

# New Zealand Journal of Marine and Freshwater Research



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

# In situ sampling reveals rapid uptake and depuration of polycyclic aromatic hydrocarbons by surf clams (Paphies subtriangulata) affected by the Rena oil spill

PM Ross, RM Fairweather, DP Culliford, S Park, CA Pilditch & CN Battershill

**To cite this article:** PM Ross, RM Fairweather, DP Culliford, S Park, CA Pilditch & CN Battershill (2016) In situ sampling reveals rapid uptake and depuration of polycyclic aromatic hydrocarbons by surf clams (Paphies subtriangulata) affected by the Rena oil spill, New Zealand Journal of Marine and Freshwater Research, 50:1, 56-69, DOI: <u>10.1080/00288330.2015.1084934</u>

To link to this article: http://dx.doi.org/10.1080/00288330.2015.1084934

Published online: 27 Apr 2016.	Submit your article to this journal 🕑
Article views: 173	View related articles 🕑
CrossMark View Crossmark data 🗹	Citing articles: 1 View citing articles



#### RESEARCH ARTICLE

# In situ sampling reveals rapid uptake and depuration of polycyclic aromatic hydrocarbons by surf clams (*Paphies subtriangulata*) affected by the *Rena* oil spill

PM Ross<sup>a</sup>, RM Fairweather<sup>a</sup>, DP Culliford<sup>a</sup>, S Park<sup>b</sup>, CA Pilditch<sup>c</sup> and CN Battershill<sup>a</sup>

<sup>a</sup>Environmental Research Institute, University of Waikato, Tauranga, New Zealand; <sup>b</sup>Bay of Plenty Regional Council, Whakatane, New Zealand; <sup>c</sup>School of Science and Engineering, University of Waikato, Hamilton, New Zealand

#### ABSTRACT

To investigate the uptake and depuration of polycyclic aromatic hydrocarbons associated with the Rena oil spill we sampled the surf clam Paphies subtriangulata at two open coast locations (6 km apart) just prior to oil coming ashore (7 October 2011), then at 1-3 week intervals for the next 4 months. Total polycyclic aromatic hydrocarbons (tPAH) increased at both sites from 1 to 96-124 µg  $kq^{-1}$  (wet weight) by 18 October before declining to low levels (<4 µg kg<sup>-1</sup>) by February 2012. Ongoing sampling throughout 2012-2014 included three additional sites to the north east (up to 30 km away) and a site 5 km to the south east revealing tPAH levels generally <10  $\mu$ g kg<sup>-1</sup> except in October 2013 where levels ranged between  $39-45 \ \mu g \ kg^{-1}$  at all sites. A comparison of PAH component profiles with oil-contaminated beach sediment indicated that the high levels observed in surf clams between October-December 2011 were clearly associated with the Rena spill. However, the October 2013 peak had a PAH profile inconsistent with weathered Rena oil, suggesting an alternative source of contamination. Our results highlight the potential for P. subtriangulata as a PAH monitoring tool but recognise more study is needed to better quantify baseline levels and uptake and depuration dynamics.

#### ARTICLE HISTORY

Received 5 May 2015 Accepted 17 August 2015

#### **KEYWORDS**

Bay of Plenty; New Zealand; *Rena*; oil spill; depuration; bioaccumulation; surf clam; tuatua; *Paphies*; shipwreck; PAHs; polycyclic aromatic hydrocarbons

## Introduction

The expansion of oil and gas operations into new locales and greater depths, combined with a dependency on ships for the transport of fuels and other goods to market, continues to generate concern over the likelihood and consequences of oil spills and our ability to deal with spills should they occur. One requirement for oil spill preparedness is the capacity to detect oil in the environment and to assess interactions between oil and marine wildlife (Kirby et al. 2014). Such abilities are relevant in the event of catastrophic oil spills, but also in detecting the cumulative environmental effects of oil-related activities in a business as usual context.

The traditional approach to measuring contaminant concentrations in the marine environment is the collection of water or sediment samples for chemical analysis (Brown et al. 1974). Although this approach can provide a point-in-time assessment of contaminants at the location of sampling, such methods do not test for bioavailability of contaminants or capture the spatio-temporal variability inherent in pollution events. Furthermore, for some contaminants, concentrations below current detection limits are capable of causing ecological damage (Fent 2006).

An alternative sampling approach, used increasingly since the 1980s, has been to measure contaminant concentrations in organisms that are considered 'biological indicators' or 'environmental integrators' (Goldberg et al. 1978; Melwani et al. 2014). These animals are typically suspension-feeding bivalves that incorporate contaminants from the water column and accumulate them within their tissues to concentrations above those seen in the environment. Consequently, this approach measures exposure over ecologically meaningful timescales and to some extent circumvents problems associated with spatio-temporal variability, detection limits and determining bioavailability.

