Intercomparison of five integrative samplers for the monitoring of indicator and dioxin-like PCBs in the laboratory and in situ (ECLIPSE project)

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Presentation of the ECLIPSE project

❖ Context:
  ➢ Innovative sampling tools needed for the monitoring of PCB in water
  ➢ Various integrative samplers available to estimate TWA concentration

❖ ECLIPSE:
  ➢ Integrative samplers for the monitoring of PCB in water
  ➢ 3 years (2009-2011)
  ➢ 5 laboratories

❖ Objectives:
  ➢ Evaluation of 5 integrative samplers to monitor PCB in water
  ➢ Comparison of performances: uptake kinetics, repeatability, accuracy

❖ Planning:
  ➢ 1st year: simultaneous calibration of samplers in laboratory
  ➢ 2nd and 3rd year: deployment of samplers in real aquatic environments

Integrative samplers studied in the ECLIPSE project

❖ Semi-permeable membrane device (SPMD)
- ➤ Layflat LDPE* tube containing triolein
- ➤ Cemagref (Lyon, France)

❖ Low-density polyethylene strip
- ➤ LDPE* strip
- ➤ Ifremer (Nantes, France)

❖ Silicone rubber
- ➤ PDMS* rubber
- ➤ Deltares (Utrecht, The Netherlands)

❖ Chemcatcher
- ➤ LDPE* membrane covering a C18 Empore disk
- ➤ BRGM (Orléans, France)

❖ Continuous-flow integrative sampler (CFIS)
- ➤ Small PDMS* pieces, use of pump and batteries
- ➤ Labaqua (Alicante, Spain)

* LDPE: low-density polyethylene, PDMS: polydimethylsiloxane

▶ 1) Simultaneous calibration of samplers in laboratory

Calibration experiment (July-Sept. 2009)

❖ Exposure conditions:
  ➢ Calibration device made of stainless steel to limit adsorption of PCB
  ➢ 200 L of unfiltered tap water
  ➢ Water velocity: about 5 cm/sec, temperature: 22.6°C (±0.1°C)
  ➢ Exposure durations: 1, 3, 7, 14 (x3), 21, 28 (x3), 56 and 91 days

❖ Concentration of each PCB in water of about 1 ng/L:
  ➢ Immersion of PCB spiked silicone sheets [Rusina et al, 2010]
  ➢ PCB_{ind}: (18), 28, 52, 101, 118, 138, 153, 180
  ➢ PCB_{D-L}: 77, 81, 105, 114, (118), 123, 126, 156, 157, 167, 169, 189

❖ Before exposure, samplers spiked with PRC (except CFIS)

❖ Dosing sheets and water sampled every 15 days:
  ➢ PCB concentrations (→, 3% < RSD < 10%)
  ➢ pH (→, 7.5 ± 0.2), conductivity (↘ from 380 to 310 µS/cm) and DOC concentration (↗ from 1.50 to 4.70 mg/L)

Stirrer engine

CFIS

Stainless steel tank
(calibration)

Polyethylene tank
(water bath)

Calibration device (2/3)

❖ Inside the tank, 6 racks immersed:

➢ 2 racks for dosing sheets

➢ 4 racks for samplers (with 4 positions on each)

Position 1: blank sampler (no PRC)

Position 2: variable exposure durations

Position 3: variable exposure durations

Position 4: 91 days exposure
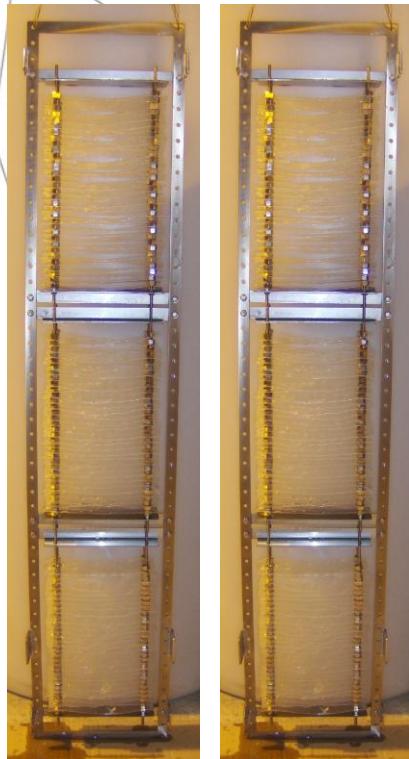
Dosing sheets (source of contamination)

