503 – The Research
Metal and Chemical Standards and the Risk Assessment

Rufus L. Chaney
USDA-Agricultural Research Service
Environmental Management and Byproducts Utilization Lab
Beltsville, MD

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Focus of this Presentation:

- 1989 503 Proposal -- Full of errors and bad science.
- After W-170 Peer Review, EPA withdrew Proposed 503.
- Ryan team worked with EPA/Rubin to provide the scientific basis for biosolids limits based on biosolids data. After more review, promulgated in 1993.
- Pretreatment of industrial wastes and reduced use of Cd in products lowered Cd and other metals in biosolids remarkably since 1980.
- Enforcement of 503 regulations favor biosolids use.
  - Assume 1000 t/ha biosolids applied for each Pathway.
- Biosolids are a remarkably valuable material for remediation of metal contaminated Superfund Areas
- Changes needed in CWA-503: Mo, As?, Cr^{6+}?, Fe?, Hg?

Problems with 1989 EPA Version of 503

- **Pathways were technically wrong for surface applied biosolids where direct ingestion occurs.**
  - Should have been mg/kg, not kg/ha.
- **Metal limits relied on soluble metal salt additions in pot studies.**
  - Several metal limits so low that allowed cumulative applications were not valuable (Cu most limiting).
- **PCB limit would have prevented biosolids use.**
  - EPA had used plant uptake data from study of PCNB (fungicide accumulated into plants), not PCBs which low uptake to plant shoots/grain/fruit.
  - Corrected PCB uptake information coupled with cessation of PCB release to sewer made it a non-issue.

Pathways for Risk Assessment of Elements in Soils, and Highly Exposed Individuals-1.

Pathway	Highly Exposed Individual
1. Soil➔Plant➔Human	Farm markets; 2.5% of food.
2. Soil➔Plant➔Human	Home gardens; 60% of garden foods for lifetime; 1000 t/ha
3. Soil➔Human	200 mg/day soil/dust ingestion; 1000 t/ha
4. Sol ➔Plant➔Animal➔Human	Farms; 45% home-grown meat; 1000 t/ha
5. Soil➔Animal➔Human	Grazing ruminants; soil is 2.5% of annual diet; 45% home-grown meat.
6. Soil➔Plant➔Livestock	100% of livestock feeds grown on soils; 1000 t/ha
7. Soil➔Livestock	Grazing ruminants; 2.5% soil in diet.

Pathways for Risk Assessment of Elements in Soils and Highly Exposed Individuals-2.

Pathway	Highly Exposed Individual
8. Soil➔Plant	Sensitive crops; strongly acidic; 1000 t/ha.
9. Soil➔Soil Biota	Earthworms; microbes; metabolic function of soil; 1000 t/ha.
10. Soil Biota➔Soil Biota Predator	Shrews; 1/3 of diet presumed to be earthworms full of soil; 1000 t/ha.
11. Soil➔Airborne Dust➔Human	Tractor operator; 1000 t/ha.
12. Soil➔Surface water➔Human	Subsistence fishers.
13. Soil➔Air➔Human	Farm households
14. Soil➔groundwater➔Human	Well water on farms.

SOIL-PLANT BARRIER

Processes in soils or plants which prevent excessive food-chain transfer of elements

- Insolubility or adsorption in soil or plants roots:
  - Cr, Pb, Fe, Hg, Sn, Au, Ag, Zr, Al, F, Ti, etc.
- Phytotoxicity limits plant yield at levels which are not toxic for lifetime consumption by livestock:
  - Zn, Cu, Ni, As, Mn, B, etc.
- Exceptions to Soil-Plant Barrier:
  - Cd, Se possible risk to humans
  - Mo, Se, Co possible risk to livestock
- Barrier can be circumvented by direct ingestion of biosolids.
  - Fe, F, Pb, Hg may comprise risk in high on surface.

