Towards a better understanding of the behaviour of pesticides in the environment: where did Allan Walker lead us and where now?

Richard Allen

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Topics

Bioavailability of Residues in Soil

Microbiological and molecular aspects of degradation

Leaching to groundwater

Fate and transport in air

Transport and dissipation processes in surface waters

Landscape-level approaches to modeling

Risk mitigation

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Bioavailability of Pesticides in Soil and Sediments

- Bioavailability from which perspective?
  - Biological Efficacy
    - Residual weed control
  - Impacts of residues on following crops
    - Herbicide damage to follow on crops
    - Residues in rotational crops
  - Impacts on non-target organisms and other environmental compartments
    - Sediment dwelling organisms
    - Groundwater
  - Factor controlling microbial degradation processes

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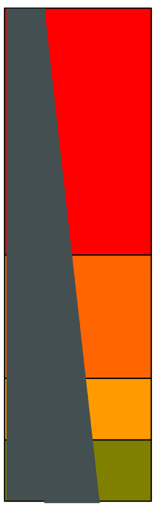
Bioavailability of Soil Acting Herbicides: Modifications of simple dose response relationships



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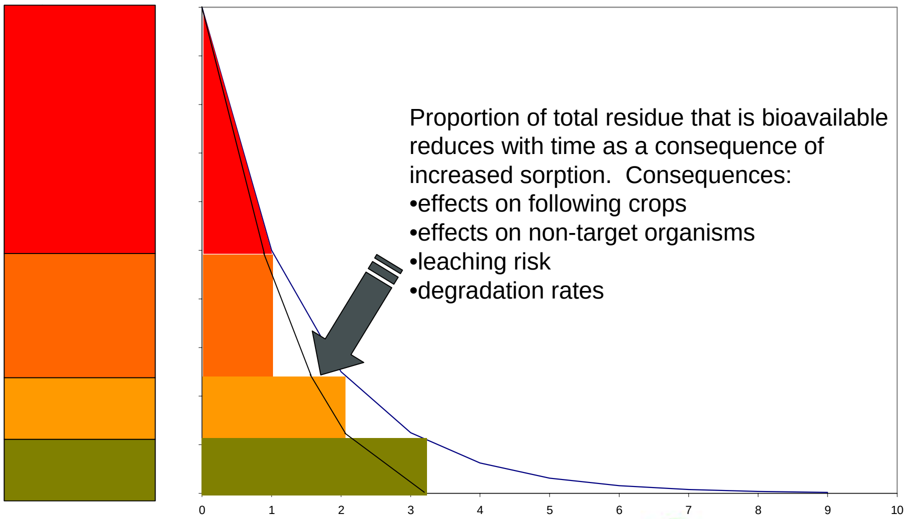
Bioavailability of Soil Acting Herbicides: with time



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Bioavailability:

Walker's early research demonstrated that bioavailability of soil acting herbicides was impacted by:

- Soil moisture
- Organic carbon content
- Distribution of residues in soil root zone
- Time of application
- Weather

Our challenges remain

- to further develop techniques and further characterize the dependency of sorption with:
  - time
  - inherent physicochemical or molecular properties
  - soil properties
- To account for these processes in refinements of pesticide risk assessment

Walker et al. (1985) Annals of Applied Biology 106, 323-334

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Development of methodologies to more accurately reflect in situ sorption at realistic soil moisture contents.

Uniformly incorporate formulated product at a range of concentrations

Incubate at -10 kPa soil water potential

Measure total residues at intervals

Centrifuge to remove soil solution and measure solution concentrations

Walker A (2001), In "Pesticide-Soil Interactions: Current Research Methods", (P Jamet; J Cornejo Eds) INRA Publications, pp. 173-177.

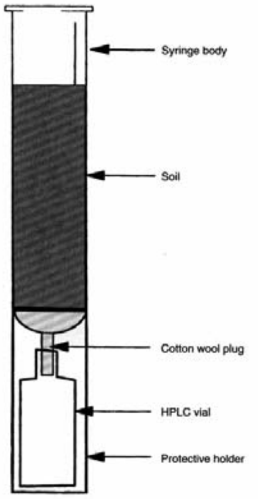

Figure 1. Centrifugation apparatus.

