Asia-Pacific
Economic Cooperation

2015/SOM3/CD/WKSP/013

# Regulation of Metals in Soils

Submitted by: University of Adelaide

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**Workshop on Metals Risk Assessment**
**Cebu, Philippines**
**28-29 August 2015**

# Regulation of Metals in Soils

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## Overview

- Sources of metals in soils
- Development of ecological soil criteria
- How to handle biomagnification?
- Example frameworks – Australian National Environment Protection Measure
- Dealing with complex historically contaminated sites (after screening level assessment)

## Sources of Metals in Soils

- **Geogenic**
  - Parent rock weathering, e.g. all metals
  - Atmospheric accessions e.g. volcanic activity, e.g., F
  - Surface or groundwater irrigation on soil e.g., As
- **Anthropogenic**
  - Mining/smelter emissions (atmosphere and to waters used for irrigation)
  - Coal combustion
  - Chemical and electronic industry waste
  - Waste disposal
  - Agricultural inputs
  - Transport
  - Urban wastes


PIVOT
Fertilisers
GIBSONS
GIBSONS GROUND SPREAD


AMAZONE


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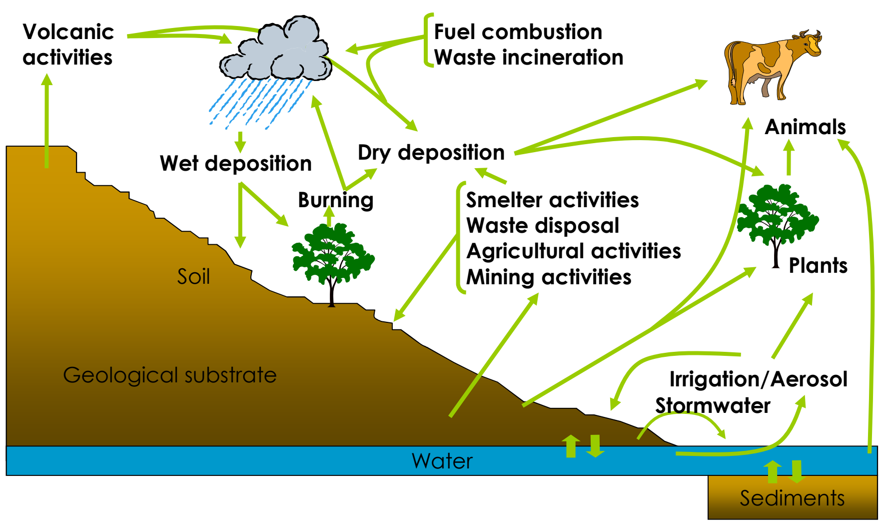
## Geochemical Cycling of Metals



## Protecting Soils from Metal/ Metalloid Contamination

**We need to control soil contamination for several reasons**

- Metals/metalloid do not degrade
- Most metals/metalloids are not easily removed from soils
- Soils are the basis for food production
- Soils are the basis of the wildlife food chain
- Most potable water passes through soil before storage

## Protecting Soils from Metal/ Metalloid Contamination

**Two scenarios to consider:**

1. Assessing presence of contamination and ecological/human risk and the need for remediation (historical contamination)
2. Predicting accumulation in soils and assessing needs for controls on emissions to soils (preventing future risk)

Both these require the development of appropriate generic or site-specific ecological soil quality standards

## Protecting Soils from Metal/ Metalloid Contamination

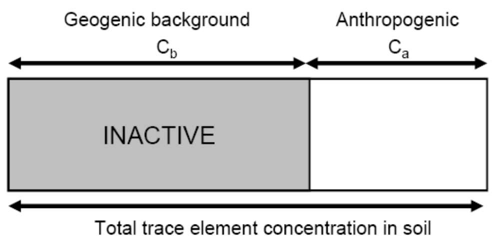
- Most soil quality standards are derived using total metal concentrations in soil
- Total metal concentration is not a good measure of metal bioavailability
- How can we merge the most recent understanding of metal bioavailability into soil quality standards?

