

THE ERIKA OIL SPILL: LABORATORY STUDIES CONDUCTED TO ASSIST RESPONDERS

Julien Guyomarc'h and François-X Merlin

*Centre de Documentation de Recherche et d'Expérimentations sur les pollutions accidentelles des eaux (CEDRE)
Rue Alain Colas BP 20413
29604 Brest, France*

Hélène Budzinski and Laurent Mazeas

*Laboratoire de Physico-Toxico Chimie des systèmes naturels (LPTC)
Université de Bordeaux I
351, cours de la Libération
33405 Talence, France*

Christian Chaumery

*Laboratoire d'Analyse de Surveillance et d'Expertise de la Marine (LASEM)
8, rue Portzmoguer
29240 Brest Naval, France*

Frank Haeseler

*Institut Français du Pétrole (IFP)
1 av Bois Préau
92500 Rueil Malmaison, France*

Jean Oudot

*Muséum National d'Histoire Naturelle (MNHN)
12, rue Buffon
75231 Paris, France*

ABSTRACT: *Immediately following the Erika oil spill, responders raised many questions concerning the identification of the fuel oil, its behavior in the water column, and physical properties, potential toxicity, environmental impacts, and the feasibility of various countermeasures to treat the spill. Several laboratories in France conducted simultaneous complementary investigations. The Laboratoire d'Analyse de Surveillance et d'Expertise de la Marine (LASEM) performed oil analyses of various samples collected at sea and on the shore for identification as well as for confirming the oil drifting predictions. The Centre de Documentation de Recherche et d'Expérimentations sur les pollutions accidentelles des eaux (CEDRE) studied oil behavior and its physical properties under realistic conditions in its flume test canal to predict the evolution of the product spilled at sea. Simultaneously, the Institut Français du Pétrole (IFP) and the Laboratoire de Physico-Toxico Chimie des systèmes naturels (LPTC) carried out oil chemical analyses of the polyaromatic compounds and the water accommodated fractions for environmental risk assessments. Finally, Muséum National d'Histoire Naturelle (MNHN) investigated the possibility for oil biodegradation through laboratory experiments. This experimental information was of great interest for response operations. Field observations validated laboratory predictions, especially those concerning physical properties.*

the subject of concern was to identify the origin of the oil patches observed on beaches including those that were not predicted to become contaminated by drift forecast models. These determinations were a key element in finding reasons to explain unpredicted observations.

As the oil reached the shoreline, concerns of the responders included the real nature of the cargo, identification of the more toxic components, and potential environmental impacts. These were addressed by physical-chemical analyses of the oil (by Institut Français du Pétrole [IFP]) and analysis of the aromatic fraction (by Laboratoire de Physico-Toxico Chimie des systèmes naturels [LPTC] and IFP), which led to the definition of a list of molecules to be monitored in the environment. Specific characteristics of the oil also made it possible to identify the origin of observed water pollution. Finally, the biodegradability of the oil was studied by the Muséum National d'Histoire Naturelle [MNHN] to provide a value of "highest biodegradation rate" conceivable. A batch of the oil that was loaded onto the tanker *Erika* at the Dunkerque refinery was received by the Centre de Documentation de Recherche et d'Expérimentations sur les pollutions accidentelles des eaux (CEDRE) within 16 hours of the accident. Identical samples also were sent to the other laboratories for complementary analyses.

Introduction

On December 12, 1999, the tanker *Erika* containing 30,000 tons of heavy fuel oil sank at 70 miles off the Brittany coast. The ship broke into two releasing about 15,000 tons of heavy fuel oil. Several questions on the fate of the oil were immediately raised: Will it sink? How and where will it drift? As the oil came ashore,

Oil behavior (CEDRE)

Small-scale laboratory tests were unable to provide realistic data to predict accurately drift and behavior of the oil at sea. To deal with this issue, an oil weathering test was initiated on December 13 at the Polludrome, a pilot scale flume test facility located at CEDRE.

Material and methods. The hydraulic canal consists of a loop in which open sea conditions can be recreated (Guyomarc'h *et al.*, 1999). Tests were conducted at ambient water and air temperature encountered at sea (11°C). The other test parameters were wind speed (3 m/s), wave height (25 cm, corresponding to about sea state 3), water volume (8 m³), and salinity (35 ppt). Guyomarc'h and Merlin (2000) previously have described the methodology for monitoring of the physical-chemical parameters of the pollutant (viscosity, density, and water content).

Results. The evolution of viscosity and water content are presented in Figures 1 and 2. The viscosity increased from 42,000 mPas to 400,000 mPas over 96 hours at 11°C and 1 s⁻¹. The final water content was close to 50% after 2 days weathering in the flume. Additional tests with demulsifiers demonstrated that this emulsion was also quite stable. Because of the tremendous viscosity of the emulsion, there was some assumption that the

inclusion of air bubbles lowered the measured densities (the emulsion density was lower than that of the initial oil). The behavior in the water column showed slight buoyancy in seawater and a great cohesion of the slick in any condition of agitation.

Conclusion. All results showed that the oil would remain at the sea surface and, therefore come ashore sooner or later: It was still buoyant even after the incorporation of water. Prior knowledge of the high viscosity of the emulsion was of great importance in the selection of appropriate mechanical strategies for recovery operations at sea. The analyses of oil slicks at sea revealed water content of about 25–30%. Samples of residual oil on the shoreline had water content close to 50%. These results showed that the flume test enhanced the emulsification process as it is not limited by the mass transfers that are slower at sea. However, it proved to be a reliable tool to predict the end points of evolutions.

