
PARTICULATES

Characterisation of Exhaust Particulate Emissions from Road Vehicles

Deliverable 8

Measurement of non-exhaust particulate matter

Version 2.0 – October 2004

A project sponsored by:



EUROPEAN COMMISSION
Directorate General Transport and Environment

In the framework of:



Fifth Framework Programme
Competitive and Sustainable Growth
Sustainable Mobility and Intermodality

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VTT	VTT Energy – Engine Technology and Energy in Transportation - FI

A project sponsored by:



EUROPEAN COMMISSION
Directorate General Transport and Environment

In the framework of:



Fifth Framework Programme
Competitive and Sustainable Growth
Sustainable Mobility and Intermodality

Publication data form

1. Framework Programme European Commission – DG TrEn, 5 th Framework Programme Competitive and Sustainable Growth Sustainable Mobility and Intermodality		2. Contract No 2000-RD.11091	
3. Project Title Characterisation of Exhaust Particulate Emissions from Road Vehicles (PARTICULATES)		4. Coordinator LAT/AUTh	
5. Deliverable Title Measurement of non-exhaust particulate matter		6. Deliverable No 8 (revised)	
7. Deliverable Responsible Dr Paul Boulter - TRL	8. Language English	9. Publication Date October 2004	
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12. Summary This report presents the findings of work undertaken to characterise airborne particles emitted by road traffic, with the aim of deriving emission factors for non-exhaust particle sources such as tyre wear, brake wear and road surface wear. The report includes a literature review which examines the state of the art in this field, and describes the formulation of an optimum methodology for determining emission factors. Wear rates for brake pads and tyres have been determined gravimetrically for in-service cars. Sampling campaigns have been carried out to collect ambient particulate matter and source materials, including road dust, tyre material and brake wear particles. Ambient airborne particles, as well as the source materials, have been characterised chemically and physically using a suite of analytical techniques including ICP/AES, ICP/MS and SEM. Levels of PM ₁₀ and PM _{2.5} have been estimated from gravimetric measurements at roadside and background sites at the University of Hertfordshire and London. The information from these campaigns and the literature review has been used to identify specific tracers for apportioning the sources of non-exhaust particles, and has assisted in the design of a main tunnel sampling campaign to derive appropriate emission factors. The main campaign has been conducted in the Hatfield Tunnel on the A1(M) motorway north of London. Emission factors for light-duty and heavy-duty vehicles have been determined using principle component analysis and multiple regression analysis.			
13. Notes			
14. Internet reference			
15. Key Words Non-exhaust particles, emission factors, receptor modelling, tyre wear, brake wear, road dust		16. Distribution statement FREE	
17. No of Pages 96	18. Price FREE	19. Declassification date	20. Bibliography NO

Acknowledgements

The authors would like to take this opportunity to thank the following for their help and advice during this project:

- Westminster City Council, London, UK.
 - Ana Deletic and David Orr, Aberdeen University, UK.
 - Professor Dick van den Hout, TNO Institute of Environmental Sciences: Energy Research and Process Innovation, the Netherlands.
 - Dr Peter Schmid, EMPA, Dübendorf, Switzerland.
 - Dr Jay Turner, Washington University, St. Louis, Missouri, USA.
 - Ms Laurel Martin at the California Institute of Technology, Pasadena, California.
 - Claire Wienburg, CEH, UK.
 - Sarah James, Nick Walsh and Jacqui Duffett, Royal Holloway College, University of London, UK.
 - Carillion-URS plc, who operate the Hatfield Tunnel on behalf of the Highways Agency and, in particular, Mr Jeff Chappell the Hatfield Tunnel manager.
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Table of Contents

1	Introduction	1
1.1	Background	1
1.2	Non-exhaust particle research in the PARTICULATES project	2
2	Review of non-exhaust particle research	3
2.1	Atmospheric particulate matter	3
2.2	Tyre wear particles	4
2.2.1	Factors affecting tyre wear	4
2.2.2	Tyre wear rates	5
2.2.3	Tyre composition	6
2.2.4	Tyre wear particle characteristics	7
2.3	Brake Wear particles	9
2.3.1	Factors affecting brake wear	9
2.3.2	Brake wear rates	10
2.3.3	Brake composition	10
2.3.4	Brake wear particle characteristics	12
2.4	Clutch wear particles	13
2.5	Corrosion particles	13
2.6	Road surface wear particles	14
2.7	Resuspension of Road Dust	16
2.7.1	Sources and composition	16
2.7.2	Factors affecting resuspension	17
2.7.3	Particle emission factors	18
2.8	Research methods	18
2.8.1	Methods for determining tyre wear and tyre particle emissions	18
2.8.2	Methods for determining brake wear and particle emissions	19
2.8.3	Methods for sampling road dust	19
2.8.4	Source apportionment methods: receptor modelling	20
2.9	Summary of literature review	23
2.9.1	Tyre wear particles	23
2.9.2	Brake wear particles	23
2.9.3	Clutch wear particles	23
2.9.4	Road surface wear particles	24
2.9.5	Resuspension of road dust	24
3	Methodology	25
3.1	Overview	25
3.2	Stage 1: Gravimetric measurement of tyre and brake wear (material loss)	26
3.2.1	Selection of test vehicles	26
3.2.2	Test schedule	27
3.2.3	Weighing of tyre and brake components	28
3.2.4	Driver logbook	28
3.3	Stages 2-5: Preliminary sampling and characterisation	28
3.3.1	Sampling of source materials	28
3.3.2	Selection of filter media for sampling airborne PM	28
3.3.3	Sampling of airborne PM	29

3.3.4	Chemical characterisation.....	30
3.3.5	Physical characterisation.....	32
3.4	Stage 6: Sampling of particulate matter in the Hatfield tunnel.....	32
3.4.1	Description of sampling site.....	33
3.4.2	Sampling of airborne particulate matter and deposited dust.....	33
3.4.3	Measurement of traffic and meteorological parameters.....	35
3.5	Stage 7: Chemical characterisation of particulate matter in the Hatfield Tunnel.....	35
3.6	Stage 8: Derivation of the emission factors for non-exhaust sources (statistical analysis and receptor modelling).....	35
4	Results and discussion.....	37
4.1	Stage 1: Tyre and brake wear tests.....	37
4.1.1	Driving information.....	37
4.1.2	Tyre wear.....	37
4.1.3	Brake wear.....	39
4.2	Stages 2-5: Preliminary sampling and characterisation.....	41
4.2.1	Metal content of tyre and brake material.....	41
4.2.2	Organic content of brake dust and road dust.....	43
4.2.3	Metal content of filter media.....	44
4.2.4	Airborne PM mass concentration.....	45
4.2.5	Chemical analysis of airborne PM.....	45
4.2.6	Physical characterisation.....	47
4.2.7	Implications for source apportionment and emission factor calculations.....	50
4.3	Stage 6: Tunnel measurements.....	50
4.3.1	Traffic measurements.....	50
4.3.2	Meteorological measurements.....	52
4.3.3	PM ₁₀ mass concentration.....	54
4.4	Stage 7: Chemical characterisation of particulate matter.....	55
4.4.1	Airborne PM - metals.....	55
4.4.2	Airborne PM – Organic compounds.....	57
4.4.3	Deposited dust.....	61
4.5	Stage 8: Statistical analysis and receptor modelling.....	62
4.5.1	Principal component analysis (PCA).....	62
4.5.2	Multiple linear regression analysis (MLRA) on absolute principal component scores.....	65
4.5.3	Derivation of emission factors.....	66
4.5.4	Comparison with results from other sources.....	68
5	Summary, conclusions and recommendations.....	71
5.1	Literature review.....	71
5.2	Measurement of tyre and brake wear rates.....	72
5.2	Preliminary sampling and characterisation.....	73
5.2.1	Chemical characterisation of source materials.....	73
5.2.2	Analysis of airborne PM at background and roadside.....	73
5.3	Tunnel measurements.....	74
5.3.1	Measured data.....	74
5.3.2	Determination of emission factors.....	75

6 Conclusions and recommendations	77
6.1 Conclusions	77
6.2 Recommendations	79
7 References	80
8 Glossary	91
APPENDIX A: Compounds present in tyre wear particles, brake wear particles and road dust particles	92
APPENDIX B: Organic compounds present in tyre wear particles, brake wear particles and road dust particles	93

1 Introduction

1.1 Background

Specific epidemiological studies have indicated a link between elevated atmospheric particle concentrations and increases in hospital admissions and death rates (Dockery *et al.*, 1993; Dockery and Pope, 1994; Vedal, 1997; Zanobetti *et al.*, 2000). The increasing weight of evidence for adverse human health effects associated with both short-term and long-term exposure to ambient particulate matter has been comprehensively reviewed elsewhere (COMEAP 1998, WHO 2000, EPAQS 2001, WHO 2003, and USEPA, 2004). However, the majority of these studies have related health outcomes with long-term ambient concentrations of the specific particulate size fraction PM₁₀. These adverse health effects include respiratory morbidity (wheeze, reduced lung function) and mortality, cardiovascular morbidity and mortality, and cancer (AQEG, 2004).

In the UK alone, emissions of airborne particles are thought to be responsible for several thousand premature deaths per annum (DETR, 1999). It is estimated that short-term exposure to the UK levels of PM₁₀ prevalent in 2002 led to 6500 deaths and 6400 hospital admissions brought forward that year, while each 1 µg/m³ decrease in PM_{2.5} over the lifetime of the current population of England and Wales will lead to between 0.2 and 0.5 million years of increased life expectancy (COMEAP, 2001). Such findings have increased concern about airborne particles, and have influenced the revision of ambient air quality standards in the United States and Europe.

One of the most important sources of particulate matter (PM), especially in urban areas, is road transport. According to the UK National Emissions Inventory, road transport accounts for over 80% of respirable PM¹ in cities (Goodwin *et al.*, 2002). However, there are still a number of uncertainties relating to the emission rates, physical properties, chemical characteristics, and health impacts of the particles derived from road vehicles. More comprehensive information would help to clarify the mechanisms by which particles affect human health and would foster the development of pollution abatement strategies.

The PM generated by road transport activity can be categorised according to its mode of formation. It is generally assumed that fuel combustion is the primary mechanism by which particles are formed, and a considerable body of research on vehicle exhaust particulate emissions has been compiled. However, there are a number of other processes, involving mechanical abrasion and corrosion, which can also result in PM being released directly to the atmosphere. These processes include:

- (i) Tyre wear
- (ii) Brake wear
- (iii) Clutch wear
- (iv) Road surface wear
- (v) Corrosion of chassis, bodywork, and other vehicle components
- (vi) Corrosion of street furniture, signs, crash barriers and fencing

The abrasion and corrosion processes can also lead to the deposition of particles on the road surface. The material which collects on the road surface, often referred to as 'road dust', may also contain exhaust particles, de-icing salt and grit deposited during winter maintenance, and matter from a range of sources that are not related to road transport (*e.g.* crustal and vegetative material, and material from industrial/commercial /domestic activity). Road dust may subsequently be suspended or resuspended in the atmosphere as a result of tyre shear, vehicle-generated turbulence, and the action of the wind. Clearly, the source apportionment and quantification of non-exhaust PM measured in the vicinity of roads is a rather complex task.

¹ Although these health effects are linked to PM it remains unclear precisely which metrics might actually be the most important.

Non-exhaust emission sources may contribute significantly to atmospheric particle concentrations. However, the data relating to the emission rate, size, and composition of particles arising from such sources are far from comprehensive, and more accurate emission factors are required for emission models and inventories. Furthermore, as exhaust emission control technology improves and traffic levels increase, the focus of attention may shift towards the emissions and health impacts of particles from these other sources. Indeed, health concerns have been noted which relate specifically to non-exhaust particles. For example, it has been reported that tyre wear is responsible for the release of around 40,000 tonnes of polycyclic aromatic hydrocarbons (PAH), in the form of respirable PM, across Europe each year (New Scientist, 1999). Miguel *et al.* (1999) found that paved road dust contains at least 20 source materials known to cause or exacerbate allergic reactions in humans, including pollen, animal dander and fungal spores. Paved road dust becomes resuspended in the atmosphere in the wake of vehicles, thus increasing allergen concentration levels above those that would prevail without the traffic movement. The study showed that between 0.5% and 12% of the allergenicity of airborne particles was attributable to paved road dust emissions. Similar findings were obtained by Chow *et al.* (1994).

1.2 Non-exhaust particle research in the PARTICULATES project

The potential importance of non-exhaust emissions has been recognised in the work programme of PARTICULATES, and a part of this project has involved the derivation of appropriate emission factors for road vehicles. The non-exhaust particle research was conducted by a UK research group comprising TRL Ltd., the Centre for Ecology and Hydrology (CEH), and the Atmospheric Science Research Group (ASRG) at the University of Hertfordshire.

The objectives of the research were to characterise particles from road vehicle non-exhaust sources, and to determine appropriate emission factors. A variety of sampling approaches, laboratory techniques and statistical procedures were employed.

Chapter 2 of this Report comprises a review of non-exhaust particle research, and updates an earlier review compiled by Warner *et al.* (2000). Various types of preliminary work were undertaken in order to develop a reliable method for determining non-exhaust particle emission rates. The preliminary work was followed by a main sampling campaign, which was conducted in the Hatfield road tunnel. The methodologies employed in both the preliminary work and the tunnel work are described in Chapter 3, and the results are provided in Chapter 4. The rationale for sampling inside a road tunnel is explained in the Report. The results from the tunnel measurements were analysed in order to apportion the particles to non-exhaust sources, and to obtain appropriate emission factors for brake wear, tyre wear, road surface wear and the resuspension of road dust. The conclusions and recommendations from the work are provided in Chapter 5.

2 Review of non-exhaust particle research

This Chapter of the Report presents a condensed and updated version of an earlier review of non-exhaust particle research compiled by Warner *et al.* (2000). The Chapter summarises the available information on wear rates (total material loss) and particle emission factors from non-exhaust sources, and discusses the sampling and analysis methodologies employed to quantify emissions from these sources. It is believed that the chemical composition of atmospheric particles may affect their toxicity (Laden *et al.*, 2000), but others have argued that chemical composition is unlikely to be a major driver of their health effects, given the similarity between dose-response relationships in different parts of the world (Harrison and Yin, 2000). It is also important that the composition of the source materials and their associated wear particles, as well as the composition of road dust, are well understood if pollutant fluxes are to be accurately determined. The chemical composition of source materials is important for another reason: tracer species can be used to apportion airborne particles according to their sources via receptor modelling. Consequently, particle sources and particle composition are important elements of the review.

2.1 Atmospheric particulate matter

Atmospheric PM displays a wide range of physical and chemical properties. It is a complex mixture of organic and inorganic substances, in solid or liquid form, which undergo modification or transformation within the atmosphere. Airborne particles range in size from less than 10nm to around 100 μ m. Particles larger than 100 μ m tend to fall out of the atmosphere rather quickly, and are generally termed 'dustfall'.

There are three recognised modes associated with the sources and size distribution of airborne particles. These are the nucleation mode, the accumulation mode, and the coarse particle mode. The nucleation mode consists of particles emitted directly from combustion sources. Nucleation mode particles typically have a diameter of less than around 50nm, but because each particle is so small this mode usually forms only a small proportion of the total aerosol mass concentration, even though the particles may be present in large numbers. Such particles reside in the atmosphere for a few hours, and are transformed by coalescence and condensation into larger accumulation mode particles. Accumulation mode particles range between around 0.05 μ m and 2.5 μ m in diameter, have atmospheric residence times of tens of days, and usually form a significant fraction of the total aerosol mass. They are also efficient light scatterers, and often dominate optical effects such as visibility. As well as being formed via the coagulation of nucleation mode particles, accumulation mode particles originate from primary emission sources and gas-to-particle transformations in the atmosphere. Particles larger than 2.5 μ m form the coarse particle mode, and include wind-blown crustal matter and material released during abrasion processes. Coarse particles have shorter residence times than accumulation mode particles, although they contribute substantially to total aerosol mass. There is negligible mass transport between the nucleation/accumulation modes and the coarse particle mode.

Atmospheric PM is derived from a wide variety of sources, both natural and anthropogenic. The contribution of different sources to total atmospheric particle concentrations varies with many factors, including locality (the number and types of the local sources), season, time of day, and both local and regional weather conditions. Particle sources are termed either 'primary', where particles are emitted directly into the atmosphere or 'secondary' where they are formed by reactions between gas-phase components. The non-exhaust processes discussed in this Report are primary, and mainly anthropogenic, particle sources. However, natural particle sources also need to be taken into account when considering resuspended road dust. Nucleation mode and accumulation mode particles primarily originate from combustion sources, such as road vehicle exhaust, waste incineration, and industrial and domestic burning. Coarse particles, on the other hand, are usually generated by mechanical processes such as erosion, construction, quarrying, and tyre wear. The main constituents of primary particles are crustal elements (*e.g.* silicon, aluminium, calcium, iron), elemental carbon, and various organic compounds. Secondary particles are mainly composed of inorganic compounds, including sulphates, ammonium and nitrates.

A number of metrics are used to define atmospheric particle samples. Prior to 1990, total suspended particulate (TSP) was commonly sampled. However, according to the UK Airborne Particulates Expert Group (APEG, 1999), such data are of limited use since TSP is an old specification for airborne particles, and it is

not necessarily relevant to those particles that can enter the human respiratory system. The parameter commonly used now is the mass concentration of the PM₁₀ fraction. PM₁₀ describes the particles which pass a sampler entry with a 50% efficiency at 10µm. To a reasonable approximation, PM₁₀ describes PM smaller than 10µm aerodynamic diameter. These particles can penetrate the larynx and enter the thoracic region of the respiratory system. Other metrics that are in common use are the mass concentrations of the PM_{2.5}, PM₁, and PM_{0.1} particle fractions.

2.2 Tyre wear particles

In 1999 more than 54 million passenger car tyres were used in the UK, equating to a total weight of more than 430,000 tonnes (Used Tyre Working Group, 2000). A new tyre on an average European passenger car weighs around 8kg, and loses roughly 1-1.5kg in weight during its service lifetime, which is typically around 3 years or 50-60,000 km. Thus, between around 10% and 20% of the rubber which goes into a tyre will disappear before the tyre is ready to scrap (Environment Agency, 1998). Similarly, Ahlbom and Duus (1994) arrived at an average rubber loss figure for Swedish roads of 17%. Based on the upper estimate for rubber loss of 20%, around 90,000 tonnes of tyre material was lost to the UK environment from passenger cars alone during 1999, mainly as a result of in-service wear. The potential environmental impact of this loss of rubber, in terms of emissions of PM to the atmosphere, could be relatively high (Environment Agency, 1998).

2.2.1 Factors affecting tyre wear

Tyre tread wear is a complex physio-chemical process which is driven by the frictional energy developed at the interface between the tread and the road pavement (Veith, 1995). The rate of wear, and hence a tyre's lifetime, varies enormously depending on its type and how it is used. The factors affecting tyre wear include:

Tyre characteristics

- Size (radius/width/depth)
- Tread depth
- Construction
- Tyre pressure and temperature
- Contact patch area
- Chemical composition
- Accumulated mileage
- Set-up (e.g. tracking, toe-in and camber)

Vehicle characteristics

- Vehicle weight and distribution of load
- Location of driving wheels
- Engine power
- Power/unassisted steering
- Electronic braking systems
- Suspension type and condition

Road surface characteristics

- Material: bitumen/concrete
- Texture pattern
- Texture wavelength - micro/macro/mega
- Porosity
- Condition including rutting and camber
- Road surface wetness
- Silt loading of road surface
- Surface dressings

Vehicle operation

- Speed
- Linear acceleration
- Radial acceleration
- Frequency and extent of braking

The construction and chemical composition of a tyre has a large impact on the way in which it wears. Almost all modern cars are fitted with radial-ply tyres, as these have a far greater rigidity for cornering, better grip in the wet, and are much less susceptible to wear than the older bias- or cross-ply type. Reclaimed rubber may be used in some new tyres, and it is possible that this will affect wear characteristics. In fact, little is now used because of performance disadvantages including poor flex and abrasion resistance, poor weathering resistance, and greater rolling resistance (Dunn, 1993). Retreaded tyres (in which remaining tread rubber is removed and replaced with new tread) may also exhibit different wear characteristics to new tyres, but there appears to be no strong evidence to confirm this. In any case, there is a poor public perception of retreaded tyres, and in virtually all European countries and the United States the market for passenger car retreads is declining.

The mileage accumulated by a tyre, particularly during the early 'running-in' phase, has an effect on its rate of wear. Using a flat-belt tyre test machine, Sakai (1996) found that after a running-in distance of approximately 300 km, the tyre wear rate (g/km) was 75% of the initial wear rate, but became almost constant thereafter. However, Sakai also observed that if the tyre is not used for three months, an additional running-in distance of

150 km is required. Extremely rapid wear during the first few hundred kilometres of a tyre's life has also been observed by Stalnaker *et al.* (1996).

The microtexture of aggregate pavement particles (*i.e.* the surface roughness on a scale of 0.01mm or less) has an important influence on tyre tread wear (Veith, 1995). Pavement microtexture is changed substantially by the weathering action of rainfall on a daily or seasonal basis. Lowne (1970) observed a large variation in the degree of tyre wear as a result of different road surfaces, where the wear on rough, harsh surfaces was approximately 3 times as severe as that on smooth, polished surfaces.

Excessive tyre wear also results from improper vehicle settings or poor maintenance. Excessive wear on the outer edges or shoulders of a tyre could be due to under-inflation, whereas excessive wear on the tyre centre could be due to over-inflation. Feathered treads are usually caused by incorrect toe-in, and excessive wear on one side of the tread is usually caused by excessive camber. Irregular depressions and bald spots can be caused by an unbalanced wheel. Other factors include worn or damaged suspension parts, overloading, incorrect steering geometry and track setting, and the improper matching of rims and tyres. With low-mileage vehicles and trailers, there is also the danger that the tyre wall can degrade (crazing and cracking) before the tread wears away, especially if the tyres are exposed to strong sunlight and moving air.

Driving behaviour and driving conditions are also well-recognised determinants of tyre wear. An aggressive driving style will tend to result in more rapid and uneven tyre wear than a 'smooth' driving style. Most tyre rubber is lost during acceleration, braking, and cornering, and the amount of rubber lost will therefore tend to be greatest near busy junctions, roundabouts and bends. Parking operations using power steering may also result in significant wear. Excessive and irregular tyre wear can result from continual high-speed cornering and hard braking. Using a tyre-testing machine, Stalnaker *et al.* (1996) simulated the effects of 'city' and 'motorway' driving conditions on the wear of radial-ply tyres. The city conditions included large numbers of turns. It was found that the city driving accounted for 63% of the tyre wear, even though it represented only 5% of the distance driven. This equated to a wear rate that was 32 times greater than that of motorway driving.

On a front-wheel drive (FWD) vehicle, the front wheels are used both for traction and steering, while the rear wheels are only responsible for rear axle control and load carriage. On a rear-wheel drive (RWD) vehicle, the front wheels serve primarily for steering, while traction is a rear-wheel responsibility. Due to these different roles, front tyres wear at a faster rate than rear tyres on a FWD vehicle, whereas the wear on the tyres of a RWD vehicle is more evenly distributed. With high performance rear-wheel drive cars, which can accelerate rapidly and be prone to wheel spin/slip, rear tyres can be worn down in as little as 4-5,000 miles.

2.2.2 Tyre wear rates

Based on the tyre usage statistics given for the UK at the start of Section 2.2, the average rate of loss of rubber is approximately 25 mg/tyre-km, or 0.1 g per vehicle-kilometre (vkm) for a passenger car. Wear rates of between 10 mg/tyre-km and 90 mg/tyre-km have been reported in the literature for car tyres (Table 2-1). These have either been derived empirically, or have been estimated from average statistics as above. Much of the variability in these wear rates can probably be explained by differences in the factors listed in the previous section, such as tyre construction, road surface characteristics, driving conditions, and vehicle load.

Table 2-1: Reported tyre wear rates for passenger cars.

Study	Estimated tyre wear rate (mg/tyre-km)
Kolioussis and Pouftis (2000)	10
Lee <i>et al.</i> (1997)	16
Legret and Pagotto (1999a)	17
Gottle (1979)	30
CARB (1993)	30
Malmqvist (1983)	30
Baekken (1993)	50
Dannis (1974)	60-90

However, it should be noted that not all of the worn tyre material will be emitted as airborne PM; some of the tyre weight loss will be in the form of carbon dioxide and water vapour (although when Cadle and Williams (1979) measured the gases emitted during continuous tyre wear tests, no significant increases in CO₂ could be measured above the background levels), and some much coarser solid material such as tyre shreds will also be removed. Annual PM₁₀ emissions from tyre wear in Germany have been estimated to be between 56,000 and 98,000 tonnes, a range that was comparable to the amount of exhaust PM₁₀ emitted by diesel road vehicles at the time (Rauterberg-Wulff, 1999). Such figures suggest that a large proportion of the material lost *is* emitted as PM₁₀, but appear to be at odds with data presented in the UK National Atmospheric Emissions Inventory (NAEI) (Goodwin *et al.*, 2002). The NAEI indicates that in 2000, tyre wear was responsible for the emission of just 700 tonnes of PM₁₀ in the UK (compared with total exhaust emissions of 26.5kt). Tyre particle size is reviewed in more detail later in this Chapter.

2.2.3 Tyre composition

A wide range of chemical compounds can be found in the tyres of road vehicles. For commercial reasons it is not usual for tyre manufacturers to release exact details of tyre composition, though some general information has been made available and this has been augmented by a number of scientific studies (*e.g.* Hildemann *et al.*, 1991; Rogge *et al.*, 1993; Kumata *et al.*, 1996 and 2000; Fishman and Turner, 1999). The bulk (40-60%) of tyre tread is composed of a variety of rubbers, including natural rubber co-polymers, butadiene rubber, styrene butadiene rubber (SBR), nitrile rubber, neoprene rubber, isoprene rubber, and polysulphide rubber. The rubber blend is usually governed by the required tyre characteristics, and for passenger cars Fauser (1999) quoted the following general composition by weight: natural rubber (40%), SBR (30%), butadiene rubber (20%), and butyl and halogenated butyl rubber (10%).

A variety of modifiers are added to the rubber mix. For example, vulcanising agents (sulphur, thiazoles, sulphenamides, selenium, tellurium, organic peroxides, nitro compounds and azo compounds) are introduced to improve the durability of tyre rubber. Vulcanising agents typically make up 1% of the tyre rubber mass. Accelerators are also introduced to speed up vulcanisation, with the main additives being zinc, calcium, lead or magnesium oxides, and a range of sulphur compounds. For example, the typical zinc oxide concentration in tyre tread has been found to be around 1-2% (Ahlbom and Duus, 1994; Smolders and Degryse, 2002). Other chemicals added to the mixture include retardants (terpene-resin acid blends), pigments (carbon black; 20-30% of the stock formula), fillers, reinforcing agents, softeners (synthetic organic oils, tars), preservatives (halogenated cyanoalkanes), anti-oxidants (amines, phenols; 1-2.5%), anti-ozonants (diamines and waxes), and desiccants (calcium oxide).

Due to changing operating temperatures, mechanical wear, oxidant and radical attack, and the loss of protective ingredients, tyre rubber is gradually altered during use (Kaidou and Ahagon, 1990; Ahagon and Kaidou, 1990). Cadle and Williams (1978) found that the wear process resulted in the devulcanisation of around 30% of the SBR in large tyre wear particles.

Despite the fact that the tyres produced by different manufacturers have different compositions, it has been shown that different brands produce similar pyrolysis products. These products, in particular benzothiazole, have been used to trace tyre wear debris in the urban atmosphere (Kim *et al.*, 1990). Fishman and Turner (1999) quoted tyre rubber benzothiazole concentrations of between 1.72 mg/g and 5.13 mg/g, with an average value of 3.02 mg/g. Because benzothiazole is of a semi-volatile nature, according to Rogge *et al.* (1993) it must be trapped as a thiazole-type compound within a tyre wear particle to actually serve as a particle-phase tracer. In a Swiss study, two tracer compounds for tyre material, 2-(4-morpholinyl) benzothiazole and N-cyclohexyl-2-benzothiazolamine (NCBA), were identified from PM₁₀ filters (Schmid, 2000). These compounds, which are degradation products of the accelerators used in the vulcanisation process, were also used as tracers for tyre material by Kumata *et al.* (1996 and 2000). These benzothiazole compounds are not easy to analyse, but they are very specific tracers for tyre wear, and the contribution of tyre wear to airborne PM can be estimated directly if the mean content of the tracer in tyres is known (Huglin, 2000). Other studies have identified the SBR component of synthetic tyre tread as useful molecular tracer for tyre dust (Pierson and Brachaczek, 1974; Cass, 1998; Fauser, 1999). VROM (1997) have reported concentrations for 10 PAHs in tyre rubber, with concentrations ranging between 0.8 and 34 mg/kg, though there appears to be no record of specific PAHs being used as tracers for tyre wear.

The metal content of tyres has been reported in a number of studies concerned with highway run-off (Malmqvist, 1983; Hewitt and Rashed, 1990; Brewer, 1997; VROM, 1997; Legret and Pagotto, 1999a). The values obtained are summarised in Table 2-2. The wide concentration ranges observed again reflect the use of different tyre recipes by different manufacturers. For example, Brewer (1997) measured the metal concentrations in five tyres from different manufacturers, and found large differences between the concentrations of Ca, Co, Fe, Pb and Sr. In some cases, the concentrations in Table 2-2 probably represent underestimates, due to the incomplete digestion of samples during analysis. For cadmium, Hewitt and Rashed (1990) have argued that the emission rate of cadmium from the road environment is underestimated, partly because of the possible underestimation of the cadmium concentration in tyres, partly because there may be underestimation of the tyre wear rate, and because there may be unidentified vehicle-based sources of cadmium.

Table 2-2: Elemental metal content of tyre rubber.

Metal	Concentration range (mg/kg)	Metal	Concentration range (mg/kg)
Ag	0.08	Mg	32-106
As	0.8	Mn	2
Al	81-420	Mo	2.8
Ba	0.9-4.1	Na	610
Ca	113-562	Ni	0.9-50
Cd	0.28-4.96	Pb	1-160
Co	0.88-24.78	Sb	2
Cr	0.4-6.73	Se	20
Cu	1.8-29.3	Sr	0.16-3.13
Fe	2.12-533	Ti	195
K	180	V	1
Li	0.23-2.3	Zn	8378-13494

(Data from Malmqvist, 1983; Hewitt and Rashed, 1990; Brewer, 1997; VROM, 1997; Legret and Pagotto, 1999).

Zinc has been used as a tyre wear particle tracer, though it does have many other sources. According to Ahlbom and Duus (1994), the particulate zinc contribution from tyre wear amounted to only 10% of the TSP zinc load in Swedish cities. Fauser (1999) identified extractable organic zinc (present in zinc accelerator complexes) as a tyre wear particle tracer since, with the exception of motor oil, tyres are the only significant contributor to organic zinc in airborne particles. Extractable organic zinc was found to be present in tyre rubber at a concentration of around 1.2 g/kg.

2.2.4 Tyre wear particle characteristics

2.2.4.1 Particle size

To repeat an earlier statement, not all of the worn tyre material will be emitted as airborne PM; some large particles and much coarser material (tyre shreds) will also be released. though a large degree of uncertainty exists in the reported size distributions of tyre wear particles.

Camatini *et al.* (2001) collected debris from the road of a tyre proving ground. They found tyre debris agglomerated to particle sizes up to a few hundred micrometers. Such particles are not airborne and are of limited interest to air pollution, but they probably contribute the largest fraction by weight of total tyre wear. Although the samples were collected in the environment of a proving ground, where tyre wear may be extreme, similar observations were also made by Smolders and Degryse (2002), who found that roadside tyre debris <100 µm had a mean diameter of 65 µm for cars and 80 µm for trucks.

However, it has been shown that both fine and coarse particles are emitted directly to the atmosphere as a result of tyre wear. For example, tests conducted by Cadle and Williams (1979) showed that airborne tyre

wear particles ranged in size from 0.01 μm to 30 μm . Several studies have also revealed that the wear particles tend to be divided into two distinct size groups: ultrafine particles with an aerodynamic diameter of less than 1 μm , and coarse particles larger than around 7 μm (Cardina, 1974; Dannis, 1974; Pierson and Brachaczek, 1974; Cadle and Williams, 1978; Fauser, 1999). A plausible mechanism for the distinction is the volatilisation (the thermal degradation of tyre polymer and the volatilisation of extender oils) and subsequent condensation of material in the ultrafine particle mode, and normal mechanical wear for larger sizes (Cadle and Williams, 1978).

The relative contributions of the fine and coarse modes to airborne PM mass appear to be rather variable. Pierson and Brachaczek (1974) showed that only 10% by mass of tyre wear particles were smaller than 3 μm aerodynamic diameter, and Cadle and Williams (1979) concurred that the larger particles dominate the total mass. More recent receptor modelling (see section 2.8.4 for a more detailed discussion of this term) work by Rauterberg-Wulff (1999), which indicated that tyre wear particles were only present in the coarse airborne PM fraction (2.5-10 μm), and the work of Moosmüller *et al.* (1997) which indicates that the products of tyre wear are dominated by particles >10 μm , appear to confirm the earlier findings. However, Fauser (1999) found that around 90% by mass of tyre wear particles had an aerodynamic diameter of less than 1 μm . Other recent PM₁₀ data from the USEPA (1995) and TNO (1997) indicate that, although tyre wear particles are mainly coarser than exhaust particles, around 70% by mass of tyre wear PM₁₀ can be classified as PM_{2.5}, 10% as PM₁, and 8% as PM_{0.1}. Dannis (1974) found that mean particle diameter decreases with increasing speed, and this may be one of a number of factors contributing to the differences in the reported findings.

2.2.4.2 Emission factors and ambient concentrations

Cadle and Williams (1979) found that airborne particles were emitted continuously during indoor tyre wear tests with a typical rate of 1 mg/tyre-km. The USEPA (1995) gives a PM₁₀ emission factor for car tyre wear of 1.2 mg/tyre-km, and its PART5 model uses a tyre wear PM₁₀ emission factor for light-duty petrol vehicles of 5 mg/vkm. This will be different for lorries and buses due to differences in the types of tyre compound used and vehicle mass. Rauterberg-Wulff (1999) determined a PM₁₀ emission factor for passenger car tyre wear of 6.1 \pm 1.1 mg/vkm, which is close to the value used in PART5. Lukewille *et al.* (2001) cite research by EMPA which indicates a PM₁₀ emission factor of 13 mg/vkm for light-duty vehicles. All these vehicle emission factors for tyre wear PM₁₀ are still considerably lower than the proposed EU type approval limit for emissions of total PM from diesel cars in 2005. Such a direct comparison is valid, as virtually all the exhaust particulates can be classed as PM₁₀ (and probably as PM₁). However, it can be assumed that tyre wear emission factors apply to all cars, whereas mass emissions of exhaust particles are only regulated for diesel vehicles (which often constitute a relatively small proportion of the fleet), and particle emissions from petrol cars are very low. This suggests that tyre wear PM₁₀ emissions may be much more important than atmospheric emissions inventories would suggest. Lukewille *et al.* (2001) also give a PM₁₀ emission factor for heavy-duty vehicles (again from EMPA) of 200 mg/vkm.

By comparing the PM₁₀ emission values given above for light-duty vehicles with the material loss values given in Table 2-1 (note these are in mg/tyre km), it appears that up to around 30 % of passenger car tyre wear material could be emitted as PM₁₀. However, using SBR as a tracer, Pierson and Brachaczek (1974) found that 2-7% of tread wear material could be classified as airborne PM, though at high-wear locations (*i.e.* near to corners) only 0.02-0.10% of estimated SBR worn from tyres was airborne PM.

