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Bioavailability Issues for Soil Organisms

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Bioavailability Issues for Soil Organisms

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Overview

- Basic chemistry of metals/metalloids
- Soil as a charged medium
- Metal/metalloid partitioning between solid and solution phases in soil
- Metal/metalloid speciation
- Natural occurrence of metals in soil – background

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Metal Bioavailability in Soil

- Compared to water systems, the behaviour of metals in soils is more complex due to the dominance of the soil solid phase controlling metal behaviour
- The solid phase in soil retains metals and reduces added metal bioavailability
- A long-term perspective is needed to protect soil from metal contamination, as
- Remediation of metal-contaminated soils is difficult, costly and time-consuming

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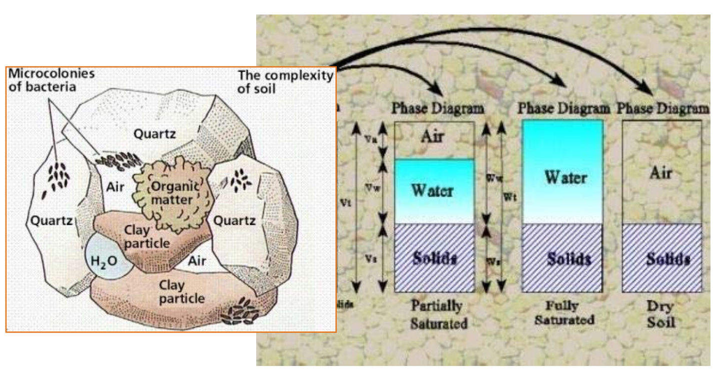
Metal Bioavailability in Soil

- Soils are more complex than waters as they have a significant solid phase (and a gaseous phase)



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Metals and Metalloids: Charged Species

Cationic Metals

- Ag^{+}
- Al^{3+}
- Cd^{2+}
- Co^{2+}/Co^{3+}
- Cr^{3+}
- Cu^{2+}
- Mn^{2+}/Mn^{4+}
- Ni^{2+}
- Pb^{2+}
- Zn^{2+}

Anionic Metalloids

- $HAsO_4^{2-}/H_3AsO_3^{0}$
- $H_3BO_3^{0}/B(OH)_4^{-}$
- CrO_4^{2-}
- MoO_4^{2-}
- $SeO_4^{2-}/H_2SeO_3^{0}/Se^{0}$
- $Sb(OH)_6^{-}/Sb(OH)_3^{0}$

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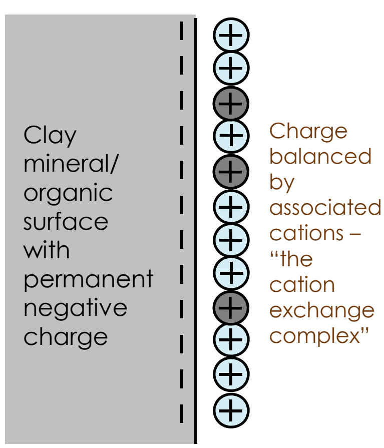
Soil: A Charged Medium

- **The solid phase in soil is predominantly negatively charged and therefore retains cationic metals and reduces added metal cation bioavailability**



There are different types of clay minerals in soils/sediments

Aluminosilictaes – kaolinite, illite, montmorillonite

Oxy-hydroxides – of Al, Fe and Mn

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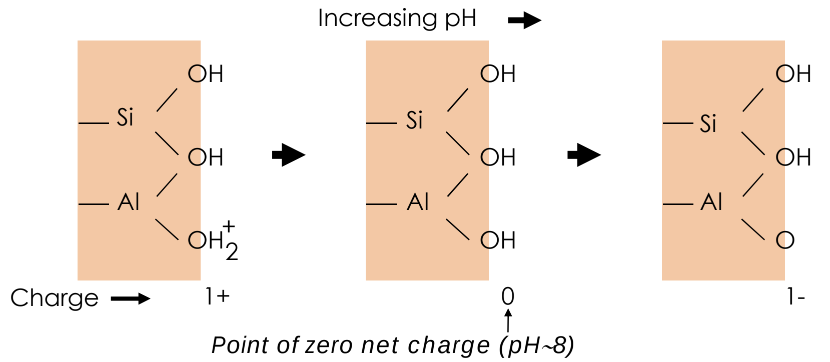
Soil: A Charged Medium

- **Anionic metalloids may react with edges of clay minerals or oxide surfaces, where positive charges are present, more at low pH**



Oxides (Fe, Mn, Al; normally positively charged) behave similarly
CEC increases, AEC (anion exchange capacity) decreases as pH rises

