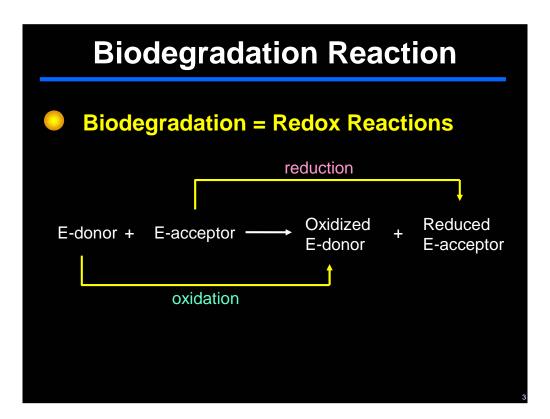
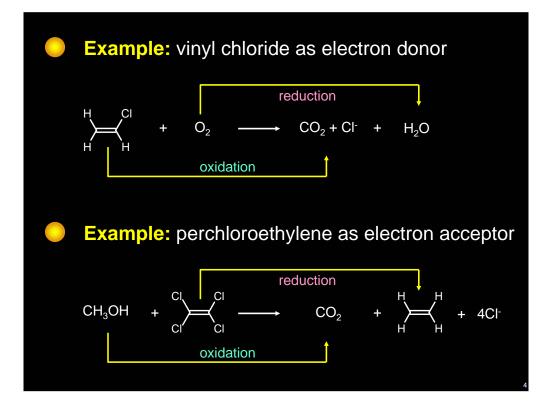
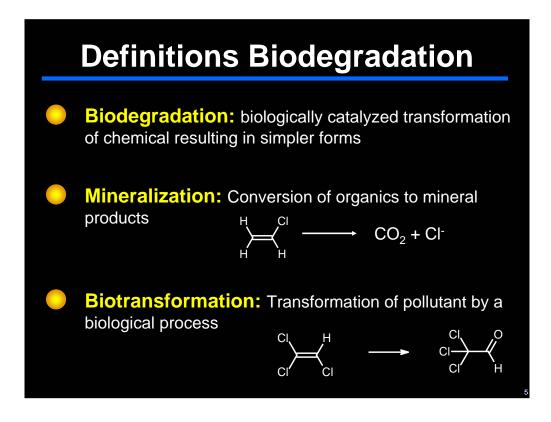


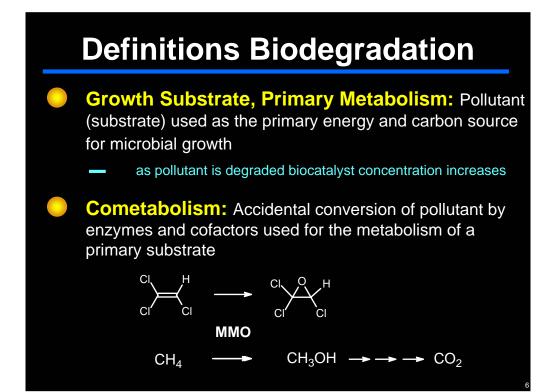
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An anoth hostingtication, distancents ands, distributions, thismatham, distancements, the experiments, the experiments of the experiments of the experiments of the experiments. Retrict of the experiments of the experimation of the experiments of the experiment	Department of Chemical and Environmental Engineering, University of Arizona, P. D. Box 210011, Tacson, Arizonas 8371-10011, USA ("anter for correspondence-a-mail: Engleditis emularizma.uke, phone: +1-520- 628-5858; fax: +1-520-621 6049)
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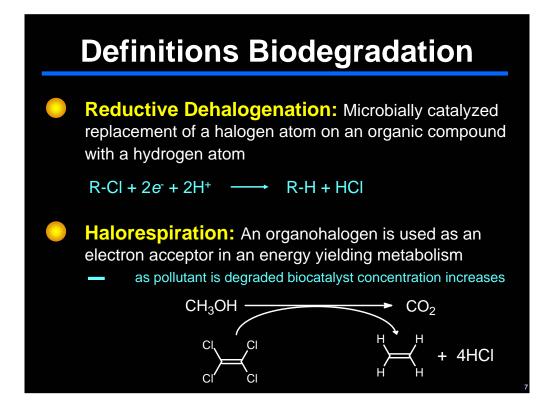
Field, J.A. & R. Sierra-Alvarez (2004) Biodegradability of chlorinated solvents and related chlorinated aliphatic compounds. *Reviews in Environmental Science & Bio/Technology* **3**:185-254.

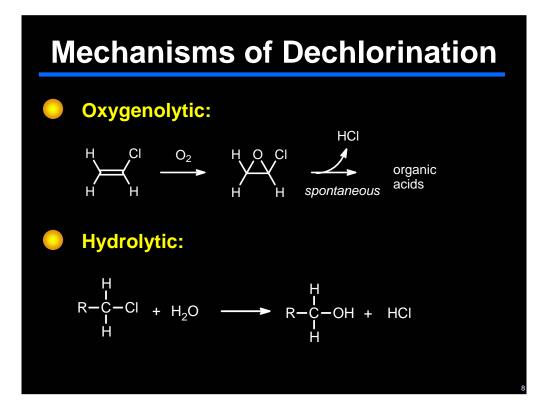








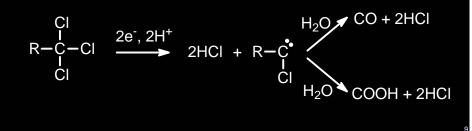




Mechanisms of Dechlorination

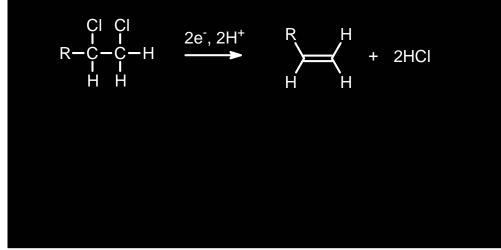
Reductive Hydrogenolysis:

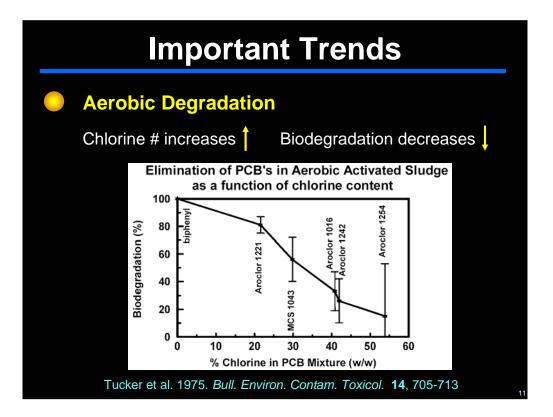
Hydrolytic Reduction:

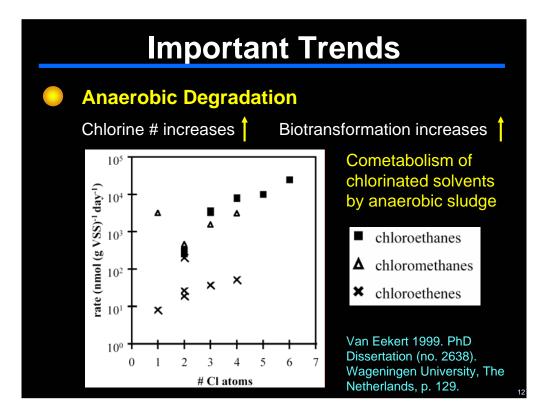


Mechanisms of Dechlorination

Reductive Dichloroelimination:

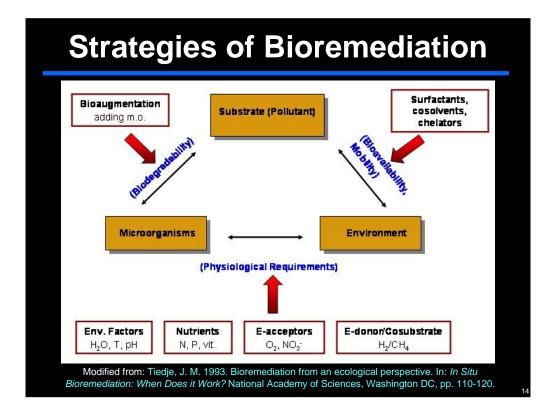




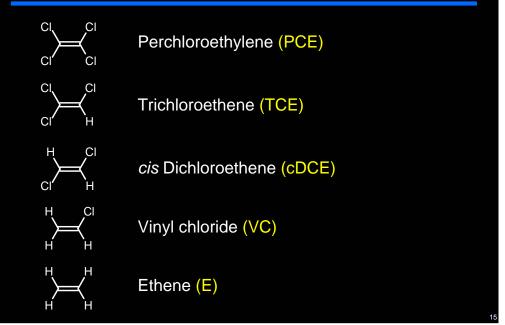


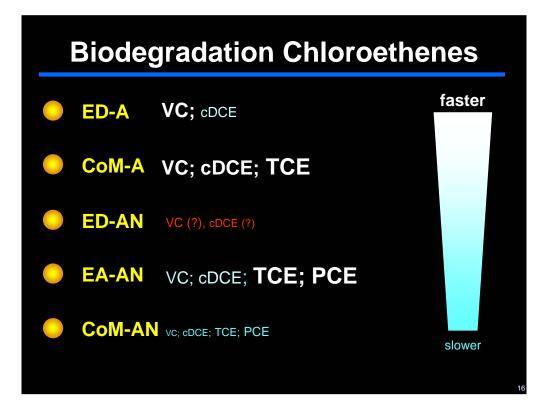
Five Physiological Roles

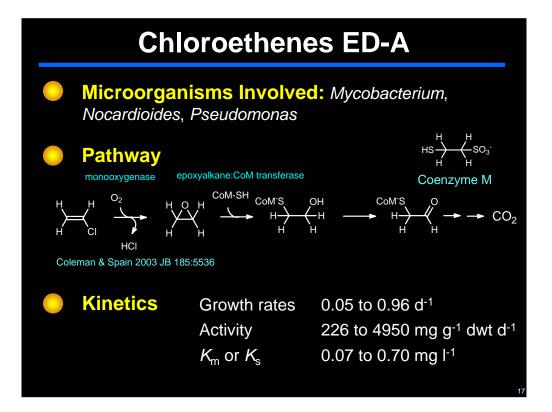
1st: aerobic carbon and energy source	ED-A
2nd: aerobic cometabolism (cooxidation)	CoM-A
3rd: anaerobic carbon and energy source	ED-AN
4th: anaerobic electron acceptor (halorespiration)	EA-AN
5th: anaerobic cometabolism (reduced cofactors)	CoM-AN

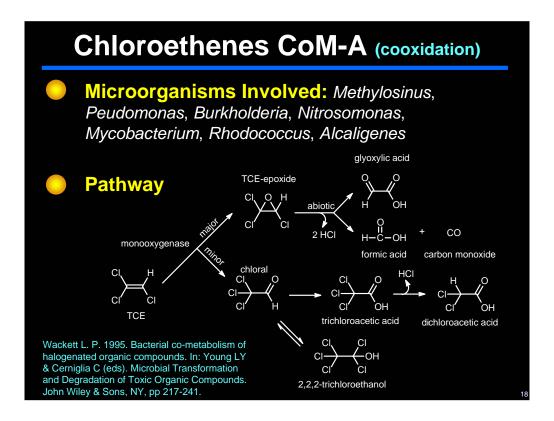


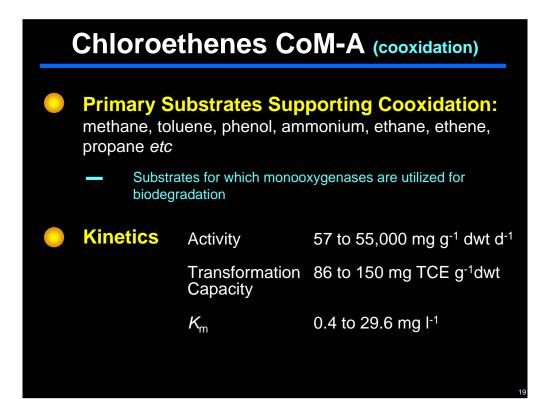
Abbreviations Chloroethenes

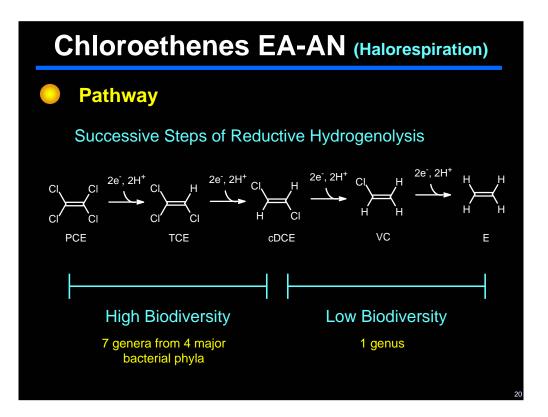












Chloroethenes EA-AN (Halorespiration)

