



SIXTH FRAMEWORK PROGRAMME

Contract n° FP6-031486



EFFORTS

23th September 2009

**“Effective operations
in ports”**

Sub-project 2:
Ports & Environment

WP 2.2.2: Aluminium pollution related to the protection of ports infrastructures

Speakers

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Organization summary of WP 2.2.2

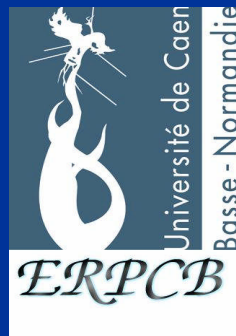
Task 2.2.2.1:
Determination of
contamination levels

Assessment of the aluminium concentration in
water, sediment and living organisms in the
port environment.

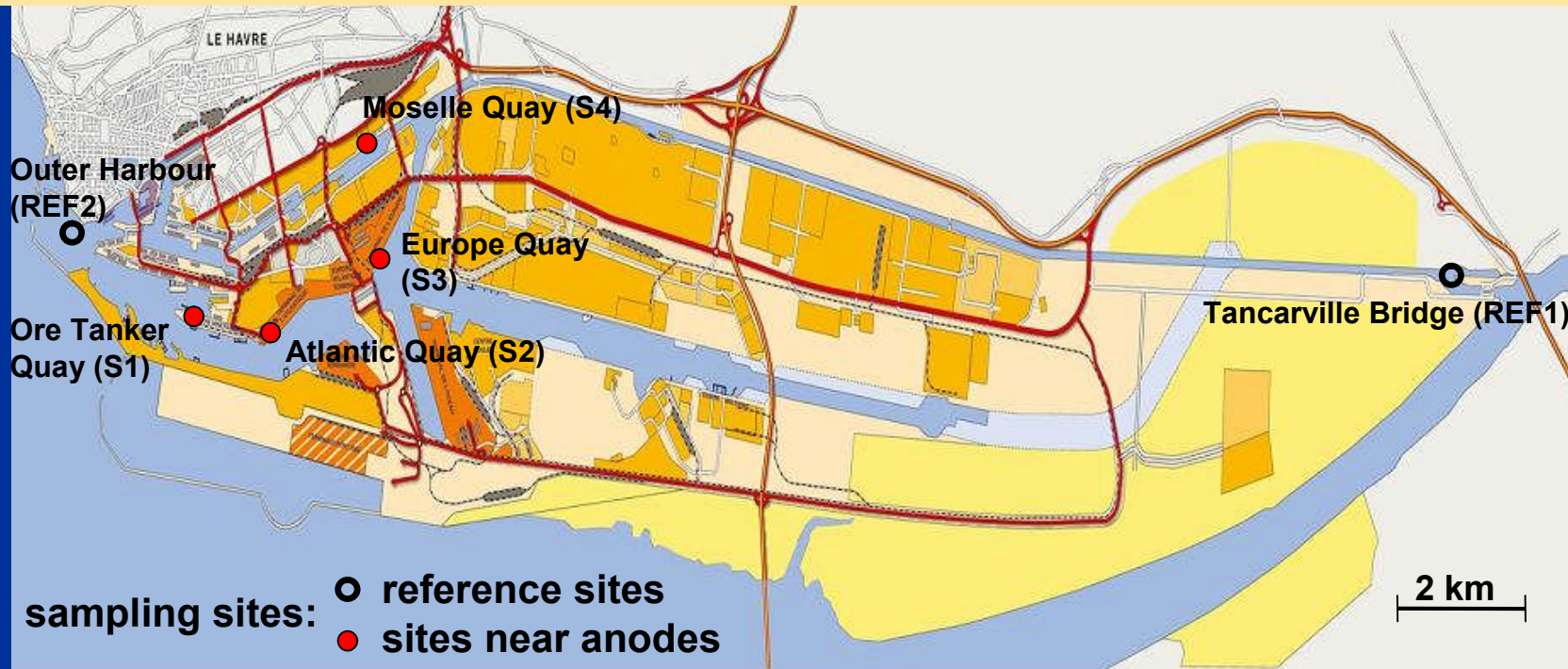
Task 2.2.2.2:
Ecotoxicological tests

Assessment of aluminium toxicity against marine
organisms and the potential environmental
impact of the use of sacrificial anodes.

