New Zealand Journal of Marine and Freshwater Research

ISSN: 0028-8330 (Print) 1175-8805 (Online) Journal homepage: http://www.tandfonline.com/loi/tnzm20

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To cite this article: WP de Lange, NPHM de Groot & VG Moon (2016) Burial and degradation of Rena oil within coastal sediments of the Bay of Plenty, New Zealand Journal of Marine and Freshwater Research, 50:1, 159-172, DOI: 10.1080/00288330.2015.1062401

To link to this article: http://dx.doi.org/10.1080/00288330.2015.1062401

NEW ZEALAND JOURNAL OF MARINE AND FRESHWATER RESEARCH, 2016
VOL. 50, NO. 1, 159–172
http://dx.doi.org/10.1080/00288330.2015.1062401

RESEARCH ARTICLE

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

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

ARTICLE HISTORY
Received 8 December 2014
Accepted 10 June 2015

KEYWORDS
depth of disturbance; GC-MS; heavy fuel oil; PAH; *Rena*; sediment contamination

Introduction

At 0220 h on 5 October 2011, the 236 m long, 37,000 tonne container ship MV *Rena* ran aground on Astrolabe Reef, 22 km offshore from Mt Maunganui in the Bay of Plenty, New Zealand. The *Rena* was carrying 1733 tonnes of heavy fuel oil (HFO 380), 22 tonnes of lubricating oil and approximately 200 tonnes of diesel fuel at the time of grounding. Initially, spillage of hydrocarbons from the vessel consisted primarily of diesel, but by midnight on 5 October, the captain reported that HFO was leaking (Hazelhurst 2014).

Oil recovery from the vessel started on 9 October, but was disrupted by a series of storms. The most severe storm in terms of oil release occurred on 11 October, resulting in a spillage of approximately 350 tonnes of HFO 380. Oil recovery finished on 15 November, with a final total of c. 1300 tonnes of HFO 380 pumped from the *Rena*. The balance of c. 80 tonnes of HFO 380 was spilt from the vessel in a series of small incidents between 5 October and the end of October, mostly during increased wave activity that caused the ship to move on the reef (Maritime New Zealand 2011a, 2011b, 2012).

The first oil was discovered on Mt Maunganui beach on 10 October, with most of the oil deposition occurring over the next week following the release of c. 350 tonnes of HFO on 11 October. In response, access to the beaches between Mt Maunganui and Maketu was

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restricted between 13 October and 16 November 2011. An official clean-up team of c. 500 NZ Defence Force staff was deployed. However, volunteers undertook the bulk of the oil removal. A total of 8000 volunteers registered with the Volunteer Engagement Team which coordinated clean-up operations with the *Rena* Incident Command Centre, marine pollution experts, health and safety officials, the NZ Defence Force, tangata whenua and community groups (Ombler 2014).

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

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

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

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

Methodology

Sediment sampling

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

There was poor sample recovery from the low-tide cores due to a high water table resulting in fluidisation of the sediment (de Groot 2014). Hence, the low-tide core sampling was not continued for the rest of the core collection. Sections of the beach were also trenched to a depth of 0.50–1.00 m, depending on the water table, to look for

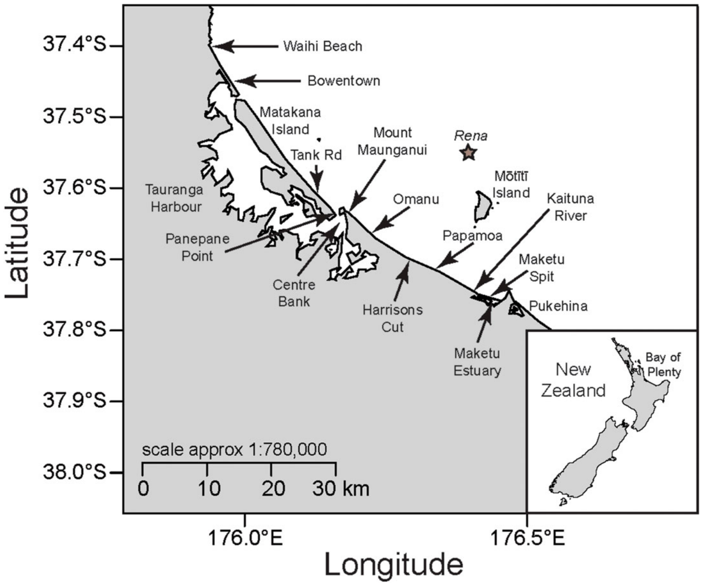

Figure 1. Map of the locations of the 12 sites sampled by vibrocoring for the purpose of assessing the extent of buried *Rena* oil and associated degradation products. Also marked are the beaches used for depth of disturbance field experiments, and the position of the source of the oil spills, the MV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

visible signs of buried oil and assess the likelihood of missing oil with random coring. While the trenching showed the presence of multiple stringers of titanomagnetite, which had the appearance of oil streaks, no visible oil was seen. A thick titanomagnetite layer was present at depths of 0.8–1.0 m below the beach surface, and this was taken to represent the extent of beach lowering during a series of severe storms in the 1970s. This layer provided a maximum possible extent for oil burial associated with the *Rena*.

