Inorganic contaminants in Soils

Itai-itai: Cadmium
Human Health Effects

Arsenicosis: Arsenic
Human Health Effects

Minamata: Methylmercury
Human Health Effects

Phytotoxicity- Zinc
Ecological Health Effects

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Phytotechnology with Biomass Production
CHE 650 Hazardous Waste Engineering Seminar
January 9-11, 2018

Terminology

- Trace elements - elements that are normally present at relatively low concentrations in soils or plants. They may or may not be essential for the growth and development of plants, animals, or humans
- Related terms – heavy metals, micronutrients, trace metals, microelements, minor elements, trace inorganics
- 78 elements in the periodic Table
- Short List - As, B, Be, Cd, Co, Cr, Cu, F, Fe, Hg, I, Mn, Mo, Ni, Pb, Se, Sn, V, and Zn

Periodic table of the elements

(shaded are NOT trace elements)

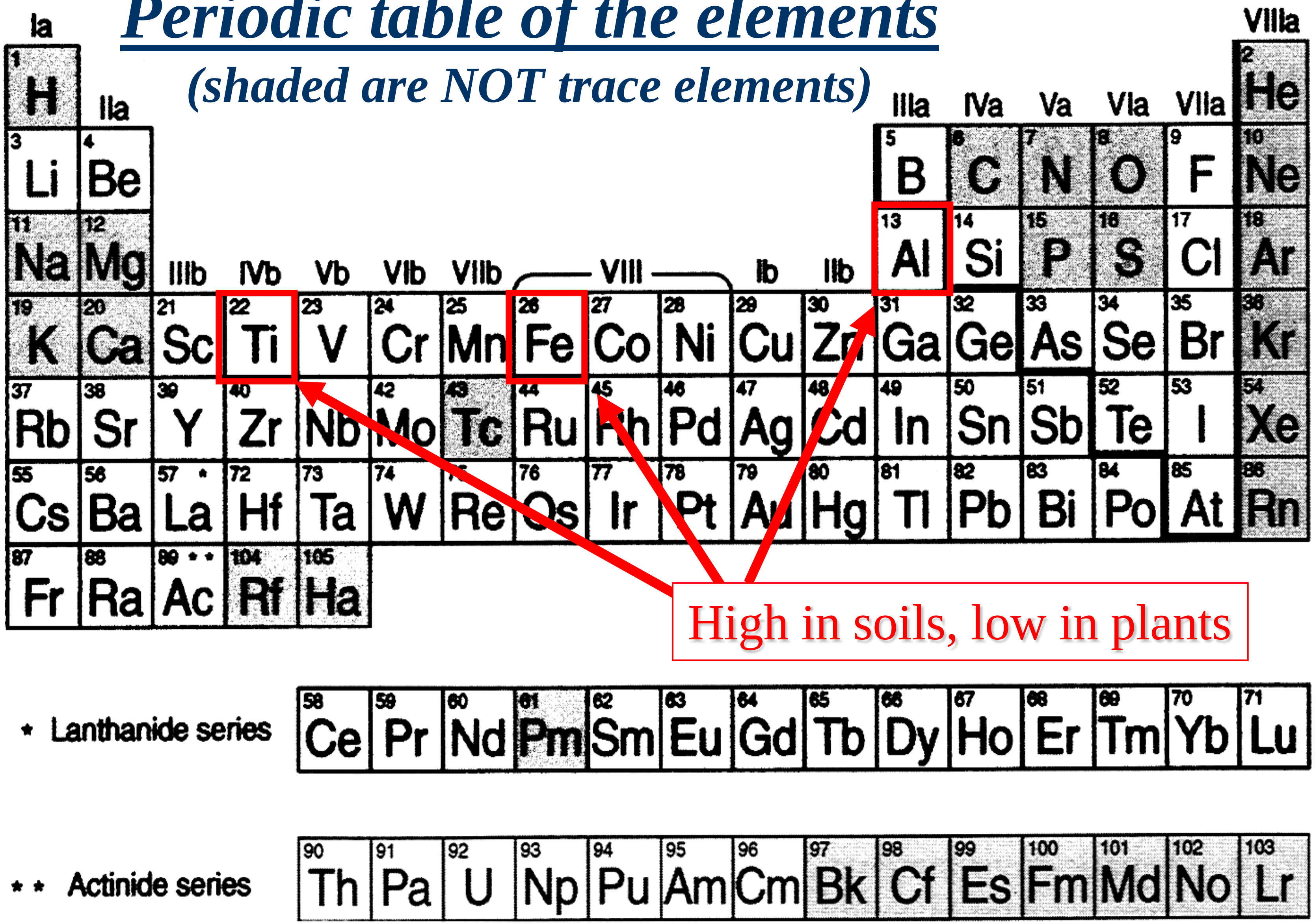

Figure 9.1

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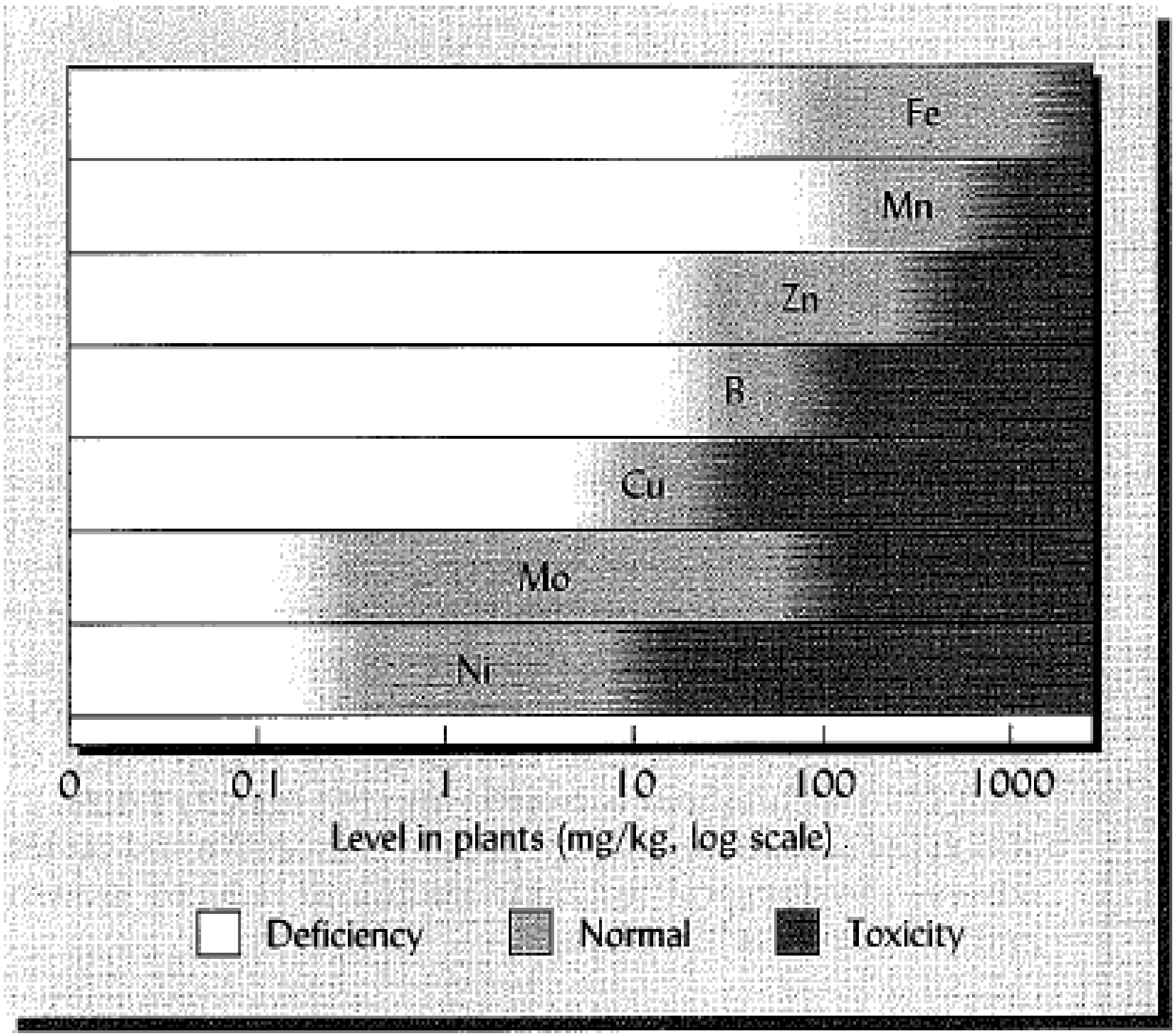
Plant essential elements (nutrients)

Nutrient – implies that the element or substance is essential for the growth and development of some organism

	Element	Chemical Symbol	Where obtained
Macro-	Carbon	C	Air/ water
Nutrients	Hydrogen	H	Air/ water
	Oxygen	O	Air/ water
	Nitrogen	N	Soil/ air
	Phosphorus	P	soil
	Potassium	K	soil
	Calcium	Ca	soil
	Magnesium	Mg	soil
	Sulfur	S	soil
Micro-	Iron	Fe	soil
Nutrients	Manganese	Mg	soil
	Zinc	Zn	soil
	Copper	Cu	soil
	Boron	B	soil
	Molybdenum	Mo	soil
	Chlorine	Cl	soil
	Cobalt	Co	soil
	Nickel	Ni	soil

Deficiency, normal, and toxicity levels in plants for seven micronutrients



Brady and Weil, 2002

TABLE 1.1

The Elemental Content (Median and Range) of Uncontaminated Soils Collected from around the World and the Mean Elemental Content of the Earth's Crust (the Valences and Aqueous Speciation of the Elements in Soil Environments Are Also Shown)

