STUDY OF THE CHEMICAL AND WEATHERING FINGERPRINTS OF THE ERIKA OIL AND CHARACTERISATION OF PAH CONTAMINATION IN GASCOGNE GULF

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ABSTRACT

The important oil spill and the grounding of oil or of its derivatives on the coasts, owing to an accident like the Erika wreck, produce an important contamination of all the parts of the marine ecosystems by hydrocarbons. The follow-up of this chemical contamination represents an important and complementary element of the actions of research and monitoring which aim at evaluating sanitary risks, damage and ecological consequences of such an accident.

A detailed chemical characterization of the composition of the fuel oil from the Erika and follow-up of the weathering of fuel oil grounded in coastal areas (intertidal rocks) were begun. These studies are the first stage and supply a reference to follow the evolution of the contamination by hydrocarbons of all the biotic and abiotic parts of the coastal areas of the northwestern Atlantic.

The analysis results supply fingerprints, features of the Erika fuel oil. These prints were obtained in the 4 chemical cuts of fuel oil of increasing polarity (F1 to F4) made by high resolution gas chromatography connected to low resolution mass spectrometry (CPG-SM). The subtle separation of the complex mixture of compounds, before the analysis CPG-SM (by chromatography of absorption), allows a better identification of the individual compounds. So, we could identify in the cuts 3 and 4 the occurrence of carbazole (nitrogenated aromatic heterocyclic structure) and its alkyl derivatives (methyl, bimethyl, trimethyl) in the Erika fuel oil. Cut 1 mainly contains aromatic aliphatic hydrocarbons of low molecular weight and the cut 2 essentially contains Polycyclic Aromatic Hydrocarbons (PAH). To date, the quantitative analyses of the PAH in the cut 2 of the oil fuel allowed to quantify the concentrations in more than 190 individual compounds. Those represent about a

fraction of 3,3 % of the fuel oil weight. However, the 16 PAH usually analysed represent only 0,3 % of the fuel oil weight. Besides, it is important to clarify that the formal identification and quantification of PAH require the use of the standards of the pure compounds. Sometimes, there are not or they are very expensive. For several compounds, the identification of the PAH in our analyses is made only by the determination of their molecular weights in CPG-SM. For an important number of compounds, the quantification is relative to the standards of quantification used.

The follow-up of the weathering of the PAH of the Erika fuel oil was done with sampling frequency of a sampling per month since December 1999, that is to say since the first oil slicks had grounded on the coasts. The analytic adjusting was developed to be able to characterize quantitatively the PAH present in the oil fuel on the rocks. Indeed, the sampled fuel oil contains water and numerous solid debris (particles of rocks, of sand, of algae, and of sediments). This occurrence can induce an error if the results are expressed in mass weight of fuel oil. The results show that this residue in the fuel oil samples significantly fluctuates and can reach more than 40 % in the weight of the sampled fuel oil.

The analysis results of the PAH reveal a loss of these compounds in the samples taken in December 1999 on the rocks or on the beaches when compared to reference fuel oil (sample of Erika oil fuel from the refinery of Flandres at Dunkerque, sent by the CEDRE). This loss was produced between the moment of the oil spill after the disaster (December 12th 1999) and the date of the first sample in the oil slick grounded at Batz-sur-Mer (December 27th 1999). The percentage of loss according to the molecular weight shows a significant linear regression. We see losses more important for the compounds with a low molecular weight and the reduction of the loss percentage for the compounds with a high molecular weight. The alkyl compounds have a more important loss percentage because they are present in a high quantity in the lightest compounds. The main causes of reduction of the concentrations probably were the solubility and the evaporation of the compounds during the first hours and days after the wreck. The losses percentages, respect to the reference sample, are on average at 18 % for the sum Σ_{16}-PAH and 32 % for the sum ΣMe-PAH.

Besides, the results show that the concentrations of the total PAH in the samples of fuel oil taken in the grounded oil slicks on the rocks between December 1999 and May 2001 fluctuate relatively little. No significant reduction is observed after the grounding of oil on the rocks for the heaviest compounds from fluoranthene. We probably observe a phenomenon of relative increase for the compounds from 5 aromatic nucleus. The low evolution of the composition of the PAH of the fuel oil in time is also revealed by the examination of a few geochemical indicators in the series of samples of the fuel oil. We notice that the geochemical indicators are constant enough, showing that the relative evolution of the composition fluctuates little and that these indicators possibly can be used to search Erika fuel oil fingerprints in the contaminated samples.

Finally, we emphasize that the quantitative analyses of fuel oil that we have done are necessary to get a mass balance of the PAH spilled in the environment. The follow-up of the qualitative and quantitative evolution of the compounds and the use of geochemical indicators allow to discriminate the chronic contamination of the coastal environment that existed before the wreck from the new contamination caused by the Erika oil spill. Finally, the identification and the precise quantification of hydrocarbons contribute to the drawing-up of a toxicological profile of the fuel oil.

Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

1. Suivi d 'altération de la composition en HAP du fuel Erika déposé sur les rochers à Batz sur Mer

2. Étude et suivi de la contamination chimique par des HAP dans le Golfe de Gascogne

Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

Naufrage de l 'ERIKA

1. Bilan de la contamination chimique par des HAP du milieu marin suite à un marée noire ?

Bilan de fioul et d'HAP	%	tonnes
Cargaison	100	30884,471
Déversement	65	~20000
Carbone aromatique	50	10000
Perte dans l'environnement	10	~ 1000
HAP dosés	3	30

→ Contamination accidentelle

Apports en Méditerranée NW

Bilans d'apports en Méditerrané	HAP (tonnes/an)
Golfe de Lion	11
NW Méditerranée	60

(Tolosa et. al. 1996)

