

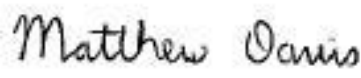


# Investigation of Contaminants in Industrial Stormwater Catchpits

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# Investigation of Contaminants in Industrial Stormwater Catchpits

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## Prepared for

Auckland Regional Council

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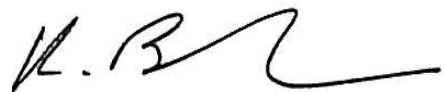
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# 1 Executive Summary

Samples of solids were collected from 19 catchpits from industrial sites in the Whau catchment, Auckland. Sampling locations were selected by Auckland Regional Council staff and were from six industry types: service stations, automotive industries, metal processors, paint manufacturers, plastic manufacturers and timber treatment.

Each catchpit was carefully drained to ensure minimal disturbance of deposited solids. Once drained, a sample was collected from the catchpit using a custom-built long handled auger. This procedure was repeated a number of times until sufficient mass of sample (2 to 5 kg) had been collected.

Bulk samples were sub-sampled and organic contaminants were assessed in sub-samples including total petroleum hydrocarbons, PAHs, phenols, and a screen for 79 semi-volatile organic compounds. A second sub-sample from each bulk samples was wet sieved into > 10 mm, 1 mm–10 mm and < 1 mm fractions. Following visual characterisation, material > 10 mm was excluded from further analyses. The < 1 mm fraction was further sieved into 0.5 – 1.0 mm, 0.2–0.5 mm and < 0.2 mm fractions for metal analysis. The metals analysed depended on the industry type and included aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, tin, zinc. Three catchpits were sampled twice and three other samples were split in order to provide information on the variability of results arising as part of the sample collection and processing methods.

The particle size distribution of the catchpit solids was extremely variable. The coarsest (1 mm – 10 mm) particle size fraction measured ranged from 10% to 64% of the total dry weight of samples. The finest (< 0.2 mm) particle size fraction constituted between 5% and 74%.

Within each sample, the highest metal concentrations most frequently occurred in the finest particle size fraction (< 0.2 mm) compared to the coarser fractions. For four samples, either copper, lead and/or cadmium was highest in the coarsest size fraction analysed (0.5 – 1.0 mm).

Zinc concentrations were 330 to 5,300 mg kg<sup>-1</sup> in 15 / 18 catchpits. Highest concentrations (18,000 to 94,000 mg kg<sup>-1</sup>) were measured in a sample from an automotive industry site. Very high concentrations were also measured in the fine fractions from a service station catchpit (9,200 mg kg<sup>-1</sup>) and from a metal processing site (17,000 mg kg<sup>-1</sup>).

Copper concentrations were 75–3,700 mg kg<sup>-1</sup> in most catchpit samples. Copper concentrations of 16,000–160,000 mg kg<sup>-1</sup> were measured in catchpits from an automotive industry and from a metal processing site.

Lead ranged from 86 to 5,200 mg kg<sup>-1</sup> with highest concentrations in solids from a metal processors and an automotive site, consistent with the elevated zinc and copper concentrations in solids from these catchpits.

Cadmium concentrations were 305 – 510 mg kg<sup>-1</sup> in fractions from a plastic manufacturers catchpit. In all other catchpits concentrations were 0.25 to 31 mg kg<sup>-1</sup>.

Mercury ranged from 0.021 to 0.71 mg kg<sup>-1</sup>, chromium from 84 to 3,000 mg kg<sup>-1</sup> and arsenic from 62 to 510 mg kg<sup>-1</sup>. Selenium was not detected in the solids analysed with a detection limit of 2.0 mg kg<sup>-1</sup>. Aluminium, nickel, silver and tin were measured in samples from the metal processors only, with one sample containing nickel, silver and tin at up to an order of magnitude higher concentrations compared to the other two samples.

All samples contained TPH in excess of 1000 mg kg<sup>-1</sup>, and five samples contained Total Petroleum Hydrocarbons (TPH) concentrations in excess of 10,000 mg kg<sup>-1</sup>. TPH was dominated by the C15-C36 fraction, comprising 88–100% of total TPH in all but one sample.

Of 18 samples tested, 16 contained at least one Semi-volatile organic compounds (SVOC) and most of these were Polycyclic Aromatic Hydrocarbons (PAHs). PAHs were exceptionally high in a sample from a service station, measuring 2620 mg kg<sup>-1</sup> dry weight (total of 16 PAHs). Phenols were detected in several samples and Pentachlorophenol (PCP) was not detected in the timber yard catchpit solids.

The analytical results for the paired samples, split at the sample collection and processing stages, generally varied by 20 – 60%, depending on parameter. This is not unexpected due to the heterogeneous nature of the samples. The difference between different samples was generally much greater than the difference between sample duplicates, particularly for the metal analyses.

## 2 Introduction

### 2.1 Overview

Stormwater from industrial sites has the potential to contain high concentrations of contaminants. When rain water washes over impervious surfaces, it collects deposited dust and debris, and associated contaminants, and transports them into the stormwater system. When not appropriately controlled or bundled, leaks and spills of industrial chemicals and petroleum products can also release contaminants into the stormwater system.

The contaminants present in the stormwater will reflect the materials used, substances stored, and activities undertaken, on the site. While the types of contaminants found in stormwater from different industrial activities can be speculated based on international studies, there has been little investigation of industrial stormwater within New Zealand.

The concentrations of common stormwater contaminants (copper, lead, zinc, and petroleum hydrocarbons) have recently been assessed in catchpits from a number of roads (Depree 2008; Moores et al., 2007, 2009). Catchpits are a standard component of most stormwater networks. They are the point to which stormwater running off roads, driveways and other impervious surfaces is collected and discharged to the reticulated pipe network. In addition to their role in the conveyance of stormwater, catchpits also provide for the removal of solids and associated contaminants from runoff prior to its discharge to the pipe system. An assessment of the contaminant types and concentrations in these catchpit solids can therefore provide information on the likely contaminants, and relative concentrations, being discharged into the stormwater system.

### 2.2 Project Scope

This report describes a pilot study to investigation contaminants in samples of solids collected from industrial catchpits in Auckland. The objectives of the study are to collect solids from catchpits located on different industrial sites representing a range of industry types and to determine the:

- ❑ particle size distribution;
- ❑ concentrations of a range of metals including common stormwater contaminants (copper, lead and zinc) and those specific to different industry types;
- ❑ concentrations of petroleum hydrocarbons, including Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs);
- ❑ concentrations of organic contaminants specific to different industry types such as pentachlorophenol (PCP); and



- occurrence of a range of common organic contaminants including pesticides and plasticisers.

The output of the study is a set of results which will aid in understanding the contaminants discharged from different industrial activities in the Auckland region.

## 3 Methods

### 3.1 Sampling Locations

Eight industries were identified for the assessment of catchpit contaminants based on a review of relevant information and discussions between ARC and NIWA. These were as follows:

- (a) metal processing,
- (b) automotive (car wreckers, repair workshops, battery manufacture),
- (c) service stations,
- (d) timber treatment plants,
- (e) tanneries,
- (f) paint manufacturers,
- (g) plastics manufacturers, and
- (h) lighting manufacturers.

The industrial sites are located within the Whau River catchment.. Potential sampling locations were selected by the ARC based on a desktop review of industrial sites within the catchment. ARC and NIWA staff then visited these sites to investigate the location of catchpits, determine the feasibility of collecting samples and to gain land owner approval.

Three catchpits were sampled for most industry types and six were sampled for the automotive industry (automotive dismantlers, panelbeaters etc), due to the large number of these sites in the catchment. No timber treatment sites were located within the Whau River catchment area, and therefore a catchpit from a timber yard (where timber is stored and sold) was sampled for this industry type. There were no tanneries or lighting manufacturers located within the study area and therefore no samples were collected for these industry types. In total, samples were collected from 19 catchpits receiving stormwater from the six different industries. Table 1 provides a summary of the catchpits sampled.

**Table 1**

Industry types for the catchpits sampled.

Industry type	Number of catchpits sampled	Catchpit Sample Numbers
Service Station	3	4, 8, 19
Automotive	6	5, 7, 9, 12, 14, 18
Metal Processing	3	1, 2, 11
Paint Manufacturers	3	3, 15, 17
Plastics	3	6, 10, 16
Timber	1	13

## 3.2 Sample Collection

Samples were collected on 16 April 2009, following a period of three dry days<sup>1</sup>. Samples were collected at each of the selected catchpits using the procedure described below.

Where necessary, the catchpit was drained with a 2 inch pump fitted with a custom-built plate over the pump hose inlet (in most cases the catchpits were relatively dry and did not require draining prior to sample collection). The plate was placed upon the upper surface of the settled catchpit solids and provided for removal of water without disturbance of the solids. The catchpit was drained until a maximum of 10-20 mm depth of water remained above the deposited solids. Figure 1 shows the pump hose and plate attachment being lowered into a catchpit and the contents of the catchpit following completion of pumping.

**Figure 1**

(a) Pump inlet hose and plate attachment being lowered into a catchpit, and (b) contents of a catchpit on completion of pumping.



Once drained, a sample was collected from the catchpit using a custom-built long handled auger. By rotating the auger it was possible to penetrate to the base of the catchpit with relatively little disturbance of the settled solids. The auger was then gently lifted to remove a sample of the full profile of deposited solids. Figure 2 shows the auger before and after sampling. This procedure was repeated a number of times until sufficient mass of sample (2-5 kg) had been collected. Care was taken to ensure repeat sub-samples were well distributed across the surface of the deposited solids. A second complete sample was taken from three of the catchpits to assess variability in the characteristics of solids within these catchpits (see section 3.5).

Sampling equipment was thoroughly rinsed with clean water following completion of sampling at each site. The samples were placed in acid washed plastic tubs with lids and transferred to NIWA's Auckland laboratory, where they were weighed and then stored at 4 °C, prior to sample processing.

<sup>1</sup> Based on rainfall recorded at ARC rainfall gauges at Oratia @ Essex St (approximately 1 km west of Whau River estuary) and Whau @ New Lynn (approximately 2 km south of Whau River estuary).

**Figure 2**

(a) Sampling auger before sampling, and (b) with a sample of catchpit solids.



### 3.3 Sample Processing

The sample processing method broadly followed that used in the assessment of contaminants in roadside catchpits (Moore et al., 2007; 2009)

The method involved the following steps. Note that all laboratory equipment was pre-washed in acid baths, unless indicated otherwise.

Sub-samples were prepared for analysis of organic contaminants by transferring the entire sample into a large shallow plastic bowl, mixing to homogenise it and collecting a sub-sample of approximately 200-300 g. This was dispatched to Hill Laboratories, Hamilton for organic analyses (see Section 3.4) and the remainder of the sample was returned to the refrigerator until required for further processing.

For particle size distribution and metal analyses, the sample was again transferred into a large shallow plastic bowl and was photographed (see Appendix 1) before being mixed thoroughly to make the sample matrix more homogeneous. A sub-sample of approximately one-quarter of the total volume of the sample was taken and wet-sieved through a 10 mm plastic sieve. The remainder of the sample was stored at  $< 4^{\circ}\text{C}$ .

This separated the sub-sample into two fractions, one with solids  $> 10\text{ mm}$  in diameter and one  $< 10\text{ mm}$ . A visual assessment of the contents of both of these two sub-samples was recorded (see Appendix 1).

The  $< 10\text{ mm}$  fraction was then further subsampled and approximately one-quarter of that volume was further wet-sieved. The remainder was transferred to an aluminium foil tray and oven dried at  $55 - 60^{\circ}\text{C}$ . When dry, these were weighed to determine the particle size distribution.

The  $< 1\text{ cm}$  subsample was further wet-sieved into the following four fractions:  $1 - 10\text{ mm}$ ,  $0.5 - 1\text{ mm}$ ,  $0.2 - 0.5\text{ mm}$  and  $< 0.2\text{ mm}$ . Each of these fractions was transferred to one or more glass jars and oven dried at  $55-60^{\circ}\text{C}$ . Once dry, each sample fraction was weighed to determine the particle size distribution. The three fractions finer than  $1\text{ mm}$  ( $0.5 - 1\text{ mm}$ ,  $0.2 - 0.5\text{ mm}$  and  $< 0.2\text{ mm}$ ) were then ground

using a mortar and pestle and a homogenised sub-sample of  $1 \pm 0.001$  g was taken for analysis of metal concentrations. Unused portions of each sample were archived for any repeat or future analyses.

### 3.4 Sample Analyses

References for the following analytical methods can be obtained from Hill Laboratories.

#### 3.4.1 Overall Scheme

Each sample was analysed for a different suite of chemical contaminants, depending on the type of industry from which it was sourced, as listed in Table 2.

**Table 2**

Parameters analysed in samples by industry type.

Parameters	Industry type					
	Metal Processing	Paint Manufacturers	Service Station	Automotive	Plastics	Timber Treatment
<b>Metals/ metalloids</b>						
Al	x					
Ag	x					
As						x
Cd	x	x			x	
Cr	x					x
Cu	x	x	x	x		x
Hg	x			x		
Ni	x					
Pb	x		x	x		
Se		x				
Sn	x					
Zn	x	x	x	x	x	
<b>Petroleum hydrocarbons</b>						
PAH		x	x	x		
TPH		x	x	x	x	
<b>Semi-volatile organics</b>						
PCP						x
Phenols	x	x				x
SVOC screen *	x	x	x	x	x	

\* Screen of 79 semi-volatile contaminants. See Section 3.4.4 for details.

#### 3.4.2 Metals

Samples of the three fractions < 0.2 mm, 0.2 – 0.5 mm and 0.5 – 1.0 mm were analysed for metal concentrations (refer to Table 2 for specific suites) at Hill Laboratories in Hamilton. Briefly, metals were extracted using USEPA Method 200.2

for Total Recoverable Digestion and analysed by inductively coupled plasma-mass spectrometry (ICP-MS). Hill Laboratories are accredited by International Accreditation New Zealand (IANZ) for these analyses in conformance with standard NZS/ISO/IEC 17025: 2005.

### 3.4.3 Total Petroleum Hydrocarbons

Samples were analysed for TPH concentrations at Hill Laboratories (Hamilton) following method US EPA 8015B and the MfE Petroleum Industry Guidelines. Samples were extracted by sonication, then subjected to silica clean-up before analysis by gas chromatography – flame ionization detection (GC-FID). This method characterises the concentrations of hydrocarbons in each of a number of different carbon chain length ranges (C7–C9, C10–C14, C15–36) and in total (C7–C36). Hill Laboratories are accredited by IANZ for these analyses in conformance with standard NZS/ISO/IEC 17025: 2005.