Other studies have indicated that the tyre rubber content of airborne PM is generally quite low. Cadle and Williams (1979) and Pollard (1997) observed tyre wear contributions of less than 1%, and Fishman and Tuner (1996) estimated that tyre wear accounted for about 1% of the PM₁₀ at Clayton, Missouri. However, Fauser (1999) has observed that tyre wear particles constitute around 5% of the TSP mass in inner city air in Denmark, and Cardina (1973, 1974) found that, again using SBR as a tracer, 2-10% of the airborne dust near a highway was tyre tread rubber. Cardina (1973) also found that dustfall near a motorway junction had a 2% tread rubber content. Rogge *et al.* (1993) reported that no more than 1.6% of road dust comes from tyres. Using tracer analysis, Huglin (2002) found that tyre wear was only a significant contributor to airborne PM at kerbside monitoring sites. A comparison of NCBA concentrations in common tyres and PM₁₀ samples from

different locations in Switzerland revealed that at a kerbside site tyre wear particles formed 7.5% of PM₁₀, and at an urban background site they formed around 2% of PM₁₀. However, because of the large amount of variation of NCBA concentrations in tyres, the results had a high degree of uncertainty.

Pierson and Brachaczek (1974) reported total suspended tyre wear particulate mass concentrations near a road and in a tunnel in Michigan of 1.2 µg/m³ and 9.6 µg/m³ respectively. The tyre wear component of airborne PM has also been measured in a number of Japanese studies. Fukazaki *et al.* (1986) reported a maximum roadside tyre wear concentration of 24 µg/m³ for PM smaller than 4.7 µm, and other researchers have reported tyre wear TSP, PM₁₀, and PM_{3,3} levels of 7 µg/m³, 2.2 µg/m³, and 0.2 µg/m³ respectively (Lee and Kim, 1989). Kumata *et al.* (1996) observed a very low tyre wear contribution (0.001 µg/m³) to TSP concentrations in a forested area approximately 500 metres from a suburban roadway in Tokyo.

2.2.4.3 Particle composition

The concentrations of a number of chemical species present in tyre wear, brake wear, and road dust particles were determined by Hildemann *et al.* (1991). The results are given in Appendix A. About half of the total particulate mass in the tyre wear sample was composed of organic compounds, with a further sixth being elemental carbon. In particular, the zinc concentration (0.04%) was thought to be lower than would normally be expected (*i.e.* around 1%). However, only a single tyre was used in the analysis. The same tyre wear, brake wear, and road dust samples were analysed by Rogge *et al.* (1993) using GC/MS techniques. The concentrations of more than 100 solvent-extractable organic compounds were determined (Appendix B). It was noted by Rogge *et al.* that tyre wear particles contain appreciable amounts of styrene and butadiene polymers, but these cannot be analysed using solvent extraction methods. Tyre wear particles were found to contain around 200 µg/g of polycyclic aromatic hydrocarbons (PAH). Rogge *et al.* noted that, for the *n*-alkanes >=C₃₅, there are few urban emission sources other than tyre wear. The *n*-alkanes >=C₃₅ were therefore considered to be a useful marker for tyre wear, and actually better than benzothiazole. In addition, it was found that PAHs in road dust were not dominated by the PAH content of tyre wear particles.

In road dust samples, Pollard (1997) observed that when tyre wear particles were present two specific compounds could be readily identified: di-pentene (limonene, C₁₀H₁₆) and styrene (C₈H₈). Di-pentene was also consistently observed by Pollard in airborne particle samples, and arises from natural rubbers or isoprene-based synthetic rubbers used in tyres. Styrene, which appeared irregularly, arises from the SBR used mainly in car tyres. The fraction of tyre rubber in the road dust was found to be 0.61%.

Hildemann *et al.* (1991) also reported that tyre wear accounts for 1.4% of the total organic carbon in the air of a heavily trafficked area. Fishman and Tuner (1996) used benzothiazole as a tracer species to estimate tyre wear contributions to ambient PM₁₀, and observed a benzothiazole mass fraction of 2.9 mg/g.

2.3 Brake Wear particles

During forced deceleration, vehicle brake linings are subject to large frictional heat generation and associated wear. This mechanically-induced wear generates brake lining particles which are subsequently released to the environment. A Swedish study found that around 934 tonnes of brake linings were used in 1993 (Malmo Environmental Health Administration, 1998). Westerlund (2001) calculated that, in Stockholm, passenger cars, goods vehicles and buses released around 45 tonnes, 7.6 tonnes, and 3.3 tonnes of brake lining material to the environment each year, respectively. The UK National Atmospheric Emissions Inventory (Goodwin *et al.*, 2002) indicates that in 2000 brake wear was responsible for 4,200 tonnes of PM₁₀ emissions in the UK. However, the brake wear component of the UK inventory is currently based on old USEPA emission factors, which are not specific to any particular vehicle type or year. The value reported in the UK inventory is therefore subject to considerable uncertainty.

2.3.1 Factors affecting brake wear

There are two main brake system configurations in current use: disc brakes, in which flat brake pads are forced against a rotating metal disc, and drum brakes, in which curved pads are forced against the inner surface of a rotating cylinder. Modern passenger cars are usually equipped with front disc brakes and either

rear disc or drum brakes. Disc brakes are also now being introduced in commercial vehicles. Many modern vehicles are also equipped with anti-lock braking (ABS). Disc brakes have a much better gradual braking efficiency than drum brakes, even though they have a smaller friction lining. The front brakes have to provide most (typically 70%) of the braking power (Garg *et al.*, 2000b), and it is therefore no surprise that front brake linings have to be replaced more frequently than rear brake linings. It has been estimated that front disc brakes last for around 35,000 miles (56,000 km) miles under normal usage, while rear brakes can be expected to last around 70,000 miles (112,000 km) (Garg *et al.*, 2000b). During a brake's lifetime, normally around 80% of the friction material will have worn away.

As with tyre wear, the composition of the friction material influences the brake wear rate. However, there is a large number of different brake pad compositions available. For example, Filip *et al.* (1997) analysed the composition of 82 brake pads on the North American market alone. Representative wear rates are therefore difficult to determine with confidence. Driving behaviour, in particular the frequency and severity of braking events, should be an important determinant of brake temperature and wear. Because brake wear only occurs during forced decelerations, the highest concentrations of brake wear particles should be observed near busy junctions, traffic lights, pedestrian crossings, and corners. Garg *et al.* (2000b) found that the mass of friction material lost per stop increased with an increase in brake temperature, though in all cases the percent of total wear detected as airborne PM was higher for a brake temperature of 100°C than for a brake temperature of 400°C.

2.3.2 Brake wear rates

Based on component size, density, and lifetime, Legret and Pagotto (1999a) estimated the wear rate of brake linings to be around 20 mg/vkm for passenger cars, 29 mg/vkm for light goods vehicles, and 47 mg/vkm for lorries. Similar results were obtained in the comprehensive study of brake wear PM conducted by Garg *et al.* (2000b), in which a brake dynamometer was used to generate brake wear particles. Garg *et al.* estimated that the total brake wear for a small car would be 11 mg/vkm, for a large car it would be 17 mg/vkm, and for a pick-up truck it would be 29 mg/vkm. In Stockholm, Westerlund (2001) estimated the amount of material lost from passenger cars and heavy goods vehicles to be 17 mg/vkm and 84 mg/vkm respectively.

2.3.3 Brake composition

The general chemical composition of brake linings is just as complex as that of tyre rubber. Linings generally consist of four main components which are stable at high temperatures: binders, fibres, fillers, and friction modifiers. Various modified phenol-formaldehyde resins are used as the binders. Fibres can be classified as metallic, mineral, ceramic, or aramid, and include steel, copper, brass, potassium titanate, glass, organic material, and Kevlar. Fillers tend to be low-cost materials such as barium and antimony sulphate, kaolinite clays, magnesium and chromium oxides, and metal powders. Friction modifiers can be of inorganic, organic, or metallic composition. Graphite is a major modifier used to influence friction, but other modifiers include cashew nut dust, ground rubber, and carbon black. In the past, brake pads included asbestos fibres, though these have now been totally removed from the European fleet.

Modern asbestos-free brake linings contain different inorganic compounds to older linings, though the metal compounds in use have remained more or less the same. The metal content of brakes determined in three studies (Brewer, 1997; VROM, 1997; Legret and Pagotto, 1999) are presented in Table 2-3. Westerlund (2001) also reported metal concentrations in the brake linings of new passenger cars (less than four years old), older passenger cars (using replaced brake disc, drums and brake linings not originally fitted to the vehicles), heavy goods vehicles and buses, based on analysis by plasma emission spectrometry (Table 2-4). The results show that significant amounts of copper (up to 14% by mass) and iron (up to 40% by mass) can be present. Other metals, notably calcium, sodium, and zinc, are also prominent. Some of the results from these studies are comparable, though the concentrations of some metals vary by several orders of magnitude, and this clearly shows that compositional information of this type is strongly dependent upon the manufacturer and lining type.

PAH concentrations in brake material samples were measured by VROM (1997), and these are shown in Table 2-5. Some compounds present in the brake lining may also be transformed during brake application; Rogge *et al.* (1993) suggested that the build-up of heat during brake application may be responsible for the additional generation of PAHs.

Table 2-3: Metal content of brake linings.

Metal	Concentration range (mg/kg)	Metal	Concentration range (mg/kg)
As	10	Mn	3,220
Al	3,770	Mo	10,000
Ba	2,640	Na	15,400
Ca	14,300	Ni	210-850
Cd	2.7-29.9	Pb	1,960-3,900
Co	6.43	Sb	10,000
Cr	162-1,200	Se	20
Cu	15,100-142,000	Sn	7,000
Fe	115,000-399,000	Sr	81.4-740
K	857	Ti	3,600
Mg	6,140	V	660
Li	55.6	Zn	270-21,800

Data from Brewer, 1997; VROM, 1997; Legret and Pagotto, 1999).

Table 2-4: Mean metal concentrations in brake linings (Westerlund, 2001).

Vehicle type	Front linings (mg/kg)						Rear linings (mg/kg)					
	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
New passenger cars	11.6	137	117,941	141	9,052	23,830	8.02	73.4	92,198	69.6	18,655	16,498
Old passenger cars	8.6	92	71,990	182	13,651	17,696	3.5	151	51,240	122	9,110	7,197
Heavy goods vehicles	Volvo	<10.3	171	15,000	118	656	14,900	As front linings				
	Scania	<1.99	157	76.9	110	158	127	As front linings				
Buses	Volvo	<10.1	<20.1	27,300	140	1,020	18,500	As front linings				
	Scania	<1.98	118	88.3	178	441	172	As front linings				

Table 2-5: PAH concentrations in brakes (VROM, 1997).

PAH	Concentration (mg/kg)	PAH	Concentration (mg/kg)
napthalene	n/a	benzo (a) anthracene	1.5
phenanthrene	0.97	benzo (a) pyrene	0.74
anthracene	n/a	benzo (k) fluoranthene	0.42
fluoranthene	0.69	indeno (1,2,3-cd) pyrene	2.6
chrysene	1.7	benzo (ghi) perylene	0.34

2.3.4 Brake wear particle characteristics

2.3.4.1 Particle size and number

As with tyre wear, not all of the worn brake material will be emitted as airborne PM (though proportionally more it seems in the case of brakes). Sanders *et al.* (2003) conducted detailed laboratory tests using a state-of-the-art experimental setup, and observed that 55-70% of the total wear material was in the form of airborne particles. The collection efficiency for wear debris was 90-100% of the wear mass. The same study identified that 3-30% of brake debris falls on the road, 16-22% is retained on the wheel, and 8-25% is retained on the brake and steering/suspension equipment. Data from the USEPA (1995) and TNO (1997) indicate that 98% (by mass) of brake wear particles can be classified as PM₁₀, whilst around 40% of the PM₁₀ is PM_{2.5}, 10% is PM₁, and 8% is PM_{0.1}. Different size distributions have been obtained elsewhere. Abu-Allaban *et al.* (2002) estimated that, for airborne brake wear particles at roadside, the PM_{2.5} share was only 5-17% of PM₁₀. Garg *et al.* (2000b) recorded airborne brake wear particle mass fractions smaller than 10µm, 2.5µm, and 0.1µm of 88%, 63% and 33% respectively, and found that, on average, around 35% of brake wear mass is released as airborne PM. However, whilst the majority of the fine particulate brake dust from disc brakes is released to the environment, small amounts of brake dust (around 10%) can be retained in the drum brake enclosure (Lohrer and Mierheim, 1983). In any case, it appears that a significant fraction of airborne brake wear particles can be classified as PM₁₀. It is possible that the high temperatures generated during braking can vaporise some of the brake pad material, and Garg *et al.* (2000b) suggested that the volatile material may condense during measurement and contribute to the fine particle fraction.

Garg *et al.* (2000b) also determined the total numbers of particles emitted during brake tests using an Electrical Low-Pressure Impactor (ELPI) and an Electrical Aerosol Analyser (EAA). With the ELPI, the average number of particles detected per stop ranged from 1.0×10^4 to 5.23×10^6 . The number of particles emitted showed a clear increase with brake temperature. When measured using the EAA, the number of particles per stop ranged from 6.9×10^{10} to 4.7×10^{12} . The higher EAA counts suggested that most of the particles were smaller than the 30nm minimum size cut-off of the ELPI. However, the numbers of particles observed at the higher brake temperatures may have been due to more frequent braking during the test procedure. As before, the large numbers of particles observed in some wear tests was attributed to condensation occurring as a result of the dilution conditions.

2.3.4.2 Particle emission factors

The PART5 model developed by the USEPA includes particle emission factors due to brake wear. However, the brake wear PM₁₀ emission factor for light-duty petrol vehicles of 7.8 mg/vkm given in PART5 is based on work conducted during the early 1980s, and using asbestos-based brakes (Cha *et al.*, 1983). Since then, the asbestos in brakes has been replaced by various other materials, and these emission factors may not be applicable to modern vehicles. Little work has been performed on emissions from brakes using non-asbestos materials, although Garg *et al.* (2000b) obtained a PM emission factor for light-duty vehicles of 3.2-8.8 mg/vkm. For the pads tested, emission rates for PM₁₀ and PM_{2.5} were calculated to be 2.9-7.5 mg/vkm and 2.2-5.5 mg/vkm respectively. In fact, the upper limit of the range for PM₁₀ emissions is very close to the older value used by the USEPA. Westerlund (2001) determined a similar emission factor for brake wear PM₁₀ from cars (6.9 mg/vkm), and an emission rate for HDVs of 41.2 mg/vkm. Lower values were obtained by Rauterberg-Wulff (1999): 1 mg/vkm for cars, and 24.5 mg/vkm for HGVs. Lukewille *et al.* (2001) cite research by Carbotech which indicated PM₁₀ emission factors for LDVs of 1.8-4.9 mg/vkm, and an emission factor for HDVs of 3.5 mg/vkm. Based on PM₁₀ measurements at a range of roadside locations, Abu-Aballan *et al.* (2003) found that LDV emission factors varied between 0 and 79 mg/vkm, and HDV emission factors varied between 0 and 610 mg/vkm. Emissions from brake wear were highest near motorway exits.

Malmqvist (1983) estimated that, of the particles emitted by brake systems, 1.5 mg/vkm are deposited on the road surface.

Although gaseous emissions do occur as a result of the mechanical abrasion of brake linings, they do not appear to be significant. During the tests conducted by Garg *et al.* (2000b), increases in the concentrations of CO, CO₂ and hydrocarbons above the background levels in the test chamber could not be detected.

2.3.4.3 Particle composition

The chemical composition of dust samples taken from inside car brake mechanisms was investigated by Hildemann *et al.* (1991) who reported the inorganic content (Appendix A), and Rogge *et al.* (1993) who reported the solvent-soluble organic content (Appendix B). However, it was found that only a small fraction of the organic fraction of brake dust could be extracted. Because brake linings have to withstand excessive mechanical and heat stress and must be resistant to possible leaking brake fluid, organic fibres and binders are used that show high boiling points and resistance to solvents. Hence it is not surprising that only a small fraction of the brake lining dust can be examined using conventional laboratory techniques. Nevertheless, potential trace compounds could still be identified in the solvent-extractable fraction.

Hildemann *et al.* (1991) found that the fine fraction of the brake dust sample consisted mainly of iron and silicon compounds, organics, magnesium, and barium. Brake abrasion dust has also been found to contain large amounts of iron in other studies (Muschack, 1990; Filip *et al.*, 1997; Garg *et al.*, 2000b). About 13% of the fine particle mass consisted of organic compounds. Hildemann *et al.* (1991) reported that brake wear may account for up to 2.3% for the total atmospheric organic carbon in air in an urban area. The identifiable portion of the brake particle organics consisted mainly of *n*-alkanoic acids (34.3%) and polyalkylene glycol ethers (56.9%), the latter being a typical component of brake fluid. By mass, the most abundant solvent-soluble organic compounds were found to be triethylene glycol monomethyl ether (2-[2-(2-methoxyethoxy)-ethoxy]ethanol) and triethylene glycol monoethyl ether (2-[2-(2-ethoxyethoxy)-ethoxy]ethanol). Again, as both compounds are used mainly in hydraulic fluids the findings suggest that the presence of these compounds is indicative of mechanical failure, and they cannot therefore be considered as reliable tracers (Rogge *et al.*, 1993).

The study by Garg *et al.* (2000b) revealed that 18% of the airborne PM was carbonaceous material. Elemental analysis indicated that metallic species, together with Si, P, S, and Cl, accounted for most of the remaining mass. The analysis showed the presence of a variety of elements that could provide a unique source profile for use in receptor models. However, a single source profile was not created since it was not known how representative the tested brake pads were of the in-service vehicle fleet. It was suggested that the analysis of a composite of brake dust samples collected from a large number of vehicles could be used as a practical way of determining an in-service brake PM emission source profile.

2.4 Clutch wear particles

The friction materials used in clutch linings are similar to those used in brake linings (*i.e.* a combination of mineral fibres, including asbestos in older vehicles, and binders). However, although some studies of the wear of asbestos-based clutches were conducted in the 1970s (*e.g.* Jacko *et al.*, 1973), there appears to be no recent information relating to the amount of material lost to the environment, or emissions of particulate matter, from this source.

It is possible that the lack of information on clutch wear and emission factors will have ramifications for the source apportionment of particulate matter via emission inventories and receptor modelling, and represents an area of uncertainty. However, the enclosed nature of the clutch mechanism probably means that much of the wear material is retained inside the housing. In any case, clutch wear as a source of particles warrants further investigation.

2.5 Corrosion particles

The corrosion of vehicle components, crash barriers, and street furniture can contribute to the dust deposited on the road surface, and hence to resuspension. Corrosion may also be a source of airborne particles, but there is little information relating to its significance.

Compositional analysis of used car body parts and fresh primer paint by Brewer (1997) revealed that a number of heavy metals are found in a range of concentrations in different vehicle body parts. The results are summarised in Table 2-6. Unsurprisingly, in all bodywork and undercarriage components (except paint) Fe is

found in the highest concentrations. Exhaust components also contain high concentrations of Pb, Zn, and Cu. Pb probably originates from the use of leaded fuel. Car paint, and other coatings, were found to contain high levels of Ba, Al, Fe, Cr, Zn, and Pb.

Legret and Pagotto (1999a) conducted a study of the corrosion of galvanised steel safety barrier on the north bypass motorway of Nantes by means of an experimental set-up consisting of a 150m long barrier equipped with a gutter. Rain water was collected and the heavy metal content was determined over a one year period. The amount of zinc removed was approximately 950 g/km/year. The corresponding fluxes for Cd, Cu and Pb were 0.16, 0.23, and 2.1 g/km/year respectively.

Table 2-6: Elemental metal content of vehicle components.

Metal	Concentration range (mg/kg)		
	Exhaust	Paint	Bodywork
Ag	3.13-5.48	559	2.8-3.2
Al	503-2,986	460-14,700	54.1-517
Ba	21.6-88.8	6,320-50,900	29.0-44.5
Ca	16.2-33,790	78,300	1.31-9.71
Cd	2.2-14.9	0.08	0.10-1.44
Co	-	15.3-352	-
Cr	250-337	18.0-4060	116-832
Cu	157-1,521	63.6	236-978
Fe	4.74-9.18x10 ⁵	5,790-218,000	0.69-1.00 x10 ⁶
K	392	129	-
Li	0.54-1.12	8.9-13.8	0.42-0.98
Mg	11.1-7,350	787-1,990	14.67-53.38
Mn	1,180-2,160	85-410	2,130-3140
Na	2,680	-	-
Ni	108-222	0.67-71.64	215-668
Pb	121-7,350	41.7-30,900	111-184
Sr	0.19-37.7	206-800	0.45-3.46
Zn	80.3-14,884	6,820-7148	150-10,500

Data from Brewer (1997).

2.6 Road surface wear particles

A range of asphalt-based and concrete-based road surfacings are in use throughout Europe. Concrete surfacings are composed of coarse aggregate, sand and cement. Asphalts are mixtures of mineral aggregate, sands, filler, and bitumen binder, though the composition can vary widely both from country to country and within countries. Generally, the stone content is around 95% and the bituminous binder around 5%. The properties of asphalt can be modified by additives such as adhesives, polymers, and different types of filler.

Bitumen is a viscous hydrocarbon material containing many chemical components, and with a mean molecular weight of around 800 (Jennings *et al.*, 1992). Its complexity makes it very difficult to characterise (Lindgren, 1996), and few workers have attempted to identify bitumen particles in the environment. The precise composition of bitumen varies according to the source of the crude oil from which it originates, and any subsequent modification (Whiteoak, 1990). Bitumen has been described as a colloidal dispersion of solid particles, known as maltenes (which are soluble in *n*-heptane) and asphaltenes (which are not), in a medium of saturated hydrocarbons with a molecular weight range of 200-600 (oils) and polyaromatic hydrocarbons with a higher molecular weight (resins). The asphaltenes have a molecular weight of up to 1000 (C₈₀) (Hagen *et al.*, 1989). It has been suggested by Fauser (1999) that asphaltenes and maltenes from bitumen, which are amongst the largest molecules present in the atmosphere, can be used as tracers for road surface wear. Fauser found that airborne bitumen particles mainly ranged in size between 0.35µm and 2.8µm, with a mean of

around 1 μm . Elvebakken (1991) attempted to use PAHs as bitumen tracers, and noted that more than 300 different PAHs are present in bitumen. However, each compound could only be found at a concentration of less than 0.1% by mass, and there is no PAH that is unique to bitumen. This lack of specificity probably renders PAHs unsuitable as tracer species for bitumen. He *et al.* (1993) and Rosenmejer (1993) used the polar aromatic and aliphatic fractions as bitumen tracers, but did not reveal a usable fingerprint profile for bitumen.

Traces of metals such as vanadium, nickel, iron, magnesium, and calcium are also present in bitumen. Lindgren (1996) determined the metal composition of bitumen (B180) and two rock minerals used in asphalt, a gabbro and a porphyry. For the bitumen, chromium, copper, and zinc were below their detection limits. A sample of stone used in the asphalt of the French A11 motorway was analysed for heavy metal content by Legret and Pagotto (1999b). The results of these studies are presented in Table 2-7.

Table 2-7: Metal analysis of asphalt constituents.

Metal	Concentration (mg/kg)			
	Gabbro ^a	Porphyry ^a	'Stones' ^b	Bitumen (B180) ^a
As	11.2	2.52	-	-
Cd	0.127	0.136	0.12	-
Cr	238	63.9	240	<35
Cu	70.5	21.9	80	<17
Ni	110	16.2	80	23 (15-100) ^c
Pb	2.75	19.8	0.6	-
V	215	24.9	-	340 (50-600) ^c
Zn	149	36.3	85	<17

^a Lindgren (1996)

^c Baekken (1993)

^b Legret and Pagotto (1999b)

- No data available

A study reported by Van Heystraeten (1996) showed that old rubber tyre material can be used in modified asphalt mixes. The amount of crumb rubber used influences the amount of bitumen added to the mix, and hence the mineral content of the material. This road surface technology was developed in Sweden with the purpose of using the rubber properties to control snow and ice. Van Heystraeten (1996) noted that several studies have been performed in Sweden to assess the resistance to abrasion and rutting of asphalt surfaces containing rubber. These tests were evaluated against asphalt surfaces containing other materials, such as conventional asphalt concrete mixes, various surface dressings and stone mastic asphalt.

Asphalt wear has been estimated by Muschack (1990) to be 3.8 mg/vkm. CBS (1998) – cited in Lukewille *et al.* (2001) – reported wear rates for LDVs and HDVs of 7.9 and 38 mg/vkm respectively, although these values also included tyre and brake wear. However, in areas where there is extensive use of studded tyres during the winter, the wear of the road surface is considerably higher. In Sweden, road surface wear due to the use of studded tyres amounts to 100,000 tonnes per year Gustafsson (2001) and an average of 24 g/vkm of asphalt is worn off during winter (Lindgren, 1996), although it was estimated by Carlsson *et al.* (1995) that the introduction of softer studs and more durable asphalt would have reduced this to 11 g/vkm by 2000. In Norway, the use of studded tyres is thought to be responsible for the wear of around 250,000 tonnes of asphalt per year (NILU, 1996).

The dust burden due to road wear and the use of studded tyres varies greatly by time and place. On cold, dry winter days near major arterial roads, the concentrations measured by NILU (1996) were often higher than the recommended air quality guideline by a factor of three to four. The highest concentrations measured were more than 600 $\mu\text{g}/\text{m}^3$ as a daily mean. By comparison, the recommended Norwegian air quality guideline is 70 $\mu\text{g}/\text{m}^3$. In these situations, an estimated 80% of the PM_{10} originates from resuspended road dust. On an annual basis calculations of annual mean concentrations of PM_{10} in the centre of the largest cities in Norway show that 20%-30% of the airborne dust comes from studded tyre wear. During wet road conditions outside the studded tyre season, the contribution from road wear is insignificant compared with the contribution from exhaust emissions (NILU, 1996).

2.7 Resuspension of Road Dust

Road dust may be suspended or resuspended in the atmosphere as a result of vehicle-generated turbulence, by tyre shear caused by rotation, and by the action of the wind (Sehmel, 1973 and 1976). Road dust therefore bears a dynamic relationship to airborne PM. At present, atmospheric emission inventories tend not to include the resuspension of road dust as a particle source due to the absence of suitable emission factors and the possibility that its inclusion results in the double counting of sources. However, studies have suggested that the resuspension of paved road dust contributes significantly to atmospheric PM₁₀ and PM_{2.5} concentrations (e.g. Rogge *et al.*, 1993; Chow *et al.*, 1995; Schauer *et al.*, 1996; Kleeman and Cass, 1999; Ruellan and Cachier, 2001).

2.7.1 Sources and composition

Road surfaces act as a repository for dustfall. Road dust is an agglomeration of material from a wide range of sources; virtually any anthropogenic and biogenic source of emissions to the urban atmosphere can contribute to the road dust complex, and it can contain particles derived from all of the following sources:

- (i) Vehicle sources
 - Exhaust particles
 - Tyre wear
 - Wear of brake linings
 - Clutch wear
 - Corrosion of chassis, bodywork, and other vehicle components
 - Material carried onto the road by vehicles
 - Discarded rubbish from road users
- (ii) Highway sources
 - Road surface wear
 - Corrosion of street furniture and crash barriers
 - Winter maintenance chemicals - road salt and grit.
 - Fertilisers, pesticides
 - Plant growth inhibitors
- (iii) Non-transport sources
 - Crustal material
 - Vegetative detritus
 - Material from industrial and commercial activity
 - Material from domestic activity
- (iv) Deposition of advected airborne particles derived from the above sources at other locations.

Legret and Pagotto (1999b) have semi-quantitatively labelled road dust as 60% 'sand', 20% 'fine sand', and 20% 'silt'. Hildemann *et al.* (1991) found that paved road dust samples consisted of 27% SiO₂, 17% organics, 11% Al₂O₃, 9% Fe₂O₃, and 4% Ca. A more detailed chemical composition of these samples is presented in Appendix A, and the detailed composition of the solvent-soluble organic component of the road dust determined by Rogge *et al.* (1993) is provided in Appendix B. The potential sources of the compounds present are also listed in this Appendix. Legret and Pagotto (1999b) found road dust to be heavily polluted by Pb, Cu, Cd, and Zn, probably originating from tyre wear, brake wear and leaded petrol. Concentrations of Cr and Ni were found to be low.

Orr and Deletic (2000) found that during the winter months, sediment loading was at its greatest, particularly when snow was present on the road surface. Heavy metal concentrations were found to be greatest in the finest particle fraction analysed (2-63µm). Miguel *et al.* (1999) found that the relative abundance of Fe, Cu, Zn, Pb and S increased with decreasing particle size.

Manoli *et al.* (2002) reported the comparison to the average compositional signatures of fine and coarse particles and showed that all signatures were significantly correlated between each other, however, the signature of road dust appeared to be more strongly correlated to coarse particles than to fine particles. This suggested a stronger contribution of road dust resuspension to the coarse particle fraction.

2.7.2 Factors affecting resuspension

An important factor influencing the rate of resuspension is the silt loading of the road. This is the mass of silt (material less than 75 μm) in a square metre of road surface. A range of silt loadings for the US is given between 0.01 and 30g/m². Little information is available for the UK, but a study carried out by Ball and Caswell (1983) show data that would equate to around 0.02g/m². If this figure were an accurate estimate, it was argued that it would result in an emission factor for PM₁₀ comparable to that of exhaust emissions from petrol engined cars fitted with a three-way catalyst. The figure is actually thought to be an over-estimate, as the environmental conditions in the UK are markedly different to the US, most notably the precipitation.

Nicholson and Branson (1990) examined the importance of traffic-generated resuspension by measuring surface concentrations of spherical silica particles of known sizes. Four nominal particle sizes were used (5, 10, 12, and 20 μm), and a fluorescent dye was attached to the particles to enable their detection. The particles were dispersed over the road surface, and allowed to settle in an enclosed volume. The surface amounts of fluorescent particles were determined shortly after their deposition, and additional measurements were made in a period which included several passes by a vehicle. The vehicle was driven so that its wheels passed either side of the test area, thus giving an indication of the effects of its turbulent wake. It was found that turbulence-induced resuspension becomes more difficult with decreasing particle size, and that large proportions of the deposited material were removed after a single passage of a vehicle.

Also, experiments with a single particle size revealed that there was a clear dependence of resuspension on vehicle speed. A proportion of the fluorescent particles remained on the road after each experiment, and it was concluded that this was associated with depressions in the road surface. A further experiment, in which the wheels passed through the test area, was used to indicate the combined effects of turbulence and tyre shear on resuspension. There was little difference in the resuspension curves to those found for vehicle-induced turbulence alone. For a busy road with fast-moving traffic, it appears that resuspension is likely to be controlled by the rate of incorporation of deposited material. Such incorporation may be most rapid when the surface is moist, such that resuspension factors resulting from turbulence of tyre shear might be greatest immediately after a road becomes dry.

Data presented by APEG (1999) showed that, within individual seasons PM₁₀ and PM_{2.5} concentrations were strongly correlated, but the percentage of PM₁₀ comprised by PM_{2.5} showed a strong seasonal dependence. The proportion of coarse particles was greatest in the spring and summer, and least in the wetter autumn and winter seasons. This was interpreted as being most probably the result of better dispersion during the hotter months, leading to lower PM_{2.5} concentrations, and more effective wind-driven suspension of coarse particles during dry weather. During wet conditions, tyre spray is an important resuspension mechanism (Smith, 1970), though this may result in more particles being deposited on the road verge than being suspended in the atmosphere.

APEG (1999) presented a comparison between particle concentrations near a busy street canyon and at an urban background location in London which revealed that, at the former site, the concentration of coarse particles was substantially higher. This was attributed to resuspension arising from traffic-induced turbulence. In mass terms, the elevation in coarse particles due to resuspension was of a similar magnitude to the elevation in fine particles due to exhaust emissions. The association of fine particles with exhaust emissions and coarse particles with resuspension was based on the observed correlations between particle concentrations and NO_x concentrations. Comparisons between particle size distributions at urban and rural locations showed that, at the rural locations, levels of both fine and coarse particles were lower. The higher level of fine particles at urban sites could be attributed to vehicle exhaust emissions. The rural air was also depleted in the larger particles which correspond to the effects of human activity, including road dust raised by traffic, construction, and industry. At other sites where PM₁₀ and PM_{2.5} concentrations were monitored

simultaneously, particle concentrations were examined in an attempt to disaggregate the wind-driven component of coarse particles from the component resuspended by traffic. Very little resuspended mass was observed at night-time, when both traffic is light and wind speeds and turbulence are lower.

2.7.3 Particle emission factors

The USEPA have derived a formula for calculating the contribution of resuspension, but it is based on old measurements near exceptionally dusty roads, in an arid environment. Such conditions are not thought to be relevant to the UK (APEG, 1999), and are probably not relevant to a number of other European countries.

In the UK, Nicholson (2000) developed a model which considered the net input and output from the road surface. Deposition and other inputs (for example, deposition from cars, transfer on tyres and wind blown material) were equilibrated with resuspension and surface run-off. The first estimate of resuspension was based on two assumptions; (i) all inputs other than atmospheric deposition were equal to removal runoff and (ii) material deposited in rain was not available for resuspension. Consequently, resuspension by traffic was equal to the dry deposition on the road. Using the model, an estimated net PM₁₀ value for resuspended material in the UK of 0.04 g/km (or 20,000 tonnes per annum based on statistics for the year 2000) was obtained. This emission factor is currently used in the UK NAEI (Goodwin *et al.*, 2002) for all vehicles. One of the main reasons for the inclusion of resuspension in the inventory is to aid the understanding of roadside pollution measurements. However, given the considerations stated earlier, resuspended PM₁₀ is reported separately in the NAEI.

If resuspended PM₁₀ were to be fully included in the UK inventory, based on the figures for 2000 it would account for 11% of PM₁₀ from all sources, and 55% of PM₁₀ from road transport. An inventory of fine particulate organic carbon emissions to the Los Angeles area atmosphere compiled by Hildemann *et al.* (1991) indicated that paved road dust was the second largest source of fine aerosol organic carbon particles. Brake linings and tyre wear were found to be the eleventh and thirteenth largest sources respectively. Kleeman and Cass (1999) found that the entrainment of road dust from paved and unpaved roads was responsible for 34% of all PM₁₀, and 20% of all PM_{2.5}. The fact that the same study showed that exhaust emissions from road vehicles were responsible for 5% of all PM₁₀, and 14% of all PM_{2.5} illustrates the potential importance of resuspension processes. It was also found that particles emitted from paved road dust sources, and crustal material other than paved road dust, dominate the 24-h size distribution for particles larger than 1µm. Until further resuspension measurements are available, this source remains a major area of uncertainty in particulate emission inventories.

2.8 Research methods

2.8.1 Methods for determining tyre wear and tyre particle emissions

The most straightforward method for determining tyre wear is the periodic measurement of tread depth. However, variations in the extent of wear across the tyre and irregularities in tyre shape render this approach rather inaccurate. Determining tyre weight loss is a more sensitive method than the measurement of tread depth, though care must be taken to avoid errors due to, for example, damage to tyres due to their removal from the vehicle and hubs, and material embedded in the tyre. This approach was adopted by Lowne (1970). To minimise damage to the tyre, Lowne (1970) weighed both the wheel and tyre simultaneously. Prior to weighing, the wheel was brushed and stones embedded in the tyre were removed.

Tyre abrasion is difficult to simulate in the laboratory. As well as speed, acceleration, tyre material, and temperature, parameters such as the road surface construction and curvature are also important (Rauterberg-Wulff, 1999). Hildemann *et al.* (1991) determined the chemical composition of tyre wear particles using a rolling resistance testing machine at a tyre testing laboratory over a period of several days. A grab sampling technique was used to collect wear particles that had accumulated on the horizontal surfaces of the machine. However, when the tyre wear particles were resuspended they became electrically charged and adhered to the walls of the sampling equipment. As a result, the attempt to re-suspend and collect only fine tyre debris particles had to be abandoned. Instead, a sample of total PM, mainly composing of coarse particle, was

collected on filters. Because tyre tread is well mixed, it was assumed that there were no compositional differences between the fine and coarse particle fractions. More recently, Camatini *et al.* (2001) have used a rotating drum method to simulate tyre wear in order to study the morphology and speciation of emitted particles.

