Heavy metals in agriculture with a focus on cadmium

Mike McLaughlin

CSIRO Land and Water

Fertiliser Technology Research Centre, Waite Research Institute,

University of Adelaide

Outline

- “Heavy” metals – definition
- Metals of concern in agriculture
- Cadmium
- Controlling cadmium in agriculture
- Cadmium in cocoa
- Conclusions

Heavy metals

- “Heavy metals” is not a rigorous term that all agree on – “contaminants” or “impurities” or “potentially toxic elements” perhaps better

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

CHEMISTRY AND HUMAN HEALTH DIVISION
CLINICAL CHEMISTRY SECTION, COMMISSION ON TOXICOLOGY*

“HEAVY METALS”—A MEANINGLESS TERM?

(IUPAC Technical Report)

Prepared for publication by
JOHN H. DUFFUS

- Some elements of potential concern in agriculture are not “heavy metals” e.g. arsenic (As), fluorine (F)

Potentially toxic elements

- Rufus Chaney's "Soil Plant Barrier" concept

Group 1 – solubility limited	Group 2 – translocation limited	Group 3 – phytotoxic	Group 4 – higher risk
Ag	As	B	Cd
Cr	Hg	Cu	Co
Sn	Pb	Mn	Mo
Ti	F	Mo	Se
Y		Ni	
Zr		Tl	
		Zn	

Chaney, R. L. and D. P. Oliver (1996). Sources, potential adverse effects and remediation of agricultural soil contaminants. Contaminants in the Soil Environment in the Australasia-Pacific Region. R. Naidu, R. Kookana, D. P. Oliver, S. R. Rogers and M. J. McLaughlin. Dordrecht, The Netherlands, Kluwer Publishers**: 456-478.**

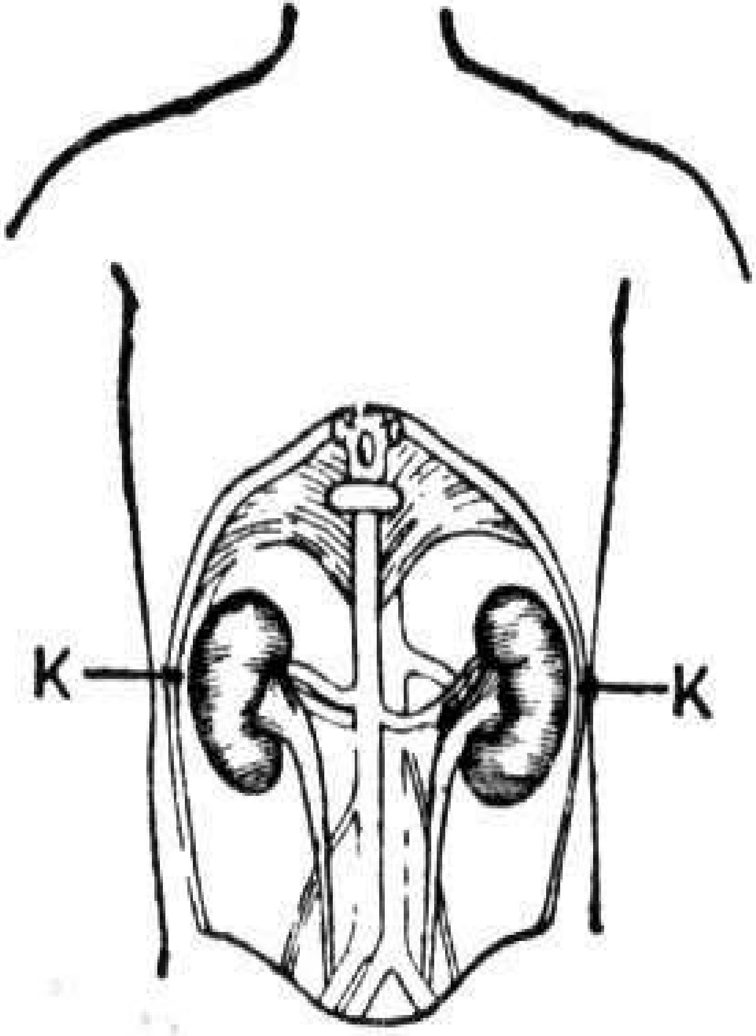
Key metal risk pathways - cadmium

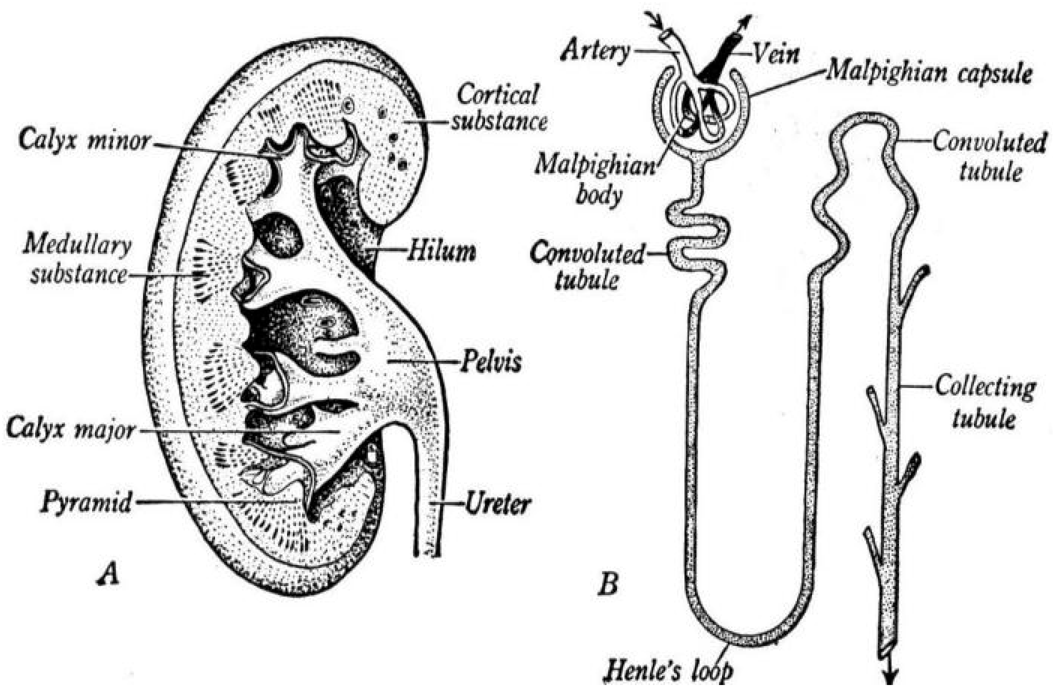
- Soil → Plant → Human ✓
- Soil → Plant ✗
- Soil → Micro-/Macroorganism ✗
- Soil → Water → Organism ✗
- Soil → Water → Plant → Human ✓

Our main concern with Cd in agriculture is food chain contamination

Cadmium

The critical organ is the kidney





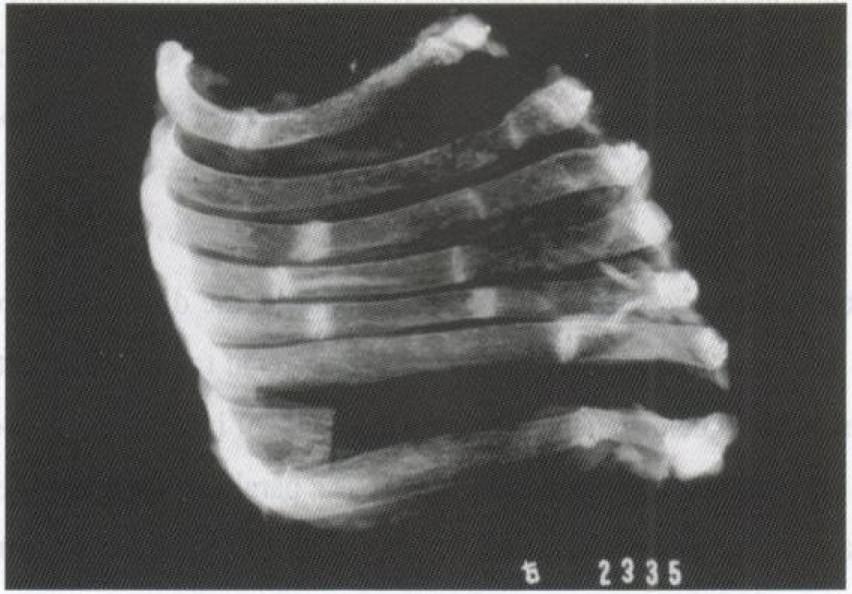


Fig. 5 Multiple Looser's zones of the ribs in an Itai-itai disease patient, autopsied material

Itai itai disease

Disease a result of irrigation of rice crops with Cd-polluted wastewater

International Food Standards

- Maximum Levels (MLs) are set by joint FAO/WHO Food Standards Program, and health risks are evaluated by the Joint Expert Committee on Food Additives (JECFA)
- CODEX MLs are developed to ensure quality in traded food commodities and prevention of non-tariff barriers to trade

codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

JOINT OFFICE: Viale delle Terme di Caracalla 00100 ROME Tel: 39 06 57051 www.codexalimentarius.net Email: codex@fao.org Facsimile: 39 06 5705 4593

Cadmium in agriculture

- Cadmium is unique amongst the trace elements in that it appears to be taken up readily by plants (despite being non-essential for crops)
- Applications at low levels to agricultural soils are widespread
- Removal from soil is not cheap or easy

Cadmium chemistry

- Present mostly as Cd^{2+} in soils
- Combines readily with Cl^- and SO_4^{2-} to form soluble complexes
- Precipitates as CdS in reduced soils (e.g. rice paddies)
- Solubility is pH dependent – more soluble in acid soils
- Does not get readily "fixed" in soil (like P, Zn, Pb)
- Similar ionic radius to Ca^{2+} so can substitute for Ca^{2+} in/on minerals, root uptake, etc.

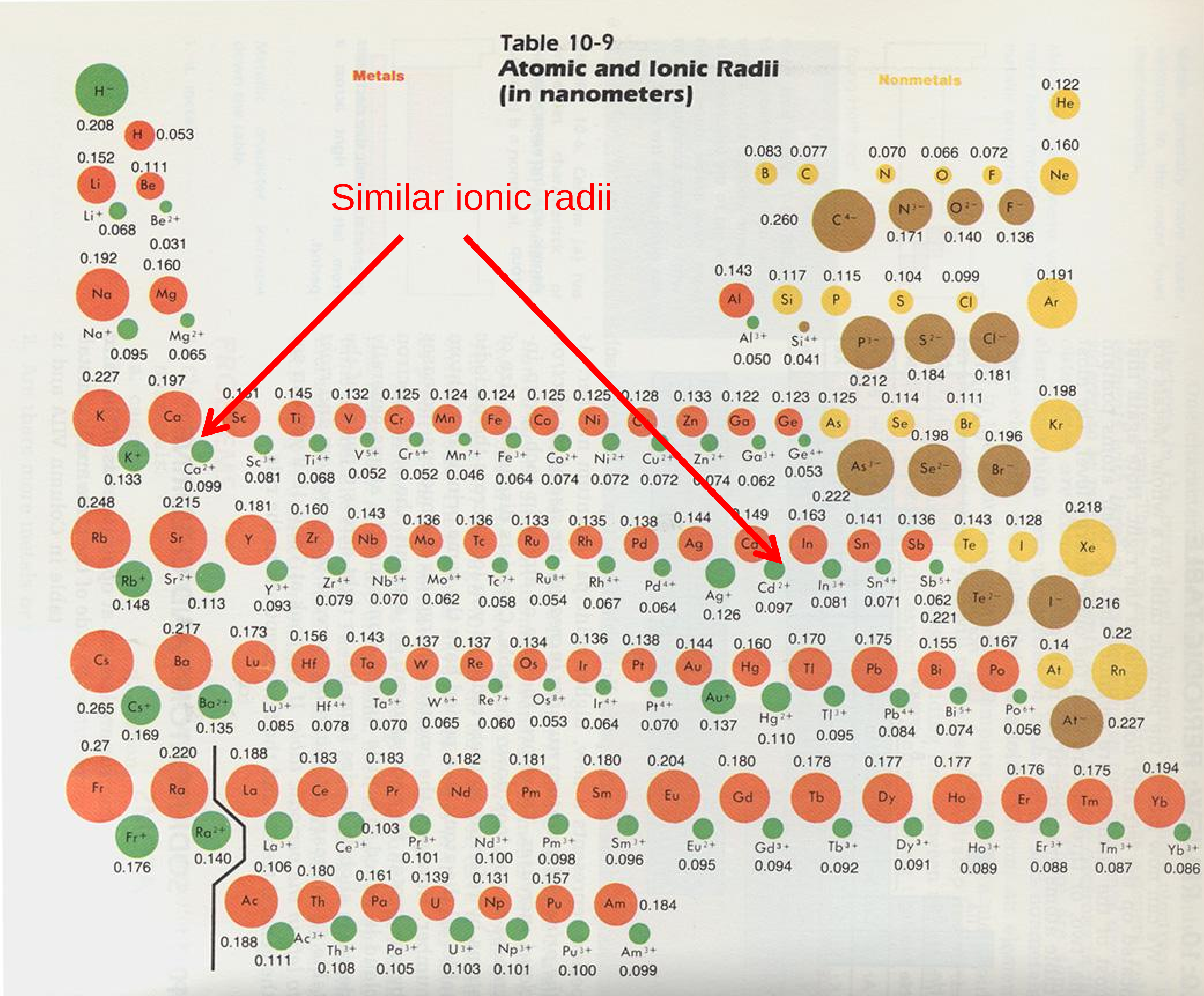
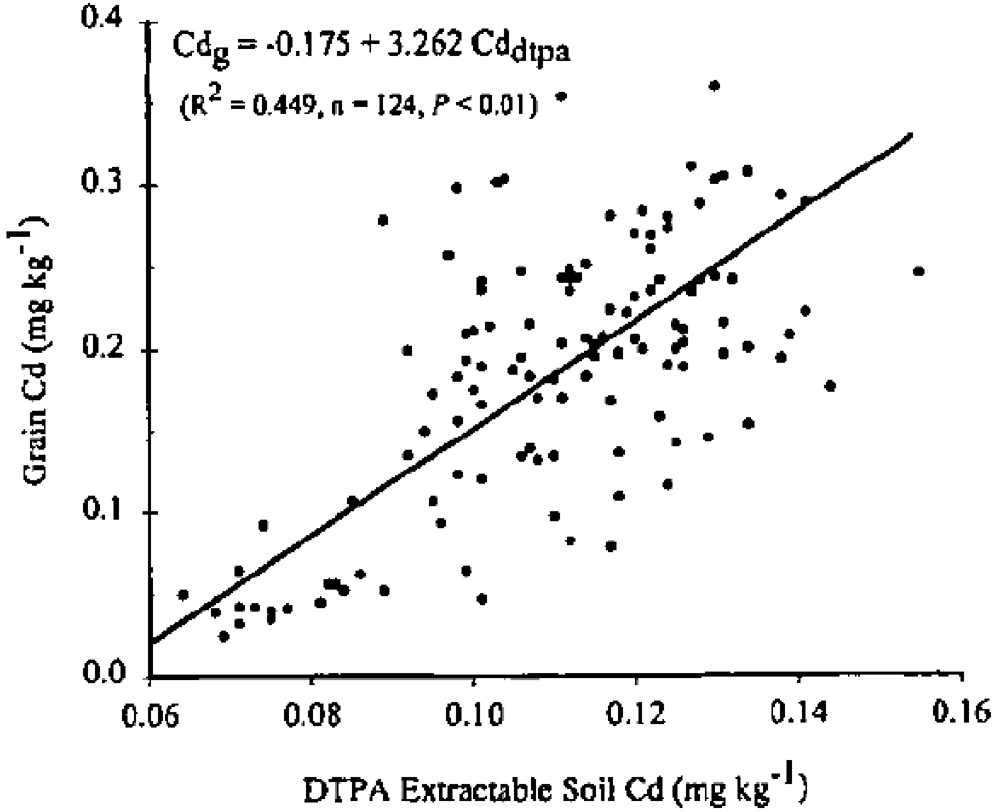


