Assessment of Natural Clean Up Processes on Oiled Rocky Shores : Development of an *In Situ* Experiment

Mr Ronan Jézéquel– Cedre – Rue Alain Colas BP 20413 – 29604 Brest
ronan.jezequel@le-cedre.fr
Secondary authors : Messrs Lénaïck Menot, François-Xavier Merlin and Roger C. Prince (*)
** : ExxonMobil Research and Engineering Co.*
1545 Route 22 East
Annandale, NJ 08801
roger.c.prince@exxonmobil.com

ABSTRACT

When exposed rocky shores are affected by oil spills, the advised cleanup option, in most cases, is to "do nothing". This assumes that natural processes will rapidly clean such shores, while remedial actions might have detrimental effects for ecological recovery. The natural cleaning timescale is one of the basic data in the decision making process for cleanup response following an oil spill (API, 1997). On rocky shores however, the quantification of natural cleaning processes remains largely based on subjective data. *Cedre* has developed an experimental concept with the aim of objectively quantifying the natural cleaning timescale of rocky shores exposed to different environmental conditions.

The experiment was conducted on an islet inside the roadstead of Brest (France) within the perimeter of the French Navy. The restricted access of the zone is ideal for long term *in-situ* studies. The two sides of a quay were used to expose artificial substrates to different conditions: the North face, exposed to wave actions and in the shade of the quay; and the South face, exposed to solar radiation but sheltered from most wave activities.

Removable artificial substrates, made of granite plates, were polluted with different oil (Arabian Light crude oil, Bunker C fuel oil, Orimulsion®), and then set on the experimental site. Plates were periodically sampled and brought back to the laboratory for analyses.

The quantity and changes in chemical composition of oil remaining were quantified. The influence of pollution on recolonisation was also monitored by assessing the density of living organisms on polluted plates and control plates (i.e without any pollutant).

Furthermore, the effect of the presence of living organisms on the plates before the oil spill was studied by applying the oil on pre-colonized plates (i.e placed in the environment for a few months before the pollution).

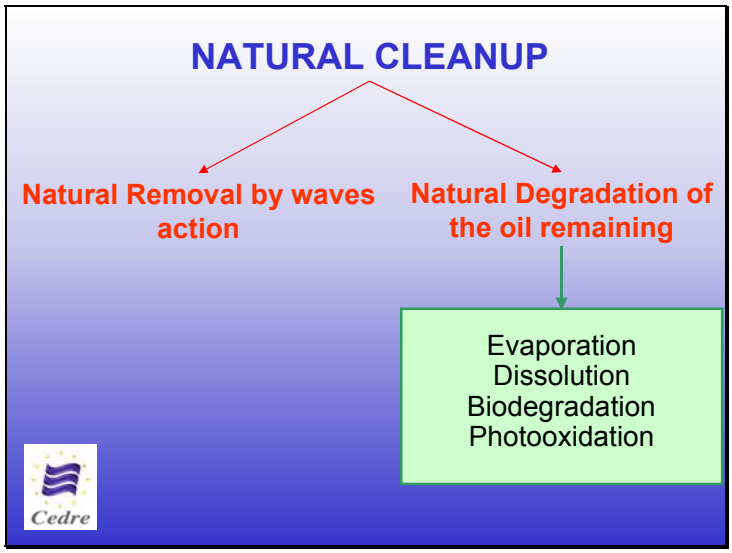
The preliminary conclusions of those studies indicate the great significance of oil type: the Arabian Light crude oil was rapidly washed, while the persistence of Bunker C fuel oil was much longer. The persistence of the oil was also a function of wave exposure: 50% loss of Arabian Light in 10 days for exposed conditions and 18 days for sheltered ones; for the Bunker C fuel oil, 50% loss occurred in 80 days for exposed and 180 days for sheltered conditions.

