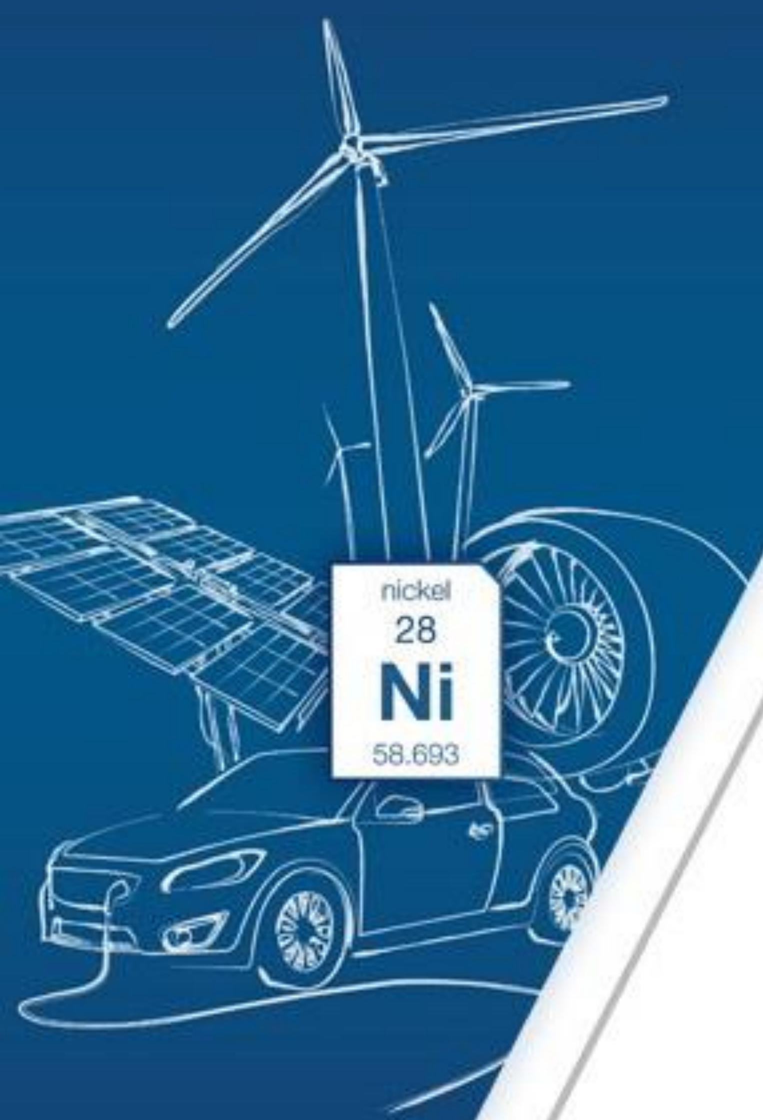
NiPERA INC.

Nickel Producers Environmental Research Association

Bioavailability based approaches for soil risk assessment of metals: Regional differences arising from distributions of soil chemical properties

EFSA/ECHA Soil Risk Assessment Workshop

Wednesday, October 7, 2015



Nickel INSTITUTE

Authors

Chris Schlekat – Nickel Producers Environmental Research Association (Durham, NC, USA)

Ilse Schoeters – Rio Tinto (Brussels, Belgium)

Robert Dwyer – International Copper Association (New York, NY, USA)

Katrien Delbeke – European Copper Institute (Brussels, Belgium)

Michael McLaughlin – Commonwealth Scientific Industrial Research Organization (Adelaide, Australia)

Yibing Ma – Chinese Academy of Agricultural Sciences (Beijing, China)

Introduction

- Introduction to soil bioavailability normalization process for metals

- Validation of concepts in Chinese soils using Chinese soil species

- Implementation of concepts in Australia

- Summary and points to consider

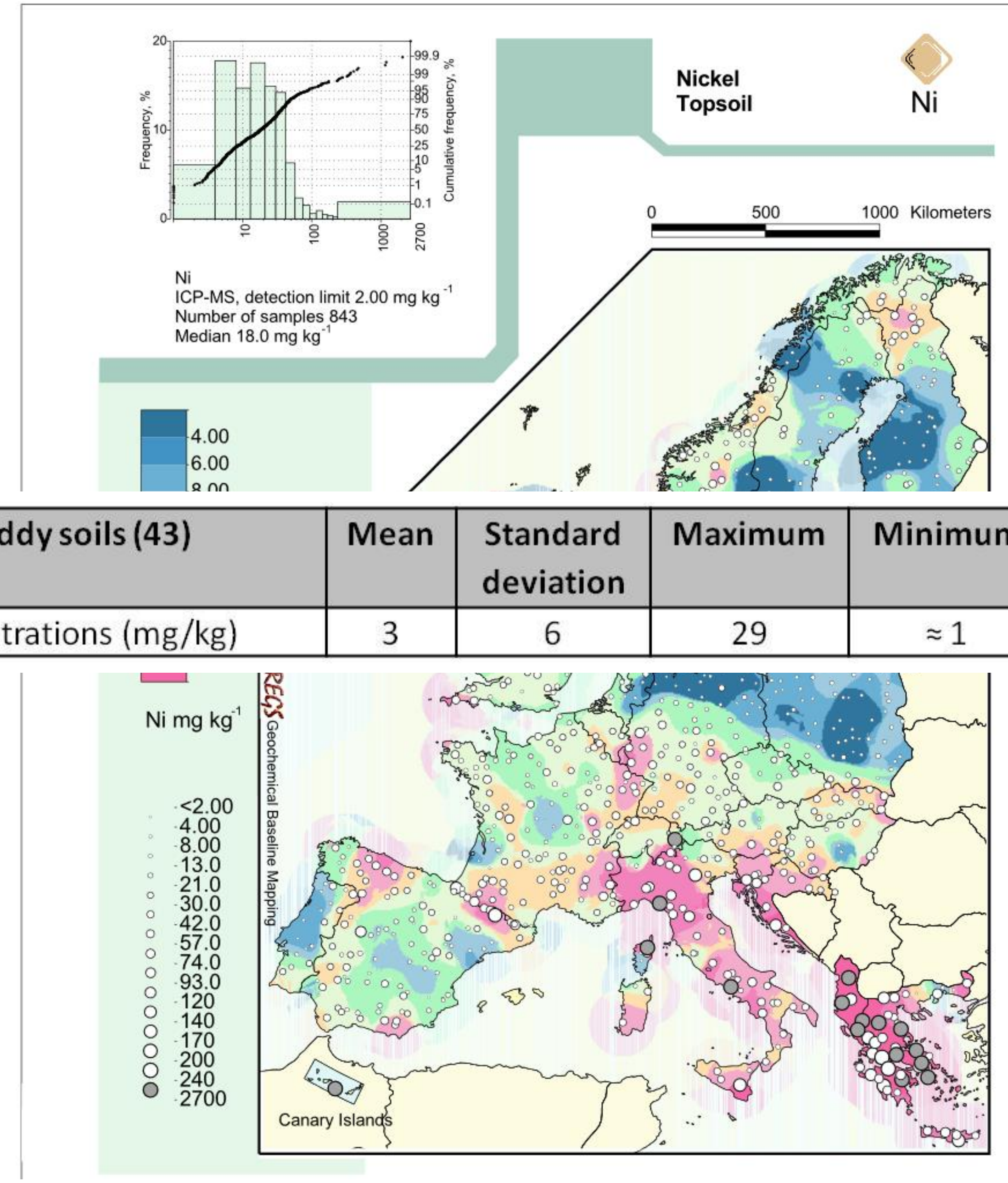
Environmental risk assessment of metals: Challenges