SPMD

Silicone rubbers

LDPE strips

Chemcatchers

Calibration device (3/3)
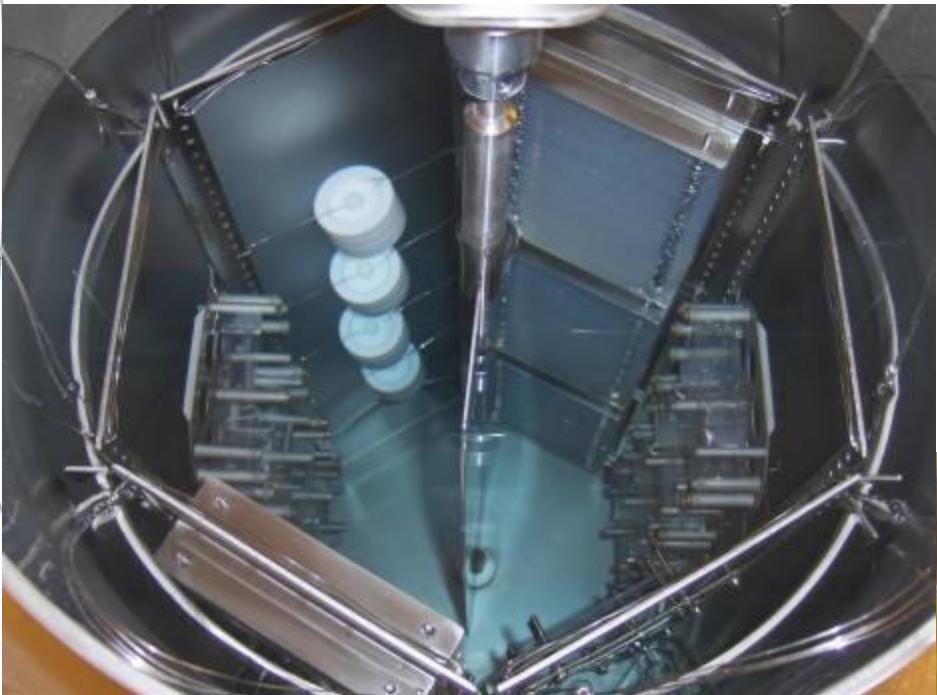
Inside the tank: dosing sheets and passive samplers

Outside the tank: CFIS

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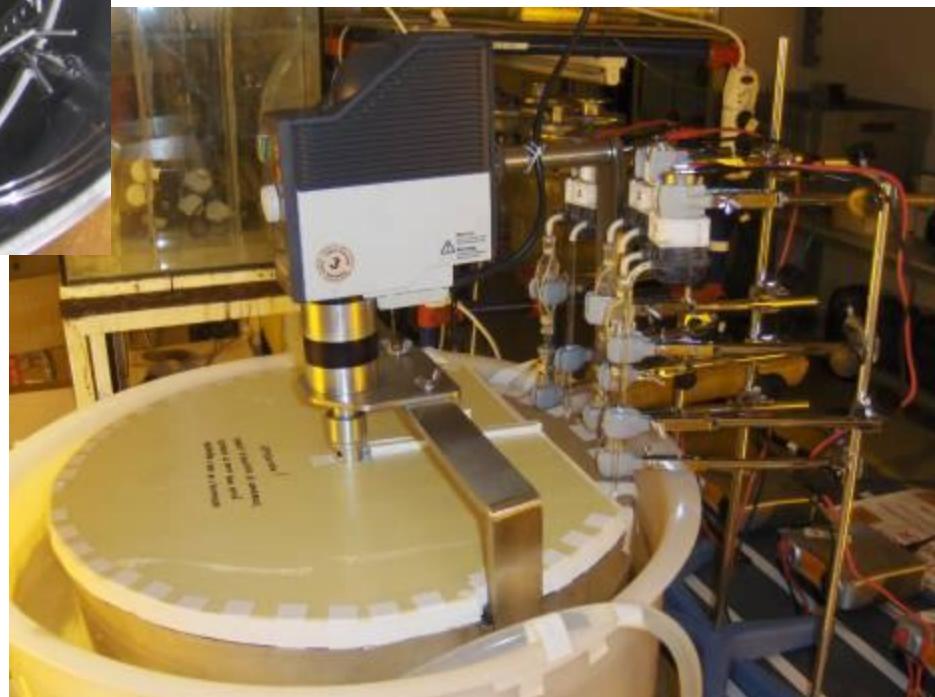
Uptake curves of PCB and release curves of PRC
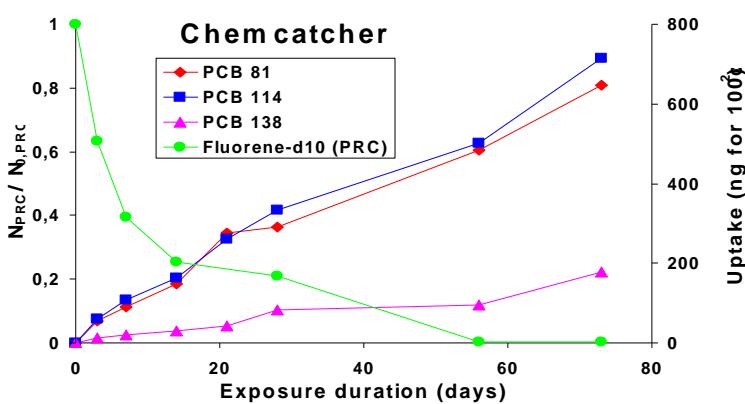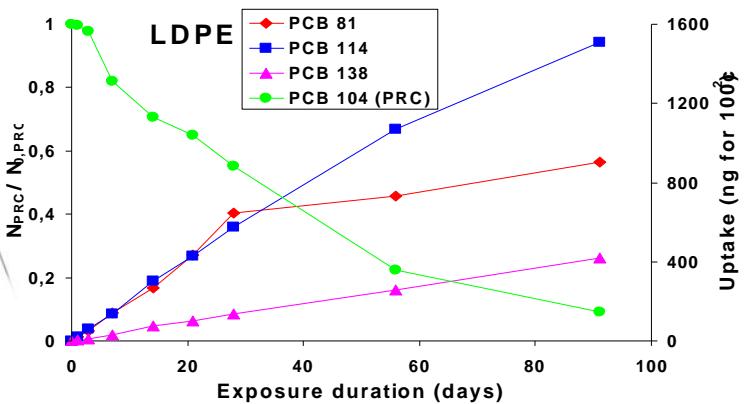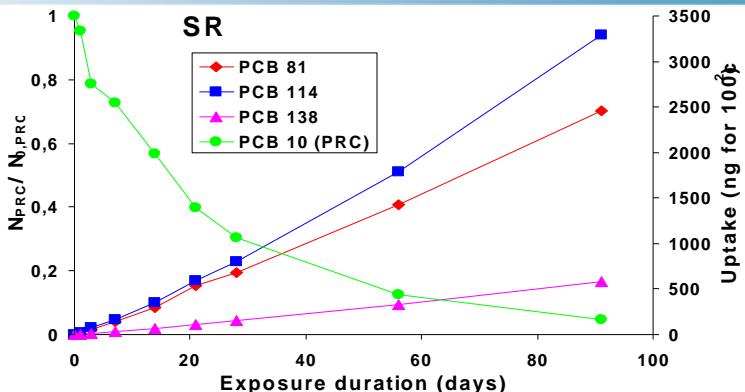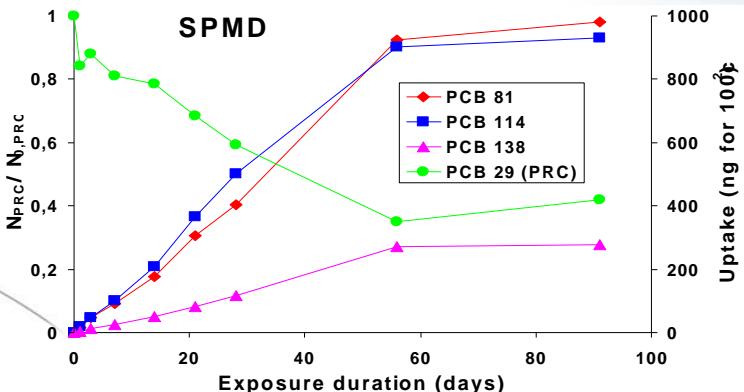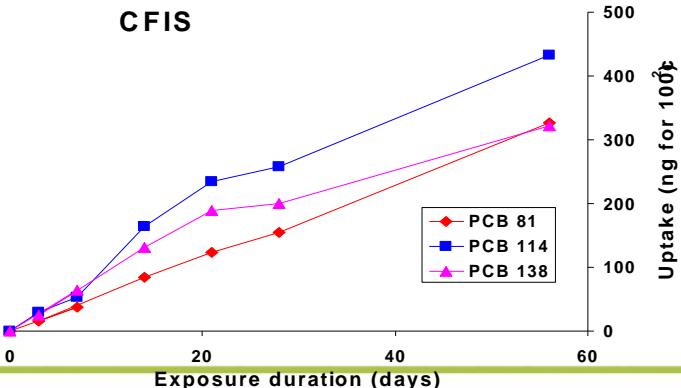
- ❖ SPMD: transfer of PCB and PRC stopped after 56 days, due to biofouling ?
- ❖ After 91 days of exposure, equilibrium reached for PCB 18, 28 and 52 in LDPE
- ❖ Overall good linearity of uptake curves

