

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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Accepted Version

Ramirez, D., Kowalczyk, R. M. and Collins, C. D. (2019) Characterisation of oil sludges from different sources before treatment: high-field nuclear magnetic resonance (NMR) in the determination of oil and water content. *Journal of Petroleum Science and Engineering*, 174. pp. 729-737. ISSN 0920-4105 doi: <https://doi.org/10.1016/j.petrol.2018.11.078> Available at <http://centaur.reading.ac.uk/81029/>

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To link to this article DOI: <http://dx.doi.org/10.1016/j.petrol.2018.11.078>

Publisher: Elsevier

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

4
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15 **Declarations of interest:** none.

16
17 *Abbreviations:* CPMG, Carr-Purcell-Meiboom-Gill; EPH, extractable petroleum
18 hydrocarbons; FID, free induction decay; FTIR, Fourier-transform infrared spectroscopy; GC-
19 FID, gas chromatography-flame ionisation detection; ICP-OES, inductively coupled plasma
20 optical emission spectrometry; NMR, nuclear magnetic resonance; NSC, oil refinery sludge;

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

25

26 **1. Introduction**

27

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

44 potentially toxic elements (PTEs) are believed to come from oil additives (de Souza et al.,
45 2014).

46 da Silva et al. (2012) reported that the composition of oil sludge is about 30 to 90% water,
47 4 to 7% sediments, and 5 to 60% oil. However, Saikia et al. (2003) stated that the typical
48 composition of oil sludge is 30-50% water, 10-12% sediments and solids, 30-50% oil. Yang et
49 al. (2005), Zhang et al. (2012), and Long et al. (2013) have agreed that oil sludge is usually
50 composed of 30-70% water, 2 to 15% sediments and solids, and 30-90% oil. Moreover,
51 Egazar'yants et al. (2015) mentioned that oil sludges can have approximately 10 to 56 wt.%
52 organic materials, 30 to 85 wt.% water and 1 to 46 wt.% solids or sediments. This shows that
53 there is no uniform agreement among authors on the detailed oil sludge composition. This is
54 not surprising since each oil sludge composition is unique, and depends on the origin of the oil
55 sludge (Viana et al., 2015). Consequently, the physicochemical characteristics vary according
56 to the nature of the oil (Oliveira et al., 2015) and the formation process and storage of the oil
57 sludge (Kadiev et al., 2015). Generally, the sediment content is less than the oil and water
58 contents. The oil usually had higher aliphatic hydrocarbon percentages (40-60%) than the
59 aromatic hydrocarbon percentages (25-40%) (Shie et al., 2004, Speight, 2006). This wide
60 variation in the composition of oil sludges has significant implications on the characterisation
61 of oil sludges because different procedures and methods have been applied to study different
62 types of sludges (Heidarzadeh et al., 2010, Wang et al., 2010, Zhang et al., 2011, Jasmine and
63 Mukherji, 2015). In turn, this is extremely relevant for quick decision-making purposes
64 regarding the appropriate treatment of this waste. Currently, the treatment of oil sludges is
65 aimed to either reduce the contaminants in the sludge or to recover the oil. The former includes
66 some methods such as encapsulation (Johnson et al., 2015), bioremediation (Wang et al., 2016,
67 Roy et al., 2018), and incineration (Gong et al., 2017) whereas the latter, the oil recovery
68 methods, include freeze/thawing (Hu et al., 2015), solvent extraction (Hu et al., 2017,

69 Nezhdbahadori et al., 2018), centrifugation (Wang et al., 2018), microwave irradiation
70 (Tsodikov et al., 2016), and surfactant enhanced oil recovery (Duan et al., 2018, Liu et al.,
71 2018). The implications of using an oil recovery technique is that the recovered oil can be
72 reused as feedstock for fuel production (Giles, 2010, Liu et al., 2011, Hu et al., 2015, Zhao et
73 al., 2017). Indeed recently, most of the sludge treatment has been focused on recycling methods
74 to recover the oil (Gumerov et al., 2017, Nezhdbahadori et al., 2018). For example, if the oil
75 sludge has a high oil content, it could be extracted and re-used as fuel (Hu et al., 2013).

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

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

90 Nuclear magnetic resonance (NMR) has been widely used in the determination of organic
91 components of oil (e.g. aromatics, paraffins, olefins) in sludges (Mazlova and Meshcheryakov,
92 1999, Pánek et al., 2014, Kadiev et al., 2015, Cheng et al., 2016, Shen et al., 2016, Uçar et al.,

93 2016, Ma et al., 2018). NMR requires only a relatively small sample amount, and it is non-
94 sample destructive (Zheng et al., 2013). It has an acceptable ^1H sensitivity, and it is easy to
95 measure (Silva et al., 2012). However, other methods used to determine the oil hydrocarbon
96 content such as azeotropic distillation need a high amount of reactants (e.g. approximately 200
97 ml of toluene) (Jin et al., 2014). Recently, low-field NMR (below 100 MHz) has been used
98 effectively for a rapid assessment of oil and water contents in the sludges (Jin et al., 2013,
99 Zheng et al., 2013, Jin et al., 2014) and in crude oil-water emulsions (LaTorraca et al., 1998,
100 Silva et al., 2012). High-field NMR is a well-established and widely available analytical
101 method that has the potential to distinguish between aliphatic and aromatic components as well
102 as to access the water-to-oil ratio in one experiment. However, to our knowledge, there are no
103 high-field NMR studies which aim to elucidate aliphatic and aromatic contributions and
104 compare water-to-oil ratios for contrasting characteristic sludges originating from different
105 sources..

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

114

115 **2. Materials and Methods**

116

117 **2.1. Oil sludges**

118

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

123

124 **2.2. Total dry matter and water contents**

125

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

131 The solid content was obtained by further heating the 105°C-dried samples at 550°C for
132 30 minutes (Taiwo and Otolurin, 2009). The organic material content was the mass lost in the
133 heating at this high temperature (Zubaidy and Abouelnasr, 2010).