## Protecting Soils from Metal/ Metalloid Contamination: Major Issues

- Need to consider background
- Need to consider “soil effect” on bioavailability (normalisation)
- Need to consider leaching/ageing factor for laboratory toxicity data
- Need to consider multiple biological species

# Background

- **One way to incorporate this issue is to use the “added risk” approach**




Soil Quality Standard = Background + Added Contaminant Limit

# Soil Bioavailability

| Species/soil process | X parameter(s) | Reference |
|---|---|---|
| *E. fetida* (eworm) | **0.79* log CEC** | Lock and Janssen, 2001 |
| *F. Candida* (collembola) | 1.14* log CEC | Lock and Janssen, 2001 |
| PNR | **0.15*pH** | Smolders et al., 2003 |
| SIN | 0.34*pH + 0.93 | Broos et al., 2007 |
| | 0.14 * pH + 0.89*log OC + 1.67 | Warne et al., 2008a |
| *T. aestivum* (wheat) | **0.271*pH + 0.702*CEC + 0.477** | Warne et al., 2008b |
| | 0.12*pH +0.89* log CEC + 1.1 | Smolders et al., 2003 |

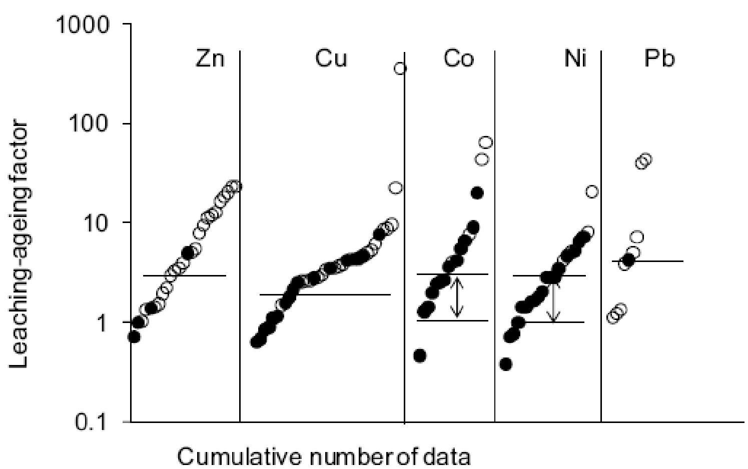
CEC = cation exchange capacity of soil

## Laboratory Bioavailability ≠ Field Bioavailability

≠

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

## Lab-to-Field Extrapolation: Leaching/Ageing




Source: Smolders et al. 2009

## Multiple Species

- **Two options:**
  1. Use toxicity data for the most sensitive organism – ensures all others (tested) are protected
  2. Aggregate toxicity data and use a species sensitivity distribution

## For Data-Poor Metals

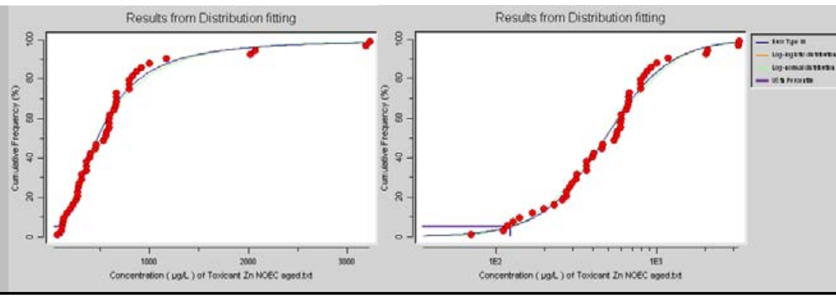
- Take the lowest toxicity value and divide it by an assessment factor (AF)
- The limit is set using the most sensitive species in the most sensitive soil
- In general, this approach sets very low ecotoxicity threshold values

| Toxicity data available | | |
|---|---|---|
| **No. species** | **No. taxonomic /nutrient gps** | **AF** |
| < 3 species | NA[a] | 500 |
| ≥ 3 species | 1 | 100 |
| | 2 | 50 |
| < 5 species | 3 | 10 |
| Field or model ecosystem data | | 10 |