Element	Atomic Mass[b]	mg kg^{-1}[a]: Soil	mg kg^{-1}[a]: Earth's Crust	ER[c]	Important Chemical Species and Oxidation States[d]
		The Most Abundant Constituents of Organic Soils and Soil Organic Matter			
O*	15.9994	490,000	474,000	1.0	O^0 [$O_2(g)$], O^{-II} [H_2O] (oxidant: $O_2(g) + 4e^- + 4H^+ = 2H_2O$)
C*	12.011	20,000 (7,000–500,000)	480	42	organic, C^{IV} [CO_3^{2-}, HCO_3^-, $H_2CO_3^0$, $CO_2(g)$]
N*	14.00674	2,000 (200–5,000) (~$^1/_{10}$ C)	25	80	organic, N^V [NO_3^-], N^{-III} [NH_4^+, $NH_3(g)$]
P*	30.97376	800 (35–5,300) (~$^1/_5$ N)	1,000	0.80	organic, P^V [HPO_4^{2-}, $H_2PO_4^-$]
S*	32.006	700 (30–1,600) (~$^1/_5$ N)	260	2.7	organic, S^{VI} [SO_4^{2-}], S^{-II} [$H_2S(g)$, HS^-, S^{2-}]
		The Most Abundant Elements in Mineral Soils			
Si*	28.0855	330,000 (250,000–410,000)	277,000	1.2	Si^{IV} [$H_4SiO_4^0$]
Al	26.98153	71,000 (10,000–300,000)	82,000	0.87	Al^{III} [Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$]
Fe*	55.845	40,000 (2,000–550,000)	41,000	0.96	Fe^{II} [Fe^{2+}], Fe^{III} [Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3^0$, and $Fe(OH)_4^-$]

Source: Essington, 2015. Soil and Water Chemistry: An Integrative Approach

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TABLE 1.1
The Elemental Content (Median and Range) of Uncontaminated Soils Collected from around the World and the Mean Elemental Content of the Earth's Crust (the Valences and Aqueous Speciation of the Elements in Soil Environments Are Also Shown) (Continued)

		Other Major Elements			
Ca*	40.078	15,000 (700–500,000)	41,000	0.37	Ca^{2+}
K*	39.0983	14,000 (80–37,000)	21,000	0.67	K^{+}
Mg*	24.305	5,000 (400–9,000)	23,000	0.22	Mg^{2+}
Na*	22.98977	5,000 (150–25,000)	23,000	0.22	Na^{+}
Ti	47.867	5,000 (150–25,000)	5,600	0.89	Ti^{IV}
Mn*	54.938	1,000 (20–10,000)	950	1.1	Mn^{2+}
		Micro and Trace Elements			
Ba	137.327	500 (100–3,000)	500	1.0	Ba^{2+}
Zr	91.224	400 (60–2,000)	190	2.1	Zr^{IV}
Sr	87.62	250 (4–2,000)	370	0.68	Sr^{2+}
F*	18.9984	200 (20–700)	950	0.21	F^{-}
Cl*	35.453	100 (8–1,800)	130	0.77	Cl^{-}
Zn*	65.39	90 (1–900)	75	1.2	Zn^{2+}
V*	50.9415	90 (3–500)	160	0.57	V^{IV} [VO^{2+}], V^{V} [VO_2^{+}, $VO_2(OH)_2^{-}$, $VO_3(OH)^{2-}$]
Cr*	51.9961	70 (5–1,500)	100	0.70	Cr^{III} [Cr^{3+}], Cr^{VI} [$HCrO_4^{-}$, CrO_4^{2-}, $Cr_2O_7^{2-}$]
Ni*	58.6934	50 (2–750)	80	0.63	Ni^{2+}
Pb	207.2	35 (2–300)	14	2.5	Pb^{2+}
Cu*	58.9332	30 (2–250)	50	0.60	Cu^{2+}
Li	6.941	25 (3–350)	20	1.3	Li^{+}
B*	10.811	20 (2–270)	10	0.50	B^{III} [$B(OH)_3^{0}$, $B(OH)_4^{-}$]
Br	79.904	10 (1–110)	0.37	27	Br^{-}
Co*	58.9332	8 (0.05–65)	20	0.4	Co^{2+}

(continued)

TABLE 1.1

The Elemental Content (Median and Range) of Uncontaminated Soils Collected from around the World and the Mean Elemental Content of the Earth's Crust (the Valences and Aqueous Speciation of the Elements in Soil Environments Are Also Shown) (Continued)

Element	Atomic Mass[b]	Soil (mg kg^{-1} [a])	Earth's Crust (mg kg^{-1} [a])	ER[c]	Important Chemical Species and Oxidation States[d]
		Micro and Trace Elements			
As*	74.9216	6 (0.1–40)	1.5	4.0	As^{III} [$HAsO_3^{2-}$], As^{V} [$HAsO_4^{2-}$, $H_2AsO_4^-$]
Mo*	95.94	1.2 (0.1–40)	1.5	0.80	Mo^{VI} [MoO_4^{2-}]
Se*	78.96	0.4 (0.1–2)	0.05	8.0	Se^{IV} [$HSeO_3^-$, SeO_3^{2-}], Se^{VI} [SeO_4^{2-}], Se^{-II} [Se^{2-}]
Cd	112.411	0.35 (0.01–2)	0.11	3.2	Cd^{2+}
Hg	200.59	0.06 (0.01–0.5)	0.05	1.2	Hg^{II} [$Hg(OH)_2^0$], Hg^{I} [Hg_2^{2+}], Hg^0 [Hg(*l*), Hg(*g*)]

[a] Soil elemental concentrations represent the median elemental content and range (in parentheses). Elemental content values for the Earth's crust represent the mean. Data are from Bowen (1979). Additional tabulations of the elemental content of soils have been compiled by Helmke (2000).

[b] Units are g mol^{-1}.

[c] ER is the enrichment ratio and is equal to the median soil content of an element divided by the mean Earth's crust content.

[d] Soluble complexes are not included.

* Denotes an essential or beneficial element for plants or animals.

Additional source (recent)- **Geochemical and Mineralogical Data for Soils of the Conterminous United States**: http://pubs.usgs.gov/ds/801/

Alternative Classification Based on Form in Soil Solution

- Cationic Metals: Ag^{+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}

- Oxyanions: AsO_4^{3-}, $B(OH)_4^{-}$, CrO_4^{2-}, MoO_4^{2-}, $HSeO_3^{-}$, SeO_4^{2-}

- Anions: F^{-}, Cl^{-}, Br^{-}, I^{-}

Terminology

- Contaminant - implies that the concentration of a substance is higher than would occur naturally but <u>does not necessarily mean that the substance is causing harm of any type</u>
- Pollutant - implies that the concentration of a substance is higher than would occur naturally and that <u>substance is causing harm of some type</u>

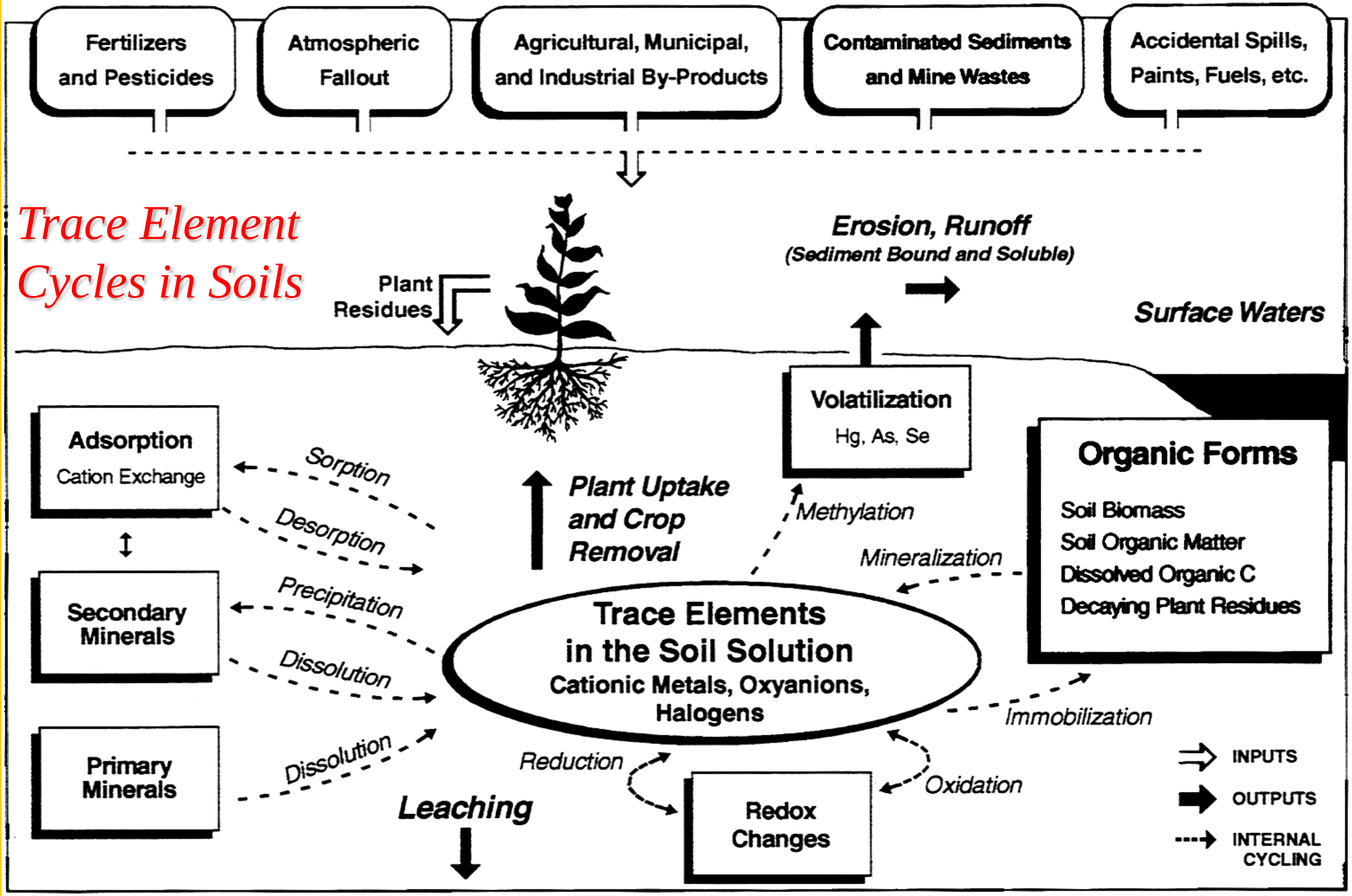
Sources of Inorganics Contamination for Soils

- Mining and smelting of trace elements
- Mining of other materials such as coal
- Land application of wastes – animal manures, biosolids, industrial wastes
- Motor vehicles - Zn and Cd from tires and Ni, Cr, V, W, and Mo from steel
- Agricultural sprays and soil amendments - Pb arsenates, Cu sulfates, etc.
- Leaded paint residues
- Military activities, etc.

