Echantillonneurs passifs du type POCIS et SBSE pour le suivi des pesticides dans deux bassins versants agricoles

Passive samplers such as POCIS and SBSE for the monitoring of pesticides in two agricultural watersheds

N. Mazzella [1], C. Margoum [2], S. Lissalde [3], B. Delest [1], F. Delmas [1], S. Moreira [1], A. Assoumani [2], L. Liger [2], M. Coquery [2]

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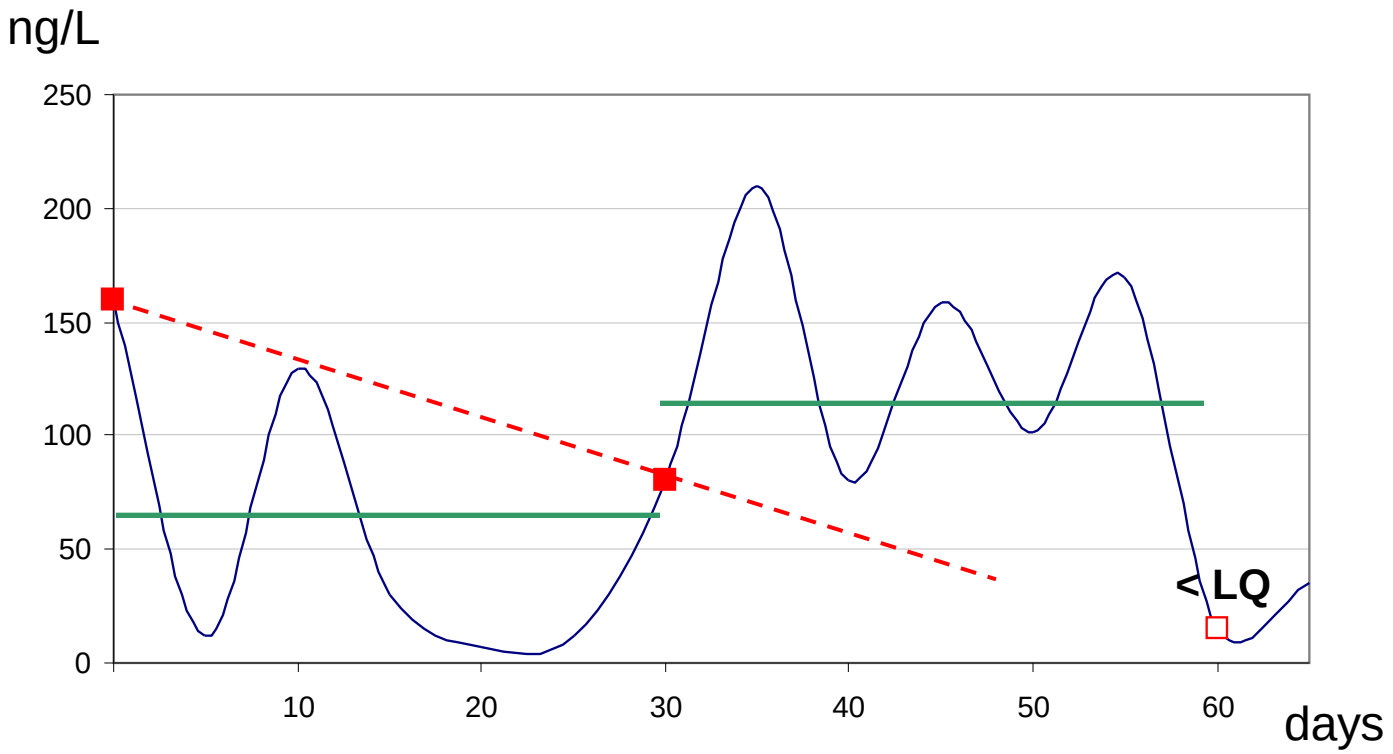
Sampling strategies



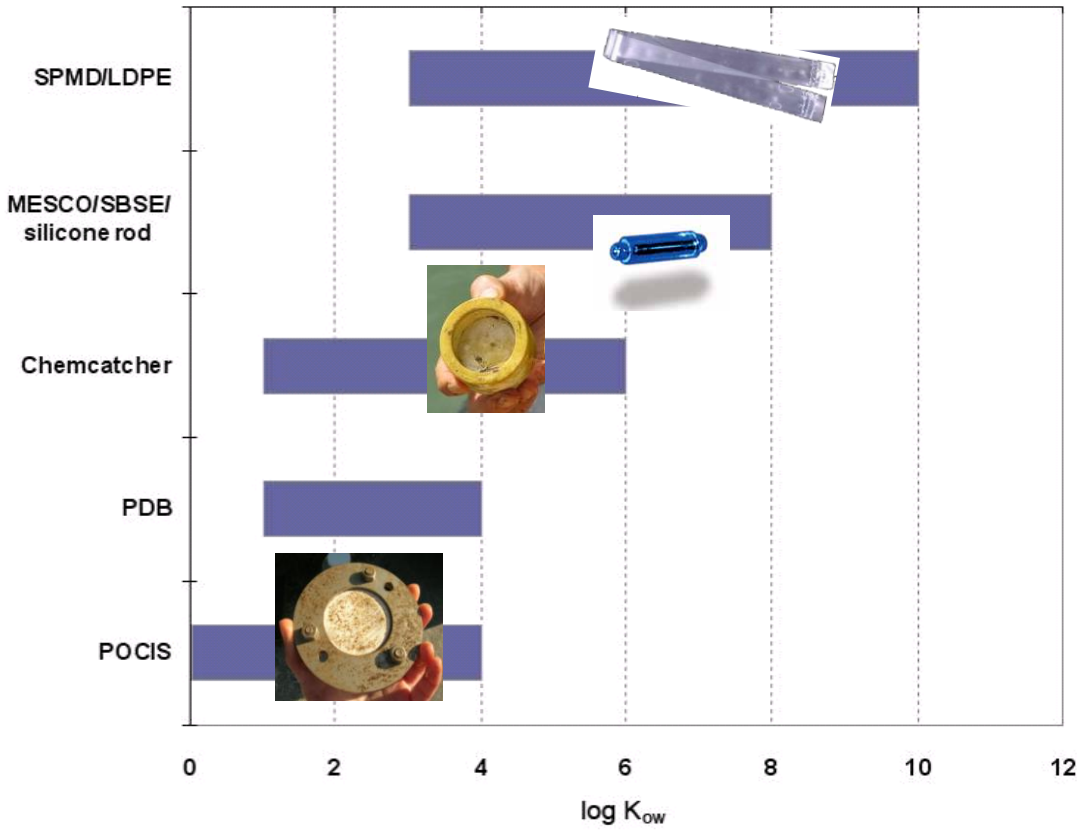
Investigative monitoring:

Trends are poorly described with spot sampling, especially at low frequency

➲ Sampling frequency increase = both analytical time and cost increase!

Mean or time weighted-average concentrations: better characterization of trends and chronic exposures

