

# Tracing experiment to evaluate the fate and behaviour of a pesticide's mixture under controlled conditions for drained systems

Adrien Marcon <sup>a,b</sup>, Florence Leprince <sup>b</sup>, Julien Tournebise <sup>a</sup>, Cédric Chaumont <sup>a</sup>, Alain Dutertre <sup>b</sup>  
a. IRSTEA Antony, UR HBAN, 1 rue Pierre-Gilles de Gennes, 92761, ANTONY.  
b. Arvalis-Institut du végétal, 3 rue Joseph et Marie Hackin 75016 PARIS.

**AIM:** Chemicals and pesticides are substances largely used in agricultural fields and could cause pollution problems. For that reason their behaviour have been studied many times to prevent or reduce the threat on the environmental media. However, many agricultural fields have the specificity of being under drainage conditions which modifies the hydraulic dynamic of the groundwater flow. Drains have influence on the watertable shape and consequently the drained flow might differ from a classical vertical water transfer. This study aims to characterize the behaviour of several pesticides in the groundwater under drainage conditions focusing on the hydraulic aspect and the solute transport. A laboratory experiment under controlled conditions will allow us to describe this part of the pesticide's leaching, but keeping in mind that differences will be highlighted compared to pesticide's leaching situation on the field, due to the fact that other processes as degradation will be ignored.



TRACING 1 (DRY SOIL, SUMMER CONDITIONS)		TRACING 2 (WET SOIL, WINTER CONDITIONS)		TRACING 3 (INTERMEDIATE SOIL, SPRING CONDITIONS)	
Commercial Product	Concentration dose (/L)	Commercial Product	Concentration dose (/L)	Commercial Product	Concentration dose (/L)
AXTER	5 µL	TOLURGAN	12.5 µL	BOXER SC 500	5 µL
NOVALL	6.25 µL	LEGURAME PM	7.5 mg	GOLTIX 70 UD	10 mg
OPUS	2.5 µL	BRENNUS PLUS	5 µL	SPORTAK	2.5 µL
GLYFONET 360	7.5 µL	PROTUGAN	6 µL	DUAL GOLD	5 µL
NIRVANA	11.25 µL	ATLANTIS WG	1.25 mg	BALMORA	2.5 µL
COLZAMID	7 µL	ALLIE EXPRESS	0.125 mg	MILAGRO	3.75 µL
AVIATOR XPRO	2.5 µL	KERB FLO	4.5 µL	DIODE	3.75 µL
		DEFI	12.5 µL	BASAGRAN	4 mg
				CASPER	0.75 mg
				ISARD	3.5 µL

Chart 1: Dose of commercial products applied depending on the field soil conditions

## RESULTS:

The isotopic tracing shows that Amino-G acid is the only of our tracers that can be considered as an ideal water tracer. His BTC is almost simultaneous with both isotopic water and Bromide 's BTC. Mass balance recovery is 99,88% for Uranine and 92,18% for Amino-G acid, this confirms that our tracing was valid. Several peaks due to either preferential flow/inlet flow rate variation (Figure 1).

## METHODS:

A 2D tracing was realised on the device MASHYNS which is a 1 m<sup>3</sup> bunk (2m\*1m\*0.5m) that simulates drainage flow. The soil in-situ is a mixture (14% clay, 30% silt, 55% sand) that results in a hydraulic conductivity of approximately 1m/day, an organic matter content of nearly 2% and in a porosity of 43%. Consequently a pore volume (PV) corresponds to 430L. The selection of the pesticides was based on agricultural practices in the Northwestern part of France. Therefore the concentrations applied were calculated knowing the practices on the field and anticipating the molecule's elution peaks. We used 4 fungicides and 23 herbicides with a wide range of sorption potentials (KOC from 15 to 2000 cm<sup>3</sup>/g).

