In-situ Phytoremediation of PCB Contamination Limited by Contaminant Concentration

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Overview

- Who are we?
- Research and Development (R&D) – Objective
- R&D Project – Timeline
- Site Background
- Polychlorinated Biphenyls (PCBs) – historical use and structure
- Site characteristics and Test plots
- Field Work Procedures
- PCB Degradation
- Effectiveness of Reed Canary Grass
- Summary and Conclusions
- Acknowledgements

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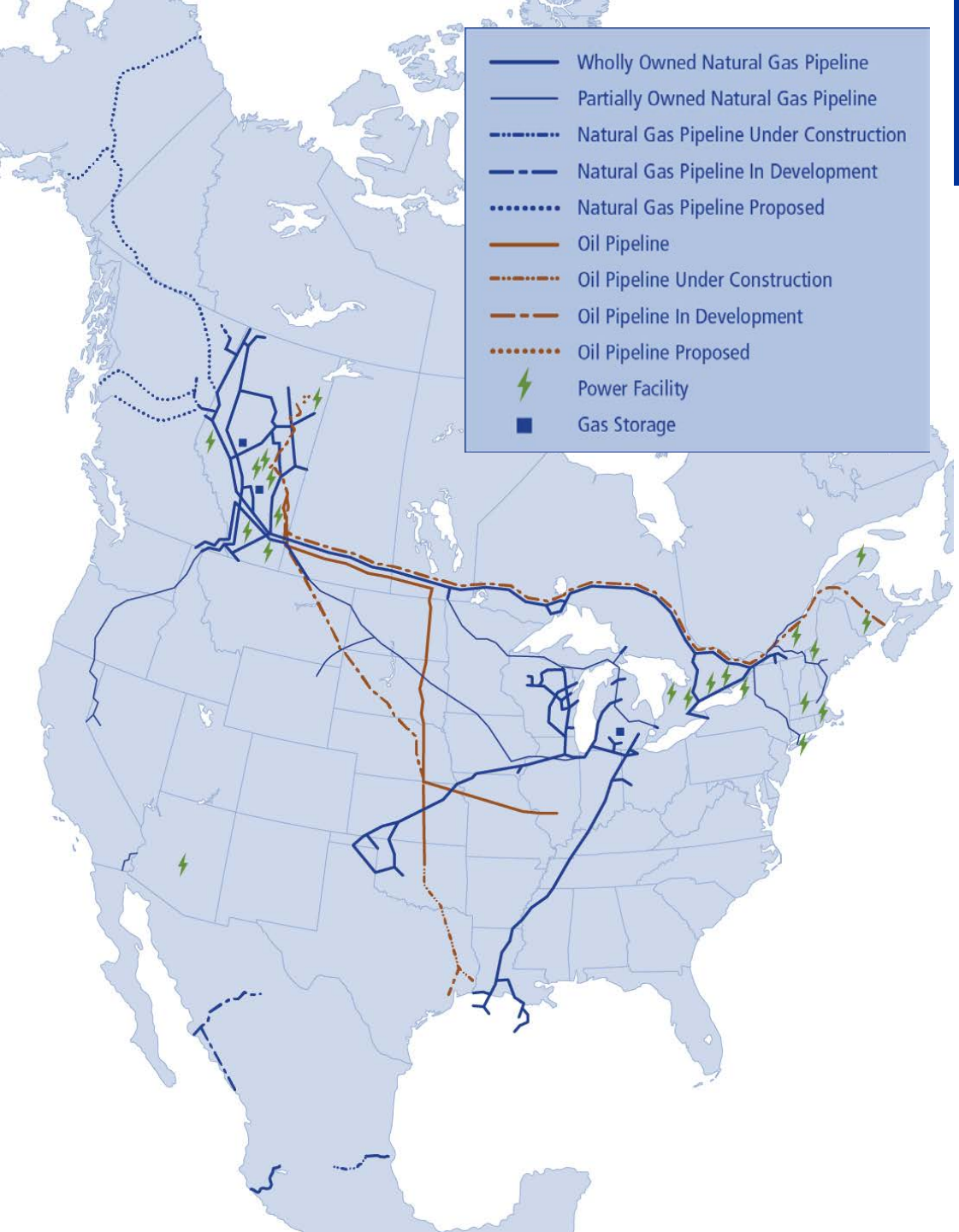
TransCanada's Assets



- **Approx 68,500 kms (42,500 mi.) of wholly owned pipelines**
- **Gas Storage: Approx 400 Bcf**
- **21 wholly or partially owned power plants**
- **> 11,800 MW of total power generation**

Research and Development (R&D) at TransCanada

- For more than 25 years the Technology Management (TM) team at TransCanada has been responsible for the management and coordination of R&D activities. Considerable investment in R&D over the last 10 years.
- TM Program grouped in five Technology Focus Areas (TFA). This project falls under Health, Safety and Environment TFA.

