

Controlling parameters for microbial pesticide degradation in subsurface and aquifers

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Warwick, 28 March 2006

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Background

- Pesticides and degradation products are detected in an increasing number of aquifers all over the world, including Europe
- Aquifer environments differ in many ways from topsoil
 - Low concentrations of the pesticides
 - EU guideline: 0.1 µg/L
 - Low content of organic matter – effect on sorption
 - Low microbial numbers, densities and activities
 - Considering hydraulic residence times in aquifers of 30-60 years, half-lives of e.g. 10 years would still be relevant
- **AIM:** Identify controlling parameters to be considered, when predicting the fate of pesticides in subsurface and aquifers

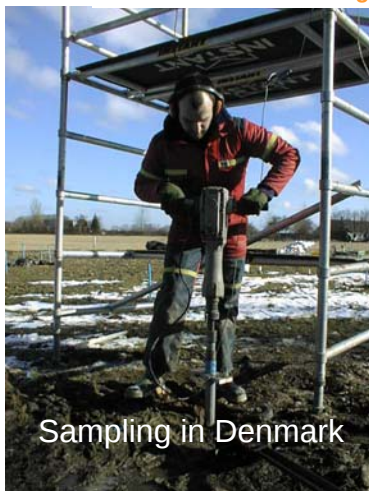
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PEGASE

Pesticides in European Groundwaters : detailed study of representative Aquifers and Simulation of possible Evolution

EU's 5th Framework Programme, key action water



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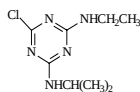
Pesticides and aquifers

Aquifers:

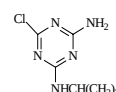


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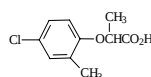
Key pesticides:



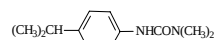
Atrazine



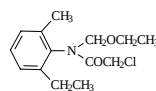
Deethylatrazine



MCPP



Isoproturon



Acetochlor

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C2, 3.15 – 3.45 m

70 cm



3 cm 2 cm 2 cm

12 cm

7 cm

6 cm 2 cm

10 cm

5 cm

DTU

Calcaire brun, fin, lité (mudstone); bioturbations (terriers) remplies de sédiments blancs



Niveau très fossilifère, poreux. Type Packstone



Calcaire fin beige, recristallisé sur les plans de fracturation, parfois poreux, souvent complètement cimenté



Delicate handling of sediment samples



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Degradation: Unsaturated zone

■ Purpose:

Mineralization of pesticides in depth profiles

■ Methods:

■ Set up:

- 33 g dry sediment, 0.70-10.64 mL water (natural water content)
- 0.5 mL ^{14}C -labelled pesticide added. Initial concentration 10 $\mu\text{g/kg}$

■ Measurements:

- $^{14}\text{CO}_2$ trapped in 2 mL 0.5 M sodium hydroxide



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Brévilles: Sediment C1, unsaturated



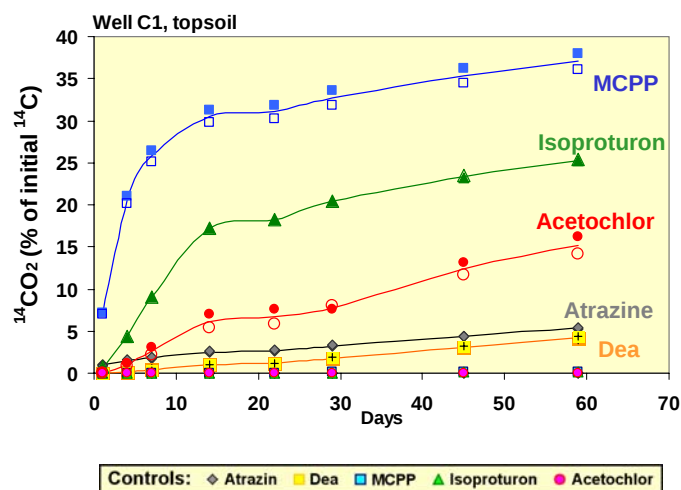
0-0.25 0.25-0.40 3.10-3.25 6.0-6.25 9.0-9.12 13.0-13.12
mbs

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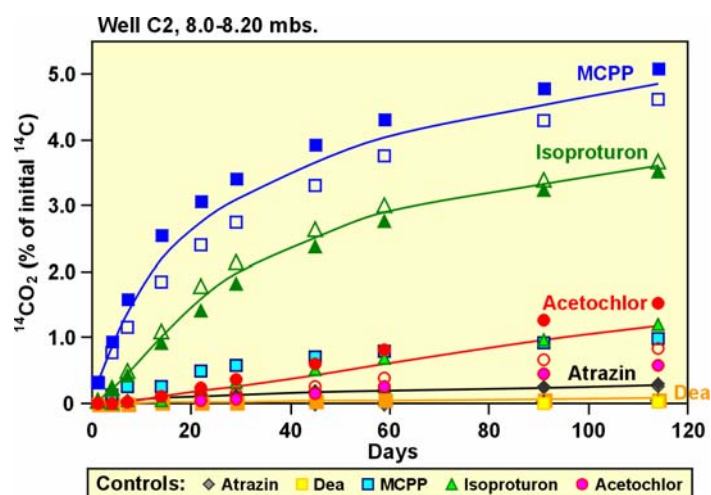
Brévilles: Unsaturated zone



