Passive sampling of pharmaceuticals and other polar emerging pollutants

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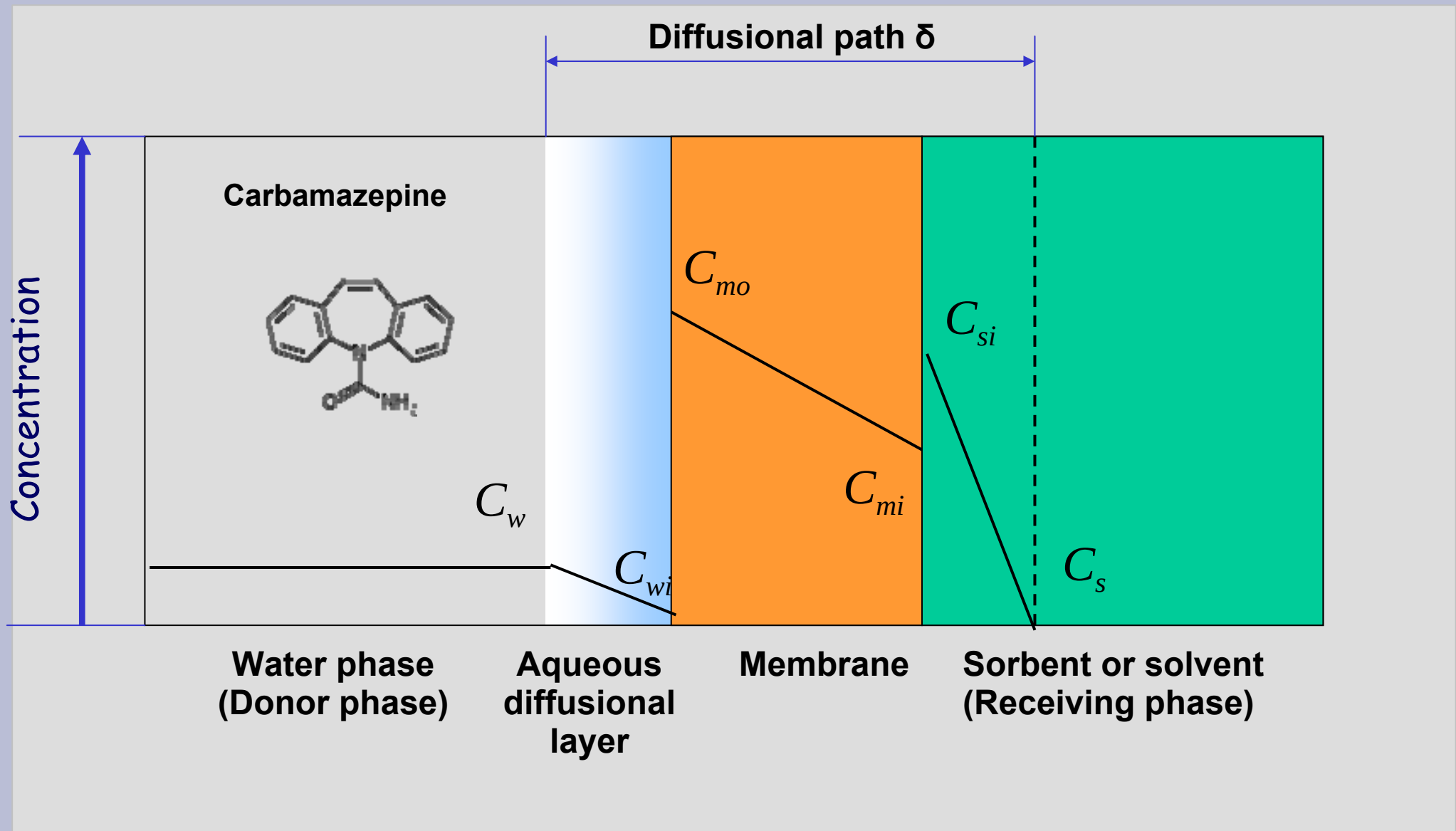
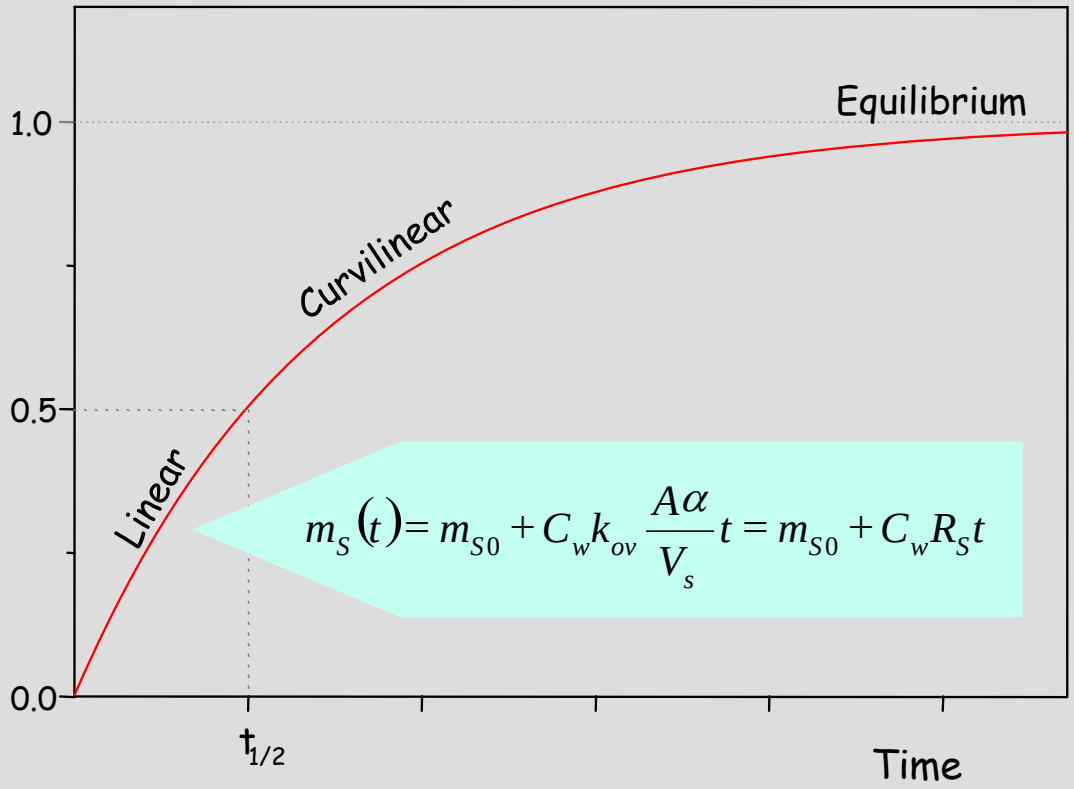
Overview

- Brief description of theory and diffusion models
- Laboratory calibration (pharmaceutical products)
  - Chemcatcher
  - POCIS (Polar Organic Chemicals Integrative Sampler)
- Limits of laboratory calibration and translation to field conditions?
- Field applications
- Perspectives and new developments?