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Methodology for measuring sorption by aggregates:

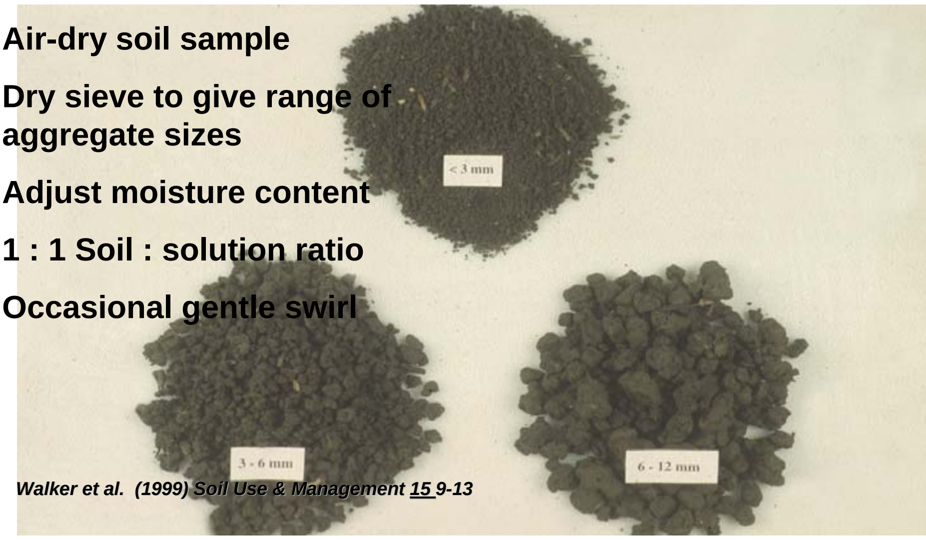
Air-dry soil sample

Dry sieve to give range of aggregate sizes

Adjust moisture content

1 : 1 Soil : solution ratio

Occasional gentle swirl



Walker et al. (1999) Soil Use & Management 15 9-13

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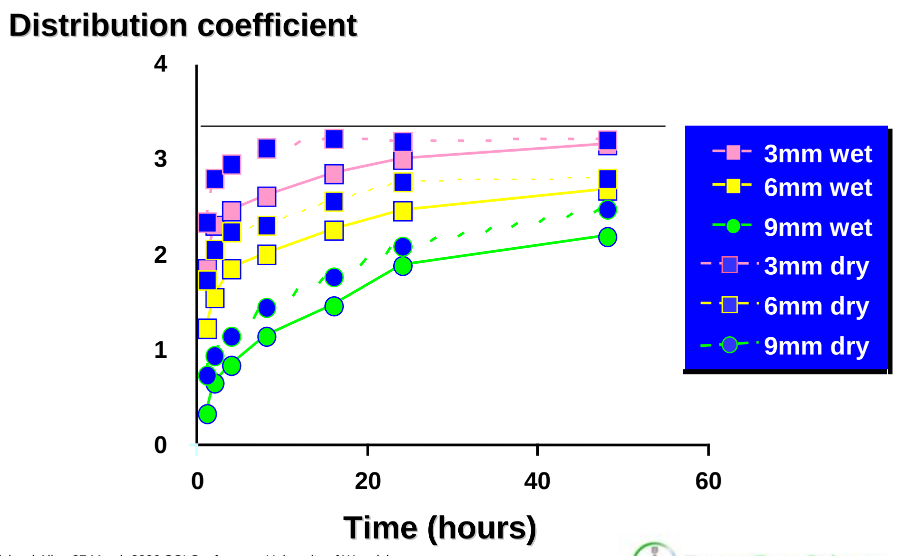
Pesticide adsorption by soil aggregates (Isoproturon; Denchworth clay)



