

## **MONITOOL PROJECT**

## **Passive sampling versatility and applications**

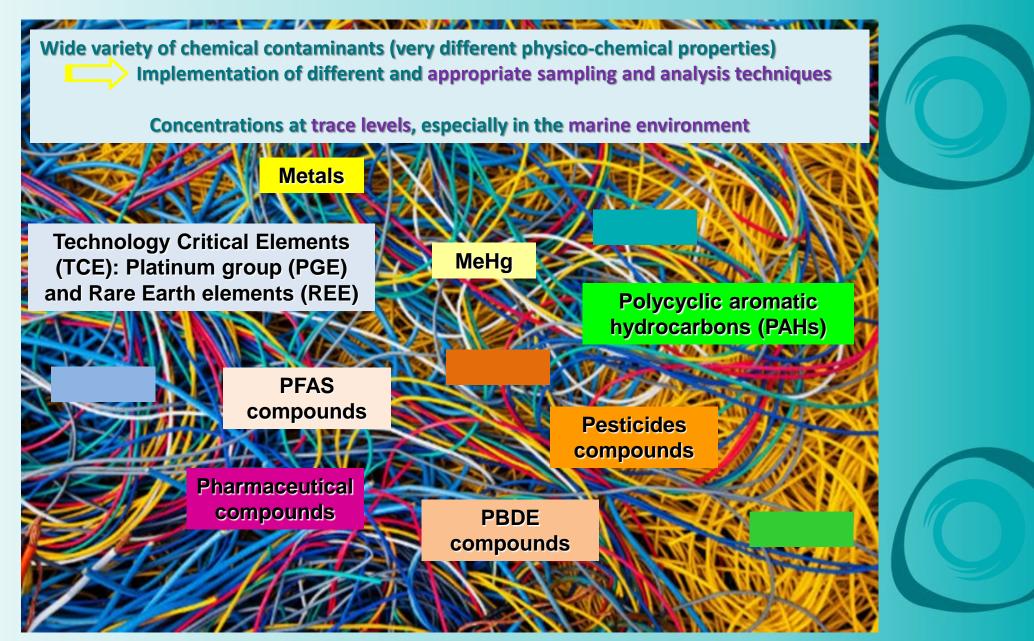
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Wide variety of chemical contaminants (very different physico-chemical properties)
Implementation of different and appropriate sampling and analysis techniques

Concentrations at trace levels, especially in the marine environment

**Metals** 

This issue is well resolved by the DGT approach (Monitool contribution)





What about other contaminants ?

MeHg

**PBDE** 

compounds

Technology Critical Elements (TCE): Platinum group (PGE) and Rare Earth elements (REE)

SANS AM

PFAS compounds

Pharmaceutical compounds

Polycyclic aromatic hydrocarbons (PAHs)

Pesticides compounds

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## There are many passive sampling (PS) techniques adapted to different families of contaminants. Some examples:

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



#### SBSE (Stir Bar Sorptive Extraction): hydrophobic organic contaminants



Equivalent technique in "integrative passive sampling" version: *Lowdensity polyethylene* (LPDE) or *silicone membrane* 

Source: Gerstel. Twister/Stir Bar Sorptive Extraction SBSE [Internet]. 2018. Available from: http://www.gerstel.com/en/twister-stir-bar-sorptive-extraction.htm Gerstel. Extractables & Leachables Medical Implants – A closer look [Internet]. 2018. Available from: http://www.gerstel.com/en/GSW15 Extractables Leachables.htm



#### SPMD (Semipermeable Membrane Device): hydrophobic organic contaminants





See presentation "Chemcatcher<sup>®</sup> – Passive Sampling for Micropollutants"







#### "Large scale" campaigns (use of 3 different techniques)

### "Prospected" sites:

 Rivers, bays, marinas, harbors, transitional waters (estuaries, etc.), coastal POCIS waters, offshore waters