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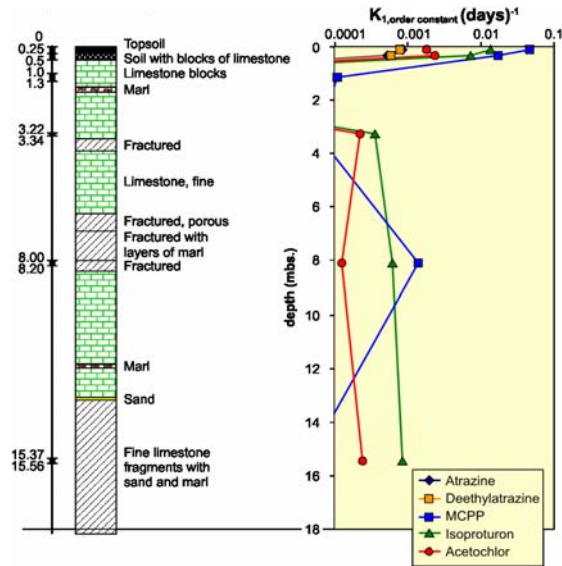
Brévilles: Unsaturated zone



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Brévilles: Unsaturated zone, C2



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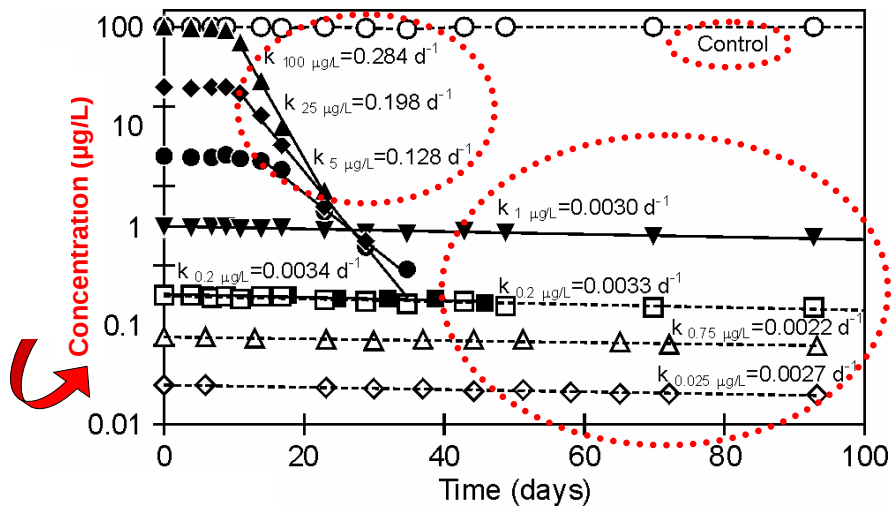
Concentration

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Degradation of 2,4-D aerobic, aquifer sediment, 10°C



Toräng et al., 2003, ES&T

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Concentration

IS IMPORTANT

- Kinetics may shift depending of concentration (µg/L)

- Thresholds: Above: faster, growth based

Below: slower, non-growth based

Implications:

- Degradation experiments to estimate rates should be carried out at relevant (low) concentrations
- Results from top soil cannot be transferred to subsurface
- Results from contaminated sites (higher concentrations) cannot be transferred to 'non-contaminated' aquifers (lower concentrations)

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Exposure

- How much – over time?

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Field injection experiment

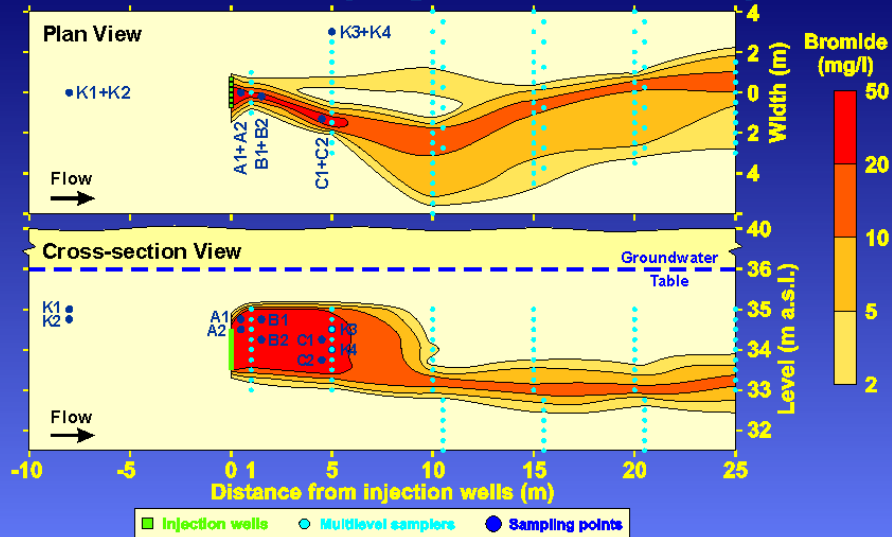
- Aquifer
 - Unconfined
 - Aerobic
- Injection
 - Natural gradient
 - Continuous injection for 216 days
 - 40 µg/L of MCPP and dichlorprop
- Sampling
 - At least every second week



