Geobotany: Exploration and Remediation

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Agenda

- Introduction
- Geobotanical Precepts
  - History
  - Plant Tolerance and Stress
- Accumulator and Indicators
- Geobotanical Exploration
- Phytoremediation
- Closing

Chinkapin Oak (*Quercus muehlenbergii*), an eastern calciphyte, usually found growing on limestone outcrops.

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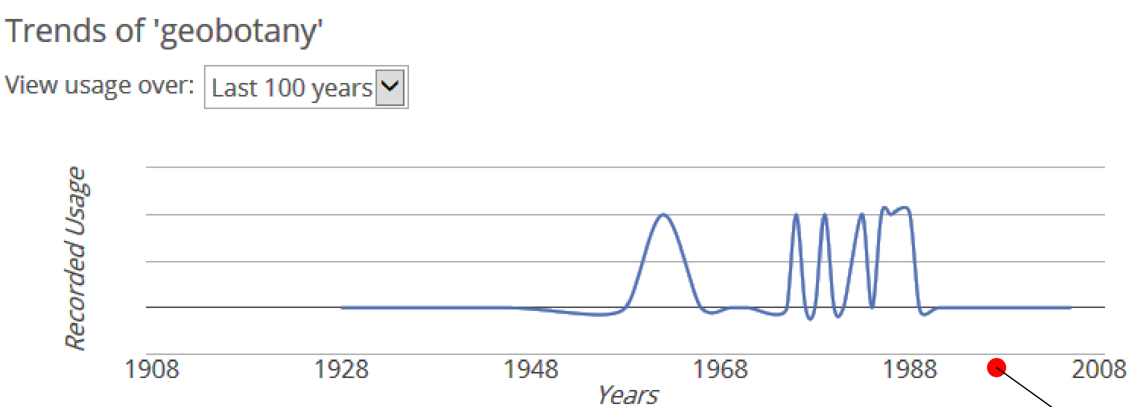
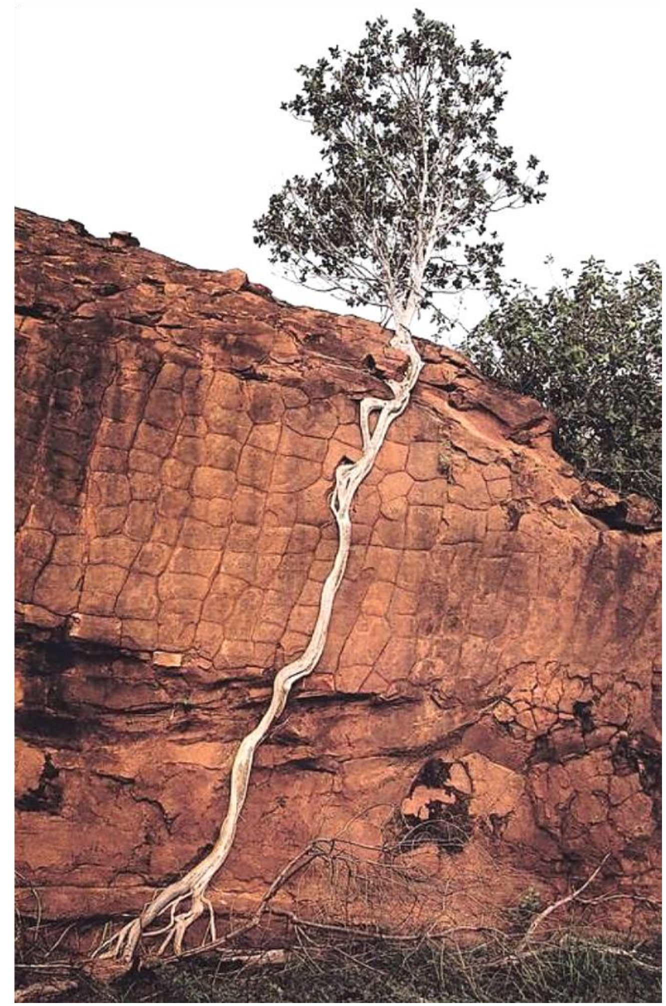
Geobotany

- Study of relationship of plants to geological substrates and habitats. Different than phytogeography.
- **Helen Cannon**, USGS (1938-1972), early proponent of discipline (selenium, uranium, lead and zinc indicators). **Robert R. Brooks**, Massey U., NZ (active late 1960’s to early 1990’s). Geo-botanical exploration of metals in New Zealand and South-Central Africa.



Birth of Phytoremediation



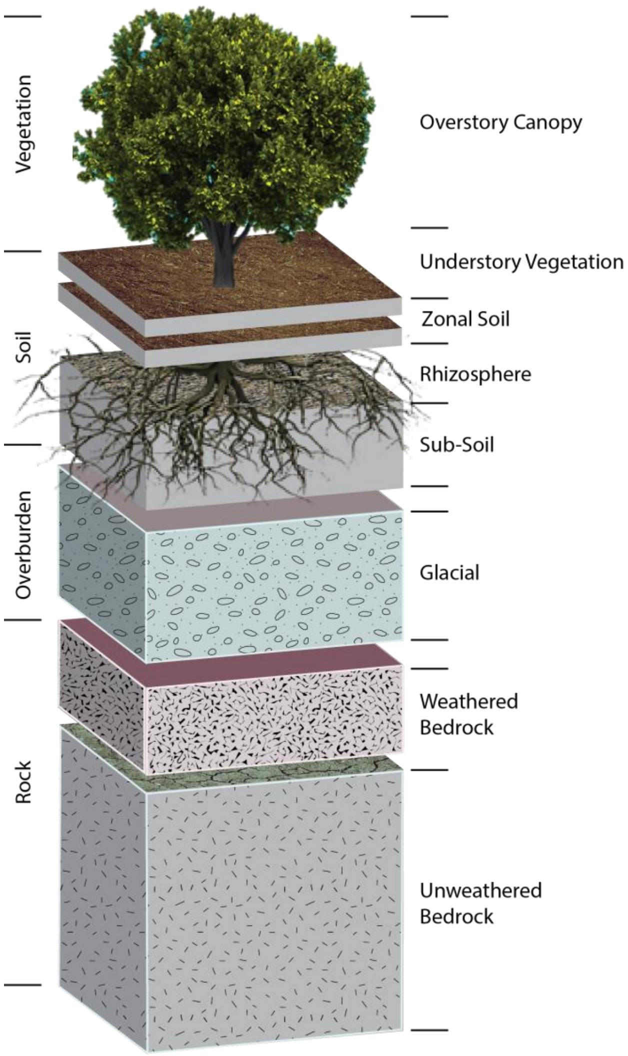
Some Geobotanical Precepts

- Natural occurring plants and plant communities reflect the geological substrates they grow upon.

- Some characteristic floras indicate regions where certain types of mineralization are likely to occur (e.g. ultramafic outcrops in NE Georgia and the serpentine barrens of the Piedmont Upland, N. Carolina).

- There are plant indicators for organics, inorganics and radionuclides. Likewise, some plants can adapt to these chemical footprints.

- Most indicator plants are accumulators, but not all accumulators are indicators.



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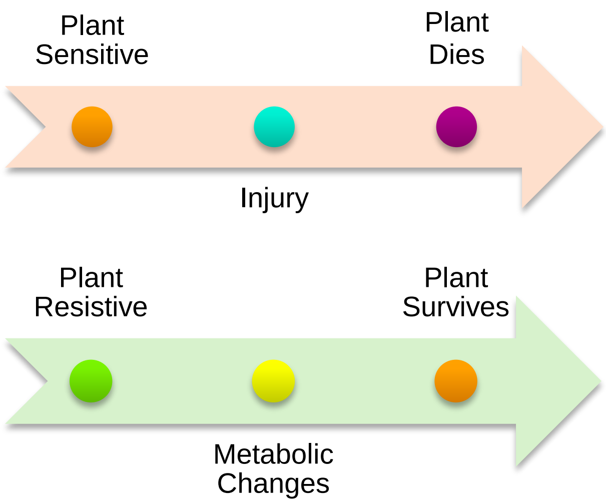
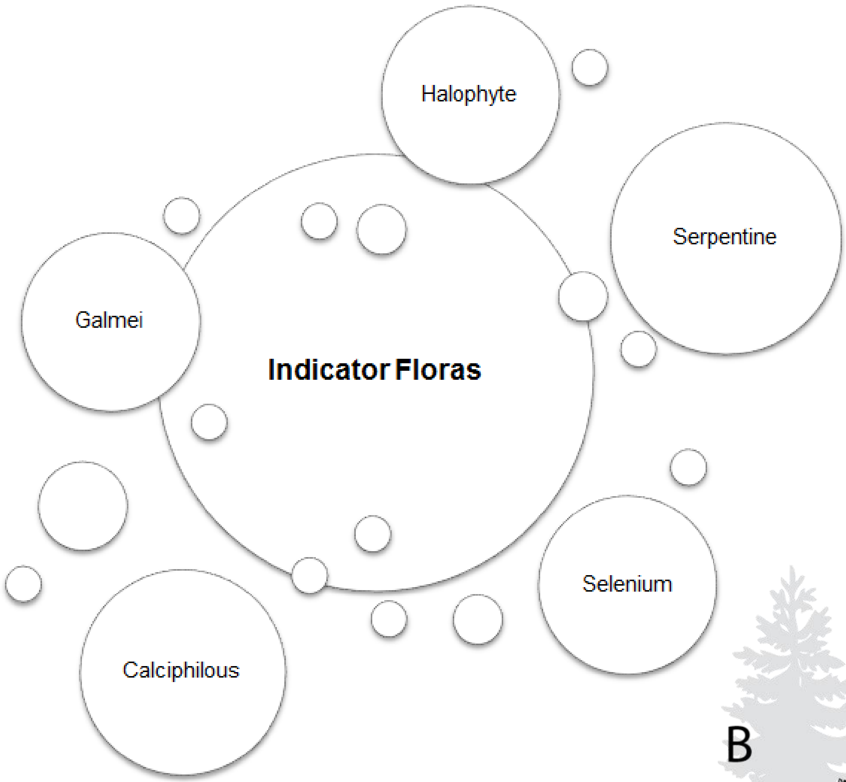
Plant Adaptation to Stress

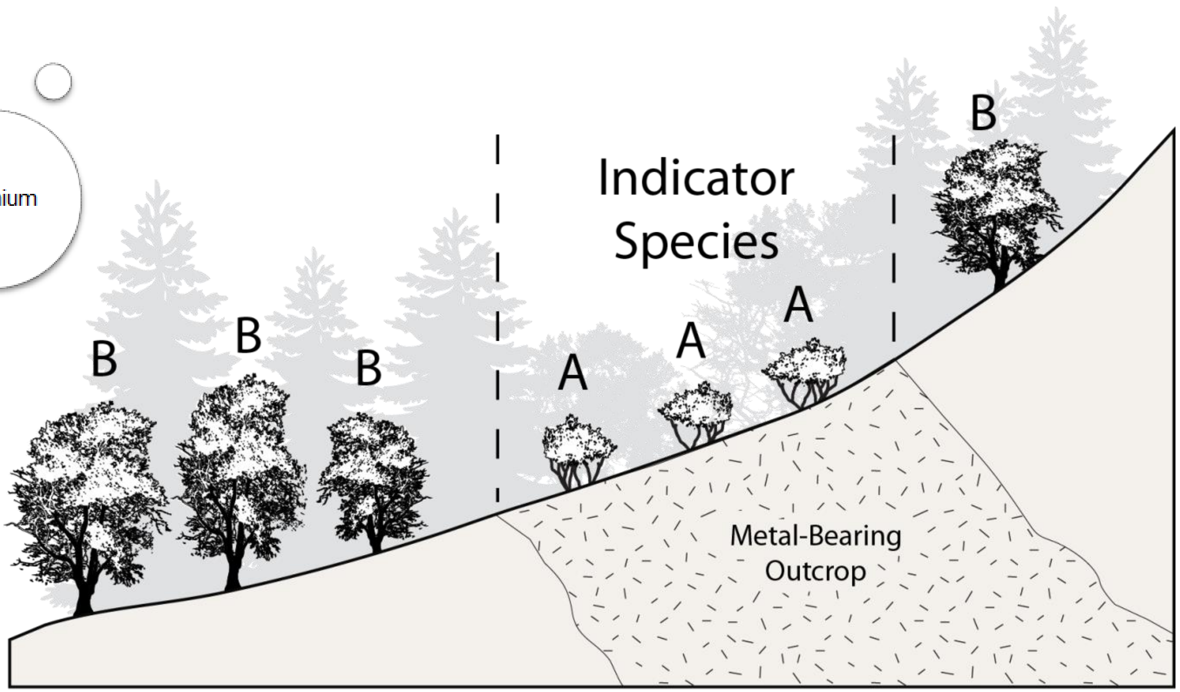
- Plant Stresses
  - Excessive Nutrients
  - Environmental Toxins
  - Ambient Conditions



Chlorotic leaf pattern developed in maple tree growing in copper-rich soil in Ely, Vermont. Photograph by Helen Cannon, USGS, 1947.

