

Final Workshop

Passive Sampler Intercomparison Exercise

C. Miège, N. Mazzella, S. Schiavone, A. Dabrin, M. Coquery: Cemagref - Lyon, Bordeaux

C Berho, J-P Ghestem: BRGM – Orleans

J-L Gonzalez, D Munaron, C. Tixier: Ifremer - La Seyne/Mer, Sète, Nantes

B. Lalere, S. Lardy-Fontan: LNE - Paris

B. Lepot: INERIS – Paris

C. Gonzalez: EMA - Ales

General aspects: Objectives, design, field campaigns

C. Miège, N. Mazzella, D. Munaron, C. Tixier, S. Lardy-Fontan, B.
Lepot, S Schiavone, C Berho, JP Ghestem, M Coquery

General objectives



The assessment of the potential role and efficiency of passive samplers for water pollutants measurements in surface and coastal water in the frame of the WFD:

- ☞ to evaluate the comparability and variability of measurements of selected priority substances with passive samplers
- ☞ to evaluate the suitability of these samplers implemented in different aquatic environments to sample selected substances
- ☞ to demonstrate the applicability of such tools to water basin managers and routine laboratories

Planning



- Year 1 (2009):
 - Constitution of an organisation committee
 - Configuration of the exercise
 - Prospection/searching for participants

- Year 2 (2010):
 - Realization of the 3 in situ campaigns
 - Centralisation of final results on the web site

- Year 3 (2011):
 - Data treatment
 - Valorisation and communication on the results (report to participants, conference at IPSW 2011, final workshop, final report for Aquaref, scientific papers)

How to design the intercomparison exercise ? (1)



1/ PS not used in France by routine lab. for monitoring programs, (especially for continental waters)

☞ necessity to limit to expert lab.

2/ Necessity to have enough data per tool/molecule/site for satisfying statistical data treatment (for evaluation of the TWAC and its uncertainty and comparison of various tools)

☞ necessity to find foreign lab.

How to design the intercomparison exercise ? (2)



3/ None detailed guideline per PS, each expert lab. has its own sampling and analytical strategy (exposure conditions, analytical treatment, quality control, PRC, calculation of TWAC, ...)

☞ Choice to let expert lab. proceed as they are used to

4/ Some participants are very far away from the location of the in situ campaigns

☞ They could either come and prepare their own PS before exposure or they send us the detailed procedure and let us prepare their own PS before exposure

How to design the intercomparison exercise ? (3)



5/ Choice of the molecules:

- Selection of priority molecules (WFD, OSPAR, good ecological status)
- Metals / Hydrophilic Organics / Hydrophobic Organics
- Selection of pesticide metabolites
- Detected in the selected sites
- Possible to be sampled by PS
- Possible to be analysed by central lab.

6/ Choice of the tools:

- Cover the most known tools: DGT, SPMD, POCIS
- Let the possibility for other tools to be compared (chemcatcher, SR, MESCO, ...)

7/ Choice of the sites:

- to test the influence of various physico-chemical field conditions for some tool/molecule/site → marine and continental water sites
- In relatively contaminated area to be sure to quantify the studied pollutants
- Well known by organising lab.
- Easy to access, protected from vandalism

24 expert laboratories participated



← 11 national and 13 international lab. (Czech republic, Germany, Italy, Netherlands, Norway, Slovakia, Spain, Sweden, United Kingdom, United States)

<ul style="list-style-type: none">• AZTI-Foundation (ES),• BRGM (FR),• Cefas (UK),• Cemagref (FR),• Deltares/TNO (NL),• Ecole des Mines d'Alès (FR),• EDF R&D/LNHE (FR),• Environment Agency, National Laboratory Service (UK),• IFREMER (FR),• Labaqua (ES),• ALS Scandinavia AB (SW), LEESU (FR),• LPTC Bordeaux (FR),	<ul style="list-style-type: none">• Marine Scotland - Science (UK),• NIVA (NO),• T. G. Masaryk Water Research Institute, Public Research Institution (CZ),• UFZ - Department of Ecological Chemistry, Helmholtz Centre for Environmental Research (DE),• Universita di Cagliari (IT),• University of Rhode Island (USA),• Water Research Institute (SK)
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Various tools and exposure systems



- Exposure system (cage or support): Commercially available or home made
- PS and main characteristics:

Substances	Tools and main characteristics
Metals	<ul style="list-style-type: none"> * DGT: binding agent (Chelex-100) with open pore or restrictive diffusive gels (thickness: 0.8 mm) * Chemcatcher (metals)
PAHs	<ul style="list-style-type: none"> * SPMD: standard, 460 cm² * LDPE: from 390 to 490 cm² * Chemcatcher (apolar), C18 : 15,9 and 17,4 cm² * SR : 5, 160 et 600 cm² * MESCO : LDPE membrane, silicone phase * CFIS (PDMS)
Pesticides	<ul style="list-style-type: none"> * POCIS: both pesticide and pharmaceutical configurations * Chemcatchers (polar), C18, SDB-XC and SDB-RPS: 15,9 cm² * SR: 5 cm² * MESCO: cellulose membrane, silicone phase

SR: PDMS sheet

N°9

Various sampling and analytical procedures



- Quality controls (those not set by the organizers):
 - Laboratory PS blank or not
 - Internal surrogates or not
 - Correction from field blanks or not

