

Session II Keynote

Recent developments in measurement and simulation for pesticide exposure and risk assessment

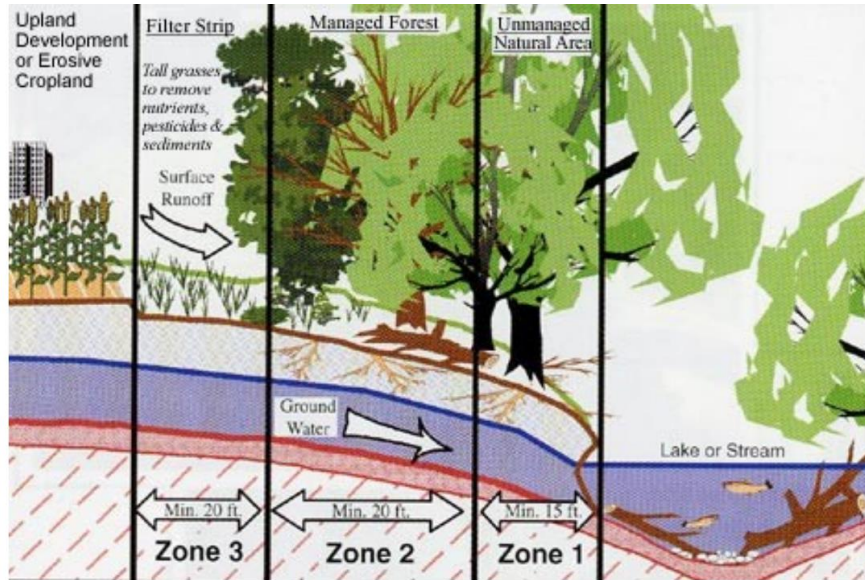
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With: A. Howe · S. Reichenberger · R. Sur



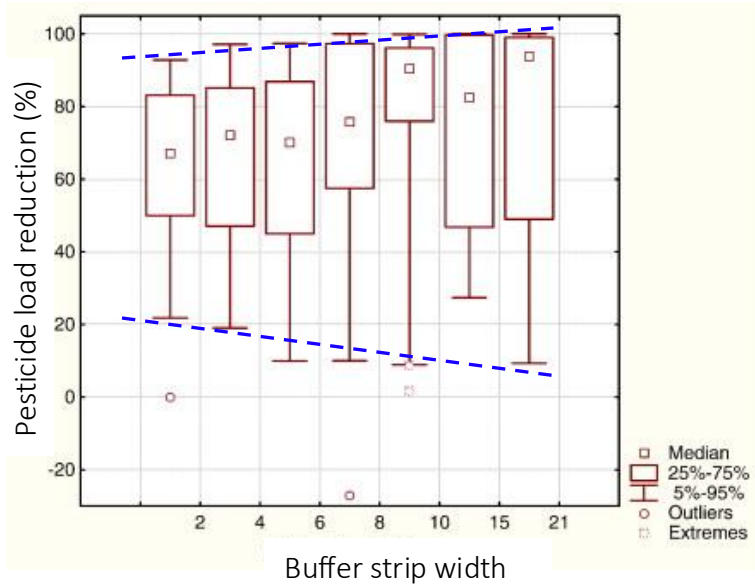


Buffer zonation after USDA NRCS

- Meeting global demand for agricultural products means plant protection products are used — and their use raises the risk of adverse impacts on off-target species.
- Vegetative filter strips are the most widely employed mitigation practice in pesticide regulatory assessments for surface runoff.
- They are widely adopted by farmers and when properly designed and maintained, among the most effective mitigation practices.
- Risk reduction is not measured field by field — it is credited through higher-tier environmental risk assessment, i.e. through a model.

So the mitigation credit is only as good as the model

VFSMOD, coupled with PRZM and TOXSWA through SWAN, is what turns a strip of grass into a number in a regulatory dossier. Every assumption inside it is doing regulatory work.



Reported pesticide load reduction vs buffer width — the spread at any width is larger than the trend

Empirical (L&M factors)

Width alone explains little. Soil, storm, vegetation and chemistry all move the answer.

What the mechanistic route buys

Physically realistic and generalizable runoff partitioning and infiltration, sediment filtration, mixing-layer leaching with dissolved and sorbed redistribution, degradation, remobilization and carry-over — event by event, over a 20-year record.

But several of its processes have never been measured

MOTIVATION

VFSMOD was built and tested on single storms. It is now used for multi-event, long-term regulatory exposure assessment — and it carries assumptions that single-event data could never test:

1

Residues between storms

the worst-case scheme returns all mixing-layer mass to the next storm

2

Vegetation as a sink

plant uptake and adsorption are assumed negligible

3

Sorption at real concentrations

linear K_d , where runoff sits far below C_{ref}

4

What the sensors actually measure

Dynamic, multi/storm patterns of flow and transport in VFS

Regulatory realism is limited by what we have actually measured — and by what the numerics can resolve.

This talk

One experimental system built to test those four assumptions directly, a bench-scale set to isolate two of them, and what the answers changed inside VFSMOD.

Hypotheses

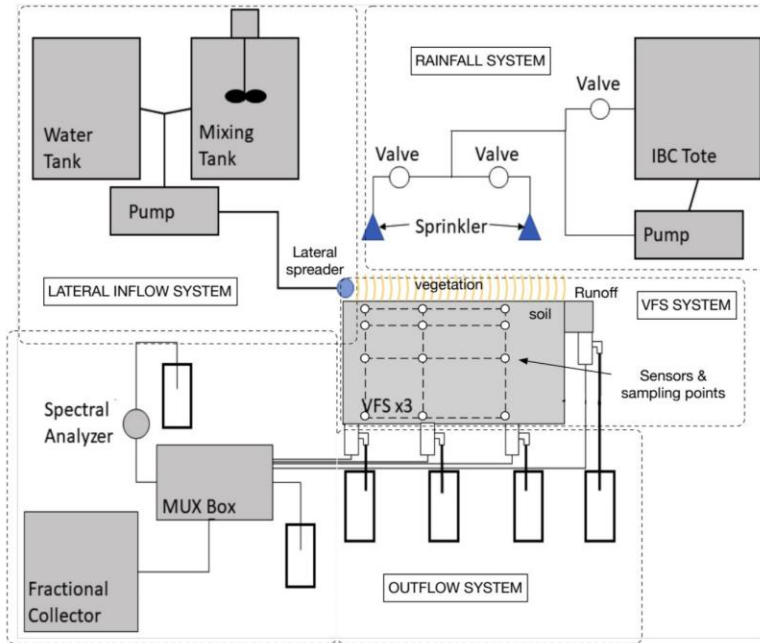
H1	A high-density 3-D sensor array in an unsaturated VFS monolith can track tracer and pesticide mass and dynamics directly, over multiple rainfall events.
H2	There is an intermediate range of K_{oc} over which pesticides are most prone to remobilization by later storms.
H3	Runoff prediction improves if the mixing layer is allowed to leach as the soil drains to field capacity after a storm.
H4	Negligible plant uptake and negligible adsorption to VFS vegetation still hold across inter-storm dry periods.

Objectives

- 1 In situ quantification**
Fate and transport of a saline tracer and three pesticides in vegetated soils, over multiple rainfall–runoff events, at high spatial and temporal resolution.
- 2 Quantify remobilization**
Measure how much of each pesticide returns to runoff in the two storms after application, and how that depends on K_{oc} .
- 3 Isolate the vegetation pathways**
Bench-scale uptake and sorption experiments to bound the two processes VFSMOD leaves out.
- 4 Close the loop**
Use the data to test — and where needed repair — the VFSMOD algorithms that regulatory assessments depend on.