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Broholm et al., 2001, WWR

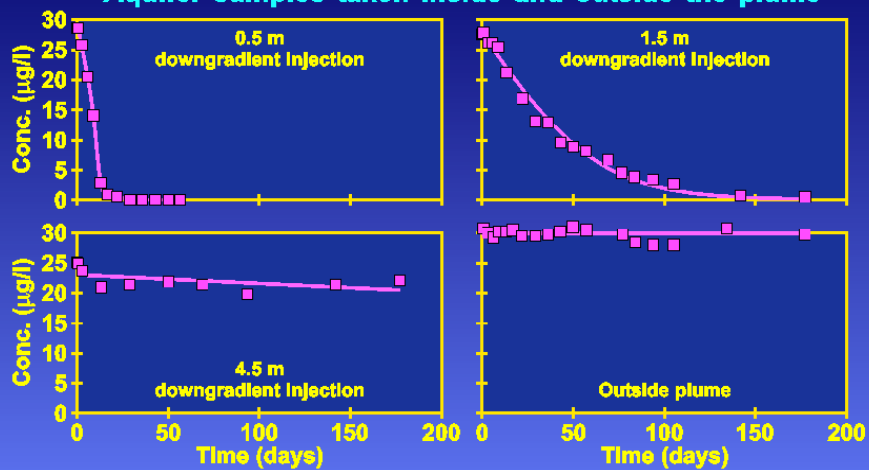
Locations of Sampling Points in Bromide-plume



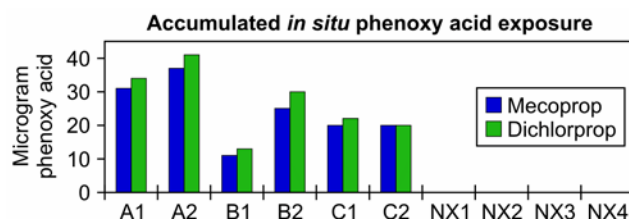
Tuxen et al., 2002, ES&T

MCPD degradation

Aquifer samples taken inside and outside the plume



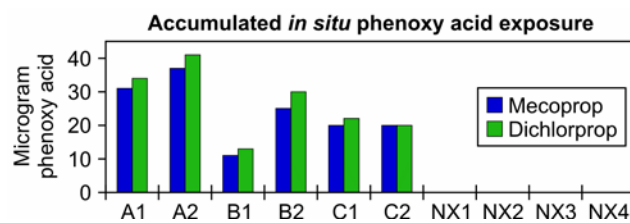
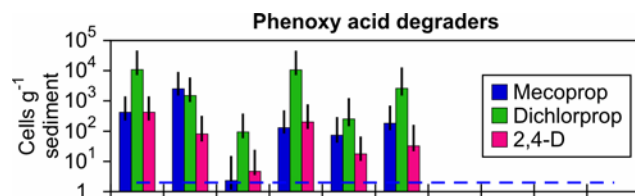
Tuxen et al., 2002, ES&T



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de Lipthay et al. (2003), AEM, 69, 461-467

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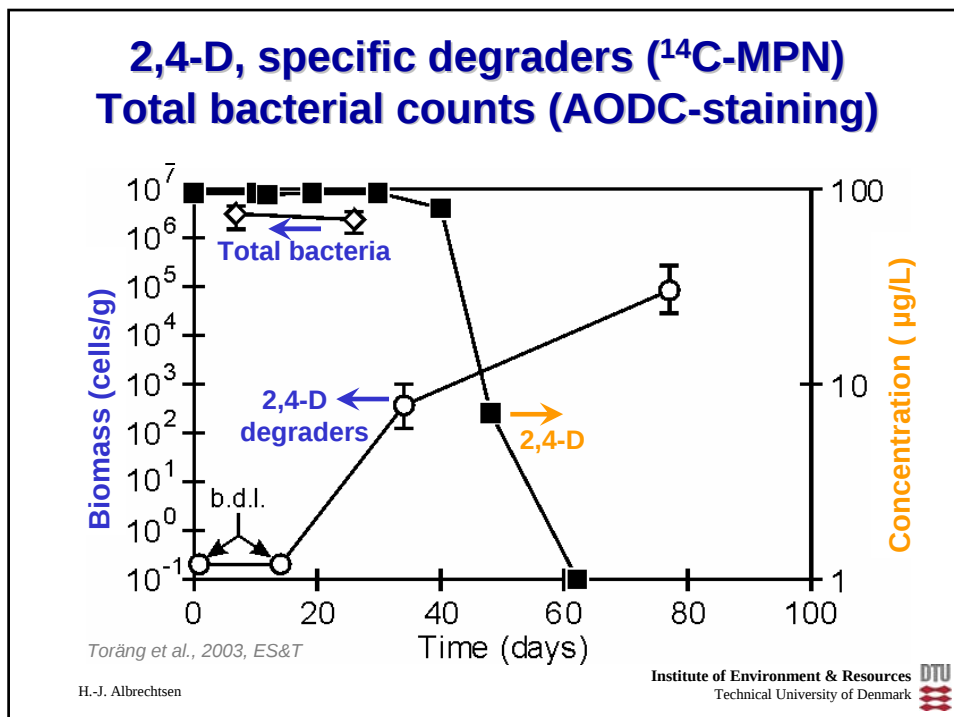
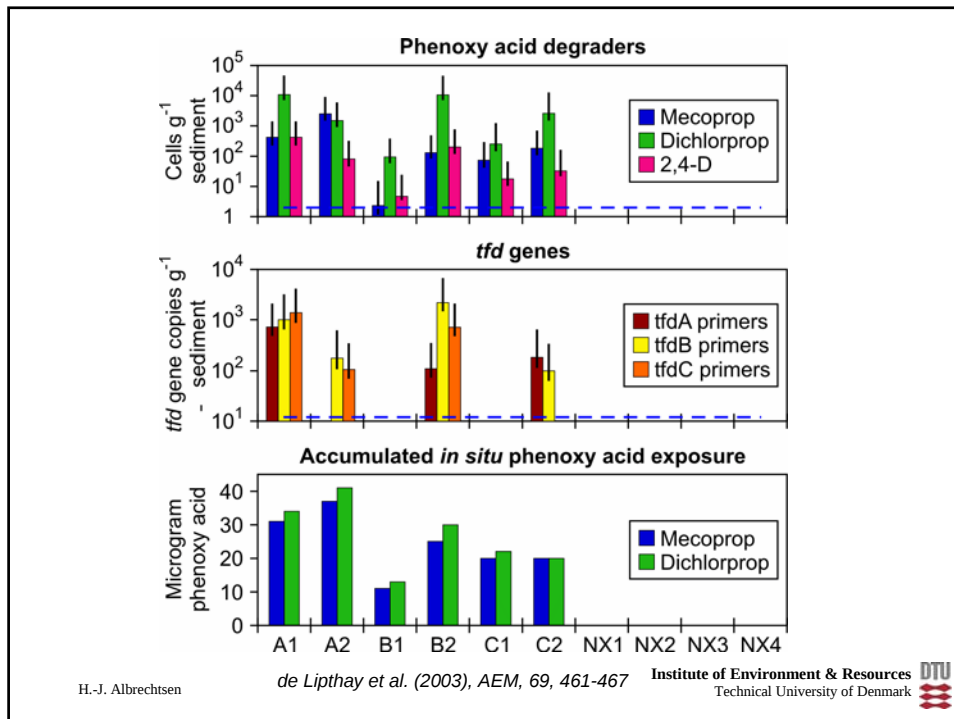