- To calculate TWAC :
 - Rs for organic chemicals: From literature or determined by the participant
 - Various models applied

- Analytical procedures:
 - Metals: ICP-MS or GF/AAS
 - Organic: ☛ purification or not
 ☛ GC-MS, GC/MS/MS or HPLC/MS/MS,
 HPLC/fluo

- PRC used or not

Target substances

- Metals (8) : Cd*‡, Ni*, Pb*‡, Zn[Ⓜ], Cu[Ⓜ], Mn, Co, Cr[Ⓜ]
- PAHs (16 EPA): naphthalene*, acenaphthylene, acenaphthene, fluorene, phenanthrene‡, anthracene*‡, fluoranthene*‡, pyrene‡, benzo(a)anthracene‡, chrysene‡, benzo(b)fluoranthene*, benzo(a)pyrene*‡, benzo(k)fluoranthene*, benzo(ghi)perylene*‡, dibenzo(ah)anthracene, indeno(1,2,3-c,d)pyrene*‡
- Pesticides (9) : acetochlor, alachlor*, atrazine* and metabolites (DEA / DIA), diuron*, isoproturon*, simazine*, S-metolachlor

Priority molecules : WFD*
OSPAR ‡
Good ecological status [Ⓜ]

Exposure durations

Pesticides

- POCIS
- SBSE
- Chemcatcher
- SR
- MESCO

← 14 days

PAHs

- SPMD
- LDPE
- Chemcatcher
- SR (PDMS sheet)
- MESCO
- CFIS




← 21 days

Metals

- DGT
- Chemcatcher

← 7 days

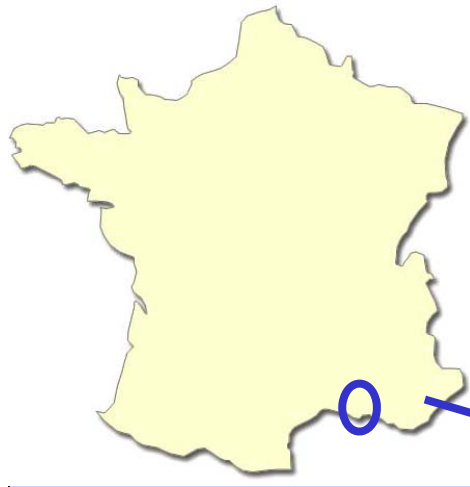
3 sampling sites

<p>Coastal waters</p>	<p>Thau (Hérault) 27th April- 18th May 2010 Pesticides, PAHs and metals</p>	
<p>River waters</p>	<p>Beillant (Charente maritime) 27th May- 10th June 2010 Pesticides</p>	
	<p>Ternay (Rhône) 17th June- 8th July 2010 PAHs and metals</p>	

Thau site

(Hérault, France)

