

Influence of the Nature and the Weathering of Oil on Surfwashing Efficiency: Experimental Study with the Shoreline Bench

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Abstract

Following an oil spill on a sandy shoreline, an alternative technique to sediment excavation consists in relocating the contaminated sediment into the surf zone. The sediments are thus subjected to the natural cleaning action of the sea. Waves break down the piles of oily sand, separate the oil from the sediment, spread out the sediment over the beach and clean it by agitation and abrasion, while moving it back up to its original location. The efficiency of this technique depends on many environmental parameters such as the nature of the substrate (particle size), wave energy, and the nature and weathering stage of the oil.

In order to assess the influence of these parameters on surfwashing efficiency, experimental studies were conducted using the “shoreline bench”, an automated tool developed at *Cedre*. Twelve replicate mesocosms, each consisting of a tank filled with a bed of medium grain sand (100 to 1000 μm) and seawater were fixed to an oscillating table (periodic movement : 30 s) to generate identical wave action in each tank. After one hour of agitation, samples of sediment were collected and the oil extracted using an automated solvent extraction system. The amount of oil remaining in the sediment was quantified by spectrophotometry. For the test involving weathered oil, the degree of degradation was assessed by gas chromatography coupled to a mass spectrometer (GC/MS).

This paper describe the methodology and the results obtained with different oils and degrees of weathering, particle sizes and use (or not) of a cleaning agent.

1 Introduction

When a substrate is contaminated by oil, the extent of its mobilisation into the water column is not only dependent on environmental factors but also on the nature of the oil. Furthermore, the degree of weathering of the pollutant directly influences its persistence. Experiments conducted on this question at *Cedre* have shown the importance of exposure to solar radiation on the persistence of heavy oil on a rocky substrate. Exposure to solar radiation leads to more rapid remobilisation of the pollutant in comparison to more shaded environments (Jézéquel et al., 2003, 2009).

In terms of soft substrates, remobilisation into the water column of a pollutant trapped within sediment is also worth studying, more specifically by assessing the influence not only of environmental parameters (sediment grain size, water/air temperature, hydrodynamics) but also the nature of the pollutant (crude oil, heavy fuel oil) and its degree of weathering. This remobilisation can either occur naturally or be encouraged by a technique known as surfwashing. This technique consists of moving polluted sediment from the upper shore down to the lower shore to promote its agitation by wave action in the surf zone and therefore the release of the oil which can then be more easily collected.

The trials presented in this paper aimed to determine the influence of the oil concentration and type, the sediment grain size and the use of a washing agent to promote the clean-up of sediment by natural agitation. The ultimate objective of this study was to obtain useful field data, in particular to decide on whether to use the surfwashing technique.

2 Material and Methods

2.1 The Shoreline Bench

The shoreline bench (Figure 1) consists of twelve tanks set on an oscillating table which generates identical wave action in each tank. To simulate tidal movements (not used during the present study), it is possible to connect each tank to a renewal tank set on a lift table. The twelve tanks (L= 40 cm; w= 20 cm; h= 30 cm) are made of stainless steel and fitted with windows to allow observation. The oscillating table consists of a stainless steel table equipped with a pneumatic jack. The periodic movement of the table can be adjusted to recreate situations ranging from a sheltered shore to an exposed marine shore (approximately sea state 3 during the present study).

