

## **Influence of Weathering of Heavy Fuel Oil on High Pressure Washing Efficiency with and without Cleaning Agent**

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### **Abstract**

Following an oil spill of rocky shores, the efficiency of high pressure washing techniques is influenced by the nature of the oil, the substrate nature and also by the weathering degree of the pollutant due to natural degradation processes. An experimental program was initiated in order to assess the influence of this natural weathering on the efficiency of high pressure washing techniques. Particularly, the need to use cleaning agents to enhance the washing effectiveness was examined according to the pressure, the temperature of the washer and the oil weathering degree.

The experimental study was conducted with a “washing robot”, an automated tool developed at *Cedre*. The rocky shores were simulated by using granite tiles coated with heavy fuel oil. The high pressure washer was similar to those available in French POLMAR stockpiles. The tests were performed in triplicates with water temperatures from 15 to 77°C at pressures ranging from 5 to 100 bars, and oil weathered from 2 to 61 days in natural environment. The amount of oil remaining on the tiles was determined by spectrophotometry and chemical analyses were performed in order to assess its degradation rate.

The experimental results highlight the importance of temperature on the efficiency of the washing technique. Without cleaning agent, for a temperature of 45°C and a pressure of 10 bars, an average of 78% of oil was removed from the tiles. With temperatures from 15 to 30°C, this rate was obtained respectively for a pressure of 100 and 60 bars. For temperatures greater than 45°C at any conditions of pressure, the application of a cleaning agent did not shown any increase in the efficiency of the washing technique.

After 61 days of natural weathering, cleaning rate did not exceed 20% for the range of temperatures and pressures tested. When a cleaning agent was used, it was possible to remove 100% of the oil when using the highest temperature and pressure settings.

### **1 Introduction**

When spilled at sea, oils are subjected to a range of environmental effects. Small and light molecules evaporate, some molecules dissolve into the sea or are photochemically oxidised, while some oil is dispersed into the water column, either naturally or following the application of dispersants, where it undergoes biodegradation (National Research Council, 2002). On rocky shores, these natural processes of degradation tend to make the pollutant stickier on the substrate and, consequently, more and more resistant to cleaning when using high pressure washing technique.

In order to assess the influence of the oil weathering degree on this cleaning

technique, an experimental study was conducted at *Cedre* by using a “washing robot”, an automated tool which recreates a reproducible high pressure cleaning as it is undertaken on the coastline after an oil spill. The aim of this study was to define the most appropriate washing conditions (pressure, temperature, application of cleaning agent) according to the weathering rate of a heavy fuel oil stranded on a rocky shoreline.

The study was conducted into two stages. The objective of the first stage was to compare the hydraulic washing efficiency of a granite substrate (Menot et al., 1999) polluted with a fresh heavy fuel oil (i.e. non weathered) according to settings of the hydraulic washer (temperatures and pressure ranging respectively from 15 to 77°C and from 2 to 100 bars). Interest of using cleaning agent was also studied during this first stage. The objective of the second stage was to assess the influence of a natural weathering of the oil during 2 to 61 days on the hydraulic washing efficiency.

## 2 Material and Methods

### 2.1 The Washing Robot

The equipment (Figure 1) is composed of the following main items:

- a stainless steel frame with an internal volume of about 300 litres,
- a trolley with the washing nozzle,
- a supporting frame with the polluted hard surfaces,
- two electric screw jacks allowing horizontal and vertical movements of the trolley,
- a high pressure washer (as it could be found in French POLMAR stocks),
- a programmable control driving the two electric jacks,
- a seawater supply.

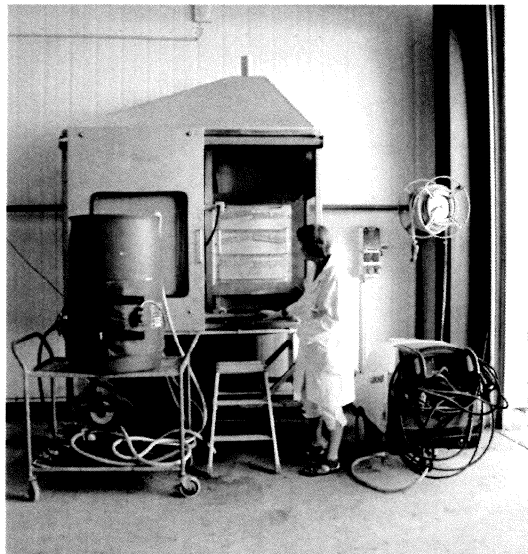


Figure 1. The Washing Robot.

This equipment ensures the same washing conditions for all the successive tests (spraying width, speed and distance). Therefore, the hard surfaces (granite tiles) were washed exactly in the same way, and comparative tests could be performed.

The settings used in the present study are presented in Table 1.

Table 1. Settings of the washing robot.

High Pressure Washer	Karcher HDS 895S
Pressure range	5, 10, 20, 30, 40, 50, 60 and 100 bars (*)
Temperature range	15, 30, 45, 60 and 77°C (*)
Nozzle	Power buse Karcher. diameter 0.55 mm, 25° angle
Sweep frequency	3.8 cm.s <sup>-1</sup>
Distance between hard substrate and nozzle	15 cm

(\*): 100 bars and 77°C are the maximum specifications available with the hydraulic washer used during the present study.

## 2.2 Hard Substrates

The rocky shoreline was simulated by using granite tiles (*Quartzite Astera Gris*) of 15 x 15 x 2 cm. The surfaces of the tiles were not smoothed down in order to recreate a substrate as natural as possible. Oil was applied on the tiles in the laboratory using a paintbrush; after oiling, the tiles were held in a horizontal position for 24 hours (impregnation time) then, in a vertical position during 96 hours to let the excess oil drain (Jézéquel et al., 2003).

The amount of oil remaining on the tiles was then quantified at  $1.56 \pm 0.19$  g ( $n=6$ ). The relatively high standard deviation value was mainly due to the surface roughness. The oil layer applied on the tiles was then estimated at 7  $\mu\text{m}$ , which is in agreement with a layer of oil which could remain on rocks after the manual scraping operations systematically performed after an oil spill.

