Toxicity Testing to Evaluate Bioremediation Endpoints at Upstream Oil and Gas Facilities

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Outline

- Background
- Objectives
- Methods
- Results
- Conclusions
- Questions

Petroleum Hydrocarbons

- Petroleum Hydrocarbons (PHC):
  - mixture of organic compounds derived from geolog substances (e.g., gas,diesel, crude oil)
  - lower MW PHC: more mobile
  - higher MW PHC: more persistent
- PHC composition at a given site:
  - Function of source, age of release, extent of degrada or transformation, weathering and site-specific facto (geology, hydrogeology etc.)

PHC Contaminated Sites

- Canada (CCME, 2000):
  - >10,000 PHC Contaminated Sites
  - Liability: ~ $10 B
- Canada Wide Standards:
  - 3-Tiered standard
  - Soil/subsoil
  - Human/environment
  - RA/RM

Elements of Risk

CCME PHC Canada Wide Standard

- PHC Fractions (CCME, 2000)
  - F1 (C6-C10)-BTEX
  - F2 (>C10-C16)-PAHs
  - **F3 (>C16-C34)-PAHs**
  - F4 (C34+)
- Standards are a function of land use, exposure pathways, soil texture (fine vs. coarse) and depth o contamination (surface vs. subsurface)

CCME PHC Canada Wide Standard

- PHC Fractions (CCME, 2000)
  - F1 (C6-C10)-BTEX
    - Coarse (HH: vapour inhalation)/Fine-(HH: gw in
  - F2 (>C10-C16)-PAHs
    - Coarse and fine-grained (HH: groundwater inges
    - Coarse-grained: Aquatic Life (water body adjace
  - **F3 (>C16-C34)-PAHs: Direct soil contact (EH)**
  - F4 (C34-C50)/F4G (C50+): Direct soil contact (EH

Upstream Oil and Gas Facilities

- Sources of PHCs:
    - Flare pits, Drilling Sumps, Wellheads, Tank Farms and Pipelines
- Hydrocarbons become issue at most Sites, based o assessment data vs. remediation guideline
- Most sources: PHC F3 (>C16-C34) CWS becomes remediation target

The Nature of PHC F3

- PHC F3 (>C16-C34): broad range of solubility, K
  - >C16-C21 subfraction (more soluble/toxic)
  - >C21-C34 subfraction (less soluble/toxic)
  - Broad range of physico-chemical properties a toxicity