Table 10-9
Atomic and Ionic Radii (in nanometers)
Metals
Nonmetals
Similar ionic radii
H^- 0.208
H 0.053
Li 0.152
Li^+ 0.068
Be 0.111
Be^{2+} 0.031
Na 0.192
Na^+ 0.095
Mg 0.160
Mg^{2+} 0.065
K 0.227
K^+ 0.133
Ca 0.197
Ca^{2+} 0.099
Rb 0.248
Rb^+ 0.148
Sr 0.215
Sr^{2+} 0.113
Cs 0.265
Cs^+ 0.169
Ba 0.217
Ba^{2+} 0.135
Fr 0.27
Fr^+ 0.176
Ra 0.220
Ra^{2+} 0.140
Sc
Sc^{3+} 0.081
Ti 0.145
Ti^{4+} 0.068
V 0.132
V^{5+} 0.052
Cr 0.125
Cr^{6+} 0.052
Mn 0.124
Mn^{7+} 0.046
Fe 0.124
Fe^{3+} 0.064
Co 0.125
Co^{2+} 0.074
Ni 0.125
Ni^{2+} 0.072
Cu 0.128
Cu^{2+} 0.072
Zn 0.133
Zn^{2+}
Ga 0.122
Ga^{3+} 0.062
Ge 0.123
Ge^{4+} 0.053
As 0.125
As^{3-} 0.222
Se 0.114
Se^{2-} 0.198
Br 0.111
Br^- 0.196
Kr 0.198
Y 0.181
Y^{3+} 0.093
Zr 0.160
Zr^{4+} 0.079
Nb 0.143
Nb^{5+} 0.070
Mo 0.136
Mo^{6+} 0.062
Tc 0.136
Tc^{7+} 0.058
Ru 0.133
Ru^{8+} 0.054
Rh 0.135
Rh^{4+} 0.067
Pd 0.138
Pd^{4+} 0.064
Ag 0.144
Ag^+ 0.126
Cd
Cd^{2+} 0.097
In 0.163
In^{3+} 0.081
Sn 0.141
Sn^{4+} 0.071
Sb 0.136
Sb^{5+} 0.062
Te 0.143
Te^{2-} 0.221
I 0.128
I^- 0.216
Xe 0.218
Lu 0.173
Lu^{3+} 0.085
Hf 0.156
Hf^{4+} 0.078
Ta 0.143
Ta^{5+} 0.070
W 0.137
W^{6+} 0.065
Re 0.137
Re^{7+} 0.060
Os 0.134
Os^{8+} 0.053
Ir 0.136
Ir^{4+} 0.064
Pt 0.138
Pt^{4+} 0.070
Au 0.144
Au^+ 0.137
Hg 0.160
Hg^{2+} 0.110
Tl 0.170
Tl^{3+} 0.095
Pb 0.175
Pb^{4+} 0.084
Bi 0.155
Bi^{5+} 0.074
Po 0.167
Po^{6+} 0.056
At 0.14
At^- 0.227
Rn 0.22
La 0.188
La^{3+} 0.106
Ce 0.183
Ce^{3+} 0.103
Pr 0.183
Pr^{3+} 0.101
Nd 0.182
Nd^{3+} 0.100
Pm 0.181
Pm^{3+} 0.098
Sm 0.180
Sm^{3+} 0.096
Eu 0.204
Eu^{2+} 0.095
Gd 0.180
Gd^{3+} 0.094
Tb 0.178
Tb^{3+} 0.092
Dy 0.177
Dy^{3+} 0.091
Ho 0.177
Ho^{3+} 0.089
Er 0.176
Er^{3+} 0.088
Tm 0.175
Tm^{3+} 0.087
Yb 0.194
Yb^{3+} 0.086
Ac 0.188
Ac^{3+} 0.111
Th 0.180
Th^{3+} 0.108
Pa 0.161
Pa^{3+} 0.105
U 0.139
U^{3+} 0.103
Np 0.131
Np^{3+} 0.101
Pu 0.157
Pu^{3+} 0.100
Am 0.184
Am^{3+} 0.099
He 0.122
B 0.083
C 0.077
N 0.070
O 0.066
F 0.072
Ne 0.160
C^{4-} 0.260
N^{3-} 0.171
O^{2-} 0.140
F^- 0.136
Al 0.143
Al^{3+} 0.050
Si 0.117
Si^{4+} 0.041
P 0.115
P^{3-} 0.212
S 0.104
S^{2-} 0.184
Cl 0.099
Cl^- 0.181
Ar 0.191

Soil factors affecting crop Cd uptake

- Soil Cd content – total and/or “available”



Note total Cd in soil is still a useful predictor if combined with other factors e.g. pH, OM, Zn, Cl

Norvell, W. A., J. Wu, D. G. Hopkins and R. M. Welch (2000). "Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium." Soil Science Society of America Journal **64: 2162-2168.**

Soil factors affecting crop Cd uptake

- Soil pH – Cd solubility is greater at low pH

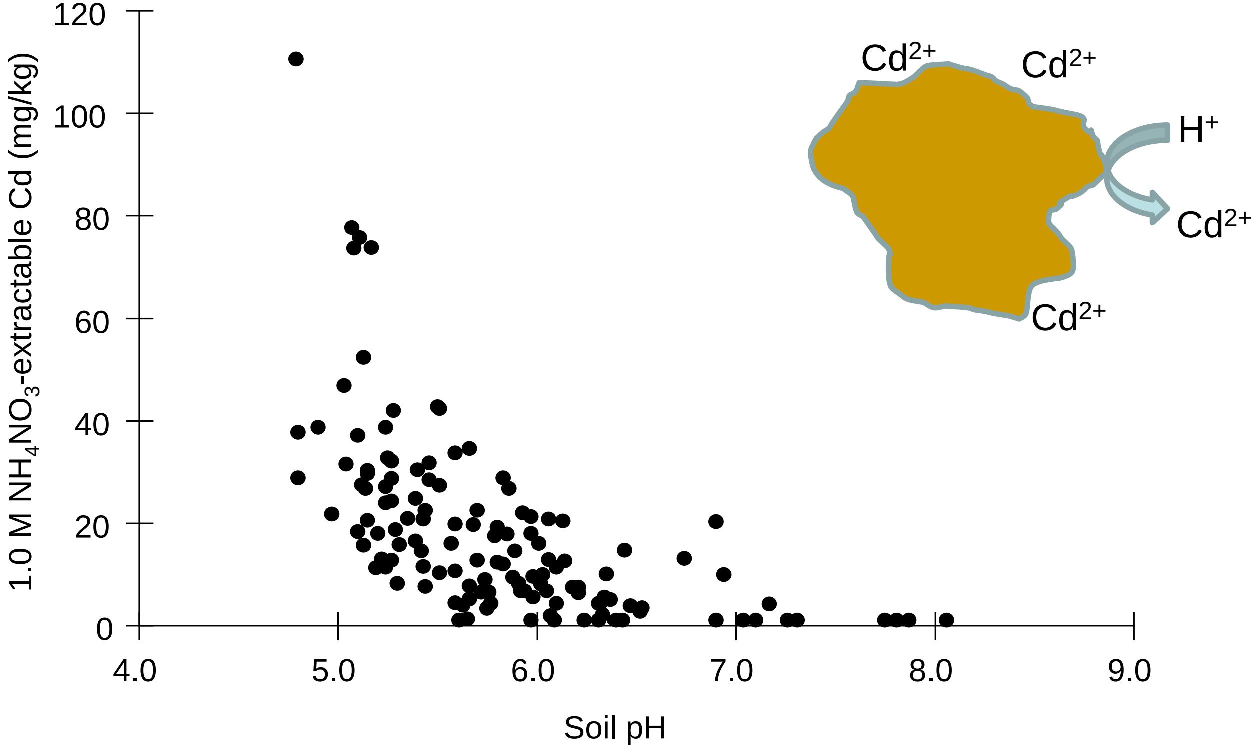
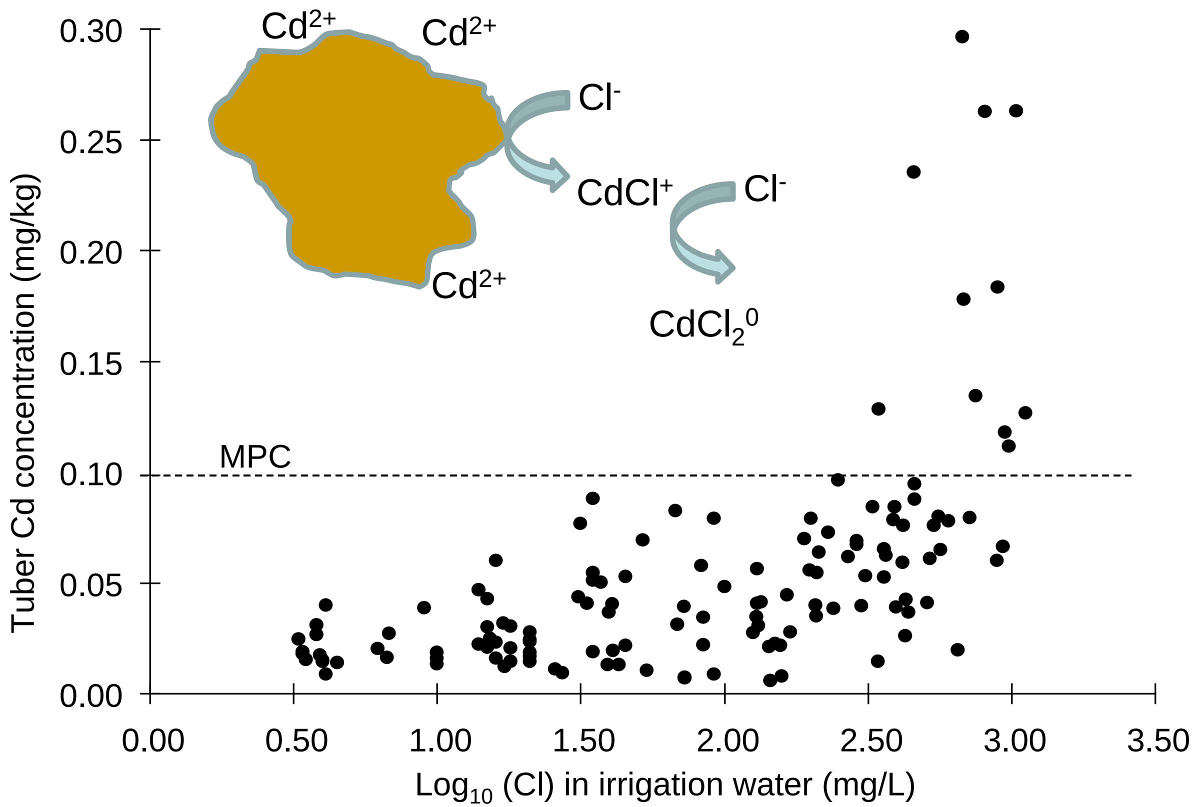


Figure 3. McLaughlin et al.

