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

Willem P. de Lange, Neeltje P.H.M. de Groot, Vicki G. Moon

Coastal Marine Group, School of Science, Faculty of Science and Engineering, The University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

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 ~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 to known PAH fingerprints of *Rena* oil and its’ degradation products. Only 7 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.

Keywords

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

Introduction

At 2:20 am on 5th of October 2011, the 236 m long, 37000 tonne container ship *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 the 5th of October, the captain reported that HFO was leaking (Hazelhurst, 2014).

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

The first oil was discovered on Mt Maunganui Beach on 10th October, with most of the oil deposition occurring over the next week following the release of ~350 tonnes of HFO on the 11th October. In response, access to the beaches between Mt Maunganui and Maketu was restricted between 13th October and 16th November 2011. An official cleanup team of ~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 that 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 personal (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 NZ, 2011a & b, 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 focussed 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 4 sites between Mt Maunganui and Papamoa during 3-7 December 2012. These locations were subjected to heavy oil contamination and ongoing reports of persistent oil buried in the beach (Maritime NZ, 2012). The trial included 3 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 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 did have 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 focussed 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 microscopic scale within the beach
sediments. Oil tends to bind with sediment particles to produce oil-mineral aggregates (OMA), 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 and 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 OMA 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 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 $H_s = 0.1-3.6$ m and $T_p = 11-16$ 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 ∼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 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 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, and one half was sub-sectioned for extraction of any oil or degradation products present in the pores, or adhered to sediment grains. The remaining 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 NZ, 2011a & b). The first 50 cm of these cores were initially sub-sectioned into 5 cm bands, which 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, sub-samples were soaked for 10 minutes 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 then 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 phen-d10 containing samples 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 (10⁻⁵g.l⁻¹). The response factor standard
was used for comparison of its component peak heights to those in the sample and 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 R J 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 petroleum aromatic hydrocarbons (PAHs) was found in any
of the ten 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. 2 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
benzo(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 half of the Omanu high tide cores
was 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 R J Hill Laboratories for quantitative GC-MS analysis of 16 specific 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...
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 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.
The results of the qualitative and quantitative GC-MS analyses are summarised in Table 2. The only sample processed by R J 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 1 of the *Rena* fingerprint PAHs, but there was no obvious pattern to the distribution of PAHs with all sites except Centre Bank having at least one PAH present. Benzo(a)anthracene and chrysene were found in a few samples (7 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 Benzo(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 between 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 (\(\beta\)) and wave angle (\(\alpha\)) into account, the DOD is related to the breaking wave height (\(H_b\)) by (Bertin *et al*, 2008)

\[
DOD = H_b \frac{0.8 \tan \beta}{\sqrt{1 + \sin(2\alpha)}}
\]

Eqn. 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 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 NZ, 2011a & b). 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 the 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) suggests 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 and 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 and Lee, 2002).

Degradation processes alter the composition of the oil within OMAs, generally initially depleting low molecular weight PAHs though 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 R J Hill Laboratories for a quantitative assessment of the 16 EPA priority PAHs. All the initial sample’s 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 C15). However, there was evidence of a greater rate of degradation than could be explained by purely 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 µg .kg^-1 dry weight) in the quantitative analysis by R J Hill Laboratories.

Phenanthrene contains 3 benzene rings (Bruzzoniti et al, 2009), has an expected half-life of around 100 days (Wilson and 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
ground water. However, this doesn’t explain why it is the most commonly detected
Rena fingerprint PAH.

Pyrene contains 4 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 right at the detection limit. 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).

Benzo(a)anthracene and chrysene are also 4 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).

Benzo(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 benzo(a)anthracene and chrysene than the
less soluble phenanthrene (Jonker et al, 2006). 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 to 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 4 of the fingerprint PAHs.
Although the combination of PAHs used to identify *Rena* oil and 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 2-3 orders of magnitude higher than measured by R J 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 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 to 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 storm water 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.

References


Figure and Table captions

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*.

Table 1 – Summary of core sampling sites and the sub-samples used for qualitative GC-MS analysis by the University of Waikato, and quantitative GC-MS analysis by R J Hill Laboratories. The locations of each core site are given as WGS84 latitude and longitude. The Omanu high tide core was initially sub-sampled 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 2nd qualitative analysis.

Table 2 – Summary of the *Rena* fingerprint PAHs detected by: (X) qualitative GC-MS analysis undertaken by The University of Waikato; and (Q) quantitative GC-MS analysis undertaken by R J Hill Laboratories. At open coast beaches, cores were taken at: (H) high tide; (M) mid tide; and (L) low tide. 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 (L) the band from 20-40 cm depth. Since benzo(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.
<table>
<thead>
<tr>
<th>Location</th>
<th>Date cored</th>
<th>Core</th>
<th>WGS84 position</th>
<th>Sample</th>
<th>University of Waikato GC-MS</th>
<th>R J Hill Laboratories GC-MS</th>
</tr>
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<td>Waihi Beach</td>
<td>10/01/13</td>
<td>H</td>
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<td>U, L</td>
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<td>M</td>
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<td>X, X</td>
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<td>Bowentown</td>
<td>10/01/13</td>
<td>H</td>
<td>37° 23.783' S, 175° 56.323' E</td>
<td>U, L</td>
<td>X, X</td>
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<td></td>
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<td>M</td>
<td>37° 23.772' S, 175° 56.336' E</td>
<td>U, L</td>
<td>X, X</td>
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<td>Tank Rd</td>
<td>10/01/13</td>
<td>H</td>
<td>37° 35.554' S, 176° 6.583' E</td>
<td>U, L</td>
<td>X, X</td>
<td>X, X</td>
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<td>Centre Bank</td>
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<td>U, L</td>
<td>X, X</td>
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