Interspill 2004
Presentation no. 462

ANALYTICAL CHARACTERIZATION AND COMPARISON OF PRESTIGE AND ERIKA'S FUEL OIL N°6

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ABSTRACT

The shipwreckage of the oil tanker Erika and Prestige occurred respectively on December the 12th 1999 in the Golf of Gascogne and on November the 19th 2002 off the coast of Galice in Spain. Both led to large oil spills: more than 10 000 tons of fuel oil n° 6 were released in the Atlantic Ocean in the south of Finistère as a consequence of the Erika and probably trice as much from the Prestige.

Detailed analytical characterisations of the fuel oils laden in both Prestige and Erika as well as of other fuel oils n°6 have been performed.

The analytical procedure used consisted in physico-chemical parameters such as viscosity, flash point, water content, concentration of insoluble compounds and distillation curves. Furthermore, this characterisation included evaluation of the chemical classes (saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltens), research for geochemical markers and quantification of polyaromatic hydrocarbons.

The characterisation was carried out on samples collected in both Ships as well as in the marine and shoreline environment.

The results obtained showed that the characterisation was quite appropriate to precisely identify the product laden in the Ships and to recognise them. It was concluded that two complementary techniques were sufficient to assess the origin of the oil sample: simulated distillation to give an overall view of the oil, on the one hand, and analysis of geochemical markers including terpanes and steranes, on the other hand.

This paper shows a detailed comparison of analytical data of those two similar oil spills. The similarities and differences are discussed in detail.

INTRODUCTION

The Institut Français du pétrole (IFP) was asked by the French Agency for Food Sanitary Security (AFSSA Agence Française de Sécurité Sanitaire des Aliments) to provide an exhaustive characterisation of the chemical composition of the heavy fuel oil transported by the tanker Erika, in view to identify and determine the real nature of the cargo and to quantify the presence of toxic compounds. Three years later a similar request came from the French Ministry of Environment concerning the heavy fuel oil transported by the tanker Prestige. The experience gathered with the first major heavy fuel oil spill was of a great help for the characterisation of the second one.

A heavy fuel oil is generally the heavy fraction from a crude oil mixed up with a lighter cut in order to adjust some parameter needed to met the commercial and administrative specifications.

The heavy fraction of such a fuel oil is most often a distillation residue:

- an atmospheric residue (distilling over 350°C),
- or a vacuum distillation residue (distilling over 550°C).

Two discrete cuts are constituting the atmospheric residue: the vacuum distillate (350 to 550°C) and the vacuum residue (550°C$^+$ fraction). Furthermore if the refinery is equipped with a conversion unit, for instance visbreaking or fluid catalytic cracking, the residues from these units may also be incorporated in the heavy fuel oil. The viscosity of those very heavy fractions is reduced by the addition of middle distillates like straight run diesel oils or light cycle oils from the fluid catalytic cracking. The origin of the different ingredients of a heavy fuel oil may vary from one refinery to the other depending on the available units, the crude used and the general market for refined oil in the influence zone of the refinery.

This study has been carried out on different samples handed over from the CEDRE (Centre de Documentation, de Recherche et d'Expérimentations sur les Pollutions Accidentelles des Eaux):

- originating from the Erika tanker:
  - a sample called cargo, originating from the refinery des Flandres (where Erika has been loaded),
  - a heavy fuel from the refinery de Normandie,
  - a heavy fuel from the refinery de Provence,
  - a sample of fuel that has reached the coast in Le Croisic on January the 19th of 2000.
- originating from the Presige tanker:
  - a sample called cargo, taken in the ship on November the 5th 2002,
  - a sample taken off shore by the Ailette on November the 18th 2002,
  - a sample taken on the beach of Le Porge on January the 1st 2003,
  - a sample taken on the beach of Mimizan on January the 1st 2003.

RESULTS

Administrative specifications of heavy fuel oils n°6 (ASTM D396-80) equivalent to fuel oil n°2 (according to French specifications) are mainly defined by their physico-chemical characteristics (A. Lewis 2002). These specifications are summarised in the table 1 together with the analytical results obtained on the product loaded into the tanker Erika and the sample from the Prestige. These results confirmed that the cargo of both tankers were fuel oil n°6.