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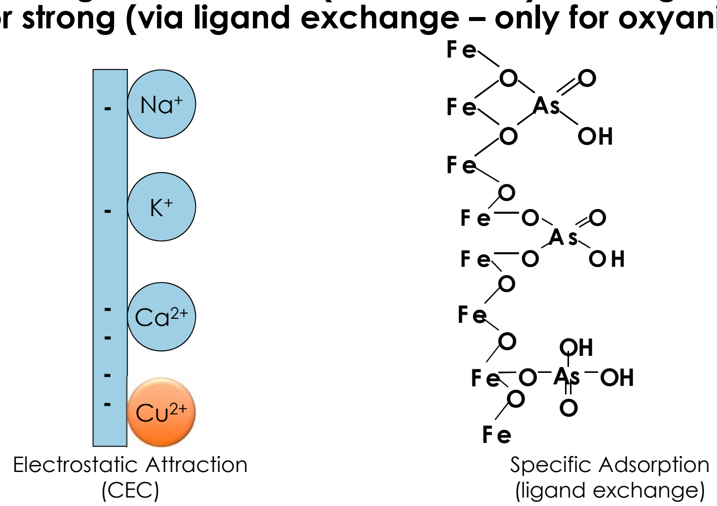
Reaction of Metals with The Solid Phase: Adsorption

- **Binding can be weak (electrostatic) to charged sites, or strong (via ligand exchange – only for oxyanions)**



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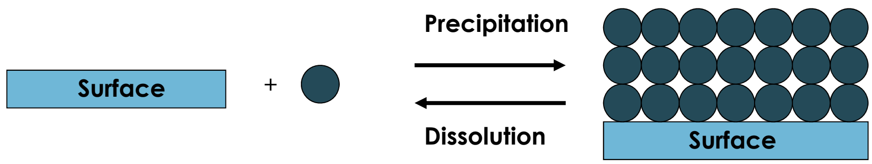
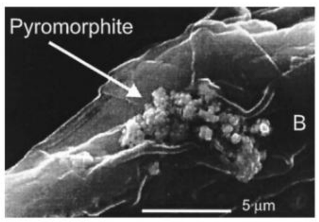
Reaction of Metals with The Solid Phase: Precipitation





Source: Traina and Laperche 1999

- Cationic metals require a complementary anion to precipitate—OH-, CO_3^{2-}, PO_4^{3-}
- Anionic metals require a complementary cation to precipitate—Fe^{3+}, Al^{3+}, Ca^{2+}

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Partitioning/Distribution Coefficient (K_d): A Crucial Concept

- **Kd is known as a partitioning or distribution coefficient**
  - Expression of how strongly an ion interacts with the solid phase in soils or sediments (either by adsorption or precipitation)
  - High Kd indicates that most of the ion is associated with the solid phase: desired case for contaminants
  - Low Kd indicates that most of the ion remains in solution
  - Kd values range from ~1 to > 50,000

$$K_D = \frac{Me_{\text{Solid Phase}}}{Me_{\text{Solution}}}$$

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Factors Affecting Partitioning

- ph, redox, temperature, pressure, ionic strength, competition with other ions, time

TABLE 1. Partitioning Coefficients (K_d in L kg^{-1}): Arithmetic Means of Untransformed K_d Values, Corresponding Standard Deviations, and Coefficients of Variability, Medians, Minimum, Maximum, log (K_d), and Number of Data Points

element	K_d (mean)	SD	CV	median	min	max	$\log_{10} K_d$	N
As	13119	65086	4.96	1825	1.6	530000	4.12	66
B	160	96	0.60	136	61	389	2.20	12
Ba	3434	3152	0.92	2455	1414	14375	3.54	15
Cd	2869	12246	4.27	390	0.44	192000	3.46	830
Cr	14920	16899	1.13	4778	125	65609	4.17	64
Cu	4799	9875	2.06	2120	6.8	82850	3.68	452
Hg	8946	5641	0.63	7500	4286	16500	3.95	4
Mo	36	19	0.52	38	14	52	1.55	4
Ni	16761	45350	2.71	2333	8.9	256842	4.22	139
Pb	171214	304089	1.78	102410	60.56	2304762	5.23	204
Se	43937	119534	2.72	15	1.6	600000	4.64	63
Sr	137	42	0.31	130	89	195	2.14	10
Zn	11615	30693	2.64	1731	1.4	320000	4.07	302

Source: Sauve et al. 2000

↑K_d: As, Cr, Ni, Pb, Zn ------ low mobility and biovailability

↓ K_d: Mo, Se, B, Cd ------ high mobility and bioavailability

Note: Kd for As, Cr, Se is redox sensitive

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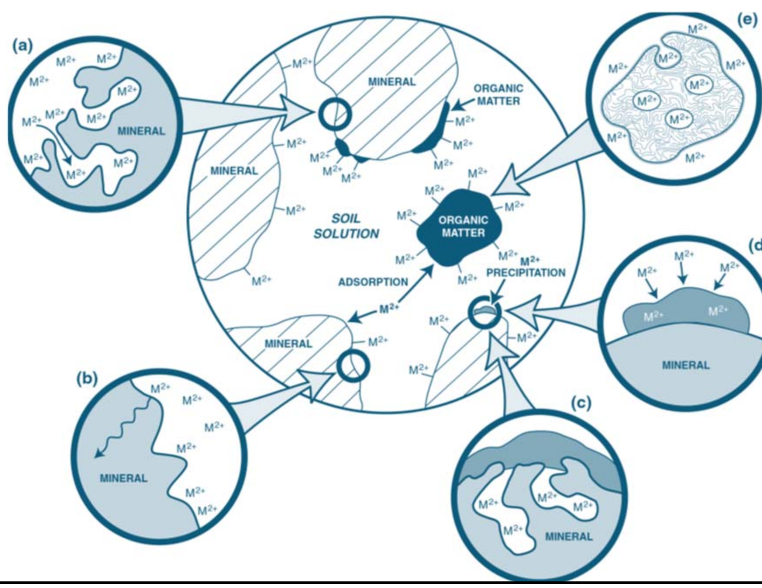
Factors Affecting Partitioning: Time (ageing)