Metal Tolerance, Accumulators and Indicator Species





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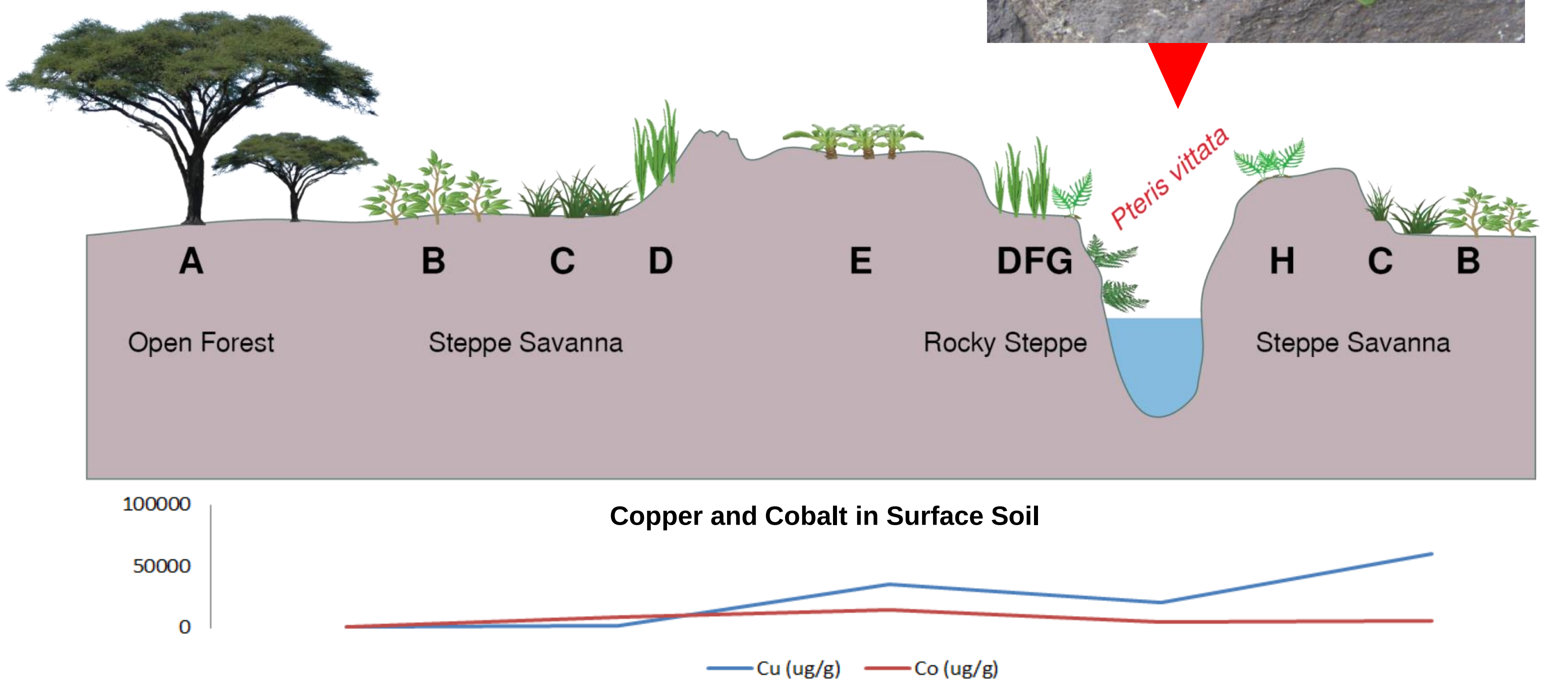
Non-Environmental Precedence for the Arsenic Fern

Pteris vittata has often been observed on arsenical mine dumps (Wild, 1974)

Schematic transect across Etoile Mine, former Zaire, showing mineral floras and environment where *Pteris vittata* is found (Malaisse and Gregoire, 1978).



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Indicator Metrics

Specific Indicator Values (SIV)

$$SIV = \frac{\text{Highest Copper Value} - \text{Lowest Copper Value (Plant Tissue)}}{\text{Average Copper Value (Soil)}}$$

$$SIV = 0.50 = \frac{100\ \text{mg/kg} - 50\ \text{mg/kg}}{100\ \text{mg/kg}}$$

$$SIV = 4.10 = \frac{500\ \text{mg/kg} - 90\ \text{mg/kg}}{100\ \text{mg/kg}}$$

SIV 4.0 or Less "Good Indicator"

Brooks, 1972

Indicator Plant vs. Accumulator Plant

INDICATOR

- Metal and Organics.
- SIV < 4.
- Can be plant species, floral community, or changes in growth, morphology and physiology of plants.
- Usually are accumulator plants.

ACCUMULATOR

- Usually Metals.
- Usually specific plant.
- Accumulate higher concentration of xenobiotic compound in tissues versus soil or groundwater.

Alpine Pennycrest (*Thlaspi sp.*) is a lead and zinc accumulator and indicator.

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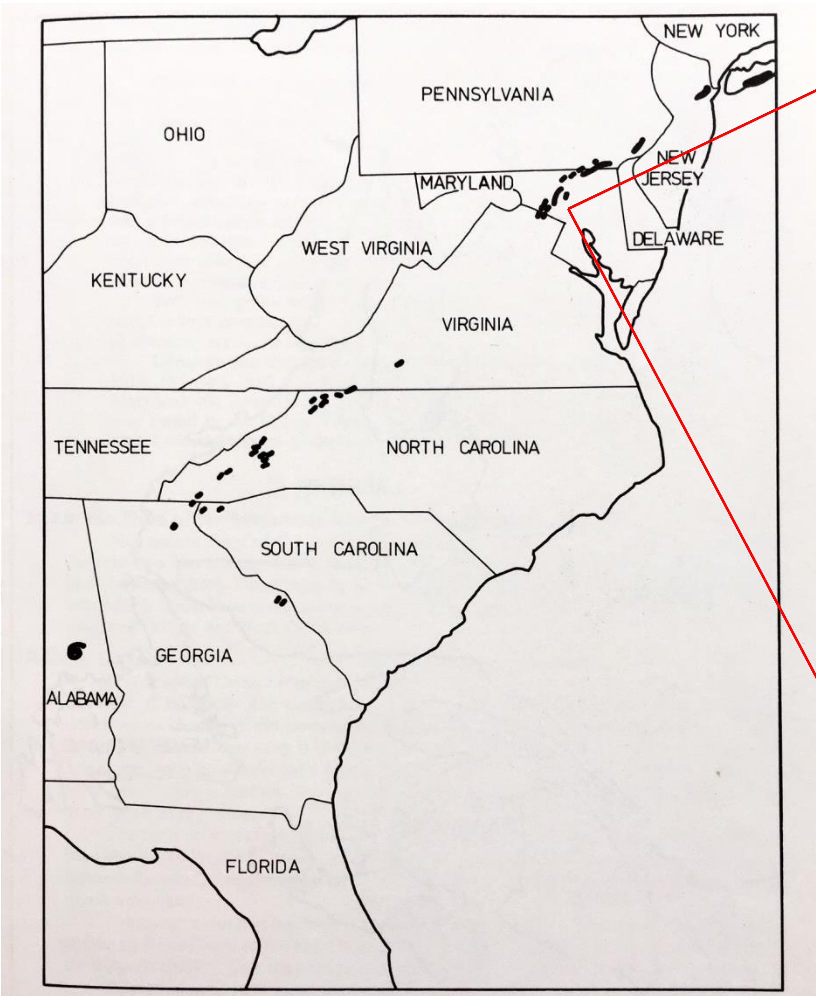
Serpentine Floras



BARREN AREA ASSOCIATION

Arabis lyrata var. *parvisiliqua*
Gerardia decemloba
Linum medium
Talinum teretifolium
Cerastium arvense f. *villosissimum**
Houstonia coerulea
Polygonum tenue

ANDROPOGON ASSOCIATION

Acerates viridiflora
Andropogon scoparius
Aristida dichomata
Aster lateriflorus
Carex glaucodea
Festuca rubra
Juncus platyphyllus
Juncus tenuis var. *dudleyi*
Oenthera tetragona var. *brevistipata*
Panicum dichotomiflorum
Poa pratensis
Sabatia angularis
Senecio smallii
Solidago juncea
Sorghastrum nutans
Viola fimbriatula
Agrostis perennans
Aristida purpurescens
Aster ericoides
Cassia fasciculata
Eleocharis tenuis
Fimbristylis autumnalis
Juncus secundus
Lobelia inflata
Panicum clandestinum
Panicum linearifolium
Polygala verticillata
Scleria pauciflora
Sisyrinchium mucronatum
Solidago canadensis
Spenopholis obtusata

ANDROPOGON—OAK ASSOCIATION

Anaphalis obtusifolium
Asclepias verticillata
Cunila origanoides
Dianthus armeria
Eupatorium perfoliatum
Hypericum gentianoides
Hypericum punctatum
Liatris graminifolia
Lobelia spicata var. *scaposa*
Phlox subulata var. *eusubulata*
Potentilla canadensis
Pycnanthemum flexosum
Quercus stellata
Sericocarpus asteroides
Vernonia noveborensis
Apocynum cannabinum
Aureolaria pedicularia
Desmodium marilandicum
Erigeron ramosus
Hieracium venosum
Hypericum perforatum
Lespedeza virginica
Linaria vulgaris
Oxalis stricta
Pinus virginiana
Prunella vulgaris
Quercus marilandica
Rosa virginiana
Verbascum blaterium
Viola pedata var. *lineariloba*

Plant Associations at Soldier's Delight Serpentine Barren, MD.
Brooks, 1987

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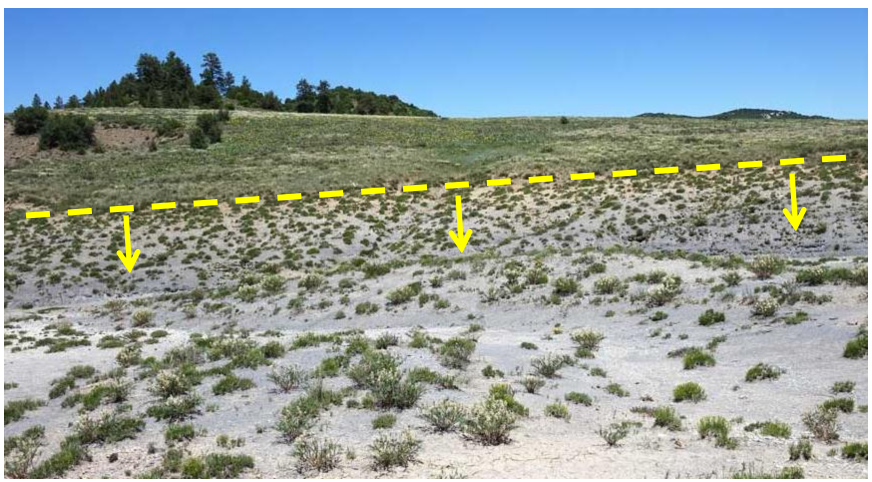
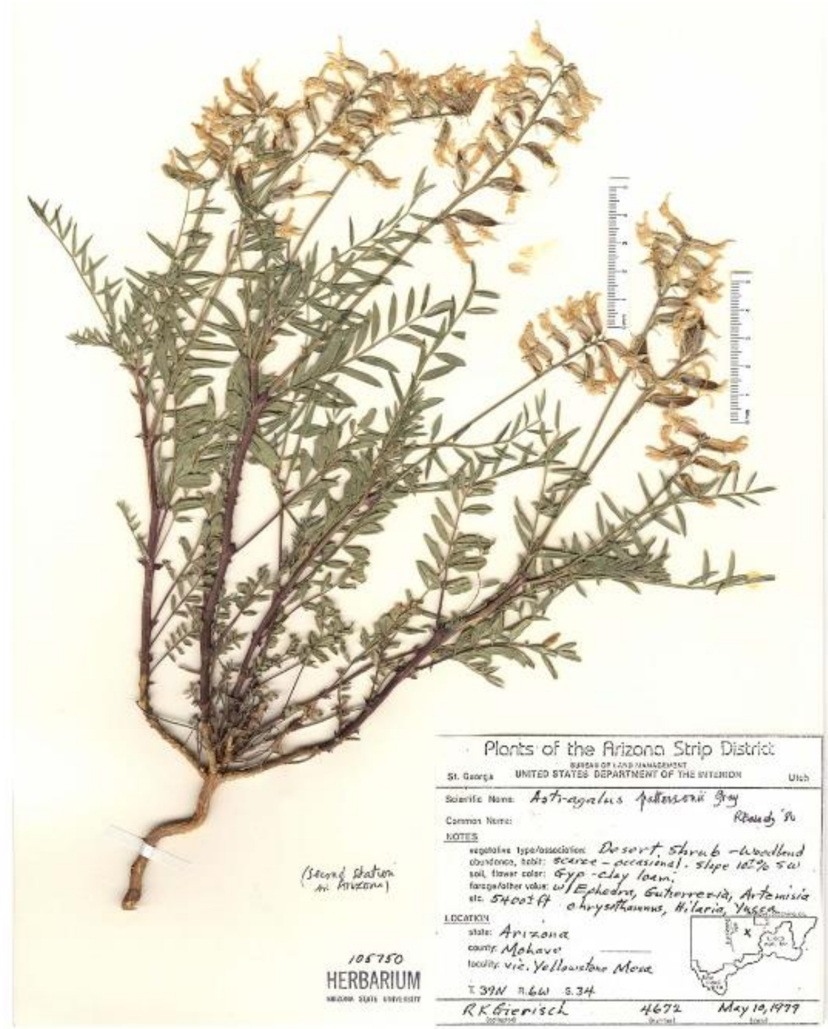
Accumulator / Indicator Plant Example

- *Astragalus pattersoni* (Milk vetch).
- Grows on natural seleniferous soils (e.g. Thompson District, Utah).
- Selenium **accumulator** (poisonous to livestock "locoweed").
- Also a uranium and molybdenum pathfinder or indicator plant.





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Indicator Plant Example

- *Eriogonum ovalifolium* (Cushenbury buckwheat or “Silver Plant”).
- Habitat within openings of Pinyon pine, Pinyon-juniper, Joshua tree and Blackbush scrub communities 4,600 to 7,900 feet in elevation on carbonate substrates, primarily in the San Bernadino Mountains mining territory.
- Cited by Henwood (1857) and Cannon (1960) as an **indicator of silver** veins in Montana.

