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PHYTOTECHNOLOGIES AND SOIL AMENDMENTS

Ecological Site Reuse

- Process by which site habitat is restored, enhanced, or created
- Soil amendments are used to bind contaminants, build soil, establish plant growth

Phytotechnology

- Use of plants to solve/mitigate environmental problems
- Construction of ecosystems (wetlands for wastewater treatment)
- Recovery of ecosystems (mine reclamation, restoration of lakes and rivers)
- Create sinks for CO2 to mitigate impacts of climate change (reforestation)
- Mitigate pollution impacts and moderate energy extremes (green roofs)

Casper, Wyoming

http://www.bp.com/genericarticle.do?categoryId=9013611&contentId=7021426

Reforestation

http://www.reforestteak.com/New-World-Eco-Trees_ep_44-1.html

Mine Reclamation

http://ecology.ucdavis.edu/programs/restoration/ecolrestore.html

Coeur D'Alene Wetlands

Source: Compton, Brown: Restoration Alternatives

The Players

- Soil
- Contaminants
- Plants

General Soil Conditions

- Nutrient Status
- Soil pH
- Organic matter content
- Soil type (clayey vs sandy soils)
- Soil Compaction
- Soil Chemistry
  - Toxicity of soil contaminants (metals)
  - Excess Na (phytotoxic)
  - Excess salts (phytotoxic)

Compaction

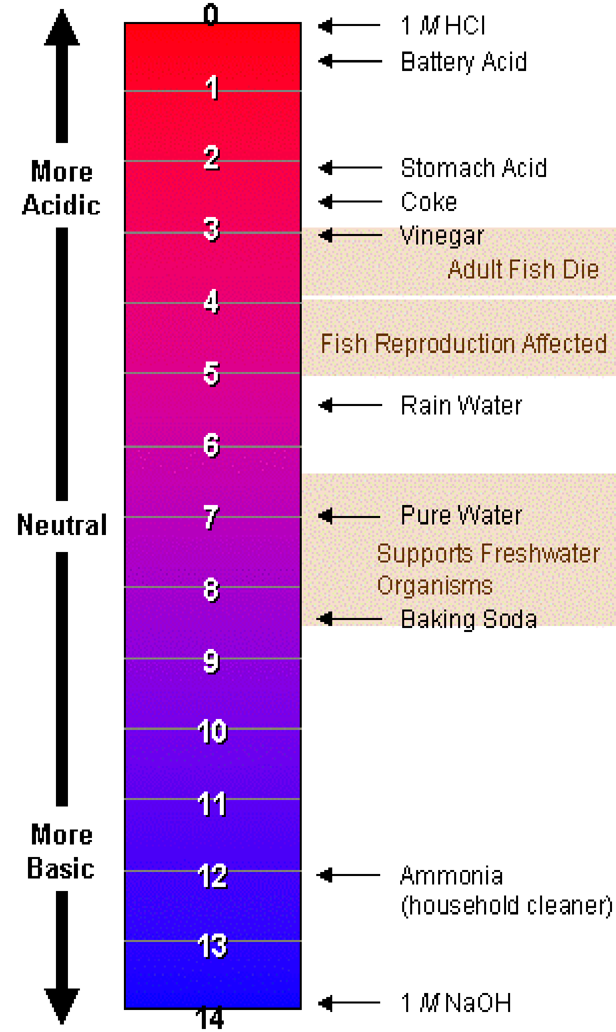
- Reduces soil porosity
- Air movement and root penetration are restricted
- Water runs off or ponds instead of infiltrating
- Roots grow sideways instead of downward
- Remedies: Tilling and addition of compost

Nutrient Status

- Nutrient status: N, P, K
- Nitrogen: healthy leaf and stem growth
- Phosphorus: important for root growth, flower production, binds metals (reduces bioavailability)
- Potassium: overall plant health

pH

- Measure of soil acidity or basicity/alkalinity
- Has a great impact on numerous soil chemical reactions
- Example: adsorption
- Low soil pH means:
  - higher mobility of cationic meta
  - ↓ lower mobility of anions



pH Adjustment

- Add lime to increase alkalinity
- Add fertilizer to increase acidity: ammonium sulfate, sulfur-coated urea

$$\underset{\text{ammonium}}{2NH_4^+} + \underset{\text{oxygen}}{3O_2} \xrightarrow{\text{bacteria}} \underset{\text{nitrite}}{2NO_2^-} + \underset{\text{water}}{2H_2O} + \underset{\text{acid}}{4H^+}$$

- Add elemental sulfur or aluminum sulfate to acidify soils

$$\underset{\text{sulfur}}{2S} + \underset{\text{oxygen}}{3O_2} + \underset{\text{water}}{2H_2O} \xrightarrow{\text{bacteria}} \underset{\text{sulfuric acid}}{2H_2SO_4}$$