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

Formation of oil–mineral aggregates

During the trial it became apparent that there was no obvious evidence of macroscopic oil or tar balls. However, oil could be present at a microscopic scale within the beach sediments. Oil tends to bind with sediment particles to produce oil–mineral aggregates (OMAs), which changes the hydraulic behaviour of the oil (Lee 2002). Generally, OMAs are stable structures and are more buoyant than the host sediment (Stoffyn-Egli & Lee 2002).

The characteristics of OMAs depend on the viscosity and composition of the oil, the composition of the sediments, salinity and the turbulent energy available for mixing. The depth to which OMAs are mixed into sediment depends on the OMAs' characteristics, water table elevation, wave conditions and, in the case of beaches, the beach morphodynamic state (Bernabeu et al. 2006). No information was available at the start of

Table 1. Summary of core sampling sites and the subsamples used for qualitative GC-MS analysis by the University of Waikato and quantitative GC-MS analysis by RJ Hill Laboratories.

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

At open coast beaches, cores were taken at high tide (H), mid tide (M) and low tide (B). Within the Maketu estuary, cores were taken (2) on the exposed flood tidal delta, and (1) 100 m further inside the estuary. Each core was split into two 20 cm subsamples: (U) the upper 20 cm; and (B) the band from 20–40 cm depth. Since benz(a)anthracene and chrysene have the same retention time in the GC-MS, it was not possible to distinguish them and they are treated as a single PAH for this table.

The locations of each core site are given as WGS84 latitude and longitude. The Omanu high-tide core was initially subsampled in 5 cm bands, before the procedure was changed to 20 cm bands. The archive half of the Omanu high-tide core was used for the second qualitative analysis.

the study for OMAs formed by mixing HFO 380 with the types of sediment affected in the Bay of Plenty, which included clays, silts and sands of predominantly volcanic origin.

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

Expected depth of burial

A review of the international literature produced no clear indication of the likely maximum depth that oil could be mixed into the sediment. Depth of disturbance (DOD) measurements were obtained from Waihi Beach and Papamoa during fair-weather conditions, and Omanu and Pukehina during a series of storm events for breaking waves ranging from significant wave height (H_s) = 0.1–3.6 m and peak wave period (T_p) = 11–16 s. DOD was measured using 10 mm diameter stainless steel disturbance rods and 5 cm^2 lead washers using the methodology of Sainia et al. (2009), combined with beach profiling with a Nikon DTM-322 Total Station (de Groot 2014).

The burial depth also depends on the variation in the cross-shore profile in response to erosion and accretion with changing beach state. Most of the beaches affected by the *Rena* oil spill are surveyed periodically by the Bay of Plenty Regional Council, which provides an indication of the extent of vertical profile migration. However, beach profiling was also specifically undertaken during this investigation to determine vertical changes within the active beach.

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

Hydrocarbon extraction and PAH identification

Even if oil particles were not visible in the cores, it was possible that microscopic residual OMAs and oil droplets were still present, or residual traces of PAHs from the water soluble fraction would be within the pore spaces. Therefore, the sediment cores were split in half: one half was subsectioned for extraction of any oil or degradation products present in the pores or adhered to sediment grains; the other half was archived in a refrigerated storage room.

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

To extract any oil present, subsamples were soaked for 10 min in dichloromethane solvent. The resulting solution was decanted off the sediment and filtered through a Pasteur pipette containing cotton wool. The extraction process was then repeated. The combined solution from the two extractions was concentrated down to approximately 10 mL using a rotary evaporator, and decanted off into a vial for gas chromatography–mass spectrometry (GC-MS) analysis.

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

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

No fingerprint of *Rena* oil PAHs was found in any of the 10 samples initially analysed for the Omanu beach high-tide core. Therefore, to increase the potential concentration of extracted oil, subsequent extractions were based on two 20 cm bands for the top 40 cm of each core (i.e. two extractions cf. 10 extractions per core).

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

After the first 19 extracted samples were processed by the GC-MS, it was discovered that the initial sample of *Rena* HFO 380 had caused a partial blockage of the GC-MS column, potentially contaminating the results. Therefore, the results were discarded and the analysis was redone. However, the archived halves of the Omanu high-tide cores were used to produce two 20 cm extractions to allow comparison of results for consistent extraction volumes. The original 5 cm extractions used to develop the extraction procedure were not reanalysed.

