Phytoremediation of petroleum and salt impacted soils: Successfully meeting generic Tier 1 standards and making green technologies work

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Partners: Cenovus; ConocoPhillips; Lone Pine Resources; Baytex; TransEuro Energy; Solaction; Shell; Talisman; PennWest; Questerre Beaver River; Imperial Oil; Seaway Energy Services; MWH; SNC Lavalin; NSERC

Waterloo Environmental Biotechnology Inc.

Earthmaster Environmental Strategies Inc.

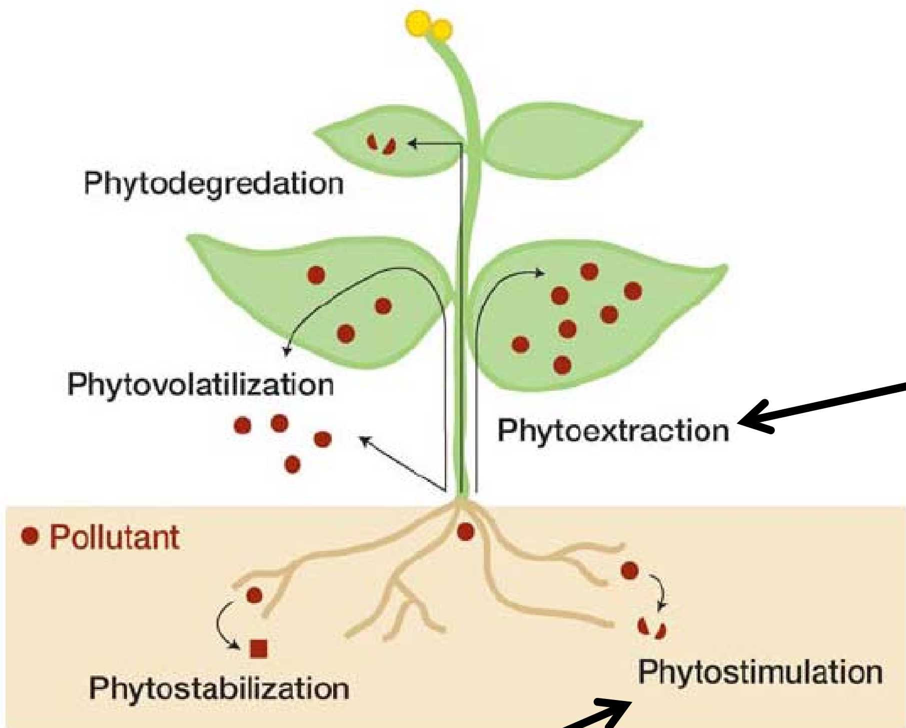
University of Waterloo

Maxxam

Outline

1. Overview of phytoremediation
2. Science of successful phytoremediation
3. Examples of full scale phytoremediation at petroleum and salt impacted sites
4. Achieving Tier 1 and Tier 2 Criteria

Phytoremediation Processes



Salt

Rhizodegradation - PHC

- Volatilization
- Phytodegradation
- Chelation/compartment in leaves

- Translocation: root symplast→ xylem
- Chelation/compartment in roots
- Plant uptake soil→root
- Rhizosphere Processes
- Bioavailability particle→water

Advantages of Phytoremediation

1. Improves the quality of soil
2. It is driven by solar energy and suitable to most regions and climates
3. It is **cost effective** and technically feasible
4. **Plants** provide **sufficient biomass** for rapid remediation; **promote high rhizosphere activity**
5. Reasonable time frames - 2 to 3 years
6. Can be used effectively at **remote sites**
7. Greenhouse gas storage: **6 tonnes per ha per year**
8. Effective for remediation of PHC and salt – relevant to the energy industry

Development, Proof, and Full Scale Application of PGPR Enhanced Phytoremediation Systems (PEPS)

Over 12 years of research with full-scale field remediations at each stage of development and application

1. **PHC:** sites in AB, BC, QC, MB, NWT and ON (2004-11)
2. **Salt:** sites in SK, AB and NWT (2007-11)

Performing full scale remediations for > 5 yrs

PEPS successful at > 25 sites

The key to phytoremediation success -
Transfer of the science from the lab to the field

1. Strategies for aggressive plant growth in impacted and poor quality soils at full scale sites
   – PEPS Deployment by highly trained scientists
2. Monitoring the progress of phytoremediation at each site – Following the chemistry
3. Continuous improvement of our phytoremediation systems through scientific research

WEBi Waterloo Environmental Biotechnology Inc.

Earthmaster Environmental Strategies Inc.

University of Waterloo

WEBi-Earthmaster-UW partnership

- Synergistic expertise in contaminated site remediation
- Developed commercial phytoremediation technologies (PEPS)
- 12 years of research, development and full scale field implementation
- Field proven systems
- Research to continually improve PEPS

WEBi
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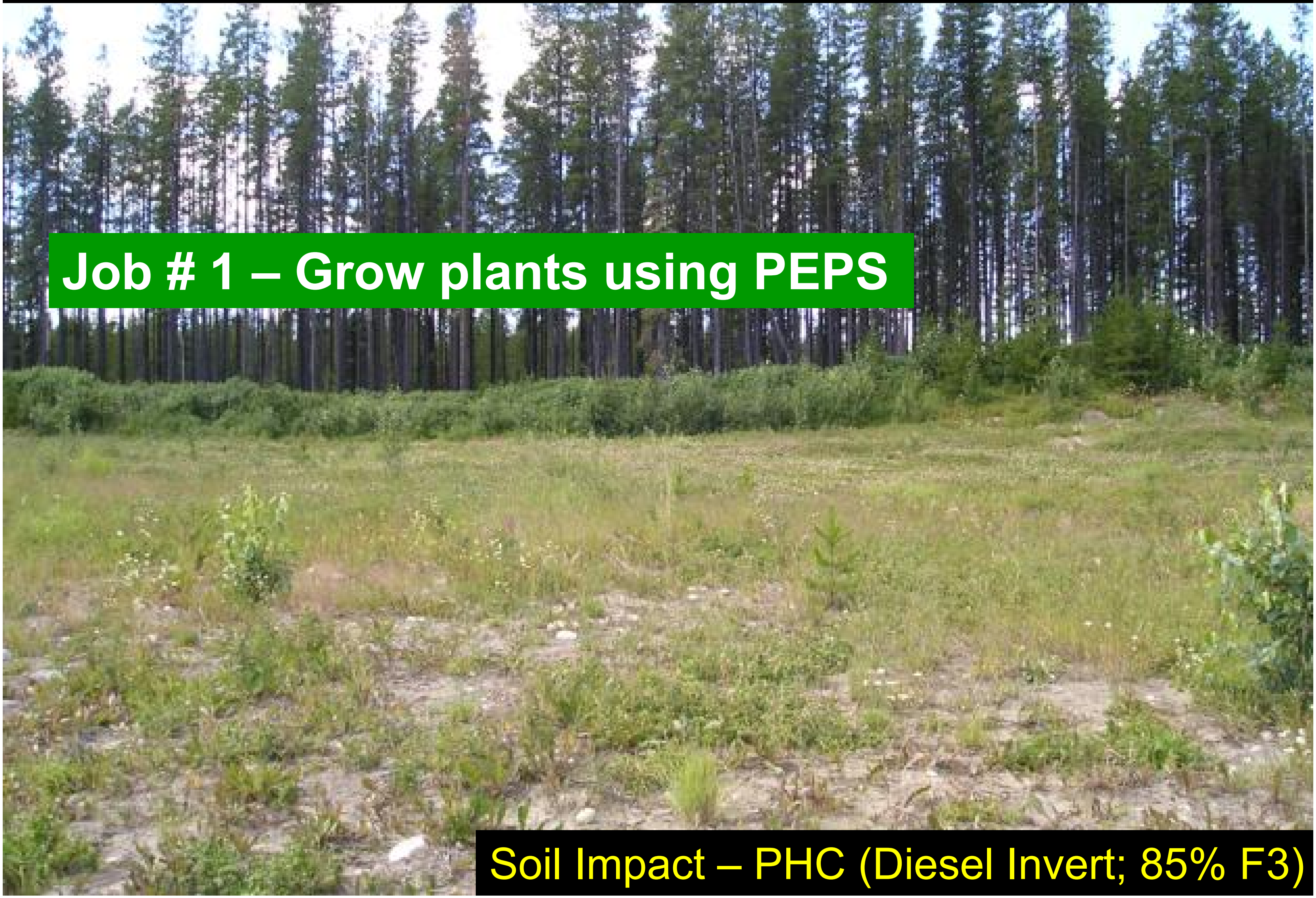
Edson, AB – Before treatment