Task 2.2.2.3:
Scientific data base & help-to-decision
tool development



Task 2.2.2.: Sampling area - The Port of Le Havre

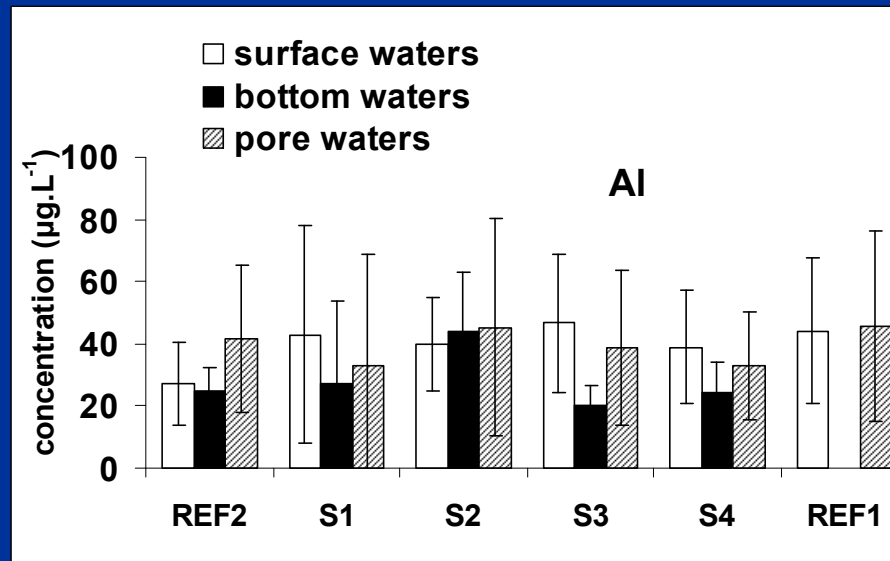


- **REF1, REF2** ⇒ to assess to the impact of the port on water/sediments/organisms quality.
- **S1, S2, S3, S4** ⇒ to assess the impact of anodes on water/ sediments/organisms in open and closed basins.

3 sampling campaigns: **Nov. 2007 (PAH1), Feb. 2008 (PAH2) and jul. 2008 (PAH3)**



Task 2.2.2.1: Aluminium concentration in waters



Mean concentrations in water column range from **20 to 47 µg/L.**

- Concentrations similar to the concentrations measured in the Thame River (England) or in Chinese estuaries (10 to 87 µg/L)
- Concentrations below **200 µg/L** (european limit recommended by decree for the water bound to the human consumption).
- No significant difference in water column between the points near the sacrificial anodes and the reference points.



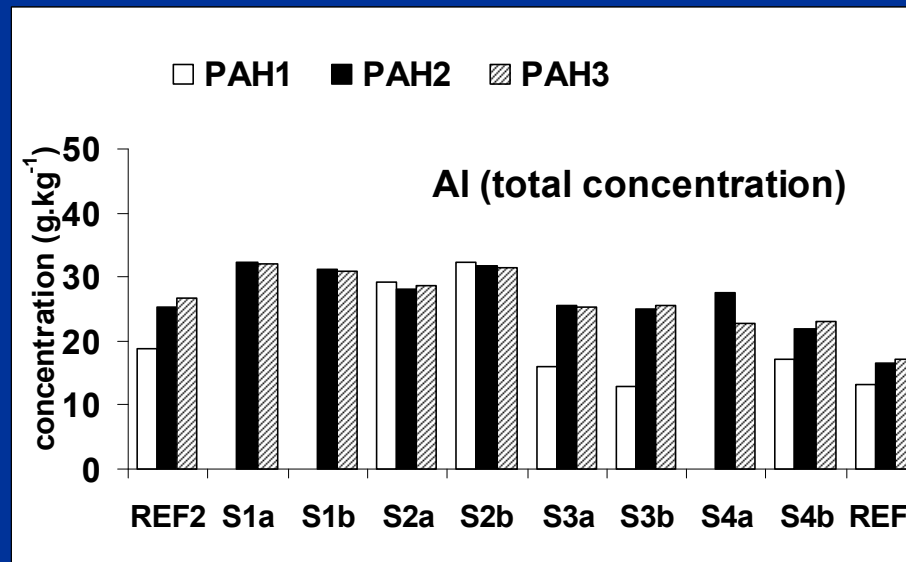
low impact of aluminium anodes on water.



