



*Metals in Particulate Material on Road Surfaces*



MINISTRY of TRANSPORT  
TE MANATŪ WAKA



# Metals in Particulate Material on Road Surfaces

Prepared for



MINISTRY of TRANSPORT  
TE MANATŪ WAKA

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## Abbreviations

Å	Angstrom
Ag	Silver
As	Arsenic
Au	Gold
B	Boron
Ba	Barium
Bi	Bismuth
Cd	Cadmium
Ce	Cerium
Co	Cobalt
Cr	Chromium
Cs	Caesium
Cu	Copper
DL	Detection limit
EU	European Union
Fe	iron
GC-ECD	Gas chromatography – electron capture detection
Ga	Gallium
Hf	Hafnium
Hg	Mercury
ICPAES	Inductively coupled plasma atomic emission spectrometry
ICPMS	Inductively coupled plasma mass spectrometry
km	kilometre
La	Lanthanum
m	Metre
mg/kg	Milligrams per kilogram (equivalent to ppm)
Mn	Manganese
Nb	Niobium
Nd	Not detected
Ni	Nickel
Mo	Molybdenum
Pb	Lead
Pd	palladium
Pt	Platinum
Rh	Rhodium
ng/g	nanograms per gram (equivalent to µg/kg or ppb)
Sb	Antimony
Sc	Scandium
Sn	Tin
Sr	Strontium
Ti	Titanium
U	Uranium
UK	United Kingdom
US	United States
USA	United States of America
V	Vanadium
Y	Yttrium
Zn	Zinc
Zr	Zirconium

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# 1. INTRODUCTION

Very few complete analyses of roadway gutter dusts have published since Pitt & Amy (1973) presented a 'complete' analyses of gutter dust samples by mass spectrometry (73 elements). Their analyses of a residential, commercial and industrial sample revealed elevated chromium (Cr), copper (Cu), Nickel (Ni), hafnium (Hf), lead (Pb), scandium (Sc) and vanadium (V) in some of the samples. Early studies such as Harrison (1979) examined street dusts in Lancaster (UK) for Pb, cadmium (Cd), Cr, cobalt (Co), Cu, Ni and zinc (Zn); Hopke et al. (1980) found elevated Cr, Ni, Pb, and Zn in the samples they examined and Ho (1979) and Lau & Wong (1982) studied the Cu, Cd, manganese (Mn), Pb and Zn concentrations in gutter dusts from Hong Kong. Data from a number of more recent studies including studies such as that of Chutke et al. (1995) who determined a wide range of elements in dusts in Nagpur are identified in this report. Although a number of elements in the samples that have been examined by the above authors showed obvious enrichment, often no indication of natural variability or baseline metal levels were presented by any author resulting in some difficulties in determining what if any the extent of enrichment was for some trace elements found in road surface particulate matter.

Sartor & Boyd (1972), Pitt & Amy (1973) and Pitt (1978) examined the distribution of a number of elements in the grain size fractions of gutter dust samples. More refined work has also been carried out on the trace element variability caused by grain size, density and magnetic properties of particles (Hopke et al. 1980; Linton et al. 1980a and Fergusson & Simmonds 1983). Different and variable trends were found for elements between the authors, demonstrating the highly variable nature of road surface and gutter dusts.

This report examined the available information on the quality of the particulate material on the surface of urban roads. This information encompasses the data obtained from the examination of contaminants in surface particulates and also the material residing in gutters of roads. The focus of the report is data obtained in New Zealand. For comparison and where data is limited, information is presented from a number of international studies.

## 2. VARIABLES & FACTORS TO CONSIDER

### 2.1 Methods

This report presents results from two studies undertaken in New Zealand in conjunction with published New Zealand and international data. The additional New Zealand data comes from two studies. The first is a series of samples collected in 1980 from streets in the Wellington region (Kennedy unpublished). The second is from samples collected from streets in Waitakere City (Auckland) during 2002 (Kennedy & Gadd 2002). Kennedy & Gadd (2002) presented results for Cu, Pb, Zn and polyaromatic hydrocarbons (not described in this report) in two fractions of street dusts collected in the City. This report discusses and presents additional data on the concentration of metals in those samples. For completeness the methods used are described here.

#### **Wellington Study**

Samples were collected from the gutter of streets in Wellington and Lower Hutt in 1980 using dustpan and brush. Typically material was collected from 3-5 areas of about 0.5 m each within the road gutter. Samples were dried at 90°C overnight, sieved through a 2 mm stainless steel sieve and then ground in a tungsten carbide ring mill. Mercury (Hg) analysis was undertaken by cold vapour atomic absorption analysis after acid digestion followed by reduction of the Hg with stannous chloride. All major and trace elements analysis were, undertaken by wavelength dispersive X - ray spectrometry (XRFS) using a Siemens SRS-1 spectrometer. Methodology is described in detail in Kennedy et al. (1983a,b). Trace elements were determined using 3.5 g of ground sample pressed

into a boric acid backed pellet (Norrish & Chappell 1967). All X-ray counts were corrected for background, interferences where needed and inter-sample matrix differences using mass absorption coefficients calculated from Compton scatter peak. Reproducibility (grinding, preparation and analytical) for the trace elements was measured as the average difference between the analysis of three duplicate samples from the study was typically 1 mg/kg for arsenic (As), cerium (Ce), Cu, gallium (Ga), lanthanum (La), niobium (Nb), Pb, rubidium (Rb), Sc, V, yttrium (Y); 2 mg/kg for Ni and Zn; 3 mg/kg for strontium (Sr); 4 mg/kg for Cr; 5 mg/kg for zirconium (Zr); 7 mg/kg for barium (Ba) and 20 mg/kg for titanium (Ti).

Results of the analyses of a range of SRMs using the techniques used for the analysis of the street dusts from the Wellington region are presented in Kennedy et al. (1983a,b) and Palmer et al. (1983). For grain size fractions, all graphics utilise the following numerical categories for identification; 1, 1-2 mm; 2, 0.71-1.0 mm; 2.5, 0.5-1.0; 3, 0.5-0.71; 4, 0.25-0.5 mm; 5, 0.15-0.25 mm; 6, 0.075-0.15 mm; 6.5, 0.038-0.15 mm; 7, 0.038-0.075 mm; 8, <0.038 mm or < 0.036 mm.

## Waitakere Study

A PacVac 2000 Contractor model vacuum cleaner was used to collect dust samples from the road surface and gutter in Waitakere City in 2002 (Kennedy & Gadd 2002). The cleaner was fitted with a plastic hose, tube and foot (stationary type foot with 6 mm long bristles). The cleaner uses disposable 2 ply paper bags capable of retaining particles to 0.3 µm. The vacuum cleaner was powered from a petrol generator fuelled by unleaded petrol.

An area of road 1 m wide was marked out using string lines. Samples were collected by vacuuming this section of road, from the left hand gutter to the right hand, by passing the vacuum cleaner four times over each section (refer following section). The area was then measured and recorded. At each location three strips were sampled at 15 m intervals. At intersections, the intervals between strips were reduced where necessary and sampling undertaken in two parts. The decision to sample the intersection in two parts was made based upon the driving behaviour within the intersection. There was insufficient information available in the published literature on road surface contaminants to indicate whether there were detectable differences in concentration or loads across the road surface. At the intersection, the lanes were identified as the entry and exit. In this study, the exit is the lane approaching the intersection and the entry is the lane leaving the intersection. These were sampled as independent samples to confirm whether there were any identifiable differences between the two sections of the road. Between roads/samples, the vacuum cleaner was cleaned by running the cleaner with a blank bag inside. The bag was run for at least 3 minutes to minimise carryover of dust. The foot of the cleaner was cleaned thoroughly by vacuum and inspected for debris or dust. The bag was replaced with a clean, unused bag for each site sample collection.

Following sample collection, individual sample bags from the same sampling location were combined and weighed. The whole sample was sieved through a 2 mm non-metal sieve, weighed and the sample fractions greater (gravel) and less than 2 mm (sand, silt and clay) weighed. The <2 mm sample was then sieved through a <63 µm non-metal sieve to provide information on the weight of sample <2 mm and >63 µm and <63 µm. The material from this sieving provided material for chemical analysis of <63 µm material.

Trace element analysis were undertaken on <63 µm and <2,000 µm fractions following nitric/hydrochloric acid digestion and ICP-MS (Perkin Elmer Elan 6000 Inductively Coupled Plasma Mass Spectrometer) according to US EPA method 200.2. A procedural blank was analysed with each batch of samples, and there was one duplicate and one spiked sample per twenty samples. An in-house reference sample was also analysed with each batch of samples. Detection limits varied for each element but were 2, 0.4 and 4 mg/kg (dry weight) for Cu, Pb and Zn respectively. Limits of detection are identified in the summary tables of the report where required.

## 2.2 Contaminant Evaluation

In this report, the available data for trace elements (and some major metallic elements such as iron and titanium) is examined to determine whether road surface particulates are readily identifiable as contaminated by that element. Data on the presence of each element is used to determine whether the element is or could be contributed by motor vehicles. To determine whether the concentration of a particular element is elevated with respect to what would be considered normal, comparison is made with concentration data for soils and sediments. When making such a comparison, two principal factors need to be taken into account. The first is ensuring that the analytical methods used for the determination of concentrations in both the road surface material and the comparative information are comparable. The second is ensuring that the comparison data comes from a similar geological provenance as the setting that the road surface particulates came from.

As described above, the two key information sources described in this report utilised two completely different analytical methods for analysis. The earlier Wellington study used XRFs a total analytical method. Other work such as that of Fergusson & Ryan (1994) used INAA, another total method. The more recent Waitakere City study (Kennedy & Gadd 2003) used strong acid digestion. This method is probably the most common method of extraction prior to analysis. For evaluation of data collected in the Wellington study, comparative element concentration data that has been obtained using the same analytical techniques has been utilised. For comparison a set of soils from Staircase Spur (Lake Ponui in the Wairarapa), a set of soils from throughout the Marlborough Sounds and a series of samples from Pauatahanui Stream and Pauatahanui Inlet (just north of Wellington, author unpublished data) were utilised. Of these, the Marlborough Sounds soils differ geologically to the Wellington road surface sample environment. For the Waitakere City samples, a data set collected by ARC on trace elements in soils in the Auckland area (ARC 2001) was used for comparison.

## 3. INDIVIDUAL INORGANIC CONTAMINANTS

### 3.1 Antimony (Sb)

#### Natural geochemistry

Antimony is a chalcophile element being found in sulphide minerals along with metals such as Pb, Cu and silver (Ag). Although there are a range of Sb minerals, stibnite ( $\text{Sb}_2\text{S}_3$ ) is the most common. Christie & Brathwaite (1993) describe the occurrence of stibnite in New Zealand. Its distribution is linked mainly to the location of gold bearing quartz in greywacke and schist and to the location of epithermal quartz associated with volcanic areas. Stibnite deposits can be found in locations such as Endeavour Inlet in the Marlborough Sounds (Christie & Brathwaite 1993). The crustal abundance of antimony is estimated to be 0.2 mg/kg (Plant & Rainswell 1983).

#### Sources

The estimated use of Sb in the United States provides an indication of its current use in society. Uses included flame-retardants, 55%; transportation, including batteries, 18%; chemicals, 10%; ceramics and glass, 7%; and other uses 10% (USDI 2003). Antimony is used in the battery industry as a hardener in lead. The metal also finds applications in solders and other alloys. Antimony trioxide is the most important of the antimony compounds and is primarily used in the flame-retardant on clothing, toys, aircraft and automobile seat covers, (Elinder & Friberg 1977, Fleming & Parle 1977). Antimony is also used for making infrared detectors and diodes. Along with its use in batteries it is also used in anti-friction alloys, type metal, small arms and tracer bullets and cable sheathing. Other Sb compounds such as oxides, sulfides, sodium antimonate, and antimony trichloride, are used in manufacturing flame-proofing compounds, paints ceramic enamels, glass, and pottery goods (Fleming & Parle 1977) (see also Christie & Brathwaite 1993).

There are few significant known uses of Sb in the manufacture of motor vehicles. Kennedy & Gadd (2000) provide information on the concentration of Sb in a selection of brake pads and tires used on vehicles in New Zealand and in bitumen (Table 3.1). The data summarised in Table 3.1 shows that there are no significant concentrations of Sb in road bitumen (both raw and on-road). Tyres were found to contain low concentrations of Sb. Brake pads and brake pad dust contained detectable concentrations with very high concentrations found in a small number of samples examined. The source of the Sb was probably the use of antimony sulphide as a lubricant in the particular commercial brake pad formulation. Industry information presented in Lohse et al. (2001) indicates that Sb compounds (total Sb concentration not identified) may comprise up to 10% of the brake lining formula. It has also been identified that Sb may be present in some of the anti-oxidant compounds used in oil and greases (Jungers et al. 1975).

**Table 3.1 - Antimony in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	6.08	0.07	29,500	12
Brake pad dust	22.4	4	133	6
Tyres	<0.2	<0.2	2.4	12
Raw bitumen	<0.2	<0.2	0.3	6
Road bitumen	<0.2	<0.2	<0.2	5

### Antimony in road dusts

The concentration of Sb in the samples of street dust examined (Table 3.2) is high compared to the concentration that could be considered normal for soils and dusts derived from greywacke and argillite.

**Table 3.2 - Antimony in gutter and road surface dusts and sediments (all results mg/kg dry weight).**

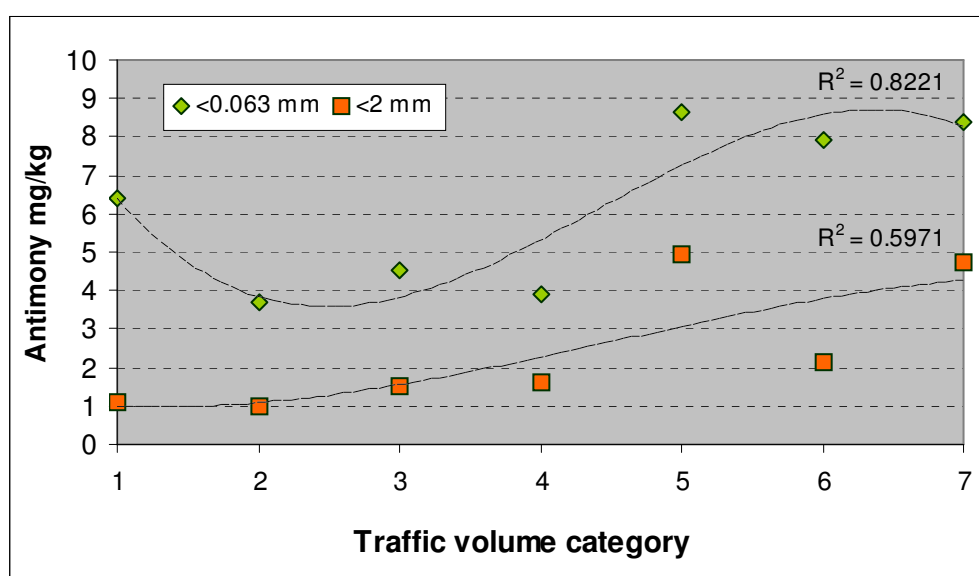
Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	C	2.2 ± 0.3	-	<0.125 mm	SA	1	Hopke et al. (1980)
London	C ~1984	15.2	14.8, 15.8	<0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	6	3.6, 8.4	<0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax	C ~1984	2	1.9, 2.1	<0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston	C ~1984	1.65	1.6-1.7	<0.963 mm	INAA	2	Fergusson & Ryan 1984
Hamburg	C	6.4	-	>0.25 mm			Dannecker et al. (1990)
Nagpur	M-1992	14.1	4.72-20.1	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R-~2000	3 ± 1	-	SC <2 mm	INAA	13	Sutherland & Tolosa 2000
Ottawa	R 1993	0.42	0.09-15.88	BP 0.1-0.25 mm	SA	45	Rasmussen et al. 2001
Christchurch	C ~1984	8.9	1.7-22	<0.963 mm	INAA	3	Fergusson & Ryan 1984
Wellington							
Lambton Quay	C	16.4	5.0-43.6	BP, <2 mm	XRFS	9	Kennedy (unpublished)
Petone	R	9.0	5.4-19.3	BP, <2 mm	XRFS	5	Kennedy (unpublished)
Gracefield	R	7.2	5.4-9.0	BP, <2 mm	XRFS	2	Kennedy (unpublished)
Gracefield	I	8.3	4.5-15.2	BP, <2 mm	XRFS	8	Kennedy (unpublished)
Lambton Quay cb	C	15.0	10.8-19.2	<2 mm	XRFS	2	Kennedy (unpublished)
Waitakere	R/C 2002	1.7	<0.4-8.3	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R/C 2002	6.25	1.9-13.0	VC <63 µm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 - median presented where available. SC – scoop; BSC – Brush and scoop; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis. ICPMS– Inductively coupled plasma mass spectrometry; cb – catchbasin.

Two samples of estuarine sediment from the Hutt estuary and one sample from the Waikanae estuary near Wellington which were examined by spark source mass spectrometry contained 2.1, 1.5 and 0.63 mg/kg respectively (Author unpublished data). The same samples examined by XRFS (also by the author) contained <1, 2.7 and <1 mg/kg Sb respectively.

One of the earliest reports of Sb in particulate matter in street gutters was by Pitt & Amy (1973) who reported Sb concentrations of 2 to 5 mg/kg by mass spectrometry. In New Zealand, Fergusson & Ryan (1984) provided results for 11 gutter samples collected worldwide (including three from Christchurch) were in the same concentration range as the data presented in Table 3.2. A low of 1.6 mg/kg was reported in Kingston, Jamaica and a high value of 22 in Christchurch (median 8.9 mg/kg). Hopke et al. (1980) reported data for Sb in a dust sample from Urbana Illinois (Table 3.2). The sample contained less than 3.3 mg/kg in all fractions except the 45 to 75  $\mu\text{m}$  fraction which contained 34.5 mg/kg. Unpublished data (D. Natusch pers comm) indicates that in the densest particles ( $>2.9 \text{ g/cm}^3$ ), the higher concentrations were found in the magnetic fraction rather than the non-magnetic. Chutke et al. (1995) reported elevated and variable Sb concentrations in dust along highways in Nagpur (Table 3.2).

The data from Waitakere City indicates that the Sb concentration in the  $<0.063 \text{ mm}$  fraction is higher than that measured in the whole sediment sample ( $<2 \text{ mm}$ ). This difference can also be seen in Fig. 3.1 that shows the median concentration of sites within a series of different categories of traffic volume ranging from  $<500$  to  $>30,000$  VPD. Given the presence of antimony in some brake pads used on vehicles in New Zealand the elevated concentration in the particulate matter collected from the streets and the relationship to traffic volume is not surprising.



**Fig. 3.1 - Antimony concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003; the traffic volume categories are 1  $<499$  VPD; 2 500-999; 3 1000-4999; 4 5000-9999; 5 10,000-19,999; 6 20,000-29,999; 7  $>30,000$  VPD;).**

### Contribution from motor vehicles

Identifiable and elevated concentrations of antimony are found in the particulate matter found on New Zealand streets. The primary source appears to be the presence of antimony in brake pads. There appear to be few other significant sources within the urban environment that could account for the concentrations measured. As such, it is likely that motor vehicles are currently contributing the majority if not all of the Sb present in particulate matter on urban road surfaces. The presence of Sb on road surfaces indicates that vehicles contribute Sb to urban stormwater. At this point in time, what proportion of the total mass load of Sb transported from catchments (natural and anthropogenic) that is contributed by motor-vehicles is not known. It is likely that the proportion is  $>75\%$ .

## 3.2 Arsenic (As)

### Natural geochemistry

Smedley & Kinniburgh (2002), reviewed As occurrence in a water, soils, sediments and rocks. Most sedimentary and metamorphic rocks contain relatively low concentrations of As. Plant & Raiswell (1983) summarised mean As concentrations in most rock types as being in the range 1-2 mg/kg. Arsenic chemistry typically follows that of sulphur with the most abundant As mineral being arsenopyrite (FeAsS). Authigenic pyrite which will contain As in some sulphur positions results in some soils containing higher concentrations of As. Boyle & Jonasson (1973) identify an average world background concentration of 7.2 mg kg As.

Fig. 3.2 summarises data from ARC (2001) that shows the As concentration in soils in the Auckland region derived from different parent materials. The median values range from 3.16 mg/kg in volcanic soils (n=38), 3.14 mg/kg in soils of the Waitemata Group (n=18) to 7.0 mg/kg for soils derived from greywacke (n=6). It can be seen from the figure that most soil types had median values in the range 3.14-6/5 mg/kg. For comparison, As in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean As concentration of 3 mg/kg (n=38) and As in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 1.7 to 9.1 mg/kg (median of location means 5.7 mg/kg, n=98) (Author unpublished data).

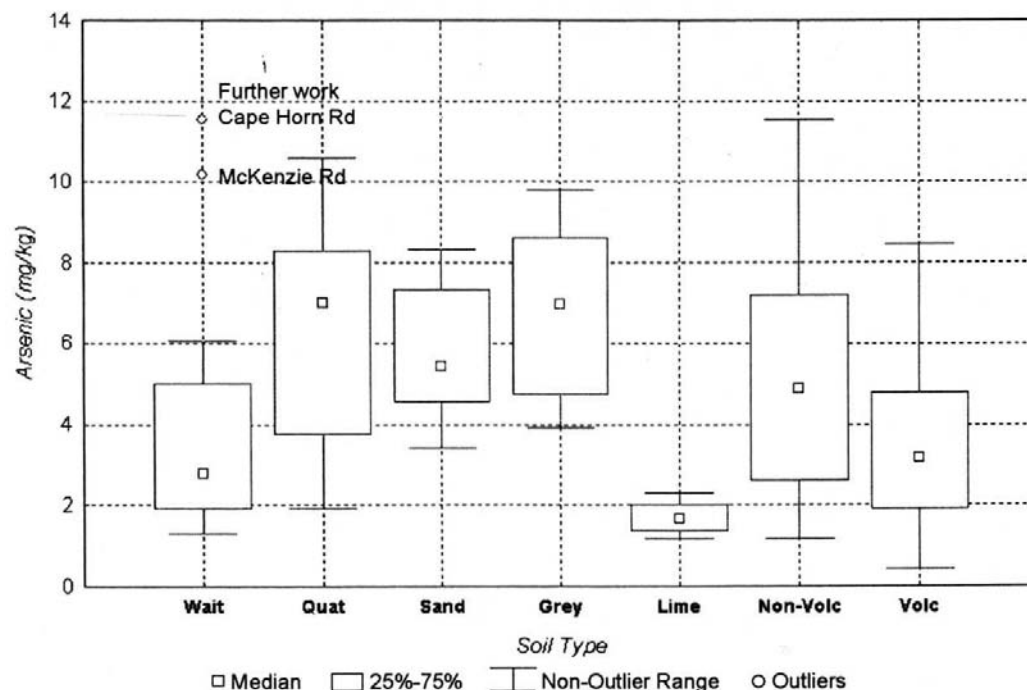


Fig. 3.2 - Arsenic concentration in Auckland soils (from ARC 2001).

### Sources

Arsenic is used in the manufacture of some non-ferrous metal alloys for use in lead acid batteries (USDI 2003) and to increase hardness and heat resistance in the manufacture of glass (Tsuchiya et al. 1977). Arsenic is also used in the manufacture of semi-conductor materials (USDI 2003). One of the principal uses in New Zealand is in arsenical wood preservatives (Cu, Cr, As) used for building and outside timbers. There are few known sources within motor vehicles. It is likely that As may be present in lead-acid batteries. Arsenic was not specifically mentioned, by Sander et al. (2000) in their review of the presence of heavy metals in vehicles. There is little information on the concentration of As in emission sources. Kennedy & Gadd (2000) reported the measurement of As in a selection of brake pads and tyres used in New Zealand and in samples of road bitumen. Table 3.3 shows that the concentration of As in tyres and in raw bitumen is low. Detectable

concentrations of As are present in brake pads and brake lining dust. Concentrations associated with wear of brake linings are variable with 50% of brake lining and dust samples examined having concentrations above 2 mg/kg. Four of 18 samples contained between 10 and 26 mg/kg As.

**Table 3.3 - Arsenic in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	<2	<2	26	12
Brake pad dust	4.85	1.7	13.9	6
Tyres	<1	<1	<1	12
Raw bitumen	<1	<1	<1	6
Road bitumen	1.5	0.9	12.6	5

### Arsenic in road dusts

Table 3.4 provides a summary of New Zealand and international information on the concentration of As in particulate matter on urban road surfaces. Concentrations of As in road surface particulates collected in at least three studies from different locations in New Zealand are similar. The concentration of As recorded in road dust samples are similar to the concentrations measured in soils and sediments in New Zealand (refer above).

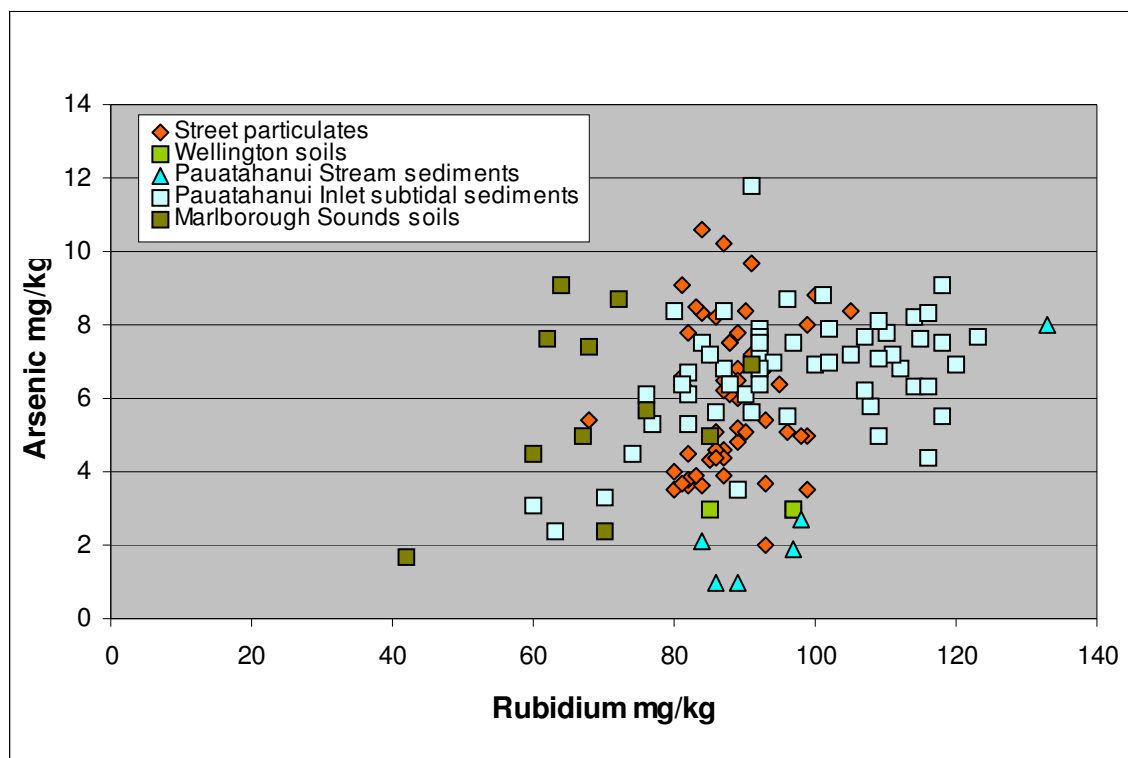
**Table 3.4 - Arsenic in street gutter and street surface dusts and sediments (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
London	C ~1984	20	12.9-27	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	4.7	4-5.4	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	7.4	5.9-8.9	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	5.1	3.5-5.3	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Urbana Illinois	~1980	11 ± 1	-	VC	INAA	1	Hopke et al. 1980
Ottawa Canada	R 1993	1.4	nd – 2.9	BP-0.1-0.25 mm	ICPMS	45	Rasmussen et al 2001
Nagpur	M-1992	14.7	14.5-21.6	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R ~2000	4 ± 1	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Wellington							
Lambton Quay	C -	4.0	2.0-6.8	BP-<2 mm	XRFS	7	Kennedy (unpublished)
Newton	C -	6.8	5.4-8.3	BP-<2 mm	XRFS	6	Kennedy (unpublished)
Karori	C -	6.1	3.7-7.8	BP-<2 mm	XRFS	7	Kennedy (unpublished)
Lower Hutt	C -	4.5	3.6-6.0	BP-<2 mm	XRFS	8	Kennedy (unpublished)
Newton	R -	7.6	4.4-10.2	BP-<2 mm	XRFS	8	Kennedy (unpublished)
Karori	R -	5.9	3.5-10.6	BP-<2 mm	XRFS	12	Kennedy (unpublished)
Taita	R -	6.2	4.0-7.2	BP-<2 mm	XRFS	7	Kennedy (unpublished)
Seaview	I -	6.5	3.7-8.8	BP-<2 mm	XRFS	9	Kennedy (unpublished)
Christchurch	C ~1984	8.25	5.3-11.2	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Auckland City	R-C, 2001-3	-	2-6	V <0.45-2 mm	SA ICPMS	~48	Ng et al. 2003 (refer below)
Waitakere	R-2002	5.5	<2-14	VC-<2 mm	SA ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	6	3-9	VC-<0.063 mm	SA ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; SC – scoop; BSC – Brush and scoop; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis. ICPMS– Inductively coupled plasma mass spectrometry. The concentration range for Auckland City is estimated from the graphical information in Ng et al. (2003) and is approximate only.

No As analysis of particulate size fractions was undertaken on the early Wellington samples by the author. Fig. 3.3 illustrates the variation in As concentration as a function of sample particle size variation (as represented by the concentration of the reference element rubidium). The figure compares the Wellington street particulate data with soil samples from two locations (Marlborough

Sounds and Lake Ponui in the Wairarapa) and also with stream sediments from Pauatahanui Inlet and with sub-tidal sediments from Pauatahanui Inlet. Fig. 3.3 suggests considerable concentration overlap between the street particulate samples from Wellington and the soil samples. Given that the typical natural range in rubidium concentration ranges from about 70 mg/kg in fine sand to 150 mg/kg in silt and clay particles, the As concentration range is not much greater than found in soils and coastal sediments in the Wellington area. However, the Pauatahanui Inlet sub-tidal sediments also used for comparison contain a higher concentration of As than the freshwater stream sediment samples examined from the inlet catchment. This difference may be attributable to particles settling within the estuary from the streams scavenging arsenic from the water (Saulnier & Mucci 2000), or iron (hydr)oxides in oxic sediments scavenging arsenate from overlying water.



**Fig. 3.3 - Arsenic concentration in road surface particle samples from Wellington compared to soils and sediments in the Region compared on the basis of their rubidium content (Kennedy unpublished data).**

The As data for particulate matter from Waitakere City Streets did not show any significant differences between <0.063 mm and <2 mm fractions. No analyses of grain size fractions for As was undertaken in relation to the Wellington area samples for which data is discussed in this report. There did not appear to be an obvious relationship with grain size (when compared to rubidium concentrations in samples) as represented by Rb in Fig. 3.3. Analysis of As in stream sediments indicates higher concentrations in fine sediment fractions compared to coarse (refer above). Similar trends in grain size fractions, of a whole street dust were reported by Corrin & Natusch (1977). However, unpublished data showing further separation by density and magnetic properties demonstrated that in the lightest fraction (<1.6, 1.6 to 2.2  $\mu\text{g}/\text{cm}^3$ ) the As content decreased from the 250 to 500  $\mu\text{m}$  separates. In the >2.9  $\text{g}/\text{cm}^3$  fraction the magnetic fraction contained twice as much As as the non-magnetic fraction (D. Natusch pers comm).

Fig. 3.4 illustrates data for road surface particulates collected in Auckland City (Ng et al. 2003). The analysis of particle size fractions from two locations indicated a general increase in the concentration of As as particle size decreased. The concentration range was small (2-6 mg/kg.) and encompassed the lower half of the range seen in samples from Wellington.



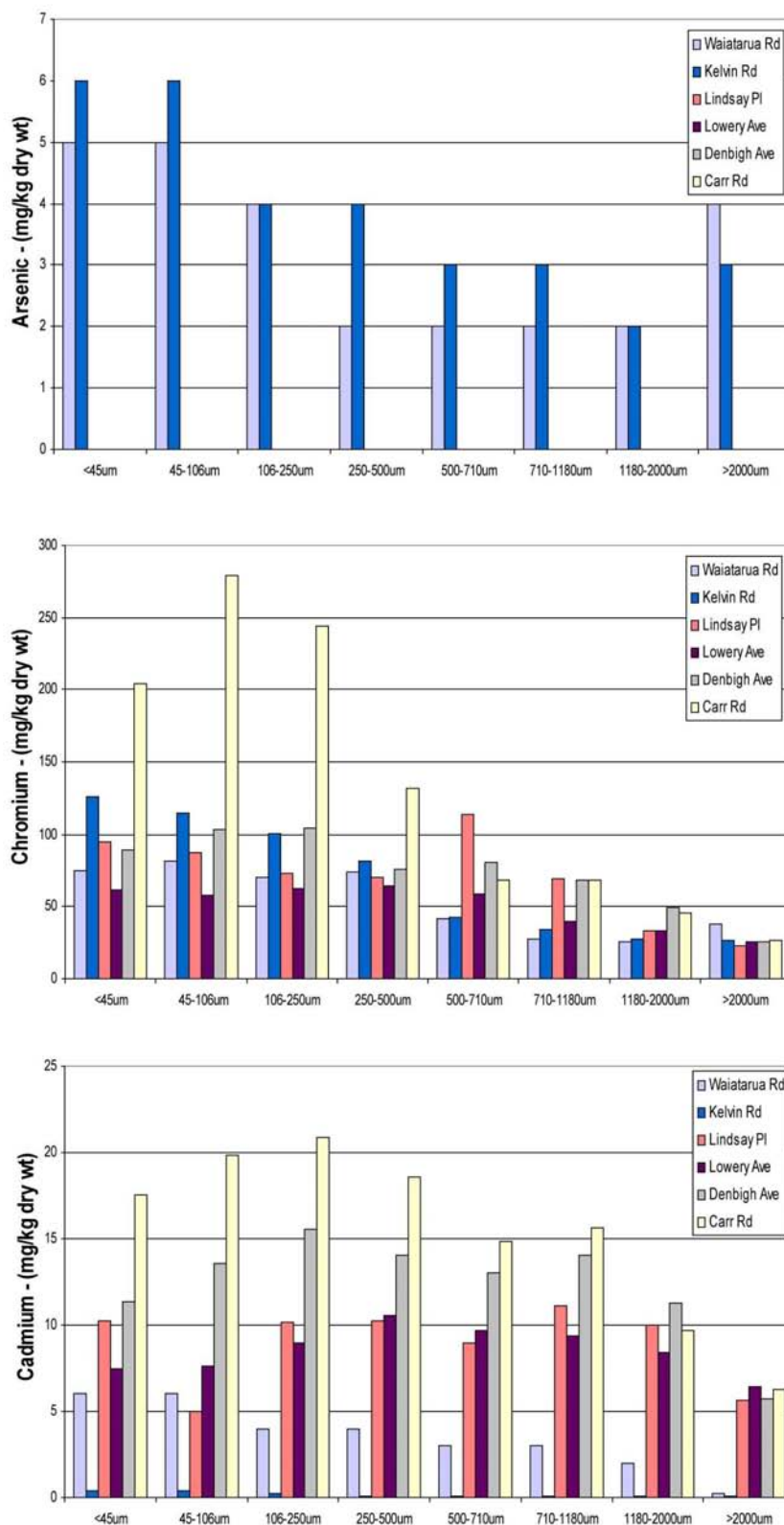
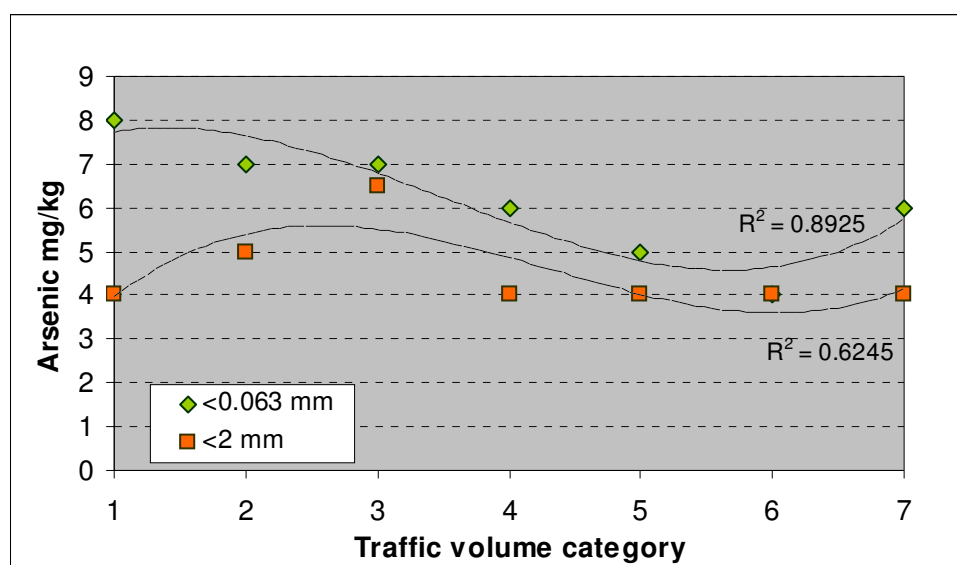


Fig. 3.4 – Arsenic, chromium and cadmium concentration in different size fractions of road surface samples from Auckland City (taken from Ng et al. 2003).

## Contribution from motor vehicles

Particulate material on road surfaces in urban areas contains variable but relatively low concentrations of arsenic. It is unclear what proportion of the As present in urban street particulates is natural or added as a consequence of activities on or adjacent to the street. Examination of emissions from motor vehicles indicates that a proportion of brake pads used on vehicles in New Zealand contain As, resulting in the release to the road environment of the arsenic in the linings. The typical concentrations measured in the brake pads is however similar to the concentrations measured in soils and sediments not enriched in arsenic in New Zealand.

The analysis of vehicle emission sources (refer above) showed that the typical concentration of As in the source samples examined were lower than the concentrations present in the road surface particles. Fig. 3.5 shows no significant positive correlation of arsenic concentration with vehicle numbers was apparent using road information for Waitakere City from Kennedy & Gadd (2003).



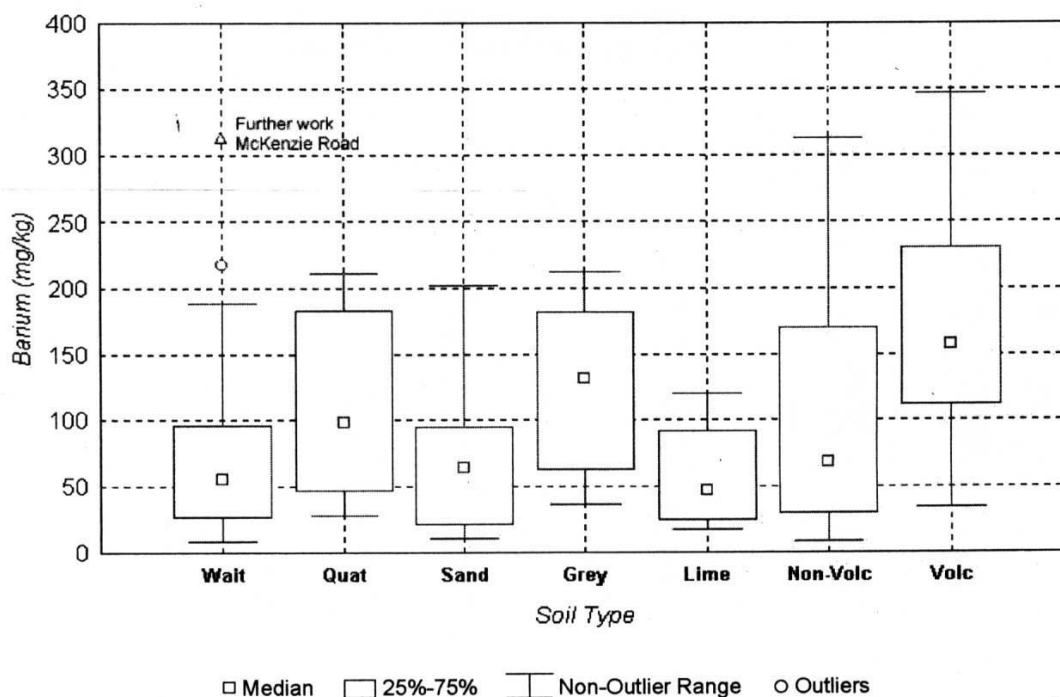
**Fig. 3.5 - Arsenic concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

Overall, although motor vehicles contribute As to the road surface through emissions from sources such as brake lining wear, vehicles do not appear to be contributing significant amounts of As to urban road surfaces that can be identified using existing data.

## 3.3 Barium (Ba)

### Natural geochemistry

Barium ( $\text{Ba}^{2+}$ ) usually substitutes for  $\text{K}^+$  in minerals (ionic radius of 1.34 and 1.33 Å respectively) and a consequence is common in potassium minerals such as biotite and potassium feldspars (Taylor 1965). This tends to result in some enrichment in many sandy sediments compared to fine sediments (as the minerals predominate in the sand fraction) such as clays and silts. The most common mineral is barite ( $\text{BaSO}_4$ ). Plant & Rainswell (1983) report an average crustal abundance of 425 mg/kg with considerable variation between rock types such as basalt with 250 mg/kg and granites with 600 mg/kg. ARC (2001) presented data for acid extractable Ba in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.6 shows that the median values range for key soil groups range from 51 mg/kg in Waitemata Group soils ( $n=18$ ), 131.8 mg/kg ( $n=6$ ) for greywacke to 157 mg/kg for soils derived from volcanic parent materials ( $n=38$ ).



**Fig. 3.6 - Barium concentration in Auckland soils (from ARC 2001).**

For comparison, Ba in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 453 mg/kg ( $n=38$ ) and Ba in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 186 to 364 mg/kg (median of location means 227 mg/kg,  $n=78$ ) (Author unpublished data).

## Sources

Barium has various uses including the manufacture of alloys, paints, soaps, paper, rubber, glass, ceramics, television picture tubes, brick and tile refractories, plastics stabilisers, fireworks and in lubricating additives (Belliles 1979). Barium sulphate (barite) is widely used in a variety of other products. It is used in radiology and it is used by the petroleum industry as a weighting agent in drilling muds – neither of these sources likely to contribute to road dust quality and stormwater. Barium is also used in paints and ceramics. Barium (as barium sulphate or sometimes as ground witherite -barium carbonate; van Alphen 1998) has been and is used in paint where it provides bulk, controls pigment settling, and improves viscosity, application properties, and surface finish. It is used as a filler in plastics and rubber products, imparts sound-deadening characteristics, and improves processing qualities when used as a backing in floor mats and carpets. It is also used in the manufacture of glass and ceramics, and as a feedstock for the production of other barium chemicals.  $BaSO_4$  is used in X-ray diagnostic tests to photograph the gastrointestinal tract (DiBello et al. 1991).  $BaCO_3$  is used in the manufacture of glass, clay, and brick products; in the manufacture of barium ferrites, which can be prepared into magnets for small motors; and also in the production of photographic papers.