Global Trace Element Cycles

- The majority of most trace elements reside in the lithosphere
- The amounts present in the hydrosphere are small but important environmentally
- Gaseous forms exist but are generally not important
- Atmospheric deposition of trace elements is an important source of contamination but this represents the deposition of particulate matter

Trace Element Cycles in Soils



Source: Pierzynski et al., 2005

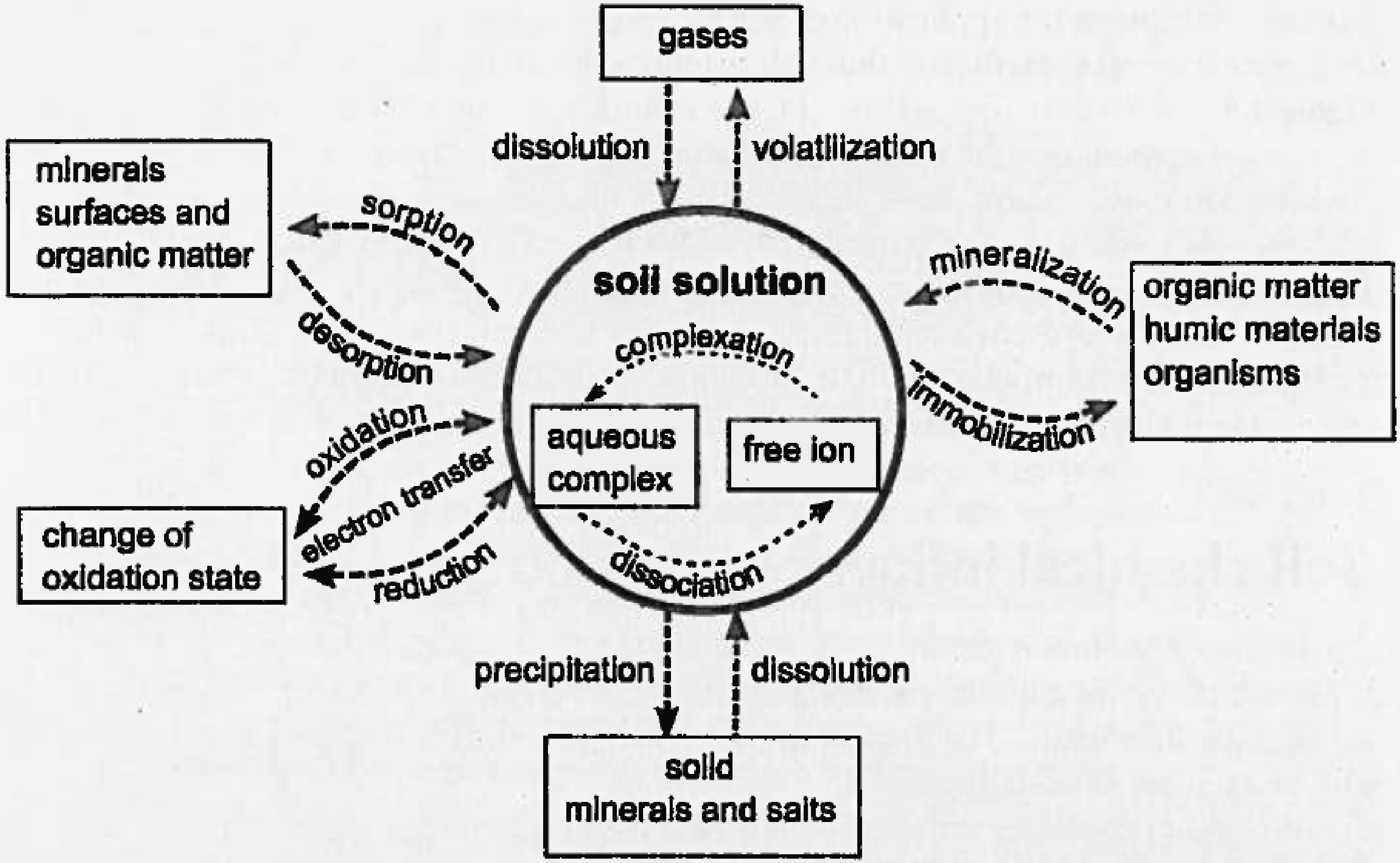


Figure 1.12 Chemical reactions in soil. Soil solution is in the center because most reactions occur between soil solution and either organisms, soil air, or solid phases.

Transformations in Soils

Source: Strawn et al., 2015 Soil Chemistry

Important transformation processes

- Adsorption/ desorption
  - important because trace elements are present at low concentrations
- Precipitation/ dissolution
  - many trace elements form insoluble compounds in soils (i.e., the formation of secondary minerals**)**
- Oxidation/ reduction
  - Some elements undergo oxidation/reduction reactions
  - All most all elements affected by oxidation/reduction of Fe, Mn and S
- Mineralization/ immobilization
- Volatilization

  Important for some trace elements (As, Hg and Se)

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Key point

- Bioavailability is very important. Bioavailability determines the risk to organisms. We may want to reduce bioavailability as part of a remediation strategy

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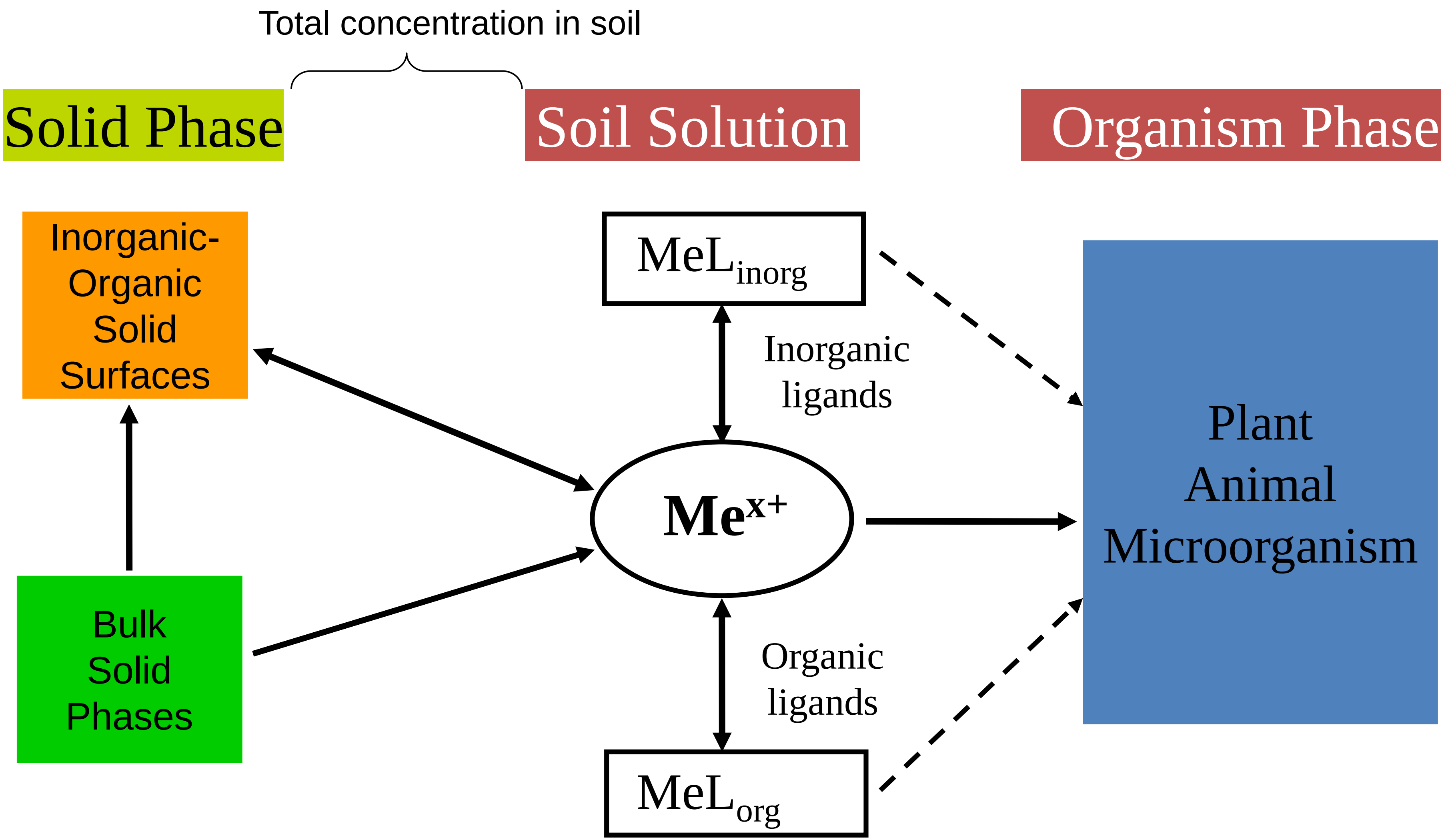
Bioavailability: Definitions

- A measure of the fraction of the chemical(s) of concern in environmental media that is accessible to an organism for absorption

American Society for Testing and Materials, 1998



The most biologically active species are usually the free, unassociated ions.
A knowledge of solid and solution speciation is important.

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Bioavailability and speciation are linked

Definition - speciation

- Determination of the exact chemical form or compound in which an element occurs in a sample, for instance determination of whether arsenic occurs in the form of trivalent or pentavalent ions or as part of an organic molecule, and the quantitative distribution of the different chemical forms that may coexist.

International Union for Pure and Applied Chemistry, 1997

Lead speciation in soil

Form	Example
A. Free metal	Pb^{2+} (lead ion)
B. Soluble complexes	$Pb(OH)^{1+}$; $Pb(OH)_2^0$; $PbCO_3^0$, $PbCl^+$ Pb-citrate
C. Polymeric organic complexes	Pb – humic acid
D. Adsorbed or incorporated metal onto soil minerals	Pb bound on, or in, microparticulate oxides or aluminosilicates
F. Precipitated metal form	Pb phosphate, Pb carbonate, Pb sulphate, Pb sulfide

High

↓

Low

Availability

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Trace Element Bioavailability in Soils

- In order for a TE to be available to an organism for uptake, it must be in a soluble form in solution. Therefore, factors that influence sorption will influence bioavailability.

