

Compositional properties characterizing commonly transported oils and controlling their fate in the marine environment†

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Oil spills relating to shipping incidents remain of substantial concern with respect to marine pollution. Whilst most frequently a reactive approach is adopted in post-incident monitoring (for the specific product involved), this paper reports important physical and compositional characteristics of commonly transported oils and oil products to afford pro-active assessments. These properties include specific gravity, viscosity, elemental composition and, of particular relevance, the relative class compositions between aliphatics, aromatics, resins and asphaltenes. The latter were determined experimentally using thin layer chromatography with flame ionization detection. Diagnostic ratios of specific compounds are reported, statistically analysed, and their significance in identification of different oil types and the weathering processes is discussed. The influence of the properties on fates under different environmental conditions (selected to represent contrasting European regional seas) are examined using the NOAA Automated Data Inquiry for Oil Spills (ADIOS2) model. Relative contributions of the different environmental conditions and properties to the fate of the oil at sea are discussed.

1. Introduction

The volume of maritime (seaborne) trade has risen in the past few decades as it affords cost effective global transport. During recent years, it amounted to about 8 billion tonnes of goods annually, of which more than 30% were crude oils and petroleum products.¹ Contrasting this increase, historical data show significant decreases in the number of large scale oil spills (>700 tonnes), from more than 25 per year in the 1970's to about 3 per year during the last decade.² However, a substantial number of tanker incidents still occur in the busiest maritime transport routes, particularly at accident blackspots with heavy traffic and/or challenging natural conditions such as the Aegean Sea, the Strait of Gibraltar, the Atlantic coast of the Iberian Peninsula,

the English Channel and parts of the Baltic and North Sea, amongst others³ (Fig. 1).

In addition to large accidental spills, many small to medium scale operational spills occur on a daily basis during routine operations in ports (*i.e.* discharging, bunkering, *etc.*) and coastal waters. This also includes waste oil spills (bilges, sludges, slops) illicitly discharged from ships. These contribute more than 40% of spills smaller than 7 tonnes and more than one-third of spills ranging from 7 to 700 tonnes.²

Therefore, despite positive trends, environmental^{4–6} and socio-economic^{7,8} impacts of oil spills on marine ecosystems and coastal regions remain an issue of great concern demanding constant efforts in terms of oil spill preparedness and response. In this respect, chemical characterization is a key tool that is indispensable for assessing risks associated with oil spills. It involves characterization of crude oils and petroleum products, as well as chemical elucidation of weathering processes that affect and change the oil composition once they are released into the marine environment.

Weathering transformations are the result of various processes; the most important being evaporation, dissolution,

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Environmental impact

The analytical technologies used produce a negligible environmental impact. Moreover, the modelling approach to predict short-term impact of oil spills does not produce any environmental impact.

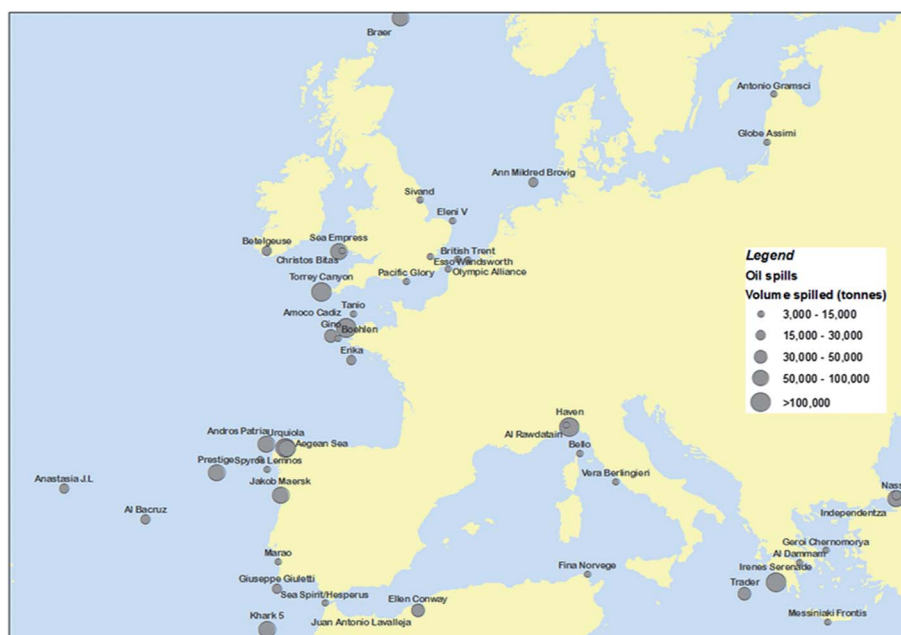


Fig. 1 Locations of major oil spills in the European waters since 1957.

emulsification, biodegradation and photo-oxidation, which can take place simultaneously or consecutively over a time scale ranging from a few hours (*e.g.* evaporation) up to a couple of months or even years (*e.g.* biodegradation).⁹ All these processes strongly depend on the characteristics of the spilled oil, *i.e.* specific gravity, viscosity, elemental composition (*e.g.* S, Ni, V), chemical classes' composition (aliphatics, aromatics, resins, asphaltenes), *etc.*

