Long-term mesocosm experiments to investigate degradation of fluorescent tracers

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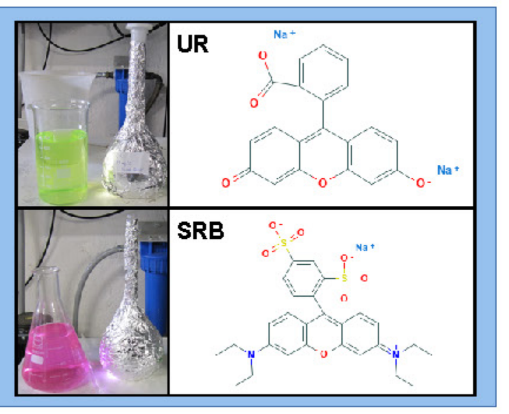
Introduction

Uranine (UR) and sulforhodamine B (SRB) are two of the most commonly used fluorescent tracers in hydrology. Their suitability to be applied as ideal tracers has been discussed since they might interact with the soil or become degraded. However, these properties have recently served to mimic processes of sorption and degradation of pollutants. The present study attempts to answer the question whether the tracers UR and SRB could be used as proxies for degradation processes in environments where saturation conditions are variable and the presence of plants might play an important role.



Goals of the study

- To investigate the fate, behavior and degradability of UR and SRB and characterize their potential dissipation pathways when they interact with the soil.
- To test whether the variations of saturation and the presence of two common types of wetland species (*Phalaris arundinacea* and *Typha latifolia*) have an influence on the processes of degradation.

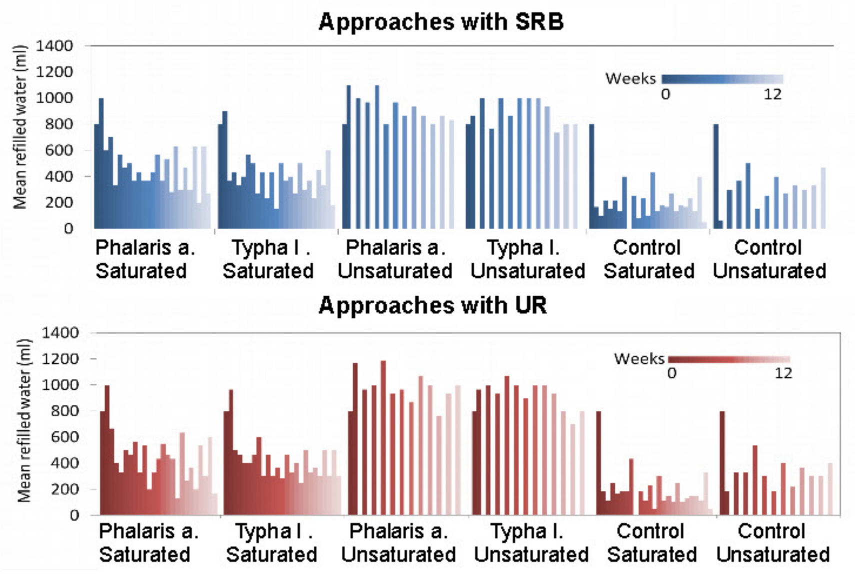
Methods

Design of the mesocosms and approaches:

The mesocosms consisted in 50 l buckets (33.5 cm x 40.4 cm x 53.9 cm) filled with a 8 cm layer of gravel (grain size of 4-8 mm) and topped with 30 cm layer of sand (grain size of 0.01-2 mm). In total, 6 different approaches with 3 replicates each were applied based on two types of hydrologic conditions (saturated and unsaturated) and the presence of two species of wetland plants (*Phalaris arundinacea* and *Typha latifolia*) plus a control without plants. The entire experiment lasted for 10 months. The first months served to ensure the adaptability of the plants and to achieve stationary conditions in the system. Then, UR and SRB were injected separately in each approach.

Types of wetland plants	Hydrologic conditions: Saturated	Hydrologic conditions: Unsaturated
Phalaris a.	Approach 1	Approach 2
Typha l.	Approach 3	Approach 4
Control	Approach 5	Approach 6

Treatments: UR SRB



Measurements:

After the injection the experiment was running for 12 weeks during which:

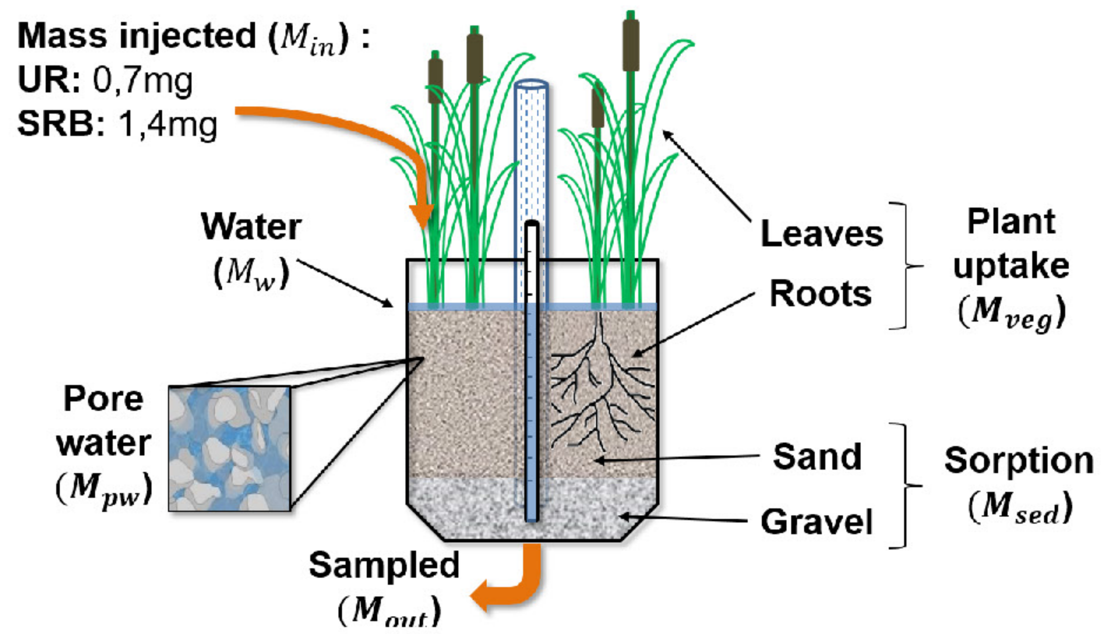
- Water level was monitored and the saturated and unsaturated approaches were refilled with water on a regular basis.
- Temperature, conductivity, nitrate and pH were measured.
- Leachate and soil samples were taken every alternate week for tracer analysis.

Plants were removed and separated into leaves and roots for tracer analysis at the end of the experiment.

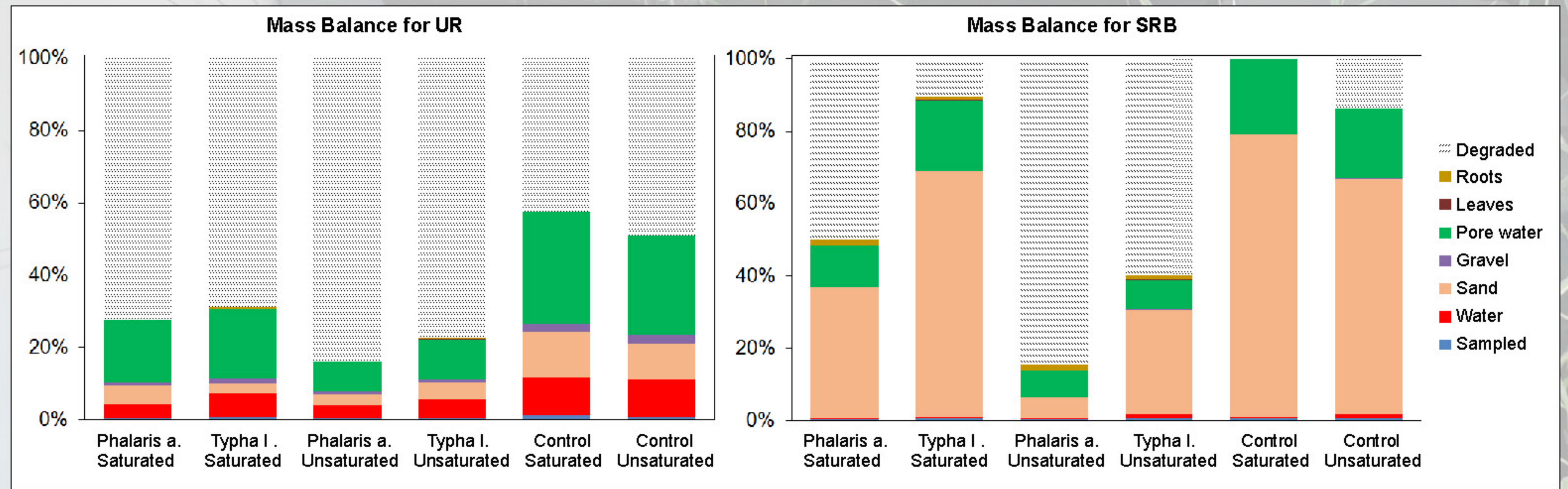
Tracer mass balance and fluorescence EEM analysis:

$$M_{deg}(\%) = \frac{M_{in} - (M_{out} + M_{sed} + M_{veg} + M_w + M_{pw})}{M_{in}} \ x\ 100$$