1. Protection goals: What are we trying to protect?
    - 95% of species?
    - Sensitive species?
    - Ecosystem function?
    - Ecosystem structure?
2. Regional variability:

- Metal toxicity varies as a function of matrix (soil, water, sediment) chemistry
- REACH (and other regulatory risk assessment guidance) requires use of sensitive conditions: Reasonable Worst Case

Environmental risk assessment of metals: Challenges

3. Dilemma:
   - Background concentrations in soils vary by an order of magnitude
   - RWC approach can lead to concentrations near natural background concentrations
   - Presents challenges in terms of environmental management
4. Solution:
   - *Bioavailability normalization*
   - Takes site-specific chemistry into account in a mechanistic way
   - Removes influence of toxicity test chemistry
   - Practical, scientific and implementable approach



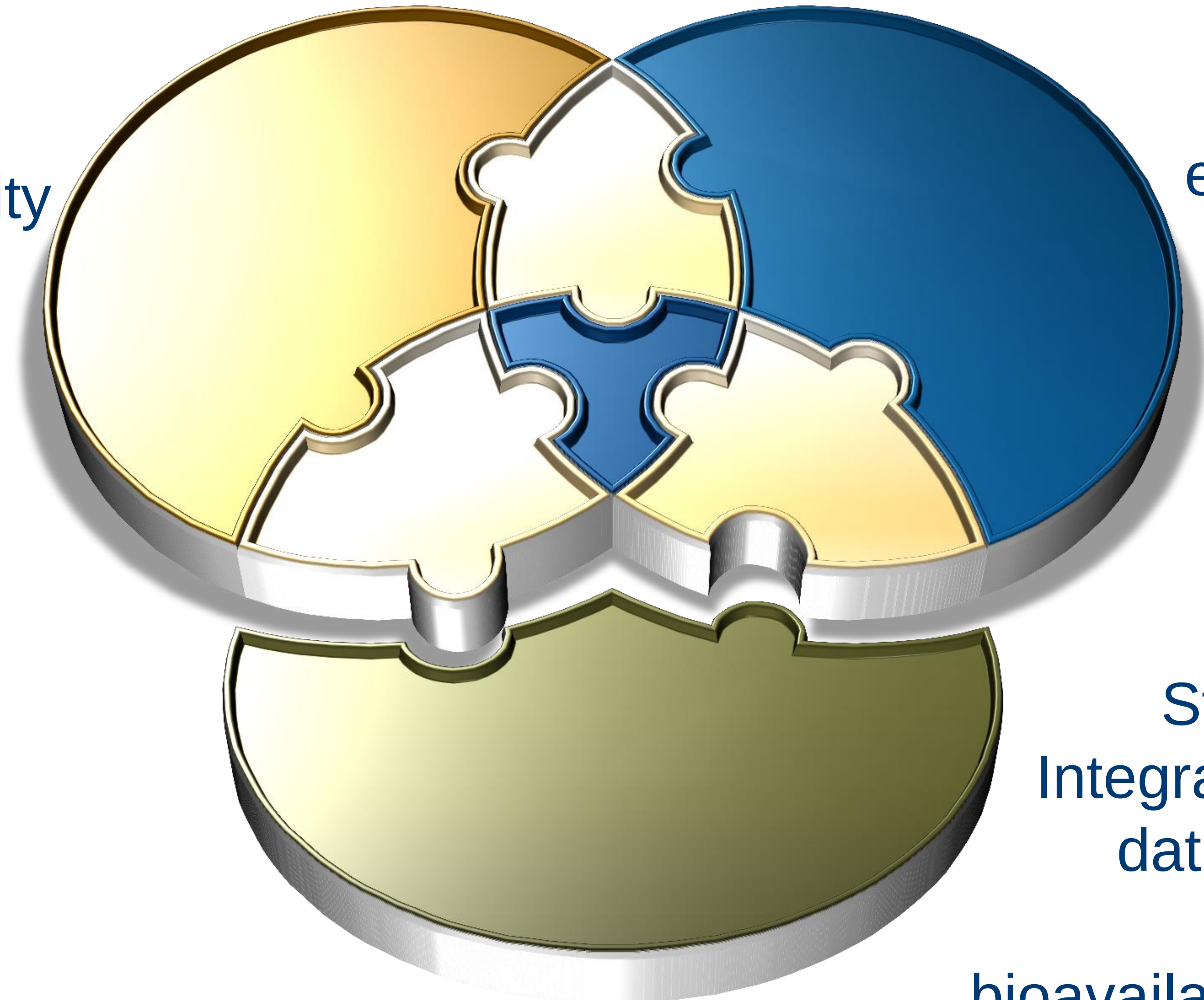
Indonesia paddy soils (43)	Mean	Standard deviation	Maximum	Minimum
Nickel concentrations (mg/kg)	3	6	29	≈ 1

