CYANIDE PHYTOREMEDIATION: REMOVAL FROM AND FATE IN SOIL-WATER-PLANT SYSTEMS

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Acknowledgements

- ALCOA
- Gas Technology Institute (GTI)
- Niagara-Mohawk Power Corp. (NIMO)
- New York Gas Group (NYGAS)

Overview

- Synopsis of cyanide chemistry & contamination
- Is cyanide phytoremediation feasible?
- Can cyanide phytoremediation be implemented in the field?
- Are there ecological risks associated with cyanide phytoremediation?
- Can the efficacy of cyanide phytoremediation be modeled and predicted?

Cyanide: sources and uses

- Biological sources
- Aluminum production
- Electroplating
- Manufactured gas industry (coal gasification)
- Ore heap leaching
- Precious metal mining
- Road salts (anticaking agent)

Cyanide speciation

- Free (CN^-, HCN) or Simple (KCN, NaCN)
  - Toxic, therefore tightly regulated
  - Among the top 30 on CERCLA list
- Cyanates ($^-$S-CN, O-CN^-)
  - Formed in the environment and *in vivo*
  - Not regulated
- Metal cyanide complexes
  - Formed in the environment or anthropogenically through reaction with cations (Fe, Zn, Ni)
  - Not regulated

Iron cyanide complexes

- Strong complexes
  - Ferricyanide, $Fe(CN)_6^{3-}$
  - Ferrocyanide, $Fe(CN)_6^{4-}$
- Iron cyanide precipitates
  - $Fe_4(Fe(CN)_6)_3$ = Prussian blue
  - $Fe_3(Fe(CN)_6)_2$ = Turnbull's blue
- Persistent
  - Slow dissociation kinetics
  - Resistant to biodegradation
  - Photosensitive to strong UV light

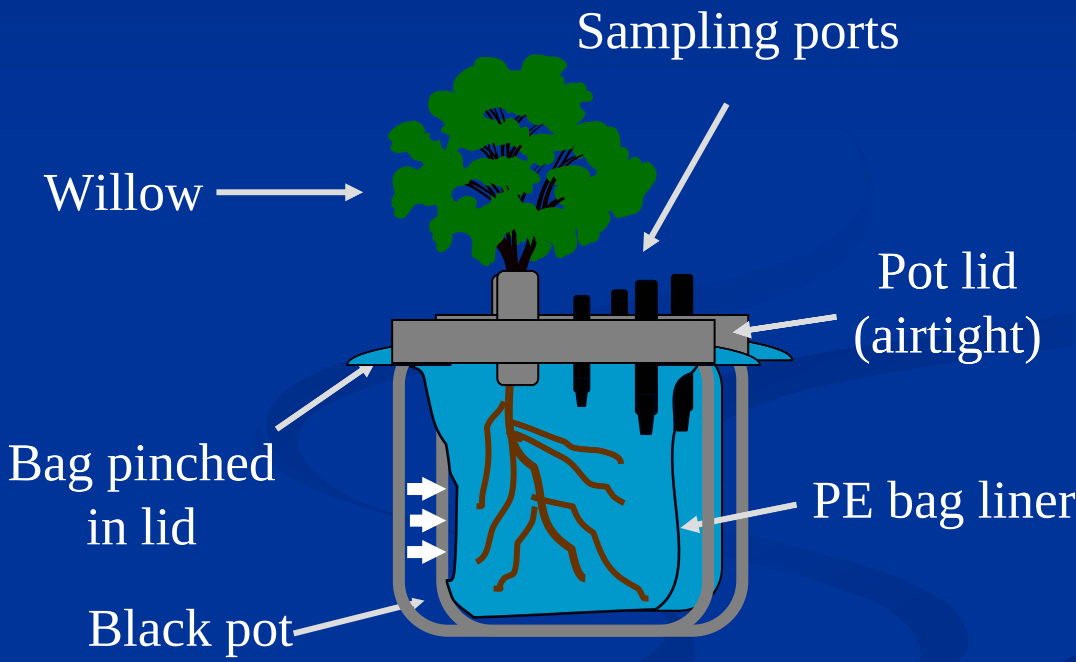
Examples: iron cyanide contamination

Former Manufactured Gas Plant site

Is cyanide phytoremediation feasible?