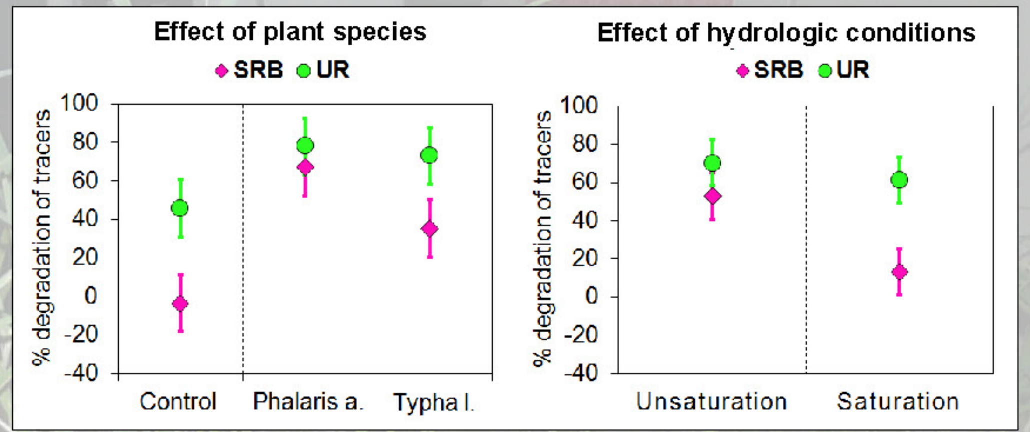
- The system was divided into 7 different compartments in which the tracers were measured.
- Mass balances were combined with excitation emission matrix (EEM) fluorescence spectroscopy to characterize dissolved organic matter in the water and soil.
- The percentage of tracer degraded was quantified by subtracting the non-degraded fraction (sorbed and uptaken by plants or remaining in the water or pore water) from the injected tracer mass.



Results



➢ Most of the SRB accumulated in the sand in agreement with its sorption affinity, while UR was mainly found in the pore water. Both tracers showed more degradation in the treatments with plants than in the controls.



➢ The effects of plant species and hydrologic conditions on the percentage of degradation for UR and SRB were analyzed with an ANOVA model (Pr(>F) < 0.05).

➢ Planted approaches had higher percentages of degradation than the controls. In terms of tracers, UR showed higher degradation rates with almost no differences between the species. SRB however, exhibited more pronounced differences with a major influence of the species Phalaris. As for the hydrologic conditions, UR showed higher rates of degradation than SRB. Here the unsaturated conditions seemed to play an important role.

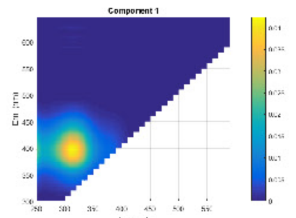
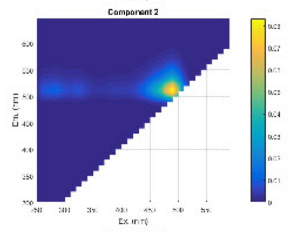
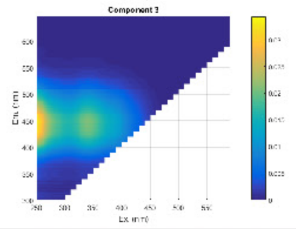
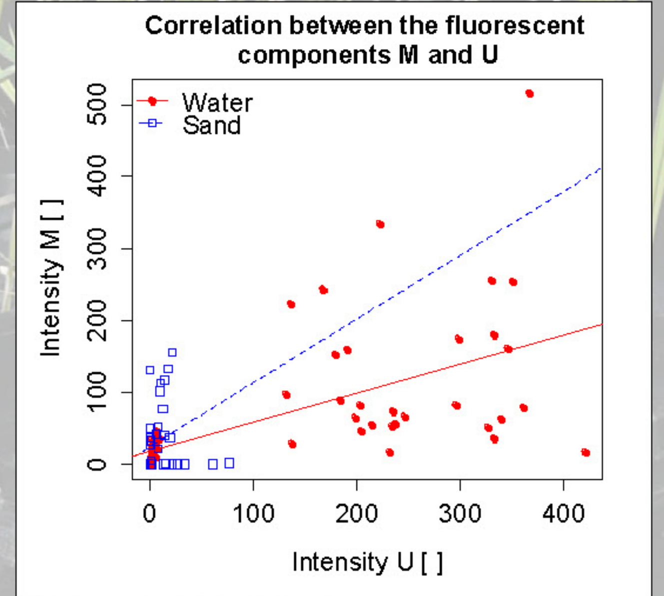
Label		EEM location	EEM	Description [2]
1	M	Ex: 310 (250)[1] nm Em: 395.5 nm		Low molecular weight, common in marine environments associated with biological activity but can be found in wastewater, wetlands and agricultural environments
2	U [3]	Ex: 490 nm Em: 512 nm		Uranine
3	A+C	Ex: 250 (340)[1] nm Em: 447.5 nm		High-molecular-weight humic, widespread, but highest in wetlands and forested environments