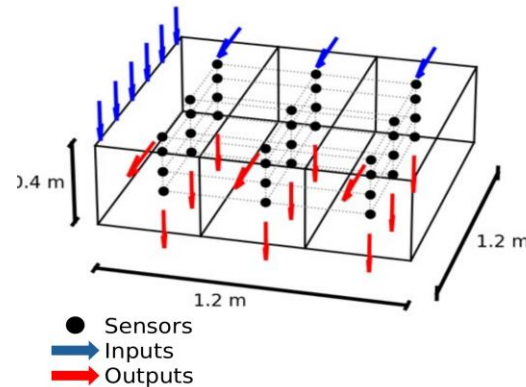
Mesoscale system: a field experiment with a lab's control

METHODS · EXPERIMENTAL



Four coupled sub-systems

- Rainfall: uniform 49 mm h^{-1} (local 10-yr, 2-h storm)
- Lateral inflow: water + sediment + tracer + pesticides



VFS system

Three replicate soil monoliths, $1.2 \times 0.5 \times 0.5 \text{ m}$, packed to uniform bulk density and topped with vegetation — 12 soil sensors each (θ , EC, temperature).

Outflow system

Three deep-drainage ports along the length plus a runoff flume; reservoirs sampled every 15 min.

Mesoscale = the representativeness of a field experiment with the control of a lab study. 36 soil sensors and 44 depth sensors feed a digital shadow of roughly 225,000 data points.

Mesoscale system: a field experiment with a lab's control

METHODS · EXPERIMENTAL

RAINFALL

49 mm h⁻¹ · 5-yr storm

LATERAL INFLOW

sediment · Br tracer · 3 PPPs

MONOLITH (VFS × 3)

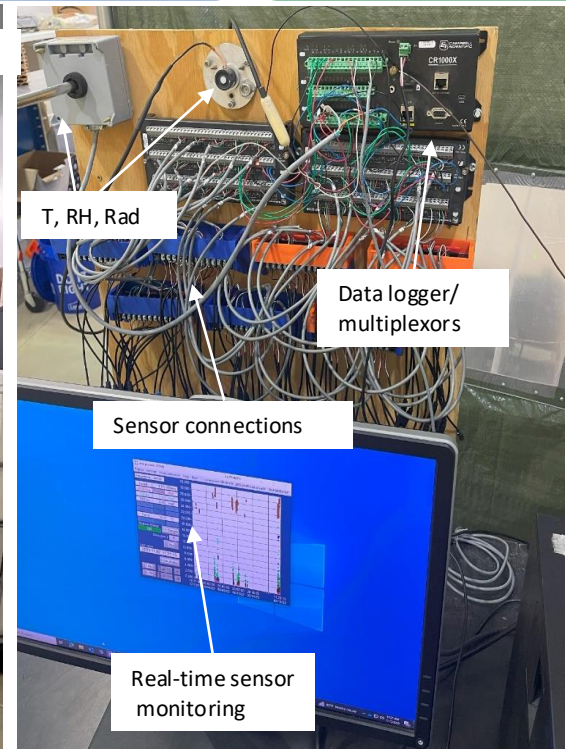
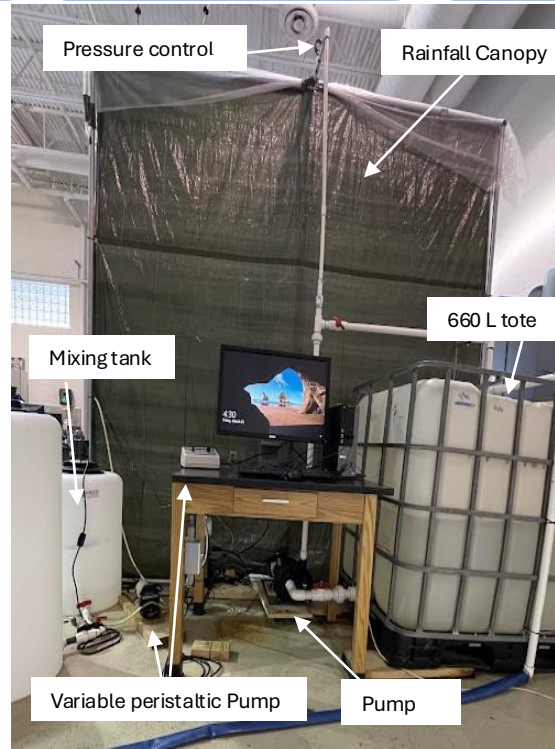
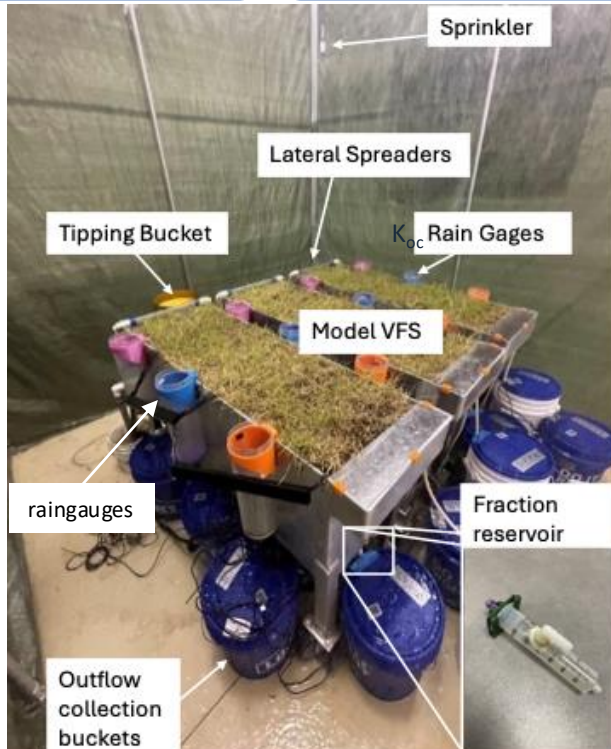
1.2 × 1.2 × 0.5 m · 36 probes

OUTFLOW

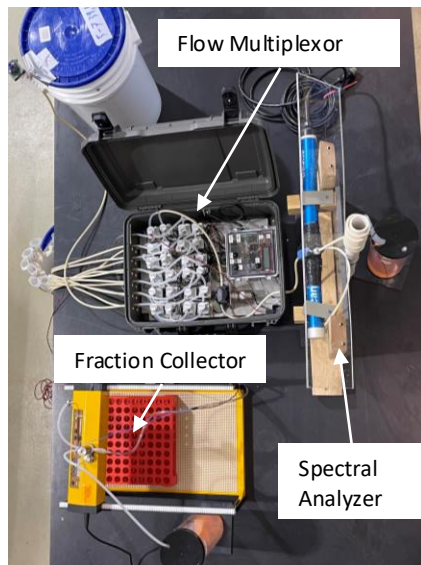
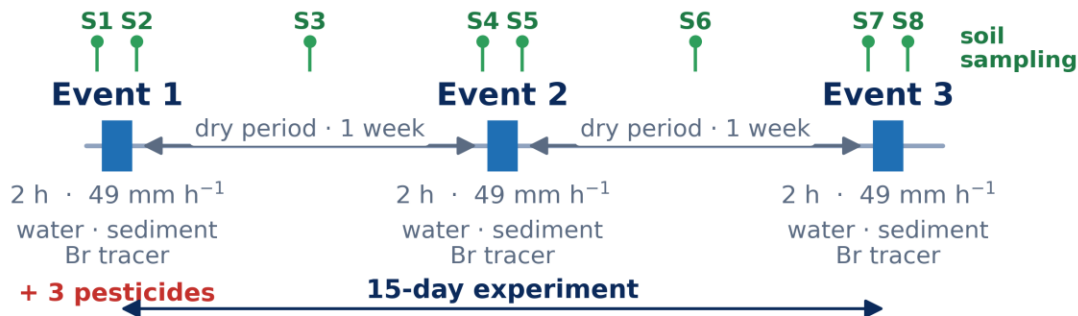
flume + 3 drain outlets

SAMPLING

30 mL every 15 min



Mesoscale system - 3 storms, 1 week apart, pesticides applied once METHODS · EXPERIMENTAL



	Sand	Loamy sand
SUMMER	run 1	run 2
WINTER	run 3	run 4

Chemical	K _{oc} (mL g ⁻¹)	DT ₅₀ (days)	Behaviour
Bromide	tracer	—	conservative
Mesosulfuron	64	313	mobile
Fluopyram	267	52.8	intermediate
Diflufenican	3791	230	strongly sorbed

Why one application in storm 1 only

Pesticides enter with the lateral inflow in **storm 1 only**. Anything measured in the runoff of events 2 and 3 is, by design, remobilized residue.