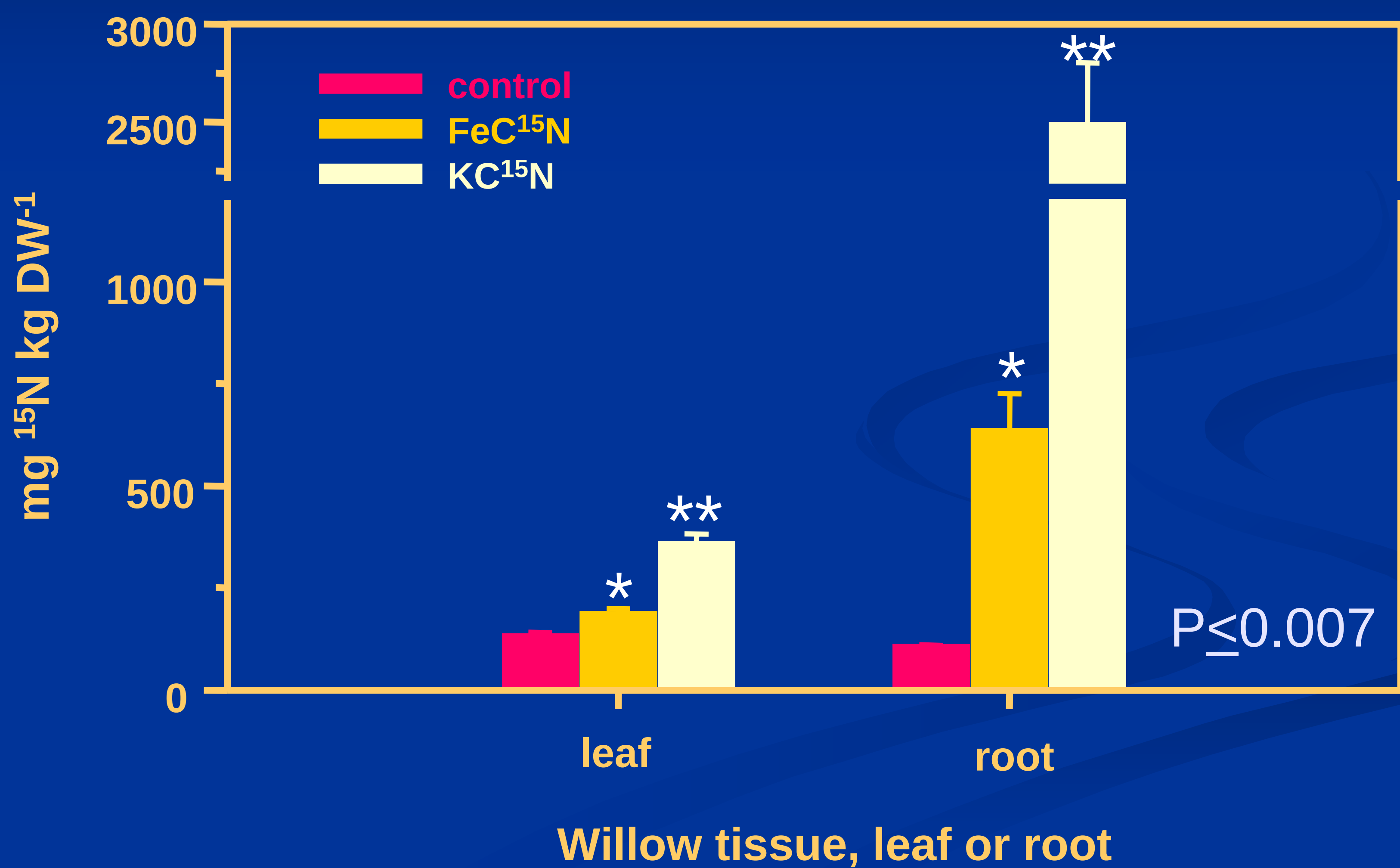
- Do plants transport cyanide?
- Do plants detoxify and/or metabolize cyanide?