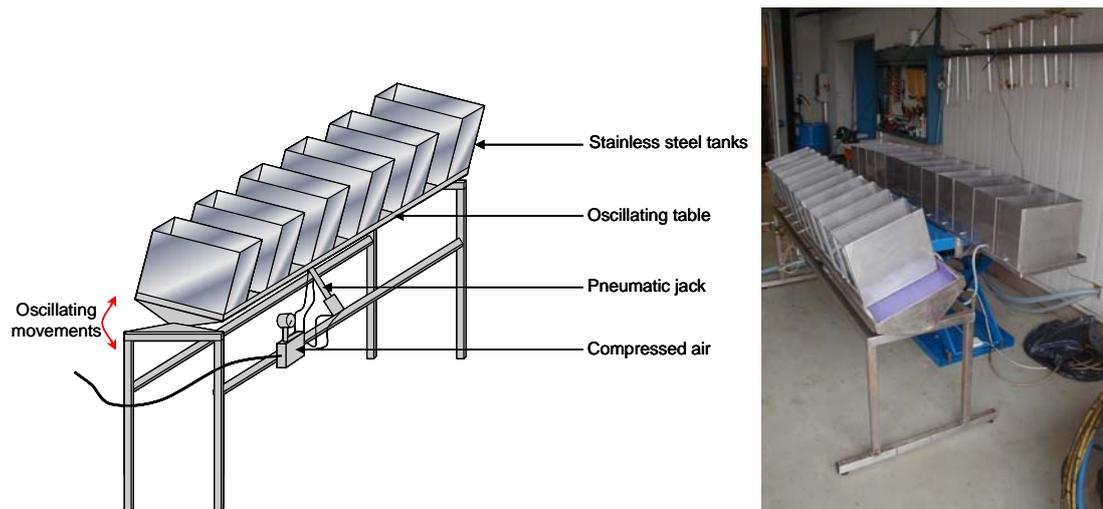


Figure 1. The Shoreline Bench (right: connected to the tidal table)

At the beginning of each test, 250 g of polluted sediment and 2 L of seawater were introduced into three tanks. After one hour of agitation (Figure 2), three samples of sediment were collected from each tank and stored at 5°C until they were analysed. Cleaning efficiencies were calculated using the ratio of the concentration of oil in the sediment after the washing operation to the concentration before the operation.



Figure 2. Oil on the walls of a tank after one hour of agitation.

2.2 Parameters Studied

The influences of the following parameters on the cleaning efficiencies were investigated:

- Natural weathering of oil,

- Oil concentrations in sediment,
- Use of cleaning agent: influence of oil concentration and soaking time.

2.3 Sediment Properties

Sediments were collected manually on the French Atlantic shoreline. The particle size distribution presented in Figure 3 is typical of fine sediment (250 – 500 μm) (AFNOR, 1997).

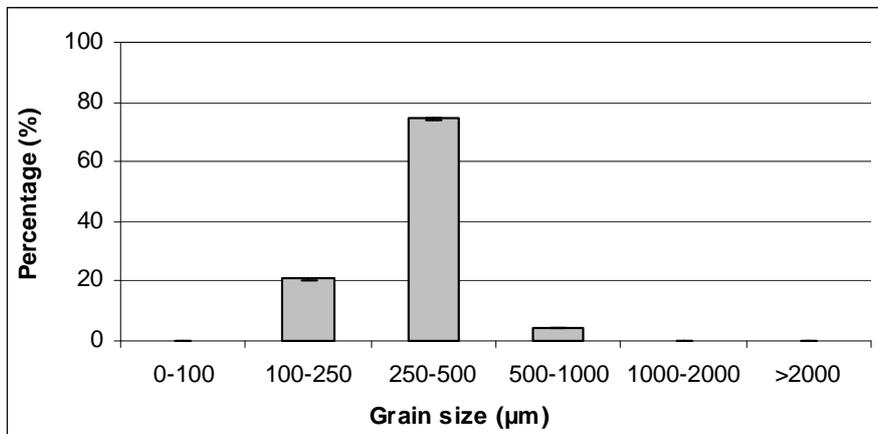


Figure 3. Particle grain size distribution of the sediment.

2.4 Physico-Chemical Properties of the Oils

The oils used during the study were a heavy fuel oil RMG 380 (classification ISO 8217, 2005) and a topped crude oil BAL 110 (Arabian Light topped at 110°C). Tables 1 and 2 present the properties of these oils.

Table 1. Physical and chemical properties of the heavy fuel oil.

	RMG 380	BAL 110	
Density	0.957 ± 0.001	0.827 ± 0.001	(ASTM, 1997)
Flash point ($^{\circ}\text{C}$)	102	57	(ASTM, 1999)
Viscosity (mPa.s) (12°C, 10 s^{-1})	$10\,000 \pm 72$	296 ± 16	

Table 2. Percentages of each chemical fraction of the oils.