Since physico-chemical properties of different crude oils and oil products vary greatly, detailed information on them is valuable to reliably estimate the environmental behavior, impact, and ultimate fate in a particular oil spill scenario. Also, this type of information is a necessary input when using oil spill models. Although such databases are available for a number of oils,¹⁰ they are often incomplete, variable and insufficiently comprehensive. Furthermore, oil spill studies are usually performed post-incident, focusing on the specific oil involved in the incident (*i.e.* a reactive approach). Databases afford a more pro-active strategy that provides characterization and weathering assessments for the selection of representative oils and oil products in advance.¹¹

In this work, 21 frequently transported crude oils and oil products were selected to cover a broad range of characteristics. Their main properties that control the environmental fate and impact were compiled from, where possible, publicly available sources (*e.g.* environmental databases, crude assays, *etc.*) and, where necessary, experimentally using elemental analysis and thin layer chromatography with flame ionization detection (TLC-FID).

Gas-chromatography mass spectrometry (GC-MS) fingerprinting was used to determine specific polycyclic aromatic hydrocarbons and biomarker molecules in the selected oils, and to calculate their characteristic diagnostic ratios which were statistically analysed using principal component analysis (PCA).

Finally, the oil properties database was used to assess short-term weathering of the oils using the publicly available Automated Data Inquiry for Oil Spills (ADIOS2) model.¹²

2. Materials and methods

2.1. Samples and sample preparation

Twenty-one (21) oil samples were obtained from local sources. They include a broad range of crude oils from Africa, America, Europe, and the Middle East, as well as different types of distilled products, creating a representative sample set of different oil classes, typically transported for the current oil market.

Samples were analysed as whole oils, without prior fractionation or sample pre-treatment except dilution with analytical grade dichloromethane (DCM, Suprasolv grade, Merck, Darmstadt, Germany).

Oil samples for GC-MS fingerprinting (120–150 mg) were prepared using two-step clean-up in an open glass column, over anhydrous sodium sulphate and neutral alumina (activated at 400 °C, 5% water deactivated), respectively, eluting with hexane (Suprasolv grade, Merck, Darmstadt, Germany). The eluate was blown down under a nitrogen stream to provide a concentration suitable for injection into the GC-MS.

2.2. Physico-chemical properties

The properties that determine the environmental behaviour (*i.e.* floating/sinking properties, evaporation, dispersion, emulsification, *etc.*) and (eco)toxicological effects were selected. They include API gravity, density, pour point, viscosity, distillation properties (boiling points), sulphur and nitrogen content and metals content (Ni, V).

Data were obtained from online databases and reports (crude assays) of relevant authorities (*e.g.* Environment Canada), oil

Table 1 Physico-chemical properties of the selected oils^{10,26-38}

Name	Origin	API ^b , °	Viscosity ^b , cSt	Density@15 °C ^a , kg m ⁻³	Pour point ^b , °C	TBP ^b , wt%(vol%)	Sulfur, %wt	Nitrogen, %wt (total, ppm)	Nickel ^b , ppm	Vanadium ^b , ppm
Arabian Light	Saudi Arabia	33.4	16.15@15 °C	865.8	-53	49@350 °C 57@400 °C	1.77 ^b	0 ^b	2.5	16
Azeri	Azerbaijan	36.6	8.21@20 °C	841.5	-3	53.97(57.64)@342 °C 59.36(62.85)@369 °C	0.12 ^a	0.16 ^a	3.7	0.3
Dalia	Angola	23.14	198@10 °C	914.5	-39	40.66(43.56)@375 °C	0.5 ^a	0.27 ^a	17	7
Diesel A	Product	38.32	3.25@40 °C	832.5	-6	(85)@350 °C (95)@360 °C	<0.1 ^a	<0.05 ^a	<0.05	<0.05
Diesel B	Product	34.8	3.25@40 °C	850	-4	(85)@350 °C (95)@370 °C	<0.1 ^a	<0.05 ^a	<0.05	<0.05
Diesel C	Product	30	7@40 °C	900	<0	(95)@405 °C	<0.1 ^a	<0.05 ^a	<0.05	<0.05
Flotta	North Sea	34.7	12@20 °C	848.7	-21	(74)@370 °C	1.01 ^b	1400 ^b	2.78	10.09
Forcados	Nigeria	29.7	17.4@10 °C	873.3	-27	58.69(61.59)@340 °C 66.89(69.58)@370 °C	0.18 ^b	1400 ^b	3.9	1
Heavy fuel oil	Product	11.47	23037.28@15 °C	988.8	-1	23.3@350 °C 33.5@400 °C	2.63 ^a	0.36 ^a	<100	<600 ^b
Hungo	Angola	28.7	26.30@20 °C	882.9	-48	43.25(48.24)@342 °C 47.55(52.47)@369 °C	0.55 ^a	0.3 ^a	19.7	16.6
Kirkuk	Iraq	35.1	13@10 °C	844.7	-22	(53)@300 °C (54)@FBP	1.97 ^b	900 ^b	12.5	28.5
Kuwait	Kuwait	31.4	25.2@15 °C	872.2	-15	(58.5)@400 °C	2.52 ^b	1400 ^b	8	30
Maya	Mexico	21.5	302.68@15 °C	924.3	-30	32@350 °C	3.4 ^b	3500 ^b	53	278
Murban	United Arab Emirates	39.73	5.9@10 °C	826	-6	59.58(63.58)@340 °C 64.78(68.53)@370 °C	0.79 ^b	(425) ^b	4.3	2.6
Nemba	Angola	39.79	8.4@10 °C	825.7	-24	62.29(66.72)@340 °C 67.22(71.41)@370 °C	1.54 ^a	0.28 ^a	11.8	4.9
Norne	North Sea	32.7	14.1@20 °C	861.5	9	61.18@375 °C	0.25 ^a	0.12 ^a	0.9	0.3
North Sea oil	North Sea	38.41	9.8@10 °C	832.4	-18	61.38(65.37)@375 °C 84.48(86.67)@550 °C	0.22 ^b	(1108) ^b	3	2
Oseberg	North Sea	37.8	6.8@10 °C	835.4	-5.6	60.11(64.27)@343 °C 87.96(89.87)@538 °C	0.25 ^b	0.098 ^b	2	2
Siberian Light	Russia	37.8	7@20 °C	835.8	-17	(46)@370 °C	0.42 ^b	900 ^b	8	15
Sirtica	Libya	43.3	3.43@40 °C	815@20 °C	-3	(73)@370 °C	0.43 ^b	1400 ^b	15	10
Sorosh	Iran	18.1	1381@20 °C	945	-12	(30)@370 °C	3.3 ^b	3000 ^b	35	101

