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Diagnostic tool for source apportionment of heavy metals around roads

Science report SC000030

SCHO0508BOCY-E-E

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Steve Killeen

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Head of Science

Executive summary

The aim of this project was to look at sources of heavy metal contamination in road dust and to apportion the relative contribution, where possible, of different sources. Objectives designed to achieve this aim included a review of current literature on sources of heavy metals in the roadside environment; identification of appropriate sampling locations which permit a separation of apportionment due to traffic from other sources of input; chemical fingerprinting of potential input sources; comparison of measured compositions with those expected from manufacturers specifications; identification of anomalies; and finally, where possible, determination of relative contribution of each source.

The first stage of the work was carried out at the Transport Research Laboratory (TRL Limited) Small Roads research facility at Crowthorne, Berkshire, UK and the second stage on the A243, south of the town of Chessington, Surrey just north of junction 9 of the M25 motorway. The two roads are similar in their density of road furniture, rural location and constancy of traffic flow along the areas sampled. Traffic flow figures for TRL research track were estimated to be less than 50 vehicles per day compared with the A243, which has an estimated 30,000 vehicles per day.

Scrapings were taken from all potential sources of contamination including lamp posts, sign posts, drain covers and grills, barrier, white lining, Surface dust samples were swept from areas adjacent to the base of lamp posts and from similar surfaces (both asphalt and concrete) as far away from the metallic sources as possible. Major elements in dusts were quantitatively determined by inductively coupled plasma (ICP) techniques.
Comparison of road dusts from both sites with their respective local soils indicates that soil is not a major component of road dust. The similarity between the heavy metal contamination in road dust at TRL and on the A243 (and other urban and rural sites) suggests that traffic has a smaller influence than currently perceived. Since soil does not play a major role, it would appear that the road surface and street furniture is a significant factor in contamination in road dust.

To investigate this further, a review was made of the literature regarding the characterisation of components present in the road environment. The materials investigated included ferrous and non-ferrous metals and alloys found in street furniture, concrete and asphalt surfacing, including aggregate and bitumen, and paint used in road markings. The result provided typical chemical compositions of the materials, which were used to assess the potential contributions of contaminants from road surface and street furniture. A comparison of trace element compositions in street furniture, associated road dust and soil demonstrated that key elements could be allocated to particular sources.

Road dust at both of the study sites contained concentrations of elements such as Cd, Cr, Cu, Ni, V and Pb similar to natural levels in gabbro, which is used in aggregate. Dust taken from the vicinity of street furniture showed elevated levels of signature elements derived from galvanising. This work provided practical proof that Cu, Ag, Cd, In, Sn, Sb, Tl, Pb and Bi are associated with galvanised Zn. Additionally, measurements showed that V, Cr, Mn, Mo, Ag, Cd, Sn, Tl and Pb in dust are associated with iron and steel. Further work is required to determine how characteristic the profile of the elements is at TRL and on the A243.

The concentration of Zn is greater on the footway than the road at TRL and the A243, suggesting that it is derived from galvanised street furniture. Other elements associated with galvanising are too low to be detected above the general background and Zn is the only element in road dust that is at sufficiently elevated concentrations to be seen as originating from a single identifiable source.

It was noted that on the A243, elements associated with galvanising were more prominent than Zn, which is the major component. Zinc is dissolved from lamp posts and barriers by rainfall and so it is proposed that less soluble metals such as Mo and Ag will remain and concentrate in the roadside environment compared to Zn.

The report concludes that soil is not a major component of road dust, and that traffic has a smaller influence than currently perceived. It would therefore appear that the road surface and street furniture are significant factors in contamination in road dust. There are four key sources of heavy metals contamination: asphalt, galvanising, iron and steel but source apportionment is difficult due to preferential dissolution of some elements during weathering and corrosion. Further work is required to study these weathering effects to ascertain the relative solubility of the heavy metals before a model can be developed to predict the relative inputs from the sources identified.

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1 Introduction

Trace elements, including some heavy metals, are found in the roadside environment at levels which are often elevated. For example, road side dusts may contain significant amounts of Zn, Pb and Cu (Jarvis et al., 2001). While the dust itself is in part derived from wind-blown local soil, the elevated concentrations can not normally be attributed to this source.

Traffic has the potential to input a vast array of heavy metals to the environment through which it travels and previous studies have tended to concentrate on the relative inputs from tyre wear, break wear, bodywork degradation, exhaust catalyst wear etc. Vehicle wear and degradation have been proposed by some workers as the main sources from which these elements are derived. However, with the complex nature of road systems, it is difficult to conclusively demonstrate that this is the case and it is likely that other types of input play an important role. For example, using data published by Legret and Pagatto (1999) it is possible to estimate the relative inputs for zinc from tyres and galvanised barriers. The zinc from corrosion of a galvanised steel barrier (1kg/km/year) is equivalent to the estimate input (in kg/km/year) from tyres on cars travelling past at a rate of 5,000 per day.

The chemical composition of materials used to construct roads and the signing, marking and construction features associated with them, is very varied and potentially provides for sources of a wide range of elements. For example road surfaces are composed of aggregate, bitumen, fillers and binders, while signs are constructed from steel with painted or galvanised surfaces. Drainage systems have grills and covers made from cast iron. The chemical composition of each component is to some extent dictated by its intended use such that an effective galvanised coating will only be durable if it falls within a particular specification for impurities in the major component, zinc.

In order for sources of road side pollution to be properly targeted in remediation schemes, or indeed to prevent toxic elements being released in the first place into the environment, the source of each pollutant must first be identified. The hypothesis to be tested in this work is that the chemical characteristics or ‘trace element fingerprint’ of the different potential input sources can be characterised. Fingerprints from a number of different sources will then mix to give the characteristic trace element composition observed in the surface dust deposits which are found on road and road-side surfaces. The aim of this work is therefore to try and unravel the complex trace element pattern found in dust deposits, and to identify and assess the relative contribution of each source.

The elements that cause most concern in the environment, such as heavy metals, may or may not be the most useful in characterising sources of contamination. In some cases, other elements may show a key signature, which is characteristic of a source, although they themselves are of little environmental impact.

An initial study carried out between June 2002 and May 2003 (Cook et al., 2003) considered the general chemical characterisation of a number of potential inputs on both private and public roads. At this stage little data was available to support the hypothesis that chemical fingerprints from input sources could be preserved in surface dust samples. A wide range of situations were sampled including the research track at TRL, major A roads, a cul-de-sac, car parks, residential road, tarmac, concrete etc with a view to gaining a general overview of the chemical variation present. This work indicated the potential of using trace elements to fingerprint source inputs and highlighted the need to be able to separate the potentially complex inputs from traffic from other sources.

The basis of this project has therefore been initially to source, characterise and understand an environment which has a limited number of potential inputs, ideally one at which the potentially most complex group of inputs, those derived from vehicles, are essentially absent. The second stage of the work has been to take the knowledge gained in this controlled environment and assess its relevance in a real road situation.

1.1 Aim

The aim of this project is to look at sources of heavy metal contamination in road dust and to apportion the relative contribution, where possible, of different sources. To achieve this aim a number of objectives were put in place.

- Review current literature on sources of heavy metals in the roadside environment including those that originate from vehicles, the road surface, road furniture, paint, soil. Potential inputs are shown in Table 1.
- Identify appropriate sampling locations which permit a separation of apportionment due to traffic from other sources of input.
- Chemically fingerprint potential input sources at each location.
- Compare measured compositions with those expected from manufacturers specifications.
- Identify anomalies.
- Determine relative contribution of each source where possible.

Table 1.1 Potential input sources of contamination to road surface deposits.

Type	Source
Vehicle	Tyres Paints Engine wear Oil & fuel Brake linings Exhaust emissions Bodywork Catalytic converters
Road surface	Sub-base aggregate Surface aggregate Bitumen Concrete
Road furniture	Barriers Paint Road signs Tunnels Drain covers Drain grills Gantries Bridges
Natural	Geology Soils Organic debris
Other	Industry Agriculture Litter

2 Methods

The first stage of the work was carried out at the TRL Limited small roads research facility at Crowthorne, Berkshire, UK and the second stage on the A243, south of the town of Chessington, Surrey just north of junction 9 of the M25 motorway. The two roads are similar in their density of road furniture, rural location and constancy of traffic flow along the areas sampled. Traffic flow figures are not available for TRL small roads system but are estimated to be less than 50 vehicles per day (Monday-Friday) compared with the A243 which has an estimated 30,000 vehicles per day. For the purpose of this work, the small roads system traffic flow is considered to be negligible.

2.1 TRL Limited

The Research Track Facility at TRL has been operational for over 50 years and is used for testing vehicle performance, operation and safety and for training drivers in specialist skills. The Facility is split into two areas, the Large Loop, which is used for a wide variety of test activities. Within the Large Loop is the Small Road System, an asphalt road laid out with features found on many public roads such as street furniture, white lining, pedestrian crossings, kerbs and footway. The small road system has straight sections of road, junctions and bends.

The small road system was selected as it is ideal for studying potential contaminant inputs into road systems. It has all the ‘features’ of a public road with one difference. The number of vehicles travelling around the system has always been very low compared with a public road. The traffic flow can be considered to be essentially zero. Thus one major potential input is absent from this system. While not realistic of a real road system, the Small Road System provides an ideal opportunity to study a number of potential inputs such as those from street furniture, white lining and road surface in a controlled environment.

Scrapings were taken from all potential sources including lamp posts, sign posts, drain covers and grills, barrier, white lining, Surface dust samples were swept from areas adjacent to the base of lamp posts and from similar surfaces (both asphalt and concrete) as far away from the metallic sources as possible.

The road surface is constructed of asphalt which has clearly been subject to repair and patching at various times. The footway is constructed of asphalt, cast concrete, concrete slabs or is grassed with no hard surface. White lining paint is used to mark junctions and central lines. There are no lining paints of other colours visible. The white lining is of various ages, some being worn thin while other areas have been recently applied. Dates of application are not recorded.

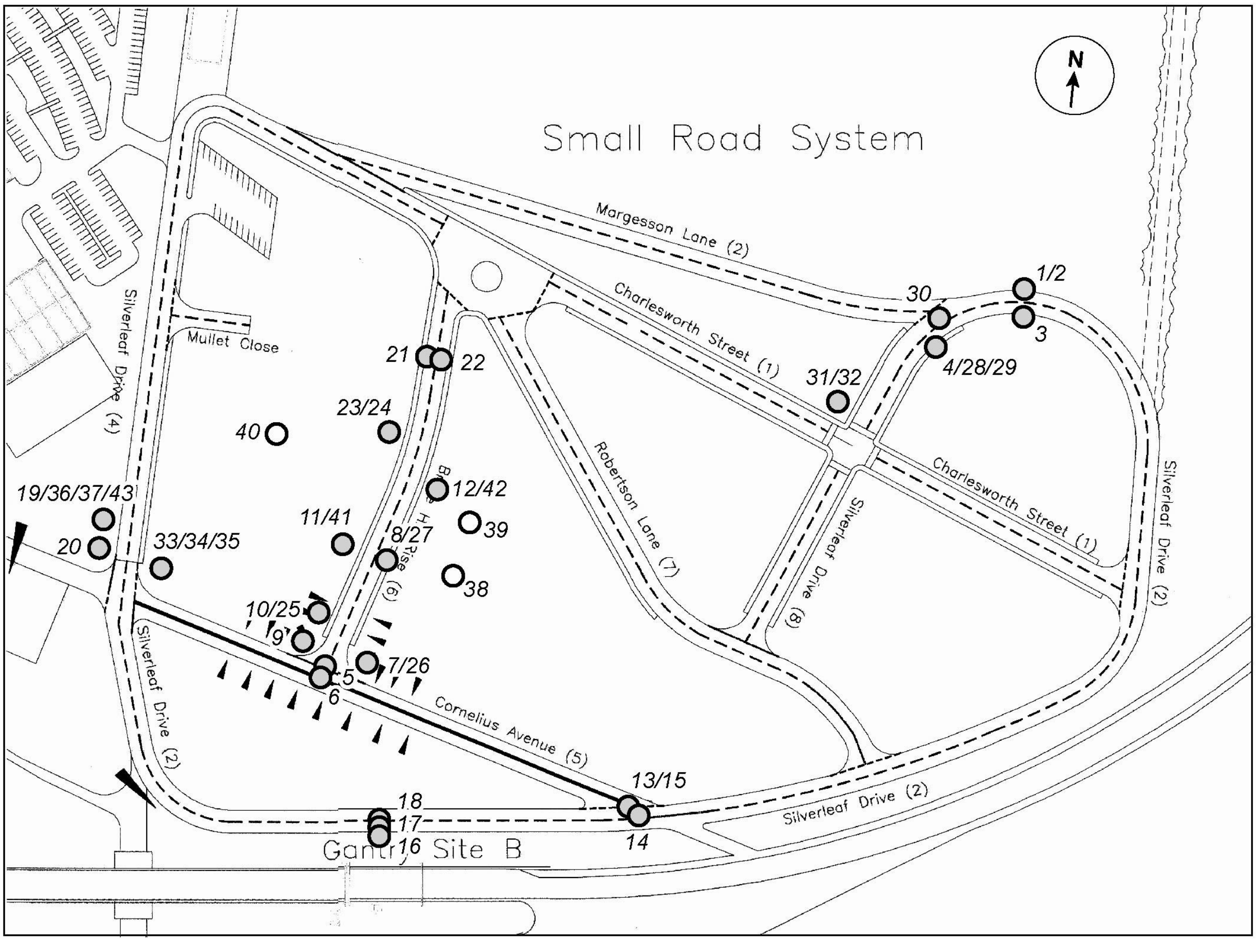


Figure 2.1: Transport Research Laboratory research track – small road system – showing sampling locations

The land adjacent to and surrounding the Research Track Facility is densely vegetated with pine forest forming an effective barrier between the Small Road System and the Large Loop, and between the Research Track and adjacent public road. The layout of the Research Track Facility is shown in Figure 2.1.