### 3.4.4 SVOC Screen

All catchpit samples excluding those from the timber site were screened for a suite of 79 semi-volatile organic compounds (SVOCs) including organochlorine pesticides, plasticisers, haloethers, phenols and polycyclic aromatic hydrocarbons (PAHs). Samples were extracted by sonication, subjected to GPC cleanup and analysed by GC-MS (full-scan). Detection limits vary for each compound, and each sample, because detection limits depend on the dry weight of sample used (refer to Tables 9-10 for compounds detected in these samples, full list provided in Appendix 2). The in-house method is a modification of USEPA 8270 and Hill Laboratories are accredited by IANZ for this analysis.

### 3.4.5 PAHs

Catchpit samples from service station, automotive and paint manufacturers were assessed for PAHs at lower detection limits ( $0.0020 - 0.024 \text{ mg kg}^{-1}$ ) than that used in the SVOC screen ( $0.1 - 1.4 \text{ mg kg}^{-1}$ ). Samples were extracted by sonication, subjected to SPE cleanup, and analysed by GC-MS-SIM, following US EPA Method 8270C. Hill Laboratories are accredited by IANZ for this analysis in conformance with standard NZS/ISO/IEC 17025: 2005.

### 3.4.6 Total Phenols

Catchpit samples from paint manufacturers, timber and metal processors were assessed for total phenols (detection limit  $0.20 \text{ mg kg}^{-1}$  dry weight). Samples were extracted by macrodistillation, following Bran + Luebbe Method No. 127-71W and APHA 5530 B, C & D (modified) 21st ed. 2005. Total phenols were quantified by segmented flow colorimetry. This analytical method does not detect 4-methylphenol,

however that phenol is included in the SVOC suite. This test is accredited by IANZ in conformance with standard NZS/ISO/IEC 17025: 2005.

### 3.4.7 PCP

Samples from the timber industry catchpit were analysed for pentachlorophenol (PCP) and 2,3,4,6-tetrachlorophenol (TCP) by LC-MS-MS after solvent extraction with sonication, dilution and online SPE (detection limit 0.05 mg kg<sup>-1</sup> dry weight). This test is not currently accredited by International Accreditation New Zealand.

## 3.5 Quality Assurance

The quality assurance programme for this project included duplicate samples at the following stages:

- ❑ Sample collection;
- ❑ Sample processing.

This is summarised in Table 3. Duplicate samples prepared by processing separate sub-samples from the same catchpit sample were submitted blind to the analytical laboratory.

The analytical laboratory has their own quality assurance and quality control programme for the analyses which can be provided on request.

**Table 3**

Summary of sample replication.

Replication	Catchpit Sample Number	Industry type
Two samples collected from catchpit	8	Service Station
	18	Automotive
	17	Paint Manufacturers
Sample split during processing	4	Service Station
	10	Plastics
	13	Timber

## 4 Results

### 4.1 Particle size distribution

The proportion of solids by dry weight in the four particle size classes 1 mm – 10 mm, 0.5 – 1 mm, 0.2 – 0.5 mm and < 0.2 mm are reported in Table 4. Figures 3 and 4 present the results as a particle size distribution for solids less than 10 mm.

**Table 4**

Proportion of catchpit sample solids in particle size classes 1 mm – 10 mm, 0.5 – 1 mm, 0.2 – 0.5 mm and < 0.2 mm.

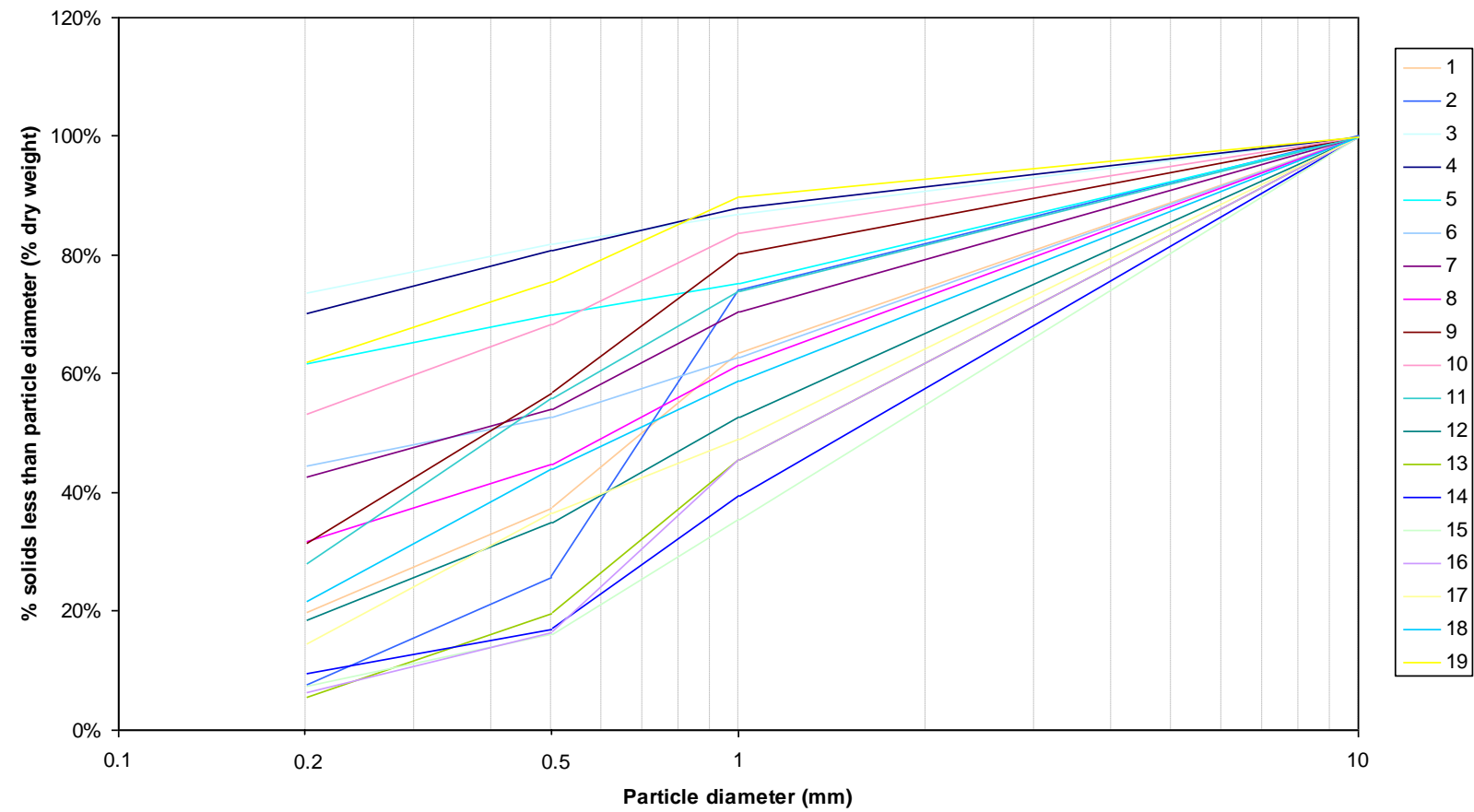
Industry type	Sample No.	Proportion of total solids by dry weight			
		< 0.2 mm	0.2 – 0.5 mm	0.5 – 1 mm	1 mm – 10 mm
Automotive	5	62%	8%	5%	25%
	7	43%	11%	17%	30%
	9	32%	25%	24%	20%
	12	18%	17%	18%	47%
	14	10%	7%	23%	61%
	18	22%	22%	15%	41%
Service Station	4	70%	11%	7%	12%
	8	32%	13%	17%	39%
	19	62%	13%	15%	10%
Paint Manufacturers	3	74%	8%	5%	13%
	15	7%	9%	19%	64%
	17	14%	22%	13%	51%
Plastics Manufacturers	6	44%	8%	10%	37%
	10	53%	15%	15%	16%
	16	6%	10%	29%	54%
Metal Processors	1	20%	17%	26%	36%
	2	8%	18%	49%	26%
	11	28%	28%	18%	26%
Timber	13	5%	14%	26%	54%

The proportion of solids with a particle size of 1 -10 mm lies in the range 10 to 61%. Samples with a relatively high proportion of these coarse solids were taken from catchpits 14 (automotive industry), 15 and 17 (paint manufacturers), 16 (plastic manufacturers) and 13 (timber treatment). The coarse (1 – 10 mm) fraction in samples from these catchpits constitutes more than half of the total dry weight of the sample. Samples collected from catchpits 4 and 19 (service stations), 3 (paint manufacturers) and 10 (plastic manufacturers) had the lowest proportion of coarse solids (all less than 20%). So while there is a great deal of difference, this difference is not industry related.



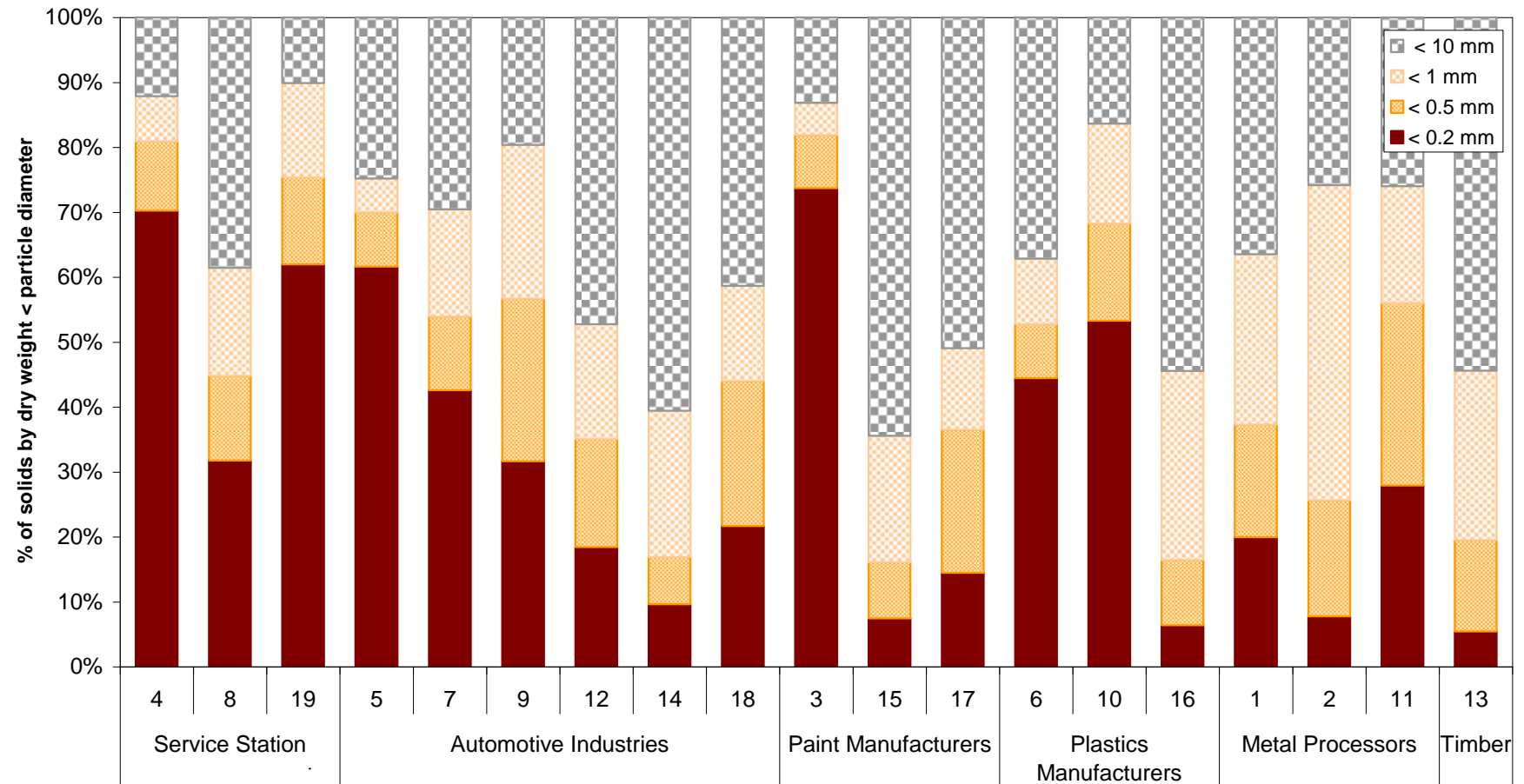
**Figure 3**

*Particle size distribution of catchpit solids samples, < 10 mm fraction.*



**Figure 4**

Particle size distribution of catchpit solids samples by industry (< 10 mm fraction).



With the exception of catchpit 2, the proportion of catchpit material with a particle size of 0.5 – 1 mm and 0.2 – 0.5 mm ranged from 5 to 29% and 8 to 28%, respectively. Catchpit 2 was from a metal processing site, and contained a higher proportion of sand-sized particles, with ca. 50% between 0.5 – 1 mm.

The proportion of solids with diameter less than 0.2 mm was between 5 and 74%. In five catchpit samples, this fraction comprised more than half of the total dry weight of the sample. These were samples 5 (automotive industry), 4 and 19 (service stations), 3 (paint manufacturers), and 10 (plastic manufacturers). In four samples, the fine sediments comprised 10 % or less of the total dry weight of the sample.

## 4.2 Metals

Concentrations of copper, lead and zinc in the 0.5 – 1 mm, 0.2 – 0.5 mm and < 0.2 mm fractions of each sample are presented in Table 5 and Figures 5 to 7.

The results indicate a wide variation in metal concentrations, between and within industry types. For example, across all industries and sediment fractions, copper concentrations ranged from 75 mg kg<sup>-1</sup> to 160,000 mg kg<sup>-1</sup>. Within each sample the highest metal concentrations most frequently occurred on the fine size fraction (< 0.2 mm) and the lowest concentrations on the coarse fraction (0.5 – 1 mm) with the middle fraction at intermediate concentrations. This is best demonstrated by mercury, where all samples follow this pattern, while for all other metals, there are noticeable exceptions to this pattern.

Zinc was measured in samples from all industries except the timber yard site (total of 18 catchpits) and ranged from 330 to 94,000 mg kg<sup>-1</sup> (Figure 5). The highest concentrations were measured in sample 14, from an automotive industry site, and ranged from 18,000 mg kg<sup>-1</sup> in the coarse fraction (0.5 – 1 mm) to 94,000 mg kg<sup>-1</sup> in the fine fraction (< 0.2 mm). Very high concentrations were also measured in the fine fraction from catchpit 19, a service station (9,200 mg kg<sup>-1</sup>) and catchpit 1, from a metal processing site (17,000 mg kg<sup>-1</sup>). In all other catchpits, the concentrations were between 330 and 5,300 mg kg<sup>-1</sup> and were typically at highest concentration in the fine sediment fractions. There was no consistent pattern in zinc concentrations for the different industry types, though the three plastic manufacturing sites contained zinc at the lower end of the range measured. However, catchpit solids from automotive industry sites contained both the highest (catchpit 14) and lowest (catchpit 7) zinc concentrations, suggesting a wide range of industrial and stormwater practices within this industry group.