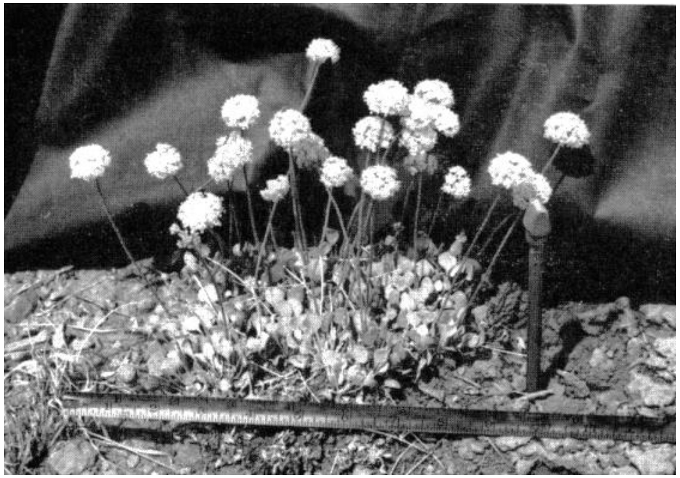
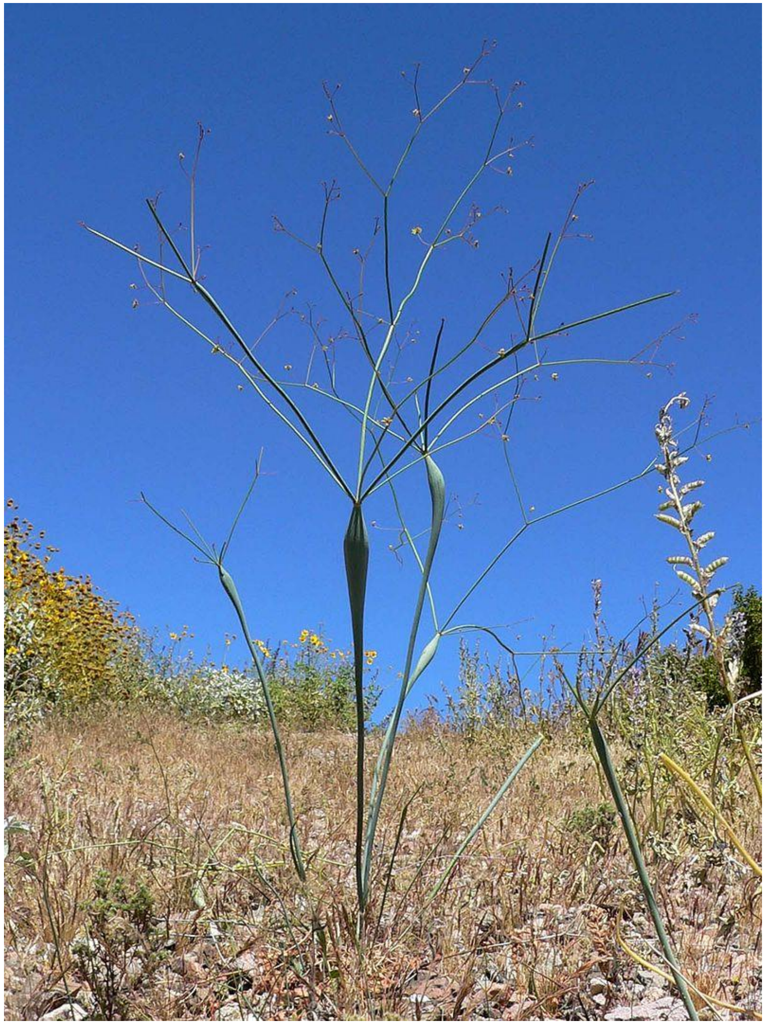


Table 1. Plants that have been used as indicators in prospecting.

Universal (U) or local (L)	Family	Genus and species	Common name	Locality	Reference
L	Buckwheat	*Eriogonum ovalifolium*	*Silver* Eriogonum	Montana	(47)

Indicator Plant Example

- *Eriogonum inflatum* (Desert Trumpet).
- Adapted for growth on evaporite- and anhydrite-rich soils. A **gypsum indicator** and medicinal plant.
- Made appearance in *Star Trek: Voyager*, Season 3, Episode 1, at around the 3 minute 47 second mark, when the character Neelix is shown to be looking at a picked specimen.



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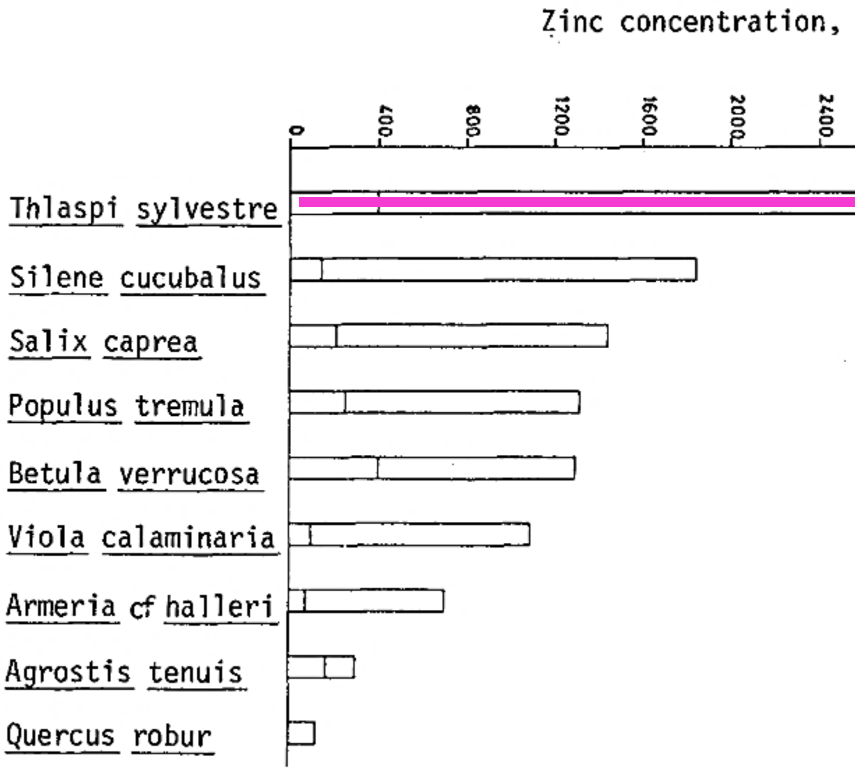
Species Accumulate Metals Differently



T. Sylvestre (Alpine Pennycrest)

Graph showing amount of zinc in leaves of different species collected from the same zinc [Galmei] biotype at Plombiéres, Belgium (from Denaeyer-De Smet, 1970).

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Factors Affecting Metal Accumulation in Plants

- Plant Species Sampled
- Plant Organ Sampled
- Age of Plant or Organ
- Health of Plant
- Soil pH
- Root Depth
- Drainage
- Aspect
- Element Availability
- Element Antagonism

TABLE 11-10 Factors Affecting Elemental Uptake by Plants and Methods of Reducing Their Effect

Factor	Relative importance	Method of reducing effect
Type of plant	Very great	Selection of plants by orientation survey
Organ sampled	Great	Selection of organ by orientation survey
Age of organ	Significant	Selection by orientation survey
Root depth	Significant	Use of ratios of two elemental concentrations in same sample
pH	Fairly significant	Selection of elemental ratios of pair of elements of same availability over pH range encountered
Health of plant	Fairly significant	Select healthy specimens only
Drainage	Fairly significant	Avoid poorly drained areas where possible; also use elemental ratios
Availability of element	Fairly significant	Use elemental ratios with both elements of same availability
Antagonism of other elements	Minor	None
Rainfall	Minor	Carry out work over short period
Variable shading	Minor	Avoid shady sites if possible or use elemental ratios
Temperature of soil	Minor	Carry out work over short period

Brooks, 1972

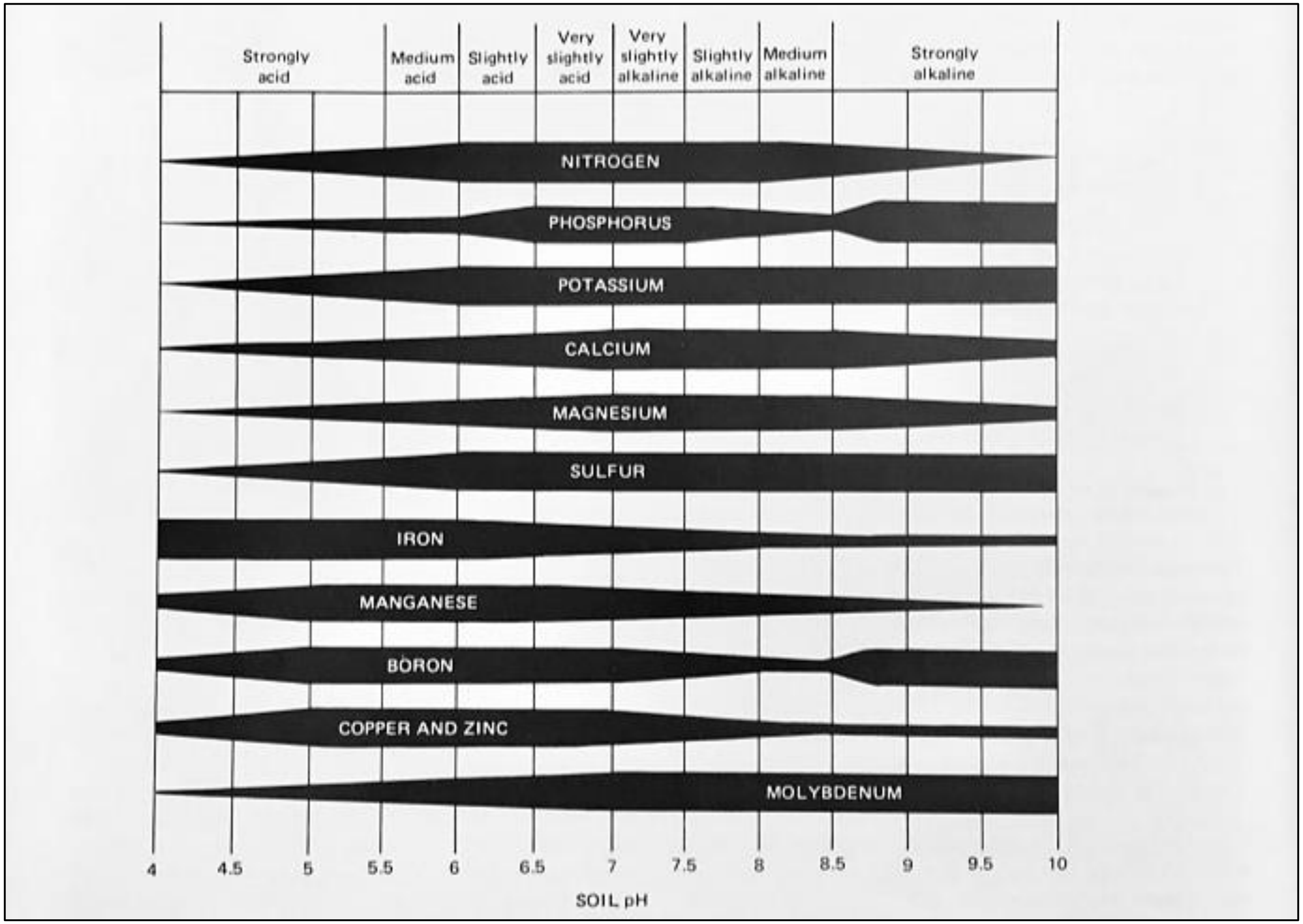
Observable Metal-Stress Plant Indicators

Physiological and morphological changes in plants due to metal toxicities.

Element	Effect	Reference
Aluminum	Stubby roots, leaf scorch, mottling	(54)
Boron	Dark foliage; marginal scorch of older leaves at high concentrations; stunted, deformed, shortened internodes; creeping forms; heavy pubescence; increased gall production	(54) (24)
Chromium	Yellow leaves with green veins	(31)
Cobalt	White dead patches on leaves	(30)
Copper	Dead patches on lower leaves from tips; purple stems, chlorotic leaves with green veins, stunted roots, creeping sterile forms in some species	(55) (16)
Iron	Stunted tops, thickened roots; cell division disturbed in algae, resulting cells greatly enlarged	(55) (56)
Manganese	Chlorotic leaves, stem and petiole lesions, curling and dead areas on leaf margins, distortion of laminae	(54)
Molybdenum	Stunting, yellow-orange coloration	(55)
Nickel	White dead patches on leaves, apetalous sterile forms	(30)
Uranium	Abnormal number of chromosomes in nuclei; unusually shaped fruits; sterile apetalous forms, stalked leaf rosette	(28) (32) (31)
Zinc	Chlorotic leaves with green veins, white dwarfed forms; dead areas on leaf tips; roots stunted	(31) (55)

Cannon, 1960

pH Influences Nutrient Availability



Modified from Bidwell, 1974

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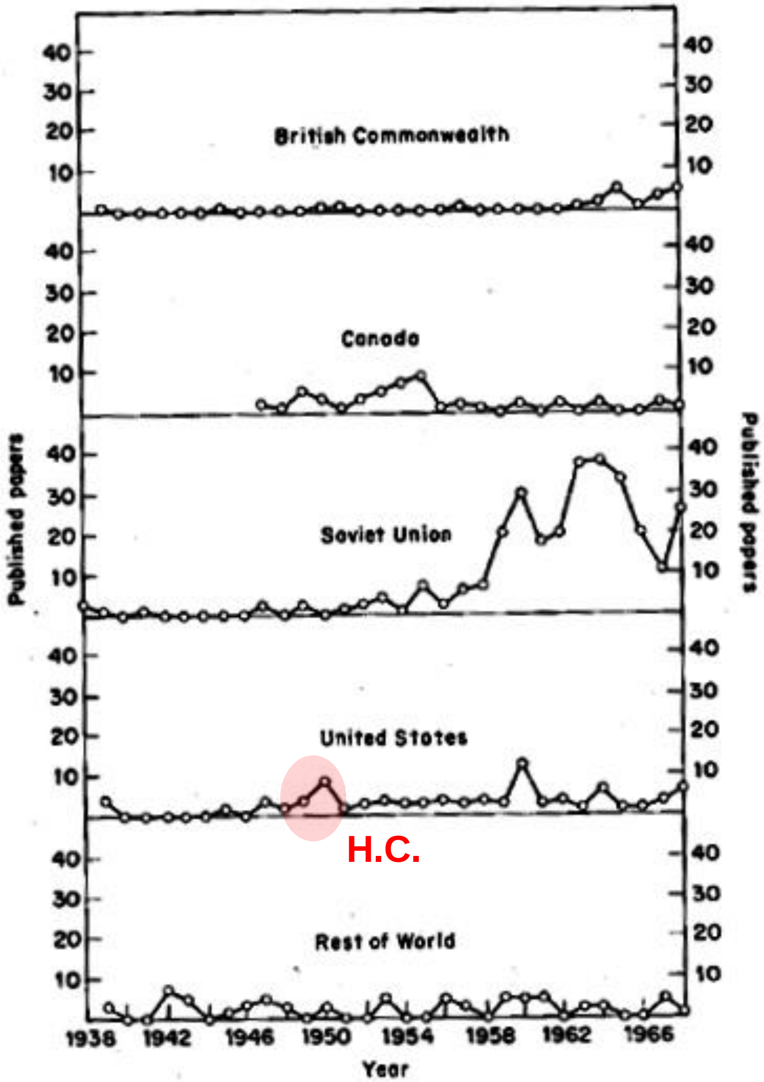
Geobotanical Exploration

- Ground-Based
  - Indicator Plant Mapping
  - Visual Observations
  - Plant and Soil Sampling & Analysis
- Aerial Reconnaissance
- Remote Sensing (Satellites)
  - Landsat 1972 – Present
    - Landsat 4 (1982-1993) MSS-TM (VIS-IR, 7 Bands) 30m Resolution
- Drones (Modern)
  - Near-IR
  - NVDI



