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Characterisation of oil sludges from different sources before treatment: High-field nuclear magnetic resonance (NMR) in the determination of oil and water content

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Abbreviations: CPMG, Carr-Purcell-Meiboom-Gill; EPH, extractable petroleum hydrocarbons; FID, free induction decay; FTIR, Fourier-transform infrared spectroscopy; GC-FID, gas chromatography-flame ionisation detection; ICP-OES, inductively coupled plasma optical emission spectrometry; NMR, nuclear magnetic resonance; NSC, oil refinery sludge;

ODS, oil drilling sludge; PTEs, potentially toxic elements; SPE, solid-phase extraction; STS, waste engine oil sludge from gravitational settling; RS, waste engine oil sludge from centrifugation; TGA, thermogravimetric analysis; UCM, unresolved complex mixture; WSS, oil-water separator sludge.

1. Introduction

Approximately 60 million tons of oil sludge are accumulated by the petroleum industry each year worldwide (Hu et al., 2013); these sludges are considered to be the most substantial waste generated in this industry (Egazar'yants et al., 2015, Shen et al., 2016). In fact, it was estimated that more than one billion tons of the sludges have been stored around the world (Mirghaffari, 2017), which considerably affects the operation of the petroleum industry and have environmental impacts. The Review of the European List of Waste has classified the oil sludges as “wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal” and “oil wastes and wastes of liquid fuels” (Okopol, 2008). Oil sludges are a mixture of oil hydrocarbons, water, and sediments, and are water-in-oil type (W/O) emulsions (da Silva et al., 2012, Hu et al., 2013). The sediment content of the sludges are formed from inorganic minerals in drilling fluids, storage tanks, discharges during testing and repairs of wells, accidental spills, and pipelines of the oil industry (Giles, 2010, Egazar'yants et al., 2015). Moreover, oil sludges can have metals, polyethers, and other chemicals obtained in the petroleum refining (Hu et al., 2013). Some metals found in oil sludges are chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). In general, oil sludges have a higher oil hydrocarbon content compared to the metal content (Hu et al., 2013). These potentially toxic elements (PTEs) are believed to come from oil additives (de Souza et al., 2014).

da Silva et al. (2012) reported that the composition of oil sludge is about 30 to 90% water, 4 to 7% sediments, and 5 to 60% oil. However, Saikia et al. (2003) stated that the typical composition of oil sludge is 30-50% water, 10-12% sediments and solids, 30-50% oil. Yang et al. (2005), Zhang et al. (2012), and Long et al. (2013) have agreed that oil sludge is usually composed of 30-70% water, 2 to 15% sediments and solids, and 30-90% oil. Moreover, Egazar'yants et al. (2015) mentioned that oil sludges can have approximately 10 to 56 wt.% organic materials, 30 to 85 wt.% water and 1 to 46 wt.% solids or sediments. This shows that there is no uniform agreement among authors on the detailed oil sludge composition. This is not surprising since each oil sludge composition is unique, and depends on the origin of the oil sludge (Viana et al., 2015). Consequently, the physicochemical characteristics vary according to the nature of the oil (Oliveira et al., 2015) and the formation process and storage of the oil sludge (Kadiev et al., 2015). Generally, the sediment content is less than the oil and water contents. The oil usually had higher aliphatic hydrocarbon percentages (40-60%) than the aromatic hydrocarbon percentages (25-40%) (Shie et al., 2004, Speight, 2006). This wide variation in the composition of oil sludges has significant implications on the characterisation of oil sludges because different procedures and methods have been applied to study different types of sludges (Heidarzadeh et al., 2010, Wang et al., 2010, Zhang et al., 2011, Jasmine and Mukherji, 2015). In turn, this is extremely relevant for quick decision-making purposes regarding the appropriate treatment of this waste. Currently, the treatment of oil sludges is aimed to either reduce the contaminants in the sludge or to recover the oil. The former includes some methods such as encapsulation (Johnson et al., 2015), bioremediation (Wang et al., 2016, Roy et al., 2018), and incineration (Gong et al., 2017) whereas the latter, the oil recovery methods, include freeze/thawing (Hu et al., 2015), solvent extraction (Hu et al., 2017, Nezhdbahadori et al., 2018), centrifugation (Wang et al., 2018), microwave irradiation (Tsodikov et al., 2016), and surfactant enhanced oil recovery (Duan et al., 2018, Liu et al., 2018). The implications of using an oil recovery technique is that the recovered oil can be reused as feedstock for fuel production (Giles, 2010, Liu et al., 2011, Hu et al., 2015, Zhao et al., 2017). Indeed recently, most of the sludge treatment has been focused on recycling methods to recover the oil (Gumerov et al., 2017, Nezhdbahadori et al., 2018). For example, if the oil sludge has a high oil content, it could be extracted and re-used as fuel (Hu et al., 2013).

Oil sludges are accumulated during the extraction, refining, storage, and transportation of oil (Wang et al., 2010, Zhang et al., 2011). The common sources of oil sludges are the bottom of crude oil tanks, oil-water separators, desalinators, and oil wastewater treatment plants (Hu et al., 2013, Egazar'yants et al., 2015). In addition, oil sludge can be formed from waste engine oils from vehicles and machines (Lam et al., 2012).

Oil sludges accumulated at the bottom of the storage tanks are the most frequently analysed (Hu et al., 2013, Mansur et al., 2016), and only a limited number of studies have studied in detail oil sludges from different sources. For instance, Jin et al. (2014) assessed the water content in oil sludges from oil storage tanks, dissolved air flotation units, biological sludge produced during wastewater treatments, and petroleum product storage tanks in the oil refinery. Another study used oil refinery tank bottom sludges and oil tank cleaning water sludges to analyse the emulsified water in these samples (Huang et al., 2014). Therefore, it is increasingly important to perform more studies with oil sludges from different sources to determine differences to standardise procedures for their rapid characterisation and subsequent treatment.

Nuclear magnetic resonance (NMR) has been widely used in the determination of organic components of oil (e.g. aromatics, paraffins, olefins) in sludges (Mazlova and Meshcheryakov, 1999, Pánek et al., 2014, Kadiev et al., 2015, Cheng et al., 2016, Shen et al., 2016, Uçar et al., 2016, Ma et al., 2018). NMR requires only a relatively small sample amount, and it is non-sample destructive (Zheng et al., 2013). It has an acceptable ^{1}H sensitivity, and it is easy to measure (Silva et al., 2012). However, other methods used to determine the oil hydrocarbon content such as azeotropic distillation need a high amount of reactants (e.g. approximately 200 ml of toluene) (Jin et al., 2014). Recently, low-field NMR (below 100 MHz) has been used effectively for a rapid assessment of oil and water contents in the sludges (Jin et al., 2013, Zheng et al., 2013, Jin et al., 2014) and in crude oil-water emulsions (LaTorraca et al., 1998, Silva et al., 2012). High-field NMR is a well-established and widely available analytical method that has the potential to distinguish between aliphatic and aromatic components as well as to access the water-to-oil ratio in one experiment. However, to our knowledge, there are no high-field NMR studies which aim to elucidate aliphatic and aromatic contributions and compare water-to-oil ratios for contrasting characteristic sludges originating from different sources..

The aim of this study was to analyse different types of oil sludges, but with the high-field NMR (500 MHz), to prove that high-field NMR could also be a rapid method to analyse the oil and water content in various sludges. Also, the oil hydrocarbon fractions, trace elements, sediment content, and PTEs were analysed. Therefore, we proposed a scheme to characterise the oil sludges in this study. Such information is crucial to make decisions regarding the most suitable treatment for these wastes. For instance, if the composition of the oil hydrocarbons in the sludge is known, the possibility to recover the oil for future fuel production could be assessed in a high degree of certainty minimising the recovery costs.

2. Materials and Methods

2.1. *Oil sludges*

Five oil sludges were used: An oil drilling sludge (ODS), an oil refinery sludge (NSC), an oil-water separator sludge (WSS), and two waste engine oil sludges (STS and RS). Oil sludge samples were stored in amber glass containers at 4°C to avoid photodegradation and volatilisation.

