Remediating soils: Bioavailability as a tool in site management

Ravi Naidu

CRC CARE

Brussels, 2014
OVERVIEW

- Introduction
  - Global estimate potentially contaminated sites
  - Current remediation strategies in Australia
- Risk based approach to managing contaminated sites
- Using bioavailability reduction as a means of managing risk and hence remediation
- Case examples of risk based approach using bioavailability reduction as the basis of remediation
- Policies and bioavailability-based guidelines
- Conclusion
Chemical contamination is one of the ten ‘planetary boundaries’ which humanity, for its own sake, ought not to transgress (Rockstrom et al (Nature 461, 2009)).

Chemical contamination is of equivalent significance with climate change (Rockstrom et al (Nature 461, 2009)).
## GLOBAL ESTIMATE OF POTENTIALLY CONTAMINATED SITES (MODIFIED FROM CEI, (2005))

<table>
<thead>
<tr>
<th>Country</th>
<th>Potentially contaminated sites</th>
<th>Value of current market</th>
<th>Future potentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>450,000 to 500,000</td>
<td>$1 trillion per annum</td>
<td>Estimated at US $650 billion over 30-35 years</td>
</tr>
<tr>
<td>Western Europe</td>
<td>600,000+</td>
<td>€50 billion, timeframe unspecified</td>
<td>0.5-1.5% of GDP likely to be spent per annum</td>
</tr>
<tr>
<td>Japan</td>
<td>500,000+</td>
<td>$1.2 billion+, timeframe unspecified</td>
<td>N/A</td>
</tr>
<tr>
<td>Australia</td>
<td>160,000</td>
<td>&gt;$3 billion per annum</td>
<td>N/A</td>
</tr>
<tr>
<td>Asia region</td>
<td>&gt;3,000,000</td>
<td>Unassessed</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Pace of remediation slow
THE SCALE OF THE CHALLENGE – AUSTRALIA

- *160,000 sites contaminated
- 60-80% within our cities, 30% government owned
- 75,000 toxic chemicals
- Complex mixtures

*Ref: Canadian Environment Industries (2005) Soil Remediation Technologies
## SITE REMEDIATION IN AUSTRALIA

<table>
<thead>
<tr>
<th>Technology</th>
<th>Type</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landfill</td>
<td>Conventional / containment</td>
<td>Increased levy to discourage landfills - all States except Qld</td>
</tr>
<tr>
<td>Solidification</td>
<td>Conventional</td>
<td>Quite common</td>
</tr>
<tr>
<td>Ex-situ soil washing</td>
<td>Conventional</td>
<td>Overly expensive</td>
</tr>
<tr>
<td>Ex-situ thermal</td>
<td>Emerging</td>
<td>Seen as suitable for highly recalcitrants</td>
</tr>
<tr>
<td>Risk based + immobilisation</td>
<td>Led</td>
<td>Most preferred approach</td>
</tr>
<tr>
<td>Bioremediation</td>
<td>Innovative</td>
<td>Green technology</td>
</tr>
<tr>
<td>Electro-kinetics</td>
<td>Innovative-emerging</td>
<td>Recent technology - still not seen as attractive</td>
</tr>
</tbody>
</table>

< 10% sites remediated during the past 20 years!
VICTORIAN EPA AUDIT RESULTS
Cleanup Methods Used

% of Audits

Excavation & Landfill  None  UST removal  Capping  Venting  Mixing  Collection & removal  Bioremediation  Landfarming  Solidification

LANDFILLS: INTER-GENERATIONAL ISSUE
NEED FOR NEW SOLUTIONS

• Current cost of remediation in Australia exceeds $3 billion per annum
• Status: < 10% of sites remediated since 1990
• Key issue: can we enhance remediation without increasing dig-and-dump?
• Need new solutions
CAN REDUCE COST BY CONTROLLING LAND USE

1990’s to current approach = fitness for use

Low Risk --- high cost

Moderate Risk

High Risk = low cost

Total Contaminant loading (mg/kg)

Cost of Clean up ($000)

residential

industrial
RISK BASED APPROACH - WHAT’S BEING PROPOSED?

