

Professor & Chair of the Department of Earth & Environmental Science

James Walker, B.Sc.

Research Assistant

MOUNT ROYAL UNIVERSITY 1910

Dr. Court D. Sandau, Ph.D., P.Chem.

Principal and Senior Chemist at Chemistry Matters Inc.

chemistry matters®

Dr. Erik Martin, Ph.D., D.A.B.T., P.Biol.

Discipline Leader, Risk Assessment and Toxicology

VERTEX™ VERSATILITY. EXPERTISE.

Alberta Upstream Petroleum Research Fund (AUPRF)

PTAC PETROLEUM TECHNOLOGY ALLIANCE CANADA

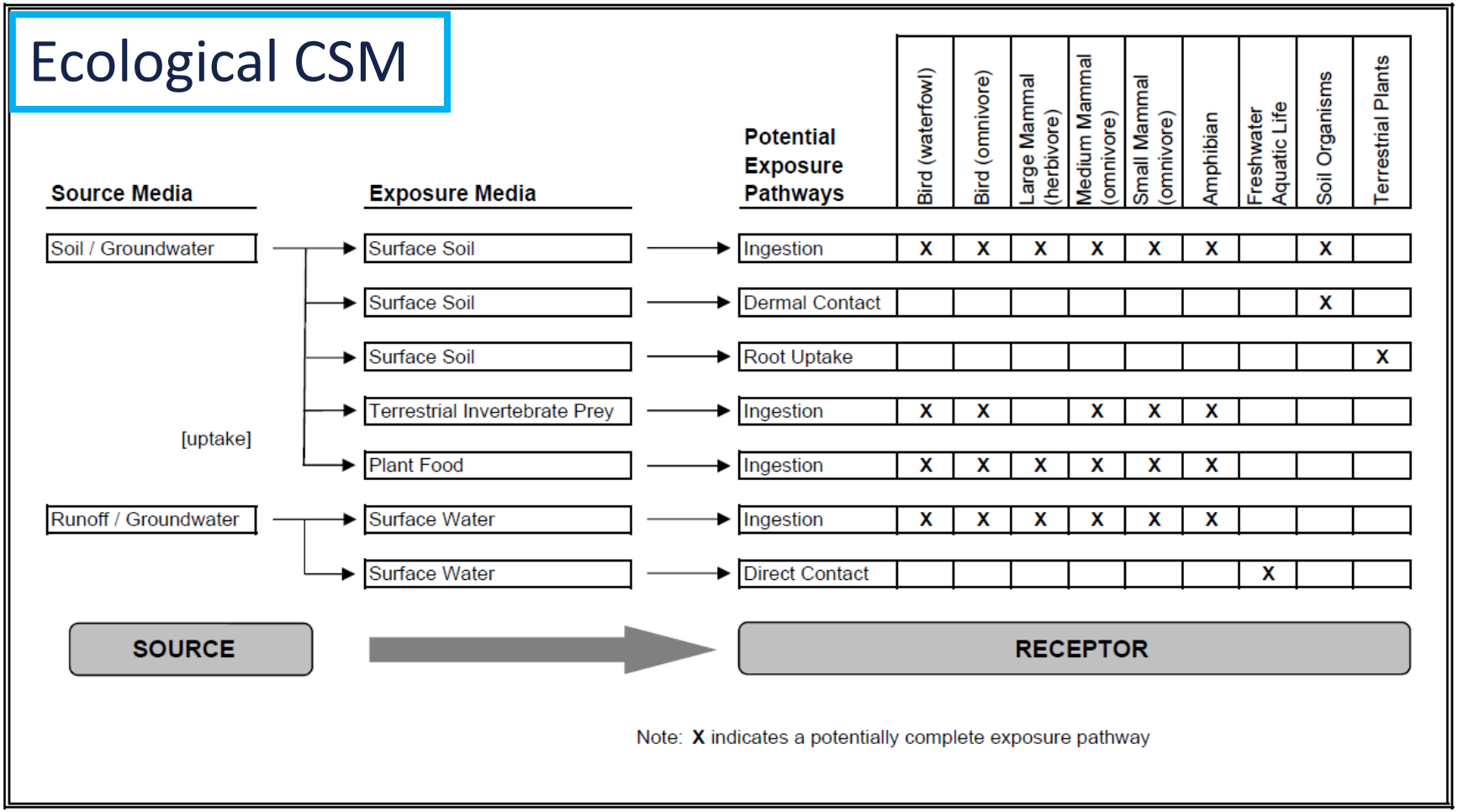
1. Project Background

Why complete this study?

- Was conducting HHERAs for Oil & Gas sites and identified potential risk for F2 associated with the '*consumption of plants*' exposure pathway.
- To complete exposure assessment (dose calculation, mg/kg-day), require concentrations of hydrocarbons in plants.
- Plant concentrations can be measured in laboratory or can use soil-to-plant uptake factors (PUFs).
- What are these factors:
  - $\log(UF_{SP}) = (1.588 - 0.578 \log(K_{ow})) \times 0.2,$ or values from literature
  - Conservative guesstimate, 10 or 20%
- A need for additional research to develop more robust PUFs that will allow for more accurate assessments of potential health effects (humans and eco receptors) from exposure to contaminants in plants.

1. Project Background

Ecological CSM



1. Project Background

Study Objectives

1. Determine the extent to which plants, four species in total, uptake PHCs and trace metals,
2. Establish PUFs (or models) for specific PHC constituents and metals, and
3. Compare calculated PUFs to PUFs obtained from the literature.

2. Work Plan and Methods

Plant Species

Functional Type	Common Name	Species	Range
Grass	Barley	*Hordeum vulgare*	Peace River Region, Central AB, and Southern/Southeastern AB
Grass	Italian ryegrass	*Lolium multiflorum*	Peace River Region, Central AB, and Southern AB (irrigation)
Grass	Corn (Maize)	*Zea mays*	Southern region of AB
Forb	Yarrow	*Achillea millefolium*	Throughout AB
Legume	Pea plant	*Pisum sativum*	Peace River Region, Central and Southern AB

- Plant species selection based on:
  - Presence in Alberta (or Canada)
  - Variety of functional types
  - Availability and ease to work with in the laboratory
  - Growth characteristics (e.g., speed of growth, time to flowering)

2. Workplan and Methods

Project Components

1. Hydroponics
    - elevated Cu, Ni, Pb, and Cr in nutrient solution
    - 9 days exposure/growth
2. Metals in Soil
    - elevated Cu, Ni, Pb, and Cr in soil
    - short-term (9 days)
    - long-term (~7 weeks)
3. Diesel Contaminated Soil
    - 9 days exposure/growth

2. Workplan and Methods

Hydroponic Systems – pros and cons

Pros

- Much of the experimental setup can be found outside of scientific supply companies, thus less expensive and more convenient.
- Nutrient media and availability can easily be controlled.
    - ➢ nutrient bioavailability changes throughout the soil matrix as nutrients bind to soil particles creating micro-environments within the soil.
- Intact roots and shoots for experimentation.

