Battelle
The Business of Innovation

Change in pesticide losses in drainflow with increasing time from application – experimental results and modelling

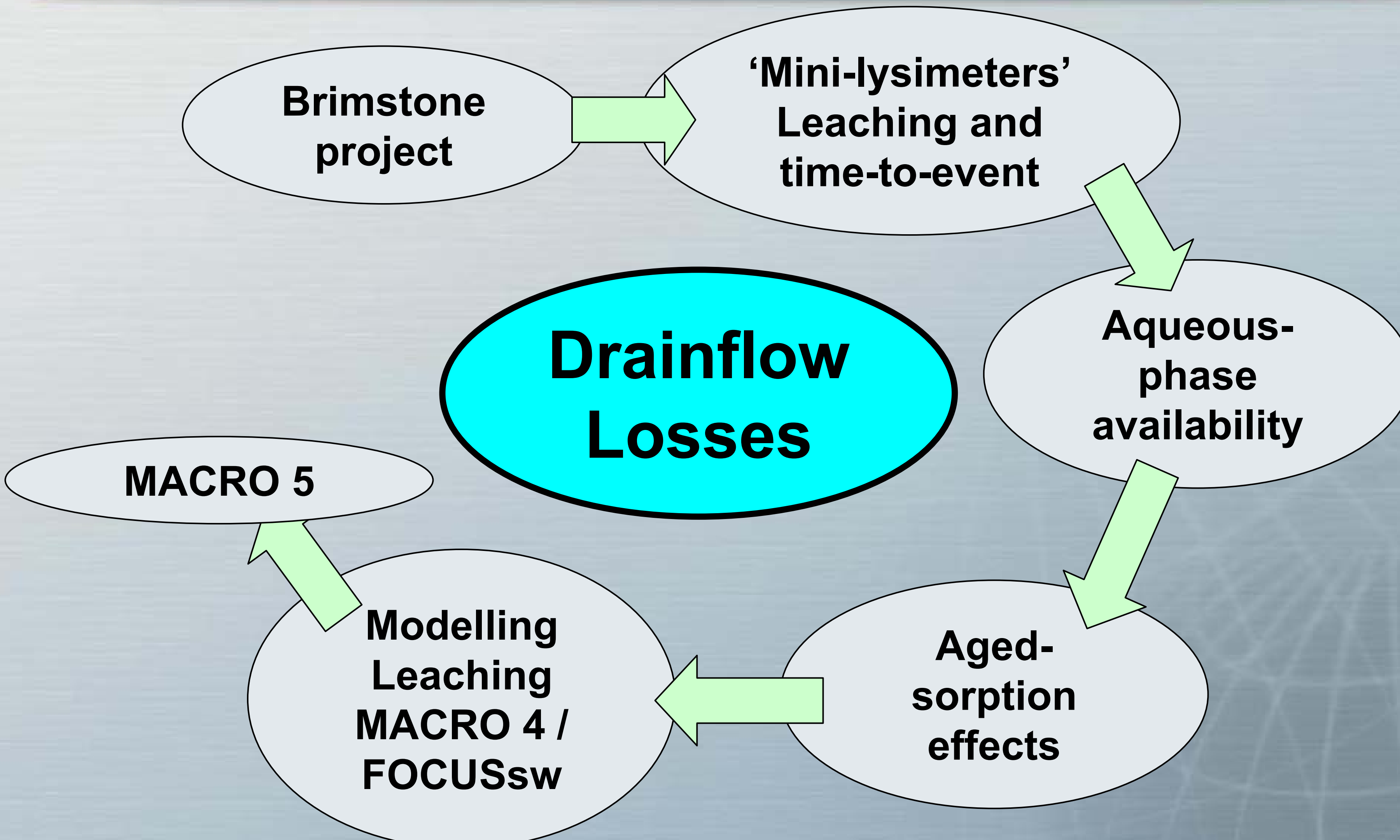
Ian Hardy

3rd European Modelling Workshop,
Catania,
17-19th February 2004

Acknowledgements

- Sabine Beulke
- Allan Walker
- Colin Brown / Fabrice Renaud
- Peter Nicholls
- Richard Bromilow
- Nick Jarvis
- The Brimstone Project team
- Chris Leake / Bayer

Overview



Brimstone project
'Mini-lysimeters' Leaching and time-to-event
Aqueous-phase availability
Aged-sorption effects
Modelling Leaching MACRO 4 / FOCUSsw
MACRO 5
Drainflow Losses

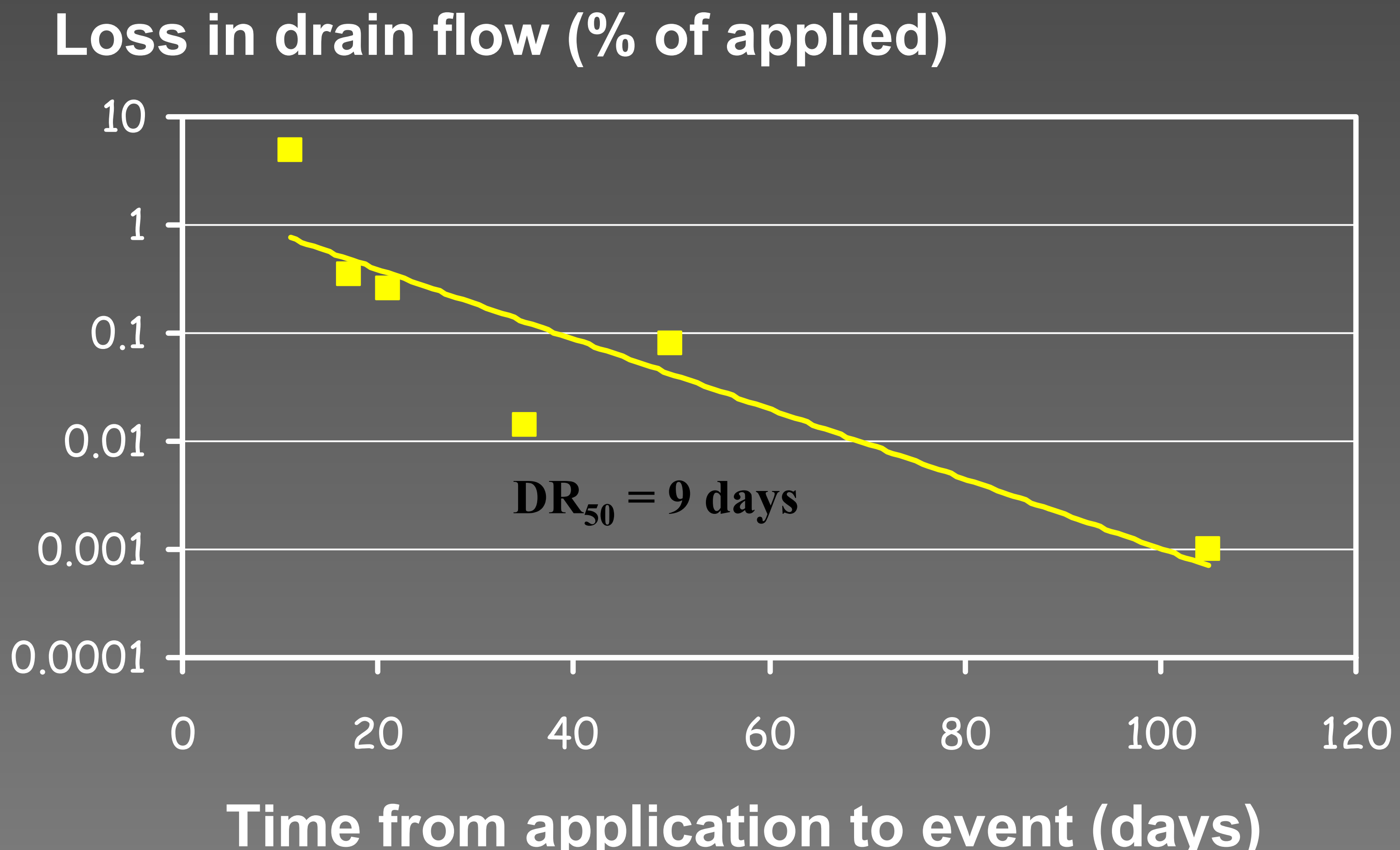
Laboratory column investigation of preferential flow of pesticides, particularly the loading and unloading of macropores

