The potential of passive sampling techniques (DGT, SBSE, POCIS) for the marine environment: Examples of "large-scale" applications (French Mediterranean coastal waters, French overseas territories)

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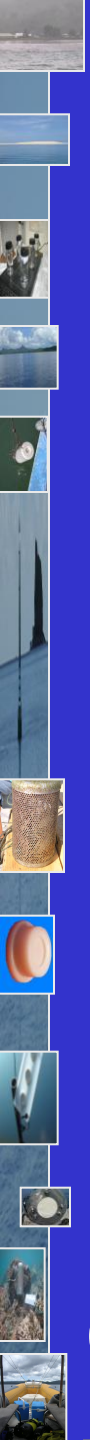


Since many years passive sampling techniques are used within the framework of various applications (speciation studies, impact studies…)

Advantages and limitations for use in connection with the implementation of the WFD ?

Numerous chemical contaminants (metals, organics) to be measured

⇒ Different methods of analysis

WFD priority substances de la DCE:

Benzene	benzène, hexachlorobenzène, pentachlorobenzène, pentachlorophénol, trichlorobenzène (*1,2,4-trichlorobenzène*)
PAH	anthracène, fluoranthène, naphtalène, hydrocarbures aromatiques polycycliques [*benzo(a)pyrène, benzo(b)fluoranthène, benzo(k)fluoranthène,benzo(g,h,i)pérylène,*
Pestic	endosulfan (*alpha- endosulfan*), alachlore, hexachlorocyclohexane (*lindane*)
Solvents	1,2-dichloroéthane, dichlorométahne, trichlorométhane
Metals	cadmium, mercure, nickel, plomb (et leurs composés)
Diverse	diphényléthers bromés, C10-C13-chloroalcanes, di(2 éthylhexyl)phtalate (DEHP), hexachlorobutadiène, nonylphénols (*4-para-nonylphénol*), octylphénols (*para-ter-octylphénol*) composés du tributylétain (tributylétain-cation)

Limits of quantification: 1/3 Environmental quality standards

p.e.: Endosulfan LD= 0.5 ng/l !!

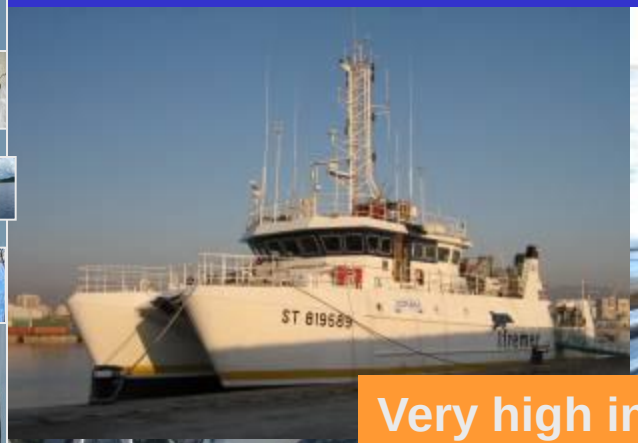
Ifremer

Very diverse origins

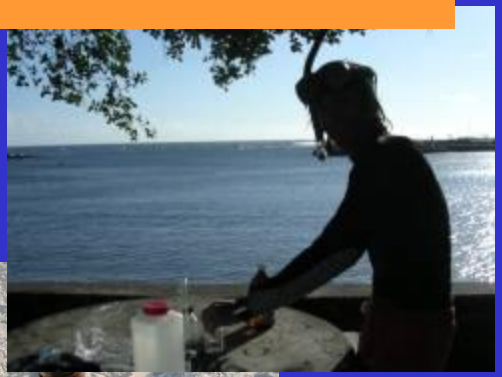
Numerous water masses to be monitored in highly diverse conditions (ground water, rivers, lakes, estuaries, sea, etc.)

Able to sample and measure in very different environments

Intervention and logistics capabilities



Very high increase in time and money spent on sampling and analysis operations



Additional difficulties related to marine waters:

- **Salt water = complex matrix**

⇨ **interferences implying an EXTRACTION step (use of solvents…)**

- **Trace concentrations (ng/L)**

⇨ **sophisticated analytical techniques and CONCENTRATION step required**

- **Spatial and temporal variability of concentrations ("transitional" waters)**

⇨ **spot sampling and / or integrated sampling**

- **Sampling operations sometimes requiring complex logistics (ships), in particular in case of bad weather. ..**

Need to develop "all terrain" techniques to extract and concentrate ***in situ*** different families of chemical contaminants

Only one stage =

Passive sampling

Operationality of these systems (on a "large scale")?

Ease of use (by non-specialist personnel)?

Objective: to test the feasibility of **using passive samplers to assess the chemical contamination of marine water masses** in the **Water Framework Directive** context

Originality: **"large scale"** testing (in various coastal environments) of the operationality of these systems in terms of **cost reduction, rapidity of results** and **ease of use** (by non-specialist **BUT TRAINED** personnel).

3 different types of samplers (contaminants, principle and implementation)

DGT (Diffusive Gradient in Thin film): trace metals

Immersion time variable

POCIS (Polar Organic Chemical Integrative Sampler): Hydrophilic organic contaminants

Collaboration with LPTC (Univ. Bordeaux I)

Immersion time (at least 2-3 weeks). Sampling rate détermination, use of reference compounds

SBSE (*Stir Bar Sorptive Extraction*): Contaminants organiques hydrophobes Collaboration with CEDRE

Spot sample extraction. Addition of internal standards

Testing in various "field conditions" using previously-trained, local personnel:

- French Mediterranean coastal water masses,

- Mediterranean lagoons

- Tropical water masses

- Tropical lagoons

-Tropical estuaries

- Harbour and urban areas

Training:

1- Realization of a "field guide"

For the deployment, recovery and conditioning of passive samplers (DGT, POCIS, SBSE)

2- Training day

Presentation of passive sampling techniques and various operations, plus hands-on experience in the field

Training operations: about 140 people

-Atlantic, Mediterranean

- Overseas Territories (La Réunion, Mayotte, Guyane, Martinique, Guadeloupe)

Field campaigns:

Logistics:

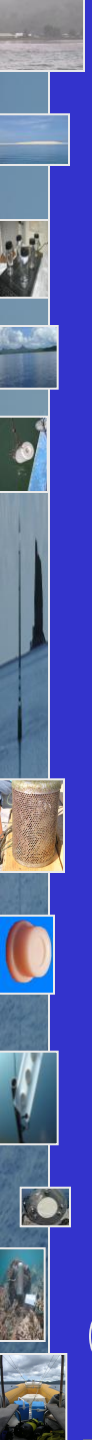
❑ Passive samplers are prepared and issued by "expert" labs (Ifremer for DGT, LPTC Univ. Bordeaux I for POCIS, CEDRE for SBSE)

❑ Local operators deal with:

- logistics (transport, deployment means, mooring adaptation to local conditions, etc.)

- deployment, monitoring, recovery and conditioning of samplers and their transport in ad hoc conditions (freezing, refrigeration)

❑ The "expert" labs are in charge of returned sampler preparation (elution, extraction, etc.), analysis and result processing.



