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RESEARCH INSTITUUT VOOR DE GROENE RUIMTE

THEORY AND APPLICATION OF LANDFARMING TO REMEDIATE PAHS AND MINERAL OIL CONTAMINATED SOILS AND SEDIMENTS

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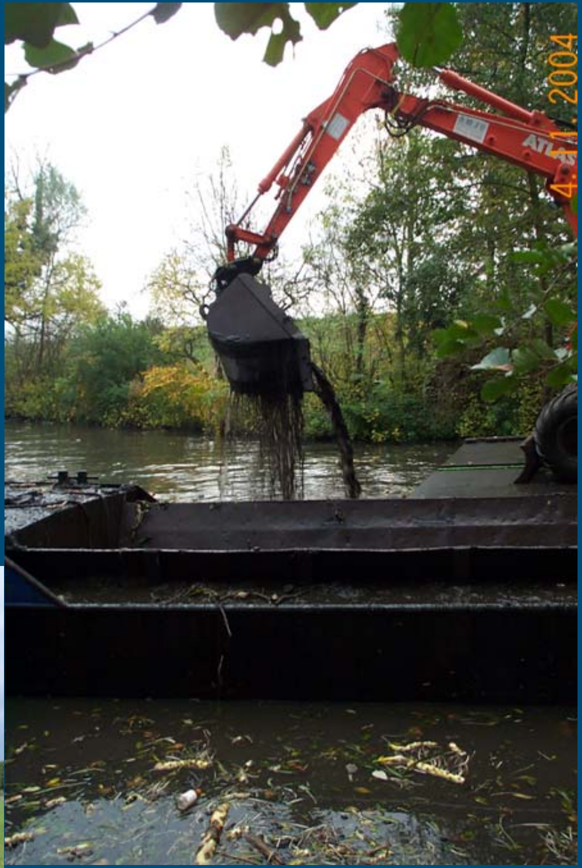
Sediments are not only harbour sediments



Contaminants

- Polycyclic Aromatic Hydrocarbons (PAHs)
  - biodegradable
- Mineral oil
  - biodegradable

Experiment Kreekraksluizen

- 14 years of measurement
- Intensive landfarming (cultivation)
- Passive landfarming (vegetation)

Results landfarm

Sediment	PAHs (mg/kg d.m.)		Mineral oil (mg/kg d.m.)	
	start	2004	start	2004
Petroleum Harbour 1994	550	22	13,500	1300
Wemeldinge 1994	45	25	2000	500
Geul Harbour 1990	52	2	8100	<200
Zierikzee 1990	65	15	630	<200

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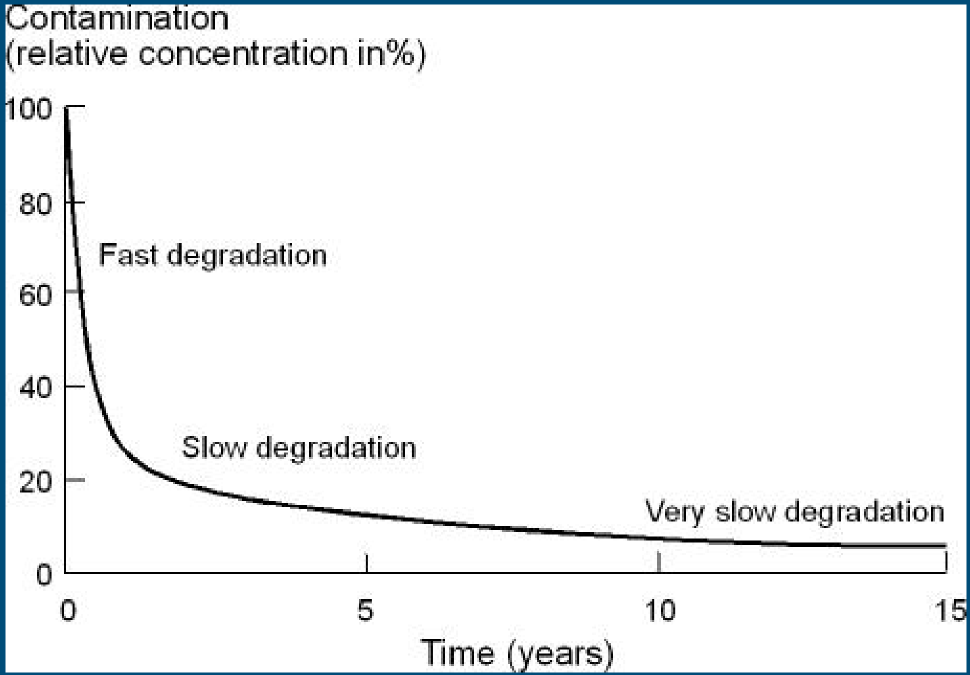
Biological degradation

