

1 **Burial and degradation of *Rena* oil within coastal sediments of the Bay of Plenty**

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5 **Abstract**

6 During the *Rena* oil spill, no data existed for New Zealand conditions on the likely depth
7 of burial and the expected degradation of oil deposited on sandy beaches. Sediment
8 cores were taken from 12 locations along the Bay of Plenty coastline ~1 year after the
9 *Rena* oil spill. No visible oil was detected in cores and trenches dug within the beaches.
10 Chemical extraction was performed on 20 cm slices from the upper 40 cm of 26 cores,
11 and the elutriates were analysed for the presence of polycyclic aromatic hydrocarbons
12 (PAHs). The results were compared to known PAH fingerprints of *Rena* oil and its'
13 degradation products. Only 7 samples contained some marker PAHs, and none had a
14 complete *Rena* profile, indicating stormwater contamination. Despite extensive
15 deposition of *Rena* oil on beaches, no evidence of ongoing contamination could be
16 located indicating that the clean-up and degradation were effective at removing the oil.

17 **Keywords**

18 PAH, GC-MS, depth of disturbance, sediment contamination, heavy fuel oil

19 **Introduction**

20 At 2:20 am on 5th of October 2011, the 236 m long, 37000 tonne container ship *Rena*
21 ran aground on Astrolabe Reef, 22 km offshore from Mt Maunganui in the Bay of Plenty,
22 New Zealand. The *Rena* was carrying 1733 tonnes of heavy fuel oil (HFO 380), 22
23 tonnes of lubricating oil, and approximately 200 tonnes of diesel fuel at the time of
24 grounding. Initially, spillage of hydrocarbons from the vessel consisted primarily of
25 diesel, but by midnight on the 5th of October, the captain reported that HFO was leaking
26 (Hazelhurst, 2014).

27 Oil recovery from the vessel started on 9th October, but was disrupted by a series of
28 storms. The most severe storm in terms of oil release occurred on 11th October,
29 resulting in a spillage of approximately 350 tonnes of HFO 380. Oil recovery finished on
30 15th November, with a final total of ~1300 tonnes of HFO 380 pumped from the *Rena*.
31 The balance of ~80 tonnes of HFO 380 was spilt from the vessel in a series of small

32 incidents between the 5th of October and the end of October, mostly during increased
33 wave activity that caused the ship to move on the reef (Maritime NZ, 2011a & b, 2012).

34 The first oil was discovered on Mt Maunganui Beach on 10th October, with most of the
35 oil deposition occurring over the next week following the release of ~350 tonnes of
36 HFO on the 11th October. In response, access to the beaches between Mt Maunganui and
37 Maketu was restricted between 13th October and 16th November 2011. An official
38 cleanup team of ~500 NZ Defence Force staff was deployed. However, volunteers
39 undertook the bulk of the oil removal. A total of 8000 volunteers registered with the
40 Volunteer Engagement Team that coordinated clean up operations with the *Rena*
41 Incident Command Centre, marine pollution experts, health and safety officials, the NZ
42 Defence Force, tangata whenua and community groups (Ombler, 2014).

43 The principal method used by the volunteers to remove the oil was manually combing
44 the beach for lumps of oil/sediment mixtures, which were bagged and transported off
45 site. Surface oil sheets and tar balls were mostly removed by shovelling by oil response
46 personal (mostly NZ Defence Force). A few other techniques were trialled, including
47 *BeachTech* beach grooming equipment (www.beach-tech.com), vacuum systems, and
48 surf washing (de Groot, 2014).

49 Although the beach clean up operations were considered to be very effective, reports of
50 persistent oil contamination of the beaches continued for at least a year after the initial
51 oil spill (Maritime NZ, 2011a & b, 2012). In particular, there were two main community
52 concerns:

- 53 1. Oil contamination was still present within the estuaries that are an important
54 source of kai moana; and
- 55 2. Oil had been buried in beaches to a depth greater than manually sieved by the
56 volunteers, by the action of storm waves during the spill events.

57 The *Rena Environmental Recovery Monitoring Programme 2011-2013* was established to
58 assess the impacts of the *Rena* oil spill, including determining the effectiveness of the
59 beach clean up response. This investigation reported in this paper was focussed on
60 assessing the residual concentrations of *Rena* sourced HFO 380 within the beach and
61 estuarine sediments within the affected area of Bay of Plenty coastline.

62 **Methodology**

63 *Sediment sampling*

64 Sediment cores were obtained with a vibrocorer from beaches and estuaries subjected
65 to *Rena* oil contamination (Figure 1) between 3 December 2012 and 26 January 2013
66 (Table 1). Initially a random sampling programme was devised. An initial trial of the
67 sampling methodology was conducted at 4 sites between Mt Maunganui and Papamoa
68 during 3-7 December 2012. These locations were subjected to heavy oil contamination
69 and ongoing reports of persistent oil buried in the beach (Maritime NZ, 2012). The trial
70 included 3 cores from low tide, mid tide and high tide locations on the beach. The core
71 barrels were 2.5 m long 75 mm diameter aluminium tubes, with a stainless steel core
72 catcher. The tubes were cleaned before use to avoid any contamination from
73 hydrocarbons before coring (de Groot, 2014).