In reef and estuarine environments, mussels and oysters have proven to be useful indicators of oil pollution (Jackson et al. 1994; Marigómez et al. 2013). However, as these taxa are absent on open soft sediment coastlines, other taxa must be used as indicators of environmental contamination. Surf clams, often one of the most abundant organisms on sandy open coasts (Haddon et al. 1996; Marsden 2000), have on at least one occasion been used to assess ecological impacts of oil spills. Following the Deepwater Horizon oil spill in the Gulf of Mexico (2010), Coquina clams (*Donax spp.*) were used to monitor oil exposure along sandy shores (Snyder et al. 2014). Although it was concluded that Coquina clams could be used to monitor exposure, there is little information available about the rates of contaminant uptake or depuration in surf clams, and how these characteristics might affect their suitability as biological indicators of oil pollution.

The October 2011 grounding of the MV *Rena* on Astrolabe Reef (Otaiti), some 25 km offshore from Tauranga, Bay of Plenty, New Zealand (37°32.4'S 176°25.7'E; Figure 1; Schiel et al. 2016) provided a rare opportunity to examine in situ hydrocarbon bioaccumulation and depuration in an intertidal surf clam. Approximately 350 tonnes of heavy fuel oil (HFO380) was released into the marine environment (Schiel et al. 2016) in the days and weeks following the grounding and breakup of the *Rena*, with much of it eventually coming ashore on Bay of Plenty surf beaches between Matakana Island and Maketu (Jones et al. 2016; Schiel et al. 2016; Figure 1). The covering of oil on beaches was spatially variable and beached oil was resuspended and deposited numerous times by tide and wave action during the following days. The removal of oil-contaminated sediments from Bay of Plenty beaches was relatively rapid with much of the clean-up conducted by hand (Lockwood 2016), removing oil that might otherwise have been forced deep into the beach sediment through the use of heavy machinery (Australian Maritime Safety Authority [AMSA] 2010; de Lange et al. 2016).

To assess the exposure of surf beach benthic fauna to *Rena* oil, *Paphies subtriangulata*, an edible, New Zealand endemic surf clam, known as tuatua in the Māori language, was collected by the Bay of Plenty Regional Council and the *Rena* Recovery Programme. The life history of *P. subtriangulata* makes this species a good candidate for use as a biological indicator. *Paphies subtriangulata* are large suspension-feeding bivalves (<80 mm). They are abundant, easily collected and occupy lower to mid-intertidal and shallow subtidal

PM ROSS ET AL.



Figure 1. Map of the Bay of Plenty, New Zealand, showing the position of Astrolabe Reef, where the MV Rena grounded, and locations where Paphies subtriangulata were collected. (•) for PAH monitoring.

beach strata, areas often heavily impacted by oil spills. The specimens examined in the present study were not explicitly collected for the purpose of assessing hydrocarbon accumulation and depuration; rather, they were collected to provide information about possible toxicity to humans if gathered for food. However, the collection of these specimens over a 3-year period, together with detailed analysis of PAH body burdens, allowed for an investigation of uptake and depuration dynamics of P. subtriangulata and their utility as a biological indicators of oil contamination.

While the data set is far from perfect—largely a consequence of the limited resources and haste with which multiple environmental monitoring programmes were implemented following the Rena grounding (Schiel et al. 2016)-the value of this study is in its uniqueness. First, it is one of only a handful of studies to document the dynamics of PAH bioaccumulation in a real-world environmental disaster situation, rather than in aquaria where results may be confounded by a lack of natural complexity and a surplus of unnatural stressors (Gronquist & Berges 2013). Second, most PAH monitoring programmes are designed against low-level, long-term contamination rather than large one-off events such as shipwrecks. Perhaps the biggest point of difference to previous studies is that here, specimen collections were made prior to the first arrival of oil to the coast and again in the days, months and years following the oil spill.

#### Methods

Paphies subtriangulata were collected from two locations on the Tauranga coast—Omanu and Papamoa Reserve—a total of 14 times over a 30-month period between October 2011

58

Collection date	Omanu	Papamoa Reserve	Papamoa Domain	Matakana Pipeline	Bowentown	Waihi
7-0ct-11	0.2	0.7	-	-	-	-
18-Oct-11	124.2	96.2	-	-	-	-
25-Oct-11	_	81.8				
7-Nov-11	24.2	54.6	-	-	-	-
14-Nov-11	12.7	39.7	-	-	-	-
21-Nov-11	5.2	61.1	-	-	-	-
12-Dec-11	25.2	18.3	-	-	-	-
18-Jan-12	6.7	6.1	-	-	-	-
21-Feb-12	3.4	0.8	-	-	-	-
10-Apr-12	5.5	3.5	-	-	-	-
7-Jun-12	7.1	11.2	10.2	7.3	6.6	6.2
2-Jul-12	2.9	4.4		-	-	-
7-Nov-12	6.4	8.2	16.4	23.6	9.1	6
8-Oct-13	39.6	41.7	41	43.8	44.6	45.3
6-Jun-14	20.7	19.3	16.6	-	-	-
Lat. (°S)	37.669	37.711	37.692	37.542	37.462	37.433
Long. (°E)	176.232	176.33	176.28	176.06	175.988	175.963

**Table 1.** Total polycyclic aromatic hydrocarbon concentrations ( $\mu$ g.kg<sup>-1</sup> wet weight) in *Paphies subtriangulata* composite samples collected from Bay of Plenty Beaches between 7 October 2011 and 6 July 2014.