Rauterberg-Wulff (1999) determined particle emission factors for tyre wear using receptor modelling in combination with measurements conducted in the Berlin-Tegel tunnel. Dichotomous samplers with PM₁₀ and PM_{2.5} inlets were used to collect airborne particles, which were then analysed thermographically for volatile organic carbon (VOC), low volatility organic compounds (LVOC), and elemental carbon (EC). The composition of tyre wear material was determined by analysing 18 samples of used tyre tread. The tread samples were washed with distilled water, dried at ambient temperature, and ground down. A chemical mass balance approach was employed to calculate the various traffic related source contributions using a simple box model, and emission factors were obtained using multiple regression analysis.

2.8.2 Methods for determining brake wear and particle emissions

As with tyres, brake wear rates can be estimated by periodic measurement of the friction surface depth or weight loss. Garg *et al.* (2000a) employed a brake dynamometer to generate brake wear particles and measure emission factors. The brake application was designed to simulate real world events by braking from 50 km/h to 0 km/h at a deceleration of 2.94 m/s². Each brake pad was preconditioned at 100°C for 200 stops, and then they were repeatedly applied (400 to 1000 stops per test) at surface temperatures of 100, 200, 300 and 400°C to simulate normal working temperatures. The brake temperature was controlled by air flow (0.85 to 5.7 m/s) and braking frequency. Seven brake pads were tested. These represented 88% of the pads used by General Motors in 1998 production. Hildemann *et al.* (1991) brushed brake dust samples from the inside of the rear drum brakes of a modern light-duty truck. The samples were then resuspended in the laboratory, and the fine particle component was obtained by filtration.

2.8.3 Methods for sampling road dust

Measurements of tyre dust in airborne particles and in road dust were made in Leeds by Pollard (1997). Road dust samples were swept from approximately 1m² of road, and on occasions when there had been at least 4 days without rain, sieved to remove coarse grit and then size-segregated to obtain the PM₁₀ fraction. Pyrolysis gas chromatography was used to resolve organic components of the samples.

As an alternative to sweeping, road dust can be sampled by vacuuming. Researchers in the US have used a dry method for sample collection. For example, Hildemann *et al.* (1991) and Rogge *et al.* (1993) reported experiments in which a vacuum sweeper was driven up and down several blocks of Pasadena-area streets to collect the road dust that had accumulated during a two-week dry period. The material was resuspended in a clean Teflon bag using purified laboratory air to maintain a slightly positive pressure in the bag. Particle-laden air was then withdrawn from the bag through cyclone separators (50% cut-off at 2µm aerodynamic particle diameter) to remove the coarse road particles. Quartz fibre filters and Teflon filters were used to collect the remaining fine particles. All quartz fibre filters were annealed at 750°C for two to four hours before use to ensure low contamination levels for organic substances. Miguel *et al.* (1999) also sampled from dry street surfaces using a commercially available wet/dry vacuum cleaner. During sample collection polyvinyl chloride gloves were used to handle the samples, and samples were returned to the laboratory in autoclaved polyethylene bags. The road dust samples were progressively sieved to yield different size fractions.

Researchers at the University of Aberdeen have developed a similar wet system (Orr and Deletic, 2000) using an industrial vacuum cleaner which is capable of removing sediment and surface water. With the Aberdeen system, a collection frame of a known size is placed on the ground where the sample is to be obtained. Portable horticultural spray equipment (usually used to deliver pesticides) with hand operated pressure control, is used to deliver deionised water to the sampling area. Attention is paid to crevices where particles may become trapped. The sides of the frame are also washed down to ensure that the whole sample is collected. The collection frame is designed to ensure that no water, and thus suspended particles, can escape. The sample is then vacuumed into a chamber unit consisting of moulded polypropylene.

2.8.4 Source apportionment methods: receptor modelling

The technique generally referred as ‘receptor modelling’, whereby particulate matter is allocated to a range of source categories, is based on the simple concept of mass conservation (Hopke 1985, 1991, 1997). If a number of sources (p) exist, and if there is no interaction between their aerosols to causes mass removal or formation, then the total airborne particulate mass measured at receptor (C), will be linear sum of the contributions of the individual sources (S_j):

$$C = \sum_{j=1}^p S_j \quad \text{Equation 2-1}$$

There are several reviews on receptor modelling which discuss in detail the theoretical basis, methodology, progress, and the uncertainties associated with these procedures (Gordan 1980a, 1980b and 1988; Hopke 1985, 1986 and 1997; Henry *et al.* 1984; Thurston and Lioy 1987; Currie 1992). At present, there are about twenty different procedures that are used for identifying and quantifying the sources contributing to the particulate mass or to its chemical constituents. Among these methods there are two generally recognised classes of source apportionment: (i) chemical mass balance (CMB) and (ii) multivariate statistical techniques. The former assigns atmospheric particles to different sources by assuming that each source emits a characteristic set of chemical species in a given relationship. It therefore requires knowledge of source composition, and assumes that the sources specified are responsible for the concentrations of the species measured at the receptor. Multivariate techniques, such as multi-linear regression, cluster analysis, discriminant analysis, and principal component analysis, can be used to identify common patterns in atmospheric data (QUARG, 1996). Table 2-8, taken from Hopke (1997), shows a summary of the available receptor modelling techniques. Table 2-9 shows the description of the some major applications of these techniques of apportionment.

Table 2-9 shows that most applications of particle source apportionment have involved the use of receptor modelling techniques to quantify the major sources of emissions in urban areas. Relatively few studies have used such methods to apportion sources of specifically traffic-related particle emissions. Rogge *et al.* (1993) have used chemical tracers coupled with CMB method to apportion sources of organic fine particles. The use of CMB techniques has also been reported by Schauer *et al.* (1996), who successfully identified a range of particle emission sources including road and tyre dust. The study relied on extensive source profile measurements. Recently, Zheng *et al.* (2002) have reported the use of CMB methods to apportion particle sources in the southern United States using organic tracers.

It has been reported that the various atmospheric processes which take place in an urban environment can seldom be identified with a single tracer. Multi-element tracers are often required to characterise the different sources of particles and their exchange between the different environmental 'compartments'. For example, in simple urban environments the association Pb-Cu-Zn-Ba can be used to evaluate the contribution of traffic more reliably than the concentration of Pb alone, and Zn-Cd reveals the influence of the corrosion of building materials. The 'natural' component of urban particulate material is especially well defined by the association of Y-Al-Ga-La-Th. However, in many instances the complexity of the situation is so great (*e.g.* in cities where there are strong and diverse industrial emission sources) that it is impossible to distinguish the influence of single sources, even with multi-element tracers (De Miguel *et al.*, 1999).

Table 2-8: Summary of available receptor models for source apportionment (from Hopke 1997).

Model	EPA model available	Requires source information	Quantitative apportionment	Source location information	Apportions secondary aerosol	Other advantages	Other disadvantages
Chemical mass balance (least squares)	Yes	Yes	Yes Propagation	No	No	Easy to use, includes error in source compositions, accepted by OAQPS	Can mis-specify sources, does not include variability in source compositions, sensitive to colinearity
Partial least squares	No	Yes	Yes	No	No	Identifies completeness of source profile set	Requires specialised software
Artificial neural networks (back propagation)	No	Yes	Yes	No	No	Least sensitive to colinearity	Requires specialised software, can be time consuming
Genetic algorithm	No	No	No	No	Yes	Uncertain	Requires specialised software, can be time consuming
Principal component analysis	No	No	No	No	No	Identification of source types, identification of unusual samples	Depends on correlation that can be driven by meteorology or co-location
Target transformation factor analysis	No	No	Yes	No	No	Does not centre, estimates uncertainties	Assumes that all sources have been identified
SAFER	No	No	Yes	No	No	Includes external constraints and other information	Assumes that all sources have been identified
Positive matrix factorisation	No	No	Yes	No	Sometimes	Treats missing and detection limit data well, estimates uncertainties	Assumes that all sources have been identified, for secondary apportionment requires correlation with other species (e.g. black carbon)
Artificial neural networks (Kohonen)	No	No	Can lead to one	Yes	Uncertain	Provides a map that can be related to geographical distribution of sources	Better with multiple source locations, needs at least 35 samples per site, time consuming
Empirical orthogonal function analysis	No	No	Sometimes	Yes	Yes	Can estimate source contributions	Requires sufficiently large spatial extent in sampling sites
Residence time analysis	No	No	No	Yes	Yes	Provides likely source areas	Needs sufficient numbers of samples
Area of influence analysis	No	No	No	Yes	Yes	Provides likely source areas	Needs sufficient numbers of samples
Quantitative trajectory balance analysis	No	No	Yes	Yes	Yes	Incorporates wet and dry deposition, combines measurements from multiple sites	Requires detailed information of precipitation along trajectory
Potential source contribution function (PSCF)	No	No	No	Yes	Yes	Provides likely source areas	Needs sufficient numbers of samples
PSCF with apportionment	No	Yes	Yes	Yes	Yes	Provides likely source areas	Needs sufficient numbers of samples, depends on quality of emissions inventory
Residence time weighted contribution	No	No	Possibly	Yes	Yes	Provides likely source areas and estimates of their relative contributions	Needs sufficient numbers of samples

Table 2-9: Some receptor model applications.

Reference	Description/Comments
Friedlander 1973	CMB (tracer element method) used to apportion TSP in Pasadena, USA
Gartrell and Friedlander. 1975	CMB (tracer element method) used to apportion TSP in five USA cities
Hopke <i>et al.</i> 1976	Common factor analysis (FA) and cluster analysis (CA) applied to apportion TSP
Kowalczyk <i>et al.</i> 1978	CMB (weighted least squares) applied to apportion TSP in Washington DC
Watson 1979	CMB (effective variance least squares) TSP and fine aerosol ($\leq 2.5\mu\text{m}$) were apportioned for samples collected in six USA cities
Dzubay 1980	CMB (weighted least squares) applied to apportion coarse and fine aerosol in St. Louis area, USA
Alpert <i>et al.</i> 1980	Target transformation factor analysis (TTFA) applied to apportion coarse and fine aerosol in St. Louis area, USA
Kowalczyk <i>et al.</i> 1982	CMB (weighted least squares) applied to apportion TSP at 10 sites in Washington DC
Espen <i>et al.</i> 1983	Principal component analysis (PCA) on elemental composition data of aerosol samples in six size fractions
Morandi <i>et al.</i> 1987	A modified factor analysis/multiple regression applied to apportion inhalable particulate matter (IPM, $\leq 15\mu\text{m}$), Pb and Fe at site in Newark, NJ.
Artaxo <i>et al.</i> 1987	CMB, PCA and multiple linear regression analysis (MLRA) applied to apportion coarse particles at six sites of Amazon Basin
Parekh <i>et al.</i> 1987	FA analysis on aerosol samples collected in Karachi, Pakistan
Negi <i>et al.</i> 1987	FA Source on aerosol samples collected in four cities of India
Pratsinis <i>et al.</i> 1988	PCA/MLRA used to apportion fine aerosol from Duarte near Los Angeles, USA
Dzubay <i>et al.</i> 1988	CMB, MLRA and wind trajectory analysis (WTA) used to apportion fine and coarse aerosol samples
Dzubay <i>et al.</i> 1989	CMB (effective variance least squares) used to apportion fine and coarse aerosol mass
Pio <i>et al.</i> 1989	PCA/MLRA applied to apportion aerosol at an industrial site of Estarreja, Portugal
Okamoto <i>et al.</i> 1990	FA/MLRA and CMB used to apportion aerosol samples collected in Tokyo, Japan
Artaxo <i>et al.</i> 1990	Absolute principle factor analysis applied to apportion coarse and fine aerosol at Antarctica basin
Kasahara <i>et al.</i> 1990	CMB (weighted least squares) applied to apportion aerosol in 9 Japanese cities
Morandi <i>et al.</i> 1991	Comparison of two source apportionment procedures a modified FA/MLRA and APCA/MLRA on IPM samples from Newark, NJ
Eltayeb <i>et al.</i> 1993	APCA on aerosol samples in Khartoum, Sudan
Andrade <i>et al.</i> 1993	APCA on coarse and fine aerosol samples in Sao Paulo, Brazil
Zelenka <i>et al.</i> 1994	TTFA is used to estimate source profiles using ambient elemental concentration data
Schauer <i>et al.</i> 1996	CMB used to apportion fine aerosol mass and organic species at four sites in Southern California, USA
Harrison <i>et al.</i> 1996	Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in Birmingham, UK using APCA/MLRA
Chan <i>et al.</i> 1999	CMB, TTFA, MLRA applied to apportion PM ₁₀ and PM _{2.5} at five sites in Brisbane, Australia
Polissar <i>et al.</i> 2001	Potential source contribution function (PSCF) analysis and WTA used to apportion PM _{2.5} in Underhill, VT (USA)
Poirot <i>et al.</i> 2001	Four source apportionment techniques compared for PM _{2.5} at Underhill, VT (USA)
Cantinho and Artaxo 2001	APFA applied to apportion winter and summer aerosol in Sao Paulo, Brazil

2.9 Summary of literature review

2.9.1 Tyre wear particles

Typical tyre wear rates of between 10 mg/tyre/km and 90 mg/tyre/km have been reported in the literature for passenger cars. Both fine and coarse particles are emitted to the atmosphere as a result of tyre wear, but not all of the worn tyre material is emitted as airborne PM, and some much coarser tyre shreds will also be removed. The distribution of the wear material between the different particle size modes appears to be rather variable. It has been shown that the mean particle diameter decreases with increasing speed, and this may be one of a number of factors contributing to the variability of the results. Also for high-wear locations such as corners, there is evidence to suggest that although the absolute level of tyre wear is high, the proportion (by mass) of finer particles is lower than at other locations. PM₁₀ appears to be released from tyres at a rate of between 4 and 6 mg/vkm for passenger cars. This suggests that generally between around 1% and 15% by mass of passenger car tyre wear material is emitted as PM₁₀, but much higher proportions have been reported in some studies. It appears that tyre wear generally accounts for less than 10% of the PM₁₀ measured in roadside air, and less than 5% of road dust mass.

Chemical species used to trace tyre wear debris in the urban atmosphere have included the following:

- benzothiazole
- 2-(4-morpholinyl) benzothiazole
- n-cyclohexyl-2-benzothiazolamine
- styrene butadiene rubber
- zinc
- extractable organic zinc

Benzothiazole compounds are not easy to analyse, but they are thought to be very specific tracers for tyre wear, and the contribution of tyre wear to airborne PM can be estimated directly if the mean content of the tracer in tyres is known. Because benzothiazole is of a semi-volatile nature, it must be trapped as a thiazole-type compound within a tyre wear particle to actually serve as a particle-phase tracer. Although zinc has been used as a tyre wear particle tracer, it does have many other sources. With the exception of motor oil, tyres are the only significant contributor to organic zinc (present in zinc accelerator complexes) in airborne particles. It has also been noted that, for the *n*-alkanes $\geq C_{35}$, there are few urban emission sources other than tyre wear. The *n*-alkanes $\geq C_{35}$ have therefore been considered to be a useful marker for tyre wear. Two specific compounds have been shown to be present in road dust samples containing tyre wear particles: di-pentene (limonene, C₁₀H₁₆) and styrene (C₈H₈).

2.9.2 Brake wear particles

The wear rate of brake linings for passenger cars has been estimated to be around 10-20 mg/vkm, and up to 3 or 4 times higher for heavy-duty vehicles. It appears that a much larger proportion of brake wear material than tyre wear material is emitted as airborne PM, but exact emission factors for different size fractions are difficult to determine because significant amounts of wear material appear to be retained on the brake, steering and suspension systems. However, PM₁₀ emission factors of between around 1-9 mg/vkm have been reported for light-duty vehicles, and around 20-40 mg/vkm for heavy-duty vehicles.

Although reasonably detailed information on the composition of brake linings and brake wear particles has been reported, no strong evidence was found in the literature of reliable tracer species for brake wear particles.

2.9.3 Clutch wear particles

It is possible that the lack of information on clutch wear and emission factors will have ramifications for the source apportionment of particulate matter via emission inventories and receptor modelling, and represents an area of uncertainty. However, the enclosed nature of the clutch mechanism probably means that much of the wear material is retained inside the housing. In any case, clutch wear as a source of particles warrants further investigation. As with brake wear particles, there appears to be no information in the literature which would help to define clutch wear emissions.

2.9.4 Road surface wear particles

Asphalt wear has been estimated at 3.8 mg/vkm. One study showed that airborne particles ranged in size between 0.35 μ m and 2.8 μ m. In areas with extensive use of studded tyres the wear of the road surface is considerably greater during winter, and wear rates of between 11 and 24 g/vkm have been reported.

It has been suggested that some of the largest molecules present in the atmosphere - maltenes and asphaltenes - could be used as tracers for road surface wear. Unsuccessful attempts have been made to derive useable fingerprint profiles for bitumen using the PAH components or the polar, aromatic and aliphatic fractions of bitumen as tracers for road wear.

2.9.5 Resuspension of road dust

At present, atmospheric emission inventories tend not to include the resuspension of road dust as a particle source due to the absence of reliable emission factors and the possibility of double counting of sources. However, recent studies in the United States have suggested that the resuspension of paved road dust contributes significantly to atmospheric PM₁₀ and PM_{2.5} concentrations. It has been estimated that resuspension of road dust accounts for a net release of 0.04 g/vkm PM₁₀ in the UK.

3 Methodology

The objectives of this research project were to characterise particles from road vehicle non-exhaust sources, and to determine appropriate emission factors. The research methodology incorporated several different stages, and a variety of sampling approaches, laboratory techniques and statistical procedures were employed. This Chapter provides an initial overview of the methodology, followed by details of these separate stages.

3.1 Overview

The main stages of the experimental work are listed below, and the interactions between these stages are shown in Figure 3-1.

Stage 1: Gravimetric measurement of wear rates for tyres and brakes on in-service vehicles.

The literature review revealed that there is a degree of uncertainty relating to the wear rates of tyres and brakes for in-service road vehicles. This part of the work was designed to provide further information on the total amount of material being released into the environment as a result of tyre and brake wear, and to link material loss rates to vehicle type and operation.

In order to identify sources of airborne particles, to apportion particles to these sources, and to estimate appropriate emission factors, a receptor modelling approach was selected, and a main measurement campaign was designed accordingly. A preliminary exploratory phase of work was undertaken in order to refine the receptor modelling methodology, and stages 2-5 reflected the requirements and design of the receptor modelling, both in terms of the need for appropriate source information and the selection of a suitable measurement method.

Stage 2: Sampling of source materials

Samples of various non-exhaust source materials - tyre tread, brake dust and road dust – were collected for characterisation.

Stage 3: Chemical and physical characterisation of source materials

The chemical characterisation of source samples was conducted in order to identify potential tracer elements and compounds which could be linked directly to specific non-exhaust sources. The work focused mainly on elemental metals, but there was also a limited qualitative analysis of the organic compounds present in samples of brake dust and deposited road dust. Particle morphology was also investigated using a scanning electron microscope (SEM).

Stage 4: Sampling of PM in ambient air

Airborne particles were sampled at paired background and roadside sites. This part of the work served to optimise the sampling method and location for the main measurement campaign. An assessment was made of a range of filter substrates and the suitability of conventional sampling equipment.

Stage 5: Chemical and physical characterisation PM in ambient air

The concentrations of a number of potential elemental metal tracers for non-exhaust emission sources were determined for the airborne PM samples collected during stage 4. This enabled the mass of sampled particles necessary for reliable source apportionment in the main campaign to be determined. Particle morphology was again investigated using a SEM.

Stage 6: Sampling of PM in a tunnel environment.

These preliminary measurements were followed by the main measurement campaign, which involved the sampling and characterisation of PM₁₀ at two locations in the Hatfield road tunnel using high-volume samplers, and the collection of dust deposited in trays.

Stage 7: Chemical characterisation of PM in a tunnel environment.

This stage of the work involved the detailed characterisation of the samples collected during stage 5.

Stage 8: Statistical analysis and receptor modelling.

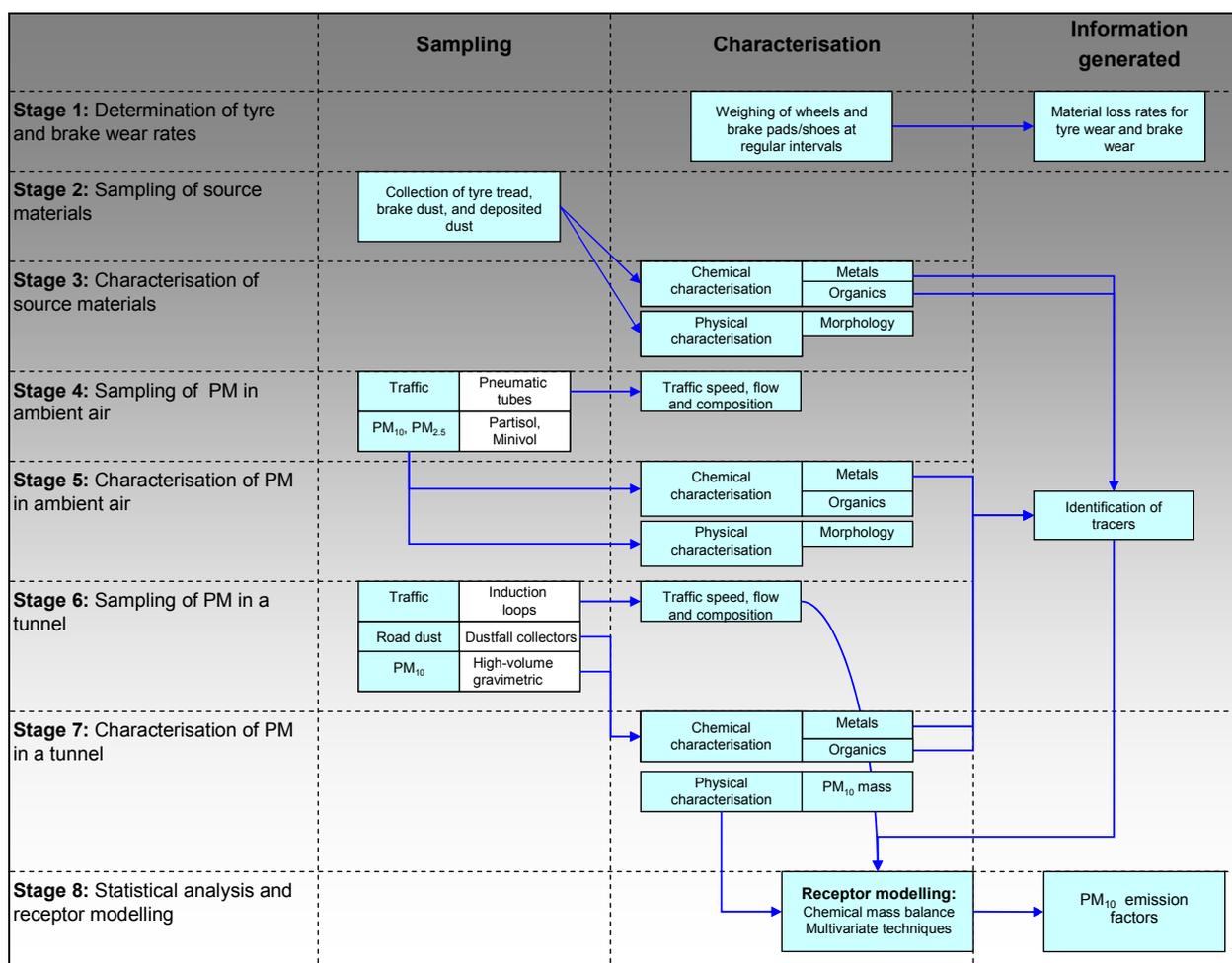


Figure 3-1: Flow diagram describing the experimental methodology.

3.2 Stage 1: Gravimetric measurement of tyre and brake wear (material loss)

3.2.1 Selection of test vehicles

Five vehicles (labelled A-E) were selected for the tests. The selection of vehicles was based primarily on driving conditions, as defined by the main type of road used by the owner and annual distance driven. All owners were members of TRL staff. The details of the vehicles used in the tests are provided in Table 3-1. The types of tyre and brake pads/shoes fitted to these vehicles are presented in Table 3-2 and Table 3-3.

Table 3-1: Test vehicles.

Vehicle ref. letter	Manufacturer	Model	Year of first registration	Engine size (cc)	Fuel type	Transmission	Initial odometer reading (km)	Annual km ¹	Road type ^{1,2}
A	Audi	A3	1998	1600	UP ³	M5 ⁴ , FWD ⁵	74,080	48,000	Motorway
B	Ford	Mondeo	1994	1800	UP	M5, FWD	205,328	32,000	Motorway
C	Peugeot	205	1990	1100	UP	M5, FWD	128,532	16,000	Urban
D	Ford	Sierra	1990	1800	UP	M5, RWD	194,390	24,000	Urban
E	Vauxhall	Cavalier	1992	1600	UP	M5, FWD	148,427	30,000	Rural

1 Reported by owner

2 Predominant type of road driven

3 UP = Unleaded petrol

4 M5 = Manual 5-speed

5 F/RWD = Front/rear-wheel drive

Table 3-2: Tyres fitted to test vehicles.

Vehicle ref. letter	Near-side front (NSF)	Off-side front (OSF)	Near-side rear (NSR)	Off-side rear (OSR)
A	Continental 195/65 R15 ¹	Continental 195/65 R15 ¹	Firestone 195/65 R15	Firestone 195/65 R15 ²
B	BF Goodrich 185/65 R14	BF Goodrich 185/65 R14	Monza HR7 185/65 R14	Continental Supercontact 185/65 R14
C	Phaser R23 145/80 R13	Phaser R23 145/80 R13	Michelin Classic 145/80 R13	Michelin MX 145/80 R13 ³
D	Roadchamp Power Racer 65H 185/65 R14			
E	Pirelli P300 175/70R	Pirelli P300 175/70R	Pirelli P300 175/70R	Pirelli P300 175/70R

1 Replaced 29/7/01 by Continental 195/65 R15

2 Replaced 14/6/01 by Firestone Firehawk 680 195 R15

3 Replaced 30/4/01 by Firestone 195/65 R15

Table 3-3: Brake pads/shoes fitted to test vehicles.

Vehicle	Front brake Type	Front brake system	Rear brake Type	Rear brake system
A	ATE H7/9	Disc (pads)	Lucas	Disc
B	- ¹	Disc (pads)	Lucas	Drum (shoes)
C	Mintex	Disc (pads)	Girling	Drum (shoes)
D	Ferrodo Target	Disc (pads)	Girling	Drum (shoes)
E	EBC	Disc (pads)	-	Drum (shoes)

1 '-' indicates that the brake type could not be identified.

3.2.2 Test schedule

Based on the typical component weights, measurement errors, wear rates, and annual driving distance, it was estimated that for reliable wear measurements, minimum periods of 57 days for tyres and 33 days for brakes would be required between successive weighings. Given these considerations, an interval of 2 months between tests represented the best compromise between maximising the amount of data collected during the study and maximising the reliability of the measurements. The dates of the tests, and the vehicles tested, are presented in Table 3-4.

Table 3-4: Test schedule.

Test reference number	Test dates	Vehicles tested				
		A	B	C	D	E
1	Feb 7-8, 2001	✓	✓	✓	✓	
2	Apr 3-4, 2001	✓	✓	✓	✓	
3	Jun 13-14, 2001	✓	✓	✓	✓	✓
4	Sep 13-14, 2001	✓	✓	✓		✓
5	Jan 14-15, 2002	✓	✓	✓		✓

3.2.3 Weighing of tyre and brake components

During each test the vehicles were taken to TRL, where the front brake pads, rear brake pads or shoes, and wheels were removed by a qualified engineer. The tyres were not removed from the wheels due to concerns that tyre material may have been detached or damaged by this process. Prior to weighing, the components were cleaned in a vehicle washing bay using water and liquid detergent. Washing continued until there were no further signs of dirt being released, and any small stones visible in the tyre tread were removed. The components were then transferred to a climatic controlled weighing room where they were dried thoroughly at room temperature. The air temperature of the weighing room was controlled ($20\pm 2^{\circ}\text{C}$), but there was no control of relative humidity. The components were weighed using two different balances; the first (Sartorius 3826, resolution 1g) was used to weigh the wheels/tyres, and the second (Sartorius LC620S, resolution 0.01g) was used to weigh the brake pads and shoes. The balances were calibrated at six-month intervals. Each component was weighed repeatedly until a stable weight was observed.

3.2.4 Driver logbook

In order to assess the impacts of driving conditions on component wear rates, the owner of each vehicle was requested to maintain a driving log. The information noted in this log included the time and odometer reading at the start and end of each trip undertaken, the types of road encountered during each trip, and any other remarks (*e.g.* the fitting of new components). This information was used to estimate the mean trip speed during the period between tests, and to confirm the main types of road used.

3.3 Stages 2-5: Preliminary sampling and characterisation

3.3.1 Sampling of source materials

Samples of tyre tread, brake lining material and brake dust were collected in order to identify potential elemental metal tracers. The tyre samples were taken from a single used passenger car tyre (make: India GT 65, size: 175/65 R14 82H). The tyre surface was grated using a hand-held grater, and the grated rubber was then passed through a cascade of mechanical sieves, with the last sieve having a $60\ \mu\text{m}$ pore size. This procedure required some care, as the charged tyre particles tended to adhere to the walls of the sieves. The brake dust samples were taken from the brake mechanism of one of the in-service vehicles used in the tyre and brake wear tests described in the previous section. Deposited dust samples were also collected from the road surface of a car park.

3.3.2 Selection of filter media for sampling airborne PM

Air filtration is the most widely used technique to collect ambient particle samples because of its efficiency, ease of handling, and economy (Snedden, 1983). However it is important that any filter used should satisfy the following conditions:

- (i) Mechanical stability
- (ii) Chemical stability
- (iii) High particle collection efficiency
- (iv) Low flow resistance
- (v) Good retention without clogging
- (vi) Low and consistent blank values and artefacts

Generally, the filter media available for the collection of ambient particles fall into three broad classes: depth or fibrous filters, membrane filters, and coated fibre filters. Depth filters are made from either glass or quartz fibres, and membrane filters are made from organic material such as Teflon (PTFE), polycarbonates and cellulose acetates. With coated fibre filters, the fibres are normally covered with Teflon. The details of the properties of various filter types can be found in Lodge (1989) and Pall (2000). The characteristics of these filter types in terms of the criteria specified above are given in Table 3-5.

Table 3-5: Summary of filter characteristics (from Pall, 2000).

Criteria	Filter type		
	Fibre	Membrane	Membrane coated fibre
Chemical stability	✓	✓	✓
High particle collection efficiency	✓	✓	✓
Low flow resistance	✓	X	✓
Good retention without clogging	✓	X ¹	✓
Mechanical stability	X	✓	✓

¹ The problem of pore clogging and re-entrainment of particles is more severe with polycarbonate membrane filters compared with Teflon filters.

Before the start of the sampling campaign, three filters were assessed in order to find the most suitable media for metal analysis. As fibrous filters are not mechanically strong and fibres are lost during handling, only filters from the remaining two categories were chosen for analysis of metal composition. The following filter types were analysed:

- (i) Pallflex EMFAB 47mm PTFE
- (ii) Pallflex Fiberfilm T60A20 47mm, glass-fibre coated PTFE
- (iii) Zylon PTFE 47mm, membrane filters

3.3.3 Sampling of airborne PM

DEFRA (2002) divides air pollution monitoring sites into eight categories: kerbside, roadside, urban centre, urban background, urban industrial, suburban, rural and remote. This categorisation is based on the source strength at the location where the monitoring station is sited, and the distance of the site from the sources of pollution. The selection of the sampling site is determined by the objectives of the study, but there are some general rules that need to be fulfilled when selecting a site (EPA, 1975):

- (i) It should be easily accessible, secure for personnel, and not prone to vandalism or tampering.
- (ii) It should not be located near obstructions, such as trees or tall buildings, which inhibit or enhance the airflow.
- (iii) The sampling intake should be high enough to avoid re-entrainment of large particles near the ground.
- (iv) Inlet should be at a height and location that reflects potential exposure.

Particles in ambient air were collected during two two-week sampling campaigns. The aim of the sampling at this stage was to assess the suitability of conventional sampling equipment and methods in the context of the aims of the project, and to identify possible roadside and background sites. The first campaign was conducted at roadside and background sites within the University of Hertfordshire (UH) campus. PM_{2.5} and PM₁₀ were collected at each site using two 'MiniVol' samplers manufactured by Airmetrics. In the MiniVol, air is drawn at 5 litres/minute through a particle size separator (impactor), and then through a 47mm filter. At the roadside site, PM₁₀ was also collected using a Partisol sampler (Rupprecht & Patashnick). The Partisol had a sample flow rate of 1 m³/h (16.7 l/min), with particles again being drawn through a 47 mm filter.

The second campaign was conducted at roadside and background sites operated by Westminster City Council in Central London. MiniVols were deployed at the London sites. The measurements at the University sites were also repeated, again using MiniVol samplers. The nominal sampling period for each filter was 24 hours. A summary of the sampling campaigns undertaken is given in Table 3-6. Figure 3-2 shows the location of the sites used in this study, and Figure 3-3 shows the roadside site at UH.

Table 3-6: Summary of preliminary sampling campaigns.

Campaign	Dates	Site & Type	Particulate sampling equipment
1	August 2001	UH background	MiniVol (PM ₁₀ , PM _{2.5})
		UH roadside	MiniVol (PM ₁₀ , PM _{2.5}) Partisol (PM ₁₀)
2	October 2001	UH background	MiniVol (PM ₁₀ , PM _{2.5}),
		UH roadside	MiniVol (PM ₁₀ , PM _{2.5})
		London background (Hyde Park)	MiniVol (PM ₁₀ , PM _{2.5})
		London roadside (Oxford Street)	MiniVol (PM ₁₀ , PM _{2.5})

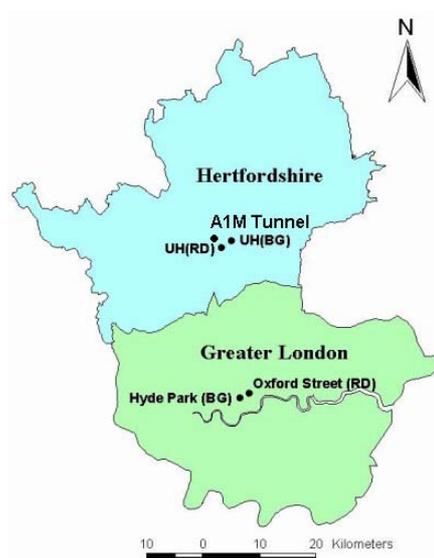


Figure 3-2: Location of the sampling sites



Figure 3-3: Photograph of UH roadside site

3.3.4 Chemical characterisation

3.3.4.1 Analysis of metal concentrations in tyre tread and brake lining

The metal content of the tyre tread, brake lining and brake dust samples was determined using inductively coupled plasma atomic emission spectroscopy (ICP/AES) and inductively coupled plasma mass spectrometry (ICP/MS). Standard reference materials (SRM) were also analysed to give an indication of typical extraction efficiencies. All tyre material, brake material, ambient PM and SRM samples were dissolved, along with blank samples, using an acid microwave digestion method (Tremper, 2001). The samples were digested using a mixture of hydrochloric acid and nitric acid (10:90 for tyre tread and brake lining, 75:25 for brake dust), and then heated for 15 minutes at 150 psi. The recovered samples were analysed along with mixed standard solutions for the metals of interest. The ICP/AES and ICP/MS techniques which were used are amongst the most sensitive for the identification of trace metals.

3.3.4.2 Analysis of concentrations of organic species in brake dust and road dust

The brake dust and road dust samples were analysed for organic content using capillary gas chromatography-mass spectrometry (GC/MS) at CEH. The species evaluated were benzothiazole, selected PAHs, and other selected compounds. The analytical procedures followed are described below.

