Comparing passive sampling, mussel caging and biomarkers for the evaluation of water quality for European Directives in Normandy coastal waters (France)

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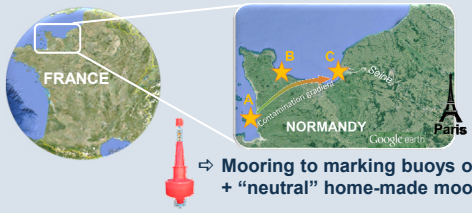
Context and Objectives

During the Water Framework Directive (WFD, 2000/60/EC) campaign of 2012-2013 for the evaluation of the Chemical Status of marine water bodies in the Seine-Normandy district, 92 % of measurements in monthly one-off seawater samples were under the limits of quantification. Moreover, 40 % of the limits of quantification were not low enough relative to the Environmental Quality Standards set in the WFD. Hence the aim of this work was to address the question of which or what association of the currently available tools would be most appropriate to evaluate the quality of Normandy waters. The tools tested were passive samplers (POCIS for hydrophilic organics, and DGT for labile trace metals), caging of mussels, and biomarkers in the caged mussels.

The objectives of this first study in Normandy were to:

1) **Test these tools for their ease of use in the Normandy coastal water bodies;**
2) **Compare the response of these tools at three contrasting sites in terms of contamination, and discuss their suitability for coastal monitoring.**

Study area and Methods



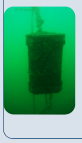
★ STUDY SITES
A ⇔ Chausey
B ⇔ Bay of Veys
C ⇔ Seine outer estuary

⇨ **Mooring to marking buoys on 3 sites + "neutral" home-made mooring in B**

TOOLS DEPLOYED AT EACH SITE:

POCIS
Polar organic Chemical Integrative Sampler
21-days immersion, analysis of 136 organics: 75 pesticides, 55 pharmaceutical molecules, 5 alkylphenols

DGT
Diffusive Gradients in Thin films
21-days immersion, analysis of 11 metals: Al, Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn

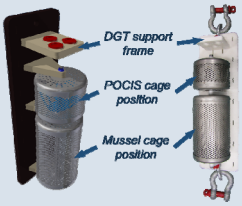


Caging of mussels
T0 and 3,5-months immersion, analysis:
⇔ **Condition index**
⇔ **7 metals:** Ag, Cd, Cu, Hg, Ni, Pb, Zn
⇔ **188 organics:** 77 pesticides, 22 PCBs, 21 PAHs, 13 PBDEs, 11 alkylphenols & furans, phthalates, solvents, dioxins, organotins, PFOA, PFOS, alkanes

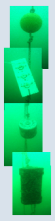
Biomarkers
Caged and/or wild mussels
Analysis of
⇔ **Lysosomal stability**
⇔ **Micronucleus assay**
⇔ **Catalase activity**

1- Immersion of POCIS, DGT and caging

A – Support device design:



Device fixed to marking buoys' chain at sites A, B, C



Tools fixed at the "neutral" mooring at site B

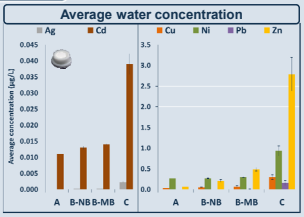
B – Tools recovered:

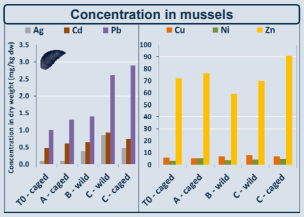
Sites	Mooring	Passive samplers		Mussels		Biomarkers
		DGT	POCIS	Caged	Wild	
A	Marking buoy	X	X	X		X
B	Marking buoy (MB)	X	X		X	X
	"Neutral" buoy (NB)	X	X			
C	Marking buoy	X	X	X	X	Caged

⇔ **POCIS membranes torn at sites A, B-MB and C ⇨ only B-NB analysed**
⇔ **Caged mussels (& devices) not recovered at site B ⇨ wild mussels analysed at site B & C**

