



Supplement of

Living cover crops alter the fate of pesticide residues in soil: influence of pesticide physicochemical properties

Noé Vandevorste et al.

Correspondence to: Noé Vandevorste (noe.vandevorste@uclouvain.be)

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S1: Raw and Supplementary Data

The pots were 30.0 ± 0.1 cm in diameter, resulting in a surface area of $7.07 \pm 0.05 \times 10^{-6}$ ha per pot. A quantity of 8.77 ± 0.44 mL of spray mixture was applied to each pot, equivalent to a dose of 1240 ± 60 L ha $^{-1}$. The composition of the spray mixture is detailed in Table S1.

5 Modalities and date of sampling are defined for each pot number in Table S2, without further reference in Tables S3 to S7.

Mefenpyr-diethyl ($LQ_{\text{soil solution}} = 0.15$ $\mu\text{g L}^{-1}$) and halauxifen-methyl ($LQ_{\text{soil solution}} = 0.03$ $\mu\text{g L}^{-1}$) were never detected in soil solution samples (ND for all samples) and were omitted from Table S4.

Where no value of K_{oc} was available in the PPDB, K_{foc} was used in Table S5 instead. Where no value of BCF was available, it was calculated using (Fu et al., 2009):

$$10 \quad \text{BCF} = \begin{cases} 10^{(-0.2(\log_{10} K_{\text{oc}})^2 + 2.74 \log_{10} K_{\text{oc}} - 4.72)} & \text{where } \log_{10} K_{\text{oc}} > 6 \\ 10^{(0.85 \log_{10} K_{\text{oc}} - 0.7)} & \text{where } 0 < \log_{10} K_{\text{oc}} < 6 \end{cases} \quad (\text{S1})$$

Table S1. Spray mixture composition.

formulated product	MAD	d_{prod}	active substance	formulation	$d_{a.s.}$
Afinto	0.32	0.26	flonicamid	500	130
Aquino	2.00	1.6	fenpicoxamid	50	80
Axial	1.20	0.96	cloquintocet-mexyl pinoxaden clopypralid	12.5	12
Bofix	4.00	3.2		50	48
				20	64
Butizyl	5.00	4.0	fluroxypyr	40	130
Capri	0.25	0.21	MCPB cloquintocet-mexyl pyroxslam	200	640
Comet New	2.50	2.0		400	1600
Frimax	0.50	0.40	pyraclostrobin cloquintocet-mexyl fluroxypyr halauxifen-methyl	75	16
				75	16
				12	4.8
Mesiofis Pro	1.50	1.2	iodosulfuron-methyl-sodium mefenpyr-diethyl mesosulfuron-methyl	280	110
				30	36
				10	12
Mizona	2.00	1.6	fluxapyroxad pyraclostrobin	30	48
Primus	0.10	0.08		200	320
Revytrex	3.00	2.4	florasulam fluxapyroxad mefentrifluconazole	50	4.0
Tebusip	3.00	2.4		66.7	160
				66.7	160
			tebuconazole	250	600

MAD: maximum authorised dose, in L ha^{-1} or kg ha^{-1} (data extracted from *phytoweb.be*);

d_{prod} : dose of the formulated product in the spray mixture, in mL L^{-1} or g L^{-1} ;

formulation: active substance content in formulated product, in g L^{-1} or g kg^{-1} ;

$d_{a.s.}$: dose of the active substance in the spray mixture, in mg L^{-1} .

Table S2. Experimental set-up raw data (**bare**: bare soil modality; **thin**: multi-species mix cover, reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80; **thick**: winter spelt cover, reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

sampling	modality	pot	fresh soil	soil DM	soil solution	sowing	biomass
day 0		1	10.03	80.2	—	—	—
		2	9.42	79.2	—	—	—
		3	10.24	80.3	—	—	—
		4	10.03	80.7	—	—	—
		5	9.25	80.3	—	—	—
day 45	bare	6	10.43	79.1	20	—	—
		7	9.80	77.7	19	—	—
	thin	8	9.82	77.7	38	—	—
		9	9.77	77.9	39	—	—
		10	9.85	77.8	0	—	—
	thick	11	10.33	78.6	56	149.1	$0.35 \pm \Delta 0.03$
		12	10.12	77.2	32	147.0	$0.32 \pm \Delta 0.02$
		13	10.21	78.4	37	147.4	$0.21 \pm \Delta 0.02$
		14	9.75	78.4	52	151.9	$0.15 \pm \Delta 0.01$
		15	9.97	78.6	40	144.1	$0.23 \pm \Delta 0.02$
	thick	16	9.40	78.2	54	190.1	$0.39 \pm \Delta 0.03$
		17	9.14	77.4	11	205.0	$0.46 \pm \Delta 0.03$
		18	9.65	78.8	17	209.1	$0.49 \pm \Delta 0.04$
		19	9.13	77.6	15	184.9	$0.41 \pm \Delta 0.03$
		20	9.06	77.9	28	174.9	$0.40 \pm \Delta 0.04$
day 80	bare	21	9.67	79.2	48	—	—
		22	9.59	79.3	17	—	—
		23	10.07	80.9	23	—	—
		24	9.55	79.4	52	—	—
		25	10.06	79.9	30	—	—
	thin	26	9.59	79.4	41	145.0	$0.33 \pm \Delta 0.02$
		27	9.33	81.1	55	144.6	$0.28 \pm \Delta 0.02$
		28	9.60	80.1	30	147.4	$0.29 \pm \Delta 0.02$
		29	9.67	80.6	0	147.9	$0.40 \pm \Delta 0.03$
		30	9.57	80.4	30	144.6	$0.50 \pm \Delta 0.04$
	thick	31	9.46	79.8	3	187.7	$1.12 \pm \Delta 0.08$
		32	9.12	79.9	16	168.3	$1.12 \pm \Delta 0.08$
		33	9.35	79.8	35	195.3	$1.10 \pm \Delta 0.08$
		34	9.50	79.5	14	196.0	$1.12 \pm \Delta 0.08$
		35	8.83	79.4	3	194.1	$1.16 \pm \Delta 0.08$

fresh soil: fresh soil mass, in kg, with a measurement error of $\pm \Delta 0.02 \text{ kg}$;

soil DM: soil dry matter content, in %, with a measurement error of $\pm \Delta 0.1 \%$ (except for 5 January 2024: $\pm \Delta 0.4 \%$);

soil solution: sampled soil solution volume, in mL, with a measurement error of $\pm \Delta 2 \text{ mL}$;

sowing: sown seed density, in $\text{kg}_{\text{seed}} \text{ ha}^{-1}$, with a measurement error of $\pm \Delta 0.1 \text{ kg ha}^{-1}$;

biomass: sampled dry matter biomass, in $\text{t}_{\text{DM}} \text{ ha}^{-1}$.