R.H. Bromilow, P.H. Nicholls and A. A. Evans

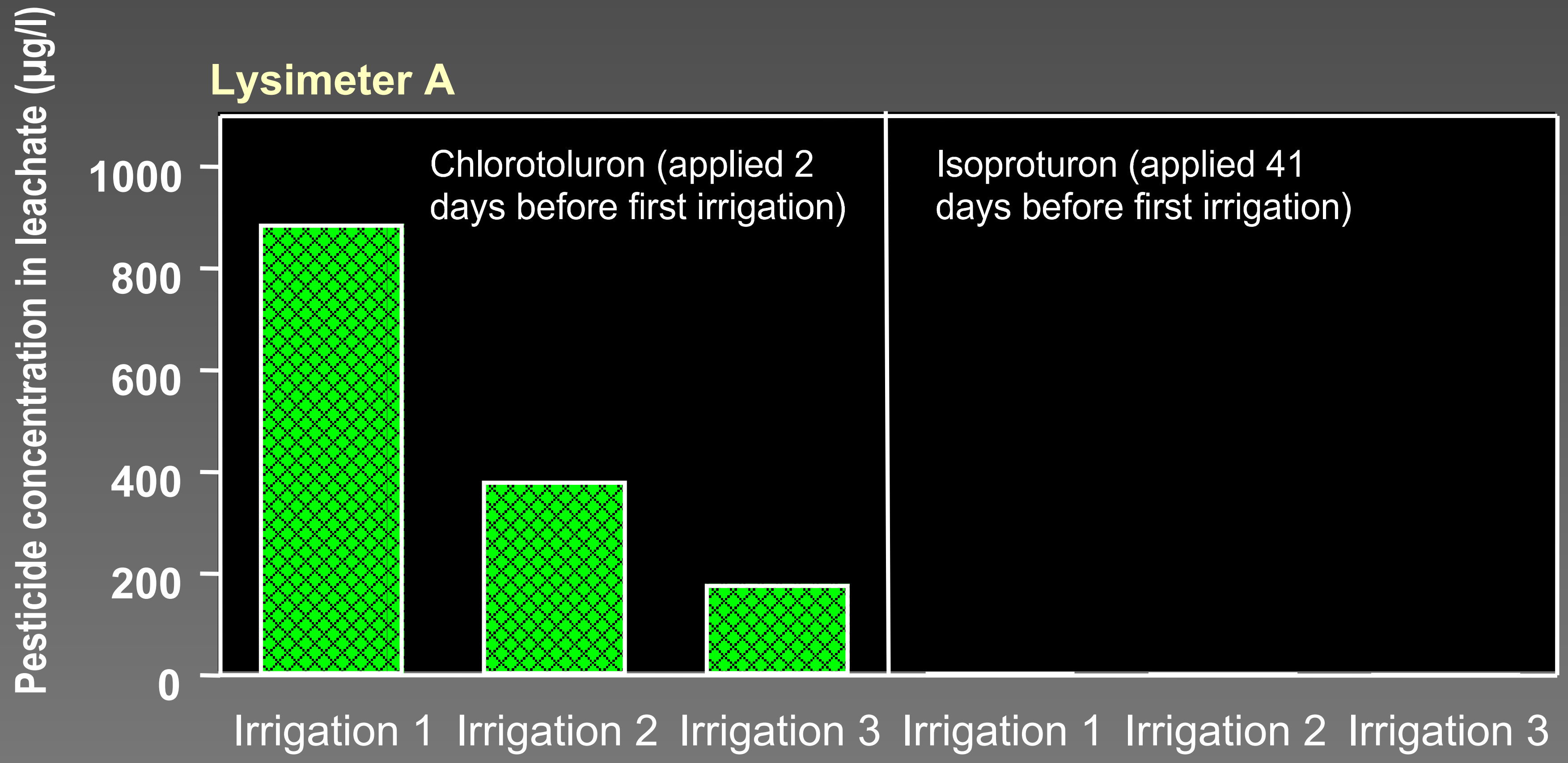
DEFRA project:- PL0540

ROTHAMSTED RESEARCH

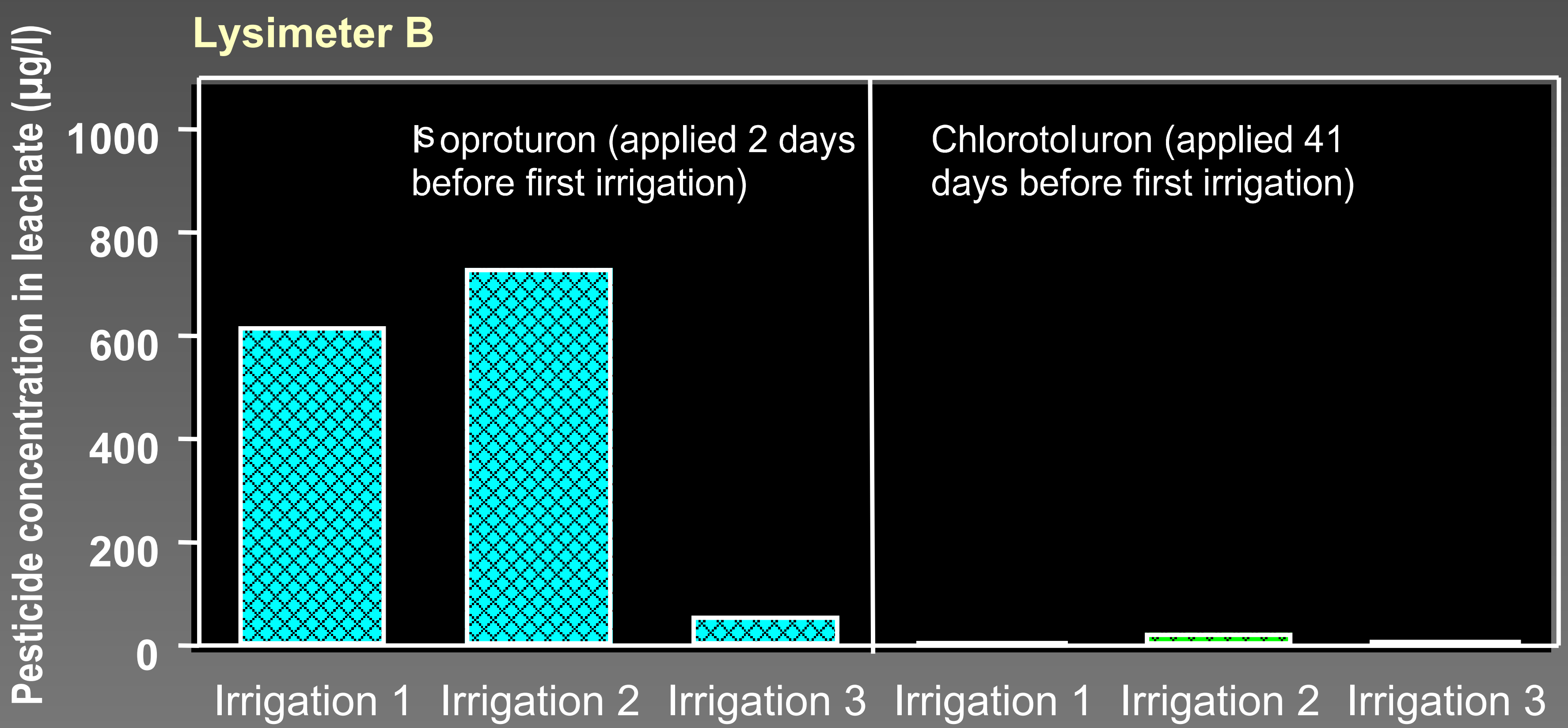
Time to first drain flow determines loss of isoproturon in drainage at Brimstone Farm



Concentration in drainage water from lysimeters (30 cm deep) of herbicides applies 2 days or 41 days before the first drainage event



Concentration in drainage water from lysimeters (30 cm deep) of herbicides applied 2 days or 41 days before the first drainage event



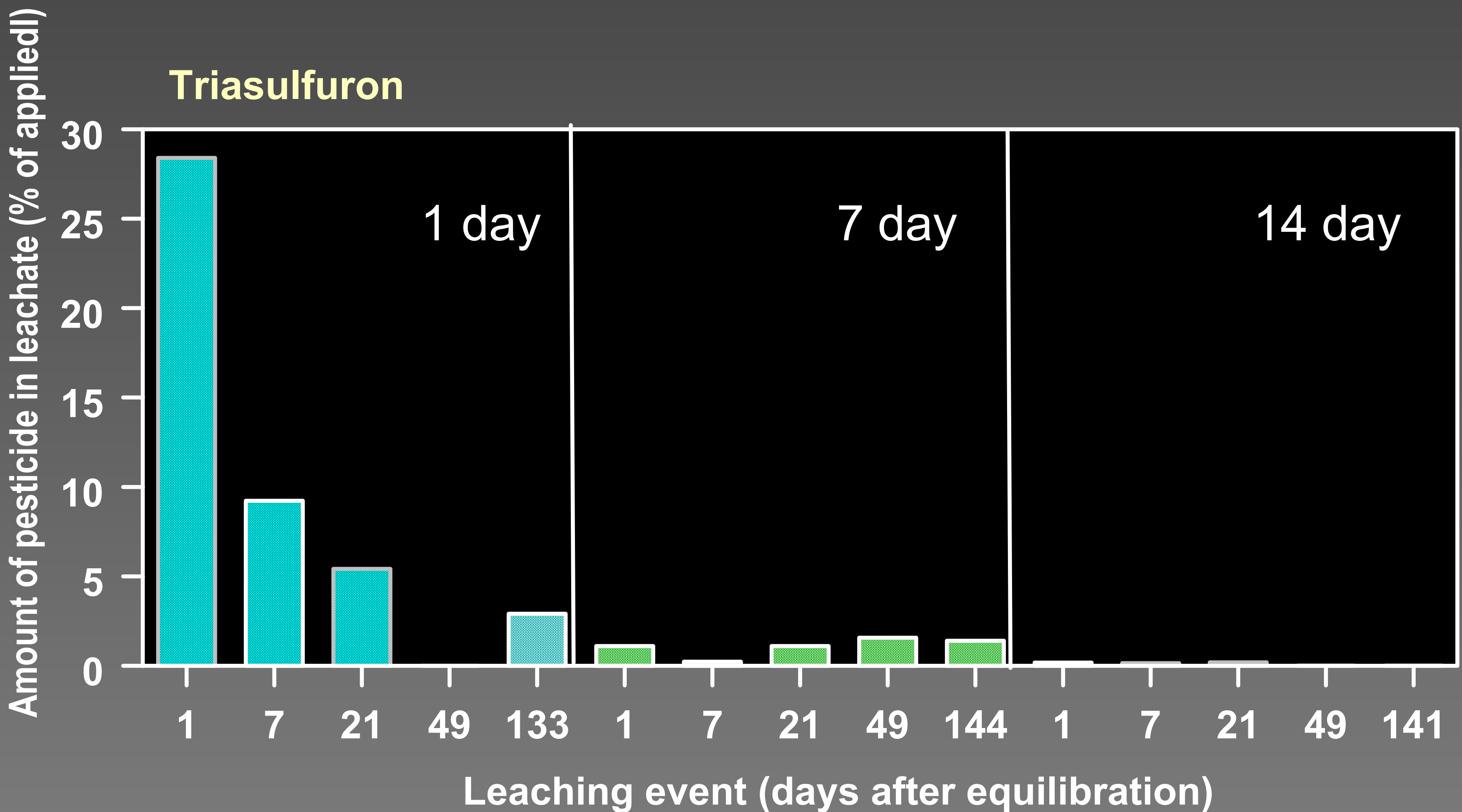
Experimental procedure for leaching tests