Microorganisms Involved: PCE to cDCE

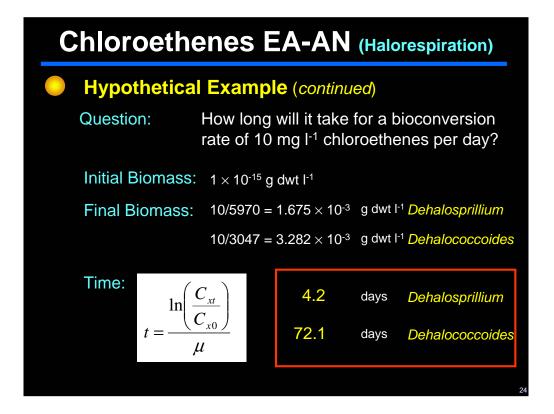
Low G+C gram +	Desulfitobacterium	H_2 , lactate, formate, etoh
	Clostridium	YE, glucose
	Dehalobacter	H ₂
δ Proteobacteria	Desulfuromonas	acetate,pyruvate
ϵ Proteobacteria	Dehalospirillim	H_2 , lacate, formate, etoh
	Sulfurospirillum	lactate
Green non-sulfur	Dehalococcoides	H ₂
Microorgania	E to E	
Green non-sulfur	Dehalococcoides	H ₂

21

Chloroethenes EA-AN (Halorespiration)				
•	 Biochemistry Reactions catalyzed by specific reductive dehalogenases All contain vitamin B12 Most are membrane bound enzymes 			
	Kinetics: PCE to TCE and/or cDCE			
		Growth rates Activity	0.23 to 6.65 d ⁻¹ 856 to 37,312 mg g ⁻¹ dwt d ⁻¹	
	Kinetics	VC to E		
		Growth rates Activity <i>K</i> _m or <i>K</i> _s	0.32 to 0.40 d ⁻¹ 3047 to 6030 mg g ⁻¹ dwt d ⁻¹ 0.16 to 0.31 mg l ⁻¹	

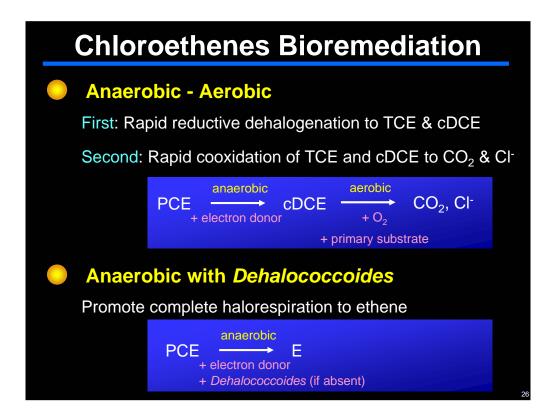
Chloroethenes EA-AN (Halorespiration)

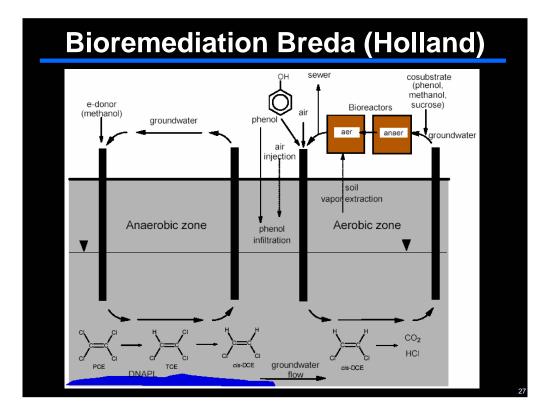
	Hypothetical Example				
	Assumptions: $t_0 = 1$ bacterium per m ³				
		1 bacter	$ium = 1 \times 10^{-12} g$	9	
		Ideal co	nditions for grow	rth	
	Kinetic data:		Dehalosprillium multivorans	<i>Dehalococcoides</i> strain VS	
	Growth rate (d-1)		6.65	0.40	
	Activity (mg g ⁻¹ d	wt d⁻¹)	5970	3047	
	Growth Equation	on: C,	$_{\rm xt} = C_{x0} e^{ut}$		
C_{x0} & C_{xt} = cell biomass conc. at time 0 & t (g dwt l ⁻¹) μ = growth rate (d ⁻¹), t = time (d)				9 & t (g dwt I ⁻¹)	



Chloroethenes CoM-AN

•	Microorg	anisms Invol	ved: Methanogens, Acetogens	6
0	- React	tions catalyzed by r	os of Reductive Hydrogenolysis educed enzyme cofactors nin B12; Nickel containing Factor 430	
	Kinetics: PCE to TCE and/or cDCE			
		Activity	0.006 to 20 mg g ⁻¹ dwt d ⁻¹	
	Kinetics: cDCE or VC to E			
		Activity	0.001 to 0.366 mg g ⁻¹ dwt d ⁻¹	
				25



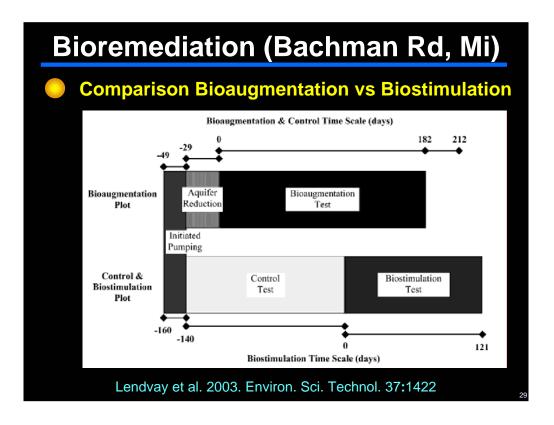


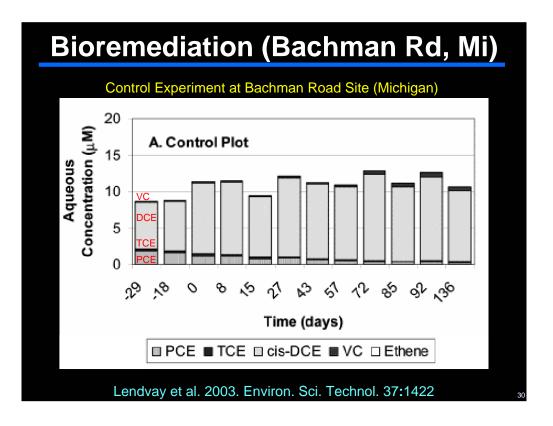
Bioremediation Breda (Holland)