74 There was poor sample recovery from the low tide cores due to a high water table
75 resulting in fluidisation of the sediment (de Groot, 2014). Hence, the low tide core
76 sampling was not continued for the rest of the core collection. Sections of the beach
77 were also trenched to a depth of 0.50-1.00 m, depending on the water table, to look for
78 visible signs of buried oil and assess the likelihood of missing oil with random coring.
79 While the trenching showed the presence of multiple stringers of titanomagnetite,
80 which did have the appearance of oil streaks, no visible oil was seen. A thick
81 titanomagnetite layer was present at depths of 0.8-1.0 m below the beach surface, and
82 this was taken to represent the extent of beach lowering during a series of severe
83 storms in the 1970s. This layer provided a maximum possible extent for oil burial
84 associated with the *Rena*.

85 After the trial, the sampling strategy was modified to obtain only the mid and high tide
86 cores, and focussed on areas of known oil deposition and ongoing community concerns
87 about residual contamination. Eventually 26 cores were obtained from 12 sites (Figure
88 1, Table 1) between northern Waihi Beach and Maketu.

89 *Formation of oil-mineral aggregates*

90 During the trial it became apparent that there was no obvious evidence of macroscopic
91 oil or tar balls. However, oil could be present at microscopic scale within the beach

92 sediments. Oil tends to bind with sediment particles to produce oil-mineral aggregates
93 (OMA), which changes the hydraulic behaviour of the oil (Lee, 2002). Generally, OMAs
94 are stable structures and are more buoyant than the host sediment (Stoffyn-Egli and
95 Lee, 2002).

96 The characteristics of OMAs depend on the viscosity and composition of the oil, the
97 composition of the sediments, salinity, and the turbulent energy available for mixing.
98 The depth to which OMAs are mixed into sediment depends on the OMA characteristics,
99 water table elevation, wave conditions, and in the case of beaches, the beach
100 morphodynamic state (Bernabeu *et al.*, 2006). No information was available at the start
101 of the study for OMAs formed by mixing HFO 380 with the types of sediment affected in
102 the Bay of Plenty, which included clays, silts and sands of predominantly volcanic
103 origin.

104 A series of laboratory trials were conducted to examine the formation of OMAs with
105 HFO 380 obtained from the last port where the *Rena* refuelled combined with
106 representative sediments obtained from Omanu Beach. These trials involved recording
107 the behaviour of sediment suspensions after vigorous mixing with the addition of 0, 10
108 and 20 ml of HFO 380.

109 *Expected depth of burial*

110 A review of the international literature produced no clear indication of the likely
111 maximum depth that oil could be mixed into the sediment. Depth of disturbance (DOD)
112 measurements were obtained from Waihi Beach and Papamoa during fair-weather
113 conditions, and Omanu and Pukehina during a series of storm events for breaking
114 waves ranging from $H_s = 0.1-3.6$ m and $T_p = 11-16$ s. DOD was measured using 10 mm
115 diameter stainless steel disturbance rods and 5 cm² lead washers using the
116 methodology of Sainia *et al* (2009), combined with beach profiling with a Nikon DTM-
117 322 Total Station (de Groot, 2014).

118 The burial depth also depends on the variation in the cross-shore profile in response to
119 erosion and accretion with changing beach state. Most of the beaches affected by the
120 *Rena* oil spill are surveyed periodically by the Bay of Plenty Regional Council, which
121 provides an indication of the extent of vertical profile migration. However, beach

122 profiling was also specifically undertaken during this investigation to determine
123 vertical changes within the active beach.

124 Since the laboratory trial and DOD results were not available when the core sampling
125 commenced, the DOD was estimated as being ~10% of an extreme 5 m breaking wave
126 height. This corresponded to a worst-case oil burial of 50 cm, and was considered
127 sufficient to account for any disturbance due to clean-up operations. Existing profile
128 data indicated that the maximum vertical change in the beach profile was of the order
129 1 m. The 2.5 m core barrels used ensured at least 50 cm of sample was retrieved, and it
130 was expected that it should span the 1.5 maximum burial expected. It was also assumed
131 that even if sand containing oil or OMAs were buried by subsequent accretion, there
132 should still be a residual trace of PAHs closer to the surface due to mixing of water
133 soluble fractions in the pore waters.

134 *Hydrocarbon extraction and PAH identification*

135 Even if oil particles were not visible in the cores, it was possible that microscopic
136 residual OMAs and oil droplets were still present, or residual traces of PAHs from the
137 water soluble fraction would be within the pore spaces. Therefore, the sediment cores
138 were split in half, and one half was sub-sectioned for extraction of any oil or
139 degradation products present in the pores, or adhered to sediment grains. The
140 remaining half was archived in a refrigerated storage room.