	RMG 380	BAL 110
Saturates	33	60
Aromatics	49	26
Resins	7	6
Asphaltens	11	8

2.5 Chemical Analyses

2.5.1 Quantification of Oil in Sediment

At the end of the washing test, 3 samples of sediment were collected from each tank and stored at -20°C until analyses. Solvent extractions of the remaining oil were performed using an ASE 350 (Accelerated Solvent Extraction, Dionex) (Table 3). The water content of each sample was assessed by weighing an aliquot of sediment before and after 24h at 50°C . Organic extracts were dried over Na_2SO_4 (activated at 400°C for 4 hours). The absorbance was measured at 580 nm using a spectrophotometer (UNICAM, UV/Vis spectrophotometer) (wavelength used to avoid absorbance greater than 1).

Table 3. Settings of the ASE 350.

Weight of sample (g)	2
Solvent	Methylene chloride
Temperature (°C)	100
Pressure (psi)	1700
Cycles	2
Heating (min)	5
Static (min)	5
Flush volume (%)	75
Purge (s)	60

2.5.2 Assessment of Oil Weathering

Analyses were performed in order to assess the degree of degradation of oil exposed to the 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, analysis was 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 into the HPLC, the asphaltens contents (% asphaltens) were gravimetrically quantified after precipitation in *n*-hexane (HPLC grade) and filtration through Whatman GF/A glass fiber filters at ambient temperature. The liquid chromatograph was an Agilent 1100 series consisting of a quaternary pump, a diode array detector (DAD) and a refractive index detector (RI). The HPLC was equipped with an aminosilica column UP5NH2 (L=250 mm, internal diameter = 4.6 mm), (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 of the aromatic fraction (% aromatics) was measured at 220 nm (mono (F1) and di-aromatic compounds (F2)), 254 nm (dibenzothiophenes and tri-aromatics (F3)) and 270 nm (compounds with a minimum of four aromatic cycles). The resin contents (% resins) were measured at 270 nm. The saturate fraction (% saturates) was detected using the refractive index detector.

Prior to injection, a calibration curve was established 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 and saturate and aromatic fractions were isolated through SPE column silica/cyanopropyl (SiO₂/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 performed 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 a conserved internal biomarker during analysis (Prince et al., 1994).

Each sample was also analysed using Scan mode in order to obtain the abundance (in hopane unit - HU) of the saturate + aromatic fractions (resolved pics + UCM). The abundance of the different chemical fractions were then calculated in hopane units (HU) using equation 1 (X=saturates, aromatics, resins).

$$X(UH) = \%X * \frac{\text{resolved pics}(UH) + UCM(UH)}{\%saturates + \%aromatics} \quad (1)$$

2.6 Statistical Analyses

Analyses of variance (one way ANOVA) with a 95% confidence limit were performed with Statgraphics Plus 5.1 software (Manugistics, USA).

3 Results and Discussion

3.1 Influence of the Degree of Weathering of the Oil

Sediments were polluted with oil at a concentration of 100 mg/g and homogenised using a cement mixer. In order to simulate the natural weathering of the oil in an upper shore area, polluted sediment was exposed in the natural environment on Cedre's artificial beach. Samples of sediment were collected after 0, 1, 4, 7, 14, 28, 41 and 56 days of weathering. For each sampling round, 3 x 250 g of sediment were collected randomly and mixed before beginning the washing operation using the shoreline bench. Figure 4 presents the washing efficiency for the sediment polluted with heavy fuel oil and crude oil according to the duration of natural weathering. Surprisingly, once the sediment had been exposed in the natural environment, the washing efficiency decreased significantly during the first 20 days of exposure. After 20 days of weathering, the washing efficiencies increased slowly from approximately 10% to 25% after 56 days of exposure. These results suggest that in real conditions, it could be interesting to wait until the oil has weathered slightly before implementing surfwashing operations.