Table S3. Quantification raw data: soil samples (in $\mu\text{g kg}^{-1}$ _{fresh soil}).

pot	clop	cloq	fenp	flon	flor	flur	flux	hala	iodo	MCPA	MCPB
LQ	5.00	0.20	0.20	0.50	0.25	2.50	0.25	0.50	0.75	0.20	2.50
1	95.43	0.50	21.45	54.04	1.68	331.97	266.78	1.35	0.99	1164.60	706.52
2	42.97	0.68	15.95	24.42	0.99	176.72	176.74	1.13	<LQ	529.15	220.53
3	45.67	0.80	18.11	30.77	0.96	171.83	167.45	0.99	<LQ	550.55	324.99
4	45.51	0.54	21.26	24.00	0.99	195.50	200.73	1.17	<LQ	627.58	211.52
5	49.55	1.65	37.80	35.80	1.18	278.57	240.80	1.77	0.83	773.60	632.97
6	<LQ	<LQ	0.60	<LQ	<LQ	3.46	102.89	<LQ	<LQ	1.21	<LQ
7	8.91	<LQ	0.50	<LQ	<LQ	5.85	107.46	<LQ	<LQ	1.38	<LQ
8	8.90	<LQ	0.49	<LQ	<LQ	7.72	92.35	<LQ	<LQ	1.26	<LQ
9	13.27	<LQ	0.45	0.61	<LQ	10.99	92.6 8	<LQ	<LQ	1.67	<LQ
10	11.04	<LQ	0.71	0.52	<LQ	6.20	86.31	<LQ	<LQ	1.52	<LQ
11	5.57	<LQ	1.02	<LQ	<LQ	4.70	164.85	<LQ	<LQ	4.10	5.15
12	7.00	<LQ	0.38	<LQ	<LQ	4.48	79.55	<LQ	<LQ	2.05	<LQ
13	9.75	<LQ	0.56	0.59	<LQ	8.10	100.73	<LQ	<LQ	2.39	2.77
14	<LQ	<LQ	0.70	<LQ	<LQ	2.93	124.64	<LQ	<LQ	1.47	2.53
15	6.46	<LQ	0.65	<LQ	<LQ	5.05	128.03	<LQ	<LQ	1.17	<LQ
16	7.00	<LQ	0.95	<LQ	<LQ	3.27	173.38	<LQ	<LQ	1.79	4.13
17	6.36	<LQ	0.49	<LQ	<LQ	<LQ	103.06	<LQ	<LQ	1.45	<LQ
18	8.43	<LQ	0.59	<LQ	<LQ	4.22	124.27	<LQ	<LQ	1.38	<LQ
19	<LQ	<LQ	0.73	<LQ	<LQ	1.81	131.26	<LQ	<LQ	1.12	2.58
20	5.91	<LQ	0.64	<LQ	<LQ	<LQ	136.20	<LQ	<LQ	1.23	2.68
21	<LQ	<LQ	0.44	<LQ	<LQ	<LQ	167.74	<LQ	<LQ	0.94	5.19
22	<LQ	<LQ	0.82	<LQ	<LQ	<LQ	255.22	<LQ	<LQ	1.84	7.90
23	<LQ	<LQ	0.75	<LQ	<LQ	<LQ	255.00	<LQ	<LQ	1.42	7.63
24	<LQ	<LQ	1.10	<LQ	<LQ	2.64	268.82	<LQ	<LQ	1.58	9.03
25	<LQ	<LQ	0.81	<LQ	<LQ	<LQ	232.44	<LQ	<LQ	1.82	8.62
26	<LQ	<LQ	0.99	<LQ	<LQ	<LQ	278.53	<LQ	<LQ	1.66	8.16
27	<LQ	<LQ	0.83	<LQ	<LQ	3.24	263.39	<LQ	<LQ	1.81	8.35
28	<LQ	<LQ	0.95	<LQ	<LQ	<LQ	270.33	<LQ	<LQ	1.61	7.26
29	<LQ	<LQ	0.81	<LQ	<LQ	<LQ	250.55	<LQ	<LQ	1.50	8.09
30	<LQ	<LQ	1.05	<LQ	<LQ	<LQ	322.96	<LQ	<LQ	1.75	9.18
31	<LQ	<LQ	0.60	<LQ	<LQ	<LQ	152.63	<LQ	<LQ	0.92	6.05
32	<LQ	<LQ	0.46	<LQ	<LQ	<LQ	135.38	<LQ	<LQ	1.00	6.40
33	<LQ	<LQ	0.28	<LQ	<LQ	<LQ	118.44	<LQ	<LQ	0.76	5.07
34	<LQ	<LQ	0.33	<LQ	<LQ	<LQ	167.76	<LQ	<LQ	0.88	5.32
35	7.01	<LQ	0.48	1.17	<LQ	<LQ	163.65	<LQ	<LQ	1.70	5.51

clop: clopyralid; cloq: cloquintocet-mexyl; fenp: fenpicoxamid; flon: flonicamid; flor: florasulam; flur: fluroxypyr; flux: fluxapyroxad;

hala: halauxifen-methyl; iodo: iodosulfuron-methyl-sodium.

ND: no detection; LQ: limit of quantification.

Table S3 (continued). Quantification raw data: soil samples (in $\mu\text{g kg}^{-1}$ fresh soil).

pot	mef.d	mef.a	meso	pino	pyra	pyro	tebu
LQ	1,00	1,25	0,50	0,20	1,00	0,25	1,00
1	<LQ	199,38	14,84	<LQ	532,09	21,13	818,24
2	<LQ	147,98	7,28	0,21	371,26	8,00	532,18
3	<LQ	121,17	7,30	0,19	293,11	10,87	477,36
4	<LQ	154,44	10,12	<LQ	413,86	10,99	643,14
5	<LQ	195,33	13,94	0,60	482,65	13,06	738,71
6	<LQ	72,80	2,76	<LQ	53,82	<LQ	285,50
7	<LQ	74,42	3,51	<LQ	42,55	0,65	280,96
8	<LQ	57,23	3,32	<LQ	48,08	0,71	236,96
9	<LQ	58,79	3,30	<LQ	42,07	1,07	244,71
10	<LQ	54,79	2,92	<LQ	52,35	0,89	252,69
11	<LQ	114,28	3,05	<LQ	98,97	0,25	444,13
12	<LQ	42,68	2,31	<LQ	34,32	0,25	178,16
13	<LQ	65,09	2,72	<LQ	60,64	0,57	262,63
14	<LQ	84,01	2,98	<LQ	70,11	<LQ	322,48
15	<LQ	77,46	3,33	<LQ	64,95	0,35	306,72
16	<LQ	139,92	3,60	<LQ	114,92	<LQ	499,47
17	<LQ	72,30	3,48	<LQ	58,23	<LQ	268,56
18	<LQ	82,09	3,04	<LQ	58,06	<LQ	360,60
19	<LQ	83,36	3,58	<LQ	68,24	<LQ	369,23
20	<LQ	85,61	3,27	<LQ	58,98	<LQ	364,14
21	<LQ	101,63	1,77	<LQ	30,05	<LQ	355,97
22	<LQ	169,24	2,51	<LQ	64,80	<LQ	557,42
23	<LQ	163,51	2,44	<LQ	61,96	<LQ	572,18
24	<LQ	179,23	3,79	<LQ	60,85	<LQ	588,86
25	<LQ	144,54	2,74	<LQ	44,87	<LQ	535,90
26	<LQ	191,77	3,29	<LQ	76,03	<LQ	657,97
27	<LQ	173,79	3,81	<LQ	68,90	<LQ	585,14
28	<LQ	184,35	3,32	<LQ	53,18	<LQ	617,68
29	<LQ	162,38	3,38	<LQ	53,48	<LQ	541,03
30	<LQ	236,07	3,67	<LQ	81,71	<LQ	730,82
31	<LQ	87,45	1,24	<LQ	31,89	<LQ	303,98
32	<LQ	89,58	1,49	<LQ	34,86	<LQ	298,62
33	<LQ	71,21	1,57	<LQ	22,50	<LQ	267,28
34	<LQ	95,99	2,24	<LQ	38,50	<LQ	360,45
35	<LQ	102,13	1,76	<LQ	31,01	<LQ	374,20

mef.d: mefenpyr-diethyl; mef.a: mefentrifluconazole; meso: mesosulfuron-methyl;

pino: pinoxaden; pyra: pyraclostrobin; pyro: pyroxsulam; tebu: tebuconazole.