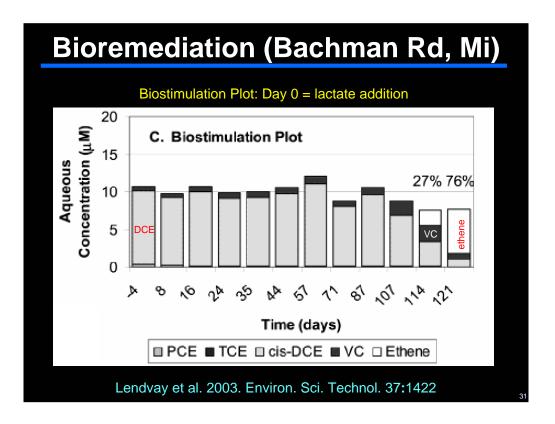
Facts about Full-Scale Bioremediation

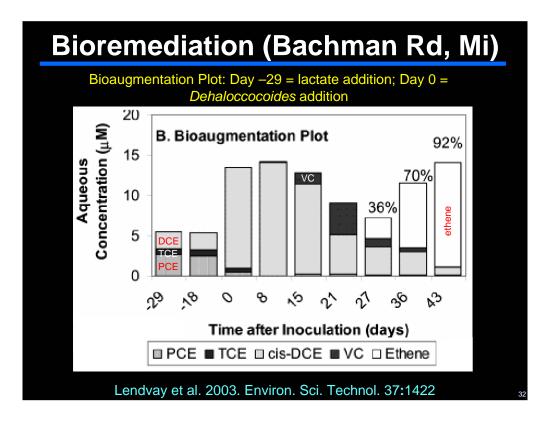
- 85% removal of PCE in situ within 6 months
- Inorganic chloride concentration in anaerobic zone increased from 1 to 6 mM
 - In the aerobic zone all of the cDCE and VC as well as injected phenol was removed
- After one year the total mass of chloroethenes decreased from 1500 to 550 mol

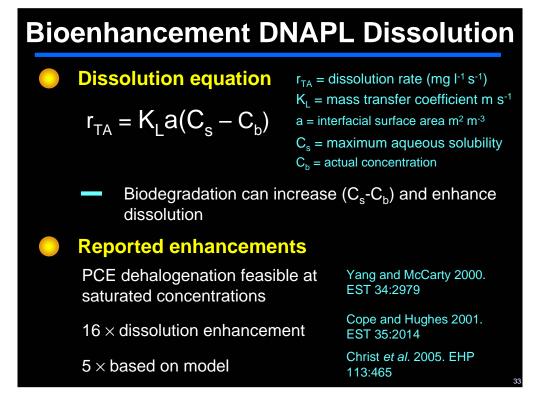
Spuij et al. 1997. Full-scale application of in situ bioremediation of PCE-contaminated soil. *4th Int. In Situ and On Site Bioremediation Symp., New Orleans, LA*, Columbus, OH: Battelle Vol 5, pp. 431–37.











Bioenhancement DNAPL Dissolution

Combine Surfactant/Cosolvent Assisted Dissolution DNAPL with Biodegradtion

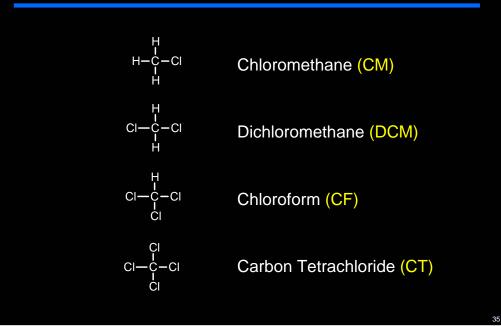
 Biodegradable surfactants/cosolvents will be used as electron donors

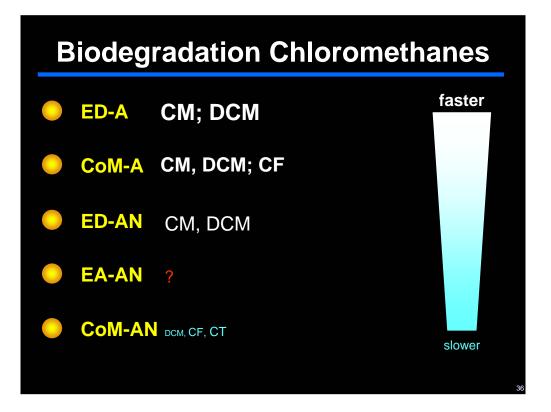
Residual PCE remaining after flushing reductively dehalogenated

Residual surfactant biodegraded

Christ et al. 2005. EHP 113:465

Abbreviations Chloromethanes





Chloromethanes CoM-AN

Microorganisms Involved: Methanogens, acetogens, fermentative bacteria, sulfate reducing bacteria, iron reducing bacteria, denitrifiers

Pathway Reductive Hydrogenolysis

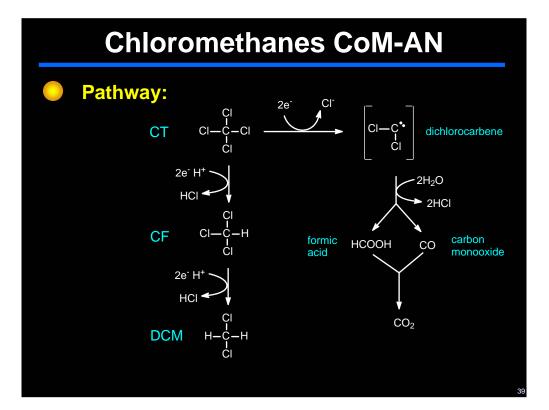
Hydrolytic Reduction

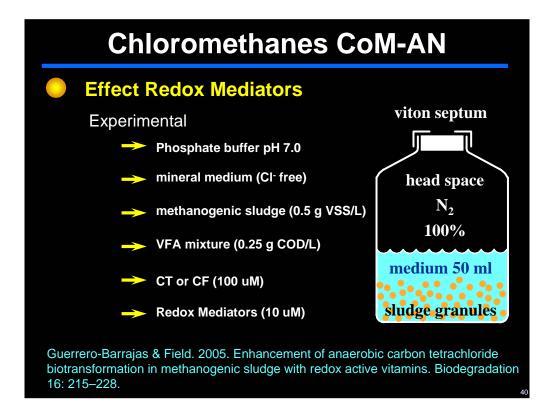
Reactions catalyzed by reduced enzyme cofactors, chelating agents, magnetite, quinones

