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Polycyclic Aromatic Hydrocarbons in Auckland's Aquatic Environment

Sources, Concentrations and Potential Environmental Risks

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Polycyclic Aromatic Hydrocarbons in Auckland's aquatic environment: sources, concentrations and potential environmental risks

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1   Executive Summary

In December 2005, NIWA was commissioned by Auckland Regional Council (ARC) to investigate potential major sources of PAHs in estuarine and stream sediments, including measurement of potential bioavailability. This report reviews existing data and relevant literature relating to the concentrations, potential sources and bioavailability of PAHs in Auckland estuaries.

Studies conducted under Auckland Regional Council's Regional Discharges Project (RDP) and long-term sediment monitoring programme have found that sediments in the Waitemata and Manukau Harbours and the Tamaki Estuary contain above-background levels of polycyclic aromatic hydrocarbons (PAHs). PAHs are a well-documented class of persistent organic pollutants that are characteristic of most urbanised and industrial areas. They derive from a variety of sources, both ongoing and historic, the majority of which are incomplete combustion of organic matter (such as from residential heating and vehicle emissions) or distillation of fossil fuels. Because PAHs are poorly water-soluble and degrade only slowly under anaerobic conditions, they tend to accumulate in sediments and in biological tissues to concentrations that may have adverse effects on resident biota.

This report reviews the current state and possible future trends of PAH contamination in Auckland's waterways, identifying predominant PAH sources and estimating whether current and future sediment PAH levels represent an elevated risk to benthic aquatic life. Furthermore, it summarises results of a field survey and laboratory analyses, conducted in 2006, to determine dominant PAH sources in Auckland estuarine sediments and ascertain their bioavailability.

Based on current sediment data, the majority of sediment PAH levels in Auckland's estuaries (Waitemata Harbour, Manukau Harbour and Tamaki Estuary) are well below ARC's environmental response criteria (ERC) of 1.7 mg/kg (for high molecular weight PAHs) and are currently not increasing, which suggests a negligible environmental risk to benthic estuarine biota. This conclusion is further corroborated by low PAH tissue levels in sentinel bivalves (oysters and mussels) and very low observed biota-sediment accumulation factors for PAHs. Further evidence for low PAH bioavailability is the low PAH extractability observed in biomimetic extractions and only weak UV-inducible phototoxicity to crustaceans in toxicity tests. The combination of generally low environmental sediment PAH levels and low observed bioavailability suggests a low risk of acute toxic effects to benthic estuarine biota that are attributable to PAHs. Nevertheless, in a small number of estuarine locations and freshwater creeks (such as Meola, Motions and Oakley Creek, the Whau River and the upper Tamaki Estuary), sediment PAH concentrations are markedly higher and close to, or higher than, ARC's ERC red criterion. Elevated PAH levels are accompanied by elevated concentrations of trace metals. In these restricted locations, first-tier risk assessment suggests that observed PAH levels, combined with other contaminants, could pose an environmental risk to resident biota. The high sedimentation rates in Auckland's estuaries and the observation that PAH levels currently appear to be at steady-state, suggests that inputs of PAHs to estuarine sediments are presently occurring at a continuous, constant level. Estimates of PAH mass loadings from likely sources rule against atmospheric deposition and run-off from petrol stations as major PAH contributors and point to road run-off as the primary source.

The sparse available data on PAH bioavailability in Auckland's estuaries indicates that there currently is only minor PAH accumulation in sentinel benthic organisms (eg, shellfish) and little

evidence for PAH-related toxicity in estuarine benthic macrofauna, even in sediments with elevated PAH levels. Given the low bioavailability of sediment-bound PAHs and their lack of biomagnification, PAH-related effects in Auckland waters appear to be unlikely for pelagic organisms (eg, plankton and nekton) and higher trophic levels, such as fish, birds and humans. Detailed studies of PAH bioavailability in sediments from seven locations using short-tem toxicity bioassays, PAH accumulation in bivalves, as well as "biomimetic extractions" to estimate the digestive availability of PAHs, suggests a lower risk of PAH-related toxicity to benthic organisms than when applying unmodified sediment quality guidelines.

Since most RDP sediments comprise substantial amounts of organic carbon (1-3 per cent TOC), it is likely that a sizable fraction of PAHs is locked up in sediment organic carbon phases and therefore not readily available for uptake by benthic organisms. However, the fact that correlation between sediment PAH concentrations and total sediment organic carbon are weak for RDP sediments, suggests that PAHs are probably not bound to the entire TOC pool, but rather to certain TOC sub-fractions. This hypothesis has been confirmed by field data showing more than 75 per cent of the PAHs are sorbed to low-density, organic carbon-rich fractions, rather than to TOC-coatings on heavier sediment particles.

Analyses of deep sediment cores in the Manukau Harbour have demonstrated that sediment PAH levels in Auckland were historically higher than they are today, probably due to the widespread use of coal for heating and power, as well as PAH-rich coal tar for road construction. While the use of coal tar largely ceased by the late 1960s, recent coring of Auckland city streets and footpaths has demonstrated that there are still considerable quantities of PAHs locked in pavements in the form of coal tar, such as found in older residential catchments upstream of the most PAH-contaminated monitoring sites. Combining advanced source identification techniques ("PAH fingerprinting") and characterisation of PAH distribution in sediment sub-fractions has provided further evidence that the majority of PAHs in high PAH catchments (eg, Motions Creek) are not derived from current vehicle or residential emissions but rather from roading coal tar. Input of PAH-rich, coal tar laced pavement material is still ongoing, explaining the high PAH levels in the adjacent creek and downstream estuary.

While currently observed PAH levels appear to pose a negligible environmental risk in most of Auckland's estuarine intertidal sediments, continued long-term monitoring is recommend for locations with sediment PAH levels >1 mg/kg to establish likely sources and bioavailability of PAHs at these locations. To this end, a targeted study involving seven estuarine and four stream sediments from the Auckland area was carried out to determine sources of PAHs, contribution from modern road run-off, bioavailability and acute toxicity of sediments.

This current study supported previous findings relating to the low PAH bioavailability of Auckland's estuarine sediments. This was confirmed by complementary "selective" extraction methods employing semi-permeable membrane devices (SPMD's) and a synthetic gut fluid "cocktail" to mimic uptake of PAHs by sediment ingesting organisms. Results from SPMD extractions revealed that only 3-7 per cent of sediment PAHs are bioavailable via pore water exposure; while gut fluid extractions showed that only 0.1-3.4 per cent of the sediment PAHs were bioavailable via sediment ingestion route.

Short-term bioassays with amphipods did not reveal pronounced PAH-related mortality, although amphipod survivability in Auckland estuarine sediments was generally lower than the control sediment (Raglan Harbour). The observed toxicity was poorly correlated to sediment PAH concentrations, which combined with an absence of enhanced UV-induced toxicity, indicated that the reduced amphipod survival was attributable to some other sediment parameter. While the experiments performed cannot provide reliable information whether

PAHs might exert chronic toxicity, the low 14d extraction efficiencies by SPMD membranes suggests that only a very limited pool of PAHs is available for uptake by organisms from porewaters

Source identification using diagnostic PAH ratios confirmed that composition of PAHs in contaminated receiving environment sediments is different to that of road run-off particulates. In agreement with previous studies, all the sediments were characterized by pyrogenic PAH compositions with strong similarity to pyrogenic source materials, such as wood soot, coal soot and coal tar. In contrast, road run-off particulates, conjectured to be a major source of anthropogenic contaminants to Auckland's receiving environments, had a mixed or "intermediate" PAH composition. The "intermediate" composition observed for run-off and air particulates is presumably due to a mixture of petrogenic (eg, road/tyre abrasion and engine oil) and pyrogenic (eg, combustion soot) source particles.

Auckland air particulates, sampled at three times throughout the year, had a very similar PAH composition to road run-off. This is consistent with these two particulate phases being linked by deposition and suspension/resuspension processes. Analysis of coal soot and wood soot marker compounds showed that whereas these combustion sources are relevant in other cities (ie, Christchurch) there is little indication that they constitute a major source of PAHs in Auckland air particulates, run-off or sediments. Concentrations and composition of PAHs in high PAH aquatic sediments is consistent with coal tar constituting over 80 per cent of the PAHs.

Despite the strong weighting due to historic coal tar inputs in some sediments, run-off from modern bituminous-based roads is likely to be an additional important source of PAHs in Auckland's urbanised cityscape, especially in catchments that were developed after the coal tar era of roading (ie, post 1960s). A further objective of this review was therefore to quantify the proportion of PAHs that derived from modern run-off particulates (ie, particles with an "intermediate" PAH composition). This analysis was performed on a suite of run-off particles collected form the Grafton Gully stormwater treatment device (SWTD). Because diagnostic PAH ratios alone did not provide sufficient resolution to quantify the various inputs, petroleum biomarker compounds known as hopanes were analysed. Using an average hopane:PAH ratio and assuming that run-off sampled from the Grafton Gully SWTD is representative of modern road run-off particulates throughout the Auckland area, the proportion of PAHs attributable to run-off particulates was estimated for Auckland receiving environment sediments.

Based on these estimates, modern road run-off particulates contributed between 4-62 per cent of the total concentration of PAHs in receiving environment sediments examined. For sediments with higher PAH levels, the contribution from modern road run-off was lower. For example, for stream sediments containing more the 4 µg/g total PAHs (of possible concern), modern run-off particulates contributed only 4-14 per cent of the total PAHs. At these sites, coal tar inputs from historic road construction practices are the major source of sediment PAHs. For sediments containing approx. 1 µg/g of PAHs, modern run-off contributed 24-62 per cent of the PAHs (with the exception of Hobson Bay). Based on these estimates, and the assumption that the existing "dilution" by inorganic and organic material continues, it seems unlikely that PAH inputs from modern road run-off have the capacity to raise PAH sediment concentrations above the ANZECC low trigger level of 4 µg/g. However, if the sediment inputs to estuaries were to become more dominated by road run-off particulates then the concentrations could theoretically exceed the ANZECC-low guidelines (based on sediments from the Grafton Gully SWTD containing 10-13 µg/g).

This preliminary study to apportion the contribution of modern road run-off to sediment PAH concentrations has important implications for future stormwater management strategies.

Further work is required to characterize "typical" concentrations of PAHs in modern run-off in other Auckland catchments since the current study is based on the run-off collected from Grafton Gully. The finding that continued inputs of modern run-off is unlikely to result in sediment levels exceeding the ANZECC low level (ie, 4 µg/g) is based on the assumption that present day inputs of diluting (ie, clean) particulate material continue in the future. Further work to determine whether this assumption is valid is recommended.

2 General Background

2.1 Brief

In December 2005, NIWA was commissioned by the ARC to produce a comprehensive report with the purpose of identifying major sources of PAHs in Auckland's estuarine and stream environments and an assessment of their bioavailability to aquatic organisms. This report will address the stated priorities of the briefing, in particular:

1. A brief discussion of possible sources of PAHs in the Auckland urban environment.

2. A brief summary of the toxicity of PAHs in waters and sediments to aquatic life including reference to water and sediment quality total and individual PAH guidelines for the protection of aquatic life.

3. An explanation of how the relative amounts of the different PAHs, and their derivatives, in a particular sample can be used to identify the source of the PAHs, ie, the PAH fingerprint.

4. Experimental results showing the "fingerprint" for each of the primary sources in the Auckland region (eg, coal tar, vehicle emissions, wood smoke etc.).

5. Identification of the primary source of PAHs in the bed sediments of the following ARC SOE long-term monitoring sites, Tamaki, Hobson, Motions, Meola, Whau Upper, Whau Wairau, Oakley and three additional stream sediments.

6. Measures of the potential bioavailability of the PAHs in each of the samples included in 5, and an explanation of how the potential toxicity of these samples can be inferred from these measures of bioavailability.

7. General concluding summary of the risks to marine benthic animals, particularly the risks to the sustainability of benthic communities and their associated food webs that can be inferred from the present PAH concentrations in the sediments.

2.2 PAHs: Definition

Polycyclic aromatic hydrocarbons (PAHs) are a diverse class of persistent organic chemicals that are widespread in marine, river and lake sediments and tend to be elevated in areas of human settlement. PAHs enter the environment by a variety of pathways, such as the diagenetic transformation of plant material, seepages or spills of crude oil and refinery products, or by incomplete combustion or distillation (pyrolytic) processes (Burgess, et al. 2003; Neff, 1979). PAHs occur in the environment as complex assemblages of compounds (typically 15-20 PAHs with concentrations > 1 ng/g dry weight), consisting of 2-6 fused benzene units. Because of their poor solubility in water, PAHs preferentially concentrate on sediment or soil particles and accumulate in the lipid-rich tissues of organisms. Owing to their aromatic structure, PAHs are

inherently stable in the environment, particularly under reducing conditions, such as encountered in sediments (Volkering, & Breure, 2003). PAHs that are commonly abundant in environmental samples include phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene and the different isomers of benzopyrene and benzofluoranthene. As a consequence of their toxic (narcotic, and often times phototoxic, endocrine, or carcinogenic) properties, sixteen PAHs have been identified by the World Health Organisation and the U.S. EPA as priority pollutants.

2.3 Sediment PAH levels in Auckland

Several studies conducted over the last two decades have measured PAH concentrations in Auckland Harbour sediments (ARC TP319, ARC TP246, ARC TP203, ARC TP193, ARC TP192, Ahrens, & Depree, 2004, Holland et al. 1993, Wilcock & Northcott, 1995). Concentrations and composition of PAHs found in Auckland sediments are similar to larger cities overseas (Fang, et al. 2003; McCready, 2000; Wang et al. 2001), with a prevalence of compounds with three or more rings. Total PAH levels measured at 27 monitoring sites in the Waitemata Harbour, Manukau Harbour and Tamaki Estuary (ARC's RDP sediment monitoring programme), range from 10-11,000 ng/g (<500 µm fraction), with a median of around 550 ng/g. Median concentrations of high molecular weight PAHs (sum of the six PAHs, benz[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene and pyrene) are approximately 250 ng/g. Sediment PAH levels at the 27 RDP monitoring sites have been more or less stable over the period 1998-2002, although analysis of deep sediment cores from Mangere Inlet suggests that PAH levels were once significantly higher, at least in the Manukau Harbour (Wilcock & Northcott, 1995). With two exceptions (Motions and Meola Creek), sediment PAH concentrations in Auckland tend to correlate strongly with concentrations of other urban stormwater contaminants, such as zinc and copper. However, the apparent absence of a temporal trend in PAH accumulation (or decrease) contrasts with the observed gradual increase of sedimentary zinc and copper concentrations in the <63 µm particle fraction over the same period at many monitoring sites (ARC TP246). Although the lack of a PAH temporal trend could be masked by greater analytical variability, it appears that PAH sources differ somewhat from those of trace metals, and PAH inputs and losses to and from the environment are currently at a steady state.

PAH sediment concentrations vary strongly from location to location and tend to reflect degree of urbanisation. Lowest PAH levels of 10-30 ng/g occur furthest away from the Auckland city centre (or having the shortest history of urbanisation), and include Browns, Awaruku, Vaughans and Te Matuku (Waiheke Island). In most parts of the Manukau Harbour, and in sediments of suburbanised creeks of the upper Waitemata Harbour, PAH levels are around 200-800 ng/g, whereas in fully-urbanised, industrialised, or high-density catchments, downstream PAH levels range between 1000-2000 ng/g. Exceptionally high sediment PAH levels, exceeding 5000 ng/g, occur along the entire length of Motions and Meola Creek and appear to have a unique origin.

Consistent with findings in Christchurch (Depree and Ahrens, 2005), the sediment concentrations of PAHs from small Auckland streams are often higher than PAH levels in estuarine sediments. Webster et al. (2004) reported sediment PAH concentrations of 350-31300 ng/g (ppb) from 16 small streams or drains within the Auckland City area. Of the 16 streams, eight contained less PAHs than the ANZECC lower trigger level of 4000 ng/g, ranging between 350-3220 ng/g, with a median concentration of 1500 ng/g. The other eight stream sediments exceeded the ANZECC SQG-low trigger level, with concentrations ranging from 5550-31,300 ng/g and a median of 16,800 ng/g (or 16.8 µg/g). These higher concentrations of PAHs in stream sediments are expected as streams are natural conduits for stormwater run-off, and compared with estuarine receiving environments, there is considerably less surface area for "dilution" of deposited run-off particulates. In addition analysis of 35 street sweeping and catchpit particulate samples showed that fine material (ie, <63 µm) made up only 6 per cent of the composite mass (Depree et al. 2007). Therefore, the majority of road run-off, and associated contaminants are likely to be exported to the aquatic receiving environment, and ultimately deposited on stream beds, explaining the high observed PAH concentrations. This is particularly important for catchments that have had historic inputs of roading coal tar; such as Motions Creek where such inputs appear to account for ca. 90 per cent of PAHs in estuarine and stream sediments (refer to Section 4.2.3 and Figure 18). Sediments from three of Auckland's most contaminated streams, namely Domain, New Market and Waiatarua have been included in this study.

2.4   PAH composition

Twenty-four PAHs are analysed routinely for the ARC RDP programme, encompassing the 16 PAHs recommended by the USEPA, as well as a small number of alkylated derivatives. PAH compositional signatures among Auckland's estuarine sediments are remarkably similar (Table 1), with a prevalence of high-molecular weight PAHs (>3 rings), notably fluoranthene and pyrene, together comprising nearly 25 per cent of total PAH concentrations. Levels of naphthalenes and alkylated PAHs are relatively low, indicative of negligible contributions from petrogenic (ie, derived from petroleum hydrocarbons) sources. The overall PAH composition in Auckland sediments is typical of material of pyrogenic origin (ie, derived from combustion of petroleum and other organic materials) and very similar to PAH signatures of many harbour sediments overseas. However, the prevalence of a pyrogenic PAH signature in sediments may also be due, in part, to the fact that petrogenically-formed PAHs, including a greater proportion of low molecular PAHs, tend to be less persistent in the environment, presumably by being bound to a more labile organic carbon matrix (Burgess et al. 2003).

Table 1
Relative PAH composition of Auckland sediments (1998 ARC RDP data).

Compound	Average	Std. deviation
Naphthalene	1.5%	1.3%

2-Methylnaphthalene	1.2%	1.0%
1-Methylnaphthalene	0.6%	0.5%
Biphenyl	0.9%	1.0%
2,6-Dimethylnaphthalene	3.1%	3.0%
Acenaphthylene	0.6%	0.2%
Acenaphthene	0.3%	0.1%
2,3,5-Trimethylnaphthalene	0.2%	0.1%
Fluorene	0.5%	0.2%
Phenanthrene	5.1%	1.2%
Anthracene	1.1%	0.3%
1-Methylphenanthrene	1.1%	0.4%
Fluoranthene	11.8%	2.4%
Pyrene	12.4%	2.9%
Benz[a]anthracene	5.3%	1.3%
Chrysene (+ Triphenylene)	6.3%	1.1%
Benzo[b+j]fluoranthene	10.0%	1.0%
Benzo[k]fluoranthene	3.5%	0.5%
Benzo[e]pyrene	5.5%	0.6%
Benzo[a]pyrene	7.3%	1.5%
Perylene	7.8%	5.5%
Indeno[123-cd]pyrene	6.2%	1.0%
Dibenz[ac+ah]anthracene	1.2%	0.2%
Benzo[ghi]perylene	6.5%	0.8%

2.5 Possible PAH sources

From first principles, it may be assumed that PAH entering the receiving environment from the full spectrum of anthropogenic sources, including transport, heating, energy generation, manufacturing and construction. Inputs of PAHs from pyrogenic origin tend to dominate in urban estuaries, except for local point sources (eg, fuel tanks). Whereas it is straightforward to distinguish between PAHs of petrogenic and pyrogenic origin by using the abundance of alkylated marker compounds (which are higher in petrogenic material), estimating the relative contributions of specific sources, such as vehicle exhausts vs. residential heating, is much more challenging. The fact that the majority of urban sediments carry a pyrogenic signature that is remarkably similar world-wide suggests that either (a) PAH sources are similar worldwide, or (b) the assemblage of PAHs produced by incomplete pyrolysis is more or less invariant, regardless of which type of organic matter is burned. Even though most human-derived PAHs are formed by combustion processes, aerial dispersal and deposition appears to contribute only marginally (ie, less than 10 per cent) to inputs. The majority of PAHs are believed to be advected into harbours and estuaries by stormwater run-off, since particulate PAH levels correlate closely with other stormwater contaminants such as zinc and copper.

In most modern cities, transport infrastructure occupies up to 30 per cent of the surface area. Particulate material that settles on these surfaces is conveyed by stormwater and discharged to the aquatic receiving environment. Larger particulates will have a tendency to settle in higher energy environments (for example streams), whereas finer particulates will settle in the low energy estuarine environments. In addition to road run-off, stormwater is furthermore comprised of run-off from roofs and overland run-off from pervious surfaces such as lawns and gardens. Whereas road and roof run-off is expected to contribute a high proportion of anthropogenic particles, run-off from grassed/dirt surfaces is expected to contribute largely clean (with respect to PAHs) particulates consisting of soil and plant detritus.

Excluding any inputs from wastewater sewers (ie, combined sewer systems), road run-off is considered to be the major source of PAHs in stormwater. Possible sources of PAHs from road run-off include tyre abrasion, pavement abrasion, oil leaks, and exhaust particulates. As mentioned in Section 1.3, PAHs can be classified into two major groups, petrogenic and pyrogenic, which provides a useful starting point for trying to identify the major sources of PAHs in road run-off. Of the sources listed above, tyres and bitumen are strongly petrogenic, whereas used oil and exhaust particulates tend to contain a combination of petrogenic and pyrogenic PAHs, leading to an "intermediate" character. This is because used engine oil (petrogenic) contains a substantial portion of engine soot deposits and/or has been thermally degraded. Analogously, exhaust particulates (pyrogenic origin) may have a significant amount of unburned petrogenic PAHs sorbed onto the surface of the soot particles. Thus, assuming road run-off is the major source of PAHs in urban sediments, it should be possible, using modern analytical source identification techniques, to estimate the proportion that different source materials contribute to the inventory and composition of sediment PAHs. Various such source identification techniques are discussed in Section 3.2 (PAH source identification).

₃ Environmental Risk

3.1 PAH toxicity

PAHs may exert various types of toxicity, ranging from narcosis, phototoxicity and hormonal disturbance to DNA and protein adduct formation and, ultimately, cancer (van Brummelen et al. 1998). While toxicity varies greatly depending on PAH compound, all PAHs share nonpolar narcosis as a common mode of toxic action. This acute, non-specific mode of toxicity (also referred to as "baseline toxicity") involves PAH molecules associating and interfering with transport processes in the cell membrane. As a general rule, narcotic toxicity increases with molecular weight. Thus, naphthalene is less toxic than fluoranthene, with a higher estimated final chronic water concentration of 322 µg/L, compared to only 12 µg/L for fluoranthene (Di Toro et al. 2000). On the other hand, while higher molecular weight PAHs are more toxic, they are less water-soluble than low molecular weight PAHs and tend to accumulate in tissues at slower rates. Acute PAH toxicity is usually due to non-polar narcosis.