Job # 1 – Grow plants using PEPS

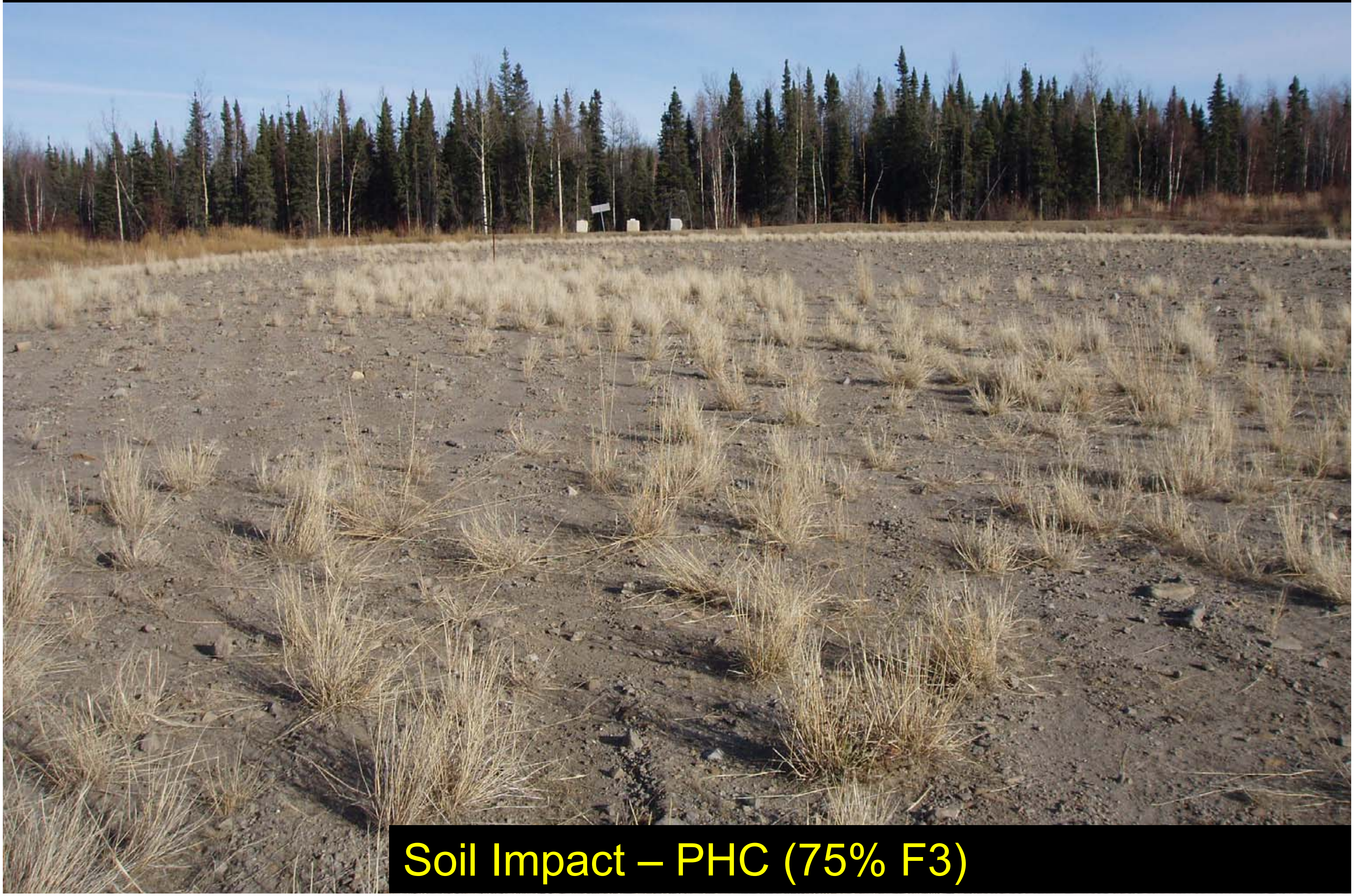
Soil Impact – PHC (Diesel Invert; 85% F3)

PEPS Deployment at Edson, AB

Mission Accomplished - excellent plant growth

Soil Impact – PHC (Diesel Invert; 85% F3)

Dawson, BC – Before PEPS treatment

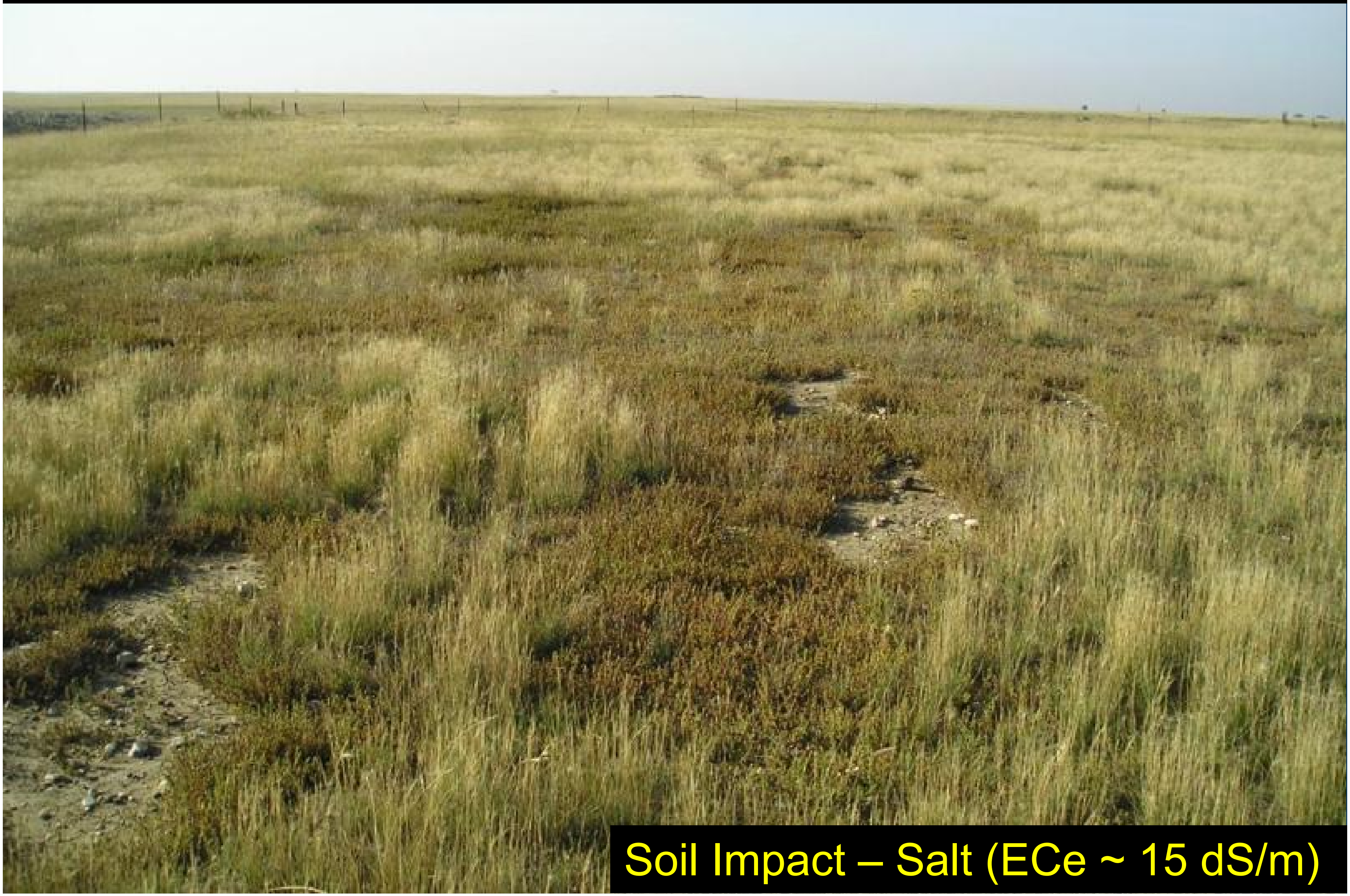


Soil Impact – PHC (75% F3)

Dawson after PEPS deployment – excellent plant growth

Soil Impact – PHC (75 % F3)