141 Since it was difficult to predict what levels could be present, the initial procedure
142 started with the high tide core from Omanu Beach that was considered most likely to
143 contain oil due to the frequency and magnitude of oiling events (Maritime NZ, 2011a &
144 b). The first 50 cm of these cores were initially sub-sectioned into 5 cm bands, which
145 was estimated to be the smallest sample size that could provide enough material to
146 analyse if significant quantities were present. The sediment from each 5 cm increment
147 was transferred to separate glass containers for oil extraction.

148 To extract any oil present, sub-samples were soaked for 10 minutes in
149 dichloromethane solvent. The resulting solution was decanted off the sediment and
150 filtered through a Pasteur pipette containing cotton wool. The extraction process was
151 then repeated. The combined solution from the two extractions was then concentrated

152 down to approximately 10 ml using a rotary evaporator, and decanted off into a vial for
153 Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

154 Before the solutions were processed in the GC-MS, phen-d10 was added to the sample
155 vials. The phen-d10 containing samples were analysed in a batch that started with a
156 sample of *Rena* HFO 380 recovered from the vessel, and ended with a response factor
157 standard. The response factor standard was diluted down with dichloromethane to
158 produce a similar peak height as the samples (10^{-5}g.l^{-1}). The response factor standard
159 was used for comparison of its component peak heights to those in the sample and all
160 components of the response factor mixes are of known weight. Hence, it provided a
161 check on detection levels, retention times and peak shapes for the GC-MS output,

162 This procedure followed the protocol established by Wilkins (2013) in order to
163 determine the GC-MS fingerprints for *Rena* oil and its' degradation products. This
164 allowed the measured profiles to be compared with the known fingerprints to
165 determine if any *Rena* oil was present. This method is more sensitive than the standard
166 quantitative GC-MS procedure used by R J Hills Laboratories. However, the
167 concentration of oil present could not be reliably determined from the GC-MS data
168 derived by this procedure.

169 No fingerprint of *Rena* oil petroleum aromatic hydrocarbons (PAHs) was found in any
170 of the ten samples initially analysed for the Omanu Beach high tide core. Therefore, to
171 increase the potential concentration of extracted oil, subsequent extractions were
172 based on two 20 cm bands for the top 40 cm of each core (i.e. 2 extractions cf. 10
173 extractions per core).

174 For each extracted sample processed by the GC-MS, a total ion chromatogram and
175 extracted ion chromatograms for naphthalene 128, phenanthrene 178, pyrene 202, and
176 benzo(a)anthracene and chrysene 228 were generated. Wilkins (2013) identified these
177 PAHs as key markers for the presence of *Rena* HFO 380 and associated degradation
178 products (*Rena* fingerprint PAHs).

179 After the first 19 extracted samples were processed by the GC-MS, it was discovered
180 that the initial sample of *Rena* HFO 380 had caused a partial blockage of the GC-MS
181 column, potentially contaminating the results. Therefore, the results were discarded
182 and the analysis was redone. However, the archived half of the Omanu high tide cores

183 was used to produce two 20 cm extractions to allow comparison of results for
184 consistent extraction volumes. The original 5 cm extractions used to develop the
185 extraction procedure were not reanalysed.

186 After the 5 cm Omanu high tide extractions were excluded, 52 sets of chromatograms
187 were produced by the GC-MS using the qualitative protocol of Wilkins (2013). A subset
188 of 18 extractions were selected on the basis of the presence of *Rena* fingerprint PAHs
189 (Table 1), and sent to R J Hill Laboratories for quantitative GC-MS analysis of 16 specific
190 EPA priority PAHs (Bruzzoniti *et al*, 2009).

191 After all the analyses were completed, the remaining sediment was returned to the
192 sampling locations from which it was obtained, as requested by the tangata whenua
193 from Maketu and Matakana Island.

194 **Results**

195 *Depth of disturbance*

196 The DOD scales with the size of the breaking waves (Bertin *et al*, 2008), so the greatest
197 disturbance is associated with storm wave conditions. Further, there were community
198 concerns that the storm waves during the *Rena* oil spills resulted in deep burial of oil in
199 Bay of Plenty beaches. Therefore, only the Omanu and Pukehina results for storm
200 conditions will be considered here.

201 The largest storm waves occurred during the Omanu DOD experiment ($H_s = 3.6$, $T_p =$
202 11 s, tidal range = 1.10 m), and were associated with DOD ranging from 1.8-7.6 cm
203 (mean = 3.82 ± 2.17 cm). Overall the beach profile eroded during the measurement
204 period, with the profile changes at the DOD rods varying between 2.4 cm accretion at
205 the high tide level, and 17.8 cm erosion at the low tide level. The average beach slope
206 for the active beach during the experiment was 3.2° . The greatest DOD (7.6 cm) was
207 associated with the largest erosion (17.8 cm) at the low tide level, indicating potential
208 burial to a depth of 25.4 cm below the pre-storm beach level. At the high tide level, the
209 maximum potential burial was 4.2 cm, due to 1.8 cm DOD and 2.4 cm accretion during
210 the storm.