134

135 **2.3. Metal elements analysis**

136

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

139 Kjeldahl digestion tube. In addition, four glass balls (1.5 mm-2mm), 10.5 ml of concentrated
140 hydrochloric acid, and 3.5 ml of concentrated nitric acid (both AnalaR grade supplied by
141 Sigma-Aldrich) were added. The tube was left overnight in a fume cupboard. After, it was
142 heated at 50°C in a digestion block.. The temperature was then increased at 5°C·min⁻¹ to 140°C.
143 The sample was left at this temperature for two and half hours and filtered into a 100-ml
144 volumetric flask using a Whatman Grade 540 filter paper (Sigma-Aldrich). The final volume
145 (100 ml) was reached with 0.5 M nitric acid and then diluted 10-fold with ultrapure water (18.2
146 MΩ·cm). An inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima
147 7300 DV) was used to analyse the sample and the multi-element and arsenic standards. The
148 data had no total metal values because this type of digestion did not dissolve any silicates,
149 therefore, analysed metals were only *aqua regia* soluble.

150

151 **2.4. High field NMR**

152

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

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

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

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

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

194

195 **2.5. Extraction of extractable petroleum hydrocarbons (EPH)**

196 ***from the oil sludges***

197

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

208

209 **2.5.1. Sample clean-up and separation of the aliphatic and**
210 **aromatic EPH fractions with solid-phase extraction (SPE)**

211
212 The silica gel (60 Å; 63 – 200 µm, GC grade) and anhydrous sodium sulphate (Fisher
213 Scientific) were activated by ultrasonication with hexane for 30 minutes, and then heated at
214 130°C for 16 hours before the SPE clean-up process. Silica gel was finally deactivated with
215 3% (w/v) of deionised water. Sand (50-70 mesh particle size) (Sigma-Aldrich) was activated
216 at 400°C during 8 hours. Silica gel (1 g), anhydrous sodium sulphate (0.5 g) and sand (1 g)
217 were added as sorbents into a SPE cartridge (Supelco). The SPE cartridge was placed in a
218 Visiprep™ vacuum manifold (Supelco) at a pressure of 250 mm Hg. Sample (0.5 ml) was then
219 transferred to the SPE cartridge, and both the aliphatic and aromatic fractions were eluted with
220 3.5 ml of hexane and 9 ml of 3% of isopropanol diluted in hexane, respectively. The eluents
221 were finally evaporated to 1 ml (40°C) with a gentle nitrogen stream.

222
223 **2.5.2. Analysis of the EPH fractions by gas chromatography-**
224 **flame ionisation detection (GC-FID)**

225
226 Samples were analysed by GC-FID (Agilent 6890) using a SPB-5 GC column (5% diphenyl
227 and 95% siloxane, 30 m, 0.32 mm, and 0.25 µm) supplied by Sigma-Aldrich. The injection
228 volume was 1 µl in splitless mode. The make-up gas was nitrogen (25 ml·min⁻¹), and the carrier
229 gas was helium (3 ml·min⁻¹). The hydrogen and air flowed at 30 and 400 ml·min⁻¹, respectively.
230 The inlet and detector temperatures were held at 285 and 320°C, respectively. The oven
231 temperature was held at 60°C for one minute, then ramped at 8°C·min⁻¹ to 290°C, and held for

232 6.75 minutes. The total programme time was 36.5 min. The calibration standards were EPH
233 aliphatic hydrocarbons and polynuclear aromatic hydrocarbons mixtures (Sigma-Aldrich). The
234 OpenLab CDS Chemstation Edition software Version C.01.07 (Agilent Technologies) was
235 used to extract and analyse the chromatograms. The EPH fractions analysed were the C₁₀-C₁₈
236 and C₁₉-C₃₆ aliphatic fractions, and the C₁₁-C₂₂ aromatic fraction. The total EPH concentration
237 was the sum of the three fractions mentioned above.

238

239 **3. Results and Discussion**

240

241 **3.1. Oil sludges**

242

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

252

253 **3.2. Characteristics of oil sludges**

254

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

258

259 **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)

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

261

262 The solid and organic material comprised the total dry contents. Figure S 1 shows the
 263 oil sludges prior to the water and total dry content determination and after heating at 105°C
 264 and 550°C to determine the water and solid contents, respectively. The highest dry matter
 265 content of 87% (± 0.02) was found in the ODS sludge arising from the high solids in the mud
 266 accumulated in the oil drilling operations. The picture of the solid content in Figure S 1 shows
 267 the drilling mud of the ODS sludge after heating at 550°C. ODS had the lowest water content
 268 (13% ± 0.02) (Table 1). Even though the STS and RS samples had the same origin (the content
 269 of organic material was not significantly different, $p = 0.104$, $\alpha = 0.05$), the paired t-test
 270 confirmed that the water content was significantly lower for RS than STS ($p = 0.015$). In
 271 addition, the solid content was significantly higher for RS than STS ($p < 0.01$).

272 According to the oven-drying method performed in this study, NSC had the lowest solid
273 content ($1\% \pm 0.07$) due to the highest dried organic material present in this sludge ($39\% \pm 2$).
274 In fact, the picture of the solid content of this sludge shows the residual ash after burning at
275 550°C (Figure S 1). The high organic material content in NSC could be partially related with
276 heavy oil hydrocarbon fractions due to the heating at 550°C . In fact, Zubaidy and Abouelnasr
277 (2010) mentioned that the oil mass fraction is an estimated value of the organic material content
278 in the sludge. Therefore, this information is important because it shows that the oil sludge has
279 the potential to be treated by an oil recovery method. In addition, NSC had the highest water
280 content ($60\% \pm 2$). However, it was expected that NSC had the lowest water content because
281 this sample was an oil-refined sludge with mostly crude oil, which was evidenced after drying
282 at 105°C (Figure S 1). This low water content can be due not only to water loss but also to the
283 volatilisation of light hydrocarbons after heating at 105°C . Therefore, the method used in this
284 study overestimated the water content value in the sludge. Jin et al. (2014) also found that the
285 oven-drying method for the assessment of water content was overestimating its content value
286 due to volatilisation of oil hydrocarbons. Even though this method was overestimating the
287 contents of water in the present study, it is suitable to determine the sediment or dry content in
288 oil sludges. If other methods such as thermogravimetric analysis (TGA) method were used to
289 determine the dry content of the oil sludge coupled with Fourier-transform infrared
290 spectroscopy (FTIR), this could distinguish water from light hydrocarbons.