Cons

- Conditions may be seen as ‘non-physiological’, and plant responses may differ when grown in alternative systems (e.g., soil).

2. Workplan and Methods

Hydroponics

1. Barley, Corn, Italian Rye, and Peas.
2. Grown for 9-days in nutrient solution.
3. Sample types for each plant:
    - spiked solutions (fertilizer + 5 x CCME irrigation guidelines for Cu, Ni, Pb, and Cr)
    - control solutions (only fertilizer)
    - evaporative controls (no plant)
4. Plants sampled on day 9.
5. Analysis with ICP-MS.

2. Workplan and Methods

Soil Metals Uptake – long-term trial

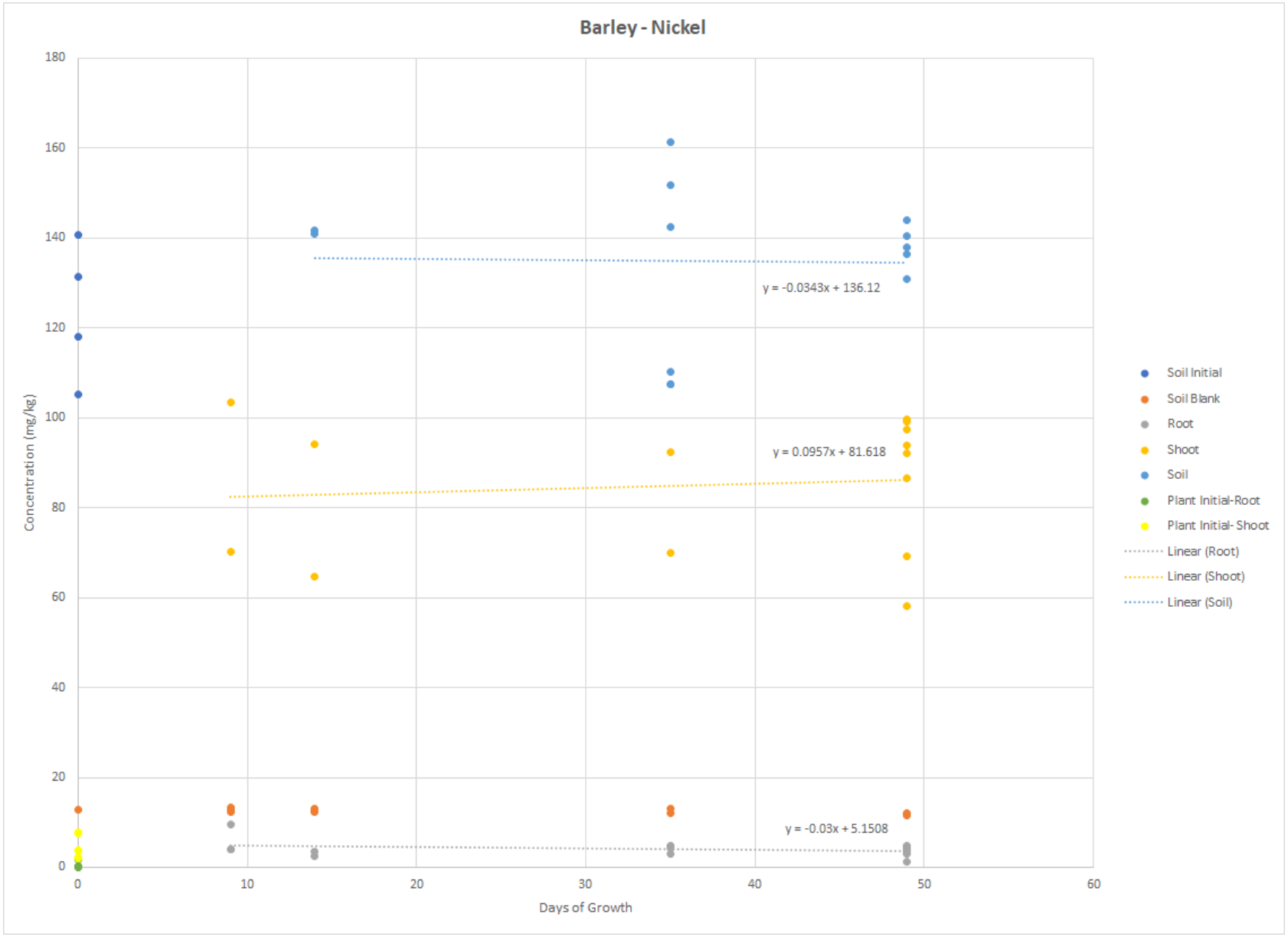
1. Barley, Italian Rye, Corn, and Peas.
2. 5 sampling points (t_0, 9 days, 2 weeks, 5 weeks, and 7 weeks).
3. Soil spiked with 2 x CCME guideline for Cu, Ni, Pb, and Cr.
4. Samples per plant type:
    - spiked soils/sampling point
    - control/sampling point
    - evaporative controls/sampling point
5. Samples collected and analyzed with ICP-MS.

