Passive samples (POCIS) in ponds and wetlands to evaluate pesticide degradation using compound-specific isotope analysis

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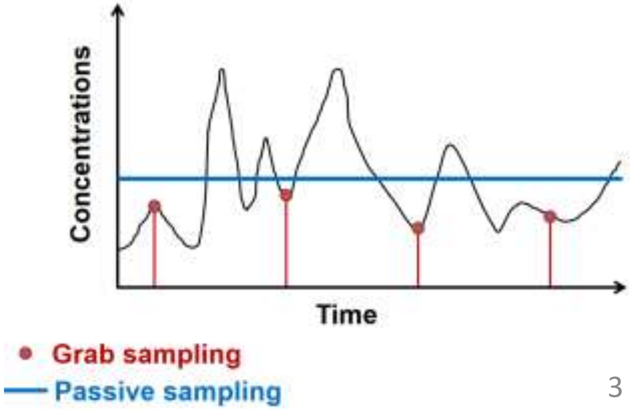
Content

- Passive samplers and compound specific isotope analysis (CSIA)
- Effect of concentrations, matrices, flow conditions and hydraulic regimes on pesticide and isotope fractination
- Field application : POCIS for pesticide CSIA in stormwater wetland

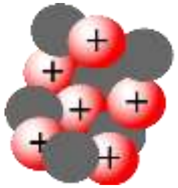
Objectives

- Develop the use of passive samples (POCIS) to facilitate CSIA analysis (preconcentration / in situ purification step) at water-sediment interface
- Collect the average isotope signature / concentration of pollutants accounting for high-concentrated short runoff events
- Compare POCIS as an alternative to grab sampling - less cost/time-consuming
- Tease apart destructive and non-destructive processes in the field with pesticide CSIA



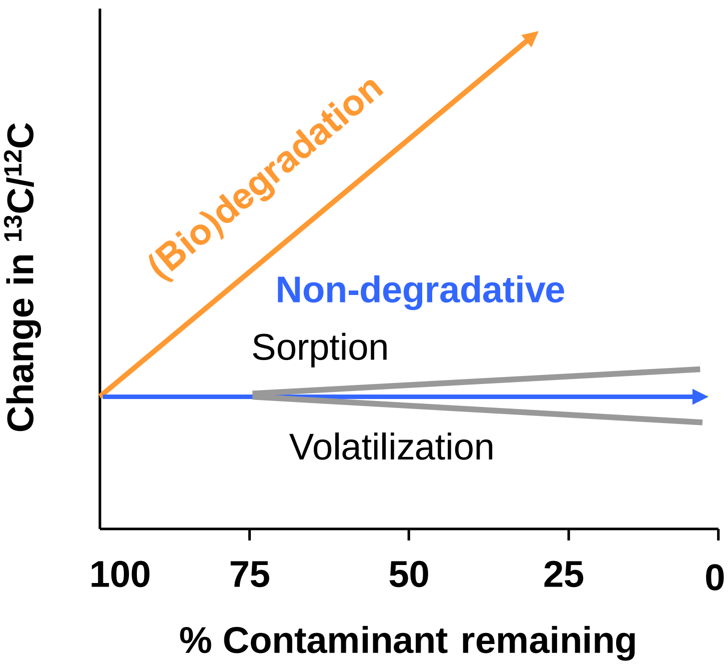
Compound Specific Isotope Analysis (CSIA)

CSIA measures the isotope ratios e.g., $^{13}C/^{12}C$ of individual contaminants

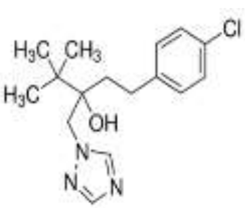


Carbon-12
6 protons
6 neutrons
98.9%

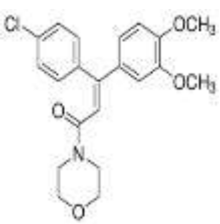
Carbon-13
6 protons
7 neutrons
1.1%



Isotopic analysis of contaminants is directly linked to degradative processes

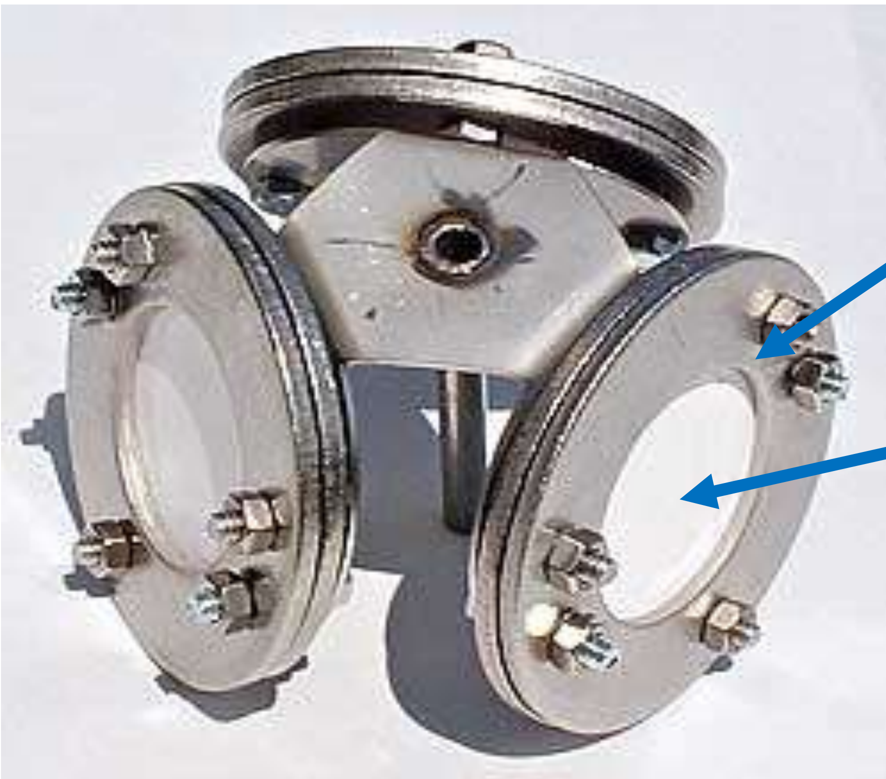


Tebuconazole



Dimetomorph

POCIS: passive sampler



Stainless steel disks

Semi-permeable polyethersulfone (PES) membrane filled with 200 mg Oasis HLB

Widely used as alternative to grab water samples for concentrations
= > Now tested for **CSIA** (this study)