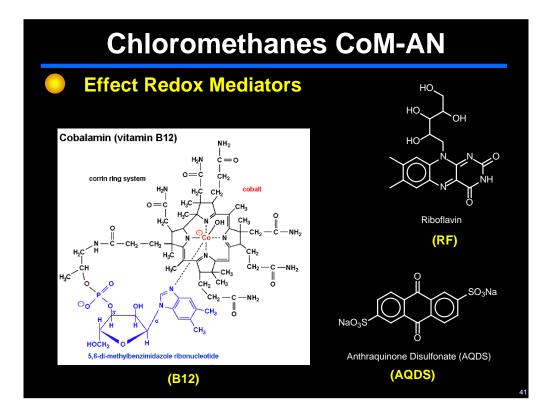
Cobalt containing vitamin B12 Zinc containing porphorinogens Pyridine-2,6-bis(thiocarboxylic acid) Quinones, humus Biogenic magnetite

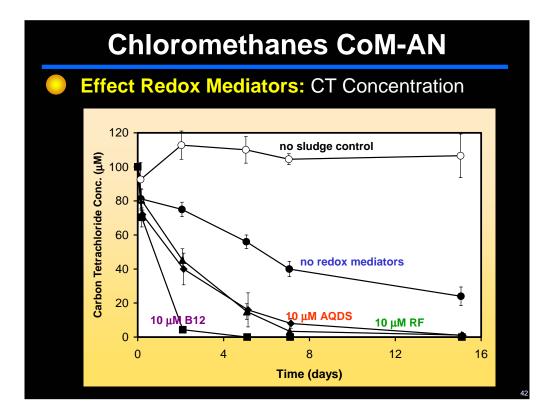
Chloromethanes CoM-AN

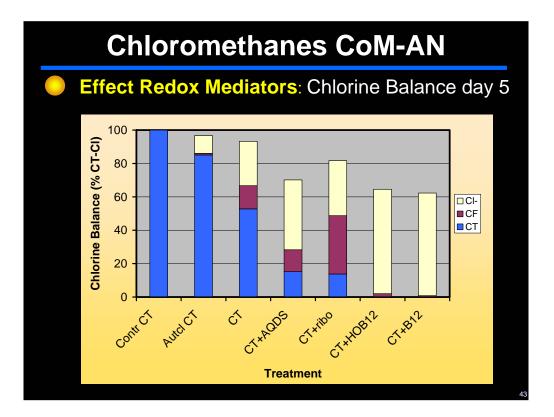
0	Kinetics: CF dechlor Activity	ination 0.3 to 36 mg g ⁻¹ dwt d ⁻¹	
0	Kinetics: CT dechlor Activity	ination 3 to 1198 mg g ⁻¹ dwt d ⁻¹	
			38

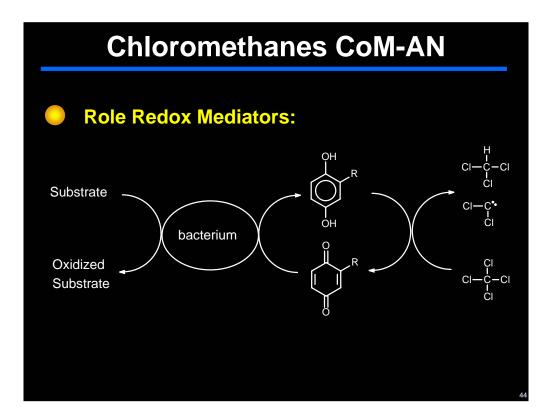


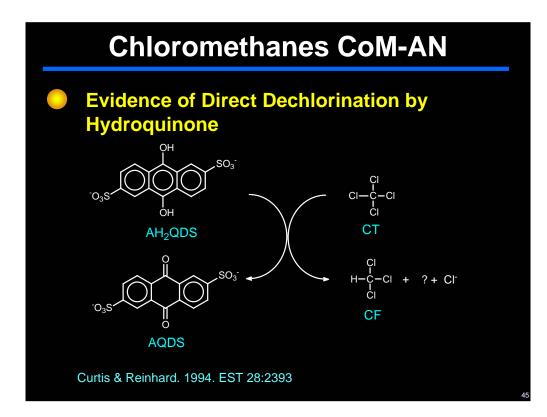












Conclusions 1

Biodegradation Chloroethenes

- High biodiversity for rapid halorespiration PCE to cDCE; halorespiration cDCE to E restricted to one genus, *Dehaloccocoides*
- Slow anaerobic cometabolism of PCE, TCE, cDCE and VC (dominant process reductive hydrogenolysis)
- Rapid aerobic cooxidation of VC, cDCE, TCE feasible
- Aerobic biodegradation of VC (and cDCE) as growth substrates feasible with newly discovered bacterial strains

Bioremediation Chloroethenes

- Anaerobic halorespiration (PCE \rightarrow cDCE) followed by aerobic cooxidation (cDCE \rightarrow CO₂, CI⁻)
- Complete reductive dechlorination with Dehaloccocoides

 $(\mathsf{PCE}\to\mathsf{E})$

Conclusions 2

Biodegradation Chloromethanes

- Rapid aerobic or anaerobic biodegradation of CM or DCM as growth substrates
- Aerobic cooxidation CM, DCM and CF feasible
- Slow Anaerobic cometabolism of DCM, CF and CT

1) hydrolytic reduction to CO_2

- 2) reductive hydrogenolysis to lower chlorinated methanes
- Redox mediators can greatly enhance anaerobic biotransformation CT, CF

Bioremediation

Anaerobic cometabolism for CF and CT

What is Phytoremediation?



What is Phytoremediation?

A solar driven, biological system that is used to Contain, Sequester, Remove, or Degrade Organic and Inorganic Contaminants in Air, Soils, Sediments, Surface Water, and Groundwater

Types of Phytoremediation

Artificial Wetlands Phytostabilization Phytoextraction Rhizofiltration Rhizosphere enhancement Phytovolatilization Phytodegradation Air purification Water and Wastewater Management Landfill caps Green Roofs Combination technologies

Wide Range of Contaminants

- **Organic:** hydrocarbons, chlorinated solvents, phenols, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), agricultural wastes
- **Inorganic:** metals, radionuclides, salinity, nitroaromatics, amines, excess fertilizers, pesticides, CCA (chromium copper arsenic)

Different Types of Impacted Media

Solid phase: soils, sediments, sludges
Liquid phase: run-off, stormwater, wastewater, groundwater, leachate
Gaseous phase: greenhouse gases, VOCs, NO_x

Advantages

Safety

Minimized emissions & effluent and low secondary waste volume

Controls erosion, runoff, rain infiltration, and dust emissions

Ecological

Habitat friendly, habitat creation, promotes biodiversity

Sequesters greenhouse gases (carbon dioxide)

Public / Regulatory

Acceptable brownfields applications

Aesthetics, green technology

Increasing regulatory approval and standardization

Limitations or Common Regulatory Issues

Depth

Only effective if within the relative rooting depth of the vegetation

Time

Requires longer periods to become effective (establishment)

May requires longer periods to reach clean up targets

Seasonal effects

Phytotoxicity

Generally considered applicable for low to moderate concentrations

In most cases, the vegetation must survive in order to operate

Media Transfer / Food Chain Impacts

Fate and transport often unclear

Air emissions, leaf litter

Harvesting, hazardous waste?