Hydroponic system schematic

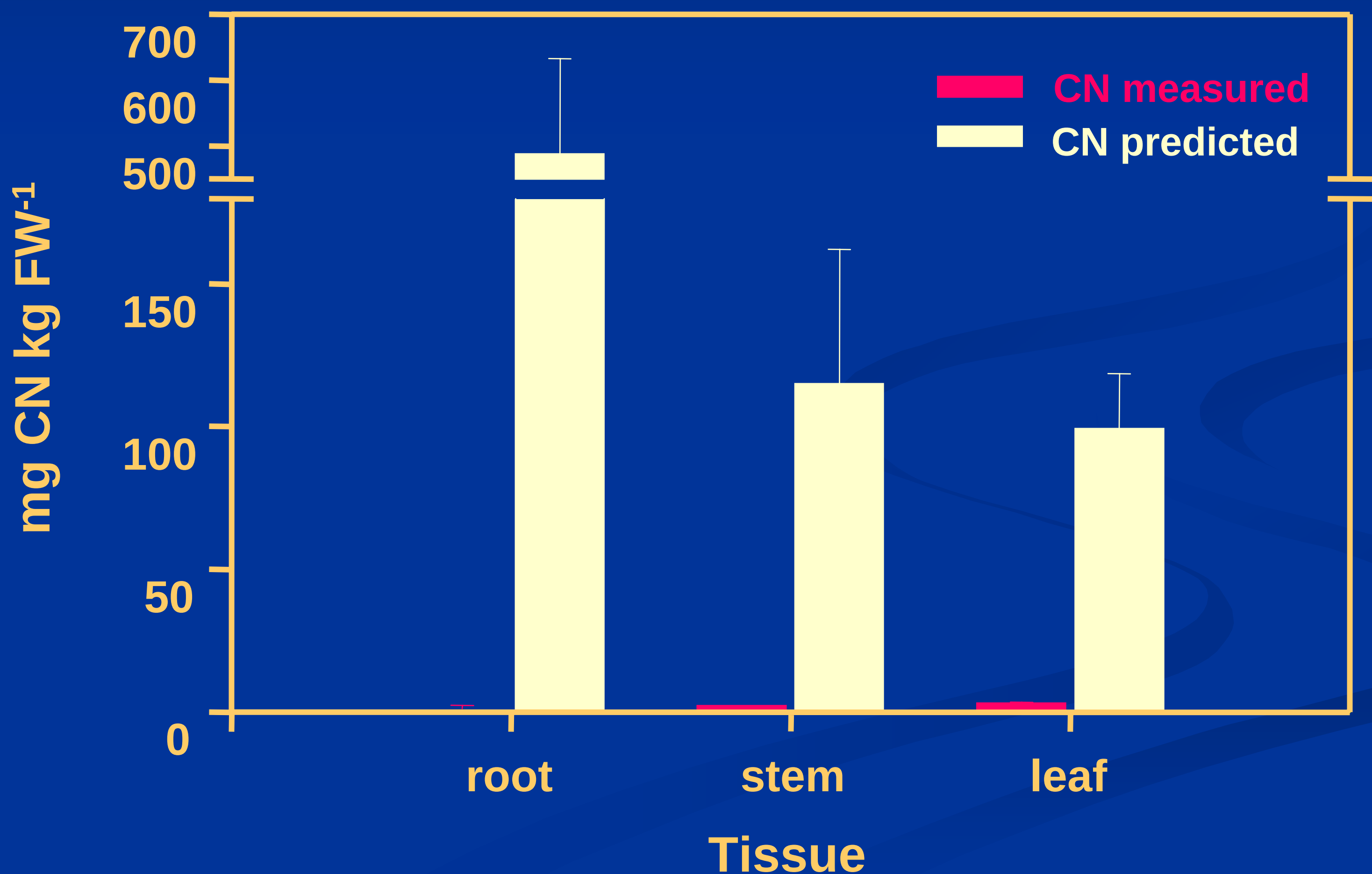


During transpiration

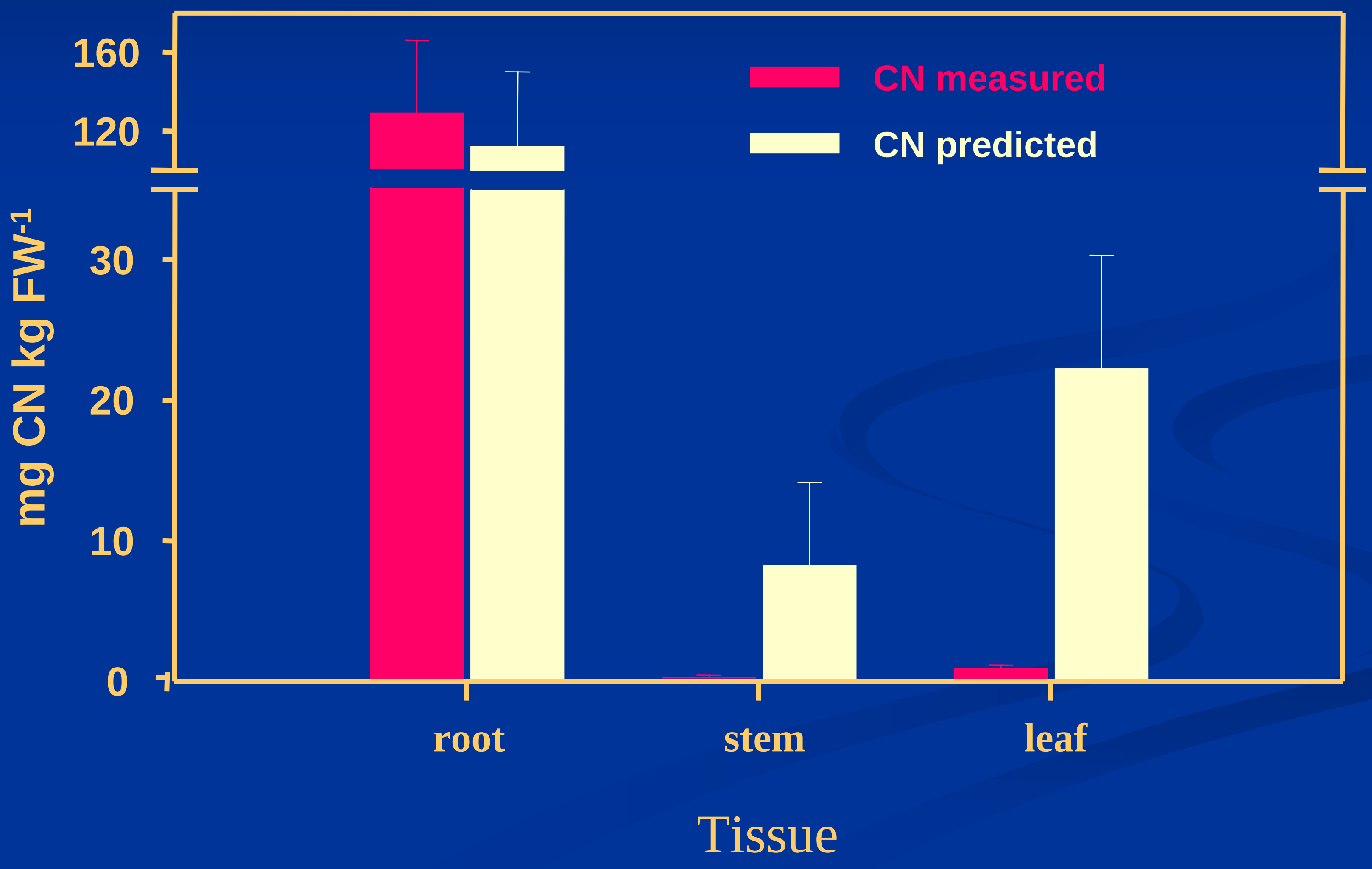
^{15}N-labeled cyanide compounds were used to assess cyanide & iron cyanide transport



^{15}N-labeled cyanide compounds were used to assess cyanide metabolism



^{15}N-labeled cyanide compounds were used to assess iron cyanide metabolism



Incorporation of ^{15}N from KCN into amino acids

Amino acid	Root ^{15}N abundance, %	Leaf ^{15}N abundance, %
Glu	30.6	2.3
Gln	12.9	1.7
Asn	30.2	2.5
Thr	5.8	2.5
Phe	22.4	9.3