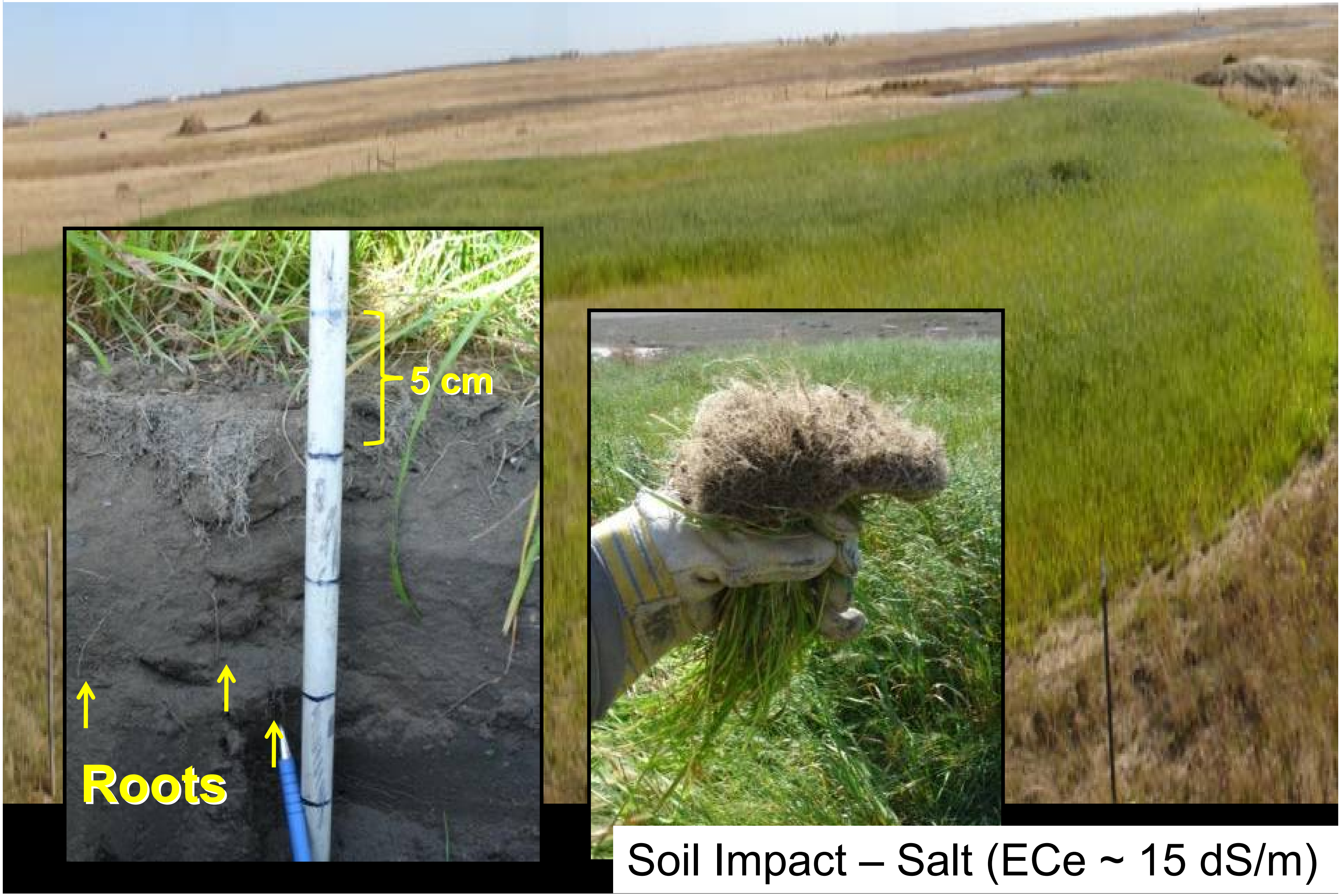
Weyburn, SK - 1: Before PEPS



Weyburn, SK - 1: PEPS utilization – 1 Month

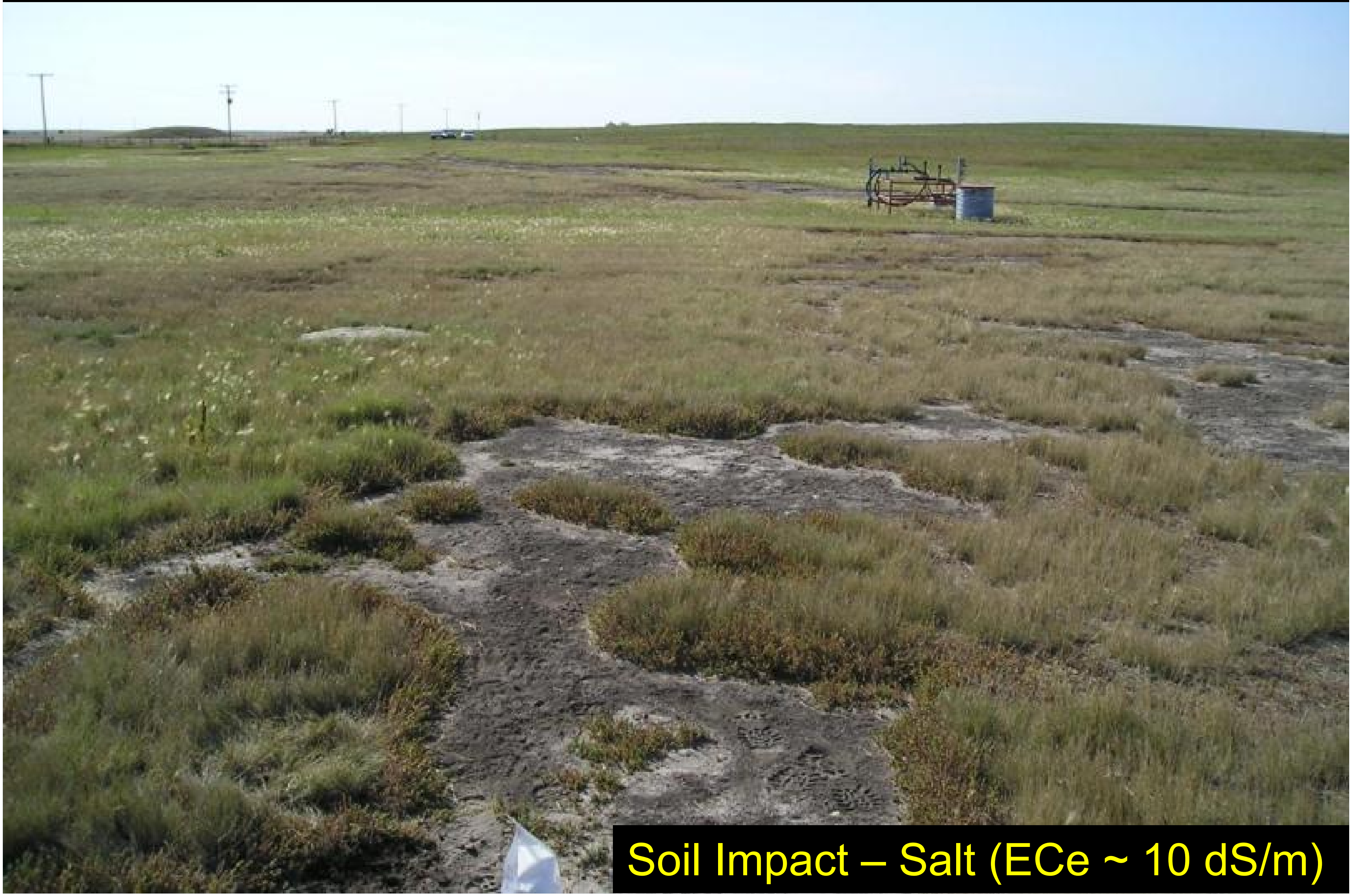
Soil Impact – Salt (ECe ~ 15 dS/m)

Weyburn, SK - 1: PEPS utilization – 3 Months



Soil Impact – Salt (ECe ~ 15 dS/m)

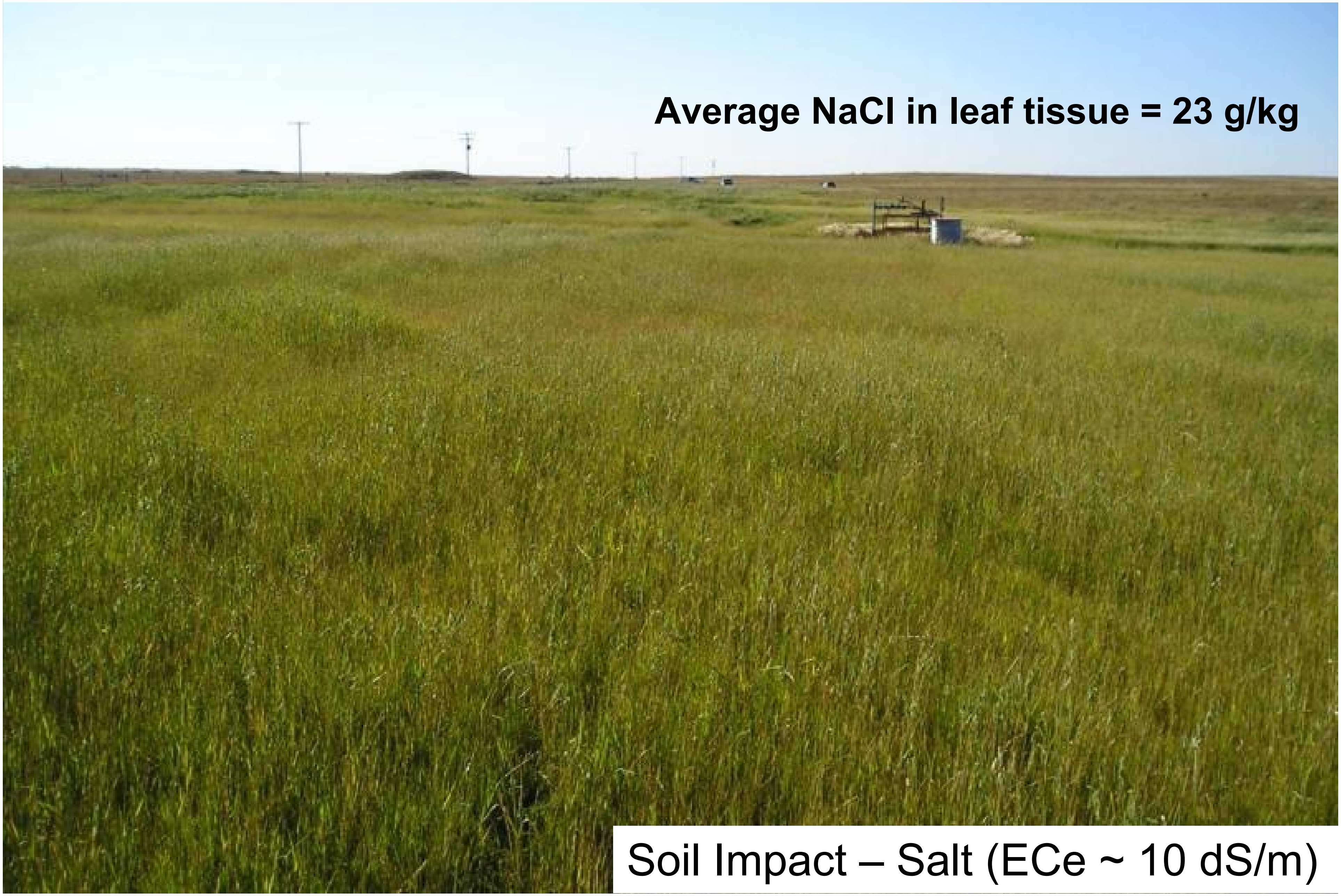
Weyburn, SK - 2: Before PEPS deployment



Weyburn, SK - 2: PEPS deployment – One month

Soil Impact – Salt (ECe ~ 10 dS/m)

Weyburn, SK - 2: PEPS deployment – 3 Months



500 kg of salt (NaCl) off the site in the plants

That is equal to the weight of a cow!