Table 1. Summary of the fluorescent components

[1] Wavelengths given in parentheses represent secondary peaks.
[2] Taken from Fellman et al., 2010
[3] Open nomenclature

➢ The analysis of the EEMs of water and sand samples with Parallel Factor Analysis (PARAFAC) resulted in three fluorescent components summarized in Table 1. According to the fluorescence characteristics one biological and/or microbial derived component (M), one related with the tracer UR (U) and one terrestrial humic-like component (A+C) could be identified.

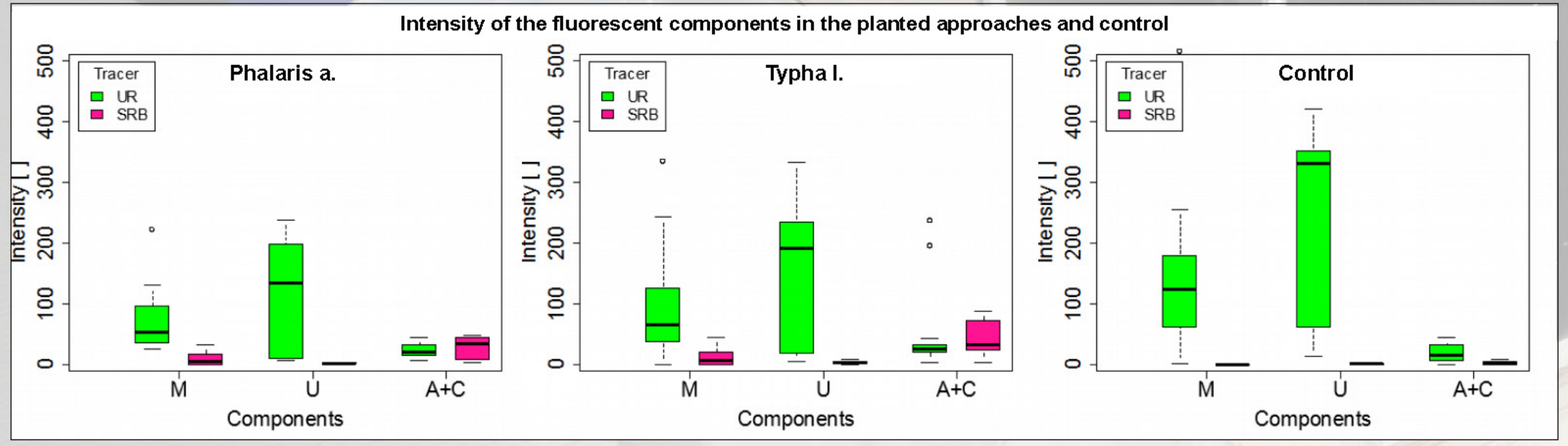


Correlations	Compartments	rho	p-value
M and U	Water	0.7959779	<0.001
	Sand	0.7233817	<0.001
M and A+C	Water	0.2403699	0.07169
	Sand	0.1786675	0.312
U and A+C	Water	0.08027872	0.5528
	Sand	0.233919	0.1824

Table 2. Spearman rank correlation between components

➢ In order to determine the strength of the relationship between the components the Spearman's rank correlation was calculated distinguishing between water and sand samples (Table 2).

➢ As a result, just the components M **(associated with biological activity)** and U **(related with UR)** showed a high positive linear correlation suggesting a possible link between them.



➢ Additionally, the intensity of the different components was analysed in the planted approaches and controls. In terms of intensity no great differences were found between the two species. In contrast, the controls showed larger mean values for the approaches with UR. Here, they exhibited the highest values of the components M and U, while they were absent in the approaches with SRB.

Conclusions

- As expected SRB remained sorbed in the sediment while UR mainly distributed in the (pore) water.
- The presence of plants and the alternation of oxic and anoxic conditions when saturation varies enhanced the degradation of the tracers.
- Results suggested a possible association of UR with microbial activity which was in agreement with the higher overall degradation rates found in this experiment.
- The combination of EEM fluorescence spectroscopy with tracer mass analysis has been revealed as a promising way to provide information on degradation processes of contaminants at the soil/water interface.

Acknowledgement
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