McLaughlin, M. J., N. A. Maier, G. E. Rayment, L. A. B. Sparrow, G., A. McKay, P. Milham, M. R.H. and M. K. Smart (1997). "Cadmium in Australian potato tubers and soils." Journal of Environmental Quality **26: 1644-1649.**

Soil factors affecting crop Cd uptake

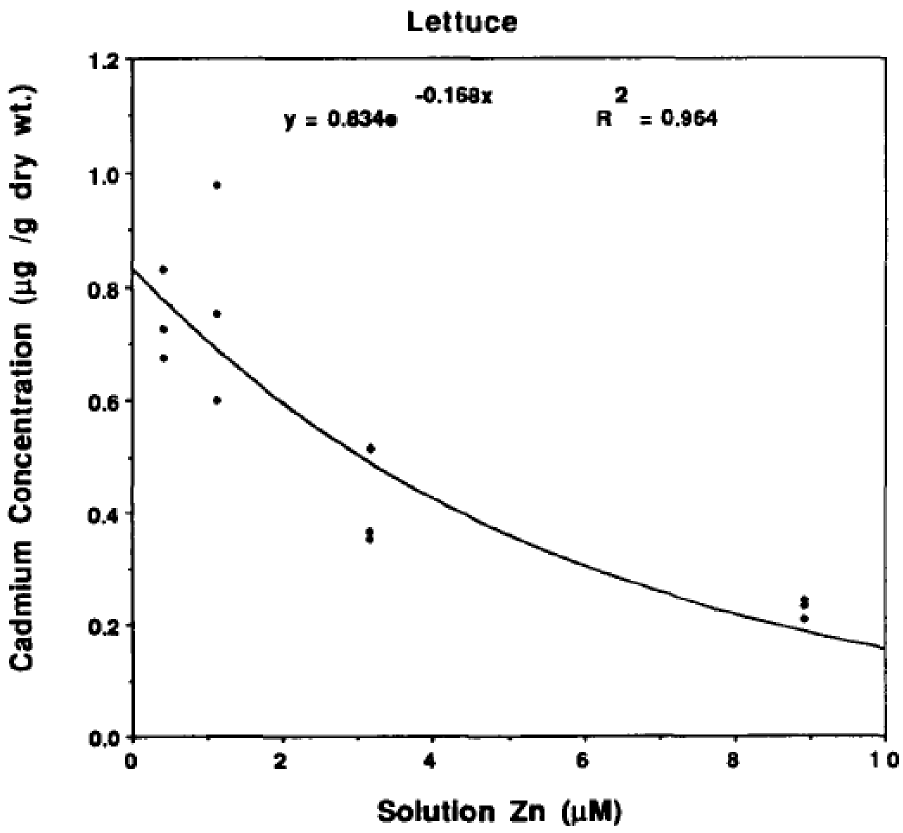
- Soil salinity – Cd solubility and plant uptake is greater with increased Cl concentrations

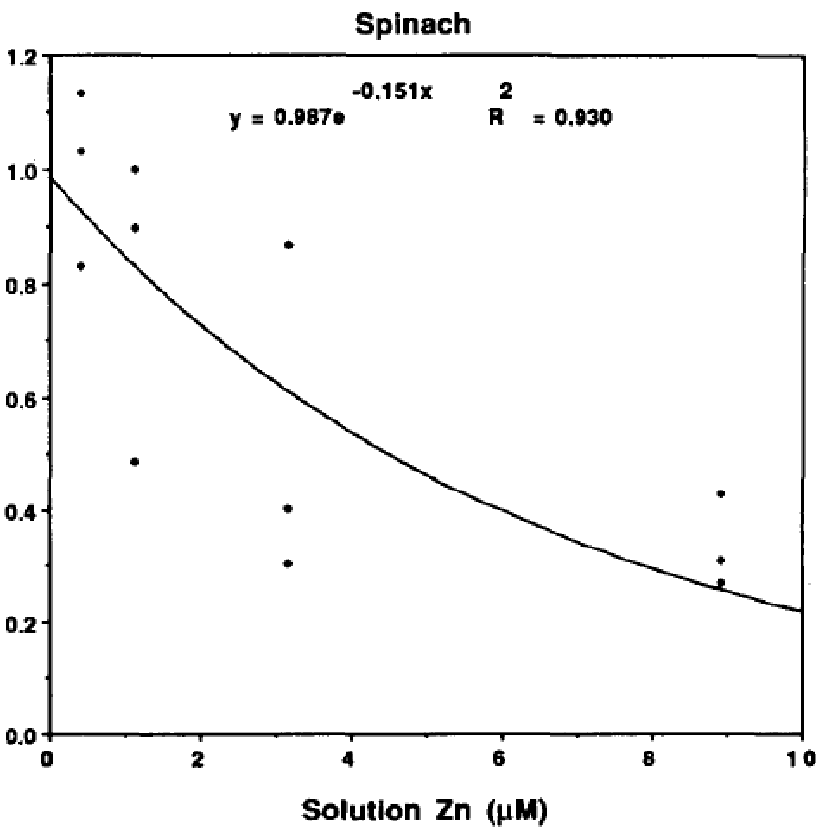


McLaughlin, M. J., N. A. Maier, G. E. Rayment, L. A. B. Sparrow, G., A. McKay, P. Milham, M. R.H. and M. K. Smart (1997). "Cadmium in Australian potato tubers and soils." Journal of Environmental Quality **26: 1644-1649.**

Soil factors affecting crop Cd uptake

- Zinc can compete for Cd uptake at root uptake sites





McKenna, I. M., R. L. Chaney and F. M. Williams (1993). "The effects of cadmium and zinc interactions on the accumulation and tissue distribution of zinc and cadmium in lettuce and spinach." Environmental Pollution **79: 113-120.**

Factors affecting Cd concentration of crops

Soil Characteristics

Crop Genetics

Soil Cd concentration

Tillage and agronomic management

Irrigation and water management

Crop Rotation

Fertilizer management

Controlling Cd in agriculture

1. Know your sources of Cd – geogenic or anthropogenic?
2. Know the distribution of Cd in soils (horizontally and vertically)
3. Understand soil and crop factors controlling Cd accumulation in your systems
4. Develop mitigation strategies based on (1) to (3) above

1. Know your sources of Cd – geogenic or anthropogenic?

Cadmium sources in soils

Atmospheric inputs

Fertilizer

Geogenic

Anthropogenic

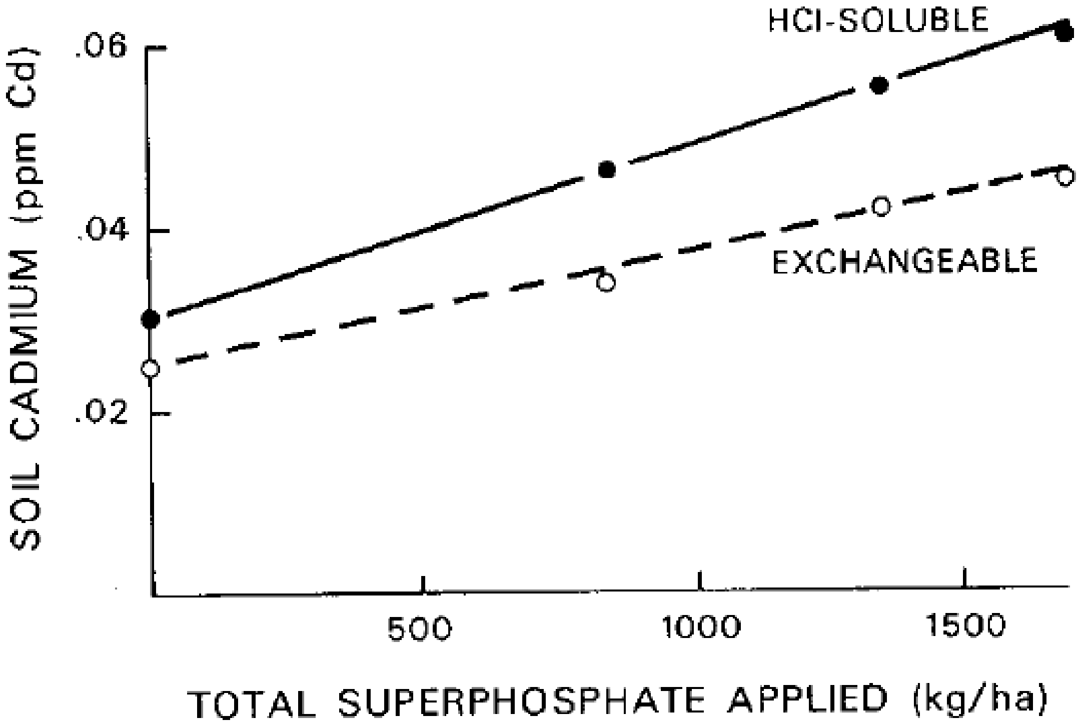
Weathering

Contaminated
irrigation water
e.g. mining

Soil
amendments
& wastes

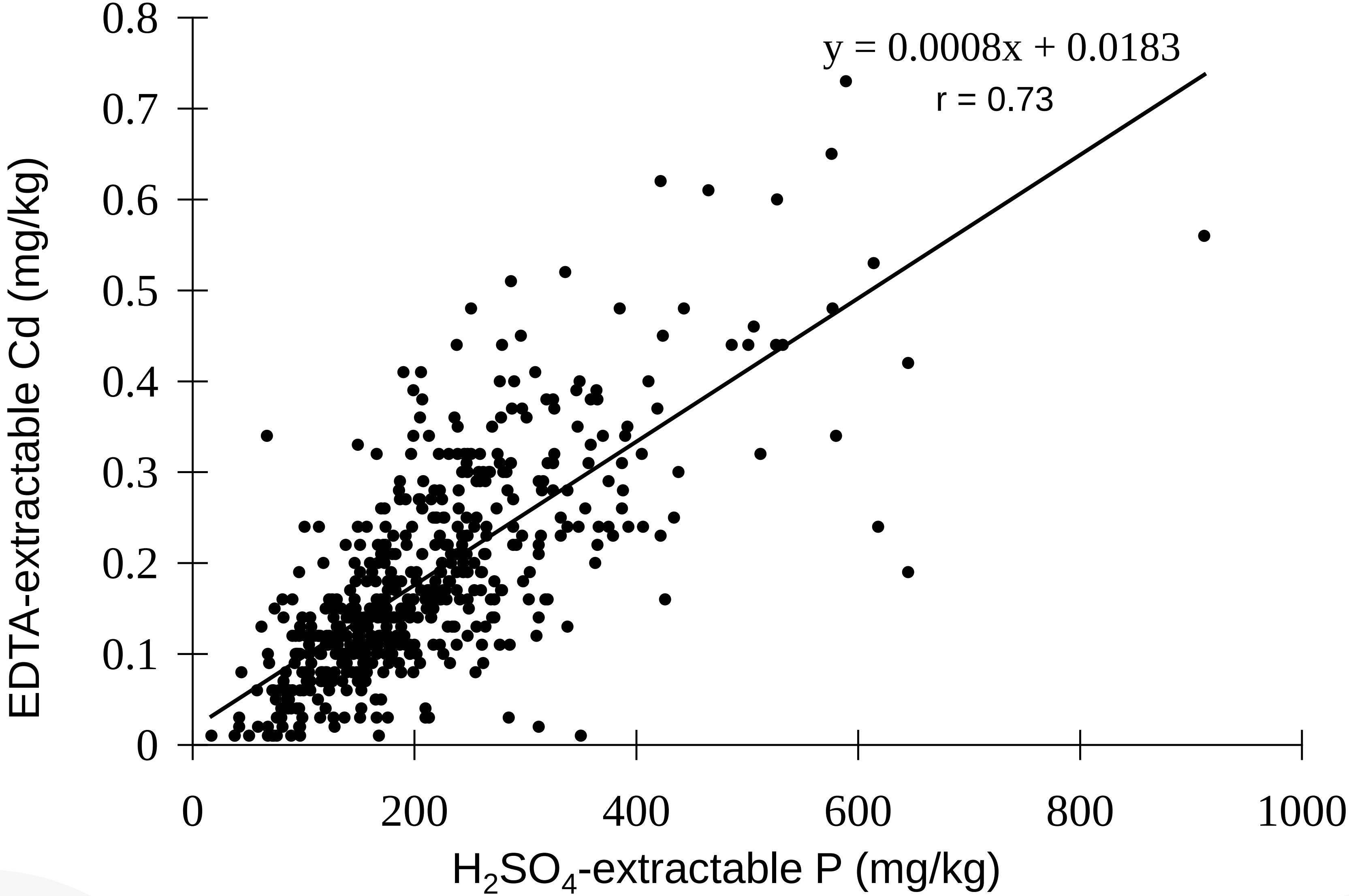
Sources of Cd in agricultural systems - Australia

- Determine the major sources of Cd input to soil in fertilizers, manures, wastes, atmospheric sources – long term trials



Williams, C. H. and D. J. David (1974). "The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants." Soil Science **121(2): 86-93.**