Due to the fact that PAHs commonly occur as complex mixtures in field samples, a substantial effort has been made to predict the toxicity of PAH mixtures rather than that of individual compounds. Based on the assumption of a common mode of narcotic action, concentration addition models have been proposed to predict the effects of exposure to PAH mixtures (Di Toro et al. 2000; Olmstead & LeBlanc, 2005). For sediments, a toxic units approach has been promoted to predict the acute toxicity of sediment-associated PAH mixtures to aquatic organisms (Swartz et al. 1997; Swartz et al. 1995; Verrhiest et al. 2001). This involves dividing the measured concentration of the respective contaminant by its respective sediment guideline value and summing the individual quotients. In general, concentration addition methods do reasonably well in predicting acute toxicity, even though they tend to both over-predict and under-predict toxic response by a factor of two to three when compared to experimental results (Olmstead & LeBlanc, 2005). Hereby, it needs to be noted that most PAH toxicity assays have determined acute toxicity over a 48-96 h exposure duration, so that concentration addition predictions apply primarily to acute, non-polar narcosis. Alternatively, synergistic toxicity models and models of "independent joint action" have been proposed that do not assume a common mode of action. These account for other aspects of PAH toxicity, such as phototoxicity and biochemical activation. For example, fluoranthene and pyrene, in addition to being narcotic, are both phototoxic and also have been shown to interfere (in separate ways) with moulting and growth of arthropods. In contrast, phenanthrene is not phototoxic, while it does decrease moult frequency in daphnid crustaceans (Olmstead & LeBlanc, 2005). As a caveat, different toxic modes operate on different time scales, so that a completely mechanistic prediction of chronic toxicity is difficult. Despite a shortage of toxicological data, empirical comparisons suggest that chronic toxicity of PAHs occurs at concentration levels 5-10 times lower than acute toxicity (van Brummelen et al. 1998).

A currently largely overlooked aspect of PAH toxicity is UV photoactivated toxicity (Ahrens et al. 2005; Ahrens & Hickey, 2002; Ahrens et al. 2002; Spehar et al. 1999; Swartz et al. 1997; Veith et al. 1995). Exposure to UV radiation, as is likely to occur on intertidal mudflats or in shallow streams with low turbidity, can enhance acute PAH toxicity by a factor of five or more in the absence of shading or UV-minimising behaviour (avoidance by burial) or morphological adaptations (opaque shell, or UV-absorbing compounds or pigmentation). Small, translucent and free-swimming or surface-dwelling organisms, such as many larvae or juveniles might be particularly vulnerable to UV-photoactivation (Pelletier et al. 1997), but are commonly not included in toxicological assessments.

Compared to benthic organisms, planktonic and other pelagic biota (organisms living in the water column) are generally less prone to exposure to high PAH concentrations, due to the typically 1000-10,000 times lower PAH levels in the water column compared to sediment. On the other hand, the reduced risk of exposure to high PAH levels in the water column might be offset by higher UV levels and lack of shelter in surface waters. This can be especially relevant for meroplanktic organisms, such as many bivalve species, having a benthic adult and a planktonic larval or juvenile stage. Maternal transfer of PAHs via egg lipids can "pre-load" planktonic offspring with PAHs, making them more vulnerable (Pelltier et al. 2000)

3.2   Sediment quality guidelines

A number of sediment quality guidelines have been proposed over the last decade for PAHs and other environmental contaminants, to define "trigger levels" at which toxicity or otherwise adverse effects are likely to occur (Di Toro & McGrath, 2000; Long et al. 1995; MacDonald et al. 1996). The currently used ANZECC (2000) quality guidelines, as well as ARC's Environmental Response Criteria (ERC), are based on primarily empirical correlations between toxicity and sediment dry weight-normalised PAH concentrations, from which threshold values are derived, such as the effects range median (ERM) and effects range low (ERL), as proposed by Long et al. (1995), or the threshold effects level (TEL) and probable effects level (PEL) of MacDonald et al. (1996). These "guidelines" are concentrations, derived from ecotoxicological datasets, at which adverse effects have been observed in 10 per cent or 50 per cent of the cases. For total (sum) PAHs, the ANZECC low trigger value is 4 µg/g dw (= µg/kg dw), whereas the high trigger value is 45 µg/g dw (ANZECC 2000). Analogously, for high molecular weight PAHs, (the sum of the six high molecular weight compounds benz[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene and pyrene, the ANZECC low and high guideline values are 1.7 µg/g and 9.6 µg/g, respectively. Guidelines for total PAHs and high molecular weight PAHs are based on a derivation by Long et al. (1995). ARC's ERC red criterion of 1.7 µg/g dw uses the summed concentration of the six aforementioned high molecular weight PAHs. Being based primarily on data from acute bioassays, current PAH sediment quality guidelines provide "safe levels" for acute PAH toxicity. As these empirical guidelines are based on dry weight-normalised concentrations of field-collected sediments or on theoretical (equilibrium partition) calculations (Di Toro et al. 1991), they lack a cause and effect

basis and make no mechanistic correction for variable bioavailability or additive toxicity. For this reason, ERL and ERM values contain a high degree of uncertainty and are probably unreasonably low (overprotective) for individual PAH compounds and for sediments with organic carbon content greater than 1 per cent or having otherwise modified bioavailability (eg, sediment containing super-sorbent black carbon phases). On the other hand, they do not predict chronic PAH toxicity, as might be caused by endocrine disruption or adduct formation, which may compensate for the "overprotection" of acute toxicity. For PAH mixtures, empirical guidelines do not differ substantially from mechanistically-derived criteria, such as those of Di Toro & McGrath, (2000), and are, thus, an acceptable option for a first-tier risk assessment to determine "potential toxicity". However, ultimate confidence about whether a sample is toxic or non-toxic can only be achieved by conducting bioassays.

3.3   PAH sub-fractions, mobility and persistence

Due to their pronounced hydrophobicity, PAHs will strongly associate with sediment particles, and in particular the organic fraction. However, unlike trace metals, PAHs in Auckland sediments do not appear to be concentrated in finer grain size fractions (Table 2). In fact, highest PAH concentrations are typically found in the coarsest (sand) grain size fractions. This finding is inconsistent with aerosolic soot particles as a major PAH source, and, instead, points to land-derived, nearby inputs. For the majority of sediments for which PAHs have been analysed in different size fractions, more than 50 per cent of the composite PAH levels are found on grain size fractions >63 μm. Size and density fractionation of Motions Creek sediment has furthermore demonstrated the majority of PAHs to be associated with low-density ($\rho < 2.15$ g/cm^3), coarser particle fractions (Figure 1): over 75 per cent of the composite PAH concentration is contributed by the light-weight fraction, which represents only approximately 3 per cent of the sediment mass. Compared to clay-sized particles, coarser particles will have a lower likelihood of being resuspended and transported over long distances, and will therefore deposit closer to their origin rather than in regions of slow water flow. Analysis of sediment PAH levels of urban creeks upstream from estuarine settling zones (in Motions and Meola Creek and in several urban streams in Christchurch) has confirmed high PAH levels in upstream sediments, indicating that PAHs do not preferentially concentrate in low energy settling zones (Depree & Ahrens, 2005).

Table 2

PAH, mass, and organic matter (OM) of size fractionated sediment samples from five Auckland locations (sum PAH*= Σ(PHE to B[ghi]P)). Unpublished NIWA data, collected by G. Mills.

Site	Size fraction (µm)	Sum PAH* (ng/g)	OM (%)	% Total mass	% Total PAH	% Total OM
Cheltenham	500-1000	6478	3.2	0.1	1.4	0.2
Cheltenham	250-500	1453	1.7	2.0	9.9	2.7
Cheltenham	125-250	383	1.4	59.3	78.6	64.2
Cheltenham	63-125	66	1.0	37.8	8.7	29.0
Cheltenham	<63	480	5.8	0.9	1.4	4.0
Cheltenham	composite	289	1.3	100.0	100.0	100.0
Hobson	500-1000	6137	2.6	0.2	5.1	0.5
Hobson	250-500	441	0.7	3.6	7.6	2.7
Hobson	125-250	44	0.6	45.7	9.6	29.7
Hobson	63-125	114	0.6	42.5	23.1	29.5
Hobson	<63	1439	4.3	8.0	54.7	37.7
Hobson	composite	211	0.9	100.0	100.0	100.0
Pakuranga	500-1000	6567	24.0	0.3	2.9	1.1
Pakuranga	250-500	1830	8.5	1.9	5.4	2.7
Pakuranga	125-250	670	2.8	11.8	12.6	5.7
Pakuranga	63-125	501	1.9	15.1	12.1	4.8
Pakuranga	<63	593	7.0	70.9	67.0	85.6
Pakuranga	composite	628	5.8	100.0	100.0	100.0
Motions	500-1000	5845	13.5	0.5	0.4	2.2
Motions	250-500	19684	3.4	4.4	11.9	5.0
Motions	125-250	9616	1.3	40.0	52.4	17.0
Motions	63-125	5894	0.7	25.3	20.4	6.0
Motions	<63	3676	7.0	29.7	14.9	69.8
Motions	composite	7335	3.0	100.0	100.0	100.0
Meola	500-1000	100353	32.5	0.1	2.2	0.5
Meola	250-500	72576	11.5	0.8	12.1	1.5
Meola	125-250	18186	3.2	5.8	21.4	2.9
Meola	63-125	10952	2.1	9.3	20.7	3.1
Meola	<63	2551	7.1	84.0	43.6	92.1
Meola	composite	4915	6.5	100.0	100.0	100.0

Figure 1

Relative contribution of seven size and density separated particle fractions to total sediment PAH concentrations in Motions Creek. L = lightweight sub-fraction ($\rho < 2.15$ g/cm^3) H = heavy sub-fraction ($\rho > 2.15$ g/cm^3). Un-sieved, density-separated bulk sediment is shown for comparison. Data from Ahrens & Depree (2004).
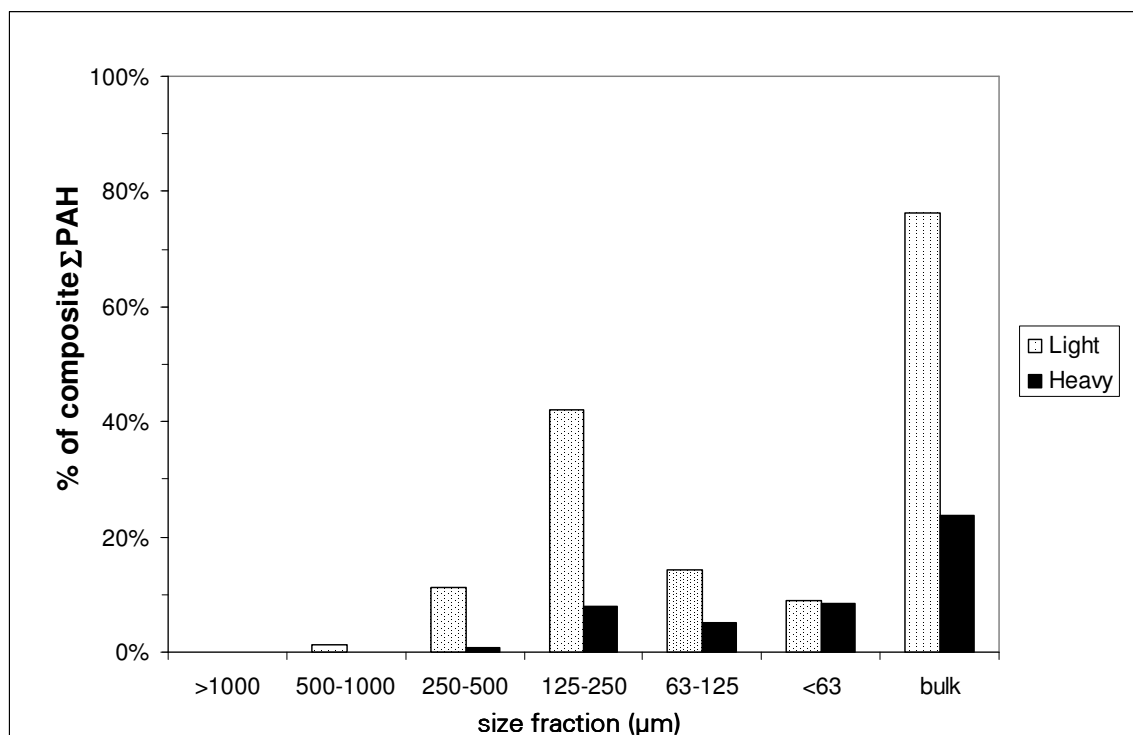
While PAH levels of Motions and Meola Creek are high and exceed both ANZECC and ARC sediment quality guidelines, the majority of current RDP sites have PAH concentrations less than 1 µg/g, falling well below the ANZECC guideline of 4 µg/g (equivalent to ca. 1.7 µg/g for high molecular weight PAHs). This suggests a low likelihood of acute and even chronic PAH toxicity for the majority of Auckland Harbour sediments. The observation that sediment PAH levels appear to be at steady state (ARC TP193, 2002), suggests no increasing risk due to ongoing PAH inputs. Furthermore, unlike other persistent organic contaminants, such as PCBs and organochlorines, PAHs do not biomagnify along the food chain, due to the ability of vertebrates to detoxify PAHs effectively. Thus, PAH levels in tissues of fish, birds and mammals are typically lower by several factors than those of invertebrates (van Brummelen et al. 1998). These findings relate to measurements made overseas and have not been verified for Auckland estuaries, since very little PAH data exist for vertebrates from Auckland waters. Noting this caveat, ecological risk emanating from PAHs is therefore likely to be restricted to lower levels of the aquatic food chain.

The persistence of PAHs in the environment is due to their chemically stable structure and the fact that microbial degradation rates are very slow, especially under anaerobic conditions (Volkering & Breure, 2003). Nevertheless, given sufficiently long time, PAH concentrations in older sediments would be expected to decrease gradually over time. This does not appear to be the case in Auckland and the finding of similar (or even higher) PAH levels in lower sediment layers of 2.5 m long cores from the Manukau (Wilcock & Northcott, 1995) suggests very low PAH bioavailability for microbial degradation. Reduced PAH bioavailability should likewise lessen the rate of PAH uptake by sediment-dwelling macroinvertebrates, thereby further diminishing the risk of PAHs reaching toxic tissue levels. In summary, the risk of PAH toxicity is therefore not determined by total PAH concentrations in the environment but to a crucial extent by PAH bioavailability. All current evidence points to PAH bioavailability being low in Auckland sediments, as will be described in the next section.

3.4 Bioavailability and bioaccumulation

Due to their hydrophobic nature, PAHs tend to accumulate in the fatty tissues of organisms, especially the benthos. Bivalve tissues from Auckland waters typically contain PAH levels of around 0.1-1 µg/g lipid. Measured bioaccumulation factors for PAHs in bivalves are considerably lower than for other persistent organic pollutants, such as PCBs. Biota-sediment accumulation factors, or BSAF (defined as the ratio of lipid-normalised tissue PAH levels to organic carbon-normalised sediment PAH levels), of mussels, oysters and cockles collected from Auckland estuaries are on the order of 0.01-0.1, compared to the theoretically expected value of around 1 (Hickey et al. 1995). While BSAFs of PAHs are known to be lower than predictions from equilibrium partition theory, these deviations are usually no greater than a factor of five (Meador, 2003). Reduced PAH bioavailability is believed to occur when PAHs are associated with super-sorbent organic material (eg, "black carbon") that has much higher sorption strength than generic organic matter. Furthermore, owing to their aromatic and planar chemical structure, PAHs are believed to penetrate deeply into intermolecular spaces of organic matter, thereby becoming less likely to desorb. Tissue PAH levels measured in oysters and mussels as part of the ARC's sentinel shellfish monitoring programme confirm the hypothesis that PAHs are not strongly bioaccumulated (relative to pristine control samples). PAH tissue concentrations range from 0.1-1 µg/g lipid in oysters from the Manukau Harbour, and 0.050-1 µg/g lipid in deployed mussels from the Waitemata, Manukau and Tamaki Estuary. It may be argued that mussels and oysters, by their lifestyle as surface-dwelling suspension feeders, are not directly exposed to sediment PAHs, and that infaunally-living organisms would therefore be more prone to higher PAH bioaccumulation. Indeed, work by Hickey et al. (1995) has shown that deposit-feeding wedge-clams (*Macomona liliana*) have up to 10 times higher tissue concentrations than suspension-feeding cockles (*Austrovenus stutchburyi*). Nevertheless, PAH levels in both bivalve species are still more than one order of magnitude below predictions based on equilibrium partition theory (as noted above). Reductions of tissue PAH levels by the organisms' own metabolism can be assumed to be negligible, as bivalves possess only weak PAH detoxification mechanisms (van Brummelen et al. 1998). It, therefore, appears that only a small fraction of sediment-

bound PAHs in Auckland sediments, on the order of 1-10 per cent, are bioavailable for uptake.

Only few studies have been conducted to quantify the trophic transfer of PAHs through the food chain. Studies to date uniformly indicate that PAHs tissue concentrations decrease with higher levels of the food chain (Wan et al. 2007), in contrast to other persistent organic contaminants such as PCBs that tend to biomagnify. This "trophically dilution" phenomenon, is a result of the well-established PAH-metabolising capabilities of the vertebrate liver. Liver enzymes (cytochrome c oxidase) quickly hydroxylate PAHs, accelerating their excretion and shortening PAH residence time in the tissue. In fact, measurement of the activity of cytochrome c-oxidase enzyme P450 1A is used as a biomarker of PAH exposure in fish (Sarkar et al. 2007). While this diminishes the likelihood of acute toxic effects, the generation of "activated", more water-soluble PAH metabolites increases the frequency of DNA-adduct formation and the likelihood of chronic adverse effects, such as cancers (Hylland, 2000).

Experiments aimed at estimating PAH bioavailability by mimicking uptake from porewater and via the digestive tract have confirmed the low extractability of sediment-bound PAHs by seawater or biological fluids. NIWA research using seawater, invertebrate gut fluids and synthetic "gut fluid cocktails" (consisting of mild detergent solutions) as extractants has found only up to 10-20 per cent of sediment PAHs to be readily extractable (Ahrens et al. 2005, Ahrens & Hickey, 2003 and Ahrens, unpublished data). This suggests that given the median PAH sediment concentration of 0.55 µg/g, only about 0.05-0.1 µg/g is available for exchange with biological tissues. Assuming equilibrium partitioning of this sub-fraction, and given a typical sediment organic carbon content of 1 per cent (equating to PAH levels of 5-10 µg/g OC), as well as typical organism lipid contents of 5-10 per cent, one would therefore expect PAH tissue levels of 0.25-1 µg/g lipid, which is about the range of lipid-normalised PAH concentrations that are in fact measured in oysters and mussels from the field. Up to now, biomimetic PAH bioavailability estimates had only been performed for sediment from Motions Creek. For generalisability, confirmatory measurements for other locations with elevated PAH levels were needed, and were conducted, as described in the next section.

3.5   PAH Bioavailability survey of Auckland sediments

In order to obtain a better understanding of PAH mobility and bioavailability in Auckland sediments, a survey of seven estuarine sediments from ARC's long-term sediment monitoring project was conducted. The objective of this investigation was to determine potential bioavailability (extractability) of PAHs in field-collected sediments using mild extraction conditions to estimate the size of the rapidly extractable and thus potentially bioavailable PAH pool. The amount of weakly-extractable PAH was compared with total PAH levels (as determined by exhaustive organic solvent extraction) to determine the percentage of PAHs potentially available for biological uptake. In addition to these "biomimetic" extractions, PAH bioavailability was

furthermore assessed in short-term toxicity assays measuring PAH toxicity of sediments to benthic microcrustanceans (amphipods).

3.5.1 Methods

Seven sediments, collected and archived for the 2001 ARC long-term (baseline) monitoring programme, were used for biomimetic extractions and toxicity tests. Selected sediments were from Hobson Bay, Whau-Upper, Whau-Wairau, Motions Creek, Meola Creek, Tamaki River and Oakley Creek. Sediments had been previously analysed for PAH and trace metal content (ARC TP192, 2002) and had been stored as freeze-dried, sieved sub-samples (<500 μm) in glass jars. For preparing uniform sediment composites, replicate samples from each site were combined in equal weight-proportion and thoroughly mixed, rendering a total composite mass of approximately 60g for each location. The seven composite sediments thus prepared were used in all subsequent bioavailability experiments.

Two types of mild extraction procedures were carried out, with the objective to simulate uptake of PAHs by pore-water route and digestion, respectively. For estimating PAH availability by pore-water, sediment-seawater slurries were incubated with triolein-filled semi-permeable membrane devices (SPMDs) acting as an infinite sink for PAHs, following general methodology of Zimmerman (2004), with modifications. SPMDs were purchased from Environmental Sampling Technologies Inc. (Missouri, USA) and consisted of 10 cm long, low-density polyethylene tubing (additive free), filled with 0.1 g triolein. Incubations were carried out in Corex glass vials, which have minimal tendency for adsorbing PAHs. For each of the seven sites, duplicates of 10 g dry sediment (<500 μm) were extracted with 40 ml of carbon-filtered seawater (35 ppt), to which was added one SPMD, corresponding to a solid/fluid ratio of 1:4. Sodium azide was added at a concentration of 77 mM to inhibit microbial activity. Vials were sealed with Teflon-lined caps and placed on a rotary shaker for 14 days at six revolutions per minute.

To simulate PAH bioavailability via the digestive route, sediments were incubated with a synthetic "gut fluid cocktail" to approximate the surface-active and protein rich conditions in the digestive tract of deposit-feeding organisms (Voparil et al. 2004,Voparil & Mayer, 2000). The gut fluid cocktail consisted of 10 mM sodium taurocholate (TC) and 0.5 per cent (w/v) bovine serum albumin (BSA), dissolved in carbon-filtered seawater. This composition has been shown to approximate the PAH-solubilisation properties of deposit-feeding polychaete gut fluids (Voparil & Mayer, 2004). Sodium azide (77 mM) was added to inhibit bacterial activity. Forty ml of synthetic gut fluid and 10 g of dry sediment were added per Corex glass vial. To envelope the range of gut passage times encountered among deposit feeders, incubations were carried out overnight (15 hours), on a rotary shaker at six revolutions per minute.

SPMDs were recovered after 14 days. To remove adhering sediment particles, each membrane was rinsed with 300 ml of distilled water, then placed in 150 ml of 1 N HCl for 10-20 sec, blotted dry, and gently wiped with an acetone-soaked paper tissue. PAHs were recovered from membranes by dialysis into 40 ml hexane for 18 h, using

200 ml capped glass jars, with an aluminium liner between jar and lid. To monitor recovery of dialysed PAHs, 500 µg of seven deuterated PAH surrogates were added to the hexane phase (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, fluoranthene-d10, pyrene-d10, benz(a)anthracene-d12, perylene-d12), spanning the range of expected PAH hydrophobicity (log K_{ow} 3-7). Dialysates were collected in round bottom flasks, and dialysis of SPMDs was repeated in a fresh volume of hexane (40ml) for another 24 h, after which both dialysates were combined and the hexane volume reduced to approximately 1ml by rotoevaporation at 40°C and 150 mbar. Sample cleanup followed the procedure described further below.

For recovery of PAHs in taurocholate-BSA (TCBSA) treatments, incubation vials were removed from the rotary shaker after 15 hours and centrifuged at 2000 rpm for three hours, which rendered a clear supernatant. PAHs were recovered from the supernatant by liquid-liquid extraction into double-distilled dicholoromethane (DCM). Two different extraction procedures were employed: replicates from the first TCBSA batch were liquid-liquid extracted in 100ml glass separating funnels, containing 30 ml of DCM and 30 ml of PAH-containing supernatant. Funnels were pre-rinsed with 20 ml DCM. Prior to adding to funnels, TCBSA supernatants were pre-filtered through GC50 filters to remove any residual suspended solids. Seven deuterated surrogates (500 µg each) were added to the DCM/TCBSA mixture, to quantify transfer efficiency and overall recovery of PAHs. Funnels were vigorously shaken for 1-minute, and then allowed to stand until phase separation was achieved. To minimize foaming and emulsification and to improve separation of the immiscible aqueous and DCM phases, 3 ml of 1.2 N HCl were added to each funnel. It was found that phase-separation could be further accelerated by gently warming the funnel walls with a hair-dryer, on a low setting. Upon phase separation, the DCM phase was drained directly into pre-conditioned clean-up columns, and the separation cycle repeated for total of three times per sample, followed by a final rinse of 10 ml DCM (total DCM volume per sample = 100 ml).

As an alternative to the separatory-funnel procedure, liquid-liquid extraction using reflux chambers was trialed for the second batch of replicates. Reflux chambers contained 150 ml of double-distilled DCM, which was continuously refluxed through the aqueous phase by a cycle of evaporated and re-condensation. As with separatory funnels, deuterated PAH surrogates (500 µg per surrogate) were added. Reflux duration was six hours.

