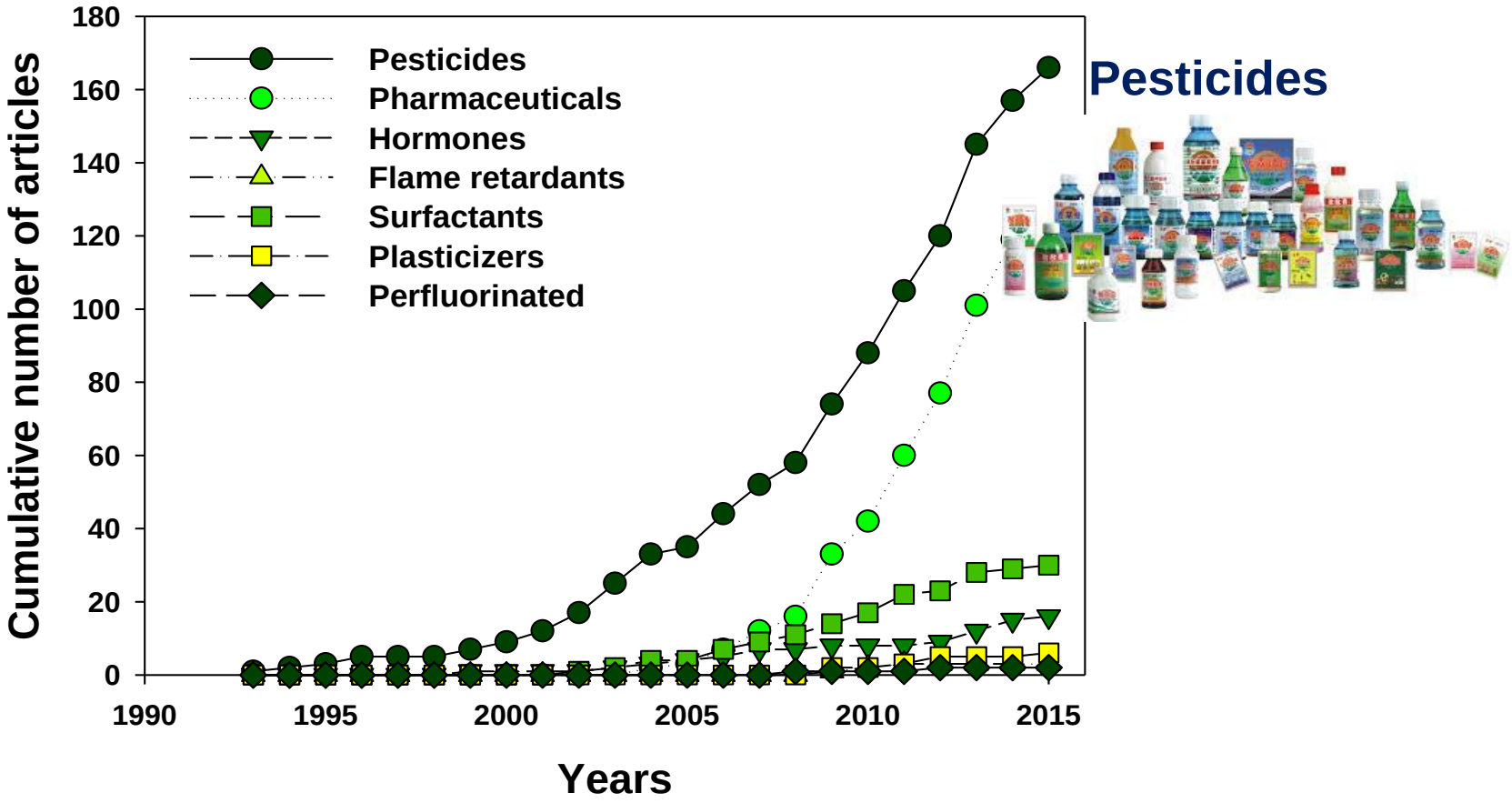
COMPARISON OF THE PESTICIDES TEBUCONAZOLE AND IMAZALIL MITIGATION IN HYDROPONIC MICROCOSMS AND MESOCOSM-SCALE CONSTRUCTED WETLANDS

Tao Lv, Pedro N. Carvalho, Yang Zhang, **Carlos A. Arias,** Hans Brix

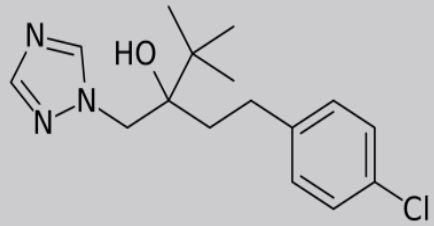
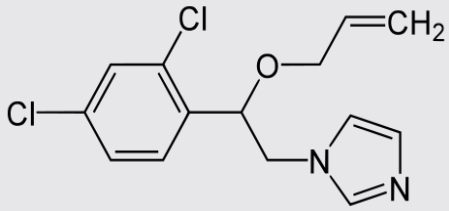
AARHUS
UNIVERSITY

Introduction – Emerging organic contaminants (EOCs)



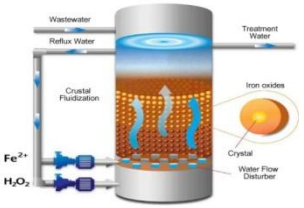
The relationship between the cumulative number of articles about EOCs treatment in CWs and year published since 1991, SCI-EXPANDED, Web of Science

