Preliminary Examination of Trace Elements in Tyres, Brake Pads and Road Bitumen in New Zealand

Ministry of Transport
Te Manatū Waka

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Prepared for

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by

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Blank

TABLE OF CONTENTS

Abbreviations

Ag	Silver
Al	Aluminium
As	Arsenic
B	Boron
Ba	Barium
Be	Beryllium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Co	Cobalt
Cr	Chromium
Cs	Caesium
Cu	Copper
Fe	iron
g	gram
Ga	Gallium
Ge	Germanium
Hg	mercury
IC-PMS	Inductively coupled plasma mass spectrometer
K	Potassium
kg	kilogram
La	Lanthanum
Li	Lithium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MoT	Ministry of Transport (New Zealand)
Na	Sodium
Nb	Niobium
Ni	Nickel
P	Phosphorus
Pb	Lead
Rb	Rubidium
Sb	Antimony
Sc	Scandium
Sn	Tin
Sr	Strontium
Th	Thorium
Ti	Titanium
Tl	Thallium
U	Uranium
V	Vanadium
W	Tungsten
Zn	Zinc

1 INTRODUCTION

It is recognized, that stormwater generated within urban areas carries a wide variety of pollutants (e.g., Williamson 1991, Kennedy 2003). Although the presence of trace elements such as lead, copper and zinc have been identified as key constituents of urban stormwater, there is little information on the actual contributions of other elements from some of the potential contributors of contaminants to stormwater. These pollutants have been implicated in a variety of effects in both freshwater and estuarine/coastal environments including the build-up of contaminant levels in sediments with the potential to cause adverse effects as a result of sediment toxicity.

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

2 METHODS

2.1 Samples and Sample Collection

Four types of material were collected for analysis. These were a selection of 12 tyres and 12 brake pads used in New Zealand, a series of six samples of raw bitumen used in road construction and five samples of bitumen from roads in the Auckland area. Given the number of brands and types of brake pads and tyres available in New Zealand, a small subset were selected following discussion with distributors to try and provide a snapshot of the types available in New Zealand.

Table 2.1 summarises the types of tyres selected and their location of manufacture and the type of vehicle the tyre is typically used on. Tables 2.2 and 2.3 provide a summary of information about the brake pads examined including the 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 2.4 summarises the types of raw bitumen sampled and Table 2.5 the location of the roads where on-road bitumen was collected.

2.2 Sample Processing

Tyres were cut to remove a cross section of each tyre selected. The tyre treads were then removed and sliced. The slices were then frozen in liquid nitrogen and smashed into small fragments while enclosed in clean cloth material. A subsample of the fragmented tread was then obtained for analysis. 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 2.1 - Tyres Examined.

Sample	Brand	Location of Manufacture	Tyre Code	Vehicle Type	Vehicle examples*
1	Dunlop	Australia	A185 R14C	Van/light truck	Various vans
2	Dunlop	New Zealand	NZ185 R14C 102/100	Van/light truck	Various vans
3	Enduro	New Zealand (retread)	P175/70 R13 82S Enduro GR2000	Car	Toyota corolla, Nissan sentra, pulsar (1.8L)
4	Yokohama	Japan	Y185/70 R14 82 Yokohama Aspec	Car	Honda prelude (2 L)
5	Roadstone	Korea	Roadstone radial A/T 31X10.5 R15	4WD	Various 4WD
6	Kelly	New Zealand	175/70 R13 82S Kelly 70	Car	Toyota corolla, Nissan sentra, pulsar (1.8L)
7	Kelly	Brazil	P195/60 R14 85S Kelly Charger	Car	Honda prelude (2 L)
8	Dunlop	Japan	235/452 R17 Dunlop Formula	Car	Holden HSVs, Nissan skyline
9	Nankang	Taiwan	N185/60 R14 82H Nankang Ex-601	Car	Honda prelude (2L)
10	Dunlop	New Zealand	P205/65 R15 95H	Car	Toyota camry, Mitsubishi V2000
11	Dunlop	Australia	8.25 R16 LT 126/124 L	Light truck	Various light trucks
12	Dunlop	Australia	10.00.R20 Steelmaster	Truck	Various heavy trucks

Note: * Examples of vehicles the tyres are used on.

Table 2.2 - Brake Pads Examined.

Sample	Brand	Place of manufacture	Part Code	Vehicle Type	Vehicles examples
1	Noki	Japan		light truck	various
2	Fras Lee	Brazil	4515 S/F	heavy truck	various
3	QH	England	DB163 S	car	BMW 500, 600, 700 series
4	Noki	Japan	DB 300 S	car	Honda Accord
5	Don Brakes	USA	DB 319 D	car	Mitsubishi cordia, galant, lancer
6	Raybestos	USA	S727S	car	Chev corvette, impalla (front)
7	Bendix	Australia	DB 1108 B	car	Ford falcon EA26F
8	Bendix	Australia	DB 308 M	car	Toyota celicia, corolla, tercell
9	MK Kashiyama Corp	Japan	DB 1308 S	car	Nissan skyline
10	Noki	Japan	XK 3337 N	light truck	Ford trader
11	Bendix	Australia	DB 340/4WD	4WD	Nissan navarra, pathfinder
12	Brakplus	Australia	DB 1085P	car	Holden commodore

Table 2.3 - Brake pad dust samples.

Sample	Vehicle make	Year	Notes
1	Mitsubishi L200	1990	150,000 km (replacement linings)
2	Toyota Corona	1984	135,401 km (replacement linings)
3	Nissan Pulsar	1991	32,758 km (Original Japanese linings
4	Honda Ascot	1989	50,012 km (replacement linings)
5	Toyota Corolla	1992	(Don linings)
6	Ford Laser	1986	(replacement linings)

Table 2.4 - Raw bitumen samples examined.

Sample Number	Bitumen Type	Notes
1	60-70-1	
2	60-70-2	
3	180/200+polymer	Contains polymer
4	180/200-1	
5	180/200-2	
6	80/100+polymer	Contains polymer

Table 2.5 - Road bitumen samples examined from North Shore City, Auckland.

Sample Number	Location
1	Ariho Road, Devonport
2	Diomede Road, Devonport
3	Barrys Point Rd, Takapuna
4	Bentley Rd, Glenfield
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 was 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 to remove dust and dirt.

2.3 Analysis

A number of methods were utilised for the overall analytical scheme including dry ashing, aqua-regia digestion and mixed acid digestion. For samples which did not require dry ashing, both total and total recoverable acid digestions were used. All digestion methods were used for all samples. Where available, both sets of digestion results are presented. However, most data has been taken from the dry ashing and acid dissolution, however some elements have been reported from the aqua regia digest because of analytical restrictions and/or QC data. All analyses were undertaken by R. J. Hill Laboratories of Hamilton, New Zealand.

Dry Ashing and Acid Dissolution (tyres, bitumen)

Samples were prepared by dry ashing and for nitric/hydrochloric acid dissolution. Approximately 2 g of sample (as received) was weighed into a glass beaker. Approximately 0.5 g (bitumen) and 0.7-0.8 g (tyres) of $MgNO_3$ was added on top of the sample in order to trap any volatile selenium and arsenic species that may get lost during the subsequent ashing procedure. The beakers and contents were then placed in an oven overnight at 103°C. Following this, the dried samples were ashed in a furnace using the following parameters: 115°C for 3 hours; 130°C for 2 hours; 150°C for 1 hour; 250°C for 1 hour; 350°C for 1 hour; 400°C for 4.5 hours. The ashed samples were allowed to cool to room temperature and then dissolved in acid which involved adding 2 ml conc. HNO_3 along with 6 mL (bitumen) or 8 mL (tyres) conc. HCl to each beaker and placing on a hotplate. The contents were allowed to gently simmer for approximately 30 minutes. After this time the beakers and contents were allowed to cool slightly and 20 mL of Type 1 water was added to each. The beakers and contents were then returned to the hotplate and dissolution allowed to continue for a further 20 minutes. Following dissolution the beakers and contents were allowed to cool to room temperature. The contents of the beakers were then transferred to the appropriate storage vessels, made to 100 mL with Type 1 water and shaken well to mix.

