On Heavy Metal Pollution from a Suburban Road Network

Sudip Kumar Pal [BSc (Hons), MEng]

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

Heriot Watt University

School of the Built-Environment

Institute of Infrastructure and Environment

Edinburgh, UK

EH14 4AS

January 2012

Abstract

In the context of urban diffuse pollution a suburban road acts as a potential source of toxic pollutants among which heavy metals are very common, are found at elevated concentrations and are generally persistent. With a lack of detailed understanding of metal emission patterns on suburban roads, a detailed study is therefore essential for gaining an improved understanding to plug the knowledge gap in terms of urban diffuse pollution management. The present understanding of pollutant build-up and wash-off processes on road surfaces elucidates that these processes are highly site specific and are hard to generalise in certain aspects. Therefore, this study aimed to characterise heavy metal emissions and associated pollution levels at several road sites on the Riccarton Campus road network using road sediment collected during dry and wet weather periods. The heavy metal concentrations of Cd, Cr, Cu, Ni, Pb and Zn, are believed to be greatly toxic and are highly abundant in road traffic environments, were determined by strong nitric acid digestion and atomic absorption spectrometry.

The study revealed that the pollutant build-up and wash-off processes were site specific and so also were the derived local build-up and wash-off parameters, as expected. However, these derived parameters were very different from those used in common urban drainage models suggesting that the default values are (significantly) inappropriate for the studied road network. The quantification of heavy metals in road sediments displayed significantly higher concentrations than local background concentrations. Their concentrations between weather types were found in the order of runoff, snow and dry road sediment, and also varied between sampling sites according to site-specific attributes, such as road lay-out inured traffic movement pattern, road surface condition and presence of road paint rather than due to traffic volume alone. The concentrations of all metals except Pb were significantly higher in finer sediment sizes than in larger sediment sizes. Correlation analyses revealed a similar pattern showing a greater number of statistically significant associations between metals in finer sediment sizes. An assessment of heavy metal contamination indicated that road sediment may likely pose a moderate to considerable level of ecological risk, if transported to the nearby water environment in the study area. The assimilation of the knowledge gained in this study should help to improve current understanding of environmental pollution from suburban roads and to provide better guidance for selecting appropriate control measures under the framework of sustainable urban drainage systems.

Dedication

This work is dedicated to my parents whose precious love, constant support and encouragement throughout this journey filled me with wonder, and who would be very proud of this achievement.

Acknowledgement

I am forever in debt to my primary supervisor Dr. Steve G. Wallis for his precious input, advice, encouragement and support throughout this study, and always having the time to review my work, checking drafts and to debate the rational of the ideas in it. It is impossible to overstate how much I have learned from him. I would like to express my heartfelt thanks to my co-supervisor Dr. Scott Arthur for his constant feedback and encouragement, and also being available, whenever I needed his guidance.

Bill Hodder is thanked for his technical and logistic support during field work. Sincere appreciation and thanks are extended to Sean McMenamy and Hugh Barras for technical assistant during laboratory work in the Environmental Chemistry Laboratory in the School of Life Sciences at Heriot Watt University. The author also thanks Dr. David A. Kelly for providing rainfall data and information. I truly appreciate the constant support from Ashiqur Rahman and Sreenivasa Rao Puwala, my good friends and colleagues, for their constant support during the field work without which a comfortable completion would not have been possible, and also their cheerfulness which made some of my most difficult days full of fun, throughout this study.

I must acknowledge Heriot Watt University for awarding prestigious ‘James Watt’ scholarship to me, which covered the tuition and living allowance in the UK. I am grateful to Dr. Adeloye giving me the opportunity to work with him as a ‘Teaching Assistant’ for several courses, which was not only an incredible teaching experience abroad but also equally improved my knowledge and skill. I would also extend my thanks to Chittagong University of Engineering and Technology, Bangladesh for granting deputation to accomplish this study in the UK.

Lastly but most importantly, I would like to express my unreserved gratitude to my dearest parents and my siblings, for their supports and unconditional love throughout this journey. In particular I thank my wife Priyanka and our daughter Shrestha, who have put up with me in spite of years of work during many evenings and weekends. I really couldn’t have done it without your costly scarifies, Priyanka.

DECLARATION STATEMENT

ACADEMIC REGISTRY
Research Thesis Submission

On Heavy Metal Pollution from a Suburban Road Network

Name*:*	Sudip Kumar Pal		
School/PGI:	Built-Environment / Institute for Infrastructure and Environment		
Version: *(i.e. First, Resubmission, Final)*	**Final**	Degree Sought (Award **and** Subject area)	PhD in Civil Engineering (Water Resources)

Declaration

In accordance with the appropriate regulations I hereby submit my thesis and I declare that:

1) the thesis embodies the results of my own work and has been composed by myself
2) where appropriate, I have made acknowledgement of the work of others and have made reference to work carried out in collaboration with other persons
3) the thesis is the correct version of the thesis for submission and is the same version as any electronic versions submitted*.
4) my thesis for the award referred to, deposited in the Heriot-Watt University Library, should be made available for loan or photocopying and be available via the Institutional Repository, subject to such conditions as the Librarian may require
5) I understand that as a student of the University I am required to abide by the Regulations of the University and to conform to its discipline.

* *Please note that it is the responsibility of the candidate to ensure that the correct version of the thesis is submitted.*

Signature of Candidate*:*		Date:	/01/2012

Submission

Submitted By *(name in capitals):*	SUDIP KUMAR PAL
Signature of Individual Submitting:	
Date Submitted:	/01/2012

For Completion in the Student Service Centre (SSC)

Received in the SSC by *(name in capitals):*			
Method of Submission *(Handed in to SSC; posted through internal/external mail):*			
E-thesis Submitted (**mandatory for final theses)**			
Signature:		Date:	

Table of Contents

Table of Contents (Continued)

Table of Contents (Continued)

CHAPTER **TITLE** **PAGE**

Table of Contents (Continued)

List of Tables

List of Tables (Continued)

List of Figures

List of Figures (Continued)

List of Abbreviations

AAS	Atomic Absorption Spectrometry
AADT	Annual Average Daily Traffic
ADD	Antecedent Dry Days
ADT	Average Daily Traffic
APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CD	Degree of Contamination
Cd	Cadmium
Cr	Chromium
Cu	Copper
EPA	Environmental Protection Agency
EA	Environment Agency
EU	European Union
FHA	Federal Highway Agency
MOUSE	Model for Urban Sewers
Ni	Nickel
PAH	Polycyclic Aromatic Hydrocarbons
PERI	Potential Ecological Risk Index
Pb	Lead
PSD	Particle Size Distribution
RDS	Road Deposited Sediment
RB	Road Bend
RSC	Road with Speed Control Measures
RI	Road Intersection
SR	Straight Road Section
SEPA	Scottish Environment Protection Agency
SNIFFER	Scotland and Northern Ireland Forum for Environmental Research
SUDS	Sustainable Urban Drainage Systems
SWMM	Storm Water Management Model
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VDS	Vehicles During Storm
VOC	Volatile Organic Carbon
VPH	Vehicles Per Hour
WFD	Water Framework Directive
Zn	Zinc

List of publications

Journal Papers

Pal, S. K., Wallis, S. G. and Arthur, S. (2011) Assessment of heavy metals emission from traffic on road surfaces. Central European Journal of Chemistry 9(2), 314-319.

Pal, S. K., Wallis, S. G. and Arthur, S. Emission patterns of traffic related metals and associated contamination in road deposited sediments. International Journal of Environmental Engineering (Article in press)

Pal, S. K., Wallis, S.G. and Arthur, S. Heavy metals in road sediment and associated contamination: a comparative assessment of the dry, runoff and snow derived sediment on road surfaces (*Under review in Water Environment Research).*

Pal, S. K., Wallis, S.G. and Arthur, S. Assessing heavy metals and associated contamination in road runoff (*Under review in Environmental Monitoring and Assessment).*

Refereed Conference Papers

Pal, S. K., Wallis, S. G. and Arthur, S. (2011) On the relationship between pollutant build-up on roads and antecedent dry days: In the proceeding CD of the 12th International Conference on Urban Drainage, 10 to 15 September, Porto Alegre, Brazil, Paper No: PAP 004880.

Pal, S.K., Wallis, S.G. and Arthur, S. (2010) Emission patterns of traffic-related metals on road: In the proceeding CD of the International Conference on Environment, 13 to 15 December, Penang, Malaysia, Paper No. 010.

Non-refereed Conference Papers

Pal, S. K., Wallis, S. G. and Arthur, S. (2011) Spatial variation of heavy metal pollution on an urban road network: In the proceeding of the SUDSnet / CIWEM National & International Conference, 11 to 13 May, The University of Abertay, Dundee, UK, pp 61-67.

Pal, S.K., Wallis, S.G. and Arthur, S. (2010) Assessment of heavy metal emissions on road surfaces: In the proceeding of the 15th International Conference on Heavy metals in Environment, 19 to 23 September, Gdansk, Poland, pp 954-959.

Chapter 1 – Introduction

1.1 Background

In recent years, urban areas have experienced severe environmental pollution. Roads, an integral part of any urban development, only use a small percentage of urban land, however they generate many types of pollutants, among which heavy metals, in particular Cd, Cr, Cu, Ni, Pb and Zn are very common (Barrett et al., 1993; Furumai et al., 2001). Heavy metals are important environmental pollutants and are regarded as potential hazards to human health and to natural ecosystems (Marcovecchio and Ferrer, 2005). The heavy metals derived from roads originate from diverse sources (Banerjee, 2003). From the study of Irish et al. (1995), atmospheric deposition, input from traffic, carriageway breakup and surrounding land uses are found to be the key sources of heavy metal pollution from roads. The urban pollution impact associated with transportation has become an important issue as road traffic in the UK has increased rapidly during last decade or so (Napier et al., 2008).

Meanwhile, much research work has been undertaken to investigate pollutants, particularly heavy metals, derived from road surfaces all over the world. For example, studies carried out in Australia and New Zealand (Ball et al., 1998; Drapper et al., 2000; Mosley and Peake, 2001; Brown and Peake, 2006), America (Sartor and Boyd, 1972; Sartor et al., 1974; Sansalone et al., 1996; Brezonik and Stadelmann, 2002; Sutherland, 2003; Lee et al., 2004), Asia (Kim et al., 1998; Lee et al., 2002) and Europe (Farm, 2002; Westerlund et al., 2003; Backstrom et al., 2003; Deletic and Orr, 2005; Crabtree et al., 2006, 2008; Robertson and Taylor, 2007; Ewen et al., 2009; Helmreich et al., 2010). Aspects of heavy metals and their quantification in road sediment are very commonly studied in the above studies. However, there is a lot of uncertainty regarding their concentrations in road sediment deposited during different types of weather, such as a dry spell, rain or snow. Such concentrations have been found to be highly variable and also appear to be site specific, being dependent on a wide range of factors including location, traffic volume, extent of antecedent dry spells, frequency of street sweeping, nature of road surface etc. Also where data is drawn from United States, Australia and Europe, these may not be very applicable to UK circumstances. While a few of the above mentioned studies of heavy metal concentrations in dry and runoff sediment have been undertaken in the UK, there is no such data available for Edinburgh City. Moreover, there is no previous data on the quantification of heavy metals and associated contamination levels in snow derived sediment from roads in the UK.

It is also well known from several studies that a significant proportion of road pollutants are associated with particulate matter, the rest being in a dissolved phase. Typically 40-70% of many heavy metals are found in the particulate fraction and about 90% of polycyclic aromatic hydrocarbon (PAHs) can be associated with particles (Marsalek et al., 1997; Starzec et al., 2005). Once deposited, road sediment could be transported from the road surfaces to nearby water bodies by different cleansing events comprising mechanical (street sweeping) and natural (air, snow and rain) events, and thus in turn make a significant contribution to the local environmental pollution. Therefore, managing sediment from roads is required to control the associated environmental pollution (Heal et al., 2006). Moreover, recent road drainage practice has seen the introduction of sustainable urban drainage systems (SUDS) for roads, replacing or modifying conventional road drainage and aiming to address the water quality and water quantity issues, as a long-term robust option for urban pollution management (Heal et al., 2009). It is therefore useful to have information on pollutant concentrations from different perspectives that may inform road drainage designs and maintenance in the context of SUDS for roads.

1.2 Justification of the Research

Pollutants derived from the road-traffic environment are seen as a major contributor to urban diffuse pollution in receiving waters. The sediment derived from roads has been found to be highly contaminated and is therefore, often studied as an indicator of environmental pollution. From reviewing literature in this field of study, it has been revealed that profiles of pollutant concentrations are highly site specific. Furthermore, variability in rainfall pattern, number of preceding dry days, and roadway maintenance, that are considered as key drivers, makes the problem more complex and unique for specific regions or sites. Furthermore, a few studies have been found that report the importance of traffic movement patterns on heavy metal emissions (Hjortenkrans et al., 2006; Ewen et al., 2009; Doung and Lee, 2011) on roads. Also from Ewen et al. (2009), it is apparent that a higher pollution level is associated with sites on suburban roads than on busy urban roads or motorways. This finding warrants further research exclusively focused on metal emission patterns for different traffic movement patterns along a suburban road network. In addition, a piecemeal approach to reporting pollutant concentrations has limited direct comparison between studies and, therefore, recommendations available from different studies may not be widely applicable (Crabtree et al., 2006). Although a few studies of heavy metal concentrations in dry and runoff sediment from the road-traffic environment have been undertaken in the UK, no such information is available for heavy metals in snow derived sediment. Moreover, in particular to Edinburgh City, there is no previous data on heavy metals and associated contamination levels in dry or wet weather (runoff and snow) derived sediment from the road–traffic environment. It is understood that the quantification of heavy metals in dry, wet weather and snow derived sediments from roads has the potential to allow an improved understanding of diffuse heavy metal pollution, which has a continuing threat to the nearby aquatic environment.

In order to meet regulatory water quality requirements set by the Water Framework Directive (WFD), a wide range of best management practices have been implemented and monitored to deal with pollution from the road-traffic environment. In Scotland the outcomes of this work practices were documented in the recently adopted road drainage guidance ‘SUDS for Roads’ (Pittner and Allerton, 2009). The performance of the various treatment options is often measured by quantifying the percentage removal of pollutant mass, and less attention has been placed on the toxicity for aquatic species in receiving waters. However, knowledge of the toxicity exerted by road runoff pollutants may be essential to accurately evaluate the effectiveness of SUDS treatment options with regard to removal of the toxic fraction of pollutants. A proper understanding of the pollutants and associated ecological risk at priority sites on a road network, to demonstrate how and where pollutants are dispersed, could be useful in selecting appropriate source/site control measures to improve stormwater runoff quality. An improved understanding of such issues particularly in the context of treatment trains would be a useful addition to the SUDS for roads manual.

1.3 Research Hypothesis

Traffic movement patterns, which are conditioned by road lay-out, have a significant influence on heavy metal emission patterns and associated pollution from the road traffic environment. It is expected that pollutant concentrations would be higher at a site, where traffic is more likely to undergo stop-start manoeuvres than at a site where traffic flows are more likely to maintain steady speeds.

1.4 Aims and Objectives

The overall aim of this research is to characterise heavy metal emissions and associated pollution at several different road-layout sites on a suburban road network during dry and wet weather events.

Major objectives to address the aim of the study are as follows:

- To investigate the influence of traffic movement patterns on metal emission patterns.
- To investigate the pollutant build-up pattern as a function of transverse sampling position and the number of antecedent dry days.
- To investigate the wash-off pattern for rainfall events also with the influence of the number of antecedent dry days.
- To measure heavy metal concentrations and associated environmental pollution in three different road sediment categories, namely dry, runoff and snow, as a function of particle size distribution.
- To undertake a correlation analysis between heavy metals and relevant key variables.

It is hoped that the findings of this study could further help to improve knowledge on environmental pollution under different site characteristics on suburban roads, and to provide better guidance to water professionals.

1.5 Scope and Limitations

The research concerns heavy metal concentrations and their distribution in different particle size fractions of dry, runoff and snow sediment for several road lay-out sites on a typical suburban road network. Furthermore, heavy metal levels associated with the above categories of road sediment are discussed addressing environmental pollution in relation to ecological risk indices. Some important issues in relation to this research are as follows:

- The research was confined to the Riccarton Campus of Heriot Watt University in Edinburgh, UK. This limits the research outcomes in terms of regional and climatic parameters. However, the generic knowledge gained is applicable outside of this region.
- The field investigations were limited to a suburban road network with a low traffic density and a combination of rural and urban land-uses. This limits the wider applicability of some of the results where specialised land uses (e.g. metal industries) may likely have a significant influence on metal emission patterns. However, the understanding of metal emission patterns gained is applicable to other urban catchments.
- The metals in focus were limited to Cd, Cr, Cu, Ni, Pb and Zn, which are often found in high concentrations in the road traffic environment. Additional constituents, including, but not limited to, metals (Al, Co, Hg and Mn), polycyclic aromatic hydrocarbons (PAHs), conventional pollutants (oil and grease, volatile suspended solids, organic matter contents, nutrients, pH, temperature etc.) and platinum group elements, are also important for road runoff pollution studies: however, they are not considered in this study for limited testing resources.
- Any seasonal variability in traffic volume was not considered during the investigation, even though this might has the influence on seasonal variability of heavy metal concentrations studied.

1.6 Organisation of the Thesis

This thesis consists of 8 chapters. Following this introductory chapter, Chapter 2 documents the outcomes of relevant published literature. It describes the background information to the research and identifies knowledge gaps. Chapter 3 outlines the study area, sampling sites, field investigations, laboratory analyses and data analysis techniques, which all together describe the materials and methods used to carry out this research. Chapters 4, 5 and 6 contain the results and discuss the investigation of the pollutant build-up and wash-off patterns and the pollution potential of dry and wet weather derived road sediments. Chapter 4 focuses on the dry road deposited sediment (RDS) and RDS heavy metal build-up patterns on road surfaces. Chapter 5 presents detailed analysis of heavy metals in RDS. Chapter 6 presents and discusses the pollutant wash-off pattern for runoff events, heavy metals in runoff and snow samples. The comparative assessment of dry, runoff and snow sediment is discussed in Chapter 7. Chapter 8 reveals the major conclusions and classified conclusions based on the results obtained in Chapters 4 to 7, and gives recommendations for further research. Following Chapter 8, a few appendices are provided that contain relevant supporting data and information, additional to the main text, and abstracts of a few published papers that were based on the work described in this thesis. Finally references cited in the text throughout the thesis are listed.

Chapter 2 - Literature Review

This chapter explores the current understanding available on urban diffuse pollution literature with the aim of identifying knowledge gaps relevant to the framework of the present study.

2.1 Background

During the 20th century, a wide range of infrastructure was built, such as roads, commercial and residential structures, urban amenities etc. At the same time, the effects of urbanisation on the response to the natural hydrological cycle were felt, for example an increased runoff volume with earlier peak discharge due to increased impervious area, and a wide range of pollutants was found in the runoff water. Part of the urbanisation process was designed to collect runoff during wash-off events (rainfall and snow precipitation), and convey it to a treatment plant by a storm sewer network, or in the absence of such facilities, in particular for road drainage, to discharge the largely untreated runoff to existing nearby surface water bodies, such as streams, lakes, rivers etc. By the end of the 1990s while point sources of pollution were well understood and reasonably controlled (SEPA, 1999), there was a concern for urban diffuse pollution that continued to pose a threat to the aquatic environment (Gray, 2004; Wilson et al., 2005). A little later, in order to control sources of pollution with the aim of improving the water quality of all water bodies, the European Union (EU) adopted the Water Framework Directive (WFD) (2000/60/EC), which, among other things, aimed to set mandatory environmental quality standards on priority pollutants. Considering the objectives of the WFD, gaining an accurate knowledge of pollutants derived from the urban environment has proved necessary (Gasperi et al., 2009). Accordingly, for mitigation processes to be efficient and productive, the reliable estimation of relevant hydrological and pollutant transport processes is deemed important. Commonly, mathematical modelling approaches were used, which required the estimation of various generic parameters. However, due to the significant variability of natural hydrology, urban settings, pollutant management strategies etc. these models often could not replicate important site-specific aspects of particular urban environments, therefore, the necessity of collecting local data and information for enhancing the application of models became recognised.

2.2 Diffuse Pollution: Urban Development

It is widely recognised that urbanisation has put huge pressures on both the quantity and quality of surface runoff. Diffuse pollution can come from many different sources, which are sometimes uniformly dispersed, but are often aggregated within a catchment. For example, pollutants entering the surface water system in urban settings are primarily derived from roads, pavements, roofs and yards, as reported by Ellis (1985, 1986); Heaney and Huber (1984); Goonettilleke et al. (2009). They also noted that diffuse pollution is closely linked to land use so that industrial, commercial, domestic and agricultural estates deliver different types of pollutants. Apart from water quality, diffuse pollution is also linked to air quality, for example acid rain in upland rural areas and impacts of industrial and traffic emissions locally in urban areas and also remotely (see atmospheric heavy metal deposition maps of the UK produced by Defra on http://pollutantdeposition.defra.gov.uk/image/tid/47). As a result of rainfall, pollutants are dislodged, transported and transformed before reaching the receiving waters. Although it seems that these sources may be individually minor, they are collectively significant. This form of diffuse source pollution has been identified as having a major adverse impact on receiving streams and rivers (Napier et al., 2008). Based on the published literature, urban surface water runoff typically contains a wide range of pollutants, among which heavy metals, for example cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), are considered to be potentially hazardous (e.g. Folkeson, 1994; Pitt et al., 1995). ‘Heavy metals’ commonly refers to metals with a specific gravity that is at least 5 times the specific gravity of water (the specific gravity of water is 1 at 4°C, where simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water).

Urban impacts associated with transportation have become increasingly important in the UK as road traffic volumes have increased. The major share of urban diffuse pollution belongs to cars and other road vehicles (Napier et al., 2008). Despite cleaner technology developed for cars and other vehicles, the volume of traffic on the roads continues to increase, tending to undo some of the benefit of individually less polluting vehicles. Pollution caused by traffic appears in different forms: in a solid form as from abrasion or wear of tyres and corrosion of metal parts of vehicles, in a liquid form as leakages or drips and in the gaseous state as vehicle exhaust (Shaheen, 1975; Herngren et al., 2006; Napier et al., 2008). Moreover, Patel and Atkins (2005) noted that the degradation of the road surface (due to ageing) and corrosion of crash barriers could also enhance metal emission in the road-traffic environment. In addition, atmospheric deposition and input from surrounding soils to the road traffic environment should not be overlooked. Runoff from roads during rainfall events carries with it many pollutants, including dirt and dust, which is associated with toxic heavy metals from the different sources mentioned above (Smolders and Degryse, 2002; Robetson and Taylor, 2007; Napier et al., 2008). Furthermore, salt from winter gritting can also act as a pollutant. Apart from heavy metals, certain aromatic hydrocarbon groups from fuel discharged from vehicle exhausts can also be accumulated on roads and other urban surfaces, from which the contaminants are washed off into the drainage system and hence threaten aquatic species (Clements et al., 2000; FHA, 2000).

2.3 Pollutant Sources in the Urban Setting

Although urban surfaces act as sinks for pollutants, these pollutants are mainly generated from various anthropogenic activities. Summarising the studies by Pitt et al. (1995) and Göbel et al. (2007), the list of key anthropogenic activities contains traffic, industrial and commercial activities, construction and demolition works, and erosion and corrosion in the built-environment. In particular to road-traffic environments, traffic, road surface, atmospheric deposition and surrounding land use are found as most influential sources, as reported by Irish et al. (1995) and presented here in a pictorial form, see Figure 2.1.