→ Contamination chronique

Conférences SaferSeas CEDRE
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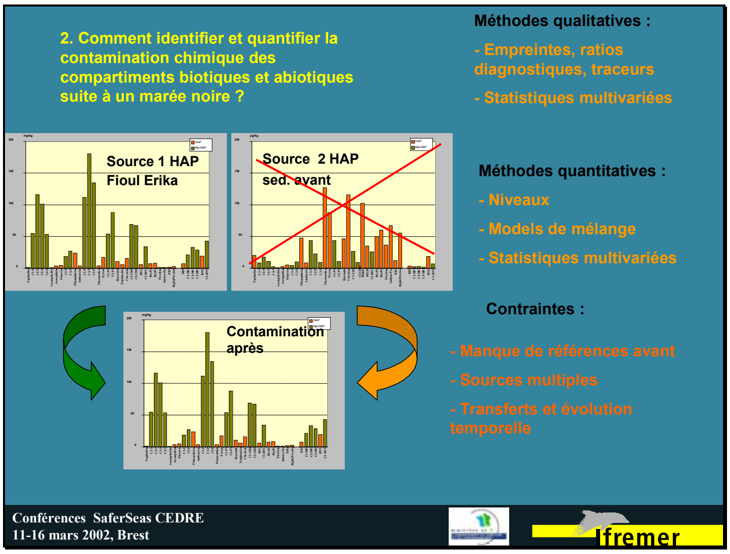
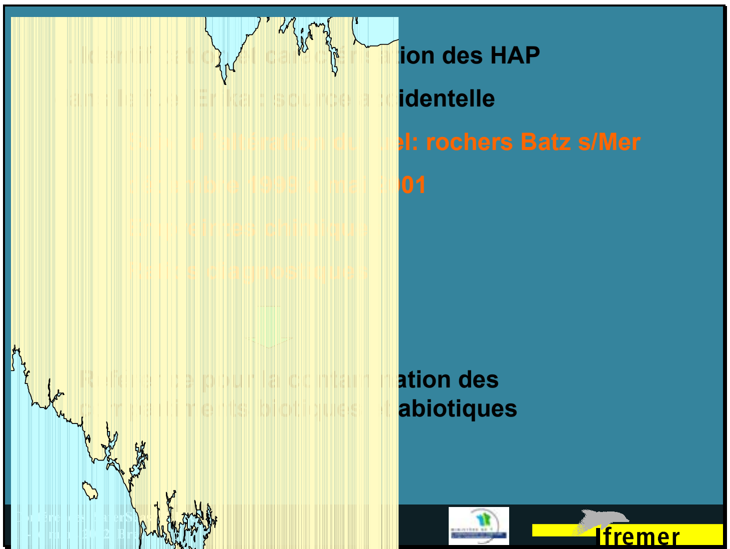
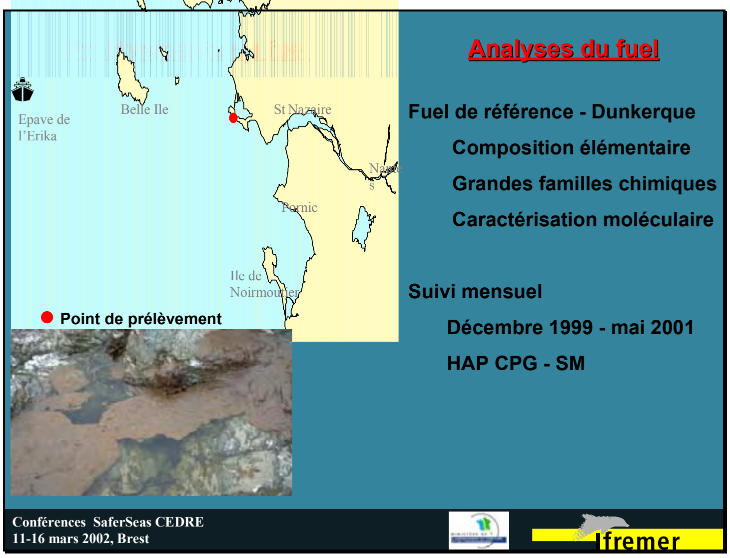
M. Jacek Tronczynski







Caractérisation de fioul Erika
Echantillon CEDRE

Analyse élémentaire CHNSO du fioul de l'Erika

Élément	Ifremer Echantillon Réf. %	IFP %
C	85,2	86,0
H	10,8	10,2
S	2,42	2,5
N	0,23	0,4 (K)
O	-	1,6
V		89 (ppm)
Ni		39 (ppm)

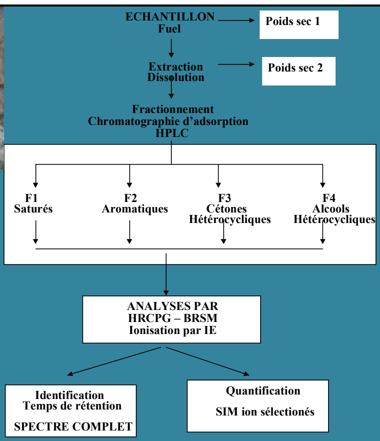
Grandes familles chimiques (IFP) %

	%
Hydrocarbures Aromatiques	55
Hydrocarbures Saturés	25
Résines	13
Asphaltènes	7

Composition moléculaire (Ifremer)

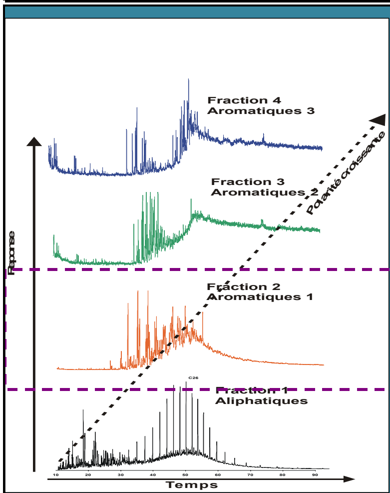
Echantillon CEDRE	Totaux mg/kg	Me-HAP %	HAP %
HAP (F2) 181 composés	32479	90	10
16 HAP	0,27 %		