http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_icpms_ni_edit.pdf

Bioavailability normalization steps

Step 1:
Develop robust,
ecologically-diverse
databases

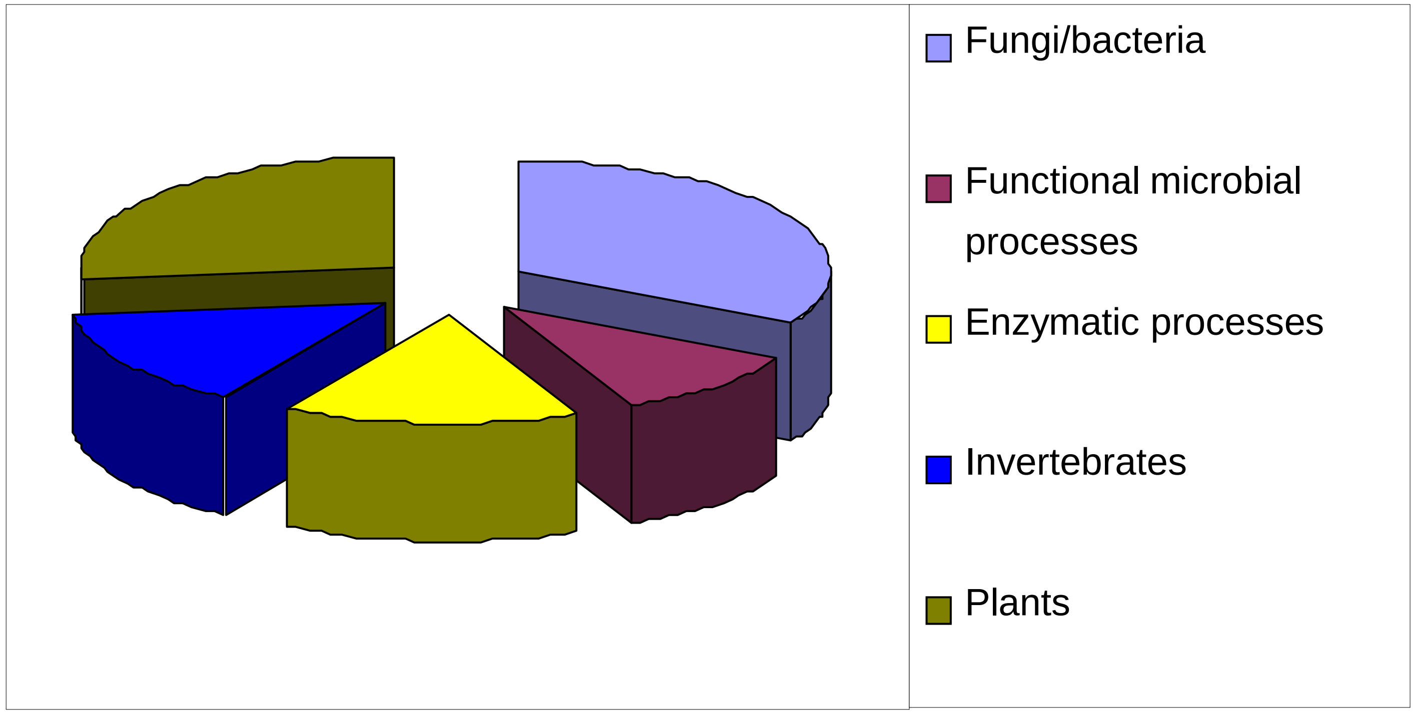
Step 2:
Develop bioavailability
models



Step 3:
Integrate toxicity
databases
and
bioavailability models

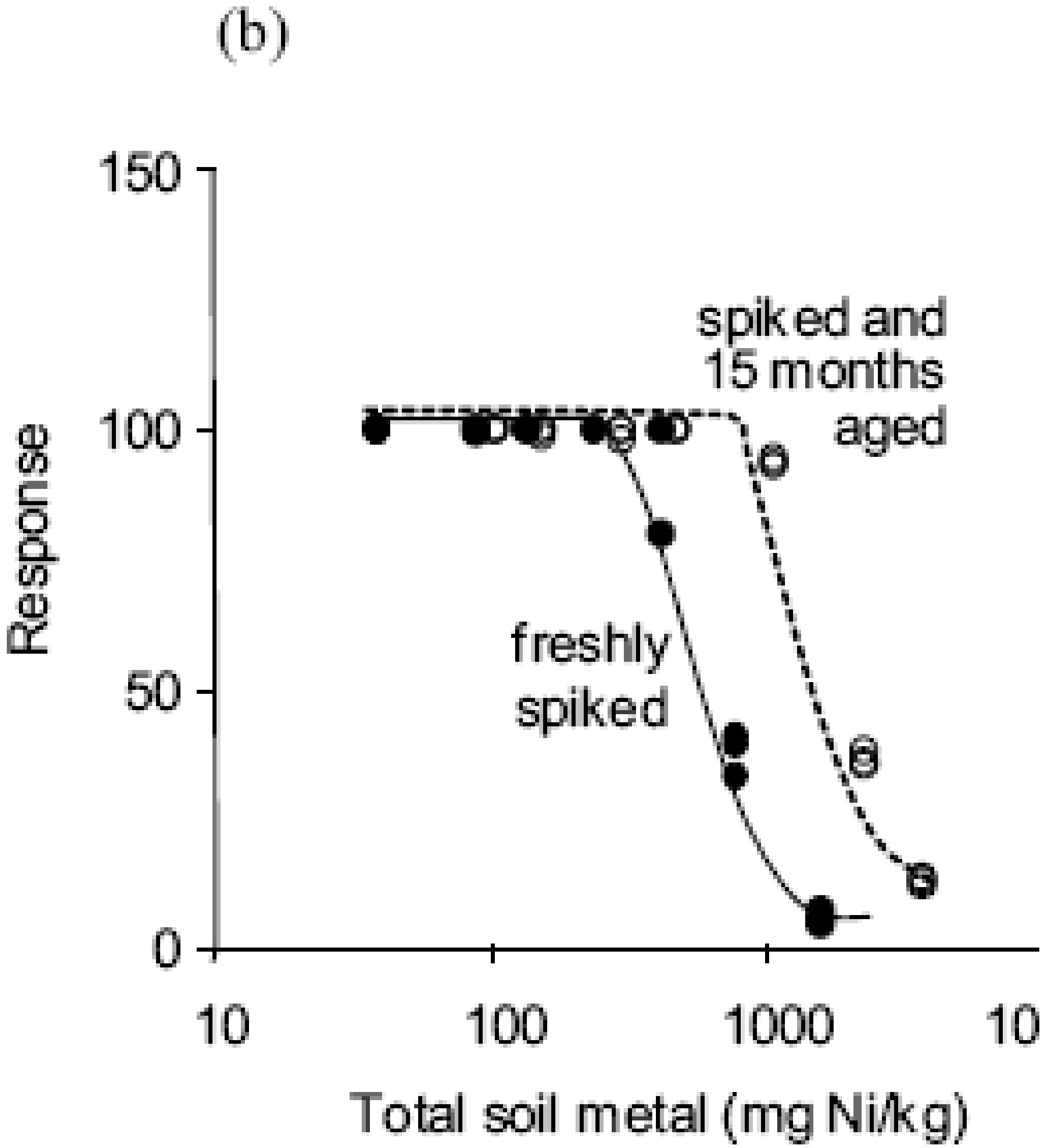
Soil databases for metals: Data-rich

- Nickel as an example
- 43 process/species
- Plants: 8 different families
- Invertebrates: 3 different taxonomic groups included
- Microbial processes:
  - 6 enzymatic activities;
  - 6 process measurements;
  - 1 biomass measurement;
  - 13 fungal species



Other metals databases (Co, Cu, Pb, Zn…): Similar taxonomic diversity and numbers of species