Complex Equilibria of Metal Ions with Components of Soil Environments

Plant Shoots

Grass Roots ↓

Deoxymugineic Acid ↓

FeOxide → Fe-PSid →

Plant Roots

Chelated to Organic Matter -- Humics; fulvics

Adsorbed on Fe/Mn

Soil Solution

$M^{2+} + L \Leftrightarrow ML$

Soil Microbes

Occluded in Fe/Mn oxides

Inorganic Solids

$Ni(OH)_2$

NiO

Ni-Silicate

Ni-Al-hydroxide

L = Ligands

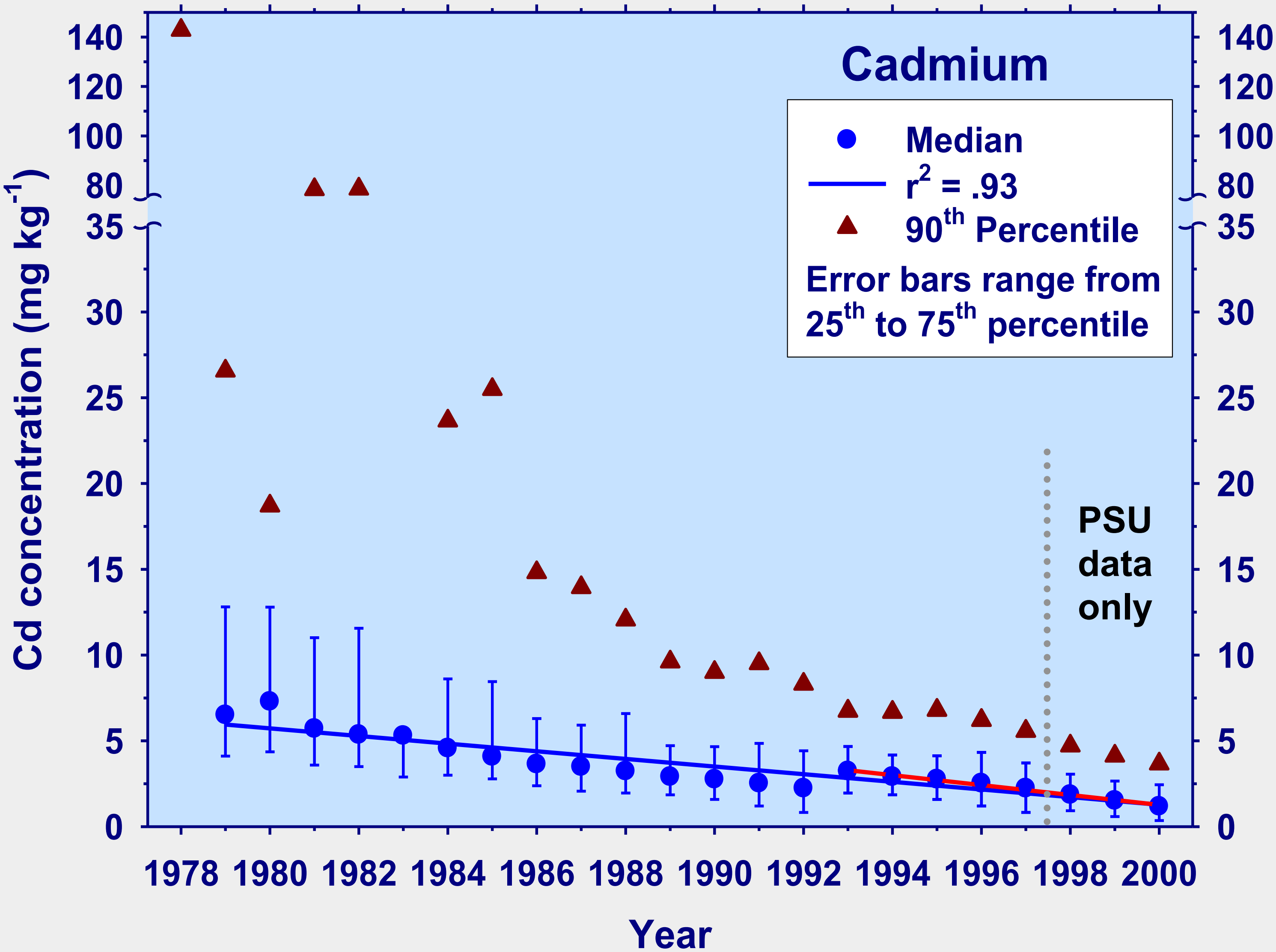
Organic

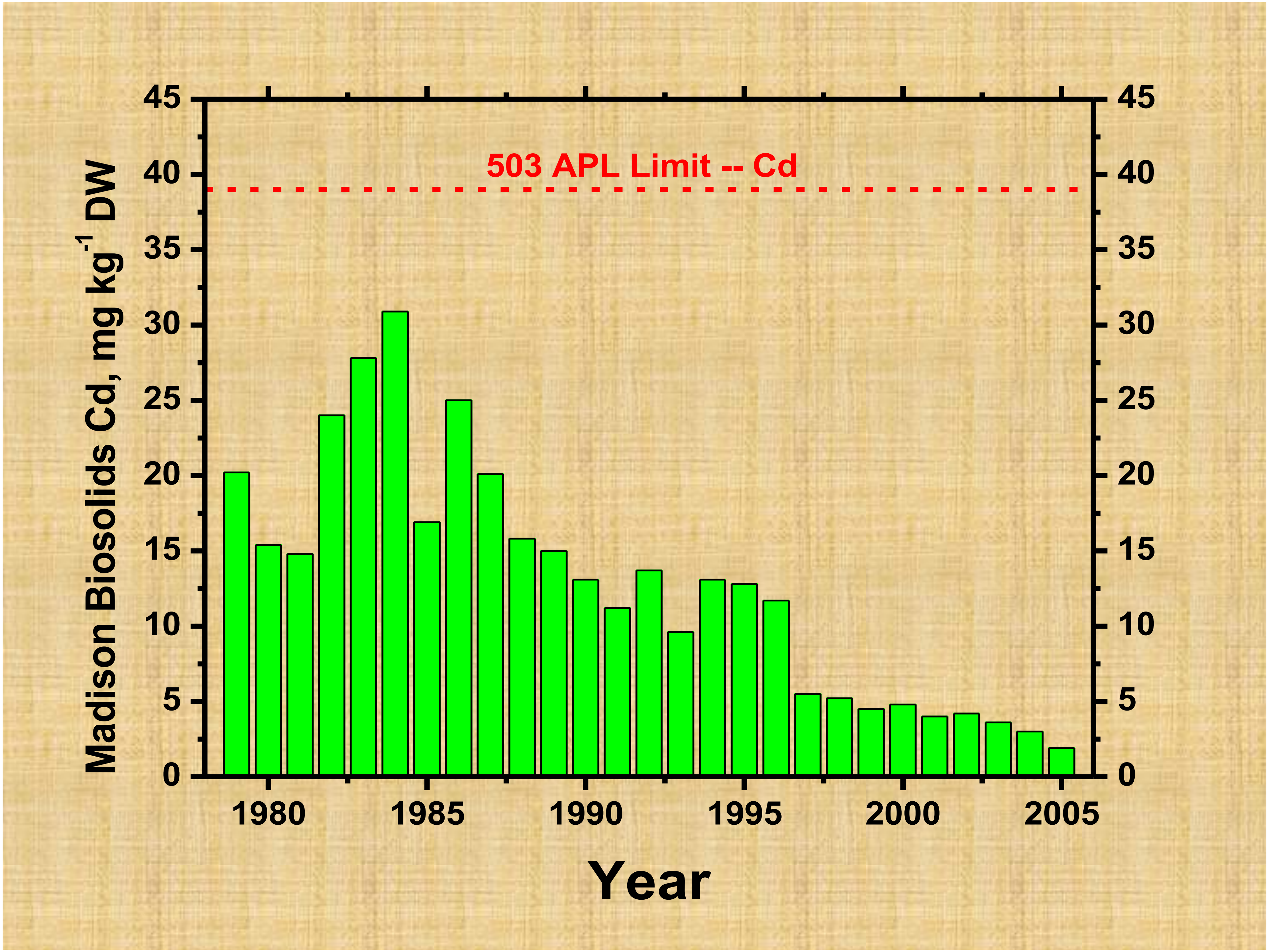
Inorganic

Comparison of 1989 Proposed 503 and PRC Review

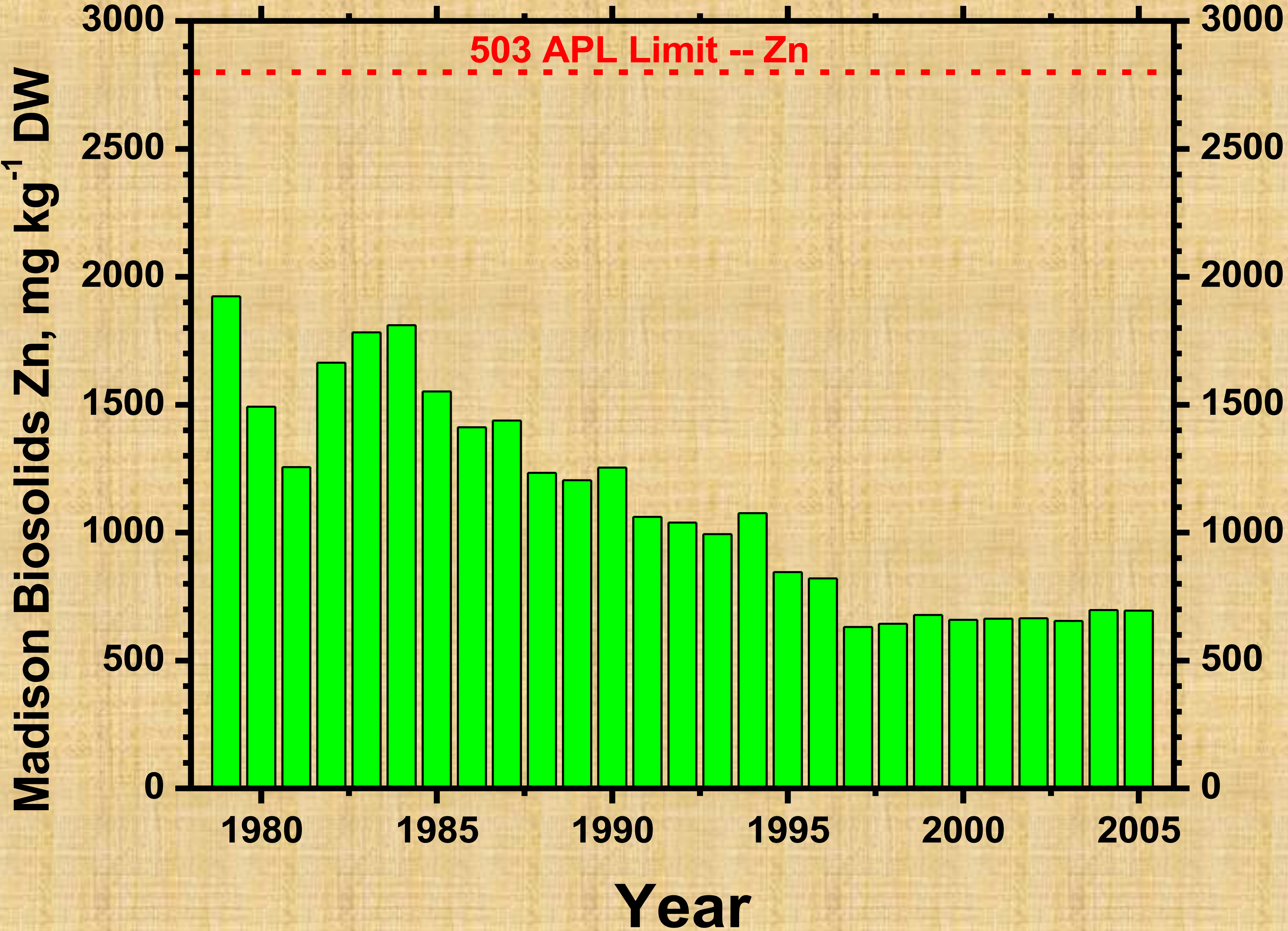
Pollutant	PRC Conclusions: Cumulative Application		PRC Conclusions: Limiting Pathway	1989 Proposed 503: Cumulative Application	1989 Proposed 503: Limiting Pathway
	kg/ha			kg/ha	
Cd	18.4	2	Garden Foods	18.4	2
Cr	>2000.	12	Ground Water	530.	8
As	1600.	3	Sludge Ingestion	14.0	3
Pb	600.	3	Sludge Ingestion	125.	9
Hg	20.	4	Livestock Feed	14.9	4
Zn	2700.	8	Phytotoxicity	172.	8
Cu	1200.	8	Phytotoxicity	46.	8
Ni	500.	8	Phytotoxicity	78.	8
Mo	35.	6	Livestock Feed	5.07	6
Se	32.	5	Livestock Feed	32.4	6
	kg/ha/yr			kg/ha/yr	
PCBs	4.93	4	Sludge Ingestion	0.0056	3
PCBs	0.573	4M	Mixture Ingestion	0.019	4

Pretreatment and Regulatory Controls Reduced Cd in PA Biosolids (Stehouwer)

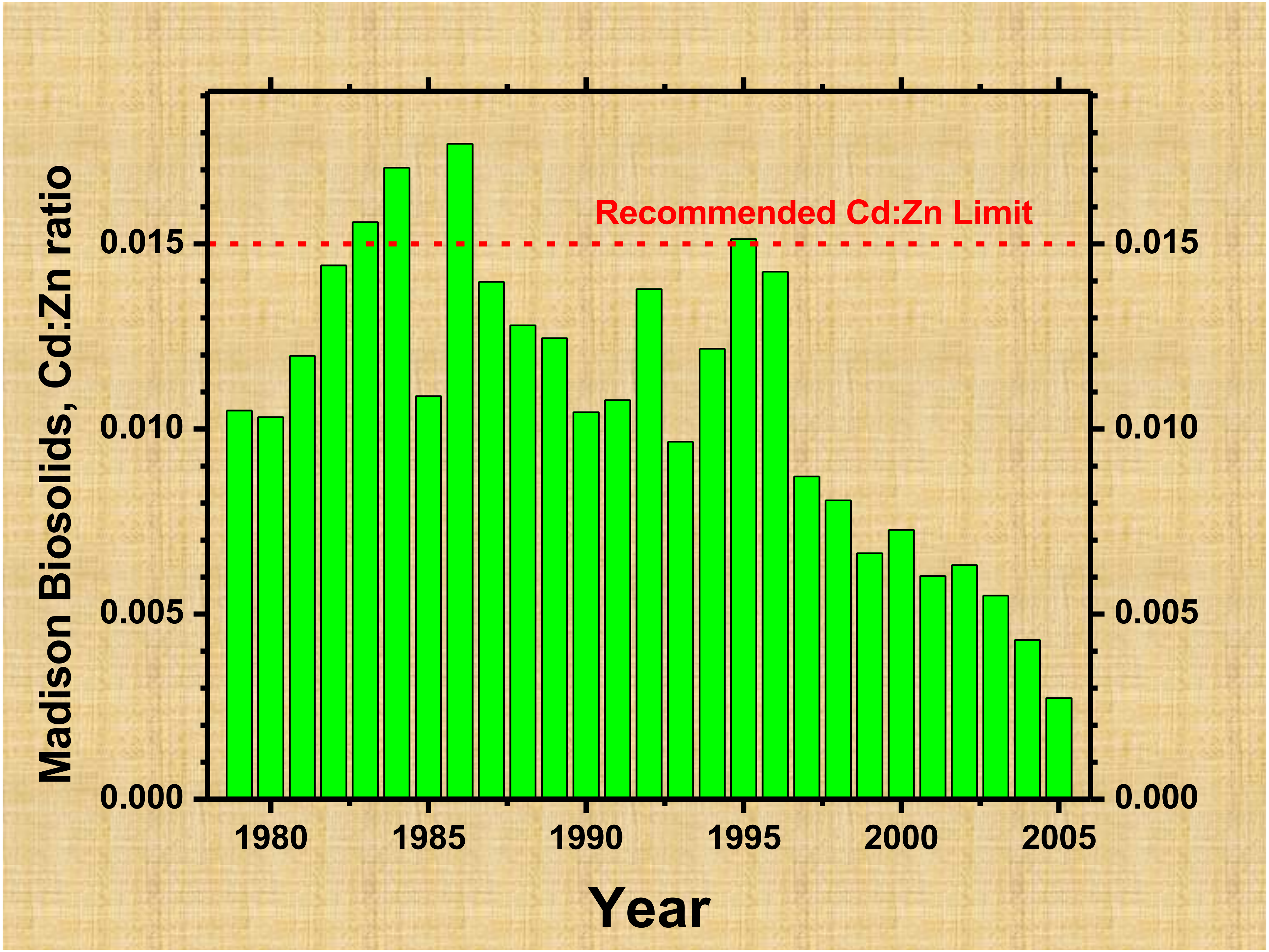




503 APL Limit -- Cd
Madison Biosolids Cd, mg kg-1 DW
Year
0
5
10
15
20
25
30
35
40
45
1980
1985
1990
1995
2000
2005



503 APL Limit -- Zn
Madison Biosolids Zn, mg kg-1 DW
3000
2500
2000
1500
1000
500
0
1980
1985
1990
1995
2000
2005
Year


Recommended Cd:Zn Limit
Madison Biosolids, Cd:Zn ratio
0.015
0.010
0.005
0.000
1980
1985
1990
1995
2000
2005
Year

Results of the TNSSS for Cd, Zn and Cd:Zn Ratio

Calculated Mean, Geo. Mean, Range for the 84 samples ignoring the population representation aspect of the TNSSS.

Element	Statistical Measure				
	Mean	GM	Min	Max	GOAL
	-------------------- mg/kg dry weight----------------				
Zn	1030.	808.	216.	8550.	<1500.
Cd	2.69	1.98	0.208	11.8	<5-10.
Cd:Zn, %	0.282	0.245	0.064	1.06	<1.5

503 Is A Defensible Rule

Pathways for Risk Assessment of Elements in Soils, and Highly Exposed Individuals

Highly Exposed Individuals
Practical Worst Case Loadings: 1000 t/ha.

SOIL-PLANT BARRIER

Processes in soils or plants which prevent excessive food-chain transfer of elements.

PHYTOTOXICITY

Possible only at very low soil pH, but sorbents in biosolids limit potential phytotoxicity—Zn Cu Ni

Potential Environmental Problems From Inadequately Regulated Use of Biosolids on Cropland and Gardens

- **Phytotoxicity from Zn (possibly Cu, Ni):**
  - Involved sensitive vegetable crops.
  - High cumulative applications and low soil pH, <<5.5
  - Highly contaminated biosolids.
- **Excessive Cd in crops:**
  - Highly contaminated biosolids (before regulations).
  - Low soil pH. High Cd/Zn ratio allow food-chain transfer.
- **Excessive PCB transfer to livestock:**
  - Highly contaminated biosolids before regulation.
  - Surface application on pastures = highest transfer.
  - Cessation of PCB use limits PCBs in biosolids.