Sources of Cd in agricultural systems - Australia

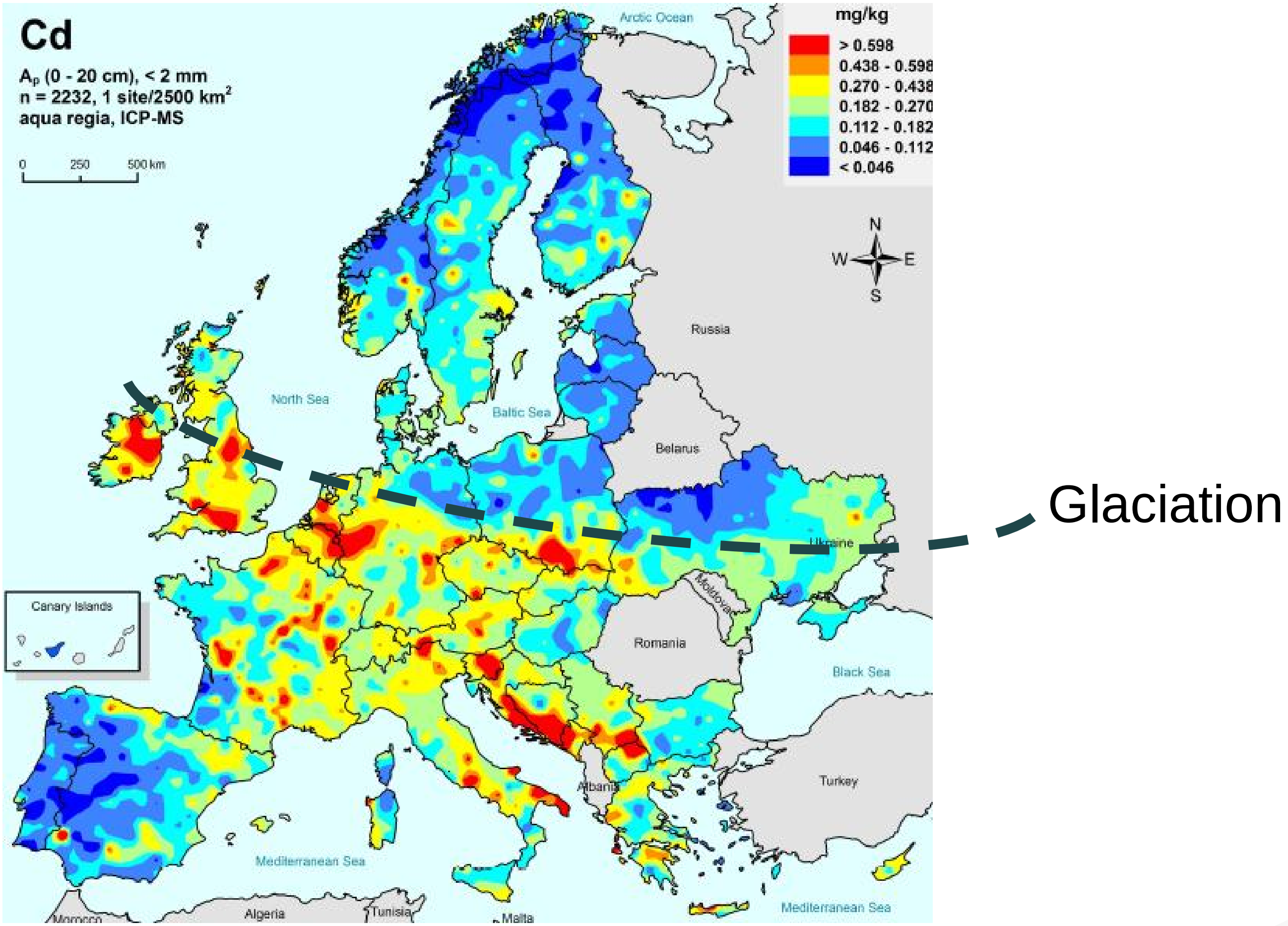


R. H. Merry (pers comm)

2. Know the distribution of Cd in soils (horizontally and vertically)

Cadmium distribution in soils - Europe

- Distribution may gives clue as to origin – geogenic or anthropogenic

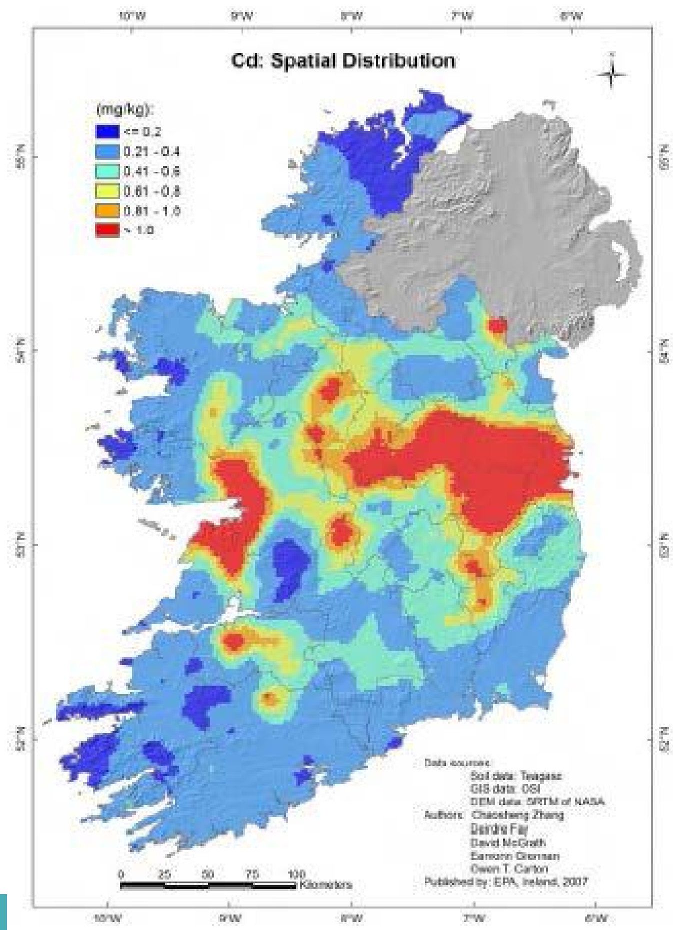


Reimann, C., P. et al. (2012). "The concept of compositional data analysis in practice - Total major element concentrations in agricultural and grazing land soils of Europe." Science of the Total Environment 426: 196-210.

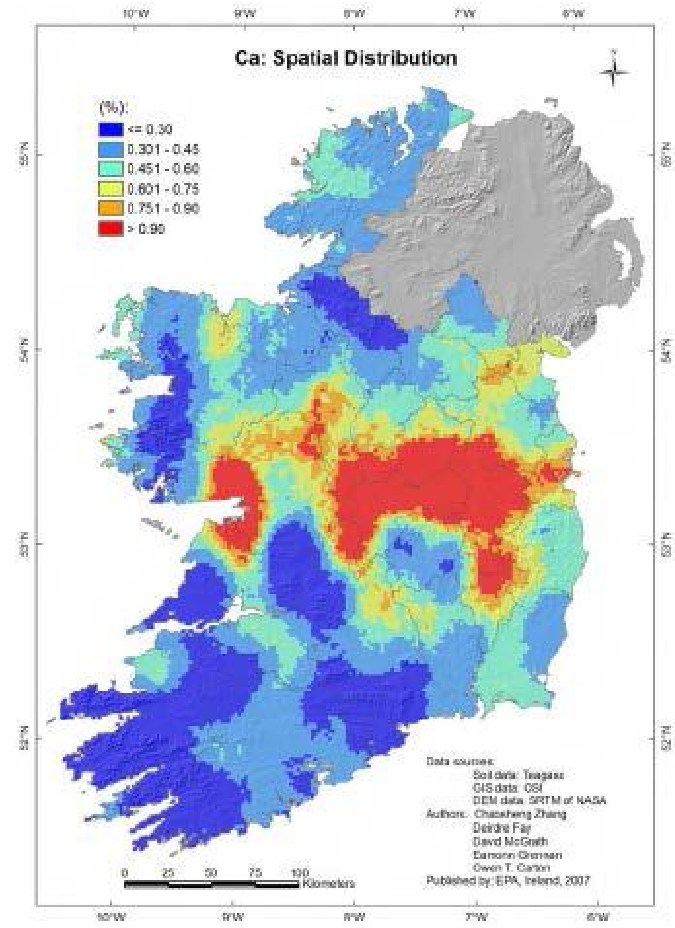
Cadmium distribution in soils - Ireland

- Distribution may gives clue as to origin – geogenic or anthropogenic

Cd

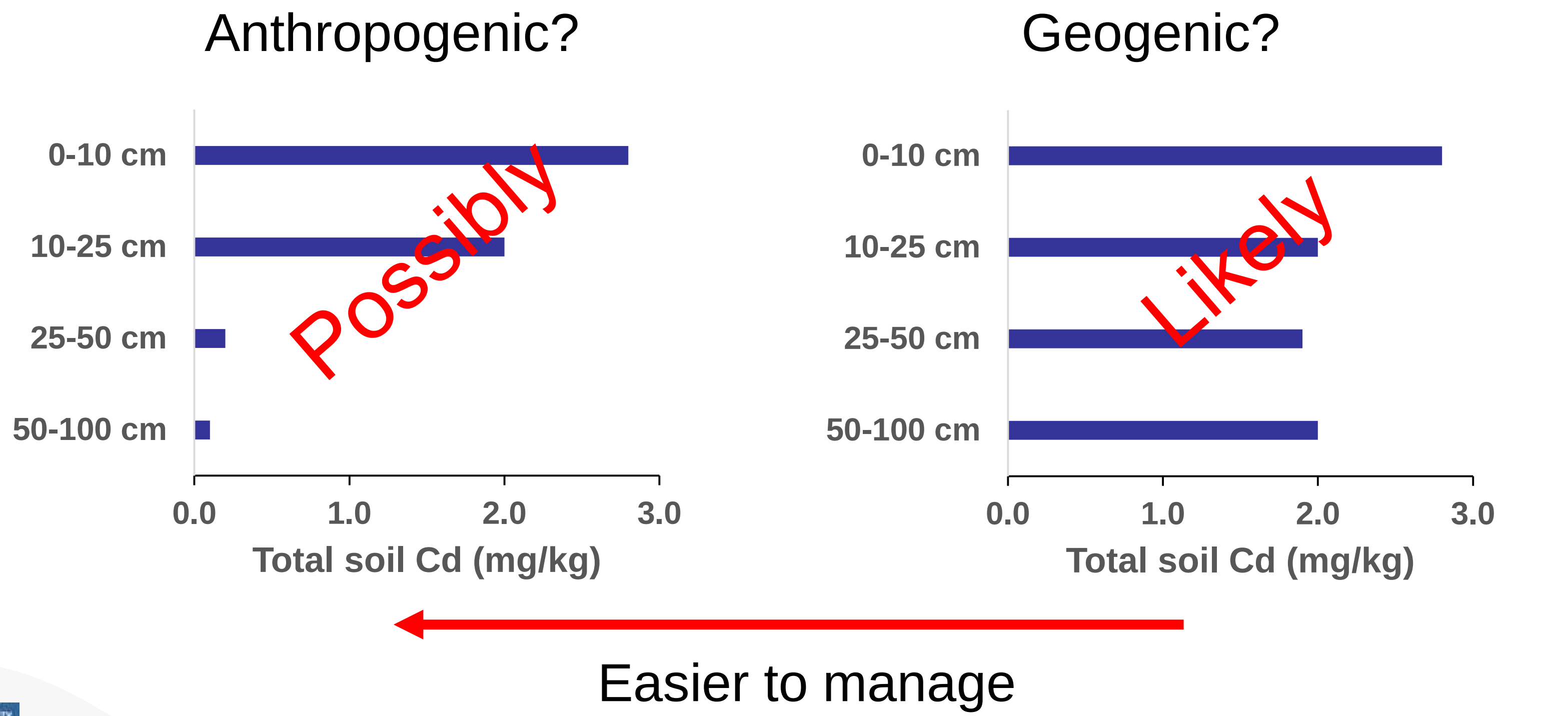


Ca



Cadmium distribution – vertical (depth)

- Gives clues as to the source/s of Cd
- Critical knowledge for developing management practices – shallow or deep?