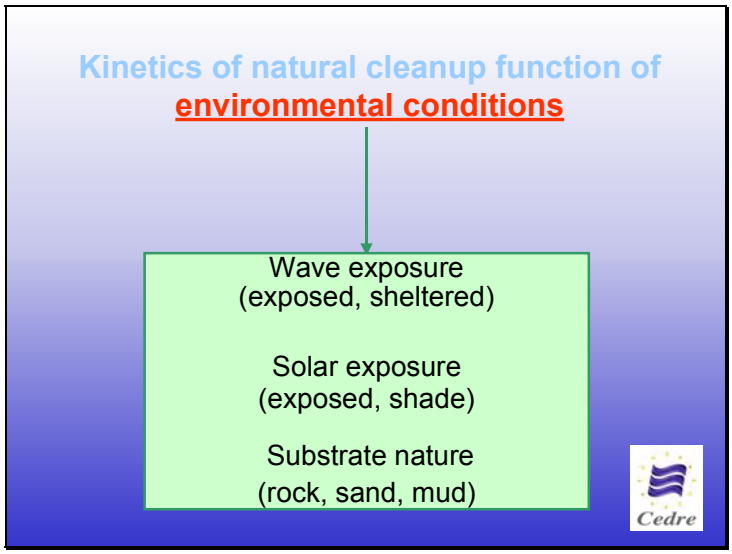
Chemical compositions were analyzed in samples exposed to the elements for 22 months. Samples in the dark, with exposure to full or reflected sunlight, and the initial oil, were analyzed by thin layer chromatography and gas chromatography coupled with mass spectrometry. The results indicate that dissolution, biodegradation and photooxidation all play important roles in the weathering process, with their respective contributions depending on the exposure. On plates facing to the North, residual oil was more biodegraded (disappearance of n-alkanes up to C_{16} and depletion of the n-alkanes from C_{17} to C_{40}) while oil remaining on plates facing to the South was more photooxidated (depletion of C3-chrysenes was more important when exposed to the South).

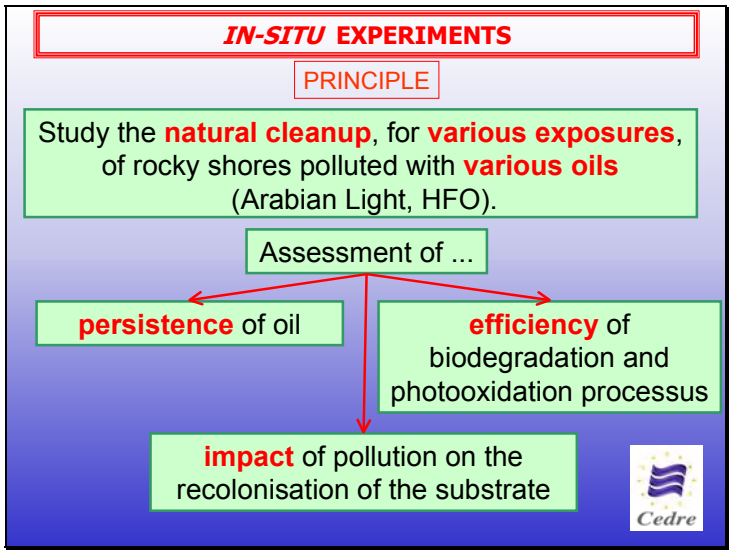
Chemical analyzes of oil remaining after 1 year also revealed the influence of pre-colonization on the rate of biodegradation: for pre-colonized plates, the biodegradation rate of alkanes was more important during the very first days than the oil remaining on non-colonized plates. This was probably due to the presence of a bacterial film on these plates at the beginning of the experiment.

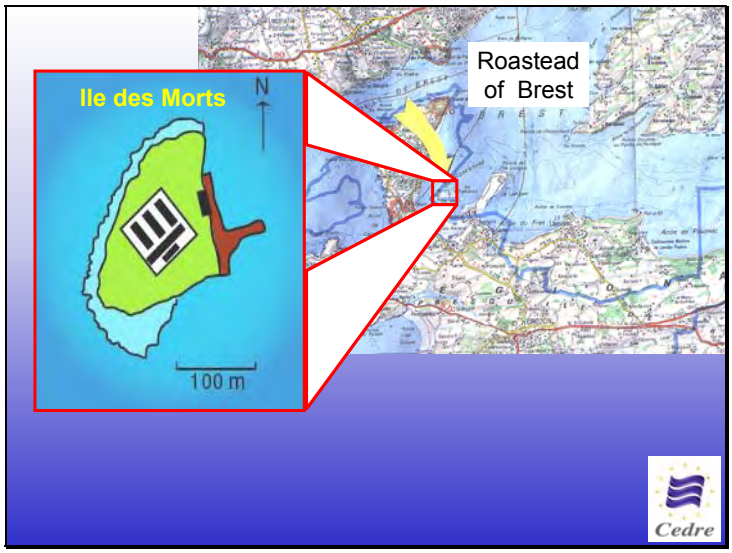
Assessment of the density of living organisms revealed that all the plates were colonized by barnacles despite the presence of pollutant.