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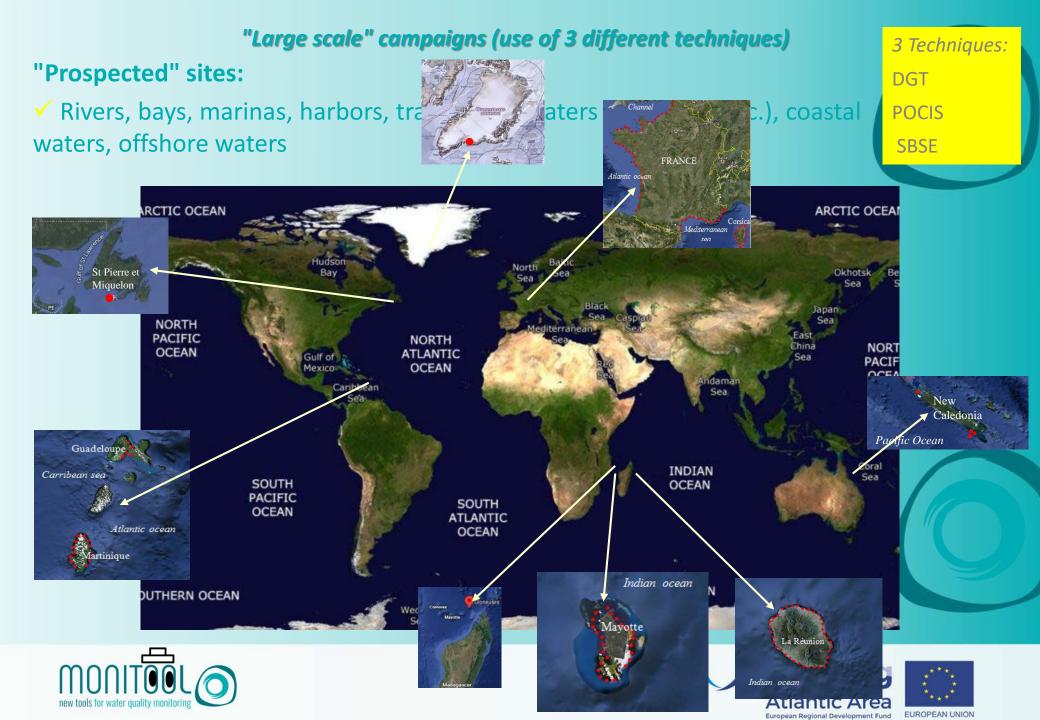




3 Techniques:

DGT

SBSE



The concentrations of metallic contaminants, hydrophilic and hydrophobic organic contaminants were measured in over 300 different bodies of water (some of which were monitored multiple times at different periods). The results obtained revealed the presence of certain organic compounds (pesticides, pharmaceuticals) at very low concentration levels (less than ng/L). Some of these data are among the first available in coastal marine environments.