ND: no detection; LQ: limit of quantification.

Table S4. Quantification raw data: soil solution samples (in $\mu\text{g L}^{-1}_{\text{soil solution}}$).

pot	clop	cloq	flon	flor	flur	flux	iodo	MCPA	MCPB	mef.a	meso	pyra	pyro	tebu
LQ	1,50	0,10	0,10	0,10	0,50	0,03	0,20	0,20	0,75	0,25	0,10	0,20	0,05	0,15
6	2,88	ND	<LQ	ND	ND	4,56	ND	ND	ND	0,36	1,16	ND	<LQ	14,42
7	24,09	ND	0,20	0,23	1,35	9,01	ND	<LQ	ND	0,57	6,78	ND	0,46	32,13
8	41,03	ND	0,48	0,39	9,88	0,46	ND	0,21	ND	ND	1,91	ND	1,75	1,21
9	47,94	ND	0,67	0,40	5,29	7,49	ND	0,31	ND	0,46	3,94	ND	1,75	24,48
11	14,81	ND	0,30	0,19	3,24	3,75	ND	0,27	ND	<LQ	2,77	ND	0,34	7,28
12	17,30	ND	0,21	0,23	3,10	1,14	ND	<LQ	ND	<LQ	1,63	ND	0,32	3,20
13	22,38	ND	0,38	0,26	5,57	3,18	ND	<LQ	ND	0,28	2,08	ND	0,70	9,90
14	20,66	ND	0,54	0,23	3,55	4,74	ND	0,23	ND	<LQ	2,78	ND	0,51	9,96
15	32,91	ND	1,81	0,58	8,98	8,40	ND	4,70	ND	0,63	4,46	ND	3,07	24,70
16	38,86	ND	0,38	0,28	8,55	2,69	ND	0,49	ND	ND	3,53	ND	1,03	6,45
17	16,12	ND	<LQ	0,20	0,85	2,59	ND	ND	ND	<LQ	3,02	ND	0,19	7,65
18	44,57	ND	4,61	0,75	42,02	2,15	<LQ	5,37	3,49	ND	5,37	ND	5,83	7,39
19	21,66	ND	0,89	0,28	4,92	0,45	ND	1,14	ND	ND	3,79	ND	1,40	2,21
20	25,82	ND	0,41	0,23	2,45	5,07	ND	0,25	ND	0,35	3,24	ND	0,80	14,81
21	15,36	ND	0,85	0,21	6,94	9,29	ND	0,57	<LQ	0,50	3,16	ND	0,87	16,09
22	12,99	ND	0,14	0,19	1,53	4,48	ND	0,23	ND	0,53	1,97	0,26	0,22	9,33
23	8,65	ND	ND	ND	0,92	4,62	ND	ND	ND	0,35	2,47	ND	0,20	8,74
24	7,18	ND	0,21	ND	1,52	8,95	ND	0,22	ND	0,68	2,59	0,48	0,19	16,62
25	5,98	ND	<LQ	ND	0,65	2,01	ND	ND	ND	<LQ	1,84	ND	0,07	4,61
26	13,52	ND	0,30	0,17	2,94	8,05	ND	0,20	ND	0,29	2,89	ND	0,42	12,80
27	1,68	ND	<LQ	ND	<LQ	2,92	ND	ND	ND	<LQ	1,66	ND	0,07	4,46
28	4,55	ND	ND	ND	0,83	3,11	ND	ND	ND	<LQ	2,21	ND	0,10	5,35
30	3,63	ND	<LQ	ND	0,98	7,40	ND	<LQ	ND	0,29	1,97	ND	0,14	13,04
31	<LQ	ND	<LQ	ND	<LQ	1,83	ND	<LQ	ND	ND	0,57	ND	<LQ	6,04
32	3,63	ND	0,13	ND	1,48	4,17	ND	0,97	ND	0,37	0,97	ND	0,17	11,90
33	6,12	ND	0,26	ND	1,82	2,93	ND	0,64	ND	<LQ	1,11	ND	0,20	9,14
34	<LQ	ND	ND	ND	ND	5,49	ND	ND	ND	0,27	1,16	ND	<LQ	15,30
35	<LQ	ND	<LQ	ND	0,51	2,20	ND	0,24	ND	<LQ	1,24	ND	0,06	8,10

clop: clopyralid; **cloq:** cloquintocet-mexyl; **fent:** fenpicoxamid; **flon:** flonicamid; **flor:** florasulam; **flur:** fluoroxypr; **flux:** fluxapyroxad;

iodo: iodosulfuron-methyl-sodium; **mef.a:** mefenitrifluconazole; **meso:** mesosulfuron-methyl; **pino:** pinoxaden; **pyra:** pyraclostrobin; **pyro:** pyroxsulam; **tebu:** tebuconazole.

ND: no detection; **LQ:** limit of quantification.

Table S5. Physicochemical properties of the active substances.

a.s.	CAS RN	DT ₅₀	log(K _{oc})	s	GUS	p	k _H	log(K _{ow})	BCF	m
clop	1702-17-6	23	0.70	7.9×10^3	3.02	1.4	1.8×10^{-11}	-2.63	1	192.00
cloq	99607-70-2	5.0	3.99	5.9×10^{-1}	0.00	5.3×10^{-3}	3.0×10^{-3}	5.20	621	335.80
fent	517875-34-2	3.5	4.73	4.1×10^{-2}	-0.29	1.2×10^{-4}	2.4×10^{-3}	4.40	18	614.64
flon	158062-67-0	3.1	0.20	5.2×10^3	1.87	9.4×10^{-4}	4.2×10^{-8}	-0.24	1	229.16
flor	145701-23-1	1.9	1.34	6.4×10^3	2.50	1.0×10^{-2}	4.4×10^{-7}	-1.22	1.5	359.28
flur	69377-81-7	13	1.83	6.5×10^3	1.03	3.8×10^{-6}	1.7×10^{-10}	0.04	62	255.03
flux	907204-31-3	183	2.86	3.4	2.57	2.7×10^{-6}	3.0×10^{-7}	3.13	36	381.31
hala	943831-98-9	1.3	3.15	1.8×10^3	1.64	5.9×10^{-6}	1.2×10^{-6}	3.76	217	345.16
iodo	144550-36-7	2.7	1.65	2.5×10^4	1.19	2.6×10^{-6}	2.3×10^{-11}	-0.70	1	529.24
MCPA	94-74-6	12	1.87	2.5×10^5	3.13	4.0×10^{-1}	1.5×10^{-1}	-0.81	1	200.62
MCPB	4-81-5	3.7	2.02	6.0×10^1	1.12	5.3×10^{-2}	9.4×10^{-5}	1.33	1	228.67
mef.d	135590-91-9	18	2.80	2.0×10^1	1.49	6.3×10^{-3}	2.6×10^{-4}	3.83	392	373.23
mef.a	1417782-03-6	268	3.54	8.1×10^{-1}	1.06	3.2×10^{-3}	1.6×10^{-3}	3.40	167	397.78
meso	208465-21-8	44	1.96	4.8×10^2	3.85	3.5×10^{-9}	3.7×10^{-12}	-0.48	1	503.51
pino	243973-20-8	0.5	2.54	2.0×10^2	-0.32	2.0×10^{-4}	9.2×10^{-7}	3.20	1	400.51
pyra	175013-18-0	42	3.97	1.9	0.05	2.6×10^{-5}	5.3×10^{-6}	3.99	706	387.82
pyro	422556-08-9	3.3	1.52	3.2×10^3	2.84	1.0×10^{-4}	6.9×10^{-7}	-1.01	1	434.35
tebu	107534-96-3	63	2.89	3.6×10^1	1.86	1.3×10^{-3}	1.0×10^{-5}	3.70	78	307.82

a.s.: active substance; **CAS RN:** Chemical Abstracts Service Registry Number; **DT₅₀:** typical soil persistence (in days); **log(K_{oc})**: soil sorption coefficient (in mL g⁻¹); **s**: water solubility at 20 °C (in mg L⁻¹); **GUS**: groundwater ubiquity score (dimensionless); **p**: vapour pressure at 20 °C (in mPa); **k_H**: Henry's law constant (in Pa m³ mol⁻¹); **log(K_{ow})**: n-octanol–water partition coefficient at pH 7 and 20 °C (dimensionless); **BCF**: biocentration factor (in L kg⁻¹); **m**: relative molecular mass (dimensionless).

