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

A. Martin, C. Guillemain, M. Le Dreau, Lucie Liger, X. Peyrard, Véronique
Gouy, C. Margoum

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

A. Martin, C. Guillemain, M. Le Dréau, L. Liger, X. Peyrard, V. Gouy, **C. Margoum**

Irstea, 5 rue de la Doua, CS 70077, 69626 Villeurbanne cedex, France – christelle.margoum@irstea.fr

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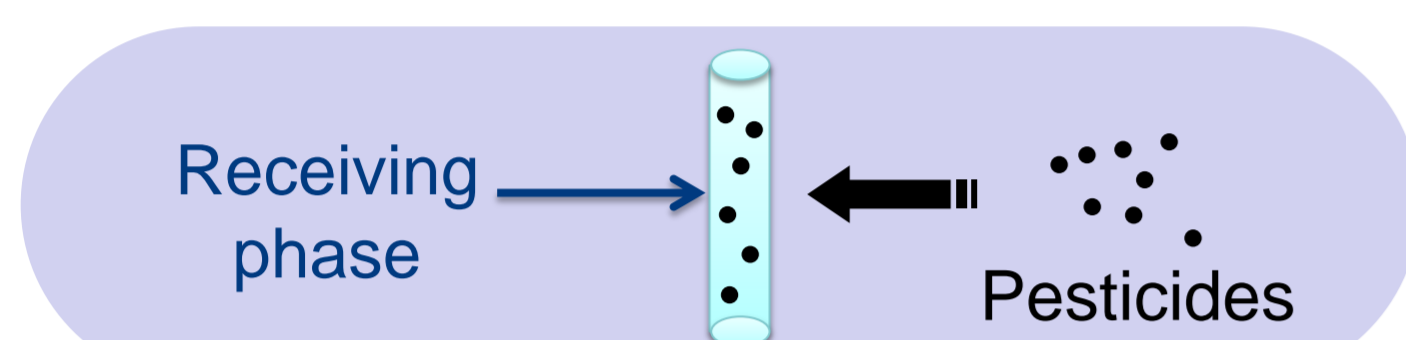
→ **How can SR be used to estimate pesticide contamination levels in surface and subsurface waters ?**
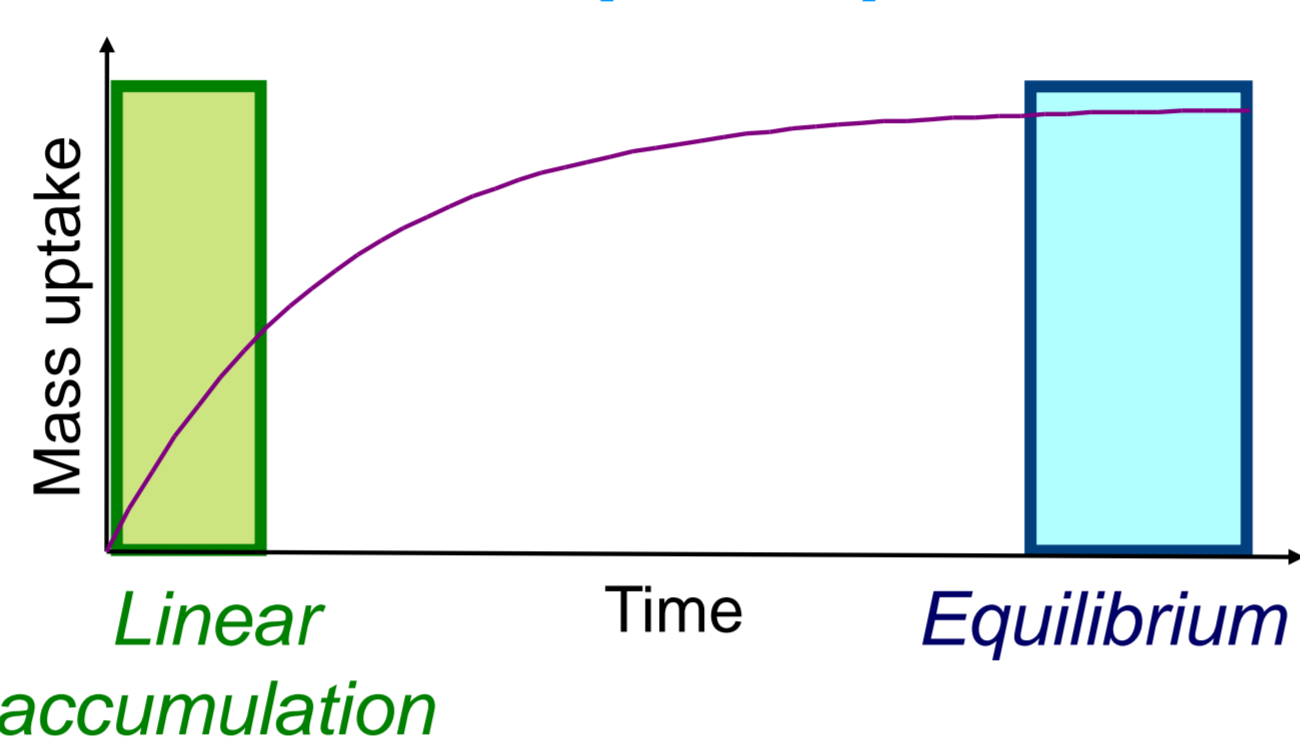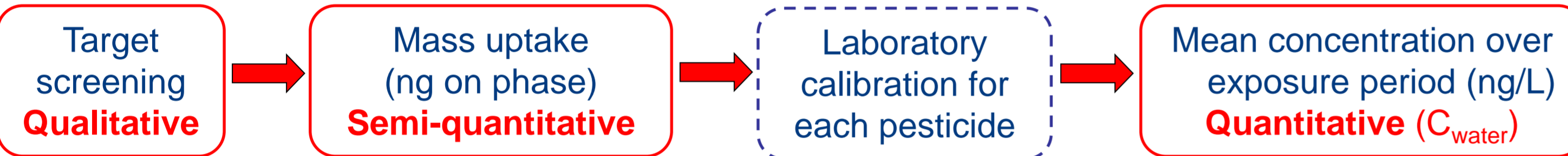
Theory and tools