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

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

Results

Depth of disturbance

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

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

The Pukehina experiment occurred during a lower energy storm event ($H_s = 2.6$ m, $T_p = 11$ s, tidal range = 1.36 m). The measured DOD ranged from 4.5–28.1 cm (mean = 12.02 ± 7.95 cm). The entire measured beach profile eroded during this storm by 4.62 ± 3.50 cm and the average beach slope of the active beach was 4.9°. Unlike Omanu, there was no correlation between the DOD and the extent of erosion. The largest DOD (28.1 cm) was associated with 4 cm of erosion at the low-tide level, indicating potential burial to a depth of 32.1 cm below the pre-storm beach level. At the high-tide level, the maximum potential burial below the pre-storm profile was 19.7 cm, with 10.7 cm DOD and 9 cm of erosion.

Formation of OMAs

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

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

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

Oil droplets between 2–5 mm settled to the bottom over 126.24 ± 5.74 s and 124.56 ± 6.18 s for 10 and 20 mL HFO 380, respectively. A few of the larger floating droplets sank to the bottom over several days, possibly due to loss of gas voids.

Distribution of PAHs

The results of the qualitative and quantitative GC-MS analyses are summarised in Table 2. The only sample processed by RJ Hill Laboratories for EPA priority PAHs that reported concentrations at or above detection limits (10 μg kg^{-1} dry weight for naphthalene and 2 μg kg^{-1} dry weight for the remaining PAHs) was the upper subsample from the high-tide Omanu beach core. The analysis found 2 μg kg^{-1} dry weight of pyrene and 8 μg kg^{-1} dry weight of phenanthrene.

Naphthalene was not present in any subsample and, hence, it is omitted from Table 2. A total of 34 subsamples contained at least one of the *Rena* fingerprint PAHs, but there was no obvious pattern to the distribution of PAHs; all sites except Centre Bank had at least one PAH present. Benz(a)anthracene and chrysene were found in a few samples (seven of 52), including all three of the low-tide level cores and both subsamples of the Maketu estuary core located furthest inside the estuary (core 1). The remaining two samples containing benz(a)anthracene and chrysene came from lightly oiled areas almost at the extreme ends of the area sampled (Bowentown and Maketu spit).

Discussion

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

However, it is clear that DOD increased with increasing beach slope. Further, since the DOD is likely to be a function of the swash zone processes, the angle between the wave crests and the shoreline at breaking is also likely to be a factor (Bertin et al. 2008). Taking beach slope (β) and wave angle (α) into account, the DOD is related to the breaking wave height (H_b) by (Bertin et al. 2008):

$$\mathrm{DOD} = H_b \frac{0.8\ \tan\ \beta}{\sqrt{1 + \sin(2\alpha)}} \tag{1}$$

The maximum DOD occurs when the waves are breaking parallel to the beach ($\alpha = 0$). For the beaches measured during the field experiment, which had beach slopes of

Table 2. Summary of the *Rena* fingerprint PAHs detected by qualitative GC-MS analysis undertaken by the University of Waikato and quantitative GC-MS analysis undertaken by RJ Hill Laboratories.

Location	Core	Sample	Phenanthrene	Pyrene	Benz(a)anthracene and chrysene
Waihi beach	H	U			
		B			
	M	U	X	X	
		B	X	X	
Bowentown	H	U			
		B			
	M	U	X	X	X
		B			
Tank Rd	H	U			
		B			
	M	U	X	X	
		B	X	X	
Panepane Pt	H	U			
		B			
	M	U			
		B	X		
Centre Bank		U			
		B			
Mt Maunganui	H	U	X		
		B	X		
	M	U	X		
		B			
	L	U	X		
		B	X	X	X
Omanu	H	U	X Q	X Q	
		B			
	M	U	X	X	
		B	X	X	
Harrisons Cut	H	U	X	X	
		B		X	
	M	U	X	X	
		B	X	X	
	B	U			
		B	X	X	X
Papamoa	H	U			
		B	X	X	
	M	U	X	X	
		B		X	
	L	U	X	X	X
		B	X	X	
Kaituna river	H	U			
		B		X	
	M	U	X	X	
		B	X		
Maketu spit	H	U			
		B			
	M	U	X		
		B	X	X	X
Maketu estuary	1	U	X	X	X
		B	X	X	X
	2	U	X	X	
		B	X	X	

X, qualitative GC-MS analysis undertaken by the University of Waikato; Q, quantitative GC-MS analysis undertaken by RJ Hill Baboratories.