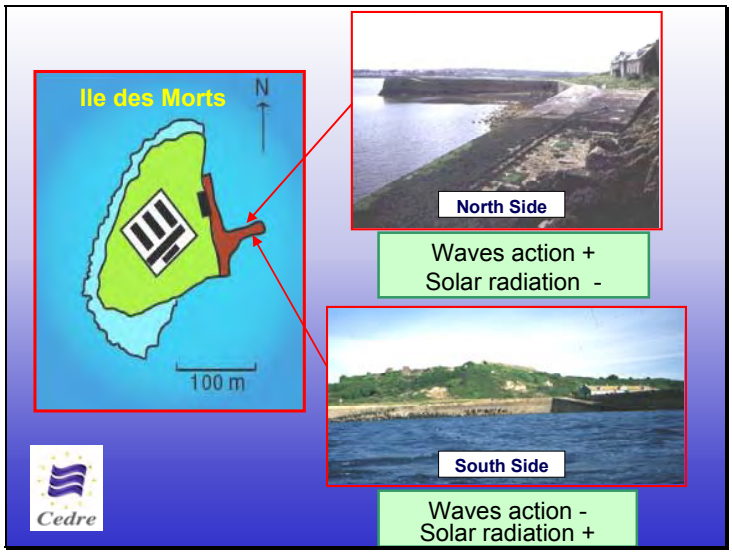

ASSESSMENT OF NATURAL CLEANING OF OILY ROCKY SHORES :
DEVELOPMENT OF AN *IN SITU* EXPERIMENT
Ronan Jézéquel, François Merlin
Lénaïck Menot
Cedre
Roger C. Prince
Exxonmobil
Technical Lessons learnt from the Erika and others
BREST, 13 - 16 March 2002

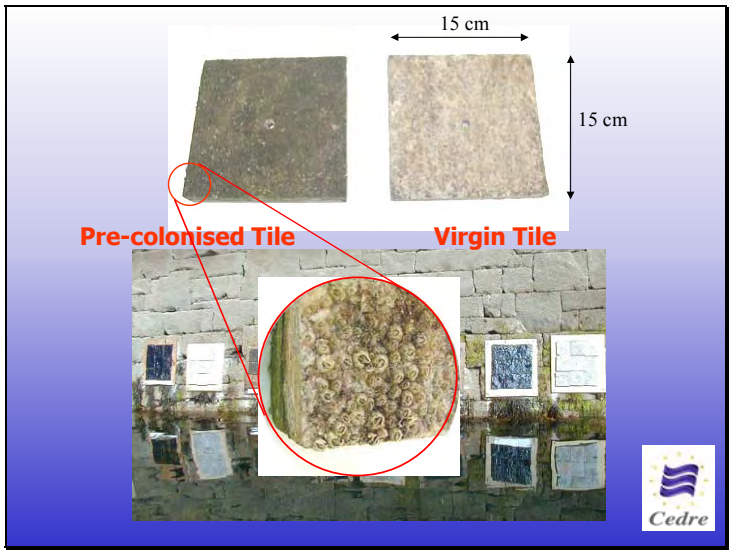

NATURAL CLEANUP
Natural Removal by waves action
Natural Degradation of the oil remaining
Evaporation
Dissolution
Biodegradation
Photooxidation
Cedre