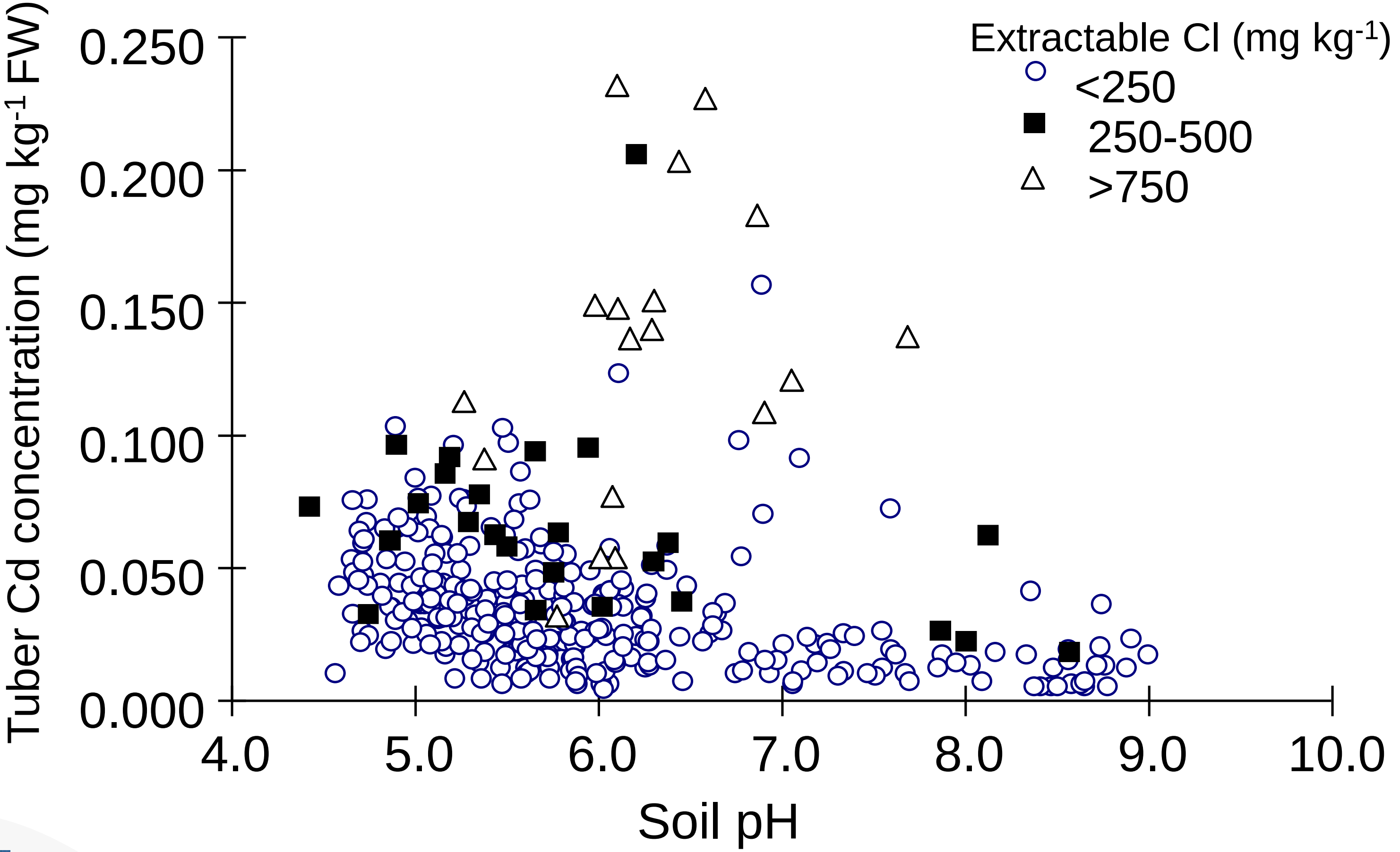
3. Understand soil and crop factors controlling Cd accumulation in your systems

Understanding crop Cd uptake

- Conduct paired soil/crop surveys – measure key soil attributes that affect Cd uptake
- Sample and analyse long-term fertilizer/lime/waste/irrigation trials – gives clues as to major Cd sources
- Sample and analyse crop variety trials – provides information to develop management strategies

Soil factors affecting crop Cd uptake

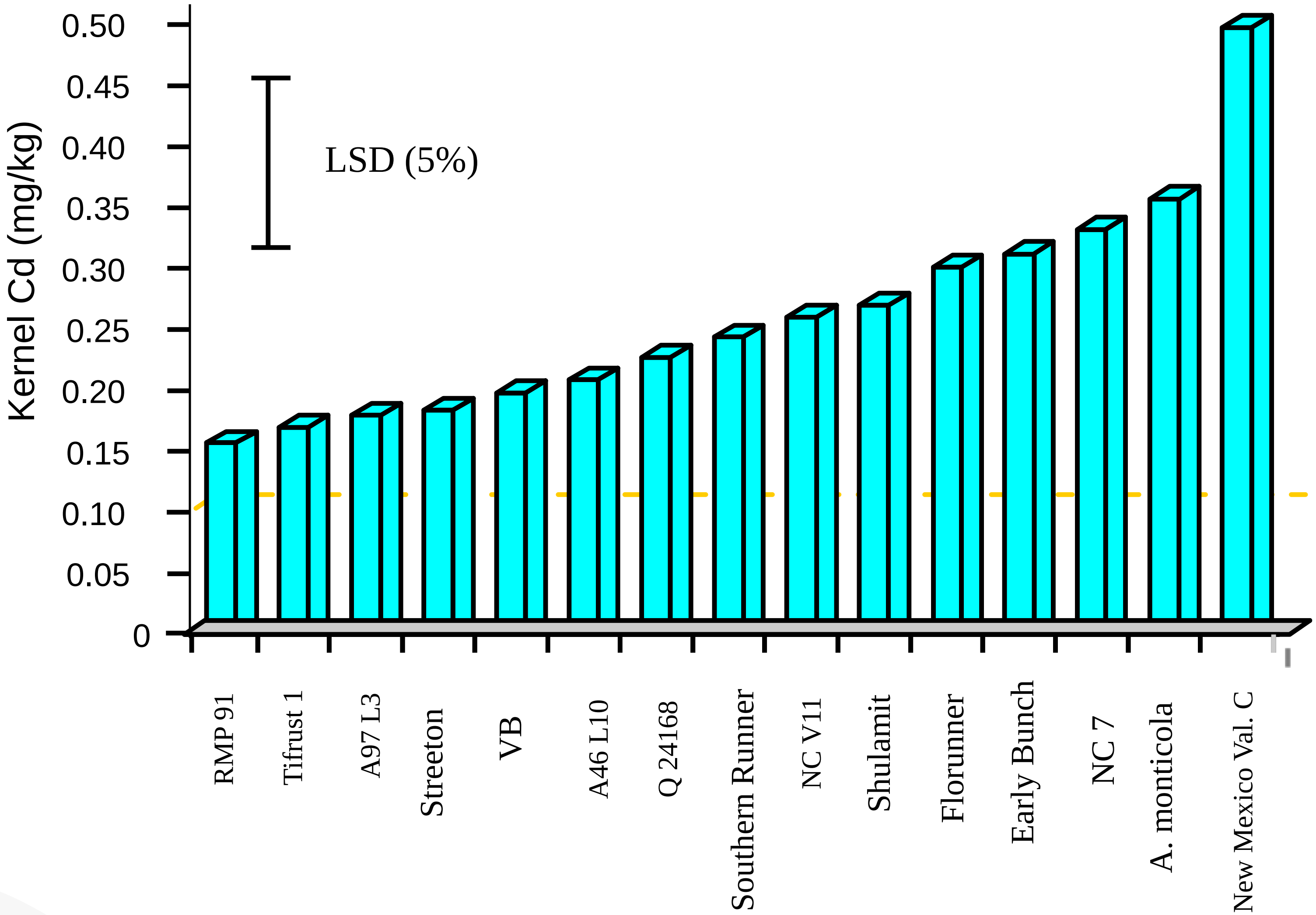
- Chloride effects greater than pH effects



McLaughlin, M. J., L. T. Palmer, K. G. Tiller, T. A. Beech and M. K. Smart (1994). "Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers." Journal of Environmental Quality **23(5): 1013-1018.**

Understanding crop Cd uptake

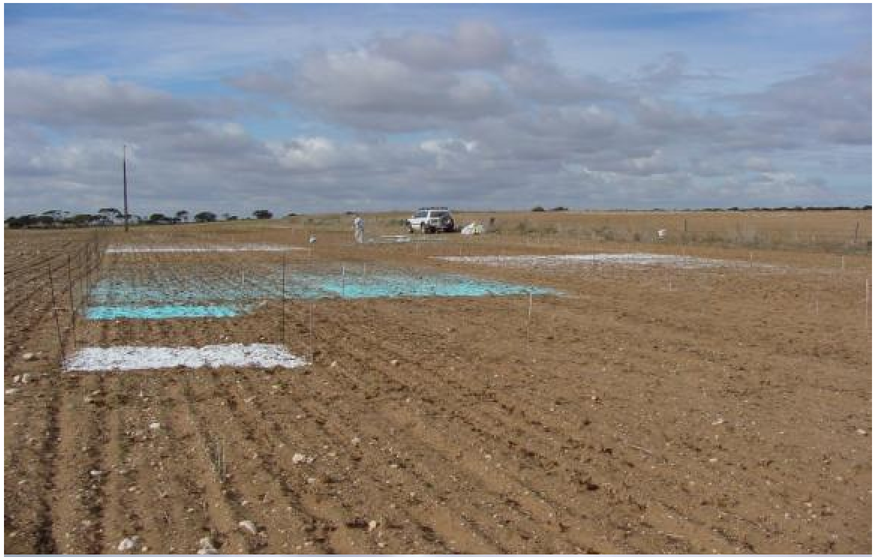
- Sample/analyse crop variety trials



McLaughlin, M. J., M. J. Bell, G. C. Wright and G. D. Cozens (2000). "Uptake and partitioning of cadmium by cultivars of peanut (*Arachis hypogaea L.*). *Plant and Soil* ***222: 51-58.***

Understanding crop Cd uptake

- Examine uptake in field



Examining the effects of cadmium, copper and zinc metal salts

Soil → Plant → Human (Cd)
Soil → Plant & Microorganism (Cu, Zn)

Examining the effects of biosolids

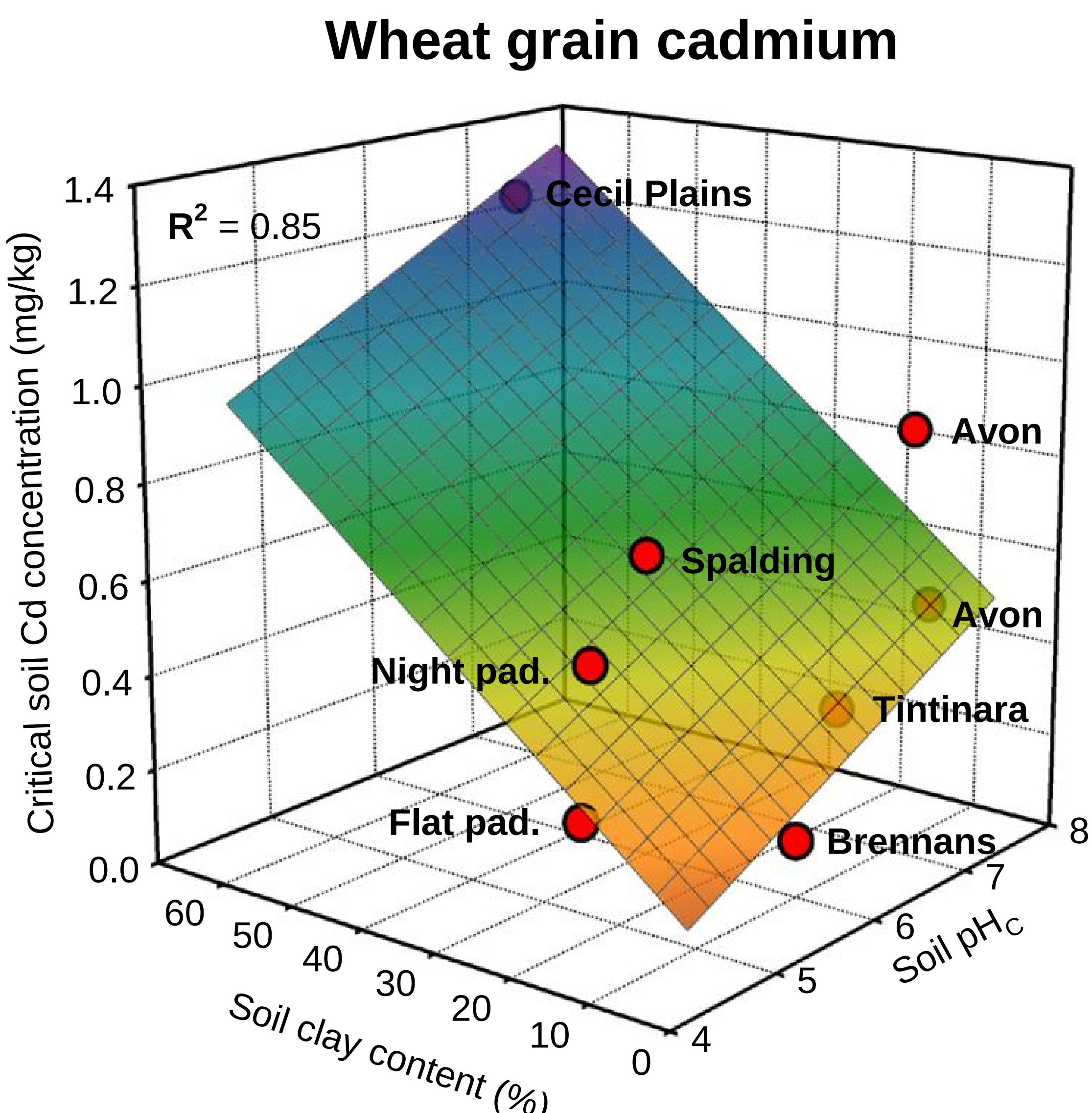
Vietnam & Thailand

Field experimental program

Australia

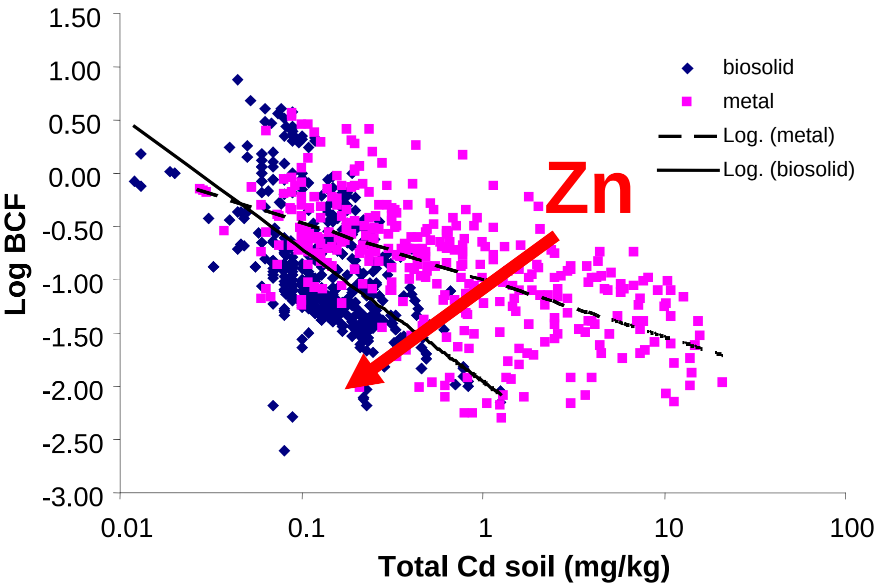
Two components examined

Food chain Cd risk for wheat grain



McLaughlin, M. J., M. Whatmuff, M. Warne, D. Heemsbergen, G. Barry, M. Bell, D. Nash and D. Pritchard (2006). "A field investigation of solubility and food chain accumulation of biosolid-cadmium across diverse soil types." Environmental Chemistry **3: 428-432.**