Sample extraction

Prior to extraction, each sampled filter was spiked with a standard of known concentration containing 7 isotopically labelled PAHs (naphthalene D8, acenaphthalene D8, phenanthrene D10, fluoranthene D10, pyrene D10, benzo[a]pyrene D12 and benzo[ghi]perylene D12) and 2-methylbenzothiazole which has been reported as an internal standard for benzothiazole (Reddy and Quinn, 1997). These deuterated internal standards were selected as the quantification references for the target particle-phase compounds in this study, based on the factors of vapour pressure, polarity and chemical characteristics, including reactivity with derivatisation reagents, mobility through GC columns and fragmentation pattern. The filter was then packed into a 100ml pre-cleaned metal extraction cell and the remaining space was filled with pre-baked sand to seal the cell. The cell was extracted under 1500 psi nitrogen at 80°C by DCM (HPLC grade) using an automatic accelerated solvent extractor (ASE300, Dionex). About 100 ml of extract was collected from the extractor. One third of this was kept as back-up for further use. The volume of extract for this analysis was reduced to about 0.5 ml by a turbo evaporator at 45°C under a gentle nitrogen stream. Around 1g of activated alumina was added and the sample was evaporated until dry.

Sample clean-up

About 1 ml of pentane was added to the sample in dried alumina, and the sample was transferred into a pre-packed chromatograph column which was prepared with 6cm silica and 3cm alumina (slurry packed in pentane) in a 1cm-diameter column, and pre-washed with 20ml pentane. The first 20ml pentane elute was discharged, then the sample was eluted with 25ml dichloromethane and collected in a measuring cylinder ready for GC/MS analysis. The cleaned-up extract was separated into 3 fractions:

- (i) Aliphatics
- (ii) Two- and three-ring aromatics
- (iii) Aromatics with greater than three rings

Fraction (i) was discarded, and fractions (ii) and (iii) were analysed by GC/MS.

GC/MS Analysis

The samples were analysed with a set of 7 deuterated quantification standards, and run together with a quantification standard for PAHs that was also spiked with the deuterated PAH standard mixture. The extracted samples were analyzed by GC/MS at CEH on a Hewlett-Packard GC/MSD equipped with a 30m-long, 0.25 mm internal diameter capillary column. The GC/MS was operated at an interface temperature of 300°C, with a scan range 50-500 amu, and with an electron ionization mode of 70eV. Helium was used as the carrier gas, with a flow rate of 1.0 ml/min. The temperature conditions were as follows: an isothermal hold at 65°C for 10 minutes, followed by a temperature ramp of 10°C per minute to 300°C, and finally an isothermal hold at 300°C for 22 minutes. Each target compound in the study was quantified by reference to a deuterated internal standard having chemical characteristics similar to the target compound. The relative response factor was calculated from the GC/MS analysis of the quantification standards mixture.

Compounds were identified by comparison of their spectra with those in the NIST MS database. Only results where the fit between the unknown spectra and the library spectra were greater than 80 (maximum fit is 100) were reported. It was not possible to obtain reliable spectra for a large number of unresolved compounds.

Quality control

For particulate samples, the recoveries of the internal standard PAHs were usually better than 50%. Samples were corrected for blanks only if the blank was higher than 5% of the target compound concentration; the levels of PAHs in the samples in this study had to be at least twice the blank value to be included in the dataset, but these were generally much higher. The recoveries of blanks spiked with deuterated PAHs were from 40% to 110%. The uncertainty for the quantification of organic compounds in ambient particulate samples was on average approximately $\pm 15\%$ (one standard deviation) according to the precisions for duplicate analyses of spiked standards, expressed as relative standard deviation.

It is worth noting here that these particulate-bound target compounds were solvent extractable. However, these only account for a small part of $PM_{2.5}$ mass concentrations. One study (Schauer *et al.*, 1996) indicated that 84% of the organic compound mass in fine particles was either unextractable or would not elute from the GC column used, while Zheng *et al.* (2002) reported that the unextractable and non-elutable organic compounds account for, on average, 88% of the total organic mass concentration. However, the organic compounds measured are sufficient to act as tracers for the road transport sources of PM.

3.3.4.3 Analysis of metal concentrations in filter media

Three filters of each type (see section 3.3.2) were analysed. The filter papers were extracted using the acid microwave digestion method described earlier. The extracted samples were then analysed with ICP/AES along with a multi-element standard, as before.

3.3.4.4 Analysis of metal concentrations in airborne PM

The concentrations of various elemental metals in the ambient PM samples was determined using ICP/AES, as described above.

3.3.5 Physical characterisation

An SEM was used to examine the size, structure and morphology of the source material and airborne PM samples. Some qualitative information on chemical composition was also available. The technique provided only elemental information, based on ratios of elemental X-ray intensities. Absolute concentrations could not be obtained.

3.4 Stage 6: Sampling of particulate matter in the Hatfield tunnel

Non-exhaust sources only account for a fraction of airborne PM, and the uncertainties associated with source identification due to meteorological effects and unidentified sources may be around 20% or more (Gehrig *et al.*, 2001). The experimental errors are partly due to the very low concentrations at which tracers for non-exhaust sources tend to be present in the environment. In order to obtain enough particle material for reliable chemical analysis, long sampling durations would normally be required. However, in order to determine emission factors receptor models require a high temporal resolution to distinguish the influence of traffic variation during the sampling period.

These factors had to be considered in the design of a suitable sampling methodology for the main campaign. In order to achieve an optimum balance between particle mass and temporal resolution, high volume sampling techniques were employed in a tunnel environment. Due to the limited dispersion and dilution of air pollution in the tunnel environment, higher concentrations than in normal ambient air tend to be observed. In addition, the influences from meteorology are reduced (John *et al.*, 1999). Consequently, a number of studies have been conducted in which tunnel measurements have been used to derive the emission factors for particulate and gaseous pollutants (*e.g.* Gillies *et al.*, 2001; Staehelin *et al.*, 1997; John *et al.*, 1999; Weingartner *et al.*, 1996; Pierson *et al.*, 1996a, 1996b, Sjödin A and Cooper C, 2001). In this study, PM emission factors were derived from measurements conducted in the Hatfield Tunnel.

3.4.1 Description of sampling site

The Hatfield Tunnel is located on the A1(M) in Hertfordshire, 0.8 km west of Hatfield town centre. The 1150 m-long Tunnel is a rectangular cut-and-cover structure on level terrain, and is equipped with two tubes: the 'A' tube which carries traffic in a south-north direction, and the 'B' tube which carries traffic in a north-south direction. Each tube has an internal width of approximately 18 metres, and a nominal cross-sectional area of 108 m². The tubes accommodate the full (uni-directional) motorway formation of three traffic lanes plus a hard shoulder. A continuous curtain wall separates the two tubes along a central line, and there is no man-access to the tubes other than through the portals, although there are emergency exit doors between the two tubes. Anti-recirculation walls are installed at the tunnel portals. The tunnel is longitudinally ventilated by the traffic, supplemented when required by 52 jet fans in each tube. There are no air extraction or inlet points other than the tunnel portals. The speed limit in the tunnel is 70 mph (113 km/h), and the total weekday traffic flow through the tunnel is approximately 100,000 vehicles. Distinct peaks in weekday traffic flow occur at 06:00–10:00 and 16:00–19:00, and traffic flows during the night-time period are relatively low. The tunnel is closed for maintenance on two nights of each month. Figure 3-4 shows the south and north portals of the tunnel.



Figure 3-4: South and north portals of the Hatfield Tunnel.

3.4.2 Sampling of airborne particulate matter and deposited dust

The sampling campaign was carried out between during October and November of 2002. PM₁₀ and deposited dust samples were collected at two locations in the 'B' tube of the tunnel. The first location was at a distance of 25 m from the tunnel entrance, hereafter referred as tunnel entrance, and the second location was at a distance of 580 m from the tunnel entrance, hereafter referred as tunnel exit. Figures 3-5 and 3-6 show the sampling locations, and Figure 3-7 is a schematic representation of the tunnel and the sampling locations.

Particles were collected on 203 mm x 254 mm (8"x10") QM-AUltra quartz filters using a high-volume sampler (Staplex) with a PM₁₀ size-selective inlet. Quartz fibre filters were used as these are known to have low background concentrations of metals and also lend themselves for organic analysis. The flow rate was set at 1.13 m³/min, and the sampling time was nominally 12 hours. Prior to sampling, the quartz filters were pre-baked in an oven at a temperature of 450°C for 5-7 hours, and then placed in a conditioned room (constant temperature and humidity) for 24 hours. They were weighed using a calibrated microbalance. At least two laboratory blank filters were weighed at the beginning and end of each weighing session. The filters were weighed again after exposure, wrapped in aluminium foil and stored in sealed glass jar bottles in a refrigerator (-20°C) for subsequent chemical analysis. Two laboratory blank filters were weighed for every 10 samples, and the analytical precisions was determined from the blank filter weights. The mean standard deviation of laboratory blanks was 80-100 µg, accounting for 0.3% of the average sampled particle weight.

Deposited dust samples were collected by placing a pre-baked quartz filter (203mm x 254mm) in a foil-lined, 45mm-deep plastic tray at both the tunnel entrance and exit, in each case at a distance of 5m from the airborne PM sampling equipment. Two filters were exposed at the tunnel entrance, and two at the tunnel exit.



Figure 3-5: Tunnel entrance site.



Figure 3-6: Tunnel exit site.

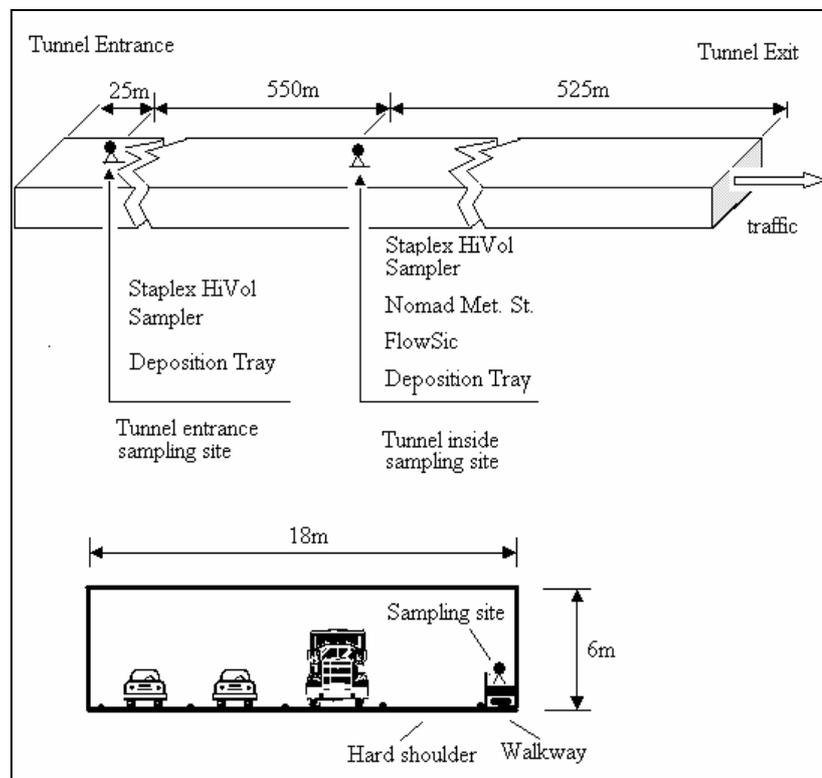


Figure 3-7: Diagram illustrating the two sampling locations and the dimensions of Hatfield Tunnel.

3.4.3 Measurement of traffic and meteorological parameters

Induction loops are permanently installed in the road surface of the Hatfield Tunnel for the purpose of characterising the traffic. The information from the loops was recorded and interpreted using a 8-loop classifier/data logger (Marksman 661) and software supplied by Golden River. As well as noting and time stamping the presence of each vehicle, and thus allowing for the determination of traffic flows over any time period (30 minute periods were used in this work), the classifier provided information on vehicle speed (km/h), vehicle headway (seconds), and vehicle length (cm). Vehicles were then grouped, according the EUR6 class scheme, into following six categories based on vehicle length, vehicle chassis height, and a signature profile, whereby:

CS1 = Motorcycle	CS4 = Rigid, heavy van or mini-bus
CS2 = Car or light van	CS5 = Artic
CS3 = Car + trailer	CS6 = Bus or coach

A limitation with this scheme is that it merges all cars and vans in categories CS2 and CS3. National data on fleet composition for motorways were used to apportion the traffic counts into the following categories:

- Motorcycle
- Car petrol
- Car diesel
- LGV petrol
- LGV diesel
- HGV rigid
- HGV artic
- Bus

The air flow velocity in the tunnel was required for the emission factor calculation (Equation 3-1), and was recorded continuously using a Flowsic 200, which measures the mean air flow velocity across the entire width of a tunnel. The device can measure flow velocities of up to 20 m/s with a typical accuracy of ± 0.1 m/s. Sender and receiver units are mounted on both sides of a tunnel at a fixed angle of inclination to the air flow. The units contain piezoelectric ultrasonic transducers which operate alternately as transmitter and receiver. The transit time of the ultrasonic pulses vary according to the flow velocity.

A Nomad portable weather station manufactured by Casella UK (incorporating cup anemometers and a wind vane) was also used to measure a number of parameters. The Nomad measured air flow velocity with an accuracy of ± 0.3 m/s below 3 m/s, and $\pm 1\%$ above 3 m/s. The Nomad simultaneously recorded temperature ($\pm 0.3^\circ\text{C}$), humidity ($\pm 3\%$) and pressure (± 1 mbar). The Nomad was co-located with Flowsic 200 and PM₁₀ sampler on the emergency walkway at the exit of the tunnel, the sensor head of the Nomad was about 1m away from the wall and 2.5m above the road. The Flowsic sensor unit, although designed for permanent tunnel installation, was temporarily installed on a wooden post fixed to the walkway hand rail. The sensor unit was about 3m above the road level. Measurements were recorded at 5-minute intervals using the Nomad and at 10-second intervals using the Flowsic.

3.5 Stage 7: Chemical characterisation of particulate matter in the Hatfield Tunnel

The concentrations of metals in the PM₁₀ filters and deposited dust samples were determined using ICP/AES and ICP/MS using the procedures described in Section 3.3.4.1. Organic species were quantified using GC/MS, using the procedures described in Section 3.3.4.2. Procedural blank quartz fibre filters were also analysed – three for metals and six for organic compounds.

3.6 Stage 8: Derivation of the emission factors for non-exhaust sources (statistical analysis and receptor modelling)

Emission factors were derived using the following procedures:

- (i) Principal component analysis
- (ii) Multiple regression analysis
- (iii) Derivation of PM₁₀ emission factors
- (iv) Derivation of emission factors for non-exhaust sources

The ‘multiple regression on absolute principal component scores’ (APC/MLR) technique was used to identify sources and quantify their contributions. This method of source apportionment was developed and applied by Thurston (1983). All the statistical analyses were performed using appropriate software (SPSS 2002). Principal component analysis was applied to identify the source categories, and the application of the Equamax rotation of the initial component matrix resulted in the determination of components that could be physically interpreted. The basis of the identification of these components as relating to given sources is discussed in Chapter 4. The component scores were saved and converted to absolute principal component scores (APCs), as suggested by Thurston (1983). The PM₁₀ mass was then regressed as a dependent variable against the APCs. The coefficients in the multiple linear regression equation, and the APCs for each source category, were used to obtain its contribution to the total PM₁₀ concentration for each sample.

The PM₁₀ emission factor (mass emitted per vehicle-km) for the entire fleet passing the tunnel during a given time interval was obtained from the following equation (Weingartner *et al.*, 1997):

$$EF_{PM_{10}} = \frac{(C_{exit} - C_{entrance}) \cdot v_{air} \cdot t \cdot A}{L \cdot N} \quad (\text{Equation 3-1})$$

where

- $EF_{PM_{10}}$ = EF of PM₁₀ (g/vkm)
- C_{exit} = PM₁₀ concentration at tunnel exit (g/m³)
- $C_{entrance}$ = PM₁₀ concentration at tunnel entrance (g/m³)
- v_{air} = velocity of the air (m/s)
- t = time duration of sampling (s)
- A = tunnel cross section (m²)
- L = tunnel length (km)
- N = number of vehicles which passed the tunnel in the time interval t .

This equation has been employed extensively to derive emission factors from the measurements at two separate locations in tunnel studies (Gillies *et al.*, 2001; Staehelin *et al.*, 1997; John *et al.*, 1999). The emission factors for non-exhaust sources were then obtained by using the PM₁₀ emission factors obtained from equation 3-1, and the fractional contributions of the sources from APC/MLR.

4 Results and discussion

4.1 Stage 1: Tyre and brake wear tests

4.1.1 Driving information

The distances completed by each vehicle between successive tests, and in total, are presented in Table 4-1. The average daily distance covered by the vehicles ranged from 30 km in the case of vehicle D to 121 km in the case of vehicle B.

Table 4-1: Distances driven between tests by vehicle.

Period	Distance driven between tests (km)				
	Vehicle A	Vehicle B	Vehicle C	Vehicle D	Vehicle E
Test 1 - Test 2	7337	6677	1714	1757	No test
Test 2 - Test 3	11617	9640	1405	1908	No test
Test 3 - Test 4	7430	11062	3501	No test	5854
Test 4 - Test 5	9619	12993	4718	No test	9105
Total	36002	40371	11337	3665	14959

The estimated average trip speeds and predominant road types for the equivalent periods are shown in Table 4-2. As not all trips were noted by the vehicle owners, these results are indicative rather than definitive. The average trip speed of each vehicle was relatively stable during the study, and reflected the type(s) of road used by the owner. For example, the highest mean trip speeds were observed for vehicles A and B, with the owners of these vehicles reporting that they had covered most of the distance between tests on motorways. Although the owners of vehicles C and D originally stated that they used mainly 'urban' roads, this was not reflected in their respective log books. For example, the owner of vehicle C almost invariably reported using 'suburban' roads, and the owner of vehicle D reported using mainly rural roads and motorways.

Table 4-2: Average trip speed for the periods between the tests.

Period	Average trip speed by vehicle (km/h)					Predominant road type by distance driven ¹				
	A	B	C	D	E	Vehicle A	Vehicle B	Vehicle C	Vehicle D	Vehicle E
Test 1 - Test 2	90.3	65.4	44.5	59.6	N/T ²	Motorway ³	Motorway	Suburban	10% Motorway 90% Rural	N/T
Test 2 - Test 3	90.6	71.9	42.9	63.6	N/T	Motorway	Motorway	Suburban	35% Motorway 65% Rural	N/T
Test 3 - Test 4	93.9	74.4	48.8	N/T	61.3	Motorway	Motorway	Suburban	N/T	Rural
Test 4 - Test 5	92.7	70.2	50.4	N/T	65.8	Motorway	75% Motorway 25% Rural	Suburban	N/T	15% Motorway 85% Rural

¹ This does not exclude trips in other areas.

² 'N/T' indicates that the vehicle was not tested.

³ Where only one road type is stated, the road type was used for more than 95% of the distance driven.

4.1.2 Tyre wear

The combined wheel and tyre weights recorded during the tests, the weight loss per kilometre, and the total weight loss of per vkm are summarised in Table 4-3. Each tyre/wheel weight value in Table 4-3 represents the mean of two measurements. It was assumed that the weight of the wheel hubs remained constant during the tests, and any weight loss was due solely to the removal of tyre rubber during driving. The sources of error in the technique used may include the possible incomplete removal of dirt during washing, corrosion or damage to the wheel body, dirt becoming bound to the wheel, and debris becoming embedded in the tyre rubber.

Table 4-3: Wheel and tyre weights.

Vehicle	Tyre	Average weight of wheel and tyre (g)					Weight loss (mg/km)					Mean total per vehicle
		Test 1	Test 2	Test 3	Test 4	Test 5	Test 1-Test 2	Test 2-Test 3	Test 3-Test 4	Test 4-Test 5	Mean by tyre	
A	NSR	17458	17388	17242	17202	17112	9.5	12.5	5.5	9.4	9.2 +/- 2.8 ⁴	56.4 +/- 7.8
	OSR	17392	17327	18185 ¹	18122	18046	8.7	- ³	8.4	7.9	8.3 +/- 0.5	
	NSF	17742	17595	17357	18264 ¹	18093	20.1	20.4	-	17.8	19.4 +/- 1.6	
	OSF	17674	17524	17277	18354 ¹	18195	20.4	21.3	-	16.6	19.4 +/- 2.8	
B	NSR	16583	16540	16477	16445	16389	6.4	6.6	2.8	4.3	5.0 +/- 1.8	66.8 +/- 15.0
	OSR	16103	16030	15918	15861	15734	11.0	11.6	5.2	9.8	9.4 +/- 2.9	
	NSF	14693	14500	14228	13991	13570	28.8	28.2	21.4	32.4	27.7 +/- 4.5	
	OSF	14646	14441	14208	14024	13673	30.7	24.2	16.6	27.0	24.6 +/- 5.9	
C	NSR	10716	10708	10690	10666	10645	4.4	12.8	6.9	4.4	7.1 +/- 3.9	85.9 +/- 35.1
	OSR	10436	11645 ¹	11626	11605	11611	-	13.5	6.0	-1.2	6.1 +/- 8.3	
	NSF	11916	11862	11816	11723	11565	31.5	32.4	26.6	33.2	30.9 +/- 2.9	
	OSF	12155	12102	12055	11949	11605	31.2	33.1	30.3	72.2	41.7 +/- 20.0	
D	NSR	14818	14724	14631	N/T ²	N/T	53.2	48.7	N/T	N/T	51.0 +/- 4.4	193.3 +/- 12.5
	OSR	15014	14946	14858	N/T	N/T	39.0	45.9	N/T	N/T	42.4 +/- 6.7	
	NSF	14977	14874	14764	N/T	N/T	58.6	57.9	N/T	N/T	58.3 +/- 0.7	
	OSF	15005	14933	14853	N/T	N/T	41.3	41.9	N/T	N/T	41.6 +/- 0.6	
E	NSR	N/T	N/T	14754	14690	14589	N/T	N/T	11.0	11.0	11.0	85.0 +/- 21.6
	OSR	N/T	N/T	14693	14635	14537	N/T	N/T	10.0	10.7	10.4 +/- 0.7	
	NSF	N/T	N/T	14802	14578	14421	N/T	N/T	38.4	17.2	27.8 +/- 20.7	
	OSF	N/T	N/T	14904	14695	14369	N/T	N/T	35.7	35.9	35.8 +/- 0.2	

1 New tyre fitted. 3

2 'N/T' indicates that the vehicle was not tested.

'-' indicates that results are not available because of a change of tyre.

4 95% confidence intervals.

For the four front-wheel-drive vehicles (A, B, C and E), the average wear rate of the front tyres was consistently greater than that of the rear tyres, with front tyre wear accounting for between 69% and 85% of total tyre material lost per vkm. The average wear rate of a front tyre on these vehicles was 28 mg/km, whereas the average rate of wear of a rear tyre was 8 mg/km. This would be expected, given the higher frictional forces associated with both steering the vehicle and providing traction. The results in Table 4-3 also indicate that the lowest tyre wear rates were observed for the two vehicles driven predominantly on motorways. These vehicles, A and B, had wear rates of around 56 mg/vkm and 67 mg/vkm respectively. Vehicles C and E had very similar wear rates (around 85 mg/vkm), although these vehicles tended to be driven on different roads and at different speeds. For the one rear-wheel-drive car included in the test programme, the average wear rates of the front and rear tyres were similar, and at 50 mg/km and 47 mg/km respectively the highest mean values observed. However, during test 3 it was found that the wheels of this vehicle were mis-aligned, and that this had resulted an uneven wear pattern on the front tyres. This may also have contributed to the higher wear rates observed, although it is not known precisely over which period the mis-alignment occurred. However, given that only one vehicle was tested it is not possible to confirm whether this reflects a more general tendency from greater tyre wear in rear-wheel drive vehicles. For the sample of five vehicles tested, the average tyre wear rate for a vehicle was 97 mg/km, though given the problems associated with the rear-wheel-drive vehicle, and the market dominance of front-wheel-drive cars, the average wear rate of 74 mg/km for the other four vehicles is probably more representative of the fleet. This value is towards the lower end of the range of the wear rates reported in the literature (Table 2-1 - note that these are per tyre).

There appear to be a number of unexpected results in Table 4-3. For example, the wear rates of the two front tyres of vehicle A appear to be lower between tests 4 and 5 than during the previous periods. This may have been a result of the fitting of new front tyres to this vehicle in July of 2001. In the case of vehicle B, the wear rates of the four tyres between tests 3 and 4 are consistently lower than those observed during the other periods. There is little evidence to indicate why this was the case, although the mean trip speed of this vehicle was highest between tests 3 and 4. The wear rates of the tyres of vehicle C between tests 4 and 5 exhibited an unusual pattern. Firstly, the OSR tyre was actually found to have increased in weight, whilst the wear rate of the OSF tyre, at more than 70 mg/km, was easily the highest observed during the study. Nothing out of the ordinary was reported by the owner during this period. Figure 4-1 shows that there was a weak negative correlation between tyre wear and average trip speed between tests for the four front-wheel drive cars. The linear regression fit to the data was characterised by an r^2 value of 0.42 (when the measurements on the rear-wheel drive car were also included, the r^2 value dropped to 0.11).

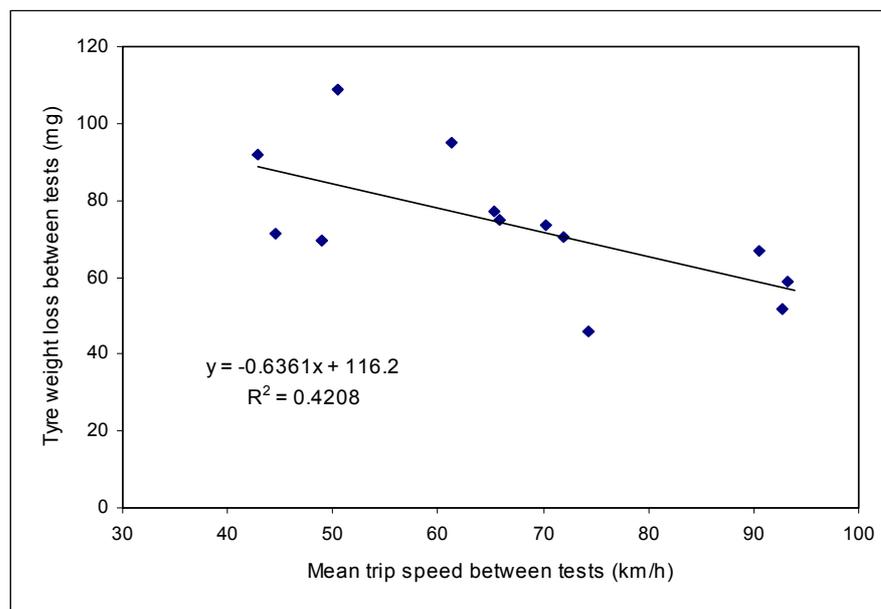


Figure 4-1: Relationship between tyre weight loss and mean trip speed between tests - front-wheel drive vehicles only.

4.1.3 Brake wear

The brake weights recorded during the tests, the amount of brake material lost per kilometre, and the total loss of brake material per vkm are summarised in Table 4-4. Again, each weight value in Table 4-4 represents the mean of two measurements. It was found that the wear of the front brakes accounted for between 77% (vehicle A – fitted with disc brakes on both front and rear wheels) and virtually 100% (vehicle E) of total brake material lost per vkm. The wear rates of individual brake pads and shoes, and the total brake wear rates per vkm, were very variable. The amount of brake material lost per vkm ranged from 1.8 mg (vehicle A) to 20.5 mg (vehicle E), the average being 8.8 mg. This is at the lower end of the range reported in the literature for passenger cars (Section 2.3.2).

Figure 4-2 shows that there was also weak negative relationship between total brake wear per vehicle and average trip speed between tests. The linear regression fit to the data was characterised by an r^2 value of 0.35. However, three of the wear values in Figure 4-2 are particularly high, and with the three high values removed, the r^2 value increased to 0.87. These three values may be outliers, but they may be indicative of events or procedures which result in high wear rates. Two of the high wear rates relate to the same vehicle, and during the period relating to one of the points, the driver of this vehicle reported having to perform an emergency stop from a high speed. In addition, new brake pads were fitted to these vehicles at the start of the corresponding periods, and this may have been a factor contributing to the higher wear rates observed. A systematic investigation of potential high-wear-rate events is required in future work.

Table 4-4: Brake weights.

Vehicle	Brake pad/shoe	Average weight of brake pad/shoe (g) ¹					Weight loss (mg/km)					
		Test 1	Test 2	Test 3	Test 4	Test 5	Test 1- Test 2	Test 2- Test 3	Test 3 - Test 4	Test 4- Test 5	Mean by pad/shoe	Mean total per vehicle
A	NSR pad, inner	209.6	209.2	204.5	203.6	203.0	0.06	0.40	0.12	0.07	0.16+/-0.16 ⁴	1.81+/- 0.84
	NSR pad, outer	207.1	206.5	207.7	207.1	206.4	0.08	-0.10	0.08	0.08	0.03+/-0.09	
	OSR pad, inner	208.8	208.2	205.0	204.4	203.6	0.09	0.27	0.09	0.08	0.13+/-0.09	
	OSR pad, outer	207.5	206.6	206.4	205.6	204.8	0.11	0.02	0.12	0.08	0.08+/-0.04	
	NSF pad, inner	327.2	323.1	317.6	316.3	313.4	0.56	0.48	0.17	0.31	0.38+/-0.17	
	NSF pad, outer	317.2	314.4	308.2	304.5	301.8	0.38	0.53	0.49	0.28	0.42+/-0.11	
	OSF pad, inner	340.8	338.1	333.8	332.2	329.6	0.36	0.38	0.21	0.27	0.30+/-0.08	
	OSF pad, outer	336.1	333.9	329.0	327.6	324.7	0.29	0.42	0.19	0.30	0.30+/-0.09	
B	NSR shoe, leading	395.6	394.7	393.9	391.1	389.2	0.14	0.08	0.25	0.15	0.16+/-0.07	4.71+/- 1.40
	NSR shoe, trailing	307.2	304.7	302.9	302.6	298.4	0.38	0.18	0.03	0.32	0.23+/-0.15	
	OSR shoe, leading	394.3	392.7	392.0	393.3	392.3	0.24	0.07	-0.11	0.07	0.07+/-0.14	
	OSR shoe, trailing	311.3	307.0	305.2	301.1	298.4	0.64	0.19	0.37	0.21	0.35+/-0.21	
	NSF pad, inner	393.9	388.7	379.1	367.5	345.1	0.78	1.00	1.05	1.73	1.14+/-0.40	
	NSF pad, outer	357.8	350.2	340.2	326.9	306.1	1.13	1.04	1.21	1.60	1.24+/-0.24	
	OSF pad, inner	393.4	388.3	381.6	371.5	359.9	0.76	0.70	0.91	0.90	0.82+/-0.10	
	OSF pad, outer	356.5	351.6	345.2	338.5	328.0	0.74	0.66	0.61	0.80	0.70+/-0.09	
C	NSR shoe, leading	267.6	267.7	267.4	267.4	267.3	-0.07	0.19	0.03	0.01	0.04+/-0.11	10.92+/- 7.06
	NSR shoe, trailing	183.2	183.0	182.6	182.1	181.7	0.12	0.29	0.14	0.10	0.16+/-0.09	
	OSR shoe, leading	266.1	266.1	265.7	265.4	264.7	0.00	0.34	0.09	0.13	0.14+/-0.14	
	OSR shoe, trailing	181.2	180.9	180.4	179.9	178.8	0.15	0.37	0.17	0.22	0.23+/-0.10	
	NSF pad, inner	287.1	279.9	280.5	272.4	267.9	4.20	-0.41	2.31	0.93	1.76+/-1.93	
	NSF pad, outer	281.9	276.5	272.7	267.4	260.8	3.17	2.71	1.54	1.39	2.20+/-0.86	
	OSF pad, inner	289.1	278.2	277.6	265.8	257.6	6.39	0.41	3.36	1.74	2.97+/-2.53	
	OSF pad, outer	284.7	275.8	270.7	260.9	251.1	5.17	3.61	2.82	2.07	3.42+/-1.31	
D	NSR shoe, leading	630.1	629.9	629.5	N/T ²	N/T	0.14	0.18	N/T	N/T	0.16+/-0.03	6.21+/- 0.61
	NSR shoe, trailing	509.4	509.1	508.7	N/T	N/T	0.16	0.24	N/T	N/T	0.20+/-0.08	
	OSR shoe, leading	618.3	618.1	617.7	N/T	N/T	0.14	0.19	N/T	N/T	0.16+/-0.05	
	OSR shoe, trailing	507.7	507.4	507.0	N/T	N/T	0.17	0.20	N/T	N/T	0.18+/-0.04	
	NSF pad, inner	265.0	262.5	260.2	N/T	N/T	1.45	1.21	N/T	N/T	1.33+/-0.23	
	NSF pad, outer	258.7	256.0	253.0	N/T	N/T	1.56	1.54	N/T	N/T	1.55+/-0.02	
	OSF pad, inner	268.2	266.1	263.86	N/T	N/T	1.23	1.15	N/T	N/T	1.19+/-0.08	
	OSF pad, outer	256.0	253.5	250.8	N/T	N/T	1.47	1.40	N/T	N/T	1.44+/-0.07	
E	NSR shoe, leading	N/T	N/T	510.7	510.9	510.6	N/T	N/T	-0.03	0.03	0.00+/-0.06	20.47+/- 10.75
	NSR shoe, trailing	N/T	N/T	414.9	415.7	417.0	N/T	N/T	-0.15	-0.15	-0.15	
	OSR shoe, leading	N/T	N/T	499.7	499.8	499.6	N/T	N/T	-0.01	0.02	0.00+/-0.04	
	OSR shoe, trailing	N/T	N/T	402.1	402.7	403.4	N/T	N/T	-0.10	-0.08	-0.09+/-0.02	
	NSF pad, inner	N/T	N/T	228.1	222.9/ 268.9 ³	223.4	N/T	N/T	0.88	5.00	2.94+/-4.03	
	NSF pad, outer	N/T	N/T	225.1	188.6/ 273.1	224.1	N/T	N/T	6.24	5.39	5.81+/-0.83	
	OSF pad, inner	N/T	N/T	249.2	193.9/ 272.4	233.1	N/T	N/T	9.45	4.32	6.88+/-5.03	
	OSF pad, outer	N/T	N/T	232.7	200.8/ 273.7	231.1	N/T	N/T	5.45	4.68	5.06+/-0.75	

- 1 Rounded to one decimal place.
- 2 'N/T' indicates that the vehicle was not tested.
- 3 Both old and new component weights displayed.
- 4 95% confidence intervals.