Toxicity of parent vs. by-products

Web Addresses

http://www.rtdf.org/public/phyto/phyto doc.htm

http://www.itrcweb.org/gd_Phyto.asp http://www.dsa.unipr.it/phytonet/ http://plants.usda.gov/

http://clu-in.org/techdrct/

http://www.acap.dri.edu/

Books

Phytoremediation (Hardcover) Tsao

Phytoremediation McCutcheon and Schnoor

Phytoremediation of Contaminated Soil and Water (Hardcover) Terry and Banuelos

Plants That Hyperaccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining (Hardcover) Brooks

Companies

Edenspace – Metals Applied Natural Sciences – Organics Phytokinetics – Organics Applied Phytogenetics – Genetically Engineered Plants Thomas Engineering - Organics Ecolotree – Landfill caps and riparian restoration Phytoextraction Associates – Metals and phytomining

Journals

International Journal of Phytoremediation Environmental Science and Technology Environmental Pollution Plant and Soil Chemosphere Journal of Environmental Quality New Phytologist Plant Physiology

Conferences

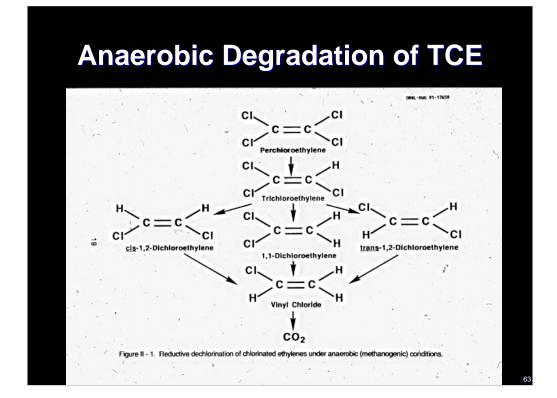
EPA International Applied Phytotechnologies Conference Battelle American Society for Agronomy American Chemical Society Association for Environmental Health and Sciences

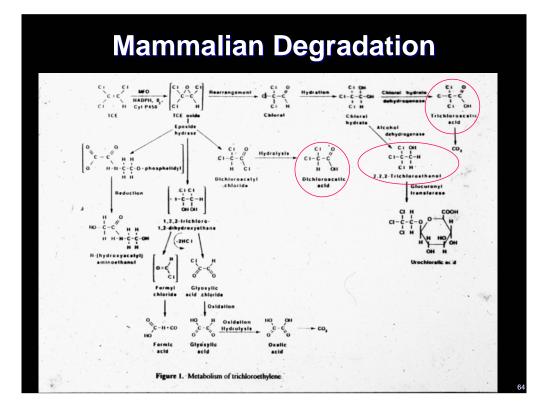
Phytodegradation

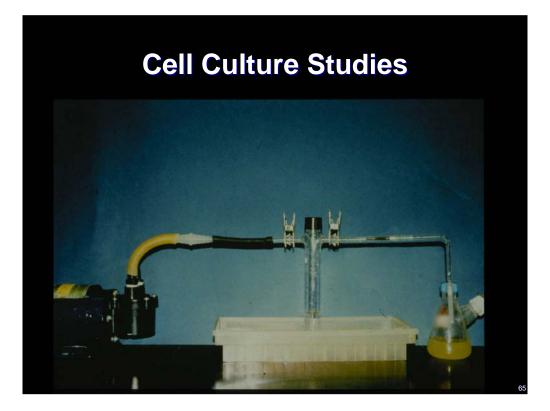
Using plants to themselves take up and degrade organic contaminants.

Enzyme Systems

Green Liver Concept P-450's Peroxidases Dehalogenases Reductases Glutathionone-s-transferases Conjugation enzymes