Task 2.2.2.1: Total concentrations in sediments

(a): under anodes

(b): at 20m



Total concentrations in sediments range from **13 to 32 g/kg**.

Values similar to values found in 2007 dredged sediments (GPMH's data)

Total concentrations not sufficient for contamination assessment, as Al = constitutive major element of naturel sediment :

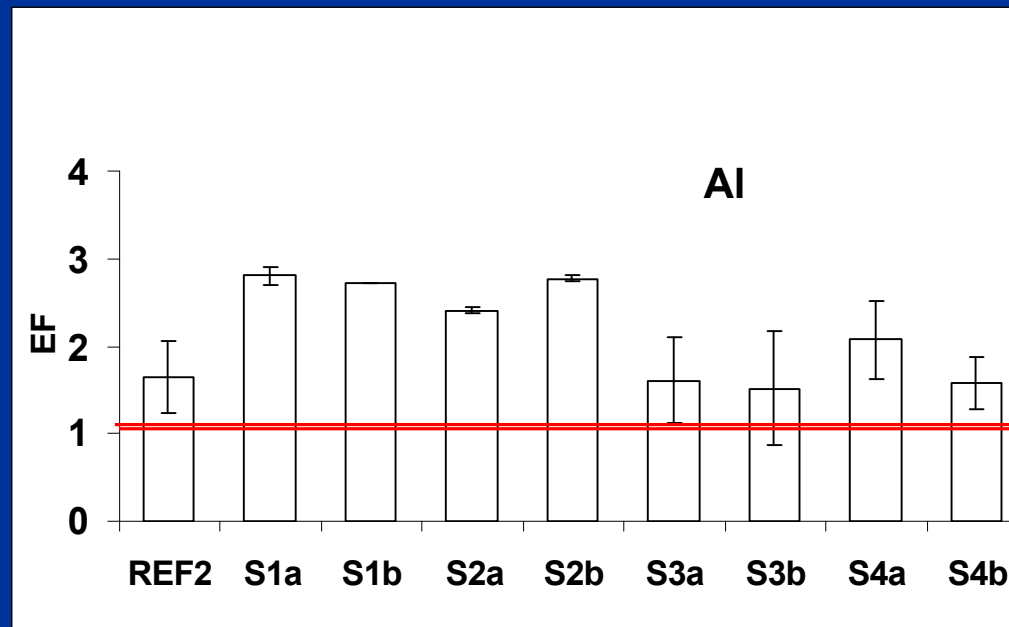



Task 2.2.2.1: Enrichment factor (EF)