PGPR Enhanced Phytoremediation Systems (PEPS)

Aggressive plant growth strategies leads to remediation

Physical soil treatment: site preparation, site preparation, site preparation

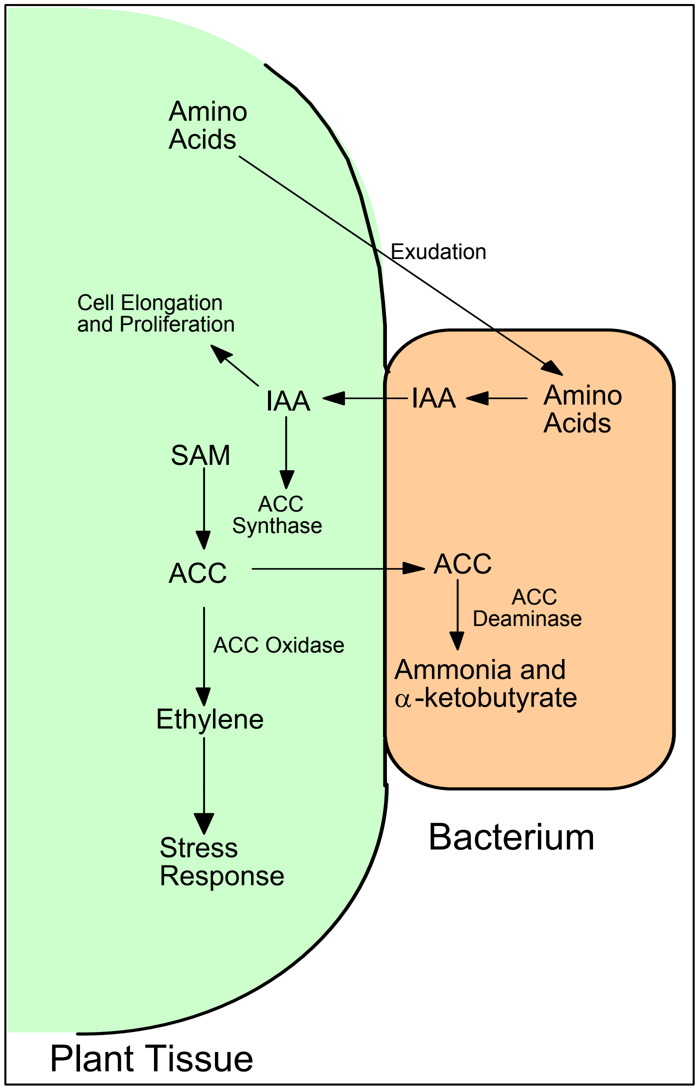
Phytoremediation: Growth of plants **with PGPR**

Monitoring and remediation assessment: Environmental chemistry to follow PEPS from start–to–finish

- <u>PGPR:</u> Plant growth promoting rhizobacteria.
- Prevent the synthesis of stress ethylene.
- <u>PGPR</u> are applied to the grass seeds prior to sowing

  $\rightarrow$ **NOT Bioaugmentation**
- Effect depth of remediation ~ 0.5 m

Interaction of a PGPR Containing ACC Deaminase with a Plant Seed or Root



Plant growth promoting rhizobacteria (PGPR)

Natural, non-pathogenic strains of PGPR (usually *Pseudomonads*)

We have isolated PGPRs from ON, AB, SK and the NWT

PGPR are applied to seeds prior to planting

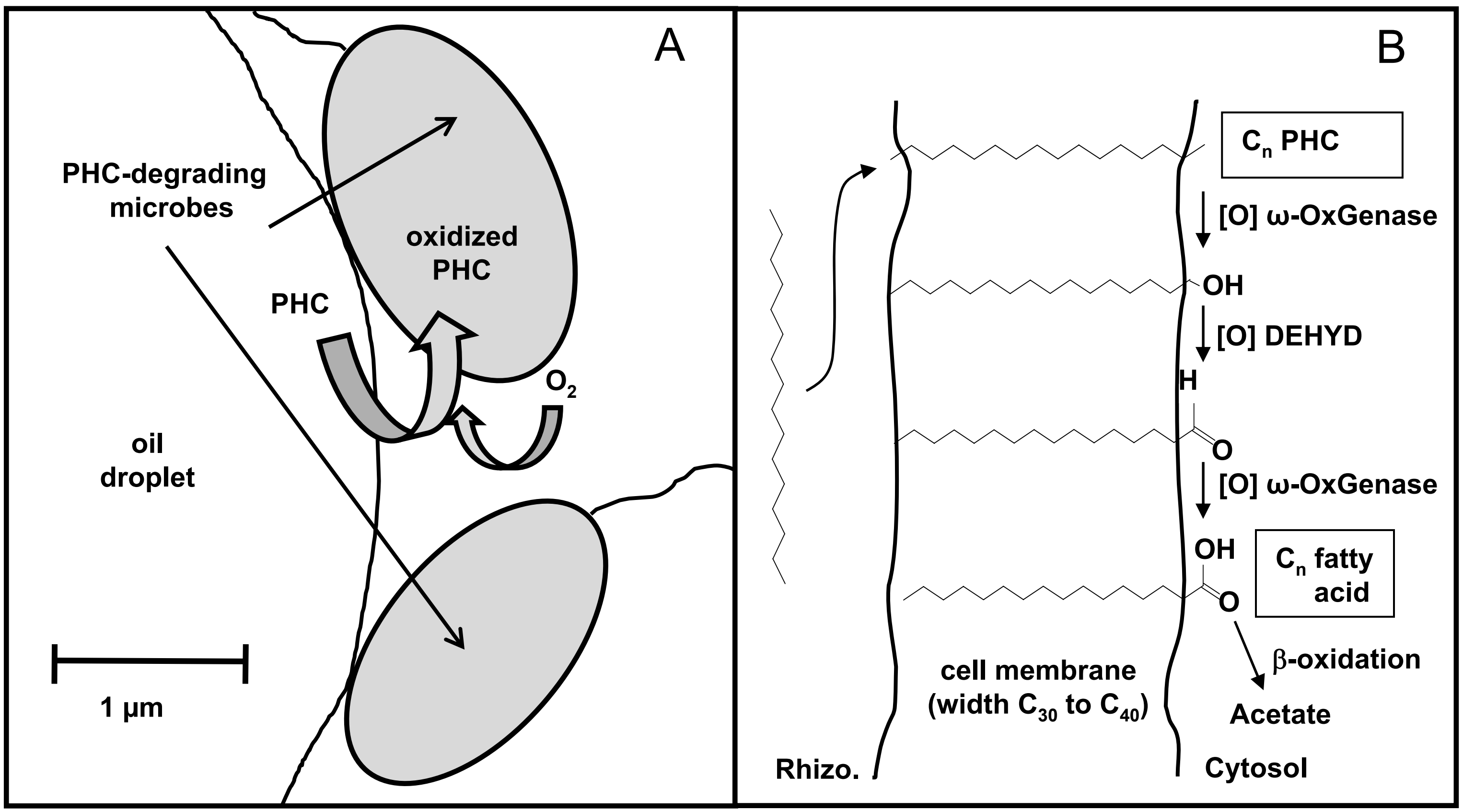
With abundant plant growth – PEPS results in PHC Remediation

- At least twice as much plant biomass due to PGPR; root growth to 50 cm below ground level
- Remediation monitored using CCME PHC analytical methods
- 30 to 40% remediation per year with PEPS; Twice as fast as plants without PGPR
- Rhizosphere microbes (esp. PHC degraders) elevated 10 to 100 fold with the PEPS - microbes and plants consume PHC
- Very low ^{14}C detected in soil microbial fatty acids – Carbon came from PHC metabolism (PHC has no ^{14}C)
- Very low ^{14}C in CO_2 that evolves from soil – PHC has been mineralized to CO_2
- No PHC detected in plant tissue as it disappears from the soil
- Tier 1 criteria (and closure) have been met at several full scale sites

Phytoremediation of PHC

(A) Microbial aerobic PHC degradation – rhizosphere supported by plants

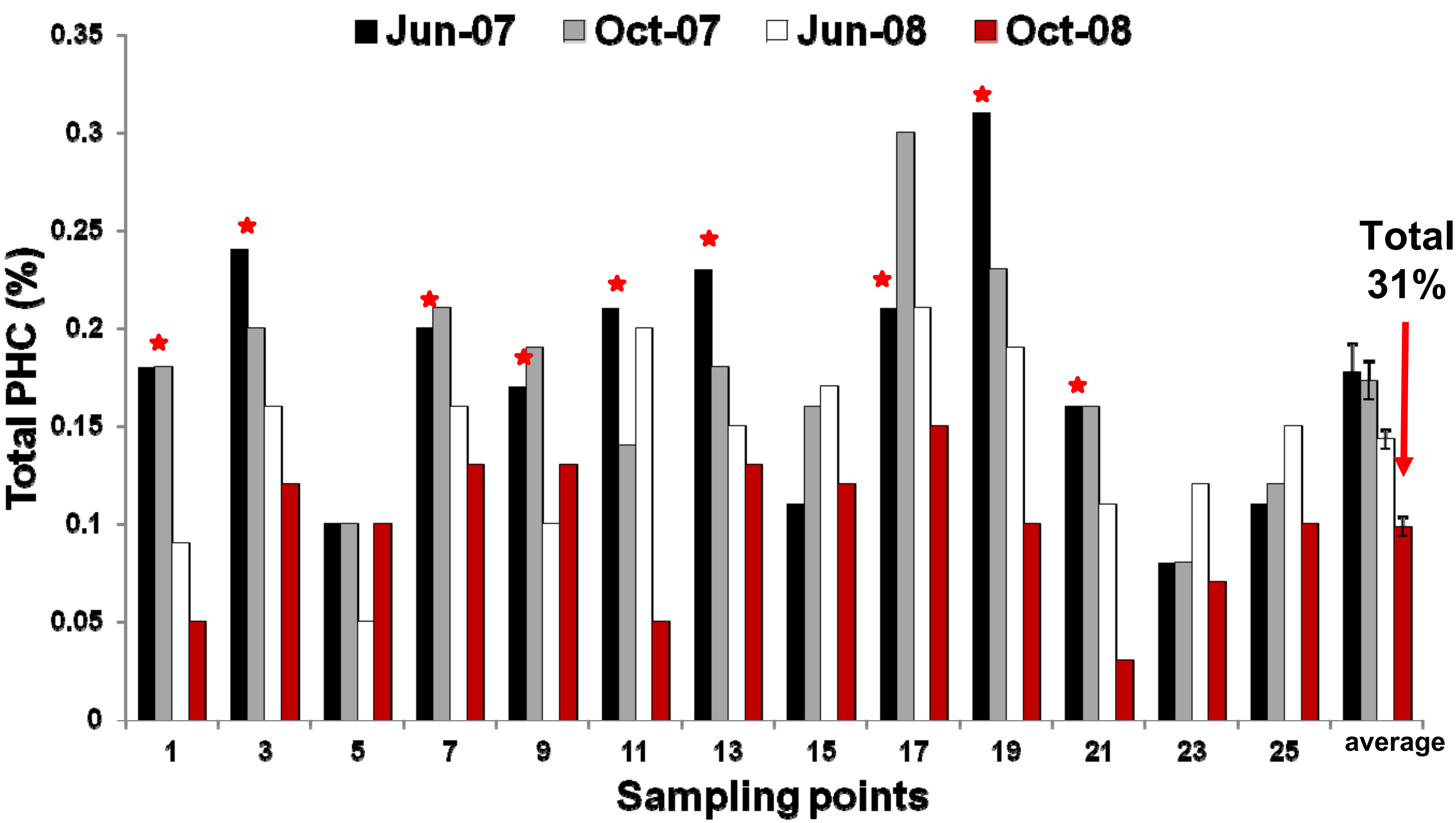
(B) Possible microbial oxygenation pathway of PHC to form a fatty acid