The various field operations were supported by public bodies in charge of implementing the WFD in mainland France and in overseas territories :

- Agence de l'Eau Rhône-Méditérranée-Corse (AERMC)

- Les Directions Régionales de l'Environnement (DEALs) de La Réunion, Guyane et Mayotte

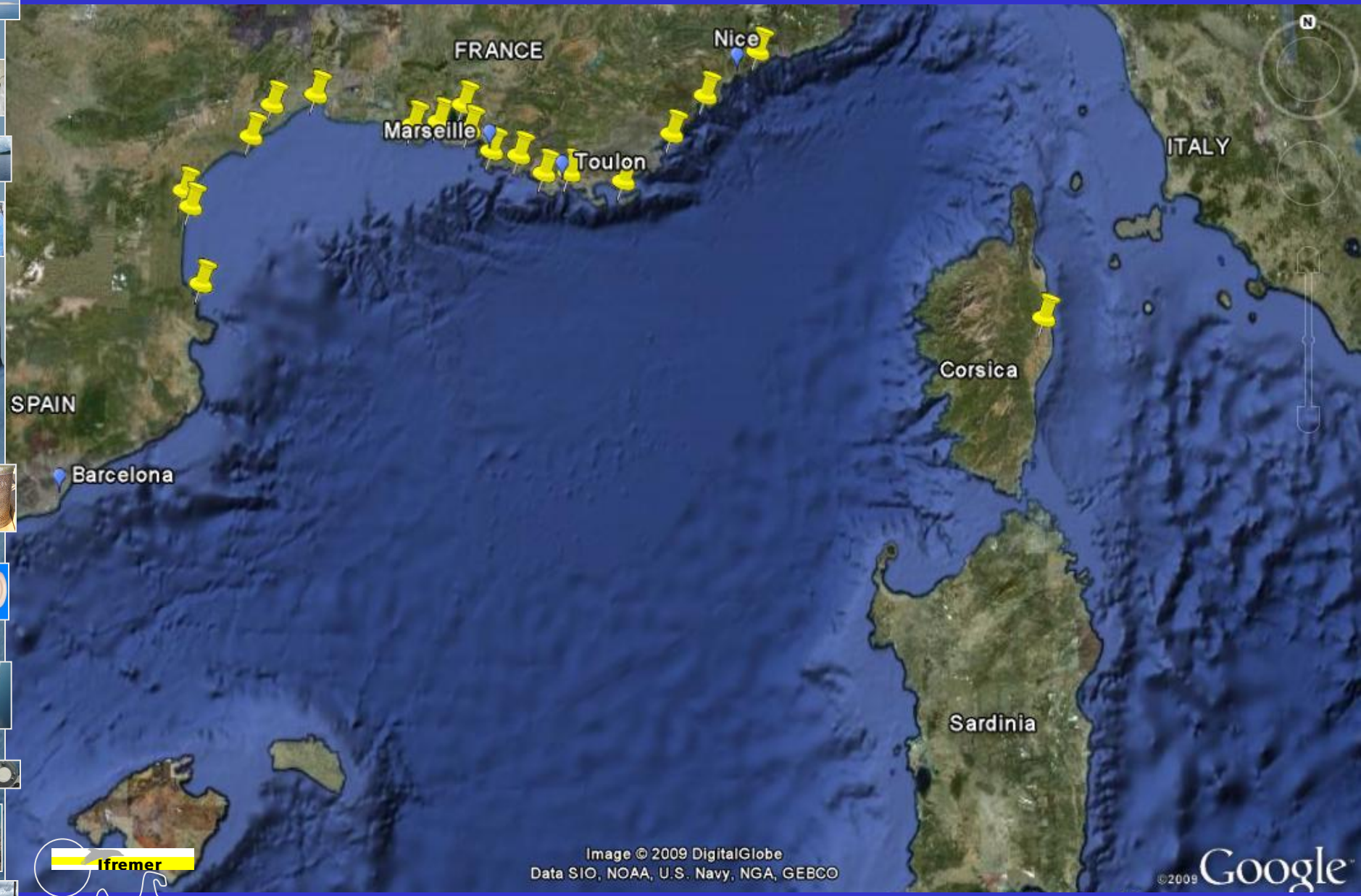
Examples of results

	Collaborations	Main Campaigns	Water masses (coastal and transition)
Mediterranean Sea	AERMC LERPAC LERLR CQ	2008: PEPS 2009: DCE 2010: Lagoons	20 36 28 (temporal variations)
La Réunion	AR DE		8
Mayotte	AR DE BR		1
Guyane	IRD DEAL	2008: Pilot study 2009: Pilot study (dry and wet season) 2011: Pilot study	4 10 22
Nouvelle Calédonie	ARVAM DEAL BRGM	2011: Biofouling study	4

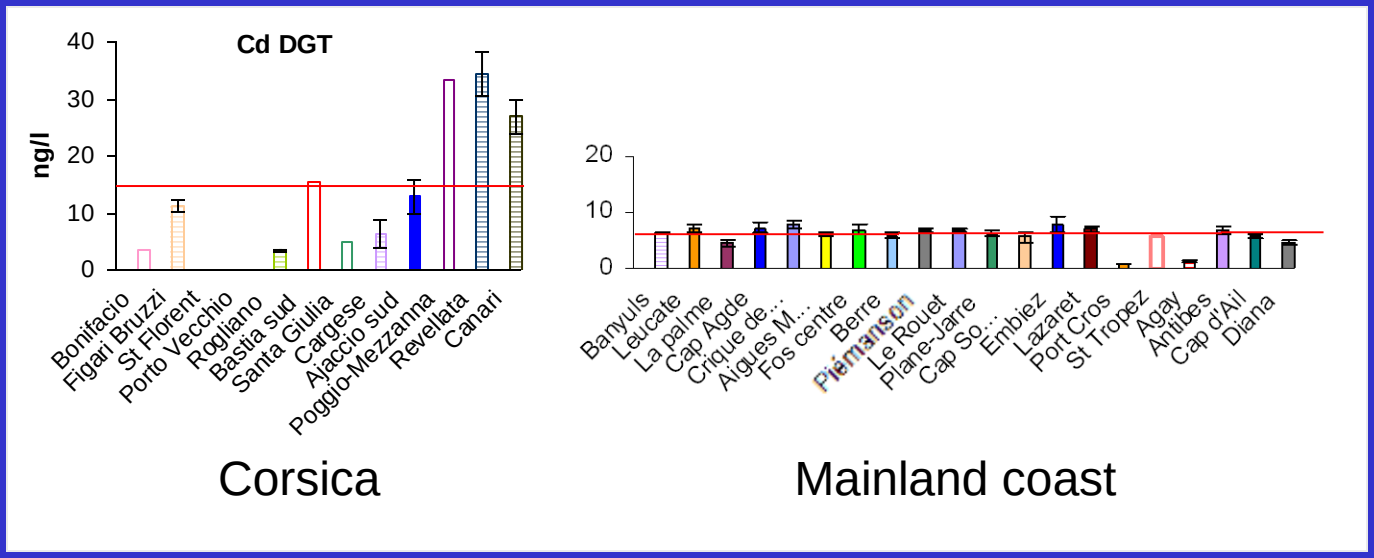
Deployment in very varied systems (about 170 different water masses):