Conférences SaferSeas CEDRE
11-16 mars 2002, Brest



Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

Analyses CPG-SM Fuel Erika



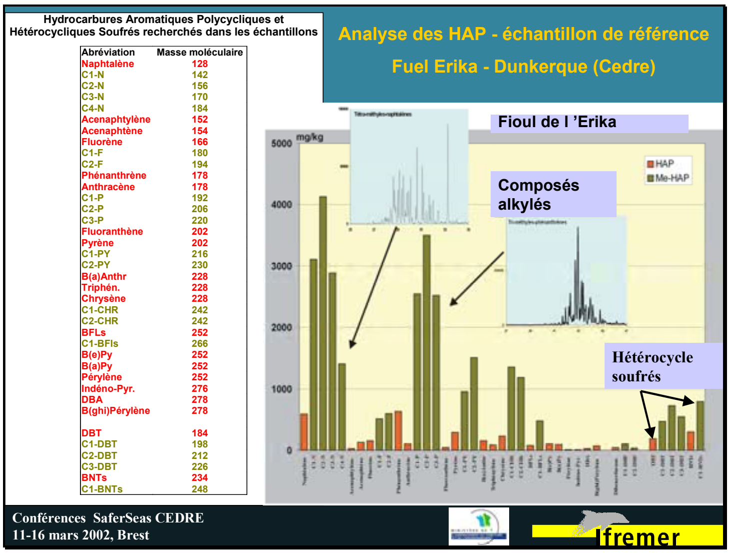
F4 Hétérocycles azotés et C1, C3

F3 Hétérocycles azotés C2

F2 HAP + Hétérocycles soufrés C1, C2, C3

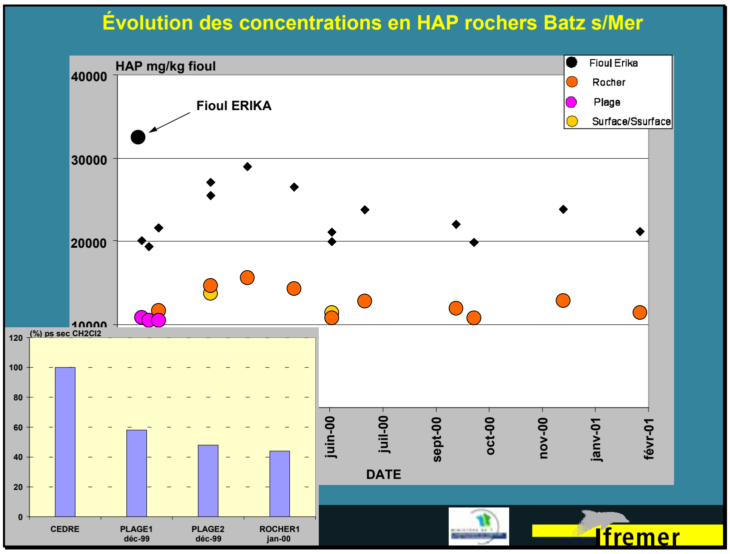
F1 Aliphatiques et mono- di-aromatiques

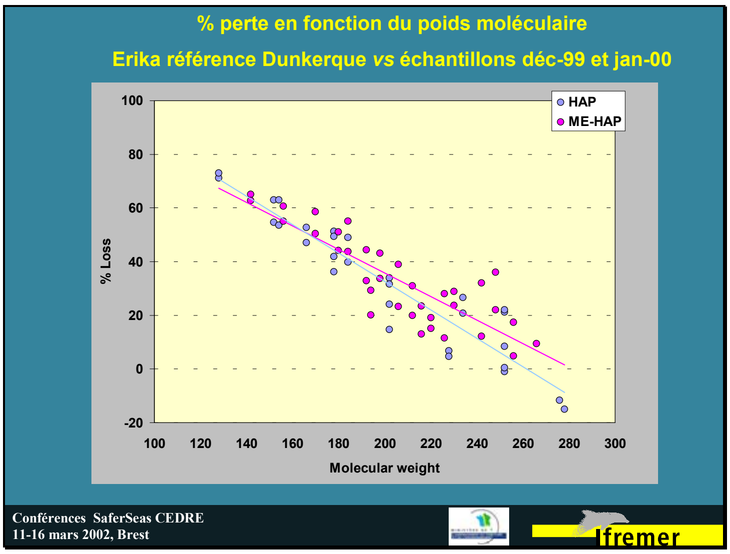
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

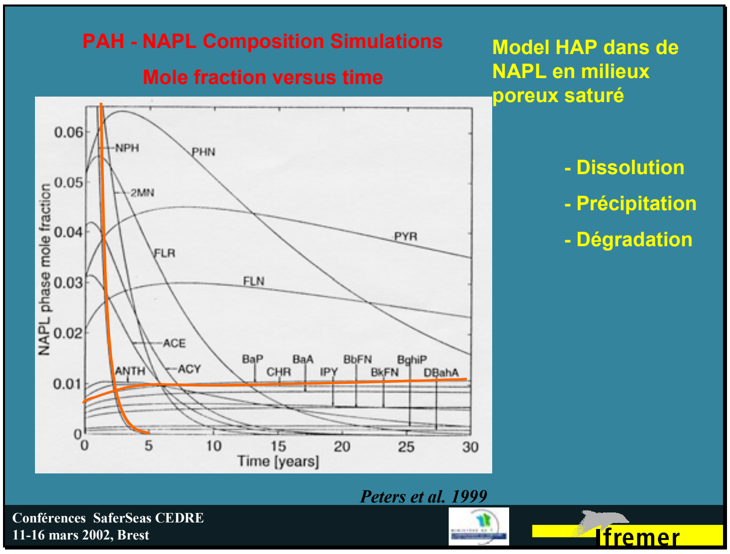


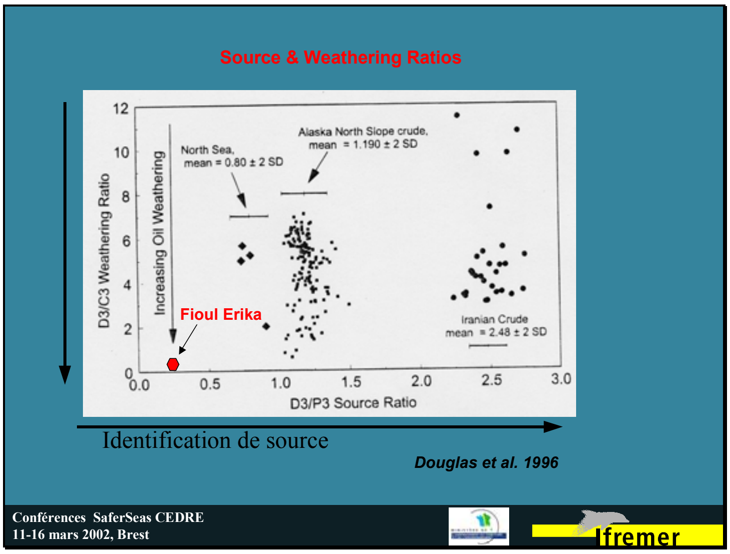
Hydrocarbures Aromatiques Polycycliques et Hétérocycliques Soufrés recherchés dans les échantillons