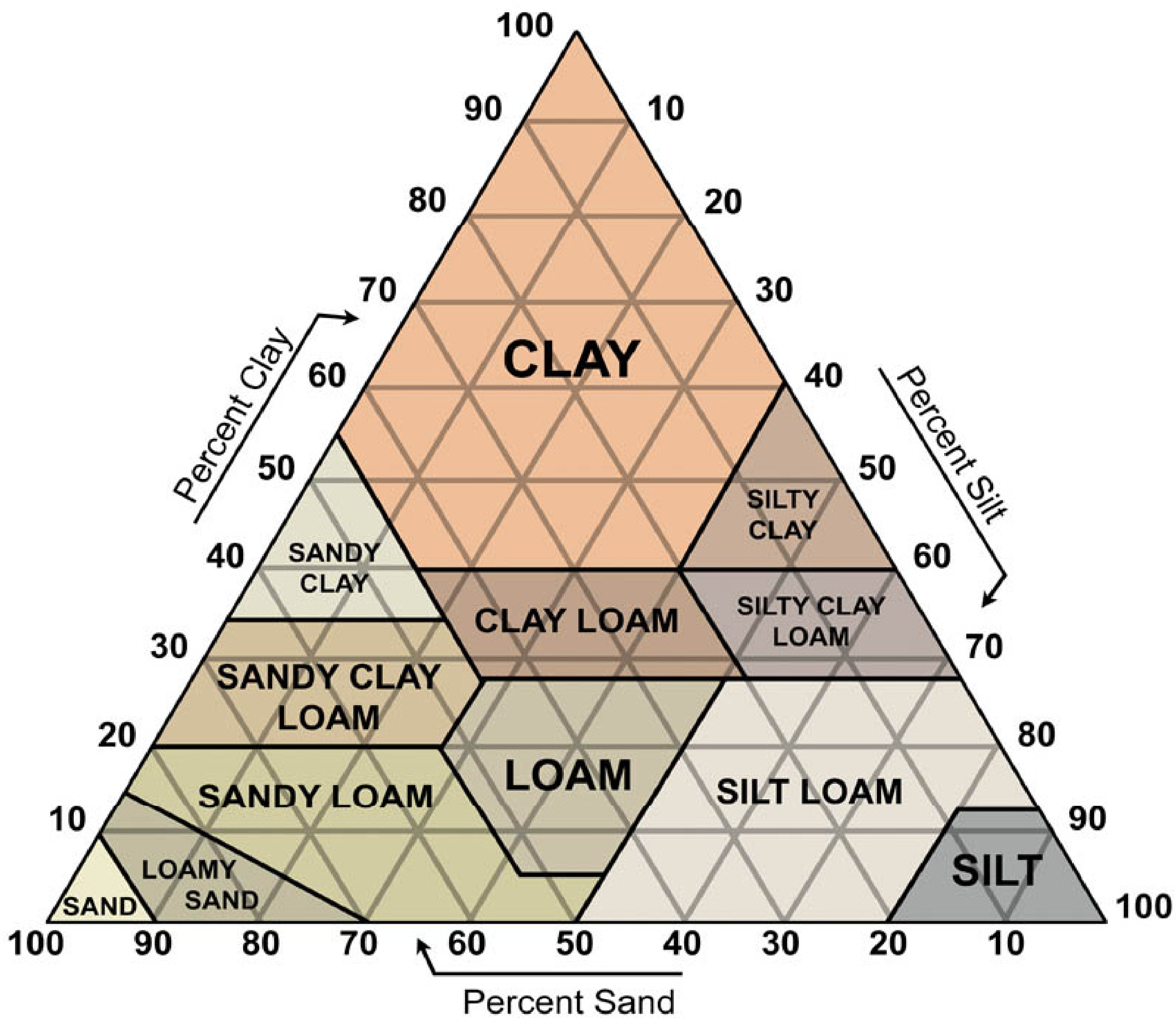
Organic Matter

- Enhances soil color
- Improves soil structure
- Improves soil drainage and aeration (clayey soils)
- Retains Water (sandy soils)
- Provides soil nutrients
- Encourages microbial activity
- Binds contaminants, reduces bioavailabilit y
- Ideal OM content depends on soil type
  Below 1-3 % OM can be considered as low

Soil Type

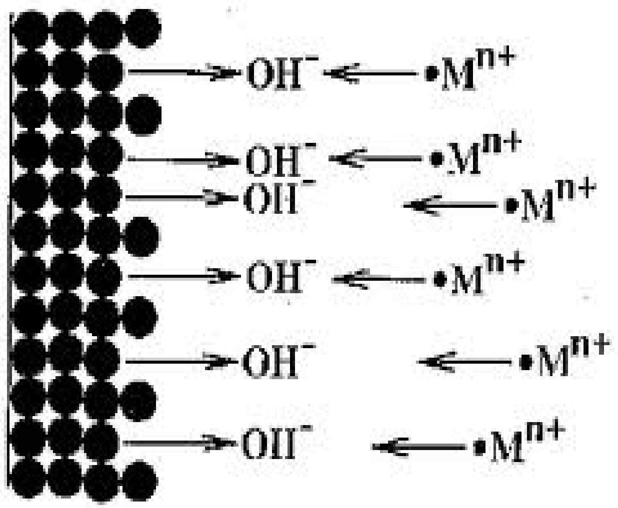
- Soils are a combination of sand, silt and clay
- Soil Type - dependant upon sand, silt and clay content

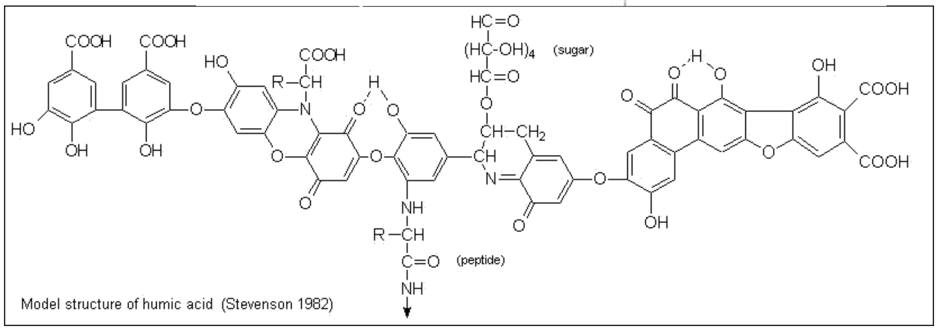
Soil Classification



Soil Type

- Clayey soils:
  - Contaminants will adsorb to the clay mineral surfaces
  - Adding OM will loosen soil, improve aeration, water infiltration, and also reduce bioavailability by binding contaminants





Model structure of humic acid (Stevenson 1982)

Soil Amendments

- Biosolids
- Manure
- Sugar beet lime
- Wood ash
- Log yard waste
- Composts

Types of Soil Amendments

Table 3: Types of Soil Amendments

Amendment	Availability	Uses	Public Acceptance	Cost	Advantages	Disadvantages	Links
Organics							
Biosolids	Sustainable supply. Higher quantities in urban areas	Nutrient source; Organic matter (OM) source; Sorbent[1] properties increase with increasing iron content.	Largely odor-driven; Pathogen concerns; Concerns largely driven by perception.	Materials generally free; Municipalities may pay for transport and use.	Multi-purpose, multi-benefit soil amendment; highly cost-effective; EPA regulated[2]; well characterized consistent quality.	Public concern/public perceptions; High nutrient loadings in some settings; Some sources have high moisture content	National Biosolids Partnership (http://www.biosolids.org/index.asp)
Manures	Sustainable supply; Higher quantities near CAFOs	Nutrient source; OM source.	Well accepted.	Materials generally free; Transport and application fee.	Widespread and readily available.	Not consistently regulated[2]; Variable quality; Not routinely treated for pathogen reduction; Generally uncharacterized.	Industry Residuals: How They Are Collected, Treated and Applied (http://www.du-in.org/studentpapers/)
Compost	Location-dependent; Volumes limited; Competing users	Nutrient source; OM source.	Readily accepted.	Product and transport costs can be high.	Readily accepted. Stable product. Can be used in or near water.	High cost; Limited availability; N quantity usually significantly lower than non-composted materials.	U.S. Composting Council (http://www.compostingcouncil.org/section.cfm?id=37) Association of Compost Producers
Digestates[3]	New material; Very location dependent	Nutrient source; OM source.	May have odor problems.	To be determined; Transport and application fee.		New enough so that not regulated[2]; Variable quality; Not routinely treated for pathogen reduction; Generally uncharacterized.	