Passive sampling

Theory [1]
- Polymeric receiving phase
- *In situ* exposure
- Pesticide diffusion and absorption in the phase

Pesticide uptake profile

Receiving phase → Pesticides

Linear accumulation — Time — *Equilibrium*

Mass uptake

Passive sampling applications

Target screening **Qualitative** → Mass uptake (ng on phase) **Semi-quantitative** → Laboratory calibration for each pesticide → Mean concentration over exposition 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**
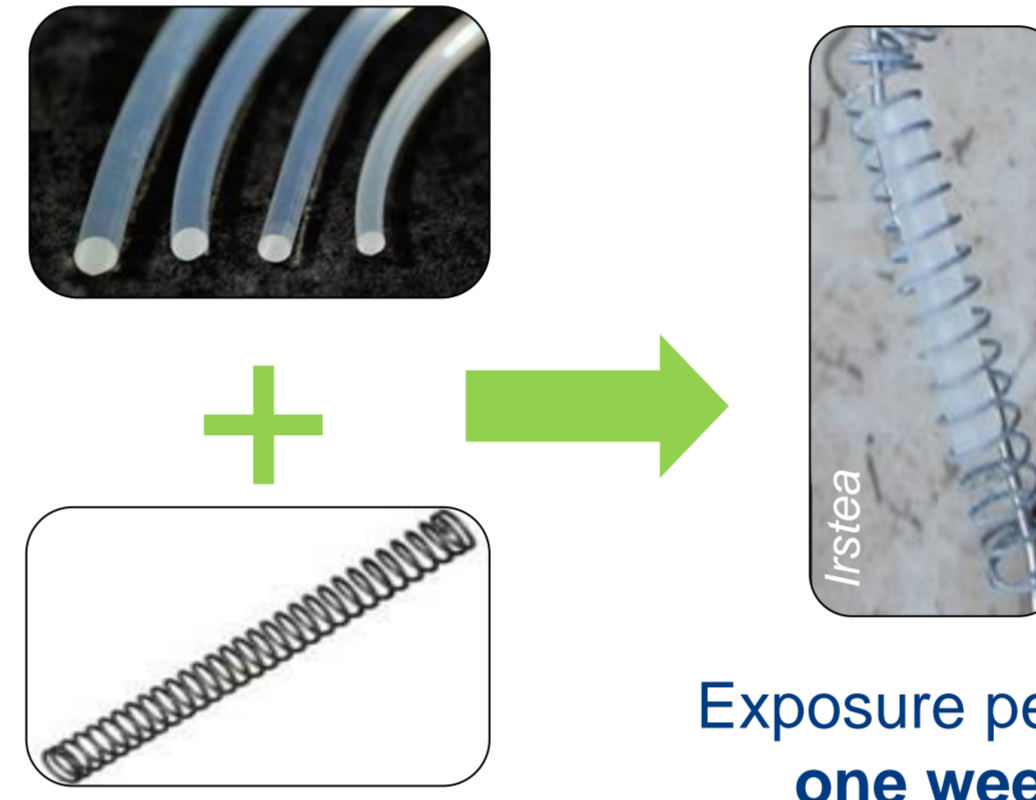
Pesticide analysis
- 24 pesticides (1.5 < log Kow < 5.51)
- Limits of quantification from 10 to 4000 ng on phase
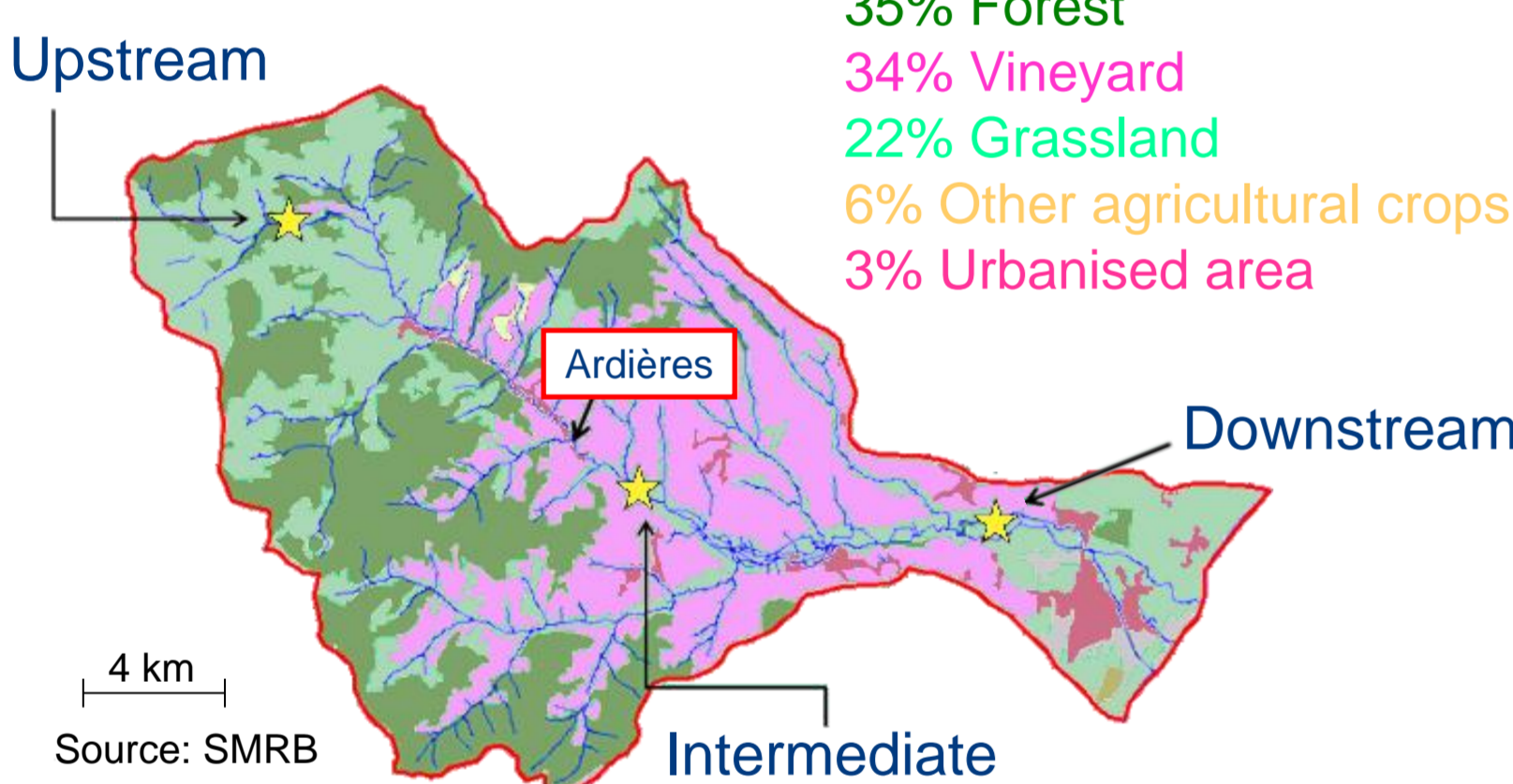- Simplified analytical procedure, from [2]