The MV *Rena* grounded on Astrolabe Reef on 5 October 2011. Oil first appeared on Tauranga beaches on 10 October 2011, 3 days after the 7 October *P. subtriangulata* collection was made.

and June 2014 (Figure 1, Table 1). Collections were also made at four additional locations -Papamoa Domain, Matakana Island, Bowentown and Waihi-three times between June 2012 and October 2013 (Figure 1, Table 1). Papamoa Domain was also sampled in June 2014. The first P. subtriangulata collections were made on 7 October 2011, 2 days after the grounding of the Rena, but 3 days prior to the first sighting of Rena oil on Bay of Plenty Beaches (Schiel et al. 2016). Rena oil was patchily distributed at Omanu and Papamoa Domain during the 18 October P. subtriangulata collection but stranded oil patches were avoided when collecting P. subtriangulata. There were no observations of unusual P. subtriangulata mortality, for example recently dead and gaping shells, on any oil-affected coastline, although no population analysis was conducted during the time oil engaged with the shore, nor in subsequent weeks (Culliford & Fairweather 2013). At each of the sampling locations on each sampling date, a composite P. subtriangulata sample was collected from the lower intertidal beach strata. Each sample consisted of approximately 30 individual *P. subtriangulata* collected haphazardly by hand over c. 100 m of shoreline. Specimens were placed in labelled bags and stored on ice prior to processing in the laboratory. P. subtriangulata were not permitted to clear their gut contents prior to analysis. Consequently, these specimens retained any fine particulate hydrocarbons consumed prior to collection. The data presented here therefore represent the total hydrocarbon exposure accessible to any organisms consuming *P. subtriangulata*. All tissue types were extracted from each specimen and all extracted tissues from each location combined to make a single composite sample for each sampling date. Tissue extractions were done by hand and empty shells were returned to the site of collection. Composite P. subtriangulata samples were stored at -20 °C then submitted to Hill Laboratories (Hamilton) for analysis. Results are reported on a wet weight basis (dry weight concentrations can be obtained by multiplying by 0.23; Ross unpubl. data). Polycyclic aromatic hydrocarbon (PAH) content was determined through a process of solvent and sonication extraction, followed by clean-up with dispersive SPE and quantitative analysis 60 👄 PM ROSS ET AL.

of 16 US Environmental Protection Agency (USEPA) priority pollutant PAHs, carried out by capillary gas chromatography mass spectrometry in selected ion mode (GC-MS SIM). Total PAH (tPAH) concentrations for Omanu and Papamoa composite samples were plotted as a time series and a correlation-based principal coordinates (PCO) analysis performed in Primer 7 to visualise chemical differences between samples. PAH concentrations were fourth-root transformed and axes normalised to enable the comparison of Euclidean distances between data points despite differences in the scales at which the different PAHs were recorded. Pearson correlation vectors (r > 0.4) were overlaid on the PCO ordination to display the PAH species contributing most to inter-sample PAH profile differences. PAH profiles obtained for two oiled sand samples were also included in the PCO analysis. These were collected at Omanu and Papamoa beaches on 2 November 2011.

#### Results

Total PAH (tPAH) concentrations in *P. subtriangulata* collected before the first *Rena* oil hit the Bay of Plenty coastline were less than 1  $\mu$ g.kg<sup>-1</sup> (Table 1, Figure 2). Eleven days later, following the arrival of oil and the removal of more than 220 tonnes of oiled sandy waste from the Tauranga coastline, tPAH concentrations of 96 and 124  $\mu$ g.kg<sup>-1</sup> were recorded in composite samples from Papamoa Reserve and Omanu, respectively. tPAH concentrations declined to 5 (Omanu) and 40 (Papamoa Reserve)  $\mu$ g.kg<sup>-1</sup> in early November before rising again to 25 and 61  $\mu$ g.kg<sup>-1</sup> in specimens collected in late November and early December. This period corresponded with heavy storm activity and release of further oil from the ship (Schiel et al. 2016). Following this second tPAH peak, concentrations declined and remained low throughout 2012 (Table 1, Figure 2).



**Figure 2.** Total PAH concentrations ( $\mu$ g.kg<sup>-1</sup> wet weight) recorded for *Paphies subtriangulata* composite samples collected at Omanu Beach (open circles) and Papamoa Reserve (closed circles) on 15 dates between 7 October 2011 and 6 July 2014. The MV *Rena* grounded on Astrolabe Reef on 5 October 2011. Oil first appeared on Tauranga beaches on 10 October 2011 3 days after the first *P. subtriangulata* collection was made.

tPAH concentrations over this period (six sampling dates) fluctuated between 0.8 and  $11.2 \ \mu g.kg^{-1}$  with a mean of 5.5 (± 0.8)  $\ \mu g.kg^{-1}$ . In October 2013, 2 years after the grounding of the *Rena* and 11 months after the previous *P. subtriangulata* collection (November 2012), higher tPAH concentrations were once again apparent. tPAH concentrations of between 39.6 and 45.3  $\ \mu g.kg^{-1}$  were recorded across the six sampling locations. These concentrations were comparable to and in some cases exceeded concentrations recorded in *P. subtriangulata* during the 2 months following oil spill. Omanu, Papamoa Reserve and Papamaoa Domain were sampled again in July 2014 and while tPAH concentrations were less than those recorded 9 months earlier, concentrations were still comparable to or greater than concentrations recorded in *P. subtriangulata* in the 2 months following the oil spill.

