Allen & Walker (1987)

Limited penetration depth in soil system with Freundlich sorption and first-order degradation

Jos Boesten

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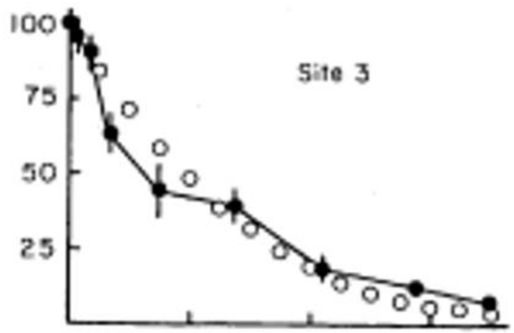
Allen & Walker (1987)

- 18 UK agricultural soils from top 10 cm
  - 14 clay loams or clays
    - limited range of textures considering other EU countries
  - organic carbon range: 0.7-2.4%
- laboratory studies with three herbicides on
  - *DegT50* at 20°C and pF = 2.5
  - Freundlich isotherm: K_F and N
- first such data set including N
- their aim: predict *DegT50* from soil properties
  - more than decade before spatially distributed modelling became popular
    - so far ahead of their time
  - prediction appeared to be difficult

Allen & Walker (1987)

Why favorite data set over 30 years ?

- Ph D supervisor Allan Walker guarantee for high-quality degradation rate measurements
  - some ***75*** field tests of Walker persistence models between 1973 and 1987
  - long, long before validation terminology and good-modelling practice guidance was developed



time

- literature information on variation in substance properties: variation also due to different methodologies
  - which part real and which part caused by scientists ?
  - Wauchope 2002 review sorption: max K_{oc} / min K_{oc} = 100 ?
  - this paper: 'true variability'

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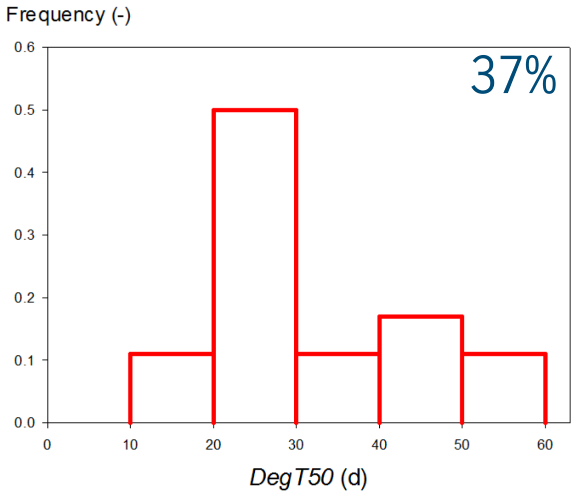
Allen & Walker (1987)

My use of the data set:

- underpinning CVs of K_{oc} and *DegT50* for spatially-distributed exposure assessments at EU level
  - observed variability minimum level for zonal or EU level
- explore causes of variation in K_{oc} and *DegT50*
- Freundlich exponent *N* (pesticide property in EU guidance)
  - variability between soils
  - testing to which extent *N* is soil or pesticide property

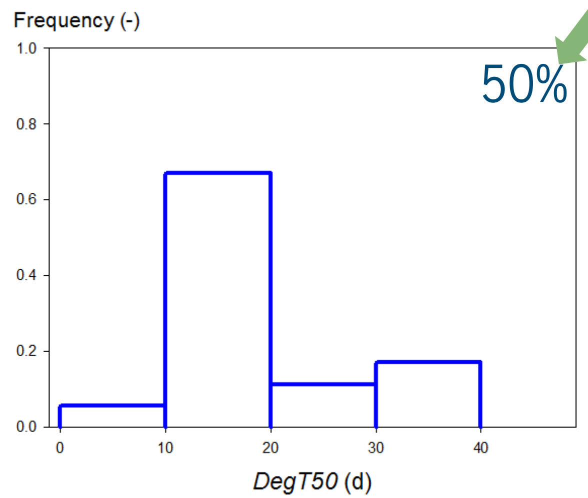
Allen & Walker (1987)

metamitron



metazachlor

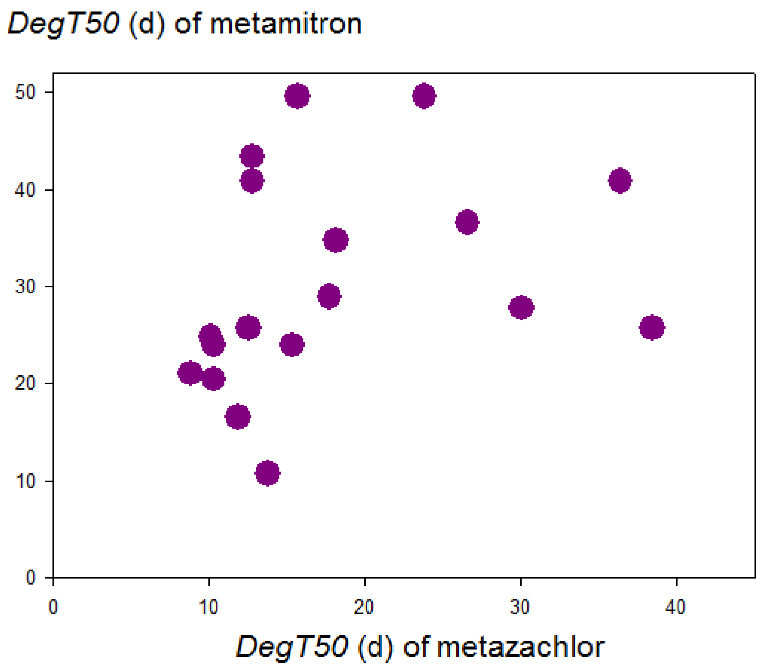
CV

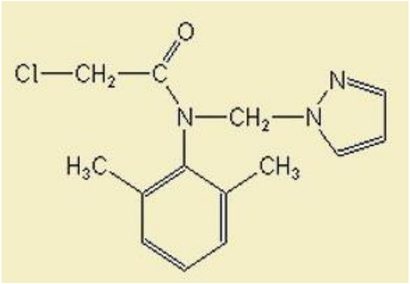


Variability in degradation half-lives

EFSA guidance assumes lognormal distribution with CV of about 50%

Allen & Walker (1987)





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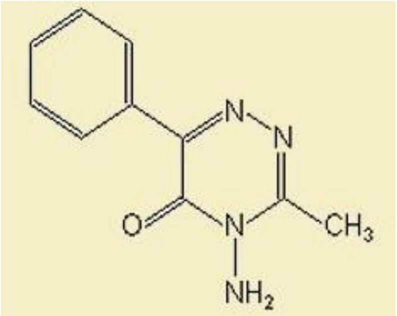
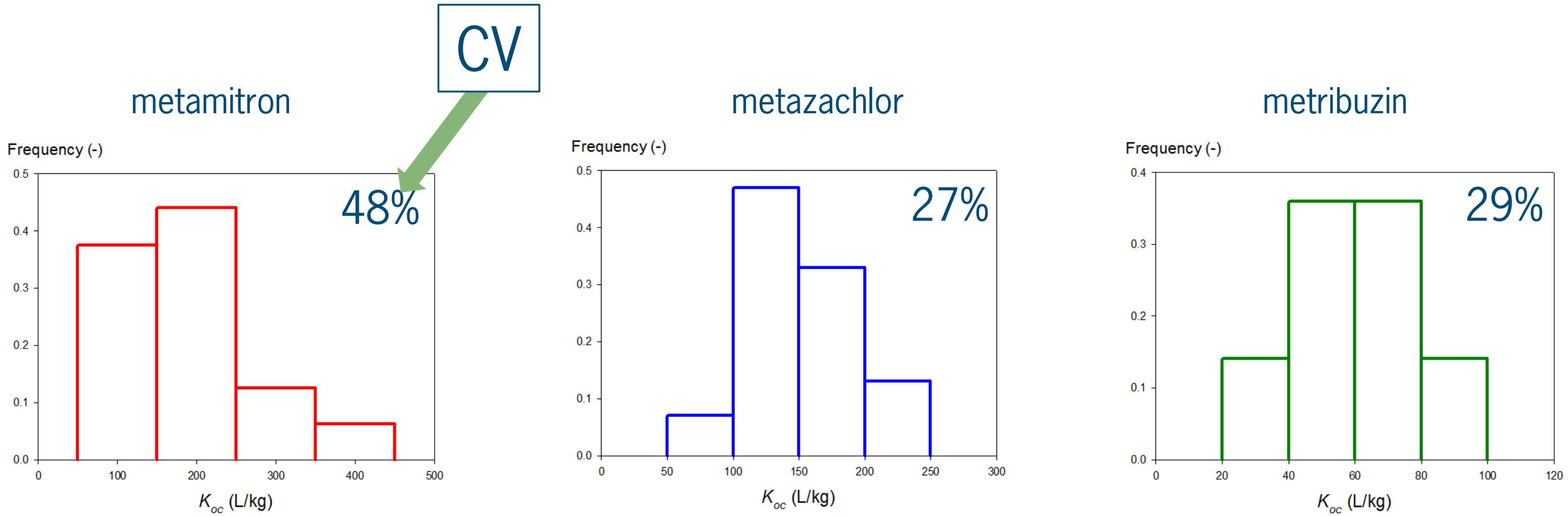


metamitron

correlation coefficient 0.30 : not significant

so spatially-distributed predictions of *DegT50* difficult

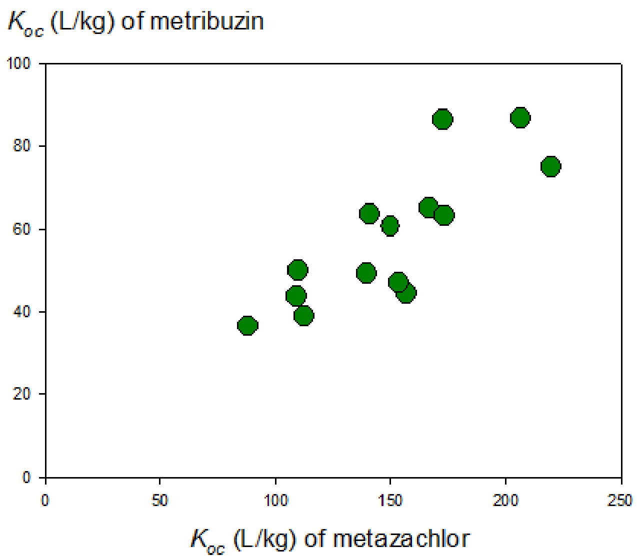
Allen & Walker (1987)