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

35% Forest
34% Vineyard
22% Grassland
6% Other agricultural crops
3% Urbanised area

Upstream
Ardières
Downstream
Intermediate
4 km
Source: SMRB

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

M.J. Capdeville, M. Le Dreau (Irstea)

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?	Pesticide	Abreviation	Type	log Kow (*)	Authorized or banned in France?
Azoxystrobin	AZS	F	2,5	authorized	3-(3,4-dichlorophenyl)-1 méthylurea	DCPMU	metab	-	-
Carbendazim	CBZ	F	1,48	banned (2009)	Flumioxacin	FMX	H	2,55	authorized
Dimethomorph	DMM	F	2,68	authorized	Isoproturon	IPU	H	2,5	authorized
Procymidon	PCM	F	3,3	banned (2008)	Linuron	LINU	H	3,0	authorized
Spiroxamine	SPX	F	2,89/5,51	authorized	Metolachlor	MTC	H	3,4	authorized
Tebuconazole	TBZ	F	3,7	authorized	Norflurazon	NFZ	H	2,45	banned (2004)
Acetochlor	ATC	H	4,14	banned (2013)	Simazine	SMZ	H	2,13	banned (2001)
Atrazine	ATR	H	2,7	banned (2003)	Chlorfenvinfos	CFV	I	3,8	banned (2007)
Chlortoluron	CTU	H	2,5	authorized	Ethyl Chlorpiryfos	CPE	I	4,7	authorized
Diflufenican	DFF	H	4,2	authorized	Methyl Chlorpiryfos	CPM	I	4,0	authorized
Diuron	DIU	H	2,46	banned (2008)	Flufenoxuron	FFX	I	5,11	authorized
3,4-dichloroaniline	DCA	metab	2,69	-	Fenitrothion	FNT	I	3,32	banned (2008)