Use of Soil Amendments

Table 1: Types of Problems Addressed by Soil Amendments

	Exposure Pathways and Adverse Effects	Interactions	Solutions
	Contaminant Bioavailability/Phytoavailability Problems		
Toxicity (inorganic)			
Aluminum (Al)	Phytotoxicity Runoff Leaching	Low pH [2] = more toxic; Low P = more toxic; High calcium (Ca) = less toxic	Raise pH greater than 6.0, add OM and P; add gypsum or other high soluble Ca source
Arsenic (As)	Soil Ingestion Runoff Leaching	High pH [2] = more toxic; High P = more soluble	Add organic matter (OM) and adjust pH to between 5.5-6.5
Borate (BO_3^{3-})	Phytotoxicity	Low and High pH [2] = more toxic	Add iron oxide and acidify (pH between 6.0-7.0)
Cadmium-to-Zinc Ratio (Cd:Zn) [1]	Food chain	High ratio = greater bioavailability (risk) of Cd	Add Zn to reduce the Cd:Zn ratio
Chromate (CrO_4^{2-})	Phytotoxicity Runoff Leaching	High pH [2] = more toxic	Add reductants, e.g., OM, biosolids; also acidify to less than 6.5
Copper (Cu)	Phytotoxicity Runoff Leaching Aquatic receptors	Low pH [2] = more toxic; low OM = more toxic	Raise pH (6.0-7.0), add P, OM, and sorbents
Lead (Pb)	Soil ingestion	Low phosphorus (P) = more toxic	With no As present, raise pH to 6.0 or greater; with As present, raise pH to 5.5-6.5; add P, and iron oxide
Manganese (Mn)	Phytotoxicity Runoff Leaching	Low pH [2] = more toxic	Raise pH greater than 7.0
Molybdenum (Mo)	Food chain Cu:Mo ratio	High pH [2] = more toxic; Low Cu = more toxic	Acidify (pH between 5.5- 6.5) and add Cu

The Use of Soil Amendments for Remediation, Revitalization, and Reuse, EPA 542-R-07-013, 2007

Use of Soil Amendments, cont.

	Exposure Pathways and Adverse Effects	Interactions	Solutions
Nickel (Ni)	Phytotoxicity	Low pH [2] = more toxic; low P = more toxic	Raise pH (7.0-8.0), add P, OM, and sorbents
Selenium (Se)	Food chain Runoff Leaching	High pH [2] = more toxic	Acidify (pH between 5.5-6.5)
Sulfate (SO_4^{2-})	Phytotoxicity to salt effects	NA	Irrigate soil
Zinc (Zn)	Phytotoxicity	Low pH [2] = more toxic; low P = more toxic	Raise pH (7.0-8.0), OM, and sorbents[3], e.g., iron and manganese oxides, WTR[4]
Toxicity (organic)			
Polycyclic Aromatic Hydrocarbon (PAH)	Soil Ingestion	Low OM [5]= more bioavailable	Add OM and tillage
Polychlorinated Biphenyl (PCB)	Soil Ingestion	Low OM [5]= more bioavailable	Add OM and tillage
	Poor Soil Health/Ecosystem Function Problems		
High or Low pH			
Active Acidity (as measured directly in a water:soil mixture)	Runoff Leaching	Controls metal solubility and microbial activity; increases metal availability [6]	Add lime and/or other alkaline soil amendments
Alkalinity	Anion solubility and metal micronutrient availability	See Mo, Se, As listed above	Add acid equivalent
Potential Acidity (total acid production capacity with time; largely from unreacted sulfides)	Runoff Leaching Metal and salt evolution and associated phytotoxicity	Similar to active acidity (above) [6]	Estimate total lime demand and add 1.25 to 1.5 times the demand
Sodicity or Salinity			
Electrical Conductivity	Phytotoxicity, plant water stress, nutrient uptake imbalances	High Na = more toxic	Irrigate; OM may help
Sodium (Na)	Phytotoxicity Sodicity[7]	High SAR = high soil dispersion	Add any Ca:Mg-rich material[1]; OM

The Use of Soil Amendments for Remediation, Revitalization, and Reuse, EPA 542-R-07-013, 2007

Addition of Soil Amendments Can Reduce Contaminant Bioavailability

Bioavailability: the fraction of the chemical(s) of concern in soil that is accessible to an organism (human or plants) for absorption

Metal contaminated soils- unamended	With Lime	With Beringite modified aluminosilicate	With Red Mud Fe oxide rich residue

Courtesy of CSIRO, Land & Water, Australia

Biosolids

- Nutrient rich organic material resulting from the treatment of domestic sewage in treatment facility
- Tested (federal biosolids rule: 40CFR Part 503)
- Biosolids can be applied as fertilizer and will improve soil structure
- Very efficient use of organic N,P by crops because of slow release throughout the growing season

Tacoma, WA

Lime+
Tagro
added

Control

Arsenic Concentrations in Soils and Lettuce Samples

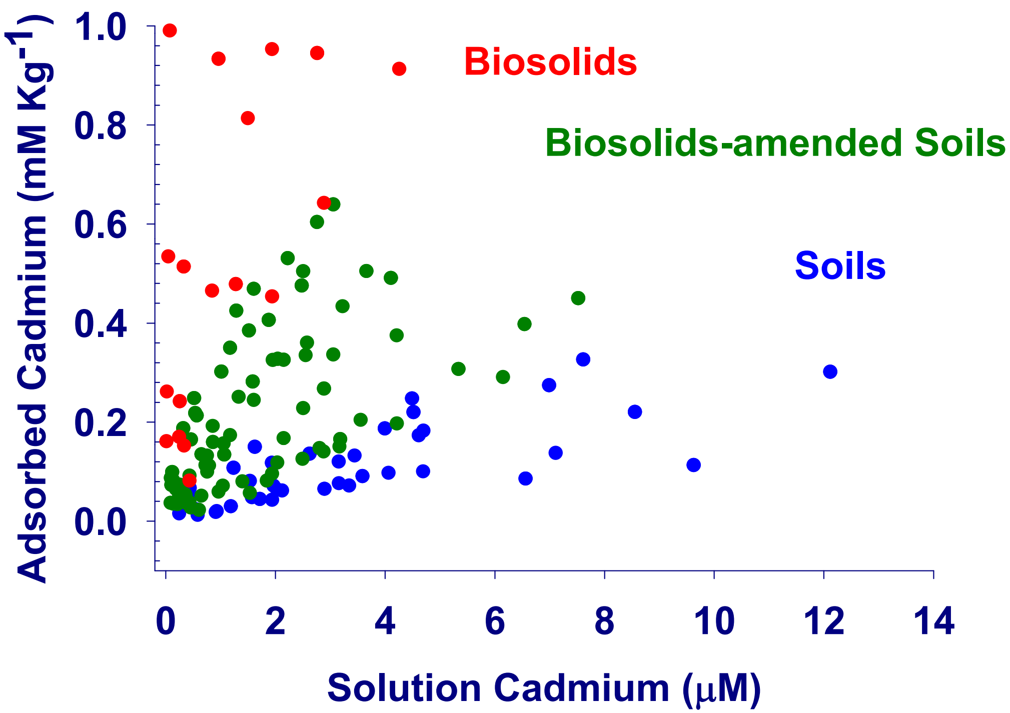
Tacoma, WA Test Plot Site

Treatment	Soil (mg/kg)†	Lettuce (mg/kg) †
Control	90	0.151
Tagro +Lime	87	0.081

†All concentrations are average of four field replicates

Unpublished preliminary data which is not released for reproduction, distribution, or publication by others

Cadmium Adsorption by Biosolids amended Soils



Ryan et al. (2003)