Natural abundance: 0.37%

Conclusions: Cyanide transport and fate

- Roots of willow transport KCN and iron cyanides

- Plants treated with iron cyanides retain parent compound in roots, but translocate a metabolite(?) containing ^{15}N

- Plants do not accumulate exogenous cyanide in leaves, it is apparently incorporated into amino acids

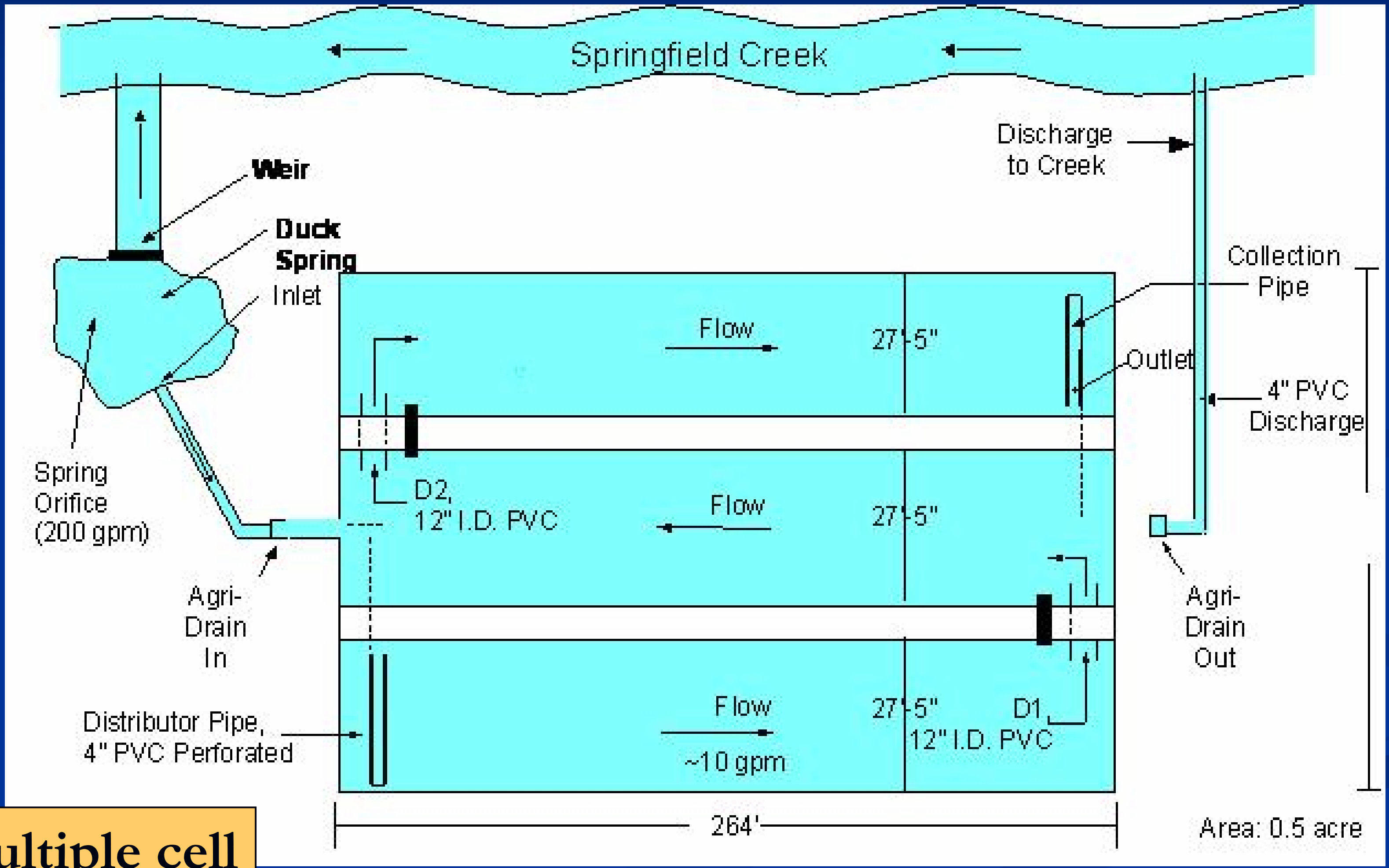
Field assessments of cyanide phytoremediation