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Metal Bioavailability in Soil: pH Effects

- **Soil pH is a "master variable" controlling metal/ metalloid bioavailability in soil through its effect on:**
  - Soil surface charge – more –ve as pH increases, more +ve as pH decreases
  - Concentrations of hydroxide (OH^-) and carbonate (CO_3^{2-})/bicarbonate (HCO_3^-) – these anions increase at high pH and can precipitate cationic metals as hydroxides or carbonates

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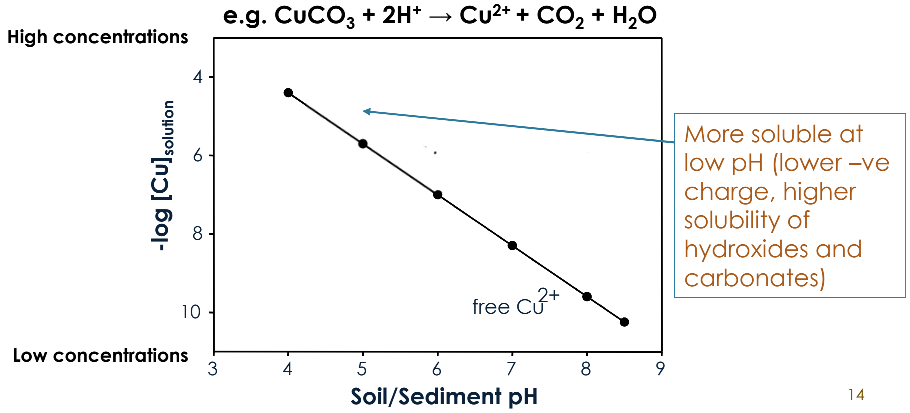
Typical pH Effects on Cationic Metal Partitioning

- **pH affects mineral/organic matter charge and hence sorption**
- **pH affects element solubility (Ksp)**

e.g. $CuCO_3 + 2H^+ \rightarrow Cu^{2+} + CO_2 + H_2O$



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Metals and Metalloids: Speciation Due to Redox Reactions

- **Redox-sensitive elements (Fe, Mn, Hg, As, Cr, Se,...): Speciation and solubility depend on redox state**

Oxidised	Reduced
Fe(III),ferric $Fe(OH)_{3}\downarrow$ (ferric)	Fe(II): Fe^{2+} (ferrous)
Mn(IV): $MnO_{2}\downarrow$	Mn(II): Mn^{2+}
Cr(VI): CrO_4^{2-} (chromate)	Cr(III): $Cr_2O_{3}\downarrow$
As(V): $HAsO_4^{2-}$ (arsenate)	As(III): $H_3AsO_3^0$ (arsenious acid)
Se (VI): SeO_4^{2-}	Se (IV), Se(0): SeO_3^{2-}, Se^0

Generally more mobile and or toxic

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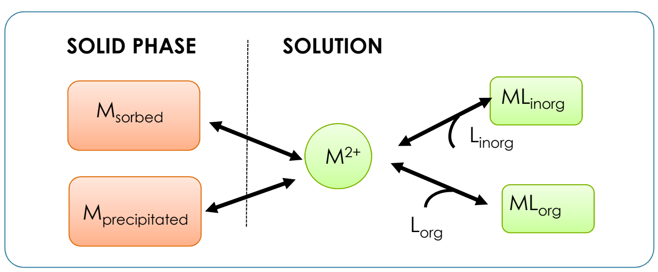
Cationic Metal Speciation in Soil: Complexation Effects



- **Two examples:**
  1. Dissolved organic matter is important in complexing Cu2+ in soil solution (increasing Cu mobility)
  2. Chloride (salinity) is important in complexing Cd and Hg in soils and increasing mobility

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Challenges to Describe Metal Bioavailability in Soil

Abiotic: Supply Term

- Background concentrations
- Soil reaction with metals reducing bioavalability
- Laboratory toxicity is greater than field toxicity

Biotic: Response Term

- Organism type
- Acceptable end-point
- Diversity of functionality?
- Element interactions
- Organism adaptation

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How should background concentrations be accounted for?