First step for sediments = dewatering



Three degradable fractions

- fast
- slow
- very slow

- 3 6 rings

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

PAHs distribution

degradation ← fast ↔ slow ↔ very slow

fast = in equilibrium with water phase

slow = diffusion to water phase

very slow = very slow diffusion to water phase

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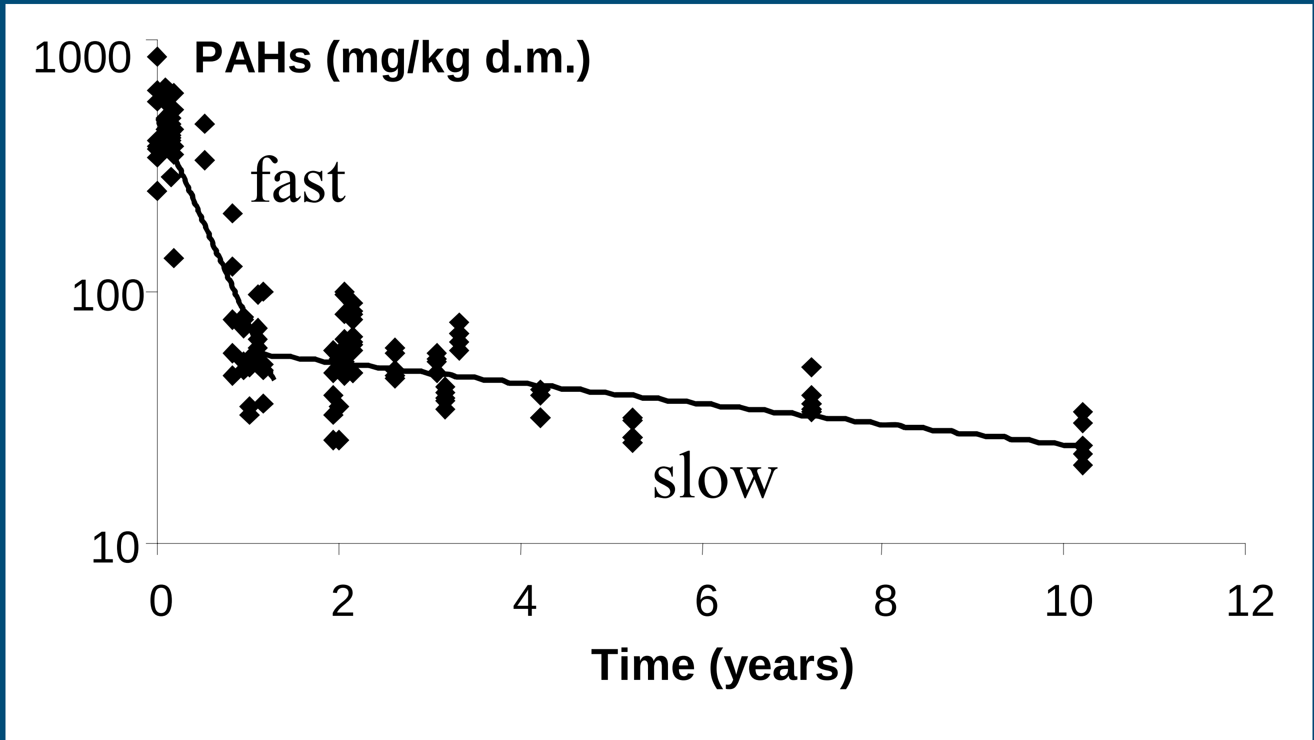
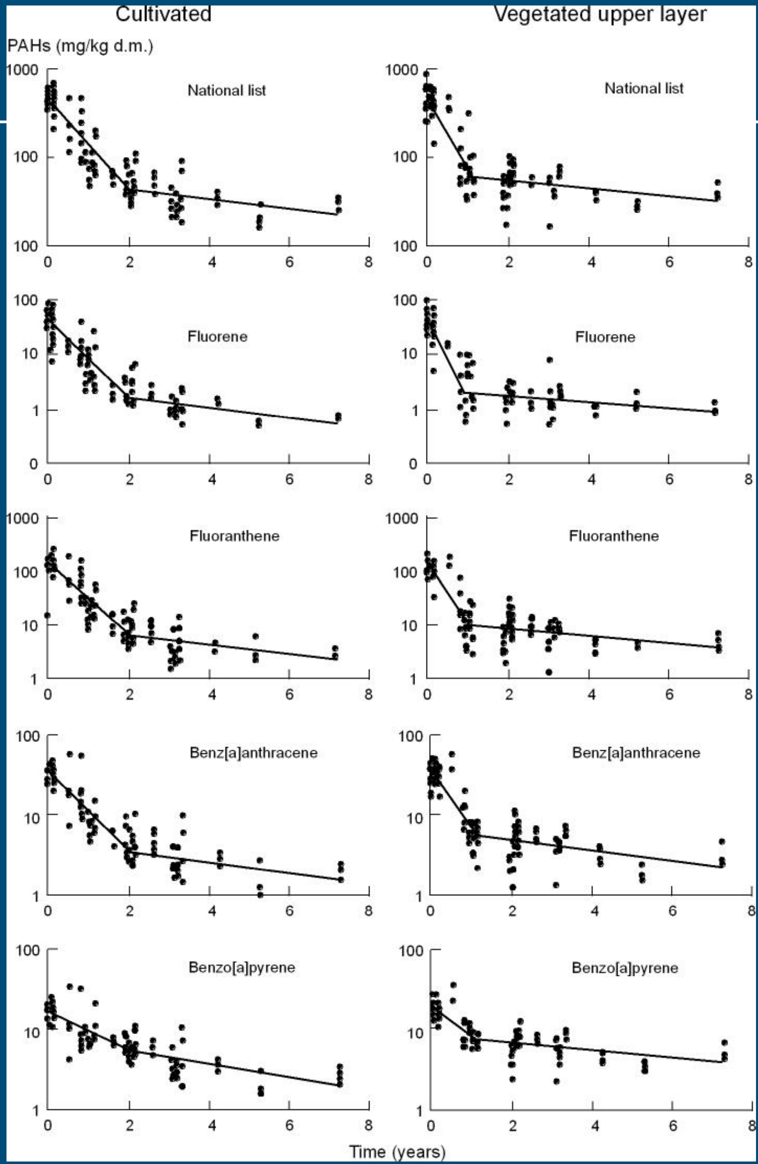
Degradation of PAHs



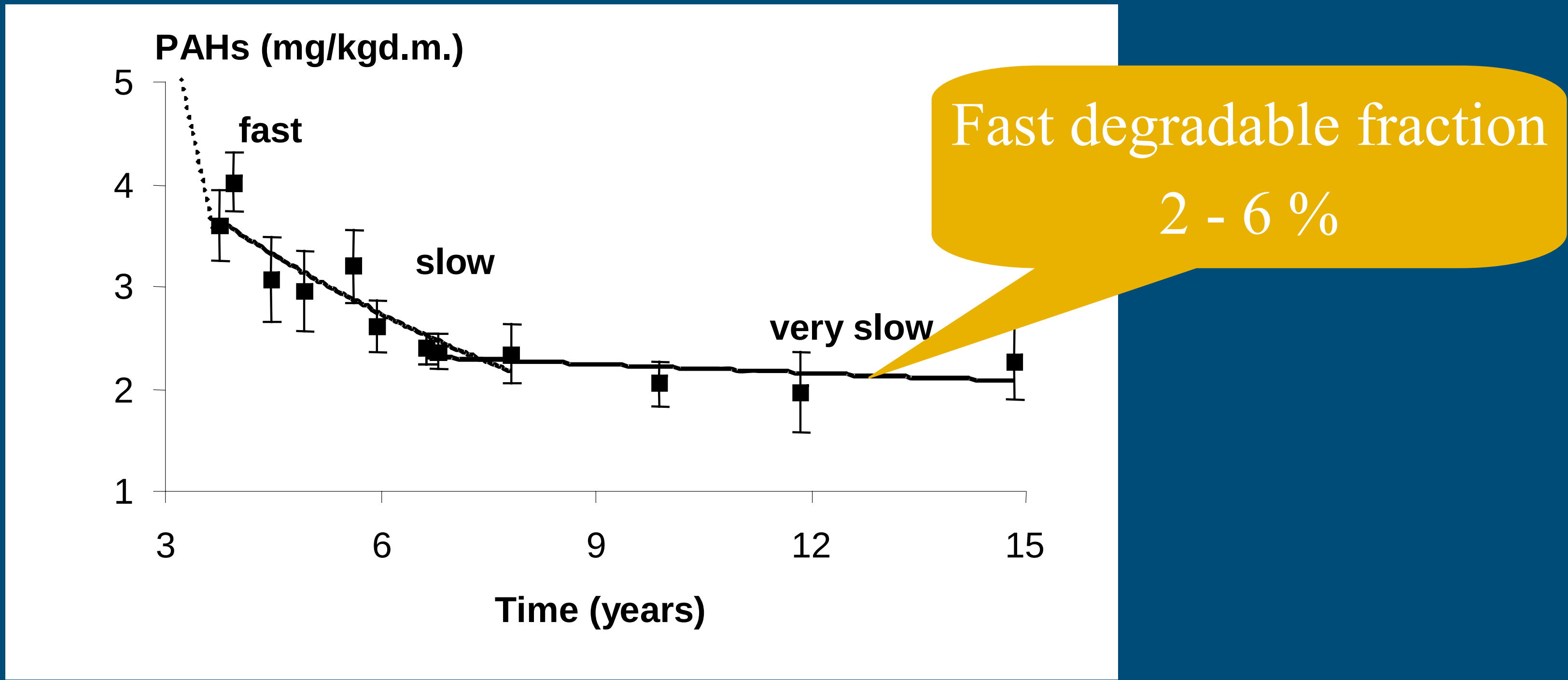
(Dutch National List) in Petroleum Harbour sediment (upper layer of vegetated sediment)