^a Values obtained by elemental analysis. ^b Values from publicly available sources, NA – not available.

companies (Total, Statoil, *etc.*), and other web-based sources (see Table 1). Where missing, elemental compositions (S and N) were determined experimentally.

2.3. Thin layer chromatography with flame ionization detection (TLC-FID)

The oil samples were analysed using TLC-FID which is well established as an efficient, fast and cost effective method to obtain quantitative data on the composition of oils, more specifically the relative contents of saturates, aromatics, resins and asphaltenes (SARA analysis).^{13,14}

Using a sample spotter SES 3202/IS-02 (Ses GmbH, Nieder-Olm, Germany), 0.8 μL of the DCM oil solution was spotted onto silica-coated quartz rods (ChromaRod®-SIII). A three-step separation was performed using 100% *n*-hexane to 10 cm, 20 : 80% *n*-hexane : toluene to 5 cm and 5 : 95% methanol : dichloromethane to 2 cm, respectively. All eluents used were of analytical grade (Suprasolv grade). After elution, the Chromarods® were dried at 40 °C for 5 min to remove solvents and transferred into a MK-5 TLC-FID Iatroscan® apparatus (Iatron Labs, Tokyo, Japan) where each Chromarod® was scanned with the FID to detect the oil compound classes separated on the silica. The hydrogen flow rate was 160–180 mL min^{-1} , the airflow rate was 2000 mL min^{-1} and the scanning speed was 30 s per Chromarod® burned.

2.4. Oil fingerprinting

Oil fingerprinting was based on a standard methodology,¹⁵ using GC-MS to measure a suite of oil specific compounds (including polycyclic aromatic hydrocarbons and molecular markers). Peak heights were used to calculate 'diagnostic ratios'.^{16,17}

GC-MS analysis was carried out with a TRACE-MS Thermo-Finnigan gas chromatograph (Manchester, UK) in the electron impact (EI) mode at 70 eV. A 20 m \times 0.18 mm capillary column coated with 0.18 μm TRB-5MS stationary phase was obtained from Teknokroma (Sant Cugat del Vallés, Spain). The carrier gas was helium, with a constant flow rate of 0.6 mL min^{-1} . The sample (1 μL) was injected in the splitless mode, the injector temperature was held at 280 °C and the purge valve was activated 50 s after the injection. The column temperature was held at 60 °C for 1 min, then the temperature was increased to 200 at 14 °C min^{-1} and finally to 320 at 7.5 °C min^{-1} , holding that temperature for 4 min. Transfer line and ion source temperatures were held at 250 and 200 °C, respectively. Data were acquired in the full-scan mode from 50 to 350 amu (10 scan s^{-1}) with 6 min of solvent delay and processed by the Xcalibur Thermo Finnigan software (San Jose, California, USA).

Twenty selected oils were analysed for 34 compounds (see Table 1, ESI†) and from their peak heights, 25 normative, oil-specific ratios were calculated.

2.4.1. Statistical analysis. Principal component analysis (PCA)¹⁸ was performed on the fingerprinting dataset using the PASW Statistics 18 package from SPSS Inc. (Chicago, IL), in order to examine the contribution of applied diagnostic ratios to differentiation between the selected oil types. Data were arranged in a matrix in which different oil types (20) were represented in columns, whereas diagnostic ratios (25) were in rows.