Fluorescent and chemical tracers (Bromide, Uranine, Rhodamine WT, Amino-G acid) and isotopic water were first tested to find the most ideal water tracer and to help determine the hydraulic flow in the device. Both tracers and pesticides were spread on top of the device through a sprinkling system and the water inlet was set up to represent the annual hydrology that happens on the field. 350mm of drained water correspond to a hydrological year but a constant high flow rate is needed to allow the complete leaching of all molecules. Pesticides and tracers are spread at 3 different steps, to which a specific watertable height corresponds according to the field conditions (Chart 1). Data are collected at the outlet drainage pipe for both tracers (spectrofluorimeter, every 15 min) and pesticides (chemical analyses).

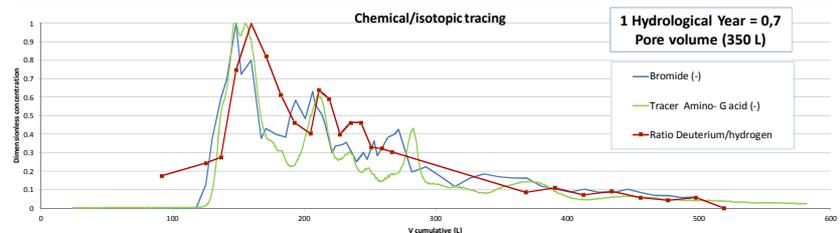
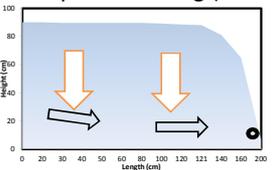


Figure 1: Leaching breakthrough curves of isotopic water, chemicals and fluorescent tracers applied on the device with a low watertable height

And final flow rate for complete leaching (30 PV):



4 steps, 90 days long experiment:

Figure 2: Watertable in Tracing 1 under summer conditions (30/06/14) with 9 pesticides and 1 tracer Amino-G acid

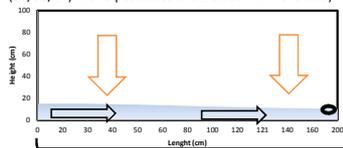


Figure 3: Watertable in Tracing 2 under winter conditions (01/07/14) with 7 pesticides and 1 tracer (Uranine)

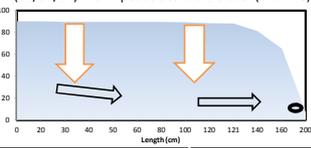
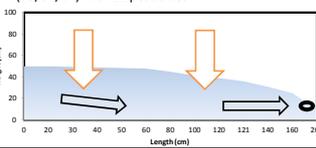


Figure 4: Watertable in Tracing 3 under spring conditions (03/07/14) with 12 pesticides



Progress of 1 hydrological year : succession of 3 steady states, total volume flowed = 350 L (0,7 PV)