Edson, AB – PHC Remediation (2007- 08)

Soil Impact – PHC (Diesel Invert; 85% F3)

*** In June 2007, 9 of 13 sampling points above Tier 1 criteria (F3 > 1300 mg/kg)**



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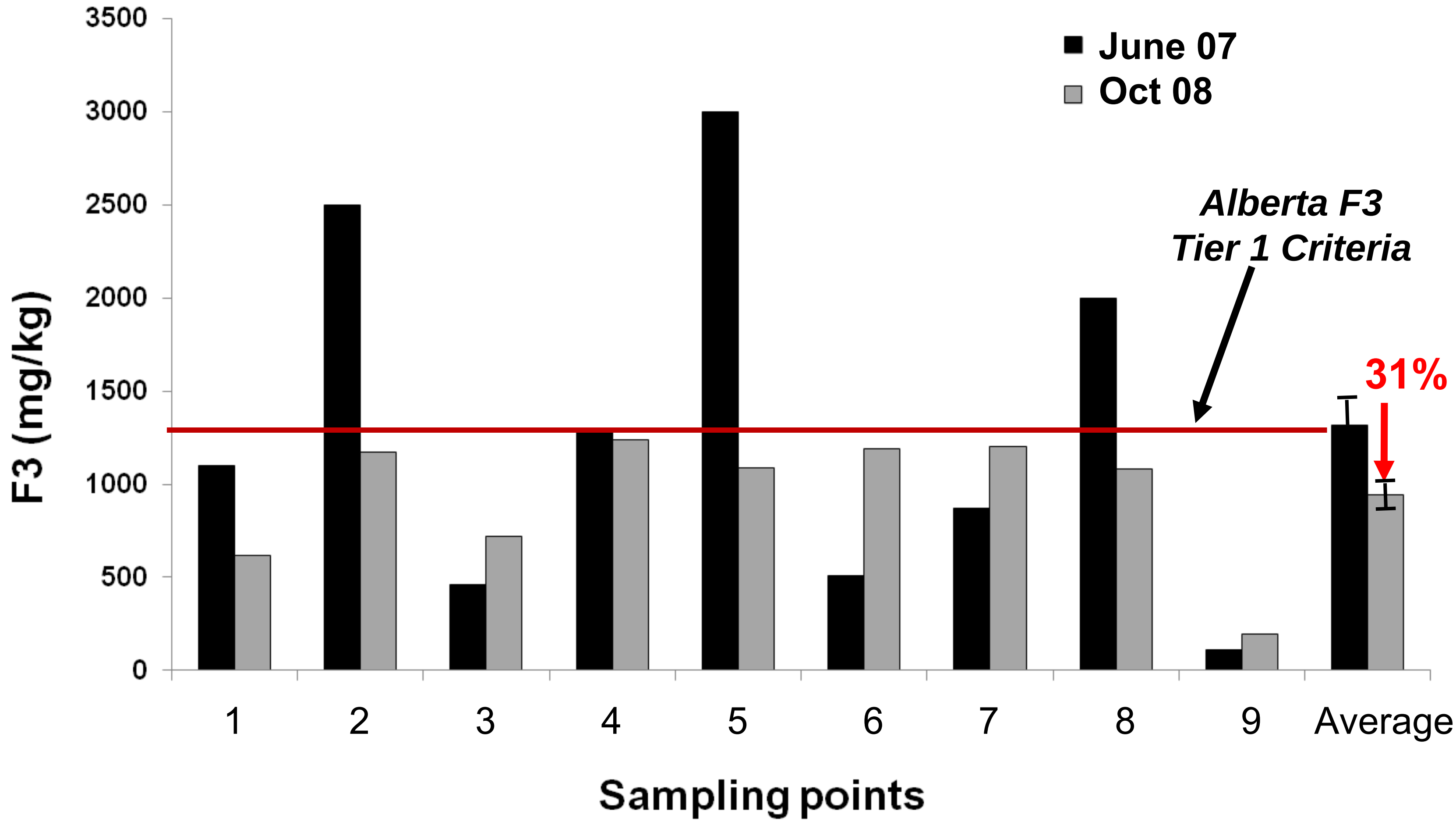


- **Remediation goals were met**
- **No points over Alberta Tier 1 criteria**

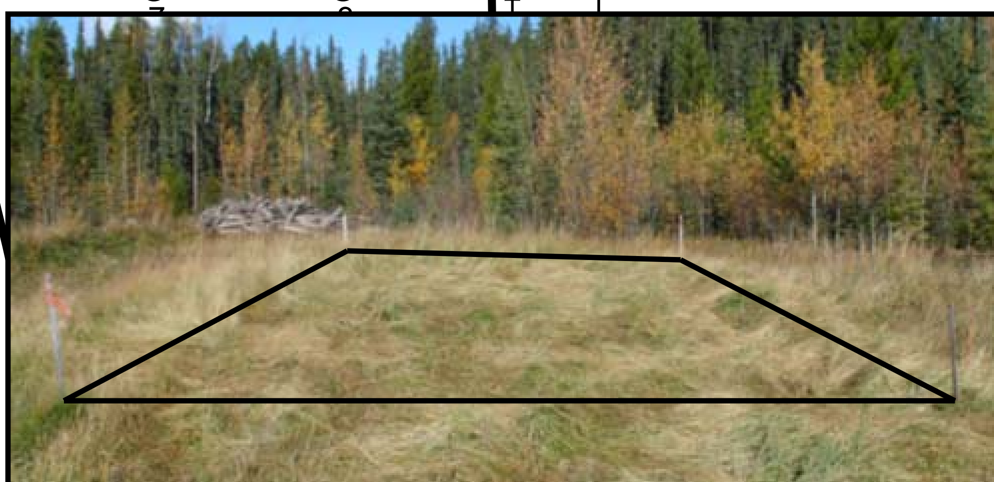
Swan Hills, AB – End of Season (2009 – 10)