Principle of Passive Sampling



Uptake of a chemical by a passive sampler



R_S = substance specific sampling rate [L d^{-1}]

Estimating TWA concentration

- TWA - time weighted average
- In the initial uptake phase, integrative sampling occurs. The TWA aqueous concentration can be estimated
- The necessary sampling rate can be determined experimentally.

$$R_s = \frac{M_S - M_0}{C_w t} \Rightarrow C_w = \frac{M_S - M_0}{R_S t}$$

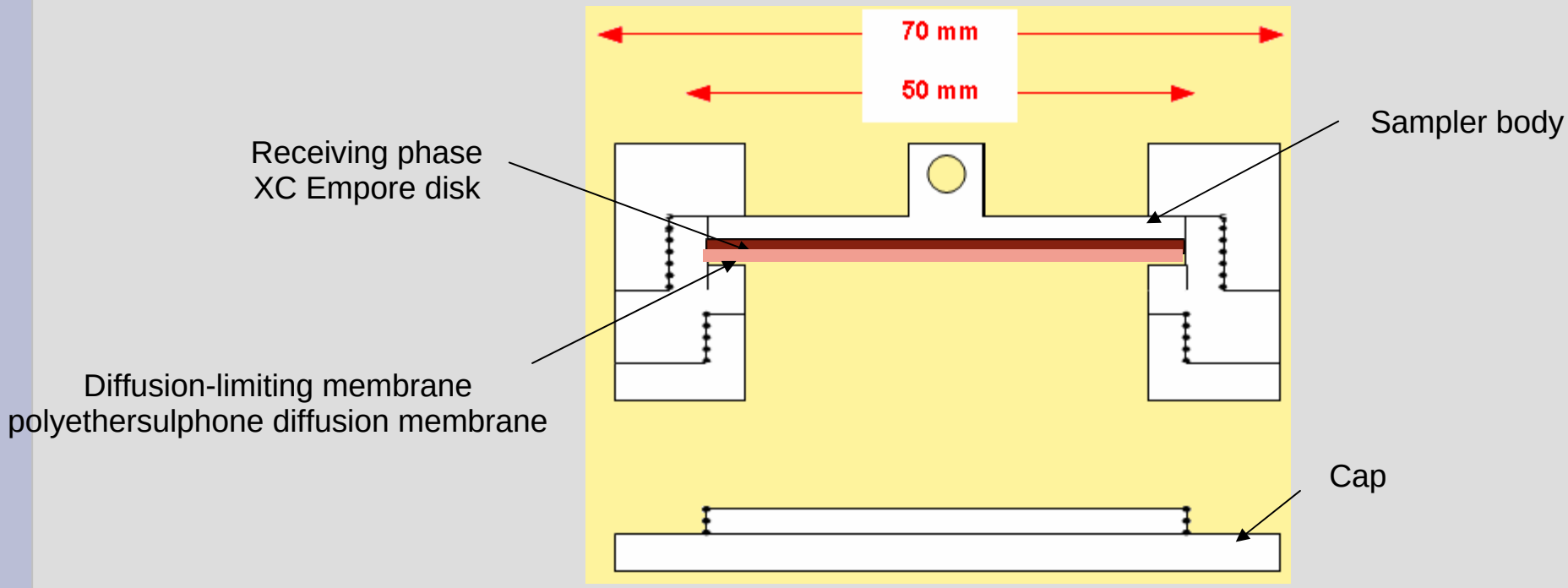
Chemcatcher ® calibration

Pharmaceutical compounds

Catherine Gonzalez (EMA, Fr)

Richard Greenwood (University of Portsmouth, UK)

Chemcatcher ®



Estimating TWA concentration

Selection of Empore disk

Empore disk recoveries

Tank experiments (lab conditions)

Sampling rates calculation

Calibration procedure

- ✓ controlled conditions
  T°, turbulence, pH

R_S ?

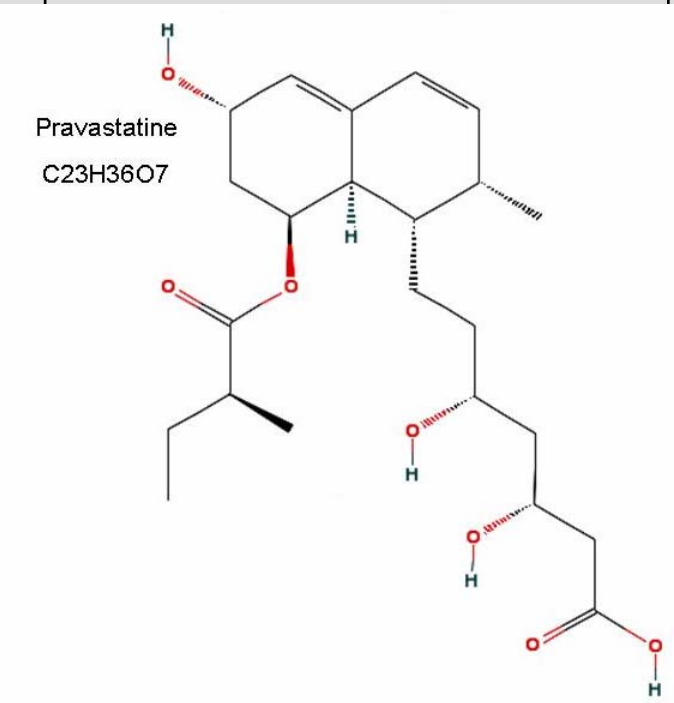
Field deployment of passive samplers

Samplers analysis

Field deployment

- ✓ various conditions
  hydrodynamic regimes
  T°, turbulence, pH

Pharmaceutical compounds

Compounds	pKa	Log Kow
	9,2	*1,7*
	7; 13,9	*2,5*
	6,1 ; 8,6	*2,3*
	4,2	*3,9*
	-	*5,3*
	5,2	*3,5*
	-	*0,9*
	13	*2,4*
	6,2 ; 8,4	*2,1*
Pravastatin	4,7	*2,2*
Propranolol	9,4	*3,5*
Tamoxifen	9,2	*6*

- Polar, hydrophilic compounds
- Dissociable compounds
- Multiple pKa value

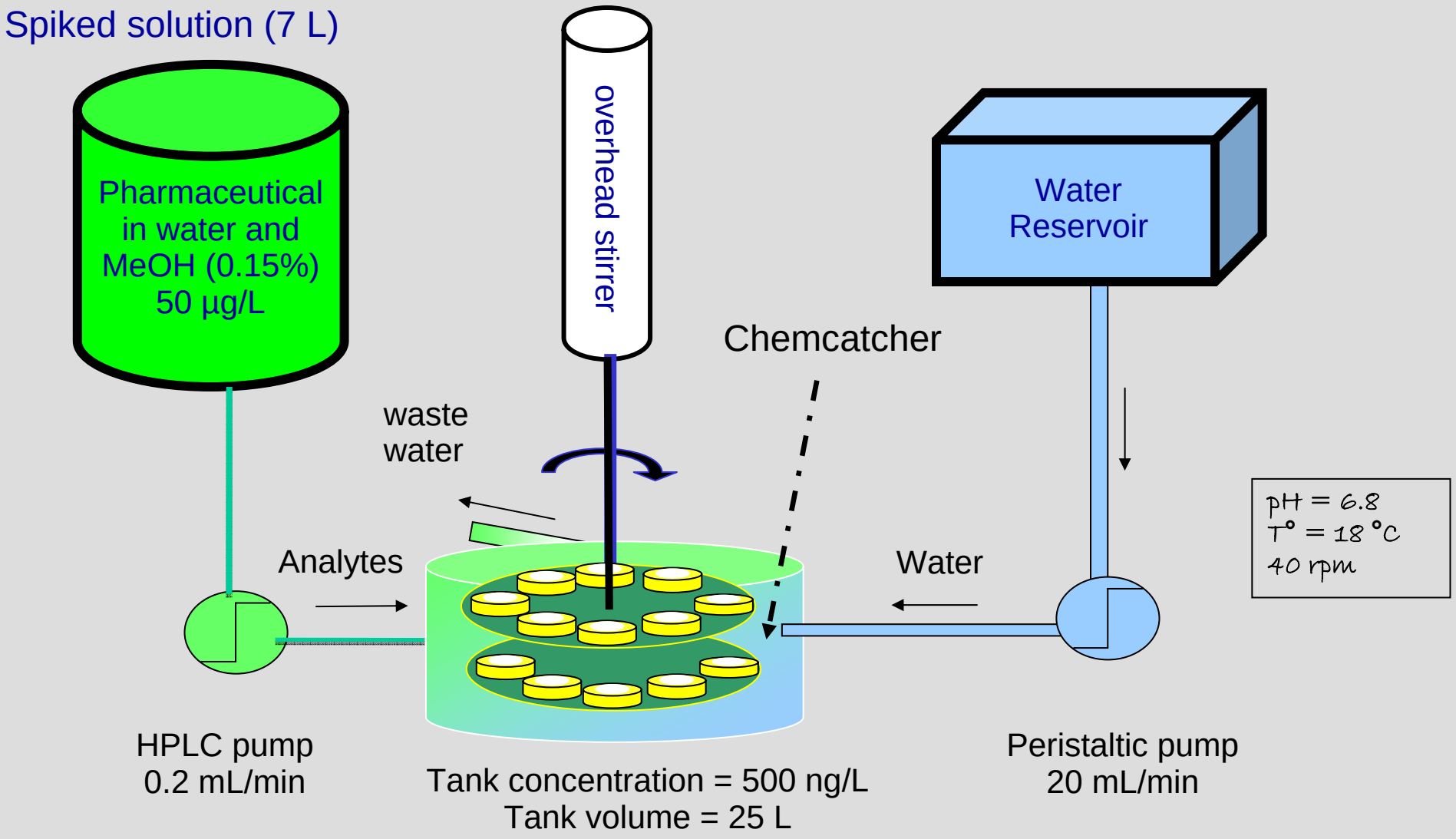
→ Selection of receiving phase?