Dr. Rajat Ghosh

Field trials of cyanide phytoremediation

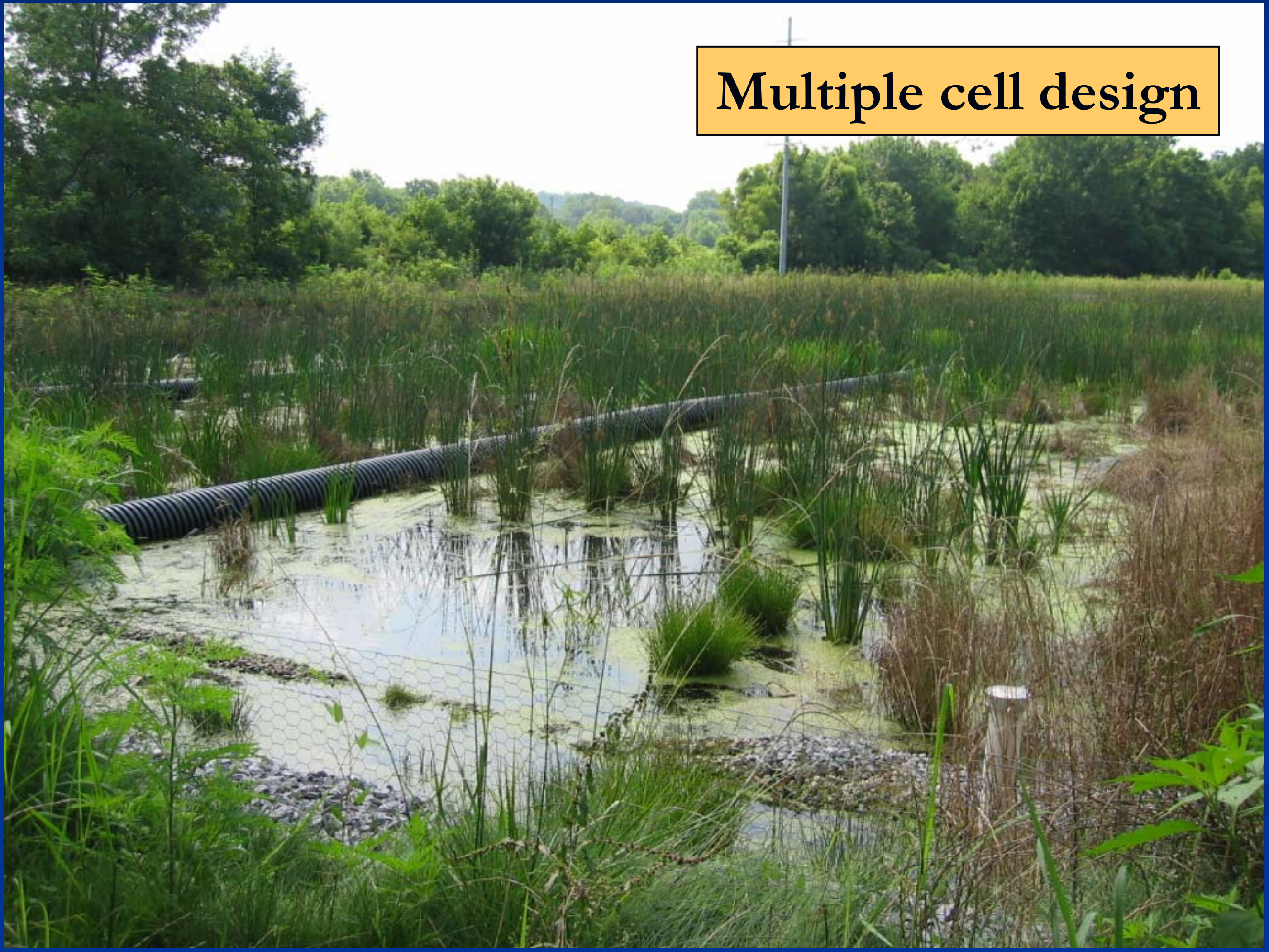
- Conducted by The Retec Group, Inc. in association with ALCOA, Inc. and others
- Tested on several sites
- Utilizes a constructed wetland approach

Cyanide remediation with constructed wetlands



Multiple cell design

Cyanide remediation with constructed wetlands



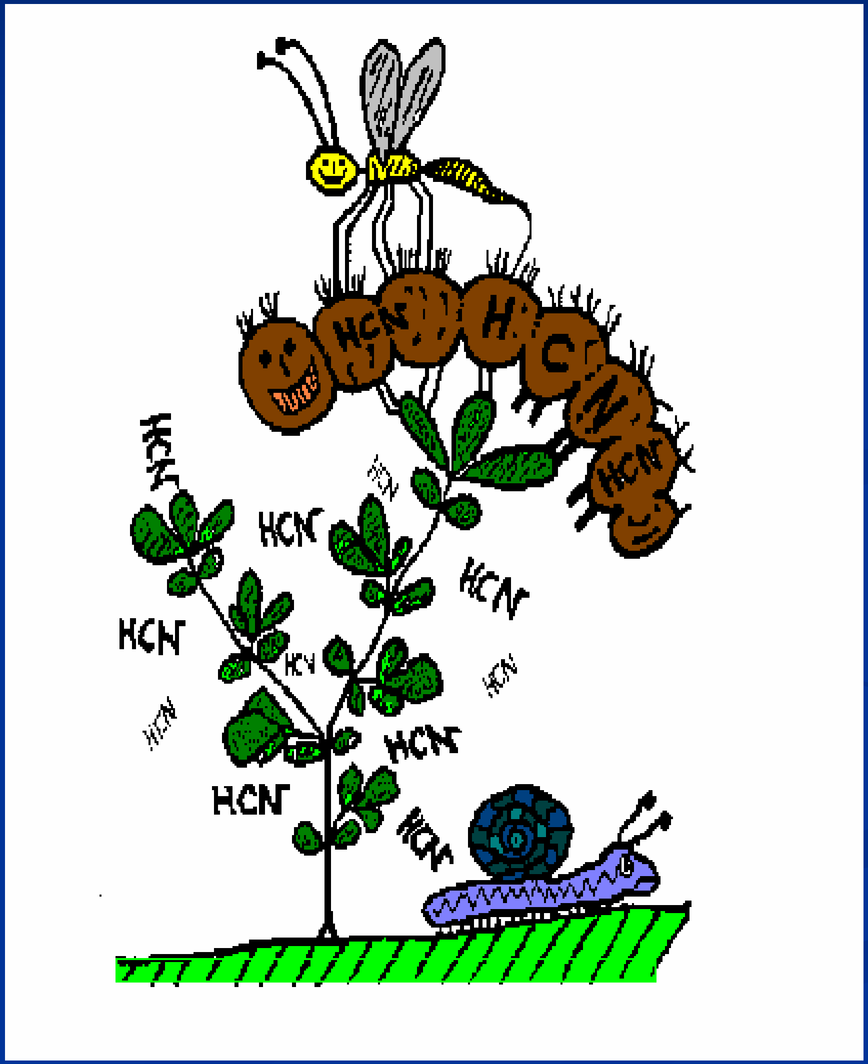
Cyanide remediation with constructed wetlands

Cyanide remediation with constructed wetlands

- Preliminary results indicate
  - High degree (>95%) of iron cyanide removal
  - Photolytic degradation a contributing factor
  - Rapid removal of cyanide by native vegetation

- Future plans
  - Deployment to various industrial scenarios

Are there ecological risks associated with cyanide phytoremediation?