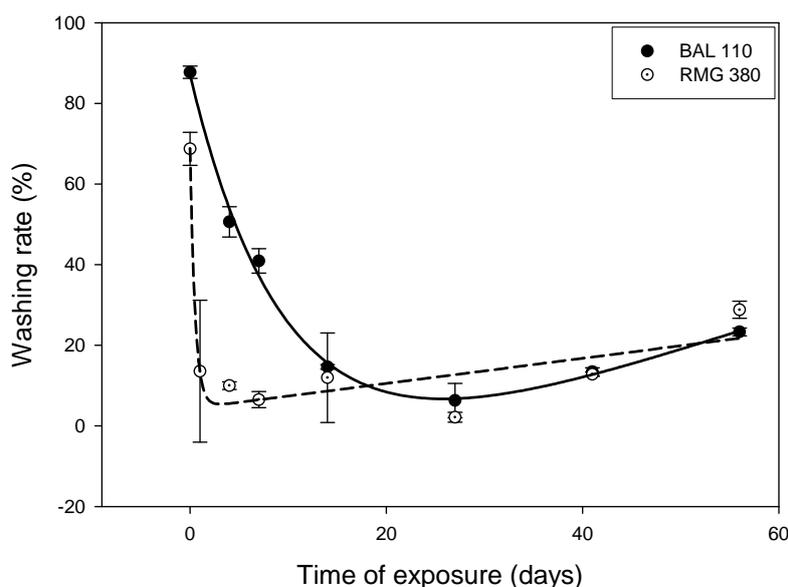


Figure 4. Evolution of washing efficiency (%) ($n=3$) for sediment polluted with heavy fuel oil and crude oil according to the time of exposure (days).

The evolution of the washing efficiency according to the time of exposure can be attributed to the influence of the natural degradation processes on the chemical composition of the oils.

The results of chemical analyses presented in Figure 5 highlight the overall degradation of the two products: after 56 days of natural weathering, the overall degree of degradation of the oils reached 47% for the crude oil and 30% for the HFO and exclusively concerned the saturate and aromatic fractions. The chemical fraction consisting of resins and asphaltens tend to increase over time due to the formation of polar compounds, especially during the biodegradation and photo-oxidation process (Garett et al., 1998, Xu and Lu, 2010). The abundance of this chemical fraction, composed of molecules with high molecular weight, induces an increase in the viscosity of the two oils which makes them especially sensitive to the abrasive nature of the sediments during the washing operations.

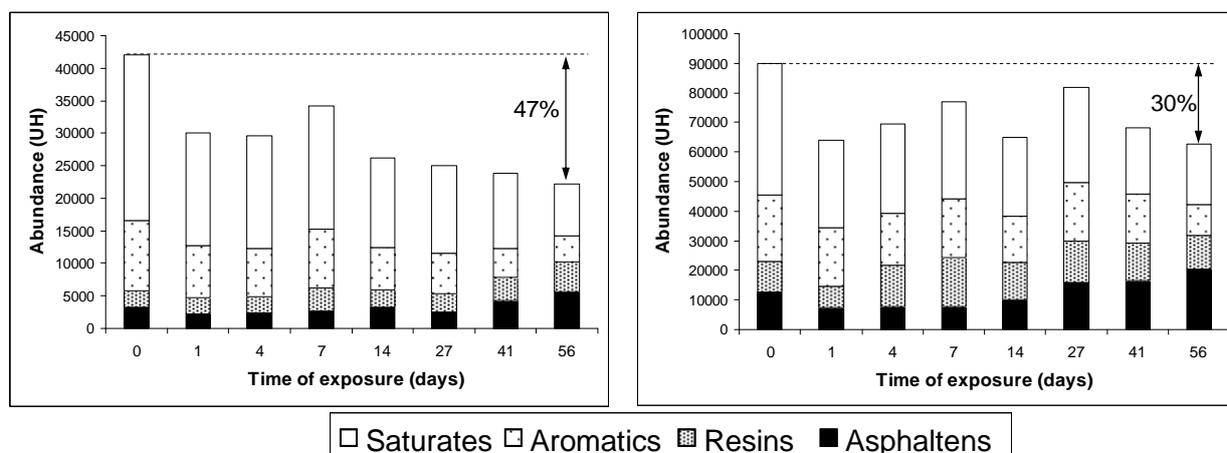


Figure 5. Evolution of the abundance of the different chemical fractions (HU: Hopane Unit) of the crude oil (left) and the HFO (right) according to the time of exposure (days) in the natural environment.

3.2 Influence of the Oil Concentrations

The tests were performed on a range of five concentrations of heavy fuel oil (10, 25, 50, 70 and 150 mg/g). Polluted sediments were exposed to the natural environment for 7 days in order to recreate light weathering of the oil. At the end of the washing operations, 3 samples of sediment were collected in each tank and were mixed. The washing efficiencies are presented in Figure 6.