Degradation of PAHs

- Fluorene
- Fluoranthene
- Benz[a]anthracene
- Benzo[a]pyrene

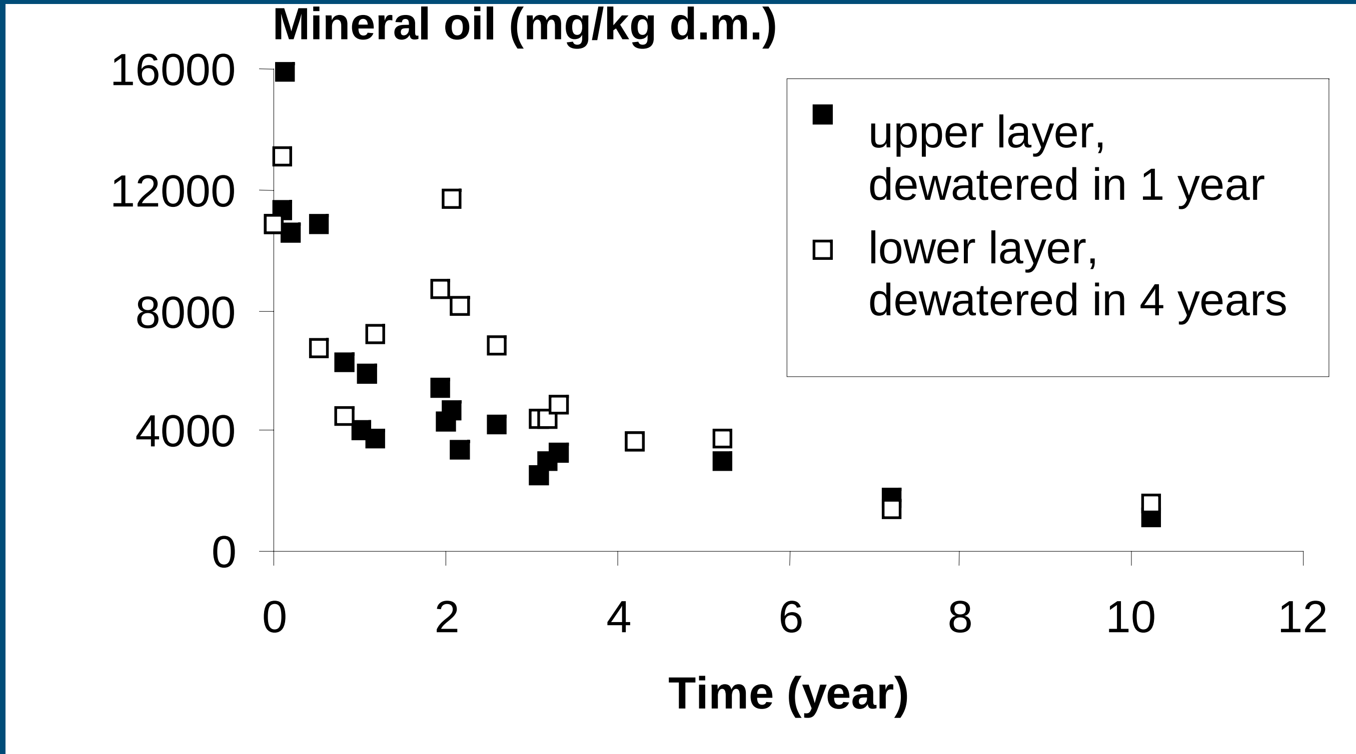


Degradation of PAHs



Geul Harbour sediment. 95% confidence values are given.

Degradation of mineral oil



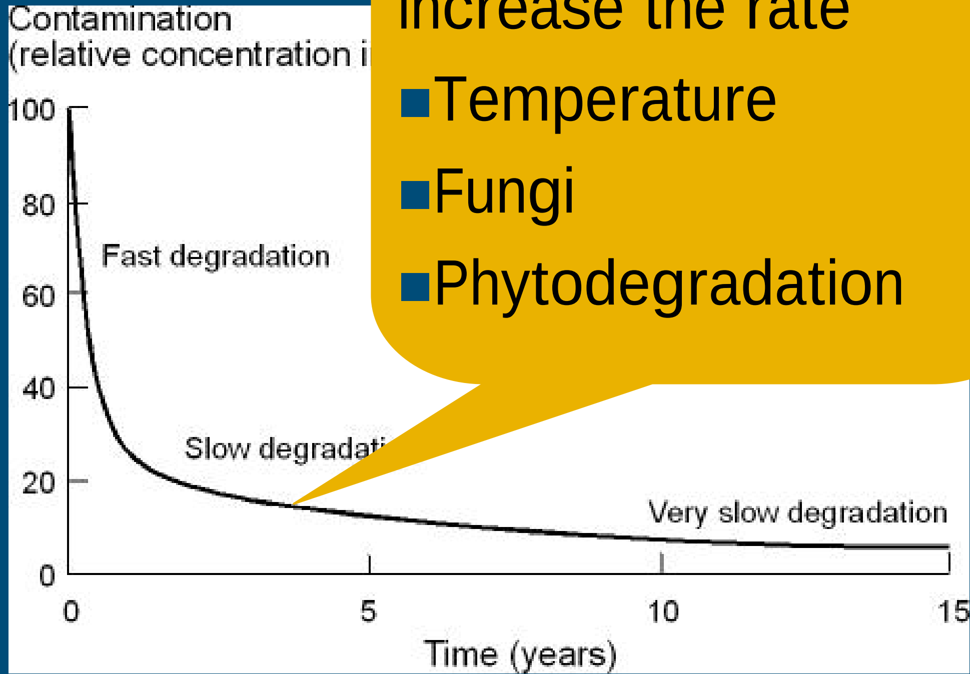
Vegetated Petroleum Harbour landfarm (upper layer and lower layer).

Biological degradation

First step = dewatering

Three degradable fractions

- fast
- slow
- very slow



Not possible to increase the rate

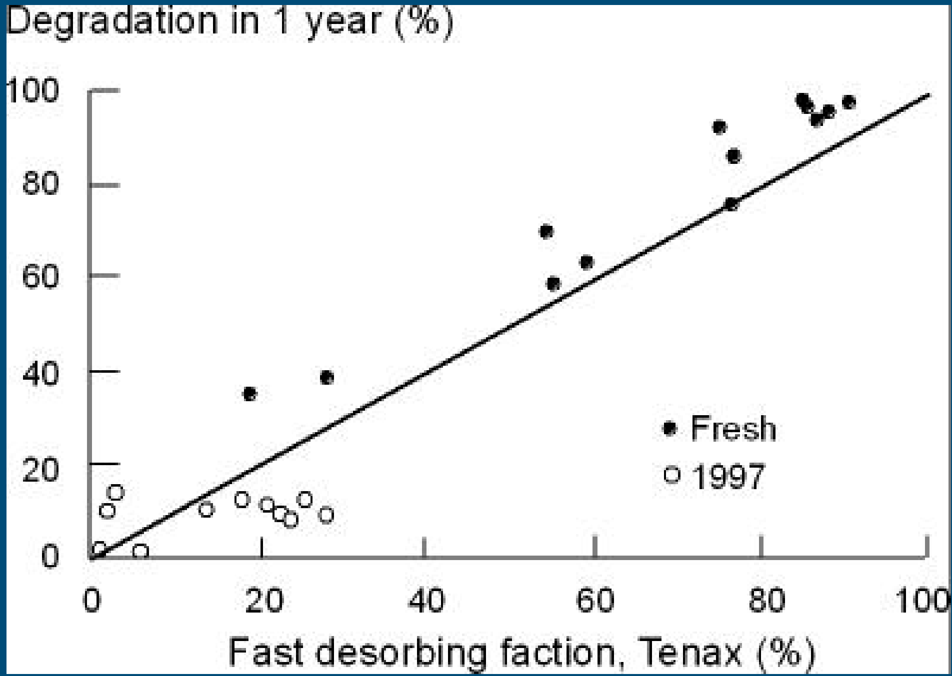
- Temperature
- Fungi
- Phytodegradation