What data do we have pertinent to the question of risk?

- Exogenous cyanide does not bioaccumulate in plant tissues
- Cyanide is assimilated largely into amino acid pools
- Cyanide volatilization is detectable, but minimal
- Wildlife (including amphibians) utilize the constructed wetlands with no apparent adverse (acute) effects

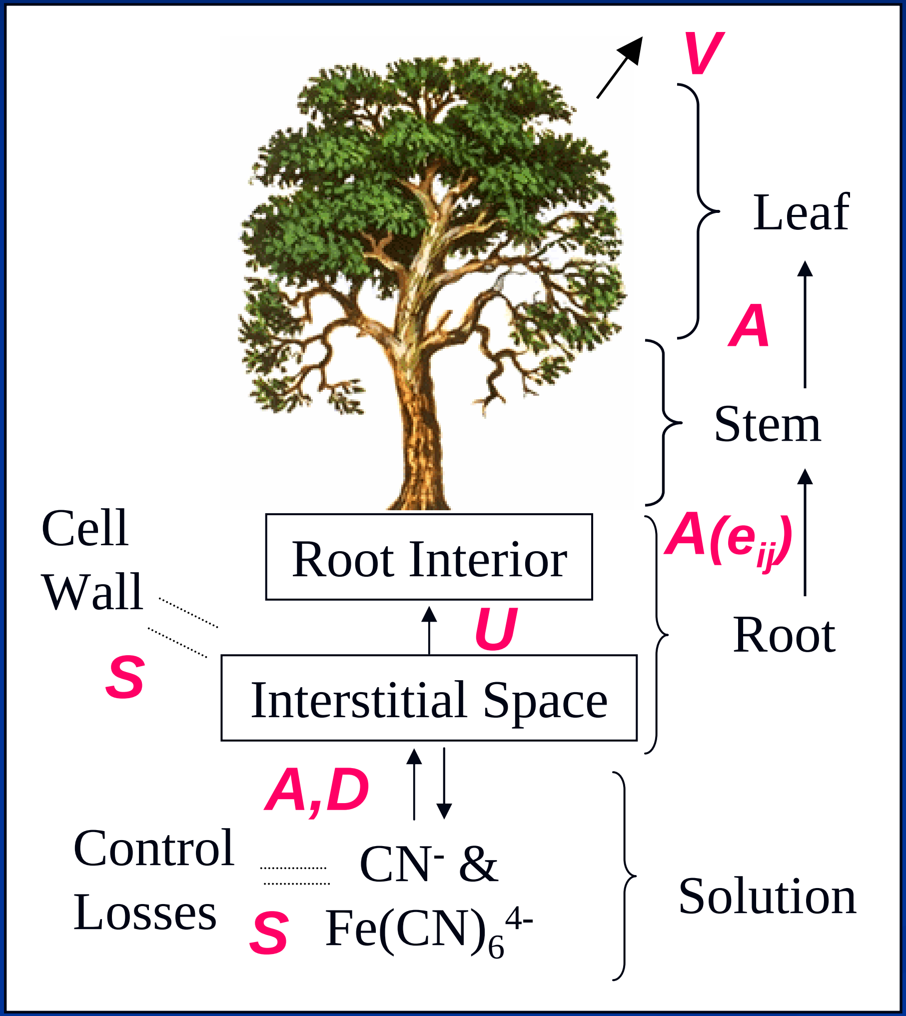
Volatile cyanide monitoring


WE'RE WORKING ON A MORE EFFECTIVE MODEL TO PROTECT WILDLIFE FROM OUR TAILINGS DAM......