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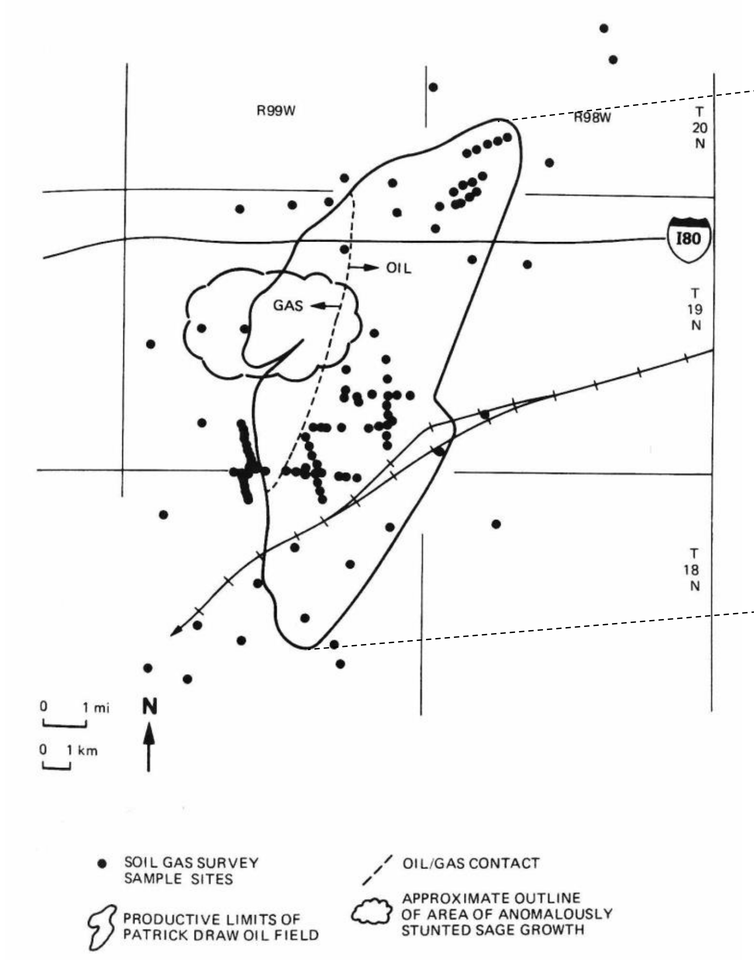
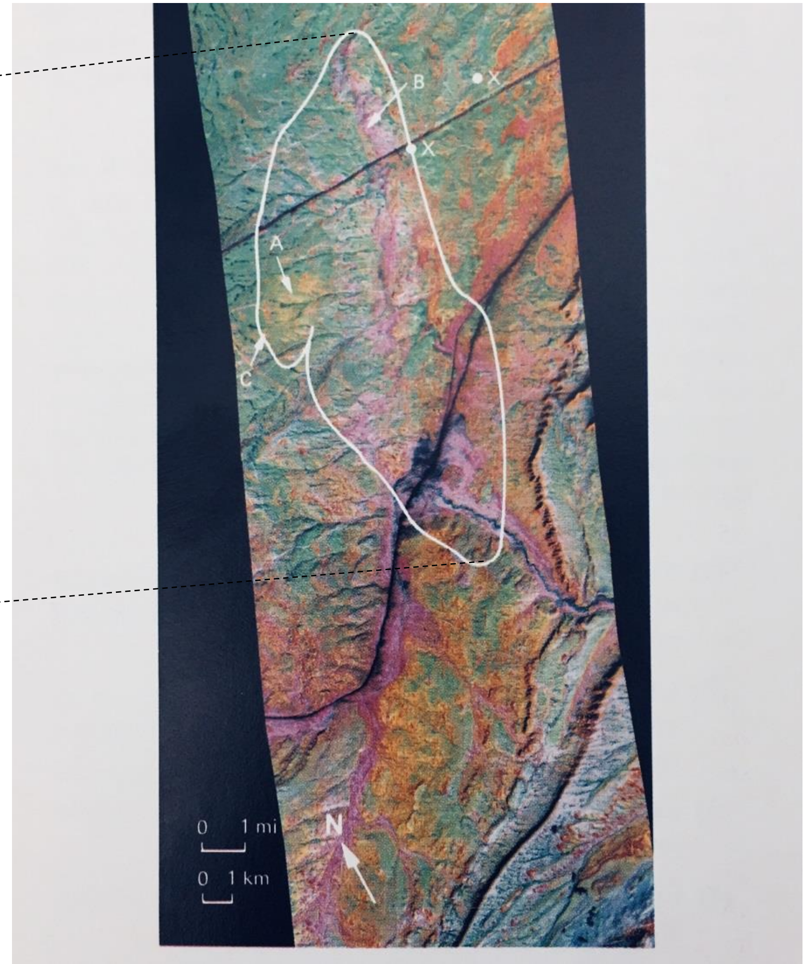
Joint NASA/GeoSat Test Report (1984)

Patrick Draw Oil Field, WY

Landsat MSS Image





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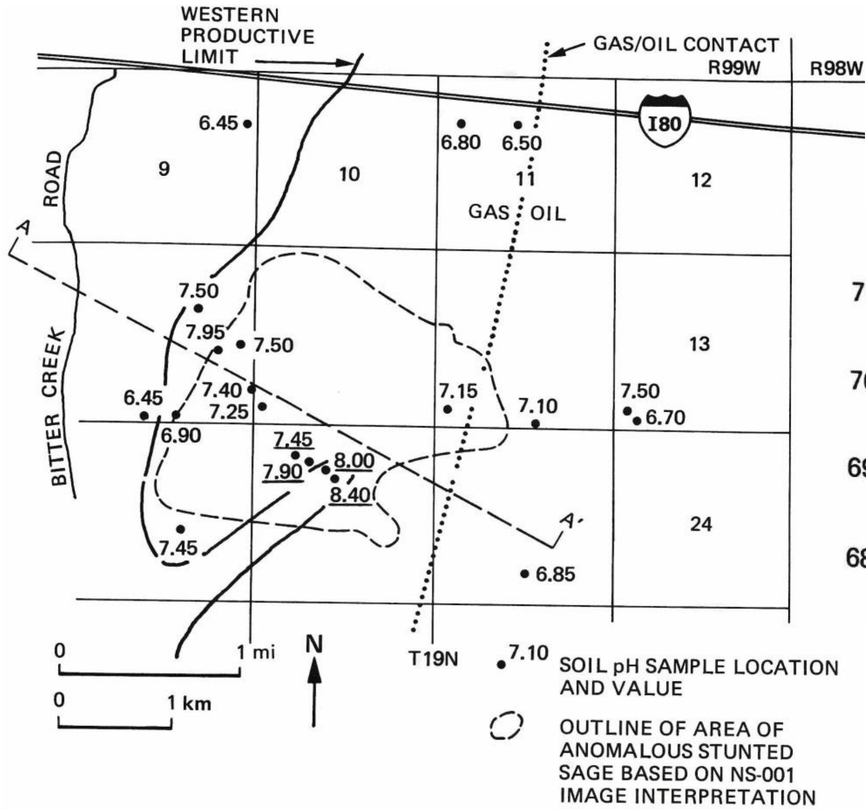
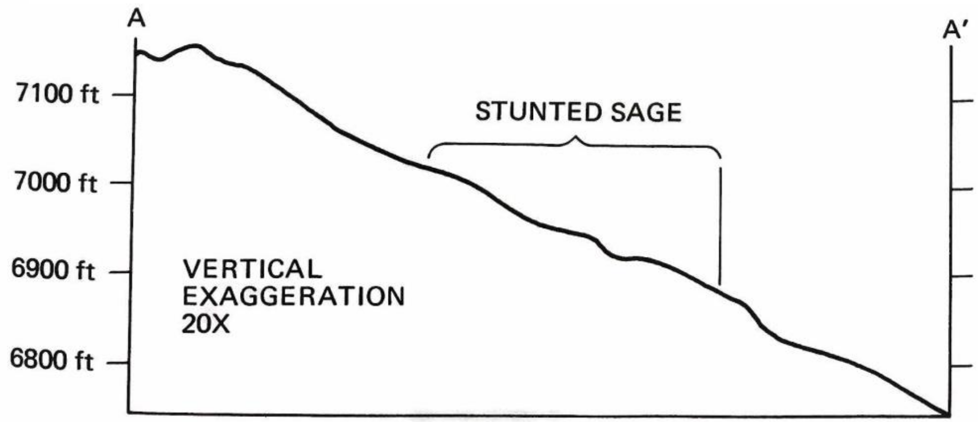
Patrick Draw Test Site 1980's





Soil pH at Stunted Sage Anomaly

Lang, et al., 1984

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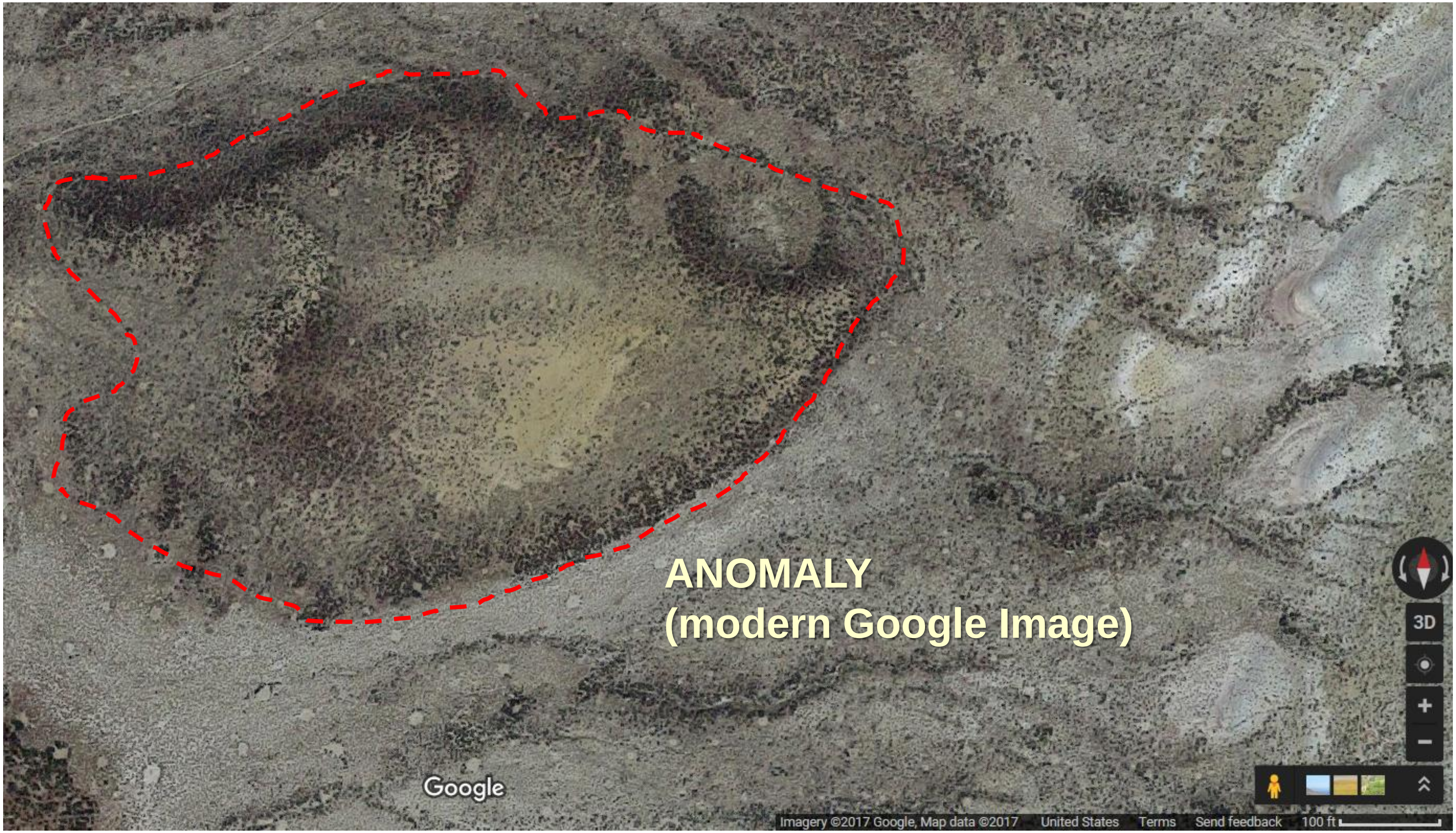
Stunted Sage (*Artemisia tridentata*) Anomaly