- 3 6 rings

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

Measured availability for predicting degradation

- Prediction of fast degradation = fast available fraction
  - Solid phase (Tenax)
  - Mild extract (Hac)
  - Mild oxidation (Cuypers)
  - XAD (Northcot Jones, Lie)
  - SFE (Hawthorne, Loibner)
  - Dextrine (Reid, Doick)
  - Mild extract (Thiele and Brunner)



Prediction of very slow available fraction is possible

Theoretical considerations

- Pollutants biodegradable at aerobic conditions
  - Passive landfarming
    - Minimal interventions
    - Dewatering for sediments
    - Biodegradation
- Potential limiting factors
  - Availability of appropriate micro organisms No problem
  - Bioavailability of the pollutants to the micro organisms
  - Supply of oxygen for the biodegradation process

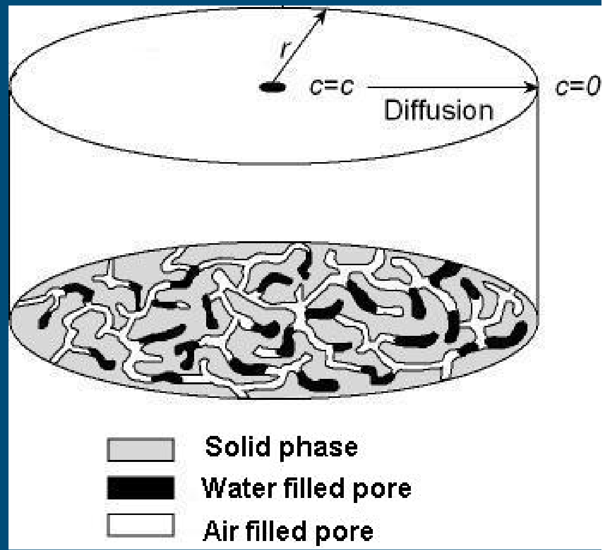
Bioavailability of pollutants: non equilibrium approach

- Mass transfer resistance in the sediment aggregate
- Simplified transport model

$$\frac{dc}{dt} = -kc$$

- *k* = first order kinetic rate constant
- *c* = average contaminant concentration

$$\frac{c_t}{c_0} = e^{-k \cdot t}$$



Rate constant k for spherical particles

$$k = \frac{6\,D_s^w}{[\,\theta + \rho_s\,(1 - \varepsilon)K_d\,]r^2}$$

- θ = internal aggregate moisture content
- ε = volume fraction of total pore space
- r = distance from the surface to the centre
- ρ_s = specific weight of the wet sediment
- D_s^W = average contaminant diffusion coefficient in sediment pore water
- K_d = partition coefficient

$$D_s^w = \eta\,\theta\,D^w$$

- η = tortuosity factor = function of θ
- D_w = diffusion coefficient of contaminant in water

Simplified expression for the rate constant

$$k \sim \frac{\theta^2}{(1-\varepsilon)r^2}$$

- Comparison slurry reactor with fresh sediment and unsaturated landfarm
  - slurry (ε = 0.7, pores 100% filled with water)
  - landfarm (ε = 0.55, pores 20 to 50 % filled with water
  - $r_{slurry} < r_{landfarm}$ Factor 2?

$k_{slurry} / k_{landfarm}$ = 12 76

- Found for slow degradation $k_{slurry\ (tenax)}/k_{landfarm}$ = 49
- To increase rate r < 0.1 1mm

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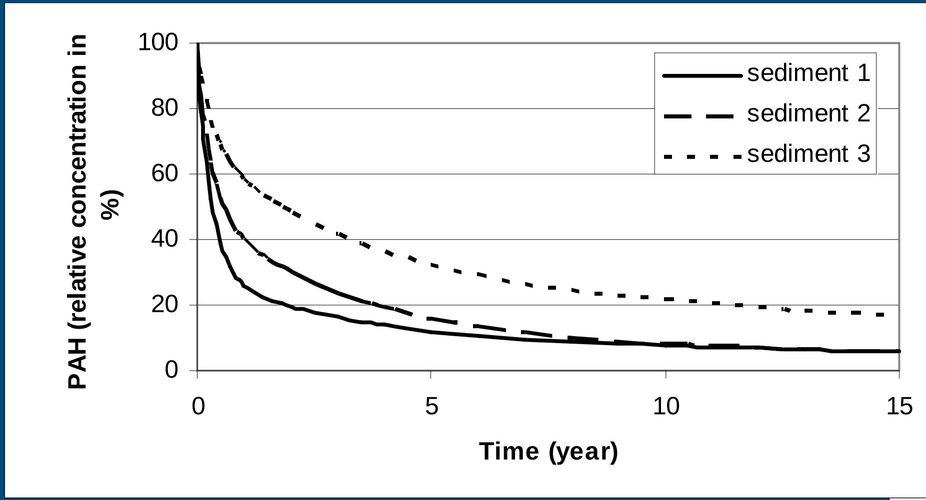
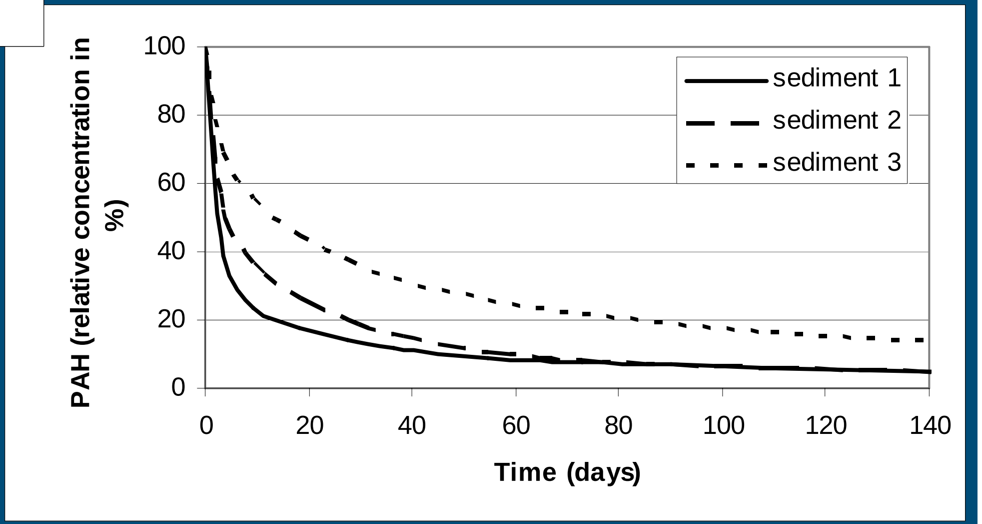
Landfarm versus bioreactor



Landfarm

Available fractions

	fast	slow	very slow
Sed 1	0.7	0.2	0.1
Sed 2	0.5	0.4	0.1
Sed 3	0.3	0.4	0.3



Bioreactor (slurry)