Mixed Acid Digestion (brake pads)

Elements reported as "Total" were performed from the following digestion procedure *(Note that all heating was performed on a hotplate).*

Approximately 2 g of the sample was weighed into 50 mL Teflon beakers and 6 mL of conc. HCl was added to each beaker. The beakers and contents were heated to just below boiling for 1 hour. After cooling, 6 mL of HNO_3 was added to each beaker. The beakers and contents were heated to near boiling for a further 30-40 minutes. After cooling, 5 mL of HF was added to each beaker. The beakers and contents were heated to near boiling for 15 minutes. After cooling, a further 5 mL HF was added to each beaker. The beakers and contents were again heated to near boiling, until only 2-3 mL of liquid remained. After cooling, 6 mL of Aqua Regia (nitrohydrochloric acid) was added to each beaker and then heated to near boiling until only 2-3 mL liquid remained. After cooling, 30 mL of Type 1 water was added to each beaker. The beakers and contents were heated gently for 15 minutes, cooled, transferred to appropriate storage vessels and made to 200 mL with Type 1 water.

Aqua Regia Digestion (brake pads, tyres, bitumen)

Elements reported as "Total Recoverable" were performed from the following digestion procedure.

Approximately 1 g of the sample was weighed into 25 x 200 mm digestion tubes. 2 mL of Type 1 water, 1.6 mL conc. HNO_3 and 5 mL conc. HCl were then added to each weighed sample. The digestion tubes and contents were then placed on a digestion block at 95°C and digested for 1.5 hours. After this time, the digestion tubes and contents were removed from the block, allowed to cool to room temperature, made up to 20 mL with Type 1 water and vortexed. Following this, the samples were transferred to 50 mL centrifuge tubes and centrifuged at 3500 rpm until residual solid material had settled.

Analysis

Analysis of the above extracts was performed by ICP-MS. The Mixed Acid digests were diluted a further 20 times prior to analysis. The Aqua Regia digests were diluted a further 10 times prior to analysis. All analyses were carried out using a Perkin Elmer Elan-6000 ICP-MS.

Quality Control

The dry ashing and acid dissolution included two procedural blanks, one sample dissolved in duplicate and one sample dissolved in triplicate with a multi-element spike on one of these. An in-house Oil QC was also included by the laboratory. The mixed acid digestion included two procedural blanks, one sample digested in duplicate and one sample digested in triplicate with a multi-element spike on one of these. A certified QC (GBW07404, chinese soil) was also included. The Aqua Regia digestion for tyres also included one sample digested in triplicate with a Hg spike.

The Aqua Regia digestion included two procedural blanks, one sample digested in duplicate and one sample digested in triplicate with a multi-element spike which included most of the elements determined in the study. A certified QC (Agal-10, river sediment) was also included.

The duplicate results are included in the tables of results in this report. Spike recoveries were carried out using a multi-element spike. However, not all elements were included in the multi-element spike.

2.4 Detection Limits

The detection limits vary by a factor of five between procedures. These are set out in Appendix A.

3. RESULTS

3.1 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 that could degrade the rubber). 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. The majority of the materials used in the manufacture of tyres are organic (antioxidants, accelerators and retarders, fillers, peptisers), however there are a number of known trace and other elements included in the manufacture process.

Environment Agency (1998) reports the presence of major elements such as calcium (calcium oxide used as a desiccant), magnesium (magnesium oxide used as an accelerant). Both silica and phosphates are also used in fillers and plasticisers. Calcium was found in low concentrations in all tyres and magnesium was present in very low concentrations in all tyres examined. No other major inorganic elements were detected in the tyres including iron, manganese and phosphorus.

A number of trace elements have been reported as being used in the manufacture of tyres (Environment Agency 1998). These include zinc and antimony. Zinc oxide is added as a vulcanisation activator (the ZnO is added as fine particles of precipitated ZnO along with stearic acid to form zinc stearate). The ZnO may also carry some other trace elements with it depending upon the process used to manufacture it (either electrochemical or precipitation). Bayer report that ZnO additive contains a small amount of lead oxide (about 5 mg/kg/). Zinc is also reported to be used, in zinc ethyl and other dithiocarbamates (used as accelerators), in zinc dibenzamide diphenyl disulphide (a peptiser) and zinc metaborate dihydrate (a flame retardant) (Environment Agency 1998).

Table 3.1 shows that the concentrations of trace elements measured in the rubber from New Zealand tyres were low. Three elements of environmental concern were consistently identified. These were cadmium, lead and zinc. Antimony was detected in two samples of tyre. One of these was a duplicate sample where no antimony was detected in the other duplicate. Environment Agency (1998) reported the use of antimony pentasulphide as a colourant in tyre production.

The median concentration of zinc was 8,310 mg/kg (0.103 % ZnO). Lead concentrations ranged from less than 1 mg/kg to 9.7 mg/kg. The concentration of cadmium was low and ranged up to 0.56 mg/kg. Fig. 3.1 shows that there was a good relationship between the zinc and cadmium concentrations in the tyres. The relationship seen in Fig. 3.1 suggests that the tyres can be placed into two groups based upon the concentration of cadmium for a given concentration of zinc. One group with a Zn/Cd ratio twice the other. If other international data is examined it is evident that there have been tyres with much higher cadmium concentrations relative to the zinc concentration. David & Williams (1975) reported the analysis of eight tyres. Two from Australia and one from Germany contained zinc and cadmium concentrations similar to the Group 2 tyres examined in this study. The other five tyres (from Japan, France, England and Ireland) contained 0.75 to 14.06 mg/kg cadmium. Similar higher concentrations of cadmium were identified by others as summarized in Table 3.2. David & Williams (1975) noted that the low concentration of cadmium in the Australian tyres examined in their study was due to the effectiveness of the electrolytic purification process used to refine zinc oxide.

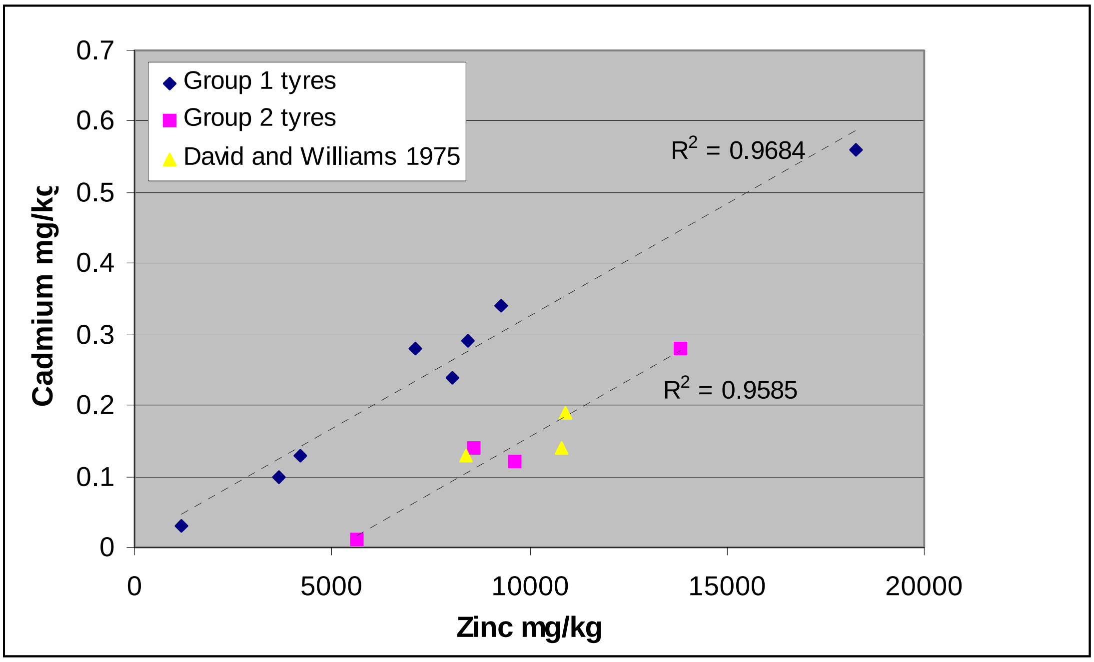

Fig. 3.1 - Relationship between zinc and cadmium in the tyres examined.