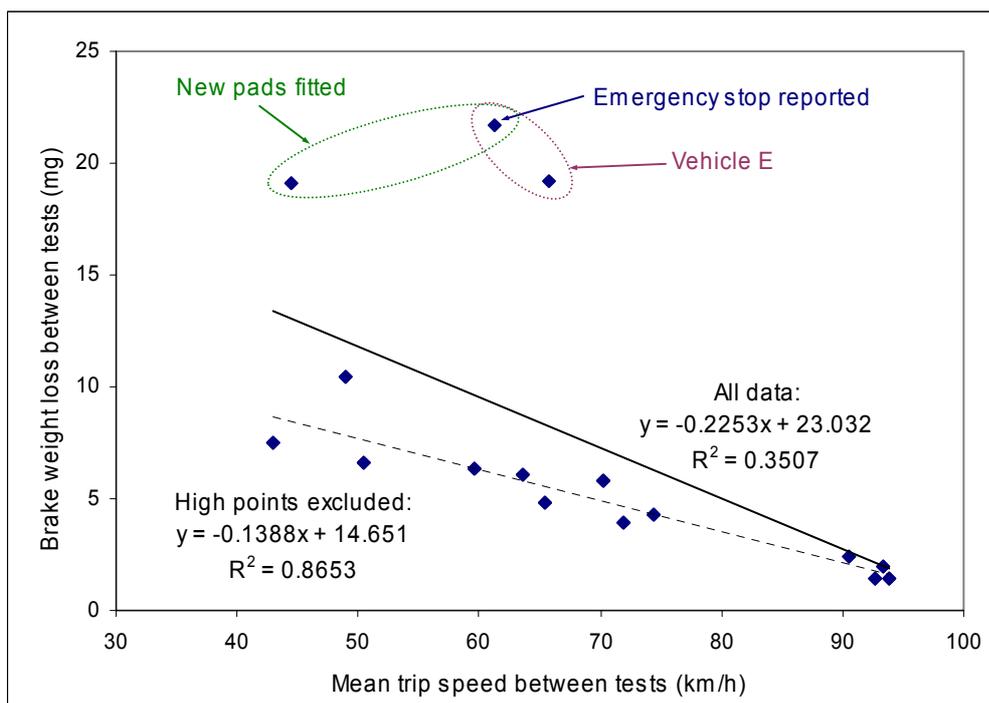


Figure 4-2. Relationship between brake weight loss and mean trip speed between tests – all vehicles.

4.2 Stages 2-5: Preliminary sampling and characterisation

4.2.1 Metal content of tyre and brake material

The average metal concentration for the tyre tread material, brake lining material and brake dust is shown in Figure 4-3. For tyre tread, the metal concentrations observed in this initial exploratory analysis agreed reasonably well with the ranges reported in the literature (given in Table 2-2). In particular, there was found to be a relatively high abundance of Zn. However, the potential use of zinc as a tyre wear tracer is confounded by the existence of many natural (*e.g.* soil) and anthropogenic (*e.g.* incineration and metallurgical processes) sources. The metal concentrations in the brake lining material and brake dust were generally of the same order of magnitude, though concentrations tended to be higher in the brake dust samples. It is possible that this was a consequence of incomplete digestion of the brake lining, but it may also be affected by the vaporisation of organic material during brake operation, and the brake dust would tend to contain material from sources other than the brake linings. The concentrations of some metals (notably Ba, Cu, Pb and Sb) were considerably lower than those found in the literature (Tables 2-3 and 2-4). For other metals, including Cr, Ni and Sr, there was a better agreement with the values in the literature.

Relative to their concentrations in the tyre tread samples, metals having substantially higher concentrations in the brake lining and brake dust samples included Ba, Cr, Sb, Sr and Zr. Again, it may be possible to use these metals as tracers for brake wear particles in the environment, but as with zinc some of these metals do have other sources, and hence the use of metal concentrations alone will not allow for a definitive identification a particular source.

De Miguel *et al.* (1999) suggested that more useful parameters as a source markers may be the ratios of metal concentrations, as these are more likely to be identifiable with a particular sources or source categories. Table 4-5 presents the ratios of the various metals that were analysed in the three types of material. These values have been included here for reference, and have not been analysed in depth given the limited number of tyre and brake samples and the variability of brake lining composition.

Furthermore, comparison with other studies (e.g. Legret and Pagotto 1999) shows that the ratios of metals can be very different, and hence, at present, they are probably not reliable for identifying non-exhaust sources. For example, a Zn/Cu ratio from the three tyre samples was determined to be 231, whereas the ratio quoted by Legret and Pagotto (1999) is 5700. Hence, it was not possible to determine typical metal concentration ratios in the wear particles, and the potential for using ratios of metals for identifying sources such as tyre and brake requires further investigation.

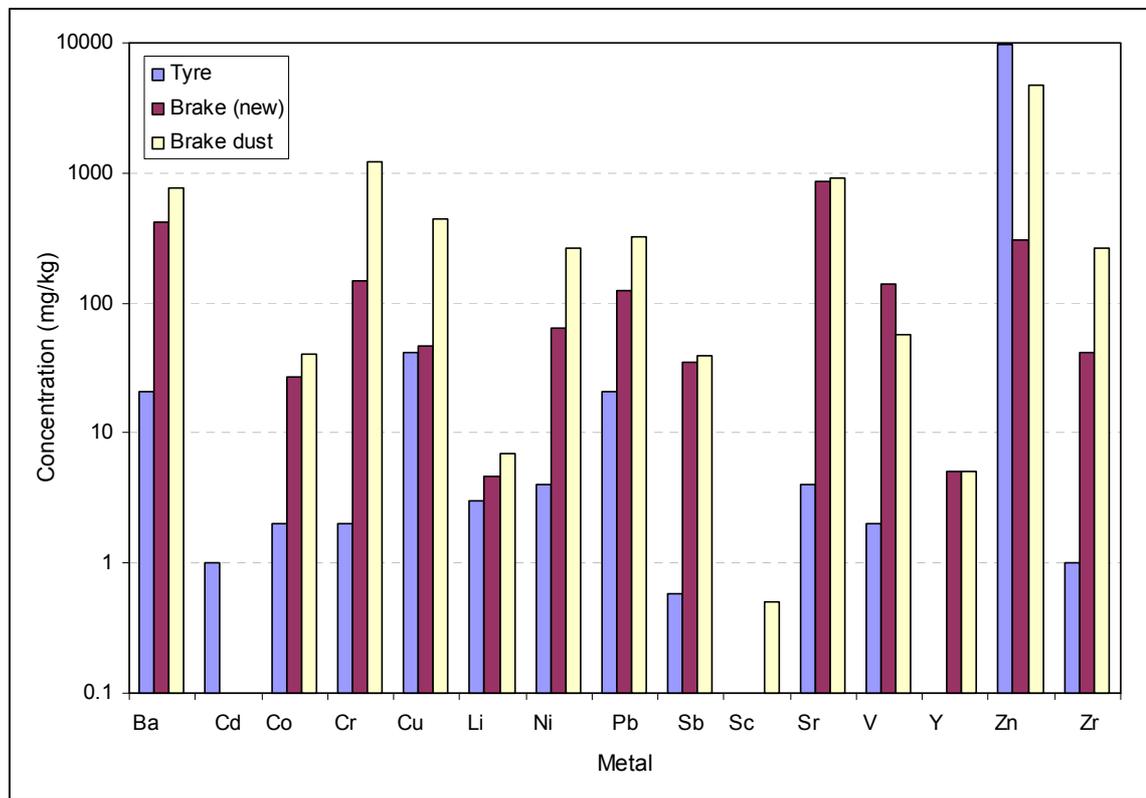


Figure 4-3: Elemental metal concentrations in tyre material, brake material, and brake dust.

Table 4-5: Ratios of various metals in the analysed tyre tread, brake lining and brake dust samples (column headers = numerator, row header = denominator).

(a) Tyre tread

	Ba	Cd	Co	Cr	Cu	Li	Ni	Pb	Sb	Sc	Sr	V	Y	Zn	Zr
Ba	1	0.05	0.1	0.1	2.0	0.1	0.2	1.0	0.03	-	0.2	0.1	-	470	0.05
Cd	20.7	1	2.0	2.0	42.0	3.0	4.0	20.6	0.6	-	4.0	2.0	-	9714	1.0
Co	10.3	0.5	1	1.0	21.0	1.5	2.0	10.3	0.3	-	2.0	1.0	-	4857	0.5
Cr	10.3	0.5	1.0	1	21.0	1.5	2.0	10.3	0.3	-	2.0	1.0	-	4857	0.5
Cu	0.5	0.02	0.0	0.0	1	0.1	0.1	0.5	0.01	-	0.1	0.05	-	231	0.02
Li	6.9	0.3	0.7	0.7	14.0	1	1.3	6.9	0.2	-	1.3	0.7	-	3238	0.3
Ni	5.2	0.3	0.5	0.5	10.5	0.8	1	5.2	0.1	-	1.0	0.5	-	2429	0.3
Pb	1.0	0.05	0.1	0.1	2.0	0.1	0.2	1	0.03	-	0.2	0.1	-	471	0.05
Sb	35.5	1.7	3.4	3.4	72.1	5.2	6.9	35.4	1	-	6.9	3.4	-	16683	1.7
Sc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sr	5.2	0.3	0.5	0.5	10.5	0.8	1.0	5.2	0.1	-	1	0.5	-	2429	0.3
V	10.3	0.5	1.0	1.0	21.0	1.5	2.0	10.3	0.3	-	2.0	1	-	4857	0.5
Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	<0.01	<0.01	-	1	<0.01
Zr	20.7	1.0	2.0	2.0	42.0	3.0	4.0	20.6	0.6	-	4.0	2.0	-	9714	1

(b) Brake lining

	Ba	Cd	Co	Cr	Cu	Li	Ni	Pb	Sb	Sc	Sr	V	Y	Zn	Zr
Ba	1	-	0.1	0.4	0.1	0.01	0.2	0.3	0.1	-	2.1	0.3	0.01	0.7	0.1
Cd	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Co	15.1	-	1	5.4	1.7	0.2	2.3	4.6	1.3	-	31.4	5.1	0.2	11.2	1.5
Cr	2.8	-	0.2	1	0.3	0.03	0.4	0.8	0.2	-	5.8	0.9	0.03	2.1	0.3
Cu	8.9	-	0.6	3.2	1	0.1	1.4	2.7	0.7	-	18.5	3.0	0.1	6.6	0.9
Li	88.6	-	5.9	31.6	9.9	1	13.6	26.8	7.4	-	184	29.6	1.1	65.4	8.8
Ni	6.5	-	0.4	2.3	0.7	0.1	1	2.0	0.5	-	13.5	2.2	0.1	4.8	0.6
Pb	3.3	-	0.2	1.2	0.4	0.04	0.5	1	0.3	-	6.9	1.1	0.04	2.4	0.3
Sb	11.9	-	0.8	4.3	1.3	0.1	1.8	3.6	1	-	24.7	4.0	0.1	8.8	1.2
Sc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sr	0.5	-	0.03	0.2	0.1	0.01	0.1	0.1	0.04	-	1	0.2	0.01	0.4	0.05
V	3.0	-	0.2	1.1	0.3	0.03	0.5	0.9	0.3	-	6.2	1	0.04	2.2	0.3
Y	82.7	-	5.5	29.5	9.3	0.9	12.7	25.0	6.9	-	171	27.7	1	61.0	8.2
Zn	1.4	-	0.1	0.5	0.2	0.0	0.2	0.4	0.1	-	2.8	0.5	0.02	1	0.1
Zr	10.1	-	0.7	3.6	1.1	0.1	1.6	3.0	0.8	-	20.9	3.4	0.1	7.4	1

(c) Brake dust

	Ba	Cd	Co	Cr	Cu	Li	Ni	Pb	Sb	Sc	Sr	V	Y	Zn	Zr
Ba	1	-	0.1	1.6	0.6	0.01	0.3	0.4	0.1	<0.01	1.2	0.1	0.01	6.2	0.3
Cd	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Co	19.0	-	1	30.7	11.1	0.2	6.6	8.1	1.0	0.01	22.5	1.4	0.1	117	6.6
Cr	0.6	-	0.03	1	0.4	0.01	0.2	0.3	0.03	<0.01	0.7	0.05	<0.01	3.8	0.2
Cu	1.7	-	0.1	2.8	1	0.02	0.6	0.7	0.1	<0.01	2.0	0.1	0.01	10.5	0.6
Li	109	-	5.7	176	63.6	1	37.6	46.5	5.7	0.07	129	8.2	0.7	671	37.7
Ni	2.9	-	0.2	4.7	1.7	0.03	1	1.2	0.2	<0.01	3.4	0.2	0.02	17.9	1.0
Pb	2.3	-	0.1	3.8	1.4	0.02	0.8	1	0.1	<0.01	2.8	0.2	0.02	14.4	0.8
Sb	19.2	-	1.0	31.0	11.2	0.2	6.6	8.2	1	0.01	22.7	1.4	0.1	118	6.7
Sc	1521	-	80.0	2459	891	14.0	526	651	79.3	1	1800	115	10.0	9390	528
Sr	0.8	-	0.04	1.4	0.5	0.01	0.3	0.4	0.04	<0.01	1	0.1	0.01	5.2	0.3
V	13.2	-	0.7	21.4	7.7	0.1	4.6	5.7	0.7	0.01	15.7	1	0.1	81.7	4.6
Y	152	-	8.0	246	89.1	1.4	52.6	65.1	7.9	0.1	180	11.5	1	939	52.8
Zn	0.2	-	0.01	0.3	0.1	<0.01	0.1	0.1	0.01	<0.01	0.2	0.01	<0.01	1	0.1
Zr	2.9	-	0.2	4.7	1.7	0.03	1.0	1.2	0.2	<0.01	3.4	0.2	0.02	17.8	1

4.2.2 Organic content of brake dust and road dust

Table 4.6 lists a number compounds identified in the brake dust and road dust samples. The analytical method used only provided a qualitative indication of the likely abundance of a particular compound in the source samples. The PAHs having the highest relative abundance in both types of sample were fluoranthene and pyrene. These compounds were also detected in abundance in tyre wear particles in a study conducted by Rogge *et al.* (1993). There is also evidence that pyrene and fluoranthene are present in automotive petrol (Miki and Sugimoto, 1998), and could thus be emitted to the environment through the car exhaust system. In a study conducted by VROM (1997) phenanthrene (0.97 mg/kg), fluoranthene (0.69 mg/kg), chrysene (1.7 mg/kg), benzo[a]anthracene (1.5 mg/kg) and benzo[a]pyrene (0.74 mg/kg) were identified in brake pad material. It is interesting to note that benzothiazole compounds, which have been considered as suitable tracers for tyre wear particles in the environment, were observed in the brake lining particles.

Table 4-6: Organic compounds identified in and road dust samples.

Brake lining dust	Road dust
PAHs from 2 to 6 rings	PAHs from 2 to 7 rings
Ethyl- and methyl- substituted PAHs from 2 to 4 rings	Ethyl and methyl substituted PAHs from 2 to 4 rings
Benzothiazole	Possible Nitro-PAHs
2-methyl-benzothiazole	2-(methylthio)-benzothiazole
3-phenyl-pyridine,	Dibenzothiophene
2-(methylthio)-benzothiazole	4-methyl-dibenzothiophene
N-ethyl, 2-benzothiazolamine	2-phenyl-benzothiazole
4-azafluorenone	4,9-dimethyl-naphtho[2,3-b]thiophene
Dibenzothiophene	Benzo[b]naphtho[2,3-d]thiophene
	Dibenzofuran

4.2.3 Metal content of filter media

Figure 4-4 shows the relative quantities of various metals analysed on the three types of filter. The results shown are the average of three filter papers from each category. The graph clearly illustrates the high metal concentrations in the EMFAB and T60_A Fiberfilm filters compared with the Zylon PTFE membrane filters. For example, the EMFAB filters contained around 100 times more zinc than the Fiberfilm filters, and 1000 times more zinc than the Zylon filters. Titanium also exhibited a similar trend. The EMFAB filters contained approximately 150 times more titanium than the Fiberfilm filters, whereas the levels in the Zylon PTFE filters were negligible. Another problem associated with the EMFAB and Fiberfilm filters was that the metal concentrations varied substantially from filter to filter.

However it was also noted that the Zylon filters resulted in a greater drop in air flow towards the end of a sampling period. Therefore, during the sampling of airborne PM other PTFE filters from same manufacturer, (TF 1000 with one micron pore size) were used, and this resolved the problem of drop in flow. These were also made of PTFE material, though the PTFE layer is thinner and has a polypropylene support. These filters were not analysed chemically at this stage, but were analysed along with each batch of airborne PM samples as procedural blanks.

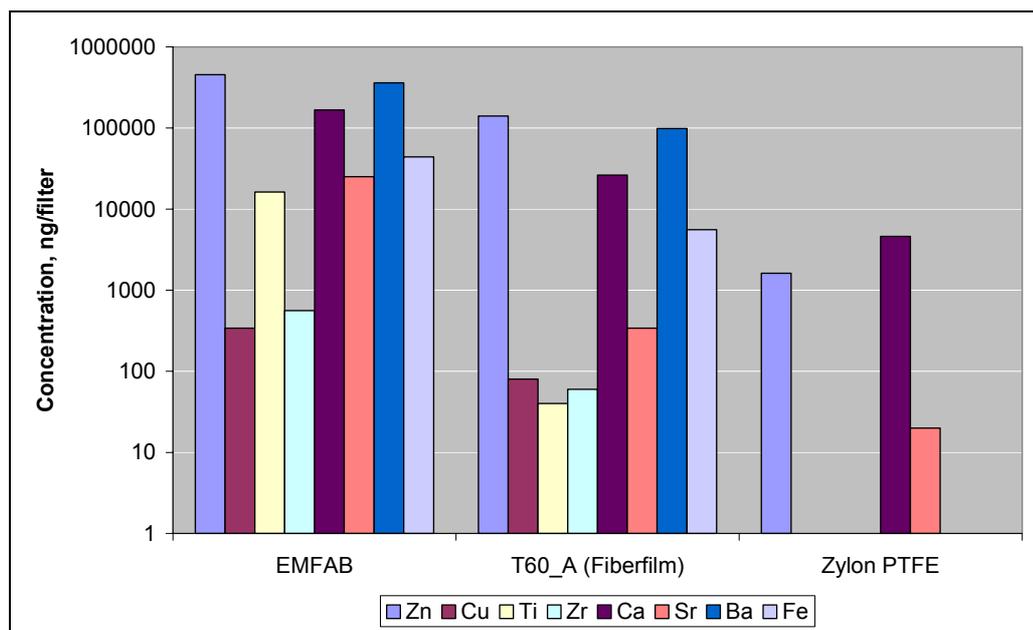


Figure 4-4: Concentration of various metals (ng/filter) in different filter types.

4.2.4 Airborne PM mass concentration

Table 4-7 shows the mass concentrations of PM₁₀ and PM_{2.5} recorded during the two preliminary campaigns at the UH and London sites. During the first campaign the PM₁₀ concentrations at the two UH sites were, rather unexpectedly, very similar. The similarity of the results may have been linked to the influence of construction work activity in the vicinity of the background site. In addition, the overall traffic flows during the sampling period were particularly low. During the second campaign, measurements were conducted at a roadside site in London where the traffic flows were substantially higher. The PM₁₀ and PM_{2.5} concentrations measured at the UH roadside site were higher than the background site by 23% and 40% respectively. The differences between the roadside and background concentrations at the London sites were much more pronounced, with the PM₁₀ concentration at the roadside being a factor of 2.8 higher than at the background site, and the PM_{2.5} concentration being almost six times higher. The observed PM₁₀ mass concentrations at the Oxford Street roadside was twice as high as the concentration at the UH roadside site, with the concentrations at both background sites being comparable.

Surprisingly, the PM_{2.5} concentration recorded at the London background site was half the value at the UH background site. The reason may be related to the size fractions of ambient particles at the two sites in that the UH samples may have consisted of relatively larger particles compared to Hyde Park site where particles will be dominated by the ultrafine fraction resulting from the large number of diesel vehicles.

Table 4-7: Particle mass concentrations at UH and London sites during two measurement campaigns.

Campaign	Site	Method	PM ₁₀ (µg/m ³)	PM _{2.5} (µg/m ³)
1	UH background	MiniVol	17.3	10.8
	UH roadside	MiniVol	17.4	3.4
		Partisol	22.8	10.9
2	UH background	MiniVol	17	10
	UH roadside	MiniVol	21	14
	London background (Hyde Park)	MiniVol	15	5
	London roadside (Oxford Street)	MiniVol	42	29

4.2.5 Chemical analysis of airborne PM

The concentrations of metals in the PM₁₀ samples collected from the roadside and background locations at UH and London are shown in Figure 4-5. The Figure indicates that higher concentrations of certain metals (Ba, Cu, Sb, Fe, Mn, Ni, Pb and Zn) were present in the roadside PM₁₀ compared with background PM₁₀.

However, in some cases this enhancement in the ambient concentration is more pronounced at the London roadside than at the roadside site of UH which is not surprising as the London site has much higher traffic levels. The difference in the elemental concentration patterns between the two roadside sites can be explained in terms of the traffic characteristics at these sites. At Oxford Street the traffic volumes are much higher, speeds are much lower, and throughout the day traffic follows a stop-start pattern. At the UH roadside site, however, the traffic flows are much lower, especially between 19:00-05:00. During other times the traffic at this site is reasonably free flowing. Braking usually occurs when traffic turns into the University Campus off the main road.

The higher levels at the London roadside site compared to background suggests that the increase in elemental concentrations – is likely to be due to road traffic emissions (including exhaust, tyre and brake) or from particles resuspended by traffic turbulence. Without similar data on exhaust emissions it is not possible to be certain that these particle-associated elements arise from non-exhaust sources, but the analysis of tyre and brake material does point to some correspondence with these source signals such as Ba/Sb ratio at Oxford Street site.

It is interesting to note that Pb concentrations at the background and roadside sites are similarly low ($\sim 10 \text{ ng/m}^3$) at both sites. As Pb has now been removed from petrol in the UK, signals resulting from traffic exhaust emissions are minimal, and any difference will most likely result from other sources including resuspension of dust. At the Oxford Street roadside site metals such as Ca, Mg and K also show significantly higher concentrations compared with the Hyde Park background site, which may indicate the influence of resuspended soil as these metals occur in high proportions in soil matrices.

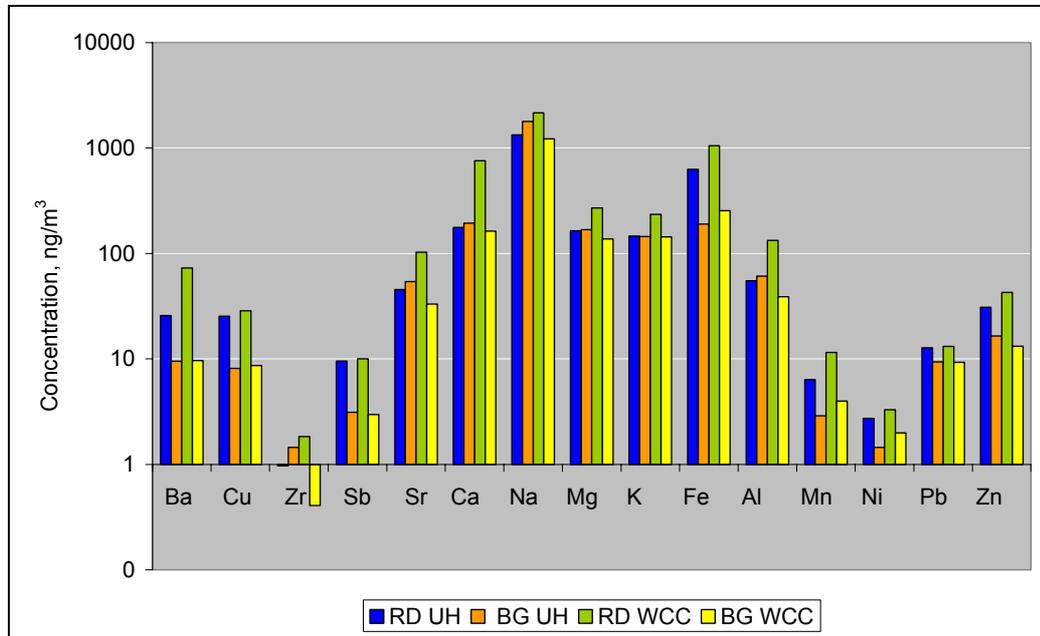


Figure 4-5: The metal concentration (ng/m^3) in the PM_{10} samples. RD UH = open roadside site at UH, BG UH = background site at UH, RD WCC = Oxford Street London, BG WCC = Hyde Park London.

As the metals in ambient particles may have a number of different origins, it is difficult to use their raw concentrations as markers for particular sources. However, as stated earlier, their concentration ratios may provide an insight into source apportionment. In order to use the ratios between metals to identify sources, it has to be assumed that the metals are associated with the same particle, or that they behave aerodynamically in a similar manner in the local atmosphere. Other studies (*e.g.* Garg *et al.*, 2000b) suggest that Ba, Sb and Zr (or their ratios) in environmental and source material samples can be used as tracers for brake wear emissions. In the work reported here, Zr was only detected at levels close to the instrument detection limit in the airborne PM samples. Therefore, only the Ba/Sb ratio in the source and ambient samples was calculated. The average Ba/Sb ratio in the three brake dust sub-samples was around 12 (see Table 4-5). To obtain this ratio at the two roadside sites the following formula was used to remove the background factor and estimate the influence of the traffic:

$$Ba / Sb (\text{traffic}) = \frac{[Ba_R - Ba_B]}{[Sb_R - Sb_B]} \quad \text{Equation 4-1}$$

where the subscripts *R* and *B* represent roadside and background respectively.

Using this formula the Ba/Sb ratios for the roadside sites of London and UH were calculated to be 9 and 2.5 respectively. The closer agreement of this ratio at the London roadside site with the that in the brake dust material might possibly be explained in terms of the traffic characteristics described earlier, in that braking is common throughout the day at this site. At the UH roadside site, in contrast, braking is infrequent. Similar methodology that is using ratios of different elements such as Ba/Cu and Zn/Cu was also employed but did not provide any additional information. Although a ratio of Cr, Y or V to Sb might prove useful for brake

material, as suggested by Figure 4-8, the concentrations for these elements were near the sensitivity limit of the instrument in the ambient samples and hence have not been used.

By comparing these with the ratios from the ambient PM samples collected in the preliminary campaigns, qualitative inferences were made concerning the likely influences of different sources at specific sites. These ratios were relatively closer at road side sites compared to background sites.

4.2.6 Physical characterisation

Figures 4-6 to 4-11 show the SEM images and x-ray spectra of material obtained from brake pad linings, brake drum dust, and tyre tread. The x-axes of the spectra shows the energy of the X-ray line characteristics of particular elements and the y-axis show the intensity of the X-ray peak, indicating the quantity of the substance.

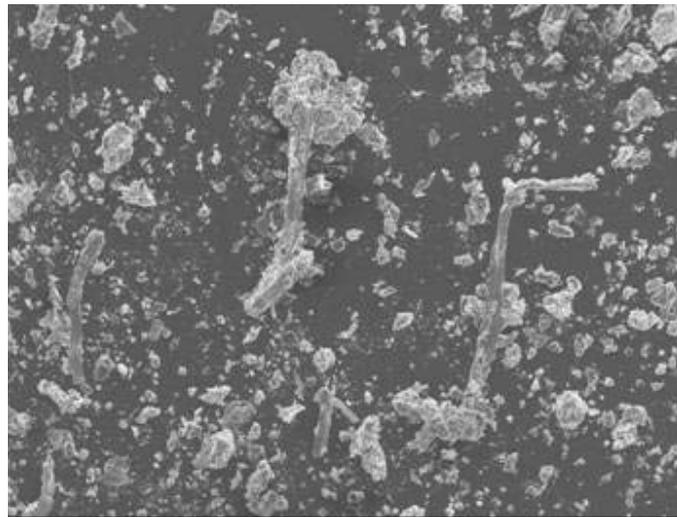


Figure 4-6: SEM micrograph of a brake pad lining particles (64x magnification).

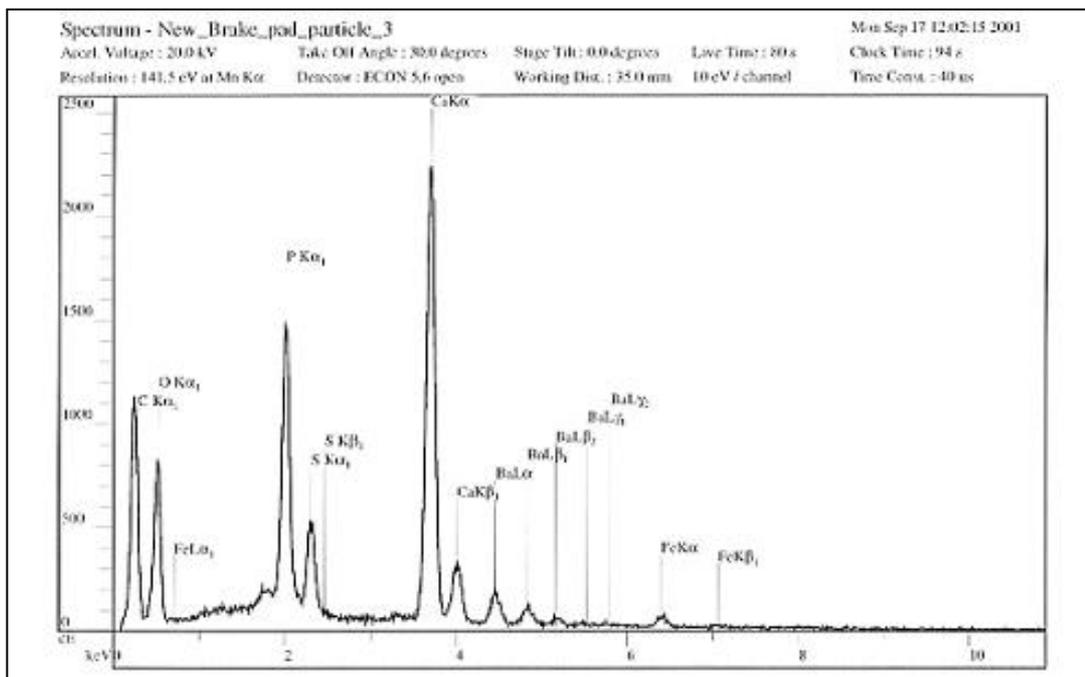


Figure 4-7: Emission line spectrum brake pad lining particles.

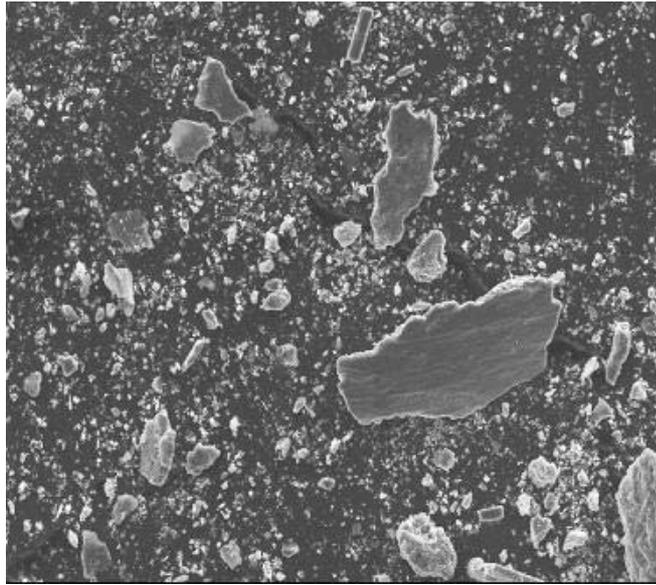


Figure 4-8: SEM micrograph of brake drum dust (64x magnification).

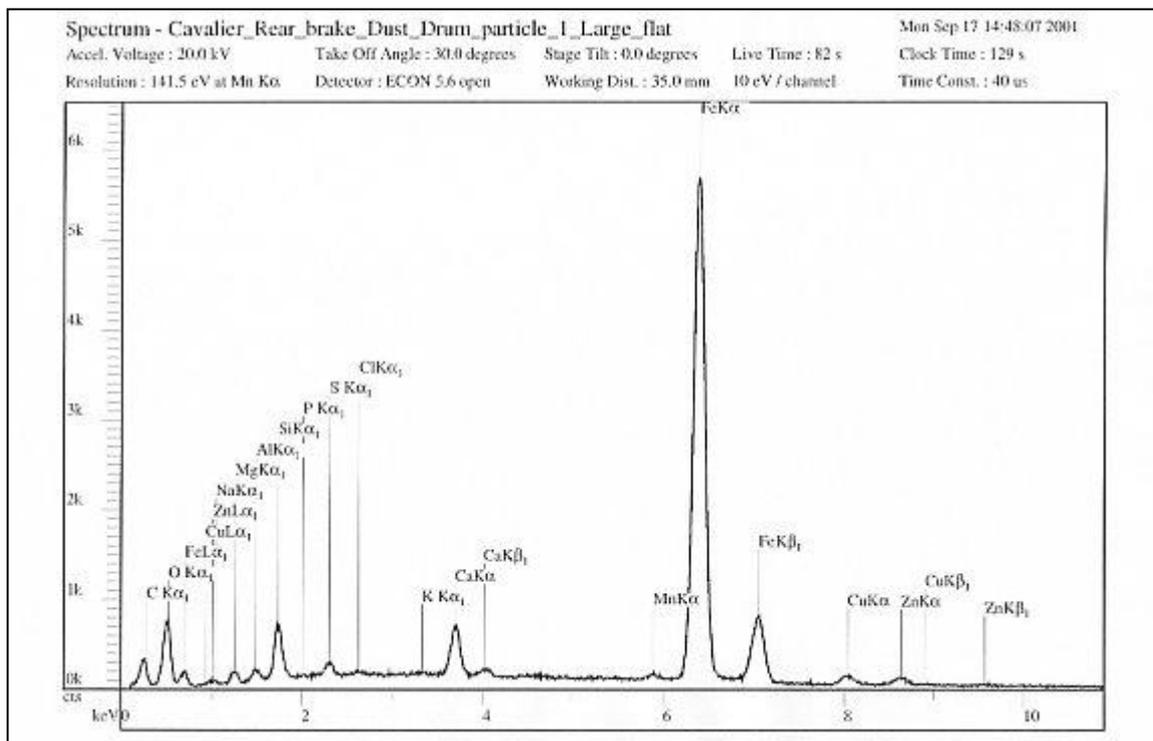


Figure 4-9: Emission line spectrum a brake drum dust particle.

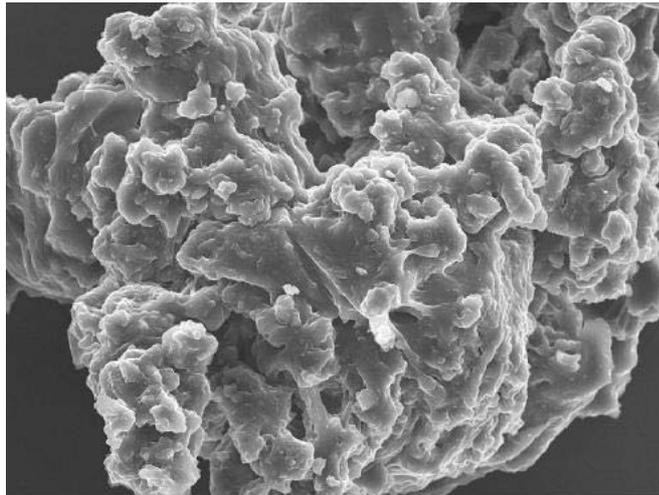


Figure 4-10: SEM micrograph of a tyre tread particle (806x magnification).