211 The Pukehina experiment occurred during a lower energy storm event ($H_s = 2.6$ m, $T_p =$
212 11 s, tidal range = 1.36 m). The measured DOD ranged from 4.5-28.1 cm (mean = 12.02

213 ± 7.95 cm). The entire measured beach profile eroded during this storm by $4.62 \pm$
214 3.50 cm, and the average beach slope of the active beach was 4.9° . Unlike Omanu, there
215 was no correlation between the DOD and the extent of erosion. The largest DOD
216 (28.1 cm) was associated with 4 cm of erosion at the low tide level, indicating potential
217 burial to a depth of 32.1 cm below the pre-storm beach level. At the high tide level, the
218 maximum potential burial below the pre-storm profile was 19.7 cm, with 10.7 cm DOD
219 and 9 cm of erosion.

220 *Formation of OMAs*

221 Mixing of *Rena* HFO 380 with sediment obtained from Omanu Beach resulted in small
222 reduction of the settling velocity of the dispersed sediment. The time taken for the
223 complete deposition of all the sand-sized sediment increased from 23.00 ± 0.85 s for
224 the control 1 l seawater cylinder, to 24.10 ± 0.56 s for 1 l seawater with 10 ml of HFO
225 380, and 24.17 ± 0.82 s for 1 l of seawater with 20 ml of HFO 380. The difference
226 between the control velocity and the presence of oil is statistically significant at the
227 95% confidence limit, but the difference between the different oil concentrations is not.
228 Visual inspection of the cylinders after the sand-sized sediment had settled suggested
229 that a higher concentration of oil droplets remained in suspension for the 20 ml tests
230 than the 10 ml tests.

231 The Omanu sediment also contained small proportions of silt and clay-sized sediment.
232 For the control tests, this material remained in suspension for more than 4 days after
233 mixing, at which stage the test was stopped. The tests for the oil-seawater mixtures all
234 cleared of fine sediment within 2 days, although a small quantity of oil droplets < 1 mm
235 in diameter remained.

236 After the sand-sized sediment had settled, oil droplets remained in suspension. The
237 droplets were spherical and varied in diameter from a maximum of 5 mm to <1 mm.
238 Larger oil droplets floated to the surface of the cylinder. Examination under a
239 microscope of suspended and floating oil droplets showed that most incorporated
240 sediment grains, and floating droplets also included voids of water or gas.

241 Oil droplets between 2 - 5 mm settled to the bottom over 126.24 ± 5.74 s and $124.56 \pm$
242 6.18 s for 10 and 20 ml HFO 380 respectively. A few of the larger floating droplets sank
243 to the bottom over several days, possibly due to loss of gas voids.

244 *Distribution of PAHs*

245 The results of the qualitative and quantitative GC-MS analyses are summarised in
246 Table 2. The only sample processed by R J Hill Laboratories for EPA priority PAHs that
247 reported concentrations at or above detection limits (10 µg.kg⁻¹ dry weight for
248 naphthalene and 2 µg.kg⁻¹ dry weight for the remaining PAHs) was the upper
249 subsample from the high tide Omanu Beach core. The analysis found 2 µg.kg⁻¹ dry
250 weight of pyrene and 8 µg.kg⁻¹ dry weight of phenanthrene.

251 Naphthalene was not present in any subsample, and, hence, it is omitted from Table 2. A
252 total of 34 subsamples contained at least 1 of the *Rena* fingerprint PAHs, but there was
253 no obvious pattern to the distribution of PAHs with all sites except Centre Bank having
254 at least one PAH present. Benzo(a)anthracene and chrysene were found in a few
255 samples (7 of 52), including all three of the low tide level cores and both subsamples of
256 the Maketu Estuary core located furthest inside the estuary (Core 1). The remaining
257 two samples containing Benzo(a)anthracene and chrysene came from lightly oiled
258 areas almost at the extreme ends of the area sampled (Bowentown and Maketu Spit).

259 **Discussion**

260 The field measurements of DOD during fair-weather and storms indicate that the
261 average DOD varied between 1-5% of the breaking wave height. This is consistent with
262 the results of Ciavola *et al* (2013) who concluded that the DOD is 2-6% of the breaking
263 wave height, and generally lower than the 4-16% of breaking wave height reported by
264 Anfuso *et al* (2000) for a wide range of morphodynamic beach states

265 However, it is clear that DOD increased with increasing beach slope. Further, since the
266 DOD is likely to be a function of the swash zone processes, the angle between the wave
267 crests and the shoreline at breaking is also likely to be a factor (Bertin *et al*, 2008).