Among the listed sources, road-traffic is an obvious source of contaminants on roads and has been regarded as the major contributor to environmental pollution in urban areas. Due to the rapid growth of urbanization and increased traffic volumes during the last decades, in particular, urban environments have been modified and stressed with increased pollution, which has driven the need for better environmental protection (Napier et al., 2008; Ewen et al., 2009). Meanwhile, several researchers reported that road surfaces act as one of the key areas from which surface runoff, polluted with a wide range of pollutants, leads to the degradation of water quality for receiving waters (e.g. Ellis et al., 1987; Barrett et al., 1998). An earlier study by Hoffman et al. (1984)

noted that up to 80% of pollutant loadings to receiving waters came via road runoff in urban areas. Following the recommendations of the EU WFD directive, it is now obligatory that water protection should be strongly integrated with other domains of environmental strategy, including the area of transportation (Crabtree et al., 2008).

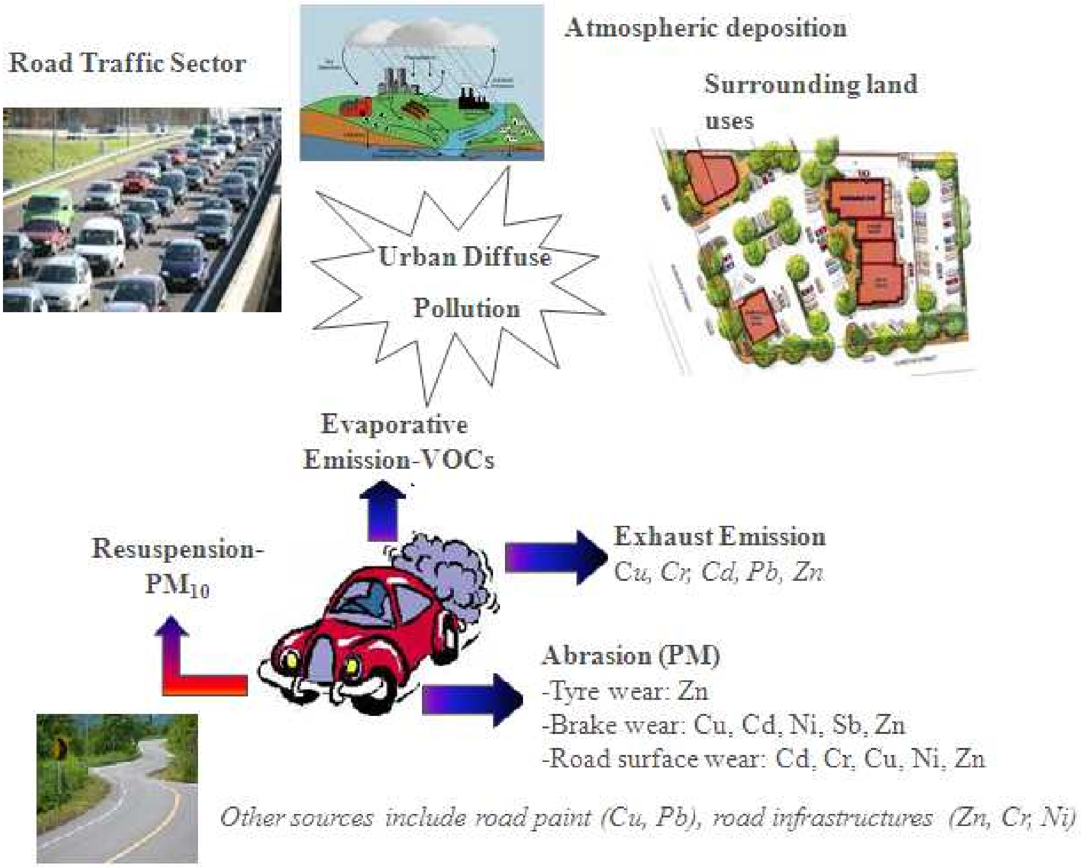


Figure 2.1: Key sources of diffuse pollutants, emphasising heavy metals, on suburban roads (VOCs: Volatile Organic Carbons; PM: Particulate Matter)

Conventionally pollutant loading has been thought to be exclusively related to traffic movement pattern, volume of traffic and type of road surface. As noted by Sartor et al. (1974), asphalt paved roads with fair to poor surface condition could have generated substantially higher pollutant loads than concrete paved roads with fair to good surface condition. Vehicle speed on roads, road geometry and surrounding road infrastructure may also affect the amount of pollutant load. Based on Novotny et al. (1985), Hjortenkrans et al. (2006) and Ewen et al. (2009) studies, it can be deduced that the amount of abrasion products derived by traffic on roads is at a higher level near traffic signals and other traffic related bottlenecks, such as bridges and bends compared to straight road section sites. Brinkmann (1985) also suggested that road geometry and traffic movement patterns might have an influence on differences in pollutant accumulation between sites.

Other than road surfaces, car parks are a large proportion of the runoff producing area in the urban environment, which are often contaminated with oil, petrol and heavy metals from vehicles. Conventionally all of this pollution would be washed off into drains, eventually polluting nearby watercourses. Industrial yards often deal with polluting substances on a larger scale than car parks, which makes them a potentially even greater producer of pollution. Oil is the cause of more than 20% of Scottish water pollution incidents. It can have serious affects on the fauna and flora of aquatic systems. Much of it comes from diffuse sources (Napier et al., 2008).

Similarly, construction and demolition activities in urban settings are also found to have a significant impact on stormwater runoff, contributing a range of materials such as cement dust, fine sand, gravels and general litter. According to the US EPA (1993), construction sites potentially generate approximately 10 to 20 times more solids than agricultural land, and 1000 to 2000 times more than forests. The report also noted that the loading may vary with the scale of construction equipment, maintenance activities and site management practices.

In addition, atmospheric deposition from industrial activities (depending on the industry type) could create much larger pollutant loadings in certain areas. The extent and type of depositions are dependent on both the nature of the industry, location and the climate. Briefly, atmospheric deposition can contribute a significant amount to pollutant load though this source of pollutant build-up is highly related with land use.

Pollution from road operation and maintenances might include some pollutants. For example, regular maintenance includes de-icing and weeds control, which involves the use of chemicals (de-icing salts and herbicides) that will be flushed from the highway surface by runoff. Winter time salting and sanding practices, for example, may leave concentrations of chloride, sodium and calcium on road surfaces (Westerlund and Viklander, 2006). Additionally, these materials usually have associated chemicals including iron, nickel, chromium, lead, zinc and cyanide (Granato, 2003; Patel and

Atkins, 2005; Pihl and Raaberg, 2000; Norrstrom and Jacks, 1998; Olli, 2003). In contrast, structural maintenance, renewal and repairs are usually well planned operations for which appropriate precautions are often taken.

Depending upon the exposure of building infrastructure such as gutters, roofs and fences to the atmosphere, wind, rainfall, and snow, corrosion from these products may result in particles that carry significant amounts of pollution (Brinkmann, 1985; Pitt et al., 1995). These corroded particles, which accumulate on the ground and on roof surfaces, are eventually washed-off in stormwater runoff (Göbel et al., 2007). When compared to road surfaces, roof surfaces are relatively less polluted (Van Metre and Mahler, 2003), however, pollutant concentrations from roof surfaces may be significant in densely populated housing areas, where houses take a dominant share of land use (Van Metre and Mahler, 2003). On the other hand, partially sealed areas, such as urban parks, porous paving, residential gardens and lawns could contribute to the stormwater pollutant load (particularly solid loads). Bannerman et al. (1993) studied the relative importance of surface type for stormwater pollution load and reported that street surfaces and parking lots are the most dominant sources for urban stormwater pollutants. They further noted that lawn areas are significant for organic loading, but roof surfaces are not significant compared to road surfaces for heavy metals.

2.3.1 Pollutant Build-up

Quantifying the relationship of pollutant build-up over antecedent dry days is difficult, but it is one of the important processes of urban environmental pollution. Based on the published studies (e.g. Egodawatta et al., 2007), it is clear that pollutant build-up is a complex process, as many variables influence the build up process. In the road environment, the pollutants primarily originate from traffic activities, the road surface itself, paints used for road markings, road side infrastructure, road operations and maintenance, and atmospheric deposition during dry and wet weather (Irish et al., 1995; Sansalone et al., 1996; Deletic and Orr, 2005). Also, road surface type, roughness, slope, antecedent dry days, land use and road lay-out play a significant role in the build-up process. The accumulation of road sediment is often regarded as a spatially uniform process. However, due to wind and traffic turbulence, road sediment is often moved towards the edge of the road and accumulates in near curb areas (Novotny et al., 1985;

Namdeo et al., 1999). To link with this issue, a few researchers highlighted that a significantly higher load of sediment (often composed of the coarse size fraction) was found near the curb, while relatively finer sediment was found towards the middle of the road (Harrison et al., 1985; Grotteker, 1987; Viklander, 1998; Charlesworth et al; 2003; Deletic and Orr, 2005; Herngren et al., 2006). Furthermore, Johnston and Harrison (1984) and Deletic and Orr (2005) reported a transverse gradient of metals indicating that particle redistribution rate is always less than the particle deposition rate on roads.

As mentioned earlier, the availability of the pollutants on road surfaces is influenced by a wide range of factors, which are associated with both natural and anthropogenic characteristics of the catchment. In the case of natural characteristics, climate variables, geomorphic characteristics, surrounding land, and the number of antecedent dry days (ADD), are a few examples, while variables that are more likely considered as anthropogenic factors include average daily traffic load (ADT) and number of vehicles during a storm (VDS). A common assumption is that the larger the ADD the higher is the sediment build-up on roads between any cleansing (e.g. street sweeping, rainfall) events. It has been considered that the ADD has a positive linear or non-linear relationship with pollutant build-up (Sartor and Boyd, 1972; Hewitt and Rashed, 1992; Irish et al. 1998; Kim et al., 2006). However, other studies found this relationship to be non-existent or insignificant (Harrison and Wilson, 1985; Kerri et al. 1985; Kim et al. 2004). In general, pollutant concentrations have been reported to be well correlated with average daily traffic (ADT) (Driscoll et al. 1990; Wu et al. 1998). However, as noted by Barret et al. (1993), ADT alone is not sufficient to describe observed sediment build-up and associated pollutant data: site specific information is also required. Additionally, the road lay-out has also been found to have a significant influence on metal emission patterns and how and where metals are dispersed (Hjortenkrans et al., 2006; Ewen et al., 2009).

Meanwhile, many researchers have also investigated the mass distribution of road deposited sediment (RDS) in different particle size ranges (e.g. Lau and Stenstrom, 2002; Charlesworth et al., 2003; Sutherland, 2003; Aryala et al., 2005; Deletic and Orr, 2005; Robertson and Taylor, 2007) and report similar findings of particles smaller than 250 µm accounting for a higher percentage of the total pollutant mass than the larger particles.

In recognition of the scope of these potential problems for cities, best management practices have identified source control of sediment generated from urban streets as a top water resources management priority. Subsequently, many field monitoring programs have been conducted in developing a set of pollution build-up models to guide selection, design and maintenance of these controls (Sartor et al., 1974; Moe et al., 1978; Driscoll et al., 1990; Sutherland and Jelen, 1996; Ball et al., 1998; Deletic and Orr, 2005; Kim et al., 2006; Li et al., 2008; Li and Barrett, 2008). Based on Sartor et al. (1974) pollutant build-up on road surfaces can be replicated with an exponential function with ADD as a primary variable. This concept continues to be used in commercial software, such as SWMM and MIKE-Urban, with ADD being the major input parameter along with the catchment surface characteristics. In contrast, Ball et al. (1998) found a power law function or a reciprocal function was a better alternative to explain pollutant build-up. However, the pattern of build-up over several dry days (commonly asymptotic with a high build-up rate initially) was consistent from both studies.

2.3.2 Pollutant Wash-off

Wash-off is the process of erosion of constituents (that build-up during dry days) from a catchment surface during a period of runoff induced by rainfall or snow. To describe the wash-off process simply, it can be divided into three main phases: firstly the surfaces get wet and soluble pollutants start to dissolve in water films, secondly sediment starts to detach from the surface and thirdly, depending on the slope and topography of the surface, sediment is either dragged along the surface by the runoff or is carried in suspension entering the drainage system in overland flow. Rainfall energy (refer to kinetic energy in relation to rainfall intensity) seems to be the main agent for particle detachment and initiation of motion (Kayhnian et al., 2002; Pitt et al., 2004; Shaw et al., 2006). In addition, other rainfall and runoff parameters (e.g. rainfall duration, rainfall volume and runoff volume) are also found to have an effect on wash-off loads (Sartor et al., 1974; Novotny et al., 1985; Mackay, 1999; Egodawatta et al., 2007).

Furthermore, it is noted that the influence of the above mentioned parameters varies widely between studies. For example, Chiew and MacMahon (1999) reported that event mean concentrations of suspended solids showed a strong positive correlation coefficient with total runoff volume, while, in contrast, Brezonik and Stadelmann (2002) and Kayhnian et al. (2002) reported that event mean concentrations of suspended solids can be better explained by the rainfall intensity. They also noted that the kinetic energy of rain drops (used to dislodge sediment from the surfaces) was strongly correlated with rainfall intensity, hence higher pollutant removal may occur with more intense rain even if it is a short duration event.

The relative importance of each factor is dependent on the type of contaminant in question. For example, Irish et al. (1998) reported that solids concentration increased with an increase in the duration of the antecedent dry period and decreased with an increase in the intensity of the previous storm event. Other studies have shown that Cu and Pb concentrations are highly influenced by the volume of traffic during a storm, Fe concentration is controlled by conditions in the preceding dry period, and Zn concentration is influenced by the traffic count during the dry period and the runoff characteristics of the preceding storm (Kayhnian et al., 2002). It is therefore necessary to understand the effect of each factor to effectively control the pollution induced by runoff. Subsequently, some of the studies also reported seasonal variations of pollutants in stormwater runoff, which demonstrated that higher pollutant concentrations (in smaller sediment load) are commonly found to occur in the summer, particularly when high intensity rain is preceded by a long dry spell, compared to winter rainfalls, which are normally less intense and more frequent (Brezonik and Stadelmann, 2002; Deletic and Orr, 2005; Hallberg et al., 2007).

Duncan (1995) followed by Pitt (2004) reported that pollutant wash-off loads (by mass) were found to be unusually high (a factor of 100 or more), if there were any construction activities nearby the catchment surface. Also, the effect of road cleaning on wash-off loads (by mass) was reported by several researchers (Sartor and Boyd, 1972; Vaze and Chiew, 2002). They found that conventional road cleaning techniques (e.g. street sweeping by brushes, municipal sweeping truck with fitted brushes) were only able to remove the larger sediment size fraction, probably significantly decreasing the wash-off mass load, however leaving sediment sizes less than the 250 µm available for wash-off in the next storm event. It has also been emphasized that smaller particle sizes could easily be blown around by the wind and, being inhalable, could pose potential human health hazards (Borrego et al., 2006 and Kaur et al., 2007). Subsequently, the wet atmospheric deposition due to rain, snow, fog, dew may also add finer substances to the road surfaces from the surrounding land use and make them available for transport with surface runoff (Göbel et al., 2007).

It has been understood that wash-off events only remove a fraction of the available pollutants from the catchment surfaces depending upon the characteristics of the runoff events. For, example, Vaze and Chiew (2002) found that only 35% of the total pollutant mass were washed-off from their controlled catchment by one event, while a subsequent event washed-off 40% of the total pollutant mass even though it had a smaller rainfall depth than the first event (there were differences in intensity and antecedent dry spells between the rain events also). A similar suggestion was also reported by Egodawatta et al. (2007).

Understanding the inherent complexity of the process, pollutant wash-off models require a wide range of information. Several mathematical equations are available to simulate wash-off load, however, the choice of which equation to use needs to be justified (Deletic et al., 1998; Massoudieh et al., 2008; Opher and Friedler, 2010). However, an exponential wash-off equation, proposed by Sartor et al. (1974) based on their research study on road surfaces in the USA, is often preferred for its ease of use and robustness (Rosener, 1982; Egodawatta et al., 2007). In terms of wash-off modelling it has been proposed that predicting the initial period of runoff, containing the ‘first flush’ (in which pollutant concentrations are believed to be significantly higher than later in the event) may well be a suitable way to explain the entire event (Lee et al., 2002; Kim et al., 2004). However, the occurrence of the ‘first flush’ is not consistently observed and it is possible that a significant amount of dissolved pollutants appear at later phases of runoff events, as reported by Hoffman et al. (1984), Harrison and Wilson (1985) and Kim and Sansalone (2008).

2.4 Road Runoff Pollutants

Road runoff has been identified as a significant source of diffuse pollution for receiving waters, and road traffic has been found to play an important role in generating such contamination in numerous research studies during the last three decades (Hedley and Lockley, 1975; Laxen and Harrison, 1977; Hoffman et al., 1985; Lee et al., 2004;

Cabtree et al., 2006). De-icers, nutrients, heavy metals, polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) are often found at elevated levels in road runoff compared to natural background levels. The study carried out by Ellis et al. (1987) estimated that drainage from road surfaces contributes as much as 50% of the total suspended solids, 16% of total hydrocarbons and between 35 and 75% of the total pollutant inputs to urban receiving waters in the UK. Deposition of oil, grease, rust, rubber particles together with wear and tear of vehicle parts are identified as common sources of these pollutants (Napier et al., 2008; Ewen et al., 2009), as also illustrated in Figure 2.1. A fraction of particulate contaminants that build up on the road surface may subsequently be dispersed by winds and/or traffic before they become washed into the road drainage system by wet weather events (rainfall or snow-melt runoff). In urban areas, the process of road cleaning, as mentioned in previous section, may also reduce the contaminant load in road runoff by rainfall or snowfall events. For, example, some particulates are permanently removed by suction devices. On the other hand washing procedures only serve to deliver pollutants to drains in sudden concentrated bursts.

2.4.1 Sources of Stormwater Pollutants

There are numerous sources of stormwater runoff pollutants from roads, including vehicles (exhaust emissions, fuel losses, lubrication system losses, brake wear and tyre wear), litter, spills, road surface wear, atmospheric deposition (dust fall and precipitation) and road operation and maintenance (salt, herbicides and road repairs) (Folkeson, 1994; Barrett et al., 1995). The most important groups of road runoff pollutants reported in the published literature include suspended particles, oxygen-consuming pollutants, nutrients, heavy metals, organic pollutants, petroleum products and microorganisms (Folkeson, 1994). A list of the most frequently studied constituents in road runoff is as follows (Folkeson, 1994):

- Total suspended solids (TSS)
- Biological Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)
- Phosphorus (P)
- Nitrogen (N)

- Cadmium (Cd)
- Chromium (Cr)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Nickel (Ni)
- Zinc (Zn)
- Hydrocarbons
- Coliform bacteria
- Sodium and chloride ions (if chemical de-icing agents are used)

A list of common pollutants and their probable sources in the road traffic environment is summarised in Table 2.1. A few of these (particularly heavy metals) is shown in Figure 2.1.

Table 2.1: Typical pollutants found in runoff from roads and highways*

Pollutants	Sources
Particulate	Pavement wear, vehicles, the atmosphere and maintenance activities, snow/ice abrasiveness and sediment disturbance
Rubber	Tyre wear
Asbestos	Clutch and brake lining wear
Nitrogen and Phosphorous	Atmosphere, roadside fertilizer application and sediments
Lead (Pb)	Leaded gasoline from auto exhaust, tire wear, lubricating oil and grease, bearing wear and atmospheric fallout
Zinc (Zn)	Tyre wear, motor oil and grease
Iron (Fe)	Auto body rust, steel highway structures such as bridges and guardrails and moving engine parts
Copper (Cu)	Metal plating, bearing and brushing wear, moving engine parts, brake lining wear, fungicides and insecticides
Cadmium (Cd)	Tyre wear and insecticide application
Chromium (Cr)	Metal plating, moving parts and brake lining wear
Nickel (Ni)	Diesel fuel and gasoline, lubricating oil, metal plating, bushing wear, brake lining wear and asphalt paving
Manganese (Mn)	Moving engine parts

* Adapted from U.S. Environmental Protection Agency. Guidance Specifying Management Measurement for Sources of Non Point Pollution in Coastal Waters, Washington, D.C.: Office of the Water, U.S. Environmental Protection Agency, 1997 and Federal Highway Administration. Sources and Mitigation of Highway Runoff Pollutants, Washington, D.C.: Federal Highway Administration, 1984.

2.4.2 Heavy Metals

Among the variety of pollutants in the road traffic environment, heavy metals have been of great concern because they are found at elevated concentrations that possibly threaten aquatic organisms and human health (Barrett et al., 1993; Furumai et al., 2001; Göbel et al., 2007; Ewen et al., 2009). Heavy metals in road runoff are the most persistent contaminants, accumulating in the environment rather than degrading and are believed to be one of the major diffuse pollutants from road and traffic activities. Emission patterns of road traffic related heavy metals need to be described and quantified in order to evaluate best management practices for optimal local treatment systems (Hjortenkrans et al., 2006; Napier et al., 2009). Heavy metals, such as Cd, Cr, Cu, Fe, Pb, Ni, and Zn, are some of the most frequently reported ones and are derived from the wear and tear of vehicle parts, road surface break up, oil and fuel drips and corrosion products, as seen in Table 2.1 and Figure 2.1 (Harrison and Wilson, 1985; USEPA, 1995; Sansalone et al., 1996, Napier et al., 2008; Ewen et al., 2009). For example, tyre wear is a source of Zn and Cd. Brake wear is a source of Cr, Cu, Ni and Pb. Engine wear and fluid leakages are sources of Cr, Cu and Ni. Vehicular component wear and detachment are sources of Cr, Fe and Zn (Ball et al., 1991; Legret and Pagotto, 1999).

Typical metal concentrations from traffic and road materials are shown in Tables 2.2 and 2.3. Apart from the road-traffic, weathering of road infrastructure, such as sign posts, road markers and galvanised railings are also noted as metal emission sources by Smolders and Degryse (2002) and Hjortenkrans et al. (2006). Moreover, adoption of catalytic convertors, to avoid release of noxious gas from exhaust emissions, is believed to result in the emission of platinum group metals (such as, palladium, platinum and rhodium) into the road-traffic environment (Wiseman and Zereini, 2009).

Table 2.2: Heavy metal concentrations (mg kg^{-1}) from traffic and road materials (adapted from Legret and Pagotto, 1999)

Sources	Cd	Cu	Pb	Zn
Vehicles				
Leaded gasoline	-	-	200	-
Unleaded gasoline	-	-	17	-
Brake linings	2.7	142,000	3900	21,800
Tyre rubber	2.6	1.8	6.3	10,250
De-icing agent	0.2	0.5	3.3	0.5

On the other hand, the concentration of Pb in runoff waters in recent years has shown a sharp decrease following the ban of tetra-ethyl lead (TEL), a petrol additive, due to health concerns (Legret and Pagotto, 1999). However, a few other studies after Legret and Pagotto (1999), for example, still reported a reasonably high Pb emission from the road-traffic environment (e.g. Deletic and Orr, 2005; Napier et al., 2008; Ewen et al., 2009). While Deletic and Orr (2005) pointed out that road paint (double yellow lines) is the probable source of this Pb, Napier et al. (2008) and Ewen et al. (2009) reported diesel fuel, car exhaust and brake pad erosion are also the likely sources.

