The risks of human made chemicals incorporated in the soil matrix.

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Contents

- Risk perception and risk communication
- Developments on bioavailability
- Spreading of sediments
- Polyacrylamide
- What do we know and need to know

Risk perception and risk communication

Fischhoff (1995): All we have to do:

1. Get the numbers right
2. Tell them the numbers
3. Explain what we mean by the numbers
4. Show them that they've accepted similar risks
5. Show them that it is a good deal for them
6. Treat them nice
7. Make them partners
8. All of the above

Chemicals in soil

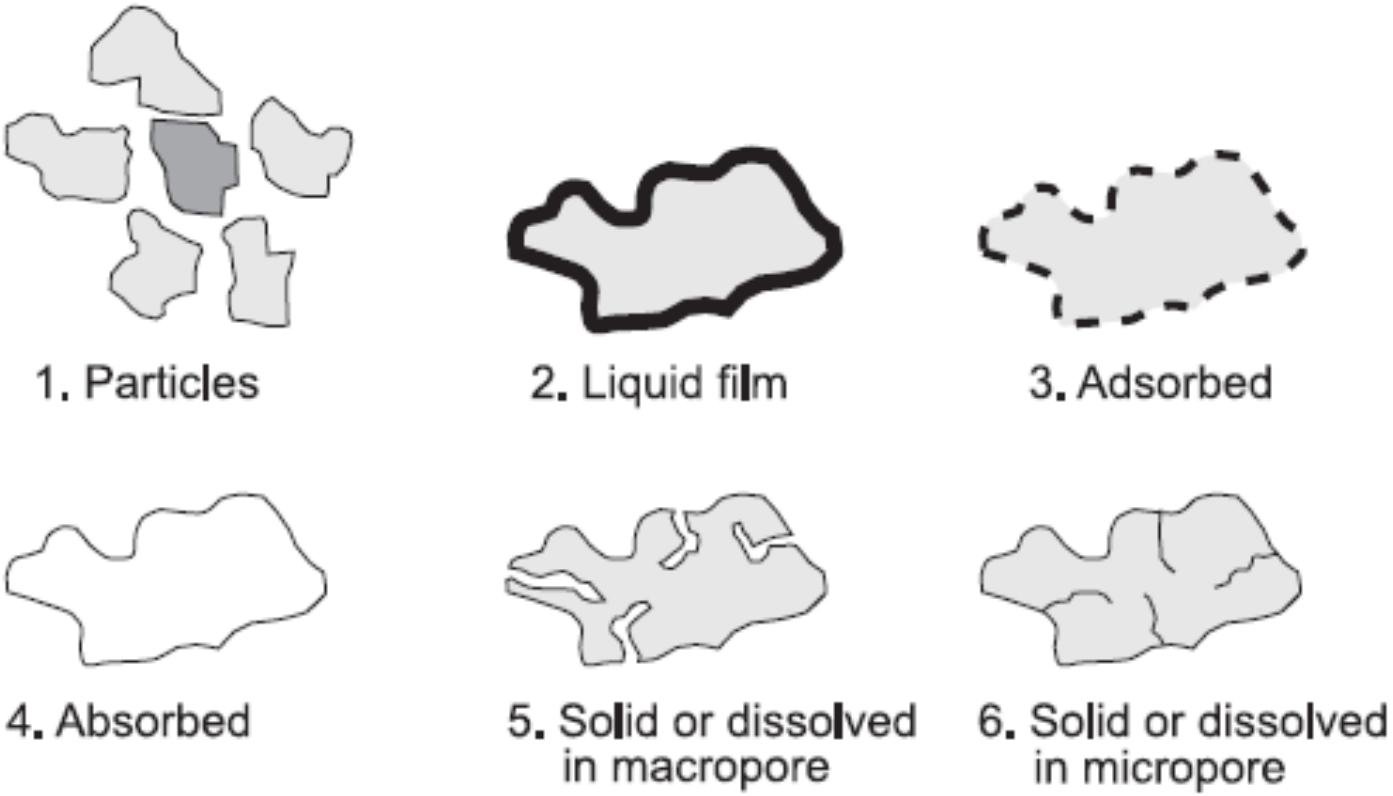
Approach in regulation

- Solved in water phase
- Adsorbed to the soil

- Partition K = concentration in soil/ concentration in water

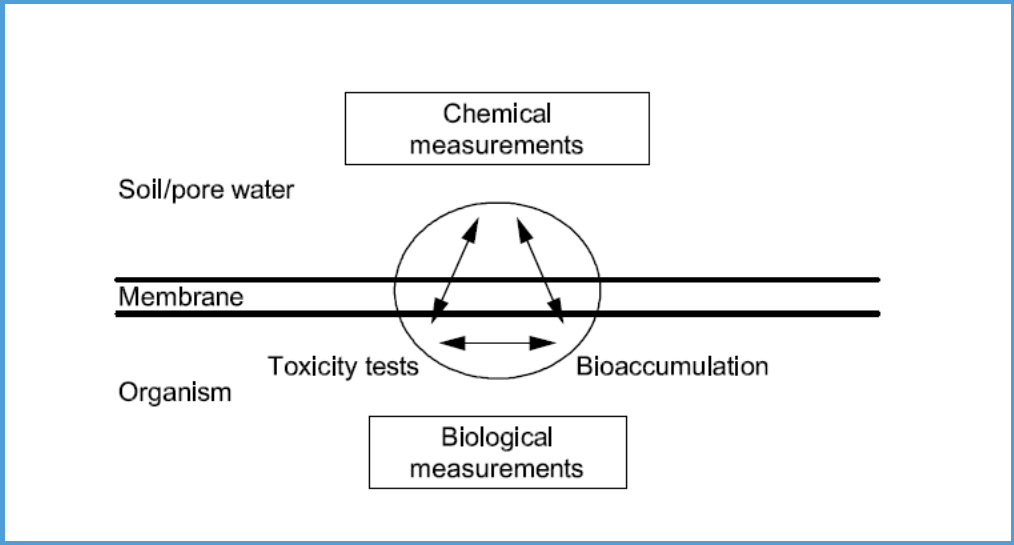
- Too simple

Appearance of contaminants in soil or sediment



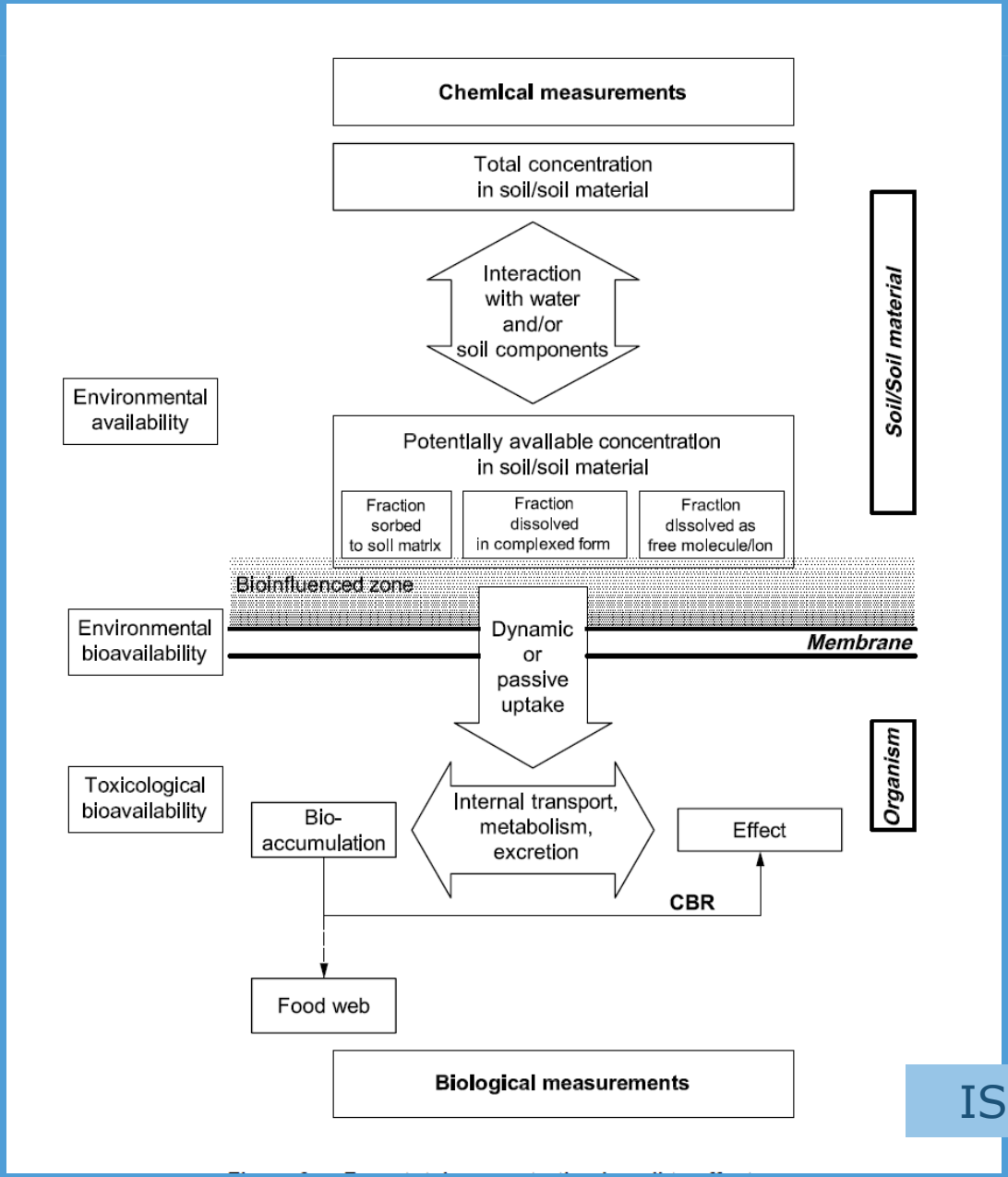
Adapted from Rulkens, (1992)