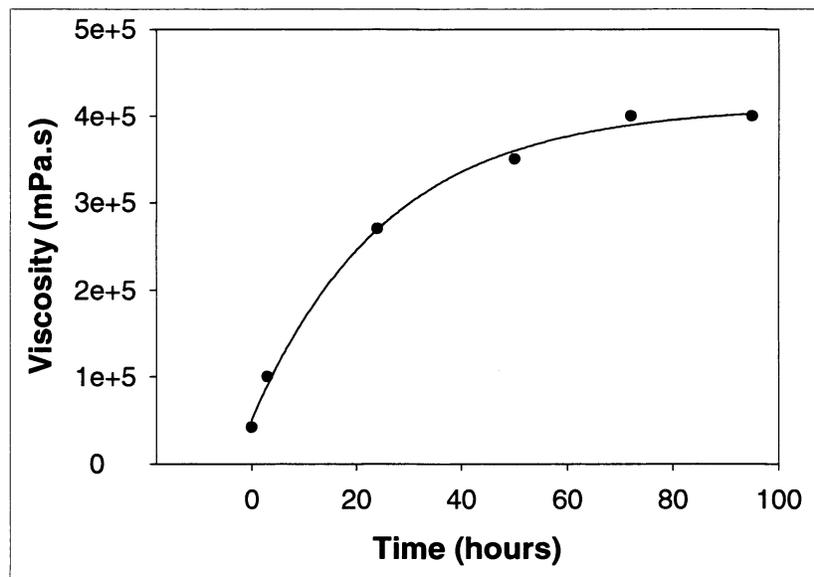


Figure 1. Evolution of viscosity versus weathering time in the Polludrome.

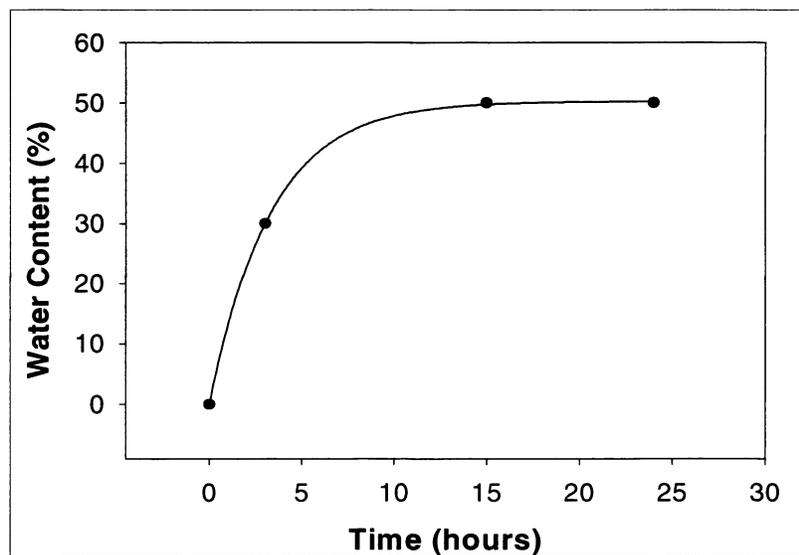


Figure 2. Evolution of water content versus weathering time in the Polludrome.

Monitoring of the pollution expansion (Laboratoire d'Analyse de Surveillance et d'Expertise de la Marine [LASEM])

Besides its rescue operations during the wreckage, the French Navy monitored the drifting of the oil slicks. Different samples were systematically collected at sea and on the shoreline, in order to verify the presence of *Erika* oil, to confirm the forecasting of the predictive models and to delineate the expansion of the impact zone. Analyses were performed at LASEM, the laboratory of the French Navy, in Brest from December 12.

Material and methods. Because of the high content of aromatic compounds (about 50%) and the objective of the analysis, a fast and reliable method by gas chromatography-mass spectrometry (GC-MS) for the identification of the origin of the samples, the fuel oil was not fractionated into saturated hydrocarbons, aromatics hydrocarbons, resins, and asphaltenes.

The identification was based on the Pristane/nC17, Phytane/nC18, and Pristane/Phytane ratio in a first step, and then, on the C1-Phenanthrenes ($m/z=192$) and C1-dibenzothiophenes ($m/z = 198$) distributions. Total hydrocarbons were extracted by CCl_4 and purified by liquid chromatography on silica gel columns. The chlorinated solvent was evaporated using a nitrogen flow and an aliquot was dissolved in hexane. The target molecules were analyzed by GC-MS using a gas chromatograph (Carlo Erba AUTO/HRCG/MS) fitted with a mass spectrometer (Carlo Erba QMD 1000). The parameters of the analysis were as follows: ionization (EI⁺) by a 70 eV electronic bombardment and acquisition in the "full-scan" mode.

Results. The Pristane/nC17, Phytane/nC18, and Pristane/Phytane ratio were respectively 0.37, 0.33, and 0.98. The determinations of the C1-Phenanthrenes ($m/z = 192$) and C1-dibenzothiophènes ($m/z = 198$) distributions were useful to confirm the origin of the samples.

Conclusion. The analyses confirmed that the oil from the refinery was identical to the cargo of the *Erika* tanker. All the other samples collected (around 100) proved to have the same origin, except one that came from the location "Ile d'Yeu" which was a light crude highly biodegraded. The first slicks impacted the coast at Penmarc'h on December 23 (Figure 3). Considering the weather and sea conditions and particularly the northwest wind, these results suggested that leakages occurred long before the tanker broke in two parts.

Oil characterizations

IFP was asked by the French Agency for Food Sanitary Security, Agence Française de Sécurité Sanitaire des Aliments (AFSSA), to provide an exhaustive characterization of the chemical composition of the heavy fuel oil transported by this tanker. The objective of this analytical characterization was:

- To quantify the presence of fuel oil and its toxic compounds
- To evaluate the transfer to water of soluble hydrocarbons

Oil composition and simulated distillation. *Material and method.* Elementary analyses were done according to ASTM D5291 for carbon and hydrogen (ASTM, 2000a), ASTM D3228 for nitrogen (ASTM, 2000b), and ASTM D5622 for oxygen (ASTM, 2000c). Sulfur was analyzed by atomic emission and nickel and vanadium were determined by plasma atomic emission.