$$EF = \frac{\frac{M_x}{Si_x}}{\frac{M_r}{Si_r}}$$

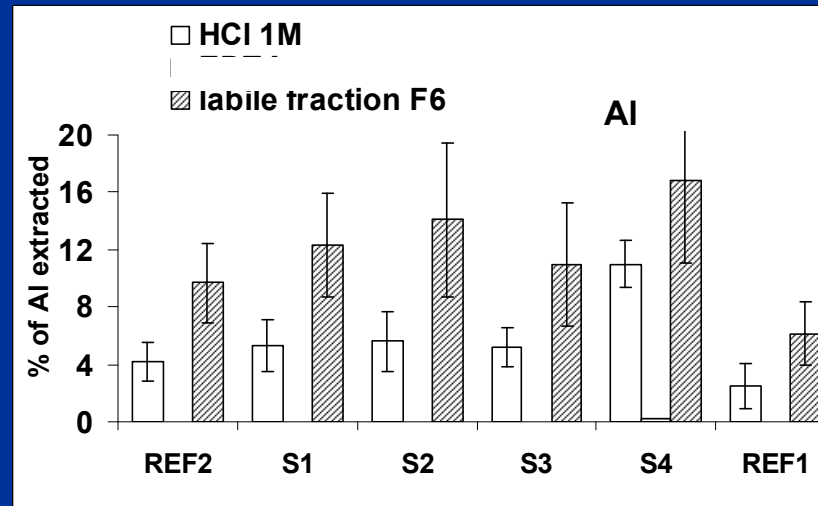
(a): under anodes

(b): at 20m



- **Al enrichment of sediments**  **Recent anthropogenic input**
Impact of Al anodes dissolution?
- Highest values found for the non-dredged sites S1 and S2
- No significant difference between values measured under anodes or at 20m

Task 2.2.2.1: Aluminium availability: single and sequential extractions



HCl labile fraction :

≤ 3% REF1 & REF2

5-10% S1, S2, S3, S4

Total labile fraction (F6) :

≤ 5% REF1

10-16% others sites

unusual value for Al mobility/availability



unusual Al speciation in the sediments



Task 2.2.2.1: Laboratory tests

water quality

No significant influence of Al sacrificial anodes dissolution in water was detected.

sediment quality

No significant Al enrichment in the sediment was also detected during this experiment.

Longer experimental time should be tested

ratio of Al anodes/sediments should be adapted to in situ conditions

Further experiments should be realised to get realistic conclusions.



Task 2.2.2.1: Conclusions

water quality

→ low impact of aluminium anodes on water quality ($[Al] < 50\mu\text{g.L}^{-1}$)

sediment quality

→ Al enrichment observed in sediments

→ increased Al mobility in surface sediments near anodes

result of:

modification of Al speciation?

and/or

anthropogenic input of mobile Al?



Task 2.2.2.1: Perspectives : water/sediment

↪ detailed investigations needed on Al speciation in water and sediments.

↪ investigations in others ports, to get statistical data.

↪ solution /alternative techniques to sacrificial anodes :

✓ regular dredging of sediments near structures protected by sacrificial anodes ⇒ *sediments re-use and valorisation techniques*

✓ cathodic protection applied by fixed current density

✓ association with organic coatings



Environmental impact?

Economical feasibility?



Task 2.2.2.2: Aluminium concentration in organisms

Task 2.2.2.2a: Determination of [Al] in *in-situ* bivalve specie: *Mytilus edulis*

=> to assess Al levels in **environmental conditions**

Task 2.2.2.2b: *in-vitro* bioconcentration test by *Mytilus edulis*

=> to assess **bioaccumulation process**

=> to identify if natural detoxification process

Task 2.2.2.2c: Ecotoxicological tests (oysters and sea-urchins)

=> to assess **toxicity effects of contaminants**



Task 2.2.2.2a: Aluminium in *in-situ* mussels

Mussels were collected *in-situ* (port of Le Havre):

Al concentration range in total tissue:

54 to 600 mg/kg DW



[Al] recorded in mussels of Le Havre are in the **medium range** levels given by **Mussel Watch** (2005) (Monitoring program)



Task 2.2.2.2a: Aluminium in *in-situ* mussels

Digestive Gland (DG) was studied because:

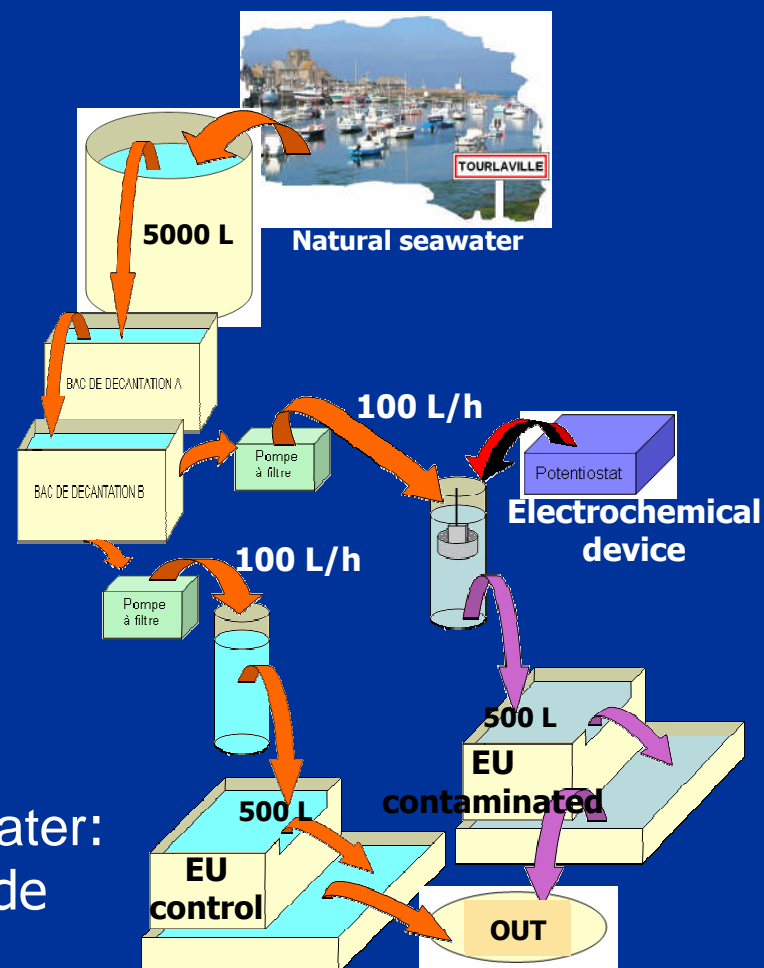
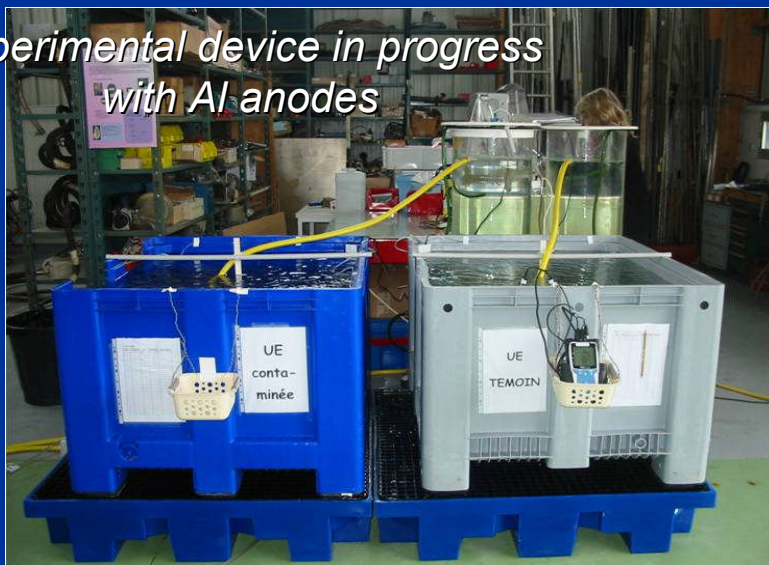
- ◆ **DG** plays a role in the intracellular and extracellular digestion and storage of nutritive substances
- ◆ the strong tendency to accumulate metals of **DG** is well documented



Task 2.2.2.2b: *In-Vitro* bioconcentration test by *Mytilus edulis*

At the « Flamands station » :

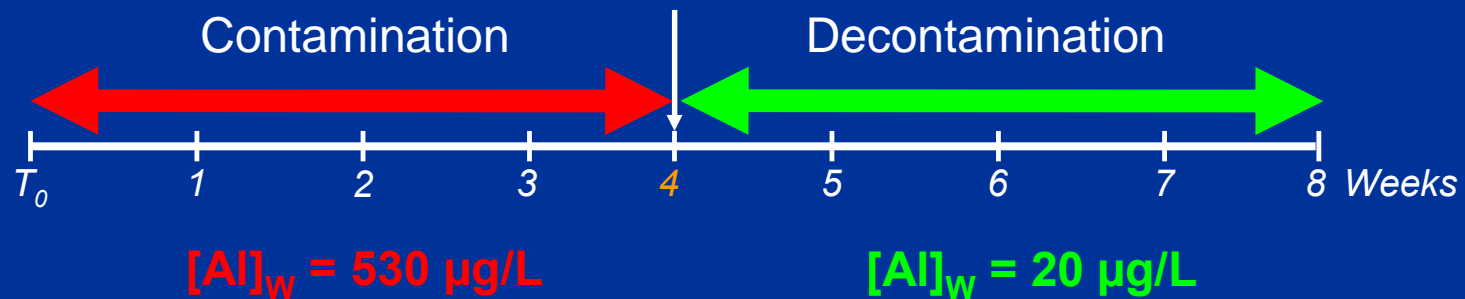
Experimental device in progress
with Al anodes