☞ PAH, Pesticides, Metals

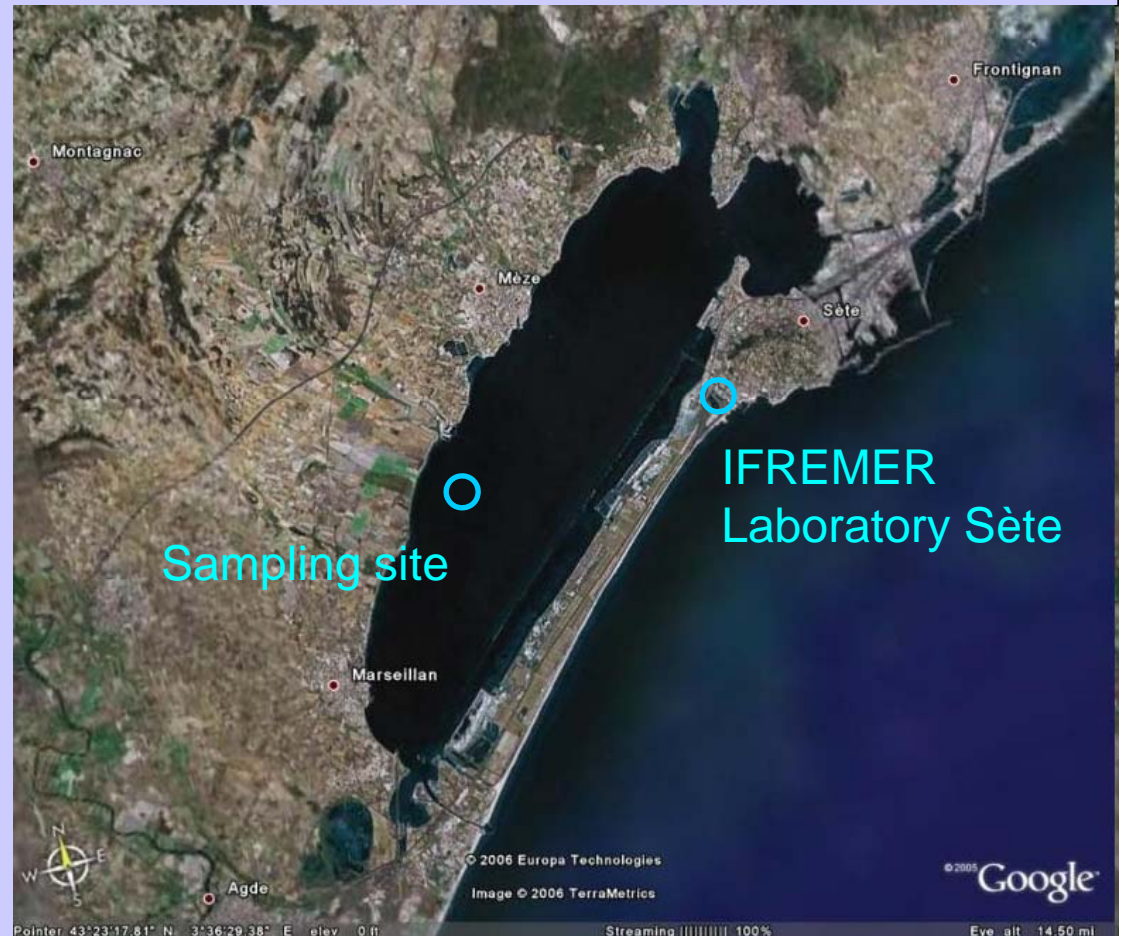


Thau lagoon: the second largest lake in France, 21 km long, 8 km wide, an area of 7 hectares, mean depth of 4.5 m, max depth of 30 m

East borders largely industrial
Northern side has villages dedicated to fishing and the production of shellfish



Oyster farming



Thau site



- Lagoon waters : mean during exercise (usual annual ranges)
 - Temperature: 17.9°C (5-26°C)
 - Salinity: 37.6 PSU (34-39)
 - Suspended solids: 0.89 mg/L
 - Flow velocity: 1.59 cm/s
 - Micropollutants concentrations in the dissolved phase:
 - ▶ Metals: > 500ng/L for Ni and Cu, ~60 ng/L for Co, < 20 ng/L for the others
 - ▶ pesticides and PAHs: < 3 ng/L
- Preparation of the PS before exposure in laboratory (at 5.5 miles from the exposure site, by boat)
- Description of the exposure area:
 - former site of oyster farming surrounded with shelf farming tables in action
 - A monitoring site of the French mussel watch program (IFREMER)