2. Workplan and Methods

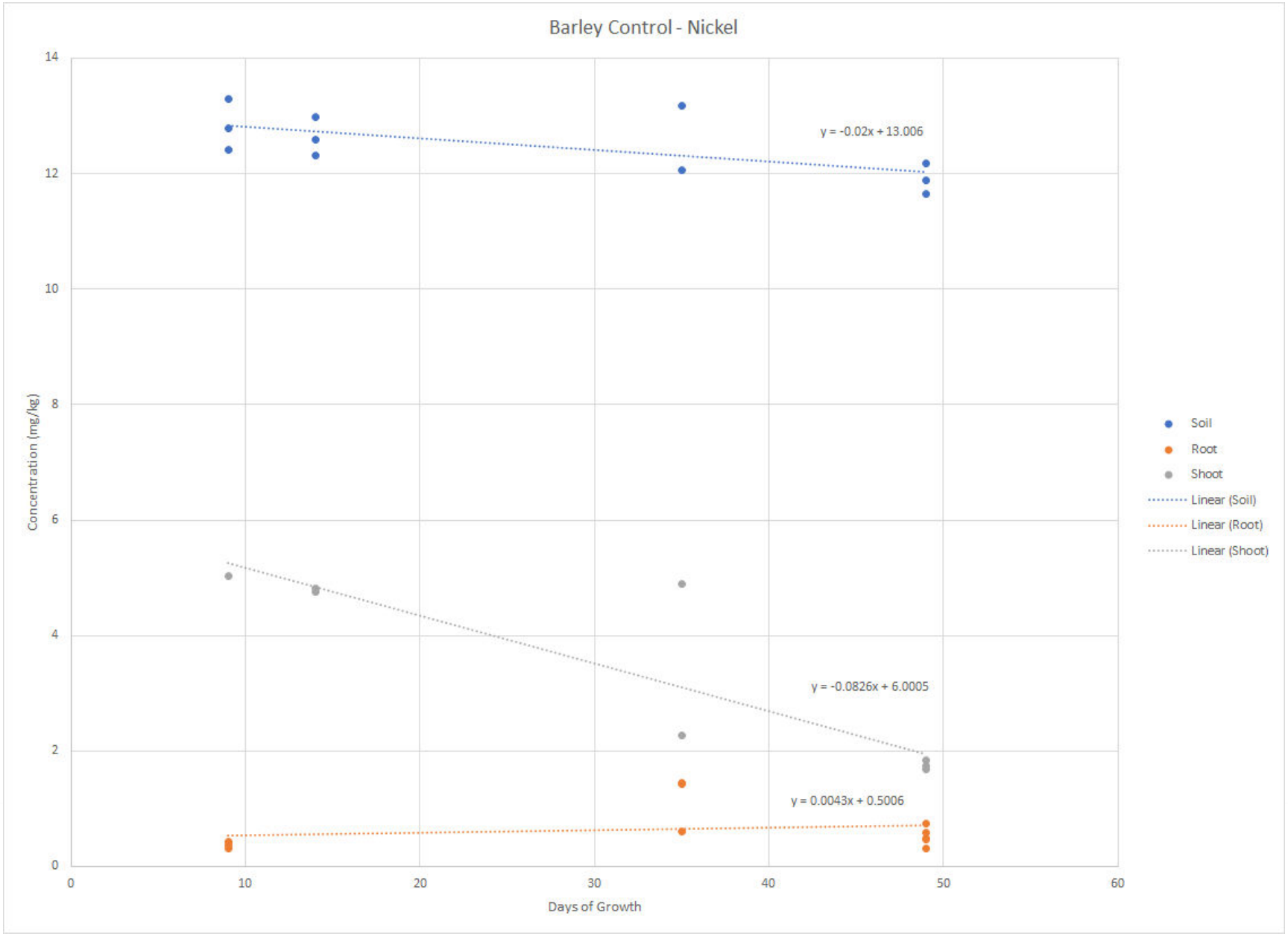
PHC Uptake

1. Barley, Italian Rye, Corn, Peas, and Yarrow.
2. 10 mg/kg of diesel (mixed with fine perlite then mixed in with soil).
3. Grown for 9 days.
4. Sample types per plant:
    - spiked soils
    - control soils
    - evaporative controls (no plant)
5. Samples extracted, cleaned and analyzed using GCxGC TOF-MS.

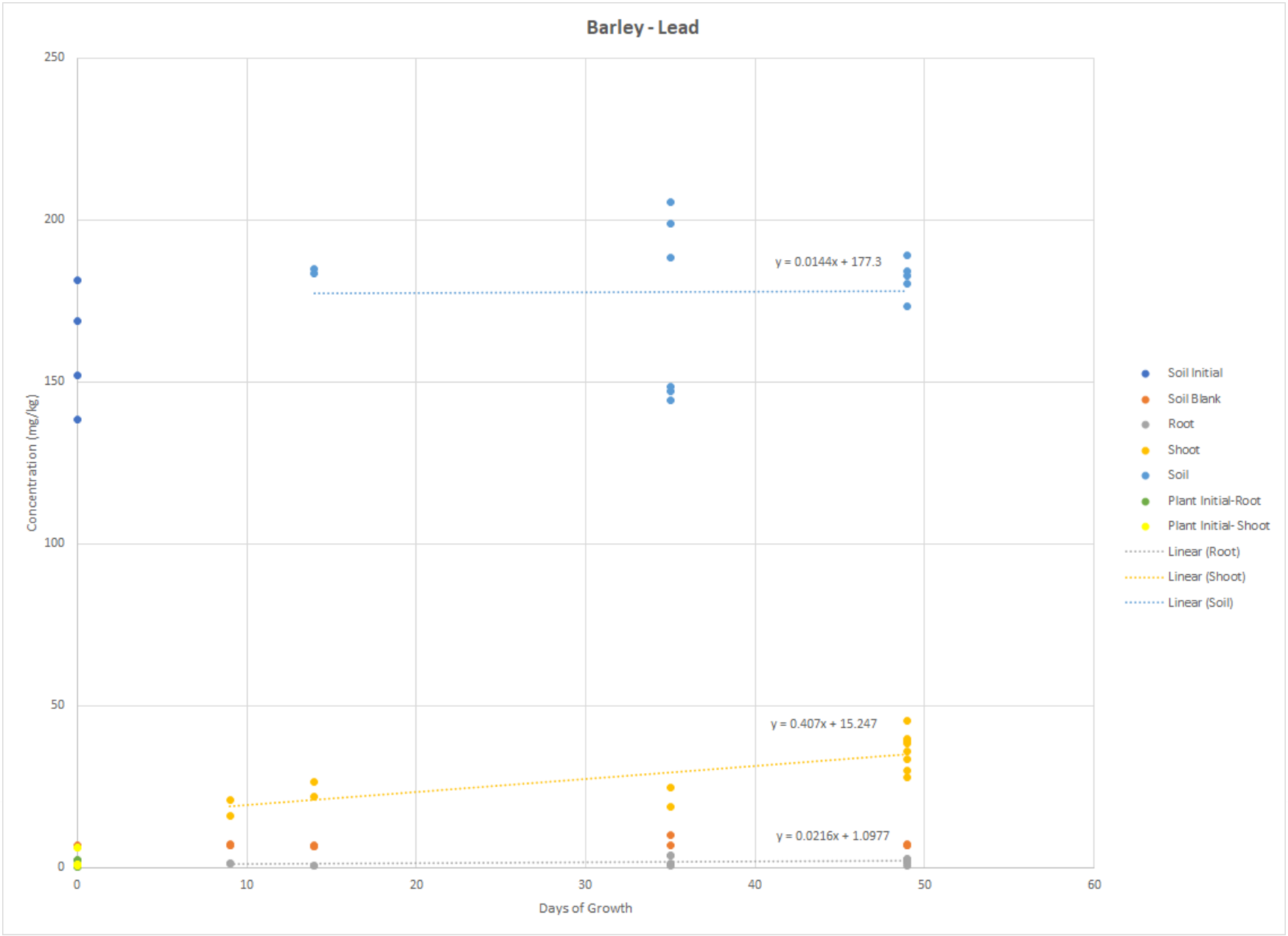
3. Findings - Soil Metals Uptake, Long-term Trial