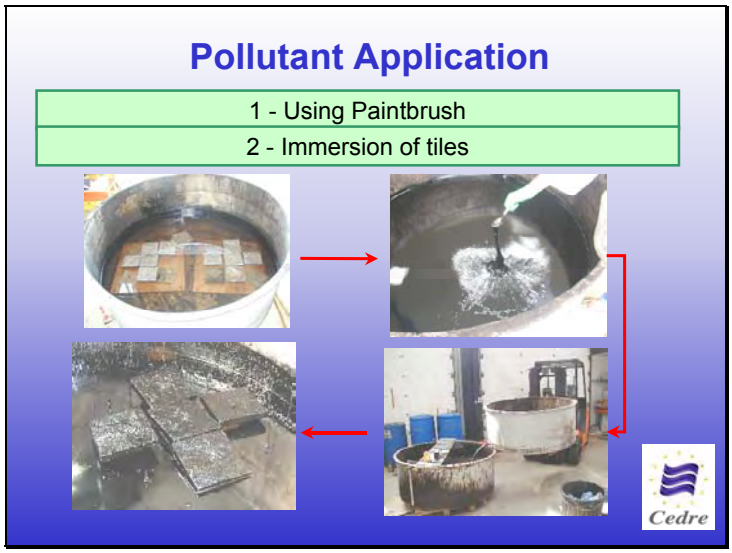

Kinetics of natural cleanup function of
environmental conditions
Wave exposure
(exposed, sheltered)
Solar exposure
(exposed, shade)
Substrate nature
(rock, sand, mud)
Cedre

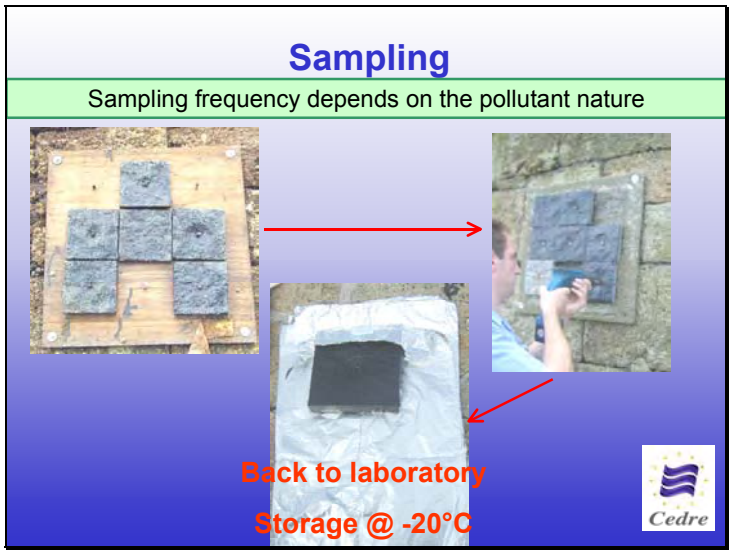

IN-SITU EXPERIMENTS
PRINCIPLE
Study the natural cleanup, for various exposures, of rocky shores polluted with various oils (Arabian Light, HFO).
Assessment of ...
persistence of oil
efficiency of biodegradation and photooxidation processus
impact of pollution on the recolonisation of the substrate
Cedre


Ile des Morts
N
100 m
Roastead of Brest
Cedre


Ile des Morts
N
100 m
North Side
Waves action +
Solar radiation -
South Side
Waves action -
Solar radiation +
Cedre


15 cm
15 cm
Pre-colonised Tile
Virgin Tile
Cedre


Pollutant Application
1 - Using Paintbrush
2 - Immersion of tiles
Cedre


Sampling
Sampling frequency depends on the pollutant nature
Back to laboratory
Storage @ -20°C
Cedre

Laboratory

1 - Pollution impact on recolonisation timescale

2 - Assessment of the natural removal by waves action

3 - Assessment of natural degradation of the oil remaining on the tiles

Laboratory

1 - Pollution impact on recolonisation timescale

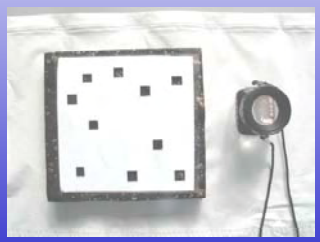
2 - Assessment of the natural removal by waves action