SDB-XC Empore disk

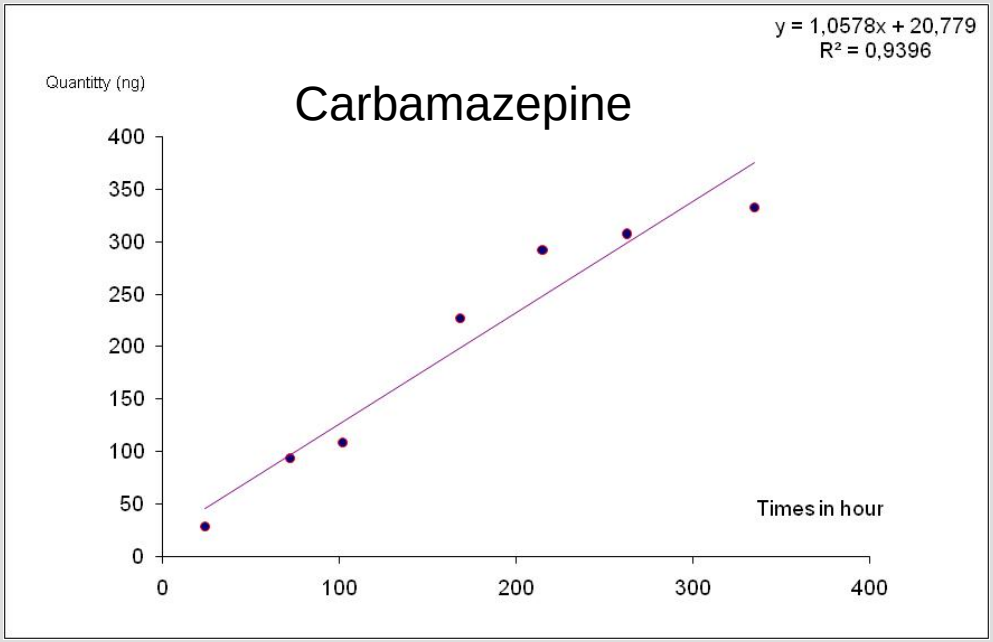
- Spiked solution : 250 mL, 500ng/L
- Elution with 20 ml of MeOH
- Analysis by LC/MS/MS
- Internal standard calibraition (Carbamazepine D10)

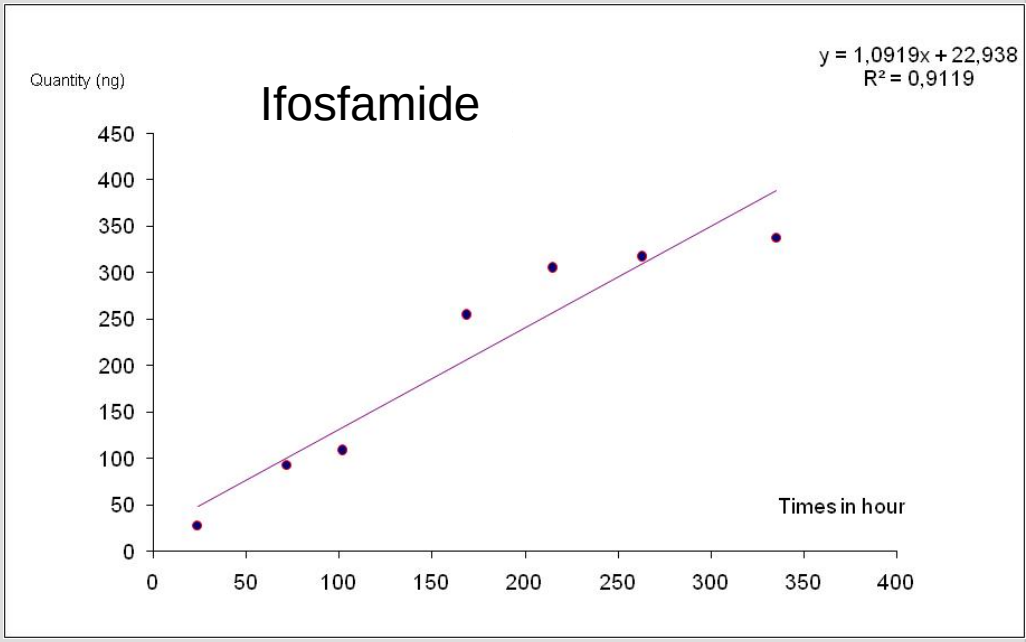
Compounds	Spiked solution (ng/l)	Recovery % Deionized water	Recovery % Tap water	Recovery % Natural water
Acebutolol	883	**76**	**61**	67
Carbamazepine	561	**83**	**83**	78
Ciprofloxacine	555	**5**	**32**	15
Diclofenac	554	**100**	**92**	100
Fenofibrate	542	**28**	**22**	37
Ibuprofene	565	**100**	**100**	100
Ifosfamide	525	**100**	**100**	86
Lorazepam	546	**82**	**78**	66
Norfloxacine	611	**1**	**20**	9
Omeprazole	604	**26**	**25**	9
Pravastatine	549	**45**	**90**	37
Propranolol	580	**83**	**51**	54
Tamoxifen	595	**17**	**15**	60

Calibration of a passive sampler in a flow-through system



Sampling rate estimation
R_S = [mL/day]