Table 3.1 - Summary of Elemental composition of a selection of 12 tyres available in New Zealand.

	1	2	3	4a,b	5	6	7	8	9	10	11	12a,b	Median
Major Elements													
Ca	60	60	360	300,530	270	330	160	100	1680	130	150	230,230	195
Mg	37	5	37	21,21	<4	25	7	<4	12	<4	15	10,11	11.25
Na	<20	80	200	120,240	70	140	450	530	120	260	530	590,590	190
K	<50	120	280	150,360	<50	210	110	110	380	410	200	430,430	205
P	<20	<20	40	<20,30	<20	20	30	<20	50	<20	120	210,200	22.5
Al	13	9	20	14,25	<5	13	21	81	129	7	51	132,145	20.5
Common Metals													
Fe	110	100	210	60,100	30	50	120	40	220	80	210	210,180	105
Mn	1.0	0.7	2.5	1.1,1.8	<0.5	1.2	1.6	0.8	1.6	1.2	3.2	6.1,5.7	1.2
Priority Pollutant Elements													
Be	0.3	0.1	0.2	0.3,0.4	0.2	<0.1	0.7	0.2	0.3	0.6	0.4	0.4,0.2	0.3
Cd	<0.05	0.10	0.34	0.21,0.37	0.13	0.28	0.14	<0.05	0.12	0.24	0.56	0.28,0.27	0.19
Co	2.4	0.4	4.1	1.8,3.3	0.3	1.6	1.1	0.5	0.7	1.4	0.9	1.0,1.0	1.05
Cr	<1	<1	1	<1,<1	<1	<1	<1	<1	2	<1	1	2,2	<1
Cu	3	1	2	<1,2	<1	<1	1	<1	2	<1	1	3,2	1
Hg	<0.01	<0.01	<0.01	<0.01,<0.01	<0.01	0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01,<0.01	<0.01
Mo	0.6	0.3	0.6	0.4,0.3	<0.2	<0.2	0.3	<0.2	1.4	0.2	1.1	0.7,0.6	1
Ni	1	<1	2	2,2	<1	1	2	3	<1	1	<1	1,1	1
Pb	0.8	1.5	3.5	2.0,3.5	1.5	2.5	4.6	5.7	1.0	2.7	9.7	3.3,3.1	2.72
Sb	<0.2	<0.2	<0.2	<0.2,0.2	<0.2	<0.2	0.9	<0.2	<0.2	<0.2	<0.2	2.4,<0.2	<0.2
Sn	0.6	<0.5	<0.5	<0.5,<0.5	<0.5	<0.5	<0.5	1	<0.5	<0.5	<0.5	<0.5,<0.5	<0.5
Zn	1190	3640	9270	6040,10900	4180	7090	8570	5650	9640	8050	18300	13700,13900	8310
Non-Essential Elements													
Ba	8.78	39.8	166	36.7,1.45	42.3	10.4	63.6	35.4	15.5	32.7	13.6	18.4,7.92	25.75
Li	<0.2	<0.2	<0.2	<0.2,0.4	<0.2	<0.2	2.6	<0.2	<0.2	<0.2	<0.2	<0.2,<0.2	<0.2
Rb	<0.2	<0.2	0.4	<0.2,0.6	<0.2	0.3	<0.2	<0.2	<0.2	0.6	0.9	1.5,1.5	<0.2
La	<0.1	<0.1	<0.1	<0.1,0.1	0.1	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	0.2,0.2	<0.1
Sr	<0.5	<0.5	2.1	<0.5,0.6	<0.5	<0.5	2.6	1.3	2.1	<0.5	0.7	1.6,1.6	0.6

Note: Not detected B, Ag, As, Au, Bi, Cs, Se Tl, U, V, W, In, Sc, Nb, Ge, Pd, Ce, Ti, Ga (refer Appendix A for detection limits).
Samples 4a,b and c and 12a, b are duplicate samples.

Table 3.2 - Comparison of published data for trace elements in vehicle tyres (all data mg/kg).

Element	This study	MoT (1996)	Legret & Pagotto (1999)	Hewitt & Rashed (1990)	Christensen & Guinn (1979)	David & Williams (1975)
Cadmium	0.19 (0.56)*	0.77	2.6	0.28-4.96	-	0.13-14.06
Copper	1 (3)	-	1.8	5.5-29.3	-	-
Lead	2.72 (9.7)	0.84	6.3	-	-	-
Zinc	8,310 (18,300)	5,624 (based on 0.7% ZnO)	10,800	-	7,300	8,400-16,600

Note: * Median and maximum from Table 3.1.

An earlier review (MoT 1996) identified typical concentrations of ZnO in tyres of 0.7% and cadmium and lead concentrations as below 1 mg/kg based on data supplied by the tyre industry. The concentrations measured in this preliminary study indicate that the zinc concentrations are generally similar to those reported previously. Cadmium concentrations may be lower than previously indicated and the lead concentrations higher (Table 3.1).

Table 3.3 provides a summary of the inter-element correlation coefficients for the tyre data-set. The summary shows that in addition to the already identified strong association between zinc and cadmium in tyres there are other correlations. It should be noted that some of the correlations are influenced by the presence of concentrations at and below detection limit. However, it is likely that the correlations of a number of these elements is a reflection of the presence of these elements in some of the materials used in the tyre manufacture process. For examples the correlation between zinc and lead may reflect the presence of lead in the zinc oxide used in manufacture.

Table 3.3 - Summary of positive inter-element correlations found in tyre element dataset.

Element	p<0.05	p<0.01	p<0.001
K	P, Cr, K, Cu, Mo, Zn	Na, Fe, Mn, Cd	
Ca		Fe, W	Mo
Fe	P, Mn, Sr, W, Zn	K, Ca, Cu	Cr, Mo
P	K, Fe, Al, Sb	Cr, Zn	Rb, Mn
Li	Be		Hg, La
Al	P, Mn, Cr	P	
Na	Cd	K, Zn	Pb
Rb	Cd	Zn	P, Mn
Mg	Cu		Co
Ba	Co		
Mn	Fe, Al, Cu, Sb	Zn	P, Rb
Sr	Fe, W		
Be	Li, La		
Cu	Mg, Mn, K, Cr, Mo	Fe	
Cd	Na, Rb, Pb	K	Zn
Cr	K, Al, Cu	P, Mo, Zn	Fe
Mo	K, Cu	Cr	Ca, Fe
Sb	P, Mn	La	
Co	Ba		Mg
Hg			Li, La
La	Be	Sb	Li, Hg
Mo	W, Mo		
W	Fe, Mo, Sr	Ca	
Pb	Cd	Zn	Na
Zn	K, Fe	Na, Rb, P, Mn, Cr, Pb,	Cd

3.2 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 and brake linings are manufactured to individual specifications. There are a very large number of brake pad manufacturers around the world and a very large variety of brake pads and linings. Armstrong (1994) indicated that there were more than 1000 different types of brake pads in the United States market. In New Zealand it is estimated that there are more than 400 different types on the 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 in 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 held together with phenolic resins and other binders and fillers. The metal is present for heat transfer and the amount present depends upon the specific heat transfer requirements. In some brake linings iron, steel (e.g., steel wool and iron sponge) and titanium are used (high heat transfer coefficients). In situations which are not so demanding such as the rear disc brakes of normal cars, the pads may contain softer metals such as copper and brass.