Barium is present in fuel additives and in fillers, which are used in the brake linings (in the form of barite) and tyres of vehicles (Hopke et al 1980). Kennedy & Gadd (2000) reported a median concentration of 2,590 mg/kg Ba in 12 brake pads used in New Zealand and a median concentration of 313 mg/kg in 6 brake pad dust samples (Table 3.5). Kennedy & Gadd (2000) also reported a median concentration of 25.8 mg/kg Ba in 12 tyres used in New Zealand. No Ba was found in raw bitumen samples in New Zealand but low concentrations were found in on-road bitumen samples (Kennedy & Gadd 2000).

**Table 3.5 - Barium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	2,590	61.4	6,810	12
Brake pad dust	313	18	8,550	6
Tyres	25.8	8.8	166	12
Raw bitumen	<0.2	<0.2	0.2	6
Road bitumen	24.1	19.2	33	5

The data from Kennedy & Gadd (2000) indicates low and relatively consistent Ba concentrations in tyres. The variable presence of barite in brake pads however results in some difficulty in determining the median concentration of Ba in the particulates worn from brake pads. Monaci et al. (2000) considered Ba one of the key elements emitted by motor vehicles. The brake pad data does show that vehicles will contribute Ba to road surfaces.

### Barium in road dusts

Table 3.6 provides a summary of Ba in street dusts in New Zealand and in dust samples from a number of locations overseas. The data in the table was obtained using different analytical methods. As a result, the Waitakere City data is considerably lower in concentration compared to the Wellington data due to the different methods of analysis used.

**Table 3.6 - Barium in gutter and road surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	253 ± 20	126-507	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	584	153-714	B 0.1-0.25 mm		45	Rasmussen et al. 2001
Oslo	M-1994	526 ± 14	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	310	-	VC	INAA	1	Hopke et al. 1980
Manoa Basin Hawaii	R ~2000	200 ± 50	-	SC-<2 mm	ICPAES	13	Sutherland & Tolosa 2000
Nagpur Wellington	M-1992	621	617-655	~<2 mm	INAA	3	Chutke et al. 1995
Lambton Quay	C	605	1406	BP <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	977	3216	BP <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	768	1717	BP <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	566	628	BP <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	568	645	BP <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	789	1043	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	576	783	BP <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	547	578	BP <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	524	528	BP <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R-LI	515	505-614	BP <2 mm	T-XRF	10	Kennedy (unpublished)
Seaview	I	606	1211	BP <2 mm	T-XRF	12	Kennedy (unpublished)
Waitakere	R-2002	67.9	28.4-199	VC <2 mm	SA-ICPMS		Kennedy & Gadd 2002
Waitakere	R-2002	147.5	82.4-333	VC <0.063 mm	SA-ICPMS		Kennedy & Gadd 2002

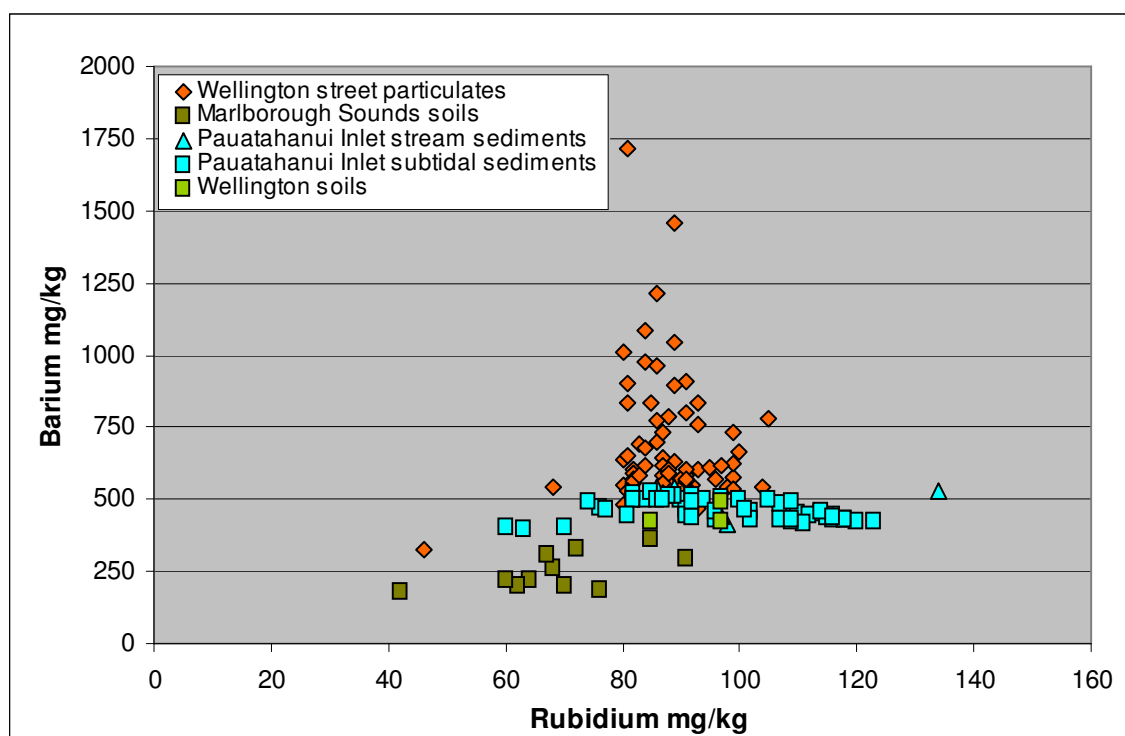
**Notes:** 1 – median presented where available; SC – scoop; BSC or P – Brush and scoop or pan; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic emission spectrometry.

There was a considerable variation in the Ba concentration of the dusts analysed (Table 3.6). The highest concentrations in Wellington were recorded in sites from commercial, residential and industrial areas. Minimum concentrations were similar in most sampling areas (400 to 600 mg/kg). In the case of the TS commercial samples, one single sample recorded 3,216 mg/kg Ba. This

sample was also elevated in a number of other metals, considered to be the result of building renovations being carried out on an adjacent building. Paint flakes that may have contained baryte may have been the cause of this increase.

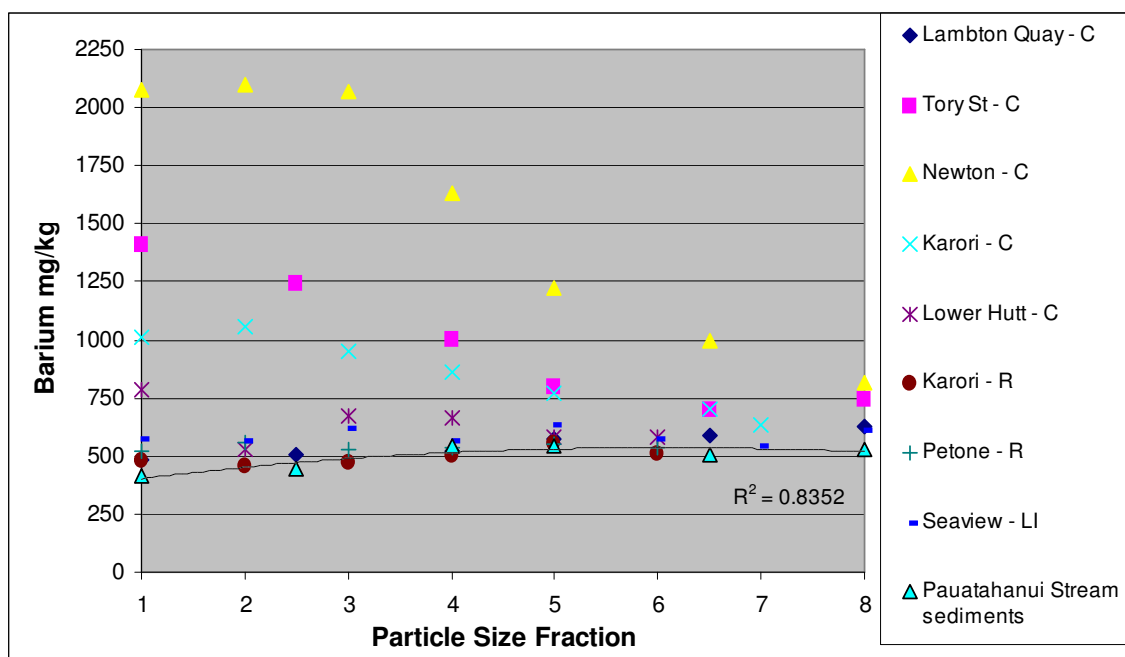
It appears from Fig. 3.7 that there are a number of samples of whole dust sampled in the Wellington region that contain high Ba concentrations. These samples were distributed throughout all sampling areas with the Newtown commercial and residential samples somewhat higher than the remainder of the samples. The whole sample Ba/Rb ratio appears to increase in samples with high Zn content. It is possible that the elevated Ba concentration is linked to the elevated Zn concentration.

Barium concentrations in <0.063 mm sized particles were about twice those measured in <2 mm particle size fractions of particle samples from road surfaces in Waitakere City (Table 3.6). Fig. 3.8 illustrates the variation in Ba concentration with changing particle size for a series of samples from the Wellington area. Three samples all from commercial areas showed elevated concentrations in coarser particle size fractions. Four sites displayed concentrations in all particle size fractions that were similar to those measured in size fractions from the stream sediments in Pauatahanui Inlet. It is likely that the high Ba concentrations in samples TS-1, K-11 and NC-5 arise from the presence of paint fragments containing barite, since most of the Ba is in the coarser particle sizes. Paints used in New Zealand on buildings may contain Ba concentrations up to several wt %.



**Fig. 3.7 - Barium concentration in road surface particle samples from Wellington compared to soils and sediments in the Region compared on the basis of their rubidium content (Kennedy unpublished data).**

Analysis of grain size separates in the work by Hopke et al. (1980) revealed similar uneven trends as those seen in the data presented in this report i.e., a low concentration in the 250-500  $\mu\text{m}$  fraction and a higher concentration in the <20  $\mu\text{m}$  fraction (Corrin & Natusch 1977). More detailed analysis, indicated considerable variability between magnetic and non-magnetic and the grain sizes between the different densities (D. Natusch pers comm).



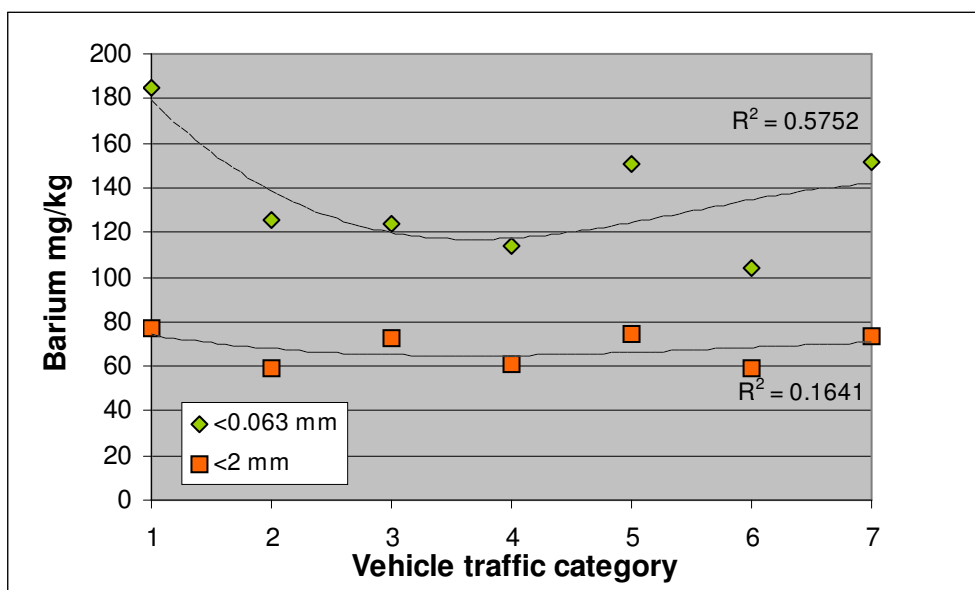
**Fig. 3.8 - Barium in size fractions of road surface particle samples and stream sediment samples from the Wellington area (Author unpublished data. Landuse abbreviations – C – commercial; R – residential, LI – light industrial).**

### Contribution from motor vehicles

Data on Ba concentrations in key vehicle emission sources shows that brake pads contain variable and often high concentrations of Ba as barite is used as a filler. The high concentrations in pads results in vehicles contributing Ba to the road environment. A proportion of all street particle samples collected in locations such as the Wellington area and in Waitakere City contain concentrations of Ba that are similar to local soils and stream sediments. However a proportion of street samples contain elevated concentrations and these are most significant in the coarser fractions of street particle samples.

The source of these elevated concentrations appears to be other urban sources such as paint fragments. Overall, motor vehicles are likely to be an important contributor of added Ba to the surface of roads principally through the wear of brake pads. The proportion of the anthropogenic Ba present contributed by vehicles is not known at this stage as other urban sources will also contribute Ba to road surfaces and to stormwater (e.g., paints on house roofs and building surfaces).

Fig. 3.9 shows the relationship between median Ba concentrations in the two grain size fractions in Waitakere City road surface particulate material and traffic volume. Although Ba is contributed by wear of brake pads, the contribution is such that it does not generate a clear concentration/traffic volume pattern. Although brake pads contain elevated concentrations of Ba compared to the concentration on road surfaces, the contribution from brake-pad wear is not evident in the Waitakere City data reported by Kennedy & Gadd (2002) as a relationship between vehicle numbers and on-road concentration.



**Fig. 3.9 - Barium concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

### 3.4 Cadmium (Cd)

#### Natural geochemistry

Cadmium has an estimated crustal abundance of about 0.2 mg/kg (Plant & Raiswell 1983). Average concentrations in common rock types are also similar. Cadmium ( $\text{Cd}^{2+}$ ) has an ionic radius of 0.97 Å which is similar in size to  $\text{Ca}^{2+}$ . Much of the Cd is typically associated with sphalerite (zinc sulphide) (Taylor 1965).

ARC (2001) presented data for acid extractable Cd in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.10 shows that the median concentrations for key soil groups range from around 0.05 mg/kg in soils derived from parent materials such as Waitemata Group soils (n=18), 0.18 mg/kg in soils derived from Quaternary materials (n=14) to 0.27 mg/kg for soils derived from volcanic parent materials (n=37). Elevated concentrations of Cd are known to be present in soil fertilisers used in New Zealand.

#### Sources

Most Cd is found in batteries (e.g., Ni/Cd batteries) with an estimated 75% of total Cd consumption being for this use (USDI 2003). Other uses for Cd include, pigments (12%), coatings and plating (8%), stabilizers for plastics (4%), and nonferrous alloys and other (1%). There are significant moves in the US and the EU to reduce Cd use especially in batteries.

Sander et al. (2000) and Lohse et al. (2001) describe the use of Cd in vehicle batteries. Cadmium is also present as an impurity in fuel additives such as zinc dithiophosphate (Lagerwerff & Specht 1980). The most significant source of Cd in vehicle parts is typically identified as tyres. Table 3.7 provides a summary of the analysis of tyres, brake pads and road bitumen by Kennedy & Gadd (2000). Negligible Cd was found in raw and on-road bitumen. Detectable concentrations of Cd were found in brake pads and brake lining dust with 9 of 18 samples having concentrations over 0.5 mg/kg and 4 of 18 having concentrations over 1 mg/kg. Tyres contain on average a lower concentration of Cd than brake pads. The Cd concentration is linearly related to the Zn concentration as the Cd is present as an impurity in the ZnO used in tyre manufacture (Kennedy & Gadd 2000). Kennedy & Gadd (2000) summarised other literature on tyre composition. Mean concentrations reported in other studies include 2.6 mg/kg (Legret & Pagotto 1999) and 0.28-4.96

mg/kg by Hewitt & Rashed (1990). As noted by Kennedy & Gadd (2000), the concentration of Cd in tyres may have decreased significantly over the last 20 years.

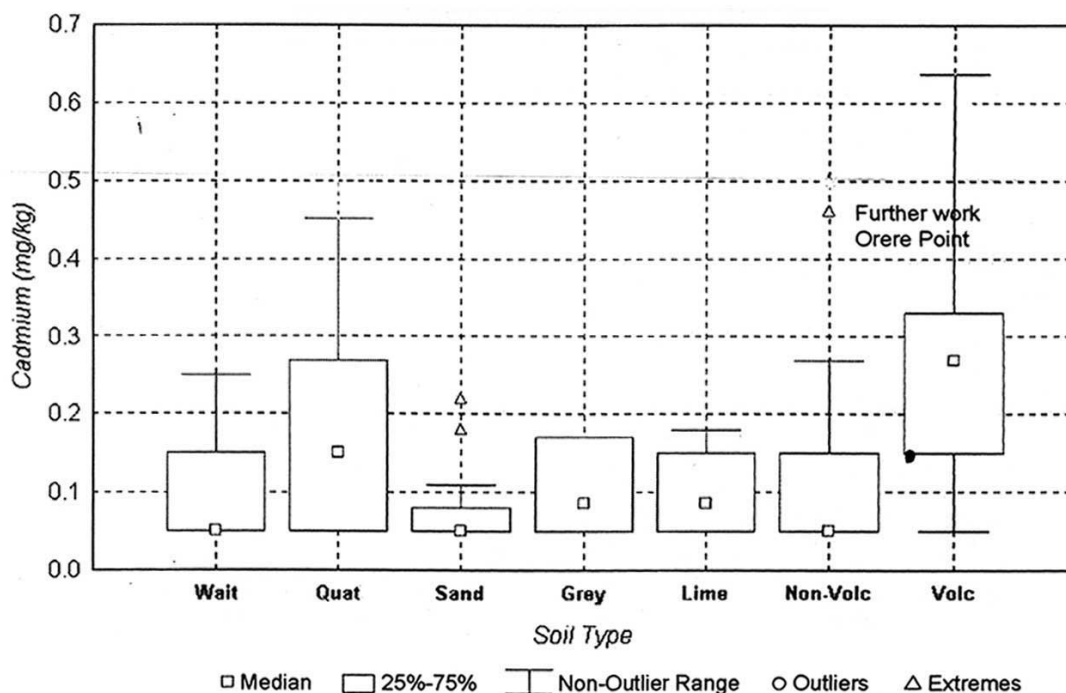


Fig. 3.10 - Cadmium concentration in Auckland soils (from ARC 2001).

Table 3.7 - Cadmium in potential sources in the New Zealand road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).

Source	Median	Minimum	Maximum	N
Brake pads	0.55	<0.1	12.3	12
Brake pad dust	0.29	<0.03	2.82	6
Tyres	0.19	<0.05	0.56	12
Raw bitumen	<0.05	-	-	6
Road bitumen	0.07	0.06	0.15	5

### Cadmium in road dusts

In New Zealand a comprehensive examination of Cd in Christchurch street dusts was carried out by Fergusson et al, (1980), Fergusson & Simmonds (1983) and also Fergusson & Ryan (1984). The concentration of Cd in New Zealand street dusts ( $1.46 \pm 0.64$  mg/kg) appears to be lower than the mean results of Harrison (1979) and Lau & Wong (1982). Harrison (1979) examined road dusts from a number of land-uses in Lancaster with mean concentrations over 2 mg/kg and Lau & Wong (1982) examined roads in a number of land-uses with mean concentrations ranging up to 11 mg/kg (Table 3.8).

Cd has been examined in the <36  $\mu$ m fraction of street surface particulates in Wellington using a dilute acid extraction (0.002 N HCl) (Author unpublished). Results were generally in the 1 to 2 mg/kg range but higher concentrations (4.5 mg/kg) were found (Table 3.8). Concentrations of Cd were much lower in the residential area (Taita), which also had lower traffic volumes. Comparison of the dilute acid extractable concentration data from Wellington with other New Zealand data indicates that much of the Cd present in road surface particles is easily extractable. Lau & Wong (1983) found a general increase in the Cd concentration in grain size separates from about 2 mg/kg for 0.25 - 0.5 mm and 16 mg/kg for <0.015 mm particles. Concentrations of Cd measured recently in Waitakere City by Kennedy & Gadd (2002) in <2 mm particle fraction of street surface material



appear low compared to the results reported in many studies. However, studies such as that undertaken in Ottawa by Rasmussen et al. (2001) report similar concentrations and the Waitakere results also include a number of samples that contained higher concentrations (Table 3.8). The comparison of the two Waitakere data sets (<2 mm and <0.063 mm) show that Cd is present in higher concentrations in the finer particles present on the road surface. Although much of the variability in Cd results between studies may be explainable on the basis of variations in particle size, it is likely that differences in sources and tyre Cd concentrations between locations will contribute to the variation seen in the data reported in the literature.

**Table 3.8 - Cadmium in gutter and road surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Birmingham	M <2003	<0.1	<0.1-13.1	B <1 mm	SA-AAS	100	Charlesworth et al. 2003
Coventry	M <2003	<0.1	<0.1-8.9	B <1 mm	SA-AAS	49	Charlesworth et al. 2003
Hong Kong	UP-~2001	3.77 ± 2.25	-	B-<2 mm	SA-ICPAES	45	Li et al. 2001
Ottawa	R-1993	0.3	0.08-1.12	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Oslo	M-1994	1.4 ± 0.2	-	B <0.1 mm	TA	14	Miguel et al. 1997
Urbana Illinois	~1980	1.6 ± 0.2	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	6.6	5.2-7.9	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	8	4.6-11.4	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	1	0.6-1.4	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	0.8	0.8-0.8	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1984	1.1	0.8-1.1	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	1.46 ± 0.64	0.5-4.33	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Karori	C	6.13 ± 2.4	4.4-8.9	B <0.036 mm	WA-AAS	3	Kennedy unpublished
Lower Hutt	C	2.32 ± 0.93	1.11-3.35	B <0.036 mm	WA-AAS	4	Kennedy unpublished
Karori	R	2.13 ± 1.60	0.18-6.23	B <0.036 mm	WA-AAS	11	Kennedy unpublished
Taita	R	0.79 ± 0.33	0.44-1.28	B <0.036 mm	WA-AAS	8	Kennedy unpublished
Auckland City	R-C, 2001-3	-	0.1-21	V <0.45-2 mm	SA ICPMS	~48	Ng et al. 2003 (refer below)
Waitakere	R-2002	0.2	0.1-10.8	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	0.55	0.7-5.4	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 - median presented where available; UP, M, C, R - streets adjacent to urban park, mixed, residential and commercial landuse; B - Brush and pan or scoop; VC - vacuum cleaner; SA - Strong acid; WA - Weak acid; INAA - Instrumental neutron activation analysis. ICPMS - Inductively coupled plasma emission spectrometry. AAS - Atomic absorption spectrometry. The concentration range for Auckland City is estimated from the graphical information in Ng et al. (2003) and is approximate only.

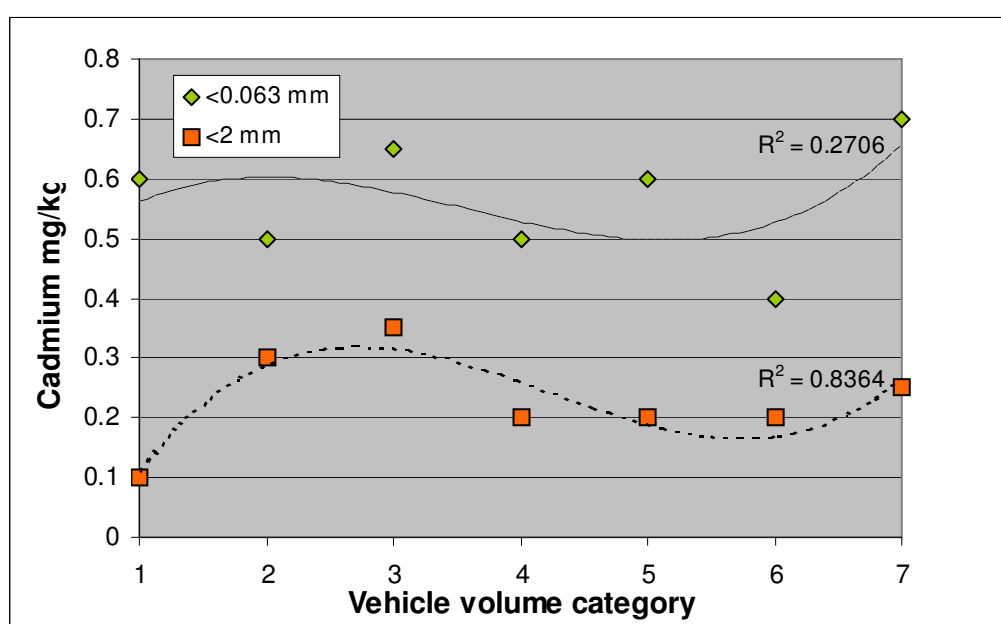
Hopke et al (1980) examined the distribution of Cd in street dusts in some detail, identifying Cd in high density magnetic particles and finer low and high density non-magnetic particles which they attributed to car exhausts and tyre wear. Corrin & Natusch (1977) found the greatest concentration of Cd in the 75-100 µm fraction (6.09 mg/kg) of a whole street dust from Urbana, Illinois. In the denser fractions of each grain size separate (>2.2 g/cm<sup>3</sup>) the Cd was higher in concentration in the magnetic fraction (D Natusch pers comm). Linton et al. (1980b) identified very high Cd concentrations in the high-density particles of street dust, especially the non-magnetic fractions (e.g., building line samples; 0-90 µm, 110 mg/kg; 90-600 µm, 76 mg/kg; curb-side <45 µm, 49 mg/kg) suggesting a dual source from both paints and vehicles in that case. The Cd that comes from the wearing of vehicle tyres is likely to be a function of the method of zinc oxide production. The hint of lower Cd levels in street dusts compared to overseas street dusts may be a result of the production of zinc oxide by an electrolytic process in New Zealand.

ARC (1992) reported Cd data for particle size fractions from two samples of gutter dust from the residential suburb of Pakuranga and one from the industrial suburb of Southdown. There were no significant differences in concentration between the samples with concentrations ranging from 0.15-0.26 mg/kg (1-2 mm) through to 0.68-1.33 mg/kg (<0.047 mm). Ng et al. (2003) recently published data for Cd in a range of particle size fractions from Auckland City. Of the six sites examined, five had significantly elevated Cd concentrations (refer Fig. 3.4). The elevated concentrations are

similar to concentrations observed in a number of samples from Waitakere City (Kennedy & Gadd 2002). The distribution of Cd in the Auckland City samples displays the highest concentrations in fine to medium sand fractions of the samples (refer Fig. 3.4). Given the lower concentrations recorded in one of the Auckland City samples and in the Waitakere City samples, it is unlikely that motor-vehicles are the Cd source in those instances.

### Contribution from motor vehicles

Cadmium concentrations in tyres and brake pads are higher than background soil concentrations. As such, vehicles will contribute Cd to road surfaces. It is evident that there are other sources of Cd in urban environments that will contribute Cd. The overall proportional contribution of vehicles to the total Cd concentration present in urban road surface particles is not known with certainty. Fig. 3.11 shows the relationship between median Cd concentrations in the two grain size fractions that were examined in particulate material on road surfaces in Waitakere City and traffic volume. As described above, Cd is contributed by wear of tyres and brake pads, no clear concentration/traffic volume pattern is apparent.



**Fig. 3.11 - Cadmium concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

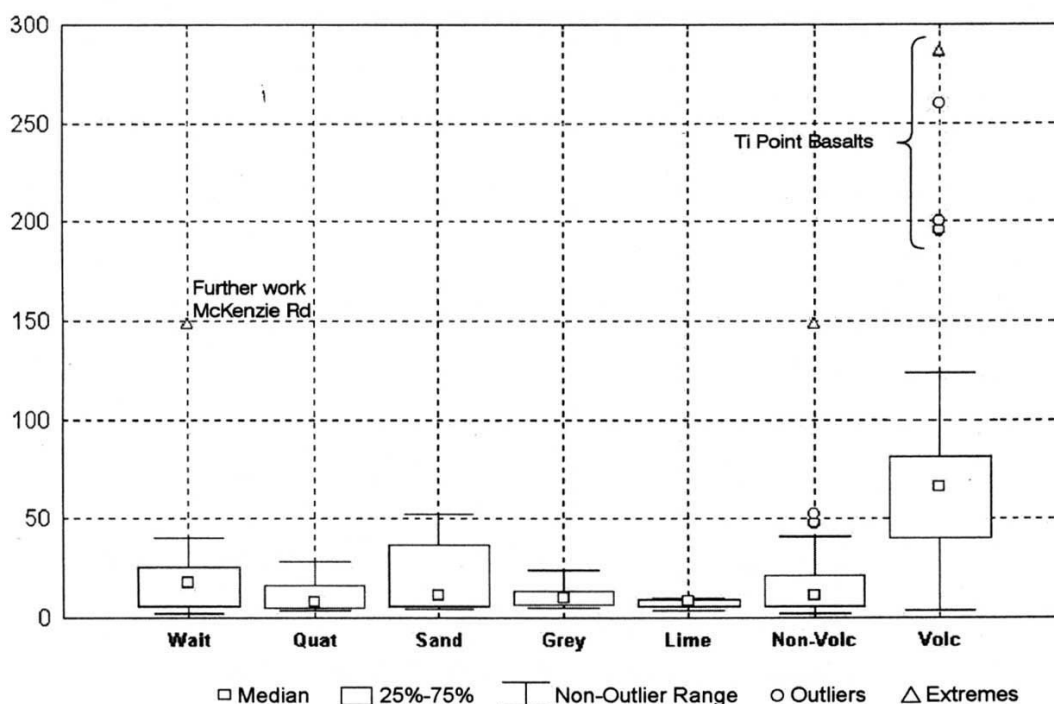
Davis et al. (2001) estimated the loadings of Cd in runoff from different sources within urban areas. They attributed the following source as contributing Cd with catchments comprised of residential brick buildings: tyre wear 4%, brake wear 10%, roofs 5%, sidings 21%, dry and wet deposition 19 and 41%. In residential areas where building sidings are composed of vinyl the sidings contribution was assessed to fall to 7% and other sources increased accordingly. In commercial catchments, the roof runoff proportion was assessed at 30%, sidings 23%, brake and tyre wear 11 and 4% respectively. Dry and wet deposition, were considered to account for 10 and 22% of the Cd.

If the non-exhaust contributions identified by Davis et al. (2001) are considered, then tyres and brake pad wear might contribute about 15% of the Cd present in urban runoff. Further work would be required to assess the proportion of Cd contributed by vehicles to the road/stormwater environment in New Zealand.

### 3.5 Chromium (Cr)

#### Natural geochemistry

Chromium ( $\text{Cr}^{3+}$ ) has a nearly identical ionic radius to  $\text{Fe}^{3+}$ . Average crustal abundance is estimated to be 100 mg/kg with a considerable range in different rock types. For example low concentrations are found in granite (4 mg/kg) and high concentrations in volcanic rocks such as basalts (200 mg/kg) (Taylor 1965). ARC (2001) presented data for acid extractable Cr in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.12 shows that the median values for key soil groups ranged from 8 mg/kg in soils derived from Quarternary materials (n=11) to 16.9 mg/kg (n=17) for soils derived from Waitemata Group materials to 61.3 mg/kg for soils derived from volcanic parent materials (n=37).



**Fig. 3.12 - Chromium concentration in Auckland soils (from ARC 2001).**

For comparison, Cr in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 38 mg/kg (n=38) and Cr in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 33 to 55 mg/kg (median of location means, 48 mg/kg, n=83) (Author unpublished data).

#### Sources

The principal consumers of Cr in decreasing order of consumption are the metallurgical, refractory and chemical industries (NAS 1974, Langard & Norseth 1977), with over 60% of the Cr used in the metallurgical industries being used in the manufacture of stainless steel (NAS 1974). Chromium is also used in the ceramics and photographic industries and in the production of paint pigments (Belliles 1979). Chromium as 2.5% dichromate has also been used as an accelerant in match heads and some brands of matches may also contain lead and zinc (Cropp et al. 1978). Because of its wide range of uses, Cr in street dusts could be derived directly from litter, paints, Cr plating wear and bodywork corrosion on motor vehicles, wear of engine components such as rocker arms, crankshaft and piston rings as well as the abrasion of brake linings (Shaheen 1975).

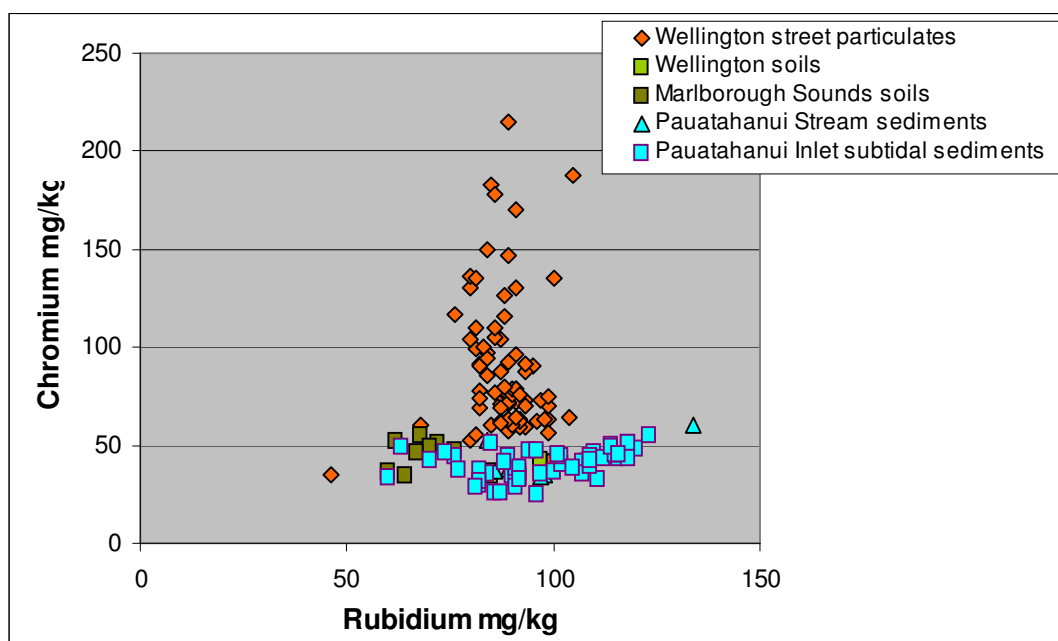
Kennedy & Gadd (2000) reported on Cr in a number of key motor vehicle emission sources. Their data summarised in Table 3.9 shows that tyres and raw bitumen contain negligible amounts of Cr. Brake pads and dust contain consistently elevated concentrations of Cr. On-road bitumen was found to contain moderate concentrations of Cr (the source is likely to be small amounts of incorporated scoria/road aggregate).

**Table 3.9 - Chromium in potential sources in the New Zealand road environment  
(All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	200	15.3	442	12
Brake pad dust	329	135	1230	6
Tyres	<1	<1	2	12
Raw bitumen	<1	-	-	6
Road bitumen	77.7	46.3	102.2	5

### Chromium in road surface particles

The range of Cr concentrations found in street dusts (Table 3.10) was greater than that found in sediments and soils of the Wellington region (Fig. 3.13). Fig. 3.14 illustrates that when compared to their particle sizes, most of the samples examined contained more Cr than was expected and the Cr concentration increases with decreasing grain size in 'clean' samples (30 to 60 mg/kg). Several road surface samples exhibited Cr concentrations in coarser fractions, with decreases in the finer grain size fractions. The LQ catch-basin sample, which was well-sorted had the most obvious decrease in concentration. This probably resulted from an accumulation of heavier metallic particles in the coarser particle sizes as a result of sorting by water in the catch basin.



**Fig. 3.13 - Chromium concentration in road surface particle samples from Wellington compared to soils and sediments in the region on the basis of their rubidium content (Kennedy unpublished data).**

Particulate material from roads in Waitakere City had a relatively narrow range of Cr (about 100 mg/kg, Table 3.10) with fine particles containing on average about 50% more Cr. Ng et al. (2003) who measured Cr in grain size separates from a number of locations in Auckland City found that fine particles (<45 µm) had about 2-3 times more Cr than coarse particles (>2000 µm) (Fig. 3.4).

This difference is similar to that seen in samples from Wellington in Fig. 3.14. The data of Ng et al. (2003) suggests that one of the sites sampled in that study may have contained Cr from another source (concentrations in three fractions were between 200 and 300 mg/kg).

**Table 3.10 - Chromium in street gutter and street surface particulates (all results mg/kg dry weight).**

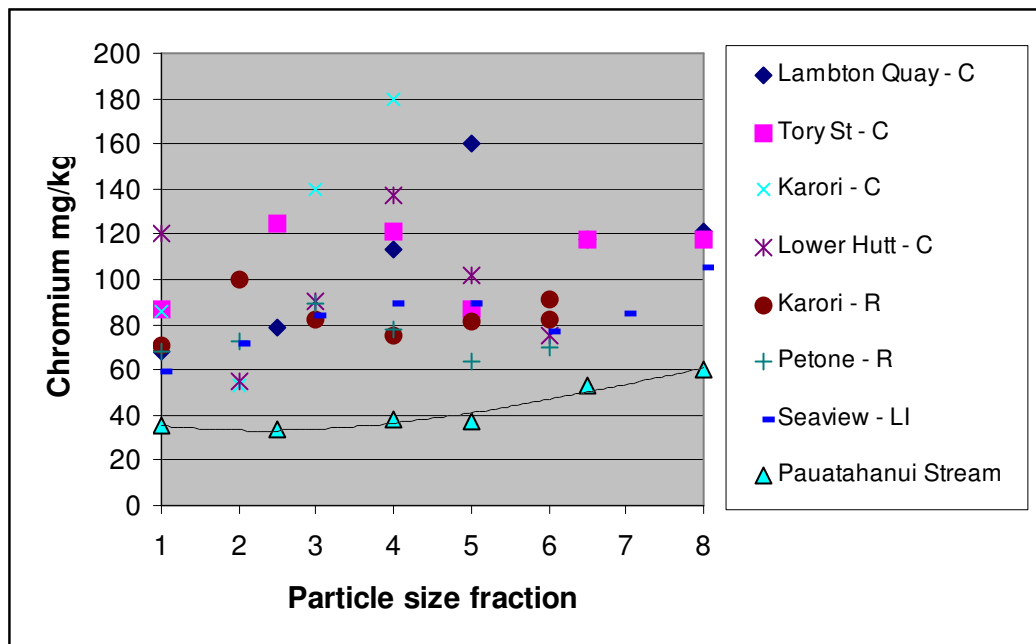
Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	124 ± 7	65.7-177	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	41.8	14.7-71.7	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	61 ± 7	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	210 ± 20	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	116	112, 120	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	125	62,188	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	69	67,71	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	24.5	22,27	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Manoa Basin Hawaii	R ~2000	273 ± 60	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Nagpur	M-1992	107	13.2-131	~<2 mm	INAA	3	Chutke et al. 1995
Christchurch	C ~1984	58	38-76	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	33.8 ± 10.6	-	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	91	53-215	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	97	77-136	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	99	60-703	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	69	59-78	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	74	57-104	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	94	70-170	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	73	42-639	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	65	52-69	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	49	35-110	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	62.5	62-63	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	62	53-76	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	121	35-178	B <2 mm	T-XRF	12	Kennedy (unpublished)
Auckland City	R-C, 2001-3	-	~20-280	V <0.45-2 mm	SA ICPMS	~48	Ng et al. 2003 (refer below)
Waitakere	R-2002	63	28-140	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	86.5	39-178	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R – streets adjacent to urban park, mixed, residential and commercial landuse; SC – scoop; BSC – Brush and scoop; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry. The concentration range for Auckland City is estimated from the graphical information in Ng et al. (2003) and is approximate only.

A number of overseas studies have included Cr in their analysis of street dusts. Wilber & Hunter (1979) found considerably more Cr in street sweepings than in river sediments in their study area. A sequential chemical extraction of the less than 63 µm street dust in that study revealed that 69.9% was present as moderately reducible iron oxide; 25% as organic, 3.1% as easily reducible manganese oxide, 1.4% as exchangeable and 0.15% was soluble.

Harrison (1979) reported that dust samples from car parks had generally higher concentrations of Cr compared to household, urban or rural dust. Chromium in rural roadside dusts and in urban dusts away from yellow road marking paint (lead chromate) had similar levels to dusts collected adjacent to yellow road markings (Harrison 1979). This suggested to Harrison that yellow paints on roadways were not a significant source of Cr. In contrast, Post & Cambell (1980) noted that road marking paints should not be ignored as a source of Cr as the contribution to the gutter could be as high as 30 g/week/curb km if all of the paint was eroded in a year. In a study conducted by Bourcier

& Sharma (1980), the Cr content of dusts was related to the total solids in street runoff events and the deposition rates for Cr on the road surface were greater than at a control site (Bourcier 1979). Pitt & Amy (1973) indicated that there were greater curb loadings of Cr in industrial areas compared to residential and commercial streets.



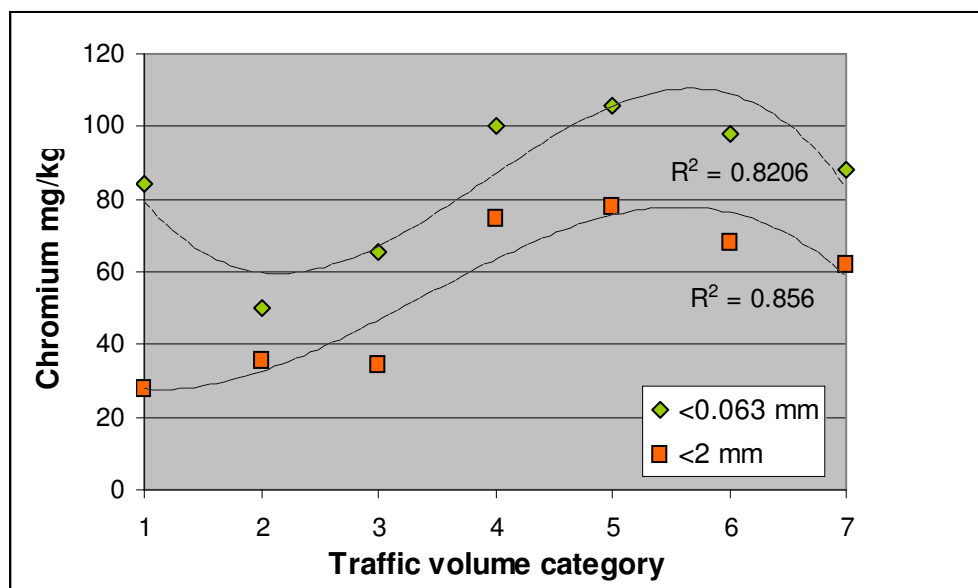
**Fig. 3.14 - Chromium in size fractions of road surface particle samples and stream sediment samples from the Wellington area (unpublished data).**

Hopke et al (1980) in characterising street dusts in Urbana Illinois, found that Cr was generally associated with low-density non magnetic particles and fine magnetic particles. This indicated that Cr was associated with a tyre wear component and it is likely that it is derived from both tyre and brake lining wear. This finding was not supported by the analysis undertaken by Kennedy & Gadd (2000) (Table 3.9). Chromium was also important in the Fe component and since Fe is so abundant in vehicle corrosion it is likely that one of the primary Cr sources is vehicle corrosion and wear.