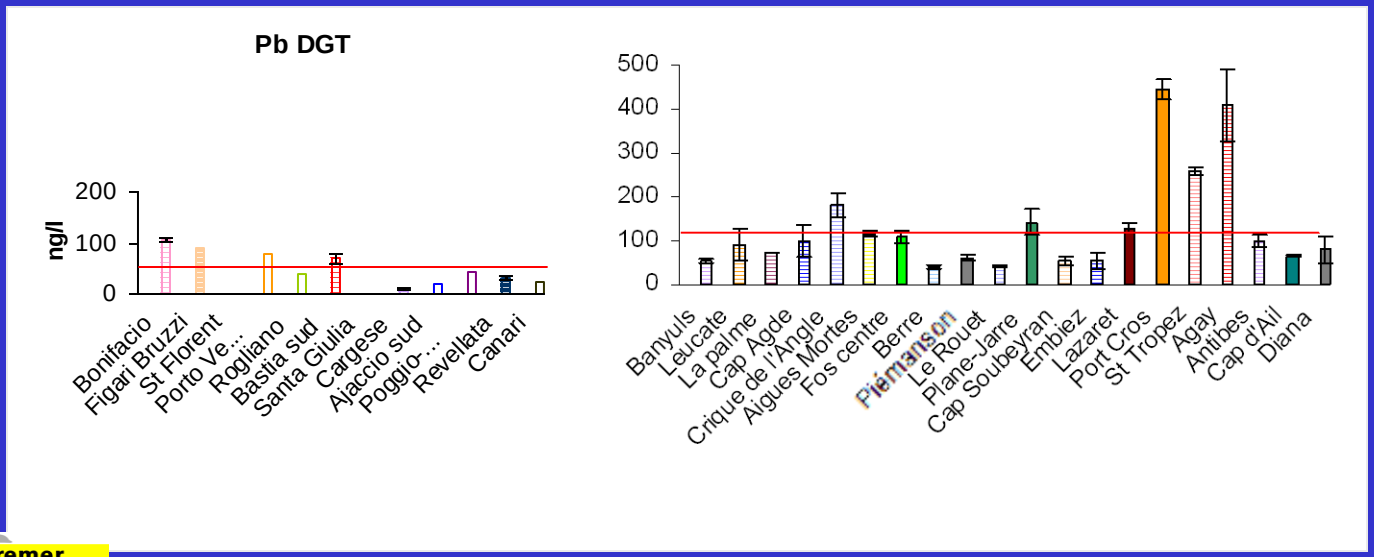
- Urban areas
- Commercial ports and marinas
- Tropical and Mediterranean lagoons
- Coastal areas
- Estuaries
- Open sea

French Mediterranean coastal water masses

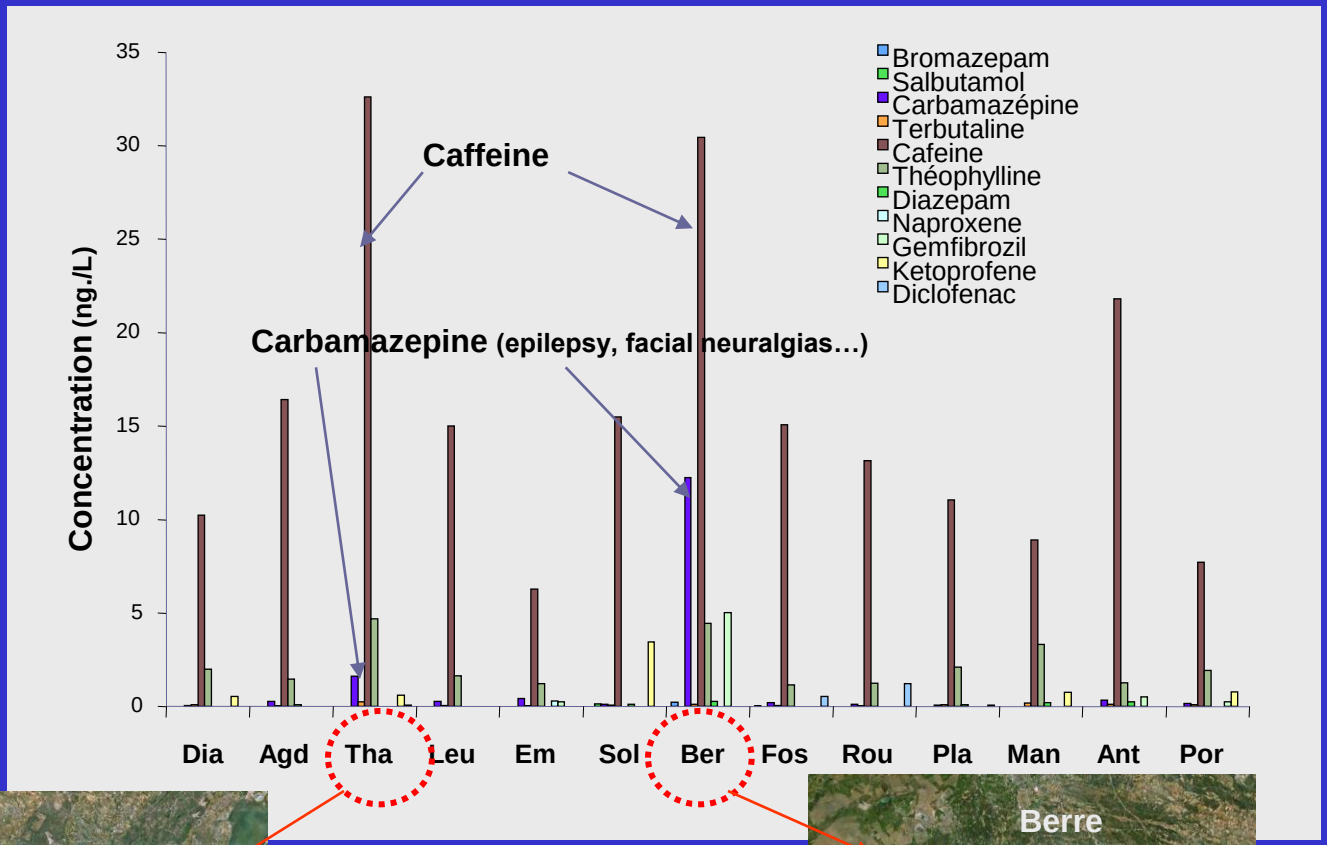


Mediterranean: Trace metals (DGT)