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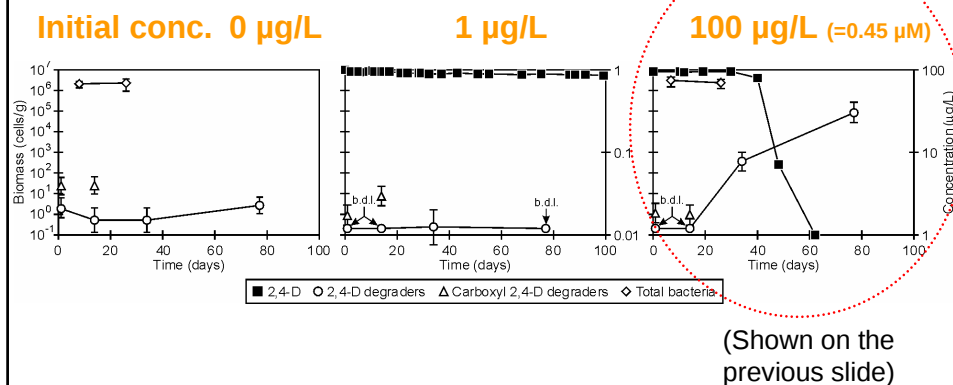
de Lipthay et al. (2003), AEM, 69, 461-467

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Degradation of 2,4-D Specific and total bacteria Unpolluted aquifer

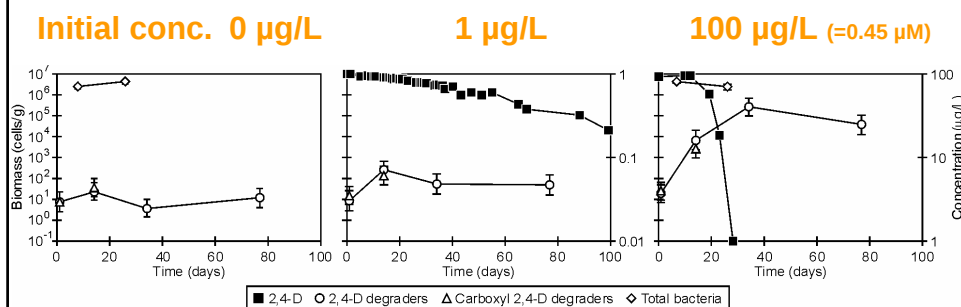


Toräng et al., 2003, ES&T

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Degradation of 2,4-D Specific and total bacteria Weakly pre-exposed aquifer

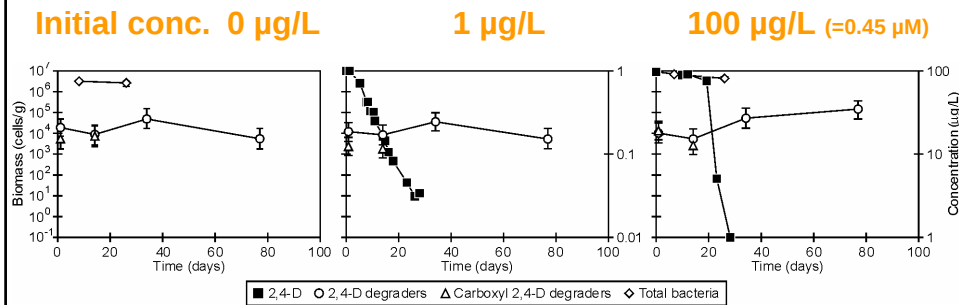


Toräng et al., 2003, ES&T

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Degradation of 2,4-D Specific and total bacteria Highly pre-exposed aquifer