Bioavailabilty



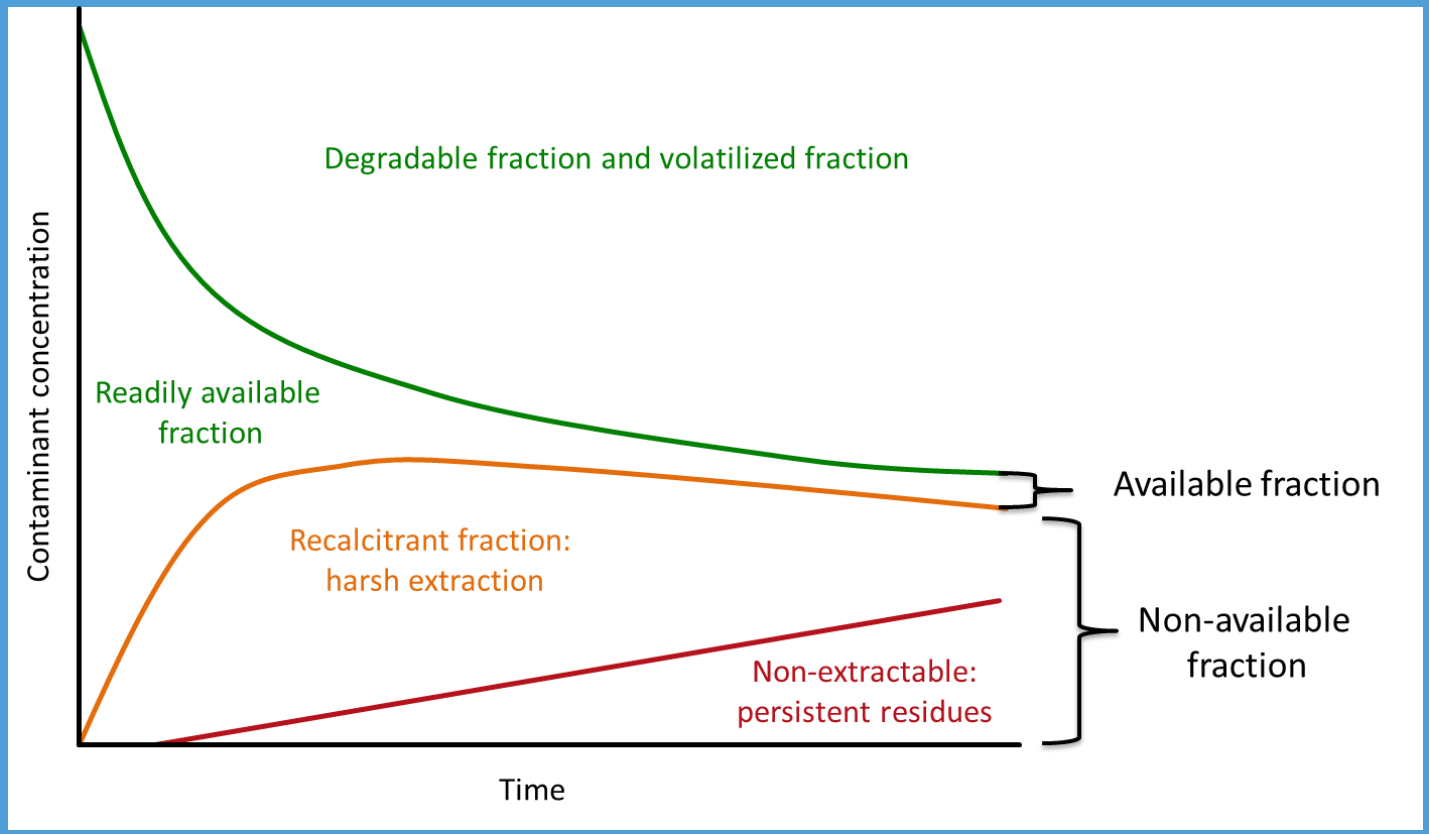
ISO 17402

Bioavailability

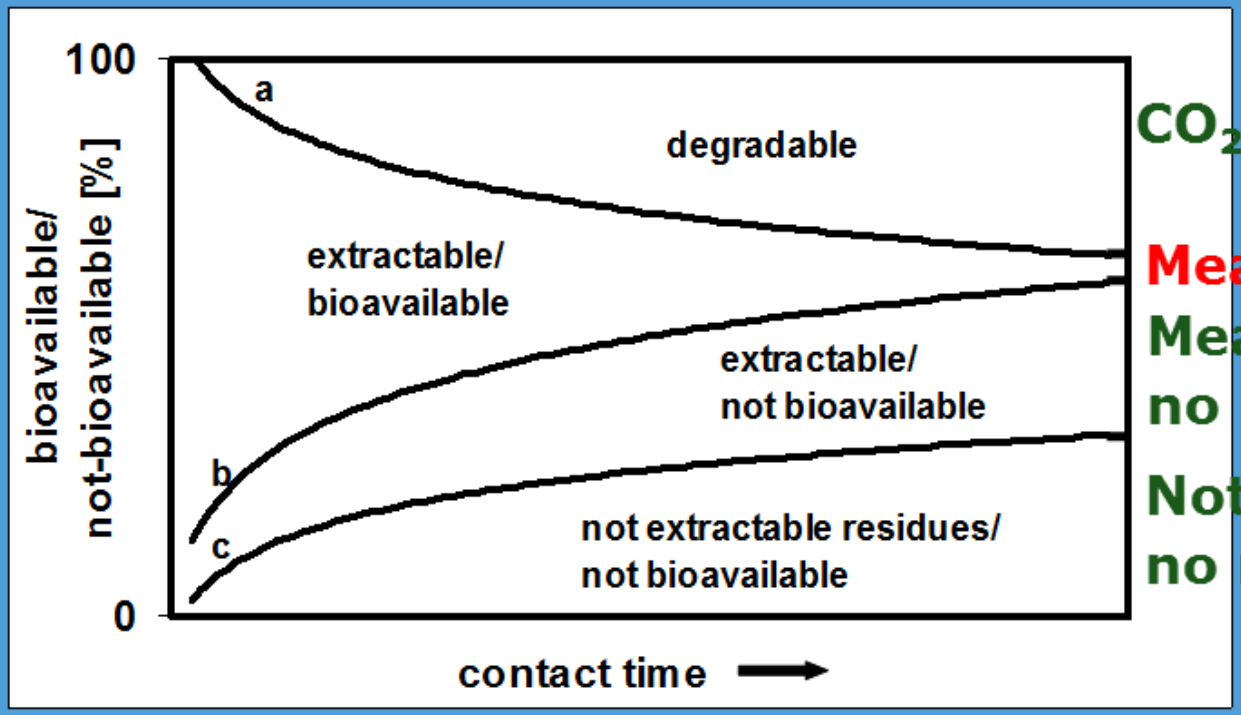


ISO17402

Redistribution in time



Bioavailability and risks



CO_2, no risks

Measurable, risks

Measurable,
no risks

Not measurable,