clop: clopyralid; **cloq:** cloquintocet-mexyl; **fent:** fenpicoxamid; **flon:** flonicamid; **flor:** florasulam; **flur:** fluroxypyr; **flux:** fluxapyroxad; **hala:** halauxifen-methyl;

iodo: iodosulfuron-methyl-sodium; **mef.d:** mefenpyr-diethyl; **mef.a:** mefentrifluconazole; **meso:** mesosulfuron-methyl; **pino:** pinoxaden; **pyra:** pyraclostrobin; **pyro:** pyroxsulam; **tebu:** tebuconazole.

Table S6. Property thresholds and data interpretation.

parameter	low	moderately low	moderate	moderately high	high	very high
DT ₅₀ soil	≤ 30		30 — 100		100 — 365	> 365
log(K _{oc})	≤ 15	15 — 75	75 — 500	500 — 4000	> 4000	
s	≤ 10		10 — 1000		1000 — 100 000	> 100 000
GUS	≤ 1.8		1.8 — 2.8		> 2.8	
p	≤ 5.0		5.0 — 10.0		> 10.0	
k _H	≤ 0.1		0.1 — 100		> 100	
log(K _{ow})	≤ 2.7		2.7 — 3		> 3	
BCF	≤ 100		100 — 5000		> 5000	

DT₅₀ soil: typical soil persistence (in days); **log(K_{oc})**: soil sorption coefficient (in mL g^{-1}), inversely proportional to soil mobility; **s**: water solubility at 20 °C (in mg L^{-1}); **GUS**: groundwater ubiquity score (dimensionless), proportional to leachability; **p**: vapour pressure at 20 °C (in mPa); **k_H**: Henry's law constant (in $\text{Pa m}^3 \text{ mol}^{-1}$); **log(K_{ow})**: n-octanol–water partition coefficient at pH 7 and 20 °C (dimensionless); **BCF**: biocentration factor (in L kg^{-1}).

Threshold extracted from Lewis et al. (2016), see sitem.herts.ac.uk/aeru/ppdb/en/docs/Background_and_Support.pdf.

S2: Pesticide quantification

Soil and soil solution samples were analysed at the laboratory of the Walloon Agricultural Research Centre (CRA-W) in Gembloux (Belgium) for quantification of the 18 applied active substances and safeners. The quantification of metabolites was not pursued due to laboratory protocol limitations.

15 Frozen soil samples were thawed and sieved to 2 mm to homogenise and remove plant fragments, stones and other debris. A 5 g subsample was extracted using the following QuEChERS method. 5 mL of Milli-Q water were added to the soil subsample, which was then vortexed and left to macerate for 30 min. 10 mL of acidified acetonitrile (2 % formic acid) were then added and the sample was shaken again and left to macerate for a further 30 min. A pre-weighed bag of QuEChERS salt (4 g MgSO₄, 1 g NaCl, 0.5 g sodium hydrogencitrate sesquihydrate, 1 g sodium citrate dihydrate; purchased from Agilent, USA) was added 20 and the mixture was shaken for 1 min at 20 Hz (using a MM400 Retch mixer mill). After centrifugation at 4800 rcf at 4 °C for 15 min, the supernatant was filtered on a 0.2 µm polytetrafluoroethylene (PTFE) filter and transferred to a glass vial. A 5 µL aliquot was analysed by liquid chromatography (LC; Nexera X2™ Shimadzu, USA) coupled to a quadrupole time-of-flight mass spectrometer (QTOFMS; X500R ABSciex, Singapore).

25 Soil solution samples were analysed within 7 d of collection. 2 mL of acetonitrile were added to 10 mL of soil solution sample, shaken manually and centrifuged at 4800 rcf. The supernatant was filtered through a 0.2 µm PTFE filter and 5 µL was analysed on the same LC-QTOFMS instrument.

30 The column used for LC was a Waters ACQUITY UPLC™ HSS T3 (100 mm × 2.1 mm, 1.8 µm particle size), maintained at 40 °C. The mobile phase gradient (at a flow of 0.3 mL min⁻¹) consisted of (A) Milli-Q water and methanol (90/10, v/v) containing 2 mM ammonium formate acidified with 0.1 % formic acid and (B) methanol containing 0.1 % formic acid. The gradient progressed from 100 % aqueous phase A to 100 % organic phase B in 4 min, was held at 100 % organic phase B for 4.5 min then returned to 100 % phase A during 6 min for re-equilibration. Analyses were performed in multi reaction monitoring (MRM) mode with electrospray ionisation in positive mode (ESI+), except for MCPA et MCPB which were quantified in negative mode (ESI-).

35 Soil quantification was calibrated using a matrix calibration curve based on pesticide-free organic soil as reference material. For each analysis sequence, three spiked reference soils (0.2, 1 and 10 µg kg⁻¹) were processed to verify extraction efficiency. Soil solution quantification was performed using a calibration curve prepared in Milli-Q water containing 20 % acetonitrile, after confirming no matrix effect.

40 Two active substances were excluded from soil solution quantification due to solubility limitations (fenpicoxamid) and non-linear responses under the conditions applied (pinoxaden). Mefenpyr-diethyl was never quantified in either soil or soil solution samples; we have no explanation for this absence.

Soil samples collected on day 0 ($n = 5$), day 45 ($n = 15$) and day 80 (random selection; $n = 3$) were thawed, sieved, QuEChERS extracted and analysed by LC-QTOFMS in duplicate one month later to assess analytical variability for fluxapyroxad, mefentrifluconazole and tebuconazole (Table S7). The average absolute difference between duplicate quantifications for these molecules was $1.7 \pm_{sd} 9.2\%$ ($n = 23$). Due to their high concentrations, these three molecules required dilution to fit within

45 the calibration range (0.1 to 20 $\mu\text{g kg}^{-1}$), introducing a potential source of variability compared to undiluted compounds. In addition, the one month interval between the first and second analyses may have contributed to the variability. For the sake of readability, this analytical variability is not repeated throughout the paper. As this assessment was not carried out for all quantified molecules, the error bars in Fig. 4, Fig. S1, Fig. S2 and Fig. S3 do not take this into account.