### Contributions from motor vehicles

Chromium concentrations in brake pads and brake pad dust are higher than background soil concentrations. As such, vehicles will contribute Cr to road surfaces. Fig. 3.15 shows the relationship between average Cr concentration for roads in Waitakere City. The data suggests that there may be a relationship between traffic and Cr concentration.

It is evident that there are other sources of Cr in urban environments that will contribute Cr. The overall proportional contribution of vehicles to the total Cr concentration present in urban road surface particles is not known with any certainty however, as a rough estimate, the Cr data in Fig. 3.15 suggests that possibly 40-50% of the Cr on roads with high traffic volumes may be associated with vehicle emissions.



**Fig. 3.15 - Chromium concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

### 3.6 Cobalt (Co)

#### Natural geochemistry

Cobalt ( $\text{Co}^{2+}$ ) has an ionic radius of 0.72 Å and is intermediate in size between Fe and Mg. Plant & Raiswell (1983) report an average crustal abundance of 25 mg/kg. Cobalt concentrations vary significantly between different rock types with granites, limestone and sandstones containing low concentrations. Greywacke typically contains about 20 mg/kg and basalts tend to contain higher concentrations (e.g., 50 mg/kg Taylor 1965, Plant & Raiswell 1983).

ARC (2001) presented data for acid extractable Co in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.16 shows that the median values range for key soil groups range typically from 4.3 mg/kg in soils derived from Greywacke (n=6) to 5.6 mg/kg (n=11) for soils derived from Quaternary materials to 45.7 mg/kg for soils derived from volcanic parent materials (n=47). The elevated Co data for Auckland soils reflects the published data for Co in geological materials such as basalts. No total Co data was available for Wellington soils as the method of preparation used for the soil samples utilised a tungsten carbide grinder (containing cobalt). The significant difference in Co content of basalt volcanic derived soils has the potential to result in localised Co content of road surface materials in some catchments.

#### Sources

Metal plating and alloys are amongst the primary uses for Co. USDI (2003) reports that 51% of U.S. cobalt use was in super-alloys (e.g., aircraft gas turbine engines); 8% was in carbides for cutting and wear-resistant applications; 19% was in various other metallic uses; and the remaining 22% was in a variety of chemical uses. Sander et al. (2000) and Lohse et al. (2001) did not identify any significant sources of Co in motor vehicles. Table 3.11 summarises data from Kennedy & Gadd (2000) on the concentration of Co in key vehicle emission sources. Median concentrations of Co in brake pads and pad dust and road bitumen were similar. Concentrations of Co in tyre rubber were low.

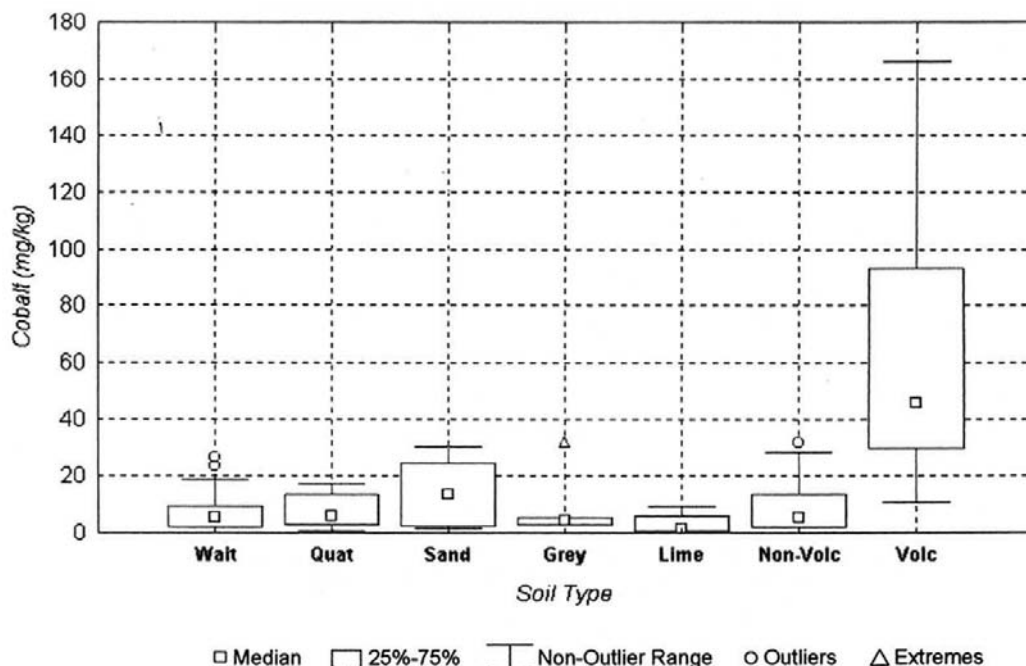


Fig. 3.16 - Cobalt concentration in Auckland soils (from ARC 2001).

Table 3.11 - Cobalt in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).

Source	Median	Minimum	Maximum	N
Brake pads	24.75	1.8	45.8	12
Brake pad dust	27.7	2.57	38.4	6
Tyres	1.05	0.3	4.1	12
Raw bitumen	<0.2	<0.2	0.2	6
Road bitumen	28.7	17.4	31.6	5

### Cobalt in road dusts

Table 3.12 provides a summary of New Zealand and international data for Co in particulate material on street surfaces. The majority of the Co concentrations presented by Fergusson & Ryan (1984) were in the range 6.7 and 12.9 µg/g. However a single sample of dust from Christchurch contained 36 µg/g compared to 9.3 and 10.3 mg/kg for two other samples which are relatively typical of Co concentrations, given the Christchurch catchment geology.

Cobalt (Co) data was reported for street dusts by Harrison (1979) and Hopke et al (1980). Both studies reported concentrations of less than 10 mg/kg although Harrison identified slightly elevated levels in car parks compared to roadway dust. Further work by Linton et al. (1980b) on high density (<math> < 3.3 \text{ g/cm}^3 </math>) particles, found high concentrations of Co in the magnetic fraction of a "building line" sample (110 - 190 mg/kg) and both non-magnetic and magnetic curb samples of <math> < 45 \text{ }\mu\text{m}</math> size (88 and 90 mg/kg respectively). Factor analysis identified vehicle sources and paint sources as the major possible sources.

### Contributions from motor vehicles

Based upon the concentration of Co in brake pads and brake pad dust, motor vehicles will contribute Co to the road environment. Median concentrations in road particulate materials in Waitakere City were higher than observed in most soils examined in the Auckland region. Fig. 3.17

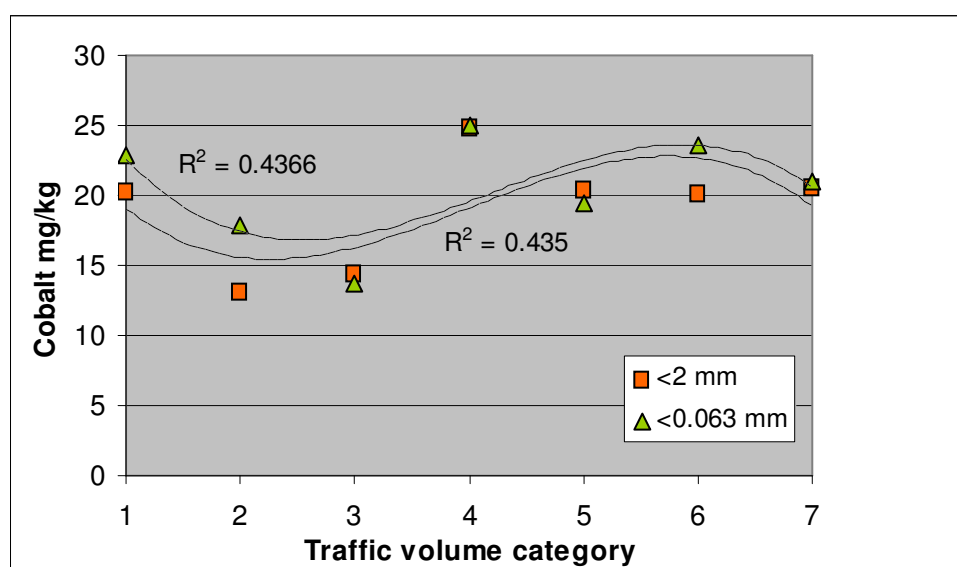


indicates that there is little apparent relationship between traffic flow and Co concentration in road surface particulates in Waitakere City. Samples of <2 mm and <0.063 mm particles had similar Co concentrations.

**Table 3.12 - Cobalt in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	9.52 ± 0.58	4.62-14.1	B <0.1 mm	T,EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	8.65	2.31-12.59	B 0.1-0.25 mm	SA, ICPMS	45	Rasmussen et al. 2001
Oslo	M-1994	19	-	B <0.1 mm	SA, ICPMS	14	Miguel et al. 1997
Madrid	M-1994	3	-	B <0.1 mm	SA, ICPMS		Miguel et al. 1997
Nagpur	M-1992	15.4	14.4-17	~<2 mm	INAA	3	Chutke et al. 1995
Urbana Illinois	~1980	6.8 ± 0.4	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	7.25	7.2-7.3	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
New York	C ~1984	10.8	8.7-12.9	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	7.9	6.7-9.1	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	7.2	6.8-7.6	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1984	10.3	9.3-36	< 0.963 mm	T,INAA	3	Fergusson & Ryan 1984
Waitakere	R-2002	20.95	11.4-32.2	VC <2 mm	SA,ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	20.25	12.9-34.3	VC <0.063 mm	SA,ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R – streets adjacent to urban park, mixed, residential and commercial landuse; SC – scoop; BSC – Brush and scoop; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.



**Fig. 3.17 - Cobalt concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

Cobalt will be contributed by other sources to the road environment. The relative contribution of motor vehicles to Co in the road environment relative to other sources is unclear at this point in time.

### 3.7 Copper (Cu)

#### Natural geochemistry

Copper has an estimated crustal abundance of about 55 mg/kg (Taylor 1965). Copper ( $\text{Cu}^{2+}$ ) has an ionic radius of 0.96 Å, which is similar to the radius of  $\text{Fe}^{2+}$  and  $\text{Na}^+$ . It tends to substitute in minerals such as plagioclase and apatite. Most common rocks have moderate concentrations of Cu ranging from lower concentrations of 10 mg/kg in granite to 100 mg/kg in basalt. ARC (2001) presented data for acid extractable Cu in Auckland soils derived from different geologic parent materials.

The data which is summarised in Fig. 3.18 shows that the median values for key soil groups typically range from 8.4 mg/kg in soils derived from Waitemata Group materials (n=22) to 15.2 mg/kg (n=11) for soils derived from Quaternary materials. Copper concentrations in soils derived from volcanic materials were higher at 48.5 mg/kg (n=42).

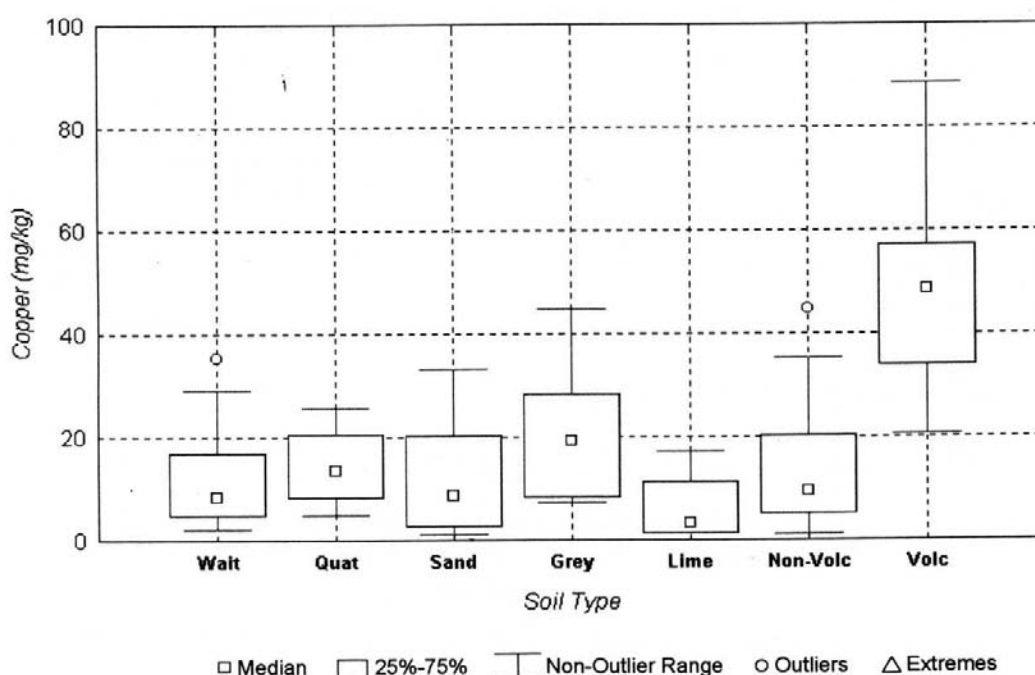


Fig. 3.18 - Copper concentration in Auckland soils (from ARC 2001).

For comparison, Cu in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 17 mg/kg (n=38) and Cu in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 14 to 44 mg/kg (median of location means 23 mg/kg, n=91) (Author unpublished data).

#### Sources

USDI (2003) reported that Cu and Cu alloy products consumed in building construction accounted for 44% of total Cu use in the US; electric and electronic products accounted for 25%; transportation equipment, 11%; industrial machinery and equipment, 10%; and consumer and general products, 10%. Metal plating and alloys are amongst the primary uses for Cu. Within urban areas one of its main uses is in electrical wiring and cables. In motor vehicles Cu can be found in bearings, bushing and brake linings, which may contain several weight percent Cu (Harrison 1979). Kennedy & Gadd (2000) found that Cu concentrations in tyres and in raw bitumen were very low. Brake pads contain extremely variable amounts of copper depending upon the

inclusion of Cu metal in the brake pad formulation. Maximum concentrations can be very high (refer Table 3.13).

**Table 3.13 - Copper in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	35.5	11	112000	12
Brake pad dust	219.5	73	1980	6
Tyres	1	<1	3	12
Raw bitumen	<1	-	-	6
Road bitumen	46.3	40.4	60.1	5

### Copper in road dusts

Table 3.13 provides a summary of New Zealand and other data for Cu in road surface particulate matter. Elevated Cu concentrations have been reported under high-voltage overhead electricity lines (Hemkes & Harton 1972) as a result of corrosion of the cables. In Wellington Cu had been observed to corrode from the overhead trolley wires of electric trains and a large number of the urban bus fleet are electric, consequently, the corrosion of trolley bus wires may have accounted for some of the elevation in the gutter dusts of Wellington City. Several areas including Taita residential and the Lower Hutt commercial area are not serviced by electric buses, but still had elevated Cu concentrations. Therefore, it is likely that most of the Cu in gutter dusts is vehicle derived, except in the case of the industrial areas examined where some elevated samples may have resulted from contamination caused by localised sources or chance contamination by metal fragments.

The analysis of whole dust samples revealed that the mean Cu concentration for all commercial samples was twice that of the residential samples (Table 3.14). The lowest concentration recorded in the residential samples was slightly higher than this range. Fig. 3.19 illustrates that for their grain size (using Rb as a reference), virtually all of the samples had Cu concentrations that were higher than would be expected. Copper concentrations appear to increase with decreasing grain size in most samples (Fig. 3.20) with the <35 µm fraction containing up to 25 times that found in 'clean' samples of soil.

In Auckland, ARC (1992) reported Cu data for particle size separates from three samples in Auckland (2 residential and one industrial). There were no significant differences between the samples with the concentrations ranging from 53-91 mg/kg (1-2 mm) though to 139-432 (<0.047 mm). Ng et al. (2003) reported data for Cu in a range of grain size separates from roads in Auckland City. Fig. 3.21 shows that Cu concentrations in the grain size separates and sites were highly variable with higher concentrations in the fractions <0.5 mm at locations in particular. A similar trend was seen in two of the three samples reported by ARC (1992).

Elevated Cu in urban street dusts have also been reported by Wilber & Hunter(1979), Harrison (1979), Lau & Wong (1982), Ho (1982) and Fergusson & Simmonds (1983). The results reported in this study for commercial areas are similar to the upper values reported by Ho (1982) for samples of street dust from Hong Kong Island. Wilber and Hunter (1979) reported that 52.3% of the Cu in the dust sample that they examined was removable as moderately reducible iron oxide; 37% in the organic fraction; 9.7% was exchangeable; 7.2% was removable as easily reducible manganese oxide and 0.05% was soluble in water.

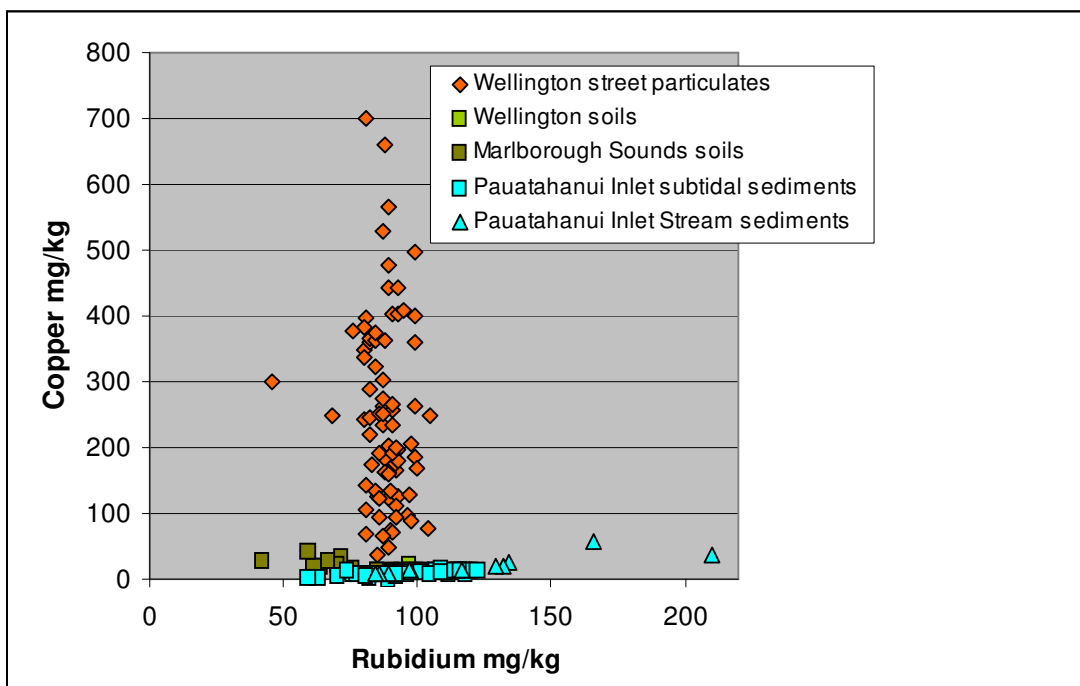
**Table 3.14 - Copper in gutter and road surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Birmingham	M <2003	165.6	16.4-6688.4	B <1 mm	SA-AAS	100	Charlesworth et al. 2003
Coventry	M <2003	151.6	49.3-815	B <1 mm	SA-AAS	49	Charlesworth et al. 2003
Hong Kong	M-2001	110 ± 4	40.9-190	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Taejon, Korea	M-1996	57	17-226	B <0.18 mm	SA-AAS	31	Kim et al. 1998
	R-1996	24	10-347	B <0.18 mm	SA-AAS	41	Kim et al. 1998
Ottawa	R-1993	29.54	4.8-249.8	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	188 ± 24	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	123 ± 13	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
London	C ~1984	197.5	191-204	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	355.5	171-540	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	86.5	54-119	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	65.5	59-72	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Nagpur	M-1992	21	14.0-21.0	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R ~2000	167 ± 46	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1984	106	48-258	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch Wellington	C ~1981	194 ± 50	110-326	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Lambton Quay	C	349	124-403	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	363	258-567	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	314	182-701	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	204	167-363	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	345	234-477	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	214	143-361	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	131	37-399	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	100	51-150	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	93	32-153	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	215	67-264	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	129	67-264	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	165	50-1572	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	442	266-498	B <2 mm	T-XRF	3	Kennedy (unpublished)
Auckland City	R-C, 2001-3	-	~60-1120	V <0.45-2 mm	SA ICPMS	~48	Ng et al. 2003 (refer below)
Waitakere	R-2002	149	48-1600	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	297	142-539	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

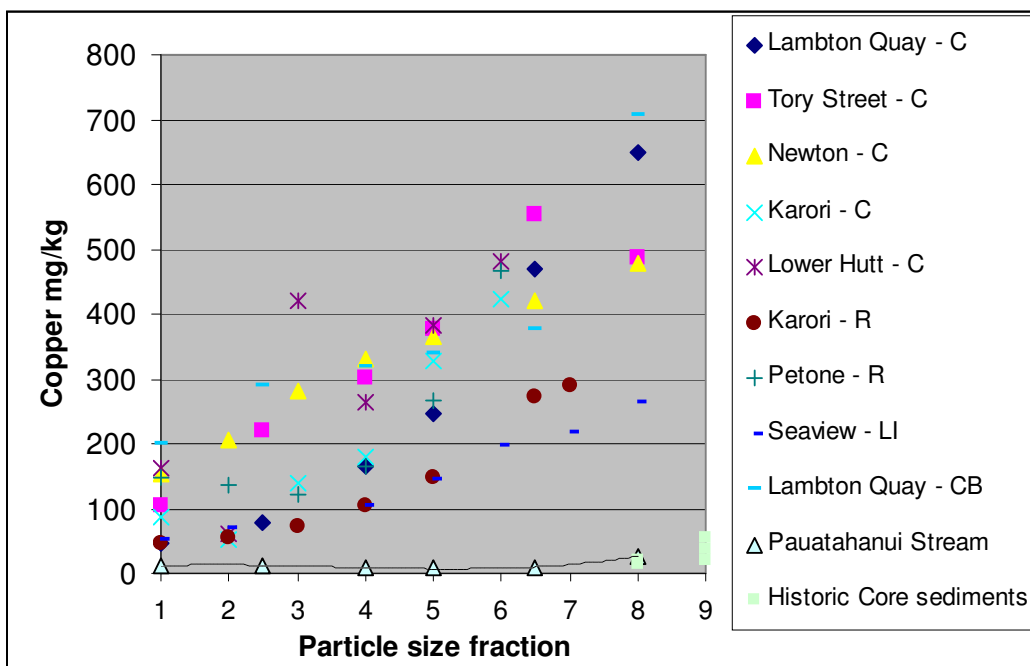
**Notes:** 1 – median presented where available; UP, M, C, R - streets adjacent to urban park, mixed, residential and commercial landuse; SC - scoop; BSC - Brush and scoop; VC - vacuum cleaner; TA - total acid; SA - Strong acid; WA - Weak acid; INAA - Instrumental neutron activation analysis. ICPMS/AES - Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS - Atomic absorption spectrometry. The concentration range for Auckland City is estimated from the graphical information in Ng et al. (2003) and is approximate only.

### Contribution from motor vehicles

The key source of Cu in non-tail pipe emission sources on motor vehicles is the wear of brake pads. This occurs because of the use of Cu metal in brake pads (Kennedy et al. 2000). It is likely that most of the Cu contributed by vehicles comes from this source. Copper is a common metal in the urban environment. The contribution of copper to road surface particulates and to stormwater from these sources has not been well assessed. Until better source data becomes available, the key source of Cu is assumed to be vehicle brake lining wear. Fig. 3.22 illustrates the relationship between traffic volume and copper concentration in particulates on Waitakere City roads. For both the <2 mm and <0.063 mm fractions the concentration increased with increasing traffic.



**Fig. 3.19 - Copper concentration in road surface particle samples from Wellington compared to soils and sediments in the Region on the basis of their rubidium content (Kennedy unpublished data).**



**Fig. 3.20 - Copper in size fractions of road surface particle samples and stream sediment samples from the Wellington area (unpublished data) (CB – catchbasin).**

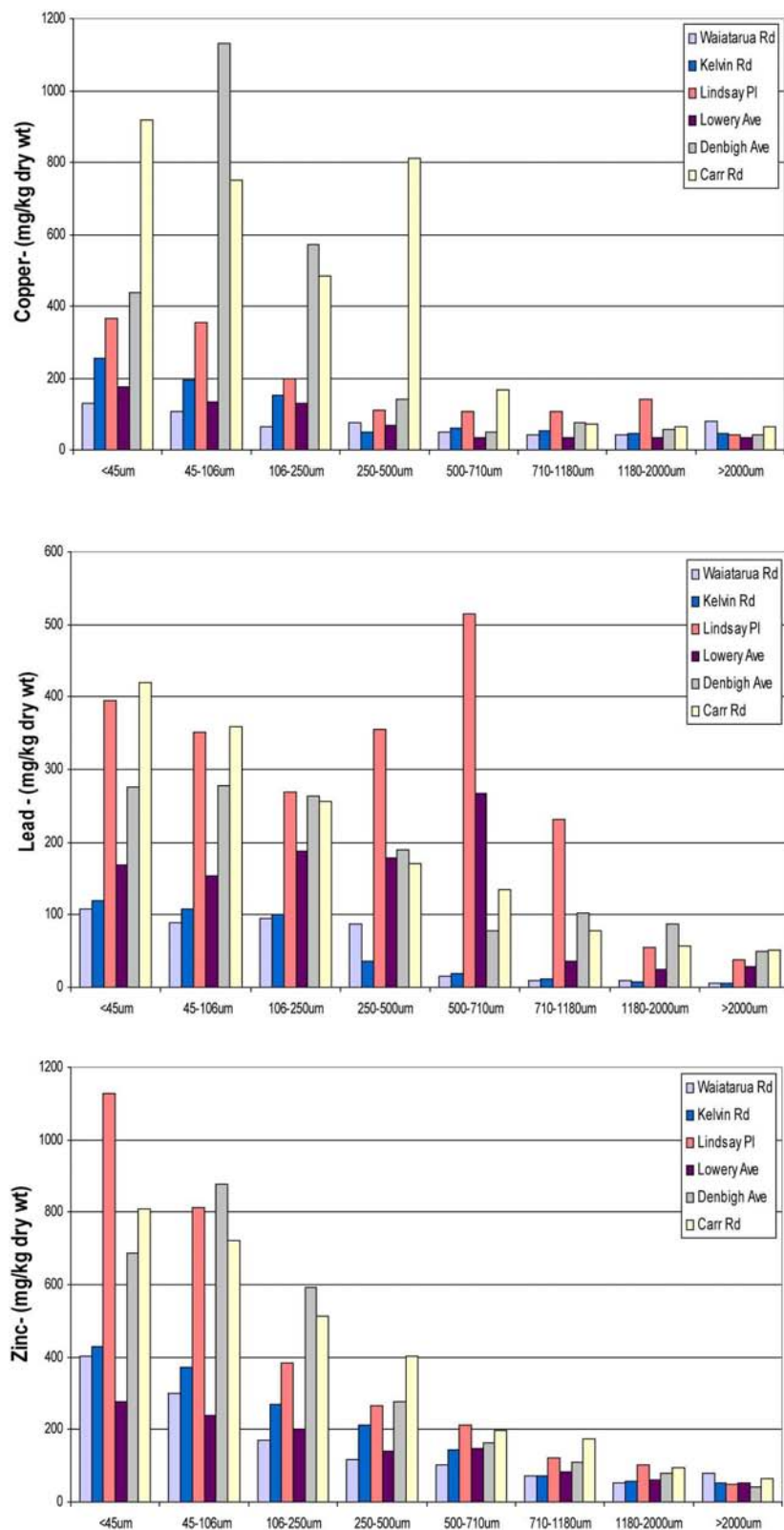
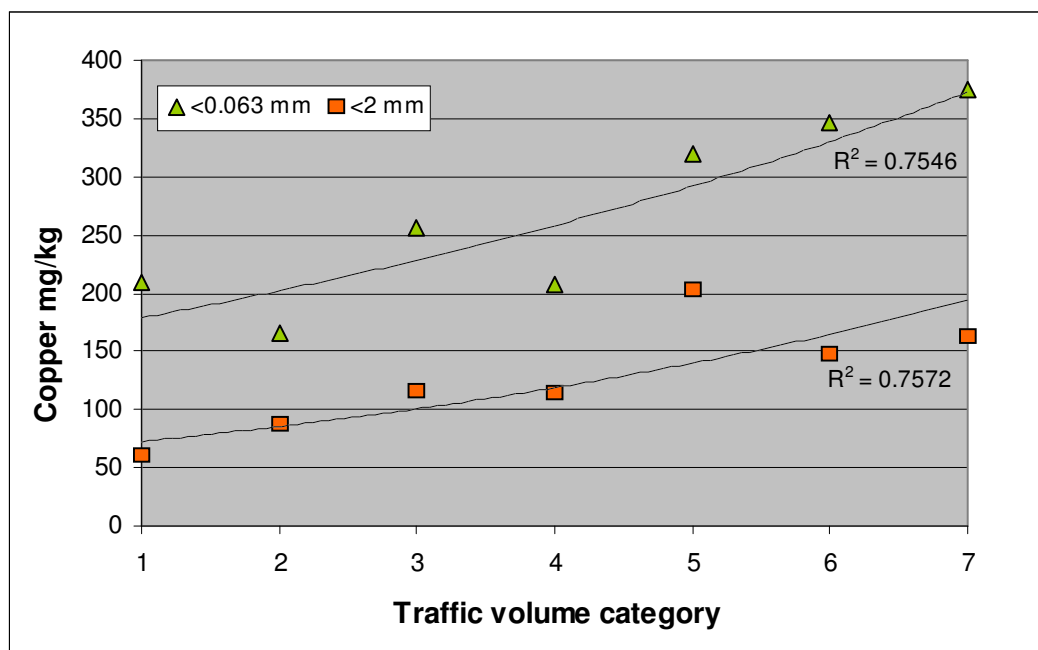


Fig. 3.21 - Copper, lead and zinc concentration in different size fractions of road surface samples from Auckland City (taken from Ng et al. 2003).



**Fig. 3.22 - Copper concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

In a recent assessment of Cu loading in Auckland City, Timperley et al. (2003) estimated that roads contributed 17% of the Cu (the 50%ile value) in stormwater runoff. Davis et al. (2001) estimated source contributions in different urban environments. For residential stormwater from brick buildings, it was estimated that brake wear contributed 47%, tire wear 1%, roofs 9%, sidings 22% and wet and dry deposition 21%. For vinyl buildings the proportions changed slightly with brake wear contributing 55%, tire wear 1%, roofs 10%, sidings 9% and wet and dry deposition 25%. Overall that study indicated that vehicles might contribute half the Cu in the road stormwater. Given that some vehicle Cu emissions will contribute to the Cu present in other sources (e.g., deposition etc.), the proportion of vehicle sourced Cu identified by Davis et al. (2001) may be higher. As a rough estimate, the Cu data in Fig. 3.22 suggests that at least 40-50% of the Cu on roads with high traffic volumes may be associated with vehicle emissions.

### 3.8 Iron (Fe)

#### Natural geochemistry

Iron is one of the common elements in all rocks and soils (the fourth most abundant element) and a key element used in urban environments. Christie & Braithwaite (1997) reviewed information on Fe as a mineral commodity in New Zealand. Iron is present in a large number of different minerals. The key minerals are hematite, magnetite, titanomagnetite, goethite and siderite. In New Zealand the most commonly observed minerals are ilmenite, magnetite and titano-magnetite in black sand beaches (especially along the west coast beaches of the North island). Crustal abundance of Fe is about 4.6% (Christie & Braithwaite 1997). Iron in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 2.37% (range 1.63-3.03%, n=17) and Fe in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 2.81 to 6.1% (median of the location means was 4.19%, n=76) (Author unpublished data).

#### Sources

Iron is an extremely common element in many materials used in urban environments. It is present in many structural materials used in buildings. As iron in most metals rusts unless treated, rust is

one of the common routes for iron to enter the general urban environment from metal products that age or break down. Analysis of Fe in key vehicle sources by Kennedy & Gadd (2000) showed that there was little Fe in tyres and raw bitumen (Table 3.15). Concentrations in brake pads were high and were higher again in brake pad dust. As noted by Kennedy et al. (2003), the higher concentrations of iron in the brake pad dust in the wheel housing may be derived from the wear of the drums and rotor surfaces. Iron is a common constituent of vehicle body-work. Loss through rusting is a potential source of iron to reach road surfaces from motor vehicles.

**Table 3.15 - Iron in potential sources in the road environment (All results % dry wt unless noted) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	1.83	0.257	61.85	12
Brake pad dust	17.65	8.88	46.8	6
Tyres (mg/kg)	105	30	220	12
Raw bitumen (mg/kg)	<20	<20	100	6
Road bitumen	3.98	2.51	4.81	5

### Iron in road dusts

Iron was the most abundant of the elements examined with concentrations in road dusts ranging from 1.64 to 4.76% (Table 3.16). Most samples contained more Fe than would be expected for samples of soil or stream sediment from the region. Fig. 3.23 compares the Fe concentrations in the road samples with a number of other sediment and soil samples. The road samples show a high degree of variation in concentration of Fe at a given Rb concentration which is typically an indication of higher than normal concentrations (at a given particle size).

Grain size fractions examined from local stream sediments contained high concentrations of Fe in the coarse sand fractions and the <35 µm fraction compared to the intermediate grain sizes (Fig. 3.24). The coarse sand fractions (0.5 to 2.0 mm) are composed of aggregated finer material containing un-weathered clays and silts. Because of this they tend to behave more like the fine silt and clay fractions in terms of their trace element content. The results from the Wellington study (Table 3.16) indicate that the whole samples were probably contaminated by at least an equal quantity of anthropogenic Fe (Figs. 3.23 and 3.24) and that most of this was in the 250 to 1000 µm size fractions.

Pitt & Amy (1973) found a variable distribution of Fe in the grain size separates that they examined, although on a mass basis, most of the Fe was present in the coarser fractions. Wilber & Hunter (1979) found an order of magnitude more Fe in street dusts compared to river sediments (using acid digestion). In that study, 96% of the Fe in the <63 µm fraction of the street dust was extracted as moderately reducible iron oxide, 2.7% as easily reducible manganese oxide and 1.2% as organic. Iron deposition has been shown to be greater on roadways compared to control areas (Bourcier 1979).

Hopke et al (1980) revealed that Fe occurred in the denser magnetic fractions of all particle sizes, but in the non-magnetic fraction the greatest concentration occurred in the high density fine and coarse and low-density coarse particles. The contribution from vehicle emissions is likely to be significant since the particles larger than 200 µm emitted from vehicle exhaust systems contain 30 to 35% Fe<sub>2</sub>O<sub>3</sub> (Piver 1977).



**Table 3.16 - Iron in street gutter and street surface particulates (all results % dry weight).**

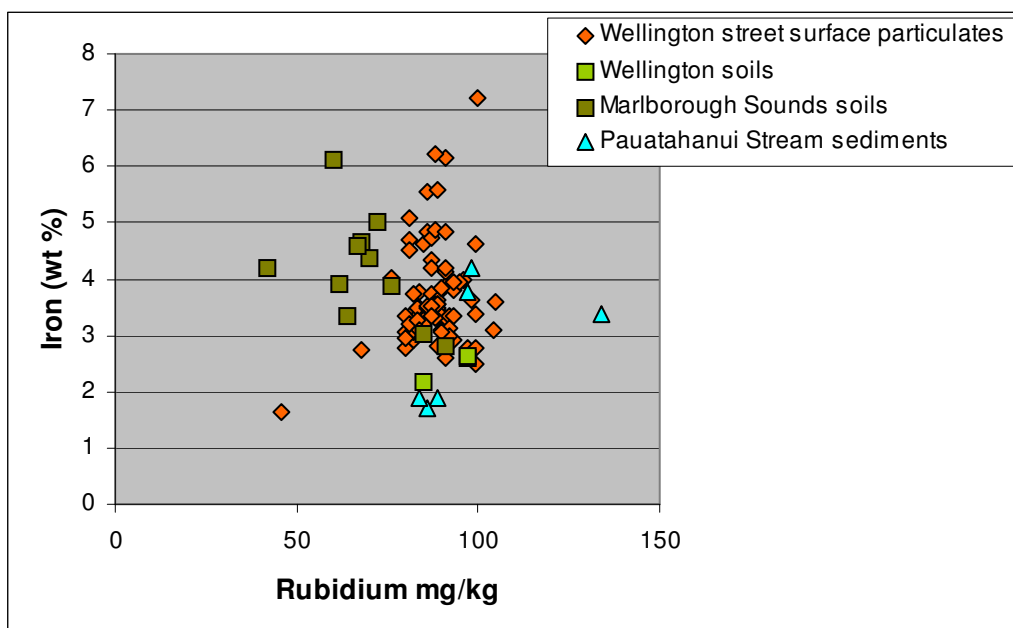
Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	1.41 ± 0.05	1.02-1.84	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	1.8	0.73-3.34	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	1.93 ± 0.18	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	5.14 ± 0.07	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	6.2 ± 0.5	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	2.35	2.28-2.42	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	3.30	3.22-3.37	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	4.53	3.21-5.86	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	3.19	2.98-3.37	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Nagpur	M-1992	6.4	5.41-7.1	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R ~2000	6.59 ± 0.79	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1984	2.39	2.36-5.82	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	2.74 ± 0.16	1.81-3.56	B< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	3.06	2.79-3.5	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	3.39	3.32-4.03	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	4.40	2.73-5.1	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	3.59	3.10-3.79	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	3.54	3.43-4.33	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	4.66	3.49-6.14	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	3.41	2.49-3.98	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	3.05	2.94-3.56	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	2.78	1.98-3.06	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	3.13	3.01-3.25	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	2.98	2.60-3.33	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	4.25	1.64-7.23	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	4.44	4.42-4.46	B <2 mm	T-XRF	3	Kennedy (unpublished)
Waitakere	R-2002	4.005	2.03-6.09	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	4.1	2.94-5.72	VC <63 µm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R - streets adjacent to urban park, mixed, residential and commercial landuse; SC - scoop; B - Brush and scoop; VC - vacuum cleaner; TA - total acid; SA - Strong acid; WA - Weak acid; INAA - Instrumental neutron activation analysis. ICPMS/AES - Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS - Atomic absorption spectrometry.

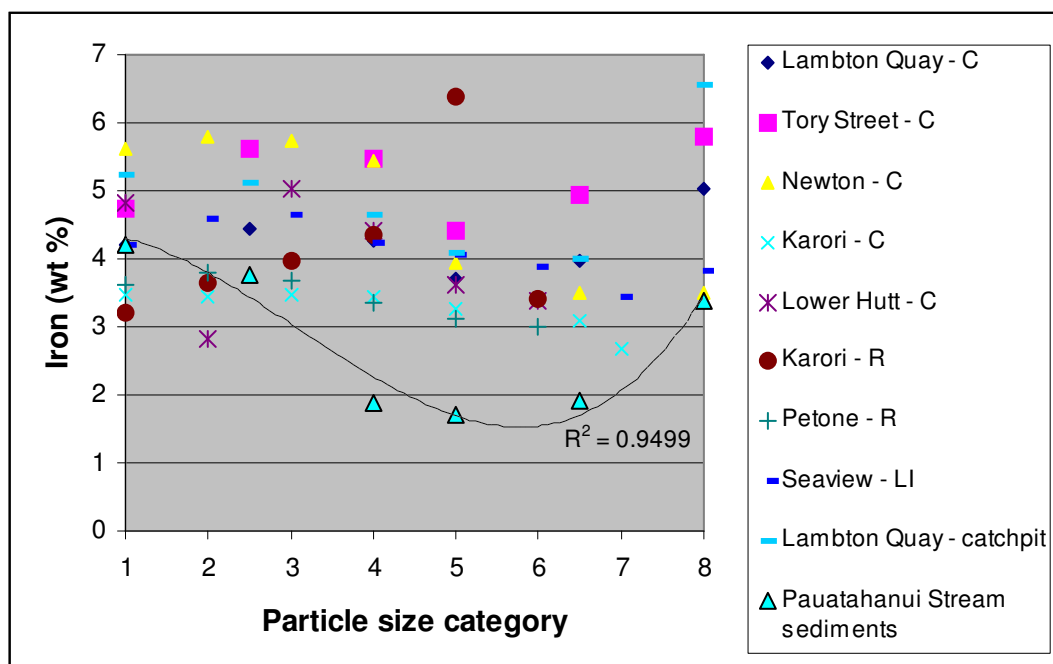
### Contribution from motor vehicles

Examination of motor vehicle emission sources has shown that vehicles release Fe through the wear of brake linings. Other vehicle emission sources are likely to only contribute minor amounts of Fe. Fig. 3.25 shows the variation in average Fe concentration on roads with different traffic volumes in Waitakere City. The data suggests that the roads with higher traffic volumes may carry a higher concentration of Fe.

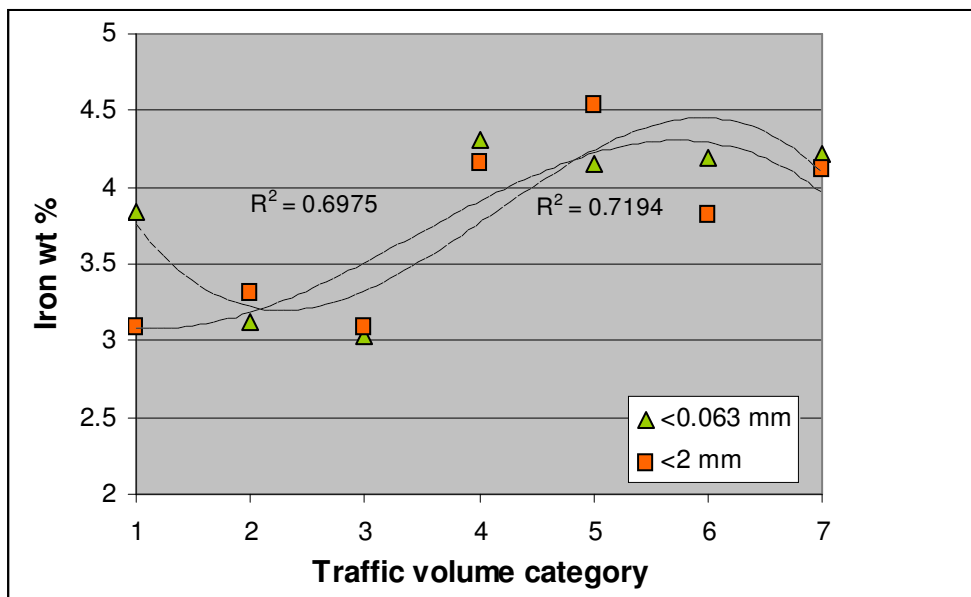
There appears to be no comparative information on the contribution made by other urban sources to the amount of anthropogenic Fe associated with urban road surface particulates. Overall, vehicles will contribute Fe to road surfaces but the proportion is not known with any certainty. As a rough estimate, the Fe data in Fig. 3.25 suggests that at least 25% of the Fe on roads with high traffic volumes may be associated with vehicle emissions.