The simulated distillation (SD) was performed by high temperature gas chromatography on a HT SimDist CB column (Chrompack, Middelburg, NL) using the Chromdis (JMBS, Fontaine, France) software according to Durand *et al.* (1999).

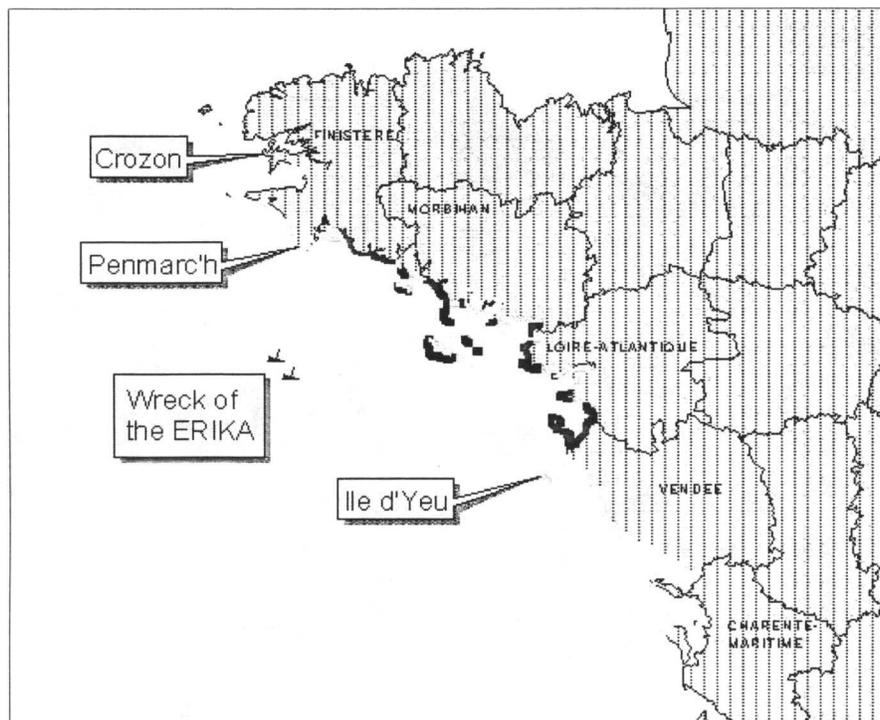


Figure 3. Impacted coast and localization of the wreck.

Results. The *Erika* heavy fuel oil contained 88.2% carbon, 10.4% hydrogen, 0.4% nitrogen, 1.6% oxygen, and 2.5% sulfur. Nickel and vanadium concentrations were respectively 89 and 39 mg/kg. The simulated distillation (Figure 4) showed that this fuel oil n°6 was composed by a mixture of light cycle oil (LCO), high cycle oil (HCO), slurry from the fluidized catalytic cracking (FCC) unit, and residue from the vacuum distillation unit (VDR):

- A light fraction distilling between 190 and 310°C corresponding to a LCO
- A medium fraction distilling between 310 and 500°C corresponding to a HCO and a slurry
- A heavy fraction distilling over 500°C corresponding to the VDR

Conclusion. These results were similar to those provided by TOTALFINA, the owner of the cargo. On the basis of compositional analysis (see also Table 1, next section) and simulated distillation, the cargo was confirmed to be a Fuel Oil No. 6 (equivalent to Fuel Oil No. 2 according to European specifications).

Analyses of the aromatic fraction and transfer to the aqueous phase. *Material and method.* The fuel was fractionated into saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes by two different techniques. The first one based on a high performance liquid chromatography (HPLC) separation after asphaltenes precipitation in *n*-heptane and the second based on a liquid chromatography on silica gel minicolumns after asphaltene precipitation in *n*-hexane according to Haeseler *et al.* (1999a). The polyaromatic hydrocarbons (PAHs) contained in the aromatic fraction were analyzed by HPLC with a fluorescence detection at specific excitation/emission wavelengths.

A contact between seawater and the fuel from the Dunkerque refinery was simulated at 20°C in a laboratory scale experiment in order to assess the maximal amount of hydrocarbons susceptible to be transferred from the oil phase to the aqueous phase. Volatile hydrocarbons were analyzed by gas chromatogra-

phy (Varian 3400) with flame ionization detection using a purge and trap injector (Tekmar 3000). Solubilized PAH were analyzed according to Haeseler *et al.* (1999b).

Results and discussion. The contents in saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes presented in Table 1 showed that less asphaltenes precipitated in *n*-heptane than in *n*-hexane and that was due to the better solubilizing capacity of heptane. But, more surprisingly, an important difference in the content of aromatic hydrocarbons and resins appeared. It is the first time in the authors' knowledge that these techniques showed a difference in the results. This certainly was due to the fact that the cut between aromatic hydrocarbons and polar compounds was not chemically well-defined otherwise as a presence in a solvent fraction after a liquid chromatography. These data showed that this oil contained in any case a large amount of aromatic hydrocarbons, which indicated that a large part of the constituents originates from the FCC unit.

The quantification of the 16 PAHs present in the EPA priority list for toxic compounds showed that these molecules are only a minor part of the fuel (0.3%) compared to the 42 to 55% of aromatic hydrocarbons. Further more, this 0.3% mainly was composed by naphthalene 1.1 g/kg and phenanthrene 0.6 g/kg so that the sum of the other 14 compounds including the genotoxic ones (like benzo[a]pyrene) represented only 1.5 g/kg.

The values of the maximal amount of hydrocarbons susceptible to be transferred from the oil phase to the aqueous phase are shown in Table 2. These values must be considered, as a maximum because the experimental setup was a closed system. In the open seas of the Atlantic, this equilibrium concentration will never be reached because of the constant renewal of water in contact with the oil phase. Furthermore, this experiment has been carried out at 20°C and the water temperature, especially in winter, is far below this value. This will also contribute to reduce the expected concentration of dissolved hydrocarbons in the seawater.

