



## Special Lecture 2

# Heavy metals in soil -plant system

An example of study on pollutants in soils and the health risks



# 土壤重金属生物有效性与食物安全

## ---土壤-作物系统中重金属生态化学探索



- WHO Project (GL.GLO.PHE.418.XD.00.4.999.00)
- 科技部“973”项目1999011808
- 教育部基础研究重点项目（教科2002012）
- 教育部人才基金项目



# 土壤中重金属的输入、积累与活化



# 主要内容

- 土壤中重金属的输入、积累与活化
- 土壤重金属与食品安全
- 土壤中重金属生物有效性若干问题
- 土壤环境重金属积累的动态问题

# 土壤-植物系统中重金属迁移难易性的分组

分组	元素	化学移动性	植物吸收性	植物毒性	(土壤)动物毒性
1	Ag, Cr, Sn, Ti, Y, Zr	很弱	可以忽略	无	不确定
2	As, Hg, Pb	被胶体吸附	弱	通常无	人类毒性, 土壤动物可能有
3	B, Cu, Mn, Ni, Zn	较易移动	中等至高	高含量时	对人类无
4	Cd, Co, Mo, Se	易移动	中等	一般无	人类潜在毒性

# 国际农业土壤环境标准中考虑的潜在有害重金属元素

国际农业土壤环境标准中考虑的潜在有害重金属元素

元素	Version 1995 <sup>1</sup>	IL EPA, 2000 <sup>2</sup>	DWS 2000 <sup>3</sup>	USEPA 503 <sup>4</sup>	EC States <sup>5</sup>	China 1984 <sup>6</sup>	WHO DWG 2000
As	×	×	×	×	× (Neth)	×	× <sup>P</sup>
Ba	×	×	×				×
Be	×	×	×				NAD
Cd	×	×	×	×	×	×	×
Cr	×	×	×	×		×	× <sup>P</sup>
F	×		×		× (UK)		×
Pb	×		×	×	×	×	×
Hg	×		×	×	×	×	×
Ni	×	×	NAD	×	×	×	× <sup>P</sup>
Se	×	×	×	×	× (Fr)		×
Ag	×	×	NAD				
Tl		×	×				
Sb		×					× <sup>P</sup>
Cu			NAD	×	×	×	×
Zn			NAD	×	×	×	
Mn							ATO <sup>P</sup>
B						×	×
Mo			×	×	× (Swiss)		×
Co					× (Swiss)		
U							× <sup>P</sup>

1 Center for Environmental Analysis Research Triangle Institute, Draft Risk assessment for cement Kiln dust used as an agricultural soil amendments., 1998

2 USEPA. Drinking Water Standards and Health Advisories EPA 822-B-00-001,2000

3 USA EPA, Land Application of Sewage Sludge, A guide for land appliers on the requirements of the Federal Standards for the use or disposal of sewage sludge, 40 CFR Part 503

4 Smith S R. Agricultural Recycling of Sewage Sludge and the Environment. Cab International, 1996

5 China Environment Protection Agency. Control standards for pollutants in sludges from agricultural use. GB 4284-84, 1984

6. Be, BCF(soybean): 0.1 ~0.5 in limed soil (pH 6.0~6.5); 0.7 ~1.2 in unlimed soil (pH 4.9~5.5)

7. Mo, toxicity to forage crops when biosolids Mo annual loading  $\geq 1.0$  kg/ha , but not directly to human

8. WHO Water, Sanition and Health,1998. Guideline for Drinking Water Quality. 2<sup>nd</sup> Edition. Geneva, Switzerland.

Those marked with “p” are provisional. ATO: provisional concerned with the taste or odor of the water.

NAD: no adequate data.

# 重金属环境释放不断加剧

上世纪 80 年代全球土壤重金属输入量 ( $10^6$  kg/yr)

来源	As	Cd	Cr	Cu	Hg	Pb	Zn
农业废弃物	5.8	2.2	82	67	0.85	26	316
木材加工废弃物	1.7	1.1	10	28	28	7.4	39
城镇丢弃物	0.4	4.2	20	26	0.13	40	60
污泥	0.25	0.18	6.5	13	0.44	7.1	39
金属加工废弃物	0.11	0.04	1.5	4.3	0.04	7.6	11
煤灰	22	7.2	298	214	2.6	144	298
报废工业品	38	1.2	458	592	0.68	292	465
肥料与泥炭	0.28	0.20	0.32	1.4	0.01	2.9	2.5
大气沉降	13	5.3	22	25	2.5	232	92
总计	82	22	898	971	8.3	759	1322

Ref: Nriagu, J. Environment, 1990, 32(7): 7~33

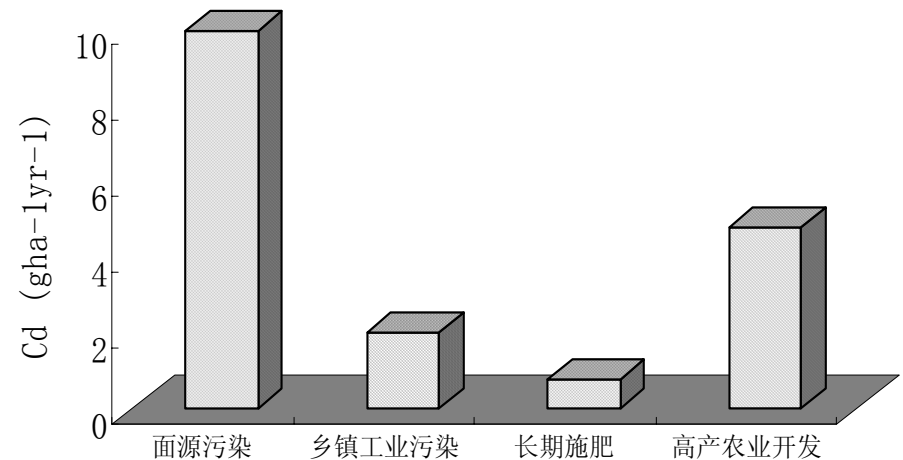
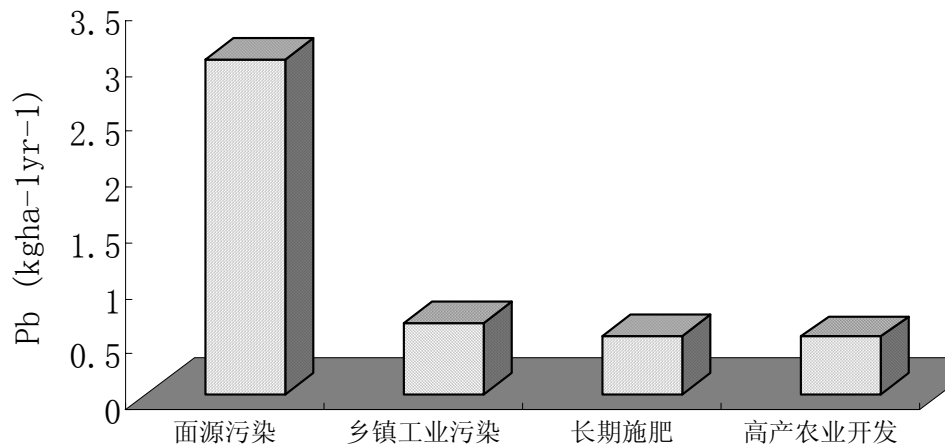
# 太湖地区农田土壤重金属年输入通量估计

## 积累速率

Cu/Zn:  $0.3 \sim 1 \text{ mg} \cdot (\text{kg} \cdot \text{a})^{-1}$ ; Pb :  $0.2 \sim 1 \text{ mg} \cdot (\text{kg} \cdot \text{a})^{-1}$ 和  
Cd:  $0.3 \sim 3 \mu \text{g} \cdot (\text{kg} \cdot \text{a})^{-1}$

## 年污染通量

Cu/Zn:  $0.5 \sim 1 \text{ kg} \cdot (\text{hm}^2 \cdot \text{a})^{-1}$ ; Pb :  $0.5 \sim 3.0 \text{ kg} \cdot (\text{hm}^2 \cdot \text{a})^{-1}$ 和  
Cd  $0.8 \sim 10 \times 10^{-3} \text{ kg} \cdot (\text{hm}^2 \cdot \text{a})^{-1}$ .





世界不同地区背景土壤中  
As, Cd, Pb 和 Zn的 95% 置信限含量范围(mg/kg)

Region	As	Cd	Pb	Zn	Data source
Florida	0.02-7.01	0-0.33	0.69-42.0	0.89-29.6	Chen et al.1999
Baseline USA	1.05-25.9	N/A	4.62-55.4	12.6-183	Shacklette & Boerngen,
California Baseline	0.63-12.3	0.05-1.34	3.96-36.3	26-188	Bradford et al., 1996
California Baseline	0.21-15.49	0-0.47	4.13-24.86	32.04-120.92	Chang, et al., 2003
China	2.5-33.6	0.02-0.33	9.95-56.0	28.5-161	Wei et al. 1990
World	(11.3)	0.40	15 (29.2)	40	Berrow, ML. et al,1984 2007- IREEA

# 世界不同地区表土重金属含量的比较 (mg/kg)

Region	As	Cd	Pb	Zn	Reference
Rio Grande, TX	2.68 (0.47-14.5)	0.49 (0.01-2.07)	3.44(0.64-9.87)	62.3(20.3-469)	Means(range), Sharma, 2000
Piedmont soils, Italy	N/A	0.01-2.0	2-30	1-900	Abollino, 2002
South Savo, Finland	2.90	0.08	7.7	N/A	Medians, Mantylahti, et al., 2002
Pearl River delta, China	N/A	ND – 1.47	10.1-180	11.1-284	Wong et al., 2002
Hunchun, China	N/A	<1-48.3	<1-24.07	21.54-146.7	Moon et al, 2000
Central German	2-14	0.1-2.1	22-152	30-369	Manz et al.,1999
California Croplands	1.52-13.76	0-1.19	13.92-27.28	28.81-107.04	This study, 95% confidence interval

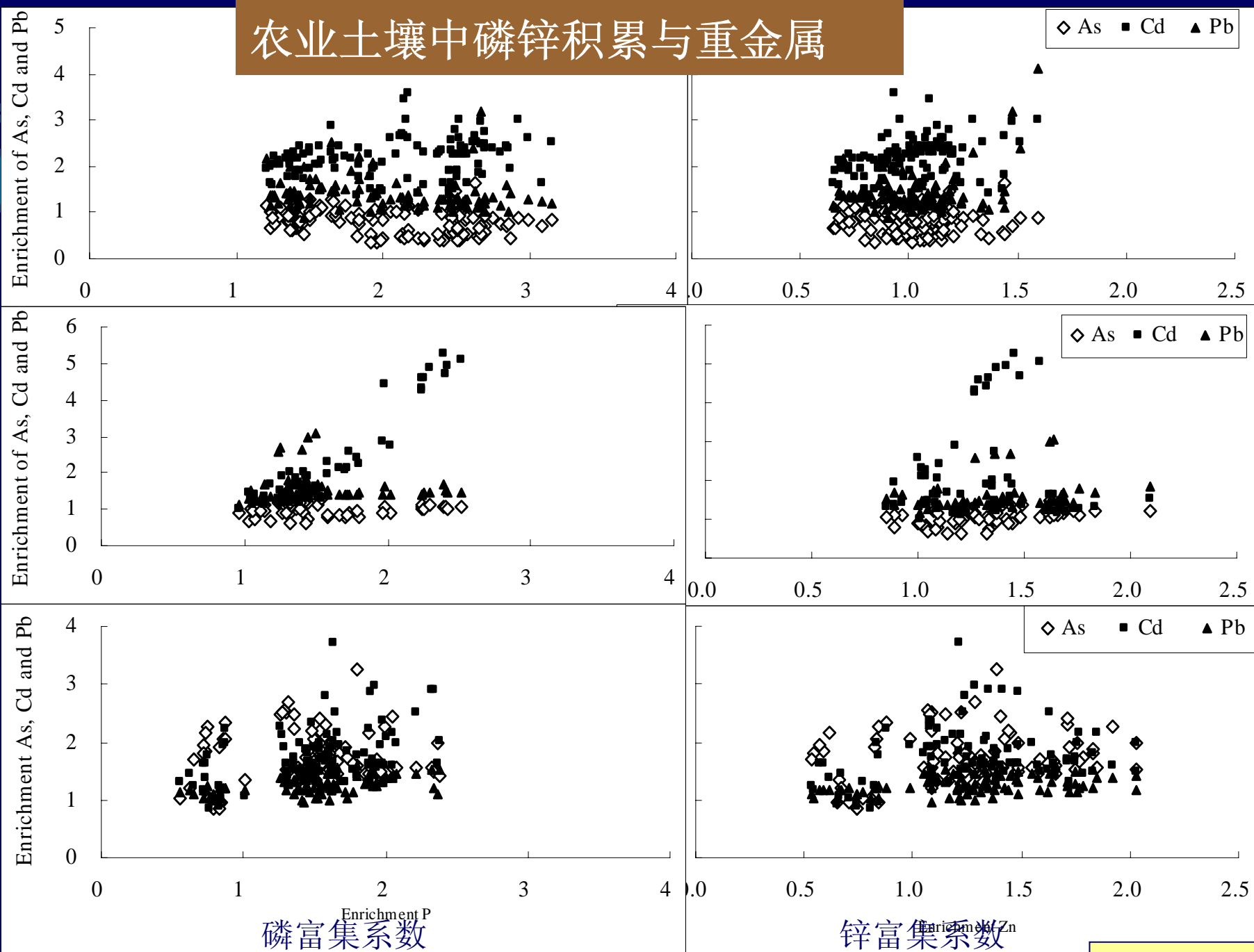
# 美国加州自然和农业土壤（均采于2001）几个重金属元素含量(mgkg<sup>-1</sup>)的统计比较

元素	As		Cd		Pb		P		Zn	
	B	F <sup>nsd</sup>	B	F <sup>A</sup>	B	F <sup>a</sup>	B	F <sup>A</sup>	B	F <sup>A</sup>
平均 值	7.85	7.64	0.23	0.50	14.4 9	15.60	612.2	843.7	76.48	67.94
极小 值	0.55	1.20	0.04	0.15	4.35	5.99	84.7	206.4	29.39	21.37
极大 值	20.3 9	18.4 0	1.15	2.38	33.4 5	62.16	2070. 6	2623. 2	167.8 3	144.6 2
中值	7.83	7.50	0.20	0.40	13.7 7	16.16	579.6	771.6	78.83	66.75
标准 差	3.90	3.12	0.12	0.35	5.29	5.96	353.7	411.8	22.67	19.95
样本 数	302	585	297	647	303	591	297	658	299	653

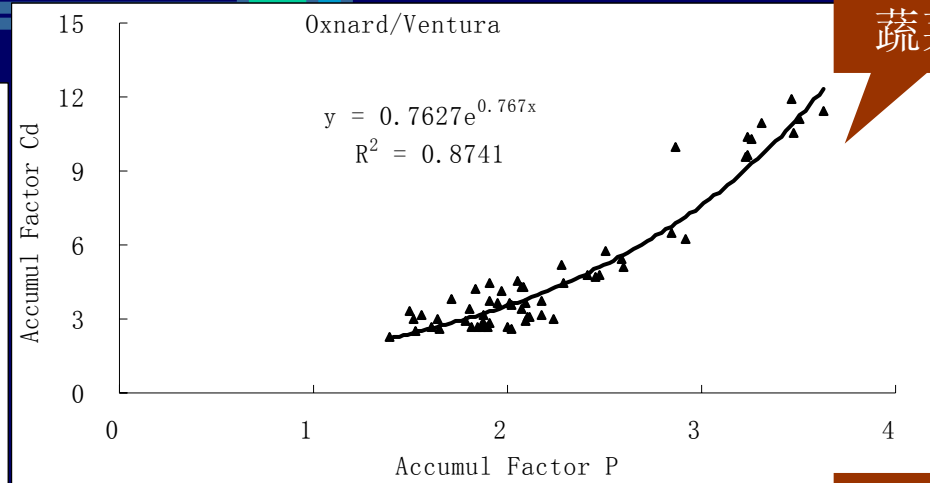
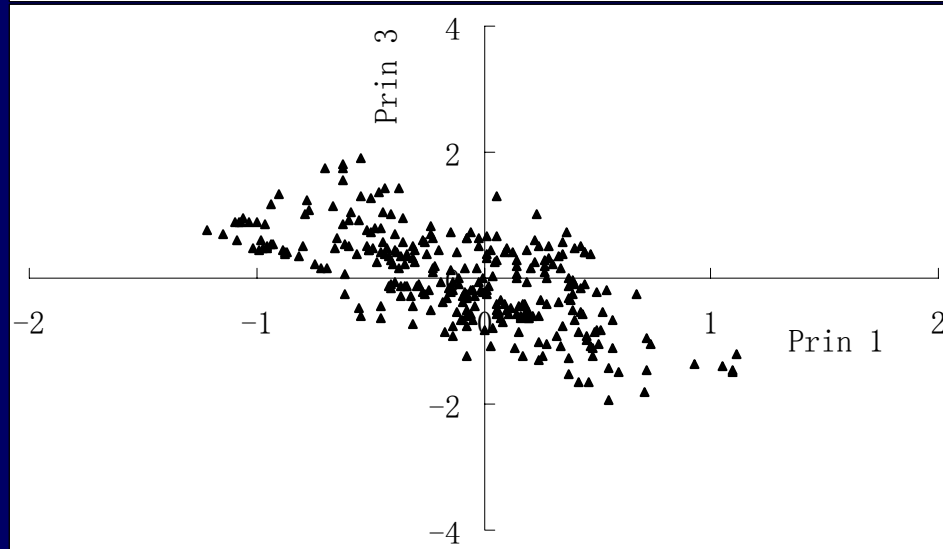
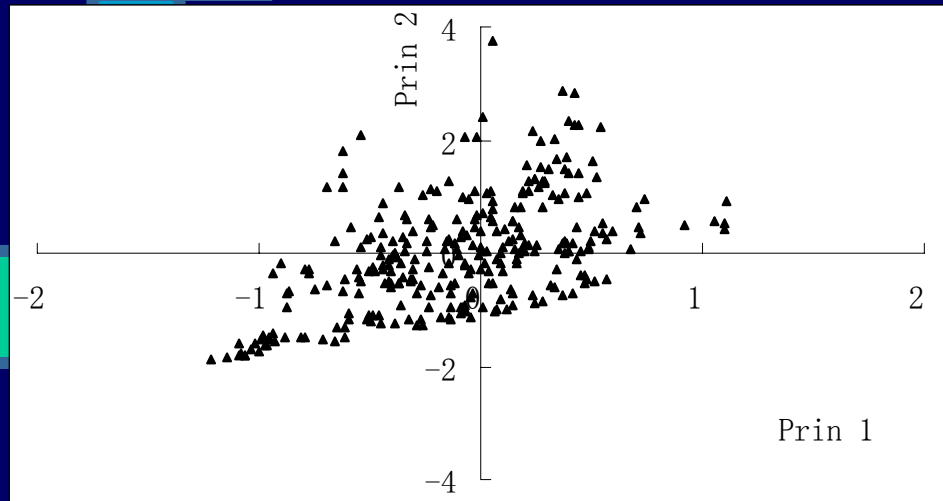
Remarks: nsd, no significant difference; a, significance at  $P < 0.01$ ; A, significance at  $P < 0.001$ .



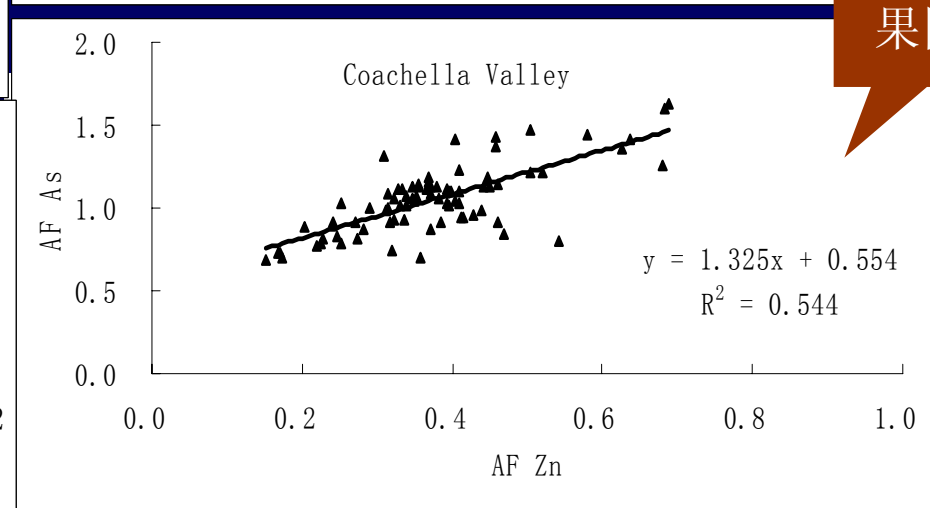
# 农业土壤中磷锌积累与重金属



# 农业经营对加州农业土壤中特定重金属积累有显著影响



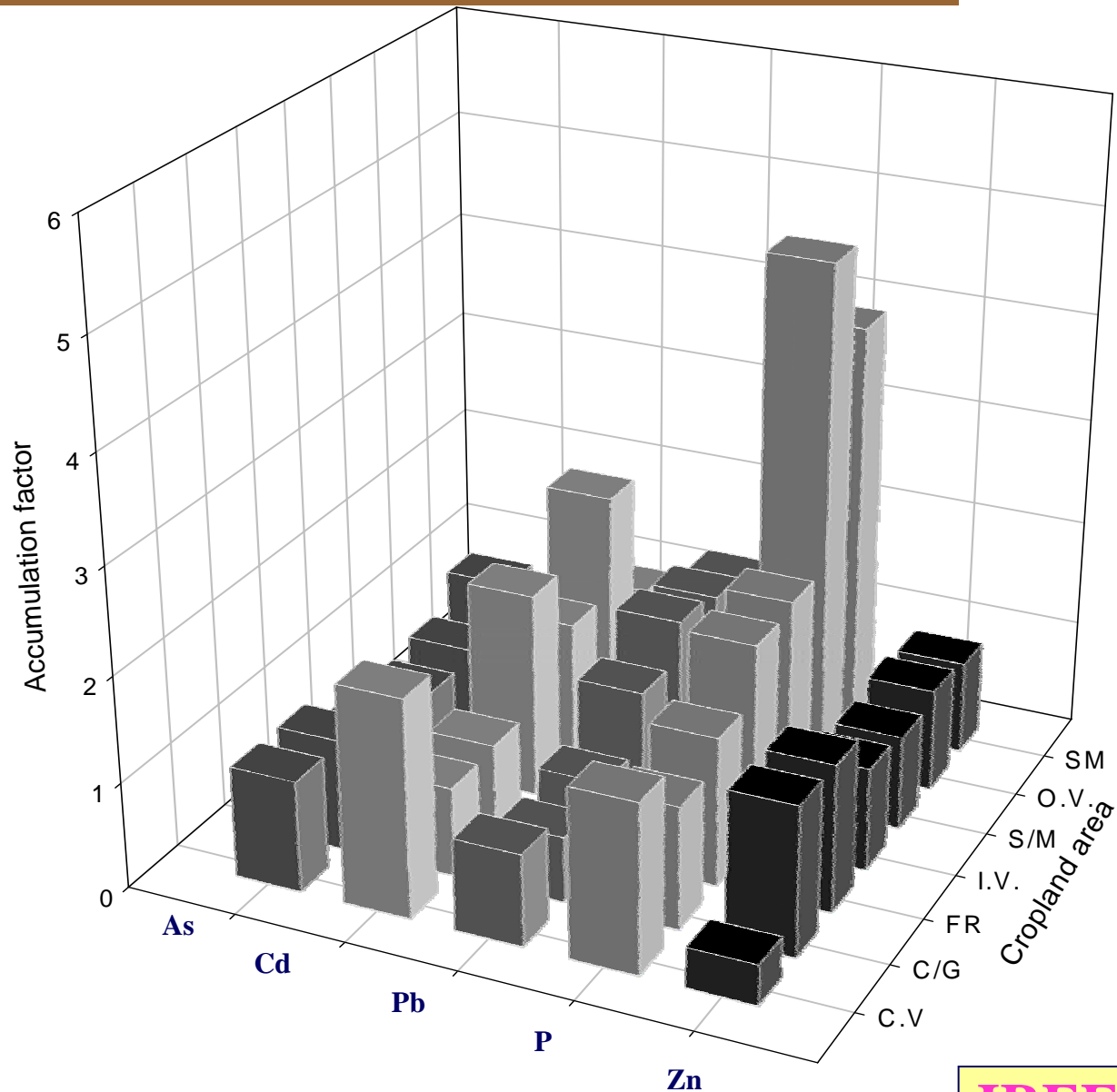
蔬菜区



果园区

Plot of PCA analysis of the benchmark soils collected in 2001. (Prin1, heavy metal accumulation; Prin 2, accumulation of P and Zn as nutrients; Prin 3, association of heavy metals with phosphorus)