Although not that popular:

(a) *In situ* management
(b) minimise exposure with the fraction of contaminant that poses risk;
(c) in place management of contaminated soil via immobilisation that minimises bioavailable fraction and potential risk to receptors.

Bioavailability reduction as a means to reducing risk = RBLM?
RISK BASED APPROACH

Source → Pathways → Receptor

Remediation
Barrier
Change of Use

Minimise bioavailability
What is the underlying basis for bioavailability reduction?

Contaminant interaction in soils
TRANSPORT AND CHEMICAL REACTION PROCESSES AFFECT REACTION RATES

1. Transport in the soil solution
2. Transport across a liquid film at the solid-liquid interface
3. Transport in a liquid-filled macropore
4. Diffusion of a sorbate at the surface of the solid
5. Diffusion of a sorbate occluded in a micropore
6. Diffusion in the bulk of the solid

Naidu et al. (2008)
BIPHASIC EFFECT OF TIME ON CONTAMINANT DYNAMICS

Effect of ageing on organic Contaminants (M. Alexander, 2000)

- Sequestration
- Slow degradation
- Rapid degradation
AGING INCREASES PARTITION COEFFICIENT = PERSISTENT POLLUTANTS

Partition coefficient vs. Reaction period (days)

- **High risk**
- **Low risk**
- Long-term cont.

**Kd** = Sorbed/solution

Bioavailability reduction

R Naidu, (unpublished)
SIMPLISTIC DEFINITIONS

Soil contact time increase:

- Highly sequestered
- Total
- Bioaccessible
- Potential bioavailable
- Recalcitrant (Extractable)

(Semple and Naidu, unpublished)
ORGANIC CONTAMINANT ATTENUATION

Key challenge: how do we minimise loss of mobile/bioavailable fraction?
KEY MESSAGE: AGEING PROCESS

As soil-contaminant contact time increases:

I. Physico-chemical behaviour changes:
   i. Bound fraction increases
      i. Chemical extractability decreases (mild)
      ii. Formation of recalcitrant but extractable fraction (harsh)
      iii. Formation of highly sequestered (bound/non-extractable) residues

II. Biological interaction decrease
   i. Uptake
   ii. Biodegradation
   iii. Toxicity
OBJECTIVE OF REMEDIATION PROCESS

- reduce the actual or potential environmental threat and
- reduce unacceptable risks to man, animals and the environment to acceptable levels (Wood, 1997)

Janssen and Beckingham 2013
• Removal risk by physical means (dig and dump) which can be prohibitively expensive and may not ultimately prove effective—leaving for future generations.

Alternative: locally change the geochemistry to stabilize and sequester the contaminants and render them biologically unavailable.
CONTAMINANT INTERACTIONS - KEY MESSAGES

• Contaminants bind via both specific and non-specific interactions
• Partition coefficient increases with increasing duration of contact with soil
• Inverse relationship between Kd and contaminant bioavailability/desorption

Bioavailability could be used as the underlying basis for risk based management
PERSISTENT ORGANIC POLLUTANT ATTENUATION:

At this stage, bioavailability is limited by the rate of contaminant transfer.

- High bioavailability
- Low Kd
- High Kd

Ageing?
Chemical Amendment?
“Could be low cost, in situ management and hence most attractive remediation technique-

Key to risk reduction: development of techniques that enable significant bioavailability reduction and this must be reliable and sustainable over long-term”
SEQUENTIAL RELEASE OF CONTAMINANTS

Soil solution (Pore water)

Non-specifically sorbed

Specifically sorbed

Immobilized

Chemically-induced

Naidu and Kim (2008)

Bioavailability

Time

Bound/immobilized

ageing
CHEMICAL IMMOBILIZATION

- Chemical species influence both the toxicity and mobility of contaminants
- Speciation is influenced by both solution and solid phase reactions
- Chemical immobilization exploits these reactions to alter and control the solubility and speciation of contaminants
- Practically accomplished *in-situ by soil amendments*
RISK BASED MANAGEMENT VIA BIOAVAILABILITY REDUCTION

