

1 Weathered hydrocarbon wastes: a risk management primer

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26 **ABSTRACT:** We provide a primer and critical review of the characterisation, risk
27 assessment and bioremediation of weathered hydrocarbons. Historically the remediation of
28 soil contaminated with petroleum hydrocarbons has been expressed in terms of reductions in
29 total petroleum hydrocarbon (TPH) load rather than reductions in risk.

30 There are several techniques by which petroleum hydrocarbons in soils can be
31 characterised. Method development is often driven by the objectives of published risk
32 assessment frameworks. Some frameworks stipulate analysis of a wide range of petroleum
33 hydrocarbons *e.g.* UK approach suggests compounds from EC₅ to EC₇₀ be examined.
34 Methods for the extraction of petroleum hydrocarbons from soil samples have been reviewed
35 extensively in the open literature. Although various extraction and analytical methods are
36 available for petroleum hydrocarbons, their results suffer from inter-method variation with
37 gas chromatography methods being used widely. Currently, the implications for risk
38 assessment are uncertain. Bioremediation works well for remediating soils contaminated with
39 petroleum hydrocarbons. As a result, the optimisation of environmental conditions is
40 imperative. For petroleum hydrocarbons in soil, international regulatory guidance on the
41 management of risks from contaminated sites is now emerging. There is also growing support
42 for the move towards compound-specific risk-based approaches for the assessment of
43 hydrocarbon-contaminated land.

44

45 **Keywords:** weathered, hydrocarbons, environmental, risk, management, remediation.

46 **1. INTRODUCTION**

47

48 Contamination of land due to anthropogenic activity, both present and historical, is a
49 global problem. It is estimated there may be as many as 100 000 contaminated sites in
50 England and Wales alone. Contaminated has become a subject of social, legal,
51 environmental and economic concern within many of the world's industrialised countries¹⁰⁷.
52 Land may be contaminated because of past industrial activity, historic disposal practices, or
53 due to an adverse event such as a chemical spill⁶². Although a large proportion of
54 contaminated land may be attributable to historical practices, modern industrial processes
55 also produce potential contaminants and thus, contamination of land is an ongoing problem
56 that requires active management.

57 Petroleum continues to be a widely utilised resource throughout the world. Its use has
58 resulted in the contamination through accidental spillage and leakage⁷¹. Certain components
59 of petroleum contamination may pose risks to human health, property, watercourses,
60 ecosystems, and other environmental receptors^{34,30}. Petroleum, in its natural state, is a highly
61 complex mixture of hydrocarbons with minor amounts of other heterogenic compounds such
62 as nitrogen, oxygen and sulphur³⁴. The composition of petroleum hydrocarbon products can
63 vary substantially depending on the nature, composition, and degree of processing of the
64 source material⁷⁰. Once released to the environment, petroleum products are subject to
65 physical, chemical and biological processes that further change its composition, toxicity,
66 availability and distribution (partitioning) within the environment (Figure 1). Such
67 degradation processes include adsorption, volatilisation, dissolution, biotransformation,
68 photolysis, oxidation, and hydrolysis^{9,30,50,70,87}. The extent of weathering experienced is
69 particularly important when characterising petroleum contamination prior to remediation¹⁰⁷.
70 Whilst there is a large literature describing the composition and properties of petroleum

71 products⁸⁷, there is a relative paucity of information on the toxicity, distribution, transport,
72 and availability of weathered hydrocarbons in the environment^{71,87}. Here, we provide a
73 primer and critical review of the characterisation, risk assessment and bioremediation of
74 weathered hydrocarbon-fuel products. Current issues are discussed.

75 As with all contaminants, their chemistry determines which environmental compartment
76 they are found in and thus analysed and is also responsible for their environmental fate and
77 transport characteristics. Analytical methods for determining concentrations of hydrocarbons
78 in the soil need to be technically and economically feasible and capable of analysing the
79 range of compounds key to the risk management protocols applied³⁰. Although various
80 extraction and analytical methods are available for petroleum hydrocarbons, their results
81 suffer from inter-method variation as illustrated by Buddhadasa *et al.* (2002)¹⁶. Additionally,
82 as discussed by Whittaker *et al.* (1995)¹⁰⁷, methods can suffer from both positive and
83 negative analytical bias⁸⁶. Gas chromatography is a widely used technique for the analysis of
84 petroleum hydrocarbons^{47,103,105}. Biodegradation of more amenable components of the
85 petroleum mixture leads to relative enrichment of the more recalcitrant species. Incomplete
86 resolution of this more recalcitrant mixture leads to a characteristic “humped” appearance
87 of the gas chromatograms output. The “hump” is the resulting signal produced by many
88 hundreds of components such as cyclic and branched hydrocarbons and is widely referred to
89 as the unresolved complex mixture (UCM). The shape and position of the UCM is not
90 constant and depends on the nature of the original petroleum contamination and the extent of
91 degradation that has taken place in the ground. These issues need to be addressed when
92 implementing a national risk-based framework, as differences in analytical approach may
93 inadvertently result in excessive or inadequate remediation being performed.

94 Risk assessment now is a well-established requirement for the management of
95 contaminated land⁴ and support tool for environmental management decisions. It is widely

96 used as a means of assessing and managing potential impacts to human- and ecosystem
97 health^{4,99}. Several risk-based frameworks for petroleum hydrocarbons in soil have been
98 published under the auspices of the Total Petroleum Hydrocarbon Criteria Working Group
99 (TPHCWG⁸⁸), the American Society for Testing and Materials (ASTM⁵), the Massachusetts
100 Department of Environmental Protection (MaDEP⁵⁵), the Environment Agency of England
101 and Wales (EA³²), the American Petroleum Institute (API³) and the Canadian Council of
102 Ministers of the Environment (CCME¹⁸), each reflecting national legislation and socio-
103 economic issues^{3,100,101}. These frameworks, and the exposure assessment methods embedded
104 within them, do not specifically address weathered hydrocarbons, although many
105 acknowledge that petroleum products released to the environment will have undergone some
106 degree of degradation^{3,6,30,32,55,87}. Weathering of fresh petroleum product makes it very
107 difficult to accurately predict the composition, toxicity and distribution of petroleum at a
108 given site⁵³.

109 Historically the remediation of soil contaminated with petroleum hydrocarbons has been
110 expressed in terms of reductions in total petroleum hydrocarbon (TPH) load rather than
111 reductions in risk. This still remains as standard practice in a number of countries, examples
112 include Portugal and the UK^{30,35}. Recent stakeholder consultations in the UK, and
113 subsequent publications from the Environment Agency, aim to adopt a risk-based framework
114 where remediation is expressed in terms of risk, consistent with other countries (e.g.
115 America⁸⁵, Canada¹⁸ and the Netherlands¹⁰)³⁰⁻³².

116 There are a plethora of approaches to, and techniques available for, the remediation of
117 contaminated land^{1,3,20,28,33,48,62,108,109}. Choice of approach depends on a number of
118 environmental, economic and human health considerations⁵¹. The UK adopts the 'suitable
119 for use' approach as the most appropriate strategy for the sustainable development of
120 contaminated sites^{23,43}. Within the land remediation sector, the EU Landfill Directive⁸⁰ is

121 now encouraging the development and implementation of alternative remediation
122 techniques⁶² and is expected to further increase the cost-effectiveness of bioremediation
123 technologies^{70,77}. This has resulted in increased interest and use of the technique for the
124 remediation of hydrocarbon-contaminated soils.

125 A complete understanding of the contaminant in question is a key component when
126 estimating potential risks to human health. To achieve this, adequate information regarding a
127 substance's environmental fate, behaviour and distribution, toxicity, concentration, and
128 potential exposure at a site is essential³⁰ (Figure 2). In this review then, we critically review
129 these considerations for the successful implementation of a risk assessment framework for the
130 bioremediation of weathered petroleum hydrocarbons.

131

132 **2. CHARACTERISATION OF WEATHERED HYDROCARBONS**

133

134 **2.1. Extraction and analysis**

135 There are several techniques by which petroleum hydrocarbons in soils can be
136 characterised. Method development is often driven by the objectives of published risk
137 assessment frameworks (Table 1)^{3,5,6,17,53,88}. Many frameworks (e.g. TPHCWG, API, CCME,
138 MaDEP) require the quantification of specific indicators and/or fractions; while others
139 consider indicator compounds or chemicals of concern (e.g. ASTM)^{3,17,53,87} (Section 3). It is
140 necessary to use analytical techniques capable of analysing specified aromatic and aliphatic
141 'fractions' as well as the specific indicator compounds selected by the different protocols
142 (summarised in Table 1 and Section 3 of this review). These compounds are known
143 carcinogens including benzene, toluene, ethylbenzene and xylene (BTEX) and the 16 EPA
144 polynuclear aromatic hydrocarbons (PAHs)^{1,17,30,53}. Some frameworks stipulate analysis of a

145 wide range of petroleum hydrocarbons *e.g.* UK approach suggests compounds from an
146 equivalent carbon number (see section 3) of 5 to 70 be examined (Table 1).