Bioavailability

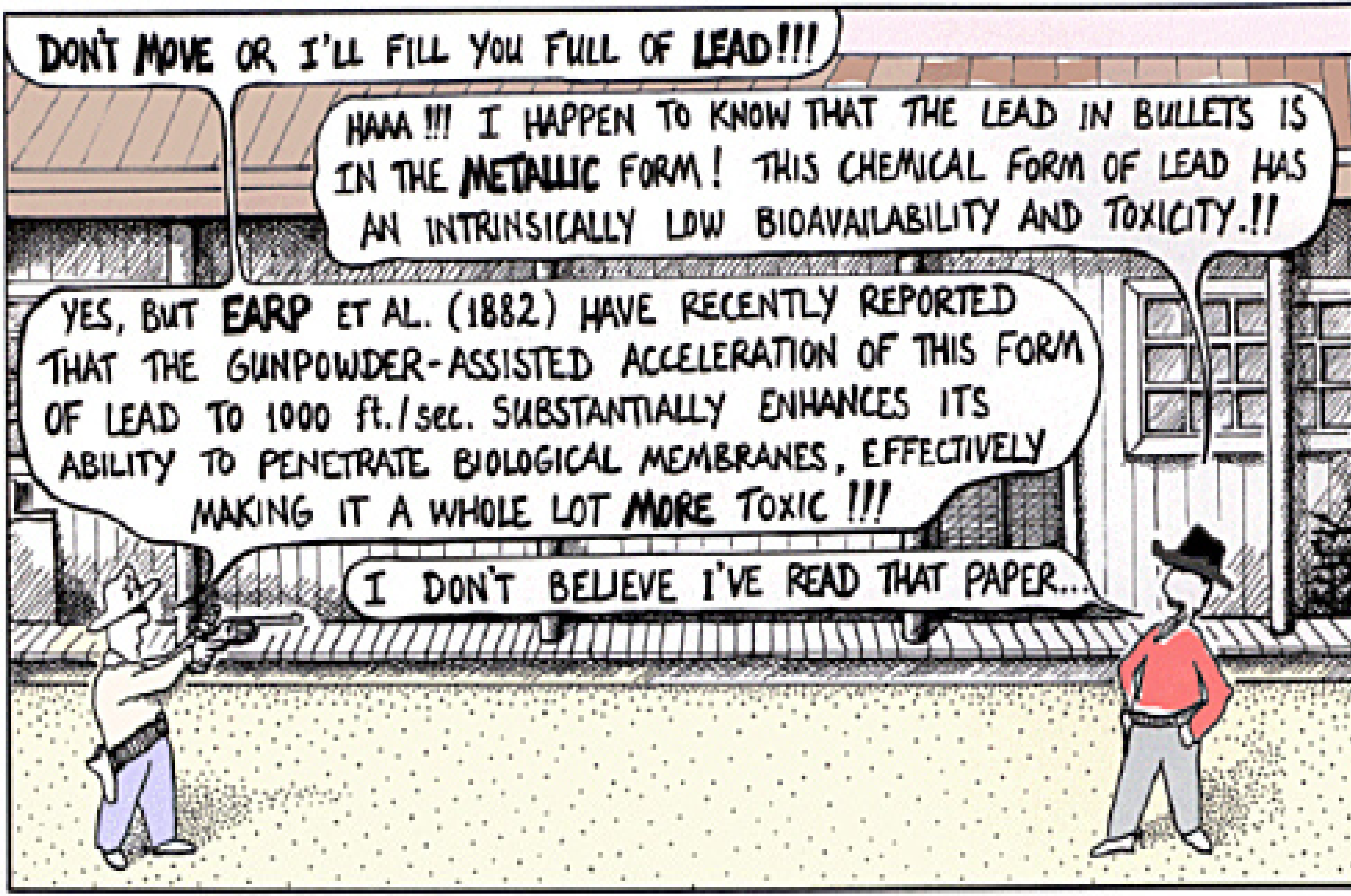
- *Describes the fraction of the chemical(s) of concern in soil that is accessible to an organism (human or plants) for absorption.*
- *Commonly thought of as one process only: Absorption Efficiency*

Sandy Soils and Zinc

Courtesy of CSIRO, Land & Water, Australia

Clayey Soil and Zinc

Courtesy of CSIRO, Land & Water, Australia



ENVIRONMENTAL SCIENTISTS IN THE WILD WEST

Galena, KS

Case Study: Galena, KS

Issues:

- Lack of vegetation
- Zn, Cd, and Pb levels in surface waters and stream sediments exceeded aquatic life criteria
- Interrelated issues: lack of vegetation promotes the movement of runoff and sediments from mining-impacted areas

Factors Limiting Vegetative Growth

- Nutrient deficiencies
- Metal toxicity
- Adverse pH conditions
- Limited water holding capacity
- Lack of microbial activity
- Poor soil chemical, physical, or biological properties

Manure Application

Photo courtesy of G. Pierzynski

Plot without Amendment

Photo courtesy of G. Hettiarachchi

Plot with Amendment

Photo courtesy of G. Hettiarachchi

Electrical Conductivity

Time	control	100 tons/acre	200 tons/acre
	------------------------------ dS/m ------------------------------		
Fall '07	0.4	30	43
Spring '08	0.4	0.8	1.0
Fall '08	0.6	0.8	1.0
Spring '09	0.3	0.5	0.6
Fall '09	0.3	0.4	0.5

Hettiarachchi G.M., and G.M. Pierzynski. 2010. USE OF PELLETIZED COMPOST MATERIALS AS AMENDMENTS OF LEAD-ZINC CHAT TAILINGS IN GALENA, KANSAS. *First Quarter 2010. Quarterly Progress Report Submitted to the Kansas Department of Health and Environment.*

Extractable Zn

Time	control	100 tons/acre	200 tons/acre
	---------------------------- mg/kg	--------------------------	
Fall '08	134	8	6
Spring '09	86	9	4
Fall '09	228	74	16

Hettiarachchi G.M., and G.M. Pierzynski. 2010. USE OF PELLETIZED COMPOST MATERIALS AS AMENDMENTS OF LEAD-ZINC CHAT TAILINGS IN GALENA, KANSAS. *First Quarter 2010. Quarterly Progress Report Submitted to the Kansas Department of Health and Environment.*

Ground Cover

Time	control	100 tons/acre	200 tons/acre
	------------------------- plants/50 ft ---------------------------		
Spring ‘09	62	62	64
Fall ‘09	65	87	88

Hettiarachchi G.M., and G.M. Pierzynski. 2010. USE OF PELLETIZED COMPOST MATERIALS AS AMENDMENTS OF LEAD-ZINC CHAT TAILINGS IN GALENA, KANSAS. *First Quarter 2010. Quarterly Progress Report Submitted to the Kansas Department of Health and Environment.*

Biomass Production

Time	control	100 tons/acre	200 tons/acre
	------------------------- g / m^2 ---------------------------		
Fall '08	13	18	16
Fall '09	37	102	107

Hettiarachchi G.M., and G.M. Pierzynski. 2010. USE OF PELLETIZED COMPOST MATERIALS AS AMENDMENTS OF LEAD-ZINC CHAT TAILINGS IN GALENA, KANSAS. *First Quarter 2010. Quarterly Progress Report Submitted to the Kansas Department of Health and Environment.*

Applicable Contaminants

- Petroleum Hydrocarbons
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Polychlorinated Biphenyls (PCBs)
- Trichlorethene (TCE) and other chlorinated solvents
- Ammunition wastes and explosives
- Heavy Metals
- Pesticides

Phytostabilization

Ground cover

- aids in soil stabilization
- prevents erosion, drift
- prevents direct contact (human, animal) with contaminants
- controls infiltration