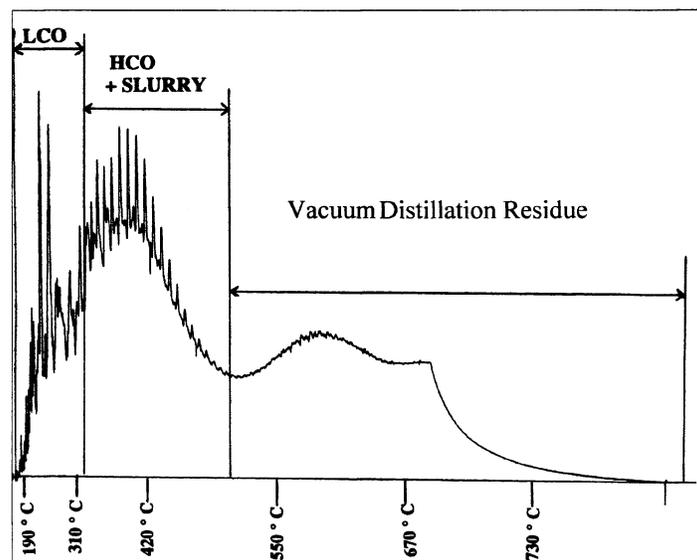


Figure 4. Simulated distillation of the *Erika* fuel oil.

Table 1. Contents in saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes.

	Concentration (%)			
	Saturated hydrocarbons	Aromatic hydrocarbons	Resins	Asphaltenes
Separation by HPLC	22.1 ± 1.1	42.2 ± 1.1	31.1 ± 1.1	4.5 ± 0.5
Separation by mini-columns	22.2 ± 0.8	55.6 ± 1.4	15.7 ± 1.8	6.6 ± 0.8

Table 2. Equilibrium concentrations at 20°C for volatile hydrocarbons and polyaromatic hydrocarbons in seawater that has been in contact with the heavy fuel oil from the Dunkerque refinery.

	Concentration (µg/L)		Concentration (µg/L)
Benzene	26	Naphthalene	131
Toluene	96	Acenaphthylene	3.1
Ethyl benzene	19	Fluorene	1.7
Meta xylene	58	Phenanthrene	9.8
Para xylene	19	Pyrene	0.6
Ortho xylene	38	Benzo(a)pyrene	0.01
Total volatile hydrocarbons	748	Sum of 16 EPA PAH	148

Furthermore, the analytical characterization done by IFP included also other parameters like:

- The light fraction including BTEX compounds (GC-FID, back flush + Carburane analysis)
- The sulfured hydrocarbons (GC-MS high resolution)
- The repartition of the different hydrocarbon families (Fischer method by high resolution mass spectrometry)

These data will be presented in works to be published in the future.

Conclusion. These elements confirmed that the dissolution of toxic compounds was limited and that contaminants in the water column would be primarily associated with oil bound to suspended particle material. This was very useful to define the analytical protocols for the spill monitoring on shoreline.

PAH fingerprint (LPTC). The LPTC performed a detailed analysis of the aromatic fraction to define a PAH fingerprint of the *Erika* oil. The objective of this study was to identify target molecules and diagnostic ratios that could lead to the identification of the origin of the water contamination.

PAHs are ubiquitous contaminants due to the multiplicity of their sources and their stability (McElroy *et al.*, 1989; Neff, 1979; Youngblood and Blumer, 1975). PAHs are major constituents of a crude oil as they represent between 25 and 40% in weight (Tissot and Welte, 1984). PAHs are the most valuable target compounds for oil spill identification (Wang *et al.*, 1999) because PAH molecular distribution exhibits differences depending on crude oil and petroleum products and because they are more resistant to weathering and biodegradation than saturated hydrocarbons. As PAHs molecular fingerprint depends on the origin of PAHs, differentiation between PAHs added after an oil spill from other background hydrocarbon sources present in the impacted area is possible (Laflamme and Hites, 1978; Lake *et al.*, 1979; Sportsol *et al.*, 1983).

Material and method. PAHs concentrations were determined in an oil sample originating from the refinery where the tanker *Erika* was loaded in an oil sample collected on December 22, 1999 in an oil slick close to where the *Erika* tanker sank and in a sample collected on December 29, 1999 on a beach in Concarneau (France). These different samples were analyzed to take into account dissolution and evaporation processes.

Twenty mg of each of those oil samples were spiked with internal standards (perdeuterated PAHs). Oil maltene fractions were isolated by asphaltene precipitation in pentane. Maltene fractions were first purified on alumina microcolumns to remove polar compounds. Saturated fractions were then separated from aromatic ones by fractionation on silica gel.

Aromatic fractions were analyzed using GC-MS. The GC was an HP 5890 Series II (Hewlett-Packard, Palo Alto, California) equipped with a split/splitless injector (Splitless time: 1 minute, flow 60 mL/min). The injector temperature was maintained at 270°C. The interface temperature was 290°C. The GC temperature gradient was from 50°C (2 minutes) to 290°C (20 minutes) at

2°C/min. The carrier gas was helium at a constant flow of 1 mL/min. The capillary column used was a CP-SIL 8 CB (Chrompack, Middelburg, The Netherlands): 50 m × 0.25 mm ID × 0.25 µm film thickness. The GC was coupled to an HP 5972 Mass Selective Detector (MSD) (Electronic Impact: 70 eV, voltage: 2000V). PAHs quantification was done using single ion monitoring mode with the molecular ion of each compound at 1.4 cycles/s. PAHs were quantified relatively to the perdeuterated PAHs introduced at the beginning of the sample preparation procedure.