Toräng et al., 2003, ES&T

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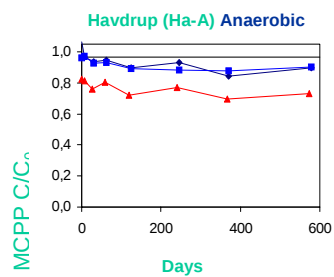
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Redox conditions

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Effect of oxygen Havdrup, MCPP

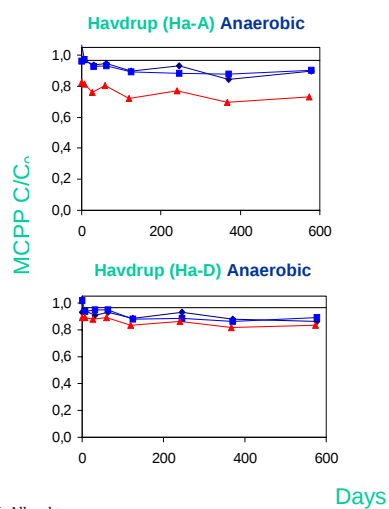


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Effect of oxygen Havdrup, MCPP

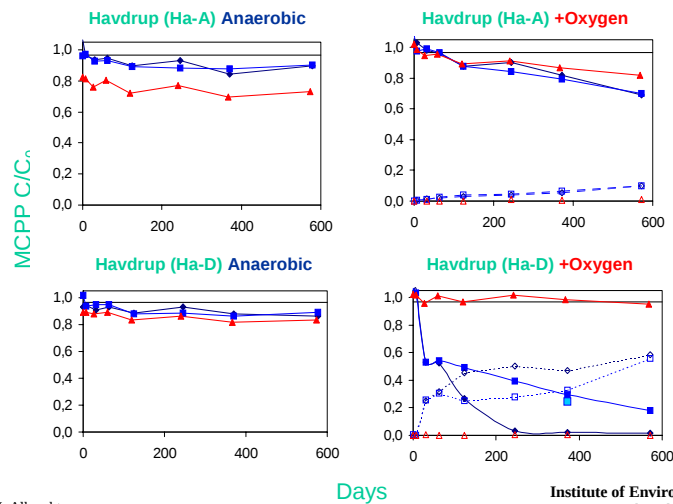


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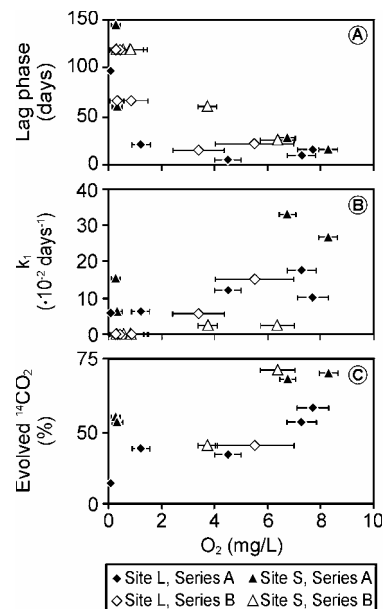
Effect of oxygen Havdrup, MCPP



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Effects of oxygen concentration on degradation



Tuxen et al., 2006, GWMR

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Sorption

Purpose:

- Determine (K_d) parameters for modelling purposes
- Investigate sorption ranges within and between aquifers
- Investigate the interactions between sorption and degradation

Methods:

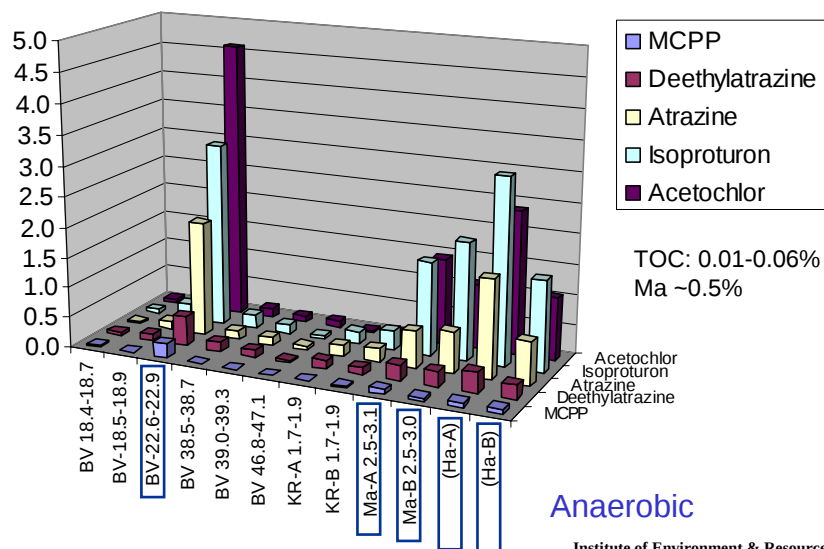
- Batch experiments: 5 mL water. 5 g sediment. 10°C. Concentrations: 50 µg/L
- Equilibrium time: 7 days (MCP, acetochlor), 14 days (atrazine, deethylatrazine, isoproturon)
- Measurements: ^{14}C -pesticide and $^{14}\text{CO}_2$