Concentration of PCB in triplicate samplers

Uptake (ng for 100cm²) — SPMD (28 days), Silicone rubber (28 days), LDPE strip (28 days), Chemcatcher (14 days), CFIS (14 days) for PCB 18, 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189.
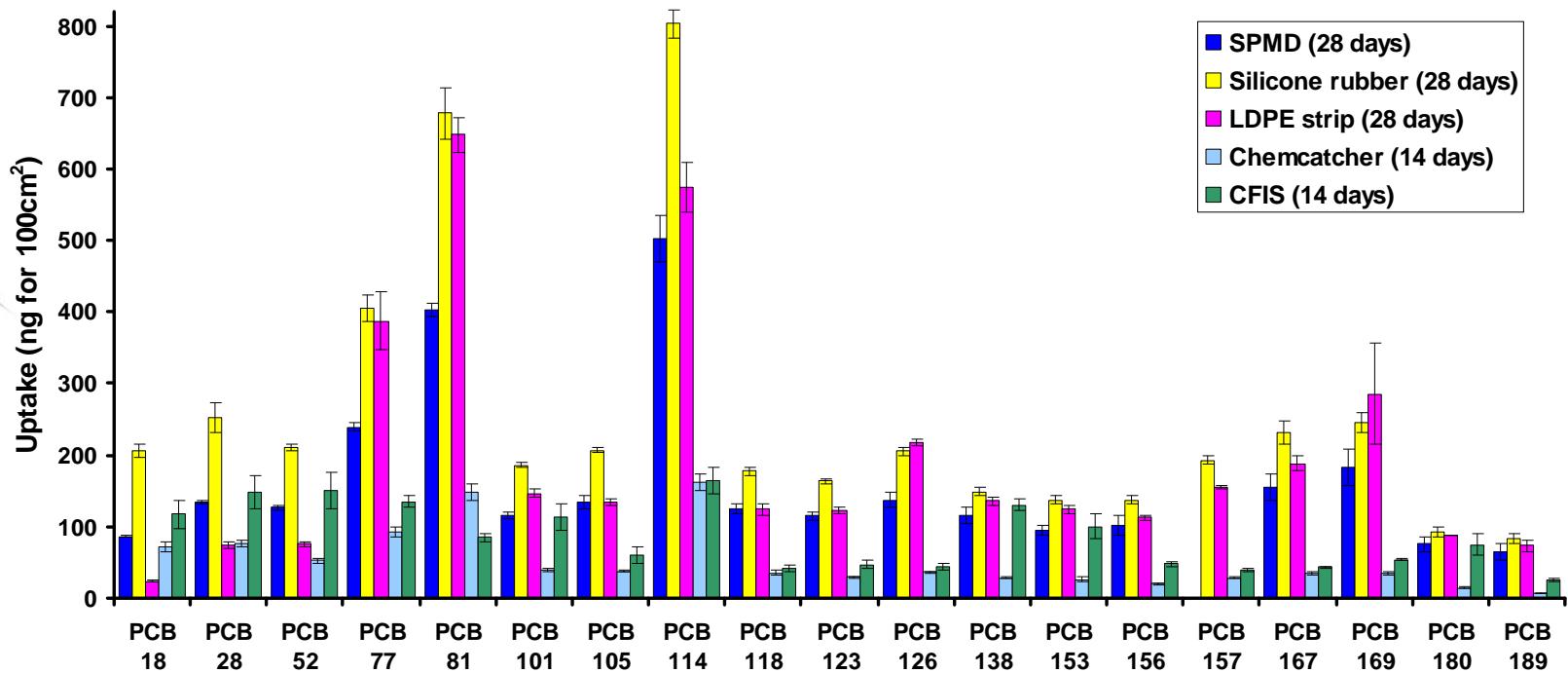
❖ Repeatability of uptake:

  ➢ SPMD: $1\% < RSD < 18\%$ (mean = 7%)

  ➢ Silicone rubber: $2\% < RSD < 9\%$ (mean = 4%)

  ➢ LDPE strip: $1\% < RSD < 25\%$ (mean = 6%)

  ➢ Chemcatcher: $3\% < RSD < 13\%$ (mean = 8%)

  ➢ CFIS: $2\% < RSD < 20\%$ (mean = 11%)
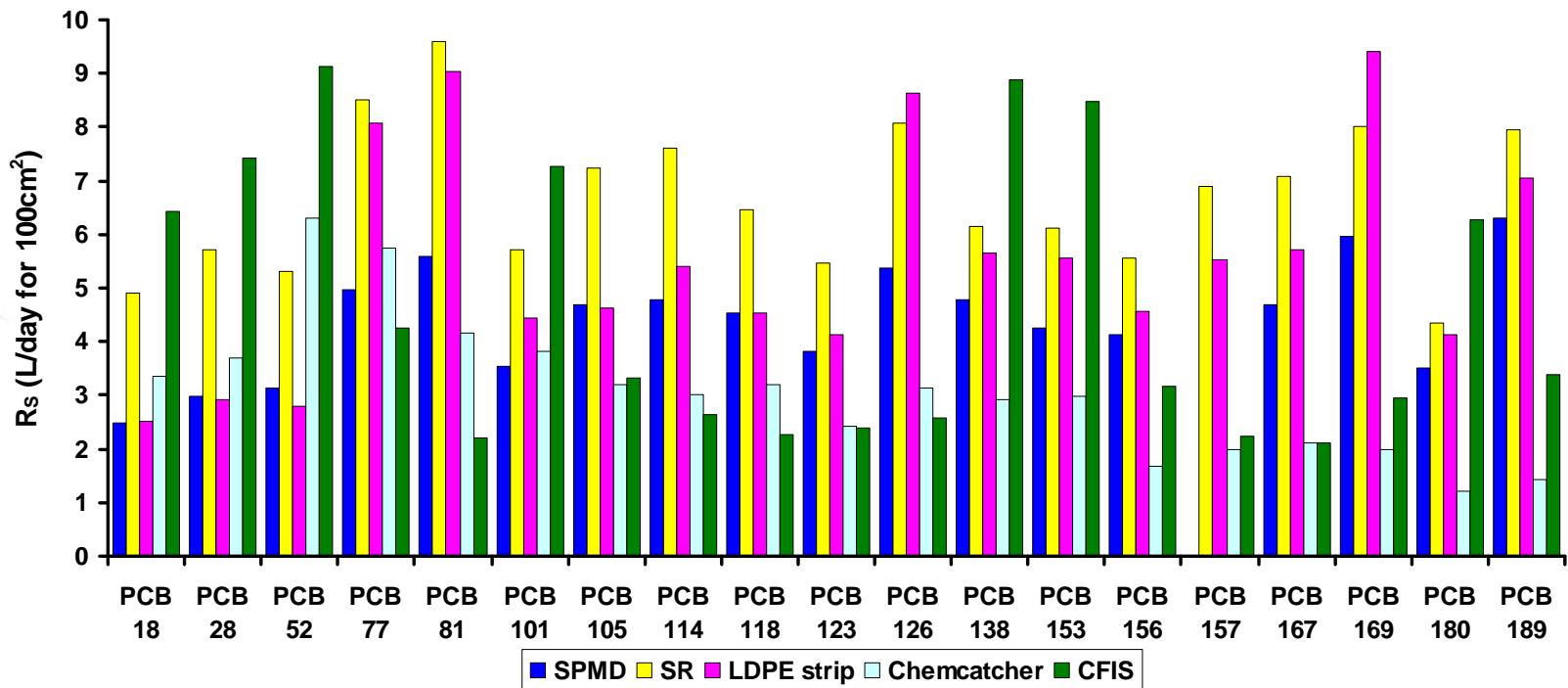
- PCB concentrations in water calculated from dosing sheets
- $N = R_S.C_W.t \Rightarrow$ when $N = f(t)$ is plotted, slope $= R_S.C_W$
- Overall trends of sampling rates:
  - CFIS: highest rates for light PCB but low rates for the others
  - Silicone rubber $\geq$ LDPE strip $\geq$ SPMD $\gg$ CFIS $\geq$ Chemcatcher
- Silicone rubber, LDPE strip and SPMD: higher sampling rates + higher surface area $\Rightarrow$ most efficient samplers to decrease LOQ