The two-dimensional PCO ordination accounted for 70.8% of the total variance in the data (Figure 3). 53.1% of the variation was explained by the first factor, or first principle component axis (PCO1), while 17.6% of the variation was explained by the second factor (PCO2). Pearson correlation vectors indicated that benzoanthracene, chrysene, benzo-fluoranthene, benzopyrene, indenopyrene, benzoperylene and dibenzoanthracene were strongly correlated with the PCO1 axis (|r| > 0.73; Table 2). Phenanthrene, anthracene, fluoranthene and pyrene were correlated with both PCO1 (|r| > 0.65) and PCO2 (|r| > 0.4) axes. In the PCO ordination, *P. subtriangulata* samples collected before the arrival of



**Figure 3.** Two-dimensional PCO ordination of the 16 US Environmental Protection Agency priority pollutant polycyclic aromatic hydrocarbons (PAHs) in *Paphies subtriangulata* collected from Bay of Plenty Beaches (Waihi, Bowentown, Matakana Pipeline, Omanu, Papamoa Domain and Papamoa Reserve) prior to (7 October 2011) and following the arrival of heavy fuel oil from the wreck of the MV *Rena*. Principle component axis 1 (PCO1) accounts for 53.1% and axis 2 (PCO2) 17.6% of total variance in the data. Lines drawn around data points are provided to indicate the *P. subtriangulata* collection time series and are of no statistical significance. Refer to Table 2 for identification codes corresponding to each PAH species.

#### 62 👄 PM ROSS ET AL.

		Pearson correlation vector r-values	
PAH species	ID code for figures	PCO1	PCO2
Naphthalene	А	0.27	-0.15
Acenaphthylene	В	0.13	-0.56
Acenaphthene	C	0.10	-0.17
Fluorene	D	-0.50	-0.42
Phenanthrene	E	-0.57	-0.62
Anthracene	F	-0.43	-0.83
Fluoranthene	G	-0.62	-0.65
Pyrene	Н	-0.68	-0.59
Benzo[a]anthracene	I	-0.95	0.16
Chrysene	J	-0.95	0.16
Benzo[k]fluoranthene	К	-0.83	0.23
Benzo[b]fluoranthene	L	-0.91	0.30
Benzo[a] pyrene	Μ	-0.94	0.24
Indeno[1,2,3-cd]pyrene	Ν	-0.93	0.22
Benzo[g,h,i]perylene	0	-0.92	0.32
Dibenzo[a,h]anthracene	Р	-0.94	0.13

**Table 2.** Identification codes used to label the 16 US Environmental Protection Agency priority pollutant polycyclic aromatic hydrocarbons (PAHs) in Figures 3 and 4. Also shown are the correlation values for Principal coordinates analysis axes PCO1 and PCO2 (Figure 3).

oil on Bay of Plenty beaches grouped in the top right corner of the ordination (Figure 3). *P. subtriangulata* collected following the arrival of oil (October–December 2011) occupied the left side and lower left corner of the ordination, predominantly due to greater concentrations of PAHs correlated with both PCO1 and PCO2 axes (Table 2). The oiled sand samples collected from Papamoa and Omanu beaches also occupied the lower left side of the ordination, positioned in closest proximity to *P. subtriangulata* collected on 18 October 2011, a week after oil first hit Bay of Plenty beaches. *P. subtriangulata* samples collected throughout 2012 occupied a more central position in the ordination due to decreasing concentrations of PCO1-correlated PAHs, while *P. subtriangulata* collected in 2013 and 2014 clustered together in the bottom right of the ordination predominantly due to greater concentrations of phenanthrene, anthracene, fluoranthene and pyrene and lower concentrations the PAHs only correlated with the PCO1 axis (Table 2).

Examination of full PAH profiles for *P. subtriangulata* samples provided further indication of temporal differences in PAH concentrations and profiles across sampling dates. Between 13 and 15 of the 16 USEPA priority pollutant PAHs were present in specimens collected immediately after the *Rena* oil spill (18 October through 11 December 2011; Figure 4). Despite being the PAH most abundant in HFO380 collected from the *Rena*'s fuel tanks in the days following the grounding (Figure 4), napthalene was not recorded in either *P. subtriangulata* or oiled sand collected from the Bay of Plenty coast. Acenaphthylene and acenaphthene were only present in the *P. subtriangulata* sample collected at Omanu on 18 October 2011, where they were recorded at relatively low concentrations (2.3% of tPAHs). Phenanthrene, pyrene, benzoanthracene and chrysene were the main PAHs present in *P. subtriangulata* making up between 67 and 71% of tPAHs in these samples by weight. The PAH profiles of the oiled sand collected at Omanu and Papamoa were similar, with napthalene, acenaphthylene and acenaphthene absent and phenanthrene, pyrene, benzoanthracene accounting for 71 and 74% of tPAHs.