# 不同农业经营下土壤中重金属元素的积累特点



# 太湖地区土壤重金属含量状况

	Cu	Zn	Pb	Cd	Hg	As	Cr	Ni
最小值	14.97	25.77	22.50	0.09	0.05	4.28	49.84	22.38
最大值	125.4	79.90	106.5	1.67	2.35	42.94	101.7	42.64
均值	35.07	49.45	36.86	0.34	0.28	7.18	69.82	30.75
标准差	16.14	12.06	12.82	0.19	0.29	3.99	10.47	4.06

太仓市农田土壤重金属含量分布(mg/kg)(董元华等, 2003)



# 太湖地区12个高产水稻丰产方若干重金属元素含量(mg/kg)的分布

样点	Cu	Zn	Pb	Cr	Ni	Co	Se	Mn
平均值	27.8	68.7	23.3	63.5	25.5	10.2	0.25	387
SD	6.6	19.8	5.6	10.6	4.9	1.7	0.04	86.4

曹志洪,潘根兴等, 2002



# 水稻土土壤环境重金属元素积累现象严重

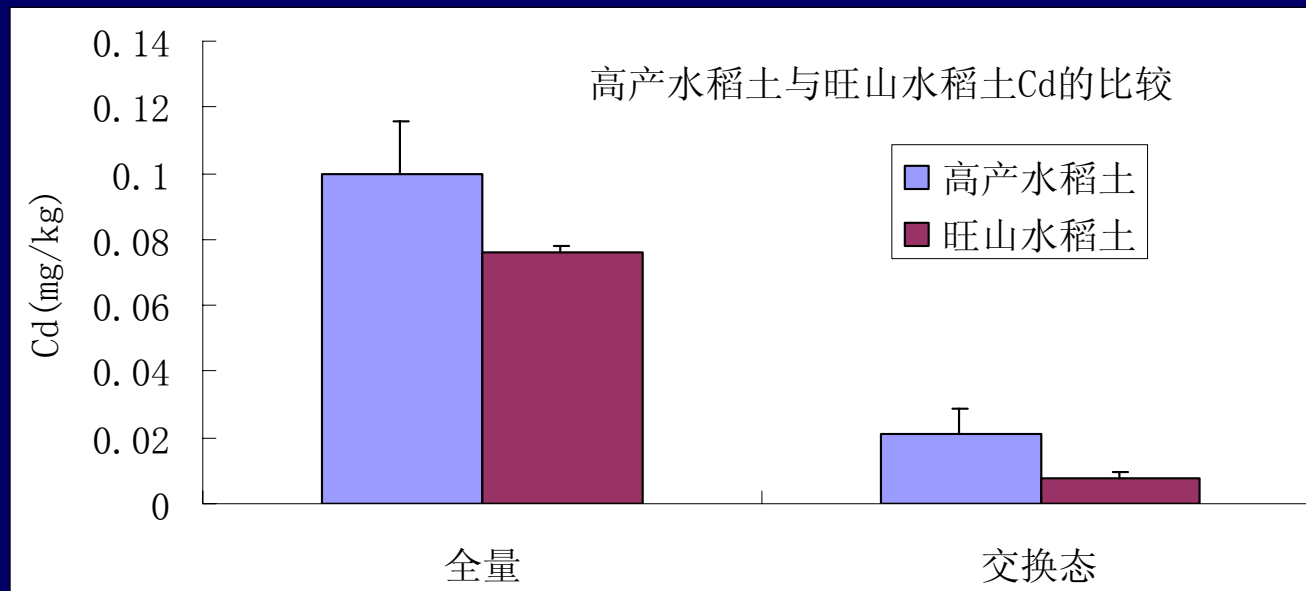
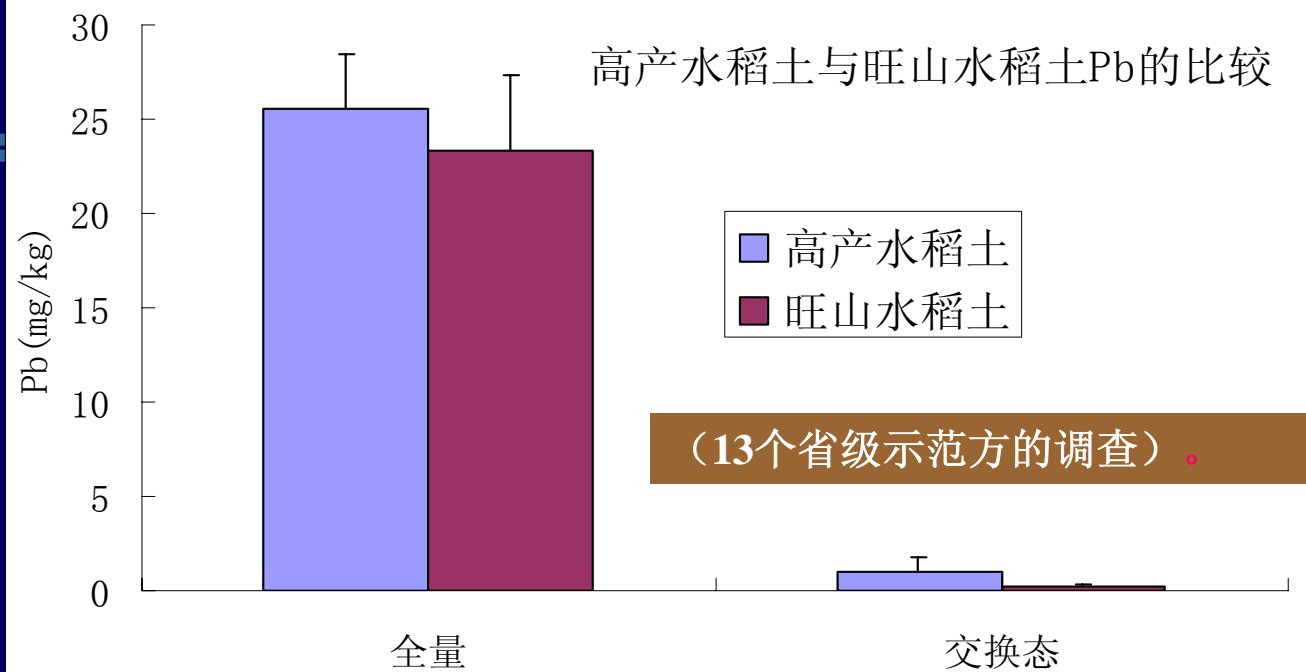
(以苏州市原吴县市为例，随机采集20余个水稻土剖面)

Depth (cm)	Zn		Cu		Pb		Cd	
	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
Range	41.52-82.72	52.13-76.73	22.67-31.38	22.67-29.38	29.08-39.08	30.08-42.64	0.50-1.10	0.58-1.20
Mean	64.12 <sup>a</sup>	66.76 <sup>a</sup>	27.24 <sup>a</sup>	26.47 <sup>a</sup>	33.94 <sup>a</sup>	32.71 <sup>a</sup>	0.58 <sup>a</sup>	0.84 <sup>a</sup>
S.D.	10.99	7.81	2.92	2.42	4.12	4.00	0.22	0.19
n	26	26	26	26	26	26	18	18
B. Value	73.72		22.78		20.39		0.11	

2000年测定； Background value in 1985

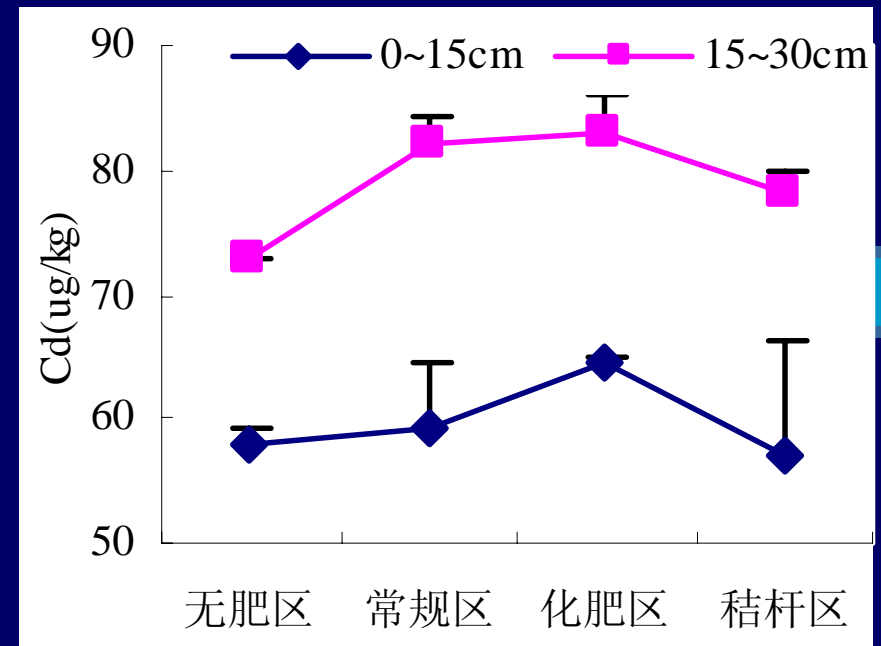
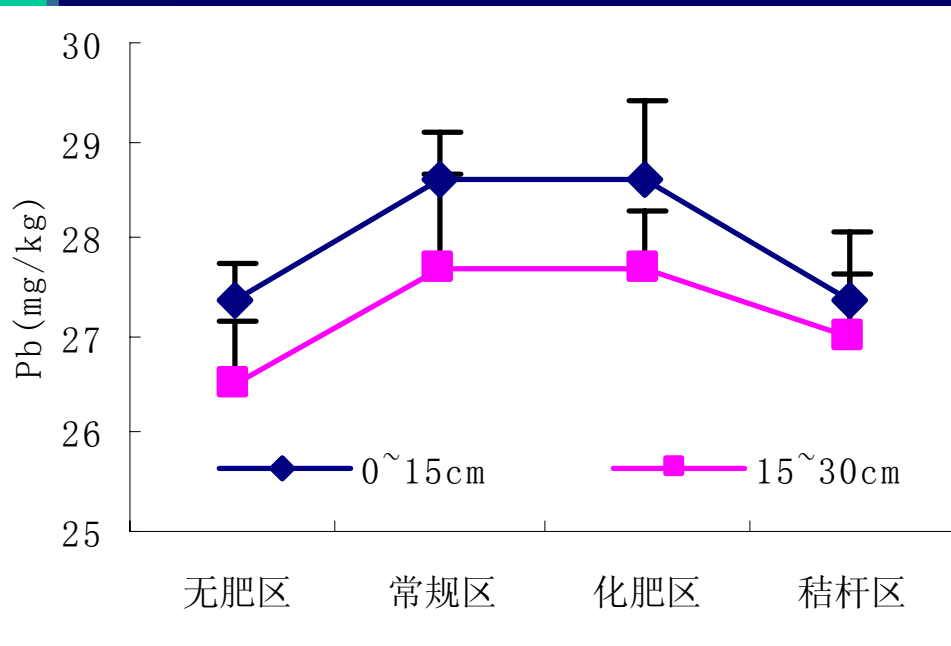


# 集约化经营与土壤重金属积累强度





# 不同施肥措施对水稻土重金属的影响 (吴江市金家坝镇1989年始的长期试验)





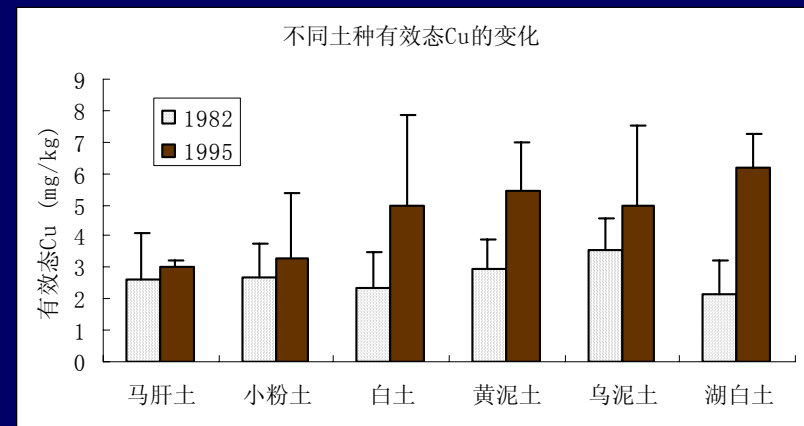
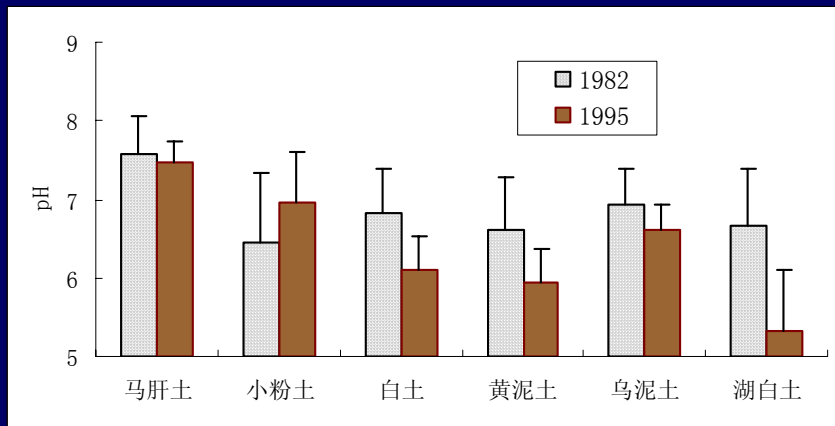
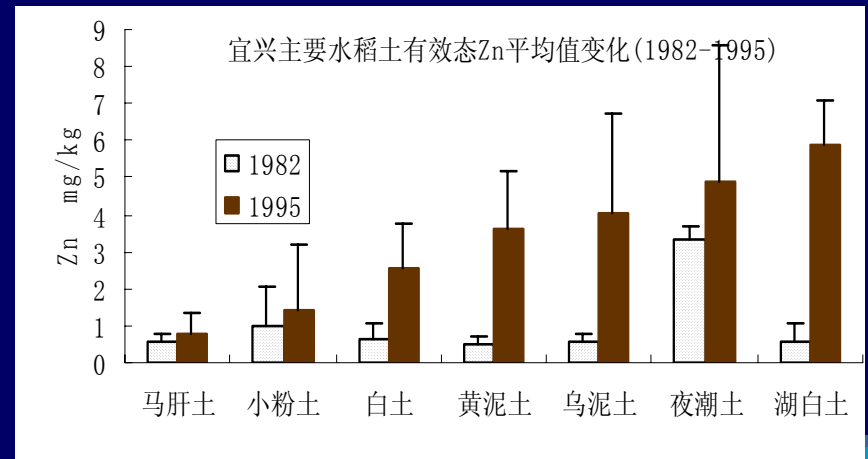
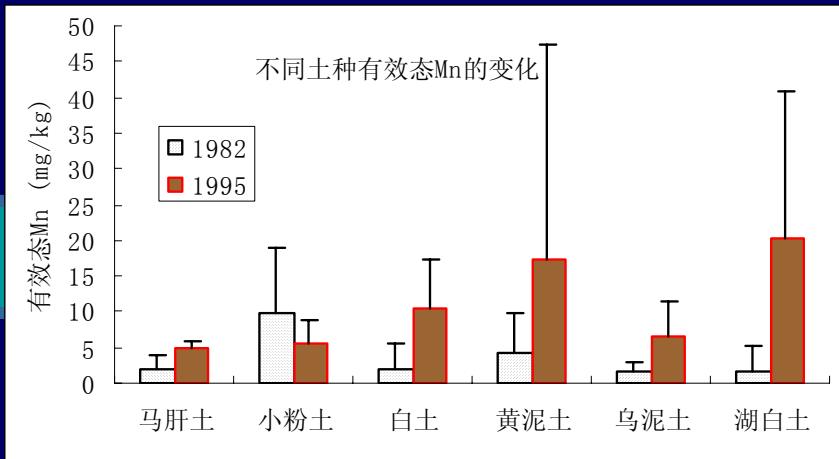
# 活性形态的急剧升高值得密切关注

宜兴市不同时限抽样调查的水稻土某些重金属有效态含量的快速升高现象 (mg/kg,  $\bar{x} \pm SD$ )

元素	1982年样本 (n=108)	1995年样本 (n=76)	上升量 mg/kg	相对幅度 %
Cu	3.17±1.63	5.12±2.20	1.95	61.51
Zn	0.81±1.39	3.94±3.03	3.13	386.4
Mn	3.73±7.10	10.56±11.30	6.83	183.1

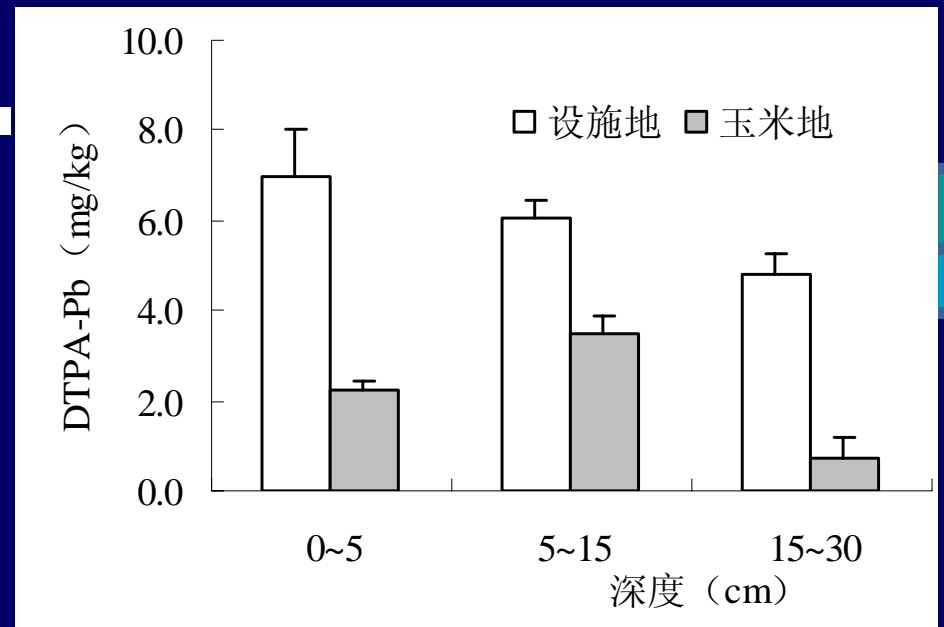
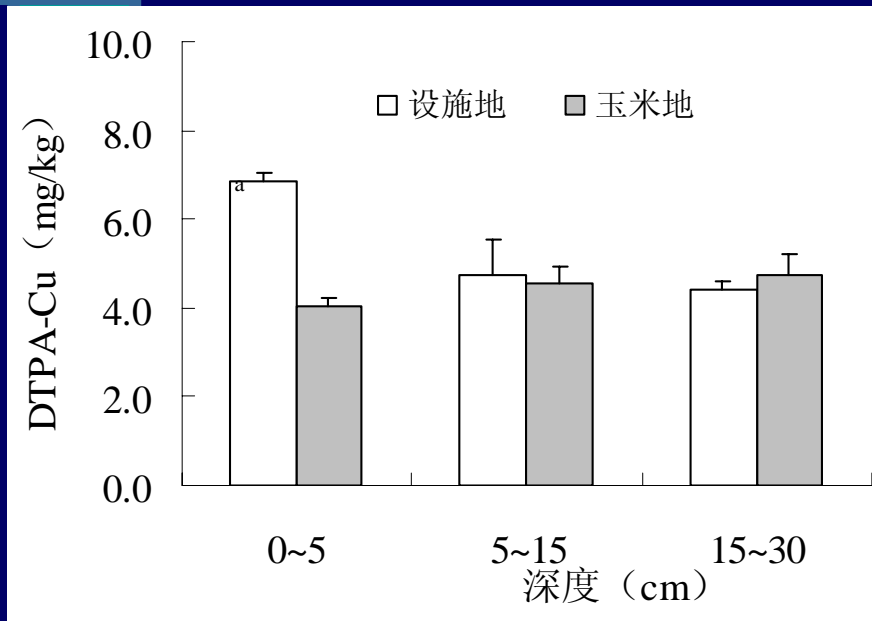


# 活性形态的急剧升高值得密切关注





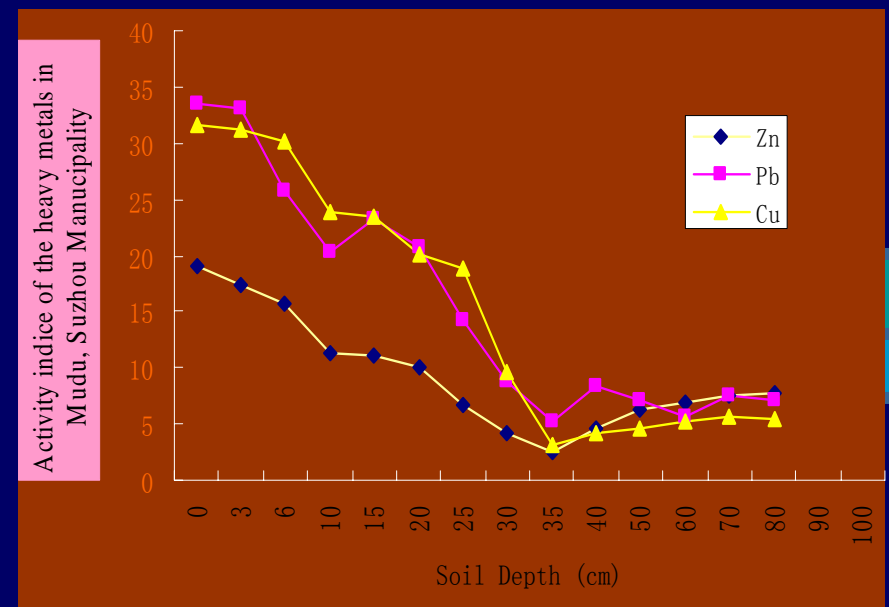
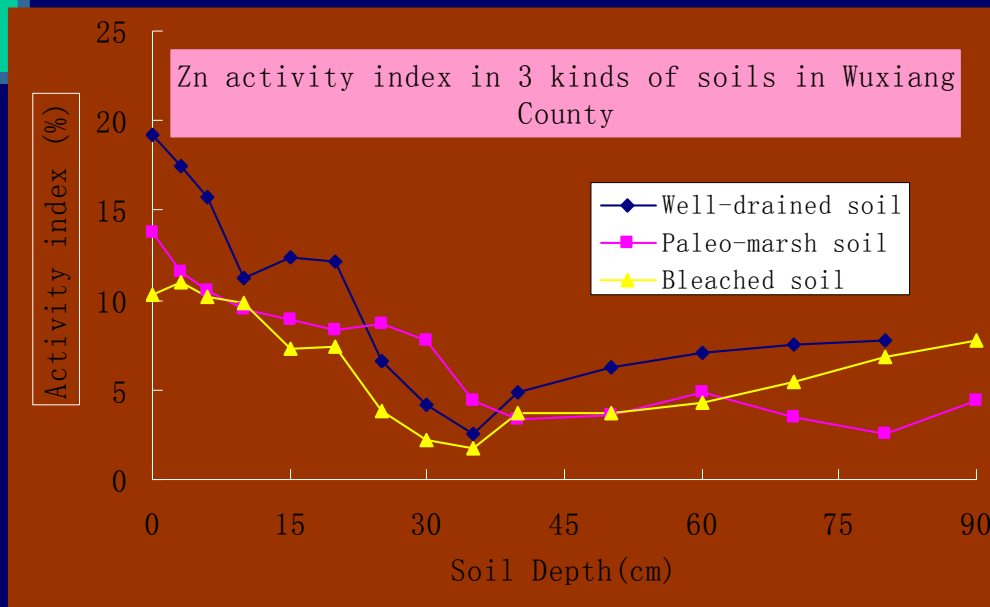
# 土地利用对土壤环境重金属积累与有效性的影响





