Modeling Transfer and Partitioning of Potentially Toxic Pollutants in Soil-Crop System for Human Food Sucuriety

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A Partial Fulfillment of the Project

-"Developing Human Health-related Chemical Guidelines for Reclaimed Wastewater and Sewage Sludge Application in Agriculture"

-A WHO Project (GL.GLO.PHE.418.XD.00.4.999.00)

Goal and Objective

- Approach to a feasible method to estimate acute pollutant uptake by human food from agricultural soils;
- A approach to developing general guidelines for controlling the human food intake of PTCs from plant food by controlling maximum concentration of PTCs in amended soils

I. Soil-plant concentration relationship

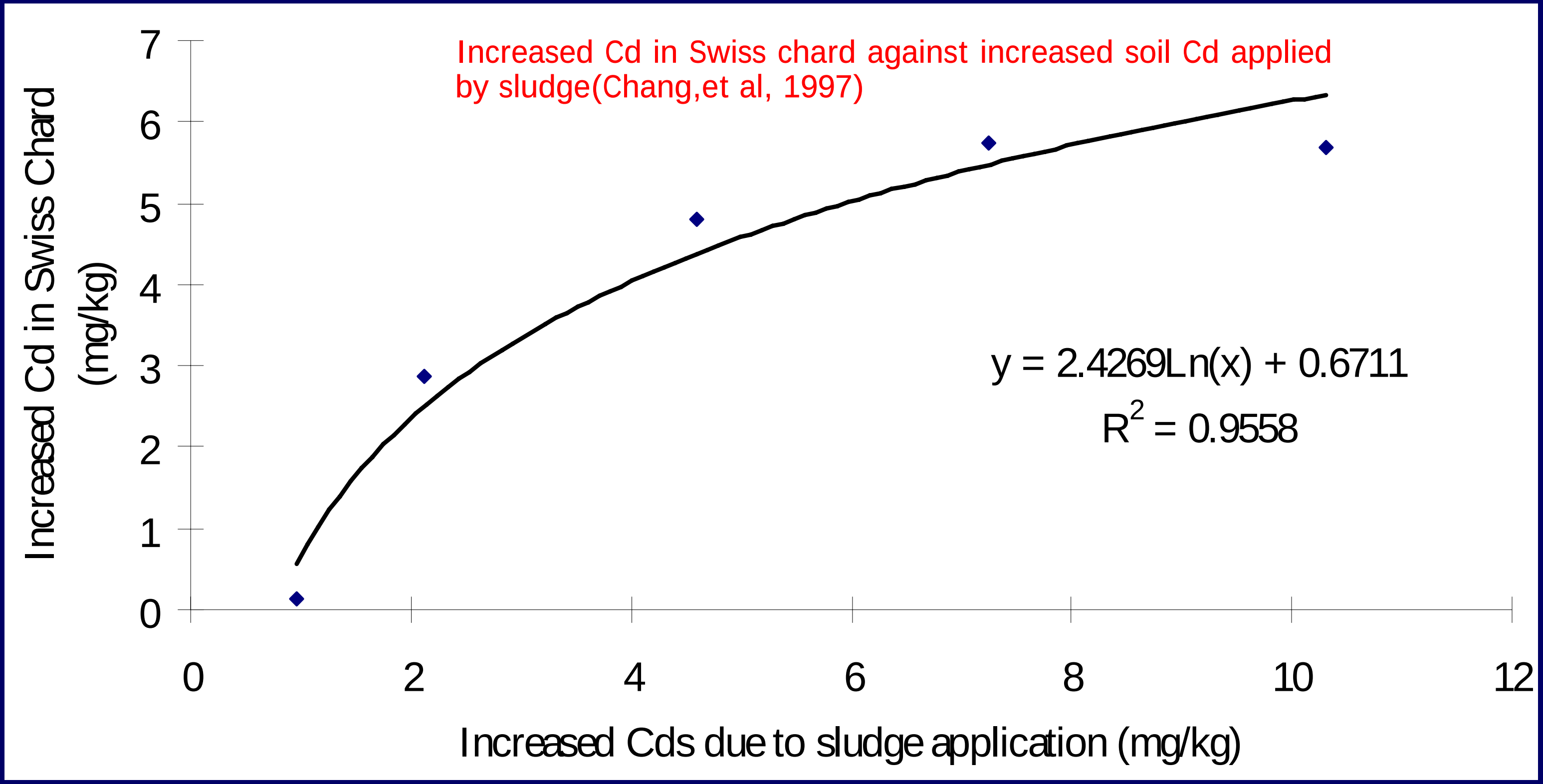
Available Data for estimating PAFs

- 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

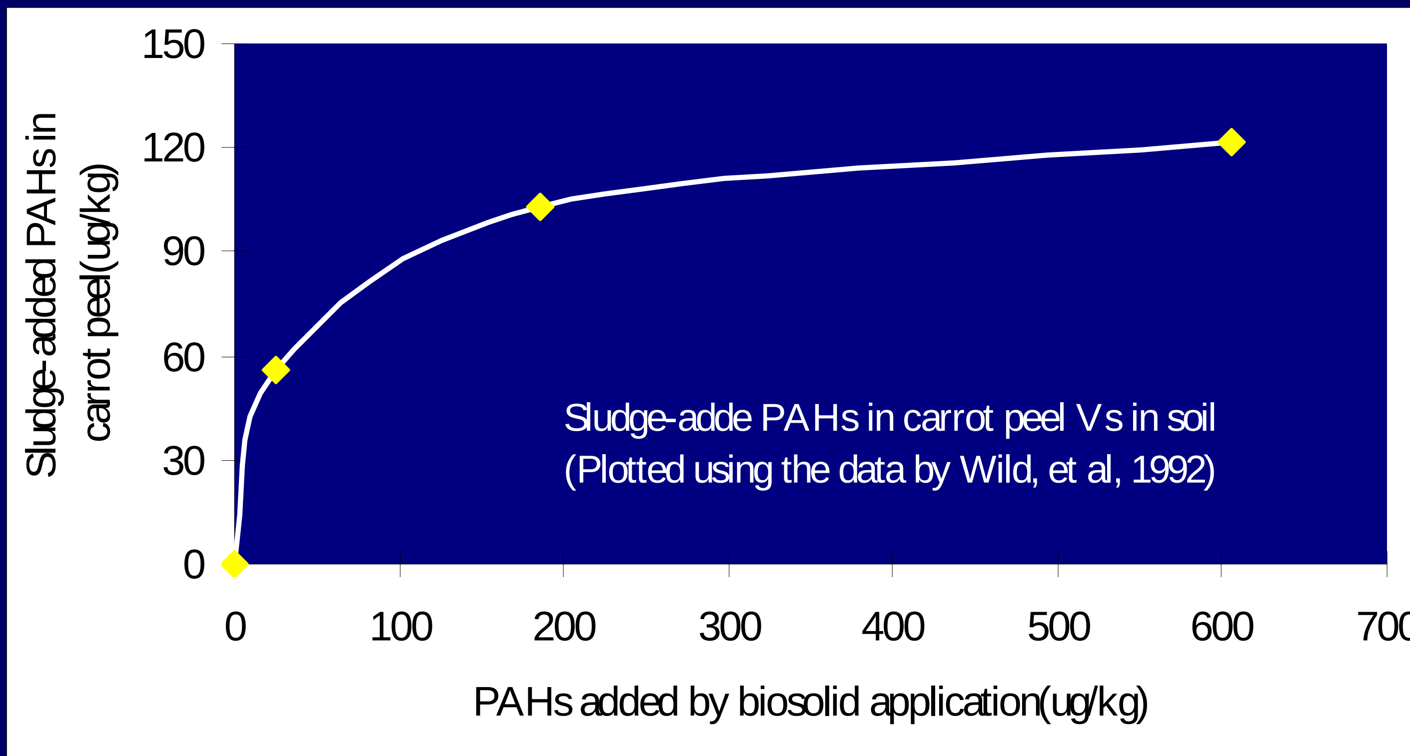
Plant uptake of PTCs depending on soil concentration (non-linear response)

- Plant control on absorption
- Soil control on mobility and availability
- Other factors associated with sludge application