**Figure 4.** Concentrations of the 16 USEPA priority pollutant PAHs ( $\mu$ g.kg<sup>-1</sup> wet weight) in *Paphies subtriangulata*, sediment samples and in the *Rena* heavy fuel oil (HFO). Plot *a* shows PAH concentrations in HFO taken from tank 3 of the *Rena* on 9 October 2011. Plot *b* shows PAH concentrations in oiled sand collected 2 November 2011 by the *Rena* Recovery Programme (Battershill et al. 2013) at Omanu (grey) and Papamoa (black). In the *P. subtriangulata* plots (*d-i*), Papamoa reserve is shown in grey, Omanu in black and other sampling locations in white (*h* and *i* only). Plot c shows PAH profiles of three Astrolabe Reef sediment samples collected March 2014 (Ross et al. 2016). Y-axis scales vary between plots. Refer to Table 2 for identification codes corresponding to each PAH species.

64 👄 PM ROSS ET AL.

Similar PAH profiles, although at much lower concentrations, were recorded in *P. subtriangulata* collected between January and July 2012, up to 9 months after the oil spill. While tPAH concentrations were an order of magnitude less, between 7 and 10 of the USEPA PAHs were still apparent and were recorded in proportions similar to those observed in earlier *P. subtriangulata* samples and in oiled sand (Figure 4).

For the 2013 and 2014 *P. subtriangulata* samples, in which tPAH concentrations were high, PAH profiles differed from those recorded up until July 2012. In October 2013, only 6 of the 16 USEPA PAHs were recorded, with phenanthrene, pyrene, benzo[a]anthracene and chrysene accounting for more than 80% of total PAHs (Figure 4). In July 2014 samples, benzo[a]anthracene and chrysene were largely absent while acenaphthylene and fluorene were recorded for the first time since December 2011. Although pyrene and phenanthrene were still the dominant PAHs and were recorded in *P. subtriangulata* at comparable concentrations to the initial post-spill samples, benzo-fluoranthene, benzopyrene, indenopyrene, benzoperylene and dibenzoanthracene, which were present in these early samples, were absent in *P. subtriangulata* collected in 2014.

#### Discussion

Because the PAH data analysed here were collected for the purpose of evaluating human health risks, *P. subtriangulata* collections were not made in the way one would expect for a scientific study aiming to assess the accumulation and depuration of hydrocarbons. First, there is no within-site replication, making it impossible to know whether differences in PAH content between locations and times are statistically significant. Second, whole *P. subtriangulata* (minus the shell) were measured for PAHs, which does not allow for differentiation between PAHs taken up into the tissue vs. PAHs associated with ingested particulate matter in the gut which is defecated out again after several hours. This may have contributed to the rapid depuration of PAHs observed immediately after the *Rena* oil spill. Better practice is to measure PAHs in the gut, including contents, and other tissues separately. However, from the literature, it appears that such protocols are seldom followed when assessing PAH exposure following oil spills (Soniat et al. 2011; Xia et al. 2012; Snyder et al. 2014). For the purposes of this discussion, the terms 'uptake' and 'depuration' are used to refer to changes in PAH concentration for entire organisms, with no differentiation made between PAHs in the gut vs. tissue body burdens.

The detection of a suite of PAHs in *P. subtriangulata* at relatively high concentrations in the days and weeks following exposure to *Rena* oil, and the observed similarity in PAH profile between oiled sand and *P. subtriangulata* tissues, suggests this species may be useful as a biological indicator of oil pollution. This is fortunate, as for New Zealand's open soft sediment coastlines, *P. subtriangulata* are probably the only candidate species that is numerous, intertidal (and therefore easily collected), relatively sedentary and suspension-feeding, all characteristics that are desirable in taxa used as biological indicators of pollution. Furthermore, *P. subtriangulata* is an important human food source so by default should be monitored for contaminants both as a matter of course and following pollution events.

PAHs may be accumulated in the tissues of marine invertebrates via a number of pathways. These include diffusion of waterborne PAHs across gills and integument, through dietary uptake, and by contact with contaminated sediment allowing diffusion through the integument (Meador et al. 1995). Following the *Rena* oil spill, PAH uptake in *P. subtriangulata* was rapid, with maximum concentrations  $(124 \,\mu\text{g.kg}^{-1})$  recorded 8 days after the first oil hit Bay of Plenty beaches. Although information about in situ PAH bioaccumulation rates for bivalves has proven surprisingly difficult to come by, laboratory studies, for which both gut and tissues PAH burdens were determined independently, have documented rapid accumulation of waterborne hydrocarbons in oysters (*Crassostrea gigas*; Bustamante et al. 2012) and estuarine clams (*Ruditapes philippinarum*, Liu et al. 2014).

Depuration of hydrocarbons from *P. subtriangulata* was observed to be equally rapid, with PAH concentrations in Omanu composite samples decreasing by two orders of magnitude over the course of 4 weeks. Further declines in PAH concentrations were recorded over the following 6 months. Similarly, rapid depuration was observed following the recent Gulf of Mexico oil spill for taxa including clams (Snyder et al. 2014), oysters (Soniat et al, 2011; Xia et al. 2012), fish, shrimp, and crabs (Xia et al. 2012). In most of these studies, PAHs were not recorded above background levels 6 months after the capping of the Deepwater Horizon wellhead.