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Sorption coefficients ($K_d = C_s/C_{eq}$)



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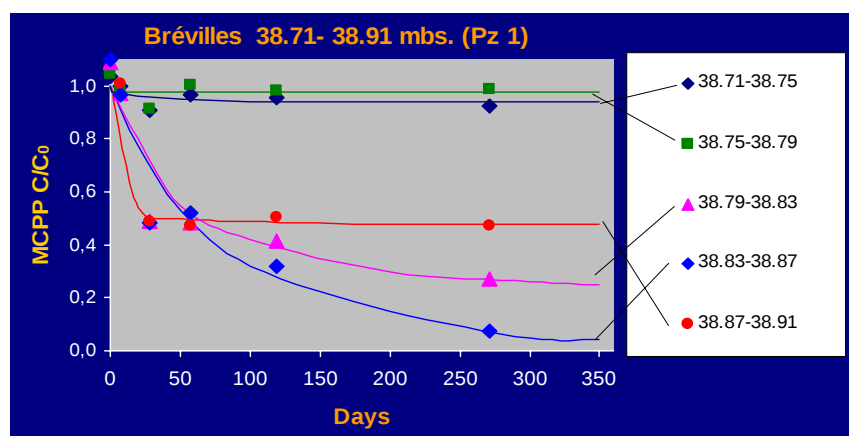
Spatial variation

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Small scale variation Degradation: MCPP



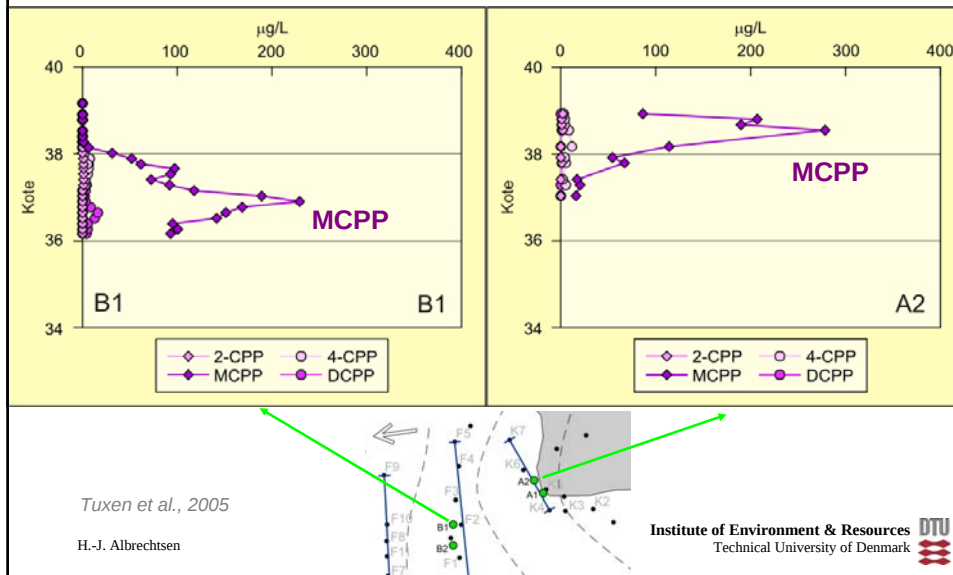
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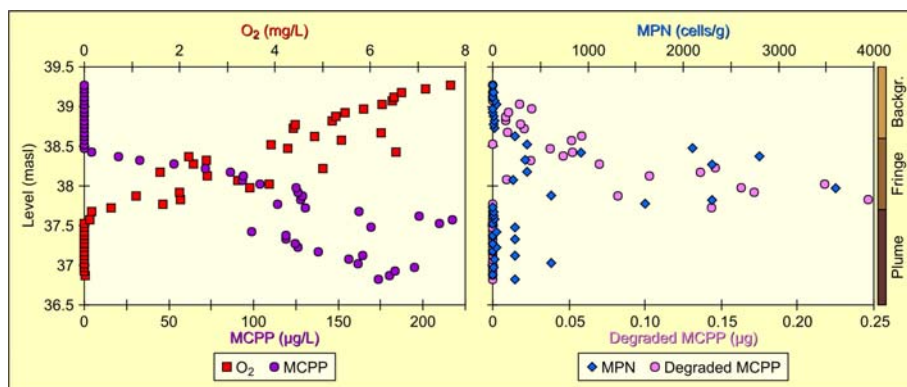