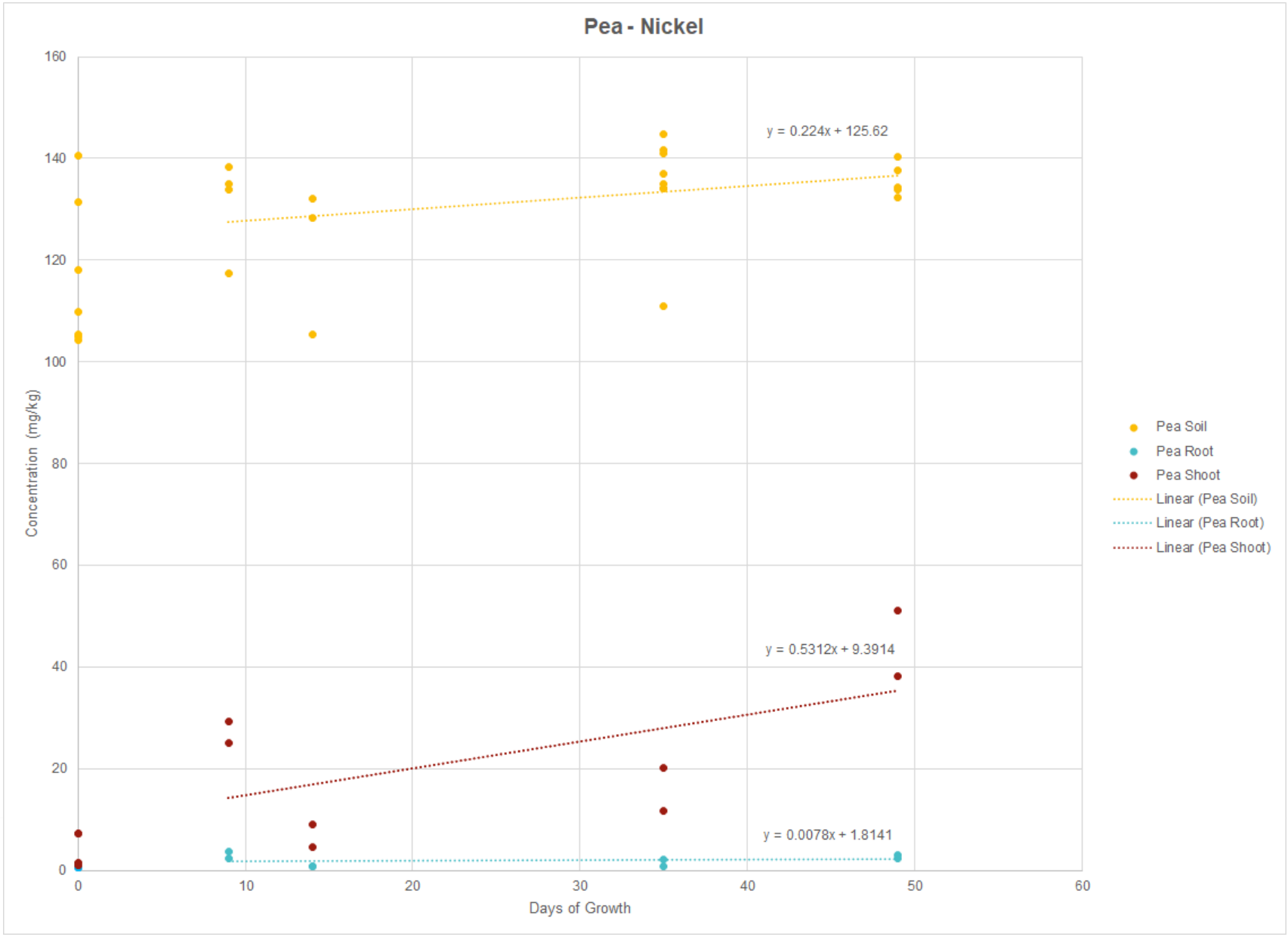
3. Findings - Soil Metals Uptake, Long-term Trial



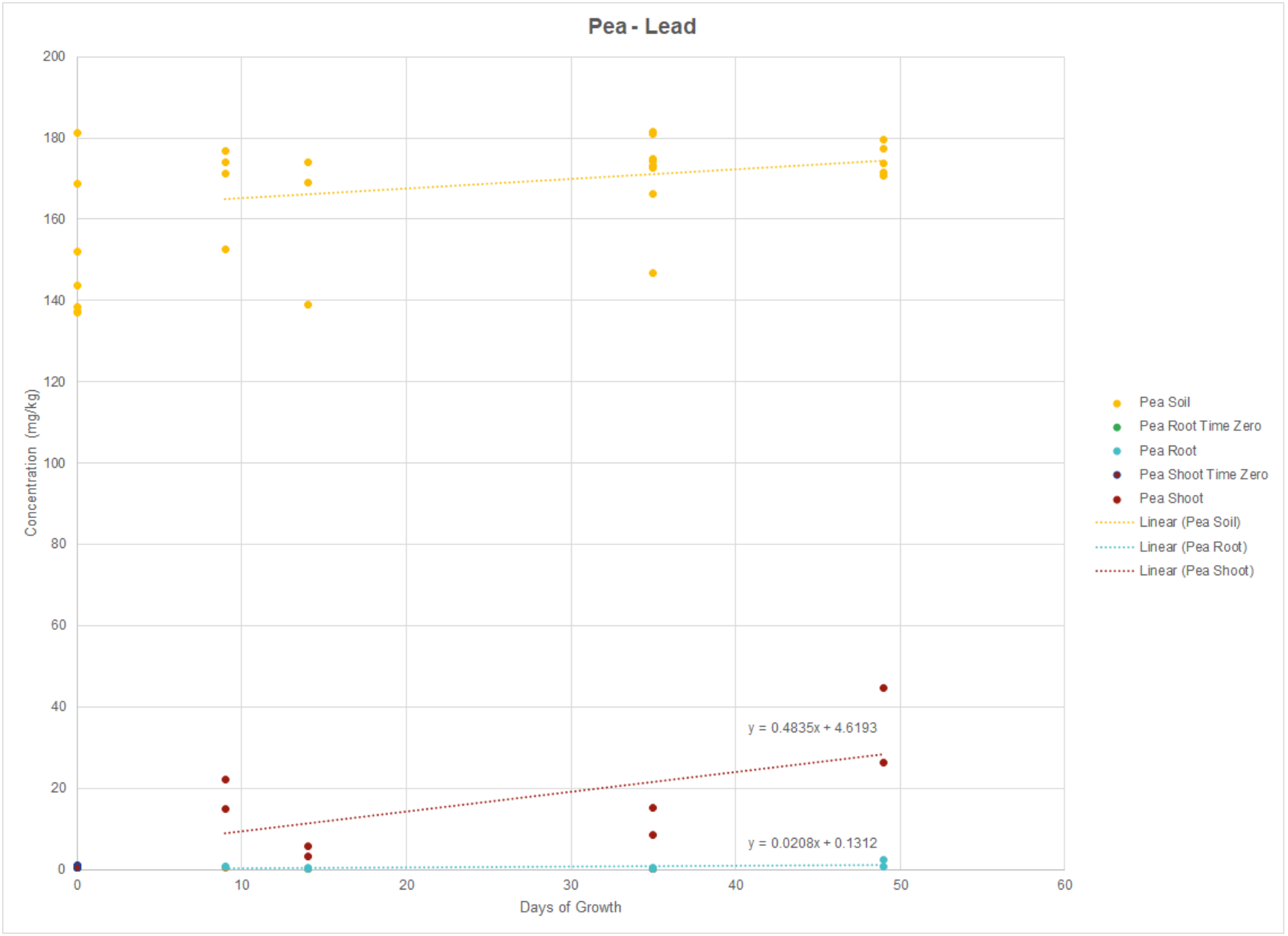
3. Findings - Soil Metals Uptake, Long-term Trial