Potential Environmental Problems From Inadequately Regulated Use of Biosolids on Cropland and Gardens

- Excess Mo or Se in forages; alkaline soils.
  - Proposed 40 ppm Mo limit would prevent.
- Lime-induced Mn deficiency:
  - Leached soils low in total Mn.
  - Calcareous soils from limed sludge or limestone applied to correct Zn phytotoxicity.
- Excess mineralizable N application
  - Nitrate leaching or lodging of small grains.
  - Prevented by regulations/mineralization data.
- Infections of livestock by parasites.

Before Regulations, Bad Practices Occurred.

Cd in Crops Grown on Long-Term Biosolids Utilization Farms in the Northeast: City 13.

Biosolids applied 1967-1975; approx. 20 t/ha
Biosolids contained 700 mg Cd/kg, Cd:Zn=10%
Field soil contained 8.2 mg Cd/kg, Cd:Zn = 15%.

Farm Trt	pH	1975 Chard	1976 Lettuce	1975 Soybean	1976 Oat	1977 Soybean	1977 Oat
		-----------------------	----------------mg/kg DW	----------------------			
Biosolids							
Nil	5.7	70.4	49.9	2.64	3.38	2.05	2.24
Limed	6.4	17.7	9.9	0.65	0.54	0.46	0.28
Control							
Nil	5.2	0.9	1.5	0.16	0.11	0.11	0.08
Limed	6.2	0.5	0.6	0.13	0.07	0.03	0.05

Cd Examples From Old Reports

- Long term sludge utilization farms in NE:
  - City 9 Elizabethtown, PA 169 Cd 0.033 Cd:Zn
  - City 13 Pottstown, PA 700 Cd 0.150 Cd:Zn
  - City 25 St. Marys, PA 970 Cd 0.780 Cd:Zn
  - City 1 York, PA 150 Cd 0.028 Cd:Zn
  - City 2 Harrisburg, PA 160 Cd 0.049 Cd:Zn
- Purdue study of high metal sludges:
  - Frankfort, IN. 284 Cd 0.042 Cd:Zn
  - Anderson, IN. 247 Cd 0.048 Cd:Zn
  - Merion, IN. 1210 Cd 0.637 Cd:Zn
- Literature reports:
  - Fort Collins, CO. 98 Cd 0.056 Cd:Zn
  - Chicago, IL 210 Cd 0.051 Cd:Zn

What should be done with contaminated biosolids application sites from before regulations?

- Before 1979, there were no Federal biosolids regulations; a few states started permitting biosolids based on metals and PCB levels.
- A few severely contaminated sites were identified and remediated using local funds and state rules.
- What about all the other sites with high soil Pb, Hg, As, Cd, etc., that are known to exist?
- I asked EPA about my recollection that the 1979 Rule required POTWs/States to investigate previous sites to look for problems? They say "Not in rules."
- States need to do something about known sites with excessive metal accumulation from biosolids.

Benefits of Biosolids

Remediation Using Biosolids

Early growth of corn on control (left) and compost amended (right) Plots on Woodstown silt loam soil (Epstein and Chaney, 1974).

Strongly wilted corn on control plot in experiment with biosolids Compost application to Woodstown silt loam (Epstein and Chaney)

Corn on biosolids compost treated soil on same day as control plot corn was strongly wilted (Epstein and Chaney).

Revegetated coal mine spoil at Frostburg, MD, treated with Composted biosolids (Armiger et al., 1975).

Photo of field test using composted biosolids and conservation grasses to revegetate barren gravel mine spoil (Walker, 1975).

Tailor-Made Biosolids Mixtures For Beneficial Use and Remediation

- **Apply mixture of limestone equivalent, metal adsorbent, organic soil amendment, and fertilizer value to correct all risks/problems of the contaminated soils:**
  - **Zn or Ni Phytotoxicity; make soil calcareous.**
  - **Food-chain risks from Cd prevented by Zn.**
  - **Soil ingestion risk from soil Pb, As, etc. remediated.**
  - **N fixation by legumes made possible.**
  - **Leaching of limestone equivalent corrects surface and subsurface soil metal phytotoxicity.**
  - **Microbes from amendments give soil life again.**
- **One treatment for comprehensive remediation.**

Bunker Hill, Idaho -- Smelter killed ecosystem Superfund Site.

Aerospreader Applying Biosolids-Wood Ash Mixture at Bunker Hill

Soil contained 12,000 ppm Zn, 2100 ppm Pb, 20 ppm Cd; pH 6.5

Highly Zn-phytotoxic smelter and mine waste contaminated soils at Bunker Hill, ID (15,000 mg Zn/kg);

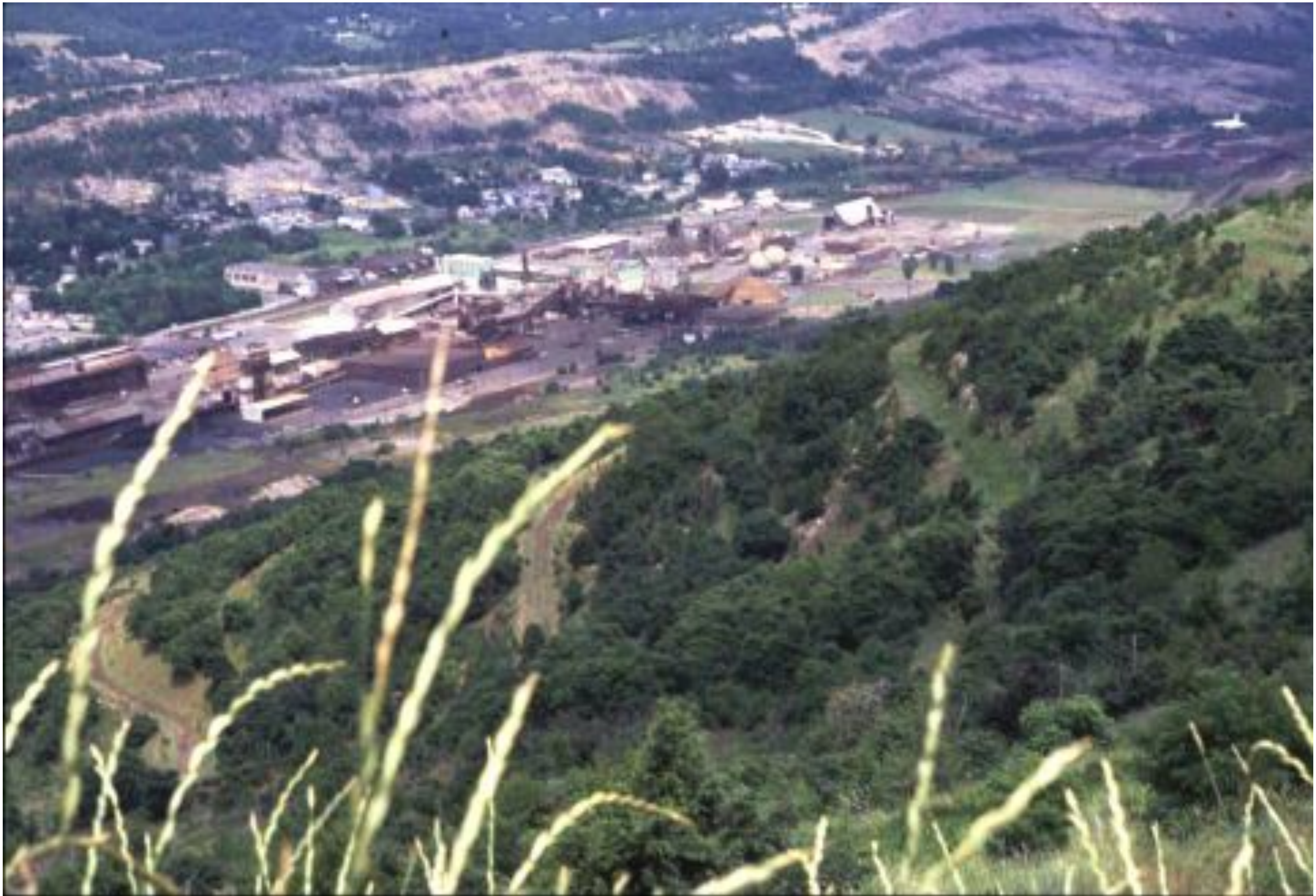
Background = Biosolids+Wood-Ash Remediated

Foreground = Seeded control hazardous soil.

Revegetation of Bunker Hill Hillsides using mixture of biosolids, woodash and logyard debris, after 2 years.

Palmerton, PA, 1980; Dead Ecosystem on Blue Mountain.

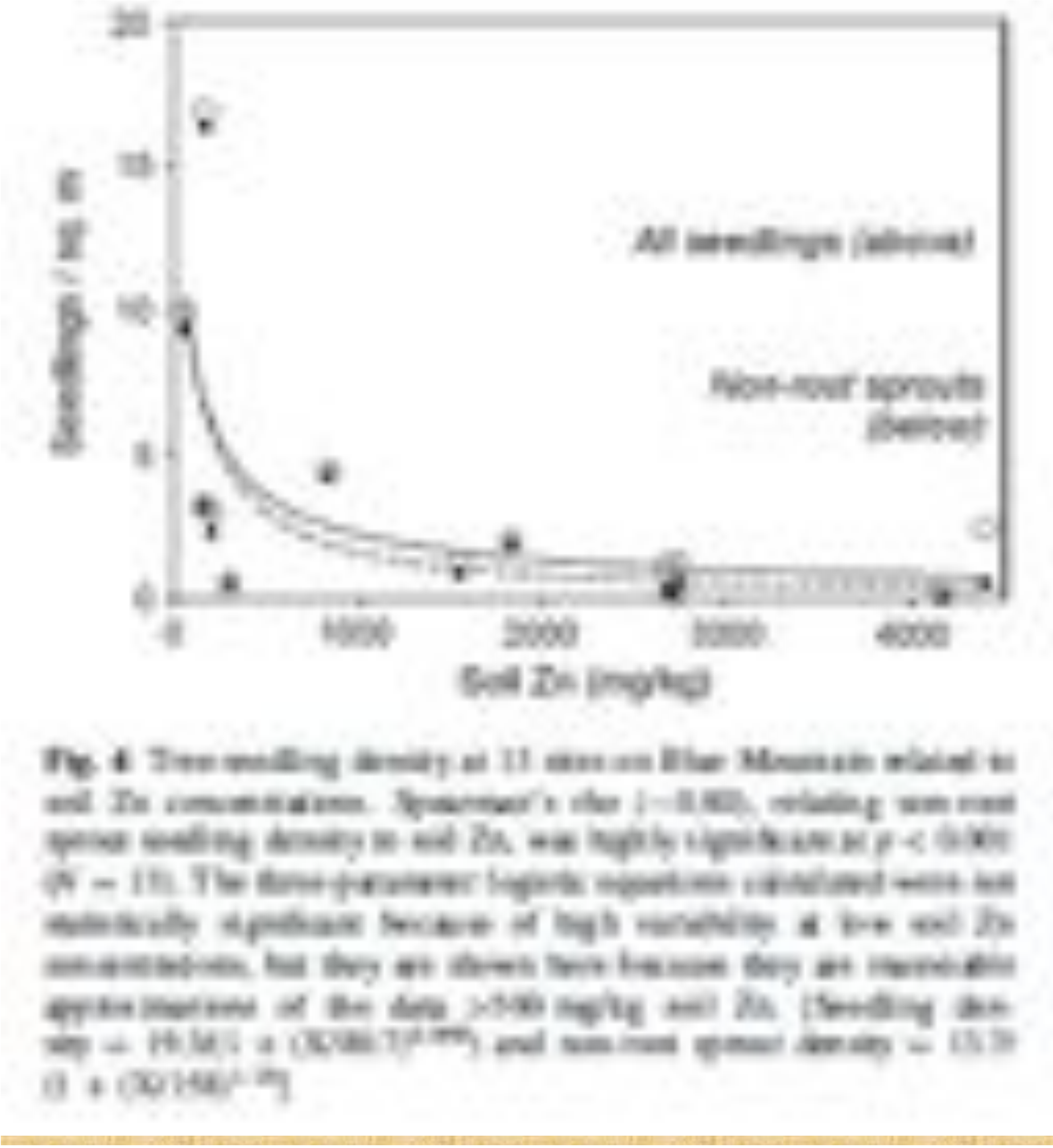
Palmerton, PA, 1990: Oyler's First Test Plot Using Biosolids + FlyAsh + Limestone, with 'Merlin' Red Fescue; adjacent control.