- Case studies
  - Cadmium in farmland
  - AFFF
  - PCB in sediments
  - DDT

Regulator requirement: outcome fulfils NEPM using OECD and other regulatory tests

Im mobilise the contaminant such that it is rendered into a non-bioavailable form
CASE STUDY 1: CADMIUM IN AGRICULTURAL SOILS

- Often Cd concentrations in farmed soils are below the regulatory guideline;
- Major concern—bioaccumulation and quality of produce.
- Remediation strategy: minimise plant uptake of contaminants by minimising bioavailability
IN-SITU REMEDIATION- Cadmium

Precipitation at pH > 8 for some metals (eg. Pb, Cd)

Decreasing bioavailability

Solution metal concentration

M²⁺(aq)

pH
CASE STUDY 2- AFFF CONTAMINATED SOILS

- Application of conventional treatment for removing PFOS from impacted soils is restricted by technical and/or economical constraints
- It is also not amenable to biological treatments.
- Immobilization of PFOS to reduce its bioavailability can be a cost effective method for managing highly contaminated sites.
Strategies to immobilize PFOS in the impacted soils.

- Develop modified natural material with capacity to immobilize PFOS
- Assess the ability of modified material to immobilize PFOS - optimization process
- An assessment of the release characteristic of the immobilized PFOS simulating field conditions
- Investigation of bioavailability of PFOS in treated soils
**PFOS CONTENT OF SOILS**

<table>
<thead>
<tr>
<th>Soil</th>
<th>PFOS concentration (µg/g dry soil)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water extract</td>
<td>solvent extract</td>
<td></td>
</tr>
<tr>
<td>Brown (Dry) RBD</td>
<td>0.26</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>Brown (Water logged) RBD</td>
<td>10.57</td>
<td>74.38</td>
<td></td>
</tr>
<tr>
<td>Red Tindal FTA 064,SB04</td>
<td>2.36</td>
<td>16.17</td>
<td></td>
</tr>
<tr>
<td>Black Tindal SS01</td>
<td>0.93</td>
<td>9.26</td>
<td></td>
</tr>
</tbody>
</table>
MODIFIED CLAY TREATABILITY STUDY - FIELD CONTAMINATED SOILS
TIME DEPENDENT DESORPTION OF PFOS FROM SOILS TREATED WITH MATCARE
### Field Remediation - PFOS in Untreated Soils