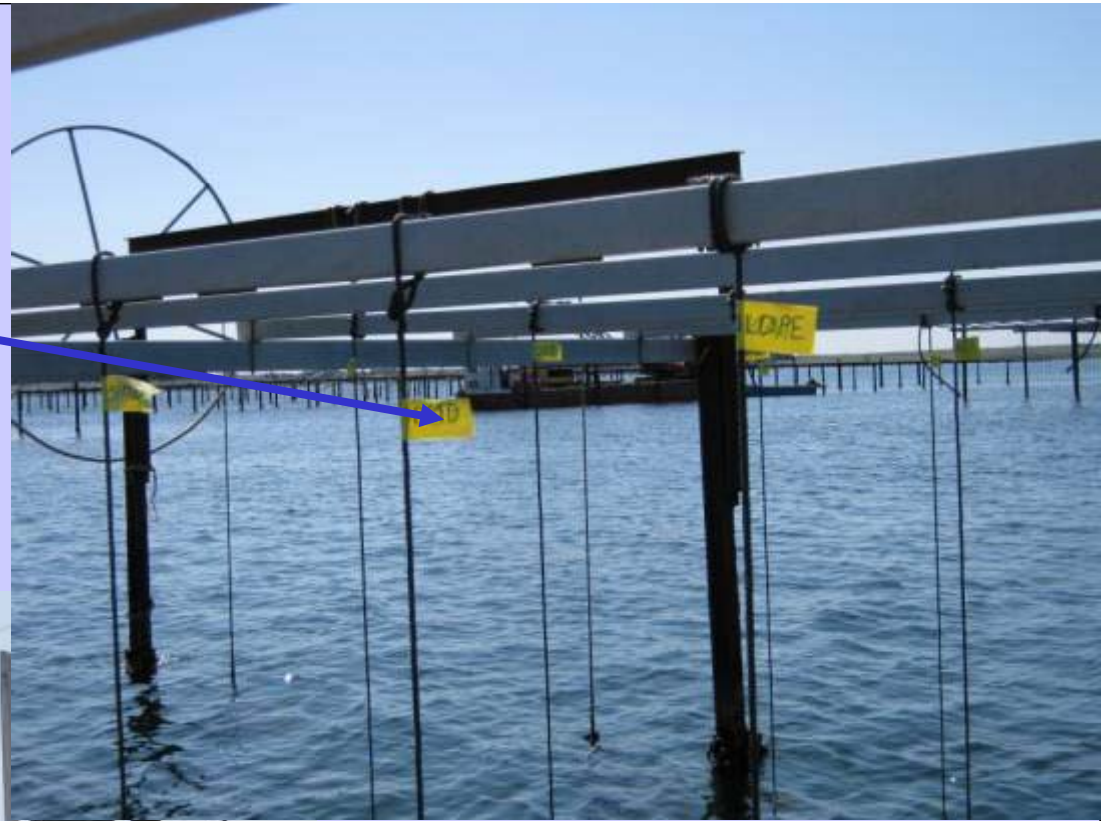


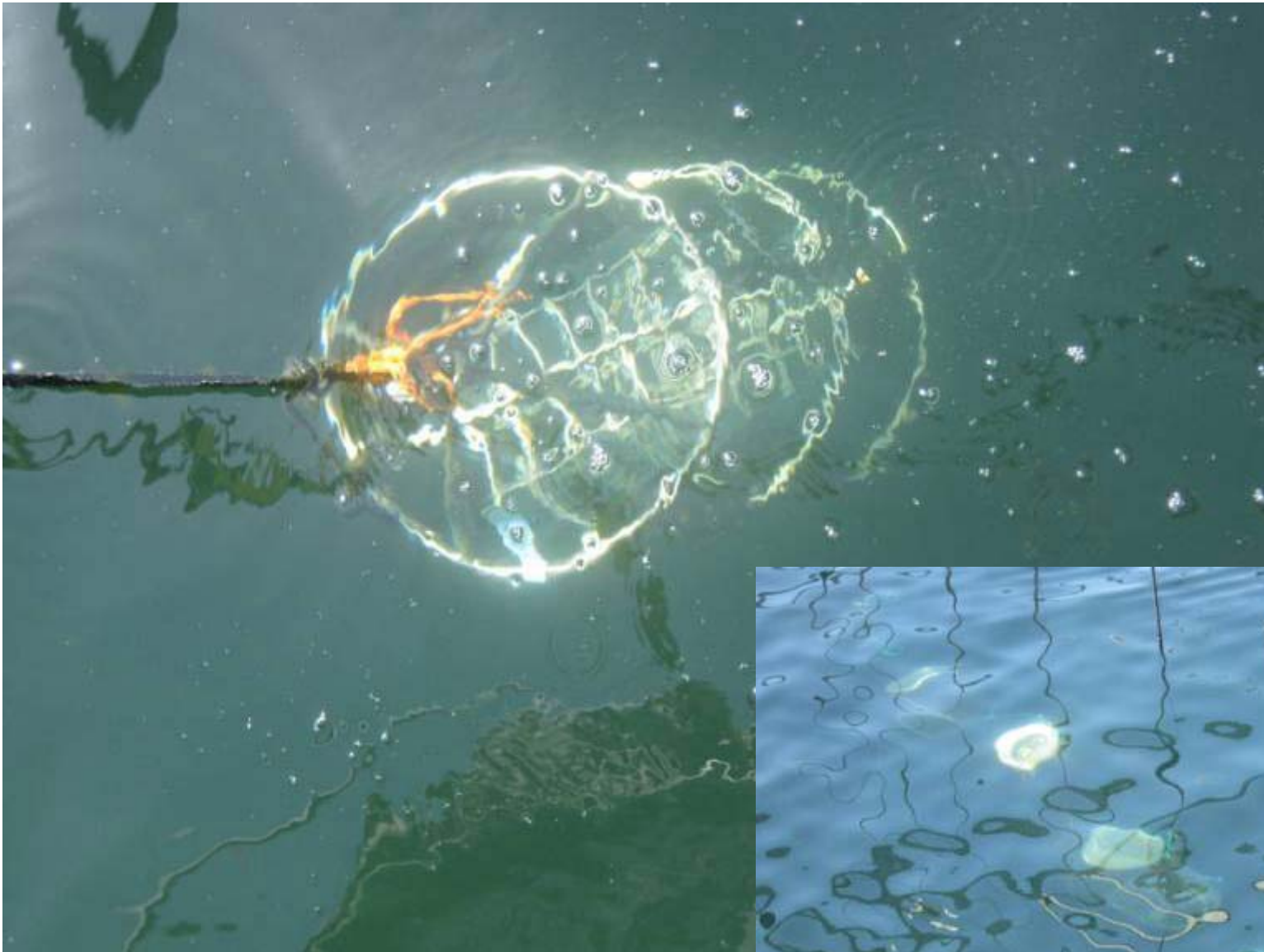
Former site of oyster farming

Rope to hang up the exposure cages of PS



Signalisation of the exposure cages of PS (tool/lab.)





Exposure cages of PS
Same depth for all PS

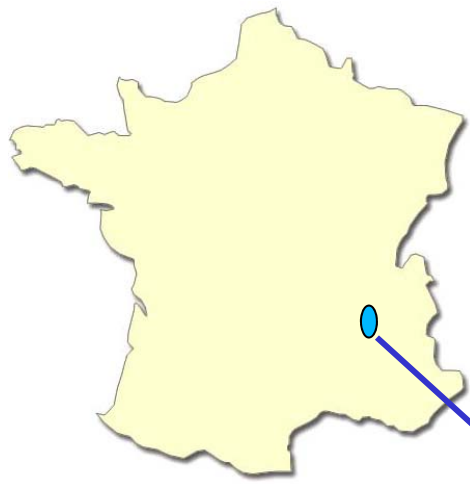


Preparation of the PS for exposure in laboratory
(at 5.5 miles from the exposure site, by boat)



Ternay site
(south of Lyon, Rhône, France)

☞ PAH and Metals



Urban area of Lyon (2 000 000 inhabitants) at around 20 km

Sampling site



Ternay site



- Rhone river waters (mean \pm sd on the 3 weeks campaign)
 - Suspended solids: $14,0 \pm 12,1$ mg/L (> Beillant > Thau)
 - Temperature: $19,8 \pm 2,7$ °C
 - Flow velocity: $0,217 \pm 0,078$ m/s (> Thau and Beillant)
 - Conductivity: 389 ± 28 μ S/cm
 - Micropollutants mean concentrations in dissolved phase:
(Metals: from 13 ng/L for Cd to 3.6 μ g/L for Mn; PAHs: < 5 ng/L)
- Preparation of the PS for exposure directly in situ, near the river Rhone (not in laboratory)
- Description of the sampling site:
 - An urban (2 000 000 inhabitants) and industrial area. The great Lyon is known for its chemical industry located between Lyon and the sampling site.
 - A Rhone river measurement station
 - PS located near the river bank