(*) from: http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm   F: fongicide   H: herbicide   I: insecticide
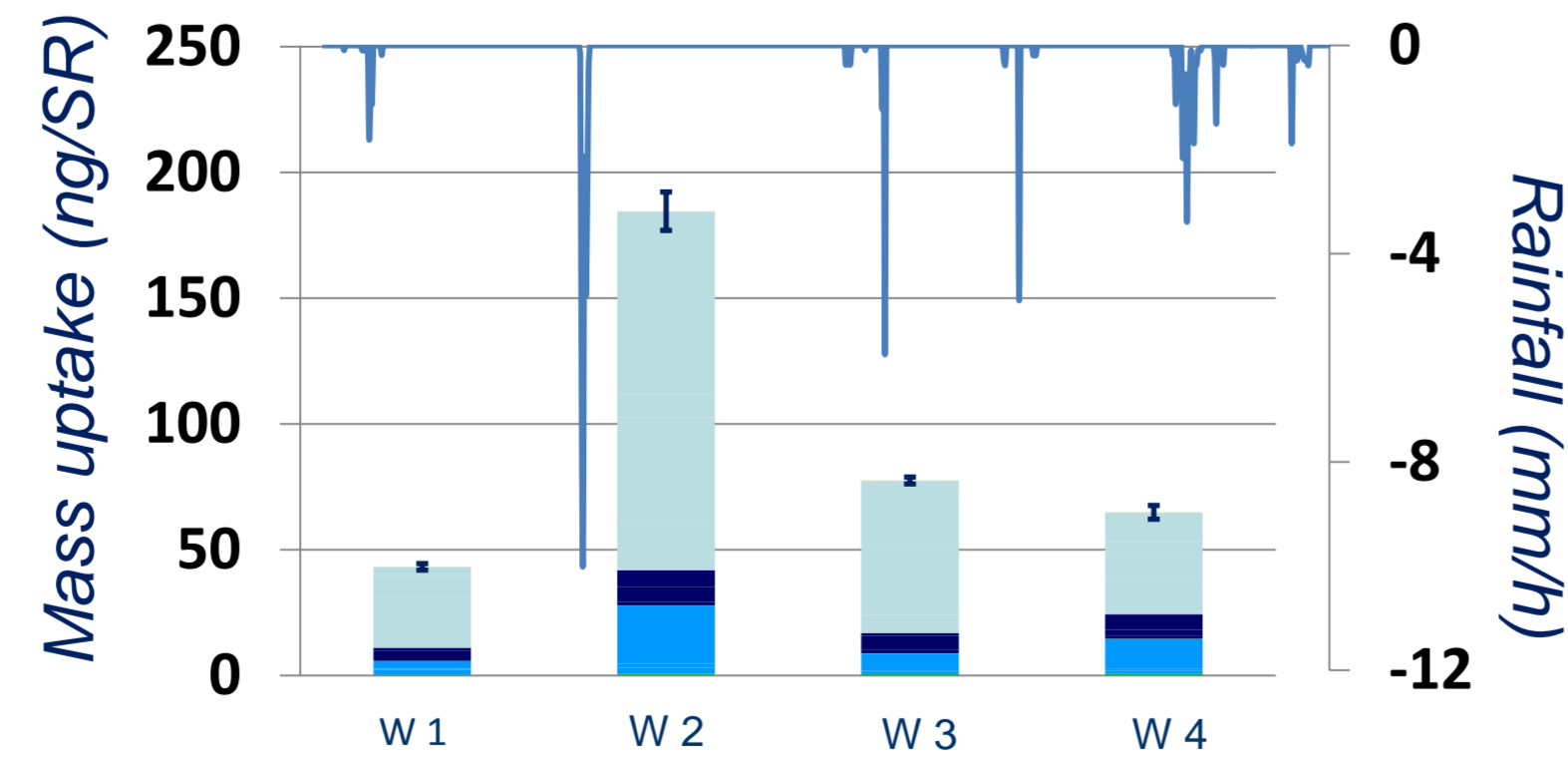
→ **SR allowed to detect:**
- 6 herbicides, 6 fungicides, 3 insecticides according to land use for vineyard
- 4 banned herbicides (ATZ, DIU, NFZ, SMZ) corresponding to persistent pesticide residues in soils
- 3 insecticides that are rarely quantified in surface waters with grab samples