CCME Ecosoil Contact Guideline

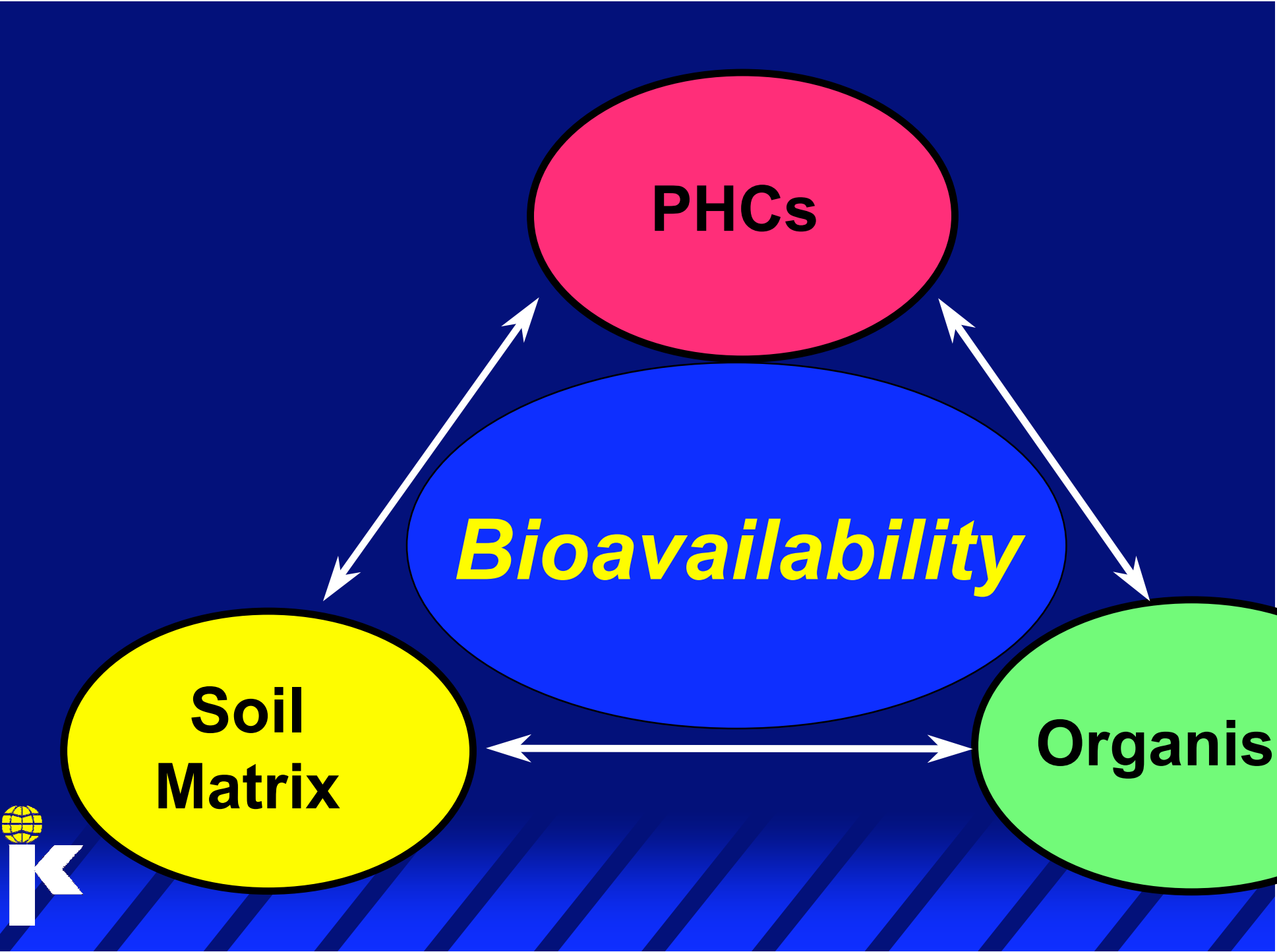
- CCME CWS ecosoil contact based on toxicity test (acute, chronic, subchronic) with distillates of Federated Crude Oil
    - Simulates fresh spill of individual fraction
- Federated Crude Oil (PHC F3):
    - >C16-C21 subfraction (45 %)
    - >C21-C34 subfraction (55 %)