Lead speciation in soil solution

Form	Example
A. Free metal	Pb^{2+}
B. Hydroxo-complexes	$Pb(OH)^{1+}$
C. Simple inorganic complexes	$PbCO_3^0$, $PbCl^+$, $PbSO_4^0$
D. Simple organic complexes	Pb-citrate
E. Polymeric organic complexes	Cd – fulvate
F. Mineral colloidal form	Pb bound on, or in, microparticulate oxides or aluminosilicates

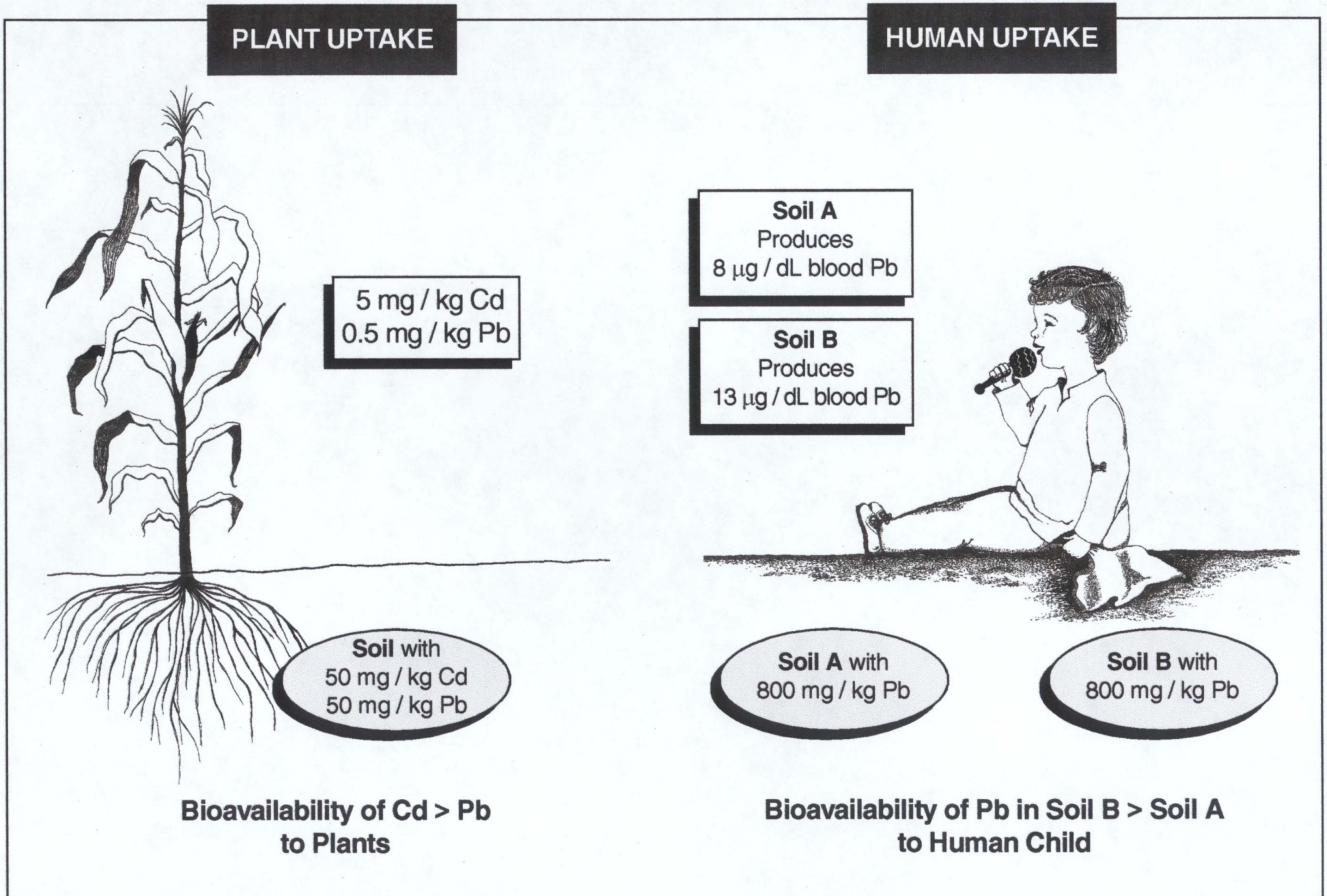
Relative Bioavailability of Pb

Pb Source	Test Organism	Relative Bioavailability
Galena (PbS)	Swine	0.01
Leaded paint	Swine	0.82
Joplin, MO (soil)	Rat	0.34
Joplin, MO (soil + P)	Rat	0.24
Bunker Hill, ID (fasting)	Humans	0.26
Bunker Hill, ID (fed)	Humans	0.03

Source: Pierzynski et al., 2005

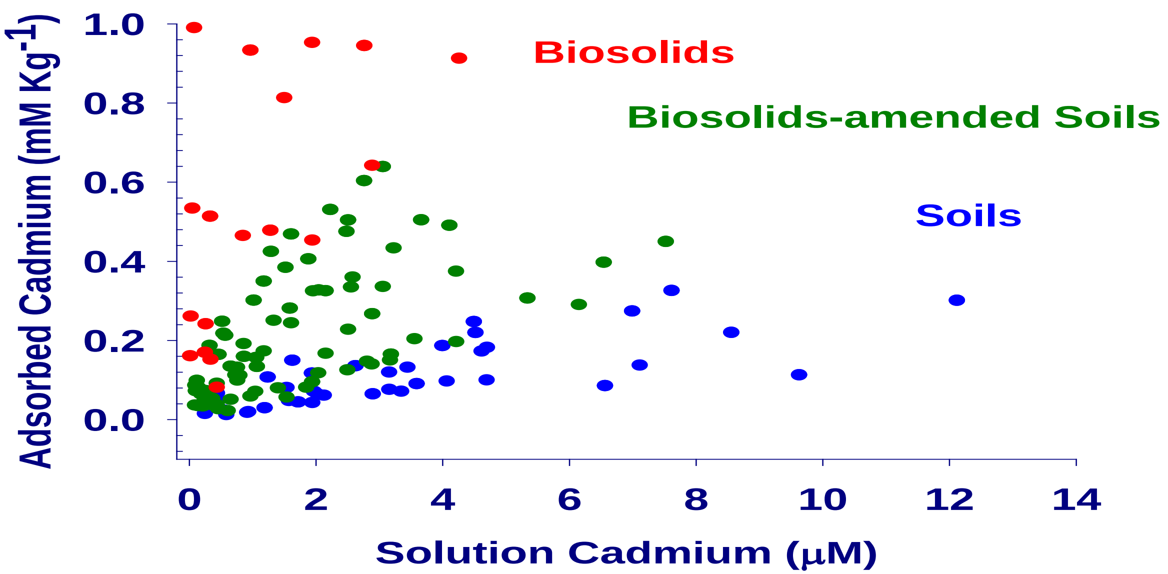
Trace Element Bioavailability in Soils

- Significant environmental effects from TEs
- Total soil TE concentrations do not correlate with organism response
- TE effects related to bioavailability
- Understanding TE bioavailability allows:
  - Better prediction of TE toxicity and deficiency
  - Prediction of exposure routes
  - Remediation strategies


PLANT UPTAKE
5 mg / kg Cd
0.5 mg / kg Pb
Soil with
50 mg / kg Cd
50 mg / kg Pb
Bioavailability of Cd > Pb
to Plants
HUMAN UPTAKE
Soil A
Produces
8 µg / dL blood Pb
Soil B
Produces
13 µg / dL blood Pb
Soil A with
800 mg / kg Pb
Soil B with
800 mg / kg Pb
Bioavailability of Pb in Soil B > Soil A
to Human Child

Factors That Influence TE Sorption and Bioavailability

- Cation exchange capacity – clay content, OM content
- Fe/Al/Mn (hydr)oxides – participate in anion adsorption



Cadmium Adsorption in amended soils

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Addition of Soil Amendments Can Reduce Contaminant Bioavailability

Metal contaminated soils- unamended

With Lime

With Beringite-modified aluminosilicate

With Red Mud Fe oxide rich residue

Courtesy of CSIRO, Land & Water, Australia

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Factors That Influence TE Sorption and Bioavailability

- pH – the master variable. pH has a profound effect on all sorption mechanisms
  - Bioavailability of cationic metals increases with decreasing pH
  - Bioavailability of some oxyanions decreases with decreasing pH

Concentrations (mg/kg) of selected elements in Alfalfa tissue as influenced by soil pH

pH	Cd	Cu	Ni	Mo
6.0	0.8	17.7	1.9	193
7.0	0.6	16.8	0.8	342
7.7	0.4	16.0	0.8	370

Source: Pierzynski et al. 2005. Soils and Environmental Quality

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Factors That Influence TE Sorption and Bioavailability

- Redox – A change in oxidation state (and chemical form) can make an element more or less likely to undergo sorption
  - Direct effects
    - SeO_4^{2-} versus SeO_3^{2-} versus Se^o versus Se^{2-}
    - AsO_4^{-3} versus $H_3AsO_3^0$
  - Indirect effect
    - Reductive dissolution of Fe/Mn minerals
    - Reprecipitaion of Fe/Mn oxides or sulfides

Example: Arsenic in rice (flooded paddy soil)