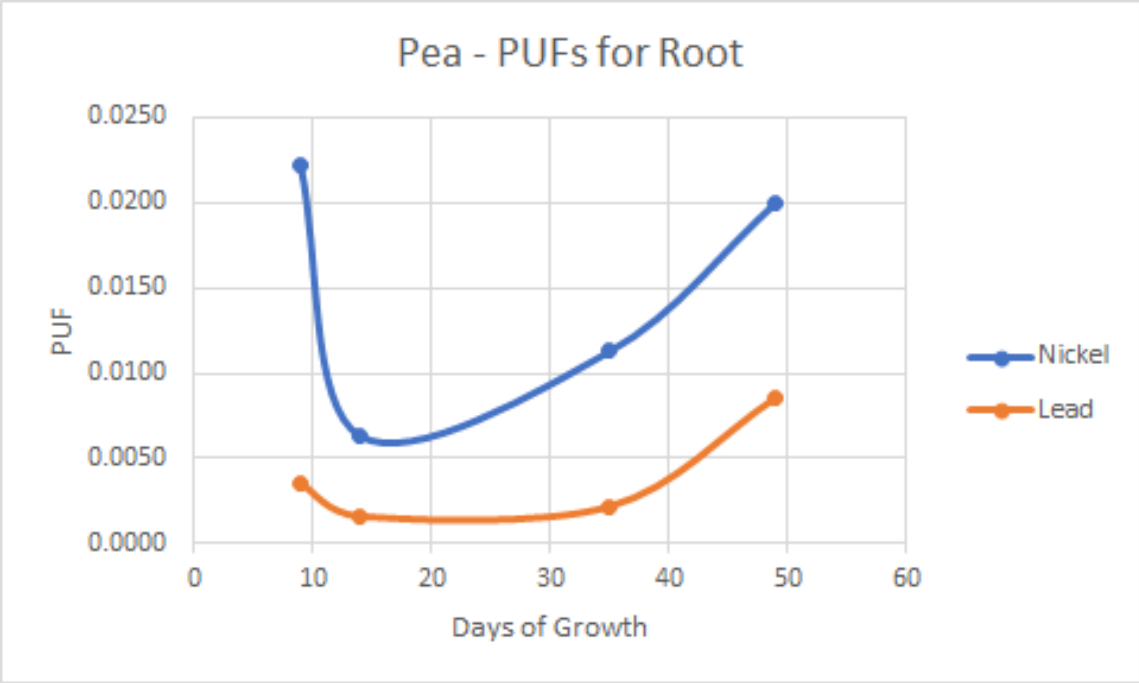
3. Findings - Soil Metals Uptake, Long-term Trial