Biodegradation of PHC

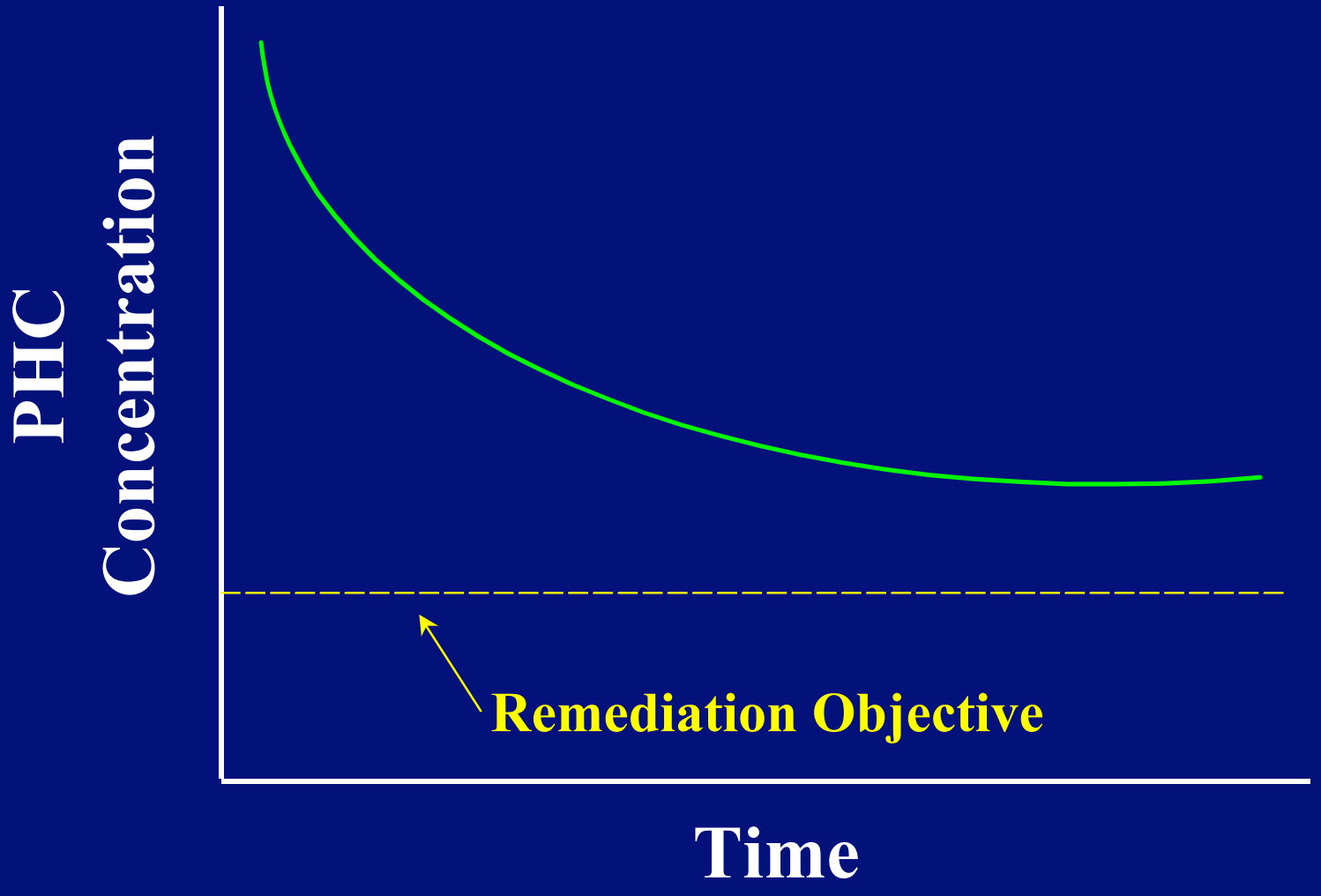
- Bioremediation of PHC contaminated media:
  - cost-effective
  - practical: can be used *in situ* or *ex situ*
  - results in mineralization or transformation of
- In many cases, residual PHC concentrations remai
  excess of Tier I remediation endpoints particularly
  PHC F3

Aging and Bioavailability of PHC

- Biodegradation of more labile (available) PHC lea
  a residual PHC fraction that is much less available
  mobile (*biostabilization*)
- *Aging phenomenon*: hydrocarbon availability withi
  geosorbents decreases with time (e.g., earthworm
  uptake and bacterial mineralization)
- *Chemical extractability versus bioavailability*: how
  you define risk-based endpoints??


PHCs
Bioavailability
Soil
Matrix
Organis

The "Aging Effect"