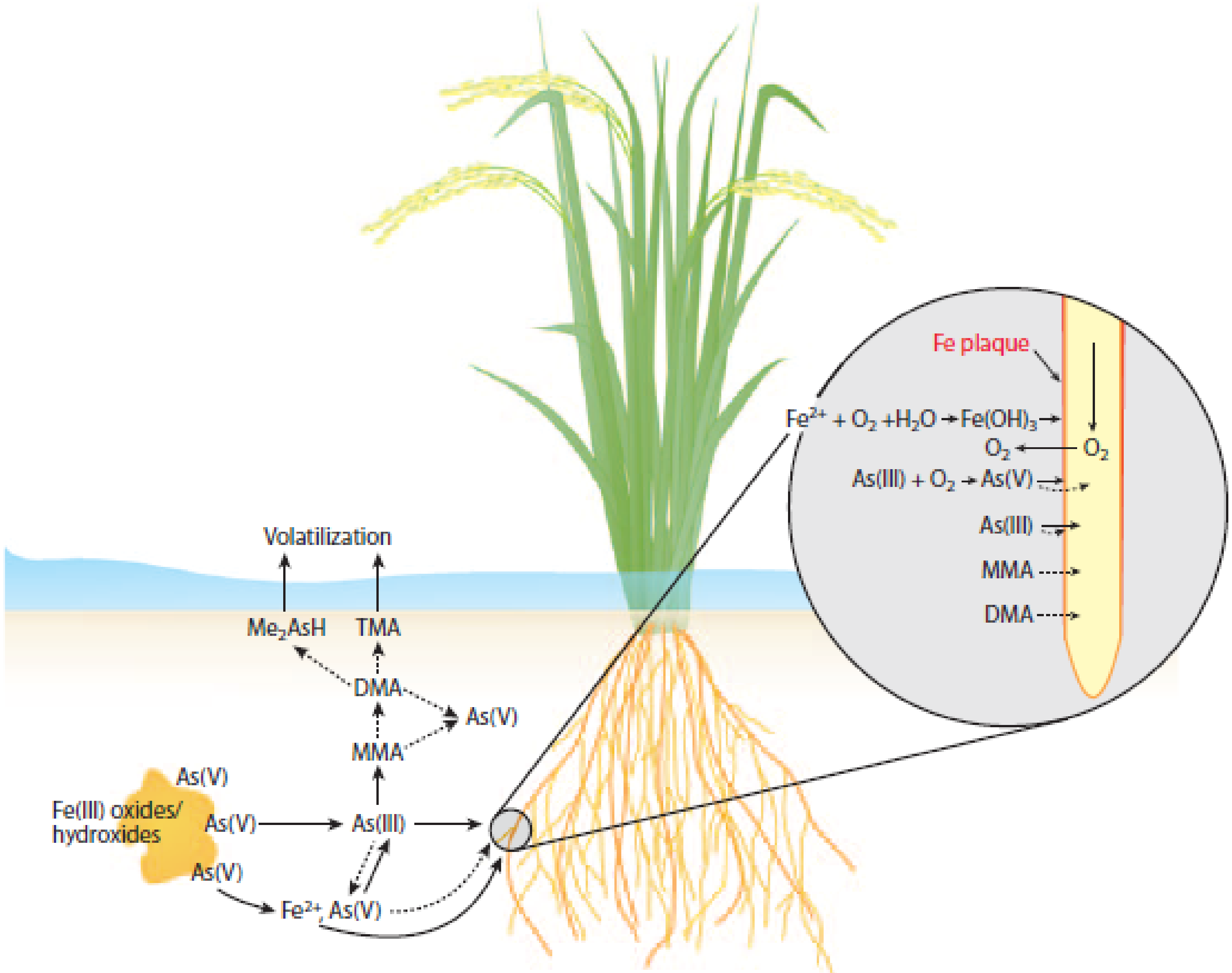
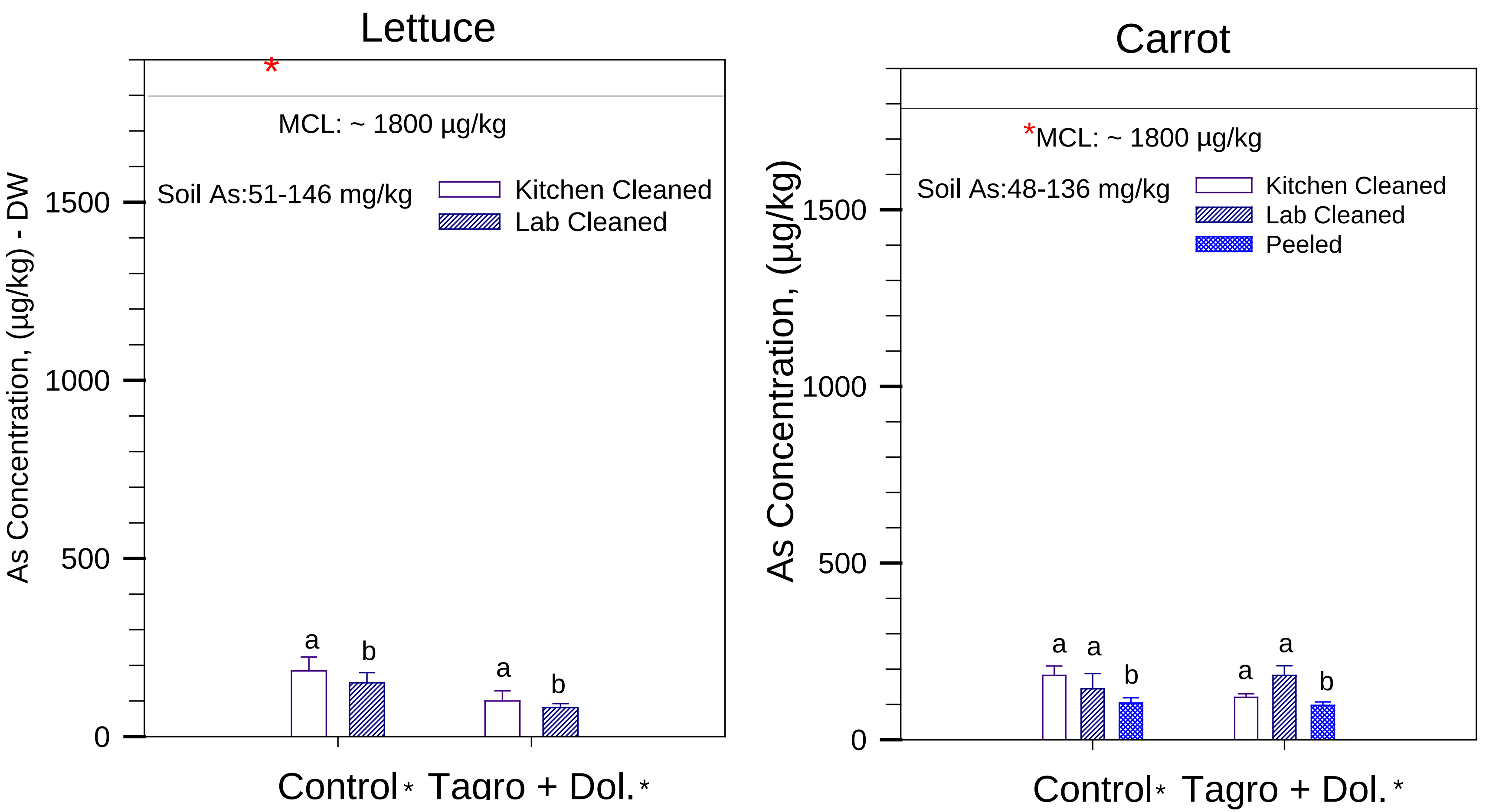


Figure 1

Arsenic mobilization and transformation in flooded paddy soil and interactions in the rice rhizosphere. Arrows with solid and broken lines indicate dominant and minor processes, respectively. For more details of the As methylation pathway, see **Figure 4*b***.

Source: Zhao, McGrath, Meharg, 2010. Annu, Rev. Plant Biol. 61: 535-559.

Arsenic in lettuce and carrot
Garden soils (well-aerated)



Vertical bars represent the means of four replicates

* Estimated using oral exposure daily reference dose limit for inorganic As

Defoe et al., *2014. J. Environ. Qual. 43: 2064-2078.*

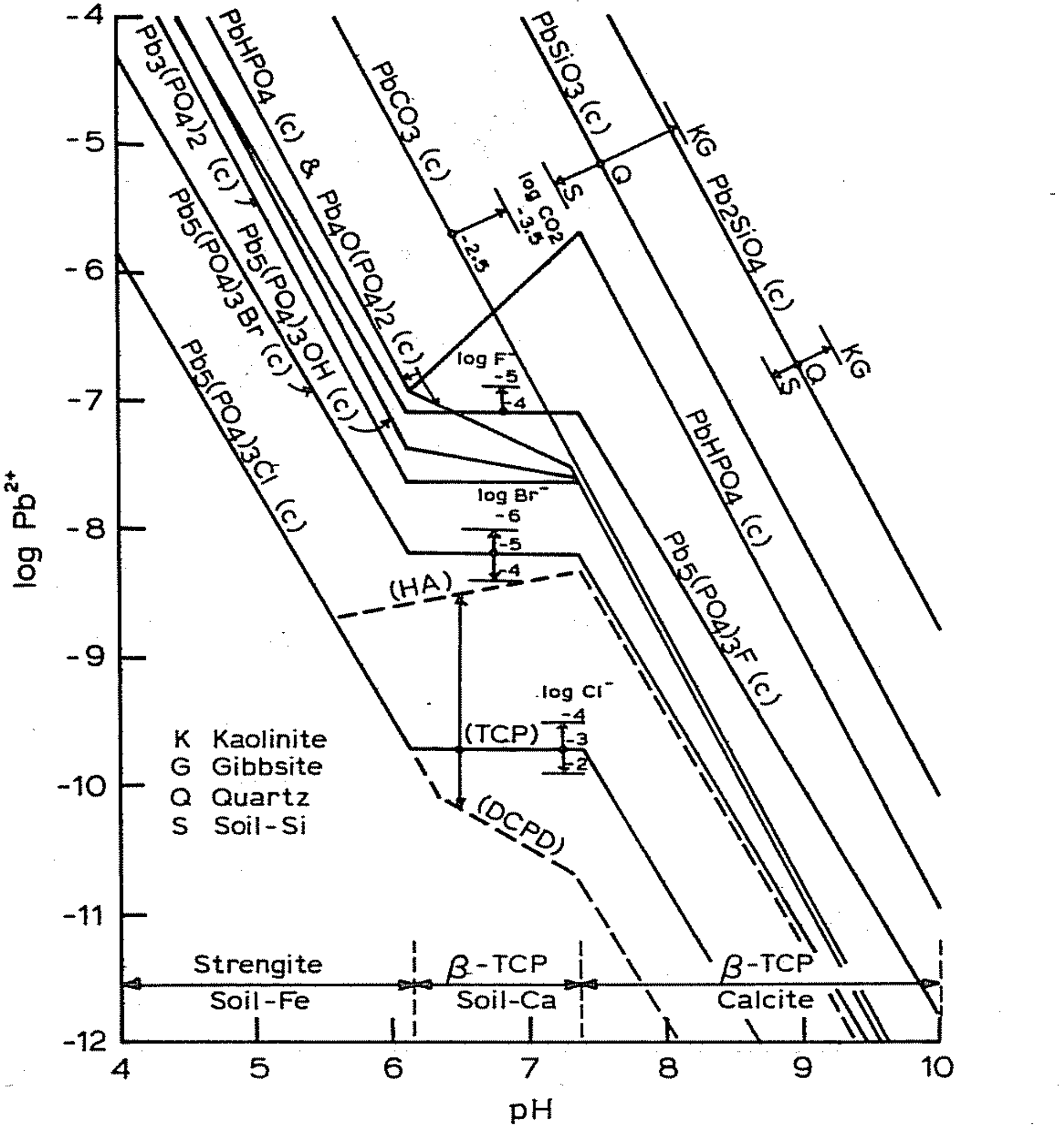


Fig. 20.2 The solubility of various lead silicates and phosphates compared to $PbCO_3$(cerussite) when phosphate is controlled by various solid phases as indicated and CO_2(g) is 0.003 atm.