Soil Impact – PHC

20 m

Impacted Plot

Planted un-impacted plot

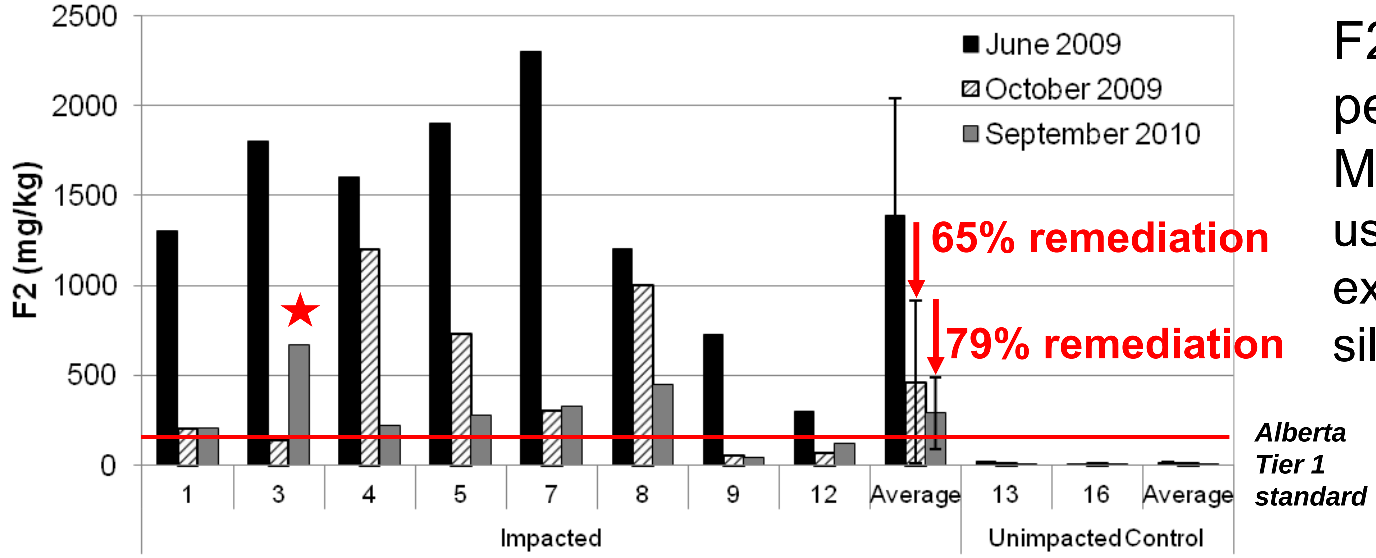


g point

Un-impacted Plot

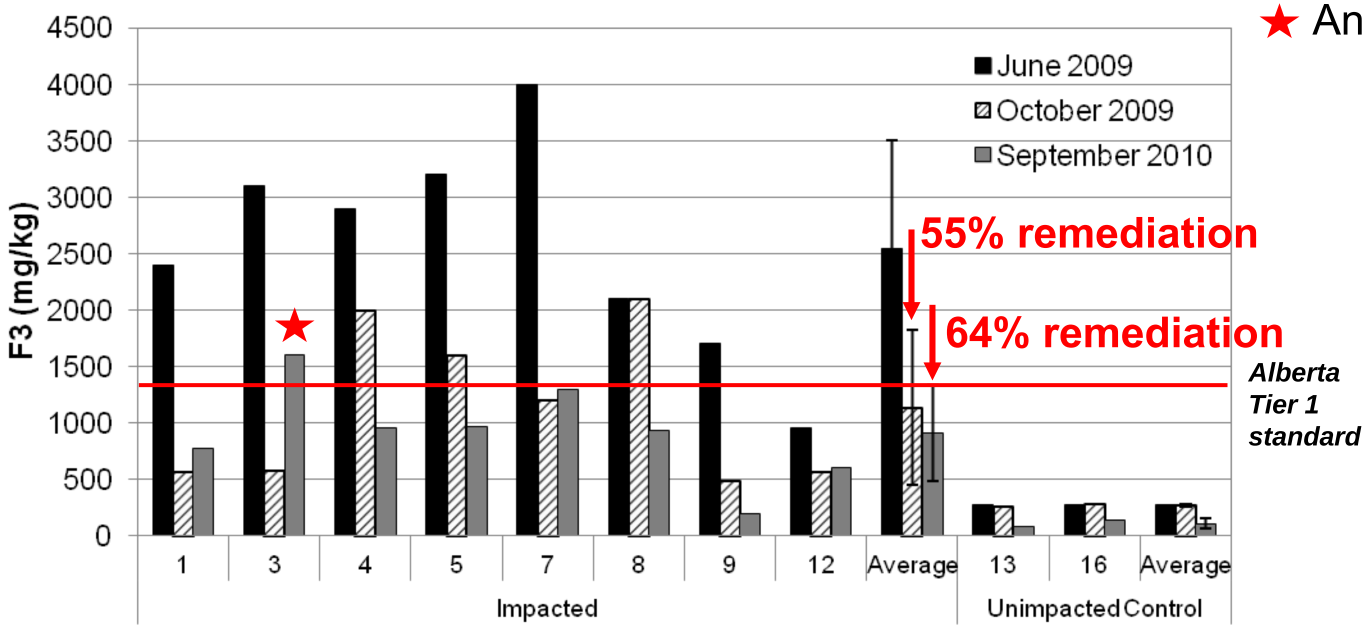
sump

Swan Hills, AB – F2/F3 Results



F2 & F3 analysis performed by Maxxam. Method used: cold shake extraction, enhanced silica-column clean-up

★ Anomalous sample point



Phytoremediation Cost analysis: Edson Site

- Volume of impacted material – 460 m^3 of diesel invert drilling mud was originally spread over 1.07 ha
- 1.07 ha impacted to a depth of 0.3 m or <u>3,210 m^3 of PHC impacted material</u>
- The costs for the entire project was: $104,000 or **$32.50/m^3**
  - Includes all Earthmaster, WEBi and 3rd party costs
  - Costs about the same at remote sites
  - Unit cost drops as volume of impacted soil increases
- Landfilling this material would have cost at least **$80/m^3**
  - 2 h truck turnaround time
  - Costs increase dramatically as the site becomes more remote

Conclusions for PHC Remediation

SUCCESS

- Achieved PHC remediation: 5 sites brought to closure, 11 second generation sites progressing well towards closure

PERFORMANCE PREDICTIONS FOR PEPS

- Fine grain soils - F3 from 2000 to 10,000 mg/kg
  - In 2 to 4 years, will meet Alberta Tier 1 standards
- Fine grain soils - F3 above 10,000 mg/kg
  - In 3 to 6 years, will meet Alberta Tier 1 or 2 standards
- Coarse grain soils - F3 above 3000 mg/kg
  - Phytoremediation will significantly lower F3
  - Tier 2 approach may be required

COST

- Actual cost for the Edson site (3,400 m^3) was \$33/m^3
- Cost to landfill (landfill 1 h from site): at least \$80/m^3

PEPS use at Salt Impacted Sites

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Plant responses to salinity

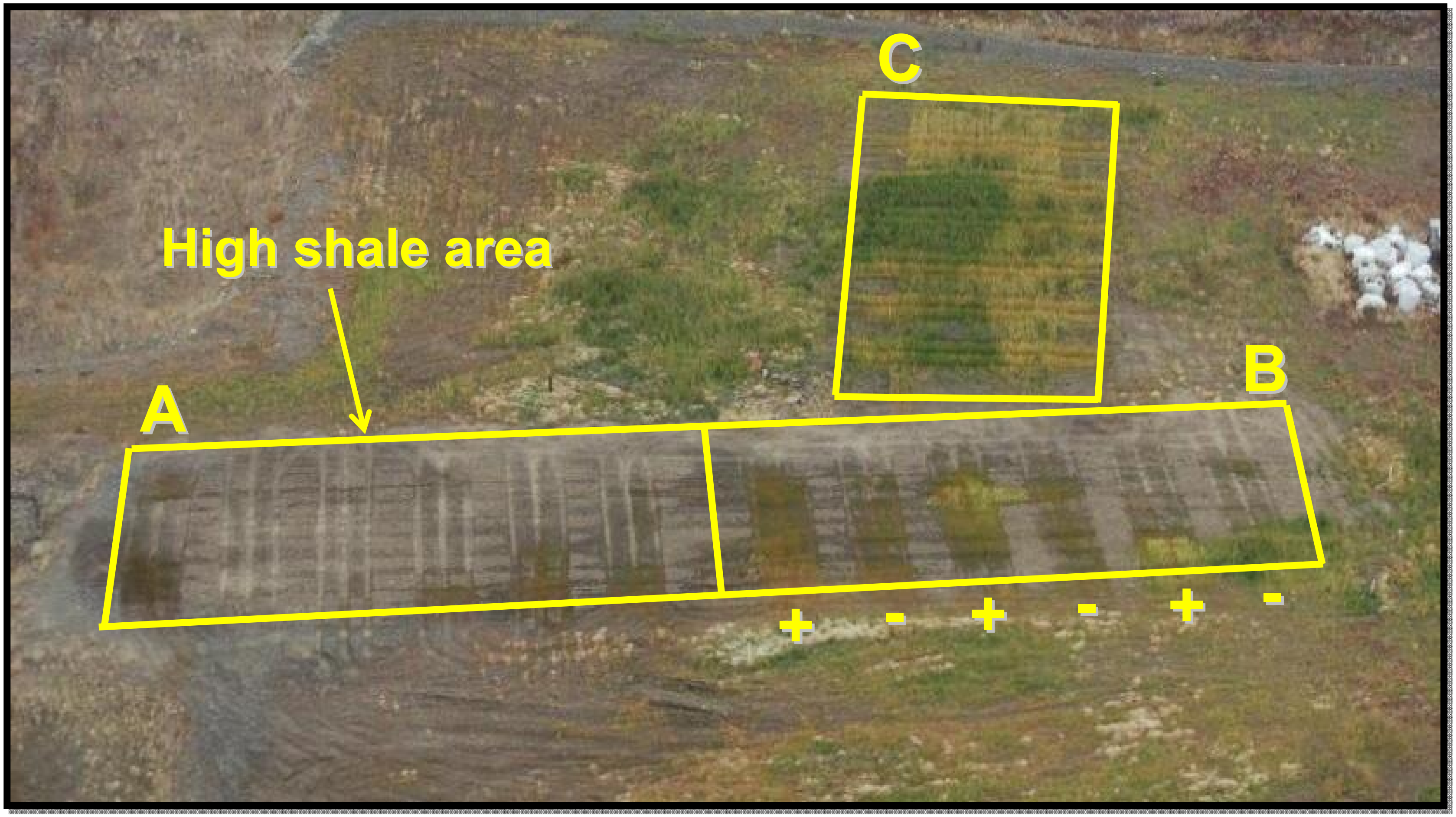
- Inhibited germination
- Decreased water uptake
- Unbalanced sodium/potassium ratios
- Inhibition of photosynthesis
- Increased reactive oxygen species (ROS)
- Increased **ethylene production**
- **PGPR doubles biomass**

Norman Wells, NWT – End of Season (2010)

Soil Impact – Salt

Norman Wells, NWT – End of Season (2008)