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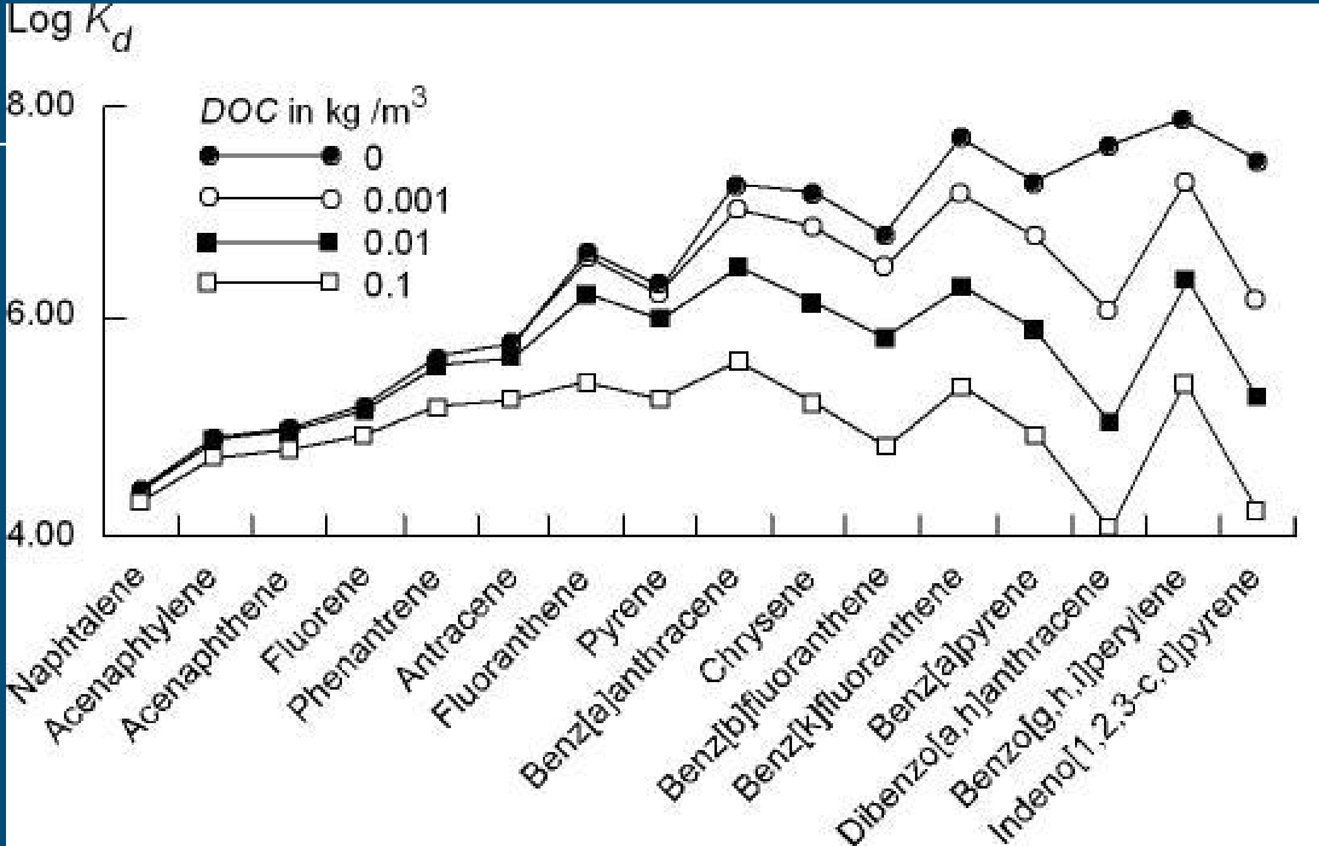
Concentration of pollutants in water phase

- Pollutants in water phase are available for biodegradation
- Partition coefficient between sediment and water phase

$$K_d = \frac{1000 \; fr_{oc} \; K_{oc}}{1 + fr_{DOC} \; K_{oc}^{DOC}}$$

- fr_{oc} = mass fraction of organic carbon in kg/kg
- fr_{DOC} = mass fraction of dissolved organic carbon
- K_{oc} = partition coefficient organic carbon and water
- K_{oc} = partition coefficient between dissolved organic matter and water



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Iudfwlrq#rujdqlf#p dwhu#lq#wkh#vhglp hqw#dp rxqw#wr#
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$$k = \frac{6 D_s^w}{[\theta + \rho_s (1 - \varepsilon) K_d] r^2}$$

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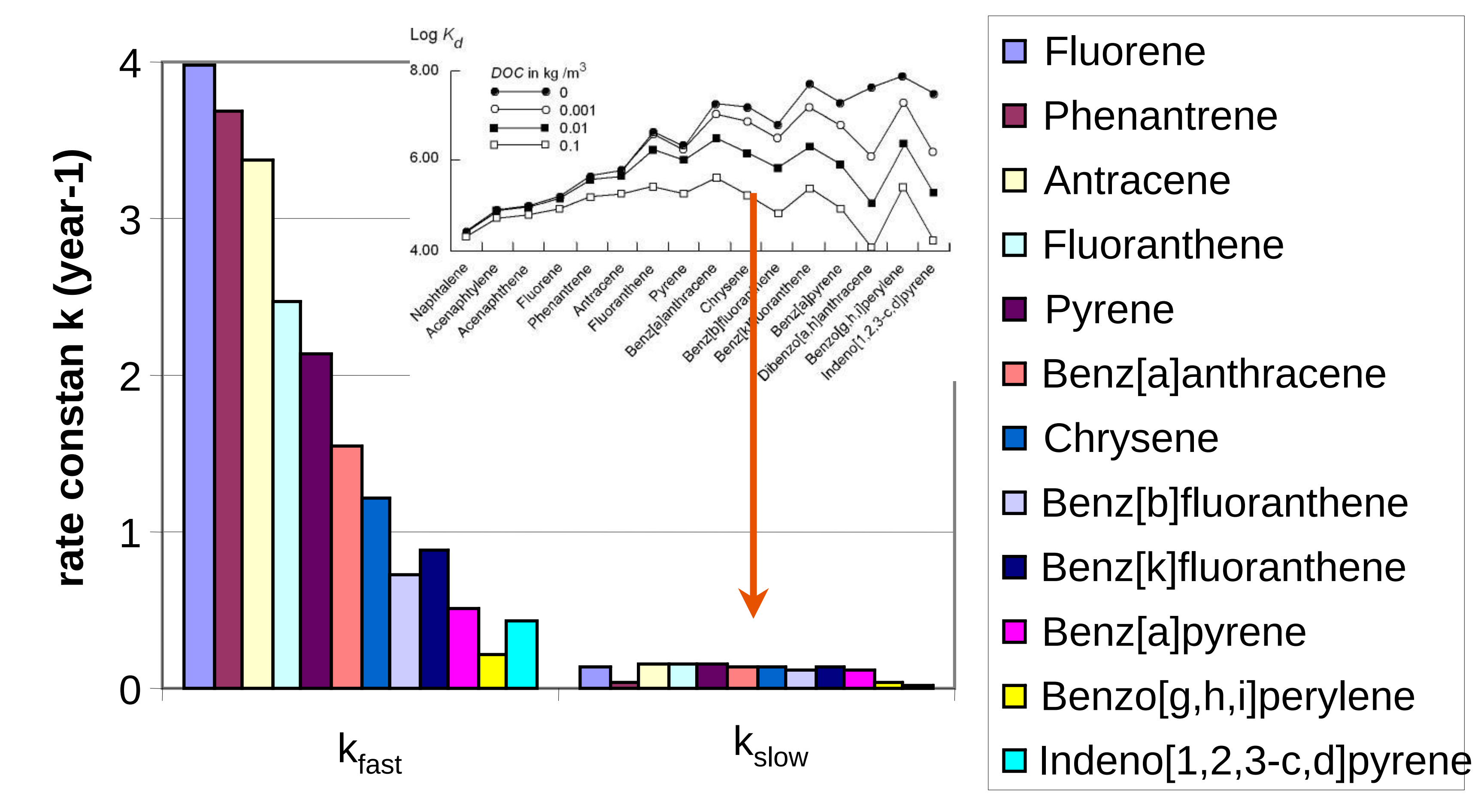
Degradation coefficients



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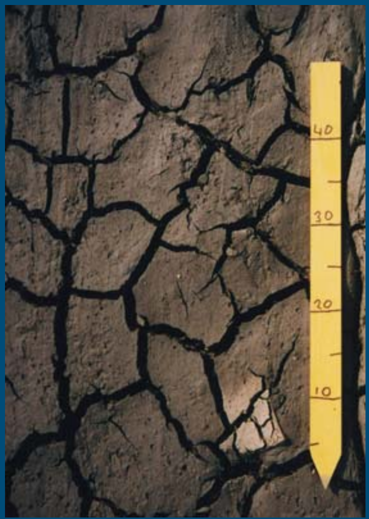
Oxygen transport

- Landfarm of sediment: dewatering and ripening
  - Compaction of the sediment layer,
  - Development of cracks between aggregates,
  - Aeration of smaller aggregates,
  - Finally a soil with vegetation.

