Sampling receiving environments close to State Highways

NIWA Client Report: 2008-035
August 2008

NIWA Project: TRZ08105

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Jacquie Reed
Craig Depree
Elizabeth Trip
Petra Chappell
Nick Talbot

NIWA contact/Corresponding author

Jacquie Reed

Prepared for

New Zealand Transport Agency (NZTA)

NIWA Client Report: AKL2008-035
August 2008

NIWA Project: TRZ08105

National Institute of Water & Atmospheric Research Ltd
269 Khyber Pass Road, Newmarket, Auckland
P O Box 109695, Auckland, New Zealand
Phone +64-9-375 2050, Fax +64-9-375 2051
www.niwa.co.nz

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Reviewed by:	*Approved for release by:*
Michael Stewart	*Ken Becker*

Formatting checked

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Executive Summary

Elevated loads of sediments and contaminants such as metals and hydrocarbons are carried via urban stormwater to freshwater and marine environments. A variety of these contaminants are the result of road run-off: New Zealand Transport Agency (NZTA) is seeking to better quantify the contribution from state highways, and has commissioned NIWA to undertake a program of research involving:

- The design of a sampling protocol.
- Collection of sediment samples at sensitive locations identified as at risk from state highway run-off.
- Assessment of sediment quality at these locations based on contaminant concentrations and diagnostic source ratios.

This report presents the results of NIWA's research program; findings are discussed in the context of land use, including the relative contribution of motorways and urban areas to the metal ratios and polycyclic aromatic hydrocarbon (PAH) levels measured in samples.

Sediment samples were taken from five sites identified as being at high risk. The catchments in which these sites were located and the neighbouring state highways are: Motions (SH16), Newmarket (SH1), Onehunga (SH1), Paremoremo (SH17) and Puhinui (SH20). The samples were analysed for PAH, TPH (total petroleum hydrocarbons) selected hopanes and total metals, including zinc and copper. A summary of the estimated contribution of modern road runoff to PAHs and metals in catchment sediments is presented in the table below and key results include:

- High zinc and copper concentrations were observed in sediments in the Motions and Newmarket catchments. Using the ANZECC (2000) guidelines, these sediment concentrations have the potential to cause harm to aquatic life. High zinc concentrations were also observed in the Puhinui catchment.
- To identify the potential source of these metals, the Zn:Cu ratio of modern road runoff was used to provide a 'crude' estimate of metal sources from roads (Reed, 2008). Land-use mapping and the Contaminant Load Model (CLM) (see Timperley and Reed, 2008) were used to assess metal sources in each catchment. So, in the Motions and Newmarket catchment, the Zn:Cu ratio observed in these catchments' sediments was lower than the Zn:Cu ratio from modern road runoff (Reed, 2008) suggesting that there are significant other metal sources in

the catchment that require investigating. An investigation of road derived sediments (RDS) would further aid the investigation of metal sources.

- High PAH concentrations were detected in sediments from the Motions and Newmarket catchments. Both of these catchments exceeded the ANZECC (2000) 'low' sediment quality guideline. However, it was estimated in this study that modern road runoff contributed approximately <5% of the total sediment concentration.

Summary Table: Estimated contribution of modern road runoff to PAHs and metals in catchment sediments.

Catchment	%of roads in catchment that are State Highways	PAH sediment levels of concern	Metal sediment levels of concern[1]	Estimated contribution of road runoff to sediment PAHs (%)[2]
Motions	40	YES	YES	2-4
Paremoremo	20	NO	NO	61-100[3]
Puhinui	15	NO	YES	100[3]
Newmarket	5	YES	YES	3-6
Onehunga	5	NO	NO	68-100[3]

[1] No estimated percentage contribution of road runoff to sediment metals; requires analysis of road derived sediment (RDS);

[2] Range is based on upper and lower quartile hopane:PAH ratios using all 10 RDS samples (blue bars; Figure 58);

[3] Estimated percent contribution was >100%.

1. Introduction

1.1 Background

Urban stormwater carries elevated loads of total suspended solids (TSS, i.e. sediments), contaminants such as metals (e.g. zinc and copper) and hydrocarbons. A substantial part of stormwater is conveyed via roadside gutters and catchpits (i.e. drain inlets) to the reticulated pipe network and discharged to streams, estuaries and harbours. A variety of contaminants that end up in freshwater and marine environments are a result of inputs from road run-off. Contaminants of particular interest include sediment, heavy metals, oils and grease, organic contaminants and debris, due to their potential for adverse effects on aquatic health.

New research by NIWA suggests that, in Auckland, estimated loads from ‘modern’ road run-off account for up to two thirds of the total amount of polycyclic aromatic hydrocarbons (PAHs) contamination (Depree and Ahrens, 2007). Treating road run-off can be expensive, and to maximise the cost/benefits of undertaking such measures, NZTA have identified a strategy for prioritising treatment of road run-off from state highways. Working with MWH (NZ) Ltd, NZTA has identified receiving environments at potential risk from state highway runoff (Gardiner *et al*., 2007).

1.2 Aims and objectives

Additional research is now needed by NZTA to better quantify the contribution of stormwater contaminants from state highways, in particular, the contribution of metals, hydrocarbons, and any other contaminants of interest to identified sensitive environments. To these ends, NZTA commissioned NIWA to undertake a research project that included the following key components: design of a sampling protocol; collection of sediment samples at specified sensitive locations; and assessment of sediment quality based on various contaminant concentrations and diagnostic source ratios. In this report we present the results found in this study, and discuss our findings in the context of land usage, including the relative contribution of motorways and urban areas to the metal ratios and PAH levels found across selected sensitive locations.

2. Materials and Methods

2.1 Site selection and sampling design

Sites selected for sampling were identified by NZTA and NIWA as having three similar characteristics: they were (1) depositional areas, (2) close to a discharge point receiving road runoff from a state highway, and (3) they drain to sensitive environments. An assessment of such sites was identified by Gardiner et al. (2007) as high risk and potentially requiring stormwater retrofit treatment options along state highways. The sites selected include outfalls that receive direct runoff (e.g., piped discharge), indirect runoff (e.g., stream/river or estuary) and/or a combination of these.

Sites selected are located in stormwater catchments in the Auckland region, discharging at:

- Meola Road (Motions catchment including SH16)
- Shore Road (Newmarket catchment including SH1)
- Captain Springs Road (Onehunga catchment including SH1)
- Vinewood Drive (Paremoremo catchment including SH17)
- Price Road (Puhinui catchment including SH2O)

Location of all five sites selected, and position of the neighbouring state highways, is presented in Figure 1. The latitude and longitude of each sample site is shown in Appendix 1. The estimated number of daily vehicle-km travelled (VKT), as a measure of urban traffic intensity at each site, is presented in Figure 2.

For each catchment, the percentage of residential, commercial and industrial land area which is occupied by roads is 16%, 20% and 20% respectively. These percentages are taken from the Contaminant Loads Model (CLM; Timperley, 2008), and are based upon studies of fully developed (urbanised) catchments. The Paremoremo catchment is still substantially rural, so the values obtained using these percentages are likely to be an overestimate.

2.2 Collection of samples

Sampling was designed with the aim of capturing the spatial heterogeneity of sediment deposited in the vicinity of the discharge at each site. At each site, 10 samples were collected randomly along a transect line ≤100m from the point of discharge, from each stormwater catchment. At each of the 10 sample locations along the transect line, the surface 1-2cm layer of sediments was scraped using a scoop, and sediments were stored wet in labelled plastic bags until return to the laboratory. Samples were stored at -20^{o}C prior to sediment processing and subsequent contaminant analysis. The approximate location of the sampled transect line is shown for each site in Figure 3 to Figure 7.

Figure 1 Map of Auckland region showing the location of the five sampling sites (red circles) and their proximity to neighbouring state highways

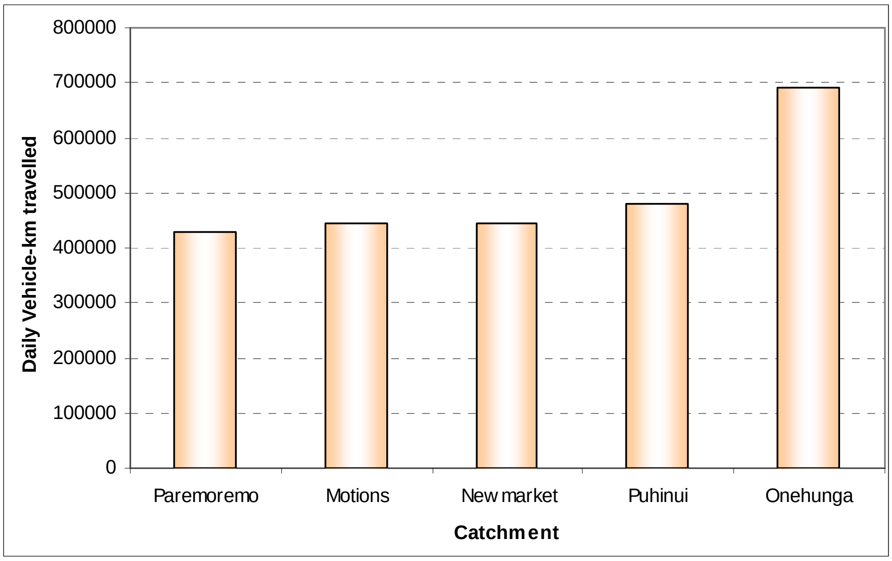


Figure 2 Estimates of number of vehicles travelling (Vehicle-Km Travelled; VKT) in the stormwater catchment only, illustrating urban traffic intensity at each of the five catchments studied. Data provided by NZTA (Greig, 2008).

2.2.1 Motions catchment (Meola Road; SH16)

The Motions Creek sampling site (Figure 3) is located 1.5 km downstream of a major stormwater culvert (2.5x2.5 m) that conveys stormwater from SH16 up to ‘Spaghetti Junction’. The site would also be impacted from numerous other smaller stormwater inputs from the surrounding residential area (Westmere).

2.2.2 Newmarket catchment (Shore Road; SH1)

The Newmarket stream sampling site (Figure 4a) is located 10m downstream of a major stormwater culvert located near Ayr Street, close to the roundabout with Brighton Road and Shore Road. The culvert conveys stormwater from the catchment (Figure 4b) including a section of SH1 in the Khyber Pass area. Sampling continued at ~10m intervals downstream to another culvert under Brighton Road. The land-use in the catchment is largely commercial (Newmarket Broadway) with recent residential infilling as flats and apartments. The sampling site would be impacted from stormwater inputs from the surrounding commercial and residential areas (Newmarket, Broadway Park, Ayr Reserve) including arterial roads.

Figure 3 Aerial view of Meola Road sampling site. Numbers show position of each of the 10 samples collected. Photo from http://www.googleearth.com .

Figure 4a Aerial view of Shore Road sampling site. Numbers show position of each of the 10 samples collected. Photo from http://www.googleearth.com .

Figure 4b Photo of Shore Road sampling site, showing mouth of culvert. Photo NIWA.

2.2.3 Onehunga catchment (Captain Springs Road; SH1)

The Onehunga sampling site is located downstream of a very large stormwater culvert (Figure 5a; black dot) along the waterfront of the Manukau harbour and located east of Alfred Street (located bottom left of Figure 5a). The culvert conveys stormwater from the Onehunga catchment including a section of SH1 near Mt Wellington. Sampling was conducted randomly along a 100m transect (Figures 5b -5d). The land-use in the catchment is a mix of commercial (Church Street, Onehunga area), industrial and a mix of old and new residential. The sampling site would be impacted from stormwater inputs from the surrounding industrial, commercial and residential areas (e.g., Te Papapa, Onehunga, Penrose, Oranga and Ellerslie), including arterial roads.

Figure 5a Aerial view of Onehunga sampling site. Photo from http://www.googleearth.com .

Figure 5b Photo of Onehunga site from the culvert showing mouth of pipe and the receiving environment of the Manukau Harbour. Photo NIWA.

Figure 5c Photo of Onehunga sampling site showing mouth of pipe and the receiving environment of the Manukau Harbour. Numbers show position of each of the 10 samples collected, only sites 1-4 shown here. Photo NIWA.

Figure 5d Photo of Onehunga sampling site showing mouth of pipe and the receiving environment of the Manukau Harbour. Numbers show position of each of the 10 samples collected, only sites 5-10 shown here. Photo NIWA.

2.2.4 Paremoremo catchment (Vinewood Drive; SH17)

The Paremoremo sampling site (Figures 6a & 6b) is located in a stormwater catchment comprising of residential areas, recreational spaces, rural areas, Massey University campus, commercial areas, several busy arterial roads and a section of SH17. Samples were collected downstream of Wilfred Pannill Park on the intertidal mudflats of Lucas Creek.

Figure 6a Aerial view of Paremoremo sampling site. Numbers show position of each of the 10 samples collected. Photo from http://www.googleearth.com .

Figure 6b Photo of sample 1 at Paremoremo. Photo NIWA.

2.2.5 Puhinui catchment (Price Road; SH20)

The sampling site is located in the Puhinui stream that flows around the quarry (Figures 7a & 7b). The catchment is largely a mixture of land uses, for example, industrial, commercial, dairying, recreational areas, some residential and various arterial roads including SH20.

Figure 7a Aerial view of Puhinui sampling site. Numbers show position of samples collected. Photo from http://www.googleearth.com .

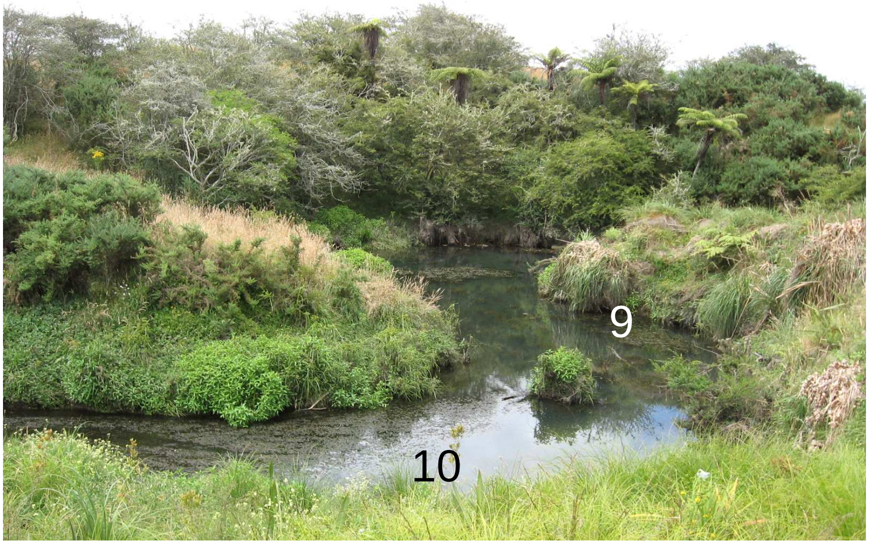


Figure 7b Photo of Puhinui sampling site (sites 9 and 10). Photo NIWA.

2.3 Sample processing

Sediments were stored at -20°C prior to processing. After thawing, each sample was homogenised, and two sub-samples were taken. One set of sediment sub-samples were immediately re-frozen, freeze-dried and sent to Hill Laboratories (Hamilton) for the analysis of PAHs (including the smoke marker compound retene), TPH and selected hopanes. The second set of sub-samples was wet-sieved to three particle sizes: 200-63 µm, 63-25 µm and <25 µm, then dried at 60°C until constant weight. The dried sediment was ground, and 1g (±0.001g) sent to Hill Laboratories (Hamilton) for analysis of total metals (including zinc and copper) using digestion method US EPA 200.2 and analysed by ICP-MS using method APHA 3125B.

2.4 Hypothesis: Contaminants in State Highway Runoff

The aim of the sediment sampling was to quantify the contribution of stormwater contaminants from State Highways to receiving environments. To achieve this aim, NIWA implemented a newly developed approach that can be used to estimate the proportion of contaminants attributable to highway runoff. This research was undertaken by Reed (2008), and Ahrens and Depree (2007), who examined contaminants (metals and PAHs, respectively) from State Highway runoff that had been deposited in a nearby stormwater retention tank. The retention tank studied was located on Grafton Road near State Highway 1, and had the distinctive feature of trapping sediments only from the surface of the new motorway, with all other contaminant sources excluded (Figure 8). As a consequence, the Grafton Road sediment contaminant concentrations and ratios provided a way of estimating the proportion of contaminants in receiving environment sediments that are attributable to modern State Highway runoff from highly trafficked streets.

In the present study, the current sampling sites are compared to the previous Grafton Road results (Reed, 2008), which are used as the ‘typical’ NZ contaminant signature’ from State Highways, having ‘high’ traffic volumes (>10,000 VKTs per day) to which this project’s sampling sites are compared to. A fundamental research question, therefore, is as follows:

> Are metal ratios and concentrations and PAH fingerprints, in sediments sampled close to discharge points in catchments with State Highways (with high VKTs), similar to contaminant ratios and concentrations from Grafton Road sediments?

In a nutshell, similar contaminant ratios are indicative that State Highway runoff is a major source of those particular contaminants in catchment sediments. If the ratios are significantly different between State Highway runoff and catchment sediments, then this indicates that a source other than State Highway runoff is a major environmental contributor of those contaminants indicating that another source is contributing disproportionately greater amounts of copper or zinc, yielding a higher or lower Zn:Cu ratio, respectively. While not quantitative, the Zn:Cu ratio provides a qualitative assessment tool for determining whether copper and zinc in receiving environment sediments are consistent with road runoff particulates being the major source.

Figure 8 Photos of Grafton Road retention tank nearby State Highway 1. Photograph A shows the position of the tank close to the state highway, and shows sample locations within the retention tank. Photo B shows an inside view of the first chamber which concentrates the coarse material, and photo C shows the main tank looking towards the forebay and inlet. Photos NIWA 2007.

2.5 Source information: Understanding the Zn:Cu ratio in sediments

Photos of Grafton Road retention tank near State Highway 1 are shown in Figure 8. Photograph A shows the position of the tank close to the state highway and sampling locations within the retention tank. Photo B shows an inside view of the inlet chamber, which concentrates the coarse material, and photo C shows the main tank. Total zinc and total copper concentrations have been measured in sediments at each site in Photo A (in three particle sizes: 200-63 µm, 63-25 µm and <25 µm) and the ratio of Zn:Cu calculated. These values are used to describe metal concentrations and ratios in sediments collected from only State Highways with high VKTs.

In this study, total zinc and total copper are measured in sediments at each sampled site and are compared to the above Grafton Road sediments. Using results shown in Figure 9 for Grafton Road, the ratio of Zn:Cu is compared to each of the 5 sampled stormwater catchments and the source of State Highway runoff assessed to help answer the research question in section 2.4 above. For example, in the case where Zn:Cu ratio differs from 6 (in the mud fraction), this may suggest the presence of other contaminating sources (without excluding the effect of State Highway runoff). The potential source of any other contaminants (other than from State Highway runoff) is discussed using land use data (data which includes percentage of area occupied by urban i.e. residential, industrial, or commercial, and/or highways) in section 3.3. This will also help answer our research question.

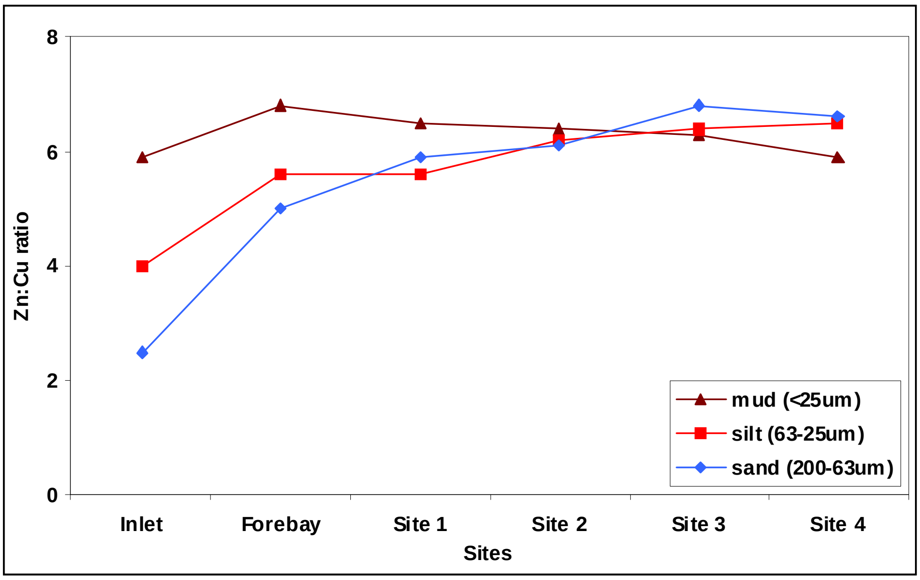


Figure 9 Grafton Road stormwater retention tank sediment analysis: zinc (Zn) to copper (Cu) ratios across the retention tank compartments for three sediment size fractions – sand (200-63µm), silt (63-25 µm) and mud (<25 µm).

2.6 Determining the contribution of road runoff to sediment PAHs

The term ‘modern’ road runoff is used to differentiate from historic road runoff that has been found to contain considerably higher concentrations (i.e. up to 100-times) of PAHs because of the practice of using coal tar binders in road construction. Accordingly, using the ratio of a suitable road runoff ‘marker’ compounds (namely, hopanes) with PAH contaminants, it is possible to estimate the proportion of PAHs in catchment sediments attributable to inputs of road runoff particulates. It is important to emphasise that this method cannot differentiate between highway and non-highway runoff since the differentiation between these roads is state vs. local government management. However, if the relative contribution of state highway runoff to total runoff into a catchment is known, then this can be used to estimate the percentage of sediment PAHs from runoff from state highways. For example, if 80% of the PAHs in catchment sediments were from modern runoff particulates, and if state highway runoff makes up 25% of the stormwater inputs into the receiving environment, then 25% of 80% equates to 20% of PAHs in catchment sediments being due to state highway inputs.

3. Results and Discussion

3.1 Heavy metal sediment concentrations by catchment

This section describes the metal concentrations and ratios in sediments at the sites sampled at the 5 catchments. Zinc and copper concentrations were measured in the mud (<25 µm), silt (25-63 µm) and fine sand (63-200 µm) size fractions. Background concentrations of zinc and copper in natural soils in the Auckland region, that is non-volcanic and volcanic soils, are also shown in the figures (see ARC, 2001; TP153).

3.1.1 Motions

Metal concentrations

The sediment concentrations of zinc and copper for the 3 particle size fractions are shown in Figure 10 and Figure 11, respectively. The median concentration of zinc in the sand, silt and mud fractions was 320, 445 and 350 mg kg^{-1}, respectively. The same trend was observed for copper, with the median concentration for sand, silt and mud fractions being 87, 110 and 80 mg kg^{-1}, respectively.

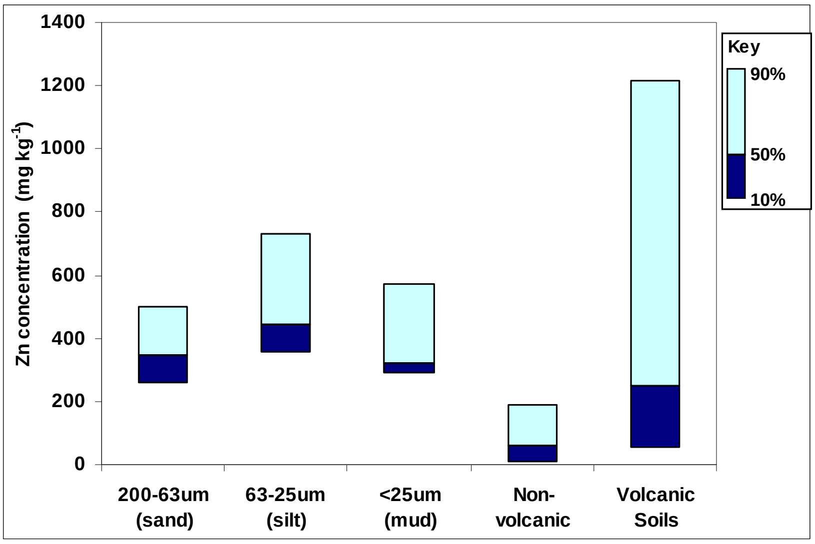


Figure 10 Zinc concentration (mg kg^{-1}) in sediments from Motions catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

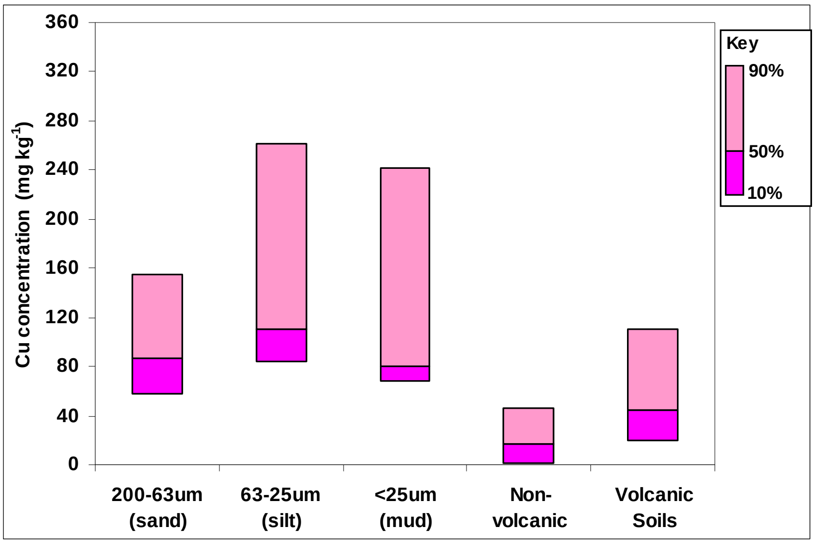


Figure 11 Copper concentration (mg kg^{-1}) in sediments from Motions catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

Zinc:Copper (Zn:Cu) ratios

The zinc to copper ratio (Zn:Cu) in the Motions catchment was constant across the 3 different particle size fractions at the 10 sampled sites, with median Zn:Cu ratios of 4.0, 4.0 and 4.1 for the mud, silt and sand sized fractions, respectively (Figure 12-Figure 13).

All three sediment types show high concentrations in both zinc and copper (Figure 10 and Figure 11, respectively). The Zn:Cu ratio remains relatively constant across locations sampled along the transect from site 4 to site 10, suggesting no spatial heterogeneity in metal contamination along the transect sampled outside the point of immediate discharge (i.e., sites 1-3) (Figure 13).

The Zn:Cu ratio in sediments sampled from this catchment was ~4. This value differs from that of the Grafton SWTD road runoff sediment where the Zn:Cu was found to be ca. 6 (refer to Figure 9), although it was noted that, in the inlet bay, the silt fraction of the Grafton SWTD sediment was closer to 4. The ratio of Zn:Cu in sediments sampled in the Motions catchment is lower than expected. This may be due to other factors, for example, an additional source of copper in the catchment other than from State Highway-only runoff and different chemical fate and behaviour processes from the Grafton Road study.

The latter study typically involved only sedimentation and contaminants binding to road-derived material rather than contaminants moving from source to the discharge point where potentially large amounts of clean sediment (from stream bank erosion) are used to bind dissolved metals to dissolved organic carbon (DOC), or where suspended sediments are entrapped, or where particulate metals are taken up by plants or aquatic animals. Implications regarding sources of heavy metals are discussed in more detail in section 3.3.

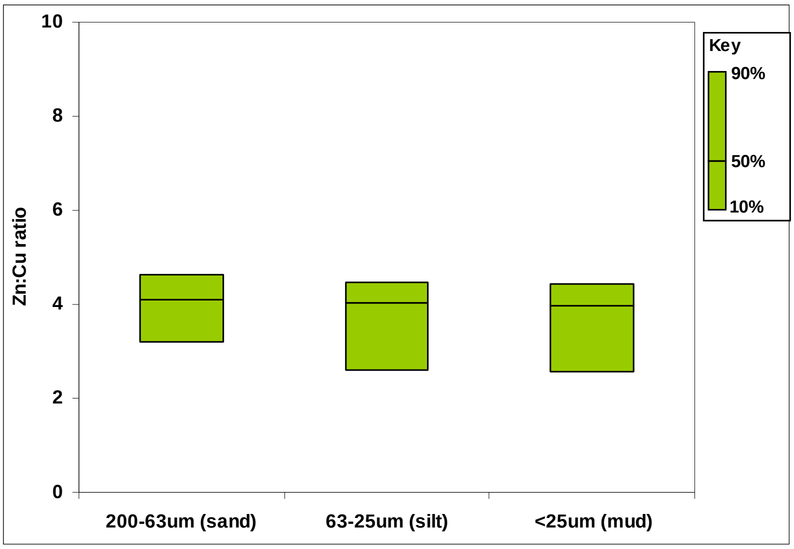


Figure 12 Ratio of zinc (Zn) to copper (Cu) in sediments from Motions catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

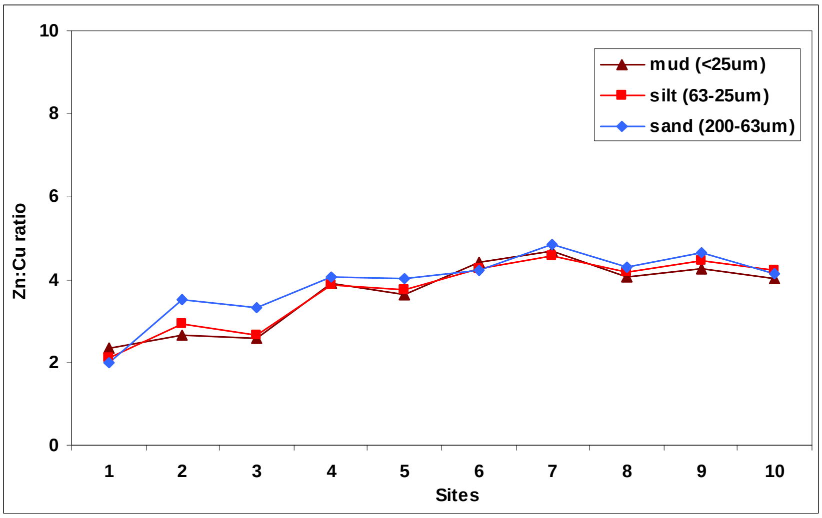


Figure 13 Variation in zinc to copper ratio across transect locations sampled in Motions catchment

3.1.2 Newmarket catchment (Shore Road; SH1)

Sediment concentrations of zinc and copper

The sediment concentrations of zinc and copper for the 3 particle size fractions are shown in Figure 14 and Figure 15, respectively. The median concentration of zinc in the sand, silt and mud fractions was 320, 750 and 700 mg kg^{-1}, respectively. A similar trend was observed for copper; with the median concentration for sand, silt and mud fractions being 115, 225 and 210 mg kg^{-1}, respectively. Highest metal concentrations were present in the finer silt and mud fractions.

Zinc:Copper (Zn:Cu) sediment ratios

The median value of zinc to copper ratio (Zn:Cu) in the Newmarket catchment remains relatively constant across sediments types, with a Zn:Cu ratio of 2.8 in the sand to 3.2 in the silt, and 3.5 in the mud section of the sediments sampled (Figure 16).