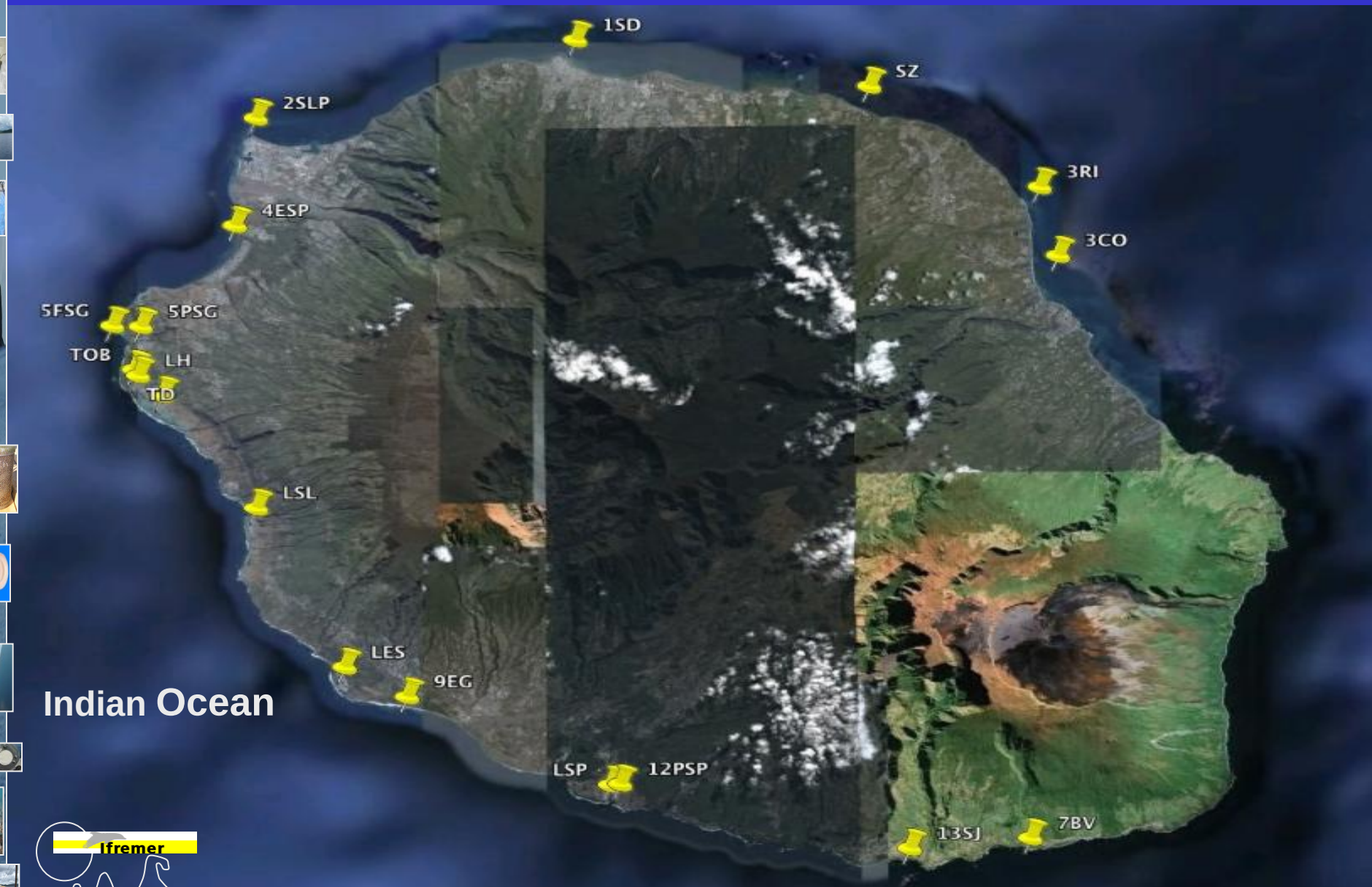




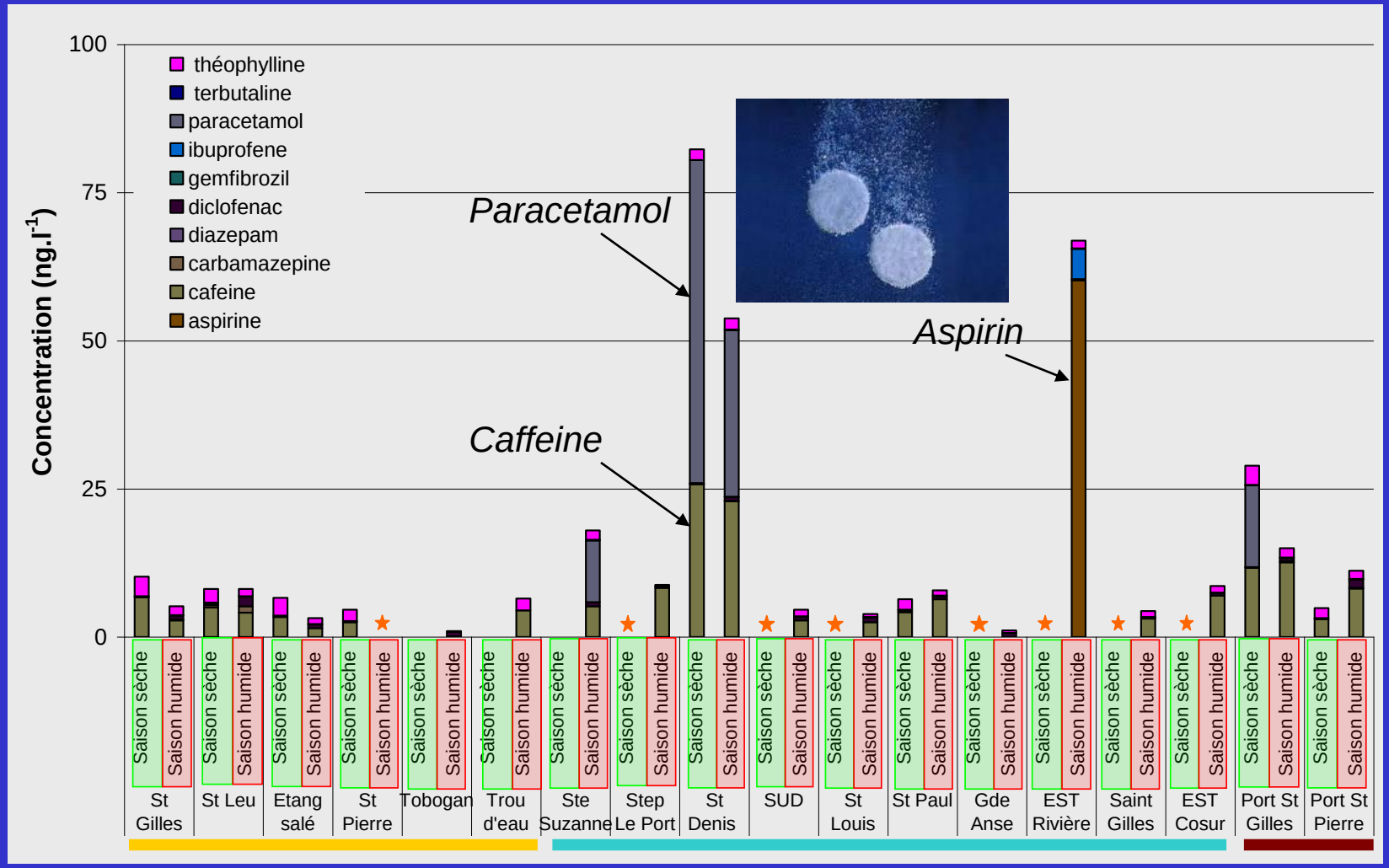
Mediterranean: Pharmaceuticals (POCIS) good markers of urban waste and "health of society"