Lab experiments

Estimate sorption and isotope signatures for different compounds under varying **pesticide concentrations, matrices, flow conditions and hydraulic regimes**

Experiment 1

Experiment 2

POCIS: sorption experiment 1

Effect of concentrations, matrices and flow conditions tested for atrazine, S-metolachlor, terbutryn, metalaxyl, dimetomorph and tebuconazole

Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
DI water Slow flow 1µg/L	RF water Slow flow 10µg/L	RF water Slow flow 1µg/L	RF water Fast flow 1µg/L	RF water Slow flow Blank
8 POCIS	8 POCIS	8 POCIS	8 POCIS	8 POCIS

DI - dionized water; RF water - stormwater water

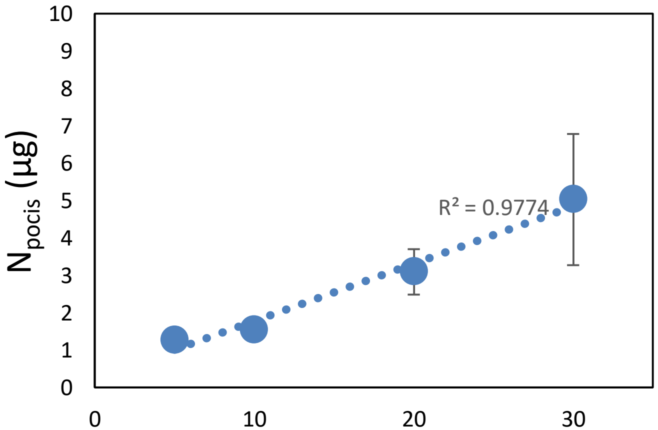
POCIS sampled after 5,10, 20 and 30 days

EXP 1. Comparison between tanks

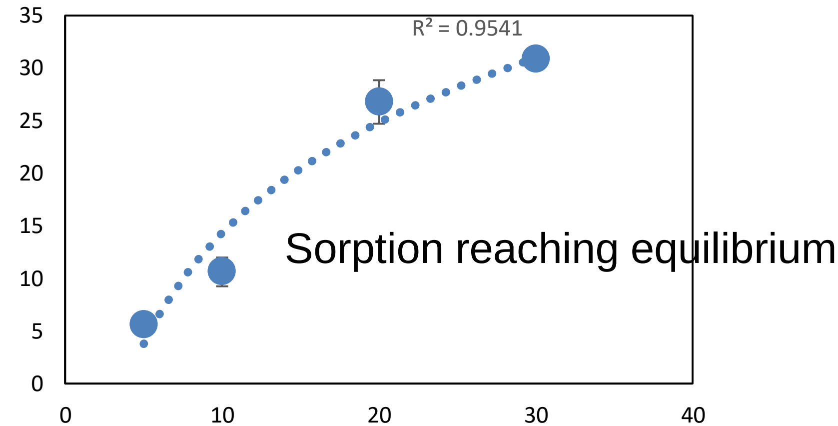
Atrazine

Tank 1	Tank 2	Tank 3	Tank 4
DI water Slow flow 1μg/L	RF water Slow flow 10μg/L	RF water Slow flow 1μg/L	RF water Fast flow 1μg/L