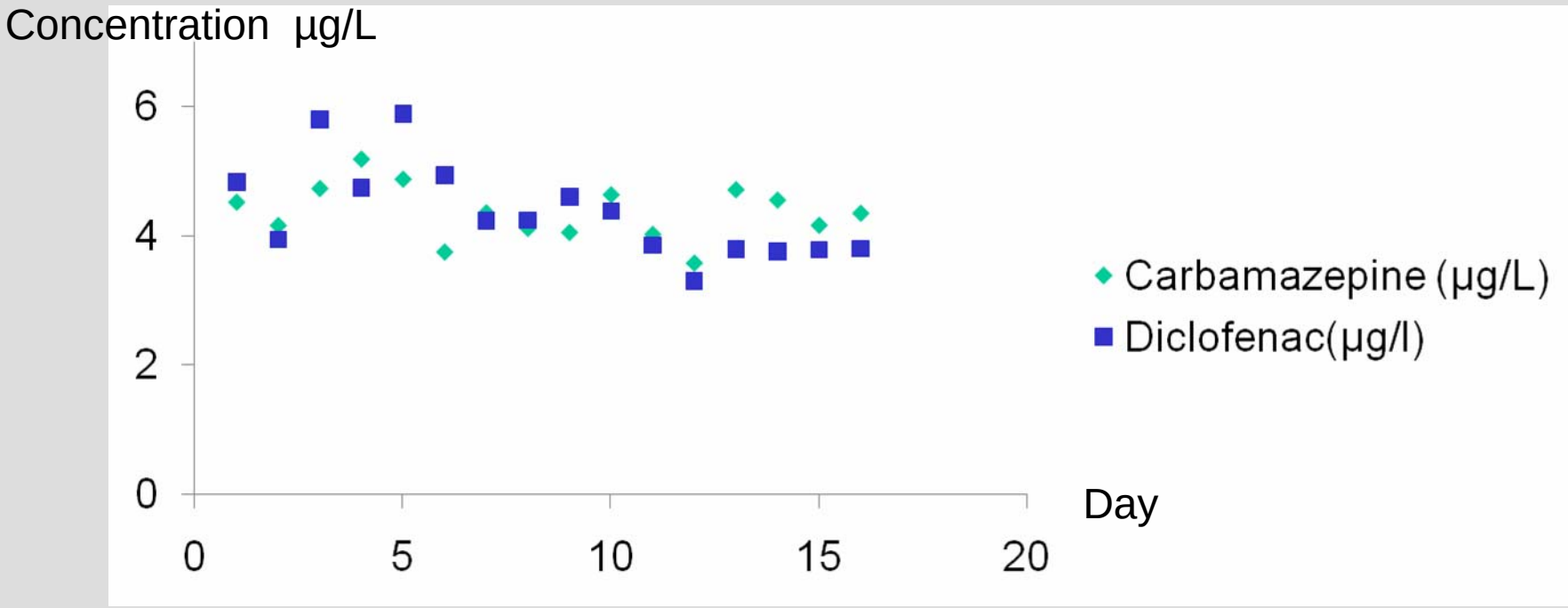
$$M_S(t) = M_0 + C_w R_S t$$

Slope = $R_S * C_W$

Cw = constant

Rs

Concentration in the tank (2 weeks)



Concentration monitored by HPLC/DAD

Sampling rates
RS = [mL/day]

Compounds	Tap water (pH = 8.2)	Deionized water (6.8)
	4	50
	49	51
Ciprofloxacine		low correlation
Diclofenac		126
Fenofibrate	2	14
Ibuprofen	63	84
Ifosfamide	53	51
Lorazepam		50
	0.1	23
		50
Pravastatin		low correlation
Propranolol		67
Tamoxifen		low correlation

Dissociable compound

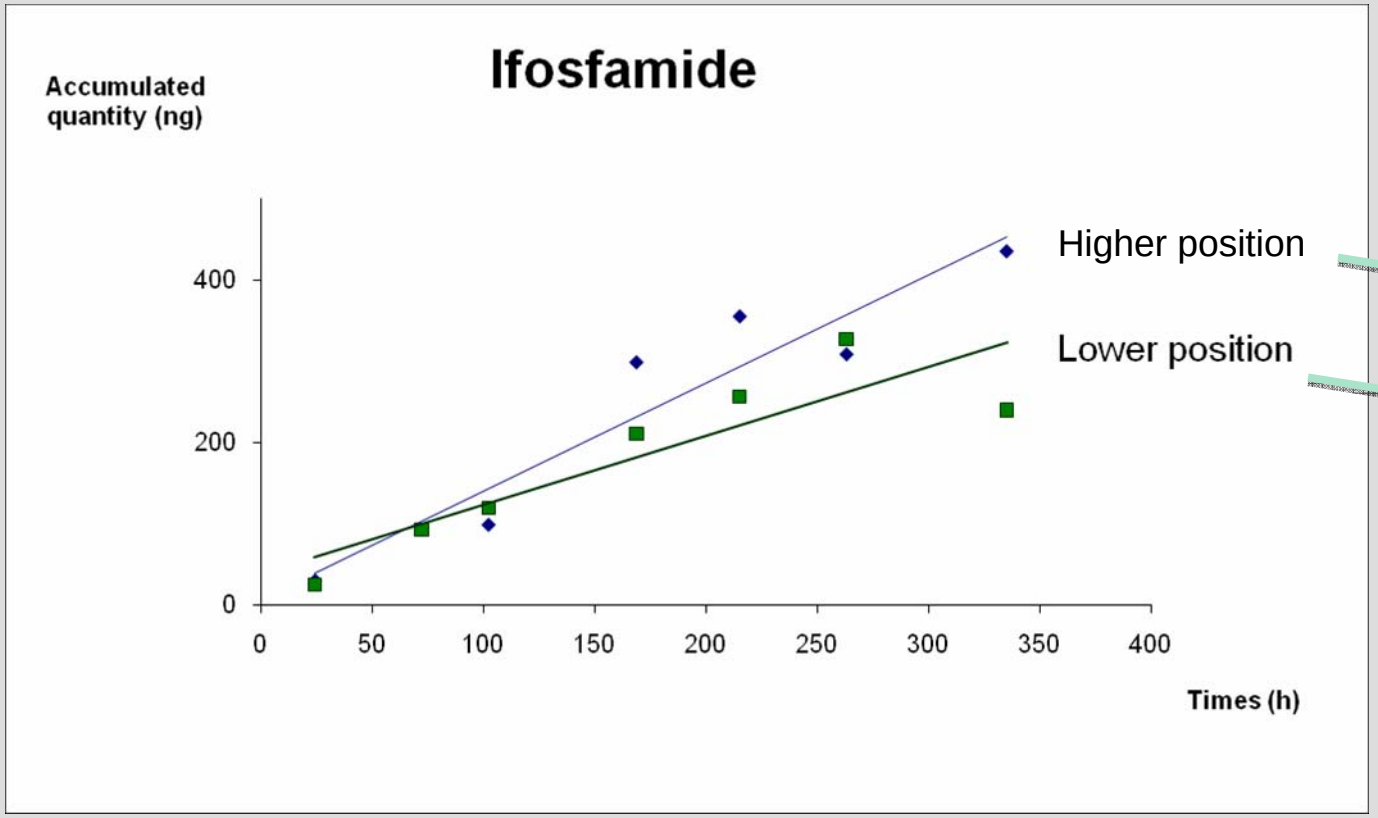
Dissociable compound

Concentration not constant

Rs: same order as polar compounds

- pesticides
- estrone

Effect of Chemcatcher® position in the tank



Higher position	Lower position
r^2 = 0,909	r^2 = 0,784
60 mL/day	50 mL/day

Diffusion of stock solution?
Position of the tube?
Solubility of compounds?
Homogeneized solution?

Difficulties in applying R_s to natural samples

Comparison of spot sampling and Cw calculated from POCIS exposure

	On lab Rs	EXP on Meuse river			EXP on Tank		
	Rs(L/day/g)	Cw from POCIS (ng/L)	Cw measured by spot sampling (ng/L)	Ratio	Ratio	Cw from POCIS (ng/L)	Cw measured by spot sampling (ng/L)
Cafeine	0,39	5145	109	4720%	452%	2863	633
Carbamazepine	1,99	107	118	91%	43%	318	736
Diazepam	1,40	72	8	903%	39%	325	828
Aspirin	0,04	1546	20,5	7539%	1368%	1775	130
Ibuprofen	0,48	388	25	1553%	49%	526	1063
Naproxen	0,72	108	16,5	652%	45%	332	738
Diclofenac	0,83	223	21,5	1038%	25%	242	987
Clenbuterol	0,40	87	3,5	2499%	191%	463	242
Ketoprofen	1,43	83	7	1182%	31%	180	578

Rs obained from lab experiment are very low in comparison with environmental conditions

Effects of water flow?