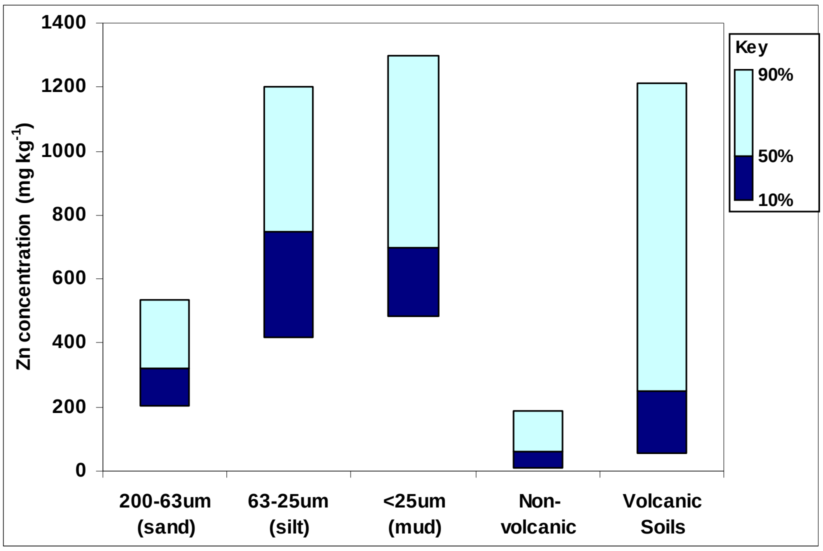


Figure 14 Zinc concentration (mg kg^{-1}) in sediments from Newmarket catchment across all sediment types (sand, silt and mud) showing median, 10% and 90% percentiles.

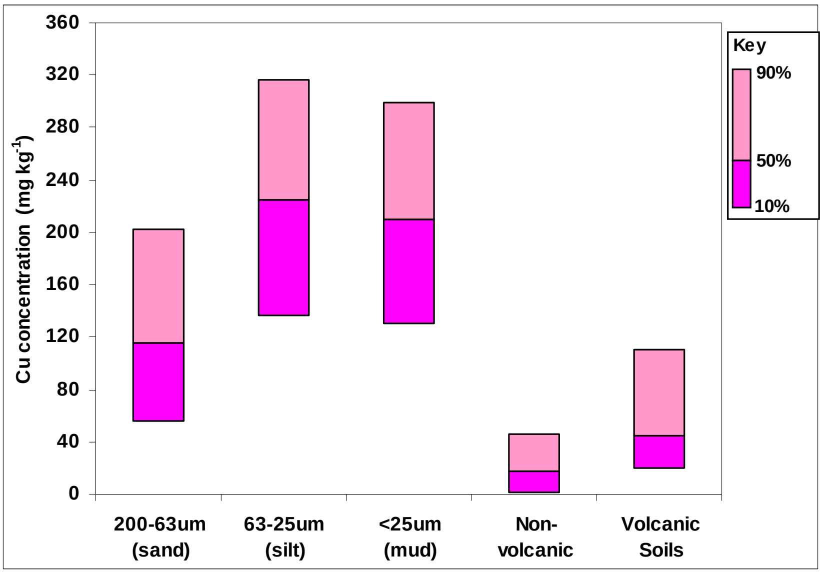


Figure 15 Copper concentration (mg kg^{-1}) in sediments from Newmarket catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

All three sediment types show high concentrations of both zinc and copper, relative to the other sites sampled in this study. Examination of the relationship between zinc and copper concentrations reveals a similar pattern in the variation of both zinc and copper in the silt and mud sections of the sediment (Figure 16). The Zn:Cu ratio remains constant across locations sampled along the transect from site 1 to site 10, suggesting no spatial heterogeneity in metal contamination along the transect sampled from the point of discharge (Figure 17).

The Newmarket Zn:Cu ratio of ca. 3 was half that observed for the Grafton Road SWTD runoff sediment. Similar to Motions, this indicates that there is either more copper than zinc in sediments or just less zinc in sediments from Newmarket than Grafton Road. Potential sources of copper include residential pipes, building material, pesticides, and possibly the sewage network. Implications regarding sources of heavy metals are discussed in more detail in Section 3.3.

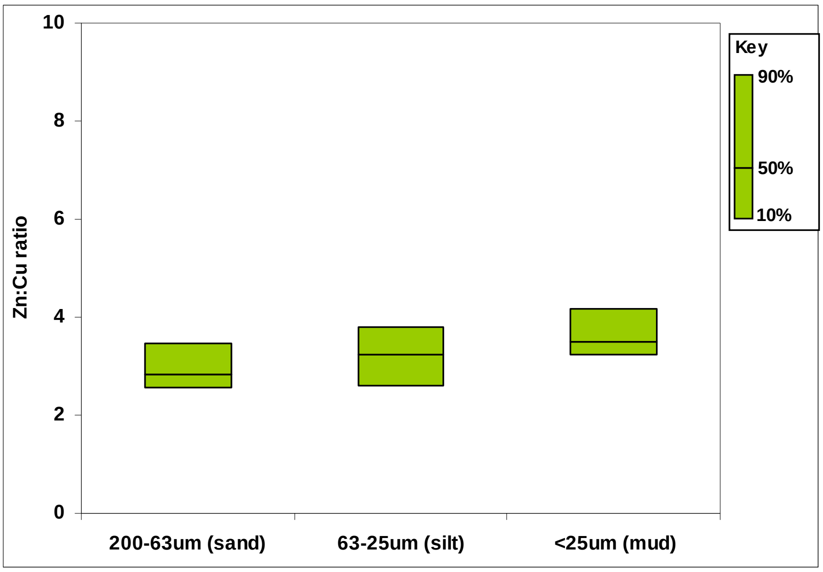


Figure 16 Ratio of zinc to copper in sediments from Newmarket catchment across all sediment types (sand, silt and mud) showing median, 10% and 90% percentiles.

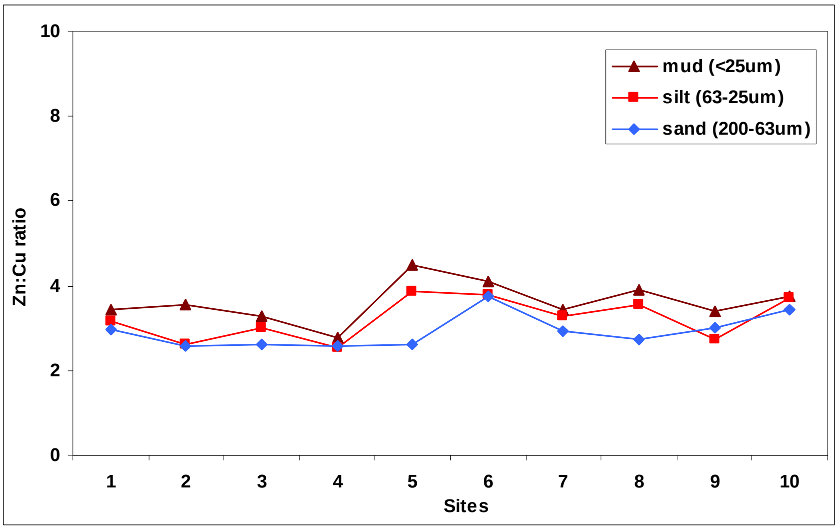


Figure 17 Variation in zinc to copper ratio across transect locations sampled in Newmarket catchment

3.1.3 Onehunga

Sediment concentrations of zinc and copper

The sediment concentrations of zinc and copper for the 3 particle size fractions are shown in Figure 18 and Figure 19, respectively. The median concentration of zinc in the sand, silt and mud fractions was 160, 140 and 170 mg kg^{-1}, respectively. A similar trend was observed for copper; with the median concentration for sand, silt and mud fractions being 26, 22 and 28 mg kg^{-1}, respectively.

All three sediment types show relatively low concentrations of both zinc and copper, and concentrations of zinc and copper are similar in all three particle size fractions of the sediments (Figure 18 & Figure 19, respectively). The results show that there are lower zinc and copper concentrations in sediments from the Onehunga catchment compared to the other catchments studied.

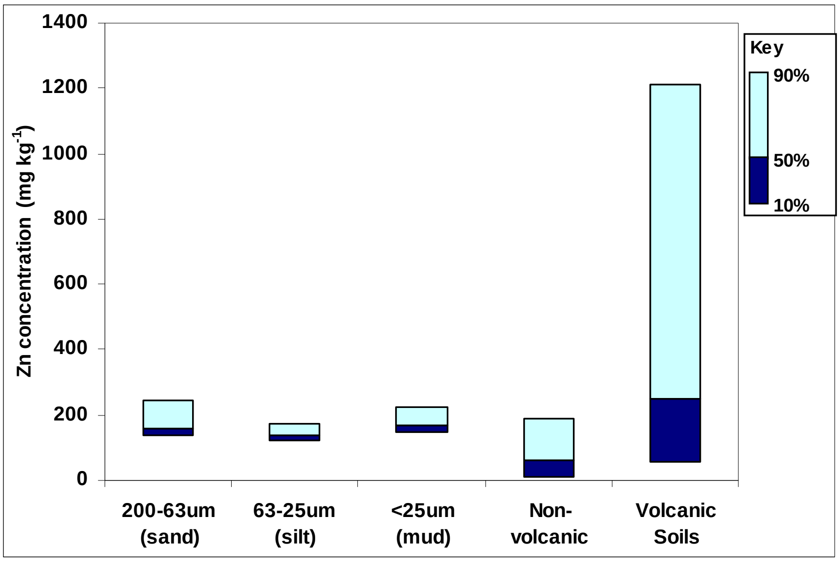


Figure 18 Zinc concentration (mg kg^{-1}) in sediments from of Onehunga catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

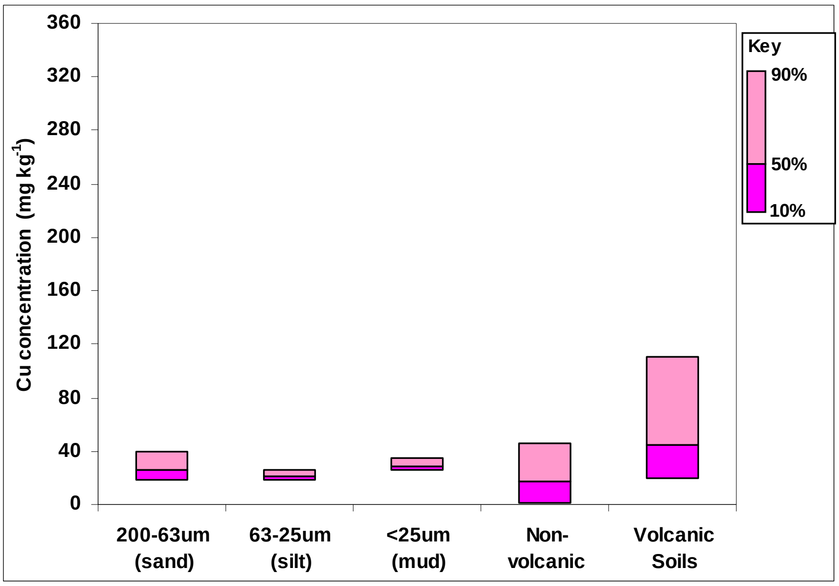


Figure 19 Copper concentration (mg kg^{-1}) in sediments from Onehunga catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

Zinc:Copper (Zn:Cu) sediment ratios

The median value of zinc to copper ratio (Zn:Cu) in the Onehunga catchment remains constant across sediments types, with a Zn:Cu ratio of 6.23 in the mud, 6.51 in the silt and 6.40 in the sand fraction of the sediments sampled (Figure 20).

The Zn:Cu ratio remains constant across locations sampled along the transect from site 1 to site 10, suggesting no spatial heterogeneity in metal contamination along the transect sampled from the point of discharge (Figure 21). This may be in response to the discharge being well-mixed and sediments having similar depositional characteristics.

The ratio of Zn:Cu was around 6 in sediments sampled from this catchment. This ratio matches that of the Grafton Road hypothesis, suggesting that the state highway runoff in the Onehunga catchment is a potentially significant source of the metal contamination found in the sediments. Implications regarding sources of heavy metals are discussed in more detail in Section 3.3.

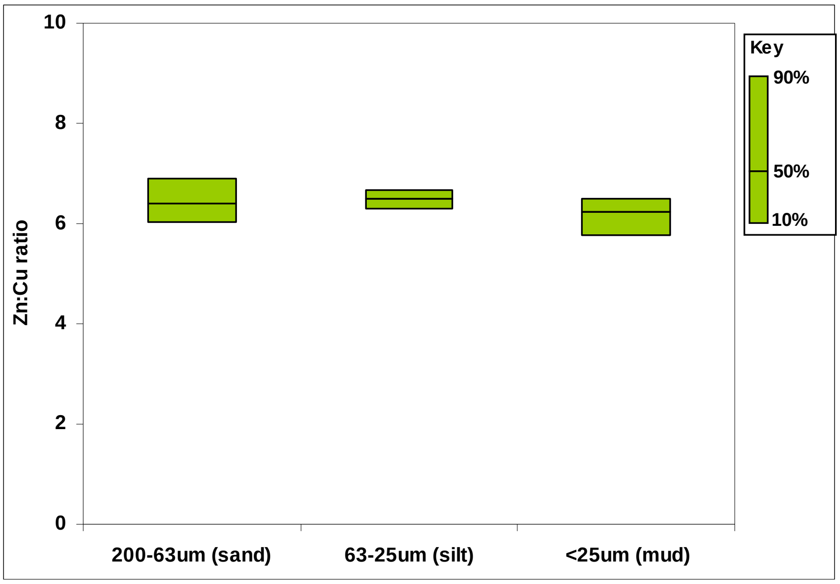


Figure 20 Ratio of zinc (Zn) to copper (Cu) in sediments from Onehunga catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles.

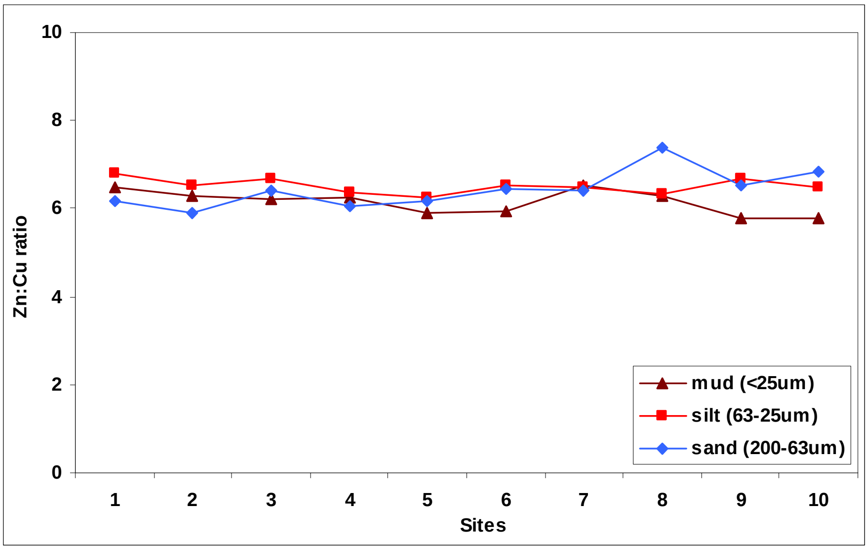


Figure 21 Variation in zinc to copper ratio across transect locations sampled in Onehunga catchment

3.1.4 Paremoremo

The sediment concentrations of zinc and copper for the 3 particle size fractions are shown in Figure 22 and Figure 23, respectively. The median concentration of zinc in the sand, silt and mud fractions was 110, 130 and 120 mg kg^{-1}, respectively. A similar trend was observed for copper; with the median concentration for sand, silt and mud fractions being 22, 24 and 21 mg kg^{-1}, respectively. All three sediment types show relatively low concentrations of both zinc and copper, and concentrations of zinc and copper are both similar in all three fractions of the sediments (Figure 22 & Figure 23, respectively).

Zinc:Copper (Zn:Cu) sediment ratios

The median value of zinc to copper ratio (Zn:Cu) in the Paremoremo catchment remains constant across sediments types, with a Zn:Cu ratio of 5.10 in the sand to 5.40 in the silt, and 5.68 in the mud section of the sediments sampled (Figure 24).

The Zn:Cu ratio remained constant across locations sampled along the transect from site 1 to site 10, suggesting no spatial heterogeneity in metal contamination along the transect sampled from the point of discharge (Figure 25).

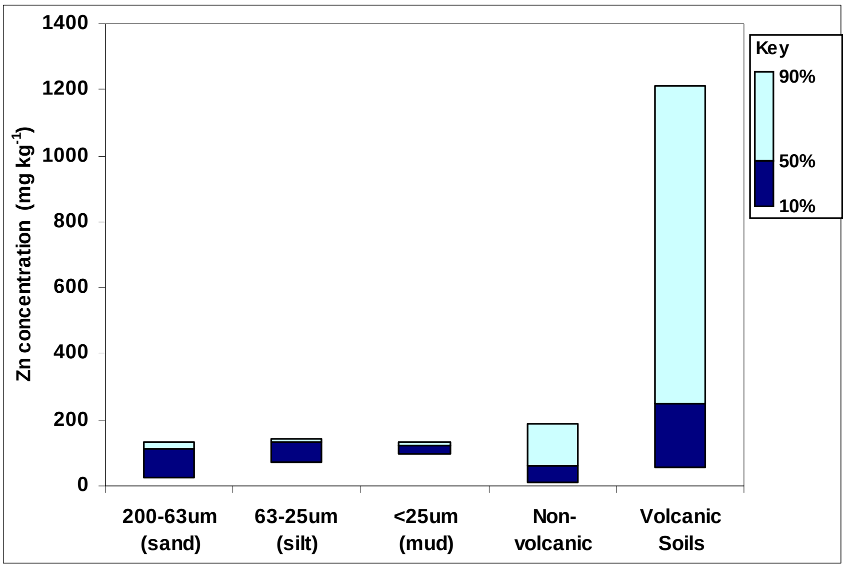


Figure 22 Zinc concentration (mg kg^{-1}) in sediments from Paremoremo catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

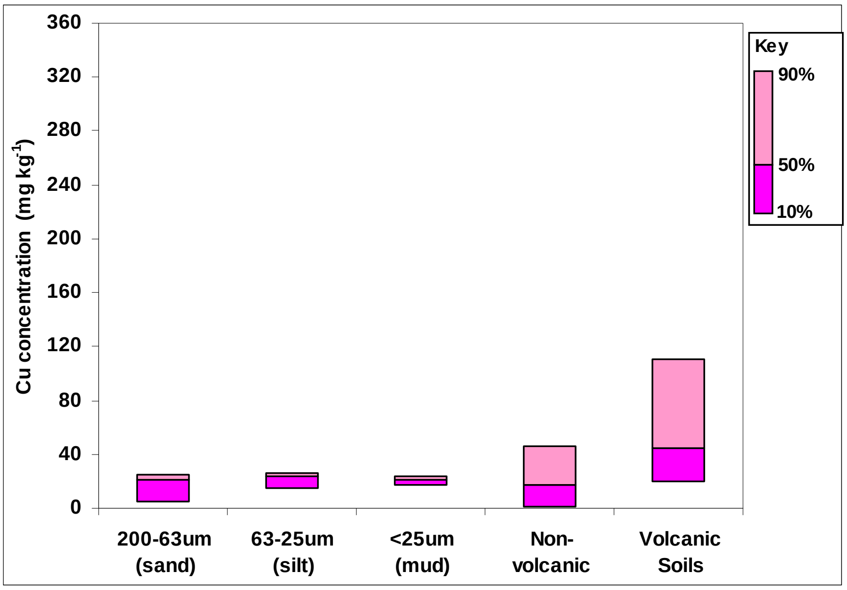


Figure 23 Copper concentration (mg kg^{-1}) in sediments from Paremoremo catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

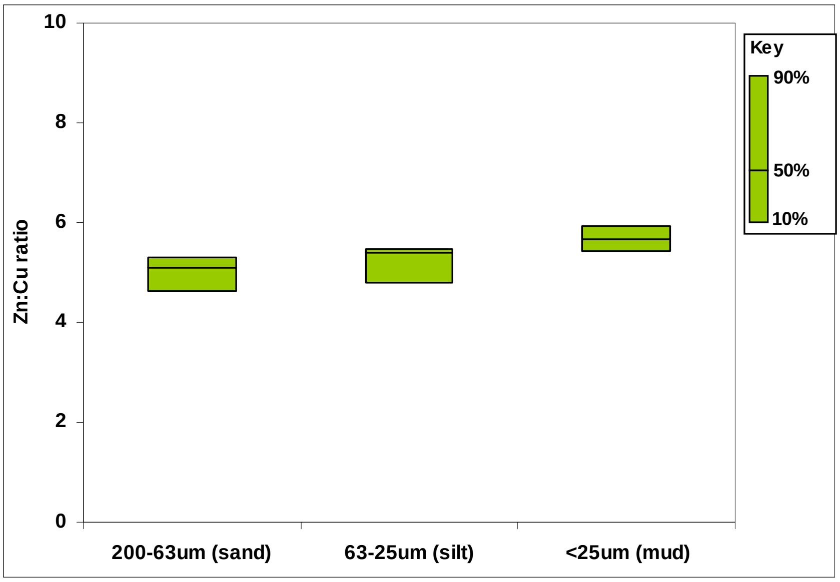


Figure 24 Ratio of zinc (Zn) to copper (Cu) in sediments from Paremoremo catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

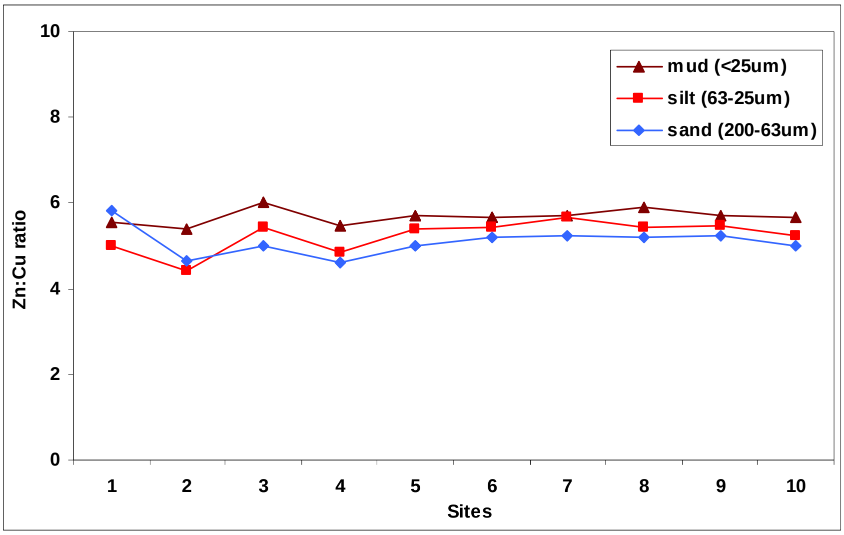


Figure 25 Variation in zinc to copper ratio across transect locations sampled in Paremoremo catchment

The ratio of Zn:Cu was 5.5 in sediments sampled from this catchment. This ratio is close to that of the Grafton Gully SWTD runoff sediments. This indicates that the neighbouring state highway 17 may affect metal contaminants ratios in the catchment. Implications regarding sources of heavy metals are discussed in more detail in Section 3.3.

However, examination of the land use reveals that 96% of the land area in Paremoremo is urban, while the remaining 4% is occupied by State Highways (Fig.12). Estimates of daily traffic intensity suggest a mean value of 427,273 vehicles km travelling (VKTs) each day on State Highway 17 in the Paremoremo catchment (Fig.2). Within the urban area, 61% of the land is occupied by residential area, while 31% is industrial and 4% is commercial (Fig.12). Zinc loads from residential (i.e., roofs and roads) and industrial (i.e., from roofs) areas are likely to influence the effect of State Highway runoff.

3.1.5 Puhinui

Sediment concentrations of zinc and copper

The sediment concentrations of zinc and copper for the 3 particle size fractions are shown in Figure 26 and Figure 27, respectively. The median concentration of zinc in the sand, silt and mud fractions was 230, 650 and 610 mg kg^{-1}, respectively. A similar trend was observed for copper; with the median concentration for sand, silt and mud fractions being 10, 35 and 36 mg kg^{-1}, respectively. Concentrations of both zinc and copper are significantly higher in the silt and mud fractions of the sediments (Figure 26 & Figure 27, respectively).

Zinc:Copper (Zn:Cu) sediment ratios

The median value of zinc to copper ratio (Zn:Cu) in the Puhinui catchment remains constant across sediments types, with a Zn:Cu ratio of 19.87 in the silt, 20.00 in the sand, and 20.71 in the mud section of the sediments sampled (Figure 28).

The Zn:Cu ratio remains constant across most locations sampled along the transect from site 1 to site 10. In one sampled location (location 6), the Zn:Cu ratio increased significantly, suggesting high spatial variability of Zn levels in local volcanic soils. The remaining samples showed similar Zn:Cu ratios, suggesting no spatial heterogeneity in metal contamination along the transect sampled from the point of discharge (Figure 29).

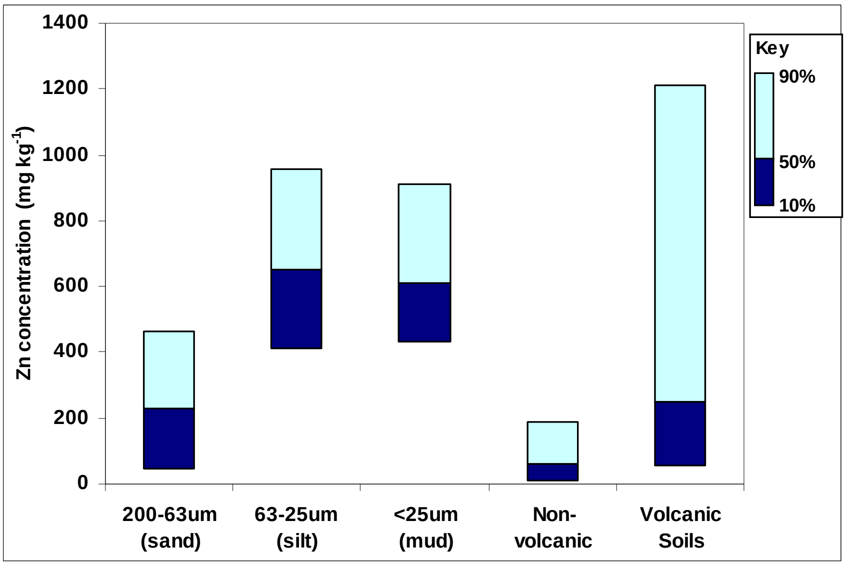


Figure 26 Zinc concentration (mg kg^{-1}) in sediments from Puhinui across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

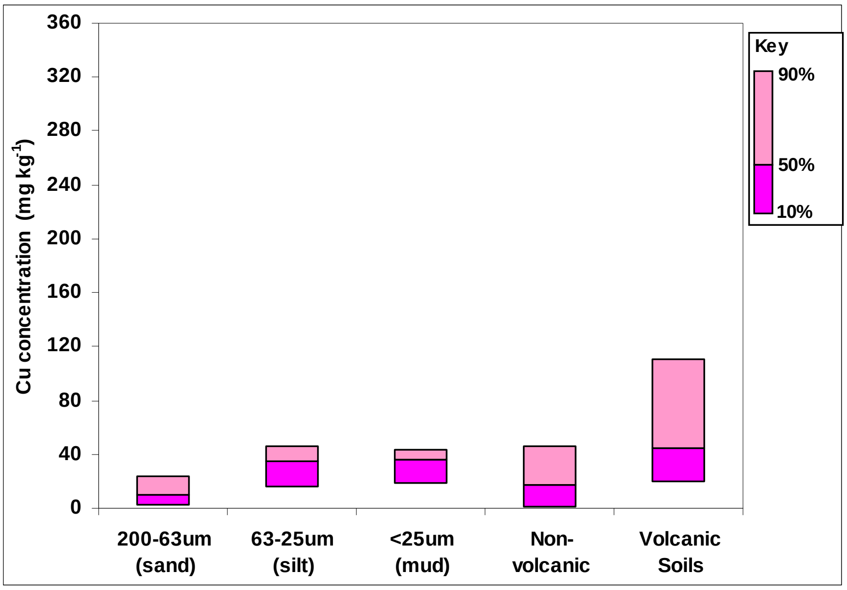


Figure 27 Copper concentration (mg kg^{-1}) in sediments from Puhinui across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

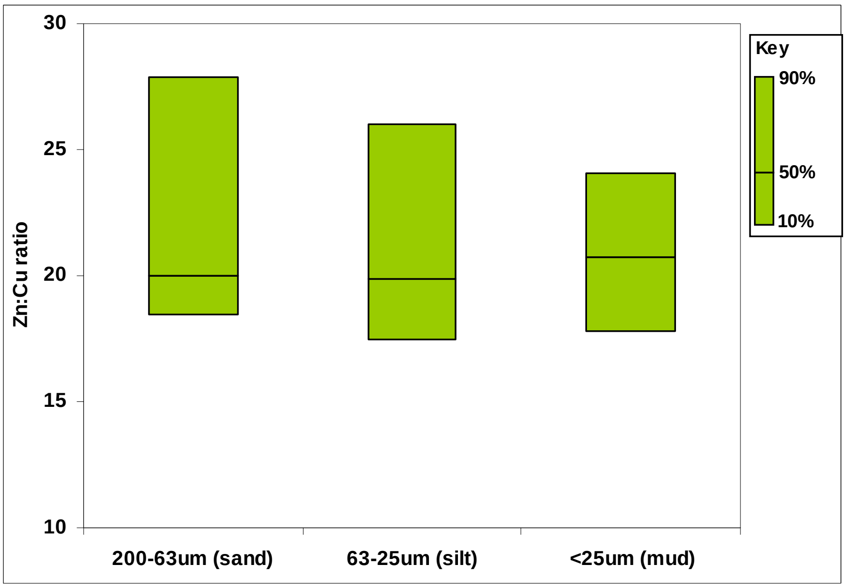


Figure 28 Ratio of zinc (Zn) to copper (Cu) in sediments from Puhinui catchment across all three sediment types (sand, silt and mud) showing median value, 10% and 90% percentiles

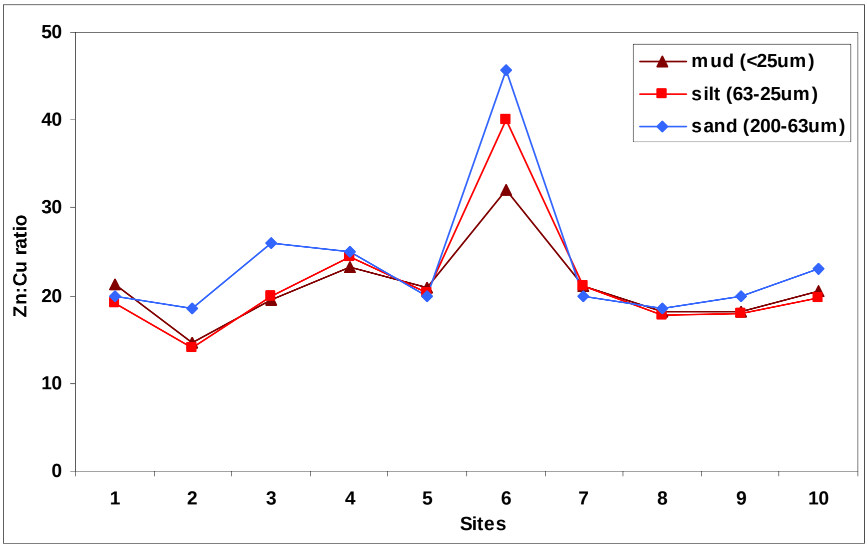


Figure 29 Variation in zinc to copper ratio across transect locations sampled in Puhinui catchment

Results show that sediments contained very high concentrations of zinc in the Puhinui catchment, containing up to ca. 1000 mg kg^{-1}. In contrast, copper concentrations were relatively low, with median values around 27-36 mg kg^{-1}. The ratio of Zn:Cu was 20 in sediments sampled from this catchment. This ratio is three to four-fold higher than in any of the other sample sites, and differs markedly from the Grafton Road study. The high values found for zinc concentration in the Puhinui catchment indicate that zinc levels are responsible for the high Zn:Cu ratio values. This is supported by organic contaminant analyses, which showed the Puhinui sediments contained very low levels of PAHs and TPH, which were in fact consistent with levels in Paremoremo. Therefore, assuming similar sources, it is reasonable to expect that Puhinui sediments would contain comparable concentrations of zinc and copper – which for Paremoremo were ca. 120 mg kg^{-1} and 22 mg kg^{-1}, respectively – however, the median zinc concentration in Puhinui sediments was ca. 5-times higher (ca. 600 mg kg^{-1}) than this. This strongly suggests there is a major source other than road runoff contributing to sediment zinc concentrations in the Puhinui catchment. The Puhinui catchment contains soil derived from volcanic origin (basalt), which may contribute to the high levels of zinc in the area. An estimated median concentration of zinc in volcanic soils was calculated by Auckland regional Council (1991) to be approximately 1,000 mg kg^{-1}.