Biosolids Cd bioavailability ≠ soluble Cd



$$BCF = \frac{\text{Grain Cd}}{\text{Soil Cd}}$$

* Biosolid Cd BCF factors are concentration dependent

Soil Cd (mg/kg)	BCF ratio (Salt/Biosolid)
1.00	9.1
0.50	5.5
0.25	3.4
0.10	1.8

McLaughlin, M. J., M. Whatmuff, M. Warne, D. Heemsbergen, G. Barry, M. Bell, D. Nash and D. Pritchard (2006). "A field investigation of solubility and food chain accumulation of biosolid-cadmium across diverse soil types." Environmental Chemistry **3: 428-432.**

Proposed soil guideline values for total Cd in soil for biosolids reuse in agriculture

pH	Clay content (%)		
	5	25	50
	mg Cd/kg soil		
4.5	0.3	0.9	1.6
5.5	0.6	1.1	1.8
6.5	0.9	1.4	2.1
7.5	1.1	1.6	2.3
8.5	1.4	1.9	2.6

4. Develop mitigation strategies

Mitigation strategies

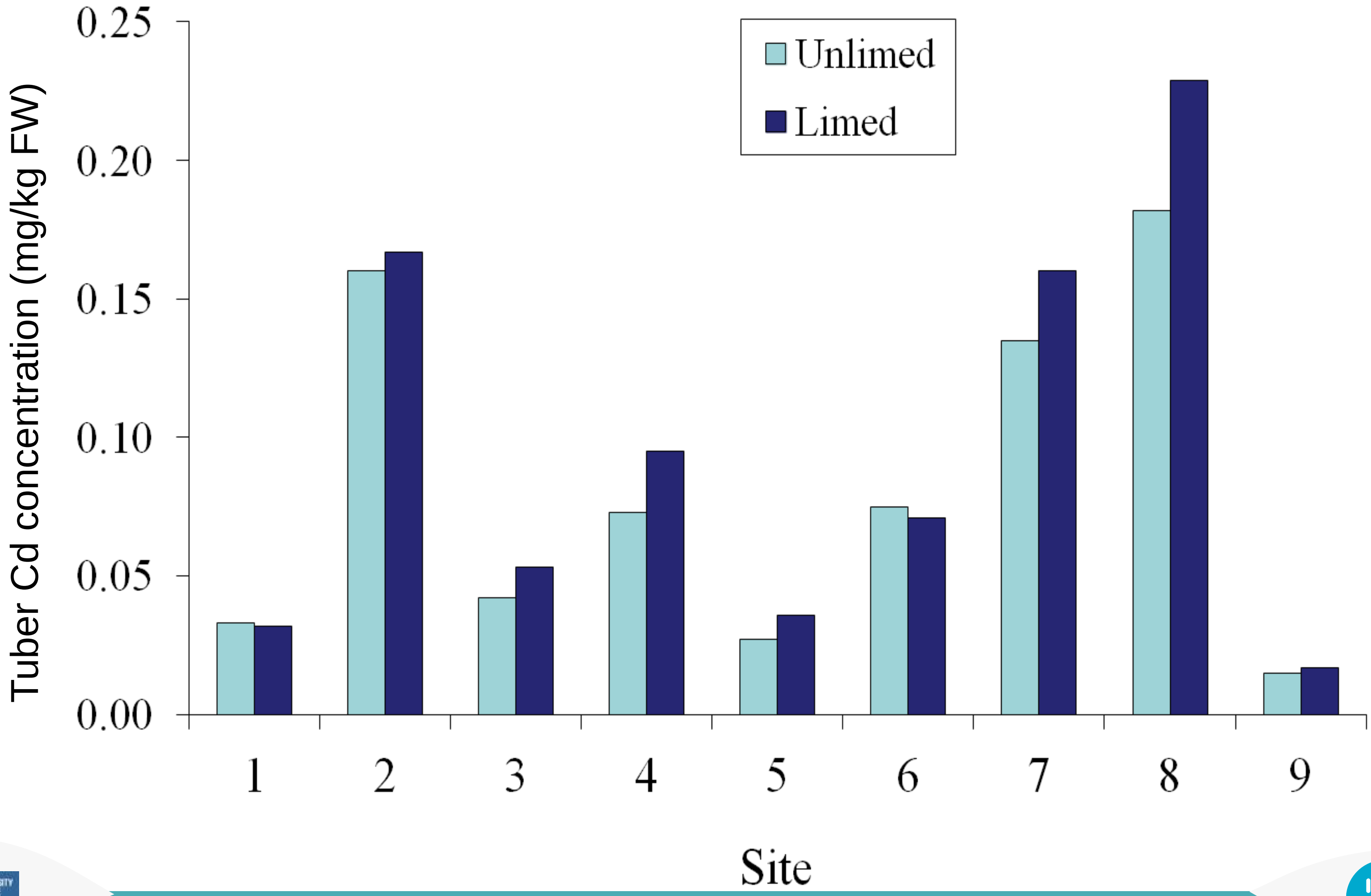
- Conduct experimental programs to determine amelioration strategies to minimize Cd uptake
  - Change cultivar/crop type
  - Add competing ions e.g. Zn
  - Liming – topsoil/subsoil (difficult)
  - Add sorbents (*in situ* remediation)
  - Add other ameliorants to soil
- Provide farmers with the information

Experimental approach

- Need robust Cd analytical capability
- Pot Cd trials ≠ field Cd behaviour
- Cd solubility ≠ Cd bioavailability
- Cd-spiked soils ≠ indigenous soil Cd
- Solution culture ≠ soil culture

Field trials are always preferable to laboratory/glasshouse trials

Mitigation strategies – liming (field trials)



Maier, N. A., M. J. McLaughlin, M. Heap, M. Butt and M. K. Smart (2002). "Effect of current-season application of calcitic lime and phosphorus fertilization on soil pH, potato growth, yield, dry matter content, and cadmium concentration." Communications in Soil Science and Plant Analysis **33(13&14): 2145-2165.**

Liming is not always successful – why?

- Ca^{2+} competition for Cd^{2+} sorption sites?
- Liming reduces availability of trace elements - ↓Zn ↑Cd?
- Time is needed for lime dissolution in soils?

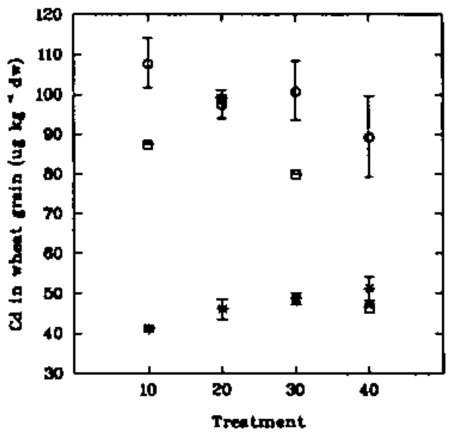
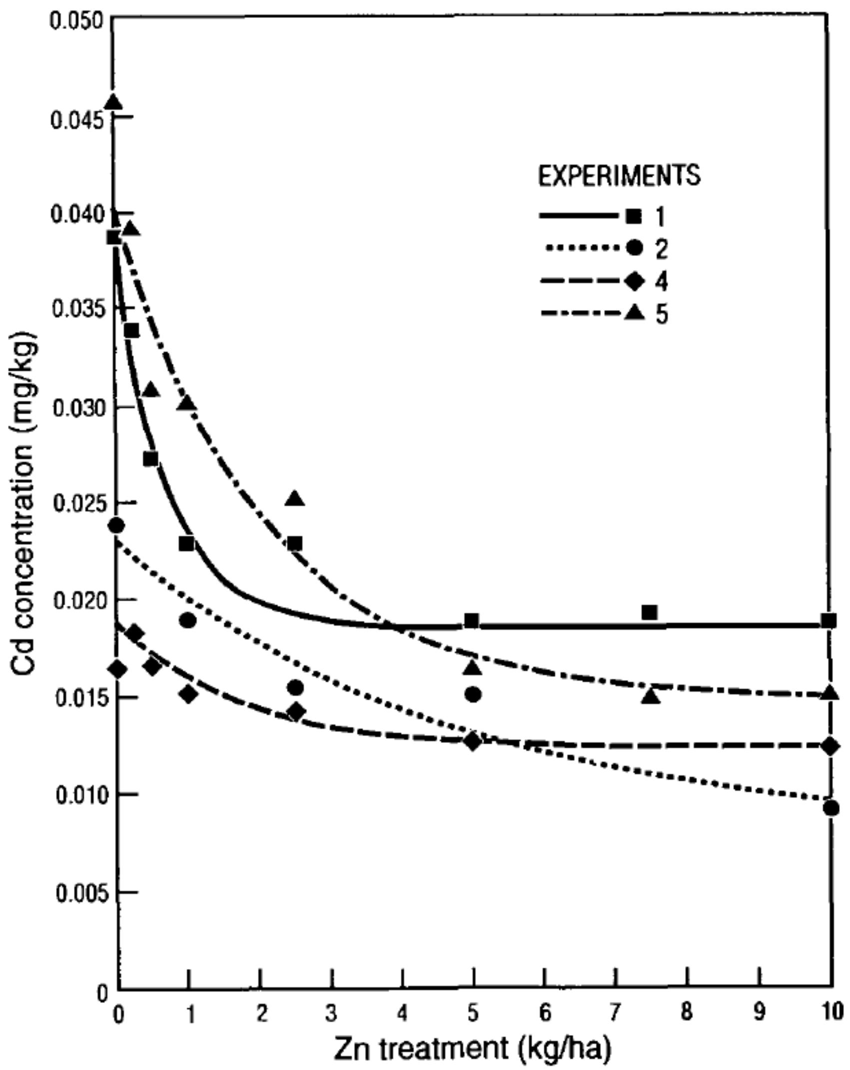


Fig. 3. Effects of liming on cadmium levels in spring wheat grain from three experimental sites Östuna (o, 2 years, p=0.06), Bro (■, 1 year) and Eckerud (*, 1 year, p=0.06). Means and standard deviations, based on results from one year and two years respectively, are shown. The treatments were unlimed (10), limed to 55 (20), 70 (30) and 100% (40) base saturation.

Oborn, I. and G. Jansson (1998). Effects of liming on cadmium contents of spring wheat and potatoes. World Congress Soil Science, Montpellier, France.