## 2.3 Natural Weathering

In order to simulate the oil weathering, polluted tiles were brought to an experimental site located in the roadstead of Brest (France). The tiles were screwed to wooden boards of 75 x 75 cm set on a pier at +5 meters over the lowest water level (French nautical chart). The tiles were exposed to tidal flushing twice a day. Sampling rounds of tiles were performed after 2, 7, 14, 31 and 61 days in the environment.

## 2.4 Chemical Analyses

### 2.4.1 Quantification of Oil Remaining on Tiles

After treatment by the washing robot, tiles with the remaining oil were stored at 5°C until analysis. The oil was removed by extraction with methylene chloride (pestipur quality) during 15 minutes in an ultrasonic bath and, after drying on sodium sulphate (activated at 400°C overnight), diluted to appropriate concentrations. The absorbance was measured at 580 nm by using a

spectrophotometer (UNICAM, UV/Vis spectrophotometer).

#### 2.4.2 Assessment of the Oil Weathering

Analyses were performed in order to assess the weathering rate of the oil remaining on tiles when exposed to natural environment. In a first step, the analyses performed by High Performance Liquid Chromatography (HPLC) provided information on the percentages of saturates / aromatics and polar fractions. In a second step, the analyses were performed by Gas Chromatography coupled to Mass Spectrometry (GC/MS) in order to quantify the abundances of *n*-alkanes and PAH compounds.

- HPLC analyses

The protocol used was adapted from Akhlaq (1993) and Pasadakis (2001). Prior to injection in HPLC, asphaltens content were gravimetrically quantified after precipitation in *n*-hexane (HPLC grade) and filtration through Whatman GF/A glass fibers filters. The liquid chromatograph was an Agilent 1100 series consisting in a quaternary pump, a diode array detector (DAD) and a refractive index detector (RI). The HPLC was equipped with an aminosilica column UP5NH2 (L=250mm, internal diameter = 4,6mm), (Interchim, Montluçon, France) and a Modulo-Cart guard column (L=10 mm, internal diameter = 4 mm) (Interchim, Montluçon, France). Hexane and chloroform were used as mobile phase during the analyses. The absorbance was measured at 220 nm (mono (F1) and di-aromatics compounds (F2)), 254 nm (dibenzothiophenes and tri-aromatics (F3)) and 270nm (compounds with a minimum of four aromatic cycles and resins compounds). Saturates fraction was detected by using the refractive index detector.

Prior to injection, a calibration curve was established by using the heavy fuel from the Erika spill (as this oil has been fully studied by many laboratories in European countries).

- GCMS analyses

Prior to GCMS analyses, samples of oil were purified through SPE column silica/cyanopropyl (SiO<sub>2</sub>/C3-CN) (1.0/0.5g, 6ml) (Interchim, Montluçon, France) (Alzaga et al., 2004).

The GC was an HP 6890N (Hewlett-Packard, Palo Alto, CA, USA) equipped with a split/splitless injector (Splitless time: 1 min, flow 50 mL/min). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 300°C (20 min) at 5°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a HP-5 MS (HP, Palo Alto, USA): 30 m x 0.25 mm ID x 0.25 µm film thickness. The GC was coupled to an HP 5973 Mass Selective Detector (MSD) (Electronic Impact: 70 eV, voltage: 1200V). *n*-Alkanes and PAH semi-quantifications were done by using Single Ion Monitoring mode with the most representative fragment (saturates) or the molecular ion (PAH) of each compound at a minimum of 1.4 cycles/s.

17 $\alpha$ (H),21 $\beta$ (H)-hopane (m/z=191) was used as conserved internal biomarker during analysis (Prince et al., 1994) . Consequently, distribution of *n*-alkanes and PAH are presented in Hopane Unit (Figures 2 and 3).

## 2.5 Heavy Fuel Oil

The oil used during the study was a RMG 380 (classification ISO8217, 2005), which corresponds to an IFO 380. Table 2 and 3 and Figures 2 and 3 present the properties of this oil.

Table 2. Physical chemical properties of the heavy fuel oil.

Density	$0.957 \pm 0.001$	(ASTM, 1997)
Flash point (°C)	102	(ASTM, 1999)
Viscosity (mPa.s)	$10\ 000 \pm 72$	
(12°C, 10 s-1)		

Table 3. Percentages of each chemical fractions of the oil.

Saturates		33	
Aromatics	F1	49	23
	F2		9
	F3		13
	F4		4
Resins		7	
Asphaltenes		11	

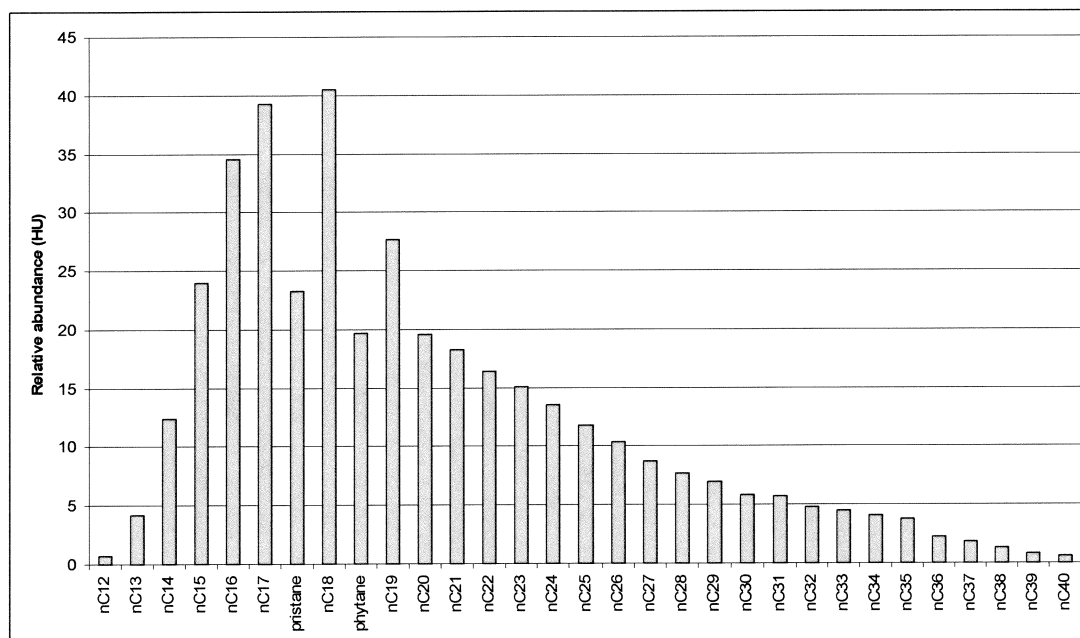


Figure 2. *n*-Alkanes distribution (Hopane Unit).