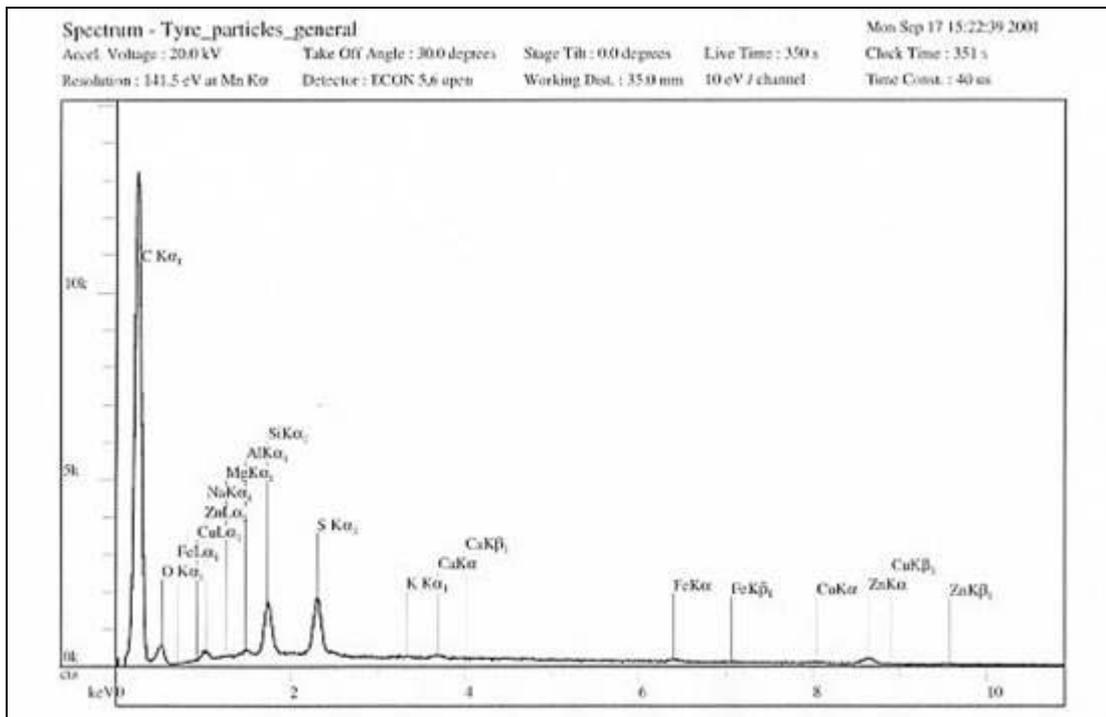


Figure 4-11: Emission line spectrum a tyre particle.

As mentioned in Chapter 3, the SEM results can only be interpreted qualitatively. However, these can be used to infer the relative abundance of some elements in particle samples. Furthermore, the analysis presented here relied on limited single particle measurements only. In the spectrum of a brake pad particle (Figure 4-6) prominent elements include C, K, P, S, Ca and Ba, though the most abundant metals present would vary by component and manufacturer. The observed spectrum partly agrees with the elemental composition of brake wear particles suggested by Hildemann *et al.* (1991). However, the appearance of P is surprising as it is reported as 0.0% in the same study. The brake drum dust particle appears to be predominantly as Fe₂O₃ showing dominant peaks at these elements. This may be the contribution of the wear of the metallic parts of the drum itself. The tyre particle, as expected, shows the largest peak at C as it is estimated that C makes over 50% of its mass. The other prominent peaks are for S and K. The predominance of S may possibly indicate the sulphur containing organic compounds such as benzothiozole which has been identified as a possible tracer for tyre wear (see section 1.2.2).

4.2.7 Implications for source apportionment and emission factor calculations

In order to identify sources of airborne particles, to apportion particles to these sources, and to estimate appropriate emission factors, a receptor modelling approach was selected and a main measurement campaign was designed based on the preliminary measurements described above.

In order to perform reliable source apportionment it is necessary to have a data set which includes mass and chemical concentrations that are temporally resolved over a period similar to the variation exhibited by the traffic (*i.e.* over time periods of less than one day). In order to apportion the particle mass to traffic sources it is expected that at least two sampling periods per day (*i.e.* each period being 12 hours long) would be necessary to pick up the variations in traffic flows. A shorter period would reduce the amount of sample collected and a longer period would average out the variations in traffic patterns. The detection limits of the ICP and GC/MS techniques, as well as data cited in the literature (e.g. Kim *et al.*, 1990), indicate that 500 mg material would be required to obtain reliable concentrations of potential tracer species, in particular organic compounds. The Partisol, for example, with a flow rate of 16.7 l/min would allow about 360 µg of PM₁₀ to be collected over 12 hours (based on a mean ambient PM₁₀ concentration of 30 µg/m³). With the MiniVol, the amount of PM₁₀ collected would be even smaller. Given the ‘interference’ arising from other ambient sources, identification of specific markers proved to be difficult with this limited mass of particles. Clearly, the preliminary measurements showed that the sampling of particles in ambient air using conventional low- or medium-flow equipment would not provide a sufficient mass of particles, or sufficient temporal resolution, for reliable source apportionment, especially for organic compounds present in low concentrations, unless sampling durations are of the order of several weeks.

As a consequence of the preliminary work, the monitoring strategy was modified, and the MiniVol and Partisol samplers were replaced by high-volume PM₁₀ samplers having a flow rate 100-200 times higher. The work also showed that the main campaign would have to be conducted at a location where particle concentrations were high. A road tunnel was selected because of the limited dispersion and dilution conditions (and elevated particle concentrations) associated with such an environment.

4.3 Stage 6: Tunnel measurements

4.3.1 Traffic measurements

4.3.1.1 Diurnal traffic flow and speed variation

Figure 4-12 shows the average diurnal variation in traffic flow and speed on weekdays, Saturdays and Sundays during the tunnel measurement campaign. The average total traffic flows on weekdays, Saturdays and Sundays were around 49000, 34000 and 33000 respectively (B tube only). During weekdays there was a large morning peak spread over the hours between 06:00 and 12:00, with a maximum traffic flow of more than 2500 vehicles per hour associated mainly with commuters travelling to London. The evening peak in the B tube was less pronounced, principally because commuters travelling home use the other tunnel tube. On

weekends there was a broader traffic peak associated with social trips and shopping activities. The diurnal flow and speed profiles on Saturdays and Sundays did not differ significantly. The average speed in the tunnel was typically around 110 km/h, except during the morning weekday peak, when it fell to around 90 km/h.

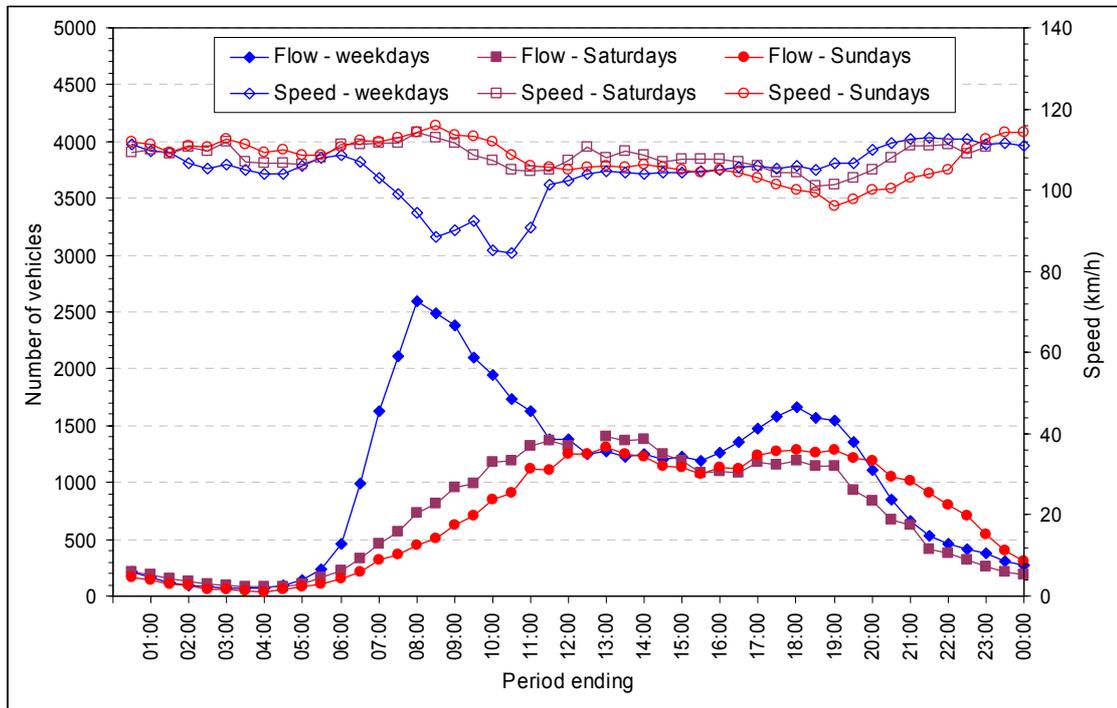


Figure 4-12 Diurnal variation of traffic flow and speed on weekdays, Saturdays and Sundays during Oct 11 – Nov 08 2002 in the B tube of Hatfield Tunnel.

4.3.1.2 Fleet distribution in the tunnel

The traffic in the tunnel was classified according to the EUR6 scheme. Table 4-8 gives the average composition of the traffic in the tunnel during the measurement campaign.

Table 4-8: Average traffic composition in tunnel on the basis of EUR6.

	Vehicle class					
	CS1 Motorcycle	CS2 Car/light van	CS3 Car + trailer	CS4 Rigid HGV/ mini-bus	CS5 Articulated HGV	CS6 Bus/coach
Percentage	0.01	86.78	0.34	7.75	4.63	0.49

The extent to which the traffic composition in the Hatfield Tunnel was representative of the UK motorway network was examined by comparison with the fleet composition for motorways in 2002 used in the National Atmospheric Emissions Inventory (Table 4-9). The vehicle categories are slightly different in the two classifications, but the total proportion of cars and vans in the Hatfield Tunnel (87.1 %) was almost identical to the national average. However, the two vehicle categories that could be compared directly (rigid and articulated HGVs) showed significant differences. This will have had an influence on the estimated emission factors, as the emission of particles tend to be higher from articulated HGVs than from rigid HGVs.

Table 4-9: National fleet composition national (motorways 2002).

Percentage of fleet	
Petrol car	65.7%
Diesel car	10.8%
Petrol LGV	1.7%
Diesel LGV	8.8%
Rigid HGV	4.4%
Artic HGV	8.0%
Buses	0.6%

Source: NAEI (2003)

4.3.2 Meteorological measurements

The descriptive statistics for the meteorological parameters measured inside tunnel using the Flowsic and the portable Nomad meteorological station are given in Table 4-10. For comparison, Table 4-11 shows the descriptive statistics for the meteorological measurements for the same period obtained from BADC (2003) for Luton airport, which is about 10 miles from the measurement site.

Table 4-10: Descriptive statistics of meteorological measurements for Flowsic and Nomad measurements.

	Flowsic	Nomad			
	Wind speed (m/s)	Wind speed (m/s)	Pressure (mbar)	Temperature (°C)	RH (%)
Mean	4.3	2.7	1000.5	20.3	80.8
Standard error	0.2	0.1	2.8	0.3	1.5
Median	4.3	2.8	1004.9	20.5	82.0
Standard deviation	1.4	0.7	19.8	2.1	10.7
RSD %	33.3	26.9	2.0	10.5	13.2
Minimum	1.0	1.2	883.9	14.4	57.9
Maximum	6.4	4.1	1019.0	23.9	95.6
95% conf. interval on mean	0.4	0.2	5.7	0.6	3.0
<i>Number of periods</i>	<i>54</i>	<i>50</i>	<i>49</i>	<i>50</i>	<i>50</i>

Table 4-11: Descriptive statistics of meteorological measurements at Luton Airport during the tunnel sampling campaign.

	Wind speed (m/s)	Pressure (Mbar)	Temperature (°C)	RH (%)
Mean	5.3	1007.9	8.8	91.3
Standard Error	0.4	1.4	0.4	0.8
Median	4.8	1009.1	9.0	92.7
Standard deviation	2.6	10.2	2.6	5.6
RSD	54.5	1.0	29.3	6.0
Minimum	1.9	980.8	2.4	77.8
Maximum	18.6	1027.9	13.7	100.0
95% conf. interval on mean	0.7	2.8	0.7	1.5
<i>Number of periods</i>	<i>54</i>	<i>54</i>	<i>54</i>	<i>54</i>

The greatest differences between the tunnel conditions and the conditions at Luton Airport related to the air temperature, in terms of both magnitude and variation. The average wind speed at Luton Airport was also higher than that determined from both the Flowsic and Nomad measurements inside the tunnel. Figure 4-13 shows the in-tunnel wind speeds plotted against the wind speeds from Luton, indicating no correlation between the two. This showed that the external wind conditions had very little influence on the wind condition inside the tunnel.

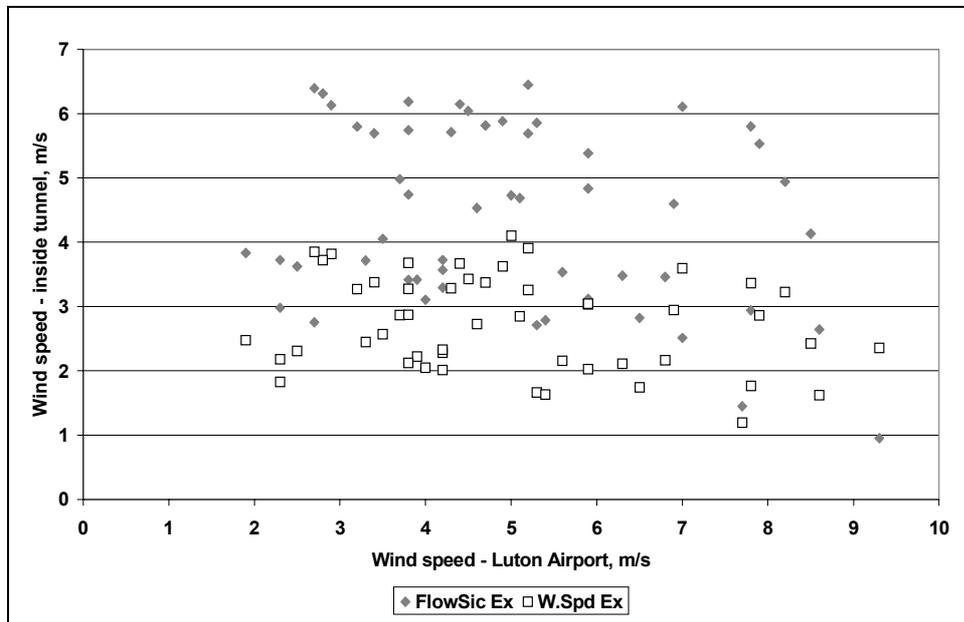


Figure 4-13: Scatter plot of wind speeds from Luton Airport and tunnel exit location.

Figure 4-14 shows that the wind speed measurements from the two instruments inside the tunnel were highly correlated. However, the wind speed measurements from the Flowsic were systematically higher than those measured by the Nomad. Whereas the Flowsic measures the average airflow velocity across the tunnel (it is designed specifically for use in tunnels), the Nomad only measures at one location - in this case near to the tunnel wall. The Flowsic measurements were therefore considered to be more reliable in this situation.

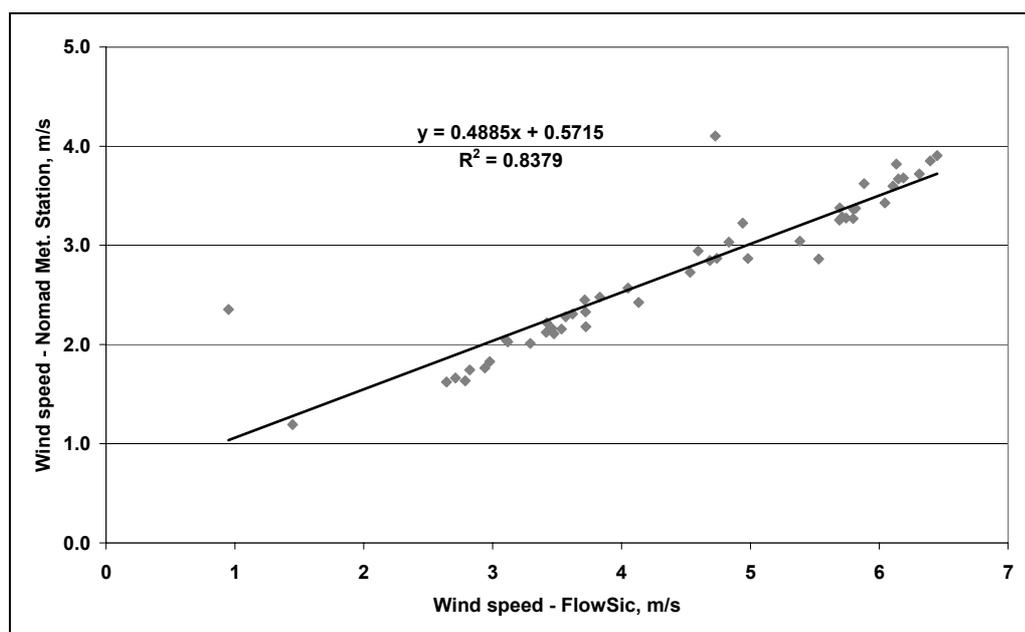


Figure 4-14: Scatter plot of wind speeds from Flowsic and Nomad.

The scatter plot between the total number of vehicles and the two wind speeds measured inside tunnel is given in Figure 4-15. This figure shows that the wind speed, from both the instruments, inside tunnel is highly correlated with the traffic flows. Figure also shows the clear clusters of the wind speeds, a cluster of high wind speeds at an average traffic flow of 35000, coinciding with the day time sample and a cluster of low wind speeds at about 10000 vehicles coinciding with the night time sample while the wind speeds for the weekend period.

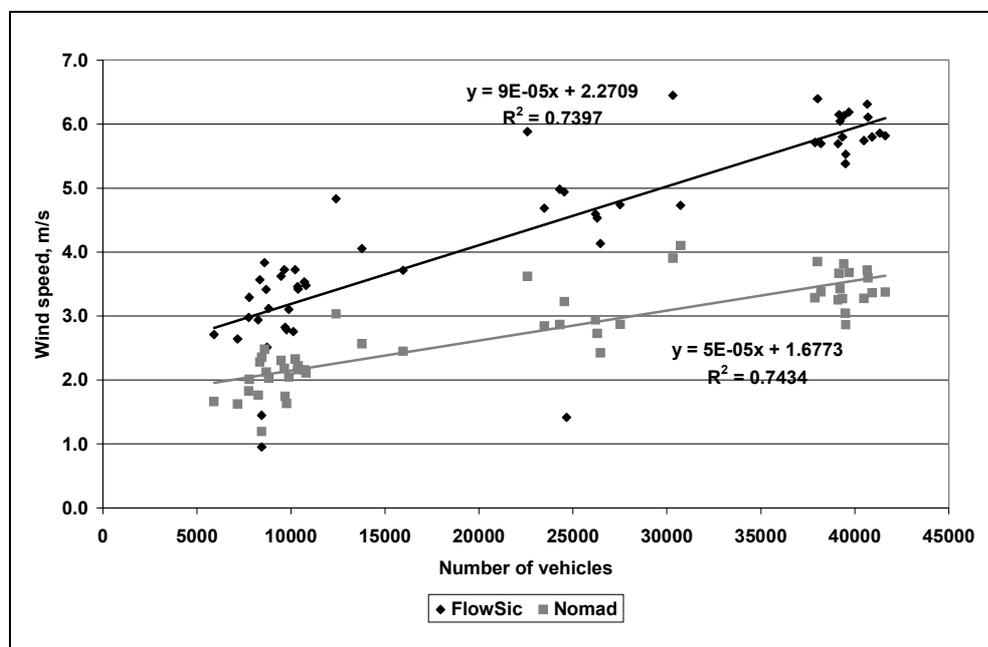


Figure 4-15: Scatter plot of number of vehicles and wind speed measurements from Flowsic and Nomad inside tunnel (for each 12 hour period).

4.3.3 PM₁₀ mass concentration

Table 4-12 gives the descriptive statistics for the PM₁₀ concentrations measured using high-volume samplers at the tunnel entrance and exit. Each PM₁₀ sample was collected during a nominal 12-hour period. The PM₁₀ concentrations measured at the tunnel exit were typically around 60% higher than those measured at the tunnel entrance. The measurements also showed that the average PM₁₀ concentration inside the tunnel was several times higher than the typical PM₁₀ concentration measured at the roadside location at the nearby University of Hertfordshire campus (Table 4-7), although the comparison is somewhat confounded by the effect of sampling during different seasons.

Table 4-12: Descriptive statistics (12-hour) of PM₁₀ measurements at tunnel entrance and exit (day = 06:00-18:00, night = 18:00-06:00).

PM ₁₀	Tunnel entrance (µg/m ³)			Tunnel exit (µg/m ³)		
	Overall	Night	Day	Overall	Night	Day
Mean	41.9	38	46	69.7	59	80
Standard Error	2.7	3.7	3.9	3.0	3.7	3.9
Median	37.2	31	42	68.0	59	77
Standard Deviation	19.9	19	20	22.3	19	20
RSD %	53.5	361	411	32.0	371	405
Minimum	13.1	13	20	34.2	34	53
Maximum	95.4	90	95	131.7	109	131
95% conf. interval on mean	5.4	7.5	8.0	6.1	7.6	8.0
Count	54	27	27	54	27	27

Figure 4-16 shows a linear regression plot of the PM₁₀ concentrations measured during the 54 paired sampling events at the tunnel entrance and exit. This relatively high correlation coefficient (0.73) confirms the influence of traffic on concentrations at both locations. In the scatter plot the slope of the regression line is almost unity. The intercept on the y-axis of 29 µg/m³ represents the average increase in the PM₁₀ concentration generated by the traffic moving between the tunnel entrance and the tunnel exit. This tunnel increment in the PM₁₀ concentration varied between 12 and 52 µg/m³. This variability was used to determine the correlation between traffic conditions and traffic-generated PM₁₀.

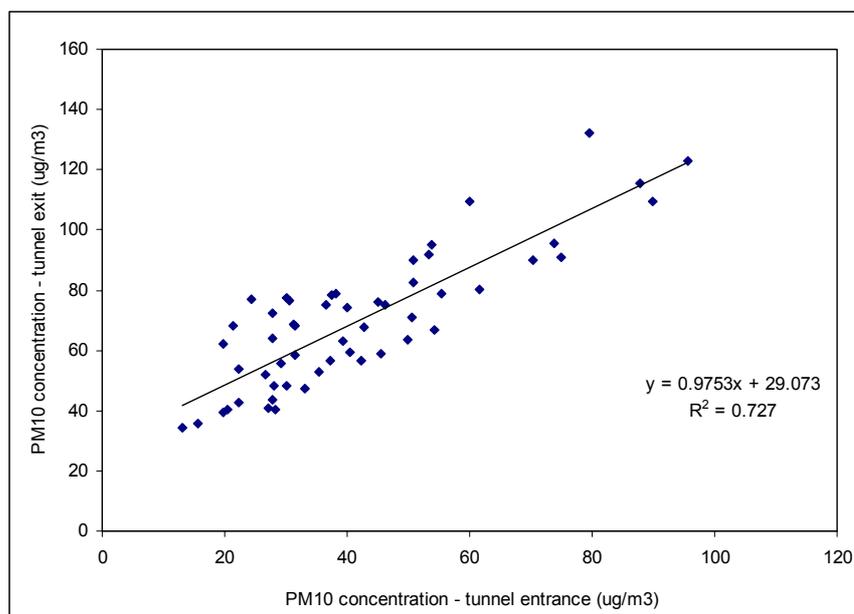


Figure 4-16: PM₁₀ mass concentration at tunnel entrance and exit.

4.4 Stage 7: Chemical characterisation of particulate matter

4.4.1 Airborne PM - metals

The descriptive statistics for the metal concentrations in the PM₁₀ sampled at the tunnel entrance and tunnel exit are given in Tables 4-13 and 4-14 respectively. The absolute PM₁₀ mass concentrations are also included for comparison. The metals analysed only accounted for 18.8% (tunnel entrance) and 13.8% (tunnel exit) of the total PM₁₀ mass. It is expected that the bulk of the PM₁₀, around 50%, will comprise of elemental and organic carbon and the other significant component will be secondary aerosol, SO₄⁻², NO₃⁻, NH₄⁺ (QUARG 1993; APEG, 1999).

The ratios of the metal concentrations at the tunnel entrance and exit are given in Table 4-15. Again, the PM₁₀ ratio is included for comparison. For the species having predominant natural sources (*e.g.* Ca, Na, Mg, K, Al) the ratio was close to unity, whereas species associated predominantly with anthropogenic sources have higher ratios. Table 4-15 also shows that the PM₁₀ concentration inside the tunnel were higher compared to all other sites in this study. The only other comparable PM₁₀ concentrations were observed at Oxford Street, London where most of the fleet comprises of buses, taxis and LGVs which almost all run on diesel and with a PM₁₀ emission factor which can be 10-40 times higher than that for petrol cars (NAEI 2003).

Table 4-13: Descriptive statistics: PM₁₀ (µg/m³) and metal concentrations (ng/m³) measured at tunnel entrance (Number of samples = 54).

	Mean	Standard error	Median	Standard deviation	RSD %	Minimum	Maximum	Confidence interval of mean (95.0%)
<i>PM₁₀</i>	41.9	2.7	37.2	19.9	47.5	13.1	95.4	5.4
Ca	1143.7	53.3	1151.2	391.7	34.2	246.3	2310.8	106.9
Na	3333.0	184.6	3625.1	1356.5	40.7	780.6	5862.9	370.2
Mg	536.5	22.7	549.2	167.1	31.1	265.8	1089.3	45.6
K	592.2	90.8	451.5	667.0	112.6	190.9	4849.2	182.1
Fe	967.0	75.5	803.0	555.1	57.4	201.2	2563.5	151.5
Al	960.4	47.6	939.6	349.6	36.4	260.8	2185.8	95.4
Ba	114.8	7.9	104.7	58.3	50.8	42.0	452.0	15.9
Cd	0.6	0.1	0.5	0.4	74.8	0.2	2.3	0.1
Co	0.2	0.0	0.2	0.2	97.3	0.0	0.8	0.1
Cr	5.6	0.4	4.7	3.0	54.3	1.6	19.4	0.8
Cu	61.8	4.9	52.5	35.7	57.8	22.0	186.6	9.7
Mn	12.8	1.0	11.4	7.6	59.2	2.9	36.0	2.1
Ni	3.2	0.3	2.5	2.2	69.4	0.6	12.6	0.6
Pb	44.1	11.3	22.9	83.1	188.4	7.6	577.0	22.7
Sb	21.9	1.9	17.9	13.9	63.3	1.7	63.7	3.8
Sr	6.2	1.6	3.4	12.1	195.4	1.9	83.8	3.3
Ti	6.4	0.7	5.4	5.5	84.9	0.0	26.2	1.5
V	1.9	0.5	0.4	3.5	186.3	0.0	19.7	0.9
Y	0.7	0.0	0.7	0.3	49.3	0.0	1.8	0.1
Zn	62.1	4.4	54.8	32.6	52.6	25.3	192.7	8.9
Zr	12.1	1.3	11.1	9.7	80.2	0.0	66.9	2.6

Table 4-14: Descriptive statistics of concentration of PM₁₀ (µg/m³) and metals (ng/m³) measured at tunnel exit (Number of samples = 54).

	Mean	Standard error	Median	Standard deviation	RSD %	Minimum	Maximum	Confidence interval of mean (95.0%)
<i>PM₁₀</i>	69.7	3.0	68.0	22.3	32.0	34.2	131.7	6.1
Ca	1427.0	89.9	1353.9	660.8	46.3	29.5	3666.7	180.4
Na	3368.1	258.9	3336.9	1902.7	56.5	0.0	11719.4	519.3
Mg	574.4	33.0	560.2	242.5	42.2	135.5	1642.3	66.2
K	618.8	87.9	471.4	646.1	104.4	158.1	4529.9	176.4
Fe	2033.8	115.7	1929.0	850.4	41.8	799.0	3726.6	232.1
Al	1053.7	67.7	1004.1	497.1	47.2	276.5	3113.1	135.7
Ba	153.6	8.1	142.8	59.4	38.7	51.8	406.0	16.2
Cd	0.9	0.1	0.8	0.4	45.1	0.2	2.3	0.1
Co	0.4	0.0	0.4	0.2	51.5	0.0	0.8	0.1
Cr	9.0	0.5	8.7	3.8	42.5	2.6	27.2	1.0
Cu	129.0	6.9	122.2	50.6	39.2	50.2	239.5	13.8
Mn	23.3	1.3	22.5	9.6	41.0	8.8	49.0	2.6
Ni	4.2	0.3	3.5	2.6	61.4	1.7	15.6	0.7
Pb	52.5	12.1	31.1	89.1	169.7	10.0	639.5	24.3
Sb	47.4	2.6	47.2	19.3	40.8	16.6	86.9	5.3
Sr	7.5	1.6	4.9	11.9	158.9	2.4	82.9	3.2
Ti	10.0	0.8	8.8	5.7	57.2	1.3	35.5	1.6
V	2.2	0.5	0.6	3.7	173.6	0.0	22.0	1.0
Y	0.6	0.0	0.7	0.4	55.2	0.0	2.3	0.1
Zn	108.6	5.6	102.1	41.2	38.0	40.6	259.2	11.2
Zr	14.2	1.2	13.2	9.0	63.4	0.0	57.4	2.5

Table 4-15: Ratio of concentrations measured at tunnel exit and entrance and other measurement sites.

	Ratio Tunnel Exit/Entrance	Ratio Tunnel Exit/ UH open roadside	Ratio Tunnel Exit/UH background	Ratio Tunnel Exit/ Oxford Street, London	Ratio Tunnel Exit/ Hyde Park, London
<i>PM</i> ₁₀	1.7	3.3	4.1	1.7	4.6
Ca	1.2	8.1	7.4	1.9	8.7
Na	1.0	2.5	1.9	1.6	2.8
Mg	1.1	3.5	3.4	2.1	4.2
K	1.0	4.2	4.3	2.6	4.3
Fe	2.1	3.2	10.7	1.9	8.0
Al	1.1	19.1	17.3	7.9	27.2
Ba	1.3	6.0	16.2	2.1	16.0
Cd	1.5	-	-	-	-
Co	1.8	-	-	-	-
Cr	1.6	-	-	-	-
Cu	2.1	5.1	15.8	4.5	14.9
Mn	1.8	3.7	8.1	2.0	5.9
Ni	1.3	1.5	2.9	1.3	2.1
Pb	1.2	4.1	5.6	4.0	5.7
Sb	2.2	5.0	15.2	4.7	16.0
Sr	1.2	4.1	3.5	1.8	5.6
Ti	1.5	-	-	-	-
V	1.2	-	-	-	-
Y	0.9	-	-	-	-
Zn	1.7	3.5	6.6	2.5	8.2
Zr	1.2	14.7	9.8	7.7	34.9

4.4.2 Airborne PM – Organic compounds

The descriptive statistics for the concentrations of organic compounds (PAHs and benzothiazoles) in the PM₁₀ sampled at the tunnel entrance and tunnel exit are shown in Tables 4-16 and 4-17. The PAH concentrations measured at tunnel exit were consistently higher than those measured at the tunnel entrance. This finding is consistent with all other tunnel studies (Wingfors *et al.* 2001). The quantified species included 31 PAHs and benzothiazole. However, it should again be noted that the mass contribution of these species towards PM₁₀ is negligible. The most important quantified species in terms of mass included pyrene, benzo[ghi]perylene, fluoranthene, cyclopenta[cd]pyrene, triphenylene, chrysene, benzo[ghi]fluoranthene, benzo[a]pyrene, phenanthrene, 2-methylphenanthrene and indeno[1,2,3-cd]pyrene.

In Table 4-18 the concentrations measured at the tunnel entrance and exit were found to be broadly comparable with those from other European and North American studies (Schauer *et al.*, 1996, Harrison *et al.*, 2003, Zheng *et al.*, 2002). In general, the concentration of heavy PAHs associated with PM₁₀ in this study such as cyclopenta[cd]pyrene, benz[a]anthracene, triphenylene, chrysene, and benzo[a]pyrene are 2-3 times higher than those reported in PM_{2.5} in South-eastern United States (Schauer *et al.*, 1996) and within the range reported elsewhere for Birmingham (Harrison *et al.*, 2003) and six states in United States (Zheng *et al.*, 2002).

However, for a number of low-molecular-weight PAHs, such as the methyl phenanthrenes, which are known to be a major component of the PAH in diesel exhaust (Rogge *et al.*, 1993), their particle-bound concentrations in this study were much lower than those reported as the sum of particulate plus vapour phase at a road side in Birmingham, UK (Harrison *et al.*, 2003) since they predominantly exist in vapour phase.

Table 4-16: Descriptive statistics of concentration of PM₁₀ (µg/m³), PAHs (ng/m³) and benzothiazole (ng/m³) measured at tunnel entrance (Number of samples = 54).

Species	Mean	Standard error	Median	Standard deviation	Min	Max	Confidence level (95.0%)
PM ₁₀	41.9	2.7	37.3	19.9	13.1	95.4	5.44
naphthalene	0.14	0.01	0.14	0.06	0.06	0.28	0.02
1-methylnaphthalene	0.09	0.01	0.09	0.06	0.02	0.49	0.02
2,6 & 2,7-dimethylnaphthalene	0.07	0.00	0.06	0.03	0.02	0.22	0.01
acenaphthylene	0.04	0.00	0.04	0.03	0.01	0.20	0.01
acenaphthene	0.02	0.00	0.02	0.01	0.01	0.05	0.00
fluorene	0.04	0.00	0.03	0.02	0.01	0.16	0.01
phenanthrene	0.66	0.05	0.59	0.37	0.20	2.00	0.10
anthracene	0.12	0.01	0.10	0.10	0.02	0.50	0.03
2-methylphenanthrene	0.38	0.03	0.32	0.21	0.09	1.14	0.06
1-methylphenanthrene	0.22	0.02	0.18	0.12	0.06	0.69	0.03
3,6-dimethylphenanthrene	0.14	0.01	0.12	0.09	0.04	0.48	0.02
fluoranthene	1.25	0.10	1.21	0.70	0.32	3.34	0.19
pyrene	1.63	0.13	1.46	0.96	0.35	4.03	0.26
2-methylfluoranthene	0.09	0.01	0.08	0.05	0.01	0.26	0.01
1-methylfluoranthene	0.15	0.01	0.12	0.09	0.03	0.49	0.03
benzo[a]fluorene	0.33	0.02	0.31	0.18	0.07	0.72	0.05
benzo[b]fluorene	0.22	0.02	0.20	0.14	0.04	0.64	0.04
1-methylpyrene	0.14	0.01	0.13	0.08	0.03	0.39	0.02
benzo[ghi]fluoranthene	0.88	0.06	0.81	0.44	0.24	2.23	0.12
cyclopenta[cd]pyrene	0.46	0.09	0.22	0.65	0.04	3.98	0.18
benz[a]anthracene	0.95	0.10	0.78	0.72	0.23	4.36	0.20
triphenylene & chrysene	1.37	0.12	1.15	0.86	0.42	5.27	0.24
benzo[b & j & k]fluoranthene	0.72	0.09	0.55	0.66	0.14	4.00	0.18
benzo[e]pyrene	0.48	0.04	0.41	0.31	0.13	1.85	0.09
benzo[a]pyrene	0.78	0.09	0.63	0.64	0.06	3.27	0.17
perylene	0.25	0.03	0.21	0.21	0.05	0.98	0.06
indeno[1,2,3-cd]pyrene	0.73	0.06	0.62	0.46	0.22	2.51	0.13
dibenz[ah]anthracene	0.08	0.01	0.07	0.06	0.02	0.32	0.02
benzo[ghi]perylene	1.20	0.10	1.01	0.70	0.32	3.91	0.19
coronene	0.52	0.06	0.39	0.43	0.12	2.59	0.12
dibenzo[a,e]pyrene	0.03	0.00	0.02	0.03	0.00	0.17	0.01
benzothiazole	0.03	0.01	0.02	0.04	0.00	0.17	0.01

Table 4-17: Descriptive statistics of concentration of PM₁₀ (µg/m³), PAHs (ng/m³) and benzothiazole (ng/m³) measured at tunnel exit (Number of samples = 54).