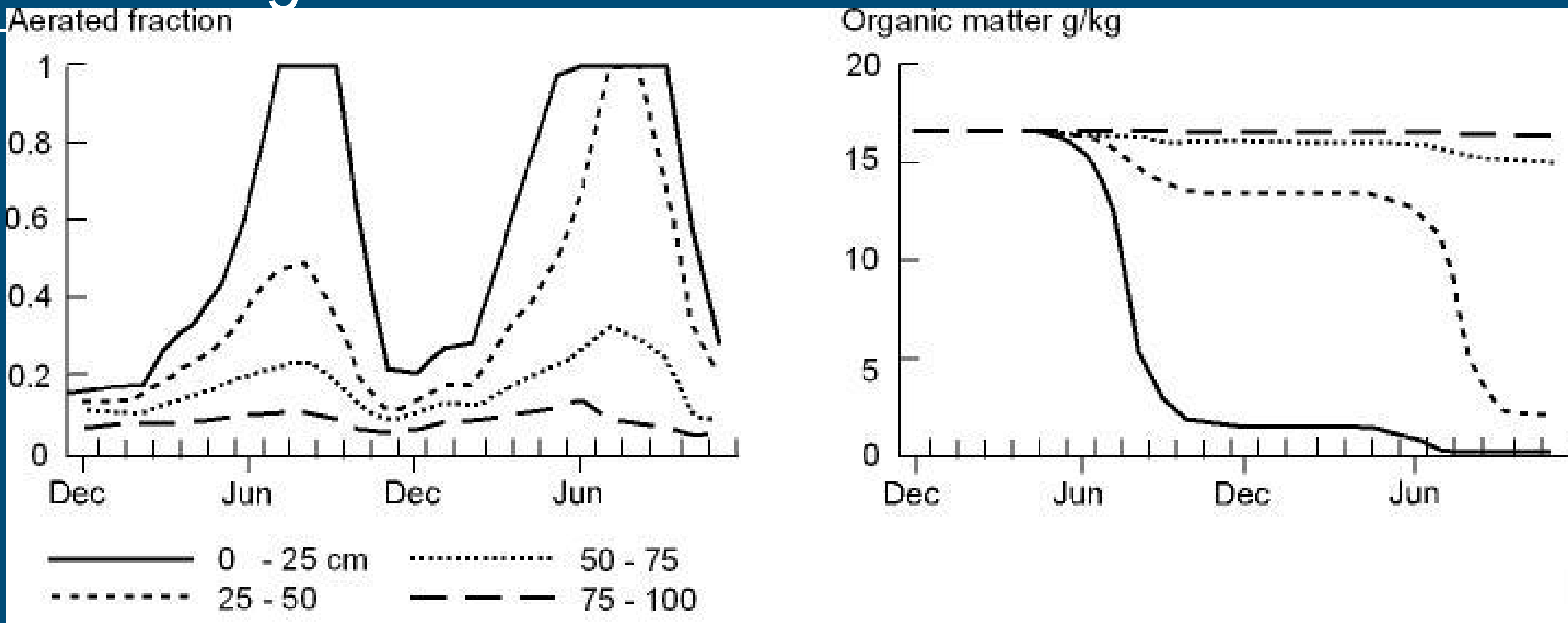


Modelling of aeration in a landfarm

Relevant physical and microbiological processes and parameters

- Formation of cracks and aeration through cracks as a result of shrinking
- Sediment moisture profile as a function of relevant properties of the sediment, presence of vegetation and period of the year
- Size of aggregates as a function of moisture potential
- Oxygen consumption due to degradation of organic matter (fast, slow and very slow degradable fractions)
- Oxygen diffusion in aggregates
- Variation of temperature during the year
- Dependency of the activity of micro organisms on temperature