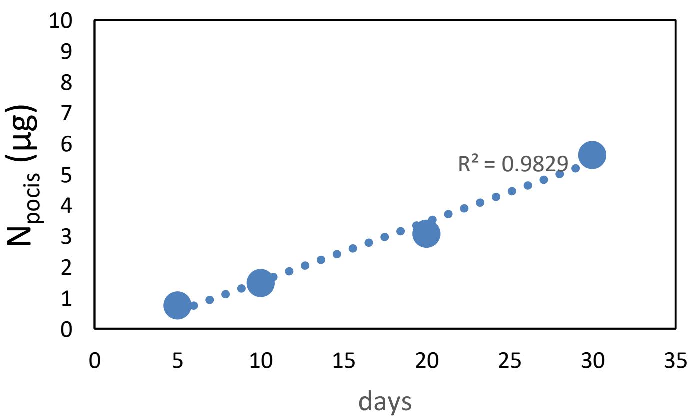
Tank 1



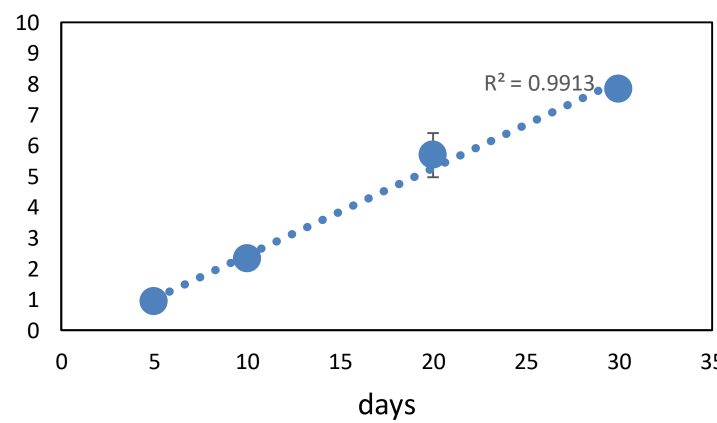
Tank 2



Tank 3



Tank 4

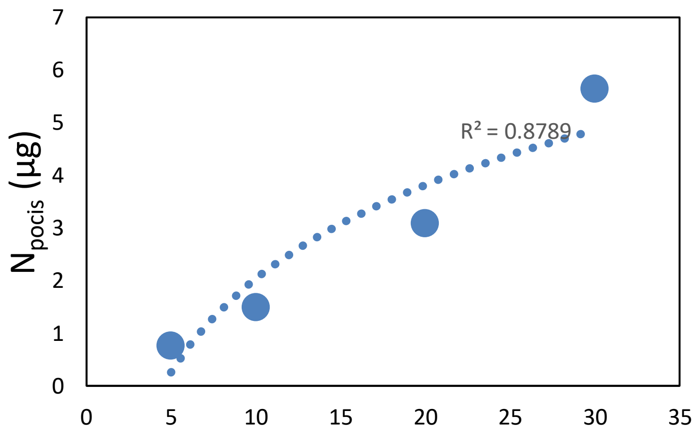


EXP 1. Comparison between compounds

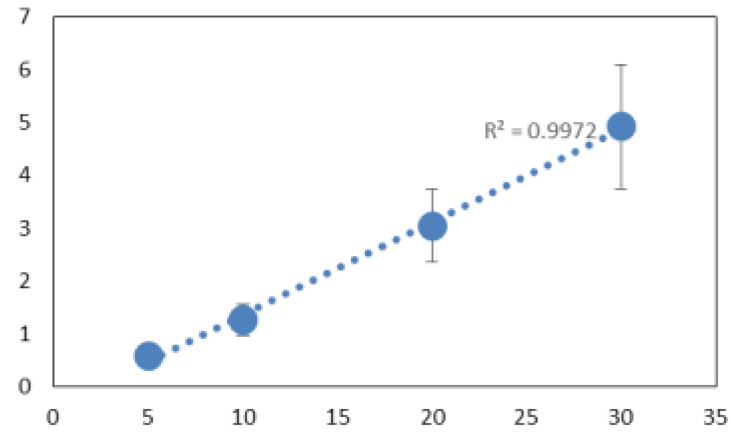
Tank 3

RF water
Slow flow
1µg/L

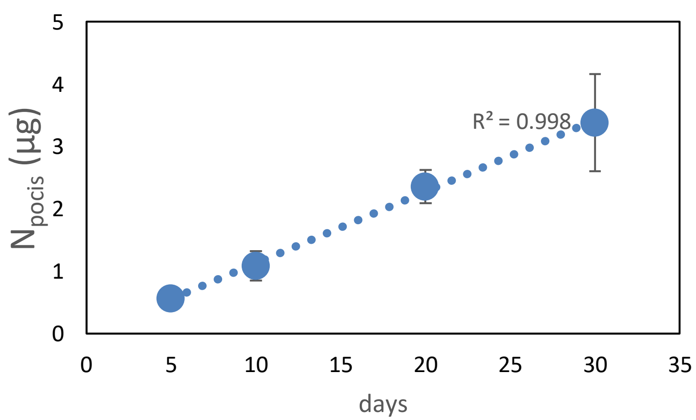
Tank 3_Atrazine



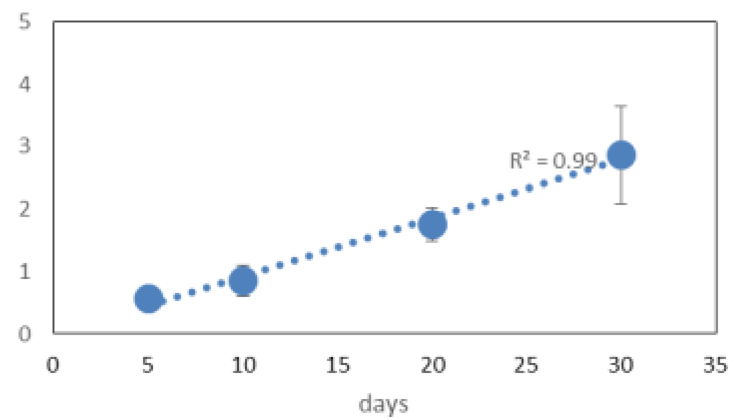
Tank 3_Metalaxyl



Tank 3_ S-Metalochlor



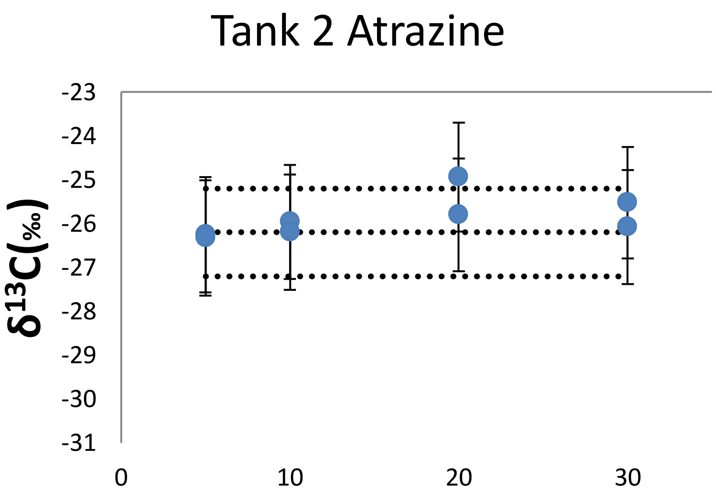
Tank 3_ Terbutryn

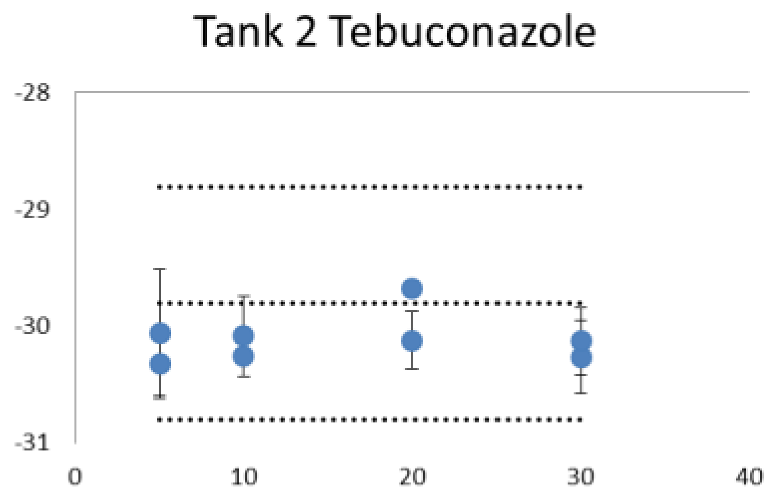


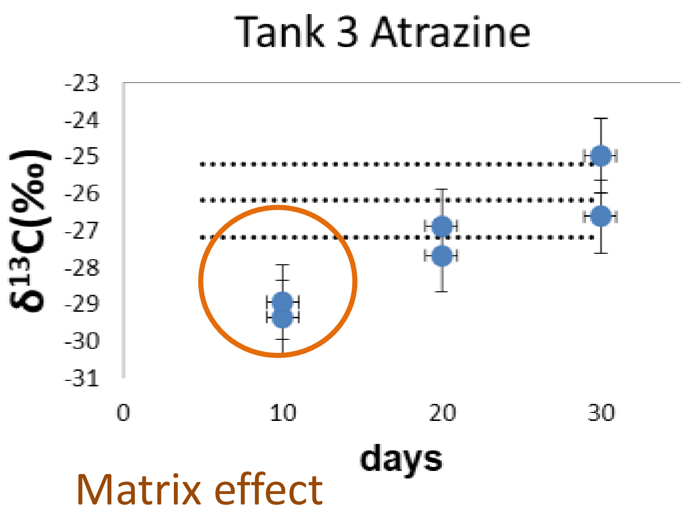
$K_{OW\ \text{Atrazine, Metalaxyl}} < K_{OW\ \text{Terbutryn, S-Metalochlor}}$

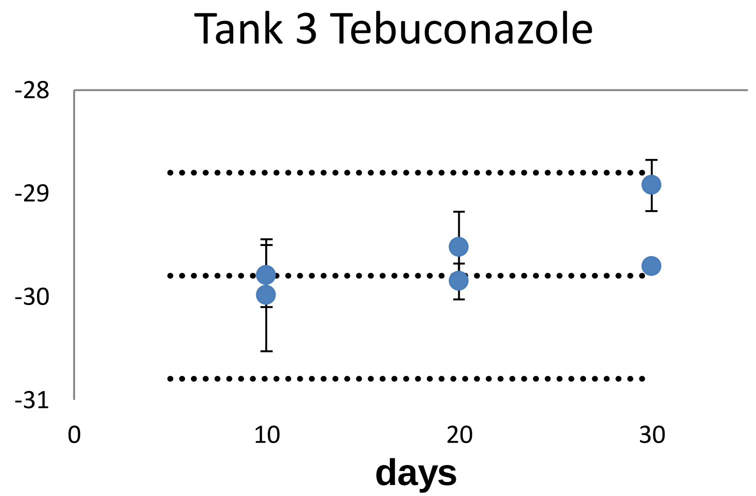