The methods by which Tauranga beaches were cleaned following the *Rena* oil spill may have contributed to the rapid decline in *P. subtriangulata* PAH body burdens. Much of the beach cleaning was done quickly and by hand (Lockwood et al. 2016), removing oil that might otherwise have been buried by wave action or the weight of heavy machinery (AMSA 2010; Schiel et al. 2016; de Lange et al. 2016), potentially recontaminating marine life if resuspended at a later date. A second peak in *P. subtriangulata* PAH contamination, shortly after the initial oiling (November 2011) was documented in this study. It is uncertain whether this peak resulted from inundation by fresh oil, recently released from the foundering ship, or from exposure to weathered oil, previously buried and resuspended by wave action.

One of the more interesting aspects of this data set is the detection of high PAH concentrations in *P. subtriangulata* more than 2 years after the *Rena* oil spill. Although it was initially feared that this was a legacy of the ship's grounding, the PAH profiles pose some questions around identifying the source(s) of these more recently recorded contaminants. More than 30 months after the grounding of the Rena, PAH profiles from sediments collected on Astrolabe Reef, adjacent to the shipwreck, contain the full suite of USEPA PAHs (Figure 4H). P. subtriangulata collected in 2013 and 2014 from Bay of Plenty beaches do not. The 2013 and 2014 P. subtriangulata samples differ in their PAH profiles both from the specimens collected in the 9 months following the Rena oil spill and from each other, possibly suggesting either some interesting temporal patterns of Rena oil weathering and resuspension or multiple sources of PAH contamination. Despite the extensive searches conducted by de Lange et al. (2016), there is no evidence that Rena oil is or was buried within Tauranga's beaches. However, in the period since the Rena grounding, there have been at least two significant oil spills from commercial ships berthed at the Port of Tauranga, a large but unquantified number of minor petrol and diesel spills from recreational and commercial vessels across the region (pers. obs.) and the discharge of PAHs derived from vehicle use and industry into the marine environment via storm water (Brown & Peake 2006).

The limited among-site variability in PAH concentrations recorded in each of the 2013 and 2014 collections lends some support to the notion of regional-scale events such as the

natural addition of PAHs via geothermal activity (Shane et al. 2006) or pulses of hydrocarbons carried by storm water during major rainfall events. Brown & Peake (2006) examined the PAHs in storm water and road debris in southern New Zealand and found the PAH profiles of run-off from an urban catchment and of sediments accumulating in the sumps underlying roadside storm water grates were dominated by phenanthrene, flouranthene and pyrene. These are the same PAHs most prevalent in *P. subtriangulata* in collected in 2013 and 2014. PAH concentrations in the *P. subtriangulata* collected immediately prior to the *Rena* oil spill were close to zero. Similarly, low PAH concentrations were not recorded in later samples. As there is no pre-*Rena* time-series, it is uncertain whether the low PAH values recorded in these first *P. subtriangulata* samples were the pre-*Rena* norm, or whether PAH body burdens typically fluctuate with stochastic events and rainfall induced pulses of hydrocarbons (Brown & Peake 2006).

PAHs are ubiquitous environmental contaminants and are produced from incomplete combustion of fossil fuels, cigarette smoking and food processing such as smoking, grilling and toasting (Panalaks 1976; Santodonato 1997; Moret et al. 1999; Stolyhwo & Sikorski 2005). In fact, tPAH concentrations of up to 164  $\mu$ g,kg<sup>-1</sup> have been recorded in barbequed meat (Panalaks 1976). Such concentrations are comparable to and in most cases greater than concentrations recorded in P. subtriangulata during the worst of the Rena oil spill. Perhaps somewhat surprisingly, according to the United States Food and Drug Administration seafood consumption guidelines, in which the concentration thresholds for concern range from 132 to 1 846 000 µg.kg<sup>-1</sup> for the 16 USEPA PAHs, the P. subtriangulata collected for this study were at no stage unsafe to eat (Xia et al. 2012). Much higher tPAH concentrations have been recorded in bivalves elsewhere. For example, tPAH concentrations of more than 500 µg.kg<sup>-1</sup> were recorded in Coquina clams in the Gulf of Mexico (Snyder et al. 2014). One possible explanation for the absence of dangerously high PAH body burdens in P. subtriangulata, is that the Rena oil reaching the Tauranga coastline, having travelled more than 20 km across open water, had already lost much of its more volatile and water-soluble/water-accommodated constituent PAHs (Prince et al. 2003; American Petroleum Institute [API] 2011). Consequently, animals not directly impacted by solid oil patches may have experienced only limited PAH exposure. The absence of naphthalene, one of the most volatile PAHs analytes, in beached oil vs. HFO taken from the Rena's fuel tanks provides support for this hypothesis. Unfortunately, a lack of within-site sample replicates, sediment samples associated with each specimen collection, or information about sample proximity to oil patches, makes it difficult to properly explore this hypothesis.