2.2. *Total dry matter and water contents*

Dry matter and water contents were assessed according to the European Committee for Standardisation (CEN) protocol (EN12880, 2003). The total dry matter content comprised the dried solid and organic material contents. Briefly, the oil sludge (5 g) was added to a crucible previously dried at 105°C for 30 minutes. The crucible was then dried at 105°C for 24 hours. The weight was continually registered until a constant mass was reached.

The solid content was obtained by further heating the 105°C-dried samples at 550°C for 30 minutes (Taiwo and Otolorin, 2009). The organic material content was the mass lost in the heating at this high temperature (Zubaidy and Abouelnasr, 2010).

2.3. *Metal elements analysis*

The elements were extracted by *aqua regia* digestion. Oil sludge (1.5 g) was dried in a fume cupboard during seven days (Chen et al., 2015), and it was then added to a 100-ml

Kjeldahl digestion tube. In addition, four glass balls (1.5 mm-2mm), 10.5 ml of concentrated hydrochloric acid, and 3.5 ml of concentrated nitric acid (both AnalaR grade supplied by Sigma-Aldrich) were added. The tube was left overnight in a fume cupboard. After, it was heated at 50ºC in a digestion block.. The temperature was then increased at 5ºC·min^{-1} to 140ºC. The sample was left at this temperature for two and half hours and filtered into a 100-ml volumetric flask using a Whatman Grade 540 filter paper (Sigma-Aldrich). The final volume (100 ml) was reached with 0.5 M nitric acid and then diluted 10-fold with ultrapure water (18.2 MΩ·cm). An inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 7300 DV) was used to analyse the sample and the multi-element and arsenic standards. The data had no total metal values because this type of digestion did not dissolve any silicates, therefore, analysed metals were only *aqua regia* soluble.

2.4. High field NMR

A Bruker Avance III 500 MHz NMR spectrometer (Bruker Biospin, Germany) operating at a Larmor frequency of 500.13 MHz (11.75 T) was used in conjunction with a Bruker broadband observe (BBO) high-resolution solution probe. Standard 5 mm diameter NMR tubes (Norell S 5-400-7) were used. A sample volume of 200 µl guaranteed that the entire sample was inside the active space of the radiofrequency coils from the BBO probe. Used motor oil (ca. 0.5 mL) diluted in 0.5 µL of deuterated benzene (Sigma-Aldrich) was the shim and lock standard. This was necessary to ensure a maximum possible homogeneity of the magnetic field and optimal and reproducible conditions for recording the NMR signal which cannot be reached using the sludges due to the numerous impurities. After the shims were calibrated with this standard, no shimming and locking was executed in the samples.

The standard 1D NMR proton spectra (oil-water calibration standards only) and the T_2 decay data were reported (all samples) at room temperature. The 90° pulse lasted 10 μs at 17 W. In total, eight signal transients were averaged in a free induction decay, FID (39,990 data points, dwell time = 3.33 μs). The spectral resolution was 3.75 Hz corresponding to a wide spectral width of 150 kHz. A full relaxation of the spins was guaranteed with a relaxation delay between 20 and 15 s.

The T_2 decay data were recorded using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. In total 128 echo cycles were used in one experiment. Each cycle consisted of an even number of echo loops with a fixed echo time of 0.26 ms (milliseconds). The number of echo loops increased non-monotonically in each consecutive cycle from 2 to 8192 to correctly cover the fast decay of oil and slow decay of water signals (e.g. frequent at short and sparse at long times). The FID signal (half of the spin echo) was registered after each cycle and was decomposed as a function of time using Fourier transformations. A 1D NMR spectrum slice was then obtained, and each slice was phase and baseline corrected prior to the integration of the full spectral range. The final T_2 decay curve for each sample comprised the series of integrals as a function of the echo time for each cycle. These data were obtained with TopSpin v. 3.5 pl 5 (Bruker Biospin, Germany).

The T_2 decay data were fitted with a decay function made from the two exponential components which corresponded to the oil and water present in the samples and a background constant using Microsoft® Excel® 2016. The T_2 decay times for oil and water, as well as corresponding signal amplitudes, were obtained from the fitting. The percentage of the amplitudes of the fit components were used to calculate the oil and water contents. This calculation was possible due to the large difference in the decay time of oil (ca. 1 ms) and water (ca. 1000 ms) signals.

This high field NMR method was validated with the relative experimental errors and R^2 values found between the NMR data and the expected percentage values of the oil and water standards. In addition, the percentage differences between the T_2 decay and 1D proton data of the oil-water calibration standards were gathered to confirm the consistency of the NMR method in calculating the oil and water contents in the oil sludges. The aliphatic to aromatic ratio in the oil sludges was calculated with the integrated intensities of the peaks in the ^{1}H NMR spectrum at the specified regions (aliphatic or aromatic).

2.5. Extraction of extractable petroleum hydrocarbons (EPH) from the oil sludges

Oil sludge (1 g) and a 10 ml acetone:hexane solution (1:1, v/v) were added to a 22 ml glass vial. Sand (50-70 mesh particle size) in ultrapure water (18.2 MΩ·cm) was used as a blank. The sample was sonicated (frequency = 38 kHz) during 15 minutes allowing the separation of soil particles and release of the EPH compounds. The sample was then agitated using a Stuart roller mixer SRT9D (Bibby Scientific Ltd.) for 60 min at 60 rpm to ensure that the sample matrix was thoroughly mixed. Deionised water (4 ml) was then added to isolate the hexane layer. The sample was frozen at -25°C to further separate water remnants from the hexane. The hexane was then separated and evaporated to 1 ml using a gentle nitrogen stream at 40°C on a sample concentrator (Bibby Scientific Ltd.). The sample was finally diluted in hexane (1:10).

2.5.1. *Sample clean-up and separation of the aliphatic and aromatic EPH fractions with solid-phase extraction (SPE)*

The silica gel (60 Å; 63 – 200 µm, GC grade) and anhydrous sodium sulphate (Fisher Scientific) were activated by ultrasonication with hexane for 30 minutes, and then heated at 130°C for 16 hours before the SPE clean-up process. Silica gel was finally deactivated with 3% (w/v) of deionised water. Sand (50-70 mesh particle size) (Sigma-Aldrich) was activated at 400°C during 8 hours. Silica gel (1 g), anhydrous sodium sulphate (0.5 g) and sand (1 g) were added as sorbents into a SPE cartridge (Supelco). The SPE cartridge was placed in a Visiprep^{TM} vacuum manifold (Supelco) at a pressure of 250 mm Hg. Sample (0.5 ml) was then transferred to the SPE cartridge, and both the aliphatic and aromatic fractions were eluted with 3.5 ml of hexane and 9 ml of 3% of isopropanol diluted in hexane, respectively. The eluents were finally evaporated to 1 ml (40°C) with a gentle nitrogen stream.

2.5.2. *Analysis of the EPH fractions by gas chromatography-flame ionisation detection (GC-FID)*

Samples were analysed by GC-FID (Agilent 6890) using a SPB-5 GC column (5% diphenyl and 95% siloxane,30 m, 0.32 mm, and 0.25 µm) supplied by Sigma-Aldrich. The injection volume was 1 µl in splitless mode. The make-up gas was nitrogen (25 ml·min^{-1}), and the carrier gas was helium (3 ml·min^{-1}). The hydrogen and air flowed at 30 and 400 ml·min^{-1}, respectively. The inlet and detector temperatures were held at 285 and 320°C, respectively. The oven temperature was held at 60°C for one minute, then ramped at 8°C·min^{-1} to 290°C, and held for

6.75 minutes. The total programme time was 36.5 min. The calibration standards were EPH aliphatic hydrocarbons and polynuclear aromatic hydrocarbons mixtures (Sigma-Aldrich). The OpenLab CDS Chemstation Edition software Version C.01.07 (Agilent Technologies) was used to extract and analyse the chromatograms. The EPH fractions analysed were the C_{10}-C_{18} and C_{19}-C_{36} aliphatic fractions, and the C_{11}-C_{22} aromatic fraction. The total EPH concentration was the sum of the three fractions mentioned above.

3. Results and Discussion

3.1. Oil sludges

The oil sludges were obtained in the UK. The sludges presented a semi-solid condition at room temperature (Figure S 1). The WSS sludge was from an oil-water separator used in an oil refinery facility. The appearance of this sludge was black and viscous. The ODS sample was a sludge from an oil drilling process with a brown and viscous appearance. The STS and RS samples were obtained from two metal removal procedures (i.e. gravitational settling for STS and centrifugation for RS) applied to waste engine oils mixed with oil additives. RS seemed more viscous than STS. The NSC sample was viscous and black and was obtained from an oil refinery process. The datasets used in this study are publicly available on the Mendeley data repository linked to this work.