- **Metals occur naturally in soils**
- **For example: Red soils in Ferrosols or Oxisols naturally contain 100–400 mg/kg Cr and 100–300 mg/kg Ni**
- **Ecosystems on these soils are adapted to these naturally occurring concentrations**

Source: http://soer.justice.tas.gov.au

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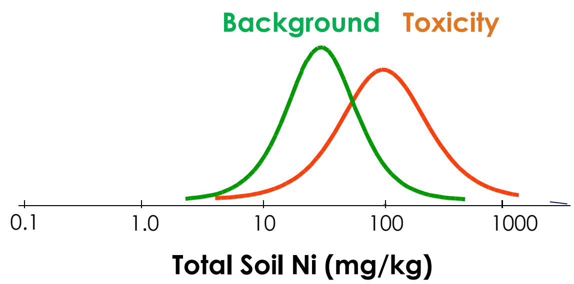
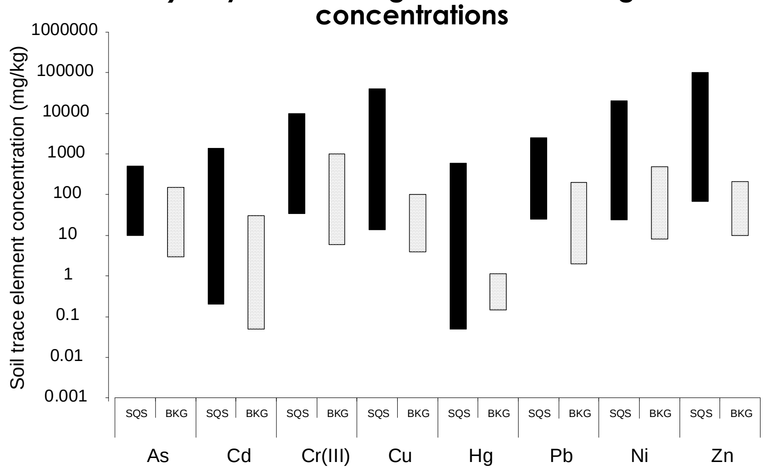
Dealing with Ambient Background

- **Dealing with ambient background concentrations is difficult**



Soil Quality Standards vs Background

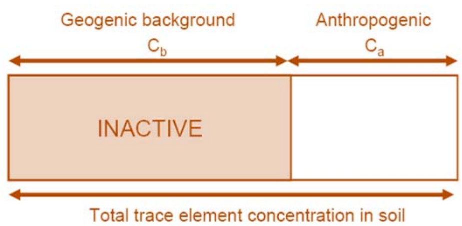
Soil quality standards (based on total concentrations in soils) vary across the globe as do background concentrations



Source: Data derived from Carlon et al. (2007) and McLaughlin (2002).

Dealing with Ambient Background

- **If total concentrations of metals are to be used for soil quality standards, the "added risk approach" is probably the best approach to use to deal with background concentrations (Struijs et al. 1997)**
- **Assume biota are adapted to geogenic background, and irrespective of background bioavailability**
- **For added risk approach, need to know, or estimate "geogenic" background concentrations to which element dose is added**



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Dealing with Ambient Background

- **Four techniques used to estimate "geogenic" background concentrations:**
  1. Measure background concentration (requires reference site)
  2. Geochemical normalisation
  3. Percentile distributions
  4. Probability graphs

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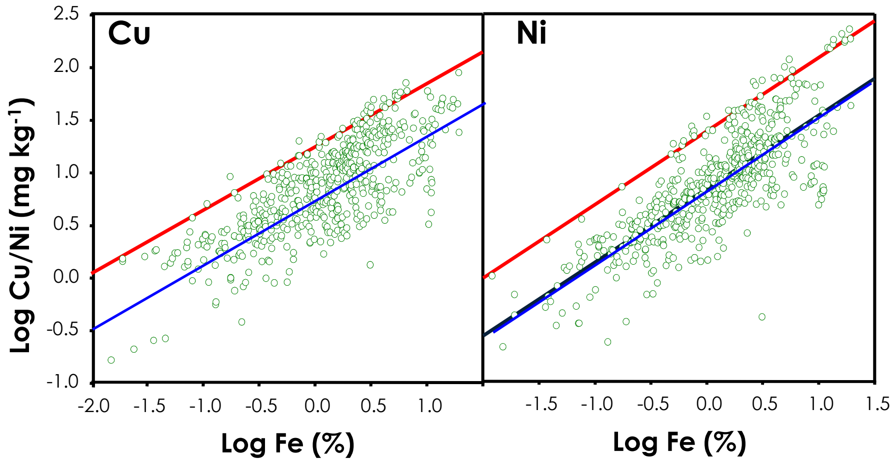
Determining Ambient Background: Geochemical Normalisation



The red and blue lines are the 95%ile and 50%ile of the relationships between log Fe and background metal concentration respectively. Other percentiles of the relationships could also be used.

Source: Hamon et al. 2004.