Herbicides applied at field rates:-

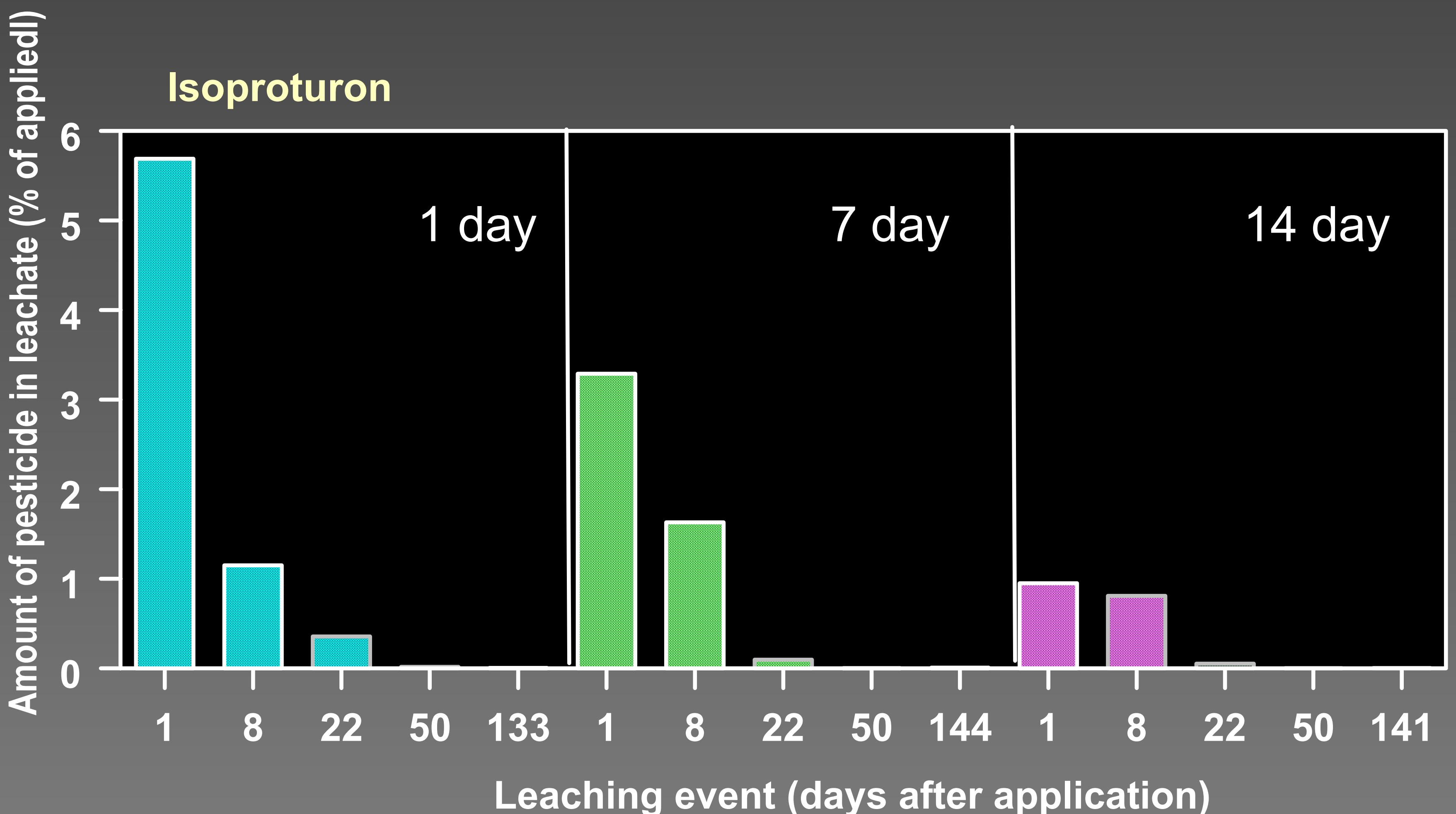
Triasulfuron (log Kow 1.6, pKa 4.64)
Chlorotoluron (log Kow 2.5)
Isoproturon (log Kow 2.48)
Pendimethalin (log Kow 5.18)

After equilibration periods at 10°C of 1, 7 or 14 days, irrigation of 27 mm was applied at 0, 7, 14 and 28 days subsequently; leachate was analysed by HPLC.

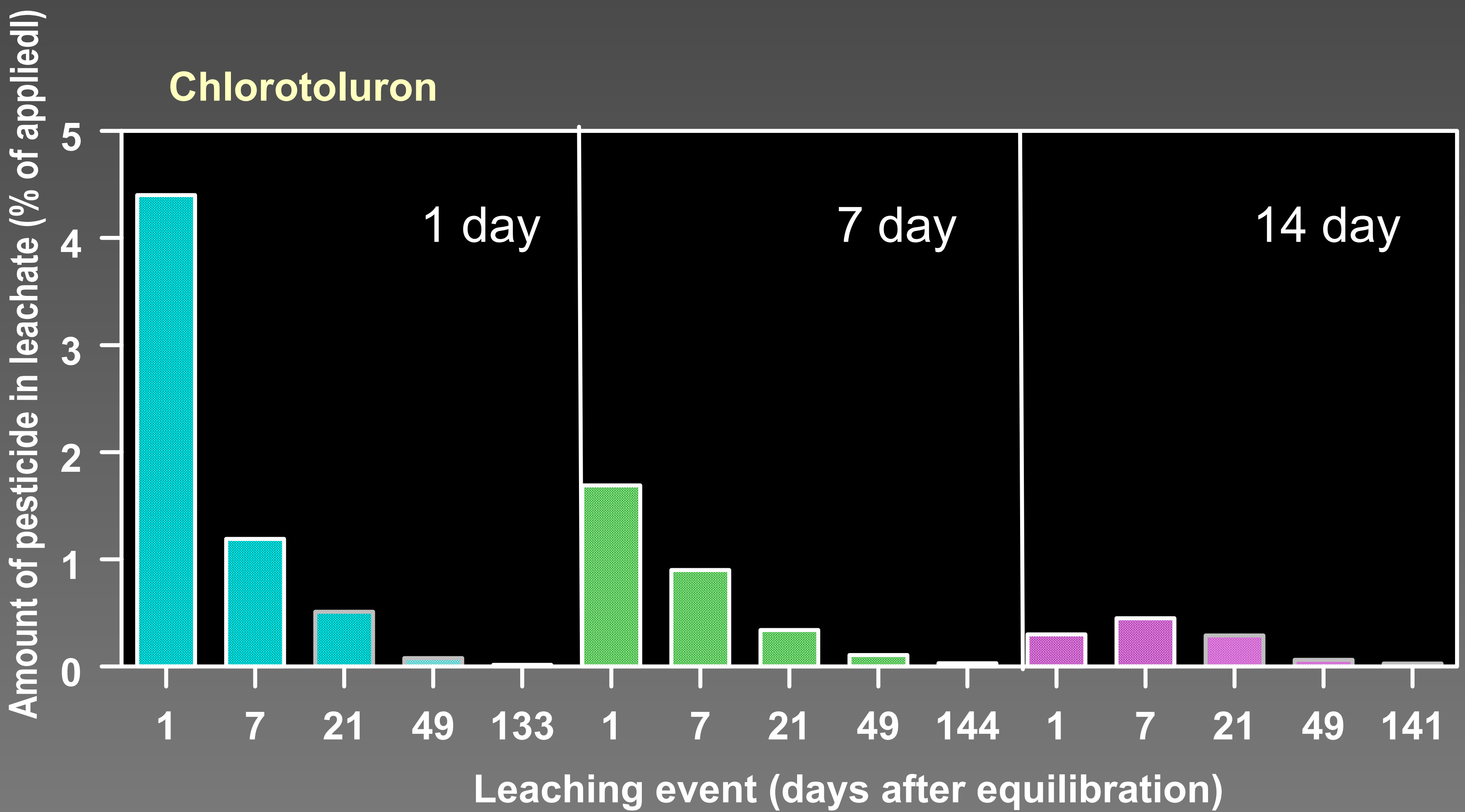
Amount lost in drainage from mini-lysimeters of herbicides applied 1, 7 or 14 days before the first drainage event



