Benefits of passive sampling for the monitoring of pesticides in surface and subsurface waters

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BENEFITS OF PASSIVE SAMPLING FOR THE MONITORING OF PESTICIDES IN SURFACE AND SUBSURFACE WATERS

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Context and objectives

The use of pesticides in agricultural fields leads to nonpoint source contamination of freshwaters by various pathways (runoff, infiltration, lateral flows…). Research programs developed to study and explain these transfer mechanisms require specific sampling strategies for each compartment of the aquatic environment. Passive sampling has been introduced as an alternative to grab or average automated sampling, in order to obtain at lower cost, more representative estimates of the contamination levels of pesticides in water. This technique allows the *in situ* accumulation of chemicals over exposition periods ranging from days to months. Two examples of application of silicone rod (SR) passive sampler are presented to answer the following question:

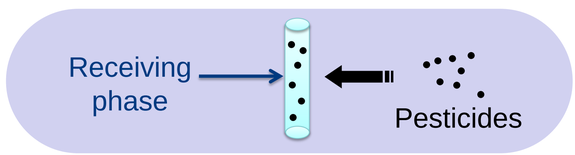
→ How can SR be used to estimate pesticide contamination levels in surface and subsurface waters ?

Theory and tools

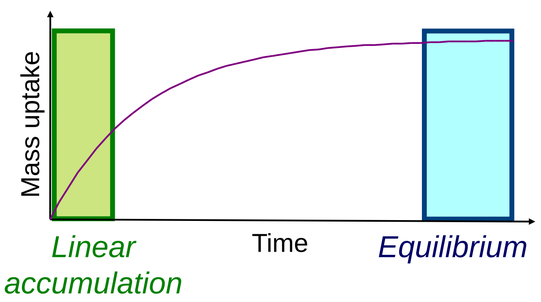
Passive sampling

Theory [1]

- Polymeric receiving phase
- *In situ* exposure
- Pesticide diffusion and absorption in the phase



Pesticide uptake profile



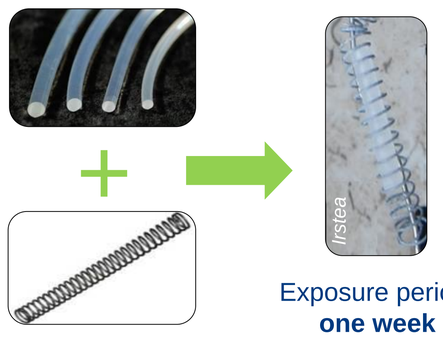
Passive sampling applications

Target screening **Qualitative** → Mass uptake (ng on phase) **Semi-quantitative** → Laboratory calibration for each pesticide → Mean concentration over exposure period (ng/L) **Quantitative** (C_{water})

Silicone Rod (SR)

SR preparation

- Silicone rubber conditioned in laboratory (heating, solvent washing)
- Put into a metal spring for protection



Exposure period: **one week**

Pesticide analysis

- 24 pesticides (1.5 < log Kow < 5.51)
- Limits of quantification from 10 to 4000 ng on phase
- Simplified analytical procedure, from [2]

Liquid desorption
Acetonitrile / Methanol 200 µL (50/50 ; v/v) in ultrasonic bath

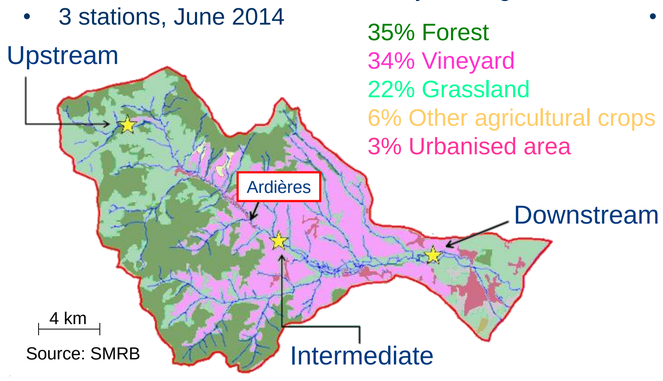
Quantification by UHPLC-MS/MS
Nexera Shimadzu, API 4000 AB Sciex

Field applications

Surface waters

Watershed and land use

- The Ardières river located in Beaujolais region, France
- 3 stations, June 2014



Field deployment

- Exposure of SR during one month (4 x 1 week)
- SR in triplicate at each station

Qualitative assessment

Pesticides analised and detected at the downstream station of the Ardières river (in color)

