Effect of long term natural weathering on oil composition: study of the 41-year-old Amoco Cadiz and 20-year-old Erika oil spills

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ABSTRACT

On 16 March 1978, the oil tanker the Amoco Cadiz, transporting 223,000 tons of crude oil and 4,000 tons of bunker fuel oil, suffered a failure of her steering mechanism and ran aground on Portsall Rocks, on the Breton coast. The entire cargo spilled out as the breakers split the vessel in two, progressively polluting 360 km of French shoreline from Brest to Saint Brieuc. This was the largest oil spill caused by a tanker grounding ever recorded in the world. The consequences of this accident were significant, and it caused the French Government to revise its oil response plan (the Polmar Plan), to acquire equipment stocks (Polmar stockpiles), to impose traffic lanes in the Channel and to create Cedre.

On 12 December 1999, the tanker Erika broke up and sank off the coast of Brittany (France) leading to the spill of 20,000 tons of a heavy fuel oil. 400 km of the French Atlantic coastline were polluted. Because of the characteristics of the oil (a very heavy fuel oil with a high content of light cracking oil) and the severe weather conditions (a centennial storm with spring tides) when the oil came on shore, the Erika spill was one of the most severe accidental releases of oil along the French coastlines. All types of habitat were concerned, and pollution reached the supratidal zone affecting terrestrial vegetation and lichens.

In 2019, respectively 41 years and 20 years after these major oil spills affecting the French shoreline, a sampling round was conducted at two sites recorded to present some residual traces of oil. Samples of weathered oil were collected, extracted with methylene chloride and then purified through an alumina-silica microcolumn. SARA fractionation and GC-MS

analyses were performed in order to assess respectively the total degradation of the weathered

oil (amount of saturates, aromatics and polar fraction) and the specific degradation of *n*-

alkanes from *n*-C_9 to *n*-C_{40}, biomarkers (such as terpanes, hopanes and steranes) and PAHs

(parents and alkylated derivatives).

INTRODUCTION

When spilled at sea, oil is subjected to a range of natural physico-chemical processes that

imply a modification of its initial chemical composition: some compounds evaporate or

dissolve, while simultaneously others are biodegraded or photo-oxidized. Year after year,

these weathering processes will gradually change the composition of the oil, reducing it to a

small amount of hard residue (asphalt pavement) (Tarr et al., 2016). Despite these changes in

composition, chemical analyses still make it possible to identify the oil, but also to assess the

degree of weathering of the oil residue compared to the initial product. Polyaromatic

hydrocarbons (PAHs) and *n*-alkanes are commonly investigated in order to assess the extent

of natural degradation due to the weathering process. Petroleum biomarkers such as hopanes,

steranes and triaromatic steroids (TAS) are also used for weathering studies as well as for

source identification (fingerprinting) as they are resistant to biotic and abiotic degradation

(Aeppli et al., 2014, CEN guideline, 2012).

The aim of this study was to evaluate the weathering degree of oil samples as well as

biomarkers' recalcitrance after long term weathering. Residues of Amoco Cadiz oil (1978,

France) and Erika oil (1999, France) were collected at two different locations in Brittany,

France in 2019. Combined with SARA (Saturate, Aromatic, Resin and Asphaltene)

fractionation, *n*-alkanes from *n*-C_{10} to *n*-$C_{35,}$ PAHs (parent and alkylated compounds),

hopane, sterane and TAS were analysed in the weathered sample as well as in reference oil

stored at Cedre since the two oil spills.

MATERIAL AND METHODS

Sampling

In 2019, two sites polluted during the Erika spill (Porz Teg, Britany, France) and the Amoco Cadiz spill (Ile Grande, Brittany, France) were visited and samples of oil were collected. Figure 1 (Portz Teg) presents a rocky shore with thin patches of asphalt pavement (sample #ER1) attributed to the Erika oil. At the Ile Grande location (salt marshes), two samples were collected: the first (Figure 2) corresponds to an accumulation of sheens and small oil droplets (2 mm diameter) collected at the water surface a few seconds after the muddy sediment was agitated. The second (Sample #AM2) was an asphalt pavement partially buried (10 cm depth) in fine sediment.

Figure 1. Patches of asphalt pavement on rocks (Sample # ER1).

Figure 2. Sheens and small oil droplets resurfacing after sediment agitation (Sample #AM1).

Figure 3. Asphalt pavement buried in salt marsh (Sample #AM2).

Concerning the initial oil samples from the Erika and the Amoco Cadiz, the first corresponds

to the sample of heavy fuel oil provided by the refinery where the Erika was loaded. The

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second corresponds to a sample of oil collected on the shoreline of north Brittany one day after the oil spill (17 March 1978) and stored at the town hall of Trebeuden (France). The sample was kindly provided in 2019 by this municipality.