Table 2.3: Total heavy metals and PAHs estimate (tonnes) from passenger cars in the UK in 2003 (adapted from Napier et al., 2008)

Metal	Tyre erosion	Brake erosion	Oil losses	Exhaust	Total vehicular
Cu	0.3	24	0.038	0.4	37.74
Pb	1.0	1.5	0.02	1.1	3.62
Zn	990	44	2.3	1	1037.30
PAHs	21.7	-	320*	130	471.70

* Value for all road vehicles

The way these metals are transported to the receiving waters is highly variable and depends on the nature/type of the metal concerned, the prevailing hydrology, and the road surface characteristics. Cd, Cu and Zn are primarily found in soluble forms and are transported with the water, while Fe and Pb are mostly attached to sediment particles which, depending on the particle sizes, may be retained on the road surfaces (Sansalone et al., 1996; Kim and Sansalone, 2008; Helmreich et al., 2010). Runoff resulting from high intensity rainfall is likely to wash off all forms of the metals deposited on the road surface and may cause severe stress to the receiving water ecology. The fractionation of the metals into particulate and dissolved phases affects the impact of the runoff since their environmental mobility and bioavailability depends upon the aqueous concentration (Mungur et al., 1995). Soluble metals usually exert the greatest impact or toxicity to aquatic life (Clements, 2000). Clearly, this has implications for the development of control strategies to protect ecological communities. In contrast, Kayhanian et al. (2007) studied a wide range of 635 rainfall events during 2000 to 2003 and reported that most of the metals in runoff were associated with the particulate phase rather than soluble forms. Based on their study, concentration of Pb was the highest proportion present in particulate (83%), while concentrations of Cd, Cr and Zn were found between 60% and 65% and Cu and Ni were between 50% and 55%.

Briefly, based on the above discussion, it can be noted that a significant variability exists between studies, which is why the need for site-specific data is extremely important. However, it can be reasonable to consider that more than half the proportion of metals may be effectively managed or removed by targeting the particulate fraction. A similar suggestion was also found from the study by Heal et al. (2006).

The quantification of heavy metals in road sediment is found to be well documented in the literature covering different parts of the world, as few of these are collated and presented in Table 2.4. It has been seen that the heavy metal concentrations have been found to be highly variable and depend on a wide range of factors including location, sediment type, sediment collection method and metal extraction technique etc. It is also apparent from Table 2.4 that road sediment contains a significantly higher concentration of most of the metals than nearby soils (see, Paterson et al., 1996 and Deletic and Orr, 2005). There are significant differences between studies (for example, Wilber and Hunter (1979) and Herngren et al. (2006), seen in Table 2.4) when viewed on a decadal basis, suggesting that changes have taken place due to changes in legislation to control road traffic pollution, such as, better road construction and maintenance practices, changes in vehicle manufacturing technology, banning of leaded fuel etc. (Napier et al., 2008).

The heavy metal concentrations in runoff and snow–melt samples from road surfaces are collated from a few previous studies, as seen in Table 2.5 along with some other pollutants. Clearly, for runoff studies (columns 2-10 in Table 2.5), there is a significant variability between previous studies, carried out in different countries, or even between different cities within the same country, which indicates the need for local data to select appropriate tools to control heavy metal pollution efficiently in the context of sustainable drainage systems at individual sites (Davis and Birch, 2010). Only two studies, from Sweden and Germany, are found for total heavy metals in snow-melt runoff and are presented in Table 2.5 (columns 11-12). Similar to runoff, snow studies are found to vary significantly. The variation in pollutant concentrations in snow is possibly linked to the nature of the winter weather in different regions and to the road-traffic management practices.

Table 2.4: Ranges or mean concentrations of heavy metals in road deposited sediments in various cities around the world (mg kg^{-1} dry weight)

Region	Type of surface	Method of collection (metal detection)	Digestion	Cd	Cr	Cu	Fe	Ni	Pb	Zn	References
Aberdeen (Scotland)	Paved residential	Wet vacuuming (FAAS)	HNO_3	1.74		530	-		1900	1040	Deletic and Orr (2005)
Aberdeen (Scotland)	Roadside soil	Soil coring (ICP-AES)	HNO_3, HCl		22.9	44.6	18116	15.9	172.9	113.2	Paterson et al. (1996)
Kavalla (Greece)	Paved urban	Dry brushing (GF-AAS)	HNO_3	0.2	232.4	172.4	-	67.9	386.9	354.8	Christoforidis & Stamatis (2009)
	Paved residential	Dry brushing (GF-AAS)	HNO_3	0.1	110.4	76.0	-	48.9	120.8	198.9	
	Urban roadside soil	Soil coring (GF-AAS)	HNO_3	0.2	240.3	48.1	-	77.4	571.3	175.0	
	Residential roadside soil	Soil coring (GF-AAS)	HNO_3	0.1	167.7	28.1	-	31.0	105.2	79.1	
Lodi (New Zealand)	Paved residential	Dry street sweeping	HNO_3	-	43	80	-	-	2110	460	Wilber and Hunter (1979)
	Paved industrial	Dry street sweeping	HNO_3	-	1450	3170	-	-	2520	2580	
	Road junction	Dry street sweeping	HNO_3	-	69	500	-	-	8300	1100	
Gold coast (Australia)	Paved residential	Dry vacuuming (ICP-MS)	HNO_3	0.002	0.012	0.50	11.38	-	0.03	1.27	Herngren et al. (2006)
	Paved industrial	Dry vacuuming (ICP-MS)	HNO_3	nd	0.044	0.70	32.10	-	0.70	1.70	
London (UK)	Road surface	Dry vacuuming (FAAS)	HNO_3	3.5	-	155	-	-	1030	680	Schwar et al. (1988)
London (UK)	Road	Dry vacuuming (FAAS)	HNO_3	0.1	-	50	-	-	570	220	Beckwith et al. (1984)
	As above	Dry vacuuming (FAAS)	HNO_3	0.9	-	50	-	-	290	280	
Birmingham (UK)	Road	Dry street sweeping (Varian 1475 AAS)	H_2SO_4, HNO_3, HCl	1.62	-	467	-	41	48	534	Charlesworth et al. (2003)
Coventry (UK)	Pelican crossing	Dry street sweeping (Varian 1475 AAS)	As above	0.9	-	226.4	-	129.7	47.1	385.7	
Manchester (UK)	Road surface	Dry street sweeping (FAAS)	HNO_3	-	-	113	10125	-	265	653	Robertson et al. (2003)
Lancaster (UK)	Roundabout	Dry vacuuming (FAAS)	HNO_3, HCl, $HClO_4$	8.6	56	76	-	76	1450	388	Harrison (1979)

Hawaii (USA)	Road side soil	Soil coring (ICP-AES)	HNO_3, HCl	0.5	436	162	-	260	313	439	Sutherland & Tolosa (2000)
Marie (Canada)	Road	Dry vacuuming (ICP-AES)	HCl	-	-	81	-	-	141	393	Stone & Marsalek (1996)
Glasgow (UK)	Road	Dry street sweeping (FAAS)	HCl	-	-	32	-	-	327	200	Gibson & Farmer (1984)
Bratislava (Slovakia)	Urban road	Dry street sweeping (ICP-AES)	HNO_3	0.4	21.3	170.7	12000	7.4	56.7	170.9	Krčmová et al. (2009)
Madrid (Spain)	Paved urban road	Dry street sweeping (ICP-MS)	HNO_3, HF, $HClO_4$	-	-	188	-	44	1927	476	De Minguel et al. (1997)
Aviles (Spain)	Paved industrial	Dry street sweeping (ICP-AES)	HNO_3, HF, $HClO_4$	22.3	42	183	-	-	514	4829	Ordonez et al. (2003)
Baoji (China)	Road	Dry street sweeping (X-ray FS)	na	-	-	123	-	49	408	715	Lu et al. (2009)
Amman (Jordan)	Urban road	Dry street sweeping (ICP-AES)	HNO_3, HCl	1.7	-	177	-	88	236	358	Al-Khashman (2007)
Xian (China)	Urban road	Dry vacuuming (FAAS)	HNO_3, HCl, $HClO_4$	-	167	95	-	-	231	421	Youngming et al. (2006)
Shanghai (China)	Urban road	Dry street sweeping (FASS)	HNO_3, HF, $HClO_4$	0.97	264	257	-	66.5	236	753	Shi et al. (2010)
Istanbul (Turkey)	Urban road	Dry street sweeping (FASS)	HNO_3	1-6.7	-	47-407	-	10-66	61-383	226-1852	Sezgin et al. (2003)
Diff. sites (Bahrain)	Road surface	Dry street sweeping (FAAS)	HNO_3	72	144	-	-	126	697	152	Akhter & Madany (1993)
Kuala Lumpur (Malaysia)	Urban road	Dry street sweeping (FAAS)	HNO_3, HCl	3.0		-	-	-	2466	344	Ramlan & Badri (1989)

Note: FAAs=Flame Atomic Absorption Spectrometry; ICP-AES=Inductively Coupled Plasma Atomic Emission Spectrometry; ICP-MS= Inductively Coupled Plasma Mass Spectrometry, FS= Fluorescent Spectrometry; GF-AAS=Graphite Furnace Atomic Absorption Spectrometry.

Table 2.5: Ranges of event mean concentrations of pollutants in road runoff from rainfall (columns 2 – 10) and in snow-melt runoff (columns 11-12) around the world

Constituent	**Rainfall runoff**									**Snow-melt runoff**	
	Driscoll et al. (1990) *USA*	Barrett et al. (1998) *USA*	Wu et al. (1998) *USA*	Drapper et al. (2000) *Australia*	Shinya et al. (2000) *Japan*	DMRB (1998) *UK*	WRc (2002) *UK*	Crabtree et al. (2008) *UK*	*Others*	Westerlund et al. (2003) Sweden	Helmreich et al. (2010) Germany
AADT (vehicles/d)	>30,000	33,465	17,300	<30,000 & >30,000	75,000	>30,000	>30,000	5,000-200,000		7400	57,000
Total Suspended Solids, TSS (mg/l)	12-135	19-129	14-215	60-1350	41-87	12-135	53-318	40-612	46[a], 9[b]	228-551	10-1050
Total Dissolved Solids, TDS (mg/l)			70-107								
Volatile Suspended Solids, VSS (mg/l)	6-25	9-36				6-25					
pH		7.1-7.2									
COD (mg/l)	28-85	37-130	24-48			28-85	70-138	48-411	80[b]		
BOD (mg/l)		4-12					6.59				
TOC (mg/l)	4-17	46			11-55	3-17					5-195
Oil and grease (mg/l)			2.7-27			1.1-3.3					
***Metals (Total)*, µg/l**											
Zn	35-185	24-222		150-1850	427-1191	35-185	53-322	34-903		83-1680	42-2500
Cd			2.5		1-3		0.47			0.1-1.90	
Ni			2.5-9		2-9		5.81			6.3-177	
Cu	10-50	12-37	2.5-150	30-340	39-100	10-50	24-64	13-242		29-465	20-610
Fe		249-2824			2.31-5.17						
Pb	24-272	3-53	6-15	80-620	17-39	24-272	4-45	0.46-114		8.5-168	
Cr			2.5-6.5		2-10						
Al					1394-2727						

Note: [a] Conventional pavement; Pagotto et al. (2000, AADT: 12,000); [b] Porous pavement highway; Pagotto et al. (2000, AADT: 12,000)

2.4.3 Polycyclic Aromatic Hydrocarbons (PAHs)

It has now been established that storm water runoff from roads is a key source of hydrocarbon load to the environment (Gray and Becker, 2002). Van Metre et al. (2000) showed that the combustion process drives the trend of PAHs in stormwater runoff. They observed that PAHs concentration increases with an increase in automobile use. However, Ngabe et al. (2000) demonstrated a close correlation of the chemical composition of PAHs in runoff with fuel, suggesting PAHs are products of the incomplete combustion of fuels.

PAHs enter either directly from the air with dust and precipitation, or particles are washed from road surfaces by runoff. PAHs are slow to degrade in the environment, and sediment, in particular, are sinks where these chemicals tend to concentrate. The following 15 PAHs are considered as a group and are reported in road runoff studies: Acenaphthene, Acenaphthylene, Anthracene Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Fluoranthene, Fluorene, Indeno(1,2,3-cd) pyrene, 2-Methylnaphthalene, Naphthalene, Phenanthrene and Pyrene (Latimer et al. (1990) cited in Maltby et al. (1995). PAHs are of major concern because of their toxic nature, which is a potential threat to fresh water organisms. For example, Maltby et al. (1995) identified PAHs as the major toxicants in sediment contaminated with road runoff. Similar results were obtained by Datry et al. (2003) in France who found all 15 types of PAHs in sediment collected from stormwater detention basins, draining road runoff from major roads without any form of treatment. Moreover they also revealed that most of the hydrocarbons were associated with the particulate phase and were very rarely found in the dissolved phase. It can be concluded that targeting the removal of sediment from storm water runoff would have a direct impact on reducing environmental pollution from PAHs. A similar suggestion was also reported by Heal et al. (2006) and Napier et al. (2009) in their studies in the UK.

2.4.4 Conventional Pollutants

Road runoff contains significant loads of other pollutants such as suspended solids, dissolved solids, organic compounds and nutrients that can affect the quality of the aquatic environment. The total solid (TS) is defined as the material residue left in a vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature (103°C-105°C). Total solids includes total suspended solids (TSS), the fraction of total solids that is retained on a filter of pore size 45 µm, and total dissolved solids, the portion that passes through the filter. Volatile suspended solids (VSS) consist of the organic fraction of TSS. Highway runoff studies typically report values for both TSS and VSS (APHA, 1998 and Irish et al., 1998). As seen for heavy metals concentrations of these pollutants show a wide variability between studies, see Table 2.5. A few of these are discussed briefly in this section.

2.4.4.1 Suspended Solids

In an urban environment, the pollutants available on paved surfaces such as roads are mostly in particulate form. These particulate pollutants are commonly referred to as suspended solids. Rainfall is found to be the key driver to transport particulate matter to the nearby receiving waters. Suspended solids from roads, a part of total road sediment, serve as a sink or carrier for toxins, such as heavy metals and hydrocarbons. Solids therefore can affect aquatic life. For example, in addition to toxicity, water with higher concentration of solids retards photosynthesis due to loss of transparency (APHA, 1998).

The wash-off of solids by rainwater depends on rainfall volume and intensity, and also depends on the size of the particulate matter that varies from very fine to large. For example, finer particles remain in suspension for a longer time than coarser ones and, hence, are more likely to reach receiving water bodies (Dong et al., 1983). Andral et al. (1999) also note that satisfactory treatment for the finer particles that have a high potential to reach receiving waters would require a solids removal efficiency of 90%. Moreover, finer particles are not only actively available in water for a long time but also they are preferentially associated with pollutants commonly harmful for aquatic life, for example heavy metals and hydrocarbons.

Relationships between pollutants and suspended solids are well understood from the literature. For example, Sartor et al. (1974) found a significantly higher percentage of nutrients and organic matter in the finer fraction (less than 43 µm) which only counted for 5.9% of the total mass of solids. The explanation of this is linked to finer particles having larger surface areas than larger ones and the presence of electrostatic charges.

Due to their importance fine particles get more attention from researchers on road runoff than coarse ones and play a significant role in designing best management practice in the field. Since the correlation of suspended solids to other pollutants is strong (Herngren et al., 2005), the use of suspended solids as a surrogate parameter to estimate other pollutants is common practice. Hence, the selection of suspended solids concentration as an indicator of stormwater quality has been advocated (Akan and Houghtalen, 2003).

2.4.4.2 Organic Carbon & Others

Organic carbon is very common in road runoff water and, if present in excessive amount, causes problems for aquatic life by significantly depleting dissolved oxygen (Warren et al., 2003). The organic content of road runoff is expressed by its biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). BOD is the measure of the amount of oxygen consumed by microorganisms in decomposing organic matter in a water sample over a specified period of time, usually five days. BOD also measures the bio-chemical oxidation of inorganic matter taking place in the sample. Higher BOD values mean that there may be insufficient oxygen left for higher forms of aquatic life to survive. COD measures the oxygen required to completely oxidise all organic materials in a sample under thorough, hot and aggressive acid digestion. TOC is the measure of organic carbon in a sample. In many cases it is possible to correlate any two or three of BOD, COD and TOC (APHA, 1998).

Gromarie-Mertz et al. (1999) found that urban road surfaces are an important source of large amounts of organic carbon, with levels depending on the number of antecedent dry days, occurrence of street cleaning or rainfall events and surrounding land uses. This is supported by a previous study by Sartor et al. (1974) who observed that organic matter accumulates on road surfaces much faster than inorganic matter. In addition Roger et al. (1998) found a high association of organic matter with the finer size fraction of road sediment, in particular for particle sizes less than 50 μm.

Other parameters such as temperature, pH, dissolved oxygen content, and faecal coliform bacteria are reported in road runoff studies (Maltby et al., 1995; Barrett et al., 1998). These and the other parameters discussed above are also good indicators of likely water quality changes in receiving waters (Barrett et al., 1998).

2.5 Factors Affecting Road Runoff Quality

It can be speculated that the increased impervious surfaces, such as roads, driveways, car parks and building yards, will aid the accumulation of contaminants or potential pollutants on these surfaces by anthropogenic activities (e.g. traffic) along with human activities. Mostly these pollutants may be discharged directly to receiving water bodies, for example, lakes, streams or rivers etc. As discussed before, the levels of contamination are highly variable and site specific, and depend upon several factors, such as volume of traffic, design of road drainage, surrounding land use, and climate and local hydrology. Among a list of factors, traffic volume would seem to be an important factor for predicting runoff quality, as research studies found major roads carrying 30,000 vehicles daily produce runoff with two to five times the pollutant concentration levels compared to rural roads carrying 5000 vehicles daily, for example (CIRIA, 1994; Sansalone & Buchberger, 1997; Wu et al., 1998; Shinya et al., 2000). Fluxes of pollutants in highway runoff can be influenced by traffic conditions, traffic movement patterns, road condition, surrounding land use and weather (Folkeson, 1994; Barrett et al., 1995). Important precipitation and atmospheric characteristics that affect the quality of runoff include seasonal rainfall patterns, dry periods between rainfall events, rainfall intensity, rainfall duration and volume of runoff. A few of the above mentioned factors are discussed below.

2.5.1 Traffic Volume

Traffic volume is seen as the primary traffic related risk factor affecting contamination in road runoff. Usually traffic volume is measured as the annual average daily traffic (AADT) and several research studies in the past have classified roads according to the level of traffic, where commonly an AADT value more than 30,000 is classified as an urban road or highway and lower than this value is for rural or residential roads (CIRIA, 1994; Sansalone & Buchberger, 1997; Wu et al., 1998; Shinya et al., 2000). The philosophy and attraction of such an approach are easy to understand. If pollutants, for example metals in stormwater, come from vehicles, the idea is that the more cars travelling over the road, the greater the metal concentrations should be. For example, as presented in Table 2.6, event mean concentrations for a variety of pollutants at different traffic volumes demonstrated that highways with an average daily traffic (ADT) value more than 30,000 have 3-5 times higher pollutant concentration than highways with ADT value less than 30,000 (Driscoll et al., 1990). This is found consistent with first 4 studies presented in Table 2.5. However, runoff pollutant data from around the world is rather inconsistent with the traffic volume and have revealed that the ADT or AADT-pollutant concentration/load relationship is considerably more complicated than originally envisioned.

Table 2.6: Typical event mean Concentration (EMC) for pollutants in highway runoff showing relationship with traffic volume [adapted from Driscoll et al. (1990)]

Pollutant	EMC for Highways with fewer than 30,000 vehicles/day (mg/l)	EMC for Highways with more than 30,000 vehicles/day (mg/l)
Total Suspended Solids	41	142
Volatile Suspended Solids	12	39
Total Organic Carbon	8	25
Chemical Oxygen Demand	49	114
Nitrite and Nitrate	0.46	0.76
Total Kjeldahl Nitrogen	0.87	1.83
Phosphate phosphorous	0.16	0.400
Copper	0.022	0.054
Lead	0.080	0.400
Zinc	0.080	0.329

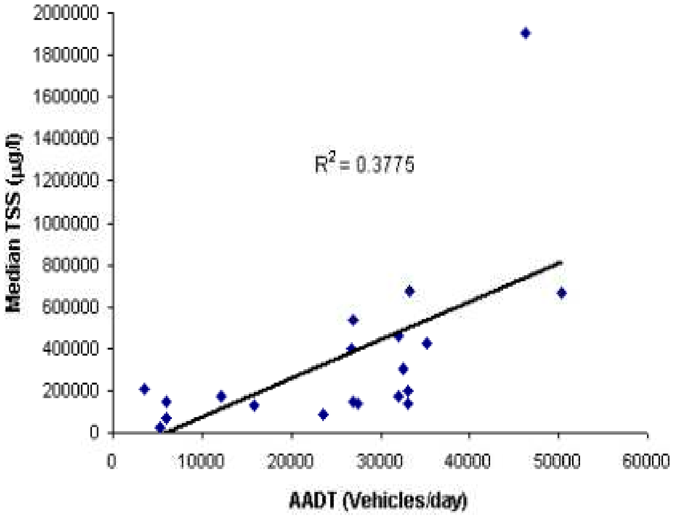


Figure 2.2: Correlation of TSS concentration to traffic volumes [Note single outlier, ignored in regression equation (adapted from Drapper et al. (2000)]

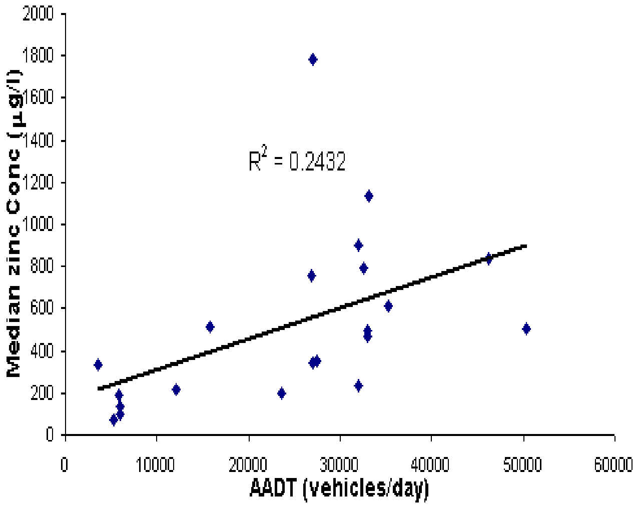


Figure 2.3: Correlation of acid-extractable zinc concentration to traffic volumes [adapted from Drapper et al. (2000)]

Moreover, McKenzie and Irwin (1983) found that Zn concentrations were higher at a medium traffic flow site (50,000 AADT) than from either a low traffic flow site (4,000 AADT) or a high traffic flow site (70,000 AADT) in a study of runoff from an urban highway in Florida, USA. They also noted that Cu concentrations at all three sites were comparable. Again these findings cast doubt on a simple relationship between ADT or AADT and pollutant loadings. A few more pieces of evidence to support this statement are also available. For example, Drapper et al. (2000) documented that in many of their study sites with AADT well below 30,000, the pollutant concentrations were as much as those from sites with higher AADT. Moreover, they found a poor correlation between chemical concentrations in road runoff and traffic volume (R^2 = 0.377 for TSS, 0.243 for Zinc), as seen in Figure 2.2 and 2.3. Although not presented, the strength of correlations for other pollutants and AADT are even smaller than 0.200.

Somewhat similar findings were found from California Department of Transportation studies (Caltrans) (Kayhanian et al., 2003; Caltrans, 2003). Here no direct linear correlations between road runoff pollutants and AADT (ranging from 1,800 to 259,000) were identified. However, they found that AADT along with site specific attributes (such as, catchment characteristics, surrounding land uses) together can better explain most road runoff pollutants concentrations.

Similar evidence was given by Miller (2005) who concluded that pollutant concentrations in road runoff were not dependent on AADT alone though it was one of the key factors. He noted an overall increase in pollutant concentrations with an increase of AADT; however, no direct relationship could be made between two. Additionally Miller found an inverse relationship between metal concentrations and the age of the road surface.

