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Supplement of

Hydrological tracers for assessing transport and dissipation processes of pesticides in a model constructed wetland system

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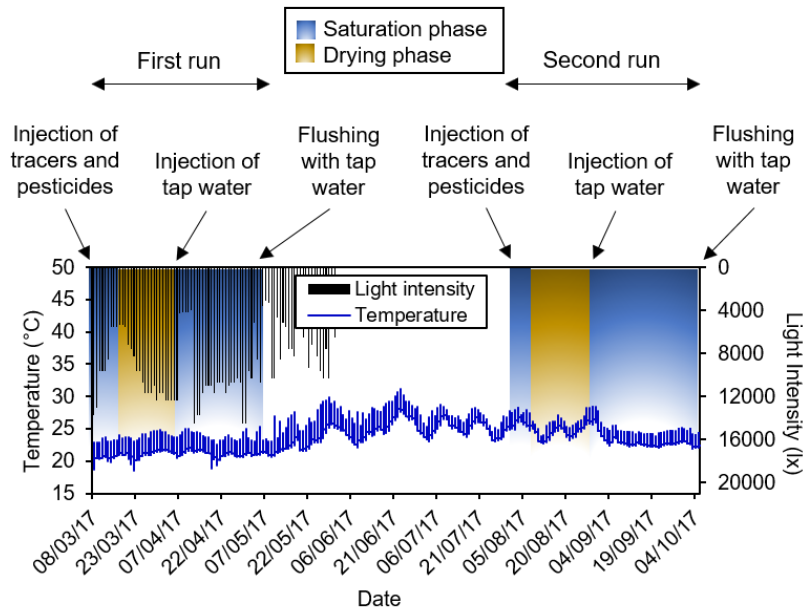


Figure S1: Air temperature and light intensity of the experimental room during the first and second run and the different phases (saturation and drying). The injections performed during each run are displayed on top of the figure. Missing data for the light intensity are due to a failure of the sensor.

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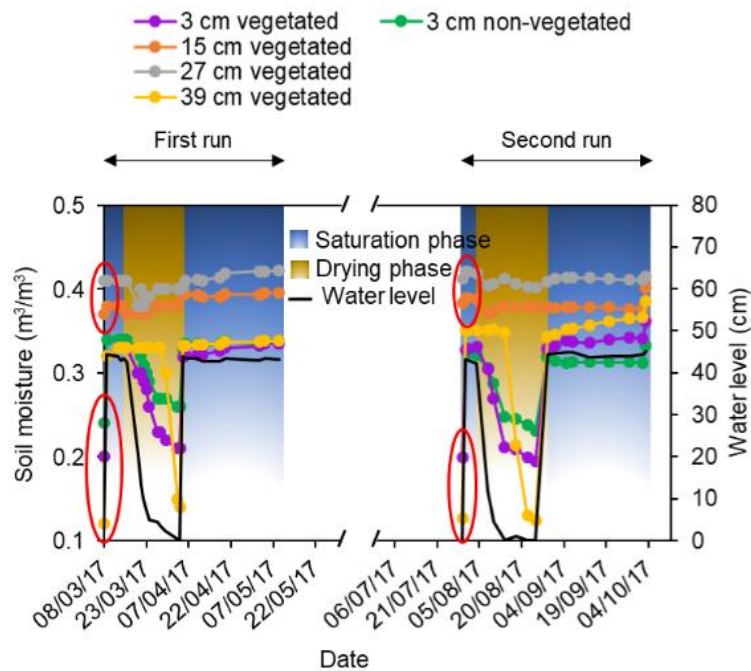


Figure S2: Soil moisture values measured in the pore water during the first and second run for the different zones, phases (saturation and drying) and depths. Water level is displayed in the second y-axis. The missing data from the sampling depths at 15, 27 and 39 cm in the non-vegetated zone is due to failures in the sensors. Red circles indicate the values previous to the injection.