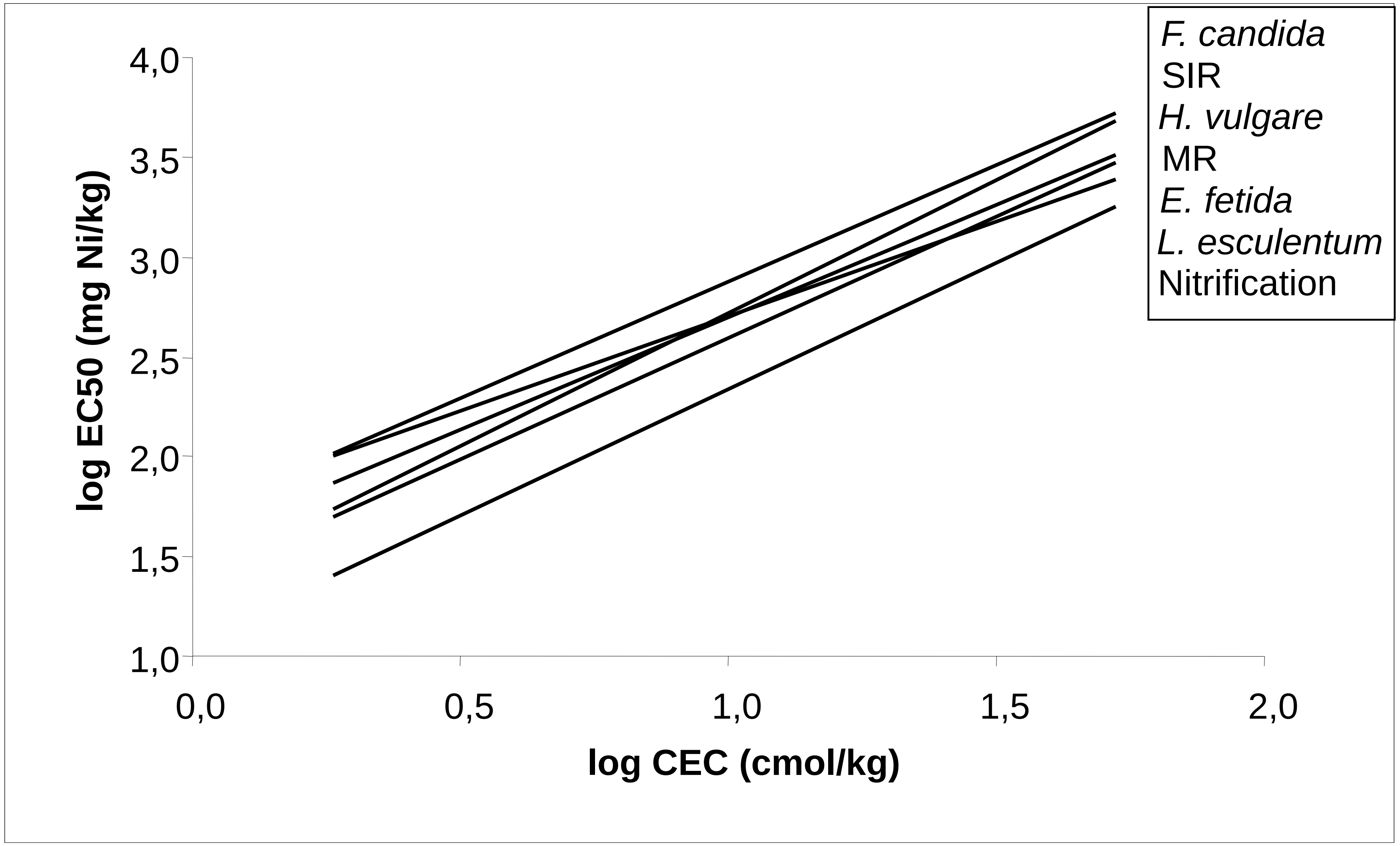
Accounting for aging processes



- Aging of soluble Ni increases with time of soil:Ni contact
- Not Ni-specific
- pH dependent: no ageing at pH<6, but up to factor of 3 at pH = 7.5

Smolders et al. 2009

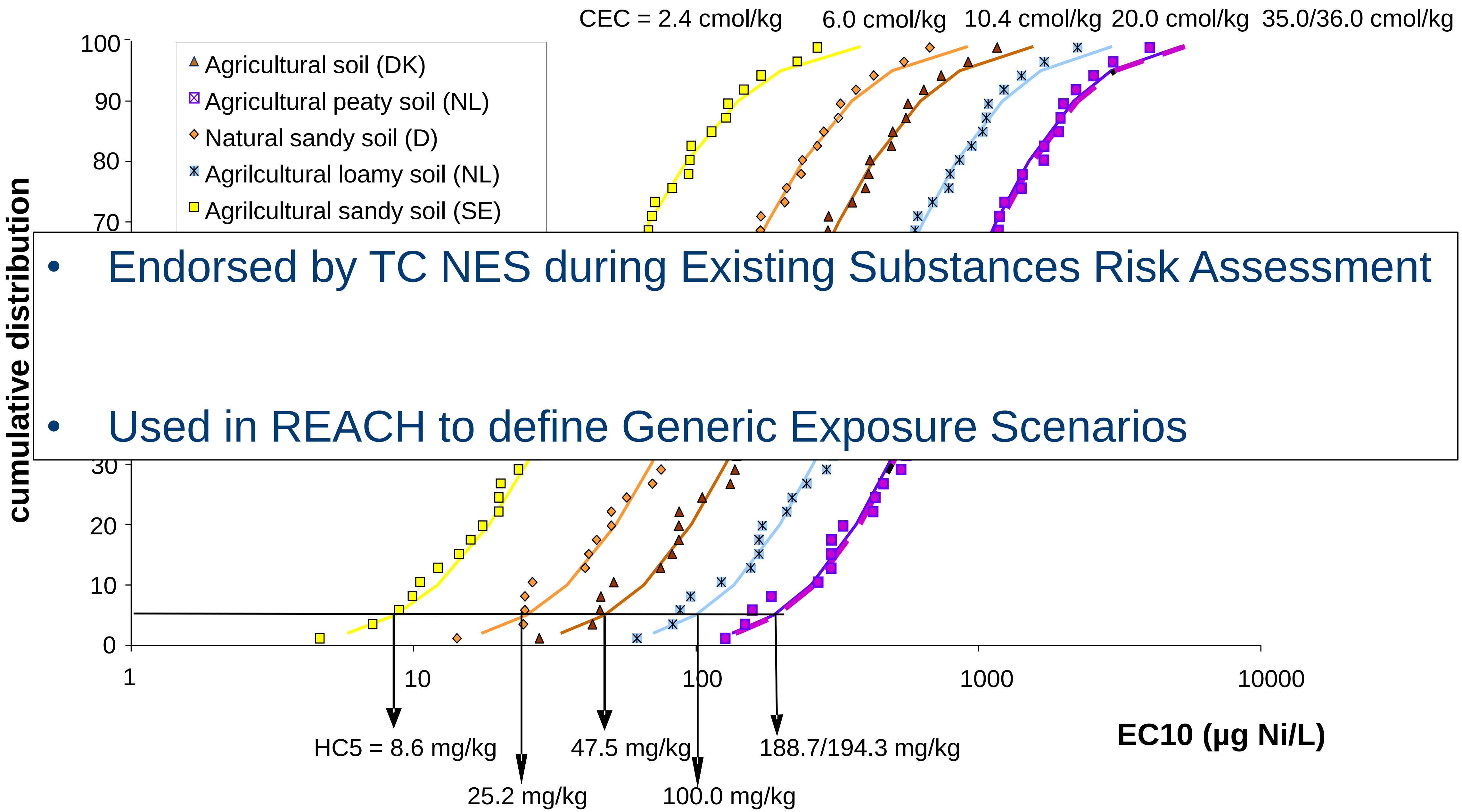
Incorporation of bioavailability: Importance of cation exchange capacity (CEC)