Introduction – Chlorinated Pesticides

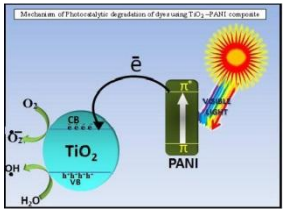
Pesticides	Applications	Toxicity
Tebuconazole 	**Agricultural Area:** Protect citrus fruits, prevent plant pathogenic fungi	Crop residence limitation of **0.01-5 mg kg^{-1}** Toxic to non-target organisms due to bio-accumulation at **0.3 µg L^{-1}**
Imazalil 	**Urban Area:** Used as biocide for wood/building protection	Crop residence limitation of **0.01-5 mg kg^{-1}** Toxic to aquatic vertebrates and invertebrates at **1-160 µg L^{-1}**

Introduction – CWs application

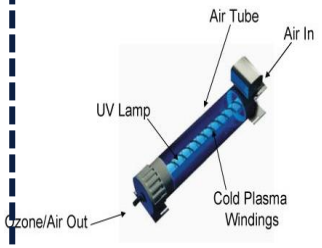
Photo-Fenton method



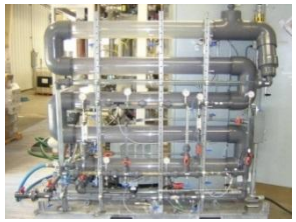
TiO_2 photocatalytic degradation method

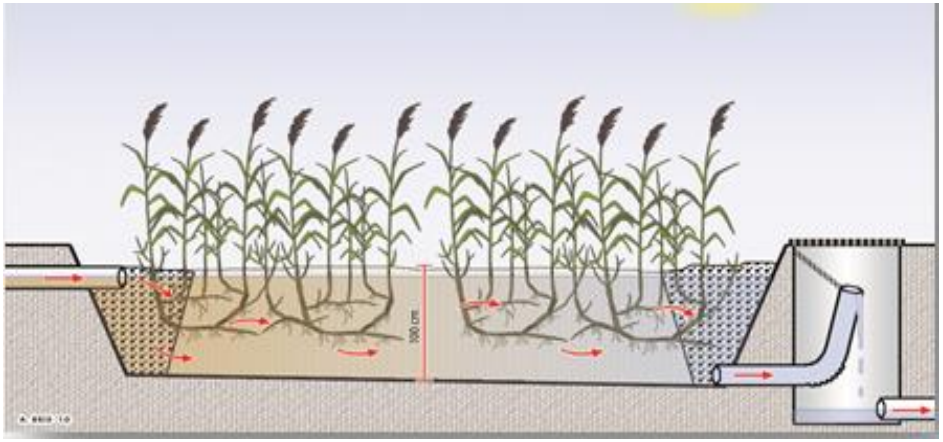


Oxidation under UV irradiation



Ozone oxidation



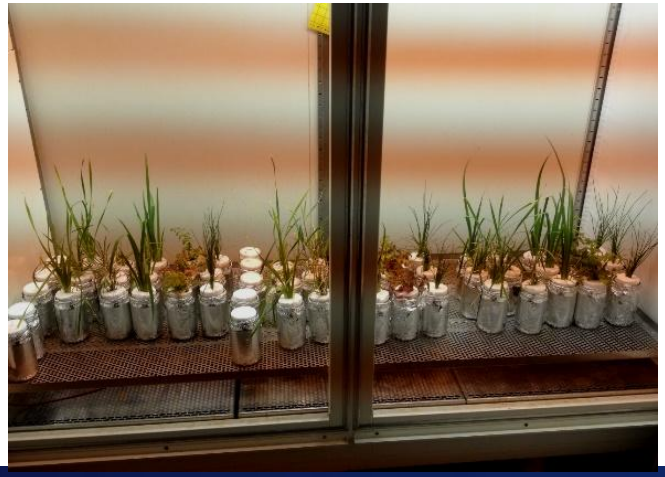


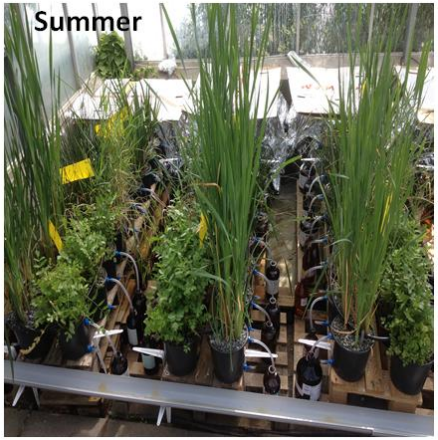
Constructed Wetland Systems

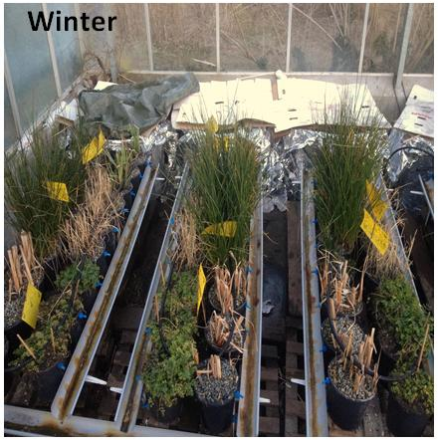
Aims

- To compare the pesticides tebuconazole and imazalil mitigation performance and kinetics in hydroponics and mesocosm-scale CWs planted with *Phragmites australis*.