Phenoxy acids

- Significant plume of phenoxy acids



Degradation across the fringe

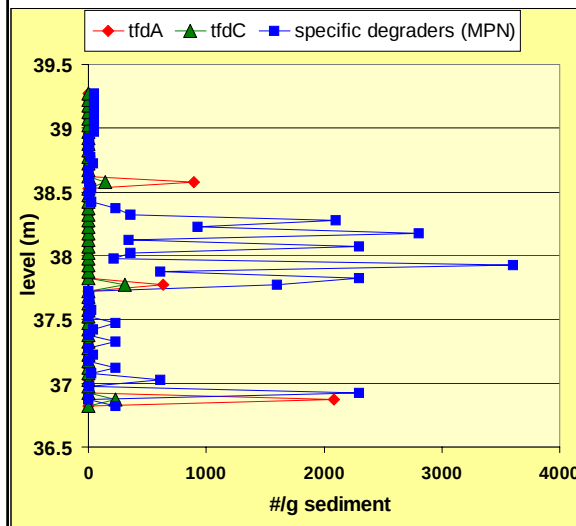


Variables

- Oxygen
- Phenoxy acid conc.
- Specific biomass



Quantification of *tfdA*, *tfdB* and *tfdC* in 50 aquifer sediment samples



tfdA: $10^2 - 10^3$ /g sediment in 3 samples (*tfdA* 100% match with *R. eutropha* JMP134 *tfdA*)

tfdC: 10^2 /g sediment in same 3 samples

tfdB: below detection limit

=> *tfdA,C* presence, but generally not correlated with MPN

Lindberg et al., 2006

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Controlling parameters in subsurface

- Concentration influences kinetics – even at very low concentrations ($\mu\text{g/L}$)
- Exposure ($\mu\text{g/L}$) increases degradation
- Spatial variation (cm) is not always just stochastic
 - Search for controlling parameters:
 - Redox, concentration
- Degradation may leave a footprint or a trace in the microbial population
 - Tfd-genes
 - Composition of microbial populations

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Funding – thanks to



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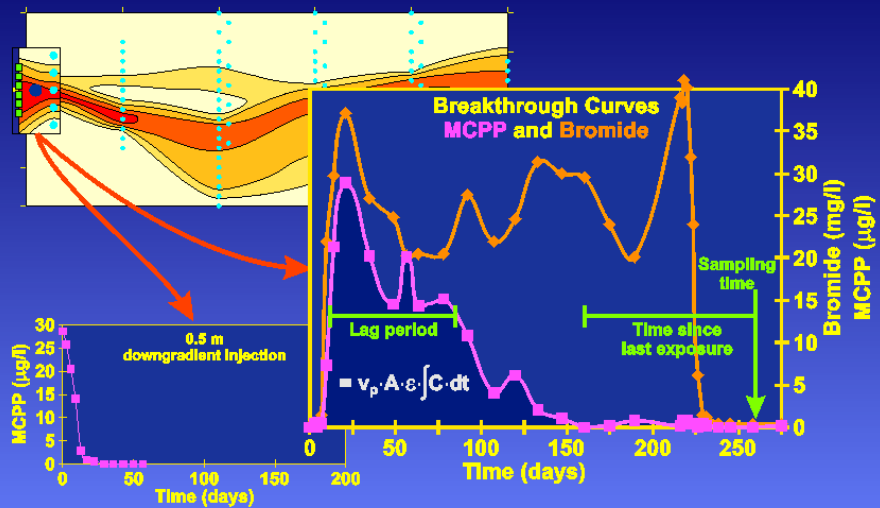


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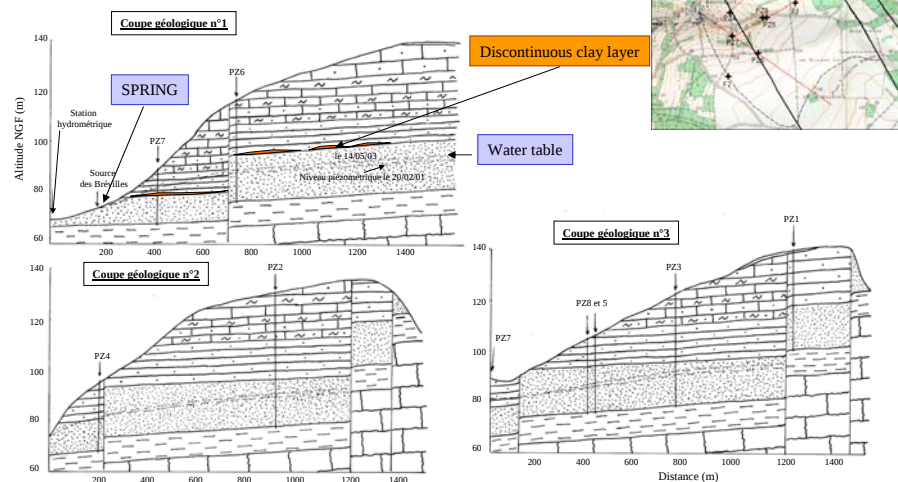