2.2 Kingston Road A243

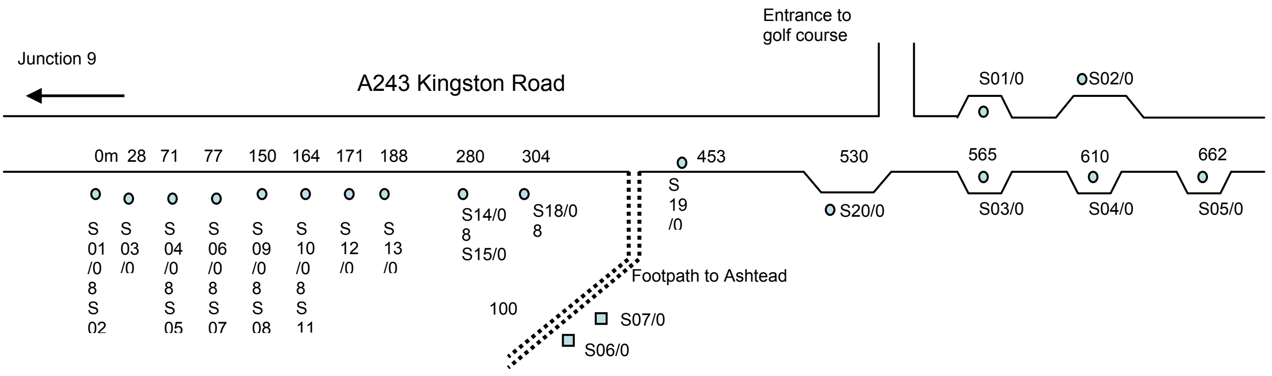
The second sampling location is on a major ‘A’ class road carrying both local and commuter traffic out to the south of London. Samples were collected specifically from the area immediately north of Junction 9 of the M25 motorway on both the north- and south-bound carriageways. There are no additional entry points for traffic within the area sampled, the nearest entry or exit point being to the north at Malden Russet crossroads. Traffic type is mixed with an estimated traffic flow of 30,000 vehicles per day.

The area sampled is characterised by abundant street furniture including large motorway indicator signs, junction distance markers, bus stops and local information signs. The road has a series of cast iron drain grills located along both carriageways to remove surface water. The centre of the carriageway is marked with a broken white line and there are remnants of white paint parallel and close to the concrete kerbs. The junction with the M25 intersection is clearly marked with white lines.

The surrounding land is heavily vegetated with mixed deciduous woodland and dense shrubs. The boundary of the Ashstead National Nature Reserve is immediately adjacent to the south-bound carriageway. The north-bound carriageway is bounded by the Leatherhead Golf Club. The general layout is shown in Figure 2.2.

Scrapings were taken from all potential sources including lamp posts, sign posts, drain covers and grills, white lining, Surface dust samples were swept from areas adjacent to the base of lamp posts principally on asphalt footway and from similar surfaces as far away from the metallic sources as possible. Surface samples taken from the A243 are potentially subject to inputs from passing traffic. However, it is not unreasonable to assume a constant input along the area sampled as traffic speed is relatively constant. Trace element input from traffic should also therefore be the same or very similar for all samples collected.

Figure 2.2 The A 243 Kingston Road – showing sampling locations



2.3 Sample collection

Samples were collected during fine dry weather. Three types of sample were collected.

2.3.1 Surface dusts

Previous studies by the authors have shown problems with the use of powered mechanical sampling devices such as vacuum cleaners. It is difficult to ensure adequate cleaning between samples thus contamination can occur and provision of an electrical supply can be problematic. So, for this study, samples were collected using a plastic pan and soft bristle brush. New or previously cleaned pans and brushes were used for each sample. The area swept depended on the amount of material available but where possible 10 g was collected. Plastic gloves were worn during collection. Samples were transferred into labelled brown paper bags for transport to the laboratory.

2.3.2 Scrapings

Samples of metal posts were taken by scraping gently with a stainless steel scalpel blade. Sample material was collected directly in a brown paper sample bag. Where rusting metal was sampled, fragments were removed by hand and placed in bags. The amount of sample collected was typically <1 g.

2.3.3 Pickings

Road aggregate samples were collected by hand by picking loose material from the surface.

2.4 Sample preparation

Surface dusts were dried at 50°C for 48 h. They were sieved to <250 µm and the coarser fraction retained for archiving. Scrapings & pickings were transferred directly to glass tubes.

Table 2.1 Sample preparation procedures used

	Alkali fusion	**HF/HClO4 digestion**	**Aqua Regia digest**	**Visual**
Surface dusts	√	√		√
Scrapings			√	√
Pickings				√

2.4.1 Alkali fusion

Surface dusts were prepared for analysis by inductively coupled plasma spectrometry (ICP-AES & ICP-MS) techniques using an alkali fusion. Powders were mixed with high purity $LiBO_2$ flux and fused in graphite crucibles for 20 min. The hot melt was poured into cold, dilute nitric acid and stirred until it was fully dissolved. The resulting solution was filtered into a volumetric flask and made to volume. This solution was further diluted prior to analysis by ICP-MS. Alkali fusion is the preparation of choice for total dissolution of soils and rocks containing highly resistant minerals such as zircon, and has been shown to give fully quantitative results for a large number of elements in a wide range of sample types. It is the preferred method if the determination of major elements, particularly SiO_2 is required and for the quantitative determination of Zr, Hf, Nb and Ta amongst others (Jarvis & Jarvis, 1992; Totland et al., 1992)

2.4.2 Hydrofluoric/perchloric acid digestion

Surface dusts were also prepared for analysis using an open, mixed hydrofluoric acid and perchloric acid digestion in PTFE beakers. For safety reasons samples were initially treated with fuming nitric acid to ensure breakdown of organic matter prior to addition of perchloric acid. Samples were heated to180°C and successive aliquots of acids evaporated until samples were fully digested. The resulting crystal mush was warmed with dilute nitric acid, transferred to a volumetric flask and made to volume. Solutions were further diluted prior to analysis by ICP-MS. This open acid digestion procedure can be used for the fully quantitative determination of chromium, zinc, cadmium, antimony and lead amongst others.

2.4.3 Aqua Regia digestion

Metal scrapings were prepared by open digestion with aqua regia in pyrex beakers. The mix was gently heated and solution transferred to a volumetric flask and made to volume. Solutions were further diluted prior to analysis by ICP-MS. Aqua regia is the acid of choice for dissolution of steels.

2.5 Sample analysis

Major elements in dusts (Si, Al, Fe, Mg, Ca, Na, K, P) were quantitatively determined in the alkali fusion by ICP-AES. Trace elements in dusts (V, Mn, Co, Ni, Cu, Ga, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sn, Cs, Ba, rare earth elements, Hf, Ta, W, Th and U) were quantitatively determined by ICP-MS. Trace elements in scrapings (Mg, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, rare earth elements, Hf, Ta, W, Tl, Pb, Th and U) were quantitatively determined by ICP-MS.

2.6 Quality

Data quality (accuracy, precision and bias) was monitored and assessed using international reference material NIST 2704 River Sediment. Major elements measured by ICP-AES were typically within +/- 1% relative of the certified reference value while trace elements determined by ICP-MS were typically within +/- 10% relative.

3 Results and observations

3.1 Characterisation of selected potential inputs

Road dust results from a number of inputs including ferrous and non-ferrous metals, rubber and plastics, as well as ‘natural’ soil and vegetation. The nature of these materials can be predicted in many cases through the specifications applied to the sources. For example, the road surface is principally asphalt containing bitumen and aggregate, or for less demanding applications, concrete. Road furniture is often constructed from steel with a zinc galvanized coating to prevent corrosion. The hypothesis is that these sources can be identified through the characteristic fingerprint relating to the materials specified in their production. We need to identify the range of materials used materials in the construction of road furniture and surfaces, and to identify relevant specification which will have an influence on their chemistry.

3.1.1 Ferrous metals

Cast iron

Plain carbon steels contain around 0.1 wt% Mn, 0.06 wt% P, 0.02-0.3 wt% Cr, 0.01 wt% As, 0.006 wt% Co, 0.05 wt% Cu, 0.01 wt% or less Mo, 0.05 – 0.1 wt% Ni, 0.05 wt% Nb, 0.001 wt% Pb, 0.001 wt% Sn, 0.01 wt% Tl, 0.01 wt% Sb and 0.002 wt% Zn. Drain covers and other simple parts of road furniture are often composed of cast iron which is a durable and cost effective material. However, in the British climate, cast iron products are subject to significant corrosion in the form of rust or iron oxide. There is therefore the potential for release of the trace components listed above.

Mild steel

The primary types of structural steel are usually classified according to the following chemical composition categories: carbon-manganese steels carbon steels (or mild structural steels) such as A36; high strength, low-alloy (HSLA) steels, such as A572 and A588; and high strength quenched and tempered alloy steel, A514. Some elements are added to steel to reduce corrosion, for example Cu is not usually less than 0.20 wt% and it is the principal anti-corrosion agent in A242 and A441. Molybdenum is typically 0.08-0.25 wt% for A588 and 0.15-0.65 for A514. Ni 0.30-1.50 wt% in A514 and 0.25-1.25 in A588.

Vanadium is a principal trace element in A572, A588 and A514 at between 0.02 and 0.15 wt%. Niobium, a relatively rare element in natural samples, occurs in A572 type steel (Wooh, 1999). Cadmium oxide has been used as anti-corrosive treatments for steel. Many elements appear as impurities, even in pure steel, which has a nominal composition of Mn 0.1 wt% Mg 0.05 wt% Cu 0.05 wt% Co 0.03 wt% Cr 0.03 wt% Mo 0.03 wt% Ni 0.03 wt% V 0.01 wt% Pb0.005 wt% Cd 0.001 wt% Bi 0.001 wt% Ag 0.0001 wt%. Many of these elements particularly Ag, Cd, Bi, Mo and Co occur in soils and rocks at relatively low concentrations, and are therefore potentially useful markers of mild steel.

3.1.2 Non-ferrous metals

Zinc

Zinc is principally used in galvanising coatings to protect steel from corrosion and to provide a visually appealing surface. High purity zinc is the standard product typically used in steel framing, agricultural and automotive applications. Electro-galvanising to produce a steel sheet with an electroplated zinc coating, results in an ultra-smooth surface finish which is desirable for surface-critical parts such as automotive exterior body panels. A majority of electro-galvanised coatings use pure zinc, although alloys with Fe or Ni are also commercialised. The main use of electro-galvanised coatings is inner panels and doors for vehicles.

The galvanising process can be by 'hot dipping', which is a batch process and can be applied to individual components. Hot dip galvanising is a process whereby steel is immersed in a bath of molten zinc (450^{O}C) to form a metallurgically-bonded zinc coating. Continuous-sheet galvanizing is also a hot dip which is used in car production. Electro-galvanized coatings are applied to steel sheet and strip by electro-deposition. This is a continuous process, and the sheet product is used in automobile bodies. Zinc plating is used for coatings deposited on small parts to large structural shapes (American Galvanizers Association, 2004a).

Steel can be galvanized continuously or in a batch operation. In continuous hot dip galvanising, coils of rolled steel are continuously unwound and fed through cleaning and preheating sections, before entering the molten zinc bath at speeds of up to 200 m/min. As the steel exits, gas 'knives' blow off the excess coating to control the coating thickness. The same process is also used to produce Zn-Al alloy coatings.

Although the term galvanised usually refers to the 'standard' continuous coating that is basically pure zinc, addition of various elements has a dramatic effect on the appearance, structure and thickness of the coating. Aluminium and Sn are added for brightness, Pb and Bi for drainage while Ni is added to reduce alloy formation. Some elements are added intentionally, while others accumulate in the bath over time.

Copper and C occur naturally in the ores which are smelted to produce zinc metal and remain as contaminants in the final product. Zinc-bath chemistry is important and there are a number of elements that have a dramatic impact on the properties of the coating. There is a small amount of Fe in Zn, and this should not exceed 0.05 wt% in ‘Prime Western Zinc’. Sheet galvanizers use 0.1-0.3 wt% Al to suppress the formation of Zn-Fe alloy layers in the coating. Aluminium is used as a brightener and it is added as a brightener bar (ASTM B-860). Other elements present in the bar include Pb (0.005 wt% max), Cd 0.004 wt% max), Cu (0.035 wt% max), Sn (0.003 wt% max). Lead is added to the bath to reduce the surface tension and to make it more fluid. The concentration is usually maintained at 1 wt%.

‘Prime Western’ or’ G.O.B’ Zn metals are pre-alloyed grades containing 0.5-1.4 wt% Pb which has a solubility of about 1.2% at 850°C. Bismuth acts in a similar manner at typical concentrations of 0.1 wt%. Nickel is used to control the galvanising reaction on reactive materials such as Si-killed steels. Typically Ni is in the range 0.04-0.07 wt%. Sn is used to brighten the coating and is primarily used at a concentration of 0.05 wt%, although some use is as high as 0.5 wt%. The ASTM specification for Prime Western Zn also permits up to 0.2 wt% Cd, although it is generally well below that level. Cu can be present but is detrimental if above 0.23 wt%. The range of concentrations for trace elements are: Fe 0.04 wt% max; Al 0.005 wt% max; Pb 0.8-1.4 wt%; Bi 0.1 wt% target;

Ni 0.040-0.07 wt%; Sn 0.05 wt% target; Cu 0.23 wt% max; and Cd 0.20 wt% max (American Galvanizers Association, 2004b)

'Galvanneal' is a Zn-Fe alloy coating with improved properties over other forms of galvanising, and is used extensively in the automotive industry because of its improved manufacturing performance with lighter and stronger grades of steel. 'Galfan' is a Zn-5%Al coating with superior corrosion resistance which is used for building panels and severely formed components such as automotive parts. Other Al/Zn coatings are Zincalume, Galvalume and Aluzinc. The chemical composition of Galvalume is 55% Al, 1.5% Si and 43.5% Zn alloy coating (Rourke, 1998). Zincanneal is a matt hot-dipped zinc-iron alloy identified as being used in automotive components.

The chemical composition of the steel is very important to the quality of the galvanised coating since a metallurgical reaction between the Zn and Fe is occurring. Carbon should be below 0.25 wt%, P less than 0.05 wt% and Mn less than 1.3 wt%. Silicon should be in the range 0-0.04 wt% of 0.15-0.25wt %. The recommended ASTM steel grades for hot dipping galvanising and structural shapes and plate are: A36, A242type2, A283, A441, A500, A501, A529, A572 or A588. Steels for sheet metal are A569 or A570. Steels for pipe or tubing are A53, A120, A595 GrA or B (Metalplate Galvanizing, 2004). A36, A424 and A283 contain a minimum of 0.20 wt %Cu according to the ASTM specification. In summary, most of the automotive use of galvanised steel is in the form of hot dip and so the steel will be A36, containing little of anything but 0.2 wt% min Cu. Zincanneal (Zn-Fe alloy) is probably used as the alloy.

Copper brasses and bronzes

Brasses are Cu alloys in which the main alloying element is Zn. Common brass contains 36% Zn. Lead is added to brass to improve its machinability at a concentration of 3 or 4 wt% (Severn Metals, 2004). Cu is also alloyed with Ni (Cu90Ni100) and this is used for hydraulic brakes in preference to steel (Copper Development Association, 2004). Copper and brass represented 1.05% of the mass of a car in 1998. Brass, iron or bronze is used in brake pads for good dissipation of heat. Powdered metal is pressed into organic binder at loadings from below 20 wt% to 60 wt%. Phosphor bronze is 3.5-4.5 wt% Sn in Cu. Copper is used extensively in brake pads in European and Japanese vehicles. A project to study the use of Cu in 'friction materials' that include disc brake pads (front and rear) and drum brake linings (rear only) resulted in an average Cu per vehicle of 40-60 g for 1998-2000 (Connick, 2001).