- The effect of CWs designs, seasons and initial/influent pesticide concentrations were taken into account when doing the comparison.

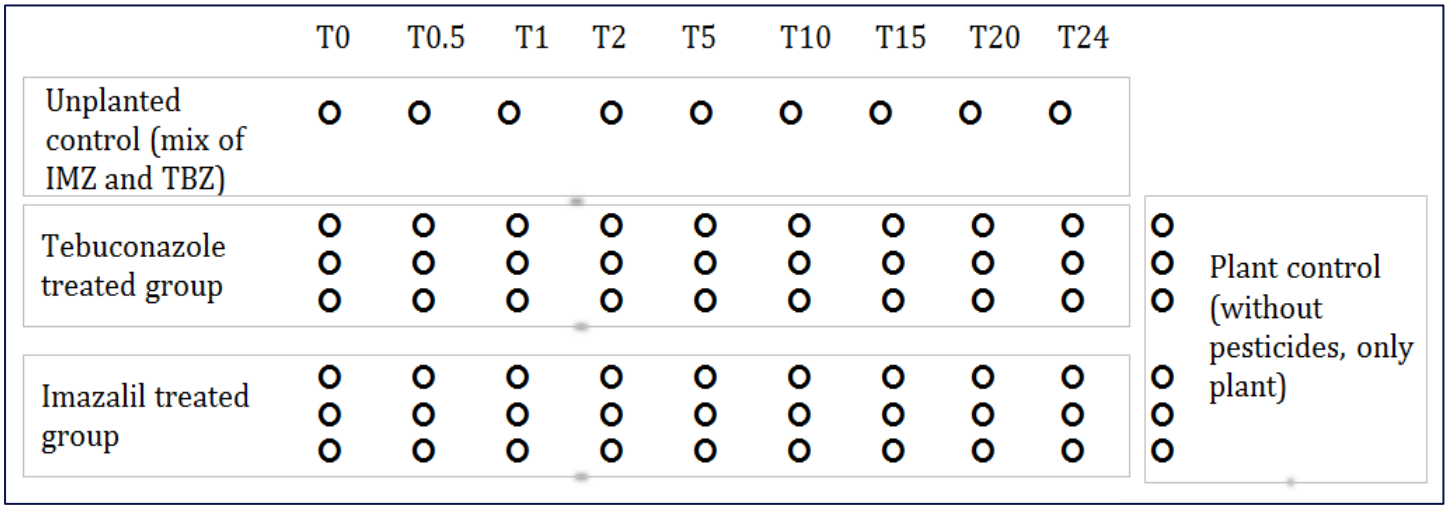






Hydroponic microcosm CWs – Exp. 1 & 2

hydroponic medium

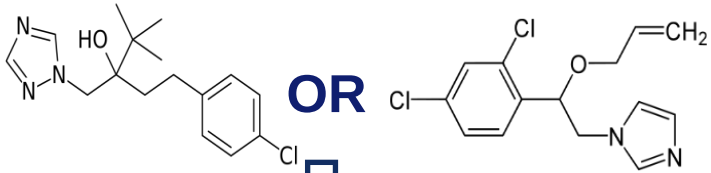


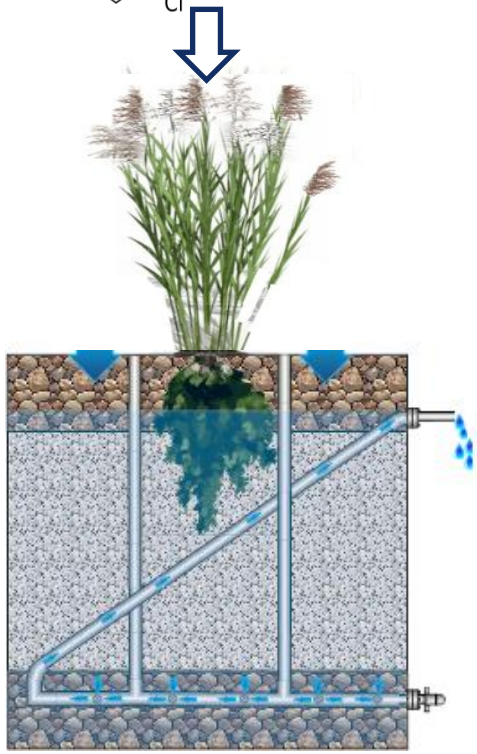
Schematic diagram of the setup for experiment 1 and 2

Experiment conditions	Experiment 1	Experiment 2
Initial spiked concentration	10 µg/L	10 mg/L
Growth Conditions	Growth Chamber	
Solution volume	500 mL	
Plant	*Phragmites australis*	
Incubation time	24 days	

