



***Preliminary Examination of Organic
Compounds Present in Tyres, Brake Pads
and Road Bitumen in New Zealand***



Preliminary Examination of Organic Compounds present in Tyres, Brake Pads and Road Bitumen in New Zealand

Prepared for



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by

Jennifer Gadd & Paul Kennedy
Kingett Mitchell Limited

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Appendix A: Summary of SVOC detection limits by compound.

Abbreviations

ASE	Accelerated solvent extraction
BTEX	Benzene, toluene, ethylbenzene, xylene
GCMS	Gas chromatograph mass spectroscopy
kg	kilogram
mg/kg	Milligrams per kilogram (= ppm)
MoT	Ministry of Transport (New Zealand)
PAH	Polyaromatic hydrocarbon
ppb	parts per billion
ppm	parts per million
SVOC	Semivolatile organic compound
TPH	Total petroleum hydrocarbon
µg/kg	Micrograms per kilogram (= ppb)
USEPA	United States Environment protection Agency

1. INTRODUCTION

It is recognised that stormwater generated within urban areas carries a wide variety of pollutants such as the trace elements copper, lead and zinc and total petroleum hydrocarbons (TPH) (e.g., Williamson 1993, Kennedy 2003). Although trace organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (e.g., Pitt et al. 1995, Marsalek et al. 1997) and BTEX (benzene, toluene, ethylbenzene and xylene) (e.g., Delzer et al. 1996, Lopes & Dionne 1998) are known to be present in urban stormwater, there is little information on the contributions of other organic compounds in motor vehicle emissions to urban stormwater.

This report presents the results of a preliminary examination of the organic composition of three key components of the vehicle-road transport system that contribute to the presence of materials and contaminants on the road surface and in stormwater. The three components are vehicle tyres, brake pads and road bitumen. Kennedy & Gadd (2000) discusses the presence of inorganic compounds in these three sources.

2. METHODS

2.1 Samples and Sample Collection

Given the number of brands and types of brake pads and tyres available in New Zealand, 12 samples of tyres and brake pads were selected following discussion with distributors to try and provide a snapshot of the types available in New Zealand. Table 2.1 provides a summary of information about the brake pads examined. That information includes their brand, the location where the pads and linings were made and the types of vehicles these particular pads are used on in New Zealand. Table 2.2 summarises the types of tyres selected and their country of manufacture and the type of vehicle the tyre is typically used on. From these samples, six were selected for organic compound analysis. Refer to Kennedy & Gadd (2000) for a list of all samples collected.

Six samples of raw bitumen used in road construction were collected and five of bitumen on roads in the Auckland area. Of them, four raw bitumen and three on-road bitumen samples were analysed. Table 2.3 summarises the types of bitumen analysed and Table 2.4 the location of the roads where on-road bitumen was collected and analysed for organic compounds.

2.2 Sample Processing

Tyres were cut to remove a cross section of each tyre selected and the tyre treads were then removed and sliced. The slices were then frozen in liquid nitrogen and disintegrated into small fragments while enclosed in clean cloth material. A subsample of the fragmented tread was then sampled.

Brake pads were processed by removing the pad from its backing and broken to remove fragments for digestion. Several small fragments amounting to about 2 g were used for the analysis.

Table 2.2 - Brake Pads Examined.

Sample Number	Manufacturer	Place of manufacture	Part Code	Vehicle Type	Vehicles Used In
1	Brakeplus	Australia	DB 1085P	car	Holden commodore
2	Don Brakes	USA	DB 319 D	car	Mitsubishi cordia, galant, lancer
3	Noki	Japan	XK 3337 N	light truck	Ford trader
4	Bendix	Australia	DB 340/4WD	4WD	Nissan navarra, pathfinder
5	Noki	Japan	DB 300 S	car	Honda Accord
6	MK Kashiyama Corp	Japan	DB 1308 S	car	Nissan Skyline

Table 2.2 - Tyres Examined.

Sample Number	Manufacturer	Location of Manufacture	Tyre Code	Vehicle Type
1	Dunlop	Australia	10.00.R20 Steelmaster	Truck
2	Enduro	New Zealand (retread)	P175/70 R13 82S Enduro GR2000	Car
3	Kelly	Brazil	P195/60 R14 85S Kelly Charger	Car
4	Dunlop	Japan	235/452 R17 Dunlop Formula	Car
5	Dunlop	New Zealand	NZ185 R14C 102/100	Car
6	Roadstone	Korea	Roadstone radial A/T 31X10.5 R15	4WD

Table 2.3 - Raw Bitumen Samples Examined.