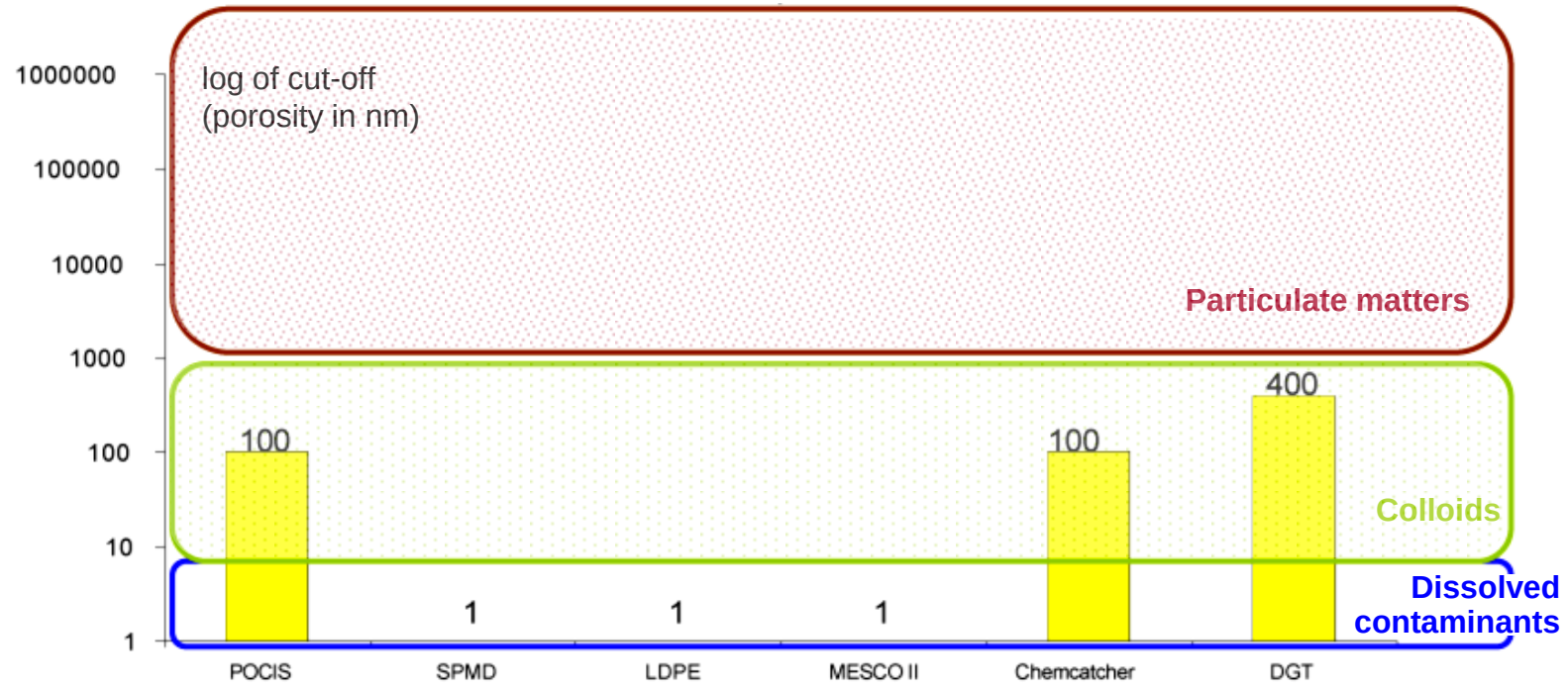
Application domains of passive samplers



herbicides	fongicides	insecticides
+	+	++
Dinitroanilines	Triazoles	Organohosphorous
Diphenylethers		**Organochlorines**
		Pyrethroïds
++	+	+
Triazines	Morpholines	**Carbamates**
Phenylureas	Strobilurins	
Chloroacetanilides	Triazoles (-)	
Amides/Anilides		

- **POCIS and Chemcatchers (polar configuration): log K_{ow}=0-4**
- **Very few calibration data for hydrophobic pesticides: log K_{ow}>4**
- **No tools for highly hydrophilic and ionic pesticides: log K_{ow} <0**

Passive samplers and contaminant partitioning



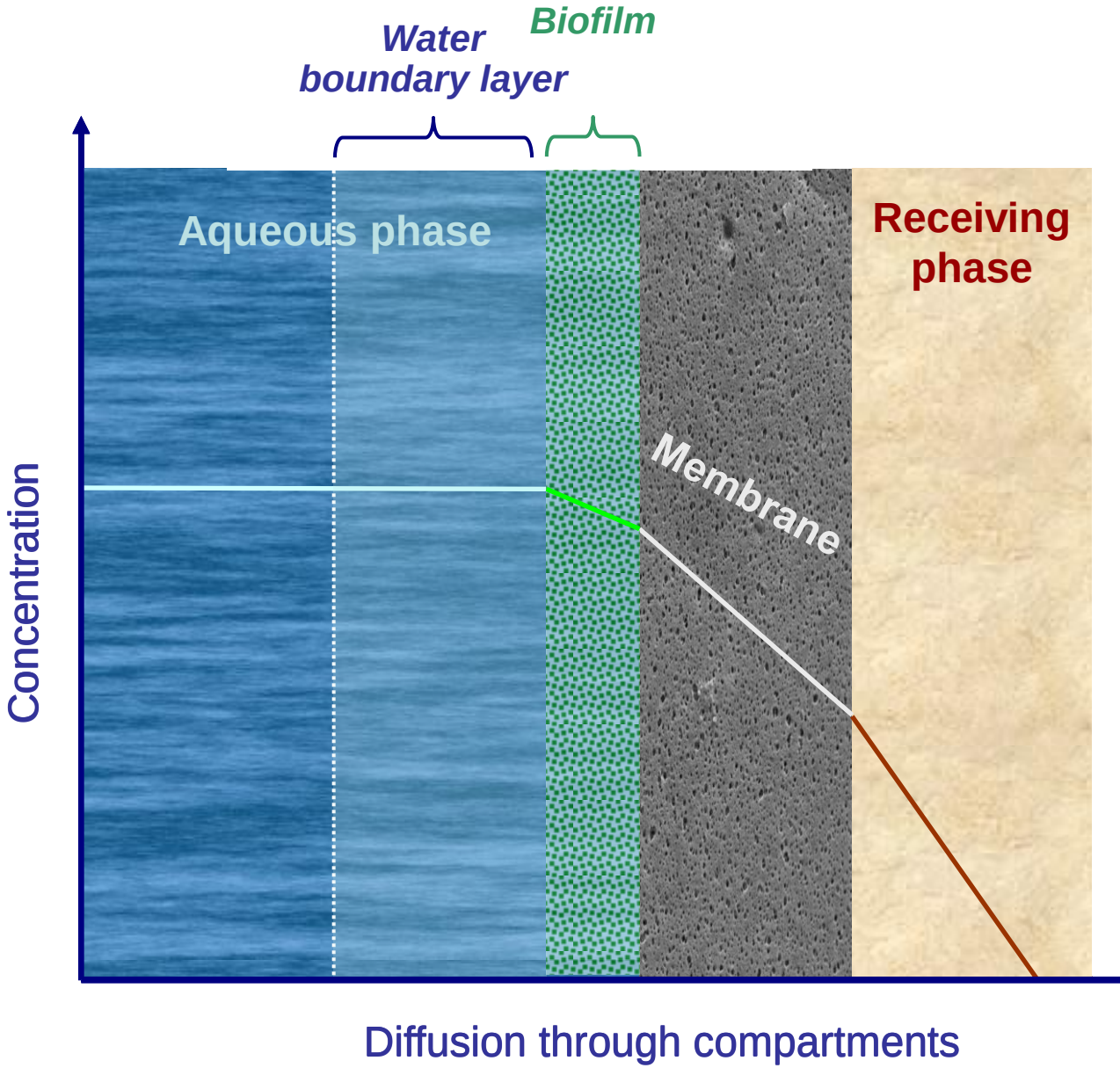
From Vrana et al., 2005 and Allan et al., 2006

➲ **Sampling of dissolved contaminants only…**

But sampling and analysis of total water is compulsory (WFD)

Relationship between isolated fraction and bioavailable contaminants?

Uptake, diffusion and kinetics of chemicals



➲ *Influence of WBL thickness and biofouling of overall kinetics*

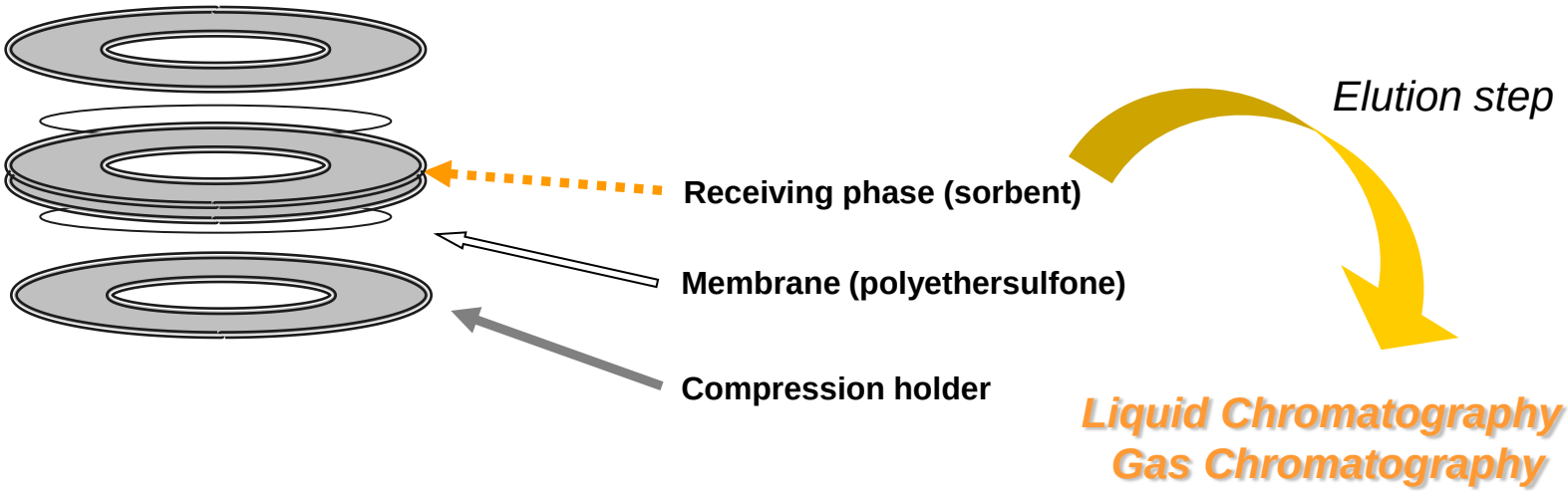
➲ *Use of Performance and Reference Compounds*

