28th September to 1st October · Donostia-San Sebastián (Spain)

DGTConference2015

"From DGT Research to Environmental Assessment"

Use and assessment of passive samplers by the French water national and regional authorities to improve the WFD implementation

ENVIRONMENTAL ASSESSMENT AND LEGISLATION, Oct. 1rst, 2015

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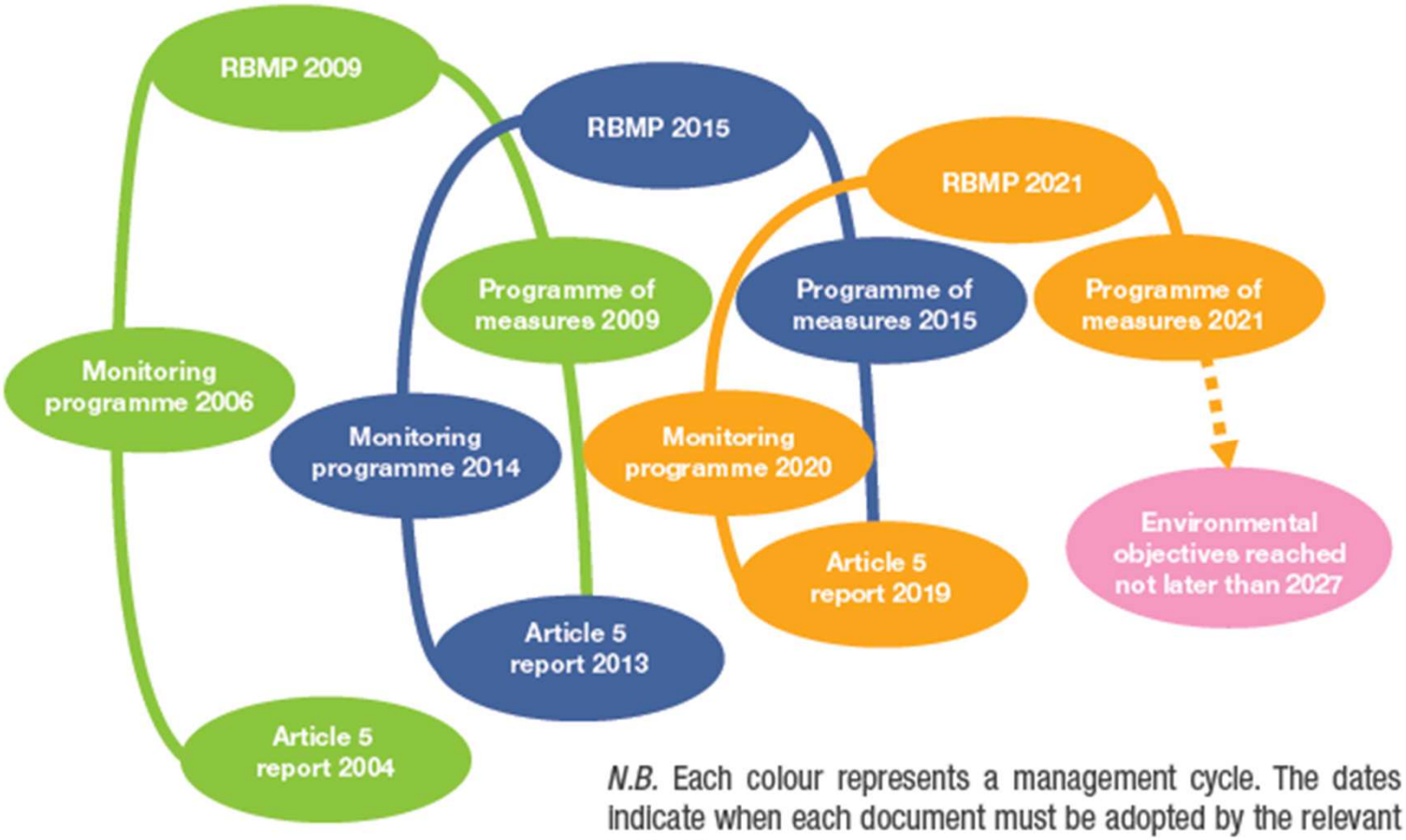
ONEMA
Office national de l'eau
et des milieux aquatiques

The Water Framework Directive (WFD)
6 years cycles process

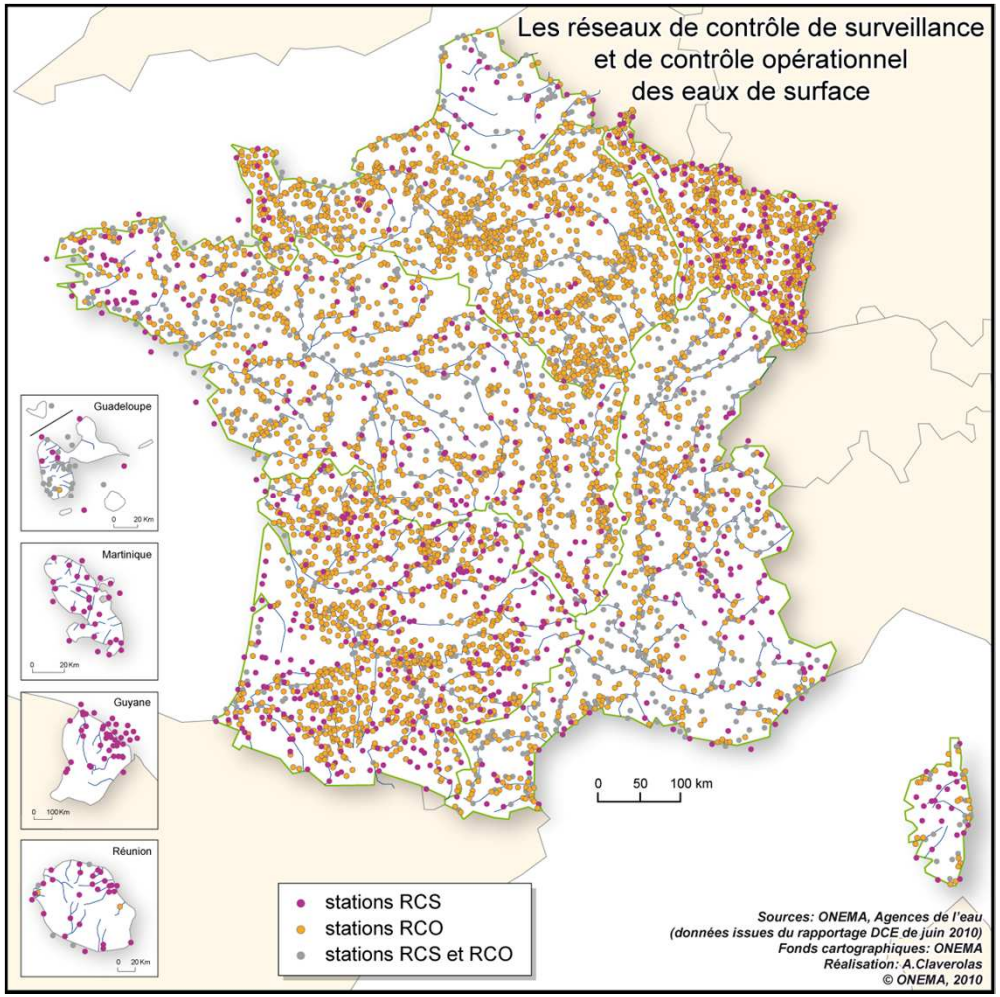


N.B. Each colour represents a management cycle. The dates indicate when each document must be adopted by the relevant authorities.