Sample Number	Bitumen Type
1	60-70-1
2	180/200-2
3	80/100+polymer
4	180/200+polymer

Table 2.4 - Road Bitumen Samples Examined.

Sample Number	Location
1	Ariho Road, Devonport
2	Bentley Rd, Glenfield
3	Diomedea Road, Devonport
3	Barrys Point Rd, Takapuna
5	Commodore Parry Rd, Devonport

Raw bitumen was provided direct from the supplier in metal containers and subsampled directly from the containers. Road bitumen samples were collected during road milling. A bulk sample of milled bitumen fragments were collected and the bulk sample sieved to assist in isolating bitumen and to remove road aggregate that was present. A sample of bitumen fragments amounting to about 250 g was hand picked. In the laboratory, the samples were distilled water washed and lightly oven dried.

2.3 Analysis

All analyses including extraction and pre-treatment were performed by Australian Laboratory Services (ALS) Melbourne and Sydney.

Extraction

Samples were extracted using accelerated solvent extraction according to USEPA method 3545. Where appropriate, 5g of sample was extracted with 10% acetone in dichloromethane using accelerated solvent extraction (pressurised fluid extraction) – the instrument being Dionex ASE 200. The extract (approximately 25 mL) was reduced under a stream of nitrogen and the extract exchanged into toluene prior to analysis

For initial bitumen analysis, 100 mg of material was dissolved in 10 mL of toluene.

Bitumen samples were prepared in Melbourne by dilution in pentane and 100 to 250 mg of material was used. Additional tyre material was extracted by ASE and the residue reduced to dryness and the amount of residue was gravimetrically determined. The dried extracts were transported to the Melbourne laboratory and redissolved in n-pentane.

SVOC (Semivolatile organic compounds) Analysis

Samples were analysed by Gas Chromatograph Mass Spectroscopy (GC-MS) according to USEPA method 8270. In brief, extracted samples are injected into a GC-MS fitted with a 30 m x 0.25 mm internal diameter DB-5 (or equivalent) column with film thickness of 1 µm. Concentration of eluted SVOCs is calculated by comparison to the closest eluting internal standard. There were 118 compounds from ten functional groups targeted in the SVOC analysis. The compounds and their detection limits are listed in Appendix A.

GC-MS Analysis was performed on HP5973 GC-MSD in the scan mode (scan range m/z 40-550). Chromatography was performed on Chrompack CP-Sil 8 CB column (or other equivalent 5% phenylmethylsilicone column). The carrier gas was helium (1.2 ml per minute – constant flow mode).

Identification of Unknown Compounds

The mass spectra of peaks detected in the GC-MS chromatogram were compared to a reference spectra library to identify unknown compounds. Where there was no match, the mass spectra of the unknowns were examined to either identify the compound or its functional group.

TPH Fractionation

TPH fractionation was performed on glass columns packed with 3 g of deactivated silica gel. Samples were dissolved in pentane. The aliphatic fraction was eluted with n-pentane and the aromatic with dichloromethane.

Aromatic speciation

Extracted samples of raw bitumen, road bitumen and tyres (subsamples of SVOC samples, extracted as above) were sent to Sydney ALS for further analysis for aromatics. Approximately 10 mg of each extracted residue was separated into its aliphatic and aromatic fractions. The aromatic fraction was analysed by GC-MS in scan mode to identify any aromatics present (Method US8270).

Quality Control

Method blanks were analysed with each batch of samples for quality control purposes. In addition, nine surrogate compounds were added to each sample before extraction and the concentration was measured along with other compounds in the GC-MS scan to determine recovery. An internal standard containing six aromatic compounds was added to each sample before analysis for unknowns. Quality control procedures were conducted according to the USEPA test method and ANZECC quality control guidelines for analytical methods. For the aromatic speciation test, a control sample blank that contained both aliphatic and aromatic compounds was separated according to the method and analysed along with each batch of samples. A sample replicate was also spiked with the mixed aliphatic/aromatic standard before separation and analysis.

3. RESULTS

3.1 Tyres

TPH

Examination of the semivolatile TPH banding revealed no hydrocarbons with n-alkane carbon numbers C10-C14. 39% of the TPH was in the n-alkane range C15-C28 and 61% was > C29. This data compares well with the results of Hildemann et al. (1991) who examined the n-alkane mass distributions in tyre dust samples and found a dominance of higher n-alkane carbon numbers. The peak in mass distribution occurs at or beyond C36 (high molecular weight).