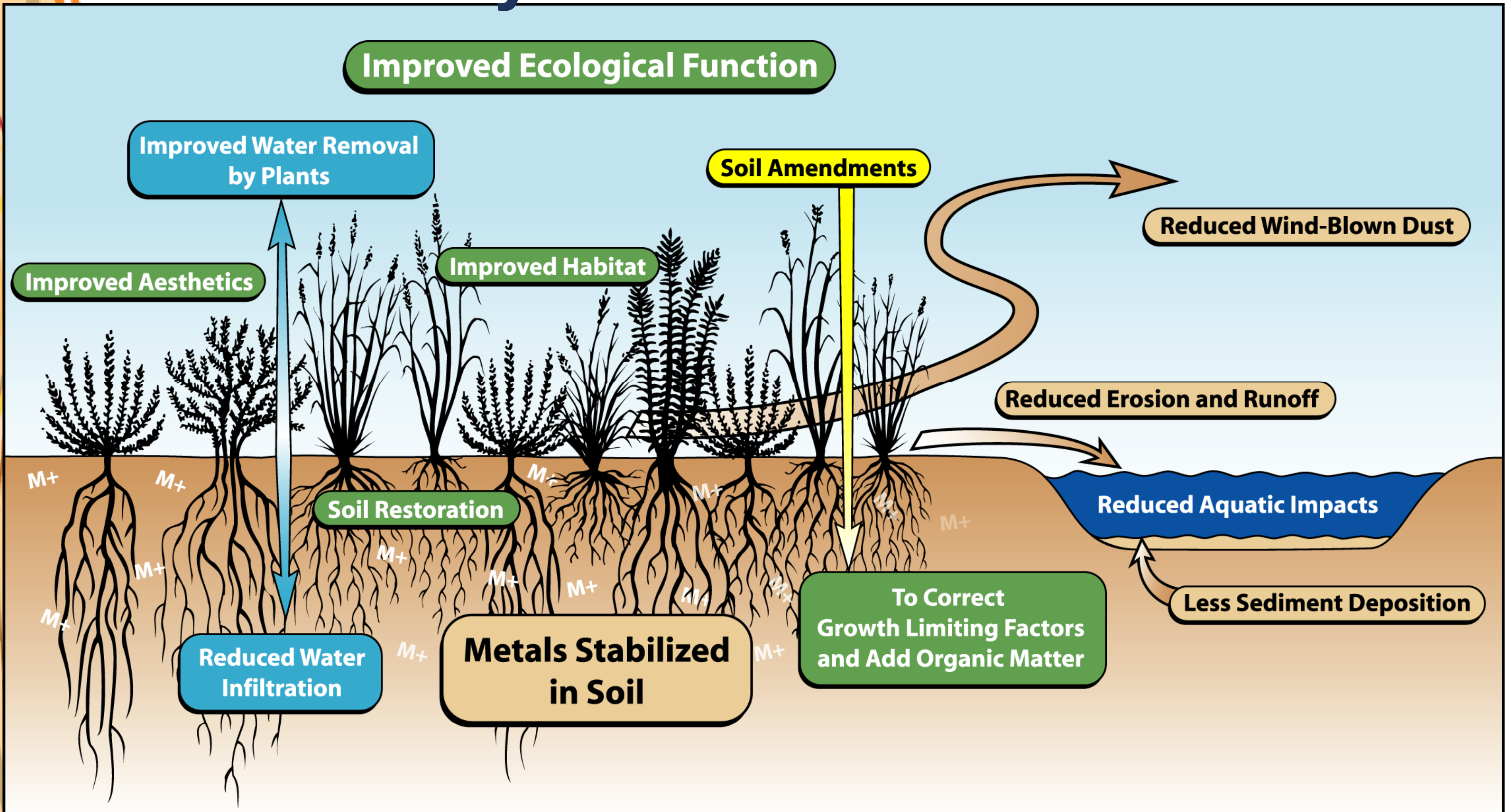
Phytostabilization, cont.

Mobility reduction of heavy metals and some organic contaminants

- Via chemical interaction in rhizosphere
  - Accumulation of contaminants at root/soil interface
  - Precipitation of contaminants within root zone
  - Adsorption of contaminants onto roots

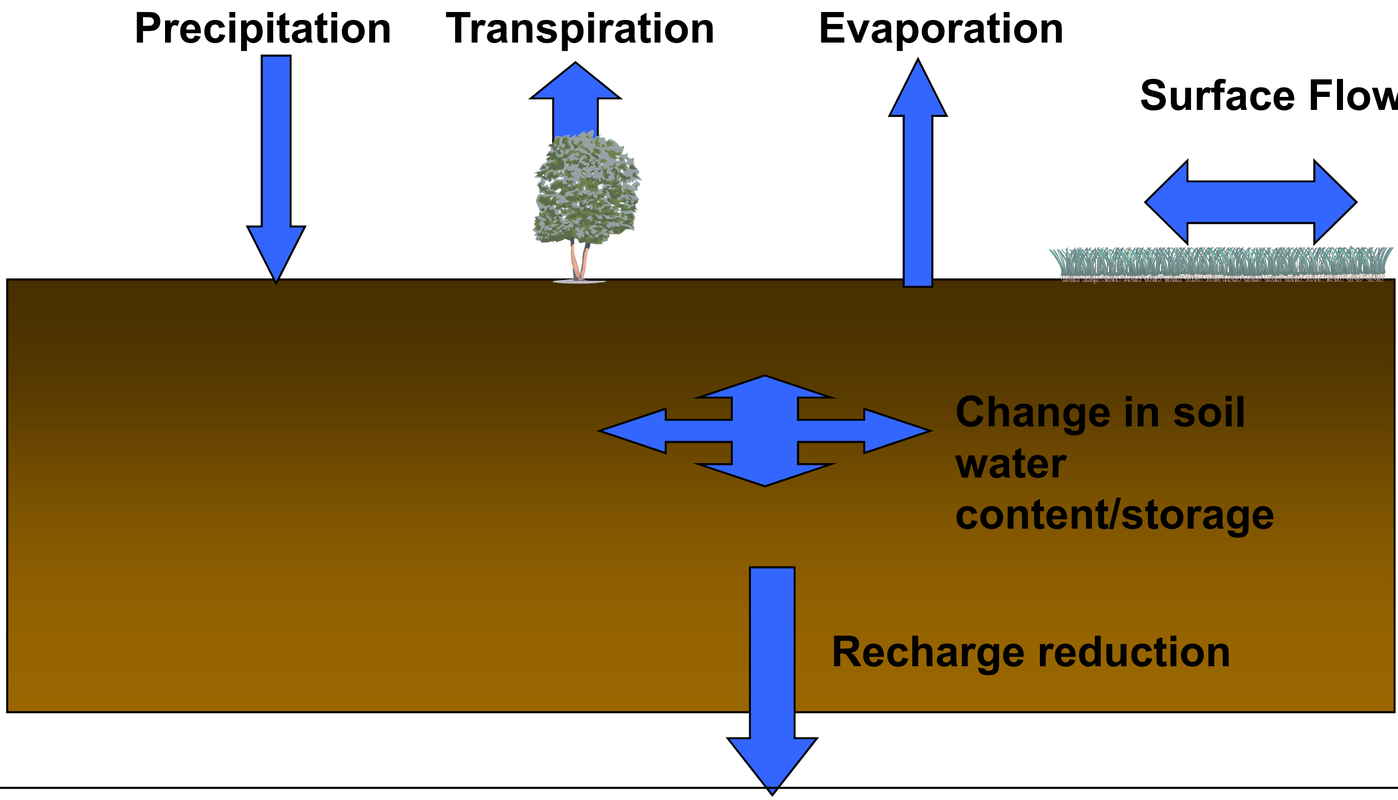
- Via soil amendments to decrease solubility of metals (phosphates, lime, OM, biosolids)