WFD Monitoring network in France

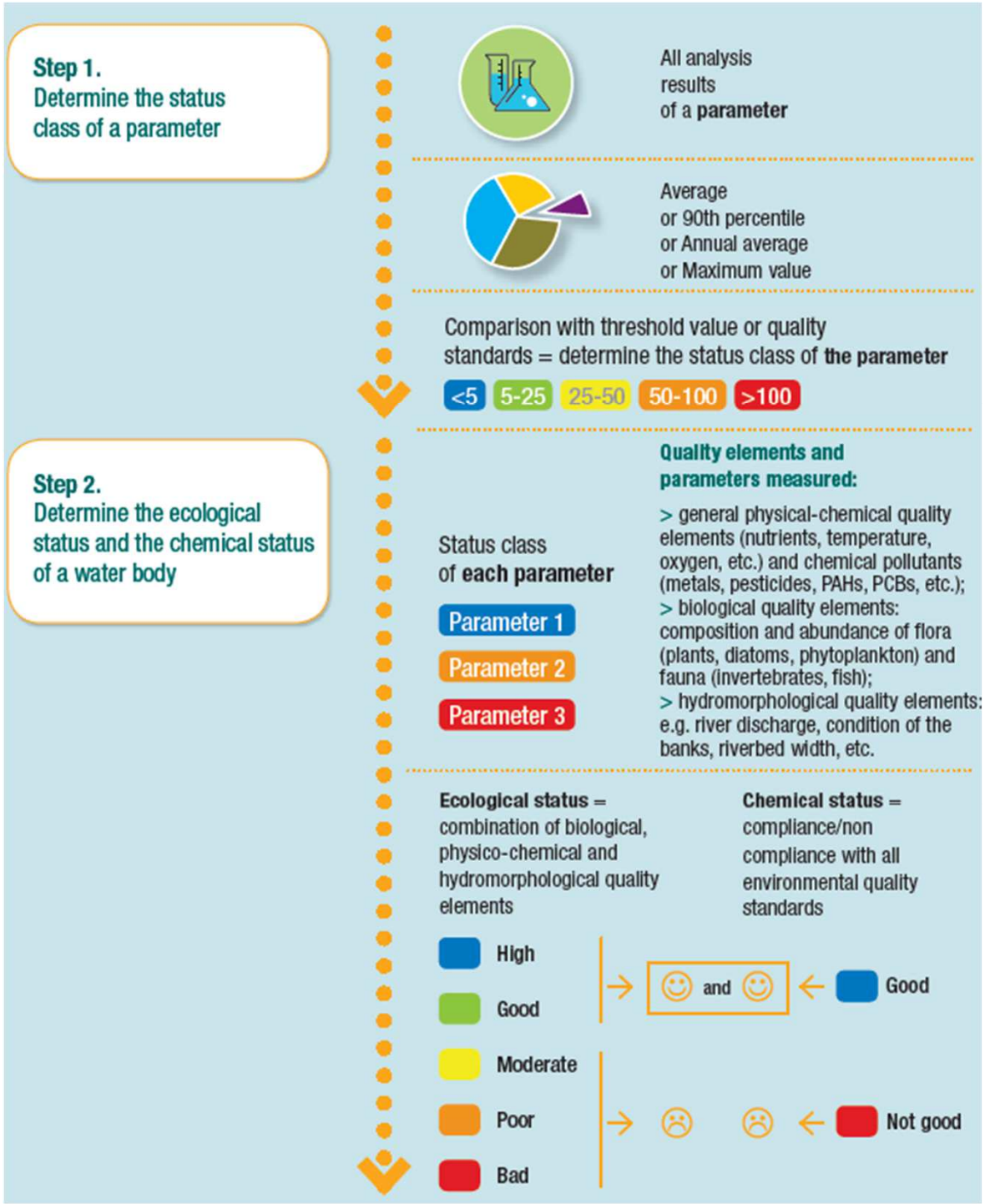
- 6 main river basins

- > 5000 monitoring points (1 point every 137 km of river)
- Around 20 to 30 samplings/site/WFD cycle

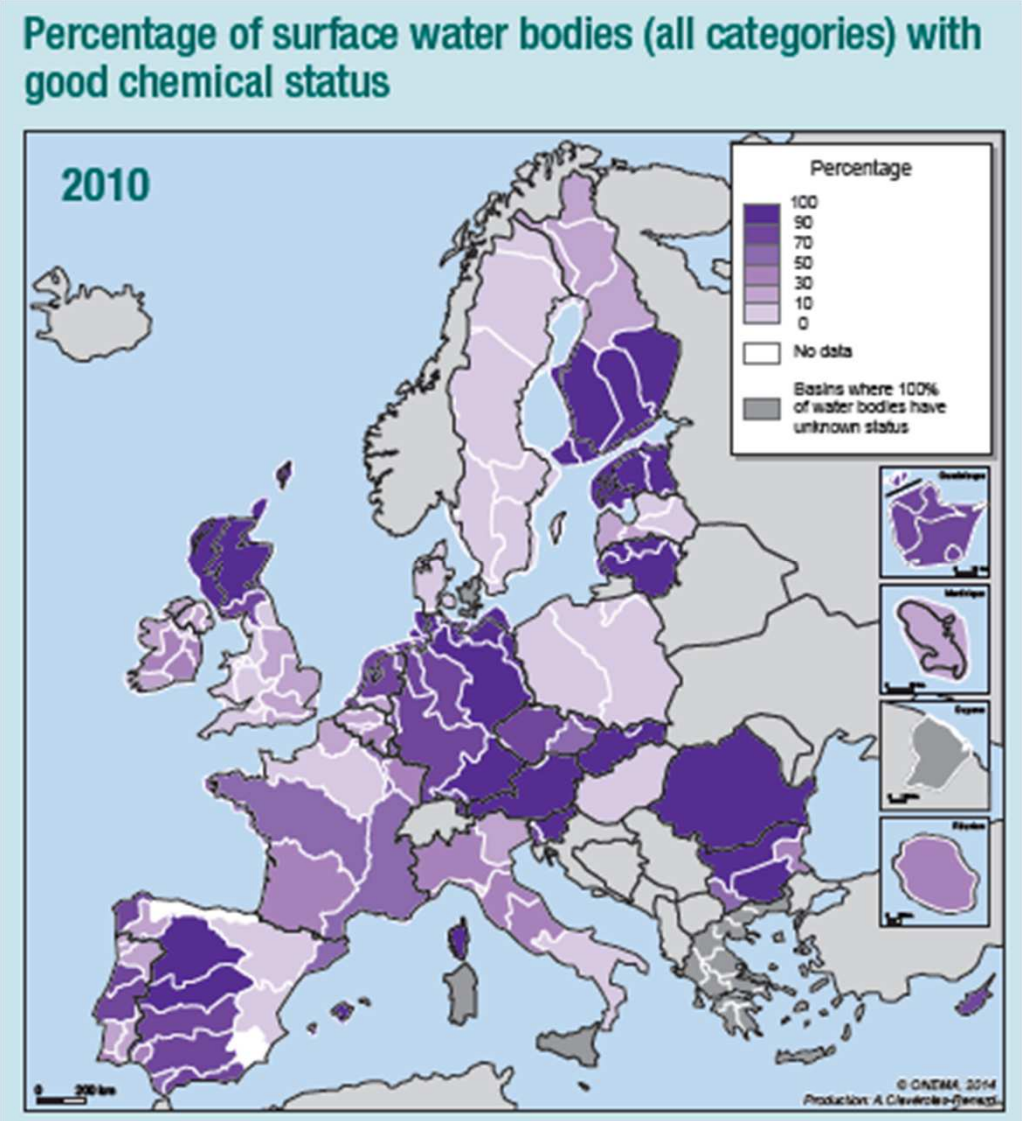


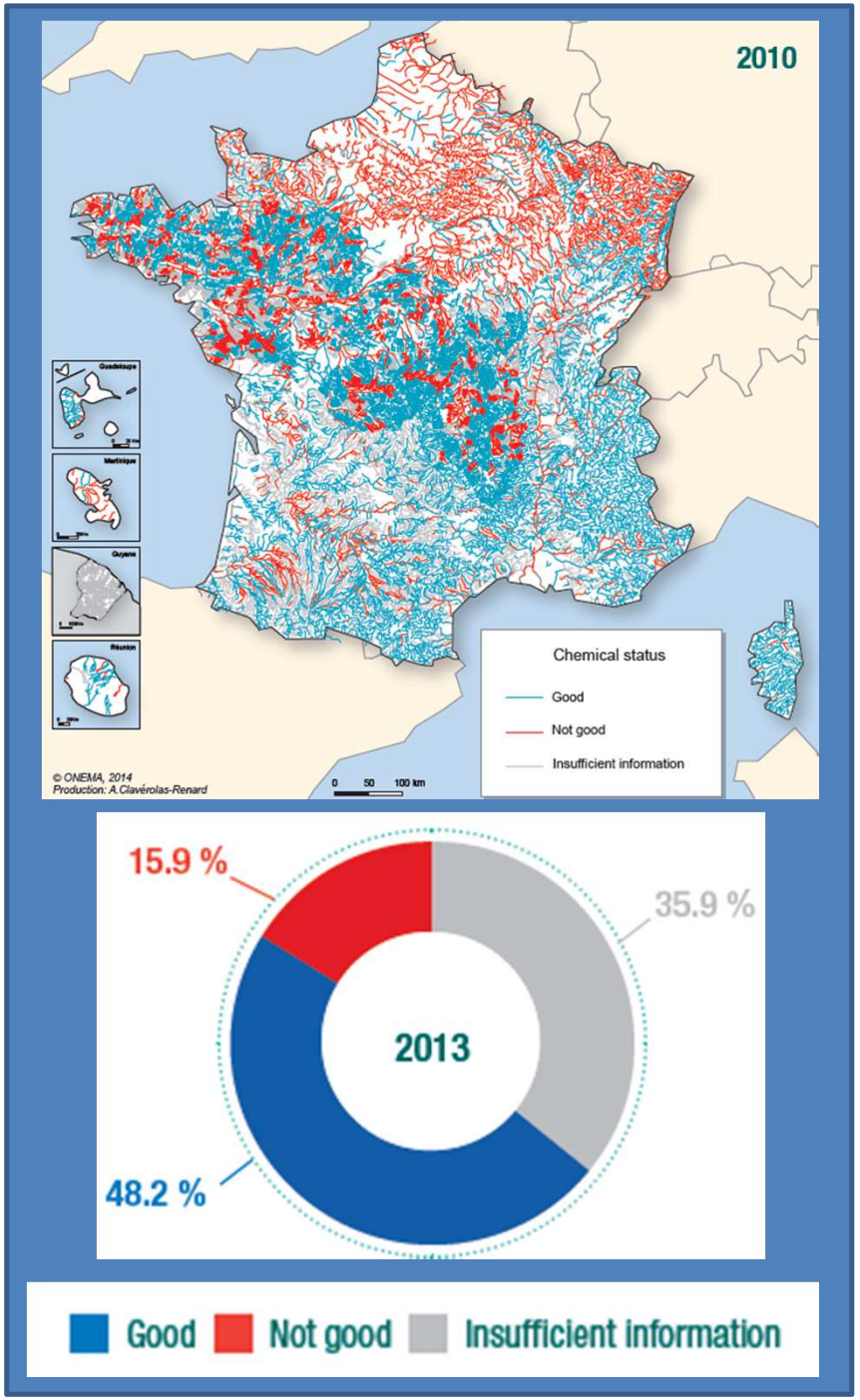
Chemical quality assessment according to WFD

- Chemical and ecological status: comparing concentration metrics (e.g. annual mean, percentiles,..) with threshold values
  - EQS for metals and organic substances
- EQS to be compared with
  - Mean annual dissolved fraction (<0.45µm) for metals
  - Mean annual whole water fraction (dissolved +suspended particulate matter SPM) for organics
- Trend monitoring for both surface and groundwaters
- QA/QC directive 2009/90/EC
  - LOQ< EQS/3
  - Uncertainty at LOQ<50%