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Determining Ambient Background: Percentile Distribution

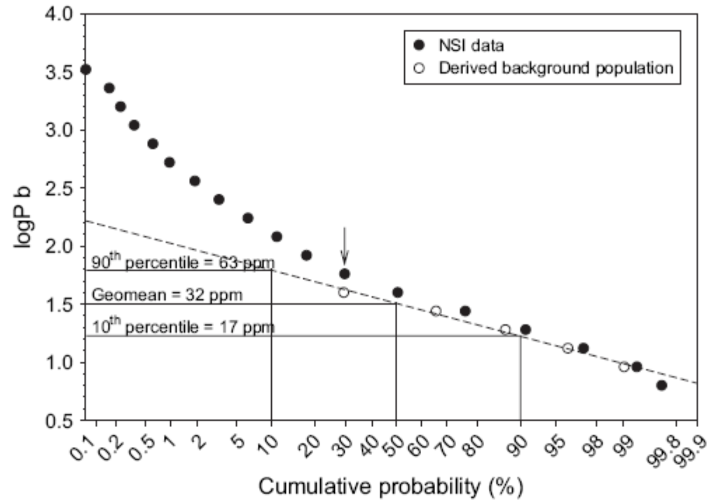
Table 4. The 95% 'Investigation Levels' determined for Thailand ($n = 318$ soils).

Element	Investigation level (mg kg^{-1})
As	30
Cd	0.15
Co	20
Cr	80
Cu	45
Hg	0.10
Ni	45
Pb	55
Zn	70

Fig. 1. Soil and plant sampling sites in Thailand.

Source: Zarcinas et al. 2004.

Determining Ambient Background: Frequency Distribution Method



Source: Zhao et al. 2007.

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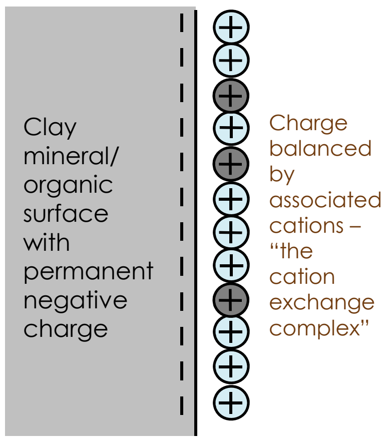
Soil: A Charged Medium

- **The solid phase in soil is predominantly negatively charged and therefore retains cationic metals and reduces added metal cation bioavailability**



There are different types of clay minerals in soils/sediments

Aluminosilictaes – kaolinite, illite, montmorillonite

Oxy-hydroxides – of Al, Fe and Mn

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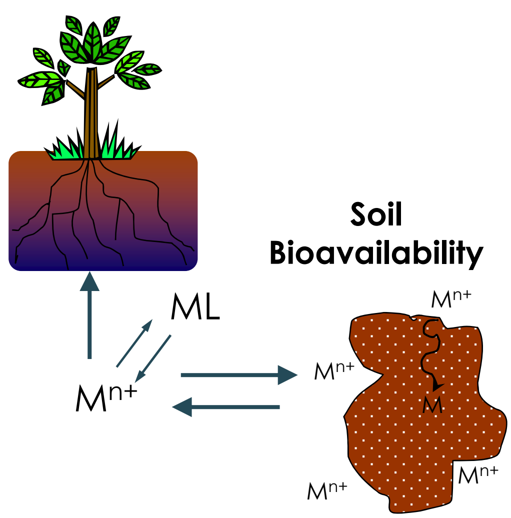
Soil Physico-chemical Parameters Affect Bioavailability



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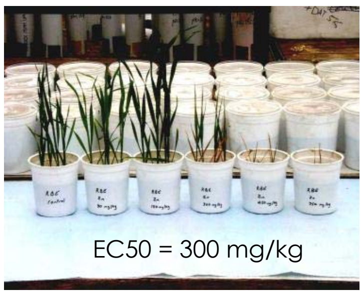
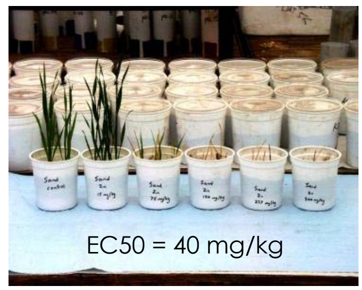
Accounting for Soil Modifiers of Toxicity

- **Soil physical and chemical parameters – pH, clay, organic matter, mineralogy, CEC, etc. have the ability to mitigate trace element toxicity (through charge and pH effects discussed earlier)**
- **Levels protective in a alkaline clay soil would be toxic in a acidic sand**





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Accounting for Soil Modifiers of Toxicity

- **There are several ways that have been tried to assess soil modifiers of toxicity**
  – Measuring dose by a partial removal of soil metal (including speciation) e.g. DGT, Mn+ in porewater (not easily predictive)
  – Retain use of total metal as dose, and normalise using soil properties (emperical)
  – Develop semi-mechanistic or mechanistic models to predict soil behaviour of metal combined with metal effect on organism (BLM)

Source: McLaughlin et al. 2000.