Passive sampling of hydrophilic pesticides

- **Polar Organic Chemical Integrative Sampler (POCIS)**

  (Alvarez et al., 2004)

Sampling of polar/moderately polar chemicals (log K_{ow}=0-4)

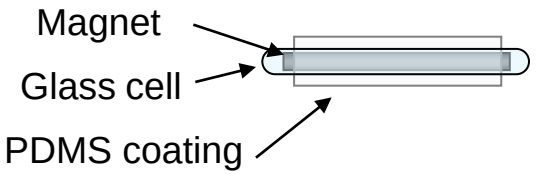


Passive sampling of hydrophobic pesticides

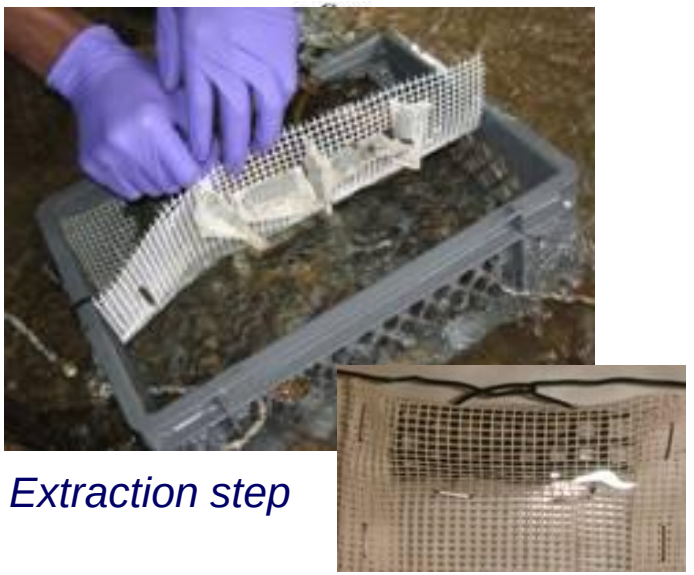
- **Stir Bar Sorptive Extraction (SBSE)**

  (Baltussen et al., 1999)

Sampling of non-polar chemicals (log K_{ow}>4)

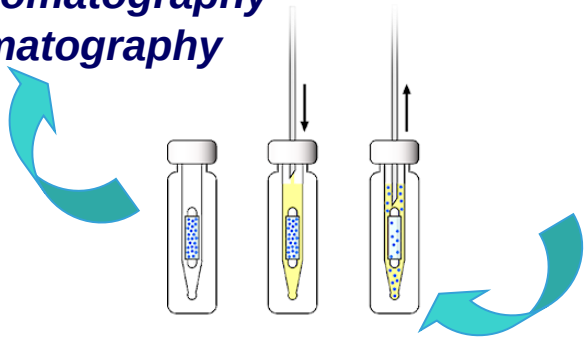


Use as *in situ* passive sampler



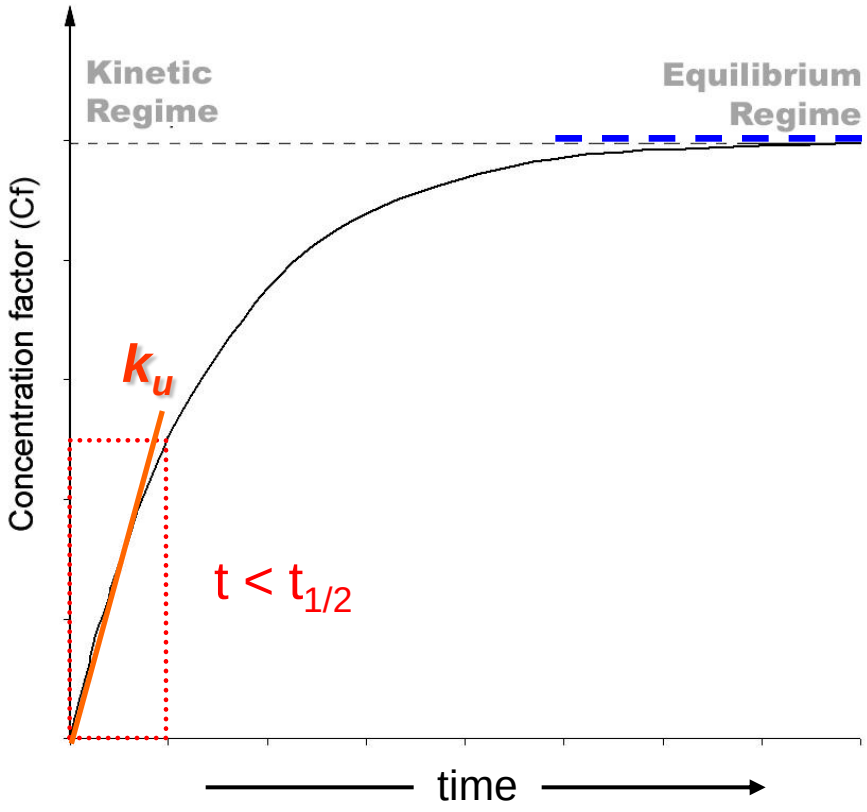
Extraction step

Liquid Chromatography
Gas Chromatography



Liquid Desorption or Thermodesorption

Uptake, diffusion and kinetics of chemicals



From Vrana et al., 2005

Equilibrium regime

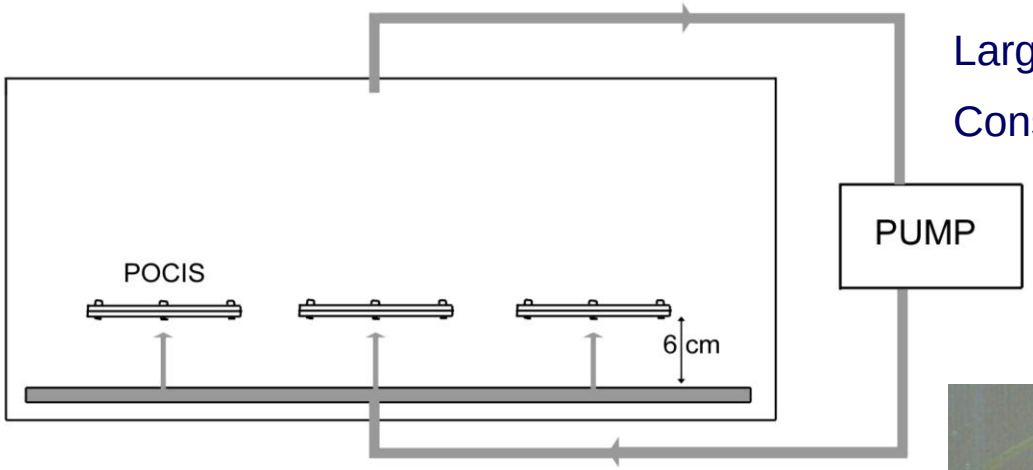
$$C_f = \frac{C_s}{C_{water}} = \frac{k_u}{k_e} = K_{sw}$$