147

148 **2.1.1 Extraction of petroleum hydrocarbons from soil and class fractionation**

149 Methods for the extraction of petroleum hydrocarbons from soil samples have been
150 reviewed extensively in the open literature. They include purge and trap (volatiles),
151 headspace (volatiles), manual shaking, Soxhlet, ultrasonic extraction, pressurised fluid
152 extraction, microwave-assisted extraction and super-critical fluid extraction⁸⁶. For heavily
153 weathered fuel oils, extraction of volatile hydrocarbons is rarely considered. Soxhlet
154 extraction is commonly used in research, yet several risk assessment frameworks adopt
155 manual shake methods, *e.g.* TPHCWG, the Agency for Toxic Substances and Disease
156 Registry (ATSDR) and the Texas Natural Resource Conservation Commission
157 (TNRCC)^{1,6,83,86}. This method involves shaking or vortexing 10g (typically) of soil with
158 10ml of an appropriate solvent (typically *n*-pentane) for 1 hour, after which an aliquot is
159 drawn for analysis^{1,59}. The popularity of manual shake/vortex methods is due to a
160 combination of convenience and cost; being quicker, easier, more accessible and cheaper than
161 Soxhlet extraction, with no concentration step required prior to analysis^{34,86}. Additionally
162 legislative analysis requirements within some countries can be met using this method rather
163 than a more exhaustive technique..

164 Soxhlet extraction^{34,86} is the benchmark method for the CCME C₁₀-C₅₀ hydrocarbon
165 range and a component of the United States Environmental Protection Agency (USEPA)
166 methods for semi- and non-volatile organics in soil^{19,91}. Soxhlet extraction is a highly
167 exhaustive extraction technique and can handle both air dried and field moist samples, the
168 latter being facilitated through the addition of chemical drying agents, such as anhydrous
169 sodium sulphate, prior to extraction. A wide range of solvent types can be employed making

170 this technique versatile for different chromatographic end points. The Soxhlet method
171 generates a relatively large volume of extract requiring concentration prior to chemical
172 analysis. This may be seen as a disadvantage due to potential contamination and losses during
173 concentration steps⁸⁶. However losses can be minimised through the use of methods such as
174 kuderna Danish.

175 The time taken to extract a sample using Soxhlet extraction and ultimately its cost has
176 initiated investigations into alternative methods. Hawthorne *et al.* (2000)⁴¹, for example,
177 reviewed methods available for the extraction of PAHs from historically-contaminated soils.
178 Methods reviewed included Soxhlet extraction, pressurized liquid extraction (PLE),
179 supercritical fluid extraction (SFE) and subcritical water extraction (at 300 and 250°C)
180 (SWE). Comparisons were made between hydrocarbon recovery, the effects on the sample
181 matrix, the presence of co-extracted (non-target) matrix material and the relative selectivity
182 for extracting different classes of target organics.

183 The authors concluded that extraction methods that are relatively simple to perform yield
184 the 'dirtiest' extracts; while those yielding cleaner more specific extracts required methods
185 that are relatively complex⁴¹. Soxhlet and PLE yielded much darker and turbid extracts
186 whereas subcritical water extracts were orange to dark orange in colour with moderate
187 turbidity. SFE extracts were light yellow in colour and clear. Soxhlet and PLE yielded more
188 artefact peaks in the gas chromatogram and, due to the extracts from these methods having a
189 high soil matrix content, more frequent cleaning of GC injection ports was required in
190 comparison to SFE extracts⁴¹. However, the development of GC techniques negates this
191 issue due to enhanced sensitivity allowing the analysis of more dilute samples. Although
192 there were minor differences in extraction efficiencies, the quantitative agreement between
193 the methods was reportedly good⁴¹. It has also been shown by Hollender *et al* (2003)⁴⁵ that
194 ultrasonic extraction and accelerated solvent extraction can achieve higher extraction

195 efficiencies when extracting PAHs than Soxhlet extraction. Saifuddin and Chua (2003)⁷⁴
196 compared Soxhlet extraction to microwave-assisted extraction (MAE)⁷⁴. Here, MAE was
197 quicker (~33mins vs. 24hrs for Soxhlet extraction), used less solvent (4ml of solvent
198 compared to 20ml for Soxhlet extraction) and capable of slightly higher extraction
199 efficiencies (82% rather than 77% for Soxhlet extraction). However, samples needed to be
200 free from metallic particles which clearly limits application of this technique to contaminated
201 soils^{22,34}. Additionally, although MAE achieved higher extraction efficiencies, there was no
202 significant difference between the data for MAE and Soxhlet extraction ($\alpha = 0.05$), thus the
203 benefit of a slight increase in extraction efficiency is questionable⁷⁴.

204 Soxhlet extraction is considered a harsh method that extracts a fraction closer to the full
205 capacity of the soil for hydrocarbons, rather than a more biologically relevant analogue of
206 extractability⁷³. It has been suggested that methods that only extract environmentally
207 relevant pollutant molecules should be used^{41,73}. Although any concentration determined by
208 extraction is operationally defined, it may be more appropriate to employ a 'weaker'
209 extraction that may determine a closer analogue of bioavailability and hence potential risk,
210 depending on the use of the data.

211 Non-petroleum based hydrocarbons may result in spurious or elevated TPH
212 concentrations especially when remediation methods employ the use of bulking materials
213 such as woodchip. In order to limit interference, it is necessary to purify samples prior to
214 analysis¹⁰⁷. The most commonly used methods of cleanup employ alumina or silica gel
215 (USEPA methods 3611B and 3630C respectively), used by the TPHCWG, ATSDR, TNRCC,
216 CCME and MaDEP risk assessment frameworks^{1,19,30,53,83}. This cleanup method also
217 facilitates fractionation into aliphatic and aromatic fractions, which is required by MaDEP,
218 TPHCWG, ATSDR and the EA^{6,30,32,53,85}. However it is likely that any moderately polar
219 compounds will be retained in the silica matrix including any which increase in polarity as a

220 result of biotransformation. This may be an issue when analysing weathered hydrocarbon
221 wastes and those undergoing remediation. Attempts to automate the fractionation procedure
222 have resulted in incomplete resolution of the aliphatic and aromatic fractions. Whilst some
223 well resolved components could be eliminated by subtraction, incomplete separation does not
224 address any UCM present. The key fractions affected involve the mono- and di-aromatics.

225 Extracted samples often need to be concentrated prior to analysis, and before and/or after
226 cleanup steps where an unacceptable level of dilution may be introduced *e.g.* Soxhlet
227 extraction^{34,86,93} and class fractionation^{34,86,98}. There are several concentration methods that
228 can be used: Kuderna Danish concentration, nitrogen evaporation, and rotary evaporation. A
229 concentration step is further source of error. For example, identification errors may occur if
230 samples are evaporated too exhaustively during sample preparation using methods such as
231 rapid nitrogen evaporation, where volatile components are most likely to be lost⁵⁰. The use of
232 a keeper solvent such as acetonitrile and methods such as Kuderna Danish, as specified by
233 the USEPA Soxhlet extraction protocol, are considered to minimise such losses⁸⁶.

234 Due to the wide carbon range covered by hydrocarbon products and the tiered nature of
235 some risk assessment frameworks, it is clear that no single analysis technique is likely to be
236 sufficient for analysing soil samples. It would seem sensible that if a tiered risk assessment is
237 used then a systematic tiered analysis strategy be matched to it, as progression to higher tiers
238 and thus higher levels of analytical complexity may not in all situations be necessary. The
239 use of tiered analytical approaches are increasingly being applied in oil spill
240 identification^{102,103}. For example, Wang *et al.* (1997)¹⁰² used a 5 tiered analytical approach
241 that enabled the identification of oil type, degree of weathering and biodegradation.

242 Many of the risk assessment frameworks for petroleum hydrocarbons specify preferred
243 extraction and analytical techniques; some having published their own recommended
244 methods (CCME, TNRCC, TPHCWG and MaDEP¹⁹; Table 1^{1,56,57,83}). The majority specify

245 manual shake or vortexing methods with an appropriate solvent to extract the sample,
246 followed by alumina or silica gel clean up and fractionation into aliphatic and aromatic
247 compounds^{1,30,53,83}. The MaDEP approach specifies volatile petroleum hydrocarbon (VPH)
248 and extractable petroleum hydrocarbon (EPH) determinations. The VPH method uses a
249 purge and trap approach, whereas the EPH method specifies extraction using
250 dichloromethane (DCM), cross-referring to the USEPA extraction method followed by silica
251 cleanup and fractionation prior to analysis^{56,57}. The CCME method specifies purge and trap
252 for the fraction range C₆-C₁₀, or Soxhlet extraction followed by silica gel clean up and
253 fractionation for the C₁₀-C₅₀ range¹⁹. However, it is stated that suitable alternative techniques
254 can be used on the condition that validation data can demonstrate that the alternative method
255 provides data comparable to the benchmark protocol¹⁹. The CCME method allows for use of
256 USEPA methods, adding further quality control measures¹⁹. Although in prescribing
257 methods the CCME is also allowing laboratories to use in-house methods, the validation
258 requirement of these methods should ensure the production of comparable data across
259 laboratories with the presumption of comparable risk assessment and remediation outcomes.
260 Neither the EA nor ASTM specify methods for the extraction of petroleum hydrocarbons in
261 risk assessment, however the EA is to adopt performance criteria rather than prescribing
262 specific approaches^{5,32}. Here, as with the CCME, the emphasis is on quality and reliability of
263 data rather than the use of specific 'gold standard' techniques.