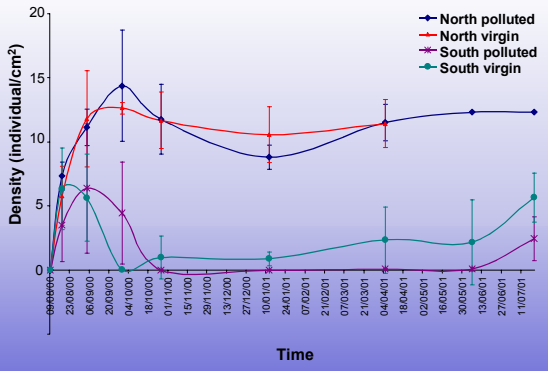
3 - Assessment of natural degradation of the oil remaining on the tiles

Impact on the recolonisation

Assessment of the density (D) of living organisms (barnacles) by counting.

D = Average barnacle number in 10 squares (1 x 1cm)





North Side (Waves +, Solar -): environment adapted to recolonisation

➥ **presence of oil has no effect on recolonisation**

South Side (Waves -, Solar +): environment hostile to recolonisation

Thickness (µm)	0	0, 21	4, 03	4,37
Density	2,40±1,51	2,50±1,43	0,40±0, 52	0

➥ **presence of oil reduces recolonisation**

! Assessment of the recolonisation was performed ONLY by counting (no study of the growth).

Laboratory

1 - Pollution impact on recolonisation timescale

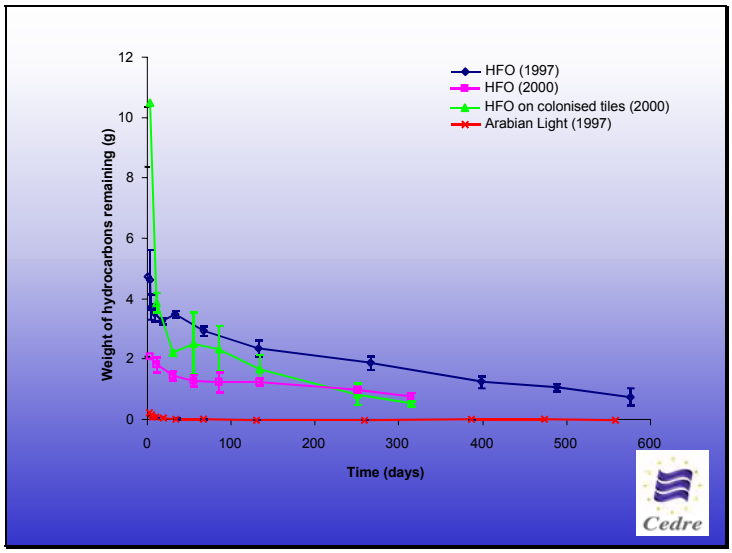
2 - Assessment of the natural removal by waves action

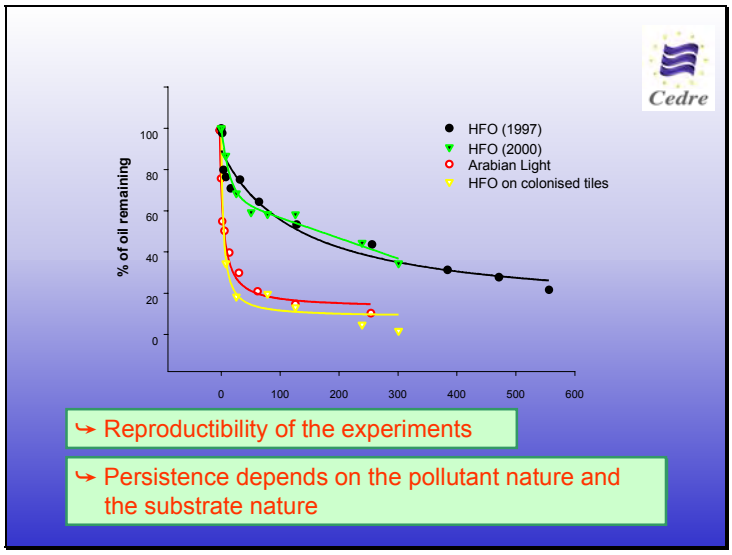
3 - Assessment of natural degradation of the oil remaining on the tiles