EXP 1. NO carbon isotope effects due to sorption on POCIS

Tank 2	Tank 3
RF water Slow flow 10µg/L	RF water Slow flow 1µg/L









Summary 1st experiment POCIS

1. Flow, pesticide concentrations and compound physicochemical characteristics, but not the matrix, affected sorption (N_{POCIS}). The equilibrium was not reached for 1µg/L condition

2. No isotope effects due to sorption on POCIS, however, changes in isotope signatures due to matrix effects at low concentrations for some compounds

3. *Projection:* POCIS (after 30 days) could allow isotope fractionation-free measurements of environmentally relevant concentrations

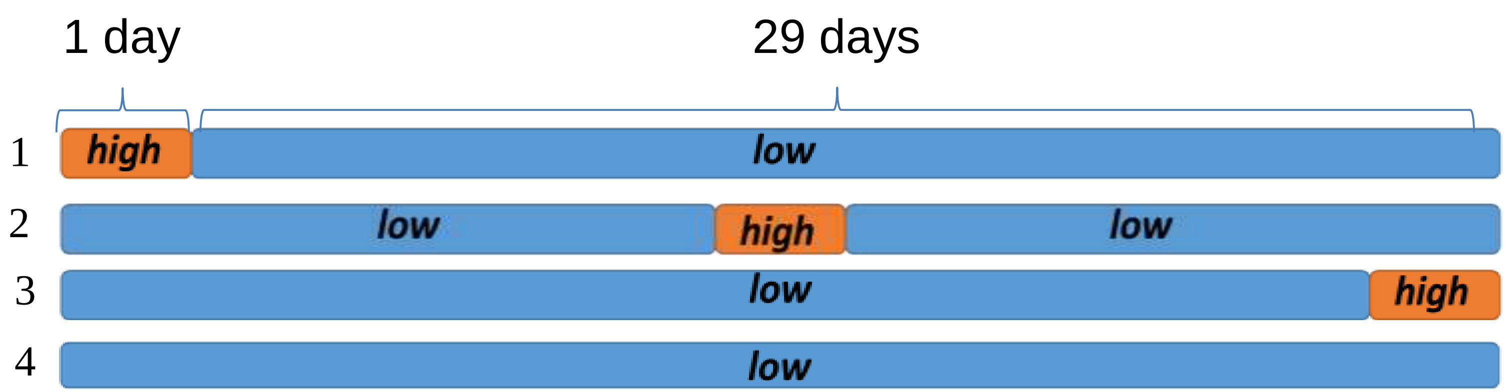
    -Atrazine, metalaxyl, terbutryn, dimetomorph at 0,3-0,5µg/L