264

265 **2.1.2. Methods for analysis of petroleum hydrocarbons**

266 The techniques used for the analysis of petroleum hydrocarbons can be grouped by their
267 measurement outcome: quantitation of the petroleum hydrocarbon load; of the concentration
268 of different groups of hydrocarbons; or the concentration of specific target compounds⁸⁶.
269 There are also methods for the rapid on-site screening of contaminated soils. However, the

270 majority of these are based on the measurement of vapours derived from the vadose zone by
271 either *in situ* soil gas measurements or headspace analysis. In the case of weathered
272 petroleum hydrocarbons, the relevance of such methods will depend upon time and alteration
273 mechanisms. Further analysis would also be required to enable the analysis of components
274 with low volatility present within weathered hydrocarbons¹⁰⁷.

275 Methods that generate total petroleum hydrocarbon concentrations and group (fraction)
276 concentrations are considered to be non-specific techniques¹⁰³. These generate basic
277 information that is a surrogate for contamination, *e.g.* a single TPH concentration. Such data
278 are not suitable for risk assessment in isolation^{34,86}. However, they are inexpensive, quick
279 and easy and, as such, can offer a useful screening tool^{34,86}. The most commonly used
280 specific methods include gas chromatography (GC), gas chromatography mass spectrometry
281 (GC-MS), gas chromatography with flame ionization detection (GC-FID), infrared
282 spectrometry (IR), thin layer chromatography (TLC) and gravimetric analysis⁸⁶. Gas
283 chromatographic methods are the most preferred TPH measurement techniques as they offer
284 relative sensitivity, selectivity, and can be used to identify risk critical compounds. As the
285 compositions of crude oil and petroleum products are highly complex and display a high
286 degree of between-oil variation, unique chemical ‘fingerprints’ for each oil can be isolated.
287 These can be used to aid identification of the source of weathered oil contamination¹⁰³.
288 Techniques such as GC require additional skills/experience compared to other methods and
289 require that samples are volatile at the operating temperature of the column²². Issues also
290 arise with co-elution of compounds as petroleum hydrocarbons comprise many isomers with
291 similar boiling points and thus retention times. Weathered hydrocarbons typically exhibit
292 low volatility, high boiling temperatures and require high column operating temperatures.
293 This can vary depending upon the starting product and whether sorbed or mobile fractions are
294 under analysis. GC techniques can be adapted to enable the analysis of specific hydrocarbon

295 ranges, such as gasoline range organics (GRO) and diesel range organics (DRO)³⁴ but are
296 often unable to resolve a large proportion of UCMs, characteristic of weathered petroleum
297 hydrocarbons¹⁰⁷. This may become an issue as more toxicological data becomes available in
298 the future.

299 Gas chromatography coupled with mass spectrometry detection (GC-MS) is routinely
300 applied for the identification and measurement of individual petroleum hydrocarbons. These
301 methods have a high level of selectivity, with the ability to confirm compound identity
302 though the use of retention time and unique spectral patterns. GC-MS requires specialist
303 operation and interpretation of the data and, as such, it can be more expensive than other GC
304 methods depending on the market forces. GC-MS offers target analyte confirmation, non-
305 target analyte identification and can be used to separate hydrocarbon classes⁴⁷. Even with
306 ready benchtop availability, some jurisdictions have felt unable to recommend GC-MS
307 analysis of petroleum hydrocarbons to inform risk assessments⁴⁷. The analysis requirements
308 of current frameworks can be easily met, relatively cheaply by GC-FID. The MaDEP
309 method adopts GC-FID methods along with the majority of risk assessment frameworks.

310 In response to the difficulties with traditional methods for the analysis of weathered
311 petroleum hydrocarbons, alternative and specialised methods have been developed¹⁰⁷.
312 Whittaker *et al.*, in reviewing both conventional and novel analytical techniques for the
313 characterisation of refractory wastes, highlighted several of these including simulated
314 distillation gas chromatography (GC-SIMDIS), thin-layer chromatography with flame
315 ionisation detection (TLC-FID), high-performance liquid chromatography (HPLC) and laser
316 desorption laser photoionisation time-of-flight mass spectrometry (L²TOFMS)¹⁰⁷.

317 The coupling of curie point pyrolysis to GC-MS (Py-GC-MS) is an alternative method to
318 conventional techniques for the analysis of non-volatile compounds such as rubbers, paints
319 and synthetic plastics and has been applied to several sample matrices including soil¹⁵.

320 Recently, Buco *et al.* evaluated this technique for the analysis of the 16 PAHs included in the
321 USEPA priority pollutant list, and demonstrated repeatability within the range of classic
322 techniques (RSD = 3.4%) with good accuracy for the measured PAHs¹⁵. This technique is
323 quick, involves no cleanup and does not require an extracting solvent. Particularly effective
324 for low-molecular-mass PAHs, high molecular mass PAH quantification was complicated by
325 reduced sensitivity. This may limit Py-GC-MS use for analysis of weathered petroleum
326 hydrocarbons¹⁵. Additionally the small sample volume used makes the homogenization of
327 samples critical for accurate analysis¹⁵. These authors concluded that Py-GC-MS is suited to
328 use as an alternative screening method for contaminated soil or sediment¹⁵.

329

330

331 **3. RISK MANAGEMENT FRAMEWORKS FOR HYDROCARBONS**

332

333 Risk assessments should provide an “objective, scientific evaluation of the likelihood of
334 unacceptable impacts to human health and the environment”⁶⁵. Where a ‘pollutant linkage’
335 between the source of a hazard and a receptor is present^{3,70,103,105}, estimates of exposure are
336 often used to characterise risks to human health, comparing the potential intake of
337 contaminants with acceptable or tolerable intakes inferred from toxicological or
338 epidemiological studies. Many risk assessment frameworks adopt a three tiered approach
339 with increasingly sophisticated levels of data collection and analysis⁵. As assessors move
340 through the tiers, the generic and conservative approach of the earlier tiers is replaced with
341 more detailed and site-specific assumptions^{3,5,30}, although each tier aims to be protective of
342 human health^{3-5,30,32,55}. The progression to higher tiers involves additional cost due to
343 increased analytical and site investigation requirements. This expenditure enables a more
344 complete characterisation of contaminants resulting in a more comprehensive risk assessment

345 and more cost-effective corrective action (risk management) plans⁵. Site-specific
346 assumptions resulting from use of the higher tiers may increase the cost-effectiveness of the
347 remediation, and so assessors need to balance the increased cost and time against potential
348 benefits before proceeding to the next level⁵. Cost-benefit analysis techniques are built into
349 some risk assessment frameworks to facilitate decision making for tier transission³.

350 Different countries and organisations consider aspects of risk assessment frameworks
351 differently. For example, residential exposure scenarios have not been considered as relevant
352 in the API framework³. This is because the most realistic future use for exploration and
353 production (E&P) sites are for ranch, agricultural or parkland land uses.

354 Hydrocarbon-contaminated soils contain many hundreds of different compounds.
355 Although it may be feasible to identify each of the compounds present, this would be
356 unnecessarily time consuming. Further, data describing the toxicity, partitioning, fate and
357 transport characteristics of the different compounds are not currently available^{3,55}.
358 Identification and assessment of all compounds would be burdensome which would not be
359 practicable for stakeholders^{30,32}. Therefore, surrogate measures for carbon fractions of
360 toxicological significance, such as boiling point and carbon number ranges, have been used to
361 simplify the assessment process⁵. Furthermore, risk management frameworks have focused
362 on a limited subset of key components, using broad observations regarding the characteristics
363 of known petroleum hydrocarbons to group compounds into fractions and identify key toxic
364 compounds for use as indicators^{3,5}. Typically, petroleum fractions are used to consider
365 threshold health effects while indicator compounds are used to evaluate non-threshold health
366 effects³².

367 Approaches such as the ASTM⁵ risk-based corrective action (RBCA) framework use
368 indicator compounds as a surrogate for risk. This approach was deemed by MaDEP⁵³ as
369 insufficient for characterising risks posed at a petroleum hydrocarbon release site and

370 fractions were introduced. The definitions of specific fractions are derived from either the
371 carbon number (C_n) or equivalent carbon (EC_n) number. For example, MaDEP uses
372 fractions to evaluate the threshold contaminants and indicator compounds (or ‘target
373 analytes’) to evaluate non-threshold toxicity^{5,30,53}. The MaDEP approach is one of the few
374 approaches that use carbon numbers. Here TPH fractions are based upon “chemical
375 structure, carbon number, and structure activity relationships”⁵⁴. The majority of
376 frameworks use equivalent carbon numbers (EC_n), *e.g.* TPHCWG³⁰ because these are
377 considered more closely related to the mobility of a compound in environmental media³⁰. As
378 such, EC_n are based on “a range of physical-chemical properties and simple partitioning
379 models”⁸⁴. In practice, the boiling point of the compound of interest on a non-polar GC
380 column is used to derive EC_n , assuming the relationship between boiling point and EC is the
381 same for both aromatics and aliphatics. In characterising the toxicity of a fraction, surrogate
382 compounds or mixtures that are well characterised and characteristic of a particular fraction
383 are often used^{30,87}.