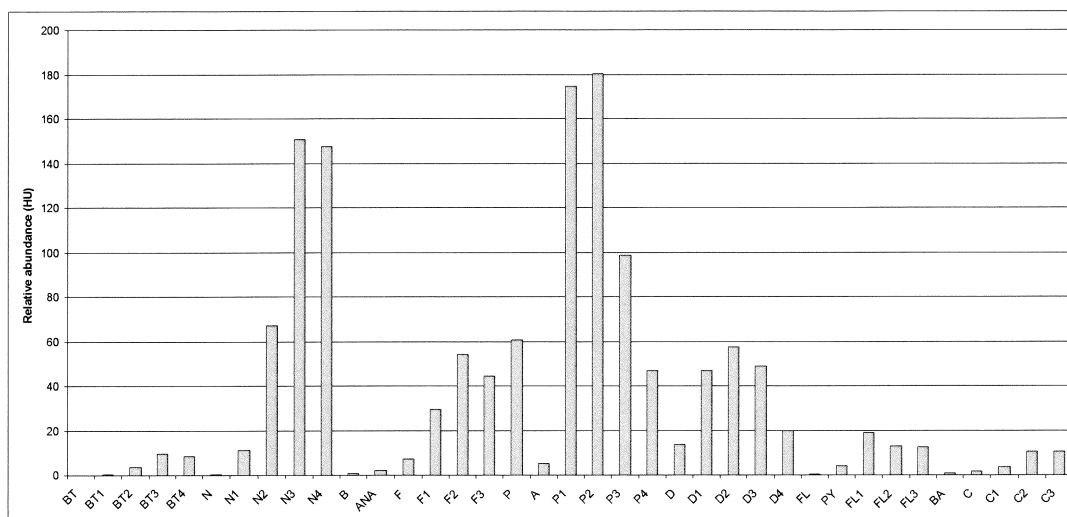


Figure 3. PAH distribution (Hopane Unit).

## 2.6 Cleaning Agent

The cleaning agent used during the study was a solvent based product. It was applied at the oil surface using a vaporizer. Polluted tiles were weighted and the cleaning agent was applied until the ratio of 1:2 between cleaning agent / oil was obtained. A soaking time of 3 minutes was set before the tiles were mounted in the robot.

## 2.7 Experimental Matrix

Table 4 summarises the overall experimental matrix.

Table 4. Experimental matrix

Stage	Weathering time (days)	Cleaning agent
1	0	No
	0	Yes
2	2	No
	7	No
	14	No
	31	No
	61	No
	61	Yes

## 2.8 Statistical Analyses

During the first stage of the study, uncertainty was estimated from the standard deviation of three trials for each condition of temperature and pressure. Analyses of variance (one way ANOVA) with a 95% confidence limit were done with Statgraphics Plus 5.1 software (Manugistics, USA).

During the second stage of the study, no replicates were performed as the number of polluted tiles which could be set in the experimental site for natural weathering was limited due to technical reason.

Figures 6, 7, 12 and 14 present regressions models obtained by using Sigmaplot 9.0 software (Systat Software, USA).

### 3 Results and Discussions

Figures 4 and 5 present pictures of tiles after washing respectively at 60°C / 100 bars and 77°C / 100 bars. The visual comparison of these pictures highlights an increase of the water jet width when using warmer water. Consequently, in order to allow comparison of results between all the parameters studied (changes of pressure and temperature), a picture of each tile were taken after washing and the surface exposed to the water jet measured using a dedicated software (ImageJ, v.1.37). Results were then corrected according to the surface really exposed to the water jet.

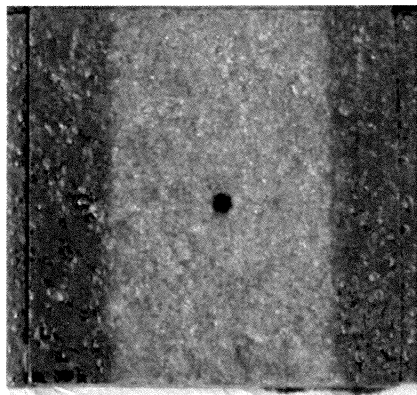


Figure 4. Polluted tiles after washing at 60°C/100 bars.

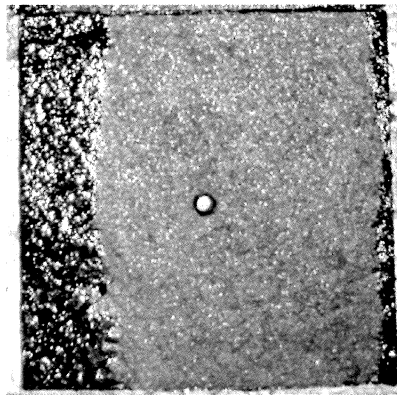


Figure 5. Polluted tiles after washing at 77°C/100 bars.

#### 3.1 Results of Washing Tests on Non-weathered Oil

Figure 6 presents the percentage of oil remaining on tiles after washings for each temperatures and pressures with and without cleaning agent. As expected, the efficiency of the oil removal from the tiles appears to increase significantly with warmer temperatures and higher pressures. With a temperature of 15°C (Figure 6A), the amount of oil removed from the substrate when a cleaning agent was used were significantly higher for pressure ranging from 10 to 50 bars. With a temperature set at 30°C (Figure 6B), these range of pressures spread from 5 to 20bars. For the other temperature tested (Figure 6C, 6D and 6E), the use of cleaning agent did not make sense as the results obtained with or without it did not differ significantly except for the lowest pressure tested (5 bars).

