Innovative passive sampling tool to facilitate the study of the transfer pathways of a wide range of pesticides in small agricultural watersheds

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Introduction

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 estimates of average concentrations of organic contaminants in aquatic environments. This technique allows the *in situ* accumulation of chemicals, 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.

Objectives

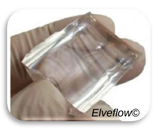
To study pesticide transfers and to assess the role of landscape features for mitigation, new sampling strategies adapted to the characteristics and dynamics of each environment are necessary.

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 organic contaminants (active substances or degradation products, with 2.3 < log Kow < 5.5) in surface or subsurface waters.

Passive sampler, experimental sites and data interpretation

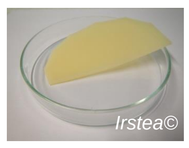
1 / Passive sampler

Material formulation



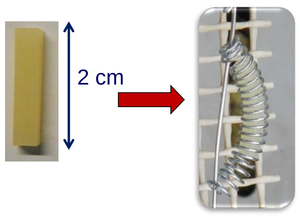
Silicone rubber (PDMS)

Porous copolymer (Oasis® HLB)



Composite material [1, 2]

Passive sampler design

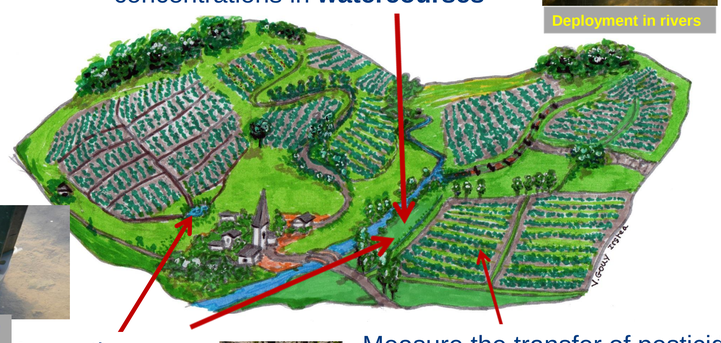


The PACSiR sampler is inserted into a spring (without any additional membrane) to facilitate in situ deployment for 1 week

2 / Deployment of PACSiR samplers in a small agricultural watershed

Evaluate spatio-temporal variations of pesticide concentrations in **watercourses**

Deployment in rivers

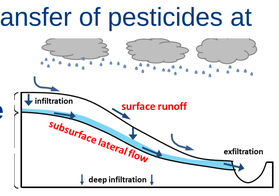


Deployment in wetlands

Asses the **effectiveness of buffer zones** (vegetative or wetlands)

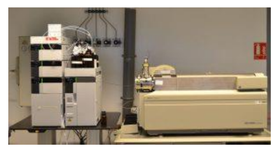
Deployment in piezometers

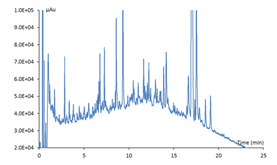
Measure the transfer of pesticides at **the plot scale via surface or subsurface** pathways



3 / How the data acquired can be interpreted?

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





Different approaches are proposed to derive information from analytical data and address the following questions:

- How many compounds are present?

→ **qualitative approach:** search for a large variety of pesticides and metabolites by targeted or suspected screening analysis

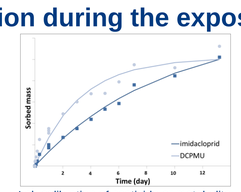
- Can we detect gradients of contamination between sampling sites?

→ **comparative approach:** comparison of the accumulated quantity of each pesticide on the PACSIR samplers (such as upstream/downstream contamination, or before/after a pesticide reduction or ban)

- What is the pesticide concentration during the exposure period?

→ **quantitative approach:**

average concentrations of target pesticides are determined after laboratory calibration of PACSIR sampler (calculation of kinetic parameters).



Lab calibration of pesticide or metabolite

Lab calibration *(linear accumulation)*

$$M_S(t) = C_W R_S t$$

Exposure period -> *time-weighted average concentrations*

$$C_{in\,situ} = \frac{M_{in\,situ}}{R_S t}$$

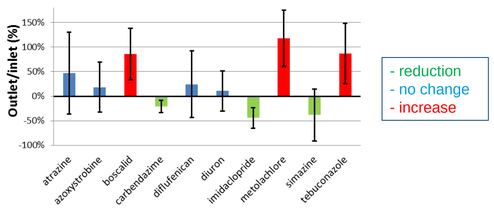
Results

3 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

Wetland buffer zone, Saint Nizier Le Désert (France)

Comparative approach: comparison of the mass of pesticides sorbed on PACSiR samplers between inlet and outlet



Qualitative approach: accumulation of a broad spectrum of contaminants on PACSiR samplers