Kinetic regime

$$C_{water}\,(t) = \frac{C_{POCIS}}{k_u \,.\, t}$$

Uptake, diffusion and kinetics of chemicals

- **POCIS calibration**

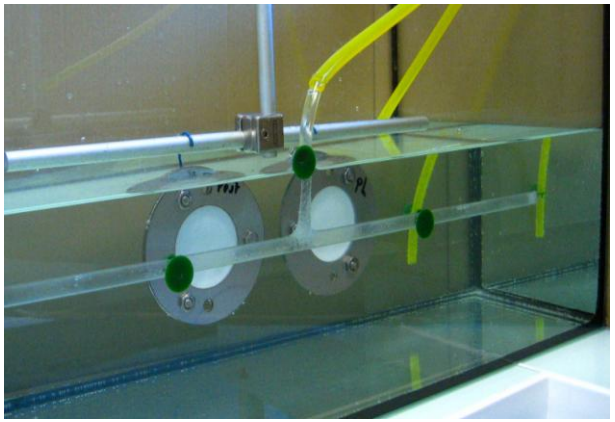


Constant temperature (17±1° C)

Obscurity

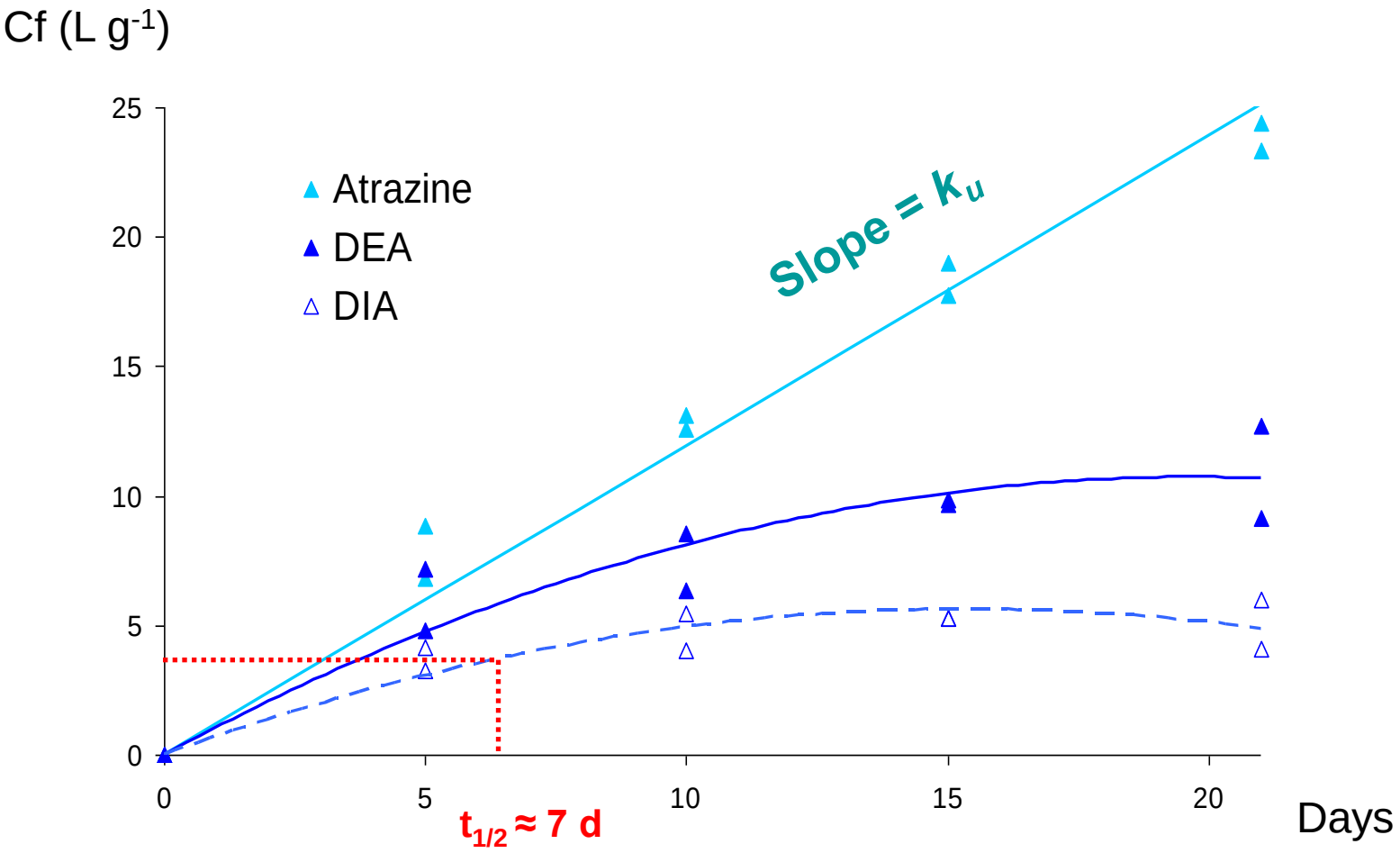
Large volume (80 L)

Constant flow velocity 2-3 cm s^{-1}



Uptake, diffusion and kinetics of chemicals

- **POCIS calibration**



Uptake, diffusion and kinetics of chemicals

- **POCIS calibration**

	$k_{u(cal)}$[a] (L g^{-1} d^{-1})	R_s[b] (mL d^{-1})	RSD (%)[c]	Linearity[d]
Acetochlor	1.206	241	14	0.98
Alachlor	1.026	205	2	0.96
Atrazine	1.138	228	18	0.98
Azoxystrobin	0.894	179	12	0.98
Carbaryl	1.217	243	19	0.97
Carbendazim[e]	N/A	N/A	N/A	N/A
Carbofuran	1.409	282	21	0.99
3-Hydroxycarbofuran	0.985	197	11	0.99
Chlorfenvinphos	1.391	278	11	0.92
Chlortoluron	0.826	165	21	0.99
Chlorpyriphos	0.626	125	6	0.97
DCPMU	0.920	184	17	0.98
DCPU	0.994	199	23	0.99
DEA	0.865	173	11	0.99
DET	1.065	213	20	0.99
DIA	0.882	176	4	0.96
Dimethoate	1.035	207	7	0.99
Dimetomorph	0.850	170	14	0.98
Diuron	0.993	199	19	0.99
Hexazinon	0.796	159	16	0.98
IPPMU	0.931	186	19	0.99
IPPU	0.923	185	15	0.98
Irgarol	1.188	238	15	0.99
Isoproturon	0.837	167	20	0.99
Linuron	1.019	204	18	0.97
Metazachlor	1.026	205	16	0.98
Methomyl	0.434	87	5	0.94
Metolachlor	0.912	182	21	0.98
Metoxuron	0.881	176	17	0.99
Pyrimicarb	0.906	181	18	0.98
Simazine	0.994	199	19	0.99
Terbuthylazine	1.192	238	15	0.98
Thiodicarb	0.840	168	11	0.97

[a] k_u: accumulation kinetic constant.
[b] R_s: sampling rate.
[c] Relative standard deviation of k_u and R_s.
[d] Correlation coefficient (linear regression).
[e] Carbendazime was not quantified with neither POCIS or SPE since the calibration was performed in tap water.