- ◆ Two different tanks with natural seawater: control and contaminated with anode
- ◆ Physical chemical parameters (pH, T, S, O₂) under control

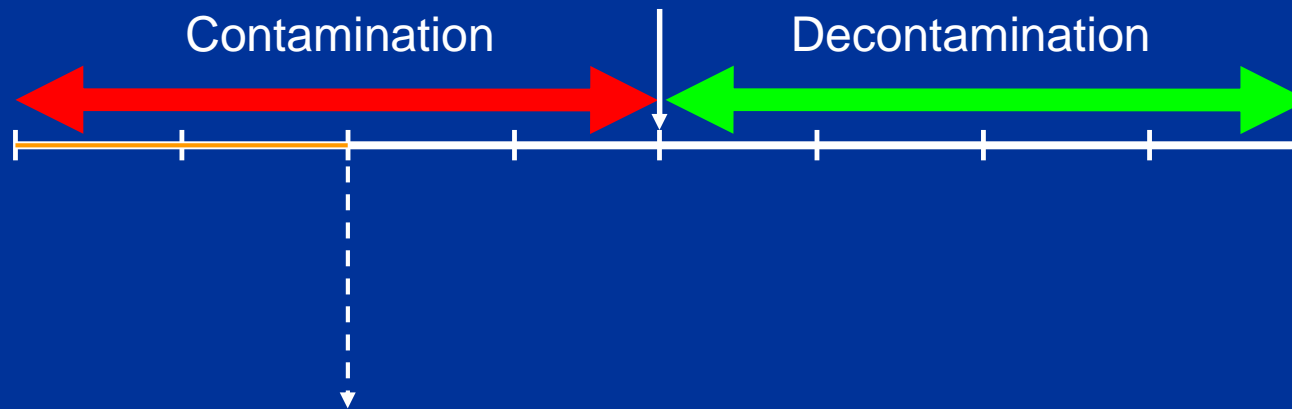
Task 2.2.2.2b: In-Vitro bioconcentration test by *Mytilus edulis*

- *In-Vitro* test in seawater - Process



Task 2.2.2.2b: In-Vitro bioconcentration test by *Mytilus edulis*

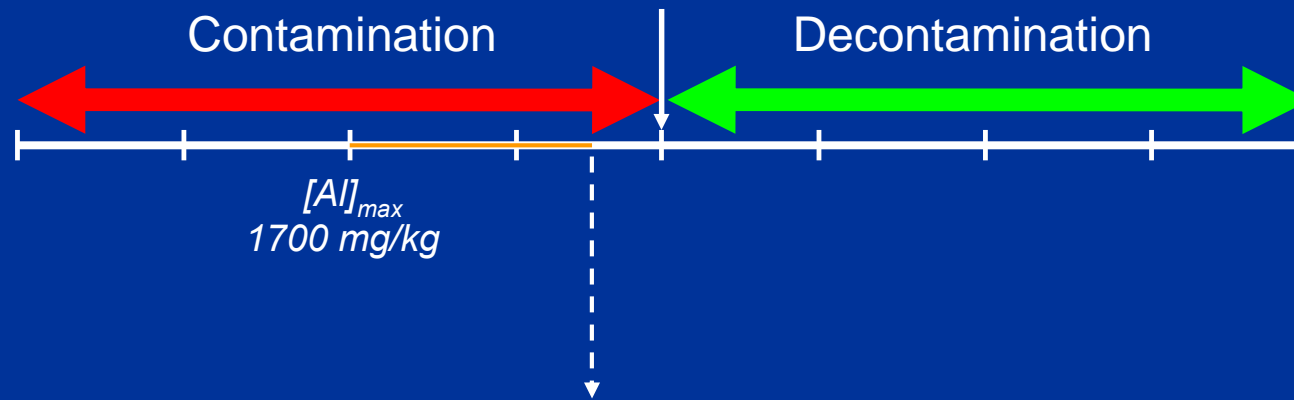
- *In-Vitro* test in seawater – Results in DG