    -Tebuconazole, S-metolachlor at 0,1-0,2µg/L

POCIS: sorption experiment 2

Estimation of sorption for each compound under distinct hydraulic patterns

- When to collect the samplers from the field and what information it will represent?
- Self-made compared to commercial POCIS



low = low flow, low concentration
high = high flow, high concentration (simulation of storm event)

Tank 1 : HIGH concentration / HIGH flow

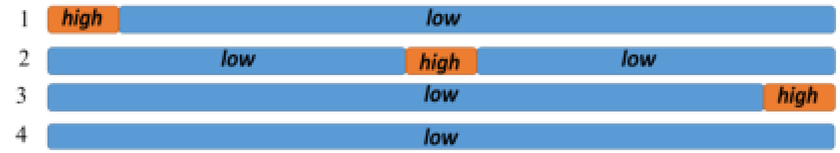
Metalaxyl (Ridgold) $\delta^{13}C$ =-29.5‰
Tebuconazole
S-Metolachlor D-11
Atrazine

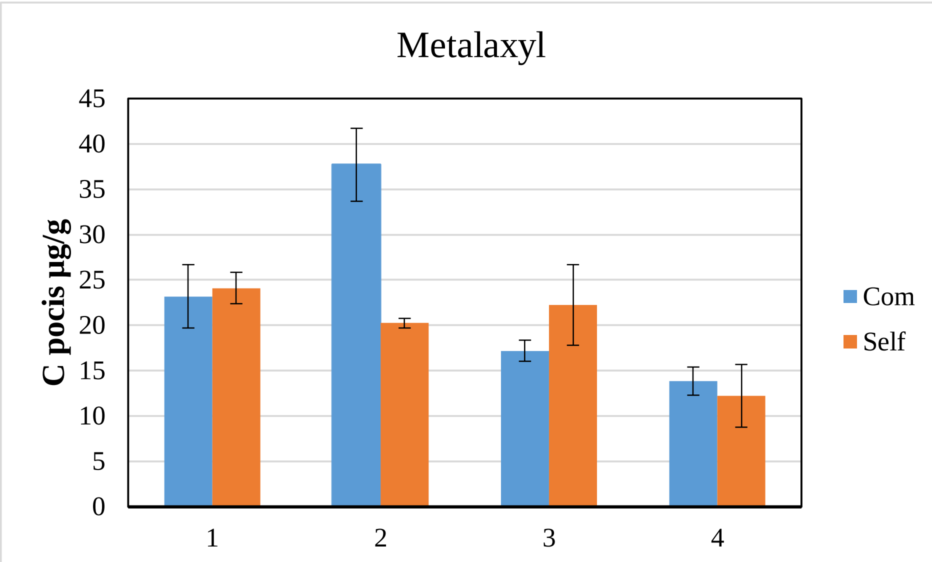
Tank 2 : LOW concentration / LOW flow

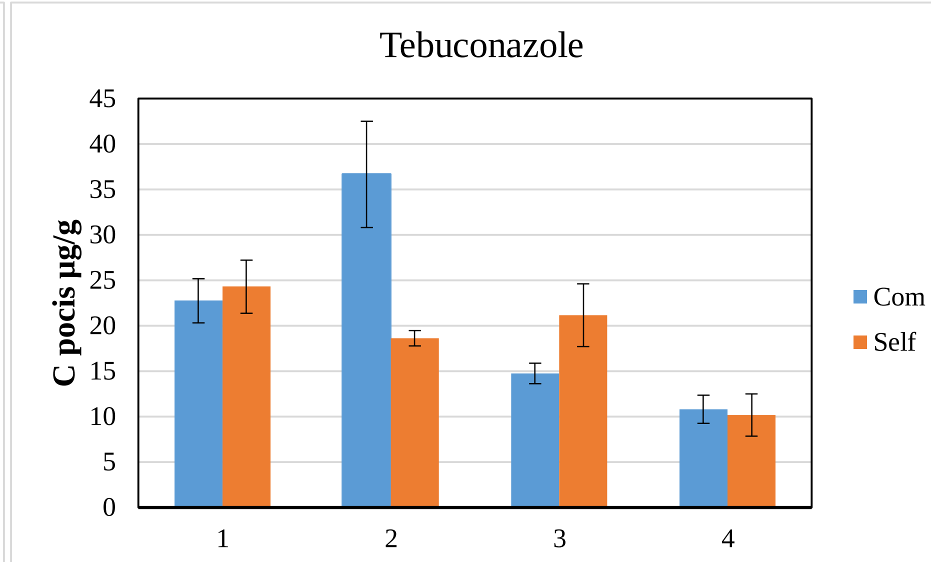
Metalaxyl (Sigma) $\delta^{13}C$ =-31.5‰
Tebuconazole
S-Metolachlor

- **Metalaxyl** proxy for mixing
- **S-Metolachlor D-11** and **Atrazine** proxy for accumulation during storm event