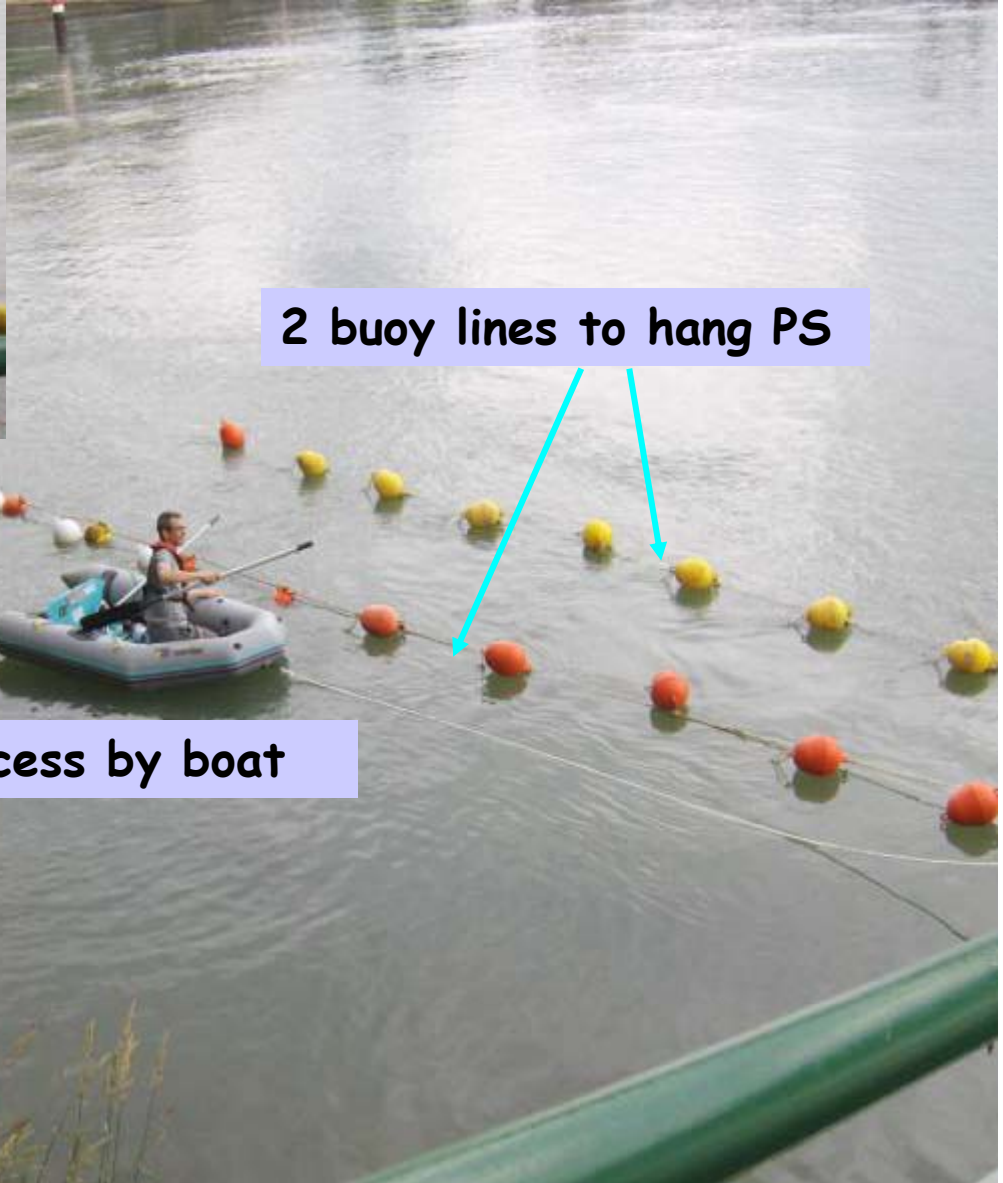
A footbridge



Industrial area



Floating platform



2 buoy lines to hang PS

Access by boat



Folding tables covered with aluminum foils



The exposure cages hanged to the buoy lines



Commercially available
exp. syst. for standard
SPMD



Home-made exp. syst.
for chemcatcher

Biofouling in SR



Exp. syst.
for SR



After exposure...



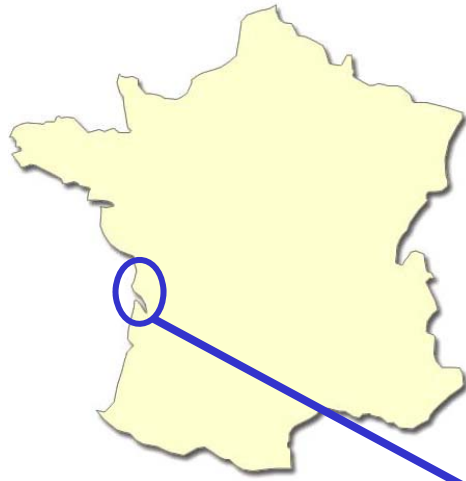
After exposure...