Solder

High purity solder is principally Sn with added Pb (37 – 80 wt%) with some added Ag (eg Sn62Pb36Ag2) or Sn with only Ag (Sn96Ag04) or Sb (Sn95Sb5). These materials are used to solder Cu, brass, Ni and Zn. The principal components are 'high purity', for example Sn99.95 wt%, Sb, Pb, Cu, Zn, Fe, As, Ag, Bi and In all below 0.01 wt% (Warton Metals, 2004).

3.1.3 Asphalt road surfaces

The bitumen binding the aggregate in asphalt surfaces is an organic material derived from petroleum products and there is little information regarding its composition at trace element concentrations. Lindgren (1996) reported trace elements such as vanadium (50-600 ppm), nickel (15-100 ppm), iron, magnesium and calcium in bitumen and found Cr <35, Cu <17 and Zn <17 ppm.

Aggregate can consist of a variety of materials, including gabbro, porphyry, coal fly ash and blast furnace slag. The gabbro has been reported to contain As 11.2 ppm, Cd 0.13 ppm, Cr 238 ppm, Cu 71 ppm, Ni 110 ppm, Pb 2.8 ppm, V 215 ppm and Zn 149 ppm (Lindgren 1996).

3.1.4 Concrete road surfaces

Roads, kerbs and pedestrian ways can be made of concrete. Concrete is made up of sand, aggregate and cement. Concrete can also contain coal fly ash. Coal fly ash commonly contains 1-25% Si, Al, Fe, Ca, Mg, Na, K and Ti; 0.001 -1% Ba, Sr, Mn, B, Mo, V, S and P; 5-50 ppm Ag, As, Cd, Cr, Cu, Ni, Pb and Zn; 10 ppm to LLD of Hg, Cl, F, Se, Be, Sb, U and Th; 1-100 ppm Cm, Cs, Rb, Ge, Sn and Co.

3.1.5 Paints

Paint is used for road furniture, road markings and on vehicles. A typical specification for white markings is 18 wt% minimum of binder, 10 wt% rutile (TiO2), 48 wt% minimum glass beads. For yellow markings the rutile is replaced with 4.0 wt% yellow pigment of lead chromate with a minimum of 50 wt% lead content. The binder is specified as maleic modified rosin ester and other plasticisers. Galvanised paint will principally consist of Zn and a range of pigments are used on vehicles, including metallic paints.

Glass

Road markings consist of glass beads embedded into the paint that is sprayed onto the road surface. Road marking materials are defined by BS EN 1424 (Premix glass beads). Glass beads are dropped into the wet paint behind the paint sprayer. They are enveloped by the paint, with the paint rising up to above the halfway point of the bead. This locks the beads into the paint and allows the paint to act as a mirror surface for the headlight that enters the glass beads at night. The glass beads are round, clear and highly efficient at reflecting light. Typical sizes for the glass beads are 1-850 micron (Trademark Swarcoflex); 1-1300 micron (Trademark Swarcolux); and 600-1500 micron (Trademark Megalux).

The approximate chemical composition of clear soda lime glass is 70-74% SiO_2, 12-15% Na_2O, 8-10% CaO, 3.5-4.5 % MgO, 0.3-0.8 % K2O, 0.0-0.2% Al_2O_3 and 0.08-0.1 % Fe_2O_3. British Glass reference material 'Soda lime-magnesia-silica glass: 71.97% SiO_2, 0.04% TiO_2 1.08% Al_2O_3 0.103% Fe_2O_3 8.63% CaO, 3.78% MgO 13.41%NaO 0.59% K2O and 0.23% S. 'Supergrit' is made from recycled soda lime so it has the same composition but it is interesting to note that As, Sb, Be, Cd, Co, Pb, and Sn are all below 0.01% and Cr is 0.02% Ni 0.01%.

3.1.6 Rubber

Zinc oxide is used in tyre manufacture and is best known as an activator during the vulcanising of rubber and it is typically 1.4% of the tyre. Ash from burning tyres has been shown to contain Pb, Cd and Zn (CIWMB, 1997). The Zn used is Special High Grade (SHG) as well as recycled Zn metal. A typical passenger car tyre contains 100 g of Zn oxide and lasts 70,000 km. The rubber industry accounts for 60% of the consumption of Zn (International Zinc Association, 2004). Cd oxide is used as a curing agent in tyres (Water UK 2001).

3.2 Visual comparison of sample chemistry

The elements which comprise any sample can be sub-divided into those which form the matrix components, major elements, and those which are present in minor quantities, the trace elements. Major element concentrations in soils are reported by convention as weight percent oxide and are all contained in most of the minerals which make up the soil composition. Their distribution tends to be rather homogenous in soil samples although relative proportions vary from one sample to another. These elements form the bulk (~95%+) of the sample, along with organic carbon and variation in one element concentration must be balanced by change in concentration of another since their total must sum to 100%.

Trace elements are more variable in concentration and may reside in only one or two of the minerals present in a soil sample. Their distribution tends to be more heterogenous than for major elements and there may or may not be interdependency between one element and another.

Although soils contain a very wide range of trace elements, albeit at significantly different concentrations, a number are relatively rare in nature and do not substitute for heavy metals in the raw ores which are used to produce refined metal products. For example, the physical properties (ionic radius and charge) of the rare earth elements (La-Lu atomic weights 139-175) cannot fit into the minerals sphalerite and chalcopyrite from which refined Zn and Cu are produced. Therefore the products which are produced from these metals are unlikely to contain these elements in any significant quantity. Similarly Ga, Th and U are largely present in soils but not in man-made materials. Thus, there are a number of elements which can potentially be identified as ‘markers’ of soil. Moreover combining data for a number of these elements can potentially produce a unique fingerprint for a particular type of sample.

A comparison of major elements in average soil from the research track and the A243 are shown in Fig 3.1. Ca, Na and K data points are missing from TRL as these elements were less then the instrument detection limit. Concentration is shown on a log scale to accommodate the wide range of values. However, the general chemical characteristics are clear with the TRL soil being higher in SiO2 than that at the A243. The relative proportions of elements such as Fe and Mg, for example, are similar for both soils.

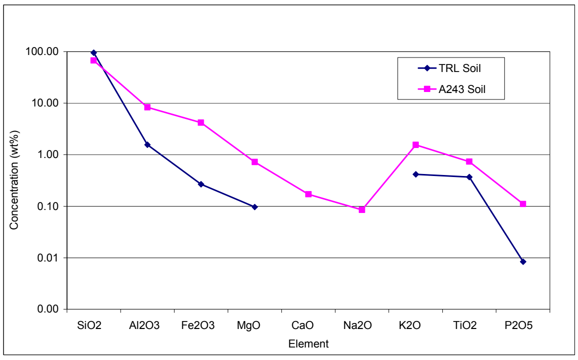


Figure 3.1 Major element soil data for TRL and A243

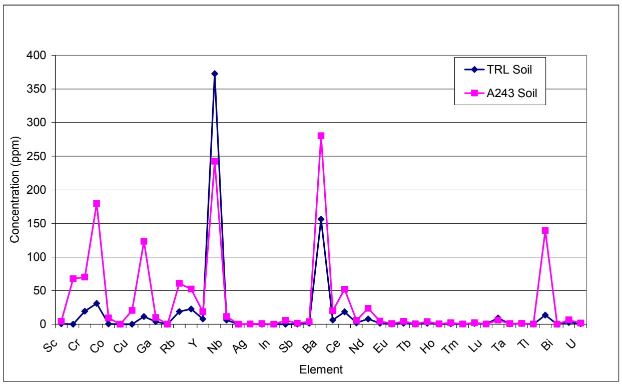


Figure 3.2 Trace element soil data

The same type of plot can be used to display trace element data (Fig 3.2) where elements are plotted for convenience in order of increasing atomic mass. Concentration scaling on this diagram is linear. Similarities and differences between the soils now become more apparent. For example, concentrations of Co, Ga and Nb for example are quite similar, while those for Zn, Zr and Pb are different. In addition, the ratio of adjacent pairs of elements varies between samples, but is reasonably consistent. In conclusion, while there are some differences between the chemistry of the soils from the different sites, these are relatively small.

A similar approach can be applied to displaying the trace element characteristics of other aspects of the roadside environment. The TRL research track has a road-side barrier located close to the junction of Bridle Hill Rise and Cornelius Avenue (Fig 2.1). Samples were collected by sweeping the upper surface of the barrier with a nylon brush and of the barrier itself by scraping with a stainless steel blade. A comparison of the trace element chemistry for the barrier and TRL soil are shown in Fig 3.3. It is reasonable to assume that some proportion of the dust deposited on the barrier surface will be wind blown soil particles and the trace element plot displays a good deal of similarity in pattern between the two samples although absolute concentrations may differ. In addition, the relative proportions of pairs of elements such as Th and U or Hf and Ta, for example, are also similar. However, there are a number of identifiable and significant differences between the two, notably the concentration and relative proportions of Nb, Mo and Ag. Unfortunately there is no Cd data available for the sweeping as insufficient material was available for analysis. These elements display a characteristic fingerprint which in the absence of any other information would distinguish these samples from each other.

The same information, but with the chemistry of the barrier scraping added, is shown in Fig 3.4. The likely origin of the characteristic Nb, Mo, Ag 'finger-print' in the barrier sweeping is clearly the barrier itself with the concentrations in the sweeping being somewhere intermediate between the two inputs of soil and barrier. The fingerprint for the sweeping appears to be a mix of soil and the barrier.

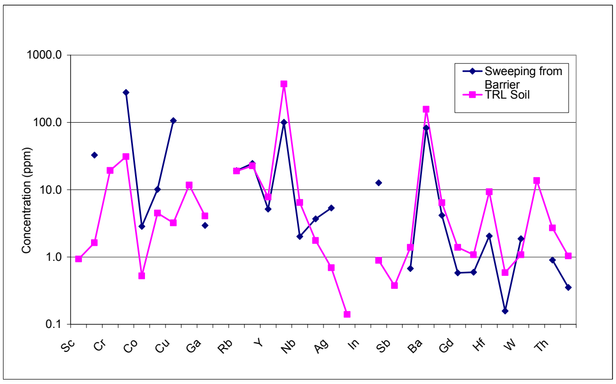


Figure 3.3 Comparison of soil composition with barrier sweeping TRL

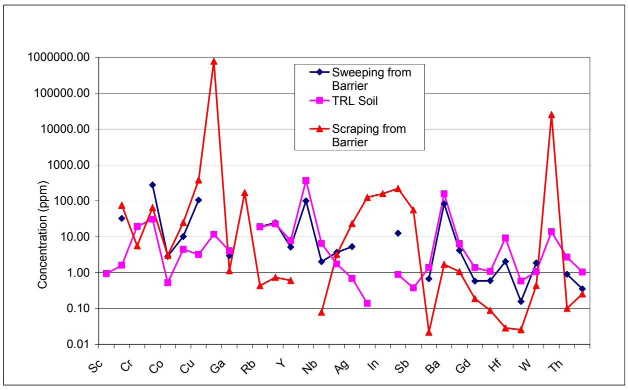


Figure 3.4 Comparison of sweeping and scraping from barrier with soil, TRL

In the same way we can also compare the chemical characteristics of the galvanised steel posts which support the street lighting at the Research track. The lamp posts are characteristically highly weathered, and in many cases the protective galvanised coating has been broken through to reveal the mild steel core which is oxidised to form a layer of rust. Scrapings were collected of both the galvanised and rusting steel core of a single lamp post. The asphalt area immediately adjacent to the base of the lamp post was also swept. In addition an asphalt surface located as far from any metal work as possible was also swept in order to provide a ‘asphalt’ trace element signature.

The trace element chemistry for the remote asphalt sweeping, sweeping under lamp post and TRL soil are compared in Fig 3.5. Whilst many elements are present in the samples at similar concentrations or show similar relationships between element pairs, a number of elements display characteristic features. For example, the relationship between Ag and Cd is characteristic such that Ag>Cd in soil, Ag<Cd in sweeping under lamp post and Ag=Cd in the sweeping from asphalt. There are similar characteristic patters for other pairs of elements such as Hf/W, Cr/V and Sn/Sb.

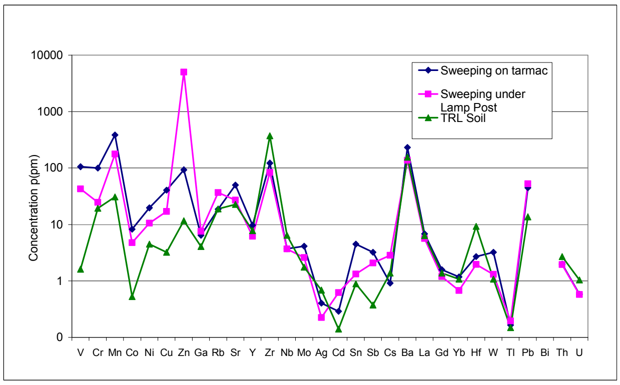


Figure 3.5 Comparison of sweepings from tarmac, tarmac under lamp post and TRL soil

These plots can be compared with the chemistry of the galvanised coating and mild steel core of the lamp post with which the sweeping is associated (Fig 3.6). Three pairs of elements stand out as being distinctively different from one part of the lamp post to another, namely Mo/Ag, Sn/Sb and Cr/V. From these plots we can see characteristics of the trace element chemistry of both the galvanised coating and steel core of a lamp post preserved in a dust swept from the asphalt surface immediately adjacent to the base. If Figs 3.5 and 3.6 are combined (Fig 3.7), the complexity of element relationships is only too apparent. It is clear that such plots are a useful starting point for the interpretation of complex chemical patterns.