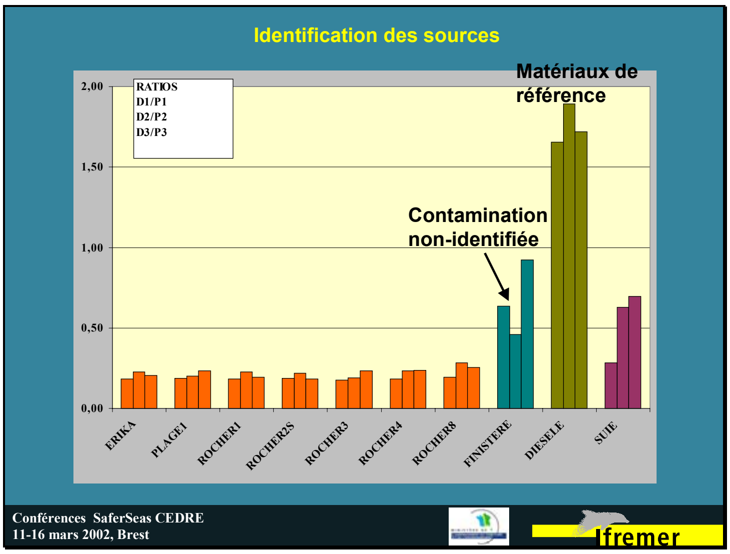
Abréviation	Masse moléculaire
Naphtalène	128
C1-N	142
C2-N	156
C3-N	170
C4-N	184
Acenaphtylène	152
Acenaphtène	154
Fluorène	166
C1-F	180
C2-F	194
Phénanthrène	178
Anthracène	178
C1-P	192
C2-P	206
C3-P	220
Fluoranthène	202
Pyrène	202
C1-PY	216
C2-PY	230
B(a)Anthr	228
Triphén.	228
Chrysène	228
C1-CHR	242
C2-CHR	242
BFLs	252
C1-BFls	266
B(e)Py	252
B(a)Py	252
Pérylène	252
Indéno-Pyr.	276
DBA	278
B(ghi)Pérylène	278
DBT	184
C1-DBT	198
C2-DBT	212
C3-DBT	226
BNTs	234
C1-BNTs	248






PAH - NAPL Composition Simulations
Mole fraction versus time
Model HAP dans de NAPL en milieux poreux saturé
- Dissolution
- Précipitation
- Dégradation
NAPL phase mole fraction
Time [years]
NPH
PHN
2MN
PYR
FLR
FLN
ACE
ACY
ANTH
BaP
CHR
BaA
IPY
BbFN
BkFN
BghiP
DBahA
Peters et al. 1999
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Source & Weathering Ratios
D3/C3 Weathering Ratio
Increasing Oil Weathering
North Sea, mean = 0.80 ± 2 SD
Alaska North Slope crude, mean = 1.190 ± 2 SD
Iranian Crude mean = 2.48 ± 2 SD
Fioul Erika
D3/P3 Source Ratio
Identification de source
Douglas et al. 1996
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Identification des sources
RATIOS
D1/P1
D2/P2
D3/P3
Matériaux de référence
Contamination non-identifiée
ERIKA
PLAGE1
ROCHER1
ROCHER2S
ROCHER3
ROCHER4
ROCHER8
FINISTERE
DIESELE
SUIE
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

Summary of oil weathering study

PAH composition of stranded oil on the inter-tidal rocks changes little during first 12 months

During this period PAH concentrations in the stranded oil decreased little

Loss of PAH in the oil immediately after spill could be related to molecular weights of the compounds