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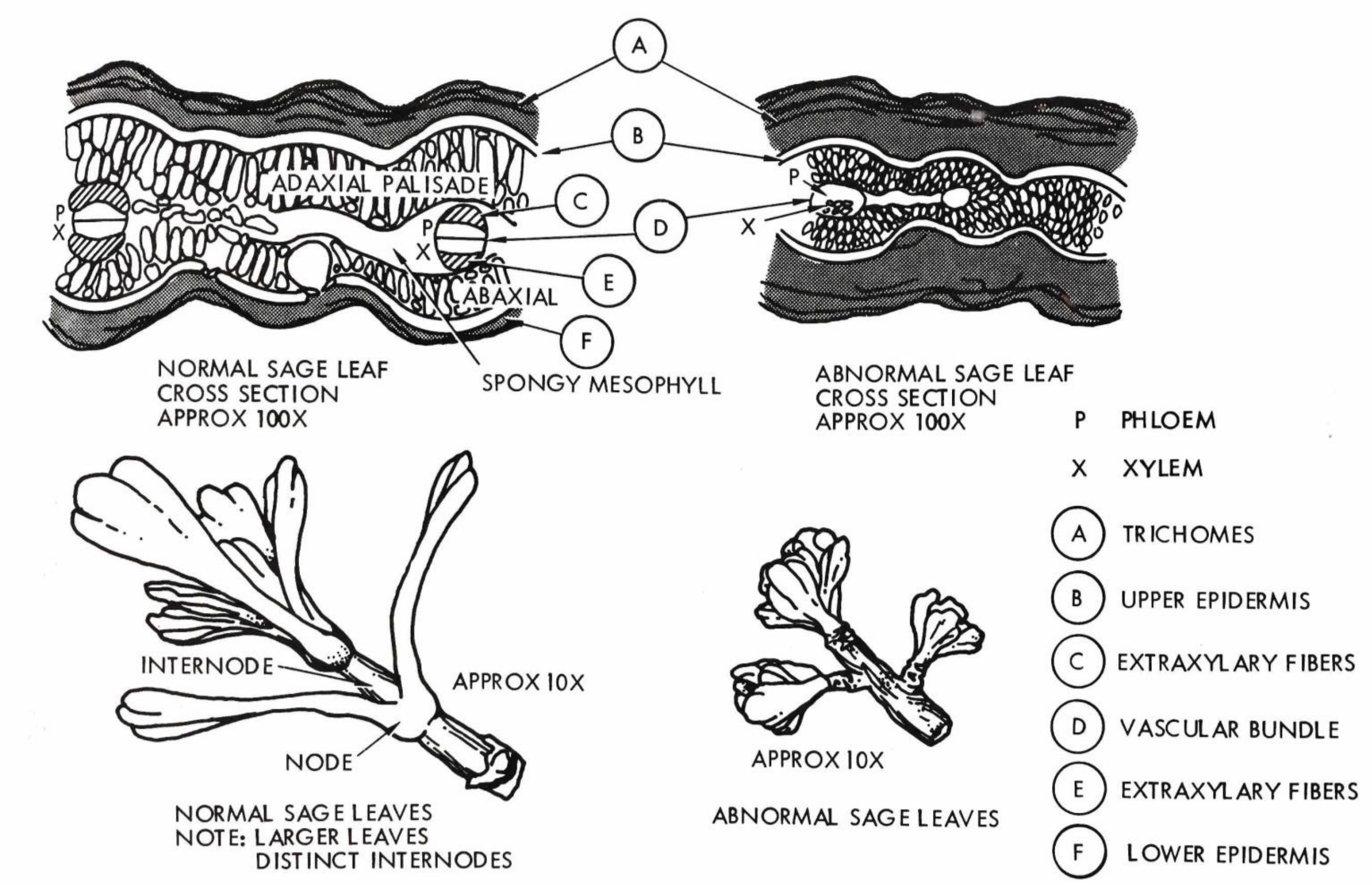
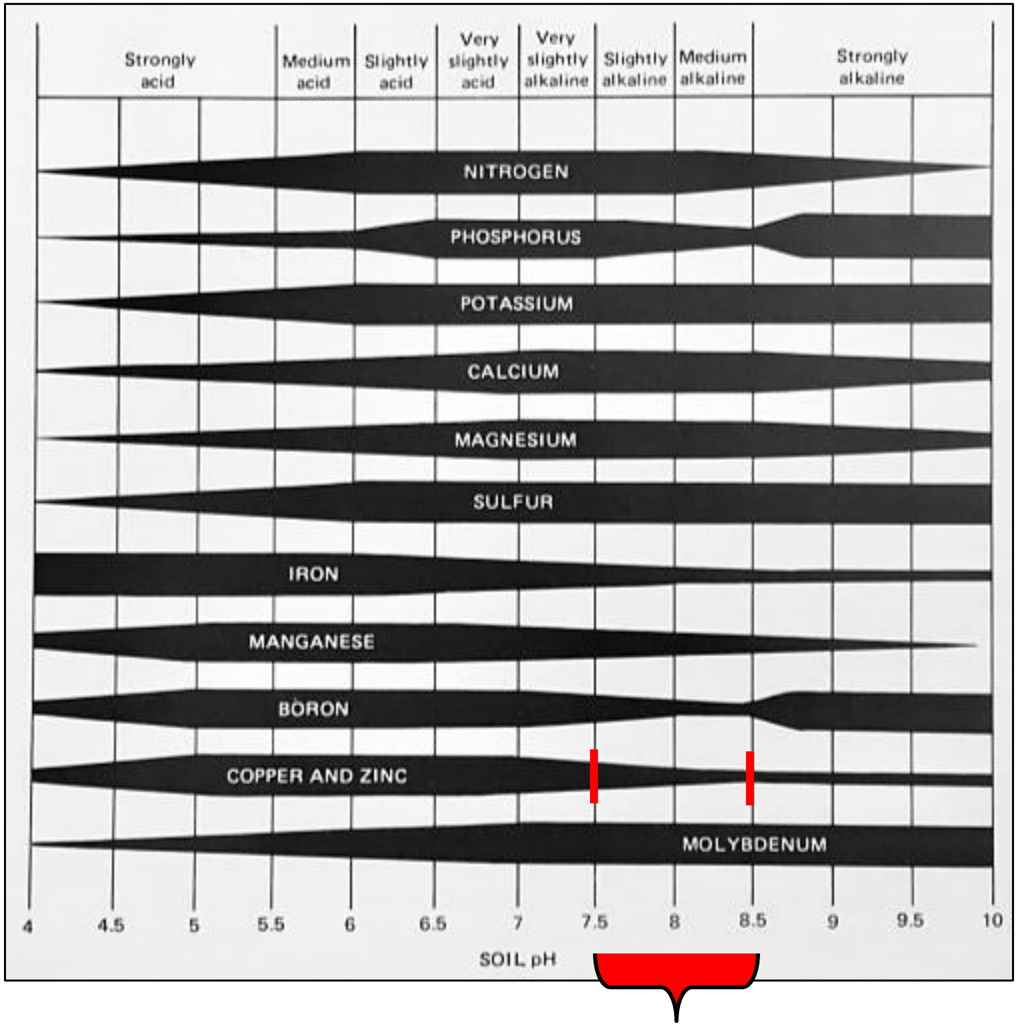
Patrick Draw Stunted Sage Test Site



Leaf cross-sections of normal and abnormal sage from the Patrick Draw Test Site, Wyoming. Note poorly developed mesophyll in stunted sage (Lang, et al., 1984).

Metal Mobility and Vegetation Stunting



Limited Metal Mobility

Zinc:

Involved in the synthesis of indoleacetic acid (IAA), a plant hormone required for normal tissue growth in plants.

Phytoremediation Mechanisms

Metals and Inorganics

- Phytosequestration
- Phytoextraction
- Phytohydraulics

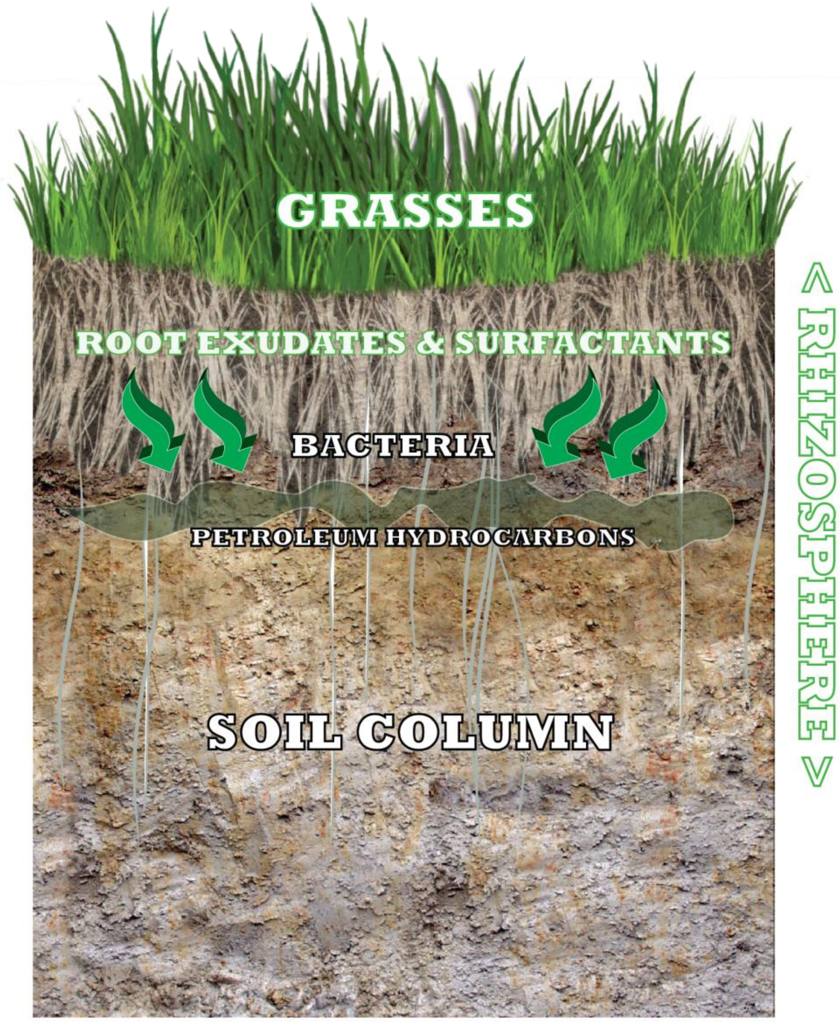
Organics

- Enhanced Rhizodegradation
  - Co-Metabolic Aerobic Degradation
  - Usually Petroleum HCs and PAHs
- Phytoextraction
- Phytovolatilization
- Phytodegradation
- Phytohydraulics
  - Barriers and ET Controls

Log $K_{ow} < 4$

Rhizospheric Remediation

- Co-metabolic breakdown of contaminants and root exudates (carbon sources) by aerobic soil-dwelling microbes.
- **Root Exudates** = Sugars, Amino Acids, Organic Acids, Fatty Acids, Sterols, Enzymes, Flavonols, Purines/Nucleotides, others misc compounds and gases.
- **Root Surfactants** = Soap-like compounds such as alkaloids and saponins
- Works on compounds amenable to aerobic breakdown pathways.
  – Fuels, Crude, Petroleum Hydrocarbons
  – Some PAHs
  – Energetic Compounds – TNT



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Why Phytoremediation?

- Promotes and encourages ecological stewardship.
- Can successfully meet target performance metrics, especially when combined in hybrid remedies.
- Plenty of precedence, case studies and success stories.
- Has gained regulatory agency and community acceptance.
- Relatively low comparative remediation costs.

RACER Cost Estimates for Phytoextraction

Federal Remediation Technologies Roundtable Estimates

SOIL TECHNOLOGY:	Phytoremediation			
RACER PARAMETERS	Scenario A	Scenario B	Scenario C	Scenario D
	Small Site		Large Site	
	Easy	Difficult	Easy	Difficult
COST PER SQUARE FOOT	$2	$7	$0.42	$1
COST PER CUBIC FOOT	$18	$66	$4	$14
COST PER CUBIC METER	$626	$2,322	$147	$483
COST PER CUBIC YARD	$479	$1,775	$112	$369

500 cu yd → 10,000 cu yd

$240K → $3.7MM

Realistic Applications

- ✓ Large open redevelopments in urban and industrial landscapes.
- ✓ Marginally impacted agricultural soils.
- ✓ Sites justifying wetland mitigation, habitat restoration or other ecological improvements.
- ✓ Site needing storm water polishing and control of overland water flow or erosion control.
- ✓ Sites having limited contaminant footprint (not mixed COC sites).

Enhanced rhizodegradation and PAH polishing using native prairie grasses at the Former Lakeside Refinery Site, Southwestern Michigan.

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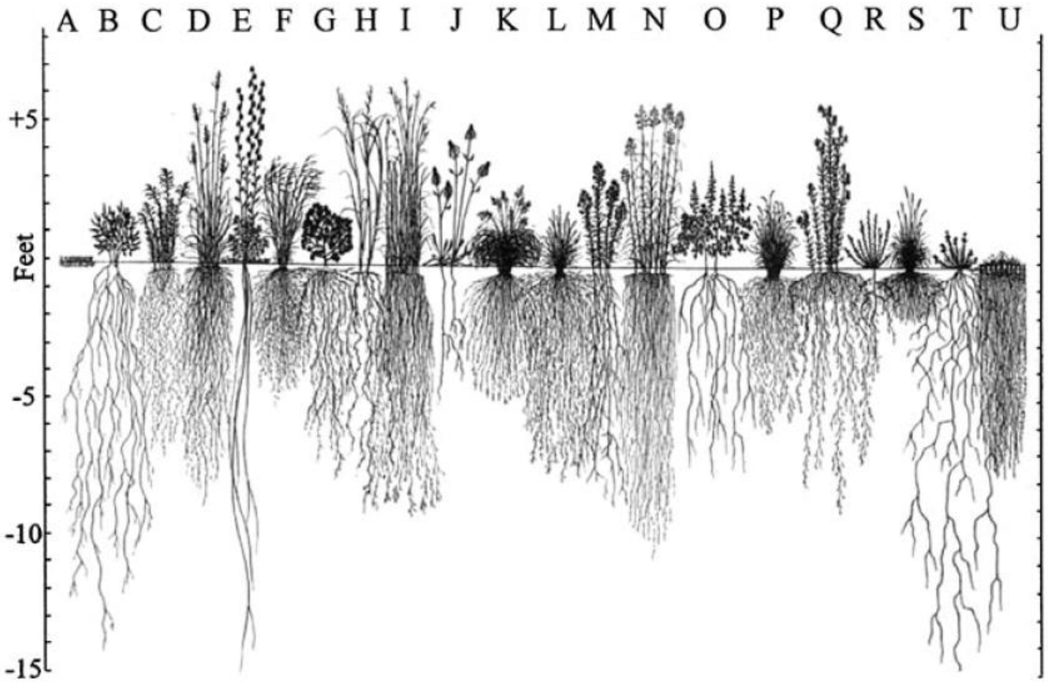
Baseline Analytical Conditions

- Impacted Media
  - Concentrations of chemicals in water and soil.
  - Distribution and depth of impacted media.
- Soil and Groundwater Geochemistry
  - pH, Cation Exchange Capacity (CEC), and Total Organic Carbon (TOC).
  - Naturally-occurring elements: Fe, Mn, Al, S, plus N, P, K and others.
  - Mineralogy (XRD).
- Soil Physics
  - Moisture, bulk density, particle grain sizes, permeability testing.
  - Soil moisture tension.