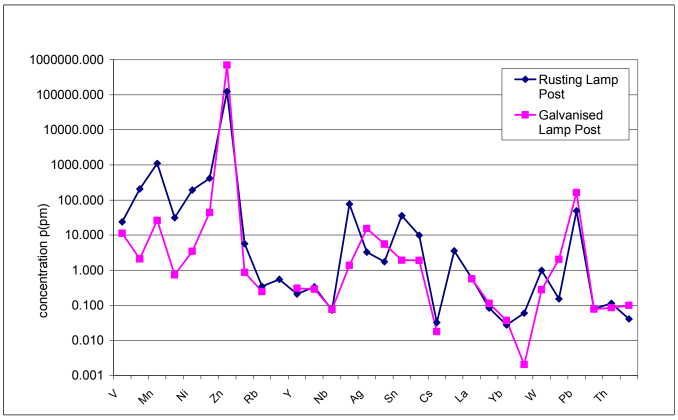


Figure 3.6 Comparison of galvanised and rusting part of lamp post at TRL

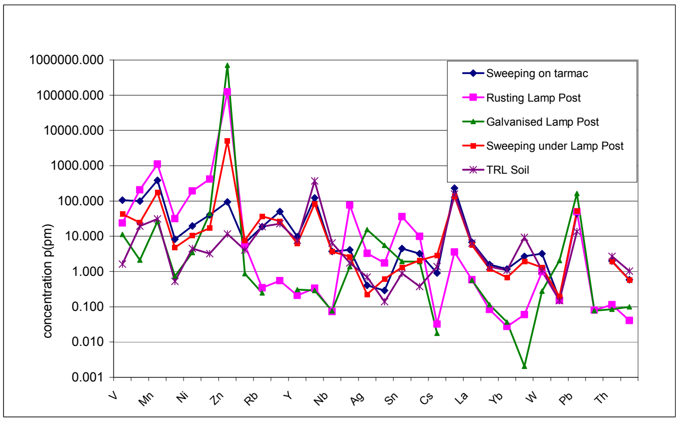


Figure 3.7 TRL fingerprints

General trace element chemistry can therefore potentially be used to permit initial characterisation of input sources to a particular sample. However, one particular group of trace elements can provide useful additional information, the rare earth elements. This group display very similar chemical properties due their ionic radius and charge. Indeed they are so similar that natural processes are unable to separate neighbouring elements from one another to any significant degree. However, some fractionation is possible across the group as a whole such that the light rare earth elements (La to Gd) may be fractionated from the heavier elements (Tb to Lu). To display this subtle fractionation, the concentration of each rare earth element present in a sample is divided by the concentration found in a meteorite sample following the recommendations of Nakamura (1974). This normalisation process removes the very large differences in concentration of neighbouring odd and even mass number elements, and subtle differences between samples become apparent.

The normalised REE patterns for sweepings from 6 asphalt and 3 concrete surfaces at TRL are shown in Fig 3.8. The sweepings from the asphalt surfaces display a very narrow range of patterns. The concrete surfaces show an overlap with the asphalt for the light REE but a distinctive and reproducible difference for elements Gd through to Lu. These REE patterns serve to characterise asphalt and concrete at TRL.

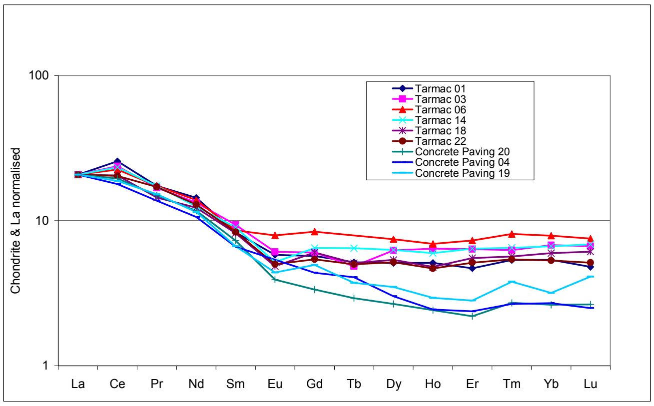


Figure 3.8 Normalised data for sweepings from tarmac and concrete at TRL

3.3 Concentration ranges

Graphic representation of the data serves to highlight general similarities and differences between individual samples. However, it is useful to compare ranges of chemical compositions for different materials and between sites. The TRL research track has essentially zero traffic flow and hence the expectation is that a real road situation such as the A243 should show enhanced levels of potentially traffic derived trace elements such as Zn, Cu and V. It is useful to identify typical elemental concentration ranges for the sites of interest particularly with a view to assessing the general effect of potential traffic inputs on the A243. Concentration ranges for all elements determined at TRL and on the A243 are given in Appendix 3.

Table 3.1 Concentration ranges (ppm) for selected elements in sweepings from asphalt surfaces compared with soil chemistry at TRL research track.

Element	Footway (n=12)	Asphalt road (n=12)	Soil (n=3)
Sc	1.4-4.0	2.2-9.2	0.5-1.2
Cr	25-105	20-617	14-23
Cu	11-78	31-86	<3
Zn	141-12900	94-322	8-15
Sr	22-79	39-70	18-26
Nb	3.3-6.0	2.9-11	5.2-7.5
Mo	<1.8-9.8	2.2-4.1	<1.8
Sn	0.9-2.8	1.0-28	<0.9
Sb	1.4-3.2	1.9-29	0.26-0.56
Ce	12-44	12-23	14-23
U	0.4-1.4	0.5-0.8	0.9-1.2

Overall, there is a generally a relatively narrow range of compositions for any particular element with concentration ranges showing significant overlap (Table 3.1). However, specific elements such as Zn display a very wide range of concentrations and highly elevated levels on the asphalt surfaces compared with local soil. The footway has concentrations in excess of 12000ppm. This pattern is reflected at the A243 although maximum concentrations are lower at ~2500ppm Zn (Table 3.2). Soil derived elements such as Ce and U have extremely similar ranges regardless of the surface type.

Table 3.2 Selected element concentration ranges (ppm) for sweepings from asphalt surfaces compared with soil chemistry at A243 site.

Element	Footway (n=6)	Asphalt road(n=7)	Soil (n=2)
Sc	4.9-10	3.5-5.5	3.2-3.5
Cr	63-257	60-90	67-73
Cu	91-170	99-187	19.5-21.6
Zn	385-2509	241-417	98-150
Sr	68-109	76-92	50-54
Nb	4.0-8.0	3.7-7.2	11.3-11.8
Mo	<1.8-12	<1.8-7.2	<1.8
Sn	3.9-17	4.1-8.2	5.8-6.0
Sb	8.9-27	7.4-18	1.3-1.7
Ce	27-32	24-32	46-58
U	1.0-1.7	0.8-1.4	1.6-1.8

3.4 Normalised data

A simple comparison of concentration ranges can be misleading when samples contain significant and variable amounts of organic material. Loss on ignition measurements have not been carried out for the sweeping samples collected for this work as insufficient material was available. In addition, variable amounts of soil incorporated in a sweeping will also produce variation in ranges which are largely controlled by soil composition. However, normalisation of the chemical data using a soil derived element can be carried out to overcome these effects. In this case, the concentration of each element in a sample is divided by the concentration of Ce in that sample, the values calculated are termed normalised concentration.

Table 3.3 Selected cerium normalised concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at TRL research track.

Element	Footway (n=12)	Asphalt road (n=12)	Soil (n=3)
Sc	0.05-0.24	0.46-0.86	0.04-0.07
V	1.4-3.8 [4.7]	4.8-9.1	-
Cr	0.6-2.9	1.4-4.4 [29,30]	1.01-1.09
Mn	10-32	17-36	1.3-1.8
Cu	0.8-1.9 [6.6]	1.8-6.1	-
Zn	19-818	4.2-17	0.48-0.82
Zr	5.2-9.9	4.0-7.5	17-28
Mo	0.06-0.26 [0.83]	0.15-0.27	-
Sn	0.07-0.10	0.07-0.20 [0.62]	-
Sb	0.04-0.18	0.15-0.35	0.01-0.03
W	0.04-0.08 [0.12]	0.07-0.14 [0.2]	0.03-0.08
Pb	1.4-5.4	2.0-3.8 [25]	0.4-1.2

- = not measured. Figures in square brackets indicate a single value lying outside of the ‘normal’ range.

Normalised concentration ranges for all sample groups below are given in Appendix 4. Selected elements are presented below for discussion.

Selected normalised concentration ranges for sweeping samples from TRL are shown in Table 3.3 9AND Appendix 4.1). Data are separated into asphalt footway, asphalt road and, for comparison, average TRL soil. The ranges for major elements are all relatively narrow, with the asphalt road often displaying higher upper values than footway or soil samples. The footway and the road are higher in Al, Mg, Fe, K and P than the local soil suggesting that the bulk of the dust is not soil derived. Trace elements show similar characteristics but with specific elements standing out as being characteristic of particular surfaces. For example, V is significantly higher on the road than on the footway or in local soil while Mn, Co, Sb and Pb are similar on the asphalt surfaces and low in the soil. Chromium, whilst having similar ranges for a majority of sweepings, is seen in 2 asphalt road samples as being exceptionally high. Surprisingly, Sc is elevated on the asphalt surfaces compared with the soil. Scandium is often used a soil indicator element but in this case is clearly not soil derived. Other soil indicator elements such as Zr, Nb and Hf are most elevated in the soil.

Perhaps, the most characteristic feature of this data set is the very large range, and elevated concentrations, of Zn from asphalt surfaces compared with soil values, particularly on the footway where normalised values exceed 800 compared with soil values of <1. In addition, the highest value seen on the asphalt road is only 17. This may suggest that the Zn is derived wholly or in part from a source close to the footway which is not influencing the asphalt road sweepings. Alternatively, the composition of the asphalt on the footway and road may be substantially different with respect to normalised Zn content.

A similar consideration of normalised data for the A243 (Table 3.4 and Appendix 4.2) shows a number of characteristics. Major element normalised concentrations are similar on both asphalt surfaces with the exception of Si, Na and Ca which are lower in the local soil, Ca significantly so. A number of trace elements, Cd, Sb, Pb, Cu, Mn, Cr, Sn and W are elevated on asphalt surfaces. The most characteristic feature of this data set is, again, the large range, and elevated concentrations, of Zn from asphalt surfaces compared with soil values, particularly on the footway where normalised values exceed 80 compared with soil values of ~3. In addition, the highest value seen on the asphalt road is only 17. This distribution of Zn is the same as that observed at TRL research track suggesting a source of Zn close to the footway which may or may not contribute to the levels observed on the asphalt road.

Table 3.4 Selected cerium normalised concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at A243 site.

Element	Footway (n=6)	Asphalt road (n=7)	Soil (n=2)
Sc	0.14-0.34	0.14-0.17	0.07-0.09
V	0.69-2.4	1.0-1.7	1.2-1.4
Cr	2.2-3.3 [11]	2.0-2.9	1.3-1.5
Mn	11-19	11-15	3.3-3.7
Cu	3.2-7.8	3.1-5.3	0.34-0.48
Zn	10-84	9.2-17	1.7-3.3
Zr	3.4-12	3.7-9.0	4.2-5.3
Mo	0.10-0.29	0.04-0.24	-
Cd	0.020-0.043	0.022-0.037	0.015-0.017
Sn	0.13-0.34 [0.74]	0.13-0.27	0.10-0.13
Sb	0.32-0.89	0.25-0.66	0.03
W	0.05-0.11	0.04-0.05	0.02-0.03
Pb	3.2-4.3	3.2-6.1	2.7

- = not measured. Figures in square brackets indicate a single value lying outside of the ‘normal’ range.

The TRL research track was chosen for the initial work due to an absence of traffic and thus potential input from vehicle wear and tear including inputs from braking and tyre wear. The A243 is similar in its ‘geography’ being surrounded by woodland and vegetated areas, and having asphalt road and footway surfaces and abundance of street furniture. Additionally it potentially has elements of input from passing traffic, with flow and speed being relatively constant. Most road systems are considerably more complex than either of the study sites, with significant changes in traffic flow, vehicle braking and acceleration, wide range of vehicle types and static traffic during rush hour for example.

A preliminary study carried out in 2003 (Cook et al., 2003) included roads and junctions with many of these more complex characteristics. Normalised data from that study are shown in Table 3.5 for sweepings from asphalt and concrete road (no footways were sampled) and for two car parks with asphalt surfaces. Normalised ranges for asphalt and concrete roads are similar with a significant degree of overlap in ranges. These ranges are in turn similar to those seen at both TRL and on the A243 for asphalt road sweepings. However, the two samples taken from car park areas show some interesting characteristics. While for some elements a similar range of values is observed, values are higher for MgO, CaO, MnO, Zn, Mo and W (Cr, Sn and Sb were not determined).

Table 3.5 Selected cerium normalised concentration ranges for sweepings from asphalt and concrete surfaces compared with samples from car parks. (Data from Cook et al., 2003)

Element	Asphalt road (n=9)	Concrete road (n=2)	Car park (n=2)
Sc	-	-	-
V	-	-	-
Cr	1.8-4.0	3.3	-
MnO	4-25	13-18	***16-27***
Cu	5.6-19	4.0-8.3	7.3-7.5
Zn	4.9-20	6.9-11	***14-27***
Ga	0.08-0.34	0.10-0.15	0.16-0.17
Zr	4.8-10 [26]	6.7-7.7	4.2-5.6
Mo	0.15-0.45	0.11-0.57	***0.41-0.69***
Sn	0.4-1.7	0.5	-
Sb	0.27-0.53	0.5	-
W	0.11-0.25	0.04-0.22	**0.36**
Pb	3.3-8.8	3.3	-

- = not measured. Figures in square brackets indicate a single value lying outside of the ‘normal’ range.

A study carried by Abeyawickrama (2003) also sampled surface sweepings from a number of asphalt roads, from mainly central London roads, but also from 4 car parks (Table 3.6). Samples were taken from a wide range of situations from local urban side streets, country roads and high traffic flow major junctions. Again, the general ranges of normalised concentrations for asphalt roads is comparable to that observed by Cook et al., (2003) and those from this study. The car park samples show characteristically high values for Cr, Cu, Zn, Mo, Sn, Sb and Ba.

Table 3.6 Selected cerium normalised concentration ranges for sweepings from asphalt surfaces compared with samples from car-parks. (Data from Abeyawickrama, 2003)

Element	Asphalt road (n=20)	Car park (n=4)
Sc	-	-
V	-	-
Cr	0.8-4.1 [6.2]	***4.4-7.6***
MnO	8-35	10-21
Cu	0.6-10	***9.8-16***
Zn	1.9-15 [25]	***14-58***
Zr	2.0-6.5 [9.8]	3.8-6.8
Mo	0.06-0.57	***0.59-1.40***

Sn	0.03-0.58	***0.33-0.99***
Sb	0.04-0.75	***0.13-1.8***
W	0.02-0.10	0.06-0.13
Pb	-	-

- = not measured. Figures in square brackets indicate a single value lying outside of the 'normal' range

A summary of the ranges and maximum and minimum normalised concentrations for selected elements in surface sweepings from asphalt roads is shown in Table 3.7. It is interesting to note that although samples were taken from a very wide number of different localities, the observed data fall within a very narrow range for each element.