Variability of K_{oc}

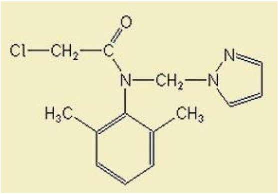
EFSA guidance assumes lognormal distribution with CV of about 50%

Allen & Walker (1987)

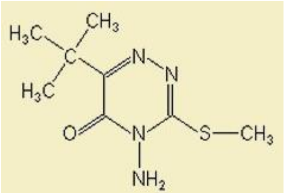


strong correlation (0.82)

metazachlor



metribuzin



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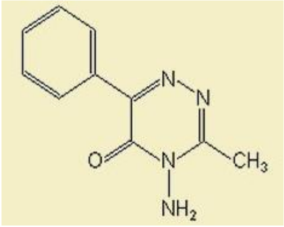
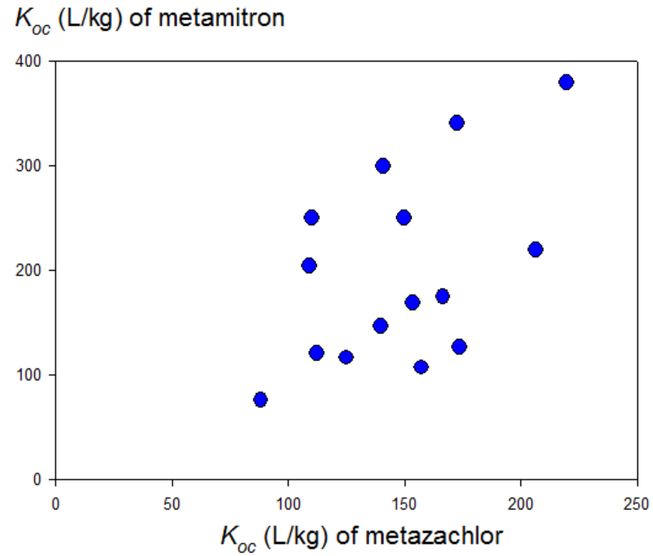


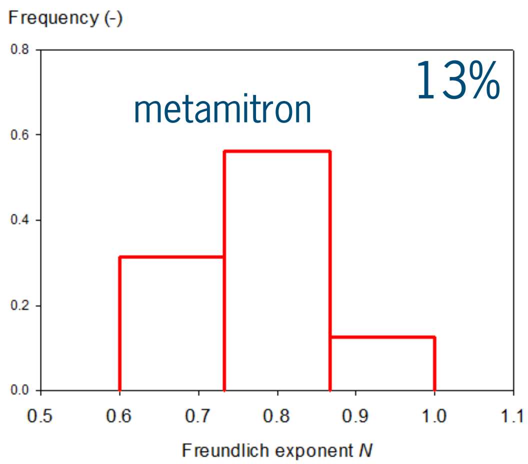


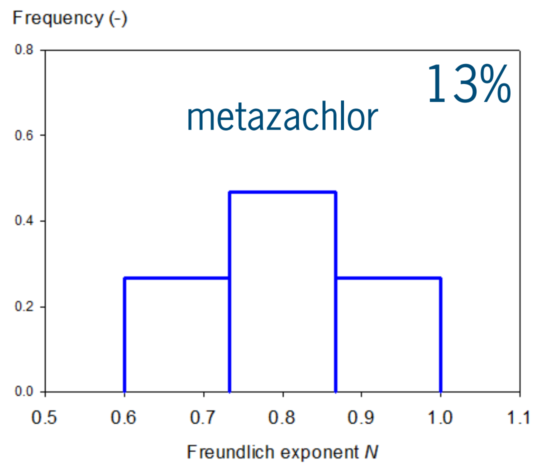
weak correlation (0.52)

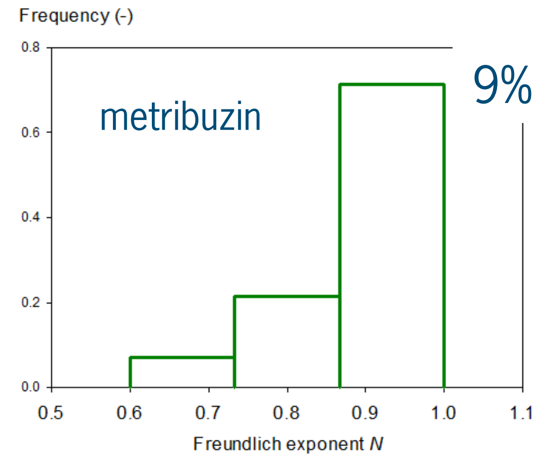
K_{oc} values correlated ?

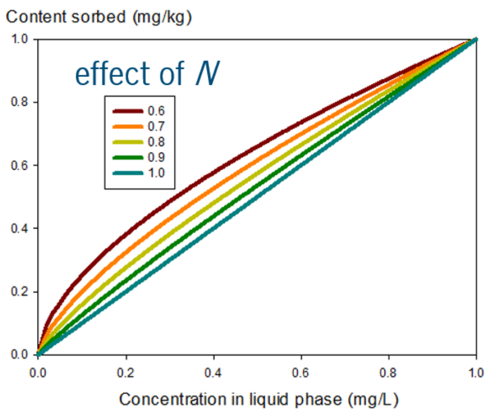
(then probably similar sorption sites)

Allen & Walker (1987)









Variability in Freundlich exponent

wide range for all three

metribuzin lower than other two

CV of three pesticides and single soil on average 12%

further statistical analysis needed to test hypothesis whether *N* is soil or pesticide property

Allen & Walker (1987)

- dataset very valuable for scientists interested in
  - pesticide degradation and sorption processes
  - spatially-distributed modelling of pesticide exposure

- my talk: effect of interaction between non-linear sorption and degradation on leaching behaviour
  - Allen & Walker one of most valuable sources for magnitude of non-linearity (*N*)

Outline

Limited penetration depth in soil system with Freundlich sorption and first-order degradation

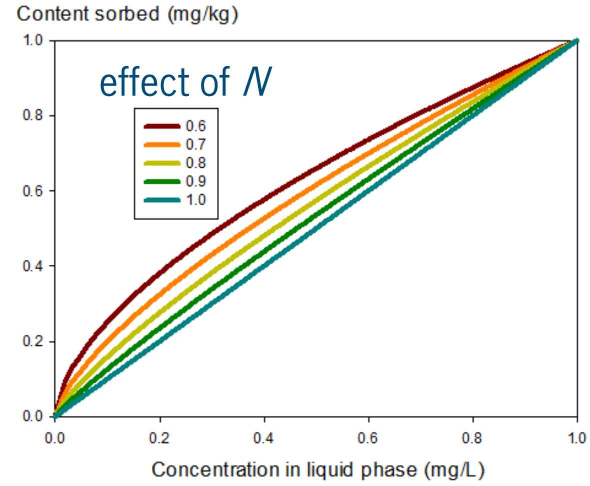
- Introduction
- Behaviour of closed Freundlich-SFO system
- Leaching in uniform soil system
- Evidence for Freundlich-SFO behaviour
- Conclusions

Introduction

- models for FOCUS groundwater scenarios all based on Freundlich isotherm and first-order degradation of total pesticide concentration in soil system, further called Freundlich-SFO system (Single First Order)
  - PELMO
  - PEARL
  - PRZM
  - MACRO

- Freundlich-SFO approach is a cornerstone of EU leaching assessment since 2000

Introduction



Freundlich-SFO system

- Freundlich sorption isotherm

$$X = K_F \; c_{ref} \left(\frac{c}{c_{ref}} \right)^N$$

X	content sorbed (mg/kg)
K_F	Freundlich sorption coefficient (L/kg)
N	Freundlich exponent (-)
c	concentration in liquid phase (mg/L)
c_{ref}	reference value of c (mg/L)