While it was not definitively assessed, there was no evidence of mass mortality in *P. subtriangulata* either during or following the *Rena* oil spill (Culliford & Fairweather 2013). The data presented here suggest that the PAH body burdens experienced by *P. subtriangulata* following the *Rena* oil spill were not high in an international context (Soniat et al. 2011; Xia et al. 2012; Snyder et al. 2014) and that Bay of Plenty *P. subtriangulata* might experience PAH contamination of a similar magnitude with some frequency, possibly derived from urban sources via storm water, geothermal activity, or from more minor vessel related fuel spills (Brown & Peake 2006; Shane et al. 2006). The apparent robustness of *P. subtriangulata* to the levels of PAH contamination generated by the *Rena* oil spill and the observed accumulation of a suite of PAHs that closely matched the *Rena* oil arriving on Tauranga's coastline suggest that *P. subtriangulata* have great

potential as biological indicator of hydrocarbon pollution. However, to be a truly effective monitoring tool, a better baseline of PAH body burden data is required, as is an understanding of the timeframes over which *P. subtriangulata* accumulate and metabolise PAHs and the contribution of gut contents to the total PAH burden in the specimens collected. Such information is essential for the interpretation of biological monitoring data and the development of Mussel Watch-style monitoring regimes (Goldberg et al. 1978; Melwani et al. 2014) that account for the timeframes over which *P. subtriangulata* metabolise PAHs.

#### Acknowledgements

We thank the following people who contributed to the open coast *Rena* research and monitoring programme of which this study is but one component. Stew Robertson, Brett Sutton, Federico Simon, Katie Franks, Nancy Van Nieuwenhove, Faust Vercetti, Nathan Capper, Mark Clayson, Ben Robinson, Luke Jacobs, Alice Morrison, Alice Podziewska, Aroha Hughes, Kelly Maxwell, Graham McCormack, Anton Williams, Stephanie Bathgate, Rob Bathgate, Dudley Bell, Nick Ling, Warrick Powrie, Kevin Eastwood, Rebecca Gladstone-Gallagher, Jen Blair, Bex Eivers, Ashlee Webby, Nick Macdonald and Christine Ulrich.

Guest Editor: Professor David Schiel.

#### **Disclosure statement**

Phil Ross is a Research Fellow at the University of Waikato. During the time that this research was conducted, Ross was contracted both by the Bay of Plenty Regional Council and by the owner (Daina Shipping Co.) and insurer (P & I Services) of the MV *Rena* to conduct environmental monitoring and report on monitoring results. Ross was called as an expert witness for the owner and insurer of the MV *Rena* at the Resource Consent hearing in November 2015.

### References

- Australian Maritime Safety Authority (AMSA). 2010. Response to the *Pacific Adventurer* incident. Report of the incident analysis team — February 2010. Operational and Technical Issues Report. Canberra, ACT: Australian Maritime Safety Authority, Incident Analysis Team.
- American Petroleum Institute (API). 2012. Heavy fuel oils category analysis and hazard characterization. Submitted to the US Environmental Protection Agency by the American Petroleum Institute HPV Testing Group. Consortium Registration #1100997. Washington, DC: API.
- Battershill C, Schiel DR, Ross PM, Fairweather R, Culliford D, Marsh R, Taiapa C, Bennet, P. 2013. *Rena* environmental recovery monitoring programme: executive summary. Tauranga, New Zealand: Te Mauri Moana; Hamilton: Environmental Research Institute, University of Waikato; [cited 2016 Mar 30]. Available from: http://sci.waikato.ac.nz/\_\_data/assets/pdf\_file/ 0008/180476/RENA-executive-summary.pdf
- Brown JN, Peake BM. 2006. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Sci Total Environ. 359:145–155.
- Brown CW, Lynch PF, Ahmadjian M. 1974. Monitoring Narragansett Bay oil spills by infrared spectroscopy. Environ Sci Technol. 8:669–670.
- Bustamante P, Luna-Acosta A, Clemens S, Cassi R, Thomas-Guyon H, Warnau M. 2012. Bioaccumulation and metabolisation of C-14-pyrene by the Pacific oyster *Crassostrea gigas* exposed via seawater. Chemosphere. 87:938–944.
- Culliford D, Fairweather R. 2013. Intertidal soft shores. In: Battershill C, Schiel DR, Ross PM, Fairweather R, Culliford D, Marsh R, editors. *Rena* environmental recovery monitoring

8 👄 PM ROSS ET AL.

programme: executive summary. Tauranga, New Zealand: Te Mauri Moana; Hamilton: Environmental Research Institute, University of Waikato; Chapter 1; p. 38–76. [cited 2016 Mar 30]. Available from: http://sci.waikato.ac.nz/research/projects-and-case-studies/rena-research/Rena-report