Modelling: reference situation

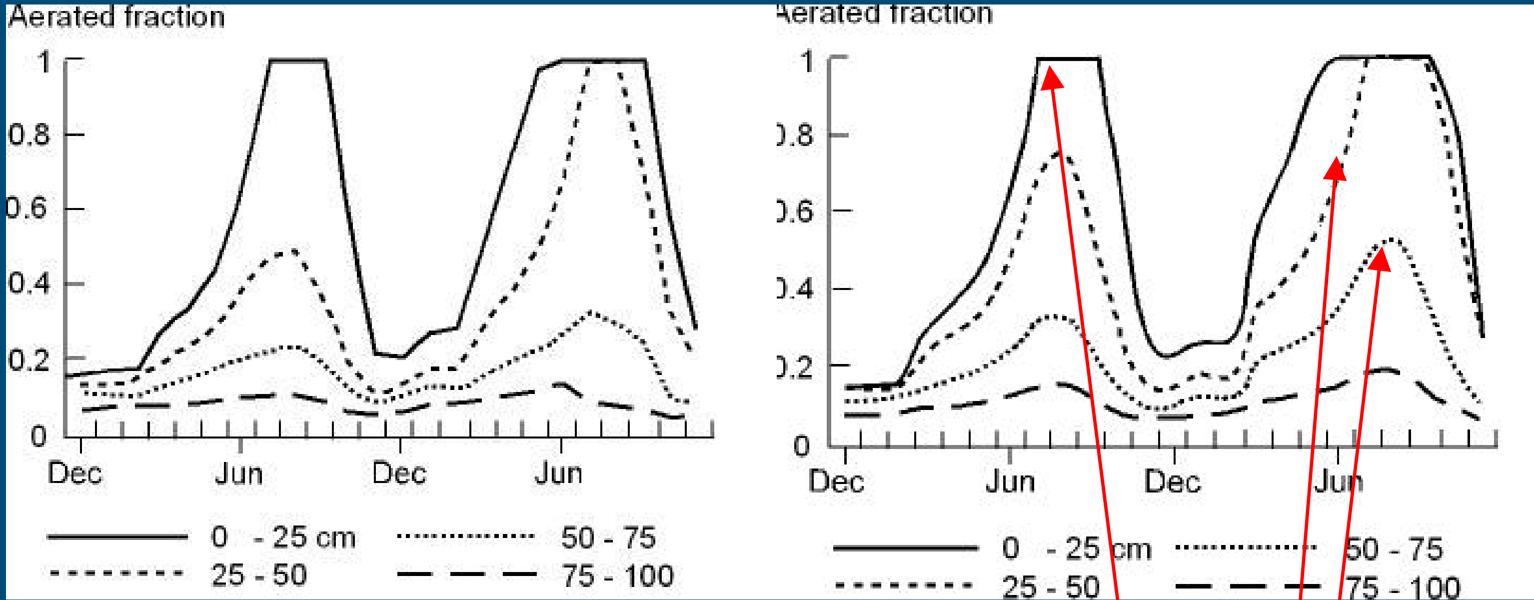


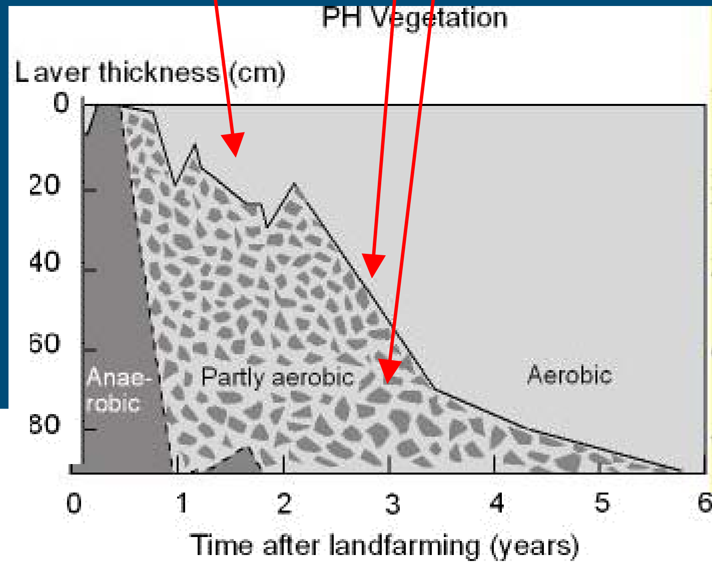
Aeration and degradation of fast degradable organic matter using the landfarm aeration model (reference situation: no cultivation and vegetation in the second year)

Modelling: root depth

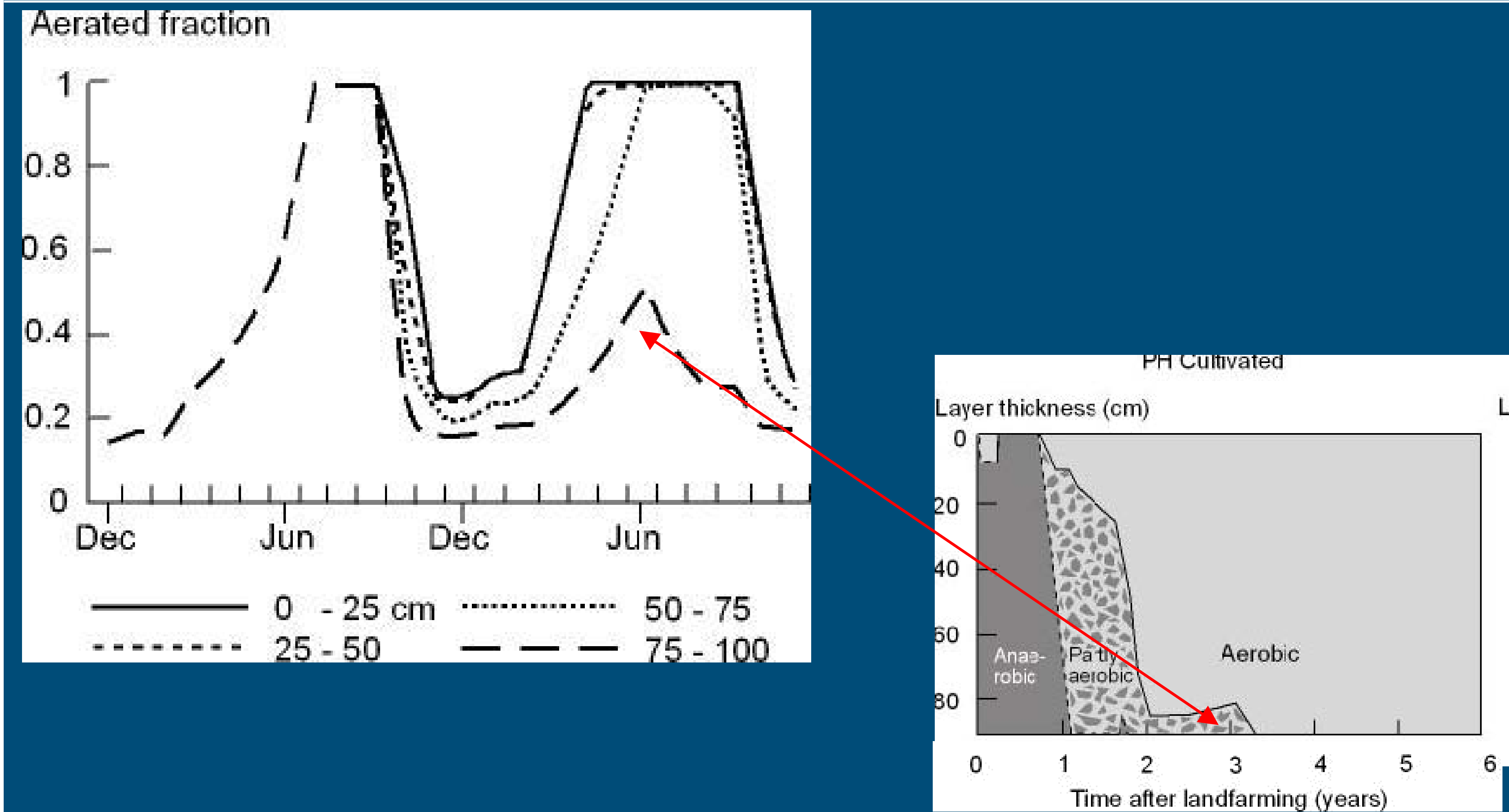
25 cm

50 cm





Modelling: Intensivation in the second year



Results landfarm aeration model

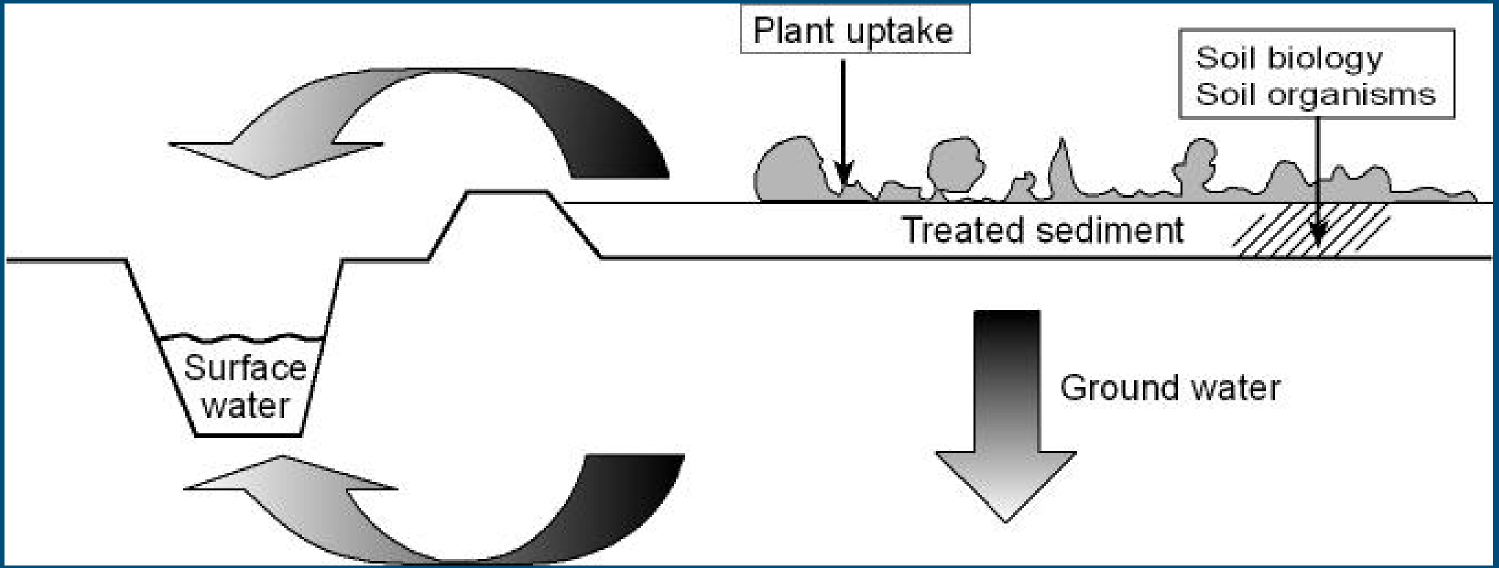
- Amount ‘Soft’ Organic matter responsible for oxygen consumption
- Increase of temperature during dewatering not effective (Too high oxygen consumption)
- Vegetation effective (Higher air filled pore volume at rooted depth)