Mesocosm-scale CWs – Exp. 3

Tebuconazole **Imazalil**





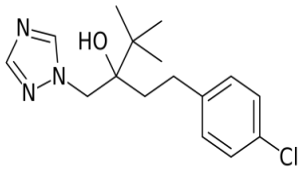
Saturated CWs

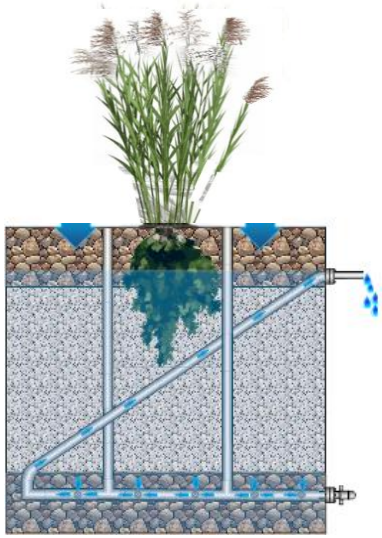
Experiment conditions	Experiment 3	
Influent pesticides concentration	10 µg/L	100 µg/L
HRT	0.25, 0.5, 1, 2 and 5 day (for each influent concentration level)	
Growth Conditions	natural environment with rain protection	
Plant	*Phragmites australis*	
Sampling time	Each influent concentration at each HRT	

Experiment conditions were the same for summer (Jul.-Oct. 2014) and winter (Jan.-Apr. 2015) study

Mesocosm-scale CWs – Exp. 4

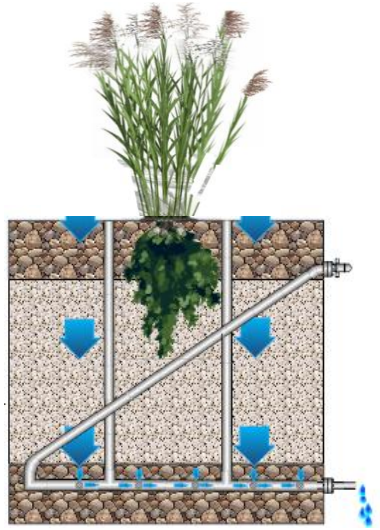
Tebuconazole





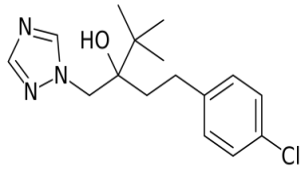
Saturated CWs

VS



Unsaturated CWs

Tebuconazole



Experiment conditions	Experiment 4	
Influent pesticides concentration	10 µg/L	100 µg/L
HRT /HLR	0.25, 0.5, 1 and 2 day / 13.6, 6.9, 3.4 and 1.8 cm/d (for each influent concentration level)	

Experiment was studied in summer (Jul.-Sep. 2015)

Calculation – removal efficiency

Evapotranspiration of the systems were considerated, so the removal rates were calculated based on mass balance,

$$\text{Removal (\%)} = \frac{C_i \times Vi - C \times V}{C_i \times Vi} \times 100$$

where, C_i and C are the pesticides influent/initial and effluent/final concentrations (µg/L or mg/L) respectively; V_i and V are the influent/initial and effluent/final sample volume (mL), respectively.

Kinetics

- **The volume-based first order kinetics removal rate constant**
  (for hydroponic microcosms and saturated mesocosm CWs comparision)

$$k = - \ln (C / C_i) / t$$

where k is the volume-based first order reaction rate constant (d^{-1}); for hydroponc microcosms C_i and C are the pesticides concentrations (µg/L or mg/L) at time zero and time t (d), respectively; for saturated mesocosm CWs C_i and C are the pesticides influent and effluent concentrations (µg/L) under HRT of t (d), respectively.

- **The area-based first order kinetics removal rate constant**
  (for unsaturated and saturated mesocosm CWs comparision)

$$k_v = - q * \ln (C / C_i)$$

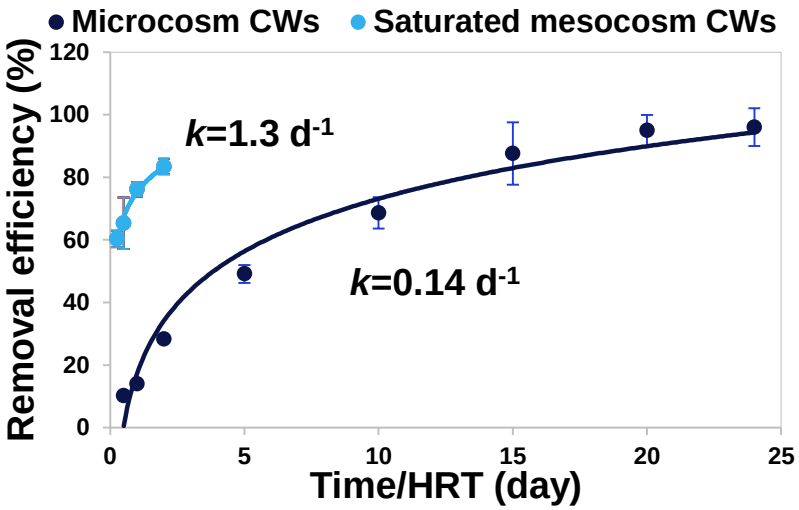
where k_v is the area-based first order reaction rate constant (cm d^{-1}), C_i and C are the pesticides influent and effluent concentrations (µg/L) under HLR of q (cm d^{-1}), respectively.