3.2 Metals: Comparison of catchments

Results of this study show high zinc concentrations in sediments in Newmarket (SH1), Puhinui (SH20) and Motions (SH16) catchments (Figure 30) and high copper concentrations in sediments in Newmarket and Motions (Figure 31). Sediment zinc concentrations ranged from ca. 100 mg kg^{-1} in Paremoremo up to ca. 700 mg kg^{-1} in Newmarket, and the copper concentration ranged from 25 mg kg^{-1} in Paremoremo up to ca. 225 mg kg^{-1} in Newmarket. Typical background concentrations of zinc and copper in soils (non-volcanic) are 35 and 7 mg kg^{-1}, respectively.

The Australia and New Zealand Environment and Conservation Council Interim Sediment Quality Guideline (ANZECC ISQG) values (ANZECC, 2000) are used to assess the degree of potential hazard posed by contaminated sediments. The ANZECC ISQG values are the most appropriate criteria to apply to this study as they are concerned with the biological responses of organisms to contaminants. The guidelines contain two concentrations, the ISQG-Low concentration (or trigger value) and the ISQG-High concentration. The trigger value is a threshold concentration below which the frequency of adverse biological effects is expected to be very low. The ISQG-High concentration is intended to represent a concentration above which biological effects are expected to occur more frequently.

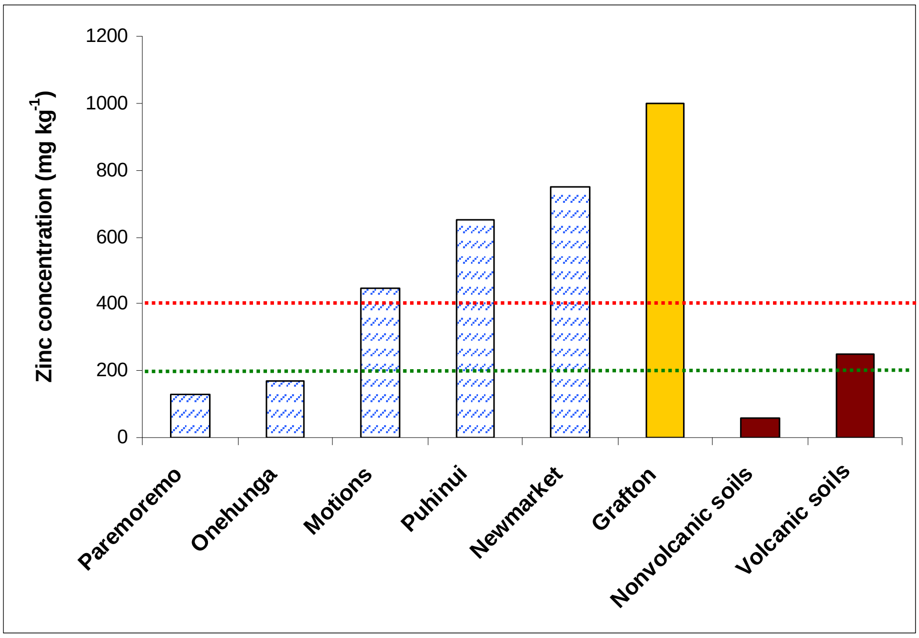


Figure 30 Median zinc concentrations in sediments (<200µm sediment size fraction) sampled from 5 Auckland catchments and at Grafton Road. Green line is ANZECC ISQG-low (200 mg kg^{-1}) and red line is ANZECC ISQG-High (410 mg kg^{-1}).

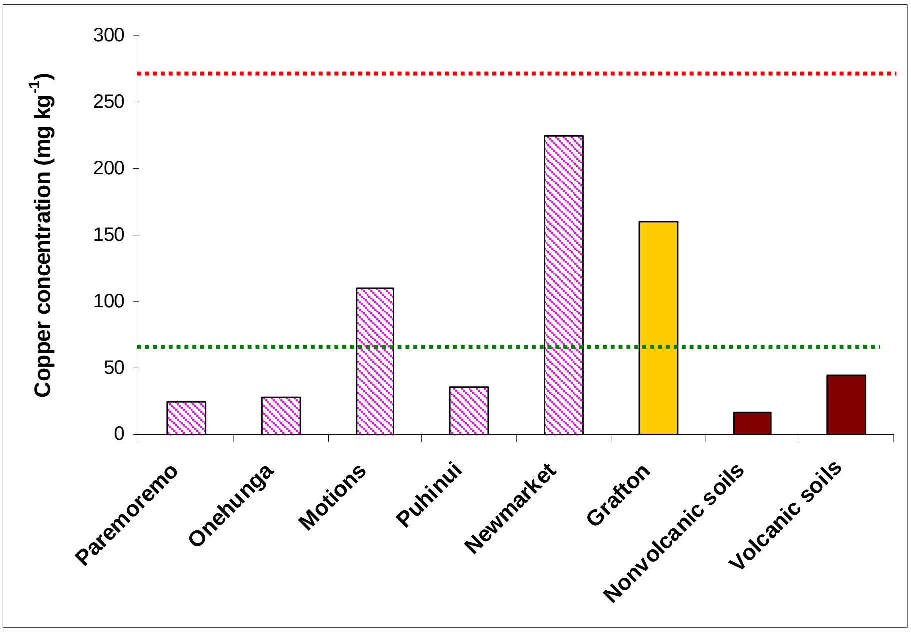


Figure 31 Median copper concentrations in sediments sampled from 5 Auckland catchments and at Grafton Road. Green line is ANZECC ISQG-low (65 mg kg^{-1}) and red line is ANZECC ISQG-High (270 mg kg^{-1}).

3.3 Estimating heavy metal sources from Zn:Cu ratio

3.3.1 Comparison of all catchments

Figure 32 shows average Zn:Cu ratio for the 5 catchments and Grafton Gully. Using the Grafton Gully Zn:Cu ratio as the basis of testing our research question, we can tentatively conclude that Grafton Gully runoff inputs are consistent with being the major input in Paremoremo and Onehunga sediments [ie. within the dashed rectangle which represents the State Highway runoff signature (ie. Zn:Cu ratio of ca. 6) from the Grafton Gully study; Reed (2008)] although a comparison with land-use information will aid this interpretation. The observation of significantly different ratios at Motions, Newmarket (lower) and Puhinui (higher) indicates there are other major ‘non-State Highway runoff’ sources contributing to sediment contaminant loading.

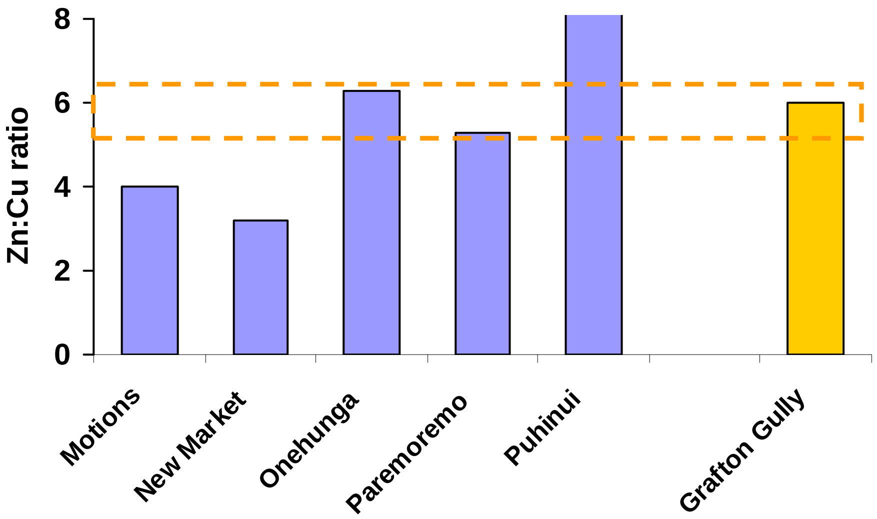


Figure 32 Summary of Zn:Cu ratios for the five study catchments (includes Grafton Gully SWTD sediment - orange bar). Note: the ratio for Puhinui is off-scale (actual value is ca. 20). Area within the dashed rectangle approximates to the Grafton Zn:Cu ratio of ca. 6.

This is consistent with the findings from the PAH contaminant apportionment results discussed in subsequent sections (refer to Figure 58), where road runoff accounted for approximately two-thirds of the PAHs in Paremoremo and Onehunga sediments (based on Grafton Gully values), but <5% for Newmarket and Motions. The unusual result for Puhinui catchment in Figure 32 was also consistent with the PAH apportionment result (refer to Figure 58), with an impossibly high value of 150% being derived for the road runoff contribution to sediment PAHs.

Motions Catchment

High levels of metal contaminants detected in the sediments of the Motions catchment reveal additional sources of contamination other than state highway-only runoff. Examination of land use in the catchment reveals that 11% of the land is occupied by state highways, and the remaining land is urban (comprised of roads, residential areas, commercial areas and industrial areas). Roads occupy 15% of the land, residential areas 53%, commercial areas only 1% and industrial areas 20%, as shown in Figure 33. Estimates of daily traffic intensity suggest a mean of 478,806 vehicles km travelling (VKT) each day on State Highway 16 discharging to the point on Meola Road adjacent to the Motions catchment (Figure 2).

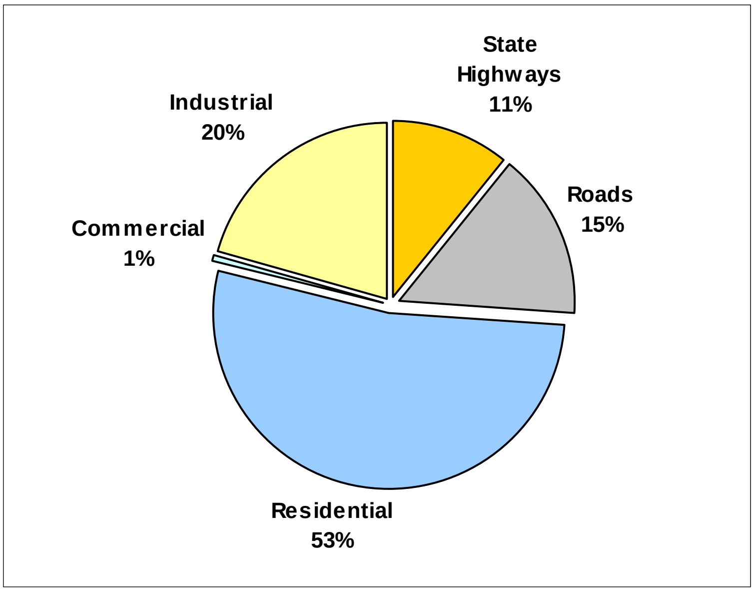


Figure 33 Summary of land-use in the Motions catchment

Results show that the Zn:Cu ratios may be primarily influenced by runoff from residential and industrial areas. These include the effects of roof-runoff from individual houses or industrial lots, and arterial road use in the urban-residential area. Projection (using the Contaminant Load Model or CLM) of the future variation in zinc load over the century from a number of sources, including roofs and roads, predicts that the zinc load originating from roofs will decrease whereas the zinc and copper load coming from road runoff will increase (Timperley, 2008).

Newmarket Catchment

Examination of land use in the Newmarket catchment reveals that nearly all of the land area is urban (roads, residential areas, commercial areas and industrial areas), with only 1% occupied by state highways. Roads occupy 17% of the land, residential areas 64%, commercial areas 4% and industrial areas 14% (Figure 34). Estimates of daily traffic intensity suggest a mean value of 444,885 vehicles km travelling (VKT) each day on State Highway 1 in the Newmarket catchment (Figure 2).

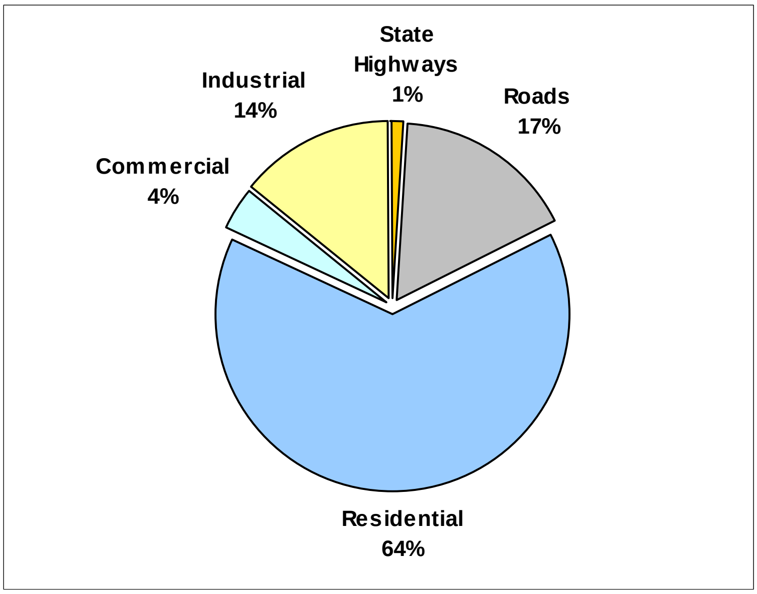


Figure 34 Summary of land-use in the Newmarket catchment

Results show that the Zn and Cu in sediments may result largely from the effect of residential and industrial runoff. Possible sources include roof-runoff (especially from industrial areas) and arterial road use in the urban-residential and urban-industrial areas. Busy arterial roads, like Khyber Pass and Broadway, for example, will have a marked impact on the metal loads in road runoff because vehicles regularly break and accelerate. Research on metal concentrations in road runoff from busy arterial roads is being conducted by Moores *et al.* (2008).

Projections of zinc loads today and in the future from a number of sources, including roofs and roads, suggest that zinc loads will increase over the next century (Timperley, 2008). This suggests that, while the metal contamination in the Newmarket catchment may show an overall decline in the future, the contribution to the contaminant concentration by road-runoff is likely to increase, with an increase in urban road use in the Newmarket catchment.

Onehunga catchment

Sediments sampled from this catchment had a Zn:Cu ratio of 6. This ratio matches that of the Grafton Road SWTD runoff sediment, which suggests that state highway runoff in the Onehunga catchment is a potentially significant source of the metal contamination found in the sediments. Examination of the land use, however, reveals that most of the land area in the Onehunga catchment is urban (roads, residential, commercial and industrial), whilst only 1% is occupied by state highways. Arterial roads comprise 17% of the land and many of these roads are 2-3 dual lanes with heavy trucks breaking and accelerating causing contaminant release to local roads. Residential areas account for 62%, commercial areas 2% and industrial areas 18% (Figure 35). Estimates of daily traffic intensity suggest a mean of 691,419 vehicles km travelling (VKT) each day on State Highway 1 in the Onehunga catchment (Figure 2).

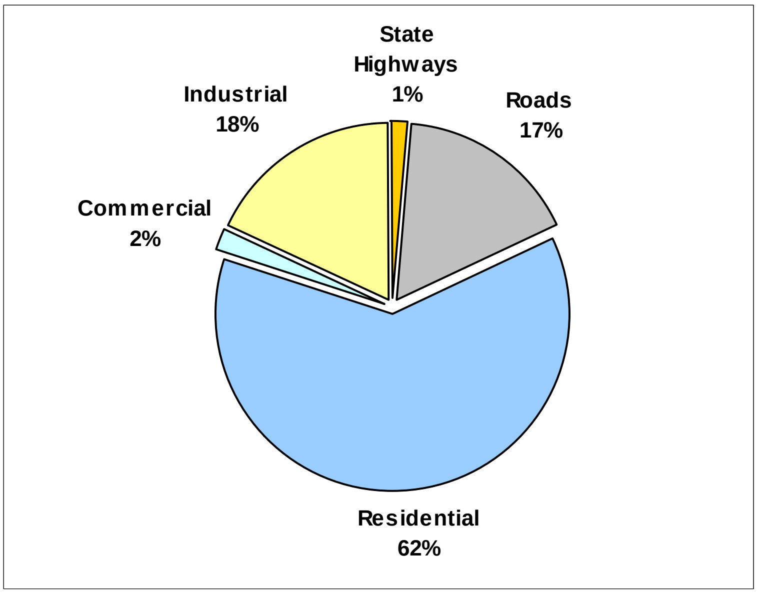


Figure 35 Summary of land-use in the Onehunga catchments

The land use data above suggests that zinc and copper in sediments may result largely from the effect of industrial and residential runoff.

Paremoremo catchment

The Zn:Cu ratio was 5.5 in sediments sampled from this catchment. This ratio is close to that of the Grafton Gully SWTD runoff sediments, indicating that the neighbouring State Highway 17 may significantly affect metal contaminants ratios in the catchment.

Similar to the Onehunga catchment however, land use examination reveals that most of the land is urban (roads, residential areas, commercial areas and industrial areas), with just 4% occupied by state highways. Roads comprise 17% of the land, residential areas 51%, commercial areas 3% and industrial areas 25% (Figure 36). Zinc loads from residential areas (i.e., from roofs and roads) and industrial areas (i.e., from roofs) are likely to markedly influence the effect of state highway runoff. Estimates of daily traffic intensity suggest a mean of 427,273 vehicles km travelling (VKT) each day on State Highway 17 in the Paremoremo catchment (Figure 2).

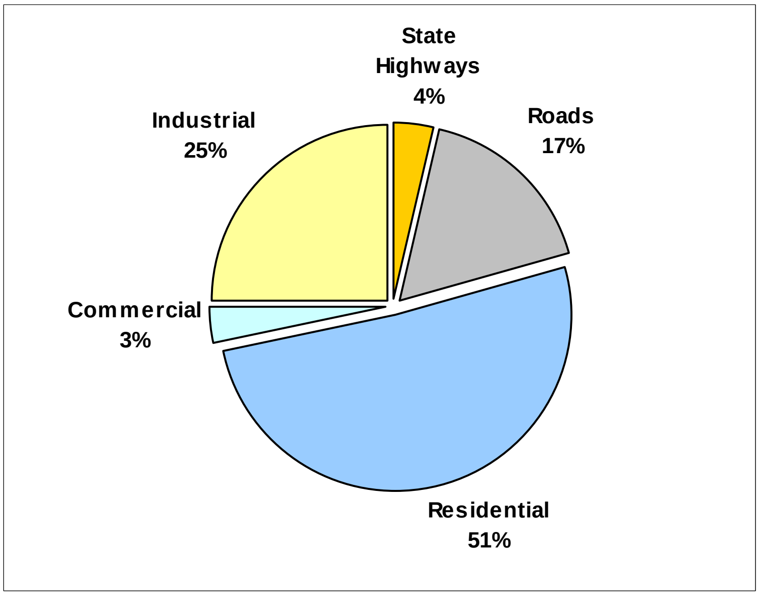


Figure 36 Summary of land-use in the Paremoremo catchments

Puhinui catchment

The very high Zn:Cu ratio in Puhinui sediments (caused by 5-fold higher than expected concentrations of zinc) strongly suggest that a source other than road runoff is responsible for much of the sediment zinc load in the catchment. Once again the majority of land in the catchment is urban (roads, residential areas, commercial areas and industrial areas), with just 3% occupied by state highways. Roads occupy 17% of the land, residential areas 45%, commercial areas 6% and industrial areas 29% (Figure 37). Estimates of daily traffic intensity suggest a mean of 481,231 vehicles km travelling (VKT) each day on State Highway 20 in the Puhinui catchment (Figure 2). Zinc and copper concentrations in this catchment may result largely from the effect of a combination of factors, including the presence of large amounts of volcanic soil, roof and arterial road runoff from residential, commercial and industrial areas, and contaminants from state highway runoff.

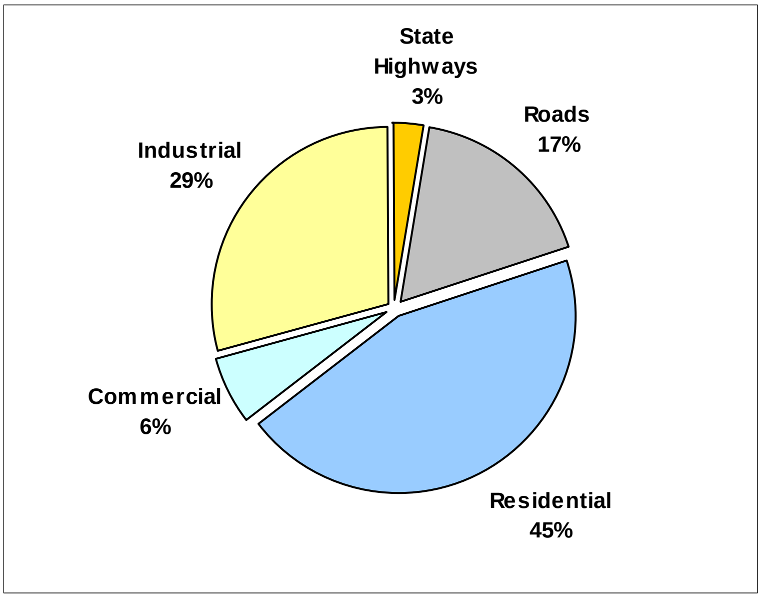


Figure 37 Summary of land-use in the Puhinui catchments

These results suggest that, while state highway runoff is likely to contribute to the contaminant concentrations and ratios in this catchment, it is not the only source and the other sources alluded to above are also likely to be major contributors.

3.4 PAHs and TPH in receiving environment sediments

3.4.1 Concentrations of PAHs and TPH for each catchment

The full analytical laboratory report for catchment sediment samples is provided in Appendix 1, which includes TPH chromatograms. Unless otherwise specified the concentration of PAHs in sediments is the sum of the 16 PAHs listed by the US EPA (Environmental Protection Agency) as priority contaminants, namely; naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i] perylene.

Motions Catchment

The concentration of PAHs at the 10 sampling sites ranged from 8.9 mg kg^{-1} to 162.6 mg kg^{-1}. The median, lower and upper quartile PAH concentrations were 18.8 mg kg^{-1}, 10.1 mg kg^{-1} and 33.0 mg kg^{-1}, respectively (Figure 38). The concentration of

PAHs varied 18-fold along the sampling transect, with the highest concentrations (sites 2 & 3) being located immediately downstream of Meola Rd. The >100 mg kg^{-1} PAH concentrations were considerably higher than the 20-30 mg kg^{-1} reported for Motions Creek sediments (Depree & Ahrens, unpublished) and ca. 10 mg kg^{-1} at the downstream Auckland Regional Council (ARC) sediment monitoring site (Mathieson et al., 2002). Depree and Ahrens have estimated that only 4% of the PAHs in Motions Estuary are attributable to modern road runoff, with the major source being proposed as historic roading coal tar (Depree & Ahrens, 2007).

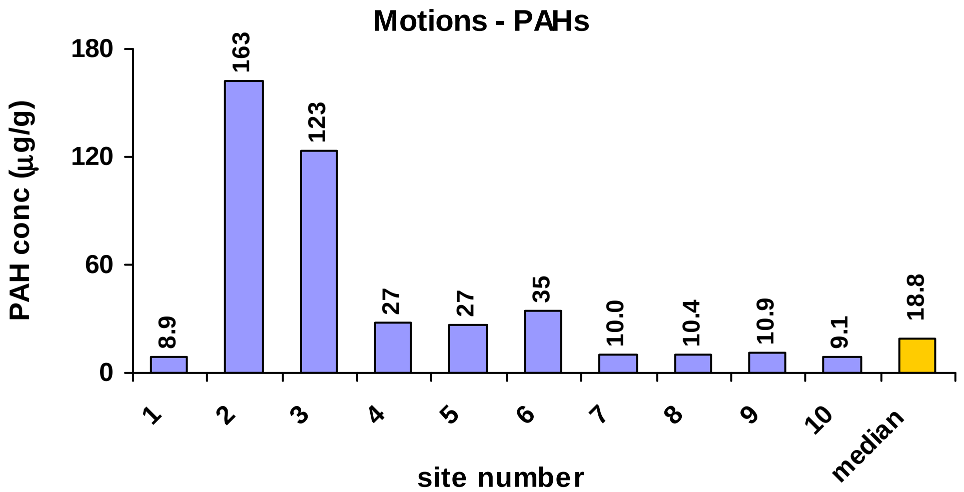


Figure 38 Sediment PAH concentrations for Motions catchment (median shown in orange)

The concentration of TPH in Motions sediments was less variable, ranging ca. 3-fold from 210 mg kg^{-1} to 670 mg kg^{-1}. The median, lower and upper quartile concentrations of TPH were 465 mg kg^{-1}, 358 mg kg^{-1} and 500 mg kg^{-1}, respectively (Figure 39). The dissimilar distribution pattern of TPH and PAHs in Motions sediments indicates either different sources, or environmental fate. Compound classes such as alkanes, which account for a large proportion of the TPH concentration, are much more easily degraded than PAHs – that is, they are less *environmentally persistent*.

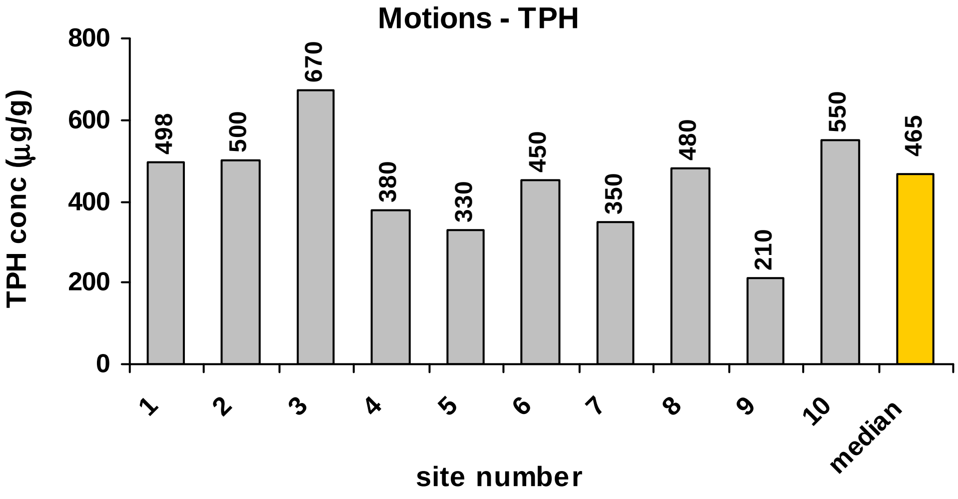


Figure 39 Sediment TPH concentrations for Motions catchment (median shown in orange)

Neither PAHs nor TPH showed any trends moving from upstream (#10) to downstream (#1) sampling sites, although the sampling transect line was relatively short compared to the distance (ca. 1.5 km) to the main stormwater outlet into Motions Creek (located just above the outflow from Western Springs, Figure 40). Furthermore, Motions Creek has, historically, been exposed to large amounts of point source industrial contamination, and the area to the North West of the sampling area used to be a landfill (Figure 40). The highest concentrations of PAHs (sites 2 & 3) were immediately downstream of discharge from Meola Rd bridge, however, because of the relatively low volume of the discharge from these sumps this is unlikely to be the reason for the high PAHs sediment concentrations at these two sites.

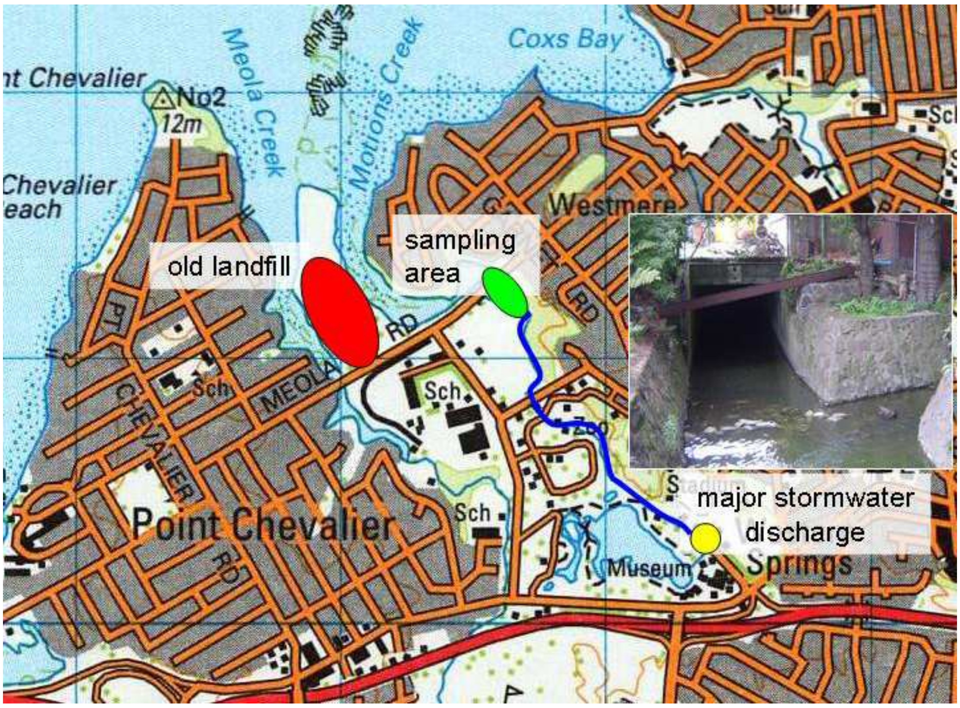


Figure 40 Location of Motions catchment sampling site relative to major stormwater outlet and historic landfill (map from MapToaster Topo). Inset photo shows stormwater box culvert merging with the outflow from Western Springs.