Why these three

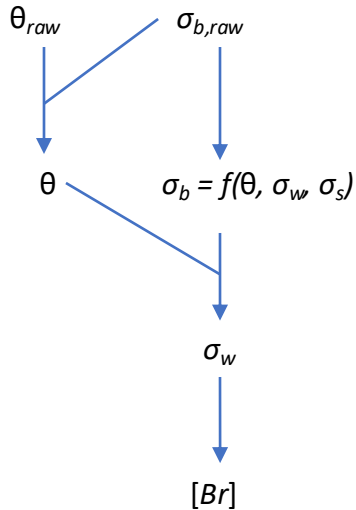
- Mesosulfuron, fluopyram and diflufenican do not interact and span a sixty-fold range in K_{oc} — 64, 267 and 3791 mL g⁻¹.
- Long half-lives (53–313 d) keep degradation negligible between sampling and analysis, isolating remobilization

Plus a tracer

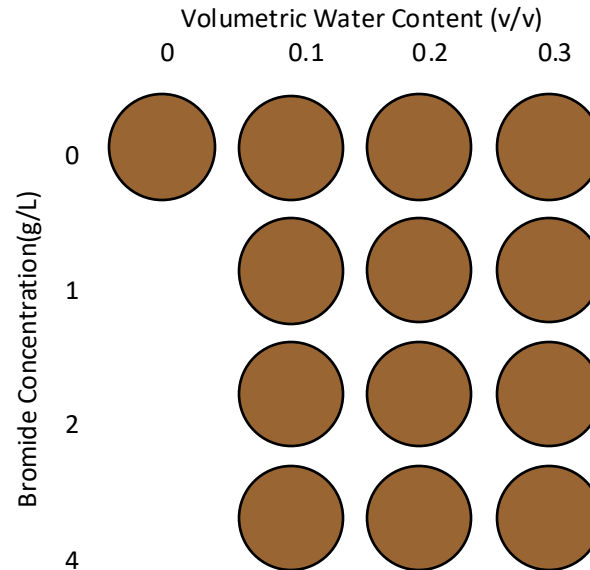
Bromide travels conservatively and marks where the water conservative chemical went.

Mesoscale system: from a raw sensor reading to [Br] tracer

METHODS · EXPERIMENTAL



TEROS 12 (x3)
Volumetric Water Content
Electrical Conductivity
Soil Temperature



Sensor Volumetric Water Content (θ_{raw})
Sensor Bulk Conductivity ($\sigma_{b,raw}$)
Volumetric Water Content (θ)
Bulk Conductivity (σ_b)
Porewater Conductivity (σ_w)
Background Conductivity (σ_s)
Bromide Concentration ($[Br]$)

Four conversions, not one

Raw θ and raw $\sigma_b \rightarrow \theta$; θ and $\sigma_b \rightarrow$ porewater conductivity σ_w ; $\sigma_w \rightarrow$ tracer concentration $[Br]$. Each step needs the soil's own calibration.

The step that is usually skipped

θ must enter the $\sigma_b \rightarrow \sigma_w$ conversion. Treating bulk EC as if it were concentration is erroneous—as this experiment could test.

Why it matters here

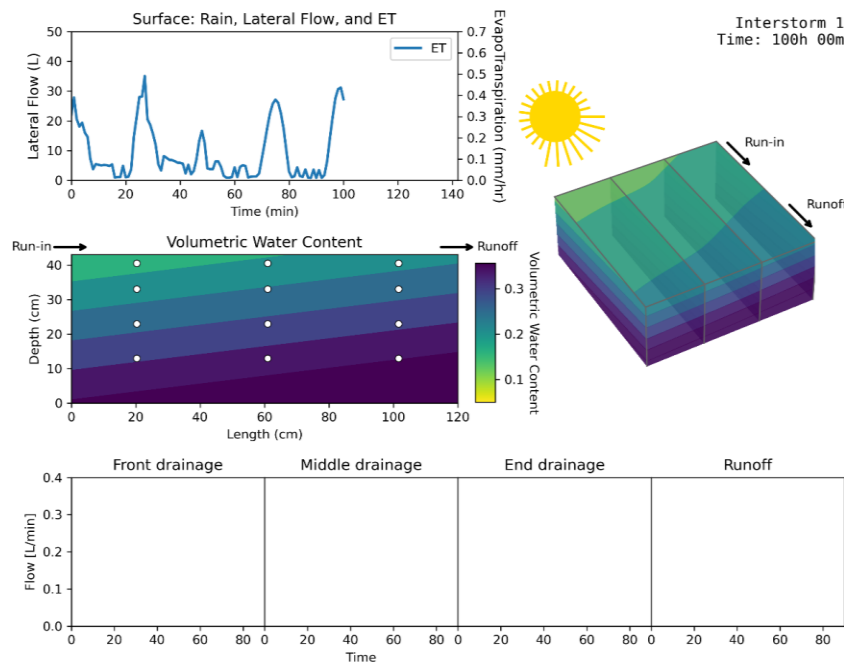
The tracer is how we know where the water and the solutes went.

TEROS 12 · calibration after Muñoz-Carpena et al. (2005) and Rusydi (2018)

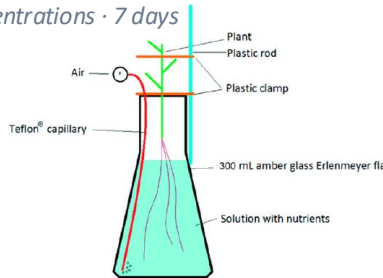
Soil-specific calibration: 13 soils $\times$ known $\theta \times$ known σ_w , three sensors each

Mesoscale system: “Digital shadow”

- Approximately 225,000 data points
- 2D and 3D representation of system measurements to augment understanding of the current system state
- Created in Python with pandas and matplotlib



Hydroponic bahiagrass · fluopyram · 3 concentrations · 7 days



Design after Lamshoeft et al. (2018) *Sci. Total Environ.* 613–614:10–19

1

Hydroponic uptake

Aerated culture, 2-day pre-conditioning, 7-day dosing, water sampled every 2 days; shoots and roots washed, split and analysed by LC-MS/MS → transpiration stream concentration factor (TSCF).

$$TSCF_{Lamshoeft} = \frac{\ln\left(1 - \frac{M_{shoots}^f}{M_{shoots}^f + M_s^f}\right)}{\ln\left(\frac{V_s^f}{V_i^f}\right)} \quad TSCF_{Briggs} = 0.7 e^{-\frac{(\log K_{ow} - 1.78)^2}{2.44}}$$

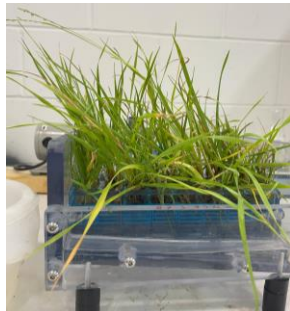
2

Batch sorption

2 g fresh grass in 50 mL solution, four concentrations, 10 min → 24 h, shaken then filtered → **hydrostatic** sorption kinetics and the equilibrium isotherm (Kd).



Batch sorption



Flow-cell

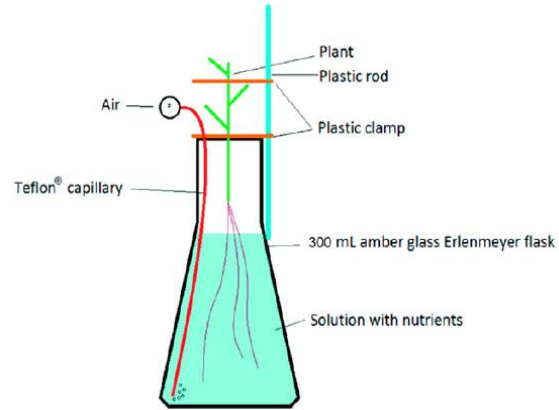
3

Flow-cell sorption

An 80-minute pulse at four inlet concentrations, sampled every 10 min over fresh grass → **hydrodynamic** (retention under moving water, not standing water).

Why benchscale at all?