384 The validity of the equivalent carbon number may be challenged. For example, the
385 TPHCWG derive EC_n using a simple empirical binomial model parameterised using data
386 describing the boiling point (T_B , °C) and carbon number of 75 key hydrocarbons; where K_1
387 and K_2 are empirical constants, and C is the intercept (Equation 1).

$$388 \quad EC_n = K_1[T_B]^2 + K_2[T_B] + C \quad (1)$$

389 At best, this provides only a rough estimate of EC_n (e.g. a measured EC value of 31.3 for
390 benzo[a]pyrene compared to the calculated value of 30.0 using Equation 1). Also, a T_B of 548
391 should relate to EC_{44} , however calculating this from Equation 1 provides a value of $EC_{34.6}$.
392 Clearly there is a disparity between the TPHCWG model and the empirical data. Different
393 parameterisations will have an effect on calculated EC_n . Figure 3 shows a series of fitted
394 binomial models based on four different parameterisation data sets. As the boiling point

395 increases, a clear disparity emerges between the *n*-alkanes and the PAHs. This can be seen
396 most clearly in the “empirical” plot (Figure 3), between boiling point 450 and 550 °C, where
397 PAHs have markedly lower EC numbers than the *n*-alkanes. Figure 3 suggests that the EC_{*n*}
398 approach is unsuitable, particularly for substances EC_{>20}. Simple empirical models, such as
399 Equation 1, do not hold true; and the theory that T_B can be used to calculate EC_{*n*}
400 representative of normalisation to the *n*-alkanes appears to be incorrect. However, the
401 implications for risk assessment are likely to be minimal, considering the heterogeneity of
402 soils.

403 Aromatic and aliphatic compounds differ in their toxicity, solubility and fate and
404 transport characteristics⁵⁵. Because of this, and the evidence shown in Figure 3, some
405 frameworks employ fractions where aliphatic compounds are considered separately to
406 aromatic, which are further fractionated by (equivalent) carbon number (Table 2). Each
407 fraction may then be treated as if it were a separate compound in the environment^{3,53,87}
408 However, the ‘New Zealand Approach’⁶⁰ only considers aliphatic fractions while the
409 aromatic fraction is addressed separately by direct measurement of BTEX and PAH
410 concentrations³⁰.

411 Toxicity values are assigned to the fractions and indicators used. This is achieved through
412 the process of review and/or extrapolation of available toxicological data on hydrocarbon
413 mixtures and specific hydrocarbon compounds⁵⁴. The number of fractions and their ranges
414 vary between frameworks (Table 2), and in general build upon or adapt the fractions defined
415 by TPHCWG and MaDEP. Various bodies have adapted these ranges. For example, The
416 New Zealand approach uses three aliphatic fractions, while the TPHCWG approach employs
417 13 analytical fractions (6 aliphatic, 7 aromatic) covering the range from EC₅ – EC₃₅^{30,55,84,85}.

418 The API extended the fractions used by the TPHCWG so that there is a >EC₂₁-EC₄₄
419 aromatic fraction and a >EC₁₆-EC₄₄ fraction along with an additional EC₄₄₊ combined

420 aliphatic and aromatic fraction (as it is not physically possible to separate hydrocarbons of
421 this size into fractions)³ (Table 2). This step was taken due to the TPHCWG fractions not
422 encompassing hydrocarbons with carbon numbers greater 35 which can make up to 60% ^{w/w}
423 of some crude oils³ and is characteristic of weathered hydrocarbons. It was also considered
424 that the TPHCWG fractions were appropriate for most refined products but not the crude oils
425 present at the majority of E&P sites³. Toxicological and fate and transport data for these
426 heavier hydrocarbons (>EC₃₅) are sparse⁵⁵. As such, the API assigned the characteristics of
427 the next closest aliphatic or aromatic carbon number fractions to the EC₃₅-EC₄₄ aliphatic and
428 aromatic ranges^{3,6,30,54,87} deriving oral and dermal reference doses of 0.03mg/kg/day and
429 0.8mg/kg/day respectively (as EC₄₄ has extremely low volatility no inhalation reference dose
430 was set by API³). The EA approach extends these carbon ranges further (Table 2), resulting
431 in 16 fractions, giving an overall range from EC₅-EC₇₀. Further to the TPHCWG fractions,
432 the EA added an aromatic EC₃₅-EC₄₄ range, an aliphatic EC₃₅-EC₄₄ range and a combined
433 aromatic and aliphatic EC₄₄-EC₇₀ range^{30,32}. Research is currently underway to examine the
434 implications of this extended set of hydrocarbon ranges⁶⁸. The use of surrogate data from the
435 next closest hydrocarbon fraction may be overly conservative and thus not cost-effective. In
436 the case of the API approach, the next closest fraction usually encompasses petroleum
437 hydrocarbons with lower molecular weights, and as such would be characterised with a
438 greater degree of mobility within the environment³. Further research into the characteristics
439 of heavier compounds may provide a more complete understanding of their behaviour within
440 the environment and potential risks to human health. It could also potentially result in a
441 reduction in the analysis and remediation requirements enabling the risk assessment to
442 become more streamlined.

443

444 **4. BIOREMEDIATION**

445

446 The bioremediation of contaminated soils has been extensively reviewed. Bioremediation
447 methods utilise naturally occurring biological processes to transform, decrease or eliminate
448 polluting substances^{13,28,33,40,62}. Theoretically, optimal conditions are provided for bacteria or
449 fungi to degrade or transform more complex compounds (*e.g.* contaminants) into relatively
450 simple constituents that may pose a lesser potential risk to humans or ecosystems. An
451 idealised bioremediation method would use harmless reagents, enable the process to be
452 carried out quickly and efficiently (on-site), and result in an acceptable soil product that can
453 be re-used with little/no further modification¹⁵. Compared to other remediation approaches,
454 bioremediation often has greater analytical and process control requirements. From an
455 engineering perspective, the processes and logistics of bioremediation are relatively simple³³.
456 Any increased expense due to greater analytical and process requirements is usually offset by
457 lower capital costs^{20,33}. In 2000, an EA survey indicated that organic pollutants accounted for
458 83% of contaminants remediated at contaminated sites in England and Wales³⁰,
459 demonstrating the applicability of bioremediation within the UK land remediation sector.

460 The disadvantages of bioremediation include the potential unpredictability of
461 performance, difficulties in scaling up from laboratory to field and relatively long
462 (weeks/months) remediation times. Bioremediation is not universally suitable for all
463 contaminants⁴⁸. High concentrations of heavy metals and other highly toxic compounds can
464 be prohibitive of microbial growth⁴⁸, or still leave the remediated soil unfit for purpose and
465 classed as contaminated due to the residual presence of inorganic contaminants. Although
466 bioremediation can breakdown potentially toxic contaminants, this process may result in the
467 formation of metabolites that are toxic in their own right³³. Contaminants need to provide an
468 energy and carbon source to enable microbial growth, and so need to be biologically

469 degradable or transformable^{27,48}. Hence, biological remediation systems are more suited to
470 organic contaminants, including weathered petroleum hydrocarbons⁴⁸.

471

472 **4.1. Bioremediation techniques**

473 The choice of bioremediation technique can depend on a number of site specific factors,
474 including the type, mobility, concentration and volume of a contaminant, the soil structure,
475 surrounding geology, the proximity to structures and potential receptors, and intended end
476 use^{13,20,28,33,62}. There is no single method for every situation and often combinations of
477 techniques are implemented at sites with multiple contamination sources. Bioremediation
478 processes can be divided into *in-situ* and *ex-situ*. *In-situ* methods include monitored natural
479 attenuation^{12,13,28,43,48,58,62}, biosparging^{13,25,62} and bioventing^{13,33,36,48,62}. They have the
480 advantage of not requiring the excavation or removal of soil^{13,20,33,62}. They are able to deal
481 with deep contamination and enable remediation both under and around buildings²⁰. These
482 techniques minimise problems with dust, and hence worker exposure may be reduced^{20,33,62}.
483 *In-situ* techniques can adapt, enhance and control bioremediation conditions. However, they
484 are limited by the degree of process control that can be used. In comparison, *ex-situ* methods
485 are contained and offer a higher degree of process control with greater control over time²⁷.
486 Techniques can be performed on or off site depending on the restrictions present at a
487 particular site²⁰. Overall, *ex-situ* methods are considered to be more efficient than *in-situ*
488 techniques¹³ and can deal with higher concentrations of contaminants²⁷. *Ex-situ* techniques
489 include landfarming, composting, biopiling and bioreactor treatments³³.

490 'Landfarming' (also known as 'land treatment') is a simple technique used to treat large
491 areas of land. Land farming has been used for the remediation of many waste types, but
492 mainly for the remediation of hydrocarbon contaminated soils^{13,20,46}. Landfarming involves
493 the excavation and spreading (to 0.3-0.5m thickness²⁸) of contaminated soil over a banded

494 area (incorporating a leachate collection system and impermeable liner material^{13,28,62}) which
495 is tilled to aerate the soil at regular intervals^{20,28,33}. Composting is an aerobic process using
496 systems that involve the construction of piles, often using bulking agents to increase porosity
497 and facilitate airflow^{13,33}. Anaerobic conditions can also be used to compost wastes;
498 however, this can result in the synthesis of unpleasant odorous compounds such hydrogen
499 sulphide²⁰ and the generation of methane. Purpose built closed reactor composting systems
500 can be used to compost wastes, and have been used as the basis of soil treatment centres in
501 mainland Europe^{13,20,62}. Here, the soil is combined with water to form a slurry which is
502 continuously mixed using mechanical agitators, giving rise to improved contact between the
503 pollutants and the microorganisms^{33,62}. Closed systems provide a high degree of process
504 control over environmental conditions and allow for the control and treatment of volatile
505 compounds. However they are more expensive than open systems such as windrows³³.