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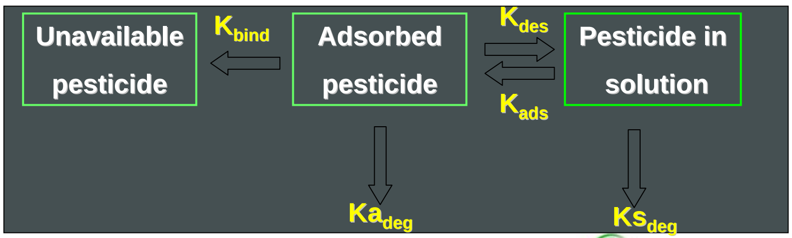
Implications of time-dependent sorption processes

- Is there still value in the standard batch equilibrium adsorption/desorption study?
- Major differences exist in rates of equilibration in structured compared with non-structured soils
- Ageing of residues leads to reduction in water-phase availability
- How should we design experiments to determine the coupled “degradation” and adsorption parameters



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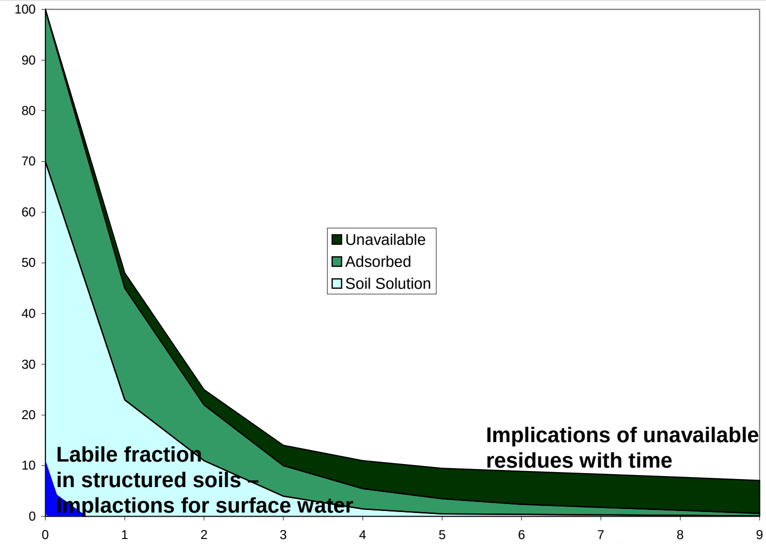
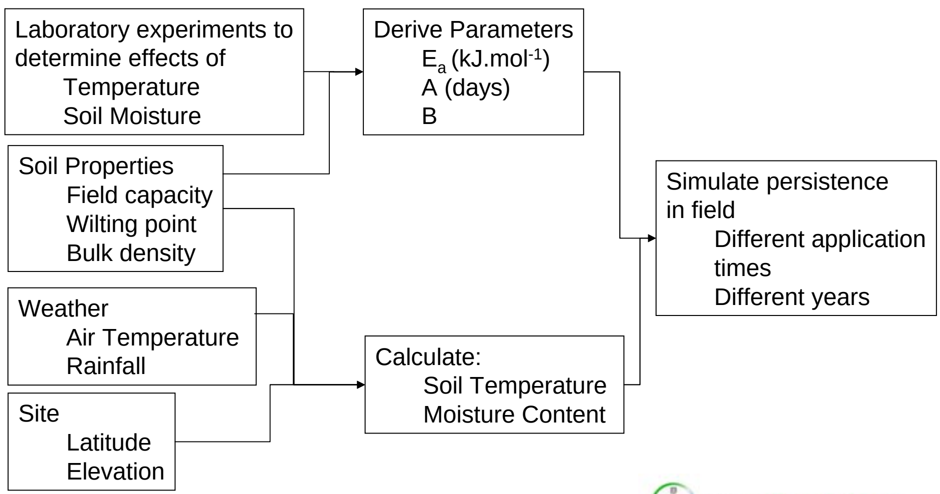
Changes in bioavailability with time



Influence of Temperature and Soil Moisture Content on Degradation Rates

- **Research driven by observations of differences in the performance and carry over effects of soil applied herbicides.**