TWA concentrations of PCB in water

❖ To calculate TWA concentrations, need for :
  ➢ Uptake models
  ➢ Choice criteria of PRC
  ➢ Low K_{SW}

❖ Models, PRC and log K_{SW} used

|	Model	PRC	Log K_{SW}
SPMD	Huckins 2006 (water boundary layer - controlled uptake model)	PCB, used when dissipation was between 20% and 80%	empirical relationship function of log K_{OW} [Huckins 2006]
SR	Rusina 2010 (non linear fit of R_S to observed dissipation)	PCB, all used with unweighted nonlinear least-squares regression [Booij 2010]	measured and modeled [Smedes 2009]
LDPE strip	Huckins 2006 (water boundary layer - controlled uptake model)	PCB, used when dissipation was between 20% and 80%	measured and modeled [Smedes 2009]
Chemcatcher	Vrana 2007 (applicable for compounds with 3.7 < log K_{OW} < 6.8)	PAH, used when dissipation was between 20% and 100%	empirical relationship function of log K_{OW} [Vrana 2006]
CFIS	none, use of predetermined R_S for PCB_{ind} and extrapolated R_S for PCB_{dl}	none, not required	none, not required

❖ Chemcatcher results (model applied for PCB with log K_{OW} < 6.8):
  ➢ 14% < RSD < 17% (mean = 15%)
  ➢ TWA concentrations of PCB up to 12 times higher than the other samplers

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TWA concentrations of PCB in water

Reference concentration in water calculated from concentration in dosing sheets (PDMS):

$$C_W = \frac{C_{PDMS}}{K_{PDMS,W}}$$
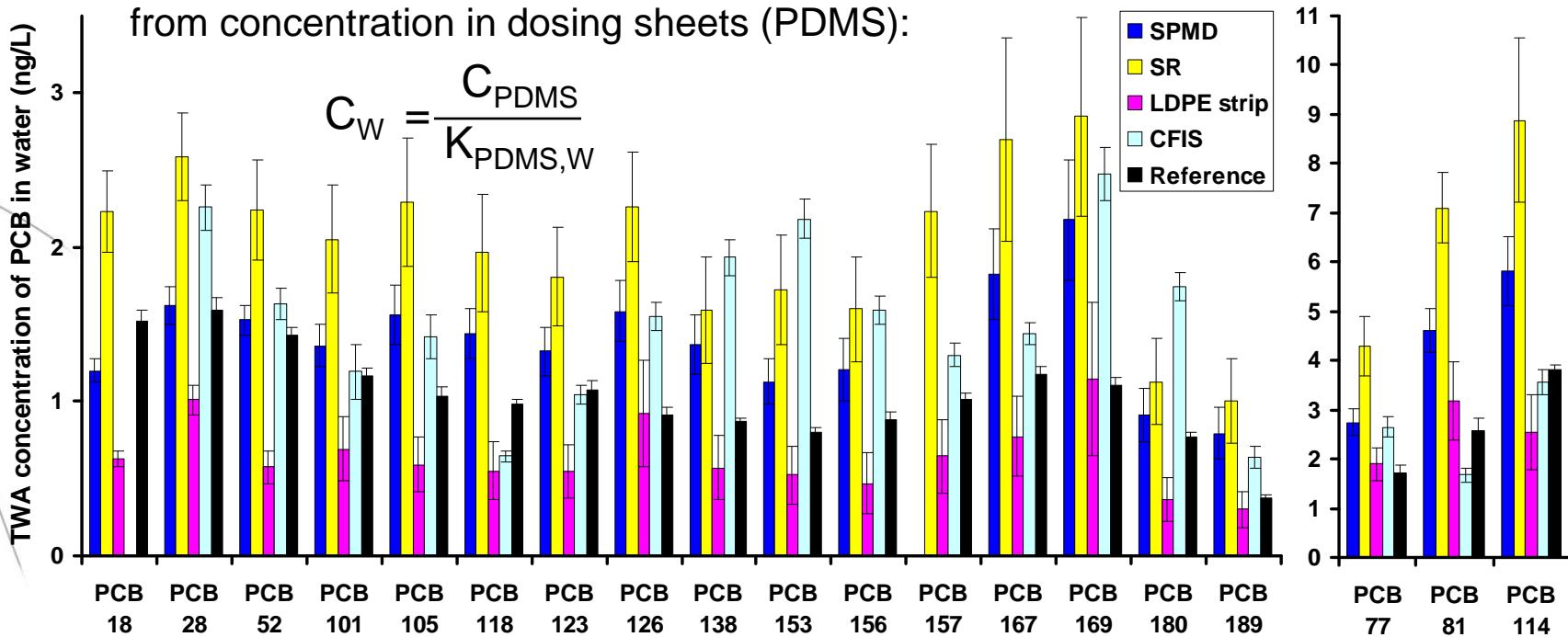
	Ratio to reference	RSD
SPMD	79% - 212% (mean = 145%)	6% - 21% (mean = 13%)
Silicone rubber	147% - 275% (mean = 207%)	10% - 27% (mean = 18%)
LDPE strip	40% - 123% (mean = 69%)	9% - 44% (mean = 30%)
CFIS	65% - 272% (mean = 146%)	5% - 15% (mean = 7%)

Conclusions about calibration

❖ Calibration experiment successfull

❖ For Chemcatcher:
  ➢ Literature model for hydrophobic compounds not applicable for PCB
  ➢ Sampling rates determined for the 19 PCB of ECLIPSE

