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Emerging pollutants in freshwater ecosystems

# An innovative composite silicone-based passive sampler to study the transfer of polar and apolar pollutants in surface waters

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## Introduction and Objectives

Passive sampling was developed as an alternative to grab or average automated sampling to obtain, at lower cost and according to a simple field protocol, more representative evaluations of average concentrations of organic contaminants in aquatic environments. This technique allows *in situ* accumulation of pollutants, resulting in ultratrace level detection and smoothed integrative sampling over exposure periods ranging from days to months.

In small agricultural catchments, pesticides are transferred from plots to the watercourse by various pathways (runoff, infiltration, lateral flows, etc.), which often induce differentiated concentration levels and dynamics.

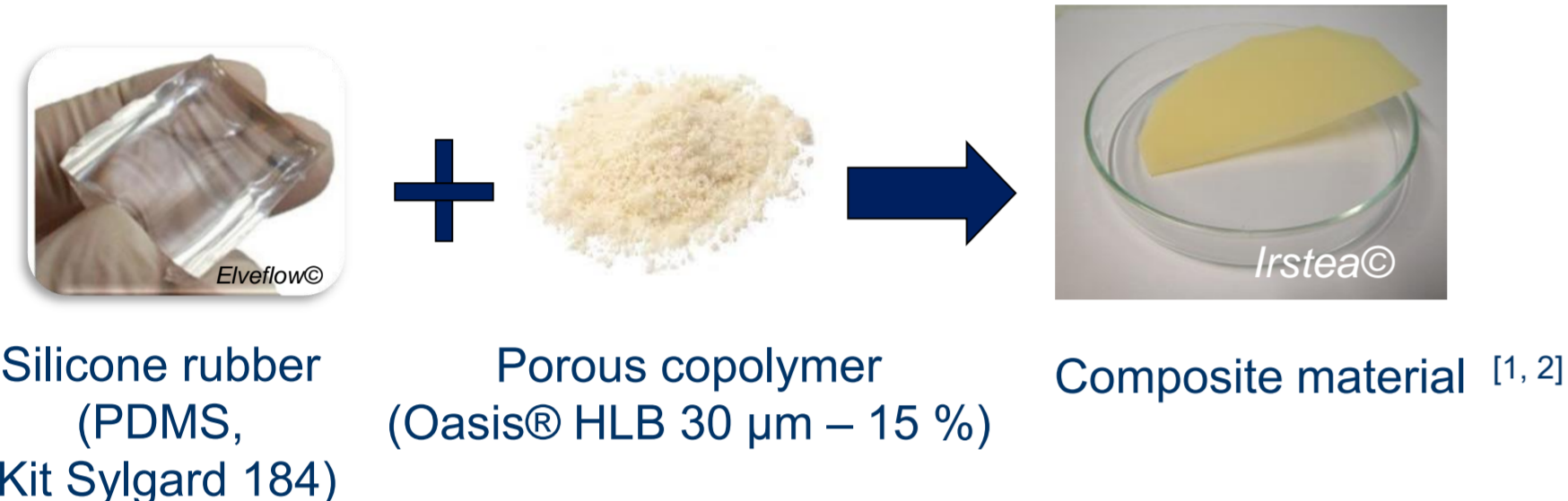
New sampling strategies adapted to local characteristics and dynamics are necessary to study pesticides transfer and assess the role of landscape features or wetland buffer zone for mitigation.

In this aim, an innovative silicone-based passive sampler - small rod made of **PACSiR**, for **Polar Apolar Composite Silicone Rubber** - was designed to address sampling, detection and quantification of a wide range of pesticides (active substances or degradation products) in waters. It was also tested for its capacity to monitor hormones and pharmaceuticals and for pollutant screening.