Comparative Results-for P amendments: Animal, *In vitro* & Human

	Animal* (Swine)	**In vitro** (pH 2.3)**	**Human*** **
% Reduction in Bioavailability	38	38	69

*Casteel et al. (2001), ** Ruby et al. (2001),

***Graziano et al. (2001)

Scientific evidence clearly shows P amended Pb-contaminated soil would cause less of an increase in blood Pb concentrations upon ingestion by children than unamended soil

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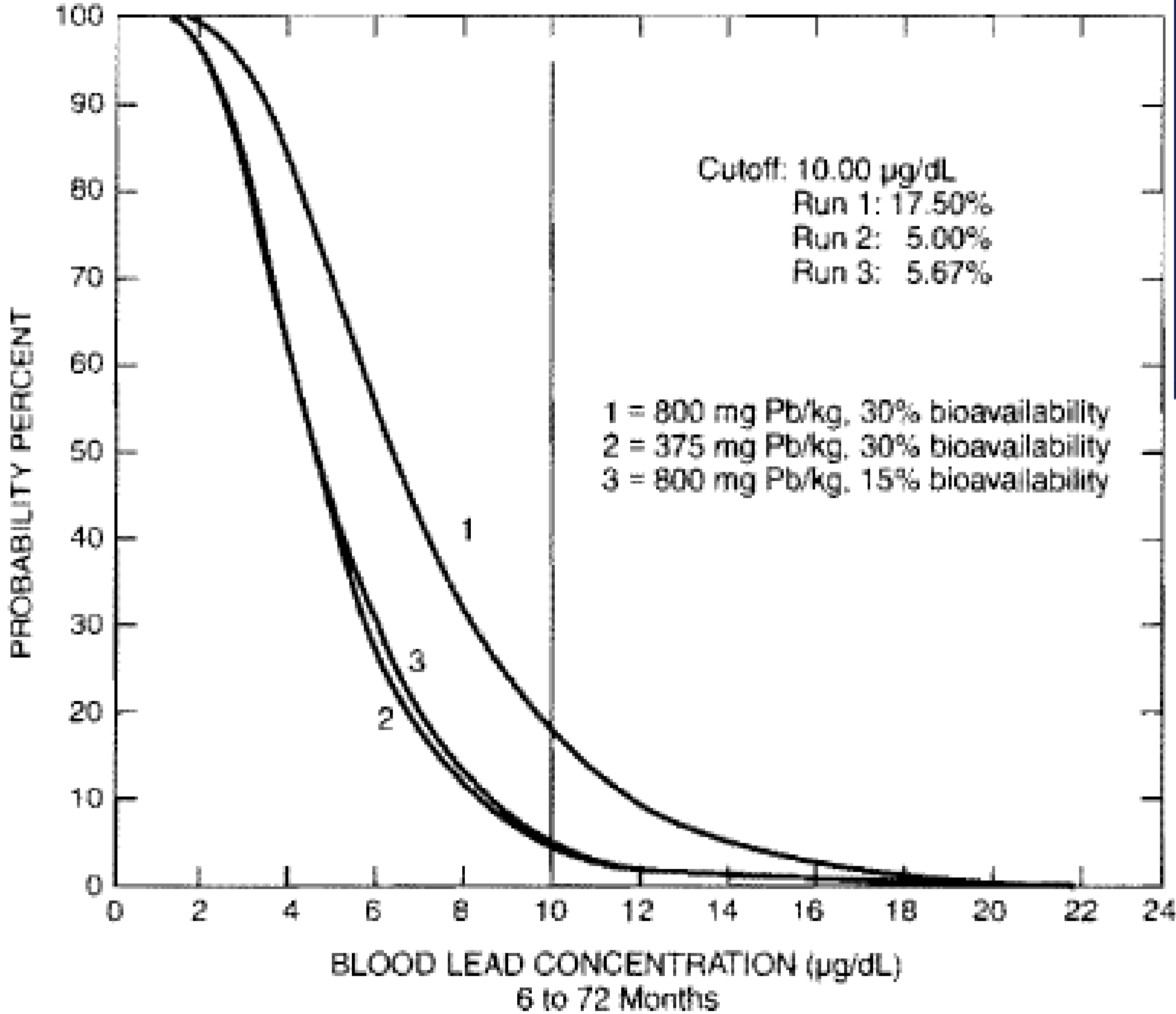
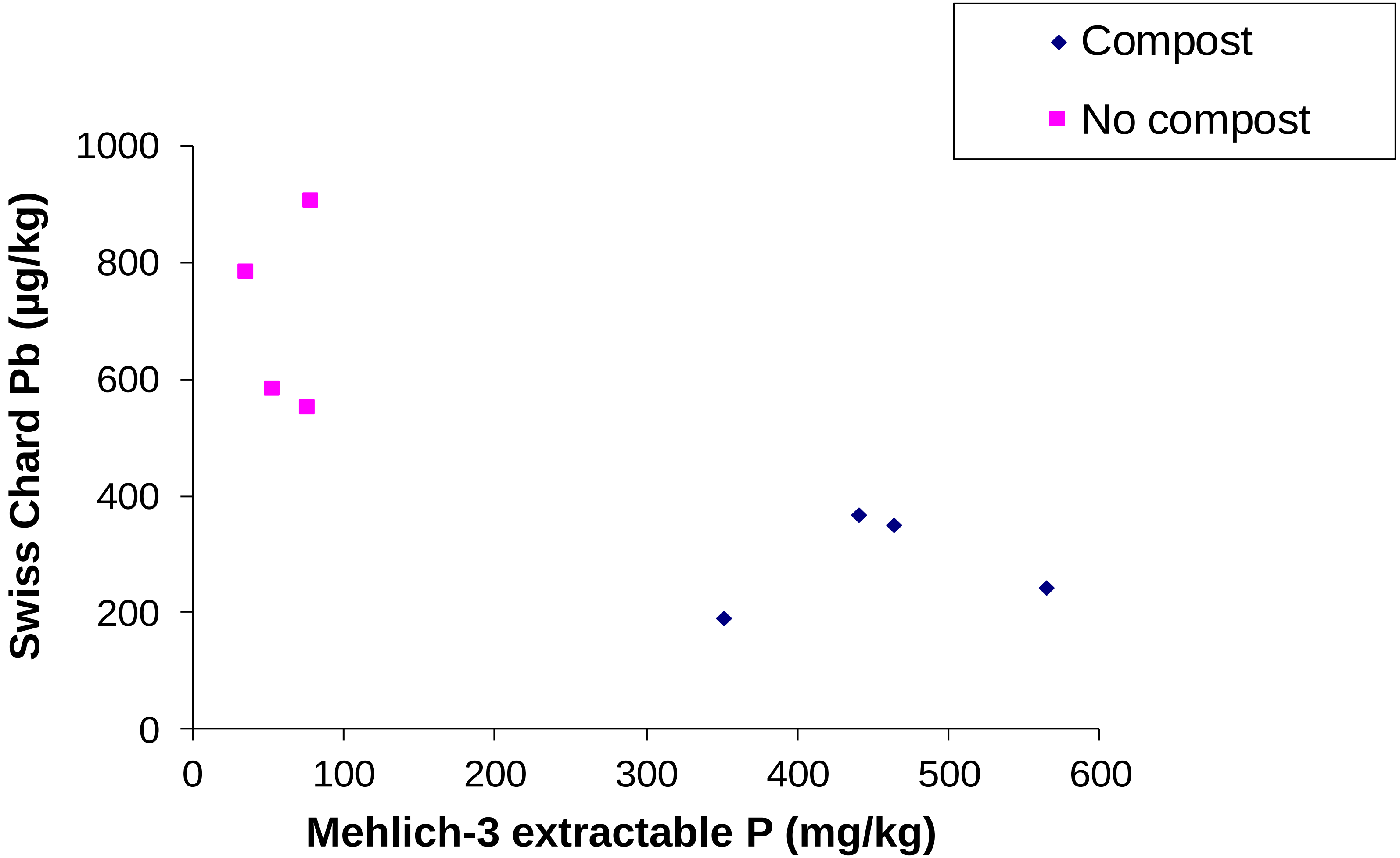


Figure 13.6 IEUBK model output showing the influence of soil Pb bioavailability on the proportion of children 6 to 72 months of age who have >10 μg/dL blood Pb concentration. Curve 1 assumes 800 mg Pb/kg soil and 30% bioavailability while curve 3 uses 800 mg Pb/kg and 15% bioavailability. Curve 2 uses 30% bioavailability and shows that soil Pb cannot exceed 375 mg/kg to have no more than 5% of the children with >10 μg/dL blood Pb concentration.