3. Findings - Soil Metals Uptake, Long-term Trial



3. Findings - PUFs



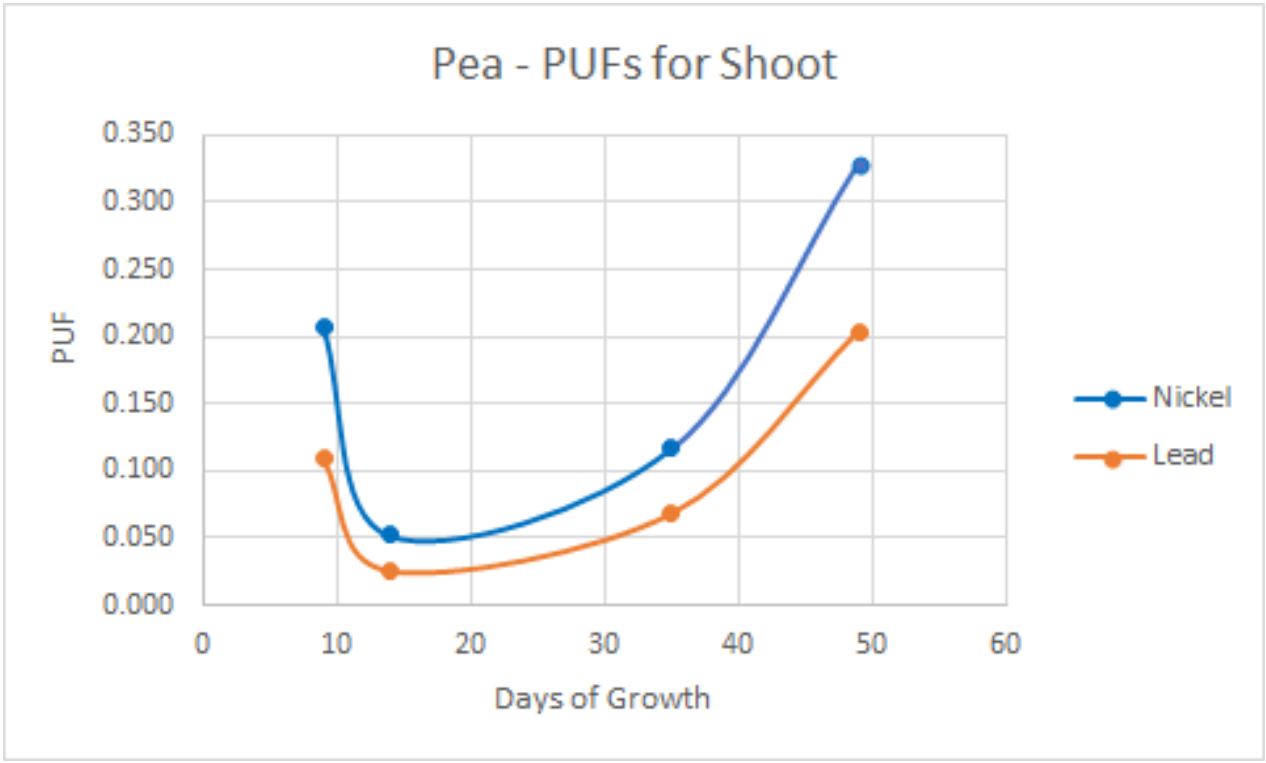
Nickel: 0.006 to 0.028

Lead: 0.001 to 0.013

Chromium: 0.001 to 0.013

Copper: 0.006 to 0.056

3. Findings - PUFs



Nickel: 0.035 to 0.38

Lead: 0.018 to 0.26

Chromium: 0.014 to 0.26

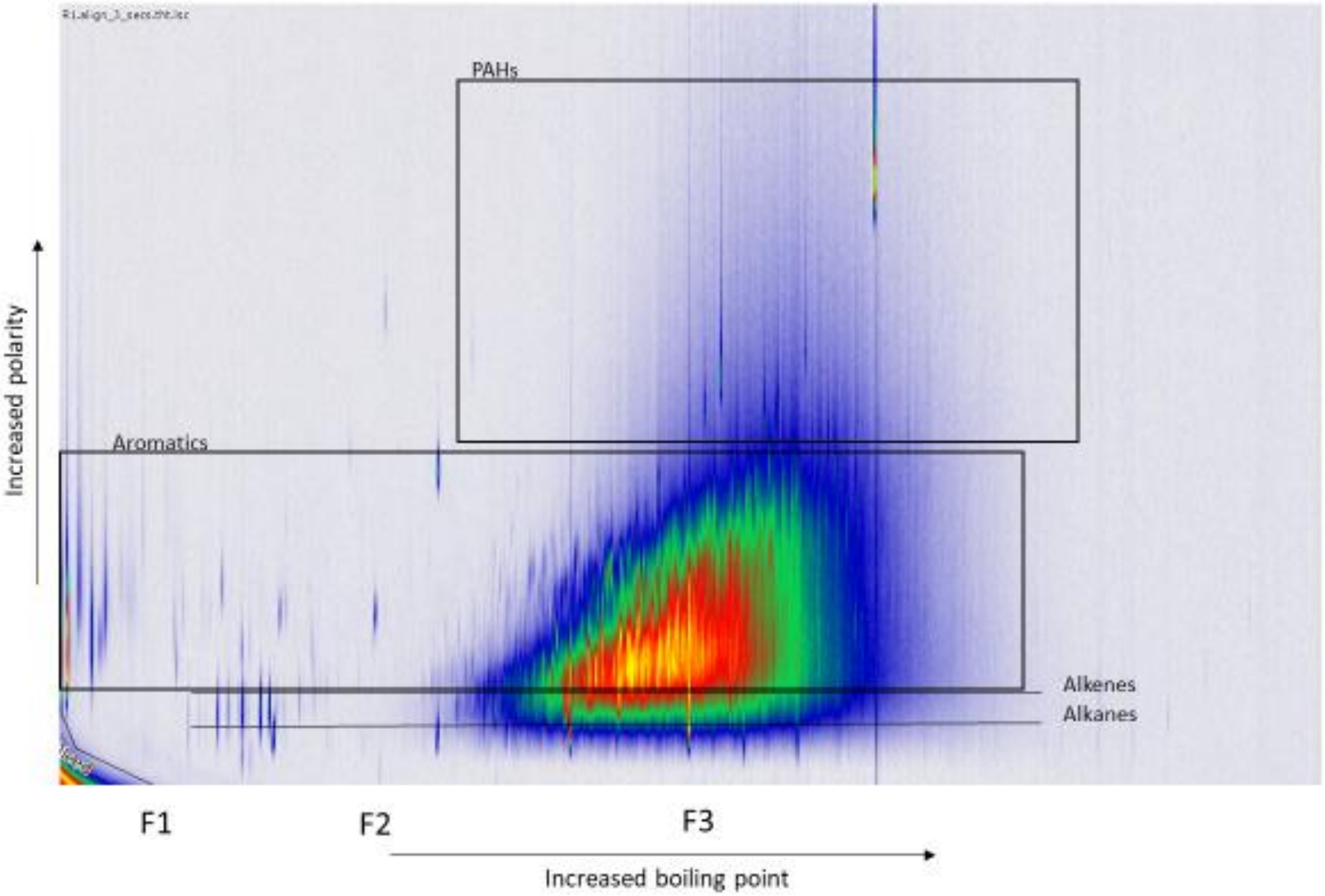
Copper: 0.052 to 0.43

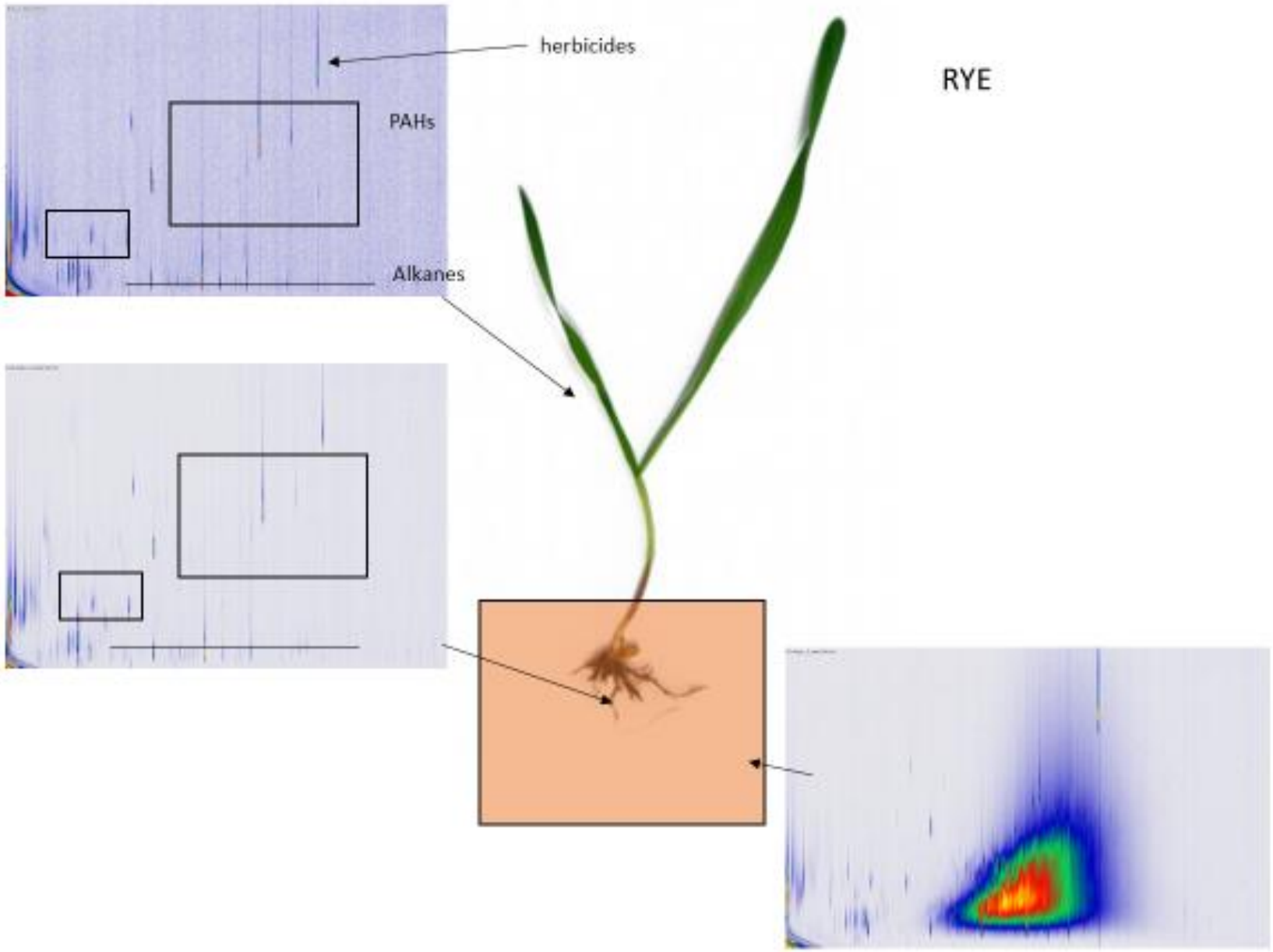
3. Findings - PUFs

Pea, PUFs for shoot vs. Literature PUFs

1. Nickel: 0.035 to 0.38
   Nickel: 0.015 to 0.06 (RAIS, Baes et al., 1984)
   Nickel: 0.1 to 0.2 (guesstimate)

2. Lead: 0.018 to 0.26
   Lead: 0.011 to 0.045 (RAIS, Baes et al., 1984)
   Lead: 0.1 to 0.2 (guesstimate)


PAHs
Aromatics
Alkenes
Alkanes
Increased polarity
F1
F2
F3
Increased boiling point


herbicides
PAHs
Alkanes
RYE

Increasing molecular weight

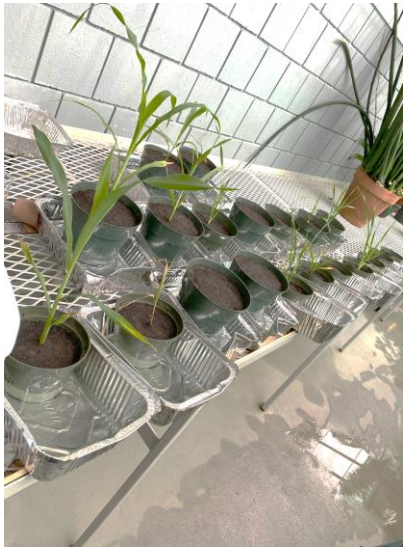
Compound class	Uptake factor-Root	Uptake factor-Shoot