❖ For CFIS:
  ➢ Sampling rates confirmed for indicator PCB
  ➢ Sampling rates determined for dioxin-like PCB

❖ TWA concentrations of PCB (except Chemcatcher):
  ➢ Good agreement between samplers (29% < RSD < 51%)
  ➢ Highest difference: a factor of 4.25 for PCB 180 between LDPE strip (0.4 ng/L) and CFIS (1.7 ng/L)
  ➢ Ratio to reference between 48% and 272%

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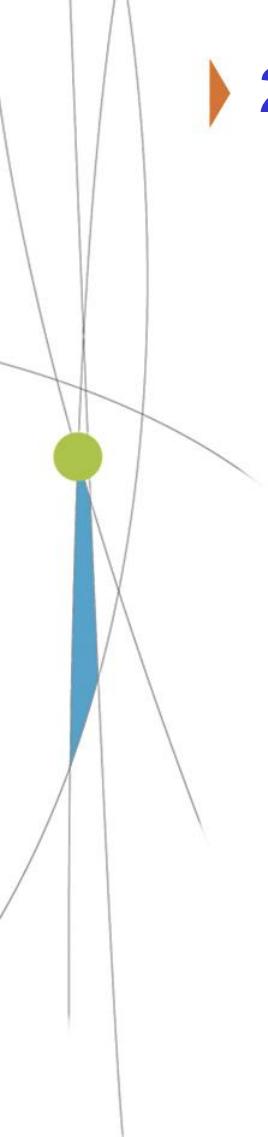
2) Deployment of samplers for field campaigns

Field campaigns

- ❖ 3 field campaigns performed in:
  - ➢ The Rhône River at Ternay (June-July 2010)
  - ➢ The Rhône River at Arles (Oct-Nov 2010)
 - ➢ The Leysse River at Bourget-du-Lac (June-July 2011)
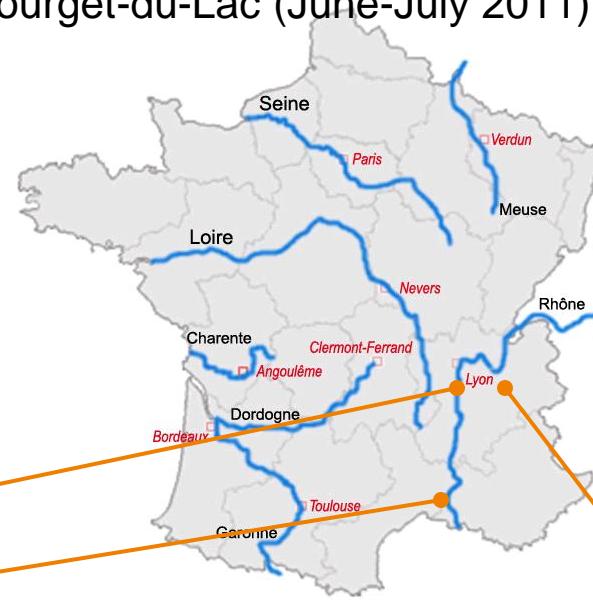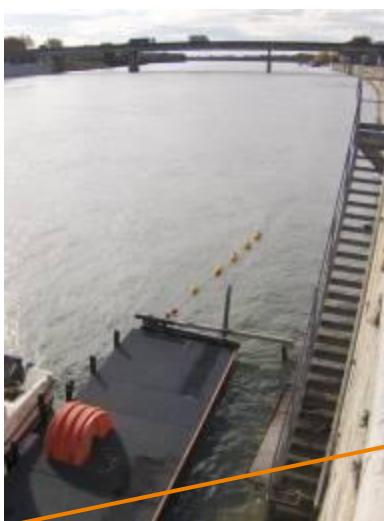

Ternay

Arles

Bourget-du-Lac

- ❖ Exposure of samplers:
  - ➢ At 1 m of depth using appropriate canisters, holders and buoys
  - ➢ During 1, 2, 3 and 4 weeks with duplicate and/or triplicate
- ❖ Monitoring of water temperature, velocity, conductivity, pH, DOC, TOC and ions concentrations