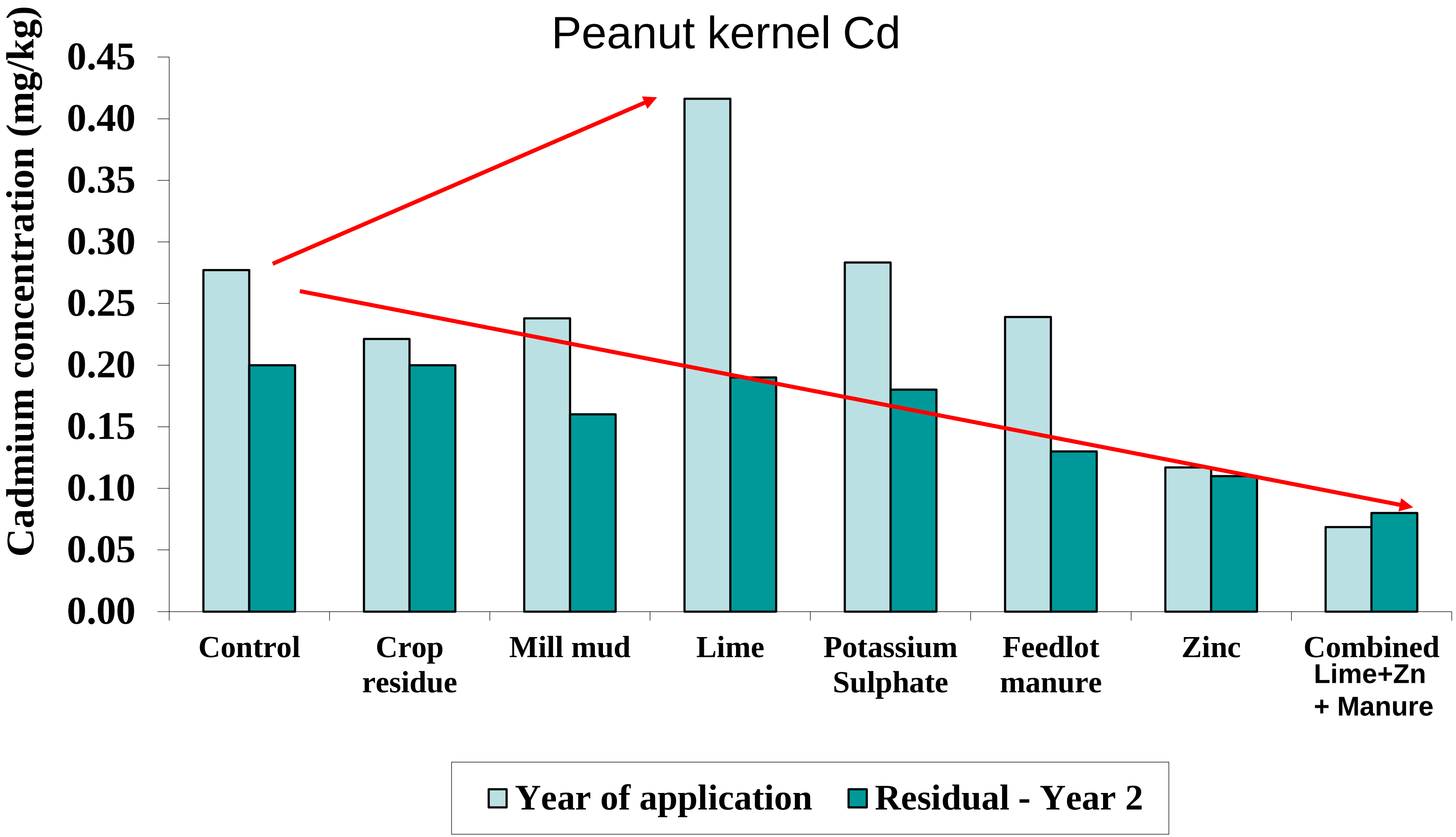
Mitigation strategies – adding Zn



Oliver, D. P., R. Hannam, K. G. Tiller, N. S. Wilhelm, R. H. Merry and G. D. Cozens (1994). "The effects of zinc fertilization on cadmium concentration in wheat grain." Journal of Environmental Quality **23: 705-711.**

Mitigation strategies – sorbents

Mitigation strategies – sorbents



Mitigation strategies – phytoremediation?

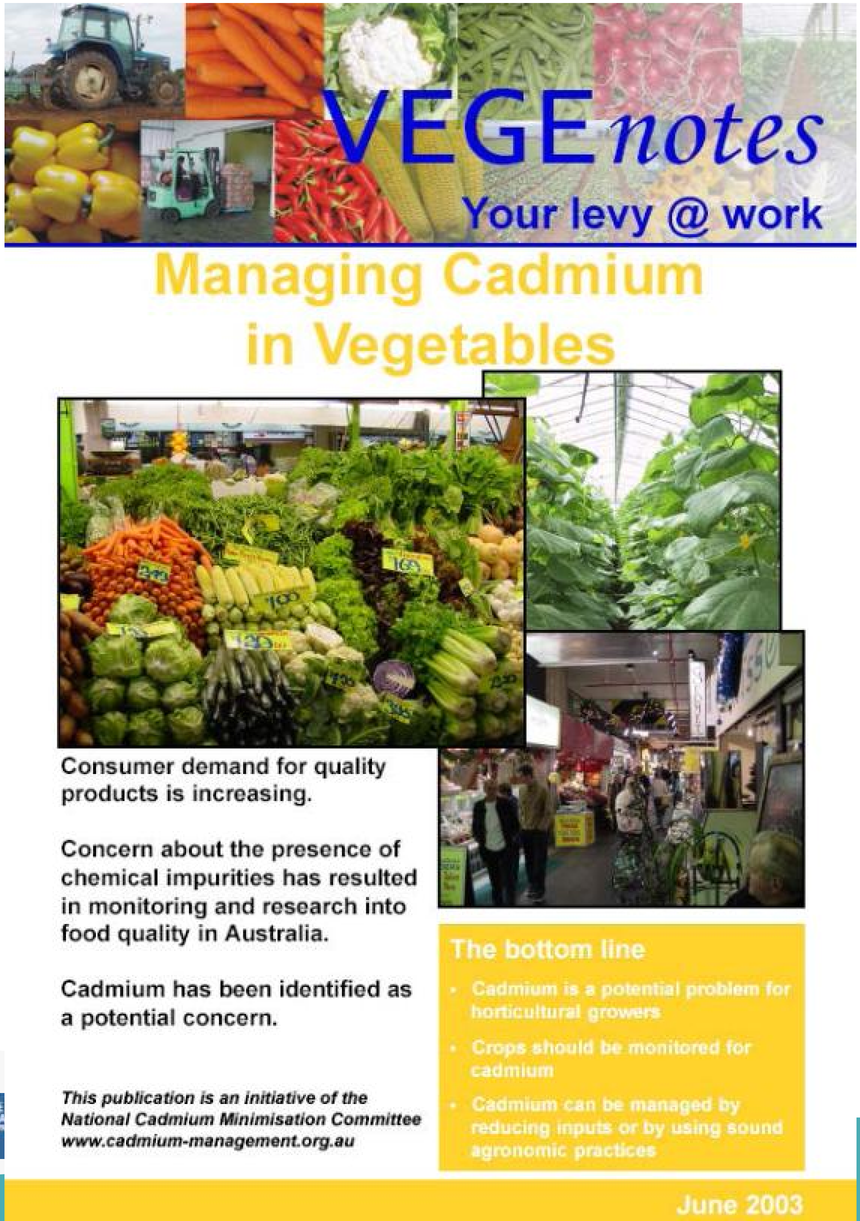
Using oilseeds ± EDTA to remove Cd from soils

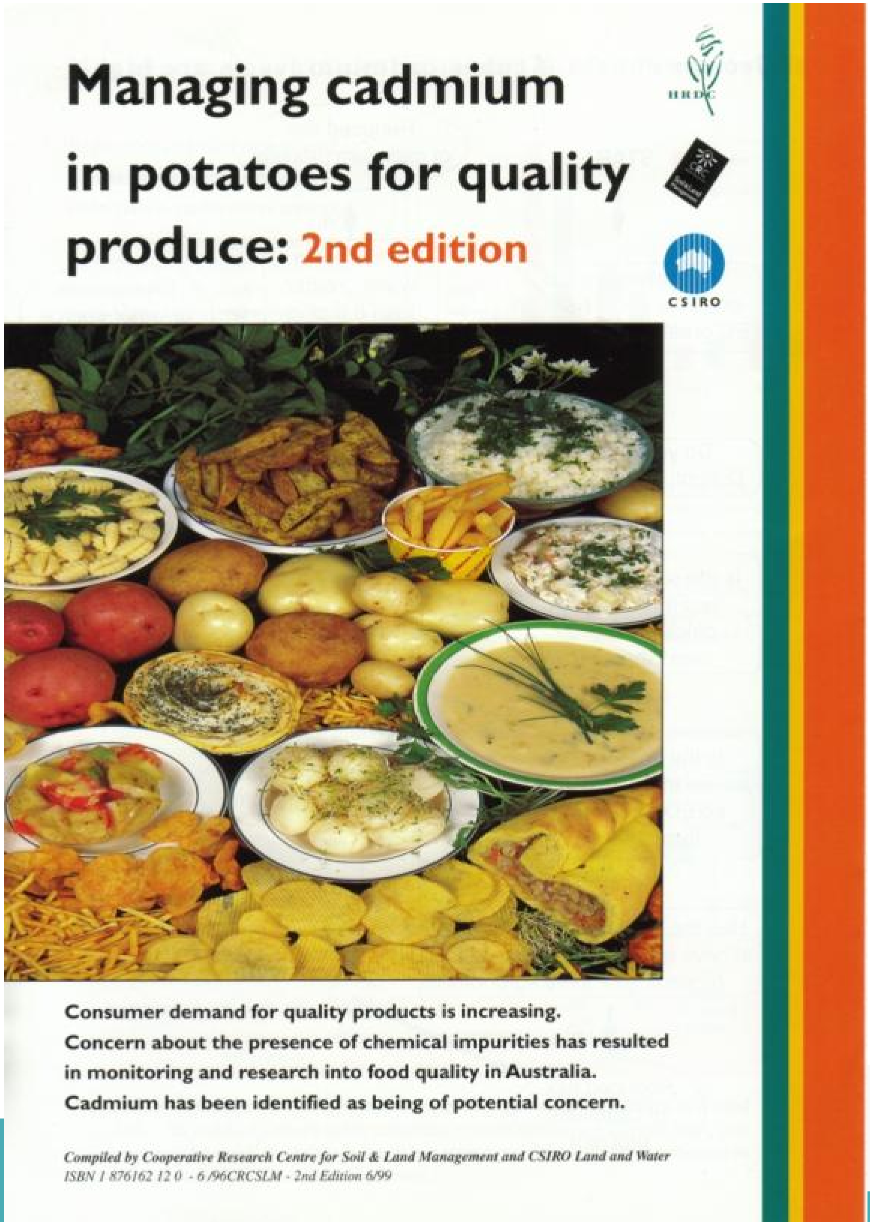
	Safflower	Mustard	Safflower	Mustard
	------- mg/kg ------		--------- g/ha --------	
Control	0.46	0.40	1.18	3.64
+EDTA	0.52	0.31	1.61	2.86
LSD ($P \leq 0.05$)	------- 0.23 -----		-------- 1.05 -------	

Removal too low to reduce tuber Cd

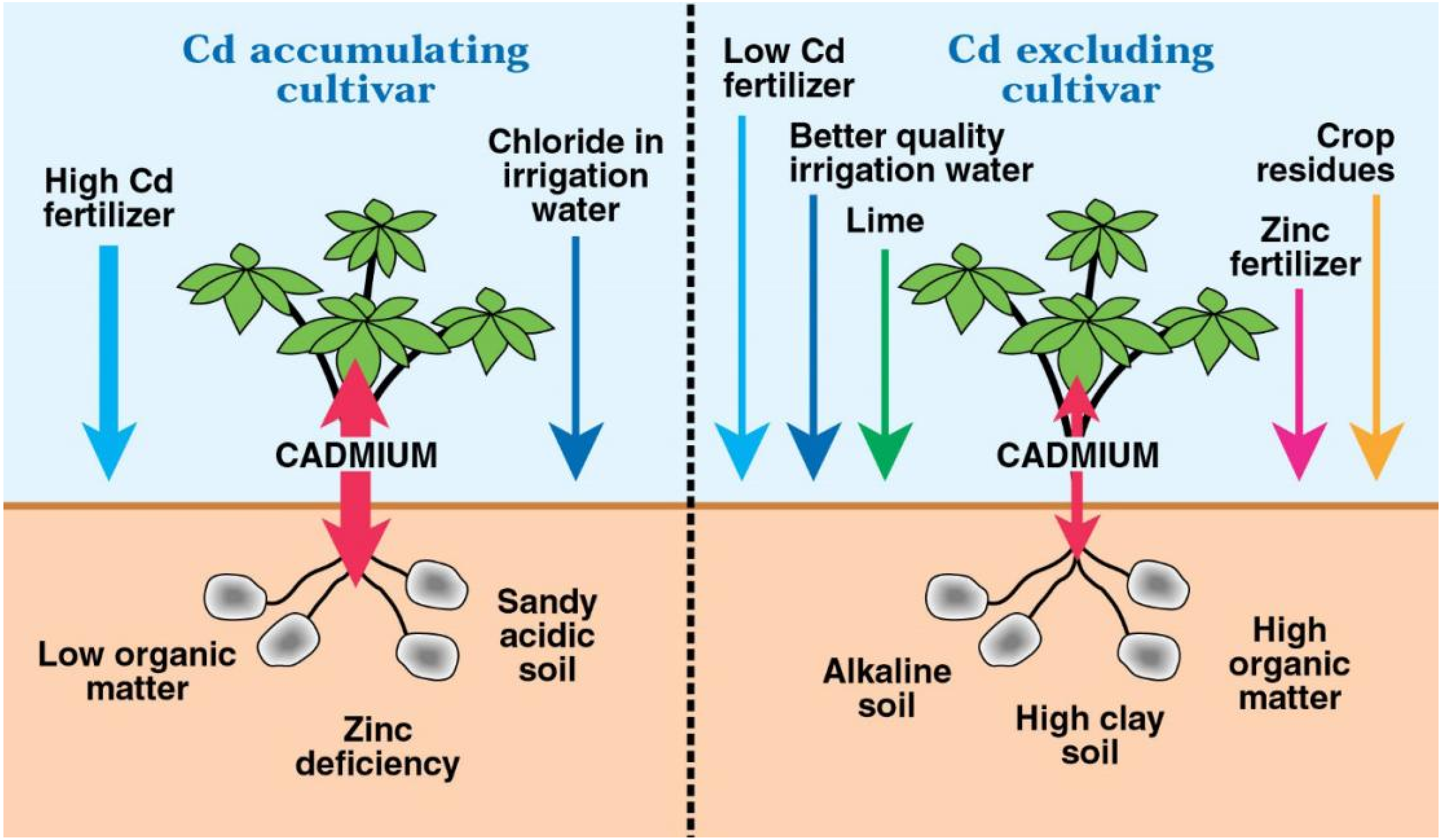
McLaughlin, M.J. et al unpublished data

Mitigation strategies – educating farmers





Mitigation strategies – extension of BMPs



Cadmium in cocoa

Cadmium in cocoa products

- Cocoa products have higher Cd concentrations than many other crop foods
- Human intake of cocoa is low, so that human health risks from exposure to Cd through cocoa consumption are low and “not of concern” by FAO/WHO(JECFA 2013 meeting)
- However no CODEX ML for cocoa or cocoa products has been set yet, so exporting countries could be affected by some country standards (e.g. EU)