Palmerton, PA, 1999: Looking down revegetated Blue Mt.

Palmerton, PA -- Revegetated Area in 1999:
Area with good wheatgrass and lespedeza cover.

Palmerton, PA: Blue Mountain – 1999; Foreground = Biosolids+Limestone+FlyAsh; Background = untreated Control



Toxicity of metals in Palmerton (Blue Mountain) soils is increasing as soil pH declines due to acidic rainfall. Plants so not survive during germination when soil Zn is too high.

Beyer et al., 2011

Mean total Zn, Cd and Pb, and DTPA-extractable Zn and Cd (at 100 mL extractant/2 g soil) in Palmerton "Revival Field" Test Plots Comparing Traditional and Biosolids Compost Remediation Treatments (Li et al., 2000).

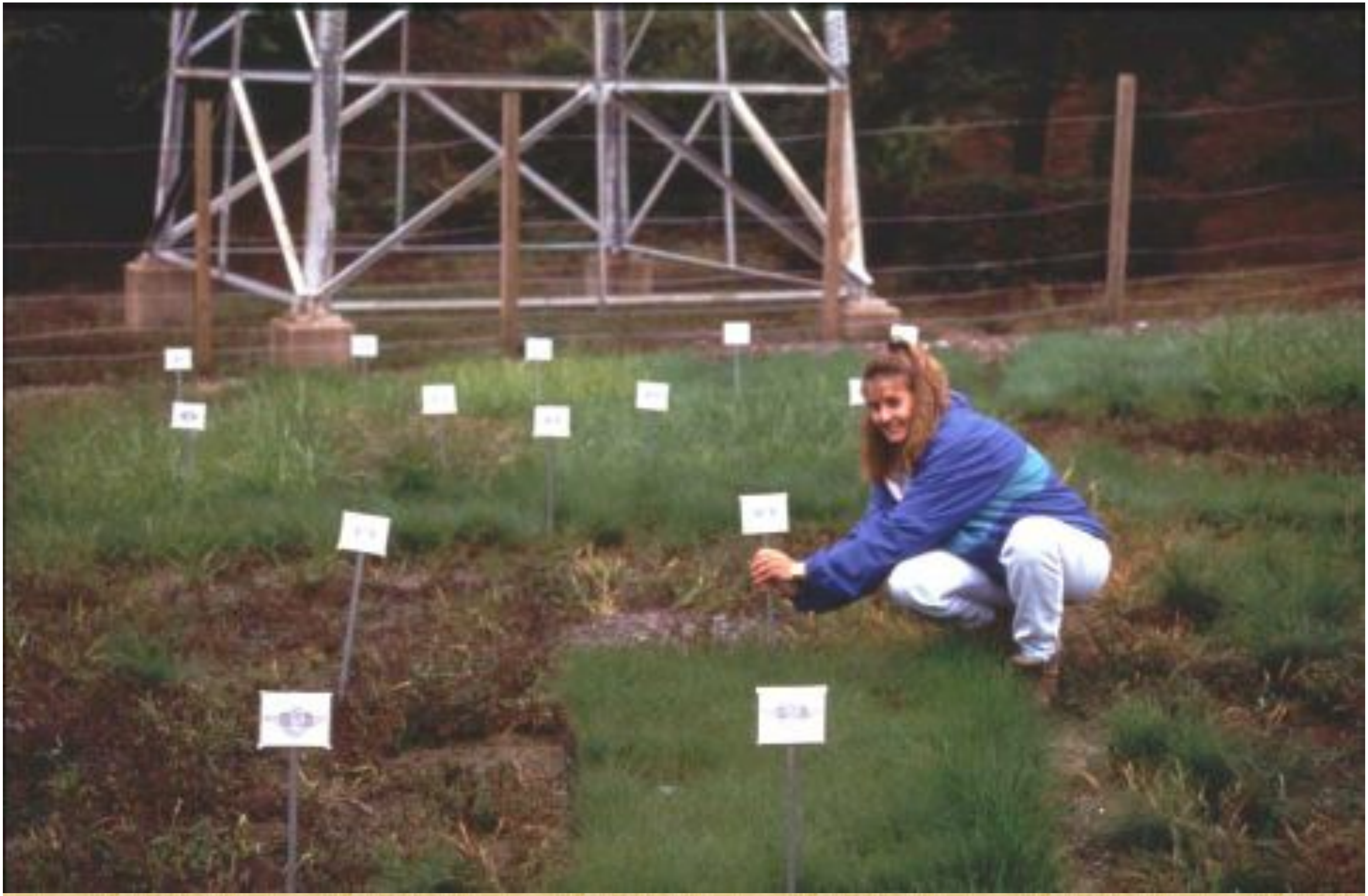
Treatment	Total			DTPA-Extractable	
	Zn	Cd	Pb	Zn	Cd
	mg kg^{-1}				
Control	14900 a†	164. a	687. a	4940. a	83.1 a
Limestone	15700 a	161. a	680. a	4980. a	82.9 a
Compost	16000 a	170. a	767. a	4550. a	69.1 b

†Treatment means followed by the same letter are not significantly different at the 5% level (Duncan-Waller-test).

Mean pH, Sr-extractable metals, pH, organic matter and oxalate Extractable Fe and Mn in Palmerton “Revival Field” Plots comparing remediation using traditional or biosolids compost methods; plots Installed in 1993, last sampled in 1998 (Li et al., 2000).

Treatment	$Sr(NO_3)_2$-Extr. Zn	$Sr(NO_3)_2$-Extr. Cd	pH	Organic Matter	Oxalate-Extr. Fe	Oxalate-Extr. Mn
	----- mg kg^{-1} ------			%	----- g kg^{-1} -----	
Control	195. a	1.99 a	5.9	4.6	5.74 a	2.12
Limestone	156. a	1.65 a	6.5	4.7	5.61 a	1.92
Compost	4.8 b	0.033 b	7.2	9.5	16.7 b	2.44

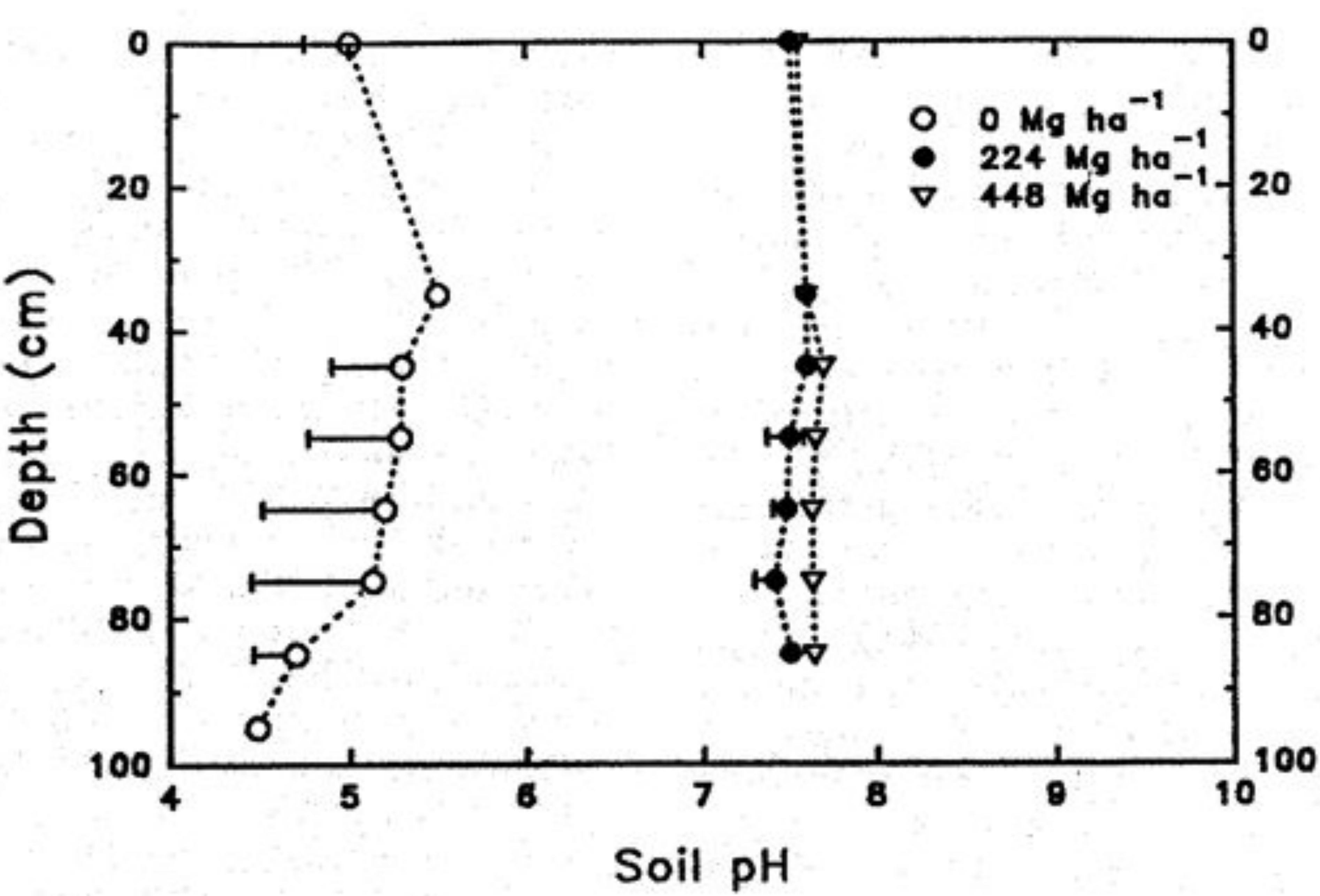
†Treatment means followed by the same letter are not significantly different at the 5% level (Waller-Duncan test.)



Palmerton, PA, Revival Field, Year-3: Grasses thrive only on Alkaline Biosolids Compost Treatment (Cooperator Bev Kershner).

Revegetation/Remediation of Heavy Metal Contaminated Soils: Solutions.

- Make Soil Calcareous Using By-Product Lime
  - Increases metal adsorption and occlusion.
  - Protects against pH falling in future.
- Increase Metal Adsorption Capacity
  - Include Fe, Mn hydrous oxides and phosphate.
  - Provides persistent increase in metal adsorption, and thus reduction in potential for metal phytotoxicity.
- Remediated Soil Must Support Legumes.
  - High pH and soil P aids legume competition, alleviating need for annual N fertilization. Legumes more susceptible to metal phytotoxicity than grasses.