Source: NEPC 2013

## Multiple Species

- **Two options:**
  1. Use toxicity data for the most sensitive organism – ensures all others (tested) are protected
  2. Aggregate toxicity data and use a species sensitivity distribution
     - Best performed on ecotoxicity thresholds normalised to "standard soil" conditions to exclude "soil sensitivity"



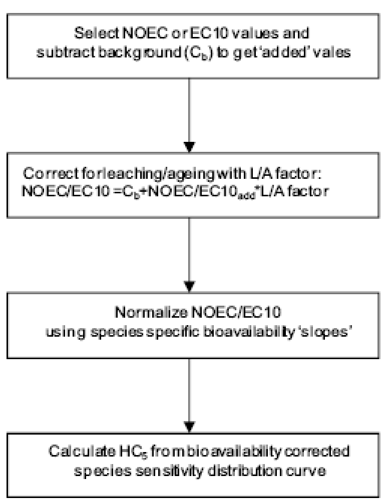

## Organism Type and Endpoint Issues

- **General agreement that higher level chronic ECx endpoints are preferable e.g., mesocosm, field ecosystem data, etc.**
- **Key limitation was data availability at higher levels so lab to field extrapolation is needed**
- **Laboratory methods need to have ecological relevance – both in terms of species selection, trophic "coverage" and, for microbial functions, functional relevance**
- **Species sensitivity distributions are generally regarded as a good integration tool as long as input data are screened for quality and relevance**

## Protecting Soils from Metal/Metalloid Contamination: Other Issues

- Biomagnification (for some elements)
- Choice of endpoints (relevance)
- Data quality screening criteria
- Choice of SSD model
- Level of protection used (HCx, AFs)
- Land use multifunctionality
- Mixtures and mixture models

## Combining Abiotic and Biotic Factors Affecting Soil Quality Standards




Source: Smolders et al., 2009

# Combining Abiotic and Biotic Factors Affecting Soil Quality Standards

- Used for development of soil amendment guidelines (sludges/wastes/manures /etc.)

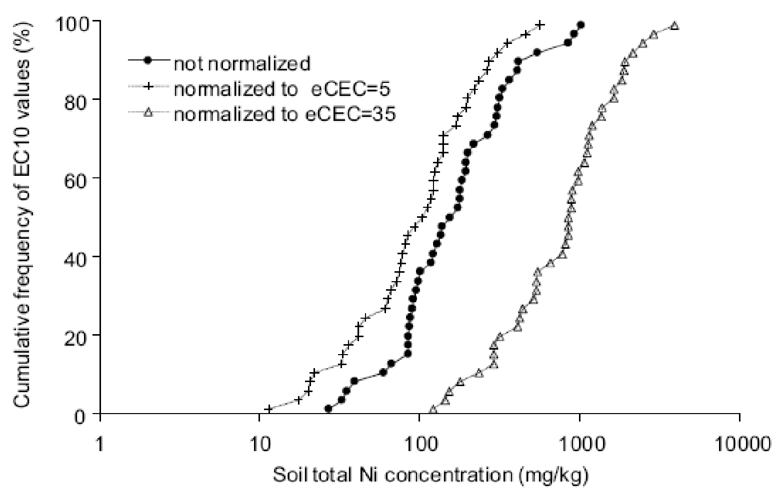
1. Collation of toxicity data and assessment of its quality and appropriateness
2. Determine if temporal changes in toxicity occur. Select the most sensitive set of toxicity data.
3. Regress toxicity data against soil properties and derive normalisation relationships.
4. Normalise toxicity data of all species to a standard soil with specific characteristics
5. Use a species sensitivity distribution method to obtain a protective concentration (added contaminant limit – ACL)
6. Calculate ACL values for a range of soils using the normalisation relationships