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11-16 mars 2002, Brest

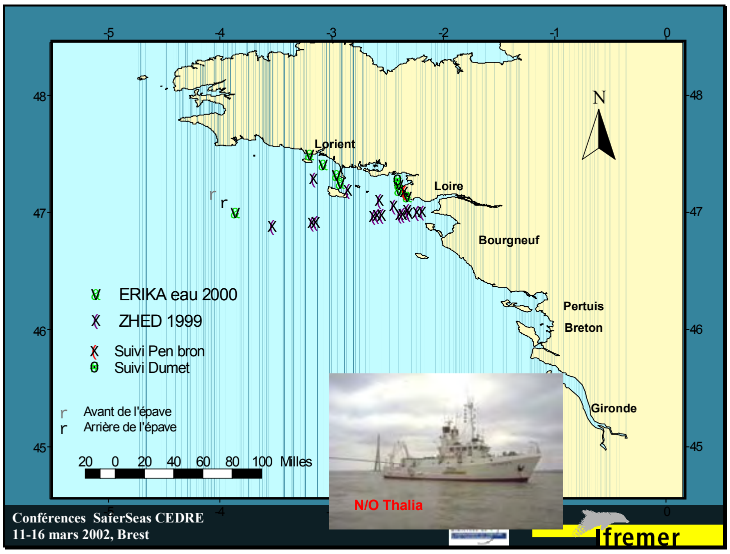
Ifremer

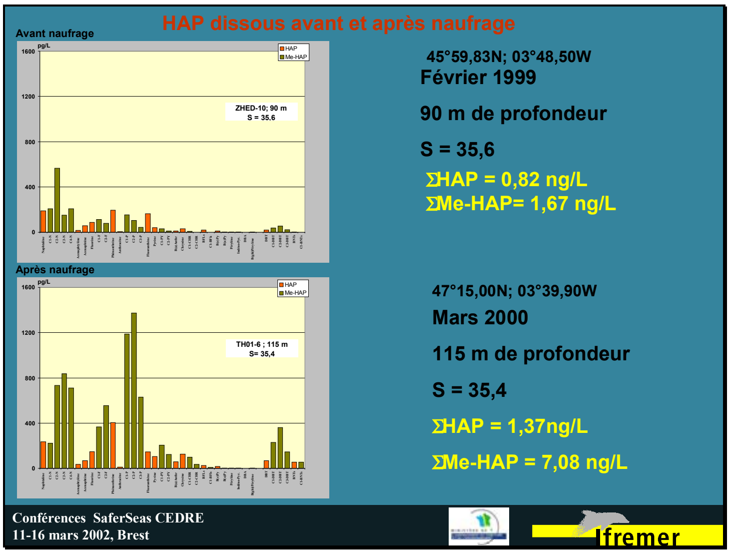
Étude et suivi de la contamination chimique par des HAP dans le Golfe de Gascogne

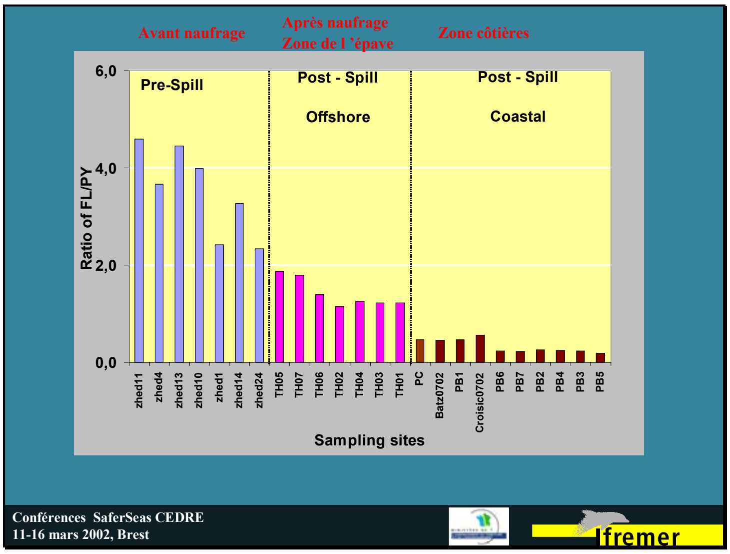
- Colonne d 'eau
- Sédiments
- Organismes marins

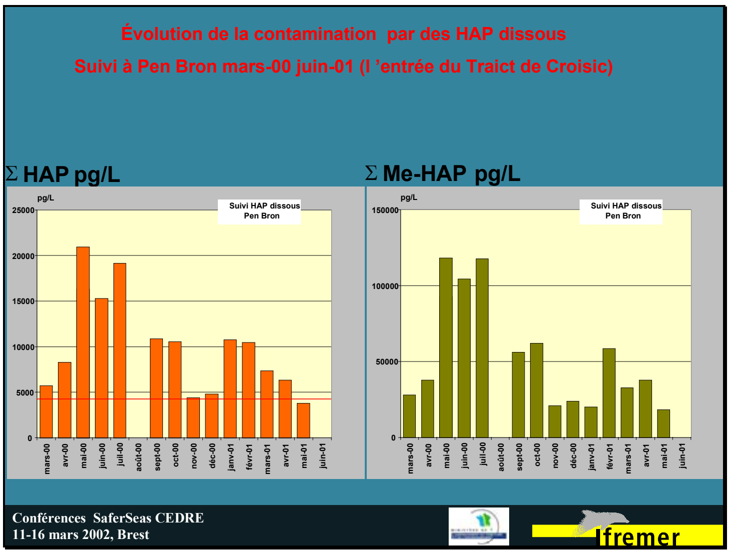
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

Ifremer

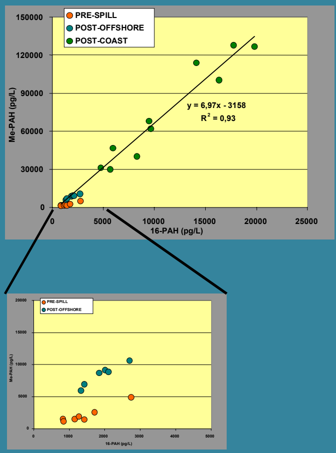



HAP dissous avant et après naufrage
Avant naufrage
ZHED-10; 90 m
S = 35,6
45°59,83N; 03°48,50W
Février 1999
90 m de profondeur
S = 35,6
ΣHAP = 0,82 ng/L
ΣMe-HAP= 1,67 ng/L
Après naufrage
TH01-6 ; 115 m
S= 35,4
47°15,00N; 03°39,90W
Mars 2000
115 m de profondeur
S = 35,4
ΣHAP = 1,37ng/L
ΣMe-HAP = 7,08 ng/L
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Avant naufrage
Après naufrage
Zone de l 'épave
Zone côtières
Pre-Spill
Post - Spill
Offshore
Post - Spill
Coastal
Ratio of FL/PY
Sampling sites
zhed11
zhed4
zhed13
zhed10
zhed1
zhed14
zhed24
TH05
TH07
TH06
TH02
TH04
TH03
TH01
PC
Batz0702
PB1
Croisic0702
PB6
PB7
PB2
PB4
PB3
PB5
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Évolution de la contamination par des HAP dissous
Suivi à Pen Bron mars-00 juin-01 (l 'entrée du Traict de Croisic)
Σ HAP pg/L
Σ Me-HAP pg/L
Suivi HAP dissous
Pen Bron
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

Relation entre HAP et Me-HAP dissous



Conférences SaferSeas CEDRE
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Ifremer

Résumé

Avant le naufrage de l'Erika

Les concentrations des HAP dissous dans les zones marines, côtières et estuariennes ont pu être déterminées : elles constituent des références;

Après le naufrage de l'Erika

Les grandes masses d'eau dans la zone de l'épave deux mois après l'accident sont toujours contaminées par les HAP principalement des composés alkylés ;

Le suivi temporel de cette contamination en zone côtière montre une persistance significative.