Ni toxicity in EU soils governed by CEC

- r^2 values for relationships range from 0.68 to 0.92
- Slopes between Ni toxicity & CEC are the same for all species
- CEC relationships can be extrapolated among different species
- Similar relationships observed for other metals, e.g., copper and zinc

Outcome of SSD bioavailability scenario analysis



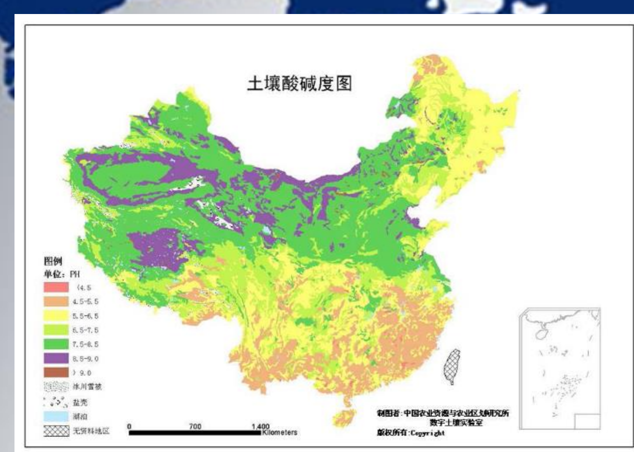
- Endorsed by TC NES during Existing Substances Risk Assessment
- Used in REACH to define Generic Exposure Scenarios

: Swedish Soil – pH ↓, CEC ↓= ***maximum bioavailability***

: Greek Soil – pH↑, CEC ↑, = ***minimum bioavailability***

Can EU approach be validated elsewhere?

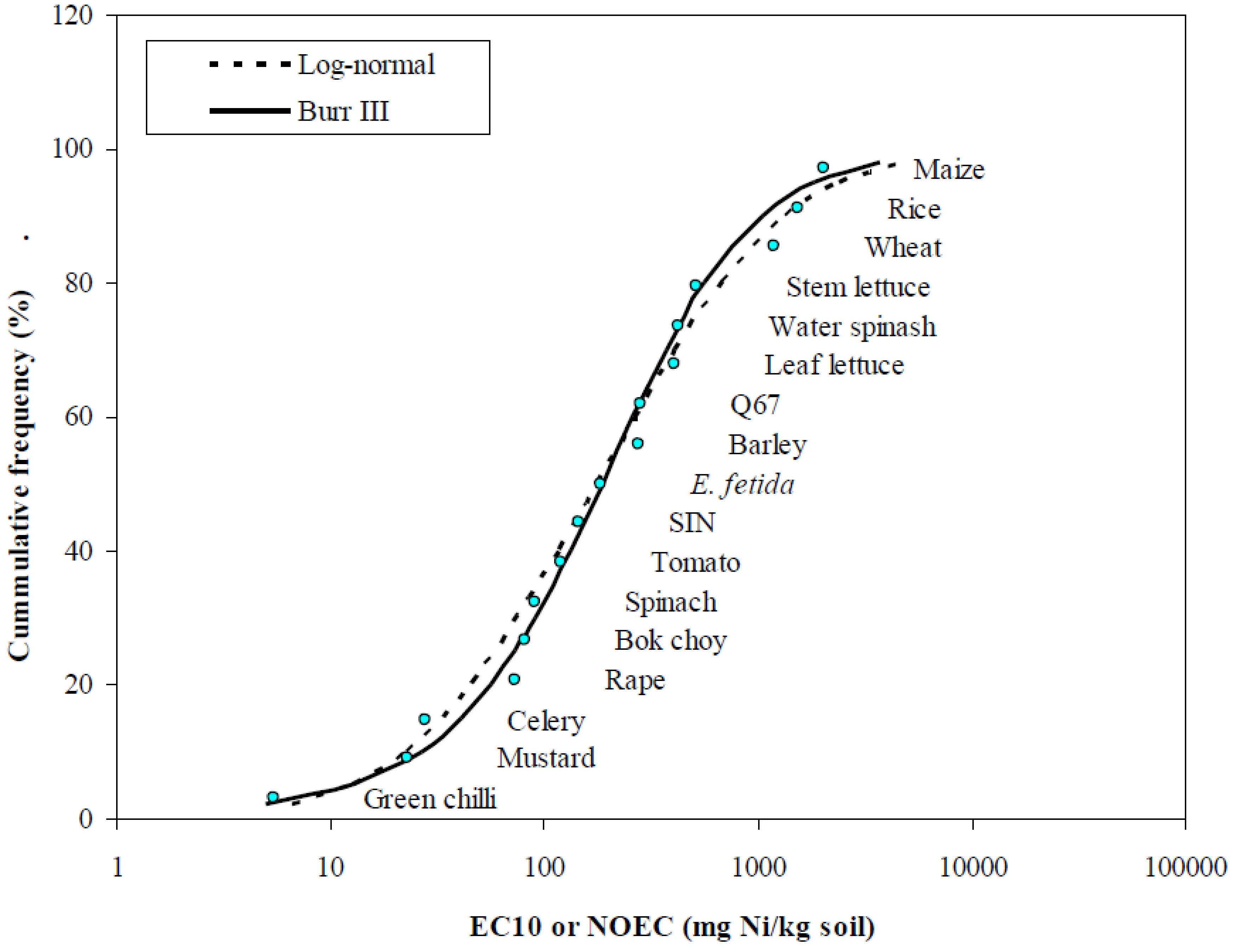
=



Metals in Asia

- Cu and Ni
- Tested 17 Chinese soils
- Used Chinese test species (plants, microbial processes, invertebrates)
- Evaluated leaching/ageing and bioavailability relationships

Species Sensitivity Distributions for Chinese soils



- 14 plant species
- 2 microbial functions
- 1 invertebrate

Metals in Asia: Laboratory Results

- Soil-specific results observed
  - Intra-species variability as high as 52-fold for some species