Table 3.7 A summary of ranges of cerium normalised concentrations recorded in surface sweepings for selected elements

	Cr	Cu	Zn	Nb
TRL	1.4-4.4	1.8-6.1	4.2-17	0.17-0.25
A243	2.0-2.9	3.1-5.3	9.2-17	0.13-0.22
Ref (a)	0.8-4.1	0.6-10	1.9-15	0.06-0.24
Ref (b)	1.8-4.0	5.6-19	4.9-20	0.11-0.25
Range	*0.8-4.4*	*0.6-19*	*2-20*	*0.06-0.30*

	Mo	Sn	Sb
TRL	0.15-0.27	0.07-0.20	0.15-0.35
A243	0.04-0.24	0.13-0.27	0.25-0.66
Ref (a)	0.06-0.57	0.03-0.58	0.04-0.75
Ref (b)	0.15-0.45	0.4-1.7	0.27-0.53
Range	*0.06-0.60*	*0.3-2*	*0.04-0.8*

Key: (a) Abeyawickrama, 2003, (b) Cook et al.,2003.

Samples of road dust and soil were taken from major roads as part of a current project for the Highways Agency and the results are presented here for the road dust, with permission. The roads sampled were A66 Stainton, A66 Brough, M62, M602, M6 Keele, M6 Coventry, A5, M5, A303, A11, A12 and A46. The data provide the opportunity to compare the heavy metals in this project with motorways and fast roads carrying very large traffic flows. Interestingly, with the exception of the M6 motorway, the concentrations of heavy metals, normalised to Ce, are within the ranges in Table 3.7. The values for the M6 motorway at Coventry are higher than the ranges in Table 3.7 for Cr [15], Cu [26], Zn [31], Nb [0.4], Mo [3.7] and Sn [1.8]. On the A 243 these elements

show higher concentrations on the footway than the road and it is inferred that street furniture is the source. On the motorway there is no footway and so any contamination from street furniture will be detected on the road.

It is particularly interesting to note that the four sites with the highest concentrations of Zn have barriers adjacent to the sampling site. Barriers are not present at the other sites. The values for all the other motorways and fast roads are within the ranges in Table 3.7. For example, the normalised heavy metal concentrations in road dust from the M5 are identical with those in road dust from the TRL research track. This would seem to confirm the hypothesis that street furniture is a more significant source of heavy metal contamination than traffic.

4 Analysis and discussion

The chemical specifications laid down either by statute, or from a practical consideration of chemistry have been reviewed above and provided a starting point for an assessment of potential trace element markers in a range of materials including galvanising, steel, asphalt and paints.

4.1 Chemical comparison of potential input sources with specifications

4.1.1 Steel

A comparison of the relative proportion of trace elements measured in steel samples at TRL with those specified for manufacturing materials highlights some important features. Typical steel chemistry is shown in Table 4.1. In general, the concentrations are similar for analysed samples and for typical levels in mild steel with between 0.0005 wt% for Tl to 0.01 wt% for As. Thus measured and predicted concentrations are rather similar.

Table 4.1 A comparison of trace element specification and measured values (TRL) for steel samples

Element	Measured (wt%)	Typical steel (wt%)
V	0.005	0.01
Cr	0.005	0.03
Mn	0.02	0.01
Co	0.001	0.03
Ni	0.005	0.03
Cu	0.02	0.05
As	0.01	0.01
Nb	0.001	0.03
Mo	0.001	0.03
Ag	0.001	0.0001
Cd	0.002	0.001
Tl	0.0005	0.01
Pb	0.02	0.005
Bi	0.00001	0.001

4.1.2 Zinc galvanising

A similar comparison can be made for some trace elements in galvanising from TRL with the maximum levels of impurities specified for manufacture (Table 4.2). The TRL galvanising is characteristically ‘clean’ with significantly lower levels of trace contaminants than the specification would suggest. Figures shown in square brackets are from a single analysis (barrier) which is significantly higher than those typically found in galvanised lamp posts. Measured levels of Cu and Cd in particular are very low at 0.005 wt% compared with maximum specified levels of 0.2 wt%.

4.1.3 Asphalt

The bulk mass of any road dust sample will be composed of a limited, and well defined number of major elements typically found in silicate materials. Thus it is useful to compare the major element chemistry of asphalt and local soil as these two inputs are the only likely source of the bulk mass of road dust. This is the case at TRL, on the A243 and will be the case at almost any location. A comparison of soil chemistry with sweepings from asphalt surfaces at TRL is shown in Table 4.3.

Table 4.3 A comparison of major elements in soil and sweepings from asphalt surfaces at TRL

Element	Asphalt (wt%)	Soil (wt%)
SiO_2	63-79	91-101
Al2O3	5.7-6.7	0.9-2.0
Fe2O3	3.6-4.3	0.1-0.5
MgO	1.5-2.2	0.08-0.12
CaO	2.3-3.7	<LLD
Na2O	0.8-1.2	<LLD
K2O	0.55-0.74	0.20-0.56
TiO2	0.29-0.34	0.26-0.26
P2O5	0.08-0.10	0.005-0.015

<LLD = less than lower limit of detection

The soil at TRL is sandy and composed almost entirely of silica. By contrast the asphalt sweepings contain lower levels of silica and higher concentrations of all other elements with the exception of TiO_2. It is clear that the chemistry of the sweeping from the asphalt is not reflecting that of local soil but that of the underlying asphalt surface. Research by Lindgren (1996) in Sweden, suggests that the chemistry of the dust produced from the erosion of asphalt surfaces (in that case via the widespread use of studded types) may reflect a combination of the chemistry of bitumen and aggregate. Basic igneous rocks such as gabbro and dolerite are commonly used as aggregate and typical gabbro composition compares well with surface sweepings from TRL (Table 4.4) although Pb concentrations at TRL are considerably higher than in typical gabbro.

Table 4.4 A comparison of trace elements in gabbro and sweepings from asphalt surfaces at TRL

Element	Asphalt sweeping (ppm)	Gabbro (ppm)*
Cd	0.29-0.39	0.13
Cr	20-99	238
Cu	34-40	71
Pb	33-418	2.8
V	96-131	215
Zn	94-248	149
Ni	16-25	110

* data from Lindgren (1996)

4.1.4 White lining

Thermoplastic road markings typically consist of 18% binder, a minimum of 10% rutile (TiO_2) pigment and 48% glass spheres. The binder is organic in nature and the spheres are soda lime glass (70-75% SiO_2, 12-16% Na_2O, 10-15% $CaCO_3$). Sweepings taken from the surface of the white lining denoting a 'zebra' crossing reflect the chemistry of the white paint with significantly higher concentrations of TiO_2 and CaO compared with those from a paint-free asphalt surface (Table 4.5).

Table 4.5 Major element chemistry of sweepings from asphalt and from surface of white line paint TRL

Element	Asphalt sweeping (wt%)	White line sweeping (wt%)
SiO_2	63-79	37-57
Al_2O_3	5.7-6.7	3.4-5.8
Fe_2O_3	3.6-4.3	2.2-3.8
MgO	1.5-2.2	3.0-3.9
CaO	2.3-3.7	6.5-7.9
Na_2O	0.8-1.2	0.5-1.1
TiO_2	0.29-0.34	0.69-1.5

4.2 Chemical signatures

At both the TRL research track and the A243 sites sweepings were collected from asphalt and concrete surfaces adjacent to metal road furniture. If metal sign posts or lamp posts are releasing metallic fragments then we would expect to see some indication in the chemical signature of dust collected adjacent to a potential source. To assess the feasibility of this approach, samples were collected of dust swept from an area adjacent to a metallic source whilst scrapings were collected from the source itself.

4.2.1 TRL research track

Lamp posts

At TRL, lamp posts are constructed of steel with a layer of zinc galvanising on the surface. Many of the lamp posts are highly weathered and rusting indicating that the galvanised layer has been ‘worn’ away or broken through to reveal the mild steel core. The steel and galvanised parts of these posts were sampled separately along with a single sweeping from around the base. The results for the analysis of galvanised areas for 4 lamp posts are given in Table 4.6 for a selection of elements. The lower part of the table shows the data for the sweepings associated with each post.

The major element present in the galvanised samples is Zn but a number of elements are present at an elevated concentration when compared with TRL average soil. When compared with the associated sweeping, Mn, Ag, Cd, Tl and Pb are present at very elevated levels while Cr, Mn, Co, Ni, Cu, Mo, Sn and Sb are also characteristic. However, of these only Zn appears at an elevated level in the sweeping. The relative proportion of these trace elements to Zn is low compared to the literature values for galvanised metal. In addition, if the relative proportions of trace elements to Zn is calculated for the galvanising and compared with those observed in the sweepings, they are all too high in the sweepings. For example Pb as a proportion of Zn in the galvanising is 0.02%, while in the sweeping is 0.8%. There is the same relationship for the other characteristic trace elements.

The major element present in the steel part of the lamp post, aside from Fe which has been omitted from this table, (Table 4.7) is Zn suggesting some mixing of the galvanising and steel components. A number of trace elements are characteristic of the steel including Cr, Mn, Ni, Cu, Mo, Ag, Sn and Sb. None of these elements stands out as being particularly characteristic in the sweeping.

Table 4.6 Chemical comparison of source and associated sweepings for selected elements in galvanised lamp posts, TRL (concentrations in mg/kg or ppm)

Sample	Reason	Type	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T24	Lamp Post	Galvanised	16.1	4.30	58.8	1.13	6.84	64.6	682373	2.57	4.88	4.28	0.03	3.37	2.33	0.29	1.82	160	0.28
T29	Lamp Post	Galvanised	40.2	393	1253	32.4	216	582	663861	87.4	3.12	1.78	0.18	47.8	12.6	2.46	0.23	129	0.34
T35	Lamp Post	Galvanised	11.4	2.10	26.4	0.73	3.45	44.2	705347	1.38	15.4	5.51	0.09	1.93	1.91	0.28	2.05	164	0.08
T37	Lamp Post	Galvanised	20.7	28.0	1175	4.56	15.4	38.0	808540	3.36	4.79	0.85	0.08	4.04	2.44	1.11	<0.033	58.4	0.13

Sample	Associated sample	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T11	T24	54.9	ND	374	7.03	38.4	78.0	ND	9.83	0.44	ND	N/D	0.97	ND	1.41	ND	ND	N/D
T04	T29	48.2	51.7	296	7.14	28.2	39.8	6456	3.96	0.40	1.036	N/D	2.81	2.45	1.86	0.32	47.9	N/D
T33	T35	42.47	24.7	176	4.75	10.6	17.0	5034	2.60	0.22	0.622	N/D	1.32	2.07	1.30	0.20	52.4	N/D
T19	T37	39.9	33.0	353	9.96	13.1	21.4	4746	2.64	0.41	0.899	N/D	1.94	1.60	1.82	0.23	37.8	N/D

Table 4.7 Chemical comparison of sources and associated sweepings for selected elements in steel lamp posts TRL (concentrations in mg/kg or ppm)

Sample	Reason	Type	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T23	Lamp Post	Steel	21.9	208	1414	32.6	197	455	114777	72.1	3.03	1.58	0.10	32.0	8.99	1.37	0.17	77.6	0.22
T28	Lamp Post	Steel	21.2	14.4	111	3.34	16.4	82.8	131107	5.94	12.4	1.19	0.10	6.12	6.34	0.68	1.60	241	0.49
T34	Lamp Post	Steel	23.7	207	1103	31.3	192	414	123608	76.8	3.29	1.75	0.14	35.8	9.90	0.99	0.15	49.3	0.08
T36	Lamp Post	Steel	10.1	819	11519	209	719	808	108559	29.0	6.28	0.89	0.27	66.4	13.9	17.3	<0.033	0.34	<0.021

Sample	Associated sample	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T11	T23	54.9	ND	374	7.03	38.4	78.0	ND	9.83	0.44	ND	N/D	0.97	ND	1.41	ND	ND	N/D
T04	T28	48.2	51.7	296	7.14	28.2	39.8	6456	3.96	0.40	1.036	N/D	2.81	2.45	1.86	0.32	47.9	N/D
T33	T34	42.47	24.7	176	4.75	10.6	17.0	5034	2.60	0.22	0.622	N/D	1.32	2.07	1.30	0.20	52.4	N/D
T19	T36	39.9	33.0	353	9.96	13.1	21.4	4746	2.64	0.41	0.899	N/D	1.94	1.60	1.82	0.23	37.8	N/D

There may be a number of explanations for these observations. The first is that there is an additional input source contributing to the dust chemistry. The second is that the concentration of Zn measured in the sweeping is lower than it should be. A study by Rourke, (1998) suggested that Zn may be solublised from metal surfaces providing a mechanism for the selective removal of only this element.

Barrier

The TRL research track has a single barrier located on the east side of Bridle Hill Rise. It is the only example of a barrier from either sampling site, and although of galvanised construction, stands out being chemically different from the other galvanised features (Table 4.8). It is characterised by very elevated levels of Cu, Ag, Cd, Sn, Sb. Pb and Bi. Lead concentrations are exceptionally high with over 25,000 ppm (2.5 wt%). Unfortunately it has not been possible to see if all of these elevated levels are reflected in the composition of the sweeping taken from the top surface of the barrier as the amount of sample available was very small precluding preparation for some of these elements. However, compared with concentrations found in the sweepings associated with lamp posts and local soil, Cu, Ag and Sn are significantly higher and may be used to characterise the contribution the barrier has made to the dust on its surface.

Drain cover and sign post

The drain cover is an example of a cast iron construction and at TRL these are badly rusted such that pieces of rusted material can easily be picked from the surface. The sign post is an example of a steel construction which is not associated with galvanising. The cast iron is characterised by significant levels of Mo, Ag, Cd, Tl and Pb and most importantly by over 770 ppm V (Table 4.9). This is the highest level of V recorded in any sample and is a distinctive feature of the cast iron at TRL. However, none of these elements are obviously enhanced in the associated sweeping. The steel sign post is characterised by many of the same elements as those found in the steel core of the lamp posts, namely Ni, Zn, Mo, Sn and Pb. Of these only Pb appears in the associated sweeping at an elevated concentration and then only at about twice other sweeping levels.