The highest washing efficiency ($20\% \pm 5$) was obtained for the sediment with the lowest concentration of oil. Except for the most polluted sediment, there were no significant differences between the other concentrations of oil. This is indeed surprising considering the observations made during the sediment pollution. It was not possible to obtain the expected concentrations of 70 and 150 mg/g due to a natural release of oil from the sediment. Consequently, the concentrations measured in the sediment before the washing operations were 65 and 112 mg/g instead of 70 and 150 mg/g.

Nevertheless, these results were confirmed visually during the test firstly, by the lack of oil on the water surface or on the walls of the tanks, as was usually found at the end of the agitation (Figure 7 left) and secondly, by the formation of aggregates of hydrocarbon and sediment which remained intact despite the agitation. Consequently, due to the formation of these aggregates, there was no remobilization of oil from the sediment to the water column (Figure 7 right).

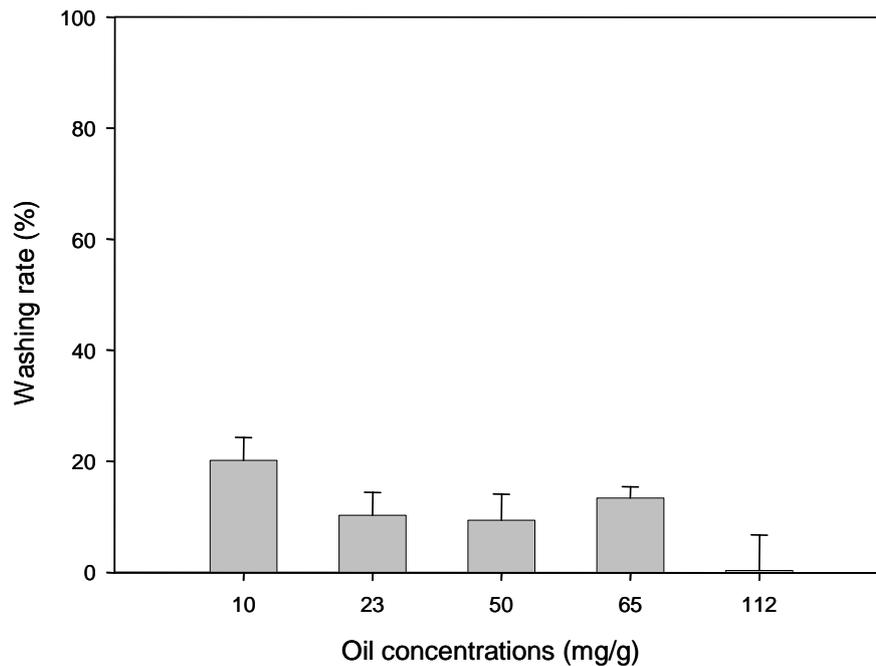


Figure 6. Evolution of washing efficiency (%) ($n=3$) according to the initial concentrations of heavy fuel oil in the sediment (mg/g).



Figure 7. Picture of tanks after one hour of agitation for a sediment polluted with heavy fuel oil at a concentration of 50 mg/g (left) and 110 mg/g (right).

3.3 Use of a Cleaning Agent

Tests with a cleaning agent were performed at 3 concentrations of heavy fuel oil (20, 50 and 100 mg/g) and 4 soaking times with the cleaning agent (1, 30, 60 and 180 minutes). The cleaning agent (a solvent based product) was applied to the polluted sediment using a vaporizer until a ratio of 1:2 (w:w) between the cleaning agent and the oil was obtained. Before the washing operations, the polluted sediment was homogenised and then set in 3 tanks. Figure 8 presents the washing efficiency for each concentration of heavy fuel oil. Washing efficiencies obtained previously without a cleaning agent (Figure 8) are indicated by a dotted line.

For the lowest pollution level (20 mg/g), the cleaning agent increased the washing efficiency significantly for a soaking time of less than 30 minutes. For a soaking time greater than 30 minutes, washing efficiencies tended to be higher but the results did not appear significant (with a 95% confidence limit) in comparison with the resultants obtained without the cleaning agent.

For a heavy fuel concentration of 50 mg/g, the soaking time had no significant influence on the washing efficiencies. Moreover, the use of cleaning agent tended to increase the washing efficiency but surprisingly, this increase was not significant. For the highest pollution level, the washing efficiencies increased with the soaking time and were significantly higher than the results obtained without the cleaning agent for a soaking time greater than 30 minutes.