Newmarket catchment

Sediments sampled from Newmarket contained relatively high concentrations of PAHs that varied by a factor of ca. 22 across the 10 sampling locations, ranging from 3.2 mg kg^{-1} to 68 mg kg^{-1}. The median, lower and upper quartile PAH concentrations were 11.7 mg kg^{-1}, 9.2 mg kg^{-1} and 37.8 mg kg^{-1}, respectively (Figure 41). The median concentration of 11.7 mg kg^{-1} was comparable to the ca. 10 mg kg^{-1} of PAHs reported for sediments sampled further upstream in 2006 by the ARC (Depree & Ahrens, 2007). In the same study, the authors estimated that 11% of the PAHs in Newmarket sediments were attributable to modern road runoff.

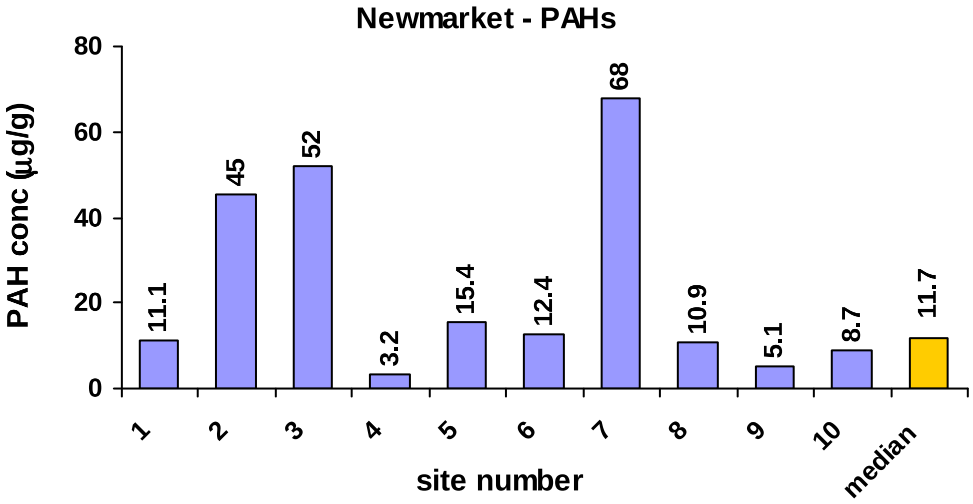


Figure 41 Sediment PAH concentrations for Newmarket catchment (median in orange)

As with the Motions catchment, there was less intra-site variability in the sediment concentration of TPH, which ranged from 190 mg kg^{-1} to 635 mg kg^{-1} – a 3-fold variation compared to the 22-fold observed for PAHs. The median, lower and upper quartile TPH concentrations were 407 mg kg^{-1}, 350 mg kg^{-1} and 535 mg kg^{-1}, respectively (Figure 42).

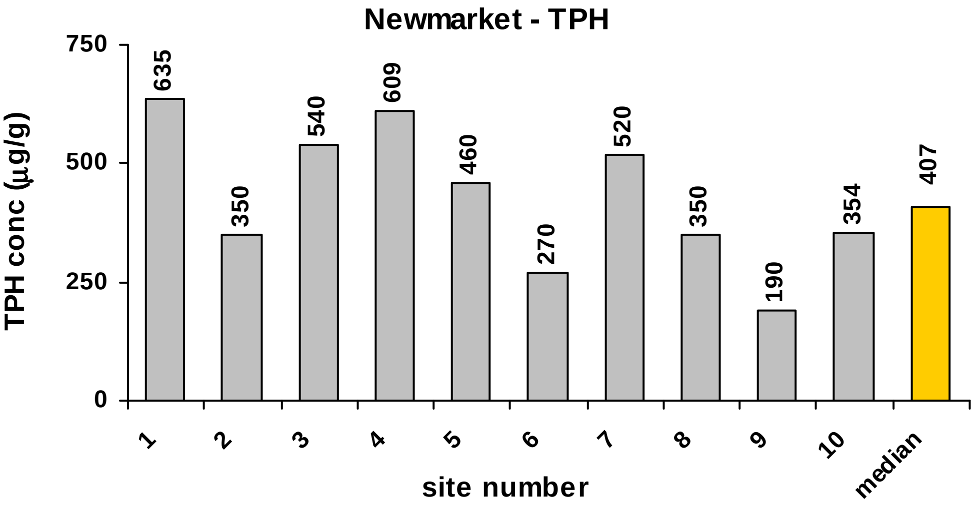


Figure 42 Sediment TPH concentrations for Newmarket catchment (median in orange)

Because the stormwater connectivity, in relation to the sampling area, is not clear, it is difficult to draw any conclusions regarding the presence or absence of any concentration trends. However, assuming the major input of road runoff is upstream of site 1, there was no decreasing trend in sediment contaminant concentrations with distance from the source. This is perhaps not unexpected given the relatively short length of sampling section (ca. 100 m).

Onehunga catchment

In contrast to the Motions and Newmarket catchments, the sediment PAH concentrations were ca. 100-times lower at Onehunga, ranging from <0.1 mg kg^{-1} to 1.0 mg kg^{-1}. The median, lower and upper quartile PAH concentrations were 0.30 mg kg^{-1}, 0.13 mg kg^{-1} and 0.35 mg kg^{-1}, respectively (Figure 43). The median PAH concentration was comparable to ARC sediment monitoring sites at Pakuranga (0.43 mg kg^{-1}), Mangere (0.40 mg kg^{-1}), Pukaki (0.22 mg kg^{-1}), Weiti (0.21 mg kg^{-1}) and Cheltenham (0.19 mg kg^{-1}) – 2001 data (Mathieson et al., 2002).

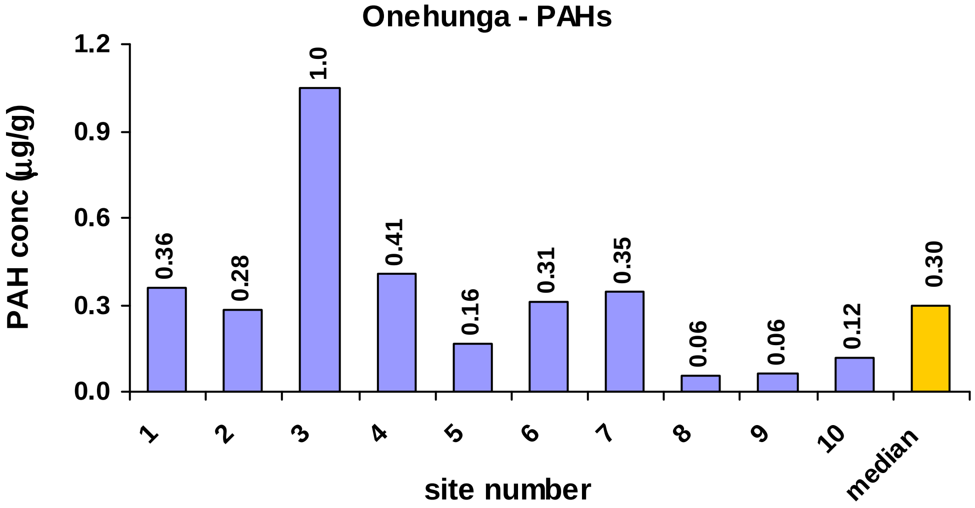


Figure 43 Sediment PAH concentrations for Onehunga catchment (median in orange)

The median concentration of TPH was lower than Motions and Newmarket catchments by a factor of 6-7. The concentrations ranged from below detection limit (ND) to 250 mg kg^{-1}. The median and upper quartile TPH concentrations were ca. 70 mg kg^{-1} and 120 mg kg^{-1}, respectively (Figure 44) – the lower quartile concentration was less than the method detection limit of ca. 30 mg kg^{-1}.

The Onehunga sampling area was a simple ‘end of pipe’ discharge and therefore a dilution gradient was expected over the ca. 100 m long sampling transect. Referring to the sampling site (Figure 5b), the sites can be divided into three groups: ‘near’ sites 1-4 were near the pipe exit; ‘mid’ sites 5-7 were mid-ground; and ‘far’ sites 8-10 were located the furthest from the point of discharge. The mean concentration of PAHs for the 'near', 'mid' and 'far' groups was 0.50 mg kg^{-1}, 0.27 mg kg^{-1} and 0.08 mg kg^{-1}, respectively. A similar decreasing trend was observed for TPH with mean concentrations of 135 mg kg^{-1}, 78 mg kg^{-1} and 'not detected' for the 'near', 'mid' and 'far' sites, respectively.

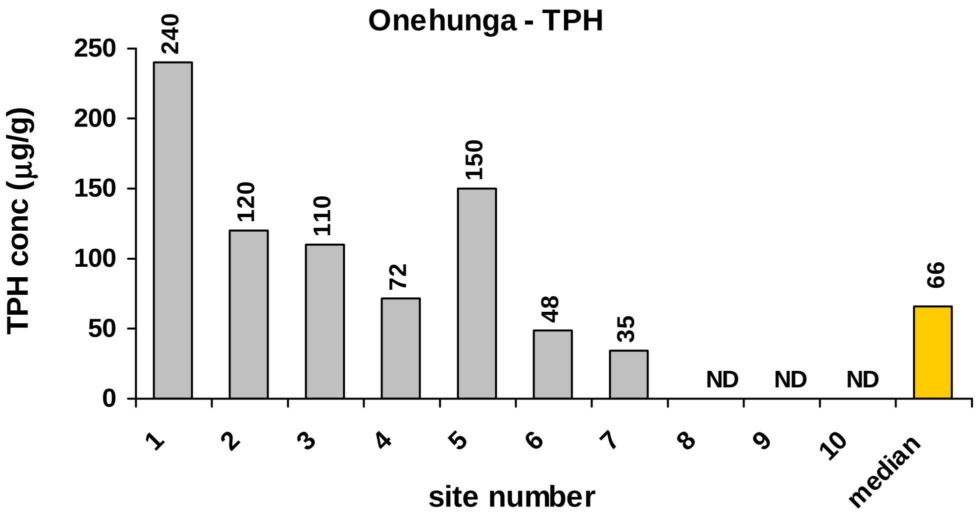


Figure 44 Sediment TPH concentrations for Onehunga catchment (median in orange)

Paremoremo catchment

Like Onehunga, sediments analysed from the Paremoremo catchment contained very low levels of PAHs, ranging from <0.1 mg kg^{-1} to 0.28 mg kg^{-1}. The median, lower and upper quartile PAH concentrations were 0.19 mg kg^{-1}, 0.15 mg kg^{-1} and 0.24 mg kg^{-1}, respectively (Figure 45). With the exception of sites 1 and 2, the sediment concentrations of PAHs along the transect were very similar, differing by only a factor of 2 (i.e. 0.14-0.28 mg kg^{-1}). The median concentration of 0.19 mg kg^{-1} of PAHs was ca. 3-times lower than the Paremoremo ARC sediment monitoring site, which for the years 1998, 1999 and 2001 had respective PAHs concentrations of 0.66 mg kg^{-1}, 0.59 mg kg^{-1} and 0.61 mg kg^{-1} (Mathieson et al., 2002).

With the exception of site 1, the concentration of TPH in sediments was very constant along the sampling transect line, ranging from 50-114 mg kg^{-1}. The reason for the 3-times higher concentration at site 1 (307 mg kg^{-1}) is unclear, especially since this site corresponding to the lowest concentration of PAHs – only 0.04 mg kg^{-1}. The median, lower and upper quartile TPH concentrations were 103 mg kg^{-1}, 91 mg kg^{-1} and 113 mg kg^{-1}, respectively (Figure 46).

As indicated for Newmarket, in the absence of a good understanding of the stormwater connectivity relative to the sampling area, it is difficult to draw any conclusions regarding the fate or dilution of contaminants relative to distance from the discharge point.

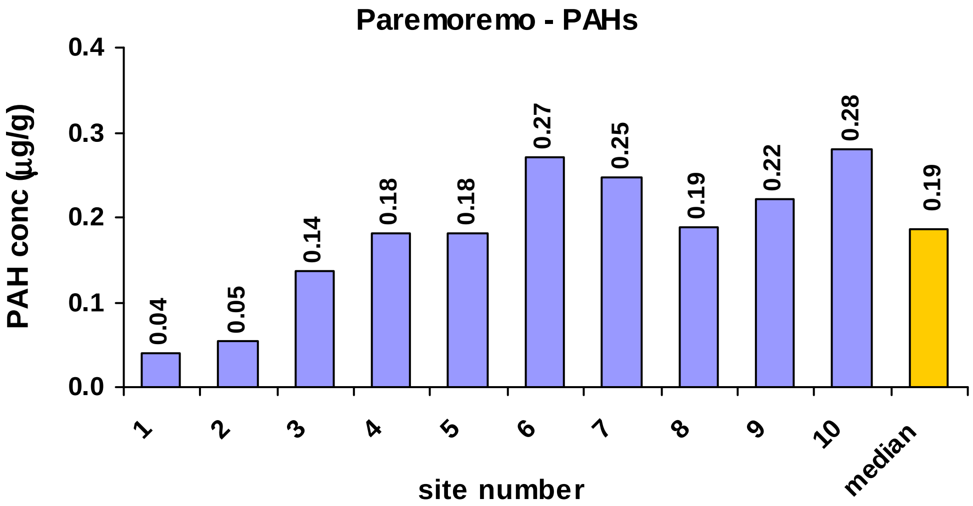


Figure 45 Sediment PAH concentrations for Paremoremo catchment (median in orange)

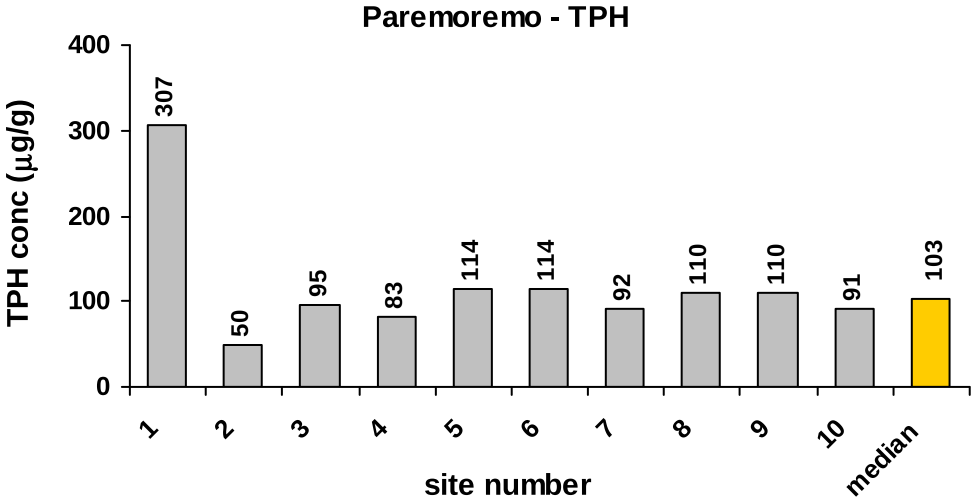


Figure 46 Sediment TPH concentrations for Paremoremo catchment (median in orange)

Puhinui catchment

Sediments from the Puhinui catchment contained the lowest concentrations of PAHs, ranging from 0.01 mg kg^{-1} to 0.24 mg kg^{-1}. Excluding site 6, the concentrations of PAHs were relatively constant between sites closest and furthest from the stormwater discharge point (sites 1 and 10, respectively – refer to Figure 7a), varying only by a factor of 2-3. The median, lower and upper quartile PAH concentrations were 0.13 mg kg^{-1}, 0.10 mg kg^{-1} and 0.21 mg kg^{-1}, respectively (Figure 47). Puhinui catchment is one of the 27 ARC estuarine sediment monitoring sites – previous concentrations of 0.15-0.21 mg kg^{-1} are consistent with the median and range of concentrations reported in Figure 47 (Mathieson et al. 2002).

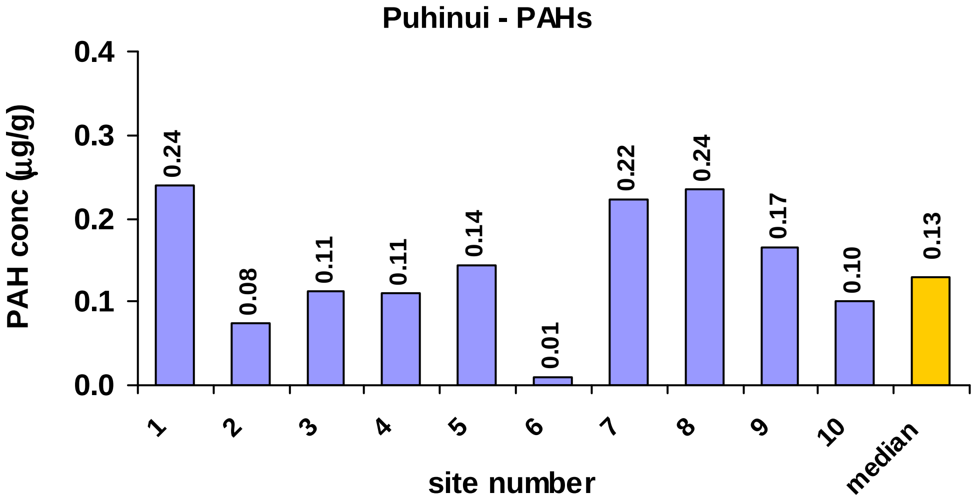


Figure 47 Sediment PAH concentrations for Puhinui catchment (median in orange)

The concentrations of TPH were highly variable, ranging from below detection limit to 500 mg kg^{-1}. The median and upper quartile concentrations were 71 mg kg^{-1} and 158 mg kg^{-1}, respectively (Figure 48) – the low quartile concentration was below the detection limit. The relatively high TPH concentration at site 7 did not correspond to an increased concentration of PAHs (Figure 47). Neither the PAH nor the TPH concentrations showed a decreasing trend between sites 1 and 10, although this is expected given the relatively short distance between sites 1-10 compared to the distance from the main stormwater discharge pipe.

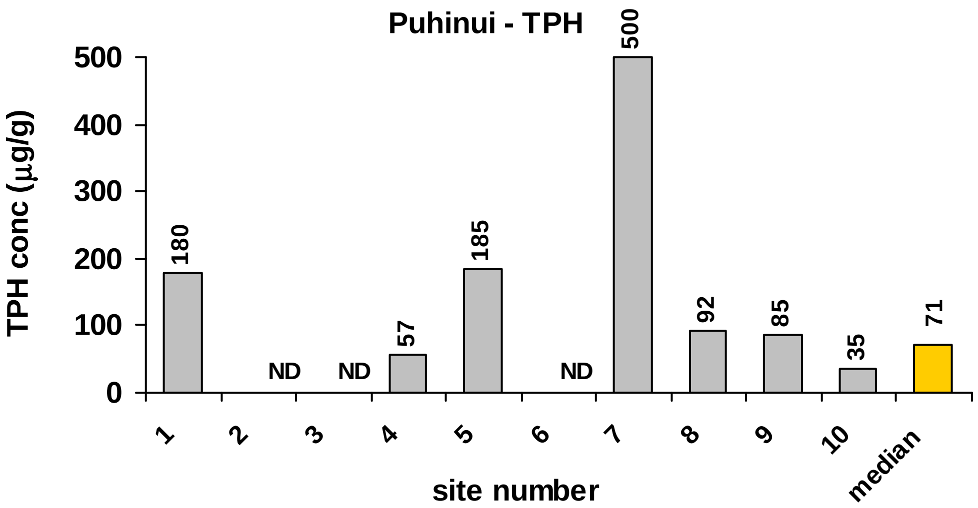


Figure 48 Sediment TPH concentrations for Puhinui catchment (median in orange)

3.4.2 Comparison of catchments: PAHs and TPH

Polycyclic aromatic hydrocarbons (PAHs)

The median sediment PAH concentrations for each of the five catchments ranged from 0.13 mg kg^{-1} for Puhinui, to 18.8 mg kg^{-1} for Motions (Figure 49). The five catchments fell into 2 distinct groups, those with elevated PAH concentrations (i.e. >10 mg kg^{-1}), namely Motions and Newmarket; and those with very low levels (i.e. <1 mg kg^{-1}), namely Onehunga, Paremoremo and Puhinui. Individual sediment PAH concentrations along the transect line at Onehunga, Paremoremo and Puhinui were reasonably constant, but there was considerable variation in concentrations at Motions and Newmarket. (evident from the large inter-quartile ranges; Figure 49).

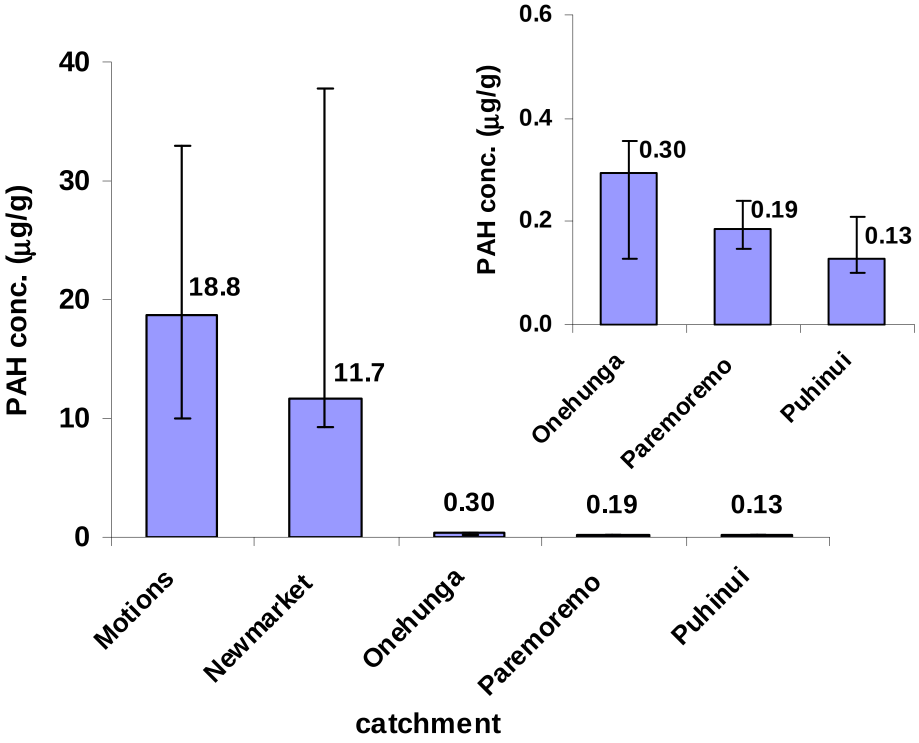


Figure 49 Median (n=10) concentrations of sediment PAH concentrations for each the five catchments. The 'error bars' represent upper and lower quartile concentrations. Inset shows detail of the 3 catchments containing low PAH concentrations (<1 mg kg^{-1})

To provide some context for the PAH concentrations presented in Figure 49, the PAH data for the 2001 ARC sediment monitoring programme (27 sites) are summarised in Figure 50 (Mathieson et al., 2002). Relative to the monitoring sites of Auckland urbanised estuaries, the concentrations of sediment PAHs reported in this study (i.e. Figure 49) were regarded as very high for Motions and Newmarket, and low for Onehunga, Paremoremo and Puhinui catchments. Sediments from reference or pristine catchments contained <0.03 mg kg^{-1} of PAHs.

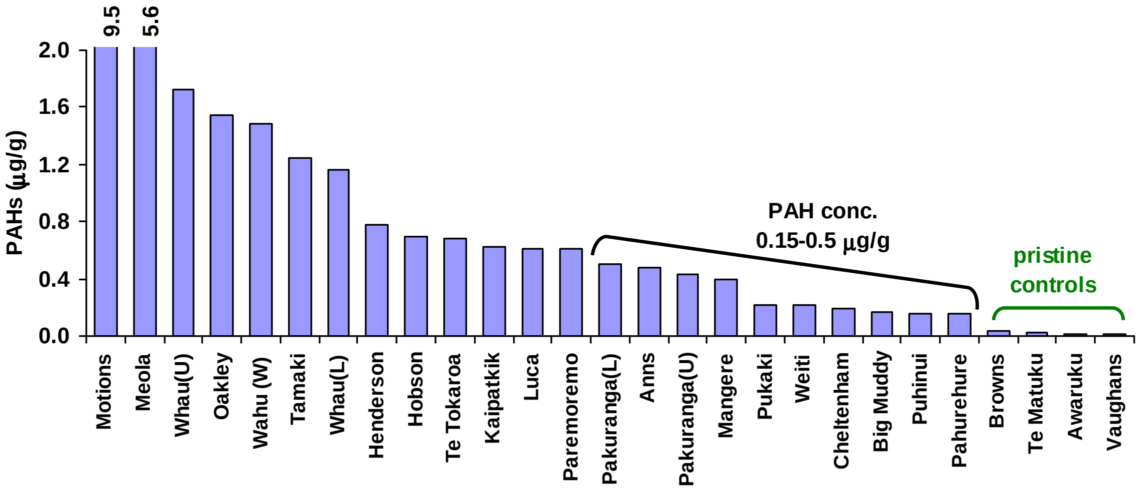


Figure 50 PAH concentrations (2001) for the 27 ARC sediment monitoring sites (Mathieson et al. 2002).

Total petroleum hydrocarbons (TPH)

The median sediment concentrations of TPH showed a similar trend to PAHs (Figure 51) with Motions and Newmarket catchments containing significantly higher concentrations (>400 mg kg^{-1}) than Onehunga, Paremoremo and Puhinui catchments (<100 mg kg^{-1}). The distribution of TPH in sediments sampled along the transect line for each catchment was less varied than for PAHs. The relatively large inter-quartile range of TPH for Onehunga and Puhinui catchments (Figure 51) was a function of many of the individual sediments having concentrations less than the method detection limit.

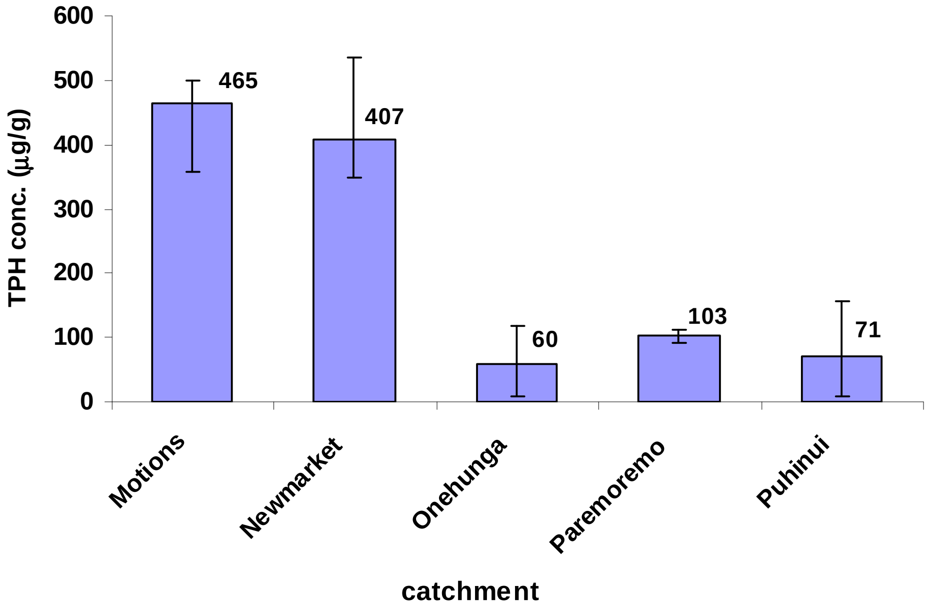


Figure 51 Median (n=10) concentrations of sediment TPH concentrations for each the five catchments. The 'error bars' represent upper and lower quartile concentrations.

3.4.3 Comparison with relevant sediment quality guidelines

The two relevant sediment quality criteria are the ANZECC (2000) quality guidelines and ARC's Environmental Response Criteria (ERC), which are summarised in Table 1. Based on the ANZECC guidelines for the 16 'priority' PAHs, sediments from Motions and Newmarket (Figure 52) have levels of PAHs that exceed the low trigger level (or 'threshold effects level' – TEL), but are below (75th percentile concentration) the high trigger value, which represents the 'probable effects level' (PEL). The median concentrations of sediments from Onehunga, Paremoremo and Puhinui were more than 10-times lower than the ANZECC low trigger value.

Table 1 Summary of ANZECC (2000) guidelines and ARC's Environmental Response Criteria (ERC)

Guideline value	Sum of 16 EPA 'priority' PAHs (mg kg^{-1})	Sum of 6 high molecular weight PAHs (mg kg^{-1})[a]
ANZECC 'LOW'	4	1.7
ANZECC 'HIGH'	45	9.6
ARC ERC 'RED'	-	1.7

[a] Sum of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[a]pyrene and dibenz[a,h]anthracene

However, based on the sum of the concentration of 6 high molecular weight PAHs (abbreviated as Σ_6PAH), the median and upper quartile concentrations of Motions and Newmarket, respectively, exceed the ANZECC high level (Figure 53). However, it must be emphasised that this comparison is based on dry weight concentrations that have not been normalised to 1% organic carbon.