291

292 The metal concentrations in the oil sludges are shown in Table S 1. The WSS sludge
293 had higher concentrations in most of the metals than the other samples. The oil sludges were
294 under the limit of acceptable concentrations in metals for landfilling purposes fixed by the
295 European Union (Kriipsalu et al., 2008). The WSS sample had higher PTE levels than other
296 samples with Cr (85 ± 0.44), Cu (142 ± 3), Zn (376 ± 7) and Ni (85 ± 0.58) ppm. The

297 concentrations were also higher than the limit in the other sludges. The higher levels of Zn in
298 all sludges were expected since this metal can be found in the porphyrin compounds from
299 petroleum (Jasmine and Mukherji, 2015). Ca and Fe were the elements with the highest
300 concentrations in all sludges ($> 1,000 \mu\text{g}\cdot\text{g}^{-1}$). For example, Fe concentrations were higher in
301 STS ($16,146 \pm 252$ ppm) and RS sludge ($13,915 \pm 278$) than the other samples. This result
302 agreed with previous analysis of a tank bottom oil sludge (Jasmine and Mukherji, 2015) who
303 proposed that the high concentrations of Ca and Fe can be due to calcite minerals and the
304 material of the tank walls, respectively. Moreover, Schirmacher et al. (1993) reported that
305 usually high concentrations of Zn, Ca, and Fe are obtained from oil sludges. Also, da Rocha et
306 al. (2010) found high Fe levels (34,500 ppm) in an oil refinery tank bottom sludge, and
307 Karamalidis et al. (2008) reported a Fe concentration of 92,179 ppm in an oil refinery sludge.
308 Other trace elements analysed included Ba, K, Li, Mg, Mn, Na, and Sr, and these levels were
309 higher for WSS than the other samples. There were no results for NSC due to the limitation on
310 the amount of the sample. These results showed the importance to consider the analysis of the
311 trace elements in the oil sludges, so this should be also considered in the decision-making of
312 the treatment of these wastes. Hu et al. (2013) mentioned the importance of the characterisation
313 of heavy metals in oil sludges. For instance, if the oil is recovered to be reused as fuel, the
314 metals can interfere with the catalysts used in thermal cracking of heavy to light oil
315 hydrocarbon fractions (Elektorowicz and Muslat, 2008, Khan et al., 2019). Also, it has been
316 reported that Ni and V in interaction with Na in the recovered oil from the oil sludge can
317 originate corrosion issues in the petroleum facilities (Abbas et al., 2010). The WSS sludge had
318 the highest concentrations of most of the PTEs, so its treatment can include a strategy to contain
319 these elements. For instance, if pyrolysis is applied to treat this sludge, the PTEs can be
320 concentrated in the char, the final solid product of the process (Shen and Zhang, 2003).

321

322 **3.3. *High-field NMR (oil and water contents)***

323

324 Firstly, different oil and water mixtures standards were evaluated to validate the NMR
325 procedure. Figure S 2 shows the ^1H spectra of these standards. All spectra showed two broad
326 resonances attributed to oil (centred at ca. 2.4ppm) and water (centred at ca. 5.4 ppm) which
327 are consequent with the expected oil and water contents in the standards. For instance, the ^1H
328 spectrum of the oil 80% + water 20% standard at the top of Figure S 2 shows the high content
329 of oil in the high intensity peak at c.a. 2.4 ppm whereas the oil 20% + water 80% (i.e. the
330 spectrum at the bottom of Figure S 2) shows a high intensity peak at c.a. 5.4 ppm attributed to
331 water. A fair resolution of the spectra allowed direct integration of the signals attributed to oil
332 and water. The peaks found in the ^1H spectra corresponded to the aliphatic carbon fraction from
333 0.5 to 4 ppm and the aromatic carbon fraction from the 6 to 9 ppm region. In the case of the
334 ^{13}C spectra (Figure S 3), the 10-60 ppm and 110-160 ppm regions corresponded to the aliphatic
335 and aromatic carbon fractions, respectively (Ancheyta et al., 2002, Trejo et al., 2005, Nakada
336 et al., 2016). Figure S 3 shows that the oil from the standards had a presence of the aliphatic
337 fraction because there are some peaks after c.a. 15 ppm to 40 ppm, and there were no signals
338 characteristic of aromatic carbons. The intensities of the peaks between 15 and 40 ppm were
339 consistent with the proportion of oil in the standard. Therefore, the standard with the highest
340 oil content (i.e. oil 80% + water 20% standard; top of Figure S 3) showed peaks with high
341 intensity. Conversely, the standards with low oil content showed peaks with low intensity.
342 These results showed the potential use of high field NMR to differentiate between aliphatic
343 and aromatic components in the ^{13}C spectra.

344 The ratio of oil and water for each standard was estimated from the ^1H spectrum directly
345 (integrals of the two resonances) and the T_2 decay which shows the decay of the signal intensity

346 (integral) as a function of the echo time. These data were compared with the expected
 347 percentage values in Table 2.

348

349 **Table 2. Oil and water mixture standards with the relative errors of the**
 350 **expected and experimental values and percentage differences of the T₂ decay**
 351 **and 1D proton spectra data.**

Std¹	Nominal values (fraction)	Experimental value (T₂ decay)	Relative error ² (T₂ 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

352 ¹ Std: Standard

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

354

355 The majority of the relative experimental errors (T₂ decay) were lower than the 15%
 356 threshold (Sivarao et al., 2014), so it can confirm that the method is appropriate to assess the

357 oil and water contents (Table 2). Two experimental errors were higher than this threshold, the
358 oil content in standard 1 (16%) and the water content in standard 4 (26%).