2.5. Short-term oil fate modelling

Automated Data Inquiry for Oil Spills (ADIOS2, version 2.0.1) software from the National Oceanic and Atmospheric Administration (NOAA) was used to perform short-term oil fate modelling for selected oils.¹² The model was populated using the database constructed for a total of 20 oils (Diesel C was not included since distillation data were not available). Three spill scenarios for a continuous release of 120 tons (109 tonnes, representing a medium scale spill) of oil during a 24 hour period were modelled for three contrasting geographical areas: the Northwest Mediterranean Sea (Tarragona buoy, 40.68° N, 1.47° E), the Northeast Atlantic Ocean (Coast of Galicia, buoy of Villano-Sisargas, 43.50° N, 9.21° W), and the Norwegian coast of the North Sea (Troll A oil platform, 60.64° N, 03.72° E). Averaged annual data were used for wind/current speed and direction, and summer water temperature.^{19–22} The wave height was computed using the model based on the wind speed. Finally, typical salinity and concentrations of the suspended particulate matter (SPM) at the three locations were inputted to the model.^{23–27}

3. Results and discussion

3.1. Physico-chemical properties

Selected physico-chemical properties for the investigated oil samples are given in Table 1. According to the EPA criteria,³⁹ petroleum-based oils that lose at least 50 percent of their volume at a temperature of 340 °C and at least 95 percent at a temperature of 370 °C are considered to be non-persistent. Out of the selected oils, only Diesel A and Diesel B (probably also Diesel C, but distillation data are lacking) could be considered to be non-persistent. The remainder are persistent^{9,39} belonging predominantly to Group 2 ($^{\circ}\text{API} = 35\text{--}45$; eight oils: Kirkuk, Azeri, Oseberg, Siberian Light, North Sea oil, Murban, Nemba, Sirtica) and Group 3 ($^{\circ}\text{API} = 17.5\text{--}35$; nine oils: Sorosh, Maya, Dalia, Hungo, Forcados, Kuwait, Norne, Arabian Light, Flotta). Only one oil, namely Heavy fuel oil (HFO), falls into Group 4 ($^{\circ}\text{API} < 17.5$).

Oil *density* determines floating/sinking characteristics of an oil spill. Normally, oils float on water, but due to changes in the water temperature and/or weathering (evaporation, dispersion, interaction with sediment particles) oil density can increase up to a point where it sinks, either to the bottom, or to a point in the water column that has higher density.⁴⁰ In some cases, *e.g.* a high particulate load with a large proportion of the oil in the dispersed phase, this is even possible for light oils such as diesels.^{41,42} Densities of the selected oils range from 815 kg m^{-3} (43.3 $^{\circ}\text{API}$) in the case of light Sirtica crude up to 988.8 kg m^{-3} (11.47 $^{\circ}\text{API}$) for residual HFO.

Viscosity and *pour point* influence the spreading of an oil slick on the sea surface. Very fluid, low viscosity oils spread rapidly making their containment difficult. If the water temperature drops below the pour point, oil will solidify and instead of spreading, it will travel large distances in the form of solid patches under the influence of currents and waves. Viscosities available for the investigated oils are somewhat difficult to compare since the temperatures at which they are measured vary widely. Notwithstanding, extreme values are observed for heavy

oils such as residual HFO (23037.23 cSt) and Sorosh crude (1381 cSt). Such oils would have severe detrimental fouling effects on marine wildlife and coastlines, but would be relatively easy to mechanically contain using booms.^{43–45} At the other extreme are highly fluid light diesel distillates (3.25 cSt) and Sirtica crude (3.43 cSt) which would spread very fast making their containment very difficult. There is only one high pour point oil (<5 °C), namely Norne (9 °C). The other oils have their pour points below 0 °C, although low water and air temperatures in cold seas can significantly limit the fluidity of such oils. In general, higher temperature will facilitate oil spreading.⁴³ Viscosity also determines oil evaporation and emulsification (see Section 3.4).

Sulfur and nitrogen concentrations can indicate the presence of heterocyclic aromatic compounds, *e.g.* carbazoles⁴⁶ and dibenzothiophenes.⁴⁷ These compounds have mutagenic^{48,49} and carcinogenic⁵⁰ activities and are found in high concentrations near oil spill sites.⁵¹ Furthermore, N and S contents also control the nitrogen and sulphur oxides release potential during any spill burning operations posing a hazard for the clean-up personnel^{52,53} and contributing to atmospheric pollution (*e.g.* acid rain). Usually, oils contain trace amounts of these elements, but some of the selected oils are characterized by increased sulphur (*e.g.* Maya) or nitrogen content (*e.g.* Maya, Sorosh), and therefore can present increased environmental risk. Light distillates (diesels) do not contain sulfur or nitrogen. Some crude oil samples also have very low S and N content (*e.g.* Azeri).

Finally, *metals* in the oils can be considered marine pollutants *per se*⁵⁴ and some afford bioaccumulation potential.⁵⁵ Most of the metals in oils are associated with porphyrins. These chelate with the metals, especially vanadium and nickel (although iron and copper chelates may also be present). Vanadium and nickel porphyrins are important molecular organic markers for petroleum maturity. Highest concentrations are found in heavy oils, with mature lighter oils containing less.⁵⁶ Hence, the heavy crudes (Maya and Sorosh) and heavy residual oils have higher metal concentrations. Furthermore, it was reported that these porphyrin complexes can play a role in oil emulsification⁵⁷ (see Section 3.4).