Sample cleanup followed standard operating procedures, using pre-baked 20 cm glass columns containing 2 g of activated alumina, 4 g of silica, and 2 g of anhydrous sodium sulphate, to remove residual water. Columns were pre-rinsed with 20 ml of DCM before sample addition, and then eluted with 3x10ml of DCM. DCM volume of the purified PAH fraction was subsequently reduced by rotary evaporation (35°C, 300 mbar). PAH fractions were exchanged into 300 µl heptane, and combined with activated copper filings to remove sulphur. Prior to transfer to GCMS target vials, 250 or 500 µg of internal standard (p-terphenyl-d14) were added.

For quality assurance, duplicate procedural blanks were run alongside the TCBSA and SPMD treatments, containing all components except sediment. Furthermore, a certified reference material (coal tar SRM 1597a, from NIST) was analysed. Measured

PAH concentrations fell within ±28 per cent of reported concentrations (average: 18 per cent), with total PAH levels being lower by about 13 per cent.

PAHs were analysed by GCMS in selected ion monitoring (SIM) mode, using standard NIWA analytical procedures. Quantitated PAH data accounted for surrogate recovery (as determined from the deuterated surrogates) and variable mass and volume extracted. Results are reported after blank-subtraction. For nomalisation, sediment total organic carbon (TOC) content was determined on freeze-dried, acidified sub-samples, using CHN analysis

Short-term (seven-day) toxicity bioassays were conducted using the benthic amphipod *Melita* sp., collected from an uncontaminated site in Raglan Harbour (Waingaro Landing). For direct comparability with mild extraction treatments, exposure conditions deviated from standard NIWA operating procedures: bioassays were carried out in 40 ml Raglan seawater (35 ppt), containing 10 g of sediment, using the same size 50 ml Corex tubes used for mild extractions with no pre-equilibration time. Control sediment was from Raglan (Waingaro Landing), sieved at a mesh size of 250 μm to remove any potentially resident juvenile amphipods. Treatments were set-up in duplicate (for ARC sediments) and five replicates for Raglan controls, with 10 adult amphipods per replicate vial. It should be noted that contaminated sediments used were previously freeze-dried and had to be reconstituted in seawater, which increased salinity compared to fresh Raglan control sediment. Thus, given the non-standard exposure procedures, toxicity test results should be interpreted as "indicative" only. Treatments were maintained at 20±1°C in a temperature-controlled room, on an 18:6 h light: dark cycle. Vials were partially covered with polyethylene wrap and constantly aerated over the seven days with whisker tubing, which maintained oxygen concentrations above 5.5 mg/l. Amphipods in all treatments were fed on day five (5 mg "GORP" per treatment). On day seven, amphipods were sieved from sediments, placed in polystyrene cups and their survival was scored as follows: any visible movement, either by the whole organisms or its appendages was scored as "alive"; motionless or missing amphipods were scored as "dead". To test for evidence of specific PAH-related toxicity, amphipods were exposed to UV radiation for two hours following initial scoring, which has been shown to enhance PAH-toxicity by up to an order of magnitude (Ahrens, 2002).

For determining sensitivity to PAH-photoactivation, amphipods were exposed to UV radiation under an array of six sunlight-simulating light bulbs (Ultra-Vitalux, Osram) for two hours. To maintain temperature between 20-23°C, amphipods were placed in polystyrene cups containing 50 ml of seawater, which were positioned in a Styrofoam rack floating on an ice-cooled water bath. UV levels under the simulator, measured with a Macam UV203 handheld radiometer, were approximately 50 per cent (UVA) and 85 per cent (UVB) of natural summer (November) sunlight (50 cm path length between bulb and detector), or approximately 16 W/m^2 UVA (320-400nm), and 3.5 W/m^2 UVB (290-330 nm). Following UV exposure, amphipod viability was assessed as described before. In previous work by NIWA, complete UV-enhanced mortality was observed in amphipods (*Chaetocorophium lucasi*) that had been exposed to fluoranthene at concentrations of 10 μg/L for 96h, followed by 1h UV exposure at UVA+UVB intensities of 21 W/m^2 (Ahrens, 2002).

3.6 Results – Mild PAH extractions

Average surrogate recoveries were 73±10 per cent (naphthalene-d8), 89±4 per cent (acenaphthene-d10), 98±3 per cent (phenanthrene-d10), 100±5 per cent (fluoranthene-d10), 96±4 per cent (pyrene-d10), 105±4 per cent (benz(a)anthracene-d12), and 112±15 per cent (perylene-d12). Due to elevated blank concentrations for low molecular weight PAH compounds (naphthalene to 2,3,5 trimethylnaphthalene), results are presented for 15 medium to high molecular weight PAHs only (fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[123-cd]pyrene, and benzo[ghi]perylene, hereafter referred to as "Σ_{15}PAH"). Among higher molecular weight PAHs, dibenz[ah]anthracene concentrations were near limits of detection in several samples and were consequently omitted. PAH extractability (per cent) was calculated by dividing the (blank-corrected) concentration of each respective PAH by the corresponding concentration as per the 2001 ARC PAH monitoring dataset (ARC TP192, 2002). Total PAH extractability (Σ15PAH) was calculated by summing the individual concentrations of the 15 OPAH analytes and dividing this sum by the corresponding sum from the 2001 ARC dataset.

Figure 2 shows extractability of Σ15PAHs (fluorene to benzo(ghi)perylene) relative to PAH levels determined by exhaustive DCM extraction. Σ15PAH extractability ranged from 3-7 per cent for SPMD extractions, and 0.1-3.4 per cent for taurocholate and BSA (TCBSA) extractions. In terms of absolute amounts of PAHs (Σ15PAH) removable by mild extraction, this corresponded to 47-293 ng/g for SPMDs and 1.7-45 ng/g for TCBSA extractions (Figures 3 and 4). Extraction efficiency for individual PAH compounds ranged from 0.02-5.9 per cent for TCBSA treatments and 1-15 per cent for SPMD treatments. Extraction efficiency by TCBSA was significantly correlated (r^2=0.53) with PAH hydrophobicity (log Kow), being lower for more hydrophobic (high molecular weight) PAH compounds (Figure 5). In contrast, PAH extractability by SPMD showed only a weak correlation with log Kow (r^2 = 0.13, Figure 5), indicating that PAH SPMDs had attained PAH-equilibrium over the 14 days.

Figure 2

Extraction efficiency of sediment-bound PAHs (Σ15PAH; fluorene to benzo(ghi)perylene) by 15-hour TCBSA and 14-day SPMD extraction; percentage as compared to 2001 ARC monitoring data; average of duplicate extractions, after blank-subtraction (error bars: mean ± 1 SD).
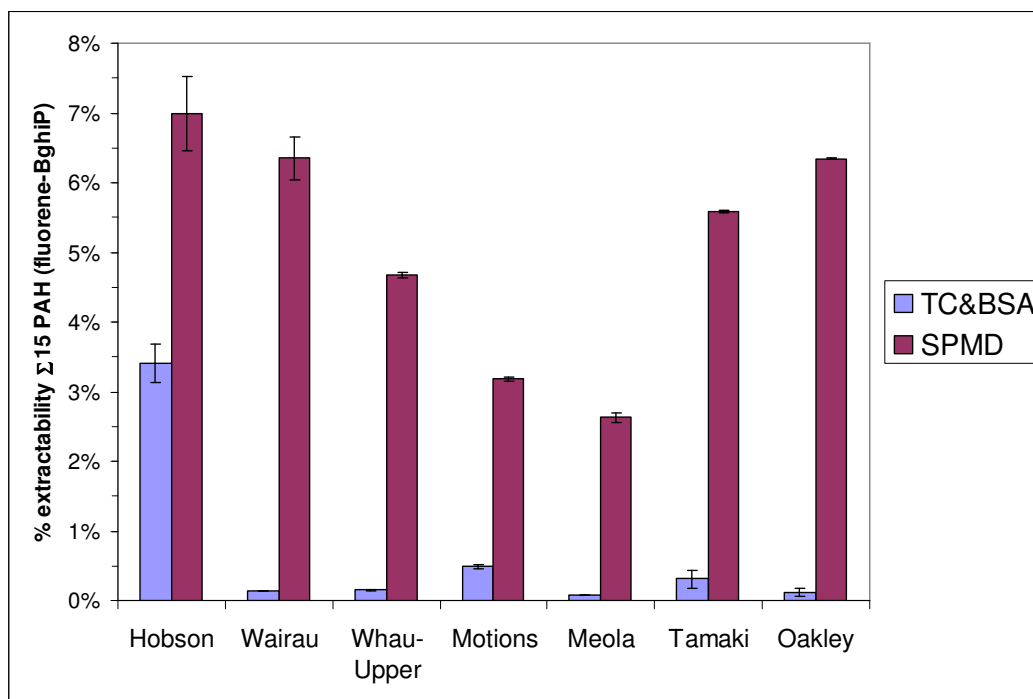

Figure 3

Extractable PAHs (Σ15PAH; fluorene to benzo(ghi)perylene, in ng/g dry sediment) by 15h TCBSA extraction (10 mM taurocholate, 0.5 per cent BSA in seawater); average of duplicate extractions, after blank-subtraction (error bars: mean ± 1 SD).
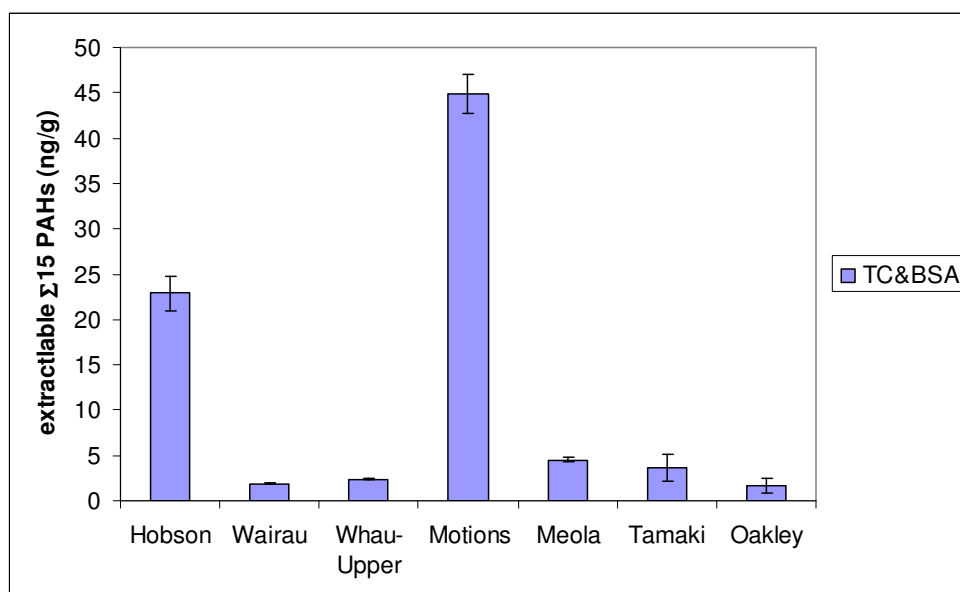
Figure 4

Extractable PAH (Σ15PAH; fluorene to benzo(ghi)perylene) by 14d SPMD extraction (10 cm polyethylene tube, 0.1 g triolein); average of duplicate extractions, after blank-subtraction (error bars: mean ± 1 SD).
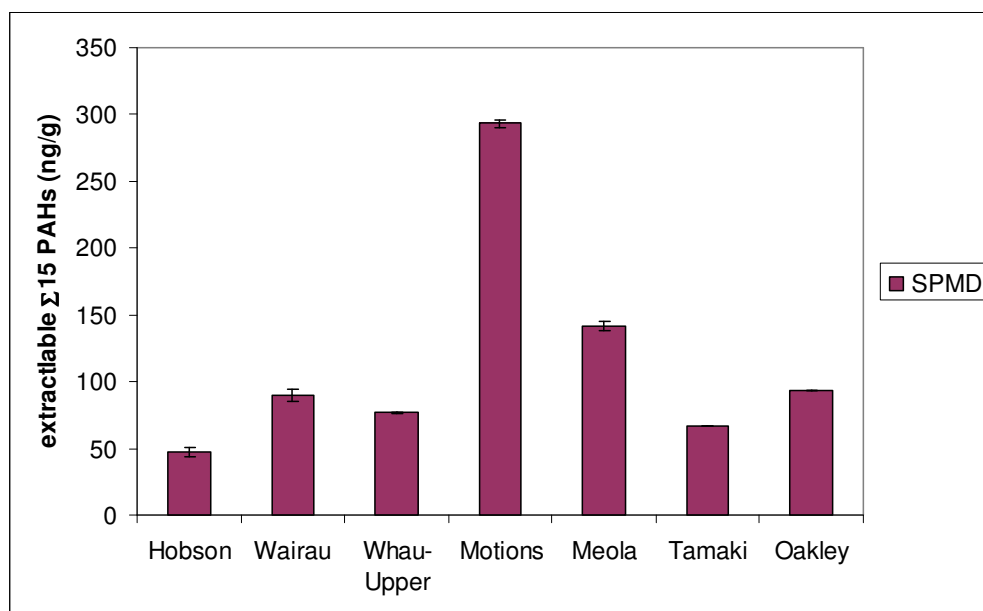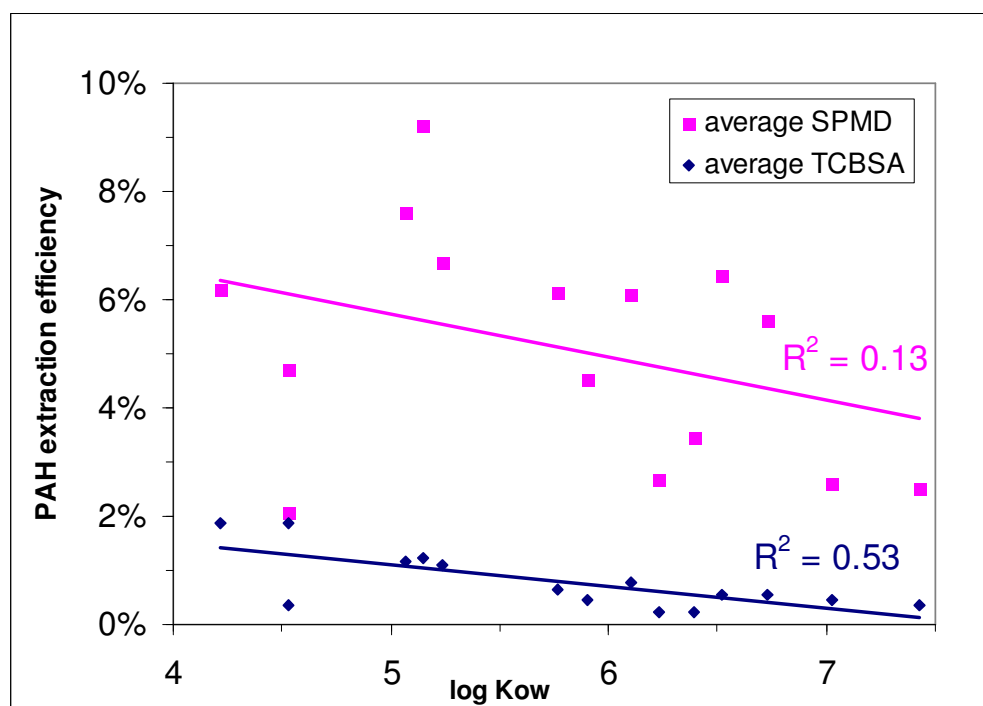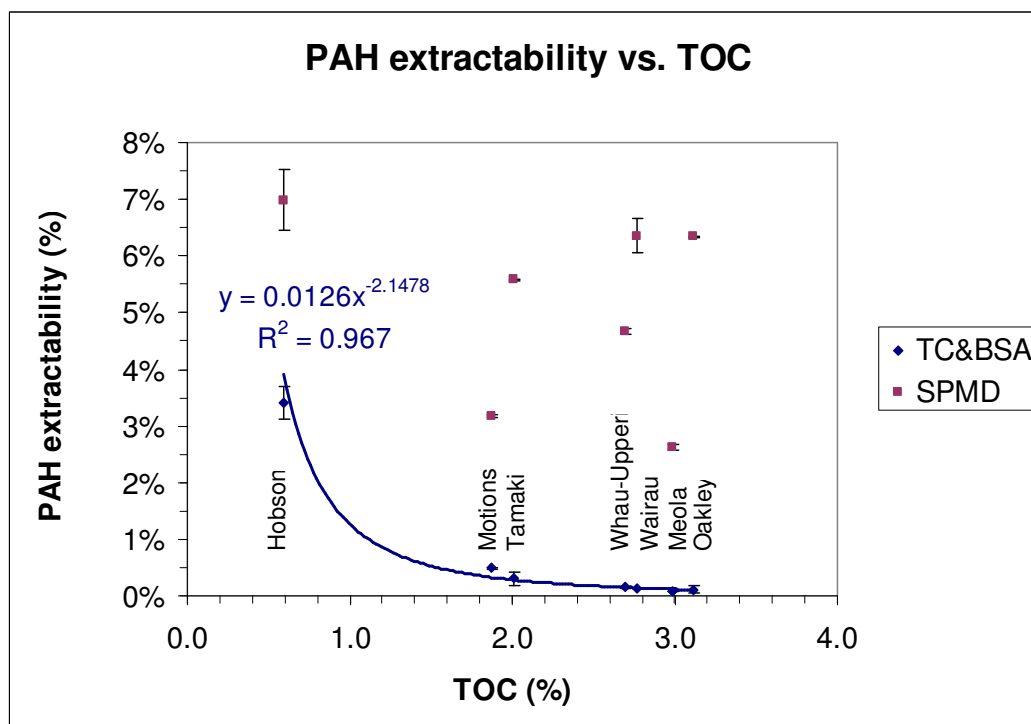

Figure 5

Individual PAH extractability (per cent compared to complete extraction, average of seven sediments) versus PAH hydrophobicity (log Kow) of 15 PAHs (fluorene to benzo(ghi) perylene). Correlation coefficients refer to linear fit.

Highest TCBSA extractability (in per cent) was observed for Hobson Bay sediment, followed by Motions Creek. The most likely explanation for the differences in sediment PAH extractability lies in their variable TOC content. As shown in Figure 6, TCBSA extraction efficiency correlated strongly with TOC content. In contrast, TOC content appeared to have little influence on SPMD extractability. This suggests that PAHs in SPMDs and sediments had come to equilibrium, with a finite PAH extractability by pore waters on the order of 3-7 per cent. Interesting in this regard is that Motions and Meola Creek, the sediments with highest overall PAH levels, showed the lowest relative SPMD extractability. While this finding, considered by itself, could be taken as indicating "absorption limitation" by the SPMD membrane (ie, a limited capacity to accommodate additional PAHs), the observation that absolute amounts of extractable PAHs were higher for both of these sediments (Figure 4) suggests that SPMDs did not limit uptake. It rather appears that a smaller fraction of PAHs in Motions Creek and Meola sediments was extractable. This could be due to a different PAH source or a different organic carbon binding phase, discussed further below.

Figure 6

PAH extractability (Σ15PAH; fluorene to benzo(ghi)perylene) by TCBSA and SPMD versus sediment TOC (per cent). Error bars: mean ± 1 SD. Sediment samples identified according to TOC content.

3.6.1 Results – Bioassays

Results of the 7d sediment toxicity tests with the amphipod *Melita* sp. are presented in Figure 7. It should be noted that these tests were non-standard by being carried out in a small water volume with minimal equilibration, to approximate the conditions of the biomimetic assays. Amphipod survival in control (Raglan) sediments was acceptable (96±5 per cent). In contrast, amphipod survival in Auckland sediment samples was generally lower and highly variable between replicates, complicating comparisons between samples. For example, 7d survival in Hobson Bay sediment was 0 per cent for one replicate whereas it was 80 per cent for the other replicate.

Figure 7

Survival (per cent) of amphipods *Melita* sp. in seven-day sediment exposures (10g in 40 ml seawater), before and after 2h of UV exposure. Error bars: average of 2 duplicates ± 1 SD; controls: 5 replicates (10 animals per replicate).
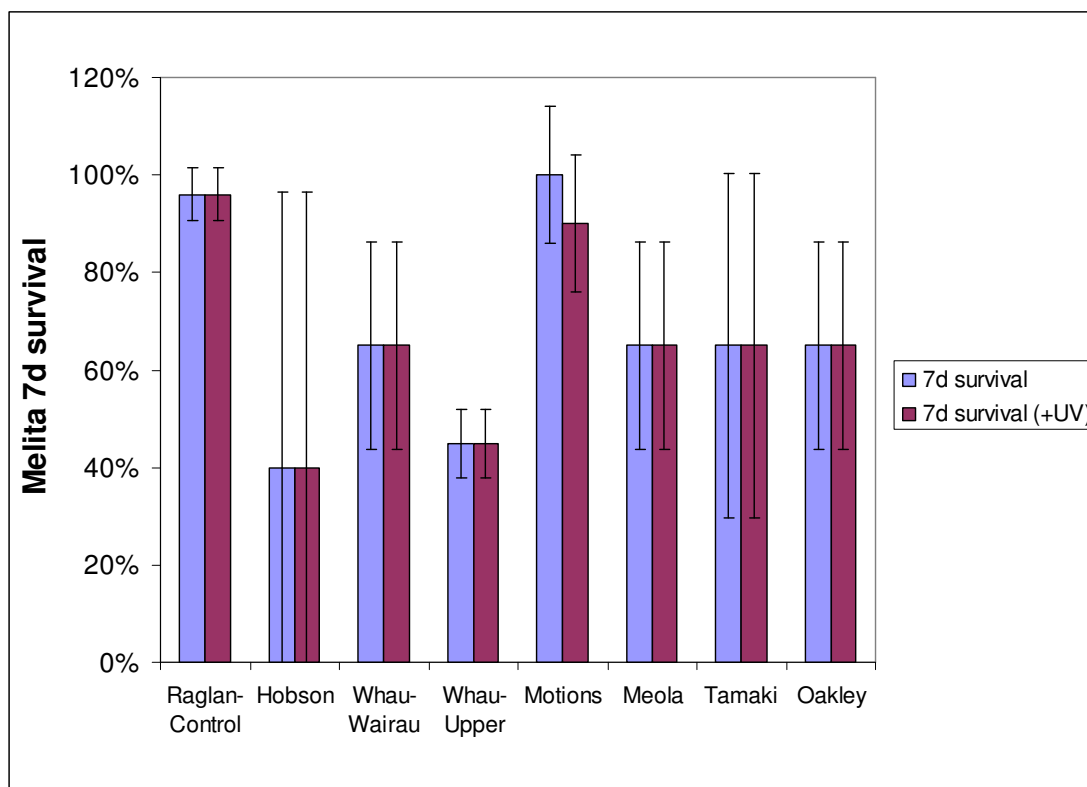
The generally lower survival in Auckland sediments might be explained, in part, by non-ideal physical-chemical conditions during the test. As shown in Figure 8, temperature, pH and oxygen levels on day seven were comparable for all treatments, ranging between 19.6-20.0°C, pH 8.18-8.33 and 5.6-6.2 mg/l, respectively. Likewise, temperature before and after UV exposure was comparable among all samples.