- ◆ First Obs. : Maxi. of [Al] concentration ($\Rightarrow T_{13}$) $[Al]_{\max} = 1700 \text{ mg/kg}$

Task 2.2.2.2b: *In-Vitro* bioconcentration test by *Mytilus edulis*

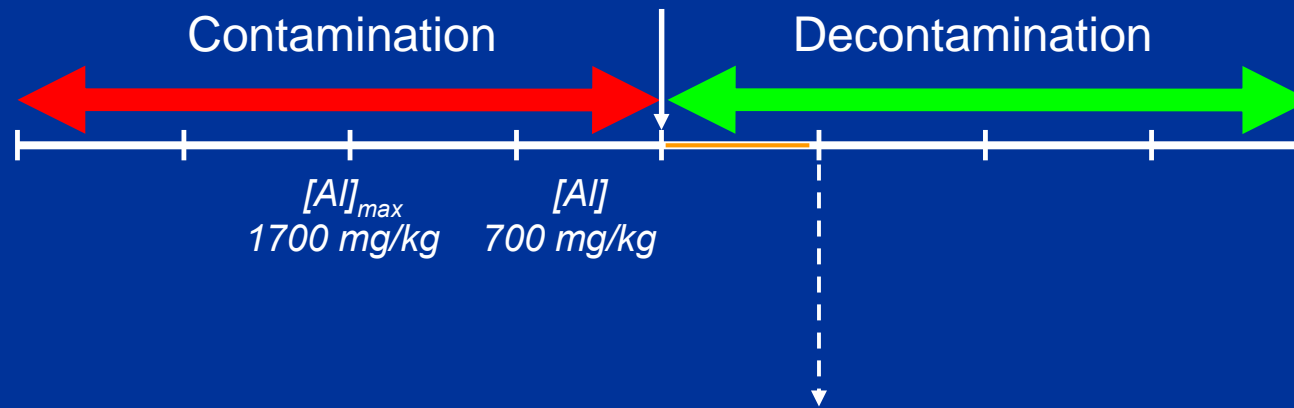
- *In-Vitro* test in seawater – Results in DG



- ◆ First Obs. : Maxi. of $[Al]$ concentration ($\Rightarrow T_{13}$)
- ◆ Second Obs. : 1st decrease of $[Al]$ **BEFORE** decontamination ($\Rightarrow T_{29}$)
 $[Al] = 700$ mg/kg

Task 2.2.2.2b: In-Vitro bioconcentration test by *Mytilus edulis*

- *In-Vitro* test in seawater – Results in DG



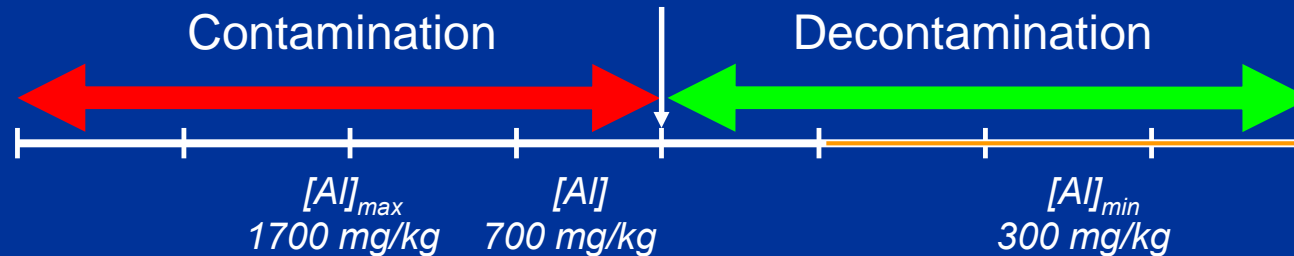
- ◆ First Obs. : Maxi. of $[Al]$ concentration ($\Rightarrow T_{13}$)
- ◆ Second Obs. : 1st decrease of $[Al]$ BEFORE decontamination ($\Rightarrow T_{29}$)
- ◆ Third Obs. : S^d decrease of $[Al]$ **AFTER** decontamination ($> T_{29}$)