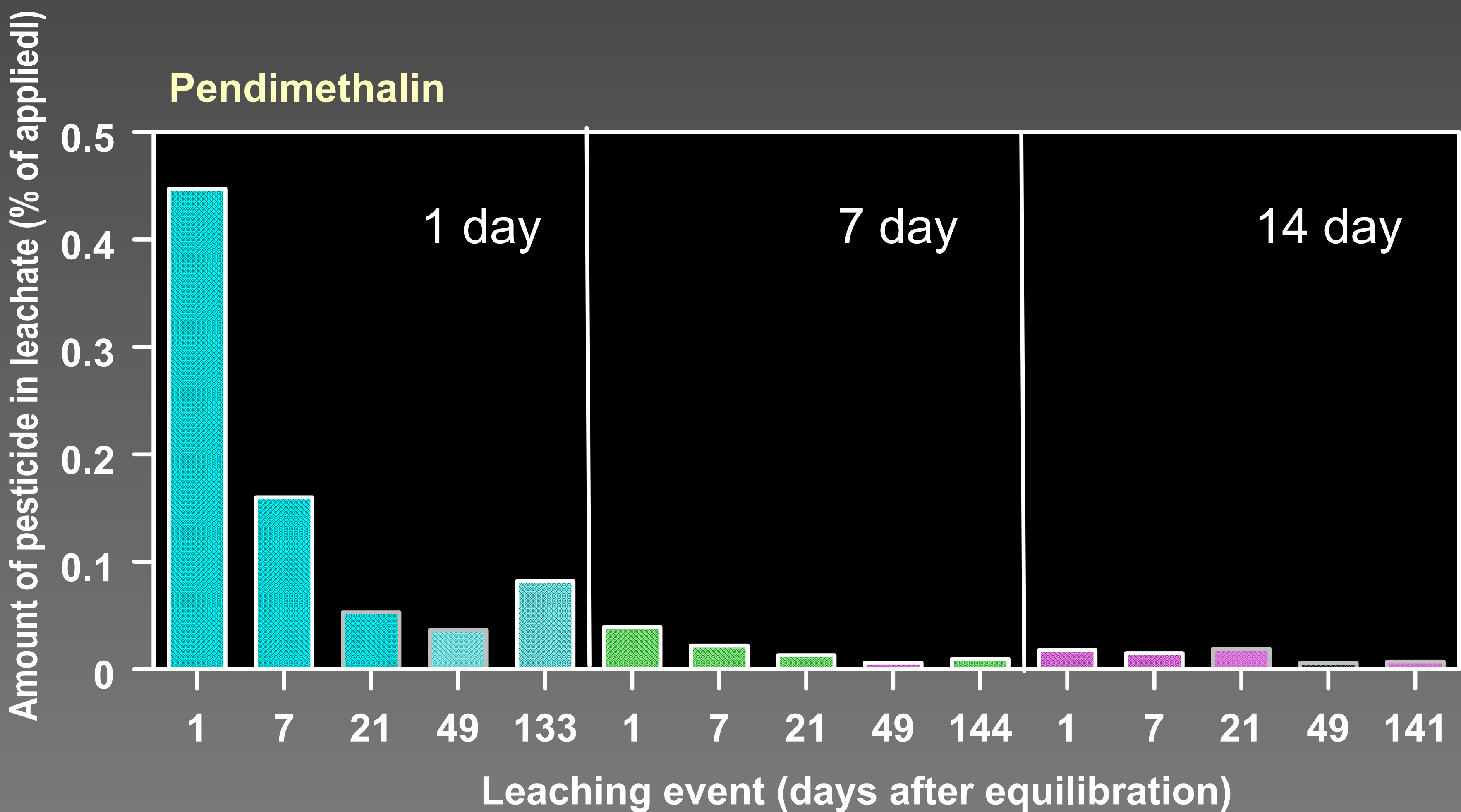
Amount lost in drainage from mini-lysimeters of herbicides applied 1, 7 or 14 days before the first drainage event



Amount lost in drainage from mini-lysimeters of herbicides applied 1, 7 or 14 days before the first drainage event



Amount lost in drainage from mini-lysimeters of herbicides applied 1, 7 or 14 days before the first drainage event



Conclusions

- Pendimethalin was only leached in small amounts
- Phenylureas were lost to a greater extent (up to 5.7%)
- Losses in later events were small especially for isoproturon
- Losses of weakly sorbed triasulfuron were larger but of a similar pattern to that of pendimethalin

Battelle

The Business of Innovation

Change in pesticide losses in drainflow with increasing time from application – experimental results and modelling – Part 3

Ian Hardy

3rd European Modelling Workshop,
Catania,
17-19th February 2004

Overview

Drainflow Losses

Brimstone project

'Mini-lysimeters' Leaching and time-to-event

Aqueous-phase availability

Aged-sorption effects

Modelling Leaching / MACRO 4 / FOCUSsw

MACRO 5

Aqueous-Phase Availability

- Many researchers have studied the aqueous-phase availability of pesticide residues with time
- Results show that residues in the aqueous phase of soils decreases more rapidly with time than the overall degradation rate in the bulk soil
- This has predominantly been considered for leaching, but will also have a significant effect on drainage losses
- At Brimstone, the decline in drainflow concentrations for IPU has an DR_{50} of ~ 9-days but the bulk soil degradation rate (DT_{50}) is ~ 30-days

Aqueous-Phase Availability

- Aggregate studies by Beulke, Brown and Fryer (Piacenza, 2003)
- Considered the effects of wet and dry aggregates on availability of IPU residues for leaching, using centrifugation techniques
- Considered the decline of residues in leachate, soil water and total soil residues :

	Initially dry		Initially wet	
	DT_{50} (days)	r^2	DT_{50} (days)	r^2
Leachate	11	0.99	10	0.98
Soil water	13	0.93	9	0.95
Total soil residues	16	0.97	17	0.96

Aqueous-Phase Availability

- Mini-lysimeter studies by Renaud, Brown, Fryer and Walker – *In-press*
- Intact soil cores (20x30cm) of four soils (Wick, Brockhurst, Hanslope and Lawford)
- Isoproturon (IPU), Chlortoluron (CTU), Triasulfuron and Bromide
- 4-Replicate cores at timepoints up to 60 days were randomly selected and irrigated with 24mm ‘rainfall’
- Degradation (intact cores and lab) and sorption studies also conducted in parallel

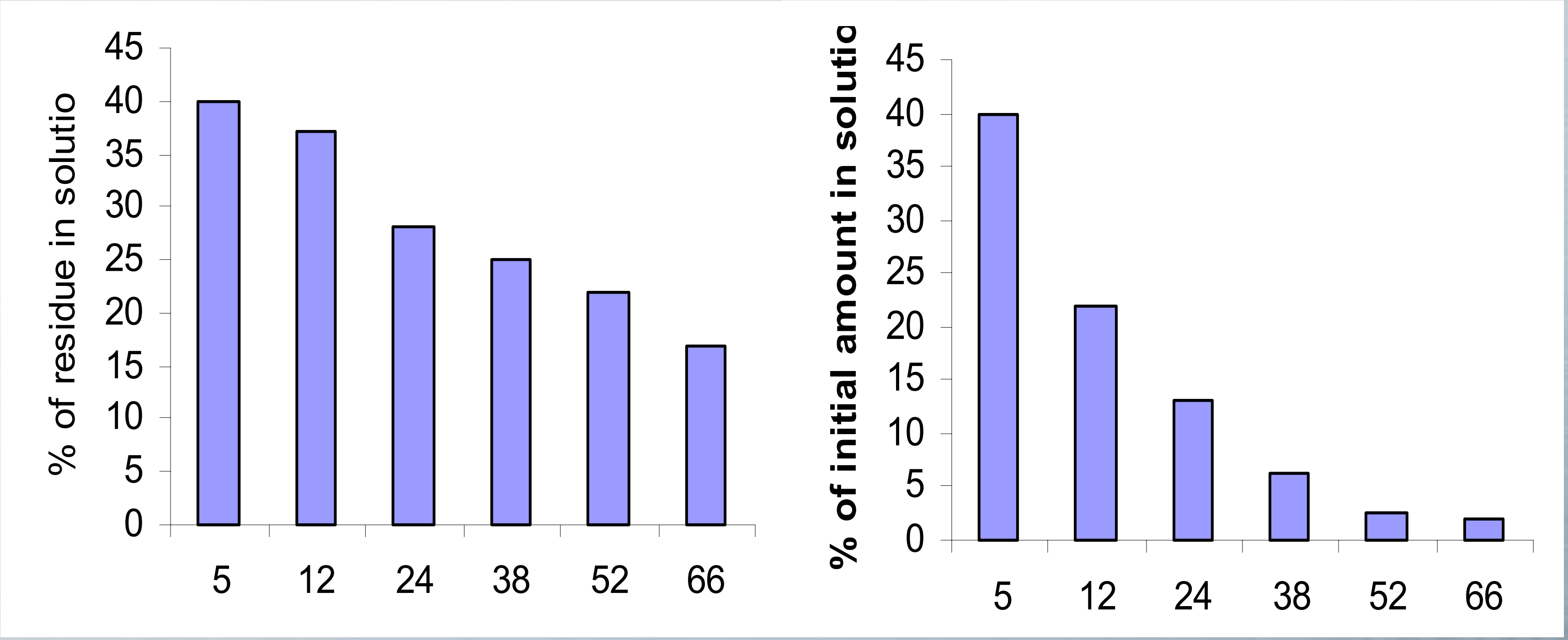
Aqueous-Phase Availability

Results for all four soils show a significantly more rapid decline in the losses in leachate for all compounds compared to the total soil degradation (lab or intact core) :

	Wick		Brockhurst		Hanslope		Lawford	
	IPU	**CTU**	**IPU**	**CTU**	**IPU**	**CTU**	**IPU**	**CTU**
LR_{50}	5.8	4.3	11.6	11	2.6	1.9	5.4	4.8
DT_{50core}	22	75	23	-	-	-	32	94
DT_{50lab}	45	97	55	118	33	-	59	-