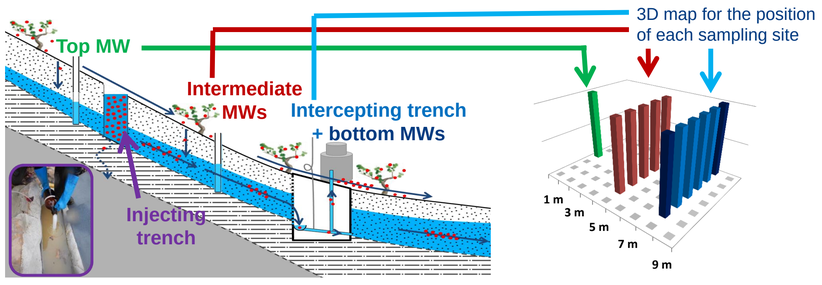
⇨ detection of pharmaceuticals from urban sources: niflumic acid, carbamazepine, diclofenac, oxazepam with the same passive sampler

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

Study lateral subsurface flow transfers

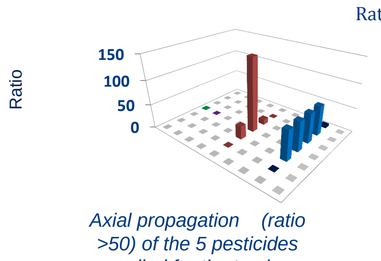
Tracing experiment [4]

- Vineyard plot (Beaujolais region, France) instrumented with injecting and intercepting trenches and 8 monitoring wells (MW)
- Tracing experiment with 5 pesticides (azoxystrobine, chlortoluron, flumioxazine, linuron and chlorpiryphos M) during a natural rainfall event (autumn 2014)
- Exposition of PACSiR samplers inside the 8 MW and intercepting trench

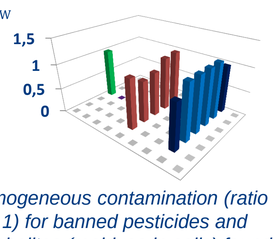


Comparative approach: significant axial subsurface transfer of pesticides used for the tracing experiment and different behaviors related to agricultural practices

$$\text{Ratio}(\%) = \frac{\text{mass}_{\text{MW or trench}}}{\text{mass}_{\text{top MW}}}$$



Axial propagation (ratio >50) of the 5 pesticides applied for the tracing experiment



Homogeneous contamination (ratio ≈ 1) for banned pesticides and metabolites (residues in soils) found with qualitative approach

PACSiR sampler: a small tool that can be used to evaluate pesticide dispersion in surface or subsurface waters without disturbing flows

Highlight dynamics of pesticide transfer in small rivers

22 target pesticides calibrated

for determination of <u>average concentrations</u> (1 week) with PACSiR sampler.

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

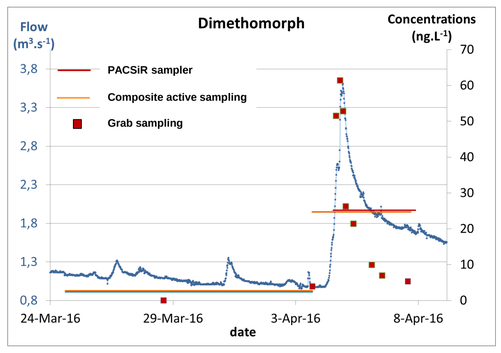
pesticide	usage	Log Kow	Rs (L.d-1)	LoQ (ng.L-1)
simazine	H	2,3	0,014	0,21
DCPMU	metab	2,3	0,010	2,02
norflurazon	H	2,5	0,012	4,48
azoxystrobin	F	2,5	0,042	0,05
chlortoluron	H	2,5	0,019	3,30
isoproturon	H	2,5	0,016	1,73
dimetomorph	F	2,7	0,010	1,84
dichloroaniline	metab	2,7	1,396	0,14
atrazine	H	2,7	0,030	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

Quantitative approach :

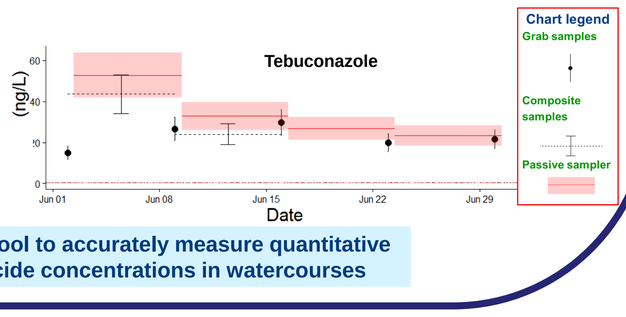
- **Pesticide concentrations during a flood event:**

Ardieres river, Beaujolais (France).

PACSiR sampling *vs.* active sampling (grab or composite)



- **Accuracy of pesticide concentration measurement 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

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
[4] Peyrard X. *et al.* (2016). *ESPR*. DOI: 10.1007/s11356-015-4917-5

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Conclusion

The new PACSiR rod passive sampler can be used for multiple **research or operational purposes**, from qualitative to quantitative approaches, thanks to the different levels of data acquisition. Its characteristics (reactive, single use and low cost) make it particularly useful for measurements within small catchments where pesticide transfers occur in **surface and subsurface waters and with rapid dynamics**.

The various *in situ* studies presented here showed that 3 main approaches – **qualitative, comparative, quantitative** - can be applied and adapted to each situation. The PACSiR sampler is indeed a flexible tool easy to use in a context of diffuse agricultural pollution.

We now plan to couple this broad spectrum passive sampling tool with suspect or non-targeted analysis (via high resolution mass spectrometry analysis) to gain access to a maximum of substances and metabolites.

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