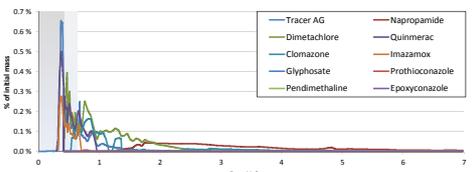


Figure 5: Leaching breakthrough curves of molecules applied during Tracing 1

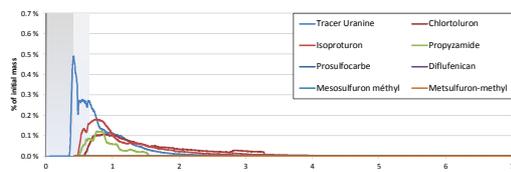


Figure 6: Leaching breakthrough curves of molecules applied during Tracing 2

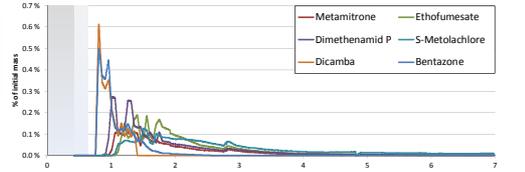


Figure 7: Leaching breakthrough curves of molecules applied during Tracing 3

	Dose applied (mg/m <sup>2</sup> )	Delay on the tracer (PV)	% recovery after 0,7 PV (1 year)	Total % recovery (after 6,5 PV)	Leaching volume (PV)	KD (cm <sup>3</sup> /g)
Quinmerac	1,60	0,01	45,7	57	0,7	1,63
Dicamba	1,02	0,02	52,1	64	1,1	0,24
Bentazone	14,23	0,02	53	75,8	2,3	1,05
Imazamox	1,02	0,04	24,9	24,9	0,4	1,27
Isoproturon	6,88	0,13	15,7	72,6	3,7	2,32
Dimetachlore	6,12	0,14	29,8	101,3	4,1	1,31
Propyzamide	5,36	0,15	7,2	28,2	1,1	15,96
Dimethenamide	6,22	0,17	19	95,3	6,5	4,37
Metamitron	19,89	0,22	7,2	59	5,3	1,46
Chlortoluron	11,95	0,22	3,2	62,3	6,5	3,8
Cimazone	0,90	0,25	14,9	79,6	4,3	5,7
S-Métolachlor	10,76	0,27	2,4	97	6,4	4,29
Ethofumesate	4,83	0,32	1,62	92,7	6,4	3,55
Napropamide	15,54	0,98	0	65,1	5,7	15,96
Glyphosate	3,46	-	-	-	-	545,3
Pendimethaline	3,50	-	-	-	-	299,1
Prothioconazole	0,07	-	-	-	-	48,56
DFP	0,04	-	-	-	-	37,9
Prosulfocarbe	21,78	-	-	-	-	32,1
Prochloraze	1,37	-	-	-	-	27,3
Epoxyconazole	0,62	-	-	-	-	20,4
Tebuconazole	1,56	-	-	-	-	14,6
Mesosulfuron-méthyl	1,7E-05	-	-	-	-	1,75
Metsulfuron-méthyl	4,3E-03	-	-	-	-	0,75
Nicosulfuron	0,36	-	-	-	-	0,4
Prosulfuron	0,02	-	-	-	-	0,27

Chart 2: Characteristics of each pesticide applied during the tracings

## References:

PPDB, [www.herts.ac.uk/aeru](http://www.herts.ac.uk/aeru)  
Pesticide transport via sub-surface drains in Europe, Brown & al., 2009

## DISCUSSIONS:

- Tracing samples recorded until 6,5 PV (3000L) which corresponds to almost 9 hydrological years.
- Complete leaching for 4 molecules, unachieved for 10 molecules, not started for 13 molecules and overleached for 1 molecule (Figures 5, 6, 7).
- Delay on the tracer varies. The lower the delay, the faster the molecule achieves its leaching. That corresponds also with the adsorption potential values. The lower the KD, the more mobile the molecule is. No special similarities within molecules that were spread at the same time, flow seems governed by the molecule's own specificities (Chart 2).
- Exception/anomalies were detected : Propyzamide has an unexpected behaviour considering it reaches the drain fast while it supposed to be sorbed. 4 molecules with very low sorption potentials didn't reach the drain (Chart 2).

## CONCLUSIONS:

Comparing results from our tracing and field data confirms that hydraulic as a key role in pesticide's leaching, but it's not the only process involved. Molecules as Bentazone or Isoproturon are detected in both cases in drainage water, but others (as DFP, Prochloraze..) didn't leach in our rexpériment even though positive concentration samples are regularly found on the field. Explanation for such a unexpected behaviour could be the particular transport via bound residues. Another huge difference appears: it's the quantity of product collected at the drain. Surprisingly many molecules flushed very easily in our experiment. But field data reach no more than 1% of applied doses, contrary to our experiment where we get on average 70%. This may highlight the existence of other processes as degradation because a non-reversible sorption is unlikely. Modelisation with HYDRUS will help set up the potential sorption under drainage conditions and the degradation process according to the mass balance recovery.