Compounds in both tanks



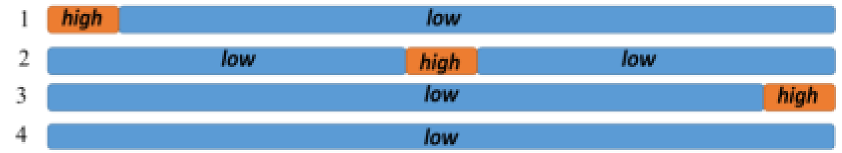


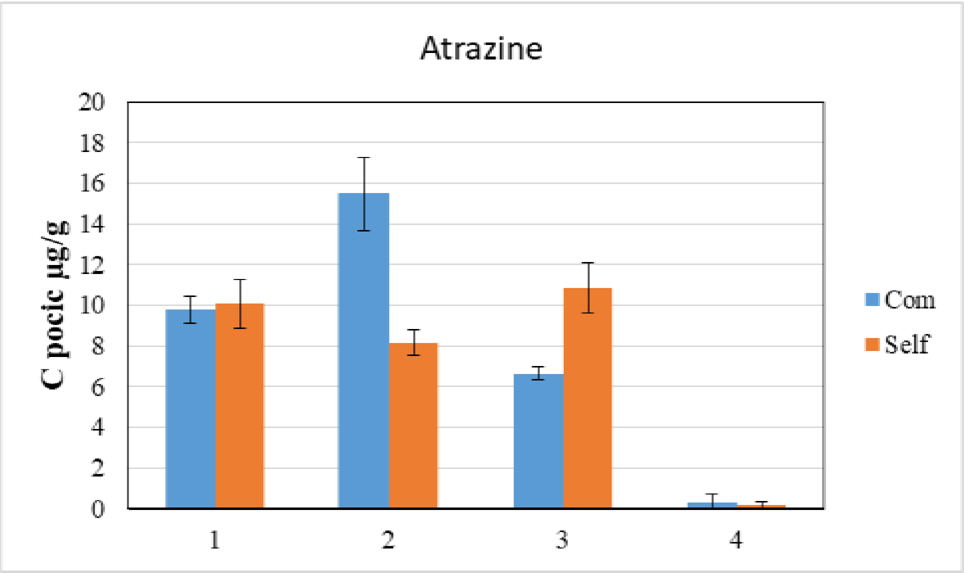


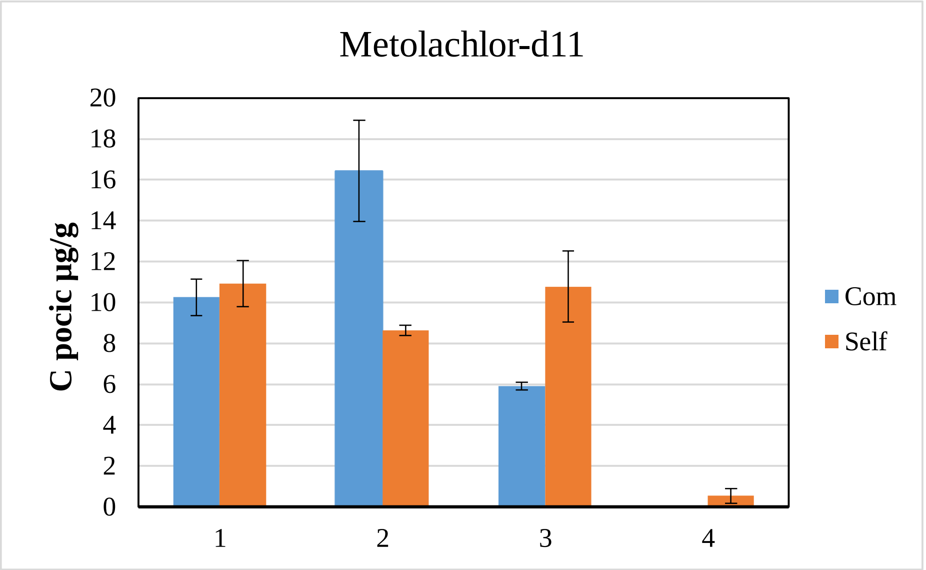
Com - commercial POCIS
Self - self-made POCIS

Similar pattern for all compounds
Self-made ≈ COM
Self-made POCIS 1≈2=3>4 as expected
Com POCIS Scenario 2>1 ≈ 3>4