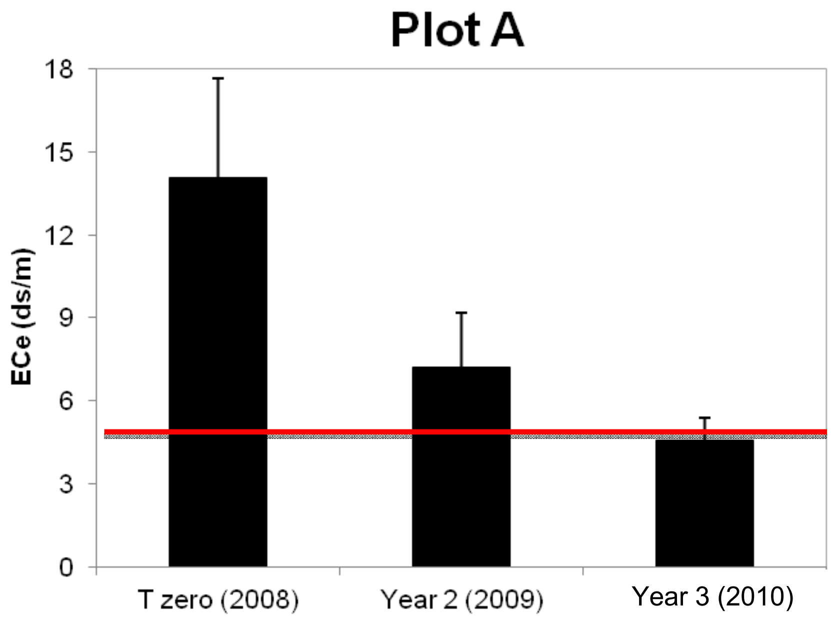
Soil Impact – Salt



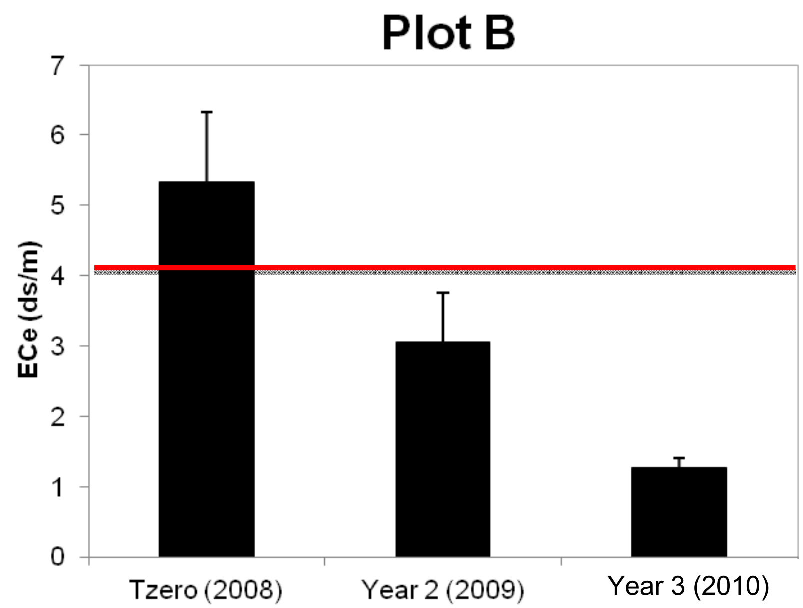
Plants used: slender wheatgrass and red fescue

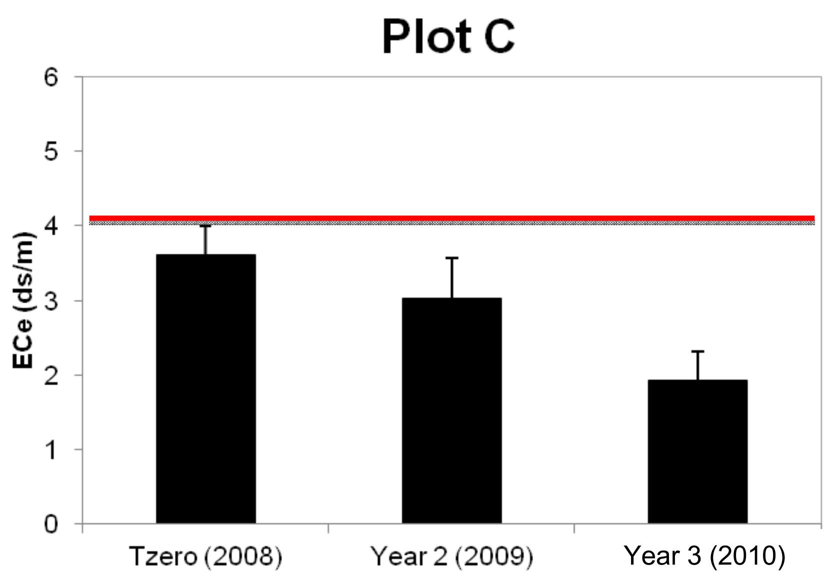
No soil conditioning

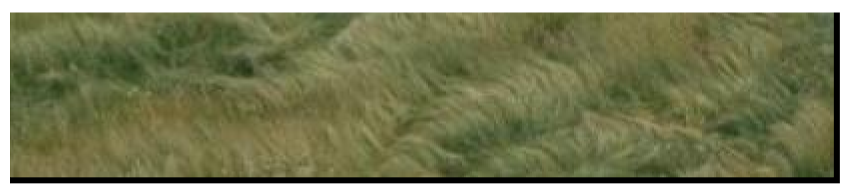
Norman Wells, NWT – End of Season (2010)



Salt Remediation







Mass balance proved salt uptake accounts for drops in ECe

Current Research to Improve PEPS

- Optimize the CCME PHC analytical protocol to remove interferences from biogenic organic compounds (BOC)
- Assess soil toxicity during phytoremediation to meet Tier 2 criteria

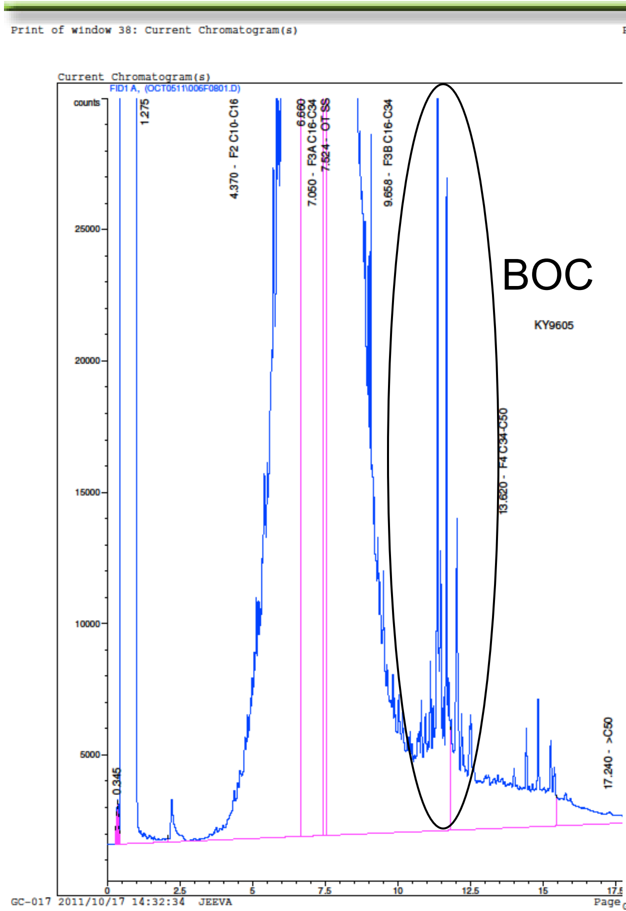
During Phytoremediation – Have to assay PHC without interferences from biogenic organic compounds (BOCs)

- Ontario MOE sampled at 180 pristine rural and old urban parkland sites
- 218 surface soil samples were selected for PHC analysis
- Only 36 of 218 were ND for F3 (For BC: will be in both and EPH_{C10-19} and EPH_{C19-32})
- 8 samples exceeded F3 criteria
- BOCs are primarily derived from plant material – **Issue for phytoremediation**

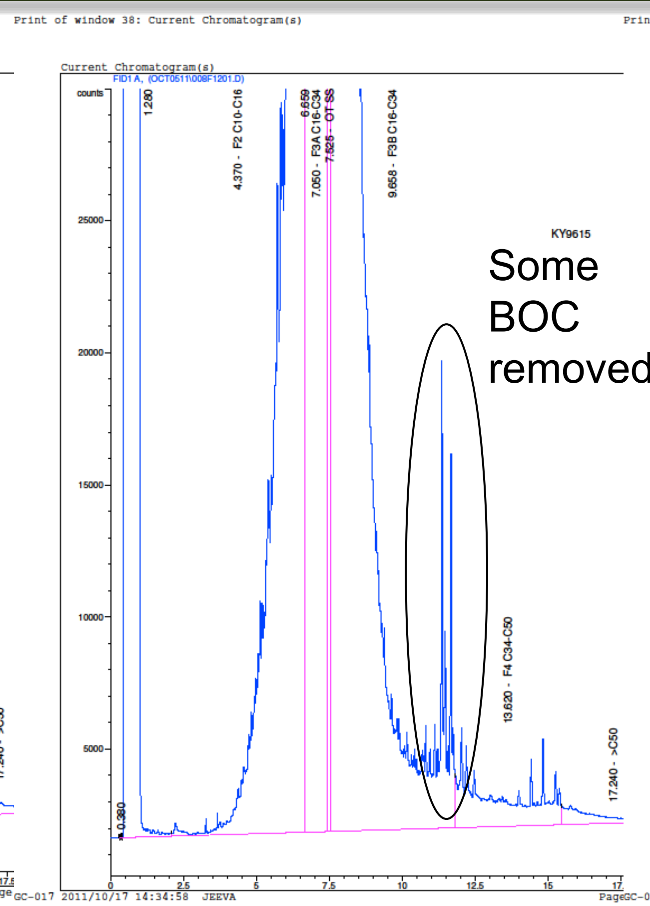
Enhanced CCME method for removal of BOCs

- The CCME method recognizes that BOCs will interfere and leads to a erroneously high PHC data (particularly F3)
- Clean up of extracts with silica gel can be used to help remove interfering BOC
- Proper use of Si cleanup can overcome most of the problems (e.g., Method 10 in BC)
- Two methods: 1. In situ Si treatment (Standard method)
  2. Ex situ Si Column clean-up (Enhanced BOC clean-up)