Effect of rates of limed digested biosolids applied to Galestown loamy Sand in 1976 on pH at soil depths in 1992 (Brown et al., 1997).

Belvidere Mountain Site, Vermont
Serpentine Asbestos Mine Wastes

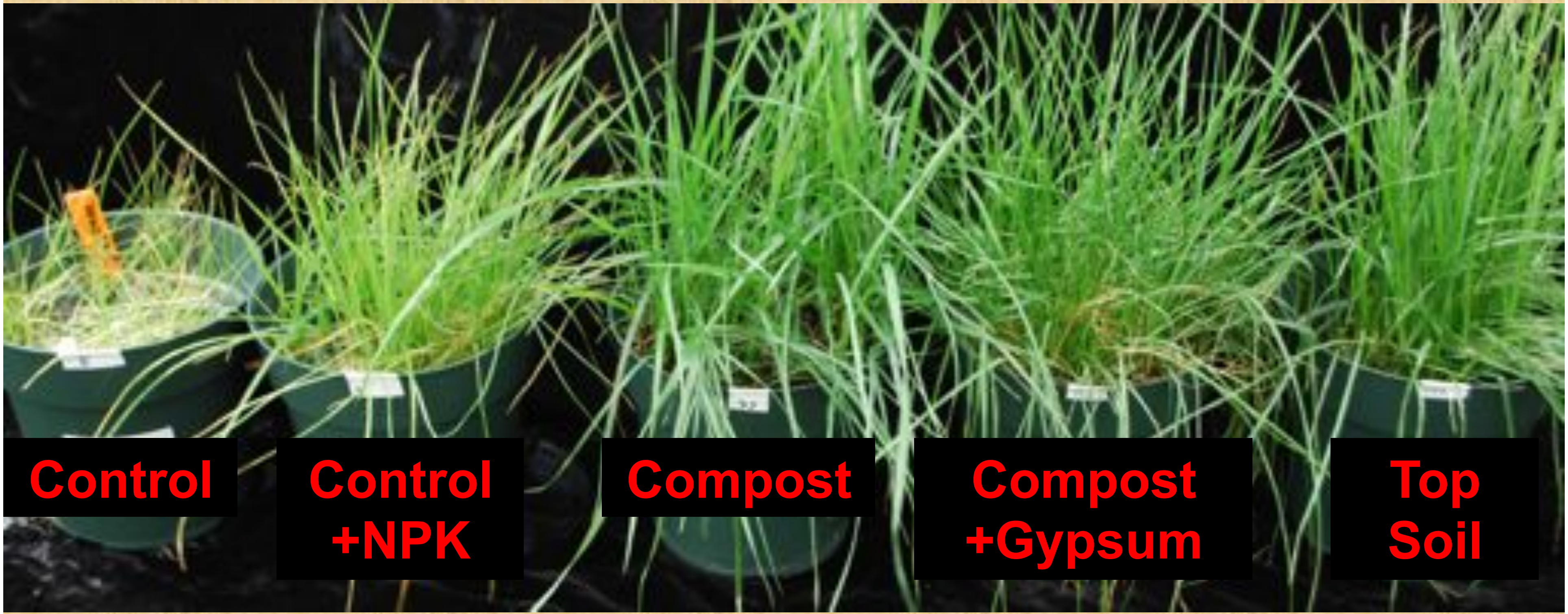
Problems at Vermont Asbestos Group Superfund Site

- 300 Acres of ground serpentinite rock, washed to recover asbestos and placed in piles <1950.
- Water and wind erosion of asbestos comprises a hazard sufficient to become Superfund.
- Serpentinite rock is Mg silicate which contains so little Ca, P, and other nutrients that plants cannot live on the site.
- Serpentinite rock also contains >2000 ppm Ni, and Cr^{3+} but because pH is >8, Ni is not toxic.
- Intensely infertile (Ca, P, N, K, B, OM, microbes).
- No plants can live on these rocks without Ca.

Treatments Tested:

- Surface Applied Soil Amendments:
  - Control
  - NPK Fertilizer (normal roadside revegetation)
  - Compost + NPK
  - Compost + NPK + Gypsum(=$CaSO_4$)
  - Topsoil + NPK
- Plant Species Tested:
  - Kentucky bluegrass
  - Perennial ryegrass
  - Tall Fescue
  - Alsike Clover

Tall Fescue 47 Days from Seeding



Preparing mixture of COMPOST (manure and yard debris), mined gypsum, NPK fertilizer plus limestone

August 24, 2011: Applying the compost mixtures to test plots; compost was raked even, then seeded with crop mix.

Vermont Asbestos Group Field plots in July, 2011 showing effective remediation using compost plus gypsum & NPK.

Strong growth of grasses and clover at VAG site in July, 2011

Rooting well into mineral layer below top-dressed compost.

Effective vegetative cover on strong slop at VAG, 7-12-2011

How Did We Achieve Success on VAG Site?

- Evaluated composition of soil for metals, pH, and nutrients before plant testing.
- Recognized severe Ca and P infertility of serpentine rock derived soil materials.
- Tested treatments and plant species on site soil in greenhouse.
- Amendment mixture included all nutrients needed for plant growth in compost.
- Added limestone to prevent acidification of compost layer over time with N-fixation.
- Included gypsum to add Ca to sub-surface soil.

Biosolids Phosphate: Plant Available but not Water Soluble.
Regulation Needs to be Based on Water Extractable P, not Soil Test P.

Rufus Chaney, Urszula Kukier and Eton Codling

USDA-ARS-EMBUL, Beltsville, MD

Northeast Residuals & Biosolids Conference

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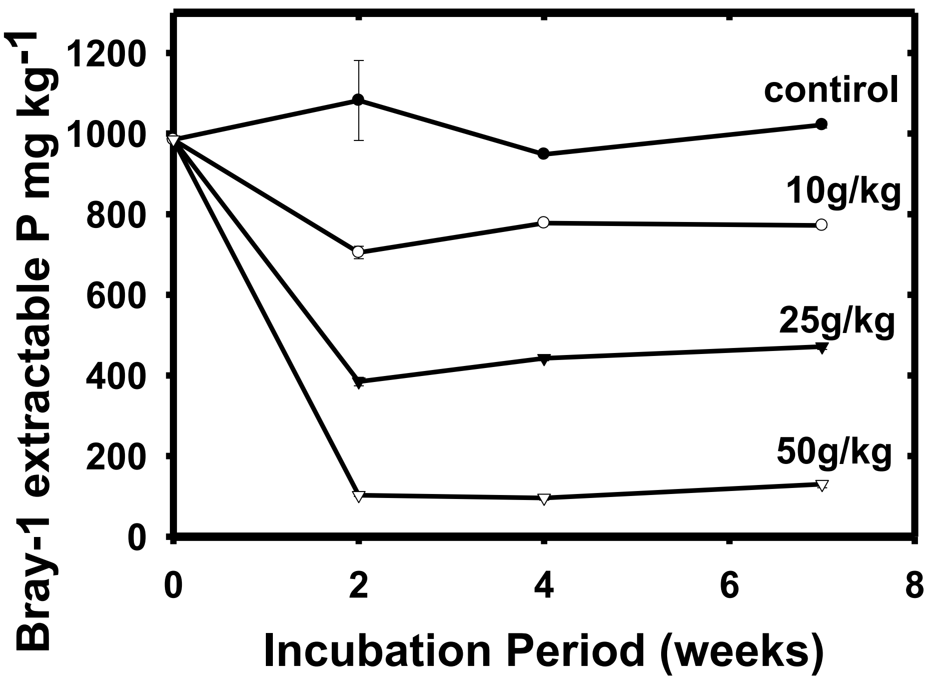
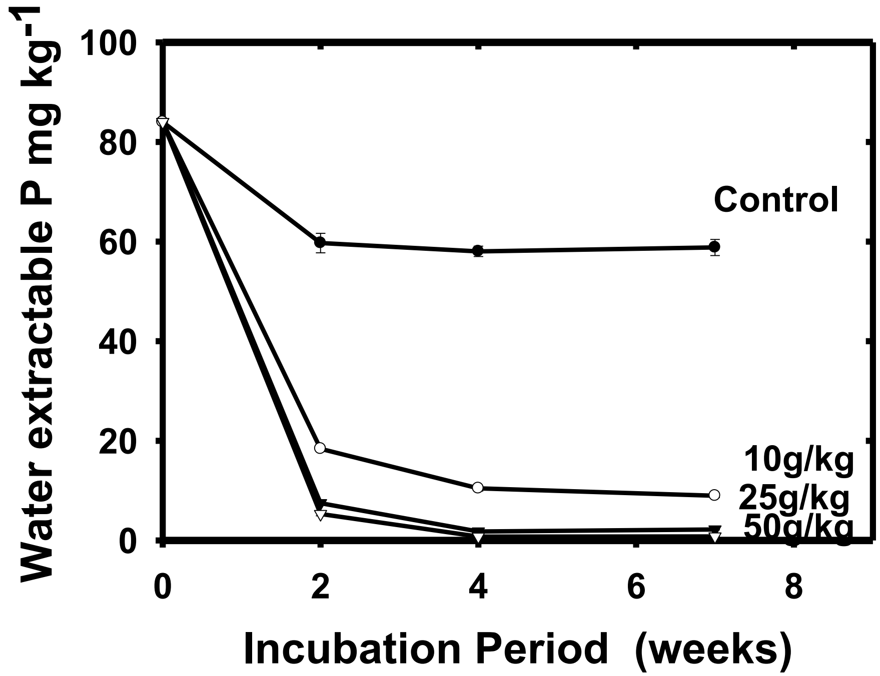
Soil Test-P based Nutrient Management Planning/Regulation

P Level in Soil	Allowed Application
Low	Apply at N-Fert Rate
Medium	Apply at P-Fert Rate
High	Replace P Removed
Very High	No P Allowed