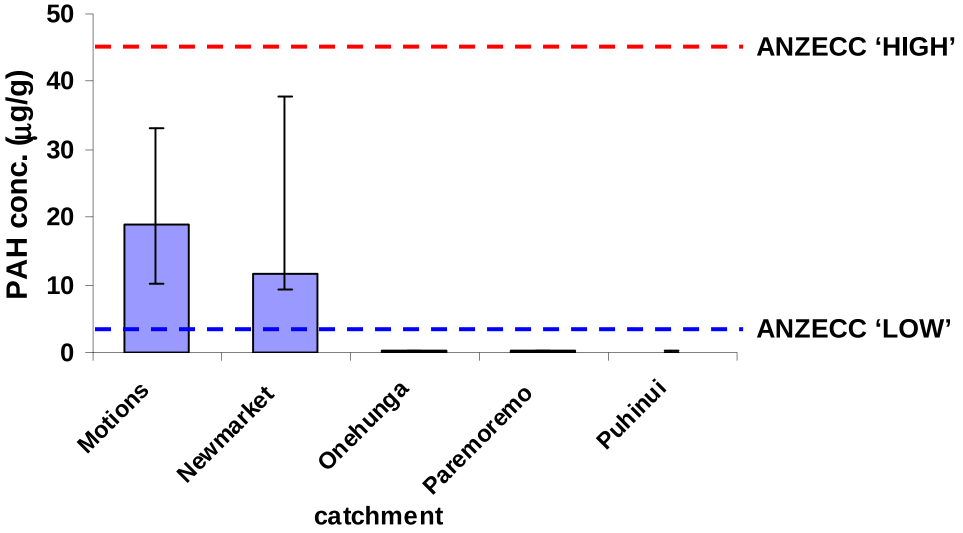


Figure 52 Comparison of sediment PAHs with ANZECC (2000) sediment quality guidelines (sum of 16 US EPA priority PAHs)

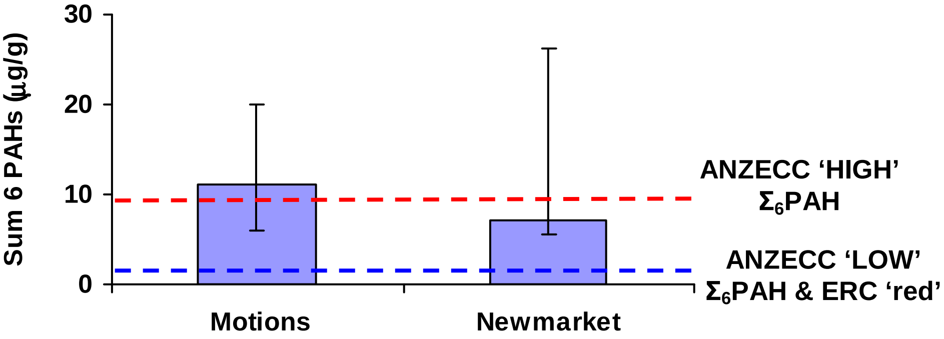


Figure 53 Comparison of Motions and Newmarket sediment Σ_6PAH concentrations with guideline values

3.4.4 PAH and TPH concentrations in road-derived sediments (RDS)

In heavily trafficked catchments, road runoff particulate material is generally considered to be the major source of sediment PAHs. To provide an indication of potential contaminants levels in this 'source' material, 11 previously collected Auckland and Hamilton road-derived sediments (Depree 2008) were re-analysed (<2mm fraction) for PAHs and TPH (refer to Appendix 2 for full laboratory data report). The median, lower and upper quartile concentrations of PAHs in the road-derived sediments (RDS) were 4.6 mg kg^{-1}, 3.9 mg kg^{-1} and 5.7 mg kg^{-1}, respectively (Figure 54). For TPH, the median, lower and upper quartile concentrations were 1300 mg kg^{-1}, 905 mg kg^{-1} and 2300 mg kg^{-1}, respectively (Figure 55).

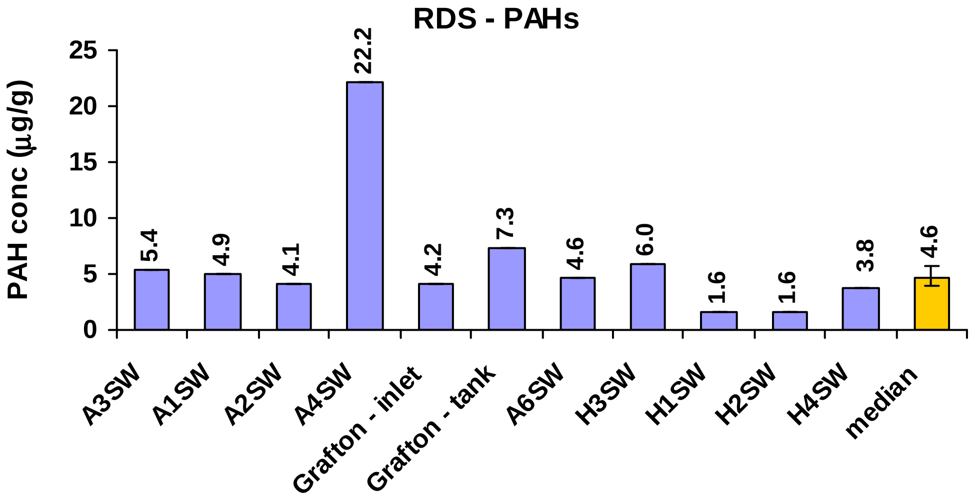


Figure 54 Concentration of PAHs in RDS collected from Auckland and Hamilton (descriptions of the RDS samples are provided in Depree 2008)

It is apparent from Figure 54 that RDS, a major source of PAHs in urban sediment, contains ca. 5 mg kg^{-1} of PAHs. The noticeably higher concentration (22 mg kg^{-1}) in sample 'A4SW' is presumably caused by inputs of coal tar (Depree 2008), which are not considered representative of 'modern' road runoff since roads are now made exclusively from bituminous binders. Assuming that 5 mg kg^{-1} is representative of the PAH concentration in road runoff particulates that are deposited in receiving environment sediment, then we can propose the following:

- modern road runoff cannot account for the level of PAHs in Motions and Newmarket sediments;

- modern runoff can readily account for the PAHs in sediments from Onehunga, Paremoremo and Puhinui catchments. On average the RDS would need to be diluted (with clean sediment) by a factor of 15-30 in order to result in the observed 0.15-0.30 mg kg^{-1} concentrations.

Based on the median concentration of TPH in RDS, a dilution factor of ca. 13-16 would be needed to produce the 60-100 mg kg^{-1} of TPH detected in Onehunga, Paremoremo and Puhinui sediments. However, less emphasis should be placed on TPH comparisons between 'source' and 'sink' because (i) many TPH components are susceptible to rapid degradation and (ii) unlike PAHs, not all sources of TPH are anthropogenic – plant wax hydrocarbons can contribute significantly to the TPH total. For these reasons more petroleum specific and refractory (environmentally persistent) petroleum molecular markers, such as hopanes, are often employed.

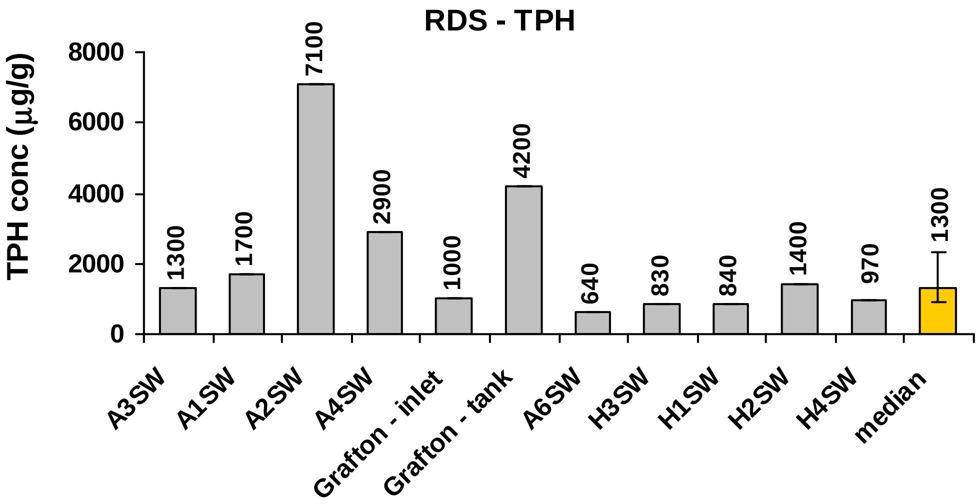
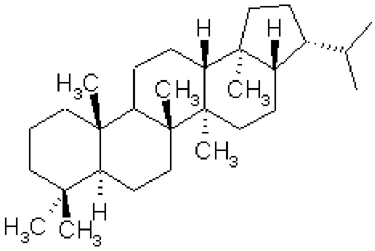


Figure 55 Concentration of TPH in RDS collected from Auckland and Hamilton (descriptions of the RDS samples are provided in Depree 2008)

3.4.5 Determining the contribution of PAHs in catchment sediments from modern road runoff

Depree and Ahrens (2007) have estimated the contribution of modern road runoff to urban stream and estuarine sediments in Auckland. The method used involved measuring the concentration of compounds called hopanes which are very stable organic compounds present in relatively high concentrations in crude petroleum, and concentrated in high-boiling fractions/residues (e.g. bitumen). The hopane quantified in this study was C_{30} 17α(H),21β (H)-hopane (structure shown below).



Because coal tar and other atmospheric sources are potentially important sources of PAHs in receiving environment sediment, the advantage of hopanes is that because they are derived from bacterial sterols, they are not present in significant concentrations in pyrogenic source materials such as soot and coal tar. Therefore, assuming that the only source of hopanes in catchment sediments is derived from road runoff, the contribution of road runoff to sediment PAHs can be estimated from the hopane:PAH ratio in modern runoff. This in-turn requires that the hopane:PAH ratio used is representative of the road runoff particulates being deposited in a particular receiving environment. Depree and Ahrens (2007) made use of a single RDS sample collected from a Grafton Gully stormwater treatment device (SWTD) – the largest stormwater settling tank in NZ. In this study, 11 RDS sediments (including Grafton Gully) were included to determine how much variability there was in the hopane:PAH ratio in modern RDS.

Concentration of hopane in catchment sediments and RDS

Note: hopane concentrations are presented as µg kg^{-1}

The concentration of hopane in sediments varied by a factor of ca. 3 across the five catchments, ranging from 60 µg kg^{-1} at Paremoremo to 203 µg kg^{-1} at Motions (Figure 56). Assuming the hopanes are a proxy for road runoff inputs to sediments, the lower variation in hopane concentrations suggests that although PAHs are ca. 100-times higher at Motions and Newmarket, the inputs of road runoff particulates may be only 2-3-times higher at these sites. It is noted, however, that this simple ‘approximation’ ignores differences in the relative loads of ‘clean’ diluting sediment being deposited.

The concentration of hopane in RDS sediments ranged from 90-340 µg kg^{-1} with median, lower and upper quartile concentrations of 1420 µg kg^{-1}, 1170 µg kg^{-1} and 1540 µg kg^{-1} (Figure 57). Based on the median hopane concentration, road runoff particulates would need to be diluted (i.e. with clean sediment) by a factor of ca. 7 at Motions and Newmarket, and 15-20-fold at Onehunga, Paremoremo and Puhinui.

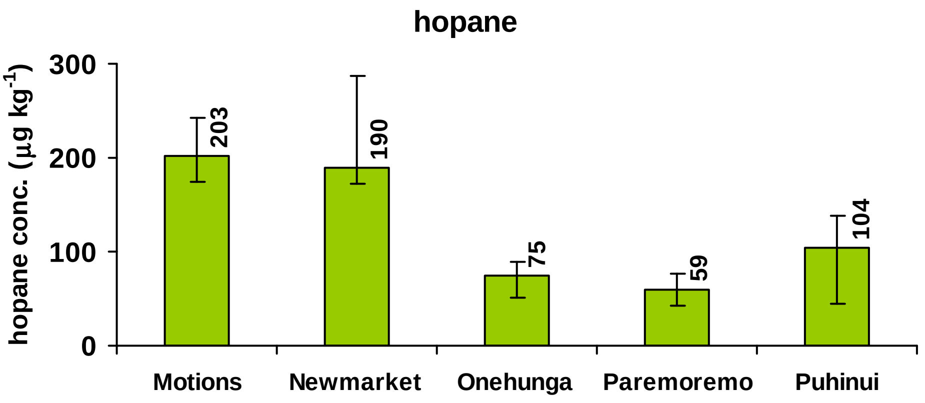


Figure 56 Median concentration of hopane in catchment sediments – 'error bars' represent the lower and upper quartile concentration (note: units are µg kg^{-1})

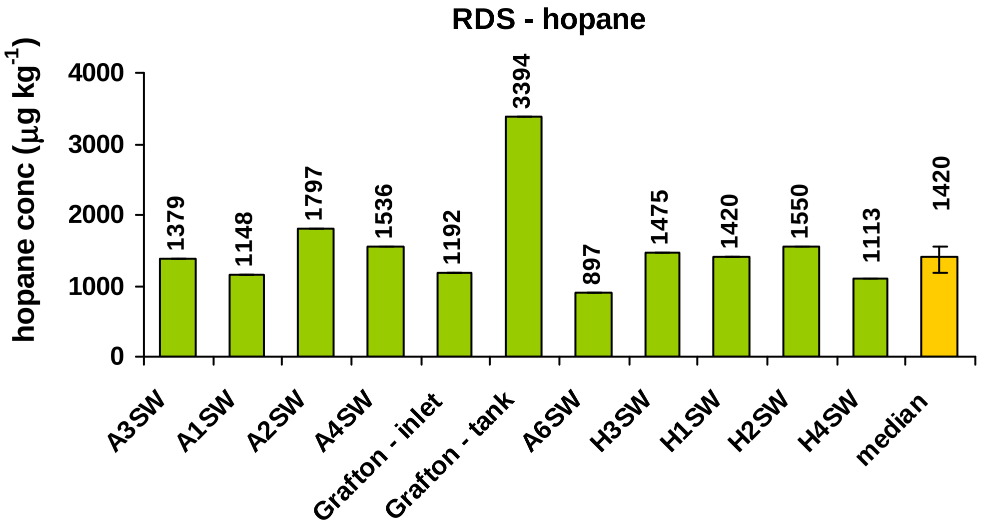


Figure 57 Hopane concentrations in road-derived sediments (RDS); median shown in orange (note: units are µg kg^{-1})

Estimating the contribution of modern road runoff to sediment PAH loadings

Using the data presented in Figure 57 and Figure 54, hopane:PAH ratios were determined for all the individual PAHs. Then because we have assumed that all the hopane in the catchment sediments is derived from road runoff, the hopane sediment concentration is simply divided by the individual ratios to estimate how much of each

PAH in the sediment is attributable to road runoff particulate. The individual concentrations are then summed and expressed as a percentage of the total measured concentration of PAHs. In contrast to a previous study (Depree & Ahrens, 2007), rather than rely on just the Grafton Gully sample as being representative of modern runoff particulates, estimations were based on the median ratios from 10 RDS samples (sample A4SW was excluded due to suspected coal tar presence).

The calculated contributions of modern road runoff particulates to the sediment loads of PAHs in the five catchments are presented in Figure 58. To give some idea of the potential variation, 3 sets of ratios have been used – (i) median from all samples (n=10), (ii) median for Hamilton RDS (n=4), and for comparison with the previous study (Depree & Ahrens, 2007), (iii) sediment from the Grafton Gully SWTD.

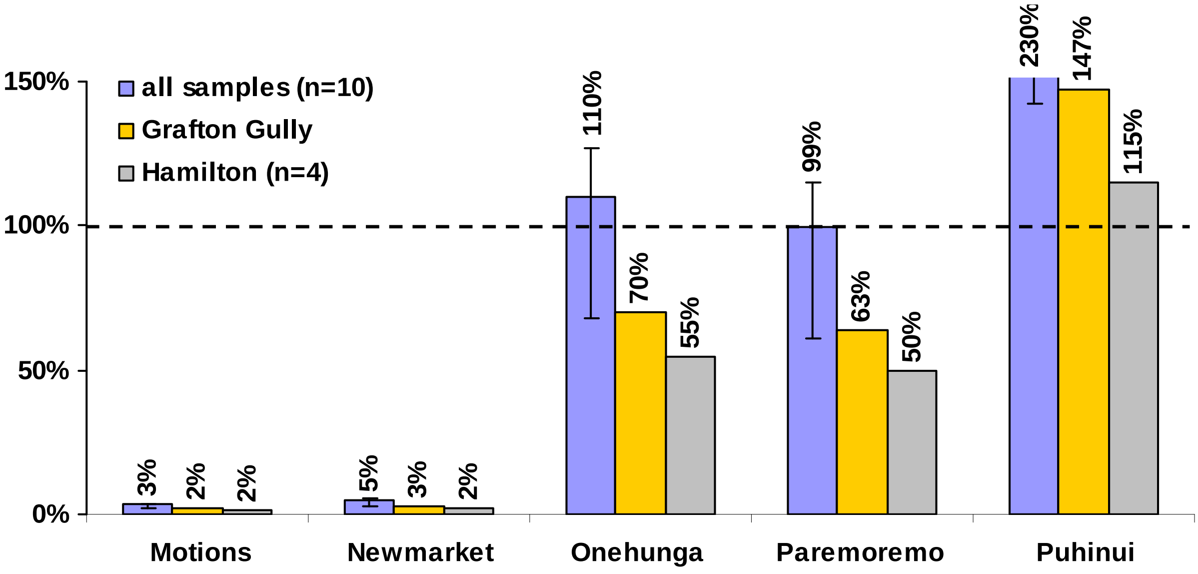


Figure 58 Estimated (based on hopane:PAH ratios) contribution of modern road runoff particulates to the concentration of PAHs in catchment sediments. Blue bars represent ‘best’ estimate using hopane:PAH ratio derived from all 10 RDS samples; alternative apportionments (orange/grey bars) using hopane:PAH ratios derived from small RDS data sets are provided for comparison

Using the ratios for ‘all samples’ the contribution of modern runoff was <5% for Motions and Newmarket, meaning that >95% of the PAHs in these sediments are attributable to another source – presumably historic (and possible ongoing) inputs of coal tar contaminated runoff particulate. For example, in Christchurch, although coal tar has not been used since the early seventies, recently deposited particulate material in channels can contain up to 200 mg kg^{-1} of PAHs caused by ongoing inputs of coal tar contaminated soils (Depree et al., 2006).

Using the ratio for ‘all samples’ (blue bars) the contribution of runoff to sediment PAHs was 110%, 99% and 230% for Onehunga, Paremoremo and Puhinui catchments,, respectively. Using the single Grafton Gully hopane:PAH ratio, road runoff accounted for 70%, 63% and >100% of the sediment PAHs from Onehunga, Paremoremo and Puhinui, respectively (orange bars).

The ca. 100% PAH contribution values obtained for Onehunga and Paremoremo were in agreement with conclusions derived from the Zn:Cu ratios – that is that sediment concentrations in these catchments are mainly due to road runoff. It is important, however, to emphasise that this does not imply state highway runoff, as it not possible to differentiate this from inputs from other modern road runoff. For the Motions and Newmarket catchments, both the Zn:Cu and hopane:PAH ratios were consistent with there being significant inputs from non-road runoff sources. For these two catchments, where the proportion of PAHs from runoff was estimated to be <5%, the Zn:Cu ratio was ca. 3, compared to the normal road runoff value of ca. 6.

The Puhinui catchment contains very low levels of PAHs, with many sites approaching the method detection limit, which tends to limit the reliability of this type of analysis. However, the main point to emphasise is that the results in Figure 58 indicate that modern road runoff could account for all of the sediment PAHs in this catchment.

It is important to point out that the contaminant apportionments estimated in Figure 58 only relate to PAHs – they cannot be applied to other contaminants such as copper and zinc. Hence, although it is estimated that <5% of PAHs in Motions and Newmarket catchment sediments are attributable to modern road runoff, the contribution to heavy metals (Cu and Zn) is probably much higher.

The >100% contributions of PAHs in sediments reflects the limitation of using a ‘single ratio approach.’ In Figure 58, the assumption is that the blue bars (‘all samples’ i.e. 10 RDS samples) best represent the hopane:PAH ratio present in runoff; however this results in road runoff accounting for 230% of PAHs. This implies there is either another source of hopanes (possible, as concentrations were 40 and 70% higher than Onehunga and Paremoremo, respectively) or the ‘all sample’ ratio is not representative of the true hopane:PAH ratio present in Puhinui catchment runoff. If the hopane:PAH ratio from Hamilton runoff (4 RDS samples) is used (grey bars, Figure 58), a more sensible PAH contribution value of 115% is produced. Irrespective of the correct ratio, as mentioned previously, the results show that all the sediment PAHs in the Puhinui catchment are probably coming from modern road runoff. Hence the amount of contaminants coming exclusively from state highways will depend on their relative contribution to total road runoff in the catchments – estimated values are given in Table 2.

A better method would have been to collect RDS samples (i.e. street sweepings and/or sump sediments) from representative highways in each of the five catchments, and derive individual hopane:PAH ratios for determining the PAH contribution in each of the catchment sediments. Despite the variation in hopane:PAH ratios, the results unambiguously showed that at sights where contaminant levels are of concern – relative to sediment quality guidelines (i.e. Motions and Newmarket) – modern road runoff containing ca. 5 mg kg^{-1} accounts for only 5% of sediment PAHs. In more recently developed catchments, which have not been exposed to historic contaminants (i.e. coal tar), modern road runoff is, as expected, a major source of sediment PAHs, accounting for between 50-100% of the total. However, in these catchments, the absolute concentration of PAHs in the sediments is well below ‘low’ ANZECC trigger levels – Onehunga, Paremoremo and Puhinui PAH concentrations were an order-of-magnitude lower than the threshold effects level (refer to Figure 52). Hence the following situations occur:

(i) sediment PAH concentrations of concern $\Rightarrow$ *<5% attributable to modern runoff*

(ii) modern runoff major source of sediment PAHs $\Rightarrow$ *concentrations well below ‘low trigger levels’ (i.e. threshold effects level)*

In either of these situations, it could be argued that treating runoff from a modern constructed road (i.e. highway) in the ‘effected’ catchment would have minimal environmental benefits with respect to PAHs. In scenario (i) treating runoff from a modern road would have little impact on sediment concentrations in the receiving environment as this source may be contributing <5% of the total. In scenario (ii) treating road runoff may reduce receiving environment loads of PAHs, however, the levels are many times lower than threshold effects levels. A summary of the modern road runoff contribution to catchment sediment PAHs, and comparison of sediment PAH concentrations relative to the threshold effects level (TEL) is presented in Table 2.

Table 2 Summary of estimated contribution of modern road runoff to PAHs in catchment sediments, and PAH concentrations relative to the ANZECC ‘LOW’ sediment quality guideline value (threshold effects level)

Catchment	Estimated contribution of road runoff to sediment PAHs (%)[1]	%of roads in catchment that are state highways	Sediment [PAH] relative to ANZECC ‘LOW’ guideline (%)	PAH sediment levels of concern
Motions	2-4	40	470	YES
Newmarket	3-6	5	290	YES
Onehunga	68-100[2]	5	7.5	NO
Paremoremo	61-100[2]	20	4.8	NO
Puhinui	100[2]	15	3.3	NO

[1] Range is based on upper and lower quartile hopane:PAH ratios using all 10 RDS samples (blue bars; Figure 58); [2] estimated percent contribution was >100%.

.

4. Conclusions

4.1 Metals

Results of this study show high zinc concentrations in sediments in Newmarket (SH1), Puhinui (SH20) and Motions (SH16) catchments and high copper concentrations in sediments in Newmarket and Motions. Zn:Cu ratios found in this study averaged between 3 and 6 in all but one catchment. The highest Zn:Cu ratio found across sampled sites was in the Puhinui catchment with a ratio of 20, which represents a three to four-folds increase relative to all other catchments studied. Results suggest that the unusually high Zn:Cu ratio found in the Puhinui catchment may be explained by the combination of natural sources, i.e. a large proportion of volcanic soils in the area, and runoff from industrial and commercial buildings, as well as of the neighbouring State Highway 20.

Onehunga catchment showed a Zn:Cu ratio close to that expected for a state highway only effect on the stormwater catchment, suggesting that the zinc and copper concentrations found in the Onehunga catchment may be markedly influenced by the state highway runoff from state highway 1. However, the land-use data indicates other urban sources of zinc and copper also make a large contribution to this ratio.

Newmarket showed high concentrations of both zinc and copper, with a low resulting Zn:Cu ratio of 3. Possible sources of contaminants in the Newmarket catchment include roof-runoff from the residential and commercial areas, old copper piped networks (a possible large source of copper), busy arterial roads and state highway 1.

Motions showed high metal concentrations in sediments but the ratio of Zn:Cu was approximately 3, so lower than the Grafton Road study. Zinc and copper concentrations in the silt and mud fraction were very high (>500 mg kg^{-1} of zinc and >119 mg kg^{-1} of copper). This concentration in sediments may cause harm to aquatic life (see Depree, 2008). Newmarket catchment also has the potential to cause harm to aquatic organisms using the above criteria. Further investigations in these catchments would assist with more detailed source tracking.

4.2 PAHs and TPH

The five catchments could be separated into two categories; ‘high’ and ‘low’ PAH contamination. Sediments from Motions and Newmarket catchments contained ‘high’ levels of PAHs, with median concentrations of 19 and 12 mg kg^{-1}, respectively.

Sediment concentrations in both of these catchments exceeded the ANZECC ‘low’ sediment quality trigger level (or Threshold Effects Concentration – TEL) of 4 mg kg^{-1}. The Motions and Newmarket PAH concentrations were significantly higher than the median of 4.6 mg kg^{-1} for samples (n=10) of road runoff particulates (i.e. RDS). In contrast, the other 3 catchments – Onehunga, Paremoremo and Puhinui – contained very low concentrations of PAHs, with median concentrations ranging from 0.13 to 0.30 mg kg^{-1}. The concentrations of PAHs in these three catchments were 13-30 times below the ANZECC ‘low’ trigger level.

Differences in the sediment levels of TPH were less pronounced between the 2 catchment groups, the ‘high’ PAH catchments (Motions and Newmarket) had concentrations of TPH ca. 400-450 mg kg^{-1}, compared to 60-100 mg kg^{-1} for the ‘low’ PAH catchments of Onehunga, Paremoremo and Puhinui. All the catchment sediment TPH concentrations were much lower than the median of 1300 mg kg^{-1} observed in road runoff particulates.

Based on the concentration data, it is apparent that (a) modern road runoff particulates cannot account for the concentration of PAHs in Motions and Newmarket sediments; (b) based on median TPH concentrations and excluding other sources, road runoff particulates would need to be diluted (with other clean sediment) by a factor of only ca. 3 – although the Auckland RDS median was ca. 2300 mg kg^{-1} which would require a ca. 5-fold dilution; and (c) Based on median PAH and TPH concentrations, modern road runoff particulates would need to be diluted by respective factors of 15-35 and 13-22 to account for the concentrations observed for the Onehunga, Paremoremo and Puhinui catchments.

Hopanes are refractory marker compounds for high boiling petroleum fractions and residues (i.e. bitumen). Based on the concentrations of 1 hopane marker, the required dilution factor of road runoff particulates was ca. 7 for Motions and Newmarket, and 15-20 for Onehunga, Paremoremo and Puhinui catchments. Using hopane:PAH ratios, the percent contribution of modern road runoff to catchment sediments was determined as: 2-4% for Motions; 3-6% for Newmarket; 68-100% for Onehunga; 61-100% for Paremoremo; 100% Puhinui.

For the three catchments – Onehunga, Paremoremo and Puhinui - where modern road runoff account for up to 100% of the sediment PAHs, it is important to emphasise that the sediment PAH concentrations in these catchments are 13-30 and 150-350 times less than the ANZECC ‘low’ and ‘high’ trigger levels, respectively. The situation is reversed for the 2 most contaminated catchments – Motions and Newmarket. Although these two catchments exceed the ANZECC ‘low’ trigger value, it was estimated that modern road runoff contributes to <5% of the total sediment concentration. Hence this study indicates that PAHs are not a major problematic contaminant class, since environmental levels arising from the discharge of road runoff particulates are well below sediment quality guideline values.