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

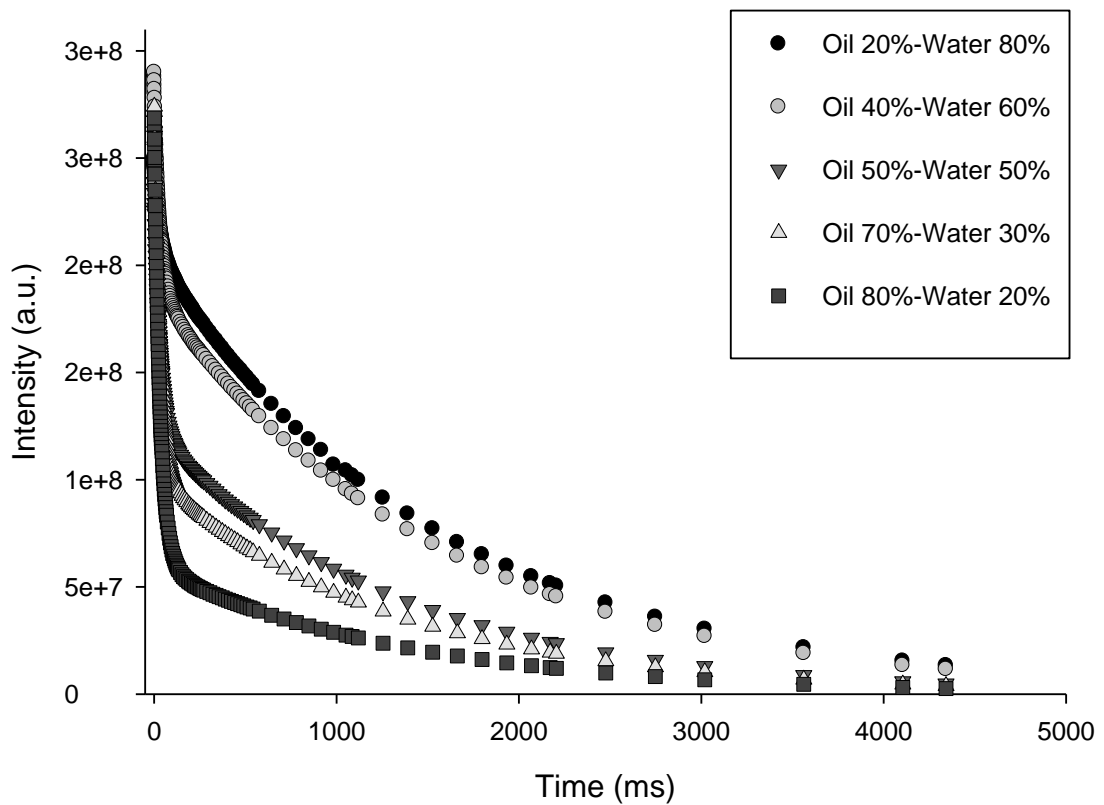
362 The differences obtained between the expected and experimental values of the standards
363 can be due to the difficulties in preparing the exact oil and water ratios. The NMR tubes were
364 very narrow (5 mm), and it was necessary to load the sample with a long-tip Pasteur pipette to
365 reach the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

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

375 The T_2 relaxation decay curves for all standards are shown in Figure 1. All curves showed
376 a bimodal decay of the NMR signal intensity as a function of time, and these were attributed
377 to oil and water in which the oil component relaxes faster than the water component (LaTorraca
378 et al., 1998). Therefore, the standards with a high oil content (i.e. oil 80%-water 20%, oil 70%-
379 water 30%, oil 50%-water 50%) showed seemingly a faster decay than the standards composed
380 by a high-water content. This trend showed that the contribution of water and oil in the decay

381 curve can be obtained by extracting the amplitudes of both components. The fraction content
382 of oil and water in each standard sample can be then calculated and results were presented as
383 showed in Table 2.

384



385

386

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

390

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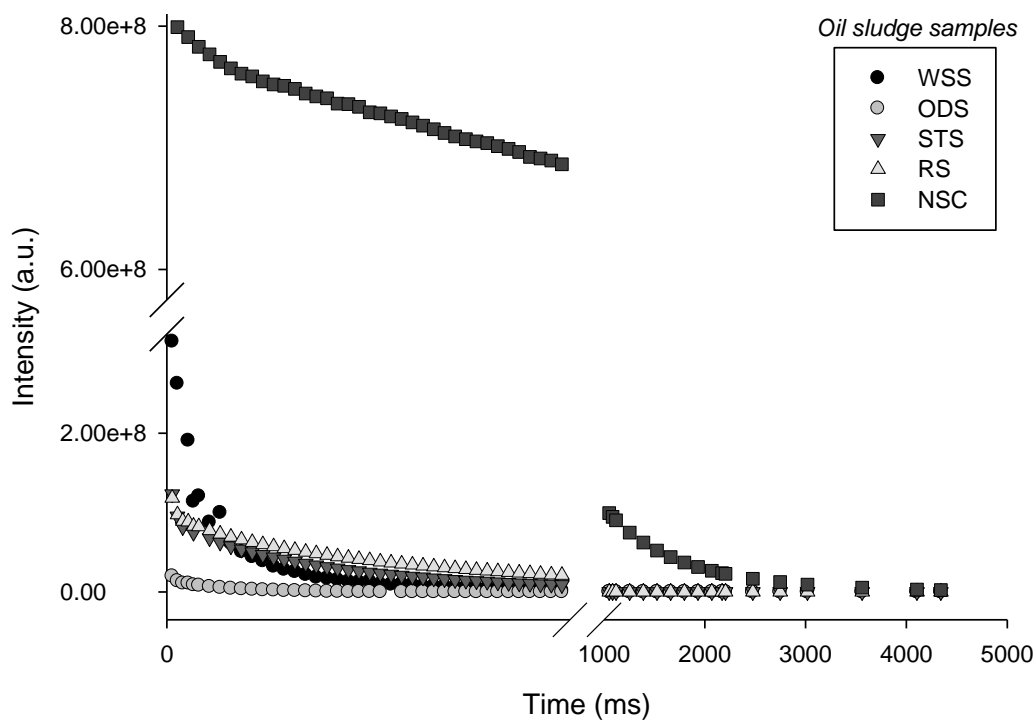
391

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

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

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

416 The oil/water fraction in sludges could only be estimated from CPMG T₂ relaxation
 417 decay curves presented in Figure 2, and the obtained results with the oil and water contents in
 418 the oil sludges are shown in Table 3.