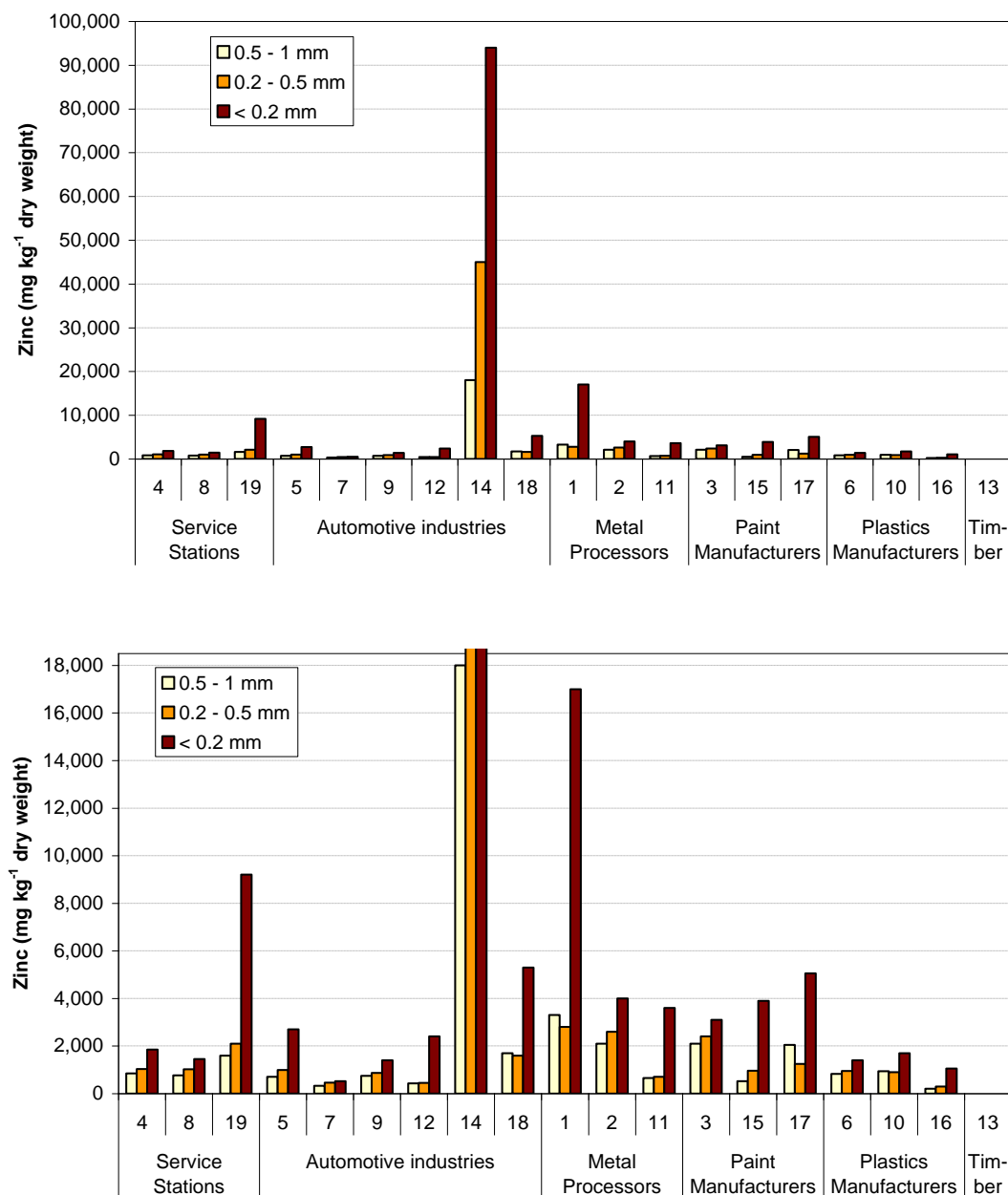
Zinc concentrations in some of these industrial catchpit samples were up to 10-fold higher than previously measured in road-side catchpit samples (Moores et al., 2007). In samples from road-side catchpits in Auckland, the highest zinc concentrations were 1380 mg kg<sup>-1</sup> in the 0.5 – 1 mm fraction, 480 mg kg<sup>-1</sup> in the 0.2 – 0.5 mm fraction and 1340 mg kg<sup>-1</sup> in the < 0.2 mm fraction and most samples contained less than 500 mg kg<sup>-1</sup> of zinc (Moores et al., 2007).

**Table 5**Copper, lead and zinc in samples of catchpit solids (mg kg<sup>-1</sup> dry weight).

Industry	Sample Number	Zinc			Copper			Lead		
		0.5-1 mm	0.2-0.5 mm	< 0.2 mm	0.5-1 mm	0.2-0.5 mm	< 0.2 mm	0.5-1 mm	0.2-0.5 mm	< 0.2 mm
Service Station	8	850	1,030	1,900	245	225	340	86	96	210
	4	765	1,020	1,500	395	395	410	240	285	395
	19	1,600	2,100	9,200	210	230	550	140	130	280
Automotive	5	710	990	2,700	240	510	540	400	300	500
	7	330	460	520	140	290	270	93	180	180
	9	750	870	1,400	300	410	630	260	320	440
	12	430	450	2,400	310	250	550	640	280	660
	14	18,000	45,000	94,000	22,000	69,000	160,000	1,200	1,500	3,700
	18	1,700	1,600	5,300	3,000	710	830	2,200	910	1,500
Metal Processing	1	3,300	2,800	17,000	16,000	15,000	50,000	1,500	720	5,200
	2	2,100	2,600	4,000	3,700	1,000	1,100	660	610	920
	11	650	710	3,600	290	190	540	320	480	590
Paint Manufacturers	3	2,100	2,400	3,100	190	190	320	-	-	-
	15	520	960	3,900	75	340	1,100	-	-	-
	17	2,050	1,250	5,100	405	625	635	-	-	-
Plastics	6	830	950	1,400	-	-	-	-	-	-
	10	940	905	1,700	-	-	-	-	-	-
	16	200	295	1,100	-	-	-	-	-	-
Timber	13	-	-	-	113	145	975	-	-	-

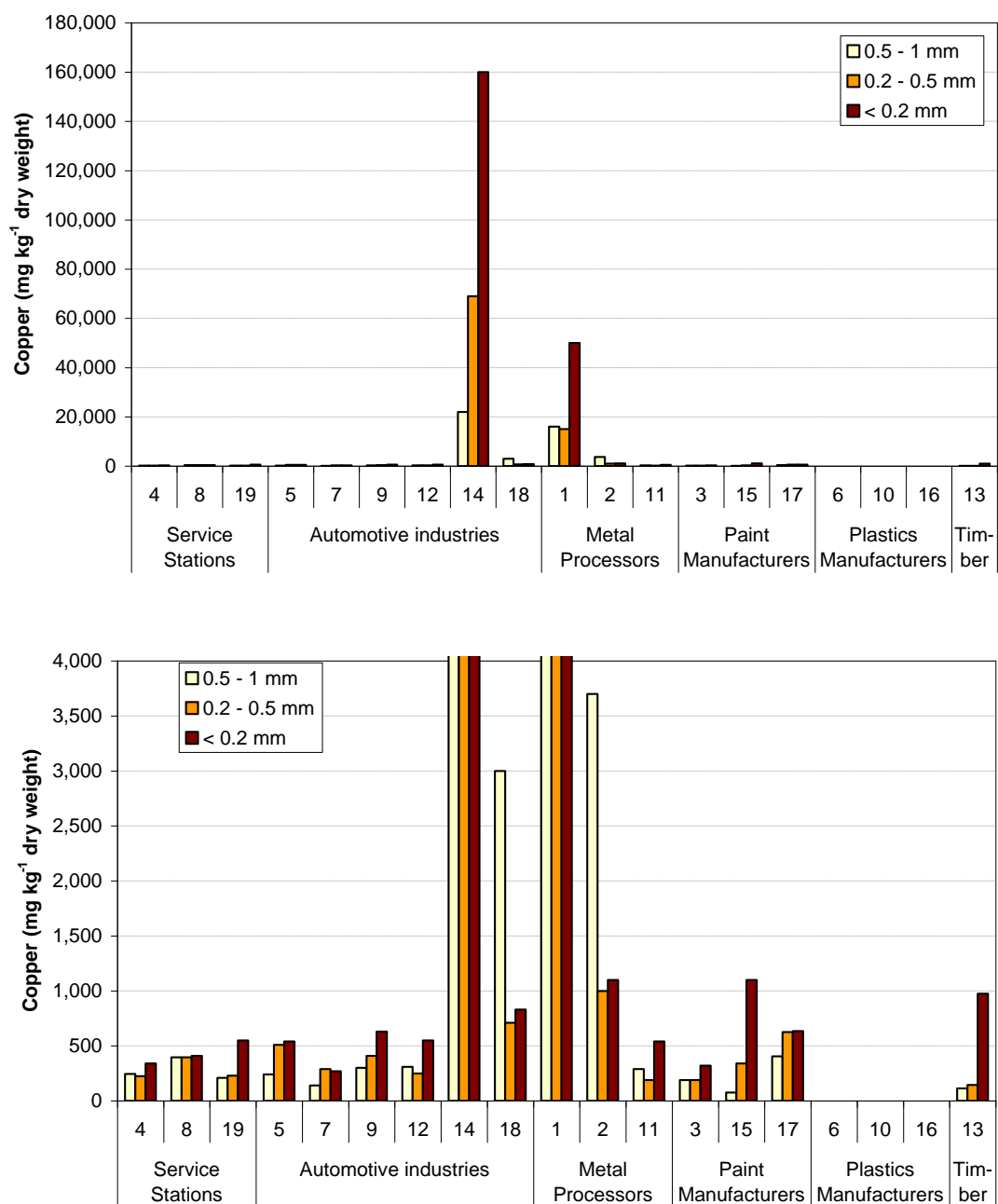
**Figure 5**

Zinc in catchpit solids, fractions 0.5 – 1 mm, 0.2 – 0.5 mm and < 0.2 mm (at full scale and at finer scale).



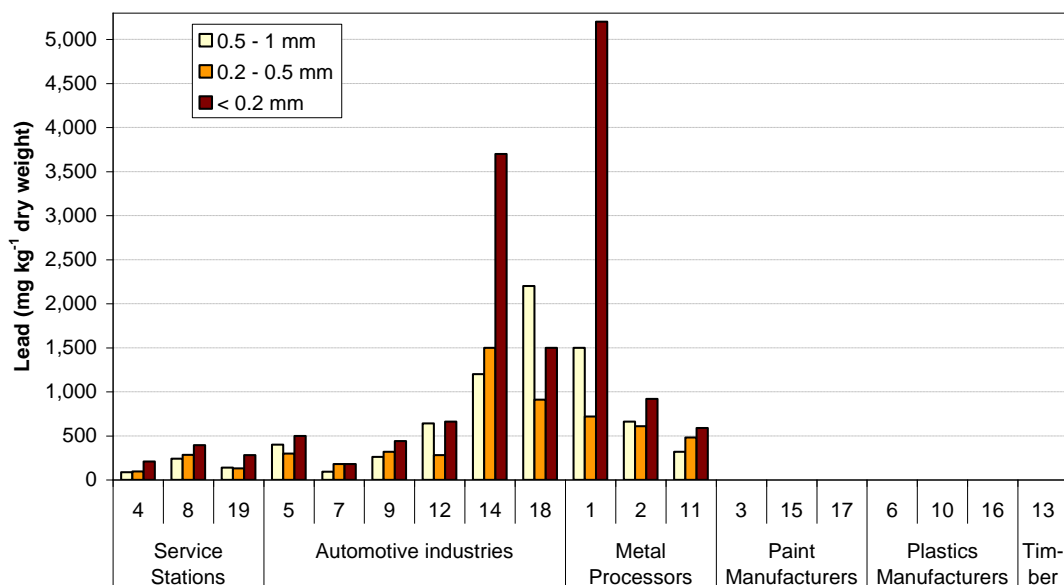
**Figure 6**

Copper in catchpit solids, fractions 0.5 – 1 mm, 0.2–0.5 mm and < 0.2mm (at full scale and at finer scale).



**Figure 7**

Lead in catchpit solids, fractions 0.5 – 1 mm, 0.2–0.5 mm and < 0.2 mm.



In addition to the high zinc concentrations, exceptionally high copper concentrations (22,000 – 160,000 mg kg<sup>-1</sup>, Figure 6) were measured in catchpit 14 and in catchpit 1, from a metal processing site (16,000 – 50,000 mg kg<sup>-1</sup>). In all other catchpits, concentrations were considerably lower (75 – 3,700 mg kg<sup>-1</sup> across all sediment fractions, Figure 6). Nonetheless, concentrations remain well in excess of the concentrations measured in from road-side catchpits in Auckland (33 – 510 mg kg<sup>-1</sup>, average 143 mg kg<sup>-1</sup> across all particle size fractions, Moores et al. 2007) and in Auckland and Christchurch (48 – 116 mg kg<sup>-1</sup>, average 85 mg kg<sup>-1</sup>, Depree 2008). Solids from one other metal processing site (catchpit 2) was also highly elevated in copper (1,000 – 3,700 mg kg<sup>-1</sup>) while the remaining catchpit had substantially lower concentrations (190 – 540 mg kg<sup>-1</sup>). Unlike the zinc results, the coarse fraction contained the highest concentrations of copper for two catchpit samples (18 and 2, from automotive and metal processor sites respectively) and may reflect the source of copper in these catchpit solids (e.g., metal fragments or large particulates from brake pads).

Lead was measured in 12 catchpit solids from three different industries (Table 5, Figure 7) and ranged from 86 to 5,200 mg kg<sup>-1</sup>. Highest concentrations were measured in solids from catchpit 1, from a metal processors; and in catchpit 14, from an automotive site, consistent with the elevated zinc and copper concentrations in solids from both catchpits. Similarly elevated lead was measured in solids from catchpit 18, also from an automotive industry site. Solids from service station catchpits contained lower lead concentrations than those from automotive industries, ranging from 86 mg kg<sup>-1</sup> in the coarse fraction to 395 mg kg<sup>-1</sup> in the fine fraction. These values are in the range of that measured in road-side catchpits in Auckland (14 – 800 mg kg<sup>-1</sup>, average 182 mg kg<sup>-1</sup> across all particle size fractions, Moores et al. 2007).