**Fig. 3.23 - Iron concentration in road surface particle samples from Wellington compared to soils and sediments in the region on the basis of their rubidium content (Kennedy unpublished data).**



**Fig. 3.24 - Iron in size fractions of road surface particle samples and stream sediment samples from the Wellington area (unpublished data).**



**Fig. 3.25 - Iron concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

### 3.9 Gallium (Ga)

#### Natural geochemistry

Gallium ( $\text{Ga}^{3+}$ ) has an ionic radii of  $0.50 \text{ \AA}$  and can substitute for  $\text{Al}^{3+}$  ( $0.57 \text{ \AA}$ ) in many minerals. Gallium distribution follows that of aluminium fairly closely but also enters  $\text{Fe}^{3+}$  positions in minerals and enters zinc sulphide (Taylor 1965). Christie & Brathwaite (1999) reviewed the natural distribution of Ga in the geosphere noting that in New Zealand that Ga is present in elevated concentrations in sinters of the North Island geothermal fields substituting for aluminium in clays. Taylor (1965) and Plant & Rainswell (1983) identified a crustal average concentration of 15 mg/kg with sandstones, basalt and granites containing averages of 12-20 mg/kg. Very low concentrations are found in limestone and ultrabasic rocks. Gallium in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 14 mg/kg ( $n=38$ ) and Ga in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 13 to 21 mg/kg (median of location means 17 mg/kg,  $n=88$ ) (Author unpublished data).

#### Sources

Gallium is used predominantly in the electronics industry with gallium arsenide (GaAs) components represented about 98% of Ga consumption in the United States (USDI 2003). About 34% of the gallium consumed was used in optoelectronic devices, including light-emitting diodes, laser diodes, photodetectors, and solar cells. Opto-electronic devices were used in areas such as aerospace, consumer goods, industrial components, medical equipment and telecommunications. Integrated circuits represented 65% of Ga demand. Integrated circuits were used in defence applications, high-performance computers, and telecommunications. The remaining small amount (1%) was used in research and development, specialty alloys, and other applications (USDI 2003).

Kennedy & Gadd (2000) presented data on the concentration of Ga in non-tailpipe motor vehicle emission sources (Table 3.17). Concentrations in tyres and raw bitumen were low. In brake pads and brake pad dust, median concentrations were low but higher concentrations were identified in some samples examined. These high concentrations were similar to concentrations identified in New Zealand soils (refer above and below).

**Table 3.17 - Gallium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	1.5	<1	16.5	12
Brake pad dust	2.2	1.2	7.9	6
Tyres	<0.1	-	-	12
Raw bitumen	<0.1	-	-	6
Road bitumen	6.6	4.4	8.3	5

### Gallium in road dusts

In undertaking Ga analysis by XRFs, some variability may result from the additional corrections made in samples with large concentrations of Pb (as in street particulate samples). Table 3.18 summarises available data for Ga in road surface particulates.

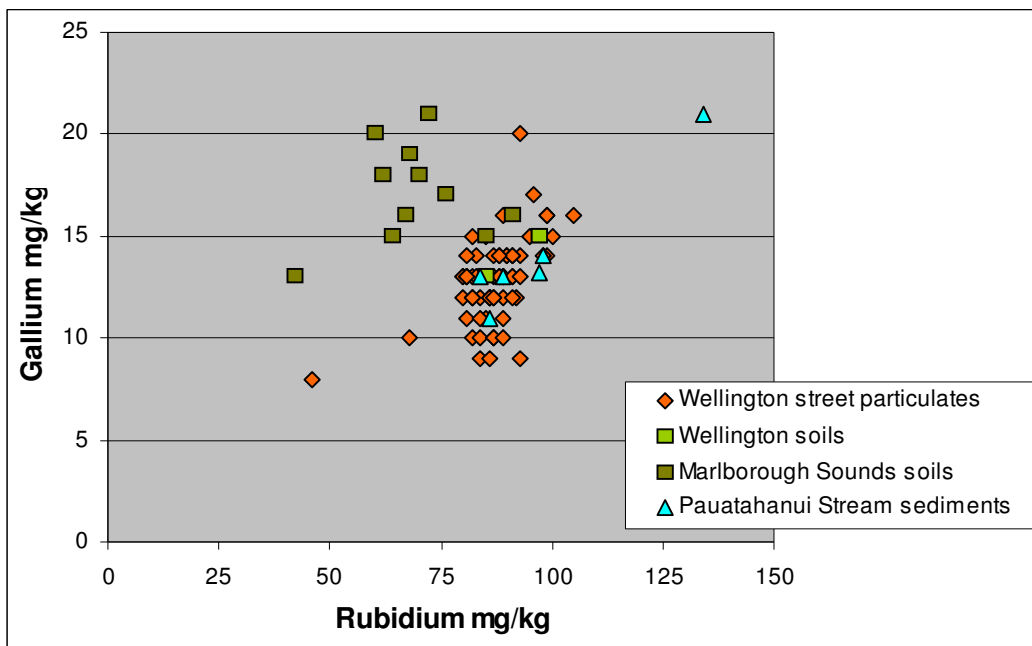
**Table 3.18 - Gallium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
US Cities	~1973	2	2-2	<6 mm	MS	3	Pitt & Amy 1973
Urbana Illinois	~1980	4.9 ± 0.9	-	VC	INAA	1	Hopke et al. 1980
Nagpur	M-1992	19	9.7-19.8	~<2 mm	INAA	3	Chutke et al. 1995
Wellington							
Lambton Quay	C	13	13-16	B <2 mm	T-XRF	7	Kennedy (unpublished)
Tory St.	C	13	12-14	B <2 mm	T-XRF	4	Kennedy (unpublished)
Newtown	C	11	9-12	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	12	9-14	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	11	10-13	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	14	9-16	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	14	11-20	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	14	12-15	B <2 mm	T-XRF	8	Kennedy (unpublished)
Seaview	I	13	8-15	B <2 mm	T-XRF	12	Kennedy (unpublished)

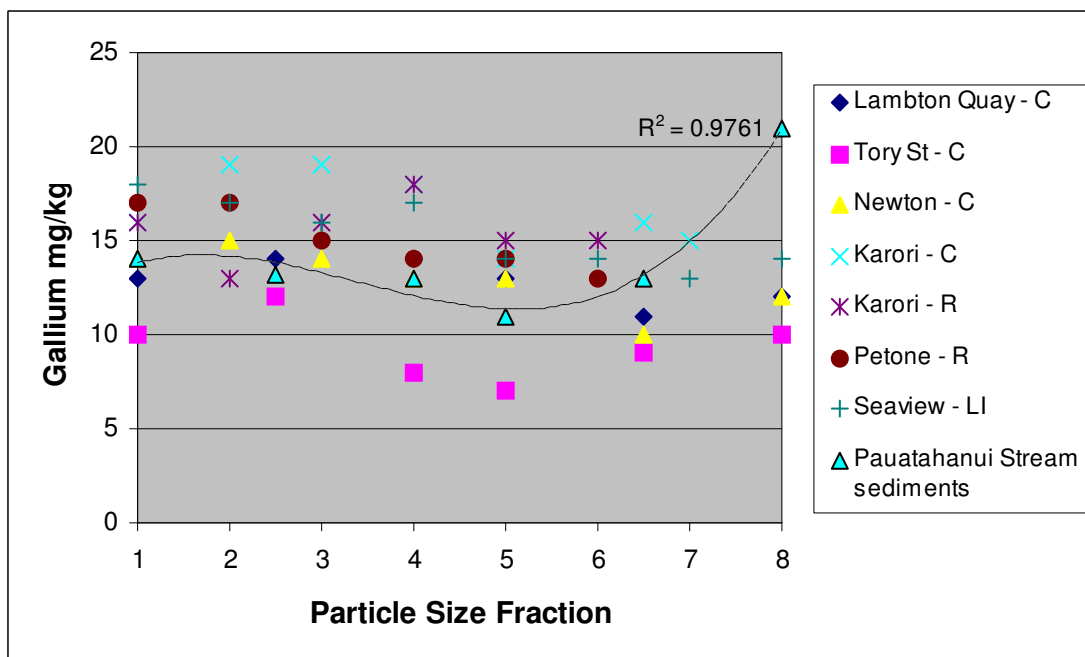
**Notes:** 1 – median presented where available; B – Brush and pan or scoop; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis. MS – mass spectrometry; XRF – X-ray spectrometry.

Fig. 3.26 shows the concentration of Ga compared to Rb for street particulate samples from Wellington along with data for soils from the region. The data shows that the concentration of Ga in the urban road surface particulates is very similar to the concentrations observed in soils from Wellington and sediments from the Wellington area. All samples in these sample sets show increasing Ga concentration as Rb concentration increases (i.e., increasing concentrations as the proportion of fine particle sized material in the sample increases). The Marlborough Sounds soils in this case have higher Ga concentrations than the Wellington samples for a given Rb concentration. As such they do not provide a suitable benchmark for assessing the likely presence of elevated concentrations of Ga in urban road surface particulate material.

Grain size separates (Fig. 3.27) show a characteristic decrease in concentration with increasing fineness, with an increase in the less than 35 µm particle size fraction. Gallium displayed little variation between grain size fractions (2.2-3.7 mg/kg) in a gutter dust sample examined by Corrin & Natusch (1977). Unpublished data for that sample indicated that Ga occurred in higher concentrations in the magnetic fractions of the denser particles over most particle sizes (D Natusch Pers. comm.).



**Fig. 3.26 - Gallium concentration in road surface particle samples from Wellington compared to soils and sediments in the Region on the basis of their rubidium content (Kennedy unpublished data).**



**Fig. 3.27 - Gallium in size fractions of street particle samples and stream sediment samples from the Wellington area (Kennedy unpublished data).**

**Contribution from motor vehicles**

Although Ga has some industrial uses in alloys, high temperature thermometers and arc lamps (Belliles, 1979) there was no indication of any increase in the Ga content of the street dusts examined, although some grain size fractions (Fig. 3.27) appear to contain higher concentrations of

Ga as that present in the same fractions taken from a non-road environment, it is likely that the concentrations observed are within the likely variability of Ga in the environment. Further work would be required to verify this.

### 3.10 Gold (Au)

#### Natural geochemistry

Gold is a relatively inert element with a very low average crustal abundance estimated to be 0.004 mg/kg. Plant & Raiswell (1983) report similar average concentrations in most rock types. Christie & Braithwaite (1997) review the geochemistry of gold in the New Zealand setting. There is little data on the natural concentrations of Au in soils and sediments in New Zealand.

#### Sources in the urban environment

USDI (2003) estimated that in the US, the main uses of Au were jewellery and arts (85%), dental (10%) and electrical and electronics (5%). Kennedy & Gadd (2000) reported no detectable Au in tyres, brake pads, brake pad dust in raw bitumen and road bitumen in New Zealand although the detection limit of 0.5 mg/kg was insufficient to identify gold concentrations above the average crustal abundance.

#### Gold in road dusts

Ferguson & Ryan (1984) reported very interesting results for gold (Au) in street dusts. Of eleven international gutter dusts examined by them, nine including three from Christchurch contained Au concentrations in the range 0.01 to 0.09 µg/g. Whereas two samples taken in New York contained surprisingly 0.38 and 2.78 mg/kg. Chutke et al. (1995) reported Au in dust samples from highways in Nagpur to contain a median of 5.8 ng/g (range 0.31-5.8).

#### Contribution from motor vehicles

Vehicle sources of gold are likely to be very minor. It is likely that particulate matter on urban road surfaces contains elevated concentrations of Au compared to crustal abundance. In cases where elevated concentrations are present it is likely that sources may be local and irregular in occurrence. Contributing sources within the urban environment have not been identified.

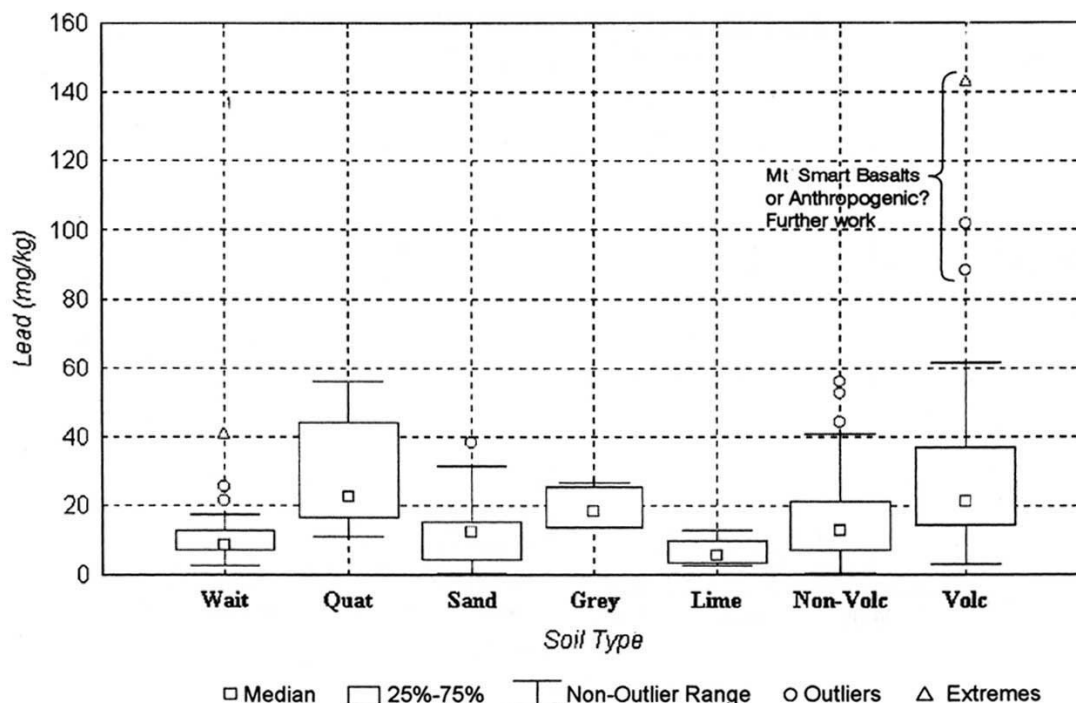
### 3.11 Lead (Pb)

#### Natural geochemistry

Lead (Pb<sup>2+</sup>) has an ionic radius of 1.20 Å mid way between Ca<sup>2+</sup> and K<sup>+</sup>. This typically results in Pb substituting for potassium in common minerals such as plagioclase and apatite. Christie & Braithwaite (1995) provide an overview of the mineral geochemistry and occurrence of lead in New Zealand.

ARC (2001) presented data for acid extractable Pb in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig 3.27 shows that the median values for key soil groups typically range from 9.64 mg/kg in soils derived from Waitemata Group materials (n=19) to 23.3 mg/kg (n=33) for soils derived from volcanic materials. As these samples were collected, from sites within urban areas with substantial contamination by Pb it is unlikely, that the data adequately represents the natural Pb concentration in the soils. ARC (2001) note that the data displayed variability with high values in rural areas and low values in urban areas.

Lead in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 14 mg/kg (n=38) and Pb in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 10 to 16 mg/kg (median of location means 12 mg/kg, n=91) (Author unpublished data).



**Fig. 3.28 - Lead concentration in Auckland soils (from ARC 2001).**

## Sources

In the US, the transportation industries have been identified as the key consumers of lead, using 76% of it for batteries, fuel tanks, solder, seals, bearings, and wheel weights. Electrical, electronic, communications uses (including batteries), ammunition, television glass, construction (including radiation shielding), and protective coatings accounted for approximately 22% of consumption (USDI 2003). The remainder of uses included ballast and counterweights, ceramics and crystal glass, tubes and containers, type metal, foil, wire, and specialized chemicals.

In New Zealand the principal source of Pb in the urban environment historically was the emission of Pb in exhaust emissions of motor vehicles using leaded fuel. In the 1980s leaded petrol in New Zealand contained 0.82 g/L of fuel. Lead emission budgets identify this source as contributing greater than 90% of the total burden to the environment in New Zealand (Day, 1977). Localised sources such as Pb based industries (Day, 1977, Ward et al., 1977, Chee 1988) and the dispersal of Pb based paint from old buildings and buildings being renovated may be locally important. Lead contamination may also occur in gutter dusts from solder and discarded batteries.

Lead also comes from the wear of tyres since Pb oxide is used as filler materials in some overseas makes of tyres (Shaheen, 1975). Plastics (rigid PVC products) stabilisers include dibasic lead stearate (up to 2%) (EPA, 1977) and Pb may also be found in colour newsprint, toothpaste tubes, cosmetics and paint on non-building materials (EPA, 1977). Overall, there are a large number of sources in urban environments able to contribute to the lead burden associated with road surface particulates.

Sander et al. (2000) and Lohse et al. (2001) provides an overview of the current uses for Pb in motor vehicles. The uses include Pb in steel in a variety of machined parts. Lead is also present in

copper alloys in bearing shells and bushes. The main uses in vehicles is in Pb sulphuric acid batteries which contain on average 15 kg of Pb. Vehicle fuel tanks may also contain Pb and Pb may be used in high pressure and fuel hoses, vibration dampers and balancing devices which vary in size from vehicle to vehicle. Until recently Pb was also used in the electrodeposited paint coatings on many vehicles. Many vehicle manufactures have changed production methods eliminating the use of Pb in paints (Sander et al. 2000). It is not known whether all paints applied to new vehicles or when re-spray is required are Pb free.

Table 3.19 summarises the data reported by Kenendy & Gadd (2000) for the concentrations of Pb in key non tail pipe emission sources to the road surface in New Zealand. Tyres and raw bitumen were found to contain relatively low concentrations of Pb. In the brake pads 3 of 18 samples contained >100 mg/kg Pb and 7 of 18 contained >20 mg/kg. There is currently no information on PB concentration of exhaust emissions in New Zealand.

**Table 3.19 - Lead in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	7.48	1.33	873	12
Brake pad dust	26	3.74	941	6
Tyres	2.72	0.8	9.7	12
Raw bitumen	<0.2	-	-	6
Road bitumen	8.33	1.89	126	5

### Lead in urban road dust

Table 3.20 summarises data for Pb in road surface dust samples collected in a range of international and New Zealand studies. The data includes locations with varying lead contents in fuels at the time of sampling. One of the earliest studies of Pb in urban dusts was by Kaye & Reznikoff in 1947 who examined roadside dusts collected before and after the introduction of leaded petrol (1924 and 1934 respectively).

Waldron & Stofen (1974) reported that the study “although having a small number of samples as indicating that the dust collected after the introduction of Pb in petrol was 50% greater (in Pb) in the later samples”. However there appears to be no statistical difference between the 1924 population (n = 5, x = 0.1187 Pb, s.d. = 0.0173% Pb) and the 1934 population (n = 5, x = 0.1764% Pb, s.d. = 0.0945%) (df = 9, T = 1.148) at the 95% confidence level. The study by Kaye & Reznikoff (1947) does point out that high amounts of Pb were found in street dusts before Pb was added to petrol. The use of Pb compounds in tyre rubber may have accounted for a proportion of this (Waldron & Stofen, 1974).

Two early studies by Giubileo (1957) and Jecklin (1956) are reported in Waldron and Stofen (1974). Both demonstrated that Pb levels in dusts collected in urban centres were greater than peripheral streets in Milan (Giubileo, 1957) and greater than rural dusts in Basel (Jercklin, 1956). Elevated concentrations in roadway dusts have been reported by a large number of authors including Ward et al (1974), Day et al (1975), Archer & Barratt (1976), Day et al (1977), Farmer & Lyon (1977), Duggan & Williams (1977), Ho (1979), Harrison (1979), Fergusson et al. (1980), Ferguson & Simmonds (1983) and Lau & Wong (1983).

The median Pb concentration (n = 94) for the samples examined in the earlier Wellington study was 1989 mg/kg which is similar to the mean Pb values found in other studies undertaken at about that time. For example, in dusts from central Christchurch (2,790 ± 1,430 mg/kg, n = 235, Ferguson et al., 1980) and Hong Kong (2974 mg/kg, n = 82, Ho, 1979). An average lead concentration of 6,340 ± 2,840 (1,780 - 12,910) mg/kg, was reported, for a busy intersection in Christchurch by Fergusson & Simmonds (1983). Reported mean values from London (Duggan and Williams, 1977), Glasgow (Farmer & Lyon, 1977), and Manchester (Day et al., 1975) were generally half of this concentration.



**Table 3.20 - Lead in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Land-use & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	1000±200	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	3031	2008-4053	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	2582	2213-2952	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	1296	674-1919	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	863	817-909	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Ottawa	R-1993	32.9	12.6-122.35	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	1927±508 <sup>#</sup>	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	180±14 <sup>#</sup>	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Coventry	C~1999	21.4	nd – 199.4	BP <1 mm	SA -AAS	49	Charlesworth et al 2003
Birmingham	C~1999	48.6	nd – 146.3	BP <1 mm	SA -AAS	100	Charlesworth et al 2003
Taejon, Korea	M -1998	52*	13-161	BP <0.18 mm	SA-AAS	31	Kim et al. 1998
Mascot, Sydney	M-1999	-	230-1600	-	SA-AAS		Brockbank et al. 1999
Gymnea, Sydney	M-1999	-	520-1600	-	SA-AAS		Brockbank et al. 1999
Hong Kong	M-2001	120±4*	-	BP <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Hong Kong	M-2001	181±92.9*	-	BP <0.1 mm	T-EDXRF	8	Li et al. 2001
Manoa Basin Hawaii	R ~2000	106±38*	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Auckland	R~1992	720	627-2524	BP <2mm	AAS	3	ARC 1992
Christchurch	C ~1984	1294	887-10,700	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	6340±2840*	1780-12,910	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	1978	719-4809	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	6421	2207-30842	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	4312	2048-7158	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	3294	1836-5624	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	5134	3258-7164	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	2583	1997-5587	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	1418	234-2999	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	1372	700-2134	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	888	207-1999	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	1904	1827-1981	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	923	639-3495	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	1353	296-6399	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	1090	850-4190	B <2 mm	T-XRF	3	Kennedy (unpublished)
Auckland City	R-C, 2001-3	-	~20-~500	V <0.45-2 mm	SA ICPMS	~48	Ng et al. 2003 (refer below)
Waitakere	R-2002	169	28.2-695	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	276	151-559	VC <63 µm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; M, C, R – streets adjacent to mixed, commercial, residential and light industrial landuse; B Brush and scoop, pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry; \* - mean/mean and standard deviation; # - mean and standard error. Nd – not detected/specified.

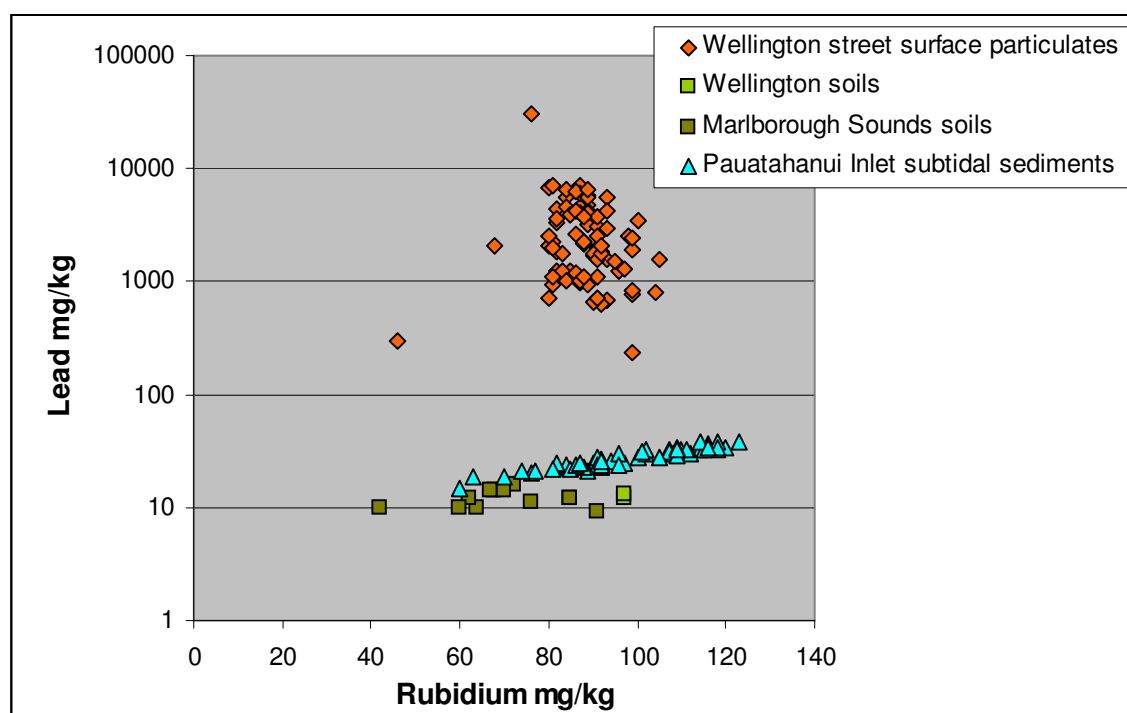
Fig. 3.27 shows the Pb concentration of street particulate samples from Wellington collected prior to the removal of Pb from petrol in New Zealand. In all samples, the concentration of Pb present was well above what would have been expected to be present naturally. The median concentration of Pb in the samples was typically >1,000 mg/kg. Data for the finer particle size fraction of road surface dusts indicates that concentrations pre-Pb removal from petrol were about 2,000 mg/kg as measured using XRFS (Table 3.21) and ARC (1992) reported concentrations of 663-3050 mg/kg in <0.047 mm particles of street dust from Auckland. The Pb concentration in whole residential road surface samples in Auckland was about 720 mg/kg (Pakuranga, ARC 1992). Comparison with samples collected over the last two years indicates that concentrations in whole dust have declined to an average below 200 mg/kg and concentrations in the finer fraction have declined to about 280 mg/kg (e.g., refer Kennedy & Gadd 2003, Waitakere City). Ng et al. (2003) have also identified Pb concentrations in <0.045 mm particles of the order of 100-400 depending upon location in Auckland City (refer Fig. 3.20). Examining the data in Table 3.20 also shows that typical Pb concentration in

road surface samples in locations where Pb is not present in petrol are low and in the range 50-200 mg/kg.

**Table 3.21 - Lead in <0.036 mm urban road surface particulate material pre-lead removal from petrol in New Zealand (all results mg/kg dry weight).**

Site	Land-use & Date	Arithmetic mean	Range	N	Reference
Wellington					
Lower Hutt	C	4488 ± 407	4101-5053	4	Author unpublished
Karori	C	4214 ± 90	3264-5240	3	Author unpublished
Karori	R	2215 ± 1127	550-4247	11	Author unpublished
Taita	R	1410 ± 633	748-2157	8	Author unpublished
Seaview	LI	1644 ± 91	527-2350	7	Author unpublished
Auckland					
Freemans Bay	R-1988	2772 ± 3233	991-10642	8	Kennedy et al. 1988
Remuera	R-1988	2180 ± 1255	285-3982	8	Kennedy et al. 1988
Clover Park	R*-1988	2644 ± 705	1674-3725	6	Kennedy et al. 1988
Glenfield	R*-1988	2379 ± 1448	853-5534	8	Kennedy et al. 1988
Clendon Park	R-1988	1676 ± 788	674-2863	10	Kennedy et al. 1988
Mangere	R*-1988	1256 ± 746	636-2481	8	Kennedy et al. 1988

**Note:** \* - adjacent to motorway.

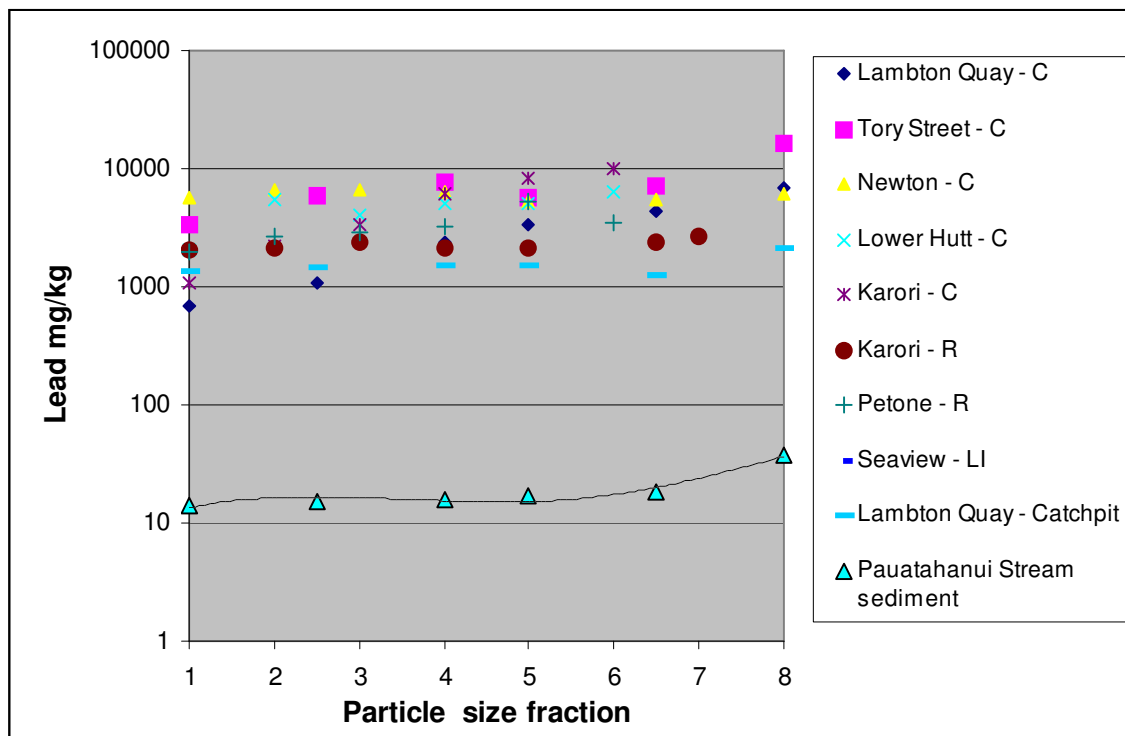


**Fig. 3.29 - Lead concentration in road surface particle samples from Wellington (pre-lead removal from petrol) compared to soils and sediments in the region on the basis of their rubidium content (author unpublished data).**

There have been substantial reductions in the Pb concentration of street surface particulate material since Pb was removed from petrol in many countries. In New Zealand, lead measured in Wellington prior to that time using XRFs recorded higher concentrations. Recent measurements in Auckland after the removal of Pb from petrol have reported median concentrations of 169 mg/kg. Similar concentrations have also, recently been reported by Ng et al. (2003) for samples from Auckland (refer Fig. 3.21). Overall, the available data indicates at least a 75% reduction in the Pb

concentration associated with particulate material on road surfaces since the removal of Pb from petrol in New Zealand.

Fig. 3.30 shows the variation with particle size for a range of samples collected from the Wellington area prior to the removal of Pb from petrol. The information in Fig. 3.30 can be compared to the data in Fig. 3.31 and Table 3.21.

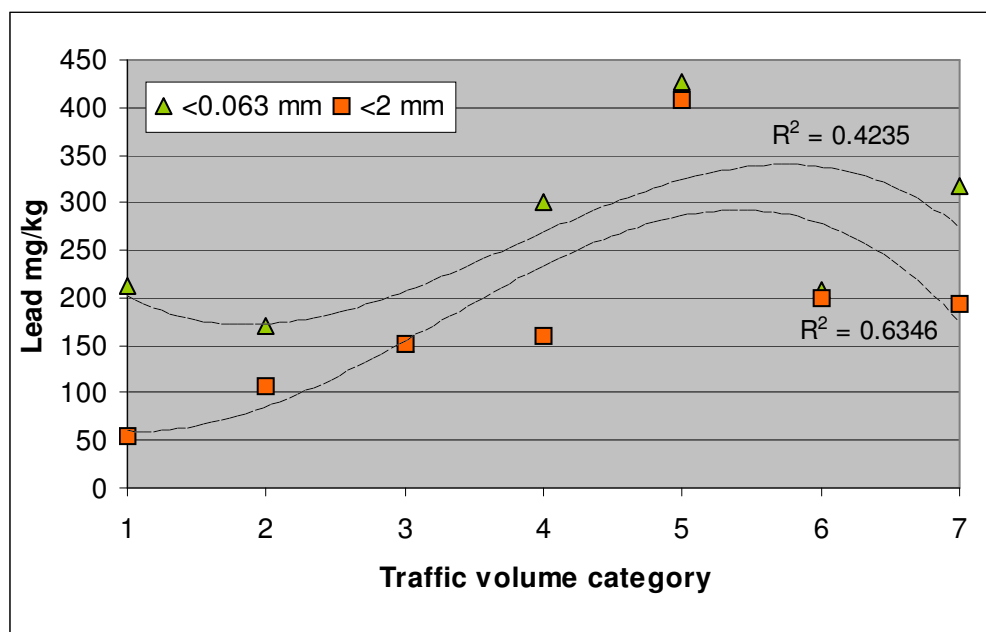


**Fig. 3.30 - Lead in size fractions of street particle samples and stream sediment samples from the Wellington area pre-lead removal from petrol (author unpublished data,).**

### Contribution from motor vehicles

Historically motor vehicles in New Zealand contributed virtually all of the Pb found on urban road surfaces. A variety of sources contribute Pb to road surfaces in urban areas. Historically the large amount of Pb-based paints used, on the exterior of houses in New Zealand was also a potential contributor in some locations. Pb is still present in the particulate matter on road surfaces. Current vehicle use still contributes Pb through the wear of brake linings and tyres. Fig. 3.30 shows the median concentration of Pb in samples in two grain-size fractions of road surface samples from Waitakere City compared to the traffic volume at the sites. Although the data shows a poor relationship with traffic volume, the three highest traffic volume categories have higher Pb concentrations than the lower four.

Davis et al. (2001) estimated source contributions to stormwater from specific sources in urban areas. For brick buildings the authors estimated that brake and tyre wear contributed 2% of the Pb, building sidings 79%, wet and dry deposition 18%. For buildings with vinyl sidings, brake and tyre wear contributed 9%, sidings 12%, roof 4% and wet and dry deposition 75%. The estimates in that study indicate that local aspects of urban character may influence the local source contributions. As a very preliminary estimate the data in Fig. 3.31 suggests that vehicles on high traffic roads may contribute 50-60% of the Pb present. The contribution from exhaust emissions is not known. In addition, contributions from soils (containing a reservoir of historic Pb deposition) adjacent to roads, is now likely to be a significant source.



**Fig. 3.31 - Lead concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

### 3.12 Manganese (Mn)

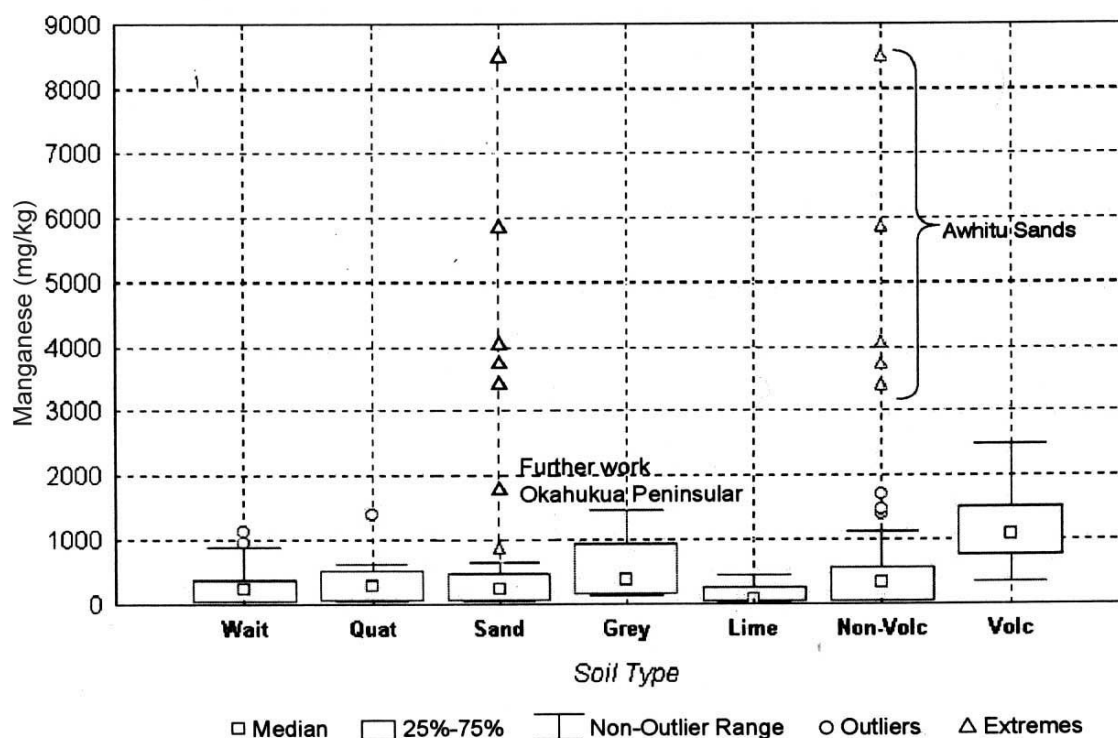
#### Natural geochemistry

Manganese is a relatively common metal with an estimated crustal abundance of 950 mg/kg (Plant & Raiswell 1983). Concentrations in key rock types range from 500 mg/kg in granites to 2,200 mg/kg in basalts. Manganese concentrations in soils vary considerably depending upon parent material and formation. ARC (2001) presented data for acid extractable Mn in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.32 shows that the median values range for key soil groups typically range from 133 mg/kg in soils derived from Waitemata Group materials (n=19) to 395 mg/kg (n=6) for soils derived from Greywacke. Soils derived from volcanic materials contained higher concentrations (median 1088 mg/kg, n=33). The mean concentration in soils from Lake Ponui in the Wellington region was 892 mg/kg (range all samples 274-1730 mg/kg) and in soils from the Marlborough Sounds, location means ranged from 372 to 1069 mg/kg (11 locations) with a sample range of 221 to 2031 mg/kg (n=82) (Author unpublished data).

#### Sources

USDI (2003) report that the main identifiable end uses of Mn were in products for construction, machinery, and transportation, which were estimated to be 29%, 11%, and 12%, respectively, of the total manganese demand (in the US). Most of the rest went to a variety of other iron and steel applications. Manganese is also used in non-metallurgical purposes such as the production of dry cell batteries, as an ingredient in plant fertilizers and animal feed and as a colorant for brick (USDI 2003).

Manganese has extensive uses including the manufacture of steel alloys, dry cell batteries, electrical coils, ceramics, glass, dyes, fertilisers, welding rods and matches (Belliles, 1979). Hopke et al. (1980) reported that Mn is possibly present in brake linings and tyres and will be released by body-work corrosion.



**Fig. 3.32 - Manganese concentration in Auckland soils (from ARC 2001).**

Table 3.22 summarises data from Kennedy & Gadd (2000) for the concentration of Mn in key non tail-pipe emission sources in motor vehicles. The data shows that tyres and raw bitumen contain negligible concentrations of Mn. Brake pads contain moderate amounts of Mn and brake pad dust higher concentrations. The higher concentrations in the post-wear particles probably reflects the addition of Mn from the drum and rotor during use of brake linings.

**Table 3.22 - Manganese in potential sources in the road environment (All results mg/kg dry wt, from Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	315.5	136	1155	12
Brake pad dust	1450	856	2870	6
Tyres	1.2	<0.5	5.9	12
Raw bitumen	<0.5	<0.5	<0.5	6
Road bitumen	543	390	654	5

### Manganese in urban road dust

Table 3.23 provides a summary of published information on Mn in urban road surface particulates. In Wellington, the total range of results was relatively small (251 to 1036 mg/kg) with all except three values lying between 400 and 800 mg/kg. Fig. 3.32 shows the variation in the road particulate samples in relation to other soils and sediments from the Wellington region. As identified above, the concentration range of Mn found in soils in the Wellington region is large, with sediments from Pauatahanui Stream at the lower end of the range and soils from Lake Ponui at the upper end (Fig. 3.33). Fergusson & Simmonds (1983) used Mn as a reference element in gutter dusts, assuming that little anthropogenic Mn was present in the gutter.

**Table 3.23 - Manganese in street gutter and street surface particulates (all results mg/kg dry weight).**

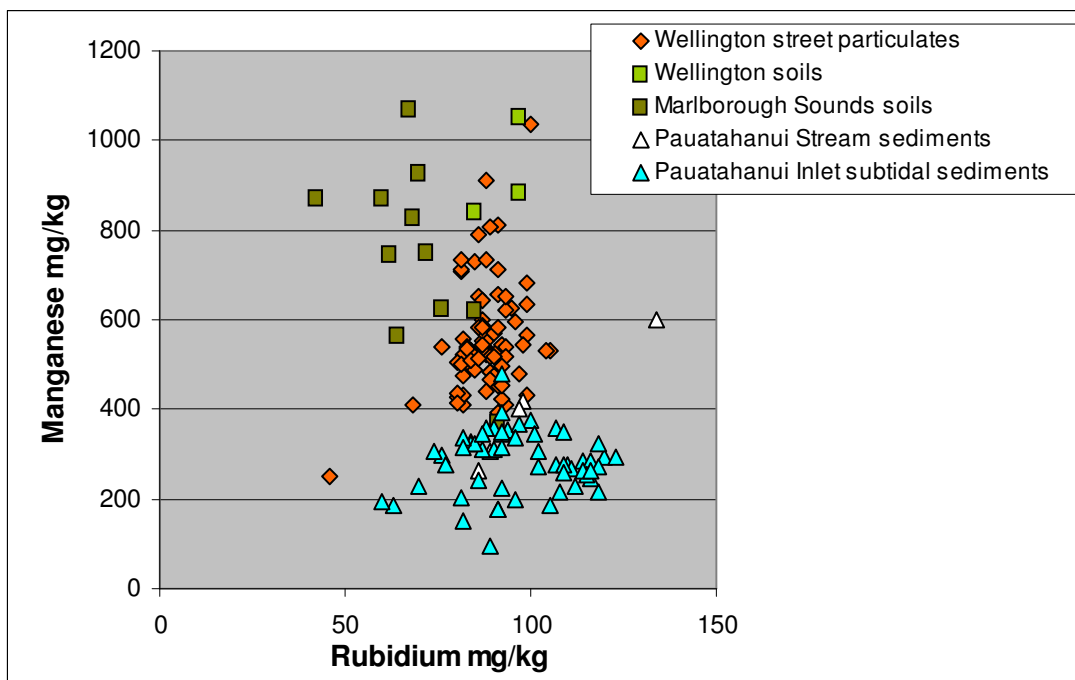
Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	594 ± 14	512-664	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Hong Kong	M-1978	373 ± 12	-	<0.75 mm	SA AAS	7	Ho 1979
Ottawa	R-1993	426.4	145.1-618.3	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	362 ± 13	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	833 ± 16	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	350 ± 30		VC	INAA	1	Hopke et al. 1980
London	C ~1984	440.5	379-502	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	453.5	391-516	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	579	474-685	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	373.5	336-411	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Nagpur	M-1992	575	524-613	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R ~2000	1035 ± 150	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1984	399	381-399	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	243 ± 67	180-408	B < 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	429	409-475	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	539	507-559	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	612	411-729	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	540	474-565	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	529	485-599	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	663	513-811	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	524	433-595	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	528	472-589	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	423	298-458	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	475	469-480	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	478	394-542	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	683	251-1036	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	635	442-653	B <2 mm	T-XRF	3	Kennedy (unpublished)
Waitakere	R-2002	557.5	412-1520	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	662	305-2710	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R - streets adjacent to urban park, mixed, residential and commercial landuse; SC - scoop; B - Brush and scoop; VC - vacuum cleaner; TA - total acid; SA - Strong acid; WA – Weak acid; INAA - Instrumental neutron activation analysis. ICPMS/AES - Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS - Atomic absorption spectrometry.