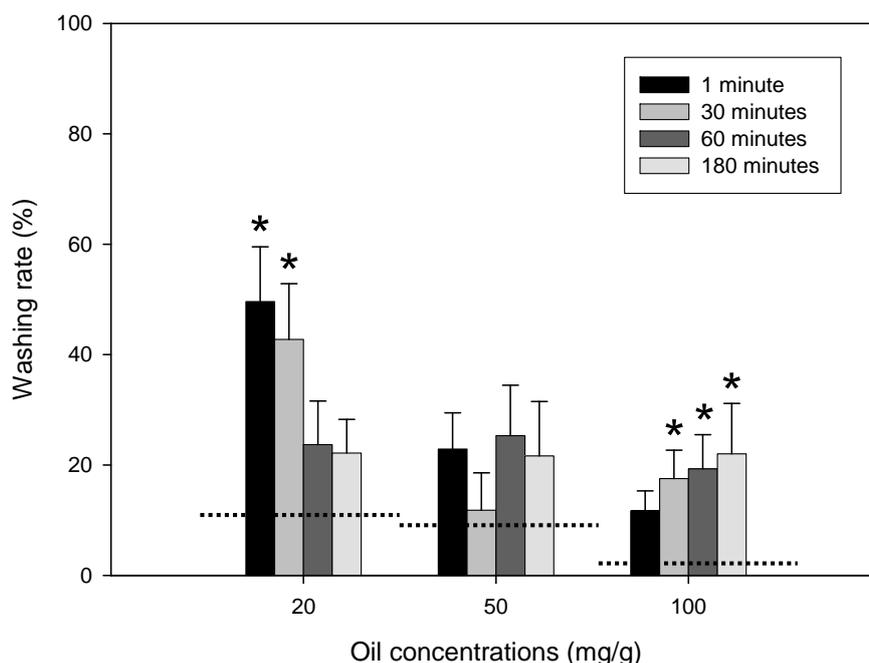


Figure 8. Evolution of washing efficiencies (%) ($n=3$) of sediment polluted with heavy fuel at different concentrations (20, 50 and 100 mg/g) according the soaking time with the cleaning agent (1, 30, 60 and 180 minutes). The dotted lines indicate the washing efficiency obtained without the cleaning agent. (* indicates statistically significant differences with a 95% confidence limit between the results obtained with and without the cleaning agent).

These results can be explained by the chemical composition of the cleaning agent and the abundance of low molecular weight compounds in this type of product. For the less polluted sediment, as the “solubilization” of oil by the cleaning agent requires little time, the cleaning operation can be performed quickly after the application of the cleaning agent. Beyond 30 minutes of soaking time, the washing efficiencies appear lower, probably due to the volatility of this cleaning agent.

For a higher concentration of oil, a delay between the treatment and washing operations appeared necessary to ensure the solubilization of the oil and significantly increased the washing efficiency.

4 Conclusion

The trials presented in this paper were conducted in order to better define the utility and limits of clean-up by agitation of oil-polluted sediments. This technique was simulated for

different oils using a shore simulation test bench. This equipment, composed of an agitation table, recreates the same agitation conditions in several tanks, enabling reproducible and repetitive tests to be conducted. The parameters studied were the oil type and concentration, its degree of weathering as well as the use of a washing agent sprayed onto the polluted sediment before its agitation. For each trial, the efficiency of sediment clean-up was calculated from oil concentrations in the sediment before and after the agitation operation.

Comparative trials performed on a heavy fuel oil (RMG380) and a crude oil (Arabian light) showed that onshore weathering of the oil could affect its mobilisation into the water column. During the first weeks of weathering, a significant drop in clean-up efficiency was observed. Thereafter, the efficiency increased with the natural weathering of the oil. From an operational point of view, the study showed that the natural weathering of the oil improved the efficiency of clean-up by surfwashing and, consequently, suggested that a certain time lapse could or even should be left before conducting sediment clean-up operations, when this does not interfere with other parameters, in particular related to site uses.