no risks ?

What can be measured (chemical methods)

- Bioavailable fraction (desorbed fraction)
- Recalcitrant fraction (extraction)

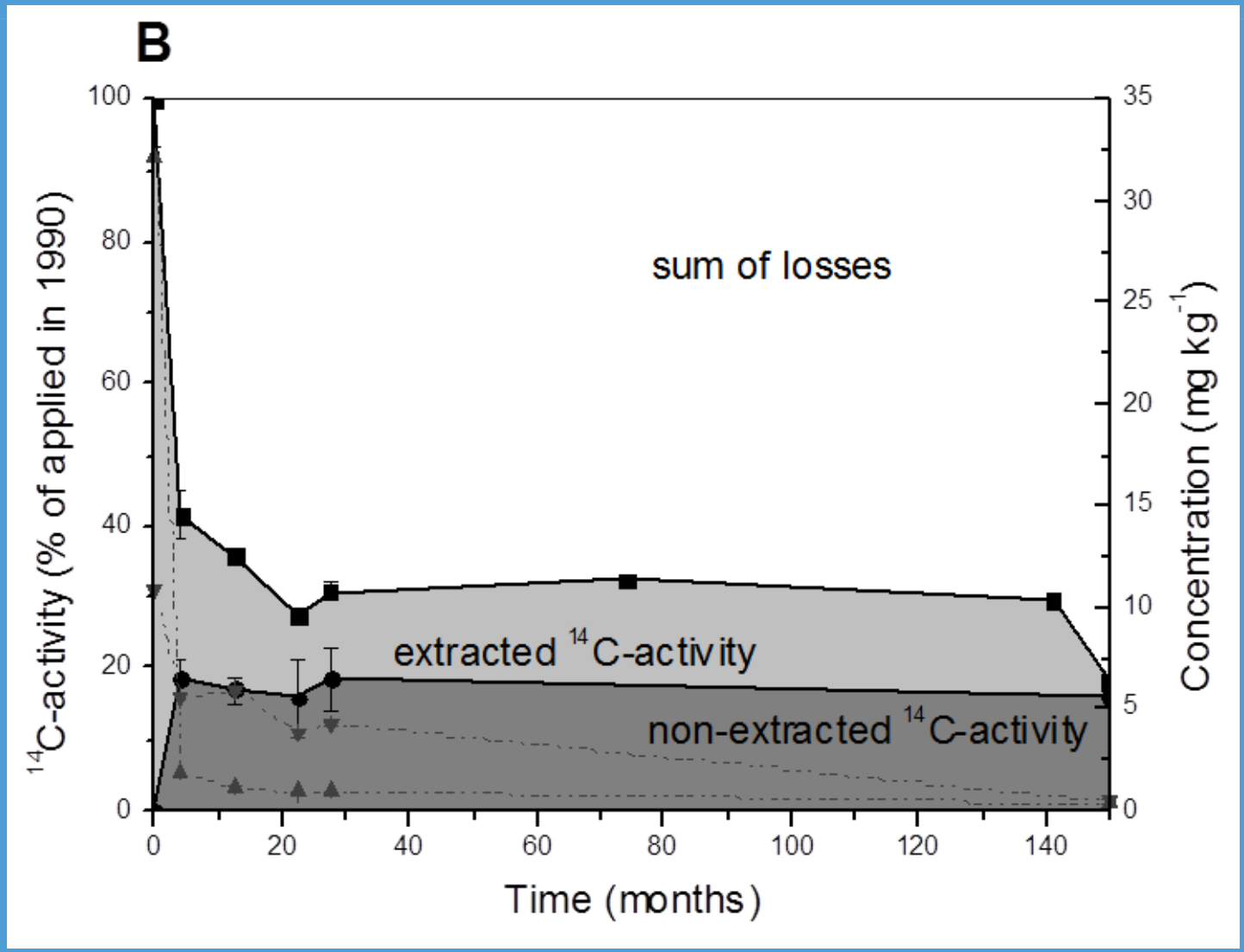
- Volatilization
- CO_2 production (mineralization of target + organic matter)