If deriving soil TVs omit steps 7 & 8

7. Derive a soil amendment (bio)availability factor (SAAF)
8. Multiply the SAAF and soil ACL values to derive ACL values for soil amendments
9. Determine the ambient background concentration (ABC) of the contaminant
10. Add the ABC to the ACL values to calculate TVs

Source: Heembergen et al., 2009

# Combining Abiotic and Biotic Issues




Source: Smolders et al. 2009

## Removing the Effect of Soil Properties

- **Normalisation equations were available so the data were normalised to the Australian reference soil (see table below)**

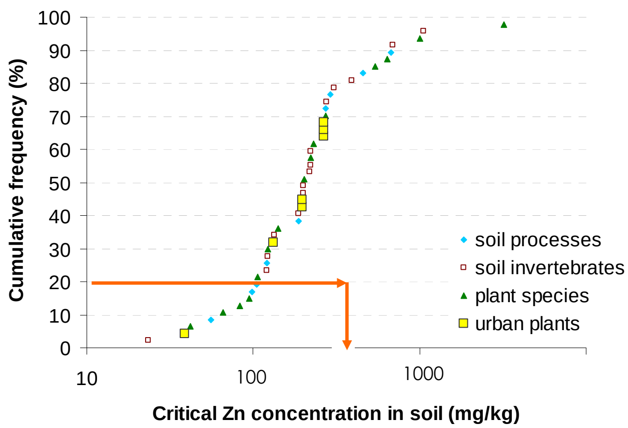
Properties of the Australian reference soil

| Soil property | Value |
|---|---|
| pH | 6 |
| Clay (%) | 10 |
| CEC ($cmol_c$/kg) | 10 |
| Organic carbon (%) | 1 |

CEC = cation exchange capacity of soil

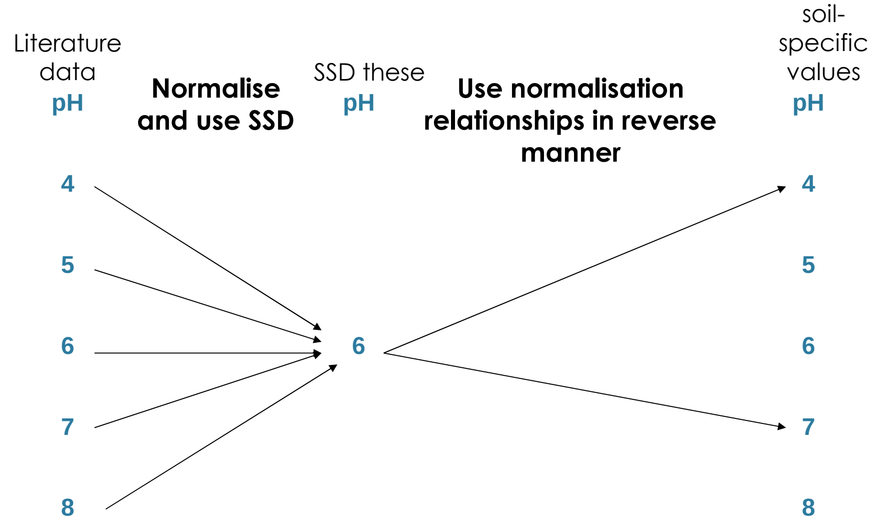
## Sensitivity of Organisms to Zn and Calculating an Added Contaminant Limit (ACL)

Normalised Zn EC30 and LOEC data




**Note:**
155 mg added Zn/kg soil is the $ACL_{(LOEC \& EC30)}$ for fresh zinc in the Australian reference soil with an urban residential land-use

## Schematic of Process e.g., pH




## Calculating Added Contaminant Limits (ACLs)

- **ACLs for zinc (mg/kg) depend on soil characteristics: pH and cation exchange capacity (CEC)**

| | CEC | | | | | |
|---|---|---|---|---|---|---|
| pH | 5 | 10 | 20 | 30 | 40 | 60 |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | **X** | | | | |
| 7 | | | | | | |
| 7.5 | | | | | | |