Table 1 : Administrative specifications concerning physical-chemical characteristics of heavy fuel oil n°6 and respective values for the products loaded in the tankers Erika and Prestige.

Physical-chemical characteristics	Administrative specifications	Fuel oil loaded into the tanker Erika	Fuel oil loaded into the tanker Prestige
Viscosity (NFT 60-100)			
- at 50 °C (cSt)	>110	565	615
- - at 100 °C (cSt)	<40	38.7	50
Sulphur content (NF M07-025) (% weight)	<4	2.5	2.6
Distillation (NF M07-002) (% of volume)	<65 at 250 °C	4.5	3.8
	<85 at 350 °C	15.5	13.9
Flash point (NFT 60-103) (°C)	≥70	141	n.d.
Dry matter in suspension (NF M07-063) (% weight)	<0.25	0.08	0.2

A simulated distillation 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).

The simulated distillation (Figure 1) showed that the fuel oils were composed by a mixture of different cuts. These profiles are characteristic of :

- Light Cycle Oil (LCO), High Cycle Oil (HCO), Slurry (all products from the Fluid Catalytic Cracking (FCC) unit) and residue from the Vacuum Distillation Unit for the Erika oil
- and a straight run diesel oil (13,9%), an intermediate distillate probably being a light fraction of the atmospheric residue (29,2%) and a heavy fraction corresponding to the heavy fraction of atmospheric residue (56,9%) for the Prestige oil.

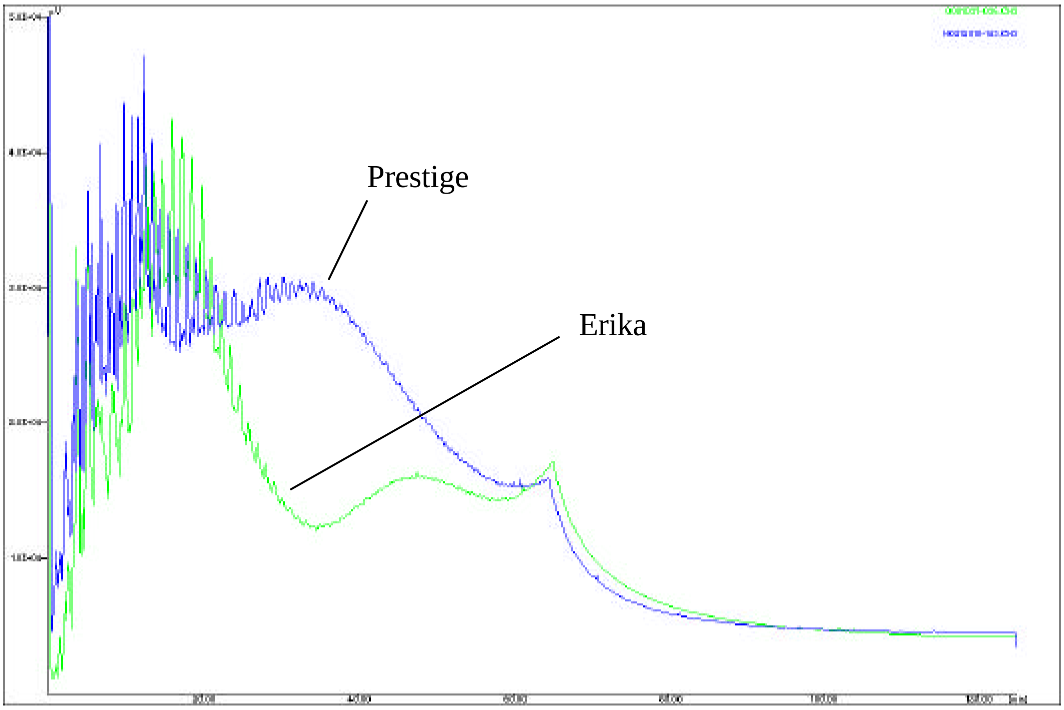

Figure 1. Simulated distillation of the Erika and Prestige fuel oils.

Haeseler et al 2002 showed that only very few differences were observed between the samples collected at the refinery des Flandres, at sea, on shore and on the wreckage in the case of the Erika spillage.

Figure 1 shows that this technique can discriminate two fuels according to their origin.