506 Engineered biopiles are an intensive static pile version of composting that enable greater
507 control over important environmental factors that effect biotransformation rates (i.e. oxygen,
508 water and nutrient levels¹³) compared to other methods. This intensive method is especially
509 useful when space is limited¹³. Details regarding biopile design and operation can be found
510 elsewhere^{11,13,20,28,40}.

511 As highlighted by some of the responses to the EAs survey²⁷, the timescale in which
512 pollutants can be remediated is an important consideration when selecting the most
513 appropriate remedial treatment to use at a given site. Cost, guaranteed insurance, and risk
514 reduction were also cited as reasons for not using bioremediation methods. Engineered
515 biopiles offer a high degree of control, have a smaller footprint and are comparatively quick,
516 yet they are not as expensive as closed bioreactor systems (~£10-40 per m³ vs. ~£30-150 per
517 m³)¹³. This makes biopiling attractive to contaminated land remediation specialists,

518 especially as the high degree of control allows the processes to be optimised for
519 biotransformation of specific pollutants of interest.

520 Bioremediation works well for remediating soils contaminated with petroleum
521 hydrocarbons^{36,49}. Most studies have reported biotransformation to be rapid in the initial
522 stages of bioremediation, with rates seen to asymptote as the weathered proportion is
523 biotransformed^{26,37,111}. Weathered petroleum hydrocarbons have typically been present in the
524 soil for a long period of time, they display relatively low bioavailability, and thus are more
525 recalcitrant in the environment⁴⁰. As a result, the optimisation of environmental conditions is
526 imperative for the remediation of land contaminated with weathered petroleum
527 hydrocarbons⁴⁰. Giles *et al.* (2001) studied the bioremediation of weathered oil sludge (C₂₀-
528 C₃₈) in composting piles. A biotransformation of 97% %^{w/w} TPH was achieved after 10
529 weeks. This study showed that indigenous bacterial populations were more suited to
530 biotransforming the sludge²⁸. Unexpectedly, the bulking agent used had a greater effect on
531 biodegradation than augmentation with a consortia of oil-degrading bacteria. The authors
532 suggested that the bulking agent achieved higher degradation rates (complete compost) due to
533 the presence of indigenous hydrocarbon-degrading microorganisms. However, this may have
534 been due in part to the increased adsorption capacity of the amended soil matrix. It was
535 suggested that this material was effective at modulating the temperature thus maintaining the
536 bacteria within their optimal range³⁸.

537

538 **4.2. Optimising bioremediation**

539 Contaminated soils usually contains a number of microbial species capable of degrading
540 the contaminants present²⁸. The degradation process can be enhanced through biostimulation
541 and bioaugmentation. The former refers to the enhancement of the bioremediation process by
542 optimising specific environmental parameters such as temperature, pH, oxygen partial

543 pressure, moisture and nutrient levels^{33,62}. The latter describes the augmentation of
544 bioremediation systems with commercially available microbial cultures which, in some cases,
545 perform specific functions^{13,28,40,62}. Bioaugmentation may be required where native microbial
546 populations are insufficient to achieve effective biotransformation. For example
547 *Phanerochaete chrysosporium* (white rot fungus) can aid in the degradation of problematic
548 recalcitrant compounds²⁸. However, it should be noted that resulting increased costs are
549 rarely justified by the benefits²⁸. Additionally, it was shown by Trindade *et al.* (2005)⁸⁹ and
550 Giles *et al.* (2001)³⁸ that indigenous micororganisms can be better adapted and more resistant
551 to the contaminants present, with greater remediation potential than foreign organisms^{28,38,89}.
552 Typically, the addition of foreign organisms are not required when degrading hydrocarbons¹¹.

553 To grow, microorganisms require an electron donor (source of energy) and an electron
554 acceptor as a means of extracting energy from the electron donor. Thus, electron acceptors
555 play a key role in the biotransformation of a contaminant (the energy source – electron
556 donor). Potential electron acceptors for microbial activity are (in order of energy yield,
557 highest first): oxygen, nitrate, iron, manganese, sulphate, carbon dioxide and organic
558 carbon⁴⁹. Clearly as oxygen yields the highest amount of energy it is the preferred electron
559 acceptor and is important to optimise its diffusion into- and concentration within the soil
560 matrix (typically need to keep oxygen in the soil gas >2%).

561 Different bacterial classes require different temperature ranges to achieve optimum
562 growth. For example, mesophiles grow from about 15° to 45°C⁴⁹ whereas thermophiles grow
563 best between 45° and 65°C^{33,49}. Typically during bioremediation mesophilic temperatures
564 are common, with Giles *et al.* (2001)³⁸ having found optimum growth for the bacteria present
565 during the bioremediation of a weathered oil sludge to be less than 45°C³⁸.

566 The pH of the soil can inhibit microbial activity and also affect the solubility of
567 important nutrients such as phosphorus^{33,49}. The typical optimum pH range for

568 bioremediation is from pH 5.0 – 9.0, with a pH of 7.0 being preferable. Giles *et al.* (2001)³⁸
569 reported a soil pH of 6.1 during the bioremediation of a weathered oil sludge, suggesting that
570 the ‘typical’ bioremediation pH range is likely to be suitable for weathered petroleum
571 hydrocarbons.

572 Water is essential for microbial growth and maintenance and also serves as a transport
573 medium through which organic compounds, contaminants and nutrients are transported into
574 the cells and waste products from the cells^{33,49}. Achieving a suitable water balance within the
575 biopile can be critical as dry zones may result in decreased microbial activity³³. Conversely,
576 saturation inhibits gas exchange resulting in anaerobic conditions³³. The typical optimum
577 water content range is within 55-80% by weight of the water-holding capacity^{13,49}. Bacteria
578 also require nutrients (carbon, nitrogen, phosphorous, and in lesser quantities potassium,
579 sodium, magnesium, calcium, iron, chloride and sulphur¹³) for the assimilation and synthesis
580 of new cell materials^{13,33,49}. The depletion of nutrients can effect the biotransformation of
581 contaminants, in response bioremediation systems can be amended with fertilisers containing
582 appropriate quantities of the rate-limiting nutrients^{11,40}.

583 It is clear that successful bioremediation relies on the optimisation of several parameters.
584 Thus, prior to the remediation of contaminated land it can be useful to assess the treatability
585 of the soil and identify requirements for bioremediation.

586

587

588 **5. DISCUSSION**

589

590 The preceding sections of this review have provided an overview of the issues for the
591 management of risks from weathered hydrocarbons. Summarising this material is insightful
592 in that it illustrates trends and approaches from a variety of perspectives. The view expressed

593 is that thirty years of research into petroleum microbiology and bioremediation have
594 bypassed an important observation - that many hydrocarbon-contaminated sites posing
595 potential risks to human health harbour weathered, 'mid-distillate' or heavy oils. These sites
596 present considerable challenges to remediation over and above those posed by fresh or more
597 refined petroleum distillates. Critically, there are important scientific components that drive
598 risk management for these wastes and specifically the partitioning of risk-critical compounds
599 within the oil/soil matrix.

600 Whilst early work suggested the recalcitrance of these wastes to microbial breakdown,
601 we now know that the risks from these wastes can be actively managed through optimising
602 treatment process parameters during bioremediation. This said, the 'in-field' verification of
603 *ex-situ* technologies such as biopiling, continues to be expressed in many countries in terms
604 of reductions in total petroleum hydrocarbon (TPH) load, or 'losses' from the soil being
605 treated, rather than by reference to reductions in risk. An observation from the UK is that the
606 absence of risk from the vocabulary of many remediation operators and remediation projects
607 reduces stakeholder (regulatory, investor, landowner and public) confidence in technology
608 performance, and in doing so, limits the market potential of these technologies.

609 For weathered hydrocarbon wastes, risk management decisions are complicated by the
610 gross complexity of the source term, the effects of weathering on the bioavailability of risk
611 critical contaminants and the variable performance of remedial technologies under authentic
612 site conditions. For heavy oils (the viscous (50-360 mPa s), high-boiling (ca. 300 - >600 °C)
613 products such as No. 6. fuel oil with carbon ranges in excess of C₂₀), their inherent
614 complexity is further compounded as they weather in the environment on account of biotic
615 and abiotic losses that shift their chemical composition towards recalcitrant, asphaltenic
616 products of increased hydrophobicity.