419
 420 **Figure 2. T₂ relaxation decay curves of the oil sludge samples (WSS, ODS,**
 421 **STS, RS, NSC). T₂ decay shows the decay of the signal intensity (integral) as**
 422 **a function of the echo time.**

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424
 425 **Table 3. Oil and water contents obtained by high-field nuclear magnetic**
 426 **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.

427

428

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

438 When comparing the oil-to-water proportions obtained by the oven drying method with
439 those from high field NMR, it was found similar trends in the data (Table 3). However, the
440 water content in NSC obtained by high field NMR was the lowest value of all the sludges which
441 was the opposite to the result found in the oven-drying method (See Section 3.2. Characteristics
442 of oil sludges). This finding established that the water content was overestimated by the oven-
443 drying method with a five-fold increase. The oil content obtained by high field NMR was the
444 highest ($88\% \pm 11$) in the NSC sample, and this was confirmed by the highest value of organic
445 material content found in the oven-drying method. Also, the lowest organic material content in
446 ODS was confirmed with the low oil content found in the high field NMR method. WSS had a

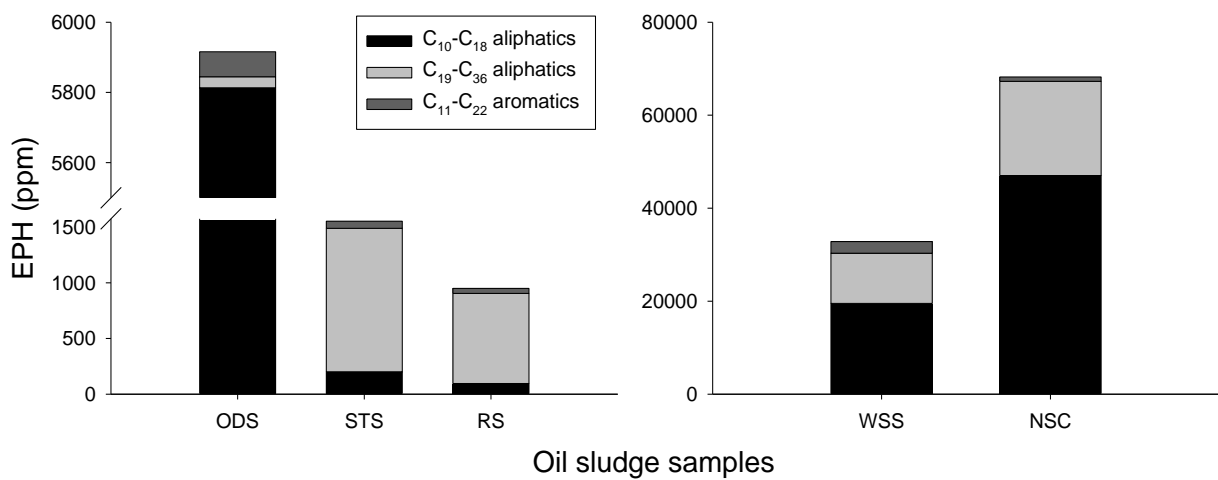
447 higher oil content compared to RS, STS, and ODS. Ramaswamy et al. (2007) mentioned that
448 oil sludges with oil contents above 10% are suitable for an oil recovery treatment from a
449 economic view. Therefore, all oil sludges samples except ODS (1% of oil content; Table 3)
450 can be treated with an oil recovery technique such as oil sludge washing with surfactants
451 (Zheng et al., 2012, Ramirez and Collins, 2018). Then, the recovered oil can be potentially be
452 reused as a feedstock for fuel production. Regarding the ODS sludge, an oil sludge contaminant
453 reduction technique can be applied such as bioremediation due to the low oil content and PTEs
454 concentrations in this sludge (Table S 1). It is necessary to emphasise that some caution has to
455 be considered when analysing NMR intensity data for the oil sludges. This is related to the
456 difficulties found with fitting the exponential function with the two components (oil and water)
457 to the oil sludge intensity data. The underlying common problem is an uncertainty in fitting
458 more than one exponential component to the experimental data. Such a problem is usually
459 related to the difficulty to reach a precise 90° pulsation which is especially important for the
460 long train of pulses in the CPMG pulse sequence. The small deviation in the pulse length may
461 adversely affect the echo intensity. The paramagnetic and salt contents contained in the oil
462 sludges could influence the variation of the precision in the 90° pulses (Simpson et al., 2011).
463 The objective of the pulse sequences is to excite the signals of the sample, so the NMR
464 spectrometer can detect them (Derome, 1987). Despite this inconvenience, the validation of the
465 method with the standards confirmed that the data was consistent within experimental errors to
466 establish the oil and water contents in the oil sludges. Also, the starting parameters for each
467 component were fixed and allowed to vary in the same range during the fit for all samples to
468 avoid unambiguity in the fitting of the exponential function to experimental data.

469

470 **3.4. Analysis of the EPH concentrations in the oil sludges**

471

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



475

476

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

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481 The total EPH concentrations were 6,000 (± 145), 1,550 (± 506), 949 (± 392), 33,000
482 ($\pm 3,000$), and 68,000 ($\pm 6,070$) ppm for ODS, STS, RS, WSS and NSC, respectively. The C₁₉-
483 C₃₆ aliphatic fraction percentage was greater in the RS and STS with values of 83 and 85%,
484 respectively, compared to the other samples (NSC, 30%; WSS, 33%; and ODS, 0.53%). ODS,
485 NSC, WSS had high proportions of C₁₀-C₁₈ aliphatic fractions with 98, 70, and 60%,

486 respectively, whereas STS had 13% and RS had 10%. All sludges showed low C₁₁-C₂₂ aromatic
487 fraction concentrations, 1% - 8% (Figure 3). In fact, the aliphatic fraction concentrations in oil
488 sludges are usually higher than the aromatic fractions (Ward et al., 2003, Jasmine and
489 Mukherji, 2015, Kadiev et al., 2015, Shahidi Rizi et al., 2017).