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R&D Project - Objective

- **Objective: to perform a proof of concept of in-situ remediation of Polychlorinated Biphenyl (PCB) contamination limited by contaminant concentration.**
- **Innovative in-situ alternative compared to typical remedial option (i.e. excavation, transportation, disposal). Opportunity to reduce risks and costs.**

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R&D Project – Timeline

- 2006: NRTC approached TransCanada; research literature and some results from work performed at NRTC showed that biodegradation and dechlorination can take place under aerobic conditions in the presence of nitrite and nitrate reduction processes.
- 2008: Site selected in Ontario
- 2009: Consultation with Ontario Ministry of Environment (MOE) to obtain a Certificate of Approval (C of A) to conduct R&D project.
- 2010: Application and receipt of Ontario MOE C of A under Section 9 (Air) of the Environmental Protection Act.
- 2011: First year of R&D Project. Establishment of six plots and site prep. Soil sampling conducted once a month, from June to Nov.
- 2012: Second year of R&D. Three soil sampling events conducted.

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Site Background

- Compressor Station located in Ontario.
- Experimental area within TransCanada property. Not posing an impact to adjacent landowners, drinking water supplies or surface water.
- Three soil investigation and groundwater (GW) monitoring programs between 2000 and 2008. No impact to GW.
- Area inaccessible to vehicles or equipment, characterized by steep slopes, rugged terrain and heavy vegetation.

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Historical Use of Polychlorinated Biphenyls (PCBs)

- Commercial production of PCB began in 1929.
- As components of lubricants PCBs are relatively fire resistant and very stable, these properties made them ideally suited for industrial use.
- PCBs are highly resistant to chemical and biological breakdown by natural processes.
- PCB manufacturing banned in 1977 in North America.
- Federal regulations introduced in 1980 and 1985 allowed for the gradual phase-out of PCBs.
- Ontario PCB Soil Standards changed in 2011 from 25 µg/g to 1.1 µg/g for industrial sites.

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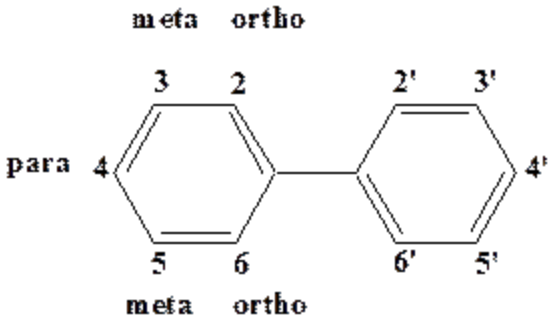
Nature of Polychlorinated Biphenyls (PCBs)

PCB Structure



Characteristics

- 209 isomers or congeners
- Stable
- Wide use as insulating and heat transfer agents
- Do not break down readily in the environment
- Toxic and toxicity persists due to stability
- Some of toxicity linked to activation of Aryl Hydrocarbon Receptor which controls gene transcription and expression

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Biodegradation of PCBs

- Aerobic and anaerobic degradation
- Aerobic processes open the rings
- Anaerobic processes dechlorinate the molecules
- Hudson River and GE
- Dutta and coworkers showed that nitrate reducing organisms degrade PCBs aerobically through dechlorination
- Nitrate reductase enzyme is the agent that dechlorinates PCB
- Therefore can achieve dechlorination and ring cleavage under aerobic conditions.

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Biodegradation of PCBs (cont'd)

- **Our laboratory work suggested that nitrate reducing organisms can degrade PCBs without prior dehalogenation**
- **Our laboratory and field studies showed that growth of reed canary grass and alfalfa stimulated hydrocarbon degradation in a landfarm – phytoremediation**

- **Wanted to apply all this knowledge *in-situ* in a field situation and compare phytoremediation to nitrate reduction based remediation.**