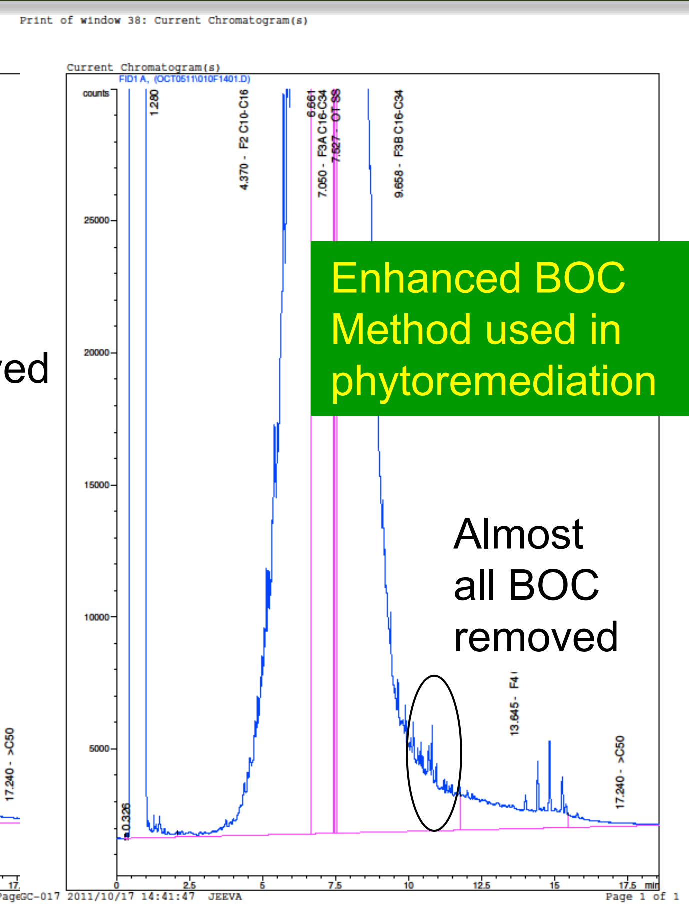
GC-FID analysis of PEPS soil samples with Enhanced BOC Method



No clean up

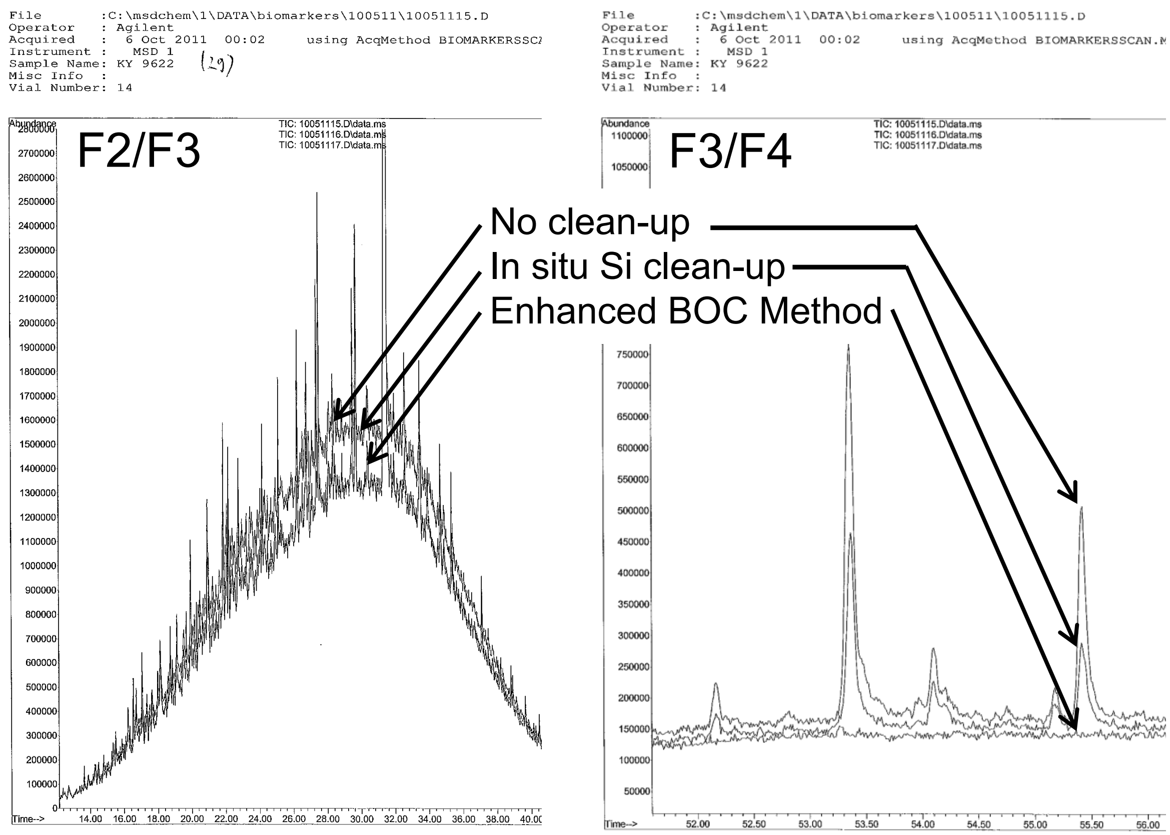


In situ Si gel clean-up



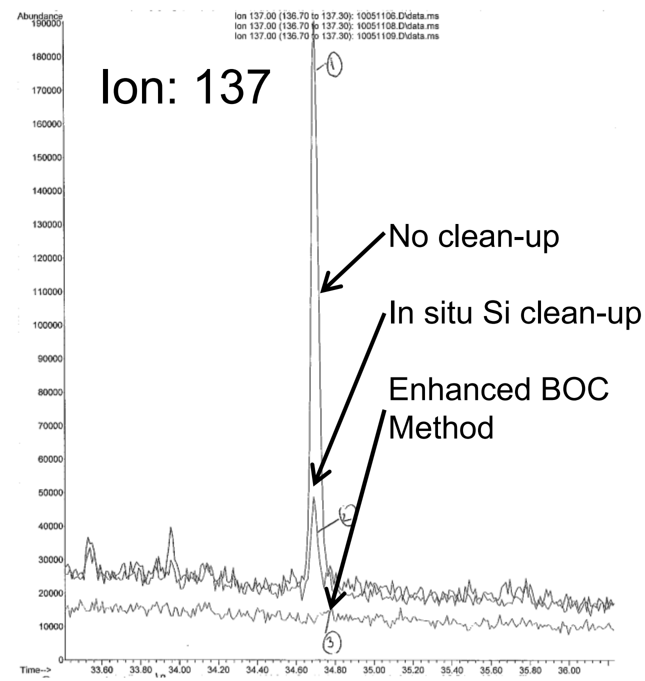
Si gel Column clean-up

GC-MS – Shows only BOC is removed by the enhanced BOC method



Total ion scan – GC-MS | Total ion scan – GC-MS

Compounds identified: plant terpenoids and plant sterols

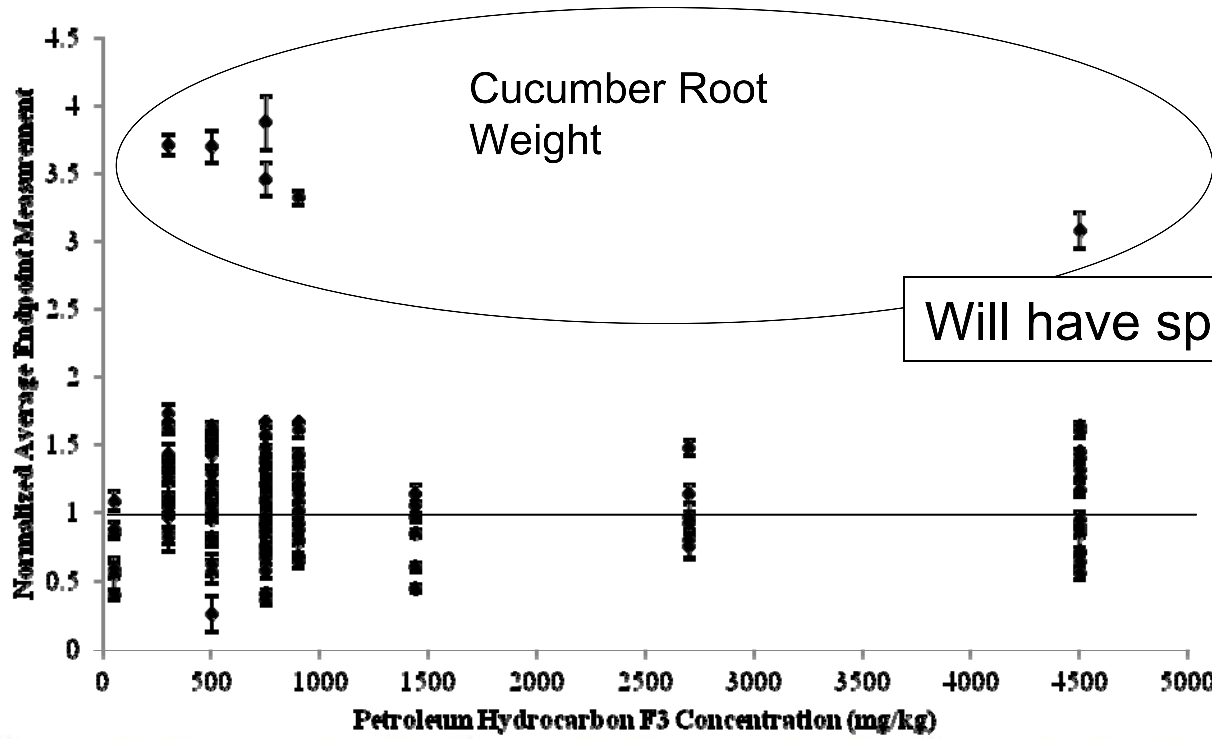


Selective ion scan – GC-MS

Plant toxicity testing – to meet Tier 2 criteria

Followed Environment Canada plant toxicity test protocol

- Plant Species
  - Cucumber, Barley, Northern Wheatgrass
- Endpoints
  - Percent Emergence (7d; 14/21d)
  - Root and shoot length/weight



Plant toxicity not correlated with F3 levels

Will have springtail data shortly

Environment Canada Protocol minimum endpoint requirements for artificial soil

Why Use Phytoremediation?

- Proven to work PHC and/or salt impacted sites.
- Remediations at all sites have been successful; > 25 sites.
- Phytoremediation costs < half the cost of landfilling.
- Liability is reduced, not transferred to a landfill.
- Cost effective at remote sites.
- Enhanced CCME BOC method – phytoremediation will meet Tier 1 criteria.
- Tier 2 approach – will work – After PEPS brings F3 levels ≤ 2500 mg/kg (no plant toxicity).

Thank you

Please visit us at the Earthmaster booth for more information

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