In a monolith mesoscale, uptake, adsorption, infiltration and sedimentation all act at once. Bench scale experiments allow separation, but there are scaling and interaction tradeoffs.



after Lamshoeft et al. (2018)



hydroponic bahiagrass

Hydroponic culture

300 mL amber flask, aerated

Pre-condition

2 days, weak nutrient

Dose 7 days

Fluopyram · 3 conc.

Sample water

every 2 days

Harvest & split

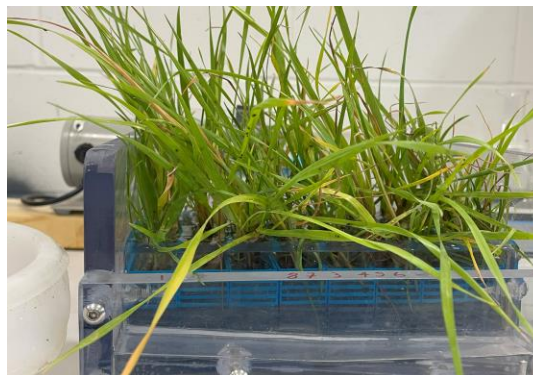
wash · above / belowground

LC-MS/MS → TSCF

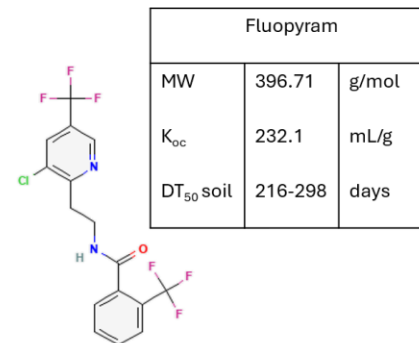
all fractions analysed



batch reactors



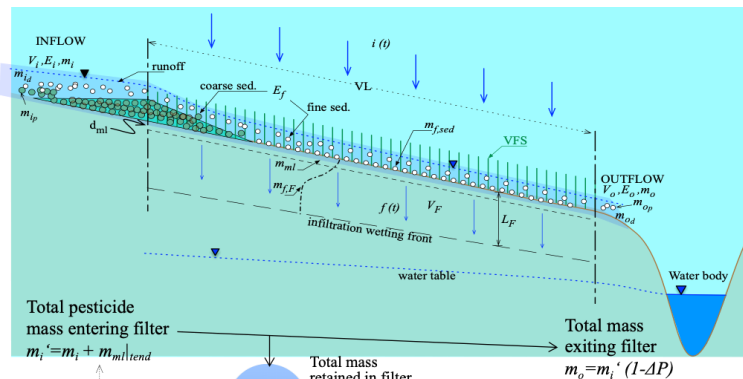
flow cell



Fluopyram



Modeling: VFSSMOD and what changed in 4.6.2.1 (new options)



Freundlich non-linear sorption

non-linear retardation solved by Newton–Raphson — because real VFS runoff sits well below $C_{ref} = 1 \text{ mg/L}$



Drained-to-equilibrium leaching

the mixing layer drains $\theta_{sat} \rightarrow \theta_{fc}$ after the storm instead of holding all pore water

Flexible multispecies degradation

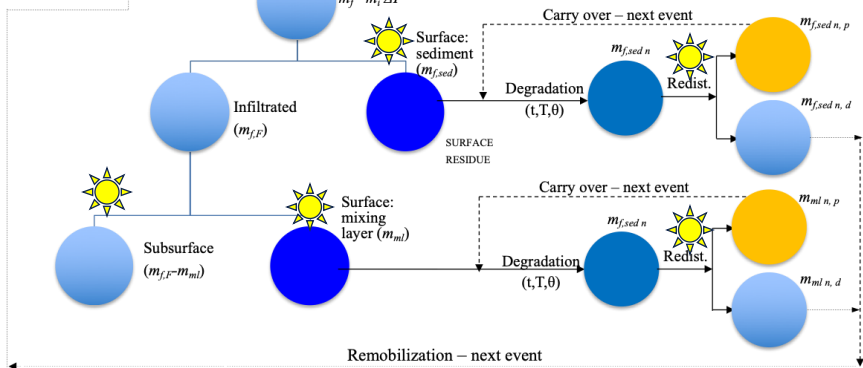
parent and products in the same simulation

Courant-based node selection

Stability, repeatability / discretization no longer a user choice

Petrov–Galerkin stabilization

non-oscillatory transport at small Péclet and Courant numbers

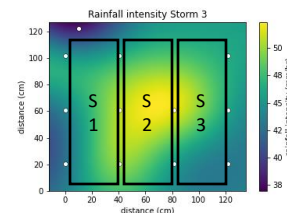
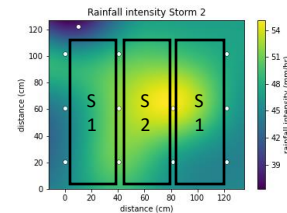
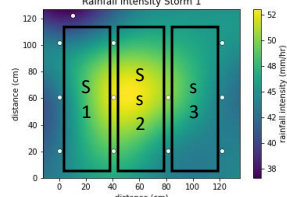
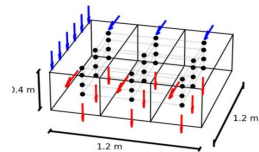


Runoff, sediment and pesticide through one segment, with residues carried to the next event

Highlighted: the two changes this experimental programme drove directly.

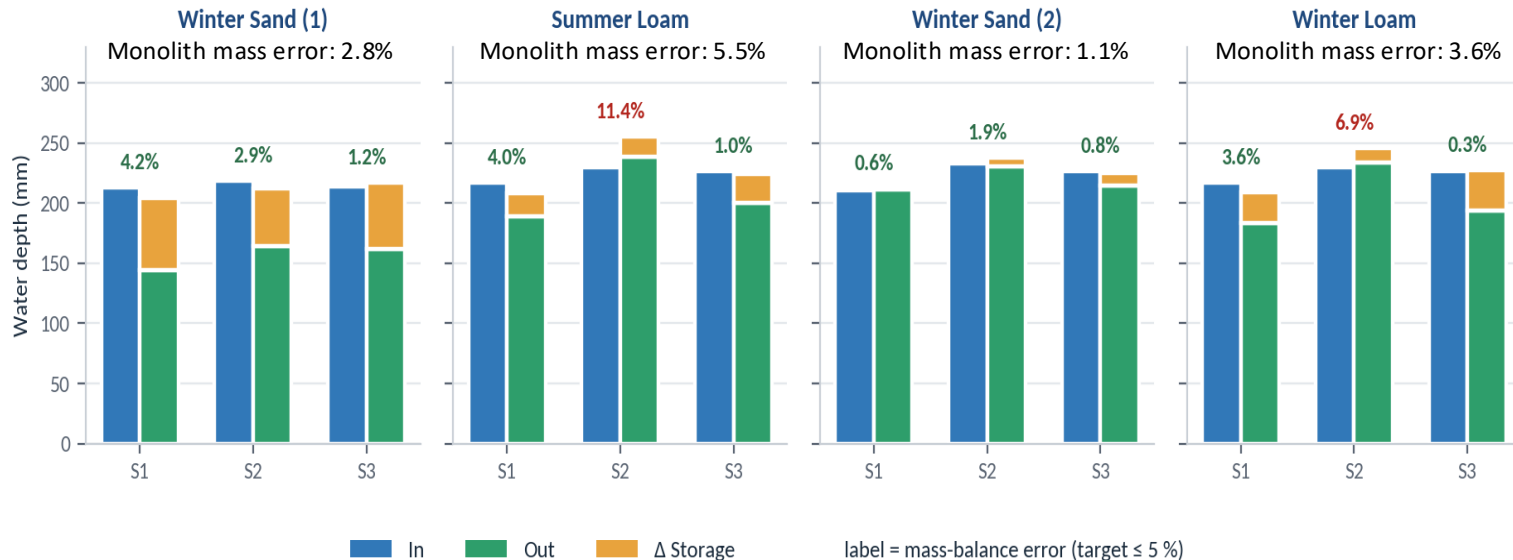
Mesoscale: water balance closes across all four experiments

RESULTS · MESOSCALE



~95 %
Christiansen uniformity
over the VFS surface

45–50
mm h⁻¹ measured
(45.1–50.2; design 49)