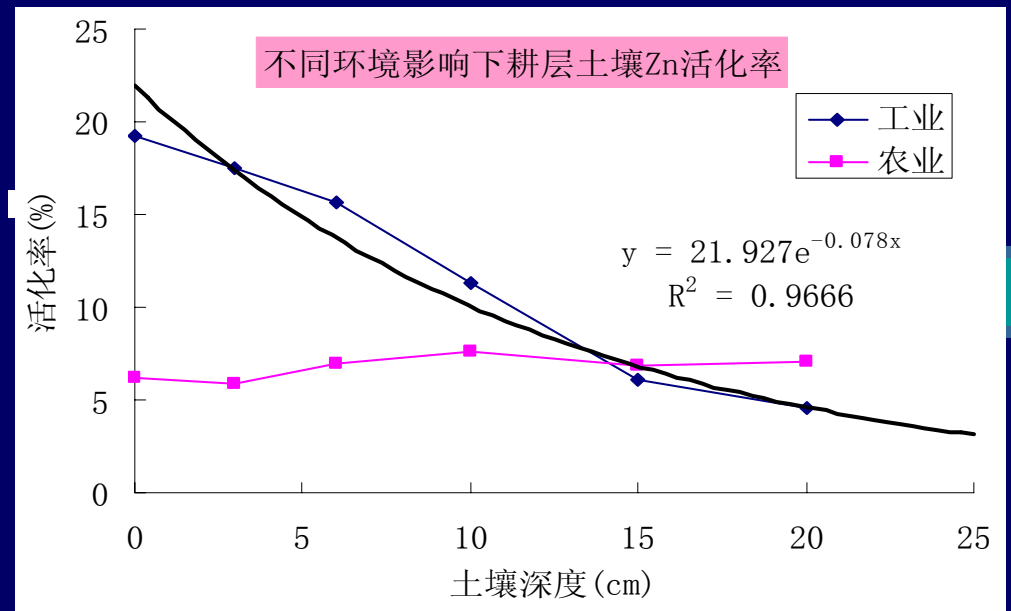
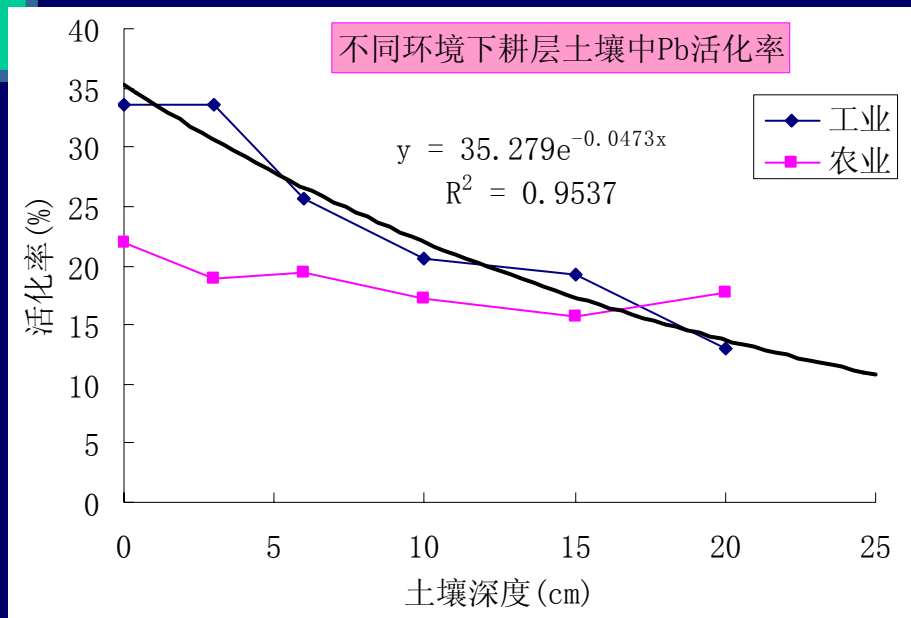
# 表土重金属富集中的活化现象

活化率：活性库的相对贡献---DTPA-extractable or 0.1 M HCl extractable divided by the total



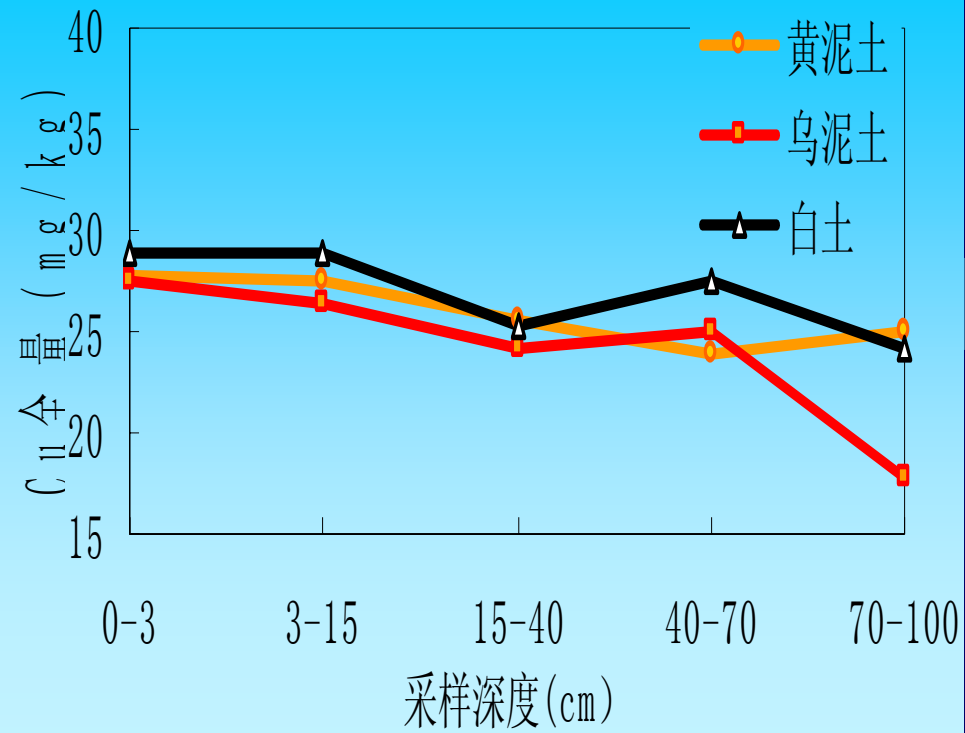
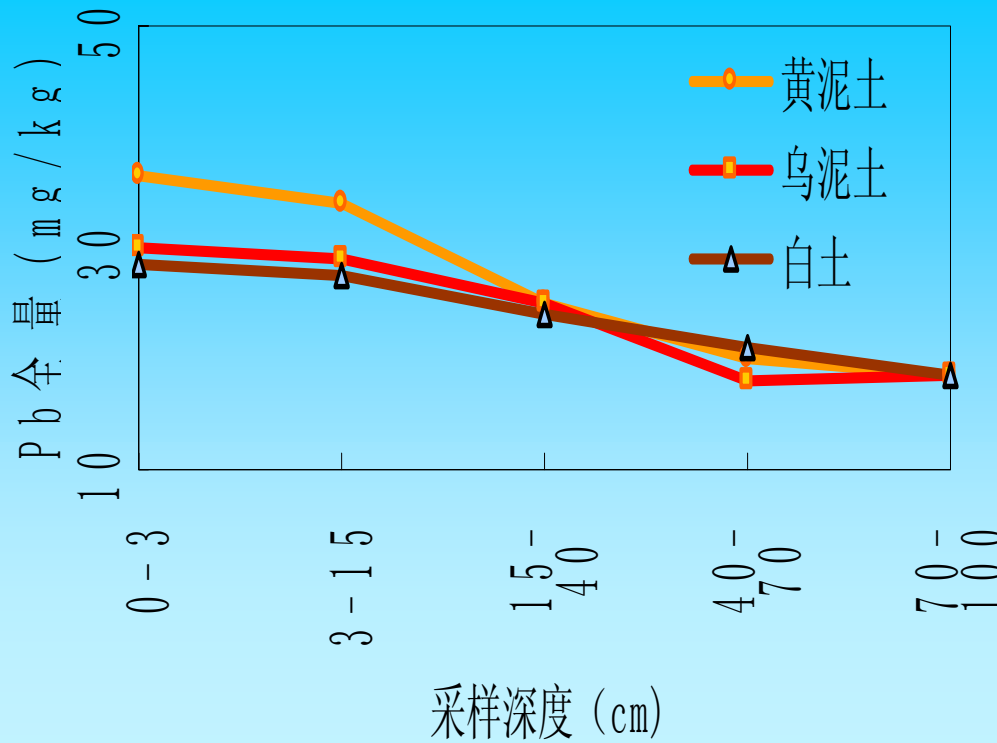


# 土壤环境重金属污染的指示





## Pb,Cd外源污染现象突出





# 工业环境有明显的污染负荷 (吴县市不同产业环境对比)

## 黄泥土表层中Pb, Zn有效态含量(mg/kg)及活化率(%)

深度 (cm)	Pb				Zn			
	有效态(工业)	有效态	活化率	活化率	有效态	有效态	活化率	活化率
		(农业)	(工业)	(农业)		(工业)	(农业)	(工业)
0-3	12.263	6.615	33.58	21.87	13.908	4.4	19.21	6.25
3~6	9.868	5.765	33.64	18.86	10.903	4.213	17.52	5.86
6~10	8.64	6.378	25.66	19.49	10.74	4.868	15.7	6.92
10~15	7.083	4.83	20.58	17.26	7.543	4.788	11.26	7.66
15~20	5.473	4.32	19.31	15.77	3.482	4.065	6.13	6.84
20-25	3.435	4.843	13.03	17.77	3.063	3.793	4.52	7.04
X	7.794	5.459			8.273167	4.3545		



# 木渎镇和光福镇两样点乌泥土表层土壤颗粒中重金属富集系数与分馏系数

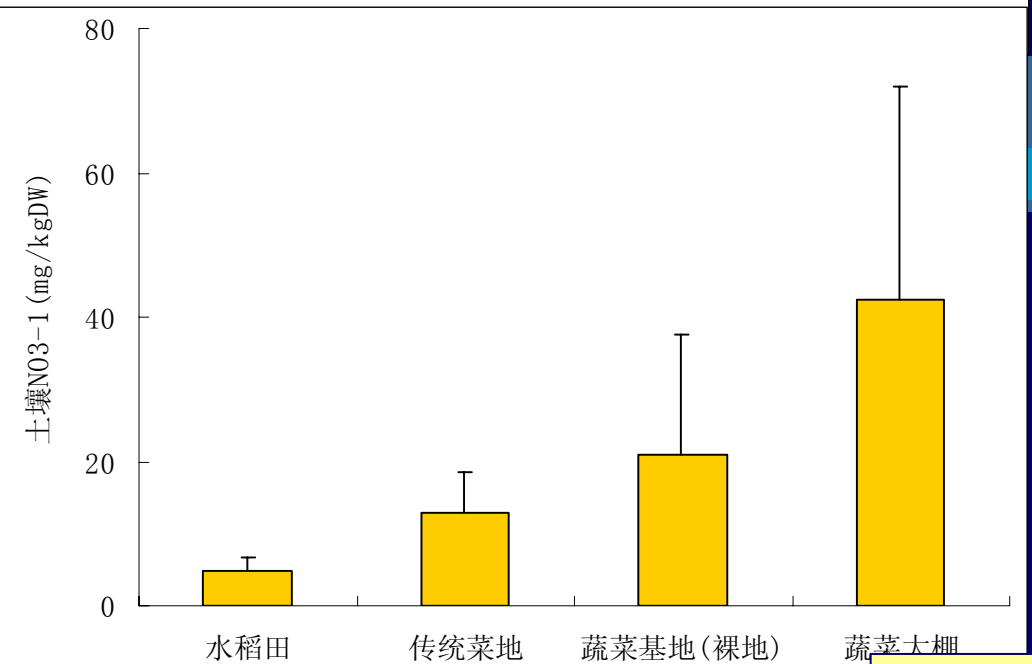
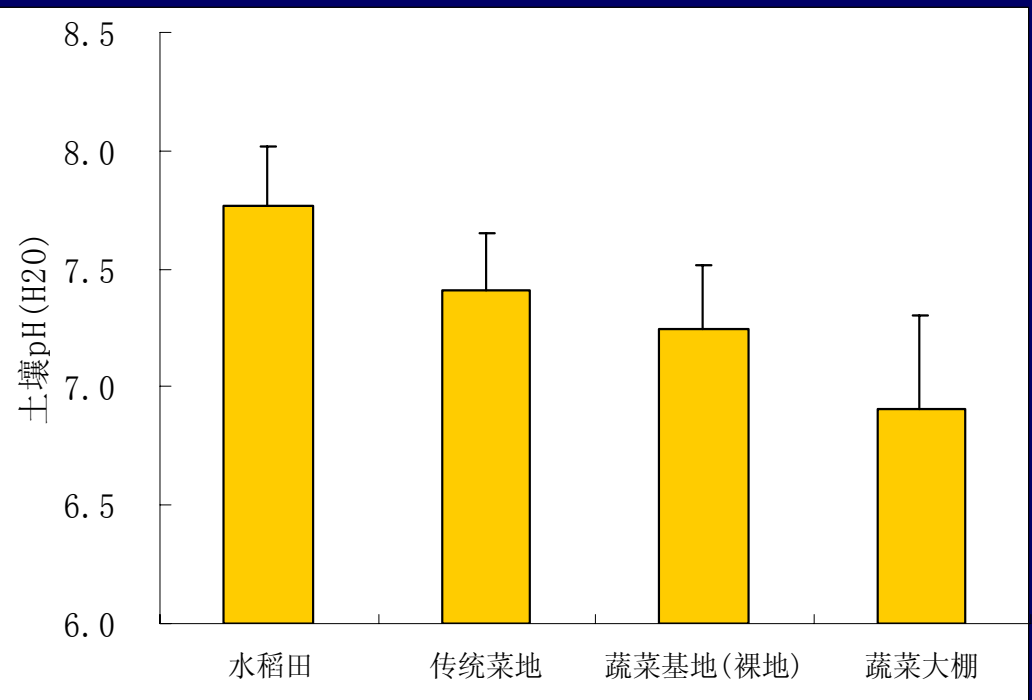
	>2		2~0.25		0.25~0.02		0.02~0.002		<0.002		分馏系数	
	A	Ap	A	Ap	A	Ap	A	Ap	A	Ap	A	Ap
Pb												
工	0.96	0.97	1.92	4.87	1.12	1.71	0.96	0.84	0.09	0.26	1.88	2.51
农	1.03	0.97	1.00	1.01	1.01	0.93	0.97	0.99	1.38	1.18	1.49	2.11
Cd												
工	0.91	1.63	3.20	7.33	0.89	2.62	0.66	1.05	0.32	0.21	7.99	15.31
农	1.68	2.00	0.68	0.75	0.99	0.44	0.82	0.45	1.22	0.70	1.71	5.36

土壤重金属污染的指示



# 土地利用中的土壤酸化

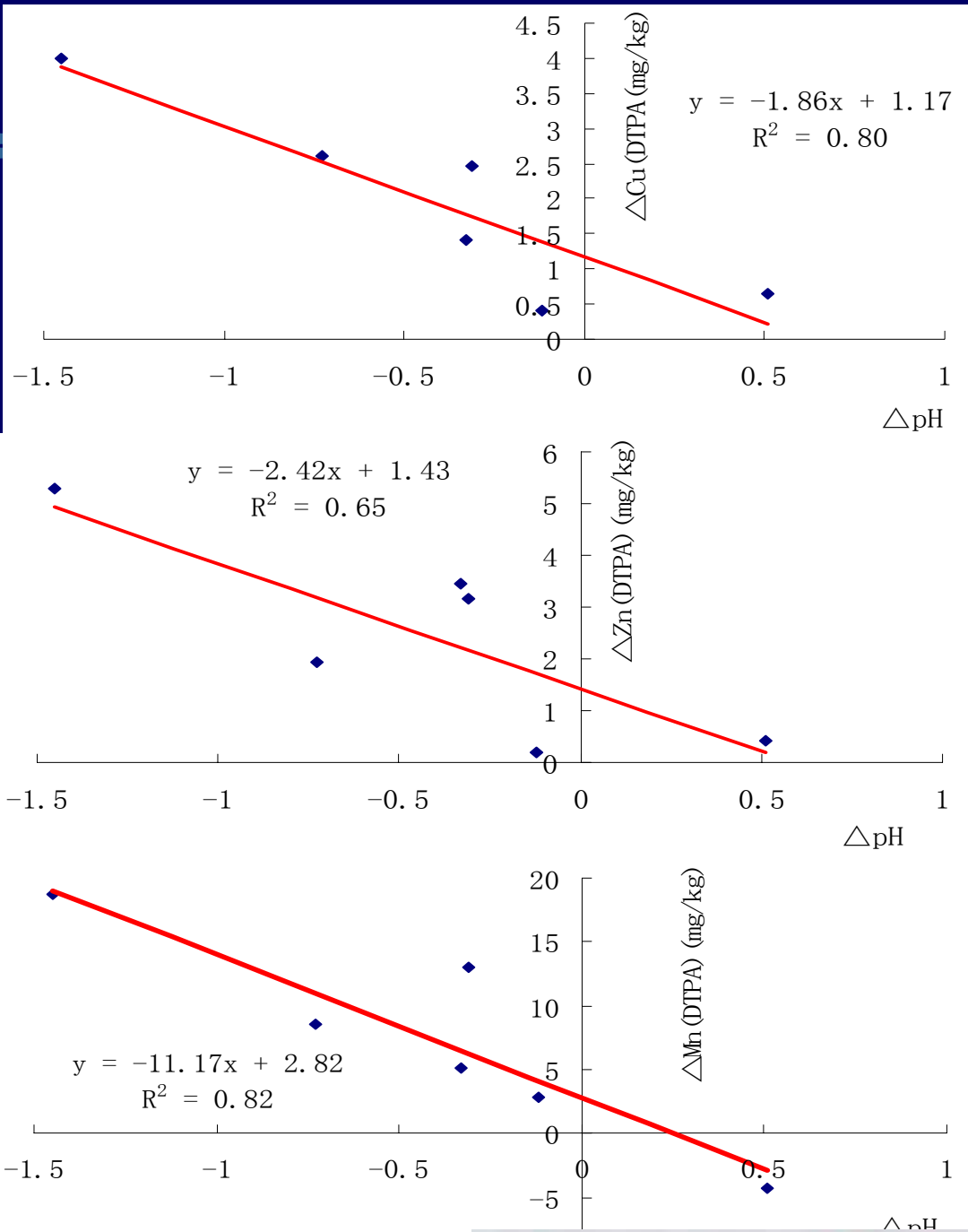
董元华  
等, 2003





# Soil acidification

土壤酸化是近10年来重金属有效性升高的重要机制



土壤酸化与重金属有效性的关系  
(宜兴市两时相水稻土的调查)



污染影响下土壤最高允许含量

Chang, A.C., Pan, G., et al., 2001

A Report submitted to WHO,  
Geneva, Switzerland, 2001

元素	允许土壤含量 (mg kg <sup>-1</sup> )
Ag	3
<b>As</b>	<b>8</b>
B*	1.7
Ba*	302
Be*	0.2
<b>Cd</b>	<b>4</b>
F	635
<b>Hg</b>	<b>7</b>
Mo*	0.6
<b>Ni</b>	<b>107</b>
<b>Pb</b>	<b>84</b>
Sb	36
<b>Se</b>	<b>6</b>
Tl*	0.3
V*	47



# 荷兰污泥用于农田的最大允许含量的变迁

元素	最大允许含量 (mg/kg d.w.)		
	Before 1/1/1991	1/1/1991 – 1/1/1995	After 1/1/1995
As	25	25	0
Cd	5	3.5	1.25
Cr	500	350	75
Cu	900	425	75
Pb	500	300	225
Hg	5	3.5	0.75
Ni	100	70	38
Zn	2000	1400	300





# 土壤环境质量国家标准 (GB 15618 - 1995)

## 污泥农用的输入土壤的 最大允许含量 (GB 4284 - 84) (mg/kg dw)

元素	农地			林地	污染元素	最大允许含量 (mg/kg dw)	
	pH < 6.5	pH = 6.5 - 7.5	pH > 7.5	PH > 6.5		(pH < 6.5)	pH > 6.5
Cd	0.3	0.3	0.6	1	As	75	75
Hg	0.3	0.5	1	1.5	B	150	150
As (水稻土)	30	25	20	30	Cd	5	20
As (旱地)	40	30	25	40	Cr	600	1000
Cu (农地)	50	100	100	400	Cu	250	500
Cu (园地)	150	200	200	400	Hg	5	15
Pb	250	300	350	500	Ni	100	200
Cr (水稻土)	250	300	350	400	Pb	300	1000
Cr (旱地)	150	200	250	300	Zn	500	1000
Zn	200	250	300	500	Mineral Oil	3000	3000
Ni	40	50	60	200	PCB	3	3

中国环境质量标准已落后！



# 土壤重金属与食品安全

1. 临界总摄入量与允许日（周）摄入量
2. 摄取途径
3. 源头控制的土壤允许含量的估计
4. 实地土壤重金属积累的摄取风险分析



# 潜在有害重金属人类暴露途径与情景 (U.S. Environmental Protection Agency, 1992)

相对重要性	暴露途径 (Exposure pathways)	暴露情景 (Exposure Scenario)
1	土壤-植物-人	植物食物摄取
2	土-植物-动物-人	家禽-家畜肉品 (植物饲料、动物土壤咀嚼)
3	土-水(地表-地下)-饮用水-人	■ 饮用地表水、地下水 (就地、异地)
4	土壤-水-动物-人	家畜饮水-肉品
5	土-人	儿童舔土(pica behaviour)
6	土-空气-人	扬尘-口鼻吸入, 尘埃飘扬-人吸入 (异地)
7	土-器具-人	皮肤粘附



# 临界摄入量: RfDs ( $\mu\text{g}/\text{kg BW day}$ ) of PTEs

Chemicals	EPA( $10^{-6}$ ) <sup>1*</sup>	WHO( $10^{-5}$ ) <sup>2</sup>	Netherl.( $10^{-4}$ ) <sup>3</sup>	Suggested( $10^{-5}$ )
Cd	5	7	1.0	7
Pb	Nd	3.5	3.6	3.5
As	0.3	0.6	2.1	0.6
Hg	0.3	0.7	0.61	0.7
Ni	20	Nd	50	20
Se	5	1	5.0	1
Ag	5	Nd	5.0	0.5
Mo	5	0.1	10	0.1
V	9	NA	2	90
Ba	70	51	20	50
F	60	Nd		600
TI	0.08	Nd	0.2	0.08
Sb	0.4	0.86	0.86	0.86

1 USEPA,2000; 2,WHO, 1999; 3, Swartjes ,1999. \* Exposure Risk level.



## 国际食物消费结构

2000年中国平均食物消费结构  
(新华社北京2001年10月16日电)

食物类	美国膳食谱 (g/人/d)		全球平均食谱 (g/人/d)
	正常食谱	素食者	
奶产品	549	584	55
动物产品	204		
肉类			111
水产品			39
谷类	331	203	405
蔬菜			194
叶菜	42	252	
豆类	51	166	
油类种子 坚果类			18
根茎类	163	43	288
水果类	242	284	235
油脂类	56	107	43
糖蜜类	65	110	59
蛋、辣椒、调味品			53
总计	1,703	1,749	1,500

食物种类	消费量(kg/a)
稻麦等粮食	206
蔬菜	110
糖	7
肉类	25.3
蛋	11.8
奶	5.5
水产	11.7

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# 人类暴露风险控制原则

- 1, 最多的人群暴露; 食物
- 2, 最经常的时间暴露; 膳食-饮水
- 3, 转移-富集最强的暴露; 植物-人; 植物-动物-人
- 4, 最敏感的人群暴露—就地 (农民、儿童)



# 依暴露重要性的重金属土壤环境指标

- 土壤-植物迁移-富集系数 (BCFs)
- 土壤-水迁移性 ( $K_p$ , 固相-液相分配)
- 可扬性与可粘性-颗粒分配 (PM10, PM2.5)



## 未污染农业土壤中生长的植物的可食部分若干重金属元素的含量 (mg/kgDW)

(Cited from: Dudka S., Miller W P., Accumulation of potentially toxic elements in plants and their transfer to human food chain. J Environ. Sci. Health, B34(4),1999:681~708)

Crop	Cd		Pb		Zn	
	Mean	95 <sup>th</sup>	Mean	95 <sup>th</sup>	Mean	95 <sup>th</sup>
Lettuce	0.44	2.1	0.19	1.0	46	78
Spinach	0.80	1.5	0.53	1.2	43	128
Potatoes	0.14	0.36	0.03	0.1	15	27
wheat	0.04	0.12	0.02	0.17	29	48
rice	0.01	0.03	0.01	0.03	15	20
Sweet corn	0.01	0.06	0.01	0.06	25	46
Field corn	0.01	0.07	0.01	0.03	22	30
carrots	0.16	0.79	0.05	0.24	20	48
onions	0.09	0.24	0.04	0.09	16	26
tomatoes	0.22	0.61	0.03	0.11	22	29
peanuts	0.07	0.21	0.01	0.03	31	42
soybeans	0.04	0.18	0.04	0.10	45	59