- SFO = single first-order kinetics

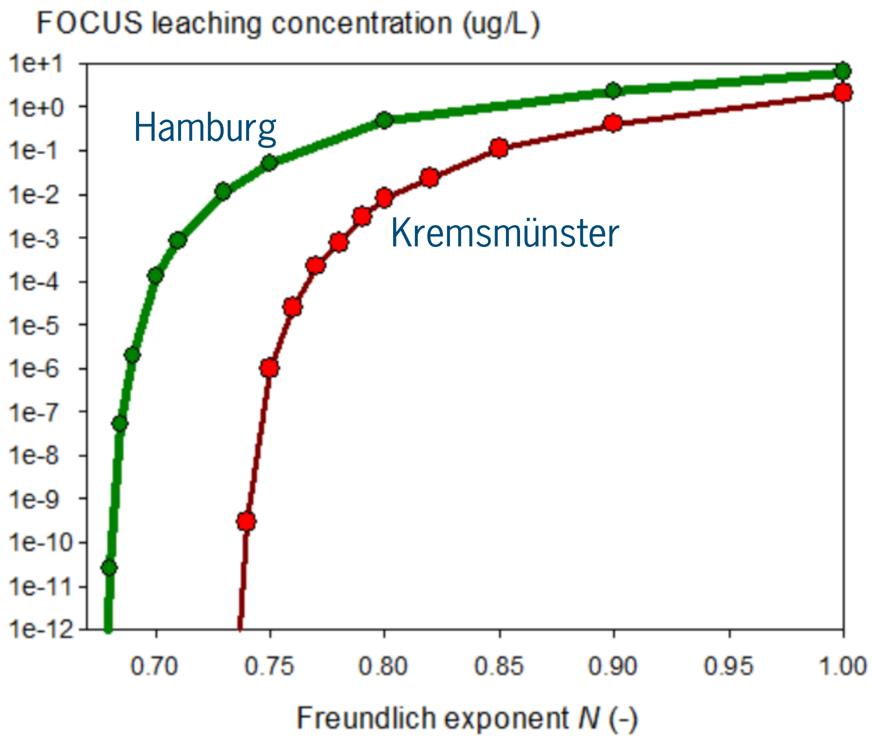
$$c^* = \theta \; c + \rho X$$

c^*	concentration in soil system (mg/L)
θ	volume fraction of water (-)
ρ	dry bulk density (kg/L)

$$\frac{d\,c^*}{d\,t} = -k\,c^*$$

t	time (d)
k	first-order rate coefficient (1/d)

Introduction



- FOCUS leaching concentration at 1 m depth
  - simulated with PEARL
- two pesticides applied in winter cereals in Hamburg and Kremsmünster
  - any pesticide-scenario combination shows same shape
- sensitivity to *N*: at some point sharp decline to zero
- why ?

Behaviour of closed Freundlich-SFO system

- e.g. incubation system for measuring degradation rate in top soil
- what is time course of fraction in liquid phase ?
- analytical approximation (ignoring mass in liquid phase):

$$f_{liq} = f_{liq,0} \exp\left(-k\,t\left(\frac{1-N}{N}\right)\right)$$

  - f_{liq} fraction in liquid phase (-)
  - $f_{liq,0}$ f_{liq} at t =0 depending on sorption coefficient etc. (-)
  - k degradation rate coefficient (d^{-1})
  - t time (d)
  - N Freundlich exponent (-)

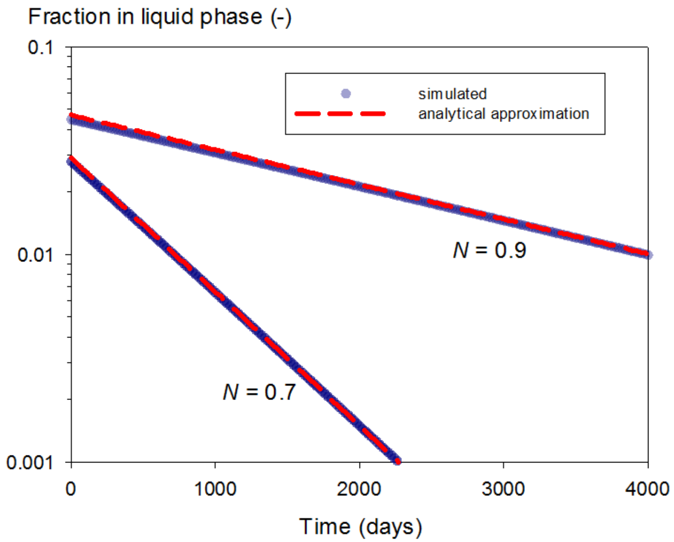
- calculations for system with $DegT50$ = 200 d and K_F = 3 L/kg

Behaviour of closed Freundlich-SFO system

- *DegT50* = 200 d and K_F = 3 L/kg
  - analytical approximation works well

$$f_{liq} = f_{liq,0} \exp\left(-k\, t \left(\frac{1-N}{N}\right)\right)$$

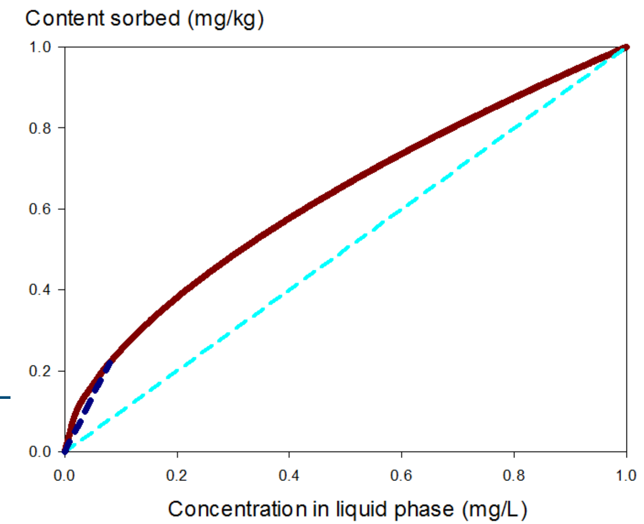
N	(1-*N*)/*N*
0.7	0.43
0.8	0.25
0.9	0.11
1.0	0



- decrease faster for higher *N*
  - *N* = 1 then f_{liq} constant

- background of decrease of f_{liq} : concentration decrease in Freundlich system leads to shift to solid phase

- background of exponential decrease of f_{liq} : content sorbed decreases exponentially



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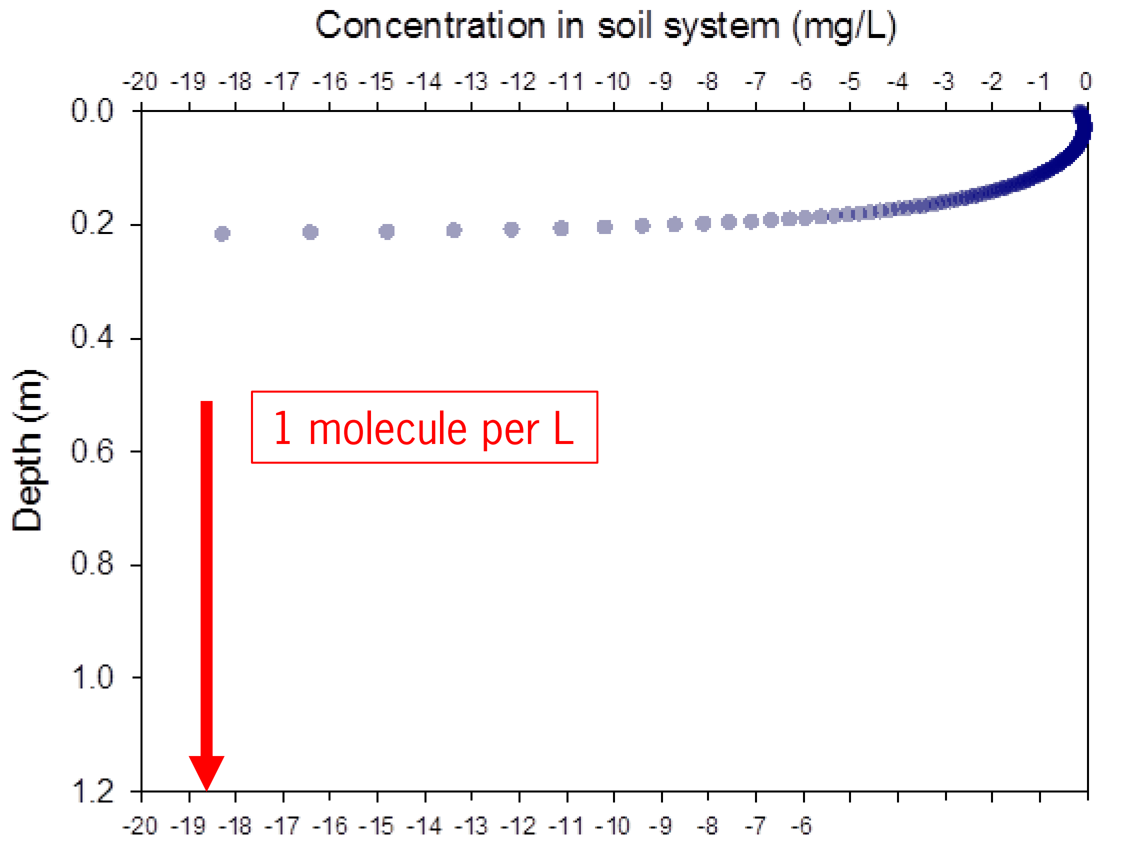
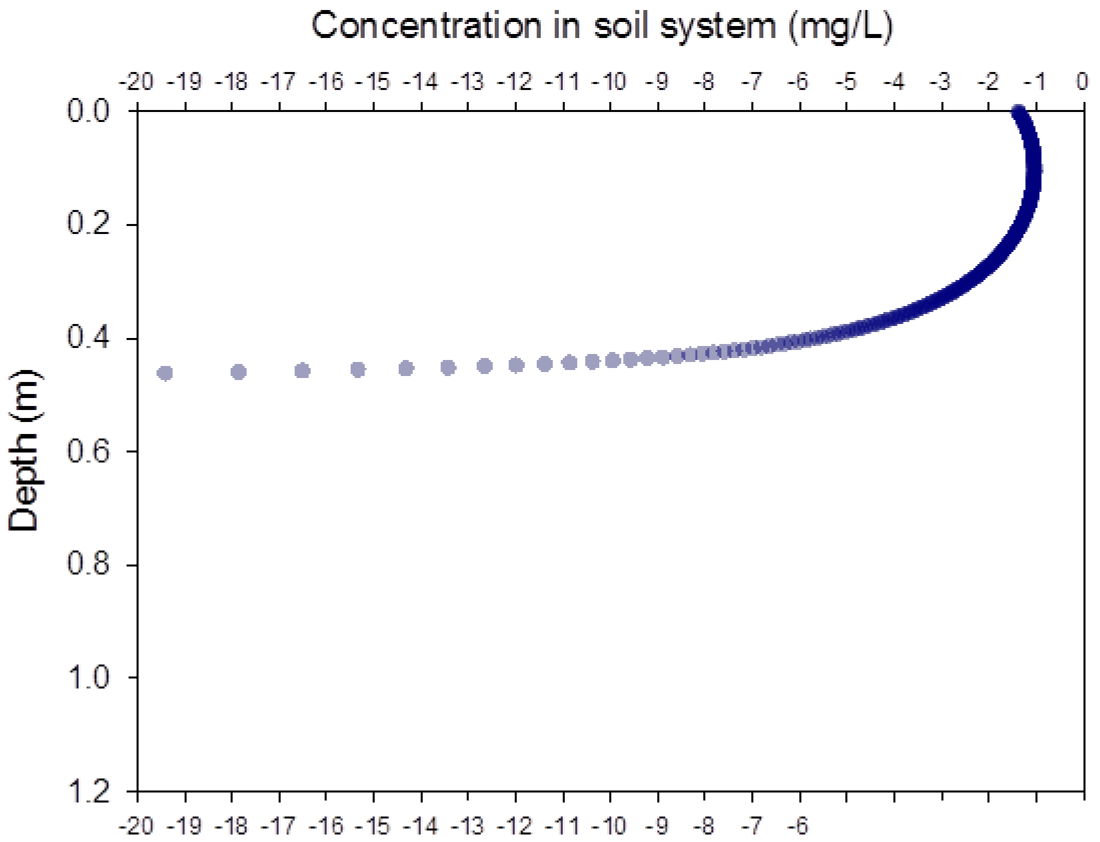
Leaching in uniform soil profile