Cadmium was measured in catchpit solids from three industries (metal processors, paint manufacturers and plastic manufacturers), and nine different catchpits (Table 6, Figure 8). Solids from catchpit 10 contained exceptionally high cadmium concentrations, measuring 510, 305 and 400 mg kg<sup>-1</sup> in the coarse, intermediate and fine fractions respectively. These concentrations are extremely elevated, both in comparison to other catchpits from the same industry (maximum 2.2 mg kg<sup>-1</sup>), other industries (maximum 31 mg kg<sup>-1</sup>) and natural soils (0.63 mg kg<sup>-1</sup>, ARC 2001).

Mercury was measured in nine catchpits from two industries (automotive and metal processors) and ranged from 0.021 to 0.71 mg kg<sup>-1</sup> (Table 6, Figure 9). For each catchpit sample, mercury was consistently at highest concentration in the fine sediment fraction (< 0.2 mm).

Chromium was measured in samples from metal processors and the timber site and ranged from 84 to 3,000 mg kg<sup>-1</sup> (Table 6). Chromium was typically at highest concentration in the fine sediment fraction (< 0.2 mm), with the exception of sample 2, from a metal processor. In this sample, chromium was highest in the coarse fraction (3,000 mg kg<sup>-1</sup>), followed by the intermediate fraction (2,400 mg kg<sup>-1</sup>) and lowest in the fine fraction (1,700 mg kg<sup>-1</sup>).

Arsenic was measured only in the samples (3 fractions) from the timber site and ranged from 62 to 510 mg kg<sup>-1</sup>, with highest concentrations in the fine sediment fraction (Table 6).

Sediment samples from the paint manufacturer catchpits were analysed for selenium, a pigment used in paint. None of the samples analysed (3 catchpits x 3 fractions) contained selenium above the detection limit of 2.0 mg kg<sup>-1</sup>.

Samples from the three metal processing sites were analysed for four additional metals: aluminium, nickel, silver and tin (Table 7). Nickel, silver and tin were substantially higher in the fine fraction of solids from catchpit 1 than in the other fractions or other two catchpits. This is consistent with the concentrations of copper, zinc and lead as described above. The coarser fractions (0.5 – 1.0 mm and 0.2 – 0.5 mm) of solids from catchpit 1 had similar nickel concentrations to those in the corresponding fractions from catchpits 2 and 11, while silver and tin was again at higher concentrations than found in catchpit 2 and 11.



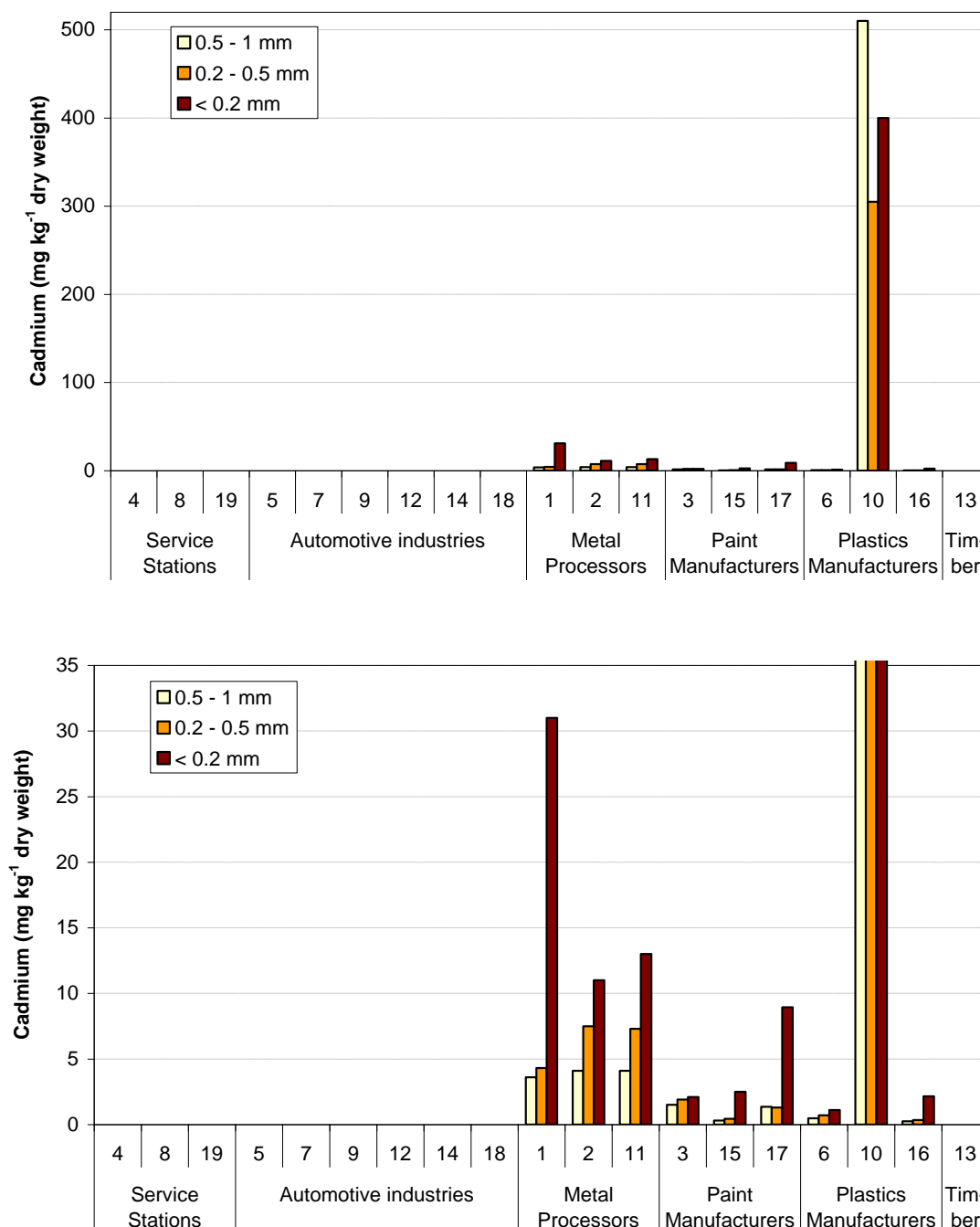
**Table 6**

Cadmium, mercury, chromium and arsenic detected in samples of catchpit solids (mg kg<sup>-1</sup> dry weight).

Industry	Sample Number	Cadmium			Mercury			Chromium			Arsenic		
		0.5-1 mm	0.2-0.5 mm	< 0.2 mm	0.5-1 mm	0.2-0.5 mm	< 0.2 mm	0.5-1 mm	0.2-0.5 mm	< 0.2 mm	0.5-1 mm	0.2-0.5 mm	< 0.2 mm
Automotive	5	-	-	-	0.048	0.060	0.13	-	-	-	-	-	-
	7	-	-	-	0.038	0.052	0.18	-	-	-	-	-	-
	9	-	-	-	0.047	0.073	0.14	-	-	-	-	-	-
	12	-	-	-	0.024	0.031	0.12	-	-	-	-	-	-
	14	-	-	-	0.021	0.051	0.25	-	-	-	-	-	-
	18	-	-	-	0.12	0.25	0.71	-	-	-	-	-	-
Metal Processing	1	3.6	4.3	31	0.019	0.023	0.15	280	260	780	-	-	-
	2	4.1	7.5	11	0.11	0.17	0.18	3,000	2,400	1,700	-	-	-
	11	4.1	7.3	13	0.045	0.054	0.13	86	84	140	-	-	-
Paint Manufacturers	3	1.5	1.9	2.1	-	-	-	-	-	-	-	-	-
	15	0.31	0.43	2.5	-	-	-	-	-	-	-	-	-
	17	1.35	1.3	9.0	-	-	-	-	-	-	-	-	-
Plastics	6	0.47	0.7	1.1	-	-	-	-	-	-	-	-	-
	10	510	305	400	-	-	-	-	-	-	-	-	-
	16	0.25	0.35	2.2	-	-	-	-	-	-	-	-	-
Timber	13	-	-	-	-	-	-	120	225	1,500	62	100	510

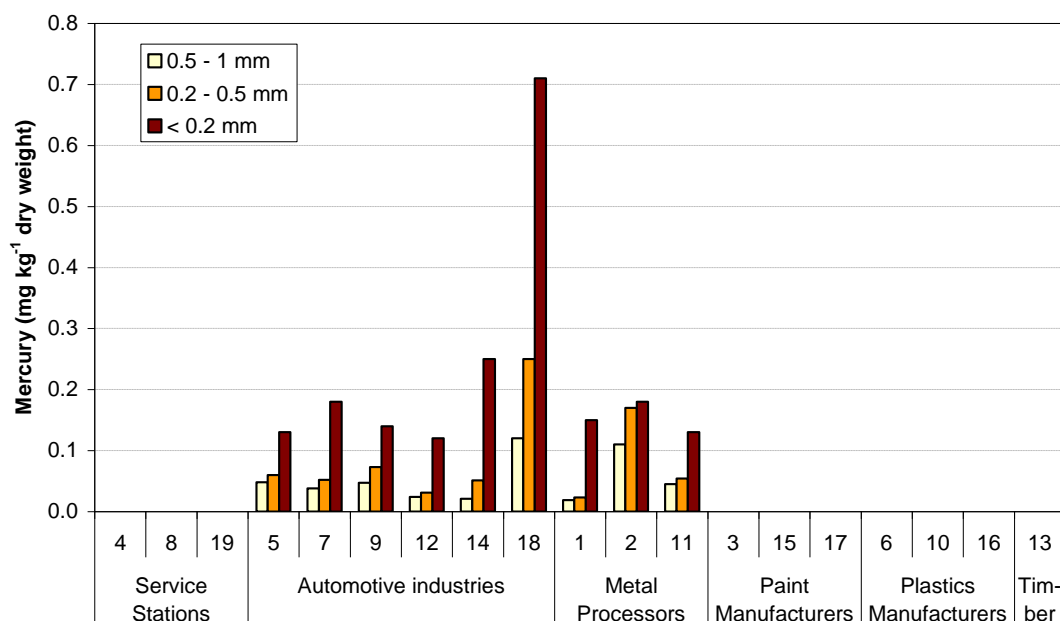
**Figure 8**

Cadmium in catchpit solids, fractions 0.5 – 1 mm, 0.2–0.5 mm and < 0.2 mm (at full scale and at finer scale).



**Figure 9**

Mercury in catchpit solids, fractions 0.5 – 1 mm, 0.2 – 0.5 mm and < 0.2 mm.

**Table 7**

Aluminium, nickel, silver and tin detected in samples of catchpit solids from metal processing sites (mg kg<sup>-1</sup> dry weight).

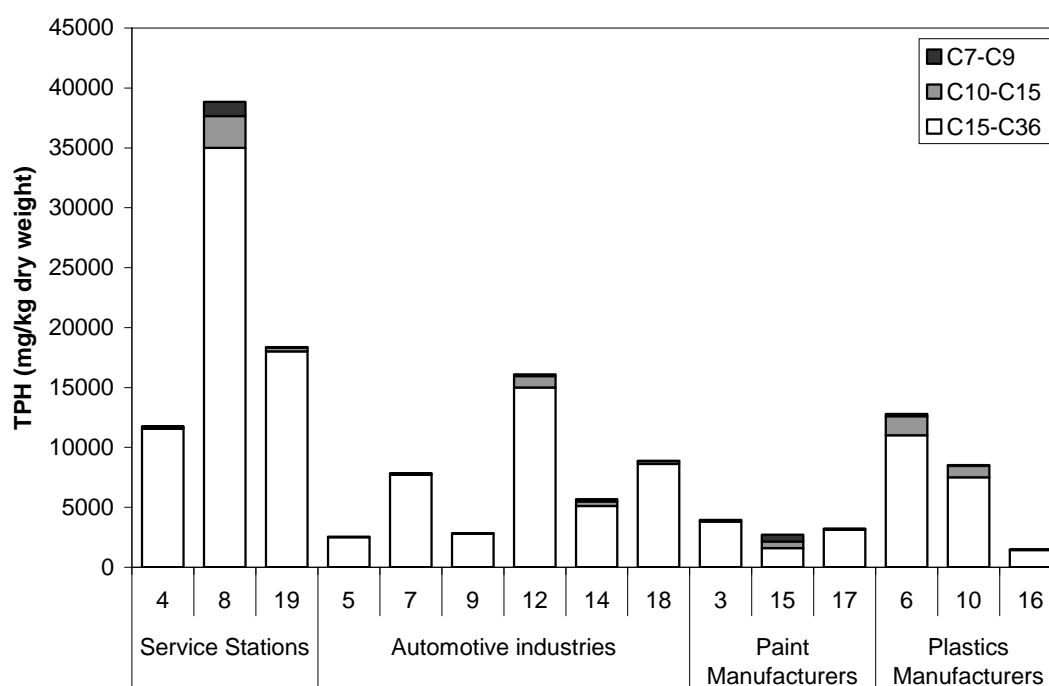
Catchpit Number	Aluminium			Nickel			Silver			Tin		
	0.5-1 mm	0.2-0.5 mm	<0.2 mm	0.5-1 mm	0.2-0.5 mm	<0.2 mm	0.5-1 mm	0.2-0.5 mm	<0.2 mm	0.5-1 mm	0.2-0.5 mm	<0.2 mm
1	17,000	5,100	30,000	830	870	3,100	7.3	10.0	40.0	650	770	2,600
2	13,000	13,000	16,000	1,700	1,400	890	3.3	3.6	4.4	490	120	130
11	17,000	13,000	22,000	130	160	120	6.2	1.0	5.4	300	310	220

### 4.3 TPHs

TPH (C<sub>7</sub>–C<sub>36</sub>) concentrations in each sample are reported in Table 8 and shown graphically in Figure 10. TPH chromatograms and concentrations within three carbon chain length ranges are provided in Appendix 3. TPH was dominated by the C<sub>15</sub>–C<sub>36</sub> fraction, comprising 88–100% of total TPH in all samples with the exception of catchpit 15 (59%). The C<sub>15</sub>–C<sub>36</sub> fraction is also the dominant fraction in diesel and lubricating oils, suggesting diesel and oils may be the major source of hydrocarbons in these samples.

**Table 8**TPHs in samples of catchpit solids (mg kg<sup>-1</sup> dry weight).

Industry	Sample Number	TPH fractions			Total
		C <sub>7</sub> -C <sub>9</sub>	C <sub>10</sub> -C <sub>14</sub>	C <sub>15</sub> -C <sub>36</sub>	(C <sub>7</sub> -C <sub>36</sub> )
Service Station	4	< 15	175	11,550	11,650
	8	1,190	2,650	35,000	39,500
	19	44	310	18,000	18,000
Automotive	5	< 16	35	2,500	2,500
	7	< 14	110	7,700	7,900
	9	< 13	< 20	2,800	2,800
	12	140	950	15,000	17,000
	14	180	390	5,100	5,700
	18	12	260	8,600	8,900
Paint Manufacturers	3	< 33	130	3,800	3,900
	15	580	530	1,600	2,700
	17	45	69	3,100	3,200
Plastics	6	180	1,600	11,000	12,000
	10	71	935	7,500	8,400
	16	16	19	1,400	1,440

**Figure 10**Dry weight concentrations of TPH fractions in catchpit solids (mg kg<sup>-1</sup> dry weight).

## 4.4 SVOC Screen

Only 28 of the 79 compounds in the screening suite were measured above detection limits in at least one sample. Of these, 17 were PAHs or a substituted PAH (i.e., 2-methylnaphthalene). PAHs were detected most frequently and at highest concentrations in catchpit solids from service stations (Table 9).