# 重金属的土壤-植物间分配关系



## 原理:

- 由土壤-植物关系反推土壤控制含量
- 考虑一个国家和地区的主要膳食结构中的作物
- 计算方程

$$C_s = 1/2RfD / \sum(PAF_i * D_i)$$

$C_s$ : ( $\mu\text{g/g}$ ) ;  $RfD$ : ( $\mu\text{g/d/pers.}$ );  $D_i$ : $\text{g/d}$



# 重金属土壤-植物间分配：区域资料的统计

考察植物重金属富集系数PAF（或BCF）与土壤含量的关系（Cd as example）；

- 确定污染起始时的作物PAF；
- 可由文献资料换算或推算其他元素或作物的PAFs

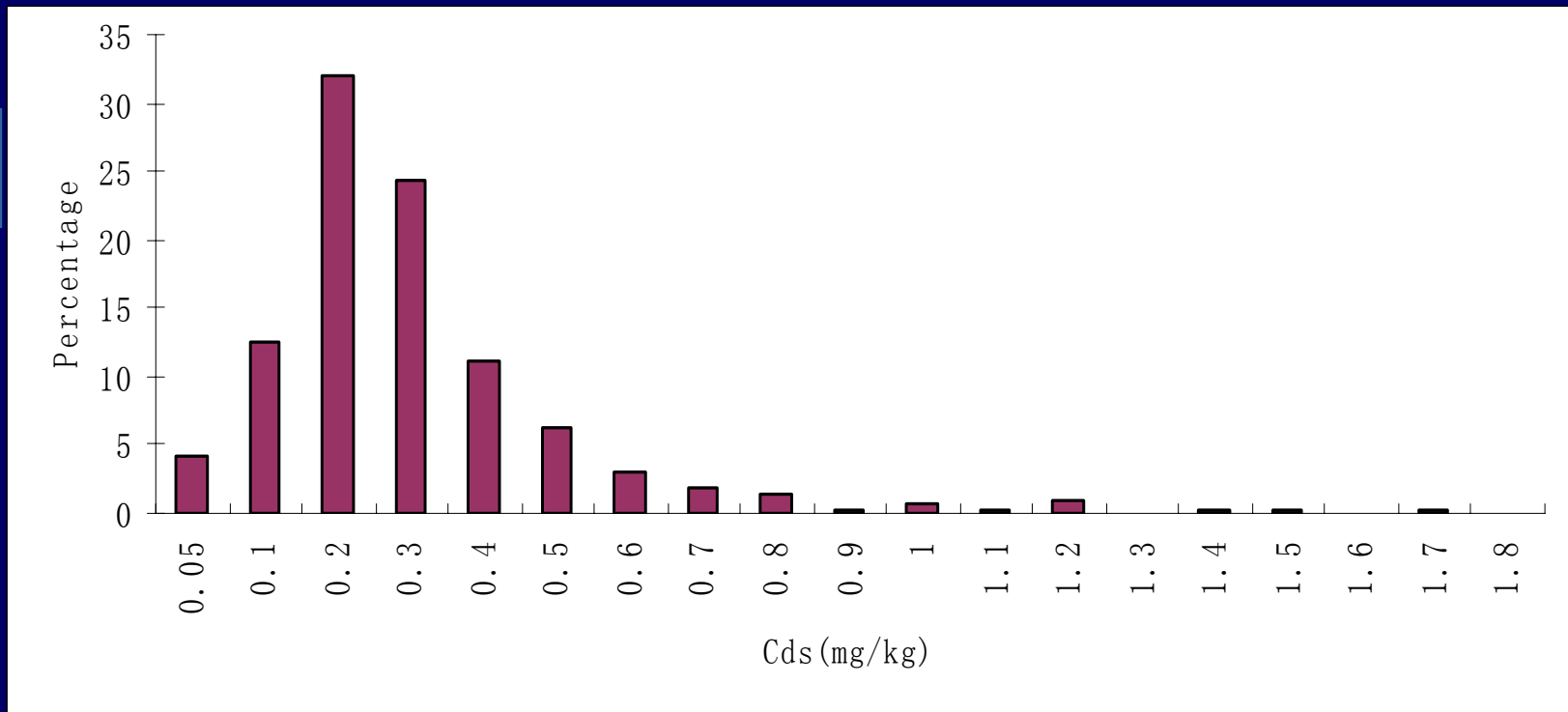


# 重金属土壤-植物 PAFs的现有参考资料

- Normal range of Trace Elements in soil and Plant ( Kabata-Pendias, 2001)
- USDA national survey data(via Dr Chaney, 2001,pers. Comm.)
- Individual references in journals



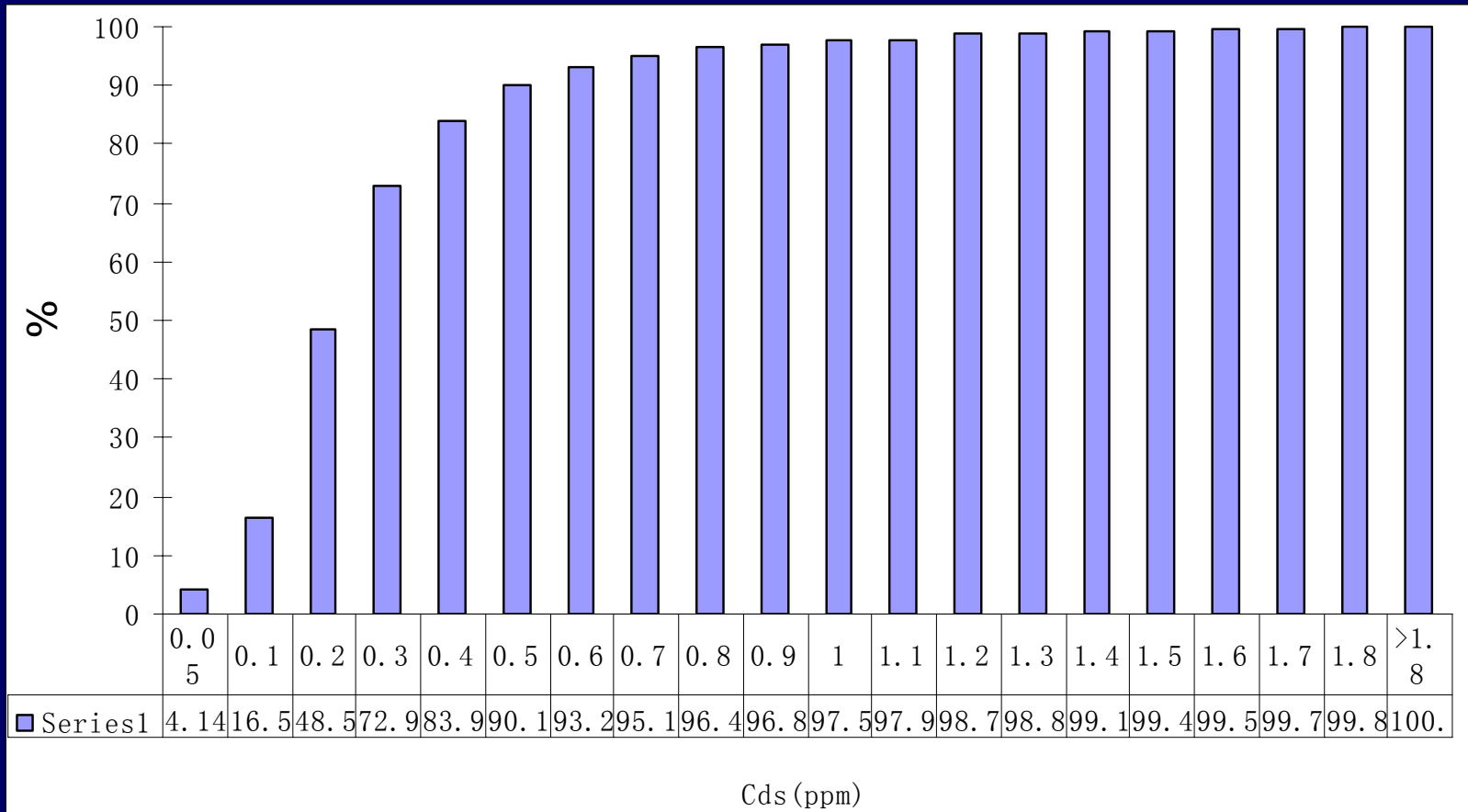
# Distribution of observation values of Cds (mg/kg)



Data source: Chaney R, 1981. Calculated by Pan G., 2001

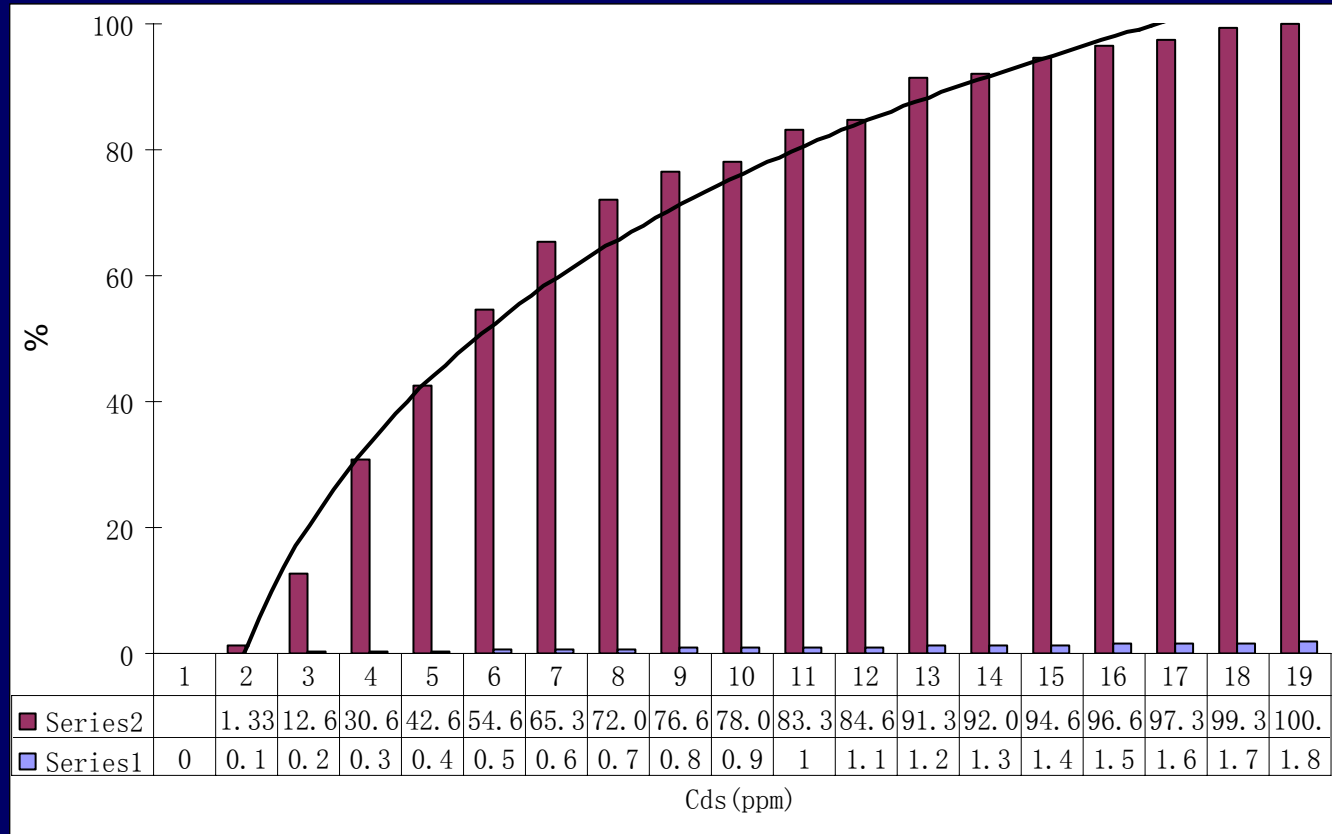


# Cds probability distribution initial pollution : 1.5ppm





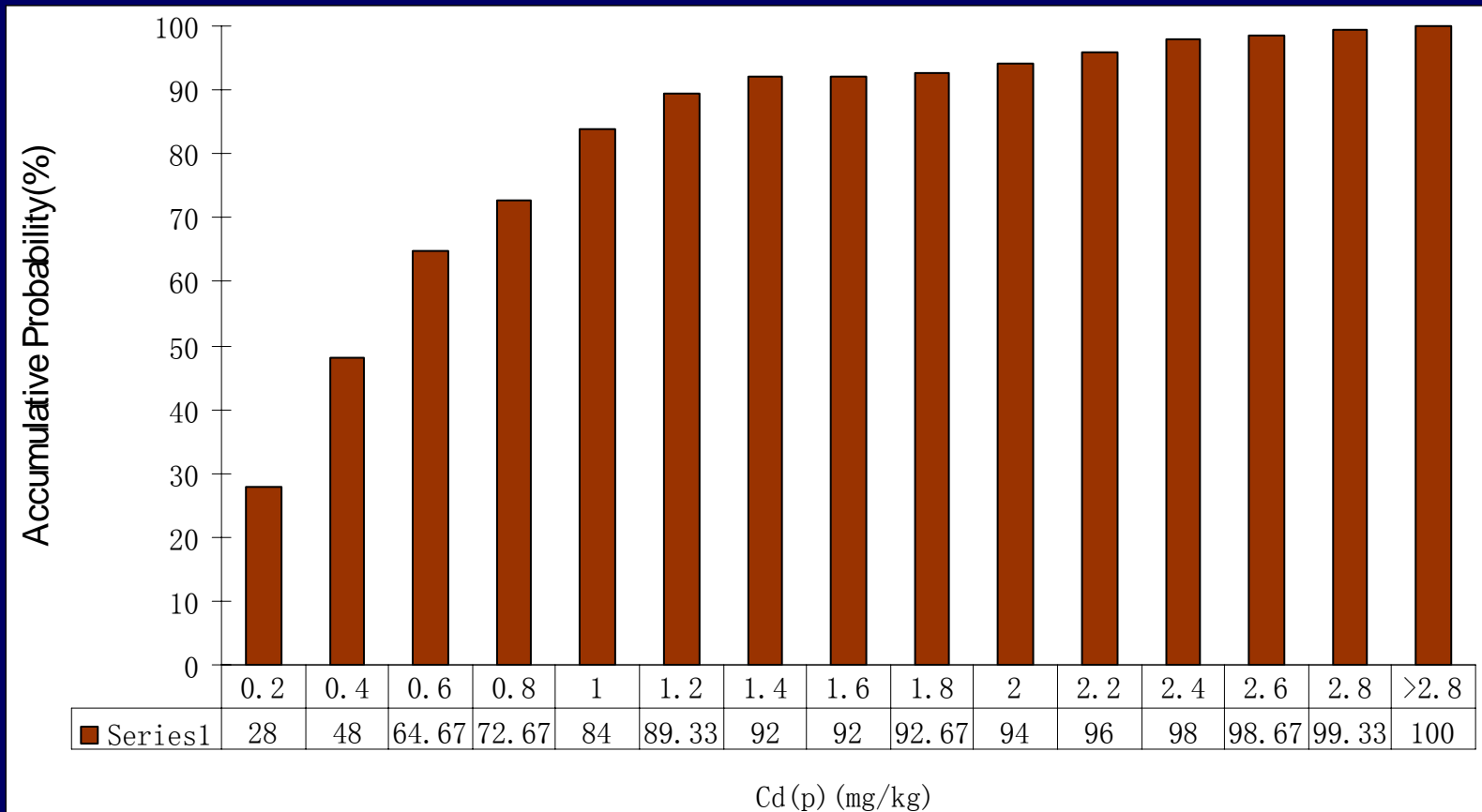
# Probability distribution of Cds in lettuce fields



Data source: Chaney R, 1981. Calculated by Pan G., 2001



# Probability distribution of Cd(p) in lettuce

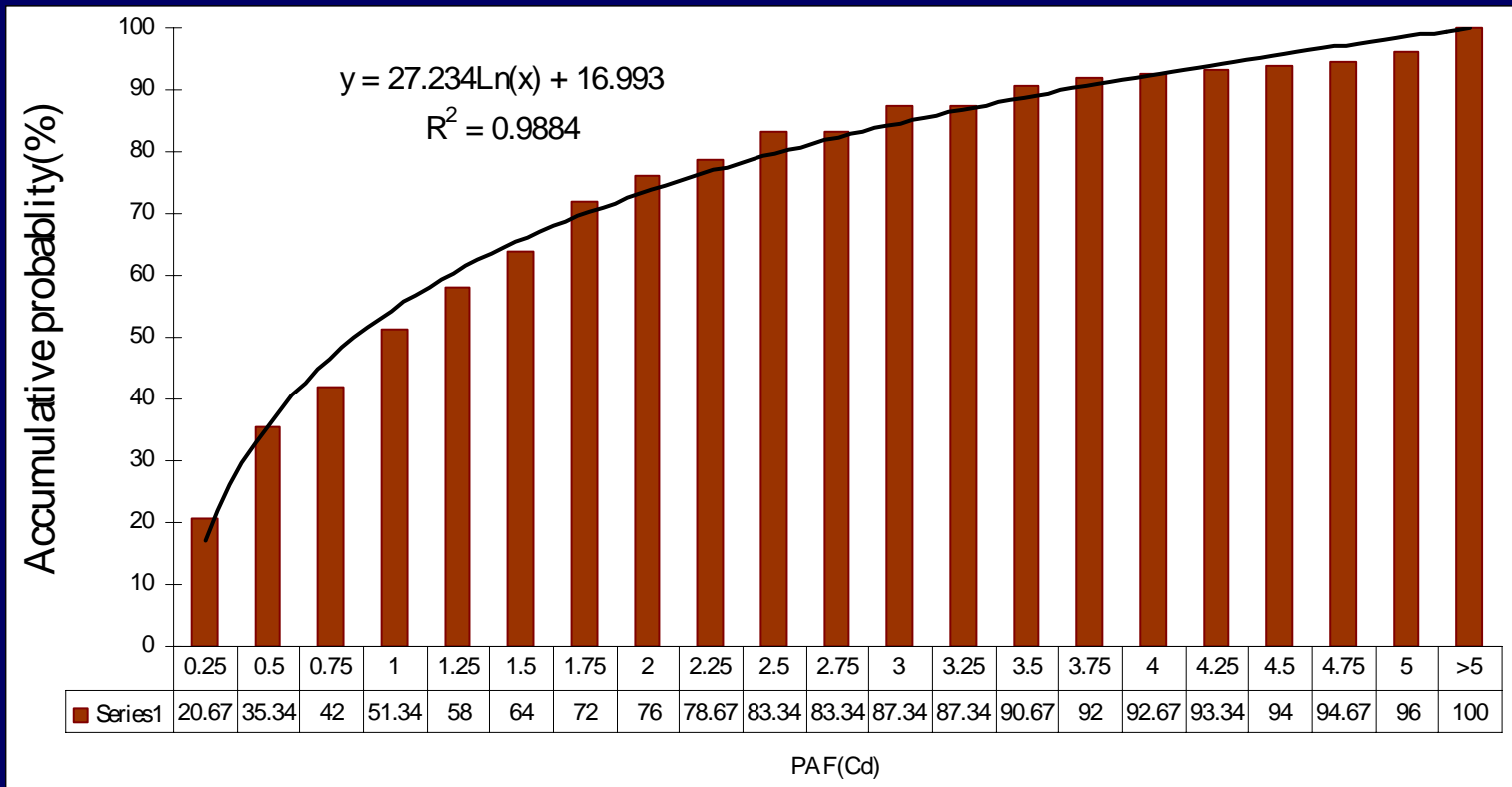


Data source: Chaney R, 1981. Calculated by Pan G., 2001





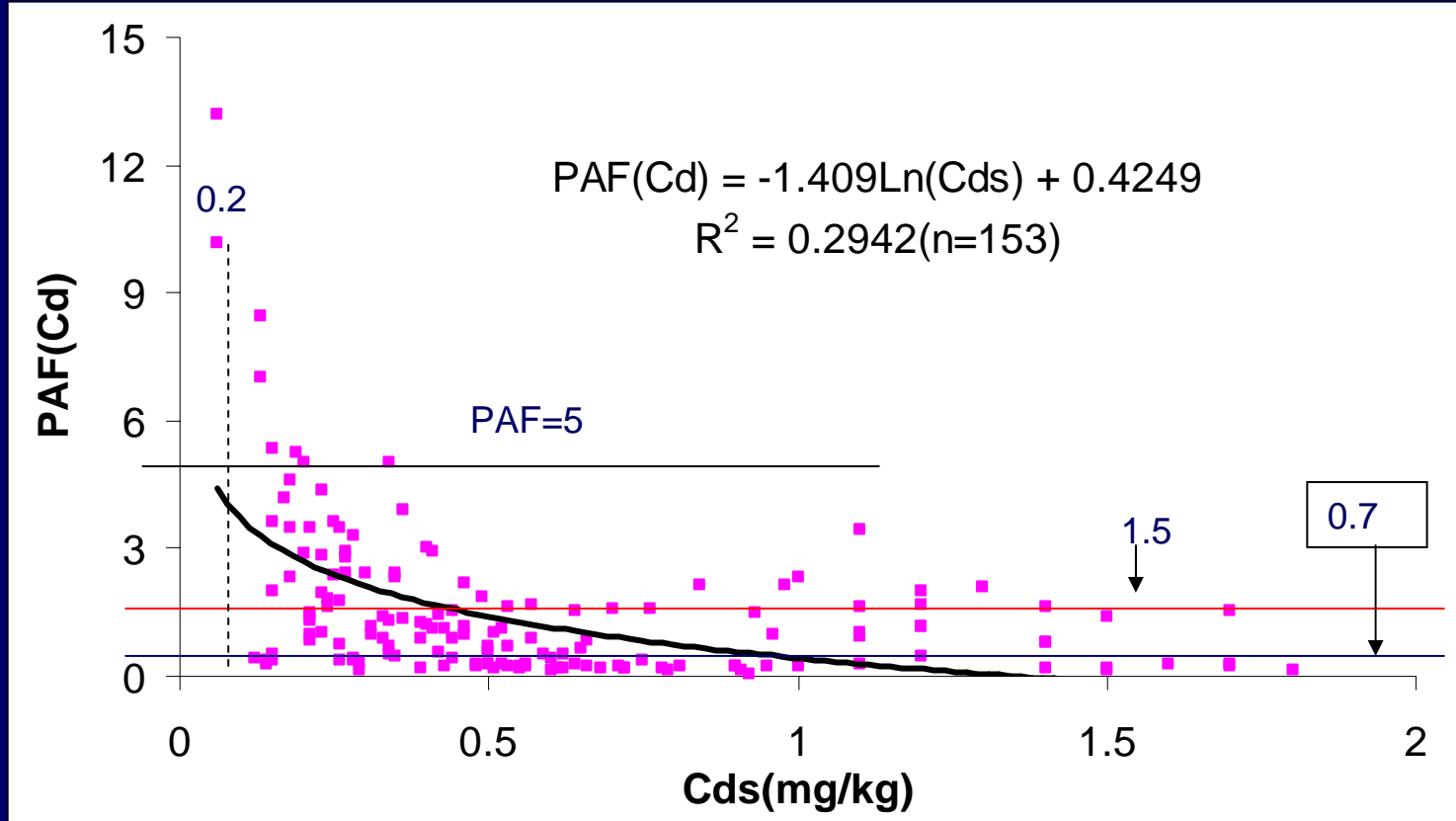
# PAF(Cd) probability for Lettuce



Data source: Chaney R, 1981. Calculated by Pan G., 2001



# PAF(Cd) as a function of Cds (lettuce)



潘根兴, Chang AC., 应用生态学报, 2002.