Pesticide	Abreviation	Type	log Kow (*)	Authorized or banned in France?
Azoxystrobin	AZS	F	2,5	authorized
Carbendazim	CBZ	F	1,48	banned (2009)
Dimethomorph	DMM	F	2,68	authorized
Procymidon	PCM	F	3,3	banned (2008)
Spiroxamine	SPX	F	2,89/5,51	authorized
Tebuconazole	TBZ	F	3,7	authorized
Acetochlor	ATC	H	4,14	banned (2013
Atrazine	ATR	H	2,7	banned (2003)
Chlortoluron	CTU	H	2,5	authorized
Diflufenican	DFF	H	4,2	authorized
Diuron	DIU	H	2,46	banned (2008)
3,4-dichloroaniline	DCA	metab	2,69	-

Pesticide	Abreviation	Type	log Kow (*)	Authorized or banned in France?
3-(3,4-dichlorophenyl)-1 méthylurea	DCPMU	metab	-	-
Flumioxacin	FMX	H	2,55	authorized
Isoproturon	IPU	H	2,5	authorized
Linuron	LINU	H	3,0	authorized
Metolachlor	MTC	H	3,4	authorized
Norflurazon	NFZ	H	2,45	banned (2004)
Simazine	SMZ	H	2,3	banned (2001)
Chlorfenvinfos	CFV	I	3,8	banned (2007)
Ethyl Chlorpiryfos	CPE	I	4,7	authorized
Methyl Chlorpiryfos	CPM	I	4,0	authorized
Flufenoxuron	FFX	I	5,11	authorized
Fenitrothion	FNT	I	3,32	banned (2008)

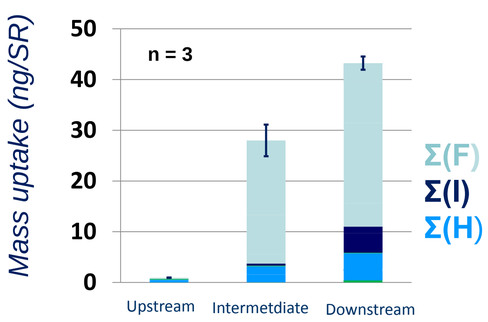
(*) from: http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm F: fongicide H: herbicide I: insecticide

→ SR allowed to detect:

- 6 herbicides, 6 fungicides, 3 insecticides according to land use for vineyard
- 4 banned herbicides (ATZ, DIU, NFZ, SMZ) corresponding to persistent pesticide residues in soils
- 3 insecticides that are rarely quantified in surface waters with grab samples

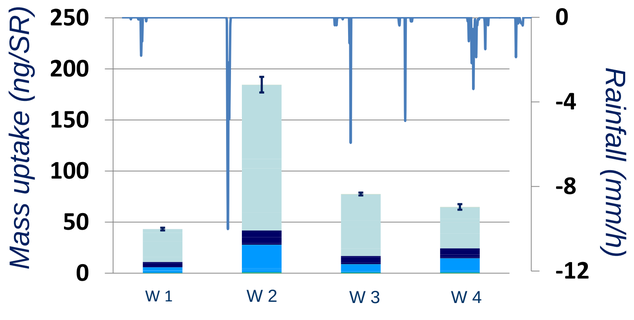
Semi-quantitative measurement

Spatial gradient (upstream to downstream, week 1)



→Strong gradient of contamination clearly shown according to the increase of vineyard

Temporal variation (downstream, weeks 1 to 4)



→Week 2: higher contamination linked to the first significant rainfall event after pesticide application

Lateral subsurface flows

Tracing experiment (Peyrard et al., Field Studies session, oral 47)

- Vineyard plot instrumented [3] with both **injecting and intercepting trenches and 8 Monitoring Wells (MW)**
- Tracing experiment with 5 pesticides (AZS, CTU, FMX, LINU, CPM) during a natural rainfall event
- Exposition of SR inside 8 MW and intercepting trench for one week

Scheme of experimental plot localised in Beaujolais region, France (autumn 2014)