3.2. Characteristics of oil sludges

The oil sludges had a wide variability of oil, water, sediment, and trace elements (including PTEs). Table 1 shows the total dry matter (organic material and solids) and water contents of the oil sludge samples.

Table 1. Percentages of water and total dry matter in the oil sludges.

Sludge	Water content	Total dry content Solid content	 Organic material
WSS	47 (±1)	23 (±0.93)	30 (±2)
ODS	13 (±0.02)	86 (±0.11)	1 (±0.10)
STS	41 (±0.16)	35 (±0.16)	24 (±0.09)
RS	35 (±2)	38 (±0.17)	27 (±2)
NSC	60 (±2)	1 (±0.07)	39 (±2)

* Each result is the mean (*n* = 3) with the standard deviation is in parentheses.

The solid and organic material comprised the total dry contents. Figure S 1 shows the oil sludges prior to the water and total dry content determination and after heating at 105°C and 550°C to determine the water and solid contents, respectively. The highest dry matter content of 87% (±0.02) was found in the ODS sludge arising from the high solids in the mud accumulated in the oil drilling operations. The picture of the solid content in Figure S 1 shows the drilling mud of the ODS sludge after heating at 550°C. ODS had the lowest water content (13% ± 0.02) (Table 1). Even though the STS and RS samples had the same origin (the content of organic material was not significantly different, $p = 0.104$, $\alpha = 0.05$), the paired t-test confirmed that the water content was significantly lower for RS than STS ($p = 0.015$). In addition, the solid content was significantly higher for RS than STS ($p < 0.01$).

According to the oven-drying method performed in this study, NSC had the lowest solid content (1% ± 0.07) due to the highest dried organic material present in this sludge (39% ± 2). In fact, the picture of the solid content of this sludge shows the residual ash after burning at 550°C (Figure S 1). The high organic material content in NSC could be partially related with heavy oil hydrocarbon fractions due to the heating at 550°C. In fact, Zubaidy and Abouelnasr (2010) mentioned that the oil mass fraction is an estimated value of the organic material content in the sludge. Therefore, this information is important because it shows that the oil sludge has the potential to be treated by an oil recovery method. In addition, NSC had the highest water content (60% ± 2). However, it was expected that NSC had the lowest water content because this sample was an oil-refined sludge with mostly crude oil, which was evidenced after drying at 105°C (Figure S 1). This low water content can be due not only to water loss but also to the volatilisation of light hydrocarbons after heating at 105°C. Therefore, the method used in this study overestimated the water content value in the sludge. Jin et al. (2014) also found that the oven-drying method for the assessment of water content was overestimating its content value due to volatilisation of oil hydrocarbons. Even though this method was overestimating the contents of water in the present study, it is suitable to determine the sediment or dry content in oil sludges. If other methods such as thermogravimetric analysis (TGA) method were used to determine the dry content of the oil sludge coupled with Fourier-transform infrared spectroscopy (FTIR), this could distinguish water from light hydrocarbons.

The metal concentrations in the oil sludges are shown in Table S 1. The WSS sludge had higher concentrations in most of the metals than the other samples. The oil sludges were under the limit of acceptable concentrations in metals for landfilling purposes fixed by the European Union (Kriipsalu et al., 2008). The WSS sample had higher PTE levels than other samples with Cr (85 ± 0.44), Cu (142 ± 3), Zn (376 ± 7) and (Ni 85 ± 0.58) ppm. The concentrations were also higher than the limit in the other sludges. The higher levels of Zn in all sludges were expected since this metal can be found in the porphyrin compounds from petroleum (Jasmine and Mukherji, 2015). Ca and Fe were the elements with the highest concentrations in all sludges (> 1,000 $\mu g \cdot g^{-1}$). For example, Fe concentrations were higher in STS (16,146 ± 252 ppm) and RS sludge (13,915 ± 278) than the other samples. This result agreed with previous analysis of a tank bottom oil sludge (Jasmine and Mukherji, 2015) who proposed that the high concentrations of Ca and Fe can be due to calcite minerals and the material of the tank walls, respectively. Moreover, Schirmacher et al. (1993) reported that usually high concentrations of Zn, Ca, and Fe are obtained from oil sludges. Also, da Rocha et al. (2010) found high Fe levels (34,500 ppm) in an oil refinery tank bottom sludge, and Karamalidis et al. (2008) reported a Fe concentration of 92,179 ppm in an oil refinery sludge. Other trace elements analysed included Ba, K, Li, Mg, Mn, Na, and Sr, and these levels were higher for WSS than the other samples. There were no results for NSC due to the limitation on the amount of the sample. These results showed the importance to consider the analysis of the trace elements in the oil sludges, so this should be also considered in the decision-making of the treatment of these wastes. Hu et al. (2013) mentioned the importance of the characterisation of heavy metals in oil sludges. For instance, if the oil is recovered to be reused as fuel, the metals can interfere with the catalysts used in thermal cracking of heavy to light oil hydrocarbon fractions (Elektorowicz and Muslat, 2008, Khan et al., 2019). Also, it has been reported that Ni and V in interaction with Na in the recovered oil from the oil sludge can originate corrosion issues in the petroleum facilities (Abbas et al., 2010). The WSS sludge had the highest concentrations of most of the PTEs, so its treatment can include a strategy to contain these elements. For instance, if pyrolysis is applied to treat this sludge, the PTEs can be concentrated in the char, the final solid product of the process (Shen and Zhang, 2003).

3.3. High-field NMR (oil and water contents)

Firstly, different oil and water mixtures standards were evaluated to validate the NMR procedure. Figure S 2 shows the ^{1}H spectra of these standards. All spectra showed two broad resonances attributed to oil (centred at ca. 2.4ppm) and water (centred at ca. 5.4 ppm) which are consequent with the expected oil and water contents in the standards. For instance, the ^{1}H spectrum of the oil 80% + water 20% standard at the top of Figure S 2 shows the high content of oil in the high intensity peak at c.a. 2.4 ppm whereas the oil 20% + water 80% (i.e. the spectrum at the bottom of Figure S 2) shows a high intensity peak at c.a. 5.4 ppm attributed to water. A fair resolution of the spectra allowed direct integration of the signals attributed to oil and water. The peaks found in the ^{1}H spectra corresponded to the aliphatic carbon fraction from 0.5 to 4 ppm and the aromatic carbon fraction from the 6 to 9 ppm region. In the case of the ^{13}C spectra (Figure S 3), the 10-60 ppm and 110-160 ppm regions corresponded to the aliphatic and aromatic carbon fractions, respectively (Ancheyta et al., 2002, Trejo et al., 2005, Nakada et al., 2016). Figure S 3 shows that the oil from the standards had a presence of the aliphatic fraction because there are some peaks after c.a. 15 ppm to 40 ppm, and there were no signals characteristic of aromatic carbons. The intensities of the peaks between 15 and 40 ppm were consistent with the proportion of oil in the standard. Therefore, the standard with the highest oil content (i.e. oil 80% + water 20% standard; top of Figure S 3) showed peaks with high intensity. Conversely, the standards with low oil content showed peaks with low intensity. These results showed the potential use of high field NMR to differentiate between aliphatic and aromatic components in the ^{13}C spectra.

The ratio of oil and water for each standard was estimated from the ^{1}H spectrum directly (integrals of the two resonances) and the T_2 decay which shows the decay of the signal intensity (integral) as a function of the echo time. These data were compared with the expected percentage values in Table 2.

Table 2. Oil and water mixture standards with the relative errors of the expected and experimental values and percentage differences of the T_2 decay and 1D proton spectra data.

Std[1]	Nominal values (fraction)	Experimental value (T_2 decay)	Relative error [2] (T_2 decay) (%)	1D proton spectra (integrals)	Difference between T2 decay and 1D proton values (%)
1	Oil (0.2)	0.17	16	0.14	19
	Water (0.8)	0.83	4	0.86	3
2	Oil (0.4)	0.34	14	0.33	3
	Water (0.6)	0.66	9	0.67	1
3	Oil (0.5)	0.47	5	0.53	12
	Water (0.5)	0.53	5	0.47	12
4	Oil (0.7)	0.62	11	0.61	2
	Water (0.3)	0.38	26	0.39	2
5	Oil (0.8)	0.77	4	0.77	0
	Water (0.2)	0.23	14	0.23	0

[1] Std: Standard

[2] $Relative\ experimental\ error = |(Experimental - Expected)/Expected| \times 100\%$.