Questions

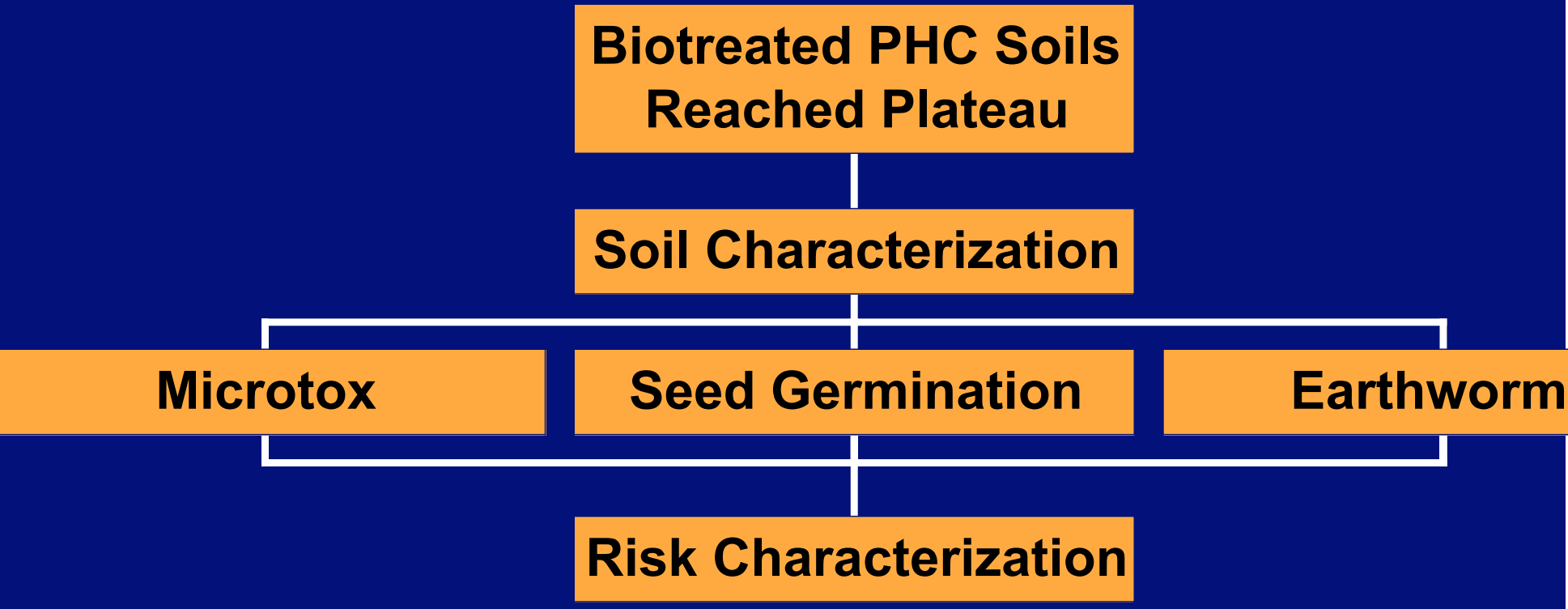
- Is the addition of freshly added hydrocarbons to so
  indicative of toxicity of weathered, aged hydrocarb
- Are remediation endpoints that we are trying to ach
  appropriate, what is the risk if we don't meet the g
- Is this mixture used in CCME CWS development
  representative of PHC F3 compositions found in
  Alberta?

Research Objectives

Using a battery of toxicity tests, we evaluated:

- Toxicity of residual PHC in four biotreated s
- CCME PHC Standards against the measured toxicity of weathered biotreated PHC contaminated soils
- Composition of PHC F3 within biotreated so vs. Federated Crude used in CWS developme

Experimental Design



Materials and Methods: Soils

PHC Contaminated Soils:

- Oil and Gas Facilities (Alberta)
- Soils A, C and D: drilling wastes
- Soil B: crude oil
- Control Soil
- PHC degradation in all soils reached plateau above Tier I

Materials and Methods: Physical-Chemical Characterization

Soil Characterization:

- particle size distribution
- pH, EC, main soluble ions
- Organic Matter
- CCME PHCs
- Polycyclic aromatic hydrocarbons
- Metals and inorganics

Bioassays and Screening Level Assessment of Earthworm Tissues

- Microtox®
- Seed Germination
  - Oat *(Avena sativa)* & radish (*Raphanus sativ*
- Earthworm (*Eisenia fetida*)
  - acute (14 days)
  - subchronic exposures (10 weeks)
  - worm tissues exposed to Soils A, D and contr
    - FAC (HPLC), PHC and metabolites (GCM

Results: Physical-Chemical Properties

	Soil A	Soil B	Soil C	Soil D	Cont
Texture	Fine*(CL)	Fine (CL)	Fine (CL)	Fine (L)	Fine
S/Si/C (%)	41/33/26	35/38/27	24/41/35	47/30/23	44/38
OM (%)	4.0	5.8	3.8	2.1	2.
pH	7.5	7.5	7.2	7.2	7.
EC (dS/m)	1.47	2.19	0.96	2.72	0.5
Metals	BC	BC	BC	BC	-