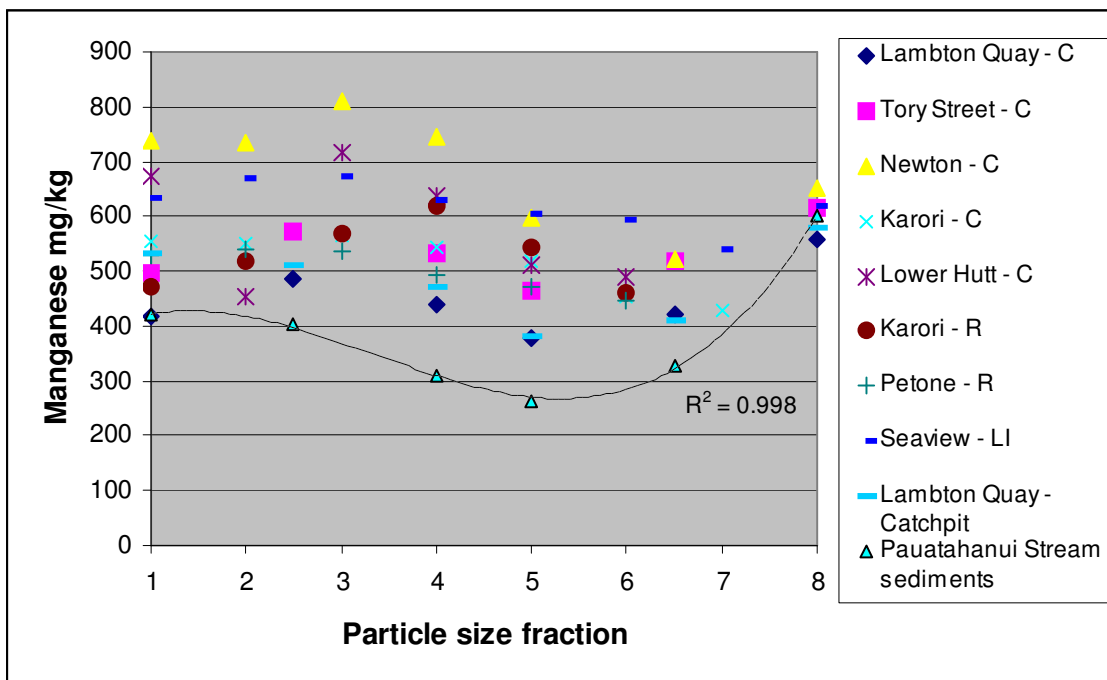
Pitt & Amy (1973) and Lau & Wong (1983) noted an increase in Mn concentration with decreasing grain size. As shown in Fig. 3.34 this increase only occurred in the finest particles. Elevated concentrations were seen in the coarser particle fractions of the dust samples from the Wellington region (fractions 2 to 4 which correspond to 0.25-0.71 mm). Hopke et al. (1980) observed a similar fraction distribution for Mn to that of Cd, with the highest concentration in the non-magnetic high density and low-density particles attributed to tyre wear and magnetic high-density particles attributed to vehicle exhausts. Corrin & Natusch (1977) presented Mn data for the analysis of grain size fractions of a street dust. The lowest concentrations were recorded in the coarser fractions with the concentration peaking at 45-75 µm. Wilber and Hunter (1979) found that most of the Mn in street dusts was extractable as moderately reducible iron oxide (61.8%), 17.8% was extractable as easily reducible manganese oxides, 11% was as organic fraction and 7.9% was exchangeable. These authors found 4-20 times more extractable Mn in street dusts compared to nearby river sediments.

Manganese in street dusts was also examined by Ho (1979) who was not able to find a great variation in the Mn concentrations of road dusts in Hong Kong, although he did observe some differences between areas examined. Similar concentrations were reported by Lau & Wong (1982)

for dusts, also from Hong Kong. No correlation was found with the annual average traffic volume and the Mn concentrations were similar to adjacent soil samples in that study.



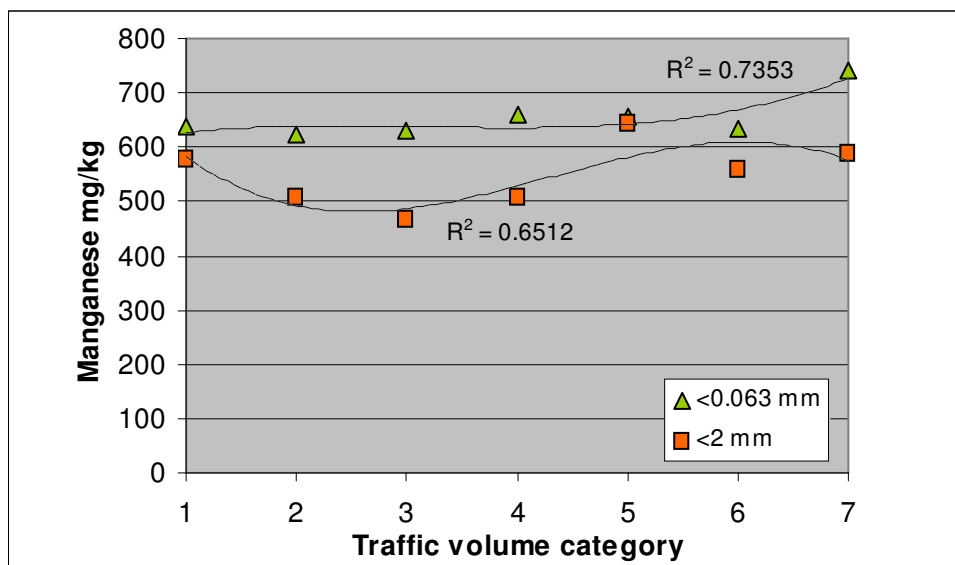
**Fig. 3.33 - Manganese concentration in road surface particle samples from Wellington compared to soils and sediments in the region on the basis of their rubidium content (author unpublished data).**



**Fig. 3.34 - Manganese in size fractions of road surface particle samples and stream sediment samples from the Wellington area (author unpublished data).**

### Contribution from motor vehicles

With Mn present in non-exhaust emission sources such as brake lining wear, vehicles have the potential to contribute Mn to road surfaces. Examination of road dust particulate Mn concentrations indicates that Mn concentrations may be elevated. The concentration of Mn in some sources such as tyres are low and these sources will potentially dilute the Mn concentration on the road surface. Particles of brake pad wear generated following contact with the brake shoe may have elevated concentrations of Mn (2-3 times the natural concentration). Fig. 3.35 shows that there was no clear relationship between Mn concentration in road surface particles on Waitakere City roads and vehicle numbers.



**Fig. 3.35 - Manganese concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

Significant natural variation within soils and sediments makes confirmation about how much anthropogenic Mn is present on road surfaces difficult. The extent of other contributing sources within the urban area is not known.

### 3.13 Mercury (Hg)

#### Natural geochemistry

Mercury has an estimated crustal abundance of 0.08 mg/kg with most rock types containing similar concentrations with the exception of shales, which tend to contain higher concentrations than most rocks (Taylor 1965). In many environments Hg tends to be associated with sulphides. Like elements such as Au, Hg tends to be diffusely distributed (geochemically). In New Zealand, geothermal and volcanic activity results in localised areas of elevated concentrations in soils, water and the atmosphere).

ARC (2001) presented data for acid extractable Hg in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.36 shows that the median values range for key soil groups typically range from 0.093 mg/kg in soils derived from Greywacke (n=6) to 0.208 mg/kg (n=12) for soils derived from Quaternary materials. Most Hg analysis is undertaken following strong acid extraction of the sample. This results in the data from most studies being more comparable than that for many other elements presented in this report where acid extraction and XRFs have been used for analysis.



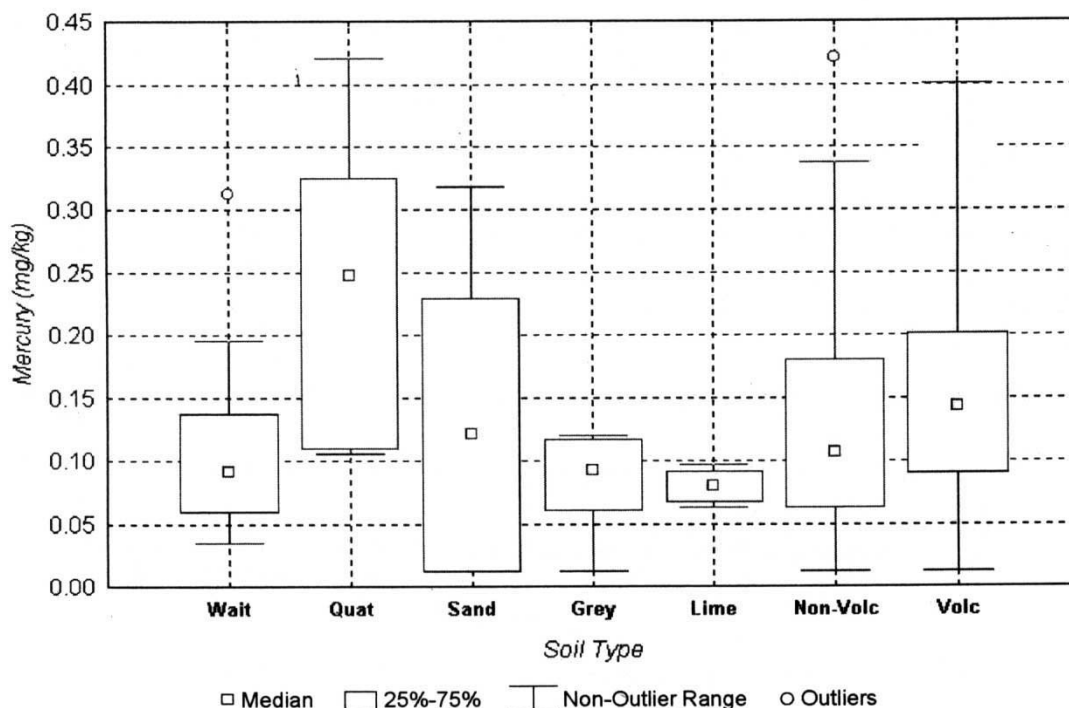


Fig. 3.36 - Mercury concentration in Auckland soils (from ARC 2001).

### Sources of mercury

Mercury in countries such as the US is now mainly derived from the recovery of mercury from items containing mercury. Sources from which Hg is recovered include batteries, chloralkali wastewater sludges, dental amalgams, electrical apparatus, fluorescent light tubes, and measuring instruments. The manufacture of chlorine and caustic soda, along with its use in electrical and electronic applications probably accounted for two-thirds to three-fourths of the mercury consumed domestically in the US in 2002. The remainder was used in other applications such as measuring and control instruments and dental amalgams. (USDI 2003). Many countries have reduced Hg use significantly because of the environmental concerns arising from the re-distribution of Hg. Hg has been eliminated from use in many products. For example, organic compounds have replaced mercury fungicides in latex paint. There are however still sources in the urban environment contributing Hg to sources adjacent to roads.

In vehicles, Sander et al. (2000) and Lohse et al. (2001) noted that some headlight bulbs (gas discharge bulbs) contain Hg (as well as scandium, sodium and Hg and possibly small amounts of thorium and thallium). Although these are sealed, the Hg may be released during accidents. Sandler et al. (2000) noted that discharge lamps may contain about 0.5 mg Hg/lamp. Kennedy & Gadd (2000) analysed for Hg in key vehicle non tail-pipe emission sources on vehicles in New Zealand. Table 3.24 provides a summary of the results obtained for Hg in tyres, brake pads and in road bitumen. Overall, the concentration of Hg in all sources examined in that study were very low.

Table 3.24 - Mercury in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).

Source	Median	Minimum	Maximum	N
Brake pads	0.2	<0.1	0.3	12
Brake pad dust	<0.015	<0.01	<0.03	6
Tyres	<0.001	<0.01	0.03	12
Raw bitumen	<0.01	-	-	6
Road bitumen	<0.01	<0.01	0.03	5

## Mercury in road dust

Few studies have reported Hg concentrations in road surface particulates. Table 3.25 provides a summary of New Zealand and the limited international data. The highest concentration of Hg was found in the three commercial areas in Wellington City were surprising. The minimum concentration of Hg in those samples was well above the values recorded for greywacke and argillite rocks ( $0.063 \pm 0.04$  mg/kg, range 0.019 to 0.148 mg/kg, author, unpublished). The other Wellington site, Newton (commercial) had variable results with 4 of 7 being at the upper end of the range for local rocks. The other three areas examined ( $n = 16$ ) had Hg values which were similar to those noted for source materials (Table 3.25). Recent data for streets in Waitakere City (Kennedy & Gadd (2002), indicated that most samples compared low concentrations of Hg similar to that reported for Ottawa by Rasmussen et al. (2001). Chutke et al. (1995) reported elevated concentrations of Hg in dusts on highways in Nagpur. The concentrations were similar to the results for dusts from residential commercial areas of Nagpur (median 0.625, range 0.05-0.89 mg/kg) and from within transport locations such as bus and train stations (0.46, range 0.15-1.02 mg/kg).

**Table 3.25 - Mercury in gutter and road surface particulates (all results mg/kg dry weight).**

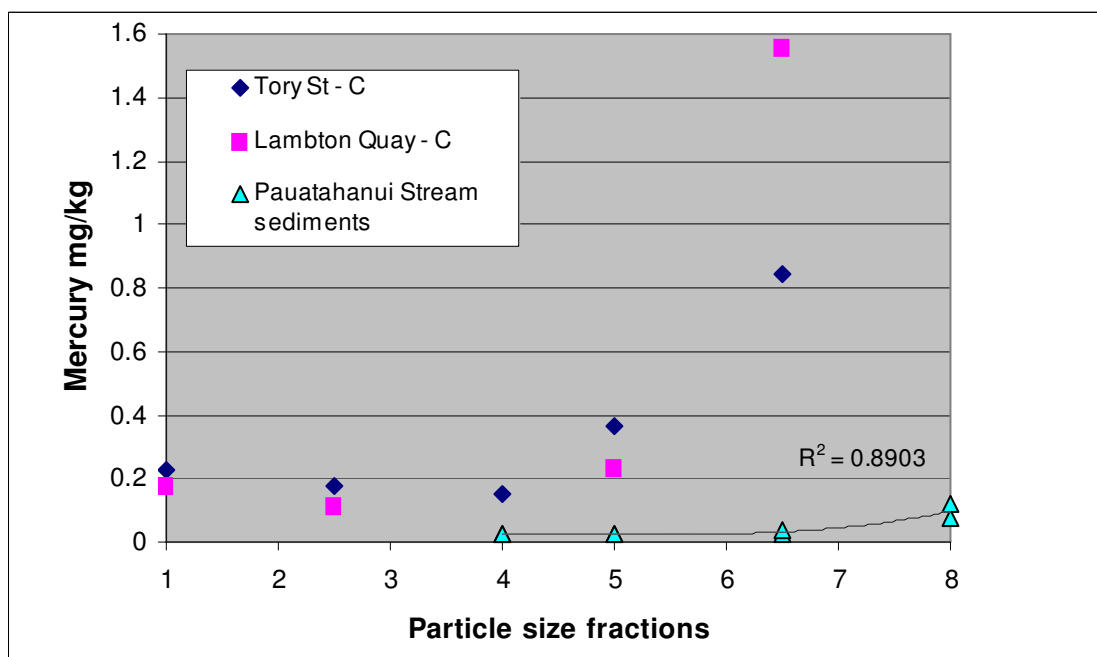
Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	0.09 ± 0.008	-	VC	INAA	1	Hopke et al. 1980
Ottawa	R-1993	0.018	0.004-0.188	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Nagpur	M-1992	0.75	0.65-0.80	~<2 mm	INAA	3	Chutke et al. 1995
Wellington							
Lambton Quay	C	1.027	0.454-6.48	B <2 mm	SA-AAS	7	Kennedy (unpublished)
Tory St.	C	0.437	0.22-1.094	B <2 mm	SA-AAS	5	Kennedy (unpublished)
Newtown	C	0.222	0.106-0.748	B <2 mm	SA-AAS	7	Kennedy (unpublished)
Lower Hutt	C	0.086	0.078-0.125	B <2 mm	SA-AAS	7	Kennedy (unpublished)
Petone	R	0.067	0.054-0.067	B <2 mm	SA-AAS	3	Kennedy (unpublished)
Gracefield	R	0.104	0.061-0.147	B <2 mm	SA-AAS	6	Kennedy (unpublished)
Lambton Quay CB	C	6.137	0.509-40.0	B <2 mm	SA-AAS	3	Kennedy (unpublished)
Waitakere	R-2002	<0.1	<0.1-0.1	VC <2 mm	SA	34	Kennedy & Gadd 2002
Waitakere	R-2002	<0.1	<0.1-0.5	VC <0.063 mm	SA	34	Kennedy & Gadd 2002

**Notes:** 1 – Median presented where available; B – Brush and scoop or pan; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis.

The analyses of a number of grain size fractions in the Tory Street and Lambton Quay samples revealed high concentrations of Hg in the finer fractions (Fig. 3.37), all of which were an order of magnitude greater than sediments from Pauatahanui Stream. Hopke et al. (1980) found that Hg was present in high concentrations in the fine dense magnetic fractions as well as in coarse light fractions with little in the dense fine non-magnetic fraction.

ARC (1992) also reported Hg in particle size fractions of three gutters sediment samples from Auckland (two residential and one industrial). They found that concentrations were low with all samples ranging from 0.03 – 0.17 mg/kg (six fractions ranged from 1-2 mm to <0.047 mm).

In the Waitakere City study (Kennedy & Gadd 2003), Hg concentrations were higher in the <0.063 mm fraction compared to the <2 mm sample. Given the predominant transport pathway of Hg in the environment (in gaseous form) it is likely that adsorption to organic carbon rich surfaces and oxide surfaces on particles would occur. As such increasing concentrations with decreasing particle sizes in sediments would be expected. In some urban situations loss of Hg (e.g., from scrap yards and from loss of Hg containing devices such as thermometers) will result in loss and deposition of Hg on street surfaces and in gutters.



**Fig. 3.37 - Mercury in size fractions of road surface particle samples and stream sediment samples from the Wellington area (author unpublished data).**

### Contribution from motor vehicles

Motor vehicle emission sources such as brake pads and tyres appear to contain little Hg. The presence of Hg in some types of vehicle headlight lamps has been reported but would only be released during accidents. Available data indicates that vehicles are only minor sources of Hg within the urban environment. However, the proportion of Hg sourced from fuel combustion is not known. It is likely that a range of other sources within the urban environment including combustion processes, weathering and loss of paints and spillage of Hg result in diffuse contributions (gaseous sources) and localised elevations (spillages). The contribution of motor vehicles to the Hg in stormwater is not known due to insufficient data for Hg. It is likely however that, vehicles are relatively minor contributors compared to other sources.

## 3.14 Molybdenum (Mo)

### Natural geochemistry

Taylor (1965) reports that  $\text{Mo}^{4+}$  will substitute for  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  and  $\text{Fe}^{3+}$  and as such will tend to be found in higher concentrations in the heavy minerals such as magnetite and ilmenite. Analysis of Mo in New Zealand soils has been reported by Vortman (1980). That study reports a median concentration of 3.5 mg/kg (range 2-9.5 mg/kg) for a series of soil samples from Lower Hutt in Wellington (e.g., Wingate and Waiwhetu silt loams).

### Sources of molybdenum in the urban environment

Molybdenum is used primarily in steel alloys, many of which are used in the automobile industry. USDI (2003) reports that major end-use applications for Mo included machinery (35%), electrical (15%), transportation (15%), chemicals (10%), in the oil and gas industry (10%) and others (15%). Molybdenum is also used in the paint industry (Friberg 1977) and also in Mo-disulphide greases. Analysis of vehicle emission sources by Kennedy & Gadd (2000) showed that tyres, raw bitumen and road bitumen contained low concentrations of Mo. A selection of brake pad samples and vehicle brake pad dust samples were found to contain higher median concentrations (refer Table

3.26). Of note were the occasional high concentrations of Mo present in some brake pads. The high concentrations probably arising from the use of Mo disulphide grease in the pads were found in 2 of 8 car pads and in a four-wheel drive pad (refer Kennedy et al. 2002).

**Table 3.26 - Molybdenum in motor vehicle and road source materials (all results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	3.6	0.4	6,000	12
Brake pad dust	29.1	5	98.9	6
Tyres	1	<0.2	1.4	12
Raw bitumen	0.45	<0.2	1.5	6
Road bitumen	1.58	1.21	1.97	5

### Molybdenum in road dust

There is little published in relation to the Mo concentrations in urban road surface particulate material. Table 3.27 summarises the available literature. The lack of data in the literature is a reflection of the generally low toxicity of Mo in the environment and the lack of known sources of Mo in the urban environment.

**Table 3.27 - Molybdenum in urban road surface dusts (all results mg/kg dry wt).**

Source	Sample	Analysis	Median <sup>1</sup>	Min	Max	N	Reference
Oslo	B, <0.1 mm	SA	4	-	-	14	De Miguel et al. (1997)
Ottawa	B, 0.1-0.25 mm.	SA - ICPMS	1.38	0.38	2.68	45	Rasmussen et al. (2001)
Wellington							
Lambton Quay – C	B, <2mm	XRF	2.1	<1	4.7	6	Kennedy (unpublished)
Waitakere	VC, <0.063 mm	SA - ICPMS	4.5	1.4	12.2	34	This study
	VC, <2 mm	SA - ICPMS	2.4	0.8	5.6	34	This study

**Notes:** 1 – median presented where available; B - Brush and pan; VC – Vacuum cleaner; SA – Strong acid extraction. ICPMS – Inductively coupled plasma mass spectrometry; XRF – X-ray fluorescence.

Six samples of road dust examined from Lambton Quay and Tory Street in Wellington contained a mean Mo concentration of  $2.4 \pm 0.5$  mg/kg (limit of detection was 1 mg/kg). There appeared to be only a slight variation in the concentration with decreasing particle size and in LQ-12 the 1 to 2 mm fraction contained less than 1 µg/g; the 0.5 to 1 mm, 2.1 mg/kg; 0.25 to 0.5 mm, 2.1 mg/kg; 0.15 to 0.25 mm, 3.4 mg/kg; 35 to 150 µm, 3.8 µg/g and in the less than 35 µm fraction the concentration was 2.6 µg/g.

Table 3.27 also summarises the results of recent analysis of molybdenum in road dusts collected in Waitakere City (Kennedy & Gadd 2003). A higher median concentration was found in the <0.063 mm compared to <2 mm fraction samples. Fig. 3.38 shows the variation in Mo concentration for samples collected from Waitakere City in relation to known traffic volumes at those sites.

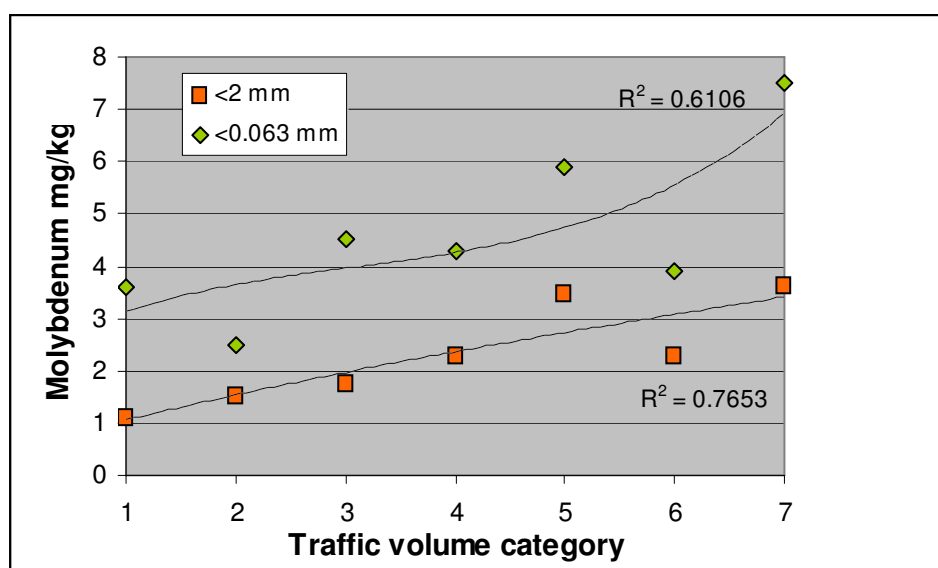
It is interesting to note that Rasmussen et al. (2001) reported the concentration of Mo garden soil and house dust in Ottawa. House dust (median 1.70 mg/kg, n=48) had a similar concentration to road surface dusts (median 1.38 mg/kg Table 3.4) but garden soils contained lower concentrations (median 0.6 mg/kg n=50). This may reflect the association of Mo with fine airborne particles possibly sourced from motor vehicles or multiple airborne sources.

### Contribution from motor vehicles

The examination of road surface dusts in Waitakere City has shown that material on road surfaces contains low and relatively consistent concentrations of Mo (80% <8 mg/kg). The examination of

motor vehicle sources indicates that motor vehicles should contribute some Mo to the road surface. This contribution comes from the wear of brake linings. Other sources such as tyres and the road sources do not appear to be significant sources of Mo and may produce wear products with concentrations lower than ambient local soils and geological materials.

Wear of brake pads produces particles containing Mo concentrations many times higher than ambient concentrations. An unknown proportion of brake pads used by the vehicle fleet in New Zealand contain Mo at concentrations significantly higher than those pads that have not had Mo purposefully added to them. It is probable that the elevated concentrations identified in Waitakere street dust samples arises from the presence of these pads in the vehicle fleet. Fig. 3.38 suggests that there may be an increase in concentration of Mo with increasing vehicle numbers. The difference between the lower vehicle volume categories and the higher categories indicates that the vehicles on the high traffic roads might contribute 40-60% of the Mo present.



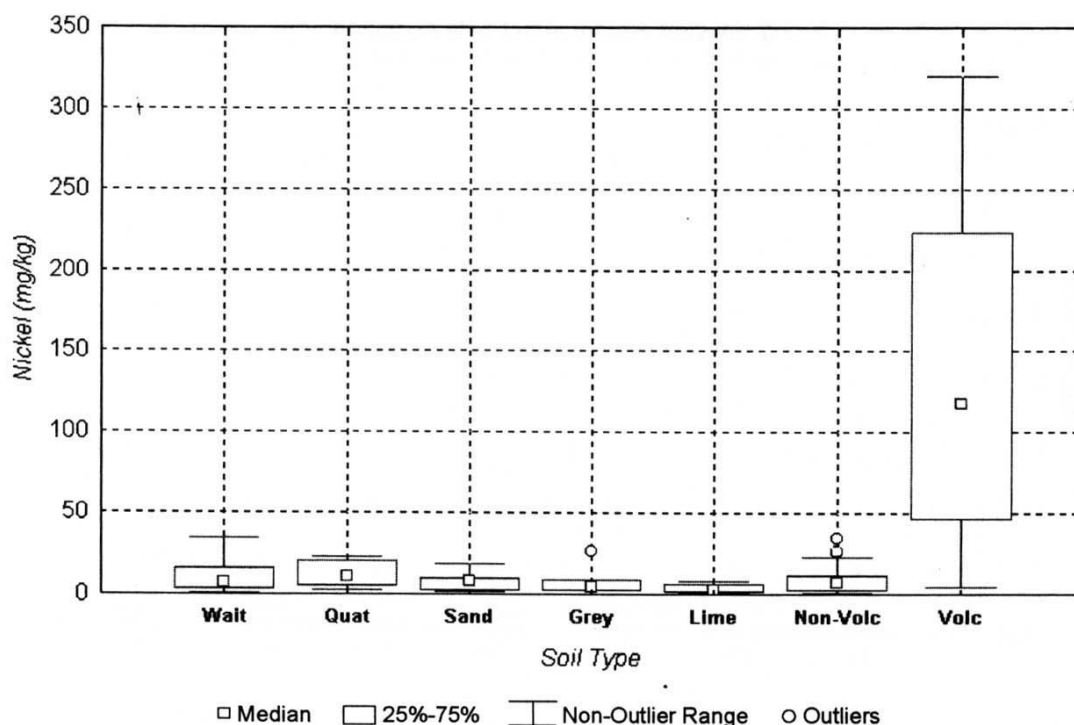
**Fig. 3.38 - Molybdenum concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

### 3.15 Nickel (Ni)

#### Natural geochemistry

Average crustal abundance of Ni is estimated to be 75 mg/kg with a considerable range among different rock types. For example, granite and basalt contain 0.5 and 150 mg/kg respectively (Taylor 1965). Ni ( $\text{Ni}^{2+}$ ) has an ionic radius of 0.69 Å which is similar to  $\text{Fe}^{2+}$ ,  $\text{Ti}^{4+}$  and  $\text{Mg}^{2+}$ . Christie & Braithwaite (1995) describe the mineral geochemistry and distribution of Ni in New Zealand.

ARC (2001) presented data for acid extractable Ni in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.39 shows that the median values range for key soil groups typically range from 4.3 mg/kg in soils derived from Greywacke (n=6) to 10.85 mg/kg (n=12) for soils derived from Quaternary materials. Soils derived from volcanic materials contained higher concentrations (median 128 mg/kg, n=33). This latter elevated concentration has the potential to influence local road surface material concentrations of Ni.



**Fig. 3.39 - Nickel concentration in Auckland soils (from ARC 2001).**

Nickel in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 13 mg/kg (n=38, range 6-24) and Ni in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 10 to 22 with one location (D'Urville Island) at 42 mg/kg (median of location means 16 mg/kg, n=89) (Author unpublished data).

### Sources of Nickel in the urban environment

Information on the use of Ni in the US (USDI 2003) shows that the main uses were; stainless and alloy steel production (42%), nonferrous alloys and superalloys (38%), electroplating (14%) and other uses (6%). Nickel has a wide range of uses including electronics, steel alloys, batteries and in the manufacture of coins. USDI (2003) indicated that the ultimate end uses included transportation (32%), chemical industry (13%), electrical equipment (10%), construction (9%), fabricated metal products (8%), household appliances (7%), petroleum industry (6%), machinery (6%) and other uses (9%). Nickel in street dusts may come from brake linings (Hopke et al. 1980), diesel fuels (Dunlap 1971), lubricating oils (Van Hassel 1979) and probably vehicle bodywork corrosion. Kennedy & Gadd (2000) examined concentrations of Ni in key vehicle non tail-pipe emission sources (Table 3.28). That study found that the concentration of Ni in tyres is low and that there are low concentrations of Ni in raw bitumen. Concentrations of Ni in brake pads and dust from brake pads is high. Road bitumen was found to contain higher concentrations of Ni compared to raw bitumen.

**Table 3.28 - Nickel in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	359	10	660	12
Brake pad dust	410.5	80	730	6
Tyres	1	<1	3	12
Raw bitumen	16	2	32	6
Road bitumen	137	77.1	153	5

## Nickel in street particulate material

Table 3.29 provides a summary of available New Zealand and international data for Ni in street surface particulates. Fig. 3.40 shows that most of the whole samples of gutter dust examined appear to contain up to twice as much Ni as would be expected when compared to the normal Ni/Rb ratios (even when soil data is considered). The highest concentrations of Ni (three times) in the whole dusts were found in samples from streets in industrial locations.

**Table 3.29 - Nickel in street gutter and street surface particulates (all results mg/kg dry weight).**

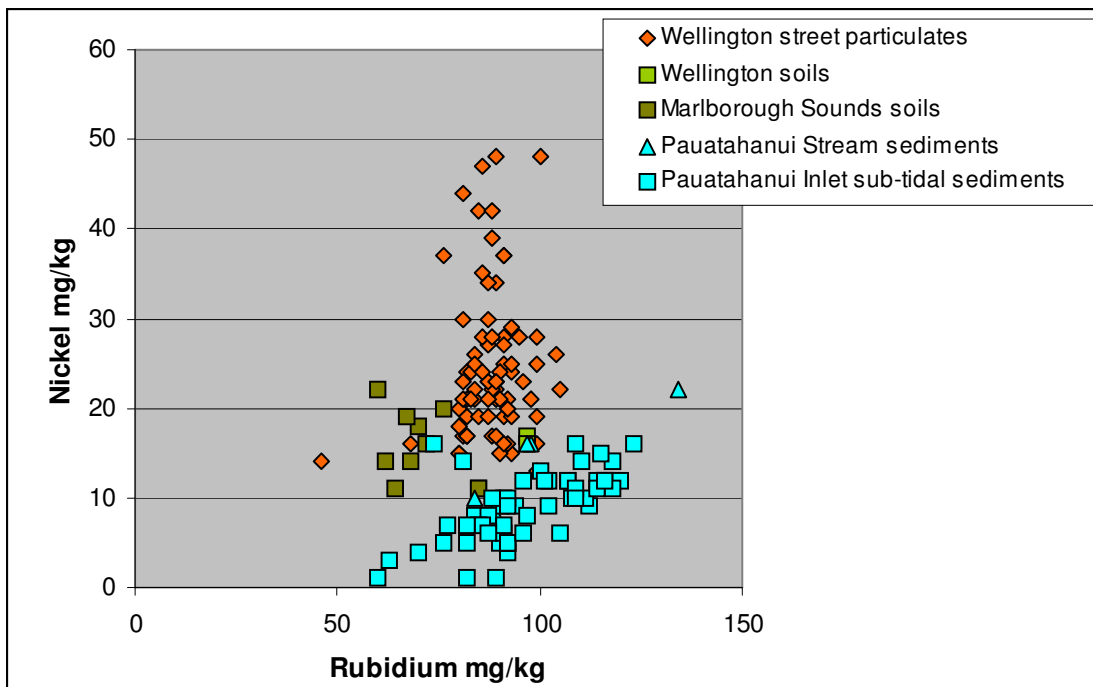
Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	28.6 ± 5.2	14-46.2	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Birmingham	M <2003	16.6	<0.1-636.2	B <1 mm	SA-AAS	100	Charlesworth et al. 2003
Coventry	M <2003	141.5	6.18-233.5	B <1 mm	SA-AAS	49	Charlesworth et al. 2003
Ottawa	R-1993	14.6	4.7-25	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Oslo	M-1994	41 ± 1	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Madrid	M-1994	44 ± 5	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	250 ± 60	-	VC	INAA	1	Hopke et al. 1980
Manoa Basin Hawaii	R ~2000	177 ± 34	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1981	19.9 ± 3.3	13.8-31.7	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	17	15-34	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	21	17-37	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	26	16-42	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	21	19-24	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	24	21-34	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	28	23-37	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	21	13-25	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	22	18-24	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	16	12-23	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	19	17-20	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	17	15-26	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	38	14-48	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	28	25-29	B <2 mm	T-XRF	3	Kennedy (unpublished)
Waitakere	R-2002	103	37-499	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	78.5	45-175	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; U, P, M, C, R – streets adjacent to urban park, mixed, residential and commercial landuse; B – Brush and scoop, pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.

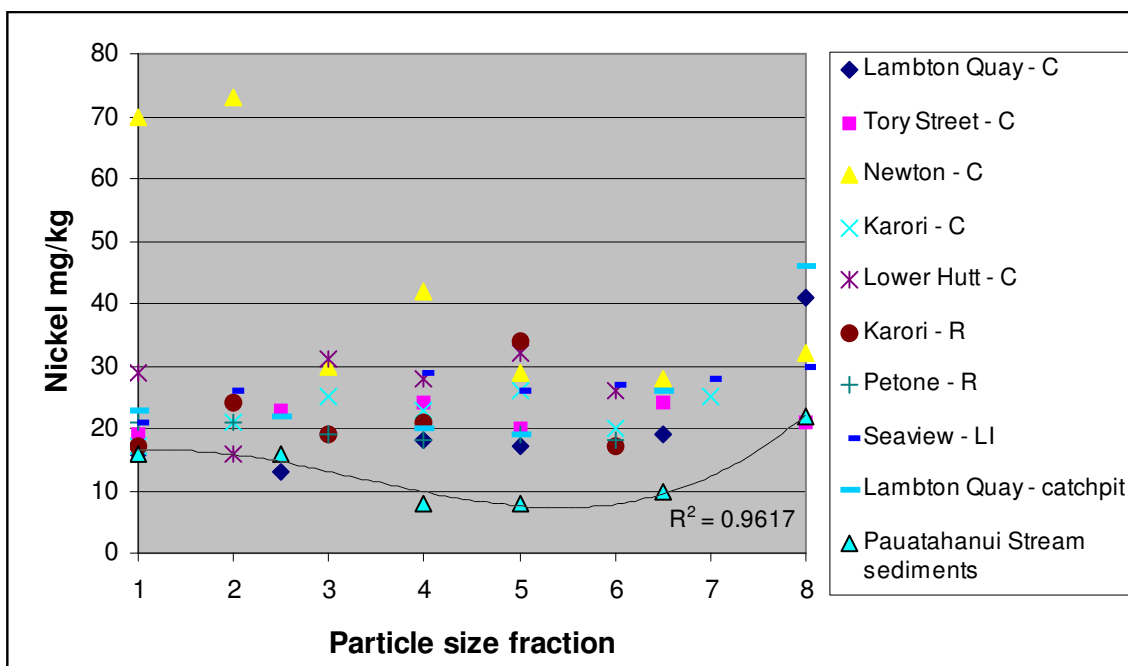
Grain size fractions of the control samples in Fig. 3.41 display the same bimodal distribution as seen for a number of metals. One sample NT-5 (commercial) displayed marked enrichment in the coarser fractions. Pitt & Amy (1973) reported that nickel concentrations in the finer fractions of street dusts were up to 100 mg/kg. Harrison (1979) found higher Ni concentrations in carpark sites compared to roadways. Wilber & Hunter (1979) reported up to ten times more acid soluble Ni in street dusts compared to adjacent river sediments and noted very high concentrations adjacent to a motor repair shop. Their <63 µm sample contained 10.3% exchangeable Ni; 9.6% easily reducible Ni; 14.2% organic; 639% moderately reducible and 1.9% soluble Ni.

There have been few analysis of Ni in New Zealand road surface particulates. Fergusson & Simmonds (1983) reported a mean Ni concentration of 19.9 mg/kg (range 13.8 to 31.7) in gutter dusts at a busy intersection in Christchurch. Recently Ng et al. (2003) reported on Ni in samples of dust from roads in Auckland City. The samples examined contained 50 mg/kg and higher concentrations. Particle fractions of 106-250 µm contained high concentrations of Ni in most of the

samples examined in that study (100 to nearly 300 mg/kg). The 50%ile of the Waitakere <2 mm data was 103 mg/kg and the 95%ile was 179 mg/kg. The Ng et al. (2003) data is very similar to the Waitakere data. However both sets of data are much higher than data obtained for Wellington and Christchurch where most location medians range from 17-28 mg/kg (Table 3.2).



**Fig. 3.40 - Nickel concentration in road surface particle samples from Wellington compared to soils and sediments in the region compared on the basis of their rubidium content (author unpublished data).**



**Fig. 3.41 - Nickel in size fractions of street particle samples and stream sediment samples from the Wellington area (author unpublished data).**

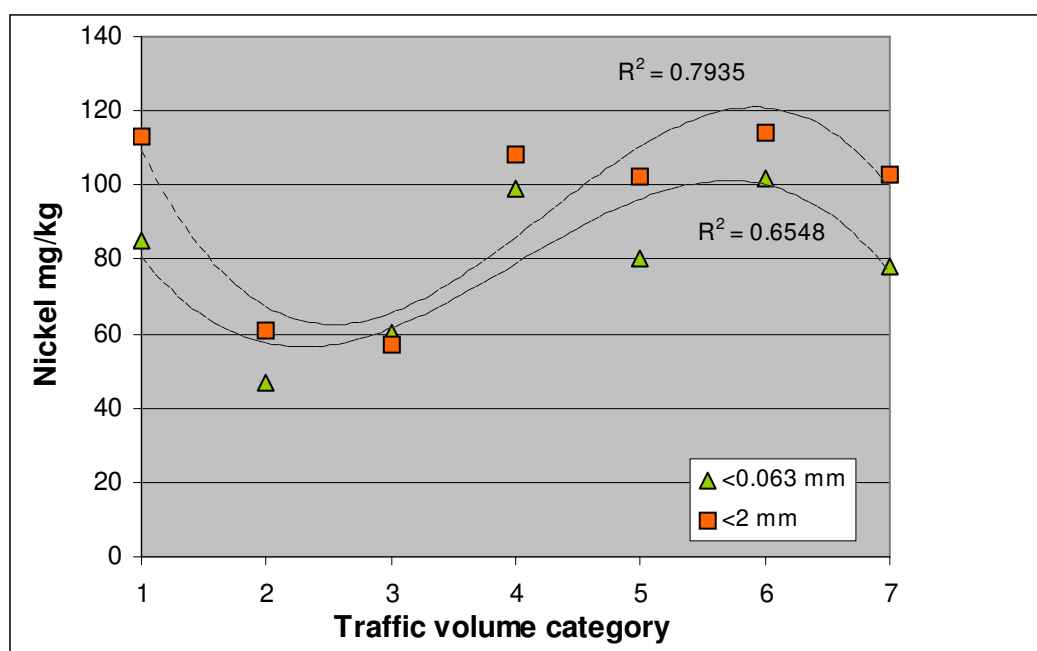


The higher concentrations of Ni in Auckland City and Waitakere suggest a contribution of Ni from either the bitumen or from volcanic scoria used in road construction (refer Fig. 3.39).

### Contribution from motor vehicles

The concentration of Ni is elevated in urban road surface particulate material. Concentrations range from low (similar to local soils and sediments to 2-3 times higher than expected). Brake pads and brake pad dusts contain elevated concentrations of Ni (up to 20 times higher than uncontaminated material on the road surface). No information is available in relation to the contribution that Ni in tail-pipe emissions makes to Ni concentrations on road surfaces. There are likely to be a range of other Ni sources in the general urban environment that could contribute to Ni on road surfaces however, there is little information on the contributions from other urban sources (e.g., combustion, litter etc.).

Overall, motor vehicles are a key contributor of Ni to road surfaces and hence stormwater. Fig. 3.42 shows the relationship between Ni concentration in road surface particles and traffic volume in Waitakere City. The figure indicates a group of high traffic volume sites with high Ni compared to two lower traffic volume sites. Although the lowest traffic volume roads had high concentrations of Ni, the high traffic roads had higher Ni concentrations compared to roads with lower Ni. Although the data is very preliminary it is possible that in the high volume traffic sites, motor vehicles contributed up to 45% of the Ni.