$[Al]_{min} = 300$ mg/kg



Task 2.2.2.2b: In-Vitro bioconcentration test by *Mytilus edulis*

- *In-Vitro* test in seawater – Results in DG



- ◆ Last 3 weeks => same $[Al]$ in mussels of 2 tanks

Natural detoxification process ignited by mussels **BEFORE** decontamination

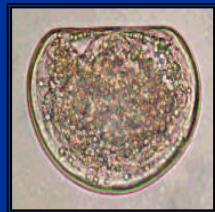
=> No bioaccumulation of Al

Task 2.2.2.c: Ecotoxicological tests

OYSTER LARVAE



(*Crassostrea gigas*)



Normal D larvae

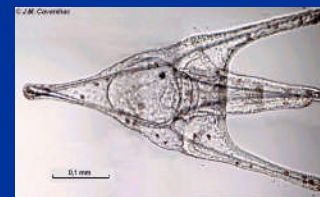


abnormality

SEA-URCHIN LARVAE



(*Paracentrotus lividus*)



Normal larvae



abnormality

- OYSTER LARVAE - Process

- ◆ % of abnormal D-larvae after eggs fertilization
- ◆ Different Al concentrations [Al₂(SO₄)₃] tested (50 to 600 µg/L)



Water Quality Guidelines :

Percentage of abnormal D-larvae	< 20%	< 25%	25 - 50%	50 - 75%	> 75%
Water Quality Status	<u>Not contaminated</u>	<u>Not much contaminated</u>	<u>Middling contaminated</u>	<u>Very contaminated</u>	<u>Highly contaminated</u>

- OYSTER LARVAE - Results

EC 50 = 110 ± 10 µg/L
(50% of abnormality after 48h)

=> EC 50 > [Al] recorded in Le Havre waters (< 58 µg/L)

Task 2.2.2.2c: Ecotoxicological tests

- SEA-URCHIN LARVAE - Process

Testing object	Duration	Endpoints
Embryos (zygote → pluteus)	72 hrs	1) larval malformations (P1) 2) development arrest (P2) 3) larval (D1) or embryonic (D2) mortality
Sperm (<i>P. Lividus</i>)	60 min	1) fertilization rate (FR)

- ◆ Two Al concentrations were tested => 1 and 10 μM (27 and 270 $\mu\text{g/L}$)
- ◆ Two Al sources were tested => Al sulfate and Al from anode



Task 2.2.2.2c: Ecotoxicological tests

- SEA-URCHIN LARVAE - Results

scarcely toxic (embryos) or non-toxic (sperm) effects of Al
from anode compared to Al sulfate



Task 2.2.2.2: Conclusions

A- Environmental conditions of Seawater:

=> [Al] recorded in Le Havre port are in the **medium range** levels

B- Laboratory tests on seawater (*in-vitro*)

=> **No bioaccumulation of Al** in mussels

C- Toxicity of Al from seawater

=> No toxicity of Al on larvae development (for [Al] < 110 µg/L)
case of port of Le Havre

=> **Lower toxicity of Al anode** compared to Al sulfate



Task 2.2.2.2: Perspectives

BUT :

=> Interactions organisms-sediment no studied:

- ◆ Ecotoxicological tests with **sediments** no performed
- ◆ *In-vitro* test with **benthos** species no performed

=> Al chemical form important to determined (difference of toxicity)



Task 2.2.2.2: Perspectives

Actions proposed for Harbours : Active Biomonitoring

◆ **Biomonitoring** of “transplanted” mussels *in-situ* from a reference site during one year

=> *caging system* :

=> near anode and sediment



◆ **Complete** with laboratory tests: *in-vitro* and *Ecotox.*)

Thanks for your
attention !