***Defined as having > 50% by mass, particles < 75 um (D_{50} < 75 um)**
BC-below criteria

Results: PHCs following Biotreatmen

PHC	CWS	Soil A	Soil B	Soil C	Soil
F1 (C6-C10)	260	-	-	-	
F2 (>C10-C16)	900	289	117	153	2
F3 (>C16-C34)	800	**3693**	**1127**	**1113**	**1**
F3(C16-C21)		896	261	231	5
F3(C21-C34)		2797	864	882	14
F4 (>C34+)	5600	2180	726	921	8

***Notes: 1) CCME standard for agricultural land use, fine textured surface soil.**

2) Historical data indicated that PHC F1 was below detection (< 5 mg/kg).

3) All units mg/kg (dw)

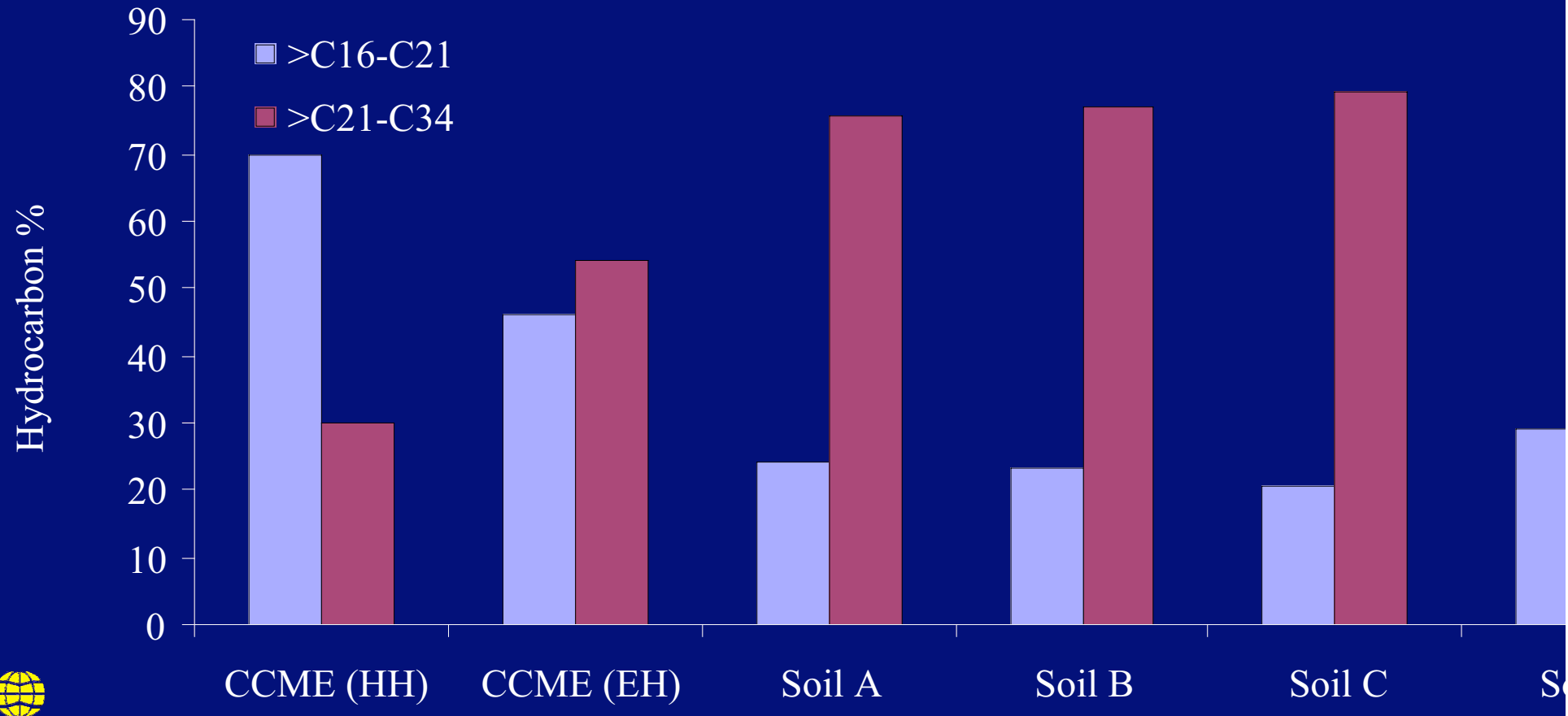
Results: PAHs following Biotreatmen

PAHs	SQG	Soil A	Soil B	Soil C	Soil D
Naphthalene	0.1	0.09	<0.05	0.07	0.10
Phenanthrene	0.1	**0.22**	<0.05	0.05	**0.13**
Chrysene	-	0.12	<0.05	<0.05	0.09