Cadmium in cocoa products

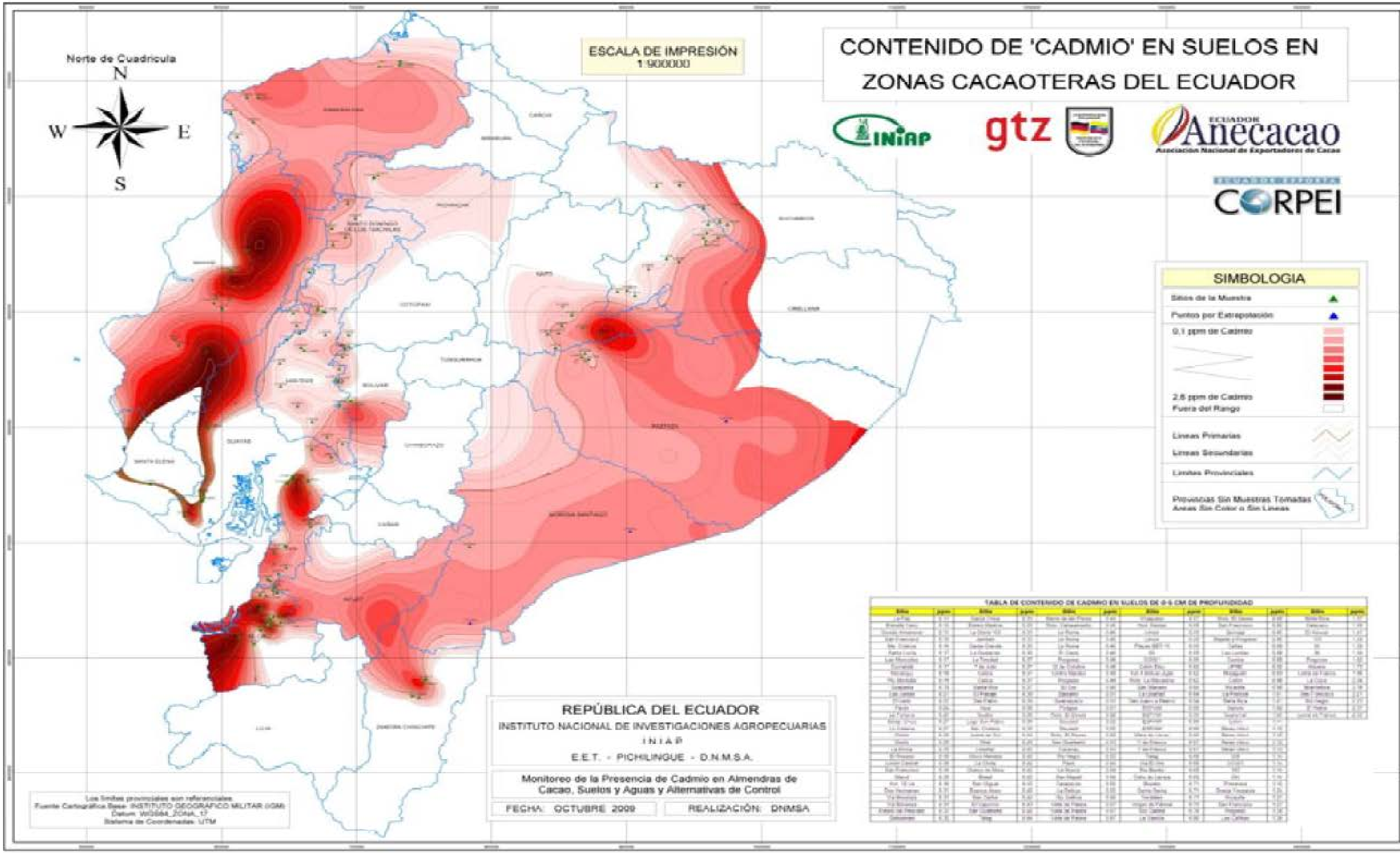
- CODEX proposed MLs for Cd are

PRODUCT	ML of Cd (mg/kg)
Cocoa liquor	3.0
Cocoa powder	4.0

- EU proposed MLs for Cd (mg/kg) are

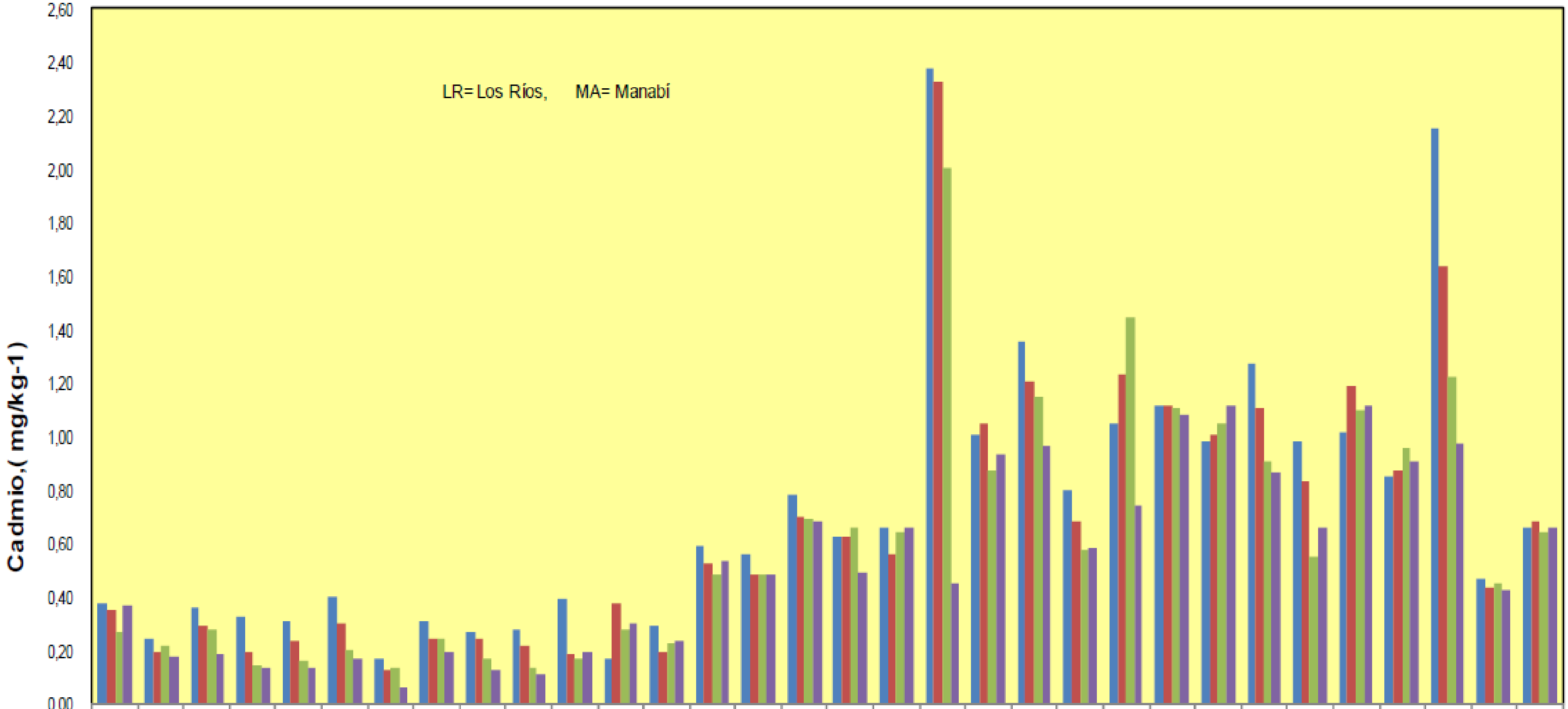
3.2.7	Specific cocoa and chocolate products as listed below ([49])	
	— Milk chocolate with < 30 % total dry cocoa solids	0,10 as from 1 January 2019
	— Chocolate with < 50 % total dry cocoa solids; milk chocolate with ≥ 30 % total dry cocoa solids	0,30 as from 1 January 2019
	— Chocolate with ≥ 50 % total dry cocoa solids	0,80 as from 1 January 2019
	— Cocoa powder sold to the final consumer or as an ingredient in sweetened cocoa powder sold to the final consumer (drinking chocolate)	0,60 as from 1 January 2019

Cadmium distribution in cocoa soils - Ecuador



Mite, F., M. Carillo and W. Durango (2010). Avances del monitoreo de presencia de cadmio en almadras de cacao, suelos y aguas en Ecuador. XII Congreso Ecuatoriano de la Ciencia del Suelo. Santa Domingo, Sociedad Ecuatoriano de la Scienca del Suelo.

Cadmium distribution in cocoa soils



	LR1	LR2	LR3	LR4	LR5	LR6	LR7	LR8	LR9	LR10	LR11	LR12	LR13	LR14	LR15	LR16
0-5 cm	0,38	0,24	0,36	0,33	0,30	0,40	0,17	0,31	0,27	0,27	0,39	0,16	0,29	0,59	0,56	0,78
6-10 cm	0,35	0,19	0,29	0,19	0,23	0,30	0,13	0,24	0,24	0,22	0,18	0,37	0,19	0,52	0,48	0,7
11-15 cm	0,27	0,21	0,27	0,14	0,16	0,20	0,13	0,24	0,17	0,13	0,17	0,27	0,22	0,48	0,48	0,69
16-20 cm	0,37	0,17	0,18	0,14	0,13	0,17	0,06	0,19	0,13	0,11	0,19	0,30	0,23	0,53	0,48	0,68

	LR17	LR18	MA1	MA2	MA3	MA4	MA5	MA6	MA7	MA8	MA9	MA10	MA11	MA12	MA13	MA14
0-5 cm	0,62	0,66	2,37	1,01	1,35	0,80	1,05	1,11	0,98	1,27	0,98	1,02	0,85	2,16	0,46	0,66
6-10 cm	0,62	0,56	2,33	1,05	1,20	0,68	1,23	1,11	1,00	1,10	0,83	1,19	0,87	1,64	0,43	0,68
11-15 cm	0,66	0,64	2,00	0,87	1,15	0,57	1,45	1,11	1,04	0,91	0,55	1,10	0,96	1,23	0,45	0,64
16-20 cm	0,49	0,66	0,45	0,93	0,96	0,59	0,74	1,08	1,12	0,87	0,66	1,11	0,91	0,97	0,42	0,66

Figura 2. Contenidos de Cd en profundidad en 32 suelos dedicados al cultivo de cacao en las provincias de Los Ríos y Manabí. Época seca, 2008.

Mite, F., M. Carillo and W. Durango (2010). Avances del monitoreo de presencia de cadmio en almadras de cacao, suelos y aguas en Ecuador. XII Congreso Ecuatoriano de la Ciencia del Suelo. Santa Domingo, Sociedad Ecuatoriano de la Scienca del Suelo.

Understanding crop Cd uptake - Cocoa

Table 6
Relationship between soil parameters and Cd concentration in cacao beans for the 0–5 and 5–15 cm depth.

Soil properties (0–5 cm)	R^2	Soil properties (5–15 cm)	R^2
M3, EC, pH. % clay, total C, TR, CEC	0.77	M3, total C, % clay, pH, TR, EC, CEC	0.84
M3, EC, pH. % clay, total C, TR	0.77	M3, total C, % clay, pH, TR, EC	0.84
M3, EC, pH. % clay, total C	0.77	M3, total C, % clay, pH, TR	0.84
M3, EC, pH. % clay	0.76	M3, total C, % clay, pH	0.82
M3, EC, pH	0.76	M3, total C, % clay	0.79*,+
M3, EC	0.73*,+	M3, total C	0.72

Nomenclature: TR = total recoverable Cd, Total C = total carbon, CEC_E = effective cation exchange capacity, EC = electrical conductivity.

* $P < 0.05$.

\+ Best model.

Chavez, E., Z. L. He, P. J. Stoffella, R. S. Mylavarapu, Y. C. Li, B. Moyano and V. C. Baligar (2015). "Concentration of cadmium in cacao beans and its relationship with soil cadmium in southern Ecuador." Science of the Total Environment **533: 205-214.**

Conclusions

- Cadmium poses a key concern as it is not highly toxic to plants or soil organisms, but accumulates in foods posing risks to human health
- Control of Cd in agricultural systems needs a combined approach to understanding soil factors leading to high Cd uptake (risk prediction), as well as intervention strategies to ameliorate soils (risk reduction)
- Field-based experimentation is essential to develop farmer-ready management strategies

Conclusions

- Ecuador has a well established research program examining Cd in cocoa soils
- High risk areas have been identified and Cd distribution in soils both spatially and to depth is known – however a whole of country geochemical survey is needed
- Some remediation strategies have been trialled but more work is needed to develop highly effective strategies using a combination of ameliorants
- Ongoing interventions at FAO/WHO CODEX are essential to ensure “sensible” MLs are adopted

Muchas Gracias!