In addition, traffic congestion likely has a strong influence on the quality of road runoff. Congestion is a function of traffic movement and road capacity, and is influenced by road type, road lay out and traffic type. Compared with free flow conditions, a heavily congested section of road may generate a higher pollutant load because braking and acceleration are known to release greater levels of pollutants compared to steady motion (Hjortenkrans et al., 2006; Napier et al., 2008; Ewen et al., 2009).

2.5.2 Sediment Particle Size and Water Quality

As mentioned earlier, not all the sediment available from road surfaces is transported during wash-off events (Egodawatta et al., 2007). Whereas finer particles are easily carried by runoff, coarse ones are retained on the road surfaces and since not all particle size fractions are equally polluted, sediment particle size has a significant influence on runoff water quality. Briefly, smaller particles (clay and silt) contain high surface areas and negative charges in chemical composition, which give them a greater opportunity for absorbing more metals into their surface compared to larger particles (sand, grit) (Ellis and Hvitved-Jacobsen, 1996). Although several particle sizes (diameter) have been defined as a borderline to separate coarse and fine sediment, commonly a sediment diameter of 63 µm has been identified (Roger et al., 1998; Charlesworth and Lees, 1999; Ellis, 2000; Sutherland, 2003; Zhu et al., 2008; Opher and Friedler, 2010). However, other classifications to separate fine and coarse particulates have also been recommended, e.g. Furumai et al. (2001) and Murakami et al. (2004) used 45 µm as a boundary, while Kim and Sansalone (2008) used 75 µm in keeping with conventions separating fine and coarse particulates specified in ASTM (2002). Furthermore, a few researchers divided sediment < 63 µm into several sizes up to as small as for example < 2 µm, and found that the smallest sizes contain even higher metal concentration than the

63 µm sediment size (Greb and Bannerman, 1997; Deletic and Orr, 2005; Sansalone and Buchberger, 1997).

Contrary to the above findings, a few other studies, for example, Stone and Marsalek (1996) and Heal et al. (2006) found that a greater amount of heavy metals and PAHs loads was associated with coarser sediment. Furthermore Marsalek (1996) found that pollutant concentrations between coarse and fine sediment size fractions were very similar. The consequences of high pollutant loads being associated with coarser sediment imply that road drainage systems should be designed not only to capture finer sediment but also to retain coarser sediment.

2.5.3 Storm Characteristics

Storms are the key driver of pollutant wash-off from road surfaces and are strongly associated with the potential impact or consequences. Storms can be described using several characteristics such as intensity of rainfall, duration of total storm and number of dry days preceding the event. Correlations between concentrations of pollutants in runoff induced by rainfall and these factors have been reported in various studies elsewhere (e.g. Brezonik and Stadelmann, 2002; Kayhnian et. al., 2002). Storm intensity has been revealed as the most important of these as many pollutants are attached to particulates. As mentioned previously, the more intense the storm (the more the kinetic energy), the greater the movement of particulate matter and so pollutants (Patel and Atkins, 2005; Kayhanian et al., 2007; Gan et al., 2008; Zhu et al., 2008; Soonthornnonda and Christensen, 2008).

2.5.4 Road Type and Surrounding land use

The effect of road paving material (e.g. conventional impervious type such as concrete and tarmac versus pervious type such as porous asphalt and paving blocks) on the quality of highway runoff has not been studied in much detail. Rob et al. (1999) and Pagotto et al. (2000) demonstrated that porous pavements improved the water quality slightly for the main pollutants in runoff water (such as Cu, Pb, Zn, solids and hydrocarbons) from Dutch and French motorways. Moreover, it is generally believed that road surface type is relatively unimportant compared to such factors such as whether the road is in a rural or urban location (Göbel et al., 2007). It has also been reported that the type of collection and drainage system, type of curbs and age of the road has a greater effect on runoff quality than road surface type (Wu et al., 1998). Road terrain (hills and bends) has a marked effect on contaminant loading. For example, Kennedy et al. (2002) quote tyre wear rates that vary from 100% on straight and level roads (representing full tyre life) to 76% on slightly hilly and curvy roads, and to 50% on hilly and curvy roads. Thus, compared with level straight sections, roads in more hilly terrain with a larger number of tight bends result in greater tyre wear, which causes increased zinc emission. Also the greater amount of braking required causes increased copper emission. Similar ideas were also reported by Ewen et al. (2009). On the contrary, Hjortenkrans et al. (2006) found no significant influence on elevated metal concentrations at road intersections, where more frequent braking is likely to occur in their study in Sweden. Therefore, it can be summarised that the effect of road type or traffic movement patterns (conditioned by road lay-out) on pollutant emission patterns are not well understood, though such information would be important in order to evaluate best management practice options for local road drainage: Clearly this needs further research.

However, land used nearby roads seems have a great impact on the characteristics of the stormwater runoff (Goonetilleke et al., 2005). Furthermore, specialised land uses such as commercial and industrial areas, agricultural property, marine environment and airports may contribute additional pollutant loading (Goonetilleke et al., 2009). Göbel et al (2007) also suggested that in-depth studies for these special land uses are needed.

2.5.5 Road Drainage Structures

The type of road drainage infrastructure (curb, channel, gutters, and catch pit) plays a key role in controlling the contaminant load in runoff leaving the road, and therefore in controlling the risk to downstream receiving environments (Sansalone et al, 1998). Evaluating the source strength in terms of contaminant load needs to take account of road drainage systems, in order to determine the actual load entering the receiving environment. For example, curb and channel drainage systems collect high volumes of runoff and finally discharge via point sources, thereby having potentially intense but local impacts on the receiving environment (Li and Barrett, 2008). On the other hand, although a significant proportion of rural roads have no storm water collection system, with the result that runoff is more spatially diffuse and because the pollutant load is distributed over a large area, the impact on nearby water bodies is unlikely higher than urban roads with conventional drainage systems. Therefore, road drainage systems have significant impacts on runoff water quality and need to be considered in studies on road runoff (Li and Barrett, 2008).

2.6 Assessing Road Sediment Contamination

Adverse effects of road runoff polluted by heavy metals and PAHs (Wilson et al., 2005) contamination on receiving waters (particularly on freshwater macroinvertebrates, aquatic species and fish species) are well documented (Clements et al., 2000; Beasley and Kneale, 2004). All of these studies reported that streambed sediments accumulated toxic pollutants among which heavy metals and PAHs are very common when runoff is associated with vehicle traffic, pavements, roofs, guttering and industry. These pollutants are believed to be persistent and often exert a wide-reaching stress on the freshwater ecosystem leading to the impairment of tolerant species and disappearance of sensitive macroinvertebrates.

To deal with potential contamination associated with urban runoff, numerous guideline values for priority pollutants (e.g. toxic metals and PAHs) have been set to improve and maintain a better quality of effluent prior to discharge to nearby water environments (Wilson et al., 2005; Gasperi et al., 2009). The standard values are set to protect freshwater ecosystems and are available for dissolved pollutants and particulate pollutants (Wilson et al., 2005). Note that at present in the UK only environmental quality standards (EQS) for dissolved metals are available from the Environment Agency (EA, 2003), and no such standard is adopted for particle bound heavy metals. However, sediment quality guidelines (SQG) suggested by the Canadian Council of Ministers of the Environment (CCME, 2007), and Flemish SQG (de Deckere et al., 2011) are relatively newly available and can be used to monitor hazard assessment relating to sediment quality. However, it has been found that two sets of trigger values from those guidelines are rather inconsistent. A point to be noted is that all these guideline values were derived for fluvial sediment with the aim of protecting fresh water ecosystems, as stated earlier. However, in the absence of particular guidelines for road sediment, these alternatives can be used to gain an impression of how hazardous the road sediment could be in relation to ecological aspects, as evident from previous use in literature (e.g. Heal et al., 2006; Shi et al., 2010).

Transforming heavy metal concentration levels into a single pollution index value is often preferred (rather than using several trigger concentration values) to derive better understanding and decision making tools in environmental pollution research. A variety of pollution indices for sediment associated heavy metals have been proposed to quantify the level of pollution and associated impacts on aquatic life (e.g. Yu et al., 2003; Huang et al., 2009). However, the degree of contamination and potential ecological risk indices proposed by Hakanson (1980) have been found to be the best tools for assessing metal pollution in more holistic way. These indices were derived for natural sediment in fresh and/or marine/estuarine waters rather than road runoff. However, their robustness makes them suitable for road sediment (even in the absence of ecological data) to obtain an impression of the ecological risk, as evident from the previous studies in the literature elsewhere (e.g. Huang et al., 2009; Shi et al., 2010; Duong and Lee, 2011). However, a point to be noted is that the results obtained using these methods may not be sufficient enough to quantify actual ecological risk posed by road sediment without other relevant data and information, such as the type of aquatic species considered, exposure time with contaminated sediment, appropriate dilution factors, metal releasing mechanisms from sediment depending upon sediment-water chemistry, etc. (e.g. Kayhanian et al., 2008; de Deckere et al., 2011).

2.7 Road Drainage - Water Quality Perspective

Based on the literature, it is clear that although roads account for only a small portion of urban land use, they generate a considerable amount of runoff during rainfall, as road surfaces are commonly impervious in nature (Ball et al., 1998). It has also been revealed that road runoff transports a wide range of pollutants that are potentially harmful to the aquatic environment if discharged to nearby waters without any form of treatment. As seen in Figure 2.3, before 1975, traditionally urban drainage was focused on controlling the quantity of water with the aim of avoiding flooding while overlooking water quality aspects. This was done by routing surface runoff through underground pipe systems to either a treatment plant or to a discharge site on a water body. However, the consequences of urban stormwater discharges for water bodies, in particular for aquatic life, came under consideration in the early 1980s. Water quality became an increasing issue in the management of stormwater drainage by the mid 1990s. The aim now was to control flooding and to ensure that surface runoff did not degrade the water quality of receiving waters.

However, in last two or three decades rapid urbanisation sees a range of infrastructures to develop and a figure is set to increase indeed. Consequently, the urban environment is becoming heavily modified and stressed with even more pollution with a wide range of pollutants (some are new, for example, in the road traffic environment after the recent innovations in both car industry and the composition of fuel), as reported by Legret and Pagotto (1999), Hjortenkrans et al. (2006) and Krčmová et al. (2009). Following on the EU WFD (2000/60/EC) formulated a guideline which requires EU countries including the UK to control diffuse sources of priority pollutants with the goal of protecting water bodies including groundwater (Legret and Pagotto, 1999; Napier et al., 2008). The EU WFD documents added the urban amenity value along with quantity and quality.

Within this context, various sustainable urban drainage systems (SUDS) have been proposed and developed over the last 15 years. These incorporate three key issues of urban drainage in the so-called SUDS triangle, namely, quantity, quality and amenity (Figure 2.4). Recently, using SUDS to deal with surface water discharges to water bodies has been enforced in law in Scotland under the ‘Water environment (controlled activities) (Scotland) Regulation 2011’ for all new development (Scotland Northern Ireland Forum for Environmental Research (SNIFFER), 2008).

Briefly, SUDS are drainage systems designed to tackle water quantity (control flood risk), to address water quality (to protect ecological status), and to restore urban amenity and biodiversity. To deal with water quality and amenity issues, several generic treatment options have also been identified, as seen in Figure 2.5. The concept of a treatment train starts with source control, then site control and finally regional control with the aim of capturing stormwater and associated pollutants at sources or sites, leaving moderately clean water to flow to a regional control where amenity and bio-diversity issues are catered for. The treatment train is a useful concept to attenuate flows, improve water quality and manage runoff close to its source (Ellis, 2000;

SNIFFER, 2008; Heal et al., 2009). Treatment in SUDS tools has focused primarily to retain water sediment and then allow sediment to undergo natural bio-chemical activity over the residence time in improving water and sediment quality.

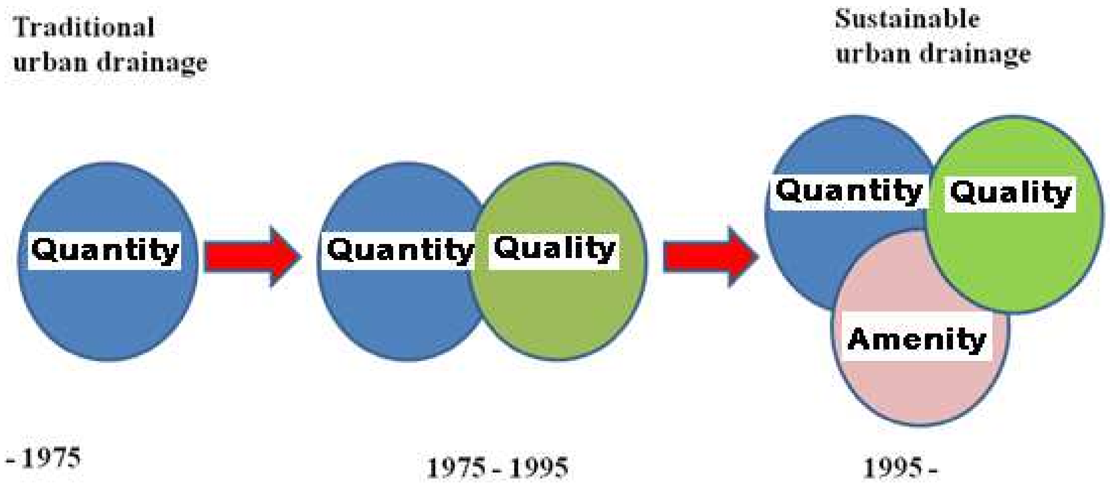


Figure 2.4: Changing concept of road drainage design over the time frame in the UK

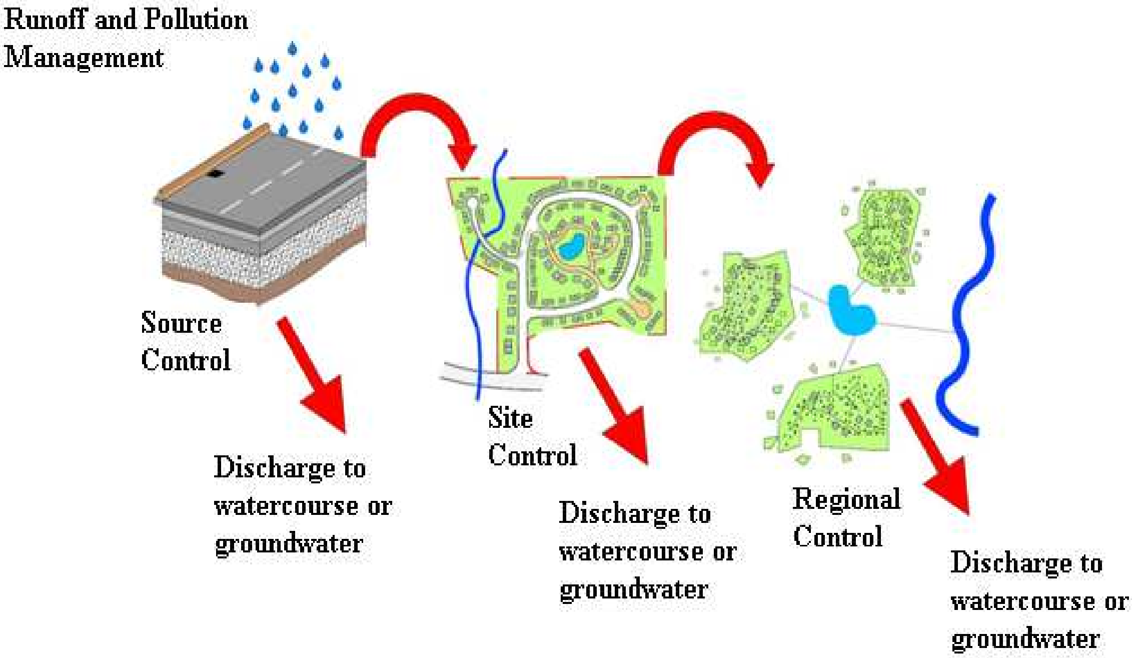


Figure 2.5: Conceptual diagram of sustainable urban drainage systems (SUDS) treatment train showing source, site and regional control (adapted from SUDS for Roads Manual)

Within the context of SUDS for roads, a number of different SUDS tools are available, for replacing or modifying conventional road drainage to address water quantity, quality and urban amenity issues, as a long-term robust option for urban pollution management. For example, filter drains, swales and permeable paving as source and site control measures, together with retention and detention ponds or wetlands as regional controls. However, source or site controls are often being preferred (SNIFFER, 2008).

A few studies are available in the UK on the performance of an individual SUDS tool or use various tools as a unit called SUDS treatment trains. For example, Heal et al. (2009) reported that SUDS treatment trains performed better than a single SUDS tool for pollutant removal efficiency based on the monitoring of four SUDS treatment trains at the Hopwood Park Motorway Service Area in Central England. Napier (2009) reported the importance of soil-based SUDS, for example, swales or infiltration, for controlling traffic-related pollutants. A few other studies conducted elsewhere have focused on treating contaminated road runoff at their sources. For example, Zhu et al. (2003) found that incorporation of a peat filtration layer in a road gully decreased Zn concentration significantly in their study in Tennessee, USA, while Lau et al. (2000) showed that insertion of a bio-filter in road drains removed over 85% of dissolved Pb and Zn from road runoff waters. However, for source or site controls, it is necessary to identify the priority locations (with data for pollutants) along the road network. It is therefore useful to have such information on pollutant concentrations handy that may inform road drainage designs and maintenance in the context of SUDS for roads.

2.8 Conclusions

Based on the current state of knowledge of urban diffuse pollution with respect to the road-traffic environment in the literature, the following conclusions can be drawn.

The focus on water quality issues associated with road runoff from the road network in a suburban area is relatively new, but a substantial amount of research has been undertaken to understand the fundamentals of the water quality issues. It is understood that urban pollution control and mitigation now needs to be more focused on diffuse source rather than point source pollution. It is recognised that a wide range of anthropogenic activities in urban areas generate a wide variety of pollutants and act as diffuse sources. Moreover, an increased area of impervious surfaces due to urbanisation generates a greater flux of pollutants to receiving waters.

Significant research has been carried out on pollutant build-up and wash-off processes, which are regarded as key mechanisms in urban water quality research. However, due to variability of pollutant build-up and wash-off processes, outcomes for most of this research are rather site-specific and often fail to fit into a general urban pollution framework. Moreover, significant variability is found between pollutant build-up and wash-off data between studies in different geographical regions and even between studies in the same region. Consequently, numerous predictive models have been developed so far for characterisation of urban stormwater quantity and quality. Although models for runoff volumes and flows are well developed, models for water quality are not reliable. For example, using default parameters embedded in available modelling tools may not always produce satisfactory results. Therefore, the information on the pollutant build-up and wash-off processes available in the literature may not be applicable for all cases, and thus needs for local data are emphasised.

The primary pollutants identified in stormwater are commonly referred to as conventional pollutants (TSS, TDS, VSS, OC, nutrients etc.), heavy metals and PAHs. Among which heavy metals are most ubiquitous and are regarded as hazardous to human and aquatic life. In addition, heavy metals are often adsorbed to the particulate matter derived from the anthropogenic activities (e.g. traffic) on road surfaces, and their concentration are found to vary with different sediment particle sizes, which is an important issue for the transport and fate of pollutants associated with road deposited sediment by natural wash-off events (rain or snow).

The sources and pathways of pollutants commonly found on urban catchment surfaces have been well documented in the literature. Among the various pollutant sources, the road traffic environment has been identified as the largest contributor to the pollutant load, although roads account for only a small percentage of urban land uses. The pollutant loading from the road traffic environment is highly variable, being influenced by several factors, among which different road lay-out, type of traffic movement patterns, traffic load, road surface condition, presence of road paints, surrounding land uses and atmospheric deposition are likely as key. Furthermore, the pollutant concentrations are also found to be influenced by different environmental conditions and are varied with road sediment derived during dry and wet weather (runoff and snow) periods. On the other hand, other urban pervious and impervious surfaces together with specialised areas (industrial and commercial sites) are found to be dominant sources of pollutants under certain conditions.

The knowledge of site-specific factors regarding pollutant emissions patterns (and associated contamination levels) from the road traffic environment is identified as a relatively new field of research. However, such information is deemed important for the design of road drainage in the context of sustainable urban drainage systems for roads in order to comply with the objectives of the EU WFD. Although a few of these studies exist in the literature, these are not particularly focused, and is difficult to transfer the results to other sites and to some extent the data is now out of date because it may not reflect recent changes to legislation (e.g. unleaded fuel use) and developments in vehicle design (e.g. catalytic convertors).

Chapter 3 – Materials and Methods

3.1 Introduction

The necessity for an in-depth investigation of pollutant processes, such as pollution build-up pattern, transformation and transportation, in stormwater quality research has been identified in Chapter 2. It has also been revealed that the techniques used to collect data in different studies, as reported in the literature, are highly variable. For example, a wide range of methods from street sweeping to vacuuming has been used to collect dry sediment from a catchment. The simplest street sweeping method is well documented in Kim et al. (1998), Charlesworth et al. (2003) and Robertson and Taylor (2007). However, street sweeping methods, although easy to use, may be biased against the collection of finer particles, as noted by Vaze and Chiew (2002) and Deletic and Orr (2005). As a result, Vaze and Chiew (2002) used dry vacuuming methods, while Deletic and Orr (2005) introduced a wet vacuuming technique with the aim of collecting dry sediment efficiently. Similarly, studies of pollutant wash-off during rainfall and snow precipitation also exhibit variability in concepts, scale, purposes of the study and apparatus used. For example, Sartor et al. (1974) used simulated rainfall for wash-off studies from roads, Vaze and Chiew (2002) sampled sediment before and after runoff during natural rainfall events and Crabtree et al. (2008) used automated water samplers at catchment outlets during rainfall.

It is therefore clear that a wide range of techniques is available to conduct investigations into stormwater quality research. Each investigation technique has its advantages and disadvantages, and the most appropriate method can be selected by rating them according to preferences, suitability and scope of the study at specific locations. Although the techniques differ, they are all scientifically recognised and verified for use in specific research environments. In this regard, this study developed field investigation methods to obtain local data from the road network in the study area over a period of 12 months. Sites were selected on the road network with the aim of capturing emission patterns of heavy metals and associated pollution that in turn enabled further information to be derived (Vaze and Chiew, 2002). Due to the absence of any previous water quality data from the road-traffic environment in the study area, it was intended to use simple approaches for the investigations, so that future work could be undertaken in a consistent manner. The apparatus for the field investigations of road sediment during dry, wet weather and snow periods were selected based on the resources available and the ease of their use considering health and safety requirements for work on roads. In addition, it was made sure that the selected methods and apparatus were reliable for their designated use.

3.2 Study Area and Sampling Sites

Edinburgh, a city in the southeast of Scotland, lies on the east coast of Scotland's central belt, alongside the Firth of Forth, as seen in Figure 3.1.

Figure 3.1: Location of the study area on Google map (UK map showing Edinburgh, Edinburgh City map showing Riccarton Campus road network at Heriot Watt University).

It has a temperate maritime climate (moderate summer and mild winter), the annual average temperature range is about 0.9 – 12.2 ^{0}C (1971-2000) and the annual average precipitation is about 668 mm (1971-2000) distributed evenly throughout the year (see Figures A4 and A5 in appendix). Heriot Watt University's Riccarton Campus (latitude: 55.91^{0} N and longitude: -3.31^{0} E) is located southwest of Edinburgh city (Figure 3.1) and has been developed during the last 40 years with good ecological and environmental perspectives. Continuing its successful progress as a provider of quality education, it is expanding with many infrastructure developments. Because it has been observed that road runoff goes directly or indirectly into the Murray Burn (see Figure 3.2 and 3.3), which is a small stream running across the campus, there is a risk of it being contaminated by traffic related pollutants. No previous research has been carried out on the pollution potential of the campus roads.