Sampling rates (volume of water extracted per day):

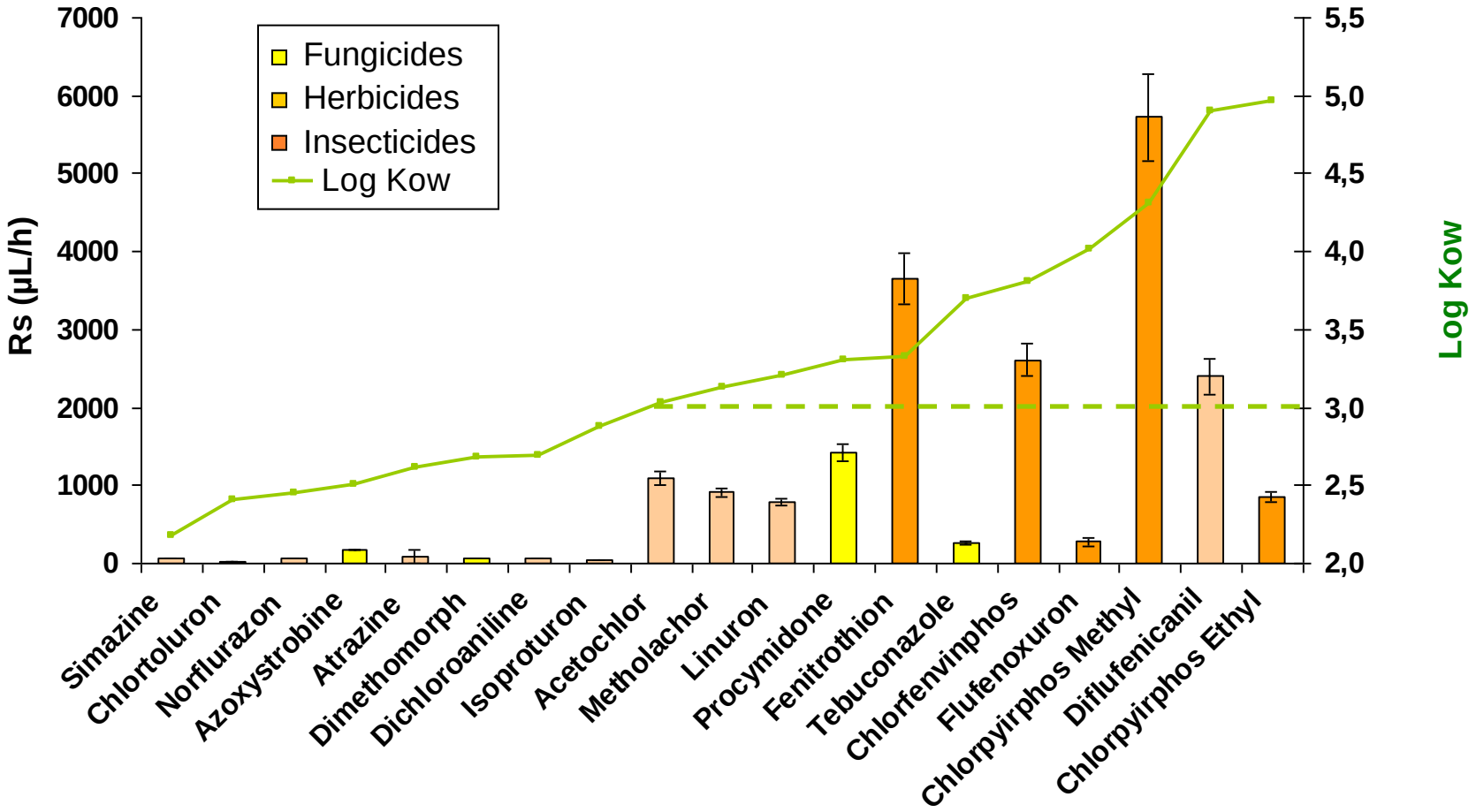
$$R_s = k_u . M_s$$

R_s~150-250 mL j^{-1}

Mazzella et al., 2007
Lissalde et al., 2011

Uptake, diffusion and kinetics of chemicals

- **SBSE calibration**



➲ R_s values ranging from 700 µL/j to 140 mL/j, increasing with hydrophobicity

➲ Linear uptake from 1.5 to 7 days (most hydrophobic pesticides)

Uptake, diffusion and kinetics of chemicals

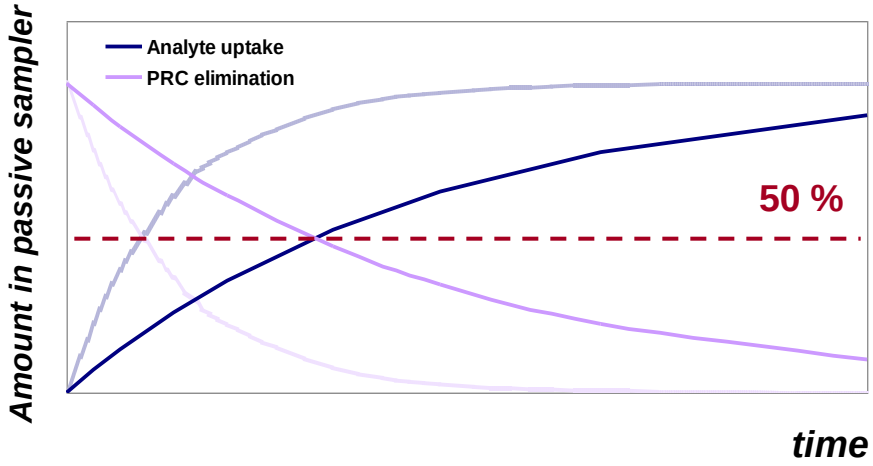
- **Performance and Reference Compound**

Observations:

k_u depends on environmental parameters (flow velocity, temperature, biofouling,…)
Real time-weighted average concentrations are under/overestimated

Suggestions:

Use of PRCs (Huckins et al., 2002)