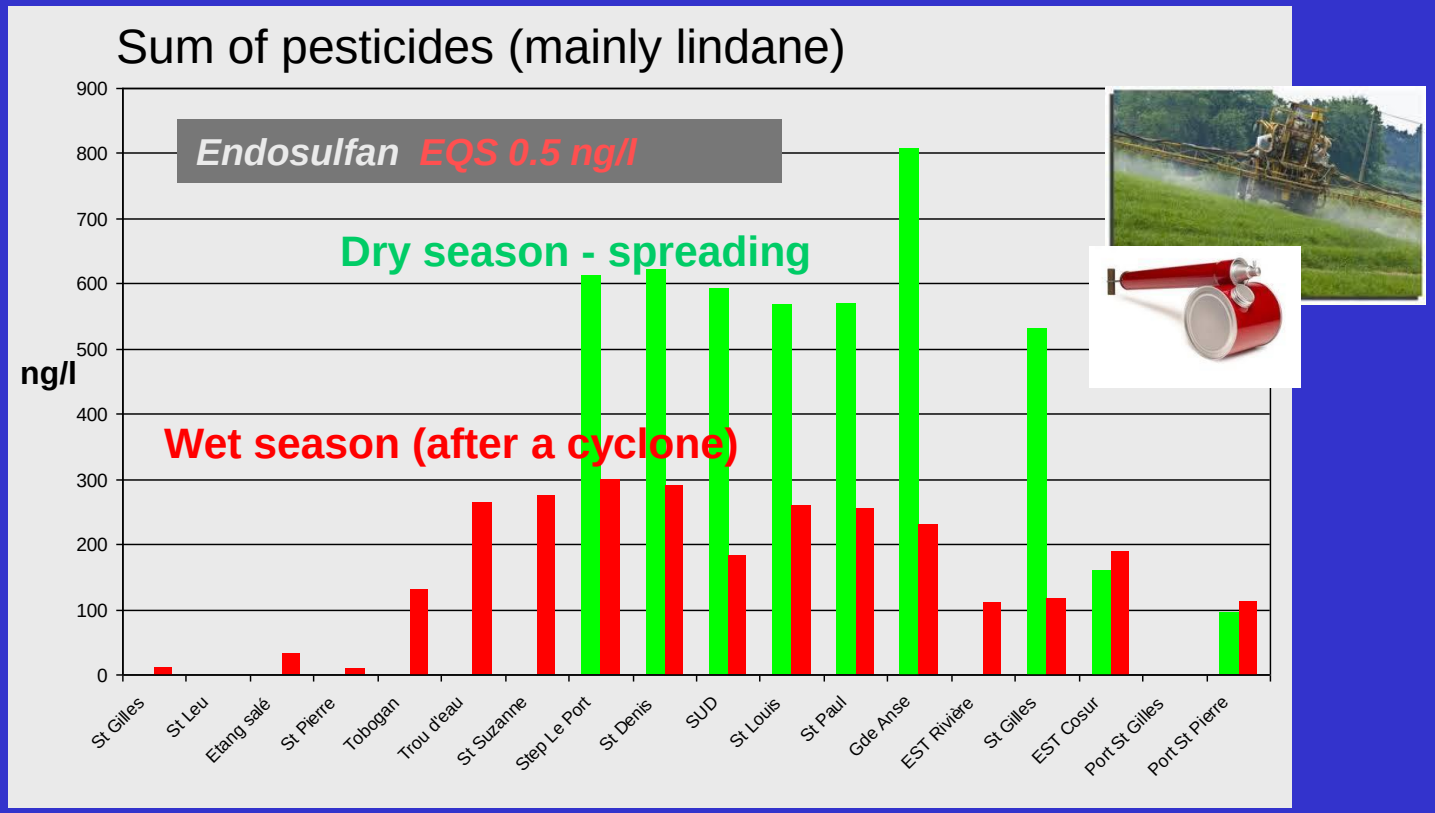
La Réunion


1SD
SZ
2SLP
3RI
4ESP
3CO
5FSG
5PSG
TOB
LH
TID
LSL
LES
9EG
LSP
12PSP
13SJ
7BV
Indian Ocean

La Réunion Pharmaceuticals (POCIS)

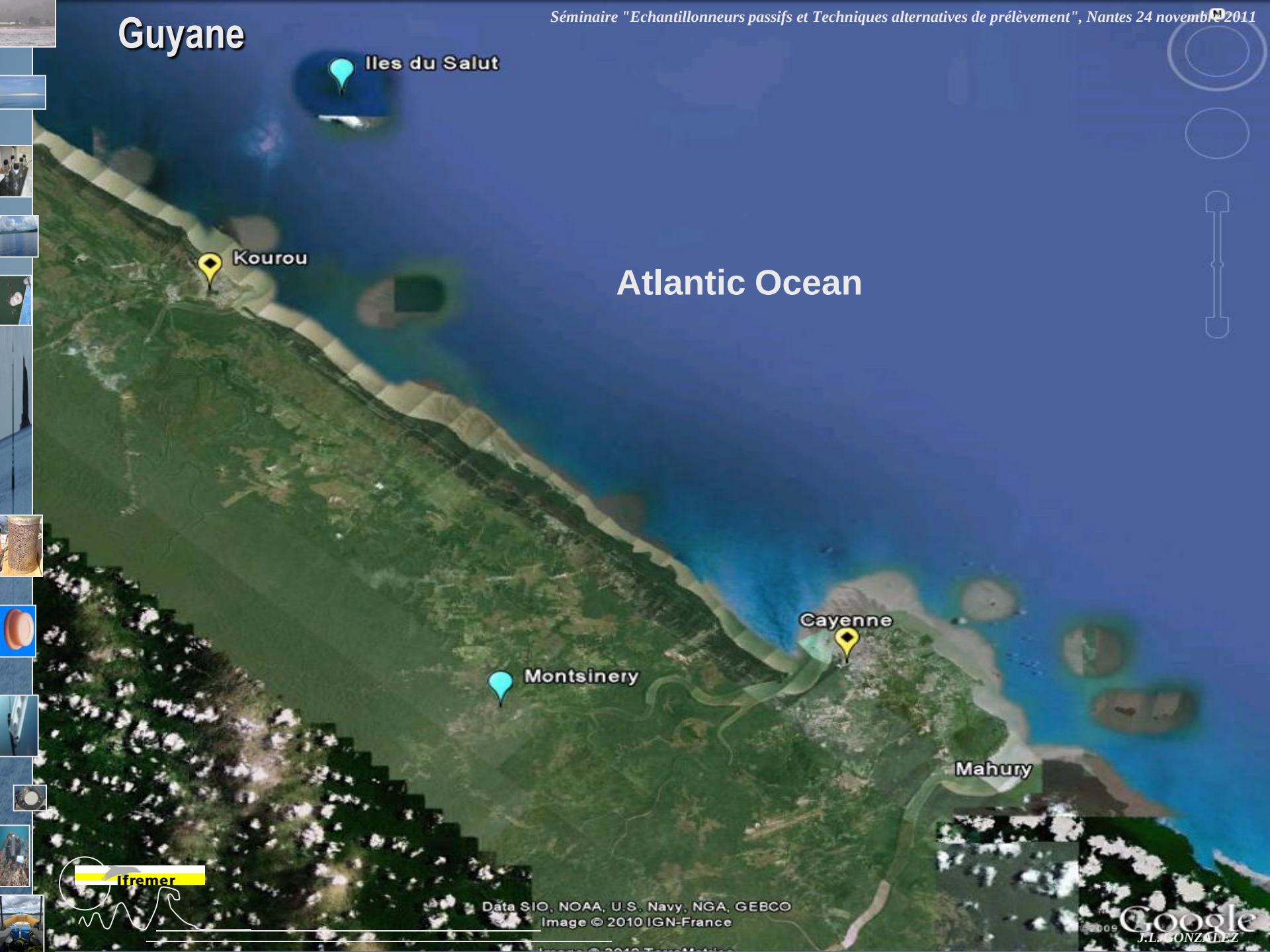


La Réunion Pesticides (SBSE)