Before rainfall **After rainfall**

Figure 3.2: Additional flow to the Murray Burn stream through Campus drainage systems during rainfall events.

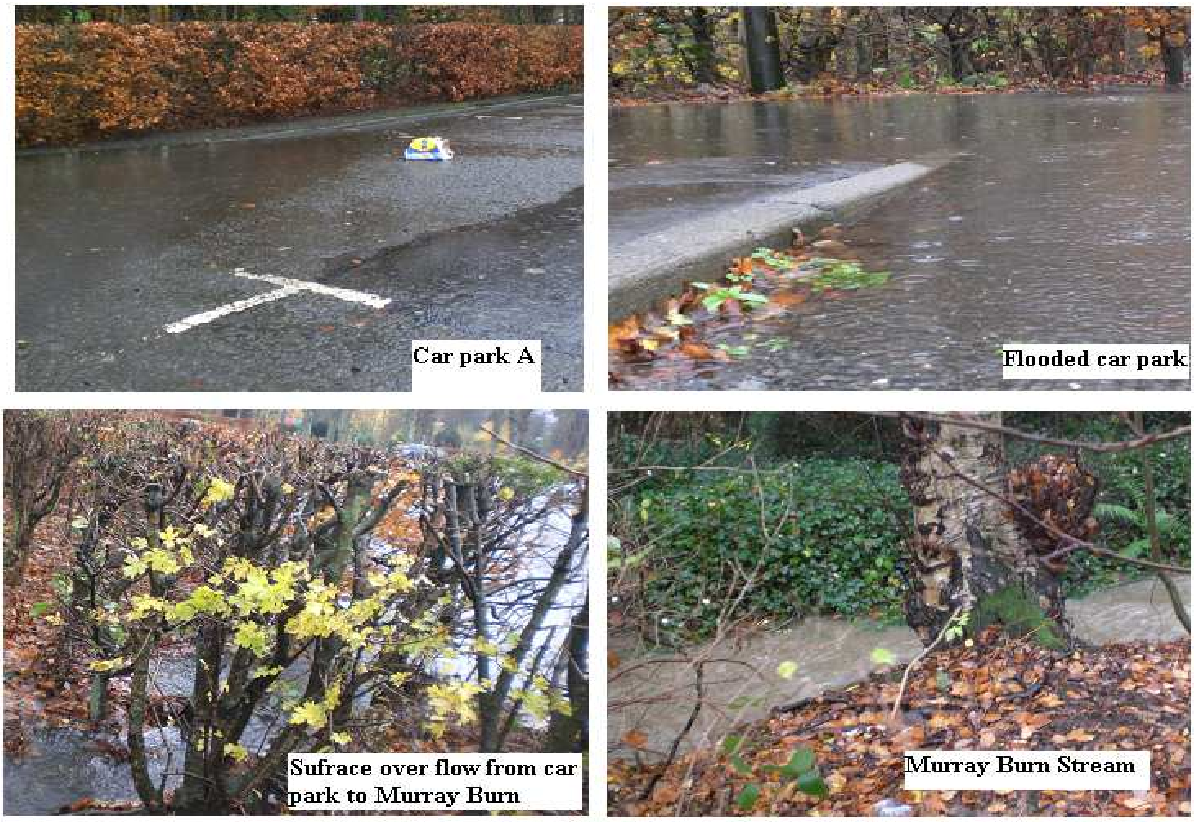


Figure 3.3: Surface overflow from Car Park A to Murray Burn during rainfall events.

12 different sites were selected on the Riccarton Campus road network to represent typical road lay-outs, as seen in Figure 3.4. The sites comprise straight sections of road, roundabouts, a road bend, a road with speed control measures (speed bumps), a road intersection, bus stops and a car park. The sites were selected after careful consideration of the aims of the field investigations, the health and safety of personnel involved in field sampling and other road users, and the quick collection and transportation samples from the field to the laboratory. Road sediment was collected from these sampling locations during dry periods between 1 to 20 days long between a rainfall and any mechanical cleansing events. However, 4 of the 12 sampling sites were further selected, based on the study objectives, for long term monitoring (over the year) of road sediment during dry and wet weather (rainfall and snow precipitation). These four sites were a road bend (Site 3: RB), a section of road with active speed control measures (Site 6: RSC), a road intersection (Site 8: RI) and a straight road section (Site 9: SR). The road surface condition of these four sites can be defined as good except for the Site 6 at which increased degradation of road surface materials and paints was observed. In addition, four other sites were selected on roads which carry no traffic, for measuring

local background values for heavy metals. These sites were located no less than 200 m north-west of Site 3 to avoid any significant influence from other sampling sites.

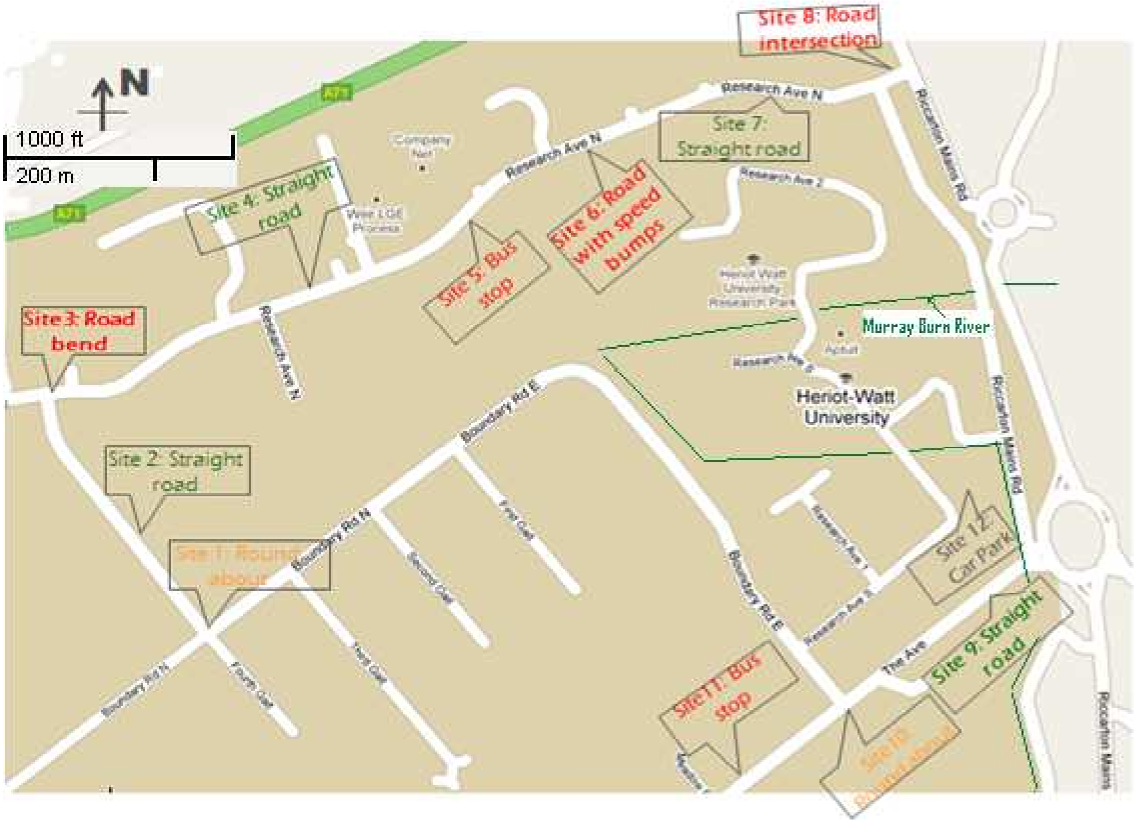


Figure 3.4: Sampling locations on Riccarton Campus road network at Heriot Watt University, Scotland (adapted from Google map).

Double yellow lines are painted along the edge of the road for most of the 12 sites and additional white markings are found at a pedestrian crossing area at Site 6 and for the stop lines at Sites 5, 8 and 11 (see Appendix A). It should also be noted that Sites 8 and 9 are very close to an entry and exit point of the campus. Based on the traffic movement pattern at the sites during the sampling period, primarily two types of ‘stop-start’ activities are found. Firstly, at a few sites, Sites 3, 5, 6 and 11, almost all traffic was observed to undergo braking as it passed through. Secondly, at a few other sites, Sites 1, 8 and 10, the traffic movement pattern was found to be more controlled in terms of ‘stop and start’ activities and therefore, a lesser degree of braking occurred than at the previous type. At all other sites except Site 12, the traffic movement pattern was consistent with a steady speed.

The roads are used by a variety of personal and commercial vehicles and some are parts of bus routes. Each of the sampling sites has 2 lanes of traffic with an asphalt road surface, with low traffic densities ranging from 200 to 650 vehicles per hour during working days mainly, as measured during the sampling period. The surrounding land area is devoted to campus buildings, some farm land, foot paths and pavements. Mechanical street-sweeping and gully cleaning occur typically twice a year on the campus by the local council.

Table 3.1: Site details on Riccarton Campus road network, Heriot Watt University, Edinburgh

Site No.	Site description	Painted lines	Road condition	Road furniture near sampling points	Traffic flow type passing sampling points	Traffic load (vph)	Surrounding areas near sampling points
1	Roundabout (G-4)	White/Red	Good	Lamp post/ signs/ gully	Stop-start	200	AA, CP, OB, FP
2	Straight Road (G-4)	Yellow	Good	None	Steady speed	200	AA, FPS
3	Road Bend (RB)	Yellow	Good	Gully/lamp post	Braking	200	AA, FPS
4	Straight Road (RAN)	Yellow	Good	Lamp post/signs	Steady speed	200	OB, FPS
5	Bus Stop (RAN)	Red/ blue/yellow	Good	Bus shelters/ sign post	Stop-start	230	OB, CP, FP
6	Road with speed controls (RSC)	White/ yellow	Poor	Lamp post/ signs/ pedestrian crossing with barriers	Braking	250	OB, CP, FPS
7	Straight Road (RP)	Yellow	Good	Sign post	Steady speed	265	OB, CP, FPS
8	Road Intersection (RI)	White/ yellow	Fair	Traffic lights/ gully	Stop-start	285	OB, MR. FP
9	Straight Road (Avenue) (SR)	Yellow	Good	Sign posts/barriers	Steady speed	650	CP, MR, FP
10	Roundabout (Avenue)	White	Good	Road barriers/ sign post	Stop-start	650	OB, FPS
11	Bus stop (Avenue)	Red/ blue/yellow	Good	Sign post	Stop-start	550	SH, OB, FP
12	Car Park	White	Fair	Lamp post	Stop-start	--	--

G = Gait No., RAN= Research Avenue North, RP = Research Park, vph = vehicle per hour, AA = Agricultural area, CP = Car park, OB = Office buildings, FP = Foot path, FPS= Foot path separated by grass strips, MR = nearby main roads linked with campus roads, SH =Student halls.

The approximate roadway width is 6 m with 2 lanes of traffic and, the speed limit is 20 mph. The age of the campus road varied between 5 to 10 years (personal communication with Estate Office, Heriot Watt University, Edinburgh). The typical road drainage pattern for campus road is found with conventional gutter and gully pot along the curb with 10 m spacing between them on both lanes. Therefore, it is assumed that 10 m × 3 m area of road draining to a road gully. However, from monitoring the sites, at no time during the study period was there any evidence of significant removal of road sediments by this process. The details of the sites are presented in Table 3.1. In addition, a photograph of each site is presented in Appendix A.

3.3 Field Sampling

3.3.1 Sampling Road Deposited Sediment (RDS)

A number of different methodologies have been used to sample road deposited sediment in earlier studies on sediment build-up with each technique having its own individual advantages and disadvantages. The most commonly used techniques are dry street sweeping using a brush and dustpan (see Kim et al. 1998; Charlesworth et al. 2003; Robertson and Taylor, 2007) and road dust collection using a portable vacuum cleaner with a view scope (see Grottker, 1987; Ball et al. 1998; Deletic and Orr, 2005; Goonnetilleke et al. 2009). For ease of use, and noting the characteristics of the sediment to be sampled, the dry street sweeping method using a brush and dustpan was used in this study, although it may be biased against the collection of the finer particle size fractions due to disturbance and mobilisation of fine sediment induced by road sweeping instrument. Previously published work reveals that a primary variable of any investigation of pollutant build-up is the number of antecedent dry days. Although several studies looking into this aspect exist, for example Sartor et al. (1974) and Ball et al. (1998), it is not clear what the optimum duration is of undertaking a pollutant build-up investigation. Based on these previous studies and knowledge of weather patterns in Edinburgh, it was decided to carry out the RDS build-up investigation over 14 days in April 2010 for this present study. The antecedent dry days considered were 1, 2, 3, 5, 7, 9 and 14 days.

Site inspection suggested that RDS particles originate primarily from vehicles, the road surface, atmospheric deposition and the surrounding land. Sampling plots comprising a 1 m^2 road surface area, near the curb and 1 m away from the curb, were initially cleaned by repeated sweeping using brushes. However, RDS from a second position (1 m away from the curb) was collected at Sites 3, 6, 8 and 9 only to characterise the transverse variability of pollutant emissions on roads, as transverse gradient of pollutant concentration was found to occur across the road width discussed in section 2.3.1. For RDS build-up investigation study (results presented in Chapter 4) there were 7 × 1 m^2 plots for both sampling positions all within the same 10 m × 3 m area of road draining to a road gully, as mentioned earlier. The RDS samples were collected at the end of each antecedent dry period by sweeping the plots using a clean plastic dustpan and brush as outlined by Kim et al. (1998), Charlesworth et al. (2003) and Robertson and Taylor (2007). Several identical dustpan and plastic brushes were used in order to minimise cross contamination between the sites. The sweeping technique was also kept consistent to avoid sample variability. During sampling, care was also taken to minimize sweeping pressure so that (artificial) detachment of road particles could be avoided. Each plot was swept 3 times to maximise sample collection efficiency, and for which approximate time spent was 10 to 15 minutes. Samples were then transported back to the laboratory using self-sealing plastic bags to avoid contamination.

3.3.2 Sampling Wet Weather Sediment

Road runoff during storm events was collected from four monitoring sites, Sites 3, 6, 8 and 9. Runoff samples were collected from 12 different rainfall events between May 2010 and April 2011.

3.3.2.1 Storm event characteristics

The focus was one of capturing data to explore monthly and seasonal variations and to cover a wide range of hydrological aspects, such as, low intensity long duration rainfall and vice versa. A range of antecedent dry periods from 15 hours to 20 days was also encountered. The details of the hydrological events monitored are summarised in Table 3.2. Data for the rain events were collected using a tipping bucket gauge which was installed on a building roof (for another research project) and located approximately 1000 m from the runoff sampling sites. The tipping bucket measures the time required to produce a single tip (0.254 mm of rainfall) and corresponding data were stored in an attached data logger, which was connected telemetrically with an office computer.

Although data collection took place without going to the rain gauge, the rain gauge site was visited regularly, and more often after any significant rain event, to ensure its efficient operation. Recorded data were then collated to determine rainfall duration, total precipitation and the number of antecedent dry days since the last event. Average rainfall intensity was calculated as total precipitation divided by the total duration of the storm event, while the number of antecedent dry days was based on the days since the last event with a minimum of 2.5 mm of precipitation (Brezonik and Stadelmann, 2002).

Table 3.2: Summary of the rain events monitored at the study sites.

Event date	Storm duration (h)	Precipitation (mm)	Average intensity (mm/h)	Peak intensity (mm/h)	Antecedent dry days (days)[1]	Runoff volume collected (*l*)
26/5/ 2010	1.70	19.30	11.35	37	2	3.75
01/7/ 2010	6.25	8.20	1.31	25	20	> 4
04/7/2010	1.83	26.60	14.50	43	2	3.95
14/7/2010	10.87	74.00	6.81	30	3	> 4
01/8/2010	1.23	13.52	10.96	33	10	3.80
12/8/2010	1.06	4.31	4.05	19	2	3.00
21/8/2010	1.42	14.42	10.18	41	1	3.50
07/9/2010	2.88	10.52	3.65	12	13	> 4
11/9/2010	2.23	17.44	7.64	40	1	> 4
20/11/2010	8.75	23.63	2.70	14	7.5	> 4
12/3/2011	5.75	37.49	6.52	24	2.5	> 4
23/4/2011	1.55	15.27	9.85	32	6	> 4
Statistics for the rainfall events						
Mean	3.79	22.05	7.46	27.4	5.73	
Median	2.03	16.35	7.23	31.00	2.75	
SD[2]	3.31	18.60	4.02	12.57	5.99	
CV[3]	0.87	0.84	0.54	0.46	1.04	

[1] days since last event with precipitation ≥ 2.5mm (Brezonik and Stadelmann, 2002)

[2] SD, standard deviation of all 12 rainfall event

[3] CV, coefficient of variance

3.3.2.2 Road-runoff collection

Each sampling site has road gullies to collect road runoff from the road surface during rainfall periods. Preliminary investigation suggested that each gully drains an approximately 30 m^2 road surface area, as noted before. The gullies at the experimental sites were modified to intercept stormwater inflow during runoff events. A trapezoidal shape plastic catch tray was designed to guide the road runoff as it left the road surface, to be collected in a 5 *l* bucket hanging inside the existing gully pot as seen in Figure 3.5. A hole at the 4 *l* mark was made to avoid flooding of the road surface caused by overflow during extreme rainfall events.

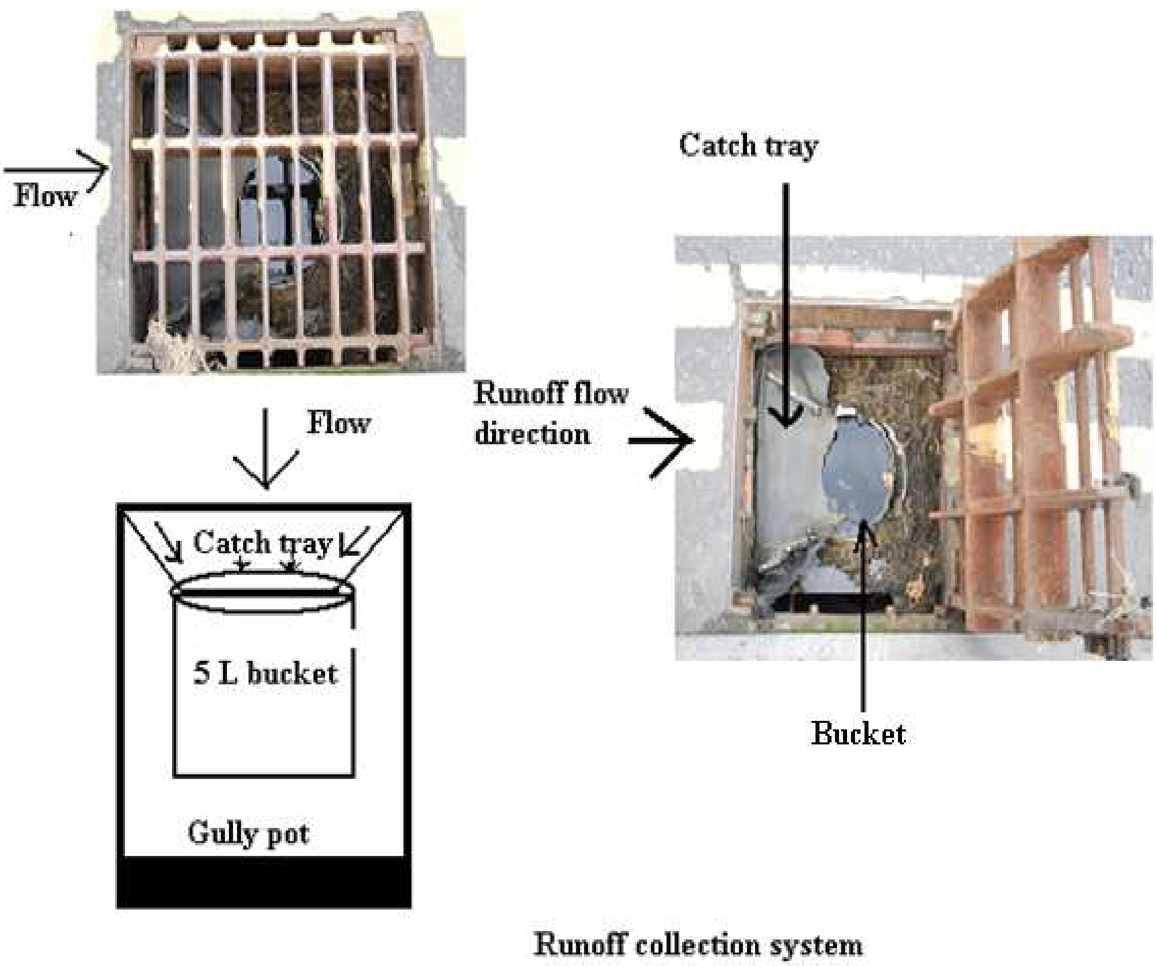


Figure 3.5: Schematic diagram and photographs of the experimental set-up used for runoff collection at sites with road gullies.

As seen in Table 3.2, runoff volume more than 4 *l* was experienced in 7 of the 12 rainfall events. Collection of 4 *l* runoff was limited by the experimental set-up adopted for this study. In such cases metal concentrations for dissolved and particulate phases, particularly for the finer sediment, may be underestimated due to loss of runoff sample as overflow. However, it may not be inappropriate to explain the pollutant loads associated with runoff samples based on the study by Stenstrom and Kayhnian (2005). They found that collection and treatment of the early phase of runoff (e.g. 1/3 of total runoff volume) is adequate for pollution control in terms of time, cost and practicality compared to monitoring entire rainfall-runoff events, which can be expensive and impractical.

Subsequently, a few field trials of the experimental set-up using manually induced runoff were conducted prior to the collection of natural runoff events and tested. Results of sediment particle size distributions from these trial experiments confirmed that a reasonable amount of sediment size fraction below 63 µm would be captured even in excessive storm events, which would well serve the present aims of the study. In addition, different set-ups were evaluated to optimise the runoff collection while avoiding leakage, and designs were modified accordingly. The gap between bucket and gully pot grid (see Figure 3.5) was sealed using water tight teflon tape. However, complete control of leakage could not be met in some circumstances.

Nonetheless, this simple approach was found to be effective for runoff collection from the road surface with little modification of the existing road drainage systems. Runoff water stored in the bucket was collected after each event as soon as was practicable and was transported back to the laboratory for further analysis. Particles attached to the catch tray were washed into the bucket by using distilled water to minimise cross contamination. The volume of distilled water required to wash–off the catch tray deposits was recorded and added to the runoff volume collected into the buckets to get total sample volume, which was then used to measure concentrations in runoff. The collection bucket was pre-washed using distilled water prior putting into experimental set-up at sites. The buckets were deployed for the period between rainfall events. The buckets were monitored regularly to remove any unwanted deposition. However, background contamination from atmospheric deposition cannot be ruled out entirely. The details of the runoff monitoring and collection procedures followed for this study can be found in the Caltrans Guidance Manual: Stormwater Monitoring Protocols (Caltrans, 2003).

3.3.3 Snow Sediment Sampling

Snow samples from five snow events between November and December 2010 were collected from four sites, Sites 3, 6, 8 and 9, by plastic scoops. The samples were taken from the whole vertical profile including dust deposition as outlined by Hricko et al. (1993) and Krčmová et al. (2009). Sampling was undertaken at the end of the snow event and a total sample of about 2 kg of snow from each site was transferred into plastic bags and transported back to the laboratory.

3.4 Laboratory Analyses

Preservation and analysis of dry, runoff and snow derived sediment samples were carried out in the analytical chemistry laboratory in the School of Life Sciences of Heriot Watt University. Standard laboratory procedures were followed for all testing and in order to ensure the accuracy of the test data standard quality control and quality assurance measures were also carried out.