617 These changes raise an important feature of hydrocarbon contaminated land that is often
618 overlooked – that the source term, the oil matrix, is itself a strong partition medium for risk
619 critical compounds and weathering imparts further hydrophobicity to the oil matrix.
620 Compositional changes dramatically affect the partitioning behaviour of these source terms
621 prior to, during and following biological treatment. Risk critical components (*e.g.* the higher
622 ring polynuclear aromatic hydrocarbons (PAH)) in weathered oils are less bioavailable
623 because they are effectively partitioned within the source term in accordance with Raoult's
624 Law. Sun and Boyd (1991)⁷⁸ first suggested the concentration of residual oil within a oil-soil
625 matrix required for it to act as a discrete partition medium (*ca.* 1000 mg/kg) and suggested
626 that this residual oil, as the original source of priority contaminants, could typically be ten
627 times more an effective partition medium than soil organic matter for hydrophobic organics.
628 This is rarely represented within the fate and transport models that support the environmental
629 exposure assessment of hydrocarbons with the possibility that regulatory exposure
630 assessment models may dramatically over estimate the availability of risk-critical compounds
631 through exposure routes. There is prior art here. Zemanek *et al.* (1997)¹¹³ showed that
632 between 71-96%^{w/w} of PAH in weathered diesel-contaminated loam soils were partitioned to
633 residual oil (at 2-6%^{w/w} of the total soil composition) in petroleum and weathered creosote-
634 contaminated soils, with 84%^{w/w} of benzo[*a*]pyrene partitioned to the residual oil phase.
635 Woolgar and Jones (1999)¹¹⁰ estimated oil - water partition coefficients (termed log K_{mw}) for
636 a series of PAH to be between 4.5 - 6.5, dependent on the source term. Under these
637 conditions, highly partitioned constituents in weathered hydrocarbon waste matrices may be
638 biologically inaccessible to microbial communities and resistant to biotransformation.
639 However, their very inaccessibility may, but not necessarily, also restrict the dose available
640 to receptors. Clearly, attempts to improve the bioavailability of these components to
641 microorganisms during bioremediation may also result in increased human exposure. In

642 estimating the fate of pollutants in complex environmental matrices, the application of
643 fugacity models⁵² for predicting the relative phase distributions and concentrations of
644 contaminants and their metabolites during treatment^{75,76} is now proving valuable for
645 informing exposure assessments and the optimisation of *in-situ* remediation. These
646 approaches have yet to be applied to the biopiling of weathered oils or to account for the
647 partitioning behaviour of PAH in weathered non-aqueous phase liquids (NAPL) within the
648 unsaturated zone. In short, the relationships between chemical presence, toxic response,
649 bioavailability and risk for weathered hydrocarbons have yet to be fully elucidated and
650 coupled into a meaningful risk management framework, though work is progressing^{29-32,81}.
651 One of the obvious research needs is to authenticate human exposures to oil/soil matrices in
652 the context of contaminated land and, in particular, to explore the bioavailability of risk-
653 critical compounds (benzene, benzo[*a*]pyrene) in light of these newly revealed partition
654 relationships.

655 The regulation of site remediation now requires adoption of a risk-based approach and
656 this extends to technology verification²⁹. Whereas the effectiveness of an environmental
657 technology in treating pollution has historically been expressed as a percentage reduction in
658 the pollutant concentration released to, or found in, a media of concern, regulators are
659 increasingly concerned with mass, toxicity and risk reductions within the multimedia,
660 multiphase environment. For petroleum hydrocarbons in soil, international regulatory
661 guidance on the management of risks from contaminated sites is now emerging. As shown in
662 this review, much of this guidance promotes the use of risk management frameworks to
663 guide decision-making, the application of reference analytical methodologies and the
664 derivation and use of acute, sub-chronic, and chronic toxicological criteria for these wastes.
665 These frameworks adopt a variety of approaches to the evaluation of risk-critical components
666 within the hydrocarbon waste-soil matrix.

667 In the US, a substantive research effort has focused on integrating hydrocarbon fate and
668 transport, petroleum microbiology and environmental diagnostics to inform regulatory
669 processes for site management under the Superfund Program. ThermoRetec (2000)⁸¹,
670 reporting for the Petroleum Environmental Research Forum (PERF), provide an authoritative
671 account of the central importance of partitioning within soil-bound hydrocarbons in
672 developing environmentally acceptable endpoints (remedial objectives). Drawing on a
673 detailed understanding of NAPL and residual oil fate and behaviour, this work is now
674 influencing the development of remediation criteria for petroleum hydrocarbon in soils in the
675 US for human health, groundwater and ecological receptors, and a reappraisal of the level of
676 residual petroleum hydrocarbons that can be left at remediated sites without posing an
677 unacceptable risk. In contrast, weathered, mid-distillate and heavier oil sources are generally
678 given a narrow treatment by these reviews and frameworks. The Environment Agency
679 (2003)³⁰ have recognised this in their recent consultation on principles for evaluating the
680 human health risks from petroleum hydrocarbons in soils, and have called for views. One of
681 the few environmental exposure assessments explicitly to address heavy oils has been
682 discussed in a recent article relating to worker and visitor exposure following the wrecking of
683 the oil tanker 'Erika' in 65 km south of the Brittany coast⁷. Here, inhalation, dermal and oral
684 PAH exposures from beached No. 6 fuel oil were estimated and found to be negligible for
685 beach cleaners and tourists (occasional visitors) coming into contact with heavy oil,
686 demonstrating the feasibility of this level of risk analysis for these problematical wastes.

687 The move towards risk-based corrective action (RBCA) has been slow in the UK and,
688 whilst some progress has been made in integrating the aspects of analysis, exposure
689 assessment and technology verification²⁹, there are gaps in the current knowledge base.
690 Specifically: (i) analytical strategies in the UK are not generally targeted at the
691 bioavailability of risk-critical components; (ii) risk assessments do not regularly account for

692 highly weathered residues encountered at many sites (API, 2001); and (iii) treatment
693 ‘success’ is still supported by reductions in hydrocarbon load in isolation of combined
694 reductions in toxicity, chemical mass and risk. In a typical study, Al Awadhi *et al.* (1996)²
695 report an 80%^{w/w} reduction in oil from heavy oil-laden landfarming plots in Kuwait over a
696 15 month research period and Milne *et al.* (1998) between 30-50%^{w/w} reductions in TPH
697 from heavy refinery sludge treated in amended composting plots over the treatment period.
698 Guerin (2000)³⁹ reports a 5 –year performance study of a land treatment facility for oil
699 wastes from heavy vehicle maintenance. Most of these studies and many of those since (e.g.
700 Tien *et al.*, (1999)⁸² and Owens and Bourgooin, (2003)⁶⁷) follow a pattern of reporting
701 reductions in TPH load as a presumed surrogate for risk reduction.

702 A contributing factor to the over-reliance on TPH as an indicator of treatment
703 performance in isolation of other parameters, has been the cost of implementing more
704 sophisticated diagnostic techniques and their low uptake within the sector. This has been, in
705 part, as result of the absence of a regulatory framework. Nevertheless, researchers have been
706 concerned with improved diagnostics methods (the analysis of specific carbon number
707 ranges); the fingerprinting of hydrocarbon wastes for source identification (for liability
708 disputes) and in tracking biotransformation; and with biological techniques as indicators of
709 the impact of hydrocarbon contamination on soil function. Recent initiatives have included
710 the development of reference methods for the analysis of petroleum hydrocarbons from nC_6-
711 C_{50} ^{19,83}, the application of biomarker analysis (*n*-alkane: substituted *n*-hopane indices) to
712 bioremediation verification^{45,61,100} and the validation of microbial bioassays for petroleum
713 hydrocarbons in soil^{24,68}. Our own work⁶⁹, building on that of Prince *et al.* (1994)⁷²
714 demonstrated that the ratio of total alkanes (Σn -alkanes) to 17 α (H)21 β (H)-hopane to be the
715 most sensitive of a series of biomarker ratios in reflecting oily waste depletion in a 256-day
716 soil microcosm study.

717

718

719 **6. CONCLUSIONS**

720

721 Risk assessment is a well-established paradigm for the management of contaminated
722 land⁴. However, the move towards risk-based corrective action has been slow. Recent
723 stakeholder consultations in the UK, and subsequent publications from the Environment
724 Agency, aim to adopt a risk-based framework where remediation success is expressed in
725 terms of risk rather than TPH load reductions.

726 There are several risk assessment frameworks for land contaminated with petroleum
727 hydrocarbons including those published by TPHCWG⁸⁸, ASTM⁵, MADEP⁵⁵, Environment
728 Agency³², API³ and CCME¹⁸. However, none of these specifically deal with weathered
729 petroleum hydrocarbons, which are widely acknowledged to have major qualitative and
730 quantitative differences compared to non-weathered petroleum hydrocarbons⁸⁷. Additionally,
731 there are variations between frameworks that may result in different recommendations e.g.
732 the level of remediation to be achieved. As shown, the use in some frameworks of deriving
733 equivalent carbon numbers from empirical relationships representative of normalisation to the
734 *n*-alkanes appears to be incorrect. In general, variations between frameworks occur in the
735 determination of the range used, how toxicity is assessed and how soil samples are analysed.

736 Beyond the regulatory perspective, researchers have been involved in improving
737 diagnostics methods (the analysis of specific carbon number ranges); the fingerprinting of
738 hydrocarbon wastes for source identification (for liability disputes) and in tracking
739 biotransformation; and with biological techniques as indicators of the impact of hydrocarbon
740 contamination on soil function. There has also been increased interest in the use of fugacity

741 models for making inferences about the fate and transport of risk-critical compounds within
742 contaminated soils.

743 Many of these advances have yet to be synthesised into regulatory tools. However, there is
744 growing support for the move towards compound-specific risk-based approaches for the
745 assessment of hydrocarbon-contaminated land.