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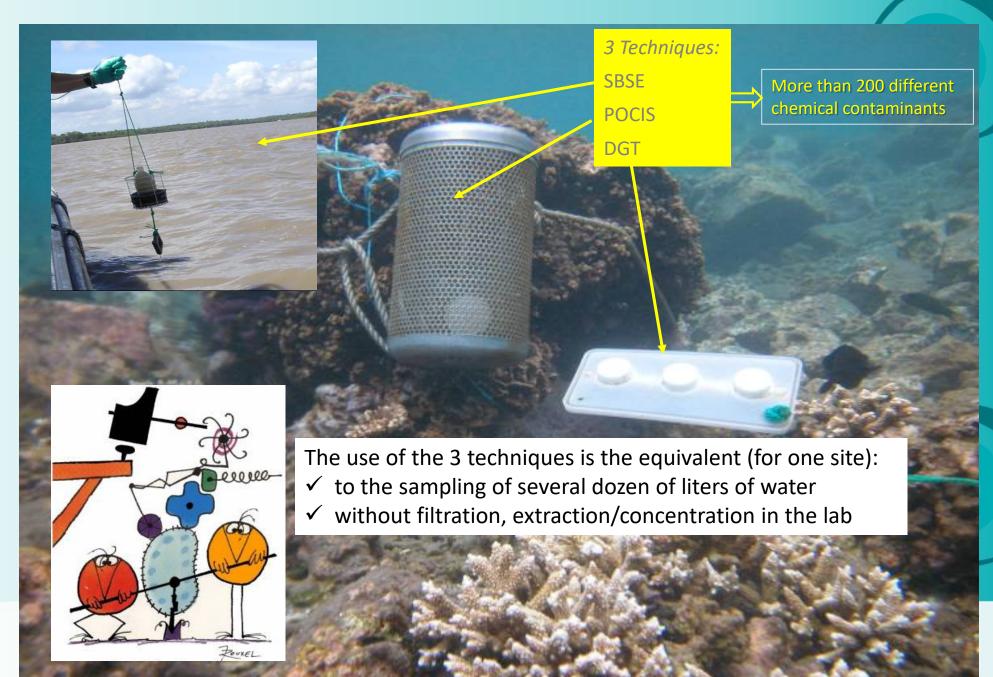
More than 200 different chemical contaminants were analyzed: trace metals, alkylphénols, PAHs, pesticides, PCBs, pharmaceutical compounds.

The initial campaigns were accompanied by training activities for the implementation of these techniques: around 300 people were trained across the various sites.

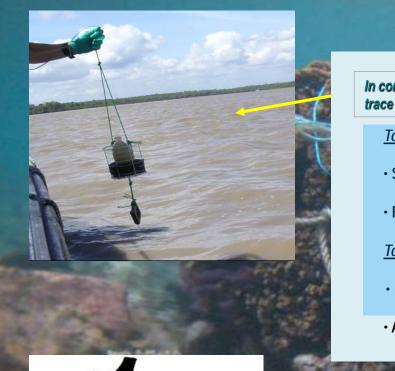




#### PS techniques greatly reduce the difficulties associated with sample collection and processing



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#### 3 Techniques:

In comparison to "conventional" techniques (spot sampling - measurement of contaminants at trace levels in dissolved form)

Steps covered by passive sampling

#### To do in the field:

- Sampling ("ultra-clean" techniques)
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CDCE

Filtration ("ultra-clean" techniques)

#### To do in the lab:

- Extraction/concentration indispensable step (due to trace levels and matrix effects)
- Analysis



The use of the 3 techniques is the equivalent (for one site):
✓ to the sampling of several dozen of liters of water
✓ without filtration, extraction/concentration in the lab





## These are "Compact" methods = ease of transport and reduction of costs

+ important point: These techniques preserve "Sample Integrity" (no possible speciation changes due to: sampling, filtration, storage conditions transport...)





For example:

7 stations (triplicate measurements)

- SBSE: pesticides, PAHs, PCBs
- DGT: trace metals: Cd, Pb, Ni, Zn...

Transportation allowed in the aircraft cabin (if no chemical reagents have been added).







#### These techniques can be implemented in a wide variety of aquatic environments







#### Adapted to the use of many means of intervention







#### "Off-road" techniques

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 The implementation protocols (field operations) of these techniques are very easy to transfer to non-specialist operators

 These methods can be implemented with very limited logistical and lab resources: with fins, by rowing, outdoors, hotel room, kitchen...





## There's more to life than just the Water Framework Directive..

#### Many other applications are possible, few exemples:

✓ Environmental impact studies: wastewaters, dredging activities, renewable marine energy (offshore wind turbines)...

✓ Assessing the occurrence and levels of emerging contaminants (Technology Critical Elements...) in coastal areas subject to anthropogenic pressures

- ✓ Study of Speciation/bioavailability relationships
- ✓ Automation (benthic stations...)
- ✓ etc...