Geoscience for a sustainable Earth

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Applications of passive samplers to water monitoring: case studies

A. Togola, BRGM

BRGM: Metrology, Monitoring and Analysis Division

Context of the study

The ultimate goal of this work is to enable state environmental agencies to alter their policies and to make it easier for managers and end users to choose passive samplers for monitoring surface water or groundwater.

Many policies are biased towards using classical spot sampling, and it may be necessary to undertake comparative studies of passive sampling devices and spot sampling techniques, or to compare passive sampling results with historical results from classical techniques.

General approaches

Masses accumulated by passive samplers
- No water concentration calculations
- No specific in lab Rs calibration

↳ Determination of key pollutants
↳ Relative comparisons of sampling stations

TARGETED COMPOUNDS:
Pesticides and their main metabolites (60 substances)
Pharmaceutical substances and metabolites (27 compounds)

PESTICIDES				PHARMACEUTICALS	
Aldicarb	Atrazine	Dimethenamide	Hexazinon	Trimethoprim	Naproxen
Imazalil	*DIA*	Carbofuran	Bromacil	Furosemide	*o desmethylnaproxen*
Tetraconazole	*DEA*	*Carbofuran 3 OH*	Chlortoluron	Diclofenac	bezafibrate
Carbendazime	Simazine	Cyanazine	Propazine	Atenolol	Carbamazepine
Metobromuron	Metoxuron	Sebuthylazine	Monuron	Metoprolol	Alprazolam
Acetochlore	Metribuzine	Terbuthylazine	Tebutam	Propanolol	Oxazepam
Chloroxuron	Monolinuron	Fluazifop p buthyl	Diuron	Diazepam	Fenofibrate
Metamitron	Napropramide	*DesethylTerbuthylazine*	Linuron	Zolpidem	Fenofibric acid
Prochloraz	Propyzamide	*Hydroxyterbuthylazine*	Oxamyl	Fluoxetine	Ibuprofen
Terbutryne	Penconazole	Fenpropimorphe	Propanil	Clotrimazole	*1-hydroxy ibuprofen*
Flufenoxuron	Propiconazole	Imazamethabenz	Alachlore	Gemfibrozil	*2-hydroxy ibuprofen*
Fluzilazole	Tebuconazole	Isoproturon	Neburon	Lorazepam	Sulfamethoxazole
Fosthiazate	Metolachlor	Isoproturon -CH3	Methomyl	Ketoprofen	Paracetamol
Hexaconazole	Desmetryne	*Isoproturon -2CH3*	Asulam		Bromazepam
Metazachlore	Prometryne	Methabenzthiazuron	Bitertanol		
		Difenoconazole	Ametryne		

General approaches

Passive samplers used:

POCIS with pharmaceutical configuration (HLB sorbent)
Comparison of regular size (disk) and groundwater format
(4 x 30 cm long, 200mg of sorbent) adapted to introduction in piezometer from 6 to 10 cm , ID)

Exposure time:

Depends on sampling sites (15 / 30 days)
Spot sampling at the beginning and at the end of passive sampler exposure

PS extraction:

PS are cleaned on site and extracted with 10 mL of methanol
Extracts are analyzed using UPLC/MS/MS and GC/MS/MS systems depending on compounds;

CASE STUDY:
Val de Loire hydrological system

Géosciences pour une Terre durable
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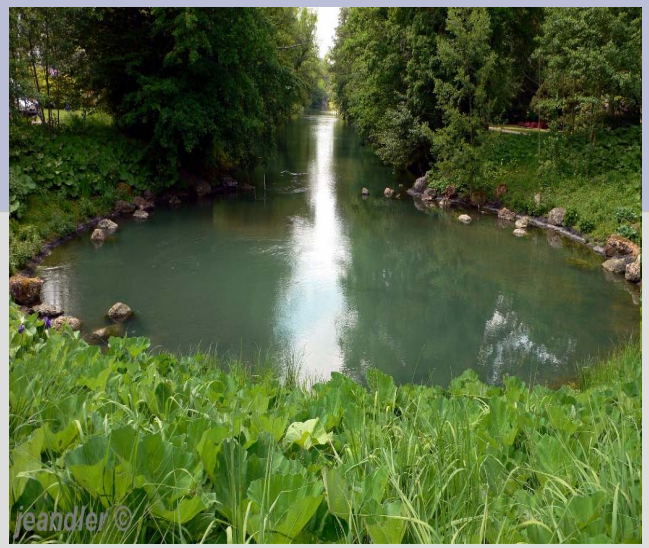
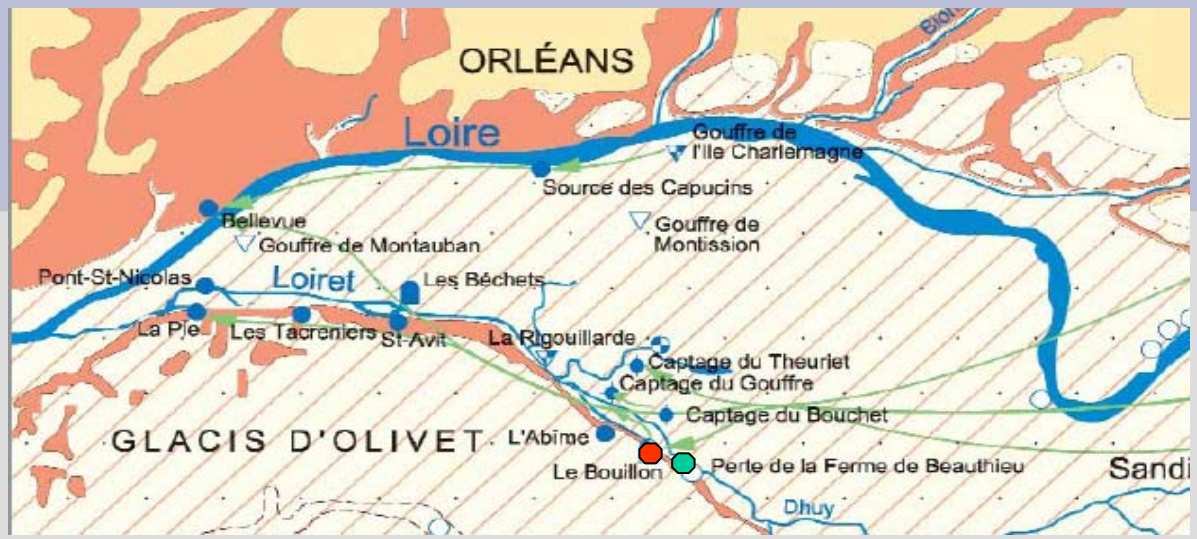
Context of the study