<table>
<thead>
<tr>
<th>Untreated Sample No.</th>
<th>Aqueous extract (µg/ml)</th>
<th>Soil (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.21</td>
<td>5.59</td>
</tr>
<tr>
<td>2</td>
<td>2.68</td>
<td>12.33</td>
</tr>
<tr>
<td>3</td>
<td>4.43</td>
<td>20.38</td>
</tr>
<tr>
<td>4</td>
<td>2.12</td>
<td>9.77</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>6.42</td>
</tr>
<tr>
<td>6</td>
<td>6.09</td>
<td>28.02</td>
</tr>
<tr>
<td>7</td>
<td>2.39</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>1.63</td>
<td>7.51</td>
</tr>
<tr>
<td>9</td>
<td>3.15</td>
<td>14.49</td>
</tr>
<tr>
<td>10</td>
<td>2.97</td>
<td>13.68</td>
</tr>
<tr>
<td>11</td>
<td>2.01</td>
<td>9.25</td>
</tr>
<tr>
<td>12</td>
<td>1.95</td>
<td>8.98</td>
</tr>
</tbody>
</table>
GLIMPSES OF THE FIELD WORK
GLIMPSES OF THE FIELD WORK
## FIELD REMEDIATION - PFOS IN TREATED SOILS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Aqueous extract (µg/ml) one week</th>
<th>Eight weeks</th>
<th>Soil µg/g one week</th>
<th>Eight weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>bdl</td>
<td>0.097</td>
<td>bdl</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>bdl</td>
<td>0.045</td>
<td>bdl</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>bdl</td>
<td>0.196</td>
<td>bdl</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>bdl</td>
<td>0.118</td>
<td>bdl</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>bdl</td>
<td>0.062</td>
<td>bdl</td>
</tr>
<tr>
<td>6</td>
<td>0.02</td>
<td>bdl</td>
<td>0.087</td>
<td>bdl</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>bdl</td>
<td>0.055</td>
<td>bdl</td>
</tr>
<tr>
<td>8</td>
<td>0.01</td>
<td>bdl</td>
<td>0.060</td>
<td>bdl</td>
</tr>
<tr>
<td>9</td>
<td>0.02</td>
<td>bdl</td>
<td>0.081</td>
<td>bdl</td>
</tr>
<tr>
<td>10</td>
<td>0.02</td>
<td>bdl</td>
<td>0.112</td>
<td>bdl</td>
</tr>
<tr>
<td>11</td>
<td>0.02</td>
<td>bdl</td>
<td>0.096</td>
<td>bdl</td>
</tr>
<tr>
<td>12</td>
<td>0.02</td>
<td>bdl</td>
<td>0.087</td>
<td>bdl</td>
</tr>
<tr>
<td>13</td>
<td>0.02</td>
<td>bdl</td>
<td>0.097</td>
<td>bdl</td>
</tr>
<tr>
<td>14</td>
<td>0.02</td>
<td>bdl</td>
<td>0.091</td>
<td>bdl</td>
</tr>
<tr>
<td>15</td>
<td>0.04</td>
<td>bdl</td>
<td>0.161</td>
<td>bdl</td>
</tr>
</tbody>
</table>

HPCD extractions
EFFECT OF IMMOBILIZATION ON EARTHWORM SURVIVAL AND UPTAKE IN TREATED SOILS

- Field soils treated with MatCARE allowed to react for 120 days were exposed to worms.
- Weight loss monitored
- Worm tissues solvent extracted

No sign of avoidance in treated soils - no bioaccumulation
No mortality
## LONG-TERM STABILITY OF MATCARE TREATED SOILS

<table>
<thead>
<tr>
<th>PFOS concentration (µg/g)</th>
<th>Key parameters for regulator approval</th>
<th>Pass criteria</th>
<th>Outcome post immobilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Bioavailability</td>
<td>TCLP test plus bioaccessibility</td>
<td>PFOS/PFOA bdl</td>
</tr>
<tr>
<td>18</td>
<td>Earthworm</td>
<td>OECD test</td>
<td>no mortality/no avoidance</td>
</tr>
<tr>
<td>16</td>
<td>Plant uptake</td>
<td>OECD test</td>
<td>No bioaccumulation</td>
</tr>
<tr>
<td>14</td>
<td>Bioindicator</td>
<td>dehydrogenase</td>
<td>No effect of contaminant</td>
</tr>
<tr>
<td>12</td>
<td>Microbial activity</td>
<td>counts</td>
<td>High</td>
</tr>
</tbody>
</table>
CASE STUDY 4: As AND DDT CONTAMINATED SOIL

• Problem
  – Former cattle tick dip site and contaminated with arsenic and organochlorines

• Remedial action plan
  – Excavate and transport to landfill
  – Bioavailability reduction via chemical immobilisation

• Regulator requirement- demonstrate
  – Using OECD tests- bioavailability reduction which is sustained over long-period
  – No leaching to TCLP
BIOAVAILABILITY REDUCTION - DDT AND ARSENIC

Chemical immobilisation using a mixture of chemicals for the immobilisation of both As and organo-chlorines