Oil sample extraction

Samples were extracted with 30 mL methylene chloride at 100°C and 2000 psi for 14 minutes using a Dionex ASE 350 accelerated solvent extractor. Extractions of sediment were performed twice for each sample. Organic extracts were dried over Na_2SO_4 (activated at 400°C for 4 hours) and concentrated to approximately 2 mL using a Syncore (Büchi Labortechnik AG, Flawil, Switzerland). Approximately 20 mg of extracts were then fractionated using SPE (Solid Phase Extraction) cartridges (silica/cyanopropyl (SiO_2/C_3-CN) (1.0/0.5 g, 6 ml) (Interchim, Montluçon, France)) (Alzaga et al., 2004): saturate and aromatic fractions were eluted simultaneously with 8 mL of methylene chloride / pentane mixture (80/20, v/v) and concentrated to approximately 2 mL under a stream of nitrogen.

Sample analysis

SARA fractionation

The evolution of the oil composition was assessed by fractionation into 4 chemical families. Asphaltenes were precipitated in *n*-pentane and were filtered on a glass fibre filter. The maltene fraction was then separated on a silica-alumina column (30 cm x 1 cm). Saturates were eluted with *n*-pentane, aromatics with an *n*-pentane/dichloromethane 80/20 mixture, and resins with a methanol/ dichloromethane 50/50 mixture. The various fractions were weighed after evaporation of the solvent and stabilization of the masses.

n-alkanes and PAH quantification

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Analyses were conducted using the gas chromatography system Agilent 7890 A with a split/splitless injector (Splitless time: 1 min, flow 50 mL/min). The GC was coupled with an Agilent 5975 mass spectrometer (Agilent Technologies, Little Falls, USA) (Electronic Impact: 70 eV, voltage: 1200 V). The injector temperature was maintained at 300°C. The interface temperature was 300°C. The GC/MS 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 an HP-5 MS: 30 m×0.25 mm ID×0.25 µm film thickness. PAHs were quantified relatively to the perdeuterated PAHs introduced at the beginning of the sample preparation procedure (perdeuterated eicosane as regards the alkanes). The target molecules, as regards the PAHs, were the 16 PAHs on the US EPA list completed with biphenyl, benzo[e]pyrene and perylene, and also two sulfured aromatics (benzothiophene and dibenzothiophene). For most PAHs, from naphthalene to chrysene, alkylated derivatives characterized by up to 4 additional carbon atoms were also quantified relatively to the parent PAH. Perdeuterated PAHs (Naphthalene-d_8, Biphenyl-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12} and Benzo[a]pyrene-d_{12}) and Eicosene $C_{20}d_{42}$ were obtained from LGC Standards (Molsheim, France). Calibration curves were established from *n*-alkanes and PAH mixtures obtained from Ultra Scientific. These mixtures contained *n*-alkanes from *n*-C_8 to *n*-C_{32}, and as regards PAHs, all 21 parent PAHs.

SRM 2779 (Gulf of Mexico Crude oil) was used as a reference oil in order to evaluate the analytical procedure.

RESULTS AND DISCUSSION

SARA distribution

Figure 4 presents the SARA distribution for the Erika oil samples: fresh oil and oil residue collected in 2019.

Saturate and aromatic fractions decrease significantly between the two samples: respectively from 22% to 7% for saturates and from 55% to 25 % for aromatics due to evaporation and biodegradation. Thus, the chemical fractions consisting of resins and asphaltenes tend to increase due to the formation of polar compounds, especially during the biodegradation and photo-oxidation processes (Garett et al., 1998, Xu and Lu, 2010). The abundance of this chemical fraction, composed of molecules with high molecular weight, is characteristic of asphalt pavement.
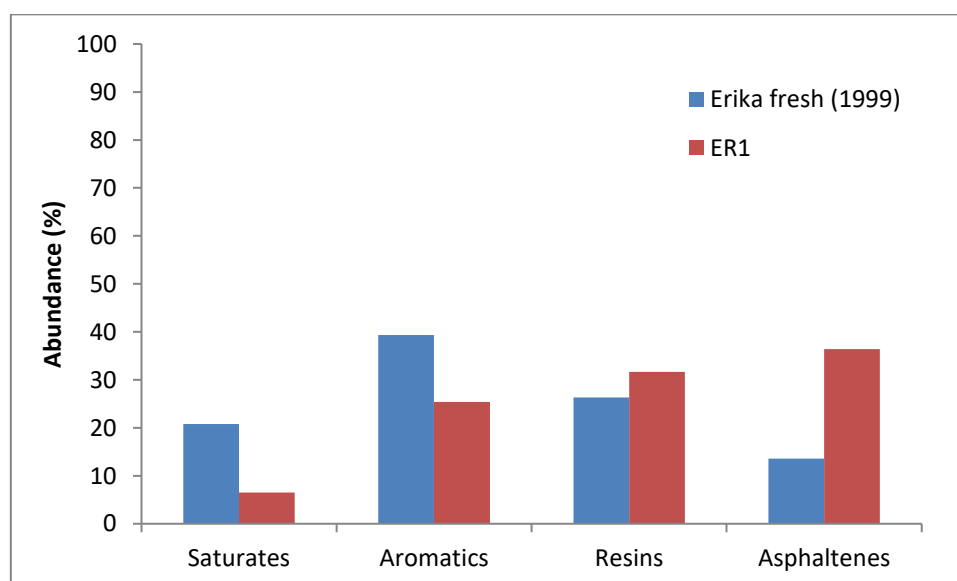
Figure 4. SARA distribution of Erika oil samples.