Semi-volatiles

Ten groups of semi-volatile organic compounds were targeted (118 compounds in total) by the analysis. A list of these compounds and their detection limits is provided in Appendix A. No phenols, phthalate esters, nitroaromatics and cyclic ketones, haloethers, chlorinated hydrocarbons, organochlorine pesticides or organophosphorus pesticides were present in concentrations above the detection limits in the tyres. The compounds detected and their concentrations are presented below in Table 3.1.

Table 3.1 - Concentrations of semi-volatile organic compounds detected in a selection of 6 tyres available in New Zealand compared to literature (all data mg/kg).

	1	2	3	4	5	6	Lit ¹	Lit ²
Polycyclic aromatic hydrocarbons								
Acenaphthylene	<10	<10	8.2	19.8	<10	<5	-	-
Phenanthrene	<10	<10	6.2	6.3	<10	<5	11.8	-
Fluoranthene	<10	9.4	14.6	28.5	<10	<5	11.1	-
Pyrene	6.3	28.8	56.3	69.7	10.8	<5	54.1	41.4
Benzofg,h,ijperylene	<10	<10	<10	<10	<10	17	nd	-
Nitrosamines								
N-Nitrosodiphenyl & diphenylamine	34	<20	60	<20	<20	18	-	-
Anilines and Benzidines								
Aniline	<10	<10	217	70.9	<10	<5	-	-

Note: ¹ from Rogge et al. 1993, ² Reddy & Quinn (1997), - not reported.

Unknowns

A number of compounds were detected in the second analysis for unknowns (i.e., compounds which were not included in the targeted semi-volatile scan). These are presented below in Table 3.2. Concentrations presented are an estimate based on the concentration of surrogate compounds and are regarded as semi-quantitative.

The results demonstrate that some major compounds are common to each of the tyres, however, there appears, based upon the results obtained, to be some differences between tyres in the additives used. The most common compounds present in the tyres were amines. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) was the most abundant compound in all six tyres analysed. A number of other benzenediamines (also known as phenylenediamines) (diphenyl phenylenediamine (DPPD), N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), methyl- and ethyl- substituted diphenyl benzenediamines) were also present in three of the six tyres.

Hexadecanoic acid, octadecanoic acid and their methyl esters were also common in the tyre samples analysed, present in all samples. Dihydrotrimethylquinoline was present in five out of six tyres and phenols were present in three out of six tyres. Benzothiazole and mercaptobenzothiazole were present in all and three out of six tyres respectively, with mercaptobenzothiazole identified as one of the most abundant compounds in the tyre extract. Most of the other compounds listed above in Table 3.2 were detected in only one tyre sample. Table 3.2 also identifies results obtained by Rogge et al (1993).

Table 3.2 - Concentrations of organic compounds identified in a selection of 6 tyres available in New Zealand (all data mg/kg).

	1	2	3	4	5	6	Lit. ¹
Long chain acids and methyl esters							
Tetradecanoic acid		33.2	17.6		9.30		634.5
Hexadecanoic acid, methyl ester	38.8				25.3		-
Hexadecanoic acid	266	1480	931	383	607	256	4818.4
Octadecanoic acid, methyl ester	17.9						-
Octadecanoic acid		1040	203	166	191	138	6009.0
Aromatic amines							
2-phenylmethylbenzenamine	20.5		33.4				-
2-methyl-N-(2-methylphenyl)-benzenamine			8.95				-
Diphenyl benzenediamine	207		300			150	-
Methyl substituted diphenyl benzenediamine	727		738			364	-

Ethyl substituted diphenyl benzenediamine	366		344			159	-
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine	1190	1480	1790	1170	1410	1050	-
N-isopropyl-N'-phenyl-p-phenylenediamine			44.3				-
Benzothiazoles							
Benzothiazole	44.7	31.3	70.4	30.8	23.5	67.9	124.3
Methylthiobenzothiazole		6.70			6.30		-
Mercaptobenzothiazole		437		430	242		-
Heterocyclic amines							
Dihydrotrimethylquinoline	7.5	28.6	37.4	72.5	14.6		-
Substituted quinolines				9.20			-
Substituted indoles				4.45			-
Isoindoleione	11.4	4.25		27.9			-
Phenols							
Propenylphenol	21.7						-
Di(methylbenzyl)phenols					627		-
Tri(methylbenzyl)phenols					715		-
Substituted methoxyphenol		22.6					-
Misc organic compounds							
Benzothiazolone	14.3						-
Isothiocyanatocyclohexane		31.8			31.4		-
Isocyanatocyclohexane						5.25	-
Sequiterpenoid compounds		17.45					-
N,N'-diphenylguanidine			135				-
1,3-bis(methylethyl)benzene				5.45			-
1,4-dimethyl-7-(1-methylethyl)azulene					110		-
bis-1,1'-(3-methyl-1-propene-1,3-diyl)benzene					9.60		-
Unknown (177 m/z)				23.2			-
tert-Butyl-hydroxyanisole						146	-
Dibenzothiophene						4.20	-
Methyldibenzothiophene						11.4	-
Unknown (M+ 346 m/z)	165				277	129	-

Note: ¹ from Rogge et al. (1993).