Table 4.8 Chemical comparison of source and associated sweeping for selected elements in a galvanised barrier, TRL (concentrations in mg/kg or ppm)

Sample	Reason	Metal	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T26	Barrier	Galvanised	75.9	5.59	64.9	3.02	25.1	379	773598	3.19	23.4	124	160	222	55.6	0.44	<0.033	25094	5.86

Sample	Associated sample	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T07	T26	32.7	ND	279	2.85	10.1	106	ND	3.68	5.33	ND	N/D	12.6	ND	1.86	ND	ND	N/D

Table 4.9 Chemical comparison of sources and associated sweepings for selected elements in an iron drain cover and steel sign post, TRL (concentrations in mg/kg or ppm)

Sample	Reason	Metal	V	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	W	Tl	Pb	Bi
T32	Drain Cover	Iron	776	35.4	149	3.92	36.9	124	<9.16	7.20	11.4	7.82	0.09	7.67	2.82	0.39	1.97	175	0.11
T25	Sign Post	Steel	34.1	78.2	582	47.8	205	260	680	37.4	1.18	2.53	0.05	20.9	4.82	1.20	0.01	278	<0.02

Sample	Associated sample																
T31	T32	48.3	86.6	840	6.38	13.0	50.3	156	3.87	0.37	0.958	N/D	28.1	3.11	2.48	0.21	51.5	N/D
T10	T25	34.1	22.3	322	5.69	15.1	21.7	355	2.69	0.41	3.73	N/D	0.92	1.36	1.01	0.18	101	N/D

TRL average Soil	<1.62	19.3	30.9	0.52	<4.49	<3.22	11.7	<1.75	0.69	<0.14	N/D	<0.89	0.37	1.08	0.15	13.7	N/D

Table 4.10 Chemical comparison of sources and associated sweepings for selected elements from A243 Kingston Road (concentrations in mg/kg or ppm)

Sample	Furniture	Type	V	Cr	Mn	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	Tl	Pb	Bi
S01/08/04	Lamp Post	Galvanised	1.86	13.7	167	731	412569	0.31	24.0	29.8	130	664	17.7	0.91	5361	3.18
S06/08/04	Lamp Post	Galvanised	0.96	3.1	55.8	538	874656	0.76	61.2	16.0	216	610	33.4	1.18	11780	9.39
S09/08/04	Manhole cover	Cast Iron	41.4	19.6	1461	137	509	7.46	0.30	<0.74	0.06	7.5	9.28	0.033	179	0.40
S15/08/04	Sign Post	Steel	40.3	120	7599	86.4	136	7.46	0.10	<0.74	0.11	24.5	2.82	0.013	8.46	0.04

Sample	Associated sample	V	Cr	Mn	Cu	Zn	Mo	Ag	Cd	In	Sn	Sb	Tl	Pb	Bi
S02/08/04	S01/08/04	71.2	76.2	571	170	2509	11.95	0.63	1.14	N/D	3.90	26.8	0.29	104	N/D
S07/08/04	S06/08/04	40.5	68.4	421	144	1189	2.92	0.60	0.86	N/D	8.94	18.3	0.20	129	N/D
S08/08/04	S09/08/04	22.2	ND	369	148	ND	4.15	0.36	ND	N/D	<0.89	ND	ND	ND	N/D
S16/08/04	S15/08/04	45.4	257	398	160	400	6.80	1.78	1.00	N/D	17.22	12.8	0.22	98.5	N/D

S12/08/04	Asphalt	59.2	93.7	498	90.7	385	4.2	0.24	0.69	N/D	4.57	8.94	0.18	89.8	N/D
Average Soil	Soil	67.6	70.2	94.5	20.6	123	<1.75	0.45	0.80	N/D	8.9	1.51	0.45	140	N/D

4.2.2 The A243 Kingston Road

Examples of sweepings with samples of galvanised lamp posts, cast iron drain cover and steel post are shown in Table 4.10. Samples of galvanised lamp posts can be compared with those from TRL. The A243 samples have significantly higher levels of contamination for Cu, Ag, Cd, In, Sn, Sb, Tl, Pb and Bi. The concentrations measured are more akin to that of the TRL barrier sample with lead levels in excess of 1.5 wt%. When compared with local soil and sweeping from asphalt remote from significant potential contamination source, Cu, Ag, Cd and Sb are elevated in the associated sweeping.

The cast iron manhole cover and steel sign post are both characterised by V, Cr, Mn, Cu, Zn and Mo. Copper and Mo appear higher in the sweeping than in either the soil or asphalt comparison sample.

However, there are a number of other elements which appear at higher concentrations in the asphalt sweepings than in any of the metal samples with which they are associated. These elements are V, Cr and occasionally Mo. This observation is consistent with them being derived from the road asphalt surface. Lindgren (1996) reports elevated concentrations of Cr (238 ppm) in gabbro aggregate, V (340ppm) in bitumen binder and up to 1% Mo in coal fly ash used as a filler in asphalt surfaces.

4.3 Discussion

The two sites studied were selected because they have similar topography but differ in the level of traffic using the roads. TRL is effectively free of traffic and it is therefore possible to compare the road dust taken at the two sites to investigate differences that may be due to non traffic-derived contaminants. Thirty-seven elements were determined in the samples. The ranges of elements measured at the two sites were remarkably similar.

The samples of road dust contain organic material. This is sometimes a small component, but at TRL the sweepings contained a high organic content. Sample sizes were often two small after sieving to carry out a ‘loss on ignition’ determination. Therefore all sample data were corrected by normalising to cerium. The effect of this normalisation was to make the range of values across the whole range of road dust samples to become even tighter.

The results are compared to twenty road dust samples collected and analysed during an earlier stage of this project (Cook et al., 2003), plus another nine samples investigated in work carried out with the authors (Abeyawickrama, 2003). The range of concentrations for both major and trace elements in road dust is quite consistent. Even thirteen samples taken from motorways and fast roads, have concentrations that lie within the same range of values. For example, the ranges for elements of interest such as Cr, Cu, Zn, Nb, Mo, Sn and Sb were just 0.8-6, 0.6-19, 2-32, 0.06-0.4, 0.06-4, 0.03-2 and 0.04-0.8, respectively.

Comparison of road dusts from both sites with their respective local soils indicates that soil is not a major component of road dust. The soil at TRL is mainly silica with just a few percent of the remaining elements in total. The profile of road dust had a maximum of 79% silica with several percent each of oxides of Al, Fe, Mg, Ca and Na, and it is highly likely that these are derived from the road surface. This is supported by the variation in major element components in asphalt surface and concrete surfaces at TRL and elsewhere. It is therefore unlikely that road dust is soil-derived.

The similarity between the heavy metal contamination in road dust at TRL and on the A243 (and other urban and rural sites) suggests that traffic has a smaller influence than currently perceived. Since soil does not play a major role, it would appear that the road surface and street furniture is a significant factor in contamination in road dust. To investigate this further, a thorough review was been made of the literature regarding the characterisation of components present in the road environment. The materials investigated included ferrous and non-ferrous metals and alloys found in street furniture, concrete and asphalt surfacing, including aggregate and bitumen, and paint used in road markings. The result provides typical chemical compositions of the materials, which can be used to assess the potential contributions of contaminants from road surface and street furniture.

The materials used in building roads and pedestrian ways, such as asphalt and concrete surfaces have characteristic elemental compositions which act as signatures in road dust. Asphalt consists of about 95% aggregate and 5% bitumen binder. Previous studies have shown that elements such as V and Ni are found in bitumen, and aggregate has high concentrations of As, Cr, Cu, Ni, Pb,V and Zn. Road dust at both of the study sites contained concentrations of elements such as Cd, Cr, Cu, Ni, V and Pb similar to natural levels in gabbro, which is used in aggregate. Dust taken on white lines showed a different signature to that from asphalt, with elevated levels of Ti from the pigment and Ca, presumably from the soda lime glass used in the reflecting glass spheres.

etals and alloys used in street furniture, such as steel and zinc galvanising, contain trace metal components that act as signatures. For example, Zn used in galvanising contains Pb, Cu, Sn, Cd and Bi. Steels contain Mn, Cu, Co, Cr, Mo, Ni, V, Pb, Cd, Bi and Ag. In this study the elemental profiles of street furniture and paint were established for a range of materials, including galvanised posts and barriers, steel posts, iron drains and rusting posts. Analyses of samples of zinc galvanising and steel taken from lamp posts at TRL showed typical elemental profiles to those found in the literature but in general were rather cleaner than expected. This was confirmed in the material samples on the A243. For example, Ni is added to the galvanising bath to improve performance and typical concentrations lie between 0.04 and 0.07%. The measured concentrations were typically 0.001%, with just one example at 0.03%. Steels may contain up to 0.03% of Cr, Co, Ni, Nb and Mo but in general all these elements were between 0.001 and 0.005% in the street furniture analysed.

Once the materials had been characterised at TRL and on the A243, it was possible to compare trace element compositions in street furniture, associated road dust and soil. A careful study demonstrated that key elements could be allocated to particular sources. For example, asphalt was shown to be the main source of V, Cr and Mo at TRL, where there is no significant traffic input.

Dust taken from the vicinity of street furniture at TRL showed elevated levels of signature elements derived from galvanising. This work provided practical proof that Cu, Ag, Cd, In, Sn, Sb, Tl, Pb and Bi are associated with galvanised Zn. Additionally, measurements have shown that V, Cr, Mn, Mo, Ag, Cd, Sn, Tl and Pb in dust are associated with iron and steel. The effect was less obvious on the A243 because there was little weathering and corrosion of the furniture, but it could still be detected.

The concentration of Zn is greater on the footway than the road at TRL and the A243, suggesting that it is derived from galvanised street furniture. Other elements associated with galvanising, such as As, Cd, In, Pb and Bi are too low to be detected above the general background. Another study by the authors provides a further indication of galvanising as the origin of Zn (Abeyawickrama, 2003). Dust samples taken from car parks show elevated levels of Zn, derived from the considerable lengths of barrier and ducting normally found in car parks.

Thirteen samples taken from high speed roads as part of a study by the authors for the Highways Agency confirmed that traffic was not a large influence on heavy metals in road dust. Moreover, the four sites that has barriers associated with the sampling points were the only ones exhibiting elevated levels of Zn and other heavy metals.

Zinc is the only element in road dust that is at sufficiently elevated concentrations to be seen as originating from a single identifiable source. The source is galvanised street furniture. This study has defined typical concentrations of heavy metals in galvanising but further work is required to determine how characteristic the profile of the elements is at TRL and on the A243.

It was noted that on the A243, other elements associated with galvanising, such as Mo, Ag and Cd, were more prominent than Zn, which is expected to be the major component. Zinc is dissolved from lamp posts and barriers by rainfall and so it is possible that the majority of Zn eroded is lost in a soluble form. It is therefore proposed that less soluble metals like Mo and Ag will remain and concentrate in the roadside environment compared to Zn. The same theory applies to rusting steel, where Fe may be lost in the soluble form but Cr and Mo may remain un-dissolved.

In summary, there are four key sources of heavy metals related to road surfaces and street furniture: asphalt, zinc galvanising, iron and steel. Many elements are components of more than one of these sources and some appear in all three, namely Cr, Mo, Cu, Ni, Cd, Sn, Sb and Pb. If the ratios of the elements were constant in the materials it would be a simple matter to apportion them to the different sources. However, with preferential dissolution of some elements it is difficult to do so at present. Further work is required to study the dissolution of zinc galvanising and steel in rainfall to ascertain the relative solubility of the heavy metals. Then it will be possible to model the relative contributions of the road surface and associated street furniture.

5 Conclusions

- Comparison of road dusts from both sites with their respective local soils indicates that soil is not a major component of road dust.

- The similarity between the heavy metal contamination in road dust at the Research Track, on the A243 and from a wide variety of urban roads suggests that traffic has a smaller influence than currently perceived.

- The heavy metal contamination in road dust from motorways, carrying very high traffic flows, reflect those measured at the experimental sites. This again confirms the view that traffic input to surface dusts is less important than predicted.

- Since soil does not play a major role, it is suggested that the road surface and street furniture are significant factors in contamination in road dust.

- Analyses of samples of zinc galvanising and steel taken from lamp posts at TRL showed elemental profiles typical of those found in the literature, but were in general rather ‘cleaner’ than expected.

- The concentration of Zn is greater on the footway than the road at TRL and the A243, suggesting that it is not traffic derived and is likely to originate from galvanised street furniture.

- This work suggests that there are four key sources of heavy metals related to road surfaces and street furniture: asphalt, zinc galvanising, iron and steel.

- Source apportionment is currently difficult to assess due to the preferential dissolution of some elements, such as zinc, during weathering and corrosion. Observed concentrations of zinc seem to be an underestimate of those predicted from the concentration of trace elements present in dust sweepings.

- Further work is required to study the dissolution of asphalt, cast iron, zinc galvanising and steel by rainfall, to ascertain the relative solubility of the heavy metals and hence their potential mobility. This information could then be used to quantify the relative importance of these different sources.

6 Recommendations

Increase the database of road dust data from other road conditions

This study has provided a very thorough characterisation of road surfaces and street furniture. The road dust from TRL and the A243 show very similar trace element profiles, despite the fact that one has no traffic and the other experiences 30,000 vehicles per day. Data from other studies support the conclusion that road surfaces and street furniture have more influence on heavy metal contamination than anticipated. However, it is important to increase the database to include a wider range of road conditions and situations.

The data from the HA road sediment project provides an excellent opportunity to quantify the relative importance of street furniture and vehicles at the sites sampled. Additional work is required to evaluate the area of total metalwork present at each site. This information will then be used to calculate the mass of heavy metal input to the road system.

Study of the relative solubility of elements in street furniture

If the ratios of the elements were constant in road surfaces and street furniture it would be a simple matter to apportion them to the different sources. However, with preferential dissolution of some elements it is impossible to do so at present. Further work is required to study the dissolution of zinc galvanising and steel in rainfall to ascertain the relative solubility of the heavy metals. This would be achieved through laboratory experiments using simulated rain and by monitoring corrosion of street furniture at TRL.

Increase the database of elemental compositions of street furniture

A number of items of street furniture such as lamp posts, drain grills, signposts and one barrier were sampled during this study but only at two sites. It is necessary to increase the database of information relating to elemental composition of street furniture. This will be particularly important once a model has been further developed to predict the relative inputs from the identified sources of contamination.

Evaluation of UNMIX™

This computer model seeks to solve a general mixture problem where the data are assumed to be a linear combination of an unknown number of sources of unknown composition which contribute an unknown amount to each sample. The program will be used to test the hypothesis that road dust is a mixture of various proportions of four key components - asphalt, zinc galvanising, iron and steel. This will permit the development of a working diagnostic tool for source apportionment of heavy metals around road systems.