Surface water chemical status in 2010: EU and France

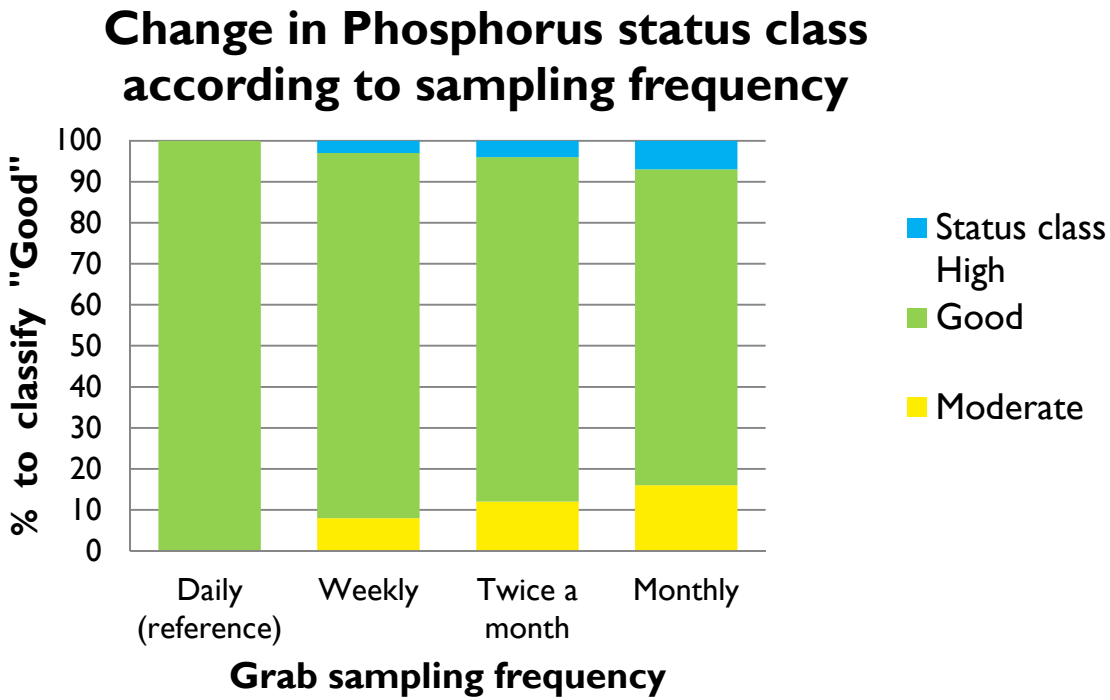




Sampling frequency vs. water quality assessment

- Illustrative example : Total Phosphorus (Ptot) in river water.
  - Consider for instance situations where Ptot metric calculated from daily monitoring produces a « Good » status class.
  - What would be the impact of degrading historical time series with lower sampling frequencies?

➢ Monte-Carlo calculation*, working on 88 years of data (8 rivers) originally monitored with a daily frequency**

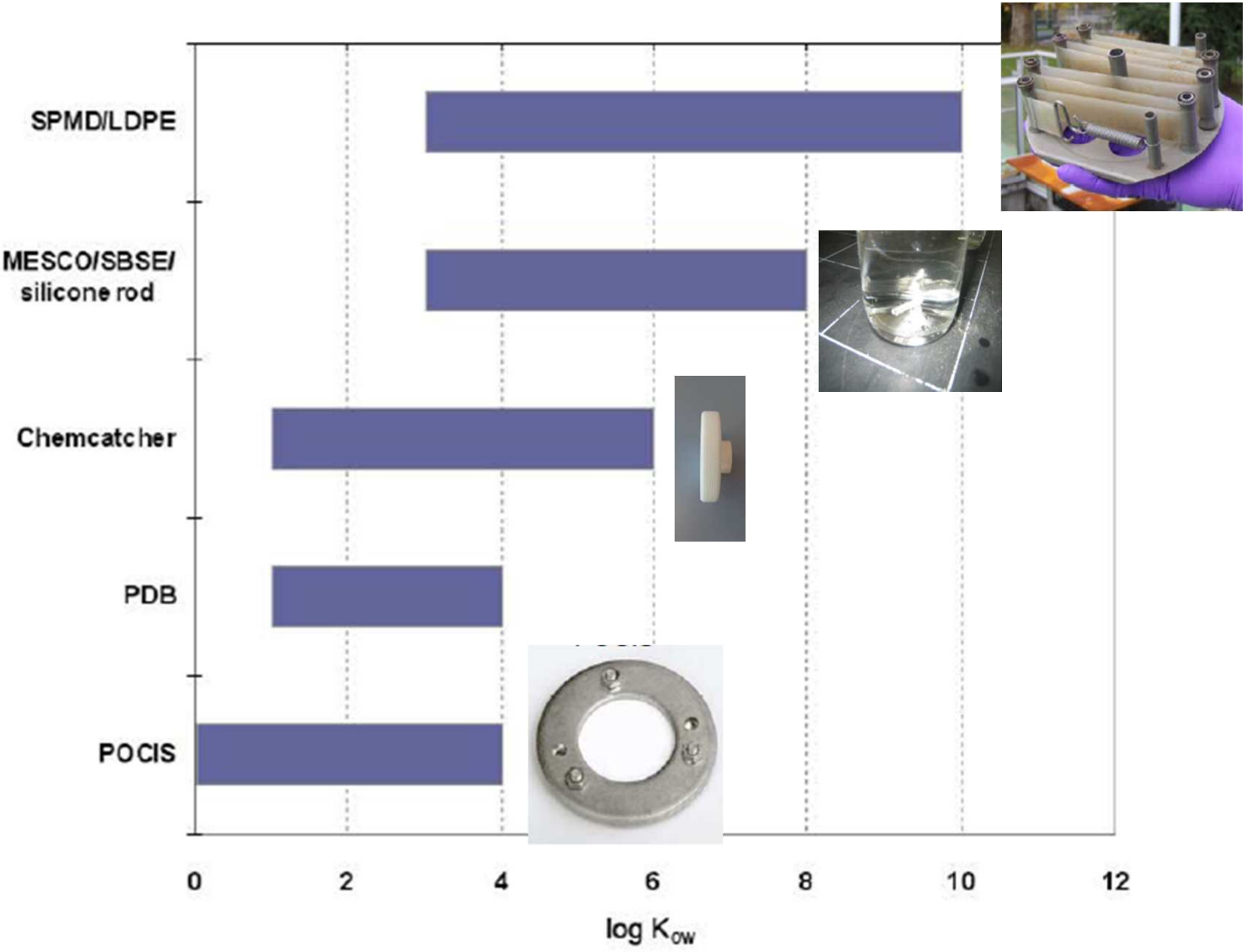


✓ Low frequency sampling significantly misleading
✓ Intensive monitoring is expensive
➢ **Interest for integrative (passive) sampling**

**Data from the Ohio tributary Monitoring Program led by the Water Quality Laboratory of the Heidelberg College, Ohio
* P.F.Staub, Université de Tours, UMR 6113 ISTO-Tours, 2007

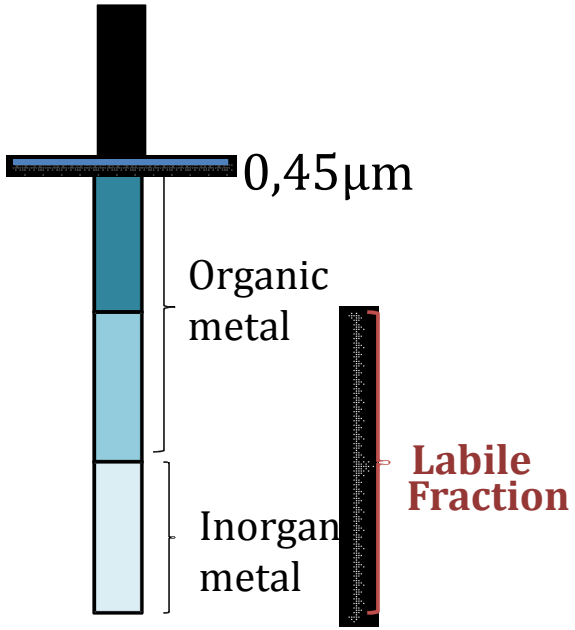
Main passive samplers (PS) assessed & used in France

DGTs for free metals



About the free dissolved chemical fraction captured by PS

- Known limits vs. WFD:
  - Hydrophobic PS do not capture SPM, whereas SPM contribute to WFD status assessment (adsorption if log Kow>5)
  - WFD requires metals to be quantified in the fraction <0.45µm. This does not correspond to the cut off limit of labile fraction captured by DGT
- However:
  - Cfree is considered to play the key role in chemical uptake by aquatic organisms, as opposed to SPM adsorbed fraction
    - By the way do EQS integrate SPM exposition?...
  - Adsorption on SPM negligible for logKow<5 (hydrophilic compounds)
  - Cfree is a more stable parameter than a concentration measured in whole water: in favor of trend assessment



What are the expected added values of PS for WFD?

- Allan, *et al*. (2006)
  - measurement of time weighted average (TWA) concentrations
  - screening of pollutant for presence or absence (with improved limits of detection and quantification, LODs and LOQs),
  - assessment of spatial and temporal trends in level of pollutants
  - identification of sources of pollution, establishment of pressure-impacts relationships,
  - integrated assessment of pollutant load across national boundaries

I.J. Allan, G.A. Mills, B. Vrana, J. Knutsson, A. Holmberg, N. Guigues, S. Laschi, A.-M. Fouillac, R. Greenwood, Trends in Analytical Chemistry, 25 (2006) 704.