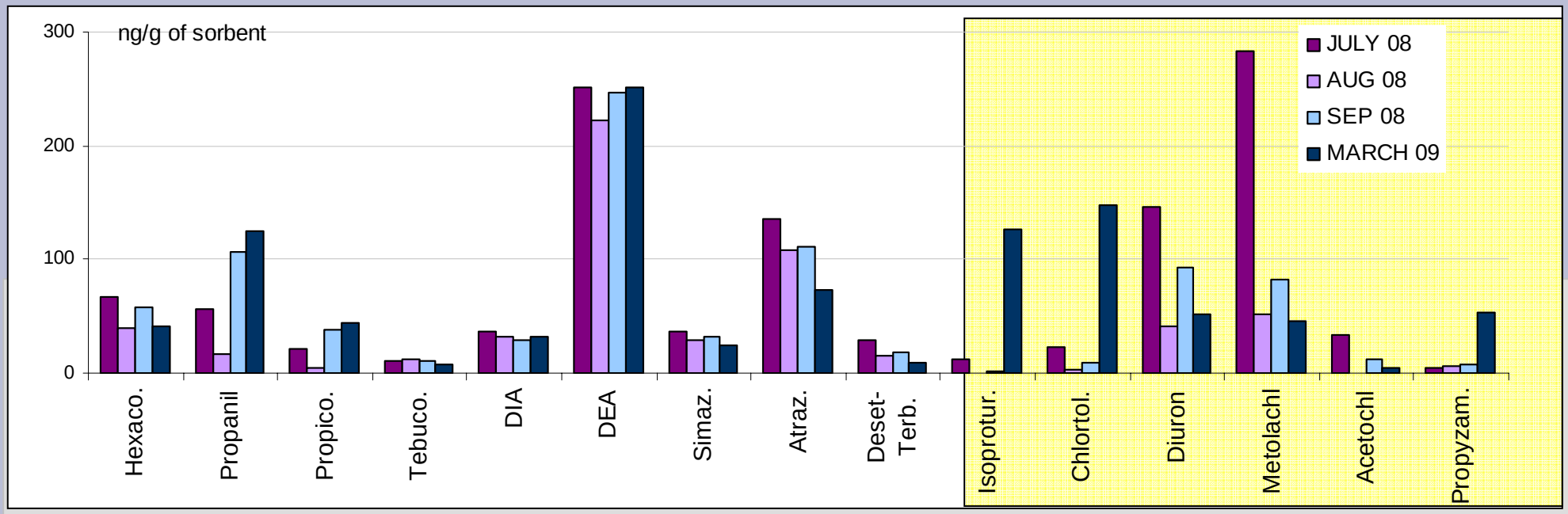


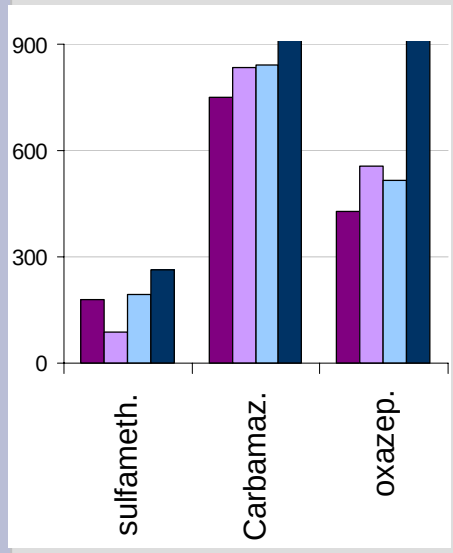
Bouillon station Dhuy station Pumping station

First case study (still under investigation) involves monthly measurements at the Bouillon station, located in the Loire river basin.

This station is located between the Loire river and several pumping stations for fresh water supply in the Dhuy river. Dhuy is an affluent of the Loire river and Bouillon is a resurgence of the Loire river, and is not connected to the Dhuy under normal circumstances.

But groundwater circulations in this area are not yet fully understood. There is an inversac phenomenon in the Bouillon spring, and this can affect the quality of water in the Dhuy river and hence water quality in the pumping stations.





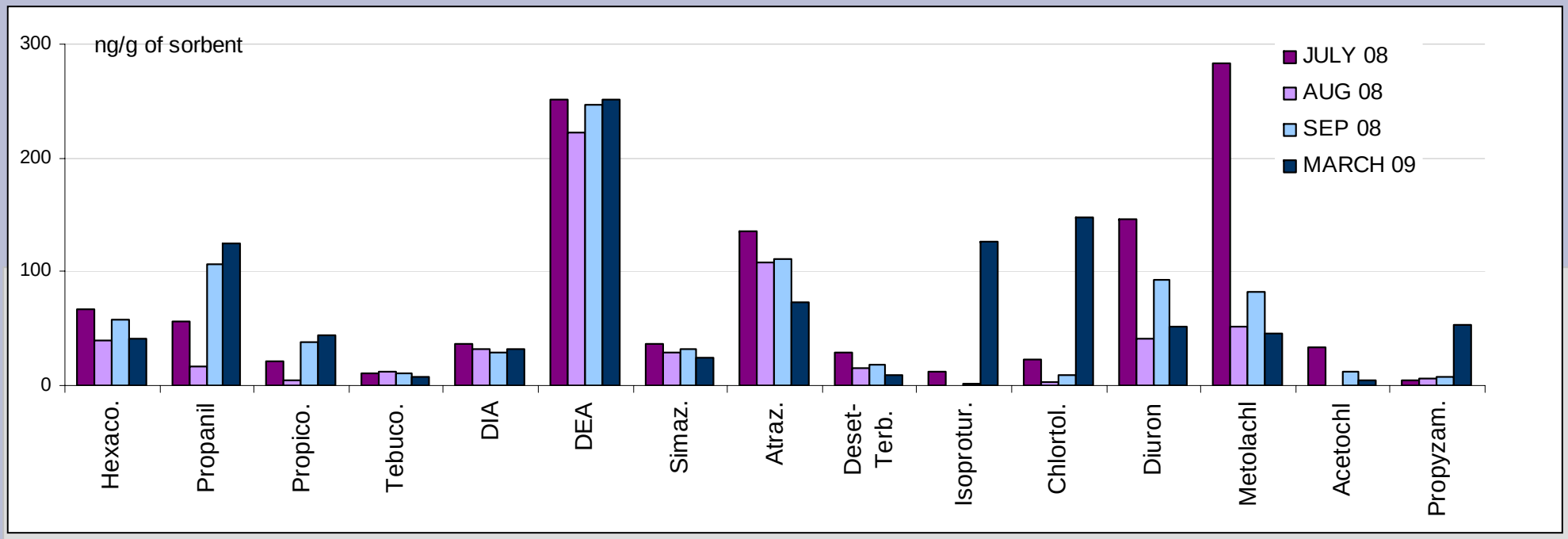
A first campaign : 3 months in summer 08

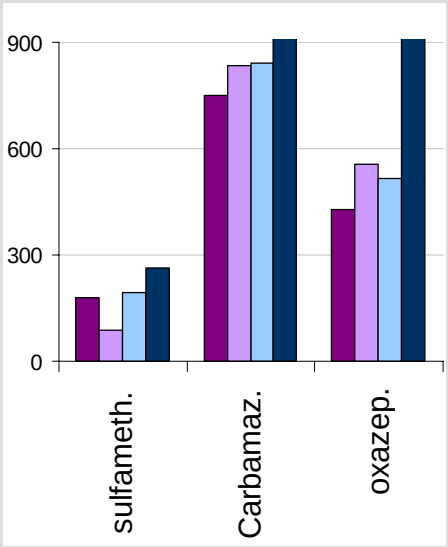
« historical pollutants » Atrazine and metabolites DIA and DEA : relative constant level, despite hydrological variations (flood in July in the Val de Loire river basin).

Same results for pharmaceuticals, highlighting local contamination by WWTP located in the watershed

hydrogeological connections are not yet elucidated.

For other compounds (metolachlor, diuron) local agricultural spreading coupled with hydrogeological changes impact water quality in the Bouillon spring, independently of the pesticide contamination of the Loire river (not shown).





A new campaign started in March 09 will connect agricultural practices, hydrological phenomenon and contamination levels in the different stations equiped with passive samplers (Loire, Dhuy and Bouillon).

With classical measurements, only Atrazine, DEA, DIA and sometimes diuron, isoproturon, carbamazepine and oxazepam have been detected. PS allows more than 25 extra compounds to be detected, and this helps us to understand the observed phenomena: such as local spreading and inputs of WWTP.