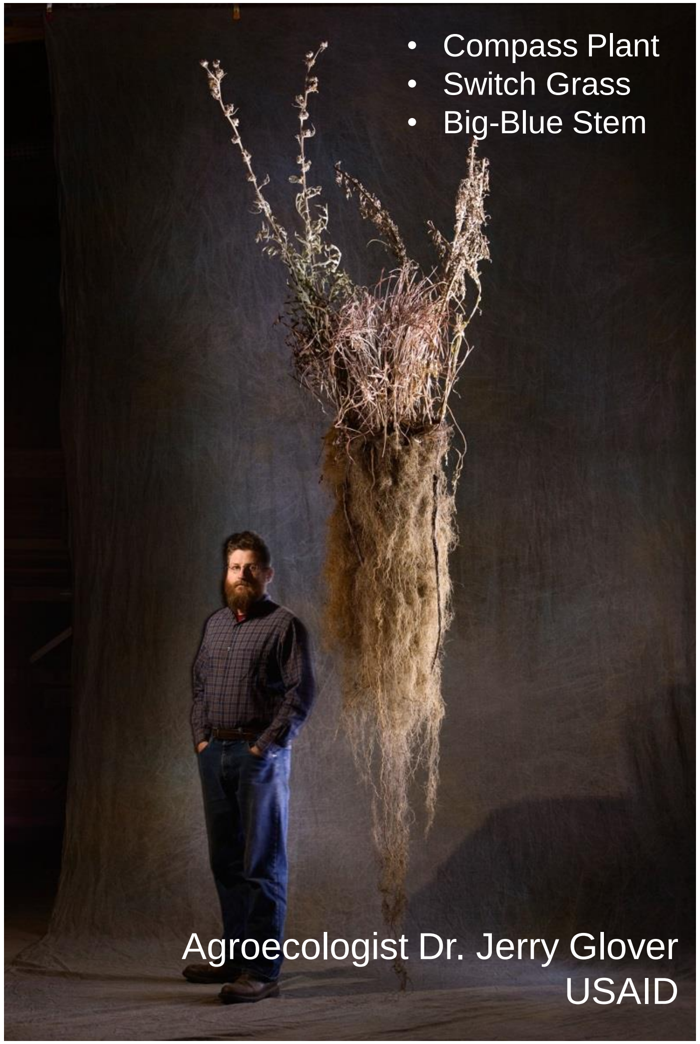
In-situ field tensiometer. Measures available interstitial water in the vadose zone.

Rooting Depths

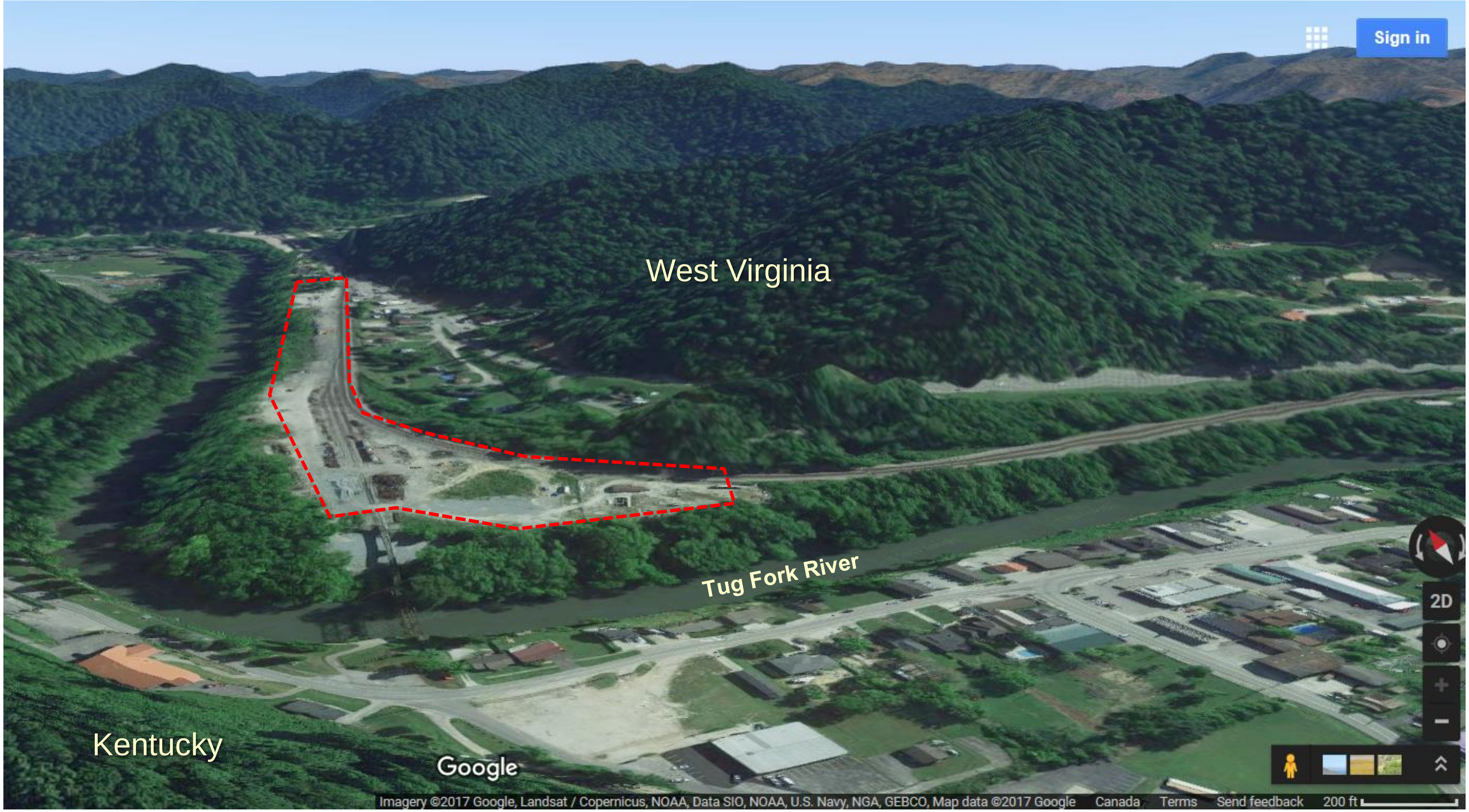


A) Kentucky Bluegrass (*Poa pratense)*
B) Lead Plant (*Amorpha canescens*)
C) Missouri Goldenrod (*Solidago missouriensis*)
D) Indian Grass (*Sorghastrum nutans*)
E) Compass Plant (*Silphium laciniatum*)
F) Porcupine Grass (*Stipa spartea*)
G) Heath Aster (*Aster ericoides*)
H) Prairie Cordgrass (*Spartina pectinata)*
I) Big Blue Stem (*Andropogon gerardii*)
J) Pale Purple Coneflower (*Echinacea pallida*)
K) Prairie Dropseed (*Sporobolus heterolepis*)
L) Side Oats Grama (*Bouteloua curtipendula*)
M) False Boneset (*Kuhnia eupatorioides*)
N) Switch Grass (*Panicum virgatum*)
O) White Wild Indigo (*Baptista leucantha)*
P) Little Blue Stem (*Andropogon scoparius*)
Q) Rosin Weed (*Silphium perfoliatum*)
R) Purple Prairie Clover (*Petalostemum purpureum*)
S) June Grass (*Koeleria cristata*)
T) Cylindric Blazingstar (*Liatris cylindracea*)
U) Buffalo Grass (*Buchloe dactyloides*)

Scheper & Tsao, 2003



Kermit Lumber Site, Grey Eagle, W.VA



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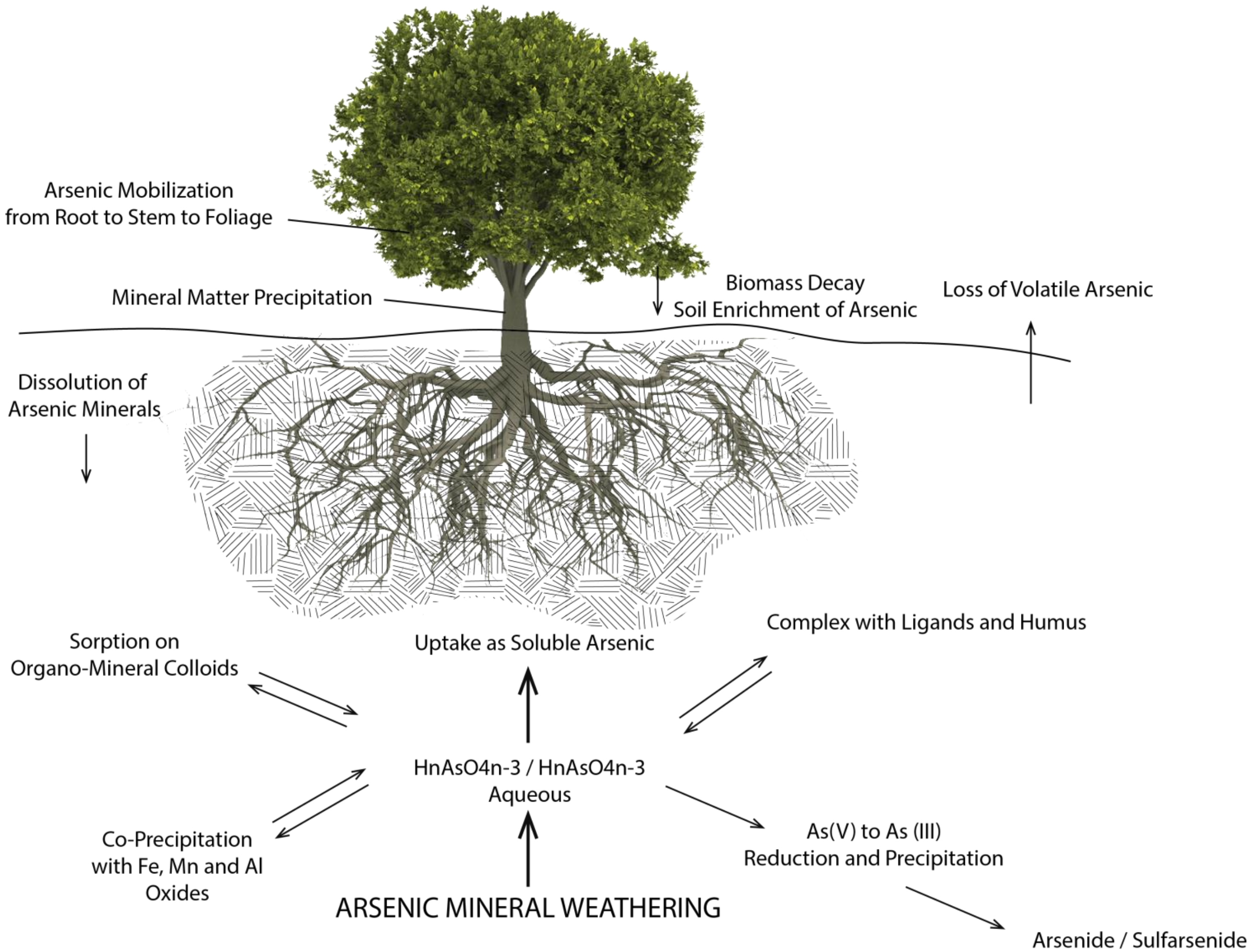
Near-Surface Arsenic Geochemistry



CONCEPTUAL MODEL OF ARSENIC CYCLING (After Stopinski, 1976)

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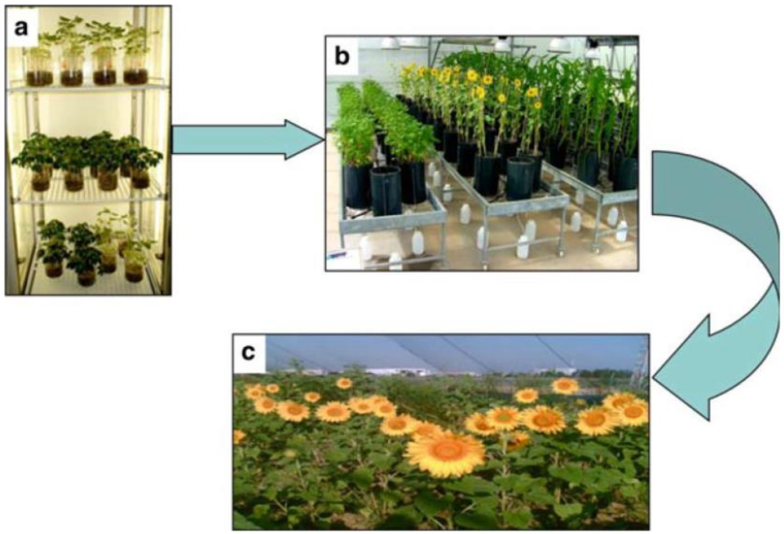
Arsenic Uptake Bench-Scale Study

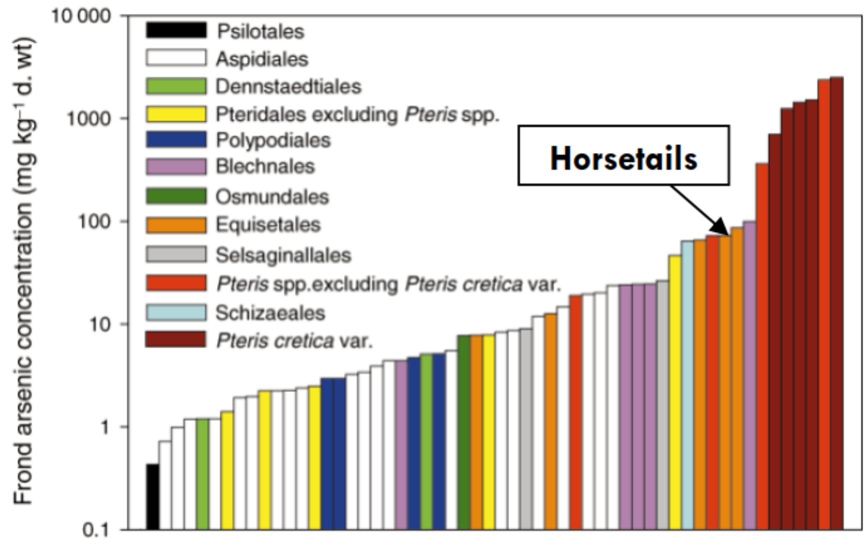
- Kermit Lumber Chromated Copper Arsenate Site, Gray Eagle, West Virginia.
- Bench-Scale Arsenic Uptake Study and White Paper “Arsenic Uptake into Primitive Plants of the Genus *Equisetum*”.
- Rough horsetails (*Equisetum hyemale*) grown in arsenic-impacted soils 100-200 mg/kg range derived from site.
- Translocation Factor approximately 3 (3x as much arsenic in plant tissue than soil over 90 days).



Site-specific feasibility assessments: (a) microcosm pot trial, (b) mesocosm pot trial, and (c) field test.

Equisetum (Horsetails) as Accumulators

- Cited in geobotanical literature as arsenic, cobalt, copper, gold, silica, and zinc accumulators.
- Next best accumulators of arsenic next to *Pteris* ferns.
- Wide-spread, tough, vigorous root system and generally unpalatable primitive plant with some medicinal merits.
- AECOM study and White Paper with Norfolk Southern indicated concentration factor of 3 (soil to leaf shoots) for *Equisetum hyemale*.



Arsenic in Pteridophytes in order of increasing arsenic concentration in fronds. Plants of the genus Equisetum are accumulators in the 100 mg/kg range (Meharg, 2003).