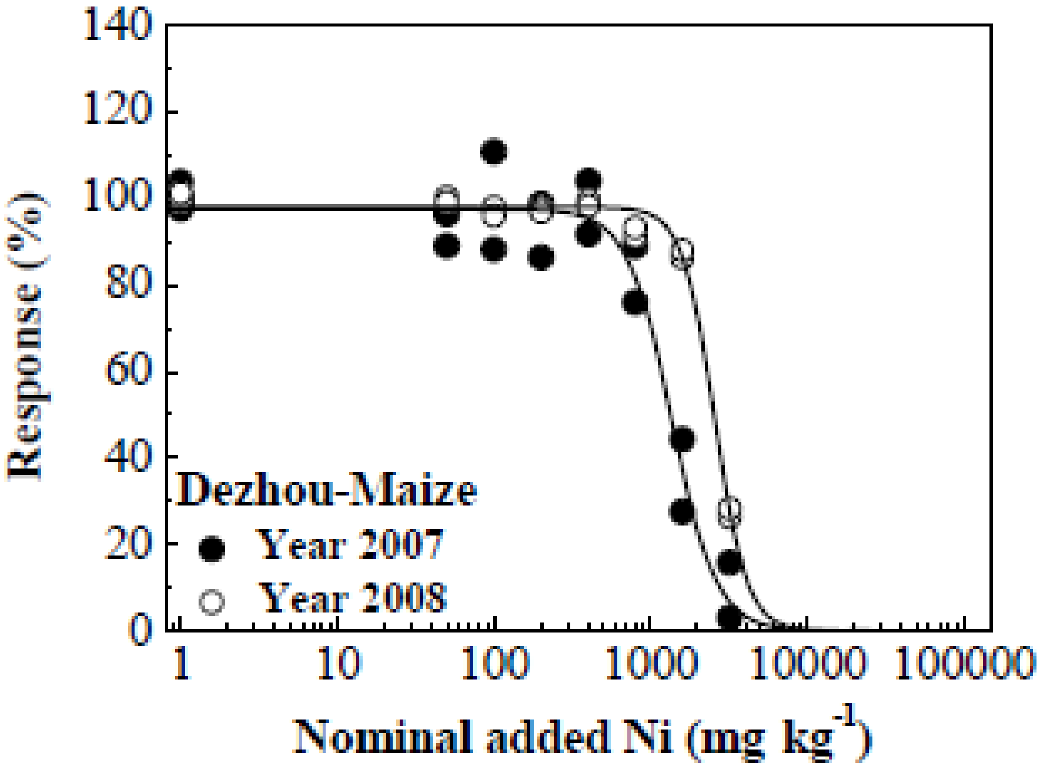
  - Relationships between soil parameters and Ni toxicity similar to that shown in EU RA soil research program

- pH related to Ni toxicity, followed by CEC
  - Together these parameters explained 80% of variability in toxicity among 17 soils (leached soils, EC_{20})

- For copper, pH, organic carbon and CEC were most important

Metals in Asia: Field Results

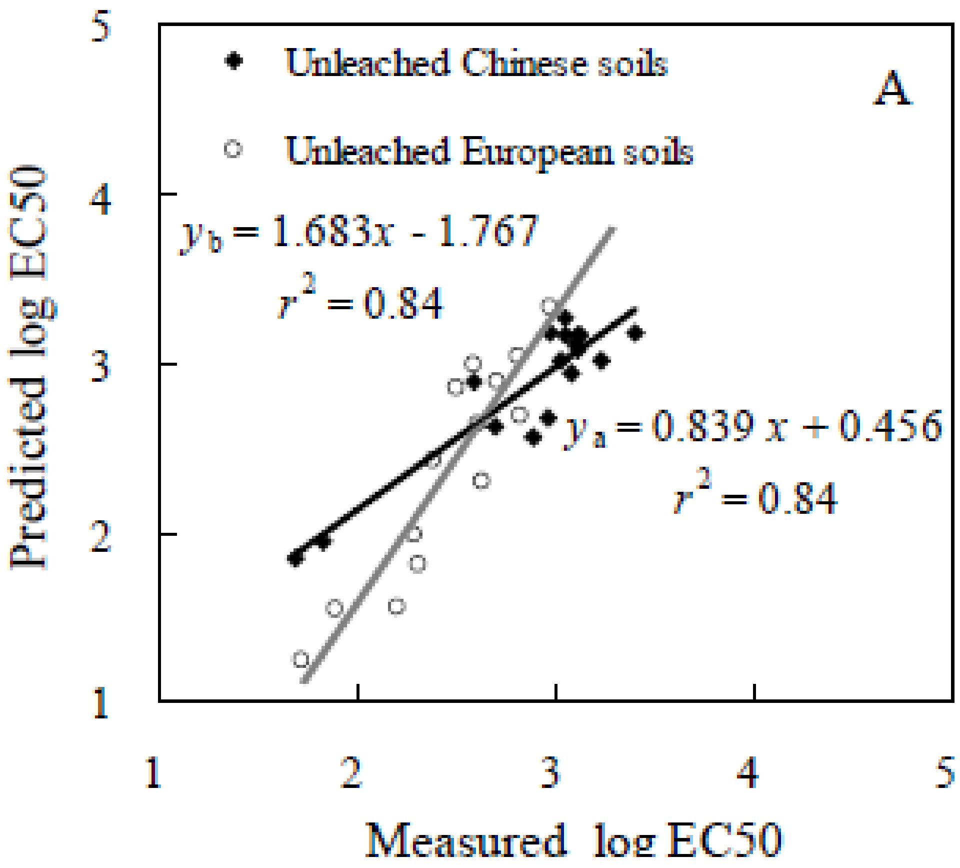
- Three field sites varying in soil parameters tested from June ’07 until September ‘08
  - pH: 5.3 to 8.9
  - CEC: 7.5 to 19.3 cmol/kg
  - Maize, wheat, rice, and rapeseed grown in each soil
- Results:
  - Decrease in toxicity in alkaline soils with time, but not in acid soil (consistent with EU data)
  - In general, L/A corrected laboratory results protective of field data



Metals in Asia: Bioavailability modeling

1. Distributions of soil parameters in Chinese soils
   - CEC and organic carbon: lower in China than Europe
   - pH: higher in China than Europe

2. Multiple regression analysis for Chinese soils
   - Variability explained mainly by pH and CEC



Australia's National Environmental Protection (Assessment of Site Contamination) Measure

- Goal: Sound environmental management of contaminated soils

- Ecological Investigation Levels (EILs)

- Contaminants covered:
  - As, Cu, CrIII, naphthalene, Ni, Pb, and Zn

- Land uses:
  - Areas of ecological interest
  - urban residential areas and public open space
  - commercial and industrial land uses

- Ecotoxicity data:
  - EC_{30}s (or LOEC)