3.2 Brake Pads

TPH

No specific banding assessment was carried out. Examination of the semivolatile scan indicated some n-alkanes in C10-C14 through to C29-C36. Hildemann et al. (1991) reported n-alkanes present in C12 through to C34 with little present at >C34.

SVOC Scan

Only three compounds were detected in the brake pad samples above the detection limit in the SVOC scan (Table 3.3). Phenol was found in all brake pad samples, with the concentration ranging from 6.9 to 1310 mg/kg. Bis(2-ethylhexyl)phthalate (DEHP) was detected in one brake pad sample at 486 mg/kg. DEHP is a commonly used phthalate plasticiser added to increase flexibility. N-Nitrosodiphenyl & diphenylamine was also present in this sample (at 24 mg/kg).

Table 3.3 - Concentrations of organic compounds identified in a selection of 6 brake pads available in New Zealand (all data mg/kg).

	1	2	3	4	5	6
Phenol	485	1310	332	6.9	158	252
Bis(2-ethylhexyl) phthalate	-	-	-	-	-	486
N-nitrosodiphenyl & Diphenylamine	-	-	-	-	-	24

Unknown Scan

Table 3.4 lists the wide range of organic compounds that were detected in the brake pads by GC-MS scan for unknown compounds. Most of the compounds were present in low concentrations. The concentration of an individual compound can be compared between samples. The nature of the analysis and quantitation method and differences in extraction efficiencies and detector response between individual compounds mean that the reported concentrations are not regarded as quantitative. A number of compounds were detected in the GC-MS scan, but their identity could not be determined and are listed below in Table 3.4 as either 'unknown' or by their functional group where this was ascertained.

Table 3.4 - Concentrations of organic compounds identified in a selection of 6 brake pads available in New Zealand compared with literature (data mg/kg).

	1	2	3	4	5	6	Lit. ¹
Long chain acids and methyl esters							
Tetradecanoic acid	1.3		6.4		1.5		8.1
Hexadecanoic acid	11	18	47	3.3			83.3
Hexadecanoic acid methyl ester		2.0			0.7		-
9 Octadecanoic acid (Z)-, ethyl ester						5.10	
Carboxylic acid (M+ 196 m/z)					1.7		-
Carboxylic acid (M+ 429 m/z)	2.4						-
Diisooctyl ester benzene carboxylic acid	190			1.0			-
Carboxylic acid (M+ 316 m/z)					64		-
Alkyl and aromatic amines and amides							
Methenamine		22					-
Trimethylbenzenamine		4.2					-
Diphenylamine						10.0	nd
Diphenyl benzenediamine				1.0			-
Methylethyl-phenylbenzenediamine						17.7	-
Aromatic amine (M+ 163 m/z)		13					-
Aminobenzophenone		1.5					-
Other nitrogen containing compounds							
Hexadecanamide						5.10	-
Alkyl amide (M+ 128 m/z)				2.0			-
Alkyl amide (M+ 281 m/z)				1.8	7.2		-
Alkyl amide (M+ 284 m/z)					11		-
Methylindoline		2.1					-
Hexadecanenitrile					1.0		-
Phenols							
Hydroxyphenylmethylphenol	126	500	403	5.5	73	201	-
Methylenebis phenol	123	303	462	4.3	123	351	-
Dimethoxyphenol	0.8						-
Alkyl phenol (M+ 344 m/z)		20					-
bis(dimethylethyl)phenol						2.55	-
bis(dimethylethyl)benzenediol			2.3		1.2		-
(Dimethylethyl)ethylphenol			47		12		-