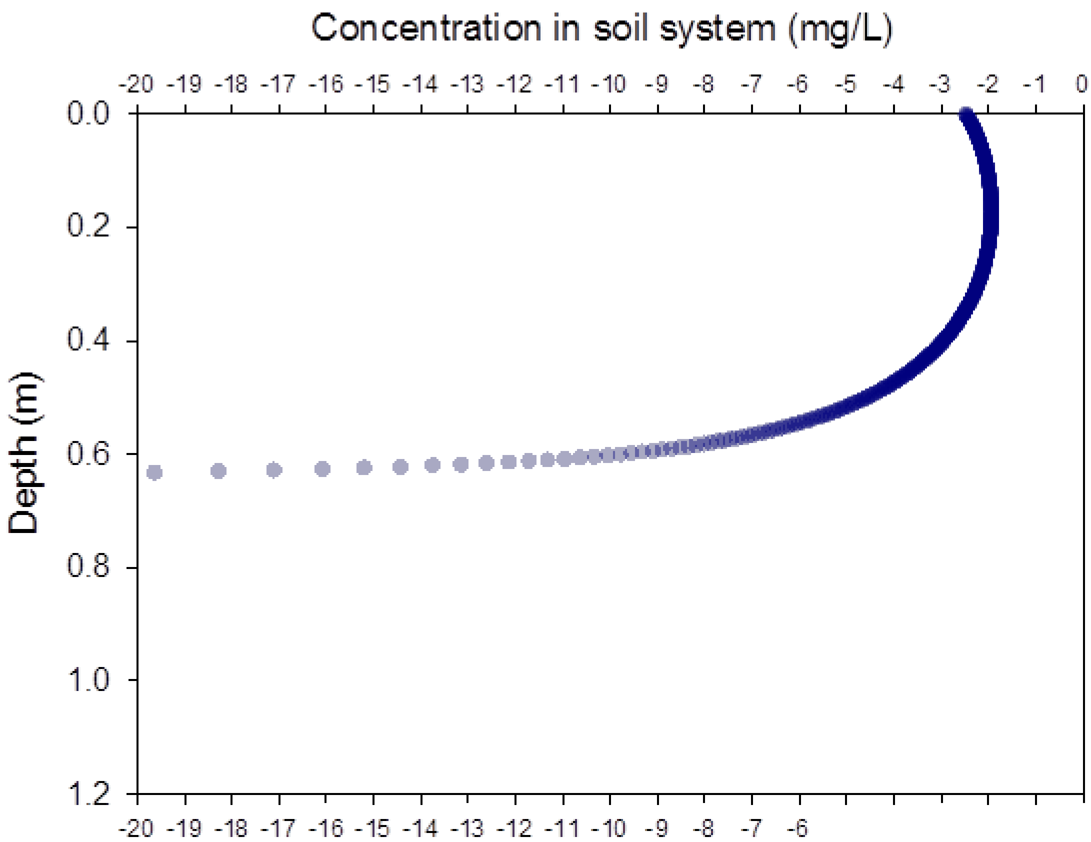
- simplified version of PEARL
- soil profile with uniform properties
  - volume fraction of water 0.25
  - water flow rate 1 mm/d
  - dry bulk density of 1.5 kg/L
  - dispersion length of 5 cm
  - no plant uptake
  - degradation and sorption uniform with depth
  - numerical compartments of 2 mm
  - single pesticide application of 1 kg/ha
- results shown for following pesticide properties
  - degradation rate based on *DegT50* = 200 d
  - Freundlich isotherm parameters: K_F = 3 L/kg and N = 0.9
- calculations for range of other pesticide properties show qualitatively always same result

11 profiles of concentration in soil system for times increasing from 100 to 9000 d