Role of vegetation (phytoremediation)

- Dewatering rate (root depth)
- Improvement of structure (aeration)
- Size of aggregate ?

- Phytoextraction
  - Not for PAHs and Oil
  - Only possible at low K_{oc} values (not present in sediment)

Risks on a landfarm



- Retention function
  - Ability to adsorb pollutants to prevent mobilization and translocation in the food chain
- Habitat function
  - Ability to serve as a habitat for soil living organisms and plants and their interaction

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Retention Function

- Water dwelling organisms
  - *Vibrio Fisheri* (Microtox)
  - *Daphnia Magna*

- Large effects in original sediment
- No effects after degradation of the fast available fraction

- Leaching tests

No measurable leaching

High fast available fraction = risk for retention function

Habitat Function

- Sediment assays
  - *Crassostrea gigas*
  - *Columphium volator*
  - *Chronomus riparius*
- Soil assays
  - *Lumbricus rubellus*
  - *Folsomia candidal*
- Bioaccumulation
  - *Oligochates*
- Biodegradation

- Biological development
  - biomass
  - incorporation of ^{3}H Thymidine and ^{14}C Leucine
  - Genetic diversity
  - Population of nematodes

Habitat function

- Slower decrease of risks
- Risks are related with fast degradable fraction
- Fast degradable fraction is degraded, but the slow degradable fraction gives a new fast degradable fraction
- No measurable risks if this fraction is small

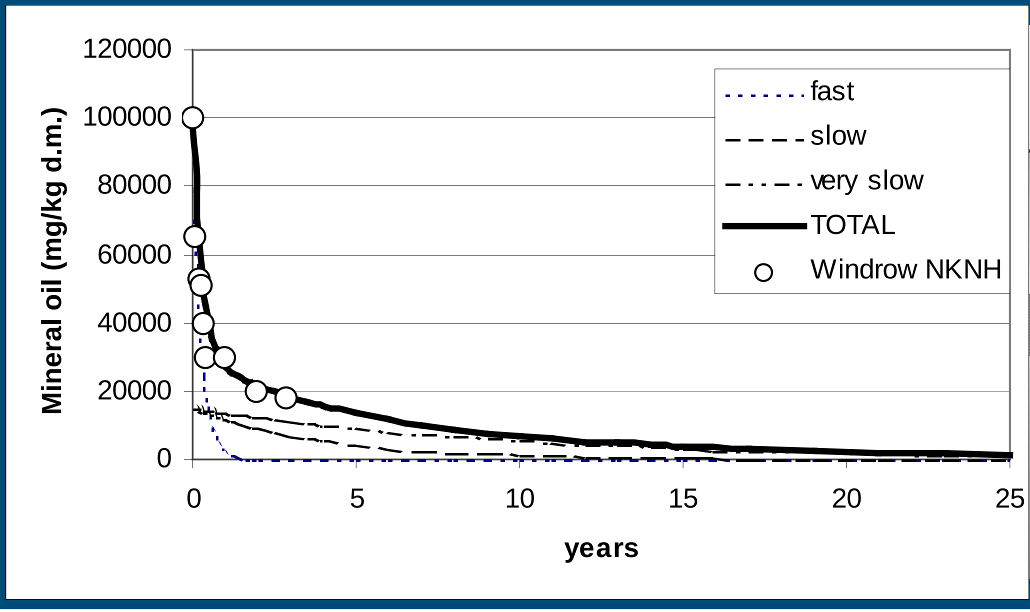
- After >5 years risks are low

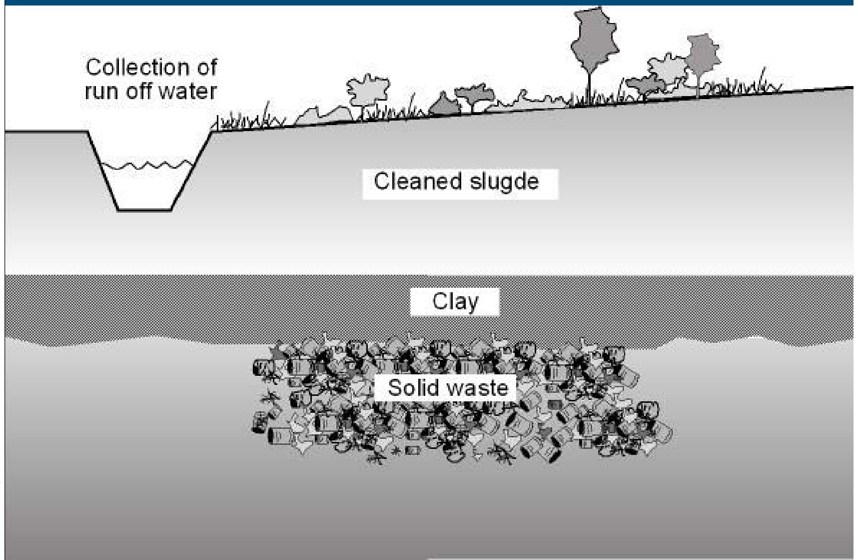
Reuse contaminated soils and sediments

Biomass production

- Oostwaardhoeve , The Netherlands
- 100 ha (1 million m^3).
- 20 Euro/m^3 – profit biomass

Contaminated sludge in Nizhnekamsk





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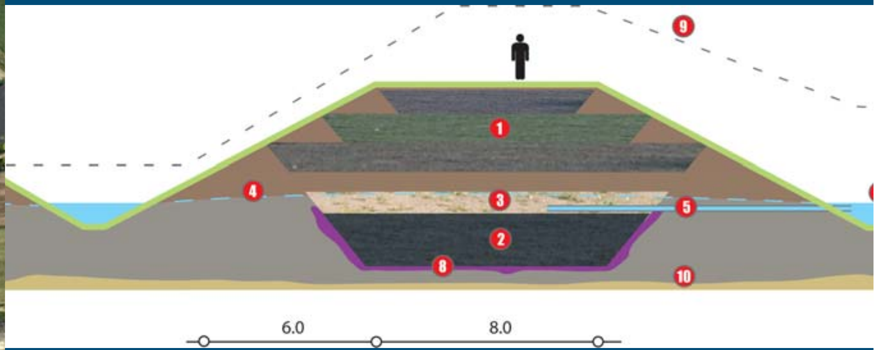
Watervast, sediments and safety (Competition)



- Area Overbetuwe, The Netherlands
- 162 km dikes = 6.5 million m^3
- Costs project 65 million Euro
- Costs for contamination 2 3 Euro/m^3

What about heavy metals?

Biodegradation and phytostabilization/extraction

Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments

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