Non-linear response to Heavy metal



Non-linear response to POPs



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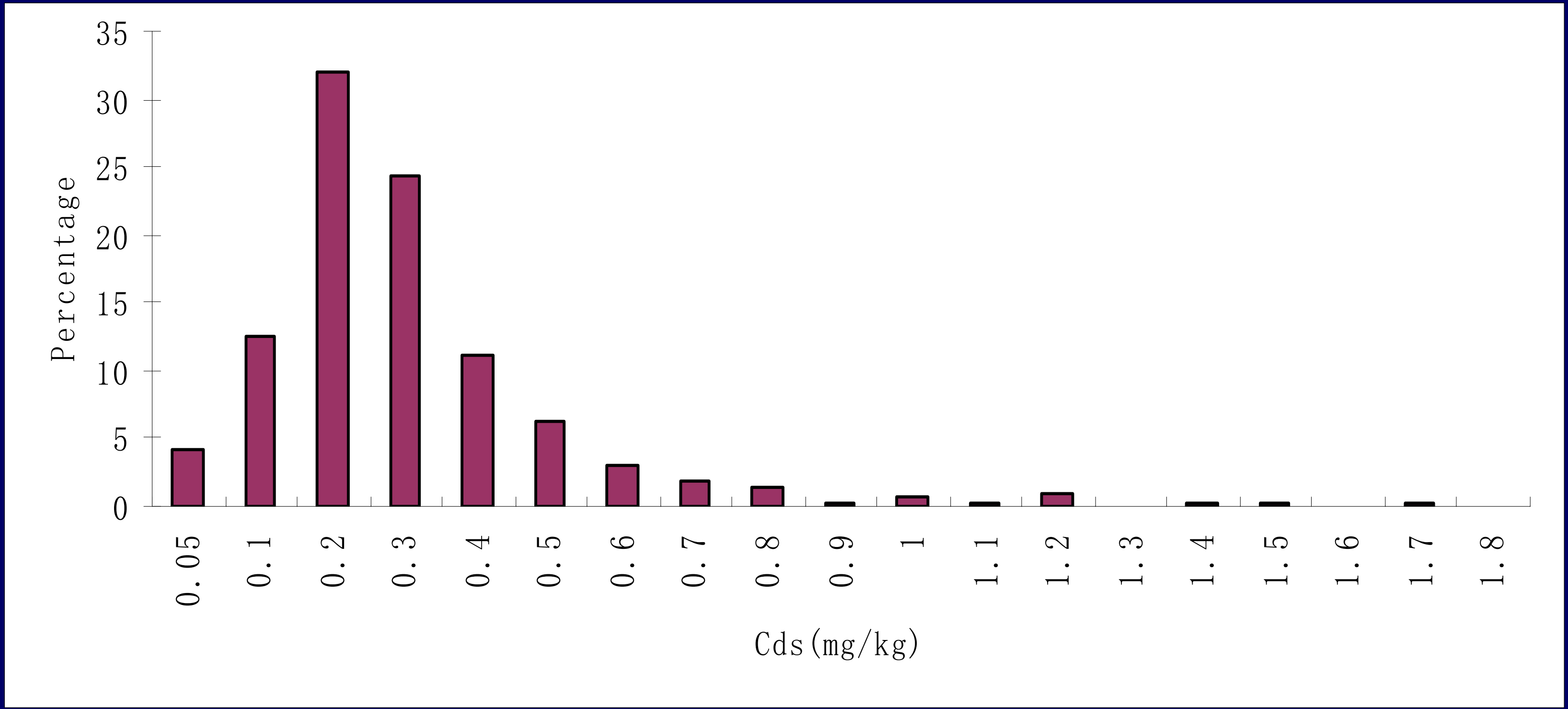
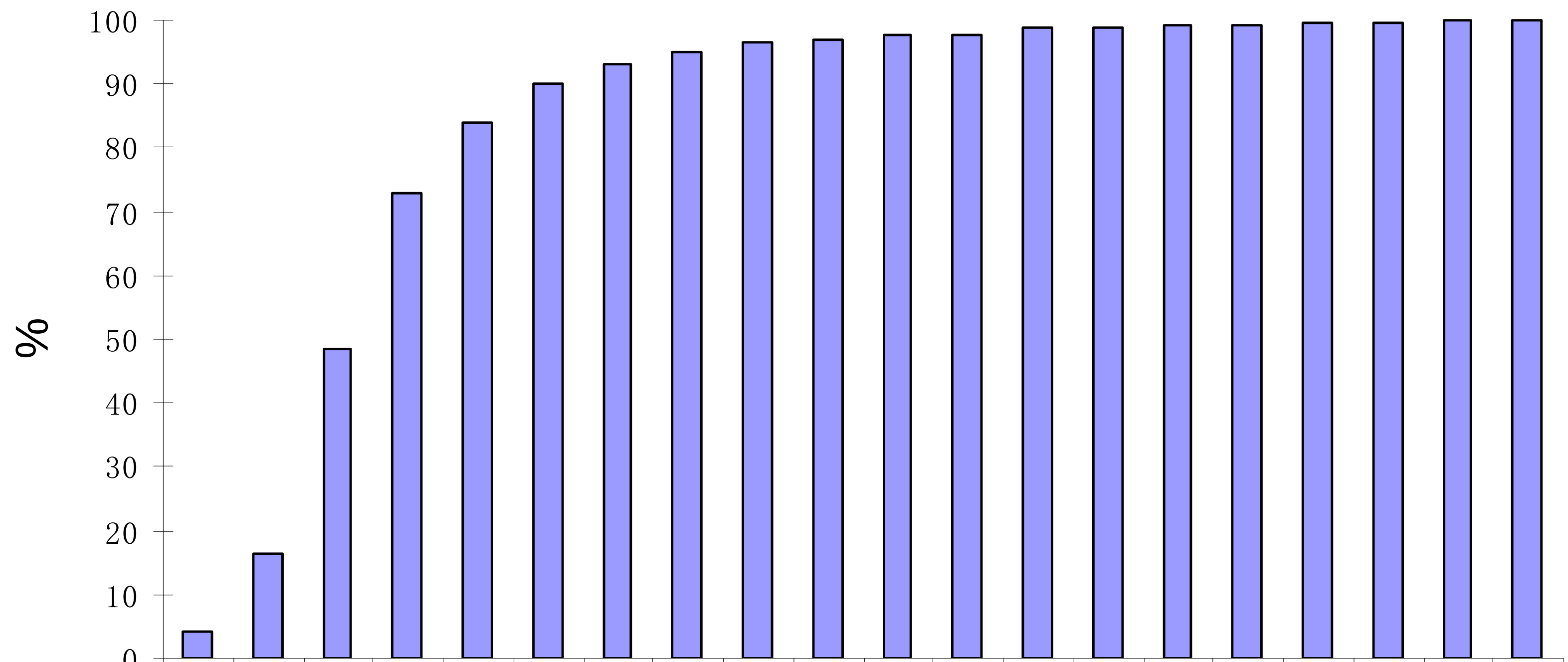
Distribution of observation values of Cds (mg/kg)