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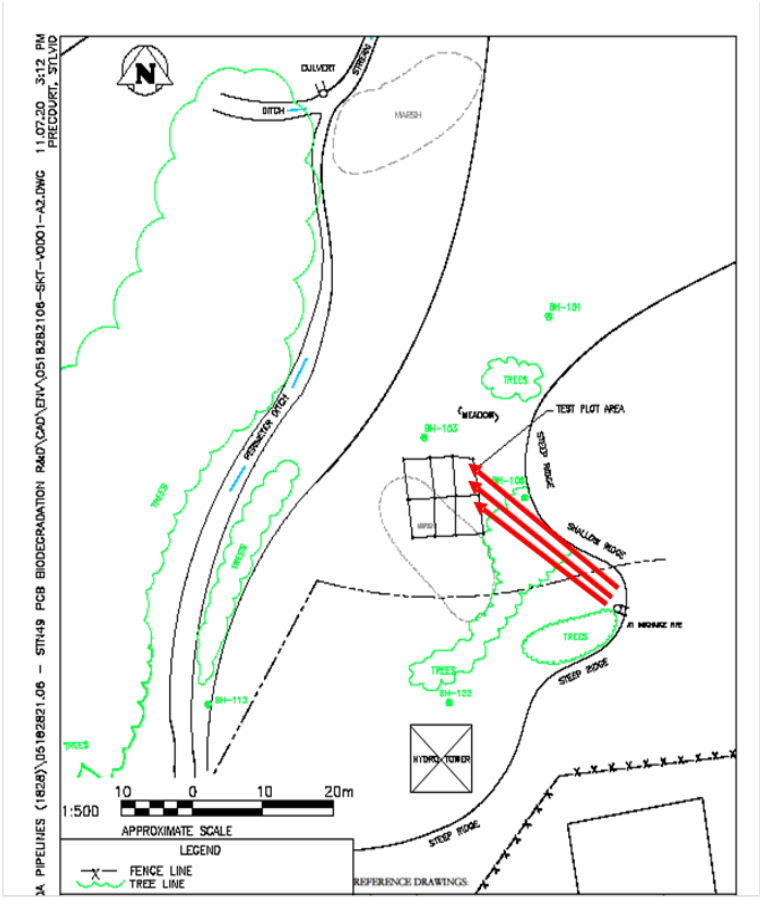
The Field Site Characteristics

- The experimental site area slopes gently to the north west.
- There is a groundwater well just north of the experimental plots to be assessed for downward migration of nutrients and contaminants to the groundwater.
- The soil is somewhat sandy comingled with organic matter and some petroleum hydrocarbon in decreasing concentrations from south east to north west.
- PCB concentration also decreases from south east to north west



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The Test Plots

Description

- **Plot 1: control – no treatment,**
- **Plot 2: nitrogen + phosphorus nutrients and covered with a tarp to induce semi-anaerobic conditions,**
- **Plot 3: nitrogen + phosphorus nutrients + aerobic conditions,**
- **Plot 4: nitrogen + phosphorus nutrients and seeded with reed canary grass – aerobic conditions**
- **Plot 5: nitrogen + phosphorus nutrients + molasses covered with a tarp to induce more anaerobic conditions ,**
- **Plot 6: nitrogen + phosphorus nutrients and seeded with alfalfa – aerobic conditions.**

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Field Work Procedure

- **Sampling locations – 5 points per plot**
- **Fertilized with nitrate and phosphorus over the summer periods for two years.**
- **Nitrogen and phosphorus added to achieve carbon:nitrogen:phosphorus ratio = 100:1.0:0.1**
- **Nitrogen and phosphorus added monthly June to November**
- **Monitored monthly over the summer periods**
  - Microbial numbers
  - PCB concentrations
  - Nutrient levels
  - Groundwater well also monitored to ensure no contamination migration to the groundwater and moving offsite