5. References

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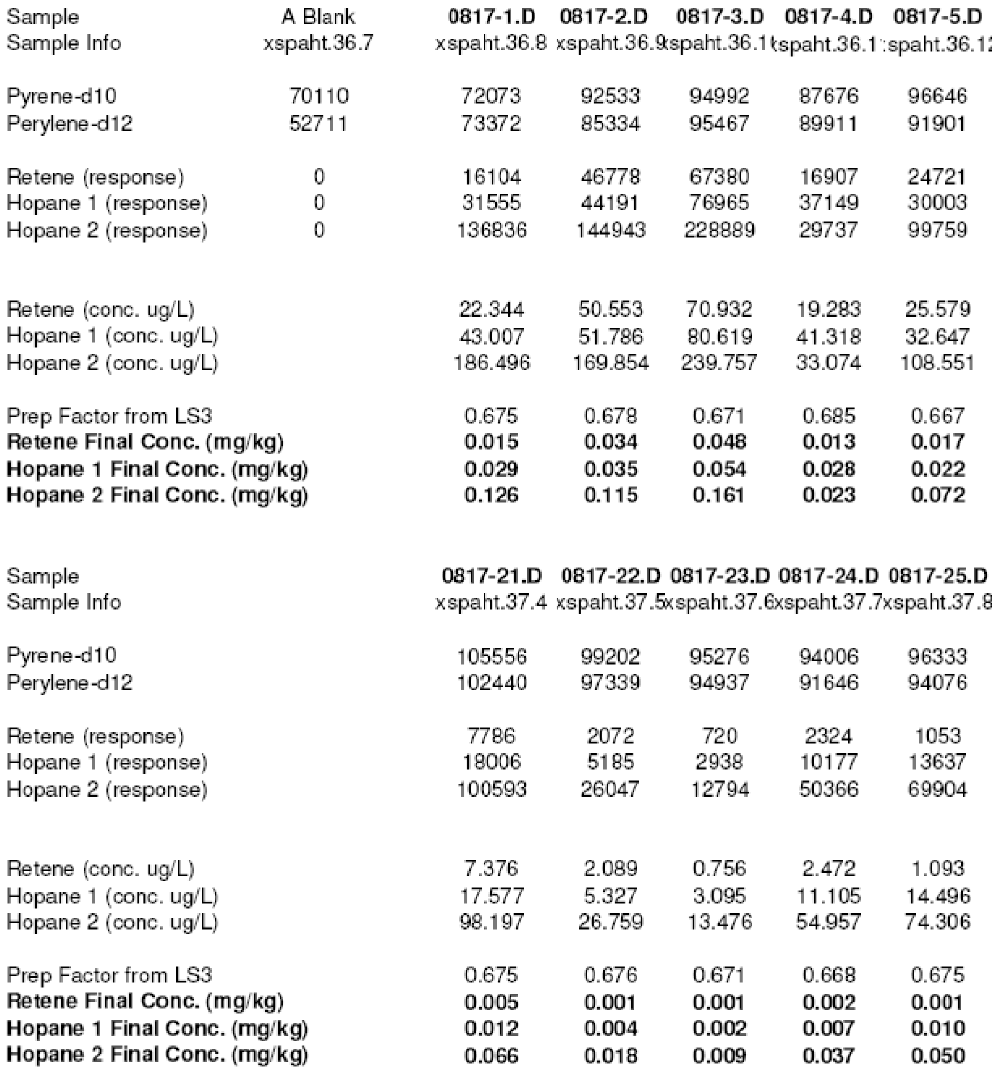
6. Appendices

Appendix 1: Latitude and longitude of sampling sites

Site	MOTIONS	NEWMARKET	ONEHUNGA	PAREMOREMO	PUHINUI
1	36° 51’ 27.14 S 174° 43’ 06.36 E	36° 51’ 50.02 S 174° 47’ 14.49 E	36° 55’ 52.00 S 174° 48’ 12.68 E	36° 44’ 12.43 S 174° 41’ 11.49 E	37° 00’ 40.69 S 174° 50’ 28.23 E
2	36° 51’ 27.19 S 174° 43’ 05.87 E	36° 51’ 49.68 S 174° 47’ 14.78 E	36° 55’ 52.24 S 174° 48’ 12.65 E	36° 44’ 12.28 S 174° 41’ 11.22 E	37° 00’ 39.20 S 174° 50’ 27.67 E
3	36° 51’ 27.68 S 174° 43’ 05.46 E	36° 51’ 49.28 S 174° 47’ 15.26 E	36° 55’ 52.55 S 174° 48’ 12.72 E	36° 44’ 11.89 S 174° 41’ 10.66 E	37° 00’ 39.63 S 174° 50’ 26.28 E
4	36° 51’ 28.16 S 174° 43’ 04.88 E	36° 51’ 49.35 S 174° 47’ 16.50 E	36° 55’ 53.05 S 174° 48’ 12.78 E	36° 44’ 11.75 S 174° 41’ 10.66 E	37° 00’ 39.97 S 174° 50’ 25.05 E
5	36° 51’ 28.61 S 174° 43’ 03.98 E	36° 51’ 49.68 S 174° 47’ 17.38 E	36° 55’ 53.86 S 174° 48’ 12.84 E	36° 44’ 11.59 S 174° 41’ 10.46 E	37° 00’ 40.59 S 174° 50’ 24.67 E
6	36° 51’ 28.66 S 174° 43’ 02.96 E	36° 51’ 49.49 S 174° 41’ 18.87 E	36° 55’ 54.66 S 174° 48’ 12.99 E	36° 44’ 11.47 S 174° 41’ 10.13 E	37° 00’ 40.96 S 174° 50’ 22.86 E
7	36° 51’ 28.32 S 174° 43’ 02.10 E	36° 51’ 49.23 S 174° 47’ 19.57 E	36° 55’ 55.29 S 174° 48’ 13.05 E	36° 44’ 11.86 S 174° 41’ 09.63 E	37° 00’ 43.05 S 174° 50’ 22.56 E
8	36° 51’ 27.38 S 174° 43’ 01.33 E	36° 51’ 48.89 S 174° 47’ 20.88 E	36° 55’ 55.84 S 174° 48’ 13.14 E	36° 44’ 12.20 S 174° 41’ 09.05 E	37° 00’ 45.40 S 174° 50’ 20.24 E
9	36° 51’ 26.91 S 174° 43’ 00.37 E	36° 51’ 48.58 S 174° 47’ 21.89 E	36° 55’ 56.68 S 174° 48’ 13.23 E	36° 44’ 12.46 S 174° 41’ 08.71 E	37° 00’ 46.56 S 174° 50’ 20.20 E
10	36° 51’ 26.92 S 174° 42’ 59.58 E	36° 51’ 48.13 S 174° 47’ 22.89 E	36° 55’ 57.71 S 174° 48’ 13.46 E	36° 44’ 12.70 S 174° 41’ 08.68 E	37° 00’ 47.86 S 174° 50’ 20.37 E

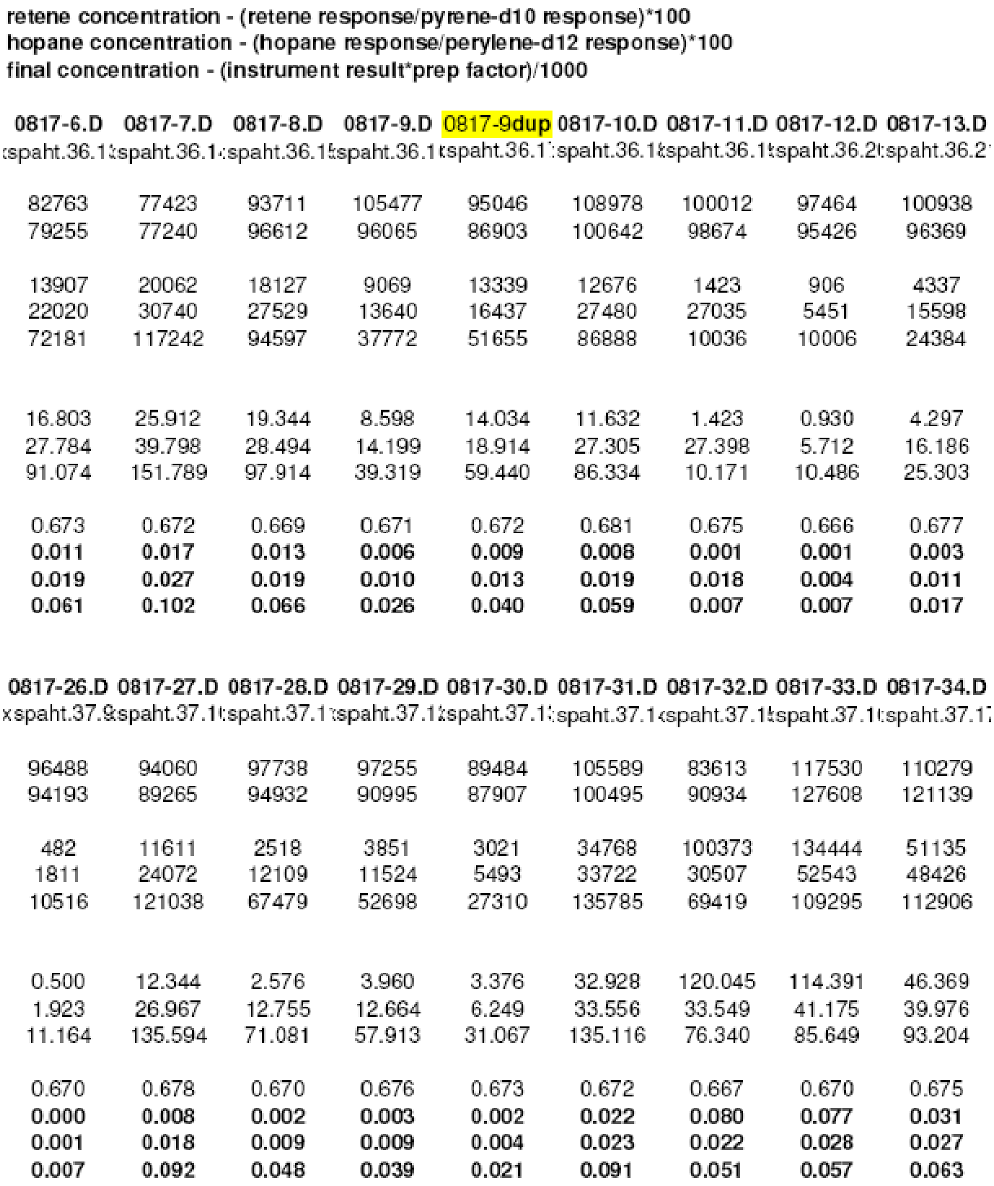
Appendix 2: Hill Laboratory report for TPH, PAH and Hopanes for catchment sediments



Sample	A Blank	**0817-1.D**	**0817-2.D**	**0817-3.D**	**0817-4.D**	**0817-5.D**
Sample Info	xspaht.36.7	xspaht.36.8	xspaht.36.9	spaht.36.1	spaht.36.1	spaht.36.1
Pyrene-d10	70110	72073	92533	94992	87676	96646
Perylene-d12	52711	73372	85334	95467	89911	91901
Retene (response)	0	16104	46778	67380	16907	24721
Hopane 1 (response)	0	31555	44191	76965	37149	30003
Hopane 2 (response)	0	136836	144943	228889	29737	99759
Retene (conc. ug/L)		22.344	50.553	70.932	19.283	25.579
Hopane 1 (conc. ug/L)		43.007	51.786	80.619	41.318	32.647
Hopane 2 (conc. ug/L)		186.496	169.854	239.757	33.074	108.551
Prep Factor from LS3		0.675	0.678	0.671	0.685	0.667
Retene Final Conc. (mg/kg)		**0.015**	**0.034**	**0.048**	**0.013**	**0.017**
Hopane 1 Final Conc. (mg/kg)		**0.029**	**0.035**	**0.054**	**0.028**	**0.022**
Hopane 2 Final Conc. (mg/kg)		**0.126**	**0.115**	**0.161**	**0.023**	**0.072**

Sample	**0817-21.D**	**0817-22.D**	**0817-23.D**	**0817-24.D**	**0817-25.D**
Sample Info	xspaht.37.4	xspaht.37.5	xspaht.37.6	xspaht.37.7	xspaht.37.8
Pyrene-d10	105556	99202	95276	94006	96333
Perylene-d12	102440	97339	94937	91646	94076
Retene (response)	7786	2072	720	2324	1053
Hopane 1 (response)	18006	5185	2938	10177	13637
Hopane 2 (response)	100593	26047	12794	50366	69904
Retene (conc. ug/L)	7.376	2.089	0.756	2.472	1.093
Hopane 1 (conc. ug/L)	17.577	5.327	3.095	11.105	14.496
Hopane 2 (conc. ug/L)	98.197	26.759	13.476	54.957	74.306
Prep Factor from LS3	0.675	0.676	0.671	0.668	0.675
Retene Final Conc. (mg/kg)	**0.005**	**0.001**	**0.001**	**0.002**	**0.001**
Hopane 1 Final Conc. (mg/kg)	**0.012**	**0.004**	**0.002**	**0.007**	**0.010**
Hopane 2 Final Conc. (mg/kg)	**0.066**	**0.018**	**0.009**	**0.037**	**0.050**

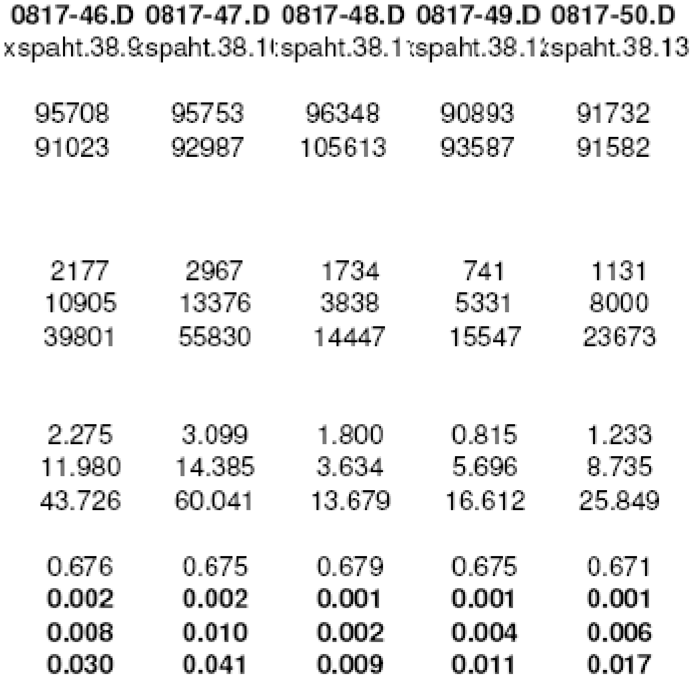
Sample	**0817-41.D**	**0817-42.D**	**0817-43.D**	**0817-44.D**	**0817-45.D**
Sample Info	xspaht.38.4	xspaht.38.5	xspaht.38.6	xspaht.38.7	xspaht.38.8
Pyrene-d10	102811	103552	98430	93255	92098
Perylene-d12	95507	96520	93923	89872	90376
Retene (response)	4278	2877	3368	2902	2657
Hopane 1 (response)	14295	13567	10339	13075	8193
Hopane 2 (response)	55368	45156	34965	43298	35512
Retene (conc. ug/L)	4.161	2.778	3.422	3.112	2.885
Hopane 1 (conc. ug/L)	14.967	14.056	11.008	14.548	9.065
Hopane 2 (conc. ug/L)	57.973	46.784	37.227	48.177	39.294
Prep Factor from LS3	0.676	0.675	0.673	0.677	0.684
Retene Final Conc. (mg/kg)	**0.003**	**0.002**	**0.002**	**0.002**	**0.002**
Hopane 1 Final Conc. (mg/kg)	**0.010**	**0.009**	**0.007**	**0.010**	**0.006**
Hopane 2 Final Conc. (mg/kg)	**0.039**	**0.032**	**0.025**	**0.033**	**0.027**



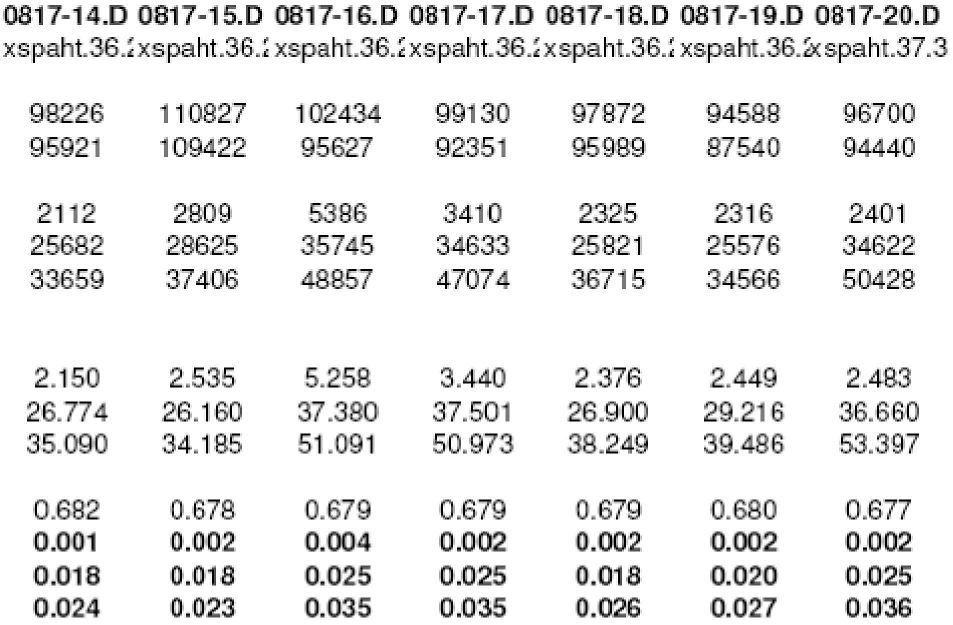
retene concentration - (retene response/pyrene-d10 response)*100
hopane concentration - (hopane response/perylene-d12 response)*100
final concentration - (instrument result*prep factor)/1000

0817-6.D	0817-7.D	0817-8.D	0817-9.D	0817-9dup	0817-10.D	0817-11.D	0817-12.D	0817-13.D
spaht.36.1	spaht.36.1	spaht.36.1	spaht.36.1	spaht.36.1	spaht.36.1	spaht.36.1	spaht.36.2	spaht.36.2
82763	77423	93711	105477	95046	108978	100012	97464	100938
79255	77240	96612	96065	86903	100642	98674	95426	96369
13907	20062	18127	9069	13339	12676	1423	906	4337
22020	30740	27529	13640	16437	27480	27035	5451	15598
72181	117242	94597	37772	51655	86888	10036	10006	24384
16.803	25.912	19.344	8.598	14.034	11.632	1.423	0.930	4.297
27.784	39.798	28.494	14.199	18.914	27.305	27.398	5.712	16.186
91.074	151.789	97.914	39.319	59.440	86.334	10.171	10.486	25.303
0.673	0.672	0.669	0.671	0.672	0.681	0.675	0.666	0.677
0.011	**0.017**	**0.013**	**0.006**	**0.009**	**0.008**	**0.001**	**0.001**	**0.003**
0.019	**0.027**	**0.019**	**0.010**	**0.013**	**0.019**	**0.018**	**0.004**	**0.011**
0.061	**0.102**	**0.066**	**0.026**	**0.040**	**0.059**	**0.007**	**0.007**	**0.017**

0817-26.D	0817-27.D	0817-28.D	0817-29.D	0817-30.D	0817-31.D	0817-32.D	0817-33.D	0817-34.D
xspaht.37.9	spaht.37.1	spaht.37.1	spaht.37.1	spaht.37.1	spaht.37.1	spaht.37.1	spaht.37.1	spaht.37.1
96488	94060	97738	97255	89484	105589	83613	117530	110279
94193	89265	94932	90995	87907	100495	90934	127608	121139
482	11611	2518	3851	3021	34768	100373	134444	51135
1811	24072	12109	11524	5493	33722	30507	52543	48426
10516	121038	67479	52698	27310	135785	69419	109295	112906
0.500	12.344	2.576	3.960	3.376	32.928	120.045	114.391	46.369
1.923	26.967	12.755	12.664	6.249	33.556	33.549	41.175	39.976
11.164	135.594	71.081	57.913	31.067	135.116	76.340	85.649	93.204
0.670	0.678	0.670	0.676	0.673	0.672	0.667	0.670	0.675
0.000	**0.008**	**0.002**	**0.003**	**0.002**	**0.022**	**0.080**	**0.077**	**0.031**
0.001	**0.018**	**0.009**	**0.009**	**0.004**	**0.023**	**0.022**	**0.028**	**0.027**
0.007	**0.092**	**0.048**	**0.039**	**0.021**	**0.091**	**0.051**	**0.057**	**0.063**



0817-46.D	**0817-47.D**	**0817-48.D**	**0817-49.D**	**0817-50.D**
xspaht.38.9	xspaht.38.1	xspaht.38.1	xspaht.38.1	xspaht.38.13
95708	95753	96348	90893	91732
91023	92987	105613	93587	91582
2177	2967	1734	741	1131
10905	13376	3838	5331	8000
39801	55830	14447	15547	23673
2.275	3.099	1.800	0.815	1.233
11.980	14.385	3.634	5.696	8.735
43.726	60.041	13.679	16.612	25.849
0.676	0.675	0.679	0.675	0.671
0.002	**0.002**	**0.001**	**0.001**	**0.001**
0.008	**0.010**	**0.002**	**0.004**	**0.006**
0.030	**0.041**	**0.009**	**0.011**	**0.017**



0817-14.D	**0817-15.D**	**0817-16.D**	**0817-17.D**	**0817-18.D**	**0817-19.D**	**0817-20.D**
xspaht.36.2	xspaht.36.2	xspaht.36.2	xspaht.36.2	xspaht.36.2	xspaht.36.2	xspaht.37.3
98226	110827	102434	99130	97872	94588	96700
95921	109422	95627	92351	95989	87540	94440
2112	2809	5386	3410	2325	2316	2401
25682	28625	35745	34633	25821	25576	34622
33659	37406	48857	47074	36715	34566	50428
2.150	2.535	5.258	3.440	2.376	2.449	2.483
26.774	26.160	37.380	37.501	26.900	29.216	36.660
35.090	34.185	51.091	50.973	38.249	39.486	53.397
0.682	0.678	0.679	0.679	0.679	0.680	0.677
0.001	**0.002**	**0.004**	**0.002**	**0.002**	**0.002**	**0.002**
0.018	**0.018**	**0.025**	**0.025**	**0.018**	**0.020**	**0.025**
0.024	**0.023**	**0.035**	**0.035**	**0.026**	**0.027**	**0.036**

0817-35.D	**0817-36.D**	**0817-37.D**	**0817-38.D**	**0817-39.D**	**0817-40.D**
spaht.37.1	spaht.37.1	spaht.37.2	spaht.37.2	spaht.37.2	xspaht.38.3
119227	104329	107283	103167	116089	102506
122596	109615	102900	95420	109416	98336
50156	25337	23170	21278	22796	16241
45847	35870	46600	43029	26606	33957
116663	130076	152581	123401	70851	114563
42.068	24.286	21.597	20.625	19.637	15.844
37.397	32.724	45.287	45.094	24.316	34.532
95.161	118.666	148.281	129.324	64.754	116.502
0.668	0.677	0.675	0.675	0.665	0.680
0.028	**0.016**	**0.015**	**0.014**	**0.013**	**0.011**
0.025	**0.022**	**0.031**	**0.030**	**0.016**	**0.023**
0.064	**0.080**	**0.100**	**0.087**	**0.043**	**0.079**

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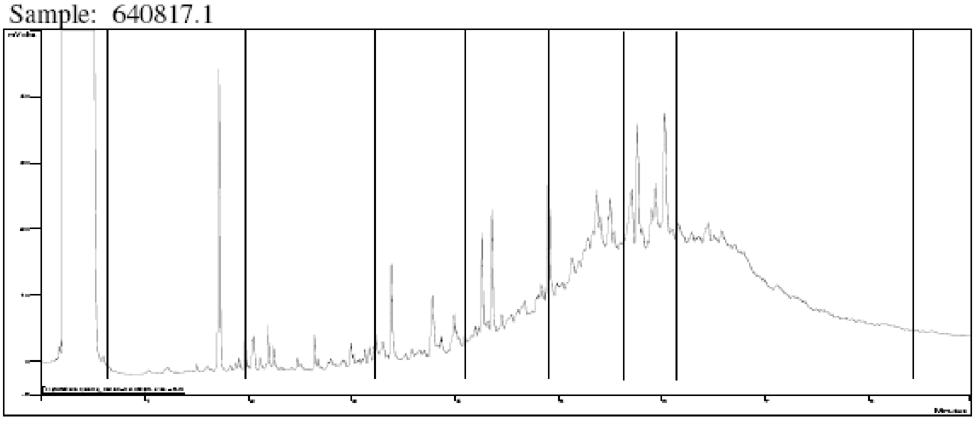

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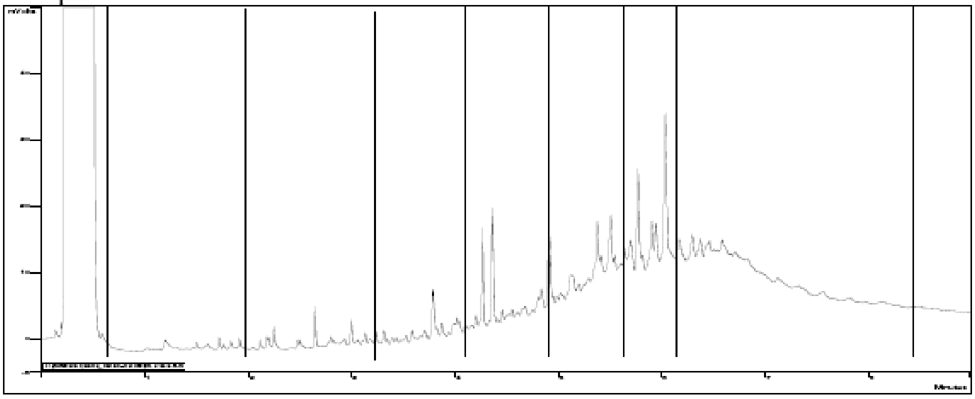

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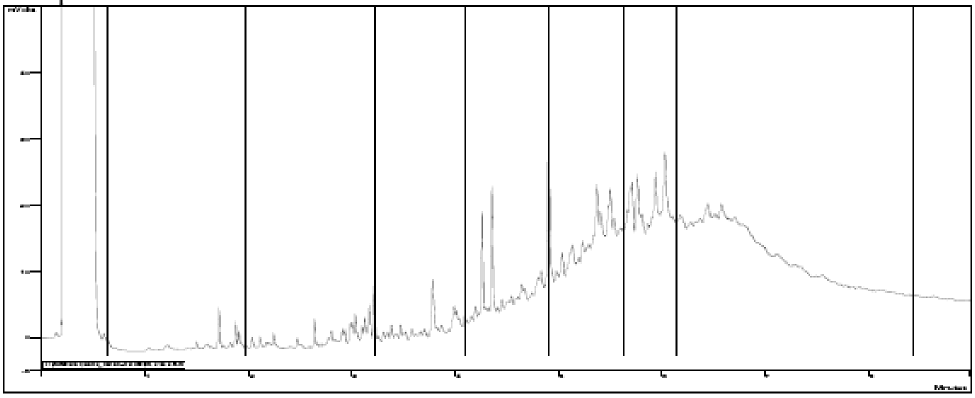

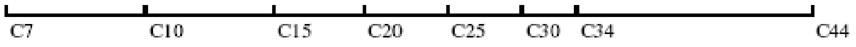

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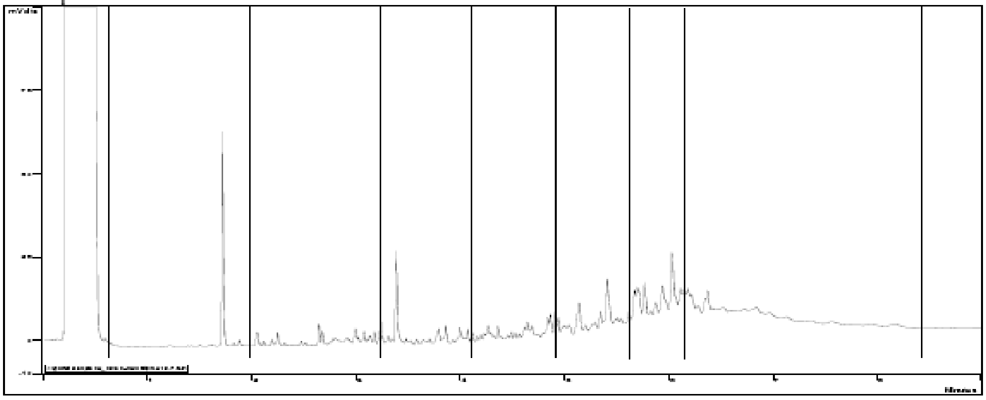

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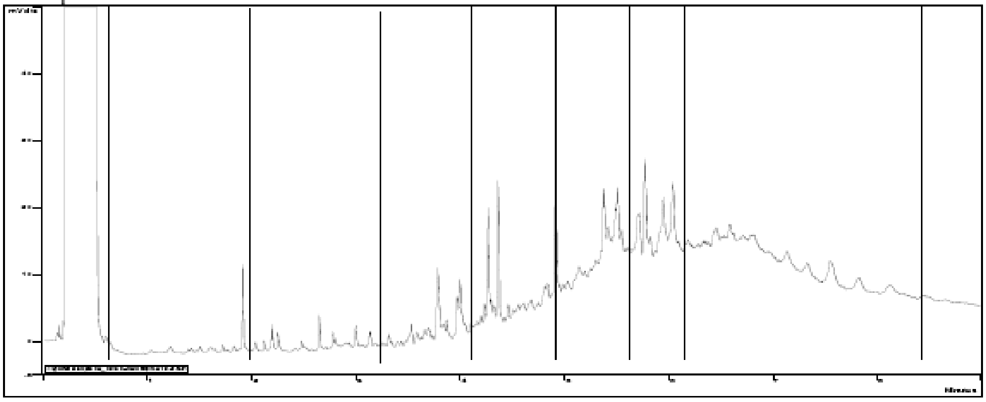

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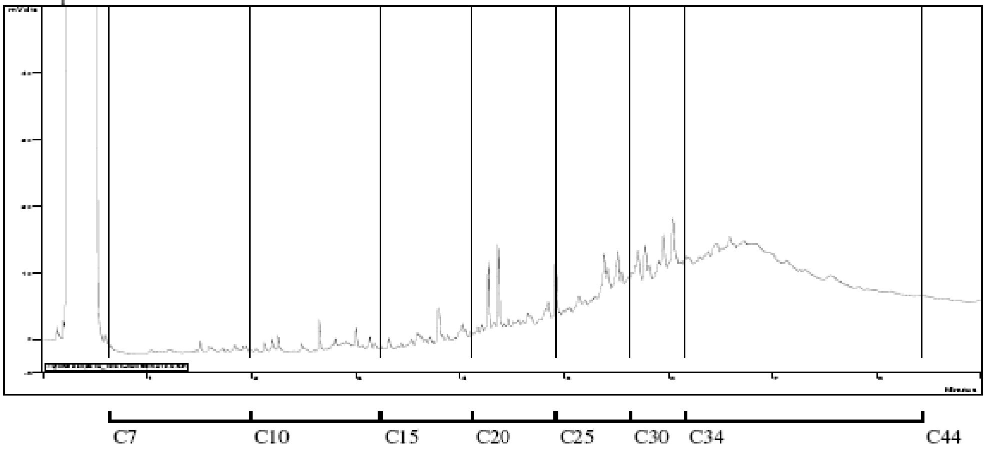

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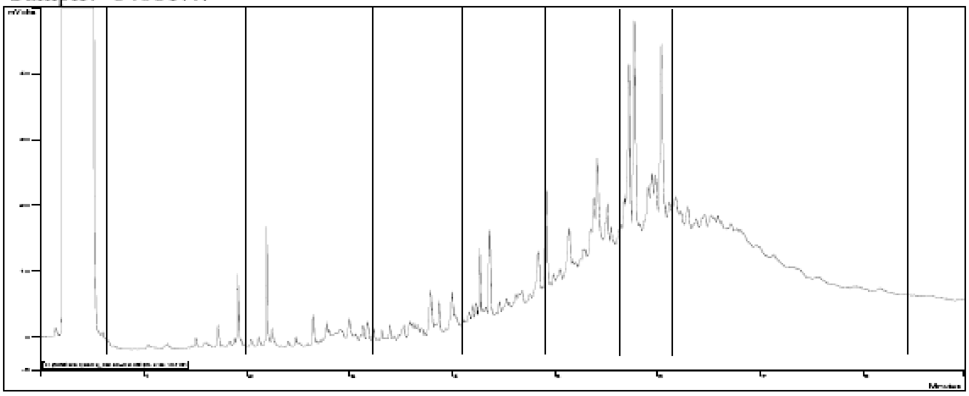

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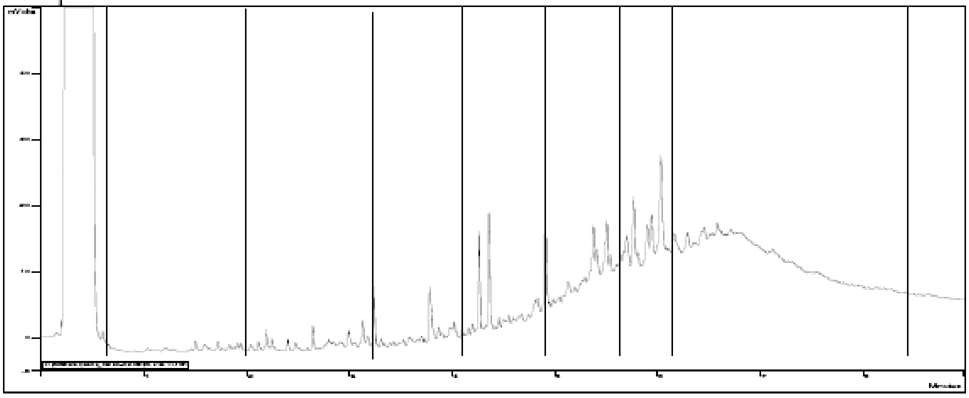

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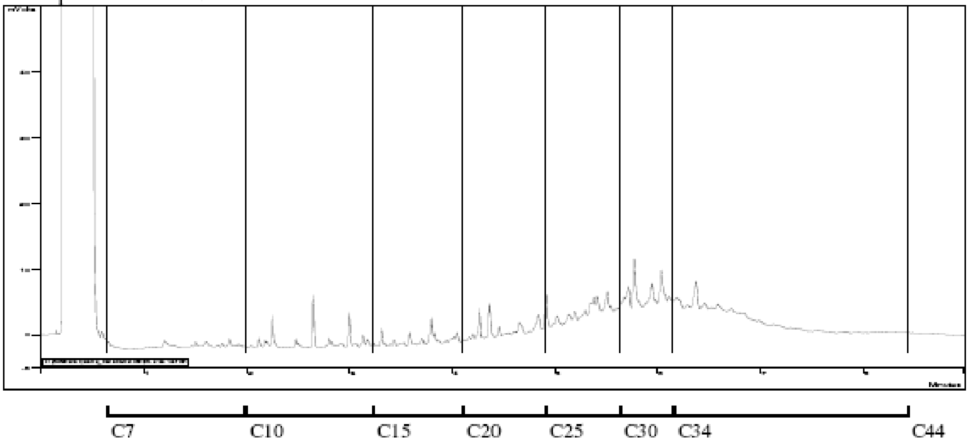