**Fig. 3.42 - Nickel concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic data from Kennedy & Gadd 2003).**

### 3.16 Niobium (Nb)

#### Natural geochemistry

Niobium ( $\text{Nb}^{5+}$ , ionic radius 0.69 Å) commonly substitutes for  $\text{Ti}^{4+}$  (ionic radius 0.68 Å) and a number of other trace elements (Taylor 1965). Average crustal abundance is estimated to be about 20 mg/kg with similar concentrations in many key New Zealand rock types. Nickel in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 7 mg/kg ( $n=20$ )

and Nb in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 6 to 10 mg/kg (median of location means 9 mg/kg, n=88) (Author unpublished data).

### Sources of niobium in the urban environment

Niobium metal has a number of important uses with USDI (2003) estimating that the key end uses of Nb were carbon steels (27%), super-alloys (27%), high-strength low-alloy steels (17%); stainless and heat-resisting steels (15%), alloy steels (13%) and other uses (1%). The super-alloys are used in applications such in jet engine components (turbine blades), rocket subassemblies, and heat-resisting and combustion equipment. Niobium alloys are also used in pipeline construction and it is used in arc-welding rods for some grades of stainless steel. Some magnets contain niobium and superconductive magnets are made with Nb-Zr alloy wire. Lithium niobate is also used for camera lenses and the coating on glass for computer screens.

Because of its bluish colour, niobium is apparently being used for "body art" products, such as navel rings (see also <http://www.tanb.org/niobium1.html>). No significant uses of Nb have been identified in motor vehicles. Kennedy & Gadd (2000) reported Nb concentrations in key motor vehicle non tail-pipe emission sources. These are summarised in Table 3.30. Concentrations were non detectable in tyres, brake pads and raw bitumen. Low concentrations were measured in brake pad dust and in on-road bitumen.

**Table 3.30 - Niobium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	<2	<2	<2	12
Brake pad dust	1.25	0.5	2.2	6
Tyres	<1	<1	<1	12
Raw bitumen	<1	<1	<1	6
Road bitumen	3.0	2.6	3.5	5

### Niobium in road dust

There appears to be very little information on Nb in the urban environment. This is not unexpected given the few uses with emission sources to the urban environment. Table 3.31 provides a summary of Nb concentrations in road surface particulate material. Tory Street sample 1 (Wellington) was the only sample with an elevated Nb concentration (15.5 mg/kg). The concentration of a number of other elements were also elevated in this sample possibly a result of an accumulation of paint fragments. The Nb content of the samples of gutter dust examined by Pitt & Amy (1973) was 10 mg/kg.

Fig. 3.43 shows the range of Nb concentrations measured in samples of road surface particulates from the Wellington area compared to their Rb concentration. The comparison shows a distinct difference when compared to a suite of coastal sediments from the region but show similar Nb/Rb ratios when compared to soil samples from the region. When grain size separates are examined (Fig. 3.44), all grain size fractions displayed a similar concentration trend with grain size changes when compared to the grain size fractions from Pauatahanui Stream.

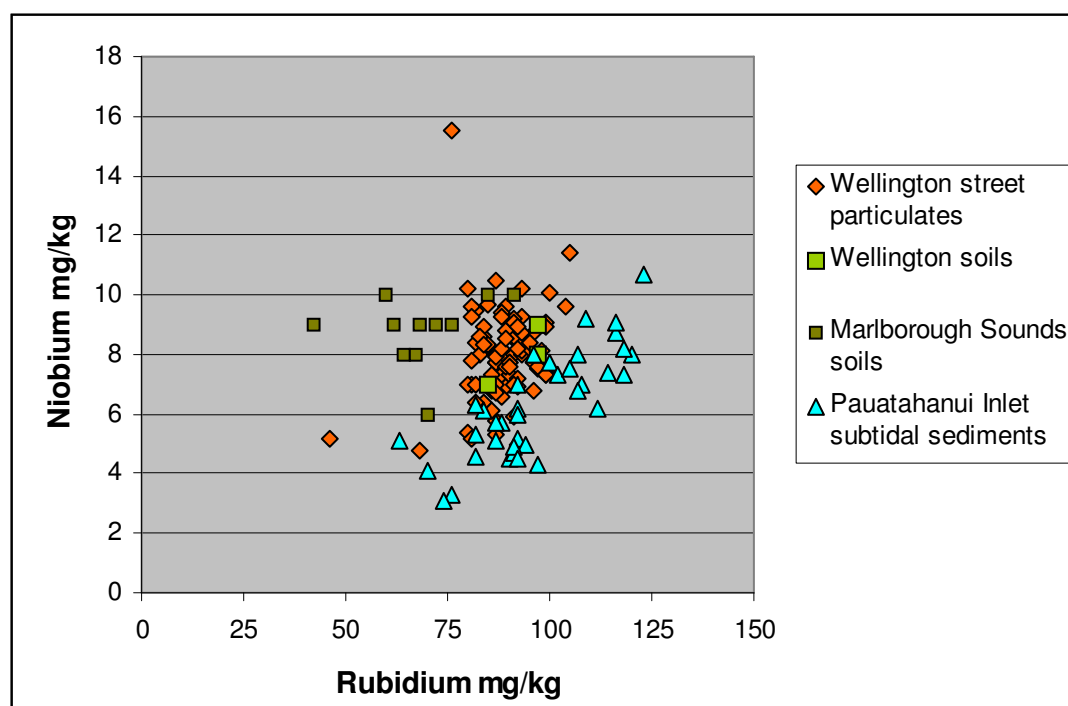
### Contribution from motor vehicles

Given the concentration of Nb measured in brake pads and tyres (key particle/contaminant emission sources) compared to the concentration in soils and sediments, it is unlikely that motor vehicles are significant sources of Nb in the urban environment. Examination of the available data for Nb in road surface particles, it is unclear whether particles on road surfaces are enriched in Nb.

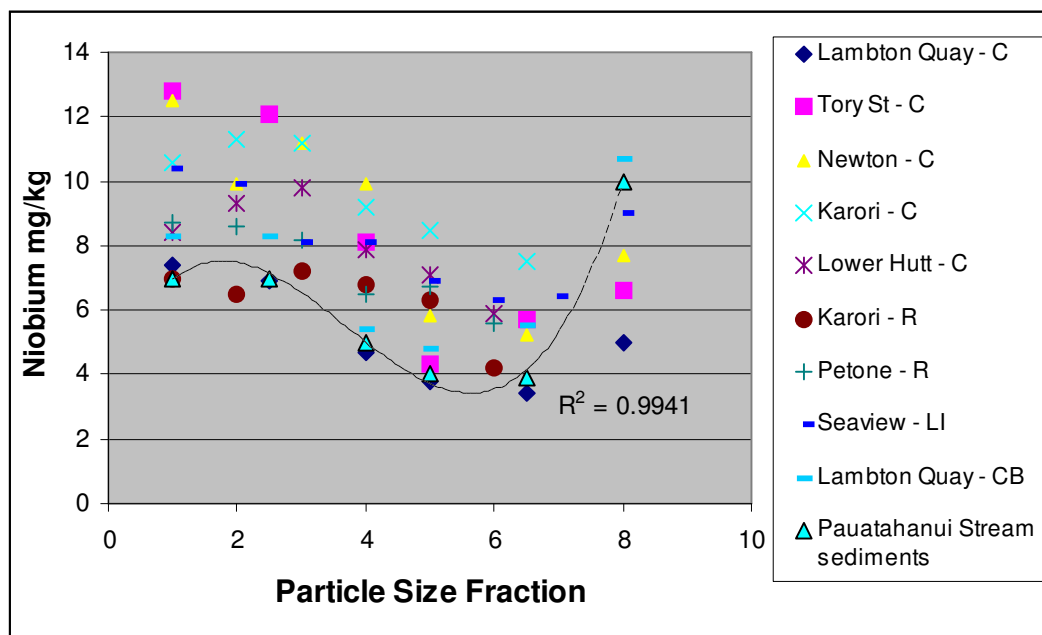
**Table 3.31 - Niobium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median	Range	Particle size	Method	N	Reference
Wellington							
Lambton Quay	C	7.7	7.0-9.5	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	8.6	6.6-15.5	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	7.9	4.8-9.7	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	8.4	6.4-9.6	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	7.1	6.4-8.0	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	7.9	6.1-9.2	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	8.1	5.2-11.4	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	7.6	6.9-8.2	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	8.3	7.7-10.5	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	6.3	5.0-7.5	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	7.6	5.9-9.6	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	8.8	5.2-10.1	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	7.4 (mean)	6.6-8.2	B <2 mm	T-XRF	3	Kennedy (unpublished)

**Notes:** 1 – median presented where available; B - Brush and pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.



**Fig. 3.43 - Niobium concentration in road surface particle samples from Wellington compared to soils and sediments in the region compared on the basis of their rubidium content (Kennedy unpublished data).**



**Fig. 3.44 - Niobium in size fractions of street particle samples and stream sediment samples from the Wellington area.**

### 3.17 Rubidium (Rb)

#### Natural geochemistry

Rubidium has an estimated average crustal abundance of 90 mg/kg (Taylor 1965). Concentrations vary depending upon rock geochemistry. Average Rb concentrations in common sedimentary rocks include shales (140 mg/kg), sandstones (60 mg/kg) and carbonates (3 mg/kg). Rubidium in greywacke-derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 91 mg/kg ( $n=38$ ) and Rb in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 42 to 91 mg/kg (median of location means 68 mg/kg,  $n=93$ ) (Author unpublished data).

#### Sources of rubidium in the urban environment

Rubidium has only limited uses in the urban environment. USDI (2003) reports that Rb products are produced from imported lepidolite ore. Small quantities of Rb, usually in the form of chemical compounds, were used mainly in research and development. Rubidium also was used in electronic and medical applications. Rubidium has few uses, except in the manufacture of photoelectric cells (Belliles 1979). Kennedy & Gadd (2000) examined Rb in key vehicle emission sources. Rubidium was present in brake pads at a low concentration probably through the presence of a number of inorganic minerals in the pads. Rubidium was not present in most tyres and was not detected in raw bitumen (Table 3.32)

**Table 3.32 - Rubidium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	2.18	0.26	76.9	12
Brake pad dust	3.78	0.7	14	6
Tyres	<0.2	<0.2	1.5	12
Raw bitumen	<0.2	<0.2	<0.2	6
Road bitumen	12.4	7.14	12.55	5

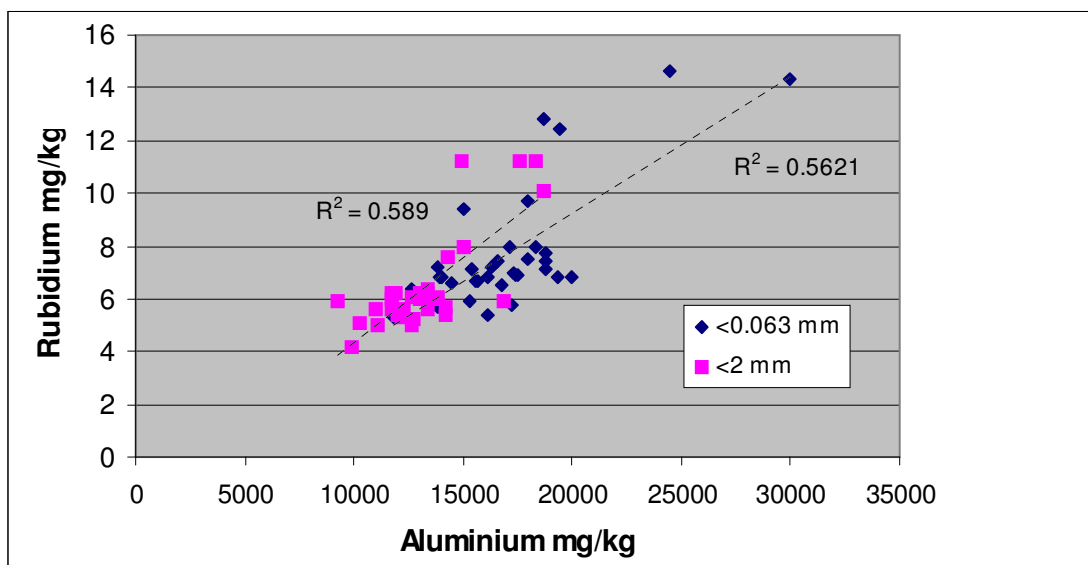
## Rubidium in road dust

Table 3.33 summarises data for Rb in road surface (gutter) particulates from the Wellington area. The data in the table shows that only a small proportion of the total Rb is soluble in strong acid (compare Wellington and Waitakere data). As indicated in previous sections, Rb is considered to be a reference element as it is geochemically 'inert' compared to most elements. Fig. 3.45 shows that the concentration of Rb in street gutter samples from Wellington are well related to the aluminium concentration. Rubidium concentrations are also very similar in concentration to that present in stream sediments in the region (Fig. 3.46).

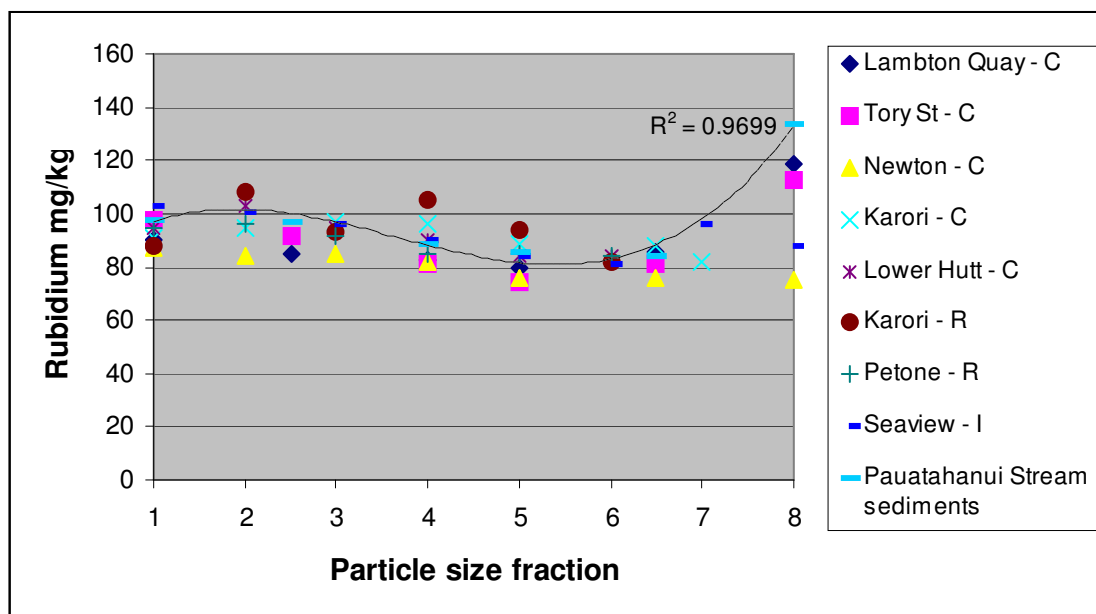
**Table 3.33 - Rubidium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Ottawa	R-1993	37.8	9.8-45.4	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Oslo	M-1994	65 ± 2 <sup>#</sup>	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	29 ± 5 <sup>#</sup>	-	VC	INAA	1	Hopke et al. 1980
Nagpur	M-1992	51.2	48.1-57.4	~<2 mm	INAA	3	Chutke et al. 1995
<b>Wellington</b>							
Lambton Quay	C	82	80-93	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	84	76-91	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	85	68-86	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	89	82-99	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	87	82-89	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	88	68-87	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	90	81-105	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	94	87-100	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	92	92-98	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	95	81-97	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	92	87-104	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	89	46-100	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	93	88-99	B <2 mm	T-XRF	3	Kennedy (unpublished)
Waitakere	R-2002	6.0	4.2-11.2	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	6.8	4.9-14.6	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** # - mean; C, R, LI- streets adjacent to commercial, residential and light industrial landuse; SC - scoop; BSC - Brush and scoop; TA - total acid; SA - Strong acid; WA - Weak acid; INAA - Instrumental neutron activation analysis. ICPMS - Inductively coupled plasma emission spectrometry.



**Fig. 3.45 - Rubidium and aluminium in road surface particulates from Waitakere City (strong acid extraction).**



**Fig. 3.46 - Rubidium in size fractions of street particle samples and stream sediment samples from the Wellington area.**

### Contribution from motor vehicles

The Rb concentration in key vehicle emission sources is low and low compared to the concentration present in soils and particulate material present on urban road surfaces. Overall, motor vehicles are likely to contribute minor amounts of Rb to road surfaces. The overall extent of anthropogenic contribution of urban activities to Rb concentrations on road surfaces is not known.

## 3.19 Silver (Ag)

### Natural geochemistry

Silver (Ag) has a low average crustal abundance (0.07 mg/kg) (Taylor 1965). Silver (Ag<sup>+</sup>) has an ionic radius of 1.26 Å and can substitute for K<sup>+</sup> in a range of common minerals. Ag<sup>2+</sup> (which has an ionic radius of 0.89 Å) however is able to substitute for Ca<sup>2+</sup>, Na<sup>2+</sup> or Fe<sup>2+</sup> in minerals. Silver behaves like copper in mineral formation and as such tends to preferentially enter sulphide phases (e.g., in minerals such as galena, pyrite). Generally in rocks silver would be expected to be present in K feldspars at low concentration. Plant & Raiswell (1983) reported an average crustal abundance of 0.07 mg/kg with most rocks containing <0.1 mg/kg Ag. Christie & Brathwaite (1996) provided an overview of silver in the New Zealand geological/minerals setting. In New Zealand silver mineralization is found in epithermal deposits such as those in the Hauraki Coromandel goldfields and in locations such as Puhipuhi. Silver is associated with most base metal sulphide deposits. There appears to be little published data on Ag in non-mineralised rocks and soils in New Zealand.

### Sources of silver in the urban environment

Silver has widespread uses in our society including the manufacture of coins, jewellery, tableware, alloys, solder and brazing alloys, the photographic industry, electrical equipment and contacts, mirroring, in batteries and in dentistry and medicine (Nordberg & Fowler 1977, Christie & Brathwaite 1996). Silver compounds are also used in filters and other equipment used to purify swimming pool water, drinking water and processing food, drugs and also drinks (WHO 2002). Silver compounds have also been used historically in a variety of pharmaceuticals (especially skin treatments). Silver is also released to the urban environment through combustion processes. Wastewater and

sludge/bio-solids from treatments plants can contain relatively high concentrations of silver. The disposal of sludge and bio-solids to land provides a mechanism for a proportion of the silver to be available for transport within the urban environment.

Kennedy & Gadd (2000) reported low concentrations of Ag in a selection of tyres, brake pads and bitumen in New Zealand (Table 3.34). Given a global non-mineralised crustal concentration of 0.07 mg/kg for silver, the average concentrations present in the motor vehicle sources are low and similar to the crustal concentration. The available data does indicate that some brake pads may contain low but measurable concentrations of silver. It is likely that the silver is present in some of the metals/alloys present in the brake pads. Overall 4 of 18 brake pad/dust samples contained elevated concentrations of Ag when compared to a crustal abundance of 0.1 mg/kg.

**Table 3.34 - Silver in motor vehicle and road source materials (all results mg/kg dry wt).**

Source	Median	Minimum	Maximum	N
Brake pads	<0.4	<0.4	3.9	12
Brake pad dust	0.09	0.06	0.71	6
Tyres	<0.2	<0.2	<0.2	12
Raw bitumen	<0.2	<0.2	<0.2	6
Road bitumen	<0.2	<0.2	<0.2	5

### Silver in road dust

Table 3.35 provides a summary of Ag concentrations in road surface particulate samples from New Zealand and from other international studies. The Ag content of street dust samples from the Wellington City commercial areas were variable, ranging from less than 1 mg/kg to 16.9 mg/kg (Table 3.37). Concentrations of Ag measured in samples from Ottawa by Rasmussen et al. (2001) are similar to those measured in Waitakere City. The majority of the samples examined from Waitakere City had non-detectable concentrations of Ag (Fig. 3.47). Lower concentrations were reported for dusts in Nagpur by Chutke et al. (1995) who reported a median of 0.05 mg/kg (range 0.03-0.91 mg/kg) in transport locations such as bus and train stations. Higher concentrations were noted in some samples at similar concentrations to those reported by Kennedy & Gadd (2000) for brake pads.

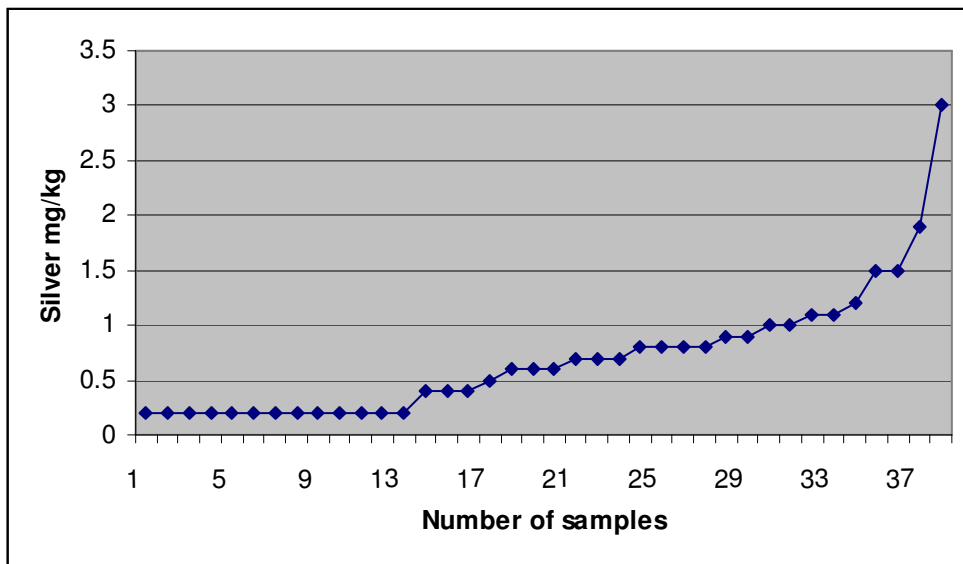
**Table 3.35 - Silver in urban road surface dusts (all results mg/kg dry wt).**

Source	Median <sup>1</sup>	Range	Sample	Analysis	N	Reference
Urbana Ill.	0.20 ± 0.09	-	VC, <0.075 mm	SA	1	Hopke et al. 1980
Ottawa	0.16	0.07-2.18	B, 0.1-0.25 mm.	SA - ICPMS	45	Rasmussen et al. 2001
Nagpur	0.07	0.01-0.09	~<2 mm	INAA	3	Chutke et al. 1995
<b>Wellington</b>						
Lambton Quay – C	2.1	<1-4.7	B, <2mm	XRF	6	Kennedy unpublished
Tory St - C	3.8	<1-10.2	B, <2mm	XRF	4	Kennedy unpublished
Newtown- C	1.4	<1-2.3	B, <2mm	XRF	6	Kennedy unpublished
All samples	2.3	<1-10.2	B, <2mm	XRF	16	Kennedy unpublished
Lambton Quay Catchpits	7.7	<1-16.9	<2 mm	XRF	3	Kennedy unpublished
<b>Waitakere</b>						
All sites	0.65	<0.2-3.0	VC, <0.063 mm	SA - ICPMS	32	This study
All sites	<0.2	<0.2	VC, <2 mm	SA - ICPMS	32	This study

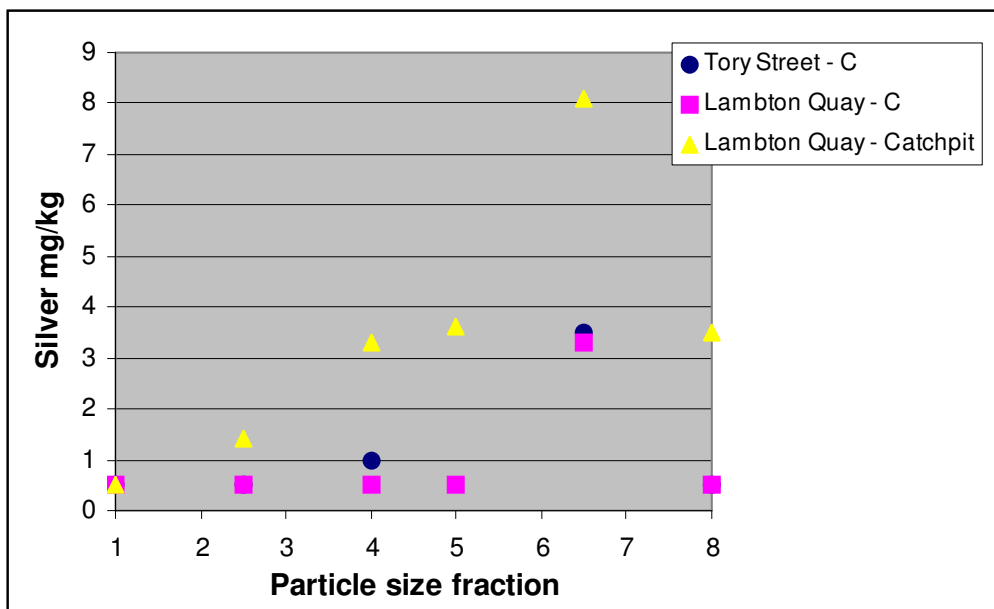
**Notes:** 1 – median presented where available; B = Brush and pan; VC – Vacuum cleaner; SA – Strong acid extraction. XRF – X-ray fluorescence.

The highest concentrations of Ag in road samples were found in stormwater catch basin samples in the older Wellington study. Examination of a series of particle fractions from selected samples from commercial land-use area indicated that peak concentrations of Ag may occur in the 0.035 to 0.15 mm fraction (Fig. 3.48). Silver in the three composite dust sample examined by Pitt & Amy (1973)

contained below 0.5 mg/kg. Samples of street dust from Waitakere City (Auckland New Zealand) contained higher concentrations of Ag in the <0.063 mm fraction compared to the whole sample. In both the Waitakere and Ottawa studies, there is evidence of a low occurrence of elevated concentrations of Ag in street surface particulate material. Similar elevated concentrations were found in the main urban areas of Wellington examined in 1980.



**Fig. 3.47 - Silver concentration in <0.063 mm fraction of road surface particle samples from Waitakere City (Note – detection limit 0.4 mg/kg, with LLD data entered as 0.5 LLD).**



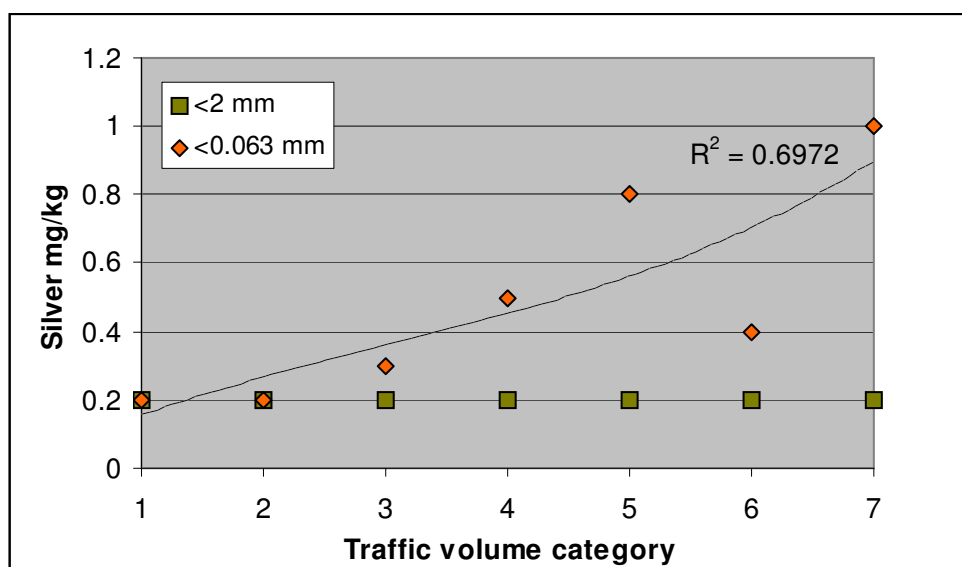
**Fig. 3.48 - Silver in size fractions of street particle samples and stream sediment samples from the Wellington area (note LLD = 1.0 mg/kg, with LLD data entered as 0.5 LLD).**



Examination of the Waitakere City samples (Kennedy & Gadd 2003) indicated that the concentration of Ag may increase with increasing traffic volume. As shown in Fig. 3.43, this was most apparent in the <0.063 mm fraction of the samples.

### Contribution from motor vehicles

Overall, there are low but detectable concentrations of Ag in vehicle emission sources such as brake pads. Fine dust on street surfaces in New Zealand contain detectable concentrations of Ag with <0.063 mm fraction containing elevated concentrations compared to the whole sample. Examination of samples from roads with different traffic volumes suggests that concentrations increase with increasing traffic count as the highest concentrations were consistently found in the samples from locations with the highest vehicle ADT (Fig. 3.49). Based upon the increase in Ag concentration in particulates from the roads with high traffic volumes it is possible that vehicles contribute a moderate proportion of the Ag identified on the road surface. The data suggests that 50% of the Ag present on the high traffic volume roads may be vehicle sourced. This figure has a great deal of uncertainty associated with it.



**Fig. 3.49 - Silver concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003) (Note – LLD 0.4 mg/kg).**

## 3.20 Strontium (Sr)

### Natural geochemistry

Strontium ( $\text{Sr}^{2+}$ ) (which has an ionic radius of 1.18 Å, is midway in size between  $\text{Ca}^{2+}$  and  $\text{K}^+$  (Taylor 1965). Average crustal abundance is estimated to be 375 mg/kg (Plant & Raiswell 1983) with considerable variation in the concentration in common rock types.

Strontium in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 137 mg/kg (n=38) and Sr in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 85 to 356 with one location (D'Urville Island) at 42 mg/kg (median of location means 194 mg/kg, n=90) (Author unpublished data).

## Sources of strontium in urban areas

The main use of strontium compounds such as strontium carbonate is in the faceplate glass of color television picture tubes (77% of the estimated use in the US), ferrite ceramic magnets (8%), pyrotechnics and signals (9%) and other applications (6%) (USDI 2003). Strontium has limited uses in the manufacture of paints, whereas most other uses, including X-ray diagnostic work and other uses such as in sugar refining are quite removed from being potential sources for street dust contamination (Belliles 1979). Kennedy & Gadd (2000) reported concentration data for Sr in tyres and brake pads and bitumen. The study found no detectable Sr in tyres or raw bitumen. Concentrations in brake pads and dust were variable with concentrations ranging from 3.8 to 652 mg/kg (Table 3.36).

**Table 3.36 - Strontium in motor vehicle and road source materials (all results mg/kg dry wt).**

Source	Median	Minimum	Maximum	N
Brake pads	166.5	22	652	12
Brake pad dust	56.75	3.8	88.4	6
Tyres	<0.5	-	-	12
Raw bitumen	<0.5		--	6
Road bitumen	94.8	64.8	120.5	5

## Strontium in road dust

Strontium concentrations were not measured in the street particulate samples collected in the Waitakere City study of Kennedy & Gadd (2003). Analysis were undertaken in a number of published studies and in samples collected in Wellington. Table 3.37 summarises the available data. Fig. 3.50 shows data for Sr in street particulates from the Wellington area along with data for soils and stream sediments from the Wellington area. The data indicates that the Sr concentrations in the road surface particulates, is similar to that seen in soils and sediments.

**Table 3.37 - Strontium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	121 ± 3	92.4-153	B <0.1 mm	T,EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	445	92-735	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Oslo	M-1994	344	-	B <0.1 mm	TA	14	Miguel et al. 1997
Urbana Illinois	~1980	250 ± 50	-	VC	INAA	1	Hopke et al. 1980
Nagpur	M-1992	195	115-210	~<2 mm	INAA	3	Chutke et al. 1995
Manoa Basin Hawaii	R ~2000	428 ± 50	-	SC-<2 mm	ICPAES	13	Sutherland & Tolosa 2000
<b>Wellington</b>							
Lambton Quay	C	256	125-266	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	251	230-268	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	241	230-259	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	245	208-292	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	225	213-245	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	239	218-243	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	246	213-362	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	215	203-257	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	227	165-259	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	227	215-239	B <2 mm	T-XRF	10	Kennedy (unpublished)
Gracefield	LI	238	215-263	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	LI	217	163-281	B <2 mm	T-XRF	12	Kennedy (unpublished)

**Notes:** 1 – median presented where available; M, C, R, LI – streets adjacent to mixed, residential, commercial and light industrial landuse; BSC – Brush and pan or scoop; VC – vacuum cleaner; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS – Inductively coupled plasma emission spectrometry. AAS – Atomic absorption spectrometry.

Examination of the grain size fractions, revealed slightly greater concentrations of Sr in the street dusts compared to the control samples; the difference was seldom greater than 50% and most samples displayed the same concentration trends as the control samples. Highest concentrations were found in the coarsest and 75 to 150 µm fractions (Fig 3.51). Similar grain size trends were found, in a street dust sample by Corrin & Natusch (1977). Pitt & Amy (1973), found that the residential dust sample that they examined contained five times the Sr as the industrial and commercial samples and this was attributed to an accidental spill on the road.

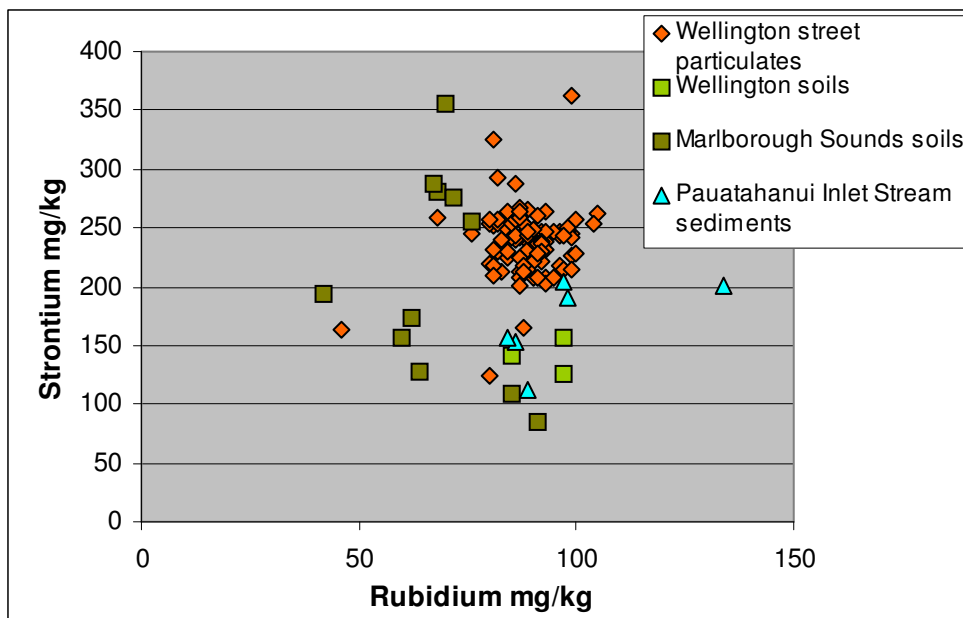


Fig. 3.50 - Strontium concentration in Wellington road surface particles (all data mg/kg).

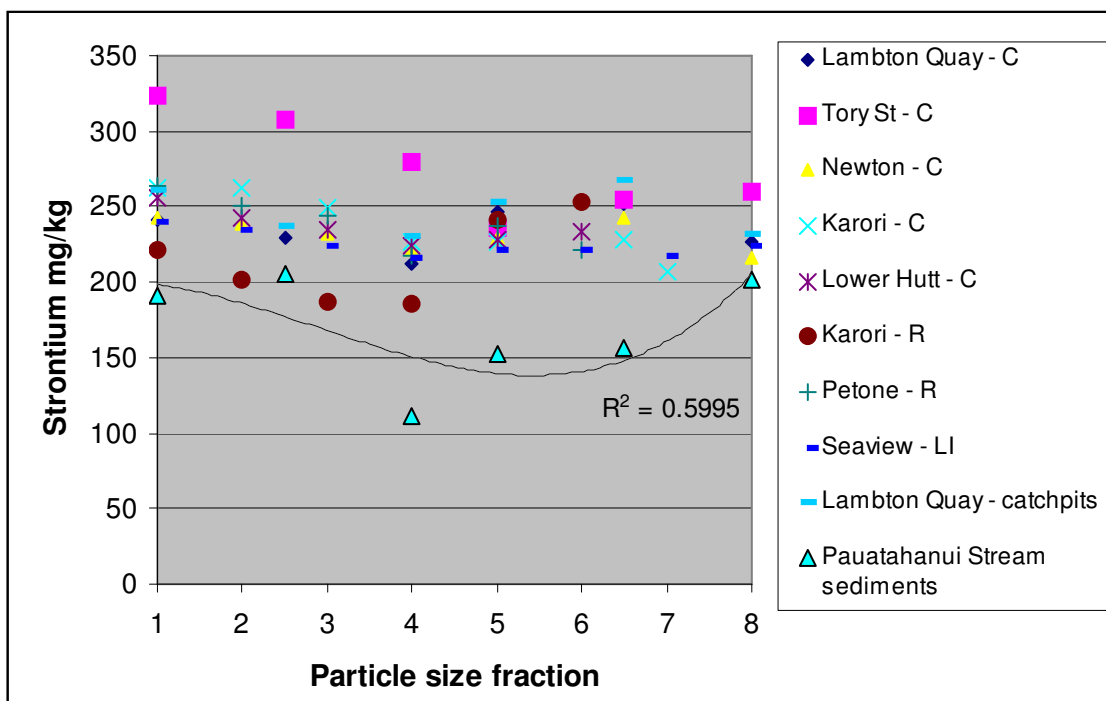


Fig. 3.51 - Strontium in size fractions of road surface particle samples and stream sediment samples from the Wellington area.

## Contribution from motor vehicles

The concentrations of Sr measured in road surface particulate samples are typically lower than the native concentration present in the soil/dust on the road surface. Although Sr concentrations appear higher in road surface particulate samples, there is no obvious source of Sr in key vehicle emission sources. There is little information on the sources of Sr within the urban and urban road environment. At this stage it appears that vehicles contribute little Sr to the road surface.

### 3.21 Tin (Sn)

#### Natural geochemistry

The ionic radii of tin ( $\text{Sn}^{4+}$ ) (0.71 Å) is similar to that of  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$ . Tin has a moderately complex geochemistry as it is found in a number of minerals such as galena and chalcopyrite. Tin has a crustal abundance of about 2 mg/kg (Plant & Raiswell 1983).

ARC (2001) presented data for acid extractable Sn in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.52 shows that concentrations are generally low ranging from median values for key soil groups ranging from 0.375 mg/kg in soils derived from Waitemata Group (n=22) to 1.5 mg/kg (n=9) for soils derived from Quaternary materials.

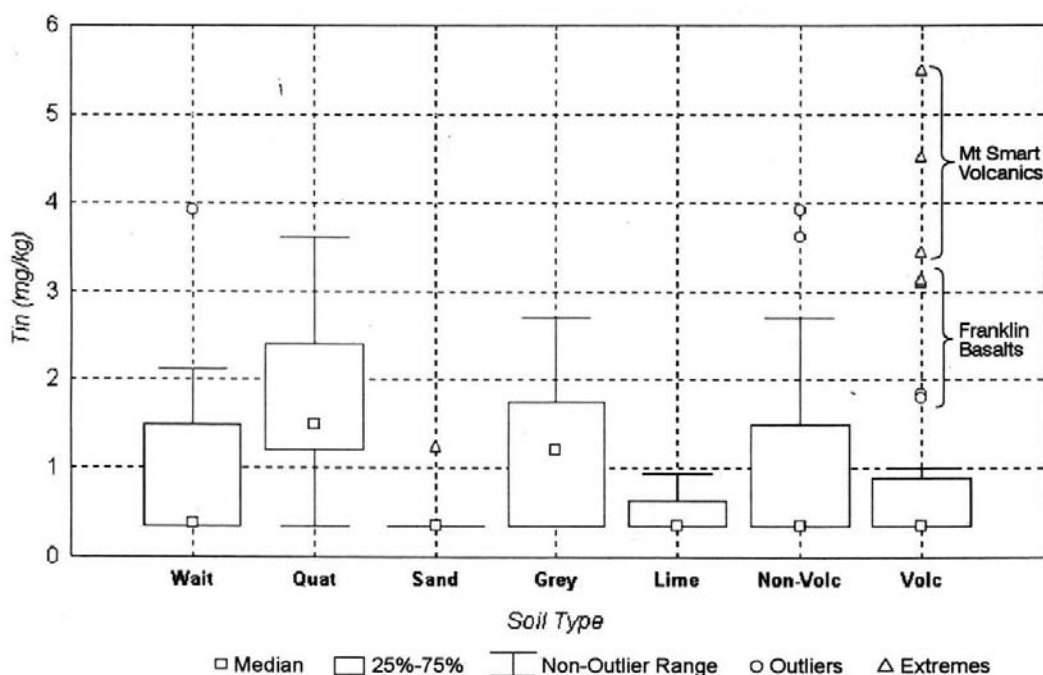


Fig. 3.52 - Tin concentration in Auckland soils (from ARC 2001).

#### Sources of tin in the urban environment

Historically, the main use of tin has been in the making of containers (tins) for food and drinks (WHO 1980). Tin is used to coat copper wire, and as a soldering material. Alloys of tin are used to make dental materials (silver-tin-mercury) (WHO 1980), bronze (copper-tin), and brass (HSDB 1989). Tin is the principal component of pewter. Inorganic tin compounds are used in the glass industry where they are used to give added strength to glass. Inorganic tin compounds also serve as the base for the formulation of colors, as catalysts, and in perfumes and soaps (WHO 1980). Tin uses also include food packaging materials, tin plate, solder, alloys as well as the textiles and plastics industry (Piscator 1977).

Organotin compounds have various industrial uses including the production of plastics including food wrap where they act as stabilizers at 0.5%-2.0% by weight (WHO 1980). Di-substituted organotins are added to polyurethane foams and silicone to increase their strength and to minimize stickiness and odors (WHO 1980). Tri-substituted organotins are useful biocides in agriculture and industry. They function as fungicides, bactericides, antihelminthics, and rodent repellents (WHO 1980). Tributyltins have historically been used as antifoulants in marine paints but their use is now prohibited in New Zealand for most craft. Bis(tributyltin)oxide has also been used as a preservative for wood products, leather, ropes, fabrics, and paper. Although tin is used in many common products little is known about its release to the environment within urban areas. The nature and extent of many of these uses is not known or poorly known in New Zealand

Tin is used in a variety of forms within motor vehicles. Tin appears to have been used in some wheel balancing weights as a replacement for lead weights (although most replacements are steel) (Sander et al. 2000). Sander et al. (2000) note that 6-15% of all PVC is stabilised with organo-tin compounds (tin content 0.4%). PVC is used extensively in motor vehicles for cable and wire coatings. PVC is less common in interior fittings. Tin is used in lead free solder used in vehicles on printed circuit boards and in larger components that required brazing during construction. Emissions from PVC in vehicles is extremely limited unless PVC fragments are lost during accidents or the vehicle is involved in a fire.