The structural materials in brake pads include metal, carbon, glass and/or kevlar fibres. The matrix of the pads is typically composed of a phenolic resin or occasionally some form of rubber (refer Table 3.4). Fillers are added and these appear to include clay and calcium carbonate. Frictional additives are included to influence the wear rate and these materials include graphite (lowers coefficient of friction) and abrasive particles (increase coefficient of friction and remove oxide coatings from the disc surface). Metal sulphides are also used to alter the coefficient of friction. Some past-manufacture products have been developed to assist in brake pad lubrication. These include lubricants containing aluminium, molybdenum disulphide and graphite.

Table 3.4: 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 sulphide (Cu_2S), lead sulphide (PbS) or antimony sulphide (Sb_2S_3)

Table 3.5 provides a summary of the results obtained for the 12 brake linings tested and Table 3.6 provides a summary of the analysis of the brake pad dust samples. Several major elements were present in significant but variable concentrations in both materials.

Table 3.5 - Summary of Elemental composition of a selection of 12 brake pads available in New Zealand (mg/kg unless noted).

	1	2	3	4	5	6	7	8a,b	9	10a,b	11	12	Median
Major Elements													
Ca %	3.99	1.75	2.9	2.07	4.43	4.86	0.182	0.272, 0.372	0.249	0.287,0.288	2.72	0.585	1.91
Mg %	12.8	7.44	1.88	9.17	10.7	1.75	12.5	2.47, 2.19	12.6	11.2,11.0	0.43	15,20	9.935
Na	400	50	490	200	160	450	400	90, 140	50	230,260	720	260	253
K	7100	<100	5400	500	200	7900	3600	300, 300	200	300,300	1300	1200	850
P	1150	150	780	80	<40	480	60	<40, <40	50	80,70	70	150	77.5
Al	11600	1840	7300	976	449	13900	883	1070, 1390	17500	818,791	4360	31900	3100
Common Metals													
Fe %	1.17	1.41	20.60	1.52	4.84	1.17	1.85	63.7, 60.0	2.20	1.85,1.78	0.257	2.95	1.83
Mn	204	136	1920	327	320	181	337	1190, 1120	311	312,309	139	481	315.5
Ti	1020	100	700	120	30	1660	50	500, 540	30	60,60	430	70	110
Priority Pollutant Elements													
Ag	<0.4	<0.4	<0.4	3.9	<0.4	<0.4	<0.4	<0.4, <0.4	<0.4	<0.4,<0.4	1.3	<0.4	<0.4
As	<2	<2	10	<2	<2	3	<2	18, 18	<2	3,3	26	<2	<2
Be	0.3	0.2	0.6	<0.2	<0.2	0.7	<0.2	<0.2, <0.2	<0.2	<0.2,<0.2	<0.2	<0.2	<0.2
Cd	0.9	<0.1	1.8	0.5	0.7	0.6	0.1	0.2, 0.5	0.1	5.0,5.1	12.3	0.1	0.55
Co	17.3	22.8	13.6	26.6	25.9	11.6	23.6	45.8, 45.7	40.4	38.6,37.6	1.8	36.3	24.75
Cr	46.0	442	166	267	123	233	86.9	40.7, 39.0	411	335,329	15.3	350	200
Cu	25	13	35	39000	11	24	56	1290, 2600	36	64,30	112000	30	35.5
Hg	0.2	0.2	0.3	0.3	0.1	0.2	<0.1	0.2, <0.1	0.2	0.2,0.2	0.1	0.2	0.2
Mo	2.3	2.8	49.4	0.4	0.7	1.0	9.2	78.3, 215	4.4	0.8,1.1	6000	4.6	3.6
Ni	45	621	44	475	342	92	294	103, 103	660	629,609	10	584	359
Pb	183	4.89	873	13.7	7.93	3.61	4.16	1.28, 1.39	7.04	67.4,65.3	84.5	5.81	7.48
Sb	6.53	0.58	1.31	2.15	0.07	4.7	35.4	144, 201	15.2	5.80,5.49	29500	14.9	6.08
Sn	<1	<1	2	6	<1	1	1	15, 15	<1	2,2	2	2	1.5
Tl	<0.2	<0.2	<0.2	<0.2	<0.2	0.3	<0.2	<0.2, <0.2	<0.2	<0.2,<0.2	<0.2	<0.2	<0.2
Zn	96	1160	352	816	948	429	34500	40, 25	1120	6270,6380	346	573	694
Non-Essential Elements													
B	950	50	30	<20	80	1230	40	100, 180	40	20,70	<20	50	47.5
Ba	3640	4650	6310	3610	413	6810	4020	2470, 2060	2400	1800,1930	61.4	2780	2590
Bi	<0.4	0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4, <0.4	<0.4	<0.4,<0.4	1.9	<0.4	<0.4
Ce	22.4	24.4	11.1	1.4	0.8	12.2	1.8	1.0, 1.1	0.6	1.0,1.0	2.2	0.9	1.6
Cs	2.88	0.04	1.96	0.25	0.09	0.91	0.23	0.03, 0.03	0.08	0.07,0.07	0.15	0.17	0.16
Ga	2	<1	5	<1	<1	4	<1	16, 17	2	<1,<1	1	4	1.5
Li	7.72	0.41	12.6	0.71	0.46	9.10	3.46	1.12, 1.52	0.45	0.85,0.78	1.68	0.68	1.06
Rb	76.9	0.26	47.0	4.61	0.73	50.6	5.85	0.89, 0.98	0.77	1.48,1.67	2.03	2.34	2.18
La	9.28	9.97	4.53	0.83	0.56	5.70	0.96	0.79, 0.80	0.31	0.42,0.41	2.95	0.59	0.89
Nb	<2	4	<2	<2	<2	<2	<2	<2, <2	<2	<2,<2	<2	<2	<2
Sc	3	4	5	4	4	3	4	<2, <2	<2	2,3	<2	3	3
Sr	303	310	163	170	22	145	652	265, 258	100	152,155	469	36	166.5
U	0.9	0.3	0.3	0.2	0.1	0.4	0.3	0.2, 0.2	<0.1	<0.1,<0.1	0.2	0.1	0.2
V	<100	<100	<100	<100	<100	<100	<100	400, 400	<100	<100,<100	<100	<100	<100
W	<1	2	1	<1	<1	<1	<1	2,2	<1	<1,<1	2	1	<1

Note: Not detected Au, Ge, In, Pd, Se (refer Appendix A 4 for detection limits).

Table 3.6 - Summary of Elemental composition of 6 brake pad dust samples (all results mg/kg unless noted).