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Ternay: uptake of PCB and release of PRC
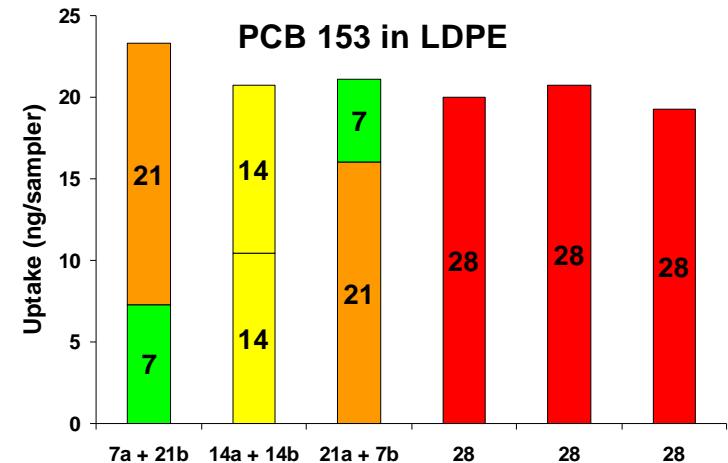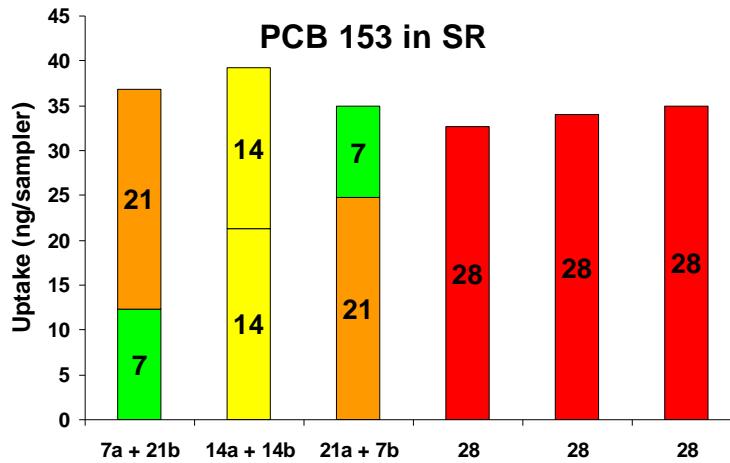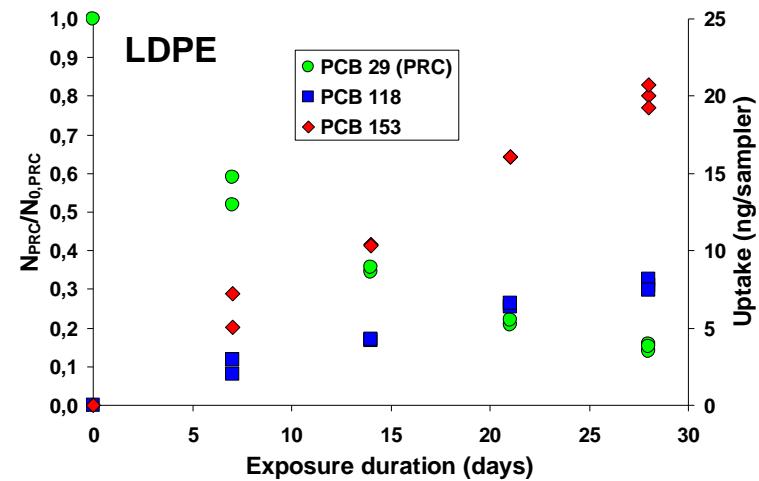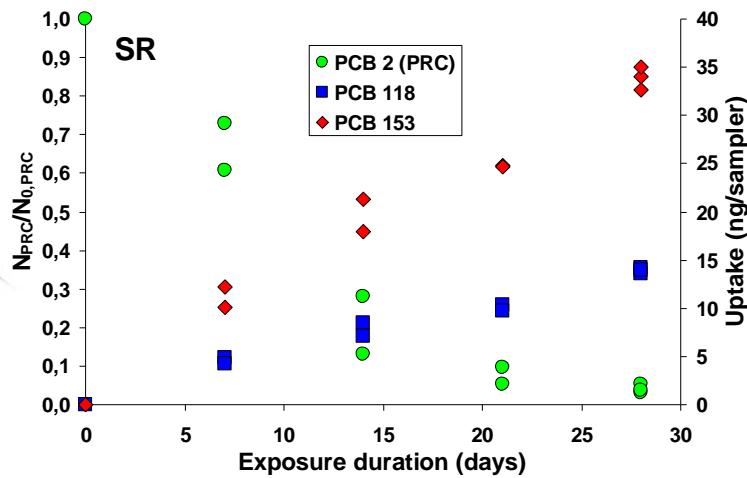
❖ Sampling in the integrative phase of uptake

Ternay: uptake of PCB

CFIS

- PCB 118
- PCB 153

Uptake (ng/sampler)

Exposure duration (days)
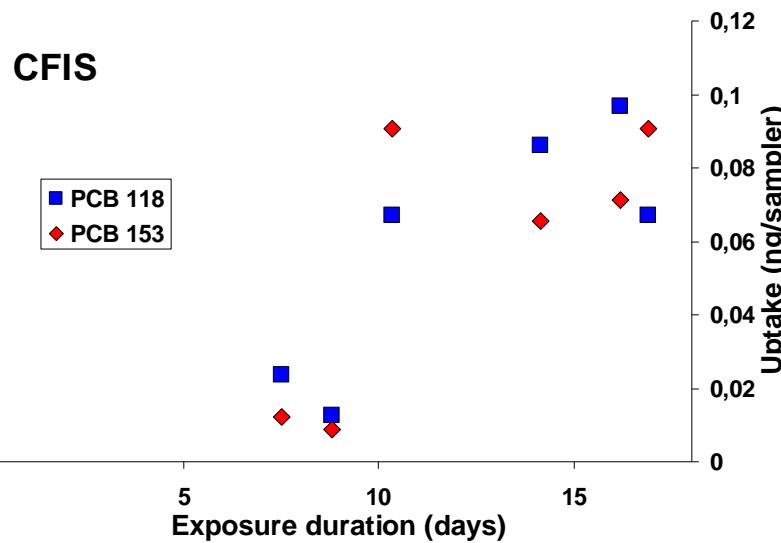
❖ SPMD: analytical problems, quantification unreliable for PRC of interest (samples currently analysed with another GC apparatus)