The majority of the relative experimental errors (T_2 decay) were lower than the 15% threshold (Sivarao et al., 2014), so it can confirm that the method is appropriate to assess the oil and water contents (Table 2). Two experimental errors were higher than this threshold, the oil content in standard 1 (16%) and the water content in standard 4 (26%).

The percentage differences between the CPMG T_2 decay data and 1D proton spectra were lower than 5% (except for standard 3 and the oil fraction in standard 1), which indicated a good agreement between both and supported the consistency of the results (Table 2).

The differences obtained between the expected and experimental values of the standards can be due to the difficulties in preparing the exact oil and water ratios. The NMR tubes were very narrow (5 mm), and it was necessary to load the sample with a long-tip Pasteur pipette to reach the bottom of the tube. It is possible that some small volume of the viscous liquid of the sample has remained in the pipette after the loading, so the exact nominal ratio was not obtained.

The linear regression of the NMR-calculated oil and water content as a function of the nominal values showed an acceptable linear correlation in both oil and water contents, and the R^2 coefficient was 0.990 which confirms that the discrepancy between nominal and experimental values were due to problems with loading the standard samples into the NMR tube. This simple analysis allowed to estimate the maximum error related to preparation and manipulation of the samples to be no larger than 20%. This value was considered for the calculation of the oil/water content experimental error in the sludges in the next step.

The T_2 relaxation decay curves for all standards are shown in Figure 1. All curves showed a bimodal decay of the NMR signal intensity as a function of time, and these were attributed to oil and water in which the oil component relaxes faster than the water component (LaTorraca et al., 1998). Therefore, the standards with a high oil content (i.e. oil 80%-water 20%, oil 70%-water 30%, oil 50%-water 50%) showed seemingly a faster decay than the standards composed by a high-water content. This trend showed that the contribution of water and oil in the decay curve can be obtained by extracting the amplitudes of both components. The fraction content of oil and water in each standard sample can be then calculated and results were presented as showed in Table 2.

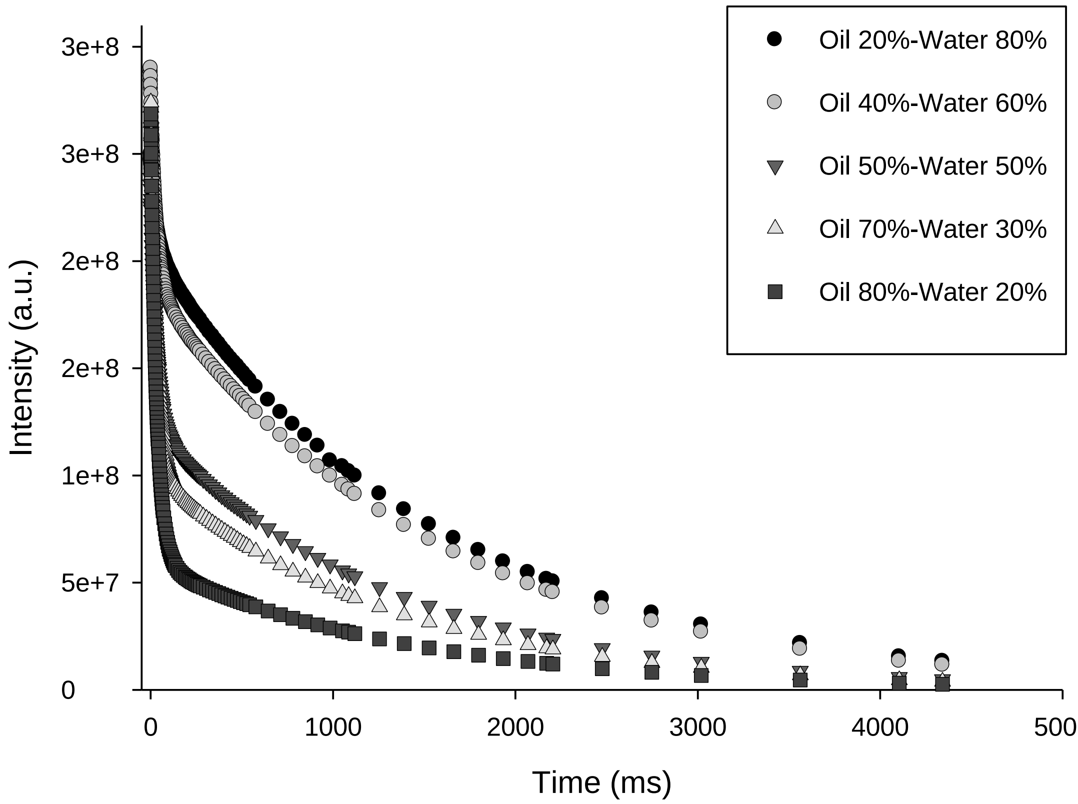

Figure 1. Carr-Purcell-Meiboom-Gill (CPMG) T_2 relaxation decay curves of the oil and water mixtures standards (%). T_2 decay shows the decay of the signal intensity (integral) as a function of the echo time.

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Examples of 1D proton spectra of the selected sludges are shown in Figure S 4. Only very broad and poorly resolved resonances were detected as a result of the presence of numerous impurities. This critical broadening of the signals, often without distinguishable structure (Figure S 4) was directly related to the presence of the metallic and paramagnetic impurities in the oil sludges as shown in the trace metal elements concentrations data (Table S 1). For instance, the ODS and RS spectra show broader signals than NSC that has more defined peaks (Figure S 4). These broad signals could probably due to the presence of more paramagnetic impurities compared to NSC. These impurities affected also the anticipated location in the 1D spectra of the oil and water peaks in the ODS and RS spectra and further prevented using them for the direct estimation of oil-to-water ratios by simple integration because appropriate regions of the spectrum were not resolved enough. Indeed, the lower the impurities content in the oil sludges, the higher the resolution of the different parts of the spectra in the high-field NMR.

Even though the paramagnetic impurities had generated broad signals in the spectra of the oil sludges, the aliphatic and aromatic ratio could be estimated in the NSC sample presumably due to a lower amount of paramagnetic impurities compared with the other sludges. Therefore, Figure S 4 shows the 1H spectrum of the NSC sludge where the aliphatic fraction was found approximately from 0 to 4.9 ppm and the aromatic fraction from 6.8 to 12 ppm (aliphatic to aromatic ratio = 0.82/0.03). The water fraction was found from 5-6.8 ppm (0.15).

In addition, the 1D carbon-13 spectra were adversely affected (poor signal-to-noise ratio due to significant broadening of the resonances) by this high content of metallic or paramagnetic impurities (data not shown). These level of metals/paramagnetic impurities can be qualitatively evaluated from the broadening of the NMR signals, but more studies with a controlled level of those impurities are required.

The oil/water fraction in sludges could only be estimated from CPMG T_2 relaxation decay curves presented in Figure 2, and the obtained results with the oil and water contents in the oil sludges are shown in Table 3.