3.4.1 Sample Preparation

The RDS samples were dried upon collection at room temperature for 24 hours and then weighed prior to particle size distribution (PSD) and heavy metal analysis. Runoff samples were sub-sampled after rigorous shaking to obtain 100 ml (out of up to 4 *l* from buckets plus added volume of water required to wash catch tray deposit, as mentioned earlier) of a representative sample, and 50 ml was used for determining total suspended solids (TSS) and another 50 ml was for total heavy metal concentrations (unfiltered runoff). The filtered water from TSS analysis was used for dissolved metal concentrations analysis. The rest of each sample was wet sieved for PSD analysis and sediment retained on sieves was analysed for particulate heavy metal concentrations. Snow samples were allowed to melt at room temperature first and then similar steps were followed as for the runoff samples.

3.4.2 Laboratory Testing

Laboratory testing for the present study was primarily focused on the mass of dry, runoff and snow derived sediment on the roads and the quantification of heavy metals in it. The influence and importance of the particle size distribution on sediment associated metal concentrations are well documented from previous studies, which reveal that greater metal concentrations are found with decreasing particle size fractions (e.g. Robertson and Taylor, 2007; Sansalone et al., 2010). Hence, particle size distribution was given priority for particle bound metal analysis. In addition TSS for runoff samples and dissolved metal concentrations for runoff and snow samples were measured. The complete set of parameters tested during the laboratory analysis was as follows: particle size distribution (PSD), total suspended solids (TSS) for runoff samples, dissolved and particle bound metal concentrations, as appropriate with different categories of road sediment.

3.4.2.1 Particle size distribution

Several techniques are available to measure particle size distributions of solids (Egodawatta, 2007). Among these methods, dry or wet sieving is most often used. Different ranges of standard sieves are used depending on study aims and purposes. The sieves used for this study included: BS 625 (20 µm), BS 350 (45 µm), BS 240 (63 µm), BS 120 (125 µm), BS 60 (250 µm) and BS 30 (500 µm). To obtain the PSDs, road sediments were passed through a range of standard sieves as mentioned above to get a representative sample mass retained on each sieve size. Sediment samples were wet-sieved to separate them into fine and coarse fractions. Wet sieving has an advantage over dry sieving of better accuracy. More details can be found in Deletic and Orr (2005), Huang et al. (2009) and Karlsson et al. (2010). The aim was to evaluate the distribution pattern of heavy metal concentrations associated with fine (<63 µm), medium (250-63 µm) and coarse (500-250 µm) sediment fractions. The author believes that using 63 µm for differentiating fine sediment from medium and coarse sediment is reasonable because the particle sizes below 63 µm (representing clay and silt) all have a large surface area and contain negatively charged particles which have a high affinity for metals. This idea is also supported by other researchers, e.g. Roger et al. (1998), Sutherland (2003), Zhu et al. (2008), Opher and Friedler (2010). However, other classifications to separate fine particles have also been found, e.g. Furumai et al. (2001) and Murakami et al. (2004) used 45 µm as a boundary sieve size, while Kim and Sansalone (2008) used 75 µm in keeping with conventions separating fine particles specified in ASTM (2002).

The mass retained on each sieve was then cleaned using distilled water, placed in a pan and left to dry for 24 hours prior to being oven dried at 103-105^{0}C for 24 hours to obtain a dried sample for further analysis. However, no sediment of the largest fraction (500-250 µm) was found in any of the runoff and snow events sampled, and hence the 250-63 µm size fraction was classified as coarse sediment, while the < 63 µm size fraction was treated as fine sediment.

3.4.2.2 Total suspended solids (TSS)

TSS concentration was analysed for runoff and snow samples. After rigorous shaking to suspend all particulate matter, a 50 ml sample was decanted from the 100 ml sub samples, which was from collection bucket to a volumetric flask. The sample was then filtered immediately through a 0.50 µm teflon filter, and TSS was analysed using a gravimetric method by weighing the oven-dried residue on the filter with a detection limit of 0.1 mg/l. The filter papers and petri dishes used for this test were pre-washed and oven dried in the laboratory for 24 hours prior use. The oven temperature was kept at 103 ^{0}C to 105 ^{0}C. The details of the TSS analysis method followed in this study can be found in APHA (1998). Briefly TSS is measured by following the steps shown below:

- Before sampling, prepare teflon filters by first soaking them in distilled water, drying them at 103^o C, and weighing and recording their weights (A).
- Place the dried, weighed teflon filter onto a filtering flask. Shake the bottle first, and then pour the sample volume of 50 ml (C).
- Dry the filter at 103 to 105 ^{0}C, let it cool to room temperature and then weigh it. Dry it, cool it, and weigh it again. Continue until the filter reaches a constant weight. Record the end weight (B).
- The increase in weight represents TSS. Calculate TSS by using the equation below.

$$\text{TSS (mg/L)} = ([A-B]*1000)/C \qquad \text{(Equation 3.1)}$$

Where A = End weight of the filter; B = Initial weight of the filter; C = Volume of water filtered

3.4.2.3 Particle bound metal concentration

Figure 3.6 shows the flow chart of the analytical method followed for the determination of heavy metal concentrations. Particle bound metal concentrations for the elements Cd, Cr, Cu, Zn, Pb, Ni were determined by strong nitric acid digestion (Anala R 70%) followed by flame atomic absorption spectrometry (AAS) using a Perkin Elmer 200 AAS analyser.

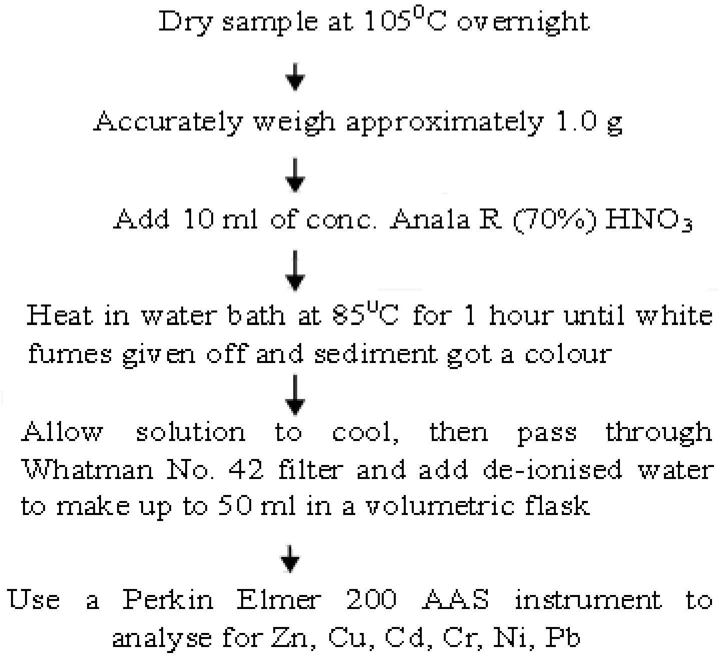


Figure 3.6: Analytical protocol for RDS metal determination.

There are numerous and varied methods of sediment bound metal extraction procedures reported in the literature. For example, Charlesworth et al. (2003) used a mix of H_2SO_4, HNO_3 and HCl, Sutherland and Tolosa (2000) used HNO_3-HCl, and Ordonez et al. (2003) used a mix of HNO_3, HF and $HClO_4$ as metal extractants in their studies. In contrast, Akhter and Madany (1993), Deletic and Orr (2005), Robertson and Taylor (2007) used HNO_3, and Gibson and Farmer (1984), Stone and Marsalek (1996) used HCl for metal extraction. A rigorous analysis of the impact of using different strength of reagents (0.05 M EDTA, 0.5 M HCl, concentrated HNO_3) for metal extraction from road sediment can be found in Sutherland et al. (2001). They suggest that in some circumstances use of weak reagents (particularly HCl and EDTA) could better quantify metal contamination compared to using a strong reagent (HNO_3). They also reported that extracting metals using strong reagents underestimated the metal contamination compared to the weaker reagents (e.g. Cu, Zn, Pb).

Within this context, selected samples for this study were initially tested using HNO_3, aqua regia (a mix of HCl-HNO_3 in a ratio of 3:1 by volume) and HCl-HNO_3-$HClO_4$. The results obtained did not exhibit significant differences (Kruskal-Wallis test; $p > 0.05$) due to the different extractants used (see appendix B). However, using aqua regia (a mix of HCl-HNO_3 in a ratio of 3:1 by volume) was found to perform better for

Cr, Ni and Pb compared to HNO_3 alone. However, popular use of concentrated HNO_3 as a metal extractant was already evident in previous research even though it is not a best alternative (Sutherland et al., 2001). To keep the metal extraction procedure consistent and logistically efficient, concentrated HNO_3 was used as the metal extractant from sediment for this study. Furthermore, two different types of acid digestion procedures are found to be followed for particulate metals. These were open and microwave digestion, with microwave digestion being preferred if available (Sutherland et al., 2001). However, in the absence of a microwave digestion facility in the laboratory used for the present study, open digestion was employed. Briefly, 0.50 to 1.0 g of sample was digested in 10 ml of concentrated HNO_3 and left for 24 hours prior to heating in a water bath at 85^0C for 1 hour. Following this, samples were cooled and filtered to a volumetric flask made up to 50 ml using deionised water.

A Perkin Elmer 200 AAS was calibrated for the range of 0-2.5 ppm for all the metals analysed for this study using standard solutions which were made up from stock solution of 1,000 ppm. Calibration curves for metal solutions were maintained with high precision ($R^2 = 0.99$). The mean of triplicate analyses was recorded as the metal concentration for all samples, for data quality purposes. Blank samples were tested repeatedly to avoid cross contamination between samples. Any sample that gave a reading beyond the calibrated ranges was diluted until a satisfactory reading was obtained. De-ionised water was used throughout for cleaning apparatus, preparing standard solutions and other related purposes of laboratory work in order to avoid cross contamination. The analytical procedure followed for this study was kept similar with Deletic and Orr (2005) and Robertson and Taylor (2007). However, necessary modifications were carried out when required in the analytical procedure. The modifications were checked with published methods, if available, otherwise they were validated in the laboratory.

The calculation of heavy metal content in sediment from mass of dried sediment and metal concentration measured from a 50 ml of samples by FAAS is as follows:

Metal concentration in mg kg^{-1} (dry weight) = $D \times E/F$ (Equation 3.2)

Where, F is the weight of sediment mass used for acid digestion (g), E is the sample volume (ml) and D is the metal concentration reading obtained from the FAAS (mg/l).

3.4.2.4 Total and Dissolved metal concentration

Total metal concentration was determined using unfiltered sub samples of runoff, as discussed in 3.4.1. The filtered water from the TSS analysis, as described in 3.4.2.2, was collected for dissolved metal concentration analysis. The filtered water was then preserved by adding 2.5 ml of concentrated nitric acid (HNO_3) to a pH level less than 2.0 for metal quantification (USEPA, 1986). Metal concentrations were determined by flame atomic absorption spectrometry (FAAS) using a Perkin Elmer 200 AAS analyser, as discussed in 3.4.2.3.

3.5 Quality Assurance

Standard laboratory quality control/quality assurance procedures were followed, which are illustrated in Caltrans (2003). The details of these procedures are discussed below under a few sub-headings.

3.5.1 Analysis of Blanks

The data for blanks presented for this study is distilled water which was tested for heavy metal concentration repeatedly to avoid cross contamination between samples. A few times (n = 10) heavy metal concentrations of Cd, Cr, Cu, Ni, Pb and Zn in distilled water were recorded. Average metal concentrations found in the distilled water were 0.1, 8.7, 1.3, 0.7, 1.1 and 12.2 µg/l for Cd, Cr, Cu, Ni, Pb and Zn, respectively (see appendix B). The results suggested that there was no significant metal contamination associated with distilled water use in the laboratory analyses.

3.5.2 Precision

Good precision of the laboratory tests were maintained and checked by analyses of replicated samples on a routine basis. Relative percent difference (RPD) between original and duplicate concentrations was estimated as follows:

$$RPD = \left|\frac{C_O - C_D}{C_O}\right| \times 100 \qquad \text{(Equation. 3.3)}$$

Where, C_O and C_D are the metal concentrations in the original and duplicate samples respectively. RPD of 10% or less for a given pollutant, are considered reasonable (APHA, 1998). However, average RPDs for the present study were found to be 5% to 10% for the samples checked on a routine basis. Moreover, good precision of the whole procedure (less than 5% relative standard deviation) was achieved.

3.5.3 Accuracy

The mean of triplicate analyses was recorded as the metal concentration for all samples, for data quality purposes. Moreover, the accuracy of the test results was determined by analysing reference material using the standard solutions prepared for metal analysis. A portion of certified reference material MESS-3 (NRC Canada Certified Marine Sediment Reference Material) was tested three times for total metal analysis of Cd, Cr, Cu, Ni, Pb and Zn by using the Perkin Elmer 200 AAS analyser. The mean of the metal concentrations from three tests was then compared with reference values, as presented in Table 3.3. As seen in the table, the mean value for each metal was very similar to their respective reference values and hence, the laboratory analysis was deemed to be accurate.

Table 3.3: Heavy metal concentrations for standard reference sample MESS-3 from the laboratory testing compared with certified values.

	Concentration of metals in MESS-3 (mg/l)		
Metal	Laboratory test (n = 3)	MESS-3 certified value	% difference
Cd	0.24 ± 0.02	0.24 ± 0.01	+0.55
Cr	106 ± 2.84	105 ± 4.00	+1.37
Cu	34 ± 2.18	33.9 ± 1.60	+0.45
Ni	47.9 ± 3.28	46.9 ± 2.20	+2.07
Pb	21.8 ± 0.40	21.1 ± 0.70	+3.28
Zn	158.4 ±9.60	159 ± 8.00	-0.40

3.5.4 Detection Limit

The detection limits of Perkin Elmer 200 AAS for trace metals analysis are presented in Table 3.4. The detection limits were determined by analysing the results of standard deviation of triplicate concentrations of analytical blank (distilled water) using a low range concentration of calibration solution (0 – 0.50 mg/l) prepared from standard stock solution (as discussed in section 3.4.2.3) for each of the six metals. The 3 times of standard deviation obtained was used as the lowest detection limit. The lower detection limit of the Perkin Elmer 200 AAS analyser allowed quantifying trace metal concentrations with sufficient accuracy. For most of the laboratory testing, metal concentrations in road sediments were found to be well above the analytical reporting limit. However, very rarely Cd (in particular dissolved Cd in runoff and snow samples) showed values below the detection limit and were recorded as ‘Not Detected’. The values recorded as ‘Not Detected’ were substituted with the lowest detection limit concentrations for further analyses (Kayhanian et al., 2002).

Table 3.4: The detection limit for trace metals analyses using Perkin Elmer 200 AAS

Metal	Detection limit (mg/l)
Cd	0.01
Cr	0.03
Cu	0.03
Ni	0.05
Pb	0.15
Zn	0.02
Fe	0.05

3.6 Heavy metals Pollution Assessment

With increasing urbanisation, the impact of heavy metal pollution on the nearby water environment has become a more serious issue, and so has received much attention in environmental research studies. A variety of pollution indices for sediment associated heavy metals have been proposed to quantify the level of pollution and associated impacts on aquatic life (e.g. Yu et al., 2003; Huang et al., 2009). The degree of contamination (CD) and the potential ecological risk index (PERI) suggested by Hakanson (1980) were applied for this study with some necessary modifications. The methods proposed by Hakanson (1980) were derived for natural sediment in fresh and/or marine/estuarine waters rather than road runoff. However, their robustness makes them suitable for road sediment (even in the absence of ecological data) to obtain an impression of the ecological risk, as evident from the previous studies in the literature elsewhere (e.g. Huang et al., 2009; Shi et al., 2010; Duong and Lee, 2011). A point to be noted is that the results obtained using these methods may not be sufficient enough to quantify actual ecological risk posed by road sediment without other relevant data and information, such as, the type of aquatic species considered, exposure time with contaminated sediment, appropriate dilution factors, metal releasing mechanisms from sediment depending upon sediment-water chemistry, etc. (e.g. Kayhanian et al., 2008; de Deckere et al., 2011). Within this context, for the present study these indices were adopted to demonstrate the level of potential hazard posed by road sediment.

The CD and PERI are defined by the equations shown below:

$$C_f^i = \frac{C_s^i}{C_B^i} \qquad \text{(Equation 3.4)}$$

where: C_f^i is the (single metal) pollution index of metal i; C_s^i is the concentration of metal *i* in the sample; C_B^i is the reference value for metal *i*. For this study, C_B^i was taken to be the local background value from road sites which carry no traffic.

$$CD = \sum_{i=1}^{n} C_f^i \qquad \text{(Equation 3.5)}$$

where *n* is the total number of metals (n=6 for this study). Categories of *CD* were adjusted and classified with modifications after Duong and Lee (2011), as seen in Table 3.5.

$$E_r^i = T_r^i \times C_f^i \qquad \text{(Equation 3.6)}$$

Where, E_r^i is the monomial potential ecological risk factor, and T_r^i is the metal toxicity factor. According to Hakanson (1980), the toxic values for each metal are in the order of Zn (= 1) < Cr (= 2) < Cu = Ni = Pb (= 5) < As (=10) < Cd (= 30) < Hg (= 40).

$$PERI = \sum_{i=1}^{n} E_r^i \qquad \text{(Equation 3.7)}$$

Where, *PERI* is the potential ecological risk index caused by the overall contamination signifying the sensitivity of the biological community to the toxic substances. As the number of pollutants considered in this study are different to Hakanson's study (As and Hg are not being used here), an adjustment of the indices was made and categories were also classified accordingly, as seen in Table 3.5. Briefly, assuming C_f^i is 1 for all the metals analysed here will give *PERI* value 48 as a low level of ecological risk. To round off the indices value, the value of 50 was taken as the lowest *PERI* instead of calculated value of 48. Furthermore, in order to minimise inherent variability associated with measurement errors, the lowest level of *PERI* value (=50) was revised multiplied by 1.5 (usually used to indicate considerable enrichment over background value), which in turn indicate a low level of ecological risk with *PERI < 75*. A similar approach of adjustment of the indices was also made by Hakanson (1980) in his study followed by others, for example, Zhu et al. (2008) and Duong and Lee (2011) in their studies elsewhere.

Table 3.5: Categorization of standards for C_f^i, CD, E_r^i and PERI

C_f^i	CD	Degree of pollution	E_r^i	PERI	Levels of potential ecological risk of the aquatic environment
$C_f^i < 3$	CD<6	Low/Unpolluted	$E_r^i<30$	PERI<75	Low
$3\leq C_f^i<6$	6≤CD<12	Moderate	$30\leq E_r^i<60$	75≤PERI<150	Moderate
$6\leq C_f^i<9$	12≤CD<24	Considerable	$60\leq E_r^i<120$	150≤PERI<300	Considerable
$C_f^i>9$	CD>24	High	$120\leq E_r^i<240$	PERI>300	High

C_f is the single metal pollution index; CD is the degree of contamination; E_r is the monomial potential ecological risk factor; PERI is the potential ecological risk index

3.7 Statistical Analyses

The present study generated a database of heavy metal analyses. In order to reveal a reliable outcome the resulting database needed to be analysed properly. The data analysis techniques were selected carefully by considering the type of data to be analysed, the capabilities of different data analysis techniques and the type of analysis to be performed based on the study objectives. These techniques were selected to understand the nature of the variability in the data and to assess the relationship between variables for predictive purposes. Microsoft Excel and SPSS 16.0 were used to compute descriptive statistics, normality tests and box plots of the results. Normality tests for all the variables in the dataset were performed prior to further analyses. As the data did not follow Gaussian distribution, the Spearman rank-order correlation coefficient (a nonparametric correlation) was used to determine relationships between variables. Only statistically significant correlations are presented in the results. The Kruskal – Wallis test, which represents a nonparametric analogy of one-way ANOVA, was used to determine whether a significant difference existed for metal concentrations between sampling sites and between size fractions. A brief description of the statistical analyses follows is given in the following sub-sections.

3.7.1 Descriptive Statistics

Range, mean, standard deviation (SD) and coefficient of variation (CV) are often used to describe the characteristics of a single data set. The range defines the array of data between the minimum and maximum values. The mean is simply the arithmetic average of the data set, while the SD represents the dispersion of the data around the mean. The higher the SD value the more scattered is the data to the mean and vice versa. Similarly the CV explains the dispersion of the data set relative to the mean and can be obtained by expressing the standard deviation as a percentage of the mean.

3.7.2 Correlation Analysis

Correlation refers to a statistical relationship involving dependence. Correlations are useful because they can indicate a predictive relationship based on the degree of relationship between variables. The degree of association is expressed by the correlation coefficient, often denoted by r or ρ or τ. The most common of these is the Pearson correlation coefficient (r), which is most relevant when there is a linear relationship between two variables. The Pearson correlation coefficient is more suitable for parametric data (when data is normally distributed).

To deal with non parametric data and non-linear relationships, other correlation coefficients have been developed that are more robust than the Pearson correlation coefficient. Rank correlation coefficients, such as Spearman's rank correlation coefficient (ρ) and Kendall's rank correlation coefficient (τ) measure the extent to which variables are associated overlooking any relationship between the variables. In general, these rank correlation coefficients are used either to reduce the amount of calculations or to make the coefficient less sensitive to non-normality in the data distributions.

The rule of thumb to interpret the statistical strength between variables using the value of the correlation coefficient is as: ± 1.0 (perfect), ± 0.90 to ± 0.99 (very high), ± 0.70 to ± 0.90 (high), ± 0.50 to ± 0.70 (moderate), ± 0.30 to ± 0.50 (low), ± 0.10 to ± 0.30 (very low) and ±0.0 to ± 0.10 (markedly low or negligible). Here the '+' and '-' signs denote positive or negative correlation, respectively, between variables. The significance of the correlation coefficients were tested each time as data was analysed. However, it should be noted that a high correlation coefficient does not necessarily define a cause and effect relationship (there may be other factors not considered in the analysis), rather it reflects a quantitative relationship that has been logically established.

3.7.3 ANOVA

Analysis of variance (ANOVA) is commonly used for testing the statistical significance of differences in means (for variables). This is accomplished by analyzing the variance, that is, by partitioning the total variance into the component that is due to true random error and the component that are due to differences between means. These latter variance components are then tested for statistical significance, and, if significant, one can then reject the null hypothesis of no differences between means and accept the alternative hypothesis that the means (for variables or groups) are different from each other. The Kruskal-Wallis test, which represents a nonparametric analogy of one-way ANOVA, was used to determine whether a significant difference existed for metal concentrations between sampling sites and between size fractions. A confidence level of 95% ($p < 0.05$) was set for the statistical significance for all analyses. The greater robustness of the Kruskal-Wallis test over other ANOVA tests makes it even more useful, for example, (1) the distributions of data do not have to be normal, (2) variances for data sets do not have to be equal, (3) it is not data intensive (as few as 6 data in a data set may be sufficient) and (4) equal sample sizes are preferred but small differences in the sample sizes in the data sets are also allowed (Corder and Foreman, 2009).

3.8 Conclusions

This study adopted a simple method to collect field samples during dry, runoff and snow events followed by laboratory analyses. The collection of dry sediment was undertaken at two transverse sampling positions from a pre-cleaned 1 m^2 area on roads for different numbers of antecedent dry days. The runoff samples for 12 different rainfall events were collected at four primary study sites using a simplified experimental set-up. Similarly, fresh snow rather than snow-melt runoff samples were collected for 5 snow events.

A part of the dry and runoff sediment data were used to study pollutant build-up and wash-off processes at the primary study sites to derive local build-up and wash-off parameters, while the remaining data were used for validation of the local parameters. The primary variable considered for the pollutant build-up was the number of antecedent dry days, while the rainfall intensity, the rainfall duration and the number of dry days between the rainfall events were used for the pollutant wash-off study.