Results and discussion. Concentrations of PAHs contained in *Erika* oil in the sample from the oil slick and in the sample collected on a beach of the Atlantic coast impacted by the *Erika* oil spill are given in Table 3. The *Erika* oil shows a classical PAHs molecular profile for a Fuel Oil No. 6 (Wang *et al.*, 1999). Phenanthrene and dibenzothiophenic compounds are present in high concentrations. Pyrene is much more abundant than fluoranthene, the ratio between the concentrations of those two isomers (pyr/fluo = 5.8) can be used as source diagnostic ratio. Chrysene and alkylated chrysene are particularly abundant; they can also be used as tracer compounds. *Erika* oil presents a high content of high molecular weight compounds such as benzo(a)pyrene, which is the most toxic PAH. The samples collected in the environment present lower PAH concentrations than the *Erika* oil because of the loss of compounds during the weathering of the samples and also to the dilution of the samples with the water contained in the emulsion formed between the oil and the seawater.

Figure 5 represents the relative distributions of phenanthrene and dibenzothiophenic compounds of various degrees of alkylation in the *Erika* oil and the two other samples collected in the environment. Phenanthrene and dibenzothiophenic compounds distributions in the sample from the oil slick and the one collected on a beach are quite close. However, the relative distributions for those samples are depleted in phenanthrene, dibenzothiophene, and methylated compounds and enriched in trimethyl compounds compared to the *Erika* oil. These modifications in the relative distributions might be due to evaporation and water washing of the samples in the marine environment.

Figure 6 represents the relative distributions of methylphenanthrenes and methyl-dibenzothiophenes determined in *Erika* oil and in the two other samples collected in the environment. Both samples from the oil slick and the one collected on a beach show methylphenanthrenes and methyl-dibenzothiophenes relative distributions similar to the *Erika* oil.

Conclusion. PAH fingerprint analysis was peculiarly useful to prove the origin of the contamination when observed ashore in some sensitive areas, such as salt ponds, where the water quality is of great importance since contaminants are concentrated during the production process (up to 35 times). The use of these ratios

Table 3. PAHs concentrations in µg/g determined in *Erika* oil in a sample from an oil slick and in a sample collected on a beach.

	<i>Erika</i> oil	Oil slick	Beach sample
Phenanthrene	598	350	194
3 MePhen	496	316	176
2 MePhen	681	457	250
9 MePhen + 1 MeAnth	465	313	173
3 MePhen	374	248	142
C1-Phen	2,017	1,335	742
3 EtPhen	54	36	19
2 + 9 + 1 + 3,6 DMPhen	221	158	87
2,6 + 3,5 DMPhen	272	196	109
2,7 DMPhen	222	174	97
1,3 + 2,1 + 3,9 + 3,1 DMPhen	682	502	284
1,6 + 2,9 + 2,5 DMPhen	458	334	193
1,7 DMPhen	211	159	90
1,9 + 4,10 + 4,9 + 2,3 DMPhen	254	194	108
1,8 DMPhen	59	49	26
C2-Phen	2,433	1,801	1,011
C3-Phen	2,117	1,739	1,008
Dibenzothiphene	233	123	67
4 MeDBT	238	136	77
3 + 2 MeDBT	268	152	84
1 MeDBT	71	43	25
C1-DBT	577	331	186
4,6 DMDBT	96	60	34
2,4 DMDBT	87	53	31
2,6 + 3,6 DMDBT	228	146	82
3,7 + 1,4 + 1,6 + 1,8 DMDBT	288	190	105
1,3 + 1,9 + 1,2 DMDBT	172	125	65
C2-DBT	871	573	316
C3-DBT	986	704	405
Anthracene	103	63	33
Fluoranthene	42	31	18
Pyrene	248	196	113
Benz[a]Anthracene	202	183	115
Chrysene + Triphenylene	357	324	205
Benzo[b+k]Fluoranthene	66	58	34
Benzo[e]Pyrene	98	90	55
Benzo[a]Pyrene	105	100	62
Perylene	37	33	21
Indeno[1,2,3-cd]Pyrene	18	17	10
Benzo[g,h,i]Perylene	40	38	23
Dibenzo[ah+ac]Anthracene	32	29	17
3 MeChrysene	611	595	341
2 MeChrysene	334	327	190
4+5+6 MeChrysene	156	152	88
1 MeChrysene	195	189	105

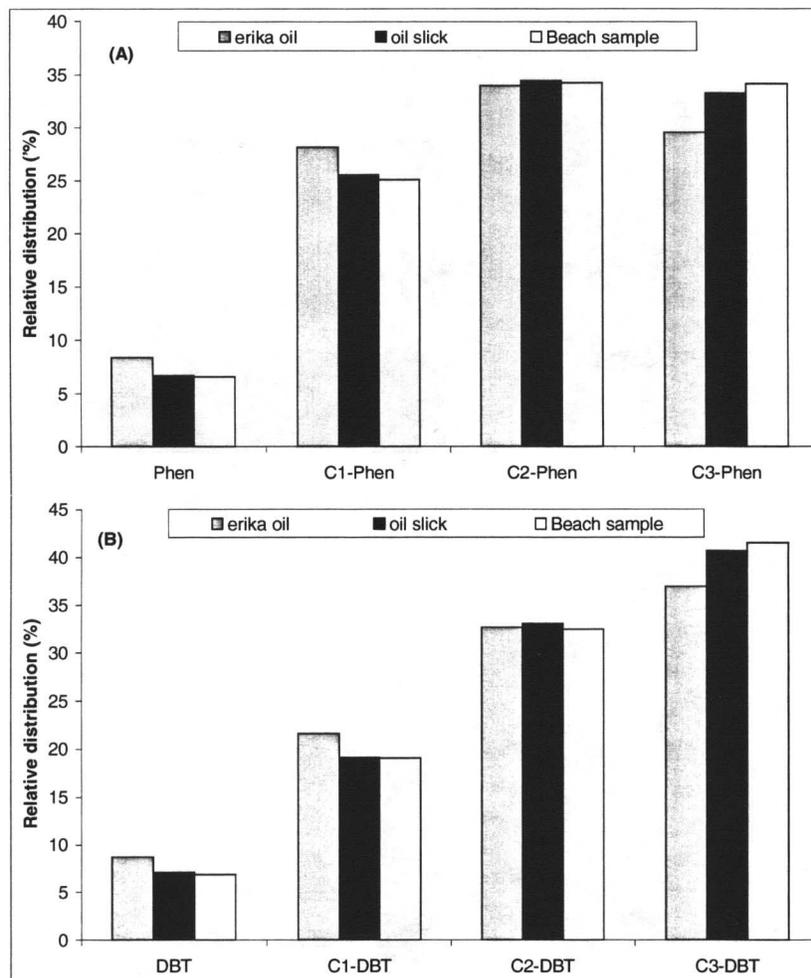


Figure 5. Comparison of the relative distribution of phenanthrenic (A) and dibenzothiophenic (B) compounds present in *Erika* oil, in a sample from an oil slick and in a sample collected on a beach.