CYANIDE
JACK

Modeling iron cyanide fate and transport in plant-soil-water systems

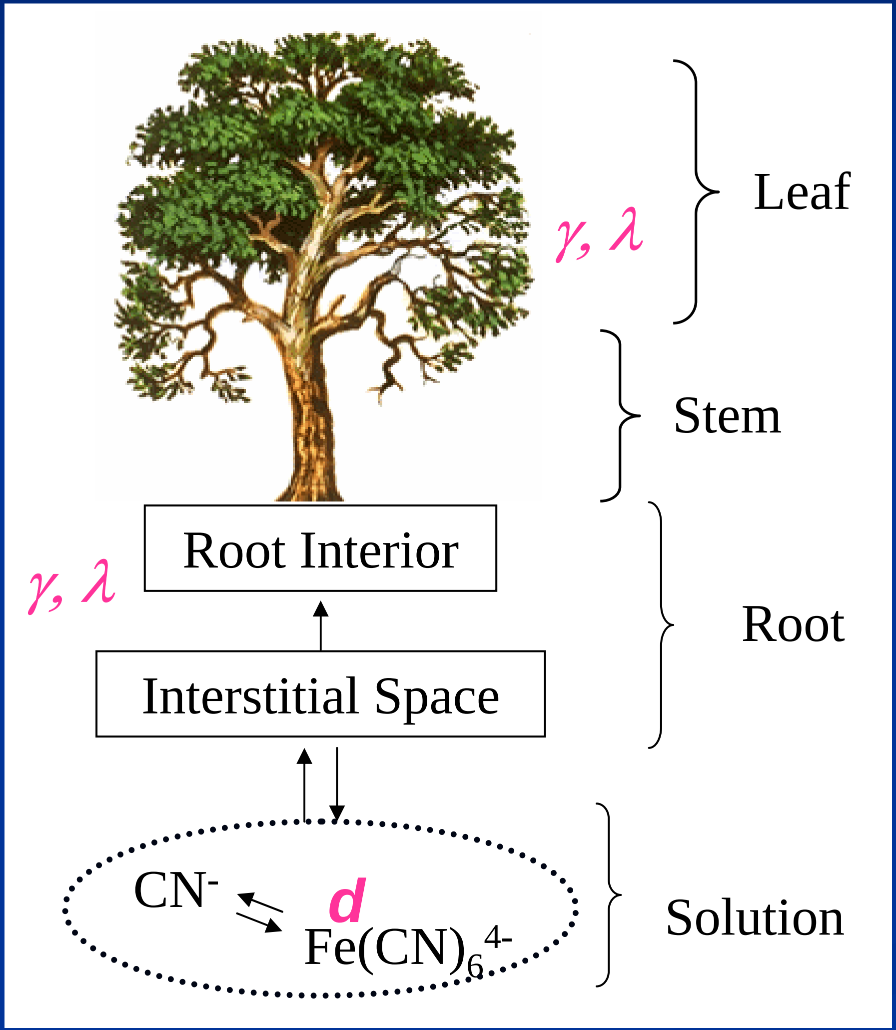
Dr. Joe Bushey

Plant Cyanide Uptake Model Development: Transfer Processes in willow



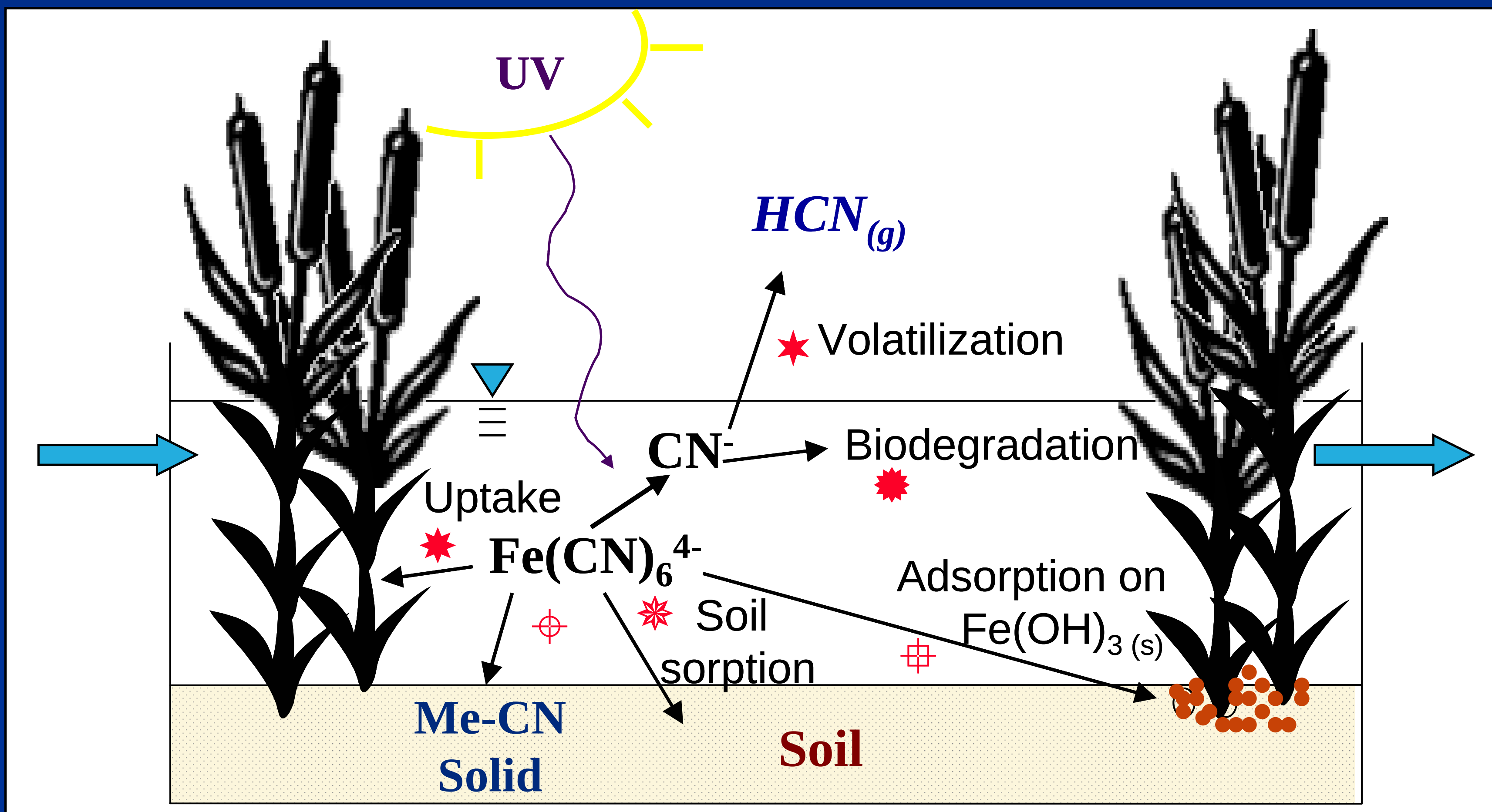
- Advection (***A***)
  - e_{ij} for root to stem
- Diffusion (***D***)
- Active uptake (***U***)
  - saturation kinetics
- Sorption (***S***)
  - 1st-order; reversible
- Volatilization (***V***)
  - HCN & assimilates
  - 1st-order