## Statistics of PAF of different crops

Crop	Min	Max	Median	Mean	Stdev	95%pr ob.
Soy-bean	0.05	7.5	0.40	0.53	0.27	1.0
Potato	0.03	6.28	1.05	0.95	0.78	2.6
Wheat	0.002	1.38	0.21	0.19	0.15	0.6
Sweet corn	0.00	1.18	0.09	0.16	0.05	0.3
Lettuce	0.06	13.2	1.53	1.86	0.97	4.8

(Data from Chaney R, 2001. Recalculated by Pan G., 2001)



## PAFs of Cd for 4 categories of crops using different soil Cd probability

Crops	PAF		
	95%	99% Prob.	99.9% Prob.
Wheat	0.03	0.002	0.001
Potato	0.11	0.010	0.004
Lettuce	0.73	0.35	0.30
Sweet corn	0.10	0.05	0.03
Soybean	0.13	0.027	0.016

Data source: Chaney R, 1981. Calculated by Pan G., 2001



# Correlating PAF to soil total concentration

Crop		Independt	Coefficient	Stdev	R <sup>2</sup>
Cdr Vs soil total Cd concentration(mg/kg)					
Soybean (n=299)		Intercept	-0.0969	0.0401	0.13
		Ln(Cds)	-0.1172	0.0237	
Potato (n=278)		Intercept	0.0890	0.0760	0.45
		Ln(Cds)	-0.1701	0.0377	
Wheat (n=291)		Intercept	-0.5566	0.1492	0.32
		Ln(Cds)	-0.9268	0.0816	
Sweet Corn (n=166)		Intercept	-0.0092	0.0297	0.17
		Ln(Cds)	-0.1558	0.0204	
Lettuce (n=150)		Intercept	0.4294	0.1905	0.29
		Ln(Cds)	-1.4090	0.1794	

Data source: Chaney R, 1981. Calculated by Pan G., 2001



## Correlating PAF(Cd) to soil properties (Data from Dr Chaney, 2001)

Crop	Variables	Coefficient	Stdev	R <sup>2</sup>
Soybean(n=299)	=0.0561-0.1706ln(Cds)			0.165
Potato(n=278)	=0.0890-0.1701lnCds			0.45
Wheat (n=291)	Intercept	-3.0702	0.5745	0.40
	Ln(Cds)	-1.8140	0.2115	
	Cds	4.7182	1.0440	
Sweet Corn (n=166)	Intercept	4.7364	1.9013	0.21
	Ln(Cds)	-0.1546	0.0206	
	pH	0.6582	0.2884	
	pH <sup>1/2</sup>	-3.5446	1.4857	
Lettuce (n= 150)	Intercept	-2.1034	0.6905	0.64
	Cds	4.3925	0.6252	
	Ln(Cds)	-3.4369	0.3597	
	CEC <sup>1/2</sup>	-0.2184	0.0260	

Data source: Chaney R, 1981. Calculated by Pan G., 2001



## 95%置信限 土壤含量的PAFs

Element	Cereals	Root/tuber	leafy vegetable	Fruit
Ag	0.01	0.01	0.01	0.01
As <sup>x</sup>	0.002	0.02	0.02	0.01
B	0.02	0.04	0.01	0.04
Ba	0.01	0.01	0.02	0.004
Be	0.01	0.02	0.01	0.01
Cd <sup>x</sup>	0.03	0.1	0.7	0.1
F	0.001	0.01	0.04	0.005
Hg	0.01	0.02	0.02	0.005
Mo	0.08	0.02	0.01	0.08
Ni	0.01	0.04	0.01	0.004
Pb <sup>x</sup>	0.001	0.001	0.005	0.05
Sb	0.001	0.001	0.005	0.005
Se	0.01	0.005	0.02	0.001
Tl	0.02	0.02	0.02	0.02
V	0.03	0.02	0.8	0.02

(cal. from Pendias, 2001) X: Adopted to the literature reported data



## The estimated C<sub>max</sub> for the major elements concerned with sludge application

Element	RfD (ug/kg BW d)	1/2RfD (ug/kg BW d)	Di (ug person/d)	C <sub>max,soil</sub> (ug/g)
Ag	0.5	0.25	15	3.38
As	0.6	0.3	18	8.21
B	0.5	0.25	15	1.48
Ba	50	25	1500	336.17
Be	0.03	0.015	0.9	0.18
Cd	7	3.5	210	8.52
F	60	30	1800	1297.53
Hg	0.7	0.35	21	4.16
Mo	0.1	0.05	3	0.10
Ni	20	10	600	98.47
Pb	3.5	1.75	105	99.23
Sb	0.86	0.43	25.8	48.74
Se	1	0.5	30	7.25
Tl	0.08	0.04	2.4	0.27
V	90	45	2700	134.45





# Calculating the Limit Concentration for Soil Cd by Using the PAF Value From Different Data Sources:

- 1, PAF data calculated from those in Pendias(2001): 1.4 ppm
- 2, Mean Cd PAF Data (USDA, R. Chany pers. 2001): 1.4ppm
- 3, Median Cd PAF(USDA, R. Chany pers. 2001): 1.9ppm
- 4, Cd PAF at 95% probability: 0.50ppm
- 5, PAF calculated as 95%pro. Cdp/95%Prob. Cds: 1.8ppm
- 6, PAF calculated by 95% probability concentration of Cds: 8.5ppm



# II. 实地土壤重金属污染的食物安全估计

A model by using soil-related  $K_p$  values



## A model by using soil-related $K_p$ values:

1. 基于土壤生物有效性变化的土壤含量控制;
- 2, 特定土壤条件下食物暴露风险估计;
- 3, 了解不同土壤如何控制生物有效性与食物安全;



# 1, The permitted daily dietary uptake :

The target for estimation of soil concentration limit (See RfD table sheet)



# 重金属植物吸收与分配

- 1, 被动吸收-质流输送-根系吸收;
- 2, 吸收后的植物目标器官分配;
- 3, 土壤水迁移-假设农田中水蒸散等于蒸腾



$$C_p = C_w * W_d * Tr \quad (1)$$

- 1,  $C_p$ : 植物含量 ( $\mu\text{g}$  metal uptake /g DM);
- 2,  $C_w$ : 与固相平衡下土壤水重金属浓度 ( $\mu\text{g}/\text{mL}$ );
- 3,  $W_d$ : 农田植物吸水量 ( $\text{mL}/\text{gDM}$ );
- 4,  $Tr$ : 食用目标器官重金属分配系数.



# 土壤固液分配作为主导因子

Convert  $C_w$  to  $K_p$

From:  $C_w = C_s / K_p$  (2)

Then:  $C_p = C_s / K_p * W_d * Tr$  (3)

- 1,  $K_p$ : the solid-liquid partitioning coefficient (L/kg);
- 2,  $C_s$ : the concentration in soil ( $\mu\text{g/g}$ ).



# Using Kp models (Cd)

- Model for Cd (Sauve, et al,2000)  
(n=751,R2=0.61,SEE=0.62):

- $$\text{Log}K_p(\text{Cd}) = 0.48 * \text{pH} + 0.28 \log(\text{SOM}) - 0.65 \quad (4)$$
- (SOM: % of soil organic matter)

- Thus: 
$$C_p(\text{Cd}) = C_s(\text{Cd}) / K_p(\text{Cd}) * W_d * Tr_i \quad (5)$$

- $$C_s(\text{Cd}) = 1/2 RfD * K_p(\text{Cd}) / \sum (D_i * W_{di} * Tr_i) \quad (6)$$
- ( $i=1 \dots 4$ )





# Relating Soil Limit Concentration to Soil Properties

$$Cs(Cd) = 210 * 10^{0.48 * pH + 0.82 * \log(SOM) - 0.65} / \sum (D_i * W_{di} * Tr_i(Cd))$$

( $i=1 \dots 4$ )

- Cs in  $\mu\text{g/g}$ ; Di in g/person/day; Wdi in gH<sub>2</sub>O/gDM; Tri dimensionless



Kp model for Pb (Janssen, et al, 1997 ):

$$\log Kp_{(Pb)} = 0.24 * pH + 0.40 * \log(Fe_{ox}) + 1.98 \quad (8)$$

(n=20, R2=0.71, SEE 0.34)

Fe<sub>ox</sub> is soil oxalate extractable iron in mmol/kg.

Then:

$$CS_{(Pb)} = \frac{1}{2} RfD_{(Pb)} * Kp / \sum (Di * Wdi * Tri_{(Pb)}) \quad (9)$$

(i=1.....4)

$$CS_{(Pb)} = \frac{1}{2} RfD * 10^{0.24 * pH + 0.40 * \log(Fe_{ox}) + 1.98} / \sum (Di * Wdi * Tri_{(Pb)}) \quad (10)$$



# Prediction of dietary uptake of metals:

- $Du = Cp * Di$  (11)

$$Du_{(Cd)} = Cp_{(Cd)} * Di \quad (i=1 \dots 4) \quad (12)$$

- $Du_{(Cd)} = Cs_{(Cd)} / Kp_{(Cd)} * \sum (Di * Wdi * Tri_{(Cd)}) \quad (i=1 \dots 4)$  (13)

- $Du_{(Cd)} (\mu g/d) = Cs_{(Cd)} / (10^{0.48 * pH + 0.82 * \log(SOM) - 0.65}) * \sum (Di * Wdi * Tri_{(Cd)})$   
( $i=1 \dots 4$ ) (14)



$$\blacksquare Du_{(Pb)} = Cp_{(Pb)} * Di \quad (i=1 \dots 4) \quad (15)$$

$$\blacksquare Du_{(Pb)} = Cs_{(Pb)} / Kp_{(Pb)} * \sum (Di * Wdi * Tri_{(Pb)}) \quad (i=1 \dots 4) \quad (16)$$

$$\blacksquare Du_{(Pb)} (\mu g/d) = Cs_{(Pb)} / (10^{0.24 * pH + 0.40 * \log(Feox) + 1.98}) * \sum (Di * Wdi * Tri_{(Pb)}) \quad (i=1 \dots 4) \quad (17)$$



# 实际食物暴露风险的估算

■ Cd:

$$\text{Exposure Risk} = D_u / RfD_f$$

其中,  $D_u = C_p * D_i$ ;  $RfD_f$  为  $RfD$  食物摄取分量, 一般取 50%。

因此, 有:

$$ER_{Cd} = D_u * 1/2 * RfD, \text{ 所以:}$$

$$ERCd = C_{S(Cd)} / (10^{0.48 * pH + 0.82 * \log(SOM) - 0.65}) * \sum (D_i * W_{di} * Tr_{i(Cd)}) * 1/2 * RfD_{cd}$$



Table 1 The parameters used for Cs estimation

	Wdi (gH <sub>2</sub> O/gDM)	Tr(Cd) <sup>a</sup> (Foliage- edible part)	Tri(Cd) <sup>d</sup> (Root-leaf- grain)	Tri(Pb) <sup>d</sup>
Cereals	600	0.11 <sup>b</sup> (0.34) <sup>c</sup>	0.005	0.11
Root	500	0.14 (0.14)	0.9	0.03
Leafy	700	1(1)	2	0.04
Fruit	800	0.29 (0.47)	0.2	0.05

a, Page & Chang, 1987. b, sludge application;

c, control; d, Adriano, 198?



## Acute plant food exposure to Cd by USA dietary

Food	US diet g/dayFW	(g/day DW)	Cd exposure( $\mu\text{g}/\text{Day}$ )	
			Median	95% pro.
Cereals	331	297.9	10.72	38.73
Root/tubers	163	32.6	4.89	13.04
Vegetable	93	4.65	2.00	10.23
Fruit	242	12.1	0.11	0.726
Total	829	347.25	17.72	62.72
% of RFD			8.44	29.90

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# The baseline Cds for cropland soils at zero risk of plant food exposure (mg/kg)

Crop	Cdp (95% probab).	Relative ratio	Permissib Cdp.	Cd in soil
Wheat	0.13	0.06	0.28	0.8
Potato	0.40	0.18	0.85	3.5
Lettuce	2.2	1	4.68	3.5
Tomato	0.53	0.24	1.12	0.6





## Kp-related soil concentration limit of Pb and Cd( $\mu\text{g/g}$ )

	pH 7		pH 5	
	5	2	5	2
SOM(%)	5	2	5	2
Cs(Cd)	9.5	5	1.0	0.5
Feox (mmol/kg)	80	50	80	50
Cs(Pb)	117.5	97.4	38.9	32.2

Cds 1.5ppm under median pH (6)& SOM(2%)(Chaney,2001,pers. Data):



# Recommendation for Sludge Application

■ Total sludge application rate

$$=(C_{dper}-C_{ds}) * W_s / C_{dslg}$$

■ Where  $C_{dper}$  is the permitted Cd concentration in soil (mg/kg);  $W_s$  is the total soil weight (kg/ha);  $C_{dslg}$  is the Cd concentration in sludge (mg/kg)



# Permissible rate for USA soil: (Normal range:pH 6.0,SOC 2%, Cds 0.8ppm)

- Permissible Cds: 1.5ppm;
- Maximum Cd in sludge:39 ppm
- Perm. Rate:
  - =  $(1.5-0.8)*1.2*10^6/39 \geq 200$  T/ha (DW)
  - = **40** T/ha for continuously 5 yrs



# Permissible rate for the case in *Chang, et al, 1997* (Ramona sandy loam)

■ If :pH 7.8, SOC 3%

■ Cds Vs application rate:

$$Cds = 0.0182X + 0.3100 \text{ (5 yrs continuously)}$$

$$Cds = 0.0146X + 2.5028 \text{ (10 yrs continuously)}$$

Cds in mg/kg; X in T/ha

To reach the 8.5 ppm of Cds, Then:

90 T/ha per yr for continuously 5 years; 40 T/ha for 10 yrs



# 土壤重金属生物有效性与食物安全

## 土壤-植物-污染的相互作用





# 重金属生物有效性

- 1, 土壤重金属总量中对生物吸收有效的部分;  
(水系、土壤动物、植物-人类吸收) (Allen, 2001)
- 2, 土壤中可以同时对生物产生暴露(exposure)的部分  
( van Straalen NM, 2001; USEPA,2000)
- 3, 植物生物有效性: 植物直接吸收而积累于体内的那部分  
(Peijnenburg W, 2000; Li,Z., Li L., Pan, G. 2004)

重金属形态分级可以描述环境化学移动性, 但不能说明生物有效性 (Tessier,1979; 张艳玲等, 2002; Li L., Pan, G. 2004 )



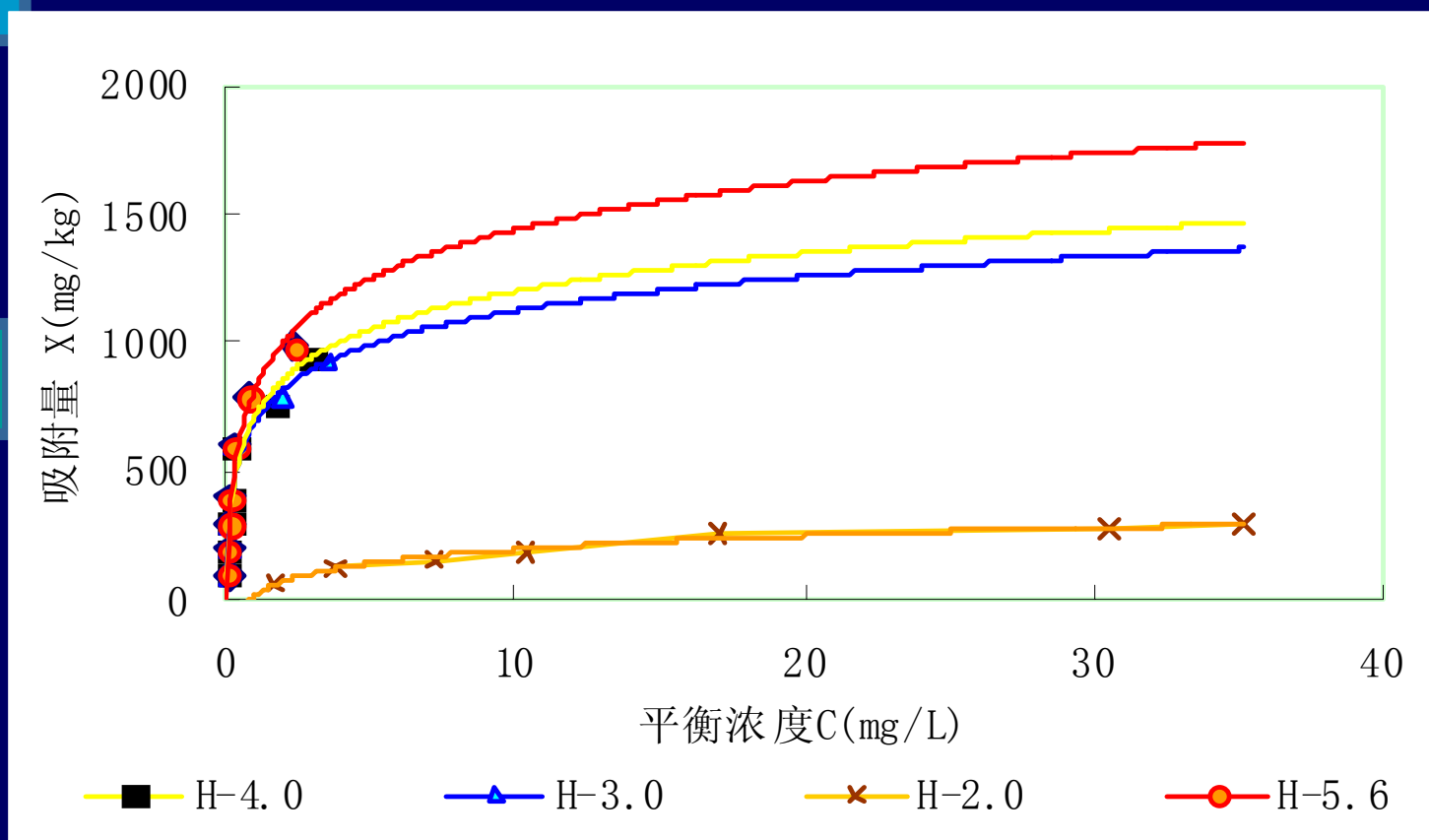
# Solid-liquid relationships:

酸化导致食物安全风险升高!

<i>Element</i>	<i>Relationship</i>	<i>R<sup>2</sup></i>	<i>No of samples</i>
<i>Cd</i>	$\log K_d = 0.48 \text{pH} + 0.82 * \log \text{SOM} - 0.65$	0.613	751
<i>Cu</i>	$\log K_d = 0.21 \text{pH} + 0.51 * \log \text{SOM} + 1.75$	0.419	353
<i>Ni</i>	$\log K_d = 1.02 \text{pH} + 0.80 * \log \text{SOM} - 4.16$	0.758	69
<i>Pb</i>	$\log K_d = 0.37 \text{pH} - 0.44 * \log \text{Pb}_t + 1.19$	0.562	204
<i>Zn</i>	$\log K_d = 0.60 \text{pH} - 0.21 * \log \text{Zn}_t - 1.34$	0.573	298



# 吸附等温线用于估计化学条件变化下（例如酸化下） $K_d$ 值变化



模拟酸雨影响下黄泥土对铜的吸附曲线



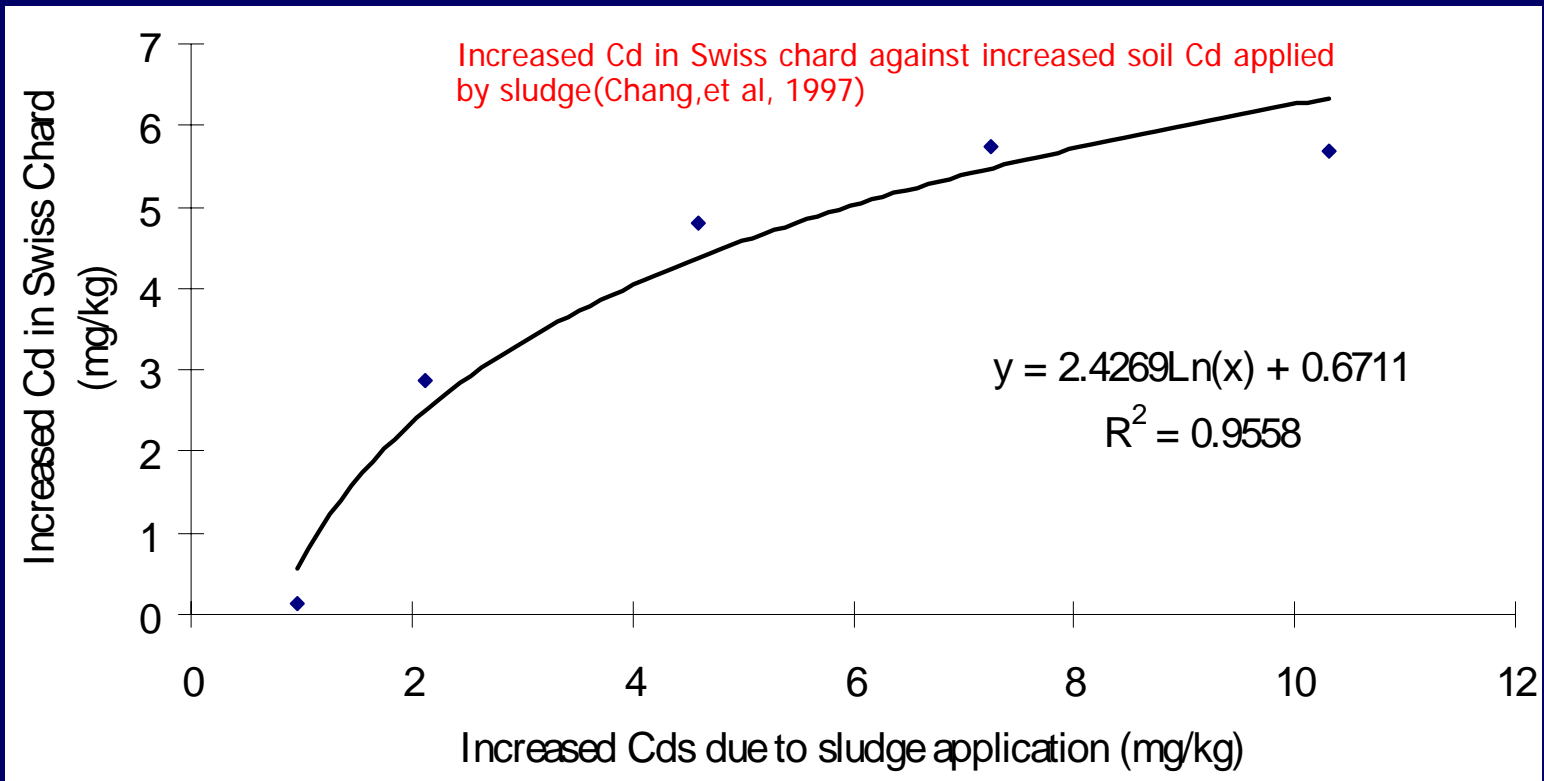


# 潜在有害元素的植物吸收：非线性响应(non-linear response)

- Plant control on absorption and partitioning
  - Soil control on mobility and availability
  - Other factors associated with metal affinity or mobility