concentration axis from 10^0 to 10^{-20} mg/L to demonstrate principle


Concentration in soil system (mg/L)
-20 -19 -18 -17 -16 -15 -14 -13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Depth (m)
-20 -19 -18 -17 -16 -15 -14 -13 -12 -11 -10 -9 -8 -7 -6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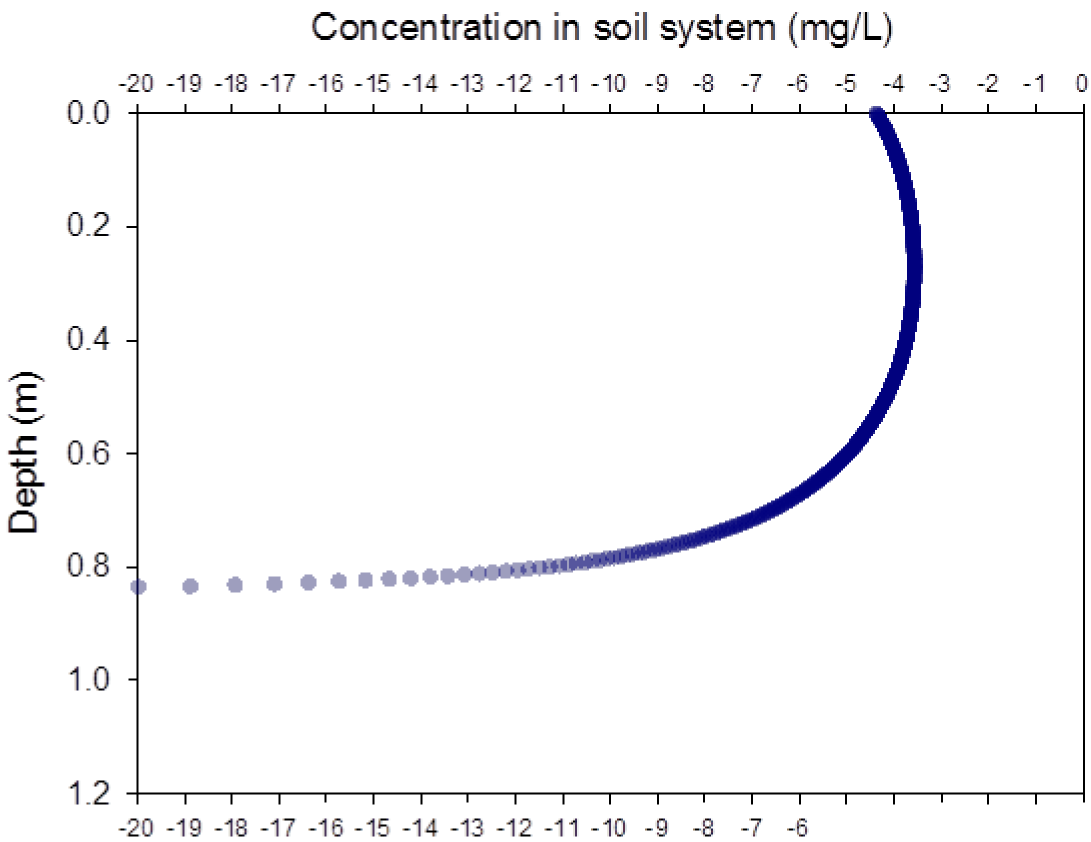
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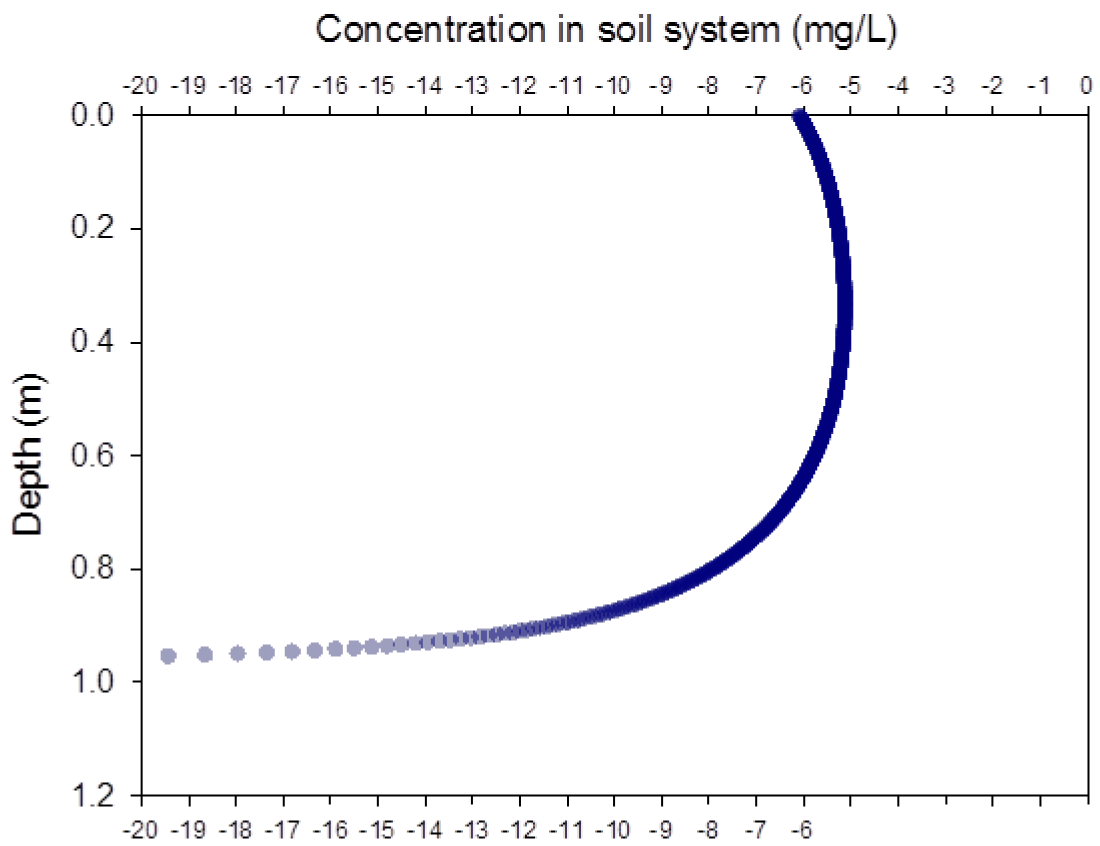

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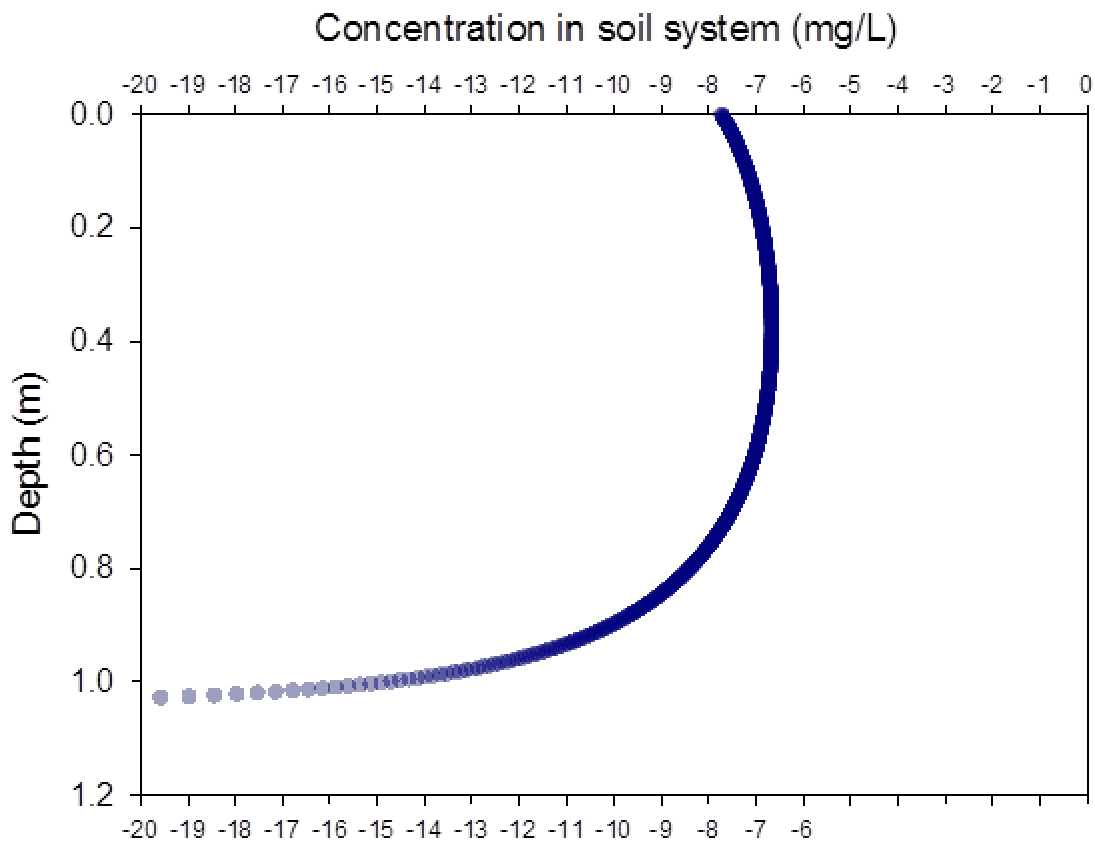
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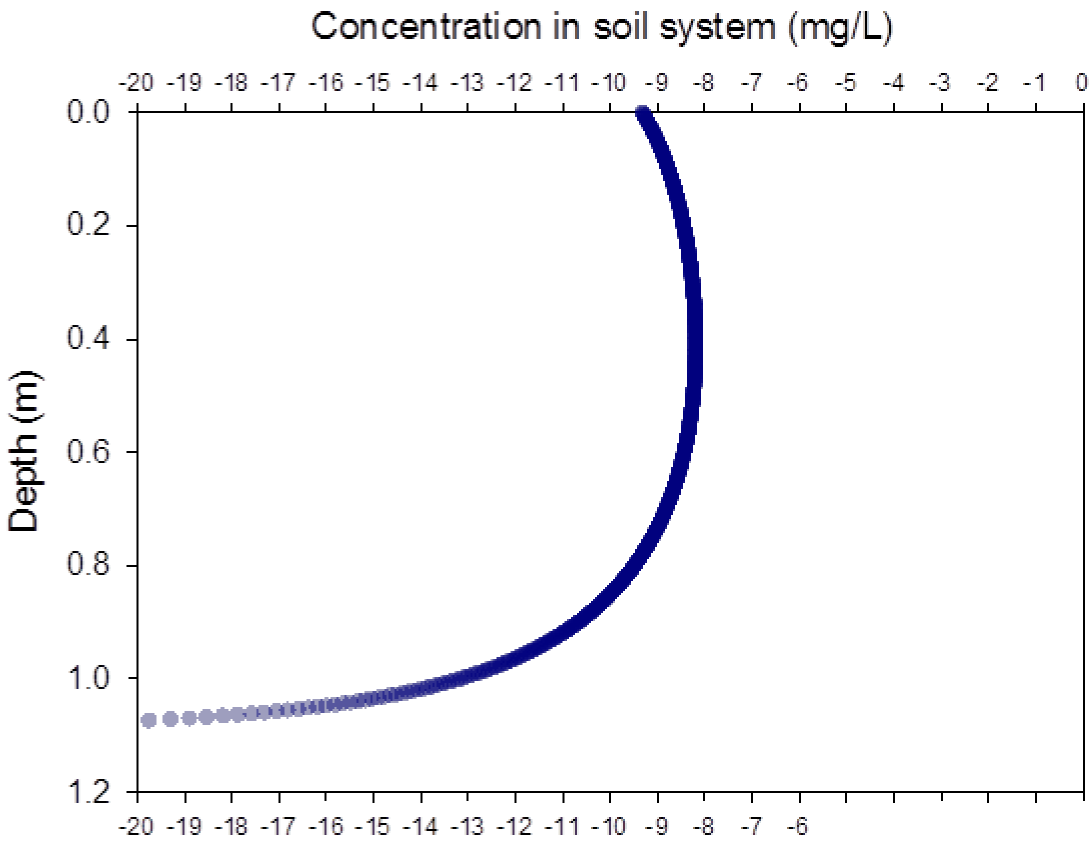