enabled the analytical laboratories to determine the origin of the possible observed contaminations and provided a method to monitor the remediation of the impacted sediments along the Atlantic coast.

Geochemical markers (IFP). *Material and methods.* The geochemical markers (e.g., terpanes and steranes) were analyzed by GC-MS using a high resolution mass spectrometer with metastable reaction monitoring (Autospec, Micromass, Manchester, Great Britain). Conditions were as follows: ionization by 70 eV electronic bombardment and resolution of 500. The identification of compounds was performed according to retention times and spectrum libraries (Willey and NIST).

Results and conclusion. The determination of the geochemical markers in the fraction of saturated hydrocarbons showed the presence of terpanes and steranes (Peters and Moldovan, 1993) as shown in Figures 7 and 8. In addition to demonstrating that the oil sample from the refinery was identical to the one loaded into the *Erika*, these compounds were successfully used to identify the origin of the fuel oil found in the different shoreline locations allowed.

Oil biodegradability (MNHN)

Microbial biodegradation is known to be an efficient process in the decontamination of oil-polluted environments. Laboratory

experiments were conducted over an 80-day period to estimate the biodegradability of the *Erika* fuel oil.

Material and methods. Three series of cultures were set up in Erlenmeyer flasks containing 150 mL of mineral medium (MM) or synthetic seawater (SS) enriched with nitrogen (N) and phosphorous (P) and 100 to 150 mg of hydrocarbons (HC).

Original fuel oil and oil-contaminated sands were used as substrates. The cultures were inoculated either with referenced HC-degrading microorganisms or by the indigenous microflora of the contaminated sands only. The series were: MM, original oil, reference inoculum; MM, polluted sand; and SS, sand, inoculum. After 8, 15, 30, 50, and 80 days, the residual oil was extracted with dichloromethane and analyzed for chemical composition by computerized capillary GC. The residue was separated on silica gel column into saturated, aromatic, and polar fractions that were weighed. Saturated and aromatic fractions were submitted to GC analyses.

Results and discussion. The polar fraction that includes the resins and part of the asphaltenes was not degraded. GC analyses showed that most compounds of the light cracking fraction were assimilated, as well as the n- and branched alkanes; hopanes were not degraded. The degradation rates of GC-resolved aromatics decreased with increasing molecular weight. Mono (alkylbenzenes) and diaromatics (alkylnapthalenes) were degraded totally,

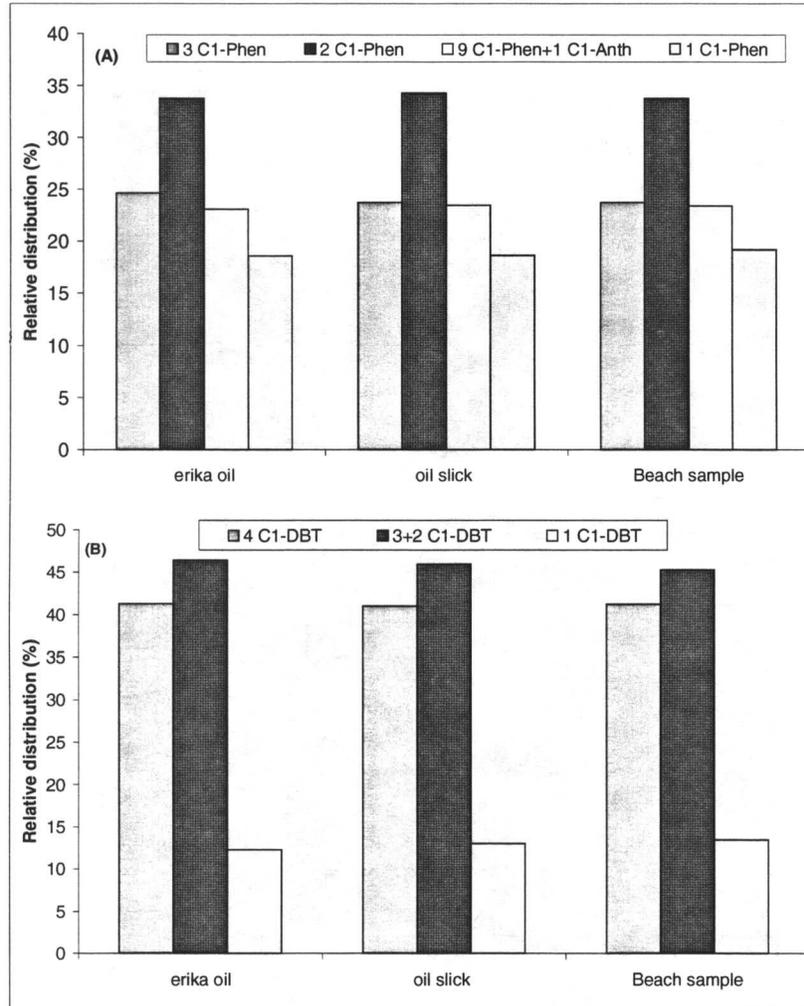


Figure 6. Methyphenanthrenes (A) and methyldibenzothiophenes (B) relative distribution determined in *Erika* oil, a sample from an oil slick and a sample collected on a beach.