The remaining compounds detected (Table 10) included four phthalates and three phenols. Phthalates are compounds used in plastics and are frequently detected in urban environments. Bis(2-ethylhexyl) phthalate was found at greatest concentration in solids from paint manufacturers, followed by plastic manufacturers. There was no apparent trend in the occurrence of the other phthalates by industry type. Phenols were detected in only two catchpits, 14 and 2, from an automotive site and metal processor respectively. It is possible that phenols were also present in other catchpits at similar concentrations, because some samples had much higher detection limits (detection limits are determined by dry matter content, analyte recovery and the presence of interferences).

Three other SVOCs were detected; benzyl alcohol, carbazole and dibenzofuran. Benzyl alcohol is commonly used as a solvent, for uses such as paint stripping; and it is produced naturally by some plants and found in fruits, teas and essential oils. It was found in two catchpits from metal processors (catchpits 2 and 11). Carbazole and dibenzofuran are found in coal tar and were detected in a service station catchpit (catchpit 19).

No organochlorine pesticides or halogenated compounds were detected in any of the catchpit solids.

**Table 9**PAHs detected in catchpit solids using SVOC screen (mg kg<sup>-1</sup> dry weight).

	Service Stations			Automotive industries						Paint Manufacturers			Plastics manufacturers			Metal Processors		
	4	8	19	5	7	9	12	14	18	3	15	17	6	10	16	1	2	11
Acenaphthene	< 0.12	< 0.78	13	< 0.58	< 0.50	< 0.49	< 0.41	< 0.40	< 0.36	< 3.0	< 0.70	0.45	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Acenaphthylene	< 0.12	< 0.78	3.2	< 0.58	< 0.50	< 0.49	< 0.41	< 0.40	< 0.36	< 3.0	< 0.70	< 0.36	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Anthracene	< 0.12	< 0.78	30	< 0.58	< 0.50	< 0.49	< 0.41	< 0.40	< 0.36	< 3.0	< 0.70	< 0.36	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Benzo[a]anthracene	0.15	< 0.78	250	< 0.58	< 0.50	< 0.49	< 0.41	< 0.40	< 0.36	< 3.0	< 0.70	0.62	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Benzo[a]pyrene (BAP)	< 0.22	< 1.4	340	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	0.64	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Benzo[b]fluoranthene	0.33	< 1.4	560	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	0.83	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Benzo[g,h,i]perylene	0.51	< 1.4	310	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.72	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Benzo[k]fluoranthene	< 0.22	< 1.4	190	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.72	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Chrysene	0.26	0.48	390	< 0.58	< 0.50	< 0.49	< 0.41	< 0.40	< 0.36	< 3.0	< 0.70	0.68	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Dibenzo[a,h]anthracene	< 0.22	< 1.4	78	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.72	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Fluoranthene	0.65	1.02	940	< 0.58	< 0.50	0.59	1.1	< 0.40	0.53	< 3.0	< 0.70	1.8	< 0.65	< 0.51	< 0.42	0.14	0.13	< 0.50
Fluorene	< 0.12	1.52	16	< 0.58	< 0.50	< 0.49	0.67	< 0.40	< 0.36	< 3.0	< 0.70	0.28	< 0.65	< 0.51	< 0.42	< 0.10	< 0.10	< 0.50
Indeno(1,2,3-c,d)pyrene	< 0.22	< 1.4	220	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.72	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Naphthalene	0.19	16	1.4	< 0.58	< 0.50	< 0.49	4.4	< 0.40	< 0.36	< 3.0	1.6	< 0.36	10	0.87	< 0.42	< 0.10	1.1	1.3
Phenanthrene	0.45	4.7	430	< 0.58	< 0.50	< 0.49	2	< 0.40	0.45	< 3.0	< 0.70	1.2	1.6	< 0.51	< 0.42	0.17	0.13	< 0.50
Pyrene	3.1	15	690	0.6	0.92	1	3	0.46	0.7	< 3.0	< 0.70	1.6	2.1	0.70	< 0.42	0.27	0.23	0.62
2-Methylnaphthalene	< 0.12	24	2.4	< 0.58	< 0.50	< 0.49	5.9	< 0.40	< 0.36	< 3.0	< 0.70	< 0.36	33	1.0	< 0.42	0.12	1.7	1.2

Note: Values in bold indicate results above the detection limit.

**Table 10**Other SVOCs detected in catchpit solids (mg kg<sup>-1</sup> dry weight).

Industry type Catchpit number	Service Station 4      8      19			Automotive Industries 5      7      9      12      14      18						Paint Manufacturers 3      15      17			Plastics 6      10      16			Metal Processing 1      2      11		
PAHs																		
2-methyl-naphthalene	< 0.11	24	2.4	< 0.58	< 0.50	< 0.49	59	< 0.40	< 0.36	< 3.0	< 0.70	< 0.37	33	1	< 0.42	0.12	1.7	1.2
Phenols																		
3 & 4-Methyl-phenol	< 0.43	< 3.3	< 5.3	< 2.4	< 2.0	< 2.0	< 1.7	2.8	< 1.5	< 12	< 2.8	< 1.5	< 2.6	< 2.1	< 1.7	< 0.40	1.1	< 2.0
2-Methyl-phenol	< 0.22	< 1.4	< 2.7	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.73	< 1.3	< 1.0	< 0.83	< 0.20	0.41	< 1.0
Phenol	< 0.44	< 3.3	< 5.3	< 2.4	< 2.0	< 2.0	< 1.7	4.7	< 1.5	< 12	< 2.8	< 1.5	< 2.6	< 2.1	< 1.7	< 0.30	< 0.34	< 2.0
Plasticisers																		
Bis(2-ethylhexyl) phthalate	130	150	55	72	26	24	77	30	13	310	360	3270	210	335	< 3.4	38	96	66
Butyl-benzyl-phthalate	1.2	2.6	< 5.3	23	< 2.0	9.3	38	63	1.8	30	41	2.3	5.3	4.4	< 1.7	< 0.30	< 0.34	4.8
Dimethyl-phthalate	< 0.44	< 3.3	< 5.3	< 2.4	7.1	< 2.0	< 1.7	< 1.6	< 1.5	< 12	< 2.8	1.1	< 2.6	< 2.1	< 1.7	1	0.62	< 2.0
Di-n-butyl-phthalate	8.5	4.2	< 5.3	7.9	< 2.0	< 2.0	< 1.7	2.9	< 1.5	< 12	4.7	17	< 2.6	6.6	< 1.7	< 0.30	1.2	13
Other SVOCs																		
Benzyl alcohol	< 2.2	< 14	< 27	< 12	< 9.9	< 9.8	< 8.2	< 7.9	< 7.2	< 60	< 14	< 7.3	< 13	< 10	< 8.3	< 1.5	2.3	50
Carbazole	< 0.22	< 1.4	88	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.73	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0
Dibenzo-furan	< 0.22	< 1.4	9.7	< 1.2	< 0.99	< 0.98	< 0.82	< 0.79	< 0.72	< 6.0	< 1.4	< 0.73	< 1.3	< 1.0	< 0.83	< 0.15	< 0.17	< 1.0

Note: Values in bold indicate results above the detection limit.

## 4.5 PAHs

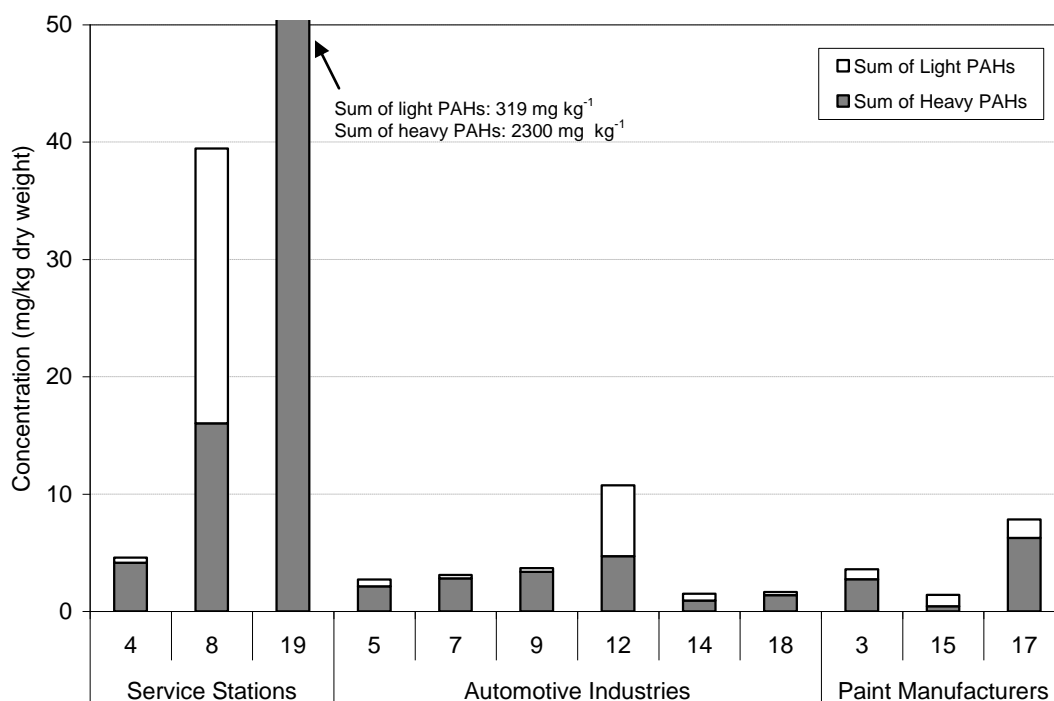
12 samples from 3 industries were assessed for PAHs at trace level (Table 11). Each sample contained measurable concentrations of PAHs. Exceptionally high concentrations were measured in the sample from catchpit 19, from a service station, with total PAHs 2620 mg kg<sup>-1</sup> (dry weight). Excluding this sample, total PAHs ranged from 1.4 to 39 mg kg<sup>-1</sup> dry weight.

Fluoranthene, pyrene, phenanthrene, benzo[g,h,i]perylene, benzo[b]fluoranthene and benzo[j]fluoranthene were the dominant compounds measured in most samples. Fluoranthene and pyrene are indicative of a petrogenic source. Napthalene was the dominant PAH in three samples (8, 12, 15) from three different industries (service station, automotive and paint manufacturing). This is reflected in the higher proportion of 'light' PAHs in Figure 11 for these three samples.

The sample from catchpit 8, a service station catchpit, contained substantially higher concentrations of napthalene and pyrene than other samples, suggesting the PAH compounds here are derived from a different source.

**Figure 11**

Concentrations of 'light' and 'heavy' PAHs in catchpit solids (sums of 6 'light' and 10 'heavy' compounds).





**Table 11**

PAHs detected in selected catchpit samples by trace analysis method (mg kg<sup>-1</sup> dry weight).

Industry type Catchpit number	Service Station			Automotive						Paint Manufacturers		
	4	8	19	5	7	9	12	14	18	3	15	17
Acenaphthene	< 0.0027	0.18	6.2	0.011	0.0041	0.0052	0.11	0.022	< 0.002	0.04	< 0.0035	0.24
Acenaphthylene	< 0.0027	0.10	0.79	0.013	0.019	0.035	0.06	0.031	< 0.002	0.033	< 0.0035	0.017
Anthracene	0.042	0.34	22	0.029	0.05	0.044	0.24	0.035	0.022	0.018	0.011	0.13
Benzo[a]anthracene	0.11	0.24	160	0.14	0.18	0.19	0.23	0.051	0.077	0.075	0.011	0.55
Benzo[a]pyrene (BAP)	0.13	0.21	160	0.1	0.19	0.31	0.15	0.038	0.062	0.065	0.012	0.41
Benzo[b]fluoranthene + Benzo[j]fluoranthene	0.3	0.55	340	0.27	0.3	0.53	0.4	0.1	0.15	0.26	0.027	1.0
Benzo[g,h,i]perylene	0.56	0.70	190	0.29	0.29	0.58	0.5	0.12	0.068	0.65	0.096	0.46
Benzo[k]fluoranthene	0.068	0.17	110	0.073	0.099	0.16	0.057	0.026	0.046	0.059	0.0065	0.28
Chrysene	0.18	0.37	200	0.16	0.18	0.26	0.23	0.057	0.11	0.21	0.015	0.49
Dibenzo[a,h]anthracene	< 0.0027	0.037	43	0.023	< 0.0025	< 0.0025	0.024	0.01	< 0.002	0.027	< 0.0035	0.11
Fluoranthene	0.39	0.66	550	0.45	0.48	0.46	0.7	0.18	0.26	0.47	0.061	1.4
Fluorene	0.040	1.7	10	0.054	0.011	0.013	0.64	0.1	0.04	0.068	0.01	0.18
Indeno(1,2,3-c,d)pyrene	0.13	0.16	140	0.079	0.15	0.15	0.11	0.027	0.033	0.058	0.012	0.31
Naphthalene	0.11	17	0.92	0.18	0.013	0.057	3.3	0.13	0.017	0.48	0.87	0.073
Phenanthrene	0.23	4.0	280	0.3	0.19	0.17	1.7	0.26	0.18	0.22	0.066	0.95
Pyrene	2.3	13	410	0.54	0.95	0.72	2.3	0.31	0.57	0.86	0.2	1.3
Total PAHs	4.6	39	2620	2.7	3.1	3.7	10.8	1.5	1.6	3.6	1.4	7.8

## 4.6 Phenols

All catchpit samples (excluding the timber yard catchpit) were screened for a range of phenols (including chlorinated and methylated) using the SVOC screen, with detection limits of 0.2 – 50 mg kg<sup>-1</sup> with several detected as described previously (Table 12).

The samples from paint manufacturers, metal processors and the timber yard catchpits were further assessed for 'total phenols' as described in Section 3.4.6 with a detection limit of 0.20 mg kg<sup>-1</sup>. Phenols were detected in all six catchpit samples from paint manufacturers and metal processors, at concentrations from 0.33 to 5.3 mg kg<sup>-1</sup>, with highest concentrations in catchpit 11, from a metal processing site. Results were not consistent with the SVOC screen results; however, this is not unexpected due to the different methods used and the different phenols detectable by each (see Section 3.4.6). Total phenols were not detected in the catchpit solids from the timber yard.