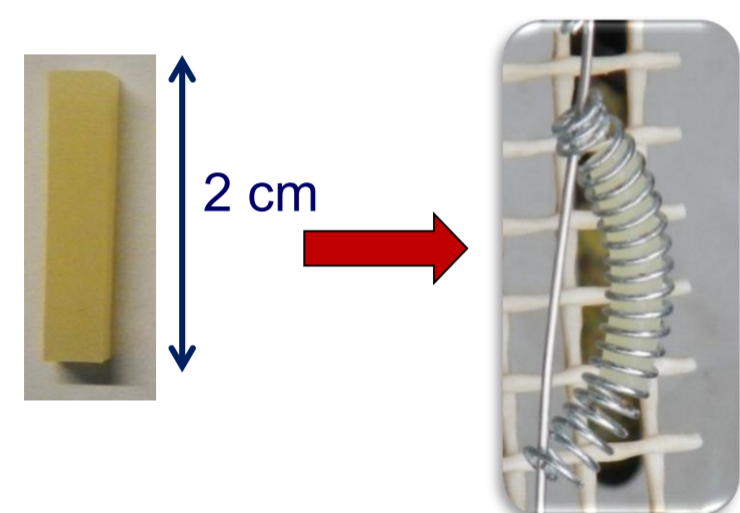
## Passive sampler design, laboratory developments and field data acquisition