At open coast beaches, cores were taken at high tide (H), mid tide (M) and low tide (B). Within the Maketu estuary, cores were taken (2) on the exposed flood tidal delta, and (1) 100 m further inside the estuary. Each core was split into two 20 cm subsamples: (U) the upper 20 cm; and (B) the band from 20–40 cm depth. Since benz(a)anthracene and chrysene have the same retention time in the GC-MS, it was not possible to distinguish them and they are treated as a single PAH for this table.

3.2° to 4.9°, Equation (1) corresponds to a DOD between 4%–7% of the breaking wave height.

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

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

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

Lee (2002) suggested that finer sediments (<2 µm) preferentially bind to HFO, and therefore enhance the transport of oil out of low-energy environments such as estuaries. The laboratory tests did demonstrate that the finer sediments were removed from suspension by the formation of OMAs, but it was not possible to test the effect this had on oil dispersal within Bay of Plenty estuaries.

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

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

Wilkins (2013) observed that the degradation profiles of the oil generally followed the expected pattern of predominantly evaporative loss of low molecular weight hydrocarbons (up to C_{15}). However, there was evidence of a greater rate of degradation than could be explained purely by evaporation, and the phenanthrene fingerprint PAH was found to be highly variable between samples. Phenanthrene was the most commonly detected PAH in the cores (Table 2) and was found in the highest concentration (8 $\mu g\ kg^{-1}$ dry weight) in the quantitative analysis by RJ Hill Laboratories.

Phenanthrene contains three benzene rings (Bruzzoniti et al. 2009), has an expected half-life of around 100 days (Wilson & Jones 1993) and is considered to be the least water-soluble PAH (Jonker et al. 2003). It is susceptible to biodegradation (Harayama et al. 2004), but no data are available on the microorganisms present in Bay of Plenty coastal sediments that could degrade oil. This suggests that although it is more likely to degrade than heavier PAHs with more benzene rings, it is not likely to migrate with groundwater. However, this does not explain why it is the most commonly detected *Rena* fingerprint PAH.

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

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

Benz(a)anthracene and chrysene are more susceptible to biodegradation than pyrene, but to a similar degree as phenanthrene (Harayama et al. 2004), which suggests that if the observed distribution was solely due to degradation, these heavier fingerprint PAHs should have been found in more locations. Some studies have demonstrated that surf washing is more effective at removing benz(a)anthracene and chrysene than the less soluble phenanthrene (Jonker et al. 2003). While this methodology was employed during the *Rena* response, it was restricted to the lower parts of the beach suggesting that these PAHs would be more likely to be found in the upper beach. Only one site (Bowentown) has detectable levels in the high-tide core, and this site did not receive much oil.

Overall, the observed distribution of PAHs is consistent with published studies of major oil spills on beaches in the Northern Hemisphere (viz. Wolfe et al. 1994), with greater degradation (loss) of PAHs in the upper parts of the beach compared with the lowest levels. The estuary results do not appear to be consistent, with Tauranga harbour samples being free of *Rena* fingerprint PAHs, and samples from Maketu estuary, which received less oil than Tauranga harbour, still having four of the fingerprint PAHs.

Although the combination of PAHs used to identify *Rena* oil and its associated degradation profiles is unique to the *Rena* (Wilkins 2013), there are other sources in the Bay of Plenty for the individual PAHs within the fingerprint. Park (2009) and BOPRC (2014) report on PAH levels in marine sediments within the Bay of Plenty, predominantly within Tauranga and Ohiwa harbours. These studies have found levels of PAHs two to three orders of magnitude higher than measured by RJ Hill Laboratories for the 18 samples analysed quantitatively. Phenanthrene, in particular, was found to occur at concentrations exceeding New Zealand guidelines (0.240 mg kg^{-1} dry weight). Fluorene was also found to occur in sediments at levels exceeding guidelines (0.019 mg kg^{-1} dry weight). This PAH was also measured above detection limits (8 µg kg^{-1} dry weight) in the upper subsample of the Omanu core.

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

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

Conclusions

No visible *Rena* oil was detected within coastal sediments sampled by this study. Chemical extraction did recover PAHs contributing to the *Rena* oil fingerprint from 34 of 52 subsamples, which represented 11 of the 12 sites cored. While the distribution of PAHs showed a greater loss due to degradation in the higher parts of the beach compared with the low-tide level, consistent with international studies, there were significant differences. In particular, lower molecular weight phenanthrene was more prevalent than was expected. Local stormwater discharges contain elevated levels of PAHs, including phenanthrene, and have probably contaminated the sediments in addition to the *Rena* oil. Therefore, it is not possible to unequivocally identify persisting *Rena* oil.

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

Acknowledgements

Guest Editor: Professor Chris Battershill.

Disclosure statement

No potential conflict of interest was reported by the authors.

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