Results – System design effect

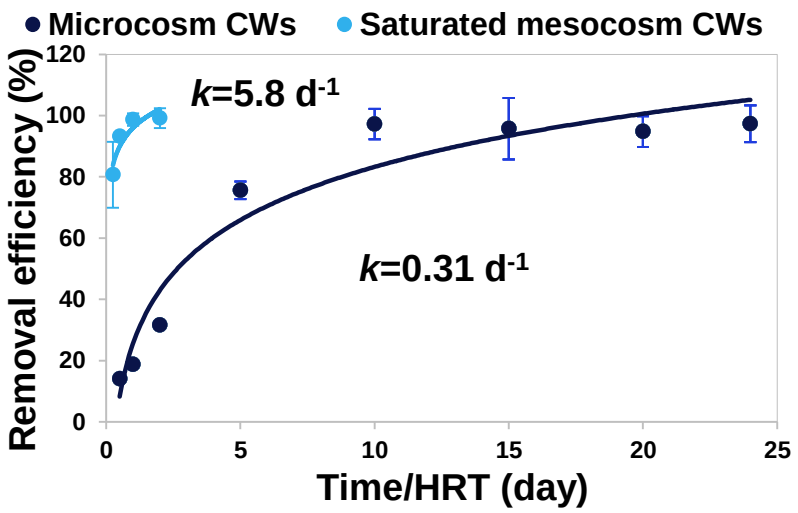
microcosm CWs ***VS*** saturated mesocosm CWs

10 µg/L initial/influent concentration level under summer (growth chamber) condition

Tebuconazole



Imazalil



1. High final tebuconazole (>85%) and imazalil removal (>98%) were observed in both systems

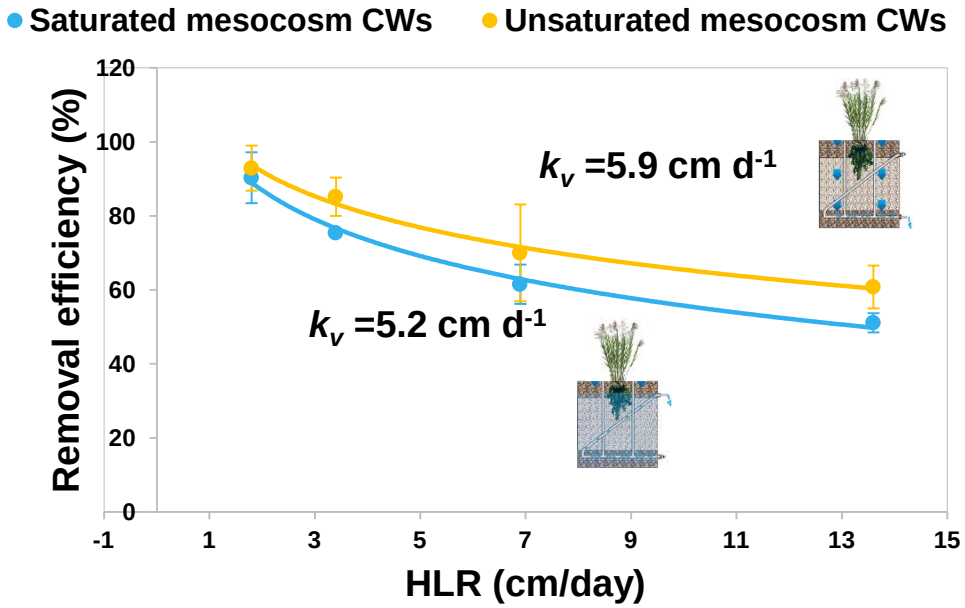
2. *k values* in mesocosm CWs were significantly higher than that in microcosm CWs for both tebuconazole and imazalil.

Results – System design effect

unsaturated mesocosm CWs ***VS*** saturated mesocosm CWs

10 µg/L influent concentration level in summer

Tebuconazole



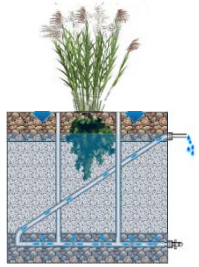
1. High tebuconazole removal (>93%) were achieved under HLR of 1.8 cm/d for both CWs.

2. k_v for unsaturated CWs was higher than saturated CWs (not significant).