Soil Test Extractable P

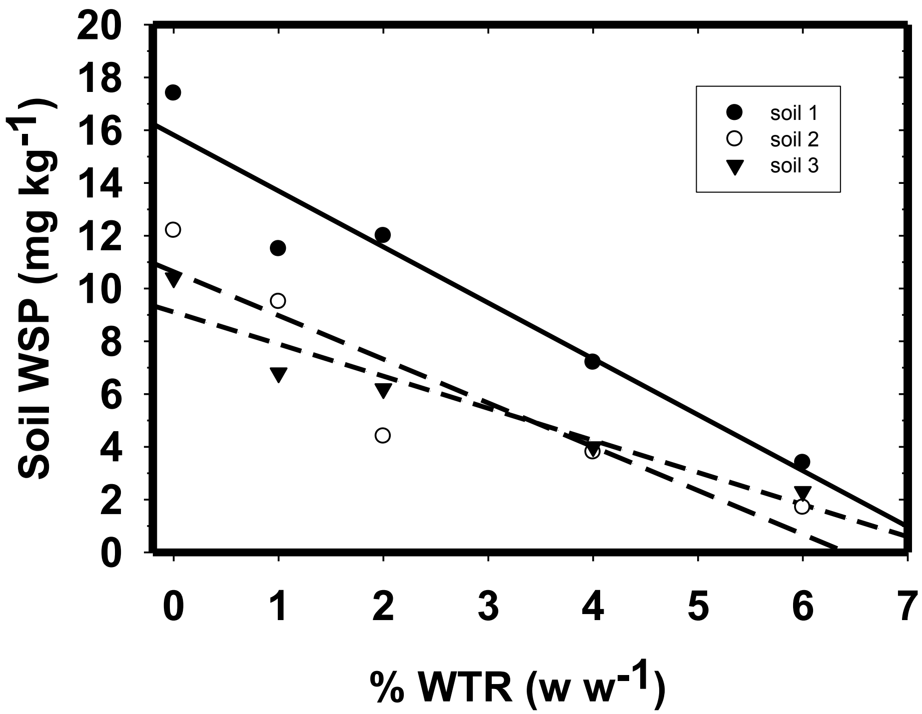


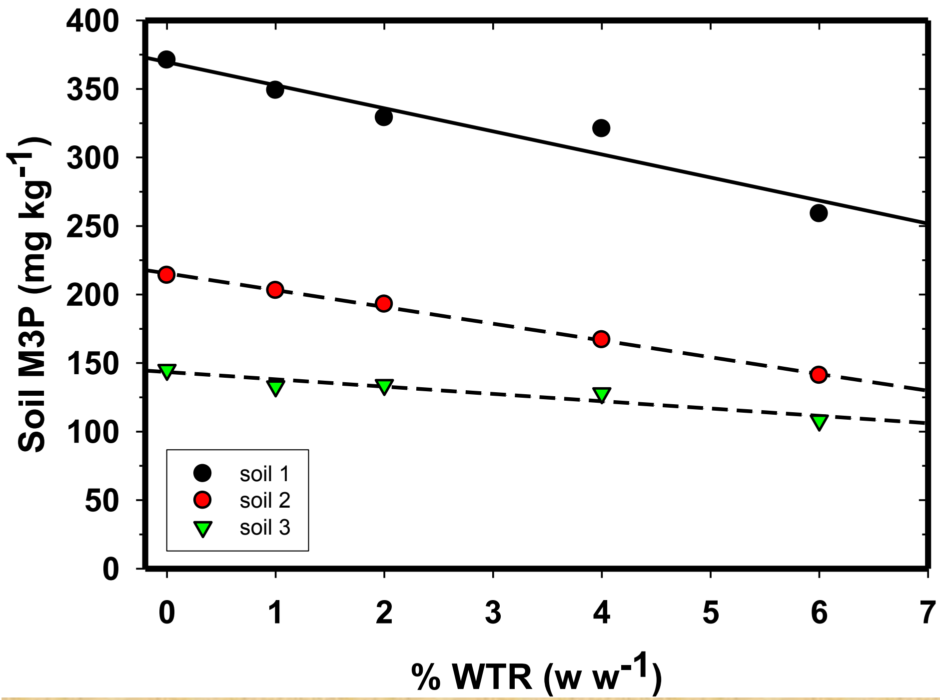
Water Extractable P



BUT, Soil Test Phosphate of Poultry Litter was less reduced by addition of Drinking Water Treatment Residual (WTR) than was Water Extractable Phosphate (Codling et al., 2000).

Regulation of Biosolids Phosphate needs to be based on Water Extractable Phosphate (WEP).





Strong reduction in Water Extractable Phosphate (WEP) of heavily manured soils by addition of varied rates of water treatment residue (WTR) and incubation for 84 days (Novak et al., 2005).

A Question Remained: "Is the Non-WEP in high Fe or Al biosolids available to plants?"

Or have we fixed the P in unavailable forms and ruined the P value of the Biosolids?

So we did an experiment.

Methods and Materials

- Soils were collected from fields that received biosolids 16-24 years earlier.
- Soil pH, Water-Extractable and Mehlich-3 Extractable phosphorus were determined.
- Wheat was planted in 15 cm pots and fertilized with N, Mg and K, but no additional P.
- Wheat was harvested at boot stage, and yield determined.
- Digested plant tissue was analyzed using ICP.

Effect of Long Term Biosolids Applications on Total, Water Extractable P, and Mehlich-3 Plant Available P.

Treatment	Rate	Total-P	WEP	M3P	pH
	t/ha	mg/kg	mg/kg	mg/kg	
MD-Control	0	646	3.5	164	6.1
MD-Heat Treated	224	4070	6.4	485	5.7
MD-Limed Compost	672	3260	5.7	568	6.3
MD-Nu-Earth	50	873	2.5	222	6.2
MD-Nu-Earth	100	1095	4.0	294	6.1
MN-Control	0	725	1.4	60	5.6
MN-Low	60	925	2.5	97	5.4
MN-Medium	120	1143	6.7	226	5.2
MN-High	180	1339	4.0	228	5.5
IL-Control	0	783	1.4	74	4.9
IL-High	643	5569	4.1	625	6.0

Wheat grown on long term biosolids amended soils from Beltsville, MD;
Plants on soil amended with limed composted biosolids are Mn deficient.

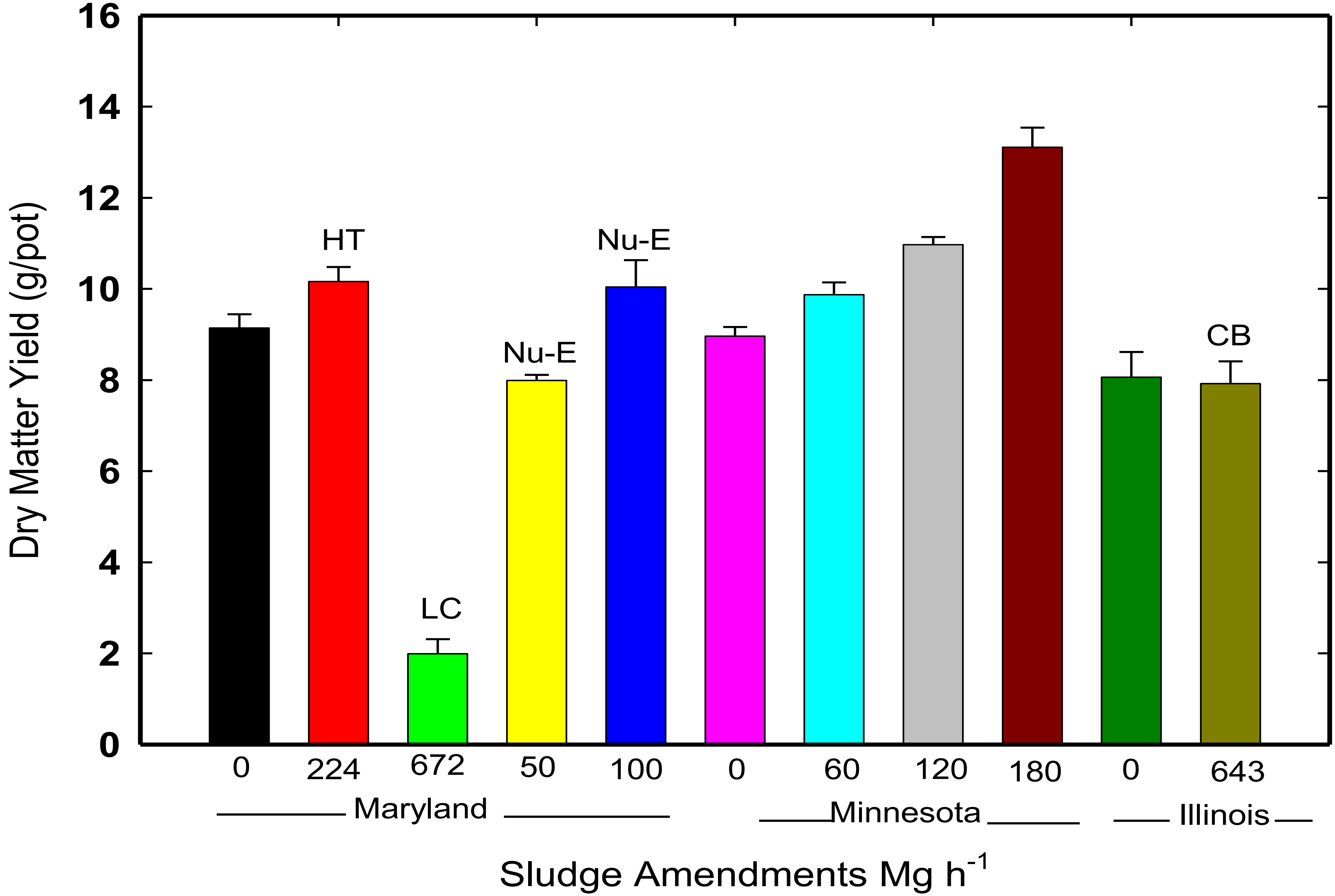


Figure 1: Dry matter yield of wheat grown on biosolids amended soils (Standard Error)

Composition of Boot Stage Wheat Shoots.

Treatment	Rate	P	Mn	Zn
	t/ha	g/kg	mg/kg	mg/kg
MD-Control	0	1.9 d	15. c	22 f
MD-Heat Treated	224	3.6 c	9.3 c	46 d
MD-Limed Compost	672	6.5 a	2.7 d	45 d
MD-Nu-Earth	50	2.2 d	16. c	33 e
MD-Nu-Earth	100	2.3 d	20. c	45 d
MN-Control	0	1.4 e	51. b	48 d
MN-Low	60	1.7 e	52. b	89 b
MN-Medium	120	2.5 d	47. b	105 a
MN-High	180	3.3 c	23. c	105 a
IL-Control	0	1.7 e	84. a	58 c
IL-High	643	5.2 b	11. c	108 a

P was adsorbed, yet plant available; High Fe induced Mn deficiency

Conclusions-Phosphate:

- Land application of biosolids may increase the potential for eutrophication of surface water, but is much less likely to do so than manure.
- Composting can increase water soluble P of manures by hydrolyzing phytate-P.
- Wheat yield increased with biosolids application with the exception of the limed composted biosolids on the Maryland soil which caused Mn deficiency; high Fe added during treatment.
- Phosphorus concentrations in the wheat shoots tissue were "sufficient" for wheat even though P fertilizers had not been applied for many years.
- Adding Fe/Al during processing helped keep P in adsorbed forms; need to balance Fe and Mn in amendments added during composting.

Risk Characterization, Assessment and Management of Organic Pollutants in Beneficially Used Residual Products.

PATHWAY 3 (Soil Ingestion by Children): PCBs Daily Intake Calculation.

$$RIA = \frac{RL \cdot BW \cdot 10^3}{q_1^* \cdot RE} = \frac{10^{-4} \cdot 16\ kg \cdot 10^3}{7.7 \cdot 1} = \frac{1.60}{7.7}$$

$= 0.208$ µg PCBs/day

where RIA = Adjusted Reference Intake (µg/day).

q_1^* = human cancer potency slope ([mg/kg BW/day]$^{-1}$).

RL = risk level = 0.0001 for EPA Proposed 503 Rule.

BW = body weight of child = 16 kg.

RE = relative effectiveness, or bioavailability.

PATHWAY 3 (Soil Ingestion by Children): PCBs Limit for D&M Products:

$$RLC = \frac{RIA}{I_S \cdot DA} = \frac{0.208}{[(0.5 \cdot 0.0286) = 0.0143] \text{ or } [(0.2 \cdot 0.0714) = 0.0143]}$$

= 14.5 µg PCB/g dry biosolids.

RLC = Reference Biosolids PCB Conc. (µg/g DW).