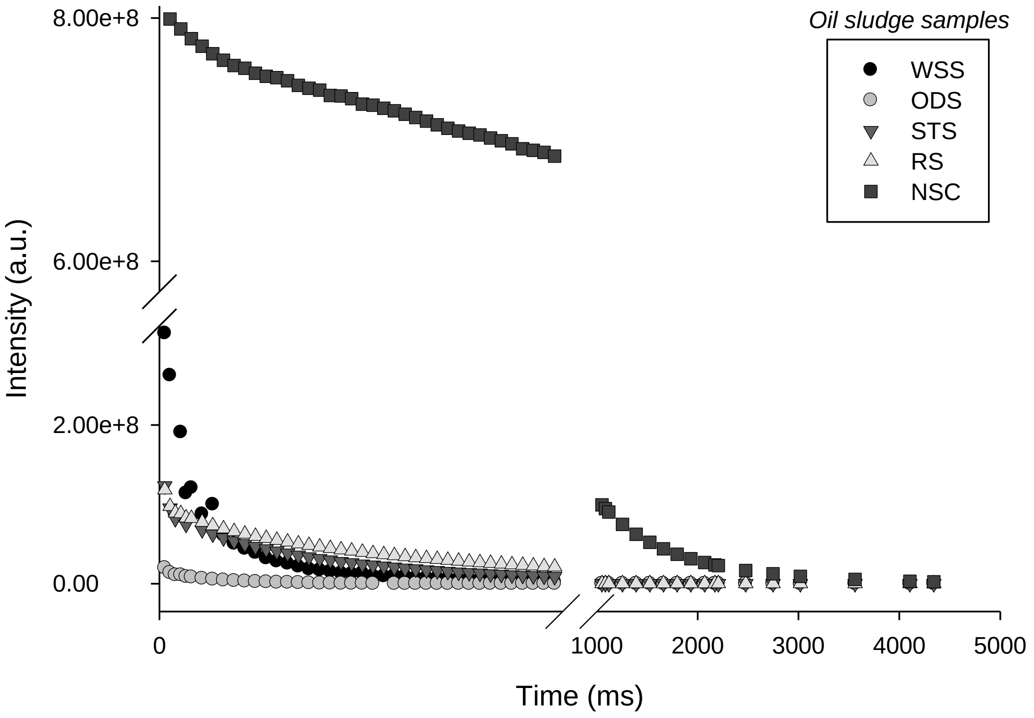

Figure 2. T_2 relaxation decay curves of the oil sludge samples (WSS, ODS, STS, RS, NSC). T_2 decay shows the decay of the signal intensity (integral) as a function of the echo time.

(THIS IS A 2-COLUMN FITTING IMAGE)

Table 3. Oil and water contents obtained by high-field nuclear magnetic resonance (NMR) of the oil sludges.

Sample	Oil (%)	Water (%)

WSS	81 (±6)	19 (±6)
ODS	1 (±0.26)	99 (±0.26)
STS	50 (±14)	50 (±14)
RS	39 (±1)	61 (±1)
NSC	88 (± 11)	12 (±11)

[*] Each result is the mean (*n* = 3) with the standard deviation is in parentheses.

The CPMG T_2 decay data (Figure 2) showed significant differences in the decay behaviour among the sludges. However, as expected all decays showed “fast” and “slow” decay components which could be attributed to oil and water (LaTorraca et al., 1998, Jin et al., 2013). For example, the decay times for the RS sludge were 2 ms for oil and 30 ms for water. The decay times of the oil and water standards results of 50 ms for the fast decay of oil and 1,500 ms for the slow decay of water. As mentioned before, the clear difference in the decay of oil and water between the oil sludge samples and standards is due to the presence of paramagnetic and metallic impurities which have tendency to accumulate in the oil sludges and as a result, shorten its relaxation.

When comparing the oil-to-water proportions obtained by the oven drying method with those from high field NMR, it was found similar trends in the data (Table 3). However, the water content in NSC obtained by high field NMR was the lowest value of all the sludges which was the opposite to the result found in the oven-drying method (See Section 3.2. Characteristics of oil sludges). This finding established that the water content was overestimated by the oven-drying method with a five-fold increase. The oil content obtained by high field NMR was the highest (88% ± 11) in the NSC sample, and this was confirmed by the highest value of organic material content found in the oven-drying method. Also, the lowest organic material content in ODS was confirmed with the low oil content found in the high field NMR method. WSS had a higher oil content compared to RS, STS, and ODS. Ramaswamy et al. (2007) mentioned that oil sludges with oil contents above 10% are suitable for an oil recovery treatment from a economic view. Therefore, all oil sludges samples except ODS (1% of oil content; Table 3) can be treated with an oil recovery technique such as oil sludge washing with surfactants (Zheng et al., 2012, Ramirez and Collins, 2018). Then, the recovered oil can be potentially be reused as a feedstock for fuel production. Regarding the ODS sludge, an oil sludge contaminant reduction technique can be applied such as bioremediation due to the low oil content and PTEs concentrations in this sludge (Table S 1). It is necessary to emphasise that some caution has to be considered when analysing NMR intensity data for the oil sludges. This is related to the difficulties found with fitting the exponential function with the two components (oil and water) to the oil sludge intensity data. The underlying common problem is an uncertainty in fitting more than one exponential component to the experimental data. Such a problem is usually related to the difficulty to reach a precise 90° pulsation which is especially important for the long train of pulses in the CPMG pulse sequence. The small deviation in the pulse length may adversely affect the echo intensity. The paramagnetic and salt contents contained in the oil sludges could influence the variation of the precision in the 90° pulses (Simpson et al., 2011). The objective of the pulse sequences is to excite the signals of the sample, so the NMR spectrometer can detect them (Derome, 1987). Despite this inconvenience, the validation of the method with the standards confirmed that the data was consistent within experimental errors to establish the oil and water contents in the oil sludges. Also, the starting parameters for each component were fixed and allowed to vary in the same range during the fit for all samples to avoid unambiguity in the fitting of the exponential function to experimental data.

3.4. Analysis of the EPH concentrations in the oil sludges

Figure 3 shows the EPH fractions of the oil sludges. A two-way ANOVA showed highly significant effects of the EPH fractions and the sludge type ($p < 0.01$), which indicated that each sludge was unique.

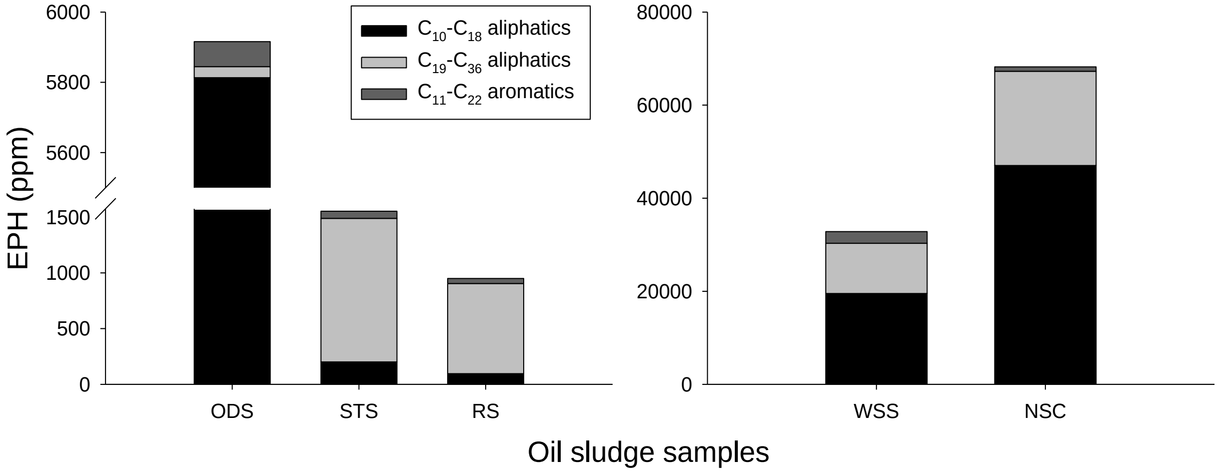

Figure 3. Mean values of the concentrations in ppm of the extractable petroleum hydrocarbons (EPH) fractions in the oil sludges.

<u>**(THIS IS A 2-COLUMN FITTING IMAGE)**</u>

The total EPH concentrations were 6,000 (± 145), 1,550 (± 506), 949 (± 392), 33,000 (±3,000), and 68,000 (± 6,070) ppm for ODS, STS, RS, WSS and NSC, respectively. The C_{19}-C_{36} aliphatic fraction percentage was greater in the RS and STS with values of 83 and 85%, respectively, compared to the other samples (NSC, 30%; WSS, 33%; and ODS, 0.53%). ODS, NSC, WSS had high proportions of C_{10}-C_{18} aliphatic fractions with 98, 70, and 60%, respectively, whereas STS had 13% and RS had 10%. All sludges showed low C_{11}-C_{22} aromatic fraction concentrations, 1% - 8% (Figure 3). In fact, the aliphatic fraction concentrations in oil sludges are usually higher than the aromatic fractions (Ward et al., 2003, Jasmine and Mukherji, 2015, Kadiev et al., 2015, Shahidi Rizi et al., 2017).