**Table 12**

Phenols detected in selected catchpit samples by trace analysis method (mg kg<sup>-1</sup> dry weight).

Industry type	Catchpit number	Total Phenols
Paint Manufacturers	3	0.85
	15	0.69
	17	0.33
Metal Processing	1	0.60
	2	1.1
	11	5.3
Timber	13	< 0.2

## 4.7 PCP

All samples were analysed for PCP at screening levels, with detection limits of 6 – 120 mg kg<sup>-1</sup> with none detected. The sediment from the timber yard catchpit was further assessed with a detection limit of 0.05 mg kg<sup>-1</sup>. Despite the lower detection level (DL), neither PCP nor TCP (Tetrachlorophenol) were detected.

## 4.8 Variability in Repeat and Split Samples

### 4.8.1 Repeat Samples

Two samples were taken from each of catchpits 8, 16 and 17. The proportion of solids falling in each size fraction were quite variable for each pair of samples, with relative percent differences (RPDs) of 2 to 76% (average 32%).

Of the 24 pairs of comparable results of the metals analysis (3 fractions for 1-3 catchpits and 4 different metals), the RPD was within 25 % for 13 pairs and all but one were within 50 %. The greatest difference was in the copper concentration in the

coarse fraction (0.5 – 1.0 mm) from catchpit 17, with one replicate measuring 580 mg kg<sup>-1</sup> and the other 230 mg kg<sup>-1</sup>, an RPD of 86 %.

The RPDs for TPH concentrations were between 34 and 139% for each pair of repeat samples. The RPDs for individual PAH concentrations were between 25 and 196% for the two pairs of repeat samples analysed (samples 8 and 17). The variation between duplicates was larger for results from the SVOC screen (0 to 185%, average 72% for 12 pairs), which is as expected for this less accurate screening test. The total phenol concentrations varied in duplicates of sample 17, with one measuring 0.56 mg kg<sup>-1</sup> and the other < 0.2 mg kg<sup>-1</sup>.

While the RPD for many of the parameters appears quite large, this is reflective of the heterogeneous nature of the catchpit solids. In general, the difference between different samples was much greater than the difference between sample duplicates, particularly for the metal analyses.

#### 4.8.2 Split Samples

The samples collected from catchpits 4, 10 and 13 were split during sample processing. The proportion of solids falling in each size fraction corresponded well for duplicates from sample 10 (RPD 4–35%), but were more variable for samples 13 (11–74%) and 4 (70 – 132%).

Of the 24 pairs of comparable results of the metals analysis (3 fractions for 1 – 3 catchpits and 6 different metals), 17 agreed well (RPD 0 – 19%). The remainder ranged from 31 to 69%. As for the repeat sampling duplicates, the pair with greatest variation (69%) was a coarse fraction (0.5 – 1.0 mm), where copper measured 330 mg kg<sup>-1</sup> in subsample 1 and was markedly lower at 160 mg kg<sup>-1</sup> in subsample 2. For all samples, the smallest differences were measured in the finest grain size fraction (< 0.2 mm), reflecting the greater homogeneity in this fraction.

The RPD for TPH concentrations was from 12 to 63% (excluding results below detection), depending on the sample or TPH fraction. In the context of TPH concentrations throughout the full set of results (< 13 – 39,000 mg kg<sup>-1</sup>), the paired sample results are broadly similar (low to moderate concentrations).

Duplicate results for sample 4 of PAHs by trace analysis showed good agreement, with RPD 0-29% (average 12% for 16 compounds). Duplicates of sample 13 analysed for PCP and total phenols returned the same results, being below detection limits (< 0.05 mg kg<sup>-1</sup> and < 0.2 mg kg<sup>-1</sup> respectively). The variation between duplicate results from the SVOC screen indicated generally good agreement (RPD 14 to 63%, average 34% for 17 pairs).

Although less variation was expected in the duplicates collected at the sample processing stage compared to the sample collection stage, there was little difference overall. Despite considerable effort to mix and homogenise samples, there was high variation in sub-samples collected during sample processing, due to the heterogeneous nature of the samples.

## 5 Conclusions

This study aimed to collect catchpit solids from a range of industries for analysis of stormwater contaminants. Catchpit solids were successfully collected from 19 catchpits, covering six industries. For five industries, at least 3 samples were collected from each industry, while only 1 sample could be collected from sites in the timber treatment industry. Samples were successfully analysed for particle size distribution, metals, TPH, SVOCs, PAHs, phenols and PCP.

The industry type had some influence on the concentration of contaminants however there was considerable variation within industry types, probably reflecting individual site activities and / or site stormwater practices. For example, the highest TPH concentration was in a catchpit from a service station, but other service station catchpits had much lower concentrations. Similarly, cadmium concentrations were extremely elevated in one catchpit from a plastic manufacturer, but much lower in other catchpits from that industry.

Copper and zinc concentrations in solids from the industrial stormwater catchpits were well in excess of concentrations measured in solids collected from road-side stormwater catchpits. Lead concentrations were similar in most industrial catchpit solids to road-side catchpit solids.

The catchpit samples were extremely heterogenous, leading to large variation between duplicates collected either at the sampling or sample processing stage. There was also considerable variation in the metal concentrations on each particle size analysed, with highest concentrations found in the < 0.2 mm fraction for most metals and most samples.



## 6 References



- ARC (2001). Background concentrations of inorganic elements in soils from the Auckland Region. Technical Publication No. 153. Auckland Regional Council, October 2001.
- Depree, C. (2008). Contaminant characterisation and toxicity of road sweepings and catchpit sediments: Towards more sustainable reuse options. Land Transport NZ Research Report 345. 114 pp.
- Moore, J., Hunt, J. and Pattinson, P. (2007). Quantification of catchpit solids and contaminants. NIWA Client Report AKL-2007-093 for Auckland Regional Council, December 2007.
- Moore, J., Pattinson, P. and Hyde, C. (2009). Richardson Rd study: measurement and sampling of runoff and catchpit solids. NIWA Client Report AKL-2009-033 for Auckland Regional Council.

## 7 Glossary



GC-MS	Gas chromatography-mass spectrometry
IANZ	International Accreditation New Zealand
PAHs	Polycyclic Aromatic Hydrocarbons, a group of compounds found in heavy petroleum products and as products of combustion. Many are toxic and some carcinogenic.
PCP	Pentachlorophenol, an organochlorine compound used as in timber preservation. Now banned.
SIM	Selected Ion Monitoring
SPE	Solid phase extraction
SVOCs	Semi-volatile organic compounds
TCP	Tetrachlorophenol
TPHs	Total Petroleum Hydrocarbons



# Appendix 1 – Sample Descriptions

<b>Catchpit number</b>	1
<b>Industry</b>	Metal processor
<b>Description of sample</b> Dark brown sand and silt, with some gravel and organic matter. 3% > 1 cm fraction, comprising 50% gravels, 30% organic (leaves and seed pods), 20% metal fragments and minor plastic (< 1%). Slight hydrocarbon odour.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	2
<b>Industry</b>	Metal processor
<b>Description of sample</b> Dark brown silt, minor organic matter. 4% > 1 cm fraction comprising 80% leaves, 10% plastic film, 5% gravel and 5% metal fragments. Slight hydrocarbon sheen and odour.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	3
<b>Industry</b>	Paint Manufacturer
<b>Description of sample</b> Black silt and mud with large proportion (> 50% by volume) plastic matter. 11% > 1 cm fraction comprising thin strips of flexible plastic wrap (90%), leaves and twigs (10%). Slight hydrocarbon odour and sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	4
<b>Industry</b>	Service Station
<b>Description of sample</b> Black silt with organic matter and litter. 14-16% > 1 cm fraction comprising 80% large gravels (10-30 mm), 10% organic material (wood, leaves, detritus), 10% plastic litter. Hydrocarbon sheen and odour.	
<b>Sample photograph</b> 	





<b>Catchpit number</b>	5
<b>Industry</b>	Automotive
<b>Description of sample</b> Dark brown mud with high organic content and minor litter. 9% > 1 cm fraction comprising 60% organic matter (leaves, twigs, detritus), 40% litter (cigarette butts, bottle caps wiring, plastic). Hydrocarbon odour and slight sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	6
<b>Industry</b>	Plastic manufacturer
<b>Description of sample</b> Very dark brown/ black silt with high proportion organic matter (mainly detritus). 5% > 1 cm fraction comprising 60% twigs and leaves and 40% plastic litter. Strong hydrocarbon odour.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	7
<b>Industry</b>	Automotive
<b>Description of sample</b> Dark brown silt, clumpy soil with high proportion organic detritus. 2% > 1 cm fraction comprising 50% twigs and other organic matter and 50% gravel. Hydrocarbon odour.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	8 – Replicate 1
<b>Industry</b>	Service Station
<b>Description of sample</b> Dark brown silt with moderate to high proportion organic matter. 10% > 1 cm fraction comprising 80% organic material (twigs, bark) and 20% litter (mainly plastic wrappers). Strong hydrocarbon odour and sheen.	
<b>Sample photograph</b> 	





<b>Catchpit number</b>	8 – Replicate 2
<b>Industry</b>	Service Station
<b>Description of sample</b> Dark brown silt with minor proportion organic matter. 4% > 1 cm fraction comprising 75% organic material (mainly leaves), 15% litter (mainly plastic film) and 10% gravel. Hydrocarbon odour and sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	9
<b>Industry</b>	Automotive
<b>Description of sample</b> Dark brown soil with minor organic and inorganic matter. 4% > 1 cm fraction comprising 50% gravel, 30% plastic film and fragments and 20% wood fragments. No hydrocarbon or anaerobic odour.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	10
<b>Industry</b>	Plastic manufacturer
<b>Description of sample</b> White to dark grey sand and clay with very little organic and plant material. 7% > 1 cm sized material comprising 80% litter (bottle caps, pens, rubber band, match sticks, cigarette butts and a large metal fragment > 40 mm), 10% twigs and 10% gravel. Hydrocarbon odour.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	11
<b>Industry</b>	Metal processor
<b>Description of sample</b> Black sand and silt. 2% > 1 cm fraction comprising 50% litter (cigarette butts and plastic fragments) and 50% organic material (sticks and detritus). Hydrocarbon sheen and odour.	
<b>Sample photograph</b> 	





<b>Catchpit number</b>	12
<b>Industry</b>	Automotive
<b>Description of sample</b> Extremely oily sandy silt with some gravel sized material. 10% > 1 cm fraction comprising 80% gravel, 10% metallic litter (screws, washers, bottle caps) 5% plastic fragments and 5% glass fragments. Strong hydrocarbon odour and sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	13
<b>Industry</b>	Metal processor
<b>Description of sample</b> Dark grey to black sandy gravel with some silt. Minor organic matter. 39% > 1 cm fraction comprising 90% gravels (5 – 35 mm) and 10% wood fragments. Slight hydrocarbon odour, no sheen.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	14
<b>Industry</b>	Automotive
<b>Description of sample</b> Dark brown gravelly silt and clay with negligible organic detritus. 9% > 1 cm fraction comprising 80% litter (wiring, bottle caps, glass pieces), 10% gravel and 10% organic material (leaves and twigs). Earthy odour, no sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	15
<b>Industry</b>	Paint manufacturer
<b>Description of sample</b> Dark grey / brown gravelly sand with some clay and minor organic detritus. 4% > 1 cm fraction comprising 70% organic material (mainly wood fragments and leaves), 15% gravel and 15% metal fragments including nails. Hydrocarbon sheen and odour.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	16 – Replicate 1
<b>Industry</b>	Plastic manufacturer
<b>Description of sample</b> Dark brown silt with some gravel. Large proportion of organic detritus and numerous small (1-5 mm) fragments white plastic. 4% > 1 cm fraction comprising 50% organic material (twigs), 40% gravel and 10% wood / board fragments. No odour.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	16 – Replicate 2
<b>Industry</b>	Plastic manufacturer
<b>Description of sample</b> Dark brown silty sandy gravel with high % organic matter. Numerous small (1-5 mm) fragments white plastic / paint. 4% > 1 cm fraction comprising 60% organic material (pine needles and leaves) and 40% gravel. Mild odour, no sheen.	
<b>Sample photograph</b> 	

<b>Catchpit number</b>	17 – Replicate 1
<b>Industry</b>	Paint manufacturer
<b>Description of sample</b> Grey-brown silty sand with some gravel. Numerous small (~ 1mm diameter) seeds. 5% > 1cm fraction comprising 80% gravel, 15% organic material (twigs) and 5% mixed litter. No odour or sheen.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	17 – Replicate 2
<b>Industry</b>	Paint manufacturer
<b>Description of sample</b> Grey-brown silty sand with some fine gravel. Numerous small (~ 1mm diameter) seeds. Very minor proportion organic material. 4% > 1cm fraction comprising 70% gravel, 15% organic material (twigs), 10% litter (plastic, metal, wiring) and 5% concrete flakes. No odour or sheen.	
<b>Sample photograph</b> 	



<b>Catchpit number</b>	18
<b>Industry</b>	Automotive
<b>Description of sample</b> Dark brown silty sandy gravel with minor organic detritus. 34% > 1cm fraction comprising 65% gravel, 30% metal fragments (bolts, wire, car parts), 5% organic material (twigs). Hydrocarbon sheen and slight odour.	
<b>Sample photograph</b> 	
<b>Catchpit number</b>	19
<b>Industry</b>	Service station
<b>Description of sample</b> Very dark brown organic silt and clay with large proportion organic detritus (< 5 mm). 2% > 1cm fraction comprising 50% litter (cigarette butts, plastic, foil wrapper), 30% twigs and leaves and 2% wood fragments. Slight hydrocarbon sheen and odour.	
<b>Sample photograph</b> 	

# Appendix 2 – Detection Limits for SVOC Screen

**Table A1**

Detection limits for SVOCs using SVOC screen method (GC-MS-FS).