Fluorene	-	0.10	<0.05	<0.05	0.05
Other PAHs		<0.05	<0.05	<0.05	<0.05

***Note: 1) CCME soil quality guideline (SQG) for agricultural land use applied.**

2) all units mg/kg (dry weight)

Results: PHC F3 Composition Following Bioremediation



Toxicity Results: Microtox Bioassay (% Survival)

	Soil A	Soil B	Soil C	Soil D	Contro
EC_{50} (5 min)	>100	>100	>100	>100	>100
EC_{20} (5 min)	>100	>100	>100	>100	>100
EC_{50} (15 min)	>100	>100	>100	>100	>100
EC_{20} (15 min)	>100	>100	>100	>100	>100

***Note: 50% diluted soil data not shown, however, data are the same as 100% contaminated soils.**

Results: Earthworm/Plant Bioassay

Worms (% Survival)

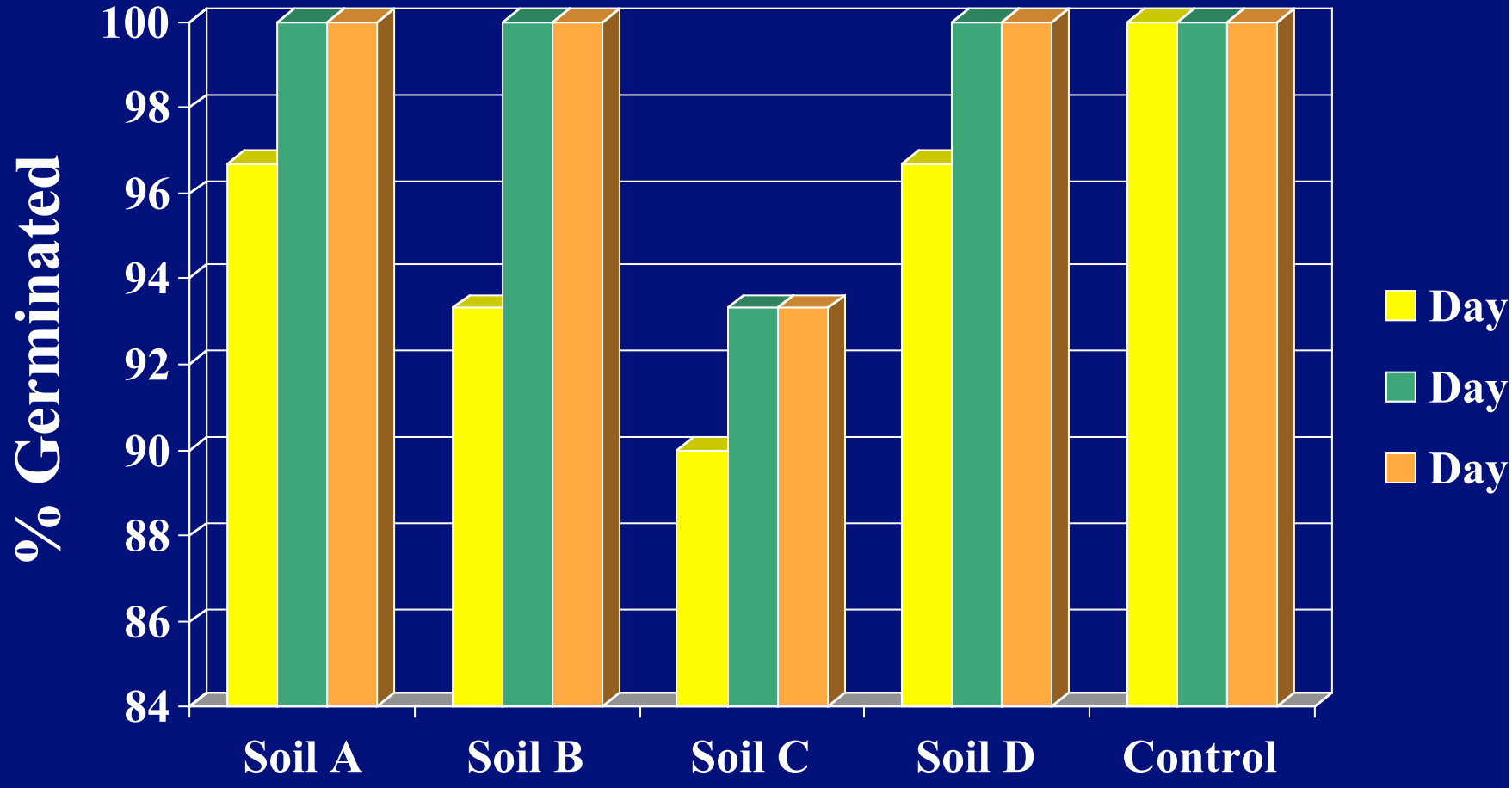
	Soil A	Soil B	Soil C	Soil D	Control
14 days	100	100	100	100	100
10 weeks	100	100	100	100	100