Figure S 5 showed the chromatograms of the aliphatic fractions. The WSS, STS, and RS chromatograms had unresolved complex mixtures (UCM) after C_{20}. The UCMs are considered to be a group of overlapped compounds which cannot be determined by GC-FID (Frysinger et al., 2003), and these are usually found in crude oils at different stages of degradation (Peters et al., 2005). For instance, some biodegradation processes could occur in the storage tanks (where oil sludges can be found) due to the action of the native and crude oil-resistant microbiota (Giles, 2010), and the water and sediments from the sludge could promote this biodegradation.

The UCMs were related with the high C_{19}-C_{36} aliphatic fraction concentrations found in STS and RS (Figure 3, Figure S 5C and D). This presence of UCMs in RS and STS could be related with the fact that these sludges had waste engine oil with oil additives which is related with the lubrication feature of the oil. In fact, Gough and Rowland (1990) mentioned that UCMs are characteristic of lubricating oils and other refined oil fractions.

The information retrieved from EPH analyses can be an initial step to anticipate the probable reuse of the oil contained in the sludge. Therefore, the recovered oil can be reused as diesel fuel if a high light aliphatic fraction concentration is present (Zhao et al., 2017). For example, NSC and WSS with their high content of C_{10}-C_{18} aliphatic hydrocarbon compounds can be treated with an oil recovery method to extract the oil and be reused. In fact, the GC profile of NSC (Figure S 5E) was similar to the GC profile of the common crude oil, which indicates that this oil is an ideal candidate for reusing purposes due to its potential quality similar to pure crude oil. For instance, Villalanti et al. (2006) mentioned that GC can be used as a rapid method for the analysis of the oil hydrocarbons fractions and gives information on the potential reuse of crude oils. In addition, Hu et al. (2015) stated that the quality of the oil can be evaluated by checking the EPH concentrations in the GC profiles. On the contrary, Giles (2010) mentioned that the quality of the oil cannot be measured directly with GC profiles, and that the oil must be fractionated by distillation methods to confirm its quality. Therefore, the use in this study of the GC profiles was not contemplated as a complete validation of the oil quality, but it was considered as an initial point to establish the potential reuse of the oil in the fuel production. Other tests can be used to evaluate directly the quality such as the API gravity, sulphur content, heat of combustion, and the pour and flash point (Zubaidy and Abouelnasr, 2010, Hu et al., 2015).

Regarding the ODS, STS, RS oil sludges, the total EPH concentrations were lower than the suggested clean-up level of 10,000 ppm in soils in industrial areas (Shelley et al., 1997), so bioremediation techniques such as landfarming and phytoremediation of these oil sludges can be used to treat these sludges by its amending to a designated soil area (Ramirez and Dussan, 2014). In addition, the PTEs concentrations of these sludges (except for Zn) were lower than the 2,500-ppm threshold (Table S 1). Higher concentrations than this threshold have been reported to be toxic for most microbiota (USEPA, 2004).

Since NSC and WSS had total EPH concentrations higher than 10,000 ppm, this bioremediation technique cannot be appropriate because these high concentrations can be toxic for the microbiota and plants. In fact, it has been reported that EPH concentrations higher than 50,000 ppm are generally toxic for most of the microbiota (USEPA, 2004). Therefore, NSC (68,000 ± 6,070 ppm) must be pre-treated first with an oil recovery technique, and then a bioremediation technique can be selected to treat the residual sludge.

4. Conclusions

The oil sludges used in this study came from different sources and presented a broad range of organic and inorganic co-contamination consistent with the high complexity present in this type of samples. It is very important to characterise in detail such complex samples because their treatment strongly depends on their composition. What is more, if the characterisation prior to treatment can be standardised for sludges from different sources, that would have a positive economic impact and more of such waste could be treated and recycled.

This study reported a use of different techniques to analyse different types of oil sludge samples, but uniquely in a uniform and standardised way, which gave complementary information about the water-to-oil ratio, aliphatic and aromatic components, sediment content, and trace elements and PTEs. Our comprehensive results showed that an oil recovery method (e.g. oil sludge washing with surfactants) can be applied in oil sludges with a high content of oil such as the NSC and WSS sludges. Also, STS and RS are suitable to be treated with an oil recovery technique because the oil contents were higher than the 10% threshold which is economically acceptable.

The high PTEs concentrations in the WSS sample suggest that pyrolysis should be considered to contain these elements in the char, which is a solid product of this treatment. Our results also showed that the ODS sludge is only suitable to be treated by an oil sludge contaminant reduction technique (e.g. bioremediation) due to its low oil content (1%) and PTEs concentrations. Low PTE concentrations are not toxic for most of the microbiota used in bioremediation processes.

This study showed that high-field NMR can be an alternative tool for waste researchers and petroleum engineers to rapidly calculate the water and oil contents, qualitatively access the concentration of the paramagnetic and metallic impurities, and in case of their absence or low concentration find the aliphatic and aromatic content of the sludges. The unquestionable advantage of this widely available analytical tool is that all that information could be potentially elucidated from a single ^{1}H NMR spectrum. However, more calibration studies are required to extend these procedures beyond the qualitative assessment.

The oven-drying method can determine the sediment content in the sludges. The assessment of oil hydrocarbons fractions by both GC-FID and high-field NMR can evaluate the possible reuse of the oil as fuel. Moreover, the gas chromatogram profiles provide evidence of a weathering condition and a possible degradation of the oil from the sludge by the presence of UCMs, as shown in the STS and RS samples. Due to the high concentration of some of the PTEs and their potentially hazardous effects, future studies should consider the analysis of these elements.

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SUPPLEMENTARY MATERIAL

Table S 1.Trace metal elements concentrations (µg·g^{-1} dry matter or ppm) of the oil sludges.

Element	WSS	ODS	STS	RS
Al	1,455 (±9)	506 (±20)	104 (±3)	116 (±1)
As*	2 (±0.24)	1 (±0.11)	0.10 (±0.03)	0.13 (±0.09)
Ba	131 (±7)	85 (±13)	40 (±2)	41 (±5)
Ca	5,811 (±44)	4,369 (±2505)	5,260 (±3033)	11,093 (±160)
Cd*	1 (±0.02)	0.08 (±0.01)	0.02 (±0.01)	0.02 (±0.01)
Co*	7 (±0.18)	0.27 (±0.02)	0.66 (±0.01)	0.21 (±0.01)
Cr*	**85 (±0.44)**	2 (±0.19)	9 (±0.30)	9 (±0.07)
Cu*	**142 (±3)**	8 (±0.08)	7 (±0.20)	12 (±0.80)
Fe	5,912 (±26)	1,536 (±867)	16,146 (±252)	13,915 (±278)
K	436 (±12)	85 (±3)	81 (±5)	116 (±6)
Li	2 (±0.01)	0.80 (±0.01)	0.65 (±0.05)	0.86 (±0.03)
Mg	502 (±5)	220 (±10)	235 (±3)	276 (±9)
Mn	142 (±3)	179 (±3)	23 (±0.47)	21 (±0.41)
Na	869 (±21)	65 (±17)	168 (±16)	241 (±3)
Ni*	**85 (±0.58)**	2 (±0.23)	2 (±0.14)	2 (±0.35)
Pb*	**101 (±0.46)**	45 (±2)	9 (±0.93)	9 (±2)
Sr	35 (±0.33)	93 (±6)	6 (±0.24)	7 (±0.07)
Zn*	**376 (±7)**	**1,683 (±22)**	**3,074 (±1814)**	**6,336 (±85)**

***** These elements are potentially toxic elements (PTEs) (Shaheen et al., 2016).

Values in bold are over the limit of the acceptable standards of landfilling of hazardous waste established by the European Union: As (25 µg·g^{-1}), Cd (5), Cr (70), Cu (100), Ni (40), Pb (50), Zn (200) (Kriipsalu et al., 2008). The mean values with the standard deviation (in parentheses) are shown (n = 3).