French WFD managers interviews on PS: level of interest grid

Functions of PS		WFD operations: Design Monitoring Network	Assess Parameter Status	Determine Trends	Follow up Prgs of Measures	Pollution in discharges	Source identification
Spatial analysis	Mapping of contamination, source localization	**High**					**High**
	Depth profiles (GrdWaters, lakes)	**High**					
Quantitation	TWA	Moderate	**High**	**High**	**High**	**High**	Moderate
	Pollution flows	Moderate	Moderate	Moderate	**High**	**High**	Moderate
Qualitative analysis	Trace detection	**High**	**High**	Moderate	Moderate	Moderate	Moderate
	Emerging contaminants screening	**High**	Moderate	Moderate	Moderate	Moderate	**High**
Time-related analysis	Trend monitoring			**High**	**High**	Moderate	
	Intermittent pollution detection		Moderate			Moderate	Moderate
Biota-related analysis	PS extracts for bioassays			Moderate		Moderate	Moderate
	Biota contamination proxy		Moderate	Moderate	Moderate		

Identified knowledge gaps & implementation challenges

- Diversity:
  - Many commercially available and home made PS… which one for which application?
  - Various practices in labs (analysis, data interpretation) or in the field.

- Technology:
  - Adsorption- based samplers (e.g. POCIS) provide semi-quantitative data only
  - Solutions for very hydrophilic and/or ionisab substances?
  - Solutions for some priority substances (e.g. PFOS)?

French chemicals monitoring organization under WFD

Regulation

European Commission

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Emerging substances

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LES AGENCES DE L'EAU
ÉTABLISSEMENTS PUBLICS DU MINISTÈRE EN CHARGE DU DÉVELOPPEMENT DURABLE

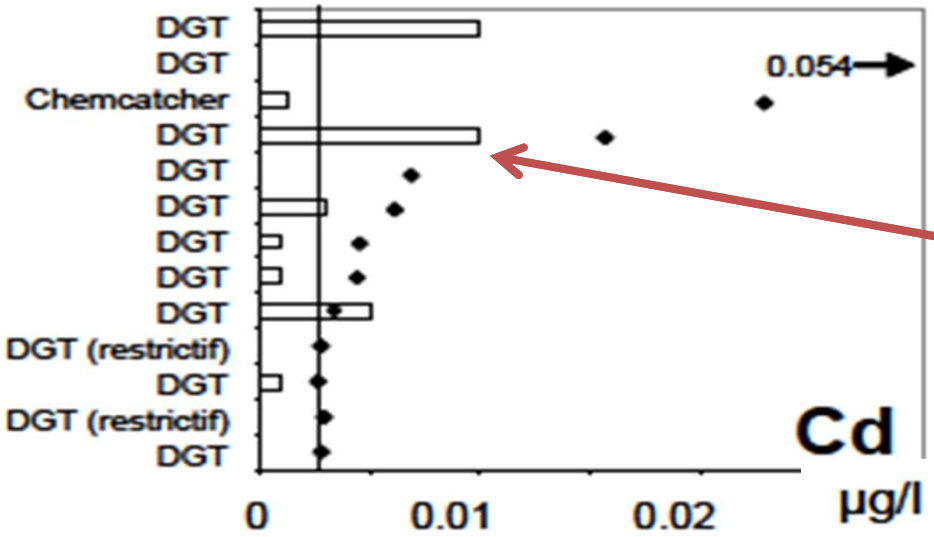
River basins monitoring programs and water quality classification

Field studies on water contamination

Validation of innovative metrology

Recent exercises and lessons in France : Aquaref interlaboratory exercise 2010

- Metals, PAHs and pesticides in surface waters. 2 rivers sites and one marine lagoon. 24 laboratories participated. Various PSs (DGT, POCIS, SPMD, SR, LDPE)
- Good overall consistency among TWA results, with satisfactory RSD considering trace levels and diversity of practices and tools
- Many PSs TWA results obtained significantly below the LOQ of classical grab sampling (for PAH, also for pesticides and metals)



➢ Field blanks issues : Cd, Cr, Pb, Zn and some PAH

C.Miège *et* al.; TrAC Trends in Analytical Chemistry June 2012, Volume 36, Pages 128-143

Large scale PS campaigns in France

- Since 2008, various regional campaigns led by Ifremer on the Mediterranean shores, and in ultra-marine locations (La Réunion, Mayotte, Antilles, Guyane) : >200 parameters, DGT & POCIS.
  - ➢ *Cf. this afternoon presentation by M.J. Belzunce-Segarra.*

Ifremer

- One nationwide campaign led by Ifremer in 2012, 40 marine sites (half in ultra-marine locations), focused on 34 polar emerging substances with POCIS : 13 were detected, 4 of them with significant frequencies, consistently with continental observations. Positive experience but :
  - ➢PS implementation strongly depends on weather conditions and hydrodynamics
  - ➢several PS losses (13%)
  - ➢exposure sometimes over-extended (waiting for good retrieval conditions)
  - ➢rust growing onto POCIS, systems laid exposed to robbery or vandalism…

Ifremer

- 20 POCIS extracts from continental sites were also collected at the same period by Ineris to further expose them to bioassays
  - ➢PS to serve ecotox screening in polluted sites identification

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Some recent PS applications by river basin water agencies

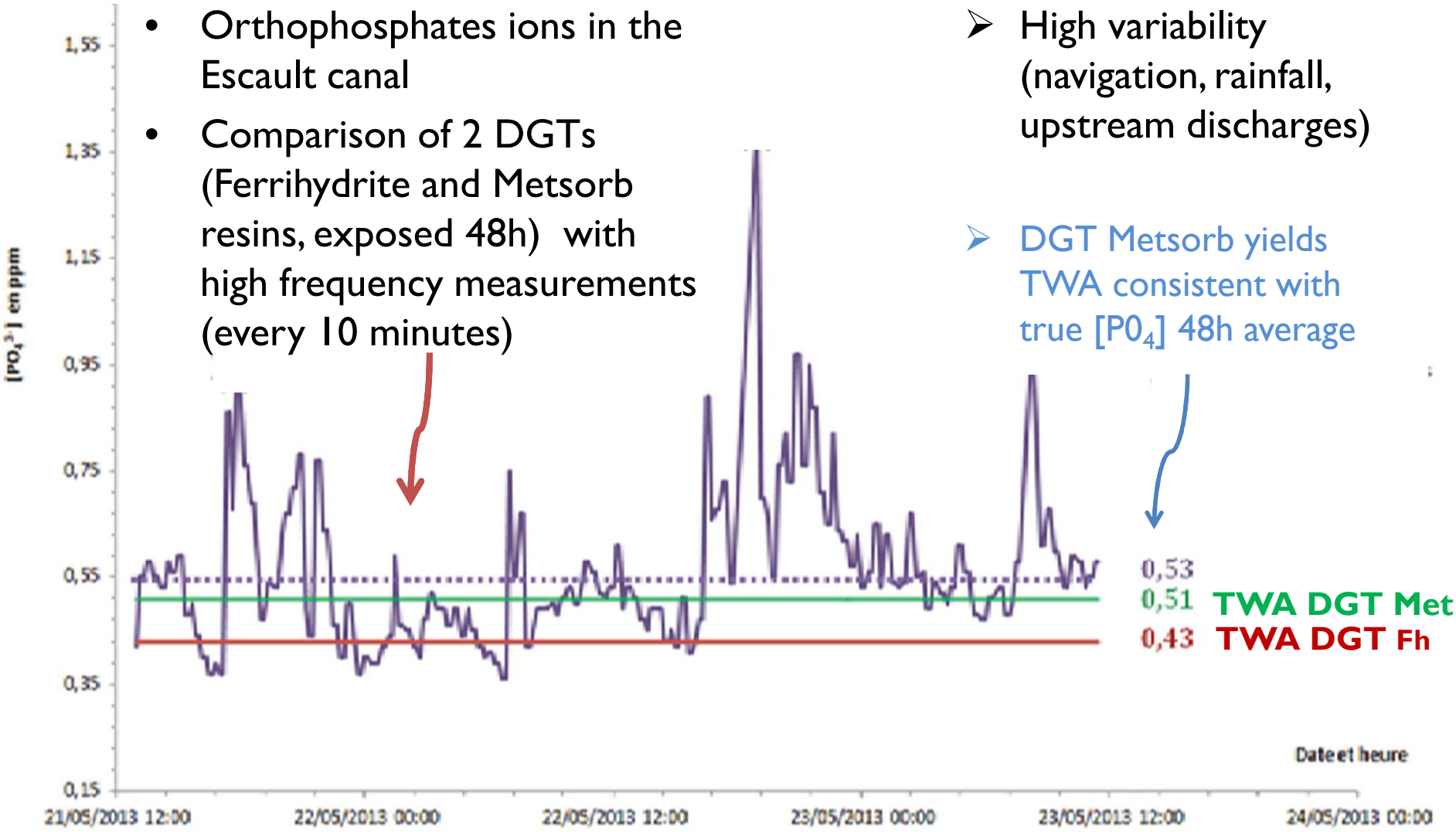
DGT representativity of phosphate mean values

www.eau-artois-picardie.fr

- Orthophosphates ions in the Escault canal
- Comparison of 2 DGTs (Ferrihydrite and Metsorb resins, exposed 48h) with high frequency measurements (every 10 minutes)

➢ High variability (navigation, rainfall, upstream discharges)