### 1 / Passive sampler

#### Material formulation



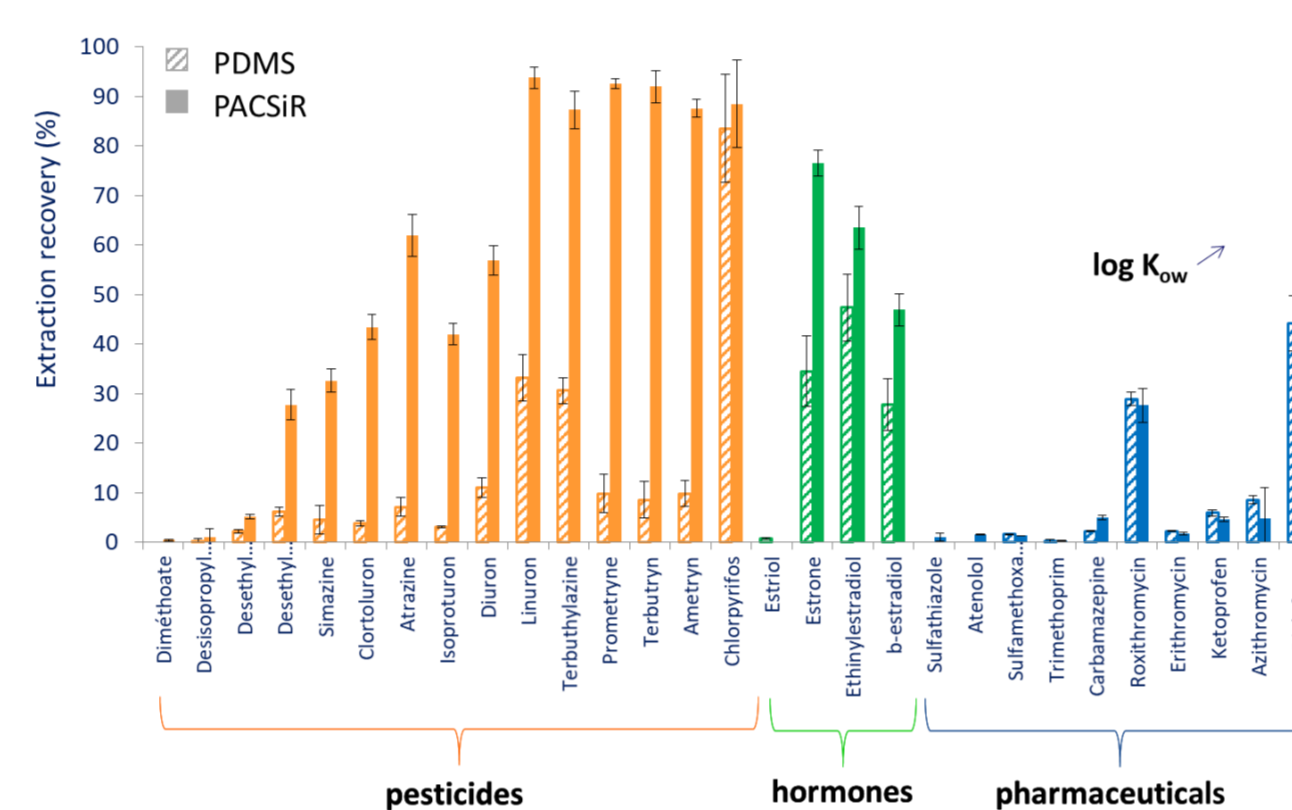
#### Passive sampler design



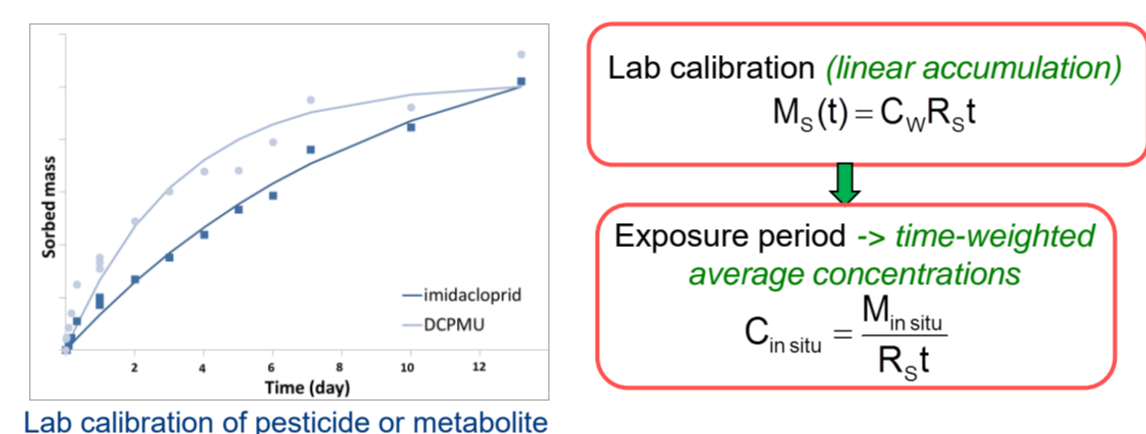
The PACSiR sampler is inserted into a spring (without any additional membrane) to facilitate *in situ* deployment

### 2 / Tests of extraction capacity and laboratory calibration of PACSiR

Comparison of simple PDMS and PACSiR for pollutants extraction recovery => better performance of PACSiR for most compounds

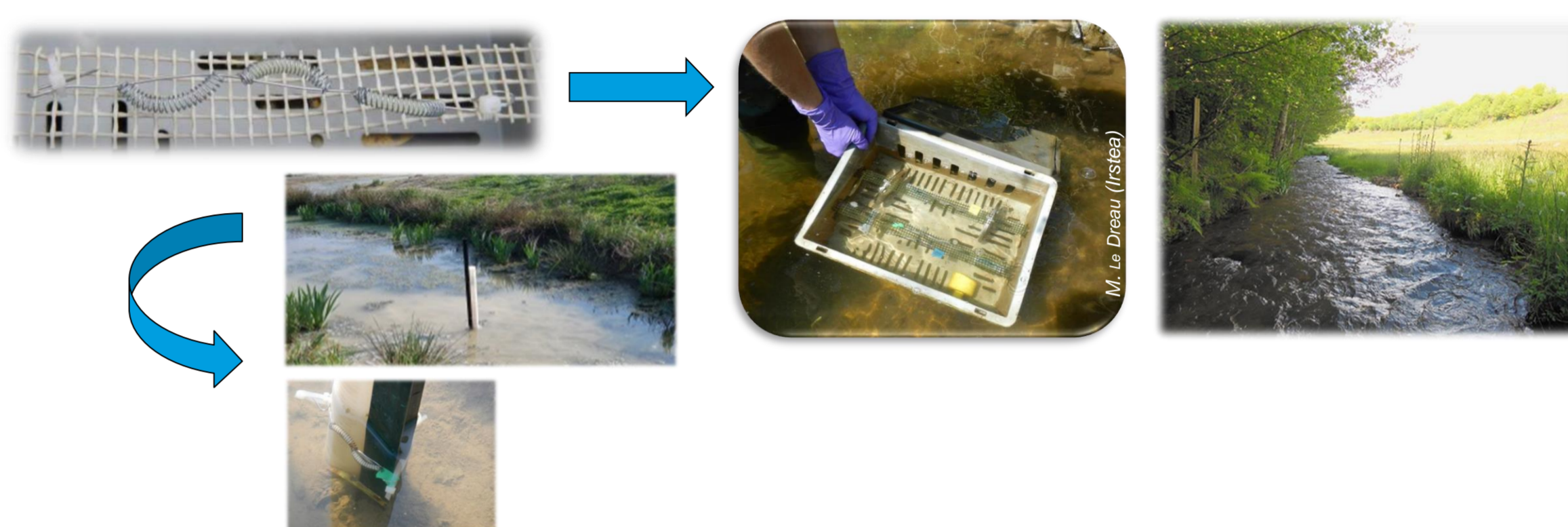


Average concentrations of target pesticides are determined after laboratory calibration (calculation of kinetic parameters)