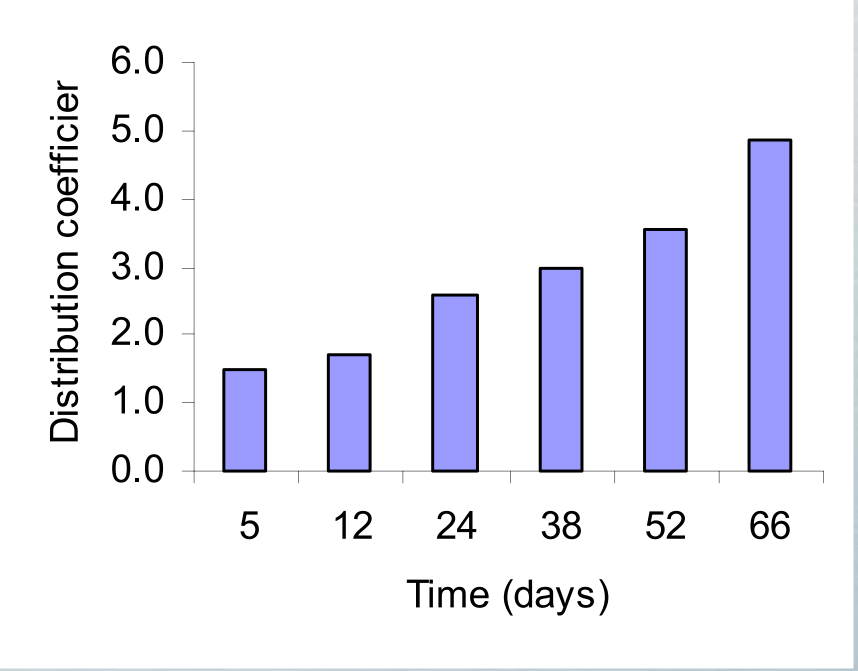
LR_{50} – half-life for leached loads (days)
DT_{50core} – half-life for total residues in soil core (days)
DT_{50lab} – lab half-life at 0.33bar and $5^{o}C$ (days)

Aqueous-Phase Availability



IPU sorption studies on Denchworth soil from Brimstone (Jones *et al*, 2000)

Aged-sorption



- Apparent increase in K_d from 1.5 to 5 for IPU on Denchworth soil

Aged-sorption

- *In-situ* K_d experiments run as part of long-term aerobic soil studies (~100 days)
  - At each timepoint soils are first extracted with $CaCl_2$ to determine C_w and then with organic solvents to determine C_s - K_d then calculated for each timepoint
- Aged-desorption studies (Leake *et al*, BCPC 2001, Cremona 1999)
- Compound applied to soil, incubated for up to 10-days and then partitioned with $CaCl_2$ (cf OECD 106)
- Multiple concentrations and times – K_{fdes} and 1/n can be determined

Aged-sorption

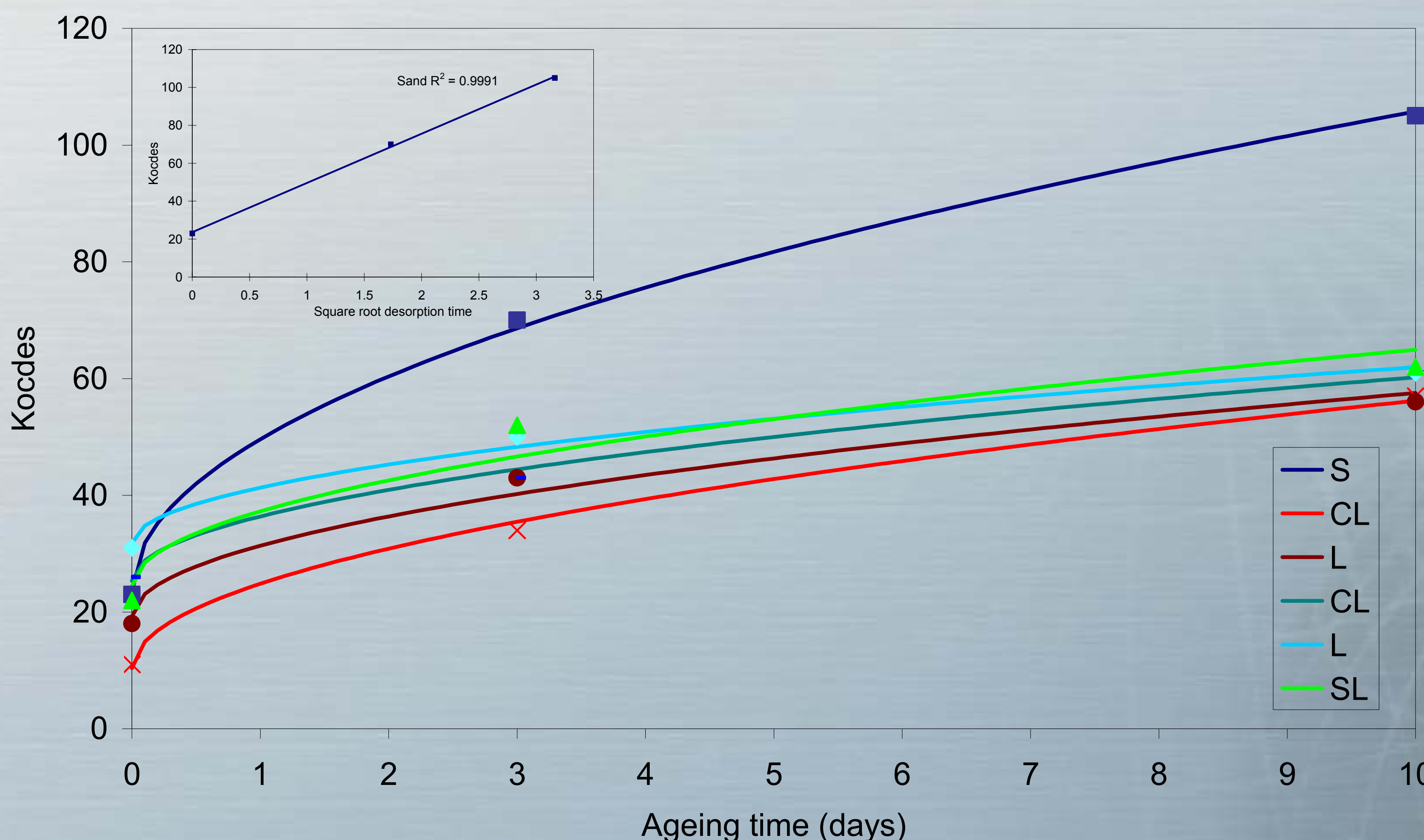
Soil reference (USDA)	Day 0 $K_{oc\ des1}$	Day 3 $K_{oc\ des1}$	Day 10 $K_{oc\ des1}$
Loam	18 (1)	43 (2.4)	56 (3.1)
Sand	23 (1)	70 (3.0)	105 (4.6)
Clay loam	11 (1)	34 (3.1)	57 (5.2)
Silt loam (sediment)	32 (1)	41 (1.3)	ND
Bologna (clay loam	26 (1)	43 (1.7)	61 (2.3)
Chazay (loam)	25 (1)	26 (1.0)	53 (2.1)
Goch (loam)	31 (1)	50 (1.6)	61 (2.0)
Manningtree (sandy loam)	22 (1)	52 (2.4)	62 (2.8)
Overall mean values	23.5 (1)	44.9 (1.9)	65.0 (2.8)

ND – Not determined. Figures in parentheses are ageing factors, calculated by dividing by the K_{ocdes1} at Day 0.

- For IPU, similar experiments show an increase of ~3-fold over the 10 days

Aged-sorption

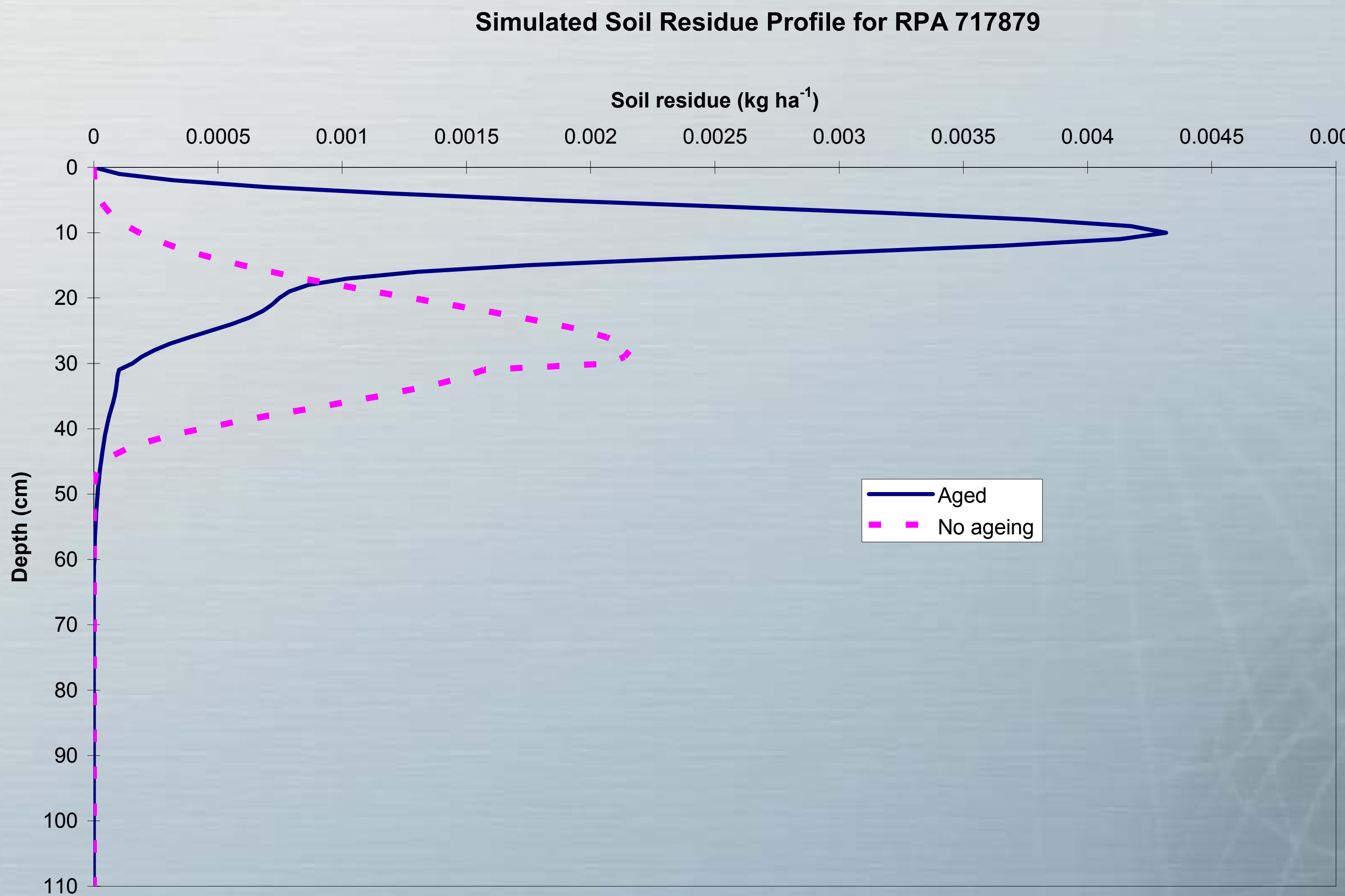
- Diffusive mechanism appears to be in operation – based on Square-root function with time :