The 'X' data point is ACL for a soil with a pH of 6 and CEC of 10 cmol/kg (from the SSD calculation)

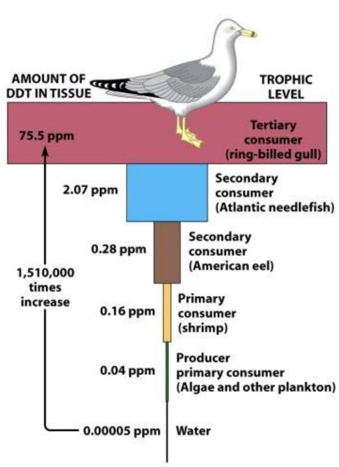
## Fresh Zn Soil-Specific Added Contaminant Limits (ACLs)

- **ACLs for fresh zinc contamination (mg/kg) in residential, urban and rural parkland land uses**

| | CEC | | | | | | |
|---|---|---|---|---|---|---|---|
| pH | | 5 | 10 | 20 | 30 | 40 | 60 |
| 4 | 27 | 44 | 72 | 96 | 118 | 157 | 27 |
| 5 | 51 | 83 | 135 | 180 | 220 | 290 | 51 |
| 6 | 95 | 155 | **252** | 335 | 410 | 545 | 95 |
| 7 | 178 | 290 | 470 | 625 | 765 | 1020 | 178 |
| 7.5 | 245 | 395 | 645 | 855 | 1045 | 1390 | 245 |

Soil Quality Standard =
Background + Added Contaminant Limit

## Biomagnification (Secondary Poisoning)




- **Options for inclusion in standards**
  - Biomagnification algorithms
  - Default biomagnification factors (BMF)
  - Increasing species protection level in the SSD

## Biomagnification (Secondary Poisoning)

- **US EPA approach**

$$SQGsp = \frac{Toxicity\ reference\ value}{FIR \cdot (P_s + BAF_{ij})}$$

**SQGsp =** soil quality guideline for secondary poisoning
**Toxicity reference value =** mg contaminant/mg prey tissue
**FIR =** food intake ratio
**Ps =** proportion of the diet that is soil
**BAFij* =** bioaccumulation factor for metal i by species j

*NOTE - BAF will vary with soil metal concentrations. For a screening value the highest BAF in the literature is used

## Biomagnification (Secondary Poisoning)

The Dutch methodology developed by Van der Plassche (1994) or Romijn et al. (1991) does not account for soil ingestion and calculates the SQG by:

$$SQGsp = \frac{NOEC\ predator}{BCFprey} \qquad \textit{(equation 16)}$$

where SQGsp is the soil quality guideline that accounts for secondary poisoning expressed in mg/kg, NOEC predator is the NOEC for a predator expressed as mg contaminant/kg prey tissue, BCFprey is the bioconcentration factor of the contaminant for a prey species expressed as a ratio of concentration in the prey and in the soil. If the BCFprey is unknown, the BCF was predicted based on the log Kow of the contaminant using QS

Source: NEPM 2013

## Biomagnification (Secondary Poisoning)

**The Australian NEPM does this in 2 ways:**

1. If the SSD approach was used (data-rich metal) the level of protection is increased by 5%
2. If the Assessment Factor approach is used (data-poor metals) then