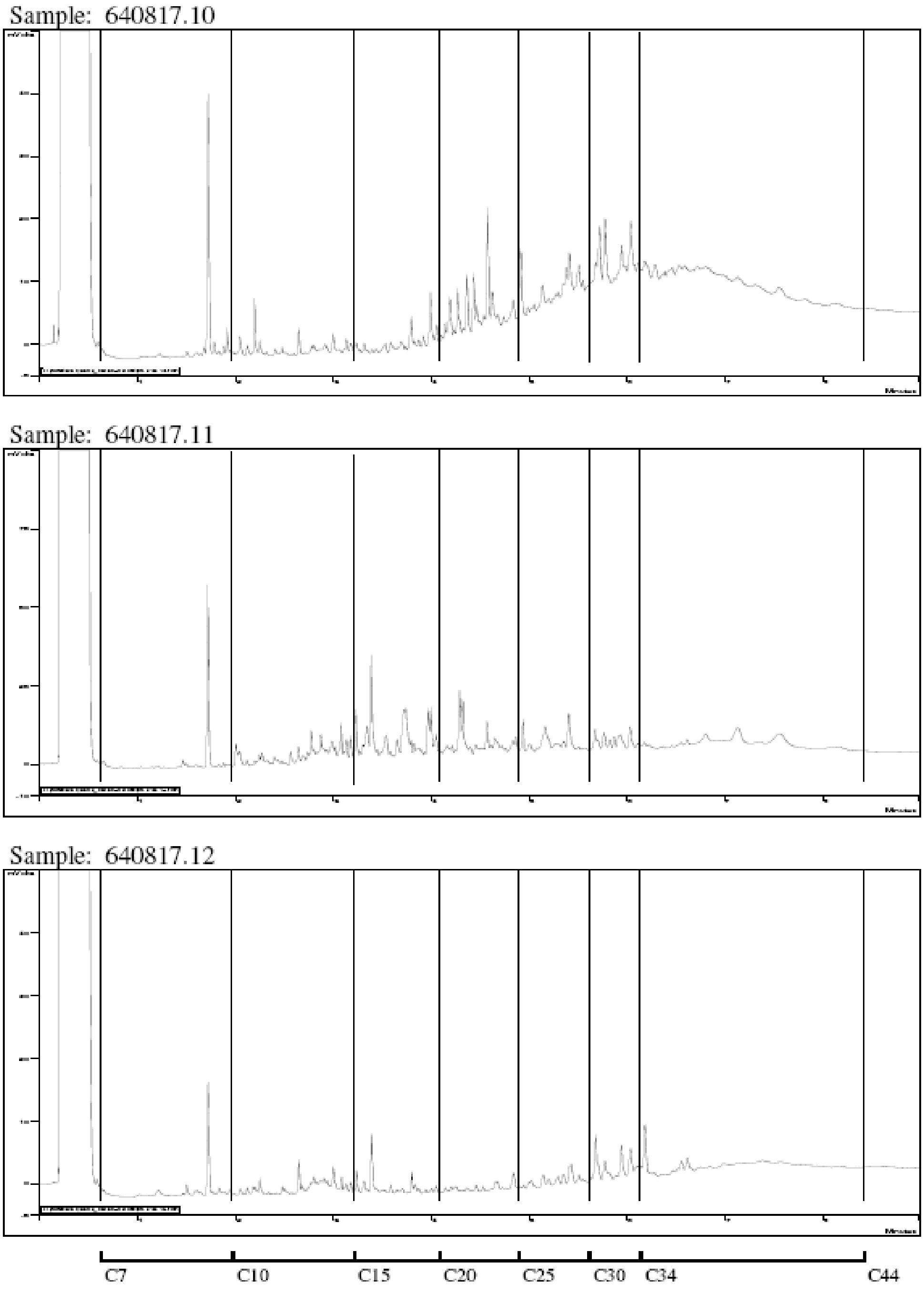

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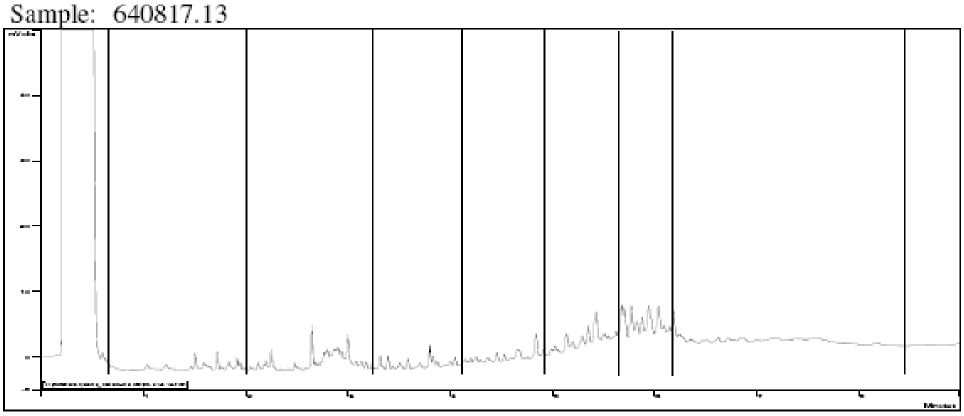
Sample: 640817.11

Sample: 640817.12

Sample: 640817.13



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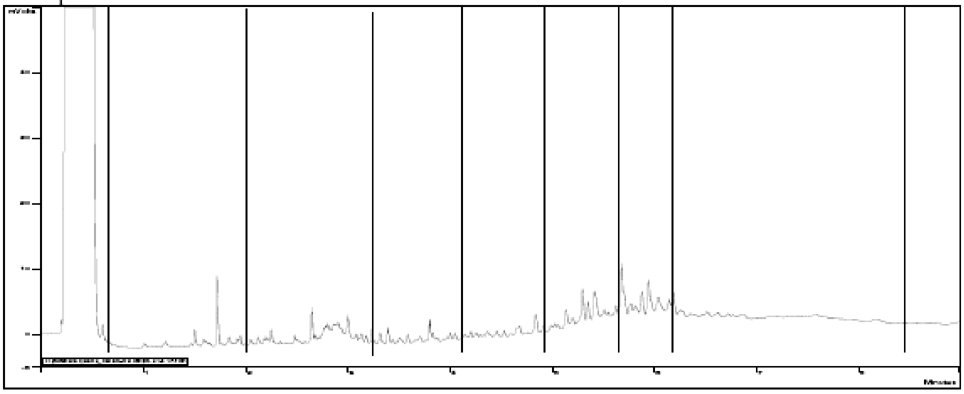

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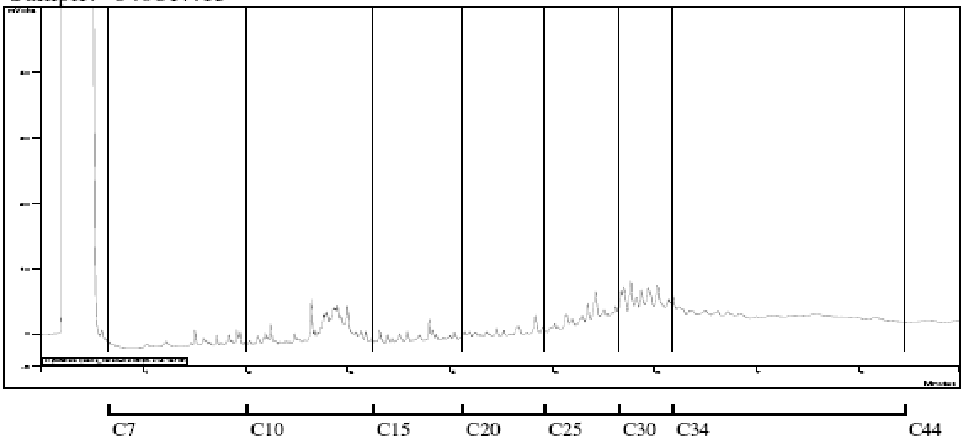

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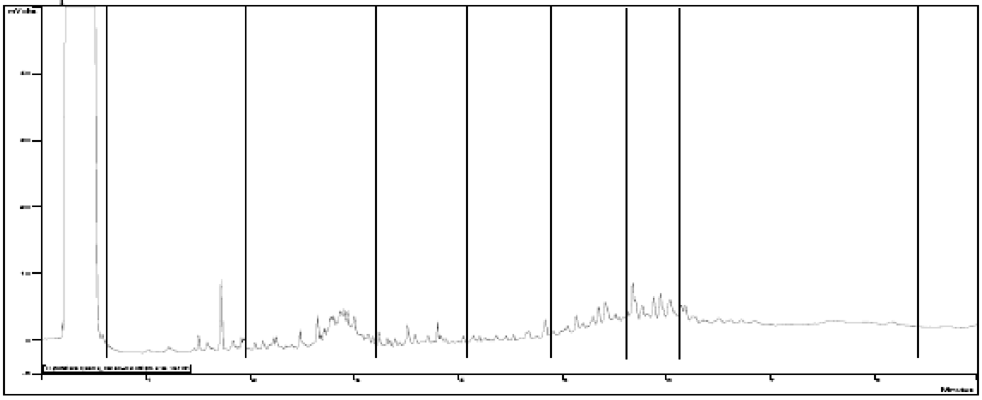

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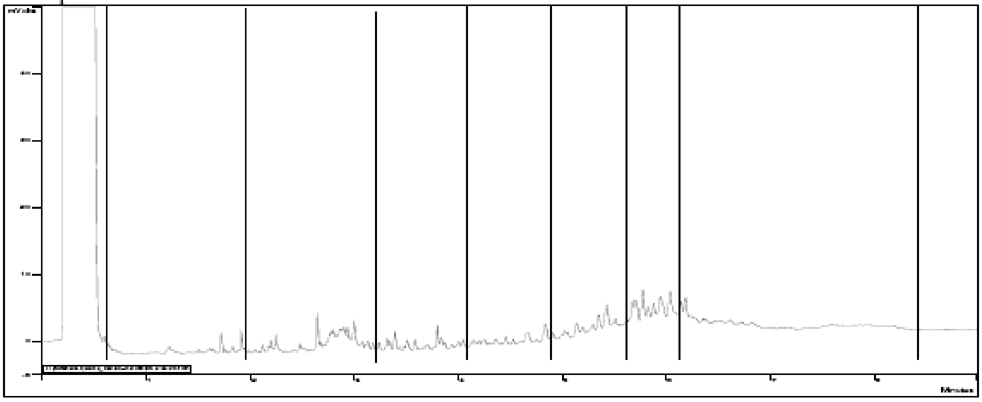

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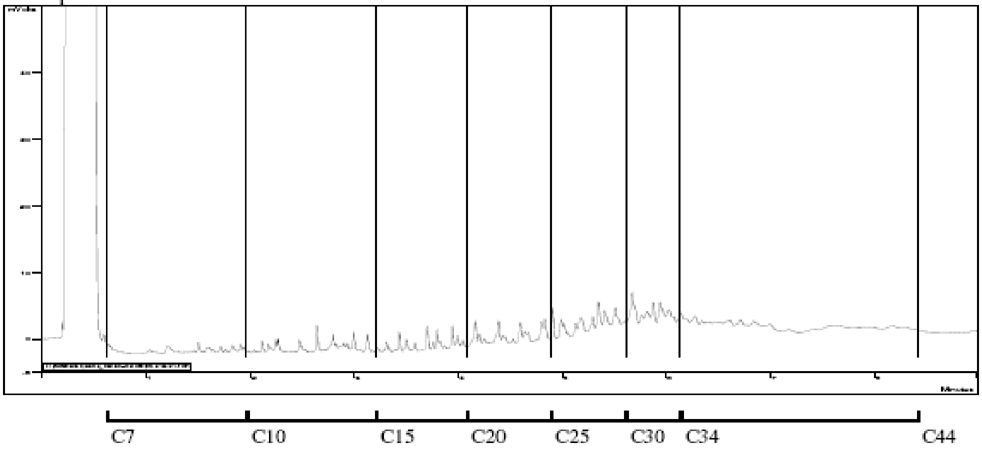

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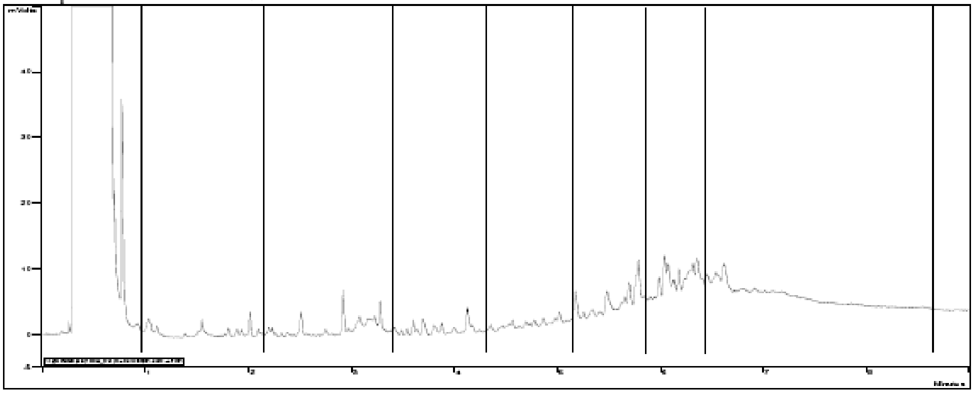

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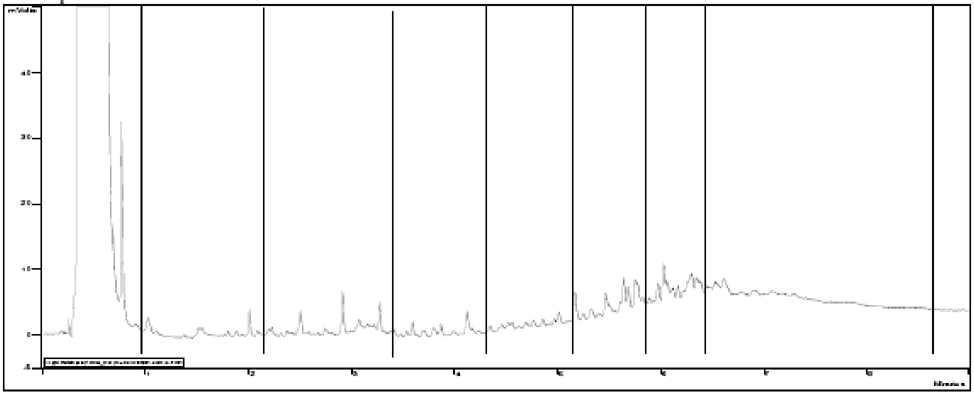

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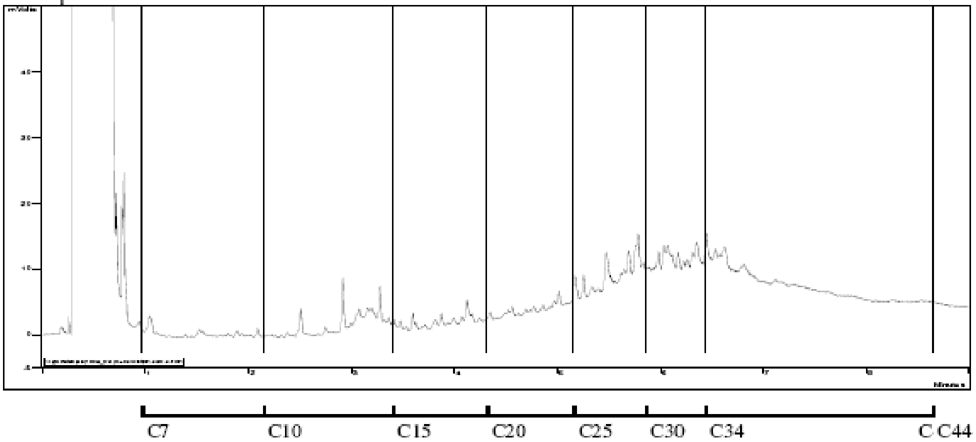

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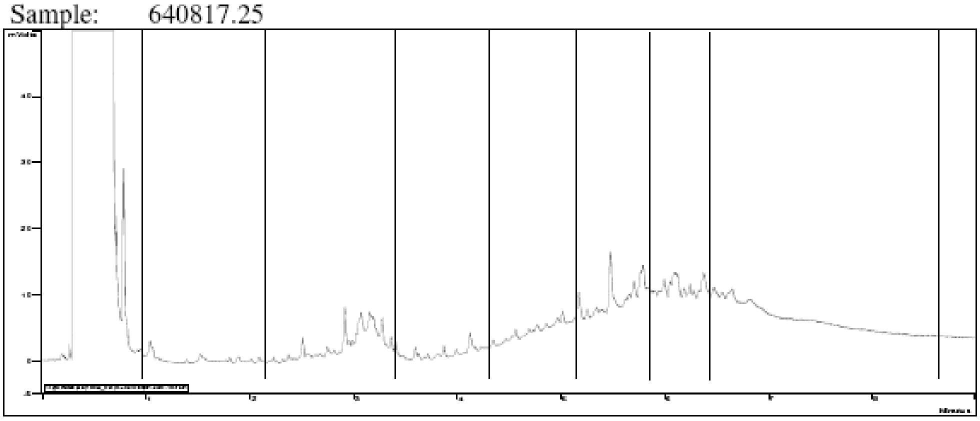

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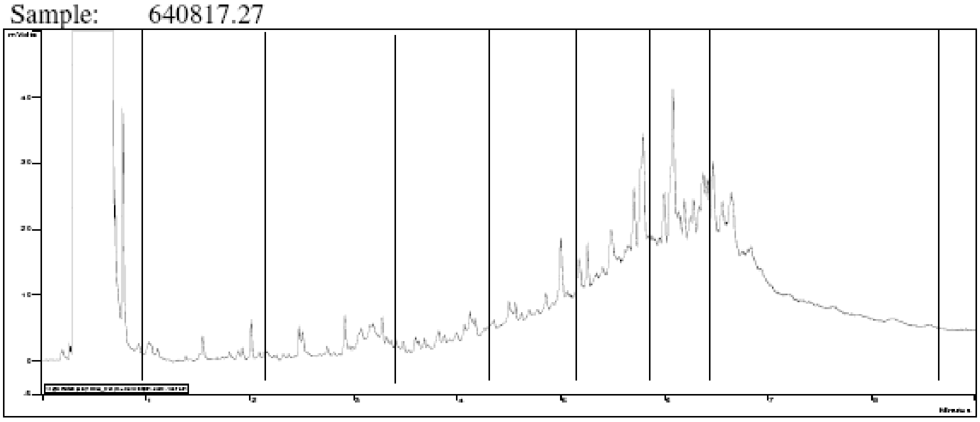

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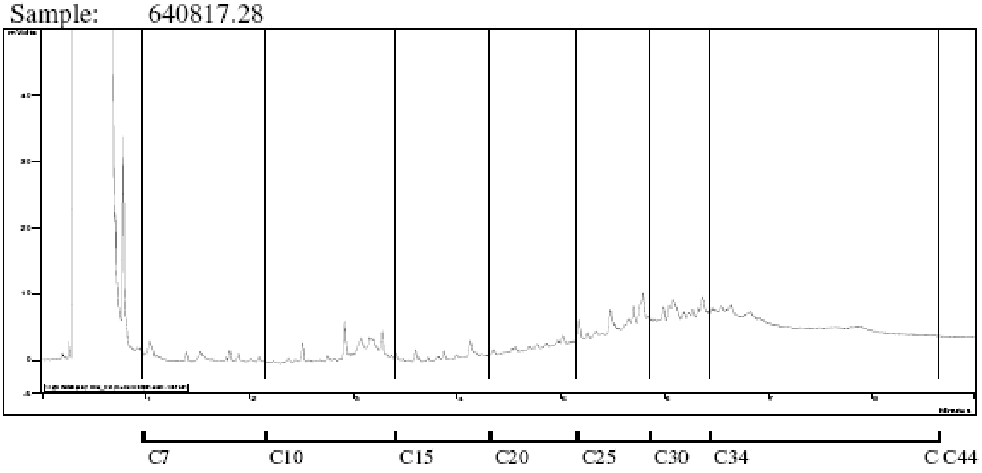

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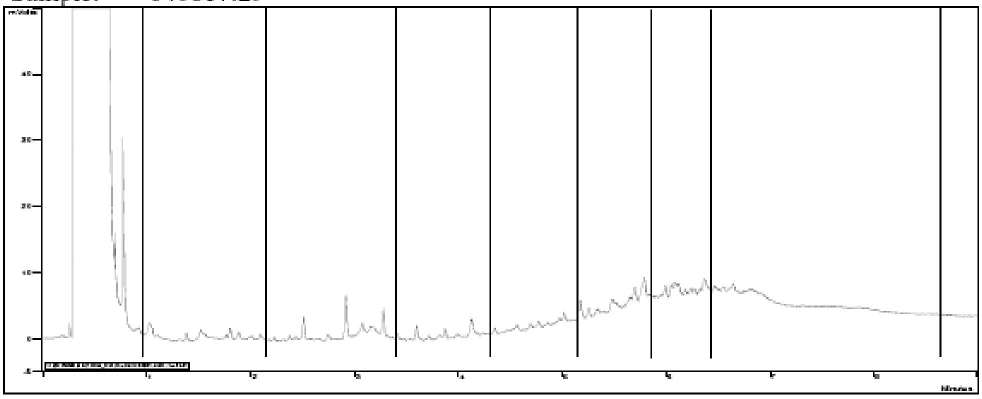

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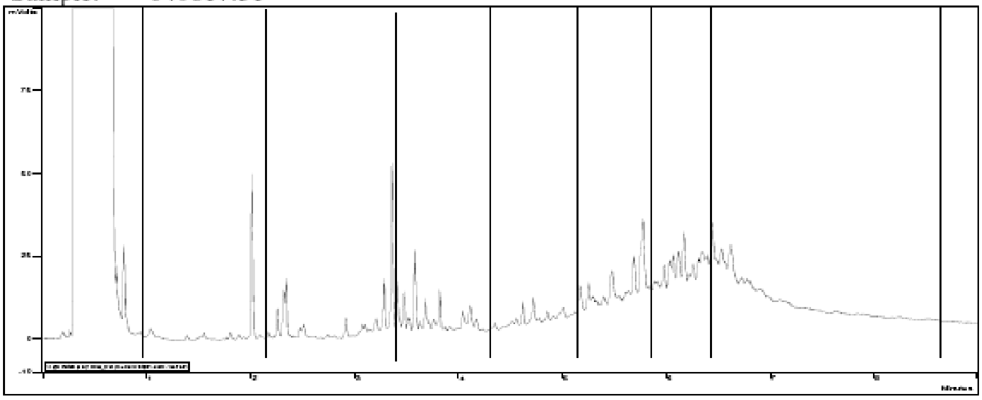

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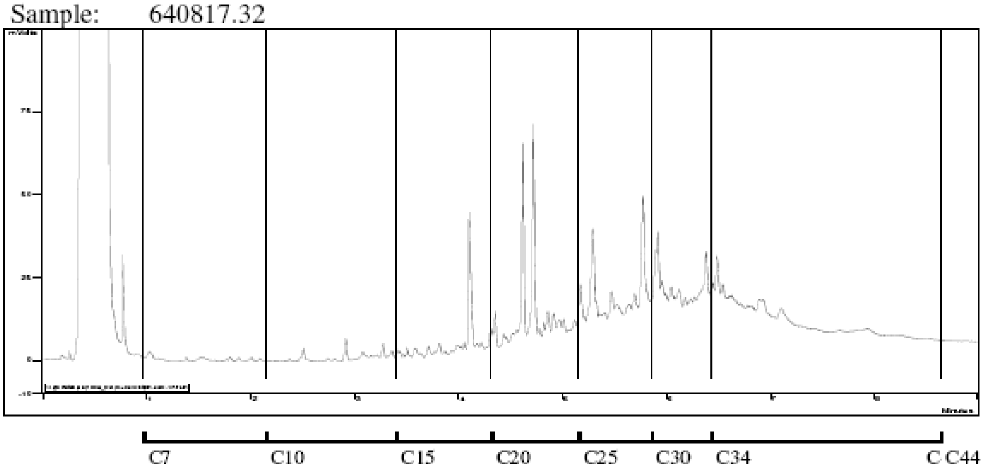
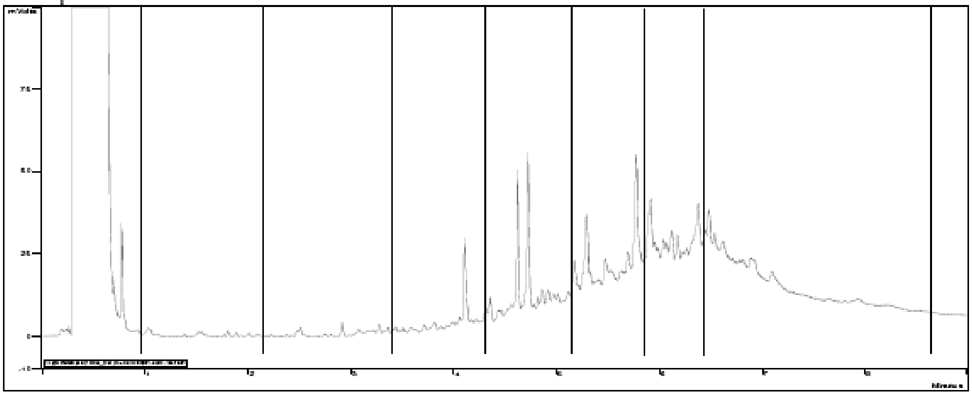


Sample: 640817.33



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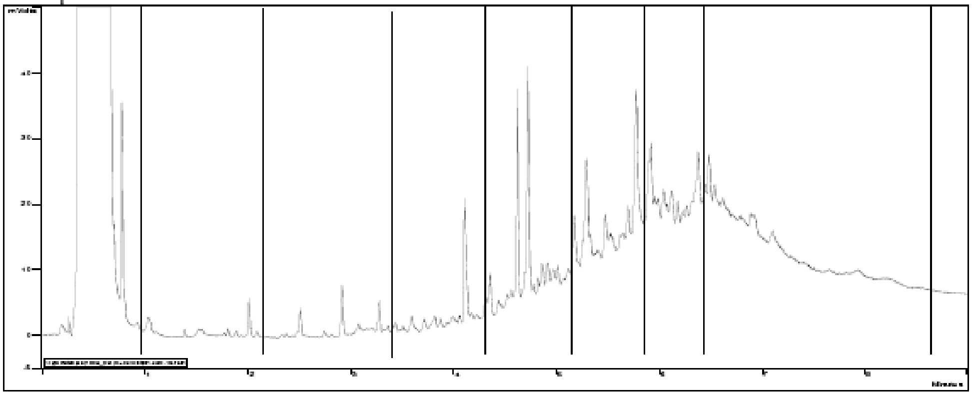
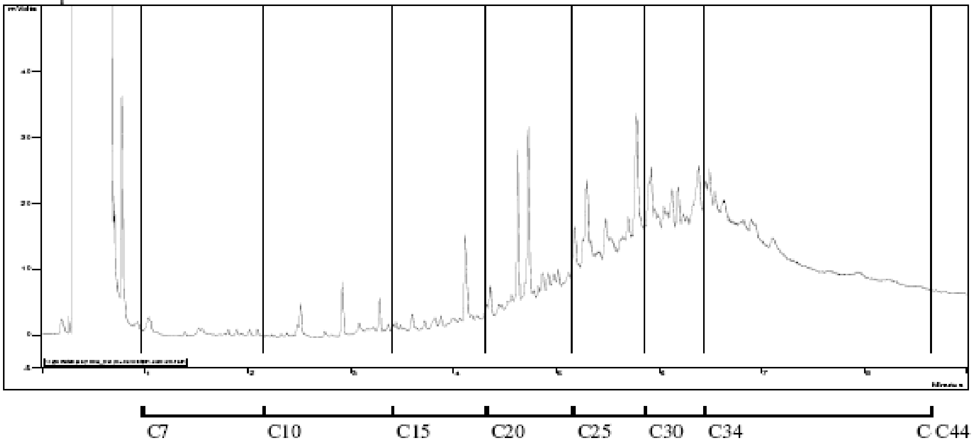


Sample: 640817.35



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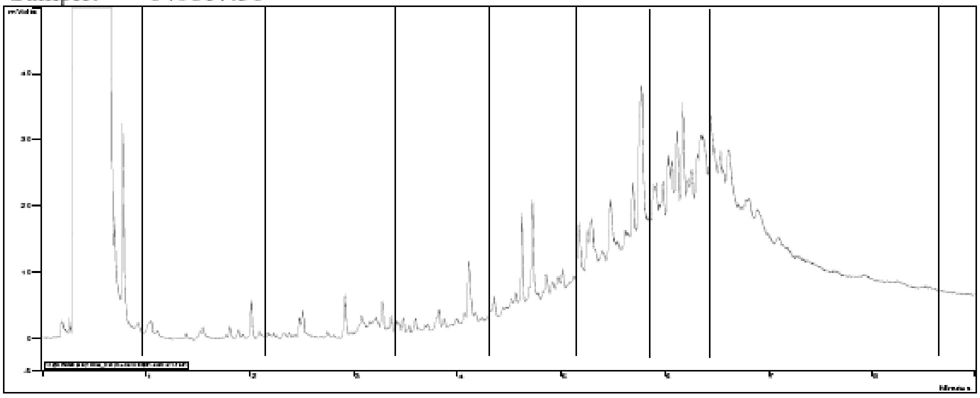

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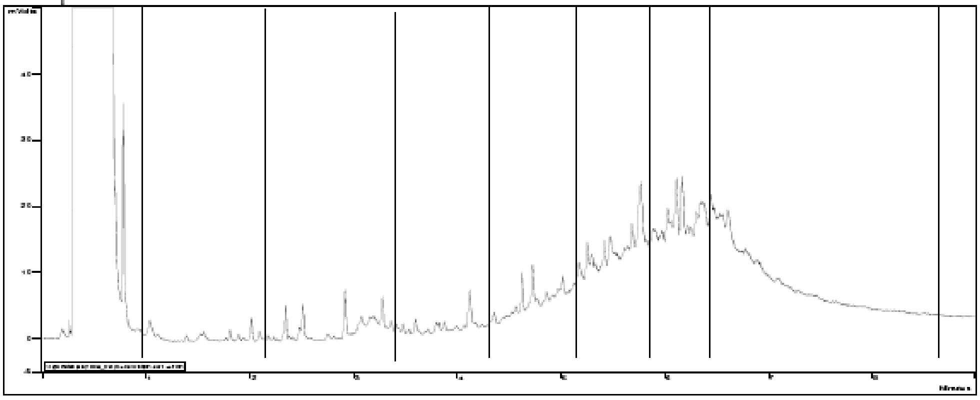