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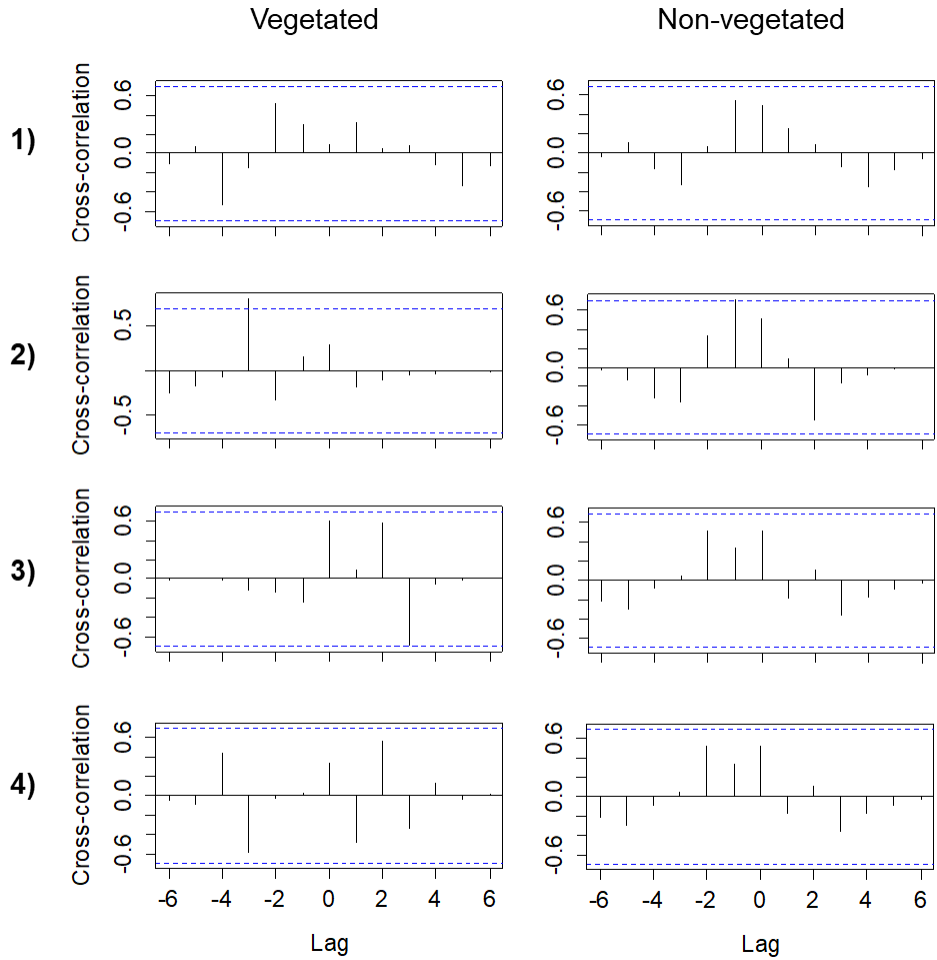


Figure S3: Lag analysis performed to the Br- breakthrough curves between the first and second run for the vegetated and non-vegetated zones and the sampling depths: 1) 3cm; 2) 15cm; 3) 27cm and 4) 39cm. The blue lines represent the approximate 95% confidence intervals.

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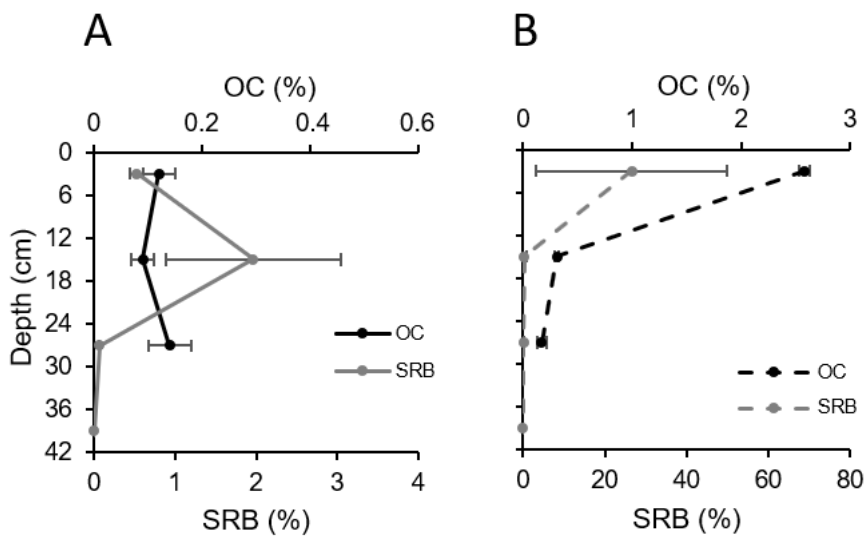


Figure S4: Selected vertical gradients of percentage of organic carbon content (OC) and SRB measured in the sediment at the end of the experiment for A) non-vegetated and B) vegetated zone. Values represent means of duplicates \pm standard deviation.