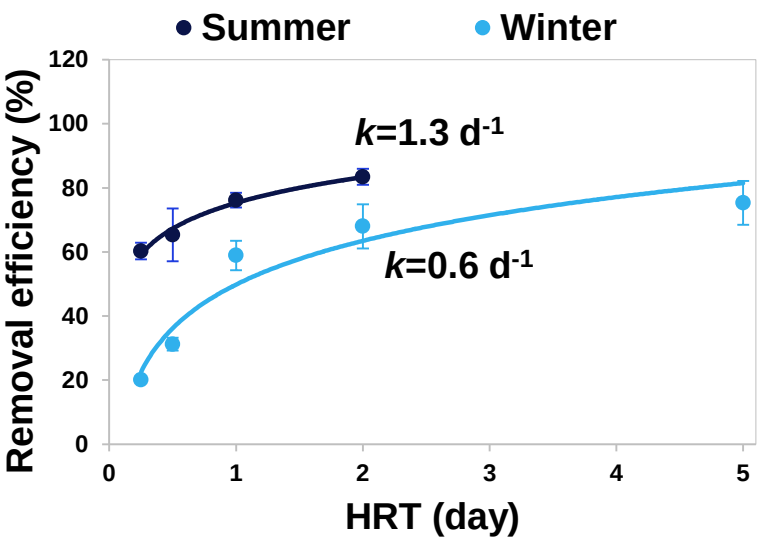
Results – season effect

Summer ***VS*** Winter

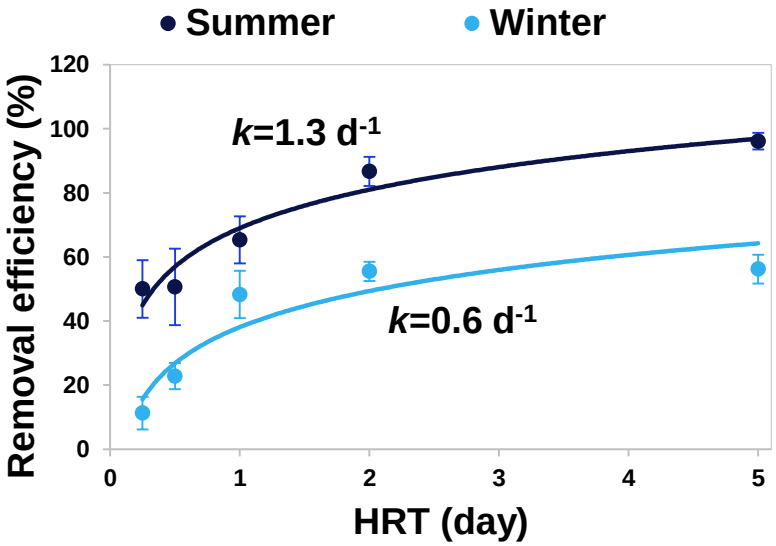
(Saturated mesocosm CWs)



influent tebuconazole of 10 µg/L



influent tebuconazole of 100 µg/L



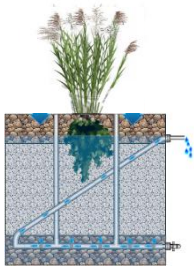
1. Tebuconazole removal efficiencies were significantly higher in summer.

1. *k* values of tebuconazole were significantly higher in summer.

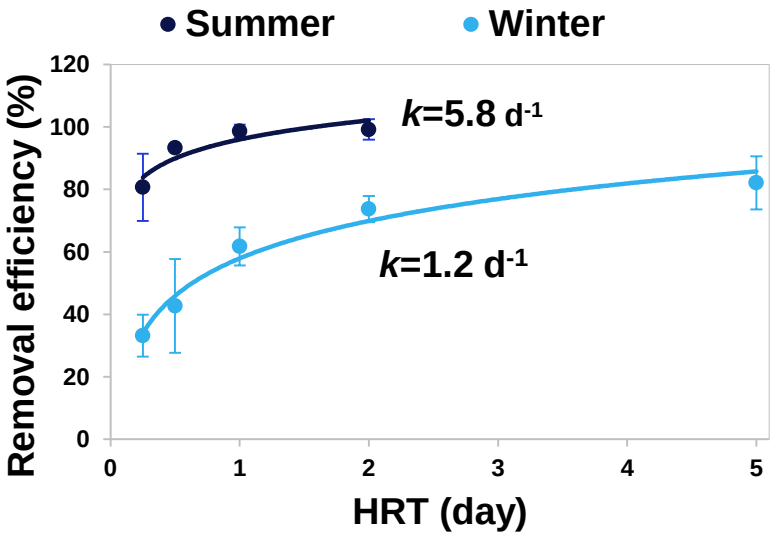
Results – season effect

Summer ***VS*** Winter

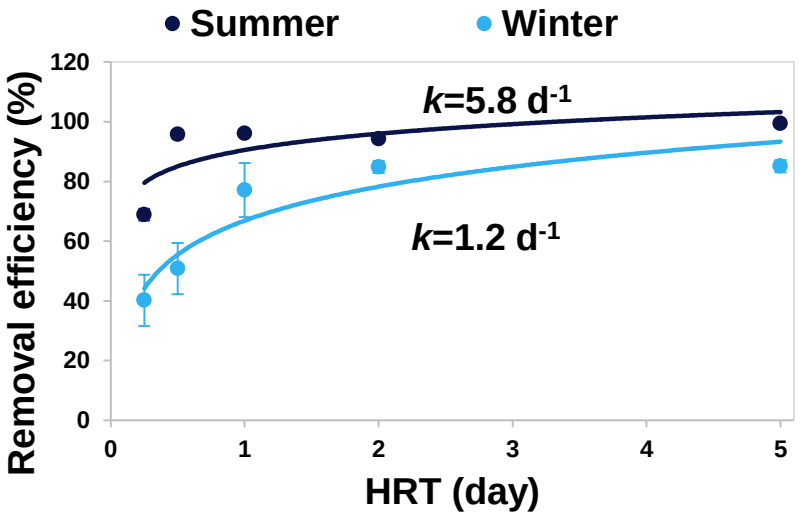
(Saturated mesocosm CWs)