Sample		1	2	3	4	5	6	Median
Major Elements								
Ca %	Total	1.04	6.50	7.70	0.11	1.07, 1.20	2.80	1.967
	TR	0.465	8.33	1.74	0.094	1.16	3.29	1.95
Mg %	Total	1.46	5.09	0.69	11.1	5.64, 5.88	5.81	5.425
	TR	0.988	4.72	0.136	10.4	6.71	6.82	5.715
Na	Total	4420	590	<800	600	540, 690	2080	615
	TR	1720	539	126	546	533	1920	542.5
K	Total	2300	500	<2000	1000	300, 400	1600	1000
	TR	790	410	410	930	230	830	600
P	Total	530	100	<800	<300	150, 160	190	172.5
	TR	416	93	50	81	122	171	107.5
Al	Total	14300	1660	15200	1420	5970, 6270	4780	5450
	TR	4500	2610	3130	1090	16300	3900	3515
Common Metals								
Fe %	Total	46.8	12.90	22.40	9.31	25.30, 25.10	8.88	17.65
	TR	36.8	11.90	4.70	8.86	21.70	8.70	10.3
Mn	Total	2870	907	1870	856	1890, 1890	1030	1450
	TR	2460	900	397	806	1730	963	931.5
Ti	Total	2570	110	<400	100	280, 350	410	315
	TR	425	58	52	81	89	164	85
Priority Pollutant and Environmentally Significant Elements								
Ag	Total	0.8	<0.4	<8	<3	<0.4, <0.4	<0.4	<0.4
	TR	0.71	0.06	0.06	0.09	0.13	0.09	0.09
As	Total	11	3	<40	<10	4, 4	<2	3.5
	TR	13.9	4.9	1.7	2.0	4.8	5.6	4.85
Be	Total	<0.3	<0.2	<4	<1	<0.2, <0.2	<0.2	<0.2
	TR	0.21	0.11	<0.02	<0.04	<0.02	0.08	0.06
Cd	Total	2.6	0.4	<2	<0.06	0.2, 0.1	0.4	0.4
	TR	2.82	0.59	0.05	0.03	0.21	0.37	0.29
Co	Total	42.4	19.7	12	38	26.7, 26.6	30.0	28.3
	TR	37.2	19.9	2.57	38.4	26.6	28.8	27.7
Cr	Total	1230	135	310	420	345, 351	204	329
	TR	861	123	70.4	376	318	201	259.5
Cu	Total	1980	348	90	470	72, 70	75	219.5
	TR	2730	298	21.8	449	62.4	69.3	183.65
Hg	Total	0.3	0.2	<2	<0.06	0.2, <0.1	<0.1	<0.15
	TR	0.03	0.02	<0.01	<0.02	<0.01	0.01	<0.015
Mo	Total	98.9	35.2	23	5	37.6, 37.0	5.8	29.1
	TR	85.2	26.4	4.13	4.66	32.2	5.35	15.8
Ni	Total	715	268	80	730	339, 333	503	419.5
	TR	693	251	16.7	692	340	469	404.5
Pb	Total	1290	35.9	62	4	16.6, 23.1	41.4	38.6
	TR	941	36.2	9.45	3.74	15.8	40.2	26.0
Sb	Total	133	10.8	39	32	12.9, 12.8	4.0	22.4
	TR	112	4.82	9.99	22.2	3.68	1.89	7.4
Sn	Total	115	6	<20	<6	5, 4	105	5.25
	TR	114	6.2	1.9	1.0	3.8	102	5.00
Tl	TR	<0.04	<0.02	<0.02	<0.04	<0.02	0.03	<0.02
Zn	Total	2460	4180	560	740	374, 346	9630	1600
	TR	2050	3520	123	599	341	8690	1325
Non-Essential Elements								
B	Total	300	220	<400	<100	40, 40	510	~260
	TR	270	212	105	17	37	469	156.5
Ba	Total	8550	464	175	18	17.3, 20.1	451	313
	TR	2540	133	15.3	12.8	19.1	318	76.4
Bi	Total	<0.7	<0.4	<8	<3	<0.4, <0.4	<0.4	<0.4

Sample		1	2	3	4	5	6	Median
	TR	0.25	0.11	<0.04	<0.08	<0.04	<0.04	<0.04
Ce	Total	528	<2	<40	<10	<2, <2	3	<2
	TR	83.1	0.9	0.4	1.2	0.7	2.9	1.05
Cs	Total	0.6	0.3	<4	<1	<0.2, <0.2	<0.2	~0.2
	TR	0.30	0.31	0.14	0.08	0.05	0.31	0.22
Ga	Total	12	2	<20	<6	6, 6	3	~.5
	TR	7.9	2.2	1.2	1.4	6.3	2.2	2.2
Ge	TR	2.3	0.5	0.4	<0.4	0.8	0.3	0.45
Li	Total	11.7	2.1	<8	21	0.9, 0.8	4.9	3.5
	TR	8.00	2.30	0.5	20.1	1.29	9.73	5.15
Rb	Total	6.8	3.0	14	4	0.5, 0.9	3.5	3.75
	TR	2.22	2.27	3.11	3.62	0.89	4.12	2.69
La	Total	11.8	<0.2	<4	<1	0.5, 0.7	1.3	~1
	TR	6.49	0.49	0.23	0.58	0.52	1.45	0.56
Nb	Total	8	<2	<40	<10	6, 6	2	~4
	TR	2.2	0.5	1.0	1.5	2.0	1.0	1.25
Sc	Total	20	10	<40	<10	20, 19	4	~15
	TR	5.2	3.1	1.9	4.2	4.4	3.2	3.7
Sr	Total	170	61	80	<6	17, 20	48	54.5
	TR	88.4	64.7	18.6	3.8	15.7	48.8	56.75
U	Total	0.4	0.2	<2	<0.6	<0.1, <0.1	0.3	~.25
	TR	0.11	0.13	0.05	0.03	0.06	0.17	0.085
V	TR	<20	<10	<10	<20	20	10	~10
W	Total	4	1	<20	<6	2, 2	1	~3
	TR	2.4	0.9	0.4	<0.2	1.3	0.7	0.8

Note: Not detected total Au, Ge, In, Pd, Tl, V; Total recoverable Au, In, Pd, Se, (refer Appendix A for detection limits).

These elements included calcium, magnesium (up to 20%) and aluminium (up to 3.19%). Sodium and potassium were present in lower concentrations. Phosphorus was present in low concentrations (<100 mg/kg) in 7 of 12 brake linings examined but was measured up to 1150 mg/kg (Table 10). Iron was one of the most abundant metals present with three samples containing more than 2.95%. These samples contained concentrations ranging from 4.84 to 63.7% (Table 3.5). A range of trace elements were detected in the brake lining and brake dust samples (Tables 3.5 and 3.6). The key results to note are:

- Cadmium concentrations in the brake pads were higher than those in tyres with up to 12.3 mg/kg being measured.
- Relatively low but consistent concentrations of cobalt were found and moderate concentrations of chromium in all brake pads.
- On average copper concentrations were low (median in new linings and dust of 35.5 and 219.5 mg/kg respectively). Copper concentrations in 4 of 18 samples were higher than 1,000 mg/kg with one sample containing 11.2% (refer Table 3.5).
- Molybdenum concentrations were generally low (median in new linings of 3.6 mg/kg) but 3 new lining samples and two dust samples contained more than 50 mg/kg with one new lining containing 6,000 mg/kg.
- Nickel concentrations were elevated in all new lining and dust samples (median concentrations of 359 and 419.5 mg/kg respectively).
- Although the median lead concentration in new linings was low (7.5 mg/kg), concentrations of up to 873 mg/kg were measured in new linings and 1,290 mg/kg in brake pad dust.
- Antimony concentrations ranged from 0.07-35.3 mg/kg in 11 of 12 samples new brake pad samples examined. The twelfth sample contained 29,500 mg/kg, suggesting the use

of antimony sulphide as a lubricant in the pad (refer below). The range in the dust samples was 1.89-112 mg/kg as TR antimony.

- Zinc was present in pads at variable but elevated concentrations. Median concentrations in both new linings and in the dust samples are around 1,000 mg/kg (Table 3.6).
- Elevated concentrations of barium were found in most linings reflecting its use in the form of the mineral baryte as a filler or friction dust.

In a pilot study examining four brake pads Armstrong (1994) reported the concentration of chromium, silver, cadmium and nickel. Analyses were then carried out on 20 pads for copper, lead and zinc. Table 3.7 provides a comparative summary of the results for these elements by Armstrong (1994) and Legret & Pagotto (1999) and this study.

Table 3.7 - Comparison of the results obtained in this study with those from the literature (all data mg/kg).

