Processes of dissipation of pesticides and hydrological tracers in a wetland mesocosm

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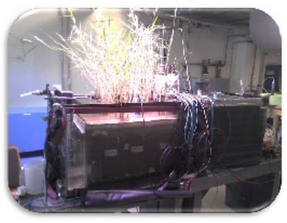
1 Introduction

The effectiveness of hydrological tracers to investigate potential dissipation pathways of pesticides in wetland systems has already been proven. However, little is known about their suitability to asses "where" and "when" such processes might take place, which ultimately represent essential information for modeling their transport and fate in the environment. Thus, we have conducted a mesocosm experiment where we have combined the analysis of three hydrological tracers (bromide, uranine and sulforhodamine B) and three pesticides (Boscalid, Penconazol and Metazachlor) with high-resolution vertical monitoring of physical and chemical gradients in a vegetated redox-dynamic environment.

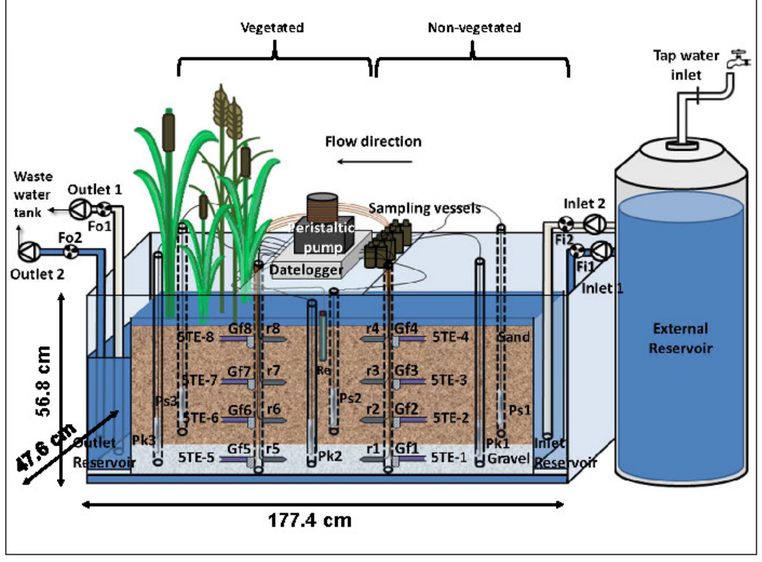
2 Method

- The mesocosm was designed as a vertical subsurface-flow system.
- One half was planted with two species of common wetland plants (Typha latifolia and Phragmites australis).
- All sensors were installed at pre-selected depths and a resolution of 12 cm.
- The experiment was running a total of 6 months during which two repetitions (injections) under identical conditions were done.



Design of the experiment

Fi: Flow meter at the inlet
Fo: Flow meter at the outlet
Ps: Piezometer (Sand)
Pk: Piezometer (Gravel)
5TE: Soil moisture, temperature and electrical conductivity sensor
Re: Reference electrode (Ag:AgCl)
r: Platinum redox electrode
Gf: Glassfilter



Chemicals and mesocosm operation

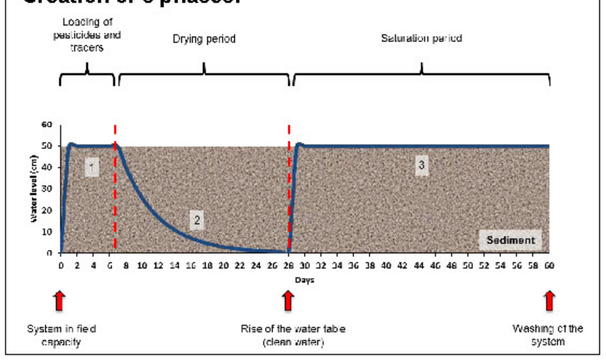
Injected substances:

Table 1. Some physicochemical properties of the tracers and pesticides.