influent imazalil of 10 µg/L

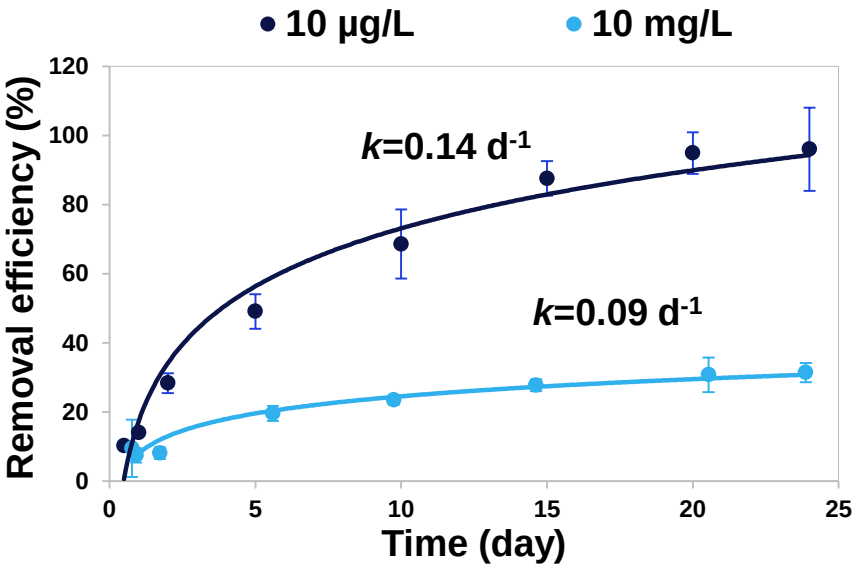


influent imazalil of 100 µg/L



1. Imazalil removal efficiencies and *k* values were significantly higher in summer.

Results – Influent/Initial concentration effect



10 µg/L **VS** 10 mg/L

Tebuconazole
Hydroponic microcosm CWs

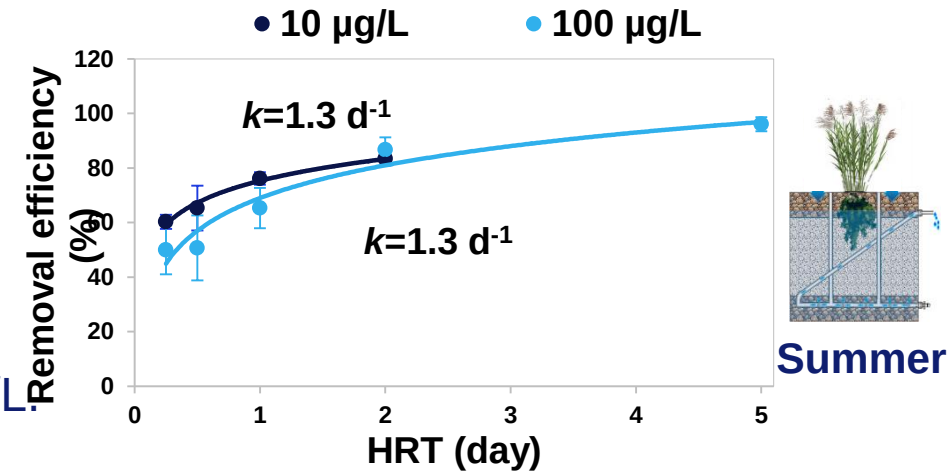
1. *k* values of tebuconazole removal were significantly higher under initial concentration of 10 µg/L than 10 mg/L.

Results – Influent/Initial concentration effect

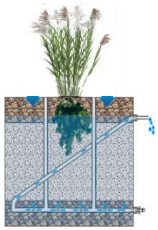
10 µg/L **VS** 100 µg/L

Tebuconazole
Mesocosm CWs

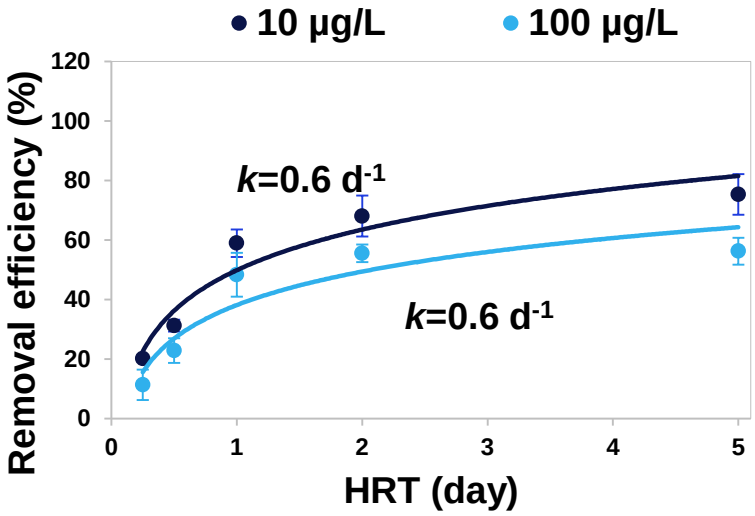
2. k values of tebuconazole removal were Slightly higher, but not significant, under influent concentration of 10 µg/L than 100 µg/L.