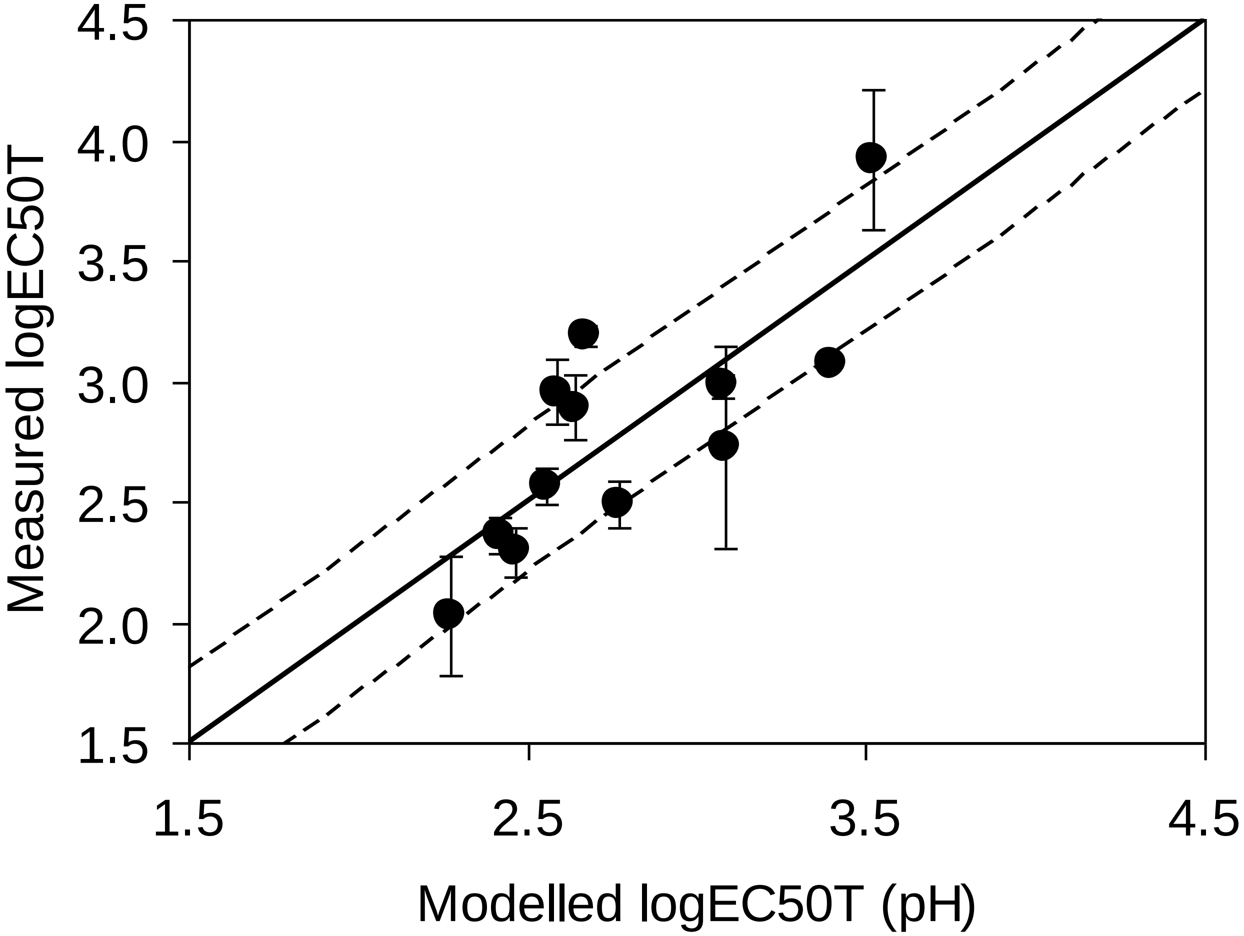
- EIL = ABC + ACL
  - ABC = ambient background concentration
  - ACL = added contaminant limit

Australia's National Environmental Protection (Assessment of Site Contamination) Measure: Normalization

- Source of soil normalization data:
  - Cu & Zn: Australian soils
  - Ni: EU soils
  - Cr(III): Indian soils

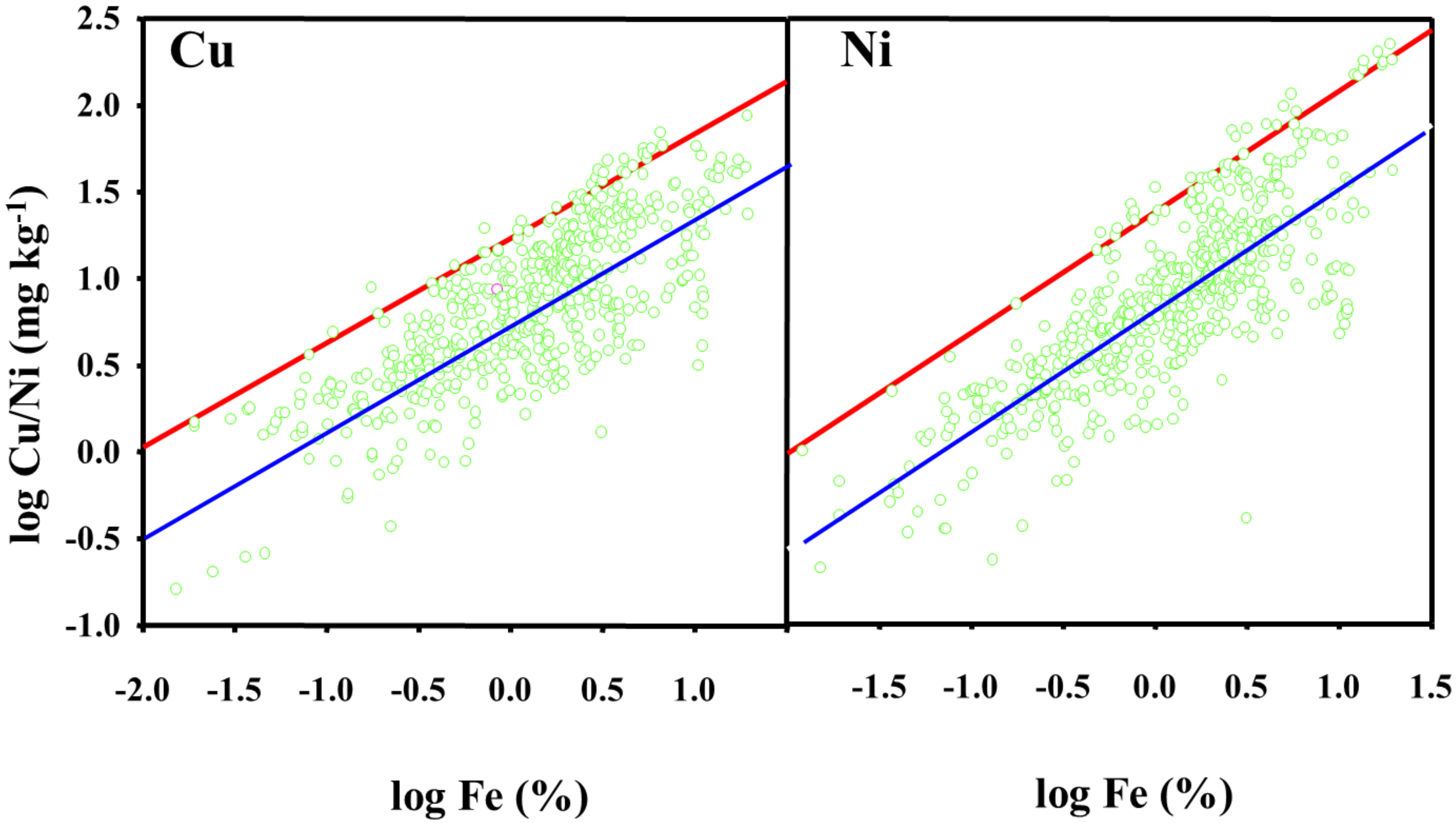
SIN Zn

logEC50T = 0.93 (0.46) + 0.34 (0.08)***pH**



Broos et al. (2007) Soil factors controlling the toxicity of Cu and Zn to microbial processes in Australian soils. *Environmental Toxicology and Chemistry* **26,** 583-590.