Concerning the Amoco Cadiz samples, Figure 5 presents the SARA distribution for the reference oil and the AM2 sample. Due to the low volume of sample AM1 (sheens and small oil droplets), it was not possible to conduct SARA fractionation on this sample. As observed for the weathered Erika oil sample, the oil residue is characterized by the abundance of polar compounds (resins and asphaltenes) that represent more than 70% of the oil residue.
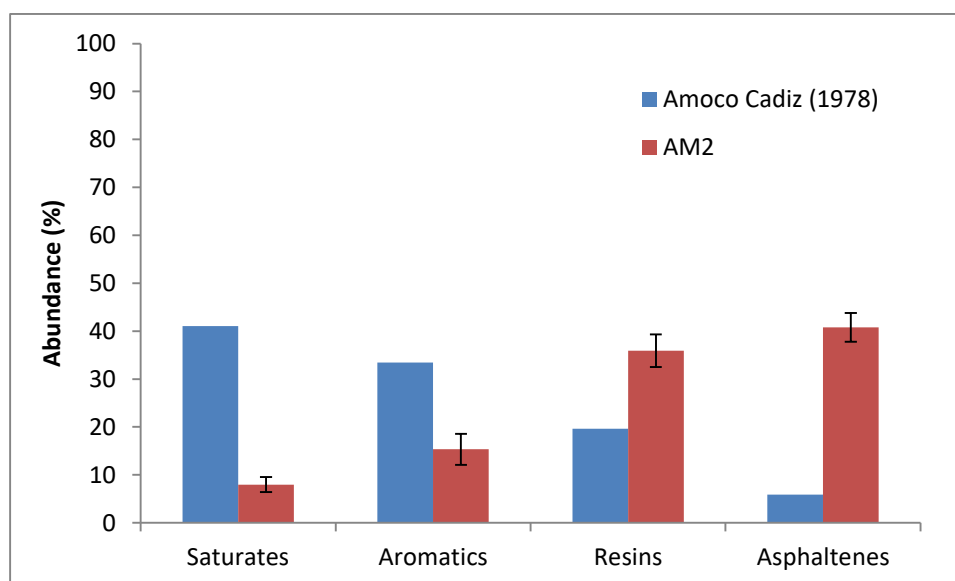
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Figure 5. SARA distribution of Amoco Cadiz oil samples.

n-alkanes and PAH quantification

Erika oil

At the molecular level, the quantifications of *n*-alkanes and PAHs in Erika fresh samples are presented in Figure 6. As regard the alkanes from *n*-C_{10} to *n*-C_{35}, the distribution is centered close to n-C_{24} which is typical of Heavy Fuel Oil (HFO) constituted by a mixture of a distillate (LCO - light cycle oil in this case) with a residue (Vacuum Distillate Residue in this case) (Guyomarch et al., 2001). PAH distribution is characterized by the abundance of the Naphthalene family (up to 40% of the total PAHs). After 20 years of natural weathering, the oil residue presents a high degree of degradation. The total degradation of *n*-alkanes reaches 99%: most of the *n*-alkanes $< n$-C_{20} are completely lost and *n*-alkanes $> n$-C_{20} are severely degraded. Concerning the PAHs, the total degradation reaches 88%. The Benzothiophene (BT – BT4), Naphthalene (N – N4), Fluorene (F - F3) and Phenanthrene (P – P4) families as well as Biphenyl (B), Acenaphthene (ANA) and Acenapthylene (ANY) are severely degraded. These compounds are known to be sensitive to natural weathering processes such as evaporation, dissolution and biodegradation (Stout and Wang, 2018). Considering the heaviest PAH (Fluoranthenes / pyrenes (FL – FL3) and Chrysene (C – C3) families as well as