Alkyl phenol (M+ 330 m/z)	1.9						-
Alkyl phenol (M+ 302 m/z)	230	114		1.5		166	-
Butylated hydroxy anisole			17		3.3		-
Butylated hydroxy toluene			21				-
Oxygen containing							
Dimethyl benzene methanol	5.8						-
Butoxy ethoxy ethanol	1.1					90.8	45.7
o-Hydroxybenzaldehyde	5.0	16	10	7.4	8.4	7.30	4.7
p-Hydroxybenzaldehyde or m-hydroxybenzaldehyde					8.6		-
Benzodioxin	16	31	34		29		-
Benzothiazole	3.5	6.9	8.0	1.5	2.8	6.85	nd
Benzothiazolone		1.3	2.0				-
Benzophenone				1.1	1.7		-
Methoxy-(phenylethenyl)-benzene						10.4	-
Misc organic compounds							
Ethenyl dimethyl benzene			6.8				-
Dimethyl(methylethyl)naphthalene	1.1	1.3					-
Diethenylbenzene			4.6				-
Tetramethyl phenanthrene			4.7				-
Aromatic acid, methyl ester (M+ 314 m/z)			44			34.2	-
Unknown aromatic compound (M+ 368 m/z)			11		13		-
Unknown organic (M+ 268 m/z)				71			-
Unknown organic compound (M+ unknown)						82.2	-

Note: ¹ from Rogge et al. (1993).

Many of the compounds were present in all or most of the six brake pads analysed. Phenols (hydroxyphenylmethylphenol and methylenebis phenol) were the most abundant group present in the brake pad extracts and were present in all six brake pad samples analysed.

Other compounds commonly detected were o-hydroxybenzaldehyde (salicylaldehyde) and benzothiazole, though at lower estimated quantities. An isomer of o-hydroxybenzaldehyde (either p-hydroxybenzaldehyde or m-hydroxybenzaldehyde) was also present in one sample. This may have been added as an impurity with the o-hydroxybenzaldehyde during manufacture.

As with the tyre samples, long chain organic acids (tetradecanoic and hexadecanoic acid) and methylesters were present in many of the brake pads samples. A number of aromatic carboxylic acids were also present. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) were present in one of the brake pad samples.

3.3 Bitumen

TPH

Examination of TPH bands revealed that most of the n-alkanes were of a high molecular weight with >C29 comprising 86%. N-alkanes of C15-C-28 made up 13% and 1% was present as C10-C14. Hildemann et al. (1991) did not examine bitumen but examined paved road dust which had a dominance of n-alkanes in the C31-C32 range. Some other sources such as plant material contributed to the presence of the C27-C32 n-alkanes in the dust.

SVOC Scan

A single sample of raw bitumen was analysed by SVOC scan. None of the 217 target compounds were present above the detection limit (generally 10 mg/kg, listed above in Section 2).

Aromatic speciation

No aromatic compounds were detected by GC-MS of the aromatic fraction of 6 bitumen samples (3 road bitumen, 3 raw bitumen).

Further PAH analysis at a second laboratory (Hill Laboratories, Hamilton) demonstrated the presence of low concentrations of PAHs in a raw bitumen sample (Table 3.5). The concentration of PAHs in this sample ranged from below detection (0.2 mg/kg) to 2.2 mg/kg for the 16 PAH compounds tested.

Table 3.5 - Summary of organic composition of a selection of raw bitumen in New Zealand (all results mg/kg).

	180/200+P
Acenaphthene	<0.2
Acenaphthylene	<0.2
Anthracene	0.2
Benzo(a)anthracene	1.0
Benzo(a)pyrene	<0.2
Benzo(b)fluoranthene	<0.2
Benzo(g,h,i)perylene	2.2
Benzo(k)fluoranthene	<0.2
Chrysene	1.2
Dibenzo(a,h)anthracene	<0.2
Fluoranthene	0.4
Fluorene	<0.2
Indeno(1,2,3-c,d)pyrene	<0.2
Naphthalene	0.3
Phenanthrene	0.3
Pyrene	2.1

4. DISCUSSION

4.1 Tyres

Tyre tread is composed primarily of hydrocarbons (natural and synthetic polymers making up the rubber), carbon black and a range of additives that are included in their manufacture to promote particular physical properties and protect against the effects of degradation (from heat, oxidation and chemicals). The various chemicals, other than the key components, amount to about 1/7th of the weight of the tyre.

Environment Agency (1998) provides an overview of the chemical composition of vehicle tyres. The bulk composition of tyres varies considerably depending upon their function. This is reflected by the large numbers of brands and types of tyres in most markets including New Zealand. Table 4.1 provides a summary of the composition of New Zealand tyres as presented in MoT (1996).

Table 4.1 - General composition of tyres.

Component	Composition (%)
Rubber	55
Carbon black	26-27
Oils	5
Resins	5
Curing Agent	3-5
Anti-ageing agent (e.g., paraffin wax)	2 (mainly side walls)
Zinc oxide	0.7
Cadmium	7.7×10^{-6}
Lead	8.4×10^{-6}

The concentrations of the compounds identified in New Zealand tyres (Table 6) are consistent with the concentrations reported by Rogge et al. (1993), despite the differences in sample preparation and analysis. In particular, the concentrations of PAHs reported by Rogge et al. (1993) and Reddy & Quinn (1997) correspond very well to the concentrations of each compound measured in the current study.