Swiss Chard Pb versus available P in Soils
(Wash. Wheatley, Kansas City, MO)



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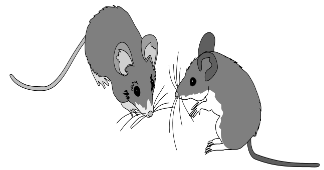
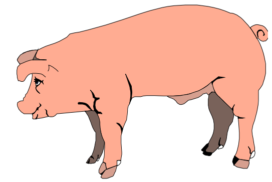
Measuring bioavailability

Humans:

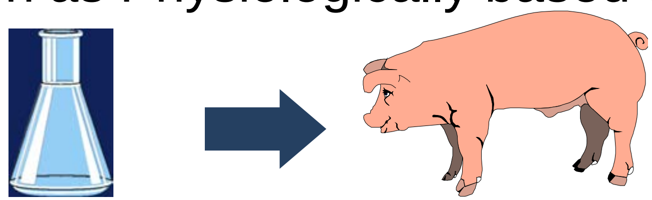
Animal feeding studies





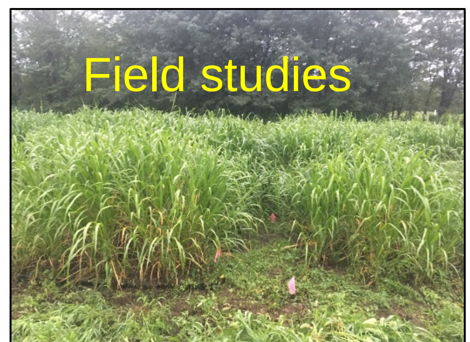
Surrogate methods:

In vitro methods – such as Physiologically based extraction test (PBET) procedure



Plants:

Plant uptake studies



Various extractions

Diffusive Gradients in Thin Films (DGT)

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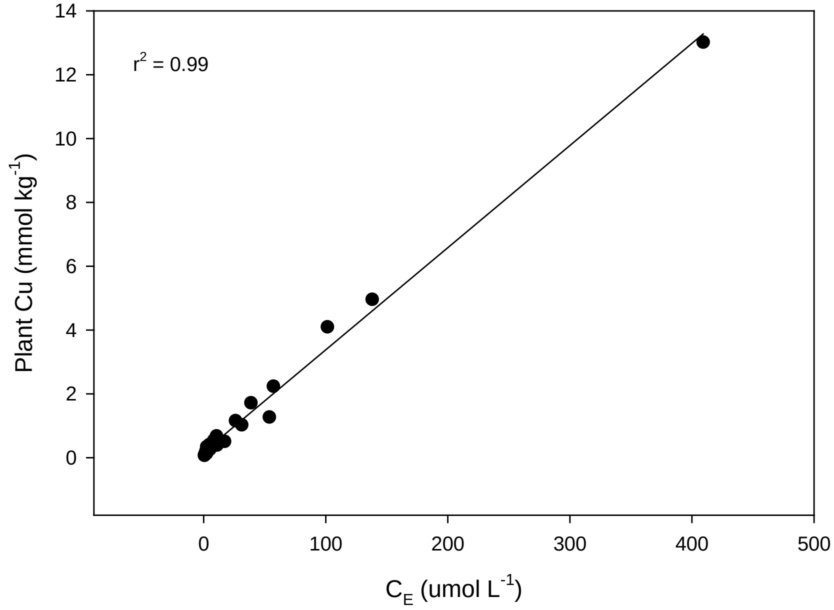

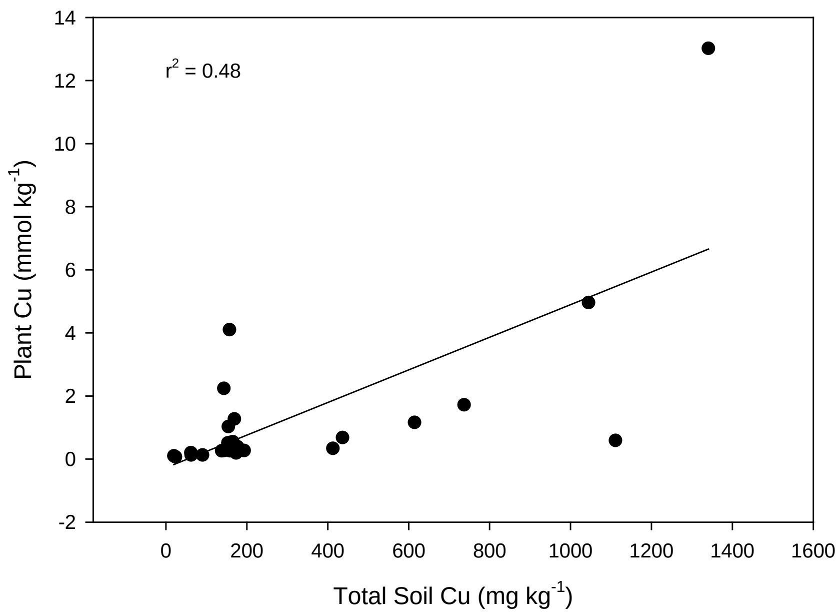

Source: Zhang et al., 2001

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Addition of Soil Amendments Can Reduce Contaminant Bioavailability

Metal contaminated soils- unamended

With Lime

With Beringite-modified aluminosilicate

With Red Mud Fe oxide rich residue

Courtesy of CSIRO, Land & Water, Australia

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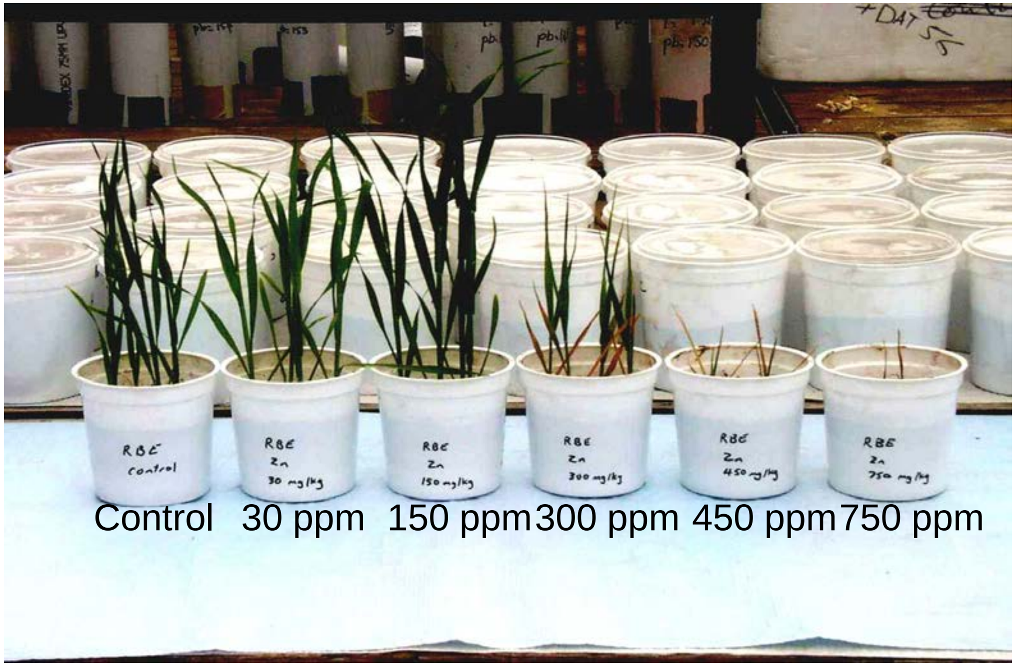
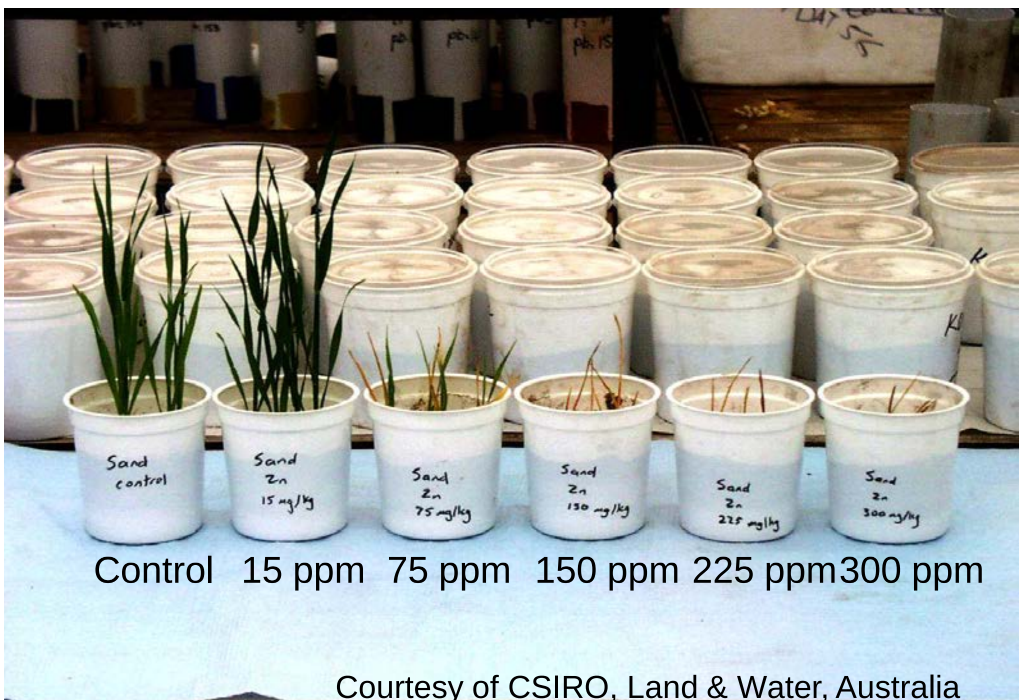
Other Key Points