Figure 2 leads exactly to the same conclusions in the case of the Prestige spillage. The high temperature chromatograms of fuel oils n°6 originating from the cargo and different samples collected on shore in Le Porge and Mimizan are very similar, only the light fraction has disappeared from the oils that were subjected to marine weathering.

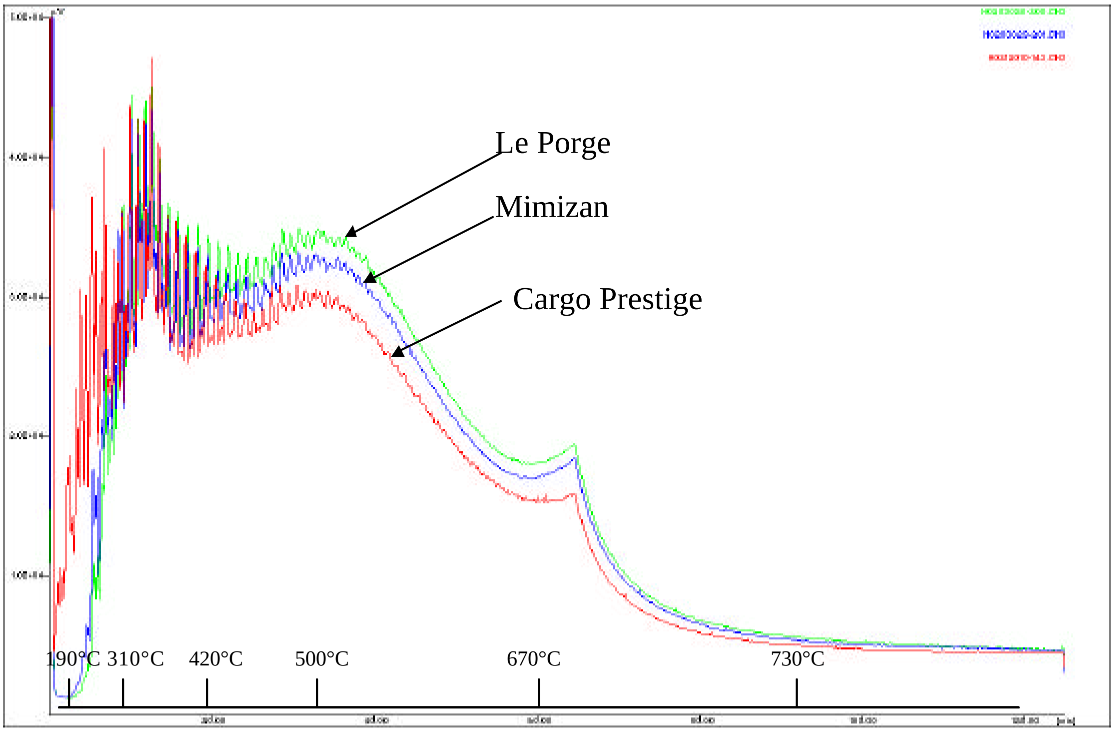

Figure 2 : High temperature chromatograms (simulated distillation) of heavy fuel oils originating from the Prestige cargo and different beaches.

The fractionation of the fuel into saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes occurred by adsorption liquid chromatography on silica gel minicolumns after asphaltenes precipitation in n-hexane according to Haeseler et al. (1999). These data (table 2) showed that the fuel oils contained a large amount of aromatic hydrocarbons, indicating that an important part of the constituents originated from a FCC unit.

Table 2 : Concentration of saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes in the fuel oils from the Erika and the Prestige tankers.

	Concentration %			
	Saturated hydrocarbons	Aromatic hydrocarbons	Resins	Asphaltenes
Erika	22,2	55,6	15,7	6,6
Prestige	23,0	54,0	12,5	10,5

For both oils the saturated and aromatic fractions represented about 75% of the total mass. These saturated and aromatic fractions have been gathered and have been analysed by **high resolution mass spectrometry** (according to Fafet et al., 1999) which gives the repartition of the different hydrocarbon families. The data presented in table 3 show for both oils approximately the same content in mono, di, tri and tetraaromatics between 7 and 10% and reveals a high proportion of sulphured compounds (15%).

The comparison of the different hydrocarbon types of the Prestige cargo and a sample taken by the Ailette (table 4) show that no significant differences can be noticed by this type of analyses for a limited weathering.