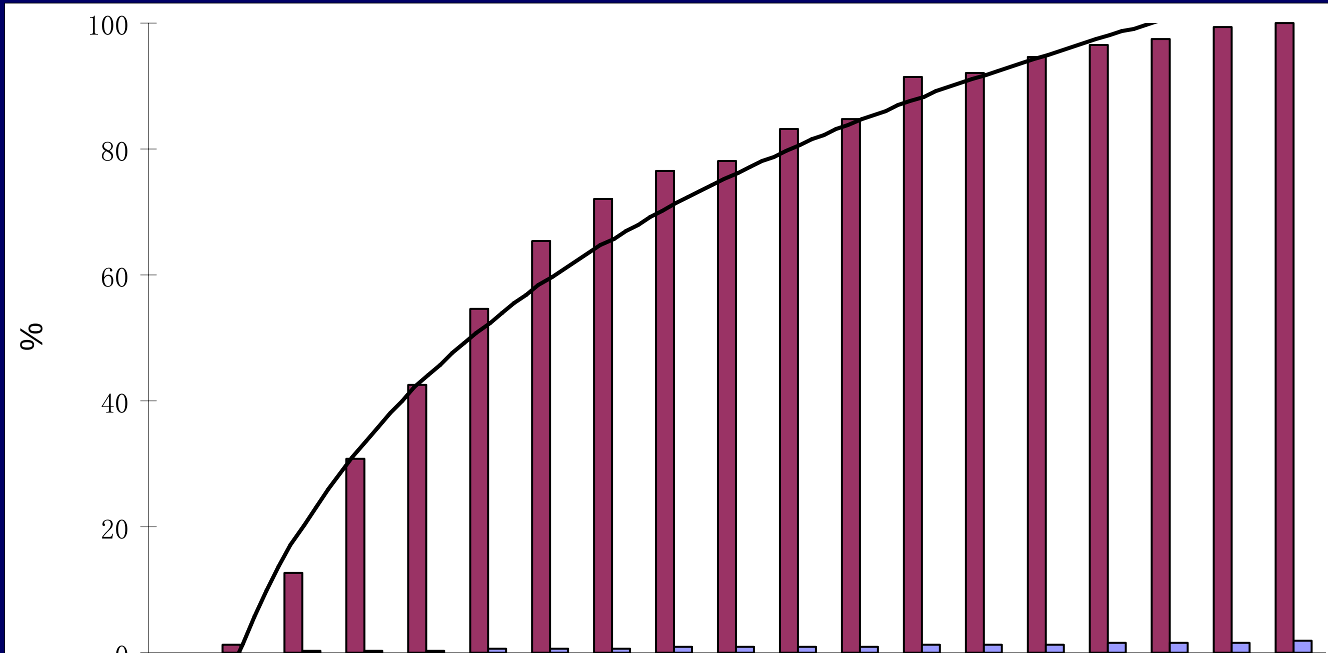
Cd*s* probability distribution initial pollution :1.5ppm



	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	>1.8
Series1	4.14	16.5	48.5	72.9	83.9	90.1	93.2	95.1	96.4	96.8	97.5	97.9	98.7	98.8	99.1	99.4	99.5	99.7	99.8	100.

Cds(ppm)

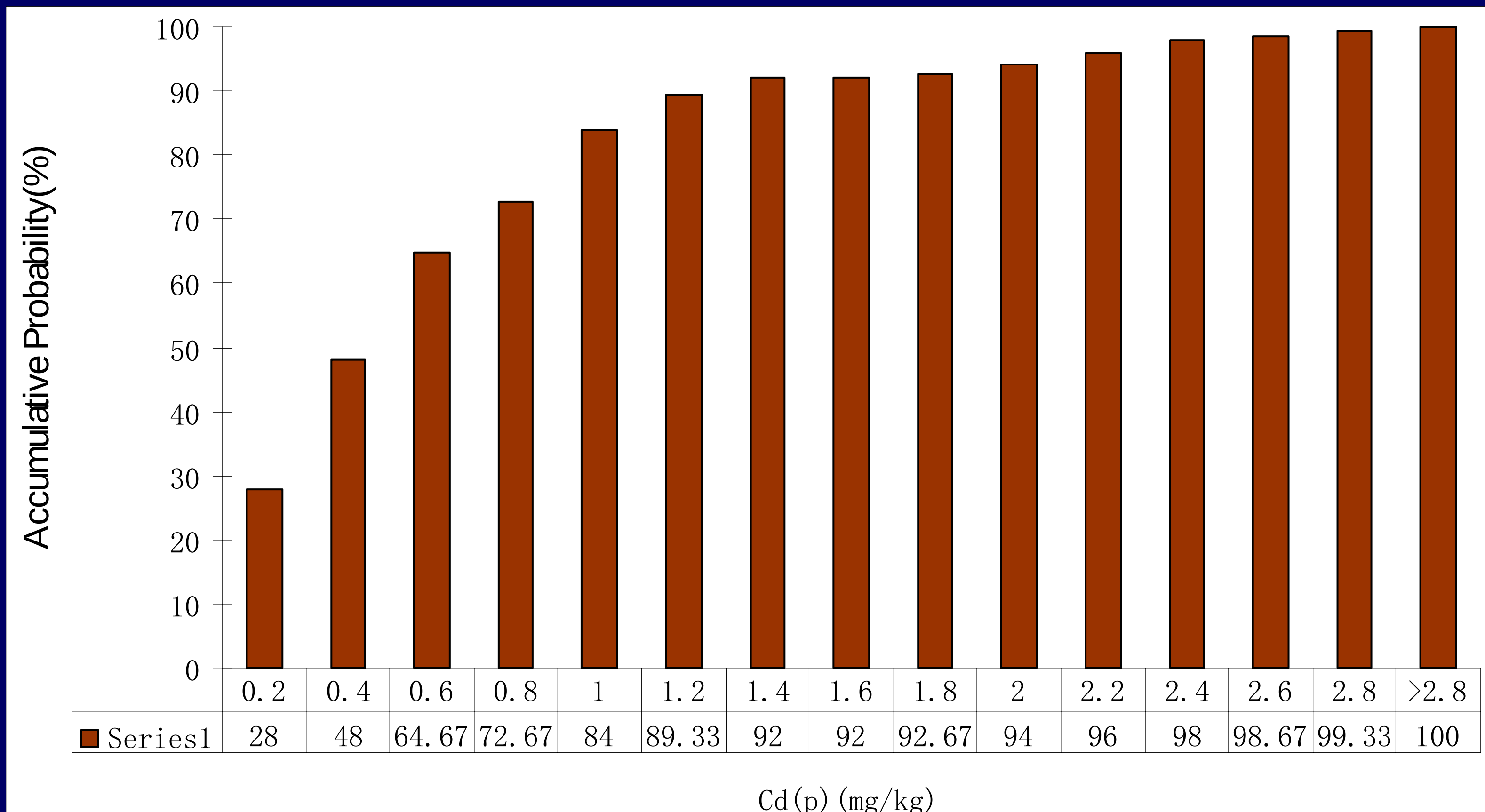
Probablity distribution of Cds in lettuce fields