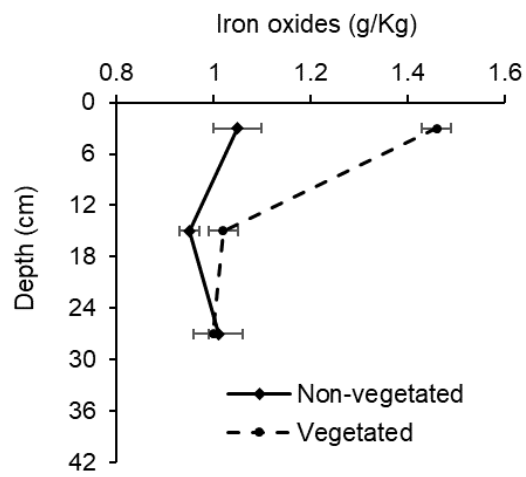


Figure S5: Selected vertical gradients of iron oxides measured in the sediment (sand) at the end of the experiment in the non-vegetated and vegetated zone. Values represent means of duplicates \pm standard deviation.

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Table S1: Mean values of the main parameters measured in the sediment (soil moisture, conductivity and temperature) and in the pore water (nitrates) during the first and second run for the different zones (non-vegetated and vegetated), phases (saturation and drying) and depths.

Parameter	Run	Phase	39 cm (gravel)		27 cm (sand)		15 cm (sand)		3 cm (sand)	
			Non-Veg	Vegetated	Non-Veg	Vegetated	Non-Veg	Vegetated	Non-Veg	Vegetated
Soil moisture [m ³ m ⁻³]	1°	Sat	-	0.32 ± 0.03	-	0.41 ± 0	-	0.38 ± 0.01	0.34 ± 0.02	0.32 ± 0.02
		Dry	-	0.30 ± 0.06	-	0.40 ± 0.01	-	0.38 ± 0.01	0.29 ± 0.03	0.26 ± 0.04
		Sat	-	0.33 ± 0.04	-	0.42 ± 0.01	-	0.39 ± 0	0.33 ± 0.02	0.32 ± 0.03
	2°	Sat	-	0.34 ± 0.04	-	0.42 ± 0	-	0.39 ± 0	0.32 ± 0	0.33 ± 0.03
		Dry	-	0.26 ± 0.10	-	0.41 ± 0.01	-	0.38 ± 0	0.26 ± 0.03	0.24 ± 0.04
		Sat	-	0.35 ± 0.05	-	0.41 ± 0	-	0.38 ± 0	0.31 ± 0.02	0.33 ± 0.03
Conductivity [dS m ⁻¹]	1°	Sat	0.19 ± 0.04	0.22 ± 0.05	-	0.17 ± 0.01	0.11 ± 0	0.30 ± 0.03	0.09 ± 0.01	0.14 ± 0.02
		Dry	0.19 ± 0.04	0.23 ± 0.07	-	0.19 ± 0.01	0.11 ± 0	0.25 ± 0.03	0.07 ± 0.01	0.09 ± 0.02
		Sat	0.20 ± 0.05	0.22 ± 0.05	-	0.17 ± 0.01	0.14 ± 0.01	0.19 ± 0	0.12 ± 0.02	0.13 ± 0.02
	2°	Sat	0.22 ± 0.05	0.20 ± 0.05	-	0.15 ± 0	0.10 ± 0.06	0.17 ± 0	0.02 ± 0.01	0.10 ± 0.01
		Dry	0.17 ± 0.13	0.18 ± 0.12	-	0.18 ± 0.01	0.15 ± 0.01	0.18 ± 0	0.02 ± 0.01	0.05 ± 0.03
		Sat	0.24 ± 0.05	0.25 ± 0.05	-	0.19 ± 0.01	0.13 ± 0.04	0.21 ± 0.01	0.04 ± 0.01	0.11 ± 0.02
Temperature [°C]	1°	Sat	20.91 ± 0.34	20.56 ± 0.24	-	20.75 ± 0.28	20.52 ± 0.34	20.05 ± 0.24	20.08 ± 0.31	20.00 ± 0.29
		Dry	21.90 ± 0.57	21.51 ± 0.60	-	21.84 ± 0.57	21.43 ± 0.53	20.91 ± 0.55	20.92 ± 0.51	20.83 ± 0.56
		Sat	22.11 ± 0.46	21.62 ± 0.49	-	22.00 ± 0.46	21.75 ± 0.42	21.11 ± 0.45	21.17 ± 0.43	20.96 ± 0.49
	2°	Sat	26.24 ± 0.50	25.77 ± 0.46	26.44 ± 0.64	26.12 ± 0.46	26.34 ± 0.31	25.36 ± 0.43	25.73 ± 0.36	25.34 ± 0.44
		Dry	25.56 ± 0.76	25.16 ± 0.71	27.20 ± 1.61	25.33 ± 0.74	25.24 ± 0.74	24.48 ± 0.73	24.51 ± 0.73	24.26 ± 0.72
		Sat	23.93 ± 1.08	23.48 ± 1.15	-	23.65 ± 1.14	23.72 ± 1.10	22.87 ± 1.14	23.05 ± 1.10	22.79 ± 1.11
Nitrates [mg L ⁻¹]	1°	Sat	3.66 ± 3.98	3.04 ± 2.79	4.49 ± 1.85	57.62 ± 35.76	12.77 ± 3.81	97.09 ± 13.05	55.66 ± 12.81	13.64 ± 4.96
		Dry	0.28 ± 0.44	1.67 ± 3.06	0.51 ± 0.29	80.61 ± 18.42	12.07 ± 4.17	86.82 ± 12.35	98.33 ± 18.99	17.53 ± 8.07
		Sat	2.81 ± 4.60	8.33 ± 4.96	0.25 ± 0.26	31.36 ± 21.23	2.43 ± 6.95	27.06 ± 18.05	34.07 ± 48.46	24.22 ± 31.96
	2°	Sat	0.08 ± 0.10	0.07 ± 0.06	0.32 ± 0.49	0.02 ± 0.02	0.31 ± 0.18	0.04 ± 0.04	9.08 ± 15.65	0.25 ± 0.24
		Dry	25.95 ± 44.80	0.19 ± 0.19	0.19 ± 0.22	0.04 ± 0.03	15.23 ± 23.04	0.07 ± 0.04	0.75 ± 0	0.04 ± 0
		Sat	5.43 ± 11.07	1.04 ± 2.02	3.95 ± 5.78	0.15 ± 0.22	0.31 ± 0.62	0.07 ± 0.10	76.22 ± 70.28	0.40 ± 0.65