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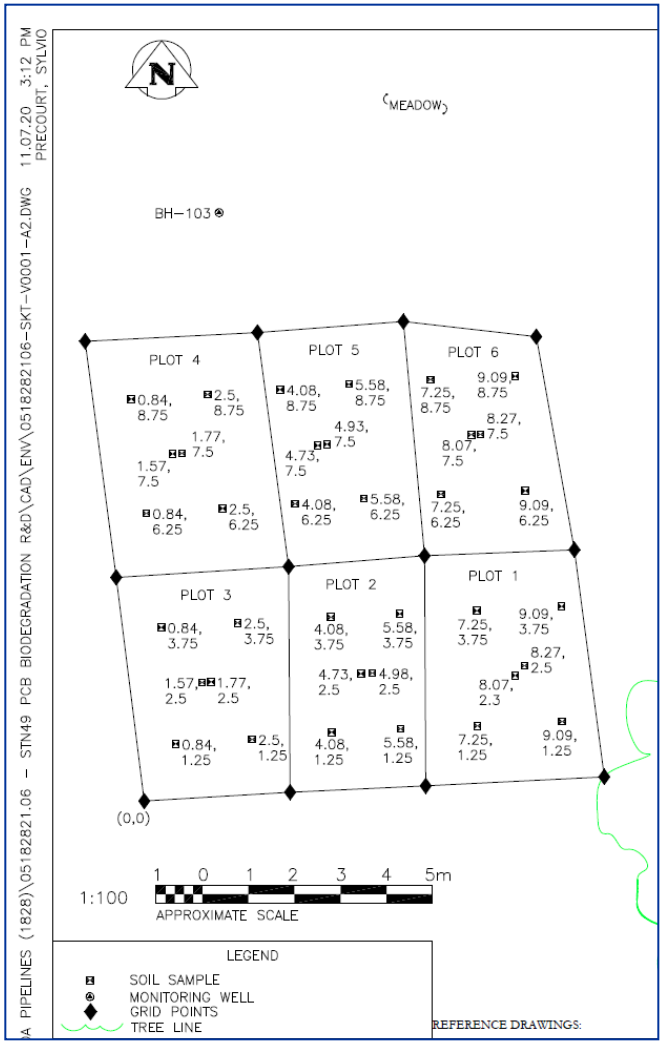
Outline of the Test Plots



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GW Well Results

- Over the two years of the study water from the groundwater well contained few PCB degrading microbes ($\leq 10^3$ microbes per mL).
- Over the two years of the study no PCBs and no PCB metabolites were found in water at the groundwater well.
- The conclusion is that neither nutrients or PCB contamination is leaching through the soil to reach the groundwater.

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Soil Results

- **To show PCB degradation is occurring we examined**
  - PCB metabolizing microbes
  - PCB concentration reduction
  - Effects on individual PCB congeners
  - PCB degradation products

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PCB Metabolizing Microbial Numbers in Test Plots

- Microbial numbers were enumerated with the most probable number dilution series technique
- Microbes were tested for growth on 4-aminobiphenyl: orange/yellow and insoluble, monitor turbidity and production of orange, soluble dinitrobiphenyl to indicate growth.

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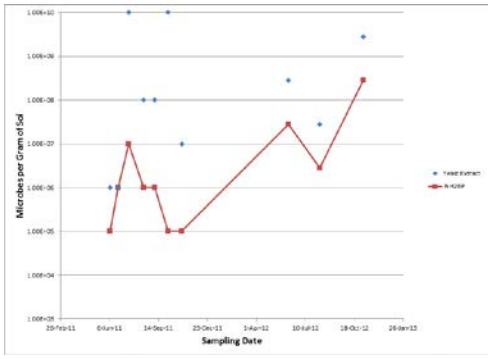
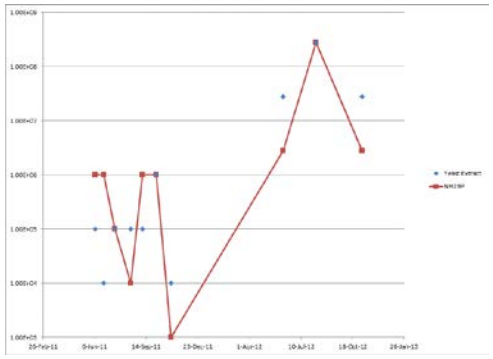
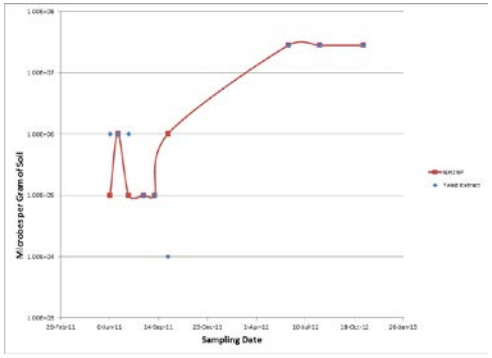
Microbial Numbers in Test Plots Over two Years