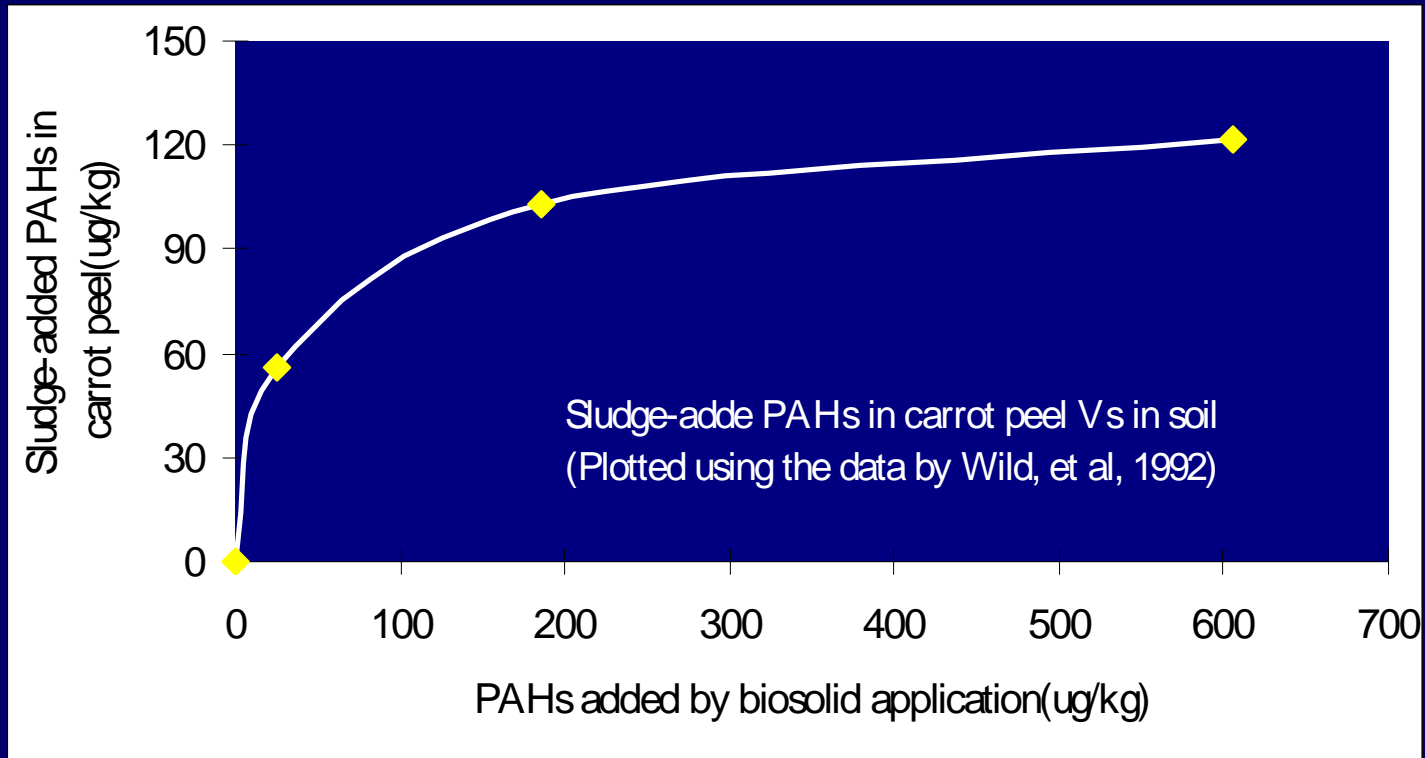


# Non-linear response to Heavy metal



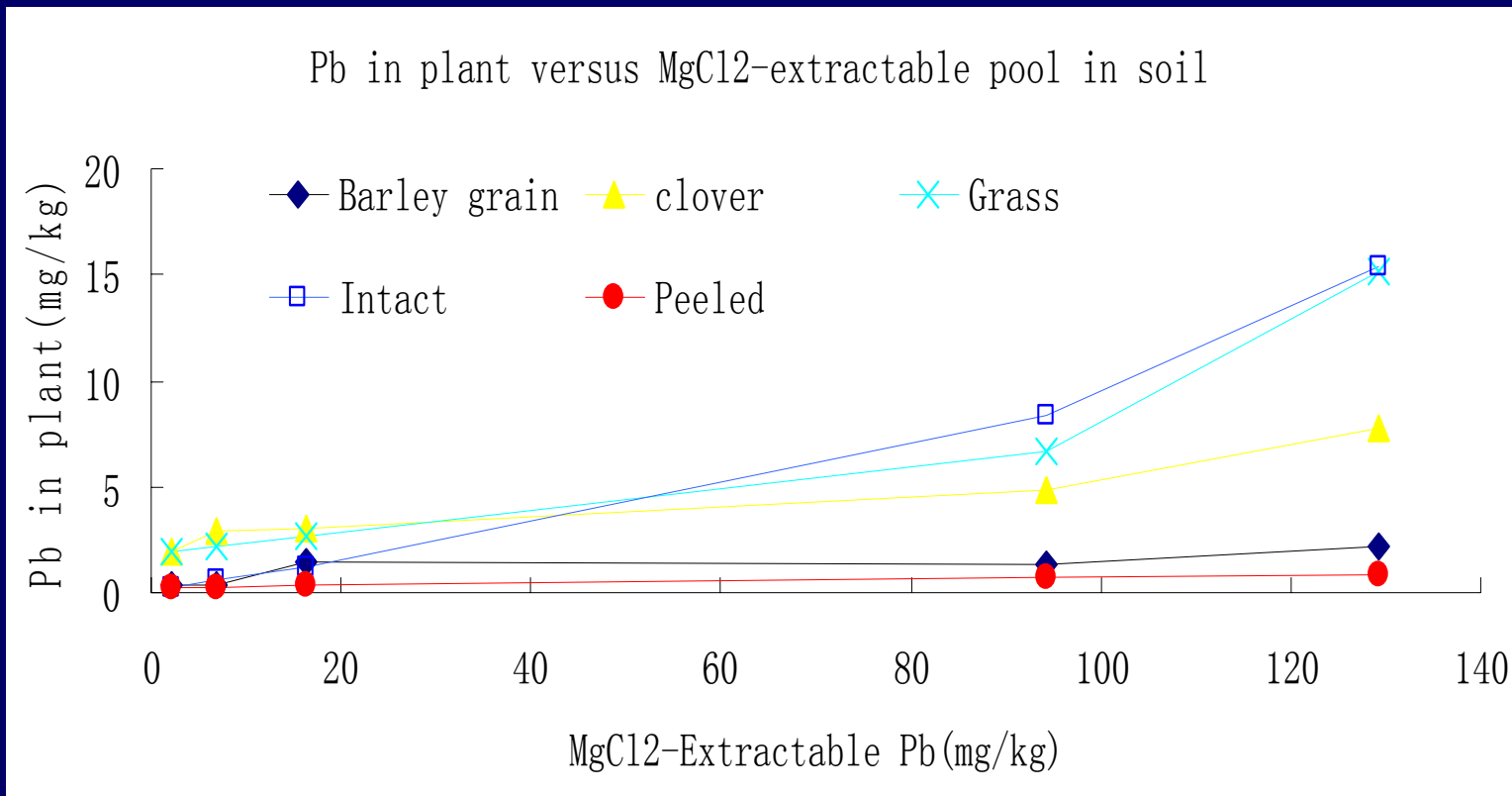


# Non-linear response to POPs





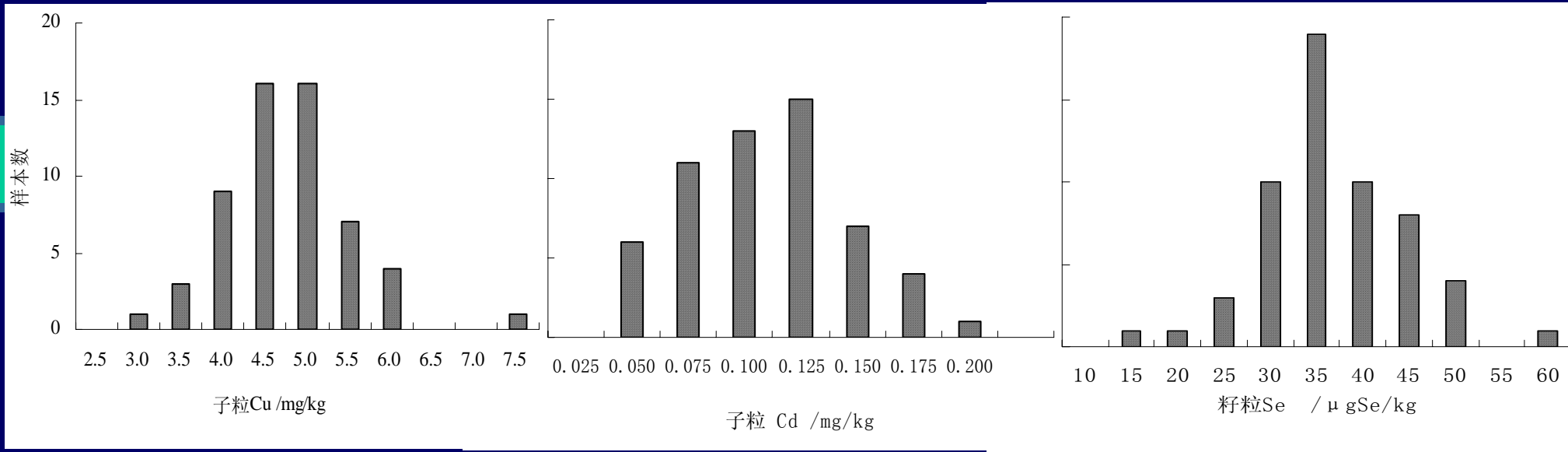
# 重金属植物吸收：依植物种类而异



Source: Dudka et al, 1996



# 同种作物的不同品种的重金属元素含量不同

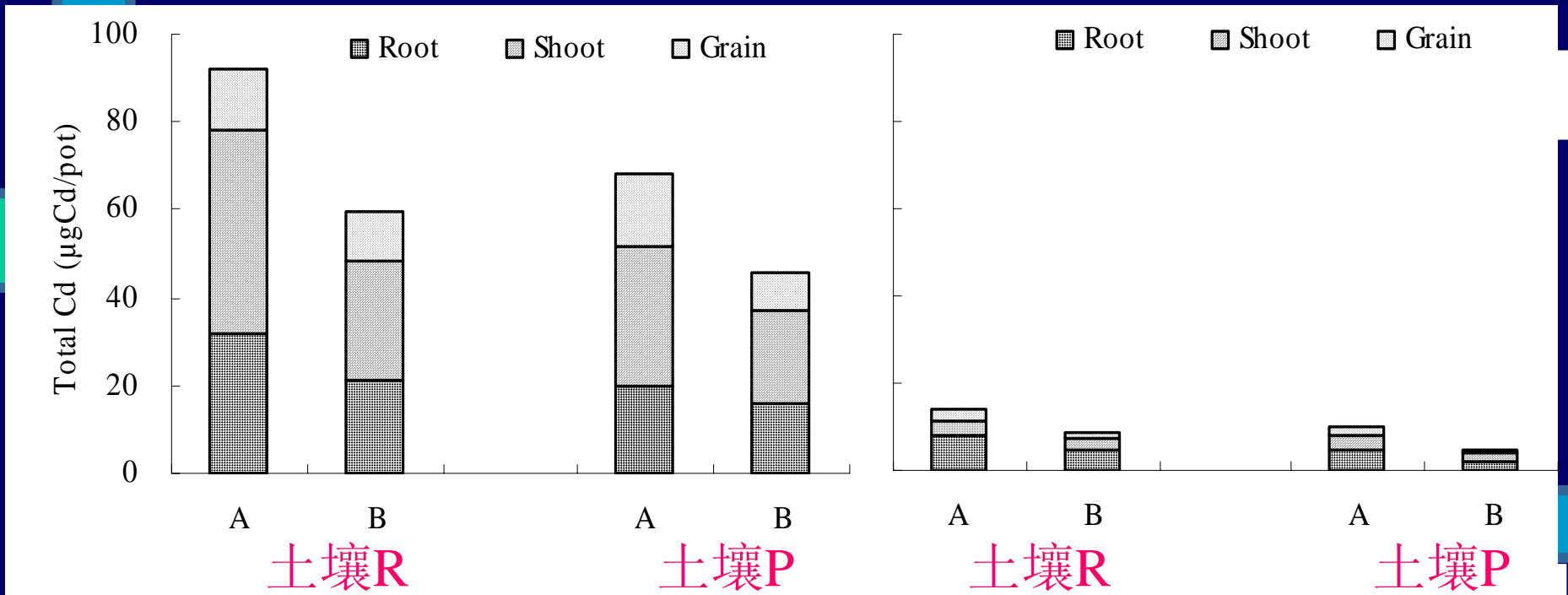


污染元素在食物器官中含量非正态分布

李正文等, 环境科学, 2003



# 为什么土壤差异影响食物安全

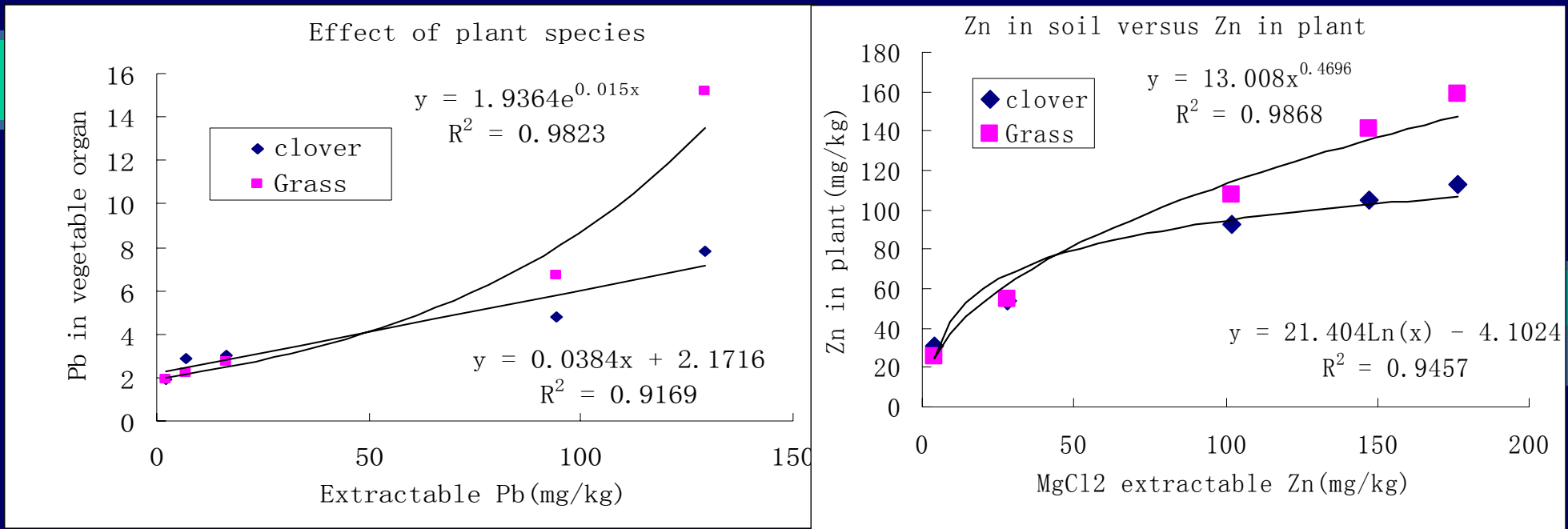


红壤性水稻土(R)pH4.95,黄泥土 (P)pH6.50. pH降低1.5,强吸收基因型水稻子粒Cd升高30%，弱基因型水稻升高60%。

Li, Z., Li, L., Pan, G. 2004. Plant & Soil. In press



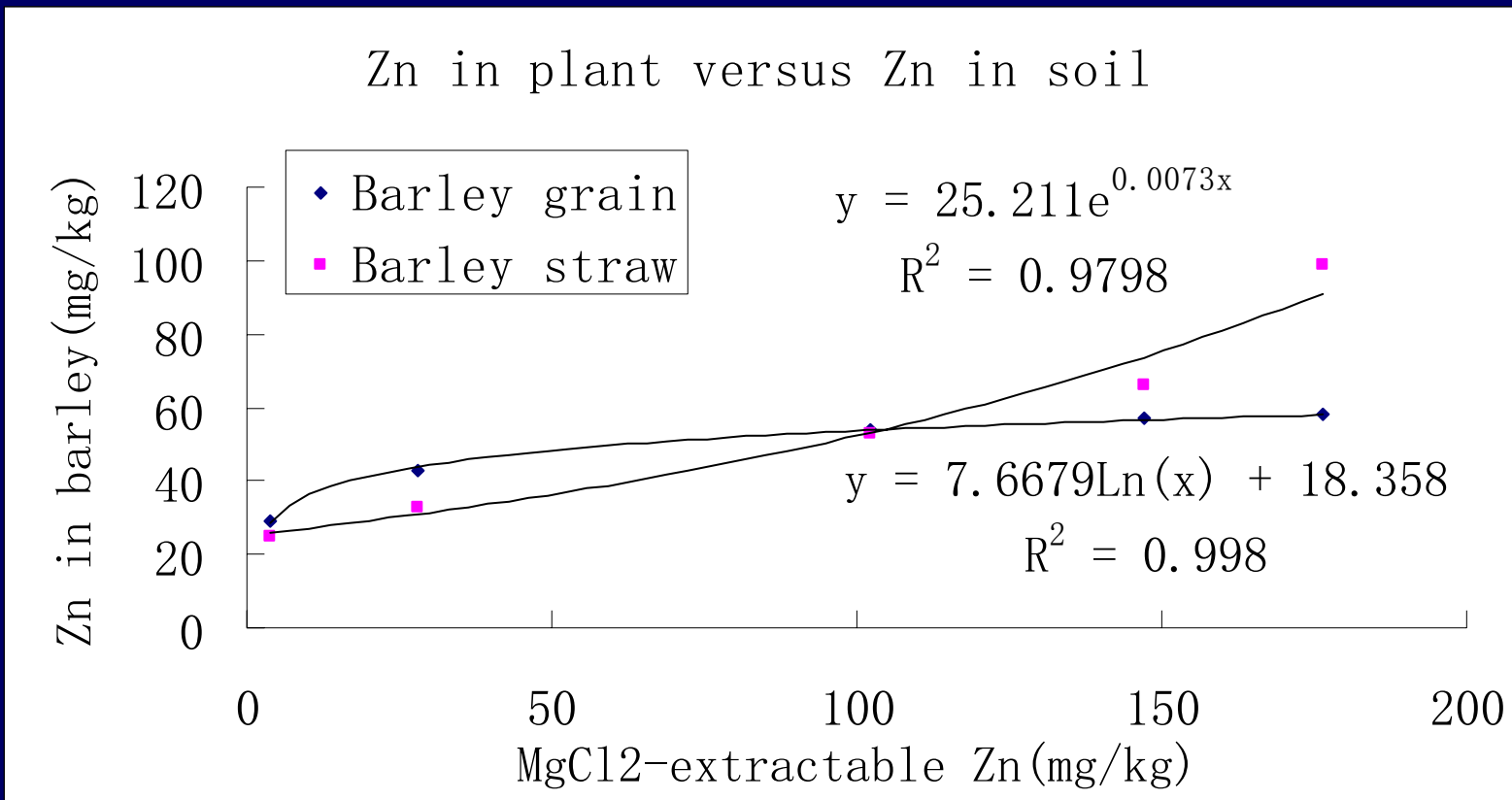
# 重金属植物吸收:依元素不同的变化



Source: Dudka et al,1999. Pot experiment with HMs amended



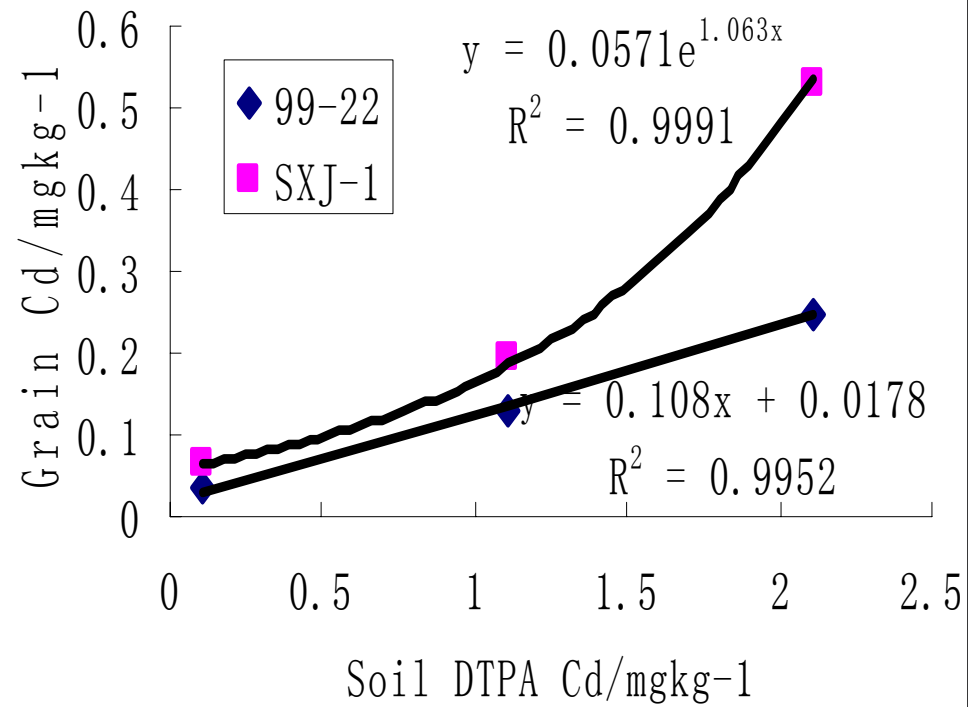
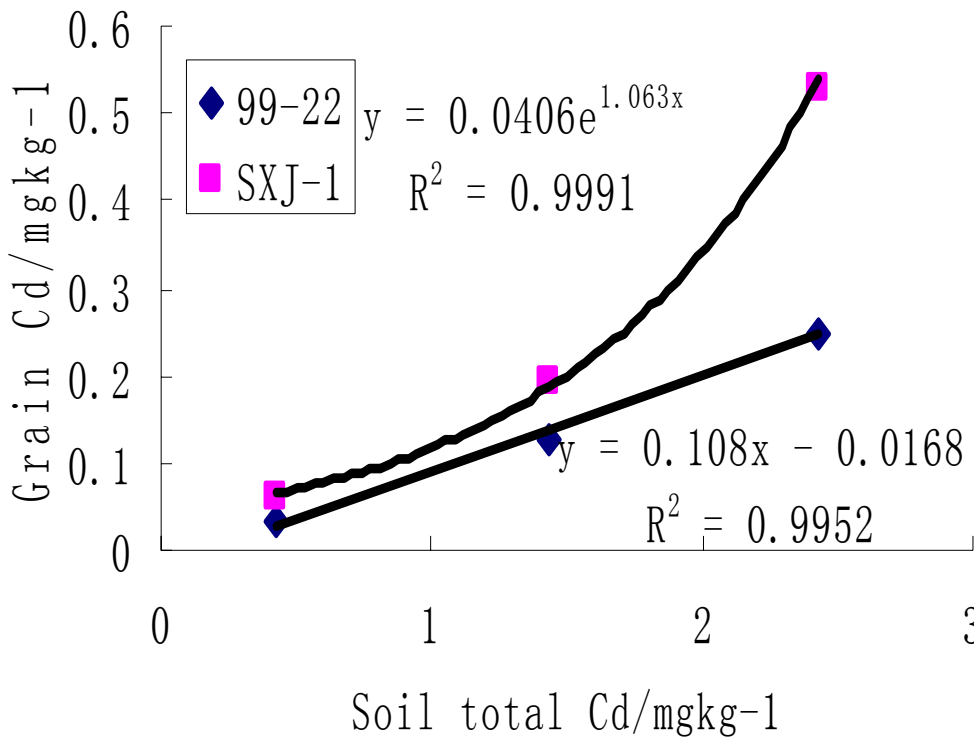
# 重金属植物吸收：植物体内转移与输送的影响







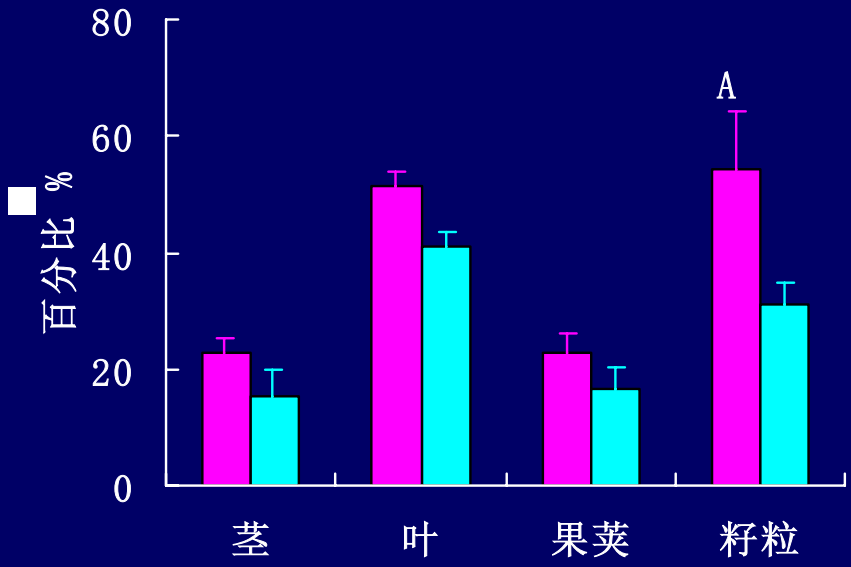
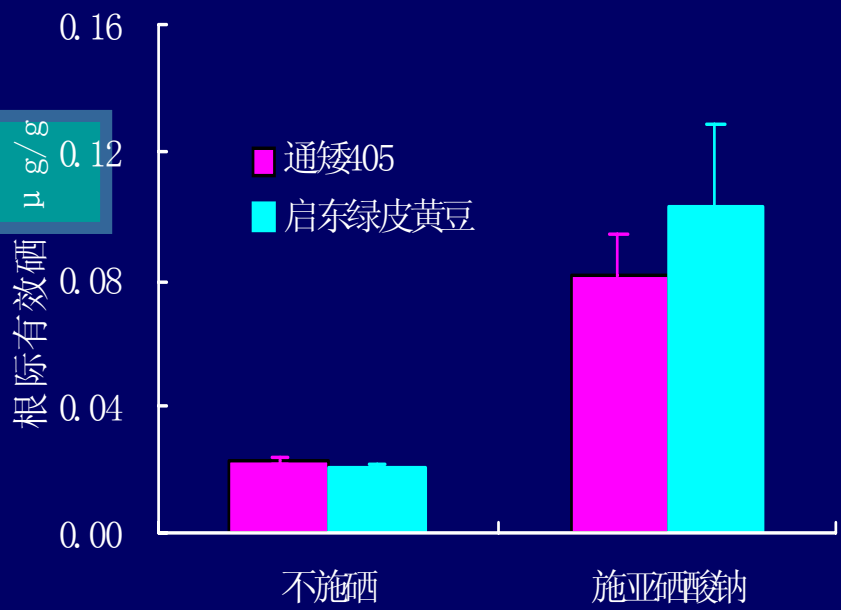
# 品种的基因型效应：吸收机制的不同