Samples collected in the field investigation were tested for six heavy metals, namely Cd, Cr, Cu, Ni, Pb and Zn, which are found abundant in road-traffic environments as reported in the literature and are toxic to aquatic species and persistent in nature. Heavy metals in sediment were determined by strong nitric acid digestion and atomic absorption spectrometry. In addition, dissolved heavy metal concentrations were measured for the runoff and snow samples. Total suspended solids concentration was measured for runoff sediment only. Particle size distributions were analysed for all categories of the road sediment.

Chapter – 4 Analysis of Dry Weather Pollutant Build-up

4.1 Introduction

The aim of this chapter is to report the results of heavy metal concentrations in dry road sediment collected from different sampling sites with the aim of examining spatial variability between sites and identifying pollutant hot spots for further in-depth investigations. Then pollutant build-up is studied in more detail for the selected (hot spot) sites (a road bend, a road with speed control measures, a road intersection and a straight road section), such as, road deposited sediment (RDS) mass build-up over antecedent dry days (ADD), and associated heavy metal build-up pattern with ADD, local build-up parameters for the relationship of RDS build-up during ADD and grain-size characteristics of RDS with respect to two transverse sampling positions, near curb and 1 m from the curb. The results presented in this chapter are based on the RDS samples collected in April 2010 over 1 to 14 ADD.

4.2 RDS Heavy Metal Concentrations

The mean concentrations of the six metals (Zn, Cu, Cd, Cr, Ni and Pb) in RDS from 12 sampling sites are presented in Table 4.1. The background concentrations of the metals from Riccarton Campus are also shown along with regional background values for Scotland (Appleton, 1995). The local background values for all the metals except Pb are similar to the regional background values. The accumulation index (AI), which is the ratio of the mean to the local background mean, is also presented in the table. The degree of contamination (CD) and the potential ecological risk index (PERI) are also shown on the bottom rows of the table for each site, which indicate the heavy metal contamination.

As seen in Table 4.1, considering all the sites the highest mean concentration of metals are found in the order of 247, 140, 92, 16, 16 and 7 mg kg^{-1} for Zn, Pb, Cu, Cr, Ni and Cd, respectively. The mean concentrations reported here are very similar to the concentrations reported previously for residential catchments in the UK (Charlesworth et al., 2003; Deletic and Orr, 2005; Robertson and Taylor, 2007) and other parts of the world (Kim et al., 1998; Sutherland, 2003). Similarly, the highest accumulation index

(AI > 1.5) of metals Cd, Pb, Zn and Cu were approximately 7, 5, 2.2 and 2, respectively, for all sites. These ratios are also found to be consistent with other studies (e.g. Hjortenkrans et al., 2006; Zhu et al., 2008). Note that the accumulation index for Ni was either significantly less than 1 or only marginally greater than 1 for all sites.

Table 4.1: Mean and standard deviation of heavy metal concentrations (mg kg^{-1}) in RDS on road network in study area

Site	1 (4)	2 (4)	3 (7)	4 (4)	5 (3)	6 (7)	7 (4)	8 (7)	9 (7)	10 (4)	11 (3)	12 (5)	Local back-ground mean [a]	Regional back-ground mean [b]
TV [c]	200	200	200	200	230	250	265	285	650	650	550	--		
Cd	1.3	0.7	1.5	0.7	7	1.7	1.3	2.0	1.8	0.4	6	1	1	1.4
SD	0.8	0.4	0.5	0.4	4	1	0.9	1	0.8	0.3	4	0.7	0.3	
AI	*1.3*	*0.7*	***1.5***	*0.7*	***7***	***1.7***	*1.3*	***2.0***	***1.8***	*0.4*	***6***	*1*		
Cr	6	12	10	13	16	12	11	11	10	12	10	4	8	n.a.
SD	3	4	5	4	10	3	4	5	4	8	7	2	2	
AI	*0.8*	***1.5***	*1.2*	***1.5***	***2.0***	***1.5***	*1.2*	*1.2*	*1.2*	***1.5***	*1.3*	*0.5*		
Cu	67	40	75	41	74	92	59	83	74	31	69	59	44	46
SD	21	19	17	22	29	23	31	25	19	11	20	30	10	
AI	***1.5***	*0.9*	***1.7***	*0.9*	***1.7***	***2.0***	*1.3*	***1.8***	***1.6***	*0.7*	***1.5***	*1.3*		
Ni	6	5	14	6	5	16	9	11	20	22	24	4	20	n.a.
SD	3	3	8	3	2	11	4	6	13	12	14	2	3	
AI	*0.3*	*0.3*	*0.7*	*0.3*	*0.3*	*0.8*	*0.5*	*0.6*	*1.0*	*1.1*	*1.2*	*0.2*		
Pb	35	77	101	112	66	140	68	62	60	35	23	43	28	115
SD	10	25	41	53	29	21	30	19	26	18	11	20	12	
AI	*1.3*	***2.8***	***3.6***	***4.0***	***2.4***	***5.0***	***2.4***	***2.2***	***2.1***	*1.3*	*0.8*	***1.5***		
Zn	225	160	212	133	205	239	213	160	247	110	167	209	107	120
SD	84	72	80	66	79	87	71	75	76	43	77	88	23	
AI	***2.1***	***1.5***	***2.0***	*1.2*	***1.9***	***2.2***	***2.0***	***1.5***	***2.3***	*1.0*	***1.6***	***1.9***		
CD	7	8	**14**	**12**	**17**	**16**	11	10	**12**	6	**12**	7		
PERI	56	46	**90**	60	**241**	**98**	68	**95**	**91**	32	**202**	51		

Value in brackets under site represents number of sample analysed

[a] metal concentrations were measured in RDS from road sites which carry no traffic

[b] Appleton, 1995

[c] TV: Traffic volume in vehicles per hour; SD: Standard deviation

AI: Accumulation index - number ≥ 1.5 in bold to identify sites where metal from anthropogenic sources may likely be key

CD: Degree of contamination – number ≥ 12 in bold suggests considerable degree of contamination

PERI: Potential ecological risk index – number ≥ 75 suggests moderate level of ecological risk

As discussed in the literature, all of the metals presented in the table above are somewhat related to the road-traffic environment. Briefly, Zn is primarily linked with tyre wear, Cr and Cu are linked with brake wear, and Cd and Pb are linked to exhaust emissions (Charlesworth et al., 2003; Ward et al., 2004; Zanders, 2005), while the relatively low concentrations of Ni may be linked with the geological background of the study site (De Minguel et al., 1997). However, significant Pb concentrations at a few sampling sites (e.g. Sites 3 and 6) are surprising, as the previous use of Pb in fuel was phased out more than a decade ago, but may be not unexpected elsewhere, as Pb is linked to road paint materials (particularly double yellow lines), as seen in Table 4.2. Pb is relied upon to provide the persistent brightness to yellow road markers exposed to any weather types before degradation. A similar suggestion was also reported by Deletic and Orr (2005) in their study in Aberdeen, UK. In contrast, elevated concentrations of Pb at some other sites (in absence of yellow lines e.g. Site 9), suggests that other traffic related inputs, such as wheel bearings, vehicle exhaust and car paints etc are likely sources of Pb in the study area (Napier et al., 2008; Ewen et al., 2009).

Table 4.2: Pb concentration (mg kg-1) in yellow paint chips collected from road surfaces on studied road network

Sample	Pb (mg kg^{-1})
1	1683
2	1710
3	1190
4	1360
5	933
Mean ±standard deviation	**1375 ± 330**

Furthermore, in relation to the above sources of metals at the study sites, it although the traffic volume varied between sites from 200 to 650 VPH, the mean metal concentrations were not found to vary accordingly. It was also observed that at some of the sites (see Table 3.1), traffic experiences frequent acceleration and deceleration, which may have an influence on larger metal emissions, as suggested by Ewen et al. (2009) for traffic undergoing ‘stop-start’ activities. As mentioned in Chapter 3, the traffic movement pattern at the sites exhibits two types of ‘stop-start’ activities, such as, at a few sites (Sites 3, 5, 6 and 11) almost all traffic was observed to undergo braking as it passed through, while at a few other sites (Sites 1, 8 and 10) the traffic movement pattern was found to be more controlled in terms of ‘stop and start’ activities, and therefore, a lesser degree of braking was required. At all other sites, except Site 12, traffic movement was at a steady speed. Hence, site-specific attributes may be the key drivers in the difference of the heavy metal concentrations across the sites rather than traffic volume alone. A similar suggestion was reported by Irish et al. (1995), Li and Barrett (1998) and Charlesworth et al. (2003).

4.3 Spatial Variability of RDS Heavy Metal Concentrations and Associated Contamination between Sites

Table 4.1 reveals that metal concentrations show site specific variability across the road network. Among the 12 different sites, Sites 5, 6 and 8 show AI ≥ 1.5 for all metals except Ni, suggesting that RDS for these sites are highly contaminated by heavy metals related to road-traffic in addition to atmospheric deposition. Based on the average value of AI for all metals (except Ni) the order of the contamination is found as: Site 5 (AI = 2.5) > Site 6 (AI = 2.2) > Site 3 (AI = 1.8) > Site 9 (AI = 1.7) > Site 8 (AI = 1.5).

The degree of contamination (CD) caused by heavy metals, ranges from 6 to 17 across the sites as seen in Table 4.1. The CD value is found to be generally consistent with previous studies of RDS elsewhere (e.g. Zhu et al., 2008; Duong and Lee, 2011). However, the maximum values of CD here are occasionally exceeded in the aforementioned studies. As seen in Table 4.1, CD ≥ 12, suggesting considerable degree of contamination, was found at Sites 3, 5, 6, 9 and 11. RDS from both Sites 5 and 11 demonstrated very high contamination by Cd, considerable contamination by Cr, and moderate contamination by Zn and Cu (Table 4.1). Similarly, Sites 3 and 6 are found contaminated mainly with Pb followed by Cr, Zn and Cu (Table 4.1).

The potential ecological risk (PERI) caused by heavy metals at different sites in the study area shows a large spatial variability, ranging from 32 to 241 across the sites. The values are consistent with previous studies carried out by Zhu et al. (2008) and Duong and Lee (2011). The assessment of ecological risk for metals in RDS for all sites (Table 4.1) reveals that both bus stop sites (Site 5: PERI = 241 and Site 11: PERI = 202) have heavy metal emissions that may have a considerable level of ecological impact if transported to the nearby water courses. Both sites are highly dominated by Cd (toxic factor =30) as mentioned earlier. Moreover, from Table 4.1, Sites 3, 6, 8 and 9 may pose a moderate level of risk (PERI = 90-100), being primarily contaminated by Pb and Cu (toxic factor, Pb = Cu = 5) along with an influence from Cd and Zn (toxic factor = 1). Metal contaminations for Sites 1, 2, 4, 7, 10 and 12, fall well below the low level of ecological risk. However, as the number of samples analysed across the sites are very small, the pollution assessment levels should be used with caution.

Considering Sites 3, 6, 8 and 9, it is interesting to note that except Site 9, all other sites experience acceleration and deceleration activities by traffic, which is likely to enhance metal emissions (Charlesworth et al., 2003; Ewen et al., 2009). Apart from these four and both bus stops sites, all other sites show average AI ≤ 1.5, CD ≤ 12 and PERI ≤ 75, suggesting that RDS in these sites is less contaminated by heavy metals and is very unlikely to pose any threats to the nearby water environment at this stage. However, it is clear that traffic volume alone is not sufficient to explain the data unless site specific attributes (e.g. road lay-out, traffic movement patterns, road surface condition, presence of road paints etc) are taken into consideration. Similar suggestions were also noted by Irish et al. (1995) and Barrett et al. (1993).

In accordance to the study objectives, 4 of the 5 hot spot sites (Site 3: a road bend, Site 6: a road with speed control, Site 8: a road intersection and Site 9: a straight road section), representing different road lay-outs with different traffic loads and road surface conditions were used for in-depth studies. These 4 sites are the primary study sites for which long term monitoring data were collected. Site 5 (bus stop) was not used because of health and safety reasons for long term monitoring.

4.4 Pollutant Build-up at Primary Study Sites

Based on the previous research on stormwater quality and road-traffic pollution, as discussed in the literature review, it is apparent that the pollutant build-up and wash-off processes on roads are very complex and a lot more research is needed for these to be well understood (Sutherland and Jelen, 1996; Zoppu, 2001; Egodawatta, 2007). This section presents the outcomes from an in-depth field investigation of RDS and RDS associated heavy metals build-up over antecedent dry days (ADD). Sampling was carried out at two transverse positions, near the curb (A) and 1 m from the curb (B), for primary study sites, a road bend (RB), a road with speed control (RSC), a road intersection (RI) and a straight road section (SR), in order to provide an insight into the influence of sampling position, typical road lay-out and road condition on metal emissions over ADD.

4.4.1 RDS Build-up

The RDS loading obtained from the primary study sites at both sampling positions A and B over 14 ADD are plotted in Figure 4.1. The RDS build-up patterns reveal site-specific rates with significant variability according to road lay-out as with an influence from road surface condition, traffic volume and surrounding land for both sampling positions, as discussed below. It was also noted that for sampling position A, at all the sites the rate of build-up was initially high and then decreased as the number of antecedent dry days increased. The asymptotic build-up pattern is consistent with current understanding of RDS build-up over ADD.

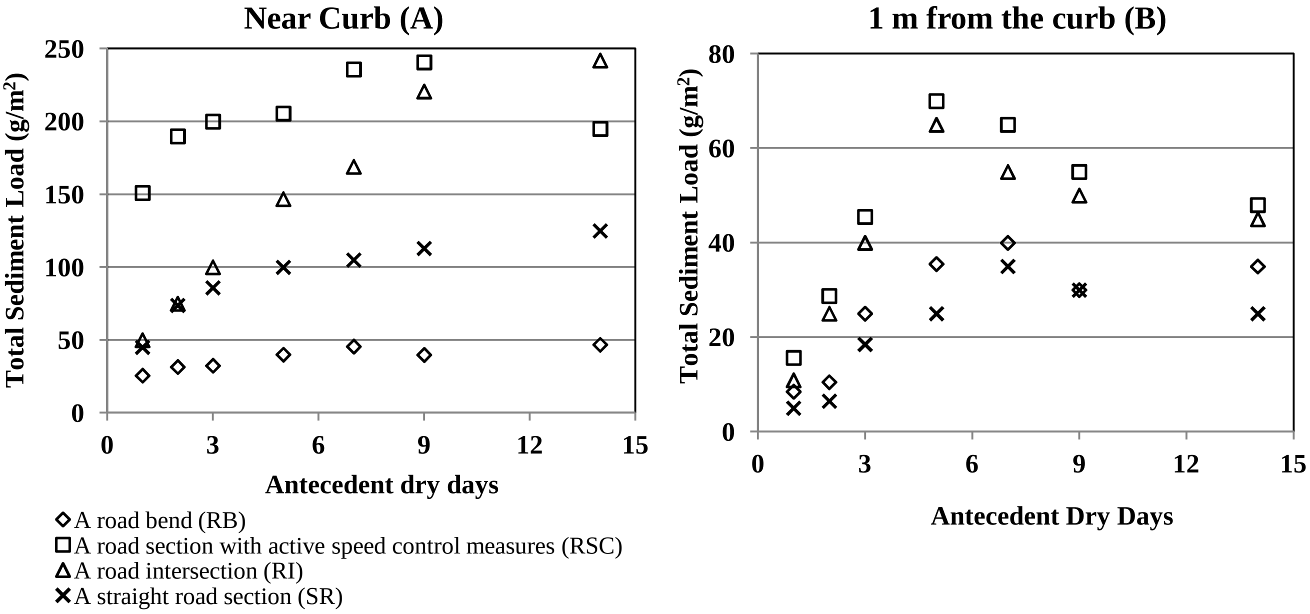


Figure 4.1: RDS build-up pattern at four different sites for both sampling positions.

In contrast, at sampling position B, RDS build-up patterns were more erratic, in particular, at the RSC and RI sites, the sediment load increased steadily for about 5 ADD and then decreased at a reducing rate over time. However, RDS build-up pattern at the RB and SR sites was similar to that for the sampling position A. The inconsistent patterns of RDS build-up at sampling position B might be due to the turbulence caused by the traffic flow (directly over this point) in addition to wind induced movement. The inconsistent patterns of RDS build-up may not be unexpected because similar inconsistent RDS build-up further away from the curb was also evident from the study by Deletic and Orr (2005).

Considering the individual sites, the sediment availability per square meter at sampling position A was in the ranges of 25 to 50 g at the RB site followed by 45 to 125 g at the SR site, 150 to 241 g at the RSC site and 49 to 242 g at the SR site over the 14 antecedent dry days. At sampling position B, they were 5 to 25 g at the SR site followed by 8 to 35 g at the RB site, 10 to 45 g at the RI site and 15 to 48 g at the RSC site (Figure 4.1). The lower sediment loads at sampling position B to A are expected and are thought to reflect the input from a single source (traffic), while one or more sources (road surface itself, traffic, foot path, surrounding land) may contribute to sediment deposition at sampling position A.

Sediment build-up at sampling position A after 1 day since the road surface was initially cleaned (Figure 4.1), was found in the range of 25 to 50 g/m^2 for the RB, RI and SR sites, while for the RSC site the initial build-up was much higher (150 g/m^2). In contrast, at sampling position B, the highest first day build-up was found as 15 g/m^2 at the RSC site followed by 10 g/m^2 at the RI site, 8 g/m^2 at the RB site and 5 g/m^2 at the SR site (Figure 4.1). The primary reasons behind the significantly higher initial build-up rate at the RSC site for sampling position A could be due to its rougher road texture (aiding the retention of RDS on the surface) and a poor road condition (providing a larger supply of non-vehicular particles) compared to all other sites.

Based on the build-up trend over 14 days for sampling position A, it appears that the rate of build-up was highest at the RI site (see Figure 4.1). This site is close to an entry and exit point of the Campus, nearby office buildings and car parks, which may have some influence on sediment deposition when compared to the lowest overall build-up rate at the RB site which has nearby open space with farm land. Build-up patterns at sampling position A for the other sites were found to follow similar trends but with different magnitudes. For example, at the SR site, surrounding trees on both sides of the road may have reduced the effect of wind turbulence thus in turn increasing the retention of sediment on the road.

Based on all sites, the sediment availability of 25 to 242 g/m^2 at sampling position A for the present study compares well with earlier studies, as Sartor and Boyd (1972) observed around 4 to 113 g/m^2 in USA, Ball et al. (1998) found 4 to 15 g/m^2 in Australia, Vaze and Chew (2002) noted 8 to 40 g/m^2 in Melbourne, Australia and

Deletic and Orr (2005) observed 150 to 225 g/m^2 in Aberdeen, Scotland. Similarly, sediment availability of 5 to 70 g/m^2 at sampling position B for the present study compared well with 20 to 115 g/m^2 at 0.75 m from the curb (data for summer months) in Deletic and Orr (2005). The variation in observed sediment loading between studies is certainly understandable, and may be due to the variability in the sample collection procedure, regional climate, road condition and road maintenance, surrounding land uses, different ADD etc. Based on the results from this study it has been revealed that the site-specific attributes (e.g. road lay-out, road surface condition, surrounding land use) have had a significant influence on RDS build-up. Also the RDS build-up varies with transverse positions.

4.4.2 Mathematical Replication of RDS Build-up

Modelling the impact of road runoff pollution on receiving waters requires various processes to be simulated. These include the pollutant build-up on road surfaces during dry periods and subsequent wash-off during rainfall and snow events, followed by the transport into and through the drainage system to the end point of discharge.

A wide variety of mathematical approaches and equations are used in commercial urban drainage models, such as MIKE URBAN, SWMM etc. in order to describe the RDS build-up on roads. For example, Sartor et al. (1974) found an exponential function to be suitable to replicate RDS build-up with reasonable accuracy and their concept was then modified and widely used in stormwater quality modelling software including SWMM (Huber and Dickinson, 1988). However, Ball et al. (1998) reported that RDS build-up could be better replicated using power law or saturation functions.

Within this context, three forms of mathematical relationship for RDS build-up were investigated in depth. Moreover, due to inconsistency in the data found at sampling position B (as seen in Figure 4.1), it was decided to use RDS data collected at sampling position A for mathematical replication of the build-up process. RDS data collected over 1 to 14 ADD in April 2010 was used to develop the model, while the model parameters were then validated by using RDS data collected during May 2010 to March 2011 from the same study sites. The three mathematical relationships used are as follows:

(a) Power function: Sediment load increases with increases in the number of ADD towards a maximum value (Ball et al., 1998; Charbeneau and Barrett, 1998; Rossman, 2004). The mathematical expression can be defined as:

$$C_t = C_1 t^n \qquad \text{(Equation 4.1)}$$

where, C_t is the sediment load (mass per unit area), C_1 is the build-up rate constant, n is the time exponent and t is the number of antecedent dry days (ADD)

(b) Exponential function: Sediment load increases to a maximum value asymptotically. The mathematical expression for exponential function is shown in equation 4.2. Sartor and Boyd (1972) introduced this function for road sediment build-up over dry days in their study, which thereafter was used by others (e.g. Grottker, 1987; Deletic et al., 2000; Egodawatta et al., 2007; Liu et al., 2010).

$$C_t = C_{max} (1 - e^{-kt}) \qquad \text{(Equation 4.2)}$$

where, C_t is the sediment load (mass per unit area), C_{max} is the maximum sediment load (mass per unit area), k is the build-up rate constant (1/day) and t is the number of antecedent dry days

(c) Saturation function: sediment load starts building-up at a linear or nonlinear rate to a maximum value recognising a saturation value. Ball et al. (1998) found this function useful for their study in Australia.

$$C_t = (C_{max} \times t)/(p + t) \qquad \text{(Equation 4.3)}$$

where, C_t is the sediment load (mass per unit area), C_{max} is the maximum sediment load (mass per unit area), *p* is the half saturation constant (days to reach half of the maximum build-up load) and t is the number of antecedent dry days.

The equations presented above were tested by developing best fit curves for each equation to the observed RDS data collected at sampling position A in April 2010, as seen in Figures 4.2 to 4.4.

To start with the power law function, the calibrated parameters are C_1 and n as seen in Equation 4.1. The values of C_1 and n were derived from the equation of the trend line derived using MS Excel. The plots are shown in Figure 4.2.