Compound	Range in Detection Limits Reported for Catchpit Solid Samples
<b>Haloethers</b>	
Bis(2-chloroethoxy) methane	< 0.15 - < 6.0
Bis(2-chloroethyl)ether	< 0.15 - < 6.0
Bis(2-chloroisopropyl)ether	< 0.15 - < 6.0
4-Bromophenyl phenyl ether	< 0.15 - < 6.0
4-Chlorophenyl phenyl ether	< 0.15 - < 6.0
<b>Nitrogen containing compounds</b>	
Aniline	< 0.30 - < 12
3,3'-Dichlorobenzidine	< 0.74 - < 30
2,4-Dinitrotoluene	< 0.30 - < 12
2,6-Dinitrotoluene	< 0.30 - < 12
Nitrobenzene	< 0.15 - < 6.0
N-Nitrosodi-n-propylamine	< 0.30 - < 12
N-Nitrosodiphenylamine	< 0.30 - < 12
<b>Organochlorine Pesticides</b>	
Aldrin	< 0.15 - < 6.0
alpha-BHC	< 0.15 - < 6.0
beta-BHC	< 0.15 - < 6.0
delta-BHC	< 0.15 - < 6.0
gamma-BHC (Lindane)	< 0.15 - < 6.0
4,4'-DDD	< 0.15 - < 6.0
4,4'-DDE	< 0.15 - < 6.0
4,4'-DDT	< 0.30 - < 12
Dieldrin	< 0.15 - < 6.0
Endosulfan I	< 0.30 - < 12
Endosulfan II	< 0.50 - < 12
Endosulfan sulphate	< 0.30 - < 12
Endrin	< 0.30 - < 12
Endrin Ketone	< 0.30 - < 12
Heptachlor	< 0.15 - < 6.0
Heptachlor epoxide	< 0.15 - < 6.0
Hexachlorobenzene	< 0.15 - < 6.0

**Table A1 contd.**

Detection limits for SVOCs using SVOC screen method (GC-MS-FS).

Compound	Range in Detection Limits Reported for Catchpit Solid Samples
Polycyclic Aromatic Hydrocarbons	
Acenaphthene	< 0.10 - < 3.0
Acenaphthylene	< 0.10 - < 3.0
Anthracene	< 0.10 - < 3.0
Benzo[a]anthracene	< 0.10 - < 3.0
Benzo[a]pyrene (BAP)	< 0.15 - < 6.0
Benzo[b]fluoranthene	< 0.15 - < 6.0
Benzo[g,h,i]perylene	< 0.15 - < 6.0
Benzo[k]fluoranthene	< 0.15 - < 6.0
2-Chloronaphthalene	< 0.10 - < 3.0
Chrysene	< 0.10 - < 3.0
Dibenzo[a,h]anthracene	< 0.15 - < 6.0
Fluoranthene	< 0.10 - < 3.0
Fluorene	< 0.10 - < 3.0
Indeno(1,2,3-c,d)pyrene	< 0.15 - < 6.0
2-Methylnaphthalene	< 0.10 - < 3.0
Naphthalene	< 0.10 - < 3.0
Phenanthrene	< 0.10 - < 3.0
Pyrene	< 0.10 - < 3.0
Phenols	
4-Chloro-3-methylphenol	< 0.50 - < 12
2-Chlorophenol	< 0.20 - < 6.0
2,4-Dichlorophenol	< 0.20 - < 6.0
2,4-Dimethylphenol	< 0.20 - < 6.0
2-Methyl-4,6-dinitrophenol	< 3.0 - < 120
3 & 4-Methylphenol (m- + p-cresol)	< 0.40 - < 12
2-Methylphenol (o-Cresol)	< 0.20 - < 6.0
2-Nitrophenol	< 0.40 - < 12
4-Nitrophenol	< 0.50 - < 12
Pentachlorophenol (PCP)	< 6.0 - < 120
Phenol	< 0.30 - < 12
2,4,5-Trichlorophenol	< 0.30 - < 12
2,4,6-Trichlorophenol	< 0.30 - < 12
Plasticisers	
Bis(2-ethylhexyl)phthalate	< 0.40 - < 12
Butylbenzylphthalate	< 0.30 - < 12
Di(2-ethylhexyl)adipate	< 0.20 - < 6.0
Diethylphthalate	< 0.30 - < 12
Dimethylphthalate	< 0.30 - < 12
Di-n-butylphthalate	< 0.30 - < 12
Di-n-octylphthalate	< 0.30 - < 12

**Table A1 contd.**

Detection limits for SVOCs using SVOC screen method (GC-MS-FS).

Compound	Range in Detection Limits Reported for Catchpit Solid Samples
Other Halogenated compounds	
1,2-Dichlorobenzene	< 0.30 - < 12
1,3-Dichlorobenzene	< 0.30 - < 12
1,4-Dichlorobenzene	< 0.30 - < 12
Hexachlorobutadiene	< 0.30 - < 12
Hexachlorocyclopentadiene	< 0.74 - < 30
Hexachloroethane	< 0.30 - < 12
1,2,4-Trichlorobenzene	< 0.15 - < 6.0
Other SVOCs	
Benzyl alcohol	< 1.5 - < 60
Carbazole	< 0.15 - < 6.0
Dibenzofuran	< 0.15 - < 6.0
Isophorone	< 0.15 - < 6.0

# Appendix 3 – TPH Chromatograms

Refer to Lab Number reported in Table A1 to identify sample results shown in chromatograms.

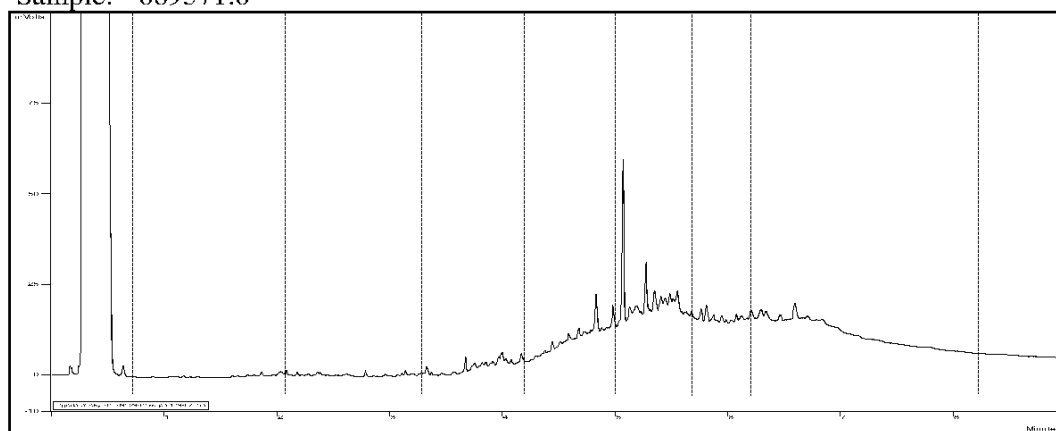
**Table A2**

Cross-reference of catchpit numbers and lab numbers

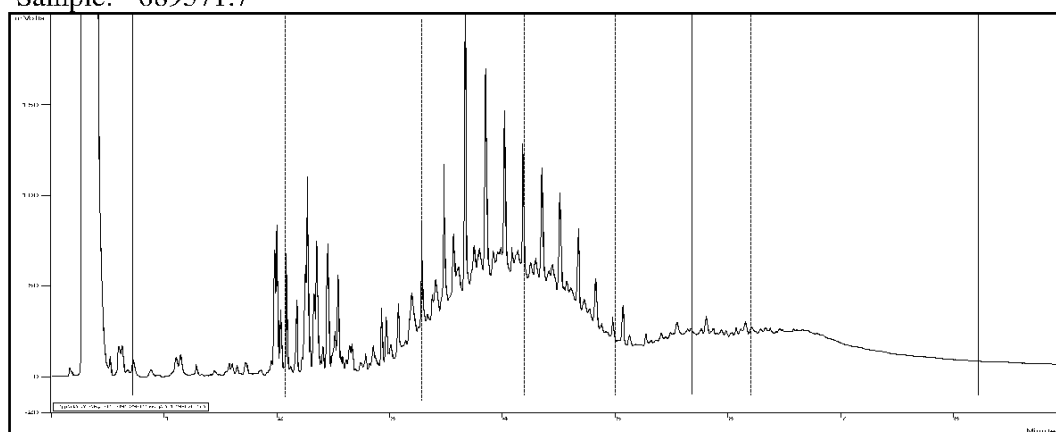
Industry	Catchpit	Laboratory Number for Organic Analyses	TPH analysed
Automotive	5	689571.6	✓
	7	689571.8	✓
	9	689571.11	✓
	12	689571.15	✓
	14	689571.18	✓
	18	689571.24	✓
Service Station	4 – Rep 1	689571.4	✓
	4 – Rep 2	689571.5	✓
	8 – Rep 1	689571.9	✓
	8 – Rep 2	689571.10	✓
	19	689571.25	✓
Paint Manufacturers	3	689571.3	✓
	15	689571.19	✓
	17 – Rep 1	689571.22	✓
	17 – Rep 2	689571.23	✓
Plastics Manufacturers	6	689571.7	✓
	10 – Rep 1	689571.12	✓
	10 – Rep 2	689571.13	✓
	16 – Rep 1	689571.20	✓
	16 – Rep 2	689571.21	✓
Metal Processors	1	689571.1	✗
	2	689571.2	✗
	11	689571.14	✗
Timber	13 - Rep 1	689571.16	✗
	13 – Rep 2	689571.17	✗

A horizontal timeline bar with tick marks at the bottom. The labels below the bar are C7, C10, C15, C20, C25, C30, C34, and C44, representing years from 2007 to 2014.