Semi-quantitative measurement

Spatial gradient (upstream to downstream, week 1)

n = 3

Mass uptake (ng/SR): Upstream, Intermediate, Downstream

Σ(F)
Σ(I)
Σ(H)
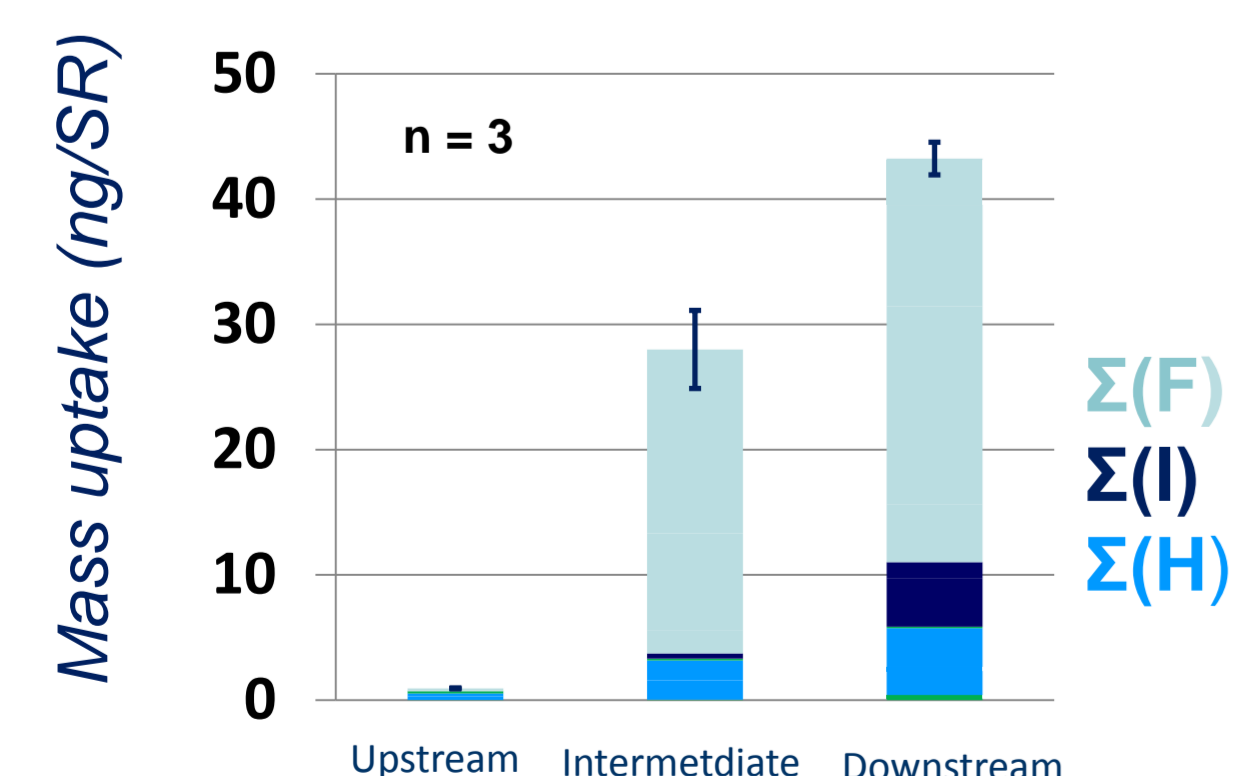
Temporal variation (downstream, weeks 1 to 4)