268 Taking beach slope (β) and wave angle (α) into account, the DOD is related to the
269 breaking wave height (H_b) by (Bertin *et al*, 2008)

270
$$DOD = H_b \frac{0.8 \tan \beta}{\sqrt{1 + \sin(2\alpha)}} \quad \text{Eqn. 1}$$

271 The maximum DOD occurs when the waves are breaking parallel to the beach ($\alpha=0$).
272 For the beaches measured during the field experiment, which had beach slopes of 3.2°
273 to 4.9° , Equation 1 corresponds to a DOD between 4-7% of the breaking wave height.

274 Considering only the DOD data measured for storm wave conditions, the maximum
275 DOD ranged from 2-11% of the breaking significant wave height. The upper limit of this
276 range exceeds the predictions of Ciavola *et al* (2013) and Bertin *et al* (2008), but is
277 lower than the maximum 16% of breaking wave height reported by Anfuso *et al* (2000).
278 Therefore, an appropriate estimate of the DOD for New Zealand mesotidal sandy
279 beaches, and hence maximum burial of oil due to wave action, is 16% of breaking
280 significant wave height.

281 Oil on the beach can also be buried as a consequence of erosion followed by accretion.
282 Generally, this occurs during post-storm beach recovery as sediment eroded from the
283 beach is transported shoreward (Masselink *et al*, 2011), but this process is slower than
284 the storm induced erosion. For the *Rena* oil spills, official and volunteer response teams
285 mostly undertook spill clean up operations soon after the oil was deposited (Maritime
286 NZ, 2011a & b). Therefore, the effects of accretion are likely to be minimal. Further, the
287 coring extended down to intact titanomagnetite placer deposits associated with severe
288 erosion during the 1970s, suggesting that no oil could have been mechanically
289 transported deeper into the beach.

290 Laboratory tests indicate that the interaction of HFO 380 and the sediments found on
291 the Bay of Plenty beaches is consistent with the behaviour reported in the literature
292 (*viz.* Bernabeu *et al*, 2010). In particular, the HFO 380 tended to rapidly bind with
293 minerals to form OMAs. The behaviour of the OMAs depended on their size, and the
294 combined impact of higher density mineral grains and lower density voids on the
295 buoyancy of the OMAs. Larger OMAs tended to float at or near the surface, and hence
296 are more likely to be deposited on the higher parts of the beach. Smaller OMAs tended
297 to sink, and are more likely to be mixed into the sediment lower on the beach.

298 Lee (2002) suggests that finer sediments ($<2 \mu\text{m}$) preferentially bind to HFO, and
299 therefore enhance the transport of oil out of low energy environments such as
300 estuaries. The laboratory tests did demonstrate that the finer sediments were removed

301 from suspension by the formation of OMAs, but it was not possible to test the effect this
302 had on oil dispersal within Bay of Plenty estuaries.

303 The formation of OMAs is important for determining the rate of oil degradation
304 (Stoffyn-Egli and Lee, 2002), primarily because they increase the surface area of the oil,
305 which enhances biodegradation, photo-oxidation and evaporation. One of the benefits
306 of surf washing, as tried with the *Rena* oil spills, is that it increases the formation of
307 OMAs, particularly if fine sediments are present (Owens and Lee, 2002).

308 Degradation processes alter the composition of the oil within OMAs, generally initially
309 depleting low molecular weight PAHs through evaporation (Nelson *et al*, 2006).
310 Therefore, in the *Rena* fingerprint, naphthalene would be expected to have been lost
311 during the first few weeks. Wilkins (2013) analysed oil samples obtained from 11 sites
312 between Matakana Island and Maketu, as well as samples directly from the *Rena*, taken
313 shortly after the initial spill (12 October 2011) until January 2012. The initial oil
314 samples for Omanu Beach and Harrisons Cut were also submitted to R J Hill
315 Laboratories for a quantitative assessment of the 16 EPA priority PAHs. All the initial
316 sample's were depleted in naphthalene relative to non-degraded *Rena* tank samples.
317 Hence, the absence of naphthalene from the core samples was expected.

318 Wilkins (2013) observed that the degradation profiles of the oil generally followed the
319 expected pattern of predominantly evaporative loss of low molecular weight
320 hydrocarbons (up to C₁₅). However, there was evidence of a greater rate of degradation
321 than could be explained by purely evaporation, and the phenanthrene fingerprint PAH
322 was found to be highly variable between samples. Phenanthrene was the most
323 commonly detected PAH in the cores (Table 2), and was found in the highest
324 concentration (8 µg
325 .kg⁻¹ dry weight) in the quantitative analysis by R J Hill Laboratories.