### 3 / Exposition in the field and analyses

Exposition of PACSiR sampler (triplicates) for 1 week in small cages or directly in the stream



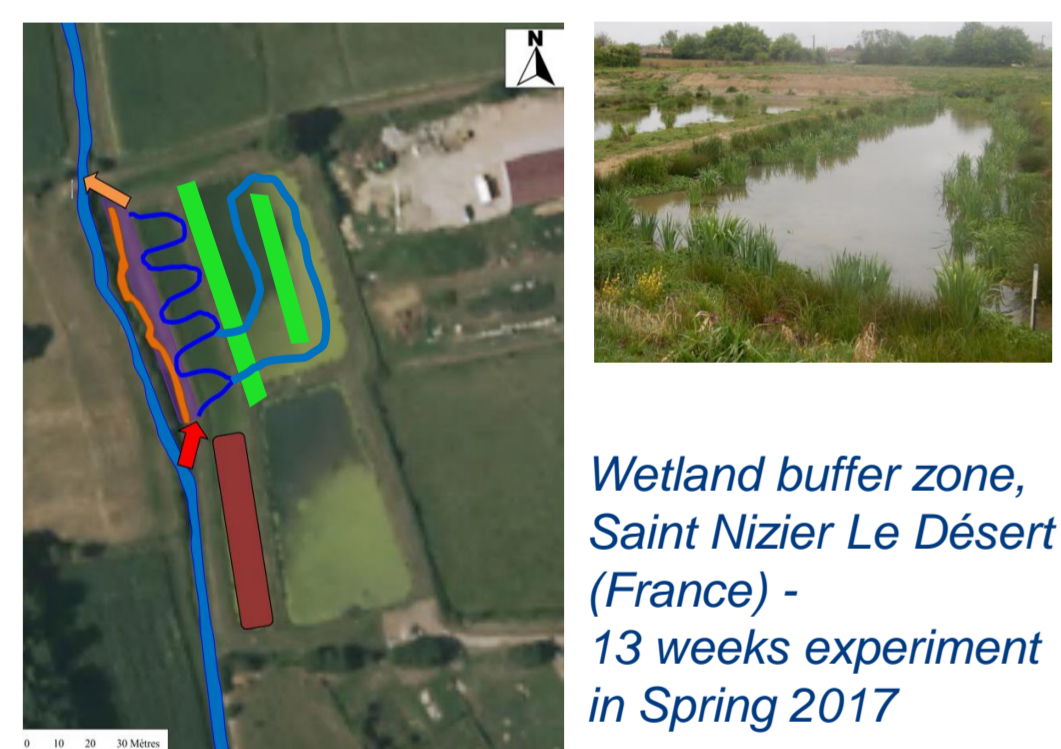
Back to the **laboratory**, pesticides and metabolites accumulated on the PACSiR sampler are desorbed with organic solvents and analyzed by UHPLC - (ESI+) MSMS [3]