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individual compounds with more than 5 aromatic rings (Benzo[b]fluoranthène (BBF), Benzo[k]fluoranthène (BKF), Benzo[e]pyrene (BEP), Benzo[a]pyrene (BAP), Perylene (PE), Indeno(1,2,3-cd)pyrene (IN), Dibenz(a,h)anthracene (DBA) and Benzo(g,h,i)perylene (BPE)), they are partially altered after 20 years of weathering processes. These compounds are known to be refractive to evaporation and dissolution but sensitive to biodegradation and especially to photo-oxidation (Jézéquel et al., 2003, Stout and Wang, 2018).
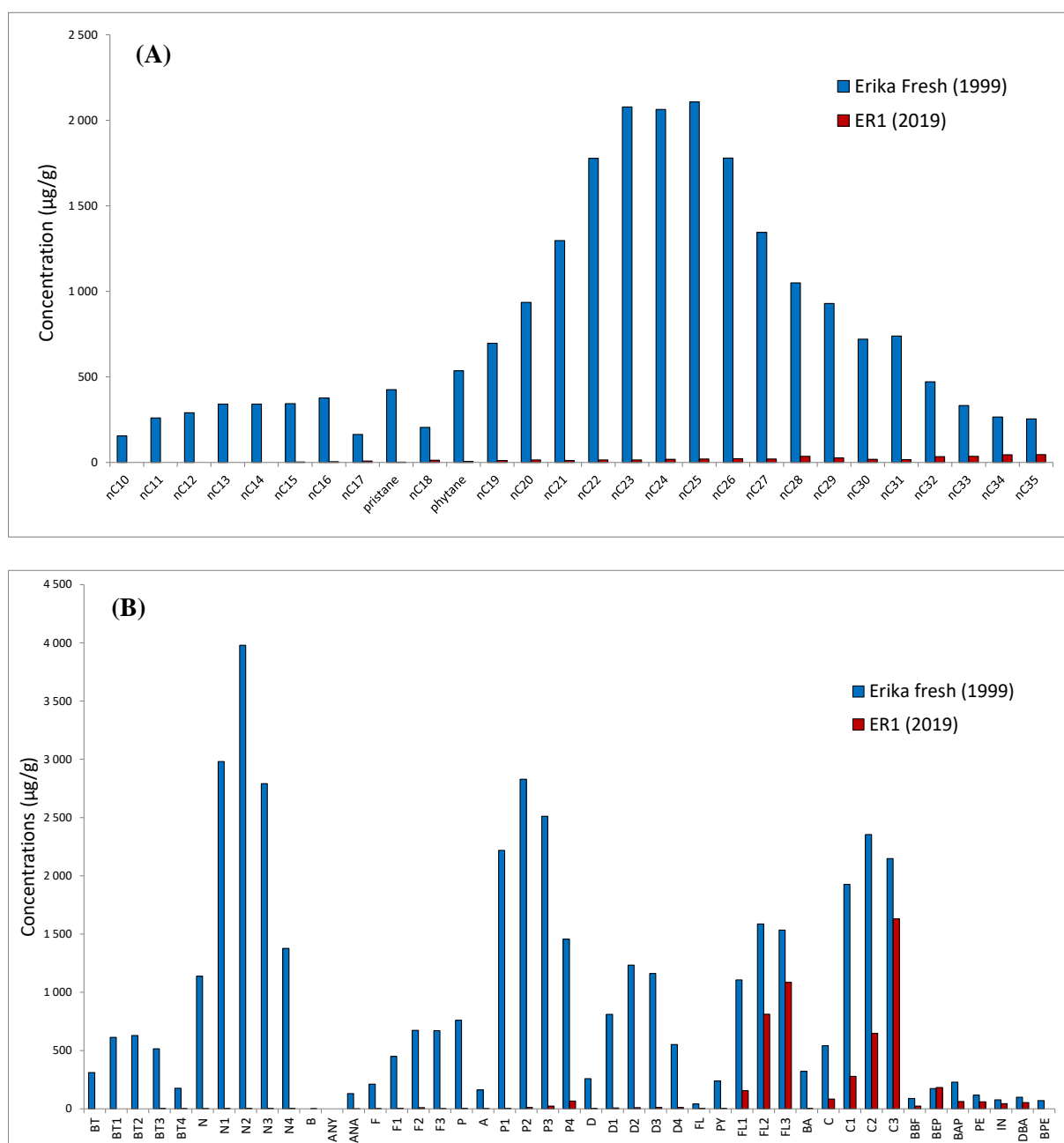
Figure 6. Chemical composition of Erika oil samples (fresh 1999 and weathered ER1), (A) n-alkane distribution, (B), PAH distribution.

The depletion rates of each family of PAHs (Figure 7) is calculated relatively to the abundance of 17α(H),21β(H)-hopane (m/z=191) used as a conserved internal biomarker (Prince et al., 1994). The depletion of PAHs decreases with the degree of alkylation: X < X1 < X2 < X3 (X<4). This is specially observed for the heaviest families (Fluoranthenes and Chrysenes) less sensitive to degradation processes. This trend is well known and has been published in previous studies (Wang et al., 1994, 1997, Michel et al., 1999, Jézéquel et al., 2003, 2011, Stout and Wang, 2018).
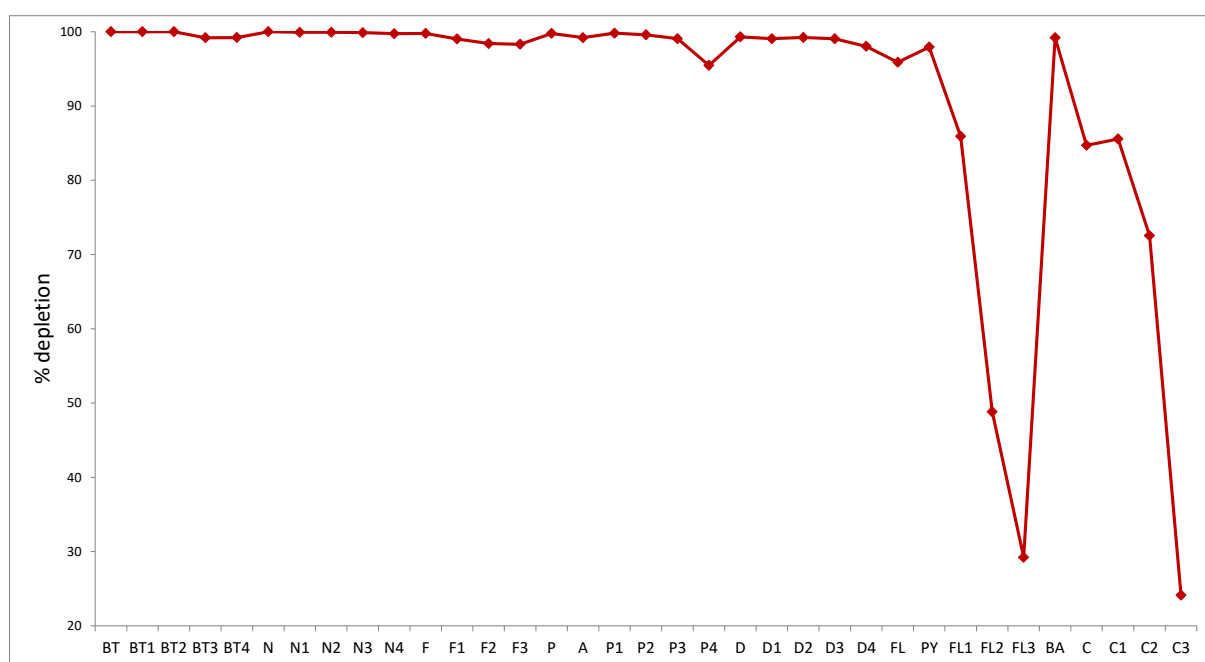