李正文, 2003



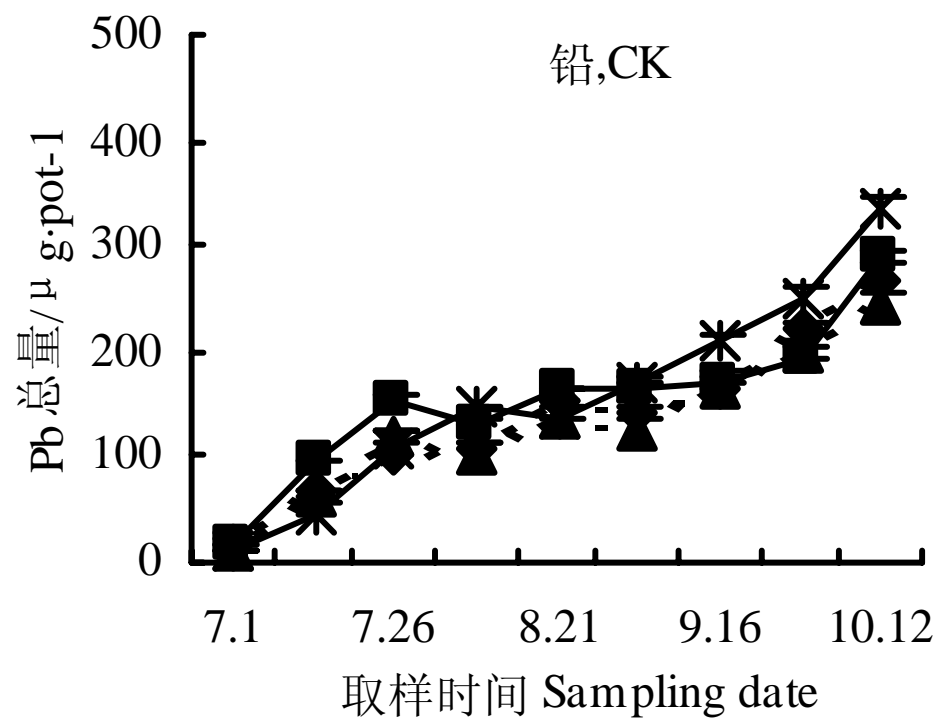
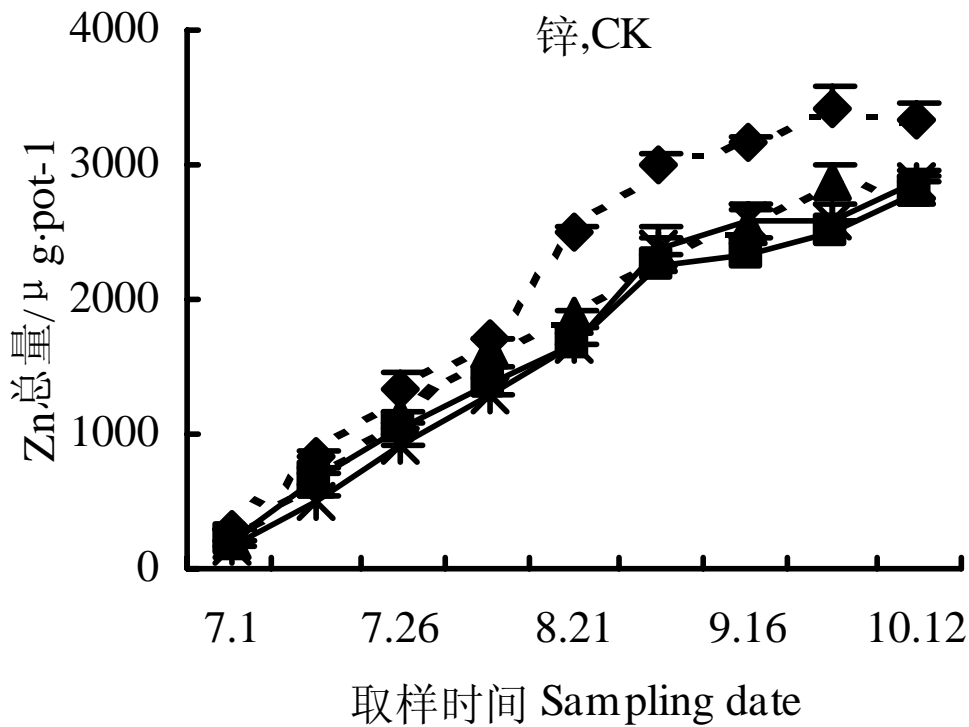
# 基因型效应：转运机制的不同



张艳玲, 潘根兴等, 南京农业大学学报, 2002



# 植物对元素的亲和性：生育期中不同的吸收选择



李正文, 南京农业大学博士学位论文, 2003



# 重金属植物吸收与食品安全:

- 土壤化学控制因素
- 植物控制因素
- (生长时期变化) ■

## ■ 估计土壤重金属的食物安全性:

(土壤环境化学模型+植物生态模型+膳食结构)  $\longleftrightarrow$  人类临界摄入量分配



# 土壤重金属环境效应：

## 稳态与突发（平台效应或定时炸弹效应）

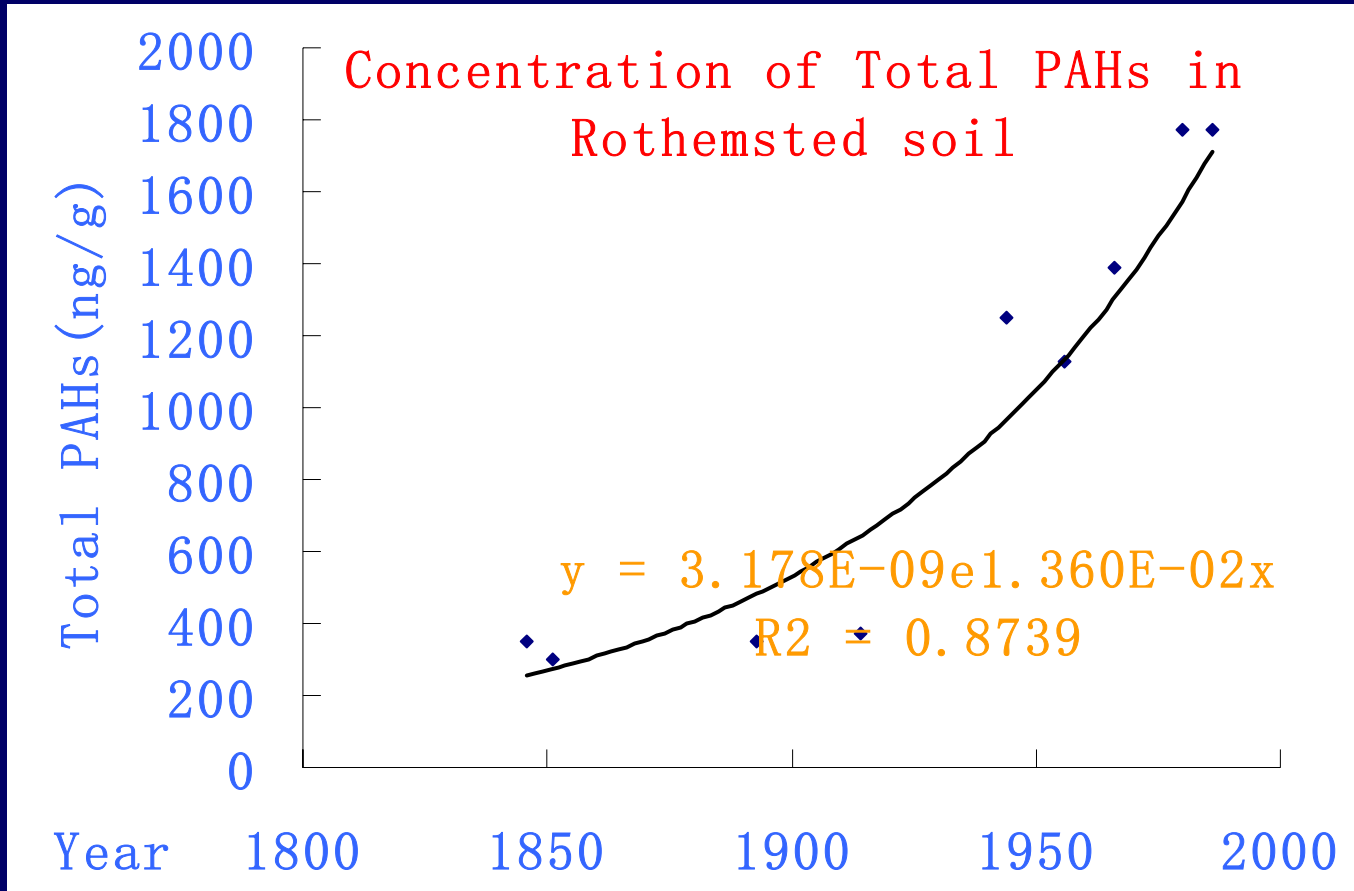
Plateau or time bomb?

- 土壤重金属的强度累积
- 活性演变与限制条件的起闭
- 长期观测效应的判断



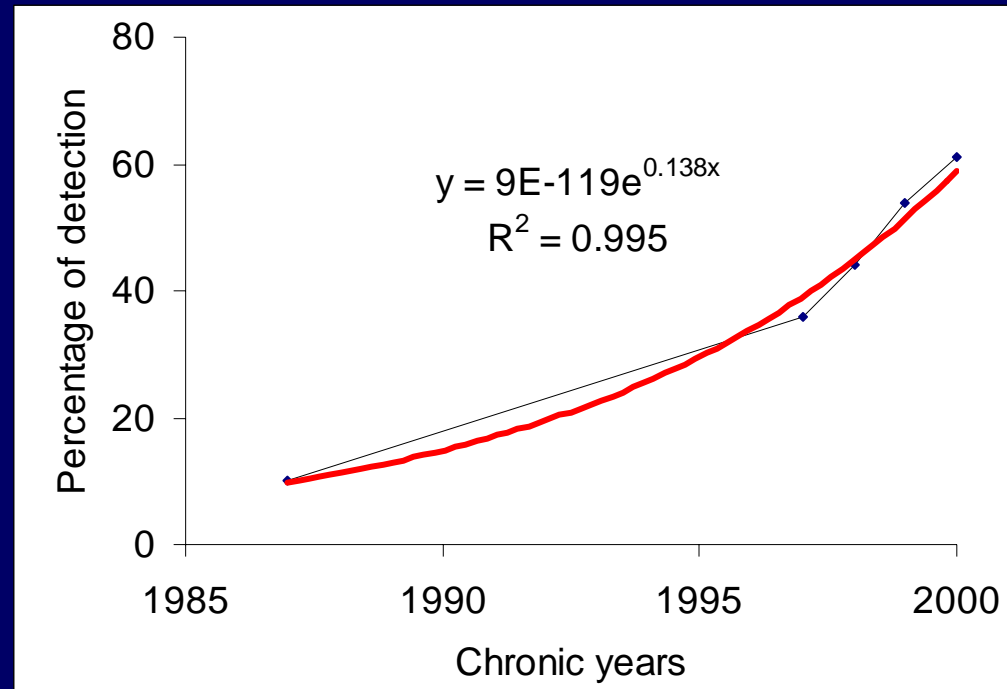


# Accumulation of OCs in Soils





# Time bomb: enhanced release with time



Pesticide residues as detected in vegetables in a chronic sequence in Hebei Province



# 定时炸弹效应：长期施用污泥土壤中重金属 Examples from Rothamsted and Xi'an long-term waste irrigation

- The Cu, Cd & Zn plant uptake slope increasing after cease of sludge application in a 25 yr continuous experiment plot

--- McGrath et al, 2000, JEQ

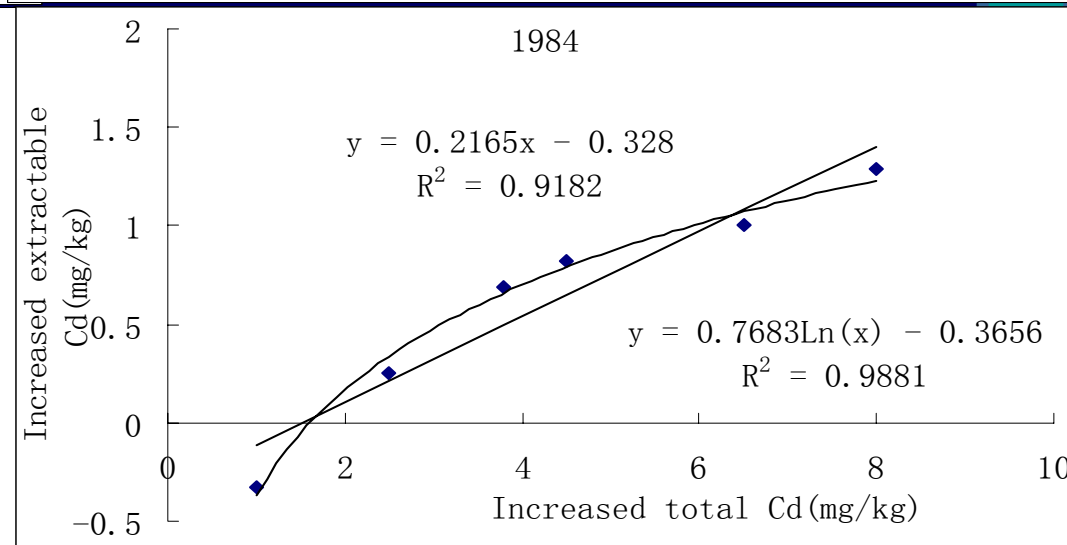
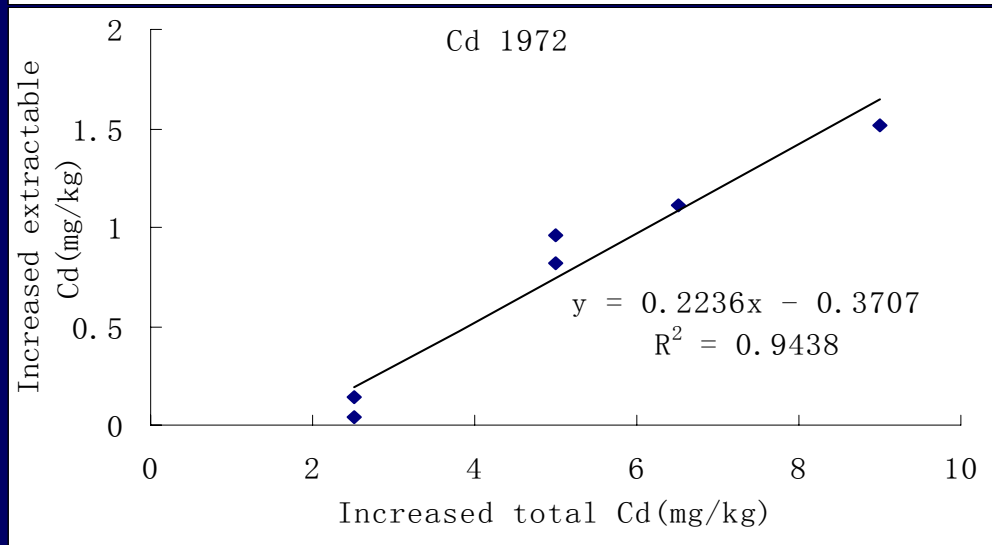
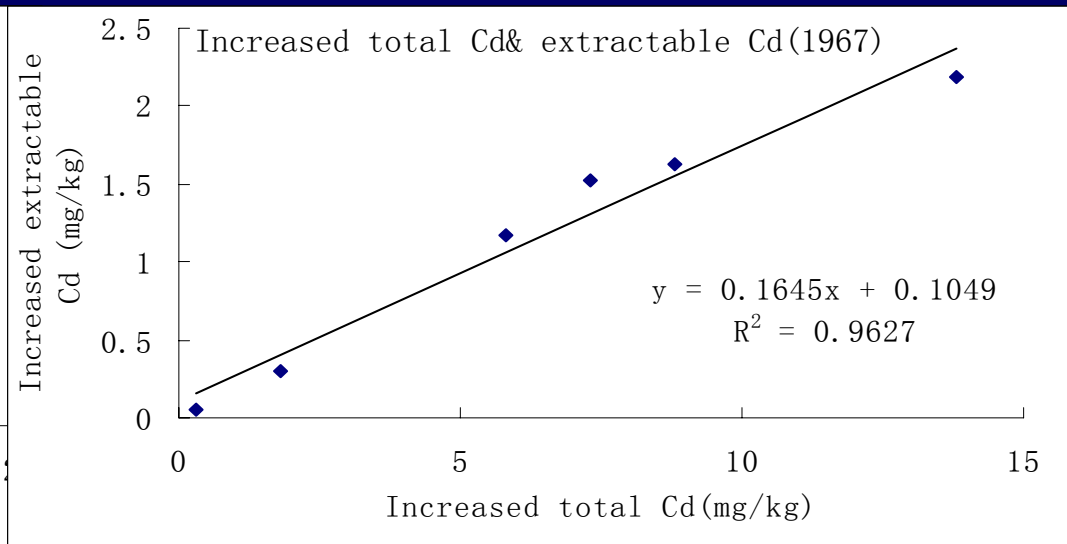
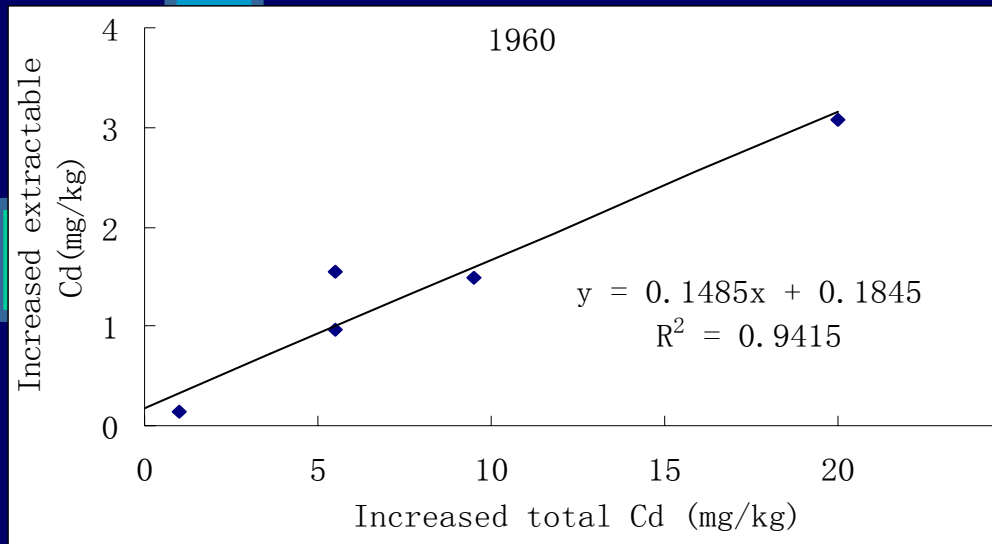
The Cu, Cd % Hg plant uptake slope keep higher in waste water irrigated lands for 30 yrs than that without waste water irrigation。 HMs in leafy vegetables exceeding the guideline for human dietary

庞奖励等, 土壤与环境, 2001, 10 (2): 94~97





# Soil Cd mobility increased with years after cease of sludge application: An example of Rothamsted experiment (McGrath et al, 2000)





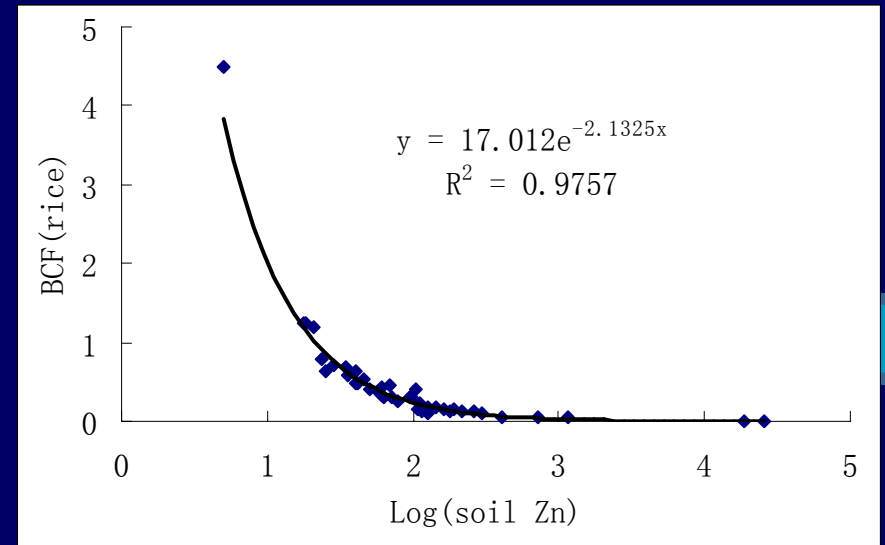
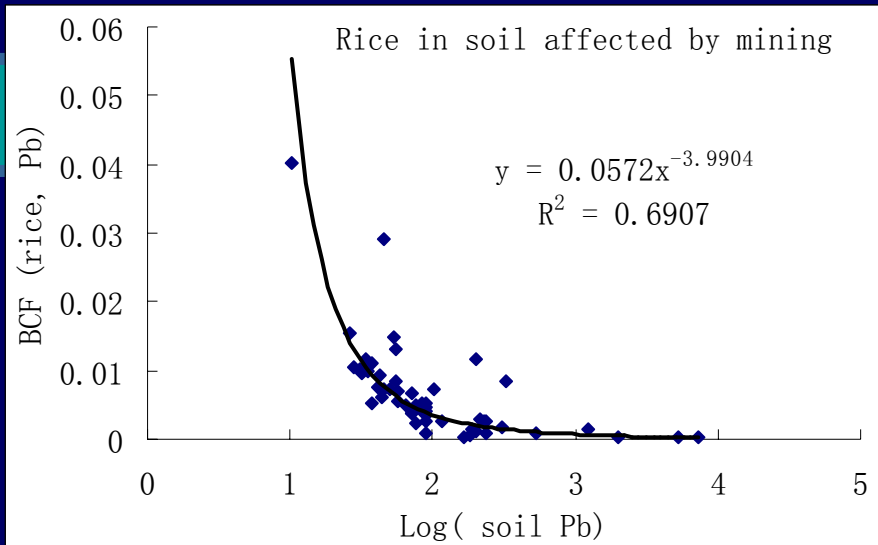
# 平台效应: Plateau theory

- 随着输入增加活性降低 Reducing mobility under increasing inputs
- 污染胁迫下生物吸收效率的降低 Depressing uptake rates by biota under increasing stress
-



# Plateau: 水稻对污染土壤中重金属的吸收

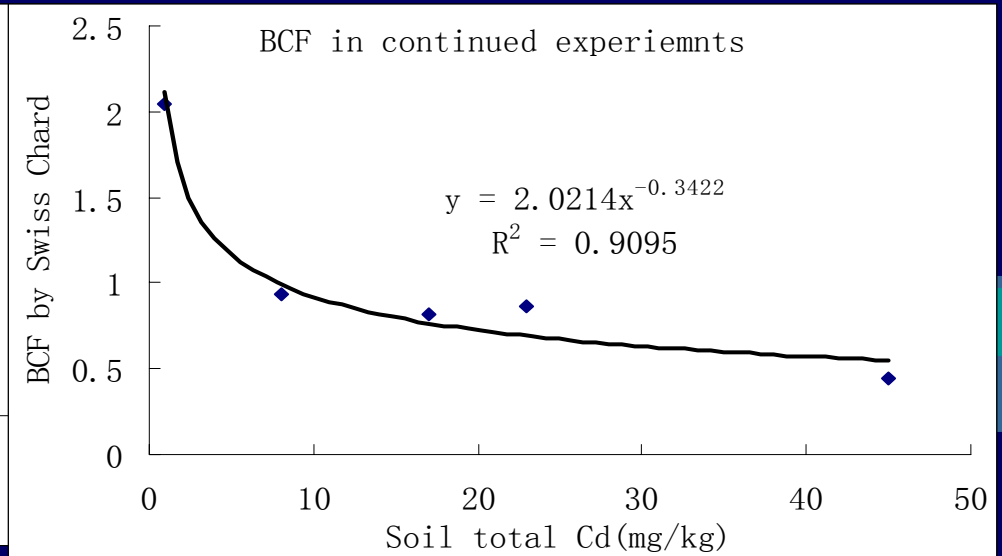
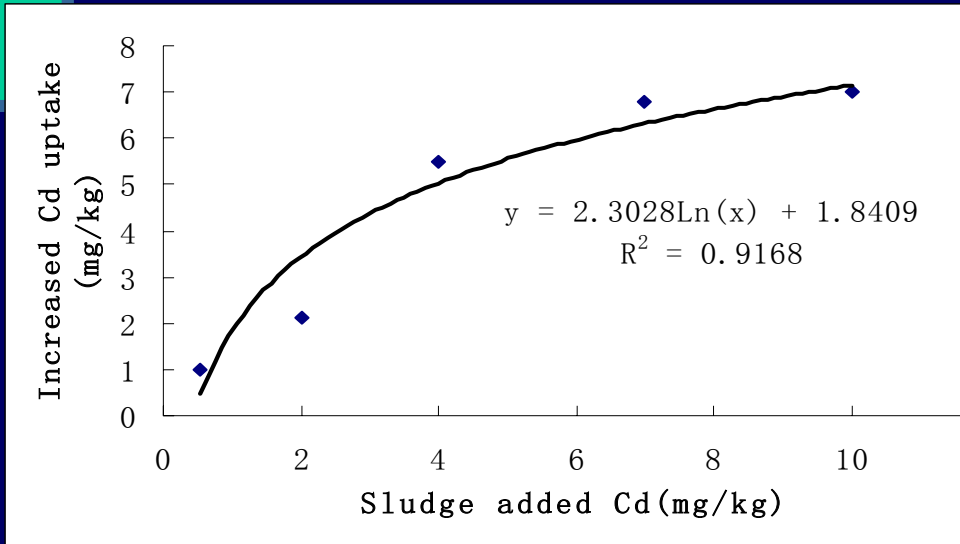
## Example of rice HMs under pollution