The results are presented as mean ± standard deviation. Missing data are due to a failure of the sensor.

Non-veg= Non-vegetated zone; Sat= saturation phase; Dry= drying phase

Table S2: LOQ/LOD values for the pesticides and TPs.

Solutes	LOD [ng L ⁻¹]	LOQ [ng L ⁻¹]
Boscalid	0.35	1.27
Penconazole	0.35	1.29
Metazachlor	0.35	1.27
Metazachlor-ESA	2.78	10.35
Metazachlor-OA	0.54	1.90

Table S3: Selected relative concentrations of Br⁻ measured during the: 1) first and 2) second run for the different zones (non-vegetated and vegetated), phases (saturation and drying) and depths.

1)		Saturation			Drying				Saturation					
	Depth (cm)	09/03	13/03	16/03	20/03	21/03	23/03	27/03	04/04	10/04	12/04	02/05	04/05	09/05
Non-vegetated	3	0.08	0.17	0.19	0.34	0.41	-	-	-	0.33	0.35	0.21	0.17	0.03
	15	0	0	0	0.01	0.02	0.04	0.09	0.23	0.15	0.18	0.06	0.04	0.01
	27	0	0	0.02	0.03	0.04	0.04	0.05	0.08	0.08	0.07	0.01	0.01	0.05
	39	0.30	0.21	0.15	0.09	0.11	0.11	0.12	0.11	0.01	0.01	0.01	0.02	0.01
Vegetated	3	0.20	0.70	0.79	0.76	0.79	-	-	-	0.48	0.55	0.45	0.39	0.08
	15	0	0	0.01	0.03	0.04	0.06	0.09	0.06	0.02	0.00	0.06	0.05	0.03
	27	0	0	0	0	0	0	0	0.01	0.02	0.02	0.02	0.02	0.08
	39	0.10	0.02	0.02	0.03	0.04	0.05	0.06	0.06	0.01	0.02	0.04	0.05	0.00