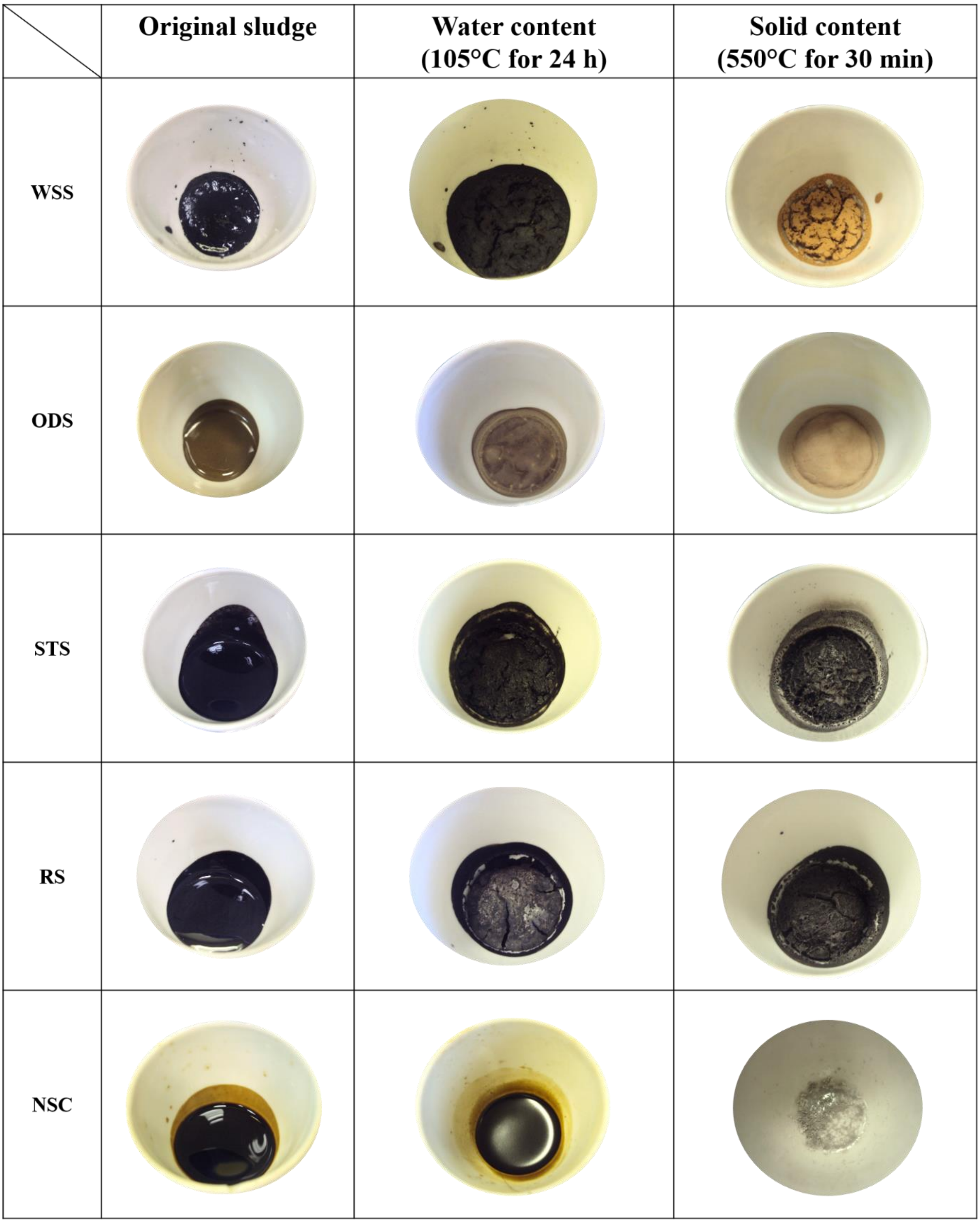

Figure S 1. Oil sludge samples before, after heating at 105°C for 24 h (water content) and 550°C for 30 min using the oven-drying method.

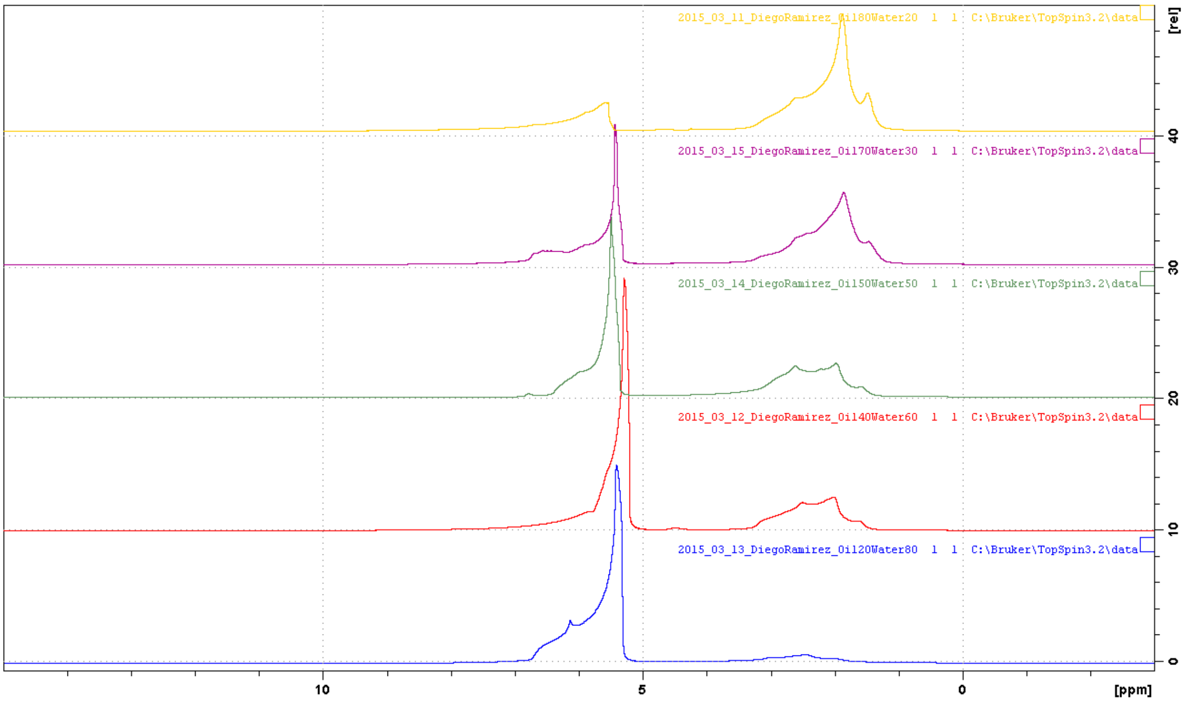

Figure S 2. ^{1}H spectra of the oil and water mixtures standards. From top to bottom: oil 80% + water 20%, oil 70% + water 30%, oil 50% + water 50%, oil 40% + water 60%, and oil 20% + water 80%.