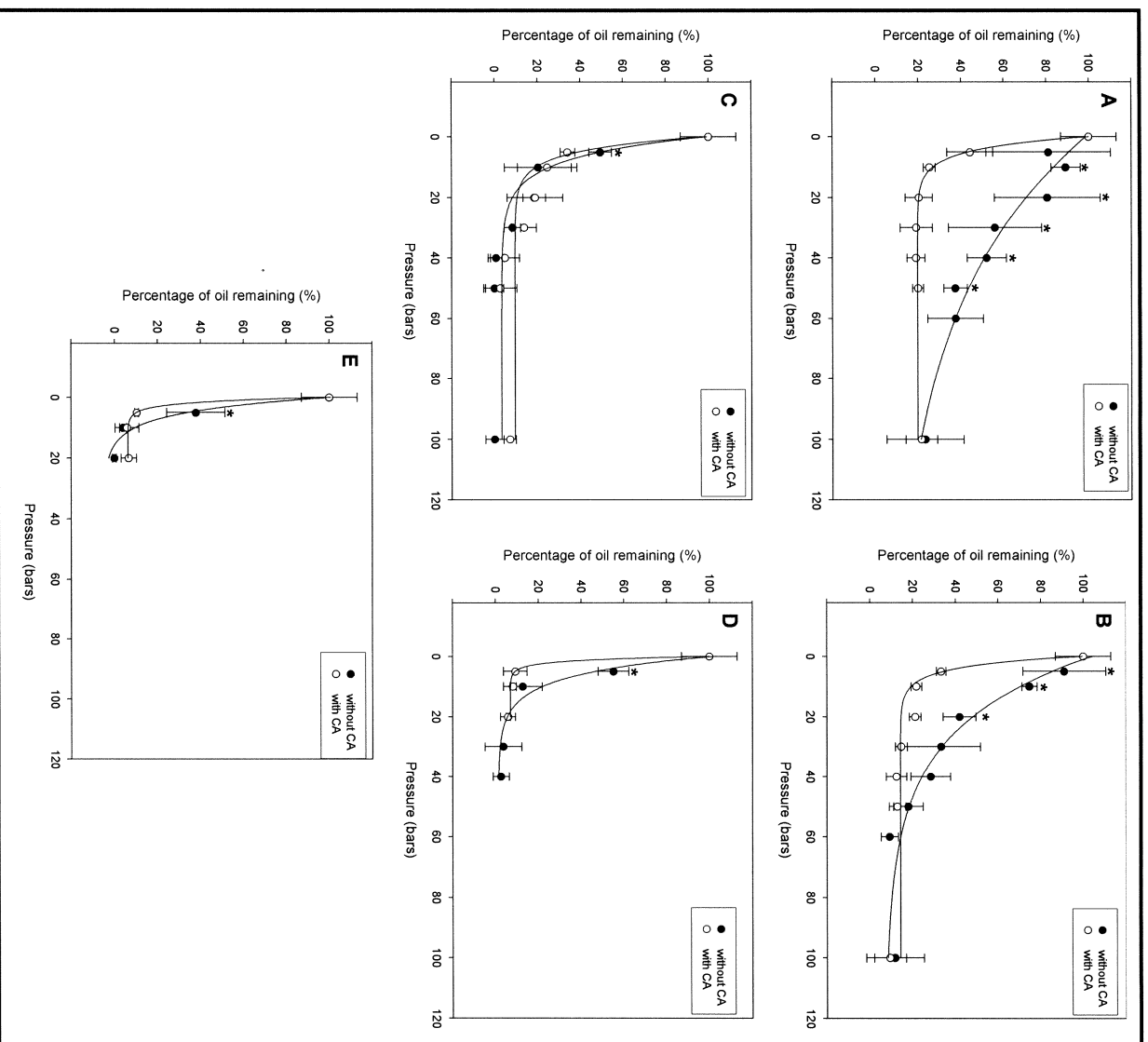


Figure 6. Mean and standard deviation ( $n=3$ ) of percentage of oil remaining on tiles after hydraulic washing with and without cleaning agent (CA) at various pressures and temperatures settings (A: 15°C; B: 30°C; C: 45°C; D: 60°C; E: 77°C). (\* indicates statistically significant differences with a 95% confidence limit between results obtained with our without CA).

### 3.2 Results of Washing Tests on Weathered Oil

During the second stage of the study, polluted tiles were set on a pier in natural environment for weathering. At each sampling round (2, 7, 14, 31 and 61 days), 25 tiles were brought back to the laboratory for washing tests and analyses of the weathering rate. Due to technical reason, it was not possible to set more tiles on the pier and consequently, no replicates were available to perform the tests of washings.



### 3.2.1 Assessment of Natural Weathering

At each sampling round, three tiles were used to quantify the amount of oil remaining. Natural cleanup by wave action appeared to be significant after 31 days of exposure in the environment (67% of oil remained on tiles) (Figure 7). At the end of the experiment, the amount of oil naturally removed from the tiles reached 42%.

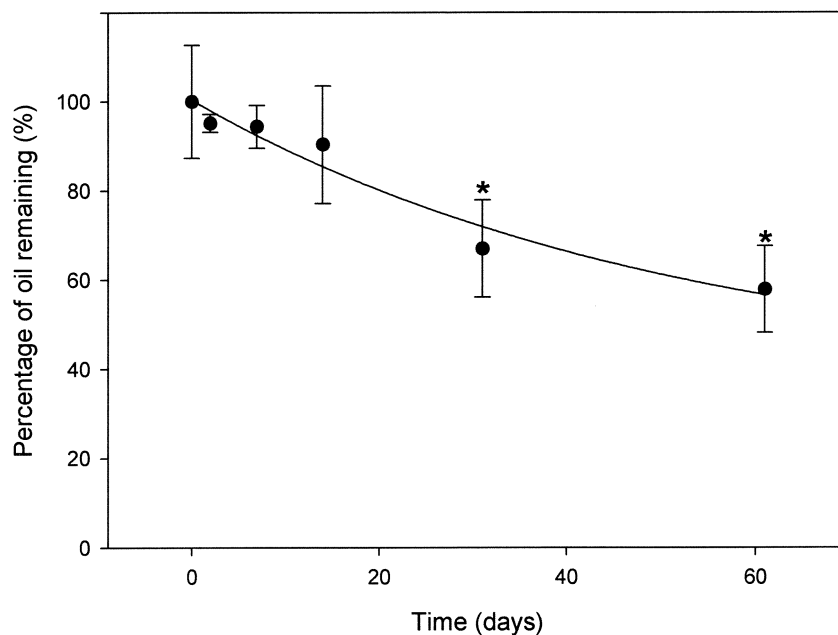


Figure 7. Means and standard deviation ( $n=3$ ) of percentage oil remaining on tiles during 61 days of exposure in natural environment (\* indicates statistically significant differences with a 95% confidence limit from results obtained at T0).