Gravimetric Analyses

Extraction of the oil remaining on the tiles

- ↪ Extraction with methylene chloride (300 mL)
- ↪ 15 minutes in an ultrasonic bath
- ↪ Solvent evaporation
- ↪ Weighing





- ↪ Reproductibility of the experiments
- ↪ Persistence depends on the pollutant nature and the substrate nature

Laboratory

1 - Pollution impact on recolonisation timescale

2 - Assessment of the natural removal by waves action

3 - Assessment of natural degradation of the oil remaining on the tiles

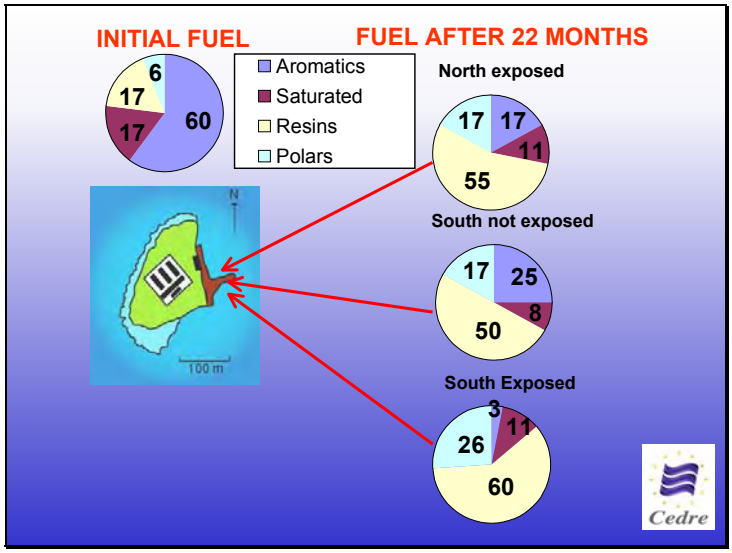
Chemical Analyses

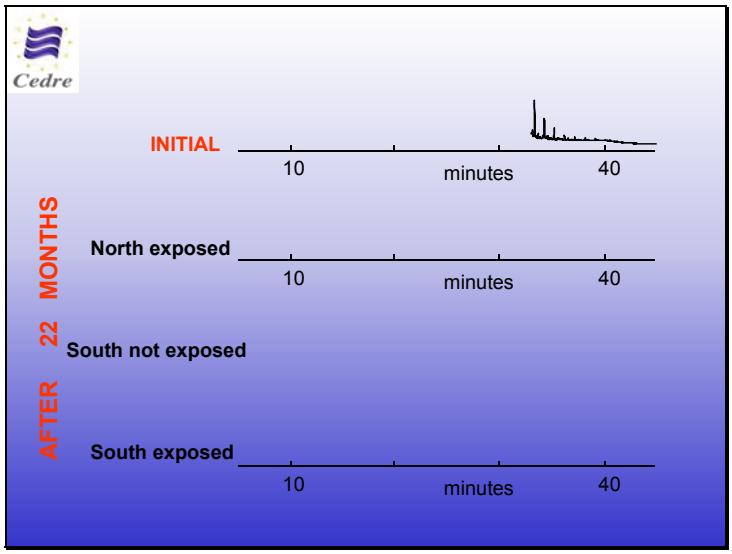
Assessment of the abundance of each chemical fraction