3.2. Thin layer chromatography with flame ionization detection (TLC-FID)

TLC-FID (SARA) analyses of the fresh, un-weathered oils reveal their compositions in terms of the main compound classes. Observed differences are the consequence of their geochemical origins or the refining processes they have undergone (Table 2).

SARA analysis is a convenient method to obtain oil compositions that can be used to make general oil spill fate and effects assessments.

For example, oils with a high content of *saturated* hydrocarbons (iso- and cyclic alkanes) will evaporate faster upon release into the marine environment, often with the remaining components being readily dispersed. As a consequence, such oils, in general, have acute short-term toxic effects on aquatic systems which are usually limited to immediate vicinity of the spill.⁵⁸

The *aromatic* fraction accounts for the majority of toxic effects since it contains numerous compounds such as polycyclic aromatic and some hetero-polycyclic compounds that have both short-term and chronic toxic effects on the marine environment.^{59–61}

Table 2 TLC-FID SARA analysis of the fresh oils

	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
Arabian Light	35.3	39.6	16.8	8.3
Azeri	84.0	3.7	10.9	1.4
Dalia	46.3	26.1	22.7	4.9
Diesel A	83.0	2.9	12.5	1.6
Diesel B	87.6	6.9	5.5	0.0
Diesel C	88.4	7.3	4.2	0.0
Flotta	14.1	10.2	74.3	1.3
Forcados	49.2	25.0	22.2	3.6
Heavy fuel oil	22.1	38.2	28.8	10.9
Hungo	39.2	9.9	41.8	9.1
Kirkuk	43.2	43.4	6.6	6.7
Kuwait	35.6	35.7	16.3	12.5
Maya	29.4	18.6	43.5	8.4
Murban	82.4	6.8	9.6	1.2
Nemba	66.7	5.8	21.9	5.7
Norne	77.2	14.7	6.3	1.7
North Sea oil	66.2	13.5	18.9	1.4
Oseberg	54.1	23.7	18.9	3.3
Siberian Light	60.4	8.7	23.3	7.6
Sirtica	64.2	5.6	25.5	4.7
Sorosh	23.7	22.4	39.4	14.6

The *resin* fraction is a heterogenous group of compounds that includes hetero-substituted aromatics, naphthenic acids, ketones, quinones, phenols, *etc.* Their main characteristic is higher polarity which, as a consequence, affords higher water solubility and bioavailability/toxicity.^{62–64} Furthermore, this fraction can also contain transformation products generated through weathering, such as oxidated polycyclic compounds which can be present at even higher concentrations than the parent compounds.⁶⁵ These have been reported in marine environmental matrices at toxic levels^{66,67} and can be persistent.⁶⁸ Consequently, it is very important to consider this fraction in post-spill assessments, even though it can be difficult to characterize in further detail.⁶⁹

The *asphaltene* fraction contains condensed aromatic macromolecules (500–5000 amu), which can contain hetero-elements (N, S, O, metals). It is the most recalcitrant oil fraction and plays an important role in the stabilization of oil emulsions.^{70,71}

Within the chosen sample set, diesel oils are dominated by saturated hydrocarbons (>80%) with a relatively low content of aromatic and polar (resin) compounds. Light distillates, in general, do not contain asphaltenes, or their content is very low (*e.g.* Diesel A). In contrast, residual oil products, such as HFO, contain increased amounts of aromatics, resins and asphaltenes. Biodegradation of these compounds can be very slow, especially when environmental conditions are not optimal (*e.g.* oxygen and nutrient limited). Under these circumstances post-spill effects can be chronic, extending for years after the incident.⁷²

As for crude oils, their compositions can vary widely. Contents of saturates range from over 80% in Azeri and Murban, down to 14.1 in Flotta, whilst aromatics range from over 40% in Kirkuk to just over 3 percent in Azeri. The resin content is highest in Flotta crude (>70%), less in Maya and Hungo blends (>40%) and even lower in Norne and Kirkuk oils (around 6%). Finally, highly asphalted oils are Sorosh and Kuwait (14 and 12%, respectively) with Murban and Flotta containing just over 1% of asphaltenes.

3.3. Oil fingerprinting

When oil pollution is detected in the marine environment, one of the priorities is to determine its origin/spill source. In order to accomplish the cumbersome task of discerning between numerous types of crude and refined oils transported which are usually transformed by weathering after being spilt, an elaborate forensic approach must be applied. It is based on profiling a series of geochemical compounds using gas chromatography coupled to mass spectrometry. These compounds, so-called biomarkers, and characteristic ratios between them, create an oil 'fingerprint', which depends on the geochemical origin of oil and/or the production process applied. This approach was introduced in 1979⁷³ and has been improved during recent decades. It is extensively used in Scandinavia and other European countries, in the form of Nordtest methodology for oil spill identification.⁷⁴ This methodology will be standardized as the European norm.¹⁵ It was applied here to fingerprint twenty (20) selected oils, by determining diagnostic ratios of 34 specific hydrocarbon compounds found in oils (Table 1, ESI†). They include *n*-alkanes and isoprenoids, polycyclic aromatic compounds, hopanes, regular steranes and diasteranes and triaromatic steranes, each selected because they are commonly present at measurable levels in oil, they produce well resolved single peaks or characteristic combined peaks (e.g. RC26TA + SC27TA), and are robust against weathering or have known weathering characteristics. From their peak heights, twenty five (25) ratios were calculated (Table 2, ESI†). This is considered the minimum useful set of ratios needed for reliable identification of oil, which is why they are referred to as 'normative' ratios.¹⁵