The differences in the sum of saturated and aromatic hydrocarbons between the data presented in table 2 and table 3 are due to the separation technique utilised: for table 2 liquid chromatography on minicolumns and for table 3 high performance liquid chromatography.

Table 3 : Repartition of the different hydrocarbon types for the Erika and Prestige oils.

	Concentration [% m/m]		
	Cargo "Prestige"	Off shore sample "Prestige"	Cargo "Erika"
Saturated hydrocarbons	**29.7 +/- 1.6**	**28.2 +/- 1.6**	**33.4 +/- 1.6**
Total of non sulfured aromatics	**31.5 +/- 1.6**	**31.0 +/- 1.6**	**30.8 +/- 1.6**
Monoaromatics	9.0	8.6	8.0
Diaromatics	9.0	8.7	7.3
Triaromatics	5.0	5.5	5.5
Tetraaromatics	6.0	5.9	7.4
Pentaaromatics	2.5	2.3	2.1
Hexaaromatics	0.0	0.0	0.5
Total of sulphured aromatics	**15.8 +/- 1.2**	**15.8 +/- 1.2**	**15.8 +/- 1.2**
Benzothiophenes	5.2	5.6	4.0
Dibenzothiophenes	4.1	3.8	5.2
Naphtalenothiophenes	4.5	4.4	5.0
Disulphured aromatics	2.0	2.0	1.6
Total (saturates + aromatics)	**77.0**	**75.0**	**80.0**

The geochemical markers: terpanes and steranes (Peter and Moldovan 1993) were analysed in the saturated fraction after elimination of the n-alkanes by insertion on molecular sieves. The analysis was performed by GC-MS using a high resolution mass spectrometer with metastable ion monitoring (Autospec Micromass, Great Britain). The compounds were identified using metastable ions scrutation mode. The presence of terpanes and steranes is shown in figures 3 and 4.

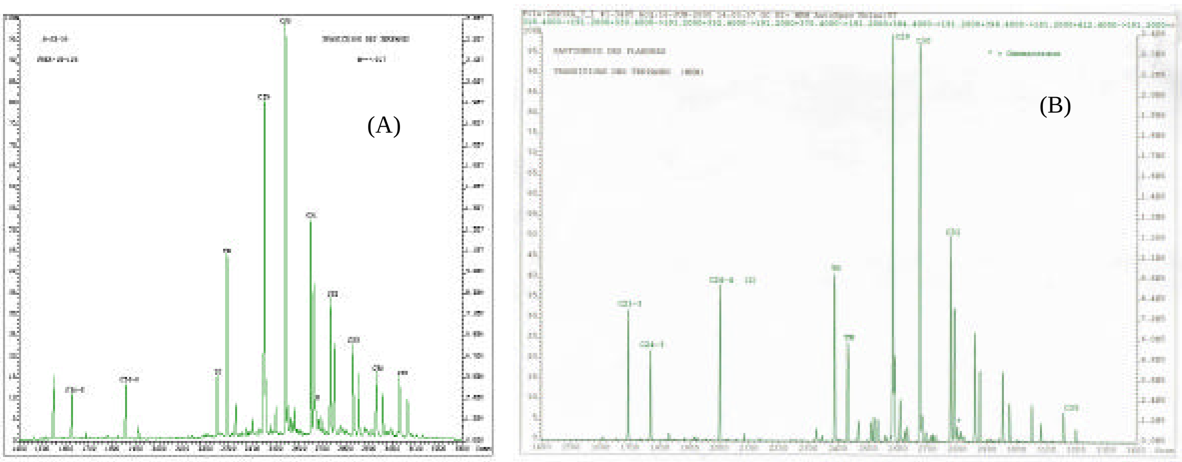

Figure 3: Terpanes chromatograms of the Prestige (A) and Erika (B) fuel oils.