Phytostabilization



Pierzynski, et al, 2002, Plant System Technologies for Environmental Management of Metals in Soils: Educational Materials, J. Nat. Resour. Life Sci. Educ., Vol. 31, p. 31-37

Vegetative Covers - Hydrologic Component



R =P - ET + S

where R= recharge, P=precipitation, ET=evapotranspiration, S=change in water storage

McMillan, 2002, Phytotechnologies Workshop Presentation, EPA Brownfields Conference, Atlantic City, NJ

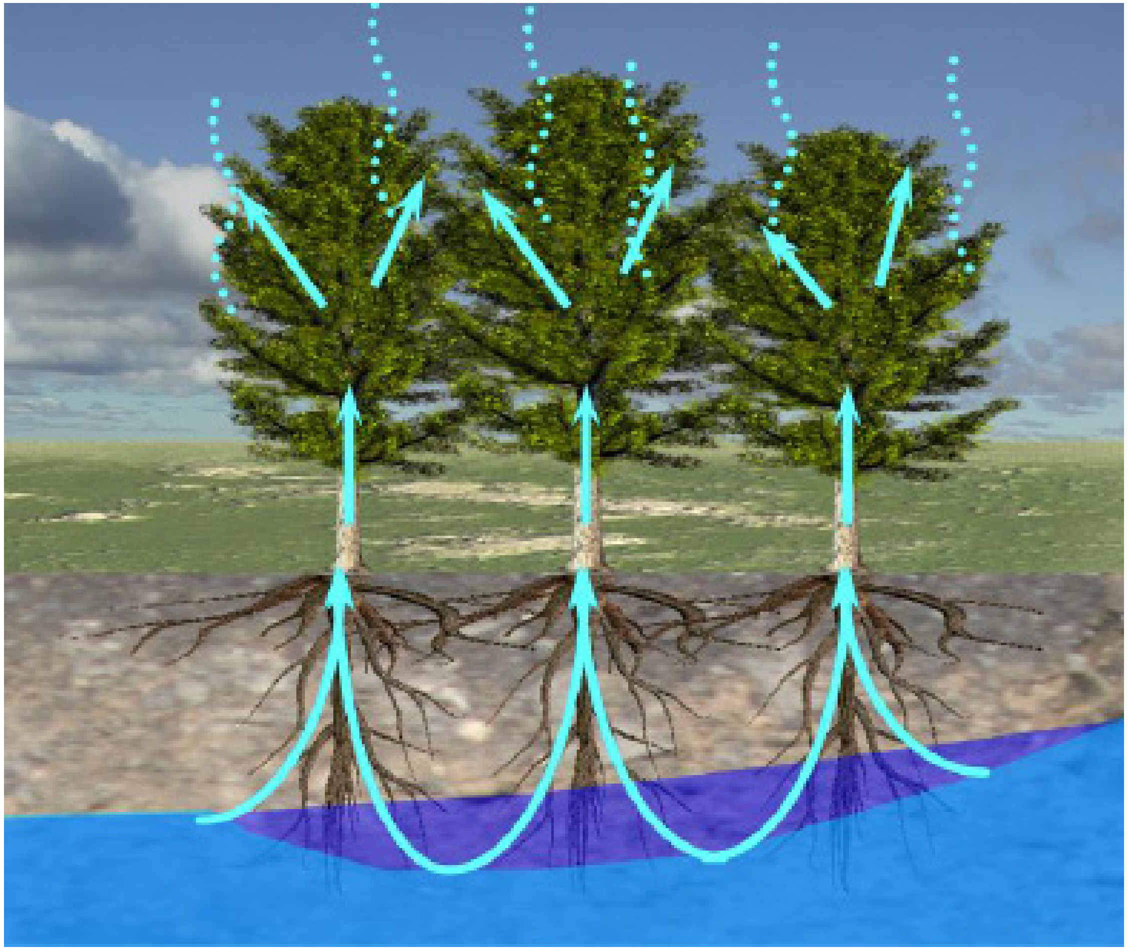
Precipitation Interception Capacity by Plants

Table 1-2. Typical water interception capacities

Plant name	Plant type	Magnitude and duration of rain	Interception capacity (%)
Natural pasture	Mixed grasses	389 mm in 5 months	14–19
Alfalfa	Agricultural crop	Unspecified	36
Tall panic grass	Prairie species	12.7 mm in 30 minutes	57
Little blue stem	Prairie species	12.7 mm in 30 minutes	50–60
Birch	Tree species	350 mm in 5 months	10
Ash	Tree species	38 mm rain (no time given)	24
Spruce-fir	Tree species	272 mm in 5 months	30

From: Phytotechnology Technical and Regulatory Guidance and Decision Trees, revised, ITRC, 2009

Phytohydraulics



From: Phytotechnology Technical and Regulatory Guidance and Decision Trees, revised, ITRC, 2009

Maximum Rooting Depths

Examples

- Indian Mustard: to 12 inches - Metals
- Grasses: to 48 inches - Organics
- Alfalfa: to 30 feet
- Poplar trees: to 15 feet - Metals, organics, chlorinated solvents

Phytodegradation

- Breakdown of contaminant molecules via plant enzymes into less or non-toxic toxic components