Figure 8

Physical-chemical conditions in amphipod exposure vials on day seven (mean ± 1SD).
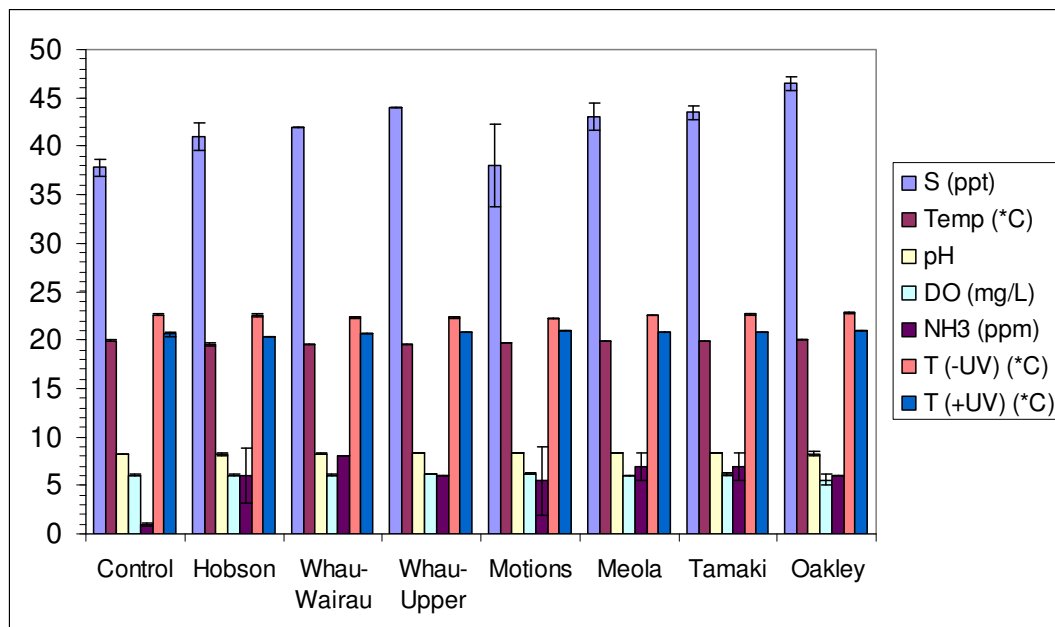
In contrast, salinity and total ammonia (NH_3 and NH_4^+) levels were significantly elevated in most Auckland sediments, relative to the Raglan control sediment. This might have represented an additional stress to animals: salinity in the seven ARC sediments ranged between 38-47 ppm on day seven (Raglan control: 37-39 ppm), and NH_3 content was 3-8 ppm (Raglan control: 1 ppm). Whereas a portion of the elevated salinity can be explained by evaporative losses over the course of the experiment (vials lost a few millilitres of water over the course of the seven days due to vigorous aeration), the majority of the excess salinity and ammonium is probably attributable to the use of freeze-dried sediments in bioassays: the freeze-drying procedure would have concentrated salts from porewaters and destroyed biological tissue and the resident nitrifying sediment microflora, enhancing nitrogen release. Since sediments were reconstituted in seawater (35 ppt, 40 ml), rather than distilled water, this would have increased salinity and afforded limited opportunity for dilution of NH_3. Furthermore, due to the absence of an established nitrifying bacterial microflora, ammonium-generating waste products would have built up quickly in the 40 ml sample volume over the seven days, further exacerbated by the addition of food on day five. The combined effect of elevated salinity and NH_3 content on amphipod survival is illustrated in Figure 9, indicating a pronounced negative influence of elevated salinity and ammonium on survival. In hindsight, a more rigorous experimental procedure would have been to pre-equilibrate sediments with a small volume of water for several days and to replace the seawater before the start of the experiment.
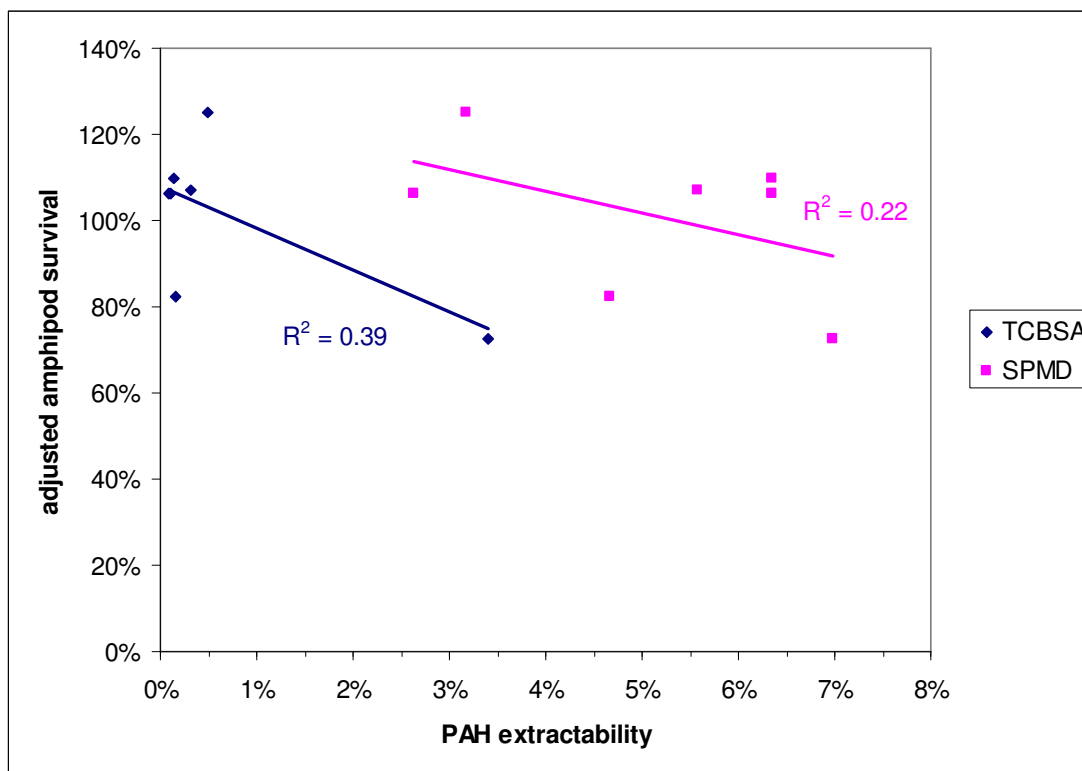
Figure 9

The combined effect of NH_3 and salinity on amphipod survival: seven-day survival plotted versus the product of NH_3 and Salinity, normalised to conditions in controls (dimensionless).
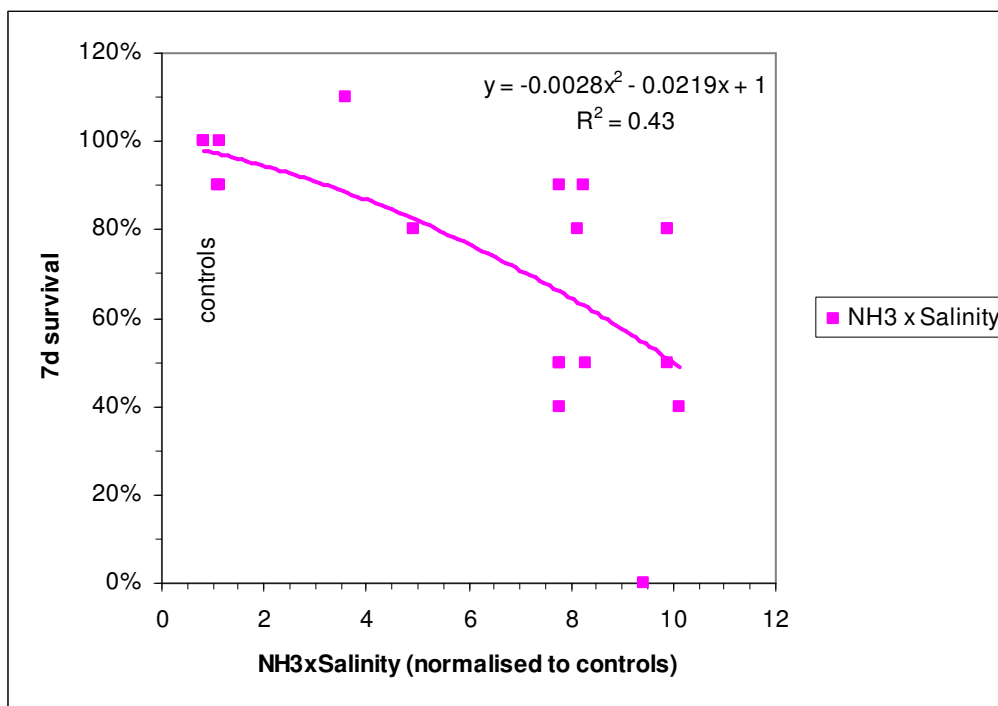
Even though a substantial portion of the observed mortality in bioassays was explainable by NH_3 and salinity effects (ie, 43 per cent of the variance), it is possible to remove the influence of these co-variables by estimating survival (using multiple regression analysis) assuming that these variables had been held constant. By subtracting mortality explained by NH_3 and salinity effects from observed mortality, it was possible to calculate an "adjusted survival" percentage, which was then related to other experimental co-variables, such as PAH bioavailability. Figure 10 plots NH_3 and salinity adjusted amphipod survival versus PAH extractability by TCBSA and SPMD. Disregarding the fact that adjusted survival was calculated to be >100 per cent in some cases (due to NH_3xS mortality being less than estimated from the curve fit in Figure 9) and focusing on relative differences, these plots indicate a weak negative correlation between amphipod survival and PAH extractability. It should be noted that these trends were driven largely by the high PAH extractability of Hobson Bay sediments, with its low TOC content. However, TOC content alone explained a smaller portion of the variance ($r^2 = 0.19$; data not shown).

Figure 10

Adjusted (average) amphipod survival (corrected for NH$_3$ and salinity effects), versus PAH extractability by TC and BSA and SPMD extraction. Correlation coefficients are for linear fits. Raglan-controls are not plotted due to lack of a corresponding x-variable.

For reasons explained below, it is unlikely that the observed correlation between PAH extractability and adjusted survival is causal; however, the pattern observed in Figure 10 is consistent with the working hypothesis that sediments with higher contaminant extractability (and thus higher bioavailability) have lower survival. When exploring the putative PAH bioavailability-survival link further, by plotting adjusted amphipod survival versus absolute amounts of PAHs extracted (Figure 11), a surprising result became evident. Contrary to expectations, high amphipod survival was observed also for sediments that had high PAH extractability, such as Motions Creek and Meola Creek. In fact, the data suggested a beneficial effect of high extractable PAH levels on (adjusted) amphipod survival. Furthermore, it was interesting to note that adjusted and observed amphipod survival showed virtually identical trends. The correlation can only be interpreted as being spurious or indirect: rather than being caused by PAH extractability, it might have been caused by other, unmeasured sediment parameters that co-varied with (absolute) PAH-extractability, perhaps nutritional lipids. Similarly, plotting amphipod survival (adjusted or observed) versus total PAH levels in sediments, revealed an unexpected, strong positive correlation (Figure 12). This suggests that high PAH levels in sediments for which high survival was observed, co-varied with other, beneficial, sediment parameters, which acted to maintain high amphipod survival over the seven-day experiment. It should be noted that for the regressions presented, correlation coefficients were calculated for average amphipod survival and were considerably lower when regressed against individual replicate data point.

Figure 11

Adjusted and observed (average) amphipod survival versus absolute PAH extractability (ng/g sediment), using TC and BSA and SPMD extraction. Correlation coefficients are for linear fits (note logarithmic x-axis, to allow comparisons). Raglan-controls not plotted due to absence of corresponding x-variable.
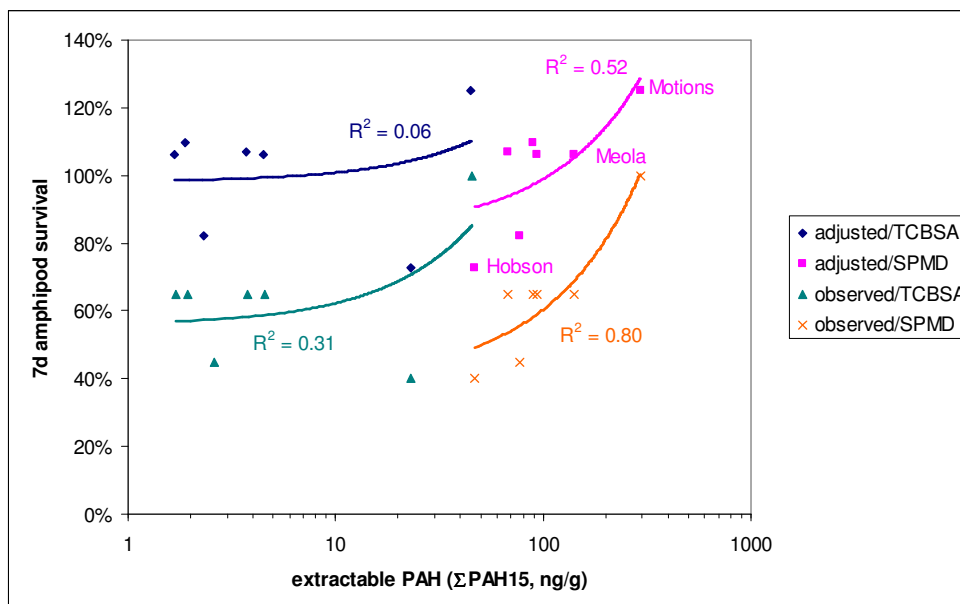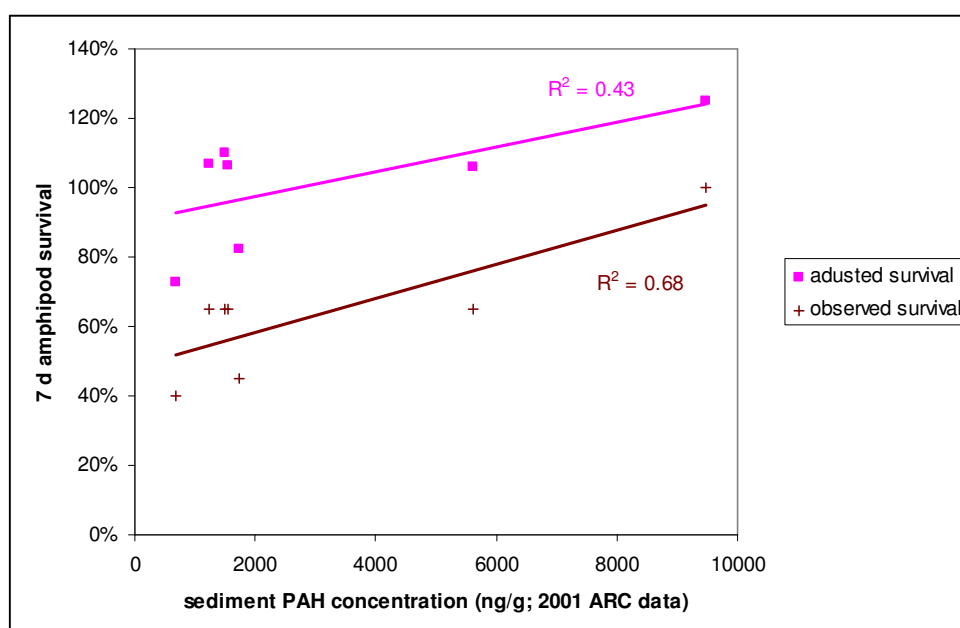

Figure 12

Average amphipod survival (observed, and (NH_3 x salinity) adjusted) versus total sediment PAH concentrations, as per 2001 ARC dataset. Regression coefficients for linear fits of average survival data (if regressed against individual replicates, regression coefficients were 0.29 (observed survival) and 0.20 (adjusted survival).

The absence of an obvious acute PAH toxic effect is further supported by the results of the UV irradiation trials: exposing amphipods to UV radiation for two hours induced virtually no additional mortality (Figure 7); with the exception of Motions Creek (one additional death), amphipods in all other replicates showed identical survival to pre-UV survival. The scarcity of evidence for UV-inducible phototoxicity supports the conclusion of low accumulation and low acute toxicity of sediment bound PAHs to amphipods over the seven days. As a caveat, given the relatively short (7d) duration of the bioassays, amphipods tissues might not have equilibrated fully with the available PAH fraction, especially if they spent the majority of their time at the sediment-water interface rather than in sediment burrows, which were seen to be scarce.

3.6.2   Conclusion

Three types of bioavailability assays with the seven selected ARC long-term monitoring sediments suggested low PAH extractability and PAH-related (acute) toxicity to benthic amphipods. Two types of mild extractions, mimicking uptake via digestion or via porewater similarly indicated PAH extractability of less than 10 per cent. This confirmed the hypothesis that only a small fraction of sediment-bound PAHs is mobile and available for biological uptake. Similarly, short-term (7d), non-standard bioassays with amphipods did not reveal any apparent PAH-related mortality, even though pronounced mortality was observed for some sediments (relative to the pristine control site). The finding that amphipod survival in toxicity tests correlated positively with total PAH levels in the sediment, suggests that high PAH levels might be offset by co-varying other sediment properties, possibly total lipid content in sediments, allowing high amphipod survival in short-term (7d) exposures. While the experiments performed cannot provide reliable information whether PAHs might exert chronic toxicity, the low 14d extraction efficiencies by SPMD membranes suggests that only a very limited pool of PAHs is available for uptake by organisms from porewaters.

4 Reducing Environmental Risk of PAHs

4.1 Knowledge gaps

While current evidence indicates little risk of adverse ecological effects due to PAH contamination for most of ARC's monitoring sites, the small number of sites having PAH levels that exceed ARC's ERC red criterion warrants further investigation of their bioavailability and toxicity. Aside from shellfish tissue data for greater harbour regions, little knowledge exists on the specific PAH bioavailability to biota at sites of concern. In intertidal regions, characterised by shallow water depths and a high incidence of solar irradiation, a risk of augmented PAH toxicity by UV photoactivation exist, particularly to transparent larval stages. Furthermore, at locations assessed to experience an elevated risk due to PAHs, strategies to reduce risk need to be developed and evaluated. Intuitively, two approaches exist to reducing environmental risk by PAHs: either (a) diminish levels of PAHs in the environment, or (b) reduce bioavailability of PAHs. Reduction of PAH loadings could be achieved by controlling PAH inputs (source reduction), or by reducing PAH concentrations (remediation). Reductions of bioavailability could be achieved by altering the amount of PAH-sorbent sediment phases or their reactivity. The first step, in both cases is improved knowledge of current PAH sources and their bioavailability.

4.2 PAH source identification

Source control of contaminants is a practical solution wherever a dominant source can be readily identified and isolated, and whenever ongoing inputs contribute measurably to observed contaminant levels in the environment. This contrast with "legacy" contamination of historic origin, such as spills or previous discharge practices. For source control of PAHs, this means that major ongoing PAH inputs need to be identified, and their magnitude placed in relation to existing sediment levels.

The goal of modern source identification techniques is to accurately apportion the PAHs found in the receiving environment to their respective sources. Source identification can also be very effective at a qualitative level, to reconcile likely and unlikely sources, which is useful for proactive contaminant mitigation (or source control) strategies. To illustrate what is meant by source reconciliation, PAHs in road run-off shall serve as an example: since road run-off is assumed to be the dominant source of PAHs in aquatic sediments, it is reasonable to expect the PAH composition of sediments to be similar to that of road run-off particulates. This implies that, without knowing the exact source make-up of the PAHs in road run-off (the presumed major source of PAHs in urban stormwater), using source identification, it should be possible to ascertain whether the composition of PAHs in the receiving environment sediments is consistent with that from the supposed major input. Establishing even this basic connectivity/linkage is essential in order to state, with some confidence, whether

elevated concentrations of PAHs in sediments of interest are attributable to ongoing inputs from road run-off.

What is interesting in this regard, is that while most urban sediments show a typical pyrogenic composition of PAHs, road run-off samples taken from highly trafficked roads have been found to have an "intermediate" PAH composition (suggesting a mixture of pyrogenic and petrogenic sources). Assuming no major post-depositional changes in the overall PAH composition to have occurred, the logical conclusion is that these run-off particulates are not the primary source of PAHs in these sediments. This being the case, we need to examine the possibility that there are other important PAH sources besides typical road run-off. This is discussed further in Sections 4.2.1 and 4.2.2.

4.2.1   PAH loading estimates

One approach to identify the dominant PAH sources involves estimating inputs (or loadings) of these sources. Given the high sedimentation rates in Auckland's settling zones, and given that sediment PAH levels have not changed significantly over the last seven years implies that a high import of PAHs (depositional flux) must be ongoing, in order to maintain the observed PAH levels. For illustration, consider the following simple estimate of PAH depositional flux: in Auckland's estuarine settling zones (such as tidal creeks), sediment accumulation rates of 20-30 mm/y are common (Vant et al. 1993; Wilcock & Northcott, 1995; Oldman and Swales, 1999; Swales et al. 1997; Swales et al. 2002). Assuming a moderate sedimentation rate of 25 mm/y for the majority of settling zones, this corresponds to a load of around 2500 mm^3 (= 2.5 cm^3) sediment per cm^2. Assuming further a water content (porosity) of around 50 per cent, this equates to around 1.25 cm^3 dry sediment being deposited per year on a 1 cm^2 large surface. Assuming further a sediment density of approximately 2.5 g/cm^3, this equates to slightly more than 3 g of (dry) sediment being deposited per year per square centimetre of tidal creek sediment. If we neglect redistribution of sediment within the receiving environment, this load of approximately 3 g/cm^2/y of sediment would therefore need to be delivered from land (or atmospheric) sources. Given a median PAH sediment concentration of, roughly, 0.5 µg/g, this corresponds to approximately 1.5 µg of PAHs depositing per cm^2 per year on a typical (median-like) Auckland Harbour settling zone. Such PAH depositional loads are high, by global comparison, yet for more contaminated sediments, such as Meola and Motions Creek, with PAH levels of >5 µg/g, depositional loads would be even ten times higher, ie, >15 µg/cm^2/y, under the (conservative) assumption that sedimentation rates are the same. From analyses of deep cores in the Manukau Harbour (Mangere Inlet), Wilcock & Northcott, (1995) calculated PAH depositional loads of 1-5 µg/cm^2/y for the total of 17 commonly occurring PAH compounds (3 or more rings), a range that agrees reasonably with our estimate of 1.5 µg/cm^2/y for a "median" Auckland settling zone. From this estimate it may, therefore, be concluded that substantial present-day PAH inputs must be occurring.

The question therefore arises, which sources are able to contribute PAH loads of this magnitude? Assuming negligible PAH inputs from marine sources (eg, ship traffic, oil spills), two pathways remain: direct atmospheric deposition and inputs from land run-

off. From first principles, it is improbable that a PAH depositional load of 1.5 µg/cm^2/y can be supplied to any significant extent by direct atmospheric deposition. For example, the atmospheric depositional flux in Paris, boasting several times the population size and density of Auckland, is 234 µg/m^2/y, for the sum of 14 USEPA priority PAHs, (Ollivon et al. 2002), which corresponds to roughly 0.0234 µg/cm^2/y. This flux is less than one sixtieth of the median depositional flux required to maintain median Auckland sediment PAH levels at steady state (1.5 µg/cm^2/y). Furthermore, the absence of pronounced atmospheric point sources, yet strong differences in absolute PAH concentrations between adjacent sampling locations, rules against significant PAH contributions due to direct aerial deposition. This leaves, by default, inputs from stormwater/catchment run-off as the most likely PAH source.

Of the range of possible land-derived PAH sources, let us first consider the likely contribution from atmospheric emissions, generated and deposited on land and subsequently transported to the aquatic receiving environment as stormwater run-off. This process may act to concentrate PAH loadings, if estuarine settling zones are smaller than the catchment area. This is, indeed, the case for all RDP sites (ARC, TP193), not considering locations on the Hauraki Gulf. Estuarine settling zones typically are 10-100 times smaller than their respective catchments, with a median scale factor of 20-fold. This would allow for a concentration of deposited PAHs by roughly 20 times. Note that this estimate assumes that all PAH deposited from the atmosphere in the catchment area ultimately make it into stormwater and downstream settling zones. A 20-fold concentration of a high (ie, Paris-like) atmospheric depositional flux of 0.0234 µg/cm^2/y would thus deliver a maximum PAH loading of roughly 0.5 µg/cm^2/y. Comparing this figure to the required median depositional flux of 1.5 µg/cm^2/y, renders a large "loading deficit" and suggests that most PAH loadings to estuaries must be derived from sources other than atmospheric deposition. Furthermore, the observation that PAH levels in settling zones are decoupled from catchment area (ie, there is only a very weak correlation between sediment PAH levels and catchment area) corroborates the conclusion that run-off from atmospheric deposition contributes only negligibly to PAH loadings. For example, Motions Creek has twice the sediment PAH levels than Meola Creek, even though its catchment area is only a fourth of the Meola catchment.