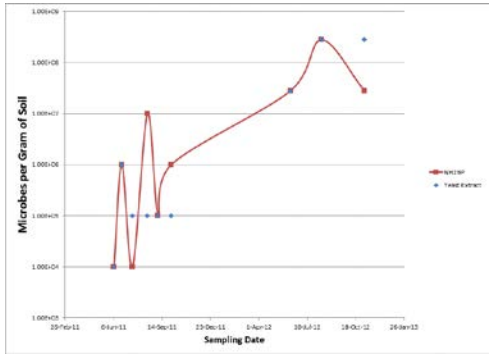
Plot 1



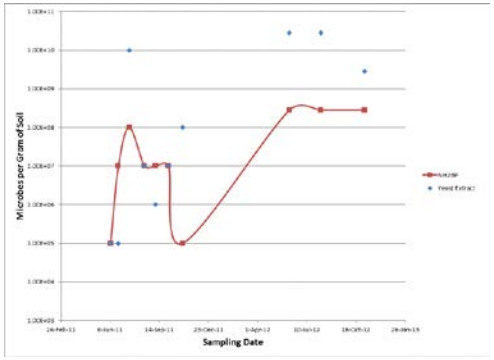
Plot 2



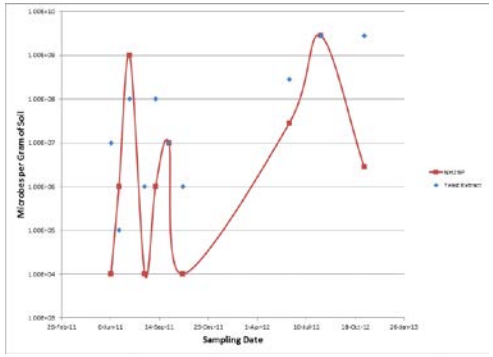
Plot 3



Plot 4



Plot 5



Plot 6

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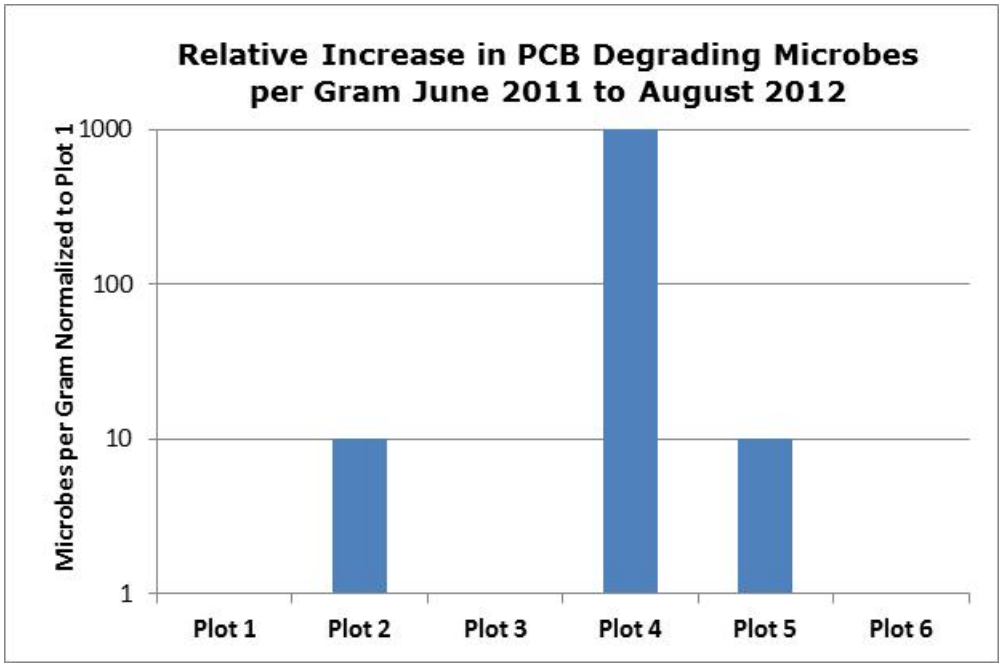
Microbial Numbers in Test Plots Over two Years (cont'd)

- Microbes including PCB degraders increased in all plots over the two yeas of the study. This occurred even in the control plot which received no nutrient supplements.
- However the increase in numbers of PCB degrading microbes was greatest in Plot 4 which received nutrients and Reed Canary Grass.