DA = Duration Adjustment for < 70 year:
5/70=0.0714 – for 0.2 g/day = 98 %ile.
2/70=0.0286 – for 0.5 g/day

I_S = Soil/Biosolids Ingestion Rate (g DW per day).

Spray application of fluid biosolids on tall fescue pastures at Beltsville, MD 1976, in cooperation with WSSC, UMD and USDA; Decker et al. (1980).

Rotation paddocks and Angus cattle grazing control or surface applied fluid biosolids treatments; Beltsville, MD 1977; Decker et al. (1980)

Surface organic layer (thatch) on orchardgrass pasture which received fluid Biosolids applications for 28 years without tillage; Hagerstown, MD, 1975.


ag-chem

PATHWAY 5: SURFACE-APPLIED BIOSOLIDS ON LIVESTOCK PASTURE: DATA ON DIETARY FAT CONSUMPTION:

Consumption of fat from grazing livestock (g dry weight/day) for different age groups and estimated lifetime average food intakes for 70 kg US adult citizens. The child age group (not reported by Pennington, 1983) was assumed to consume the average of that consumed by toddlers and teens.

Food Group	Age Grouping						
	Baby	Toddler	Child	Teens	Adult	Older	Lifetime
Age:	0-1	1-6	6-14	14-20	20-45	45-70	0-70
	------------------------- g dry weight/day -------------------------						
Beef Fat	2.45	6.48	11.34	16.22	20.40	14.07	15.50
BeefLiverFat	0.05	0.07	0.08	0.10	0.29	0.33	0.25
Lamb Fat	0.14	0.08	0.07	0.06	0.31	0.22	0.21
Dairy Fat	38.99	16.48	20.46	24.43	18.97	14.51	18.13

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN):
1. Calculate allowed lifetime daily intake:

$$RIA = \frac{RL \cdot BW \cdot 10^3}{q_1^* \cdot RE} = \frac{10^{-4} \cdot 70\ kg \cdot 10^3}{7.7 \cdot 1}$$

= 0.909 µg PCB/day

RIA	=	adjusted reference intake (µg/day)
q_1^*	=	human cancer potency ($[mg/kg/day]^{-1}$)
RL	=	risk level = 0.0001 for 503 Rule
BW	=	body weight = 70 kg
RL	=	Relative Effectiveness or bioavailability.

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN): Calculate allowed feed PCBs concentration:

$$RFC = \frac{RIA}{\Sigma(UA_i \cdot DA_i \cdot FA_i)}$$

RFC = reference feed concentration (µg PBCs/g DW)

RIA = adjusted reference intake (µg/day)

UA_i = uptake response slope of pollutant in the animal tissue food group i for organics, on a fat basis,

= 2 (µg PCB/g fat)•(µg PCB/g feed DW)$^{-1}$ for biosolids-borne PCBs added to test diets.

DA_i = Daily dietary consumption of the animal tissue food group i, g dry wt.

FA_i = Fraction of the food group i assumed to be derived from livestock grazing biosolids amended soil - lifetime.

Assumes a high fraction of the dietary fats (44% of meat fat and 40% of dairy fat) came from cattle raised on the biosolids-treated pastures for 70 years.

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN): Calculate Human exposure from animal fat:

Pathway 5 calculation of $\Sigma(UA_i \cdot DA_i \cdot FA_i)$ needed to estimate human exposure to PCB in fat of meat from grazing livestock. UA value from Baxter et al. (1983), based on feeding cattle 10% biosolids for 270 days at which time equilibrium of PCB in fat that in the diet would have been reach according to Fries (1982).

	Biosolids PCB in Diet of Grazing Livestock			
	DA_i	UA_i	FA_i	$\Sigma(UA_i \cdot DA_i \cdot FA_i)$
Food Group	g/day			Estimated Lifetime
Beef fat	15.50	2.0	0.44	13.64
Beef liver fat	0.25	2.0	0.44	0.22
Lamb fat	0.21	2.0	0.44	0.18
Dairy fat	18.13	2.0	0.40	14.50
3Fat-grazing	34.09			28.54

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN): Calculate Allowed Feed PCBs Concentrations:

$$RFC = \frac{RIA}{\Sigma(UA_i \bullet DA_i \bullet FA_i)} = \frac{0.909}{28.54}$$

= 0.0319 µg PCBs/g DW

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN):

Whole grazing season mean adherence of spray-applied fluid biosolids to tall fescue (Decker et al., 1980) or 'Pensacola' bahaigrass (Bertrand et al., 1981), and biosolids content of feces of cattle which rotationally grazing these pastures.

Study Treatment	Solids content	Application Rate	Biosolids in/on Forage	Biosolids in Feces
	%	cm	% DW	% DW
Decker et al. (1980)†				
1976 21-day-biosolids	4.4	20 X 0.51	5.39	7.1
1976 1-day-biosolids	4.8	20 X 0.51	22.3	18.6
1977 21-day-biosolids	2.9	20 X 0.51	2.18	7.7
1977 Compost			(0.74)‡ 6.5	
1978 21-day-biosolids	3.7	24 X 0.51	2.91	6.1
1978 Compost			(0.50)‡	2.0

PATHWAY 5 (Surface Application--Grazing) BIOSOLIDS→LIVESTOCK→HUMAN): Calculation of Maximum Allowed Biosolids PCB Concentration – Surface Application

RSC = RFC/FS

RSC = Reference Biosolids PCB Concentration
RFC = Reference Feed PCB Concentration
FS = Biosolids fraction of livestock diet.

For 100% of pastures treated each year:

RSC = 0.0319/0.025
= 1.28 µg PCB/g dry biosolids.

For 33% of pastures treated each year:

RSC = 0.0319/0.015
= **2.13 µg PCB/g dry biosolids.**

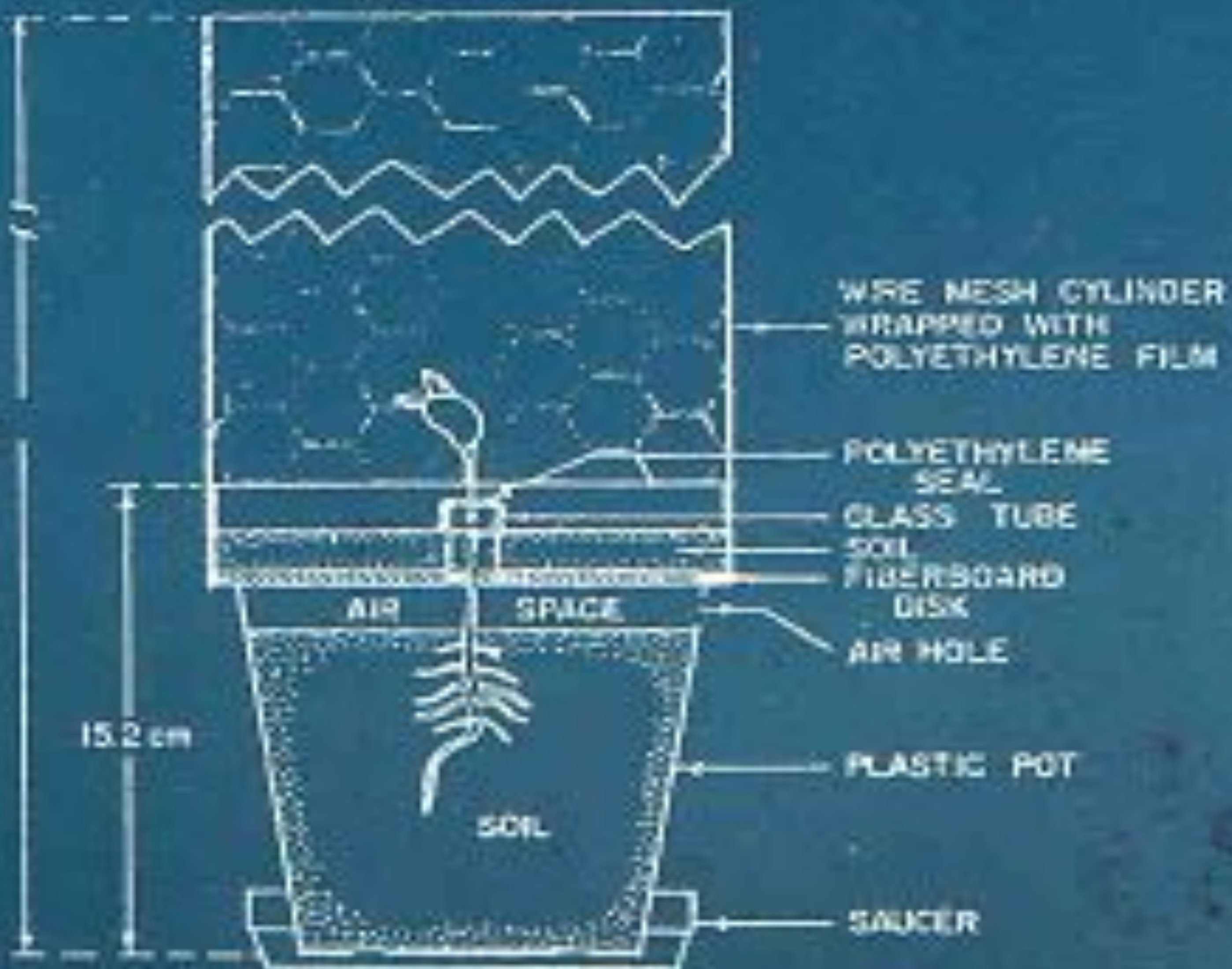


Fig. 1. Longitudinal section of pot designed to provide a solid, liquid, and vapor barrier between surface and subsurface soil treatments.