Ratios of linear and branched alkanes can serve as indicators of both geochemical origin, as well as some weathering processes (i.e. biodegradation). Pristane to phytane ratios characterize different crude oils, based on the redox conditions present in the source rocks during their formation. It is accepted that ratios higher than 1 indicate oxic, and lower than 1 anoxic conditions.⁷⁵ Extremely high pristane to phytane ratios (>3) can be an indicator of abundant terrestrial organic matter, whilst extremely low values (<0.8) suggest hypersaline, anoxic conditions in the source rocks.⁷⁶ Out of the investigated oils, eight crudes have pristane to phytane ratios lower than one, five of them with extremely low (<0.8) ratios, suggesting anoxia/hypersalinity during their formation. In the rest of crude oils, pristane to phytane ratios are higher than one, ranging from 1.03 in Siberian Light to 2.71 in Forcados, indicating oxic formation.

Changes in ratios of heptadecane to pristane and octadecane to phytane can be very useful to identify the onset of biodegradation of oil spilt in the environment. It has been observed that bacterial communities preferentially degrade straight chain alkanes to branched ones (pristane, phytane). Hence, the ratios of C17/Pris and C18/Phy (diagnostic compounds and ratios abbreviations are given in the ESI,† Table 1) in a biodegraded oil will be lower than in the respective fresh oil.⁷⁷

Characteristic distributions and ratios of polycyclic aromatic hydrocarbons (PAH) can be used to distinguish between different crude oils as well as to identify refining products. In this respect, particularly useful are methyl substituted dibenzothiophenes and phenanthrenes, monitored by selective ion traces at *m/z* 198 and 192, respectively. For example, as a result of

cracking processes in the refinery, the ratio of 2-MP to 1-MP in HFO is higher than in the starting crude oil, while at the same time the ratio of 4-MD to 1-MD is lower than in the crude oil. Furthermore, weathering processes produce characteristic changes in MP and MD ratios. For example, 2-MP is more soluble than 1-MP, so in aqueous environments, their ratios will change accordingly. Also, dissolution will affect heterocyclic compounds (dibenzothiophenes) more than aromatic compounds.⁷⁸ On the other hand, 9-MP and 4-MD appeared to be more resistant to biodegradation than the others.⁷⁹ Four ring aromatics, such as fluoranthenes and pyrenes, are also used since they can vary significantly among different oils. Methylpyrene ratios can also serve as indicators of photooxidative weathering, because 4-Mpy and 1-Mpy are more affected by irradiation than 2-Mpy. Sulphur containing heteroaromatics such as benzo-naphthothiophene can also serve as oil-type specific indicators, characterizing sulphur rich oils.⁸⁰ For example, oils with increased sulphur content, such as Kirkuk and HFO, also have high BNT to tetramethylphenanthrene ratios. However, there are other sulphur containing compounds, such as C3- and C2-dibenzothiophenes, which are not included in normative ratios, because they cannot be resolved as single peaks with the applied GC-MS methodology. Therefore, it is not recommended to draw direct conclusions about the sulphur content in oil solely based on the BNT/T-M-phen ratio.

Retene is another aromatic hydrocarbon which can be very useful for oil identification, because it provides a geochemical indication that the oil in question was formed from biomass containing conifer plants.⁷⁶ This is illustrated for the analysed oils, where it can be observed that the highest retene to T-M-phen ratios are found in the oils from the north of Europe (Oseberg, Norne, Siberian Light, Flotta), a region with rich conifer vegetation. Furthermore, retene can be used to identify heavy, residual oils, because it is strongly reduced during refinery cracking. In the investigated HFO, a retene peak at mass 234 could not be found.

Oleanane is a natural triterpenoid, and is another plant-derived geochemical marker indicating flowering vegetation inputs during oil formation.¹⁷ It has been reported as a characteristic feature of Nigerian crude oils.¹⁷ This is confirmed with Forcados, the only Nigerian oil in our sample set, which had the highest oleanane peak. Other crudes with oleanane detected were Dalia and Nembra from Angola, and Azeri from Azerbaijan.

The diagnostic biomarkers used for calculating normative diagnostic ratios include hopanes (pentacyclic triterpanes), steranes (regular and rearranged, i.e. diasteranes) and triaromatic steranes. These biomarkers are particularly useful because of their specificity, diversity and resistance to biodegradation and weathering.⁸¹ In this respect, particularly important is 17 α (H),21 β (H)-hopane, which is used, due to its stability, as a natural internal standard to normalize other biomarker compounds.⁸² Fidelity of their ratios can be compromised in the case of refinery products, i.e. they are absent or found at very low levels due to losses during refining processes. Biomarker patterns can be altered due to the mixing of different oil production streams, as observed for diesel oils and HFO.