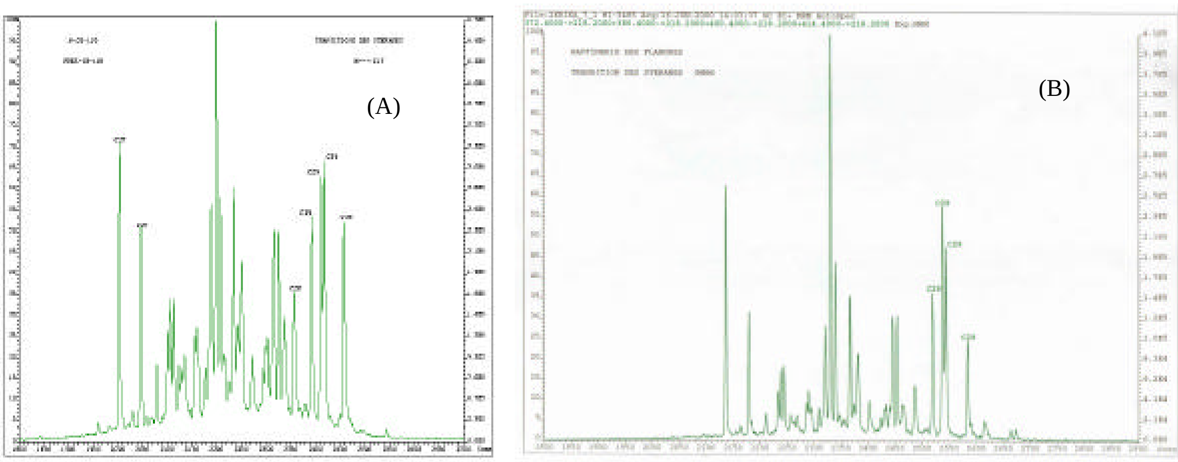

Figure 4: Steranes chromatograms of the Prestige (A) and Erika (B) fuel oils.

The table 5 summarises quantitatively the chromatograms presented in the figures 3 and 4. The geochemical markers were also successfully used to identify the origin of the fuel oil collected in different shoreline sites. Moreover, the a and ß oleananes and the C_{24} terpanes were very good markers to segregate the fuels. The same conclusions appears to be drawn by the *ad hoc* working group from the CEN which is doing an important normative work concerning oil spill identification that will soon lead to CEN guidelines.

All sample suspected to be originating from the Prestige (sampled soon after the ship wreckage) appeared to present the same molecular signature on saturated markers. Furthermore, heavy fuel originating from different refineries including the Erika cargo appeared to present different and also specific ratios in particular for C29hopane/C30hopane ratio, the C35hopane(R+S)/C34hopane(R+S) ratio as well as the diagenesis indexes (Peters and Moldovan 1993) for C27 and C29 steranes. These ratios are not influenced by weathering in the case of both oil spills (Erika and Prestige) and they are also not influenced by biodegradation (Haeseler and Ballerini 2002, Benoit and Haeseler 2004). According to these data the discriminating hopane and sterane ratios may be used for assessing the origin of oil even after very long periods.

Table 5: Terpanes and steranes distribution in different fuel oils n°6 (Prestige: cargo and weathered, Erika cargo and two other refineries).

	TERPANES						STERANES								
							C27			C29					
	C24-3/24-4	TS/TM	olea(α+β)/C30hop	Gammacérane*100/C30 Hop	C29hop/C30hop	C35 Hop(R+S)/C34 Hop(R+S)	(S/R+S)	ββ/αα+ββ	dia index	(S/R+S)	ββ/αα+ββ	dia index	% C27	% C28	% C29
Prestige Cargo	0,77	0,34	-	7,20	0,72	0,97	0,47	0,51	0,56	0,50	0,55	0,33	41	24	35
Off shore sampling	0,78	0,37	-	7,40	0,79	0,97	0,47	0,50	0,54	0,50	0,51	0,34	40	24	36
Beach Le Porge	0,69	0,31	-	7,50	0,83	0,97	0,47	0,52	0,52	0,50	0,55	0,31	41	24	35
Beach Mimizan	0,67	0,27	-	7,41	0,80	0,96	0,47	0,52	0,52	0,50	0,55	0,32	41	24	35
Flandres/ Dunkerke (Erika)	0,48	1,84	-	-	0,91	0,70	0,48	0,49	1,12	0,54	0,53	0,79	47	20	33
Povence / Fos	0,46	1,65	1,32	-	0,96	0,53	0,48	0,44	0,74	0,74	0,36	0,32	47	19	34
Normandie / Gonfreville	0,40	1,78	0,41	-	0,88	0,77	0,51	0,49	2,13	0,74	0,39	0,96	47	17	36