$$ACL_{Biomagnification} = \frac{ACL}{BMF}$$

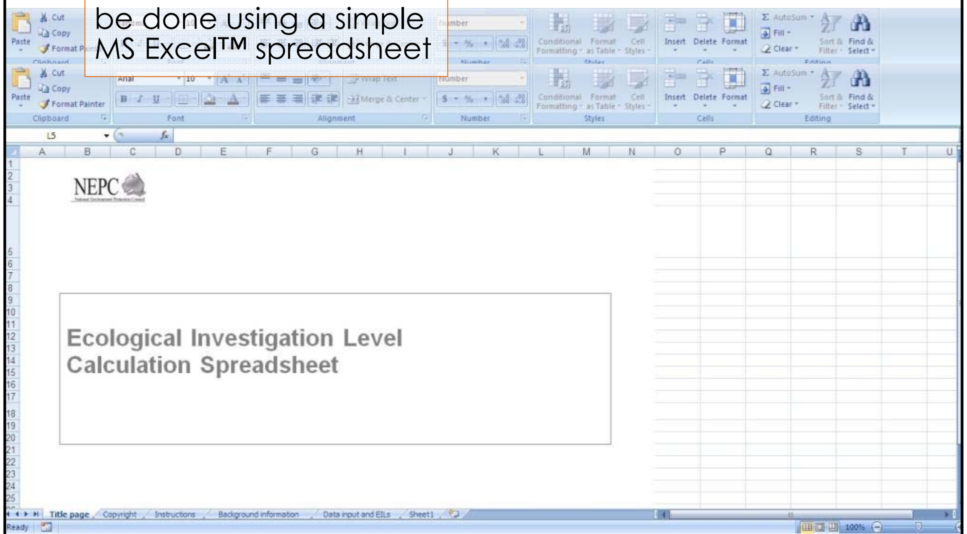
– The Biomagnification Factor (BMF) is taken from literature data (80$^{th}$ percentile of all data)

## Biomagnification (Secondary Poisoning)

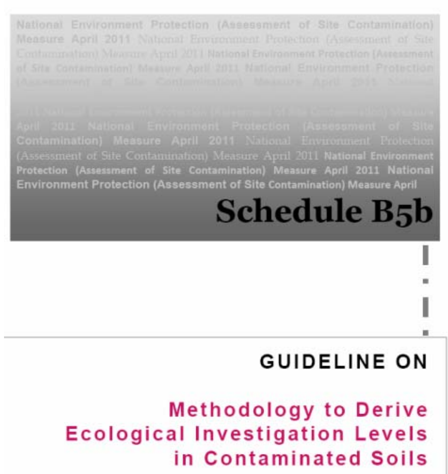
- **The Australian NEPM does not consider As, Cr, Cu, Ni, Pb or Zn to biomagnify**
- **Obviously some elements can biomagnify e.g., As, Hg but this is more commonly observed in aquatic systems than in terrestrial systems**