Alkanes	0.46 (±0.14)	0.19 (±0.03)
Tetramethyl benzenes	1.02 (±0.2)	0.9 (±0.5)
Methyl Naphthalene	0.6 (±0.2)	0.35 (±0.11)
Dimethyl Naphthalene	--	--
Trimethyl Naphthalene	0.03 (±0.03)	0.01 (±0.01)

4. Conclusions

- Developing a comprehensive database for PUFs.
  - 2 plant growth methods
  - 4 plant species
  - roots and shoots
  - 5 time points
- A lot of data analysis remains.
- Our PUF values appear to be elevated versus literature values (based on analysis of a small portion of our dataset).

5. Future Research Plans

- Plant uptake studies with additional hydrocarbon doses and parameters (F3?).
- Conduct field studies to evaluate whether laboratory PUFs will correctly determine the concentration of PHCs and metals in plants.
- Evaluate how the newly derived PUFs may (or may have) influenced the risk assessment process.



Questions?

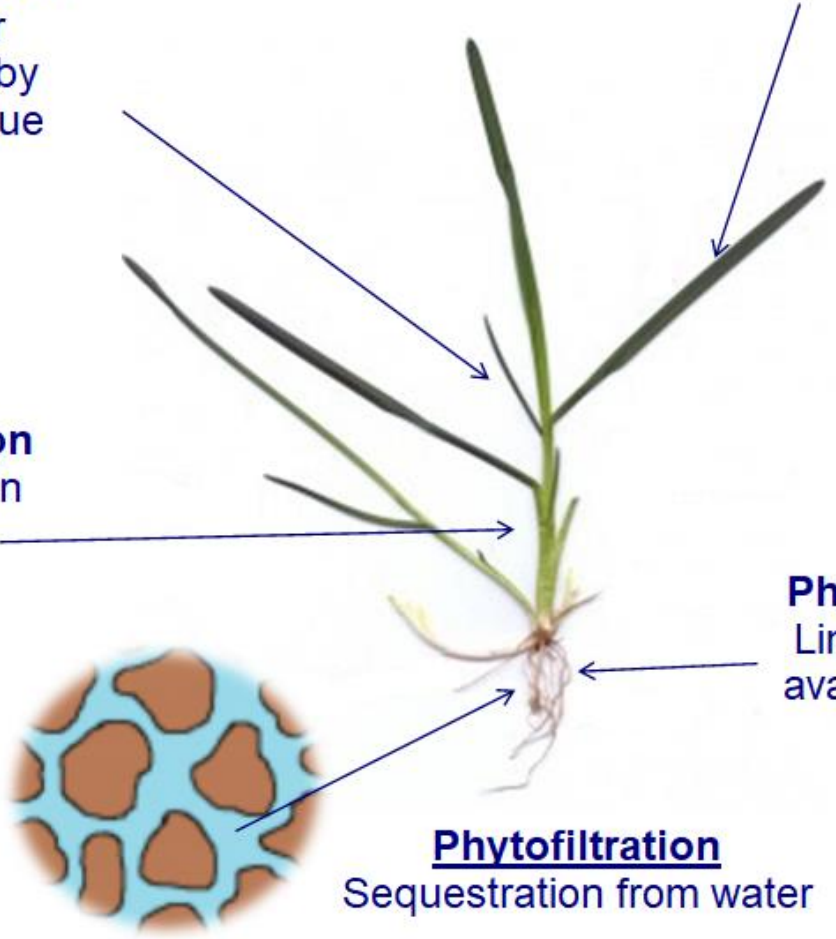
Thank You!