What can be measured (radio labelled)

- Bioavailable fraction (desorbed fraction)
- Recalcitrant fraction (extraction)

- Volatilization
- CO_2 production (mineralization of target ~~+ organic matter)~~
- Residue in soil (NER)
    - Sorbed target
    - Sorbed degradation product
    - Biomass

^{14}C distribution, PAH



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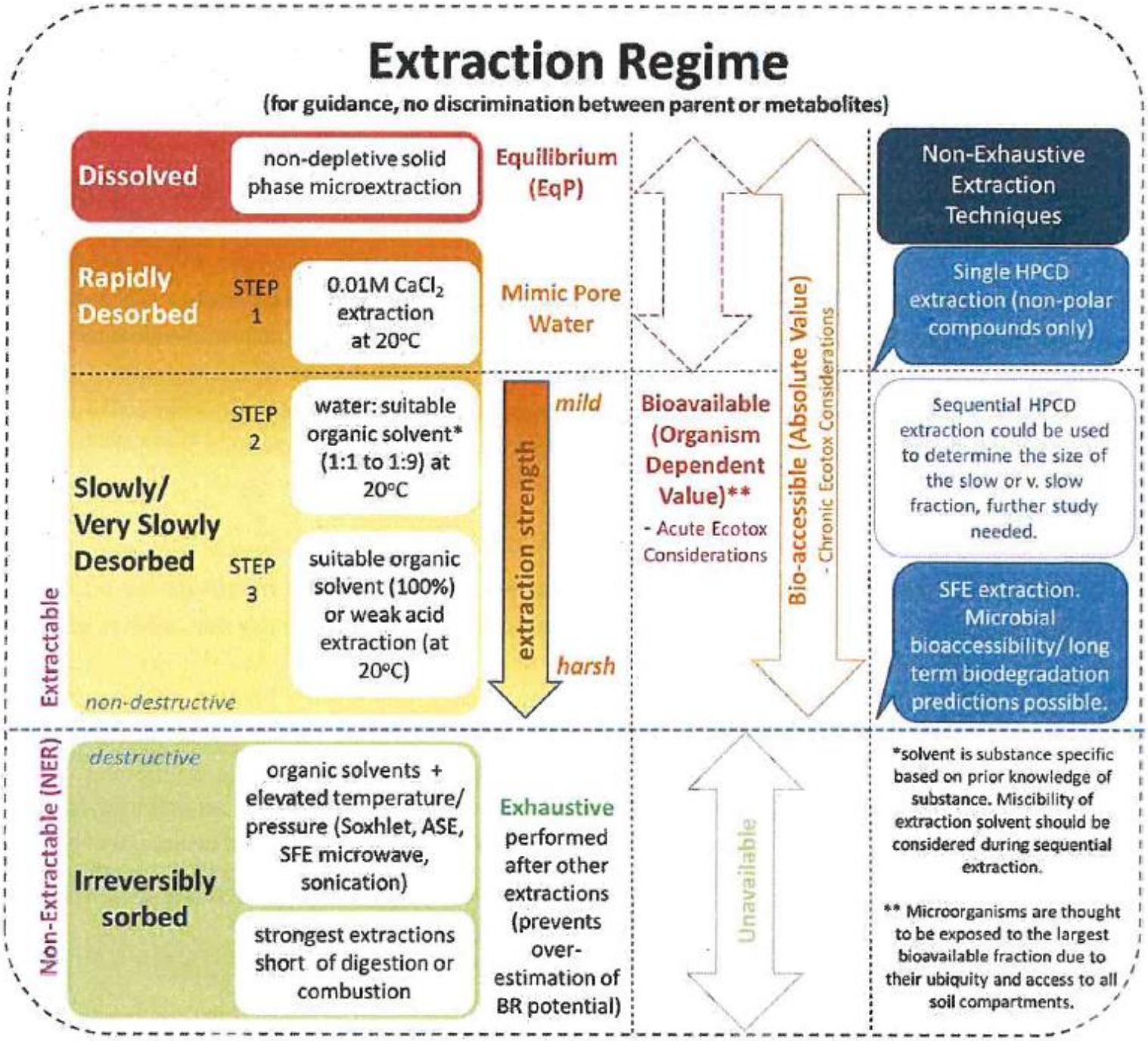
Semple


Extraction Regime
(for guidance, no discrimination between parent or metabolites)
Dissolved
non-depletive solid phase microextraction
Equilibrium (EqP)
Rapidly Desorbed
STEP 1
0.01M $CaCl_2$ extraction at 20°C
Mimic Pore Water
Slowly/ Very Slowly Desorbed
STEP 2
water: suitable organic solvent* (1:1 to 1:9) at 20°C
STEP 3
suitable organic solvent (100%) or weak acid extraction (at 20°C)
non-destructive
Extractable
extraction strength
mild
harsh
Bioavailable (Organism Dependent Value)**
- Acute Ecotox Considerations
Bio-accessible (Absolute Value)
- Chronic Ecotox Considerations
Non-Exhaustive Extraction Techniques
Single HPCD extraction (non-polar compounds only)
Sequential HPCD extraction could be used to determine the size of the slow or v. slow fraction, further study needed.
SFE extraction. Microbial bioaccessibility/ long term biodegradation predictions possible.
destructive
Irreversibly sorbed
organic solvents + elevated temperature/ pressure (Soxhlet, ASE, SFE microwave, sonication)
strongest extractions short of digestion or combustion
Non-Extractable (NER)
Exhaustive performed after other extractions (prevents over-estimation of BR potential)
Unavailable
*solvent is substance specific based on prior knowledge of substance. Miscibility of extraction solvent should be considered during sequential extraction.
** Microorganisms are thought to be exposed to the largest bioavailable fraction due to their ubiquity and access to all soil compartments.