## Results

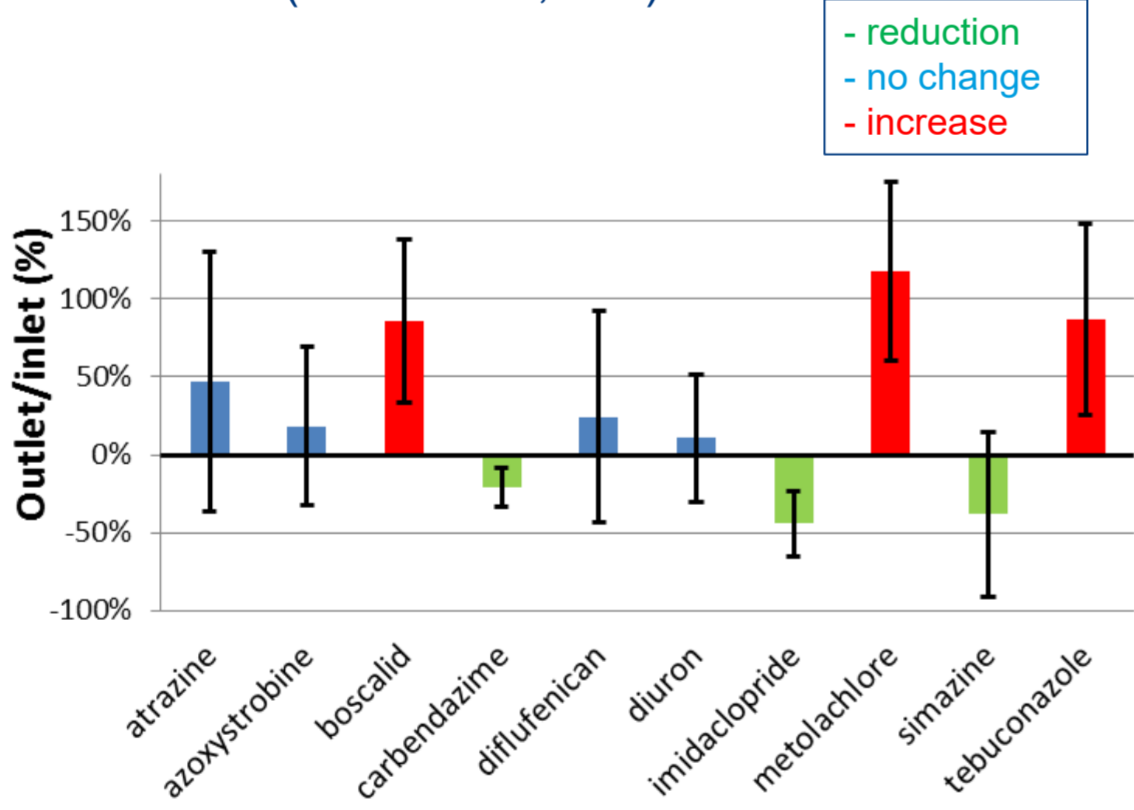
Two examples to illustrate how the PACSiR sampler could be used for research purposes or to address operational issues

### Evaluate the role of a wet buffer zone



#### Comparative approach:

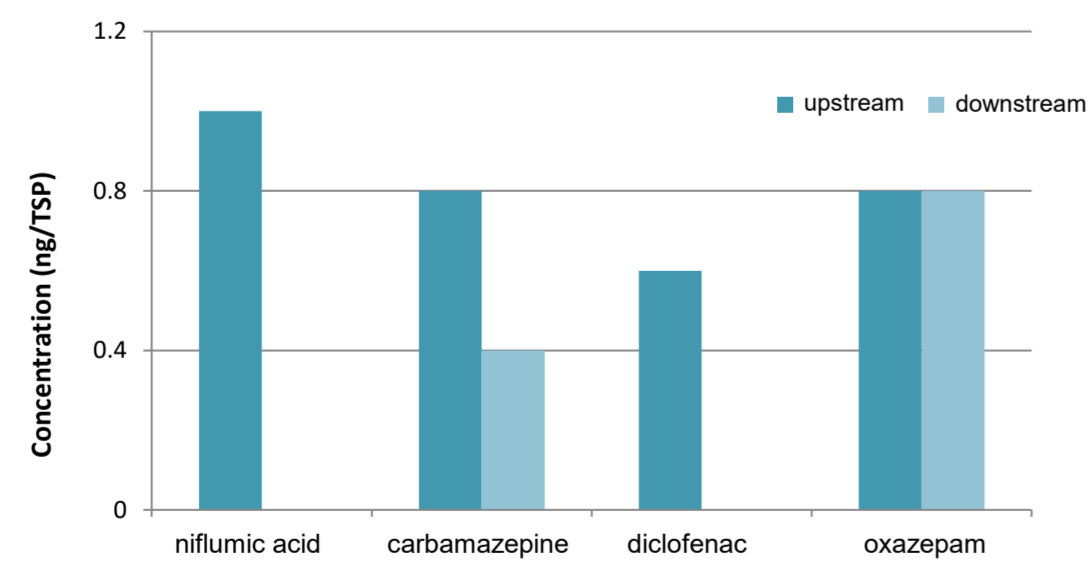
Comparison of the mass of pesticides sorbed on PACSiR samplers between inlet and outlet of the buffer zone (mean ± std, n=6)



#### Qualitative approach:

Accumulation of a broad spectrum of contaminants on PACSiR samplers.

In addition to the quantified pesticides, detection of pharmaceuticals from domestic sources (WWTP outlet): niflumic acid, carbamazepine, diclofenac, oxazepam.