CASE STUDY:
VILAINE River, WWTP influence

Géosciences pour une Terre durable
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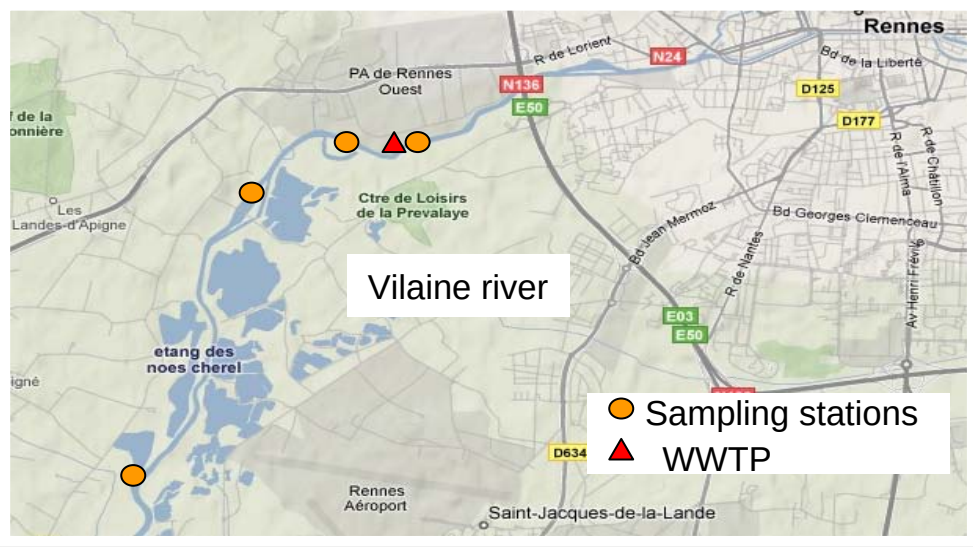
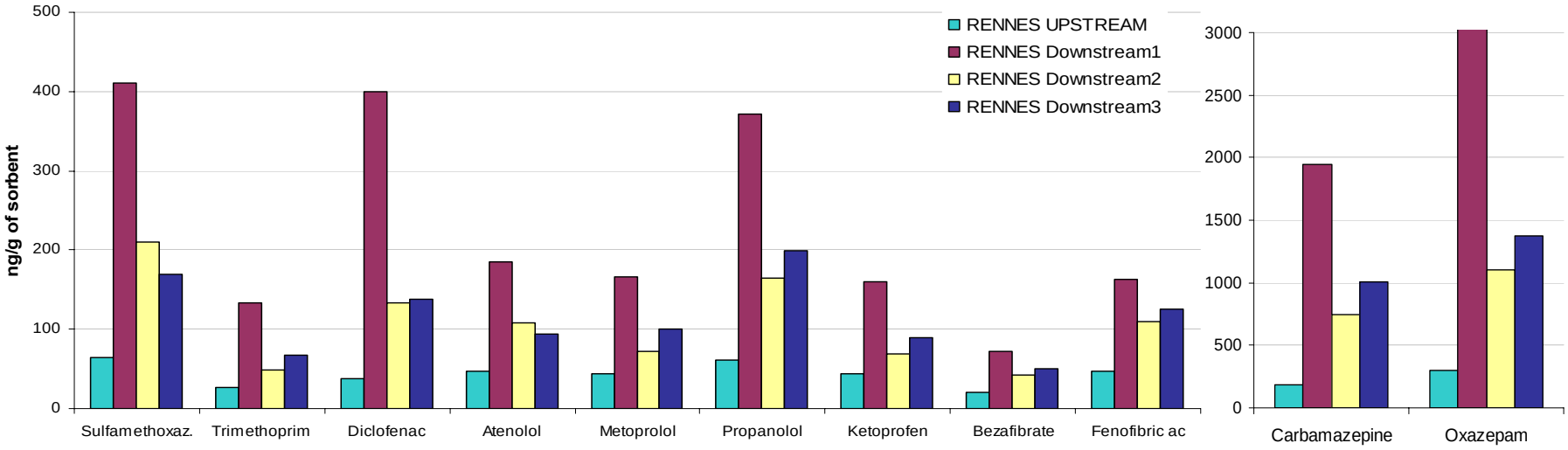
Context of the study



CASE STUDY: Water quality in the Vilaine river

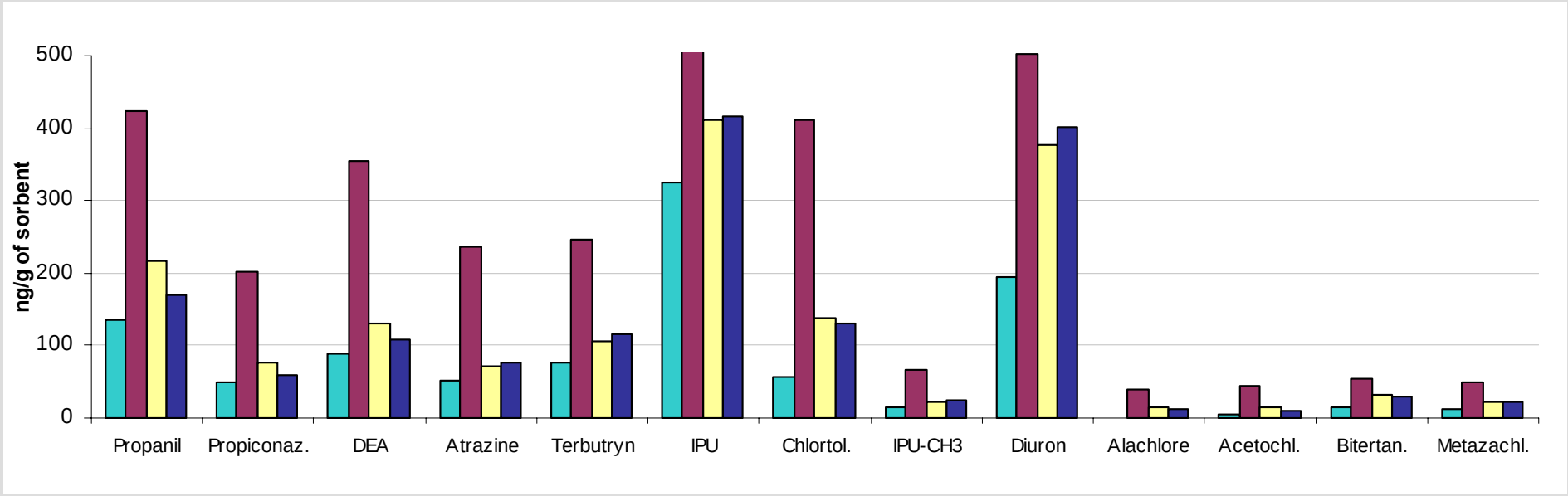
Second case studies (still under investigation) is the longitudinal measurements of the Vilaine river, with 4 station located upstream of a WWTP (300 000 EqH) for the first one and 500 m, 2 km and 5 km downstream for the others. The aim is to identify “4 or 5 key pollutants” than can allow a qualitative monitoring of the water quality in this river. Degradation of pollutants can also be monitored to determine the impact area of the WWTP effluent, that can affect diverse uses of the river (nautical leisure centre, protected natural area) located in the downstream part of the river.