490 Figure S 5 showed the chromatograms of the aliphatic fractions. The WSS, STS, and
491 RS chromatograms had unresolved complex mixtures (UCM) after C₂₀. The UCMs are
492 considered to be a group of overlapped compounds which cannot be determined by GC-FID
493 (Frysiner et al., 2003), and these are usually found in crude oils at different stages of
494 degradation (Peters et al., 2005). For instance, some biodegradation processes could occur in
495 the storage tanks (where oil sludges can be found) due to the action of the native and crude oil-
496 resistant microbiota (Giles, 2010), and the water and sediments from the sludge could promote
497 this biodegradation.

498 The UCMs were related with the high C₁₉-C₃₆ aliphatic fraction concentrations found
499 in STS and RS (Figure 3, Figure S 5C and D). This presence of UCMs in RS and STS could
500 be related with the fact that these sludges had waste engine oil with oil additives which is
501 related with the lubrication feature of the oil. In fact, Gough and Rowland (1990) mentioned
502 that UCMs are characteristic of lubricating oils and other refined oil fractions.

503 The information retrieved from EPH analyses can be an initial step to anticipate the
504 probable reuse of the oil contained in the sludge. Therefore, the recovered oil can be reused as
505 diesel fuel if a high light aliphatic fraction concentration is present (Zhao et al., 2017). For
506 example, NSC and WSS with their high content of C₁₀-C₁₈ aliphatic hydrocarbon compounds
507 can be treated with an oil recovery method to extract the oil and be reused. In fact, the GC
508 profile of NSC (Figure S 5E) was similar to the GC profile of the common crude oil, which
509 indicates that this oil is an ideal candidate for reusing purposes due to its potential quality

510 similar to pure crude oil. For instance, Villalanti et al. (2006) mentioned that GC can be used
511 as a rapid method for the analysis of the oil hydrocarbons fractions and gives information on
512 the potential reuse of crude oils. In addition, Hu et al. (2015) stated that the quality of the oil
513 can be evaluated by checking the EPH concentrations in the GC profiles. On the contrary, Giles
514 (2010) mentioned that the quality of the oil cannot be measured directly with GC profiles, and
515 that the oil must be fractionated by distillation methods to confirm its quality. Therefore, the
516 use in this study of the GC profiles was not contemplated as a complete validation of the oil
517 quality, but it was considered as an initial point to establish the potential reuse of the oil in the
518 fuel production. Other tests can be used to evaluate directly the quality such as the API gravity,
519 sulphur content, heat of combustion, and the pour and flash point (Zubaidy and Abouelnasr,
520 2010, Hu et al., 2015).

521 Regarding the ODS, STS, RS oil sludges, the total EPH concentrations were lower than
522 the suggested clean-up level of 10,000 ppm in soils in industrial areas (Shelley et al., 1997), so
523 bioremediation techniques such as landfarming and phytoremediation of these oil sludges can
524 be used to treat these sludges by its amending to a designated soil area (Ramirez and Dussan,
525 2014). In addition, the PTEs concentrations of these sludges (except for Zn) were lower than
526 the 2,500-ppm threshold (Table S 1). Higher concentrations than this threshold have been
527 reported to be toxic for most microbiota (USEPA, 2004).

528 Since NSC and WSS had total EPH concentrations higher than 10,000 ppm, this
529 bioremediation technique cannot be appropriate because these high concentrations can be toxic
530 for the microbiota and plants. In fact, it has been reported that EPH concentrations higher than
531 50,000 ppm are generally toxic for most of the microbiota (USEPA, 2004). Therefore, NSC
532 (68,000 ± 6,070 ppm) must be pre-treated first with an oil recovery technique, and then a
533 bioremediation technique can be selected to treat the residual sludge.

534

535 **4. Conclusions**

536

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

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

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

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

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

571

572

573 **5. Acknowledgements**

574

575 Diego Ramirez would like to thank the Colombian Administrative Department of Science,
576 Technology and Innovation, Colciencias, for the financial support from the Call 529 (2011)
577 during his PhD studies. The funding source did not have any involvement in design,
578 development and production of this study.

579

580 **6. References**

581

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SUPPLEMENTARY MATERIAL

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Table S 1. Trace metal elements concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry matter or ppm)

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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)

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

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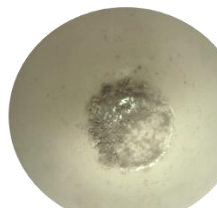
Values in bold are over the limit of the acceptable standards of landfilling of hazardous waste established by the European Union: As (25

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 $\mu\text{g}\cdot\text{g}^{-1}$), Cd (5), Cr (70), Cu (100), Ni (40), Pb (50), Zn (200) (Kriipsalu et al., 2008). The mean values with the standard deviation (in

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parentheses) are shown ($n = 3$).

	Original sludge	Water content (105°C for 24 h)	Solid content (550°C for 30 min)
WSS			
ODS			
STS			
RS			
NSC			

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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.