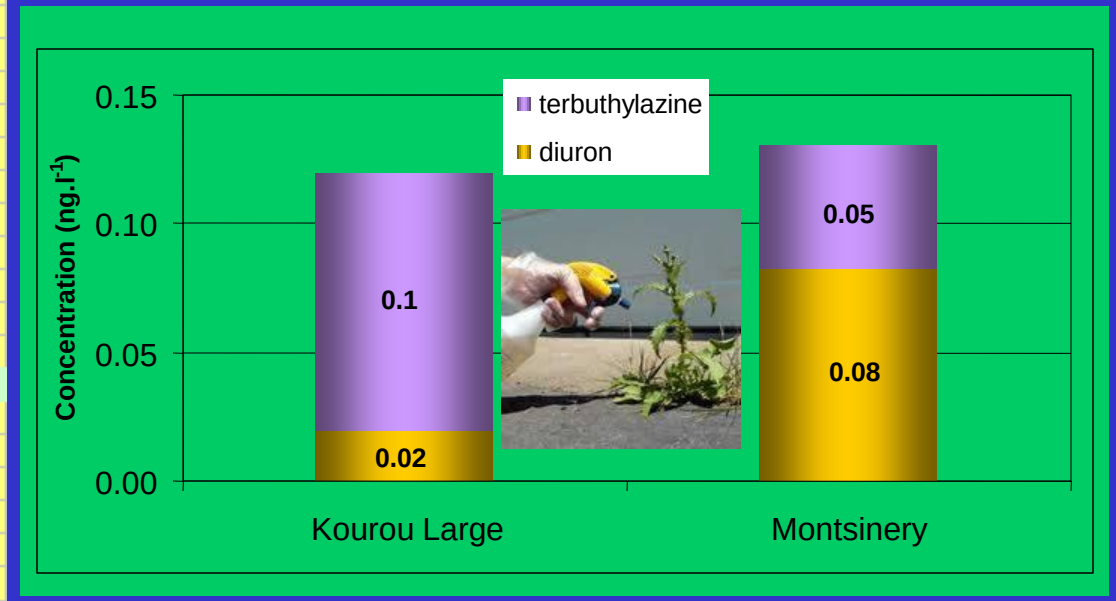
Lindane (insecticide) $t_{1/2}$ water: 30 to 300 days

Endosulfan (insecticide) prohibited use since 2007. $t_{1/2}$ 4 à 7 days in water (60 days in soils).


Guyane
Iles du Salut
Kourou
Atlantic Ocean
Cayenne
Montsinery
Mahury
Ifremer
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image © 2010 IGN-France
Google

Guyane: Pesticides *(POCIS)*

Metazachlore
Irgarol
Chlorfenvinphos
Phosmet
Bifenthrine
Phosalone
Lambda-cyhalothrine
Acrinathrine
Permethrine
Cyfluthrine
Cypermethrine
Deltamethrine
Fenvalerate+esfenvalerate
Tau-fluvalinate
Pymethrozine
Temephos
diuron
linuron
chlorsulfuron
nicosulfuron
isoproturon
chlorotoluron
DCPMU
metoxuron
124 dichlorodiphenylurée
134 dichlorodiphenylurée



Dichlorvos
Trichlorfon
Chlormephos
Propachlore
Ethropophos
Deisopropyl-atrazine
Desethyl-atrazine
Dimethoate
Simazine
Atrazine
Cyromazine
Propazine
Terbuthylazine
Diazinon
Dimetachlore
Acetochlore
Chlorpyrifos-methyl
Tolclophos-methyl
Alachlore
Promethrine
Terbutryn
Fenithrothion
S-Metolachlore
Malathion
Chlorpyrifos-ethyl
Cyanazine

Terbuthylazine (herbicide) prohibited use since 2004 ($t_{1/2}$ soils 46 days)

Diuron (herbicide) prohibited use since 2008 ($t_{1/2}$ soils 372 days).
Antifouling products