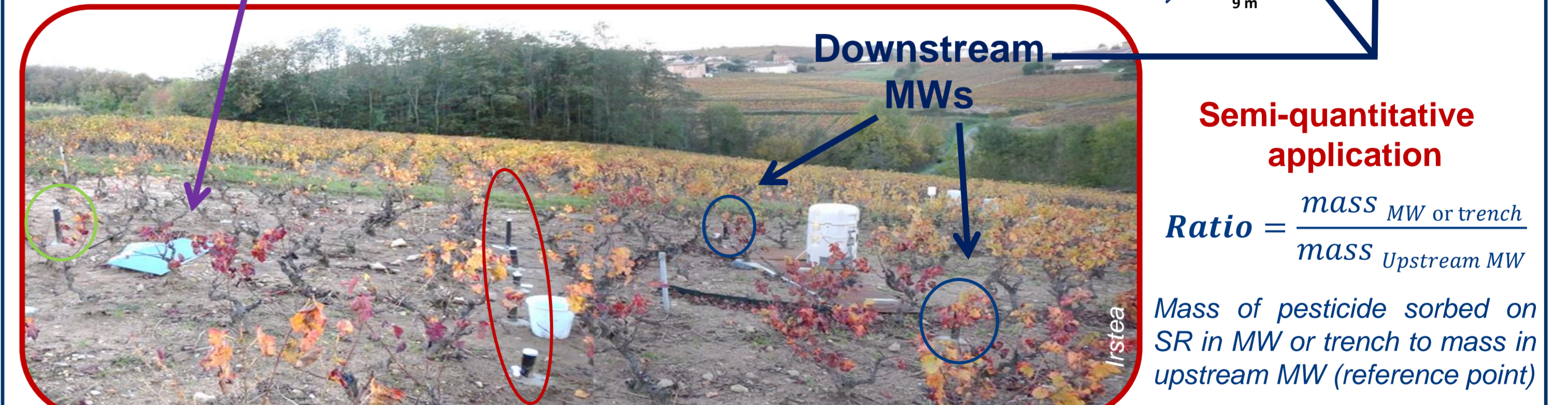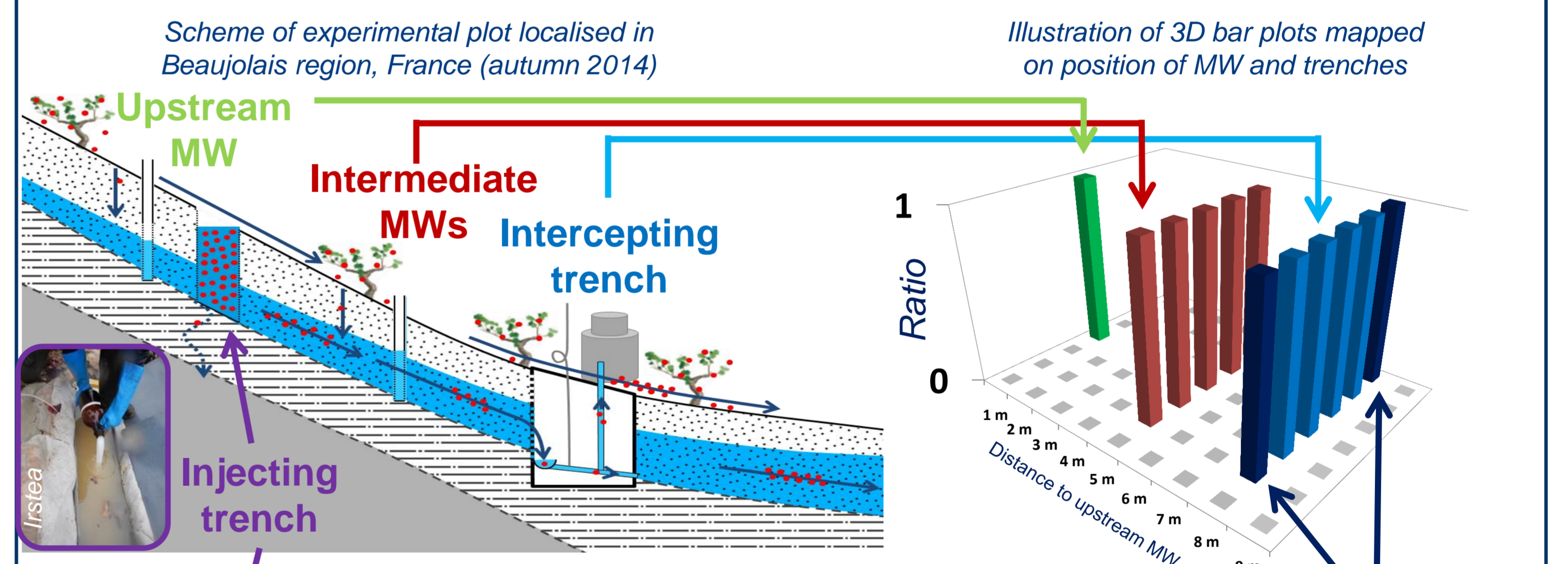Mass uptake (ng/SR) — W1, W2, W3, W4 — Rainfall (mm/h)