Figure 7. Evolution of the degree of PAH degradation for the Erika oil sample collected in 2019.

Amoco Cadiz samples

Figure 8 presents the distribution of *n*-alkanes for the samples of Amoco Cadiz oil collected in 1978 and 2019. The *n*-alkanes ranged between *n*-C_{10} and *n*-C_{34}, with *n*-C_{24} being the most abundant compound. The low abundances of the lightest alkanes (*n*-C_{10} to *n*-C_{14}) can be attributed to a slight evaporation of the oil as this sample was collected on the French shoreline, one day after the spill.

After 41 years of natural weathering, the *n*-alkanes appeared highly degraded to more than 99% for each sample. Concerning the PAHs, the degradation rate reaches 97% for the AM2 sample (asphalt pavement) and not more than 55% for the AM1 sample (oil droplets trapped in sediment). For this sample, the concentrations of the heaviest phenanthrene (P4) and dibenzothiophene (D4) as well as the fluoranthene / pyrene and chrysene families increase between the AM1 sample and the reference oil. As the results are presented in µg of PAHs /g of oil, the increase in the concentrations of the heaviest PAHs is due to the degradation of the lightest PAHs, which implies a relative increase in the abundance of the heaviest PAHs in the weathered residue compared to the reference oil.
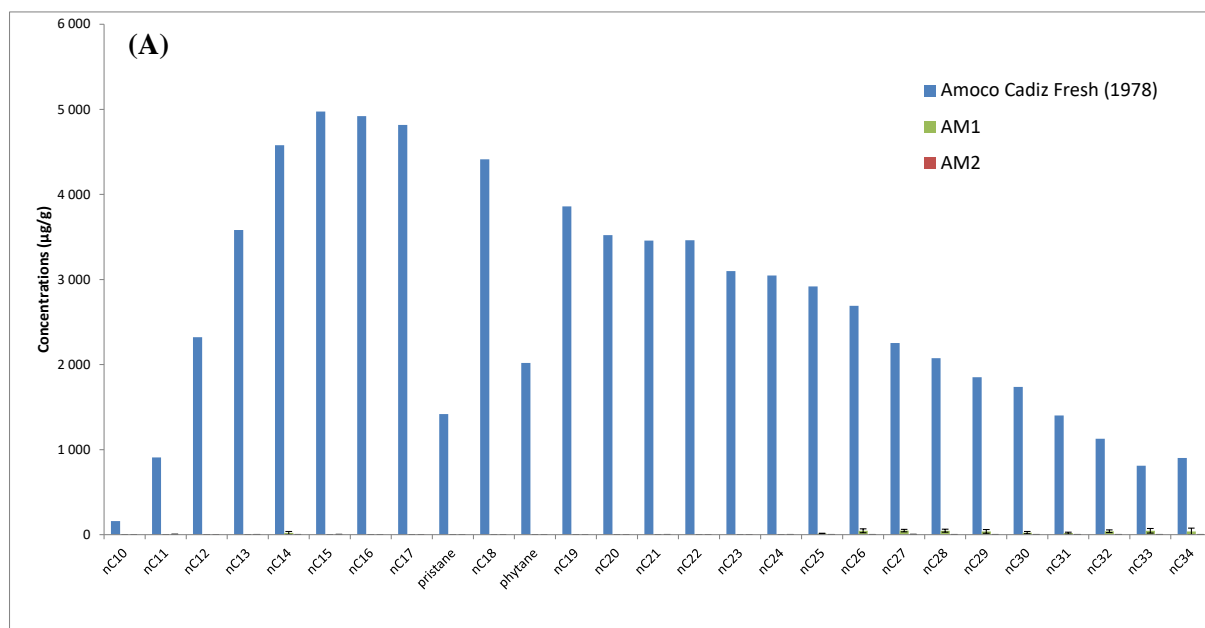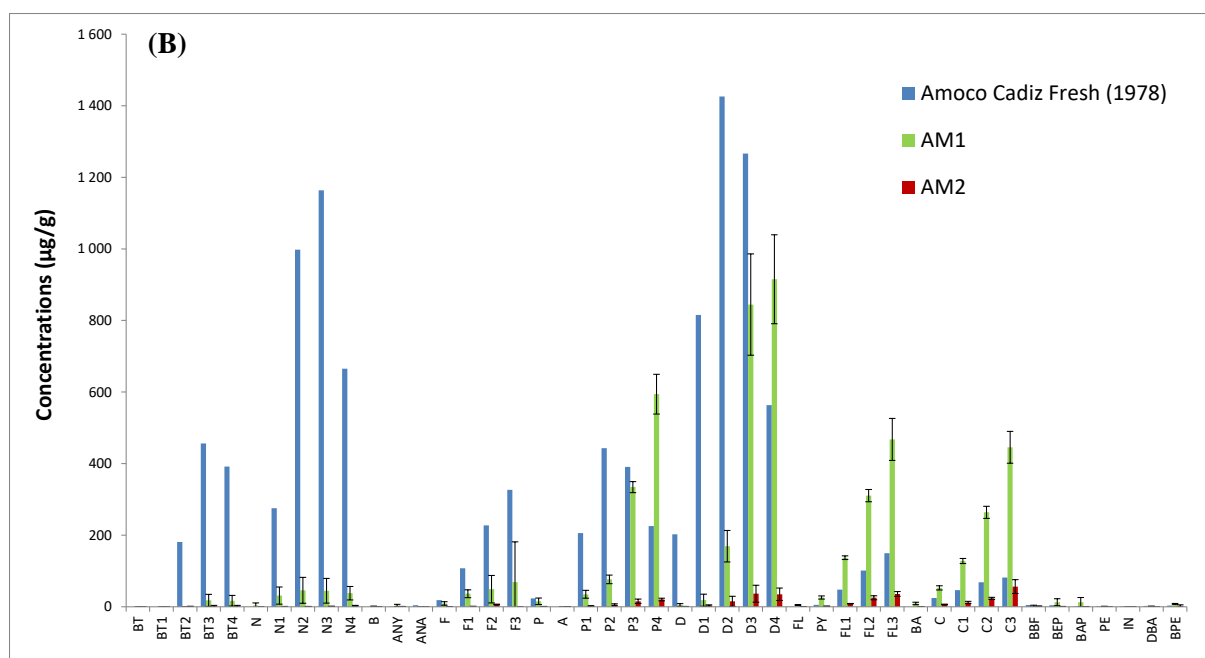
Figure 8. Chemical composition of Amoco Cadiz oil samples (fresh 1978 and weathered samples #AM1 (*n*=3) and #AM2 (*n*=3)), (A) *n*-alkane distribution, (B), PAH distribution.

When considering the depletion rates of each PAH (calculated in hopane units) for the two weathered oil samples relatively to the reference oil, PAH depletion is significantly higher for the AM2 sample (asphalt pavement) compared to #AM1. This difference in weathering can be attributed to the difference in environmental conditions between these samples. AM1 sample corresponds to oil droplets trapped in a muddy sediment located in a salt marsh. For this type of environment and anoxic sediment, it is established that weathering of oil is generally very weak.
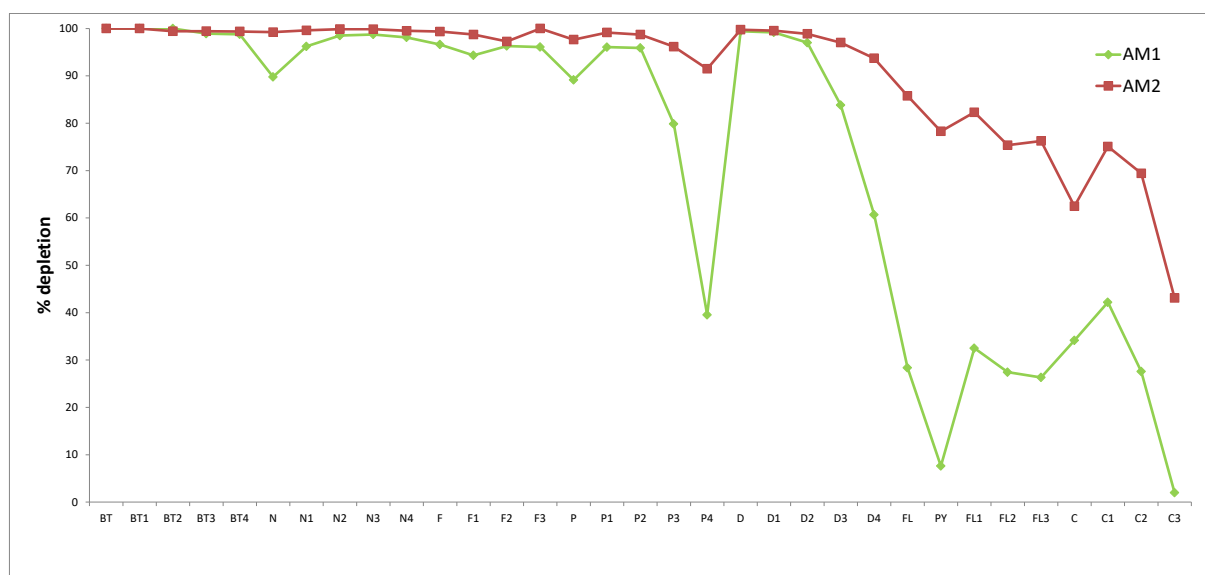
Figure 9. Evolution of the degree of degradation of PAH families for Amoco Cadiz oil samples collected in 2019.