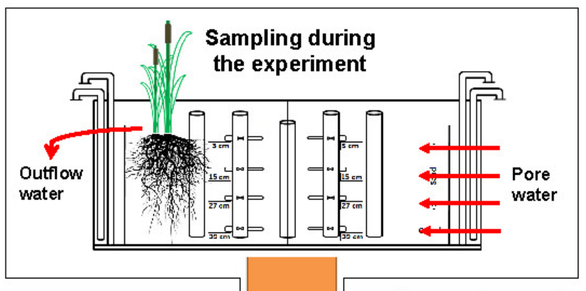
		UR	SRB	Br	Boscalid	Penconazol	Metazachlor
Chemical formula	-	$C_{20}H_{18}O_5Na_2$	$C_{27}H_{29}N_2NaO_7S_2$	NaBr	$C_{18}H_{12}Cl_2N_2O$	$C_{13}H_{15}Cl_2N_3$	$C_{14}H_{16}ClN_3O$
Molecular mass[a]	g mol^{-1}	376.3	580.7	102.89	343.21	284.18	277.75
Aqueous Solubility	g L^{-1}	300[c]	10 [10°C][c]	850[c]	0.0046[d]	0.073[d]	0.450[d]
Photolytic Stability (DT_{50})	days	0.5[c]	34[c]	stable[c]	30[d]	4[d]	stable[d]
Hydrolytic Stability (DT_{50})	days	stable[c]	stable[c]	stable[c]	stable[d]	stable[d]	stable[d]
Soil Retention (K_d)	mL g^{-1}	0-0.4[b]	1.2-3.2[b]	-	-	-	0.78[d]
Organic carbon - water partitioning (K_{OC})	L kg^{-1}	0-62[b]	147-498[b]	-	772.0[f]	2205[f]	134.0[f]

[a] ChemID database (2017), [b] Sabatini (2000), [c] Leibundgut et al. (2009), [d] IUPAC, [e] Merck Millipore (http://www.emdmillipore.de), [f] PAN Pesticides Database („pesticideinfo.org/Search_Chemicals.jsp), [g] Martin et al. (2017)

Creation of 3 phases:



Data Collection



Samples of pore water and at the outflow were taken every two days

Temperature, water content, conductivity and redox potential were continually monitored

Sampling at the end of the experiment

3 Results and Discussion

Temporal & spatial evolution:

- The development of the physicochemical parameters was driven by the changes produced during the drying and rewetting phases.

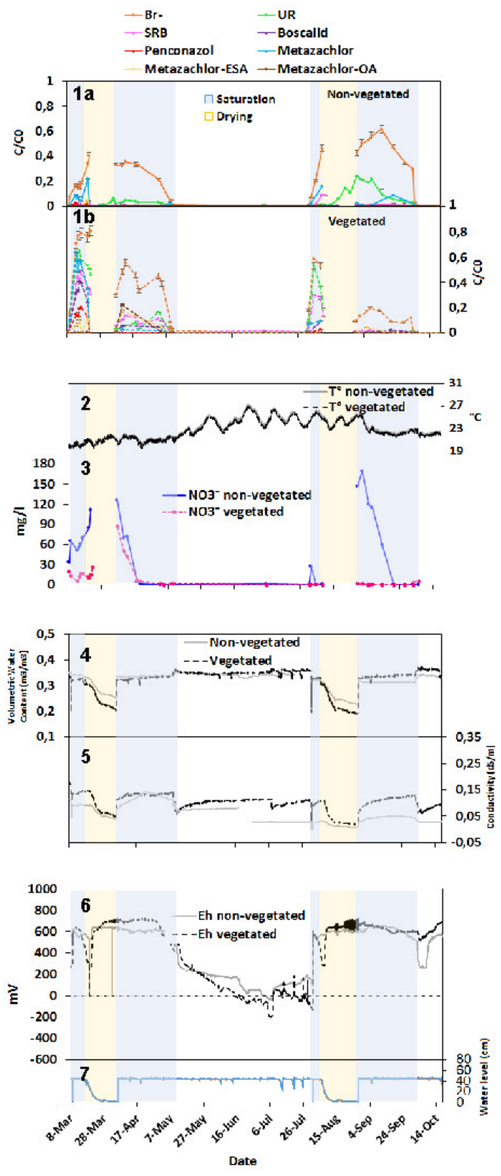
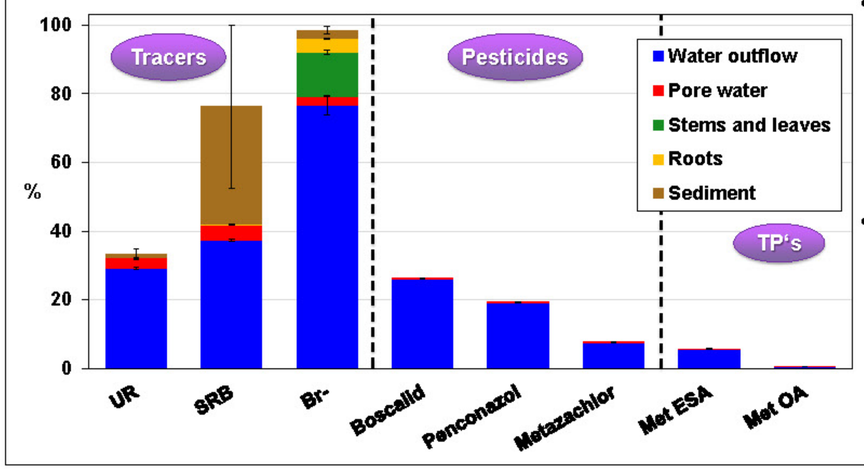