Results of HPLC analyses are presented in Figure 8. After 61 days in the environment, the compositions of the oils extracted from tiles were very different from that of the initial oil. While the saturate fraction did not seem to be altered, the percentage of the aromatic fraction decreased significantly from 49% for the initial oil to 25% at the end of the experiment.

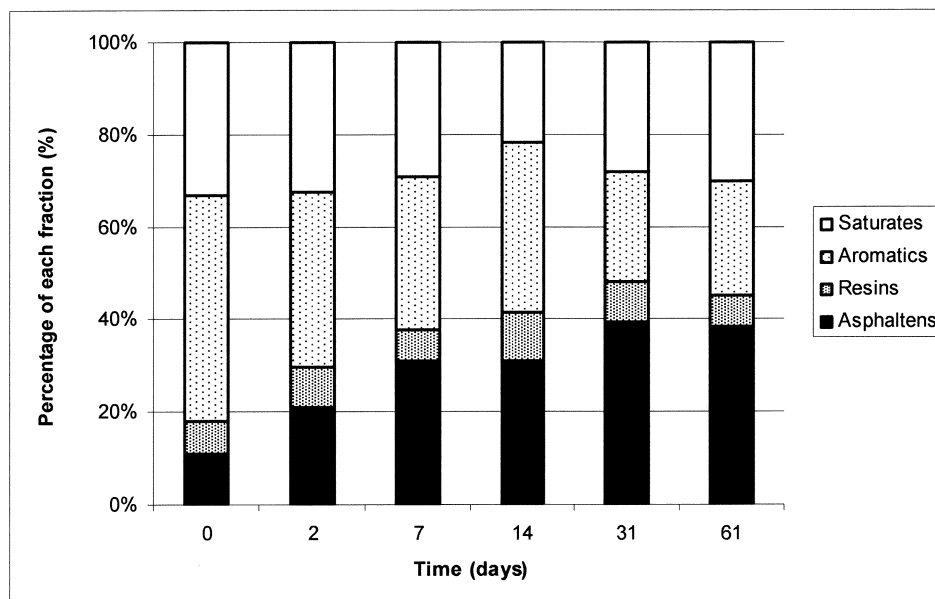


Figure 8. Distribution of different chemical fractions according to the time of exposure in natural environment.

The GCMS analyses highlight the nature of the oil-degradation processes which occurred during the 61 days of exposure. Figure 9 present the variations of the abundance of total n-alkanes ( $m/z=57$ ) and the  $n\text{-C}_{17}$ /pristane ratio from the samples of oil collected during the study. During the first 14 days of exposure, as the value of  $n\text{-C}_{17}$ /pristane did not change, the loss of n-alkanes could be attributed to evaporation and dissolution processes. From 14 to 61 days, as the ratio decreased, process of biodegradation contributed to the loss of n-alkanes in the oil remaining on tiles (Le Floch et al., 1999).

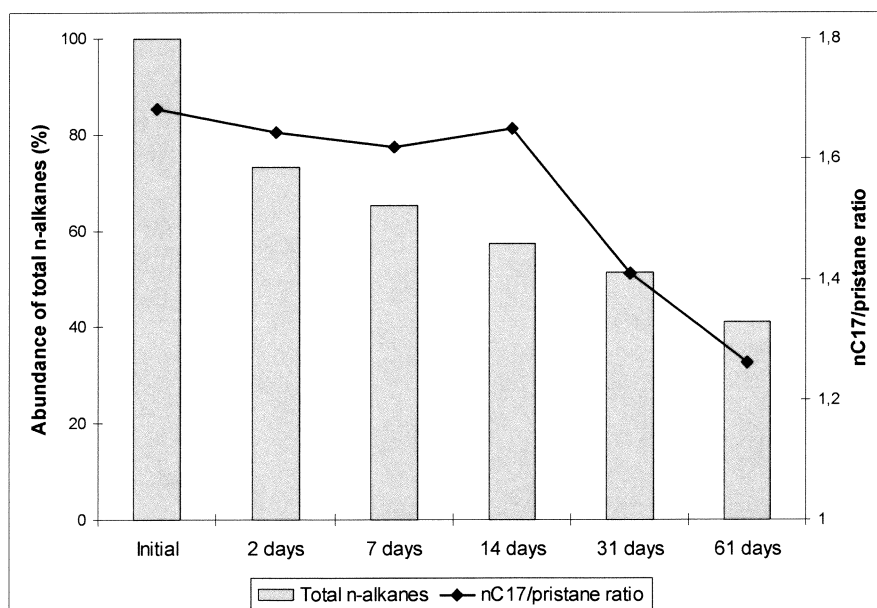


Figure 9. Abundance of total n-alkanes ( $m/z=57$ ) and  $n\text{-C}_{17}$ /pristane ratio according to time of exposure.

As shown in Figure 10, PAH compounds have been classified into three classes: the first class includes the lightest PAH such as benzothiophenes and naphthalenes families; the second class includes fluorenes, phenanthrenes / anthracenes and dibenzothiophenes families; the last class includes the heaviest PAH, fluoranthenes and chrysenes families. Each family of PAH includes parent PAH and the alkylated homologues.

While lightest PAH were highly degraded after 2 days of exposure due to evaporation and dissolution processes, the second and third classes of PAH were gradually degraded until 31 days of natural weathering. For the second class of PAH, the degradation could be attributed to dissolution, evaporation and also biodegradation processes as previously described with *n*-alkanes. Concerning the heaviest PAH, laboratory literature have shown that ultraviolet illumination of thin films of oil can lead to the disappearance of aromatic compounds from the oil (Garrett et al., 1998). This effect is more pronounced for larger polycyclic compounds and for the more alkylated forms. This is indeed what Figure 11 presents for chrysenes family and consequently, evidences that photooxidation occurred during the time of exposure in natural environment.