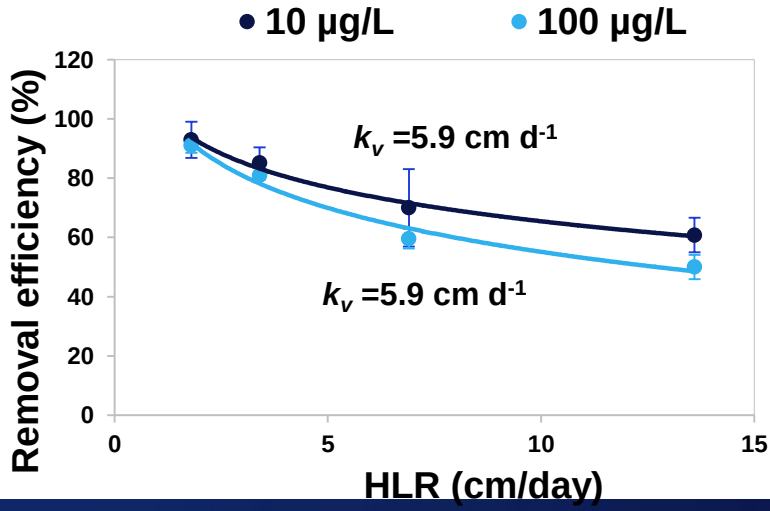


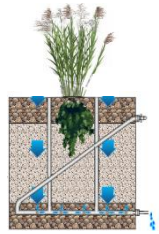
Summer



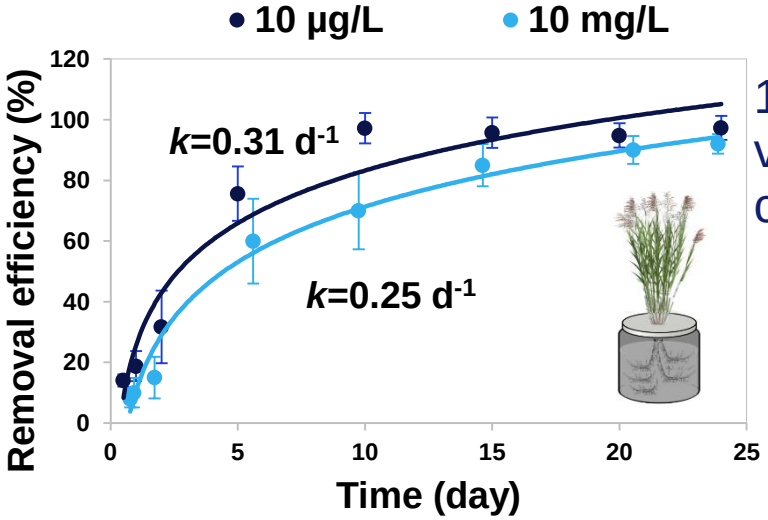
Winter





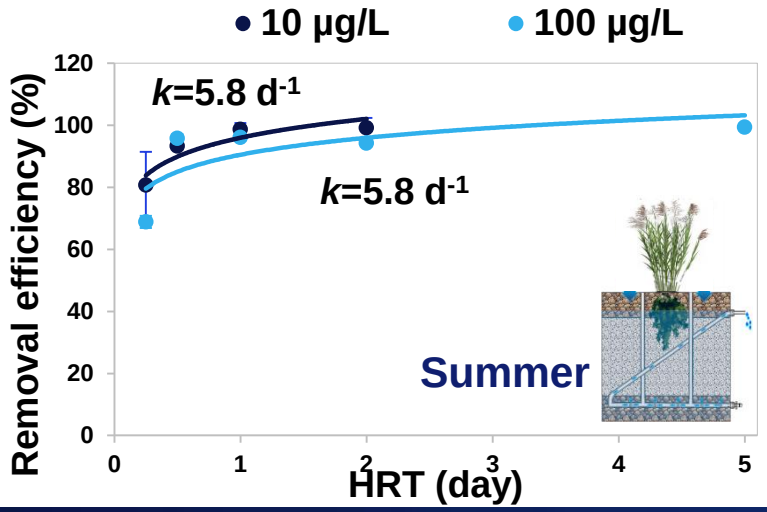


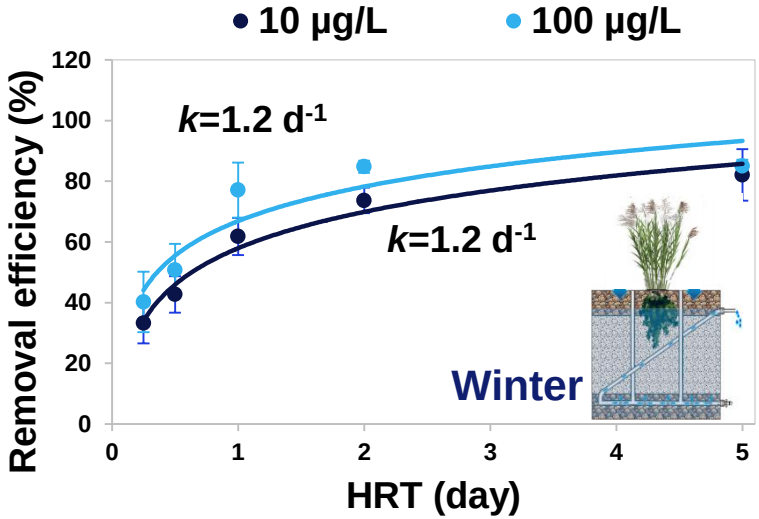
Results – Influent/Initial concentration effect



1. Imazalil removal in Hydroponic microcosm CWs, *k* values is significantly higher under 10 µg/L initial concentrations.

2. Imazalil removal in mesocosm CWs, *k* values are not significantly different under 10 µg/L and 100 µg/L influent concentrations.





Conclusions

- *Phragmites australis* planted microcosm CWs and mesocosm CWs showed high removal (>90%) of the pesticides.
- Mesocosm CWs presented significantly higher pesticides removal rate than that in hydroponic microcosm CWs.
- Tebuconazole removal efficiencies and removal rate s were higher, but not significant, in unsaturated than saturated mesocosm CWs.
- Removal efficiencies and removal rate constants of the pesticides observed in the mesocosms were significantly higher In summer than that in winter.
- Initial/influent pesticides concentrations had generally negative influence on the pesticides removal rate constants in microcosm CWs, but not in mesocosm CWs.


THANKS …