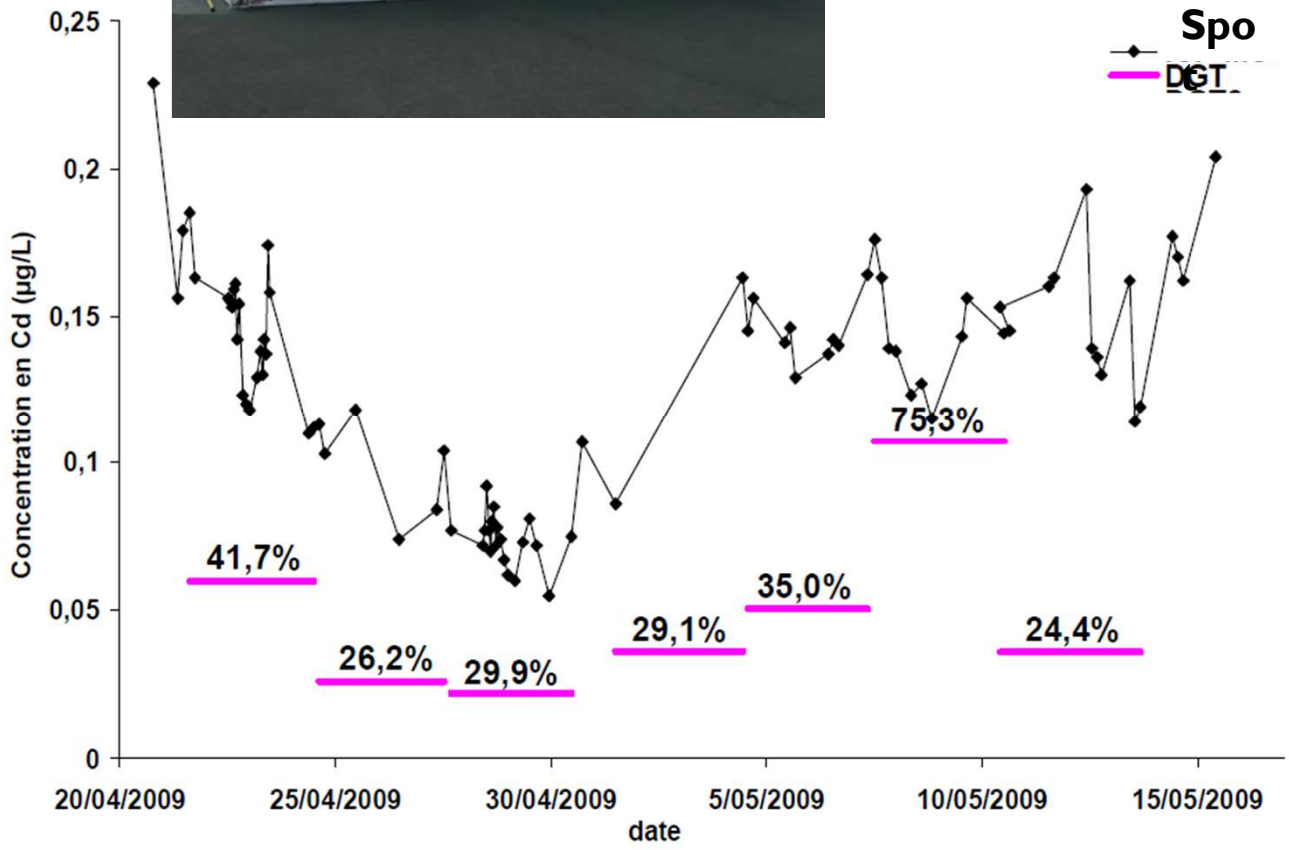
➢ DGT Metsorb yields TWA consistent with true [PO_4] 48h average



Dynamics of metal lability

- Deûle canal, downstream of a former metal industry plant
- 1 month study: Cd Pb Cr Mn Fe Co Ni Cu Zn As
- 3 spot samples in water/day
- DGT 72h
- DGT/spot= %age of labile metals, varies much
  - ➢ labile fraction can't be predicted by regular spot sampling
  - ➢ significance vs. bioavailabilty?
  - ➢ some ratio>>100%?? (Pb, Mn)

On-site portable clean room



DGT for Organo-Tin (anti fouling)

- Tributyl-Tin (TBT) exceeded EQS in Bidassoa water-body in 2009, confirmed by oysters anlaysis (Ifremer)
- Investigative control will be carried out (2016) thanks to DGTs, in continuous monitoring mode (several weeks).

Study program:

- Development & calibration of a **TBT DGT** in fresh&marine waters
- In-situ testing in Aracachon harbour & Bidassoa
- Search for point sources (10 monitoring sites)
- Simultaneously: caged clams will be set up aside of DGTs to check out bioavailability.

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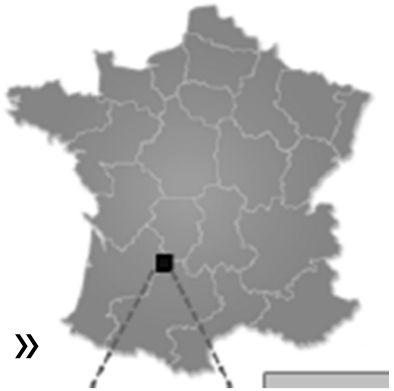
Field blanks studies for DGT



- River basins of the Trec and Auvézère
- Metals investigation with DGT (2013 & 2014)
- Blanks contamination studies
  - Measured concentrations in rivers below the « River LOQ » values for Cd, Cu and Ni: no results could be validated.

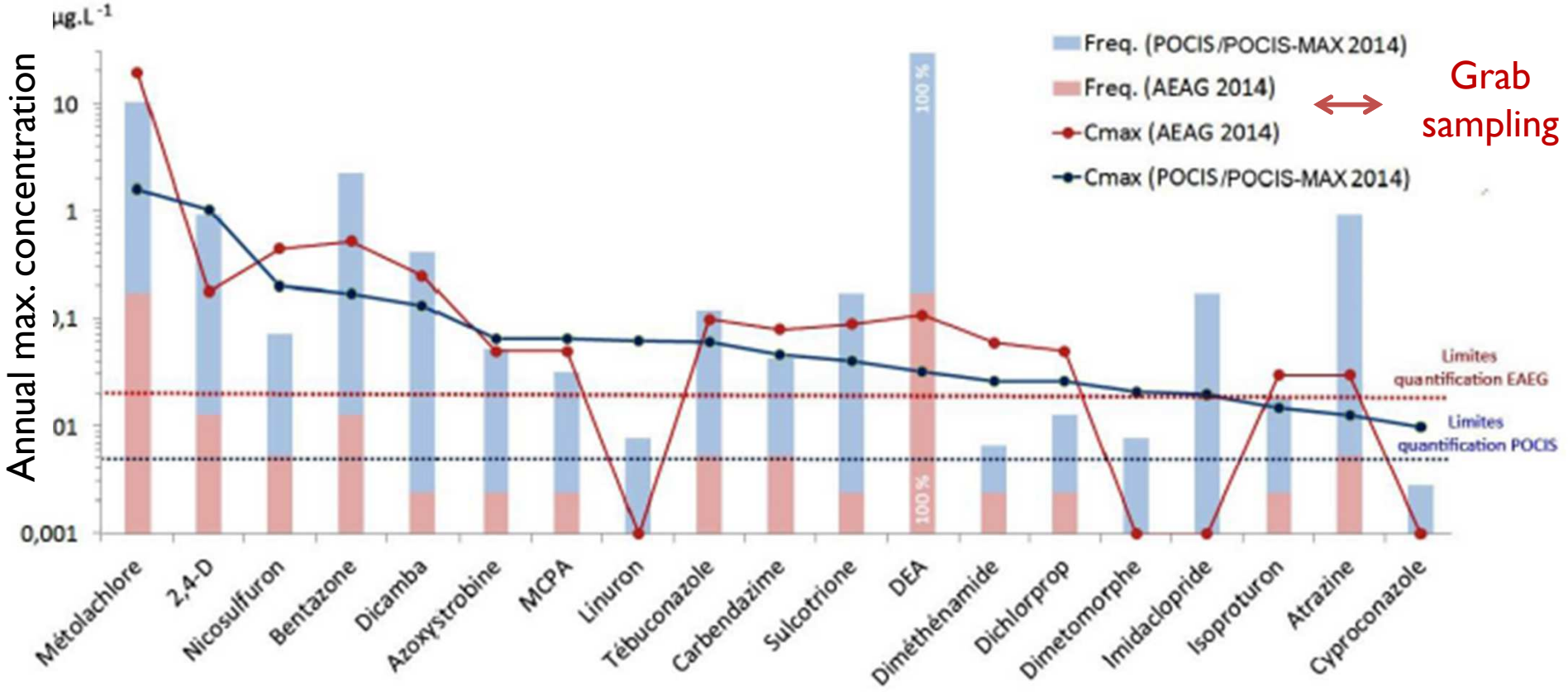
➢ **Importance of validating methodology for operational LOQ**

	Unité ($ng.L^{-1}$)	As	Cd	Cu	Ni
Analysis only →	LQ « analytique »	6	0,2	4	9
Resin fab. process →	LQ « fabrication »	6	0,9	14	19
PS mount/dismount operations →	LQ « rivière » 2013	6	0,9	700	19
	LQ « rivière » 2014	6	30	900	1000

irstea Université de Limoges GRESE Groupement de Recherche Eau Sol Environnement AGENCE DE L'EAU ADOUR-GARONNE ETABLISSEMENT PUBLIC DU MINISTERE DU DEVELOPPEMENT DURABLE

Comparison POCIS vs. grab sampling for 20 pesticides. River basin of the Trec –Canaule.