Element	Armstrong (1994)	Legret & Pagotto (1999)	This study
Ag	<10	-	<0.4 (<0.4-3.9)
Cd	<2.5	2.7	0.55 (<0.1-12.3)
Cr	NR (30 – 160)	-	200 (15.3 – 442)
Cu	~250 (<62.5 – 200,500)	14,200	35.5 (11 – 112,000)
Ni	NR (60 – 140)	-	359 (10 – 621)
Pb	<100 (<100 – 119,000)	3,900	7.48 (1.28 – 873)
Zn	1,835 (100 – 188,000)	21,800	694 (25 – 34,500)

Note: NR, not reported.

Sutherland & Tolosa (2000) identified that the major source of antimony in road sediments may be the wear of asbestos free brake linings which may contain 1-4% (Helmers 1996, Dietl et al. 1996). A single brake pad examined in this study contained antimony within this range. 11 other pads contained low but detectable concentrations of antimony. Table 3.8 provides a summary of the positive inter-element correlations found in the brake pad analysis data-set. Although the correlations have not been explored in detail (using multivariate statistics), it is evident that there are a number of associations based upon chemical properties. These strong correlations include elements such as potassium, rubidium and caesium. This relationship is probably related to the ionic radii of these elements and the common substitution of the smaller elements in minerals containing potassium. As with tyres there is likely to be some materials used in brake pad manufacture that are carried over as contaminants in the major compounds used in the manufacture.

3.3 Bitumen

Tables 3.9 and 3.10 provide a summary of the concentration of inorganic constituents in six samples of raw bitumen (prior to application to road surfaces) and five samples of bitumen collected from road surfaces. The raw bitumen samples include two samples with added polymers. The road bitumen samples will include some material that has been incorporated into the bitumen surface as a result of the action of vehicles driving on the road surface and some inorganic material that was included with the bitumen when it was milled (the bitumen often coated very small aggregate particles).

Table 3.8 - Summary of positive inter-element correlations found in brake-pad element dataset.

Element	p<0.05	p<0.01	p<0.001
Ca	Ti, K, Li, Rb, P, B, Be, Cs, La, U		
Mg		Ni	
Na	Li, K, Bi, Cd, Cu, Mo, Sb		
K	Na, Ca, La, Th, Ce	Ba, U	Ti, B, P, Rb, Li, Be, Cs
Fe	As, W	Mn	Sn, V, Fe, Ga
P	Ti, Ca, B, Ba, Pb,	Be, La, Ce	K, Li, Rb, Cs, U
B	Ca, Li. P, La, Cs	Be, U, Th	Ti, K, Rb
Li	Ca, Na. B, U,	Ti, Ba, Pb	K, Rb, P, Be, Cs
Ti	P, Ca, Ba, Cs, U	Li, Th	K, Rb, B, Be
Rb	Ca, Ba, La, Ce	Be	Ti, K, Li, B, P, Cs, U
Ba	Rb, P, Ti, Th, Ce, Ce	K, Li	Be
Mn	Ga	Fe, Pb	
Sr		Zn	
As	Fe, Bi, Cd, Cu, Ga, Bi, Cd, Sn	Mo, W, Sb	
Be	Ca, Cs, La, Pb, Ce	Rb, P, B, Th	Ti, K, Li, Ba
Bi	Na, Fe, As		Cd, Cu, Mo, Bi
Cu	Na, As		Bi, Cd, Mo, Sb
Cd	Na, As		Bi, Cu, Mo, Sb
Ce	K, Rb, Ba, Be, Cs, Nb	P, U	La
Co	Sn, V		
Cr	Ca		Ni
Cs	Ti, B, Ca, Be, La, Pb, Ce		K, Li, Cs, Rb, P, U
Ga	As, Mn, W		Sn, Fe, V
La	Ca, K, Rb, B, Be, Cs, Nb	P, U	Ce
Mo	Na	As	Bi, Cd, Cu, Sb
Nb	La, Ce		
Ni		Mg	Cr
Pb	P, Be, Cs	Li, Mn	
Sb	Na	As	Bi, Mo, Cu, Cd
Sc	Ba		
Sn	As, Co, W		Fe, V, Ga
Th	K, Ba	Ti, B, Be	
U	Ti, Ca, Li, V	K, B, La, Ce	Rb, P, Cs
V	As, W		Sn, Ga
W	Fe, V, Sn	As	
V	As		Fe
W	Fe		
Zn		Sr	

Table 3.9 - Summary of elemental composition of a selection of raw bitumen in New Zealand (all results mg/kg).

	60/70-1	60/70-2	180/200-1	180/200-2	180/200+P	180/100+P	Median
Major Elements							
Na	<20	20	<20, <20	20	20	<20	<20
Al	7	<5	<5, <5	<5	6	<5	<5
Common Metals							
Fe	20	<20	<20, <20	<20	100	40	<20
Priority Pollutant Elements							
Co	<0.2	0.2	<0.2, <0.2	0.2	<0.2	<0.2	<0.2
Mo	<0.2	0.6	0.4, 1.6	1.5	0.3	0.2	0.45
Ni	2	17	9, 36	32	15	3	16
Sn	4.0	<0.5	<0.5, <0.5	<0.5	1.3	1.1	~0.6
Zn	6	3	2, 10	<2	99	34	5.5
Non-Essential Elements							
Ba	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Li	<0.2	<0.2	<0.2, <0.2	<0.2	0.7	2.9	<0.2
V	<50	60	<50, 110	110	<50	<50	<50

Note: Not detected Ca, Mg, K, Rb, P, B, Mn, Ti, Ag, As, Au, Be, Bi, Cd, Ce, Cr, Cs, Cu, Ge, In, Hg, La, Pb, Pd, Nb, Sb, Sc, Se, Sr, Tl, Ti, U, W (refer Appendix A for detection limits).

Table 3.10 - Summary of elemental composition of a selection of road bitumen in Auckland New Zealand (all data mg/kg unless stated).

	1	2	3	4	5	Median
Major Elements						
Ca	9520	8270, 8080	7820	8490	6310	8175
Mg	26300	28900, 29100	26300	26100	15000	26300
Na	14100	10900, 9920	10400	10300	5520	10400
K	2570	3760, 3260	2970	3470	1600	2970
P	1840	1210, 1110	1220	1180	843	1180
Al%	2.21	1.87, 1.79	1.74	1.82	1.24	1.82
Common Metals						
Fe %	4.81	4.05, 3.91	4.05	3.66	2.51	3.98
Mn	654	558, 545	543	518	390	543
Ti	3360	3940, 3830	3580	3580	2310	3580
Priority Pollutant Elements						
As	1.5	1.0, 1.4	0.9	1.5	12.6	1.5
Be	1.23	0.71, 0.58	0.63	0.66	0.49	0.645
Cd	0.07	0.05, 0.05	0.15	0.06	0.15	0.07
Co	31.6	30.0, 29.1	28.7	26.9	17.4	28.7
Cr	46.3	106, 98.4	77.7	90.7	48.8	77.7
Cu	46.3	41.2, 38.7	53.4	40.4	60.1	46.3
Hg	<0.01	<0.01, 0.01	<0.01	<0.01	0.03	<0.01
Mo	1.97	1.61, 1.48	1.58	1.65	1.21	1.58
Ni	137	154, 152	138	134	77.1	137
Pb	8.33	1.99, 4.16	146	1.89	126	8.33
Sb	<0.2	<0.2, <0.2	<0.2	<0.2	0.3	<0.2
Sn	0.7	0.6, 0.7	0.9	0.5	1.3	0.7
Tl	0.03	0.03, 0.03	<0.02	0.03	<0.02	0.03
Zn	64.1	50.9, 49.4	53.5	47.4	79.9	53.5
Non-Essential Elements						
Ba	24.1	25.1, 40.9	19.2	30.2	22.4	24.1
Ce	46.2	29.5, 29.5	29.4	29.5	20.1	29.5
Cs	1.56	2.26, 3.10	0.32	2.67	0.99	1.56
Ga	8.3	6.8, 7.0	6.4	6.6	4.4	6.6
Li	5.03	3.88, 4.74	3.72	3.78	4.39	4.31
La	9.28	9.97	4.53	0.83	0.56	4.53
Nb	2.6	3.0, 3.0	3.0	3.1	3.5	3.0
Rb	12.6	13.3, 11.8	10.1	12.4	7.14	12.4
Sc	3.2	3.2, 3.8	2.8	3.6	2.5	3.2
Sr	119	102, 139	88.3	94.8	64.8	94.8
U	0.67	0.35, 0.32	0.34	0.37	0.32	0.34
V	80	80, 70	80	70	60	75

Note: Not detected Ag, Se, Au, B, Bi, Ge, In, Pd, W (refer Table Appendix A for detection limits).