In all cases, particular attention should be paid to the initial pollutant concentration as, beyond a certain oil concentration, the efficiency of this clean-up technique will drop considerably due to the formation of oil-sediment aggregates which prevent the pollutant from being remobilised. During the trials conducted, beyond a concentration of 70 mg/g in fine grain sand, no remobilisation of the heavy fuel oil was observed. For lower concentrations, efficiencies of less than 50% (in the case of coarse grain sand), or even as little as 20% (in the case of fine grain sand polluted by a slightly weathered heavy fuel oil) were obtained, indicating that, in the field, surfwashing operations will need to be repeated to ensure sufficient cleaning of the sediment.

When the decision is made to use a washing agent, our trials showed that their use could improve the efficiency of surfwashing, especially in the case of a heavy fuel oil that is not easily remobilised. It is nevertheless important to leave the cleaning agent to work on this type of heavy pollutant for at least 30 minutes. In the case of crude oil, this soaking time should be reduced to a minimum and the product should be applied only a few minutes before the surfwashing operation. In all cases, the use of this technique should be adapted on a case-by-case basis according to the nature of the pollutant and its concentration while taking into account the possible ecological impact that the use of a cleaning agent may have.

5 References

AFNOR, NF EN 933-1 Décembre 1997, Essais pour déterminer les caractéristiques géométriques des granulats - Partie 1 : détermination de la granularité, Analyse granulométrique par tamisage, Afnor Editions : Saint Denis La Plaine, 1997.

Akhlaq, M.S., “Rapid Group-type Analysis of Crude Oils using High Performance Liquid Chromatography and Gas Chromatography”, *Journal of Chromatography*, 644: 253-258, 1993.

Alzaga R., P. Montuori, L. Ortiz, J.M. Bayona and J. Albaiges., “Fast Solid-phase Extraction-gas Chromatography-mass Spectrometry Procedure for Oil Fingerprinting. Application to the *Prestige Oil Spill*”, *Journal of Chromatography A*, Vol. 1025, Issue 1, pp. 133-138, 2004.

American Society for Testing and Materials (ASTM), “D70-97 Standard Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials (Pycnometer Method)”, *1997 Annual Book of ASTM Standards – Road and Paving Materials; Vehicle-Pavement Systems*, Vol. 04.03, Philadelphia, Pennsylvania, 1997.

American Society for Testing and Materials (ASTM), "D93-02 Standard Test Methods for Flash-Point by Pensky-Martens Closed Cup Tester", *1999 Annual Book of ASTM Standards – Petroleum Products and Lubricants (I)*, Vol. 05.01, Philadelphia, Pennsylvania, 1999.

Garrett, R.M., I.J. Pickering, C.E. Haith, and R.C. Prince, "Photooxidation of Crude Oils", *Environ. Sci. Technol.*, 32: 3719-3723, 1998.

International Organization for Standardization, ISO 8217, *Petroleum Products -- Fuels (class F) -- Specifications of Marine Fuels, Edition: 3, Stage: 90.92*, 13 p., 2005.

Jézéquel, R., L. Menot, F.X. Merlin, and R.C. Prince, "Natural Cleanup of Heavy Fuel Oil on Rocks: An In Situ Experiment", *Marine Pollution Bulletin*, 46 (8), 983-990, 2003.

Jézéquel R., J. Lebastard, and F.X. Merlin, "Influence of Weathering of Heavy Fuel Oil on High Pressure Washing Efficiency with and without Cleaning Agent", *Proceedings of the 2009 Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environnement Canada, Ottawa, Ontario, 2009.

Pasadakis, N., V. Gaganis and N., Varotsis, "Accurate Determination of Aromatic Groups in Heavy Petroleum Fractions Using HPLC-UV-DAD", *Fuel*, 80, 147-153, 2001.

Prince, R.C., D.L., Elmendorf, J.R. Lute, C.S. Hsu, C.E. Haith, J.D. Senius, G.J. Dechert, G.S. Douglas and E.L. Butler, "17 α (H), 21 β (H)-hopane as a Conserved Internal Marker for Estimating the Biodegradation of Crude Oil", *Environ. Sci. Technol.*, 28: 142-145, 1994.

Xu, Y. and M. Lu, "Bioremediation of Crude Oil-contaminated Soil: Comparison of Different Biostimulation and Bioaugmentation Treatments", *Journal of Hazardous Materials* 183: 395–401, 2010.