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Series2		1.33	12.6	30.6	42.6	54.6	65.3	72.0	76.6	78.0	83.3	84.6	91.3	92.0	94.6	96.6	97.3	99.3	100.
Series1	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8

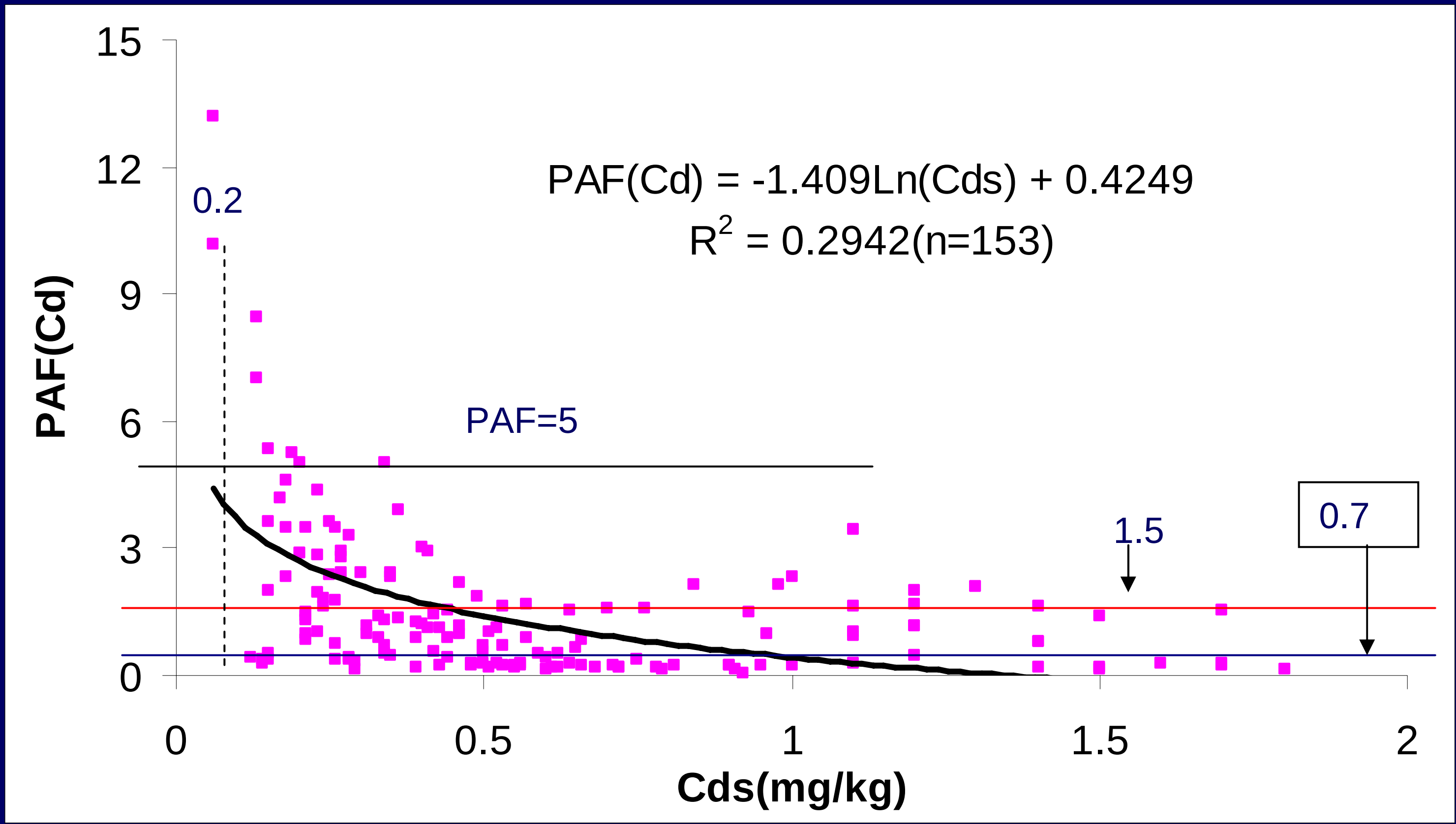
Cds(ppm)