Table S7. Quantification raw data: soil samples (in $\mu\text{g kg}_{\text{fresh soil}}^{-1}$); duplicated quantification for analytical variability analysis.

pot	flux	mef.a	tebu
1	255,18	192,64	752,12
2	187,21	144,67	529,58
3	170,65	137,29	508,84
4	201,93	162,88	612,37
5	232,69	182,82	676,60
6	114,86	71,98	302,11
7	107,84	71,11	284,69
8	83,66	55,53	199,90
9	97,98	61,63	255,77
10	90,82	59,46	246,56
11	155,09	108,42	394,38
12	93,42	45,53	219,62
13	107,92	66,80	260,04
14	126,21	83,96	316,39
15	111,87	60,08	278,49
16	151,67	92,11	421,23
17	121,19	71,89	301,65
18	137,92	93,33	361,15
19	137,25	78,93	347,53
20	142,55	87,21	361,14
23	253,17	165,11	601,26
28	276,38	186,24	625,86
33	134,48	69,30	270,45

flux: fluxapyroxad; **mef.a:** mefentrifluconazole;

tebu: tebuconazole.

S3: Selection of three contrasted molecules

50 In order to analyse the behaviour of active substances under the different cover types, we selected a subset of compounds that serve as representative examples of the pesticides used. This selection was based on two main criteria: (1) contrasting physicochemical properties and (2) consistent detection over time in soil samples. In order to maximise the contrast between the 18 applied active substances in this selection process, we chose not to use PCA clustering—which tends to produce average values from cluster centres—and instead used archetypal analysis (Cutler and Breiman, 1994¹).

55 Archetypal analysis is a statistical method that synthesises multivariate observations by identifying a set of extreme points (archetypes) or their closest observed counterparts (archetypoids) that lie on the boundary of the data set. Mathematically, it is an unsupervised learning approach that identifies extreme observations that are convex combinations—linear combinations with positive coefficients that sum to one—of the data set. The analysis was performed using the *archetypes* package in *R* (Eugster and Leisch, 2009²).

60 To distinguish between different environmental transfer mechanisms, we selected physicochemical properties relevant to key fate processes (data extracted from the PPDB, Table S5): typical soil persistence (DT50_{soil}, in days) and soil sorption coefficient (K_{oc}, in mL g^{-1}) for persistence and mobility in soil, respectively; water solubility at 20 °C (s, in mg L^{-1}) and groundwater ubiquity score (GUS, dimensionless) for transfer to soil solution and tendency to leach; vapour pressure at 20 °C (p, in mPa) and Henry's law constant (k_H, in $\text{Pa m}^3 \text{mol}^{-1}$) for transfer to air; n-octanol–water partition coefficient (i.e. 65 lipophilicity) at pH 7 and 20 °C (K_{ow}, dimensionless), bioconcentration factor (BCF, in L kg^{-1}) and relative molecular mass (m, dimensionless) for uptake in plants.

To ensure representativeness while avoiding bias towards highly persistent molecules, we prioritised compounds detected in at least 25 % of samples on day 0 and day 45, rather than selecting only those consistently quantified across all sampling dates. This approach allowed the inclusion of compounds that became undetectable in a compartment by day 80. Recognising the 70 limitations associated with our low LQ in soil solution, we chose not to impose consistent quantification in soil solution samples as a selection criterion. The archetypal analysis algorithm was run 50 times to avoid convergence to a local minimum and the first three archetypes identified were selected: mesosulfuron-methyl, MCPA and mefenitrifluconazole. These three substances exhibit low volatility (consistent with their high detection rates) but have distinct physicochemical profiles in terms of water solubility, soil persistence and molecular mass:

75 — Mesosulfuron-methyl (systemic post-emergence herbicide): has moderate soil mobility, moderate water solubility, very low volatility and high molecular weight.

— MCPA (systemic post-emergence herbicide): has high soil mobility, very high water solubility, low volatility and low molecular weight.

— Mefenitrifluconazole (systemic fungicide): has very low soil mobility, low water solubility, low volatility and moderate 80 molecular weight.

¹Cutler, A., Breiman, L.: Archetypal analysis. *Technometrics*, 36 (4), 338–347, <https://doi.org/10.1080/00401706.1994.10485840>, 1994

²<http://CRAN.R-project.org/package=archetypes>

S4: Influence of cover types for three contrasted molecules

In order to analyse the behaviour of active substances under the different cover types, we selected a subset of compounds that were consistently detected in soil samples, examining their behaviour under the different cover types, that serve as representative examples of the pesticides used: mesosulfuron-methyl, MCPA and mefenitrifluconazole (see Supplement S3).

85 Mesosulfuron-methyl (a systemic post-emergence herbicide with moderate soil mobility, moderate water solubility, very low volatility and high molecular mass) showed uniform behaviour in all modalities in soil samples on day 45, with a soil content of ca. $3 \mu\text{g kg}^{-1}$ (i.e. ca. 30 % of the initial applied mass on day -14; Fig. S1a). By day 80, the average content in soil samples under the thin cover was $32 \pm \Delta 37\%$ higher than under the control (p -value < 0.05), whereas it was $37 \pm \Delta 22\%$ lower under the thick cover (p -value < 0.05). In the soil solution on day 45, the average concentration under the cover types 90 was not different from the control, with a soil solution equivalent content of ca. $0.7 \mu\text{g kg}^{-1}$ (i.e. ca. 7 % of the initial mass). However, by day 80, the average soil solution content under the thick cover had decreased by $58 \pm \Delta 14\%$ compared to the control (p -value < 0.01).

95 MCPA (a systemic post-emergence herbicide with high soil mobility, very high water solubility, low volatility and low molecular mass) also showed a uniform behaviour in all modalities in soil samples on day 45, with a soil content of ca. 1.5 $\mu\text{g kg}^{-1}$ (i.e. ca. 0.25 % of the initial mass; Fig. S1b). By day 80, the average content in the soil samples under the thin cover was equivalent to that of the control, whereas it had decreased by $31 \pm \Delta 30\%$ under the thick cover (p -value < 0.05). In the soil solution, concentrations were at or below the LQ for all modalities on both dates, limiting further interpretation. Compared to mesosulfuron-methyl, average soil and soil solution equivalent contents were significantly lower for MCPA 100 (below 0.5 % of the initial mass), suggesting that a greater share of the initial mass was either transferred out of the system or degraded. The observed reduction in soil samples under the thick cover supports hypothesis (2), while the limited rhizofiltration effect under the thin cover (hypothesis 1) was likely due to the high soil mobility and very high solubility of MCPA.

105 Mefenitrifluconazole (a systemic fungicide with very low soil mobility, low water solubility, low volatility and moderate molecular mass) also showed a uniform behaviour in all modalities in soil samples on day 45, with a soil content of ca. 75 $\mu\text{g kg}^{-1}$ (ca. 55 % of the initial mass; Fig. S1c). By day 80, the average content in the control soil samples had increased by 95 $\pm \Delta 19\%$, reaching ca. $150 \mu\text{g kg}^{-1}$ (ca. 110 % of the initial mass), due to changes in soil sampling. On day 80, the average content in the soil samples under the thin cover was $25 \pm \Delta 31\%$ higher than under the control (p -value < 0.05), whereas it was 41 $\pm \Delta 14\%$ lower under the thick cover (p -value < 0.01). As for MCPA, concentrations in the soil solution were at or below the LQ for all modalities on both dates. The results are, again, consistent with our hypotheses, showing (1) a significant increase in pesticide content under the thin cover compared to the control by day 80, hypothetically driven by an evapotranspiration-induced rhizofiltration, and (2) a very significant decrease under the thick cover, likely due to biodegradation facilitated by microorganisms stimulated by the developed rhizosphere.