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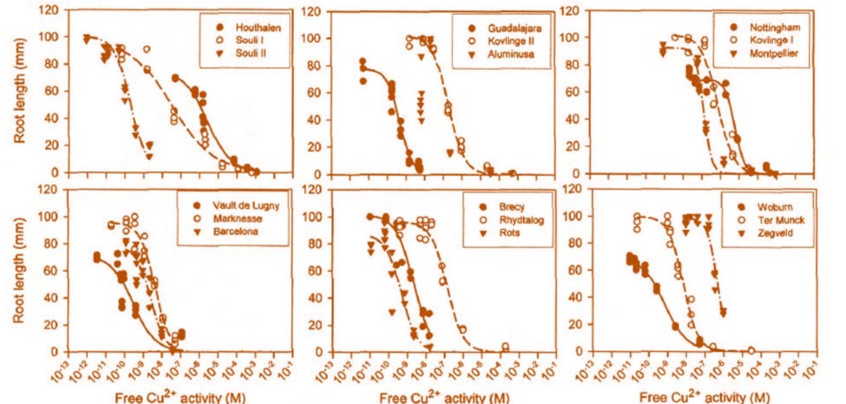
Accounting for Soil Modifiers of Toxicity: Partial Extractants

- **EC50 values based on DGT-Cu varied less (CV 42%) than those based on total soil Cu (72%), soil solution Cu (125%) or free Cu^{2+} activity (290%)**



Source: Zhao et al. 2006.

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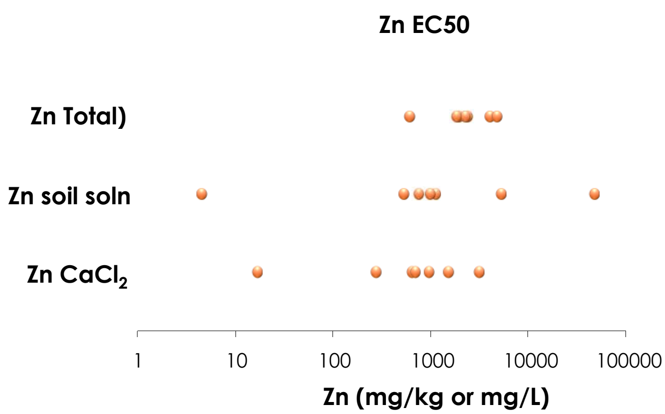
Accounting for Soil Modifiers of Toxicity: Partial Extractants



	Min	Max	Range
Zn Total)	609	4900	8
Zn soil soln	5	47600	10250
Zn $CaCl_2$	17	3107	185

Source: Broos et al. (2007).

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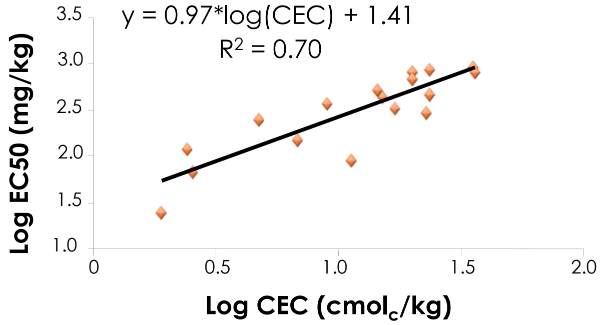
Emperically-Derived Models

- **Total Cu EC50 phytotoxicity for a wide range of European soils**



Source: Rooney et al. (2006).

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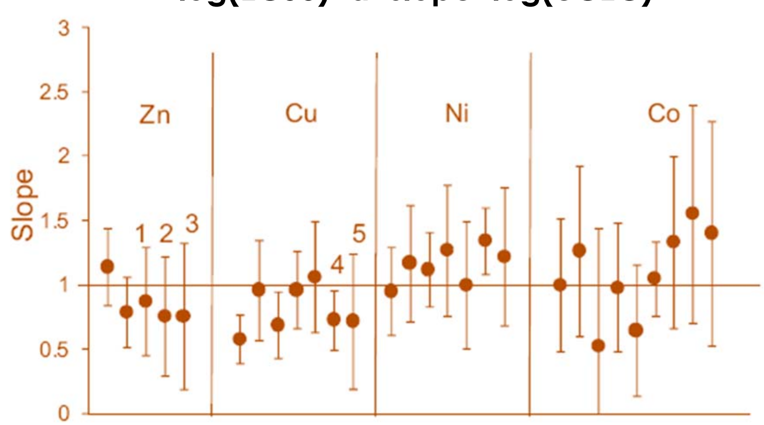
Emperically-Derived Models using Effective Cation Exchange Capacity (eCEC)

log(EC50)=a+slope•log(eCEC)



Source: Smolders et al. 2009.

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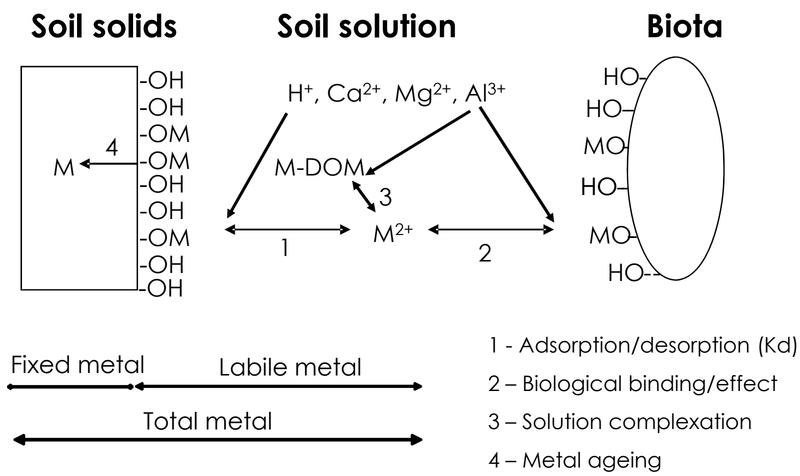
Mechanistic Models: Terrestrial Biotic Ligand Model



Source: Modified from Smolders et al. 2009.