The light fraction including benzene, toluene, ethylbenzene and xylenes (BTEX) was analysed by GC-FID under Carburane condition according to Durand et al, 1995. Using an injection technique with back flush, it was possible to perform this analysis by injecting directly the fuel in the GC avoiding losses by evaporation which otherwise would have occurred during fractionation steps. The chromatograms of these analyses realised on the Prestige fuel oil are presented for the C_{20}^{-} fraction in the figure 5 and the C_9^{-} fraction including the BTEX in the figure 6. This analysis shows very clearly the presence of volatile hydrocarbons in this oil even though it is a heavy oil. These volatile hydrocarbons are certainly originating from the middle distillates (straight run diesel oil for the Prestige and light cycle oil for the Erika tanker) used to fluidise the heavy oil fractions.

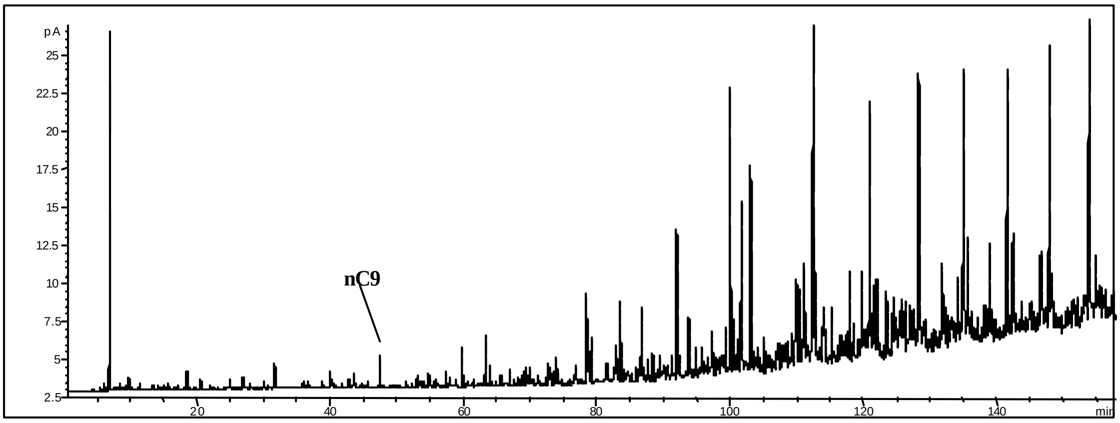

Figure 5: GC chromatogram of the C_{20}^{-} fraction of the Prestige fuel oil n°6.

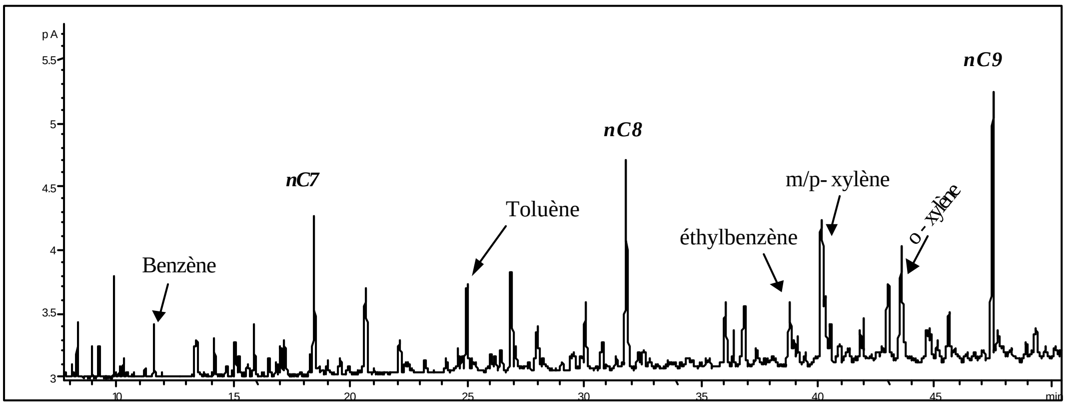

Figure 6: GC chromatogram of the $C9^-$ fraction of the Prestige fuel oil n°6.