Large screening (> 500 molecules) on 2 PACSiR samplers exposed upstream and downstream the wetland buffer zone (week 9)

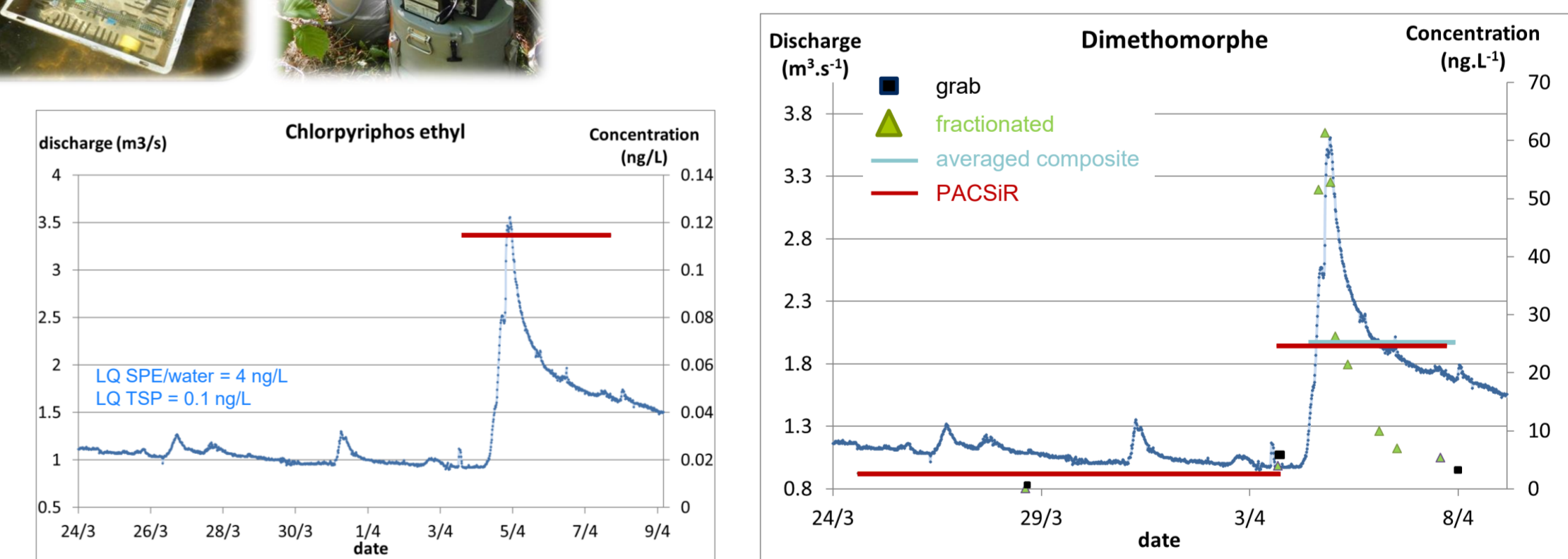
PACSiR sampler: an easy-to-use integrative tool to assess the effectiveness of buffer zones

