Limited penetration depth in soil system with Freundlich sorption and first-order degradation
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
  - $D_{egT50}$ at 20°C and pF = 2.5
  - Freundlich isotherm: $K_F$ and $N$

- first such data set including $N$

- their aim: predict $D_{egT50}$ 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

- 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’
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)

Variability in degradation half-lives

EFSA guidance assumes lognormal distribution with CV of about 50%
correlation coefficient 0.30 : not significant
so spatially-distributed predictions of $DegT50$ difficult
Variability of $K_{oc}$

EFSA guidance assumes lognormal distribution with CV of about 50%
Allen & Walker (1987)

$K_{oc}$ values correlated?
(then probably similar sorption sites)
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)

- The dataset is 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 is one of the most valuable sources for magnitude of non-linearity ($N$)
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
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
  \[ X = K_F \cdot c_{\text{ref}} \left( \frac{c}{c_{\text{ref}}} \right)^N \]

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

- SFO = single first-order kinetics

  \[ c^* = \theta \cdot c + \rho \cdot X \]

  - \( c^* \): concentration in soil system (mg/L)
  - \( \theta \): volume fraction of water (-)
  - \( \rho \): dry bulk density (kg/L)

  \[ \frac{d c^*}{d t} = -k \cdot c^* \]

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

[Diagram showing the effect of \( N \) on the sorption isotherm]

WAGENINGEN UNIVERSITY & RESEARCH
**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):

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

  - \(f_{liq}\): 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

- \( \text{DegT50} = 200 \text{ d} \) and \( K_F = 3 \text{ L/kg} \)
  - analytical approximation works well

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

- decrease faster for higher \( N \)
  - \( N = 1 \) then \( f_{\text{liq}} \) constant

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

- background of exponential decrease of \( f_{\text{liq}} \): 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 in soil system (mg/L)

Depth (m)

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

1 molecule per L
later concentration profiles all converge to same depth
Leaching in uniform soil profile

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

average penetration depth:
- 50% above and 50% below this depth
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

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

- \( k \) and \( N \) are known but \( f_{\text{liq}, 0} \) unknown so \( f_{\text{liq}, 0} \) estimated from start of linear phase
Leaching in uniform soil profile

- Fraction in liquid phase in soil profile decreases at about the same speed as in a 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.

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

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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
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!