Rogge et al. (1993) also reported high concentrations of alkanes, containing from 19 to 40 carbon atoms. These were not detected in the current study due to the different analytical method. Hildemann (1991) found that different types of dusts within urban environments (e.g., tyre, road, cigarette smoke) each have a unique organic fingerprint, which can be used to distinguish aerosols from different sources.

There were a number of compounds detected in the current study that were not reported by Rogge et al. (1993), however many were identified in only one or two of the tyre samples analysed, demonstrating the wide variation in tyre composition. Many of the compounds identified in the analysis reported in Section 3 are tyre additives. The majority of the additives used in the manufacture of tyres are organic (antioxidants, accelerators and retarders, fillers, peptisers) but a number of trace elements are also used. Environment Agency (1998) reports the presence of organic compounds such as amines, organic acids and phenol derivatives in tyres. Amines such as N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), diphenyl benzenediamine (DPPD), N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), methyl- and ethyl- substituted diphenyl benzenediamines were present in many of the tyres. These compounds are antioxidants possessing antiozonant properties, which are added to rubber tyres in order to protect against stress, heat, oxidation and ozone attack.

Bayer (<http://www.rubber.bayer.com>) lists the quinoline dihydrotrimethyl-quinoline as a staining antioxidant added to tyres for protection against oxidation and heat. Environment Agency (1998) reports the use of phenol derivatives as hardeners in tyres. Substituted phenols such as di(methylbenzyl)phenol were identified as present in three out of six tyres in this study.

Benzothiazole and mercaptobenzothiazole are used as accelerators, to speed up the curing process. Mercaptobenzothiazole was one of the most abundant compounds in some tyre extracts in this study. Benzothiazolone is a breakdown product of these antioxidants. The concentrations of benzothiazole, 2-hydroxy benzothiazole (HoBT) and 2-(4-morpholino)-benzothiazole (24MoBT) have been quantified in rubber particles and urban runoff by Reddy & Quinn (1997). They measured concentrations of 171 ± 21 mg/kg of benzothiazole in recycled crumb rubber from automobile tyres (~150 μ m in diameter). The rubber also contained 80.9 ± 3.2 mg/kg HoBT and 3.76 ± 0.78 mg/kg MoBT. The Reddy & Quinn (1997) results were similar to earlier results obtained by Rogge et al. (1993) (Table 6). Kumata et al. (1997) reported 2 mg/kg HoBT in particles of tyre wear. Although these results may seem to be inconsistent with the concentrations measured in rubber particles in the current study

(23.5 to 70.4 mg/kg) it is not outside the range of concentrations expected when the differences in method are considered (i.e., quantitative (Reddy & Quinn 1997) compared to semi-quantitative (this study)).

Diphenylguanidine, present in one of the tyres, is also used as an accelerator (Bayer (<http://www.rubber.bayer.com>)). Other abundant compounds in the tyres were hexadecanoic acid and octadecanoic acid. These are long chain organic acids and have been used in the past as retarders (Environment Agency 1998).

There were a number of differences between the tyres in the types of chemicals added to them. Tyres 1 and 3 contained a number of benzenamines and benzenediamines as antioxidants whereas tyre 4 contained quinolines as antioxidants. Tyres 2 and 5 contained only 6PPD as an antioxidant, but contained more accelerators (mercaptobenzothiazoles). The differences in tyre composition may be due to the different uses of the tyres (i.e., truck, car, 4WD).

4.2 Brake Pads

Brake pads and linings have undergone many changes over the years. The composition, which was dominated by asbestos 20 years ago, now comprises numerous materials. Brake linings are manufactured to specific applications depending on size, wear and noise. There are a very large number of brake pad manufacturers around the world and a very large variety of brake pads and linings. In New Zealand it is estimated that there are more than 400 different types on the market. Armstrong (1994) indicated that there were more than 1000 different types of brake pads in the United States market.

Brake linings can be grouped into three key categories. These are semi-metallic, organic and non-asbestos organic. There are however a wide range of specialised brake pads/frictional materials on the market which typically cater for non automotive applications, or particular vehicle uses such as race and luxury cars (e.g., the use of paper, carbon, resin bonded graphite and the use of ceramic particles in metal matrices).

Semi-metallic linings are a mixture of fragments or powdered metal and phenolic resins and other binders or fillers. The metal (such as iron, steel, copper and brass) is present for heat transfer, while the phenolic resins hold these fragments together. Phenolic resins tend to be the most common matrix of the brake pad. Some forms of rubber are also occasionally used for this purpose. Table 4.2 presents a summary of the common materials present in brake pads.