### Highlight dynamics of pesticide transfer in small rivers



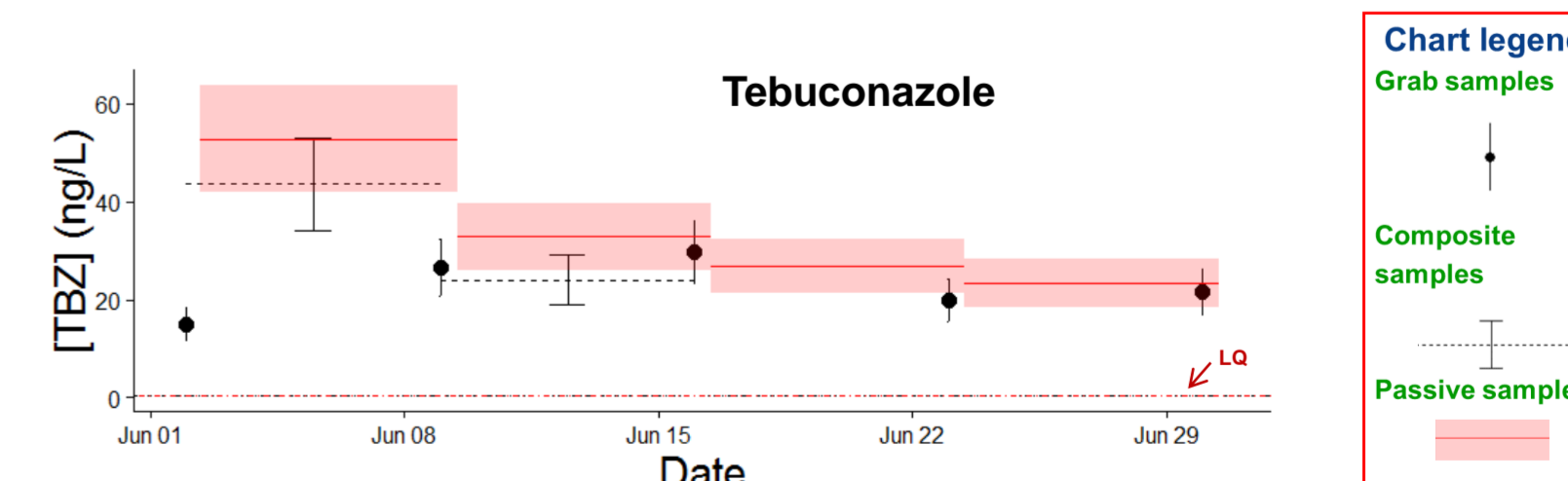
#### Quantitative approach:

Pesticide concentrations during a flood event: Ardères River, Beaujolais (France) – Spring 2016



#### Accuracy of pesticide concentration measurements with PACSiR:

4 consecutive one-week studies with grab and composite sampling or PACSiR samplers, with associated uncertainties



PACSiR sampler: a reactive tool to accurately measure quantitative time-weighted average pesticide concentrations in watercourses

22 target pesticides calibrated for determination of average concentrations (1 week) with PACSiR sampler.

Corresponding sampling rates (Rs) and limits of quantification in water are listed below:

pesticide	use	Log Kow	Rs (L.d <sup>-1</sup> )	LoQ (ng.L <sup>-1</sup> )
simazine	H	2.3	0.014	0.21
DCPMU	metab	2.3	0.010	2.02
norflurazon	H	2.4	0.011	4.48
azoxystrobin	F	2.5	0.042	0.05
chlortoluron	H	2.5	0.019	3.30
isoproturon	H	2.5	0.016	1.73
dimetomorph	F	2.7	0.010	1.84
dichloroaniline	metab	2.7	1.40	0.14
atrazine	H	2.7	0.030	0.52
diuron	H	2.9	0.028	2.25
boscalid	F	3.0	0.102	0.46
linuron	H	3.0	0.149	0.13
procymidone	F	3.3	0.142	1.54
fenitrothion	I	3.3	0.277	1.36
metolachlor	H	3.4	0.123	0.30
tebuconazole	F	3.7	0.070	0.34
chlorfenvinphos	I	3.8	0.228	0.08
chlorpyrifos methyl	I	4.0	0.298	0.11
acetochlor	H	4.1	0.128	0.43
diflufenican	H	4.2	0.263	0.14
chlorpyrifos	I	4.7	0.276	0.12
spiroxamine	F	5.5	0.082	0.18

H: herbicide, F: fungicide, I: insecticide, metab: metabolite

## References:

- [1] Patent: FR 3 047 992 (2017)
- [2] Martin, A. et al. (2016). *J. Sep. Science*. DOI: 10.1002/jssc.201600502
- [3] Margoum C. et al. (2013). *Talanta*. DOI: 10.1016/j.talanta.2013.04.066

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## Conclusions

PACSiR is a sensitive receiving phase for sampling of polar and apolar pesticides (2.3 > Log Kow > 5.5) and other emerging pollutants such as hormones and pharmaceuticals. This composite material can greatly improve sorption properties compared to PDMS and permitted to reach lower limits of quantification for polar pesticides.

Results of field studies showed that the new PACSiR rod passive sampler can be used for multiple **research or operational purposes**. Its characteristics - reactive, single use and low cost - make it particularly useful for measurements within small agricultural catchments where pollutants transfer occurs in **surface and subsurface waters and with rapid dynamics**.

We plan to couple this broad spectrum passive sampler with suspect or non-target analyses (via high resolution mass spectrometry) to gain access to a maximum of emerging substances and metabolites.

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