Kennedy & Gadd (2000) reported analytical data for tin in the key motor vehicle emission sources. The summary of their data in Table 3.38 indicates that although the concentration of tin in tyres and brake pads is low, brake pads or brake pad dust contained occasional high concentrations due to the use of tin metal in the pad. Five of 18 samples contained tin concentrations of >5 mg/kg and two had concentrations >100 mg/kg.

**Table 3.38 - Tin in motor vehicle and road source materials (all results mg/kg dry wt) (Source Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	1.5	<1.0	15	12
Brake pad dust	5.0	1.0	114	6
Tyres	<0.5	<0.5	1.0	12
Raw bitumen	5.5	<2	99	6
Road bitumen	<0.7	0.5	1.3	5

### Tin in urban road dust

All Sn results for the Lambton Quay commercial, Petone and Gracefield residential samples were above the normal concentrations for Sn in sediments and soils derived from greywacke and argillite (limit of detection 4 mg/kg by XRFs). Pitt & Amy (1973) reported a concentration of 20 mg/kg in the urban street dusts examined by them. Examination of tin in samples collected from road surfaces in Waitakere City (refer Kennedy & Gadd 2003). The analysis of the Waitakere samples showed that finer particles on the road surface contained twice as much Sn as the whole coarser sample (Table 3.39).

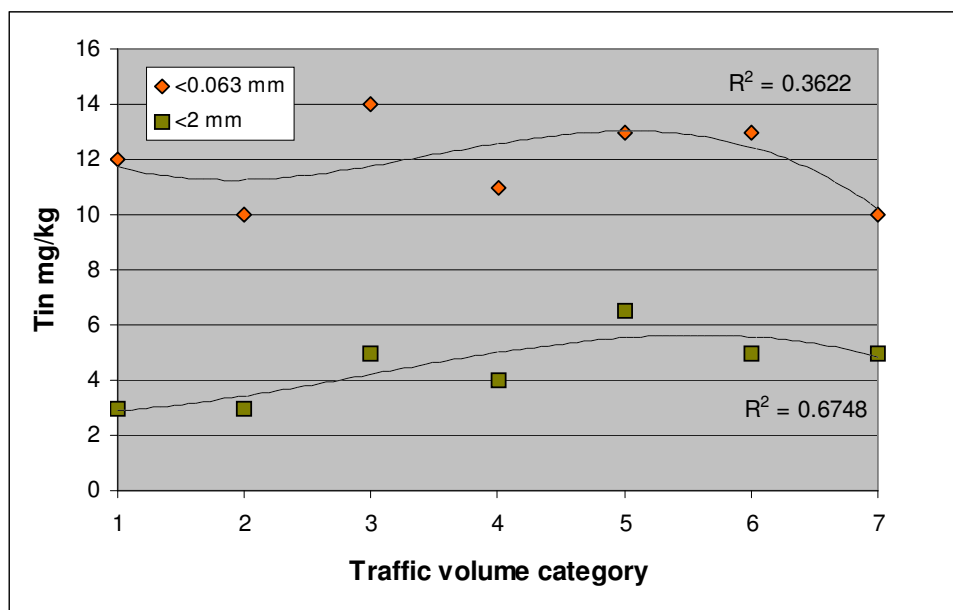
High concentrations of Sn in urban street dusts are not unexpected, considering the wide range of uses that Sn has in the urban environment (refer above). The highest concentration of Sn found in the earlier Wellington study were in the catch basin samples; a characteristic already noted for a number of other metals.

Examination of the relationship between Sn concentrations in Waitakere City samples and traffic volume suggests that there is little relationship between the amount of Sn present and the ADT (Fig. 3.53).

**Table 3.39 - Tin in urban road surface dusts (all results mg/kg dry wt).**

Source	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Ottawa	R-1993	1.19	0.3-25.09	B, 0.1-0.25 mm.	SA - ICPMS	45	Rasmussen et al. 2001
<b>Wellington</b>							
Lambton Quay	C	13 ± 3	7-14	B, <2 mm	XRF	8	Kennedy (unpublished)
Petone	R	11 ± 7	4-23	B, <2 mm	XRF	5	Kennedy (unpublished)
Gracefield	R	9	8-9	B, <2 mm	XRF	2	Kennedy (unpublished)
Catchbasins	C	32 ± 43	32-115	SC, <2 mm	XRF	3	Kennedy (unpublished)
<b>Waitakere</b>							
All sites	R-2002	5	6-48	VC <2 mm	SA	34	This study
All sites	R-2002	11.5	1-233	VC <0.063 mm	SA	34	This study

**Notes:** 1 – median presented where available; C, R, – streets adjacent to residential and commercial landuse; B = Brush and pan; VC – Vacuum cleaner; SA – Strong acid extraction. XRF – X-ray fluorescence.



**Fig. 3.53 - Tin concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

### Contribution from motor vehicles

Analysis of vehicle sources for Sn has shown that motor vehicles are sources of Sn to the road surface environment. As shown in Fig. 3.53, Sn concentration is related to the grain size characteristics of the sample but appears to be poorly correlated to the ADT volume. If the <2 mm fraction variation provides an indication of traffic effects then the data would suggest a possibly 40% contribution in areas of high traffic. However this estimate is considered speculative. There is little information on source of Sn to road surfaces from urban environments.

## 3.22 Titanium (Ti)

### Natural geochemistry

Titanium is one of the key metals in rocks and soils. Christie & Braithwaite (1998) provide an overview of the geochemistry and occurrence of Ti in New Zealand. Titanium in the form of ilmenite is very common in New Zealand as beach sand concentrates. Titanium in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 2,342 mg/kg (n=38) and Ni in

soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 3670 to 6776 mg/kg (median of location means 4,674 mg/kg, n=75) (Author unpublished data).

### Sources of titanium in the urban environment

USDI (2003) reported that in 2002 about 65% of the titanium metal used in the US was used in aerospace applications. The other 35% was used in armor, chemical processing, power generation, marine, medical, sporting goods, and other non-aerospace applications (USDI 2003). It was also reported that in 2002, titanium dioxide pigment (a white pigment) was used in paint, varnishes, and lacquers (49%), paper (16%), plastics (25%), and other uses (10%). Other uses of titanium dioxide included catalysts, ceramics, coated fabrics and textiles, floor coverings, printing ink, and roofing granules (USDI 2003). It is also used as a colour additive in foodstuffs and in cosmetics because of its effectiveness as an ultraviolet sun screen. Titanium is also used in steel alloys, magnets, welding rods and lamp filaments (Berlin 1977, Belliles 1979). Titanium is also used in roadmarking paints with some 800 tons used annually for this purpose alone in Sweden (Horkeby & Malmquist 1977).

Table 3.40 summarises data from Kennedy & Gadd (2000) for the concentration of Ti in key vehicle non tail-pipe emission sources. No Ti was measured in tyres or raw bitumen. Low but variable concentrations of Ti were found in brake pads and brake pad dust.

**Table 3.40 - Titanium in motor vehicle and road source materials (all results mg/kg dry wt) (Source Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	110	30	1660	12
Brake pad dust	315	100	2570	6
Tyres	<10	<10	<10	12
Raw bitumen	<10	<10	<10	6
Road bitumen	3580	2310	3885	5

### Titanium in urban street surface particulate matter

The Ti results for whole gutter dusts fell into the upper range of results for soils and sediments from the Wellington region (Table 3.40). As with other elements the sample from the Tory Street commercial area which was contaminated with paint fragments had a Ti content three times what could be regarded as normal (Table 3.40 and isolated sample result in Fig. 3.54). High concentrations of Ti have previously been identified in the non-magnetic ( $>3.3 \text{ g/cm}^3$ ) fractions of dust taken alongside buildings compared to curbside samples (presumably as a result of the presence of paint fragments in the sample) (Linton et al 1980).

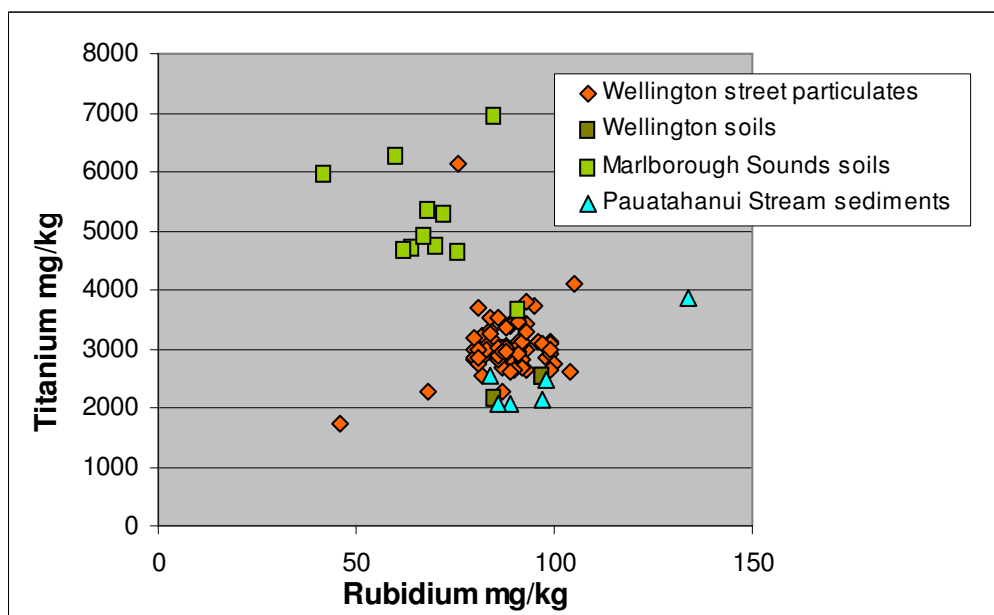
Initial examination of the data in Fig. 3.54 suggests that the Wellington samples have higher concentrations than expected based upon comparison with the Wellington soils and the Pauatahanui Inlet sediments. However, the vehicle source information indicates that on average none of the sources could contribute Ti such that it would increase the concentration of Ti in the road particulates. However, the maximum concentrations identified (Table 3.40) are high enough to contribute Ti to the road surface.

Most of the grain size fractions examined in this study displayed the same trends in Ti concentration as seen in the control samples, with a decrease in the Ti content from the 1 to 2 mm to the 150 to 250  $\mu\text{m}$  fractions, increasing again to the  $<35 \mu\text{m}$  fraction (Fig. 3.55). In the gutter dusts, there appeared to be greater concentrations of Ti in the very coarse fractions which may have been due to contamination by paint fragments and possibly Ti associated with rust fragments. As noted above, the source of the Ti cannot be clearly identified based upon available vehicle source data.

**Table 3.41 - Titanium in street gutter and street surface particulates (all results mg/kg dry weight unless noted).**

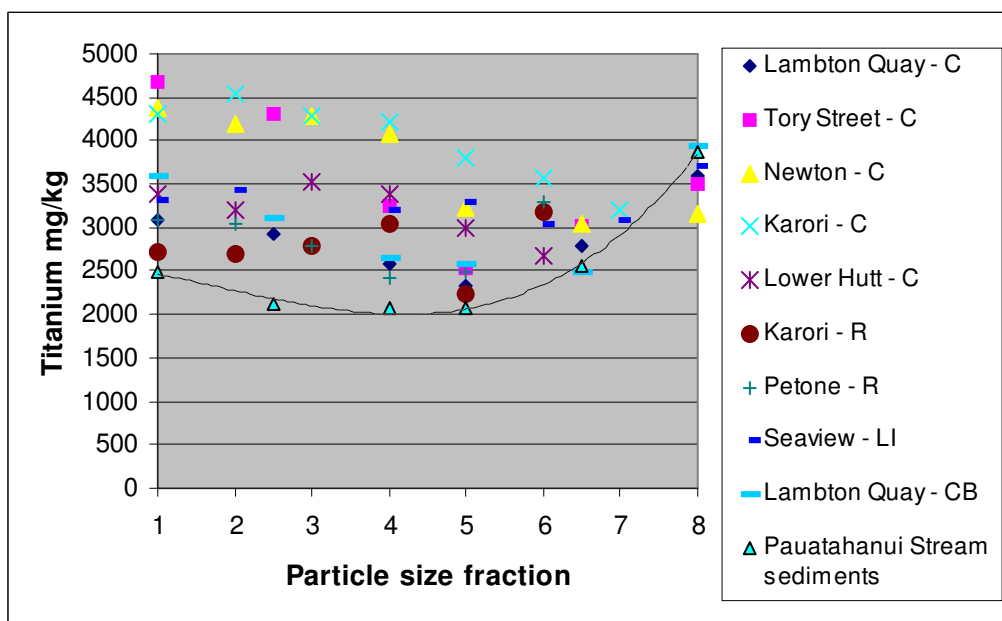
Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	2370 ± 50	1790-2970	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Madrid	M-1994	1100 ± 90	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	7452 ± 123	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
London	C ~1984	1626	1465-1787	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	2475	2210-2740	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	2886	2811-2961	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	764	533-996	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Manoa Basin Hawaii	R ~2000	1.54 ± 0.27%	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch Wellington	C ~1984	548	429-996	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Lambton Quay	C	2910	2710-3410	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	3192	2934-6152	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	3192	2279-3679	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	2990	2544-3386	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	2969	2780-3030	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	3065	2927-3538	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	3023	2743-4118	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	2995	2735-3120	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	2697	2384-3154	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	2789	2498-3080	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	2692	2282-3117	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	3153	1726-3794	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	2980	2950-3300	B <2 mm	T-XRF	3	Kennedy (unpublished)

**Notes:** 1 – median presented where available; M, C, R, LI – streets adjacent to mixed, residential, commercial and light industrial landuse; B – Brush and scoop, pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.



**Fig. 3.54 - Titanium concentration in Wellington road surface particles (all data mg/kg).**





**Fig. 3.55 - Titanium in size fractions of road surface particle samples and stream sediment samples from the Wellington area.**

### Contribution from motor vehicles

Although Ti is a relatively common element in urban areas, concentrations in vehicle sources such as brake pads were low (on average typically 10% of the concentration in particulate matter found on road surfaces). It is likely that motor vehicles contribute a small amount of Ti to road surfaces. Natural concentrations are high.

## 3.23 Vanadium (V)

### Natural geochemistry

ARC (2001) presented data for acid extractable V in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.56 shows that the median values range for key soil groups typically range from 36.45 mg/kg in soils derived from Greywacke (n=6) to 57.9 mg/kg (n=12) for soils derived from Quaternary materials. Soils derived from volcanic materials contained higher concentrations (median 155 mg/kg, n=33). This latter elevated concentration has the potential to influence local road surface material concentrations of V.

Vanadium in greywacke-derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 70 mg/kg (n=38) and V in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 92 to 220 mg/kg (median of location means 151 mg/kg, n=82) (Author unpublished data).

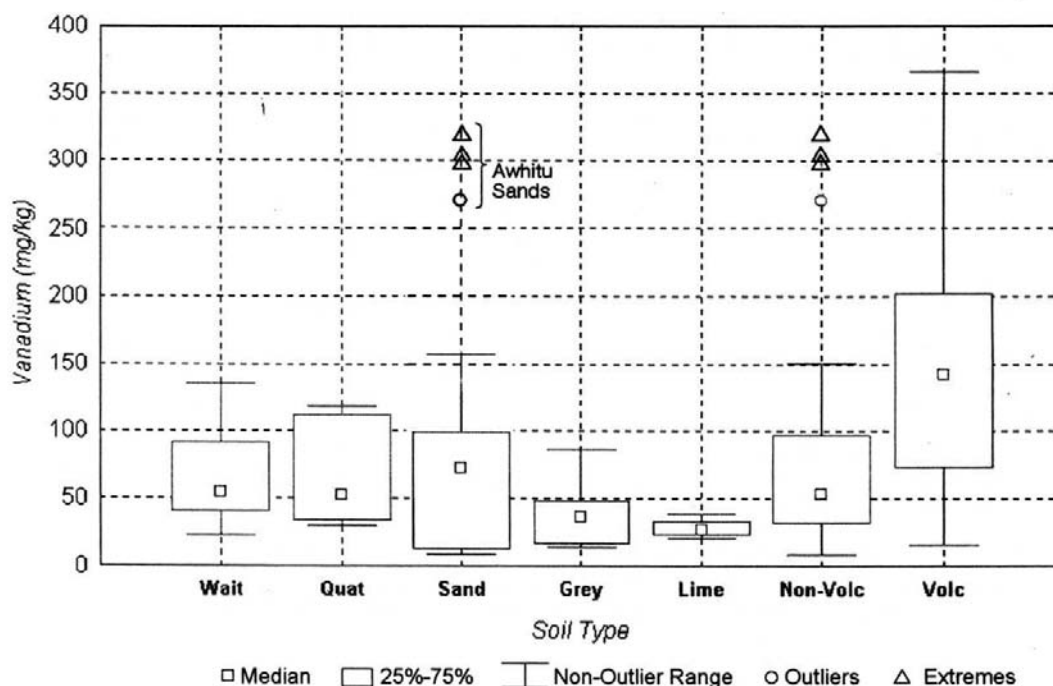


Fig. 3.56 - Vanadium concentration in Auckland soils (from ARC 2001).

### Sources of Vanadium in the urban environment

Most (about 90%) of the V used in the US is used as an alloying agent for iron and steel. Of the other uses for vanadium, the major non metallurgical use was in catalysts for the production of maleic anhydride and sulfuric acid (USD1 2003). Vanadium compounds are used in steel hardening and in non-ferrous alloys and will therefore come from vehicle bodywork corrosion. Vanadium is also used in the manufacture of pigments and in photography (Belliles 1979) and V is also present in petroleum products. Kennedy & Gadd (2000) examined V in key non-exhaust vehicle emission sources. The poor detection limit precluded accurate data being obtained (Table 3.42). The results showed that overall the concentrations in all possible sources were low.

Table 3.42 - Vanadium in motor vehicle and road source materials (all results mg/kg dry wt) (Source Kennedy & Gadd 2000).

Source	Median	Minimum	Maximum	N
Brake pads	<100	<100	400	12
Brake pad dust	~10	<10	20	6
Tyres	<50	<50	<50	12
Raw bitumen	<50	<50	110	6
Road bitumen	75	60	80	5

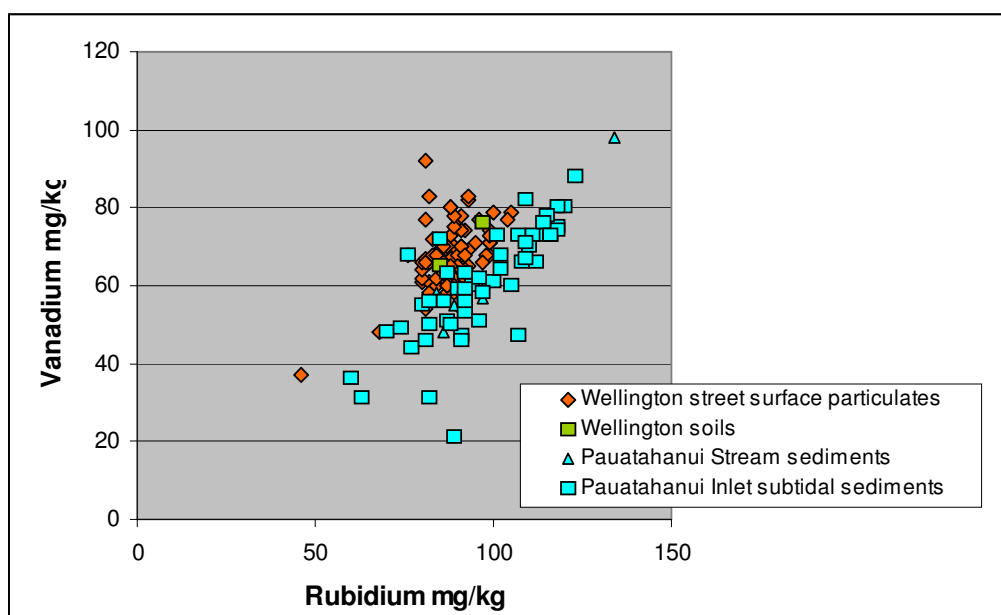
### Vanadium in street surface particulate matter

Fig. 3.57 shows that V in whole gutter dusts appeared to be within the expected range for soils and sediments of the region. Trends in the V concentration of the grain size fractions were generally similar to the control samples, but in the medium sand fractions the concentration appeared to be some 50 to 100% greater than the control samples (Fig. 3.58).

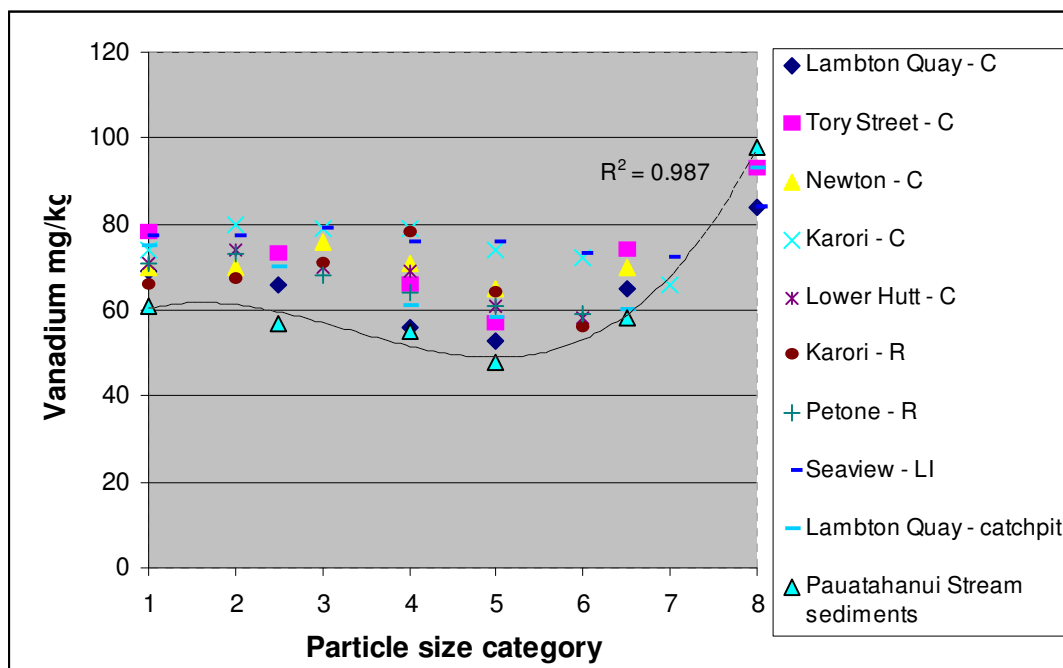
**Table 3.43 - Vanadium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Hong Kong	M-2001	36.6 ± 2.4	14.5-51.5	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Ottawa	R-1993	34.2	13.8-56.2	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	17 ± 2	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
London	C ~1984	71	62-80	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	73	60-86	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	142	78-206	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	113	97-129	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Manoa Basin Hawaii	R ~2000	203 ± 25	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1984	48	41-68	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Wellington							
Lambton Quay	C	61	58-83	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	68	66-73	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	63	48-69	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	67	65-74	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	60	58-69	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	74	66-78	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	69	66-74	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	71	64-72	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	66	57-73	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	61	54-68	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	65	54-77	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	75	37-92	B <2 mm	T-XRF	12	Kennedy (unpublished)
LQ CB	C	73	65-83	B <2 mm	T-XRF	3	Kennedy (unpublished)
Waitakere	R-2002	<100	<100-529	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	117	<100-417	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R – streets adjacent to urban park, mixed, residential and commercial landuse; B – Brush and scoop, pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.



**Fig. 3.57 - Vanadium concentration in Wellington road surface particles (all data mg/kg).**



**Fig. 3.58 - Vanadium in size fractions of road surface particle samples and stream sediment samples from the Wellington area.**

### Contribution from motor vehicles

Data on the concentration of V in non-exhaust emission sources indicates that motor vehicles may contribute some V to the road surface. The amount is uncertain due to analytical detection limits in analysis undertaken being high compared to the expected natural concentration. Examination of V data in New Zealand road surface particulate samples indicates that concentrations may be elevated compared to what might be expected naturally. The proportion of anthropogenic V present on road surfaces is not known with any certainty. Vehicles may contribute V through several sources but the amount and proportion of the overall urban contribution is not known. Examination of the Waitakere City data did not show any significant changes in V concentration with increasing vehicle numbers at the sites sampled.

## 3.24 Yttrium (Y)

### Natural geochemistry

Yttrium ( $Y^{3+}$ ) with an ionic radius of 0.92 Å is similar in size to  $Ca^{2+}$ . As a result it typically occupies Ca positions in minerals (Taylor 1965). Crustal abundance is estimated at about 30 mg/kg with a moderate range in concentration in common rock types (e.g., 25 mg/kg in basalt, 30 mg/kg in greywacke to 40 mg/kg in granite).

### Sources in the urban environment

Yttrium has a wide range of uses. USDI (2003) reports the key uses of Y as lamp (trichromatic fluorescent lights) and cathode-ray-tube phosphors (in colour televisions and computer screens) (82%), oxygen sensors and laser crystals (13%) and ceramics and abrasives (5%). AS described by USDI (2003), "yttrium was also used as a stabilizer in zirconia, in alumina-zirconia abrasives, wear-resistant and corrosion-resistant cutting tools, seals and bearings, high-temperature refractories for continuous-casting nozzles, jet engine coatings, oxygen sensors in automobile

engines, and simulant gemstones. In electronics, yttrium-iron-garnets were components in microwave radar to control high frequency signals. Yttrium was an important component in yttrium-aluminium garnet laser crystals used in industrial cutting and welding, medical and dental surgical procedures, temperature and distance sensing, photoluminescence, photochemistry, digital communications, and nonlinear optics. Yttrium was also used in heating element alloys, superalloys, and high-temperature superconductors”.

Yttrium was not determined by Kennedy & Gadd (2000). Yttrium has no identifiable uses that are likely to be sources for urban environmental contamination, except that it is released after the combustion of coal and petroleum products (Dunlap 1981).

### Yttrium in urban dusts

Table 3.44 presents a summary of Y concentration data for street particulate samples collected in the Wellington area. Initial examination of the data in the table suggests that the concentrations are relatively similar. Comparison of the Y/Rb ratio of soils and sediments from the region indicated no difference in the Y content of the gutter dusts examined (Fig. 3.53).

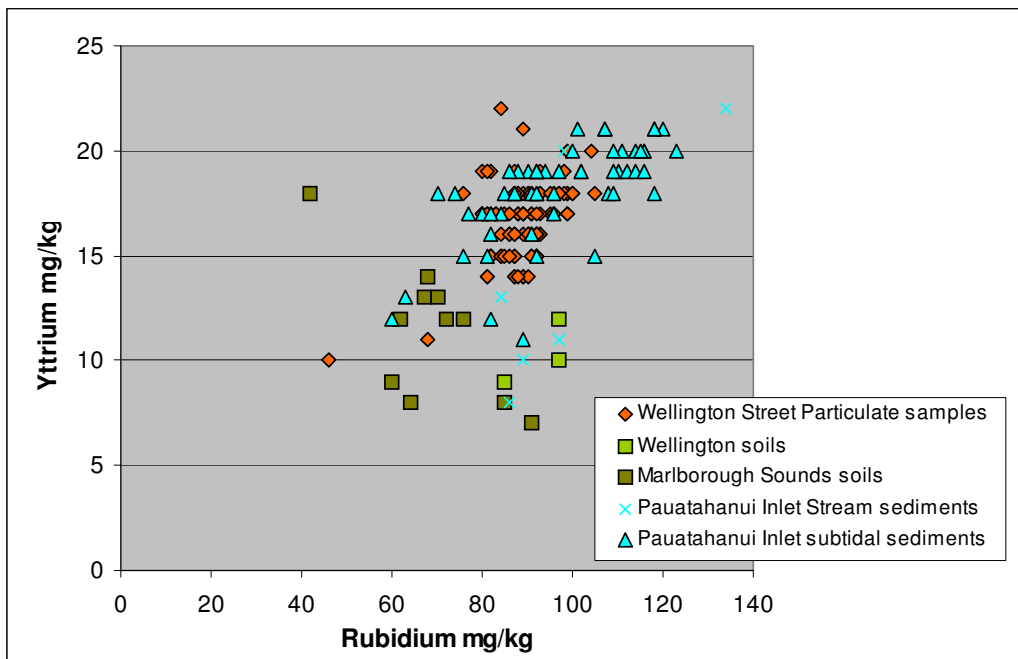
**Table 3.44 - Yttrium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median	Range	Particle size	Method	N	Reference
Wellington							
Lambton Quay	C	17	17-21	B <2 mm	T-XRF	8	Kennedy (unpublished)
Tory St.	C	18	16-22	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	15	11-17	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	16	14-18	B <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	15	14-17	B <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	16	14-18	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	17	14-19	B <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	18	16-20	B <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	18	14-18	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	17	16-18	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	LI	20	15-20	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	LI	19	10-19	B <2 mm	T-XRF	12	Kennedy (unpublished)
Lambton Quay CB	C	18	17-19	B <2 mm	T-XRF	3	Kennedy (unpublished)

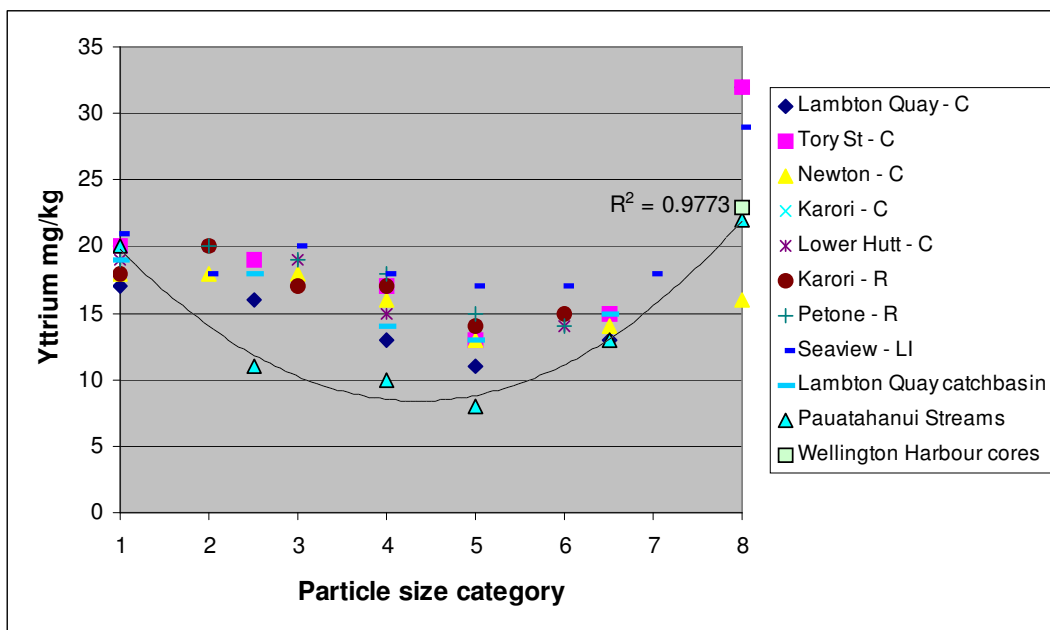
**Notes:** SC – scoop; BSC – Brush and scoop; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis.

### Contribution from motor vehicles

There is no indication that Y is emitted in even minor amounts by vehicles. Concentrations in road surface particulates in New Zealand do not show any identifiable change in concentration compared to soils and sediments.



**Fig. 3.59 - Yttrium concentration in Wellington road surface particles (all data mg/kg).**



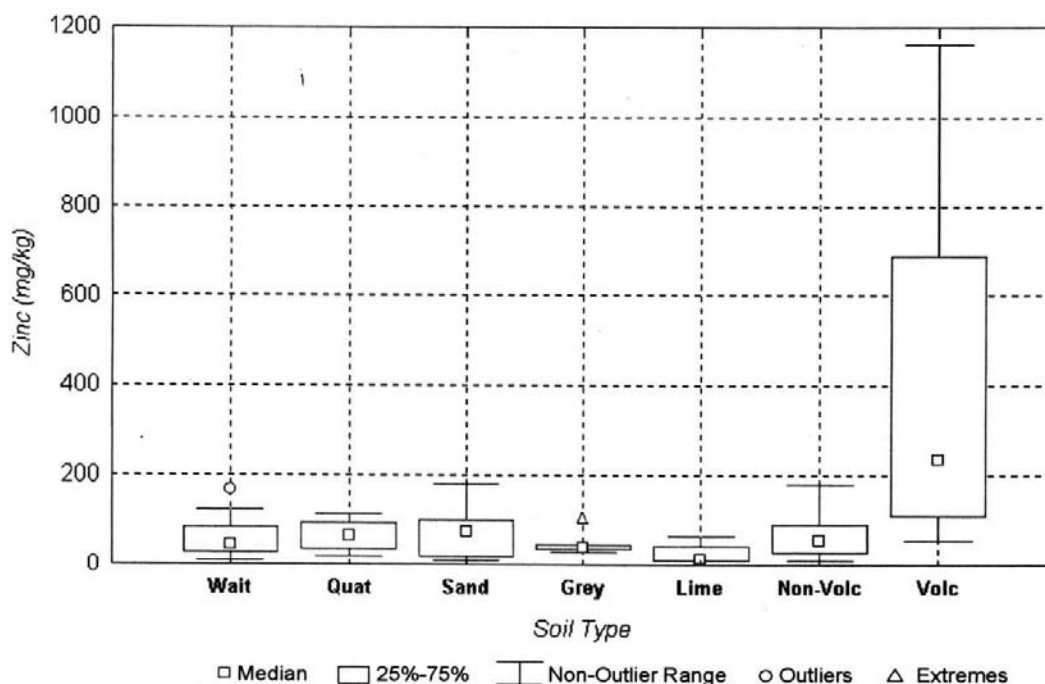
**Fig. 3.59: Yttrium in size fractions of street particle samples and stream/coastal sediment samples from the Wellington area.**

### 3.25 Zinc (Zn)

#### Natural geochemistry

ARC (2001) presented data for acid extractable Zn in Auckland soils derived from different geologic parent materials. The data which is summarised in Fig. 3.59 shows that the median values range for key soil groups typically range from 39.15 mg/kg in soils derived from Greywacke (n=6) to 280

mg/kg (n=33) for soils derived from volcanic materials. This latter elevated concentration has the potential to influence local road surface material concentrations of Zn.



**Fig. 3.60 - Zinc concentration in Auckland soils (from ARC 2001).**

Zinc in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 66 mg/kg (n=38) and Ni in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 46 to 98 mg/kg (median of location means 76 mg/kg, n=91) (Author unpublished data).

### Zinc sources in the urban environment

USDI (2003) reported that of the total Zn consumed in the US, about 55% was used in galvanizing, 17% in zinc-base alloys, 13% in brass and bronze, and 15% in other uses. Zinc compounds and dust were used principally by the agriculture, chemical, paint, and rubber industries. Zinc is used in a wide variety of materials including galvanising on iron products, in alloys, in rubber, glazes, enamels, paper and glass (Belliles 1979).

Shaheen (1975) noted that organo-zinc compounds are added to motor oils as stabilisers. Because of its relative mobility, it is likely that some redistribution of Zn will occur in gutter dusts, hence its identification in the other two main phases; soil and cement, by Hopke et al. (1980).

Table 3.45 summarises data from for Zn in key vehicle emission sources (from Kennedy & Gadd 2000). Raw bitumen and road bitumen were found to have relatively low concentrations of Zn. Tyres contain significant amounts of Zn as a consequence of the use of Zn oxide in the vulcanisation process. Concentrations in brake pads and brake pad wear dust were high and highly variable.

**Table 3.45 - Zinc in motor vehicle and road source materials (all results mg/kg dry wt) (Source Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	694	32.5	34,500	12
Brake pad dust	1600	360	9,630	6
Tyres	8,310	1190	18,300	12
Raw bitumen	5.5	<2	99	6
Road bitumen	53.5	47.4	79.9	5

### Zinc in urban street particles

Table 3.46 and Fig. 3.62 illustrate the obvious difference between the Zn content of the street dusts examined and the normal range of Zn found in soils and sediments in the Wellington region. Zinc concentrations recorded in this work are generally similar to the averages recorded in other studies of urban gutter dusts. Results from recent studies in England, Hong Kong, The United States Japan and New Zealand are summarised in Table 3.46. Asami (1982) presents further data for Zn in street dusts from Osaka, Tokyo, Nagoya, Shizuoka and Ube. Mean Zn concentrations were in the range 500 to 800 mg/kg with one outlying sample from Tokyo recording 9,120 mg/kg. Harrison (1979) recorded higher Zn concentrations in car park dusts compared to roadway dusts. Variations within each land use category are high in all studies examined.

Examination of the grain size data revealed that for most samples there was an increase in the Zn concentration in the finest fraction, which was a similar trend to that seen in the control samples (Fig. 3.63). The catch basin sample had a high Zn concentration in its coarse fraction, probably resulting from the accumulation of Zn containing metal fragments in the catch basin. Linton et al. (1980) found higher concentrations of Zn in the non-magnetic fractions of a street dust compared to the magnetic fraction, with the greatest concentration of 14,000 mg/kg in the <45 µm non-magnetic fraction. The elevation of Zn in the samples examined in this study suggests paint as a source in some samples in addition to car tyres (as seen in the correlation of elevated Ba data in a number of samples, the abundance of these elements in the coarser fractions and the presence of rubber fragments). Zinc was also well correlated with elevated Fe in some samples (possibly metal fragments) and the correlation with general soil elements suggests the re-association of Zn with soil particles.

ARC (1992) reported Zn data for six particles size fractions from a residential suburb (2 samples) and one sample from an industrial suburb. Concentrations ranged from 198-278 mg/kg (1-2 mm) to 305-811 mg/kg (<0.047 mm). Samples from roads in Waitakere City contained more than twice the zinc concentration in the <0.063 mm fraction compared to the <2 mm sample (Table 3.46). The difference is comparable to data reported by Ng et al. (2003) for Auckland City (Refer Fig. 3.21).

Zinc appears to be present in gutter dusts in four main phases (Hopke et al. 1980). One of the major forms is derived from tyre wear (intermediate size, low density and non-magnetic particles). Zinc associated with large high-density non-magnetic particles may be from galvanising materials or possibly lead zinc solders (Linton et al 1980). Galvanising chips have also been found in urban dusts by Weiner & Malinoski (1970). Small high-density particles containing Zn identified by Hopke et al. (1980) are probably derived from car exhausts

### Contribution from motor vehicles

Zinc is one of the most common metals associated with road surface particulate matter. Examination of non-tailpipe emission sources in vehicles shows that there are high concentrations of Zn in sources such as tyres and brake pads relative to natural Zn in soil concentrations. Motor vehicles are a key source of Zn to road surfaces in urban areas. Table 3.64 shows the median zinc concentration for the sites of different traffic volume in Waitakere City. The <2 mm fraction showed a steady increase in concentration as traffic volume increased. The <0.063 mm fraction showed a similar increase except for the elevated concentration in one of the lower traffic volumes.



**Table 3.46 - Zinc in gutter and road surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Birmingham	M <2003	388.4	81.3-3164.8	B <1 mm	SA-AAS	100	Charlesworth et al. 2003
Coventry	M <2003	300	93-3038.2	B <1 mm	SA-AAS	49	Charlesworth et al. 2003
Hong Kong	M-2001	3840 ± 70	2250-6380	B <0.1 mm	T-EDXRF	8	Yeung et al. 2003
Hong Kong	UP-~2001	1450 ± 869	-	BP-<2 mm	SA-ICPAES	45	Li et al. 2001
Taejon, Korea	M-1996	214	67-495	B <0.18 mm	SA-AAS	31	Kim et al. 1998
	R-1996	107	59-373	B <0.18 mm	SA-AAS	41	Kim et al. 1998
Nagpur	M-1992	656	461-841	~<2 mm	INAA	3	Chutke et al. 1995
Ottawa	R-1993	98.7	28.7-302.5	B 0.1-0.25 mm	SA-ICPMS	45	Rasmussen et al. 2001
Madrid	M-1994	476 ± 30	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Oslo	M-1994	412 ± 61	-	B <0.1 mm	TA-ICPMS	14	Miguel et al. 1997
Urbana Illinois	~1980	320 ± 30	-	VC	INAA	1	Hopke et al. 1980
London	C ~1984	1173.5	1171-1176	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
New York	C ~1984	1811	984-2638	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	467.5	315-620	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	764.5	533-996	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Manoa Basin Hawaii	R ~2000	434 ± 94	-	SC-<2 mm	INAA	13	Sutherland & Tolosa 2000
Christchurch	C ~1984	429	365-850	< 0.963 mm	INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1981	482 ± 115	277-795	< 0.25 mm	SA-AAS	147	Fergusson & Simmonds 1983
Wellington							
Lambton Quay	C	690	243-4377	B <2 mm	T-XRF	9	Kennedy (unpublished)
Tory St.	C	993	609-3126	B <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	952	504-2332	B <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	521	251-805	B <2 mm	T-XRF	7	Kennedy (unpublished)
Karori	C	1271	751-1764	B <0.063 mm	T-XRF	4	Kennedy (unpublished)
Lower Hutt	C	785	433-911	B <2 mm	T-XRF	8	Kennedy (unpublished)
Lower Hutt	C	1144	895-1233	B <0.063 mm	T-XRF	4	Kennedy (unpublished)
Newtown	R	1041	668-1330	B <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	684	177-2670	B <2 mm	T-XRF	12	Kennedy (unpublished)
Karori	R	1316	432-4246	B <0.063 mm	T-XRF	11	Kennedy (unpublished)
Taita	R	639	229-3067	B <2 mm	T-XRF	8	Kennedy (unpublished)
Taita	R	965	411-3983	B <0.063 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	428	141-2297	B <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	364	260-467	B <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	I	434	263-1658	B <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	I	680	147-1621	B <2 mm	T-XRF	12	Kennedy (unpublished)
Seaview	I	1043	395-2304	B <0.063 mm	T-XRF	7	Kennedy (unpublished)
LQ CB	C	1317	695-1349	B <2 mm	T-XRF	3	Kennedy (unpublished)
Auckland							
Freemans Bay	R	1052	657-2377	B <0.063 mm	SA-AAS	8	Kennedy et al (1988)
Remuera	R	768	303-2315	B <0.063 mm	SA-AAS	8	Kennedy et al (1988)
Waitakere	R-2002	326	130-983	VC <2 mm	SA-ICPMS	34	Kennedy & Gadd 2002
Waitakere	R-2002	723	267-2690	VC <0.063 mm	SA-ICPMS	34	Kennedy & Gadd 2002

**Notes:** 1 – median presented where available; UP, M, C, R – streets adjacent to urban park, mixed, residential and commercial landuse; B – Brush and scoop, pan; VC – vacuum cleaner; TA – total acid; SA – Strong acid; WA – Weak acid; INAA – Instrumental neutron activation analysis. ICPMS/AES – Inductively coupled plasma emission spectrometry/atomic absorption spectrometry; AAS – Atomic absorption spectrometry.