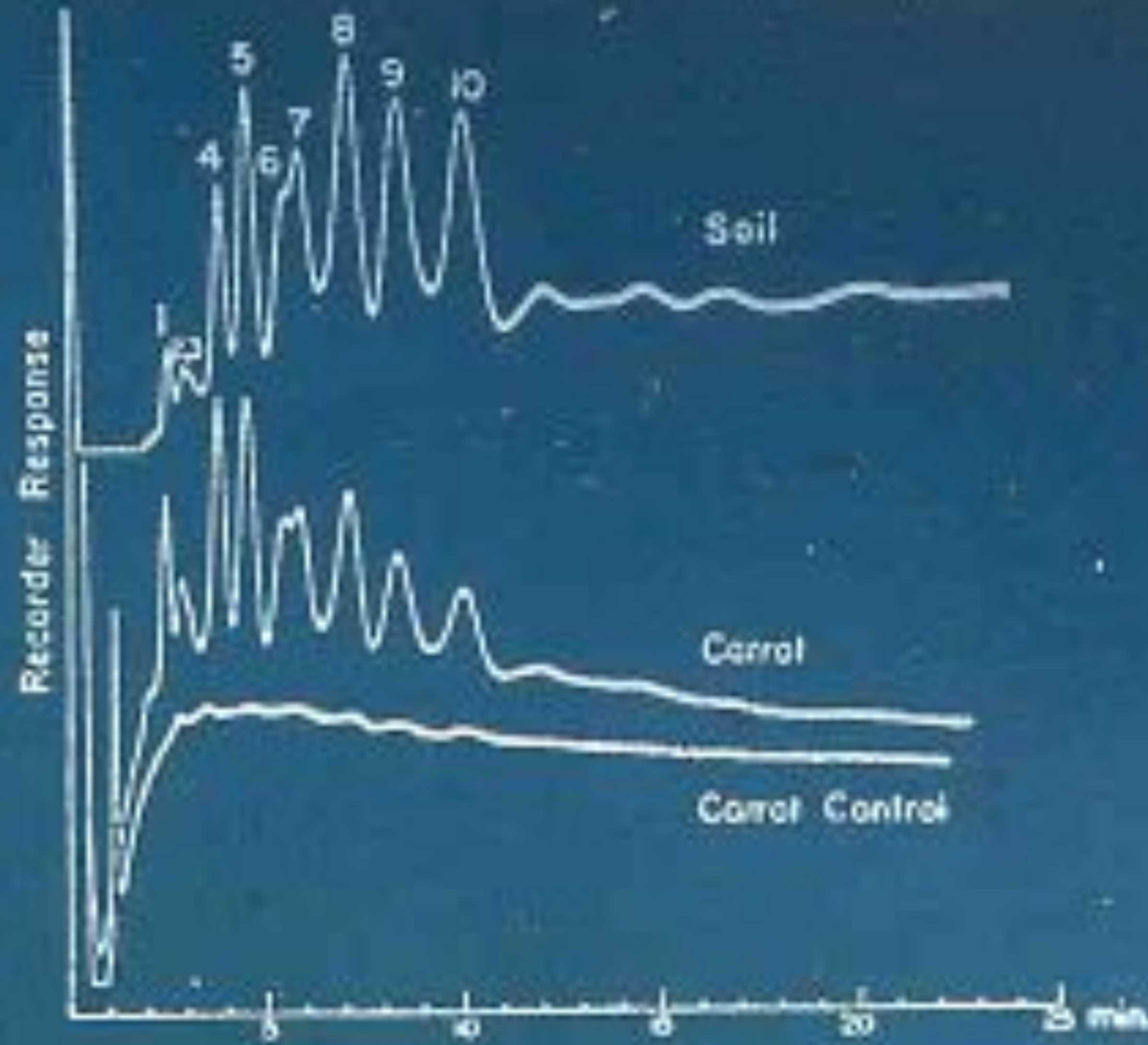


Fig. 1--Electron-capture gas chromatogram of extractives from 40 µg of field-treated soil, 400 µg of carrot root grown in field-treated soil, and 400 µg of carrot root grown in untreated field soil.

Guidelines Were Developed To Protect Against Excessive Biosolids Ingestion by Grazing Livestock:

- Waiting period after application before livestock entry: 30+ days
- Requirement to cut or graze forages to low height before biosolids application.
- Requirement to limit certain elements and any toxic organics more severely if surface applied: (also important for Fe, F, Pb, Hg).
- Recommendation to inject or incorporate biosolids to minimize exposure.

US-EPA 503 Rule Provides High Protection Against Adverse Effects of Biosolids-Applied PCBs.

- **Modern biosolids usually contain <0.1 mg PCBs/kg DW.**
- **But the most limiting pathway was 2.13 mg/kg (surface applied on pastures) or 9.09 mg/kg for bagged biosolids products ingested by children.**
- **Biosolids used at 10 t/ha/yr apply less than 1% of the allowed PCB applications (which was defined to provide protection at the 1 in 10^4 level).**
- **Thus the Highest Risk pathway gives 10^6 protection against risk to Highly Exposed Individuals.**

Corrected Limits for Biosolids-Applied PCBs if PCBs had been included in the Final 503 Rule:

Pathway	Limit	Units
2 Garden Foods	17.	mg/kg soil maximum
	2.3	kg/ha•yr
3 Soil Ingestion	14.	mg/kg Biosolids
4 Livestock Feed	18.	mg/kg soil maximum
	2.4	kg/ha•yr
5 Grazing Livestock	2.1	mg/kg Biosolids (surface)
Home-Grown	0.29	kg/ha•yr (annual incorp)
10 Predator Wildlife	4.0	mg/kg soil maximum
	0.54	kg/ha•yr

PCB Risk Models Apply to PPCPs

- Lipophilic compounds can be accumulated in biosolids at measureable concentration.
- Hydrophilic compounds mostly in effluent.
- Detergents retained in anaerobic digesters are rapidly biodegraded in soils or aerobic systems.
- Applying 503 risk assessment methods shows that direct ingestion of biosolids on forages or on soil surface is most sensitive pathway for risk.
- Plant uptake is minor to irrelevant.
- Lipophilic compounds bound to biosolids humics.
- Aged PPCPs bound to OM lowers possible uptake.
- No evidence of risk at levels in crops/worst case.

Colgate Total Toothpaste, 0.30 % Triclosan = 3000 ppm

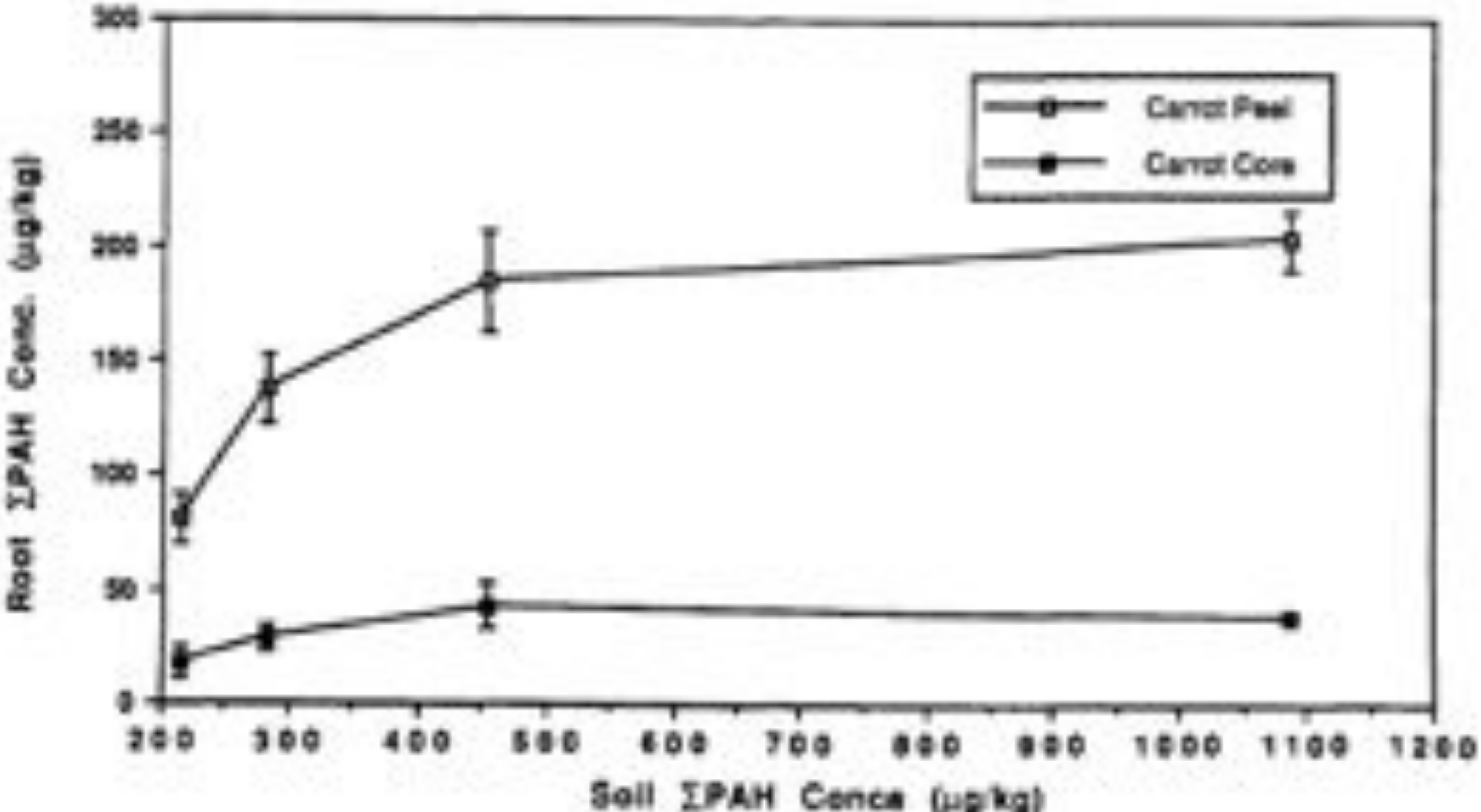
Triclosan in US Biosolids

Property	Concentration
	mg/kg DW
Minimum	0.33
Maximum	133.
Mean	16.1
Median	3.86
95th Percentile	62.2
If 100 mg/kg (ppm) in biosolids:	
@10 t/ha (P rate)	0.44
Incorporated (15 cm)	
Toothpaste	3,000.
Soap	10,000.

UK Approach

THE SAFE SLUDGE MATRIX

Guidelines for the Application of Sewage Sludge to Agricultural Land



Accumulation of biosolids-applied PAH by carrot: Biosolids organic matter strongly adsorbs PAHs in soil, which limits PAH uptake by carrot peel; protection (Wild and Jones, 1992).

Summary—Biosolids Xenobiotics

- PPCPs causing alarm for some environmentalists
  - But levels in biosolids are low.
  - Either strongly adsorbed by biosolids or in effluent.
  - Uptake to edible crop tissues miniscule.
  - If there are risks, they are at point of use, not biosolids.
- EPA's focus on As gives soil As limits lower than background levels in US soils!
  - Seeking 17-fold lower MCLG for DW.
  - But DW gets practical MCLs.
  - Old soil limit was 0.43 mg/kg; new = 0.025 mg/kg.
  - Normal levels in US soils: 5^{th} to 95^{th} = 2-12 mg/kg.
- Incorporation or Injection prevents worst case.

Summary

- **Risk Assessment of contaminated soil:**
  - Soil-Plant Barrier.
  - Phytoavailability related to soluble metal level.
    - Affected by pH, sorbents (Fe, Mn, OM) and competition.
  - Bioavailability of metals in ingested soil requires test correlated with bioavailability to animals.
    - Important risk for Pb, As, F, and some others.
- **In situ remediation using byproducts to reduce phytoavailability, bioavailability and improve agronomy.**
  - Alkalinity to reduce metal solubility.
  - Organic matter/N to improve fertility.
  - Diverse microbial inocula.
  - Support growth of perennial grasses and legumes.

What Does it Take To Develop Local Tailor-Made Remediation Products?

- Risk assessment and value information from evaluation of field studies of product utilization.
- Courageous agencies and businesspersons who will seek out such combinations of biosolids, byproducts, and valuable commercial uses of the products.
- Organized valid risk assessment information on:
  - Phytoavailability of applied and soil elements in field.
  - Bioavailability of soil and crop elements.
- Improved risk communication, and honest risk assessments. Examples from Cd food-chain risk, soil Pb and As risk, and phytotoxicity risks from biosolids show massive errors of conservative assumptions.

Summary

- **One Shot Remediation of Metal Toxic Soils:**
  - For Zn, Cu, Ni rich acidic soils causing phytotoxicity.
  - Make contaminated soil depth calcareous
  - Provide enough P, K, and other nutrients to support diverse vegetation, and enough organic-N to achieve stable ecosystem which includes legumes.
  - For Pb or As co-contaminated soils have to reduce bioavailability of Pb or As in ingested soil.
    - Phosphate and composts can reduce soil Pb bioavailability.
    - Iron oxides can reduce soil As bioavailability
  - With normal <1:100 Cd:Zn ratio, Zn limits plant growth before Cd accumulated in plants is a risk to foods.
  - If slope of the site is to high for tillage, can combine biodegradable amendments with alkaline organic amendments and surface apply; allow rainfall to leach soluble alkalinity into soil profile.