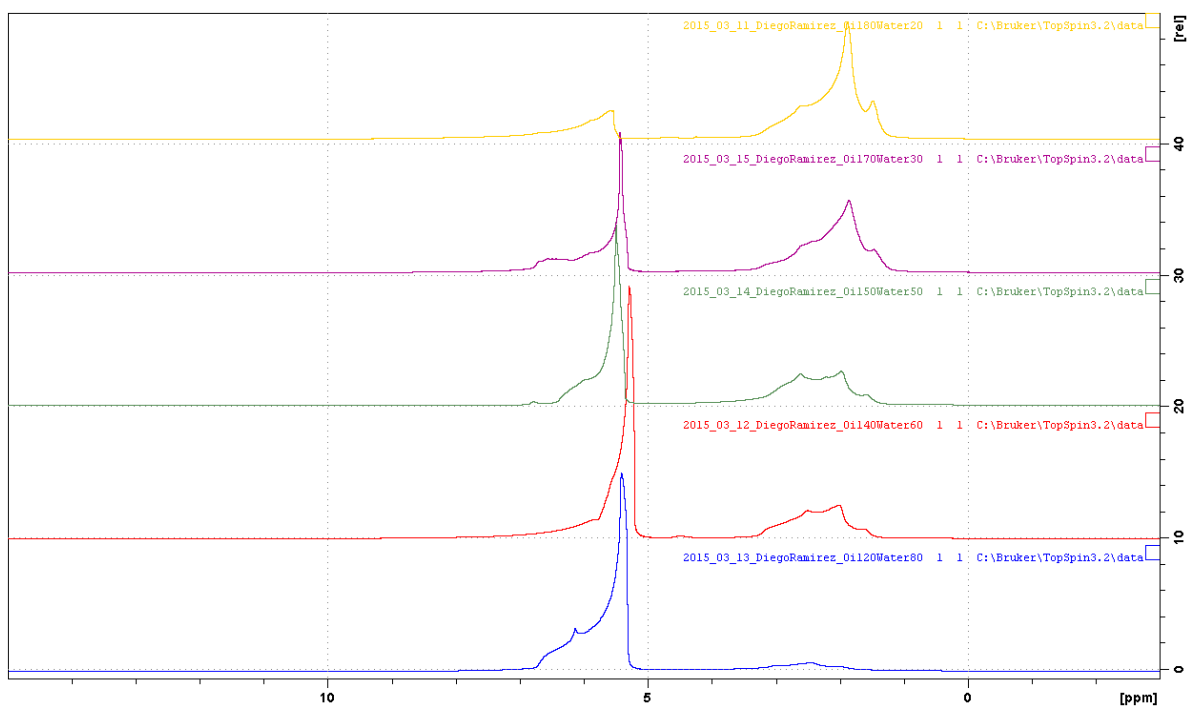


Figure S 2. ¹H spectra of the oil and water mixtures standards. From top to bottom: oil 80% + water 20%, oil 70% + water 30%, oil 50% + water 50%, oil 40% + water 60%, and oil 20% + water 80%.

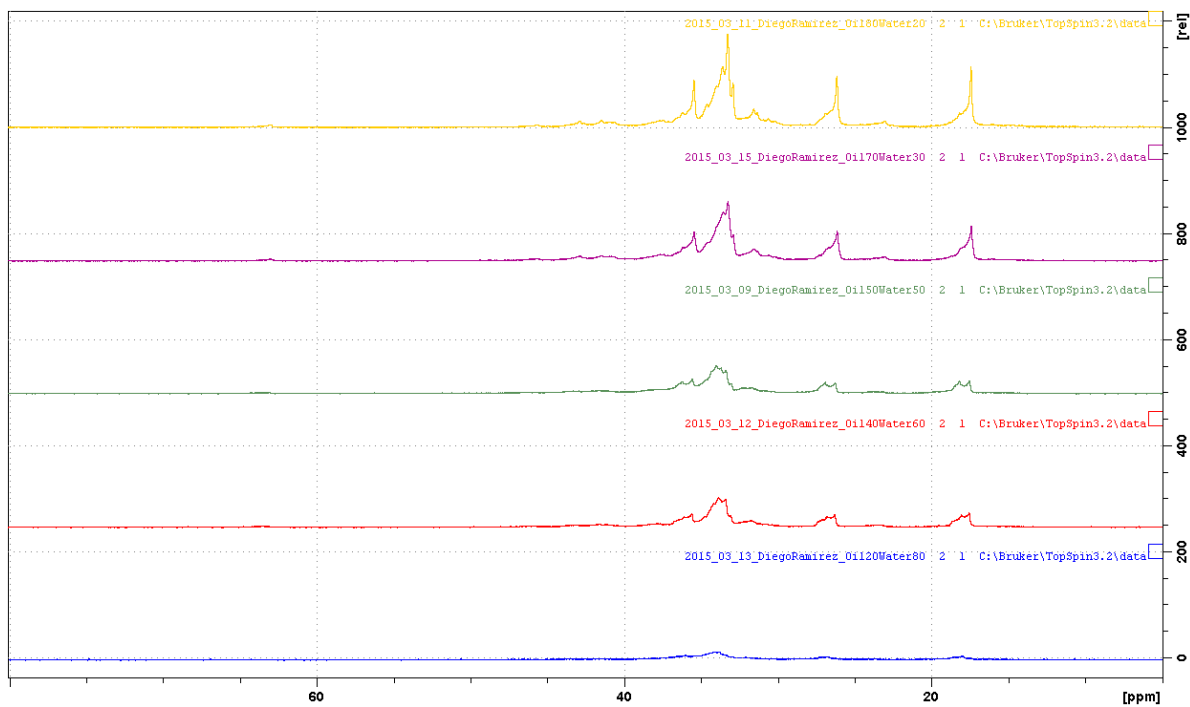


Figure S 3. ^{13}C spectra of the oil and water mixtures standards. From top to bottom: oil 80% + water 20%, oil 70% + water 30%, oil 50% + water 50%, oil 40% + water 60%, and oil 20% + water 80%.