326 Phenanthrene contains 3 benzene rings (Bruzzoniti *et al*, 2009), has an expected half-
327 life of around 100 days (Wilson and Jones, 1993), and is considered to be the least
328 water-soluble PAH (Jonker *et al*, 2003). It is susceptible to biodegradation (Harayama
329 *et al*, 2004), but no data are available on the microorganisms present in Bay of Plenty
330 coastal sediments that could degrade oil. This suggests that although it is more likely to
331 degrade than heavier PAHs with more benzene rings, it is not likely to migrate with

332 ground water. However, this doesn't explain why it is the most commonly detected
333 *Rena* fingerprint PAH.

334 Pyrene contains 4 benzene rings (Bruzzoniti *et al*, 2009) and was the second most
335 commonly detected *Rena* fingerprint PAH. It was also found by the quantitative
336 analysis, although right at the detection limit. Pyrene is resistant to biodegradation, and
337 therefore tends to persist in sediments after an initial decline due to evaporation.
338 Pyrene from the *Exxon Valdez* was still detectable after 6 years (Wolfe *et al*, 1994).

339 Benzo(a)anthracene and chrysene are also 4 ring PAHs (Bruzzoniti *et al*, 2009) like
340 pyrene, but are considered to be more resistant to degradation due to their greater
341 molecular weight. However, these PAHs were not present in most of the samples
342 analysed. When they were present, they occurred in areas that did not receive
343 significant deposits of oil, such as the low tide level (Mt Maunganui, Omanu, and
344 Harrisons Cut), within Maketu Estuary, or the margins of the affected area (Bowentown
345 and Maketu Spit).

346 Benzo(a)anthracene and chrysene are more susceptible to biodegradation than pyrene,
347 but to a similar degree as phenanthrene (Harayama *et al*, 2004), which suggests that if
348 the observed distribution was solely due to degradation, these heavier fingerprint
349 PAHs should have been found in more locations. Some studies have demonstrated that
350 surf washing is more effective at removing benzo(a)anthracene and chrysene than the
351 less soluble phenanthrene (Jonker *et al*, 2006). While this methodology was employed
352 during the *Rena* response, it was restricted to the lower parts of the beach suggesting
353 that these PAHs would be more likely to be found in the upper beach. Only one site
354 (Bowentown) has detectable levels in the high tide core, and this site did not receive
355 much oil.

356 Overall, the observed distribution of PAHs is consistent with published studies of major
357 oil spills on beaches in the northern hemisphere (*viz.* Wolfe *et al*, 1994), with greater
358 degradation (loss) of PAHs in the upper parts of the beach compared to the lowest
359 levels. The estuary results do not appear to be consistent, with Tauranga Harbour
360 samples being free of *Rena* fingerprint PAHs, and samples from Maketu Estuary, which
361 received less oil than Tauranga Harbour, still having 4 of the fingerprint PAHs.

362 Although the combination of PAHs used to identify *Rena* oil and associated degradation
363 profiles is unique to the *Rena* (Wilkins, 2013), there are other sources in the Bay of
364 Plenty for the individual PAHs within the fingerprint. Park (2009) and BOPRC (2014)
365 report on PAH levels in marine sediments within the Bay of Plenty, predominantly
366 within Tauranga and Ohiwa Harbours. These studies have found levels of PAHs 2-3
367 orders of magnitude higher than measured by R J Hill Laboratories for the 18 samples
368 analysed quantitatively. Phenanthrene, in particular, was found to occur at
369 concentrations exceeding New Zealand guidelines (0.240 mg.kg⁻¹ dry weight). Fluorene
370 was also found to occur in sediments at levels exceeding guidelines (0.019 mg.kg⁻¹ dry
371 weight). This PAH was also measured above detection limits (8 µg.kg⁻¹ dry weight) in
372 the upper subsample of the Omanu core.

373 Park (2009) and BOPRC (2014) attributed elevated PAHs to stormwater discharges
374 containing PAHs from sources such as coal tar, asphalt and combustion engine
375 exhausts. Additional contributions were due to minor oil spillages within marinas and
376 at wharves and boat ramps. The sites sampled for this study were then assessed for
377 their proximity to stormwater discharges, and the following sites were located within
378 20 m of stormwater outfalls or stream discharges: Waihi Beach, Omanu, Harrisons Cut,
379 and Kaituna River. The other sites were further from stormwater sources, but all were
380 located within 1500 m of a potential source.

381 Therefore, it is considered likely that all the sites sampled are subject to some degree of
382 PAH contamination from sources other than the *Rena* oil spills. Hence, with all sites
383 showing a weak to negligible match to the expected PAH fingerprint profile, and
384 potential contamination from other sources it was not possible to unequivocally
385 identify persisting *Rena* oil.

386 **Conclusions**

387 No visible *Rena* oil was detected within coastal sediments sampled by this study.
388 Chemical extraction did recover PAHs contributing to the *Rena* oil fingerprint from 34
389 of 52 subsamples, which represented 11 of the 12 sites cored. While the distribution of
390 PAHs showed a greater loss due to degradation in the higher parts of the beach
391 compared to the low tide level, consistent with international studies, there were
392 significant differences. In particular, lower molecular weight phenanthrene was more

393 prevalent than was expected. Local storm water discharges contain elevated levels of
394 PAHs, including phenanthrene, and have probably contaminated the sediments in
395 addition to the *Rena* oil. Therefore, it is not possible to unequivocally identify persisting
396 *Rena* oil.