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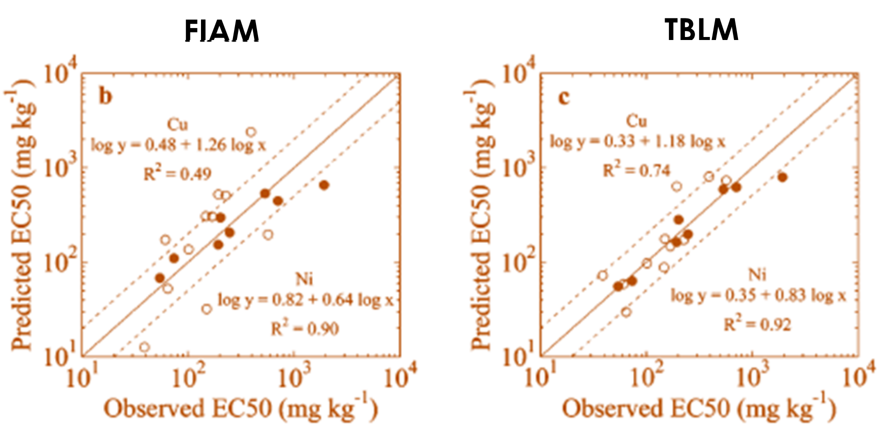
Mechanistic Models: Terrestrial Biotic Ligand Model



Source: Thakali et al. (2006).

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Challenges to Describe Metal Bioavailability in Soil

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Laboratory Bioavailability ≠ Field Bioavailability

≠

- **Two key differences between laboratory-based and field-based experiments are**
  1. Short-term artifacts induced in laboratory toxicity experiments
  2. Long-term artifacts—ageing of metals

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Laboratory bioavailability ≠ field bioavailability

- **There are two major reasons for this:**
  1. Metal toxicity is often studied in the laboratory by spiking soil with soluble metal salts. This creates unusually high metal bioavailability compared to field soils – can be reduced by leaching soluble salts
  2. Laboratory experiments are often conducted shortly after spiking soils with soluble metal salts, thus not allowing metals to "age" as occurs in the field
- Laboratory data can be corrected using a **leaching/ageing** factor

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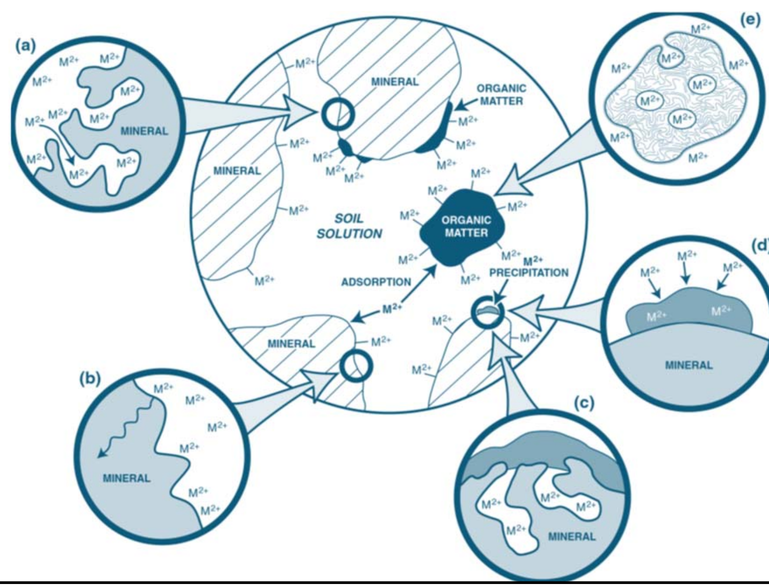
Factors Affecting Partitioning: Time (ageing)



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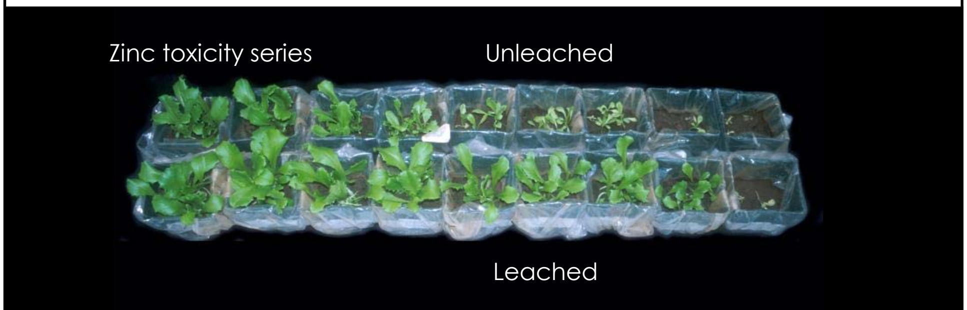
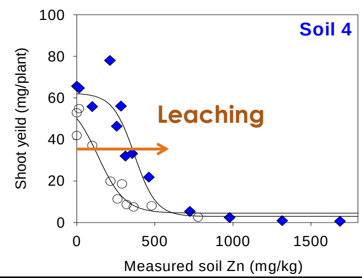
Laboratory Artifacts: Salt Effects





Source: Stevens DP et al. (2003).