2)		Saturation			Drying				Saturation					
	Depth (cm)	01/08	04/08	08/08	10/08	14/08	18/08	22/08	25/08	29/08	05/09	13/09	27/09	03/10
Non-vegetated	3	0.07	0.20	0.46	-	-	-	-	-	0.43	0.53	0.62	0.35	0.03
	15	0.01	0.01	0.02	0.06	0.18	0.31	0.42	-	0.39	0.41	0.30	0.15	0.02
	27	0.01	0.01	0.03	0.02	0.04	0.07	0.11	0.15	0.14	0.10	0.07	0.05	0.00
	39	0.29	0.19	0.19	0.19	0.20	0.21	0.21	0.20	0.02	0.02	0.02	0.02	0.00
Vegetated	3	0.18	0.59	0.53	-	-	-	-	-	0.09	0.16	0.18	0.08	0.01
	15	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.03	0.04	0.04	0.02
	27	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.06	0.04	0.03	0.02	0.00
	39	0.02	0.01	0.01	0.03	0.06	0.10	0.10	0.09	0.01	0.02	0.02	0.02	0.00

Table S4: Spearman rank correlation between the breakthrough curves of Br⁻ and the conductivity values of the probes located at the same depth for the first and second run and the different zones.

Depth (cm)	Zones	First run		Second run	
		rho	p-value	rho	p-value
3	Non-vegetated	-0.34	0.19	0.60	0.02 *
	Vegetated	0.07	0.80	-0.2	0.49
15	Non-vegetated	0.83	<0.001 ***	-	-
	Vegetated	-0.39	0.13	0.84	<0.001 ***
27	Non-vegetated	-	-	-	-
	Vegetated	-0.18	0.51	0.82	<0.001 ***
39	Non-vegetated	-0.07	0.81	0.05	0.86
	Vegetated	0.32	0.23	0.54	0.04 *

Signif. Codes: 0.001 ***; 0.01 **; 0.05 *

Table S5: Spearman rank correlation between the breakthrough curves of the different solutes at the vegetated and non-vegetated zones for the first and second run and the different depths.

Depth (cm)		First run		Second run	
		rho	p-value	rho	p-value
3	Br _{nv} : Br _v	0.43	0.09	0.53	0.05*
	UR _{nv} : UR _v	0.30	0.26	0.33	0.25
	SRB _{nv} : SRB _v	0.79	0.26	0.32	0.26
	BOS _{nv} : BOS _v	0.79	0.06	0.76	0.03*
	Pen _{nv} : Pen _v	0.46	0.35	-	-
	Met _{nv} : Met _v	0.59	0.22	0.58	0.13
	Met-ESA _{nv} : Met-ESA _v	0.40	0.43	-	-
	Met-OA _{nv} : Met-OA _v	-	-	-	-
15	Br _{nv} : Br _v	0.49	0.06	0.63	0.02*
	UR _{nv} : UR _v	0.53	0.04*	0.05	0.86
	SRB _{nv} : SRB _v	0.51	0.04*	-0.01	0.98
	BOS _{nv} : BOS _v	-	-	-	-
	Pen _{nv} : Pen _v	-	-	-	-
	Met _{nv} : Met _v	-	-	-	-
	Met-ESA _{nv} : Met-ESA _v	-	-	-	-
	Met-OA _{nv} : Met-OA _v	-	-	-	-
27	Br _{nv} : Br _v	0.58	0.02*	0.97	<0.001***
	UR _{nv} : UR _v	0.85	<0.001***	0.78	<0.001***
	SRB _{nv} : SRB _v	0.67	0.004**	0.64	0.01**
	BOS _{nv} : BOS _v	-	-	-	-
	Pen _{nv} : Pen _v	-	-	-	-
	Met _{nv} : Met _v	-	-	0.76	0.03*
	Met-ESA _{nv} : Met-ESA _v	-	-	-	-
	Met-OA _{nv} : Met-OA _v	-	-	-	-
39	Br _{nv} : Br _v	0.53	0.03*	0.27	0.35
	UR _{nv} : UR _v	0.84	<0.001***	0.95	<0.001***
	SRB _{nv} : SRB _v	-0.06	0.83	0.73	0.003**
	BOS _{nv} : BOS _v	-	-	-	-
	Pen _{nv} : Pen _v	-	-	-	-
	Met _{nv} : Met _v	0.40	0.44	0.76	0.03*
	Met-ESA _{nv} : Met-ESA _v	-	-	-	-
	Met-OA _{nv} : Met-OA _v	-	-	-	-

Signif. Codes: 0.001 ***; 0.01 **; 0.05 *

nv = non-vegetated; v = vegetated