Non Extractable Residue, NER

- Strongly bounded, no risks
- May become available, chemical time bomb

- Not measurable, indirect prove
  - What is available?
  - What is non- available?
  - What are effects?

Spreading of sediments in The Netherlands

Spreading on agricultural land

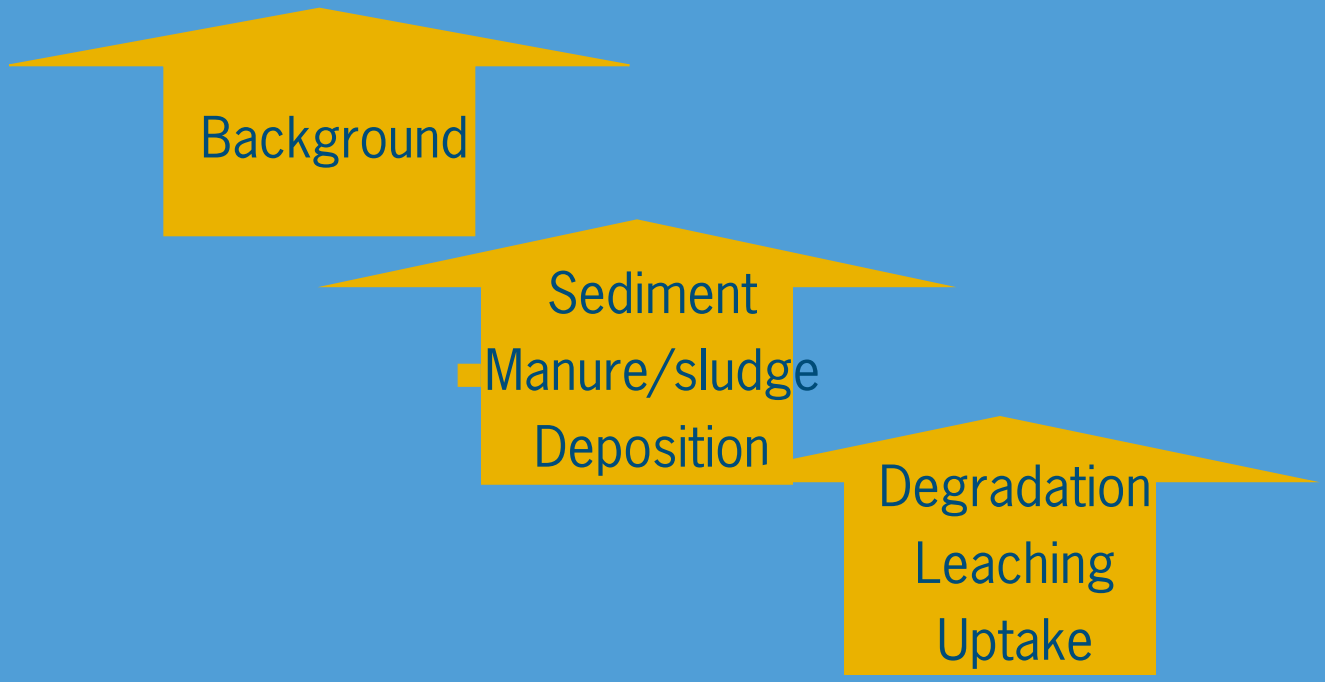
Practice since centuries. Increase of fertility of the soil

Effect of contamination?

clean | contaminated

Modelling: accumulation PAH and heavy metal

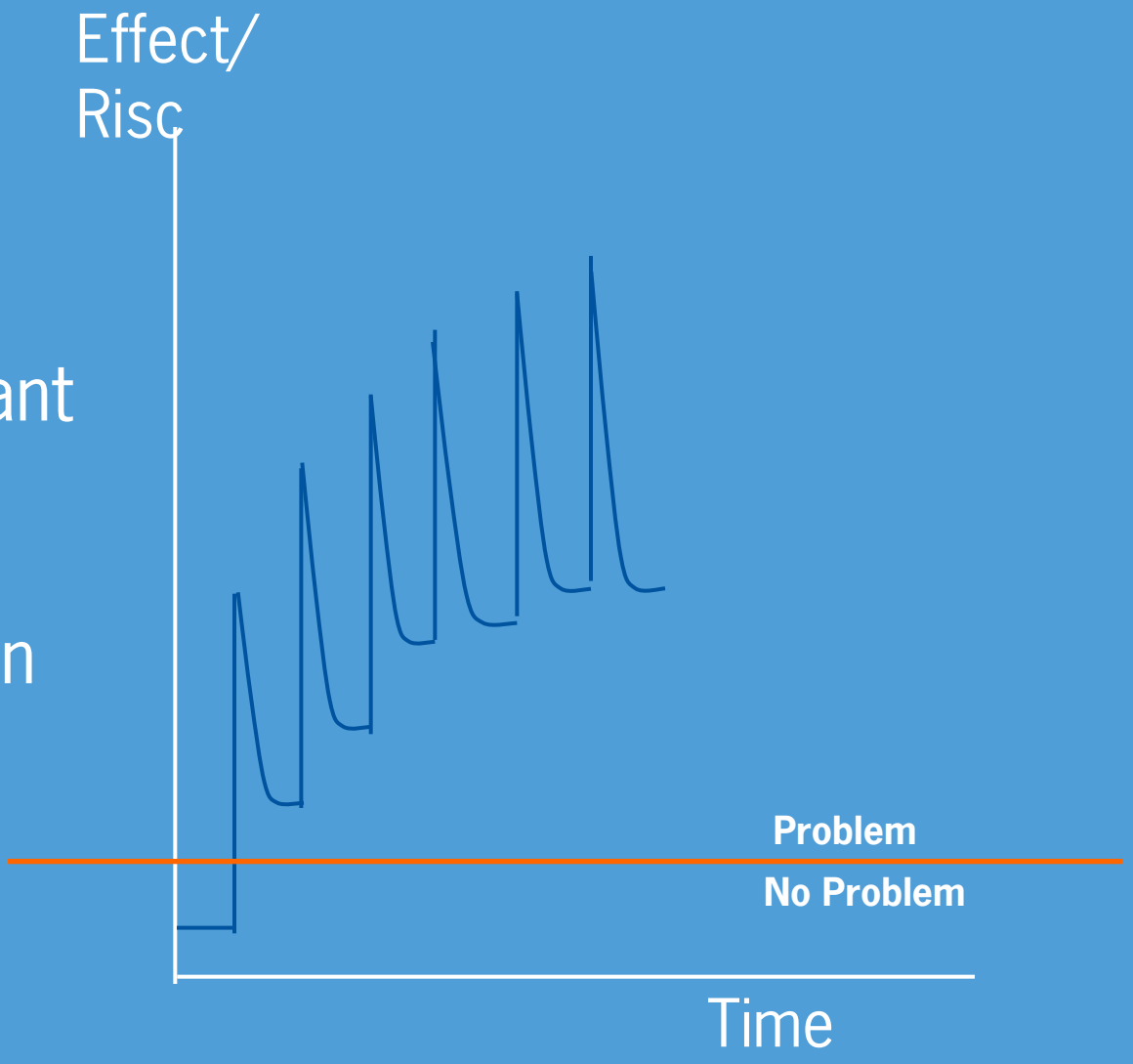
Concentration= Present + Supply – reduction