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

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

Lateral subsurface flows

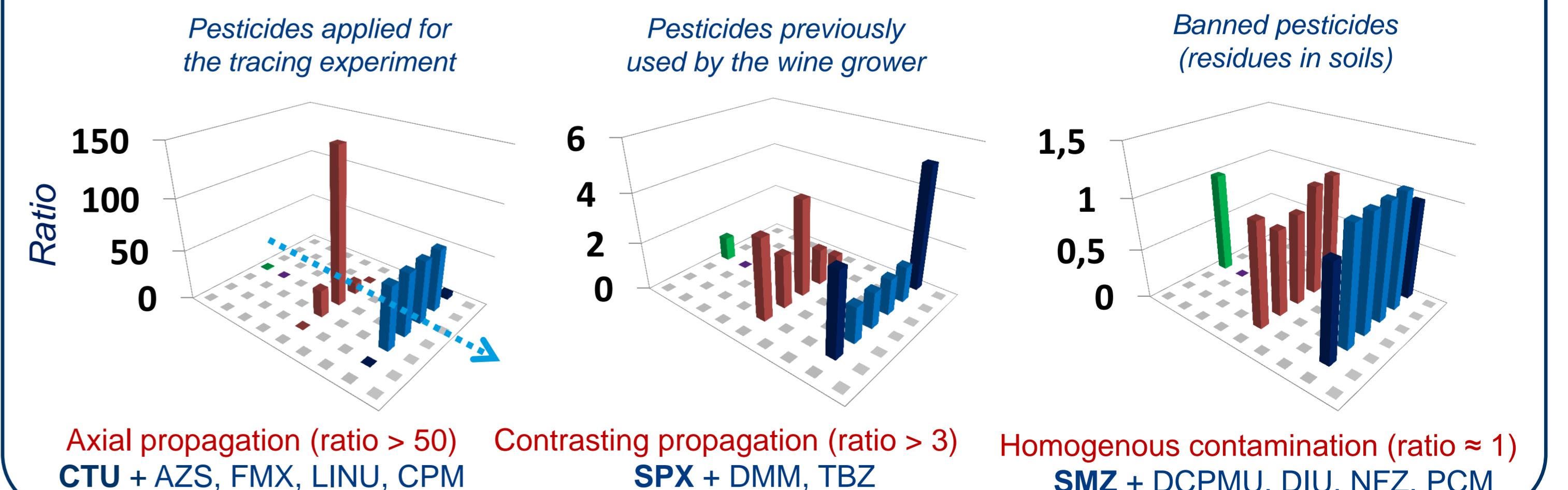#### Tracing experiment (Peyrard et al., Field Studies session, oral 47)
- Vineyard plot instrumented [3] with both **injecting and intercepting trenches and 8 Monitoring Wells (MW)**
- Tracing experiment with 5 pesticides (AZS, CTU, FMX, LINU, CPM) during a natural rainfall event
- Exposition of SR inside 8 MW and intercepting trench for one week

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

Upstream MW
Intermediate MWs
Intercepting trench
Injecting trench
Downstream MWs

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

Ratio — Distance to upstream MW

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)

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

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.
[3] X. Peyrard, L. Liger, C. Guillemain, V. Gouy (2015). Environmental Science and Pollution Research (accepted).

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