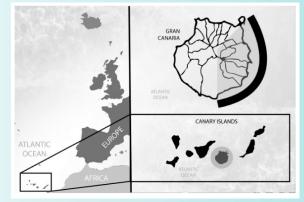
# Inputs of Total and Labile Dissolved Metals from Six Facilities Continuously Discharging Treated Wastewaters to the Marine Environment of Gran Canaria Island (Canary Islands, Spain)

*Work published in:* International Journal of Environmental Research and Public Health. 2021; 18(21):1158 https://doi.org/10.3390/ijerph182111582

**Objective:** To demonstrate that the **limitations of low-frequency spot sampling**, such as the lack of representativeness in dynamic systems such as discharges, can be compensated with the inclusion of **complementary methodologies**, such as DGTs.

**6** different **final discharges** (wide range of physico-chemical conditions) were studied (July 2020):

- TP-1: large WWTP, domestic WW
- TP-2 and TP-3: medium size WWTP, mixed household/industrial WW
- TP-4: little size WWTP, industrial WW
- TP-5: a coastal thermal power plant outlet
- TP-6: an indoor seawater aquaculture (fish) farm



**10 metals** were targeted:

- Cd, Ni and Pb: as priority substances
- Cr, Cu and Zn: as preferential substances
- Al, Co, Fe, Mn: for their important role in the marine environment



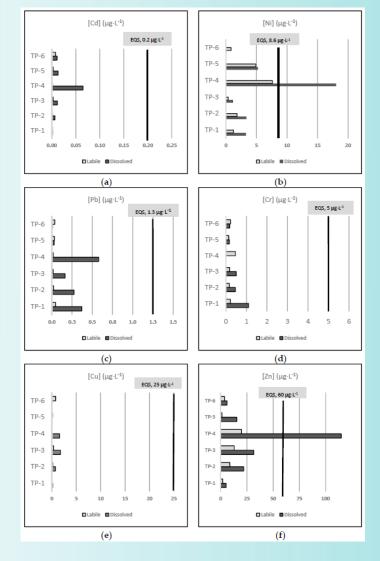






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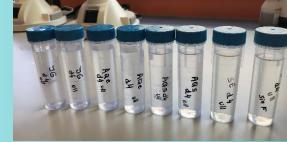




#### Following the MONITOOL standardized methods:

- **Spot sampling** (Day 0, 2 and 4): For total dissolved metal concentrations by ICP-MS.
  - Passive sampling by DGT: 4 days exposure, Chelex-100 metal extraction and ICP-MS for labile metal concentration.



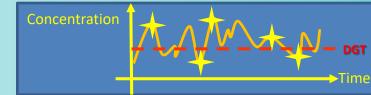




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#### Main conclusions:

- The robustness of the DGT technique.
- The spot sampling can miss some peaks and/or decreases and may not properly monitor the wide variation in the total dissolved metal content.
- <u>The advantage of using DGT devices to measure time-weighted</u> <u>average concentrations over the deployment period providing more</u> <u>representative results.</u>







Is passive sampling more expensive? (In any case, it's much prettier...)

Requires 2 field trips: deployment and recovery

Preparation time for sampling, filtration...equipment ("ultra-clean" quality) No filtration and extraction/concentration operations (in the case of spot sampling: performed under "ultra-clean" conditions by highly skilled personnel).

Volumes of reagents used (environmentally sound methods)

#### Analysis: same methods











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### "New" DGTs, new possibilities !

### new "configurations" (different diffusion gels and resins)

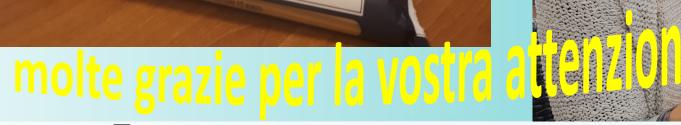


- Spéciation: Hg; Cr (III, IV); As (III, V)...
- Rare Earths Elements
- Organics: antibiotics; pharmaceutical coumponts...); bisphenols; pesticides...
- ≻ ...
- DGT "sediments"









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