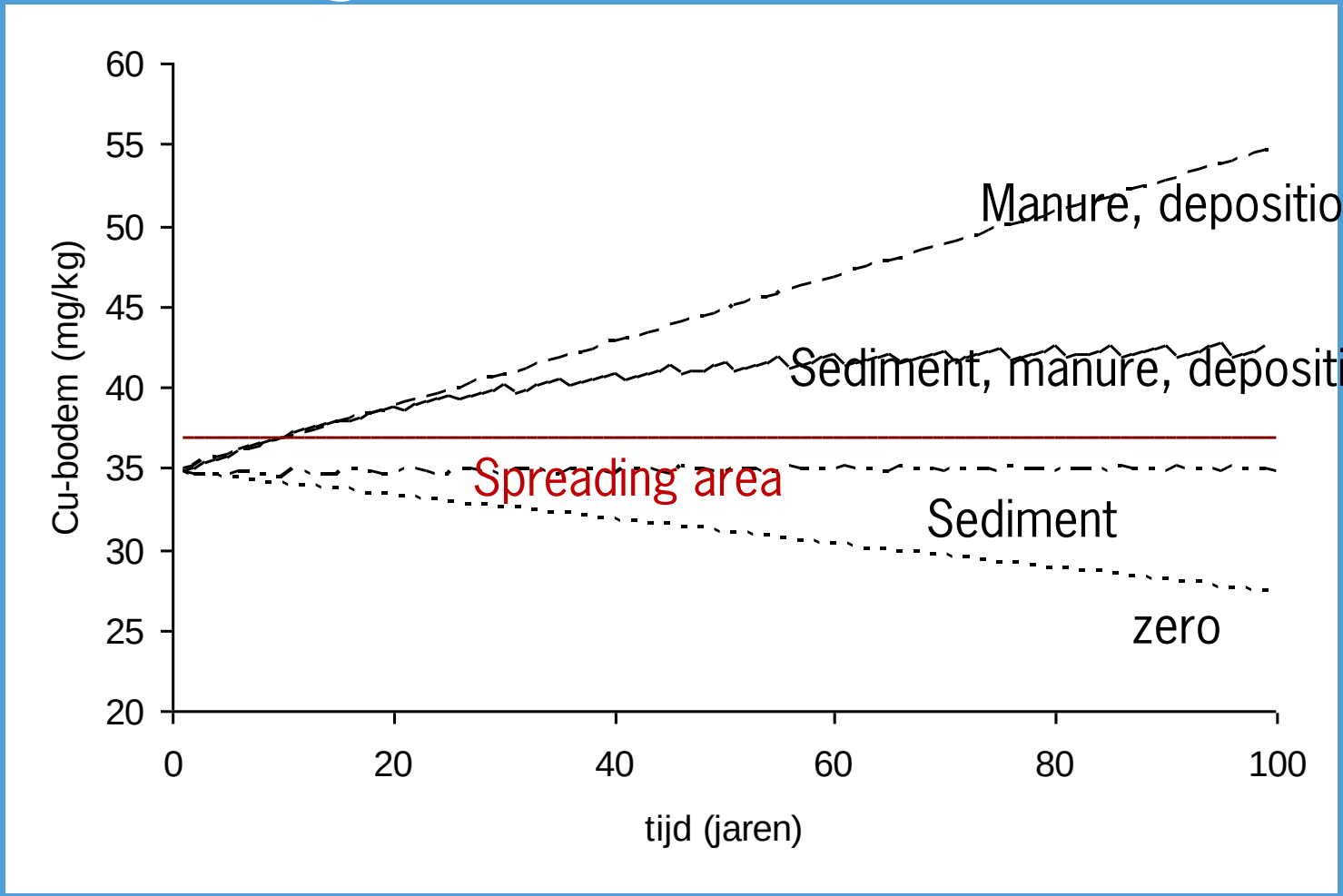
Accumulation

Measurable effect of spreading?

Increase of contaminant concentration after spreading
Decrease (degradation uptake, leaching) in following period