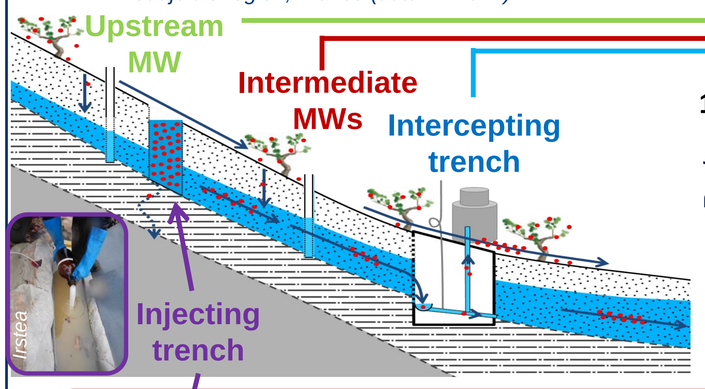
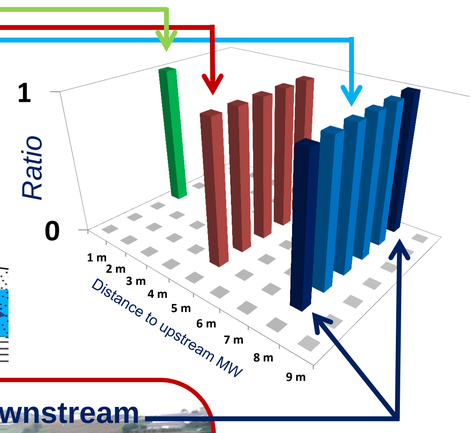
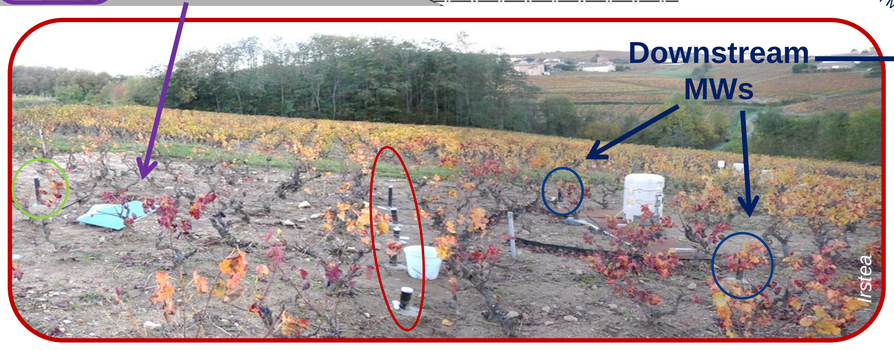


Illustration of 3D bar plots mapped on position of MW and trenches





Picture of the experimental plot instrumented with MW in Beaujolais region, France

Semi-quantitative application

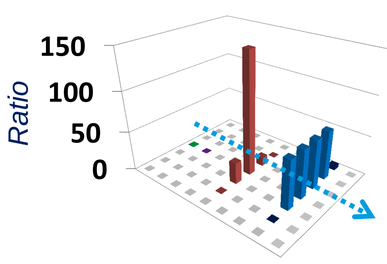
$$Ratio = \frac{mass_{\ MW\ or\ trench}}{mass_{\ Upstream\ MW}}$$

Mass of pesticide sorbed on SR in MW or trench to mass in upstream MW (reference point)

Spatial dispersion of pesticides

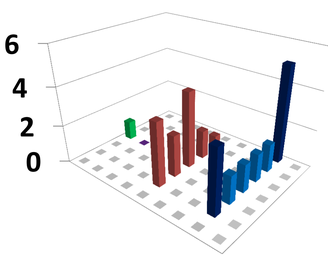
- **Qualitative:** 13 pesticides detected in subsurface waters
- **Semi-quantitative:** significant axial subsurface transfer of pesticides used for the tracing experiment
- Different behaviours of pesticides on SR related to pesticide-use practices

Pesticides applied for the tracing experiment



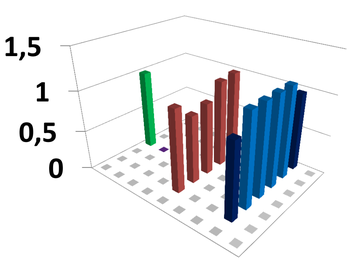
Axial propagation (ratio > 50)
CTU + AZS, FMX, LINU, CPM

Pesticides previously used by the wine grower



Contrasting propagation (ratio > 3)
SPX + DMM, TBZ

Banned pesticides (residues in soils)



Homogenous contamination (ratio ≈ 1)
SMZ + DCPMU, DIU, NFZ, PCM

Conclusion

Silicone rods are an alternative to estimate pesticide contamination levels in surface and subsurface waters and can be applied for different applications:

- **Qualitative: target screening for 24 pesticides and very well adapted to detection of non polar pesticides**
- **Semi-quantitative: spatial and temporal variations can be estimated using SR during one week**
- **Quantitative: laboratory calibration needed *(see Martin et al., Monitoring session, poster 5)***

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[1] B. Vrana, G.A. Mills, I.J. Allan, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison, R. Greenwood (2005). Trends in Analytical Chemistry 24, 845-868.
[2] C. Margoum, C. Guillemain, X. Yang, M. Coquery (2013). Talanta 116, 1-7.
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