Other key points: Soil type affects bioavailability



Clayey Soil



Sand

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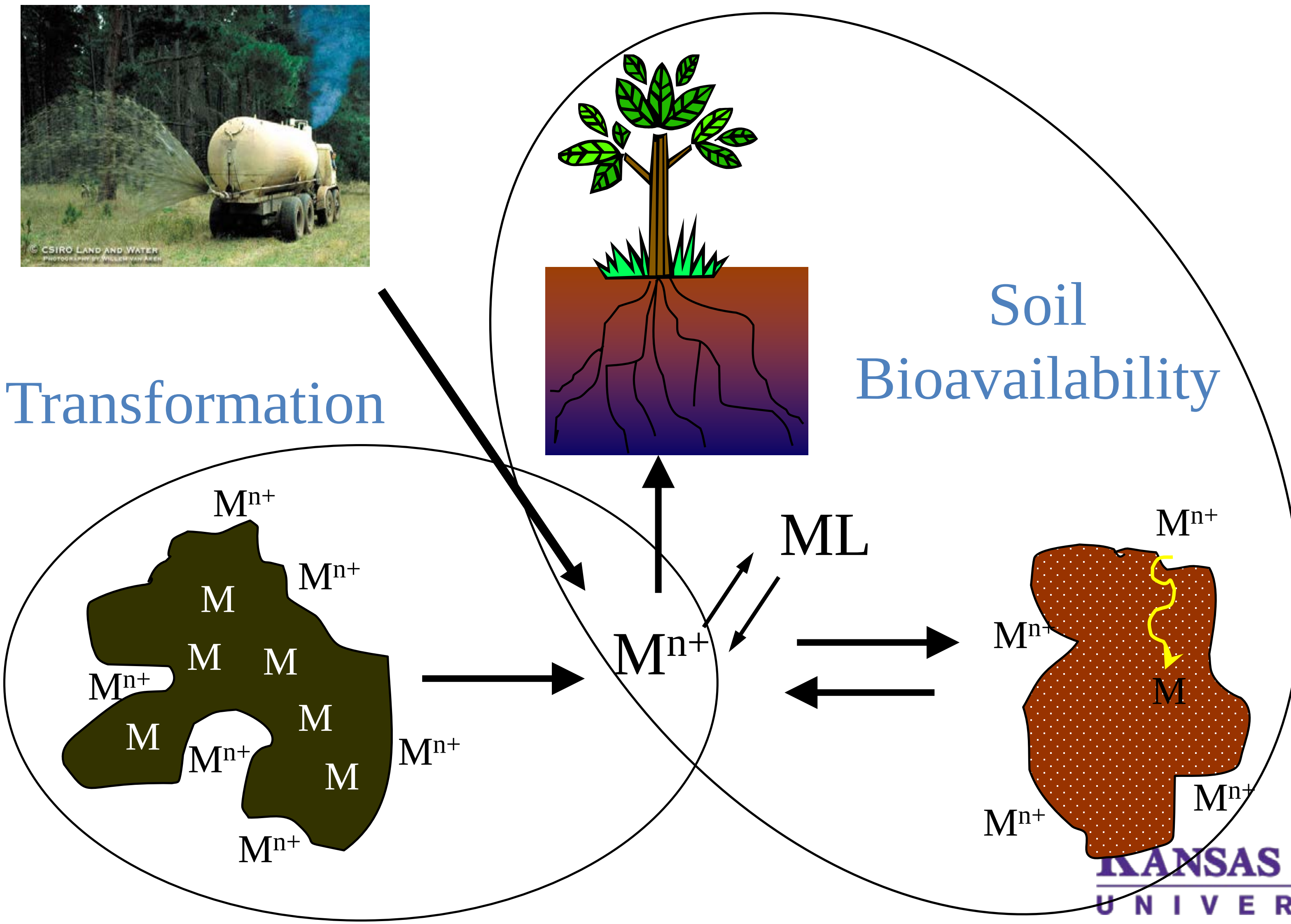
Contaminant form affects bioavailability
Example: Biosolids vs. metal salt



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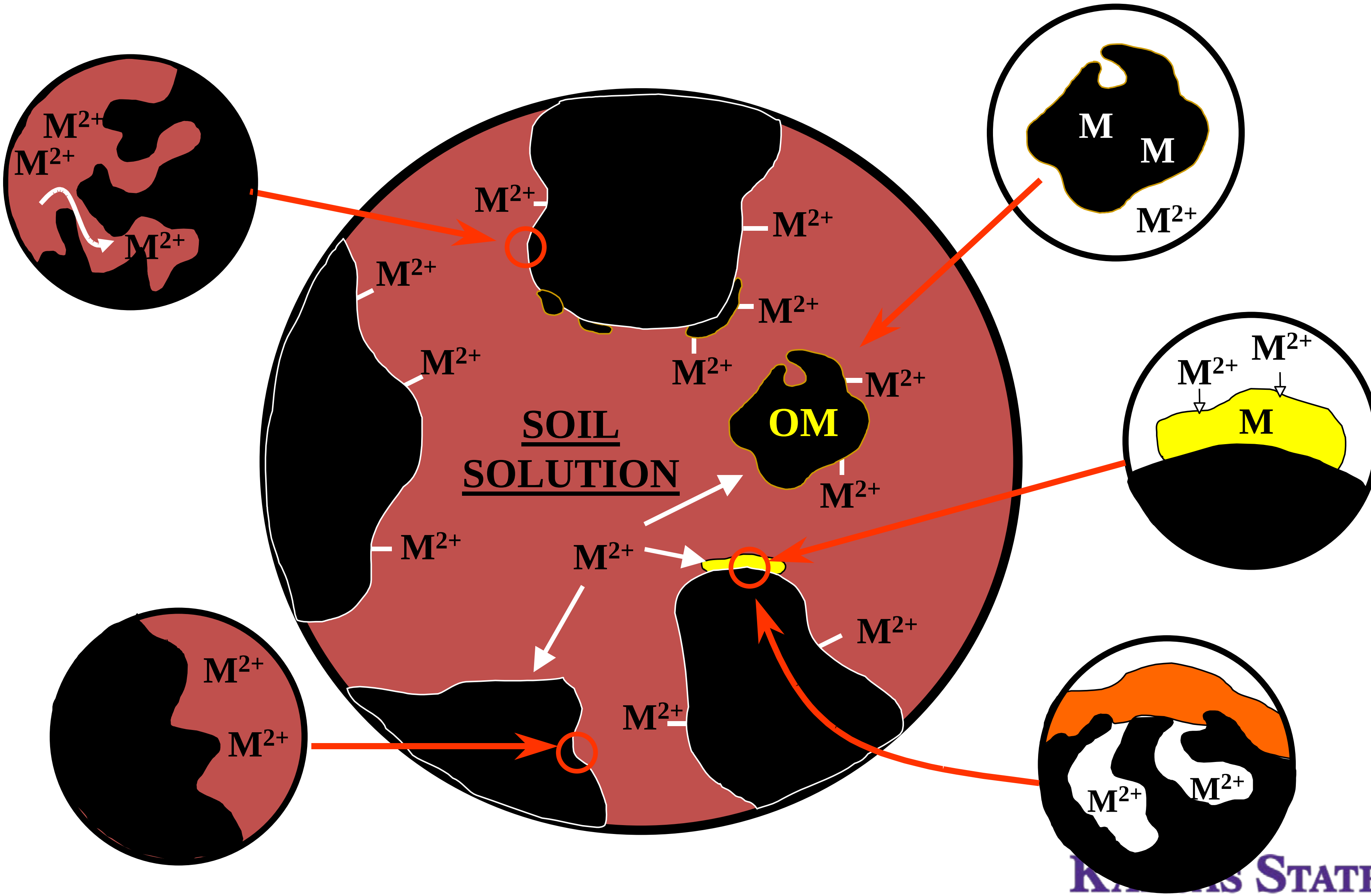
Nutrient/contaminant attenuation in soil



Slow diffusion/ageing reactions with time

Nutrient/contaminant attenuation in soil

Example: root elongation on soil contaminated by Cu

Field transect

Fresh spike

Species differences in tolerance

Rice

Barley

Mustard

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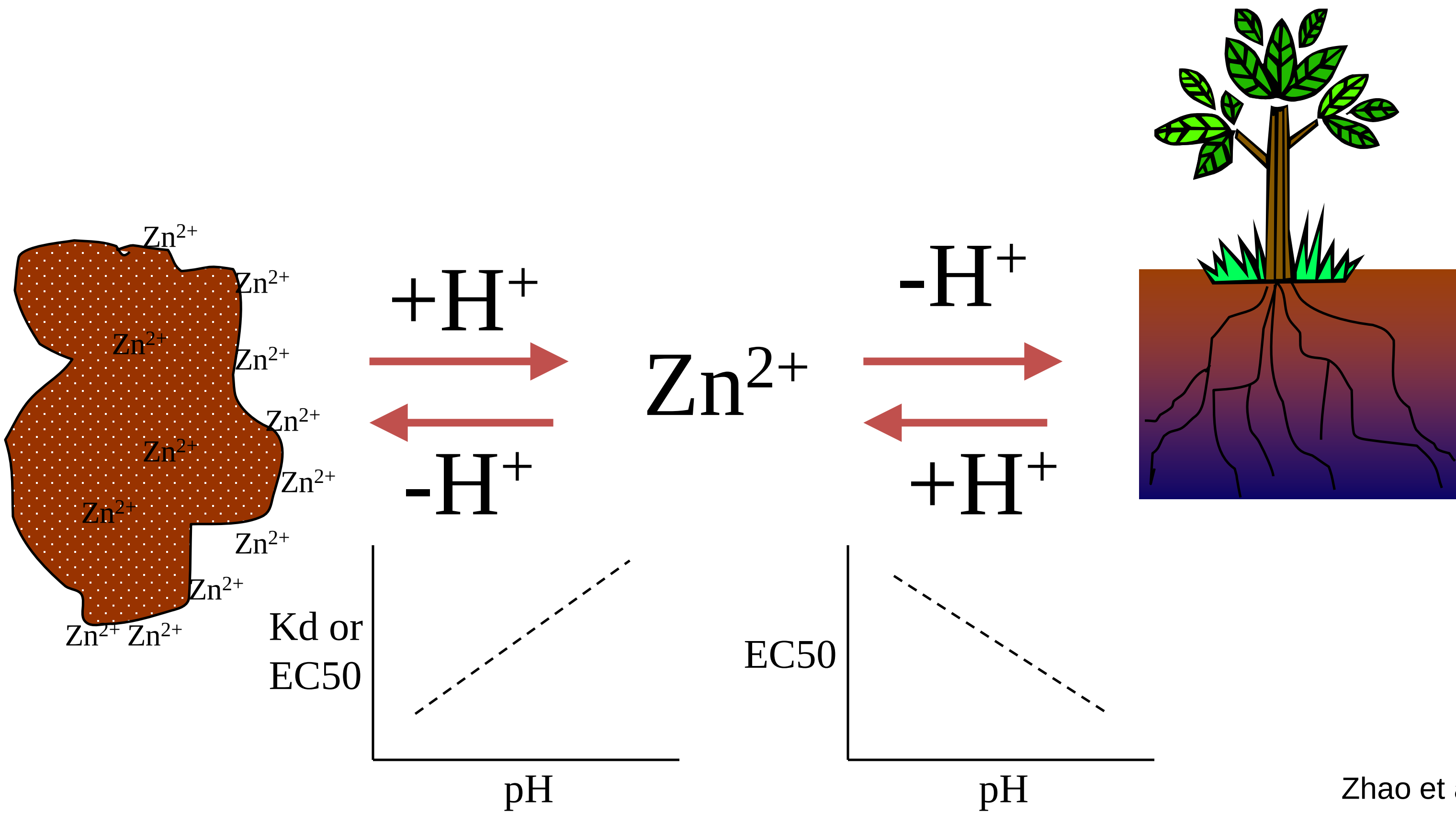
Soil chemistry alone is not enough

- We know that pH is important in modifying metal toxicity – however 2 effects are apparent



Zhao et al. 2006

EC50: The concentration of an element, which produces 50% of the maximum possible effective response for that element