❖ Chemcatcher: low and erratic PCB accumulation

Ternay: TWA concentrations of PCB in water
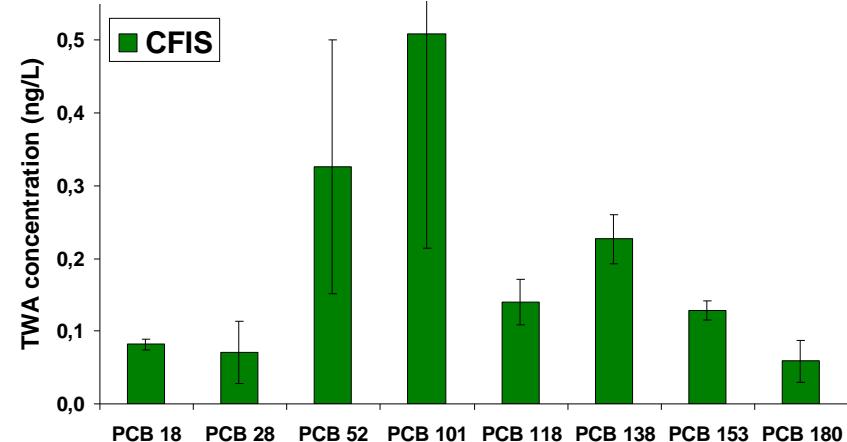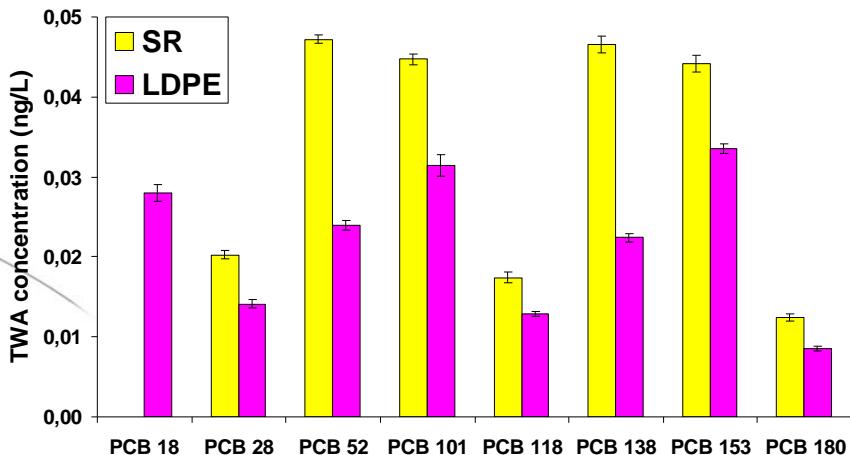
❖ Close results for SR and LDPE:

  ➢ $[PCB]_{SR} / [PCB]_{LDPE} < 2$

  ➢ RSD < 4%

❖ CFIS:

  ➢ $[PCB]_{CFIS} / [PCB]_{SR} < 11$

  ➢ 9% < RSD < 61%
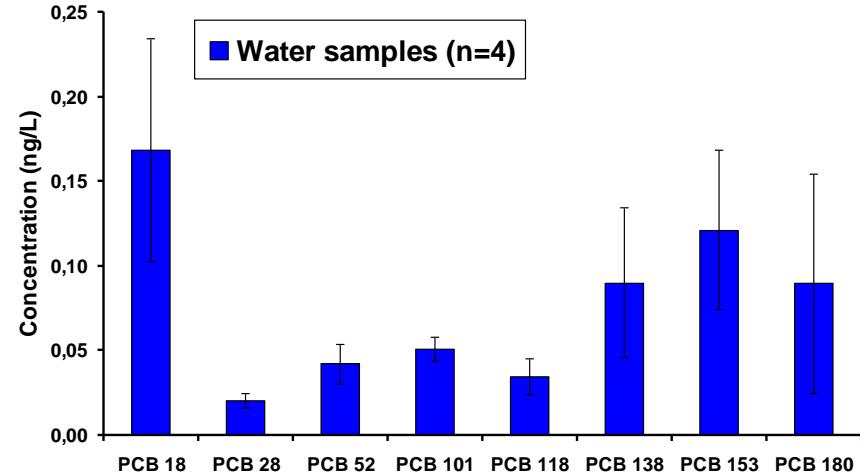
Conclusions about field campaign

❖ Similar results for SR and LDPE strips with good repeatability
  ➢ Results for dioxin-like PCB ?

❖ Higher TWA concentrations measured with CFIS
  ➢ Longer exposure durations to increase accumulated amounts ?

❖ Low and erratic uptake with Chemcatcher
  ➢ Probably not suitable for PCB monitoring

❖ Problem during analysis of SPMD extracts
  ➢ Use of another GC equipped with two columns in parallel

❖ Results of Arles and Lac-du-Bourget campaigns ?
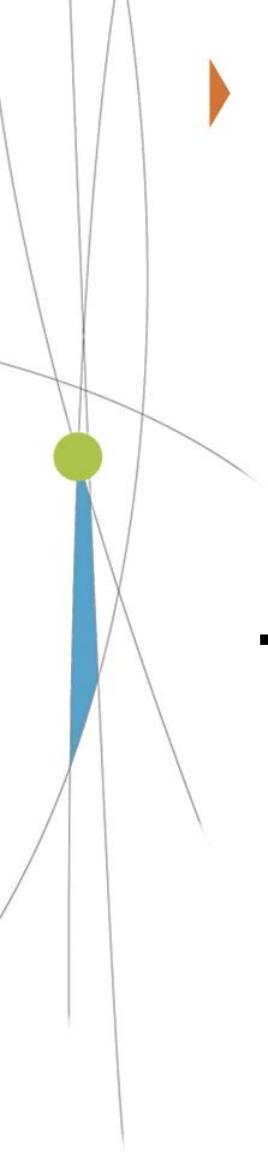
Thank you for your attention

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