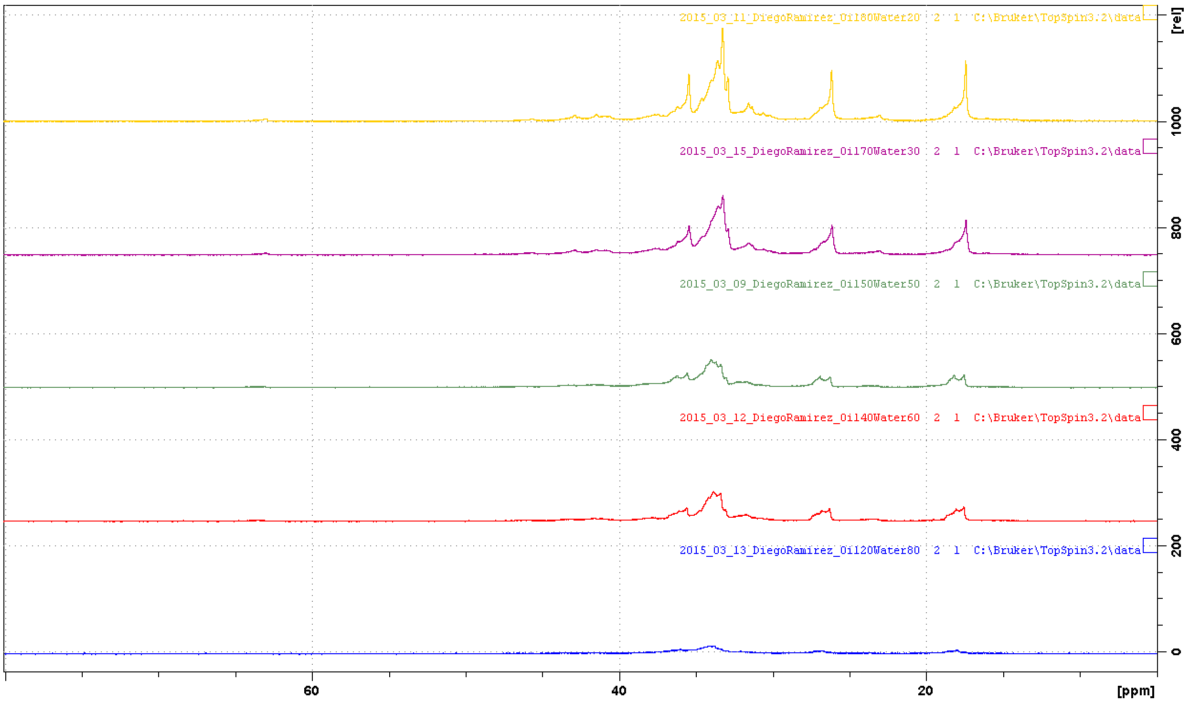

Figure S 3. ^{13}**C spectra of the oil and water mixtures standards. From top to bottom: oil 80% + water 20%, oil 70% + water 30%, oil 50% + water 50%, oil 40% + water 60%, and oil 20% + water 80%.**

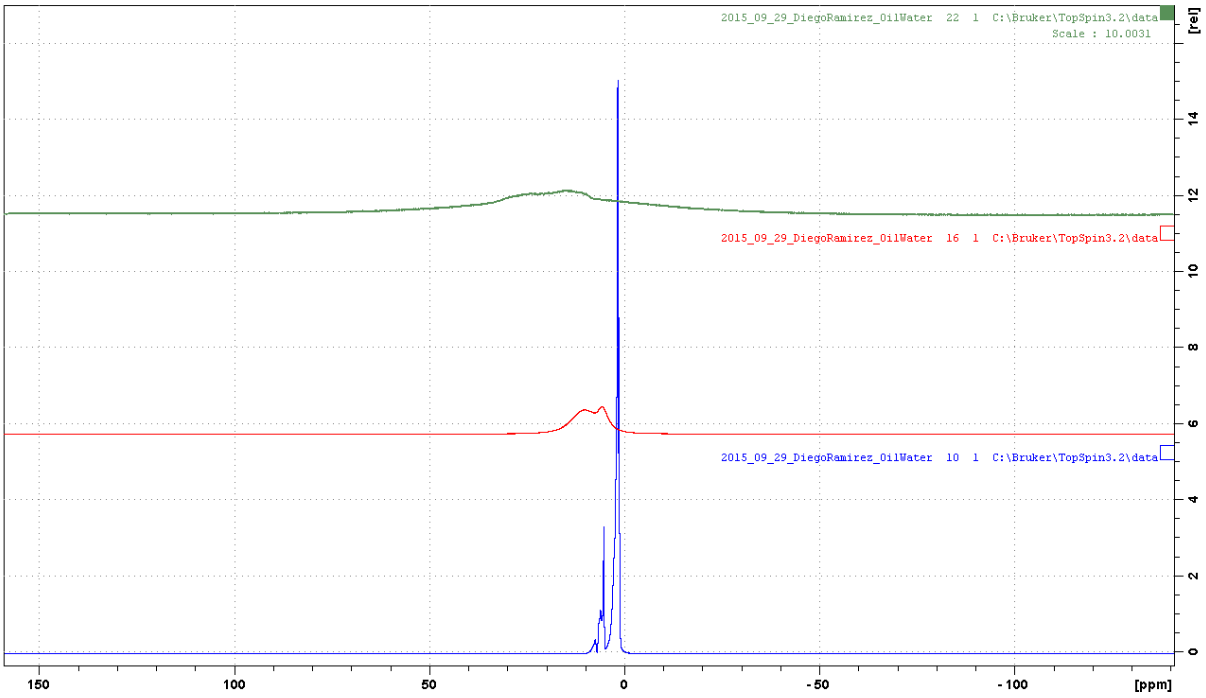

Figure S 4. 1D spectra of the sludges. From top to bottom: ODS, RS and NSC.

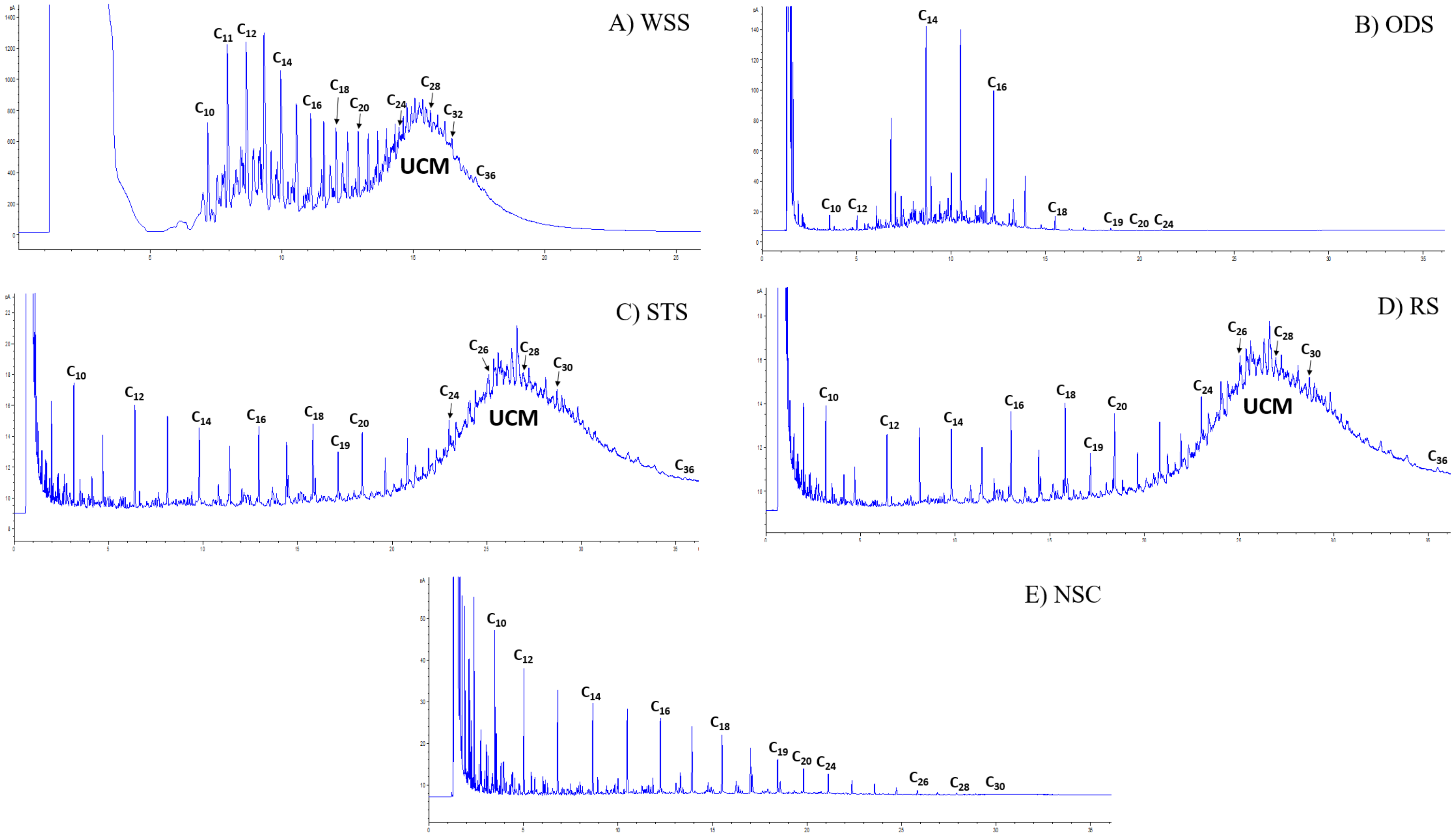

Figure S 5. Gas chromatograms of the EPH aliphatic compounds for all the analysed oil sludges. The retention times (min) are shown on the x-axis. The signal magnitude of the peaks was pA (picoamps; y-axis). The unresolved complex mixtures (UCM) are indicated.