Plants (% Germination)

	Soil A	Soil B	Soil C	Soil D	Control
Radish	100	100	100	100	100
Oats	100	100	93.3	100	100

***Note: 50% diluted soil data not shown, however, data are the same as 100% contaminated soils.**

Results: Seed Germination - Oats



Screening Level Assessment of Earthworm Uptake

HPLC/Fluorescence Detection

- No clearly distinguishable FACs
- Could not discriminate earthworms exposed to PHC from control

GC/MS Analysis

- Complex but similar total ion chromatograms for all samples
- Trimethylnaphthalene and two isomers of ethoxypheny acetone found in all samples.

Discussion

- Residual PHC F3 concentrations in all soils in excess of standard: ***chemically extractable PHC***
- No observed toxicity (Microtox®, seed germination, earthworms) from exposure to PHC contaminated soils: ***bioavailable fraction of PHC***
- Incorporation of weathered hydrocarbon data should be considered
- Results of screening level assessment indicate better con (e.g., OECD Soil) necessary for evaluation of earthworm tissues

Discussion

- Achieving PHC F3 (>C16-C34) standard may prove difficult through bioremediation; however measured toxicity not observed
- CWS for PHC F3 may not accurately represent risk t ecological health:
  - Assumes fresh spill of distilled fraction
  - Assumes F3 composition with high level of C16-C21 subfraction vs. study soils
  - Federated Crude not representative of all hydrocarbon mix
  - Does not consider interactions amongst fractions, weather and limitation in bioavailability

Conclusions

- Risk of toxicity from weathered PHC (F3) in biotreat loam to clay loam soils may be overestimated by curr CCME Tier I PHC standards