Table 4.2 - Summary of materials present in brake pads (adapted from Gudmand-Hoyer et al. 1999).

Component	Material
Fibre	Organic (aramid), fibreglass, kevlar
	Metal
Fillers	Baryte, friction dust and vermicullite
Metals	Brass
Abrasives	Zirconium sulphates
	Aluminium oxides
Binders	Resin, rubber
Metal sulphides	Copper (Cu ₂ S), lead sulphide (PbS) or antimony sulphide (Sb ₂ S ₃)

Phenols were the most abundant group present in the brake pad extracts. Phenolic resins are one of the major components of non-asbestos organic material brake pads, as they are used to bind the metallic constituents together. Salicylaldehyde (o-hydroxybenzaldehyde) was present in all samples and is used as a flame retardant in some applications. Benzothiazole was identified in the previous section as an accelerator used in tyre manufacture and it is possible that it may be added to the brake pads to aid the manufacturing process. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are antioxidant preservatives and are commonly found in rubber and petroleum products (Merck 1996).

There were also apparent differences between the compounds present in the brake pads. Samples 1 and 3 contained no amines or amides, whereas the other 4 samples contained between 2 and 5 compounds from these groups.

As with the tyre samples, the concentrations of identified compounds is consistent with those reported by Rogge et al. (1993). Again, there were differences generally in the types of compounds reported, with Rogge et al. (1993) reporting further benzaldehydes than the present study and a number of polyglycol ethers in addition to butoxyethoxy ethanol found in this study.

4.3 Bitumen

No organic compounds were detected in the 6 bitumen samples analysed by SVOC and aromatic speciation. Polycyclic aromatic hydrocarbons (PAHs) were detected in one sample analysed by a separate laboratory using lower detection limits. The concentrations present in this sample were lower than the detection limit used in the SVOC scan (detection limit 10 mg/kg for PAHs). If PAHs are present in all bitumen samples at similar concentrations this would explain why no PAHs were detected in the SVOC scan. The aromatic speciation test used a lower detection limit than the SVOC scan (2 mg/kg). This remains higher than the concentration of most of the PAHs detected in the raw bitumen sample.

Although bitumen historically contained high concentrations of PAHs, due to their natural presence in the heavy fraction of hydrocarbons that bitumen was refined from, modern bitumen is quite different. In addition to lower concentrations of PAHs, it contains synthetic polymers such as SBS (styrene butadiene styrene), which are added to bitumen to improve its properties. Herrington et al. (1993) reported concentrations of PAHs in Safaniya bitumen used in New Zealand (Table 4.3). These were low (often close to the detection limit) and similar to concentrations measured in the current study.

Table 4.3 - Comparison of polyaromatic hydrocarbon concentrations in New Zealand bitumen (All data mg/kg).

Polyaromatic hydrocarbon	Concentration in this study	Concentration in Safaniya bitumen
Fluoranthene	0.4	det.
Pyrene	2.1	det.
Benzo(a)anthracene	1.0	det.
Chrysene	1.2	ND
Benzo(b)fluoranthene	<0.2	12.1
Benzo(k)fluoranthene	<0.2	0.10
Benzo(a)pyrene	<0.2	0.15
Dibenzo(a,h)anthracene	<0.2	ND
Benzo(g,h,i)perylene	2.2	1.7

Notes: ND not detected. Det – detected.

The composition of bitumen has been described previously (e.g., Jones 1993), however these are mainly for bitumen used overseas and differ from that used in NZ. Nonetheless, in the absence of New Zealand data, this data is of use. Jones (1993) reports polar aromatics in bitumen between 18.7 and 52.7% and naphthene aromatics between 22.4 and 46.6%. Naphthene aromatics would include any PAHs in the bitumen. Other components of bitumen include aliphatic sulphides and thiophene derivatives (Herrington et al. 1994).

In summary, this study demonstrated that PAHs were present in a bitumen sample at low concentrations, however, further testing at lower detection limits is required to confirm their presence in other samples.

5. SUMMARY AND CONCLUSIONS

A diversity of organic compounds, were detected in the tyres and brake pad samples. These were similar to compounds already reported in the international literature and those reported by manufacturers. Concentrations of the compounds found in this study (semi-quantitative) were consistent with those reported in quantitative studies. In contrast, bitumen samples contained fewer compounds than tyres and brake pads.