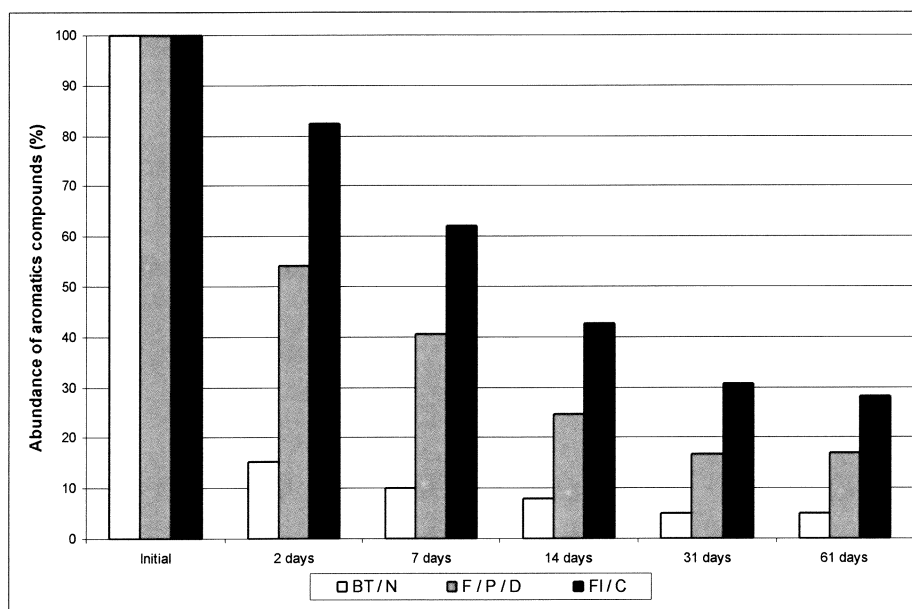


Figure 10. Abundance of class of PAH according to time of exposure.

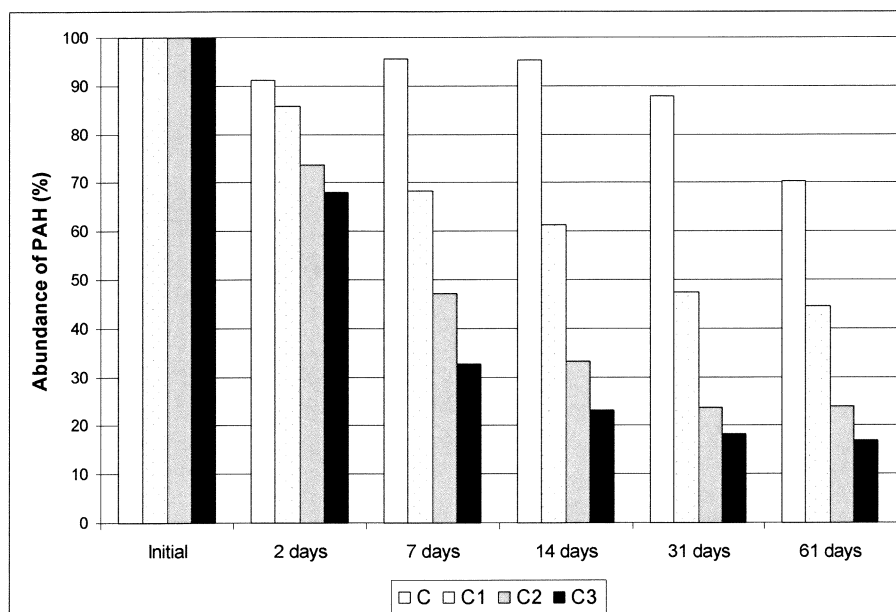


Figure 11. Abundances of chrysenes and some of its alkylated forms (C1, C2 and C3 refer to methyl-, dimethyl- and ethyl-, and trimethyl-, methyl-ethyl and propyl-chrysenes, respectively) from the oils washed from the tiles.

### 3.2.2 Washing without Cleaning Agent

Figure 12 presents the results obtained for the tiles exposed during 0 to 61 days to natural weathering. It must be noticed that results obtained for fresh oil were not similar to those obtained previously with the same oil during the phase 1 of the study (see §3.1.1). Although the oil used during these two stages was the same, it was assumed that differences of results were due to ambient temperature: stage 1 was performed during winter and, consequently, as the oil was more viscous, the amount of oil remaining on tiles at the end of the pollution protocol was greater (around 1.56g) than during stage 2 performed at the end of the summer (around 1g).

As presented in Figure 12, the effectiveness of hydraulic washing decreases dramatically as the oil weathering increases. After 2 days of exposure, a maximum of 75% of oil was washed from the tiles with the settings 77°C/20 bars. This maximal effectiveness decreased gradually to 43% after 14 days, 21% after 31 days and finally, 18% after 61 days.