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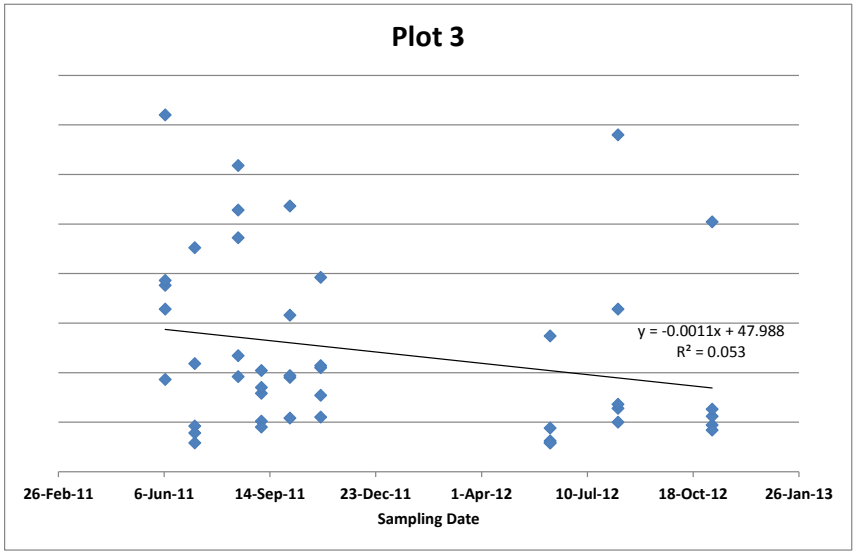
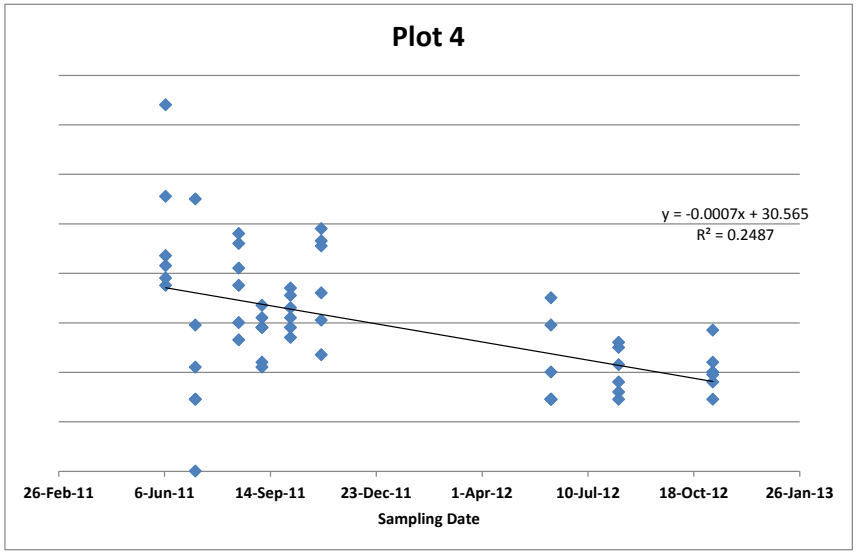
PCB Concentration Reduction

Statistical analysis of PCB concentrations in the test plots over the two years did not support a statistically significant PCB removal. The scatter in the data at each sampling point was too large to allow significance. Only in Plot 4 was the PCB loss marginally significant. The correlation in Plot 4 was 5 - 10 x better than in other plots.





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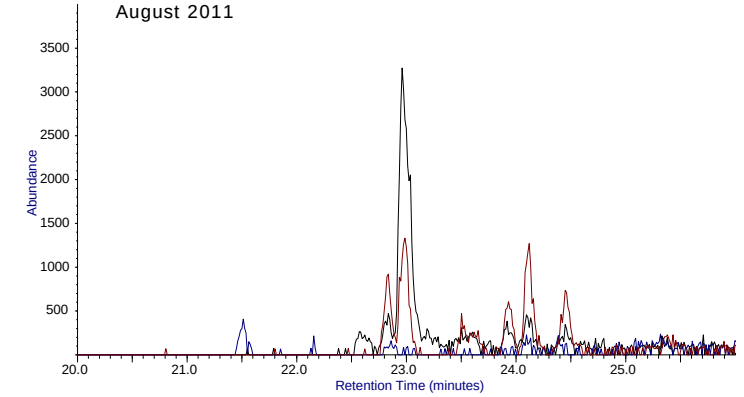
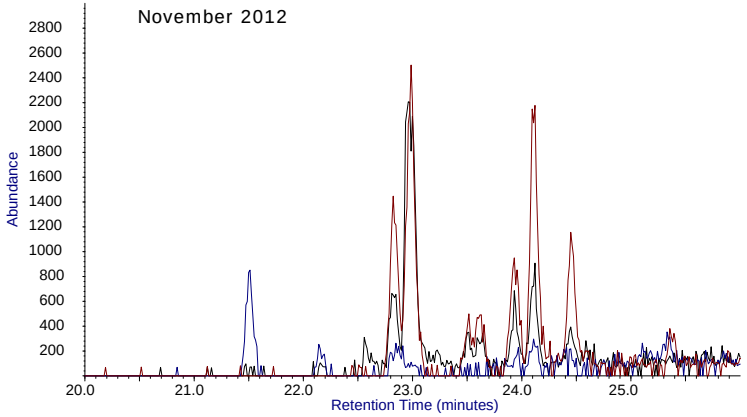
Effects on Individual PCB Congeners