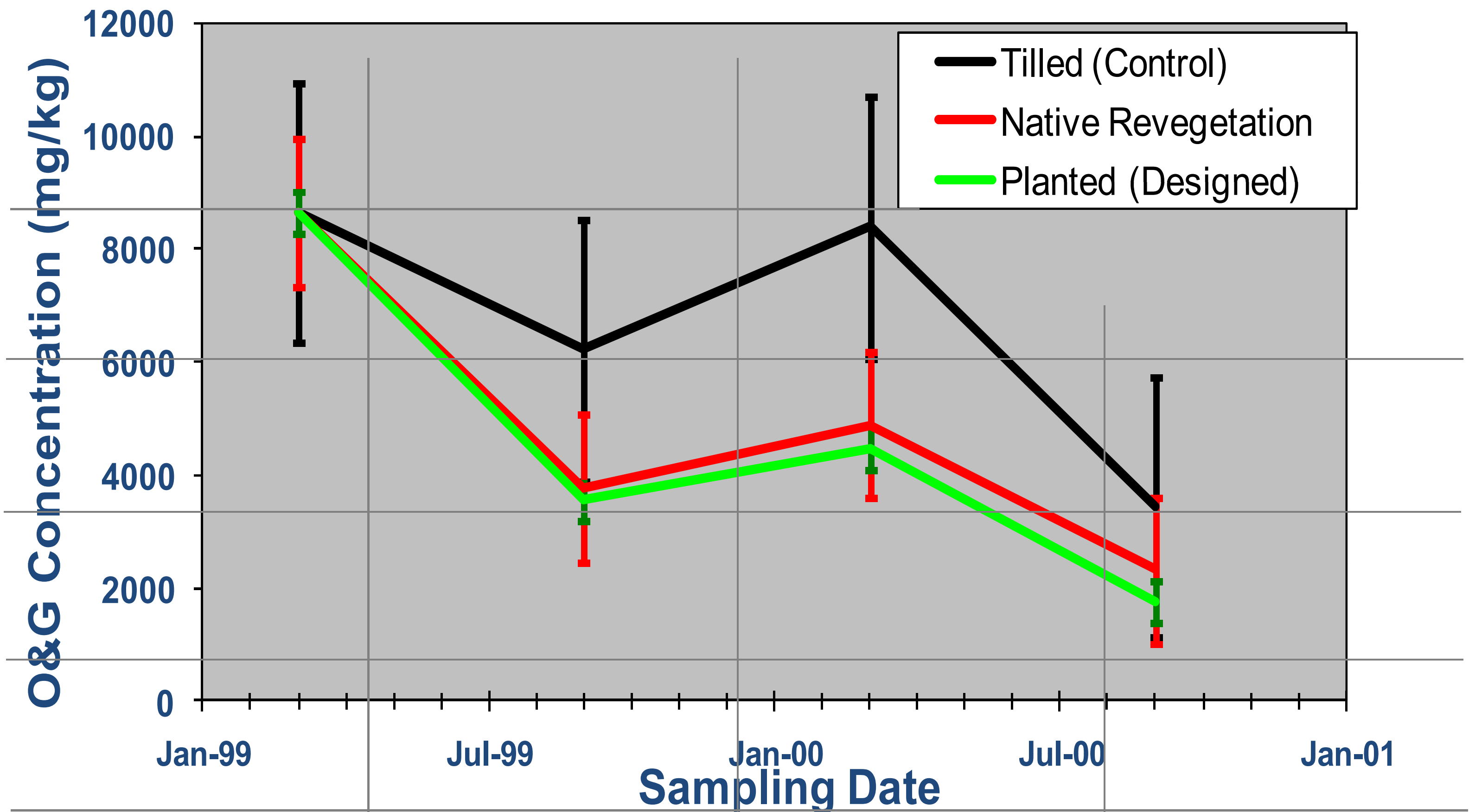
  Examples:
- Hybrid Poplar Trees break down TCE into water, CO2 and chloride ions (Schnoor et al. 1995)
- Poplars partially break down TNT

Phytotransformation
Organic Contaminants (examples)

- Petroleum Hydrocarbons – TPH, PAHs, BTEX
- Pesticides
- Chlorinated Solvents – usually involving groundwater
- PCPs
- PCBs

BIODEGRADING HYDROCARBONS

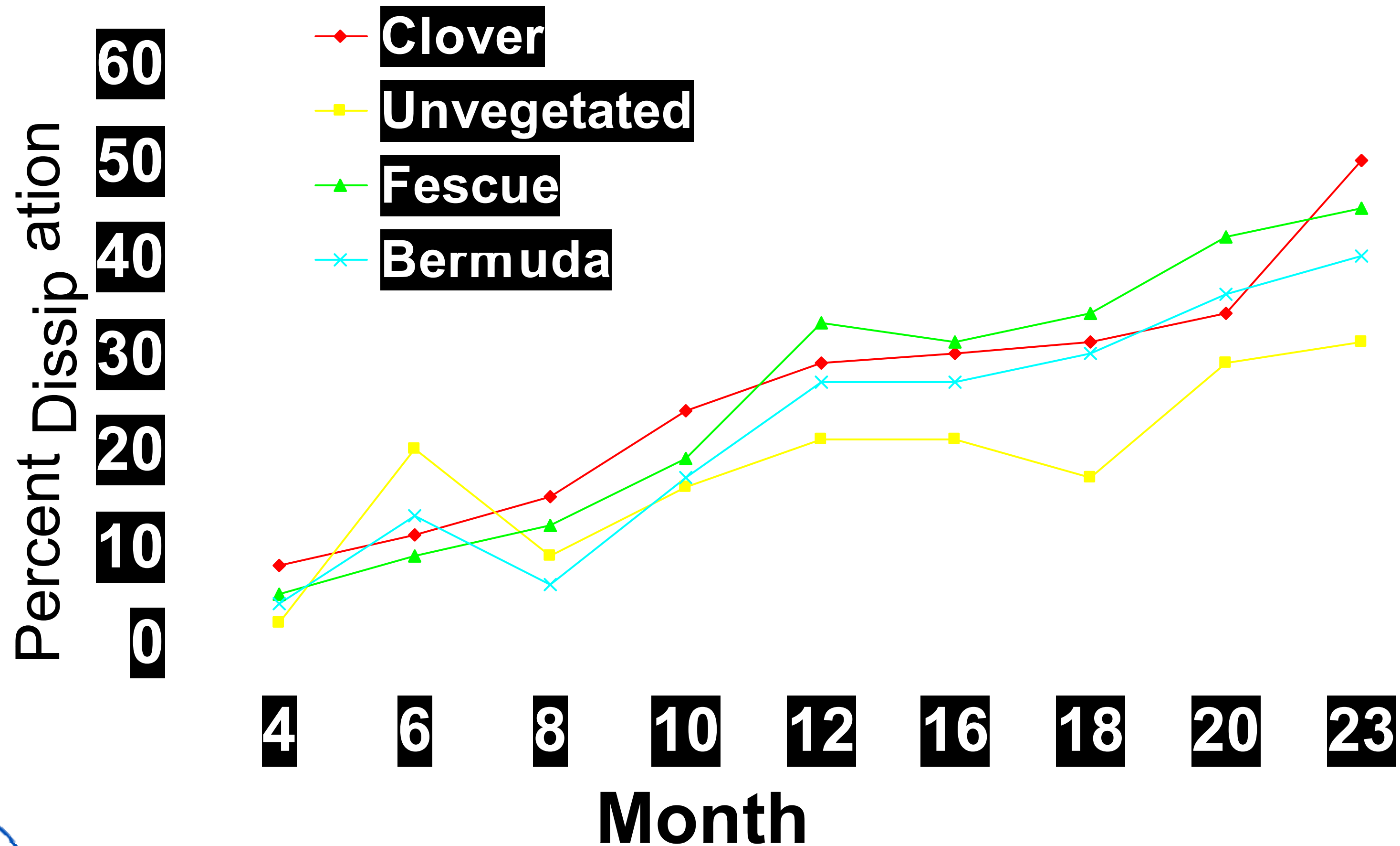
(Texas City)