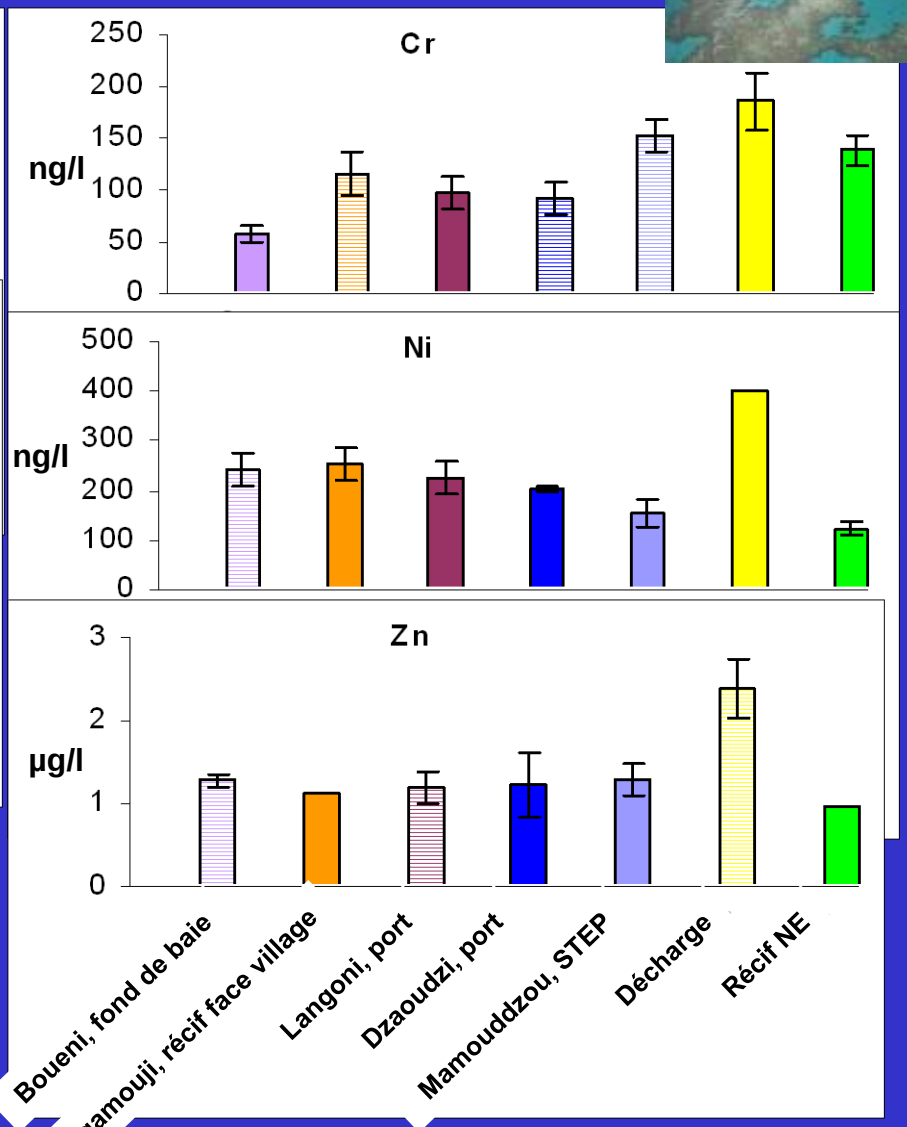
MAYOTTE

Ifremer

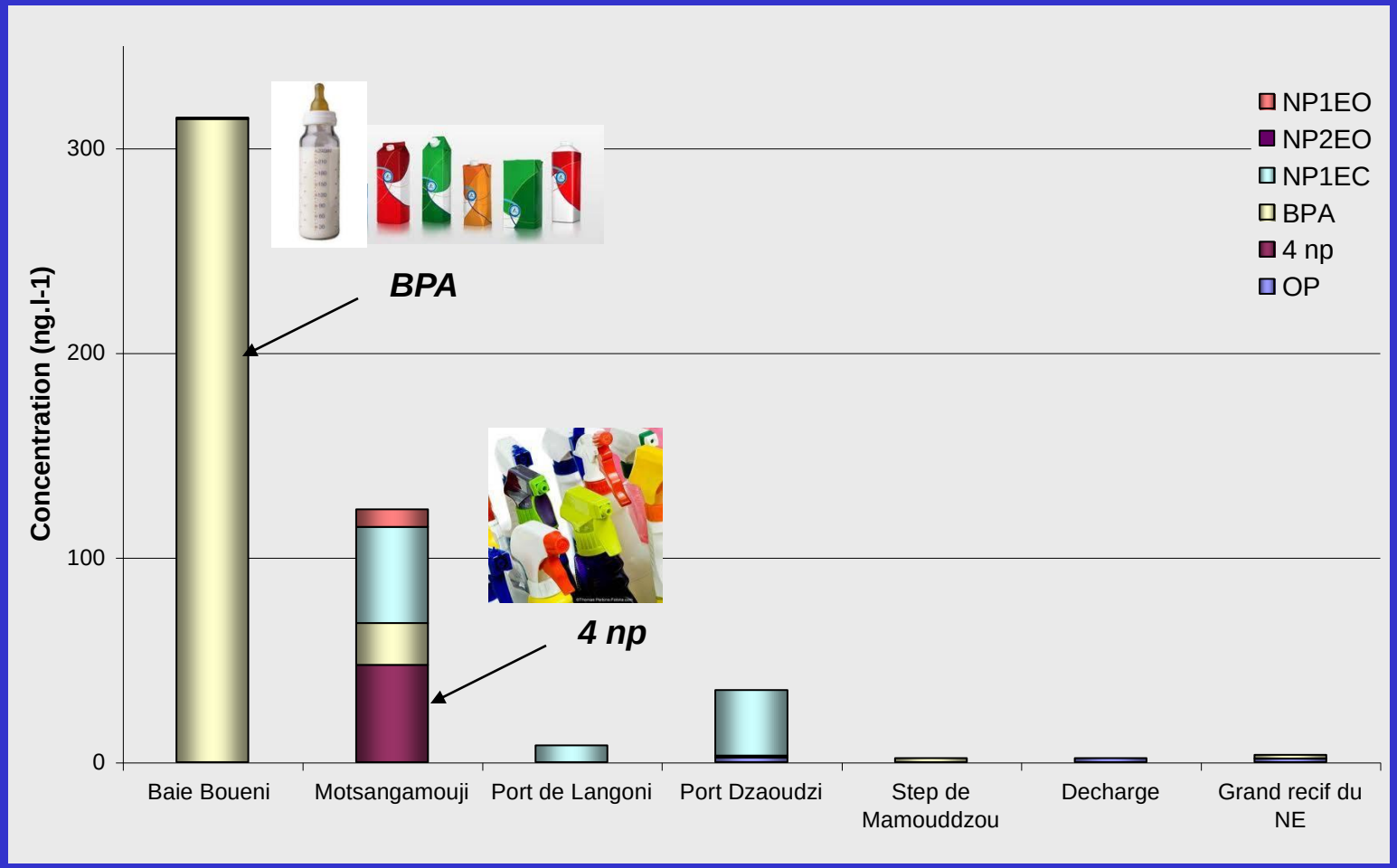
J.L. GONZALEZ

Mayotte: Trace metals (DGT)

commercial port



Mayotte: Alkylphenols (POCIS)



BPA Bisphénol A. Component of plastic (polycarbonate, will tétra Pak, feeding-bottles…) prohibited since 2010

4 np Nonyl phénol. Surfactant (textile industry, detergents, cleaning products ...)

In conclusion

- "all terrain" techniques, simples, robust and easy to use
















Deployment in very varied systems:

- Urban areas
- Commercial ports and marinas
- Tropical lagoons
- Coastal areas
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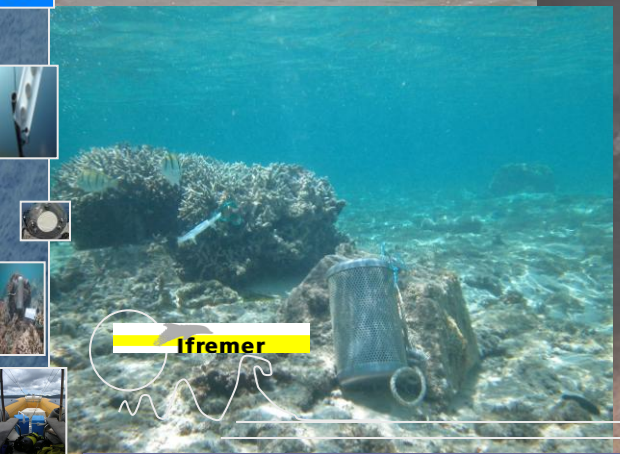
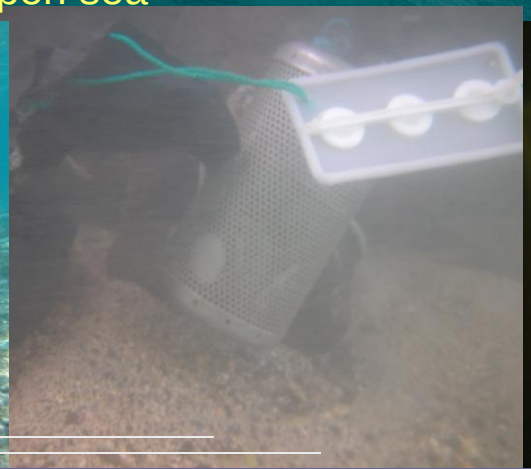
- Open sea





operationality in very different conditions

large vessels, small boats, by car, by feet and by flippers…

In conclusion

- "all terrain" techniques, simples, robust and easy to use
- Simplification of problems related to sampling, contamination and filtration, quantification limits, encountered with usual techniques