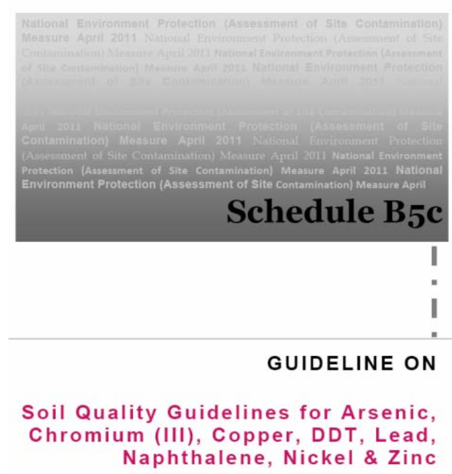
# Simplifying Complexity

All the calculations can be done using a simple MS Excel™ spreadsheet

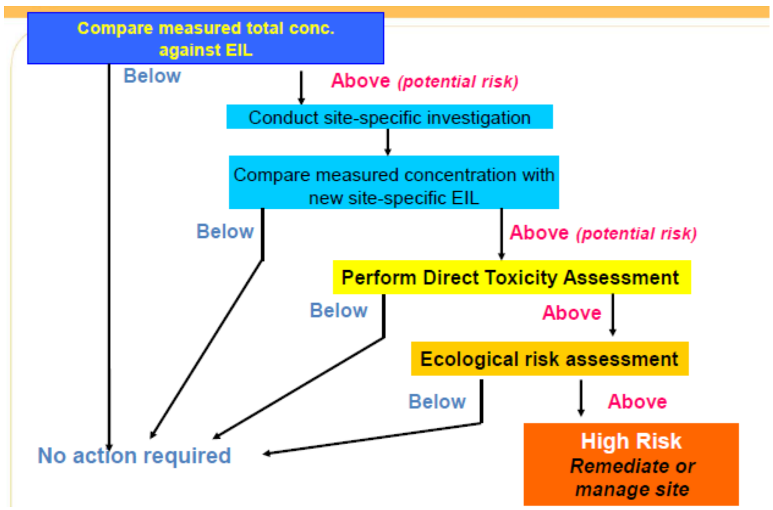



# Framework Adopted in Australia

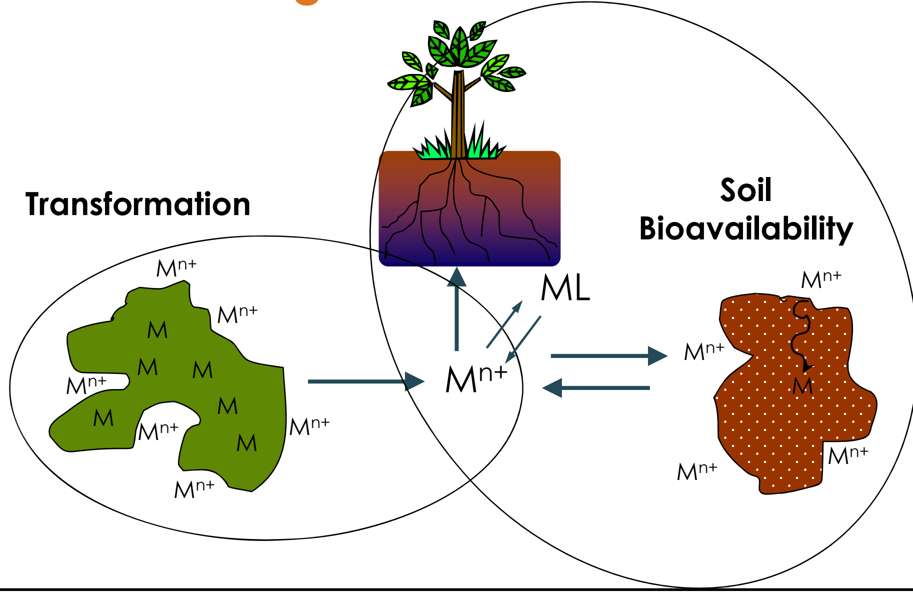


## Hierarchy of Decisions in Australian NEPM



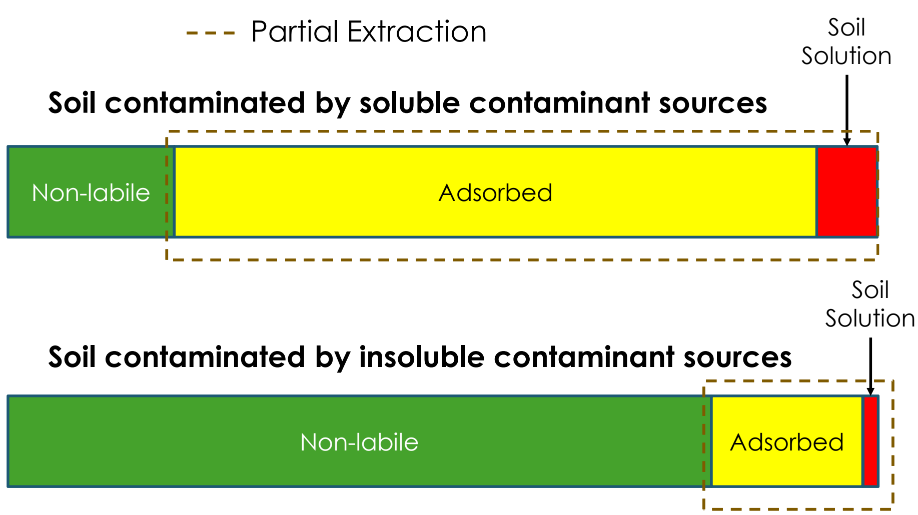

## What next? If the soil fails the screening level risk assessment?



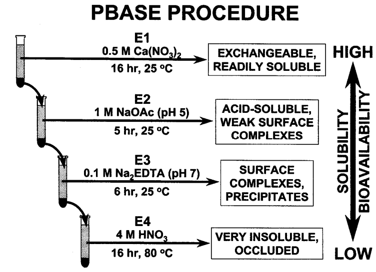
## Different Sources of Contaminants at Contaminated Sites Increase Complexity

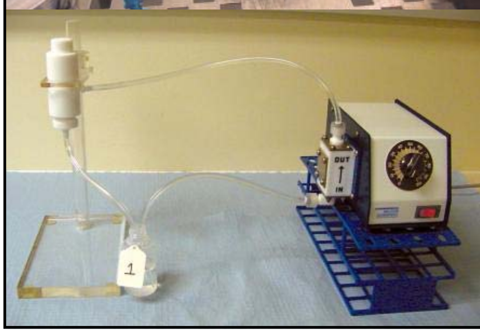
- At contaminated sites some contaminant sources may be highly soluble e.g. galvanised runoff, plating effluents, etc.
- Others are highly insoluble e.g. vitreous slags, pure metallic waste (Pb shot), etc.
- Total concentrations treat these sources similarly
- Modelling to predict dissolution is complex
- Selective extraction offers a simple screening tool prior to more detailed risk assessment

## Metal/Metalloid Pools in Contaminated Sites



# Extraction of a Bioavailable Fraction



# Partial Extractants (standard methods)

- 1.0 M $NH_4NO_3$ (DIN 19730)
- 0.01M $NaNO_3$
- 0.001 M $CaCl_2$

INTERNATIONAL STANDARD **ISO 19730**

First edition 2008-12-01

**Soil quality — Extraction of trace elements from soil using ammonium nitrate solution**

*Qualité du sol — Extraction des éléments traces du sol à l'aide d'une solution de nitrate d'ammonium*

TECHNICAL SPECIFICATION **ISO/TS 21268-1**

First edition 2007-07-15

**Soil quality — Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials —**

Part 1:
**Batch test using a liquid to solid ratio of 2 l/kg dry matter**

*Qualité du sol — Modes opératoires de lixiviation en vue d'essais chimiques et écotoxicologiques ultérieurs des sols et matériaux du sol —*