Influence of Temperature and Soil Moisture Content on Degradation Rates

- Walker's concepts, if not specific algorithms, utilized in most simulation models
- Walker's principles used in derivation of model input parameters according to FOCUS guidelines
- Algorithms derived from a large number of studies of the degradation of herbicides in soil under controlled laboratory and field conditions:
  - e.g. Walker (1978): Simulation of the persistence of **eight** soil-applied herbicides. Weed Research <u>18</u>, 305-315
- Collaborative experiments with many coauthors
  - e.g. Walker et al. (1983): EWRS Herbicde Soil Working Group Collaborative Experiment on simazine persistence in soil. Weed Research <u>23,</u> 373-384
  - **16 sites** in multiple countries
- Experimentally derived, well validated quantitative descriptions of processes stand the test of time

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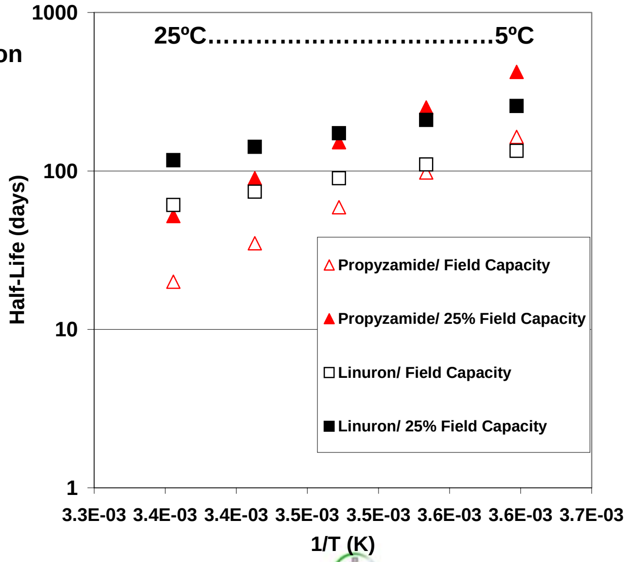
Dependence of Degradation Rates on Temperature

Classical Arrhenius Equation

Activation Energy (Ea) Dependent upon molecular structure and degradation routes/mechanisms

⇒Q_{10} = 2 to 3

Experimental derivation of the values here require 20 degradation studies!



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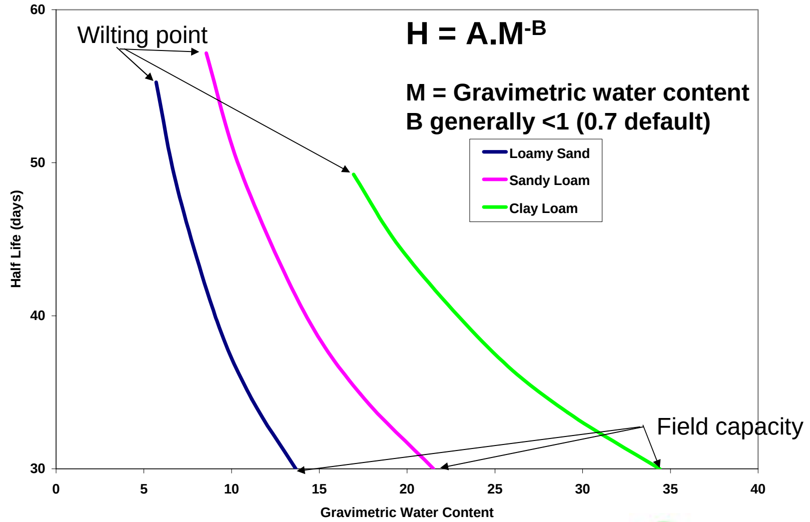
Dependence of Degradation Rates on Soil Moisture



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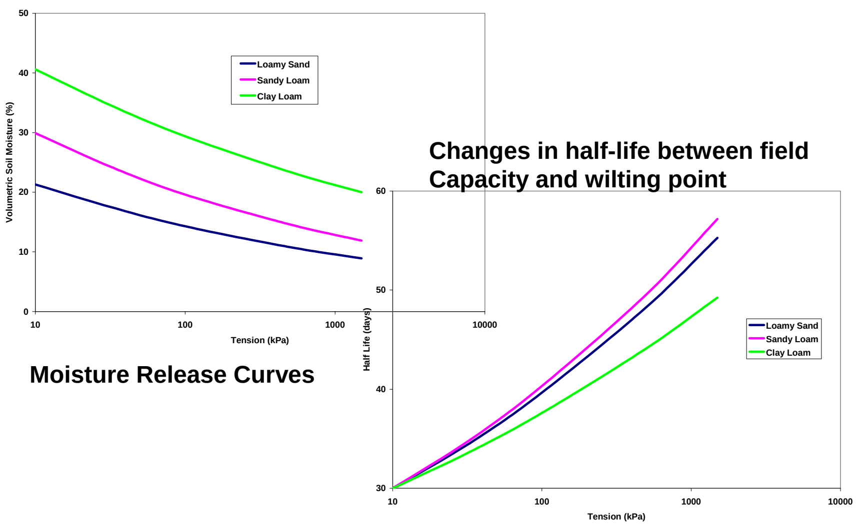
Dependence of Degradation Rates on Water Tension