Australia's National Environmental Protection (Assessment of Site Contamination) Measure: Background concentration



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

Australia's National Environmental Protection (Assessment of Site Contamination) Measure

- Ambient background concentration determination hierarchy:
  1. Measure trace metals at reference site, or
  2. Use soil Fe and/or Mn to estimate soil Cu, CrIII, Ni, Pb, and Zn, or
  3. Use 25th percentile of urban monitoring database values

- Added contaminant limit determination:
  - Based on soil pH, CEC, and clay content

Soil physicochemical property	CrIII	Cu	Ni	Zn
pH		✓		
CEC		✓	✓	✓
% clay	✓			

Australia-specific relationships determined

EU relationships read across

India relationships read across

Australia's National Environmental Protection (Assessment of Site Contamination) Measure: Example for Cu

Table 1B(2) Soil-specific added contaminant limits for aged copper in soils

Cu added contaminant limits (ACL, mg added contaminant/kg)					
Areas of ecological significance					
CEC ($cmol_c$/kg)[a] based					
5	***10***	***20***	***30***	***40***	***60***
30	65	70	70	75	80
pH[b] based					
4.5	***5.5***	***6***	***6.5***	***7.5***	***8.0***
20	45	65	90	190	270
Urban residential/public open space[1]					
CEC ($cmol_c$/kg)[a] based					
5	***10***	***20***	***30***	***40***	***60***
95	190	210	220	220	230
pH[b] based					
4.5	***5.5***	***6***	***6.5***	***7.5***	***8.0***
60	130	190	280	560	800
Commercial/industrial					
CEC ($cmol_c$/kg)[a] based					
5	***10***	***20***	***30***	***40***	***60***
140	280	300	320	330	340
pH[b] based					
4.5	***5.5***	***6***	***6.5***	***7.5***	***8.0***
85	190	280	400	830	1200

Notes:

1. Urban residential/public open space is broadly equivalent to the HIL A, HIL B and HIL C land use scenarios in Table 1A(1) Footnote 1 and as described in Schedule B7.
2. The lower of the CEC or the pH-based ACLs for the land use and soil conditions is the ACL to be used.
3. Aged values apply to contamination present in soil for at least two years. For fresh contamination refer to Schedule B5c.
4. The EIL is calculated from summing the ACL and the ABC.

a = CEC measured using the silver thiourea method (Chabra et al. 1972).

b = pH measured using the $CaCl_2$ method (Rayment & Higginson 1992).

Migration of EU soil RA: Lessons learned

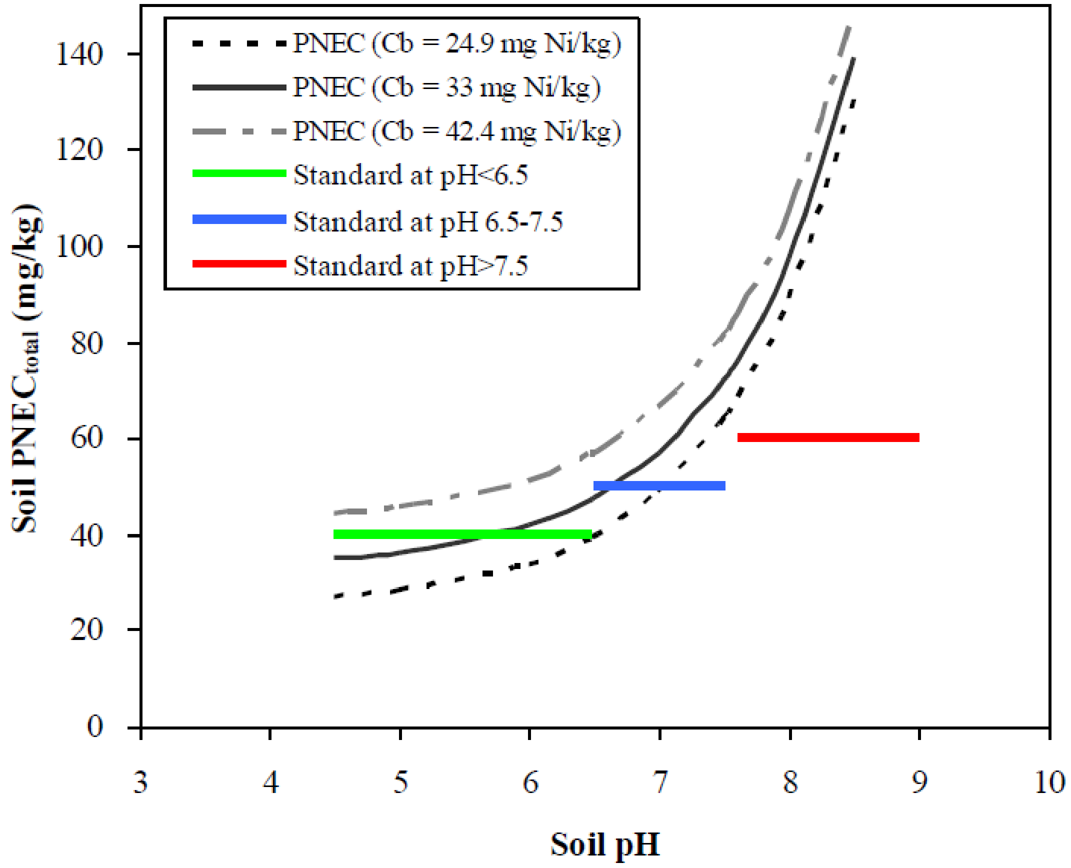
1. General approach for bioavailability correction developed in the EU can be applied in other areas, taking regional factors into account

2. Consideration of regional protection goals
   - Bok choy, green chili and other species not considered in EU testing were sensitive to metal exposure

3. Evaluation of regional influences on ageing, leaching, and bioavailability
   - Soil pH and organic carbon explained variability among Chinese soils

4. Regional ambient background concentrations must be determined
   - HC_5s from species sensitivity distributions may be over-protective for some protection goals

Bioavailability-based approach for Chinese soils?



Thank you

- For additional information please contact me at cschlekat@nipera.org