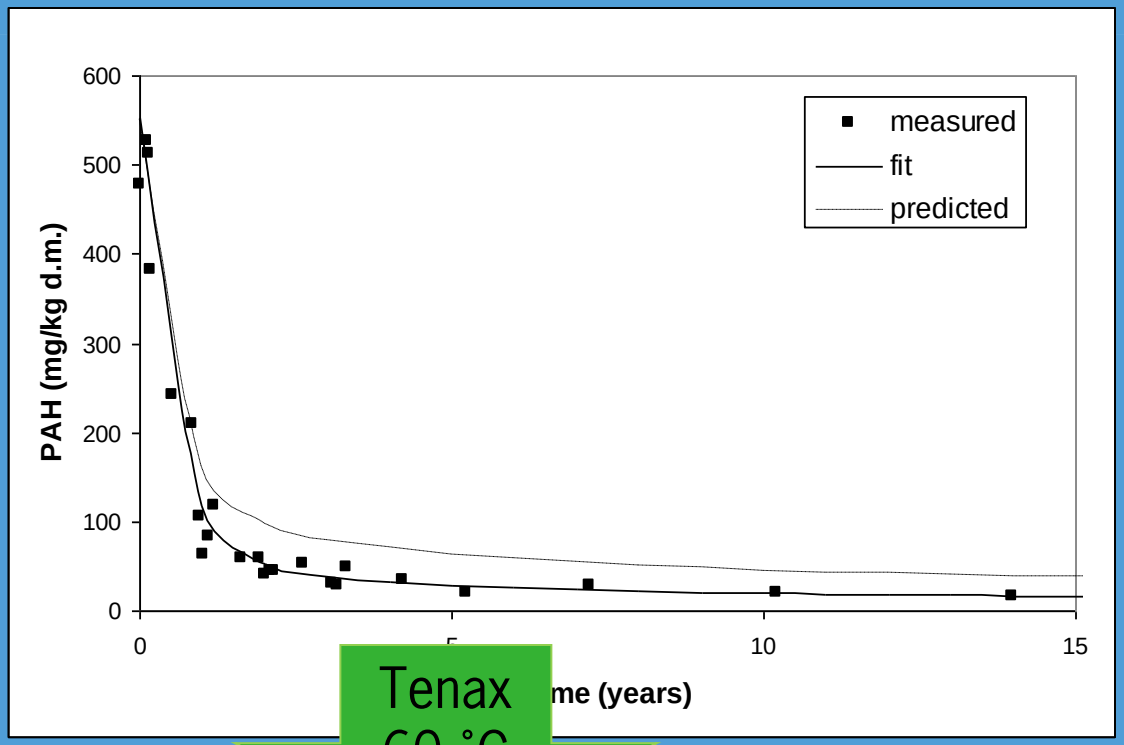


Modelling



Copper Location D2

PAH degradation



Tenax 60 °C

$$\frac{C_t}{C_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\ slow} \cdot e^{-k_{very\ slow} \cdot t}$$

Tenax 20 °C

Half life time very slow degradation = Approx. 25 years

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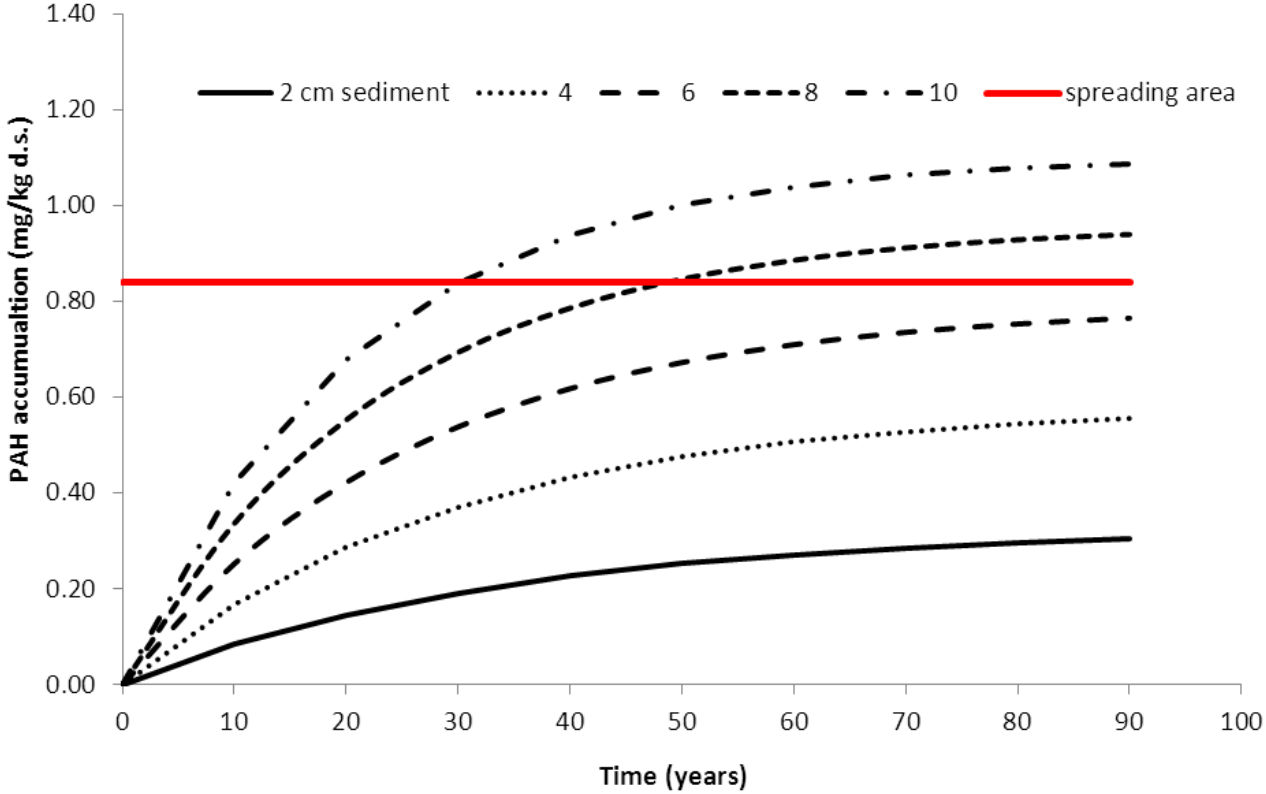
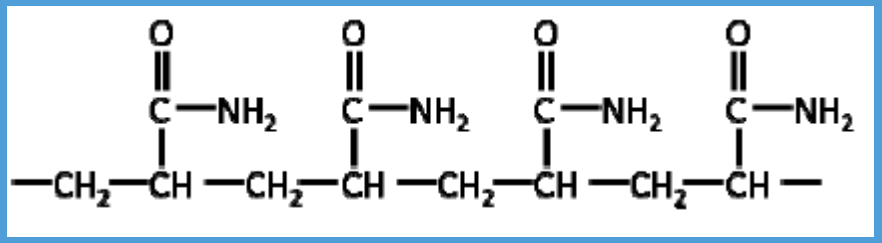
Effect sediment layer on accumulation of PAHs



6-8 cm is realistic

Polyacrylamide



M =1,000,000

- Difficult measurable compound
- In soil not measurable (non detectable)

- Non-extractable (NER)?
  - Non-extractable with organic solvents
  - Extractable with 0.5 M NaOH (Fraunhofer) (together with humic acid = stable component of agricultural soil/German soil)