Field deployment of POCIS

5.5 km² watershed with 4.7 km² for agriculture
Mainly maize and wheat cultures

Field deployment of POCIS

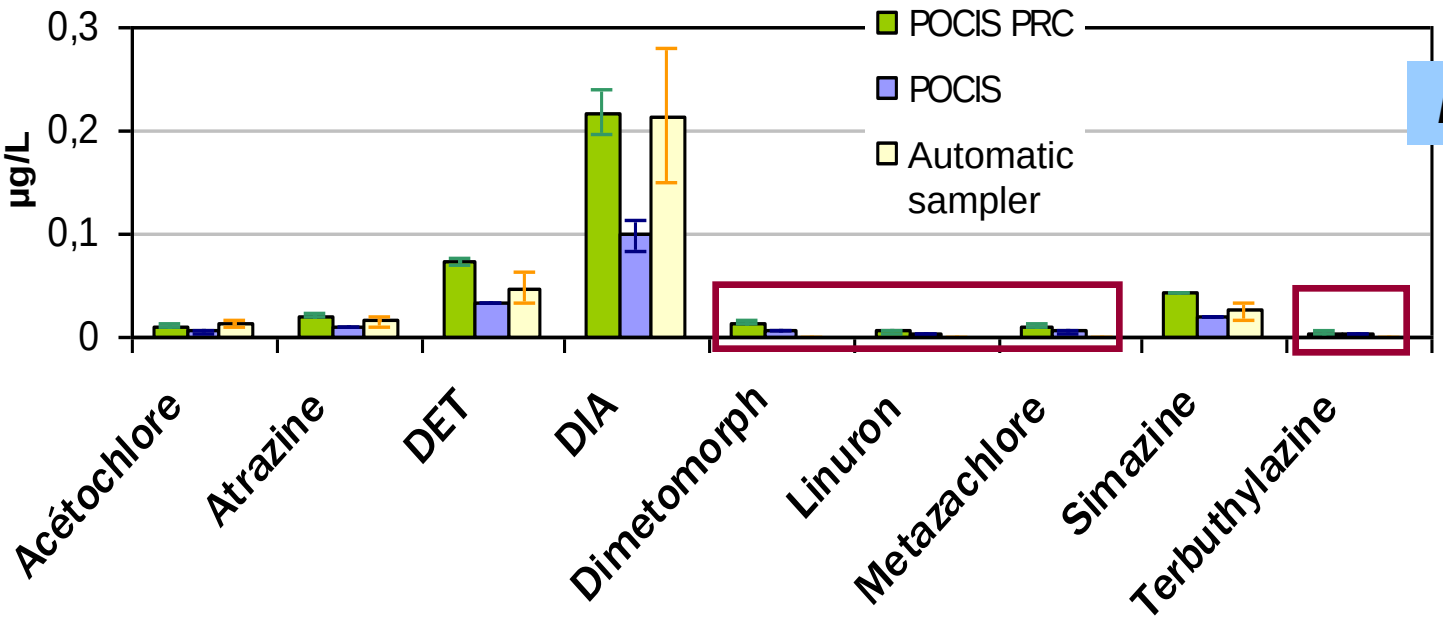
Reference mean concentrations

Automatic sampler

t_0 → 14 days

POCIS TWAC

Field deployment of POCIS



Ruiné - Charente

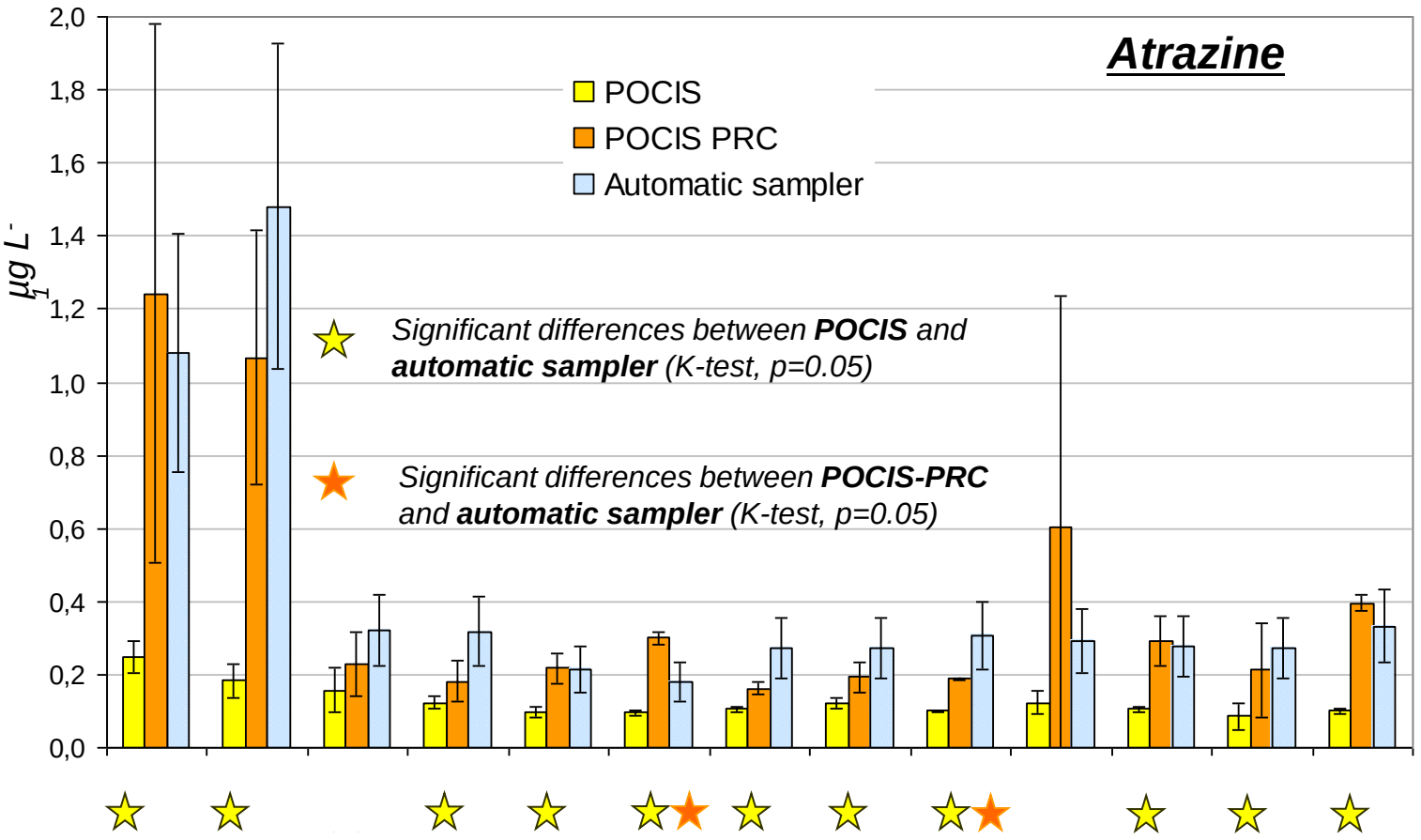
1er - 15 juin 2009

➲ ***Better comparability with PRC correction***

➲ ***Traces of contaminants were not detected in water samples collected with the automatic sampler***

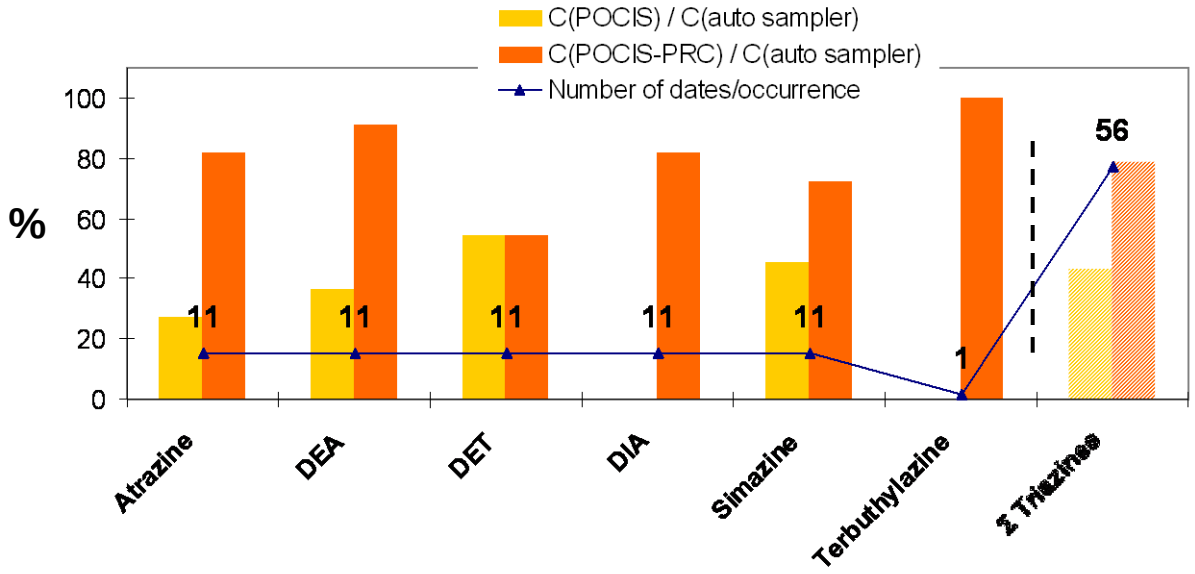
Field deployment of POCIS

- **Comparison for one chemical and several 14-d exposures**



➲ **Higher number of comparable populations with the PRC correction**

Field deployment of POCIS



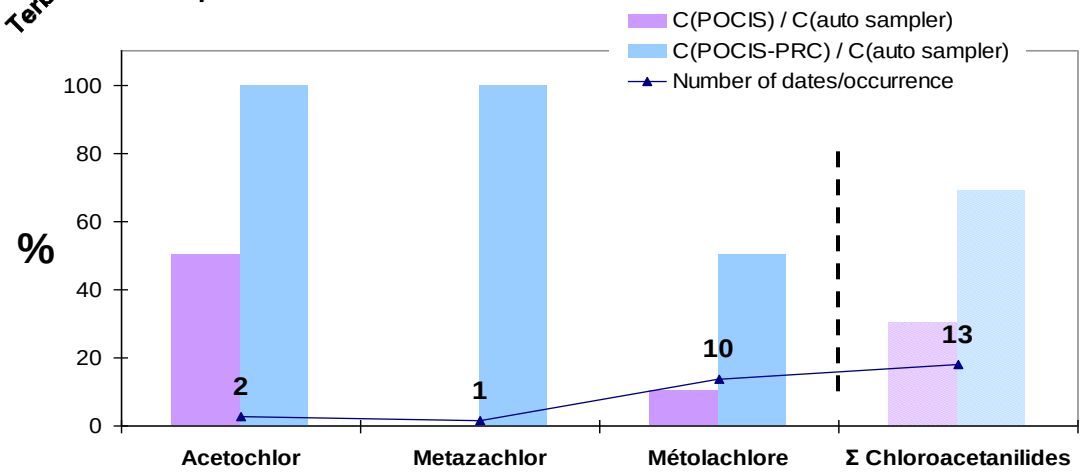
Percents of equivalent populations:

$C_{POCIS} / C_{automatic\ sampler}$

or $C_{POCIS\text{-}PRC} / C_{automatic\ sampler}$

% RSD C_{POCIS}	% RSD $C_{POCIS\text{-}PRC}$
14-18	17-34

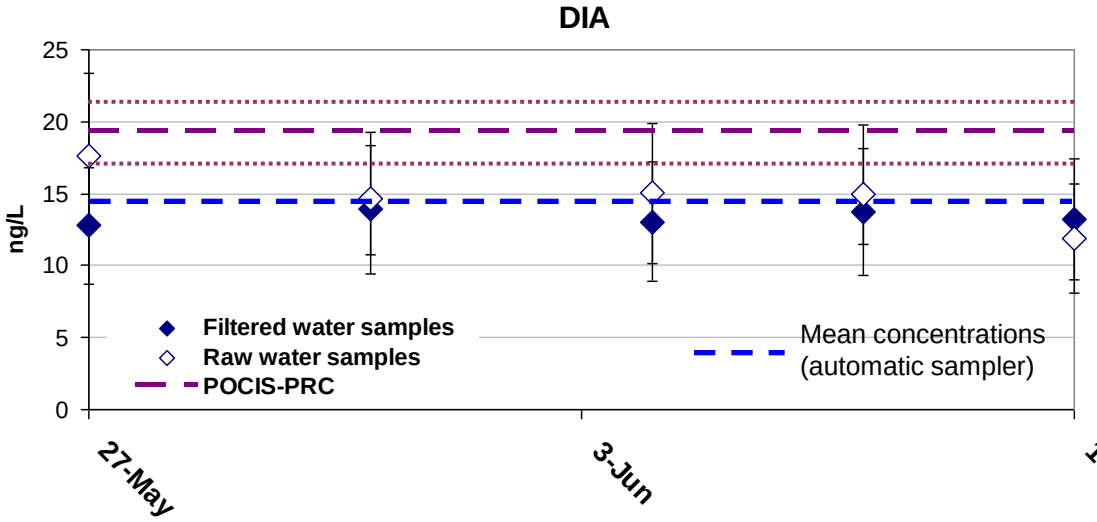
% RSD SPE
15-32



- Significant improvement of quantitative comparison with PRC approach
- Application to other polar pesticides (phenylureas, triazoles, etc.)?
- Comparability with unfiltered water samples?

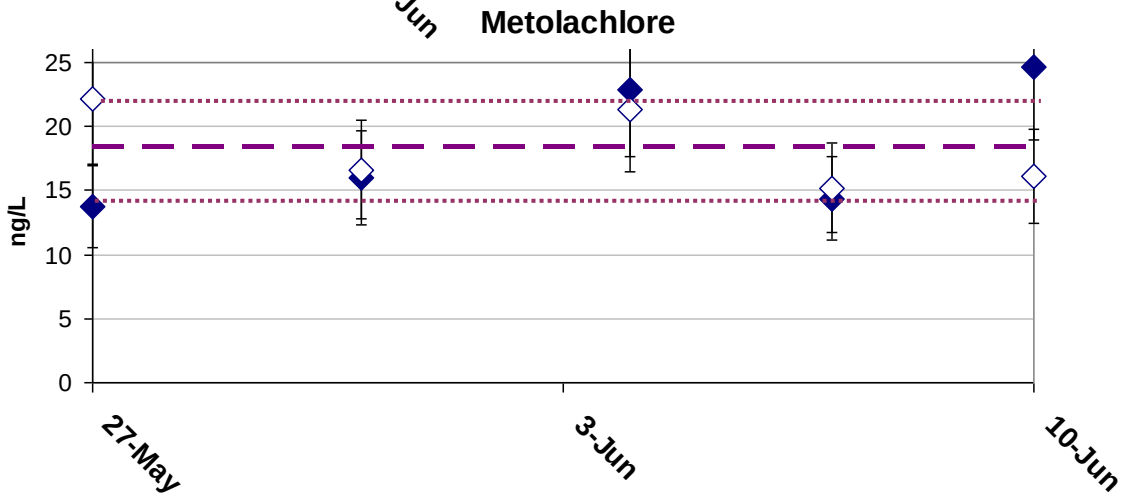
Field deployment of POCIS

- **POCIS vs. filtered and raw waters (spot sampling)**



Charente River water:
- SPM = 6.4-7.6 mg/L
- TOC = 2.9-5.1 mg/L

➲ ***No significant differences between mean concentrations and TWAC derived from POCIS***

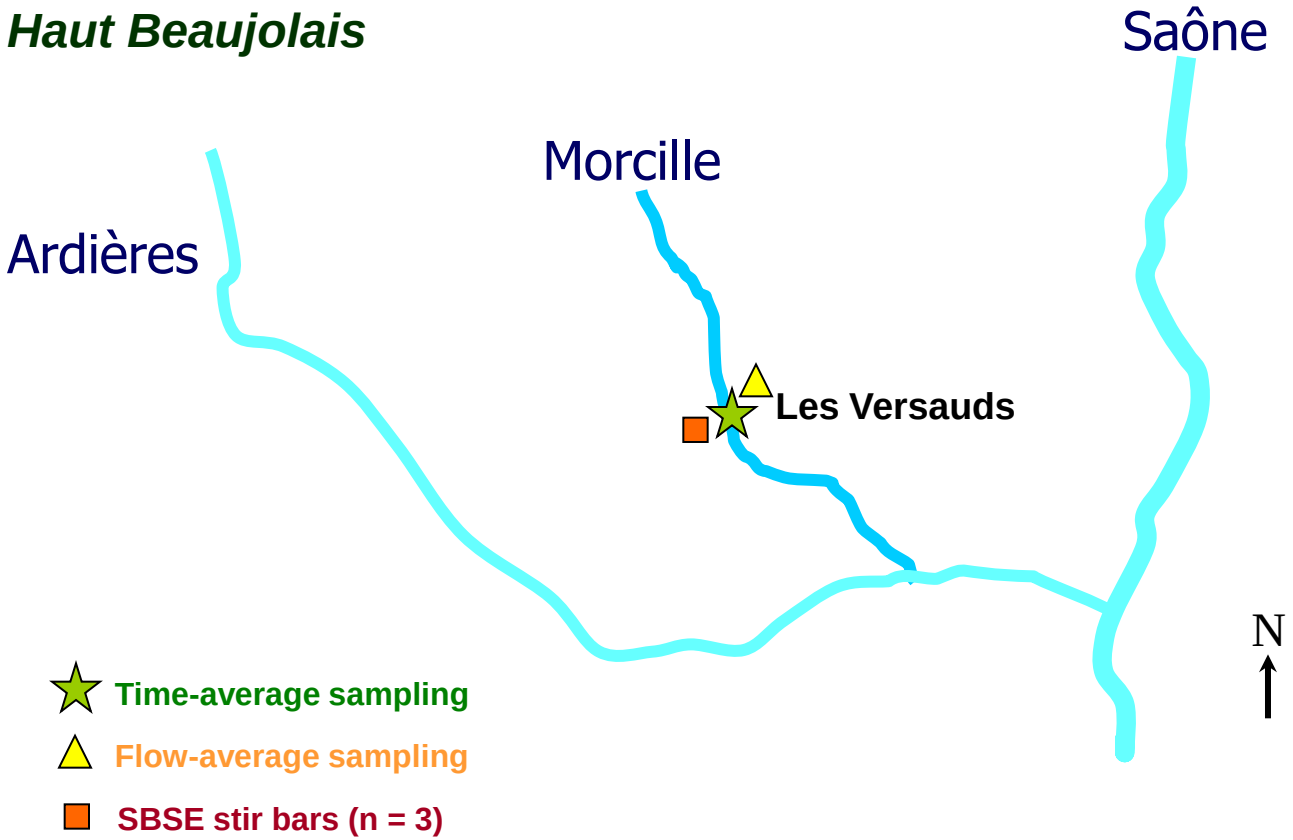


➲ **Good agreement with raw water for some hydrophilic pesticides…**
more hydrophobic compounds (organophosphorous, organochlorines, etc.)?