Loss of individual PCB congeners in gas chromatograms

Examination by GCMS of PCB congeners in extracts of the soil from the test plots did not show losses of individual PCB congeners over time in Plots 1, 2, 5 and 6, implying that no PCB degradation was occurring in these locations. See data for Plot 5 below.





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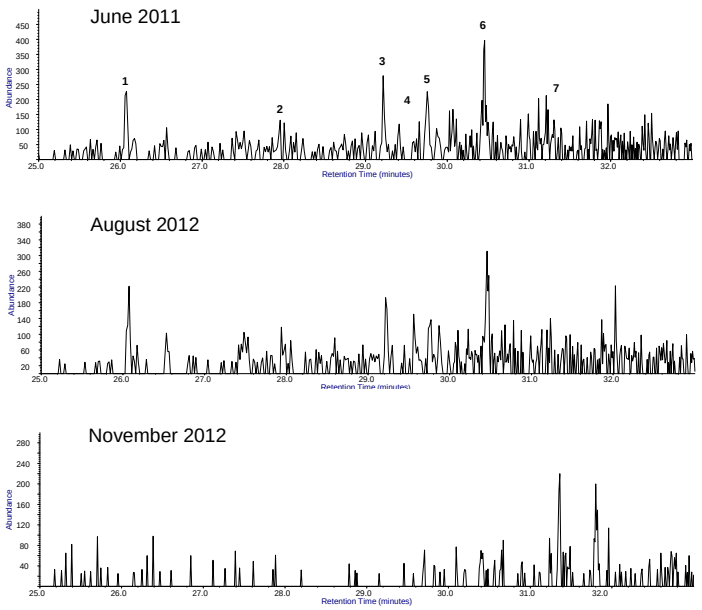
Effects on Individual PCB Congeners (cont'd)

GCMS analysis of extracts of soil from Plot 4 showed significant loses of individual PCB congeners over the two years of the study. By November 2012 there were only traces of extractable PCBs left in the soil from this plot.



Peaks:

1 = Tetrachlorobiphenyl

2 = Pentachlorobiphenyl

3, 4, 5, 6, 7 = Hexachlorobiphenyl

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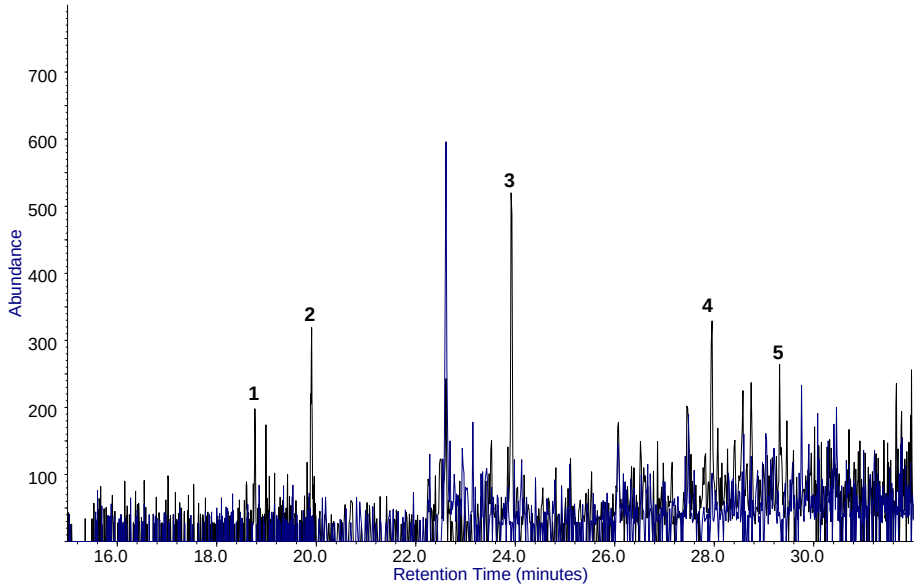
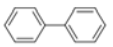
PCB Degradation Products

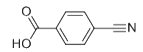
Degradation Products Found in Plot 4



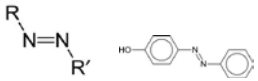
1 Biphenyl



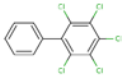
2 4-cyanobenzoic acid

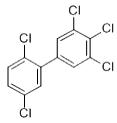


3 Azo-compound



4, 5 Pentachlorobiphenyls





Plot 4 was the only plot where these products were found. The presence of degradation products supports degradation of the PCBs in this plot.