- Tyres and bitumen contribute TPH containing a predominance of n-alkanes of higher molecular weight compared to brake pads.
- A range of compounds were identified in the tyres examined. Composition was dominated by long chain acids. Additives such as benzothiazole were also found.
- PAH concentrations in bitumen are low and the results obtained in this study are comparable to other published data. Tyres contain PAH and the concentrations vary between brands of tyres. Pyrene was identified as the most common PAH in tyres. Low concentrations of n-alkyl substituted PAHs were found.
- A number of organic compounds were found in the brake linings examined. Phenol and phenol derivatives were found in all samples and one phthalate was found in one tyre sample.

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Appendix A: Detection limits of target compounds in the SVOC analysis.

Compound	Detection Limit (mg/kg)
Phenols	
Phenol	10
2-Chlorophenol	10
2-Methylphenol	10
3- & 4-Methylphenol	10
2-Nitrophenol	10
2,4-Dimethylphenol	10
2,6-Dichlorophenol	10
4-Chloro-3-methylphenol	10
2,4,6-Trichlorophenol	10
2,4,5-Trichlorophenol	10
Pentachlorophenol	20
Polycyclic aromatic hydrocarbons	
Naphthalene	10
2-Methylnaphthalene	10
2-Chloronaphthalene	10
Acenaphthylene	10
Acenaphthene	10
Fluorene	10
Phenanthrene	10
Anthracene	10
Fluoranthene	10
Pyrene	10
N-2-Fluorenylacetamide	10
Benz(a)anthracene	10
Chrysene	10
Benzo(b) & (k)fluoranthene	20
7,12-Dimethylbenz(a)anthracene	10
Benzo(a)pyrene	10
3-Methylcholanthrene	10
Indeno(1.2.3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(g,h,i)_perylene	10
Phthalate esters	
Dimethyl phthalate	10
Diethyl phthalate	10
Di-n-butyl phthalate	10
Butyl benzyl phthalate	10
Bis(2ethylhexyl) phthalate	100
Di-n-octyl phthalate	10
Nitrosamines	
N-Nitrosomethylethylamine	10
N-Nitrosodiethylamine	10
N-Nitrosopyrrolidine	20
N-Nitrosomorpholine	10
N-Nitrosodi-n-propylamine	10
N-Nitrosopiperidene	10
N-Nitrosodibutylamine	10
N-Nitrosodiphenyl & diphenylamine	20
Diallate	10
Methapyrilene	10
Nitroaromatics and cyclic ketones	
2-Picoline	10
Acetophenone	10
Nitrobenzene	10
Isophorone	10
2,6-Dinitrotoluene	20
2,4-Dinitrotoluene	20
1-Naphthylamine	10
4-Nitroquinoline-N-oxide	10
5-Nitro-o-toluidine	10

Compound	Detection Limit (mg/kg)
Azobenzene	10
1,3,5-trinitrobenzene	10
Phenacetin	10
4-Aminobiphenyl	10
Pentachloronitrobenzene	10
Pronamide	10
Dimethylaminoazobenzene	10
Chlorobenzilate	10
Haloethers	
Bis(2-chloroethyl)ether	10
Bis(2-chloroethoxy)methane	10
4-Chlorophenylphenylether	10
4-Bromophenylphenyl ether	10
Chlorinated hydrocarbons	
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
Hexachloroethane	10
1,2,4-Trichlorobenzene	10
Hexachloropropylene	10
Hexachlorobutadiene	10
Hexachlorocyclopentadiene	50
Pentachlorobenzene	10
Hexachlorobenzene	20
Anilines and Benzidines	
Aniline	10
4-Chloroaniline	10
2-Nitroaniline	10
3-Nitroaniline	20
Dibenzofuran	10
4-Nitroaniline	10
Carbazole	10
3,3'-Dichlorobenzidine	10
Organochlorine pesticides	
alpha-BHC	10
beta-BHC & gamma-BHC	10
delta-BHC	10
Heptachlor	10
Aldrin	10
Heptachlor epoxide	10
Endosulfan 1	10
4,4'-DDE	10
Dieldrin	10
Endrin	10
Endosulfan 2	10
4,4'-DDD	10
Endosulfan sulfate	10
4,4'-DDT	10
Organophosphorus pesticides	
Methanesulfonate methyl	10
Methanesulfonate ethyl	10
Dichlorvos	10
cis-Isosafrole	10
trans-Isosafrole	10
Safrole	10
Dimethoate	10
Diazinon	10
Chlorpyrifos methyl	10
Malathion	10
Fenthion	10
Chlorpyrifos	10
Pirimiphos ethyl	10
Chlorfenvinphos-E	10

Compound	Detection Limit (mg/kg)
Chlorfenvinphos-Z	10
Prothiofos	10
Ethion	10