Probability distribution of Cd(p) in lettuce

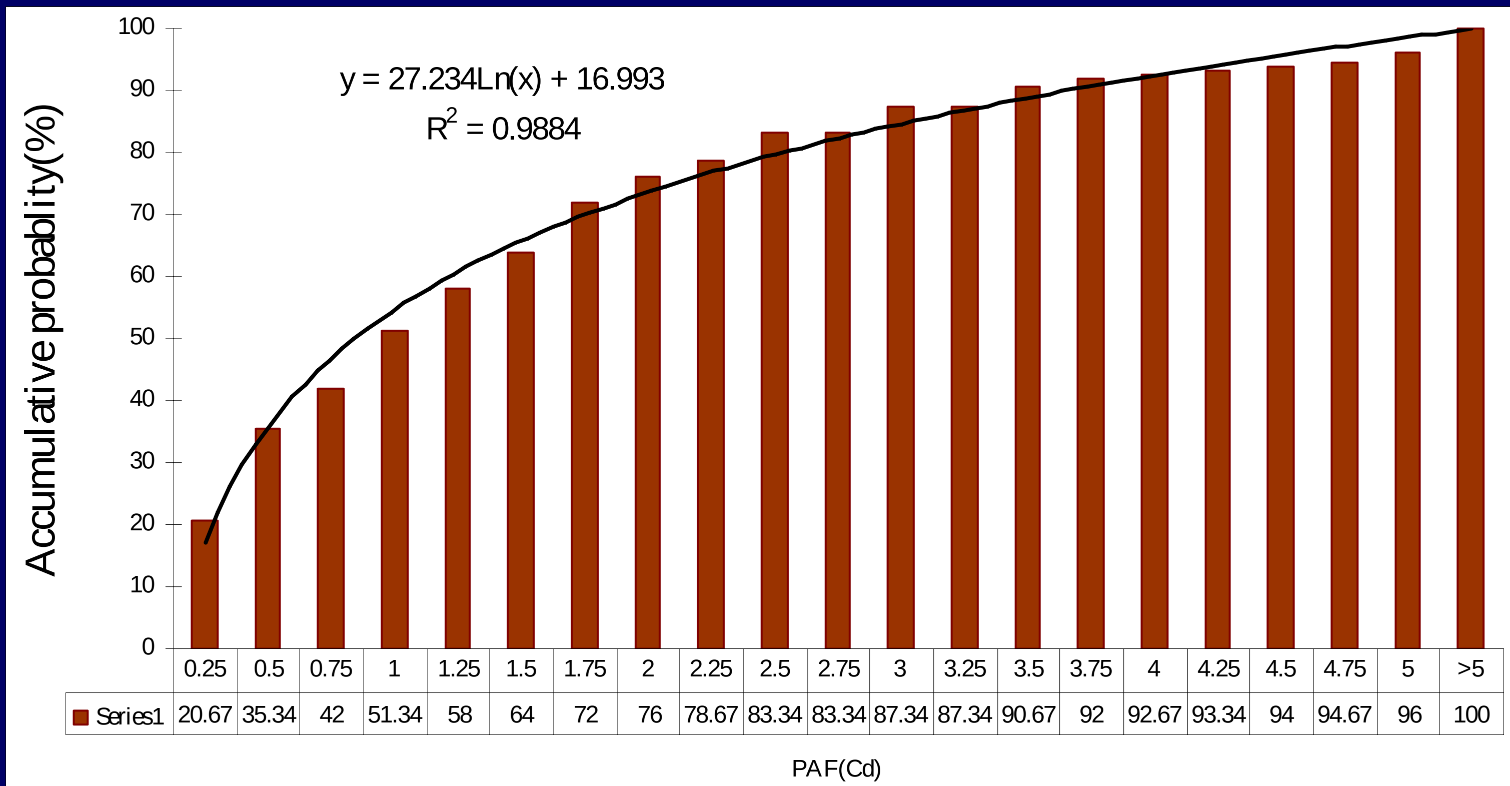


	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8	2	2.2	2.4	2.6	2.8	>2.8
Series1	28	48	64.67	72.67	84	89.33	92	92	92.67	94	96	98	98.67	99.33	100

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



PAF(Cd) probability for Lettuce



Statistics of PAF of different crops (Source: Chaney, 2001)

Crop	Min	Max	Median	Mean	Stdev	95%prob.
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

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

Correlating PAF to soil total concentration

Crop		Independt	Coefficient	Stdev	R^2
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	

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

Crop	Variables	Coefficient	Stdev	R^2
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	
	$pH^{1/2}$	-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	
	$CEC^{1/2}$	-0.2184	0.0260	

Estimated PAFs(cal. from Pendias,2001) at a 95% probability concentration

Element	Cereals	Root/tuber	Leafy vegetab	Fruit
Ag	0.01	0.01	0.01	0.01
As[x]	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[x]	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[x]	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

X: Adopted to the literature reported data

The estimated Cmax for the major elements concerned with sludge application

Element	RfD (ug/kg BW d)	1/2RfD (ug/kg BW d)	Di (ug person/d)	Cmax, soil) (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: 8.5

Estimating Soil Concentration Limit For Sludge And Waste-water Application In Agriculture

II. A model by using soil-related Kp values

A model by using soil-related Kp values:

- 1. To specify the soil-dependent concentration limit；
- 2, To evaluate the possibility of predicting food exposure risk in given soil conditions;
- 3, To understanding the practical approaches for enhancing sound waste application in agriculture;

1, The permitted daily dietary uptake：

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

Metals in Food Crop

- 1, Absorbed by water consumption;
- 2, Partitioning between plant organs;
- 3, Evapor-transpiration equal to Transpiration in crop fields

$$Cp = Cw * Wd * Tr \qquad (1)$$

- 1, Cp :metal concentration in plant(μg metal uptake /g DM);
- 2,Cw: metal concentration in soil pore water in equilibrium with soil solid phase(μg/mL);
- 3,Wd : the total water uptake by plant during life-time in field(mL/gDM);
- 4,Tr : partitioning factor of a given metal between in root and in the edible organs.

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 (μg/g).