Remediation in 2002 and still no sign of DDT and As mobility

Naidu and Smith (2002)
## CONTAMINANT LEVELS IN SOILS

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Total arsenic (mg/kg)</th>
<th>Bioavailable arsenic (%)</th>
<th>Solvent extractable DDT (mg kg(^{-1})-total)</th>
<th>Bioavailable DDT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 10</td>
<td>&gt;3,000</td>
<td>bdl</td>
<td>106</td>
<td>1</td>
</tr>
<tr>
<td>10 to 20</td>
<td>1,450</td>
<td>bdl</td>
<td>76</td>
<td>bdl</td>
</tr>
<tr>
<td>20 to 40</td>
<td>250</td>
<td>bdl</td>
<td>22</td>
<td>bdl</td>
</tr>
<tr>
<td>40 to 60</td>
<td>50</td>
<td>bdl</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>60 to 80</td>
<td>10</td>
<td>bdl</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

Naidu and Smith (2002)- confidential report
CASE STUDY 5; PCB REMEDIATION IN SEDIMENTS (SUN AND GHOSH, 2012)
CONCEPTUAL FRAMEWORK - BIOAVAILABILITY REDUCTION USING ACTIVATED CARBON (SUN AND GHOSH (2012): CASE STUDY 2

Legacy contaminants in exposed sediment contaminate the food chain through bioaccumulation in benthic organisms, flux into the water column, and uptake in the pelagic food web.

Activated carbon amended to surficial bioactive sediments reduces contaminant exposure to food chain through reduced bioaccumulation in benthic organisms and reduced flux into water column and uptake in the pelagic food web.

In the long term (>5 years), the carbon amended layer is covered with clean new sediment deposit and continues to serve as a barrier to the release of legacy contaminants to surficial sediments and water column.
ACTIVATED CARBON REDUCES PCB BIOACCUMULATION FOR FIVE BENTHIC ORGANISMS
RECOMMENDATION

✓ Application of activated carbon to immobilise PCB and hence reduce its bioavailability to benthic organisms.

✓ Has it worked?- yes from data available– long-term success yet to be demonstrated.
PAHs IMMobilization: AC VS MODIFIED MATERIAL

Residual PAHs remaining after extraction with butanol
PAHs IMMobilization: AC vs Modified Material

Residual PAHs remaining after extraction with butanol
CHEMICAL IMMOBILISATION = CHANGING SPECIATION OF POLLUTANTS IN THE SOIL

Diagram adapted from NRC 2003; Semple et al. 2004

Soil processes properties

Bioaccessibility

Bioavailability processes

Bound Contaminant

Released Contaminant

Association

Dissociation

Biological membrane

Absorbed contaminant in organism

Site of biological response

A, B and C occur internally – for example at the gut lumen
D is uptake across a physiological membrane

A, B, C and D defined as bioavailability processes

Physiology – organism specific; gastric pH, rate of absorption, pre-exposure
Physico-chemical – contaminant properties, mineralogy, soil particle size, soil properties

Diagram adapted from NRC 2003; Semple et al. 2004
Towards bioavailability-based soil criteria: past, present and future perspectives


*Environmental Science and Pollution Research International* (2013)
CONTAMINATED LAND POLICY: BIOAVAILABILITY-BASED GUIDELINES

• Current guidelines based on total contaminant loading
  → Conservative outcomes
  → Remediation of sites that may be safe from an exposure perspective

• Bioavailability could inform decisions on remediation

• Key to a bioavailability-based guideline is:
  • Science underpinning bioavailability
  • Reliable tools for measuring bioavailable fraction
  • Recognition and acceptance by regulators
  • Careful consideration of liability inc. community acceptance
  • Policies and bioavailability-based guidelines
CLEANUP 15 CONFERENCE
MELBOURNE 13 TO 17TH SEPTEMBER

- Social, legal and economic
- Policy innovation
- Characterisation, monitoring and risk assessment
- Site management and closure
- Green and sustainable remediation
- Chemical oxidation/reduction technologies
- In-situ delivery approaches
- Physical/chemical treatment/barrier technologies
- Biological technology
- Vapor intrusion
Acknowledgements:

- Dr Thava Palanisamy
- Dr Dawit Bekele
- Dr Yanju Liu
- Dr Luchun Duan
- Prof Joop Harmsen
- Prof Jose Ortega
- Prof Kirk Semple

Thank you!