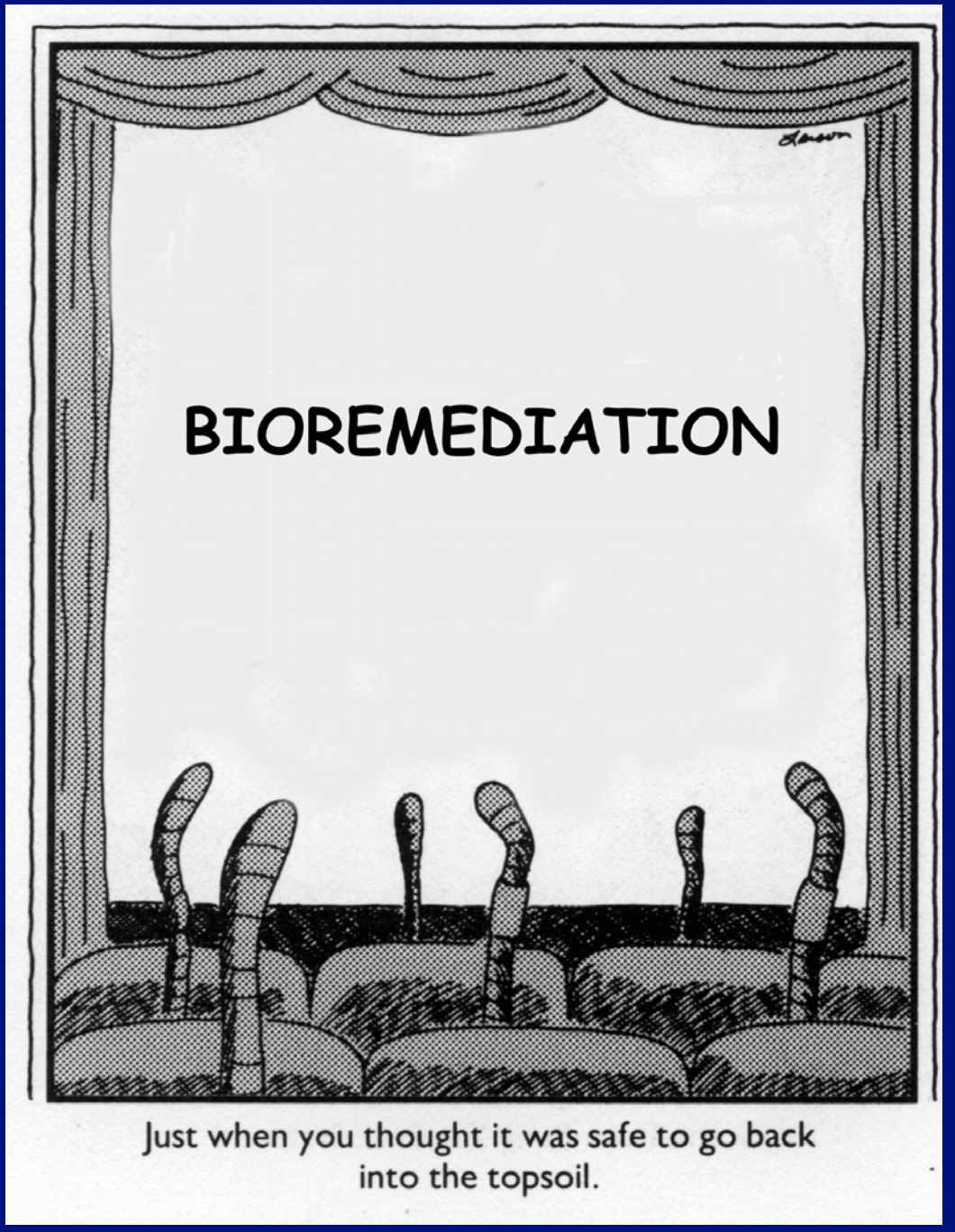
- Coupling site-specific toxicity data with chemical characterization can assist in achieving protective, an obtainable remediation endpoints

Future Directions

- The refinement of standards requires data relating PHC concentrations in aged samples containing complex hydrocar mixtures to measured toxicity in soil organisms
- Evaluating CCME PHC standards (particularly F3) versus additional weathered biotreated PHC data
  - ***PTAC in process of completing***
- Inventory of other products (e.g., crude oils) to see if Federat Crude Oil composition representative
- Appropriate controls for earthworm toxicity studies (OECD)

Acknowledgments

- Komex International Ltd., Edmonton, Alberta
- Norwest Labs- for performing chemical and physical analyses of soils
- EnviroTest Labs- for performing earthworm analyses
- Bill McGill (UNBC) and Sumithrai Vasanthan (University of Alberta)- who performed seed germination and earthworm bioassays


BIOREMEDIATION
Just when you thought it was safe to go back into the topsoil.