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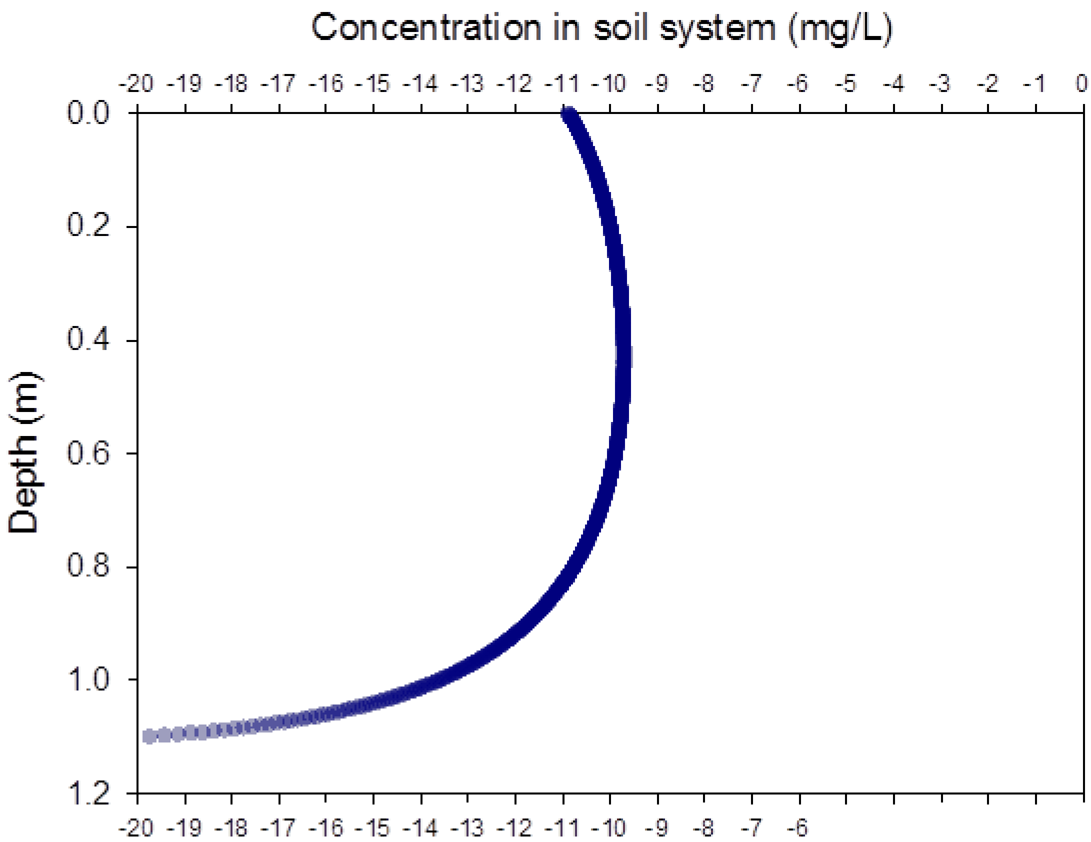
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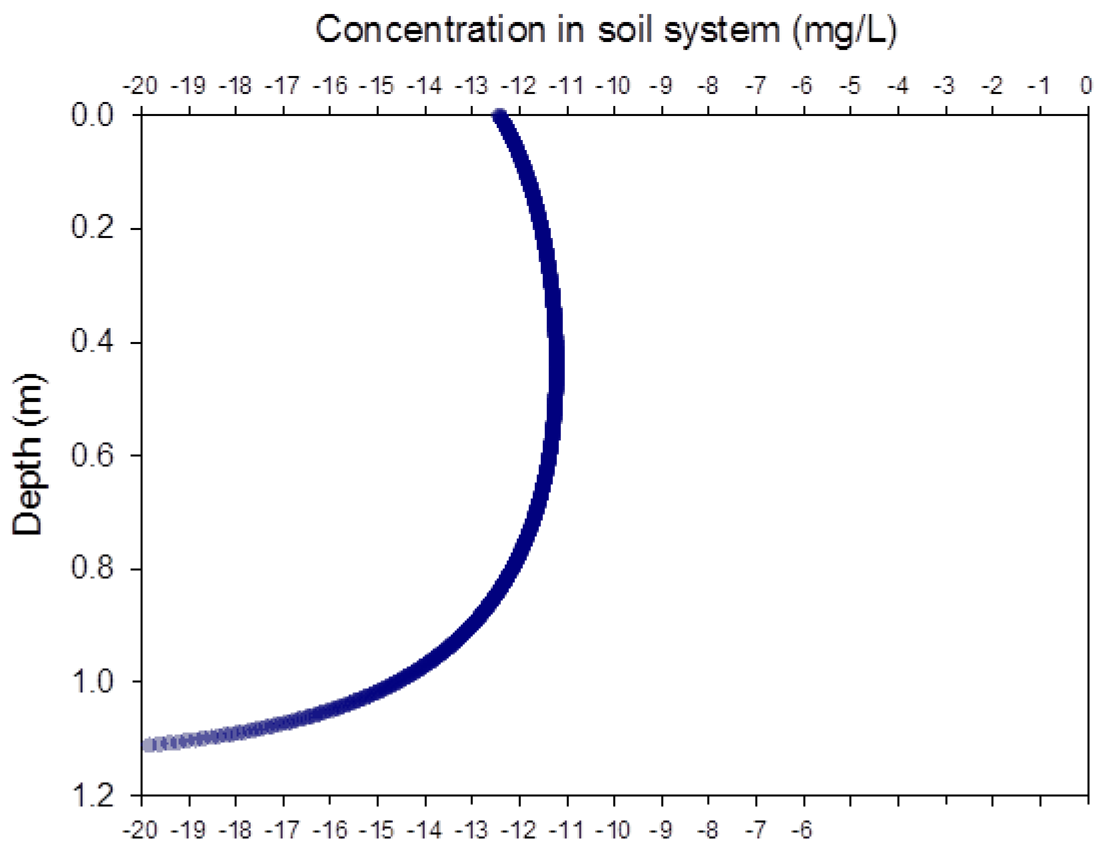

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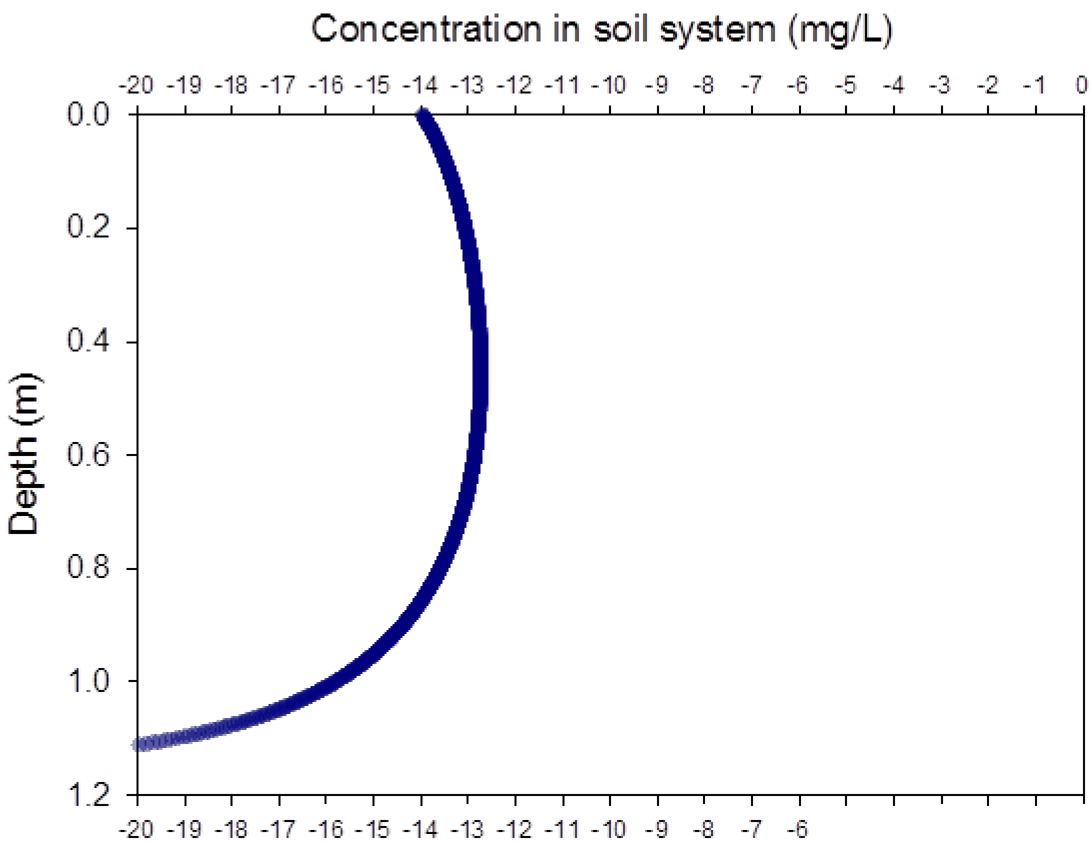
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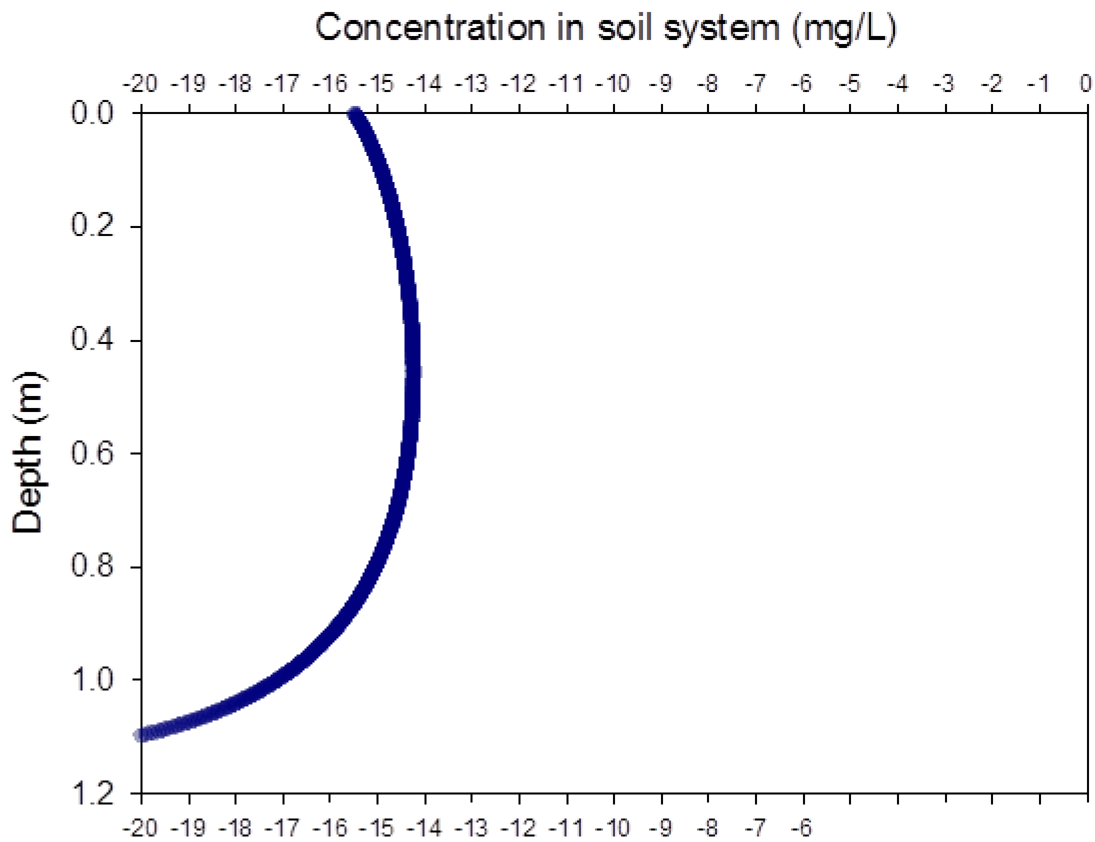