2- Comparison of results between tools

METALS



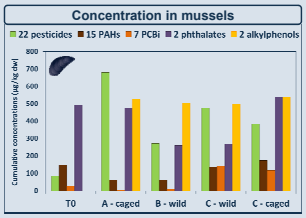


⇔ Results in water showed increasing concentrations of all metals from sites A < B << C.
⇔ Concentrations in caged mussels show increasing concentrations for silver, cadmium, copper, lead, zinc between sites A and C. Levels were slightly higher at site A than C for nickel.
⇔ In wild mussels, concentrations where higher at site C than B for all metals. At site C, concentrations were higher in wild mussels compared to caged mussels for silver, cadmium, and copper.
⇔ **Results confirmed the higher concentration at site C influenced by the Seine inputs. Results more contrasted in the DGT results than in mussels' (problem of metabolic regulation).**

ORGANICS

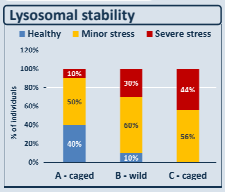
Average water concentration at site B-NB

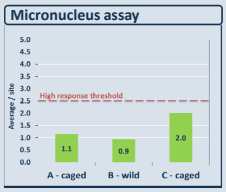
Substances type	Substances	Concentration (ng/L)
Pharmaceutical	Carbamazepine	3,5
	Acebutolol	2,1
	Cetirizine	0,8
Pesticides	Metolachlor ESA	34,8
	Desethylatrazine (DEA)	12,3
	Acetochlor ESA	11,7
	Metolachlor OA	5,6
	Chlortoluron	3,6
	Atrazine-2 hydroxy	3,3
	Atrazine	1,6
	Carbendazime	1,4
	Metazachlor	0,5
	Diuron	0,5
	Carbetamide	0,3
	DMSA	0,2
	Hexazinone	0,1

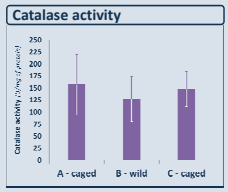


⇔ In water at site B, 3 pharmaceutical residues and 13 pesticides quantified. Most quantified pesticides were metabolites of banned substances.
⇔ Concentrations in caged mussels show increasing concentrations for Polycyclic Aromatic Hydrocarbons (PAHs), PolyChloroBiphenyls (PCBs). Pesticides, phthalates and alkylphénols were present at all sites.
⇔ **Results confirmed the higher contamination of site C influenced by the Seine inputs for PAHs and PCBs. Pesticides, phthalates and alkylphénols were ubiquitous.**

BIOMARKERS







⇔ No "healthy" mussels were found in site C with lysosomal stability.
⇔ "Severely stressed" mussels found at site A, even though often used as a reference for low contamination.
⇔ Similar response at site A and B with micronucleus assay. Higher response at site C but not exceeding the threshold.
⇔ No significant difference between sites for the catalase activity response.
⇔ **The lysosomal stability indicator gave the most informative response relative to the health status of mussels, highlighting worsening from site A to C in consistency with above results.**

Conclusion

This work highlighted the **operational challenge of deploying passive samplers and caging** in open coastal waters in the Channel:

- DGTs resisted relatively well to the immersion during 21-days, beyond the recommended 4-5 days.
- POCIS did not resist to the immersion at all sites when moored to the marking buoys.
- The lysosomal membrane stability biomarker was the most revealing indicator of the health status of mussels between all sites.

These results represent **new data on substances that are of high concern**:

- A confirmed increasing gradient in trace metal, PAHs, and PCBs concentrations from sites A to C and worsening health status of mussels.
- Banned pesticides metabolites were the most detected molecules in water at site B, with two pharmaceutical residues. Pesticides, phthalates and alkylphenols were present at all sites.

Acknowledgments

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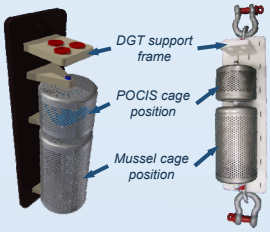
B
C
A
Seine
Contamination gradient
NORMANDY
Paris


DGT support frame
POCIS cage position
Mussel cage position