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Appendix 1

Small Road System, TRL Limited Research Track, Bracknell – sampling details

Sample number	Date	Detailed location	Type of sample	Description	Reason for sample
T01/05/2004	12/05/04	Silverleaf Drive at junction with Margesson Lane, E side of track taken from north side of road	Sweeping	Taken from asphalt surface, old central white line has been over-painted. Concrete kerb, grass growing to kerb edge. Pine trees approx 3m from kerb edge. Little loose surface material, road surface un-patched. Brown seeds	Asphalt
T02/05/2004	12/05/04	Same as 01	Picking	Small pieces of aggregate from surface of road, not very abundant, most are well stuck down.	Aggregate
T03/05/04	12/05/04	South side of road from 01	Sweeping	Same as 01	Asphalt
T04/05/04	12/05/04	Junction of Silverleaf Drive and Margesson Lane at E side of track	Sweeping	Taken from an area within 15cm of lamp post base. Under surface is concrete slabs	Lamp Post
T05/05/04	17/05/04	J of Cornelius Ave & Bridle Hill Rise	Sweeping	From surface of white lining including the surface of the dotted line across junction, and junction triangle. Sample includes centre of triangle which is unpainted asphalt.	White line
T06/05/04	17/05/04	J of Cornelius Ave & Bridle Hill Rise	Sweeping	Taken adjacent to 05 as far from white line as possible. Pair with previous sample for comparison. Taken from entirely on asphalt surface.	Asphalt
T07/05/04	17/05/04	East side of Bridle Hill Rise	Sweeping	Taken from top surface of barrier at junction with Cornelius Ave. Very little material	Barrier
T08/05/04	17/05/04	Bridle Hill Rise	Sweeping	Taken from surface of cast iron drain grill (5 covers)	Drain Grill
T09/05/04	17/05/04	Junction of Cornelius Ave and Silverleaf Drive west side of track	Sweeping	Taken from area around base of lamp post and up side of rusting area	Lamp Post
T10/05/04	19/05/04	J of Cornelius Ave & Bridle Hill Rise. 11m from junction on W side.	Sweeping	Taken from around base of a plastic coated (steel?) sign post. Post is located in cast iron base. Plastic coating very weathered and cracked exposing the under metal surface to weathering. Lots of dry vegetation. Difficult sample to take, mostly organic material. Have cleared base of post after sampling to permit future collection on hard surface.	Sign Post
T11/05/04	19/05/04	Bridle Hill Rise, 23m from junction with	Sweeping	Taken from base of lamp post, galvanised but rusting. Lot of dry vegetation but sample taken from clear area	Lamp Post

Sample number	Date	Detailed location	Type of sample	Description	Reason for sample
		Cornelius Ave on W side		between post and gutter where rain appears to have kept ground clear. Not seeping kerb stone. Lamp post itself also swept. Asphalt	
T12/05/04	19/05/04	Bridle Hill Rise, 16m from sample 11	Sweeping	Taken from base of lamp post. Same appearance as 11/05/04. Sample taken from asphalt surface. No sweeping on kerb stone. Lamp post itself also swept.	Lamp Post
T13/05/04	19/05/04	Junction of Cornelius Ave & Silverleaf Drive, west side of SRS	Sweeping	Taken from on surface of white line marking the junction of Cornelius Ave. Area swept is approx 8mx0.5m	White Line
T14/05/04	19/05/04	Junction of Cornelius Ave & Silverleaf Drive, west side of SRS	Sweeping	Taken from asphalt surface on Silverleaf Drive between white line (sample 13) and central white line parallel to sample 13 but more than 0.5m away from it.	Asphalt
T15/05/04	19/05/04	Junction of Cornelius Ave & Silverleaf Drive, west side of SRS	Picking	Pieces of white paint breaking off sample 13	White Paint
T16/05/04	19/05/04	Silverleaf Drive, south side of SRS, close to 'Tolling Site B'	Sweeping	Taken from top of concrete kerb (opposite 'Stop Gate' where traffic can pass under main track)	Kerb
T17/05/04	19/05/04	Silverleaf Drive, south side of SRS close to 'Tolling Site B'	Sweeping	Taken from gutter on asphalt at base of concrete kerb, same location as 16	Gutter
T18/05/04	19/05/04	Silverleaf Drive, south side of SRS, close to 'Tolling Site B'	Sweeping	Taken from asphalt surface midway between sample 17 and white line in middle of road	Asphalt
T19/05/04	19/05/04	Silverleaf Drive, N of cross road with Cornelius Ave, west side of SRS	Sweeping	Taken from paving at base of lamp post on west side of road (near entrance gate)	Lamp Post
T20/05/04	19/05/04	Silverleaf Drive, N of cross road with Cornelius Ave, west side of SRS	Sweeping	Taken from paving away from lamp post sample 19 as possible	Concrete Paving
T21/05/04	24/05/04	Bridle Hill Rise, Zebra crossing	Sweeping	Taken from surface of white lines defining zebra crossing. Little material to collect. Very fine with some aggregate from asphalt	White Line
T22/05/04	24/05/04	Bridle Hill Rise, Zebra crossing	Sweeping	Taken from 'black' parts of zebra crossing ie asphalt and no paint! Loose grit and fine dust (VIDEO)	Asphalt
T23/05/04	24/05/04	Bridle Hill Rise, west	Scraping	Taken from rusting area of lamp post (associated with	Lamp Post

Sample number	Date	Detailed location	Type of sample	Description	Reason for sample
		side, 40m from J with Cornelius Ave		Sample 11). Note: ground surface will now be contaminated with scrapings	
T24/05/04	24/05/04	Bridle Hill Rise, west side, 40m from J with Cornelius Ave	Scraping	Taken from non-rusting area of lamp post sample 23. Loose on surface but goes back to a nice shine!	Lamp Post
T25/05/04	24/05/04	J of Cornelius Ave & Bridle Hill Rise. 11m from junction on W side.	Scraping	Taken from base holder of ‘speed control hump’ sign close to J of Bridle Hill Rise and Cornelius Ave (from same site as sample 10)	Sign Post
T26/05/04	24/05/04	East side of Bridle Hill Rise	Scraping	Taken from top surface of barrier just down from J of Cornelius Ave and Bridle Hill Rise on east side	Barrier
T27/05/04	24/05/04	East side of Bridle Hill Rise	Scraping	Taken from 5th drain down hill on east side close to samples 23 & 24 (associated with sample 8)	Drain Grill
T28/05/04	24/05/04	Junction of Silverleaf Drive and Margesson Lane at E side of SRS	Scraping	Taken from rusting area of lamp post (associated with Sample 4). Note: ground surface will now be contaminated with scrapings	Lamp Post
T29/05/04	24/05/04	Junction of Silverleaf Drive and Margesson Lane at E side of SRS	Scraping	Taken from non-rusting area of lamp post (associated with Sample 4). Note: ground surface will now be contaminated with scrapings	Lamp Post
T30/05/04	24/05/04	Junction of Silverleaf Drive and Margesson Lane at E side of SRS	Picking	Taken from white line marking junction of Silverleaf Drive with Margesson Lane	White Paint
T31/05/04	24/05/04	Junction of Charlesworth Street & Silverleaf Drive at the Traffic Lights	Sweeping	Taken from surface of two cast iron drain covers close to traffic lights, very rusty, not much dust, vegetation. Drain covers set into concrete paving slabs	Drain Cover
T32/05/04	24/05/04	Junction of Charlesworth Street & Silverleaf Drive at the Traffic Lights	Picking	Pieces of rusty drain cover from same cover as sample 31	Drain Cover
T33/05/04	24/05/04	Junction of Cornelius Ave & Silverleaf Drive, west side of SRS	Sweeping	Taken from around base of rusting lamp post on north corner of Cornelius Ave opposite main entrance	Lamp Post
T34/05/04	24/05/04	Junction of Cornelius Ave & Silverleaf Drive, west side of SRS	Scraping	Taken from Lamp post sample 33 from rusting part of lamp post	Lamp Post
T35/05/04	24/05/04	Junction of Cornelius Ave & Silverleaf Drive,	Scraping	Taken from Lamp post sample 33 from non-rusting part of lamp post	Lamp Post

Sample number	Date	Detailed location	Type of sample	Description	Reason for sample
		west side of SRS			
T36/05/04	24/05/04	Silverleaf Drive, N of cross road with Cornelius Ave, west side of SRS	Scraping	Taken from lamp post at sample 19. Rusting part sampled	Lamp Post
T37/05/04	24/05/04	Silverleaf Drive, N of cross road with Cornelius Ave, west side of SRS	Scraping	Taken from lamp post at sample 19. Non-rusting part sampled	Lamp Post
T38/09/04	06/09/04	E side of Bridle Hill Rise at 90 deg off from lamp post 40m down. Sample from within woods 30m from J of Bridle Hill Rise with Cornelius Ave	Soil	Leaf litter removed and dug down to soil under 15cm of peat. Very dry, silver grey	Soil
T39/09/04	06/09/04	As above but 30m further down BHR travelling parallel to the road. Opposite T junction	Soil	As above but only 10cm of peat	Soil
T40/09/04	06/09/04	W side of BHR between T38 & T39 on opposite side of road. Midway between BHR and Silverleaf Drive	Soil	As above but only 5cm of peat	Soil
T41/09/04	06/09/04	Repeat of 11/05/04	Sweeping	Very little material, asphalt with high aggregate content	Lamp post
T42/09/04	06/09/04	Base of lamp post believed to be repeat of 12/05/04 on east side of BHR about 40mdown. The first one you come to on that side.	Sweeping	Asphalt repair with fine aggregate different from T41. White quartz? present	Lamp post
T43/09/04	06/09/04	Base of lamp post on Silverleaf Drive (4) just north of junction with Cornelius Ave, west	Sweeping	Paving slabs concreted in. New white lines in gutter next to it, confirmed new since visit	Lamp post

Sample number	Date	Detailed location	Type of sample	Description	Reason for sample
		side. Same as sample 19/05/04			

Appendix 2

A243 Kingston Road - sampling details

Sample number	Date	General Location	Detailed location	Sample Type	Description	Reason
S01/08/2004	12/08/04	0 m	1st lamppost along road from M25 junction. Located between the asphalt footway and the 1 m grass verge separating it from the road. Continuous white line along the edge of the road (3 m from lamppost) and vegetation on the other side of the footway.	Scraping	Scraping from a plain galvanised lamppost with no signs of corrosion.	Lamp Post
S02/08/2004	12/08/04	0 m	Same as 01/08/04	Sweeping	Sweeping from asphalt area up to 1 m from the base of the lamppost. Very little material.	Lamp Post
S03/08/04	12/08/04	28 m	Green road sign indicating local route. Located between footway and vegetation along road	Scraping	Paint from the pole supporting the roadsign. Grey, plastic type of paint.	Sign Post
S04/08/04	12/08/04	71 m	100 metre distance sign (/). Located between grass verge and asphalt footway.	Scraping	Taken from area at post base. Dirty coating at a height of 20 cm on post base. Continuous white line at edge of the road and drain in gutter a few metres further up the road.	Sign Post
S05/08/04	12/08/04	71 m	Same as 04/08/04	Sweeping	Surface of asphalt footway within 1 m of sample 04/08/04	Sign Post
S06/08/04	12/08/04	77 m	2nd lamppost along the road. Located between grass verge and asphalt footway.	Scraping	Lamppost looks the same as 01/08/04. Has a dirty layer (perhaps inhibitor) similar to 04/08/04	Lamp Post
S07/08/04	12/08/04	77 m	Same as 06/04/08	Sweeping	Asphalt surface within 1 m of the lamppost. New asphalt in the area immediately at the base of the lamppost.	Lamp Post
S08/08/04	12/08/04	150 m	Manhole cover located at edge of grass verge in asphalt footway	Sweeping	Clarksteel EN 124 Class D400 Ductile. Good condition cast iron. Weathered but not rusted. Sweeping of the cover itself.	Manhole cover
S09/08/04	12/08/04	150 m	Same as 08/08/04	Scraping	Same as 08/04/08	Manhole cover
S10/08/04	12/08/04	164 m	Sign post for 40 mph limit in the vegetation at the side of the road.	Scraping	Rust from the post	Sign Post

Sample number	Date	General Location	Detailed location	Sample Type	Description	Reason
			1 m from footway and 4 m from the road.			
S11/08/04	12/08/04	164 m	Same as 10/08/04	Picking	Grey paint peeling off the post	Sign Post
S12/08/04	12/08/04	171 m	Sign post for 200 m marker (//)	Sweeping	Asphalt surface on footway between grass verge and roadside vegetation. Area where quite a lot of metalwork.	Asphalt footway
S13/08/04	12/08/04	188 m	Sign post for motorway traffic	Scraping	Taken from large (25-30 cm) post located on the vegetation side of the asphalt footway.	Sign Post
S14/08/04	12/08/04	280 m	Sign Post 'Welcome to Leatherhead' on the footway.	Scraping	Painted rusty post, like 10/08/04. Scraping of the coating.	Sign Post
S15/08/04	12/08/04	280 m	Same as 14/08/04	Scraping	Scraping of rust sample	Sign Post
S16/08/04	12/08/04	280 m	Same as 14/08/04	Sweeping	Asphalt footway surface by 14/08/04	Sign Post
S17/08/04	12/08/04	304 m	Manhole cover in the middle of asphalt footway.	Sweeping	Sweeping of the cover itself. 'Nevilles Aldridge'. Good condition.	Manhole cover
S18/08/04	12/08/04	304 m	Same as 17/04/08	Scraping	Scraping of the surface.	Manhole cover
S19/08/04	12/08/04	453 m	Drain in layby.	Sweeping	Close to white line. Some grass and concrete kerb.	Drain grill
S20/08/04	12/08/04	530 m	Bus stop opposite Leatherhead Golf Club	Scraping	Very little – aluminium post in a concrete/asphalt base.	Bus Stop
S01/09/04	06/09/04	565 m	Drain area 15m N of GC entrance, W side of road before bus stop	Sweeping	On concrete by cast iron drain cover	Concrete
S02/09/04	06/09/04	610 m	Leatherhead GC bus stop	Sweeping	On concrete by sign in lay-by 35m N of S01/09/04	Concrete
S03/09/04	06/09/04	565 m east side of road	Opposite side of road to S02/09/04	Sweeping	On asphalt in drain area beside cast iron drain cover	Asphalt
S04/09/04	06/09/04	610 m east side of road	45m N of S03/09/04	Sweeping	On asphalt in drain area beside cast iron drain cover	Asphalt
S05/09/04	06/09/04	662 m east side of road	52m N of S04/09/04	Sweeping	On asphalt in drain area beside cast iron drain cover	Asphalt
S06/09/04	06/09/04	100m from road,Ashtead Common NR	Oak woodland. Footpath to Ashtead Gap. Soil sample on east side of footpath, 20m south of signpost/map	Soil	Vegetation removed and top 5cm soil taken with plastic trowel	Soil
S07/09/04	06/09/04	100m from road on Ashtead Common	Oak woodland. Footpath to Ashtead Gap. Soil sample on east side of footpath, 5m north of signpost/map	Soil	Vegetation removed and top 5cm soil taken with plastic trowel	Soil

Sample number	Date	General Location	Detailed location	Sample Type	Description	Reason
		Nature Reserve				

Appendix 3

Appendix 3.1 Concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at TRL research track.