Modelling - Leaching

- Mobility in soil measured under field conditions compared to PELMO modelling predictions using site-specific degradation, soil, sorption and weather data
- Mobility under field conditions could only be simulated by taking into account the increase in sorption with time
- Soil residues confined to 0-10cm (with two low level detects in 10-20cm)

Modelling - Leaching

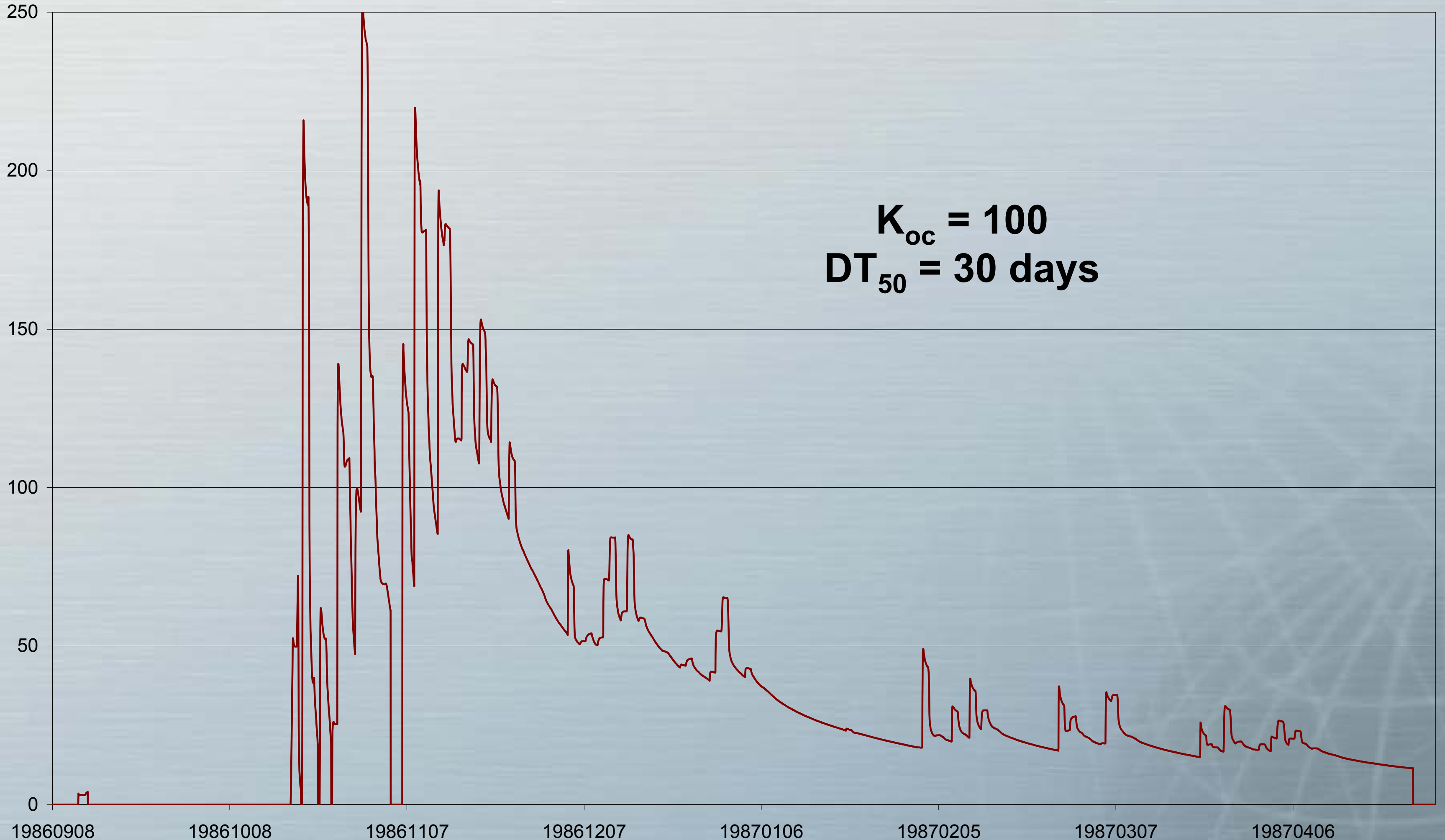


Battelle
The Business of Innovation

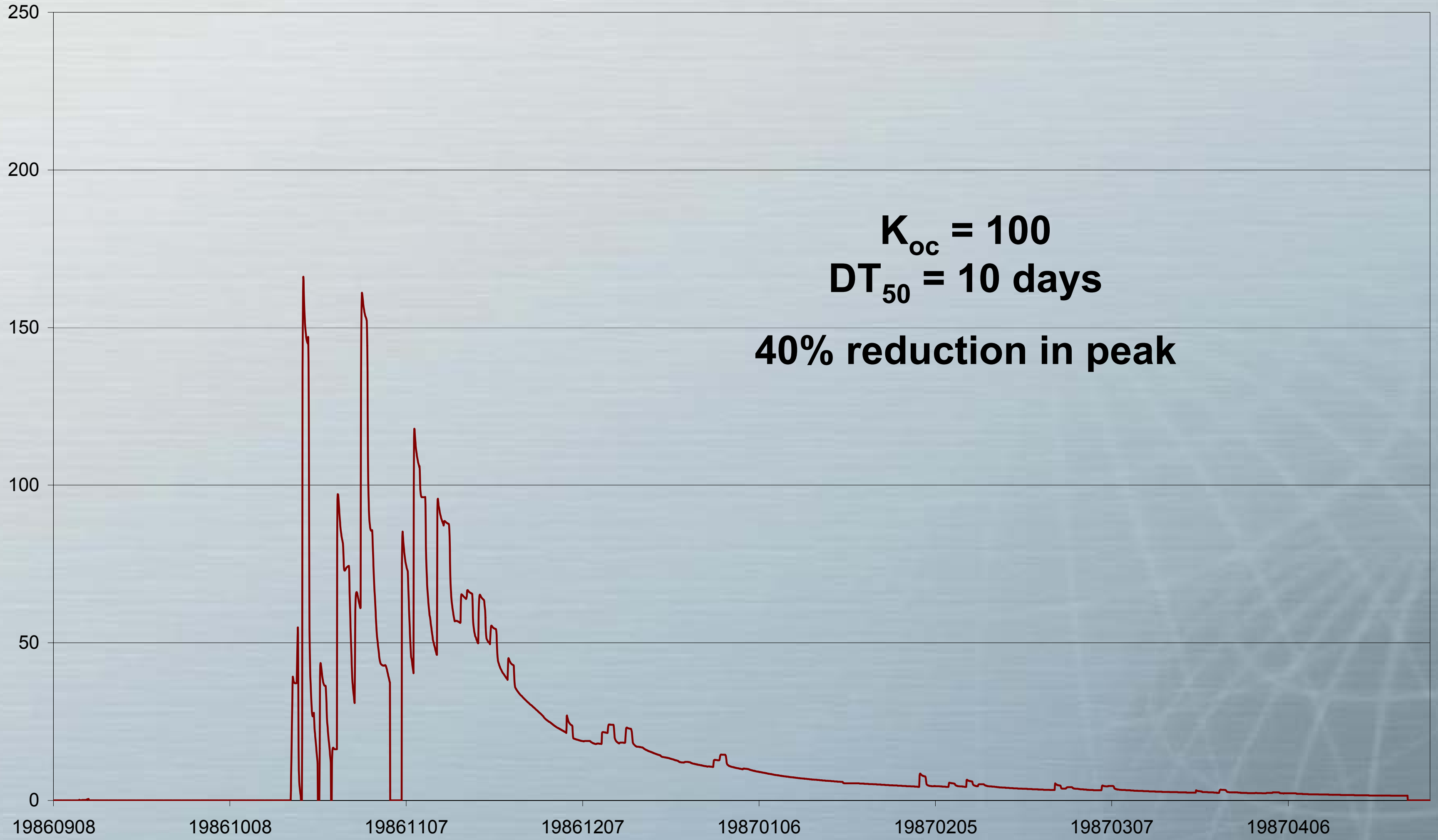
Modelling – Drainage Concentrations

- What impact do aqueous availability and increases in sorption with time have on drainflow concentrations ??
- Measured drainflow concentrations at Brimstone ‘drop-off’ more rapidly than predicted using bulk soil DT_{50} and K_{oc}
- Some simple comparisons run using the FOCUSsw D2 (Brimstone) MACRO scenario
- 1kg/ha to winter cereals on day 283 (mid-Oct), K_{oc} = 100 and DT_{50} =30 days