Petroleum biomarkers

The abundances of hopanes (m/z = 191), steranes (m/z = 217), diasteranes (m/z = 218) and triaromatic steroids (TAS) (m/z = 231) were analyzed in both samples of Erika and Amoco Cadiz oils. These families of chemical compounds are often investigated in order to assess the weathering degree of environmental samples or to identify an oil source (fingerprinting) (CEN guidelines, 2012). The abundance of each biomarker was calculated relatively to the sum of the hopane / homohopane categorized as the most stable (Aeppli et al., 2014, Yang et al., 2018): 17α(H), 21β(H)-30-norhopane (29ab), 17α(H), 21β(H)-hopane (30ab), 17α(H), 21β(H), 22S-homohopane (31abS), 17α(H), 21β(H), 22R-homohopane (31abR), 17α(H), 21β(H), 22S-bishomohopane (32abS), 17α(H), 21β(H), 22R-bishomohopane (32abR).

Figure 10 presents the biomarkers correlations between Erika fresh oil sample (1999) and ER1 sample. After 20 years of natural weathering, the hopanoids compounds of the Erika oil are affected to different degrees : 27Ts, 30 ab, 31ab (S+R) and 32 ab (S+R) are preserved while 27Tm and 29ab appear depleted in the samples collected in the environment. Regarding

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the other families, TAS were strongly degraded but not all the TAS were affected in the same way (RC26TA+SC27TA are more impacted than RC27TA and RC28TA). The diasterane family is also highly impacted: 27bbR+S appeared more depleted than 29bbR+S or 28 bbR+S.
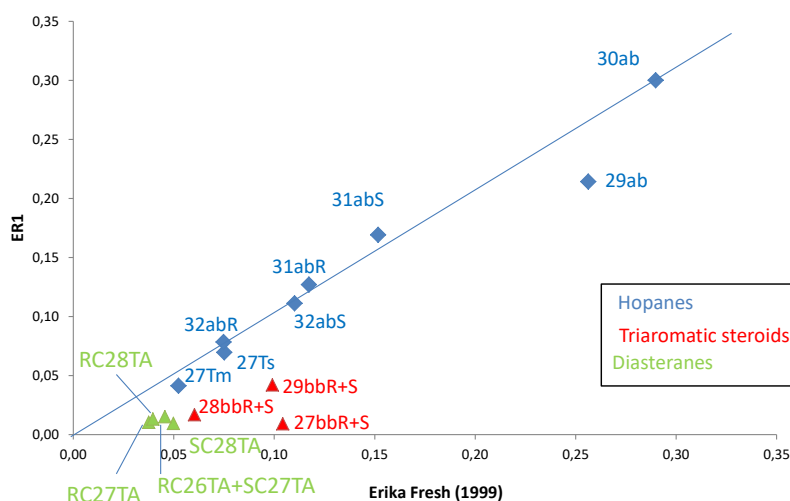

Figure 10. Biomarker correlations between Erika samples.

After 41 years of weathering, the same trends are partially confirmed for the Amoco Cadiz oil samples (Figure 11 and 12). For the hopane family, 30 ab, 31 ab (S+R) and 32 ab (S+R) compounds are not altered but Ts, Tm and 29ab appear depleted for the AM2 sample (asphalt pavement). Regarding TAS, surprisingly these compounds are preserved in the AM1 sample and slightly degraded for the AM2 sample compared to the degradation rates observed for the Erika oil. However, it must be noted that the Amoco Cadiz reference oil corresponds to a sample of oil collected on the shoreline, one day after the spill. As TAS are known to be highly sensitive to photo-oxidation (CEN guideline, 2012, Aeppli et al., 2014), it is possible that photo-oxidation occurred and that the TAS were already partially depleted in the oil that reached the shoreline compared to the initial oil. Moreover, as the AM1 samples correspond to an oil trapped in a muddy sediment located in a salt marsh and the AM2 samples correspond to an asphalt pavement buried in the same sediment, we can assume that the oil was not exposed to solar radiation for the 41 years in natural environment and that photo-

oxidation did not occur. The abundance of the heaviest PAHs in this sample (Figure 8), a

class of compounds sensitive to photo-oxidation (Prince et al., 1998), confirmed that the

photo-oxidation did not contribute in the degradation of the Amoco Cadiz oil collected at the