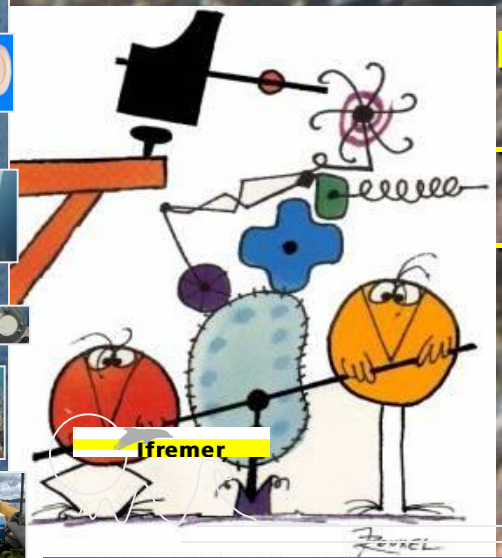












Equivalent:

- to the sampling of several hundred liters of water
- and filtration, extraction / concentration in the lab

In conclusion

- "all terrain" techniques, simples, robust and easy to use
- Simplification of problems related to sampling, contamination and filtration, quantification limits, encountered with usual techniques
- Reduction of the costs













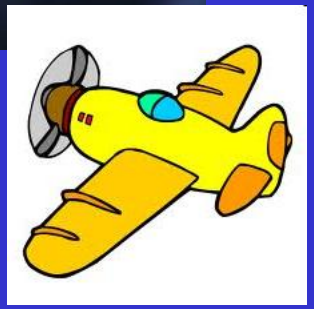
"Compact" techniques = easy transport and reduction of the costs

7 stations in triplicate:

pesticides, PAHs, PCBs (SBSE)

=

Trace metals: Cd, Pb, Ni, Zn…(DGT)



cheaper transport to the lab for direct analysis, more representative sample, minimum sample interference

In conclusion

- "all terrain" techniques, simples, robust and easy to use
- Simplification of problems related to sampling, contamination and filtration, quantification limits, encountered with usual techniques
- Reduction of the costs
- A sample less "disturbed" - Extraction / concentration in situ
- After extraction (simple step in the lab): a concentrated "matrix". Direct analysis
- Measurement of very low concentrations in water
- Easy transfer of these techniques use by non-specialist BUT previously TRAINED).
- **Environmental interest:** reduction (or elimination) of the volumes of reagents and solvents used by the "classic" methods

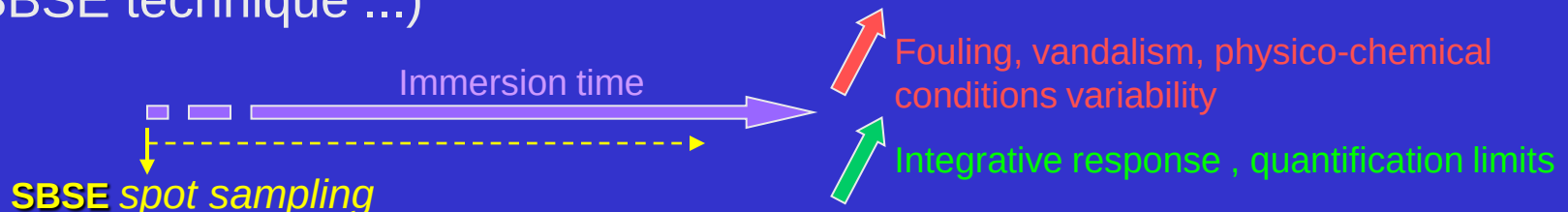
Main problems and limitations:

- Necessity to adapt moorings lines to local conditions (very strong hydrodynamic conditions, vandalism in lagons)
- "biofouling" is a potential problem for long immersion periods
- all passive samplers are not at the same level of development
- all contaminants are not measurable (developments to do)
- concentrations calculation (calibration, fouling, hydrodynamics ...)
- standardization of protocols

Outlook

- DGT for Hg (one of the WFD priority metal): choice and validation of analytical technique
- Improvement POCIS technique: fouling, hydrodynamics, compactness

- Developments in order to adjust the immersion time (achieving measurable levels more quickly, reduce fouling, integrative measures with the SBSE technique ...)



❑ Automation of sampling techniques (DGT, SBSE, POCIS):

Example: *FRAME* (benthic sation) automation to measure the impact of "extreme" events on water mass contamination

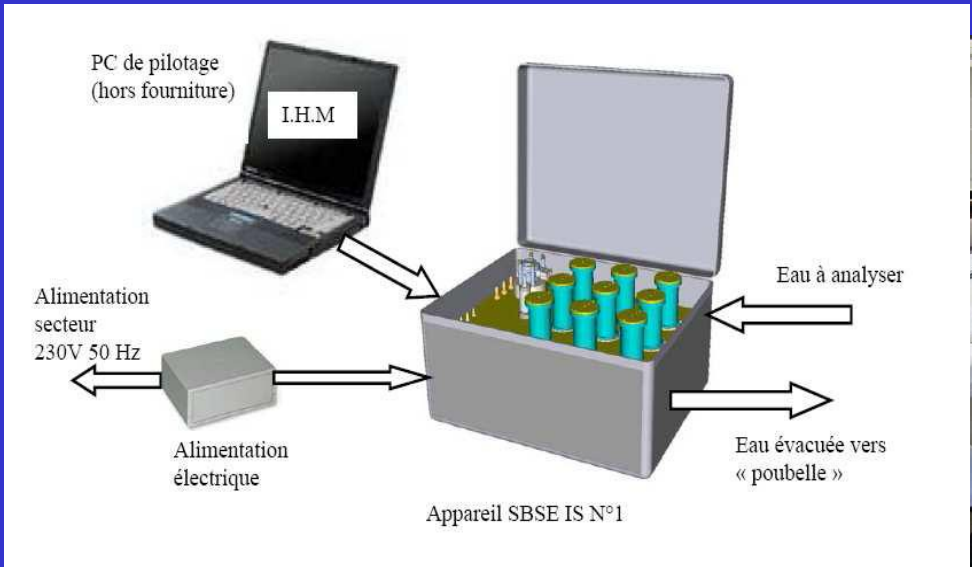
DGT module

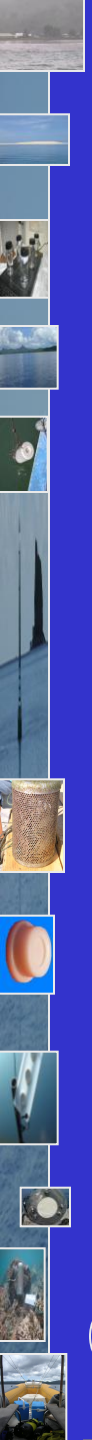
SBSE module

SBSE suitcase:

- water sampling and automatic extraction

- extraction of hydrophobic and hydrophilic compounds (in situ derivatization) with the same technique





❑ Definition of "passive samplers" EQS

PS concentrate and isolate a mixture of compounds (according to their physico-chemical properties) potentially toxic.

Test these extracts on "model" organisms (freshwater, marine ...) ⇒ EQS more realistic and directly comparable to measurements.


Thank you for your attention