Another possible PAH source candidate is traffic-related petroleum discharges, excluding atmospheric emissions, which have been considered already. Smith et al. (2000) measured PAHs in stormwater run-off from four locations in an urban area in Virginia, USA: a gas station, a highway off-ramp, and a low- and a high-traffic volume parking lot. The gas station site produced the highest total PAH loading (2.24 g/m^2/y), followed by the high-traffic-volume parking lot (0.0556 g/m^2/y), the highway off-ramp (0.052 g/m^2/y), and the low-traffic volume parking lot (0.0323 g/m^2/y). To calculate the contributions from petrol stations in the Auckland area, consider the following estimate. According to the Yellow Pages (2005/06), there are 182 petrol stations in the greater Auckland region (88 Auckland City, 42 Manukau City, 24 North Shore City, 28 Waitakere City). Assuming a loading of 2.24 g/m^2/y and an average fuelling area of approximately 1000m^2, one petrol station will generate approximately 2240 g of PAH per year. For 182 stations this amounts to 407 680 g/y. For the Auckland region, this PAH loading is distributed over an area of 6546 km^2, which amounts to an average PAH loading of roughly 63 g/km^2/y, which is 63 µg/m^2/y, or 6.3 ng/cm^2/y. Applying the

catchment concentration factor of 20, one could therefore expect a PAH loading to estuarine settling zones on the order of 0.13 µg/cm^2/y due to fuel run-off from petrol stations, assuming an even petrol station density of approximately one station per 36 km^2. Within the immediate Auckland metropolitan area, petrol station densities are significantly higher, approximately one station every 7 km^2 (88 stations per 637 km^2). Consequently, allowing for a 5-fold higher station density in urbanised catchments, would bring the PAH loading to approximately 0.6 µg/cm^2/y. While this estimate could account for a sizable fraction of the "PAH loading deficit" for "median" settling zones, it is still well below the loading required to maintain a steady-state loads in higher level sediments such as those from Motions and Meola Creek, or the Whau River. Furthermore, the typical pyrogenic PAH signature of sediments argues against significant contributions from petrogenic sources, such as petrol station run-off.

To estimate the PAH contributions from ordinary road dust, ie directly deposited soot particles and tyre material, we again employ the data collected by Smith et al. (2000). This study reported PAH loadings of approximately 0.05 g/m^2/y for highway or parking lot run-off. Making the assumption that roads cover 10-20 per cent of an urbanised catchment, this would amount to a catchment-wide PAH export of 0.005-0.01 g/m^2/y, or 0.5-1 µg/cm^2/y due to stormwater run-off. This PAH load could subsequently concentrate further in estuarine settling zones by a factor of 20 (assuming complete sedimentation), generating hypothetical depositional PAH loads of 10-20 µg/cm^2/y. While this would be of a magnitude more than adequate to sustain the required PAH loadings in most RDP sediments, there is one caveat: PAH levels of source material appear to be too low, unless road debris makes up a significant weight fraction of the 3 g/cm^2/y of dry sediment deposited annually. NIWA research has determined PAH concentrations of 5 µg/g in dry gutter material, collected from the off-ramp of the Northwestern Motorway. If we assume that the majority of PAHs enter stormwaters in particulate form, this would mean that roughly 0.3 g of pure (dry) road gutter material would need to deposit for every 3 g of dry sediment accumulating, in order to generate depositional loads of 1.5 µg/cm^2/y. In other words, 10 per cent of a settling zone's sediment dry mass would need to be comprised of road run-off material. This seems like an improbable assumption that does not match casual observation of sediment composition. Furthermore, in sediments with high PAH levels of 5 µg/g or more, an even more improbable 3 g of road run-off particulates would have to deposit per square centimetre per year.

4.2.2   Missing PAH sources?

From the foregoing, it appears that there exists unaccounted-for PAH sources that contribute to high PAH depositional fluxes in Auckland sediments, other than atmospheric deposition or inputs from petrol stations or regular road run-off. Using simple mass balance arguments, as well as the observation that typical estuarine sediments are largely composed of inorganic sand and clay particles and only a small fraction of road debris (such as evidenced by glass microspheres, used in road marking), one may postulate the existence of a highly PAH enriched source material, of which only minute quantities are necessary to deliver sufficiently-high PAH fluxes. The following sections will demonstrate that this material is likely to be coal tar rich

particulates from older pavement layers. This hypothesis is supported by a combination of evidence, including characteristic patterns of certain diagnostic PAH marker compounds, microscopic inspection and analysis of selected sediment particles, and the observation that concentrations of PAHs in certain sediment fractions are so high that they can only be accounted for by coal tar as a source material. In addition to our experimental results, it has been recently reported (Mahler et al. 2005) that the use of coal tar sealcoats on parking lots in the City of Austin, Texas (USA) is the major source of PAHs in stormwater run-off, despite these surfaces only occupying 1-2 per cent of the watersheds in the study. The authors estimated that the total amount of PAHs coming from these watersheds would be reduced to 5-11 per cent of the current loading if the parking lots were not sealed with coal tar products. The prevalence of coal tar sealer use in North America may account for the high parking lot yields (ie, 0.05 g/m^2/y) reported by Smith et al. (2000) in Section 4.2.1.

4.2.3 Diagnostic marker compounds

The inherent analytical variability of PAH measurements and the general similarity of sediment PAH signatures among sites sets a limit to the ability to resolve source contributions from observed sediment PAH patterns. Nevertheless, by combining information on relative PAH distributions and absolute PAH concentrations, as well as ancillary environmental parameters (eg, particle size, density, mineralogy, trace metal content), it is possible to extend inferences about sources.

One approach to delineate sources is to utilise the relative proportion of different PAH compounds. Petrogenic PAH sources (such as diesel, engine oil and bitumen), tend to have a greater proportion of alkylated PAH homologues (such as methylphenanthrenes) compared to pyrogenic sources (eg, roading coal tar). An example is given in Figure 13.

Figure 13

Compositional PAH profile (relative proportion of total binder content) of coal tar binder seal layer (Finch Street) and bitumen binder seal layer (School Road), from streets samples within the Motion Creek Catchment, Auckland. Methylphenanthrenes are circled to highlight differences between the petrogenic and pyrogenic sources.
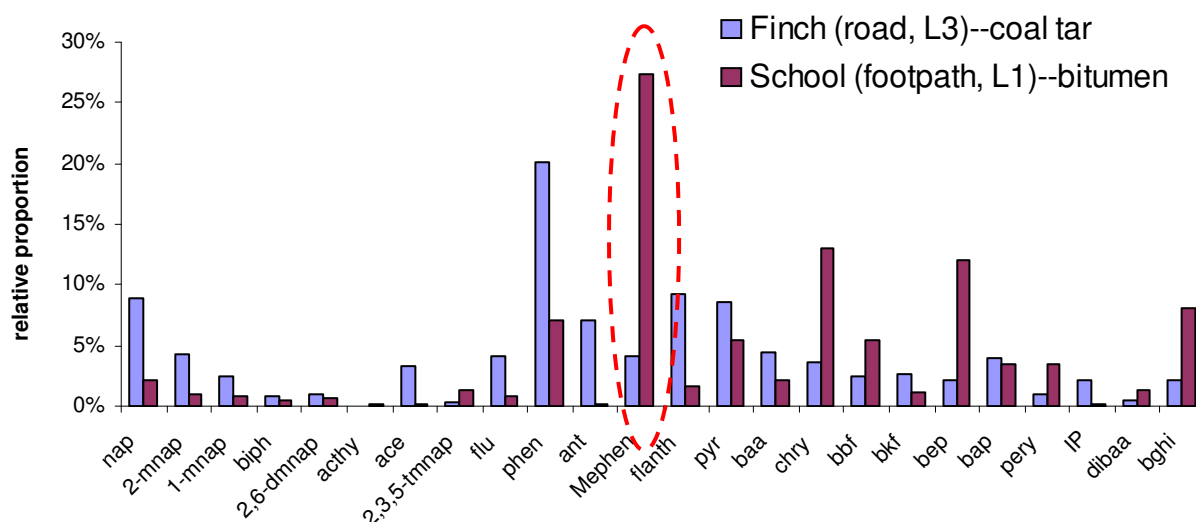

While a comparison of relative PAH composition of different pavements may provide a good qualitative measure for estimating petrogenic or pyrogenic origin, this approach proves to be cumbersome when larger numbers of samples need to be compared, or when the objective is to estimate the proportion of different source components of interest. One practical approach is to calculate the ratios of certain diagnostic PAH compounds, such as the proportion of methylated phenanthrenes to phenanthrene (MP/P). A problem with this approach is that the molecular masses and physico-chemical properties (eg, volatilisation) of the different compounds are not identical, so that they may not behave the same upon deposition in the environment, leading to the potential for post-depositional changes of the ratio.

A solution to this is to use the ratios of PAH isomers, that is, compounds with the same mass but a different molecular ring structure. The advantage of comparing ratios of PAH isomers is that mass-related, confounding factors that may affect the ratio, such as volatility, adsorption and water solubility (which are related to mass and hence identical for isomer pairs) are minimised. Because isomer pairs will differ subtly in their energies of formation, their relative proportion in source material will differ depending on the temperature conditions under which they were generated. For example, the four-ring PAH benz(a)anthracene (MW 228) is favoured over its isomer chrysene (MW 228) at higher (>1000 °C) combustion temperatures. Thus, a higher proportion of benz(a)anthracene to chrysene is measured in materials of pyrogenic origin, such as soot and coal tar. Conversely, a low benz(a)anthracene to chrysene ratio is characteristic of PAHs of low-temperature origin, such as in petroleum. As a general rule, thermodynamically favoured PAH isomers (ie, isomers with a lower heat of formation), such as chrysene, pyrene, benzo[e]pyrene (BeP) or benzo[ghi]perylene,

tend to prevail in material of low-temperature, petrogenic origin, whereas "kinetically-favoured" isomers (having a higher heat of formation, but faster reaction kinetics), such as benz[a]anthracene, fluoranthene, benzo[a]pyrene (BaP) and indeno[1,2,3-cd]pyrene attain higher proportions in pyrogenic material (Yunker et al. 2002). Isomer ratios are commonly used for PAHs with three or more rings, because of their higher molecular weight and hence lower rate of volatilization, which minimizes the likelihood of post-depositional modification.

Figure 14

Two-dimensional PAH ratio plot of potential PAH source materials and urban sample collected from Auckland. Ratio of indenopyrene/benzo(ghi)perylene plotted against the ratio of benz(a)anthracene/chrysene.
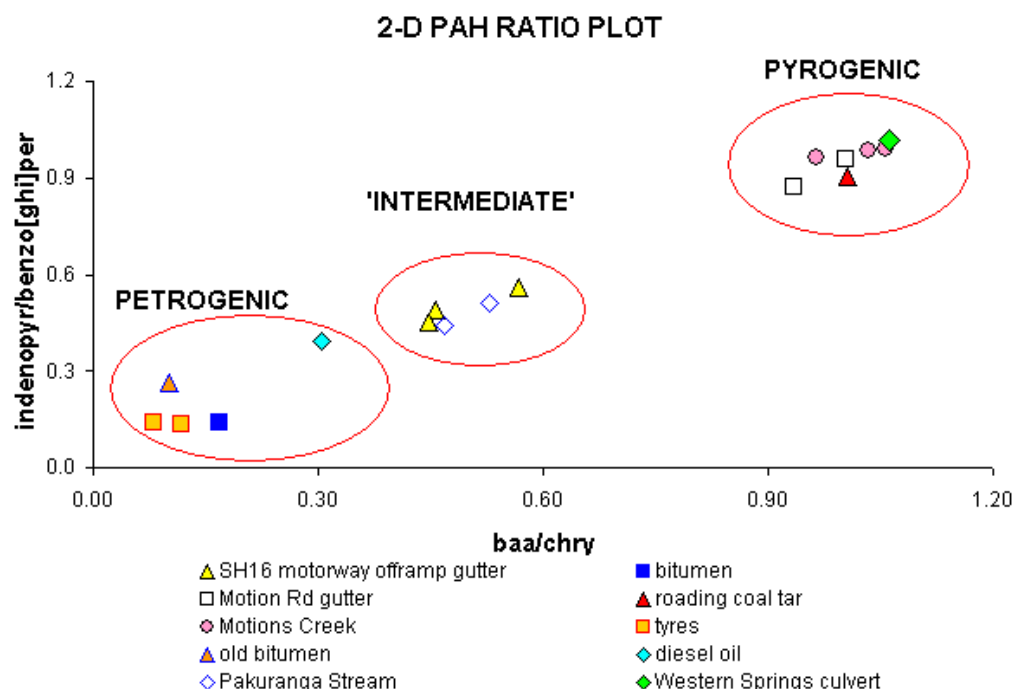
To resolve differences between PAH source materials beyond the dichotomous petrogenic/pyrogenic classification, it is informative to employ 2-D isomer ratio plots, for which the indeno[1,2,3-cd]pyrene/benzo[ghi]perylene ratio is plotted against the benz[a]anthracene/chrysene ratio. Figure 14 shows the isomer ratios of number of potential urban source materials (diesel oil, tyres and coal tar) and Auckland urban samples. This 2-D plot resolves both the petrogenic samples from the pyrogenic samples, and reveals the "intermediate" nature of run-off particulates (gutter particulates) collected from the off ramp on the Northwestern Motorway (SH16). This "intermediate" PAH composition has also been observed in run-off material sampled from SH1 in Hamilton and is presumed to be representative of "modern" road run-off particulates from New Zealand roads. The term "modern" is used to imply that there is no influence from historic sources of coal tar, which, as discussed later, only requires very small quantities to dominate the PAH ratio values. The three samples of SH16

run-off particulates analysed contained only 3-4 µg/g of PAHs, which is considerably lower than the 10-15 µg/g of PAHs present in the estuarine sediments of Meola and Motions Creek. Furthermore, the intermediate PAH composition of the modern run-off is inconsistent with the strongly PAH pyrogenic signature found in the receiving environments. In marked contrast to motorway run-off, gutter particulates sampled from Motions Road, which has much lower vehicle traffic, contained 15-16 µg/g of PAHs and had a similar pyrogenic composition to adjacent stream sediments. Based on these findings, we can conclude the following:

- modern run-off particulates are not the major source of PAHs entering the Motions Creek catchment;

- run-off particulates from Motions Rd have similar concentrations and composition of PAHs as adjacent sediments. Because roads are commonly swept approximately every four weeks, the Motions Rd run-off particulates are representative of recently deposited material. Therefore, it is probable that the levels in Motions Creek are due to ongoing inputs;

- there appears to be a different source of PAHs contributing to the run-off particulates at Motions Rd compared to SH16, which is not related to vehicles (since SH16 site has a considerably greater traffic volume). All data, to date, indicate this source to be historic coal tar binders; and

- similarity of concentration and composition between Motions Rd particulate samples and a Western Springs culvert sediment sample (refer to Figure 33b) indicates that the coal tar inputs are occurring on a catchment scale. The possible involvement of contaminated roadside soils as a possible source is discussed in Section 3.3.

It is interesting to note that sediments analysed from Pakuranga Stream in the Tamaki catchment (at two locations) had sediment PAH compositions and concentrations that are consistent with "modern" road run-off particulates as the primary PAH source. The persistence of the "intermediate" PAH composition in stream sediments provides at least some evidence to support the assumption that post-deposition changes in PAH composition are not significant.

To take source identification and apportionment further, it is informative to consider more specific PAHs, such as 1,7-dimethylphenanthrene (1,7-DMP), which is a marker compound for wood or coal smoke, or investigate completely different source-specific compound classes. We have successfully used the marker compound 1,7-DMP (Figure 15a) to determine whether coal and/or wood soot are the major contributors to PAH levels in Christchurch soils and run-off particulates. Because soot from fireplaces and furnaces contains relatively high levels of this particular isomer these marker compounds should be present in relatively high concentrations if soot from furnaces were a major source of PAHs in the environment. The selected ion chromatograms (m/z = 206) of 1,7-DMP in Figure 15b clearly show that wood and coal burner soot was not a major source of PAHs in the Christchurch samples, whereas coal tar was a very good match.

Figure 15

(a) Formation of 1,7-dimethylphenathrene in wood and coal soot (Benner et al. 1995). (b) Dimethylphenanthrene GC traces of Christchurch environmental samples (centre) compared to potential source materials, soot (left) coal tar (right).
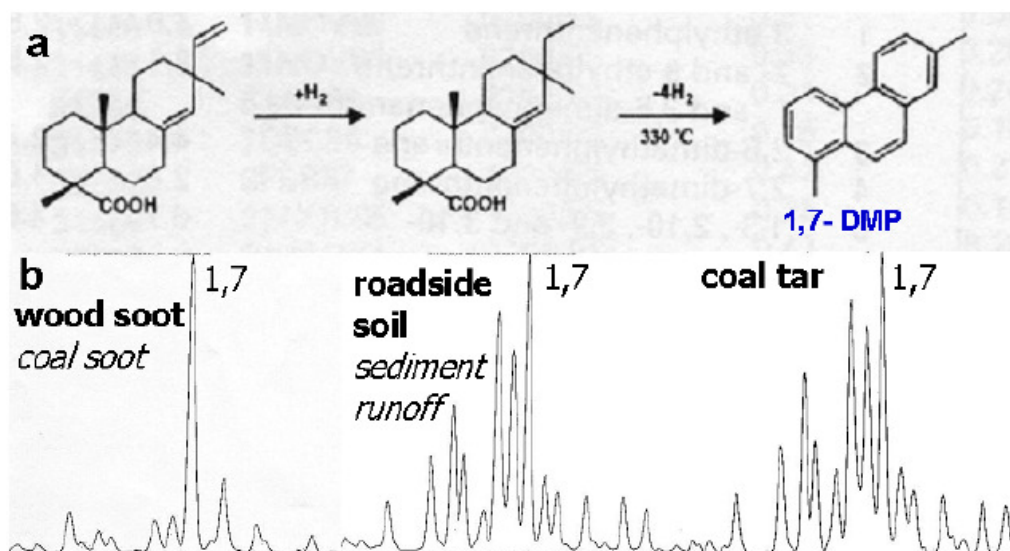
Other marker compounds NIWA has used to help distinguish PAH sources are hopanes. These are refractory compounds present in crude oil, but due to their low volatility, they are concentrated in high boiling fractions, meaning that they are present in very high concentrations in bitumen. A combination of a low concentration of petrogenic PAHs, combined with high concentration of hopanes gives a very high certainty that the source material is bitumen.

Other more specialised marker compounds include benzothiazole compounds (Kumata et al. 2000) that are used in the rubber vulcanising process when making car tyres. These man-made compounds are unique to tyre making. Consequently, the presence of benzothiazoles in sediment or run-off particulate can be used to apportion the amount of PAHs derived from tyre abrasion. In previous research at NIWA, we have synthesised the appropriate reference standards required for these analyses and have analysed PAHs and benzothiazoles in a number of New Zealand tyres. This has led to a good understanding of typical PAH concentrations in abraded tyre rubber.

Auckland (Motions Creek catchment) road coring case study

To confirm the presence of high PAH coal tar in road and footpath seal layers, in March of 2006, NIWA cored a number of roads and footpaths within the Motions Creek catchment. As with previous Christchurch road coring studies, many of the roads and footpaths contained coal tar binders in the lower seal layers. Unlike modern bitumen binders that contain only 20-30 µg/g of PAHs (US EPA 16 listed PAHs), coal tar binders in subsurface seal layers contained up to 200,000 µg/g of PAH (binder-basis). PAH levels in some surface wearing layers were as high as 2000 µg/g. Based on the findings that coal tar surfaces on parking lots covering just 1-2 per cent of a catchment

can contribute over 90 per cent of PAHs in run-off (Mahler et al. 2005), it is possible that the levels of PAHs in run-off in the Motions catchment may have been up to 100-fold higher in the last century, when much more coal tar binder was on the top wearing layer of the roads and footpaths. However, similar to findings in Christchurch, NIWA research has shown that coal tar derived particulates are still an ongoing source of PAHs in road run-off, which we believe is largely attributable to the ongoing release of contaminated roadside soils (discussed further in Section 3.3). The remainder of this section reviews the Auckland road and footpath coring, with an emphasis on the development of a bitumen/coal tar binder mixing model based on a number of diagnostic PAH ratios.

Table 3

Useful diagnostic PAH ratios for distinguishing road bitumen from coal tar (abbreviations: BaA= benz(a)anthracene, Chry=chrysene, BaP=benzo(a)pyrene, BeP=benzo(e)pyrene, IP= indeno(1,2,3-cd)pyrene, Bghi=benzo(ghi)perylene.

Isomer ratio	No. of rings	Mass	Coal tar	Bitumen
BaA/(BaA+Chry)	4	228	0.55	0.15
BaP/(BaP+BeP)	5	252	0.65	0.20
IP/(IP+Bghi)	6	276	0.55	0.25

Diagnostic ratios have been applied successfully to delineate PAH contamination by coal tar in sediments from Christchurch and Auckland (Depree & Ahrens, 2005; Ahrens & Depree, 2006; Depree et al. 2006). In a detailed analysis of pavement material from the Motions Creek catchment in Auckland, it was found that diagnostic ratios of the three isomer pairs, listed in Table 3, fell within a consistent, narrow range and were highly correlated with each other. When plotting two diagnostic ratios against each other in a 2-D plot (Figure 16), all sample points fell along a curve described by coal tar and bitumen as end members. As is apparent from Figure 16, Motions Creek sediment (fractionated by grain size) showed diagnostic PAH ratios similar to coal tar.