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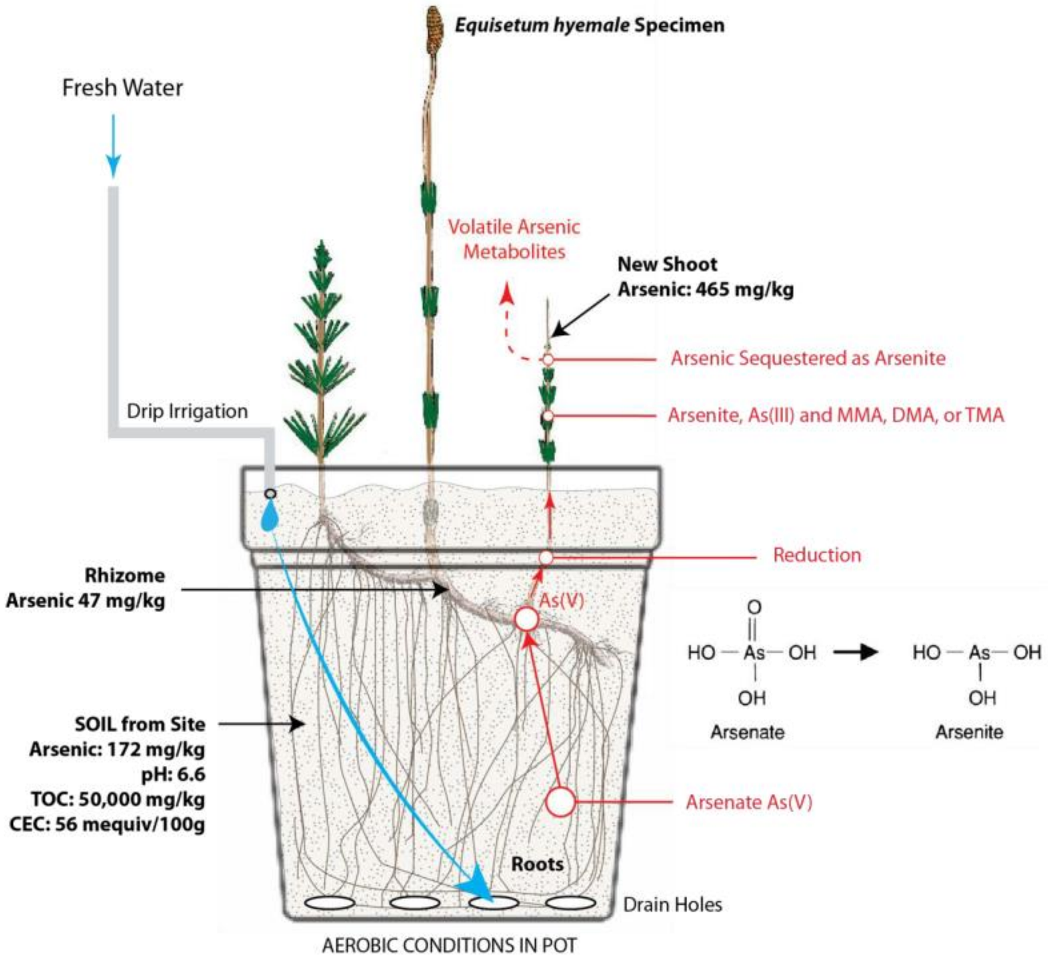
Arsenic Uptake into Rough Horsetail

Soil to Shoot Ratio (CF) = 2.7



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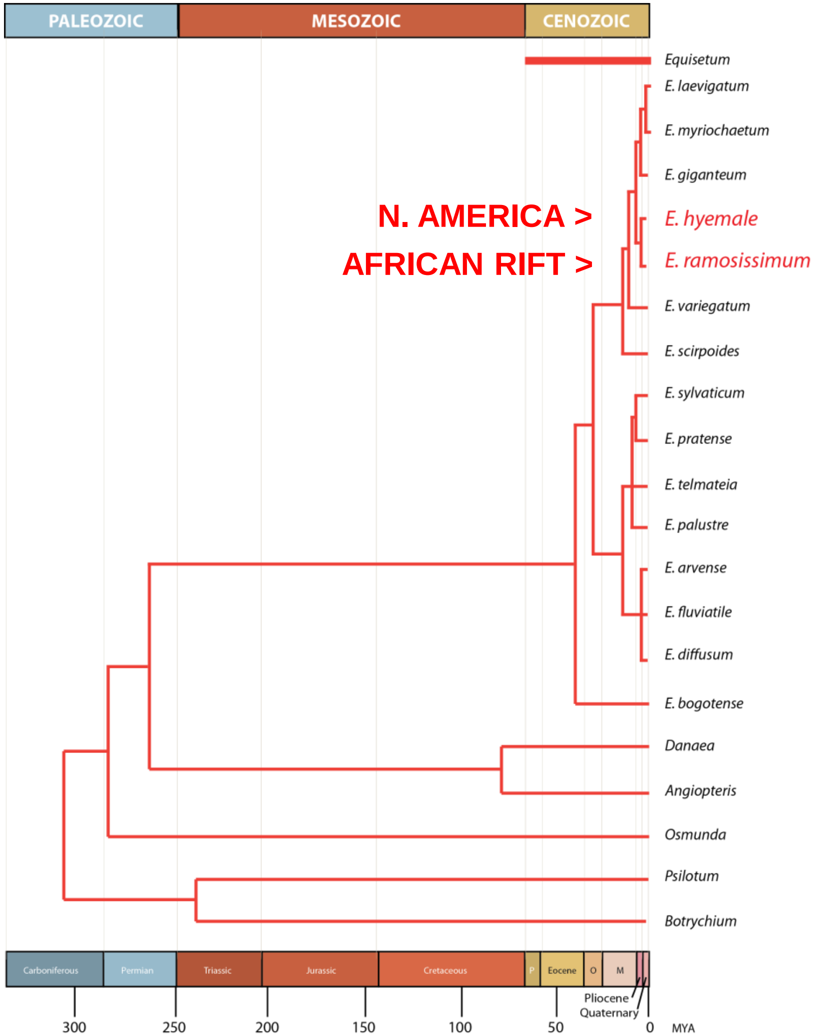
Evolutionary Basis for Arsenic Uptake in *E. hyemale*

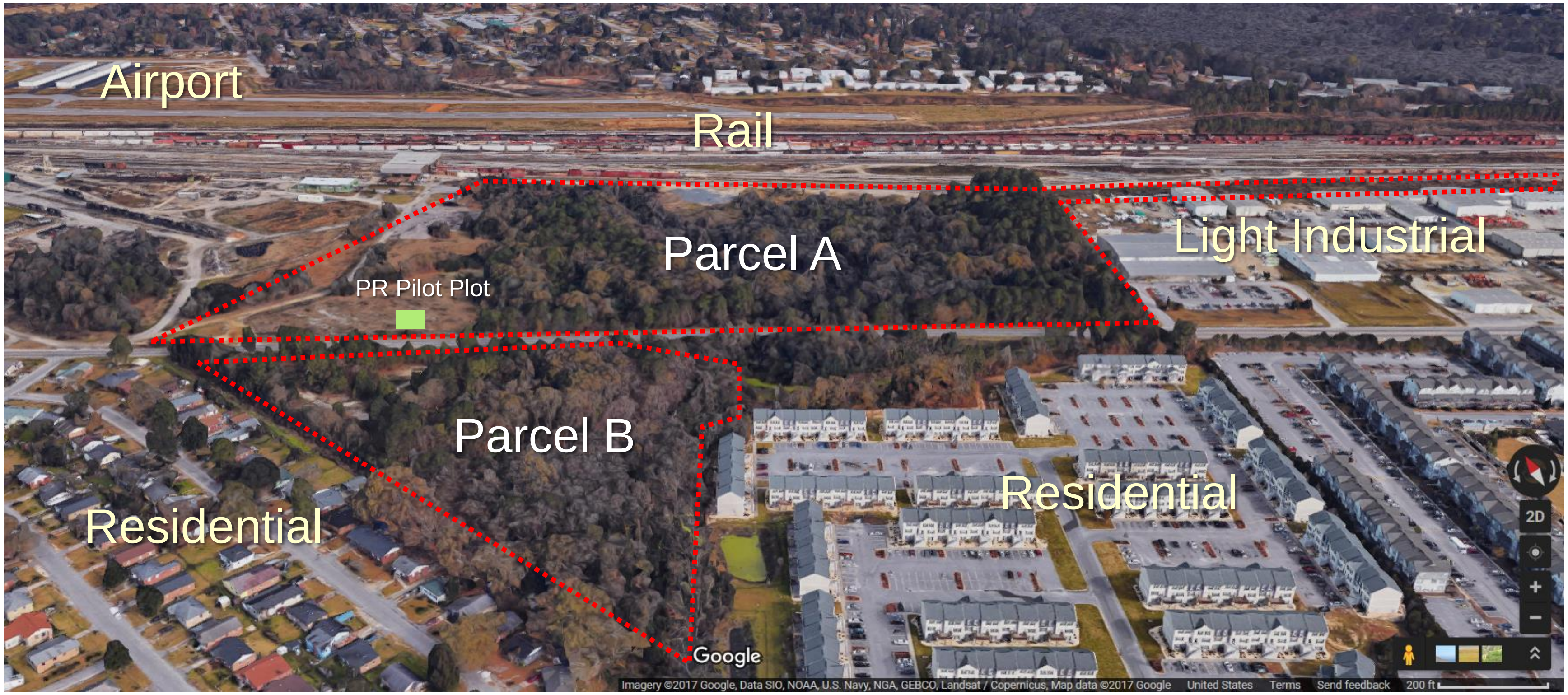
E. hyemale

E. ramosissimum



Columbia Wood Preserving (CWP) Site, S.C.

- Wood treating site from 1949 – 1977.
- COIs: As, Cr6 – Parcel A; As, Cr6 and PCP – Parcel B.
- Remedy: Dig and Haul, with evaluation of Phytoremediation for As.



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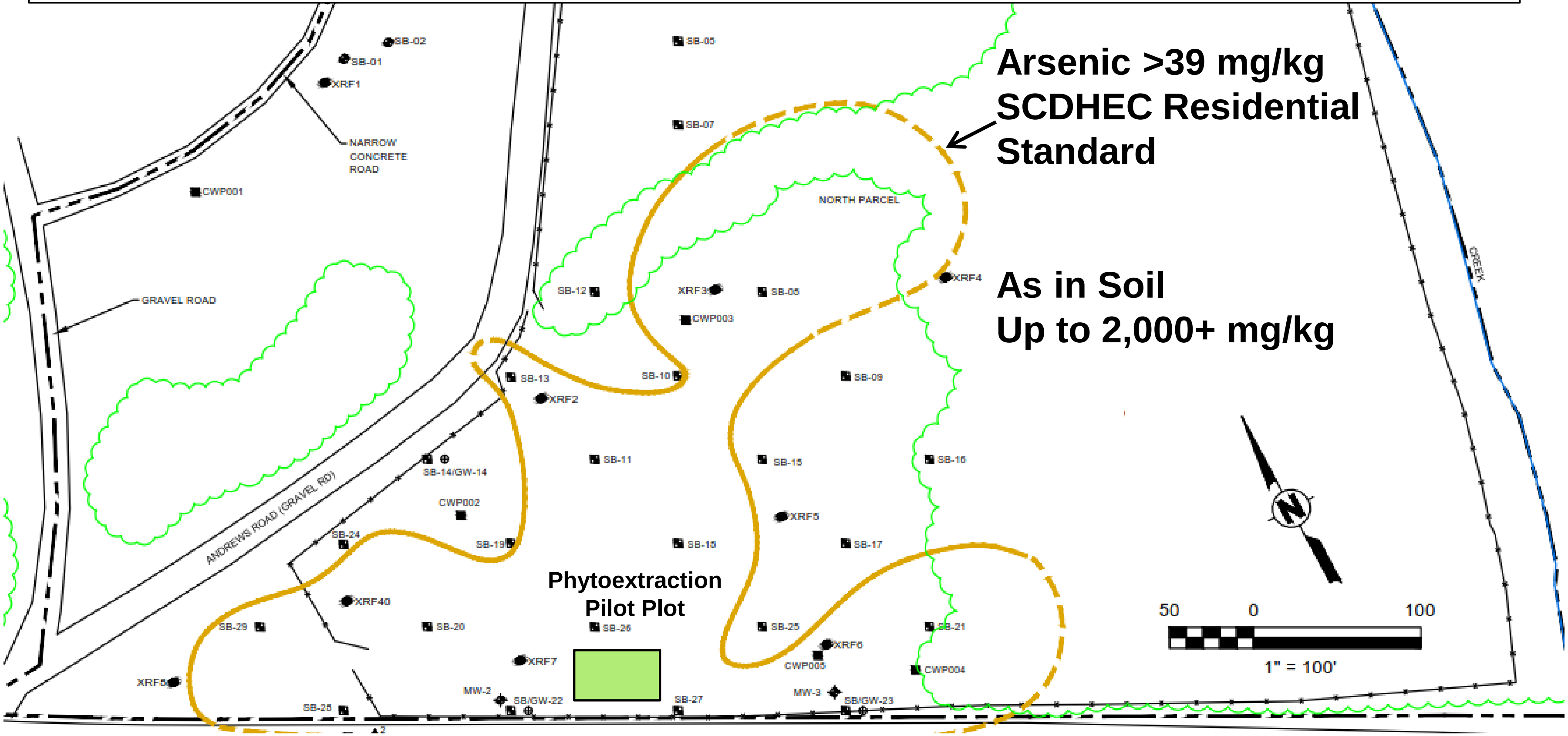
Columbia Wood Preserving Site

Case Study: Pilot Design for Arsenic Site

Chromated Copper Arsenate (Lumber Treating) Site, in Piedmont of South Carolina. Arsenic in near-surface (top 2-feet) ranging from 3 mg/kg to 2,000+ mg/kg. Dig and haul primary remedy, with phytoextraction pilot study.