397 However, the measured PAH distributions indicate that the beach response teams were
398 very effective at cleaning the *Rena* oil spills from the beaches, and any residue that
399 remained has either been removed or greatly reduced by natural degradation.

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466 **Figure and Table captions**

467 Figure 1 – Map of the locations of the 12 sites sampled by vibrocoreing for the purpose
468 of assessing the extent of buried *Rena* oil and associated degradation products. Also
469 marked are the beaches used for depth of disturbance field experiments, and the
470 position of the source of the oil spills, the *MV Rena*.

471

472 Table 1 – Summary of core sampling sites and the sub-samples used for qualitative GC-
473 MS analysis by the University of Waikato, and quantitative GC-MS analysis by R J Hill
474 Laboratories. The locations of each core site are given as WGS84 latitude and longitude.
475 The Omanu high tide core was initially sub-sampled in 5 cm bands, before the
476 procedure was changed to 20 cm bands. The archive half of the Omanu high tide core
477 was used for the 2nd qualitative analysis.

478 Table 2 – Summary of the *Rena* fingerprint PAHs detected by: (X) qualitative GC-MS
479 analysis undertaken by The University of Waikato; and (Q) quantitative GC-MS analysis
480 undertaken by R J Hill Laboratories. At open coast beaches, cores were taken at: (H)
481 high tide; (M) mid tide; and (L) low tide. Within the Maketu Estuary, cores were taken
482 (2) on the exposed flood tidal delta, and (1) 100 m further inside the estuary. Each core
483 was split into two 20 cm subsamples: (U) the upper 20 cm; and (L) the band from 20-
484 40 cm depth. Since benzo(a)anthracene and chrysene have the same retention time in
485 the GC-MS, it was not possible to distinguish them and they are treated as a single PAH
486 for this table.