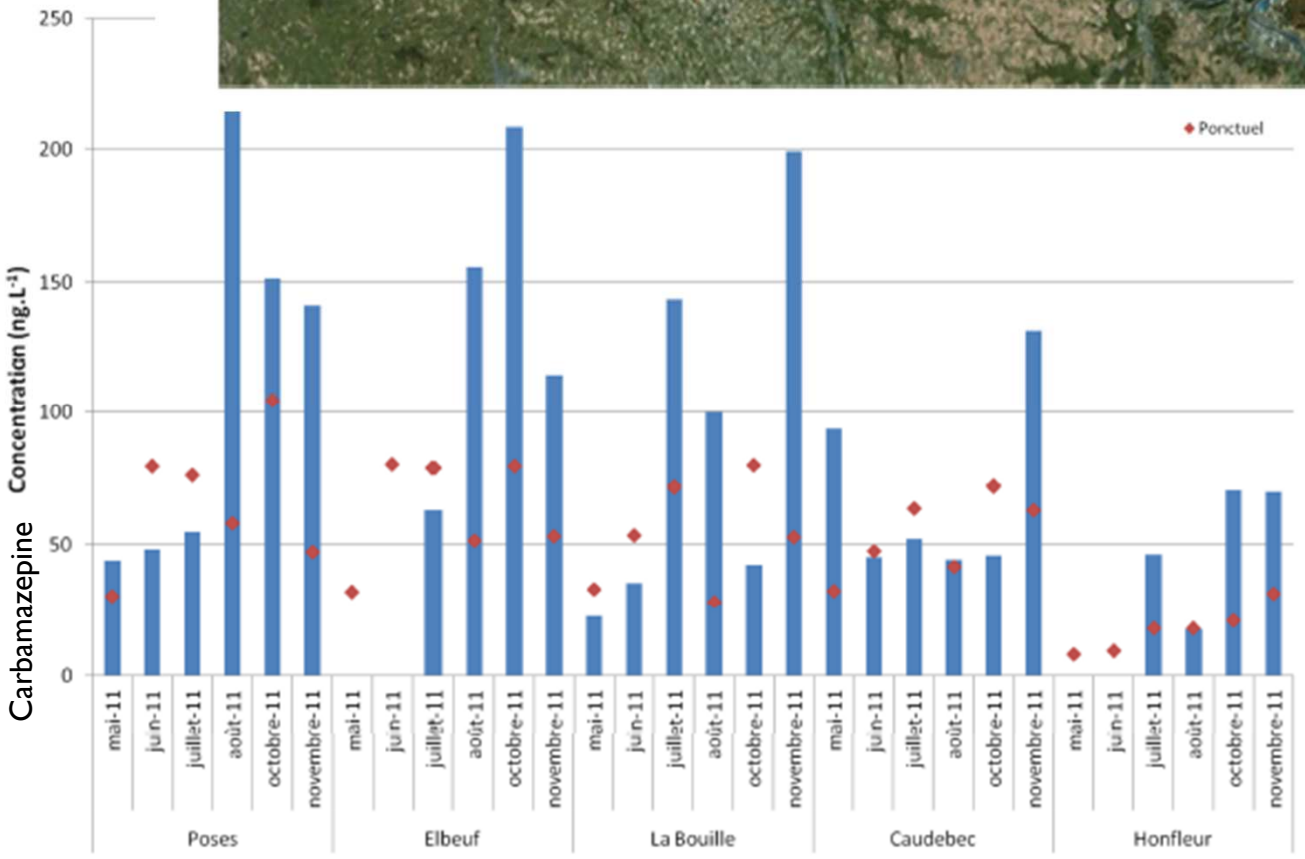
- Successive POCIS 2 weeks exposures in 2014
- Clear plus for POCIS in terms of environmental sensitivity: Higher quantification frequencies, more molecules detected
- Similar max concentration profiles for POCIS and grab, but POCIS attenuates maximum values



Pharmaceutical residues seasonal dynamics in the Seine river estuary (MedSeine program 2012)

- 5 study river-sites, influenced by 4 WWTP, from spring to fall 2011.
- POCIS adapted for 53 molecules

➢ Similar values as grab sampling, but different seasonal profiles: integrative info brought by POCIS



eau seine NORMANDIE

Seine-Aval
GROUPEMENT D'INTÉRÊT PUBLIC

Needs identified to convince policy-makers to accept passive sampling in regulatory monitoring

Trends in Environmental Analytical Chemistry 8 (2015) 20–26

Contents lists available at ScienceDirect

Trends in Environmental Analytical Chemistry

journal homepage: www.elsevier.com/locate/teac

Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment – Achievements to date and perspectives

Cécile Miège [a,*], Nicolas Mazzella [b], Ian Allan [c], Valeria Dulio [d], Foppe Smedes [e,f], Céline Tixier [g], Etienne Vermeirssen [h], Jan Brant [i], Simon O'Toole [j], Hélène Budzinski [k], Jean-Philippe Ghestem [l], Pierre-François Staub [m], Sophie Lardy-Fontan [n], Jean-Louis Gonzalez [o], Marina Coquery [a], Branislav Vrana [e]

Needs identified to convince policy-makers to accept passive sampling in regulatory monitoring

- Drafting of guidelines and clear Quality Assurance/Quality Control rules
  - blank management, calibration, TWA calculations , exposure duration and frequency, installation and removal, …

- New interlaboratory comparison scheme to mimic PS routine use. Twostep exercises:
  1. Proficiency Test (PT) for the analysis extracts of PS
  2. Intercomparison of PS field-deployment and analysis+TWA by profiecient labs

- Certified PSs to demonstrate lab performances (i.e., conservation, extraction, purification and analytical steps)

- PS-based assessment criteria in relation to existing EQS

- Better share experience between marine and continental water expert communities.

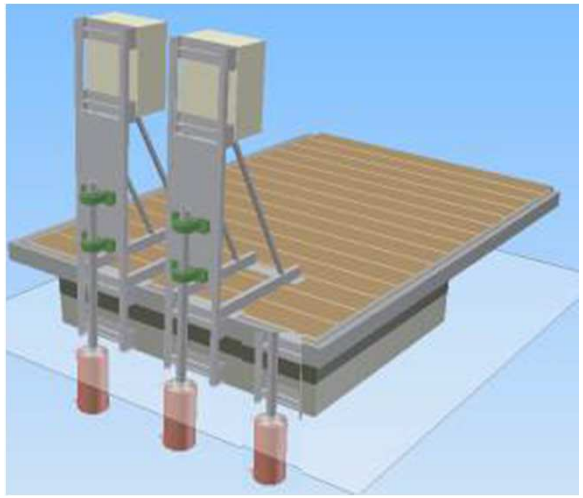
French PS developments and expertise brought by Aquaref

Does PS sensitivity comply with WFD EQS requirements?

- WFD analytical sensitivity target: LQ<EQS/3
- Comparison of PS LQs with grab sampling from French labs active in WFD surveillance
- 56 regulated (non volatile) molecules investigated for marine waters assessment
  - 37 hydrophobic (log Kow > 3)
    - 24 of which exhibit sensitivity issues using classical grab sampling
      - 14 of which cannot either be monitored in biota (no biota EQS)
    - **35 of which could be met adequately with PS (SPMD, SR of LDPE)**
  - 11 hydrophilic (log Kow < 3)
    - 8 of which can be adequately measured by either grab sampling or POCIS
    - 3 for which neither grab nor POCIS meet specs
  - 8 metals
    - sensitivity with usual grab sampling is problematic for As and Cu
    - DGT meets all specs, but specific DGT required for As
    - Hg to be monitored in biota for WFD status assessment, but other apps exists
- Overall:
  - PS offer clearly better analytical sensitivity compliance for hydrophobics compounds,
  - for other substances PS and grab sampling are equally compliant, PS providing better representativity

New designs for PS

- Solutions to limit fouling (copper grid around POCIS), on-site water agitators to stabilise sampling rates…
- Developments to improve PS sensivity and reliability:
  - test of new materials, like PVMQ silicone elastomer rods, for pesticides with medium-high hydrophobicity
  - new DGT for Hg and methyl-Hg using new diffusive and resin layer, allow low blank contamination
    - cf. pres. by Aymeric Dabrin, last sept 29th



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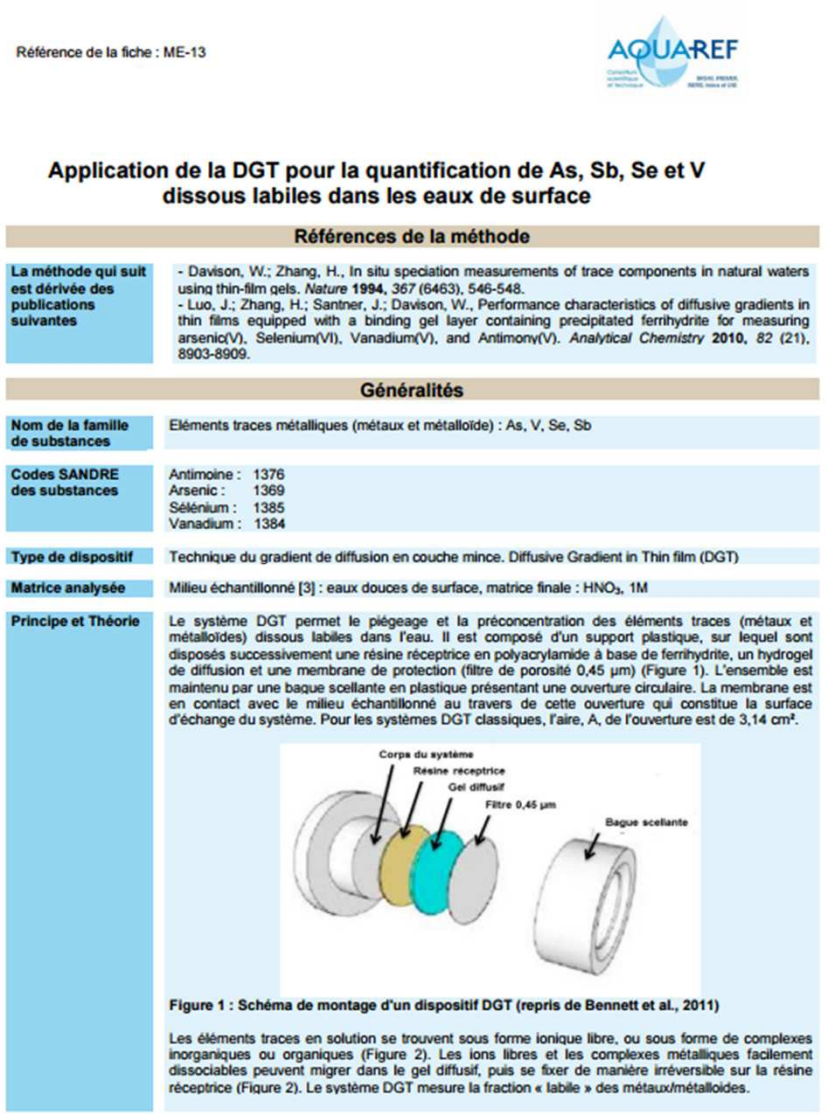
Aquaref reference protocols : www. aquaref.fr