Use of polyacrylamide

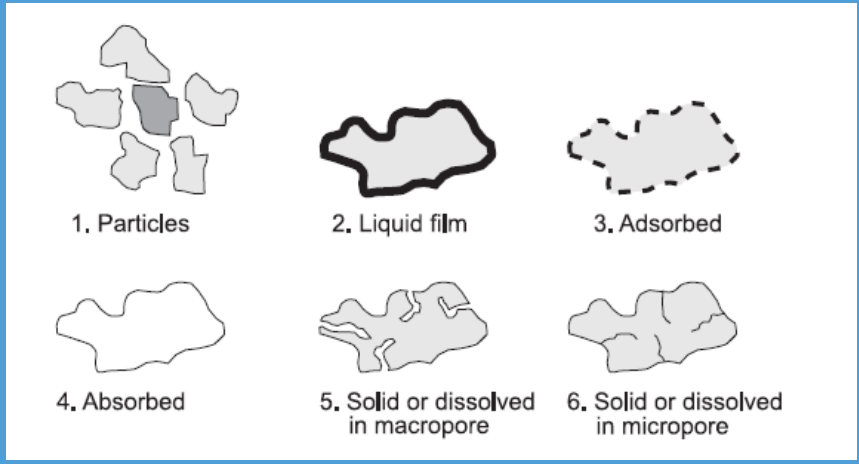
Flocculants, coagulants

Body care, shampoo

Fate in soil

- Associated with particles, organic matter
- Long molecule, polar interaction
- Different interactions, strong binding

- Nothing in water phase
  - No leaching (no risk)



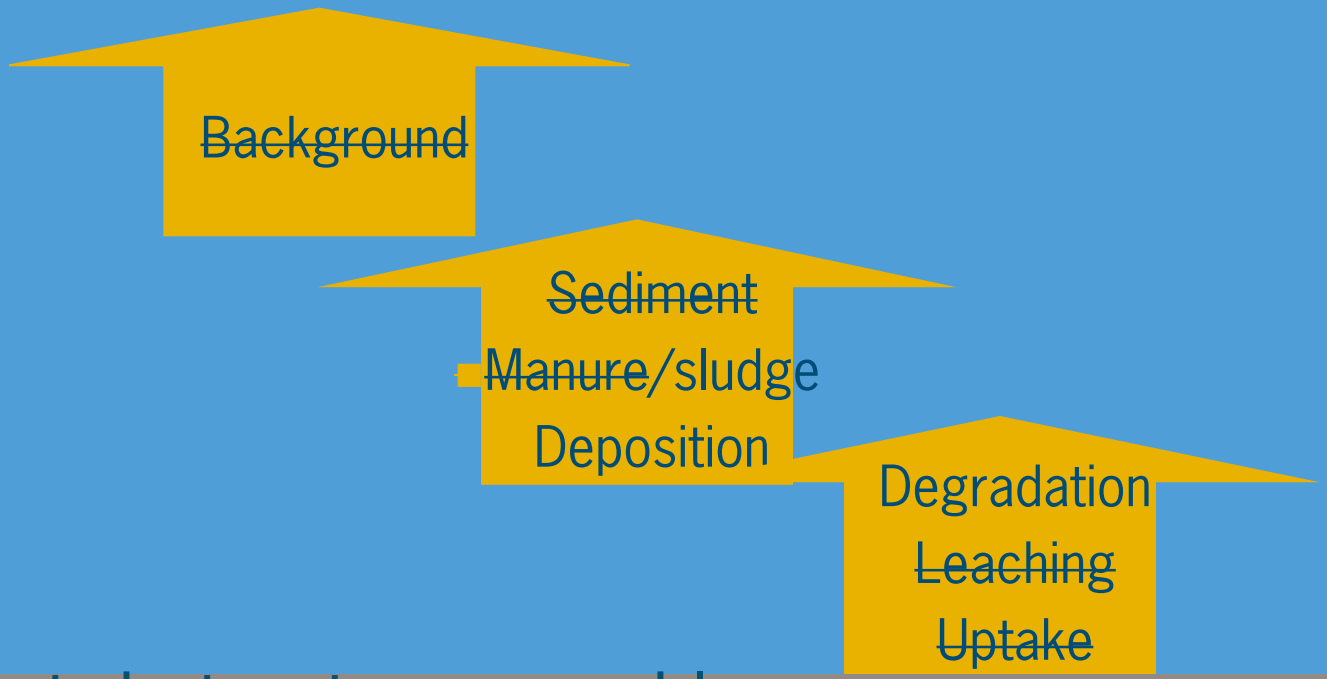
Traces of Acrylamide

- High Solubility
- Low K_{ow}
- High Degradability (Days to weeks)
- Toxicity (high)

- No problem in sludge amended soil
    - If present in sludge, fast degradation

Modelling: accumulation polyacrylamide

Concentration= Present + Supply – reduction



Is present, but not measurable

Accumulation

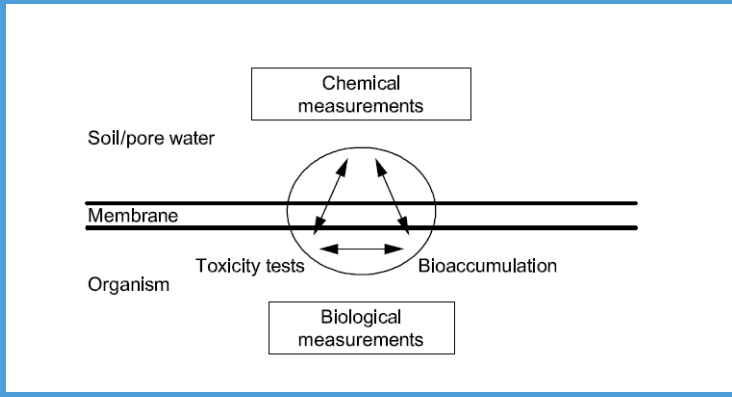
- Degradation: how much wil degrade in about 20 year
  - ^{14}C experiment for a long period
- Equilibrium concentration
  - Amount in sludge added to soil
  - Degradation rate

- No degradation
- Increasing concentration
  - Amount in sludge added to soil

Reliable data to enable decissions

Chemical measurements

- Concentration in soil by calculation
  - Amount used, sludge produced and sludge used
- NER (not measurable)
  - Not available, so not a risk
  - Chemical time bomb,
    - Stable organic matter



Biological measurements

- Set of bioassays
- Measurable, no toxicity measured
- No uptake by vegetation/crops

Knowledge gaps

- Degradation rate (very slow degradation)
  - Biodegradation
  - Chemical oxidation
  - UV degradation
- Degradation under field conditions
- Only possible with ^{14}C

- Toxicity of aged polyacrylamide (acrylamide is degradable in days to weeks)
  - Avoidence test

Risks of polyacrylamide

- If degradation occurs, accumulation in soil can be predicted. Acceptable yes/no
- No leaching
- No toxicity
- Not extractable (no bioavailble fraction)
    - Accumulation is not measurable

- How much of an inert substance is acceptable in soil?
    - Stones, micro-plastics

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