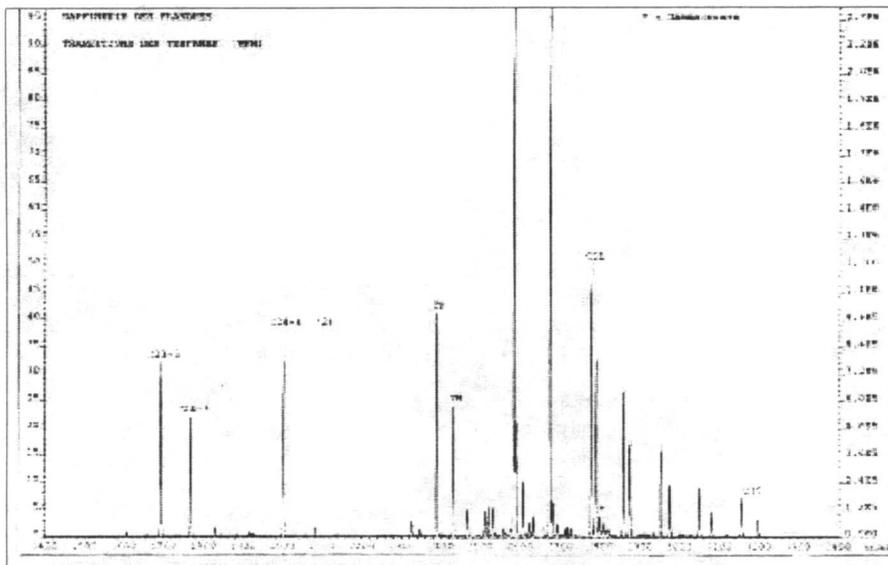


Figure 7. Terpanes distribution of the *Erika* fuel oil.

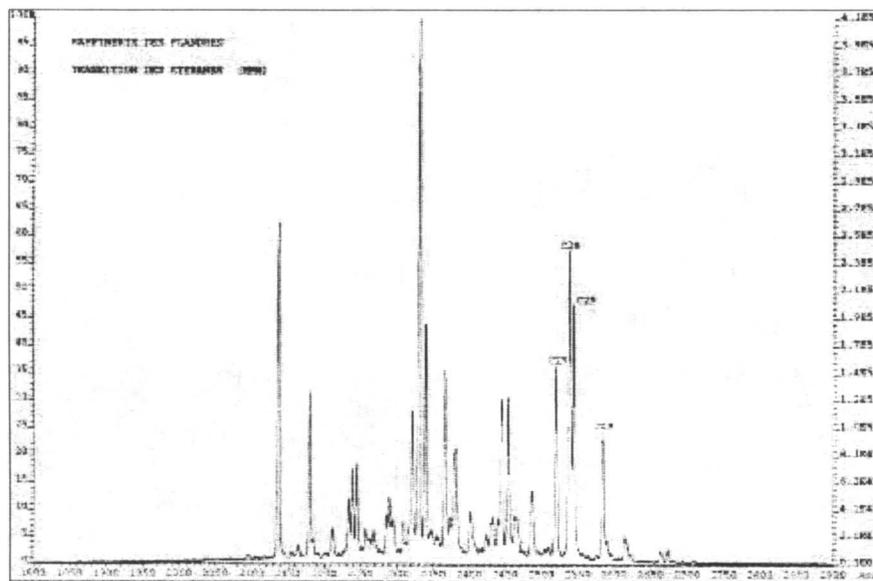


Figure 8. Steranes distribution of the *Erika* fuel oil.

whereas alkylchrysenes were not significantly altered. The biodegradation rate of alkylphenanthrenes and alkyldibenzothiophenes was intermediate and varied according to the number of methyl substitutions (Table 4). The unresolved complex mixture UCM that contains polycyclic saturated and aromatic compounds was not degraded (Table 5). No significant difference was observed between the three series indicating that the indigenous microflora of the polluted sands contained HC-degrading strains able to assimilate all of the degradable fraction of the fuel oil.

Conclusion. The *Erika* fuel oil was composed of 90% of a heavy distillation residue and 10% of a light fraction resulting from catalytic cracking used to lower the viscosity of the fuel.

After 80 days, the total fuel was only 11% degraded. The saturated fraction was 32% degraded and the aromatic fraction 12%.

The very low biodegradation rate of the fuel is attributable to its chemical composition, being rich in biodegradation resistant or refractory compounds like resins, asphaltenes, and polycyclic saturated and aromatic compounds. For comparison, an Arabian light crude oil was 65% degraded under similar conditions and gas oil over 85%. This information confirmed that the *Erika* heavy fuel oil would be highly persistent in the environment and reinforced the need for physical cleanup operations excluding bioremediation processes.

Table 4. Extent of biodegradation for GC-resolved aromatic compounds after 80 days.

GC-resolved aromatic compounds	T0 (ppt)	T80 (ppt)	Biodegradation (%)
Alkylbenzenes	6.94	0	100
C1-Naphtalenes	3.55	0	100
C2-Naphtalenes	4.69	0	100
C3-Naphtalenes	3.89	0	100
C4-Naphtalenes	2.31	0.26	89
C1+2-Fluorenes	2.43	0.31	87
C1-Dibenzothiophenes	2.01	0.49	77
C2-Dibenzothiophenes	2.39	0.76	68
C3-Dibenzothiophenes	2.90	1.31	55
C1-Phenanthrenes	3.26	0.51	84
C2-Phenanthrenes	1.56	0.79	49
C3-Phenanthrenes	4.04	2.67	34
C4-Phenanthrenes	4.13	3.58	13
C1-Chrysenes	2.62	2.45	6
C2-Chrysenes	2.48	2.37	4
C3-Chrysenes	1.58	1.49	6
Total	68	28	59

Note: ppt, part per thousand.

Table 5. Extent of biodegradation for specific fractions of the *Erika* oil after 80 days.