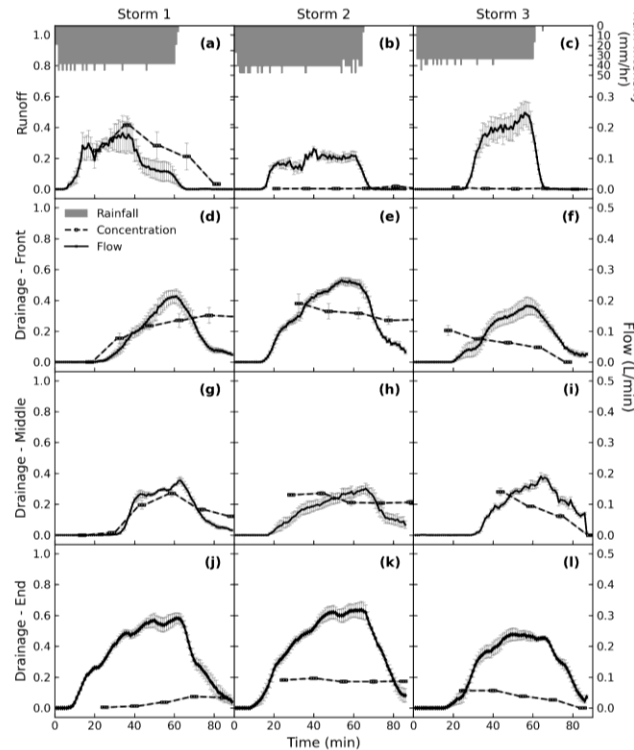
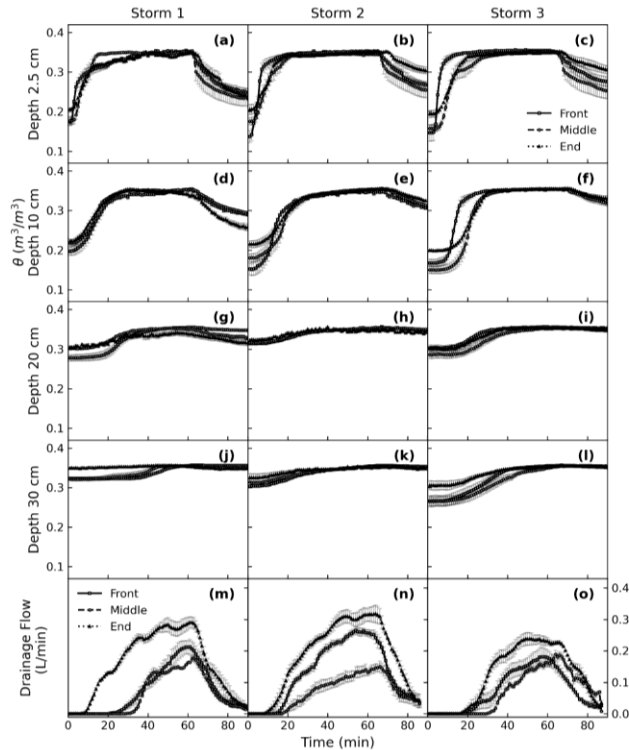
The target was ~5 %

Monoliths meet target. Ten of the twelve boxes meet storm water balances, too. Those that did not are both loam -storm 2, possibly because of some heterogeneity in finer texture soils.

Antecedent moisture condition affects balance

Winter Sand (1) holds 49–60 mm per storm (some water remains in soil) and almost nothing (full drainage) on (2). Same soil class, different antecedent state.

Drawn from the water mass-balance table, SETAC Europe 34th Annual Meeting poster (Howe, Muñoz-Carpena & Sur, 2024)



- Constant rainfall measured, small error in the hydrographs
- Saturation is delayed with depth — near-piston flow
- Difference in drainage along flow, more at end (wall effect)
- Hydrographs peak and the soil drains at 60 min when rainfall stops
- Three-event breakthrough curves show no remobilization of the tracer

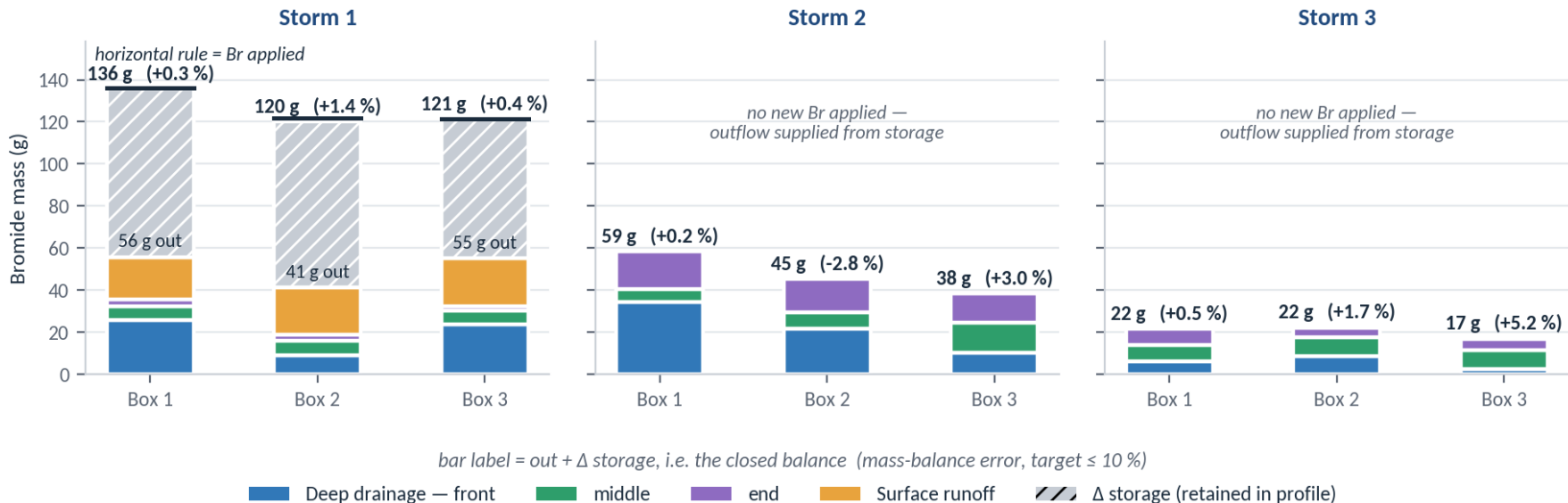
Reading it

The conservative tracer arrives, passes through, and does not come back. Whatever returns in storms 2 and 3 is therefore a property of the chemical, not of the water.

Left: volumetric water content by depth, three storms. Right: runoff and breakthrough curves.

Bromide mass balance: where the tracer actually went

RESULTS · MESOSCALE



Storm 1

Runoff and the front port dominate. Forty per cent of applied Br leaves in the event itself; 225 g stays in the profile.

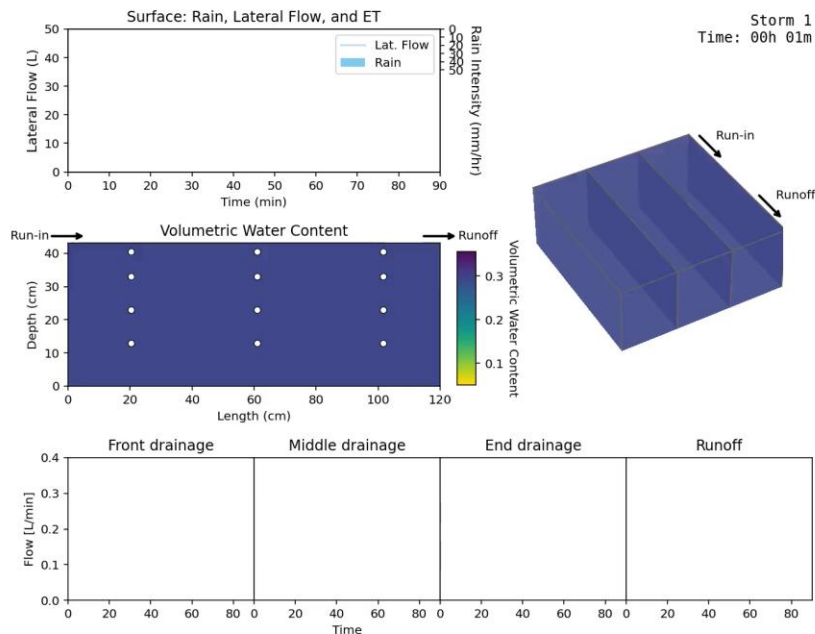
Storms 2 and 3

Runoff is essentially zero. What leaves does so through the profile: this is leaching, not remobilization.