Compounds in High tank



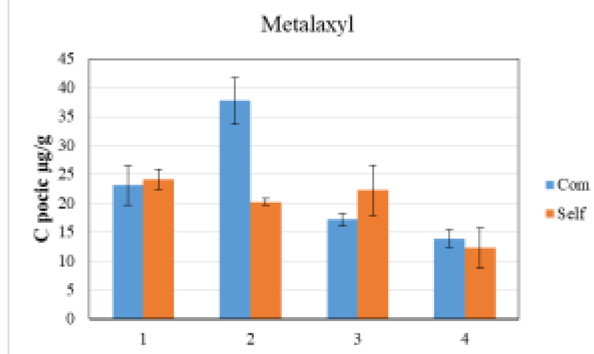


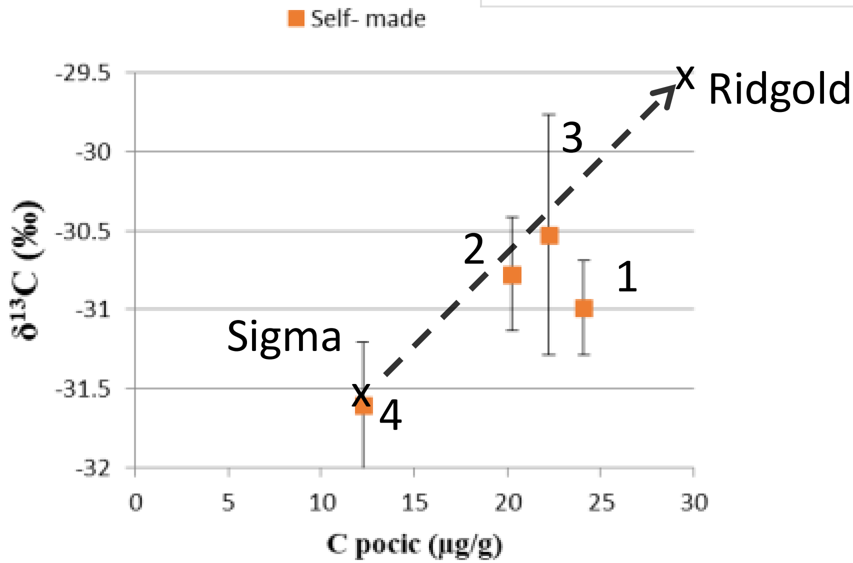


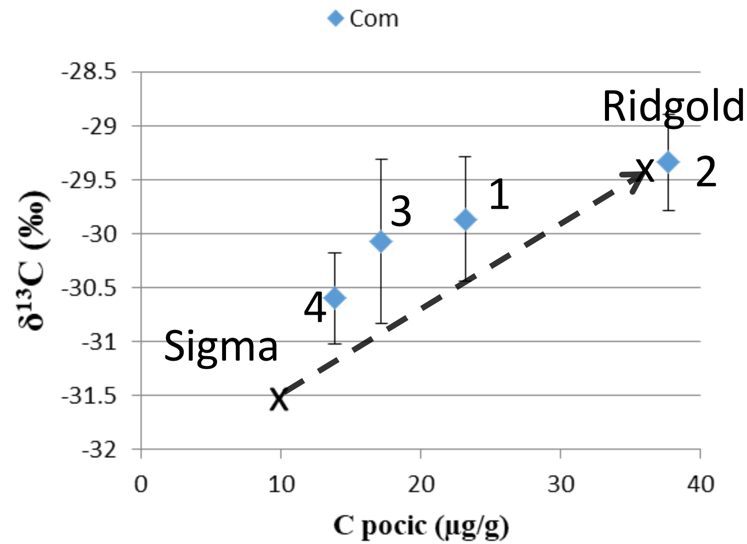
Com - commercial POCIS
Self - self-made POCIS

Same pattern as before

Isotope analysis / Mixing



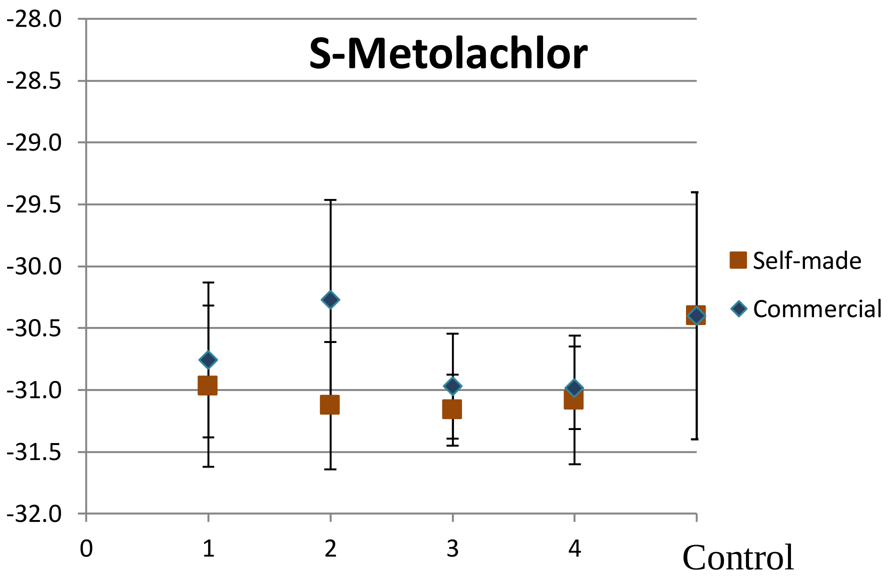


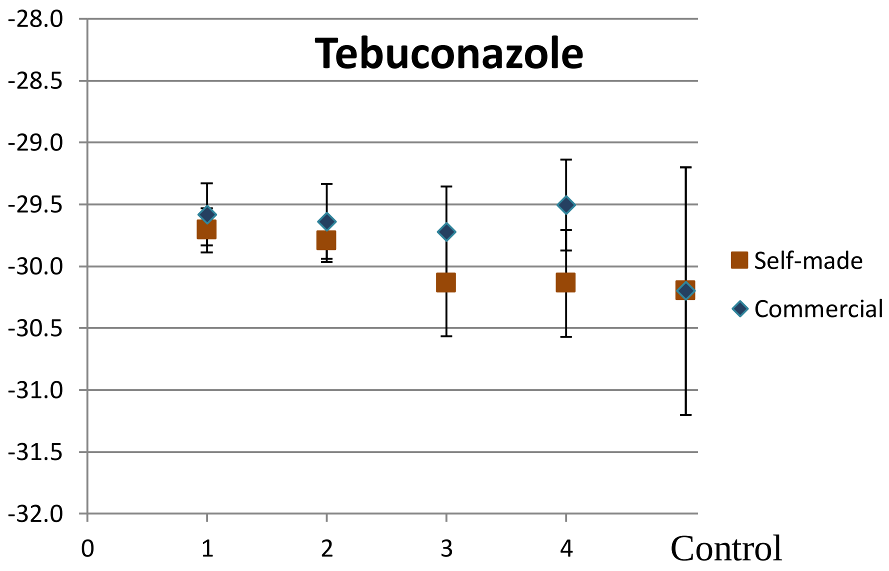


- ~ Δ1‰ in Self-made between Series 4 and 1,2,3
- ~ Δ1‰ in COM between Series 4 and 2

- Tank1,2,3 are influenced by High flow tank
- Isotope values : generally between Ridgold and Sigma sources

No isotope effects due to sorption on POCIS as in experiment 1





S-Metolachlor and Tebuconazole - stability in all tanks

Summary 2nd experiment POCIS

- Self-made POCIS have similar sorption (except for scenario 2) as commercial
- Isotope analysis were identical and concentration were identical for all mixed regime regardless HIGH/LOW mixtures scenario
- No isotope effect caused by sorption on POCIS, similar to experiment 1