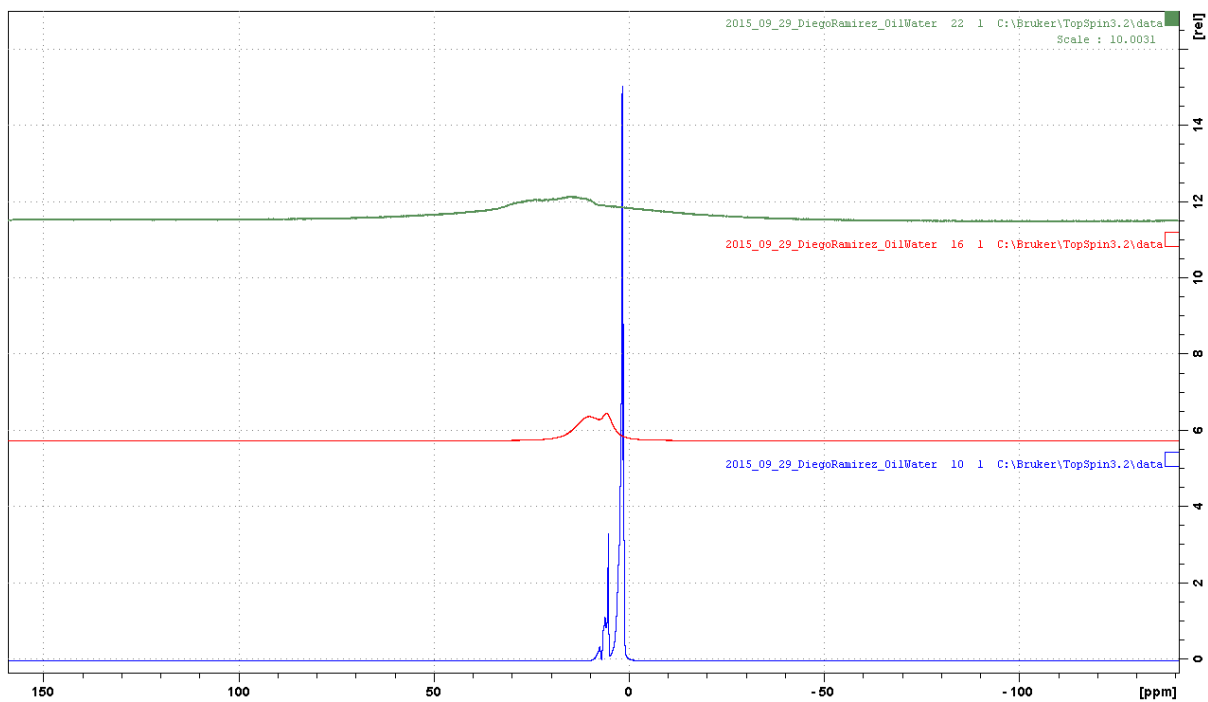


Figure S 4. 1D spectra of the sludges. From top to bottom: ODS, RS and NSC.

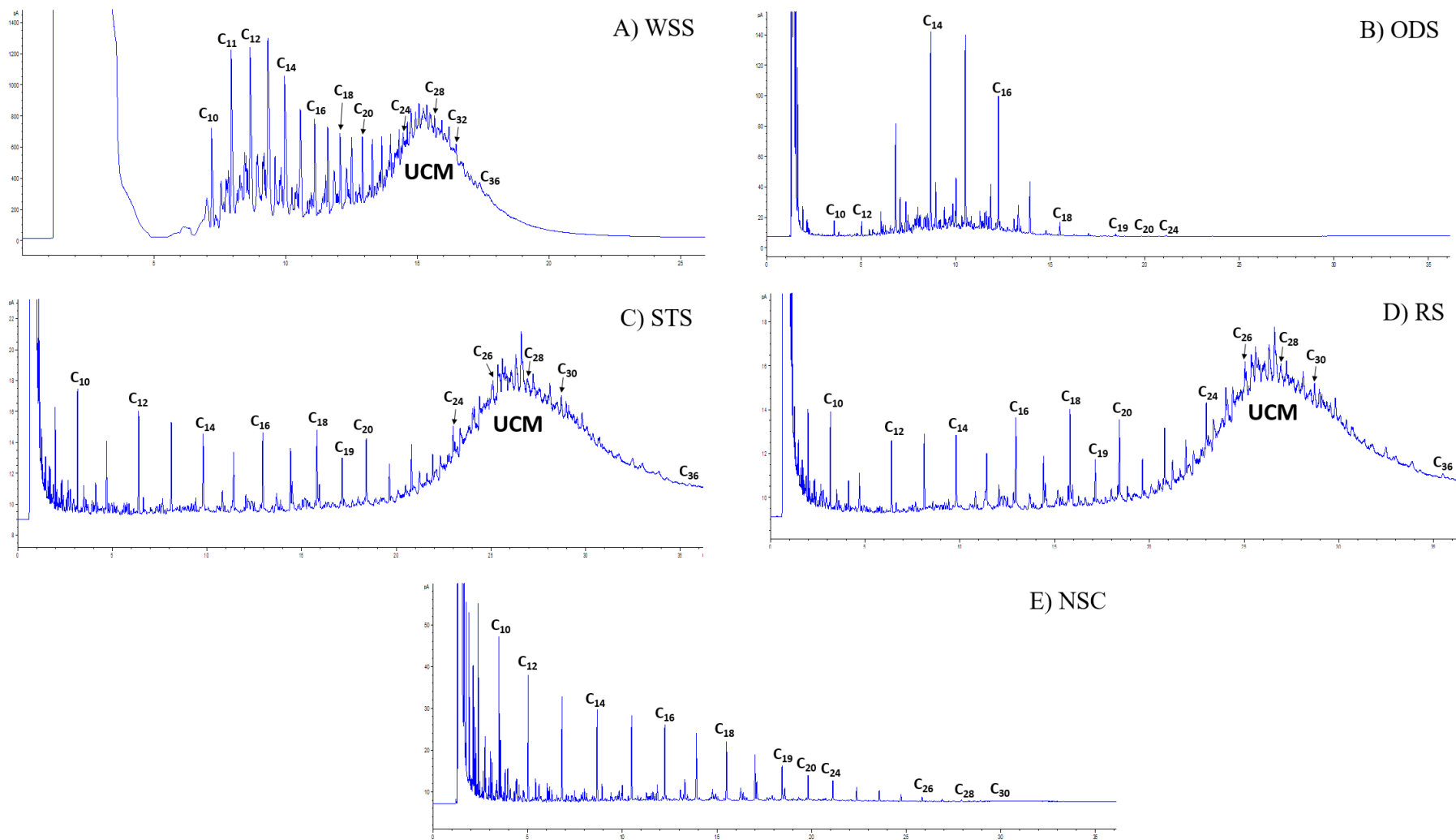


Figure S 5. Gas chromatograms of the EPH aliphatic compounds for all the analysed oil sludges. The retention times (min) are shown on the x-axis. The signal magnitude of the peaks was pA (picoamps; y-axis). The unresolved complex mixtures (UCM) are indicated.