Species	Mean	Standard error	Median	Standard deviation	Min	Max	Confidence level (95.0%)
PM ₁₀	69.7	3.04	68.0	22.3	34.2	131.7	6.09
naphthalene	0.31	0.02	0.29	0.13	0.01	0.56	0.03
1-methylnaphthalene	0.15	0.01	0.14	0.06	0.05	0.32	0.02
2,6 & 2,7-dimethylnaphthalene	0.15	0.01	0.13	0.08	0.05	0.39	0.02
acenaphthylene	0.09	0.00	0.08	0.04	0.04	0.20	0.01
acenaphthene	0.03	0.00	0.03	0.01	0.01	0.08	0.00
fluorene	0.09	0.01	0.09	0.05	0.02	0.28	0.01
phenanthrene	1.78	0.12	1.48	0.88	0.67	4.12	0.24
anthracene	0.35	0.03	0.29	0.19	0.11	0.82	0.05
2-methylphenanthrene	1.29	0.10	0.96	0.75	0.43	3.24	0.20
1-methylphenanthrene	0.74	0.06	0.53	0.43	0.25	2.03	0.12
3,6-dimethylphenanthrene	0.52	0.05	0.39	0.33	0.17	1.52	0.09
fluoranthene	3.71	0.29	3.09	2.14	1.06	9.55	0.58
pyrene	5.27	0.43	4.65	3.15	1.29	13.34	0.86
2-methylfluoranthene	0.25	0.02	0.22	0.14	0.07	0.66	0.04
1-methylfluoranthene	0.45	0.03	0.39	0.25	0.14	1.30	0.07
benzo[a]fluorene	0.90	0.06	0.86	0.45	0.24	2.18	0.12
benzo[b]fluorene	0.56	0.05	0.51	0.33	0.16	2.14	0.09
1-methylpyrene	0.40	0.03	0.37	0.19	0.11	0.86	0.05
benzo[ghi]fluoranthene	2.27	0.11	2.37	0.78	1.12	4.54	0.21
cyclopenta[cd]pyrene	2.80	0.18	2.94	1.33	0.65	5.83	0.36
benz[a]anthracene	2.11	0.11	1.89	0.83	0.81	4.71	0.23
triphenylene & chrysene	2.72	0.13	2.47	0.95	1.24	5.86	0.26
benzo[b & j & k]fluoranthene	1.12	0.08	1.03	0.56	0.33	3.11	0.15
benzo[e]pyrene	0.91	0.05	0.83	0.35	0.32	2.14	0.10
benzo[a]pyrene	1.86	0.10	1.70	0.76	0.83	4.12	0.21
perylene	0.66	0.06	0.56	0.43	0.23	2.36	0.12
indeno[1,2,3-cd]pyrene	1.28	0.07	1.18	0.53	0.47	3.00	0.14
dibenz[ah]anthracene	0.14	0.01	0.11	0.08	0.05	0.42	0.02
benzo[ghi]perylene	3.88	0.38	3.25	2.79	1.44	17.47	0.76
coronene	1.13	0.09	0.94	0.70	0.37	3.84	0.19
dibenzo[a,e]pyrene	0.04	0.01	0.03	0.04	0.01	0.26	0.01
benzothiazole	0.04	0.00	0.03	0.03	0.00	0.12	0.01

Table 4-18: Ratio of PAH concentrations measured at tunnel exit and entrance, and comparison of PAHs measured at tunnel entrance in this study and in other studies (ng/m³).

Compounds	Ratio Tunnel Exit/ Entrance	PM ₁₀ concentration at the entrance of Hatfield Tunnel			Fine particles concentration in USA ^a		Sum of particulate & vapour, Birmingham, UK ^b	PM _{2.5} concentration in Southeastern United States ^c	
		Mean	Min	Max	Min	Max	Mean	Min	Max
naphthalene	2.2	0.144	0.056	0.279	-	-	-	-	-
1-methylnaphthalene	1.7	0.091	0.025	0.491	-	-	-	-	-
2,6 & 2,7-Dimethylnaphthalene	2.1	0.067	0.023	0.219	-	-	-	-	-
acenaphthylene	2.3	0.043	0.014	0.195	-	-	4.180	-	-
acenaphthene	1.5	0.022	0.009	0.050	-	-	1.410	-	-
fluorene	2.3	0.036	0.006	0.163	-	-	9.140	-	-
phenanthrene	2.7	0.657	0.196	1.995	-	-	21.910	-	-
anthracene	2.9	0.124	0.019	0.496	-	-	4.660	-	-
2-methylphenanthrene	3.4	0.378	0.091	1.140	-	-	5.650	-	-
1-methylphenanthrene	3.4	0.222	0.062	0.690	-	-	-	-	-
3,6-dimethylphenanthrene	3.7	0.141	0.035	0.482	-	-	-	-	-
fluoranthene	3.0	1.252	0.324	3.339	0.070	0.150	8.290	0.030	0.450
pyrene	3.2	1.633	0.353	4.026	0.120	0.260	7.660	0.020	0.560
2-methylfluoranthene	2.8	0.091	0.015	0.261	-	-	-	-	-
1-methylfluoranthene	3.0	0.149	0.034	0.495	-	-	-	-	-
benzo[a]fluorene	2.7	0.327	0.065	0.719	-	-	-	-	-
benzo[b]fluorene	2.5	0.222	0.044	0.642	-	-	-	-	-
1-methylpyrene	2.9	0.141	0.027	0.390	-	-	-	-	-
benzo[ghi]fluoranthene	2.6	0.884	0.242	2.231	0.110	0.390	-	0.010	0.260
cyclopenta[cd]pyrene	6.1	0.456	0.039	3.984	0.040	0.410	-	0.010	0.070
benz[a]anthracene	2.2	0.950	0.232	4.358	0.090	0.290	0.730	0.020	1.790
triphenylene & chrysene	2.0	1.365	0.423	5.274	0.230	0.610	1.240	0.030	2.550
benzo[b & j & k]fluoranthene	1.6	0.718	0.136	3.997	0.330	1.200	1.090	-	-
benzo[e]pyrene	1.9	0.484	0.125	1.845	0.380	0.970	0.570	0.050	3.180
benzo[a]pyrene	2.4	0.780	0.059	3.269	0.180	0.440	0.440	0.030	2.500
perylene	2.6	0.252	0.046	0.978	-	-	-	0.040	0.500
indeno[1,2,3-cd]pyrene	1.8	0.730	0.216	2.515	0.070	0.430	0.690	0.040	1.580
dibenz[ah]anthracene	1.8	0.078	0.021	0.318	-	-	0.120	-	-
benzo[ghi]perylene	3.2	1.200	0.322	3.911	1.120	4.470	1.420	0.040	2.180
coronene	2.2	0.518	0.122	2.585	2.410	-	0.470	0.010	0.700
dibenzo[a,e]pyrene	1.3	0.025	0.003	0.168	-	-	-	-	-
benzothiazole	1.3	0.027	0.000	0.167	-	-	-	-	-

- a. Schauer *et al.*, 1996
b. Harrison *et al.*, 2003
c. Zheng *et al.*, 2002

4.4.3 Deposited dust

Four samples of deposited dust were collected in the tunnel – two at the tunnel entrance and two at the exit. The deposition rates at the tunnel entrance during the two measurements were 146.4 $\mu\text{g}/\text{m}^2/\text{min}$ and 119.4 $\mu\text{g}/\text{m}^2/\text{min}$. The deposition rates at the tunnel exit were lower, at 86.5 $\mu\text{g}/\text{m}^2/\text{min}$ and 70.7 $\mu\text{g}/\text{m}^2/\text{min}$. The overall average dust deposition rate was 106 $\mu\text{g}/\text{m}^2/\text{min}$. It is important to note that this values is based on the filters which were placed alongside other sampling equipment on the walkway at a height of about 1.5 m from the road surface. The dust deposit rate for the actual road surface may well be higher.

Two filters were analysed for metals, and two for organic constituents. The average chemical composition of the deposited dust for inorganic and organic species is given in Table 4-19 and 4-20. Ca, K, Fe and Al were present in quite high concentrations. Other important elements to mention in this matrix include Cu, Pb, Ti and Ba. Amongst the organic species fluoranthene, pyrene, triphenylene/chrysene and benzo[ghi]perylene were present in relatively higher proportions in the analysed dust.

Table 4-19: The concentrations of metals in the deposited dust.

Metal	Concentration ($\mu\text{g}/\text{g}$ of deposited dust)	
	Tunnel Exit	Tunnel Entrance
Ca	30,777	19,309
Na	2,090	617
Mg	2,595	1,457
K	12,535	4,944
Fe	18,247	12,482
Al	18,067	11,937
Ba	381	79
Cd	9	4
Co	8	6
Cr	46	27
Cu	480	294
Mn	380	270
Ni	26	17
Pb	360	262
Sb	61	27
Sr	103	74
Ti	468	325
V	36	27
Y	4	3
Zn	4,788	1,189

Table 4-20: The concentrations of PAHs and benzothiazole in the deposited dust.

Compound	Concentration ($\mu\text{g}/\text{g}$ of deposited dust)	
	Tunnel Exit	Tunnel Entrance
naphthalene	1.67	0.67
1-methylnaphthalene	0.81	0.36
2,6 & 2,7-dimethylnaphthalene	0.43	0.19
acenaphthylene	0.56	0.20
acenaphthene	0.24	0.07
fluorene	0.13	0.05
phenanthrene	2.37	1.02
anthracene	0.43	0.18
2-methylphenanthrene	0.98	0.40
1-methylphenanthrene	0.68	0.25
3,6-dimethylphenanthrene	0.43	0.13
fluoranthene	3.93	1.45
pyrene	5.00	1.73
2-methylfluoranthene	0.14	0.04
1-methylfluoranthene	0.25	0.10
benzo[a]fluorene	0.60	0.24
benzo[b]fluorene	0.38	0.09
1-methylpyrene	0.21	0.09
benzo[ghi]fluoranthene	1.52	0.58
cyclopenta[cd]pyrene	0.65	0.21
benz[a]anthracene	2.52	0.90
triphenylene & chrysene	4.51	1.67
benzo[b & j & k]fluoranthene	1.71	0.84
benzo[e]pyrene	1.68	0.64
benzo[a]pyrene	2.30	0.67
perylene	0.94	0.32
indeno[1,2,3-cd]pyrene	2.30	0.78
dibenz[ah]anthracene	0.36	0.10
benzo[ghi]perylene	3.92	1.39
coronene	2.29	0.81
dibenzo[a,e]pyrene	0.13	0.04
<i>benzothiazole</i>	<i>1.41</i>	<i>0.43</i>

4.5 Stage 8: Statistical analysis and receptor modelling

4.5.1 Principal component analysis (PCA)

The concentrations of PM and chemical species measured at the tunnel entrance were subtracted from those measured at the tunnel exit, yielding ‘tunnel increment’ data. This methodology was adopted to minimise the influence of possible external (non-traffic) sources. PCA was then performed on the tunnel increment data to identify the most important particle sources, according to the method suggested by Thurston (1983). One criterion for this type of analysis is that the number of samples should be at least twice the number of input variables, and therefore only those variables, in this case chemically characterised species and PM₁₀ concentrations, were selected which were either known to be unique tracers or which are predominantly associated with a source type expected to influence concentrations in the tunnel. In the final analysis, 23 variables were included. The Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy Test and Bartlett's Test were performed to check the suitability of the dataset for PCA and the results are given in Table 4-21. The KMO test measures the overall magnitude of intercorrelations amongst input variables, and a value of greater than 0.6 indicates that it is appropriate to apply PCA. The null hypothesis in the case of Bartlett's Test is that non-zero correlations only arise from errors. However, on the basis of the calculated significance value (0.000), the null hypothesis was rejected. This indicated that the correlation amongst the input variables was likely to be real, and therefore that the application of PCA was appropriate.

The communalities of the entered variables are given in Table 4-22. The communality is the sum of the square of the loadings for each entered variable in a factor matrix (as shown in Table 4-24). The initial communality is the sum of the loadings on all the components (equal to 1) and the extraction communality is the sum of the square of the loadings on the retained components.

Table 4-21: Result of KMO and Bartlett's Test.

Test	Result
Kaiser-Meyer-Olkin Measure of Sampling Adequacy	0.802
Bartlett's Test of Sphericity	Approx. Chi-Square df Significance
	1818.856 253 0.000

Table 4-22: Communalities of entered variables (initial communalities = 1).

Species	Extraction	Species	Extraction
PM ₁₀	0.859	Ca	0.898
		Al	0.953
phenanthrene	0.972	Ba	0.917
anthracene	0.795	Zn	0.657
2-methylphenanthrene	0.954	Cu	0.816
1-methylphenanthrene	0.942	Sb	0.742
3,6-dimethylphenanthrene	0.940	Ti	0.654
benzo[a]fluorene	0.921	Ni	0.493
benzo[b]fluorene	0.757	V	0.841
benzo[ghi]fluoranthene	0.819		
benz[a]anthracene	0.721	Benzothiazole	0.767
benzo[a]pyrene	0.925		
coronene	0.742		
indeno[1,2,3-cd]pyrene	0.868		

Table 4-22 shows that for most of the variables the communality after extraction was quite high, indicating that most of the variance was explained by one or more of the retained components. PCA reduces the number of input variables to a smaller number of ‘components’, which can be interpreted as the underlying cause or source. All the principal components having an Eigenvalue of 1 or more were retained for further interpretation, as suggested by Hopke (1989). Table 4-23 gives the variance explained by all the principal components and by the retained components, before and after rotation.

Table 4-23: Eigenvalues and variance explained by the components.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	11.221	48.786	48.786	11.221	48.786	48.786	6.643	28.883	28.883
2	3.332	14.489	63.275	3.332	14.489	63.275	3.896	16.940	45.823
3	2.214	9.626	72.901	2.214	9.626	72.901	3.385	14.717	60.540
4	1.156	5.024	77.925	1.156	5.024	77.925	2.968	12.904	73.445
5	1.030	4.479	82.405	1.030	4.479	82.405	2.061	8.960	82.405
6	0.860	3.738	86.142						
7	0.695	3.020	89.162						
8	0.601	2.615	91.777						
9	0.484	2.105	93.882						
10	0.345	1.502	95.384						
11	0.248	1.077	96.461						
12	0.189	0.824	97.284						
13	0.156	0.679	97.963						
14	0.134	0.584	98.548						
15	0.104	0.454	99.001						
16	0.064	0.279	99.281						
17	0.056	0.244	99.525						
18	0.040	0.173	99.697						
19	0.035	0.152	99.849						
20	0.019	0.082	99.931						
21	0.009	0.038	99.969						
22	0.005	0.024	99.993						
23	0.002	0.007	100.000						

Table 4-24 shows the loadings of the five retained components after rotation. Only loadings ≥ 0.2 or ≤ -0.2 are shown, as these are likely to be significant (Hopke, 1989). The loadings of species used to interpret a source are marked with grey shading. The physical interpretation of the principal components is given at the foot of each column in Table 4-24, and this interpretation is explained more fully in the following paragraphs.

Principal Component 1: This component had the highest loading for PM₁₀. It also had loadings for the phenanthrenes, which are constituents of diesel exhaust (Rogge *et al.*, 1993) and have been used as tracers to identify this source in other studies (Harrison *et al.*, 2003). Other PAHs present in diesel exhaust also had high loadings (around 0.8) on this component. The component was therefore interpreted as the diesel exhaust source.

Principal Component 2: This component had very high loadings for PAHs relating to petrol exhaust, such as benzo[a]pyrene, indeno[1,2,3-cd]pyrene and coronene. The component was therefore interpreted as the petrol exhaust source.

Principal Component 3: This component had loadings of more than 0.9 for Ca, Al and Ba. These elements, particularly Ca and Al, are reasonably reliable tracers for crustal material. It was shown in Table 4-18 that Ca and Al were present in high concentrations in the deposited dust collected in the tunnel. This component also has minor loadings for many other metals. The component was therefore interpreted as resuspended soil.

Principal Component 4: This component had the highest loading for benzothiazole, which was been identified as an organic tracer for tyre wear particles, and also had a significant loading for Zn the metal that has been used as inorganic tracer for this source (Ahlbom and Duus 1994, Fauser 1999). However, this component also had significant loadings for Sb and Cu, which are constituent elements of brake linings, and loadings of 0.3 or more for PAHs that are present in tyre and brake wear particles. The component was therefore interpreted as mixed tyre and brake wear source, and it was not possible to resolve separate tyre and brake wear contributions.

Principal Component 5: This component had the highest loadings for two metals, Ni and V. Both these metals have been considered as relevant tracers of refuse oil burning (Lioy *et al.*, 1985). However, there were clearly no major sources of refuse oil burning in the tunnel. Asphalts, on the other hand, are composed of a mixture of mineral aggregates, sands, fillers and bitumen binder, and bitumen is the crude residue of fossil fuel. It has therefore been assumed that V and Ni appearing together in this way points to road surface wear as the source relating to this component. The loadings on the component agree reasonably well with the source profiles of the asphalt constituents given in Table 2-7. There were also minor loadings for a number of PAHs, which are associated with fossil fuel, of which coal tar is a crude end product. Therefore, the component was interpreted as a road surface wear source.

Table 4-24: Rotated component matrix.

	Component				
	1	2	3	4	5
PM ₁₀	0.577	0.241	0.243	0.485	0.416
phenanthrene	0.812	0.218		0.401	0.295
anthracene	0.737	0.281		0.335	0.222
2-methylphenanthrene	0.814	0.223		0.381	0.267
1-methylphenanthrene	0.830			0.358	0.258
3,6-dimethylphenanthrene	0.846	0.227		0.305	0.222
benzo[a]fluorene	0.787	0.386		0.313	0.220
benzo[b]fluorene	0.808				
benzo[ghi]fluoranthene	0.438	0.699		0.359	
benz[a]anthracene	0.379	0.711			
benzo[a]pyrene	0.310	0.881			
coronene		0.817	-0.242		
indeno[1,2,3-cd]pyrene	-0.246	0.891			
Ca			0.905		0.262
Al			0.964		
Ba			0.932		
benzothiazole				0.854	
Zn	0.521	0.263	0.388	0.381	
Cu	0.673		0.203	0.443	0.296
Sb	0.683	0.235		0.420	
Ti			0.353	0.679	0.245
Ni			0.371		0.584
V					0.905
Eigenvalue	6.64	3.90	3.39	2.97	2.06
% variance	28.88	16.94	14.72	12.90	8.96
Assigned Source	Diesel exhaust	Petrol exhaust	Resuspended soil	Tyre & brake wear	Road surface wear

4.5.2 Multiple linear regression analysis (MLRA) on absolute principal component scores

Absolute Principal Component Scores (APCS) were obtained according to the methodology suggested by Thurston (1983). These APCS are proportional to the impact of each source for the sample in question. MLRA was performed using PM_{10} as the dependent variable and the APCS as independent variables. The model summary for this MLRA is given in Table 4-25, and Table 4-26 gives the coefficients of the independent variables. The R square value for the regression is significant at 99.9% level indicating a good fit.

Table 4-25: Model summary of MLRA (dependent variable PM_{10} , predictor variables constant, Absolute Principal Component Scores for components 1-5).

R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
				R Square Change	F Change	df1	df2	Sig. F Change
0.909	0.827	0.809	5.2	0.827	46.785	5	49	0.000

Table 4-26: Coefficients of predictor variables ($\mu\text{g}/\text{m}^3$).

Assigned sources	Unstandardized Coefficients		Standardized Coefficients	t	Sig. Level	
	B	Std. Error	Beta			
(Constant)	Unidentified	2.152	2.023		1.064	0.293
APCS1	Diesel Exhaust	6.954	0.751	0.551	9.253	0.000
APCS2	Petrol exhaust	3.135	0.705	0.265	4.448	0.000
APCS3	Resuspension	4.423	0.952	0.277	4.647	0.000
APCS4	Tyre & brake wear	8.983	1.173	0.466	7.661	0.000
APCS5	Road surface wear	3.522	0.744	0.288	4.734	0.000

The regression equation constructed from these coefficients is:

$$PM_{10} = 2.2 + 7(de) + 3.1(pe) + 4.4(rs) + 9(tb) + 2.5(rsu) \quad \text{Equation 4-2}$$

Where: *de* = diesel exhaust
pe = petrol exhaust
rs = resuspended soil
tb = tyres and brakes
rsu = road surface

Table 4-27 shows the contribution of each identified source and the constant (representing unidentified sources). The contributions were obtained by multiplying the regression coefficient for the source and its average principal component score. The largest percentage contribution to PM_{10} was from the diesel exhaust source, and lowest contribution from resuspended soil and unassigned sources. The two exhaust sources combined amounted to almost 47% of all contributions. The non-exhaust sources accounted for 46% of all PM_{10} , and around 8% of total PM_{10} mass remained unaccounted for.

Table 4-27: Contribution from identified sources to measured tunnel increment PM₁₀.

	Constant (unidentified)	Diesel exhaust	Petrol exhaust	Resuspended soil	Tyre and brake wear	Road surface wear
Coefficient (µg/m ³)	2.15	6.95	3.14	4.42	8.98	3.52
Avg. PC score		0.98	1.88	0.66	0.69	0.95
Contribution (µg/m ³)	2.15	6.82	5.88	2.93	6.16	3.33
% contribution	7.9	25.0	21.6	10.7	22.6	12.2

4.5.3 Derivation of emission factors

The total PM₁₀ emission factor for each source was obtained by applying Equation 3-1 to each of the 54 paired PM samples collected inside the tunnel. The total PM₁₀ emission factor for each sample was then apportioned using the fractional contributions of the identified sources from Table 4-27. The descriptive statistics for the estimated emission factors are given in Table 4-28. The emission factors for two exhaust sources, diesel and petrol, have been combined. The average emission factor for total PM₁₀ was 48.4 mg/vkm, with a range of 11-98 mg/vkm. The highest emission factor for a single source was that for exhaust emissions, at 22 mg/vkm. The emission factor for the combined tyre and brake wear source was 11 mg/vkm while, the emission factors for the two remaining non-exhaust sources, resuspended soil and road surface wear, were each around 6 mg/vkm. Unidentified sources were responsible for 4.3 mg/vkm. This Table shows that, at this site, the exhaust and non-exhaust emissions were roughly equivalent. This highlights the importance of non-exhaust emission sources, with obvious implications for policy and control of PM₁₀ in urban areas.

Table 4-28: Descriptive statistics of the estimated emission factors, mg/vkm, (number of samples = 54).

	Constant	Exhaust emissions	Resuspended soil	Tyre & brake	Road surface	PM ₁₀
Mean	4.3	21.8	5.7	10.7	5.9	48.4
Standard Error	0.3	1.1	0.9	1.1	0.8	1.9
Median	3.6	21.8	4.1	11.6	4.0	49.9
Standard Deviation	2.1	8.1	6.8	7.8	5.7	13.7
RSD %	49.8	37.2	117.7	73.3	96.0	28.4
Minimum	1.1	5.5	0.0	0.0	0.0	11.3
Maximum	11.2	36.5	38.9	29.6	26.0	98.9
95% conf. interval on mean	0.6	2.2	1.8	2.1	1.6	3.8

Given that the traffic composition had been recorded in the tunnel at the time of the measurements, it was also possible to estimate separate emission factors for LDVs and HDVs for each source using further multiple regression analyses. The results of these analyses are shown in Table 4-29. For each source the regression equation is:

$$E_{tot} = \text{constant} + (e_{LDV} \cdot N_{LDV}) + (e_{HDV} \cdot N_{HDV}) \quad \text{Equation 4-3}$$

Where:

E_{tot}	=	Total emissions from the traffic contributing to the PM ₁₀ sample (mg/km)
N_{LDV}	=	Number of HDVs
N_{HDV}	=	Number of LDVs
e_{LDV}	=	Emission factor for LDVs (mg/vkm)
e_{HDV}	=	Emission factor for HDVs (mg/vkm)

An attempt was made to split the LDV component into the petrol and diesel fractions using national fleet composition data for the motorways. This analysis therefore included three independent variables: HDV, LDV_{petrol} and LDV_{diesel}. However, the LDV_{petrol} component was not found to be significant.

Table 4-29: Model summary and coefficients by PM₁₀ source and vehicle type.

Source	Variables		Model summary				Coefficients					
							Unstandardized coefficients		Standardized coefficients	t	Sig.	
	Dependent variable	Independent variables	R	R ²	Adjusted R ²	Std. error of estimate	B	Std. err.	Beta			
Exhaust	TOT_EXEM	LDV, HDV	0.940	0.884	0.879	114482.3	Constant	1062	31788		0.033	0.973
							LDV	13.9	3.114	0.489	4.449	0.000
							HDV	79.3	18.197	0.479	4.355	0.000
Resuspension	TOTRESUS	LDV, HDV	0.592	0.351	0.310	49775.3	Constant	59983	15266		3.929	0.000
							LDV	0.8	1.771	0.152	0.447	0.658
							HDV	14.4	10.774	0.451	1.333	0.192
Tyre and brake wear	TOT_TRBR	LDV, HDV	0.821	0.674	0.657	123293.3	Constant	5057	38520		0.131	0.896
							LDV	6.9	3.786	0.375	1.814	0.078
							HDV	49.7	21.945	0.468	2.263	0.029
Road surface wear	TOT_RDSR	LDV, HDV	0.610	0.372	0.344	122557.3	Constant	2647	34755		0.076	0.940
							LDV	3.1	3.368	0.244	0.934	0.355
							HDV	29.0	19.831	0.382	1.465	0.150

TOT_EXEM = Total exhaust emissions for the sample
TOTRESUS = Total emissions for the sample from resuspension
TOT_TRBR = Total emissions for the sample from tyre & brake wear
TOT_RDSR = Total emissions for the sample from road surface wear
LDV = Number of LDVs (EUR CS2 & CS3, all cars and vans) for the sample
HDV = Number of HDVs (CS4-CS6, all HGVs and buses) for the sample

The *B* coefficients in Table 4-29 (the shaded values) can be treated as the emission factors for LDVs and HDVs. For example, the PM₁₀ emission factors for exhaust emissions from LDVs and HDVs were found to be 13.9 mg/vkm and 79.3 mg/vkm respectively.

It is important to note that some of these results, particularly those for the non-exhaust sources, ought to be treated with caution as they are not significant at the 95% confidence level. However, even the non-significant results should provide a reasonable estimate of the magnitude of the emission factors, albeit under a fairly limited range of vehicle operation conditions.

4.5.4 Comparison with results from other sources

4.5.4.1 Exhaust emissions

The emission model in the UK Design Manual for Roads and Bridges (Highways Agency, 2003) was used to estimate emissions for the traffic in the Hatfield Tunnel at the time of the study. The emission factors used in the DMRB are based on emission tests conducted in the laboratory, and for PM they are identical to those used in the NAEI 2002 edition. The modelling took into account the traffic composition and speed during each PM sampling period. The average modelled fleet-weighted emission factor was 61.5 mg/vkm, almost three times higher than the fleet average emission factor derived in the Hatfield Tunnel (21.8 mg/vkm).

The PM₁₀ emission factors for exhaust emissions from LDVs and HDVs in the Hatfield Tunnel were found to be 13.9 mg/vkm and 79.3 mg/vkm respectively. These values are compared with the exhaust emission factors for UK vehicles on motorways, derived from the NAEI (2003), in Tables 4-30 and 4-31.

Table 4-30: Particulate exhaust emission factors (mg/vkm by legislative class).

	Pre-Euro I	Euro I	Euro II	Euro III	Euro IV
Petrol Car	18.0	8.8	5.3	5.3	5.3
Diesel Car	188.2	85.6	63.2	44.2	22.1
Petrol LGV	68.2	14.1	4.7	4.7	4.7
Diesel LGV	401.4	217.6	217.6	174.1	106.6

Source: NAEI (2003).

Table 4-31: Particulate exhaust emission factors for motorways (mg/vkm by legislative class).

	Pre-1988 models	1988 - 1993 models	Euro I	Euro II	Euro III	Euro IV	Euro IV+ (2008)
HGV rigid	853.4	408.5	210.6	127.5	91.8	19.1	19.1
HGV artic	580.1	508.4	554.0	331.9	239.0	49.8	49.8
Buses	655.4	284.3	198.0	120.2	86.6	18.0	18.0

Source: NAEI (2003)

Most LDVs in the Tunnel would have been mainly petrol passenger cars, with the remainder being diesel cars and diesel LGV. Euro I to Euro III technologies would have dominated the fleet. The average emission factor for LDVs, estimated using DMRB based on national fleet composition statistics for motorways, was 33.0 mg/vkm. HGVs would have been mainly Euro II technology, with the remainder being Euro I and Euro III. The average emission factor for HDVs, estimated using DMRB, was 254.2 mg/vkm, more than a factor of three higher than the Hatfield Tunnel estimate. It is worth highlighting here that the traffic measurements reported in this study indicate that the fleet composition on A1(M) is different to the national fleet in some respects, in particular the relative proportions of rigid and articulated HGVs (Section 4.1.3.2).

4.5.4.2 Tyre and brake wear

The PM₁₀ emission factors for combined tyre and brake wear emissions from LDVs and HDVs in the Hatfield Tunnel were found to be 6.9 mg/vkm and 49.7 mg/vkm respectively. These values are compared with values from the literature in Table 4-32. For LDVs, typical values for tyre wear reported in the literature are between 5 and 13 mg/vkm, and values for brake wear are between 1.0 and 7.8 mg/vkm. The combined tyre and brake wear emission factor from the Hatfield Tunnel study of 6.9 mg/vkm appears to be at the lower end of the range of values reported elsewhere. For HDVs, a wide range of tyre wear and brake wear values have been found in the literature: 7.5-200 mg/vkm for LDVs, and 0 to 610 mg/vkm for HDVs. The combined value in the Hatfield Tunnel study was 49.7 mg/vkm, and again this is towards the lower end of the range of reported values. According to Abu-Allaban *et al.* (2003), brake wear emissions of PM in tunnels are minimal, as vehicles tend to be operated in a 'steady-state' mode.

Table 4-32: Comparison of PM₁₀ emission factors for tyre and brake wear.

Study	Method/comments	Vehicle category	PM ₁₀ emission factor (mg/vkm)		
			Brake wear	Tyre wear	Combined brake & tyre wear
<i>This study</i>	<i>Tunnel measurements and PCA</i>	<i>Fleet in Hatfield Tunnel</i>			10.7
		<i>LDV</i>			6.9
		<i>HDV</i>			49.7
<u>Tyre wear – light -duty</u>					
USEPA (1995)		LDV		5.0	
Rauterberg-Wulff (1999)	Tunnel measurements	LDV		6.1	
EMPA (2000)		LDV		13.0	
<u>Tyre wear – heavy -duty</u>					
USEPA (1995)		HGV rigid		7.5	
USEPA (1995)		HGV articulated		22.5	
Rauterberg-Wulff (1999)	Tunnel measurements	HDV		31	
EMPA (2000)		HDV		200	
<u>Brake wear – light -duty</u>					
Cha <i>et al.</i> , 1983	Asbestos brakes	LDV	7.8		
Rauterberg-Wulff (1999)	Tunnel measurements	LDV	1.0		
Carbotech (1999)		LDV	1.8-4.9		
Garg <i>et al.</i> (2000b)	Wheel dynamometer	LDV	2.9 - 7.5		
Westerlund (2001)		LDV	6.9		
Abu-Allaban <i>et al.</i> (2003)	Roadside measurements and CMB		0-79		
<u>Brake wear – heavy-duty</u>					
Rauterberg-Wulff (1999)	Tunnel measurements	HDV	24.5		
Carbotech (1999)		HDV	3.5		
Cadle <i>et al.</i> (2000)	Wheel dynamometer	HDV	7.6		
Westerlund (2001)		HDV	41.2		
Abu-Allaban <i>et al.</i> (2003)	Roadside measurements and CMB	HDV	0-610		

4.5.4.3 Resuspension

Table 4-33 compares the emission factors estimated in this Hatfield Tunnel with values from other studies, although given the extremely wide range of values quoted in the literature for this particle source, no conclusions have been drawn from the comparison. It is very difficult to derive general emission factors for resuspension, as it is strongly related to local conditions, and the method used to determine resuspension emission factors is undoubtedly crucial.

Table 4-33: Comparison of PM₁₀ emission factors for resuspension.

Study	Method/comments	Vehicle category	PM ₁₀ (mg/vkm)
<i>This study</i>	<i>Tunnel measurements and PCA</i>	<i>Fleet in Hatfield Tunnel</i>	5.7
		<i>LDV</i>	0.8
		<i>HDV</i>	14.4
Nicholson (2000)			40.0
USEPA (1993)		LDV	0.28-0.79
		HDV	6.93
Abu-Allaban <i>et al.</i> (2003)	Roadside measurements and CMB	LDV	2247
		HDV	224

4.5.4.4 Road surface wear

Only limited information on PM emission factors arising from road surface wear is available in the literature. The PM₁₀ values obtained in the Hatfield Tunnel are compared with the results from other studies in Table 4-34. The comparison is not necessarily direct – it is not always clear exactly what is being defined in terms of ‘road surface’ particles, and in some studies these may include resuspended particles.

Table 4-34: Comparison of PM₁₀ emission factors for road surface wear.

Study	Method/comments	Vehicle category	PM ₁₀ (mg/vkm)
<i>This study</i>	<i>Tunnel measurements and PCA</i>	<i>Fleet in Hatfield Tunnel</i>	5.9
		<i>LDV</i>	3.1
		<i>HDV</i>	29.0
CBS (1998)	Includes tyre, brake and road surface wear	LDV	7-9
		HDV	38
Muschack (1990)			3.8*

* PM rather than PM₁₀

5 Summary, conclusions and recommendations

The research work presented in this Report was carried as a part of the EU PARTICULATES project to derive a set of emission factors for the non-exhaust sources of road transport, with particular emphasis on tyre wear, brake wear, road surface wear and resuspended dust.

The subject of non-exhaust particles was explored in an initial literature review, and the review helped to define the scope of the experimental work in the project. In the first stage of the experimental work the wear rates for the tyres and brakes of in-service vehicle were estimated by weighing components at regular time intervals.

Samples of source materials (tyre tread, brake lining and brake dust), ambient airborne particles and road dust were then chemically and physically characterised using a suite of techniques (ICP/MS, GC/MS and SEM). The results of these preliminary campaigns were used to refine the sampling and analytical methodologies for estimating emission factors of non-exhaust particle sources. In order to identify sources of airborne particles, to apportion particles to these sources, and to estimate appropriate emission factors, a receptor modelling approach was selected, and a main measurement campaign was designed based on various preliminary measurements.

The preliminary measurements showed that the sampling of particles in ambient air using conventional low- or medium-flow equipment would not provide a sufficient mass of particles, or sufficient temporal resolution, for reliable source apportionment, especially for organic compounds present in low concentrations, unless sampling durations are of the order of several weeks. The work also showed that the main campaign would have to be conducted at a location where particle concentrations were high. A road tunnel was selected because of the limited dispersion and dilution conditions (and elevated particle concentrations) associated with such an environment.

5.1 Literature review

Typical tyre wear rates of between 10 mg/tyre/km and 90 mg/tyre/km have been reported in the literature for passenger cars. Both fine and coarse particles are emitted to the atmosphere as a result of tyre wear, but not all of the worn tyre material is emitted as airborne PM, and some much coarser tyre shreds will also be removed. The distribution of the wear material between the different particle size modes appears to be rather variable. It has been shown that mean particle diameter decreases with increasing speed, and this may be one of a number of factors contributing to the variability of the results. Also for high-wear locations such as corners, there is evidence to suggest that although the absolute level of tyre wear is high, the proportion (by mass) of finer particles is lower than at other locations. PM₁₀ appears to be released from tyres at a rate of between 5 and 13 mg/vkm for light-duty vehicles. This suggests that up to around 30% by mass of LDV tyre wear material is emitted as PM₁₀, but much higher proportions have been reported in some studies. It appears that tyre wear generally accounts for less than 10% of the PM₁₀ measured in roadside air, and less than 5% of road dust mass. Chemical species used to trace tyre wear debris in the urban atmosphere have included benzothiazole compounds, styrene butadiene rubber, zinc, and extractable organic zinc. It has also been noted that, for the *n*-alkanes $\geq C_{35}$, there are few urban emission sources other than tyre wear.