The inorganic composition of the bitumen is dependent upon the source of the bitumen. Historically, some of the material used on New Zealand roads was sourced from materials such as gas-works tar. Some tar from these sources may still be present on New Zealand roads but nearly all will have been replaced or buried. Bitumen composition will depend on the source of the original petroleum product.

Bitumen was historically obtained from the New Zealand Refining Company and as such the composition depended upon their source. Bitumen is also imported into New Zealand by, the companies using it with one company currently sourcing Venezuelan bitumen. Bitumen is predominantly a high molecular weight aliphatic hydrocarbon with the amount of other organic compounds (e.g., polyaromatic hydrocarbons) present depending upon source and manufacture.

The analysis of the raw bitumen showed that the bitumen had a low inorganic content with few metallic elements such as iron, nickel and zinc present in elevated concentrations. None of the elements detected were elevated when compared to the concentrations measured in either tyres or brake pads. Comparison of bitumen samples containing polymer (e.g., 180/200 + polymer) with bitumen samples not containing polymer (e.g., 180/200 – 1) demonstrated some differences in the concentration of two elements. These elements were iron and lithium. This comparison suggests that these elements (iron and lithium) may be either contained in or added along with the polymer.

The nickel and vanadium concentrations are similar to the concentrations of 18 and 65 mg/kg reported by Herrington (2001) for Safaniya bitumen.

Table 3.10 summarises the data for the analysis of samples of bitumen milled from five roads in North Shore City. A wider range of elements were detected in the road bitumen samples compared to the raw bitumen samples. Concentrations of the major elements (Ca, Mg, Na, K and P) were much higher than in the raw bitumen samples. Concentrations were generally similar between the five road bitumen samples. A number of priority pollutant elements were detected in the road bitumen samples (14 compared with only 5 in raw bitumen). Concentrations of Co, Zn, Mo, Ni and Sn (present in raw bitumen) were higher in the road bitumen samples than raw bitumen.

4. DISCUSSION

The analysis of the three potential vehicle contaminant sources revealed a wide range of concentrations of the constituents that were tested for. For the constituents tested in this preliminary survey, there were some limitations with respect to detection limits for a number of elements (notably vanadium and selenium). The range of elemental composition was also very large with respect to some of the samples of the materials tested and the differences between the different materials was also significant in some cases. The examination of tyres and brake pads confirmed the presence of the key elements known to be present as a result of the manufacture of those materials. The two key environmentally significant elements are copper and zinc. Table 4.1 provides a summary of the median composition of the types of materials tested in this study. The table also contains some information on the crustal abundance of those constituents. For further comparison, the concentration expected in a fine greywacke sediment (one of the key geological rock types in New Zealand) is also presented. The presence of higher concentrations of any element in a vehicle source might indicate that an increase in the concentration of that element in sediment may occur following entry of stormwater into a receiving environment. Further evaluation is required for these elements in relation to the potential for adverse effects to arise due to their possible accumulation in the environment.

The analysis of the bitumen samples showed that the raw bitumen contained very low concentrations of both major and trace elements. For all constituents the median concentrations obtained were lower than those measured in the road bitumen. Of all of the elements measured only nickel and strontium were found to be present in concentrations higher than other elements. The concentrations were however similar to or lower than crustal abundance.

Examination of the road bitumen found a larger range of detectable elements. No elements were measured that were present at concentrations higher that the upper of the crustal or greywacke abundance data in Table 4.1.

Table 4.1 - Comparative summary of tyre, brake pad and bitumen composition with elemental crustal abundance (all results mg/kg, unless noted).

		Tyre	Brake Pad	Brake Pad dust	Bitumen	Road Bitumen	Crustal abundance	New Zealand Greywacke
Major Elements								
Ca	Total	195	19100	19670	<50	8170	-	5000
Mg	Total	11.25	9.935%	5.715%	<4	26300	-	7060
Na	Total	190	253	607	<20	10400	-	19996
K	Total	205	850	1000	<50	2970	-	2.45%
P	Total	22.5	77.5	172.5	<20	1180	-	700
Al	Total	20.5	3100	545	<5	1820	-	8.627%
Common Metals								
Fe	Total	105	18300	17.65%	<20	39800	-	3.38%
Mn	Total	1.2	315.5	1450	<0.5	543	950	600
Ti	Total	<	110	315	<10	3580	5700	3870
Priority Pollutant and Environmentally Significant Elements								
Ag	Total	<0.2	<0.4	0.09	<0.2	<0.2	0.07	-
As	Total	<1	<2	4.85	<1	1.5	1.8	8.9
Be	Total	0.3	<0.1	0.06	<0.1	0.645	2.8	-
Cd	Total	0.19	0.55	0.29	<0.05	0.07	0.2	~0.1
Co	Total	1.05	24.75	28.3	<0.2	28.7	25	-
Cr	Total	<1	199.5	329	<1	77.7	100	60
Cu	Total	1	35.5	219.5	<1	46.3	55	26
Hg	Total	<0.01	0.2	<0.015	<0.01	<0.01	0.08	0.06
Mo	Total	1	3.6	29.1	0.45	1.58	1.5	-
Ni	Total	1	359	419.5	16	137	75	22
Pb	Total	2.72	7.48	38.6	<0.2	8.33	12.5	37
Sb	Total	<0.2	6.08	22.4	<0.2	<0.2	0.2	-
Se		<10	<10	<20	<10	<20	0.05	-
Sn	Total	<0.5	1.5	5.25	<0.5	0.7	2	-
Tl	TR	<0.02	<0.2	<0.02	<0.02	0.03	0.45	-
Zn	Total	8310	694	1600	5.5	53.5	70	104
Non-Essential Elements								
Au		<0.5	<1	<0.1	<0.5	<0.5	0.004	-
B	Total	<10	47.5	269	<10	<10	10	-
Ba	Total	25.75	2590	313	<0.2	24.1	425	528
Bi	Total	<0.2	<0.4	<0.04	<0.2	<0.2	0.17	-
Ce	Total	<1	1.6	1.05	<1	29.5	-	52
Cs	Total	<0.1	0.16	0.22	<0.1	1.56	3	-
Ga	Total	<0.5	1.5	2.2	1.5	6.6	15	21
Ge	TR	<1	<2	0.45	<1	<1	1.5	-
In		<1	<2	<0.2	<1	<1	-	-
La		<0.1	0.89	0.56	<0.1	4.59	-	4
Li	Total	<0.2	1.06	5.15	<0.2	4.31	20	-
Nb		<1	<2	1.25	<2	3.0	-	10
Pd		<1	<2	<0.2	<1	<1	-	-
Rb		<0.2	2.18	2.69	<0.2	12.4	-	134
Sc	Total	<1	3	3.7	3	3.2	-	10
Sr	Total	0.6	166.5	54.5	<0.5	94.8	375	~300
U	Total	<0.05	0.2	0.085	0.05	0.34	2.7	3.6
V	TR	<50	<100	<10	<50	75	135	98
W	Total	<0.5	<1	0.8	<0.5	<0.5	1.5	-

Nickel was found to be present in concentrations higher than the average greywacke concentration data presented in Table 4.1. This higher value may have been affected by the incorporation of any element associated with residual roading aggregate in the sample (especially if any of the aggregate was volcanic in origin). However, the examination of the raw and aggregate bitumen samples did show that based upon the samples collected that the concentrations of elements in the bitumen are generally low. Consequently, road wear was unlikely to result in the discharge of elements to receiving environments that would result in increased concentrations of those elements in that environment.