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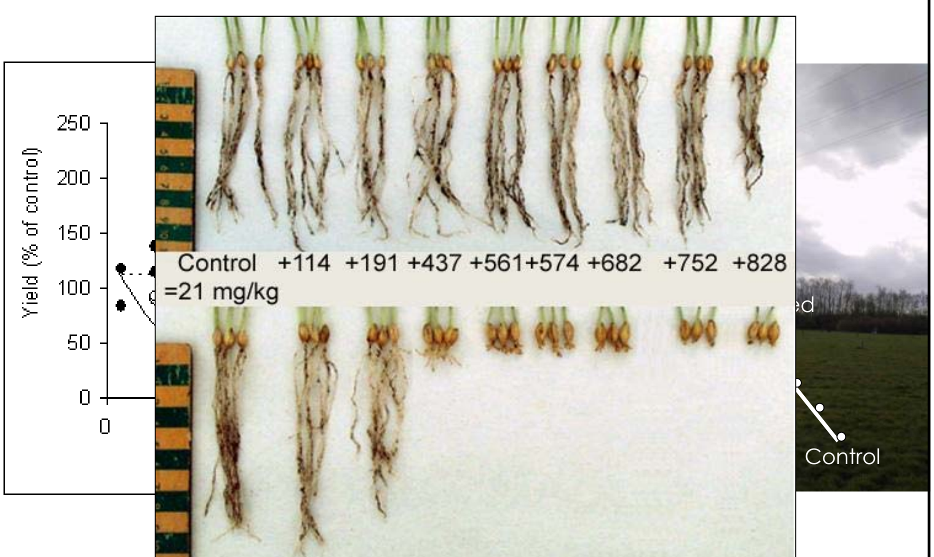
Ageing Affects Bioavailability



Source: Smolders et al. (2004).

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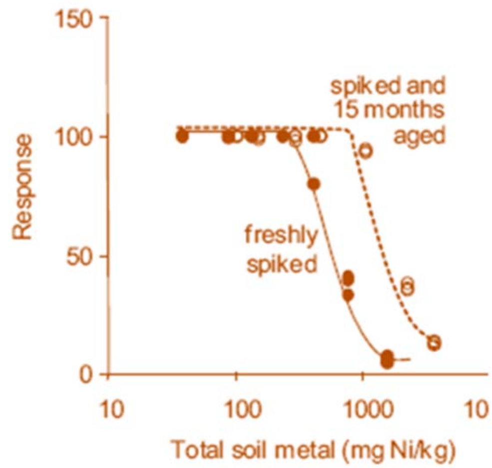
Ageing Affects Bioavailability



- Aging of soluble metals increases with time of soil:metal contact
- Generally Ni,Co > Zn, Cu > Cd

Source: Smolders et al. (2009).

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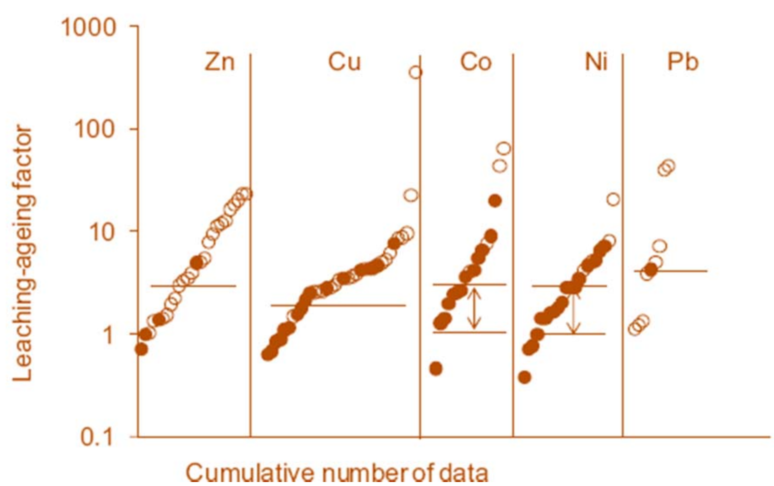
"Leaching-ageing" Factors for Soluble Metals in Soils



Source: Smolders et al. (2009).

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Conclusions

- Two key issues for metal contamination of soils – background and bioavailability – can now be predicted and used for regulatory assessments
- The bioavailability models appear to work for a range of trophic levels in soils
- The range of metals covered by these models is still limited
- Further work is needed to develop bioavailability models for more metals/metalloids
- Some local validation is recommended prior to adoption in different jurisdictions

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