746

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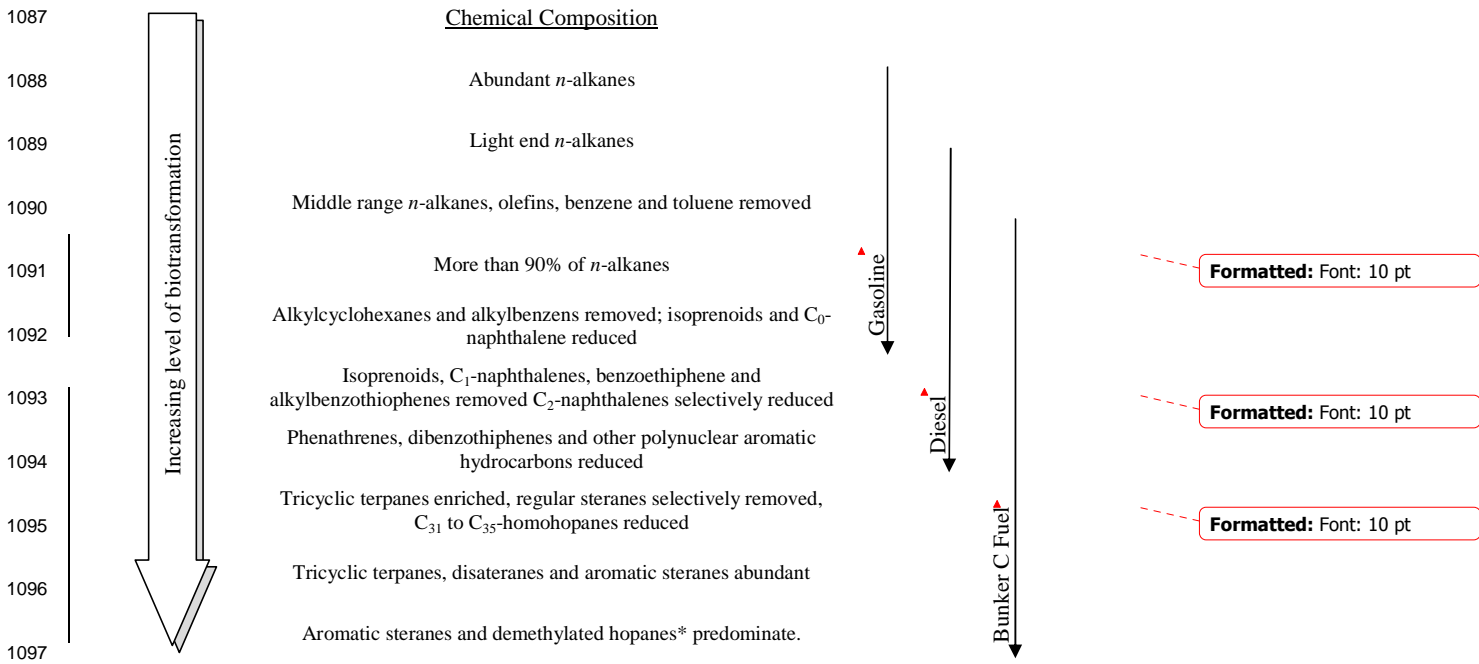
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1084 **FIGURES & TABLES:**

1085 *Figure 1: General petroleum hydrocarbon degradation pattern (modified after Kaplan et al.,*
 1086 *(1996)⁵⁰)*



* Present under special conditions only.

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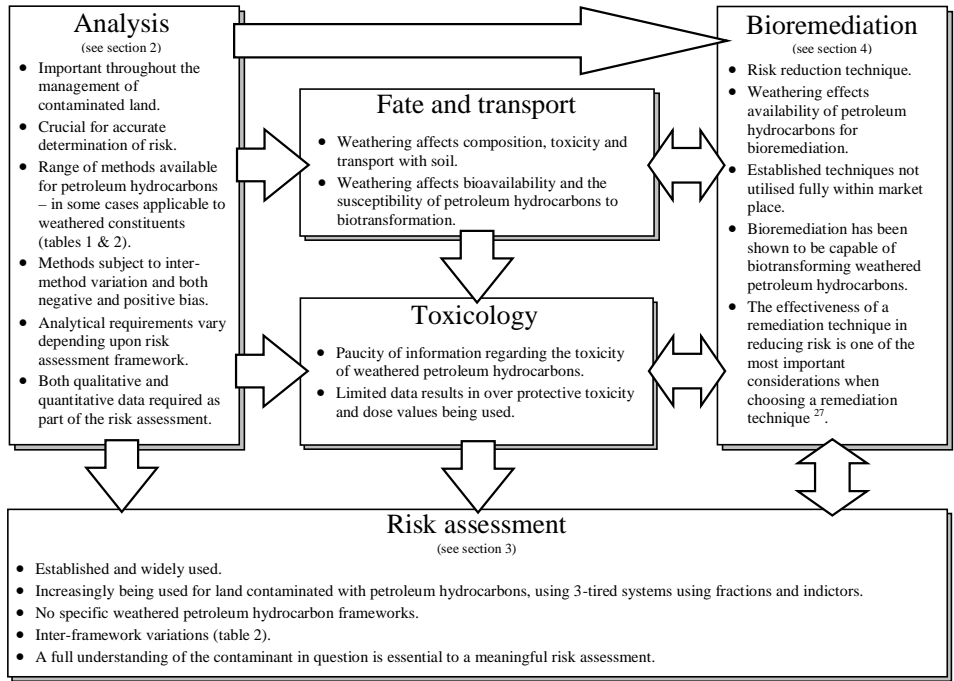
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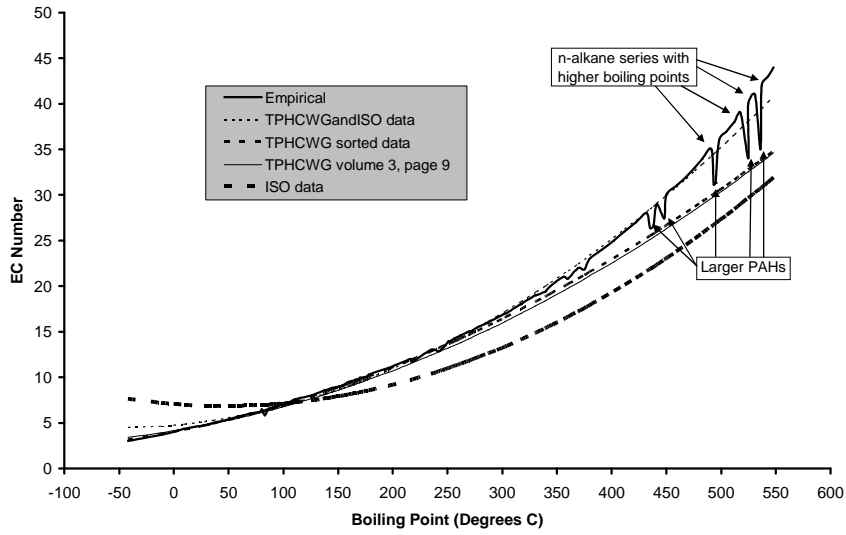
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1108 *Figure 2: Illustration of the interactions of the key elements involved in remediation of*
 1109 *weathered petroleum hydrocarbon contaminated land.*



1133 Figure 3: Estimated equivalent carbon number using Equation 1 parameterised with four
1134 different data sets. The measured data are also provided for comparison.

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1140 *Table 1: Summary of the analysis methods developed for several risk assessment frameworks*

	Massachusetts Department of Environmental Protection ⁵⁴	Total Petroleum Hydrocarbon Criteria Working Group ⁸⁵⁻⁸⁹	Canadian Council of Ministers of the Environment ¹¹⁸	New Zealand ⁶¹	New South Wales ⁶⁴
Description	Use of two methods. Volatile petroleum hydrocarbon (VPH) method ⁵⁷ and extractable petroleum hydrocarbon (EPH) method ⁵⁶ developed by MaDEP. The EPH method refers to USEPA methods for sample extraction ^{57,98} .	Use of 'The Direct method' (AEHS) ¹ developed for the TPHCWG framework. Based upon USEPA SW-864 test methods ⁹⁷ and MaDEP EPH method ⁵	Recommends the use of benchmarked methods ¹⁹ , however also allows the use of non-benchmarked methods providing that validation data demonstrate that the substitute method provides data comparable to the benchmark method.	Permits the use of a variety of methods, including those prepared by the Oil Industry Environmental Working Group (1999) ⁶⁷ which outlines methods for several different petroleum products often referring the reader to USEPA documentation ^{67,99} .	Recommends the use of methods specified in the National Environmental Protection Councils (NEPC) Schedule B(3): Guideline on Laboratory Analysis of Potentially Contaminated Soils (1999) ⁶³ . Where no suitable analytical method is available it recommends the use of USEPA ⁹⁷ , or equivalent methods ⁶⁴ . All chemical analysis should be carried out in laboratories currently accredited by the national association of testing authorities (NATA).
Reported Range	C ₅ to C ₃₆	C ₆ to C ₃₅	C ₆ to C ₅₀	C ₆ to C ₃₆	C ₇ to C ₃₆
Sample collection	EPH method uses amber glass wide mouth sample jars with Teflon lined screw caps. These are cooled immediately after collection and extracted within 14 days of receiving the sample. VPH method uses specially designed air tight collection vials with Teflon-lined septa screw caps stored at 4°C and preserved with methanol before analysis within a maximum of 28 days.	Wide mouth glass jars with Teflon lined caps stored at 4°C. Analysis must be performed within 14 days of sample collection.	Wide mouth glass jars with aluminium foil or Teflon-lined lids. Samples must completely fill the jars. Samples are not chemically preserved but are cooled to 4°C. Laboratory sample handling procedure is also outlined.	100ml (volatiles) and 250ml (semi-volatiles) Borosilicate jars with Teflon-lined cap and completely filled. Stored at 4°C in the dark.	Use of USEPA ⁹⁷ or equivalent methods