Using Kp models

- Model for Cd (Sauve, et al,2000) (n=751,R2=0.61,SEE=0.62):
- $LogK_p(Cd) = 0.48*pH + 0.28log(SOM) - 0.65$ (4)
- (SOM: % of soil organic matter)
- Thus: $C_p(Cd) = C_s(Cd)/K_p(Cd)*W_d*Tr$ (5)
- $C_s(Cd) = 1/2\ RfD*K_p(Cd)/\Sigma(D_i * W_{di}*Tr_i)$ (6)
- (i=1•••••4)

Relating Soil Limit Concentration to Soil Properties

- $Cs(Cd) = 210 * 10^{0.48*pH+0.82*\log(SOM)-0.65} / \sum (D_i * W_{di} * Tr_i(Cd))$ $(i = 1 \cdots\cdots 4)$

- Cs in µg/g; Di in g/person/day; Wdi in gH2O/gDM; Tri dimensionless

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

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

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

Fe_{ox} is soil oxalate extractable iron in mmol/kg.

Then:

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

$$(i=1 \cdots\cdots 4) \qquad (9)$$

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

(10)

Prediction of dietary uptake of metals:

- $Du = Cp * Di$ (11)

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

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

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

- $Du_{(Pb)}=Cp_{(Pb)}*Di \quad (i=1\cdots\cdots 4)$ (15)
- $Du_{(Pb)}=Cs_{(Pb)}/Kp_{(Pb)}* \sum(Di * Wdi*Tri_{(Pb)}) \quad (i=1\cdots\cdots 4)$ (16)
- $Du_{(Pb)}(\mu g/d) =Cs_{(Pb)}/(10^{0.24*pH+0.40*\log(Fe ox)+1.98})* \sum(Di * Wdi*Tri_{(Pb)})$ $(i=1\cdots\cdots 4)$ (17)

Table 1 The parameters used for Cs estimation

	Wdi (gH2O/gDM)	Tr(Cd)[a] (Foliage-edible part	Tri(Cd)[d] (Root-leaf-grain)	Tri(Pb)[d]
Cereals	600	0.11[b] (0.34)[c]	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?

Kp-related soil concentration limit of Pb and Cd(μg/g)

	pH 7		pH 5	
SOM(%)	5	2	5	2
C*s*(Cd)	9.5	5	1.0	0.5
Fe*ox* (mmol/kg)	80	50	80	50
C*s*(Pb)	117.5	97.4	38.9	32.2

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

Acute plant food exposure to Cd by USA dietary

Food	US diet g/dayFW	(g/day DW)	Cd exposure**(μg/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

Estimating Soil Concentration Limit of Organic Pollutants for Sewage Sludge and Wastewater Application in Agriculcture

- Using available models of Ocs incorporating their physico-chemical properties

Rational: The transfer pathways of organic chemicals to plant tissue

- A, soil pore water to plant roots(soil-root pathway)
- B, soil– air to leaves of plant via volatilization(soil-air-foliage pathway)

However, the second pathway is only valid for volatile compounds at very high pollution loading, as in case of >500 ng/kg of PCDDs (Trapp, S. 1997)

Calculation of TSCF
(transpiration stream concentration factor)

1, Model by Burken et,al, 1998:

$$TSCF = 0.756 * Exp(-(logKow-2.5)/2.58) \qquad (1)$$

(the expression in their paper was wrong)

2, Model by Briggs, et,al, 1982:

$$TSCF = 0.784 * Exp(-(logKow-1.78)/2.44) \qquad (2)$$

TSCF is transpiration-soil concentration factor:

$$TSCF = C_{\text{transpiration stream}} / C_{\text{soil solution}}$$

Calculating RCF:

1, Model by Burken et,al, 1998:

$$\log(RCF-3.0)=0.65 * \log Kow-1.57 \qquad (3)$$

2, Model by Briggs, et al, 1982:

$$\log(RCF-0.82)=0.77 * \log Kow-1.52 \qquad (4)$$

RCF is root soil concentration factor:

$RCF= C_{root} / C_{soil\ solution}$

Calculating crop uptake of OCs:

- Vegetable Uptake(μg/g)= TSCF * Wr * W_d * C_{sln} (5)
- Root uptake (μg/g)=RCF * R*pc**C_{sln} (6)

C_{sln} is concentration of OC in soil solution (μg/ml)

R*pc* is partitioning factor of peel-core of root crop

Calculation of C_{sln} limit:

C_{sln}=1/2 RfD * 60/(TSCF* $\sum$ Wd_i*D_i * Wr + RCF * R_{pc}* D_{root}) (7)
(i=1• •••3)

1,Wd_i is the water consumption (gH_2O/g DM) for the food crop *i*, Di is the daily dietary consumption (g/day) of the food crop *i*. D_{root} is the daily dietary consumption of root/tuber crop.

2, 100% of the water consumption is through transpiration by crop under irrigated farm system.