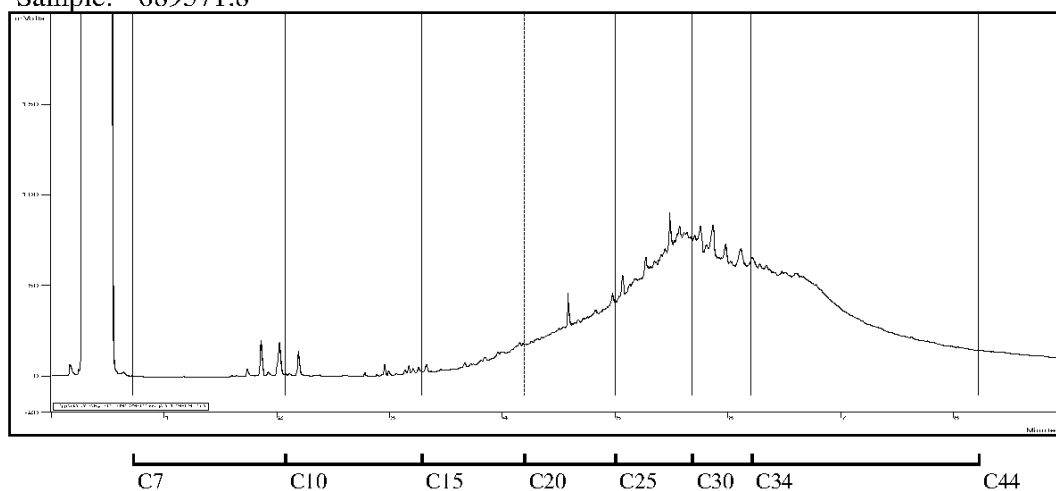
Sample: 689571.6



Sample: 689571.7

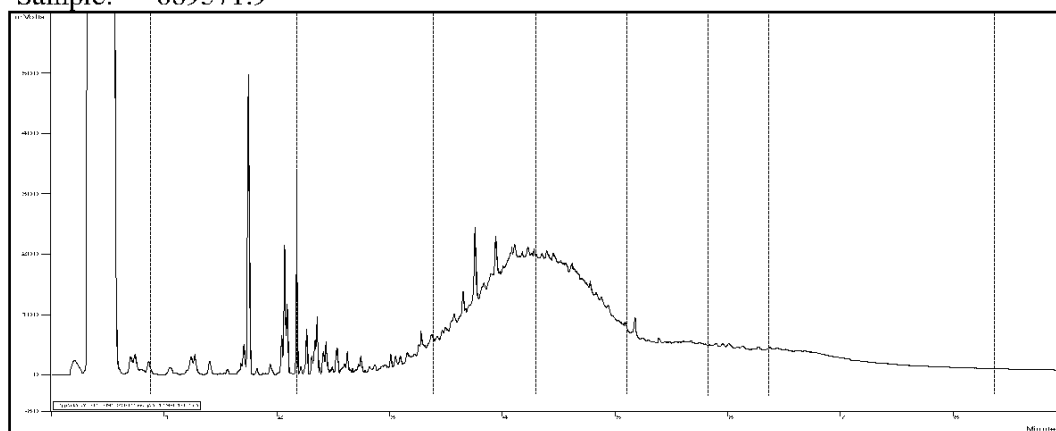


Sample: 689571.8

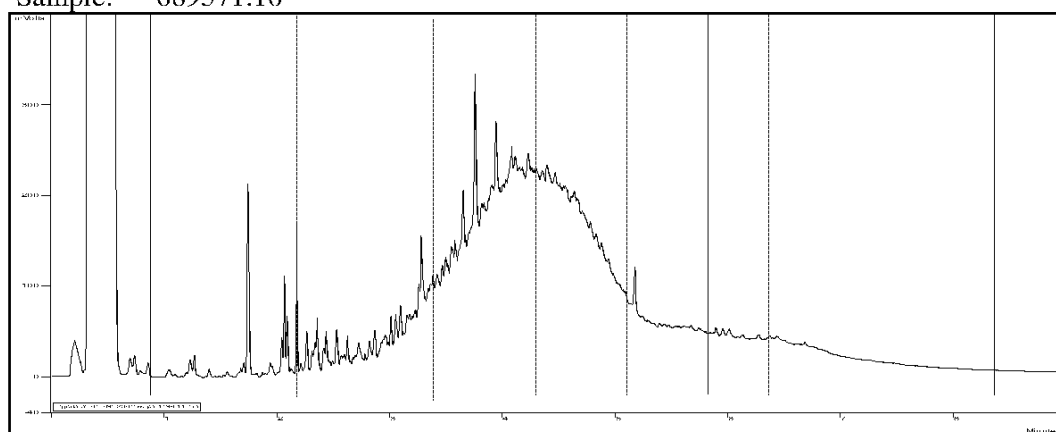


C7 C10 C15 C20 C25 C30 C34 C44

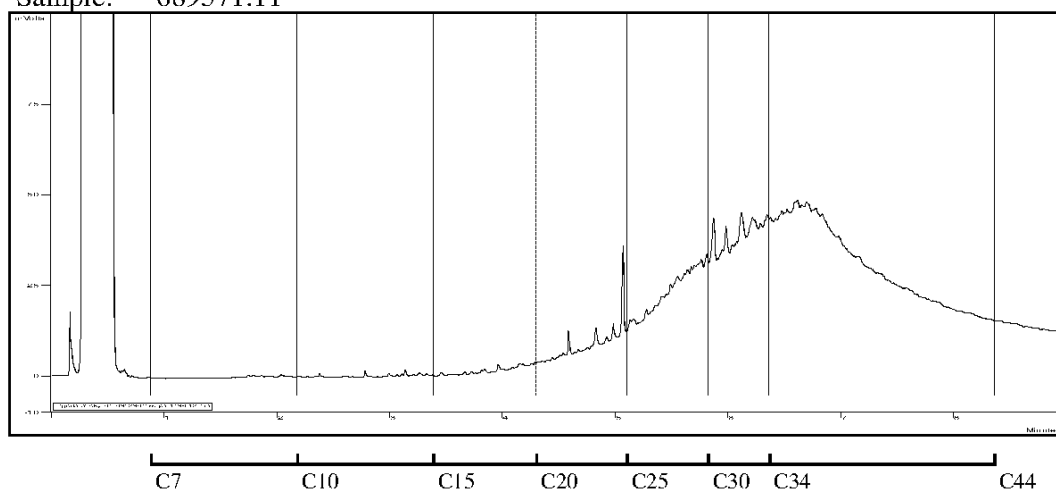
Sample: 689571.9



Sample: 689571.10



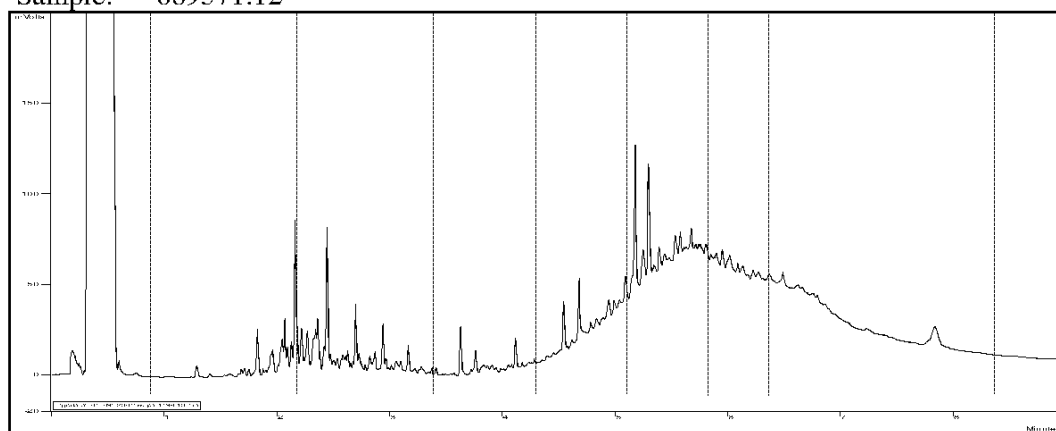
Sample: 689571.11



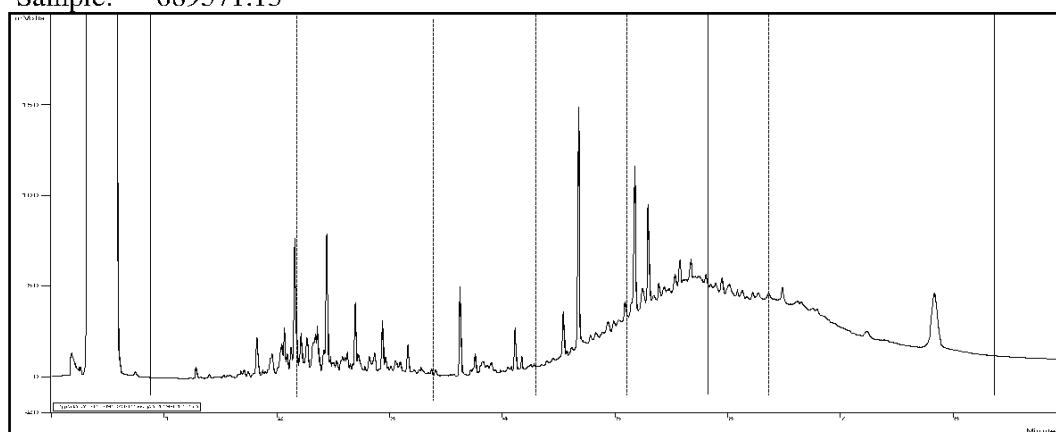
C7 C10 C15 C20 C25 C30 C34 C44



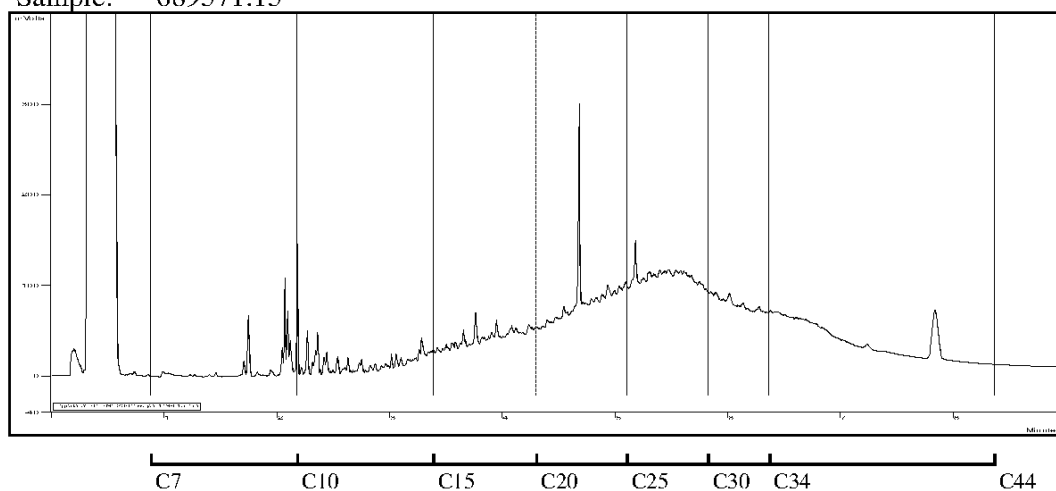
Sample: 689571.12



Sample: 689571.13

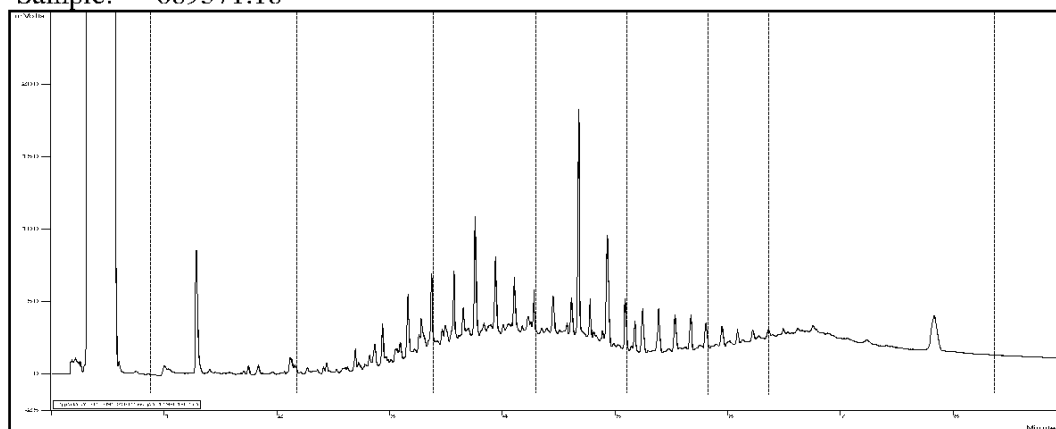


Sample: 689571.15

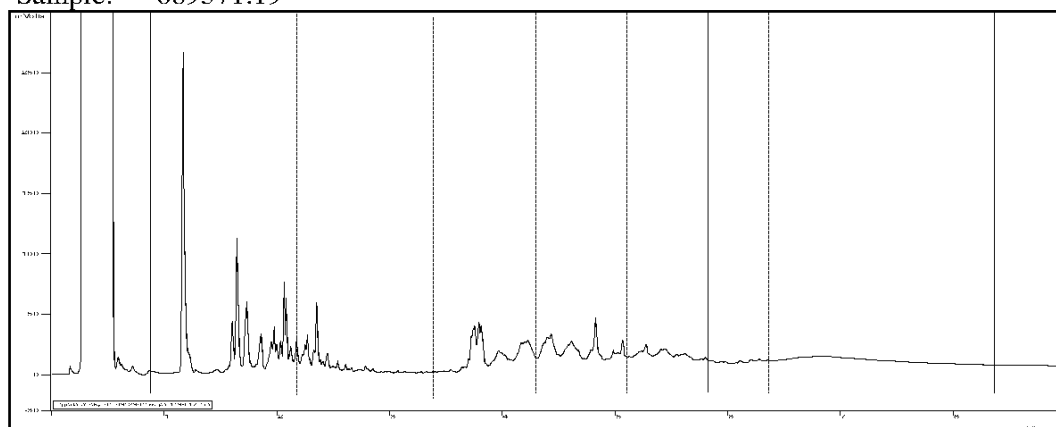


C7 C10 C15 C20 C25 C30 C34 C44

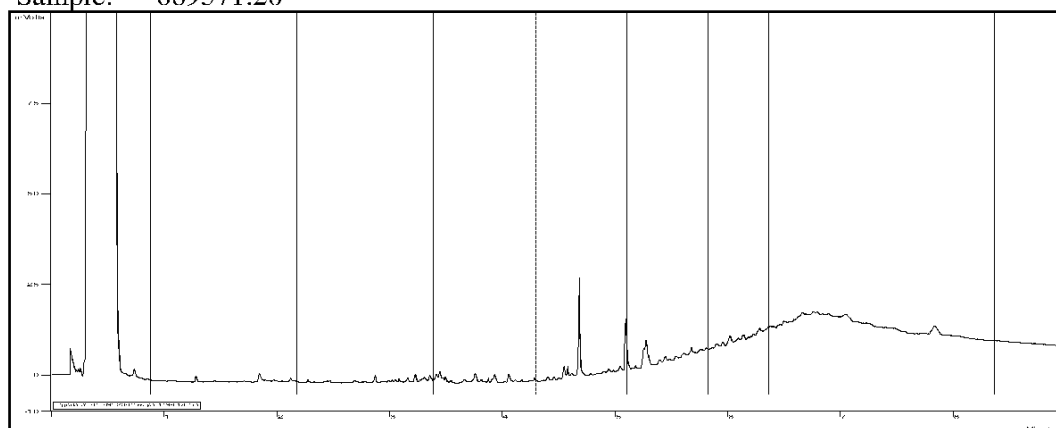
Sample: 689571.18



Sample: 689571.19

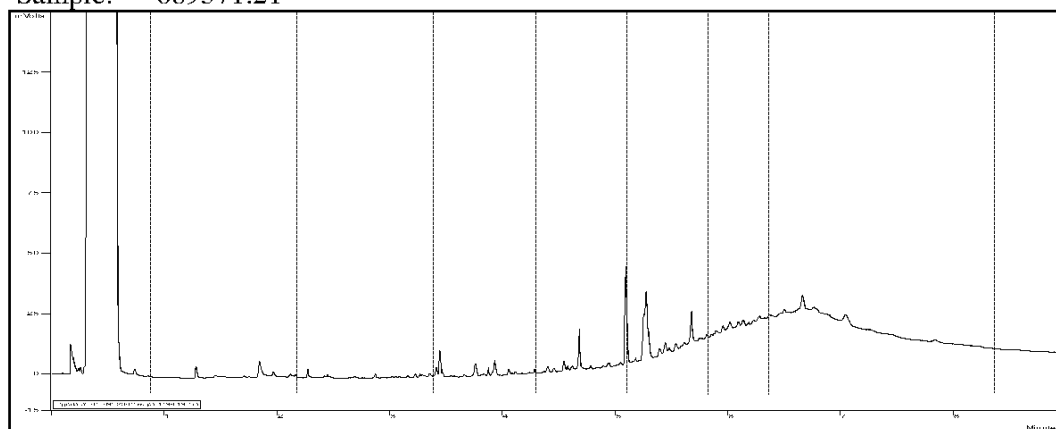


Sample: 689571.20

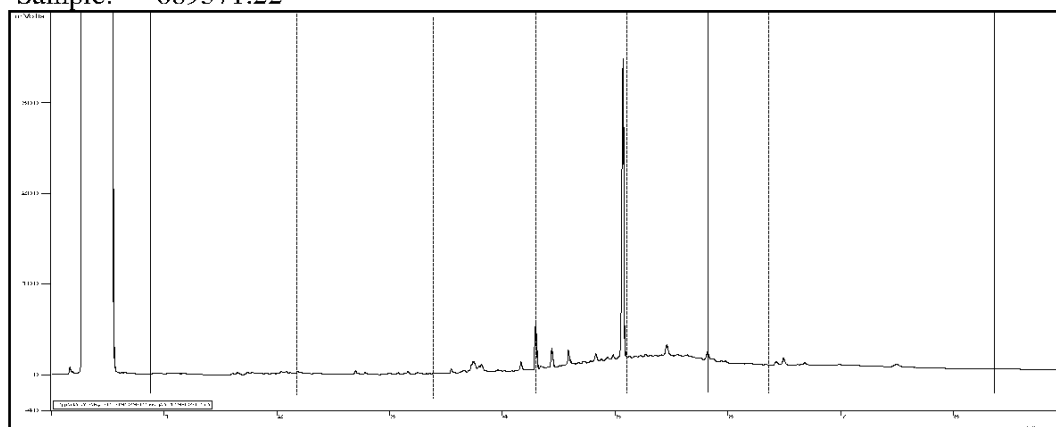


C7 C10 C15 C20 C25 C30 C34 C44

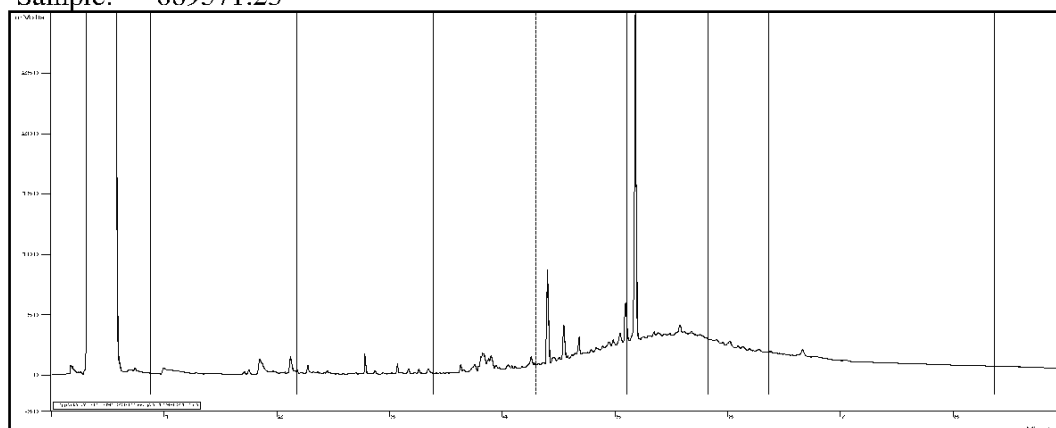
Sample: 689571.21



Sample: 689571.22



Sample: 689571.23



C7 C10 C15 C20 C25 C30 C34 C44