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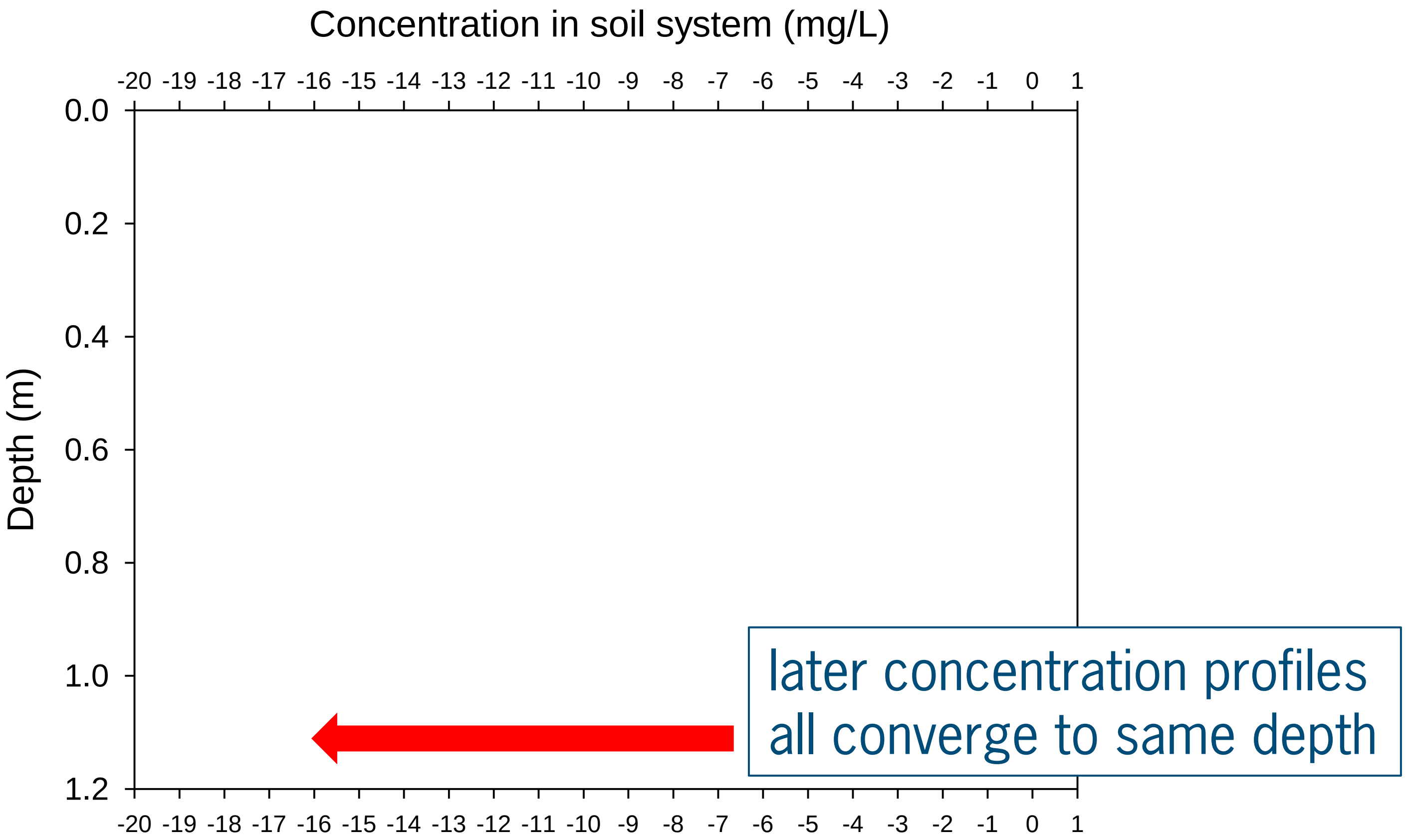
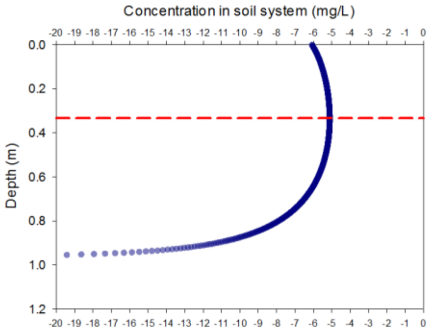


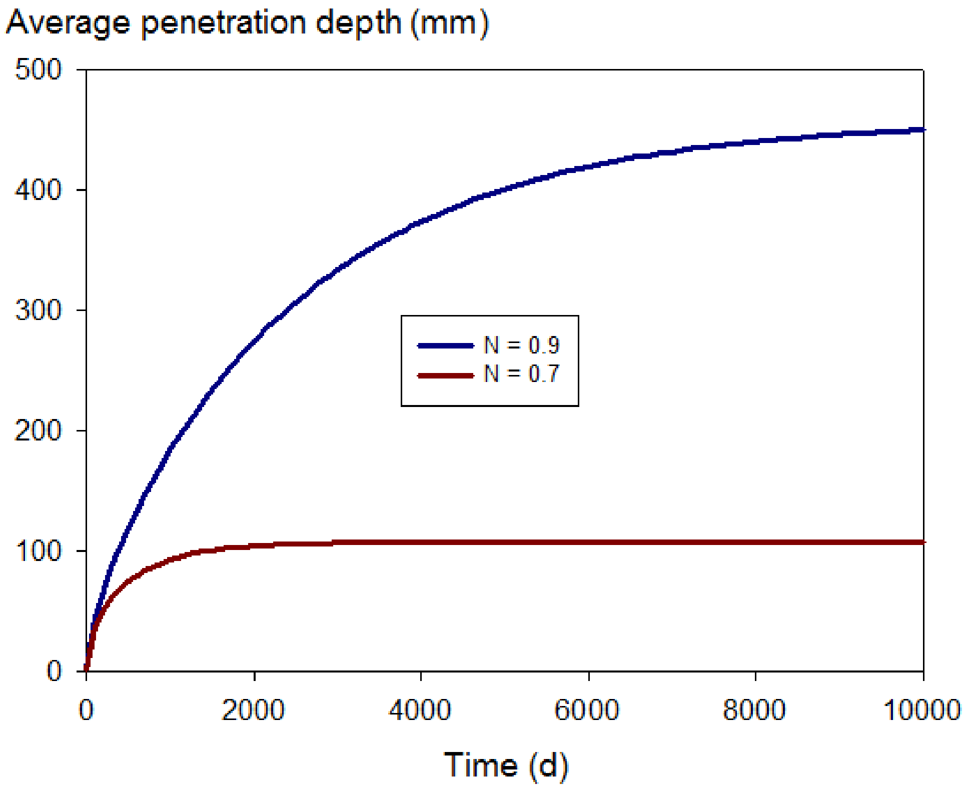
Concentration in soil system (mg/L)
-20 -19 -18 -17 -16 -15 -14 -13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1
Depth (m)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
later concentration profiles all converge to same depth