*Partie 1: Essai en bâchée avec un rapport liquide/solide de 2 l/kg de matière sèche*

# Partial Extractants

Ecotoxicological calibration data???

## Partial Extractants of Soil

- **Most research on partial extractants has focussed on correlations of extracted concentrations with concentrations in terrestrial plants**
- **For ecological receptors, there is a paucity of calibration data against toxicological endpoints**
- **It is unknown if critical values derived from extracted concentrations will need to be normalised using other soil physicochemical properties – this is a research gap**

## Partial Extractants

- **Advantages**
  - They account for bioavailability of the contaminant source
- **Disadvantages**
  - There are many methodologies in the literature and it has not been resolved which is "best"
  - Very little calibration data for ecotoxicity thresholds
  - Intra-laboratory differences of these measures are higher than that for total concentration measurements

## References


- Heemsbergen, D.A., M.S.J. Warne, K. Broos, M. Bell, D. Nash, M. McLaughlin, et al. 2009. Application of phytotoxicity data to a new Australian soil quality guideline framework for biosolids. Sci. Total. Environ. 407: 2546–2556.
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- NEPC. 2013. National Environment Protection (Assessment of Site Contamination) Measure 1999 (2013 Amendment), Volume 8, Schedule B5c. Ecological Investigation Levels for Arsenic, Chromium (III), Copper, DDT, Lead, Naphthalene, Nickel & Zinc In: N. E. P. Council, editor Australian Commonwealth Government.
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