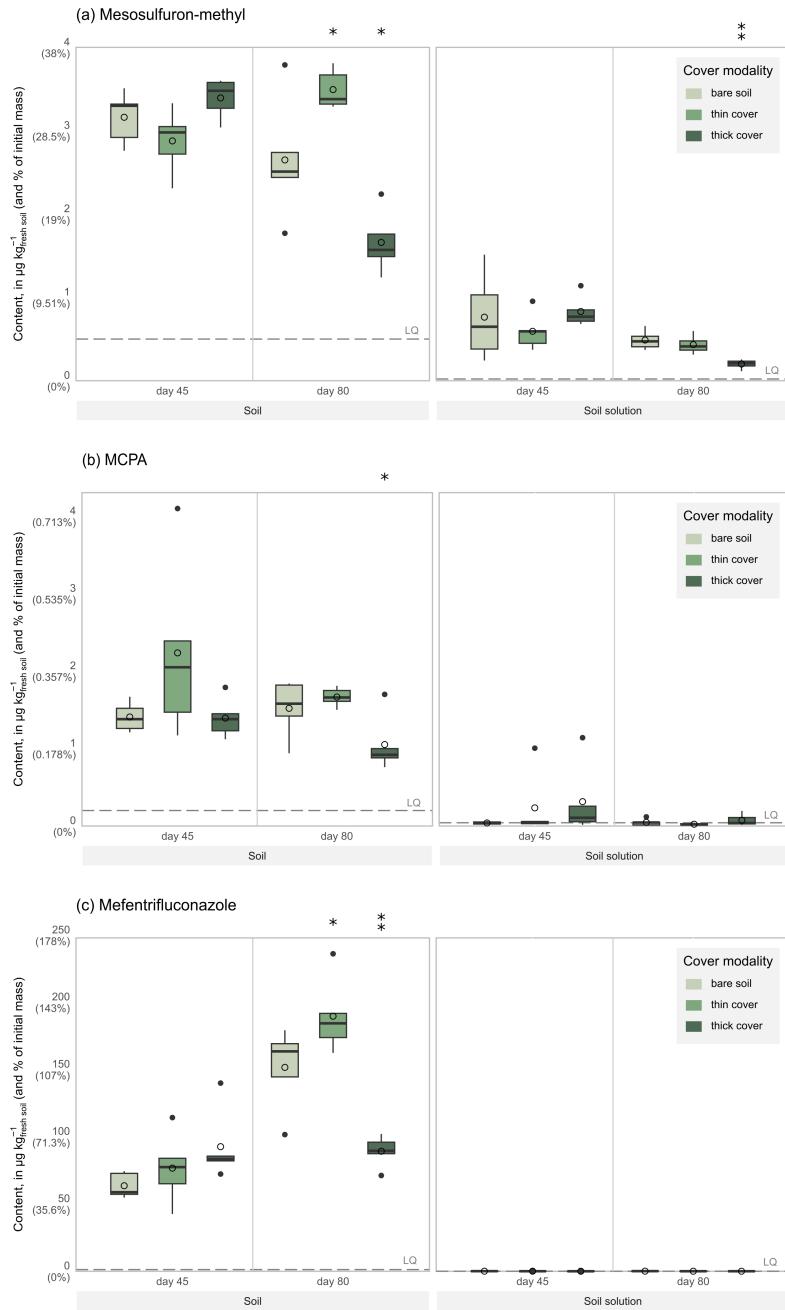


Figure S1. Active substance contents (in $\mu\text{g kg}^{-1}$ and in proportion of the initial applied mass on day -14) for three contrasting molecules (mesosulfuron-methyl, a; MCPA, b; mefenitrifluconazole, c) under three cover modalities (bare soil, thin cover and thick cover) in two compartments (soil and soil solution) at two dates (day 45 and day 80). Stars above the graphs depict statistically significant unilateral differences between the cover types and the control (bare soil) at each date (*: $0.05 \geq p\text{-value} > 0.01$; **: $0.01 \geq p\text{-value} > 0.001$). The *thick cover modality* refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80) and the *thin cover modality* refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

S5: Minimal sampling size

Minimal sampling size was evaluated for unilateral testing assuming normal distribution, using the formula:

$$n = \frac{2(Z_{1-\alpha} - Z_\beta)^2}{d^2} \quad (\text{S2})$$

115 where n is the minimum sample size for each modality to achieve a test power of $1 - \beta$ at a threshold of α , where $Z_{1-\alpha}$ and Z_β are the quantiles of order $1 - \alpha$ and β of the standard normal distribution $\mathcal{N}(0, 1)$ and where d is Cohen's d measuring the effect size of the modality (Cohen, 2013):

$$d = \frac{\mu_1 - \mu_2}{\sqrt{\frac{(n_1 - 1)\sigma_1^2 + (n_2 - 1)\sigma_2^2}{n_1 + n_2 - 2}}} \quad (\text{S3})$$

120 where μ_i are the means of the contents in the cover modality and the control, σ_i their standard deviations and n_i their sample sizes. Values of $\alpha = 0.05$ and $\beta = 0.20$ were used throughout the analysis.

We calculated the minimum sample sizes required to achieve at least 80 % statistical power under similar conditions of active substance levels, variances between independent replicates and cover development. These sample sizes are presented in Table S8 by date, cover type, compartment and active substance.

Table S8. Sample size (n) tested in our experiment (with associated statistical significativity obtained) and minimal sample size (Min. n) needed to reach a statistical power of at least 80 %.

	Substance	Soil			Soil Solution		
		n tested	p-val.	Min. n	n tested	p-val.	Min. n
day 45	Thin cover	clopyralid	5 vs 5	.	12	5 vs 5	46
		cloquintocet-mexyl	5 vs 5		57	5 vs 5	–
		fenpicoxamid	5 vs 5		32	5 vs 5	–
		flonicamid	5 vs 5		28	5 vs 5	40
		florasulam	5 vs 5		–	5 vs 5	251
		fluroxypyr	5 vs 5		22	5 vs 5	286
		fluxapyroxad	5 vs 5		29	5 vs 5	98
		MCPA	5 vs 5	.	13	5 vs 5	35
		mefentrifluconazole	5 vs 5		26	5 vs 5	71
		mesosulfuron-methyl	5 vs 5		19	5 vs 5	85
		pyraclostrobin	5 vs 5	.	13	5 vs 5	–
		pyroxsulam	5 vs 5	*	6	5 vs 5	99694
		tebuconazole	5 vs 5		33	5 vs 5	29
		clopyralid	5 vs 5	.	9	5 vs 4	17751
		cloquintocet-mexyl	5 vs 5		39	5 vs 4	–
Thick cover	Thin cover	fenpicoxamid	5 vs 5	.	15	5 vs 4	–
		flonicamid	5 vs 5	**	3	5 vs 4	31
		florasulam	5 vs 5		–	5 vs 4	75
		fluroxypyr	5 vs 5	*	4	5 vs 4	38
		fluxapyroxad	5 vs 5	*	5	5 vs 4	13
		MCPA	5 vs 5		2896	5 vs 4	22
		mefentrifluconazole	5 vs 5	*	7	5 vs 4	8
		mesosulfuron-methyl	5 vs 5		18	5 vs 4	339
		pyraclostrobin	5 vs 5	*	7	5 vs 4	–
		pyroxsulam	5 vs 5	*	3	5 vs 4	56
		tebuconazole	5 vs 5	*	5	5 vs 4	11

Sample size tested: $n_{\text{cover type}}$ vs n_{control} ; **p-value:** $0.1 \geq \cdot > 0.05 \geq * > 0.01 \geq ** > 0.001$; **Minimum sample size:** n for both cover and control (–: no detection). The **thick cover** refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80) and the **thin cover** refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

Table S8 (continued). Sample size (n) tested in our experiment (with associated statistical significance obtained) and minimal sample size needed to reach a statistical power of at least 80 %.