- DGT: metals (Ag, Al, Se, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn), and more recently As,Sb, Se and V
- Polar compounds with POCIS
  - including herbicides (with HLB, and more recently with Ion Exchange Sorbent resin) , pharmaceuticals,
- Hydrophobic compounds with SPMD in surface water and wastewater (e.g. PAHs and PCBs)



Référence de la fiche : ME-13

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Application de la DGT pour la quantification de As, Sb, Se et V dissous labiles dans les eaux de surface

Références de la méthode

La méthode qui suit est dérivée des publications suivantes	- Davison, W.; Zhang, H., In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature* **1994,** *367* (6463), 546-548. - Luo, J.; Zhang, H.; Santner, J.; Davison, W., Performance characteristics of diffusive gradients in thin films equipped with a binding gel layer containing precipitated ferrihydrite for measuring arsenic(V), Selenium(VI), Vanadium(V), and Antimony(V). *Analytical Chemistry* **2010,** *82* (21), 8903-8909.

Généralités

Nom de la famille de substances	Eléments traces métalliques (métaux et métalloïde) : As, V, Se, Sb
Codes SANDRE des substances	Antimoine : 1376 Arsenic : 1369 Sélénium : 1385 Vanadium : 1384
Type de dispositif	Technique du gradient de diffusion en couche mince. Diffusive Gradient in Thin film (DGT)
Matrice analysée	Milieu échantillonné [3] : eaux douces de surface, matrice finale : HNO_3, 1M
Principe et Théorie	Le système DGT permet le piégeage et la préconcentration des éléments traces (métaux et métalloïdes) dissous labiles dans l'eau. Il est composé d'un support plastique, sur lequel sont disposés successivement une résine réceptrice en polyacrylamide à base de ferrihydrite, un hydrogel de diffusion et une membrane de protection (filtre de porosité 0,45 µm) (Figure 1). L'ensemble est maintenu par une baque scellante en plastique présentant une ouverture circulaire. La membrane est en contact avec le milieu échantillonné au travers de cette ouverture qui constitue la surface d'échange du système. Pour les systèmes DGT classiques, l'aire, A, de l'ouverture est de 3,14 cm².

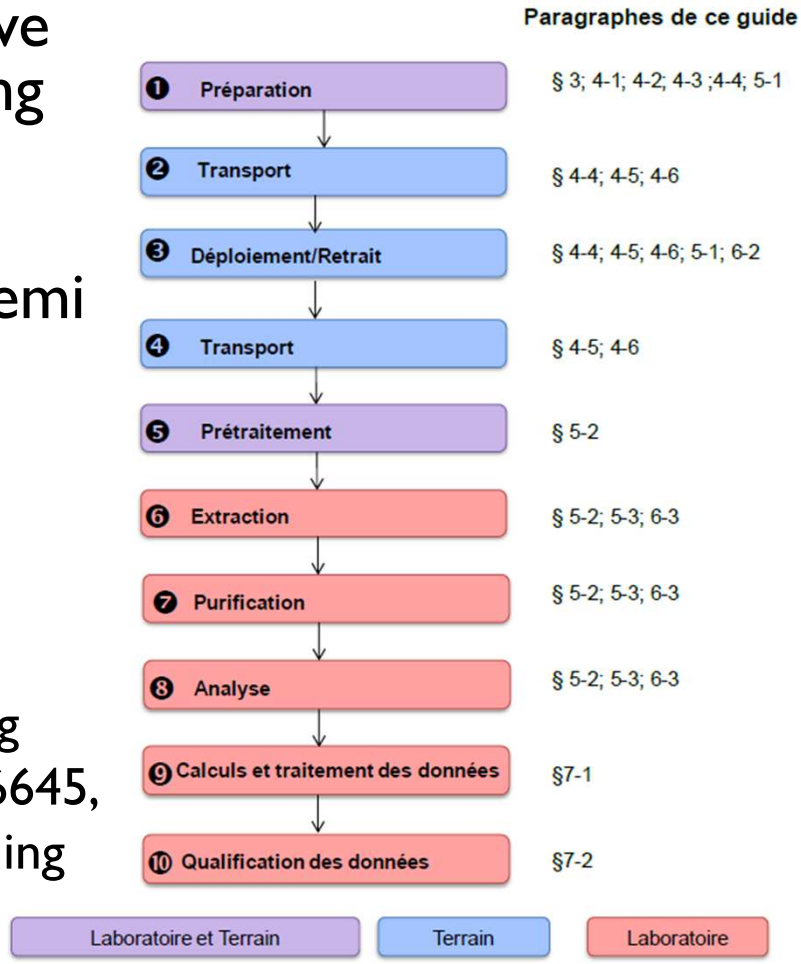
Figure 1 : Schéma de montage d'un dispositif DGT (repris de Bennett et al., 2011)

Les éléments traces en solution se trouvent sous forme ionique libre, ou sous forme de complexes inorganiques ou organiques (Figure 2). Les ions libres et les complexes métalliques facilement dissociables peuvent migrer dans le gel diffusif, puis se fixer de manière irréversible sur la résine réceptrice (Figure 2). Le système DGT mesure la fraction « labile » des métaux/métalloïdes.

Aquaref guidance documents on PS

- To complement the ISO 5667-23 which only gives general guidelines for passive sampling in surface waters, and existing USGS guidance (SPMD & POCIS)
- Aquaref Guidance for an operational monitoring of aqueous system with semi permeable membrane device SPMD

- Under work: Method for the measurement of metal concentration with passive sampling by diffusive gradient in thin films
  - ➢ Similar content as above but for metals
  - ➢ Document structure adapted from existing standards for chemicals in air (CP CEN 16645, ISO1600-6…), which integrate both sampling and analysis
    - ➢ Investigation about standardization opportunities…



Field training

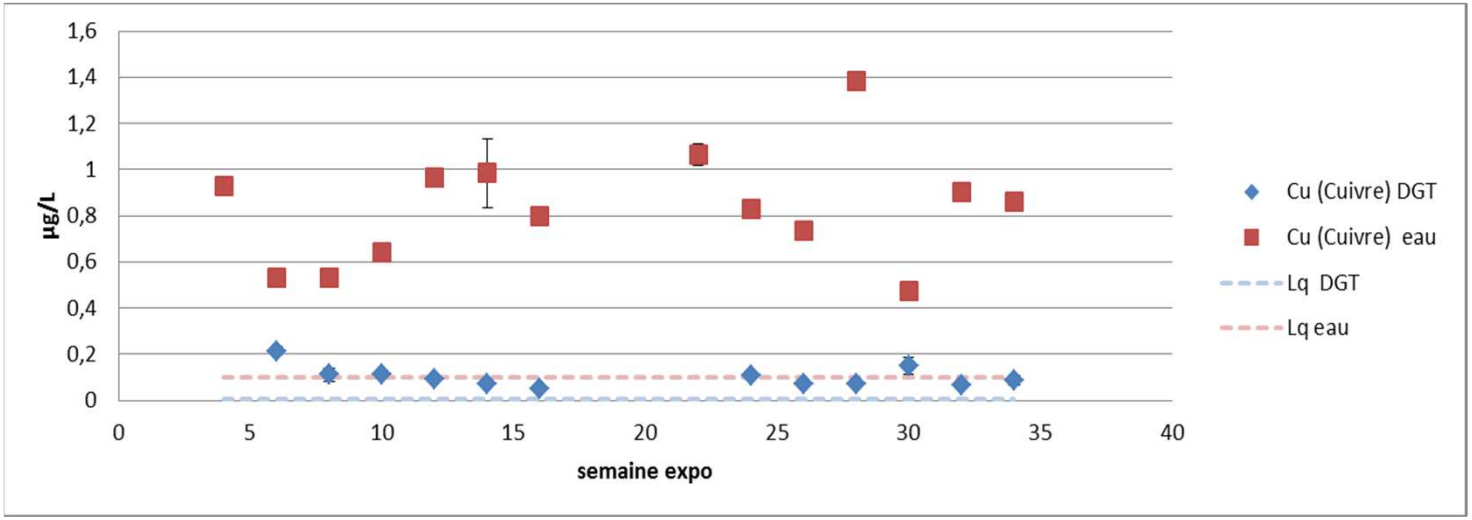
- Training needs mainly driven by data collection campaigns performed since 2008 by Ifremer in marine waters, in continental Europe and ultra-marine territories.
- More than 250 people, non-experts, have already been taught by Ifremer: campaign implementation teams, consultancies, WFD monitoring program managers,..
- Theory, and practice DGT, POCIS : PS preps, in-water setting up, retrieval, conditionning before shipment to labs…
- Tutorial documents also about to be converted into a generic Aquaref guidance for marine PS operations…
- Training through Aquaref is now scheduled in 2016 for continental waters poeple (in preparation of a demonstration exercise 2017-2018).