Element	Footway (n=12)	Asphalt road (n=12)	Soil (n=3)
SiO_2	32-81	37-76	92-101
Al_2O_3	1.5-4.7	3.2-6.7	1.0-2.0
Fe_2O_3	1.7-7.3	2.2-4.3	0.1-0.5
MgO	0.3-0.8	0.4-3.9	0.08-0.12
CaO	0.5-3.3	0.9-7.2	<LLD
Na_2O	0.02-0.25	0.10-1.2	<LLD
K_2O	0.4-1.2	0.4-1.0	0.2-0.6
TiO_2	0.1-0.3	0.2-1.5	0.3-0.5
P_2O_5	0.09-0.47	0.07-0.22	0.005-0.015
Sc	1.4-4.0	2.2-9.2	0.5-1.2
V	33-85	48-131	14-23
Cr	25-105	20-617	14-23
Mn	176-670	320-840	26-34
Co	5.7-10.0	7.0-11.2	0.4-0.8
Ni	<5-99	13-25	<5
Cu	11-78	31-86	<3
Zn	141-12900	94-322	8-15
Ga	4.9-9.4	6.0-9.5	2.6-6.2
Rb	12-42	13-30	6-25
Sr	22-79	39-70	18-26
Y	4.1-13	7.3-11	6.6-9.2
Zr	64-251	60-163	312-423
Nb	3.3-6.0	2.9-11	5.2-7.5
Mo	<1.8-9.8	2.2-4.1	<1.8
Ag	0.21-8.1	0.16-0.40	0.60-0.80
Cd	0.6-4.0	0.5-1.2	<0.14
Sn	0.9-2.8	1.0-28	<0.9
Sb	1.4-3.2	1.9-29	0.26-0.56
Cs	0.7-5.3	0.5-1.1	0.3-2.4
Ba	77-505	127-251	122-176
La	3.0-18	4.4-9.8	3.7-9.4
Ce	12-44	12-23	14-23
Eu	0.30-0.80	0.31-0.45	0.25-0.37
Lu	0.08-0.23	0.13-0.21	0.17-0.19
Hf	1.7-7.8	1.2-3.7	8.3-10.2
Ta	0.20-0.56	0.27-0.80	0.46-0.66
W	0.50-2.7	1.1-3.6	0.80-1.3
Tl	0.18-0.35	0.08-0.21	0.10-0.20
Pb	38-103	27-68	11-22
Th	1.3-3.9	1.4-2.4	2.2-3.1
U	0.4-1.4	0.5-0.8	0.9-1.2

Concentrations for major elements as wt% oxide and trace elements as ppm

Appendix 3.2 Concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at A243 site.

Element	Footway(n=6)	Asphalt road(n=7)	Soil (n=2)
SiO_2	73-79	70-81	67
Al_2O_3	3.4-5.2	3.7-6.8	7.9-8.8
Fe_2O_3	3.1-3.7	3.6-5.4	4.1-4.2
MgO	0.9-1.1	0.8-1.4	0.71-0.73
CaO	2.9-4.4	2.6-4.2	0.17
Na_2O	0.25-0.48	0.22-0.78	0.05-0.12
K_2O	0.39-0.65	0.45-1.1	1.4-1.7
TiO_2	0.23-0.42	0.27-0.48	0.68-0.79
P_2O_5	0.08-0.16	0.09-0.18	0.11
Sc	4.9-10	3.5-5.5	3.2-3.5
V	22-71	29-50	63-71
Cr	63-257	60-90	67-73
Mn	330-571	304-442	170-189
Co	5.7-9.4	5.4-9.3	8.2-10.7
Ni	<4.5-22	<4.5-14	<4.5
Cu	91-170	99-187	19.5-21.6
Zn	385-2509	241-417	98-150
Ga	4.1-7.5	4.0-5.9	10.0-10.3
Rb	17-34	14-26	58-64
Sr	68-109	76-92	50-54
Y	8.9-16	7.7-13	17-20
Zr	103-477	99-225	238-247
Nb	4.0-8.0	3.7-7.2	11.3-11.8
Mo	<1.8-12	<1.8-7.2	<1.8
Ag	0.2-1.8	0.31-0.72	0.43-0.47
Cd	0.7-1.1	0.7-1.2	0.76-0.84
Sn	3.9-17	4.1-8.2	5.8-6.0
Sb	8.9-27	7.4-18	1.3-1.7
Cs	1.1-4.0	0.9-3.1	3.0-4.8
Ba	233-369	236-317	272-288
La	7.8-17	7.9-12	18-22
Ce	27-32	24-32	46-58
Eu	0.5-4.1	0.5-0.7	0.9-1.1
Lu	0.17-0.35	0.12-0.29	0.33-0.37
Hf	2.6-12	2.4-7.3	6.2
Ta	0.35-0.65	0.31-0.66	0.86
W	1.4-3.2	1.0-1.7	1.1-1.2
Tl	0.18-0.29	0.15-0.25	0.44-0.45
Pb	90-141	85-198	121-158
Th	3.2-5.6	2.7-4.5	6.2-6.5
U	1.0-1.7	0.8-1.4	1.6-1.8

Concentrations for major elements as wt% oxide and trace elements as ppm

Appendix 4

Appendix 4.1 Cerium normalised concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at TRL research track. Figures in square brackets indicate a single value lying outside of the ‘normal’ range

Element	Footway (n=12)	Asphalt road (n=12)	Soil (n=3)
SiO_2	1.5-5.7	3.0-4.8	4.4-6.7
Al_2O_3	0.04-0.24	0.26-0.46	0.07-0.11
Fe_2O_3	0.06-0.22 [0.62]	0.17-0.30	0.01-0.03
MgO	0.01-0.04	0.07-0.15	0.004-0.006
CaO	0.02-0.16	0.10-0.25	-
Na_2O	0.002-0.006	0.04-0.08	-
K_2O	0.03-0.05	0.03-0.04	0.010-0.013
TiO_2	0.009-0.015	0.013-0.031	0.019-0.021
P_2O_5	0.004-0.016 [0.039]	0.004-0.011	0.0002-0.0008
Sc	0.05-0.24	0.46-0.86	0.04-0.07
V	1.4-3.8 [4.7]	4.8-9.1	-
Cr	0.6-2.9	1.4-4.4 [29,30]	1.01-1.09
Mn	10-32	17-36	1.3-1.8
Co	0.22-0.40 [0.60]	0.37-0.78	0.02-0.04
Ni	0.5-2.3 [3.3]	0.88-1.7	-
Cu	0.8-1.9 [6.6]	1.8-6.1	-
Zn	19-818	4.2-17	0.48-0.82
Ga	0.20-0.48	0.29-0.59	0.18-0.27
Rb	0.7-2.3	0.8-1.3	0.04-1.4
Sr	1.7-2.2	2.3-4.2	1.1-1.3
Y	0.29-0.48	0.44-0.78	0.40-0.48
Zr	5.2-9.9	4.0-7.5	17-28
Nb	0.16-0.26	0.17-0.25	0.32-0.36
Mo	0.06-0.26 [0.83]	0.15-0.27	-
Ag	0.01-0.04 [0.46]	0.01-0.02	0.03-0.06
Cd	0.01-0.05 [0.24]	0.01-0.06	-
Sn	0.07-0.10	0.07-0.20 [0.62]	-
Sb	0.04-0.18	0.15-0.35	0.01-0.03
Cs	0.06-0.12 [12]	0.04-0.13	0.02-0.10
Ba	6.5-14	10-17	7.6-9.1
Hf	0.10-0.23	0.09-0.16	0.44-0.68
Ta	0.013-0.023	0.016-0.022	0.027-0.036
W	0.04-0.08 [0.12]	0.07-0.14 [0.2]	0.03-0.08
Tl	0.004-0.015	0.006-0.010	0.006-0.011
Pb	1.4-5.4	2.0-3.8 [25]	0.4-1.2
Th	0.09-0.15	0.09-0.13	0.13-0.15
U	0.03-0.06	0.03-0.04	0.05-0.07

- = not measured

Appendix 4.2 Cerium normalised concentration ranges for sweepings from asphalt surfaces compared with soil chemistry at A243 site. Figures in square brackets indicate a single value lying outside of the ‘normal’ range

Element	Footway (n=6)	Asphalt road (n=7)	Soil (n=2)
SiO_2	1.7-3.3	2.4-2.8	1.2-1.5
Al_2O_3	0.12-0.23	0.13-0.17	0.14-0.19
Fe_2O_3	0.11-0.17	0.10-0.12	0.07-0.09
MgO	0.03-0.05	0.03-0.04	0.01
CaO	0.07-0.15	0.10-0.16	0.003-0.004
Na_2O	0.01-0.03	0.01-0.02	0.001-0.003
K_2O	0.02-0.04	0.01-0.02	0.02-0.04
TiO_2	0.010-0.014	0.009-0.012	0.012-0.017
P_2O_5	0.003-0.006	0.002-0.005	0.002-0.003
Sc	0.14-0.34	0.14-0.17	0.07-0.09
V	0.69-2.4	1.0-1.7	1.2-1.4
Cr	2.2-3.3 [11]	2.0-2.9	1.3-1.5
Mn	11-19	11-15	3.3-3.7
Co	0.21-0.31	0.18-0.29	0.18
Ni	0.30-0.56 [0.9]	0.32-0.45	-
Cu	3.2-7.8	3.1-5.3	0.34-0.48
Zn	10-84	9.2-17	1.7-3.3
Ga	0.14-0.25	0.15-0.19	0.18-0.22
Rb	0.6-1.1	0.58-0.81	1.0-1.4
Sr	2.1-3.6	2.5-3.2	0.9-1.1
Y	0.28-0.42	0.29-0.41	0.34-0.37
Zr	3.4-12	3.7-9.0	4.2-5.3
Nb	0.14-0.25	0.13-0.22	0.19-0.26
Mo	0.10-0.29	0.04-0.24	-
Ag	0.01-0.02 [0.08]	0.01-0.02	0.008-0.009
Cd	0.020-0.043	0.022-0.037	0.015-0.017
Sn	0.13-0.34 [0.74]	0.13-0.27	0.10-0.13
Sb	0.32-0.89	0.25-0.66	0.03
Cs	0.04-0.10	0.03-0.10	0.05-0.10
Ba	7.2-13	7.8-11	4.6-6.4
Hf	0.09-0.28	0.09-0.23	0.11-0.14
Ta	0.016-0.022	0.011-0.020	0.015-0.019
W	0.05-0.11	0.04-0.05	0.02-0.03
Tl	0.006-0.010	0.005-0.008	0.008-0.010
Pb	3.2-4.3	3.2-6.1	2.7
Th	0.11-0.16	0.10-0.14	0.11-0.14
U	0.04-0.05	0.03-0.04	0.03-0.04

- = not measured

Appendix 4.3 Cerium normalised concentration ranges for sweepings from asphalt and concrete surfaces compared with samples from car parks. Figures in square brackets indicate a single value lying outside of the ‘normal’ range. (Data from Cook et al., 2003)

Element	Asphalt road (n=9)	Concrete road (n=2)	Car park (n=2)
SiO_2	1.2-4.1	1.3-2.4	1.1-2.3
Al_2O_3	0.06-0.16	0.09-0.12	0.12
Fe_2O_3	0.04-0.17	0.08-0.13	0.09
MgO	0.005-0.076	0.015-0.031	***0.06-0.11***
CaO	0.007-0.98	0.08-0.25	***0.31-1.7***
Na_2O	0.013-0.026 [0.14]	0.010-0.011	0.010-0.021
K_2O	0.02-0.04	0.018-0.028	0.024-0.031
TiO_2	0.008-0.061	0.011-0.014	0.011-0.013
P_2O_5	-	-	-
Sc	-	-	-
V	-	-	-
Cr	1.8-4.0	3.3	-
MnO	4-25	13-18	***16-27***
Co	0.14-0.25	0.17-0.18	0.26
Ni	0.57-0.93	0.70-0.85	1.10
Cu	5.6-19	4.0-8.3	7.3-7.5
Zn	4.9-20	6.9-11	***14-27***
Ga	0.08-0.34	0.10-0.15	0.16-0.17
Rb	0.50-1.6	0.81-0.91	1.1-1.3
Sr	2.4-11	2.2-3.6	5.2-12
Y	0.17-0.62	0.30-0.39	0.31-0.61
Zr	4.8-10 [26]	6.7-7.7	4.2-5.6
Nb	0.11-0.25	0.15-0.19	0.16-0.17
Mo	0.15-0.45	0.11-0.57	***0.41-0.69***
Ag	-	-	-
Cd	-	-	-
Sn	0.4-1.7	0.5	-
Sb	0.27-0.53	0.5	-
Cs	0.02-0.08	0.03-0.05	0.04-0.07
Ba	6.6-28	6.9-12	15-29
Hf	0.10-0.24 [0.55]	0.14-0.18	0.11-0.13
Ta	0.01-0.05	0.02-0.04	0.02-0.06
W	0.11-0.25	0.04-0.22	**0.36**
Tl	-	-	-
Pb	3.3-8.8	3.3	-
Th	0.07-0.14	0.12-0.13	0.11-0.12
U	0.03-0.08	0.04	0.04-0.09

- = not measured

Appendix 4.4 Ce normalised concentration ranges for sweepings from asphalt surfaces compared with samples from car-parks. Figures in square brackets indicate a single value lying outside of the 'normal' range. (Data from Abeyawickrama, 2003)

Element	Asphalt road (n=20)	Car park (n=4)
SiO_2	0.35-1.7	0.60-1.1
Al_2O_3	0.04-0.12	0.05-0.07
Fe_2O_3	0.04-0.12	0.09-0.29
MgO	0.01-0.05	0.01-0.04
CaO	0.01-0.14	0.10-0.23
Na_2O	0.005-0.022	0.013-0.035
K_2O	0.007-0.028	0.014-0.019
TiO_2	0.003-0.009	0.005-0.008
P_2O_5	-	-
Sc	-	-
V	-	-
Cr	0.8-4.1 [6.2]	***4.4-7.6***
MnO	8-35	10-21
Co	0.09-0.45	0.21-0.32
Ni	-	-
Cu	0.6-10	***9.8-16***
Zn	1.9-15 [25]	***14-58***
Ga	0.07-0.30	0.13-0.16
Rb	0.34-1.3	0.56-0.90
Sr	1.1-5.5	3.1-5.9
Y	0.25-0.49	0.25-0.40
Zr	2.0-6.5 [9.8]	3.8-6.8
Nb	0.06-0.24	0.11-0.26
Mo	0.06-0.57	***0.59-1.40***
Ag	0.03-0.09	0.03-0.09
Cd	0.005-0.03	0.02-0.03
Sn	0.03-0.58	***0.33-0.99***
Sb	0.04-0.75	***0.13-1.8***
Cs	0.02-0.07	0.03-0.04
Ba	4.1-12 [17]	***9.5-36***
Hf	0.06-0.24	0.09-0.17
Ta	0.006-0.024	0.006-0.021
W	0.02-0.10	0.06-0.13
Tl	-	-
Pb	-	-
Th	0.07-0.13	0.07-0.11
U	0.02-0.04	0.03-0.04

- = not measured

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