	Substance	Soil			Soil Solution		
		n tested	p -val.	Min. n	n tested	p -val.	Min. n
day 80	Thin cover	clopyralid	5 vs 5	–	4 vs 5		15
		fenpicoxamid	5 vs 5	20	4 vs 5		–
		flonicamid	5 vs 5	–	4 vs 5		43
		florasulam	5 vs 5	–	4 vs 5		84
		fluroxypyr	5 vs 5	296	4 vs 5		52
		fluxapyroxad	5 vs 5	·	9	4 vs 5	438
		MCPA	5 vs 5	44	4 vs 5		25
		MCPB	5 vs 5	59	4 vs 5		–
		mefentrifluconazole	5 vs 5	*	8	4 vs 5	*
		mesosulfuron-methyl	5 vs 5	*	6	4 vs 5	62
		pyraclostrobin	5 vs 5	·	12	4 vs 5	–
		pyroxsulam	5 vs 5	–	4 vs 5		53
		tebuconazole	5 vs 5	*	9	4 vs 5	65
		clopyralid	5 vs 5	–	5 vs 4	**	3
		fenpicoxamid	5 vs 5	*	4	5 vs 4	–
		flonicamid	5 vs 5	–	5 vs 4		31
		fluroxypyr	5 vs 5	–	5 vs 4		19
Thick cover	Thin cover	fluxapyroxad	5 vs 5	**	2	5 vs 4	·
		MCPA	5 vs 5	*	8	5 vs 4	61
		MCPB	5 vs 5	*	4	5 vs 4	–
		mefentrifluconazole	5 vs 5	**	2	5 vs 4	*
		mesosulfuron-methyl	5 vs 5	*	5	5 vs 4	**
		pyraclostrobin	5 vs 5	*	4	5 vs 4	–
		pyroxsulam	5 vs 5	–	5 vs 4		14
		tebuconazole	5 vs 5	**	2	5 vs 4	118

Sample size tested: $n_{\text{cover type}}$ vs n_{control} ; **p -value:** $0.1 \geq \cdot > 0.05 \geq * > 0.01 \geq ** > 0.001$; **Minimum sample size:** n for both cover and control (–: no detection). The **thick cover** refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80) and the **thin cover** refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

S6: Additional Figures

125 In order to allow a direct comparison of the levels of active substances between the two compartments, we have converted the concentrations in soil solution to equivalent fresh soil content (in $\mu\text{g kg}^{-1}$) by multiplying them by the fraction of soil solution per unit mass of fresh soil, bearing in mind that the soil content also includes some of the soil solution concentration. Refer to section 2.3 for more detail.

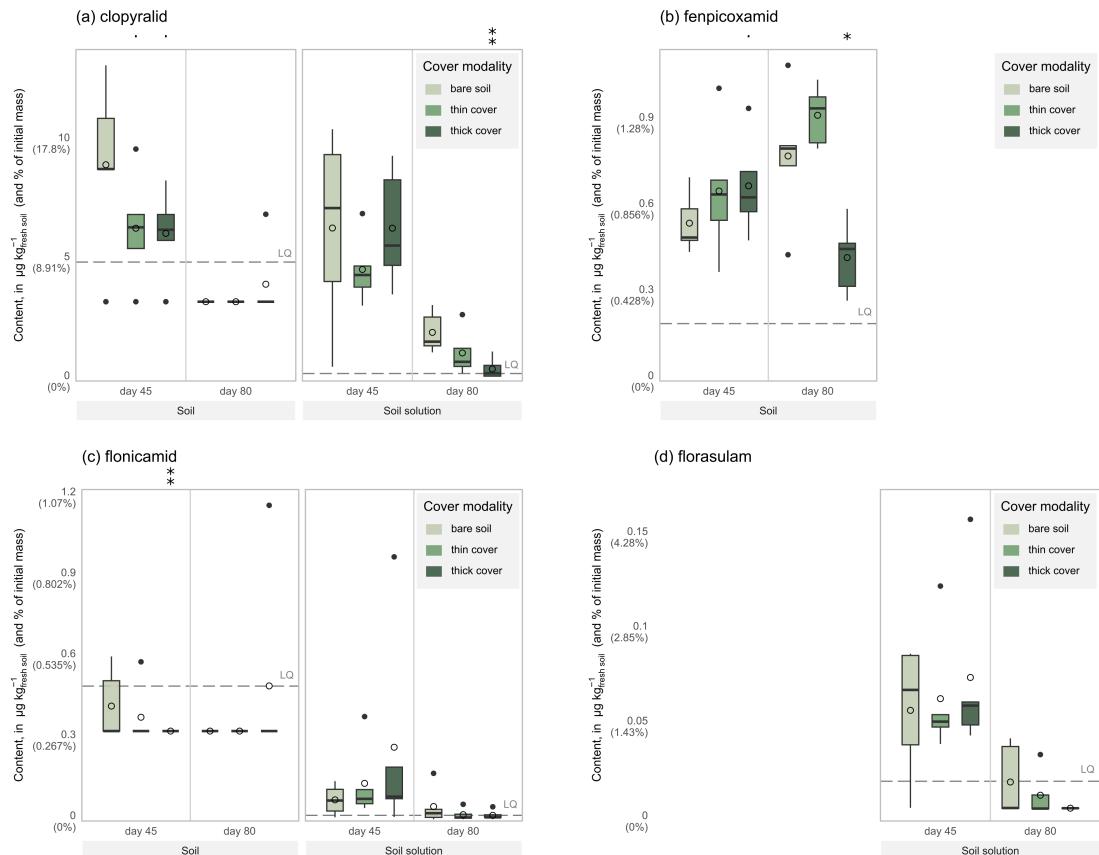


Figure S2. Active substance contents (in $\mu\text{g kg}^{-1}$ and in proportion of the initial applied mass on day -14) under three cover modalities (bare soil, thin cover and thick cover) in two compartments (soil and soil solution) at two dates (day 45 and day 80). Stars above the graphs depict statistically significant unilateral differences between the cover types and the control (bare soil) at each date (p -value: $0.1 \geq \cdot > 0.05 \geq * > 0.01 \geq ** > 0.001$). The *thick cover modality* refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80) and the *thin cover modality* refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