3.3.1. Statistical analysis. The database of normative diagnostic ratios for the selected twenty oils has been created in accord with CEN methodology. It provides unique 'fingerprints'

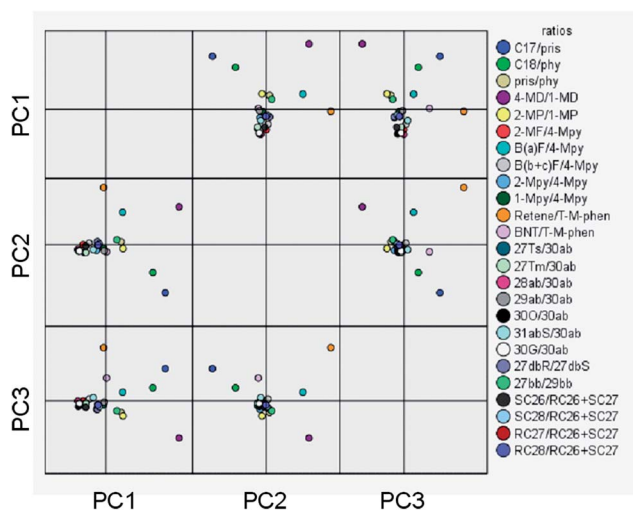


Fig. 2 PCA score plots.

that can be used for identification of the oils in the environment. Furthermore, the dataset can be investigated in order to determine which of the 25 normative diagnostic ratios in the analysed samples most significantly reflect oil-type differences. In this way, the most characteristic ratios could be used in cases of oil spills with numerous potential sources to screen and discard sources whose 'critical' ratios differ. Detailed fingerprinting could then be limited to the samples that appear reasonably 'suspicious'.

For the purpose of this study, a data matrix was created where diagnostic ratios were presented row-wise and oil samples column-wise. Dimension reduction was then performed using PCA. As a result, three principal components with eigenvalues greater than one (which explain 87.52% of the total variance)

were obtained. Fig. 2 is a matrix scatter plot showing mutually contrasted scores of the three principal components with the greatest variance. In all score plots it can be observed that the majority of normative ratios are clustered together, and that there are six ratios with obvious deviations from that clustering and from each other. These are C17/pris, C18/phy, 4-MD/1-MD, B(a)F/4-Mpy, BNT/T-M-phen and retene/T-M-phen, suggesting that they govern oil type differentiation in the analysed sample set. This can be explained by the fact that these ratios are very characteristic; ratios of linear to branched alkanes depend on the geochemical origin of the oil, four ring aromatics (fluoranthenes/pyrenes) vary between oils, sulphur heteroaromatics (MD and BNT) ratios depend on the sulphur content of the oil (and change during oil refining), while retene is only found in oils with conifer biomass origin. It is reminded, however, that some ratios can be altered by weathering, *e.g.* C17/pris and C18/phy due to biodegradation and 4-MD/1-MD by dissolution. Hence, caution is advised when using a limited set of ratios for source identification, particularly if the samples are extensively weathered.

3.4. Short-term oil fate modelling

The ADIOS2, software from the NOAA, is the most widely used computer program that models the behaviour of spilled oil, *i.e.* processes such as evaporation and dispersion. Evaporation is estimated using a pseudo-component evaporation model which models crude oils and refined products as a relatively small number of discrete, non-interacting components.⁸³ For dispersion it applies the Delvigne–Sweeney model.⁸⁴ So far it has been used on numerous small and experimental spills and shows reasonable agreement with field observations.⁸⁵ Successful oil spill modelling depends on the quality of the data used; therefore testing of model simulations in real scenarios is crucial. In this

Table 3 Modelled oil budget of applied spill scenarios and emulsification prediction for selected oils

	NW Mediterranean Sea			NE Atlantic Ocean			North Sea			Emulsification		
	Evaporated (%)	Dispersed (%)	Remaining (%)	Evaporated (%)	Dispersed (%)	Remaining (%)	Evaporated (%)	Dispersed (%)	Remaining (%)	Mousse (% evap.)	Ni + V (ppm)	Tendency
Arabian Light	44	12	45	41	11	48	42	16	42	6	18.5	Yes
Azeri	48	10	41	45	12	43	45	18	37	22	4	No
Dalia	19	2	79	18	2	80	18	3	79	2	24	Yes
Diesel A	83	9	8	81	13	6	88	10	2	100	NA	No
Diesel B	82	9	9	81	13	6	88	10	2	100	NA	No
Flotta	47	10	43	41	9	50	40	13	47	21	12.87	No
Forcados	45	15	40	41	18	42	38	27	36	19	4.9	No
Heavy fuel oil	15	0	85	14	0	86	14	0	86	100	<600	Yes
Hungo	44	3	53	42	3	56	44	4	52	4	36.3	Yes
Kirkuk	47	14	39	44	14	42	42	20	37	6	41	Yes
Kuwait	38	8	54	35	7	58	34	11	55	5	38	Yes
Maya	27	0	73	26	0	74	26	1	73	1	331	Yes
Murban	54	19	27	50	23	28	48	31	21	23	6.9	No
Nemba	48	6	47	55	16	29	54	22	24	8	16.7	Yes
Norne	35	10	54	32	13	55	31	22	48	20	1.2	No
North Sea oil	51	15	34	48	16	37	53	20	27	23	5	No
Oseberg	54	17	29	51	19	30	54	24	22	23	4	No
Siberian	33	21	47	29	21	50	29	29	43	23	NA	NA
Light												
Sirtica	64	7	29	61	7	32	62	10	29	25	NA	NA
Sorosh	28	0	72	26	0	74	27	0	73	1	136	Yes