Davis et al. (2001) estimated source contributions for Zn in urban areas. They determined that for brick buildings, tire wear contributed 25% of the Zn; brake pad wear 3%; dry and wet deposition 5%; roof runoff 7% and building sidings 59%. For buildings with vinyl sidings tire wear contributed 58%; brake pad wear 8%; dry and wet deposition 12%; roof 16% and sidings 4%. Timperley et al. (2003) determined that roads contributed on average 16% of the Zn in urban runoff in Auckland City. The relationship between Zn concentration in road surface particulates in Waitakere City was not strong. However, in the <2 mm samples, the relationship suggests that high traffic may account for 40% of the Zn present in the road surface.

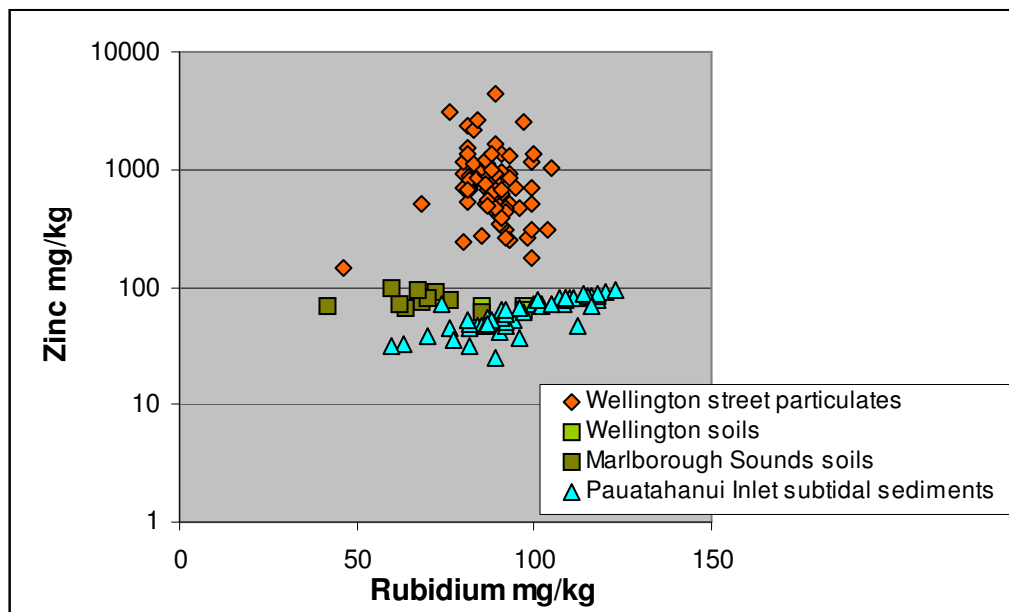


Fig. 3.62 - Zinc concentration in Wellington road surface particles (all data mg/kg).

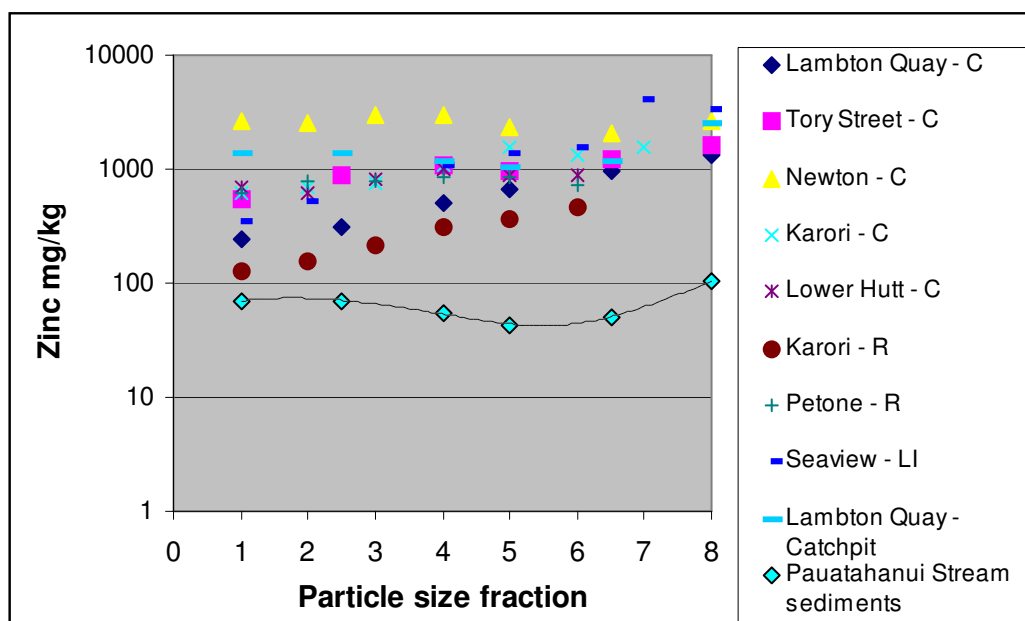


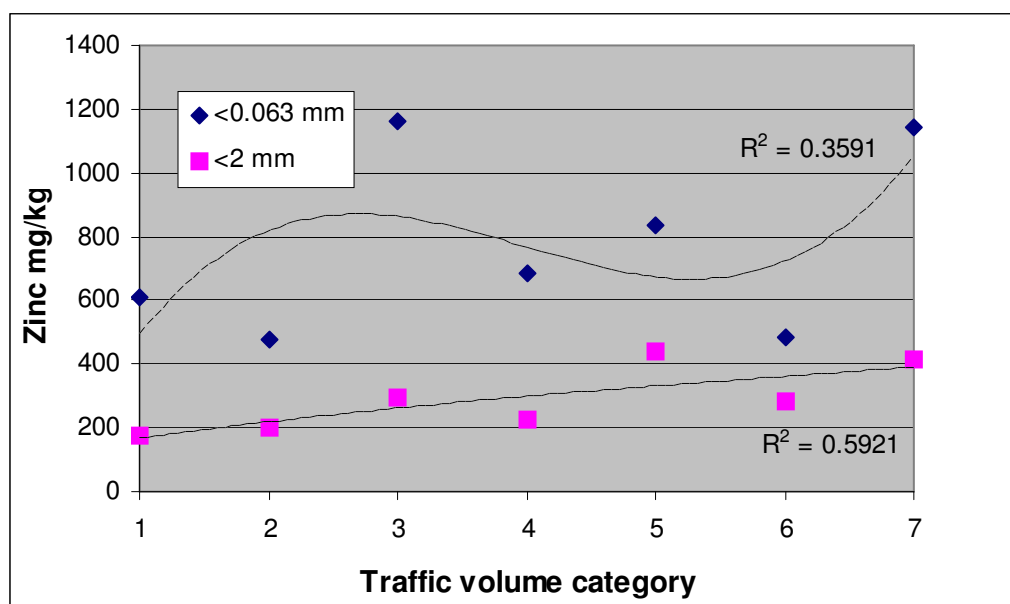
Fig. 3.63 - Zinc in size fractions of road surface particle samples and stream/coastal sediment samples from the Wellington area.

### 3.26 Zirconium (Zr)

#### Natural geochemistry

Because of the ionic radii (0.79 Å) and the charge balance of Zr ( $Zr^{4+}$ ) Zr tends to form a separate mineral phase (zircon –  $ZrSiO_4$ ) with limited substitution for  $Ti^{4+}$  ( $r = 0.68\text{Å}$ ) in other minerals. The crustal abundance of Zr is about 165 mg/kg with most rock types having similar concentrations with some exceptions (Taylor 1965). As Zr is found in zircons it tends to have a particular particle size distribution as zircons are commonly found in the fine sand fraction of many soils and sediments.

Zirconium concentrations in greywacke derived soils from Lake Ponui in the Wairarapa contained a mean concentration of 209 mg/kg (n=38) and Ni in soils from 11 locations in the Marlborough Sounds had mean concentrations ranging from 120 to 219 mg/kg (median of location means 203 mg/kg, n=90) (Author unpublished data).



**Fig. 3.64 - Zinc concentration in road surface particles at sites of different traffic volumes in Waitakere City (site and traffic Kennedy & Gadd 2003).**

## Sources

Zirconium has a number of uses in the manufacture of pigments, water repellent textiles, ceramics, abrasives (e.g., for sandblasting), cigarette lighter flints, medical cosmetics and in the past it has been used in television tubes and incandescent lighting (Belliles 1979). The largest uses for Zr are in ceramics, opacifiers, refractories and foundry applications (USDI 2003) and it is also used in welding rods, welding rod coatings. There do not appear to be any significant uses for Zr in motor vehicles (Sander et al. 2000).

## Zirconium in urban street dusts

Zirconium was identified by Pitt & Amy (1973) as being one of the elements that varied considerably in gutter dusts. This is not surprising given its geochemical/mineralogical distribution (refer above). Available data for Zr in road surface particulates is presented in Table 3.47. Most of the dust samples examined displayed similar trends to the control samples and the whole dust results fell into the expected range for soils of comparable grain size (Fig. 3.65).

Fig. 3.66 shows the high concentration of Zr in the 35 to 150  $\mu\text{m}$  fraction of the control samples due to the presence of zircons.

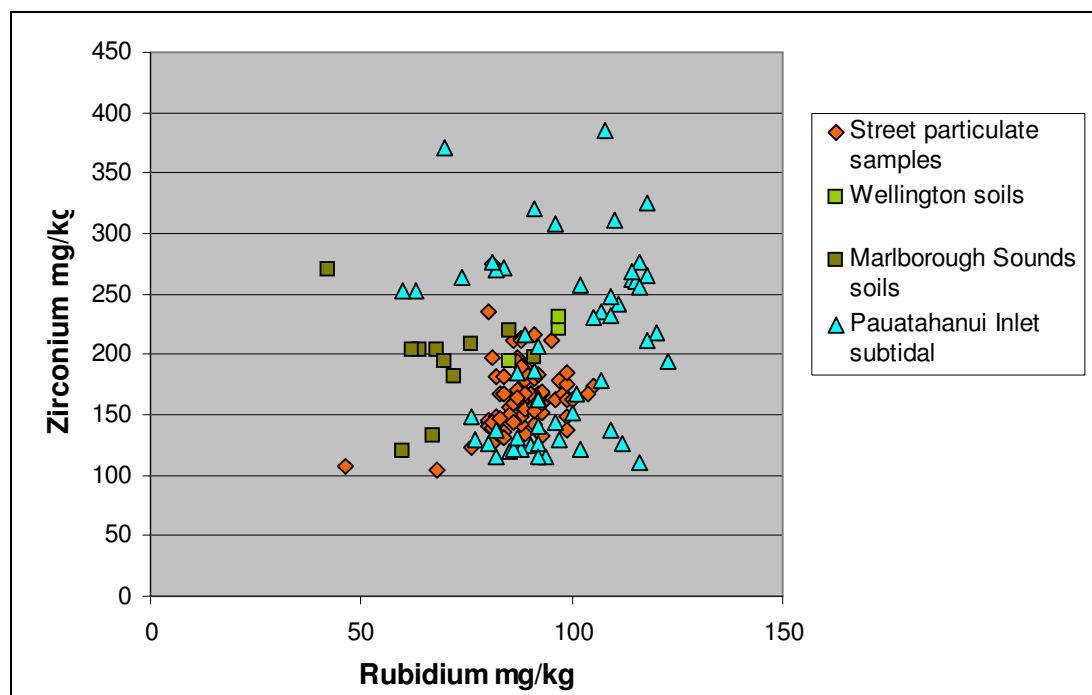
## Contribution from motor vehicles

It is unlikely that motor vehicles are contributors of Zr to road surfaces. There is little information on the contribution that urban activities make to the Zr on road surfaces.

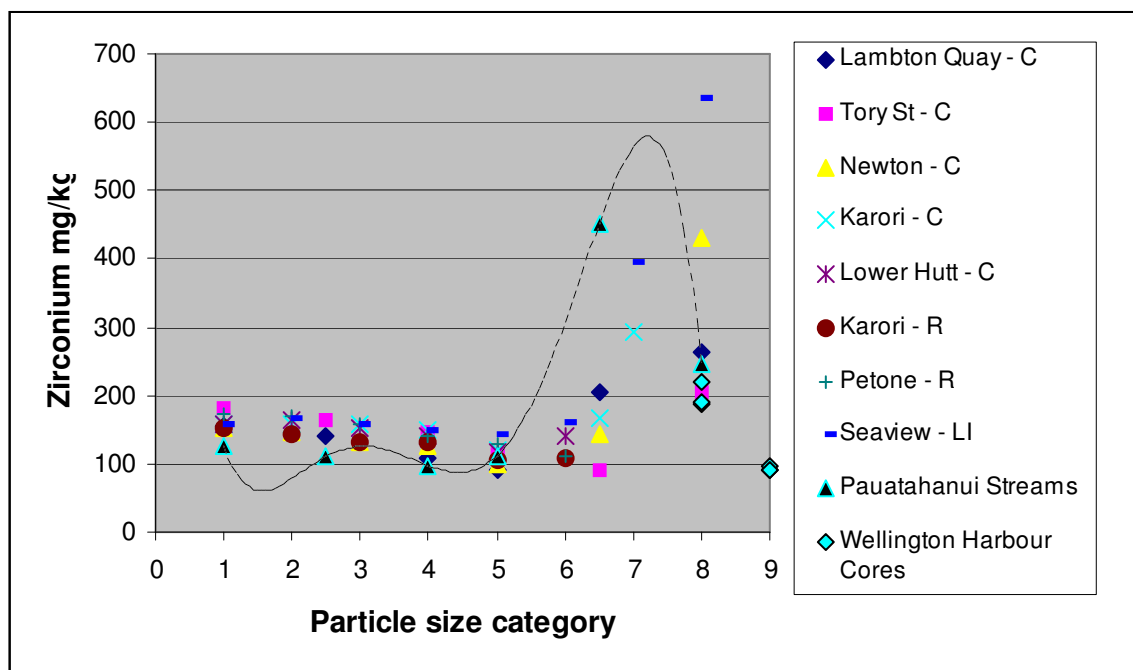
**Table 3.47 - Zirconium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	120 ± 14	-	VC	INAA	1	Hopke et al. 1980
Germany	1999	64 ± 3.2	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	11.3 ± 5.65	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	83 ± 4.15	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	72 ± 3.6	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
Wellington							
Lambton Quay	C	145	127-236	B, <2 mm	T-XRF	8	Kennedy (unpublished)
Tory St.	C	140	123-142	B, <2 mm	T-XRF	5	Kennedy (unpublished)
Newtown	C	143	104-170	B, <2 mm	T-XRF	6	Kennedy (unpublished)
Karori	C	149	133-163	B, <2 mm	T-XRF	7	Kennedy (unpublished)
Lower Hutt	C	182	159-198	B, <2 mm	T-XRF	8	Kennedy (unpublished)
Newtown	R	160	143-198	B, <2 mm	T-XRF	8	Kennedy (unpublished)
Karori	R	165	138-173	B, <2 mm	T-XRF	12	Kennedy (unpublished)
Taita	R	187	153-211	B, <2 mm	T-XRF	8	Kennedy (unpublished)
Petone	R	160	134-178	B, <2 mm	T-XRF	6	Kennedy (unpublished)
Gracefield	R	180	157-203	B, <2 mm	T-XRF	2	Kennedy (unpublished)
Gracefield	LI	168	153-210	B, <2 mm	T-XRF	11	Kennedy (unpublished)
Seaview	LI	203	108-275	B, <2 mm	T-XRF	12	Kennedy (unpublished)

**Notes:** 1 – median presented where available; B – Brush and pan; VC – vacuum cleaner; SA – Strong acid; INAA – Instrumental neutron activation analysis; ICP-AES – Inductively coupled plasma atomic emission spectrometry.



**Fig. 3.65 - Zirconium concentration in Wellington road surface particles (all data mg/kg).**



**Fig. 3.66 - Zirconium in size fractions of street particle samples and stream/coastal sediment samples from the Wellington area.**

### 3.27 Platinum Group Elements (PGMs)

None of the published New Zealand studies have examined road dusts for the presence of the platinum group (platinum, palladium and rhodium) metals (PGM). Given the introduction of PGM in catalytic converters (refer Moncrieff & Kennedy 2002 for more detail) since 1975 (in the US), there have been a number of studies that have examined the distribution/presence of these elements in the road environment. Table 3.48 provides a summary of a selection of published information.

Petrucci et al. (2000) identified increases in the PGMs in roadside dust in Rome. They identified a concentration of 0.9-0.5  $\mu\text{g}/\text{m}^3$  Pt in airborne particulates in 1991 and 6.4-25.0  $\mu\text{g}/\text{m}^3$  in 1998-1999. Work on Pt in airborne dust over roads in Germany has reported 0.6-130  $\mu\text{g}/\text{kg}$  Pt (Alt et al. 1993). Schafer et al. (1999) reported Pt, Rh and Pd concentrations in the ranges 112-166, 16.6-43.3, <0.4-27.2  $\mu\text{g}/\text{kg}$  respectively in airborne dust just above the ground adjacent to a road in Karlsruhe, Germany.

Hodge & Stallard (1986) reported on the release of Pt and Pd to the roadside environment from motor vehicles (Table 3.49), reporting that the accumulation on surfaces (e.g., leaves) may result in the wash-off of this material to aquatic systems. The authors reported higher concentrations on plant surfaces close to heavily trafficked roads compared to those roads with less traffic. The authors reported a close correlation with Pb concentrations.

Ely et al. (2001) and Jarvis et al. (2001) have reported on the distribution of PGM in roadside soils in the United States and United Kingdom respectively and identified a correlation with other key vehicle source elements (e.g., Cu, Zn etc.). Jarvis et al. (2001) identified concentrations up to 500  $\mu\text{g}/\text{kg}$  in road dusts and surface dust samples. Farago et al. (1998) identified Pt in road dusts in the United Kingdom in the range 11.2-23.7  $\mu\text{g}/\text{kg}$ . Higney et al. (2002) presented results for Pt in roadside dusts in Scotland. Concentrations varied significantly between high traffic roads such as motorways/dual carriageways (12.2-335.1  $\mu\text{g}/\text{kg}$ ) and residential areas (1.8-14.8  $\mu\text{g}/\text{kg}$ ).

**Table 3.48 - PGM group metals in road surface dust samples (all results ng/g dry weight).**

Location	Pt	Pd	Rh	Reference
San Diego California (dust on roadside plants)	37-680	15-280	-	Hodge & Stallard 1986
Australia West Coast Highway	53.5	58.2	8.8	Whitley et al 2003
Australia Leach Highway	161.2	132.7	31.5	Whitley et al 2003
Australia Collick St	123.6	168.5	24.5	Whitley et al 2003
Australia Leach Highway	229.6	150.1	45.1	Whitley et al 2003
Australia South Street	224.4	293.5	42.7	Whitley et al 2003
Australia Wanneroo Street	164.9	224.3	56.0	Whitley et al 2003
Australia Marmion Street	181.3	211.7	44.9	Whitley et al 2003
Australia Freat eastern Highway	419.4	440.5	91.4	Whitley et al 2003
Australia Graham Farmer Freeway tunnel dust	141.5	114.5	22.5	Whitley et al 2003
Australia Background	1.21	1.62	0.31	Whitley et al 2003
Madrid	317	-	74	Gomez et al. 2002
Goteborg	325.5	70.8	101.8	Gomez et al. 2002
Sheffield	57.7	-	-	Gomez et al. 2002
London	73.7	-	-	Gomez et al. 2002
Rome	34	202.7	4.8	Gomez et al. 2002
Munich	178.8	-	31.2	Gomez et al. 2002
Madrid	317 ± 109	-	74 ± 21	Gomez et al. 2001
Germany 1994	-	13.5-113.7	-	Boch et al. 2002
Germany 1997-98	-	32.9-100.5	-	Boch et al. 2002
Germany 2001	-	138.2-281.6	-	Boch et al. 2002
Germany 1999 Saarbrueken	135 ± 15	90 ± 8	30 ± 5	Djingova et al 2002
Germany 1999 A-1 (30 km from Koeln)	303 ± 40	95 ± 2	42 ± 3	Djingova et al 2002
Germany 1999 A-61 (near Bonn)	280 ± 20	82 ± 7	40 ± 2	Djingova et al 2002
Germany 1999 B-262 (parking area Koblenz)	269 ± 20	60 ± 4	38 ± 1	Djingova et al 2002
East Kirkbride Scotland, motorway	13-338.1	-	-	Higney et al. 2003
East Kirkbride Scotland, residential	1.8-11.8	-	-	Higney et al. 2003

Zereini et al. (1997) reported a concentration of 148 µg/kg Pt in tunnel dust in Frankfurt, Germany. Other studies such as Zereini et al. (1998) have identified that the highest concentrations of PGMs occur at road junctions and intersections. Schafer et al. (1999) reported up to 1,100 µg/kg Pt in dusts on urban city roads in Karlsruhe. Petrucci et al. (2000) identified Pt concentrations in the <63 µm fraction of roadside dust in Rome in the range 14.4-62.2 µg/kg (2-5 µg/kg considered background).

Examination of the particulates released from catalytic converters has shown that 99% of the Pt is in the metallic state and about 1% is present as oxidised Pt<sup>4+</sup> and the Pt is typically attached to larger alumina particles. Other work has shown that the PGMs in roadside dusts are not in metallic form suggesting that the PGMs undergo transformation when emitted from the exhaust system (Jarvis et al. 2001). Pt is also more soluble than Pd resulting in a solubility/transport related environmental distribution (Jarvis et al. 2001). Alt et al. (1993) reported 31-43% of the total Pt as acid soluble (0.07 mol/L HCl). This contrasts with 10% water soluble reported in Hodge & Stallard (1986). Jarvis et al. (2001) also examined solubility of Pt, Rh and Pd in water and simulated rainwater at pH 3. The respective solubilities for Pt, Rh and Pd were 0.14 and 0.48%; 0.57 and 1.21%; 5.9% and 35.4%. The authors also reported a faster dissolution rate for Pd compared to the other PGMs. As such, deposition to the road and soil environment results in some chemical change to the PGMs. This process probably involves formation of PGM chloride species but may also involve organic complexing agents (Jarvis et al. 2001). Zereini et al. (1997) carried out studies of PGM solubility and showed that the solubility is relatively constant in the pH range 3-9. At typical roadside soil pHs the solubility is very low with 0.01-0.025% for Pt, 0.05% for Rh.

Although there is no New Zealand data for PGMs in road surface particulates, PGMs will be present at similar concentrations. The concentrations present will be related to the proportion of vehicles in the fleet that have catalytic converters fitted.

## 3.28 Rare earth elements and Lanthanides

### 3.28.1 Cerium (Ce)

#### Natural geochemistry

Cerium ( $Ce^{4+}$ ) is a rare earth element with ionic radius of 0.94 Å (Taylor 1965). Cerium has an average crustal abundance of about 60 mg/kg with many rock types such as basalts and granites containing less (Plant & Raiswell 1983). Christie et al. (1998) describe the geology of the rare earth elements (of which Ce is a member) and their geological sources within New Zealand. Fig. 3.67 provides an indication of the natural variation on Ce concentration in different particle size fractions of freshwater sediments from Wellington.

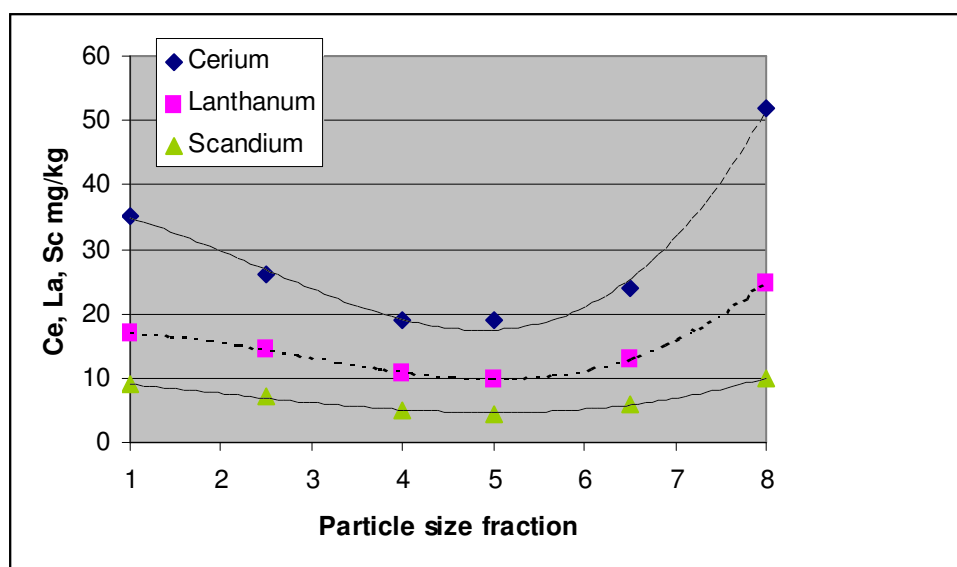


Fig. 3.67 – Cerium, lanthanum and scandium in size fractions of steam sediment from Pauatahanui Inlet Wellington (Kennedy unpublished data).

#### Sources

Cerium has limited uses in industry, although one of its more common uses is in the manufacture of photo-electric cells (Belliles 1979). The approximate use in the included glass polishing and ceramics (34%); petroleum refining catalysts (16%), automotive catalytic converters (15%), metallurgical additives and alloys (14%), rare-earth phosphors for lighting, televisions, computer monitors, radar, and X-ray intensifying film (9%), permanent magnets (8%), and other use (4%) (USDI, 2003).

There appear to be few uses for Ce in vehicle components. Kennedy & Gadd (2000) reported Ce concentrations in key non-exhaust emission sources. No detectable Ce was reported for tyres and raw bitumen. Low concentrations of Ce were found in most brake pads and dusts with a small number (3 of 18) containing over 20 mg/kg (Table 3.49).

**Table 3.49 - Cerium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	1.6	0.6	24.4	12
Brake pad dust	1.05 (TR)	0.4	83.1	6
Tyres	<1	-	-	12
Raw bitumen	<1	-	-	6
Road bitumen	29.5	20.1	46.2	5

**Note:** TR – total recoverable result.

### Cerium in road dusts

The mean concentration for the five TS-commercial samples was  $40 \pm 2$  µg/g, which at the upper end of the range identified for stream sediments (Fig. 3.67). Three samples of gutter dust from Christchurch examined by Fergusson & Ryan (1984) contained 34-76 mg/kg. Estimates of the Ce content of gutter dusts overseas include Pitt & Amy (1973) (20 mg/kg), Hopke et al (1980) and Fergusson & Ryan (1984) all of which reflect local geological conditions.

**Table 3.50 - Cerium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	29 ± 1	-	VC	INAA	1	Hopke et al. 1980
Manoa Basin Hawaii	R ~2000	50 ± 6	-	B, <2 mm	INAA	13	Sutherland & Tolosa 2000
Nagpur	M-1992	62	14.7-69	~<2 mm	INAA	3	Chutke et al. 1995
London	C ~1984	17.9	10.8-25	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
New York	C ~1984	24.5	21-28	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	41	38-44	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	22	-	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1984	49	34-76	< 0.963 mm	T,INAA	3	Fergusson & Ryan 1984
Germany	1999	25.1 ± 0.7	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	68.7 ± 2.06	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	58.5 ± 1.75	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	38 ± 1.14	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
Wellington, Tory St	C ~1980	40 ± 2	-	B <2 mm	T-XRF	5	Kennedy (unpublished)

**Notes:** 1 – median presented where available; B - Brush and pan; VC— vacuum cleaner; INAA - Instrumental neutron activation analysis; ICP-AES - Inductively coupled plasma emission spectrometry; SA - strong acid; T – total. XRF – X-ray fluorescence spectrometry.

### Contribution from motor vehicles

Measured concentrations of Ce in non tail-pipe motor vehicle emission sources are low. Given the natural concentration of Ce and the measured concentration of Ce in road surface particulates, there is little evidence of Ce contributions to road surfaces. There is little information on the contribution from exhaust systems. Further quantitation of emissions from exhaust systems is required.

## 3.28.2 Lanthanum (La)

### Natural geochemistry

Christie et al. (1998) provide an overview of rare earth element geochemistry (La is a member of the rare earth group). Lanthanum (has an ionic radius of 1.14 Å (the largest of the rare earth elements) and a crustal abundance of 30 mg/kg (Taylor 1965) which is similar to the concentrations



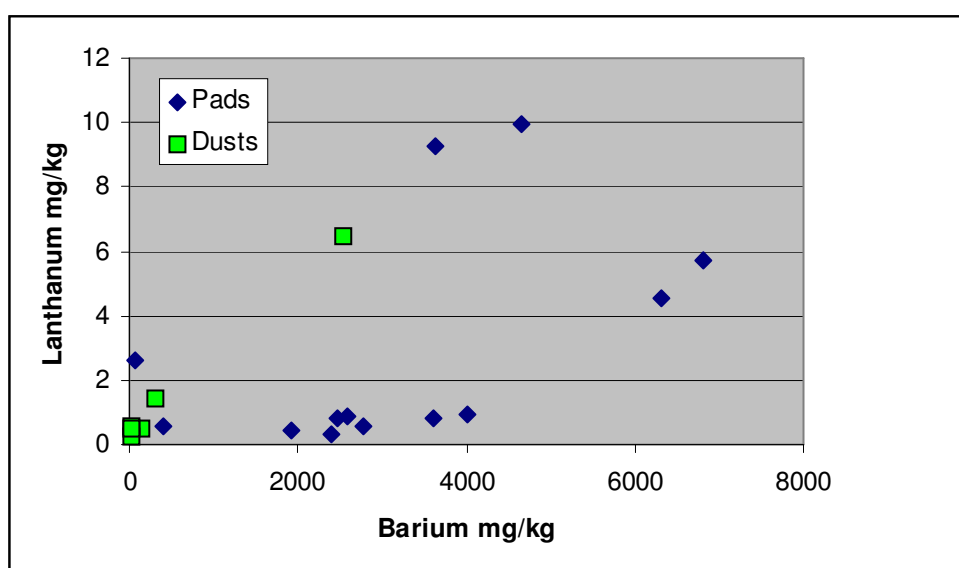
found in granites and shales. Taylor (1965) provides more information on the fractionation chemistry of La. Fig. 3.67 illustrates the natural variation in La concentration in stream sediments from the Wellington region.

## Sources

Lanthanum is used in a variety of applications such as glazes used on ceramics, microwave crystals, capacitors, glass polishing and optical glass and lenses (Christie et al. 1998). There do not appear to be any significant sources of La used in motor vehicles. It is possible that some La is present in ceramic components within the vehicle. Kennedy & Gadd (2000) measured La in brake pads, tyres and road bitumen. The results summarised in Table 3.51 show that tyres and raw bitumen contain no detectable La. Low concentrations of La were found in brake pad samples and in brake dust. La may be present in one of the mineral components commonly added to brake pads as a filler. Barite may be the source of La in the pads. Fig. 3.68 shows the relationship of the Ba/La data for the brake pad samples examined by Kennedy & Gadd (2000).

**Table 3.51: Lanthanum in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	0.89	0.31	9.97	12
Brake pad dust	0.56	0.23	6.49	6
Tyres	<0.1	-	-	12
Raw bitumen	<0.1	-	-	6
Road bitumen	4.53	0.56	9.97	5



**Fig. 3.68 - Lanthanum and barium in brake pad and brake pad dust samples (data from Kennedy & Gadd 2000).**

## Lanthanum in road dusts

The mean concentration of La in 5 samples of dust from Tory Street (commercial) in Wellington was  $19 \pm 2$  mg/kg (Table 3.52). Fig. 3.678 shows the natural variation in La concentration with grain size. Like Ce, concentrations were at the upper end of the range when compared to the stream sediments. Examination of the less than  $35 \mu\text{m}$  fraction of a sediment sample from a catch basin sump in Lambton Quay in Wellington contained 83 mg/kg La (2 to 9 times more La than any

other sample). It was already mentioned that this sample contained high levels of several trace elements, probably as a result of the particle sorting processes that operate in catchpits: however, the reason for the elevated La is obscure.

Three samples of street dust from Christchurch contained 12.7-15.6 mg La/kg (Ferguson & Ryan 1984). A single sample of dust analysed by Hopke et al. (1980) contained 10 mg/kg La; three pooled samples of street dust examined by Pitt & Amy (1973) contained 10 to 20 mg/kg and a number of street dusts collected worldwide by Ferguson & Ryan (1984) contained 6.9-16.5 mg La/kg.

Analysis of grain size fractions by Corrin & Natusch (1977) produced a very similar trend in La concentrations to those seen in this study with 10.3 mg/kg in the 250-500 µm fraction decreasing to 8.9 mg/kg in the 100-250 µm fraction then increasing from 14.3 and 14.2 to 19.1 and 40.7 mg/kg in the 75-100, 45-75, 20-45 and <20 µm fractions respectively. Generally higher concentrations of La were found in the magnetic fraction of the denser particles, although the highest La concentration was recorded in the non-magnetic >2-9 g/cm<sup>3</sup>, 20-45 µm fraction (78.6 mg/kg).

**Table 3.52 - Lanthanum in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	10 ± 1	-	VC	INAA	1	Hopke et al. 1980
Manoa Basin Hawaii	R ~2000	19 ± 3	-	B, <2 mm	INAA	13	Sutherland & Tolosa 2000
Nagpur	M-1992	30	19.7-34	~<2 mm	INAA	3	Chutke et al. 1995
London	C ~1984	11.6	9.4-13.8	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
New York	C ~1984	7.05	6.9-7.2	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	16.45	16.4-16.5	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	10.95	10.1-11.8	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1984	15.2	12.7-15.6	< 0.963 mm	T,INAA	3	Fergusson & Ryan 1984
Germany	1999	10.8 ± 0.324	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	34.5 ± 1.035	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	27.5 ± 0.825	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
	1999	18.8 ± 0.564	-	<2 mm	SA,ICP-AES	-	Djingova et al. (2002)
Wellington, Tory St	C ~1980	19 ± 2	-	B <2 mm	T-XRF	5	Kennedy (unpublished)

**Notes:** 1 – median presented where available; B - Brush and pan; VC— vacuum cleaner; INAA - Instrumental neutron activation analysis; ICP-AES - Inductively coupled plasma emission spectrometry; SA - strong acid; T – total; XRF – x-ray fluorescence spectrometry.

### Contribution from motor vehicles

There is little evidence of increased concentrations of La associated with particulate material on urban road surfaces. Current information indicates that vehicles contribute little if any La to urban road surfaces. Further information is required in relation to La emissions from vehicles.

### 3.28.3 Scandium (Sc)

#### Natural geochemistry

Scandium (Sc<sup>3+</sup>) has an ionic radius (0.83 Å) similar to that of Fe<sup>3+</sup> (0.83Å) and Mg<sup>2+</sup>. Scandium is found in minerals such as pyroxenes, mica and amphiboles. Taylor (1965) notes that its geochemistry is relatively complex and Short (1958) notes that soil profile information suggests some mobility of scandium. Taylor (1965) identified an average crustal abundance of 16 mg/kg with Sc concentrations in rocks of 5 mg/kg for granites to 38 mg/kg for basalts. Fig. 3.67 provides an indication of the natural variation in particle size fractions of stream sediments from the Wellington area.

## Sources of scandium in the urban environment

Principal uses for Sc include were aluminium-Sc alloys for sporting equipment, metallurgical research, high-intensity metal halide lamps, analytical standards, electronics and laser research (USDI 2003). Recent developments using Sc include welding wire, scandium-aluminium baseball and softball bats, and scandium-aluminium bicycle frames. Although, there appear to be few identifiable uses for Sc in motor vehicles, Lohse et al. (2001) noted that small amounts of Sc were present in some vehicle lights (gas discharge bulbs). Kennedy & Gadd (2000) examined Sc in a number of key emission sources. These are summarised in Table 3.53. Scandium was not detected in tyres or raw bitumen and only low concentrations were measured in brake pads and dust and on-road bitumen.

**Table 3.53 - Scandium in potential sources in the road environment (All results mg/kg dry wt) (From Kennedy & Gadd 2000).**

Source	Median	Minimum	Maximum	N
Brake pads	3	<2	5	12
Brake pad dust	3.7	1.9	5.2	6
Tyres	<2	<2	<2	12
Raw bitumen	<2	<2	<2	6
Road bitumen	3.2	2.5	3.6	5

## Scandium in road dust

Fergusson & Ryan (1984) reported Sc data for street particle samples from a number of cities around the world. Sample concentrations ranged from 3.7-6.4 mg/kg for 10 samples from London, New York, Halifax, Kingston and Christchurch. A further single sample from London was found to contain 25 mg/kg Sc (Table 3.54).

**Table 3.54 - Scandium in street gutter and street surface particulates (all results mg/kg dry weight).**

Site	Landuse & Date	Median <sup>1</sup>	Range	Particle size	Method	N	Reference
Urbana Illinois	~1980	17.2	11.1-21.3	VC	INAA	1	Hopke et al. 1980
Nagpur	M-1992	51.2	48.1-57.4	~<2 mm	INAA	3	Chutke et al. 1995
London	C ~1984	14.35	3.7-25	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
New York	C ~1984	4.05	4.0-4.1	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Halifax, Canada	C ~1984	5.85	5.3-6.4	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Kingston, Jamaica	C ~1984	5.3	4.8-5.8	< 0.963 mm	T,INAA	2	Fergusson & Ryan 1984
Christchurch	C ~1984	5.3	4.0-5.6	< 0.963 mm	T,INAA	3	Fergusson & Ryan 1984
Wellington, Tory St	C ~1980	19 ± 2	-	B <2 mm	T-XRF	5	Kennedy (unpublished)

**Notes:** 1 – median presented where available; B - Brush and pan; VC— vacuum cleaner; INAA - Instrumental neutron activation analysis; ICP-AES - Inductively coupled plasma emission spectrometry; SA - strong acid; T – total. XRF – X-ray fluorescence spectrometry.

A street dust sample from Urbana, Illinois examined by Hopke et al. (1980) contained  $4.2 \pm 0.3$  mg/kg and the range found by Pitt & Amy (1973) was 5 to 20 mg/kg. The average concentration of Sc in five street surface particulate samples from Tory Street in Wellington area was  $8 \pm 1$  mg/kg (Table 3.54). This is within the range seen for freshwater sediments (Fig. 3.67).

## Contribution from motor vehicles

Concentrations of Sc in key vehicle emission sources are low. There is no evidence that vehicles contribute Sc to the road environment. Analysis of limited numbers of road surface particulate

samples in New Zealand does not indicate any identifiable contamination with Sc either by vehicles or other urban sources.

### 3.28.4 Rare earth elements

The rare earth elements Europium, Samarium (Sm) and Dysprosium were measured in street dusts by Corrin & Natusch (1977). No abnormal grain size trends were apparent for these elements. Normal soil grain size distributions (increasing concentration with decreasing grain size) were noted for Sm, Hafnium (Hf) and Thorium by Ferguson & Ryan (1984) (this included three samples from Christchurch). Djingova et al. (2002) also reported data for Neodymium (Nd) in highway and parking area dusts in Germany. The study identified that the higher concentrations were found in the samples from higher traffic area. The source of the Nd was not identified.

Hafnium has been measured in street dusts by Linton et al. (1980b). The fractionation of the  $>3.3 \text{ g/cm}^3$  separate by those workers revealed a wide range of Hf concentrations. Although factor analysis revealed a high loading for a soil component for Hf, vehicle sources were also important. Further factor analysis with the removal of a building line sample which contained paint particles from the analysis, revealed significant loadings for Hf possibly derived from vehicles (probably associated with one of the major metals). The highest Hf concentration in that study were in the curb non-magnetic  $<45$  and  $45$  to  $250$   $\mu\text{m}$  fractions ( $550$  and  $280 \mu\text{g/g}$  respectively). The non-magnetic building line sample of  $0$ - $90 \mu\text{m}$  recorded  $200 \mu\text{g/g}$  and the curb magnetic  $<45 \mu\text{m}$  sample  $36 \mu\text{g/g}$ . Other fractions examined by Linton et al. (1980b) contained between  $0.8$  and  $3.6 \text{ mg/kg}$ .

Chutke et al. (1995) reported on the concentration of Cs, Eu, Hf, Lu, Ta, Tb, Th and Yb in dusts along highways in Nagpur.

It is possible that motor vehicles emit small amounts of rare earth elements to the road environment. The source is likely to be a result of the presence of small amounts of rare earth elements in some materials present in emission sources such as brake pads. Further work would be required to evaluate the potential and environmental significance of any release within the road environment.

## 4. DISCUSSION

Road surfaces are the recipient of a wide range of inorganic pollutants (trace elements/metals) sourced from motor vehicles on the roads and from the adjacent urban environment. The range of elements deposited on the road surface is extensive. The key questions arising in the assessment - is what are the key elements and where are they coming from?

Answering the first question requires knowledge of the environmental significance of the elements. This is restricted to some extent by current knowledge of the importance of some elements in the environment. There are a number of elements that have become increasingly utilised by our society (especially for electronic components) for which there is very limited information about their release and fate in the urban environment. In relation to motor vehicles, a wide range of elements are present, in vehicles and have the potential to reach the road surface if released. A good example of the changing environment in relation to elements emitted by motor vehicles include the introduction of catalytic converters (releasing Pt, Pd, Rh and possible Ce) and the use of high temperature control units on diesel vehicles to control emissions of PAHs (these may release a number of rare earth elements).

Table 4.1 provides a summary of the elements that are present in motor vehicle emissions (focussing on the non tail-pipe sources), their environmental significance and the relative significance of vehicles as a source of that contaminant on road surfaces (and hence in stormwater). Environmental significance is signalled by an orange or red highlight. Red indicating a known environmental significance. An orange highlight indicates possible environmental significance. The rating is dependent upon environmental circumstance and the particular environment. The shading should not be identified as absolute or as applying to any other

circumstance or particular environment. It provides a general indication of probable significance. Environmental concerns and effects associated with the presence of these elements on road surfaces and in stormwater runoff from roads is discussed further in Kennedy (2003). The overall indicative vehicle contribution is indicated by green (low), yellow (un-quantified), and purple moderate to high contribution.

**Table 4.1: Summary of key motor vehicle contaminant contributions.**

Element	Presence in non tail-pipe vehicle sources	Environmental Significance	Extent of motor vehicle contribution to road surface particulates (rough order estimate from text identified)
Arsenic	Low		Low
Antimony	Yes		>75%
Barium	Yes		? not quantified
Cadmium	Yes		15%
Cerium	Low		Negligible
Cobalt	Yes		? not quantified
Copper	Yes		40-50%
Chromium	Yes		40-50%
Gallium	Low		Low to ?50%
Gold	Low		Negligible
Iron	Yes		25%
Lanthanum	Low		Negligible
Lead	Yes		50-60%
Manganese	Yes		? not quantified
Mercury	Yes		? not quantified
Molybdenum	Yes		40-60%
Nickel	Yes		45%
Niobium	Low		Negligible
Palladium	Low##		>75%
Platinum	##		>75%
Rhodium	##		>75%
Rubidium	Low		Negligible
Scandium	Low		? not quantified
Selenium	??		?
Silver	Low		?<50%
Strontium	Low		Low
Tin	Yes		? not quantified ~40%
Titanium	Yes		Low ? not quantified
Uranium	Low		Low
Vanadium	Low		? not quantified
Yttrium	Low		negligible
Zinc	Yes		40%
Zirconium	Low		Low

**Note:** # PGE sourced from exhaust system.

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