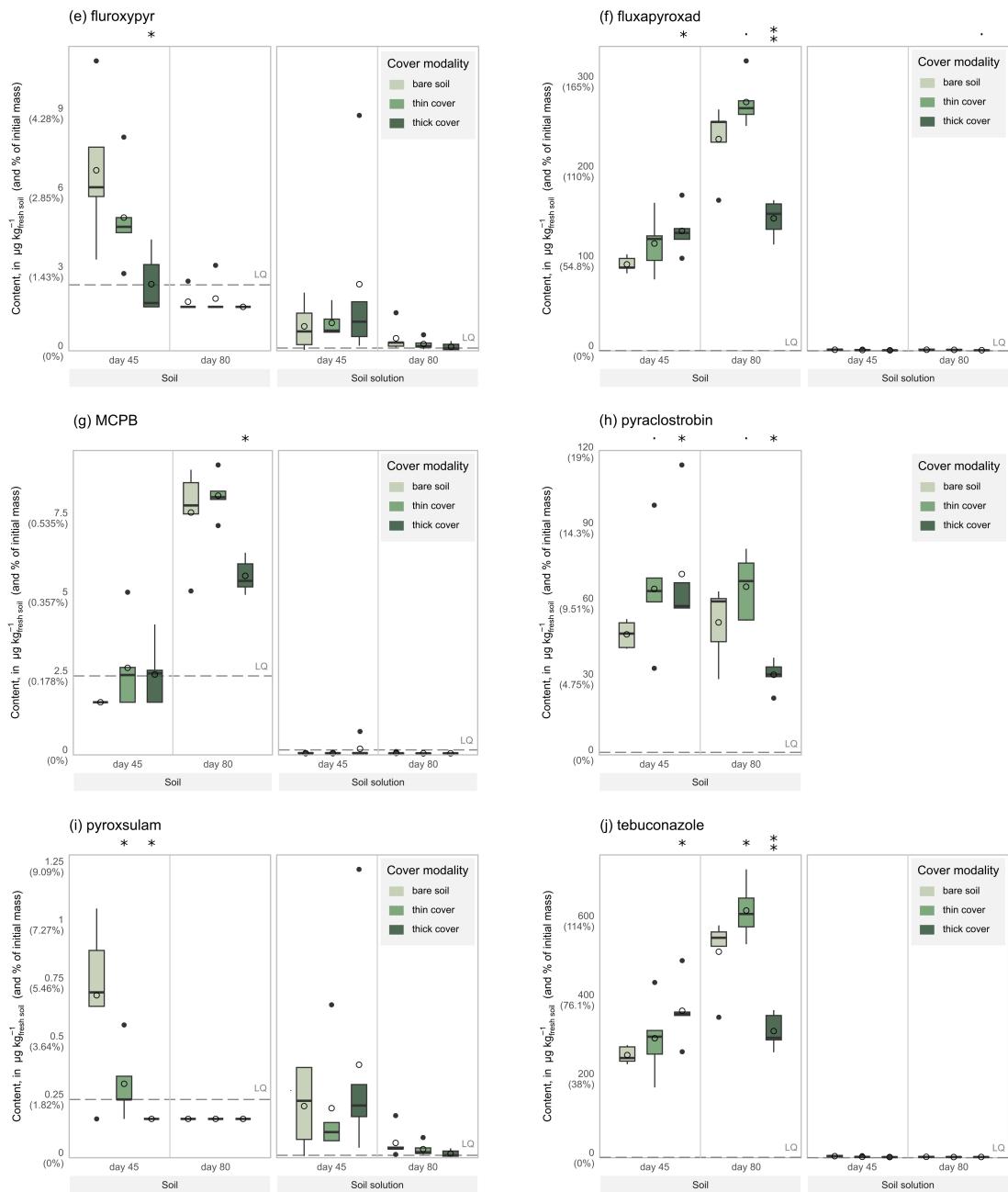


Figure S2 (continued). Active substance contents (in $\mu\text{g kg}^{-1}$ and in proportion of the initial applied mass on day -14) under three cover modalities (bare soil, thin cover and thick cover) in two compartments (soil and soil solution) at two dates (day 45 and day 80). Stars above the graphs depict statistically significant unilateral differences between the cover types and the control (bare soil) at each date (p -value: $0.1 \geq \cdot > 0.05 \geq * > 0.01 \geq ** > 0.001$). The *thick cover modality* refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80) and the *thin cover modality* refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{\text{DM}} \text{ ha}^{-1}$ on day 80).

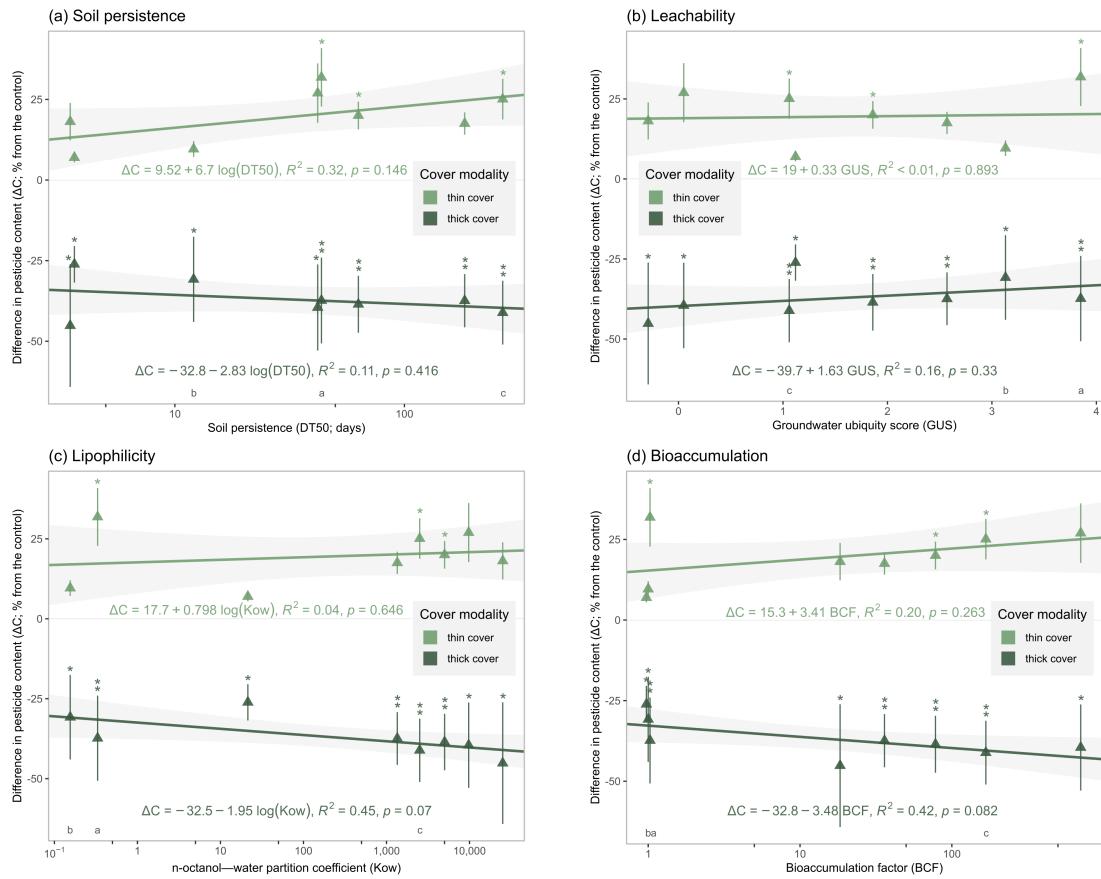


Figure S3. Differences in active substance soil contents compared to the control (bare soil) on day 80, for the eight active substance with 100 % quantification rate and for both cover types, in function of the active substance's: (a) soil persistence (as $\log(DT_{50})$), (b) leachability (GUS), (c) lipophilicity (as $\log(K_{ow})$) and (d) bioaccumulation (BCF). The coloured lines represent linear fits for both cover types, with 90 % confidence intervals. Stars above the error bars depict statistically significant unilateral differences between the cover type and the control at each date (*: $0.05 \geq p\text{-value} > 0.01$; **: $0.01 \geq p\text{-value} > 0.001$). Three contrasting molecules (see Supplements S3 and S4) are tagged with a letter below them (mesosulfuron-methyl: a; MCPA: b; mefenentrifluconazole: c). The *thick cover modality* refers to the winter spelt cover (reaching a shoot biomass of $1.12 \text{ t}_{DM} \text{ ha}^{-1}$ on day 80) and the *thin cover modality* refers to the multi-species mix (reaching a shoot biomass of $0.36 \text{ t}_{DM} \text{ ha}^{-1}$ on day 80).