Table 4 Environmental data at selected locations used for modelling

	Wind speed (m s^{-1})	Wind dir ($^{\circ}$)	Water temp. ($^{\circ}\text{C}$)	Curr. speed (m s^{-1})	Curr. dir ($^{\circ}$)	Salinity (psu)	Water sediment load (mg L^{-1})
The NW Mediterranean Sea	5	123	26	0.2	195	38	16
The NE Atlantic Ocean	7	158	19	0.1	29	36	0.5 ^a
The North Sea	9	160	17	0.3	45	35	0.3 ^a

^a ADIOS2 does not permit decimal values, so 0 mg L^{-1} was used.

respect, the approach applied here, where an extensive customised oil database has been built using experimental results and oil assays to provide model inputs, is useful.

Oil budget data including evaporated, dispersed, and the remaining percentage of spilled oil after 5 days (the maximum time following spillage permitted by the model) were calculated (Table 3). Major environmental effects of any oil spill will most certainly last much longer than this period, however, the estimations obtained by the model are invaluable for successful planning of the immediate response activities, both in terms of clean up personnel safety, as well as in the decision making process and selection of the appropriate mitigation measures (e.g. use of dispersants, mechanical containment, *etc.*). Moreover, an estimation of the quantity of remaining oil is a valuable piece of information in the assessment of the possible medium- to long-term effects of the spill and the planning of monitoring activities.

The marine conditions at three locations (Table 4) were selected to be characteristic of regional seas within Europe with the potential to influence oil spill behaviour.

Turbulence of the water mass is more intense in seas with strong winds and high waves, which in turn promotes oil dispersion. Wind speed is also a limiting factor for emulsification, *i.e.* a wind speed of at least $3.6\text{--}5 \text{ m s}^{-1}$ is necessary for emulsification to take place (although other emulsification factors also need to be present).⁹ This is confirmed by the model results, as the highest percentage of dispersed oil, in most cases, was observed for the North Sea scenario, where the wind is strongest. HFO, Maya and Sorosh oils do not show a tendency for dispersion in all three modelled scenarios owing to their high viscosities.

Evaporation rates are influenced by various factors including viscosity (fluid oils spread fast, creating a large thin surface which facilitates evaporation), oil composition (lighter compounds evaporate more quickly), temperature, wind and wave conditions (as for dispersion, rough seas facilitate evaporation). These complex interactions are reflected in the model results. As expected, light, low viscosity oils such as Sirtica and Diesel A and B, evaporate extensively and after five days 61 to 88% of oil has evaporated. In most cases oils' evaporation loss is similar for the three scenarios; notwithstanding it is slightly higher in the Mediterranean due to the warmer waters.

In addition to wind-speed (as noted above), emulsification of oils depends on their viscosity and composition. Emulsions readily form in oils that have more than 0.5% of asphaltenes,⁹ and when the sum of nickel and vanadium concentrations exceeds 15 ppm. Besides reflecting their less mature (heavier) nature, Ni/V porphyrin complexes are more oil-soluble and tend to act as natural surfactants, thus stabilizing water-in-oil emulsions.⁵⁷ In the sample set, light distillates (diesels) will not emulsify since they do not contain

asphaltenes or metals. Also, very viscous oils (about 10 000 cSt) with high asphaltene contents (>10%) do not form stable emulsions, but rather uptake entrained water which is then lost with time.⁸⁶ HFO is a typical oil of this type. It does not emulsify, but rather forms tar balls after a certain amount of weathering. As for the rest of oils, the limiting factors (viscosity, asphaltenes, and metals) permit emulsification, although it commences only after an amount of weathering (evaporation), as predicted by the ADIOS2 model. Heavy crudes (Maya, Sorosh, Dalia, Hungo) emulsify as fresh (unweathered) spillages, whilst other lighter crudes (e.g. Murban and Oseberg) only emulsify after heavy weathering. According to the ADIOS2 model, in the case of Murban and Oseberg crudes, this occurs after 23% of the oils evaporate. This result corroborates previously reported values obtained experimentally (25% weathering).⁵⁷

4. Conclusions

The dataset compiled from both the literature and experimental work includes a broad range of various oil types from different continents. It provides the most important properties necessary for post-spill assessments.

The majority of the selected oils can be considered to be persistent, the most recalcitrant being residual fuel oil and heavy crude oils. These also have increased contents of toxic and persistent components.

Normative diagnostic ratios of biomarkers to fingerprint the oils are reported to facilitate identification of oil spills in the environment. Statistical analyses of the ratios afford assessment of relative performance in differentiating between oil types.

Finally, short-term modelling is shown to estimate the influence of different marine conditions on the fate of spilled oil. More extreme environmental conditions (elevated temperature and turbulence *etc.*) promote processes such as evaporation and dispersion. Furthermore, the majority of oils have compositional properties that facilitate emulsification, although for some, severe weathering is necessary to make this process possible.

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