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Support for a Conclusion that PCB Degradation is Occurring

- **The following lines of evidence demonstrate that PCB degradation is occurring in Plot 4:**
  - Increase in PCB degrading microbes
  - Total PCB concentration reduction (70%)
  - Loss of individual PCB congeners in gas chromatograms of soil extracts
  - The presence of PCB degradation products in the soil.

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Why Is Reed Canary Grass Effective?

- Reed canary grass has an extensive root system.
- Root system provides exudates for microbial growth and stimulation.
- The root system provides colonizing sites for microbial growth.

Comparison of root mass of Reed Canary Grass, Alfalfa and Clover

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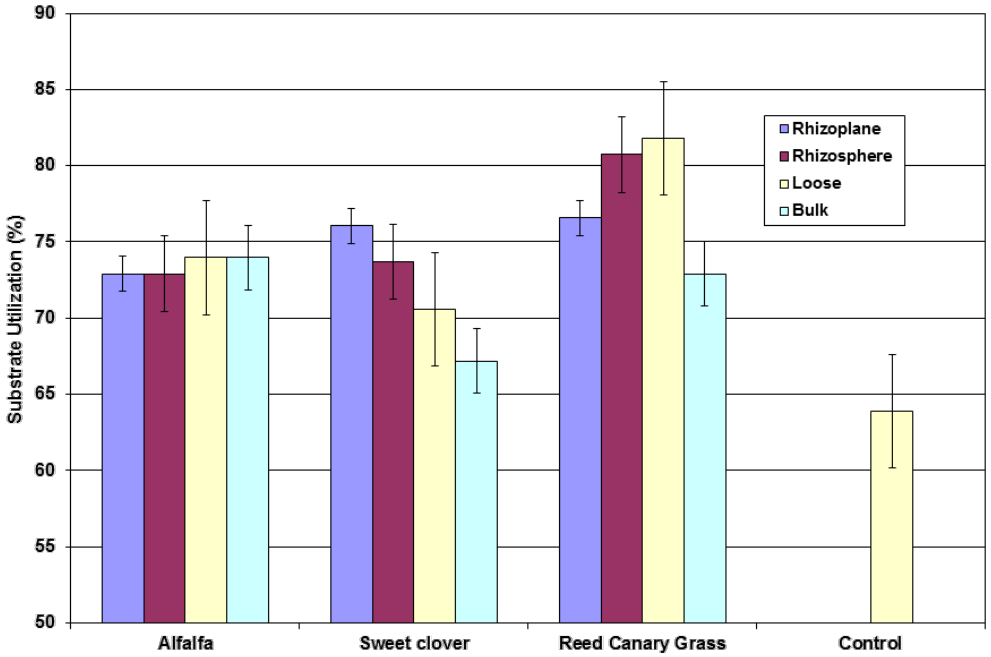
Why Is Reed Canary Grass Effective? (cont'd)

Comparison of metabolic capability of rhizosphere populations of Reed Canary Grass, Alfalfa and Clover

- **The rhizosphere population of Reed Canary Grass is more diverse than that of Alfalfa or Clover or of the bulk soil.**



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Summary and Conclusions

- PCB degrading organisms increased in all test plots, including the control, over the course of the field study.
- PCB degrading organisms increased the most in Plot 4 treated with fertilizer and reed canary grass.
- PCB degradation products, including biphenyl, accumulated in Plot 4 treated with nitrate and phosphate fertilizer and reed canary grass.
- Loss of particular PCB molecules and accumulation of less chlorinated species were observed in Plot 4.
- A minor increase in numbers of PCB degraders in the other test plots did not produce overall PCB concentration losses, individual PCB congeners were not removed and PCB degradation products did not accumulate.
- At the end of the study PCB peaks were mostly removed from the soil in Plot 4 and this confirmed the observation of general PCB reduction in that plot.

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Acknowledgements

- We thank TransCanada Pipelines for financial support and for providing a site for this research project.
- We thank the Analytical Group at NOVA Chemicals Research and Technology Centre for excellent technical assistance.

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