The wear rate of brake linings for passenger cars has been estimated to be around 10-20 mg/vkm, and several times higher for heavy-duty vehicles. It appears that a much larger proportion of brake wear material than tyre wear material is emitted as airborne PM, but exact emission factors for different size fractions are difficult to determine because significant amounts of wear material appear to be retained on the brake, steering and suspension systems. However, PM₁₀ emission factors of up to 79 mg/vkm have been reported for light-duty vehicles, and up to 610 mg/vkm for heavy-duty vehicles, the latter value being considerably higher than the highest *total* brake wear rate reported in the literature. Although reasonably detailed information on the composition of brake linings and brake wear particles has been reported, no strong evidence was found in the literature of reliable tracer species for brake wear particles.

It is possible that the lack of information on clutch wear and emission factors will have ramifications for the source apportionment of particulate matter via emission inventories and receptor modelling, and represents an area of uncertainty. However, the enclosed nature of the clutch mechanism probably means that much of the wear material is retained inside the housing. In any case, clutch wear as a source of particles warrants further investigation. As with brake wear particles, there appears to be no information in the literature which would help to define clutch wear emissions.

Asphalt wear has been estimated to be between 3.8 and 38 mg/vkm. One study showed that airborne particles ranged in size between 0.35 μm and 2.8 μm . In areas with extensive use of studded tyres the wear of the road surface is considerably greater during winter, and wear rates of between 11 and 24 g/vkm have been reported. It has been suggested that some of the largest molecules present in the atmosphere - maltenes and asphaltenes - could be used as tracers for road surface wear. Unsuccessful attempts have been made to derive useable fingerprint profiles for bitumen using the PAH components or the polar, aromatic and aliphatic fractions of bitumen as tracers for road wear.

At present, atmospheric emission inventories tend not to include the resuspension of road dust as a particle source due to the absence of reliable emission factors and the possibility of double counting of sources. However, recent studies in the United States have suggested that the resuspension of paved road dust contributes significantly to atmospheric PM_{10} and $\text{PM}_{2.5}$ concentrations. It has been estimated that resuspension of road dust accounts for a net release of 40 mg/vkm PM_{10} in the UK.

5.2 Measurement of tyre and brake wear rates

The average wear rate of tyre material per passenger car was found to be 97 mg/vkm (74 mg/vkm for the front-wheel drive cars, and 193 mg/km for the rear-wheel drive car). Given the problems associated with the rear-wheel-drive vehicle during the tests, and the market dominance of front-wheel-drive cars, the average wear rate of 74 mg/km for the other four vehicles is probably more representative of the fleet. This value indicates a wear rate for individual tyres that would be towards the lower end of the range of values observed in the literature. Front tyre wear accounted for between 69% and 85% of total tyre material lost per vkm for front-wheel drive vehicles, depending on the vehicle. The average brake wear per vkm was around 9 mg, again towards the lower end of the range of values observed in the literature, although the wear rates of individual brake pads, and indeed the totals for the five vehicles, were very variable. It was found that the wear of the front brakes accounted for between 77% and virtually 100% of total brake material lost per vkm.

There was a weak negative correlation between tyre wear and average trip speed between tests for the four front-wheel drive cars. The observed decrease in tyre wear with increasing trip speed appears to contradict some previous laboratory studies (*e.g.* Dannis, 1974; Saki, 1996). One explanation for this maybe that the average speeds reported here include a wide range of operational modes, including accelerations, decelerations and idling, whereas in laboratory studies steady speeds were used. Furthermore, low-speed driving tends to be associated with more stopping, starting and turning than high-speed-driving. Stalnaker *et al.* (1996) simulated the effects of different driving conditions on the wear of tyres, and found that the city driving accounted for 63% of the tyre wear, even though it represented only 5% of the distance driven. The variability in the data will also have been increased by various factors, including the different absolute weights of the tyres and wheels of the vehicles, different rubber compounds, different road surfaces and the weather. There was also weak negative relationship between brake wear and average trip speed between tests for the cars. Given the observed reduction of tyre and brake wear with increasing trip speed, it could be argued that the comparatively low mean tyre and brake wear rates measured in the study may simply reflect the fact that most of the distance covered by the test vehicles was driven on motorways.

The average wear rates observed in this study, 74 mg/vkm for tyres and 9 mg/vkm for brakes. These values can be compared with the 2000 and 2005 Type Approval exhaust emission limits for total particulate matter from diesel light-duty vehicles of 50 mg/vkm and 25 mg/vkm respectively. There are currently no legal requirements for the control of exhaust particle emissions from light-duty petrol vehicles (particle mass emissions from such vehicles are very low). Given that all road vehicles are potential sources of tyre and

brake wear particles, this illustrates the potential scale of emissions from these sources. However, it should also be noted that not all of the worn tyre and brake material will have been emitted as airborne particles. Some tyre rubber may have been deposited directly onto the ground as coarse shreds, or as larger particles which rapidly fall out of the atmosphere, and many of the wear particles from the rear brakes of vehicles fitted with drums will probably be retained in the mechanism.

5.2 Preliminary sampling and characterisation

5.2.1 Chemical characterisation of source materials

For tyre material, the metal concentrations observed in the initial exploratory analysis agreed reasonably well with the ranges reported in the literature. In particular, there was found to be a relatively high abundance of Zn in the tyre material. However, the potential use of zinc as a tyre wear tracer is confounded by the existence of many other sources.

Metal concentrations in new brake material and brake dust were generally of the same order of magnitude, though concentrations tended to be higher in the brake dust samples. It is possible that this was a consequence of incomplete digestion of the new brake lining material. The concentrations of some metals (notably Ba, Cu, Pb and Sb) were considerably lower than those found in the literature. For other metals, including Cr, Ni and Sr, there was a better agreement with the values in the literature. Relative to their concentrations in the tyre material, metals having substantially higher concentrations in the brake lining and brake dust samples included Ba, Cr, Sb, Sr and Zr, and it may be possible to use these metals as tracers for tyre and brake wear particles in the environment. However, as with zinc some of these metals do have other sources, and hence the use of metal concentrations alone will not allow for a definitive identification a particular source. The ratios of metal concentrations may be more likely to be identifiable with particular source categories, though some of the ratios obtained in this study were very different to those obtained in some other studies.

A semi-quantitative analysis of organic compounds in brake dust and road dust samples revealed the presence of a PAHs, and provided some evidence to support the use of benzothiazole as a tracer compound for tyre wear.

Although a small amount of information on the chemical characterisation of such source materials has been obtained in this study, the research in this area is far from advanced. Clearly, much more information is required for PM source apportionment studies.

5.2.2 Analysis of airborne PM at background and roadside

Preliminary gravimetric measurements of ambient PM₁₀ and PM_{2.5} concentrations were carried out at the roadside and background sites at the University of Hertfordshire and Westminster, London. During the first campaign the PM₁₀ concentrations at the background and roadside UH sites were, rather unexpectedly, very similar. The similarity of the results may have been linked to the influence of construction work activity in the vicinity of the background site. In addition, the overall traffic flows during the sampling period were particularly low. During the second campaign, measurements were conducted at a roadside site in London where the traffic flows were substantially higher. The PM₁₀ and PM_{2.5} concentrations measured at the UH roadside site were higher than the background site by 23% and 40% respectively. The differences between the roadside and background concentrations at the London sites were much more pronounced, with the PM₁₀ concentration at the roadside being a factor of 2.8 higher than at the background site, and the PM_{2.5} concentration being almost six times higher. The observed PM₁₀ mass concentrations at the Oxford Street roadside was twice as high as the concentration at the UH roadside site, with the concentrations at both background sites being comparable.

Analysis of the PM₁₀ samples collected at the background and roadside sites showed that most of the metal concentrations were significantly higher at the roadside sites compared with the background sites. At this stage it was not possible to quantify the contributions from the various traffic sources to the measured metal levels. Ratios between the concentrations of various metals in the ambient particles were compared with the

ratios in the raw source material, and a close agreement was observed between the Ba/Sb ratio in the brake material and that at the London roadside site, a site where braking is a routine throughout the day. A similar agreement for the tyre material could not be found for the ratios of the measured metals. As these are preliminary results the data are not conclusive as to the usefulness of elemental ratios as possible markers for non-exhaust emission sources. However, when combined with organic tracers then they should allow identification of the main non-exhaust sources.

Physical characterisation of the ambient and source material samples using SEM has given some qualitative information regarding the relative abundance of various elements in these matrices. Brake pad particle showed relatively larger peaks for C, K, P, S, Ca and Ba which is in reasonable agreement with the composition reported by Hildemann *et al.*, 1991 except for P which was not observed by these authors. Tyre particle, as expected, show the largest peak for C which makes over 50% of the particle matrix with other major peaks for S and K also being detected. Benzothiozole, which is recommended as a tracer for tyre material, will also contribute to the S signal. The analysis of spectra from ambient particles, 2 and 5 μm , show clear differences in their composition while in 2 μm C is the most dominant peak, indicating its carbonaceous origin whilst the 5 μm particle appears to be richer in metals such as Fe along with C indicating a mixed origin.

5.3 Tunnel measurements

In order to obtain enough particle material for reliable chemical analysis, long sampling durations would normally be required. However, in order to determine emission factors receptor models require a high temporal resolution to distinguish the influence of traffic variation during the sampling period. These factors had to be considered in the design of a suitable sampling methodology for the main campaign. In order to achieve an optimum balance between particle mass and temporal resolution, high volume sampling techniques were employed in a tunnel environment. In this study, PM emission factors were derived from measurements conducted in the Hatfield Tunnel.

PM₁₀ and deposited dust samples were collected at two locations in the B tube of the tunnel, the entrance and the exit. Each PM₁₀ sample was collected during a nominal 12-hour period, and 54 paired samples were obtained in total. Induction loops permanently installed in the road surface of the tunnel were used for the purpose of characterising the traffic. The air flow velocity in the tunnel was required for the emission factor calculation, and this was recorded continuously using a Flowsic 200 ultrasonic device. The concentrations of metals in the PM₁₀ and deposited dust samples were determined using ICP/AES and ICP/MS

Emission Factors were derived using the ‘multiple regression on absolute principal component scores’ technique to identify sources and quantify their contributions.

5.3.1 Measured data

The diurnal traffic profiles between weekdays and between weekend days did not differ significantly. The average total traffic flows on weekdays, Saturdays and Sundays were around 49000, 34000 and 33000 respectively (B tube only). During weekdays there was a large morning peak spread over the hours between 06:00 and 12:00, with a maximum traffic flow of more than 2500 vehicles per hour associated mainly with commuters travelling to London. The evening peak in the B tube is less pronounced, principally because commuters travelling home use the other tunnel tube. On weekends there was a broader traffic peak associated with social trips and shopping activities.

The extent to which the traffic composition in the Hatfield Tunnel was representative of the UK motorway network was examined by comparison with the fleet composition for motorways in 2002 used in the National Atmospheric Emissions Inventory. The total proportion of cars and vans in the Hatfield Tunnel was almost identical to the national average. However, the two vehicle categories that could be compared directly (rigid and articulated HGVs) showed significant differences. This will have had an influence on the estimated HDV emission factors, as the emission of particles tend to be higher from articulated HGVs than from rigid HGVs.

The PM₁₀ concentrations measured at the tunnel exit were typically around 60% higher than those measured at the tunnel entrance. The average PM₁₀ concentration inside the tunnel was several times higher than the typical PM₁₀ concentration measured at the roadside location at the nearby University of Hertfordshire campus, although the comparison was somewhat confounded by the effect of sampling during different seasons. The tunnel increment in the PM₁₀ concentration – the difference between the concentration at the tunnel exit and that at the tunnel entrance - varied between 12 and 52 µg/m³. This variability was used to determine the correlation between traffic conditions and traffic-generated PM₁₀.

The various metals analysed in the PM₁₀ samples from the tunnel only accounted for 18.8% (tunnel entrance) and 13.8% (tunnel exit) of the total PM₁₀ mass. It is expected that the bulk of the PM₁₀, around 50%, will comprise of elemental and organic carbon and the other significant component will be secondary aerosol, SO₄²⁻, NO₃⁻, and NH₄⁺. The ratios of the metal concentrations at the tunnel entrance and exit were calculated. For the species having predominant natural sources (*e.g.* Ca, Na, Mg, K, Al) the ratio was close to unity, whereas species associated predominantly with anthropogenic sources had higher ratios.

The quantified species included 31 PAHs and benzothiozole. However, it should again be noted that the mass contribution of these species towards PM₁₀ was negligible. The most important quantified species in terms of mass included pyrene, benzo[ghi]perylene, fluoranthene, cyclopenta[cd]pyrene, triphenylene, chrysene, benzo[ghi]fluoranthene, benzo[a]pyrene, phenanthrene, 2-methylphenanthrene and indeno[1,2,3-cd]pyrene. PAH concentrations measured at tunnel exit were consistently higher than those measured at the tunnel entrance.

Four samples of deposited dust were collected in the tunnel – two at the tunnel entrance and two at the exit. The deposition rates at the tunnel entrance during the two measurements were 146.4 µg/m²/min and 119.4 µg/m²/min. The deposition rates at the tunnel exit were lower, at 86.5 µg/m²/min and 70.7 µg/m²/min. The overall average dust deposition rate was 106 µg/m²/min. It is important to note that this values is based on the filters which were placed alongside other sampling equipment on the walkway at a height of about 1.5 m from the road surface. The dust deposit rate for the actual road surface may well have been higher. Two filters were analysed for metals, and two for organic constituents. Ca, K, Fe and Al were present in quite high concentrations. Amongst the organic species, fluoranthene, pyrene, triphenylene/chrysene and benzo[ghi]perylene were present in relatively higher proportions in the analysed dust.

5.3.2 Determination of emission factors

Principal Component Analysis was performed on the tunnel increment data. Twenty three variables, PM₁₀, 12 PAHs, Benzothiozole and nine metals were included in the analysis. Five principal components (PM sources) were identified:

- diesel exhaust
- petrol exhaust
- resuspended dust
- combined brake and tyre wear
- road surface wear

Separate emission factors were estimated for LDVs and HDVs for each source (except petrol exhaust) using further multiple regression analyses. These are listed below, but it is important to note that some of these results, particularly those for the non-exhaust sources, ought to be treated with caution as they are not significant at the 95% confidence level. However, even the non-significant results should provide a reasonable estimate of the magnitude of the emission factors, albeit under a fairly limited range of vehicle operation conditions.

The PM₁₀ emission factors for exhaust emissions from LDVs and HDVs were found to be 13.9 mg/vkm and 79.3 mg/vkm respectively. The emission model in the DMRB was used to estimate emissions for the traffic in the Hatfield Tunnel at the time of the study. The modelling took into account the traffic composition and

speed during each PM sampling period. The average modelled fleet-weighted emission factor was 61.5 mg/vkm, almost three times higher than the fleet average emission factor derived in the Hatfield Tunnel (21.8 mg/vkm).

The PM₁₀ emission factors for combined tyre and brake wear emissions from LDVs and HDVs in the Hatfield Tunnel were found to be 6.9 mg/vkm and 49.7 mg/vkm respectively. Both these values are towards the lower ends of the ranges values reported in the literature. One reason for this may be that vehicles tend to be operated in a 'steady-state' mode inside tunnels.

The emission factors for resuspension were 0.8 mg/vkm for LDVs and 14.4 mg/vkm for HDVs. There is an extremely wide range of values quoted for resuspension in the literature. It is very difficult to derive general emission factors for resuspension, as it is strongly related to local conditions, and the method used to determine resuspension emission factors is crucial.

For road surface wear, the LDV and HDV emission factors were found to be 3.1 mg/vkm and 29.0 mg/vkm respectively. No direct comparison could be made with the values reported in the literature, mainly because it is not always clear exactly what is being defined in terms of 'road surface' particles, and in some studies these may include resuspended particles.

6 Conclusions and recommendations

6.1 Conclusions

Material loss rates: literature

- Typical tyre wear rates of between 10 mg/tyre/km and 90 mg/tyre/km have been reported in the literature for passenger cars. Both fine and coarse particles are emitted to the atmosphere as a result of tyre wear, but not all of the worn tyre material is emitted as airborne PM, and some much coarser tyre shreds will also be removed.
- According to the literature, the wear rate of brake linings for passenger cars has been estimated to be around 10-20 mg/vkm, and several times higher for heavy-duty vehicles. A much larger proportion of brake wear material than tyre wear material is emitted as airborne PM.
- Asphalt wear has been estimated to be between 3.8 and 38 mg/vkm. In areas with extensive use of studded tyres the wear of the road surface is considerably greater during winter, and wear rates of between 11 and 24 g/vkm have been reported.

Material loss rates: experimental work in the study

- In tests, the most representative average wear rate of tyre material was found to be 74 mg/vkm. The average tyre wear value was towards the lower end of the range of values observed in the literature. Front tyre wear accounted for between 69% and 85% of total tyre material lost per vkm for front-wheel drive vehicles.
- The average brake wear per vkm was around 9 mg, again towards the lower end of the range of values observed in the literature, although the wear rates of individual brake pads, and indeed the totals for the five vehicles, were very variable. It was found that the wear of the front brakes accounted for between 77% and virtually 100% of total brake material lost per vkm.
- There was a weak negative correlation between tyre wear and average trip speed between tests for the four front-wheel drive cars. This may have been due to the nature of low-speed driving, which involves more stopping, starting and turning than high-speed driving. There was also weak negative relationship between brake wear and average trip speed between tests for the cars, probably for similar reasons.

Characterisation of source materials and tracer identification

- According to the literature, the chemical species used to trace tyre wear debris in the urban atmosphere have included benzothiazole compounds, styrene butadiene rubber, zinc, and extractable organic zinc. It has also been noted that, for the *n*-alkanes $\geq C_{35}$, there are few urban emission sources other than tyre wear. Although reasonably detailed information on the composition of brake linings and brake wear particles has been reported, no strong evidence was found in the literature of reliable tracer species for brake wear particles.
- For tyre material, the metal concentrations observed in the initial exploratory analysis agreed reasonably well with the ranges reported in the literature. In particular, there was found to be a relatively high abundance of Zn in the tyre material. However, the potential use of zinc as a tyre wear tracer is confounded by the existence of many other sources.
- Metal concentrations in new brake material and brake dust were generally of the same order of magnitude, though concentrations tended to be higher in the brake dust samples. It is possible that this was a consequence of incomplete digestion of the new brake lining material. The concentrations of some

metals (notably Ba, Cu, Pb and Sb) were considerably lower than those found in the literature. A semi-quantitative analysis of organic compounds in brake dust and road dust samples revealed the presence of PAHs, and provided some evidence to support the use of benzothiazole as a tracer compound for tyre wear.

- Although a small amount of information on the chemical characterisation of such source materials has been obtained in this study, the research in this area is far from advanced. Clearly, much more information is required for PM source apportionment studies.

PM₁₀ source apportionment

- In this study, it was found that the combined use of metal and organic tracers and receptor modelling techniques provides a reasonably robust means of identifying non-exhaust sources and determining appropriate emission factors.
- Five main sources were identified as contributing to the PM₁₀ tunnel increment concentration: diesel exhaust, petrol exhaust, resuspended dust, combined brake/tyre wear and road surface wear. With the exception of petrol exhaust, it was possible to derive separate LDV and HDV emission factors for each source.

PM₁₀ emission factors

- According to the literature PM₁₀ appears to be released from tyres at a rate of between 5 and 13 mg/vkm for light-duty vehicles. This suggests that up to around 30% by mass of LDV tyre wear material is emitted as PM₁₀, but much higher proportions have been reported in some studies.
- For brake wear, PM₁₀ emission factors of up to 79 mg/vkm have been reported for light-duty vehicles, and up to 610 mg/vkm for heavy-duty vehicles, the latter value being considerably higher than the highest total brake wear rate reported in the literature.
- The PM₁₀ emission factors for exhaust emissions from LDVs and HDVs in the Hatfield Tunnel were found to be 13.9 mg/vkm and 79.3 mg/vkm respectively. The average fleet-weighted emission factor derived using the DMRB model was 61.5 mg/vkm, almost three times higher than the fleet average emission factor derived in the Hatfield Tunnel (21.8 mg/vkm).
- The PM₁₀ emission factors for combined tyre and brake wear emissions from LDVs and HDVs in the Hatfield Tunnel were found to be 6.9 mg/vkm and 49.7 mg/vkm respectively. Both these values are towards the lower ends of the ranges values reported in the literature. One reason for this may be that vehicles tend to be operated in a 'steady-state' mode inside tunnels.
- The emission factors for resuspension were 0.8 mg/vkm for LDVs and 14.4 mg/vkm for HDVs. There is an extremely wide range of values quoted for resuspension in the literature. It is very difficult to derive general emission factors for resuspension, as it is strongly related to local conditions, and the method used to determine resuspension emission factors is crucial.
- For road surface wear, the LDV and HDV emission factors were found to be 3.1 mg/vkm and 29.0 mg/vkm respectively. No direct comparison could be made with the values reported in the literature, mainly because it is not always clear exactly what is being defined in terms of 'road surface' particles, and in some studies these may include resuspended particles.
- The emission factors for non-exhaust sources of road transport can be of the same order of magnitude as those for exhaust emissions. For example, the 2000 and 2005 Type Approval exhaust emission limits for total particulate matter from diesel light-duty vehicles of 50 mg/vkm and 25 mg/vkm respectively. There are currently no legal requirements for the control of exhaust particle emissions from light-duty petrol

vehicles (particle mass emissions from such vehicles are very low). Given that all road vehicles are potential sources of tyre, brake and road surface wear particles, this illustrates the potential scale of emissions from these sources. This will have implications in terms policy planning and control strategies for PM_{10} .

6.2 Recommendations

The methodology used in this study to estimate emission factors for fleet, exhaust and non-exhaust sources has shown a promising applicability. However this needs to be improved upon to obtain more accurate emission factor estimates. Some of the steps listed below could be taken to confirm and improve the findings of this study. Once more robust and detailed information becomes available, it should be possible to begin to formulate control policies for non-exhaust sources.

- *More detailed source characterisation*

Only a limited analysis of source materials was possible in this study. A more extensive examination of the composition of the tyres and brakes available on the European market is required. It would also be useful to examine the extent to which tyre tread and brake lining material are altered during use, and to analyse the tyres, the brake lining, and the brake dust from same in-service vehicles at regular intervals.

- *Use of chemical mass balance for source apportionment*

This would support the principal component analysis approach in the identification of sources, but it would require the determination of adequate source profiles, as described above.

- *Investigation of vehicle operation effects*

One of the limitations of the research was that it only related to a particular set of traffic conditions (*i.e.* those on the A1(M) motorway). These conditions will be associated with typical tyre wear and brake wear rates. It is not known to what extent these reflect traffic conditions on other road types, but they appear to be lower than urban driving. Brake wear in particular may be underestimated.

- *Sampling of particulate matter in at least two size fractions, such as PM_{10} and $PM_{2.5}$*

- *Real-world studies of tyre, brake and road surface wear emissions using instrumented vehicles*

Attempts should be made to determine emissions from these sources by direct measurement, including particle size distributions and fluxes.

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8 Glossary

APC	Absolute principal component score
APEG	Airborne Particles Expert Group (UK)
AQEG	Air Quality Expert Group (UK)
CMB	Chemical mass balance
DCM	Dichloromethane
DMRB	Design Manual for Roads and Bridges (UK)
FWD	Front-wheel drive
GC/MS	Gas chromatography/mass spectrometry
HDV	Heavy-duty vehicle
HPLC	High performance liquid chromatography
ICP/AES	Inductively coupled plasma atomic emission spectroscopy
ICP/MS	Inductively coupled plasma mass spectrometry
LDV	Light-duty vehicle
MLRA	Multiple linear regression analysis
NAEI	National Atmospheric Emissions Inventory (UK)
NCBA	N-cyclohexyl-2-benzothiazolamine
NIST	National Institute of Standards and Technology
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PM ₁₀	Airborne particulate matter with an aerodynamic diameter of less than 10 µm
PM _{2.5}	Airborne particulate matter with an aerodynamic diameter of less than 2.5 µm
PM ₁	Airborne particulate matter with an aerodynamic diameter of less than 1 µm
RWD	Rear-wheel drive
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
TSP	Total suspended particulate
USEPA	United States Environmental Protection Agency
vkm	vehicle.kilometre

APPENDIX A: Compounds present in tyre wear particles, brake wear particles and road dust particles

Table A-1: Species determined in tyre wear, brake wear and road dust particles (Hildemann *et al.*, 1991)

Species	Tyre Wear (% of mass)	Brake Wear (% of mass)	Road Dust (% of mass)
Al	0.047	0.033	5.890
Si	0.180	6.790	12.400
P	0.000	0.000	0.072
S	0.110	1.280	0.560
Cl	0.052	0.150	0.170
K	0.038	0.019	1.870
Ca	0.200	0.110	4.440
Ti	0.056	0.360	0.560
V	0.000	0.066	0.027
Cr	0.003	0.120	0.017
Mn	0.010	0.170	0.120
Fe	0.460	11.500	6.230
Ni	0.005	0.066	0.012
Cu	0.049	0.037	0.056
Zn	0.043	0.027	0.150
As	0.000	0.001	0.002
Se	0.002	0.002	0.001
Br	0.002	0.004	0.005
Rb	0.000	0.005	0.013
Sr	0.004	0.074	0.130
Ba	0.037	7.440	0.076
Pb	0.016	0.005	0.110
EC	15.3	2.61	1.06
OC	36.0	10.7	13.5
Mg ²⁺	0.036	8.300	0.170
Na ⁺	0.068	0.008	0.150
Cl ⁻	0.060	0.150	0.150
NO ³⁻	0.150	0.160	0.250
SO ₄ ²⁻	0.250	3.340	1.200
NH ₄ ⁺	0.019	0.003	0.053

APPENDIX B: Organic compounds present in tyre wear particles, brake wear particles and road dust particles

Table B-1: Organic species in tyre wear particles, brake wear particles and road dust (Rogge *et al.*, 1993).

Organic Compound	Tyre wear particles (µg/g)	Brake wear particles (µg/g)	Road dust	
			(µg/g)	Possible source(s)
<i>n</i>-Alkanes				
Nonadecane	40.70	2.00	14.30	Vehicle exhaust emissions
Eicosane	58.30	2.40	15.00	
Heneicosane	47.70	1.70	28.80	
Docosane	62.50	1.40	35.70	
Tricosane	70.70	3.20	34.90	
Tetracosane	114.00	1.90	39.50	
Pentacosane	175.10	5.70	90.70	
Hexacosane	185.90	3.30	51.10	Vegetative detritus
Heptacosane	227.00	2.10	100.80	
Octocosane	268.50	2.00	47.10	
Nonacosane	389.30	3.30	214.70	
Triacontane	546.00	2.10	61.90	
Hentriacontane	742.90	2.30	150.70	
Dotriacontane	969.00	1.60	84.30	
Tritriacontane	1229.80	1.60	98.50	Tyre wear
Tetratriacontane	1556.20	0.80	42.70	
Pentatriacontane	2005.80	0.67	44.10	
Hexatriacontane	2253.90	0.42	31.30	
Heptatriacontane	2301.50	0.00	34.20	
Octatriacontane	2181.20	0.00	34.40	
Nonatriacontane	1428.00	0.00	20.50	
Tetracontane	1157.70			
Hentetracontane	831.10			
<i>n</i>-Alkanoic Acids				
Hexanoic	122.00	82.10	71.40	Vegetative detritus
Heptanoic	3.00	35.40	28.60	
Octanoic	31.10	60.50	57.70	
Nonanoic	90.90	87.40	135.40	
Decanoic	37.80	18.40	55.40	
Undecanoic	187.40	41.10	146.90	
Dodecanoic	136.50	12.50	105.30	
Tridecanoic	11.60	3.20	33.60	
tetradecanoic (myristic acid)	634.50	8.10	171.80	
Pentadecanoic	86.00	3.20	64.40	
hexadecanoic (palmitic acid)	4818.40	83.30	1216.70	
Heptadecanoic	150.60	4.10	61.30	
octadecanoic (stearic acid)	6009.00	79.50	689.00	
Nonadecanoic	16.60	0.83	27.00	
Eicosanoic	127.00	1.80	119.00	
Heneicosanoic	0.00	0.87	20.90	
Docosanoic	0.00	2.10	70.20	
Tricosanoic	0.00	1.90	23.60	
Tetracosanoic	0.00	1.60	116.20	
Pentacosanoic	0.00	0.34	21.90	
Hexacosanoic	0.00	0.69	93.40	

Table B-1 continued:

Organic Compound	Tyre wear particles (µg/g)	Brake wear particles (µg/g)	Road dust	
			(µg/g)	Possible source(s)
Heptacosanoic	0.00	0.36	20.60	Vegetative detritus
Octacosanoic	0.00	0.55	124.00	
Nonacosanoic	0.00	0.00	21.50	
Triacontanoic	0.00	0.00	120.30	
Hentriacontanoic	0.00	0.00	12.50	
Dotriacontanoic	0.00	0.00	48.90	
<i>n</i>-Alkenoic Acids				
Oleic acid	1115.50	10.70	130.90	Vegetative detritus
Linoleic acid	163.70	0.00	129.10	
Linolenic acid	0.00	0.00	17.30	
<i>n</i>-Alkanals				
octocosanal	0.00	0.00	144.40	Plant wax
triacontanal	0.00	0.00	232.20	
dotriacontanal	0.00	0.00	85.90	
<i>n</i>-Alkanols				
Hexacosanol	0.00	0.00	61.70	Plant wax
Octacosanol	0.00	0.00	152.90	
Benzoic Acids				
Benzoic Acid	74.80	31.90	114.10	Vehicle exhaust, meat cooking, tyre wear, brake wear, plant material
4-methyl-benzoic acid	0.00	2.60	5.20	
3,4-dimethoxybenzoic acid	0.00	0.00	5.50	
Substituted Benzaldehydes				
2-methylbenzaldehyde	4.10	0.48	0.00	Vehicle exhaust, meat cooking, tyre wear, brake wear, plant material
3-methylbenzaldehyde	1.40	0.11	0.00	
4-methylbenzaldehyde	2.30	0.30	0.00	
3-methoxybenzaldehyde	0.00	13.00	0.00	
3,4-dimethoxybenzaldehyde	0.00	0.45	0.00	
2-hydroxybenzaldehyde	0.00	4.70	0.00	
Polyalkylene Glycol Ethers				
2-(2butoxyethoxy)ethanol	0.00	45.70	0.00	Vehicle exhaust, meat cooking, tyre wear, brake wear, plant material
2-[2-(methoxyethoxy)ethoxy]ethanol	0.00	248.10	0.00	
2-[2-(2-ethoxyethoxy)ethoxy]ethanol	0.00	403.60	0.00	
2-[2-(2-butoxyethoxy)ethoxy]ethanol	0.00	181.70	0.00	
Thiazoles				
benzothiazole	124.30	0.00	4.40	Vehicle exhaust, meat cooking, tyre wear, brake wear, plant material
Polycyclic Aromatic Hydrocarbons (PAH)				
phenanthrene	11.80	0.97	3.90	Vehicle exhaust, meat cooking, tyre wear, brake wear, plant material
anthracene	0.00	0.00	0.84	
methyl(phenanthrenes, anthracenes)	23.60	0.67	1.50	
dimethyl(phenanthrenes, anthracenes)	38.50	0.66	3.10	
fluoranthene	11.10	0.69	6.90	
pyrene	54.10	1.10	9.40	
benzacenaphthylene	0.00	0.00	0.23	
2-phenylnaphthalene	0.00	0.00	0.16	
2-benzyl naphthalene	0.00	0.00	0.00	
methyl(fluoranthenes, pyrenes)	24.40	0.89	2.10	
benzo[<i>a</i>]fluorene/benzo[<i>b</i>]fluorene	1.30	0.26	0.37	
benzo[<i>ghi</i>]fluoranthene	6.30	0.34	1.30	

Table B-1 continued:

Organic Compound	Tyre wear particles (µg/g)	Brake wear particles (µg/g)	Road dust		
			(µg/g)	Possible source(s)	
benz[<i>a</i>]anthracene	0.00	1.50	1.20		
chrysene/triphenylene	8.20	1.70	7.70		
methyl(benz[<i>a</i>]anthracenes, chrysenes, triphenylenes)	18.70	2.20	1.30		
dimethyl(fluoranthenes, pyrenes)	19.00	0.00	0.00		
benzo[<i>k</i>]fluoranthene	0.00	0.62	5.50		
benzo[<i>b</i>]fluoranthene	0.00	0.42	4.40		
benzo[<i>e</i>]pyrene	5.20	0.84	2.70		
benzo[<i>a</i>]pyrene	3.90	0.74	2.30		
Perylene	0.00	0.00	0.48		
indeno[1,2,3- <i>cd</i>]fluoranthene	0.00	0.00	1.20		
benzo[<i>ghi</i>]perylene	0.00	2.60	2.10		
Polycyclic Aromatic Ketones and Quinones					
Fluorenone	0.00	0.82	0.72		Combustion
Phenanthrenequinone	0.00	0.31	0.41		
Anthraquinone	0.00	0.48	1.10		
Phenanthrone/anthrone	0.00	0.46	0.00		
Xanthone	0.45	0.00	0.00		
4-cyclopental[<i>def</i>]phenanthren-4-one	0.00	0.00	0.62		
7 <i>H</i> -benzo[<i>de</i>]anthracen-7-one	0.00	0.58	0.98		
6 <i>H</i> -benzo[<i>cd</i>]pyren-6-one (benzol [<i>cd</i>]pyrenone)	0.00	0.36	0.00		
Regular Steranes					
Cholestanes	13.50	0.30	12.10	Engine oil, vehicle exhaust, tyre wear, brake wear	
Cholestane	10.70	0.26	13.80		
Ergostanes	20.70	0.99	17.30		
Sitostanes	29.30	0.00	12.50		
Pentacyclic Triterpanes					
22,29,30-trisnorhopane	29.60	0.35	10.10	Engine oil, vehicle exhaust, tyre wear, brake wear	
17β (<i>H</i>),21β(<i>H</i>)-30-norhopane	161.60	0.69	21.20		
17α(<i>H</i>),21β(<i>H</i>)-30-hopane	199.20	1.20	38.30		
22 <i>S</i> -17α(<i>H</i>),21β(<i>H</i>)homohopane	107.40	0.41	16.70		
22 <i>R</i> -17α(<i>H</i>),21β(<i>H</i>)homohopane	73.90	0.18	10.30		
22 <i>S</i> -17α(<i>H</i>),21β(<i>H</i>)bishomohopane	69.80	0.13	9.50		
22 <i>R</i> -17α(<i>H</i>),21β(<i>H</i>)bishomohopane	42.90	0.10	8.30		
Natural Resins					
Dehydroabietic acid	7970.30	10.10	6.80		
abietic acid	69.60	0.00	0.00		
7-oxodehydroabietic acid	10.10	0.00	0.00		
13β-ethyl-13-methylpodocarp-8-en-15-oic acid	291.30	0.00	0.00		
13α-isopropyl-13-methylpodocarp-8-en-15-oic acid	255.80	0.00	0.00		
13β-isopropyl-13-methylpodocarp-8-15-oic acid	916.20	0.00	0.00		
Amides					
4-phenylbenzenamine	12.90	0.00	0.00		
Pesticides					
iridomyrmecin (insecticide)	0.00	0.00	18.40	Roadside gardens	
simazine (herbicide)	0.00	0.00	22.60		

Table B-1 continued:

Organic Compound	Tyre wear particles (µg/g)	Brake wear particles (µg/g)	Road dust	
			(µg/g)	Possible source(s)
Chlorinated Organics				
<i>α</i> -chloroindane	3.40	0.00	0.00	
2,4,5'-trichlorobiphenyl	1.90	0.00	0.00	
Other Compounds				
hydroxymethylphthalimide	54.50	0.00	0.00	
<i>p</i> -octylphenol	17.60	0.00	0.00	
isopulegol	0.00	0.00	296.10	Tress, flowers
<i>α</i> -terpineol	0.00	0.00	27.40	
<i>β</i> -citronellol	0.00	0.00	71.30	