Figure 16

2-D plot of diagnostic PAH ratios, IP/(IP+Bghi) versus BaA/(BaA+Chry), of road pavement material from Auckland (17 samples, collected at different depth). Diagnostic ratios of Motions Creek sediment plotted for comparison. The line labelled "mixing model" is an estimate from a mixing model described further below in the text.
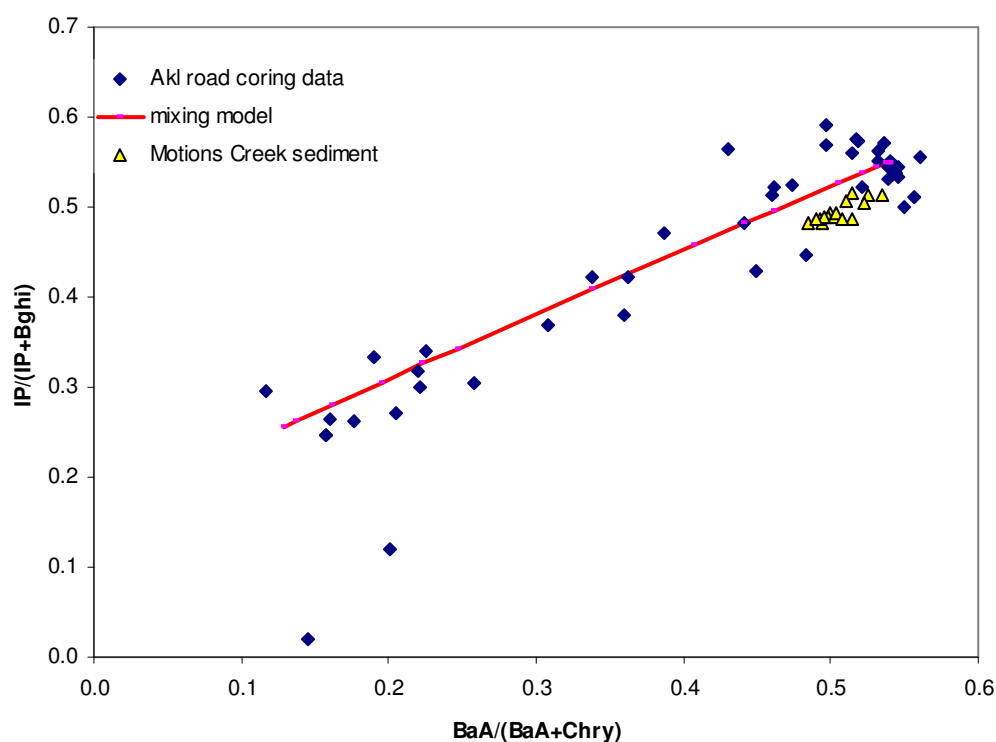
It was noted that PAH levels in some road pavement material were extremely high, and high PAH concentrations tended correlate with high diagnostic ratios resembling those of coal tar. Figure 17 demonstrates that when plotting each diagnostic ratio versus the concentration of the sum of its isomers, all points generally fell along a curvilinear function that saturated with a diagnostic ratio of coal tar. For example, the BaA/(BaA+Chry) and (IP/IP+Bghi) ratios saturated around a value of 0.55 (data not shown), whereas (BaP/BaP+BeP) saturated around 0.65.
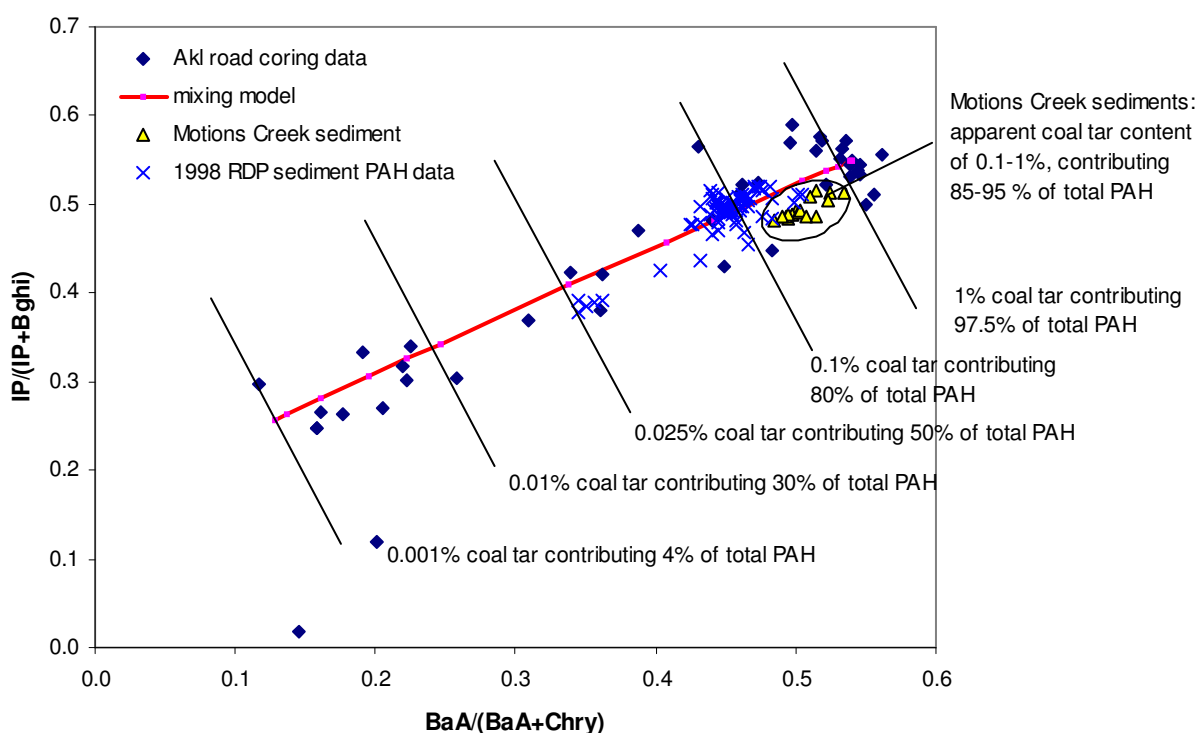
Figure 17

Diagnostic ratio (BaP/BaP+BeP) of road pavement material versus the sum of its isomer concentration, showing a close relationship between isomer ratio and PAH concentration. Curve represents estimate from mixing model, described below (ie, it is not a regression). Note log scale.
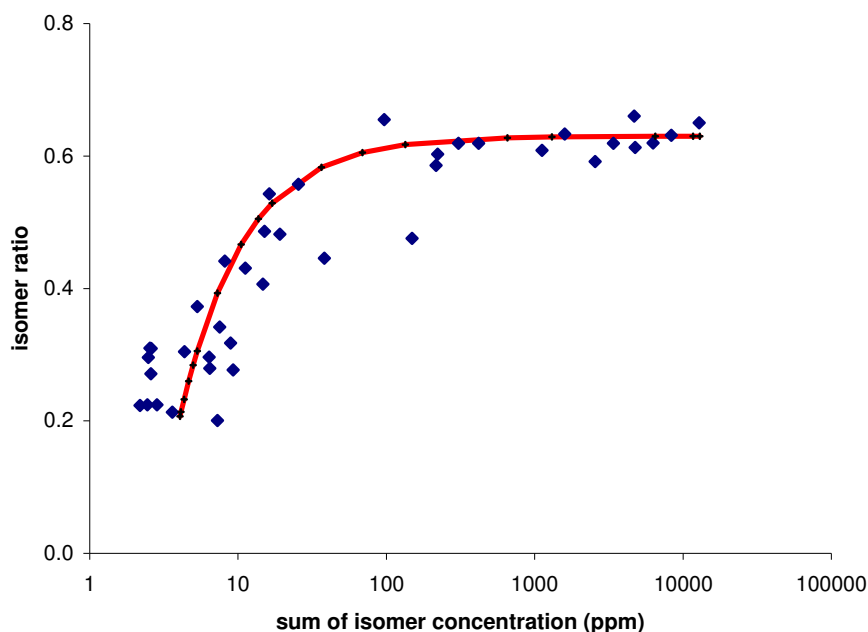
The tight correlation among the three diagnostic ratios, as well as the tight curvilinear relationship between isomeric ratios and total (isomer) PAH levels led us to postulate a common underlying relationship explaining our pavement PAH data. The observation that isomer ratios plotted along one line, with the ratios of coal tar and bitumen as end members, was taken as an indication that conservative mixing of these two source materials is occurring to explain the observed relationship. A weighted mixing model was therefore developed (Ahrens & Depree, 2006), using coal tar and bitumen as end members, and accounting for a greater numeric influence of coal tar as a consequence of its extremely high PAH concentrations. Model estimates for different hypothetical pavement mixtures agreed closely with observed ratios and showed the same curvilinear relationship when plotted against isomer PAH levels. Furthermore, plotting the modeled ratios of one isomer pair against another isomer pair, produced a single mixing line that coincided with the observed field data, confirming that PAH levels and composition in pavement material can be accurately estimated by assuming conservative mixing between coal tar and bitumen source material. Moreover, application of the mixing model made it possible to estimate the likely proportion of the two assumed end member materials in producing an observed ratio, as well as their contribution to total PAH levels (Figure 18).

Figure 18

2-D plot of IP/(IP+Bghi) versus BaA/(BaA+Chry) ratios of Auckland road pavement material (Ahrens & Depree, 2006). The "mixing model" line was estimated from a weighted mixing model, which also allowed estimating the proportion of coal tar to bitumen in producing any observed point along the mixing line. Dark lines perpendicular to mixing model line indicate approximate proportion of coal tar to bitumen. Diagnostic ratios of Motions Creek sediment (Ahrens & Depree, 2004) and the 1998 PAH dataset from the ARC long-term sediment monitoring (RDP) programme are plotted for comparison.

As is evident from Figure 18, even trace amounts of coal tar have strong leverage on the respective diagnostic ratio, due to the approximately 4000 times higher PAH concentrations of coal tar. Thus, as little as 0.1 per cent coal tar (in proportion to bitumen) is necessary for a diagnostic ratio of approximately 0.5 and accounting for 80 per cent of the PAHs in a sample (corresponding to PAH levels of approximately 2500 ng/g dw). Diagnostic ratios of field sediments conspicuously fell along one mixing line. Even though it is likely that there are more than two main sources of PAHs in Auckland sediments, it may be argued that stormwater draining off street pavements and footpaths need only carry away a very small proportion of coal tar particles into adjacent streams to significantly elevate the PAH concentration and alter the PAH composition of downstream sediments. This is likely to be the case in the Motions Creek catchment, with its steep topography, combined with the old age of many of its residential streets, providing a readily erodible pool of PAH-enriched coal tar particulates.

Applying all the aforementioned principles, a source identification investigation was undertaken to attempt to determine the major contributors of PAHs to selected Auckland stream and estuarine sediments.

4.3 Source identification of PAHs: results from the 2006 study

Samples of estuarine and stream sediments were provided by ARC. Samples were analysed for a suite of PAHs (including methylated analogues) and the petroleum indicator compounds hopanes at the NIWA organic analytical laboratory (Hamilton). To aid in source identification, a number of potential source materials were also analysed, including wood soot, diesel soot, coal soot, air particulates, bitumen, coal tar, abraded tyre material and road run-off particulates.

4.3.1 Methods

The samples analysed in the study are summarized in Table 4. All wet particulates (stream and road run-off samples) were freeze-dried and sieved to 1 mm. Archived estuarine sediments had been previously freeze-dried and sieved to 1 mm. A brief description of the sampling procedures of the various sediments and source samples is outlined below.

Table 4
Environmental and source samples included in the study.

Sample name	Sample description
Sediments	
Hobson	ARC estuarine sediment (<1 mm) sampled in 2001
Whau – Wairau	ARC estuarine sediment (<1 mm) sampled in 2001
Whau – Upper	ARC estuarine sediment (<1 mm) sampled in 2001
Motions	ARC estuarine sediment (<1 mm) sampled in 2001
Meola	ARC estuarine sediment (<1 mm) sampled in 2001
Tamaki	ARC estuarine sediment (<1 mm) sampled in 2001
Oakley	ARC estuarine sediment (<1 mm) sampled in 2001
Portland	Urban stream sediment (<1 mm) sampled in 2005
Waiatarua	Urban stream sediment (<1 mm) sampled in 2005
New Market	Urban stream sediment (<1 mm) sampled in 2005
Domain	Urban stream sediment (<1 mm) sampled in 2005
Run-off particulates	
Inlet	Grafton Gully SWTD sediment (<1 mm) – inlet chamber
Forebay	Grafton Gully SWTD sediment (<1 mm) – forebay chamber
Tank1	Grafton Gully SWTD sediment (<1 mm) – main tank (ca. 7 m)
Tank2	Grafton Gully SWTD sediment (<1 mm) – main tank (ca. 25 m)
Tank3	Grafton Gully SWTD sediment (<1 mm) – main tank (ca 45 m)

Sample name	Sample description
Tank4	Grafton Gully SWTD sediment (<1 mm) – main tank (ca. 65m)
Tank5	Grafton Gully SWTD sediment (<1 mm) – main tank (ca. 80 m)
Air particulates	
Auckland – Mar 10	High volume, 24-hr particulate sample (summer/autumn) – 36.8 mg
Auckland – Apr 6	High volume, 24-hr particulate sample (autumn) – 35.6 mg
Auckland – Aug 1	High volume, 24-hr particulate sample (winter) – 30.5 mg
Christchurch – Feb 27	High volume, 24-hr particulate sample (summer) – 17.0 mg
Christchurch – Mar 29	High volume, 24-hr particulate sample (summer/autumn) – 7.2 mg
Christchurch – July 10	High volume, 24-hr particulate sample (winter) – 100.4 mg
Christchurch – July 12	High volume, 24-hr particulate sample (winter) – 86.2 mg
Christchurch – July 14	High volume, 24-hr particulate sample (winter) – 18.2 mg
Source materials	
Tyre	Composite sample of powdered truck and car tyre
Engine oil	Composite sample of used oil from diesel engines
Bitumen	Sample of "new" bitumen provided by Fulton Hogan
Coal tar	RT-12 grade roading coal tar from US supplier
Diesel soot (10 t)	Composite sample removed from exhaust pipes of 10 t Hino trucks
Diesel soot (3.5 t)	Composite sample removed from exhaust pipes of 3.5 t Isuzu trucks
Diesel soot (2.5 t)	Composite sample removed from exhaust pipes of 2.5 t Isuzu trucks
Wood soot1	Wood soot sample provided by chimney cleaning firm
Wood soot2	Wood soot sample provided by chimney cleaning firm
Wood soot3	Wood soot sample provided by chimney cleaning firm
Coal soot1	Coal soot sample provided by chimney cleaning firm 1
Coal soot2	Coal soot sample provided by chimney cleaning firm 1

4.3.1.1 **Estuarine Sediments**

Archived 2001 sediments, collected as part of the ongoing ARC sediment monitoring programme, were used for this study (ARC TP192, 2002). From the 27 potential sites, the client selected the following seven high-PAH estuarine sites: Hobson; Whau – Wairau; Whau – Upper; Motions, Meola; Tamaki and Oakley. For all sites except Oakley and Whau-Upper, a composite sample was prepared from three site replicate samples. For Oakley and Whau-upper, the composite was comprised of two replicate samples. Based on previously determined concentrations of PAHs in the individual replicate samples, the average concentration of PAHs in the composite samples are shown in Table 5.

Table 5

Average (calculated) concentrations of PAHs in composite estuarine samples used – based on 2001 data for the individual sediment replicates.

ARC estuarine sediment	Average PAH concentration (µg/g)
Hobson	0.7
Whau-Wairau	1.5
Whau-Upper	1.7
Meola	5.6
Motions	9.5
Tamaki	1.2
Oakley	1.4

4.3.1.2 **Stream sediments**

Four stream sediments known to contain >10 µg/g of PAHs were provided by the client. The sediments were from the following streams: Portland; Waiatarua; New Market and Domain.

4.3.1.3 **Run-off particulates**

Although road run-off is not a "pure" source material, a representative particulate sample of "modern" run-off was required to compare the PAH compositions with Auckland receiving environment sediments. The road run-off particulate samples were obtained from the approximately 3-year old Grafton Gully storm water treatment device (SWTD). The concrete structure is the largest SWTD in the country, with 100 m length, 10 m width and 2.5 m height. The tank consists of an inlet bay, forebay and a large ca. 85 m settling tank. The SWTD was constructed as part of the Grafton Gully motorway development and commissioned in 2003. Accordingly, the road (or motorway) run-off entering the tank contains no historic roading coal tar and therefore should be representative of road run-off particulates in the Auckland area.

Samples of road run-off particulates were collected in June 2006. Samples were taken from the inlet, forebay and at five sampling points along the length of the settling tanks at approximately 15-20 m intervals (Figure 19).

Figure 19
Grafton Gully storm water treatment device (SWTD) showing the approximate location of the seven sampling sites.


4.3.1.4 Air particulate samples

Air particulate samples from Auckland and Christchurch were kindly provided by Dr. Jo-Anne Cavanagh from Landcare Research (Lincoln). The air particulate samples were collected over different seasons during 2005. The samples were collected by high volume samplers over a 24-hr period (ca. 1600 m^3 of air) and the material analysed was the particulate fraction trapped on the glass fibre filter (masses are given in Table 4). Although not a "pure" source material, atmospheric particulates are closely linked to run-off particulates via deposition and suspension/resuspension processes and are therefore a potentially important source component of PAHs in Auckland's aquatic receiving environments. Christchurch air particulate samples have been included as these are known to be impacted by domestic solid fuel burning (primarily wood, as well as coal) in the winter months under smog-forming weather conditions (Figure 20). The comparison of Christchurch air particulates with Auckland air particulates, allowed to determine whether soot emissions from heating were important sources of PAHs in the Auckland environment.

Figure 20

High volume air particulate filters showing the pronounced contribution of soot particulates from solid fuel burning by domestic heating appliances. The sample on the left is typical for Auckland air particulates, whereas the sample on the right is from a winter "smog" day in Christchurch.
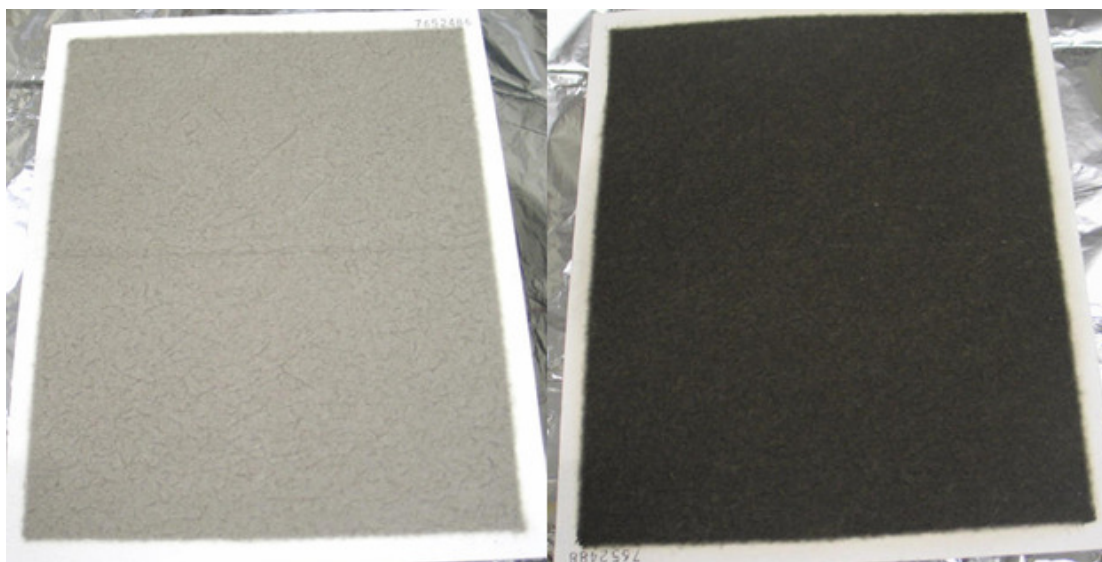
4.3.1.5 PAH source materials

Coal soot and wood soot samples were provided by two Waikato chimney sweeping companies. The wood soot samples were taken from fireplaces in Hamilton whereas the coal soot samples were obtained from fireplaces in Huntly. The soot samples were taken from the uppermost part of the chimney (ie, as near as possible to the chimney opening) and from domestic fireplaces that burned predominately either wood or coal. The wood soot and coal soot samples were analysed as received.

Diesel soot samples were obtained using a bottle brush to remove weakly adhered soot deposited near the opening of the exhaust pipe on the following trucks: Hino (10 tonne), Isuzu (3.5 tonne) and Isuzu (2.5 tonne). At least two trucks within each weight range were sampled.

A selection of car (8), 4x4 (1) and truck tyres (2) where collected and powdered using a belt sander. A composite was prepared consisting of eight parts car tyre:2 parts 4x4 tyre:8 parts truck tyre.

Samples of bitumen (Fulton Hogan, Hamilton), coal tar (RT-12 grade roading coal tar, Railworks, USA), and diesel oil (composite from diesel mechanic workshop, Auckland) had been obtained previously.

4.3.1.6 Analysis

Standard methods for extraction and analysis were used throughout. Briefly, with the exception of engine oil, bitumen and coal tar (which were extracted by dissolving the matrix in dichloromethane solvent), all the samples were extracted with

dichloromethane using an accelerated solvent extraction instrument (ASE, Dionex). Prior to extraction seven deuterated PAH surrogate compounds were added to the sample to monitor recoveries of target analytes. Extracts were "cleaned up" via silica column chromatography, and the volume reduced and exchanged into heptane solvent (ca. 1 ml). Activated copper was added to remove any elemental sulfur before the addition of internal standards and transferal to GC vials. The analytes were quantified using selected ion monitoring (SIM) GCMS, using two calibrations curves (one for standard PAHs and one for the methyl PAHs) consisting of 4-6 calibration points. Contaminant concentrations were corrected for surrogate recoveries, which on average, were: naphthalene-d_8, 91 per cent; acenaphthene-d_{10}, 93 per cent; phenanthrene-d_{10}, 97 per cent; fluoranthene-d_{10}, 100 per cent; pyrene-d_{10}, 98 per cent; benz[a]anthracene-d_{12}, 93 per cent; and perylene-d_{12}, 90 per cent.

4.3.2 Results and discussion – PAH source identification study

The purpose of the study was to analyse a wide range of PAHs in order to attempt to ascertain the major source of PAHs in Auckland sediments. Previous work has shown that the majority of Auckland sediments have a strongly pyrogenic PAH composition of PAH, which is in contrast to samples of "modern" (ie, no coal tar) road run-off that have a composition that lies between the pyrogenic/petrogenic extremes of the 2-D PAH ratio plot (refer to Figure 14). An "intermediate" PAH profile would be expected, considering run-off is comprised of both pyrogenic (ie, vehicle exhaust, home and industrial combustion emissions) and petrogenic (abraded tyre, bitumen, engine oil deposition and unburned diesel sorbed to exhaust particulates) source materials. The persistence of strongly pyrogenic PAH compositions in many of Auckland's receiving environments are thought to be the result of historic coal tar inputs. For coal tar at least, the concentrations of pyrogenic PAHs are so high, that the pyrogenic signature "swamps" the intermediate profile of incoming "modern" run-off particulates (refer to Figures 16 to 18, Ahrens & Depree, 2006). Because the swamping effect of coal tar contamination limits the usefulness of diagnostic PAH ratios for fine-scale source apportionment, the concentration of petroleum derived hopanes was also analysed.

Hopanes are very stable organic compounds present in relatively high concentrations in crude petroleum, not degraded under most conditions. Oil companies use hopanes as maturity markers in the search for new oil fields. The origin of most hopanes is the bacterial C_{35} tetrol compound, tetrahydroxybacteriohopane. This undergoes a very slow transformation to hopanes, which consist of five fused aliphatic (as opposed to aromatic) rings. The structure of the major hopane, 17α(H),21β (H)-hopane is given below:
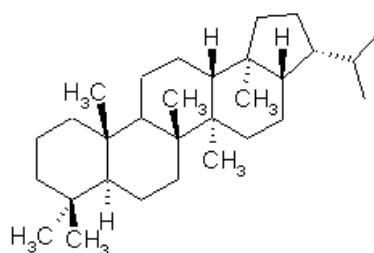
17α(H),21β (H)-hopane

The major usefulness of hopanes is that while they are relatively abundant in high boiling fractions/residues of crude petroleum, they are only present at trace levels in coal tar. Accordingly, they provide an alternative method for detecting petrogenic inputs in receiving environment sediments that is independent of PAH diagnostic ratios that are often too insensitive, depending on the sources that need to be resolved.

4.3.2.1 Concentrations of PAHs in sediment, particulate and source samples

As a first tier of a PAH source apportionment, it is essential to consider the absolute concentration of PAHs in environmental samples in comparison to potential source samples. The primary reason for this is that is prevents the over-interpretation of diagnostic ratios. For example, if a sediment sample contains 100 ug/g of PAHs and a suspected source material contains only 5 ug/g of PAHs, then irrespective of any diagnostic ratio match, the potential source material cannot be the major contributor of PAHs to that sample.

Although more than 40 PAHs were quantified, unless otherwise indicated, the PAH totals in this report refer to the sum of the 16 PAHs listed as priority contaminants by the US EPA. The 16 PAHs (with three letter abbreviations) are; naphthalene (nap), acenaphthylene (acy), fluorene (flu), phenanthrene (phe), anthracene (ant), fluoranthene (fln), pyrene (pyr), benz[a]anthracene (baa), chrysene (chy), benzo[b]fluoranthene (bbf), benzo[k]fluoranthene (bkf), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (idp), dibenz[ah]anthracene (dba) and benzo[ghi]perylene (BgP).