Modelling – Drainage Concentrations



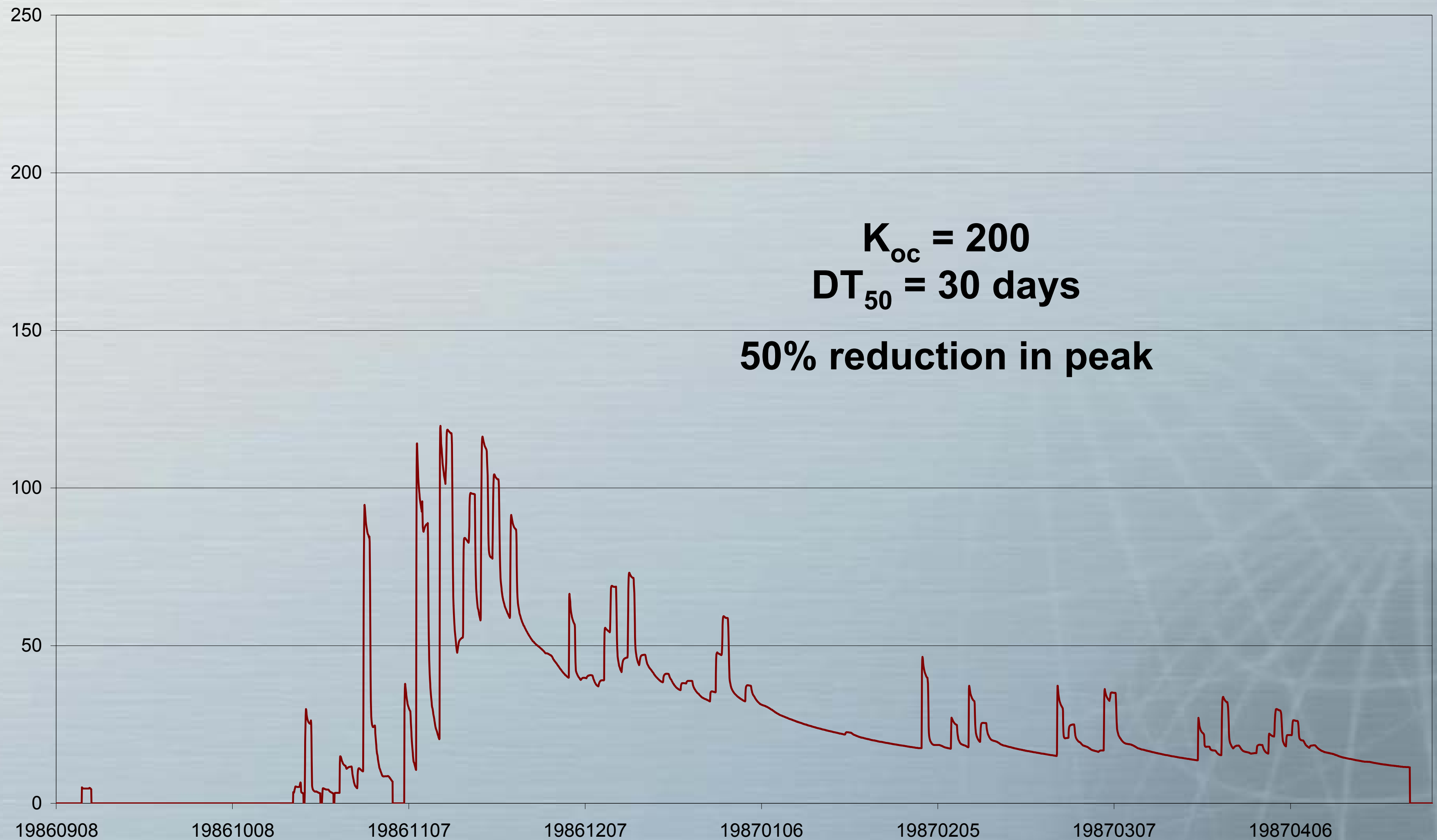
Modelling – Drainage Concentrations



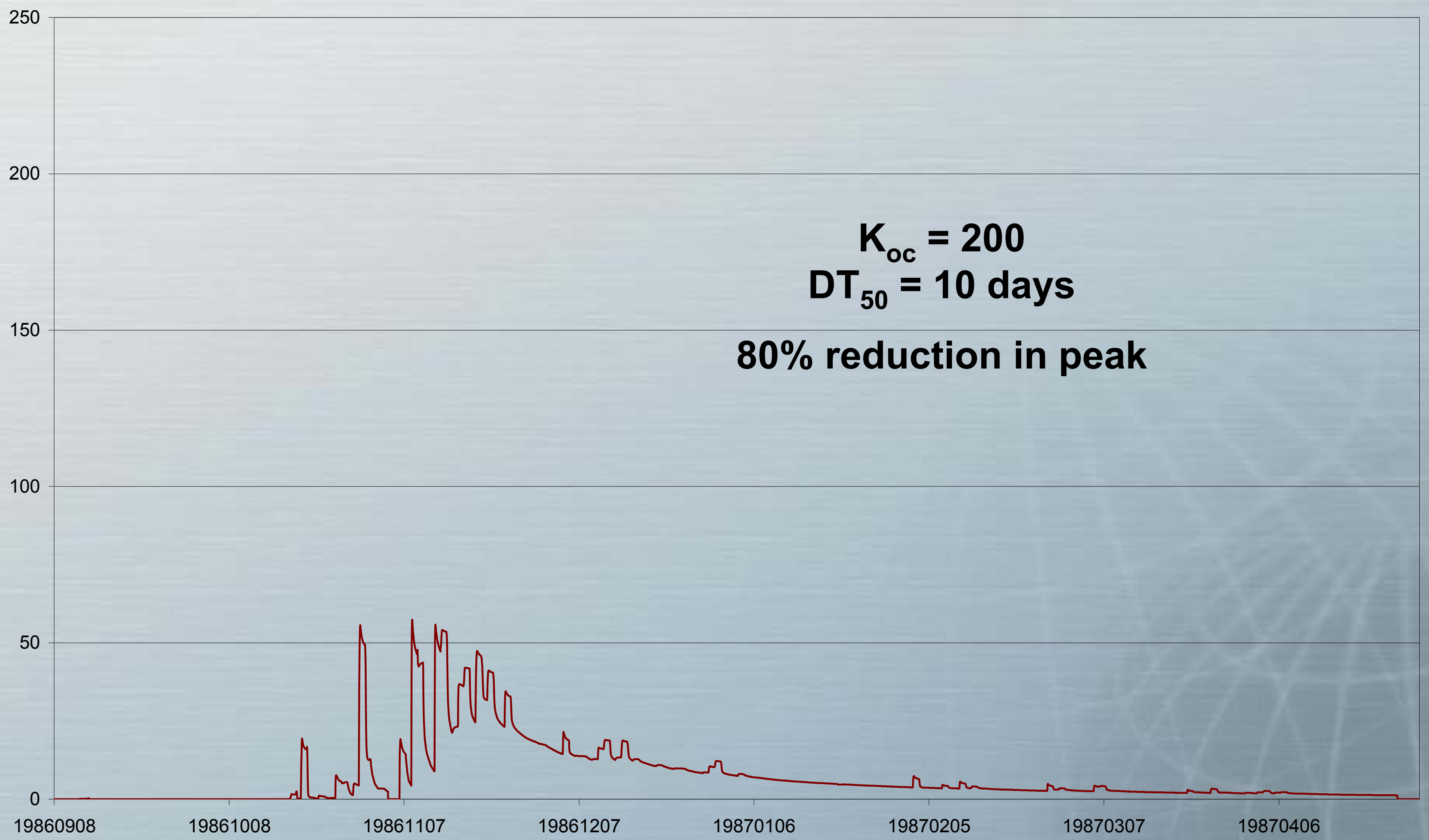
K_{oc} = 100
DT_{50} = 10 days

40% reduction in peak

Modelling – Drainage Concentrations



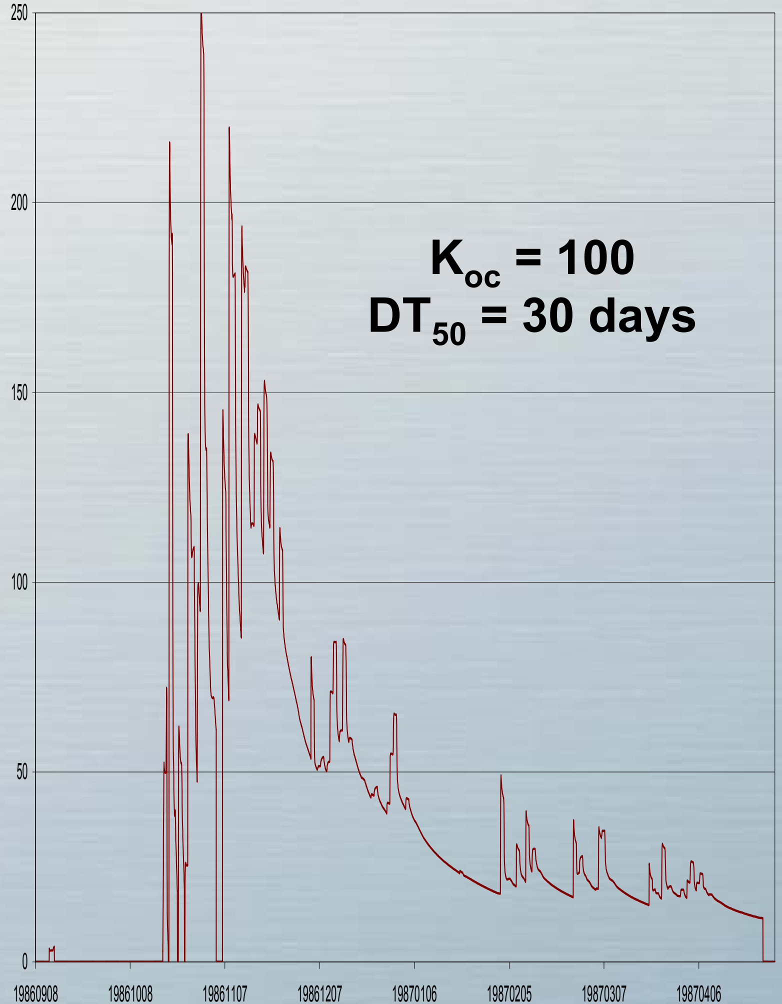
Modelling – Drainage Concentrations

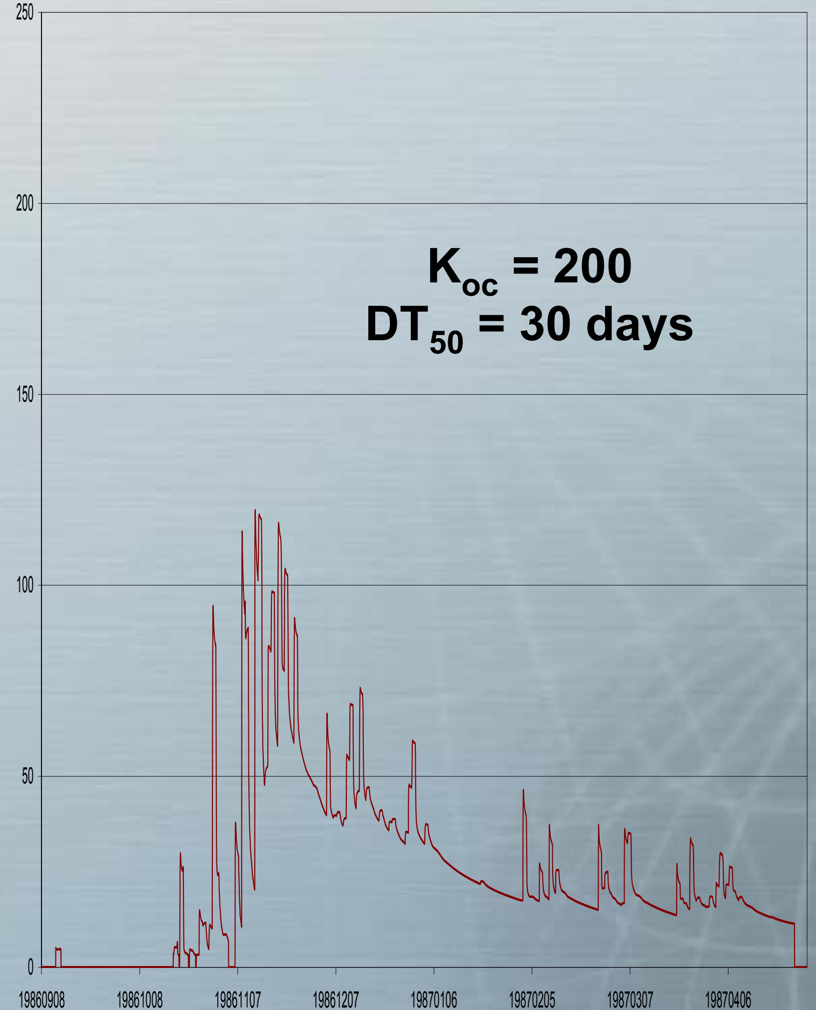


K_{oc} = 200
DT_{50} = 10 days

80% reduction in peak

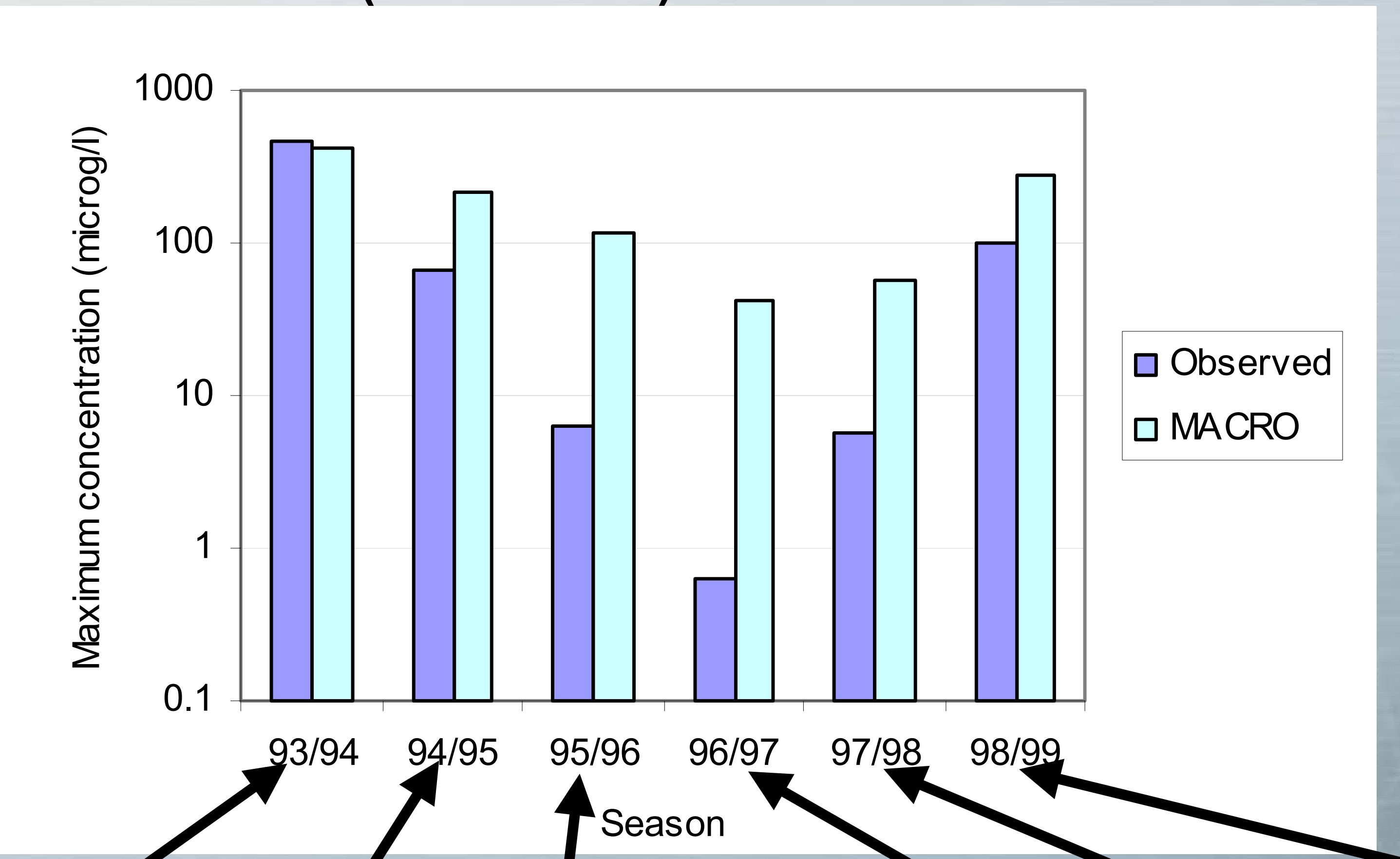
Modelling – Drainage Concentrations





Modelling – Drainage Concentrations

- Predicted (MACRO) vs observed conc. At Brimstone



Early-Dec Early-Dec Early-Jan Mid-Feb Late-Dec Late-Oct

Modelling – Drainage Concentrations

- MACRO 4 predicted maximum IPU drainage concentrations quite well for those years where drainflow started relatively ‘shortly’ after application
- For those years where drainflow started significantly later (95/6, 96/7 and 97/8), MACRO significantly over-predicted the IPU losses in drainflow by 1-2 orders of magnitude
- Aqueous availability and Increased / kinetic sorption effects ???

Modelling – MACRO 5

- Nick Jarvis has implemented kinetic sorption into MACRO 5 (similar system to PEARL)
- Project is underway to analyse the Brimstone dataset and assess the impact of kinetic sorption to drainage losses
- Initial thoughts suggest that the reduction at Brimstone is due to enhanced microbial degradation following repeated applications (based on the analysis of plot 9 data only)
- Pete Nicholls does not agree !! - rapid decline in drainage losses seen in early years
- Likely to be a significant effect for ‘coarser’ soil types in reducing drainage loss predictions