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CWP: Pilot Soil Baseline Conditions

UGA extension

Ag & Environmental Services Labs
Soil, Plant, and Water Laboratory

2400 College Station Road
Athens, GA 30602
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http://aesl.ces.uga.edu

Completed: May 25, 2017

Soil Samples

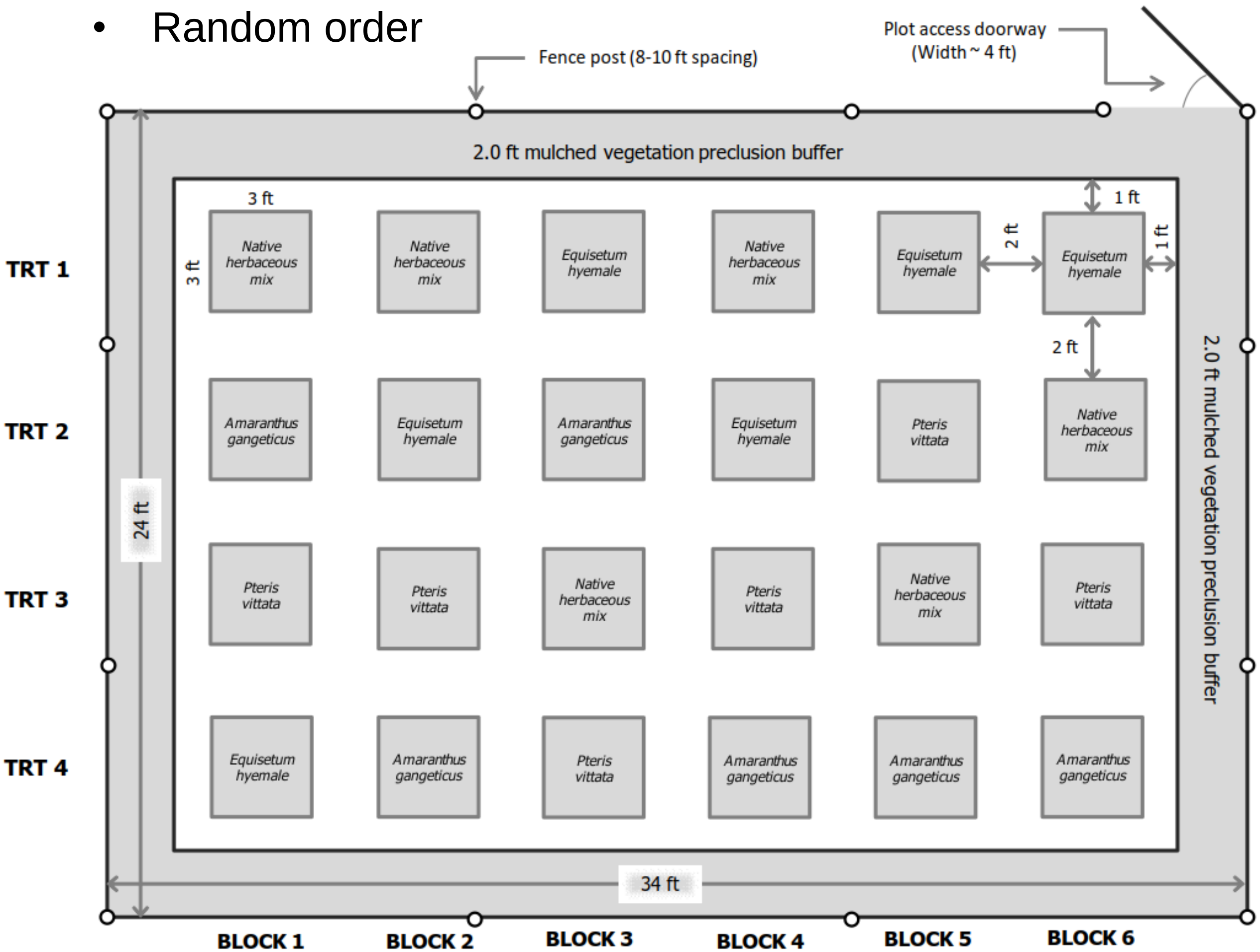
					%	meq/ 100g	Mehlich 1 mg/kg (ppm)														%
Lab	**Samp**	**LBC [1] (ppm $CaCO_3$/ pH)**	**pH $_{CaCl2}$ [2]**	**Equiv. water pH**	**Base Satur-ation**	**CEC**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**	**Pb**	**Zn**	**OM [3]**
62597	11	N.A.	7.55	8.15	100.0	11.8	2279	0.04	5.62	9.91	38.82	35.0	37	15.91	<0.03	11.2	0.14	11.4	2.00	6.72	1.32
62598	15	N.A.	7.52	8.12	100.0	12.1	2325	0.04	6.01	10.29	42.49	35.0	39	16.92	<0.04	10.0	0.14	12.2	2.07	6.88	1.03
62599	18	N.A.	7.58	8.18	100.0	13.5	2609	0.04	5.98	10.18	38.02	40.4	41	17.78	<0.04	11.2	0.14	11.1	1.80	7.07	1.25
62600	19	287	7.47	8.07	100.0	12.5	2360	<0.04	5.65	9.87	45.02	42.0	67	16.44	<0.04	11.1	0.13	13.6	2.21	6.78	1.04
62601	PM	3253	6.05	6.65	93.6	103.8	7519	<0.20	2.88	2.40	98.37	759.3	6825	31.43	<0.20	171.5	0.28	155.0	0.97	9.64	74.97

1. Soil Testing: Measurement of Lime Buffer Capacity (http://www.caes.uga.edu/Publications/displayHTML.cfm?pk_id=7335)
2. Soil Testing: Soil pH and Salt Concentration (http://www.caes.uga.edu/Publications/displayHTML.cfm?pk_id=7336)
3. Organic Matter is determined by the "loss on ignition" method for 3 hours at 360° C. Results are reported in percent by weight.
N.A.: Not applicable

	Total Elemental Analysis by Nitric Acid Digestion EPA Method 3051																			
	Al	B	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	P	K	Si	S	Zn	Pb	As	Se
Samp	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
11	3624	3.1	2997	< 1.0	158	37.0	3801	404.2	79.6	< 1.0	< 50.0	1.52	116	248	947	164	27.0	15.1	101.5	< 3.05
15	3692	2.6	2861	< 1.0	150	29.3	3486	385.4	76.6	< 1.0	< 50.0	1.31	113	238	1016	100	30.1	11.8	92.8	< 3.05
18	3872	2.7	3094	< 1.0	162	42.8	3797	407.1	82.9	< 1.0	< 50.0	1.90	121	267	1021	110	61.5	13.0	107.5	< 3.05
19	3766	2.9	3065	< 1.0	159	31.2	3870	398.7	81.1	< 1.0	< 50.0	1.83	119	272	1141	106	26.2	14.2	97.0	< 3.05
Gravel	2374	4.4	1690	< 1.0	208	6.4	6497	1385	145.35	< 1.0	< 50.0	3.24	291	596	256	63	22.6	0.5	< 3.05	< 3.05

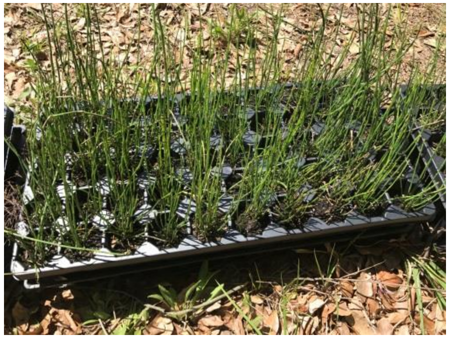
CWP: Designing a Statistically Robust Pilot Study

- Use of six replicates (blocks)
- Four test groups
- Random order



Test Plants Groups:

- *Equisetum hyemale*
- *Pteris vittata* Edenfern™
- *Amaranthus gangeticus*
- Native Herbaceous Mix



Nutter & Associates
environmental consultants

Ladder or Brake Fern (*Pteris vittata*)

- True arsenic hyperaccumulator plant (TF > 10). Tropical and non-native.
- Patent US6280500 B1, Lena Q. Ma et al., U of FL, 2001: *Methods for removing pollutants from contaminated soil materials with a fern plant.*
- Patent US7065920 B2 (Pteris and additional Ferns *Chielanthes sinuta, Adiantum raddianum, Polystichum acrostichoides, Actiniopteris radiate, Pellaea rotundifolia, Nephrolepis cordifolia, and Dennstaedtia punctilobula).*

EdenFern™ representation of *Pteris vittata* licensed through University of Florida.

CWP: Pilot Study Native Grass and Flower Mix

Native Grass and Forb Mix

Species	Common Name	Percentage
Rudbeckia hirta	Blackeyed Susan	0.12
Helenium autumale	Common Sneezeweed	0.04
Echinacea purpurea	Purple Coneflower	0.15
Coreopsis lanceolata	Lanceleaf Coreopsis	0.20
Agrostis perrenans	Upland Bentgrass	0.11
Andropogon virginicus	Broomsedge	0.07
Panicum virgatum	Switchgrass	0.11
Andropogon gerardii	Big Bluestem	0.18
Helianthus maximiliani	Maximilian Sunflower	0.02

CWP: Pilot Study Photograph, June 2017

Study Area from B6-T1 inward

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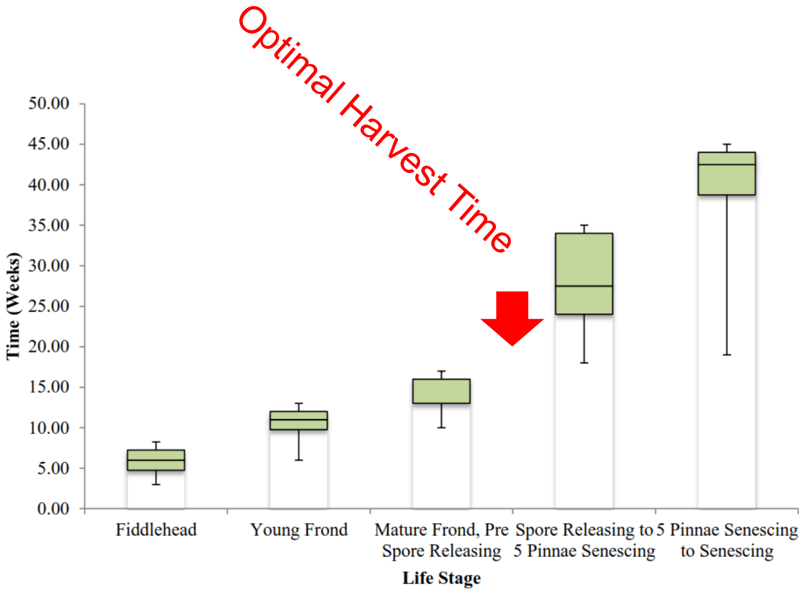
Plant Harvesting

- Irrigate and Monitor Plant Growth.
- Apply fertilizer as needed.
- Plant tissue harvesting and soil analyses:
  - Mid-season and fall
  - Roots and Fronds
  - Root, Shoots and Leaves
- Review data and assess translocation factors (ratio of what is in soil versus what is in plant tissue).
- Repeat data collection as needed….



The Life and Times of *Pteris vittata*: Investigating Frond Life Stage and Harvest Techniques to Optimize Phytoremediation with an Arsenic Accumulating Fern

Benavides, 2015.

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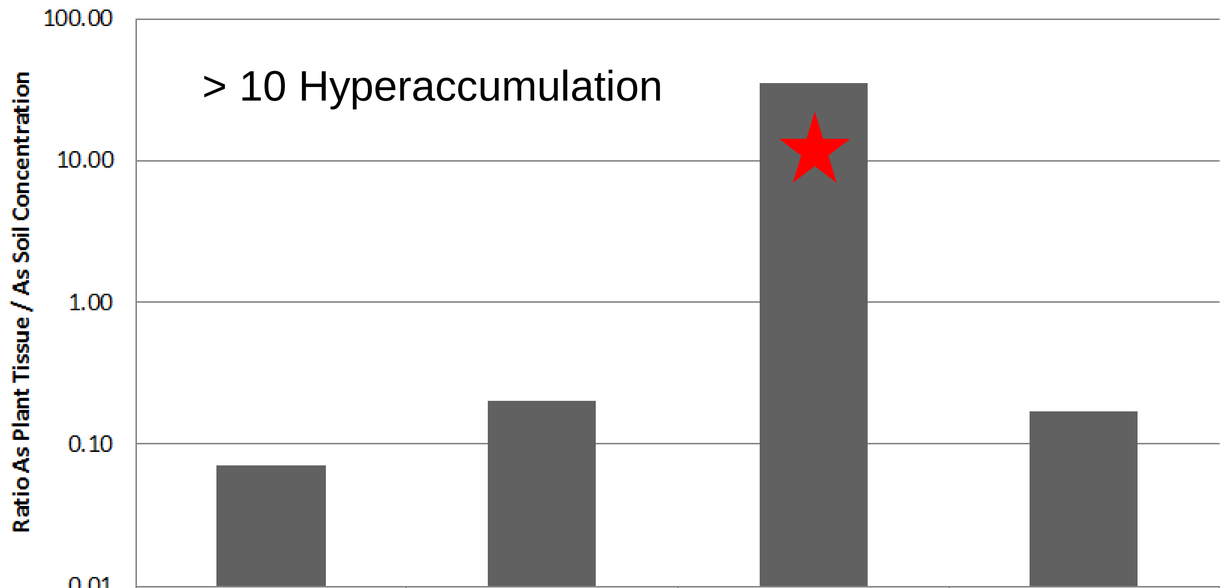
Mid-Season Harvest Results

Arsenic Translocation Factors



	Control	Amaranth	Pteris	Equisetum
TF	0.07	0.20	34.93	0.17

Photo 1. Harvesting horsetail.

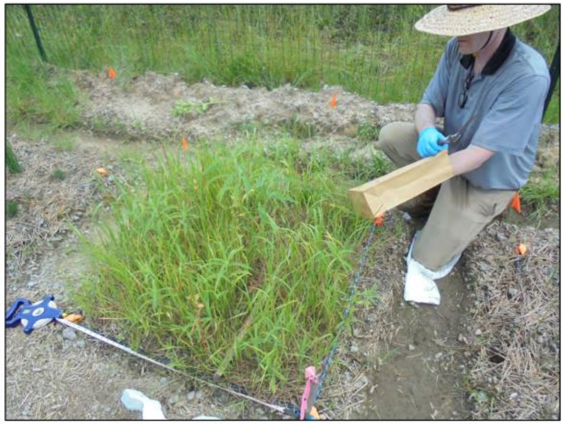


Photo 2. Harvesting a Control Plot.

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Key Points

- The applied discipline of economic geobotany dates back to the early 20th Century, but is rarely applied by practitioners today.
- Geobotanical precepts may be safely applied to other disciplines including environmental remediation.
- Phytoremediation is usually a supportive remedy best used in synergy with other technologies that address source zone remediation.
- Land use synergies for phytoremediation include landscaping, wetland mitigation, ecological habitat restoration, land conservation, biomass reclamation, storm water treatment and Brownfield-type redevelopments.
- Applied phytoremediation requires diverse multi-disciplinary team or niche-firm specializing in phytotechnologies practice.

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Fern Exhibit - Royal Botanical Gardens
Sydney, Australia

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