Calculating soil total concentration limit for OCs :

$$C_s = C_{sln} \times K_p(\text{soil}) \qquad (8)$$

- And:
- $K_p(\text{soil}) = Koc * foc \qquad (9)$

Where Kp is the soil solid to liquid partitioning factor of a OC, *foc* is the fraction of soil organic carbon (%/100)

Then :

- $C_{soil} = C_{sln} * Koc * foc \qquad (10)$

Water consumption by crops under irrigation conditions

(Teare Peat. 1983, Crop water relations. John Wiley and Sons, Inc., New York. pp 307~350)

Crop	Growth time (d)	Water consumption (Wd, gH_2O/g DM)	ET(mm)
Wheat	112	613	473
Potato	128	532	532
Beet	113	703	599
Tomato	?	800 (?)	711

Results of calculation of Cs of OCs (1)

Chemicals	Adopted RfD(10^{-5})	1/3RfD (μg/day)	Kow	Koc	TSCF	RCF	Cs(5%SOC)	Cs(1%SOC)
Aldrin	0.03	0.010	7.20E+06	4.84E+04	7.67E-07	3.52E+01	7.16E-01	1.43E-01
Benzene	0.43	0.143	1.51E+02	5.51E+01	4.57E-01	9.60E-01	2.21E-04	4.42E-05
PAHs	12.5	4.167	2.20E+06	2.49E+06	4.88E-05	2.37E+01	2.26E+04	4.52E+03
Chlorodane	0.5	0.167	1.21E+06	5.18E+04	2.41E-04	1.94E+01	2.21E+01	4.41E+00
chlorobenzene	85.7	28.567	3.51E+06	2.28E+02	1.13E-05	2.77E+01	1.22E+01	2.45E+00
chloroform	200	66.667	90	60	4.94E-01	8.08E-01	1.03E-01	2.07E-02
Dichlorobenzene	107	35.667	2.80E+03	3.84E+02	2.13E-01	2.55E+00	8.18E-01	1.64E-01
2,4-D	10	3.333	99	50	4.87E-01	8.34E-01	4.37E-03	8.74E-04
DDT	0.25	0.083	1.38E+06	3.09E+04	1.74E-04	2.03E+01	6.39E+00	1.28E+00
Dieldrin	0.05	0.017	5.13E+05	1.26E+04	1.52E-03	1.46E+01	5.27E-01	1.05E-01
Heptachlor	0.1	0.033	1.67E+05	6.81E+03	9.10E-03	1.00E+01	2.51E-01	5.02E-02
Hexachlorobenzene	1	0.333	3.51E+05	4.58E+04	2.98E-03	1.28E+01	3.18E+01	6.37E+00
Pyrene	300	100.000	1.04E+05	7.06E+04	1.64E-02	8.54E+00	4.86E+03	9.73E+02

Results of calculation of Cs of OCs (2)

Chemicals	Adopted RfD(10^{-5})	1/3RfD (μg/day)	Kow	Koc	TSCF	RCF	Cs(5%SOC)	Cs(1%SOC)
Lindane	500	166.667	5.30E+03	1.50E+03	1.62E-01	3.16E+00	1.96E+01	3.92E+00
Methoxylchlor	5	1.667	4.53E+04	7.89E+04	3.87E-02	6.47E+00	4.17E+01	8.34E+00
Pentachlorophenol	9	3.000	1.21E+05	5.45E+04	1.37E-02	8.98E+00	1.31E+02	2.62E+01
PCBs	1	0.333	2.59E+06	1.26E+06	3.00E-05	2.50E+01	8.70E+02	1.74E+02
Tetrachloroethane	40	13.333	2.45E+02	8.00E+01	4.20E-01	1.13E+00	3.24E-02	6.49E-03
Tetrachloroethylene	100	33.333	3.82E+02	1.97E+02	3.84E-01	1.31E+00	2.18E-01	4.37E-02
Toluene	223	74.333	4.82E+02	1.39E+02	3.64E-01	1.42E+00	3.62E-01	7.24E-02
Toxaphene	0.009	0.003	1.97E+03	888	2.43E-01	2.27E+00	1.40E-04	2.79E-05
2,4,5-T	3	1.000	9.02E+04	4.06E+04	1.93E-02	8.14E+00	2.43E+01	4.86E+00
Trichloroethene	24	8.000	1.26E+02	8.56E+01	4.70E-01	9.04E-01	1.86E-02	3.72E-03
Phthalate	25	8.333	3.27E+09	4.27E+04	9.70E-39	2.73E+02	6.80E+01	1.36E+01
Styrene	7.7	2.567	8.92E+02	9.12E+02	3.12E-01	1.74E+00	9.58E-02	1.92E-02
Dioxins(TCDD)	0.00001	0.000	4.62E+06	5.38E+06	4.33E-06	3.04E+01	3.07E-02	6.15E-03

Recommendation for Sludge Application

- Total sludge application rate

  =(Cd*per*-Cds)* Ws/Cd*slg*

- Where Cd*per* is the permitted Cd concentration in soil (mg/kg); *Ws* is the total soil weight (kg/ha);Cd*slg* 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 sludeg:39 ppm
- Perm. Rate:
- = (1.5-0.8)*1.2*106/39 $\geq$ 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 (5 yrs continuously)

Cds=0.0146X+2.5028 (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

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

Recommendation for Future Guideline Development

- Developing models of PAFs for estimating the crop food exposure, possibly incorporating the mass balance and taking in account of root absorption parameters;
- More well performed experiment results are needed for other metals as Hg, As and Tl;
- Soil-related estimation model may be practical for regional or national guidelines based on the relevant dietary patterns

Recommendation for Research of Environmental Issues With Sludge Application

- Enhanced aging and sequestration of toxic chemicals by sludge-amended soil;
- The positive interaction between the sludge added particles and organic materials with soil, esp.monitoring of the dynamic effects; (eg. Soil carbon problem)
- Well performed field trials needed for understanding fate and transfer to plant of less frequently studied chemicals (in case of insufficient data)

- Making Biosolids Application in Harmony With Soil !

- Thank you !