Table 1

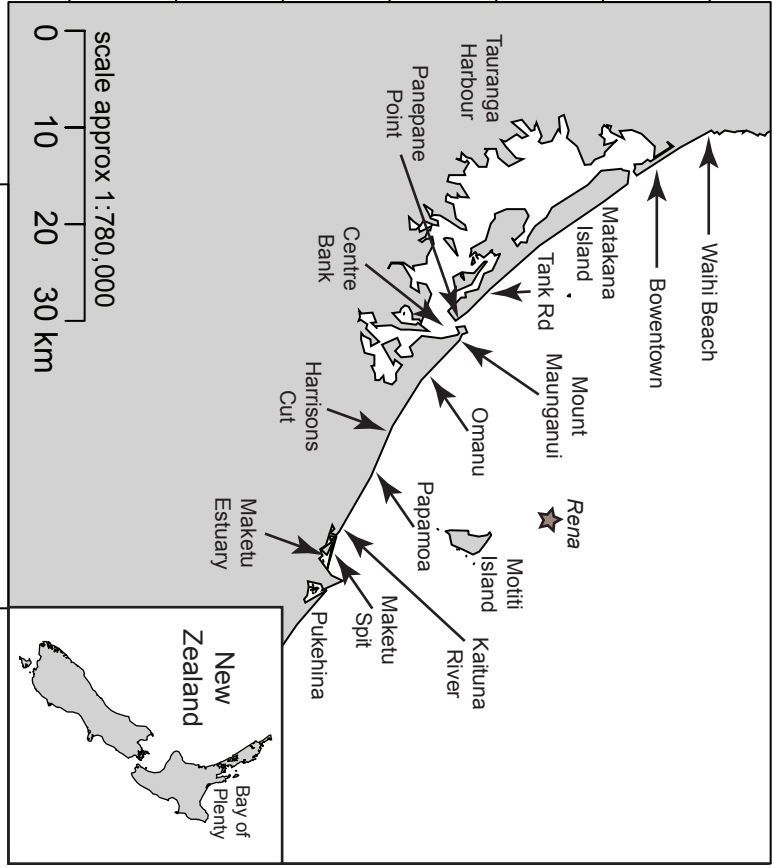
| Location | Date cored | Core | WGS84 | | University | R J Hill |
|----------------|------------|------|----------------|--------|---------------------|-----------------------|
| | | | position | Sample | of Waikato GC-MS | Laboratories GC-MS |
| Waihi Beach | 10/01/13 | H | 37° 23.749' S | U | X | X |
| | | | 175° 56.297' E | L | X | X |
| | 10/01/13 | M | 37° 23.747' S | U | X | |
| | | | 175° 56.326' E | L | X | |
| Bowentown | 10/01/13 | H | 37° 23.783' S | U | X | X |
| | | | 175° 56.323' E | L | X | X |
| | 10/01/13 | M | 37° 23.772' S | U | X | |
| | | | 175° 56.336' E | L | X | |
| Tank Rd | 10/01/13 | H | 37° 35.554' S | U | X | |
| | | | 176° 6.583' E | L | X | X |
| | 10/01/13 | M | 37° 35.546' S | U | X | |
| | | | 176° 6.591' E | L | X | |
| Panepane Pt | 26/01/13 | H | 37° 38.165' S | U | X | X |
| | | | 176° 9.662' E | L | X | X |
| | 26/01/13 | M | 37° 38.154' S | U | X | |
| | | | 176° 9.675' E | L | X | |
| Centre Bank | 12/12/12 | | 37° 38.583' S | U | X | X |
| | | | 176° 10.425' E | L | X | X |
| Mt Maunganui | 6/12/12 | H | 37° 37.510' S | U | X | |
| | | | 176° 10.406' E | L | X | |
| | 6/12/12 | M | 37° 37.844' S | U | X | |
| | | | 176° 10.686' E | L | X | |
| | 6/12/12 | L | 37° 37.840' S | U | X | |
| | | | 176° 10.689' E | L | X | X |
| Omanu | 7/12/12 | H | 37° 39.514' S | U | X - 2 nd | X |
| | | | 176° 12.944' E | L | X - 2 nd | X |
| | 7/12/12 | M | 37° 39.508' S | U | X | |
| | | | 176° 12.953' E | L | X | |
| Harrisons Cut | 3/12/12 | H | 37° 41.442' S | U | X | |
| | | | 176° 16.425' E | L | X | |
| | 3/12/12 | M | 37° 41.416' S | U | X | |
| | | | 176° 16.430' E | L | X | |
| | 3/12/12 | L | 37° 41.412' S | U | X | |
| | | | 176° 16.436' E | L | X | |
| Papamoa | 7/12/12 | H | 37° 42.620' S | U | X | |
| | | | 176° 19.653' E | L | X | |
| | 4/12/12 | M | 37° 42.603' S | U | X | |
| | | | 176° 19.636' E | L | X | |
| | 4/12/12 | L | 37° 42.371' S | U | X | |
| | | | 176° 19.391' E | L | X | X |
| Kaituna River | 8/1/13 | H | 37° 44.860' S | U | X | |
| | | | 176° 24.975' E | L | X | |
| | 24/1/13 | M | 37° 44.866' S | U | X | |
| | | | 176° 24.975' E | L | X | |
| Maketu Spit | 6/12/12 | H | 37° 45.271' S | U | X | X |
| | | | 176° 26.985' E | L | X | X |
| | 6/12/12 | M | 37° 45.263' S | U | X | |
| | | | 176° 26.985' E | L | X | X |
| Maketu Estuary | 8/1/13 | 1 | 37° 45.428' S | U | X | X |
| | | | 176° 27.088' E | L | X | X |
| | 8/1/13 | 2 | 37° 45.412' S | U | X | |
| | | | 176° 27.053' E | L | X | |

Table 2

| Location | Core | Sample | Phenanthrene | Pyrene | Benzo(a)anthracene and chrysene |
|----------------|------|--------|--------------|--------|------------------------------------|
| Waihi Beach | H | U | | | |
| | | L | | | |
| | M | U | X | X | |
| | | L | X | X | |
| Bowentown | H | U | | | |
| | | L | | | |
| | M | U | X | X | X |
| | | L | | | |
| Tank Rd | H | U | | | |
| | | L | | | |
| | M | U | X | X | |
| | | L | X | X | |
| Panepane Pt | H | U | | | |
| | | L | | | |
| | M | U | | | |
| | | L | X | | |
| Centre Bank | | U | | | |
| | | L | | | |
| Mt Maunganui | H | U | X | | |
| | | L | X | | |
| | M | U | X | | |
| | | L | | | |
| | L | U | X | | |
| | | L | X | X | X |
| Omanu | H | U | X Q | X Q | |
| | | L | | | |
| | M | U | X | X | |
| | | L | X | X | |
| Harrisons Cut | H | U | X | X | |
| | | L | | X | |
| | M | U | X | X | |
| | | L | X | X | |
| | L | U | | | |
| | | L | X | X | X |
| Papamoa | H | U | | | |
| | | L | X | X | |
| | M | U | X | X | |
| | | L | | X | |
| | L | U | X | X | X |
| | | L | X | X | |
| Kaituna River | H | U | | | |
| | | L | | X | |
| | M | U | X | X | |
| | | L | X | | |
| Maketu Spit | H | U | | | |
| | | L | | | |
| | M | U | X | | |
| | | L | X | X | X |
| Maketu Estuary | 1 | U | X | X | X |
| | | L | X | X | X |
| | 2 | U | X | X | |
| | | L | X | X | |

Latitude

37.4°S
37.5°S
37.6°S
37.7°S
37.8°S
37.9°S
38.0°S



Longitude

176.0°E
176.5°E