VERTEX

ADBE

Phytovolatilization
Converts to volatile form, releases to atmosphere through leaf surface

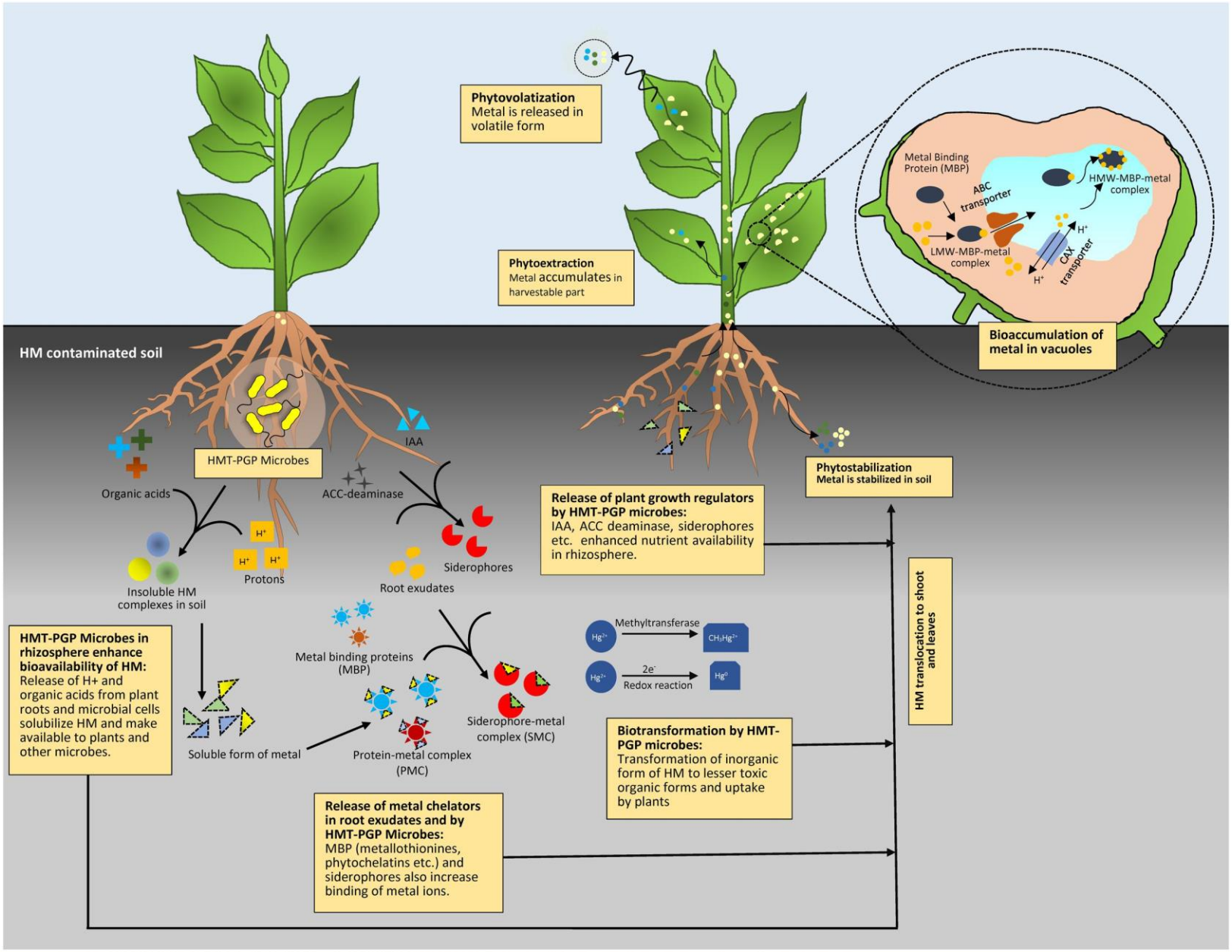
Phytodegradation
Breakdown or transformation by enzymes in tissue



Phytoextraction
Accumulation in shoots

Phytostabiliaztion
Limits mobility and availability in soil by roots

Phytofiltration
Sequestration from water


Phytovolatization
Metal is released in volatile form
Phytoextraction
Metal accumulates in harvestable part
Metal Binding Protein (MBP)
ABC transporter
HMW-MBP-metal complex
LMW-MBP-metal complex
CAX transporter
H+
Bioaccumulation of metal in vacuoles
HM contaminated soil
HMT-PGP Microbes
IAA
Organic acids
ACC-deaminase
Siderophores
Root exudates
Protons
Insoluble HM complexes in soil
Phytostabilization
Metal is stabilized in soil
Release of plant growth regulators by HMT-PGP microbes:
IAA, ACC deaminase, siderophores etc. enhanced nutrient availability in rhizosphere.
HMT-PGP Microbes in rhizosphere enhance bioavailability of HM:
Release of H+ and organic acids from plant roots and microbial cells solubilize HM and make available to plants and other microbes.
Metal binding proteins (MBP)
Methyltransferase
2e-
Redox reaction
Soluble form of metal
Protein-metal complex (PMC)
Siderophore-metal complex (SMC)
HM translocation to shoot and leaves
Biotransformation by HMT-PGP microbes:
Transformation of inorganic form of HM to lesser toxic organic forms and uptake by plants
Release of metal chelators in root exudates and by HMT-PGP Microbes:
MBP (metallothionines, phytochelatins etc.) and siderophores also increase binding of metal ions.