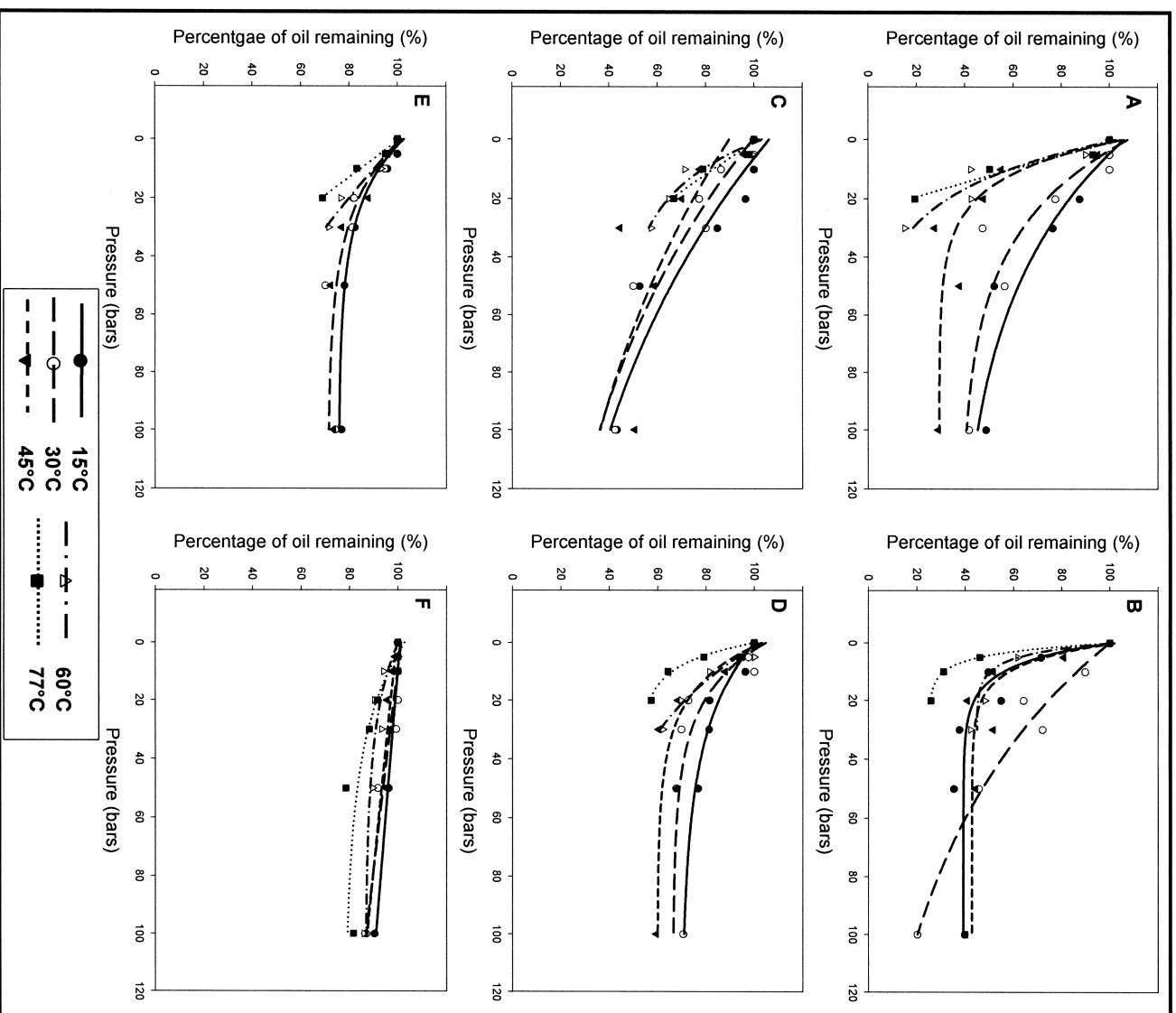


Figure 12. Percentage of oil removed from the substrate according to water jet temperature ( $^{\circ}\text{C}$ ), pressure (bars) and time of exposure to natural environment (A: 0 days; B: 2 days; C: 7 days; D: 14 days; E: 31 days; F: 61 days).

In order to highlight the influence of weathering on the hydraulic washing efficiency, Figure 13 presents an example of results obtained for a single temperature setting ( $45^{\circ}\text{C}$  in this case). As the oil progressively weathered, the effectiveness of the hydraulic washing decreased at a maximum of 60% of oil washed out after 2 days of weathering, 56% after 7 days, 41% after 14 days, 28% after 31 days and 13% for 61 days of weathering. As presented previously (Figure 8), chemical analyses demonstrated the oil degradation (especially for the aromatic

fraction) which implied an increase of the abundance of the polar fraction (resins and asphaltens) at a maximum of 48% compared to 18% for the fresh oil. This was visually confirmed during each sampling round; as the oil weathered, the thin layer of oil looked like a bitumen becoming more and more sticky on the substrate.

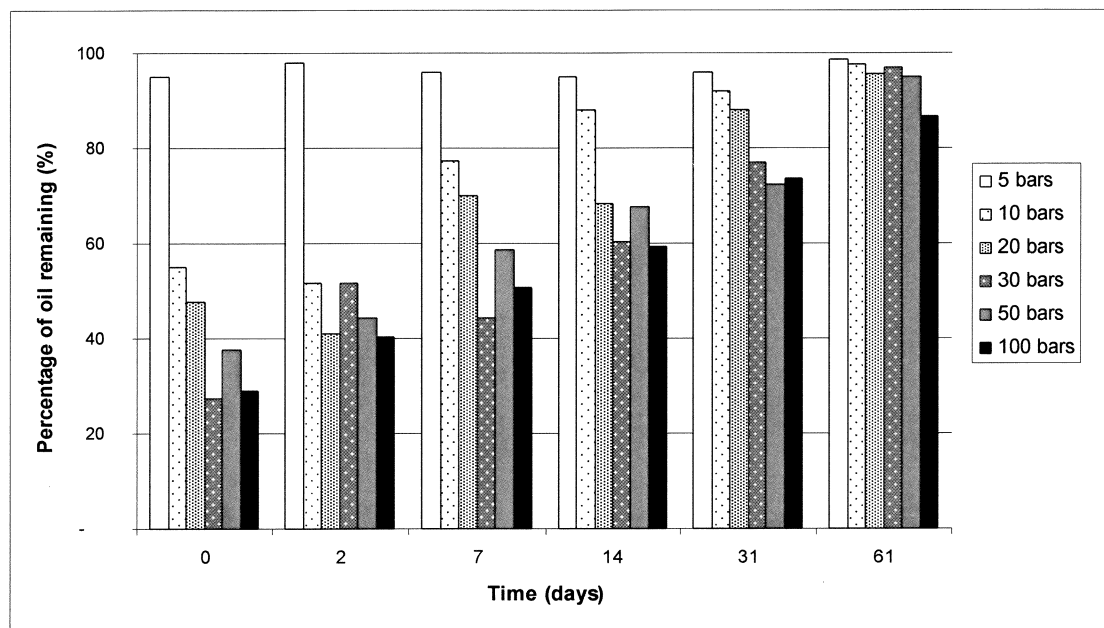


Figure 13. Percentage of weathered oil remaining on tiles after exposure to a water jet temperature set at 45°C and different level of pressure (bars) without cleaning agent.

### 3.2.3 Washing with Cleaning Agent

Tests with cleaning agent were performed on tiles exposed during 61 days in the environment. Figure 14 compares for each temperature tested the results obtained with and without cleaning agent according to the water jet pressures. These results clearly show the advantage of using a cleaning agent for a heavy fuel oil that has weathered for 2 months in the natural environment. Thus, for a water jet at a pressure of 50 bars, the average effectiveness obtained in the tested temperatures range is 10% without cleaning agent against 70% with cleaning agent. For a temperature of 77°C, this effectiveness increased from 14% to 86%.