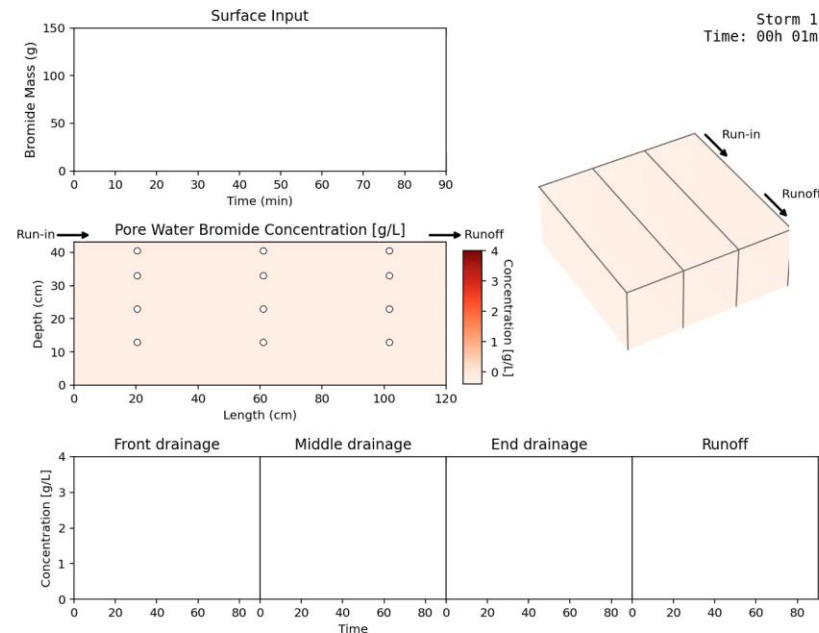
Closure

Series mass error 1.5 % on the concentration basis, against a 10 % target for the tracer.

Hydrological Digital Shadow



Tracer Digital Shadow



- Approximately 225,000 **data points** used

H1

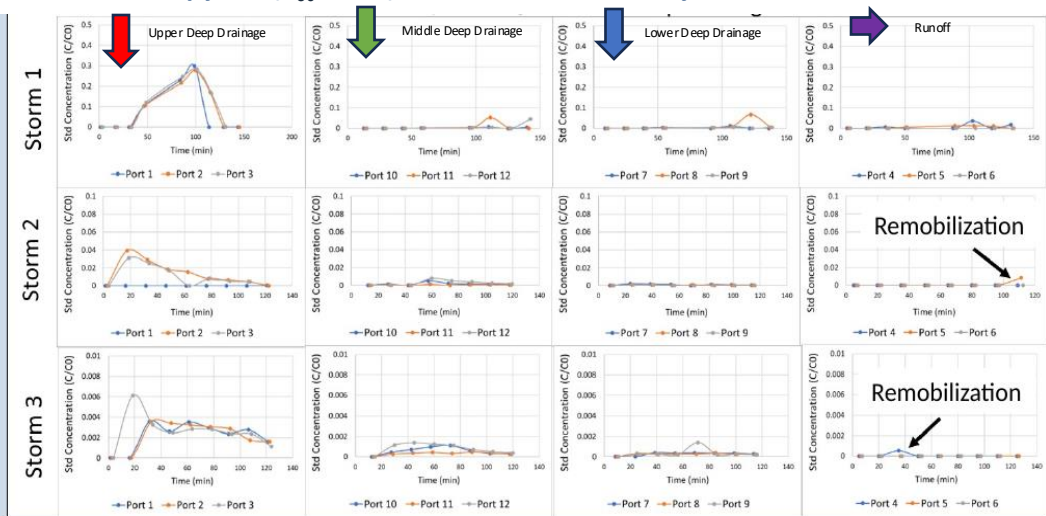


Novel insights from hi-res experiments.

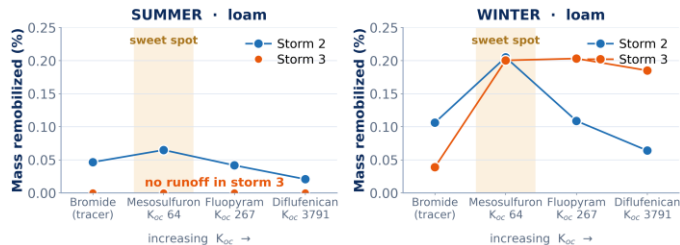
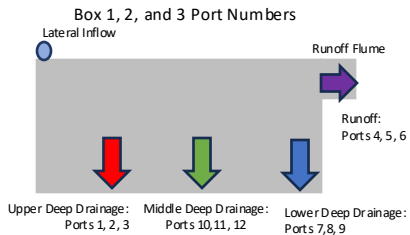
Pesticides: only the middle of the K_{oc} range comes back

RESULTS · MESOSCALE

Fluopyram ($K_{oc} = 267$) — soil concentration by outlet and storm



The remobilization signal — pesticide in the runoff column with no new application — appears in storms 2 and 3



Bromide very low K_d

High mobility — moves with the water and leaves the mixing layer quickly. No remobilization

Mesosulfuron $K_{oc} 64$

High intermediate mobility — moves with the water but some in mixing layer quickly. Higher net remobilization

Fluopyram $K_{oc} 267$

Intermediate — the only pesticide seen in Winter Sand runoff in events 2 and 3.

Diflufenican $K_{oc} 3791$

Strongly sorbed — stays bound in the top-layer soil samples. No remobilization.

H2 : ✓ remobilization has a K_{oc} window.

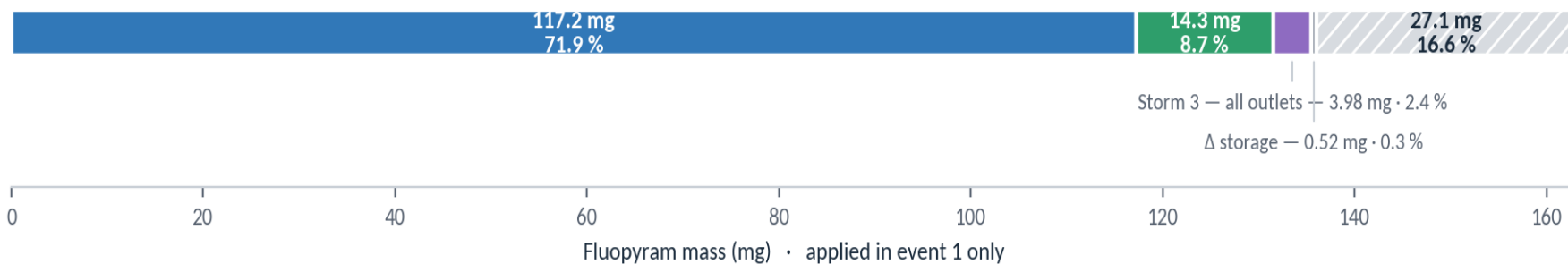
Fluopyram: a further 11 % left in the two storms that followed

RESULTS · MESOSCALE

Drawn from the fluopyram mass-balance table (Winter Sand 1), SETAC Europe 34th Annual Meeting poster, 2024

Applied: 163.08 mg

Recovery 83.4 % · mass error 16.6 % (target ≤ 20 % for pesticides)



Storm 1 — all outlets Storm 2 — all outlets Storm 3 — all outlets Δ storage Unaccounted

The first storm

72% of the applied fluopyram left in the event it was applied in — most of it, but not all.

The two storms that followed

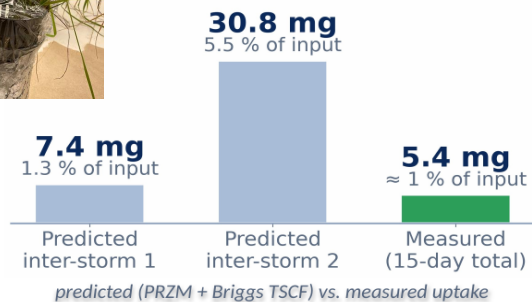
A further 8.7 % and 2.4 % left with no new application — mostly by deep drainage.
The runoff-borne part, which is what remobilization means for exposure, is very small (<0.25%).