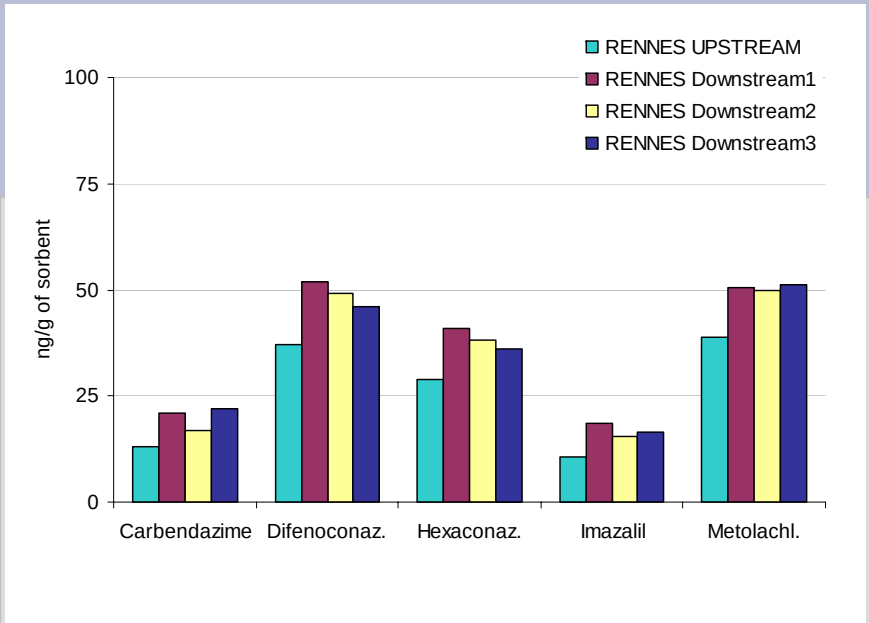


Main part of the pollution comes from WWTP effluent (Vilaine downstream 1), more important for pharmaceuticals than for pesticides. Pesticide contamination comes from the both sources.

Degradation phenomena are highlighted by occurrence of IPU-CH3 , or DEA.

These results will be compared with summer measurements.





For some pesticides, the impact of WWTP effluent are completely negligible. Vilaine pollution is mainly due to agricultural watersheld.

FIRST RESULTS ATTEMPTED FOR THIS CASE STUDY:

More than 36 compounds have been detected in this study compared with 15 by spot sampling;

Helpful for identification of pollution sources

Better under understanding of degradation phenomena occurring

Potential use for specific measurements in area with high vulnerability.

Conclusions and perspectives

Factors affecting the calibration (laboratory conditions)

- Properties of pharmaceutical compounds
  - pKa, Log Kow, solubility, degradation?
  - Investigation of specific receiving phases
- T°, turbulence, pH, matrix effect
  - Use of PRC: rate of PRC loss during an exposure is related to the target compound uptake
- Chemcatcher® and POCIS
  - Accumulation of PPs is based on adsorption and not on partition process
  - Under these circumstances it is difficult to use performance reference compounds

Translation to field applications?

- Factors affecting field applications
  - water velocity/turbulence/hydrodynamic regimes
  - Flow rate (river)
  - Temperature
  - Biofouling
  - Matrix effects (SPM, humic substances?)
- Determination of Rs?
  - *In-situ* validation?
  - Spot /passive sampling analysis
  - Use of same principal as PRC?
    - Measure of “tracer/labelled compound” loss rates during calibration studies and field exposures

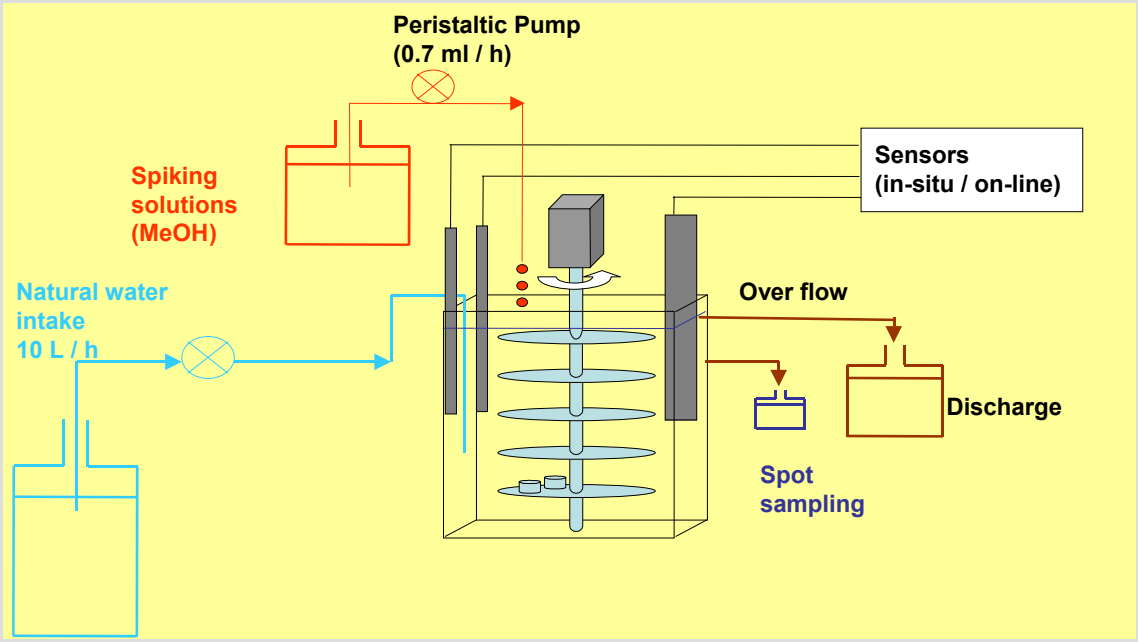
How to simulate environmental conditions?

- Artificial channel
  - Flow rate and the concentration could be monitored
  - Calibration model? Rs determination?
- Deployment of passive samplers in reference sites
  - Pollutants concentration are well known
  - Matrix effect well characterized (SPM, DOC, pH,…)
  - Comparison of different passive samplers (same conditions, same period of time,…)
- Tank experiment with natural water (cf SWIFT)

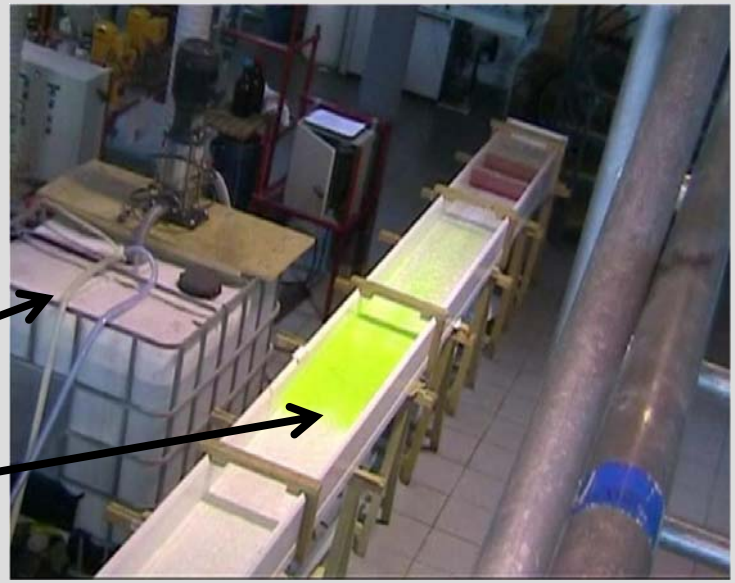
Reference sites?

Pilot site : WWTP + lagoon system

Design of the tank in continuous mode
SWIFT project : UoP, BRGM, RIZA(Eijsden)



Artificial channel



Water reservoir

Hydrodynamic regime

Factors affecting the use of PS as new tool for monitoring

What are regulatory barriers to using passive samplers to assess ground water contamination ?

- Environmental Quality Levels determination
- What is really measured by PS (which fractions?)
- Sampling frequency adopted ?

Acknowledgments

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