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Simulation of Environmental Degradation and Sorption processes – our challenges

- **Recognition of the sensitivity of parameters to the objective of the simulation**
- **Improve our knowledge of the behaviour of compounds at the boundaries of environmental conditions:**
  - **At or around field capacity**
  - **dry conditions**
  - **structured soils**

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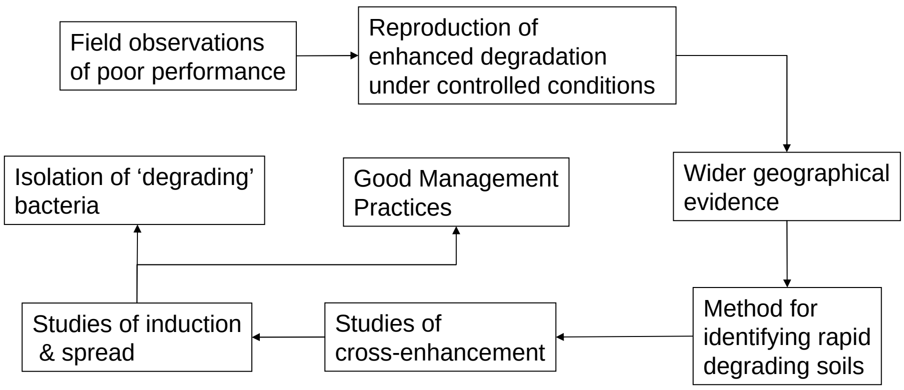
Enhanced Biodegradation

- Walker's research initiated by observations of loss of effectiveness of dicarboximide fungicides against *Sclerotium cepivorum* (white rot) in onions and leeks
  - Summarized by Walker & Welch (1990)ACS Symposium Series No. 426, pp 53-67



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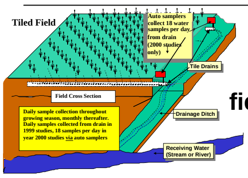
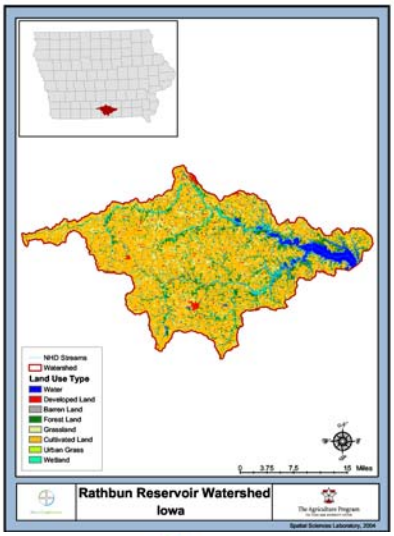
Current perspectives for microbiological and molecular aspects

- Continue to need good management practices to manage resistance and enhanced degradation
- Behaviour of pesticides in the rhizosphere – impact of crops
- Greater understanding of the processes controlling behaviour of pesticides in sub-soils and aquifers

Spatial Variability



field………….. watershed



Watershed – 350,000 Ac.
Reservoir - 11,000 Ac.