根据张乃明资料整理



# Plateau: 植物对污染重金属的非线性响应 plant uptake in exponential response to increasing inputs



根据 Chang et al, 1997, JEQ资料计算

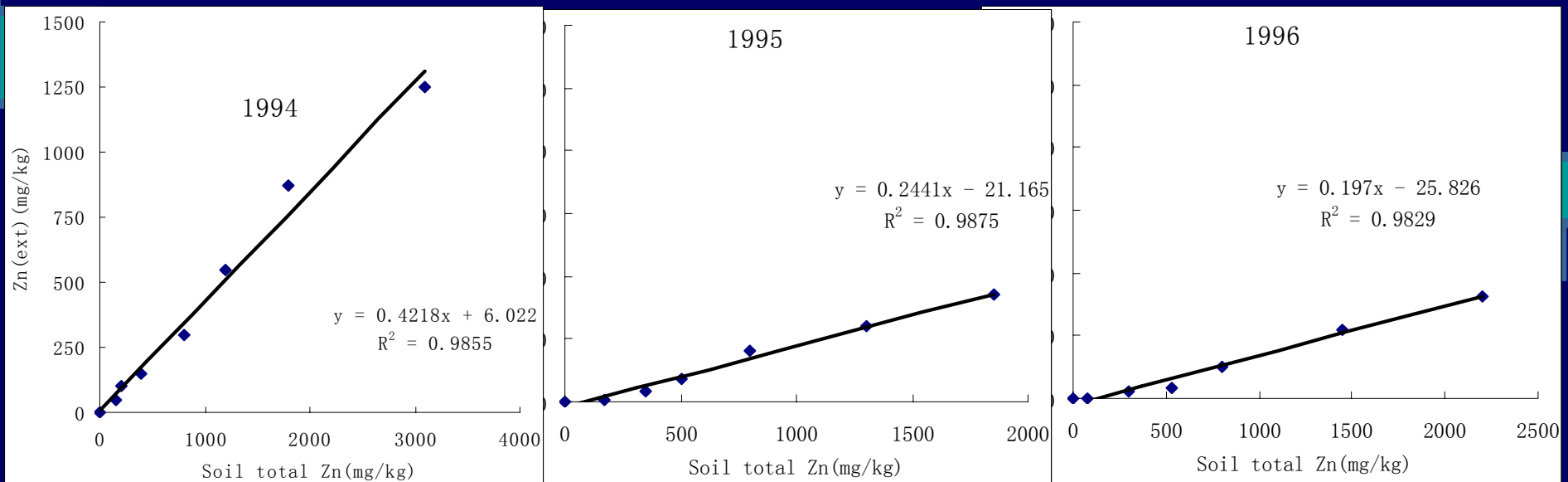


# 土壤的平抑机制： Soil mechanism for plateau

- Soil aging 土壤老化
- Soil sequestration 土壤固定
- Enhanced degradation (有机污染物)



# 土壤老化：污染输入重金属可浸提性的年际降低 Rapidly reducing of soil extractability of amended heavy metals ()

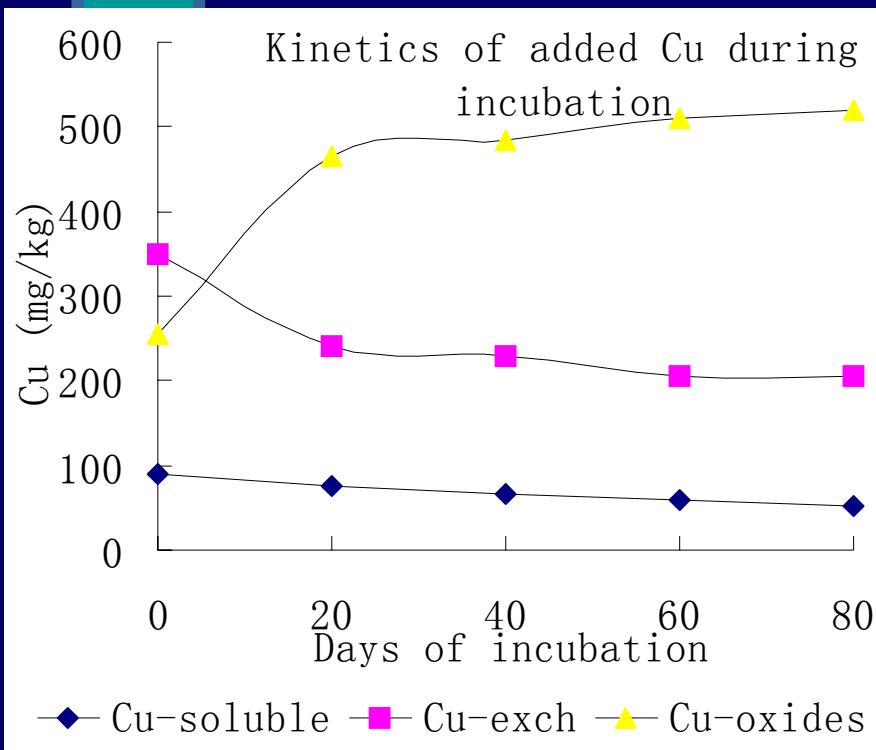


Average  $\text{CaCl}_2$  extractable Zinc concentration as a function of total concentration of the test field plots amended with different amount of  $\text{ZnCl}_2$



# Kinetics of fractionation in soil during spiked experiment

Ref: Darmawan and Shin-Ichiro Wada. Kinetics of speciation of copper, lead, and Zinc loaded to soils that differ in cation exchanger composition at low moisture content. *Comm. Soil Sci. plant Anal.* 30(17&18),1999:2363-2375



Soil:

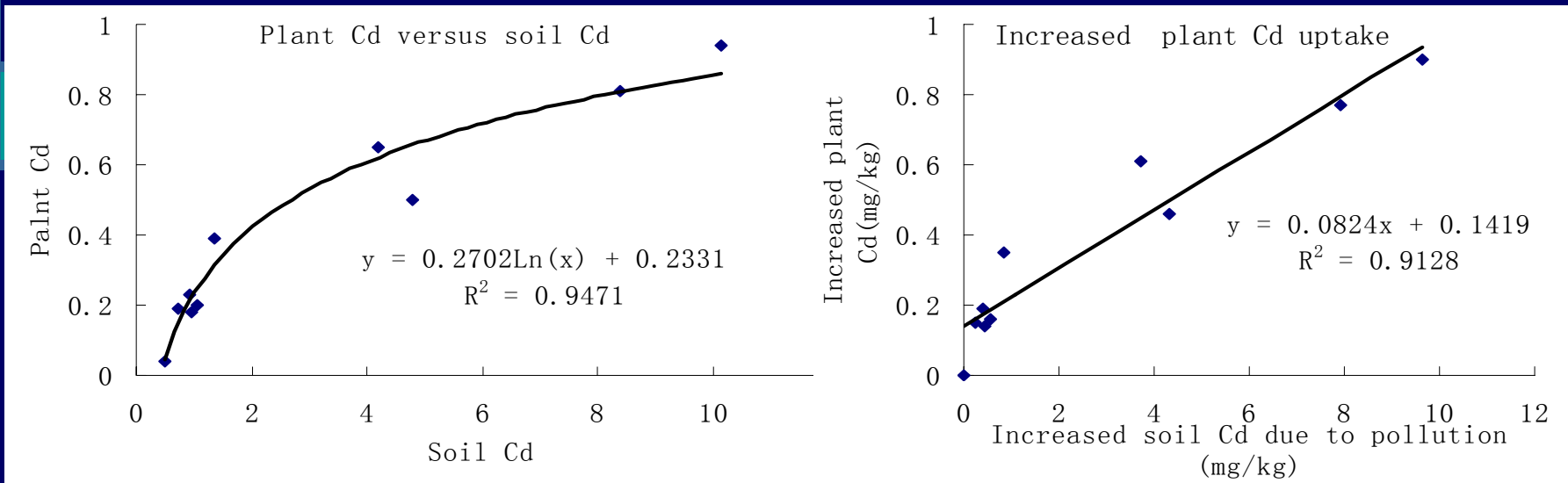
pH 6.1; SOC 8.81g/kg; Clay 44.4%; CEC 9.2 cmol/kg; silicate mineralogy



# 土壤老化与固定：植物吸收降低的可能机制

## Soil aging and sequestration:

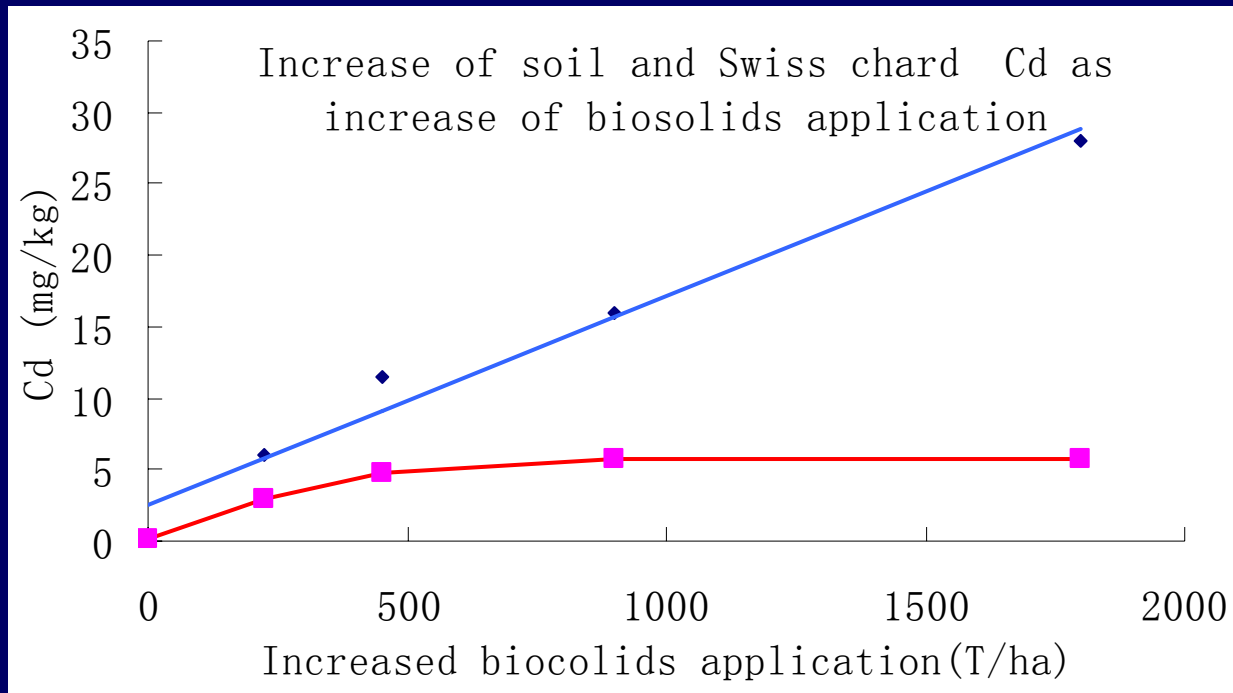
a mechanism for preventing plant uptake in excess







# Soil aging and sequestration: a mechanism for preventing plant uptake in excess

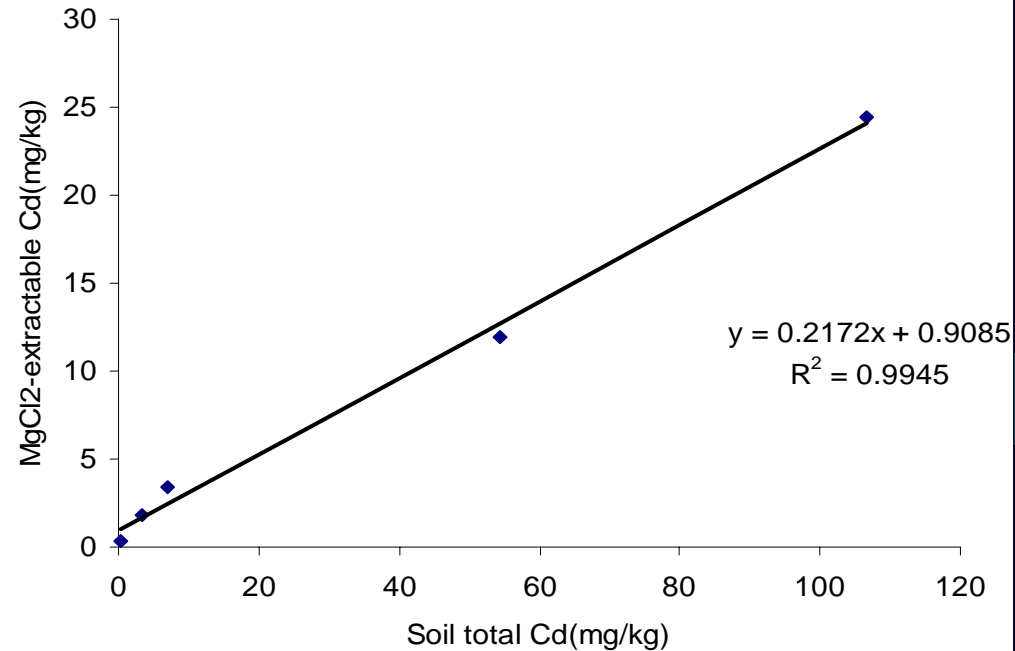
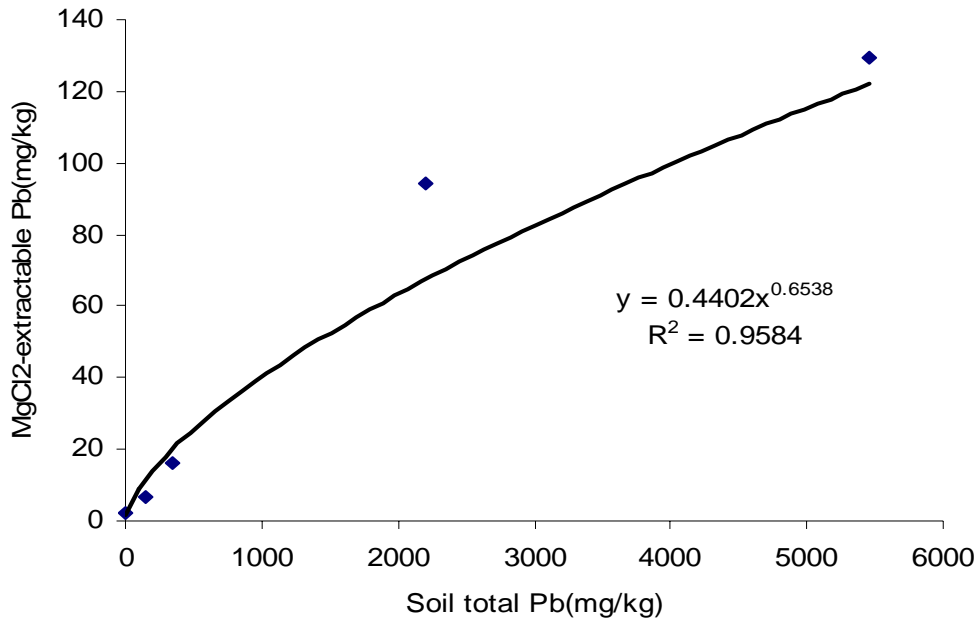


Data source : Chang et al, 1997



# 土壤老化与固定因元素而异

## Aging of HMs in soil: varying with elements

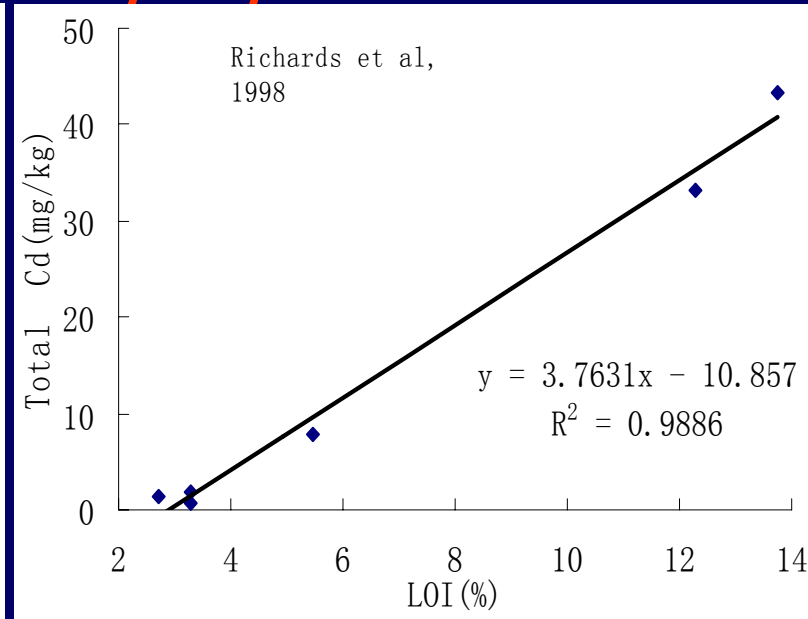
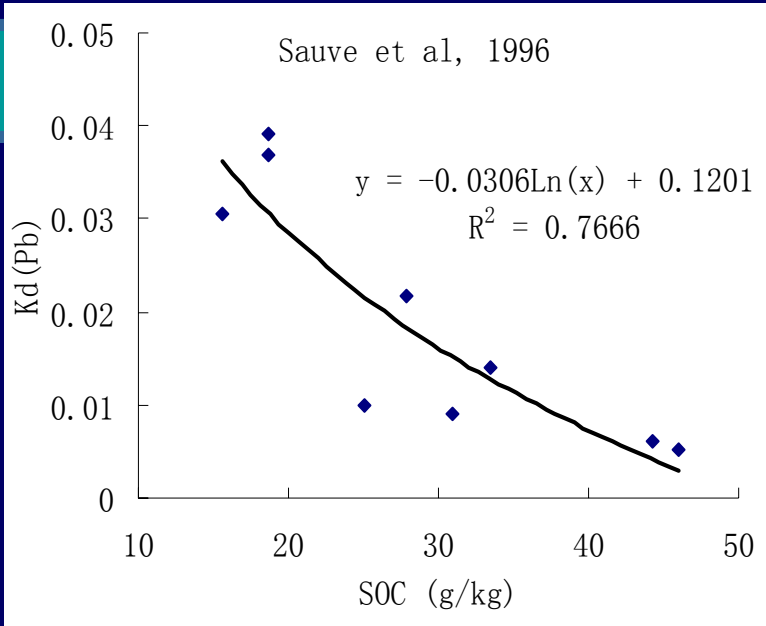


The MgCl<sub>2</sub> extractable as related to the total HM pool analyzed at the end of pot experiment for one cropping with initially spiked HMs(Dudka et al, 1999)



# 土壤固定与有机质和吸附相性质有关

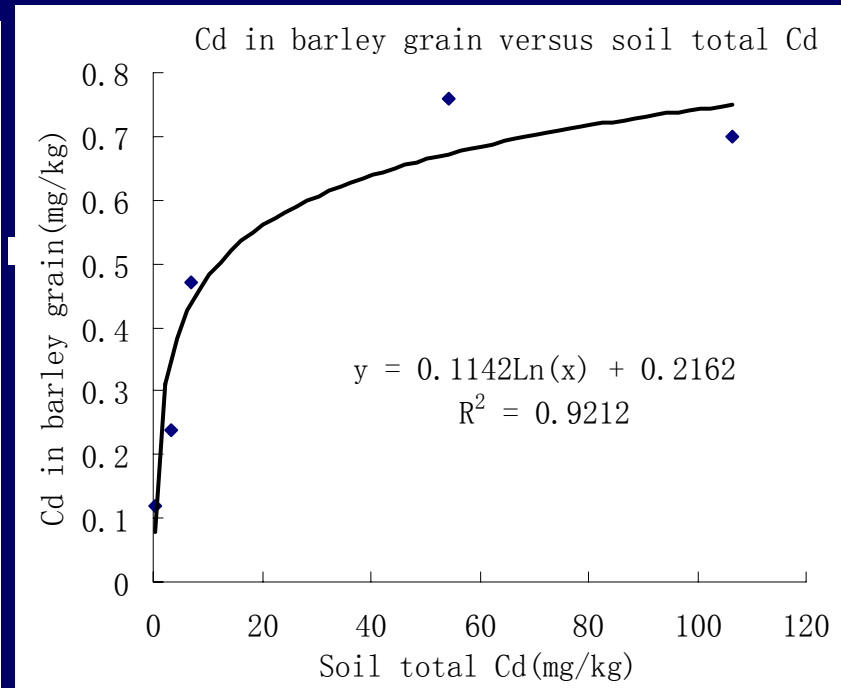
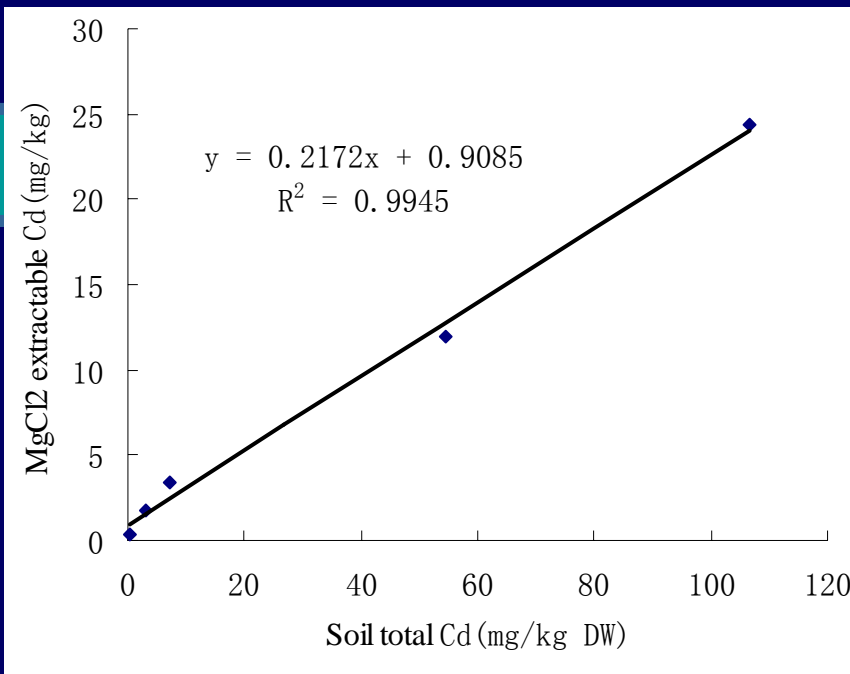
## Sequestration of heavy metals: Effect of SOC and oxy-hydrates





# 植物平抑机制：有效态库的非决定性

## Plant uptake: function of soil available pool?



Data source: Dudka et al, 1996)



作业：

按下列关键词：土壤-作物（植物），**重金属**，**食物安全**，**土壤环境**，环境标准，迁移-分配，土壤环境过程，基因性差异等

有选择地写一段综述论文

# ■ 使人类对土壤的利用与土壤-植物系统的耦合与和谐！

■ Making soil use in Harmony With Soil-Plant system !

■ 谢谢！ 欢迎讨论！