The following conclusions can be drawn in relation to the concentration data obtained in this preliminary examination of brake pads:

- The iron concentration of the brake pad dust samples is higher than that in the original pads.
- The barium, cadmium and mercury concentration was elevated (compared to crustal abundance) in the new brake pads examined.
- The chromium, copper and tin concentrations were elevated (compared to crustal abundance) in the brake pad dust samples compared to the new brake pads.
- The boron, molybdenum, nickel, antimony and zinc concentrations were elevated in both new brake pads and brake pad dust compared to crustal abundance.

The following conclusions can be made in relation to the preliminary examination of tyres:

- Zinc appears to be the only element present in tyres in concentrations that significantly exceed crustal abundance.
- Although cadmium is present in tyres, the concentrations appear low compared to crustal abundance.

These elements have the potential to accumulate in depositional environments if associated with particulate materials. The potential effects of any of these elements is related to the concentration in the material lost from motor vehicles and the concentration in the receiving environment and the relative toxicity and or adverse effects associated with that element. However, if the concentration of any element (e.g., cadmium) is particularly low in sediments of the receiving environment then the contribution from motor vehicles may result in changes in the receiving environment.

The limited information on cadmium in tyres indicates that there appears to have been a decline in the concentration of cadmium in tyres. In 1975 an Australian study identified a considerable difference between the cadmium concentration in tyres made in Australia compared to imported tyres with one tyre containing 14 mg kg^{-1}. The examination of a limited number of tyres available in New Zealand found that the cadmium concentration in the tyres was low by comparison with the 1975 study. The tyres appeared to fall into two groups one with a higher cadmium concentration than the other.

This preliminary examination of the inorganic contaminants that may be released to the environment from some of the key motor vehicle contaminant sources has shown that there are several elements that may be released to the environment in amounts that could result in accumulation/exposure to those contaminants. The analysis of the samples carried out to-date has also shown that the variability in all constituents is very high and dependent upon the specifications of the manufactured brake-pads/linings. Because of this variability, the median results presented in this report provide only preliminary data for use in estimating loads of contaminants released from motor vehicles. To produce more accurate data for the New Zealand vehicle fleet, systematic and representative sampling of a larger number of samples of tyres and brake-pads will be required to ensure that the concentration factors used in emissions assessments are representative. This can be carried out, by matching samples tested, to the make up of the New Zealand vehicle fleet by, type and manufacturer.

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Appendix A: Summary of analytical methods and detection limits by element (all data mg/kg).

Parameter	**Sample**	**Method Used**	**Detection Limit**
Total calcium	T, B,	Dry Ash followed by nitric / hydrochloric acid dissolution ICP-MS.	50
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	100
Total recoverable calcium	BP, RB	Nitric / hydrochloric acid digestion	10
Total magnesium	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	40
Total recoverable magnesium	T, BP, RB, B	Nitric / hydrochloric acid digestion	4
Total sodium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution .	20
	BP	Hydrochloric/nitric/hydrofluoric acid/Aqua Regia digestion	40
Total recoverable sodium	RB	Nitric / hydrochloric acid digestion	4
Total potassium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	50
	BP	Hydrochloric/nitric/hydrofluoric acid/Aqua Regia digestion	100
Total recoverable potassium	RB	Nitric / hydrochloric acid digestion	10
Total lithium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	0.4
Total recoverable lithium	BP, RB	Nitric/hydrochloric acid digestion	0.04
Total rubidium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	0.4
Total recoverable rubidium	BP, RB	Nitric/hydrochloric acid digestion	0.04
Total phosphorus	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	20
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	40
Total recoverable phosphorus	RB, BP	Nitric / hydrochloric acid digestion	4
Total boron	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	10
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	20
Total recoverable boron	BP	Nitric/hydrochloric acid digestion	2
Total iron	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	20
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	40
Total recoverable iron	BP, RB	Nitric/hydrochloric acid digestion	4
Total manganese	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	1
Total recoverable manganese	BP, RB	Nitric/hydrochloric acid digestion	0.1
Total silver	T, BP, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution .	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	0.4
Total recoverable silver	BP	Nitric/hydrochloric acid digestion	0.04
Total aluminium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digest	10
Total recoverable aluminium	BP, RB	Nitric/hydrochloric acid digestion	1
Total arsenic	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	2
Total recoverable arsenic	BP, RB	Nitric / hydrochloric acid digestion	0.2
Total gold	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	1
Total recoverable gold	BP	Nitric/hydrochloric acid digestion	0.1
Total barium	BP,	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4

Parameter	Sample	Method Used	Detection Limit
	B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
Total recoverable barium	T, RB, BP	Nitric / hydrochloric acid digestion,.	0.04
Total beryllium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.2
Total recoverable beryllium	RB, BP	Nitric / hydrochloric acid digestion	0.02
Total bismuth	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4
Total recoverable bismuth	BP	Nitric/hydrochloric acid digestion	0.04
Total cadmium	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.05
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.1
Total recoverable cadmium	BP	Nitric/hydrochloric acid digestion	0.01
Total cobalt	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4
Total recoverable cobalt	RB, BP	Nitric / hydrochloric acid digestion	0.04
Total chromium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	2
Total recoverable chromium	BP, RB	Nitric/hydrochloric acid digestion	0.2
Total caesium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.2
Total recoverable caesium	BP, RB	Nitric/hydrochloric acid digestion	0.02
Total copper	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	2
Total recoverable copper	RB	Nitric / hydrochloric acid digestion	0.2
Total mercury	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.1
Total recoverable mercury	T, RB, B, BP	Nitric / hydrochloric acid digestion,	0.01
Total lanthanum	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.2
Total recoverable lanthanum	BP, RB	Nitric/hydrochloric acid digestion	0.02
Total molybdenum	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4
Total recoverable molybdenum	RB	Nitric / hydrochloric acid digestion	0.04
Total nickel	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	1
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	2
Total recoverable nickel	RB	Nitric / hydrochloric acid digestion	0.2
Total lead	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4
Total recoverable lead	BP, RB	Nitric/hydrochloric acid digestion	0.04
Total antimony	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.4
Total recoverable antimony	BP	Nitric/hydrochloric acid digestion	0.04
Total selenium	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	10
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	20
Total recoverable selenium	BP	Nitric/hydrochloric acid digestion	2
Total strontium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	1

Parameter	Sample	Method Used	Detection Limit
Total recoverable strontium	RB, BP	Nitric / hydrochloric acid digestion	0.1
Total tin	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	1
Total recoverable tin	BP	Nitric/hydrochloric acid digestion	0.1
Total thallium	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.2
Total recoverable thallium	T, RB, B, BP	Nitric / hydrochloric acid digestion	0.02
Total uranium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.05
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	0.1
Total recoverable uranium	RB, BP	Nitric / hydrochloric acid digestion	0.01
Total vanadium	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	50
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	100
Total recoverable vanadium	RB, BP	Nitric / hydrochloric acid digestion	10
Total tungsten	T, RB, B	Dry Ash followed by nitric / hydrochloric acid dissolution	0.5
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	1
Total recoverable tungsten	BP	Nitric/hydrochloric acid digestion	0.1
Total zinc	T, B	Dry Ash followed by nitric / hydrochloric acid dissolution	2
	BP	Hydrochloric/nitric/hydrofluoric acid/aqua regia digestion	4
Total recoverable zinc	RB	Nitric / hydrochloric acid digestion	0.4