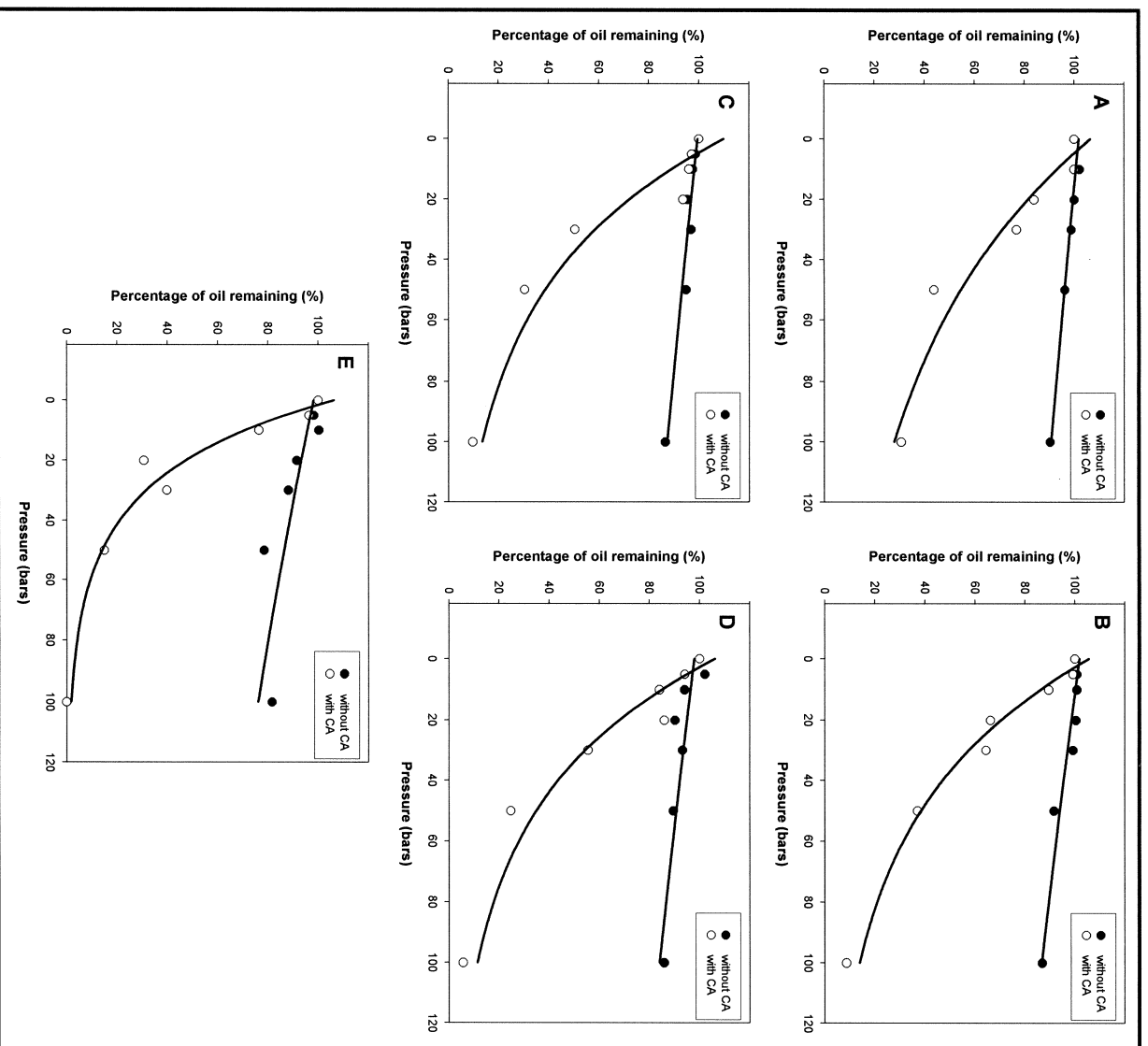


Figure 14. Efficiency of cleaning agent (CA) for a 61 days-weathered oil according to water jet pressure (bars) and temperature (A: 15°C; B: 30°C; C: 45°C, D: 60°C and E: 77°C).

#### 4 Conclusion

The objective of the experimental study presented in this paper was, first, to determine the performance of cleaning high pressure water jet on a rocky shores polluted with heavy fuel oil (RMG 380) by varying the range of temperature and pressure of the water jet. Secondly, the aim was to assess the influence of the oil weathering degree on the effectiveness of hydraulic washing technique. The advantage of using a cleaning agent was also tested on non-weathered oil and oil weathered during 2 months in natural environment. To conduct this experiment, the polluted rocky shoreline was simulated by coating granite tiles with a heavy fuel oil. The hydraulic washing was simulated using the “washing robot”, an automated tool

developed at *Cedre*.

The results of tests performed on the fresh oil illustrated the expected influence of temperature and pressure of the water jet on the hydraulic washing effectiveness. These tests have also revealed, for each temperature tested, the optimal settings of pressure beyond which the effectiveness of cleaning did not appear significantly higher. The settings thus defined can remove from 63% to 96% of the pollutant respectively for temperatures of 15°C and 77°C (maximum temperature of the hydraulic washer used during the study). When using a cleaning agent, effectiveness increased significantly only for temperatures lower than 30°C. For higher temperatures, the use of a cleaning agent did not make sense to wash rocky shores polluted with a non weathered heavy fuel oil.

For the weathered oil, the results showed surprisingly that after 2 days of natural weathering, effectiveness of hydraulic washing decrease in the range of temperatures and pressures tested. Chemical analyses performed on each samples collected showed that natural degradation processes occurred on the pollutant layer resulting in the persistence of a residual heavy fuel oil becoming more and more sticky to substrate. Therefore, the effectiveness decrease to 20% of oil removed from the substrate with the highest temperature and pressure settings. The use of cleaning agent on this weathered oil has shown its interest as it lead to an increase of hydraulic washing effectiveness for the range of temperatures and pressure tested.

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