The concentrations of PAHs (μg/g) in the 38 samples listed in Table 4 are presented in Figure 21. The concentrations of PAHs ranged from 0.7-10.4 μg/g for the estuarine sediments (good agreement with calculated concentrations, Table 5), 10-66 μg/g for the stream sediments, 4-14 μg/g for road run-off particulates (Grafton Gully SWTD), 40-188 μg/g for Auckland air particulates (cf to 84-1800 μg/g for Christchurch air particulates) and from 10->200,000 μg/g for potential source materials. As expected, coal tar contained at least two-orders of magnitude higher PAH concentrations than the next highest material, which in this study was coal soot with 2600 μg/g of PAHs. Accordingly, the widespread historic use of coal tar binders in road construction, combined with extremely high concentrations of PAHs, make coal tar a prime candidate as a major source of PAHs in sediments. Note that the maximum PAH content of 200,000 μg/g relates to pure coal tar binder; in road seal layers with an average coal tar binder content of 10 per cent, the maximum composite PAH concentration would be approximately 20,000 μg/g.

Figure 21

Total concentrations of PAHs in environmental and source samples (note: logarithmic scale on y-axis – concentrations less than 1 µg/g appear as the corresponding "negative" logarithmic value below the x-axis). ANZECC sediment guideline values are shown in blue (low = 4 µg/g) and red (high = 45 µg/g).
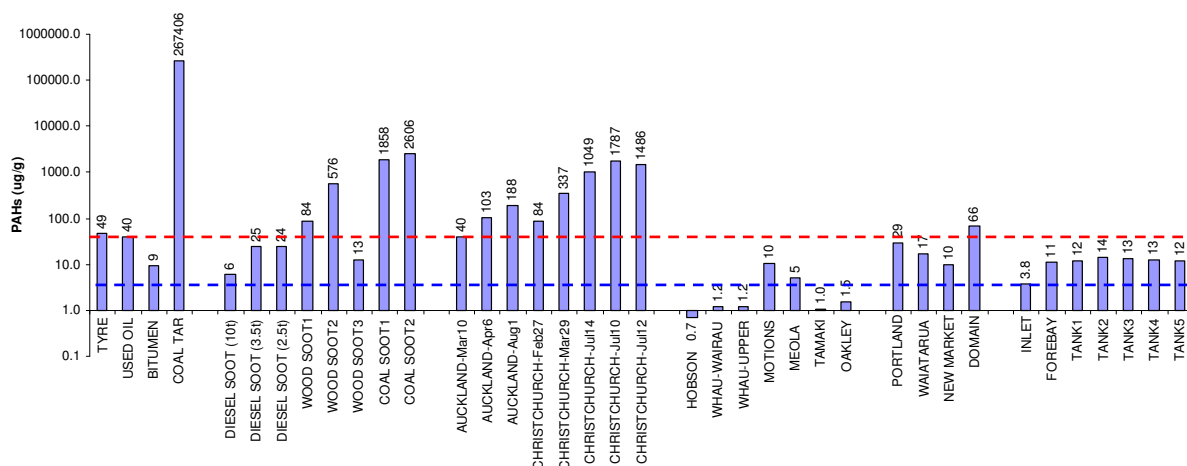
4.3.2.2 Concentration of hopanes in sediment, particulate and source samples

In this report, the concentration of hopanes refers to the sum of the two major hopanes, $17\alpha(H),21\beta(H)$-30-norhopane and $17\alpha(H),21\beta(H)$-hopane. The concentration of hopanes is presented in Figure 22, with those samples with concentrations less than 1 µg/g appearing as the corresponding "negative" logarithmic value (ie, below the x-axis). As expected, the petrogenic source materials, tyre, used oil and bitumen all contained very high levels of hopanes (60-500 µg/g). Hopanes were below the detection limit for coal tar. However, this was largely because the extract was so dilute on account of the very high concentrations of PAHs in the material. Although coal tar will contain some hopanes, the amount is insignificant compared to the concentration of PAHs, which enables useful comparisons using hopane:PAH ratios since the ratio for coal tar is <<1 (Section 4.3.2.4). Other than the petrogenic source materials, coal soot, containing 6 µg/g, was the only other source material that contained significant amounts of hopanes. The other "combustion" soot samples, diesel soot and wood soot, only contained 0.1-0.6 µg/g of hopanes.

Road run-off particulates from the Grafton Gully SWTD contained higher concentrations of hopanes (ie, 3-11 µg/g) than either the estuarine sediments (0.1-0.6 µg/g) or the stream sediments (0.9-1.9 µg/g). The coarse-grained inlet SWTD particulates, which might be expected to deposit in higher energy stream receiving environments, contained 2.8 µg/g of hopanes, which is comparable to the hopane concentration to Domain stream sediment (ie, 1.9 µg/g).

The concentration of hopanes in Auckland air particulates (median 11.4 µg/g) was very similar to that found in the fine road run-off particulates (ie, forebay and tank particulates; 9-11 µg/g of hopanes). Similarities between air particulates and road run-off particulates are expected since they are related via deposition and

suspension/resuspension processes. However, a simple relationship between the two particulate types is quickly ruled out since, despite similar hopane concentrations, air particulates contained ca. 10-fold higher PAH concentrations than run-off (discussed further in Section 4.3.2.4).

Figure 22

Total concentrations of hopanes in environmental and source samples (note: logarithmic scale on y-axis).
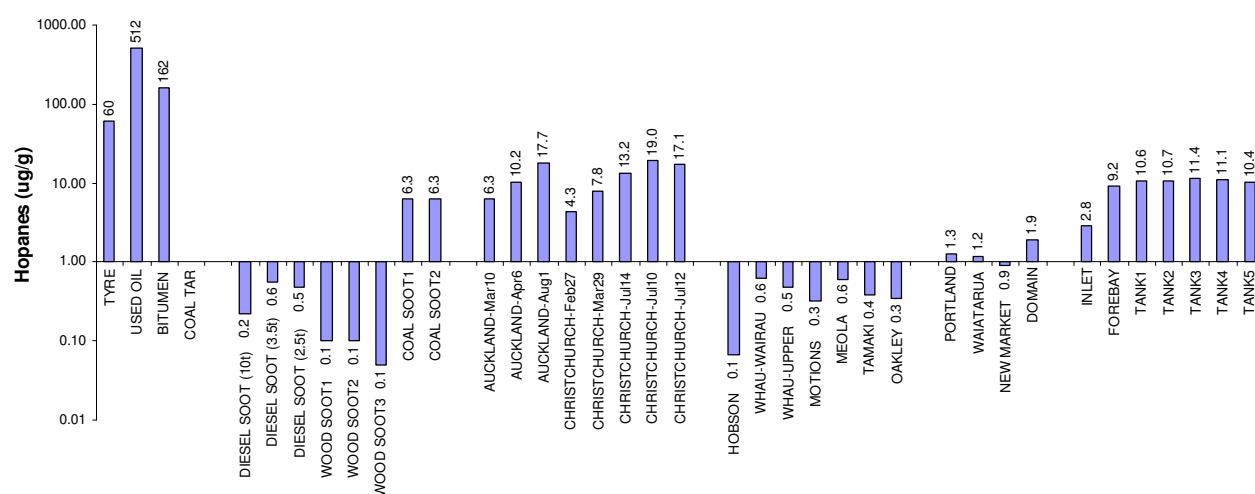

4.3.2.3 2-D PAH ratio plot: pyrogenic vs petrogenic composition

To further complement the PAH source identification, we shall examine a number of diagnostic ratios of key indicator compounds. A useful starting point for source identification is a 2-D isomer ratio plot analogous to Figure 14, which plots the indeno[1,2,3-cd]pyrene/benzo[ghi]perylene (or idp/BgP) ratio against the benz[a]anthracene/chrysene (or baa/chy). As shown previously, such plots are informative for quickly separating samples into categories that are predominately pyrogenic, petrogenic or show an "intermediate" or "mixed" PAH composition. Isomer ratios from this study are shown in Figure 23. These clearly show that source samples could divided into the three aforementioned regions – petrogenic (lower left), pyrogenic (upper right) and the central "intermediate" region. Analogous to Figure 14, the 2-D ratio plot classified both the Auckland estuarine and stream sediments as containing strongly pyrogenic PAHs, which is consistent with the current hypotheses that historic coal tar is the dominant source of PAHs in many of these receiving environment sediments. However, in addition to coal tar, coal soot and wood soot exhibit similar pyrogenic characteristics, and therefore cannot be eliminated as potential sources. Further differentiation of these pyrogenic source materials is discussed in Section 4.2.3.4.

Figure 23

2-D PAH ratio plot – benz[a]anthracene:chrysene versus indeno[1,2,3-cd]pyrene:benzo[ghi]perylene.
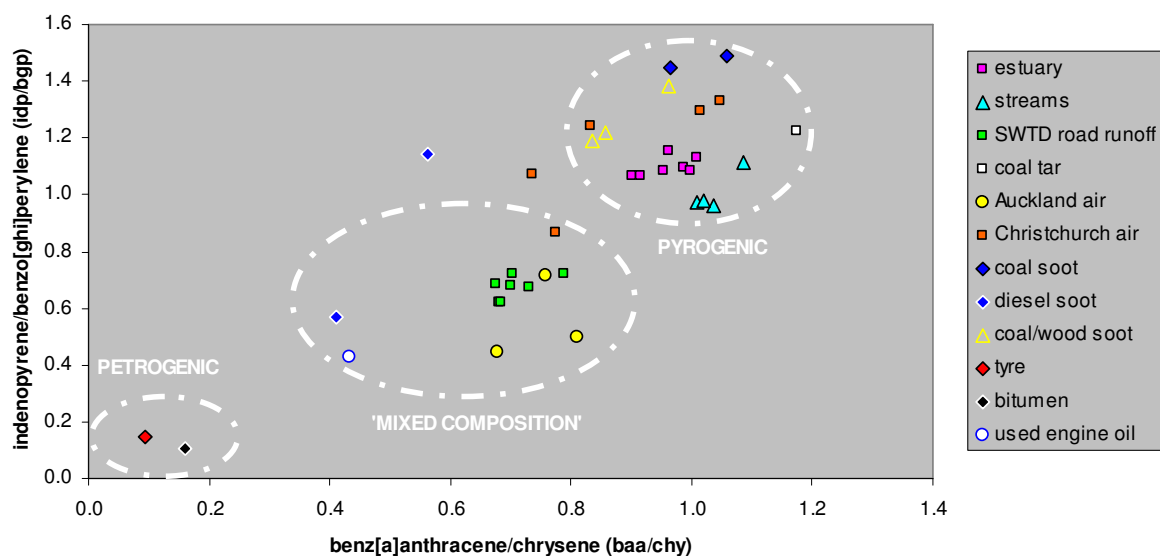
The 2-D plot highlights the compositional differences between the run-off particulates ("mixed" or "intermediate") and the Auckland sediment samples (pyrogenic). The "intermediate" composition of run-off is expected since run-off is likely to be derived from a combination of pyrogenic (eg, combustion soot etc.) and petrogenic (eg, bitumen, tyres and oil) source materials (Figure 23). The intermediate profiles of Grafton Gully run-off particulates are similar to Pakuranga Stream sediments and SH16 gutter particulates shown in Figure 14, suggesting that intermediate PAH isomer ratios are typical of modern run-off.

The only source materials shown to have an intermediate PAH composition were used engine oil and diesel soot, although the composition of the latter was highly variable between samples. Diesel soot samples were collected from exhaust pipes; thus, it is not clear how representative these samples are of vehicular soot released to the atmosphere. As mentioned, the "intermediate" composition of run-off particulates is likely to be due to a mixture of petrogenic and pyrogenic source materials, as opposed to a source material with an "intermediate" PAH composition.

Figure 24 illustrates the potential sources contributing to road run-off and air particulates, and the link between these two particulate compartments via deposition and suspension/resuspension processes. The schematic shows that the composition of PAHs in atmospheric particulates is dependant on the relative contribution of the individual sources/inputs. For example, the PAH composition in winter Christchurch air particulates is dominated by inputs from wood and coal burning, whereas in summer, the dominant anthropogenic input is likely to be from vehicle exhaust and suspension/resuspension of fine particulates. The influence of winter heating on the composition of atmospheric PAHs is apparent in Figure 23 – the summer air sample is the single red square in the "mixed composition" area, whereas the winter air

particulates are the red squares in the pyrogenic area, with a similar composition to the coal soot and wood soot samples. In contrast, Auckland air particulates had a fairly constant intermediate PAH composition all year round, with no obvious impacts from winter heating emissions.

Figure 24
Schematic showing the connectivity and inter-relationships between different anthropogenic source materials, atmospheric particulates, and road run-off particulates.
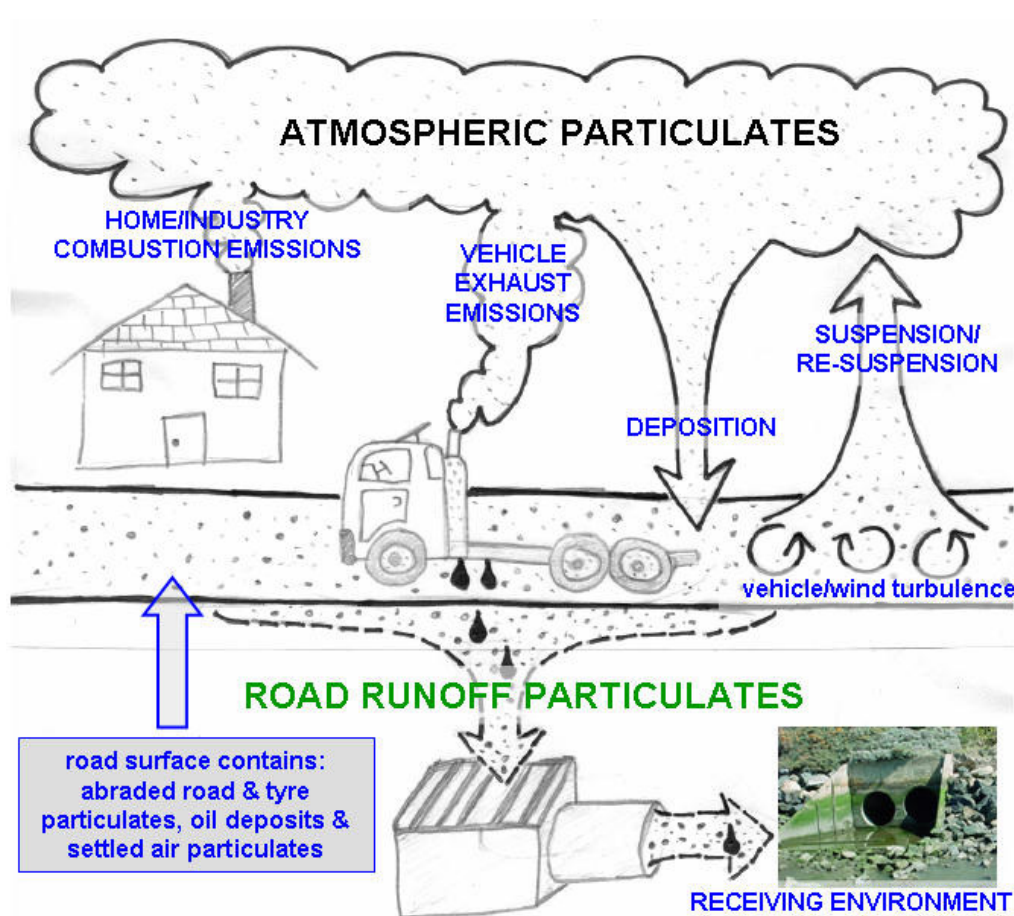
The only other "pure" source material that exhibited a "mixed" pyrogenic/petrogenic composition of PAHs was used engine oil. The used motor oil in this study was a composite of eight samples taken from diesel engines. The mixed profile is a consequence of new oil being petrogenic, but over time, combustion products containing pyrogenic PAHs being incorporated into the oil. It is therefore not surprising to find a mixture of both low molecular weight petrogenic PAHs and medium/high molecular weight pyrogenic PAHs in used oil. It is interesting to note that Zakaria et al. (2002) suspected used engine oil to be a major source of PAHs in riverine and estuarine sediments in Malaysia. The authors noted that Malaysia, unlike many developed countries, has no recycling programme for used sump oil, and consequently large amount are improperly stored and consequently released (either accidentally or

deliberately) into waterways. While a significant percentage of the total volume of engine oil sold in NZ is unaccounted for, the amount of waste oil dumping (or fugitive losses) is likely to be substantially lower in New Zealand cities. Accordingly, the sediment compositions are not consistent with used engine oil being a major source of PAHs. If used oil were a major contributor of PAHs in road run-off or receiving environment sediments, much higher concentrations of hopanes would be expected on account of used engine oil containing >500 µg/g of the two hopanes quantified in this study. However, most of Auckland's receiving environment sediments contained less than 1 µg/g of hopanes, and run-off particulates contained only 10 µg/g (refer to Figure 22), which is <2 per cent of the hopane levels measured in used engine oil.

The similarity between Auckland run-off particulates and air particulates (Figure 23) is consistent with the assumption that these two particulate materials are linked via deposition/resuspension processes (Figure 24). Based on the proposed schematic, the following assumptions can be made about the composition of air and run-off particulates:

- Air particulates consist predominantly of fine particulate materials and will be enriched in fine, combustion-derived PAHs (ie, pyrogenic) relative to the PAH composition in road run-off particulates.

- Relative to air particulates, run-off particulate material will consist of coarser, road derived particulate material, such as abraded tyre and roading surface, resulting in an enrichment of petrogenic PAHs.

- In addition to the coarse material described above, run-off will contain fine material from atmospheric deposition that is eventually washed off the road surface. This fine material contributes a significant proportion of the total PAHs in road run-off.

- The combination of road-derived petrogenic particulates and atmospheric-released pyrogenic particulates (ie, combustion soot) is the reason why road run-off particulates have a mixed or "intermediate" PAH composition.

4.3.2.4 Wood/coal soot contribution to Auckland air and road run-off particulates

In addition to the diagnostic procedures mentioned above, other chemical markers can be used delineate PAH sources. Two methods used to identify coal and wood soot PAHs in road run-off were based on retene and the relative abundance of 1,7- and 2,6-dimethylphenanthrenes (DMP). Retene (a C4-phenanthrene; see structure below) is a characteristic marker compound for wood smoke/soot – Figure 25 shows the utility of the retene/C1-pyrene ratio for identifying wood soot inputs. The conspicuous difference in the retene/C1-pyrene ratio illustrates the impact that wood burning has on Christchurch air particulates. More importantly, it highlights the absence of such sources in Auckland air particulates, run-off particulates and sediments.
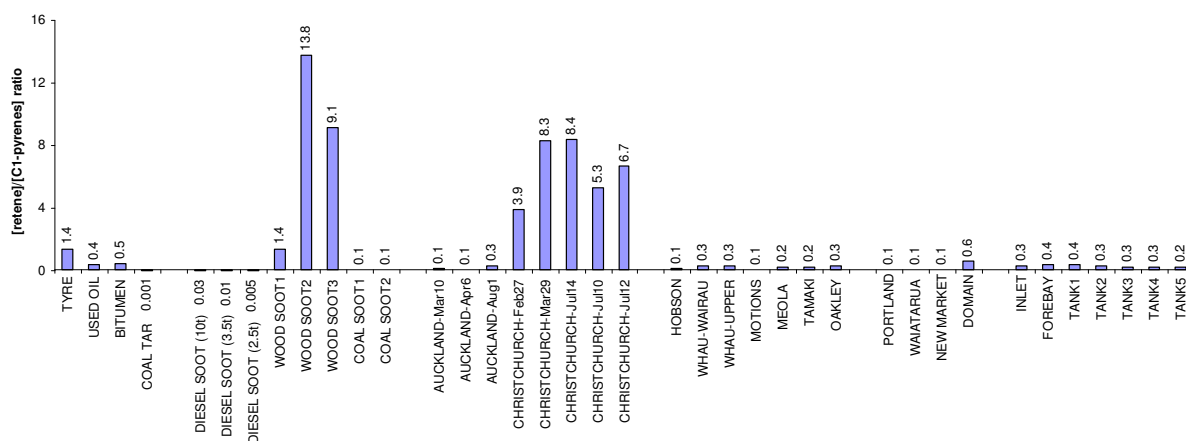

Retene

As with retene, the 1,7-DMP/2,6-DMP ratio is largely an indicator for wood smoke/soot, but coal soot also contains elevated ratios (Figure 26). As with retene, the

1,7-DMP/2,6-DMP ratio shows significant contribution of wood/coal soot to Christchurch air particulates, but not in Auckland air particulates, run-off particulates or sediments. Thus, it may be concluded that wood/coal soot is not a major contributor of PAHs in road run-off in Auckland.

Figure 25
Retene/C1-pyrene ratio: a high ratio indicates a significant contribution from wood soot.


4.3.2.5 Coal tar versus coal soot

The 1,7-DMP/2,6-DMP ratio is less specific than retene for wood smoke. On the other hand, it has a wider dynamic range and can be used to distinguish coal soot from coal tar or pyrogenic materials (tyres, oil, bitumen). Coal soot has a relatively high 1,7-DMP/2,6-DMP ratio of ca. 5 compared to coal tar, with a ratio of ca. 0.6, or tyres and bitumen, with ratios of 2.1 and 3.4, respectively (Figure 26). The 1,7-DMP/2,6-DMP ratio in Auckland sediments ranged between 1.4-2.3, and was 1.2 in road run-off particulates. While this low ratio does not preclude coal and wood soot, it suggests a relatively low contribution of these source materials.

Figure 26

1,7-Dimethylphenanthrene (1,7-DMP)/2,6-dimethylphenanthrene (2,6-DMP) ratio: a high ratio indicates a significant contribution from wood/coal soot.
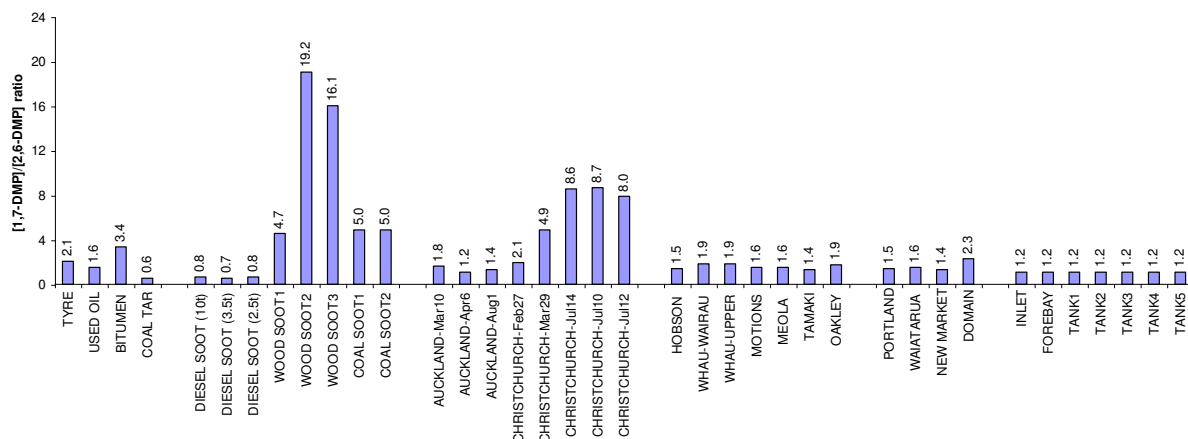
Even though they are low molecular weight PAHs, the acenaphthylene (acy)/acenaphthene (ace) ratio possibly provides the best differentiation between coal tar and coal soot source materials (Figure 27). Based on the high acy/ace ratio of >20 for coal tar soot, if it were a major source of PAHs, then higher acy/ace ratios would be expected in receiving environment sediments. In contrast, sediments had an average acy/ace ratio of only 1.7, precluding substantial contributions from coal and wood soot.