- de Lange P, de Groot N, Moon VG. 2016. Burial and degradation of *Rena* oil within coastal sediments of the Bay of Plenty. New Zeal J Mar Freshwat Res. 50:159–172.
- Fent K. 2006. Worldwide occurrence of organotins from antifouling paints and effects in the aquatic environment. In: Konstantinou IK, editor. Antifouling paint biocides. Berlin: Springer; p. 71–100.
- Goldberg ED, Bowen VT, Farrington JW, Harvey G, Martin JH, Parker PL, Risebrough RW, Robertson W, Schneider E, Gamble E. 1978. The Mussel Watch. Environ Conserv. 5:101–125.
- Gronquist D, Berges JA. 2013. Effects of aquarium-related stressors on the zebrafish: a comparison of behavioral, physiological, and biochemical indicators. J Aquat Anim Health. 25:53–65.
- Haddon M, Willis TJ, Wear RG, Anderlini VC. 1996. Biomass and distribution of five species of surf clam off an exposed west coast North Island beach, New Zealand. J Shellfish Res. 15:331–339.
- Jackson TJ, Wade TL, McDonald TJ, Wilkinson DL, Brooks JM. 1994. Polynuclear aromatic hydrocarbon contaminants in oysters from the Gulf of Mexico (1986–1990). Environ Pollut. 83:291– 298.
- Jones HFE, Poot MTS, Mullarney JC, de Lange P, Bryan KR. 2016. Oil-dispersal modelling: reanalysis of the *Rena* oil spill using open-source modelling tools. New Zeal J Mar Freshwat Res. 50:10–27.
- Kirby MF, Gioia R, Law RJ. 2014. The principles of effective post-spill environmental monitoring in marine environments and their application to preparedness assessment. Mar Pollut Bull. 82:11–18.
- Liu D, Pan L, Li Z, Cai Y, Miao J. 2014. Metabolites analysis, metabolic enzyme activities and bioaccumulation in the clam *Ruditapes philippinarum* exposed to benzo[a]pyrene. Ecotox Environ Saf. 107:251–259.
- Lockwood S, Weaver CK, Munchi D, Simpson M. 2016. The self-organising of youth volunteers during the *Rena* oil spill in New Zealand. New Zeal J Mar Freshwat Res. 50:28–41.
- Marigómez I, Garmendia L, Soto M, Orbea A, Izagirre U, Cajaraville MP. 2013. Marine ecosystem health status assessment through integrative biomarker indices: a comparative study after the Prestige oil spill 'Mussel Watch'. Ecotoxicology. 22:486–505.
- Marsden ID. 2000. Variability in low tide populations of tuatua, *Paphies donacina*, in Pegasus Bay, Canterbury, New Zealand. New Zeal J Mar Freshwat Res. 34:359–370.
- Meador JP, Stein JE, Reichert WL, Varanasi U. 1995. Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. Rev Environ Contam Toxicol. 143:79–165.
- Melwani AR, Gregorio D, Jin Y, Stephenson M, Ichikawa G, Siegel E, Crane D, Lauenstein G, Davis JA. 2014. Mussel Watch update: long-term trends in selected contaminants from coastal California, 1977–2010. Mar Pollut Bull. 81:291–302.
- Moret S, Conte L, Dean D. 1999. Assessment of polycyclic aromatic hydrocarbon content of smoked fish by means of a fast HPLC/HPLC method. J Agr Food Chem. 47:1367–1371.
- Panalaks T. 1976. Determination and identification of polycyclic aromatic hydrocarbons in smoked and charcoal-broiled food products by high pressure liquid chromatography and gas chromatography. J Environ Sci Health B. 11:299–315.
- Prince RC, Garrett RM, Bare RE, Grossman MJ, Townsend T, Suflita JM, Lee K, Owens EH, Sergy GA, Braddock JF, et al. 2003. The roles of photooxidation and biodegradation in long-term weathering of crude and heavy fuel oils. Spill Sci Technol Bull. 8:145–156.
- Ross, PM, Battershill, CN, Loomb C. 2016. The wreck of the MV *Rena*: spatio-temporal analysis of ship-derived contaminants in the sediments and fauna of Astrolabe Reef. New Zeal J Mar Freshwat Res. 50:87–114.
- Santodonato J. 1997. Review of the estrogenic and antiestrogenic activity of polycyclic aromatic hydrocarbons: relationship to carcinogenicity. Chemosphere. 34:835–848.

- Schiel DR, Ross PM, Battershill CN. 2016. Environmental effects of the MV *Rena* shipwreck: crossdisciplinary investigations of oil and debris impacts on a coastal ecosystem. New Zeal J Mar Freshwa Res. 50:1–9.
- Shane P, Sikes EL, Guilderson TP. 2006. Tephra beds in deep-sea cores off northern New Zealand: implications for the history of Taupo Volcanic Zone, Mayor Island and White Island volcanoes. J Volcanol Geoth Res. 154:276–290.
- Snyder RA, Vestal A, Welch C, Barnes G, Pelot R, Ederington-Hagy M, Hileman F. 2014. PAH concentrations in Coquina (*Donax* spp.) on a sandy beach shoreline impacted by a marine oil spill. Mar Pollut Bull. 83:87–91.
- Soniat TM, King SM, Tarr MA, Thorne MA. 2011. Chemical and physiological measures on oysters (*Crassostrea virginica*) from oil-exposed sites in Louisiana. J Shellfish Res. 30:713–717.
- Stolyhwo A, Sikorski ZE. 2005. Polycyclic aromatic hydrocarbons in smoked fish—a critical review. Food Chem. 91:303–311.
- Xia K, Hagood G, Childers C, Atkins J, Rogers B, Ware L, Armbrust K, Jewell J, Diaz D, Gatian N, Folmer H. 2012. Polycyclic aromatic hydrocarbons (PAHs) in seafood from areas affected by the Deepwater Horizon oil spill. Environ Sci Technol. 46:5310–5318.