Target for pesticides < 20%

16.6 % unaccounted, against a 20 % target for pesticides. Soil-sample placement along the profile is the likely contributor.



H4- first half



Predicted vs measured uptake, mesoscale VFS: 15 days, 3 storms

Mass balance held

Error below 0.5 % in the hydroponic system — all mass accounted for, degradation negligible.

The measurement

Over 15 days and three events, **less than 1 %** of incoming fluopyram was recovered in grass biomass — below the uncertainty of the other fate and transport processes.

A measured TSCF that cannot be right

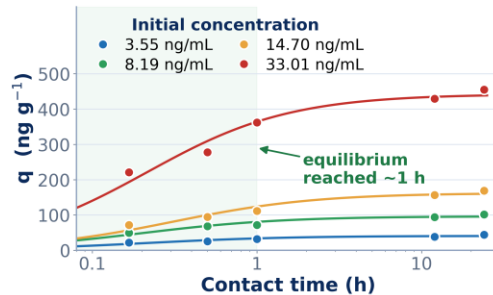
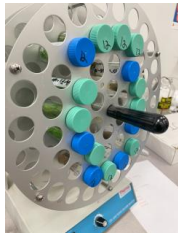
The hydroponic TSCF came out at 1.2–1.35 — more mass in the shoots than was present in the water transpired. Briggs' TSCF = 0.304 was used instead for all model comparisons.

And a warning about the alternative

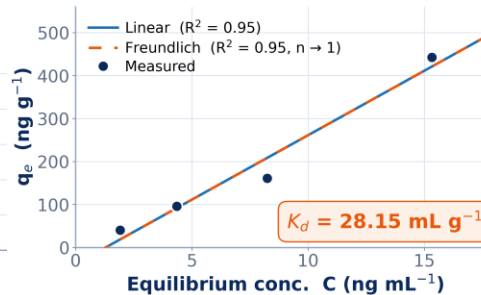
PRZM allows unbounded uptake over long time frames — unrealistic, non-conservative, and PRZM's own documentation warns against it. Leaving uptake out of VFSMOD is the safer choice, not the lazy one.

Bench-scale: adsorption to vegetation is fast, linear and minor

RESULTS · BENCH SCALE



kinetics · 4 initial concentrations



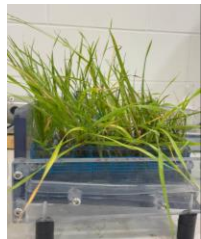
equilibrium isotherm

$$K_d = 28.15 \text{ mL g}^{-1}$$

Three to nine times published values.
With $f_{oc} \approx 0.44$ the apparent K_{oc} is 62–66 against 230–460 — only 13–28 % of the plant's organic carbon is accessible.

Kinetics and isotherm

~2nd-order kinetics ($R^2 = 0.97$ – 0.98) best fits linear close (0.91 – 0.94). Equilibrium ~1 hr, faster than 6–12 hour storms used in exposure assessment $\approx$ instantaneous runoff sorption. Linear $\approx$ Freundlich fit ($R^2 = 0.95$, $n \rightarrow 1$), nosaturation.



lowest inlet conc.
 0.0037 mg L^{-1}

2.28 % retained on vegetation

highest inlet conc.
 0.0377 mg L^{-1}

0.23 % retained on vegetation

0 25 50 75 100 %
% of incoming mass, after 80 min of flow

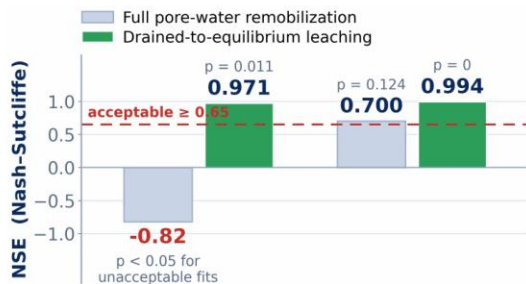
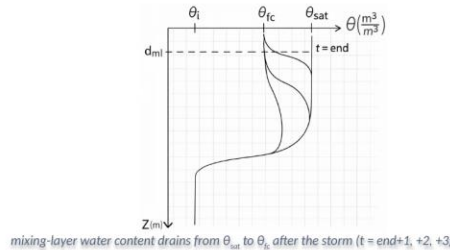
Under moving water

Retained mass did not rise with inlet concentration: the sorbent, not the solute, controls uptake. A minor sink.

H4 : ✓ Both VFS plant assumptions hold.- and neglecting them is risk-conservative

Back to the model: the mixing layer has to be allowed to drain

4 METHODS · THE TWO ALGORITHMS



NSE by FITEVAL · full pore-water over-predicted bromide by more than 400 % (NSE = -0.82 across all chemicals)

What the experiment showed

Bromide leaves the mixing layer between storms — it does not sit in the pore water waiting for the next event. The old algorithm returned all of it to runoff.

What was changed

The layer now drains from θ_{sat} to θ_{fc} after the storm, and only the residual pore-water mass returns to runoff. Everything else in the algorithm is untouched.

Model Fit
(NSE=non-linear
 $R^2 + <0$ values)

0.700

full pore-water
(pesticides, p = 0.124)

0.994

drained-to-equilibrium
(pesticides, p = 0)

H3

✓ drain-to-equilibrium after storm improves runoff prediction for low K_{oc}

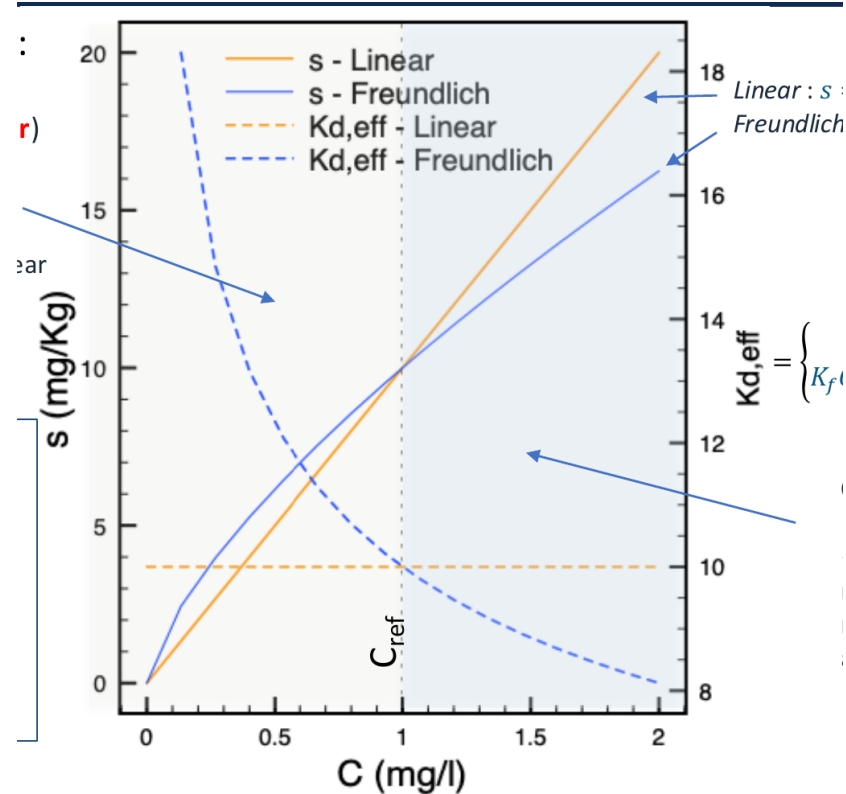
And sorption is not linear at the concentrations that matter

$C < C_{ref}$ (typical porewater)

Freundlich $K_{d,eff} > \text{linear } K_d$
→ more sorption
→ shallower leaching
→ more mass near the surface