Figure 27

Acenaphthylene (acy)/acenaphthene (ace) ratios for the source materials and environmental samples.
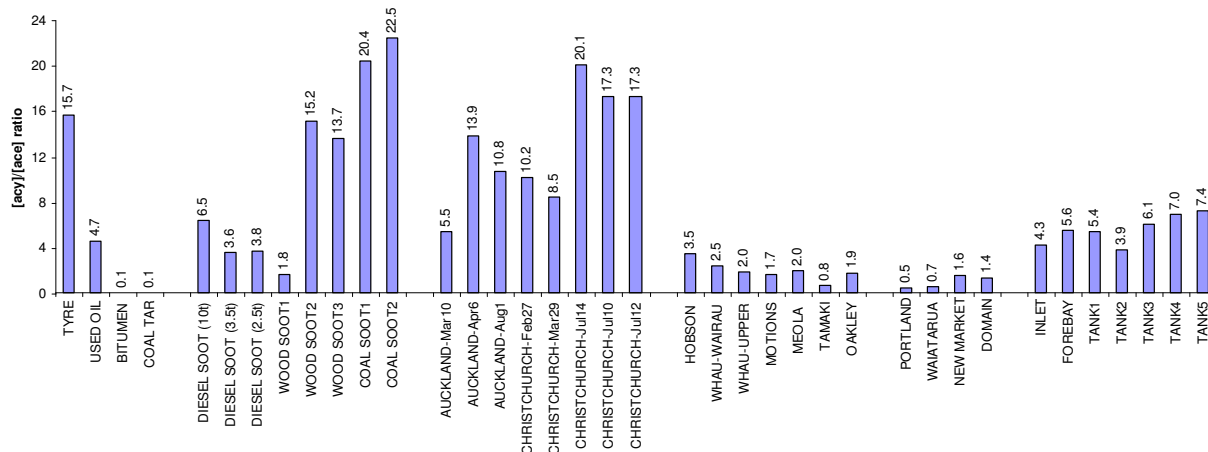
Unlike coal soot, the importance of coal tar as a major source of PAHs is supported by road cores taken within the Motions Creek catchment (Ahrens and Depree, 2006) and identified coal tar coatings on particulates from Motions Creek stream sediments (Figure 28). The presence of tar coated grit, as shown in Figure 28, accounted for the very high levels of PAHs in the 1-2 mm size fraction (ca. 70 µg/g). While not a major

component of estuarine settling zone sediments, these coarse particulates are potentially important (ie, ecologically and chemically) fractions in urban stream sediments.

Figure 28
Sediment particle from Motions Creek Stream (1-2 mm) with visible tar coating containing ca. 28,000 µg/g of PAHs.


4.3.2.6 Contribution of petrogenic compounds to run-off –hopane ratios

As mentioned in Section 4.3.2.3, deposition of engine oil and abrasion of road surface and tyres is expected to result in an enrichment of petrogenic PAHs in road run-off particulates. For resolving contributions from petrogenic sources, hopanes were employed in concert with PAHs for source identification. In general, petrogenic sources contain low to moderate concentrations of PAHs but high concentrations of hopanes, whereas many pyrogenic materials such as coal tar contain very high concentrations of PAHs and low concentrations of hopanes. Accordingly, the relative amount of these two classes of compounds can be used for identifying petrogenic inputs. Rather than using total PAHs, which includes low molecular weight PAHs that are susceptible to volatilization (ie, air particulate sampling) and solubilisation (ie, sediments), the ratio of hopanes to benzo[e]pyrene (BeP) has been employed to improve consistency across the sample types (Figure 29). In brief, the higher the Hopanes/benzo[e]pyrene ratio – the more petrogenic the sample is. Conversely, the lower the ratio – the more pyrogenic the sample is.

Figure 29

Hopanes/benzo[e]pyrene (BeP) ratios for the source materials and environmental samples (off-scale values for used oil and bitumen are 273 and 70, respectively).
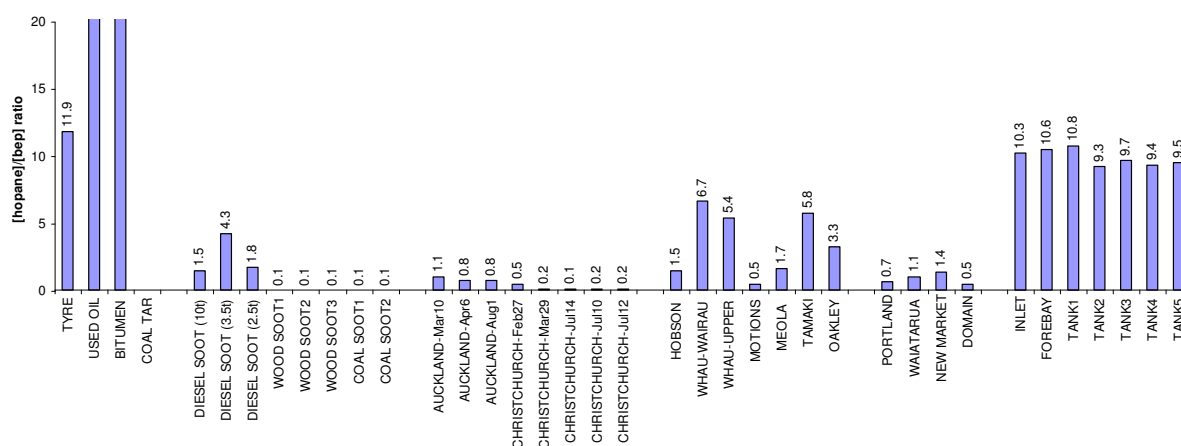
As anticipated, the run-off samples from the Grafton Gully SWTD contain much higher ratios (ca. 10) of hopanes/BeP, than the Auckland air particulates (ca. 1), which is consistent with higher inputs of strongly petrogenic source materials (eg, tyres, used oil and bitumen). From the ratios in Figure 29 it is clear that many of the Auckland receiving environment sediments are substantially more pyrogenic in nature than the run-off particulates, indicating that "modern" road run-off is not the dominant source of PAHs in these environments. This is certainly the case for Motions Creek estuarine sediment (hopane/BeP ratio of 0.5), which has been shown to have a large proportion of the PAHs attributable to coal tar (Ahrens and Depree, 2006). In contrast, other receiving environments, such as Whau-Wairau, have much higher petrogenic ratios – approaching that of the road run-off particulates.

4.3.2.7 Possible composition of road run-off

Using complementary hopane and PAH data it is possible to not only estimate the contribution of "modern" road run-off to total PAHs in receiving environment sediment (Section 2.6), but also to derive possible source compositions of road run-off particulates. One such source apportionment example for road run-off is given below.

Using a weighted mass balance of four different source materials, it is possible to calculate mixtures having the observed concentrations of hopanes and BeP of run-off material. A possible composition of road run-off consisting (by weight) of: 7 per cent air particulates; 3 per cent tyre; 1.5 per cent bitumen; and 1 per cent engine oil, which fits both the ratio and absolute concentrations of hopanes and benzo[e]pyrene is given in Table 6. The remaining ca. 90 per cent is inorganic minerals (both anthropogenic and natural) such as pavement aggregate, sand and soil, combined with organic material (detritus and humic coatings on inorganic particles).

Table 6

Example calculation showing a possible composition of anthropogenic particles in (modern) road run-off that is consistent with hopane and benzo[e]pyrene concentrations and ratios

Sample	Hopanes (µg/g)	BeP (µg/g)	Ratio
Run-off particulates (mean)	10	1.1	9
Auckland air particulates (mean)	11	13	1.2
Abraded tyre	60	5	12
Bitumen	160	2	70
Engine oil	500	2	274
Scenario: 7% air particulates; 3% tyre; 1.5% bitumen; 1% engine oil			
7% Auckland air particulates (mean)	0.7	0.9	
3% abraded tyre	1.8	0.15	
1.5% bitumen	2.4	0.03	
1% engine oil	5.0	0.02	
Composite total	9.9	1.1	9

4.3.2.8 Estimates of the proportion of PAHs in Auckland sediments derived from "modern" road run-off.

Making the assumption that the hopanes/PAH ratio in the run-off particulates (Grafton Gully SWTD) is representative of the road run-off particulates entering Auckland's receiving environments, the amount of PAHs attributable to run-off can be calculated (Figure 30). Estimates of modern road run-off contributions to total PAHs ranged from 4 per cent to 63 per cent. The very low contribution of modern road run-off for Motions Creek estuarine sediment is consistent with the previous finding that up to 95 per cent of the PAHs may be coal tar derived (Ahrens and Depree, 2006). Similarly, modern run-off contributed less than 11 per cent of PAHs to the four stream sediments analysed. In the Tamaki and Whau estuaries, modern road run-off could account for one-half to two-thirds of the sediment PAHs. However, at these locations, the current sediment PAH concentration is only 1.2 µg/g, well below the ANZECC-low trigger level (4 µg/g total PAHs). Thus, if two-thirds of the PAHs found in the Whau-Wairau estuary are due to modern road run-off, then continued or even slightly increasing inputs of road run-off into this receiving environment are unlikely to elevate sediment PAH concentrations beyond the ANZECC-low trigger level of 4 µg/g.

Figure 30

Calculated percentages of PAHs derived from "modern" (no coal tar) road run-off particulates for Auckland receiving environment sediments.
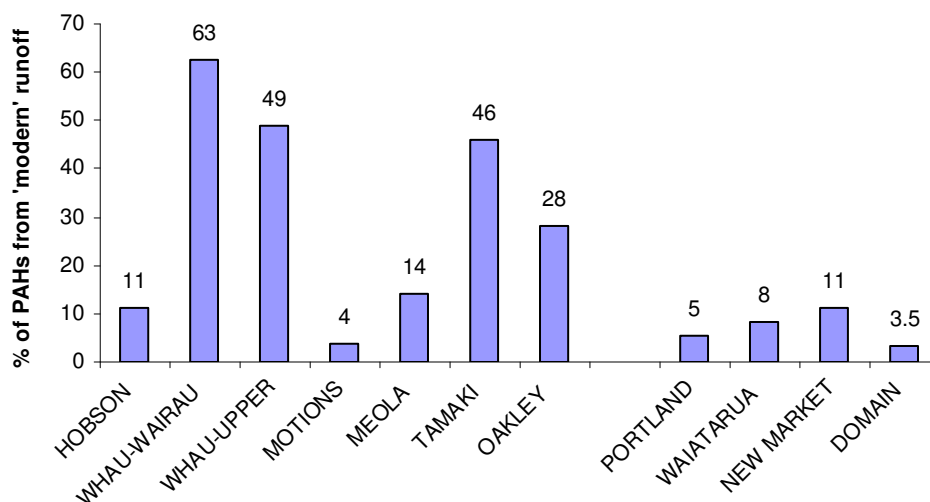
Note that the higher percentages of road run-off contributions in Figure 30 do not signify larger absolute PAH inputs of modern run-off particulates, but rather the fact that these sites experience smaller inputs of historic pyrogenic PAH inputs (ie, from roading coal tar inputs). This is illustrated in Figure 31, showing that stream sediments contained 3-times higher hopane levels than estuarine sediments despite having a 4-fold lower percentage of PAHs contributed from modern road run-off. The low "modern run-off percentage values" for stream sediments can be explained by the observation that coal tar binders are enriched in the more coarse size fractions of road run-off, and that these coarse size fractions are preferentially deposited in high energy stream environments (as opposed to low energy estuarine settling zones).

Figure 31

Hopane concentrations in Auckland receiving environment sediments. For comparison, the concentration of hopanes in coarse run-off (Grafton Gully – INLET) and fine run-off particulates (mean of Grafton Gully FOREBAY and TANK samples) have been included.
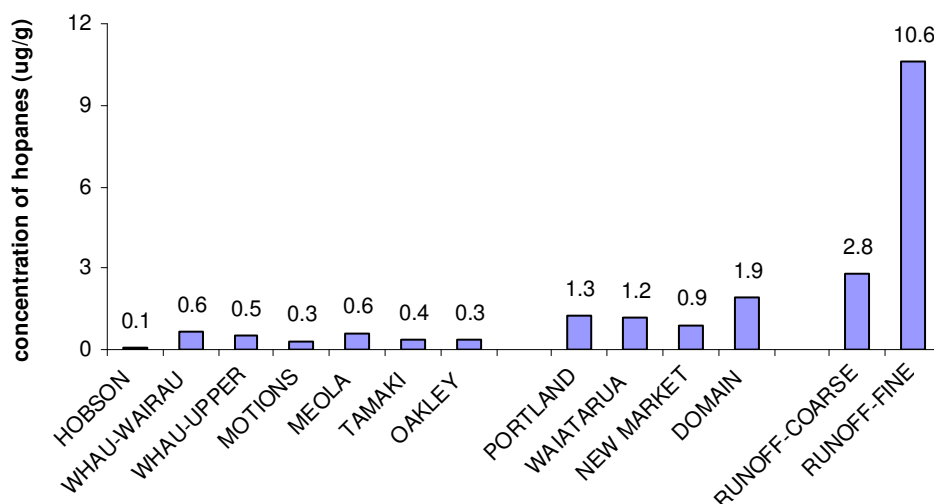

4.4 Reducing PAH inputs

Based on this and previous study there appear to be only a small number of locations in Auckland where sediment PAH levels are currently exceeding the ANZECC-low sediment guideline value for PAHs of 4 µg/g. Of the estuarine sites the only sites of concern are Motions and Meola. However all four stream sites analysed exceeded 4 µg/g. At these locations, source identification techniques strongly implicate PAH contamination by coal tar as a likely input. Accordingly, the percentage of PAHs arising from "modern" road run-off is very low in these samples, typically being less than 10 per cent. The calculations presented here indicating that modern road run-off is not a major contributor of PAHs to sediments with high PAH concentrations have important implications for stormwater contaminant management and mitigation options. As can be seen from Figure 32, those sites that have a large estimated proportion of the PAHs coming from "modern" road run-off (≥50 per cent; such as Whau and Tamaki sites) have total PAH sediment concentrations of only 1-2 µg/g. This indicates that inputs from "modern" road run-off are unlikely to result in sediment PAH levels that exceed guideline values (ie, 4 µg/g), providing the existing "dilution" by inorganic and organic material continues. However, if the sediment inputs to estuaries were to become more dominated by road run-off particulates then the concentrations could exceed both the ANZECC-low guidelines (Figure 21).

Figure 32

PAH concentrations and estimated "modern" road run-off contributions to total PAHs for Auckland stream and estuarine sediments.
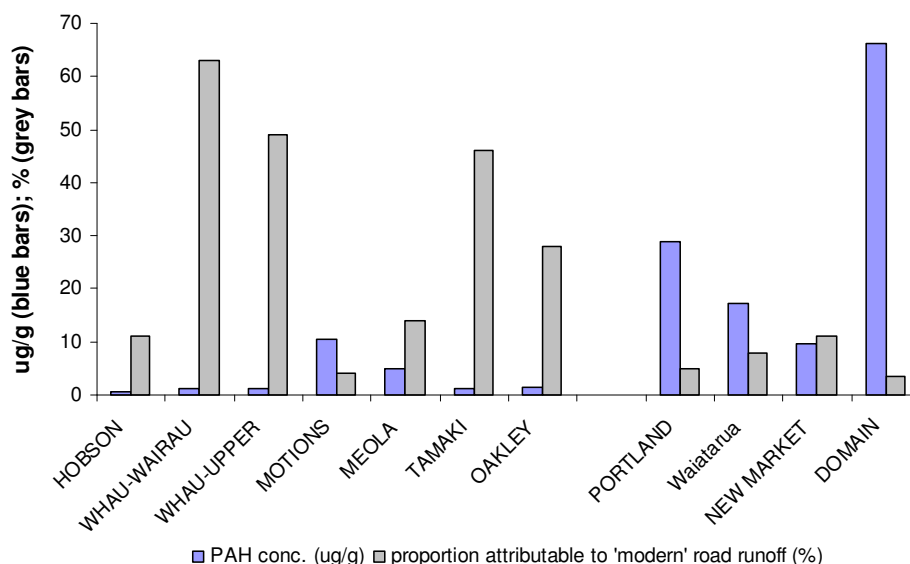
Sites with elevated PAH concentrations are contaminated either by entirely historic inputs (no-longer occurring) or, coal tar contaminated material is still being mobilised in the catchment and contributing to the high levels of PAHs. Mitigation strategies aimed at reducing PAH loads in these locations might therefore best focus on reducing inputs from coal tar pavements, since even removing small amounts goes a long way. This could be achieved by sealing or reconstruction of coal tar contaminated roads and footpaths or the installation of catchpit filters, since PAH-rich pavement particulates tend to be coarse and should be captured readily by these devices. Although ongoing erosion of surface pavements is demonstrably contributing coal tar derived PAHs (Figure 33a), road coring in Auckland and Christchurch has found the majority of coal tar to be buried under more recently applied bitumen layers, greatly reducing the inputs of coal tar particulates from these seal layers. On the other hand, Christchurch data showed a good correlation between PAH concentrations in roadside soils and run-off particulate material (Figure 33c), indicating that coal tar derived PAHs have accumulated in roadside soils, and that these soils represent an ongoing source of high levels of PAHs in run-off particulates. In other words, soils within the roading corridor can function as large PAH reservoirs of particulate material containing historic coal tar.

Figure 33

(a) broken pavement with coal tar material exposed (De Luen St., Point Chevalier), (b) Western Springs stormwater box culvert (c) correlation of shoulder soil PAHs with gutter particulates PAHs (Christchurch data).

surface shoulder vs gutter
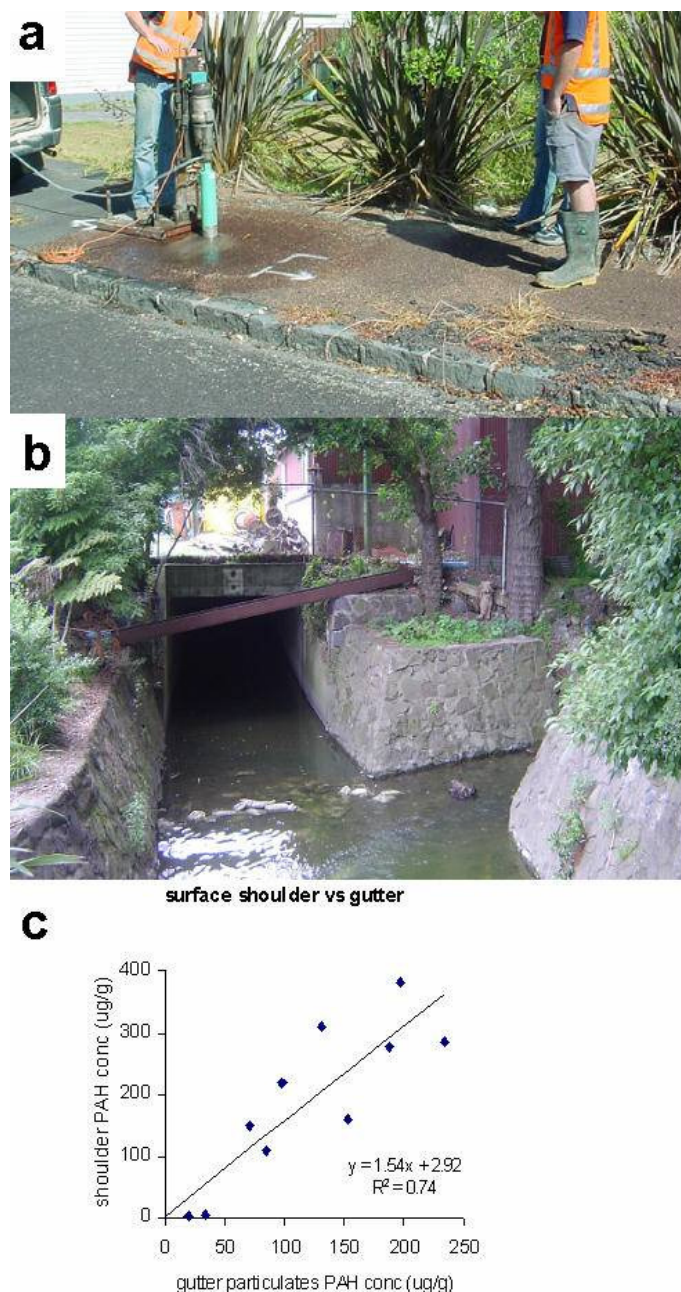
Although the Christchurch situation is somewhat unique because of the presence of shoulder soils (grassed verge between road seal edge and the gutter channel), it is important to point out that even the berm soil (grassed area between footpath and front boundary of property ca. 4-5 m from road seal edge) typically contained between 60-100 µg/g of PAHs. Accordingly, Auckland roadside soils (with coal tar histories), might contain relatively high levels of PAHs as well. If this hypothesis were to be confirmed in Auckland, roadside soils could be an important vector for ongoing,

elevated levels of PAHs in road run-off that could be diminished by targeted proactive mitigation (or "source control") strategies.

Ongoing input of coal derived PAHs in older Auckland catchments has been confirmed for Motions Creek. Run-off particulates collected from Motions Rd (near bridge that crosses Motion Creek) contained 15-16 µg/g of PAHs, with a strongly pyrogenic signature. These levels compare with only 3-4 µg/g of PAHs in run-off particulates collected from nearby SH16 motorway off ramp (intermediate PAH composition). Data collected to date are consistent with the conclusion that ongoing input of coal tar-derived material is accounting for the four to five times higher concentrations of PAHs at the Motions Road site. The concentration and composition of PAHs in Motions Road gutter particulates was comparable to that of sediment sampled from the large box culvert (just upstream of the main Western Spring outlet, Figure 33b), suggesting the high PAH inputs are occurring on a catchment-wide scale. Based on these preliminary findings, further work is warranted to confirm the source of these elevated PAHs and, at the very least, roadside soils should be analysed to determine whether they contain elevated levels of PAHs.

4.5 Remediation

An alternative to reducing loadings is to attempt to reduce the levels of deposited PAHs in situ, by dredging or capping, or enhancing the degradation of PAHs. Due to the much greater costs and efforts associated with remediation, this reactive approach to PAH risk reduction seems advisable only for severely contaminated, localised PAH hot spots. No location in Auckland Harbour, including Motions Creek, currently seems to warrant in situ remediation. Furthermore, dredging or capping of PAH-contaminated sediments would be of little environmental benefit, because of the continuous nature of PAH inputs and deposition. Furthermore, assuming PAHs in most sediments have low bioavailability, as shown for Motions Creek, the benefit of artificially enhanced in situ microbial degradation would probably be minimal. Targeted source control/input minimisation therefore seems a more cost-effective approach, wherever risks from PAHs appear to require management action.

4.6 Reducing bioavailability

A further (theoretical) alternative to reducing PAH effects on settling zones is to modify the bioavailability of introduced PAHs. This could be accomplished by increasing the pool of organic matter that PAHs can adsorb to, or increasing the specific binding capacity of organic matter. NIWA research has shown that increasing dissolved organic carbon levels by introducing plant litter leachate can measurably diminish concentrations of freely dissolved PAHs, which will entail lower PAH bioavailability. Similarly, higher sediment organic carbon content is likely to diminish freely dissolved PAH concentrations in pore water, since a greater fraction of PAHs would be bound to organic matter. This outcome could be achieved by increasing organic carbon loadings to settling zones. The obvious drawback is that increased organic matter inputs would

probably lead to greater microbial degradation and biochemical oxygen demand in the receiving environment, potentially leading to hypoxia or anoxia, with undesirable ecological consequences. A solution and optimisation of this approach is not to introduce ordinary, labile organic matter, but rather, refractory carbonaceous material, such as black carbon (soot, activated charcoal), as demonstrated by Zimmerman et al. (2004). This carbon fraction would not be susceptible to microbial degradation and therefore persist in sediments while creating little oxygen demand. Furthermore, the up to 100-fold greater PAH-binding affinity of black carbon compared to labile organic carbon (Koelmans et al. 2006) is likely to lead to a compounded reduction in PAH bioavailability, by locking-in PAHs even more tightly, all assuming that deposited PAHs re-partition into the black carbon material that is introduced. Given that, without any additions, black carbon generally comprises around 9 per cent of total organic carbon in many (urbanised) sediments, reductions of PAH bioavailability are probably occurring already in many instances. This phenomenon would, therefore, merely be amplified by enhancing the proportion of black carbon.

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