Discussion Points

- Aged-sorption studies generally indicate a diffusive mechanism – is this consistent with the 'kinetic sorption' implementation ?
- Can occur even for compounds that exhibit pseudo first-order degradation in soil (eg IPU, CTU)
  - Bi-phasic kinetics not a pre-requisite
- Impact on FOCUSsw predictions ?
  - Maybe not a large impact on 'Level 1' assessments
  - Significant impact on higher-tier evaluations
- Implementation / validation in MACRO 5

References

- S Beulke, C D Brown and C J Fryer, **2003**
  'Influence of Kinetic sorption and diffusion on pesticide movement through aggregated soils'. Piacenza 2003
- C R Leake, C M Burr, I A J Hardy, S L McMillan-Staff, G Reinken and R J Wicks, BCPC No. 78, 2001
  'The measurement of time-dependant desorption and its influence on modelling movement of a pesticide metabolite through soil to groundwater'
- R L Jones, D J S Arnold, G L Harris, S B Bailey, T J Pepper, D J Mason, C D Brown, P B Leeds-Harrison, A Walker, R H Bromilow, D Brockie, P H Nicholls, A C C Craven, C M Lythgo, Pesticide Outlook 2000
  'Processes affecting movement of pesticides to drainage in cracking clay soils' Final report of the Brimstone Farm Project
- F G Renaud, C D Brown, C J Fryer and A Walker, in-press
  'A lysimeter experiment to investigate temporal changes in the availability of pesticide residues for leaching'
- C R Leake, I A J Hardy, S L McMillan-Staff, P Lowden and G Reinken, Cremona 1999
  'The influence of aged and unaged adsorption and desorption constants on the assessment of xenobiotic leaching potential'