Field application stormwater wetland Rouffach

Sampling from June 2nd to September 22nd 2020

- Weekly sampling of grab water (10L), inlet/outlet (autosampler)
- Monthly sampling of water from piezometers in gravel filter (GF) (12L)
- Monthly sampling of plants, sediment, **POCIS**

↓

- Concentration and isotope analysis of all samples to establish mass balance and monitor degradation

Installation of POCIS in the field

Metal pole inserted into sediment

POCIS hanged with a fishline on a metal pole

Protective cage installed

3 POCIS kept in water and replaced every 4 weeks

Preliminary results Rouffach campaign

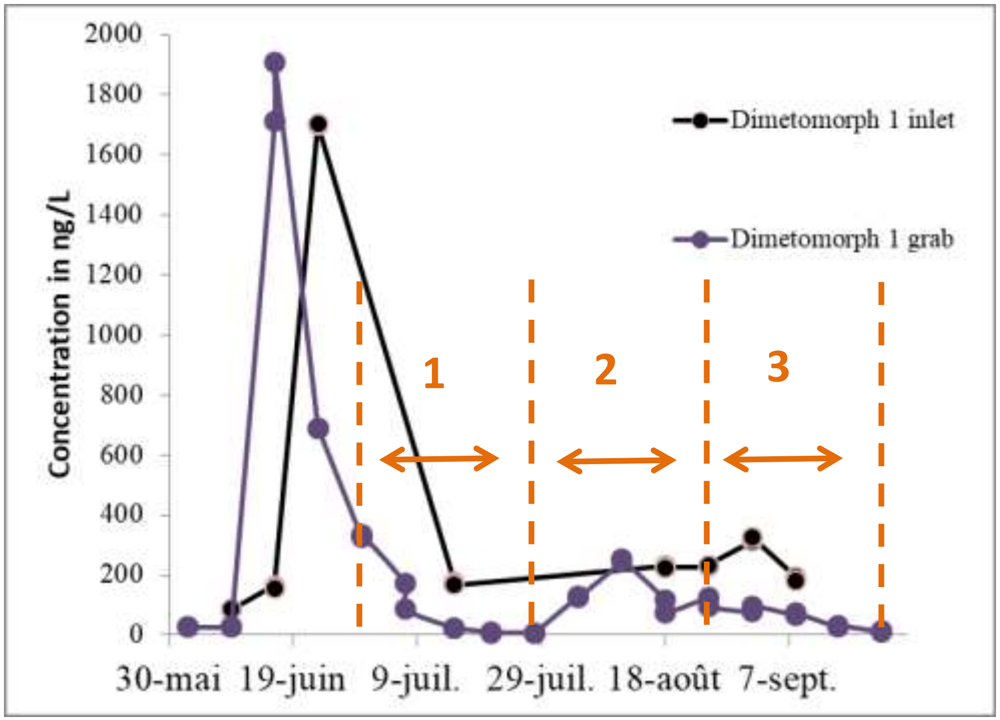
Almost all compounds detected in water were found in POCIS

Matrix	Dimetomorph	Metalaxyl	S-met.	Cyprodynil	Tetraconazole	Pyrimethanil	Terbuthylazine	Atrazine	Myclobutanil/ Tebuconazole	Pendimethalin
Water	+	+	+	+	+	+	+	+	+/+	+
POCIS	+	+	+	+	+	+	+	+	-/+	-
Plant	+	+	-	-	-	+	-	-	-	-
Sediment	-	-	-	+	-	-	-	-	-	-

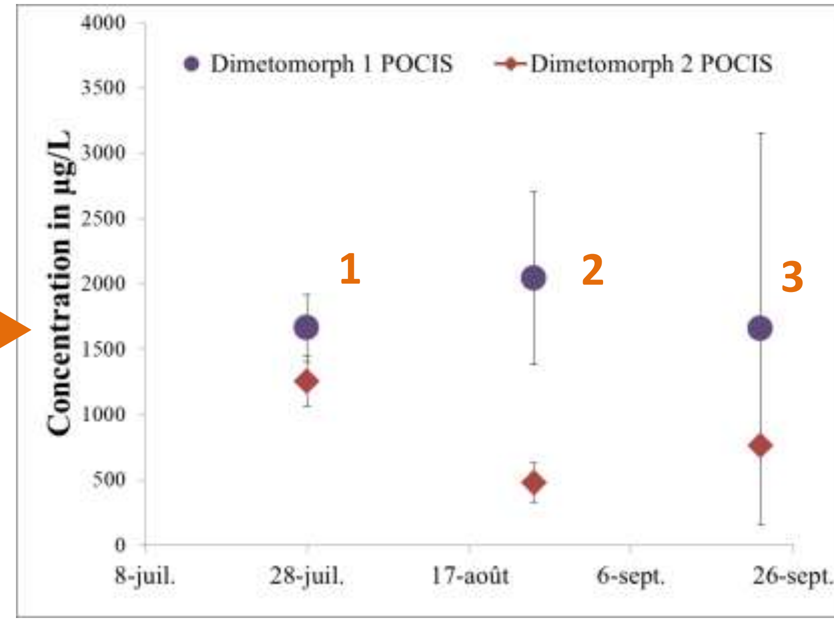
+ detected - not detected

Preliminary results Rouffach campaign

Period of POCIS application



POCIS concentration



Average concentration in the pond ~100 ng/L = ~2000 µg/L in POCIS extract

Conclusions

- POCIS : a suitable alternative to grab sampling - less cost/time consuming sampling. Up to 20’000 times preconcentration of dimetomorph in the sampling campaign in stormwater catchment.

- POCIS collected the average isotope signature/ concentrations of pollutants and account for high-concentrated short runoff events.

- Sorption of tested pesticides on POCIS : no isotope effects and is linear at environmental concentrations.

- High pre-concentration factor of POCIS allows CSIA of micropollutants => insight into pesticide dissipation processes in the water column/ at water-sediment interface.

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