Calculations of exposure



Tuxen et al., 2002, ES&T

Brévilles

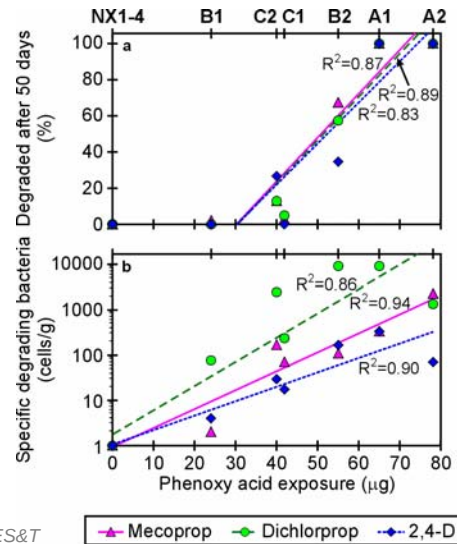


BRGM

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Effect of exposure

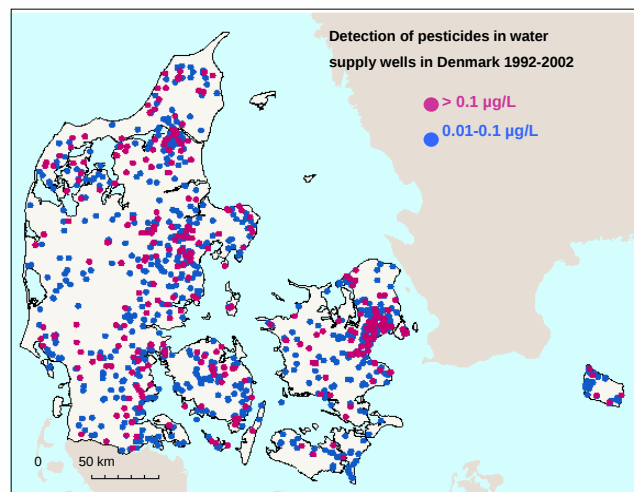


Tuxen et al., 2002, ES&T

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Detection of pesticides in water supply wells in Denmark 1992-2002



(GEUS, 2003)

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Pesticides in groundwater, USA

Investigation period: 1993-1995

Pesticides present

in 54% of the 1034 sites sampled

in both agricultural (56%) and urban (47%) settings

39 pesticides detected of the 46 examined

Top 5:

Atrazine (38%) - 18% > 0.1 µg/L

Deethylatrazine (34%) – metabolite

Simazine (18%)

Metolachlor (15%)

Prometon (14%) – urban area

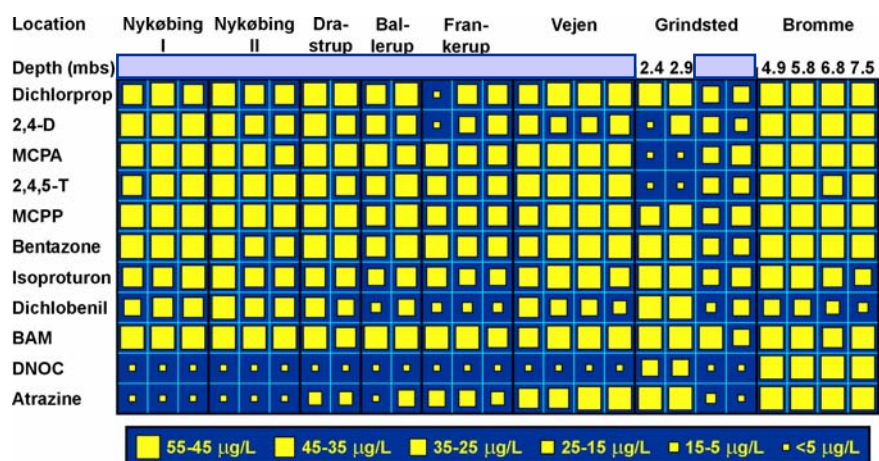
Sites with pesticides: 73% ≥ 2 pesticides (25% ≥ 4)

Kolpin et al., 1998, ES&T

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Danish aquifer sediments concentration after 1 year incubation

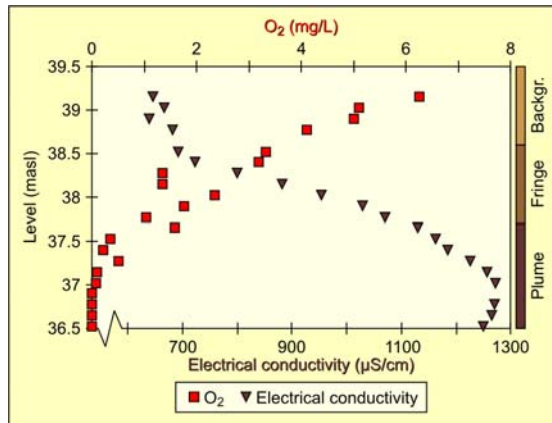


P.G. Pedersen, Thesis

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Zone of degradation at fringe?



Sediment core

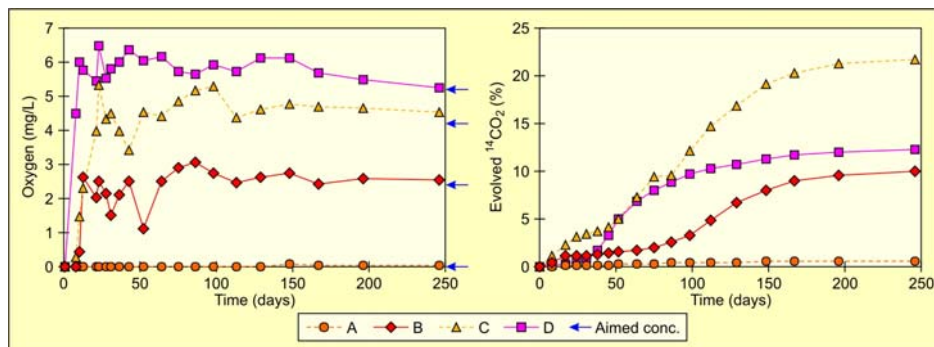
- 5 cm pieces
- 50 microcosms

H.-J. Albrechtsen Tuxen et al., 2005



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Microcosm studies



- Oxygen control
- ¹⁴C-labelled MCP
- Evolved ¹⁴CO₂

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