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	Massachusetts Department of Environmental Protection	Total Petroleum Hydrocarbon Criteria Working Group	Canadian Council of Ministers of the Environment ¹⁸	New Zealand	New South Wales
Extraction technique	<p>VPH method uses Purge and trap with methanol.</p> <p>EPH method uses DCM for extraction and solvent exchanges into hexane. Using USEPA methods 3540C⁹² (Soxhlet), 3545A⁹³ (pressurised fluid extraction (PFE)), 3541⁹⁰ (Automated Soxhlet extraction), 3546⁹⁵ (Microwave extraction) and 3570⁹⁶ (microscale solvent extraction (MSE)).</p>	Vortex or shaker method using <i>n</i> -pentane.	Purge and trap for C ₆ to C ₁₀ range using methanol. Soxhlet is the benchmarked method for the C ₁₀ to C ₅₀ range.	For the C ₁₀ to C ₃₆ range any method that can be demonstrated to meet the performance criteria can be used. For the C ₆ to C ₉ range purge and trap is used.	USEPA methods 3540B ⁹⁷ or C ⁹² (Soxhlet extraction), 3550B ⁹⁴ (sonication extraction) or sequential bath sonication and agitation described by NEPC ⁶³ .
Evaporation	<p>The EPH method uses those specified by the USEPA. However, after fractionation the use of gentle stream of air or nitrogen is recommended to bring the sample to the required volume.</p> <p>Evaporation is not applicable to the VPH method.</p>	N/A	Uses an evaporation vessel after extraction for the C ₁₀ to C ₅₀ range. After silica gel cleanup rotary evaporator is the benchmarked method to reach the required sample volume.	Permits the use of any method that can be demonstrated to meet the performance criteria.	USEPA methods specified for extraction using Kurderna-Danish (K-D) evaporation.
Clean up /fractionation	<p>Silica gel clean up for EPH method.</p> <p>Not applicable to VPH method.</p>	Extract fractionation using alumina or silica.	One of two specified clean up steps for C ₁₀ to C ₅₀ range, not fractionated.	Clean up steps and fractionation are optional as this may not be required for each sample/analytical approach.	Solvent exchange into hexane followed by K-D evaporation and treated with silica gel as described in USEPA method 1664 ^{64,97} .
Analysis Technique	<p>EPH uses GC/FID[*].</p> <p>VPH may use either GC/FID[*] or GC/PID[#].</p>	GC/FID [*]	GC/FID [*]	For the C ₁₀ to C ₃₆ range GC/FID [*] is used and for the C ₆ to C ₉ range GC/MS [§] is used.	GC/MS [§] , or GC/FID [*] , however the use of GC/MS [§] to identify unusual mixtures is noted as being necessary when analysing by GC/FID [*] .

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*GC/FID refers to gas chromatography with flame ionisation detection

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#GC/PID refers to gas chromatography with photoionisation detection

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§GC/MS refers to gas chromatography with mass spectroscopy detection

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1149 Table 2: Summary of risk assessment used by several different jurisdictions (modified after Environment Agency, (2003)³⁰)

	American Society for testing and materials ⁵	Massachusetts Department of Environmental Protection ⁵³	Total Petroleum Hydrocarbon Criteria Working Group ⁸⁴⁻⁸⁸	Agency for Toxic Substances and Disease Registry ⁶	Canadian Council of Ministers of the Environment ¹⁸	American Petroleum Institute ⁵	Environment Agency ³²	New Zealand ⁶⁰	New South Wales ⁶⁴	National Institute for Public Health and the Environment ¹⁰
Indicator Compounds	Uses 'chemicals of concern' only.	Use most toxic and those most frequently tested for.	Uses most toxic compounds only.	Uses most toxic compounds only	Uses most toxic and those most frequently tested for	Uses most toxic compounds only	Most toxic and most prevalent in petroleum hydrocarbon-contaminated environment	Use of 'contaminants of concern' to address most toxic substances and aromatics	Individual compounds identified	Uses most toxic and those most frequently tested for
Fractions Number	None	6 Analytical fractions (3 aromatic, 3 aliphatic), using 4 toxicity values(3 aliphatic, 1 aromatic.	13 analytical fractions (6 aliphatic, 7 aromatic), using 7 toxicity values (3 aliphatic, 4 aromatic).	Similar to TPHCWG. Minor modification to aromatic groups to include BTEX compounds in same fraction	4 fractions, based on TPHCWG, separate evaluation of aliphatic and aromatic compounds not required	14 fractions based on TPHCWG (7 aromatic, 6 Aliphatic and 1 aliphatic and aromatic combined)	16 fractions based on TPHCWG and API (7 Aliphatic, 8 Aromatic and 1 aliphatic and aromatic combined)	3 aliphatic fractions	2 petroleum hydrocarbon fractions	7 fractions based on toxicity values (3 aliphatic and 4 aromatic)
Basis	N/A	Carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Not defined	Equivalent carbon number
Application of approach	RBCA 3 tiered look-up tables for tier 1 and increasing use of site-specific information in tiers 2&3.	Not tiered as appropriate method is selected prior to assessment. 3 methods can be used – increasing specificity with methods 1 generic 3 site-specific.	RBCA 3 tiered look up tables for tier 1 and increasing use of site-specific into in tiers 2&3.	RBCA 3 tiered look up tables for tier 1 and increasing use of site-specific into in tiers 2&3.	RBCA 3 tiered look up tables for tier 1 and increasing use of site specific information in tiers 2 &3.	Modified TPHCWG approach.	Modified TPHCWG approach within UK context.	Use of a 3-tired approach, moving from generic guidelines to less conservative values using site-specific information.	None specified	Use of a tiered approach, moving from generic to less conservative values using site-specific information in tiers 2 and 3.

	American Society for testing and materials ⁵	Massachusetts Department of Environmental Protection	Total Petroleum Hydrocarbon Criteria Working Group	Agency for Toxic Substances and Disease Registry	Canadian Council of Ministers of the Environment	American Petroleum Institute	Environment Agency	New Zealand	New South Wales	National Institute for Public Health and the Environment
Analysis	No recommended method of analysis	Use of two methods developed by MaDEP for volatile petroleum hydrocarbons (VPH) ⁵⁷ and Extractable petroleum hydrocarbons (EPH) ⁵⁶	The 'Direct Method', developed by AEHS. ¹	The 'Direct Method' ¹	Benchmarked methods for the C ₆ to C ₁₀ and C ₁₀ to C ₅₀ ranges ¹⁹ .	Modified 'Direct Method' for C ₄₄₊ range.	No specified methods, however are to adopt performance criteria - MCERTS ³²	Use of method prepared by the Oil Industry Environment Working Group ⁶⁶ .	Dependent on source of threshold concentration. Using NEPC methods ⁶³ .	Single analytical method (NEN 5733) recommended.
Additivity effects	Not recommended	Precautionary based on addition of hazard quotients across fractions	Precautionary based on addition of hazard quotients across fractions	Precautionary. Developing index of concern based on addition of hazard quotients across fractions for compounds affecting same target organs of systems	Not advised due to different toxicological end points and exposure pathways of different fractions	Precautionary based on addition of hazard quotients across fractions	Assumes additivity of toxicological effects across all fractions, unless there are scientific data to the contrary.	Additivity of excess lifetime cancer risk for non- threshold substances. Precautionary approach, as for ATSDR	Not discussed in guidance document	Precautionary approach, based on addition of hazard quotients across fractions
Range		<i>n</i> C ₅ - <i>n</i> C ₃₆ Aliphatics, <i>n</i> C ₉ - <i>n</i> C ₂₂ Aromatics	EC ₅ -EC ₂₁ Aliphatics, EC ₅ -EC ₃₅ Aromatics	EC ₅ -EC ₂₁ Aliphatics, EC ₅ -EC ₃₅ Aromatics	EC ₆ -EC ₅₀	EC ₆ to EC ₄₄₊	EC ₅ to EC ₇₀	EC ₇ to EC ₃₆	EC ₆ to EC ₄₀	EC ₅ to EC ₃₅

1151	List of main acronyms and definitions	
1152	API	American Petroleum Institute
1153	ASTM	American Society for testing and materials
1154	ATSDR	Agency for Toxic Substances and Disease Registry
1155	BTEX	Benzene, toluene, ethylbenzene and xylene
1156	CCME	Canadian Council of Ministers of the Environment
1157	EA	Environment Agency (UK)
1158	EPH	Extractable petroleum hydrocarbon
1159	GC	Gas Chromatography
1160	GC-MS	Gas Chromatography mass spectroscopy
1161	GC-FID	Gas Chromatography with flame ionisation detection
1162	MaDEP	Massachusetts Department of Environmental Protection
1163	PAH	Polynuclear aromatic hydrocarbons
1164	RIVM	National Institute for Public Health and the Environment
1165	TNRCC	Texas Natural Resource Conservation Commission
1166	TPH	Total petroleum hydrocarbon
1167	TPHCWG	Total Petroleum Criteria Working Group
1168	UCM	Unresolved complex mixture
1169	USEPA	United States Environmental Protection Agency
1170	VPH	Volatile petroleum hydrocarbon
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