Conférences SaferSeas CEDRE
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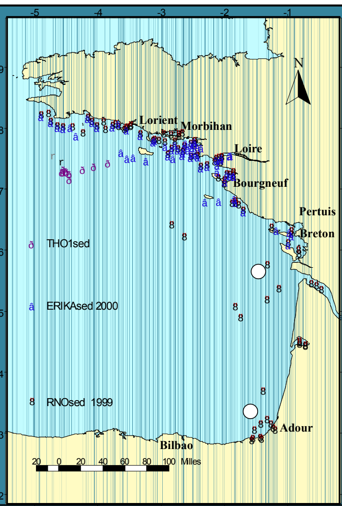


Campagnes de prélèvements

RNO-SED 1999

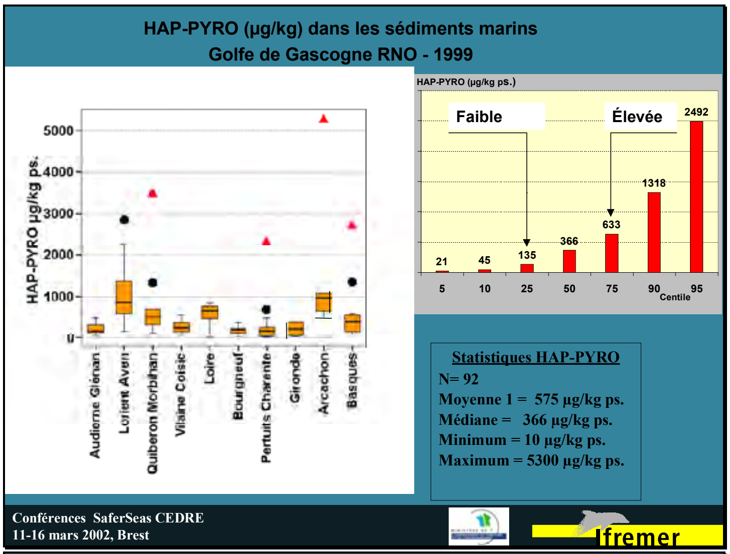
ERIKA TH-01 2000

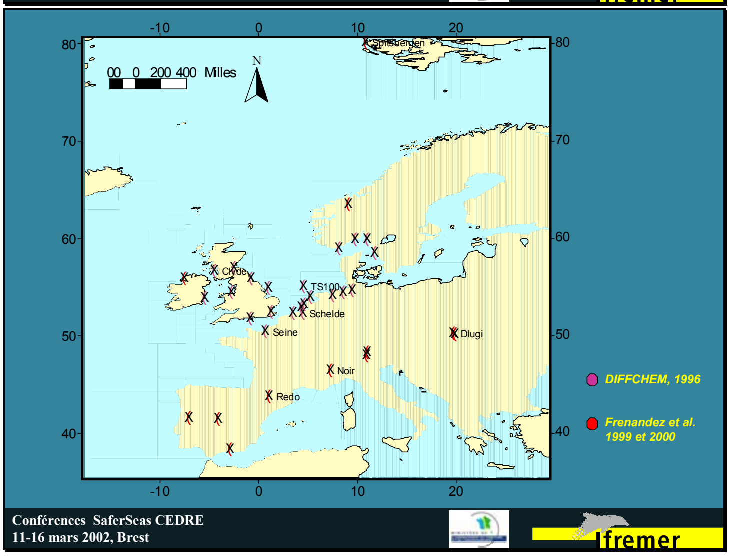
ERIKA TH-02 2000

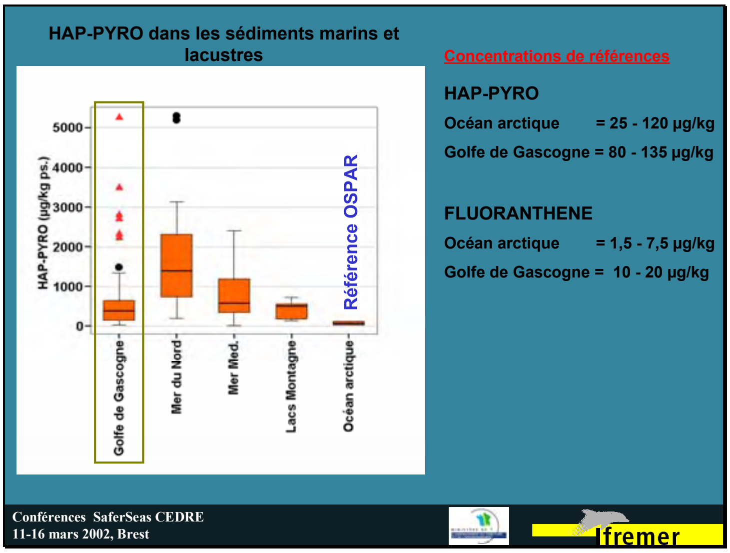
N/O Thalia

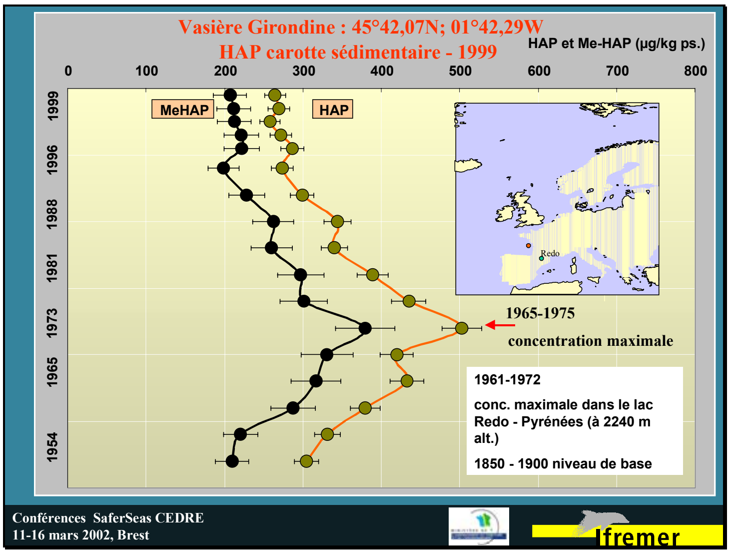
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest

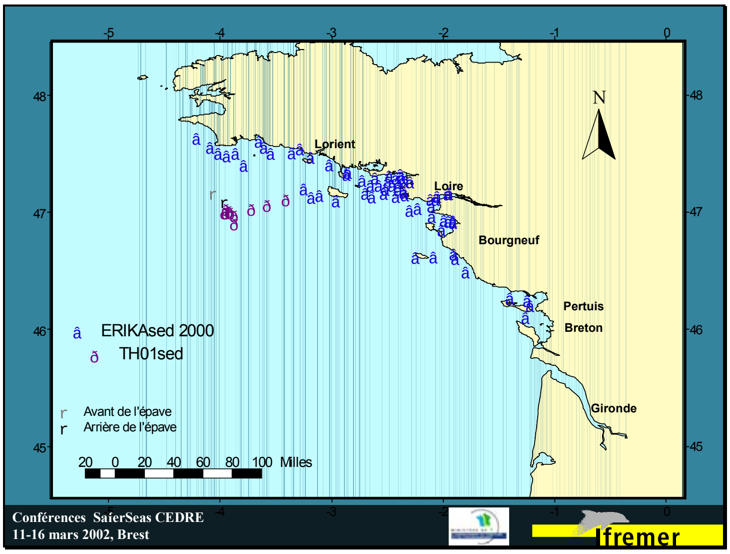
Ifremer

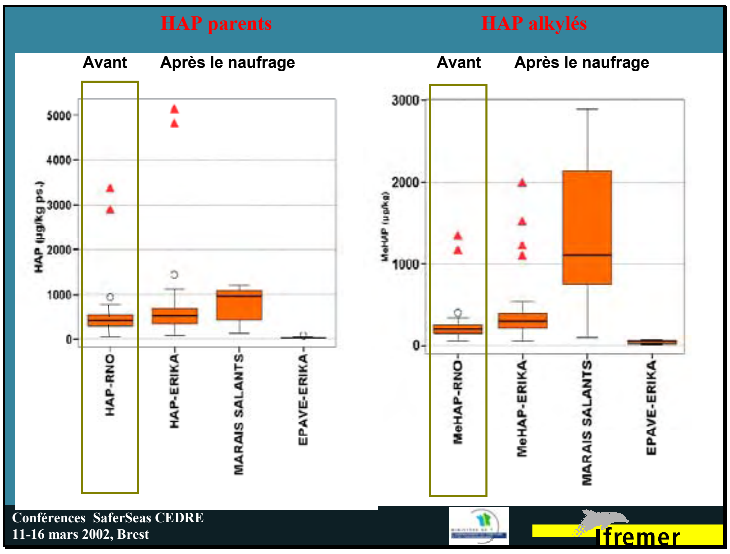

HAP-PYRO (µg/kg) dans les sédiments marins
Golfe de Gascogne RNO - 1999
HAP-PYRO µg/kg ps.
5000
4000
3000
2000
1000
0
Audierne Glénan
Lorient Aven
Quiberon Morbihan
Vilaine Croisic
Loire
Bourgneuf
Pertuis Charente
Gironde
Arcachon
Basques
HAP-PYRO (µg/kg ps.)
Faible
Élevée
21
45
135
366
633
1318
2492
5
10
25
50
75
90
95
Centile
Statistiques HAP-PYRO
N= 92
Moyenne 1 = 575 µg/kg ps.
Médiane = 366 µg/kg ps.
Minimum = 10 µg/kg ps.
Maximum = 5300 µg/kg ps.
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

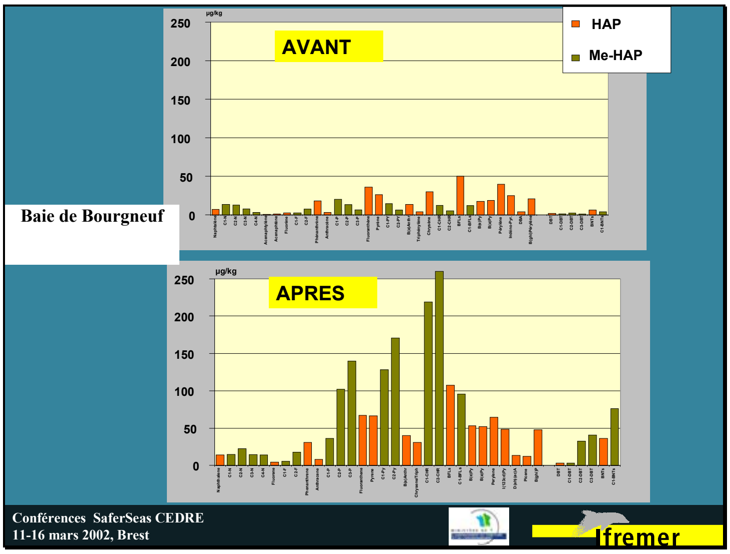

Milles
N
Clyde
TS100
Schelde
Seine
Dlugi
Noir
Redo
DIFFCHEM, 1996
Frenandez et al. 1999 et 2000
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

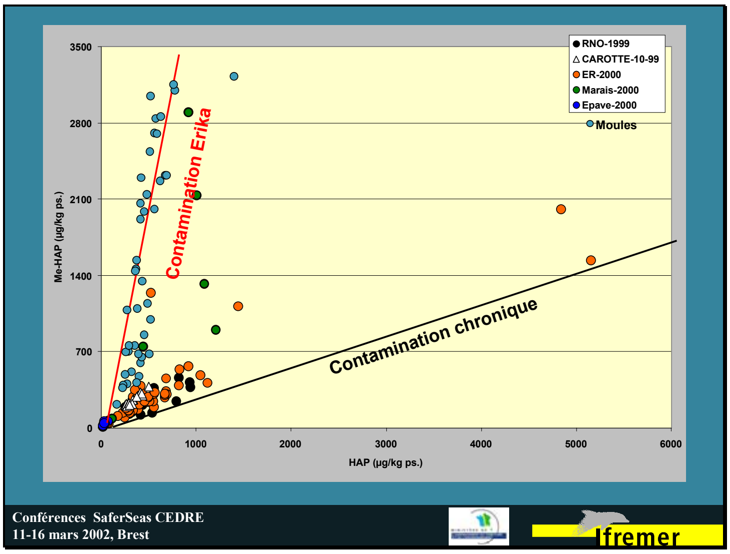

HAP-PYRO dans les sédiments marins et lacustres
HAP-PYRO (µg/kg ps.)
5000
4000
3000
2000
1000
0
Golfe de Gascogne
Mer du Nord
Mer Med.
Lacs Montagne
Océan arctique
Référence OSPAR
Concentrations de références
HAP-PYRO
Océan arctique = 25 - 120 µg/kg
Golfe de Gascogne = 80 - 135 µg/kg
FLUORANTHENE
Océan arctique = 1,5 - 7,5 µg/kg
Golfe de Gascogne = 10 - 20 µg/kg
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