Field deployment of POCIS and SBSE

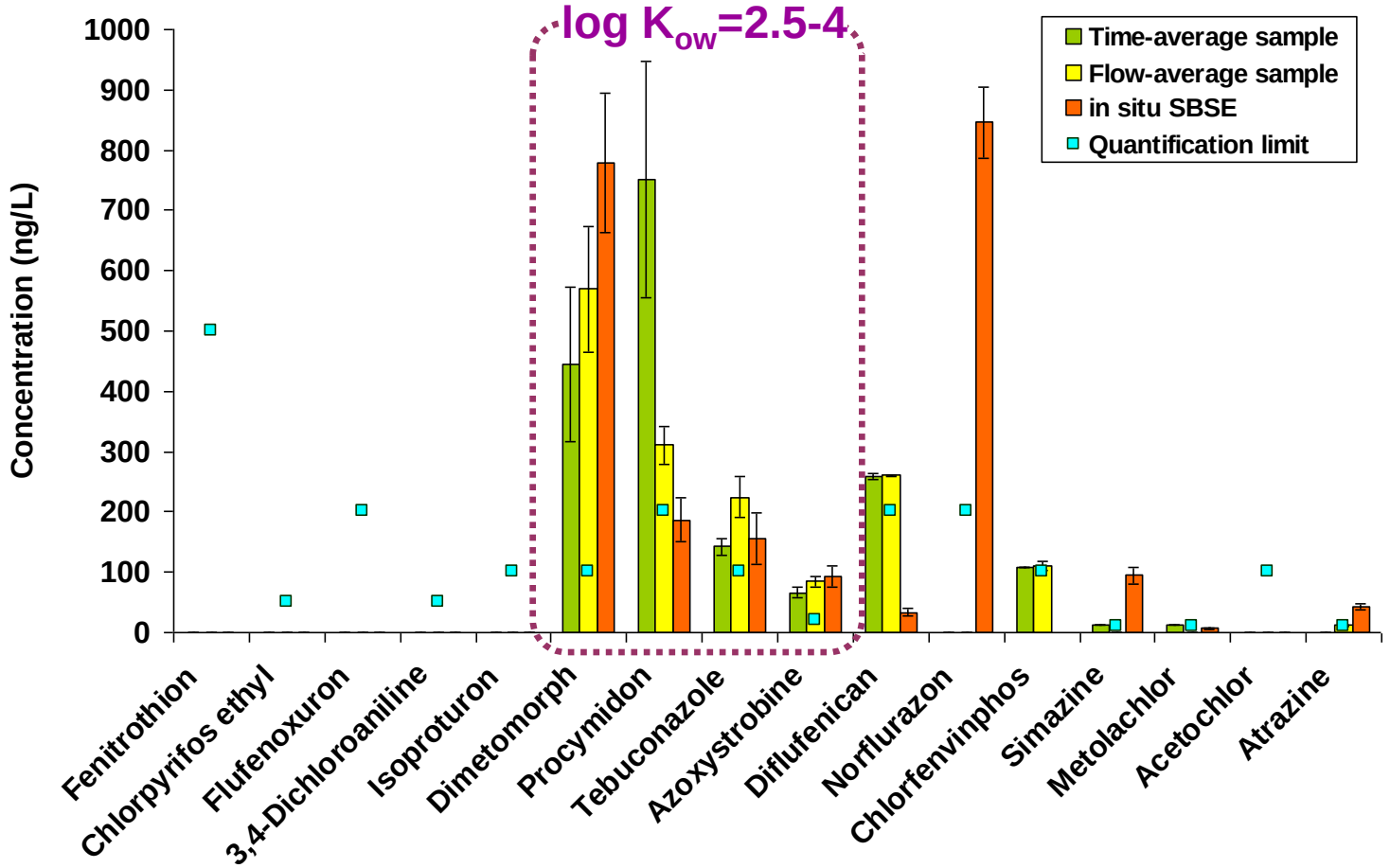
Morcille river: located in a watershed in the Beaujolais region

Watershed of the Morcille river: 8 km², 70 % of the area dedicated to wine-growing



Field deployment of POCIS and SBSE

- One week exposure of SBSE

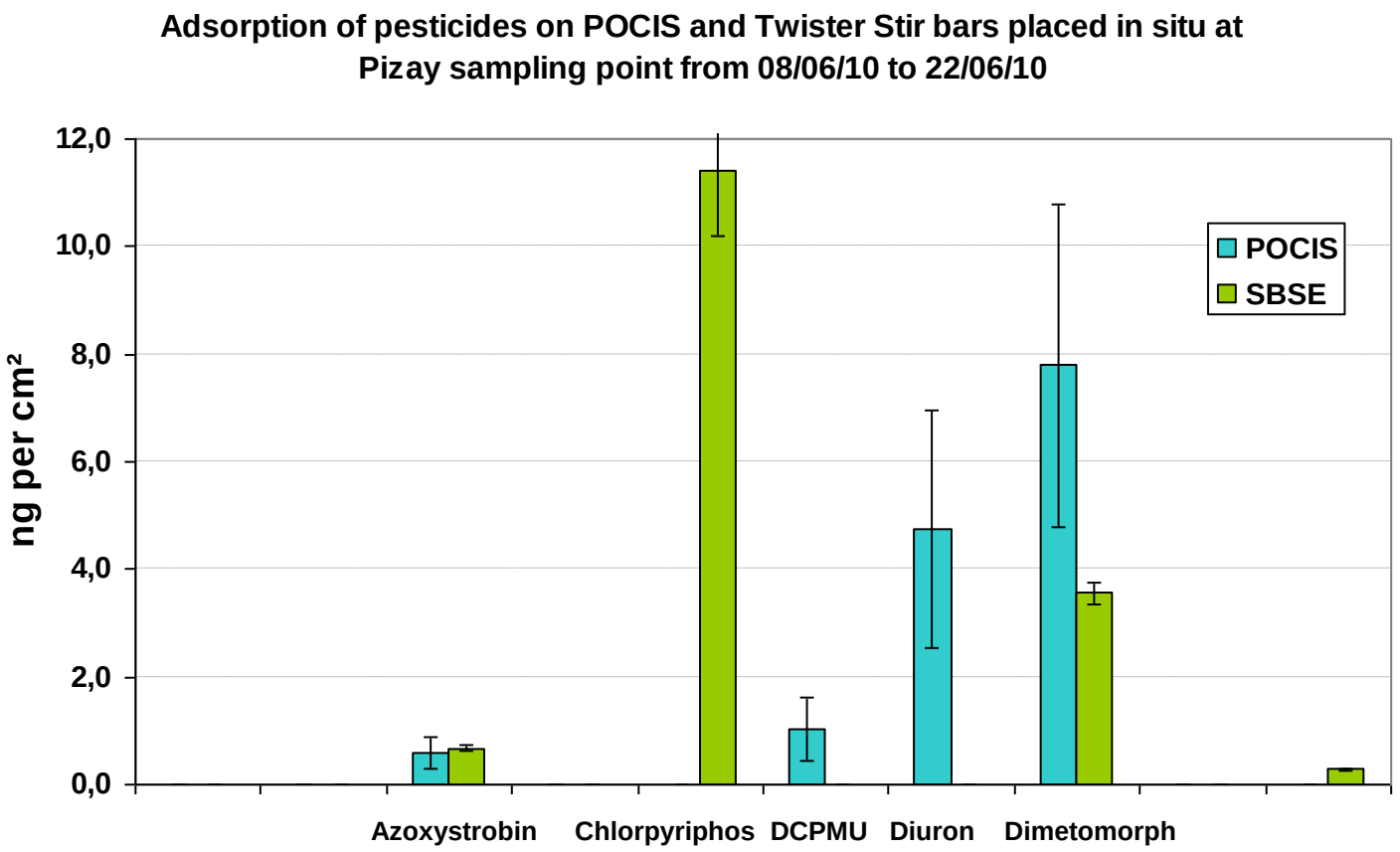


➲ Same information as active sampling techniques (filtered water) for one week

➲ Receiving phase amount should be increased for longer exposure times

Field deployment of POCIS and SBSE

- **Sampling domains of POCIS and SBSE**



➲ **complementary tools regarding to pesticide polarity**

➲ **Application of PRC approach for SBSE (or any PDMS tool)**

Conclusion and further developments

POCIS and hydrophilic pesticides

Application of PRC approach to other polar pesticides, various *in situ* conditions

Study of accumulation/desorption mechanisms, lag times

Calibration or development of a new tool for ionic organic pesticides

SBSE (or PDMS tools) and hydropobic pesticides

Increasing the receiving phase amount for longer exposure periods

Application of PRCs?

More generally

Characterization of the isolated fractions (dissolved contaminants)

Comparability with the filtered/raw water for a wide range of pesticides

Determination of uncertainties (calibration step, field deployment)

Acknowledgements

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AQUAREF

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AGENCE DE L'EAU
ADOUR-GARONNE
ÉTABLISSEMENT PUBLIC DU MINISTÈRE
DE L'ÉCOLOGIE ET DU DÉVELOPPEMENT DURABLE

And you for your attention !