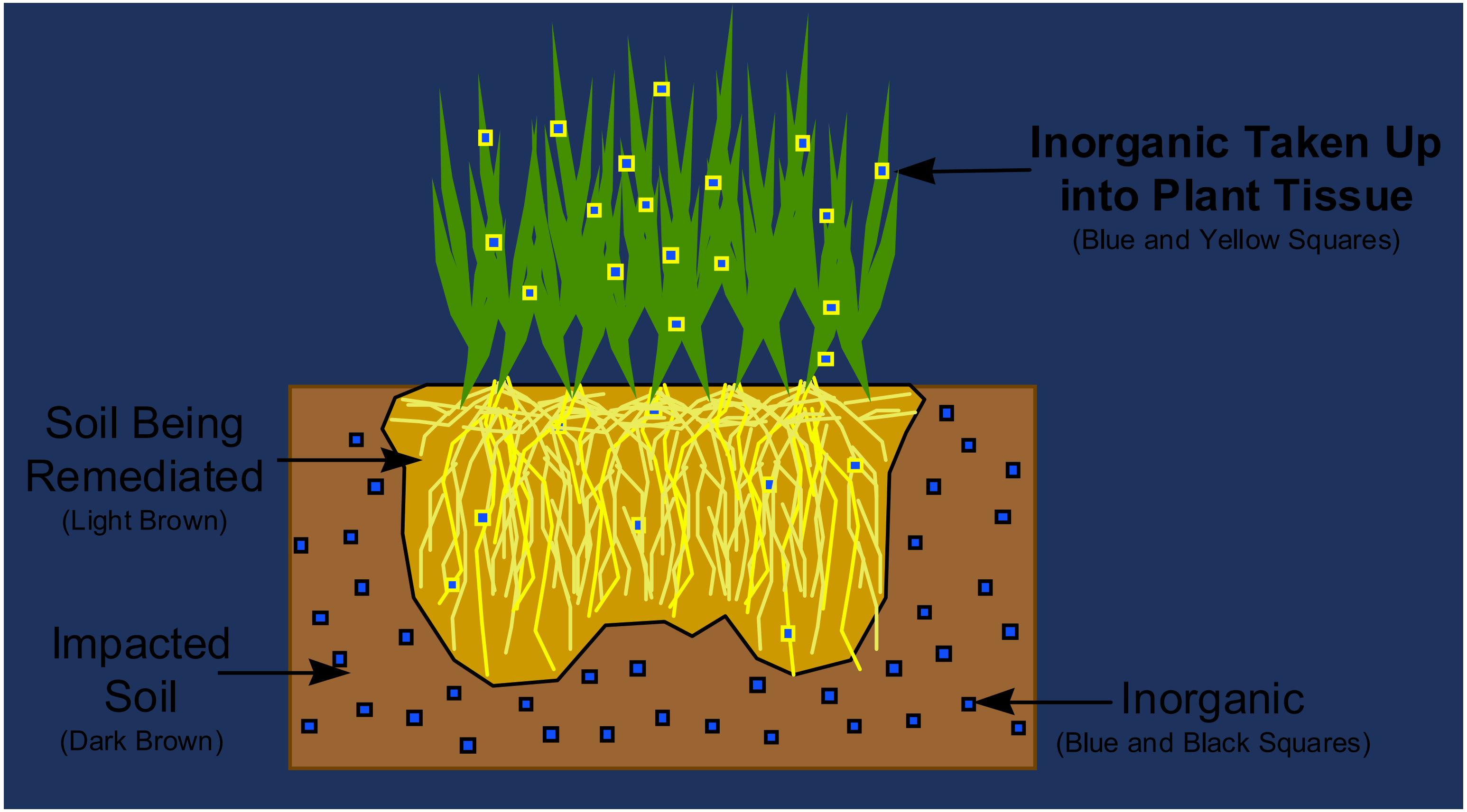
Kulakow, 2002, Phytoremediation of Organics in Soil, ITRC Workshop Presentation

TPH Dissipation in Craney Island, VA Study

Banks, 1999, *in* Kulakow, 2002 ITRC workshop presentation



Phytoextraction



Rock and Tsao, 2002, Introduction to Phytotechnologies, ITRC Workshop Series Presentation

Phytoextraction of Heavy Metals

- Ag, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, W, Zn
- Hyperaccumulating plants can treat metals in soil at ~1,000 ppm range
  - Must prevent eco exposure and leaching, and dispose of properly
- Treatment depth generally ~ 1 foot
- Phytotoxicity
  - physical or chemical amendments required for extraction or stabilization strategies

Natural Hyperaccumulators of Metals

- Barley
- Sunflowers
- Tall Fescue
- Hydrangea
- Rapeseed

http://en.wikipwedia.org/wiki/phytoremediation

Hyperaccumulators

Hyperaccumulators table – 1

hyperaccumulators and contaminants : Al, Ag, As, Be, Cr, Cu, Mn, Hg, Mo, naphthalene, Pb, Pd, Pt, Se, Zn – accumulation rates

Contaminant	Accumulation rates (in mg/kg dry weight)	*Latin name*	English name	H-Hyperaccumulator or A-Accumulator P-Precipitator T-Tolerant	Notes	Sources
Al-Aluminium	A-	*Agrostis castellana*	Highland Bent Grass	As(A), Mn(A), Pb(A), Zn(A)	Origin Portugal.	[1]
Al - Aluminium	1000	*Hordeum vulgare*	Barley	xxx	25 records of plants.	[2] [3]
Al - Aluminium	xxx	*Hydrangea* spp.	Hydrangea (a.k.a. Hortensia)	xxx	xxx	xxx
Al - Aluminium	Al concentrations in young leaves, mature leaves, old leaves, and roots were found to be 8.0, 9.2, 14.4, and 10.1 mg g1, respectively.[4]	*Melastoma malabathricum* L.	Blue Tongue, or Native Lassiandra	P competes with aluminium and reduces uptake.[5]	xxx	
Al-Aluminium	xxx	*Solidago hispida (Solidago canadensis L.)*	Hairy Goldenrod	xxx	Origin Canada.	[2] [3]
Al-Aluminium	100	*Vicia faba*	Horse Bean	xxx	xxx	[2] [3]
Ag-Silver	xxx	*Brassica napus*	Rapeseed plant	Cr, Hg, Pb, Se, Zn	Phytoextraction	[6] [7]
Ag-Silver	xxx	*Salix* spp.	Osier spp.	Cr, Hg, Se, Petroleum hydrocarbures, Organic solvents, MTBE, TCE and by-products;[7] Cd, Pb, U, Zn (*S. viminalix*);[8] Potassium	Phytoextraction. Perchlorate (wetland halophytes)	[7]

http://en.wikipwedia.org/wiki/phytoremediation

Phytovolatilization

- Soluble contaminants are taken up with water via plant roots, transported to the leaves and volatized.
- Chlorinated hydrocarbons volatize well, gasoline components do not (Davis et al., 1998)
- Poplar saplings concentrate and transpire MTBE

Phytovolatilization cont.

- Selenium – after conversion to dimethylselenide (Neumann et al. 2003)
- Mercury – after conversion to elemental Hg by microbes (example Yellow Poplars Rugh et al. 1996, 1998)

Critical Factors for Implementing Ecological Revitalization

- Type and concentration of contaminants
- Depth of contamination
- Toxicity
- Transfer of contaminants
- Leaching/mobilization of contaminants
- Size and other physical constraints of site

Critical Factors for Implementing Ecological Revitalization(cont.)

- Natural soil and climate conditions
- Availability of suitable plant material
- Expertise
- Proper risk management, monitoring
- Cost
- Acceptability
- Seasonality of plant activity
- Sampling requirements

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