Open thoughts

- New PS for polar molecules (Acidic herbicids, Pharmaceuticals, Perfluorinated compounds, …)
  - DGT-HLB, Ion Exchange Sorbent in POCIS, …
- Experimental studies to characterise the response dynamics of POCIS-HLB to pollution peaks (medium polar pesticides logKow = 3 to 5)
  - varying concentrations, flow rates, exposure durations…

Applicability of DGT in groundwater context

- Adour Garonne Basin
- Agricultural area (low metals concentrations)



- Lowering of LOQ with DGT confirmed (factor 10 vs. grab sampling)
- But low ratios DGT/ICPMS, in spite of low particulate fraction in groundwater, opens questions:
  - Impact of low flow rates in wells (diffusion boundary layer)?: estimated <50%
  - Impact of speciation: How to relate the sampled DGT fraction to groundwater toxicological threshold (drinking water)?

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Roadmap towards Quality Assurance for PS: what are the needs?

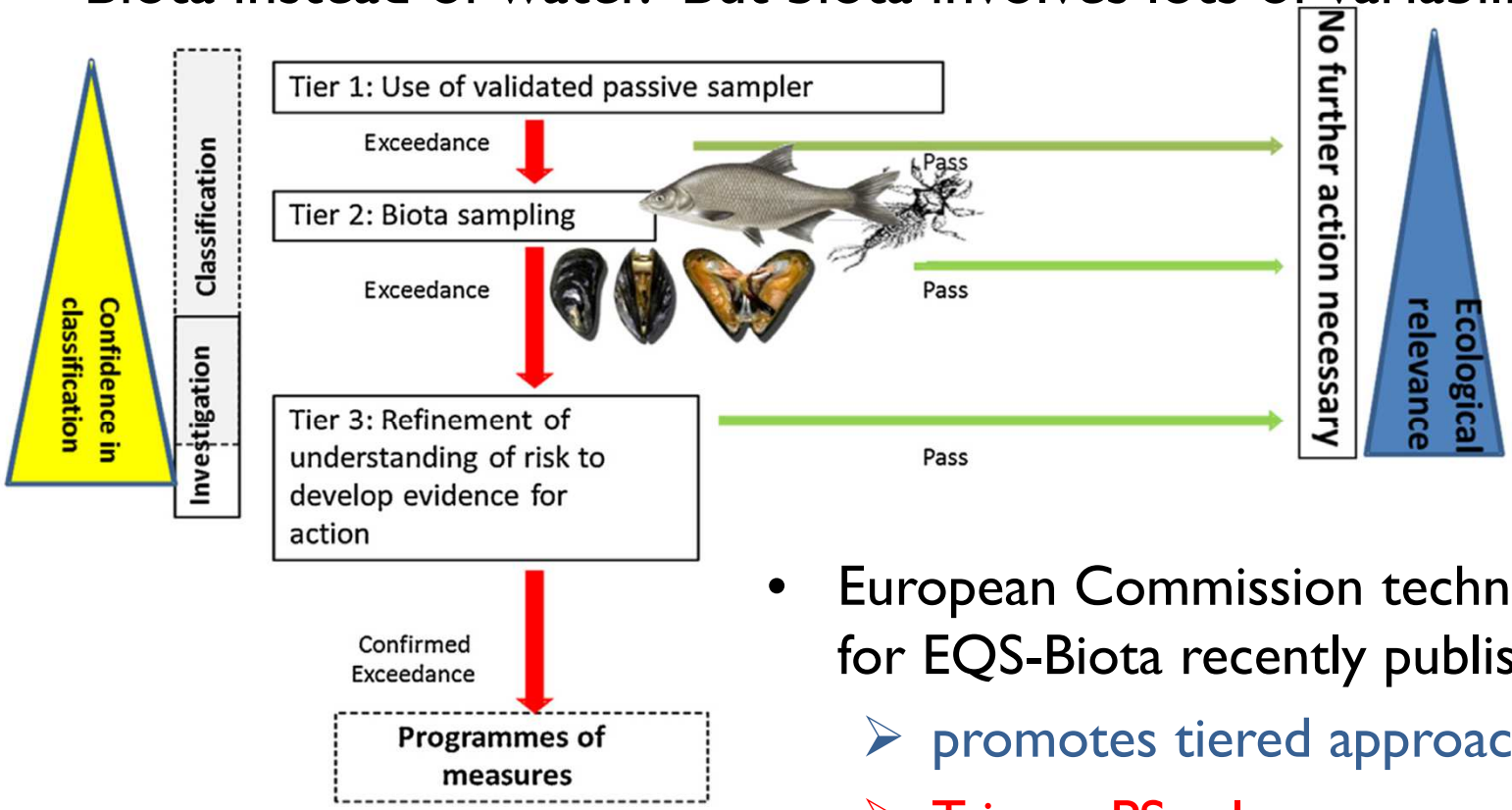
- Integrate PS specific requirements into French Accreditation guidances (Cofrac) dedicated to sampling and analysis, e.g. defining:
  - which PS for which compound in which water? which reference method to analyse it?
  - who provides and warrants the PS?
  - which metadata should come along with the compound results?
  - who is in charge to compute the TWA?

- Some training & guidances strategies, including for accreditation assessors!
- Standardization of PS calibration procedures
- Refine ISO 5667-23
- Define specific requirements of PS vs. method validation, CRM, quality control (blanks, replicates..)
- Promote intercomparison trials

Some outlooks to conclude…

PS assistance to WFD EQS-biota compliance checking

- Several bioaccumulative WFD priority substances to be monitored in Biota instead of water. But biota involves lots of variabilities...



- European Commission technical guidance for EQS-Biota recently published*
  - promotes tiered approach involving PS
  - Trigger PS values are needed…

** EC, Guidance Document No. 32, 2014-83 ON BIOTA MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE*

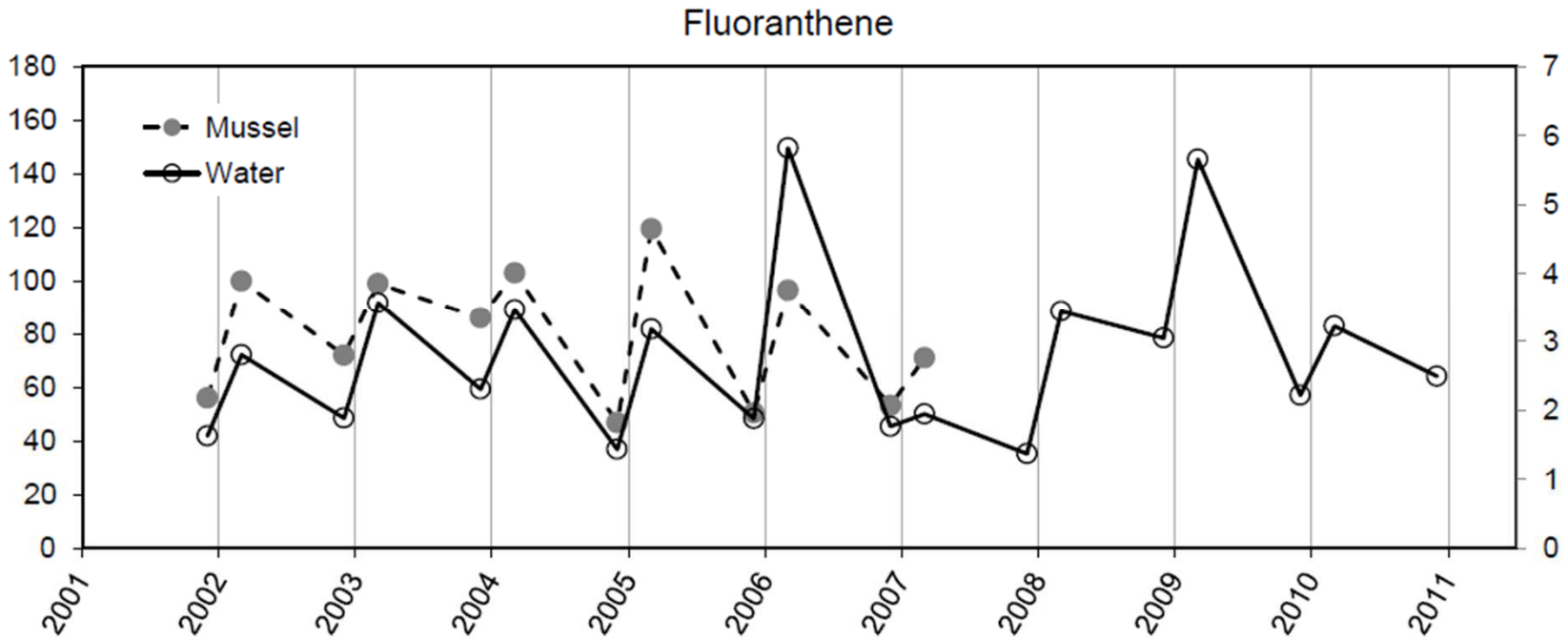


Figure A.4.1 A time series of Fluoranthene concentrations in the mid Western Scheldt for mussels

[µg/kg dry weight, grey dots, (left axis) and free dissolved concentrations in water determined through passive sampling (ng/L, open circles, right scale). Note that connecting lines are only to guide the eye and do not represent intermediate concentrations. Measurements in mussels were ceased in 2007.]

Looking forward

- Promote demonstration projects/case studies of representative dimension, (contexts & seasons) with passive sampling undertaken together with spot sampling and biota monitoring, associating trained but non-expertWFD operators, in order to demonstrate their practical & economical applicabilities for various (but precise) WFD operations. *National exercise under prep. in France, to proceed in 2017-2018.*
- Develop more the argument about PS fraction better relevance in regards of EQS … (a dedicated position paper?)
- Establish a European repository (database) to better share PS monitoring data & metadata: PS used? conditions of deployment? analytical method? method to treat the results? concentration in the PS and the TWA?...

  The NORMAN* European association already works upon a specific template, used in the recent Joint Danube Survey
- Stimulate production of commercial PS systems and CRMs, of established and controlled physical properties which would require minimal calibration experiments by end-users.

* http://www.norman-network.net/

Thank you!

Gracias!

Milesker anitz!

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