Leaching in uniform soil profile



average penetration depth:

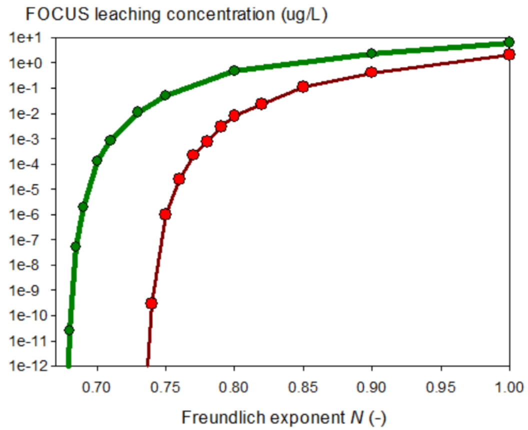
50% above and 50% below this depth



- approaches plateau
  - consistent with behaviour of concentration profiles
- for $N = 0.7$ plateau is shallower and reached quicker

Leaching in uniform soil profile

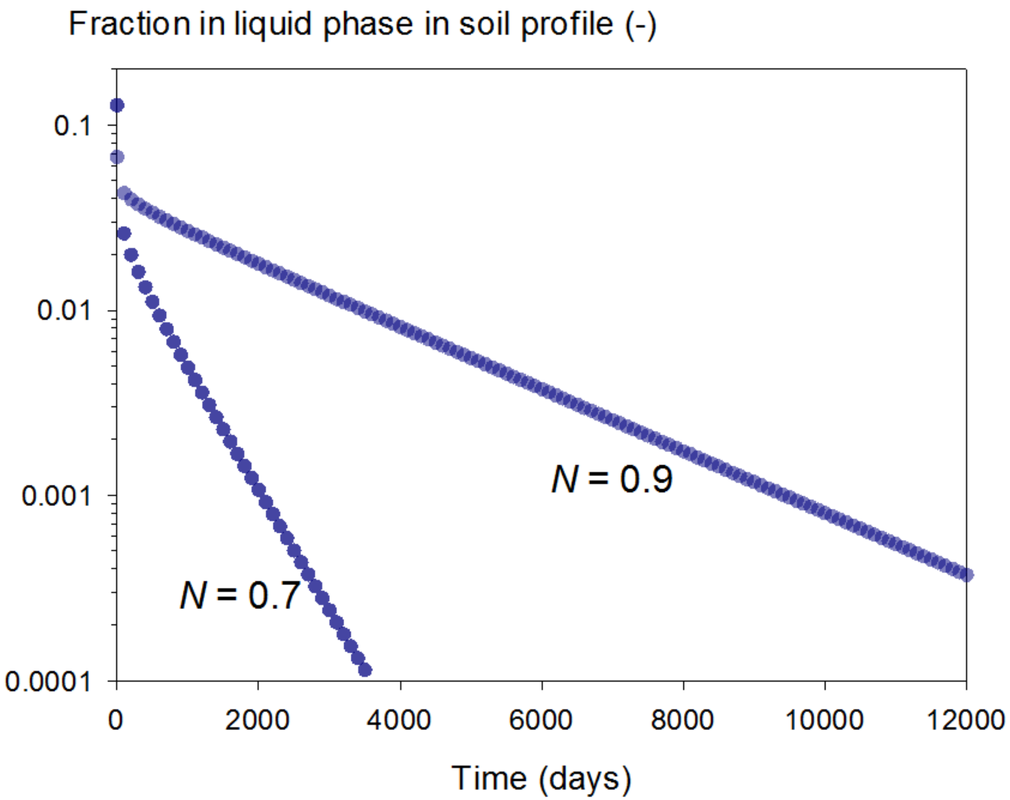
- so pulse in Freundlich-SFO leaching system with constant properties has finite penetration depth
  - beyond which no pesticide molecule will ever pass
- this causes probably the drastic drop in FOCUS leaching concentration when *N* decreases



Leaching in uniform soil profile

- finite penetration depth, so speed of pulse goes to zero
- this speed is proportional to fraction of pesticide in liquid phase
  - only molecules in liquid phase move
- so let us examine fraction of pesticide in liquid phase for total mass of pesticide present in this leaching system

Leaching in uniform soil profile

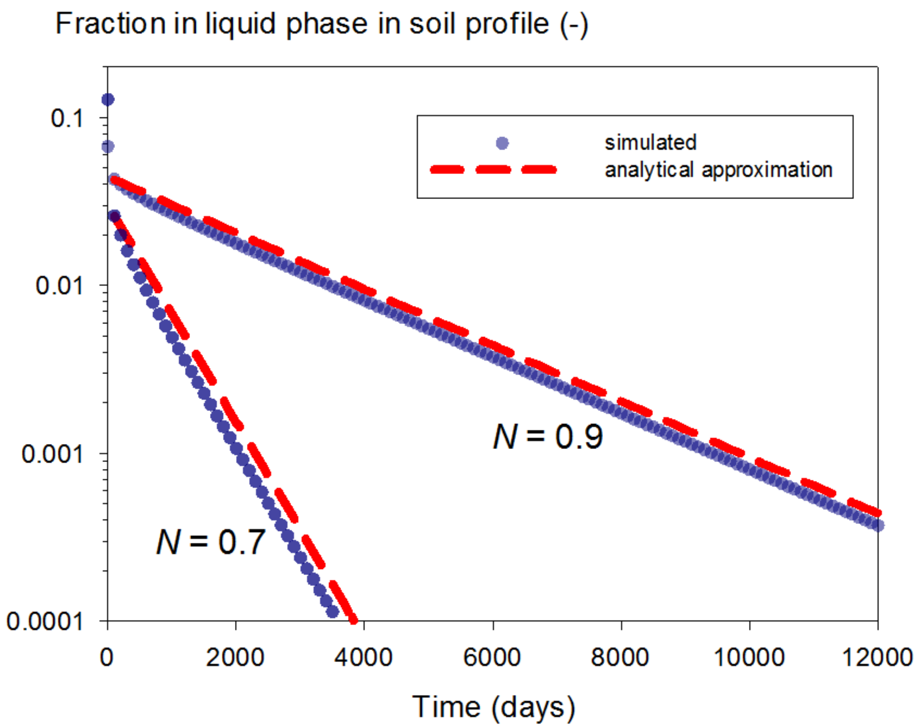


- exponential decrease similar to closed system

$$f_{liq} = f_{liq,0} \exp\left(-k\,t\left(\frac{1-N}{N}\right)\right)$$

- k and N are know but $f_{liq,0}$ unknown so $f_{liq,0}$ estimated from start of linear phase

Leaching in uniform soil profile



$$f_{liq} = f_{liq,0} \exp\left(-k\, t \left(\frac{1-N}{N}\right)\right)$$

- fraction in liquid phase in soil profile decreases at about same speed as in closed system
  - after an initial phase with a more rapid decline
- exponentially decreasing fraction in liquid phase gives exponentially decreasing speed of the pulse
- therefore a pulse has a finite penetration depth in a Freundlich-SFO soil system

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Evidence for validity of Freundlich-SFO concept

- finite penetration depth after infinite time counterintuitive
- sound underpinning needed of this cornerstone of EU leaching assessment
- Freundlich-SFO has historical roots in pesticide world
  - hundreds of measurements of degradation rate measured by extraction with solvent from 100% to some 5% show nice SFO behaviour
- problem: for simulating leaching at 0.1-ppb level the models have to extrapolate orders of magnitude below this 5%

Evidence for validity of Freundlich-SFO concept

- H_0: hypothesis Freundlich-SFO: degradation rate proportional to concentration in total soil
  - for most substances equivalent to: rate proportional to amount sorbed
- H_a: alternative hypothesis: degradation rate proportional to concentration in liquid phase
  - my perception: main-stream microbiological thinking since about 1985
  - considerable amount of indirect evidence (e.g. paraquat behaviour)
  - very large consequences for leaching assessment
    - Beltman et al. (2008) Water Resour. Res. 44, W05417

Evidence for validity of Freundlich-SFO concept

- degradation rate measurements needed that can distinguish between H_0 and H_a
  - not easy, but doable: e.g. study substances with low N values that show very rapid microbial degradation
- to best of my knowledge, no measurements are available that support preference of H_0 over H_a
  - but I am happy to be proven wrong

Conclusions

- leaching of pesticide pulse in uniform Freundlich-SFO soil system results in limited penetration depth
  - which decreases with increasing curvature of isotherm
- this is caused by exponentially decreasing fraction in liquid phase

Conclusions

- this exponentially decreasing fraction is caused by Freundlich-SFO assumption that degradation rate is proportional to total amount in soil instead of amount in liquid phase

- experimental tests of this Freundlich-SFO degradation rate concept required because
  - above results are counterintuitive
  - indirect evidence in favour of alternative concept

Thank you for your attention !

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