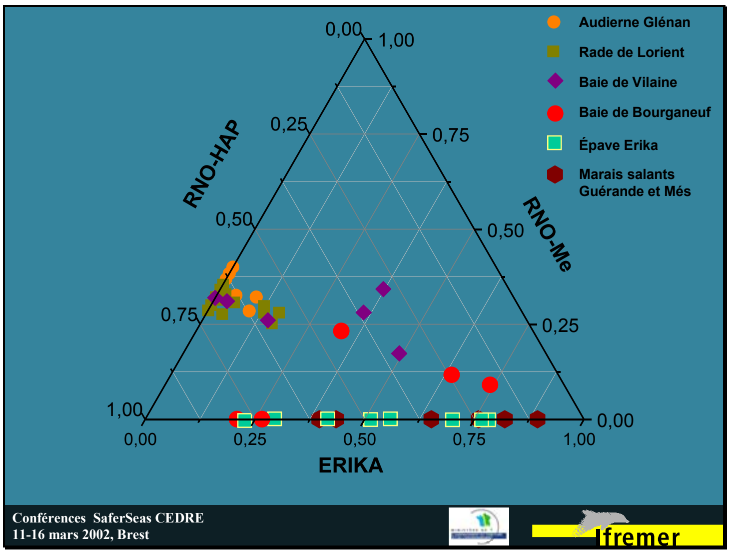

Vasière Girondine : 45°42,07N; 01°42,29W
HAP carotte sédimentaire - 1999
HAP et Me-HAP (µg/kg ps.)
0 100 200 300 400 500 600 700 800
1999 1996 1988 1981 1973 1965 1954
MeHAP
HAP
Redo
1965-1975
concentration maximale
1961-1972
conc. maximale dans le lac Redo - Pyrénées (à 2240 m alt.)
1850 - 1900 niveau de base
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer

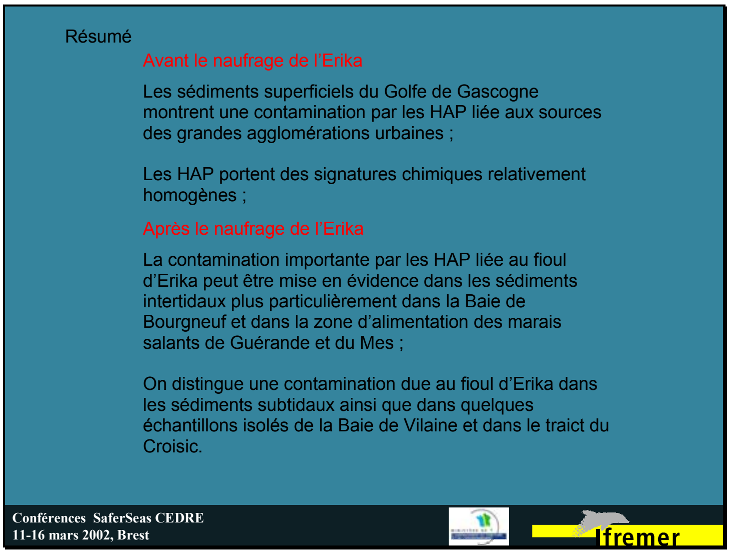

Lorient
Loire
Bourgneuf
Pertuis
Breton
Gironde
N
ERIKAsed 2000
TH01sed
Avant de l'épave
Arrière de l'épave
20 0 20 40 60 80 100 Milles
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


HAP parents
HAP alkylés
Avant
Après le naufrage
HAP (µg/kg ps.)
HAP-RNO
HAP-ERIKA
MARAIS SALANTS
EPAVE-ERIKA
MeHAP (µg/kg)
MeHAP-RNO
MeHAP-ERIKA
MARAIS SALANTS
EPAVE-ERIKA
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Baie de Bourgneuf
AVANT
APRES
µg/kg
HAP
Me-HAP
250
200
150
100
50
0
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


RNO-1999
CAROTTE-10-99
ER-2000
Marais-2000
Epave-2000
Moules
Contamination Erika
Contamination chronique
Me-HAP (µg/kg ps.)
HAP (µg/kg ps.)
3500
2800
2100
1400
700
0
1000
2000
3000
4000
5000
6000
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Audierne Glénan
Rade de Lorient
Baie de Vilaine
Baie de Bourganeuf
Épave Erika
Marais salants
Guérande et Més
RNO-HAP
RNO-Me
ERIKA
0,00
0,25
0,50
0,75
1,00
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer


Résumé
Avant le naufrage de l'Erika
Les sédiments superficiels du Golfe de Gascogne montrent une contamination par les HAP liée aux sources des grandes agglomérations urbaines ;
Les HAP portent des signatures chimiques relativement homogènes ;
Après le naufrage de l'Erika
La contamination importante par les HAP liée au fioul d'Erika peut être mise en évidence dans les sédiments intertidaux plus particulièrement dans la Baie de Bourgneuf et dans la zone d'alimentation des marais salants de Guérande et du Mes ;
On distingue une contamination due au fioul d'Erika dans les sédiments subtidaux ainsi que dans quelques échantillons isolés de la Baie de Vilaine et dans le traict du Croisic.
Conférences SaferSeas CEDRE
11-16 mars 2002, Brest
Ifremer