These volatile compounds are also the hydrocarbons presenting the most important solubility in water. For this reason, they may present an impact on the water quality. The concentration of BTEX were about the same order of magnitude for the Prestige and Erika fuel oils: respectively 300 and 360 mg/kg (cf. Table 6). The significantly more important concentration of naphthalene and methyl-naphthalenes in the Erika fuel can be explained by a higher content of light cycle oil or a more paraffinic crude oil used in the refinery that produced the Prestige fuel oil.

These significant concentration of volatile hydrocarbons can also constitute a danger for the persons involved in the decontamination of the spill both off- and on-shore. These toxic substances can impact the human health through different exposure pathways like inhalation or cutaneous transfer during the decontamination works. In particular, the clean up of oiled birds often realised in not ventilated, warm rooms (in order to reduce the temperature looses of the birds) and without gloves (in order to reduce their stress) is susceptible to harm the people involved in that kind of veterinarian actions.

Table 6: BTEX and Naphthalene concentration in the Prestige and Erika fuel oils (according the normalised method IFP 9413).

Hydrocarbons	Concentration [mg/kg]	
	Prestige	**Erika**
Benzene*	≤ 12	≤ 29
Toluene	41	60
Ethyl Benzene	38	39
Meta/para Xylene	129	153
Ortho Xylene	79	77
Total BTEX	**298**	**358**
Naphthalene	350	1 026
1 methyl Naphthalene	1 373	2 297
2 methyl Naphthalene	715	3 363

** : partial co-elution with methyl-1 cyclopentene*

The 16 polyaromatic hydrocarbons (PAH) from the US-EPA priority list for toxic compounds were analysed by HPLC with fluorescence detection at specific excitation/emission wavelengths. The concentration of these compounds are presented in table 7. It appears that they are a minor part of both the fuel oils (between 0.2 and 0.3%) compared to the total content of aromatic hydrocarbons representing more than 50%. Furthermore, these 0.2 or 0.3% were mainly composed by naphtalene and phenanthrene, so that the sum of the other 14 compounds including the genotoxic ones like benzo(a)pyrene represented only 1 g/kg for the Prestige fuel oil and 1.5 g/kg for Erika's. Even though the five and six rings PAH are not predominant in these fuel oils, they have to be considered as important regarding their toxicity and their potential of accumulation in the trophic chain. They may also have an impact through cutaneous transfer and should be considered by all the workers during the clean up measures.

Table 7 : Concentration of polyaromatic hydrocarbons (PAH). Analyses by HPLC with fluorimetric detection (PAH from the US-EPA priority pollutant list).

	Concentration [mg/kg]	
Polyaromatic hydrocarbons (PAH)	Prestige	Erika
Naphtalene	519	841

Acenaphthylene *	n.d.	n.d.
Acenaphthene	66	134
Fluorene	82	141
Phenanthrene	438	629
Anthracene	56	71
Fluoranthene	293	328
Pyrene	18	96
Benzo(a)anthracene	22	18
Chrysene	6	335
Benzo(b)fluoranthene	115	2
Benzo(k)fluoranthene	3	34
Benzo(a)pyrene	62	172
Dibenzo(a,h)anthracene	4	<1
Benzo(g,h,i)perylene	13	52
Indeno(c,d)pyrene	217	246
Sum of 16 EPA PAH	1 914	2 987

** : acenaphthylene is not detected by fluorimetric detection*

For getting a more complete picture of the PAH in oil, a more extensive characterisation including also the alkylated homologues of the PAH in addition to the 16 EPA PAH can be beneficial. For instance a detailed analysis of the aromatic fraction using GS6MS techniques to define a PAH fingerprinting of the Erika oil has been presented by Guyomarc'h et al. (2001).

CONCLUSIONS

The physico-chemical characterisation showed that the oils loaded into both of the tanker Erika and Prestige were fuel oil n°6.

All the data presented in this paper allowed to define a specific fingerprinting of the fuel oils from both tankers which could successfully be used to prove the origin of the contamination observed at sea or ashore.

Some of these data (aromatic hydrocarbons) were useful to assess the toxicity and the environmental impact of the fuel oil and to evaluate its potential biodegradability.

The comparison between the cargo of the Erika and the Prestige tankers showed similar concentration levels in various hydrocarbon compounds and in particular in aromatic hydrocarbons. According to this, the same protection measures as those set up for the Erika spillage have been suggested for the Prestige oil spill in order to protect the targets on the shore line and off shore.

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