CFIS

Beillant site (Charente maritime, France)

☞ Pesticides



The watershed area is occupied by almost 80% of agricultural lands

PS exposed in Charente river



376 km long, watershed of about 10 050 km²

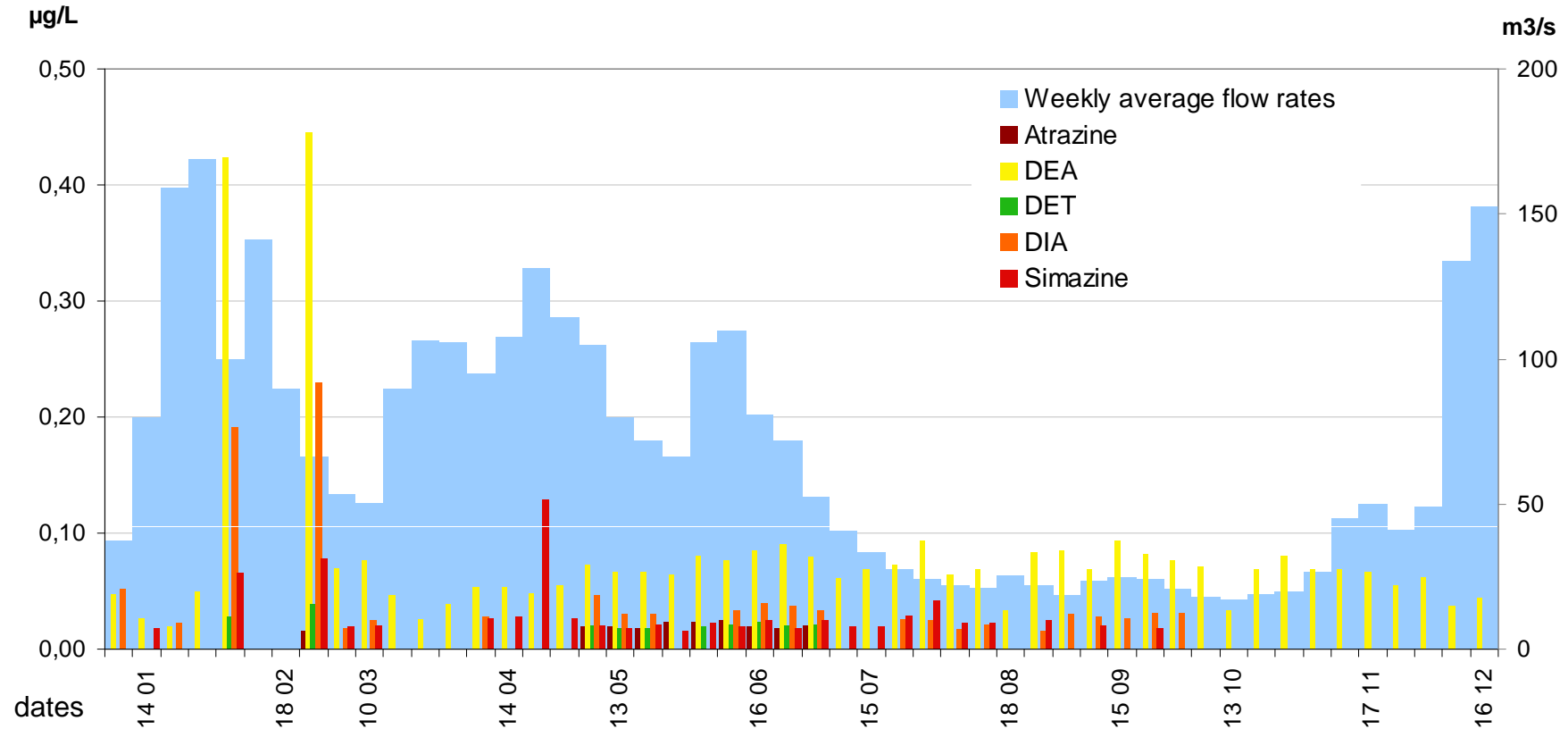
Mean annual flow of 68 m³.s⁻¹ (at Beillant, 2008)

Beillant site



- Charente river waters (mean \pm sd on the 2 weeks campaign) :
 - Suspended solids: 7 ± 0.7 mg/L
 - Temperature: 19.4 ± 1.1 °C
 - Flow velocity: 0.01-0.02 m/s
 - Conductivity: 539.8 ± 10.8 μ S/cm
 - Pesticide mean concentrations in dissolved phase: 10 to 50 ng/L for DIA, MET, DEA, < LQ for others
- Preparation of the PS for exposure in laboratory (at 150 km from the exposure site)
- Description of the sampling site:
 - The watershed area is occupied by almost 80% of agricultural lands
 - A very well known site for Cemagref Bordeaux
 - PS located near the river bank