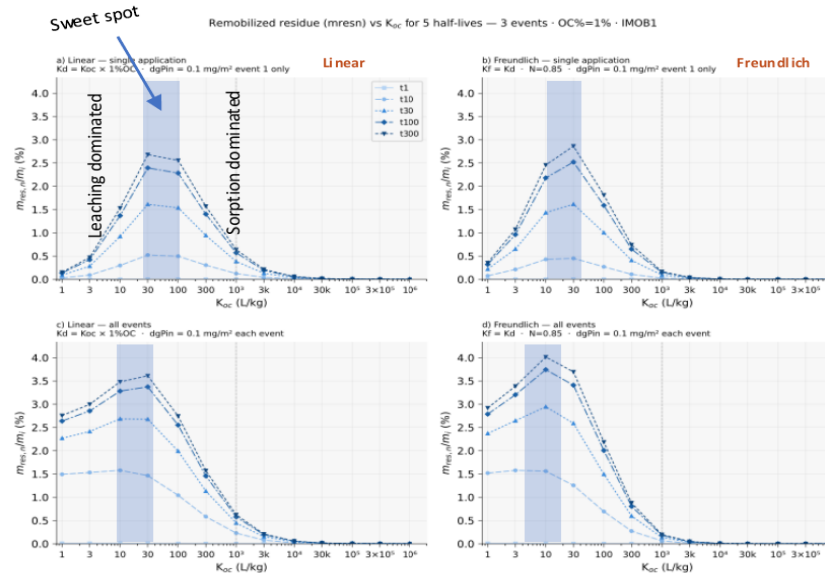
Why it belongs in this talk

The bench isotherm said linear and Freundlich fit the vegetation equally well. The soil is a different matter: at real VFS runoff concentrations the effective K_d is not the linear one, and that changes both what is trapped and what comes back.



$C > C_{ref}$

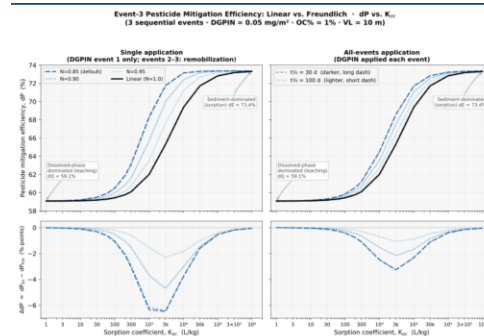
Freundlich $K_{d,eff} < \text{linear } K_d$
→ less sorption
→ leaching below the mixing layer
→ less available at the surface



Simulated residue remobilized vs K_{oc} — the shaded bands mark the peak

The experiment said

- Mesosulfuron (K_{oc} 64) returned; Bromide, K_{oc} 256 and 3791 did not
- Model peak near K_{oc} 10–30 (with 1% OM); measured return at 67 (<0.5% MO). In the monolith the peak also shifted between storms 2 and 3. Open work.



Mitigation efficiency dP vs K_{oc}

Same mechanism, same shape

The model also puts remobilization at intermediate K_{oc} , suppressed at both ends — already leached away below, still sorbed above. Independent agreement on the mechanism.

dP envelope

$dQ \leq dP \leq dE$. Left limb leaching-dominated, right limb sediment-dominated.

H2 : ✓ (2) remobilization has a K_{oc} window

Conclusions

1

Calibration is not a formality — it is a result

A soil-specific equation for θ that uses both raw θ and raw σ_b is required in unsaturated, variable-conductivity systems. Using σ_b as if it were concentration leads to erroneous interpretation of tracer transport; converting properly to σ_w and [Br] removes the artefacts and cut the series mass-balance error from 5.6 % to 1.5 %.

2

Soil type sets the direction of transport

Sandy soil moves the plume vertically; loamy sand moves it down and laterally. The same buffer is a different filter on a different soil.

3

Maximum remobilization has a K_{oc} window (“sweet spot”)

Neither mesosulfuron (64) nor diflufenican (3791) appeared in later-storm runoff; fluopyram (267) did. A further 11 % of applied fluopyram left the system across storms 2 and 3, mostly by drainage. H2 supported.

4

The vegetation pathways can stay out of VFSSMOD

Less than 1 % of incoming fluopyram was recovered in biomass; sorption to fresh grass is fast, linear and minor. Neglecting both is risk-conservative — H4 holds.

5

And the data changed the model – drained to equilibrium after storm & Freundlich adsorption

Drained-to-equilibrium leaching raised remobilization NSE from 0.700 to 0.994; Freundlich sorption is now implemented through the full VFSSMOD chain. Both are in 4.6.2.1.

Sept 2024

VFSMOD Workshop, Piacenza

Regulators, industry and model developers agree a list of open technical questions and resolutions.

Since

Resolutions published

Technical report issued and archived (zenodo.org/records/17942850); each resolution mapped to a code or documentation change.

2026

Peer-reviewed publication

Reichenberger et al., "Update of vegetative filter strip scenarios for pesticide risk assessment in Europe", STOTEN 1039:181906.

Now

Guidance and harmonization

A regulatory guidance pathway is being pursued to broaden VFSMOD acceptance across EU authorities.

The detail is in these talks and posters

Fri 09:40

SPOTMOD I — Theoretical background and hydrological consistency validation

R. Muñoz-Carpena

Fri 10:00

SPOTMOD II — Case studies using real application maps

J. Olivares-Rivas

Fri 11:40

VFSMOD — Joining the Path Forward?

R. Sur

Poster

Adsorption to vegetation and plant uptake in dense vegetation buffers

A. Howe (S1PO3)

Poster

VFSMOD remobilization assumptions vs high-resolution mesoscale data

A. Howe (S2PO8)

Poster

FLUXMOD — process-based pesticide volatilization from soil

S.M. Hong

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Thank you

“... all models are wrong, some are useful.”

G. Box

“... and remember — GIGO!”

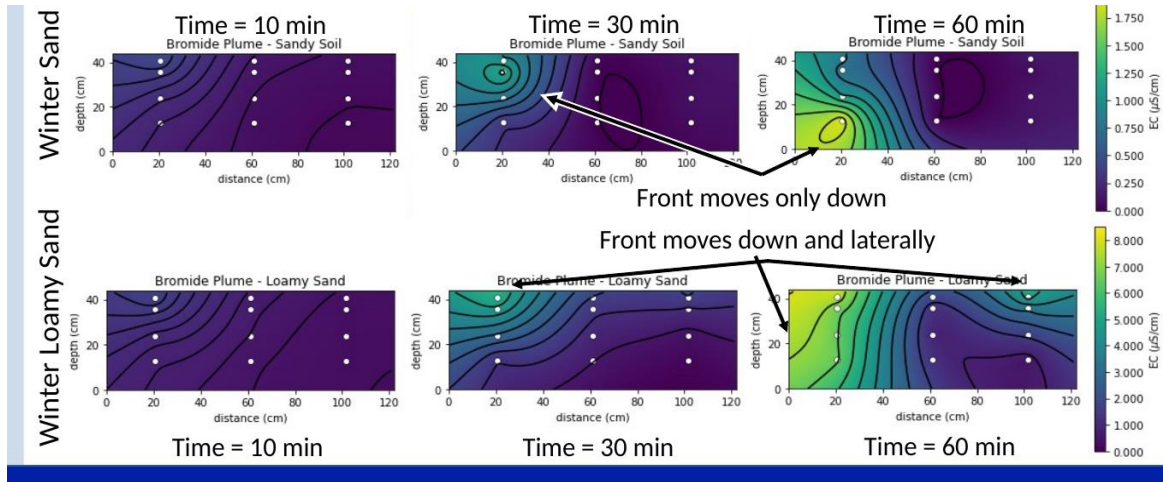
W.E. Deming

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Backup

The soil decides the direction of transport

RESULTS · MESOSCALE



Bromide plume at 10, 30 and 60 min — sandy soil (top), loamy sand (bottom). Panels are colour-scaled in bulk EC, and the two rows use different scales: read the geometry, not the magnitudes.

Implication

Same rainfall, same inflow, same geometry — the only thing that changed is the soil, and it reverses the direction the plume travels.

Sand

The front moves down. Bromide travels quickly through the profile and flushes out.

Loamy sand

The front moves down and laterally. Slower movement, more lateral transport, and residues that stay in the system.

H1

:✓ Novel insights — from hi-res experiments.