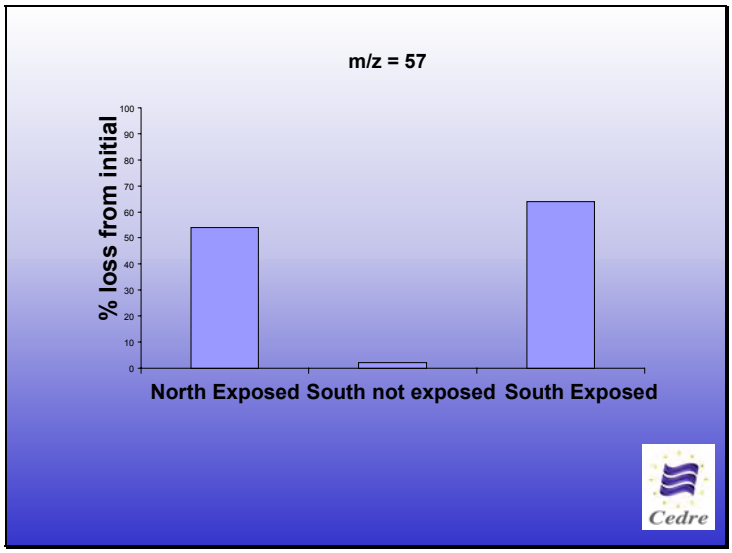
➥ Iatroscan

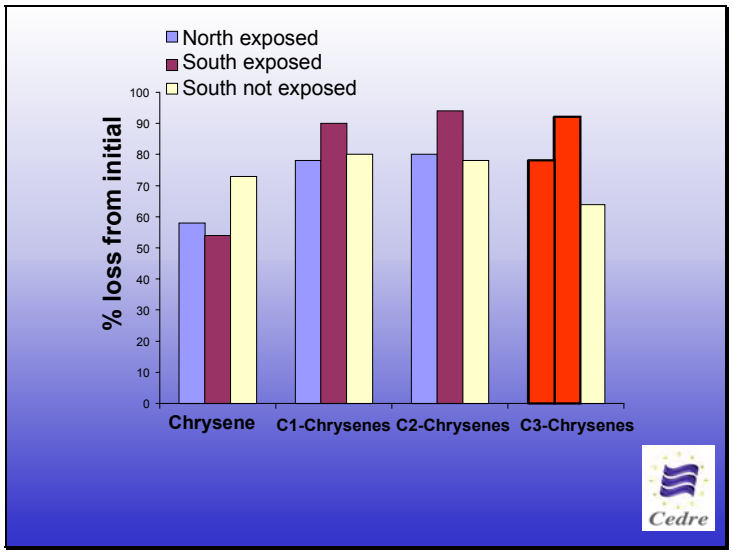
Assessment of the degradation of the Saturated and Aromatic Fractions

➥ GC - MS




Cedre
INITIAL
10
minutes
40
AFTER 22 MONTHS
North exposed
10
minutes
40
South not exposed
South exposed
10
minutes
40


m/z = 57
% loss from initial
100
90
80
70
60
50
40
30
20
10
0
North Exposed
South not exposed
South Exposed
Cedre


North exposed
South exposed
South not exposed
% loss from initial
100
90
80
70
60
50
40
30
20
10
0
Chrysene
C1-Chrysenes
C2-Chrysenes
C3-Chrysenes
Cedre

Conclusions

North exposed sample:	photooxidation + biodegradation +
South not exposed sample:	photooxidation - biodegradation ++
South exposed sample:	photooxidation ++ biodegradation -

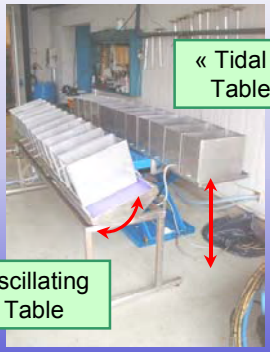
FUTURE

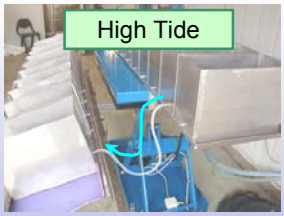
- Study on the influence of substrate nature
  ↳ **Experiment with various substrates**
  (wood, calcareous, concrete, marble)

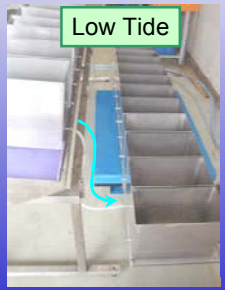
- Development of experimentations in mesocosms (« banc d'essais » *Cedre*) before *in situ* experiment.

Oscillating table generating identical waves action in 12 tanks. Each one is connected to another aquarium (renewal tank) by a small hose to recreate tidal cycles.

« BANC D' ESSAIS »







Water movement


ACKNOWLEDGEMENTS
Marine nationale
COMMISSION D'ETUDES PRATIQUES DE LUTTE ANTIPOLLUTION
CEPPOL
Cedre