Ile Grande site. Regarding diasteranes, as observed for the Erika oil, this family appears

highly degraded and 27bbR+S appears more depleted than 29bbR+S or 28 bbR+S.
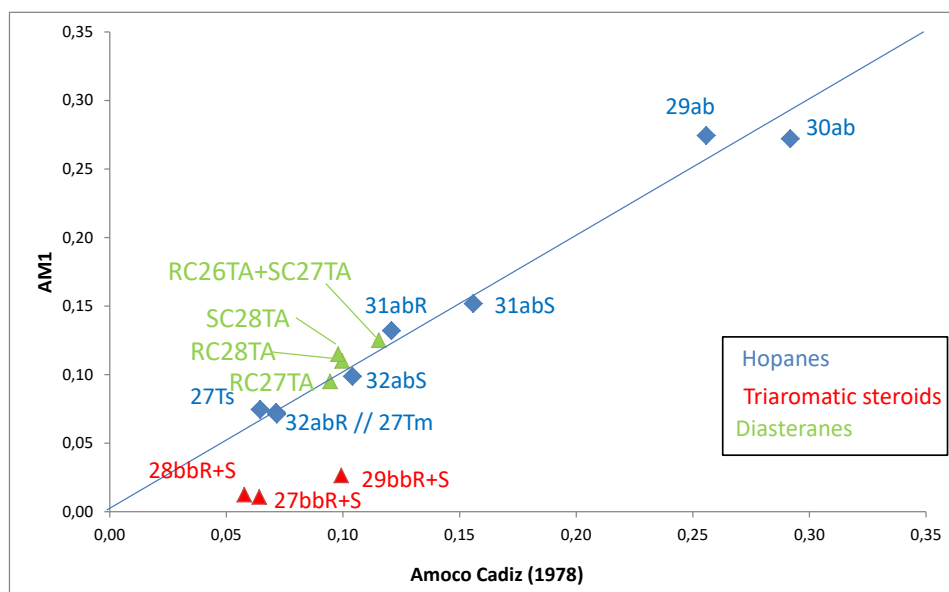
Figure 11. Biomarker correlations between Amoco Cadiz reference sample and AM1 sample.
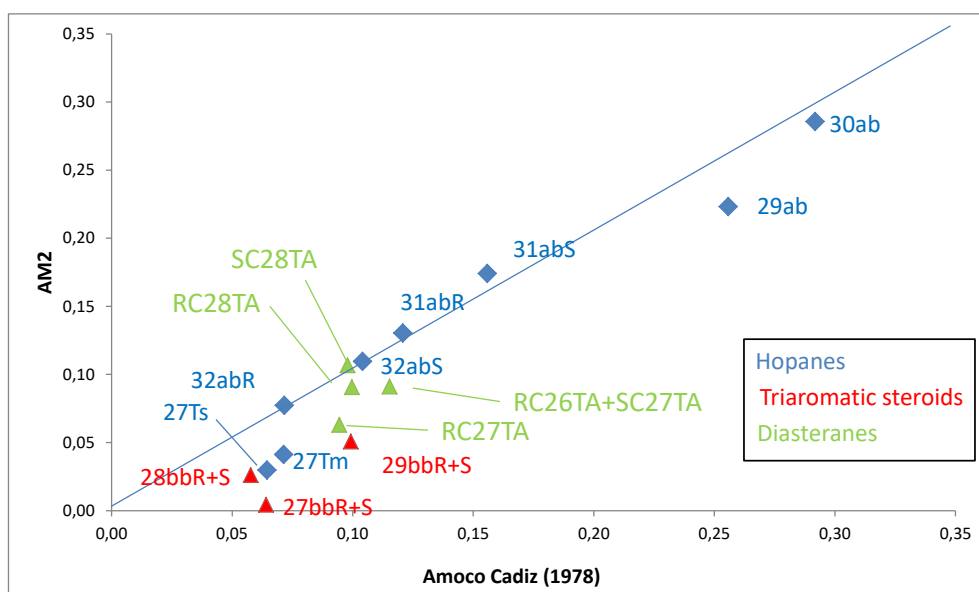

Figure 12. Biomarker correlations between Amoco Cadiz reference sample and AM2 sample.

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CONCLUSION

Respectively, 20 years and 41 years after two dramatic oil spills along the French coastline, samples of oil were collected in order to assess their degree of weathering. SARA fractionation, *n*-alkanes, PAHs as well as biomarker abundances were investigated. The SARA distributions of the Erika sample and Amoco Cadiz asphalt pavement (sample #AM2) highlight that the samples are mainly characterized by the abundance of the asphaltene family (more than 50%). This is due to the very high degree of weathering of the other families (saturates, aromatics and resins). The degradation rates of *n*-alkanes and PAHs reach 99% for both the Amoco Cadiz and Erika oils. Regarding the biomarkers, these results confirm that even after 41 years of natural weathering, 17α(H), 21β(H)-hopane (30ab) can be considered as an internal conservative biomarker. It can be used in order to fingerprint weathered oil and to assess petroleum degradation in the environment.

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