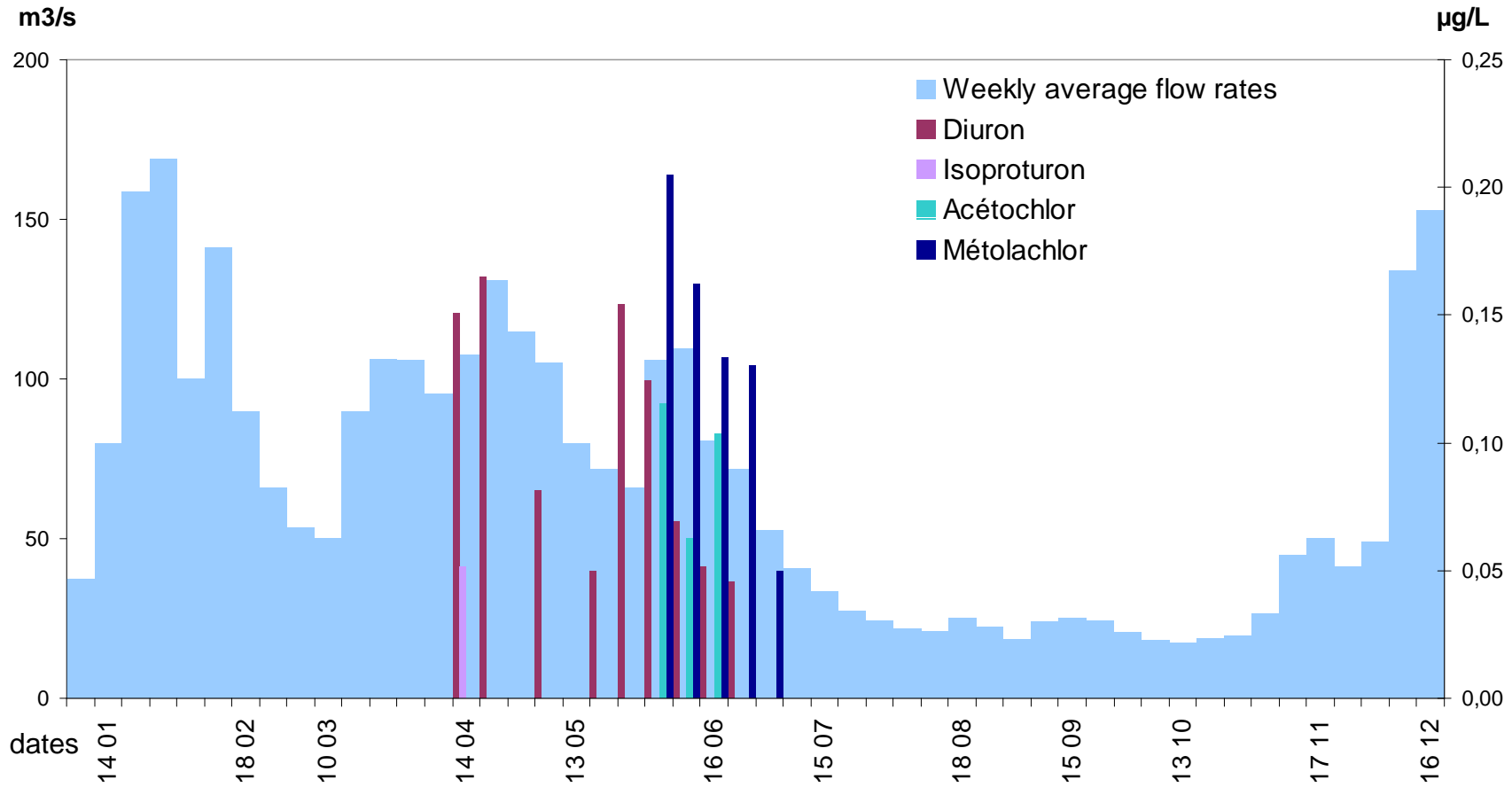
Triazine concentrations (2008)



Background levels and low fluctuations of concentrations

Metabolites (DEA and DIA) are generally more abundant than parent compounds

Phenylurea and chloroacetanilide concentrations (2008)



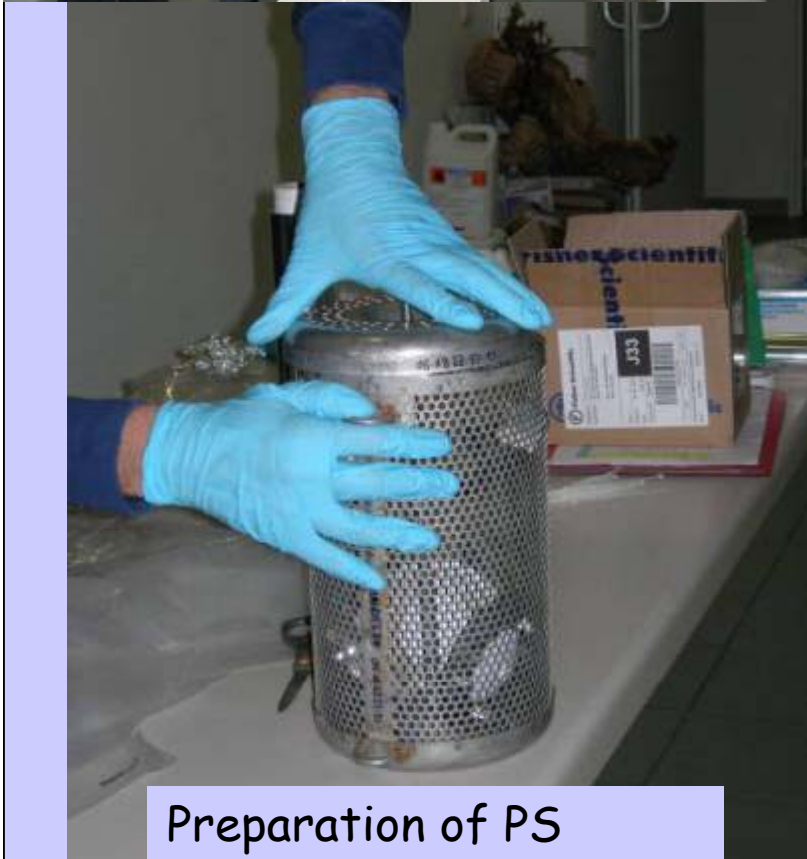
Applications and detection typically during the spring



The Charente
river at Beillant



The lab. at 150 km from the sampling site



Preparation of PS



Receipt of PS from participants

Access by boat...