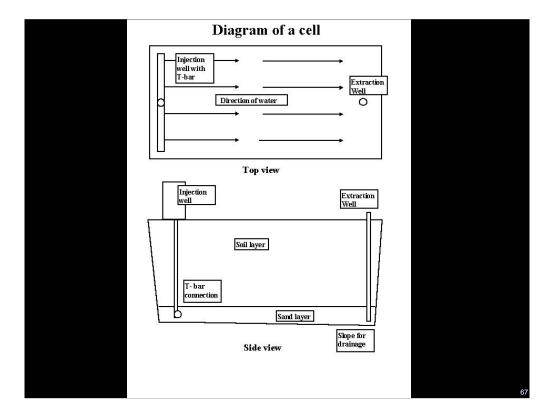






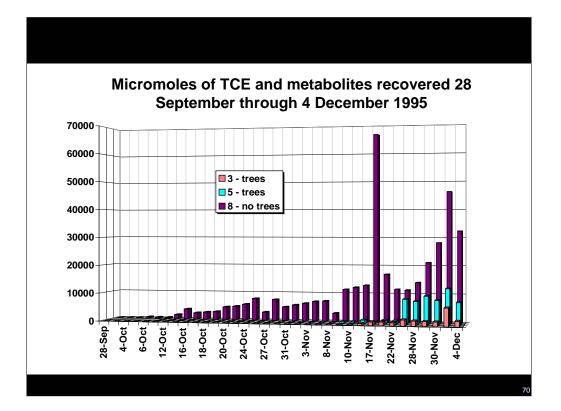
Greenhouse Studies

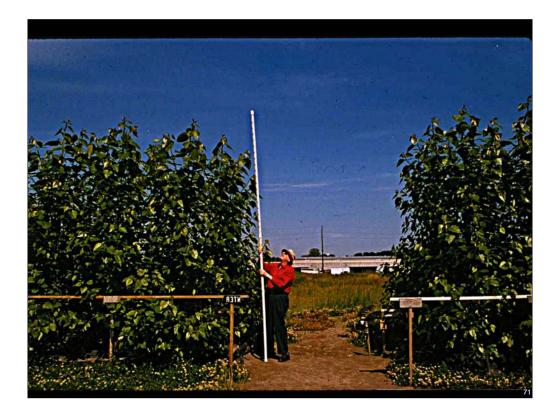


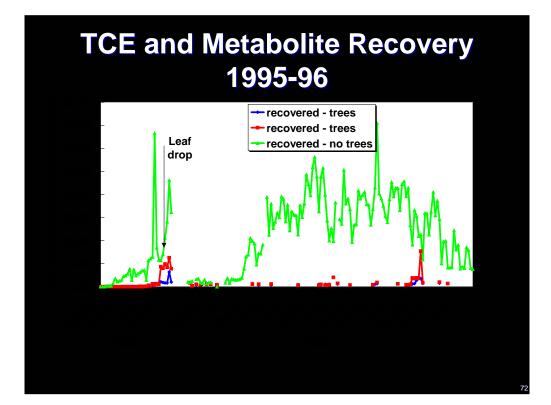






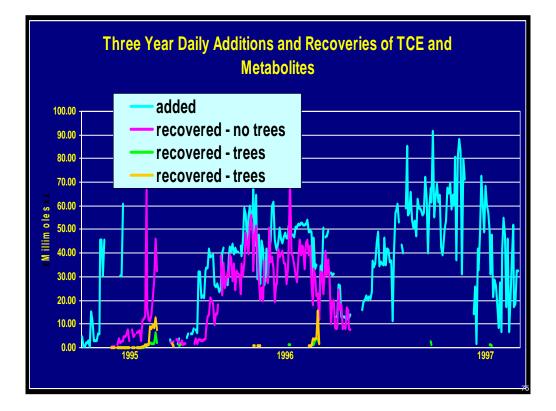


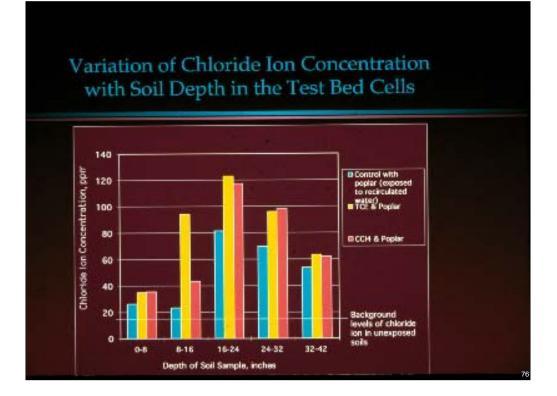


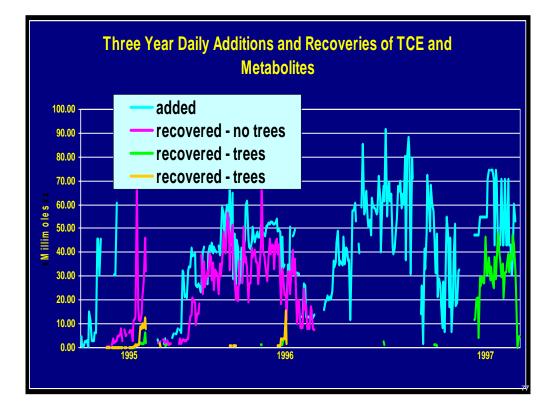












Other Compounds

MtBE , Benzene, other gasoline additives Pesticides; Ethylene dibromide, lindane Explosives; TNT, RDX, perchlorate Solvents; TCE, CT, PCE Deicing agents; benzotriazoles

Regulatory Concerns

How to convince the regulators that this is a good idea.

Regulatory Issues

Regulator unfamiliarity with process Not knowing all the answers to assure the regulator

Testing and Monitoring

How often What needs to be tested Soil Air Water Plant tissues How do you analyze these crazy samples???

Unusual Monitoring Parameters

Tree health or why are all my plants brown? Water issues Nutrient availability Is the soil itself killing the plants Fungus, bugs and other munching critters Convincing the regulators that plant health is a measurable criteria for success Where do those roots go?



Weather Impacts on Monitoring

Why doing transpiration measurements in the rain is not a good idea.
Temperature and light intensity have strong effects on plant metabolism and thus your test results.

What do you mean by success? Do you need different standards for success? What are actually testing? Plant survival Root depth Root penetration Transpiration Presence of metabolites Groundwater depression Soil analysis Transpiration rates

Security Issues

Securing a field can be more challenging than securing a building.
Squatters/Vagrants on the site.
Community member access on sites.
Involving the community with site protection.
Problems with radical groups.



Food chain transfer

Insects munching Animals munching on the plants or insects Local people taking the plants



And children want to play



Decision making

How to decide if phytoremediation is right for the site.

Site Evaluation

Evaluating a site as a potential phytoremediation site involves some different parameters.

Weather

Water availability

Soil fertility

Toxicity

Site Evaluation

Will phyto work with the contaminant I have on the site?

How will the plants and contaminants interact?

Is this acceptable to the regulators?

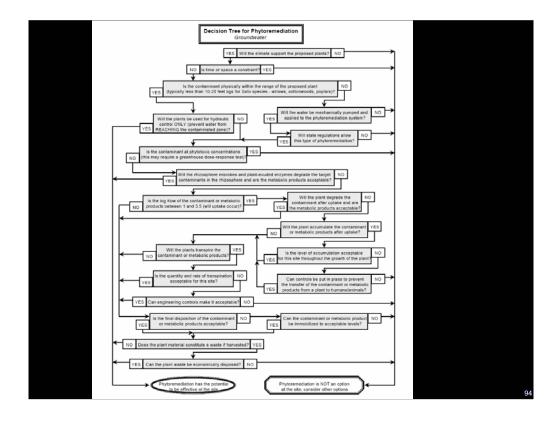
Site Evaluation

Is the site now, or could it be, applicable to plant growth?

Blacktop and plants do not mix

Shade/sun issues

Soil toxicity that is not related to contaminant



Designing a site

How do we make this work?

Unique Site Prep Problems

Concrete is not dependent on soil nutrients, but your plants will be. Soil compaction can be an issue for planting. Shades from buildings or other plants can be a major issue.

Security Issues

Securing a field can be more challenging than securing a building.Squatters/Vagrants on the site.Problems with radical groups.

Weather

Why doing transpiration measurements in the rain is not a good idea.
Temperature and light intensity have strong effects on plant metabolism and thus your test results.

Working With Mother Nature

- Construction can go on anytime of the year, but planting has to be in sync with the seasons.
- When dealing with natural systems we have to deal with all of nature (ie. bugs and birds are now a fact of life).

Selecting Plants For Your Site

You need to research and find the plant type that can handle the contaminant you are dealing with on the site

You need to find a plant that will SURVIVE on your site, or why brown trees don't impress anyone...





Before You Install, or Why Feasibility Testing is a Good Idea

Better to have a few plants die in the greenhouse, rather than have a field full of dead plants.....

Preparing the Site for Planting, or Why You Need to Learn to Think Like a Farmer

Weather plays an important role Why plowing mud is a BAD idea... Plants have their own time schedules, and you have to meet theirs, not the other way around

Sometimes That Extra Plowing is NOT a Good Idea...