Fig 1. Temporal evolution of the relative concentration of tracers and pesticides in 1a) non-vegetated zone and 1b) vegetated zone, 2) temperature, 3) nitrate concentration, 4) volumetric water content, 5) conductivity, 6) redox potential and 7) water level.

Mass Balance:



- The overall tracer mass balance revealed that the main dissipation processes were degradation, sorption and plant uptake.
- Two transformation products from Metazachlor were detected: Metazachlor ethane sulfonic acid (ESA) and oxanilic acid (OA).

Process evaluation:

1. Transport:

- Transport processes predominated over the experiment as shown by the high overall correlations between bromide and the tracers and pesticides.
- Correlation become weaker at the end of the drying phase and beginning of saturation.
- Results were similar for the two injections indicating constant dissipation rates.

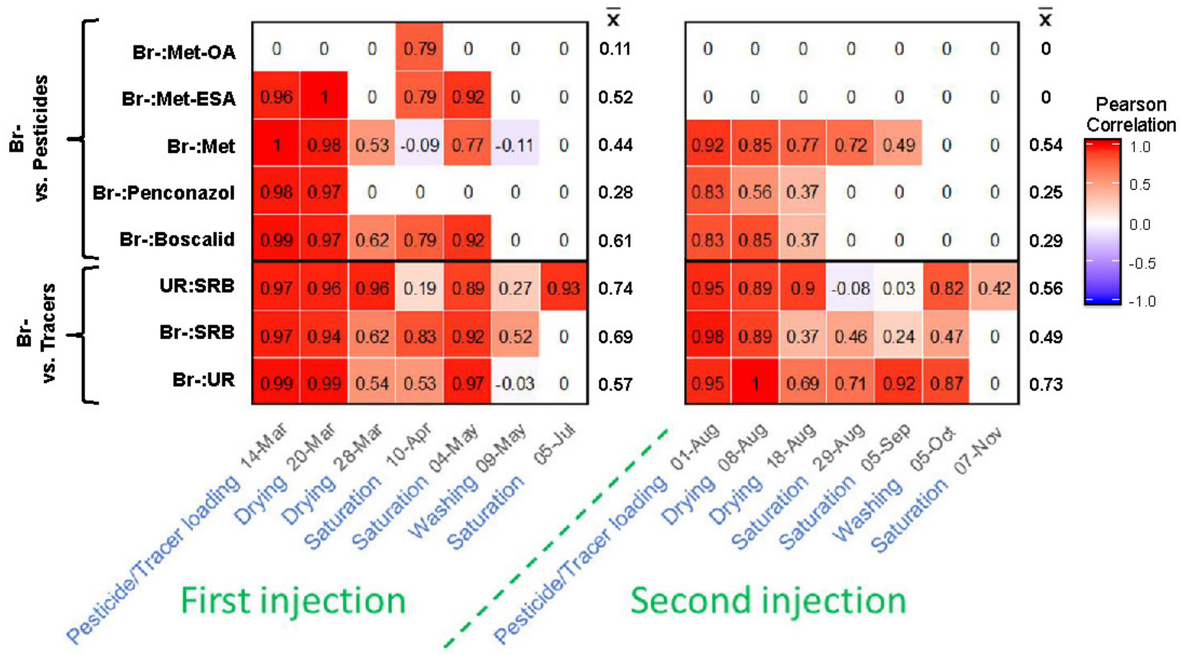


Fig 2. Correlation matrices between bromide and tracers and bromide and pesticides for the different phases of the experiment and the two injections.

2. Degradation:

- Correlation matrices indicated a different behavior depending on the depth of the layer and the availability of oxygen.
- Transformation products of Metazachlor were formed in the uppermost layer (3 cm) under oxic conditions.
- UR and Metazachlor were anaerobically degraded in the deeper layers according to their negative correlations with Eh and nitrate.

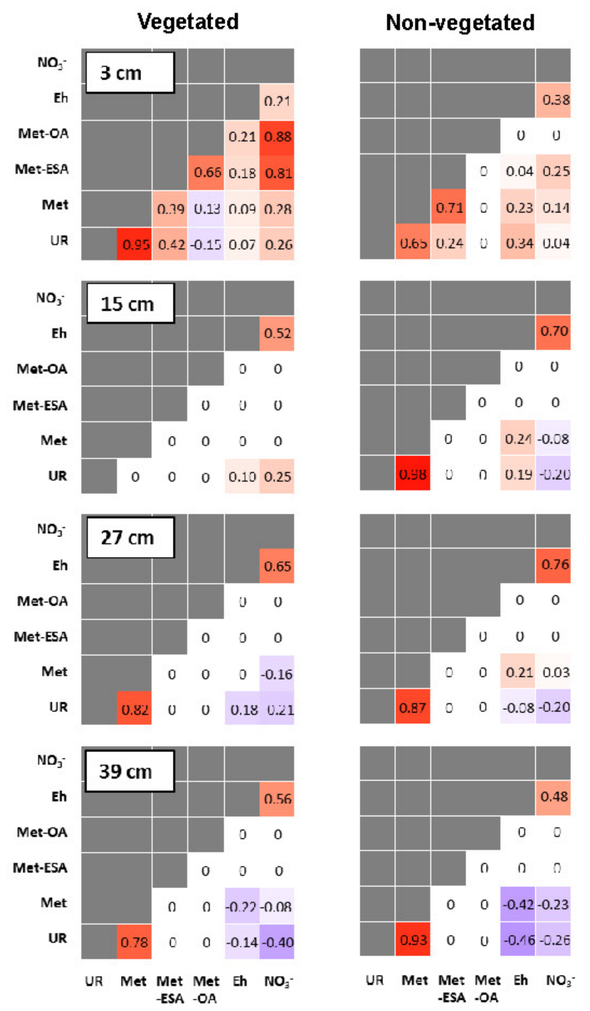


Fig 3. Correlation matrices between UR, Metazachlor, the degradation products of Metazachlor, nitrate and redox potential (Eh).

4 Conclusion

- Degradation, sorption and plant uptake were the main dissipation processes found in this study. However, transport has dominated most of the time with the exception of a transition period from drying to saturation when other processes, presumably sorption and degradation were more prominent.
- Similar recoveries of tracers and pesticides in the two injections suggested that the system did not evolve in terms of a more specialized microbial community.
- Degradation was the main dissipation pathway of UR and Metazachlor in the sediment under both aerobic and anaerobic conditions.

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