	T0 (ppt)	T80 (ppt)	Biodegradation (%)
Saturates	243 ± 12	165 ± 11	32
n-alkanes	20 ± 1.4	3.6 ± 1	82
Iso-alkanes	17 ± 2	10.7 ± 1.1	37
Aromatics	588 ± 20	473 ± 17	12
PAH + alkyl PAH	18.4 ± 2	15.5 ± 2	16
Light Cracking fraction	98 ± 17	59 ± 13	40
Light Cracking Peaks	36 ± 6.2	8 ± 2	78
UCM	320 ± 60	330 ± 33	0
Polar Compounds	209 ± 17	246 ± 25	-17
Total HC	1,000	890 ± 10	11

Note: ppt, part per thousand.

Conclusion

The analyses and studies performed on the *Erika* fuel oil by the different laboratories were used to select optimal response strategies. Realistic studies on the behavior of the oil in the water column conducted at the pilot scale accurately predicted that the oil would remain at the sea surface and come ashore. In addition, field data on the spatial distribution of oil explained why some sites were impacted unexpectedly in contrast to the results of predictive models. Results of the study team suggest that leakage of oil from the tanker occurred prior to its breakup and sinking.

All analyses of the aromatic compounds were essential to assess the toxicity and the environmental impact of the oil, to establish a list of the most specific compounds that characterize water or sediment pollution because of the *Erika* fuel oil and, in the long term, to monitor the success of remediation procedure and the extent of contaminated site recovery. Finally, the biodegradability studies provided evidence that physical cleanup operations were required to remove residual oil from the *Erika* as bioremediation strategies would be ineffective.

Acknowledgements

The authors would like to thank IFP colleagues J-P. Durand, A. Fafet, E. Robert, and M. Da Silva for skillful participation to the analyses; V. Gouriou from CEDRE for providing map and information about the drifting; and Ken Lee, for his comments that improved the paper.

References

1. ASTM (American Society for Testing and Materials). 2000a. D5291-96 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants. *2000 Annual Book of ASTM Standards—Petroleum Products and Lubricants (II)*, Vol. 05.03. American Society for Testing and Materials, Philadelphia, PA.
2. ASTM (American Society for Testing and Materials). 2000b. D3228-96 Standard Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils By Modified Kjeldahl Method. *2000 Annual Book of ASTM Standards—Petroleum Products and Lubricants (II)*, Vol. 05.02. American Society for Testing and Materials, Philadelphia, PA.
3. ASTM (American Society for Testing and Materials). 2000c. D5622-95 Standard Test Methods for Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis. *2000 Annual Book of ASTM Standards—Petroleum Products and Lubricants (II)*, Vol. 05.03. American Society for Testing and Materials, Philadelphia, PA.
4. Durand J-P., A. Bré, J-J Béboulène, A. Ducrozet, and S. Carbonneaux. 1999. Improvement of Simulated Distillation Methods by Gas Chromatography in Routine Analysis. *Oil & Gas Sci. Technol. Rev IFP*, 54-4:431-438.
5. Guyomarc'h, J., and F-X. Merlin. 2000. Methodology for Assessing Oil Weathering in a Dedicated Hydraulic Canal: Evolution of Physical-Chemical Properties and Dispersibility of Various Crudes. *Proceedings*, 23rd Arctic and Marine Oilspill Program (AMOP) Technical Seminar. Environment Canada, Ottawa, Ontario. pp. 37-57.
6. Guyomarc'h, J., O. Kerfourn, and F-X. Merlin. 1999. Dispersants and Demulsifiers: Studies in the Laboratory, Harbor and Polludrome. *Proceedings*, 1999 Oil Spill Conference. American Petroleum Institute, Washington, DC. pp. 195-202.
7. Haeseler, F., D. Blanchet, V. Druelle, P. Werner, and J-P. Vandecasteele. 1999a. Analytical Characterization of Soils from Former Manufactured Gas Plants. *Environ. Sci. Technol.* 33:825-830.
8. Haeseler, F., D. Blanchet, V. Druelle, P. Werner, and J-P. Vandecasteele. 1999b. Ecotoxicological Assessment of Former Manufactured Gas Plants Soils: Bioremediation Potential and Pollutant Mobility. *Environ. Sci. Technol.* 33:4379-4384.
9. Laflamme, R.E., and R.A. Hites. 1978. The Global Distribution of Polycyclic Aromatic Hydrocarbons in Recent Sediments. *Geochimica et Cosmochimica Acta*. 42:289-303.
10. Lake, J.L., C. Norwood, C. Dimok, and R. Bowen. 1979. Origins of Polycyclic Aromatic Hydrocarbons in Estuarine Sediments. *Geochimica et Cosmochimica Acta*. 43:1847-1854.
11. McElroy, A.E., J.W. Farrington, and J.M. Teal. 1989. Bioavailability of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. Ed Varanasi U., CRC Press, Boca Raton, FL. pp. 1-40.
12. Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Sources, Fates and Biological Effects. Applied Science Publishers Ltd., London, England.

13. Peters, K., and M. Moldovan. 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice-Hall, Englewood Cliffs, NJ.
14. Sporstøl, S., N. Gjos, R.G. Lichtenthaler, K.O. Gustovsen, K. Urdal, F. Oreid, and J. Skel. 1983. Source Identification of Aromatic Hydrocarbons in Sediments using GC/MS. *Environmental Science and Technology*. 17:282–286.
15. Tissot, B.P., and D.H. Welte. 1984. *Petroleum Formation and Occurrence*. Ed. Springer-Verlag, Berlin, Heidelberg, New York.
16. Wang, Z., M. Fingas, and D.S. Page. 1999. Oil Spill Identification. *Journal of Chromatography A*. 843:369–411.
17. Youngblood, W., and M. Blumer. 1975. Polycyclic Aromatic Hydrocarbons in the Environment: Homologous Series in Soils and Recent Marine Sediments. *Geochim. Cosmochim. Acta*. 39:1303–1314.