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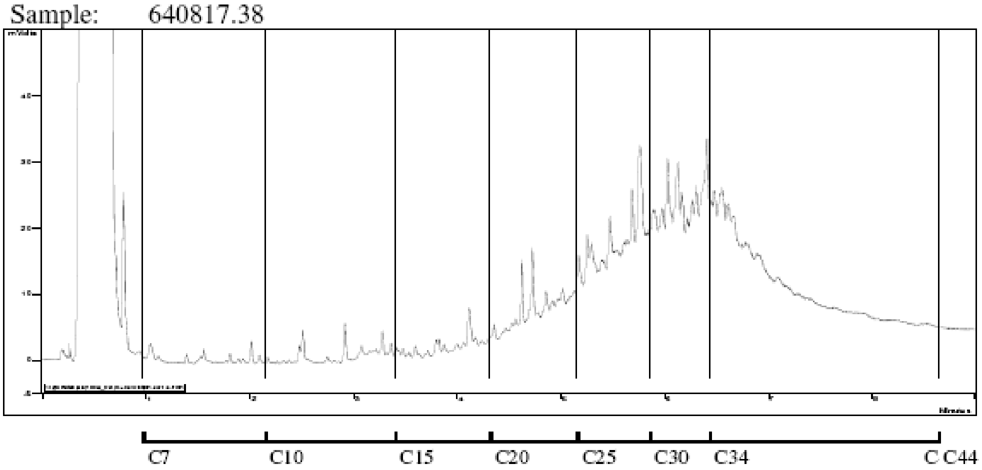

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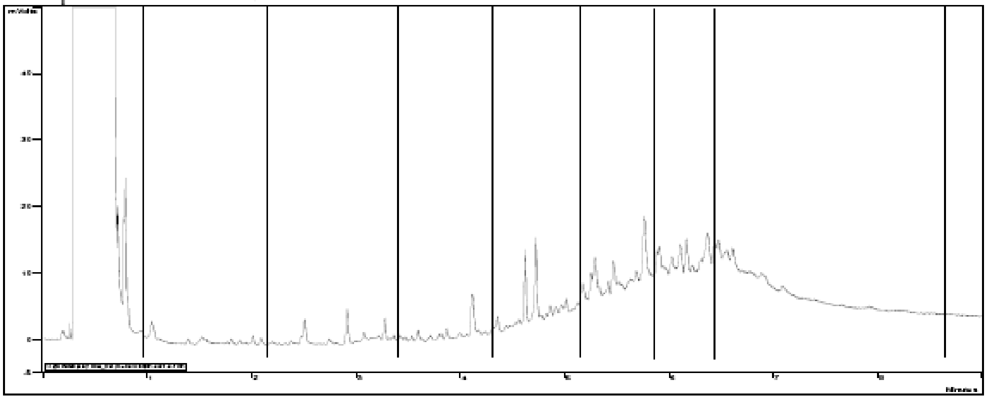
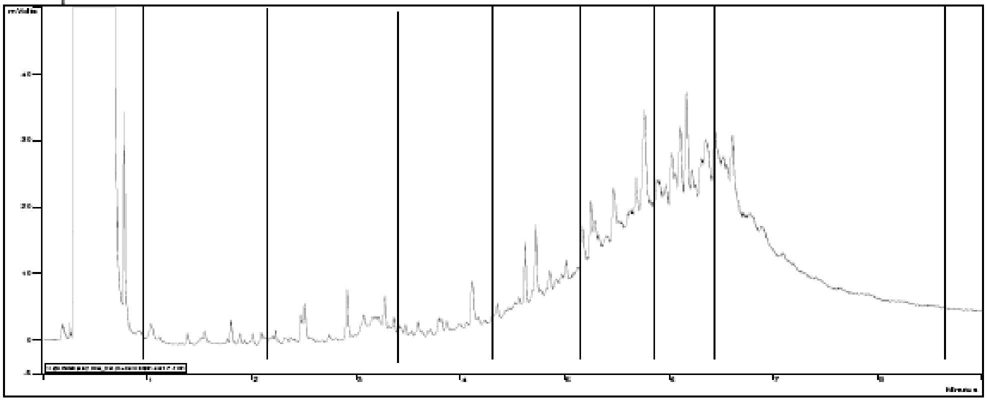
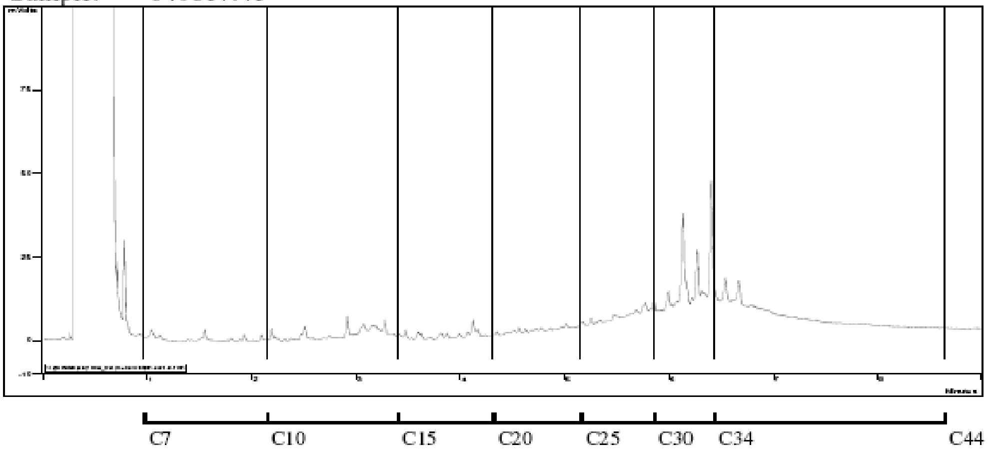


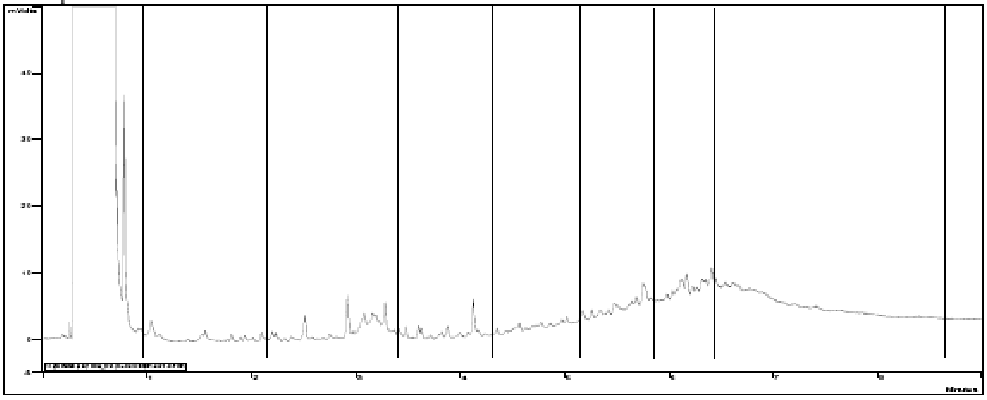
Sample: 640817.40



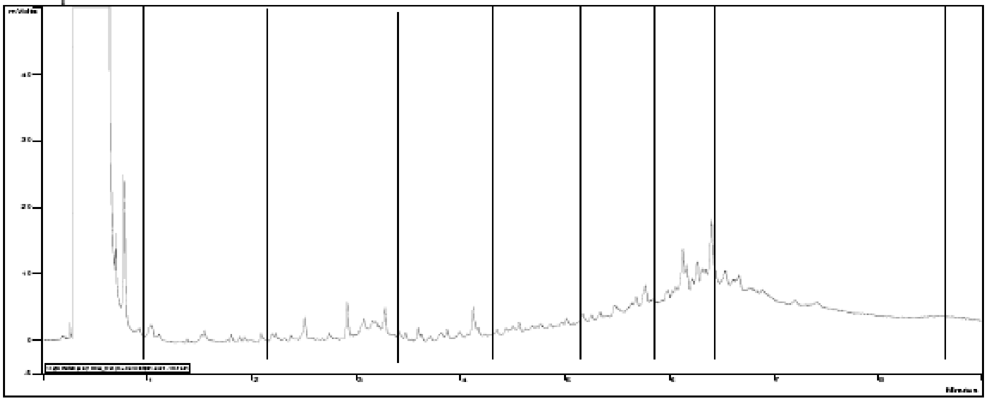
Sample: 640817.41



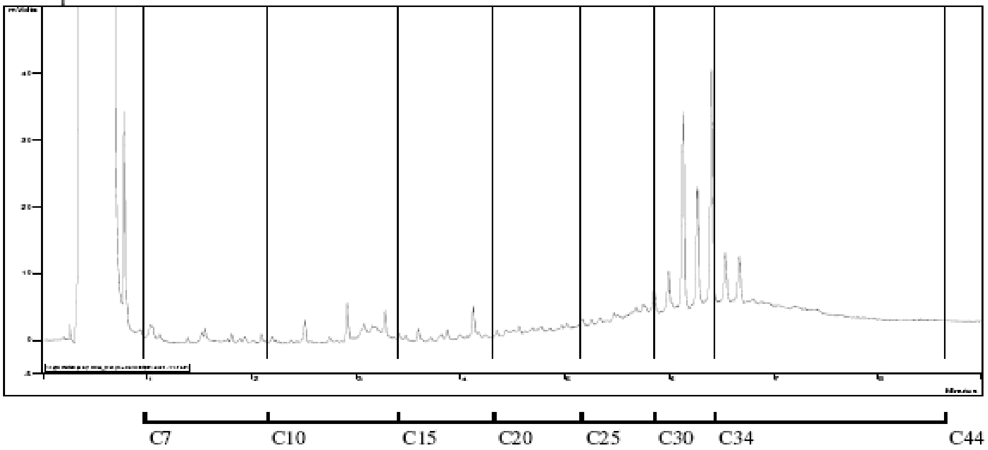
Sample: 640817.42

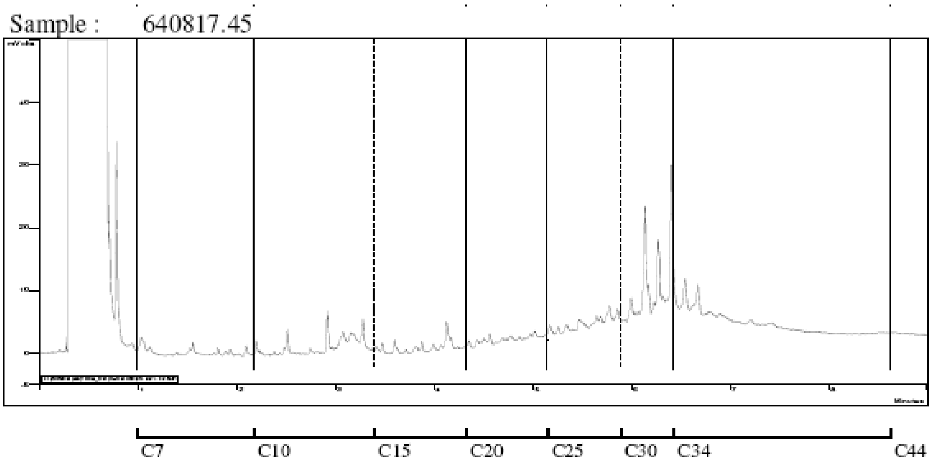


Sample: 640817.43

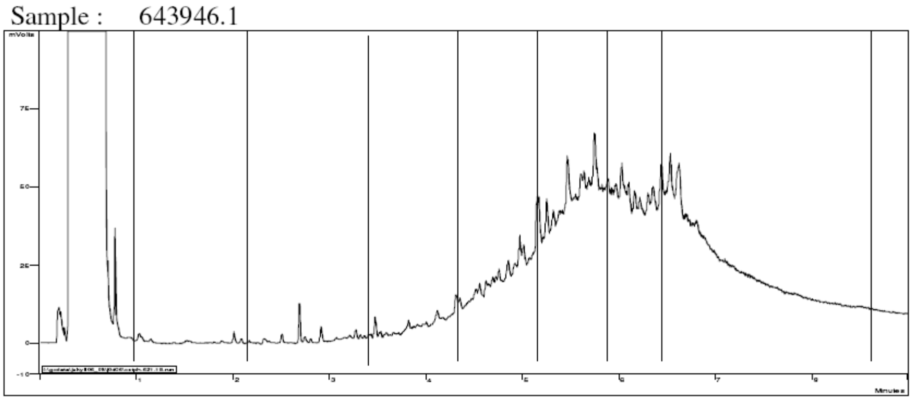


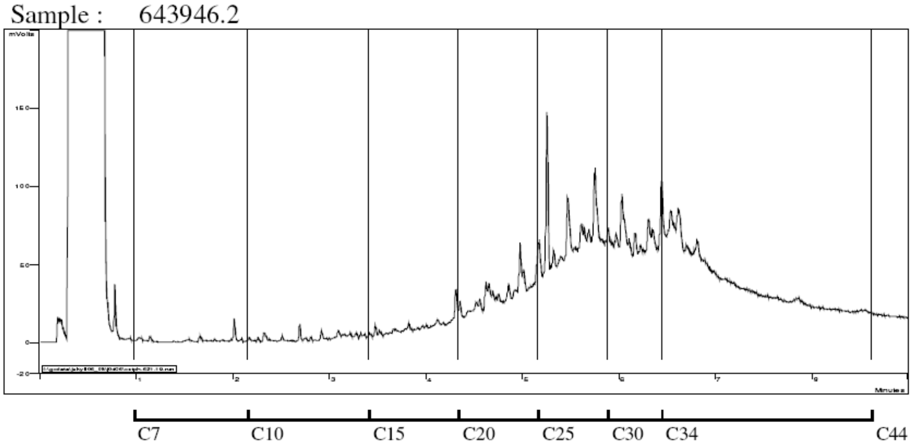
Sample: 640817.44

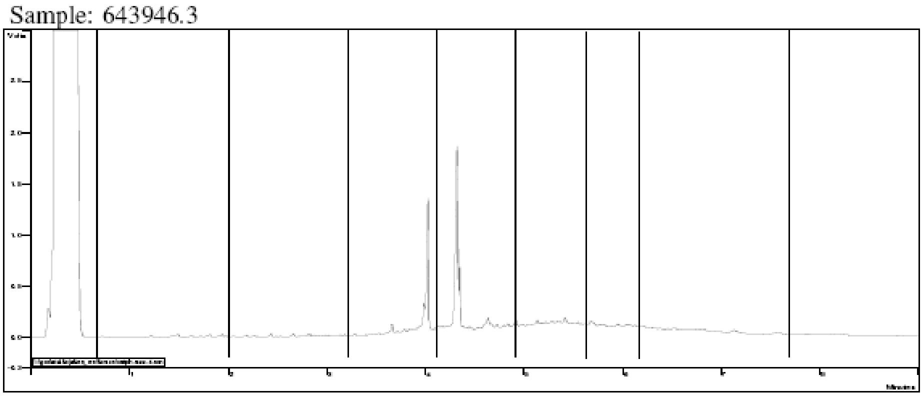



Sample : 640817.45
C7
C10
C15
C20
C25
C30
C34
C44

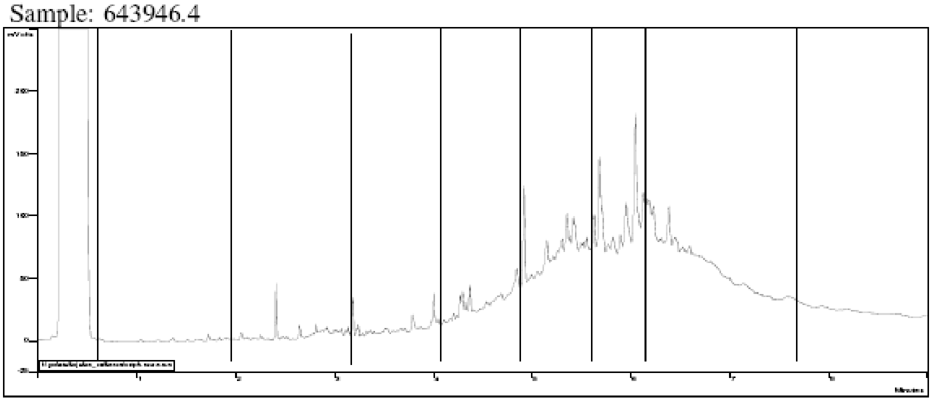
Appendix 3: Hill Laboratory report for TPH, PAH and Hopanes for road-derived sediments (RDS)



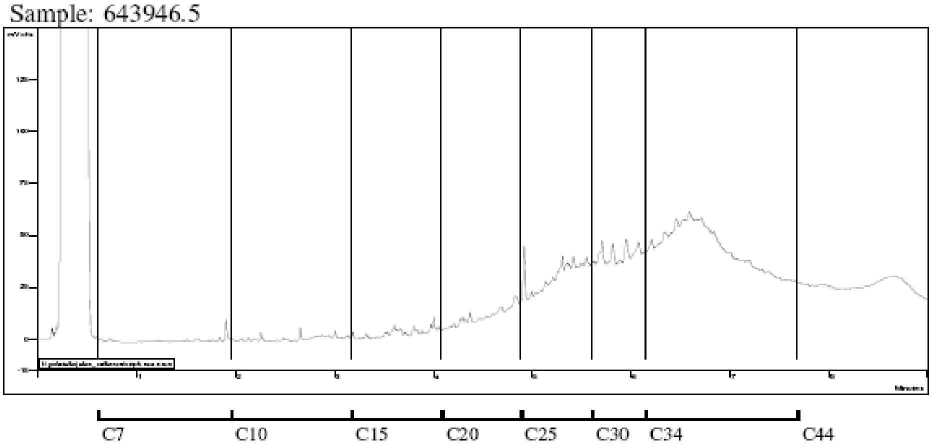




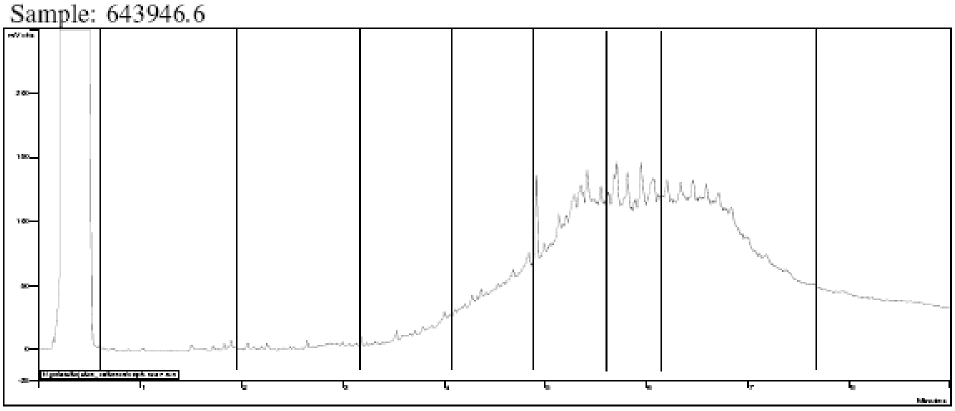
Sample: 643946.4



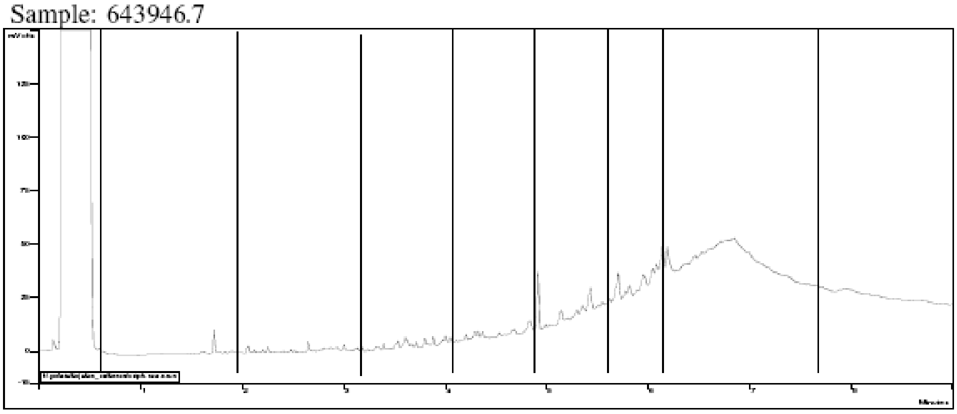
Sample: 643946.5



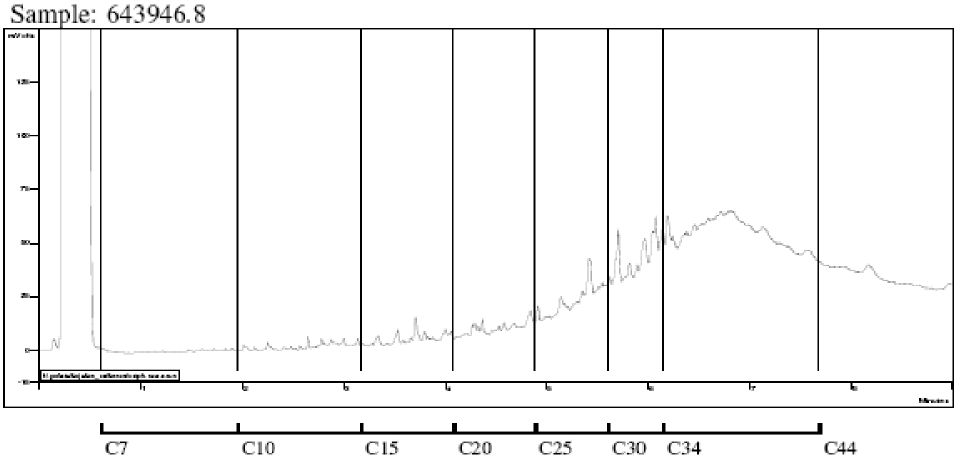
Sample: 643946.6



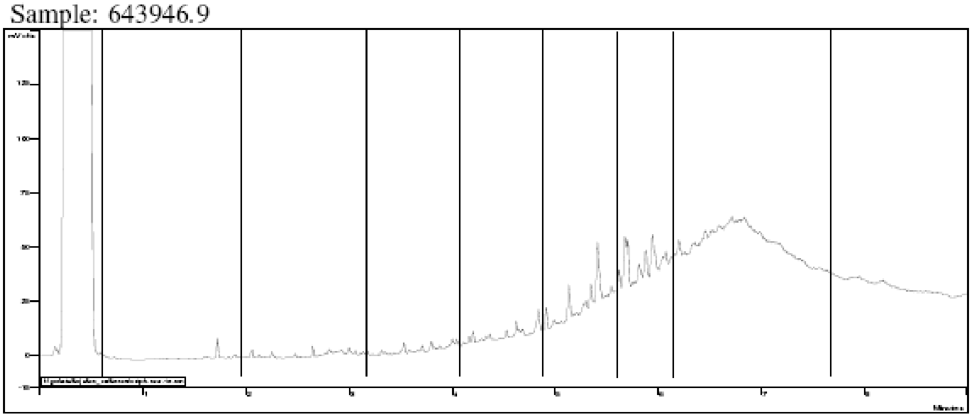
Sample: 643946.7



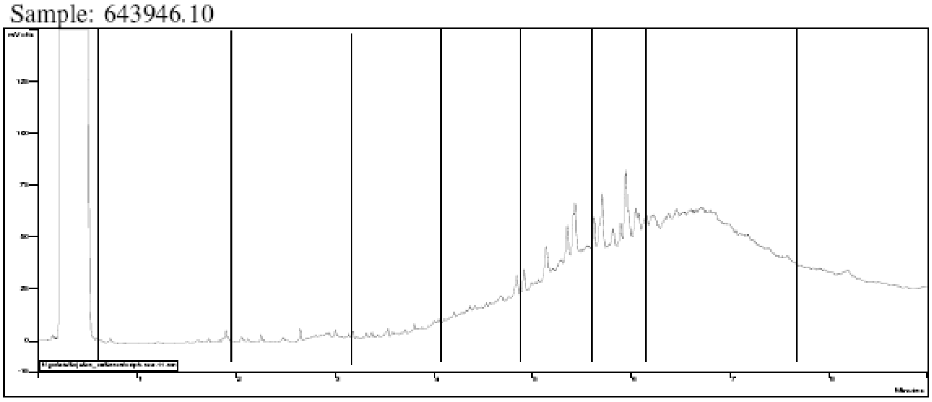
Sample: 643946.8



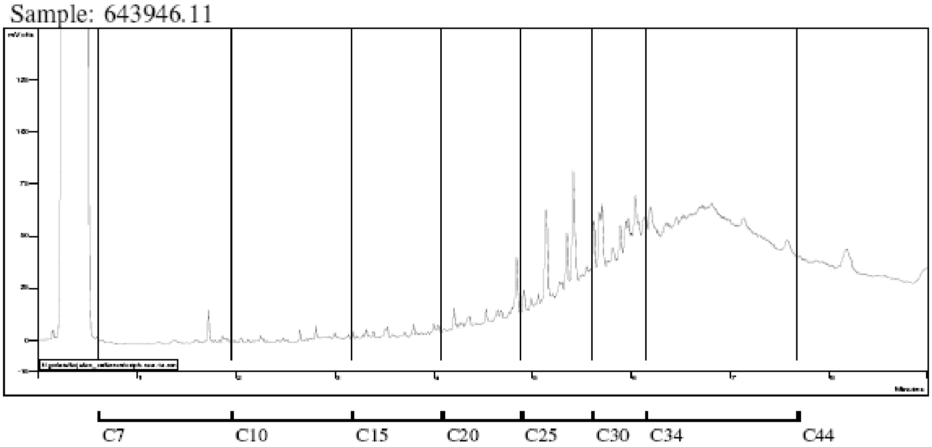
Sample: 643946.9

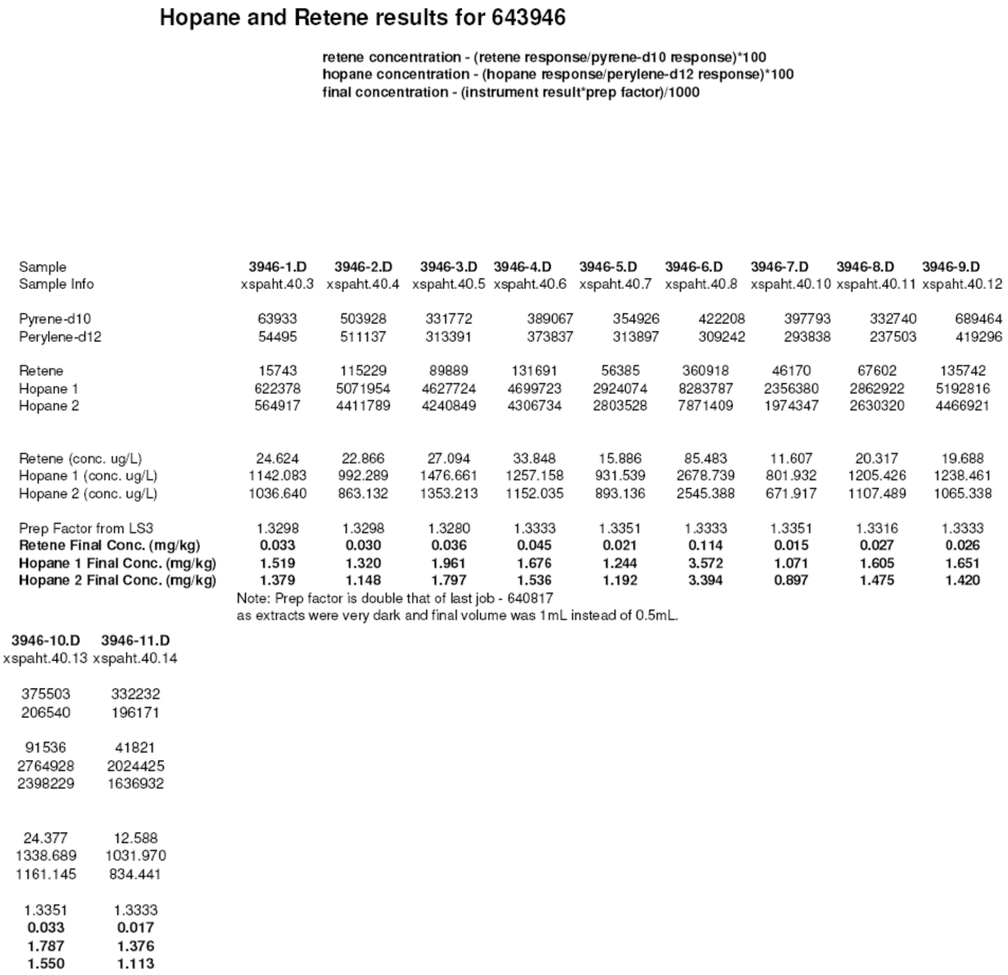


Sample: 643946.10



Sample: 643946.11





Hopane and Retene results for 643946

retene concentration - (retene response/pyrene-d10 response)*100
hopane concentration - (hopane response/perylene-d12 response)*100
final concentration - (instrument result*prep factor)/1000

Sample	**3946-1.D**	**3946-2.D**	**3946-3.D**	**3946-4.D**	**3946-5.D**	**3946-6.D**	**3946-7.D**	**3946-8.D**	**3946-9.D**	**3946-10.D**	**3946-11.D**
Sample Info	xspaht.40.3	xspaht.40.4	xspaht.40.5	xspaht.40.6	xspaht.40.7	xspaht.40.8	xspaht.40.10	xspaht.40.11	xspaht.40.12	xspaht.40.13	xspaht.40.14
Pyrene-d10	63933	503928	331772	389067	354926	422208	397793	332740	689464	375503	332232
Perylene-d12	54495	511137	313391	373837	313897	309242	293838	237503	419296	206540	196171
Retene	15743	115229	89889	131691	56385	360918	46170	67602	135742	91536	41821
Hopane 1	622378	5071954	4627724	4699723	2924074	8283787	2356380	2862922	5192816	2764928	2024425
Hopane 2	564917	4411789	4240849	4306734	2803528	7871409	1974347	2630320	4466921	2398229	1636932
Retene (conc. ug/L)	24.624	22.866	27.094	33.848	15.886	85.483	11.607	20.317	19.688	24.377	12.588
Hopane 1 (conc. ug/L)	1142.083	992.289	1476.661	1257.158	931.539	2678.739	801.932	1205.426	1238.461	1338.689	1031.970
Hopane 2 (conc. ug/L)	1036.640	863.132	1353.213	1152.035	893.136	2545.388	671.917	1107.489	1065.338	1161.145	834.441
Prep Factor from LS3	1.3298	1.3298	1.3280	1.3333	1.3351	1.3333	1.3351	1.3316	1.3333	1.3351	1.3333
Retene Final Conc. (mg/kg)	**0.033**	**0.030**	**0.036**	**0.045**	**0.021**	**0.114**	**0.015**	**0.027**	**0.026**	**0.033**	**0.017**
Hopane 1 Final Conc. (mg/kg)	**1.519**	**1.320**	**1.961**	**1.676**	**1.244**	**3.572**	**1.071**	**1.605**	**1.651**	**1.787**	**1.376**
Hopane 2 Final Conc. (mg/kg)	**1.379**	**1.148**	**1.797**	**1.536**	**1.192**	**3.394**	**0.897**	**1.475**	**1.420**	**1.550**	**1.113**

Note: Prep factor is double that of last job - 640817
as extracts were very dark and final volume was 1mL instead of 0.5mL.