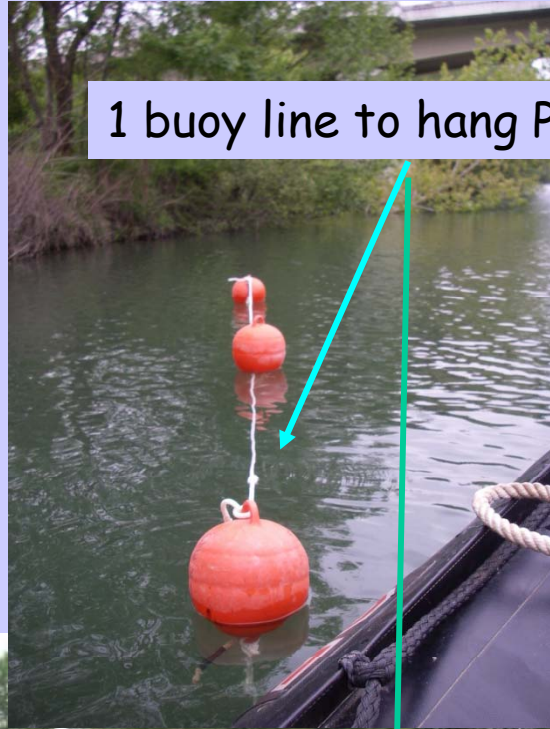


Access by boat...





Home made
exp. syst. for
Chemcatcher



1 buoy line to hang PS



Other aspects:

- ➡ A web site
- ➡ Water monitoring
- ➡ Quality assurance

A web site

The screenshot shows the website interface for the EIL (Essais Inter Laboratoires) program. At the top left, there are logos for the French Republic and the Ministry of Ecology, Sustainable Development, and Urban Planning. The main header features the EIL logo and the text 'Essais Inter Laboratoires'. On the right, there are links for 'Liens utiles', 'Contacts', and 'Connexion', along with the INERIS logo and the tagline 'maîtriser le risque pour un développement durable'. Below the header, there is a navigation menu with 'Home', 'Programmes', and 'Help'. The main content area is titled 'INTERLABORATORY TRIAL PASSIVE SAMPLERS 2010'. It contains a section for 'April-July 2010 : Passive samplers intercalibration exercise: 2010' with descriptive text. A yellow banner with the URL 'www.ineris.fr/eil/passivesamplers.php' is overlaid on the text. To the right of the text is a 'RESULTS REPORTING' section with a login form. The login form includes fields for 'Login', 'Password', and a 'Choose your trial' dropdown menu, with an 'OK' button and a message indicating 'You have 3 attempt(s) remaining'. Below the login form, there are links for 'Already registered : Forgotten your password?' and 'Application for Registration'.

- To register
- To collect results and information (sampling and analytical strategy) from participants

6 central lab. for water analysis



- BRGM (PAH at Ternay),
- Cemagref of Bordeaux (pesticides, physico-chemical parameters at Beillant),
- Cemagref of Lyon (metals, physico-chemical parameters at Ternay),
- EPOC-LPTC of Bordeaux (pesticides and PAHs at Thau site),
- IFREMER of Sète (physico-chemical parameters at Thau site),
- IFREMER of Nantes (LBCM) (metals at Thau site).

Monitoring of the exposure water conditions



- Ionic composition
- pH, suspended matter, conductivity, salinity (for Thau), DOC, TOC, temperature, water velocity, pluviometry, discharge, dissolved oxygen (for Thau).
- Concentrations of the target compounds in the dissolved and total phases (spot sampling):

	Beillant	Ternay	Thau
Metals	/	50 mL Direct analysis by ICP-MS LQ from 0.01 for Cd to 0.5 for Zn	500 mL Danielson method (1982) ICP-MS LQ from 0.1 ng/L for Cd to 10 for Cu and Zn
PAHs	/	5L samples LLE (dichloromethane) HPLC-Fluo LQ: 0.4 ng/L except ACE and PHE at 2 ng/L	2 L SPE (C18) GC-MS LQ: 0.1 ng/L
Pesticides	50 mL samples SPE (Oasis HLB) HPLC-MS-MS LQ from 10 to 20 ng/L	/	2L SPE (Oasis HLB) HPLC-MS-MS LQ from 10 to 20 ng/L

Quality controls and Quality assurance



- Each sampler exposed in triplicate
- 1 field blank per sampler and per site, participant are free to subtract or not this blank from their measurements
- A reference solution to evaluate the accuracy and precision of the instrumental analytical step
- Because of the design of the trial, implementation of QC based on reference PSs (spiked and then distributed to all participants) was not technically possible (too many different PSs studied).

👉 A questionnaire measuring satisfaction will be sent to you

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Thank you for your attention !!