Department of Energy – Ash Basin

Understanding how your preparations will affect the site



Know How Your Treatment Will Work





Consider Combination Technologies

- Pump and irrigate
- Water management behind a plume containment wall
- Reactive barriers and plants
- Combined bioremediation and phytoremediation
- Using plants to minimize recharge zones



Tritium Irrigation System

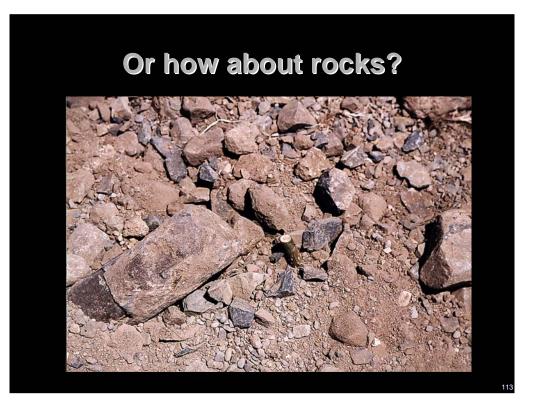


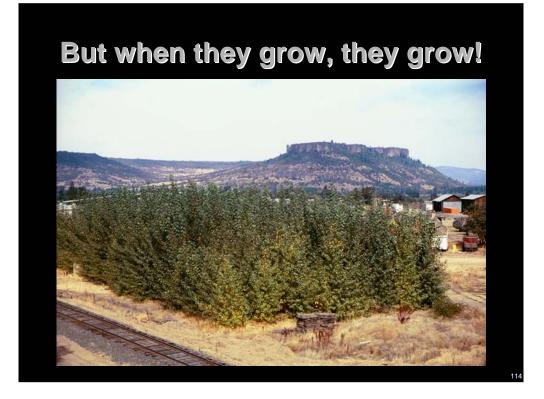
Medford

Timing of the installation can be critical Timing the herbicide application to remove existing vegetation can be vital Digging up irrigation lines does not help

Mud, Anyone?







Navy Base I

Plowing and moving mud Meeting unrealistic time schedules Why a wood chip road is NOT a good idea Hydrologic problems

Poplars don't swim real well

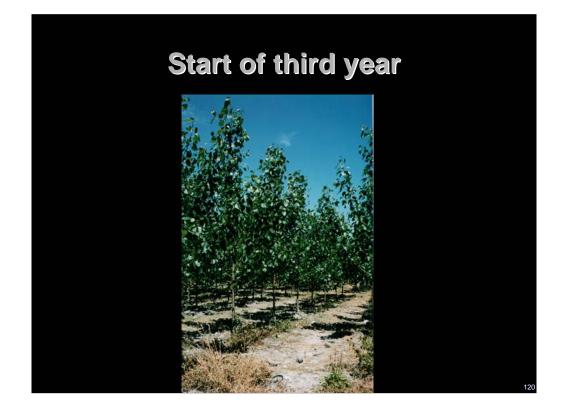
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Wood Chips are Not Always a Good Idea





Saginaw Mill

Drainage problems Trees and deer don't mix well The problems with weeds Why community knowledge is a good thing





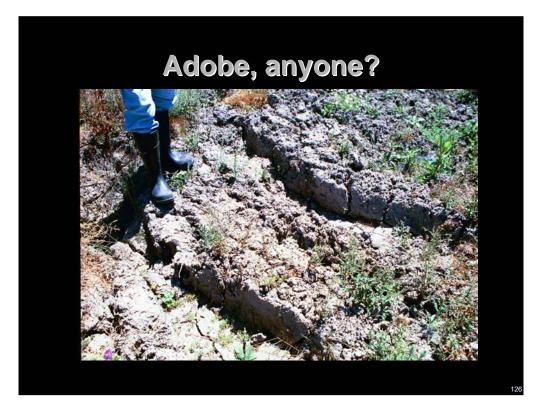
And finally they grow

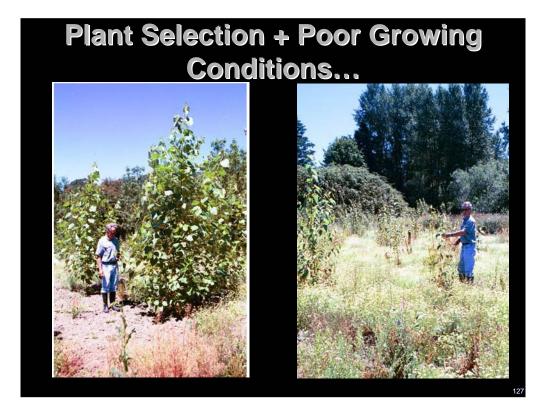




Portland

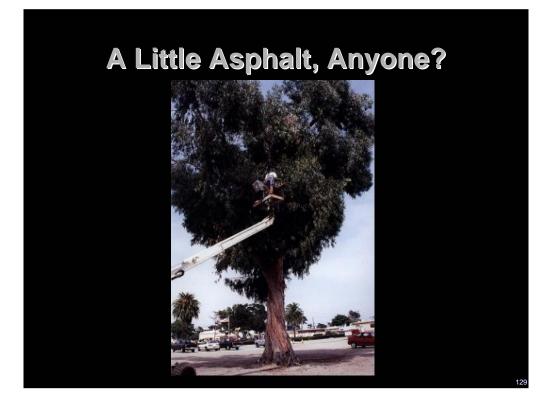
Why plowing mud is a bad idea or adobe is not a good growing medium Plant selection can be crucial





Navy Base II

You need to know what is happening all around you, even if it is not related to what you are doing



Vale

What do you mean there is too much fertilizer or when wood chips ARE a good idea

Didn't you say the pesticides were burned?

Why more mixing is not always better

A Little of Everything...





Wood Chips Just Might be a Good Idea Here!



And Then There Were Pesticides...



Still Not a Good Idea...



Okay, the Plants are Finally in the Ground and Growing. What Can Go Wrong Now???

Mechanical breakdowns Invaders of the four-legged kind Don't forget the "Save the Trees Society" Nutrient needs Droughts are Mother Nature's way of saying "Gotcha!"

Poplars Can't Swim!







Sigh.....

Plants are Growing, Everything is Looking Green and Healthy. Time to Start Testing. Now What?

Weather can still be a big issue Sample collection can pose some unique problems (getting liquid nitrogen into the field is NOT fun)

Where do I ship the samples for analysis?

Tell Me Again.....

WHY Do I Want to Put Myself Through This???

Less expensive

Citizens groups LIKE trees

Many regulatory agencies are looking favorable at groups that try innovative technologies

Because it is a great technology that will have you constantly learning as you go

Have faith in the trees!