Plant Cyanide Uptake Model Development: Chemical Considerations in willow

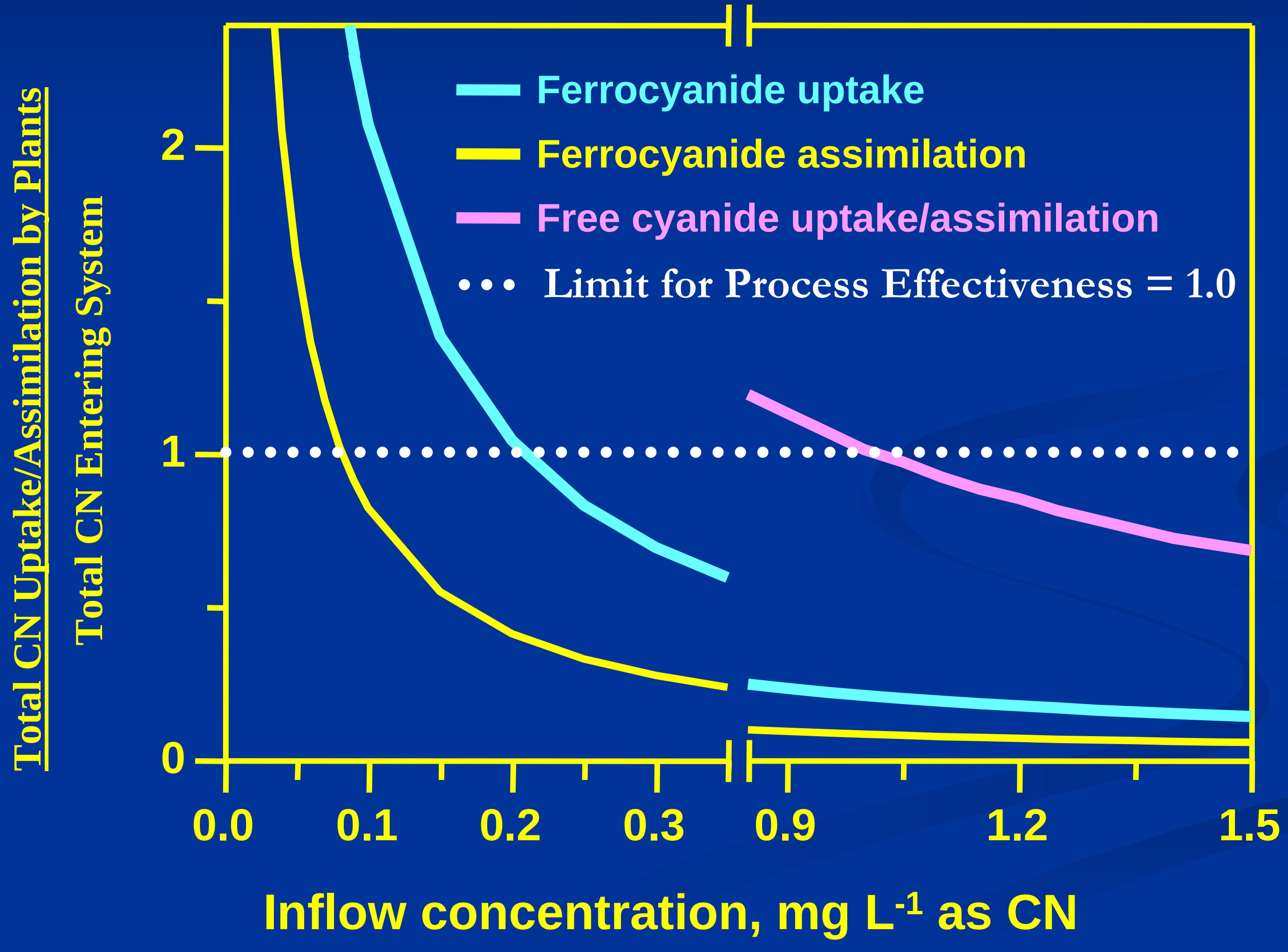


- $Fe(CN)_6^{4-}$ dissociation
  - Chemical/Reversible (*d*)
  - 1st-order enzymatic (γ)
- CN^-
  - 1st-order assimilation (λ)
- Assimilates move with transpiration stream
- Ignored solid formation & plant growth

Wetland fate model



Engineering Feasibility
Normalized uptake & assimilation



Engineering Feasibility
Normalized uptake & assimilation

- Normalizing data and adjusting parameters provides a means of applying the model to different scenarios

- A value of 1.0 represents the boundary of efficacy
  - $> 1.0 \rightarrow$ plants not reaching full potential
  - $< 1.0 \rightarrow$ results in breakthrough

- Results applicable to systems with
  - Ferrocyanide input ≤ 0.2 mg L^{-1} as CN
  - Free cyanide input ≤ 1.2 mg L^{-1} as CN

Thank you!