Land Cover
- Cropland – 31 %
- Grassland – 50 %

Soil
- Class-C – 68 %
- Class-D – 20 %
- Class-B – 10 %

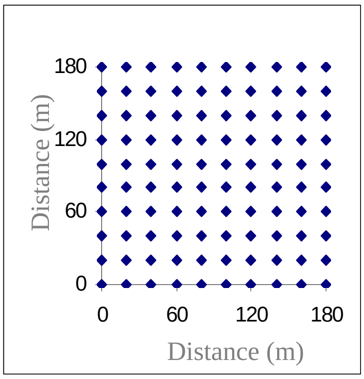
Spatial variability in pesticide/soil interactions

(Walker et al. (2001). Environmental Pollution 111, 407-415)

Geostatistical techniques allow us to:

Quantify the scale and structure of the variation that occurs

Predict behaviour at the field scale



Soil sampling:
100 samples taken on a regular grid at a spacing of 20 m

Soil properties:
Organic matter
pH
Dehydrogenase activity

Pesticide behaviour:
DT50 and Kd for isoproturon
DT50 for chlorpyrifos and chlorothalonil

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Spatial variation in pesticide sorption and degradation

Sorption of isoproturon:

Kd range from 0.42 to 1.08

Average = 0.80 ; Standard deviation = 0.17

Degradation rate:

DT50 range for IPU from 6.4 to 33 days (15 C; 40% MWHC)

Average = 19.0 ; Standard deviation = 6.95

DT50 range for chlorpyrifos from 25 to 120 days

DT50 range for chlorothalonil from 15 to 55 days

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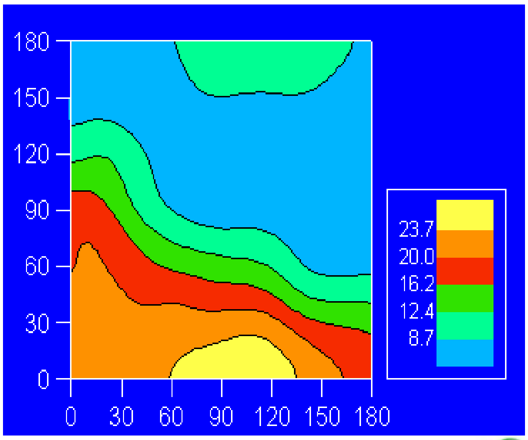
Spatial distributions of DT50 values for three pesticides

Isoproturon



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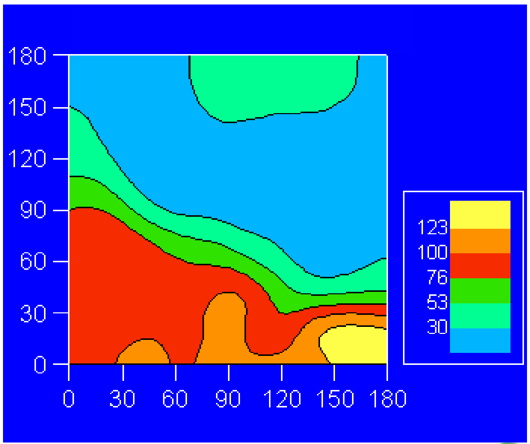
Spatial distributions of DT50 values for three pesticides

Chlorpyrifos



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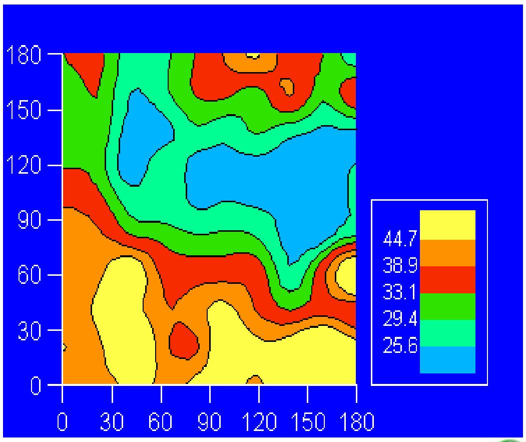
Spatial distributions of DT50 values for three pesticides

Chlorothalonil



Key lesson and our challenge – account for variability!

- Improve our understanding and description of the environment, esp. hydrology and how it influences the behaviour of pesticides
- Take account of the variation in environmental parameters at an appropriate scale and their sensitivity to different objectives/endpoints
- Develop and validate exposure assessment techniques that take account of these variations
- Develop risk assessment procedures that account for the distribution in exposure

Thank you for your attention!