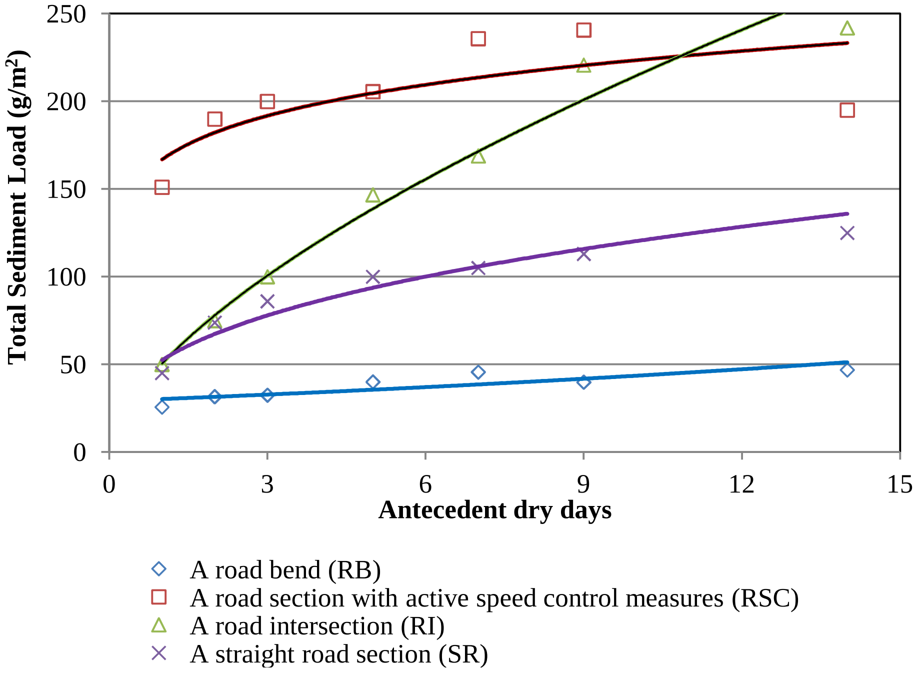


Figure 4.2: Road deposited sediment build-up parameters estimation using **power function.**

The exponential function calibration parameters are C_{max} and k (build-up rate constant). The largest value of the 7 RDS loads for each study site was taken as the C_{max} (maximum sediment load per square meter area). To estimate the k value, equation 4.2 was re-arranged as shown below. The final form of the equation generates a straight line and the slope of this line gives k directly. The graphs were plotted accordingly, as seen in Figure 4.3.

$$\frac{Ct}{Cmax} = 1 - e^{-kt}$$

$$e^{-kt} = 1 - \frac{Ct}{Cmax}$$

$$\mathrm{k} = -\frac{1}{\mathrm{t}}\ln(1 - \frac{\mathrm{Ct}}{\mathrm{Cmax}})$$

$$-\ln(1 - \frac{\mathrm{Ct}}{\mathrm{Cmax}}) = \mathrm{kt}$$

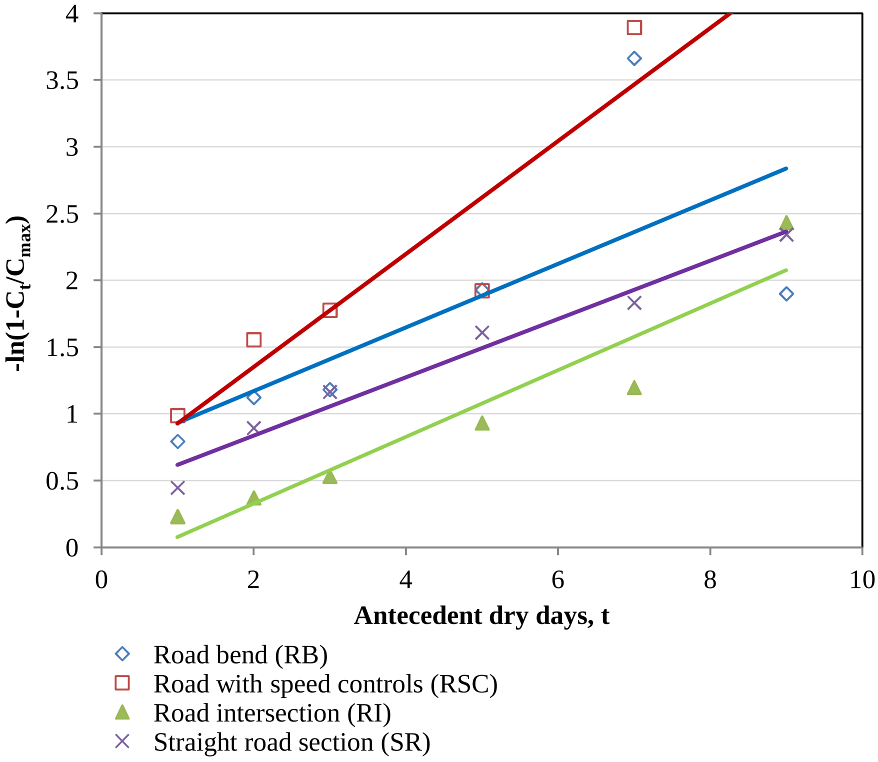


Figure 4.3: Road deposited sediment build-up parameters estimation using **exponential function.**

Using the saturation function for pollutant build-up the only calibration parameter is *p* (half saturation constant). To estimate *p* equation 4.3 was modified as shown below and a graph was plotted, as seen in Figure 4.4. The final form of the equation, as shown below, indicates a linear relationship, from which *p* can be calculated by taking the reciprocal of the slope of the trend line (Figure 4.4).

$$Ct = \frac{Cmax \times t}{p + t}$$

$$\frac{Ct}{Cmax - Ct} = \frac{t}{p}$$

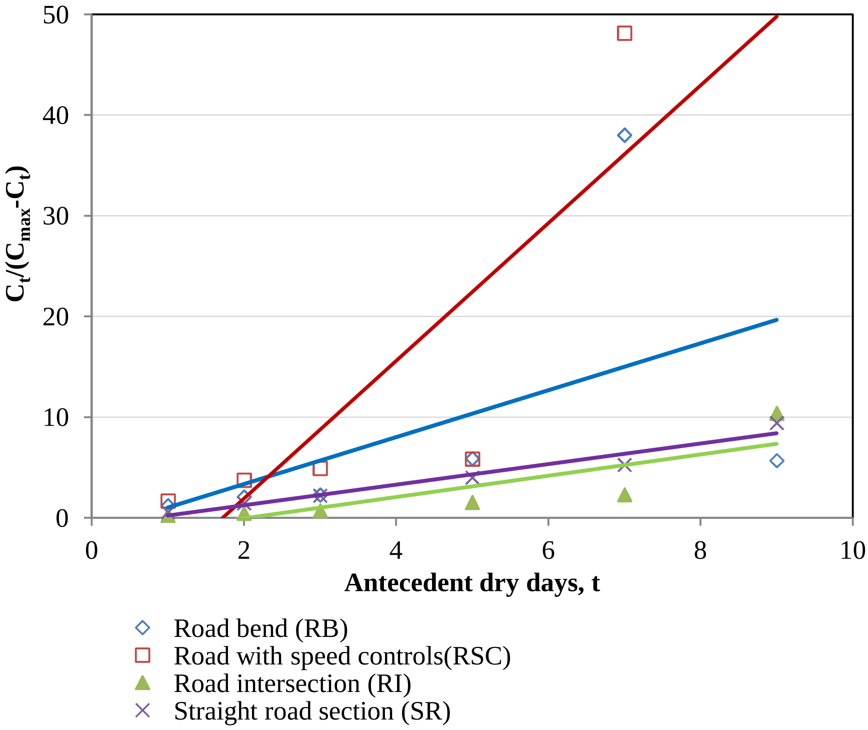


Figure 4.4: Road deposited sediment build-up parameters estimation using **saturation function.**

The build-up parameters derived from the above three models are presented in Table 4.3. As seen in the table, there is a marked variability between sites for all the derived build-up parameters. The highest RDS build-up rate (C_1) of 167 g/m^2 was at the RSC site followed by 52, 50 and 26 g/m^2 at the SR, RI and RB sites, respectively. The parameter, n (time exponent of build-up) was highest at the RI site (0.630) and lowest at the RSC site (0.127). The maximum sediment build-up load (C_{max}) of 242 g/m^2 was at the RI site, which was very close to 241 g/m^2 at the RSC site, but was 2-times as high as 125 g/m^2 at the SR site and 5-times that of 47 g/m^2 at the RB site. With the exception of the RSC site (0.423), the k (build-up rate constant (1/day)) at other sites did not exhibit significant variation (0.219 – 0.250). Similarly, *p* (half saturation constant (day)) was very close to 1 day at the RI and SR sites, while it was as low as 0.15 day (4 hours) and 0.43 day (10 hours) at the RSC and RB sites, respectively. These findings reconfirm that site specific attributes, such as road lay-out and road surface condition are the key drivers to explain the variability between calibrated parameters. As mentioned earlier (Table 3.1), the road surface condition was very poor at the RSC site (especially for sampling position A), where a larger supply of loose road particles was observed during sample collection compared to the other sites. Clearly, this is consistent with the magnitude of the build-up parameters at this site compared to the other sites in this study, as seen in Table 4.3. The significant influence of road texture and traffic flow condition on pollutant build-up on roads was also reported by Mahbub et al. (2010) in their study in Gold Coast region of Australia.

Table 4.3: Local build-up parameters estimation for near the curb sampling positions from field monitoring data

Site	C_1 (g/m^2)	n	C_{max} (g/m^2)	k (1/day)	*p* (day)
Road bend (RB)	26	0.228	47	0.238	0.43
Road with speed controls (RSC)	167	0.127	241	0.423	0.15
Road intersection (RI)	50	0.630	242	0.250	0.95
Straight road (SR)	52	0.362	125	0.219	0.98

C_1: build-up rate constant for Power law function, n: time exponent for build-up, $C_{max:}$ maximum sediment build-up load, k: build-up rate constant for Exponential function, *p*: half saturation constant

The RDS build-up parameters are now compared to the default values found in commercial urban drainage software and published results from previous studies elsewhere, as presented in Table 4.4. It appears that the build-up parameters derived for this study vary significantly with the default values used in MOUSE and SWMM5 commercial software, and with other studies listed in the table. All the derived parameters except k are found to be significantly higher than their default values in MOUSE and SWMM5. The variability of the build-up parameters from other studies elsewhere is also evident, as presented in Table 4.4.

Table 4.4: Comparison of estimated local build-up parameters with the default values from MOUSE and SWMM5 and other studies

Parameters	Description	Default values		This study	Other studies		
		MOUSE	SWMM5		Liu et al. (2010)	Hossain et al. (2010)	Deletic et al. (2000)
Maximum build-up (g/m^2)	The threshold of RDS build-up	50	5	47 - 242	37.50	2.75 - 5.30	10 - 100
Build-up rate ($g/m^2/d$)	Accumulation rate (MIKE URBAN)	5	-	7.5 -19	3.20	-	-
Build-up rate constant, k (1/d)	Exponential rate (SWMM)	-	0.4	0.219 – 0.423	-	0.210 – 0.382	0.045 – 0.100

RDS: Road deposited sediment, * irrespective of sampling positions

Based on the discussion above, it can be inferred that the large variations of these derived parameters are primarily due to the different site specific charcteristics with an influence from RDS sampling procedures between build-up studies elsewhere (e.g. Deletic et al., 2000; Liu et al., 2010; Mahbub et al., 2010). In addition, as RDS build-up patterns are rather different at the two transverse sampling positions, as discussed in section 4.4.1, the transferability of the derived parameters must be questioned.

4.4.3 Validation of Build-up Equations

In order to check the accuracy of the build-up equations, which were derived from the site investigation data collected in April 2010, simulated values from the equations were compared with observed values from RDS at sampling position A, undertaken during May 2010 to March 2011. Exponential and power law functions were chosen for validation purposes because these methods were found to be used frequently in pollutant build-up studies in the literature (e.g. Ball et al., 1998; Deletic et al., 2000; Liu et al., 2010). Figures 4.5 and 4.6 show the observed and the predicted sediment build-up values. As seen in the figures (left hand side), for most of the cases, the ratio of observed and simulated solid loads fluctuates within the ratio of 0.5 to 1.5, which suggests that the simulated sediment loads are in close agreement with the observed data.

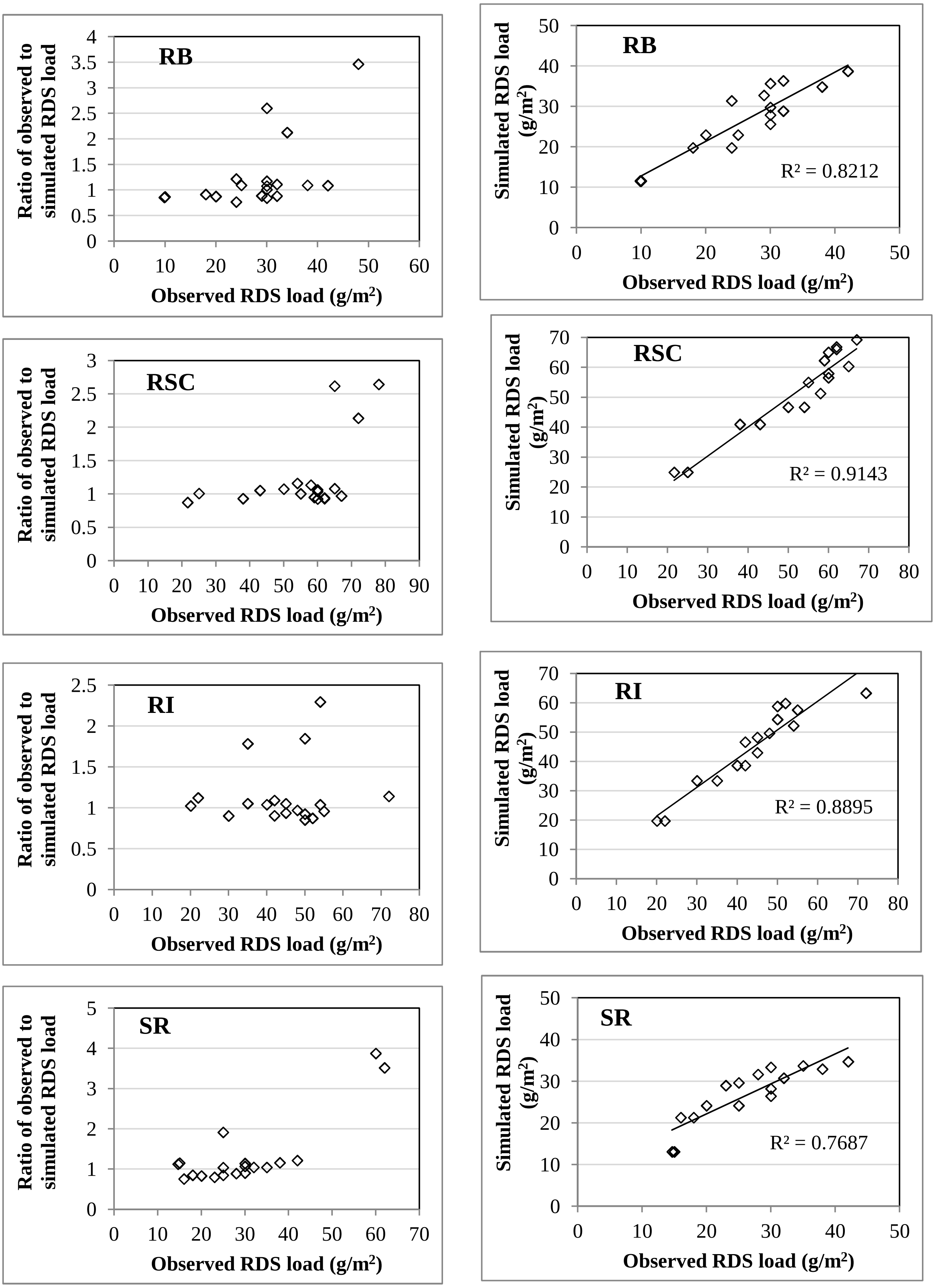


Figure 4.5: Comparison of simulated RDS load using the **power law function** with observed RDS load at primary study sites (RB: road bend; RSC: road with speed control; RI: road intersection; SR: straight road section).

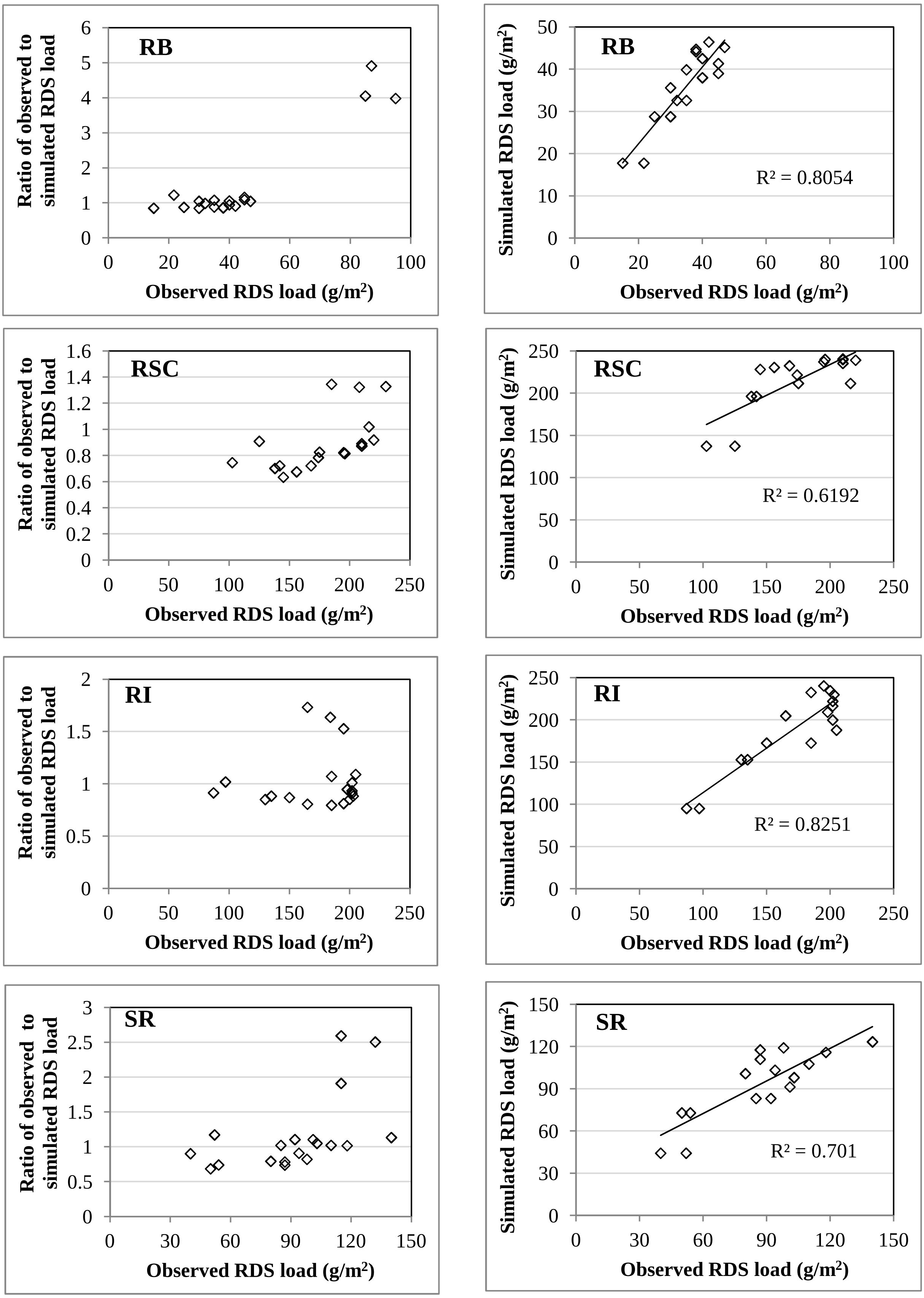


Figure 4.6: Comparison of simulated RDS load using **exponential function** with observed RDS load at primary study sites (RB: road bend; RSC: road with speed control; RI: road intersection; SR: straight road section).

In contrast three specific cases were found for which the ratio of observed and simulated build-up loads are greater than 2. These occur for data collected during the winter season (typically, November to January) when normally road grit and salt were spread over the road surfaces, hence increasing the sediment load (by mass) significantly. This observation is a reminder that seasonal variations in road maintenance and degradation operations may have an influence on the water quality of road runoff.

Removing outliers (ratio above 2.0) from the data, the simulated sediment loads are plotted against the observed data using the power law and the exponential function for all the primary study sites in Figures 4.5 and 4.6 (right hand side). The R^2 values range from 0.77 to 0.91 using the power law function, while they are between 0.62 and 0.82 using the exponential function, suggesting that simulated sediment build-up loads obtained from either model are reasonable. Comparing the two models, the power law is found to perform a little better than the exponential function for the present study. It is therefore clear that the derived parameters can provide guidance in the application of commercial software packages for urban drainage at a particular location instead of using the default values. Indeed, appropriate estimation of the local build-up parameters is crucial to ensuring the accuracy of water quality modelling, as noted by Egodawatta et al. (2007) and Liu et al (2010).

4.4.4 Particle Size Distribution of RDS

Table 4.5 displays particle size distributions for road deposited sediment (RDS) by averaging over all four primary study sites for both sampling positions A and B. As before, data is shown over a time span of 14 ADD. In general particle sizes of 250-63 µm (medium to fine sand) are dominant at both sampling positions. At sampling position A weight percentage of the RDS varied over time from approximately 36% to 41% (with an average value of approximately 38%) for the 500 - 250 µm size fraction, followed by approximately 56% to 60% (with an average of 58%) for the 250 - 63 µm size fraction and approximately 3% to 4.5% (with an average value of 3.75%) for the < 63 µm size fraction. At sampling position B, the RDS comprised approximately 21% to 26% (with an average value of 23.5%) for the size fraction of 500 - 250 µm, approximately 71% to 75% (with an average value of 73%) for the size fraction of 250 - 63 µm and approximately 3% to 4% (with an average value of 3.5%) for the size fraction of < 63 µm. Therefore, sediment collected at sampling position B contained, on average, approximately 15% more mass for the 250 - 63 µm size fraction compared to sampling position A, while the reverse trend was found for the size fraction 500 - 250 µm (course to medium sand). There was no significant difference between the sampling positions for the < 63 µm size fraction.

Table 4.5: Grain size distribution of RDS at both sampling positions averaged over all four primary study sites.

Antecedent dry days	**Near Curb** (A) Percentage by weight at size fraction (µm)			**1 m from the Curb (B)** Percentage by weight at size fraction (µm)		
	500-250	**250-63**	**<63**	**500-250**	**250-63**	**<63**
1	36.6	58.9	4.5	26.4	70.9	2.7
2	36.3	59.1	4.3	25.0	71.9	3.1
3	36.5	59.3	4.1	24.2	72.4	3.4
5	37.3	58.9	3.6	23.0	73.4	3.6
7	38.1	58.9	3.5	22.6	73.5	3.9
9	38.7	58.1	3.1	21.5	74.4	4.1
14	40.5	56.5	2.9	21.0	75.1	3.9

The particle size distributions suggest that finer fractions (particularly 250-63 µm size fraction) are more dominant (by mass) at sampling position B, while larger particles are predominant (by mass) at sampling position A. This finding is consistent with previous studies elsewhere, for example, Shaheen (1975), Ellis and Revitt (1982), Grottker (1987), Viklander (1998), Deletic and Orr (2005), Mahbub et al. (2010). In particular, sampling near the curb, Sartor et al. (1974) reported approximately 6% particles were smaller than 45 µm and 43% were below 250 µm in their study in the USA, while Ball et al. (1998) found 10 to 30% of particles were less than 200 µm on suburban road surfaces in Sydney. In contrast, sampling further away from the road, Deletic and Orr (2005) noted approximately 50% of the RDS were smaller than the 250 µm size in their study in Aberdeen, Scotland. The amount of sediment in the < 63 µm size compared to the total load (by mass) for both sampling positions was a little lower than reported in the studies by Ball et al. (1998), Deletic and Orr (2005) and Vaze and Chew (2002). This variation may likely be caused by local conditions found at the sites and the methods of sediment collection. As noted by Deletic and Orr (2005) common methods used to collect road sediment, such as dry vacuuming, brushing and sweeping the surface may not be very reliable for the collection of very small particles.

Furthermore from Table 4.5, the grain size distribution did not show a marked temporal variation over the antecedent dry periods. However, it appears that some small degree of particle redistribution did occur. At sampling position B, as dry days progress the sediment becomes finer (4% and 1.4% increase in weight for 250-63 µm and < 63 µm sizes, respectively over 1 to 14 ADD). However, a reverse picture of redistribution for RDS at position A was observed. As discussed earlier, based on the general driving pattern on roads, sediment deposited along the curb sides is unlikely to undergo agglomeration of particles, as noted by Mahbub et al. (2010) in their studies.

Particle size distribution curves for both sampling positions for each site are shown in Figure 4.7. The values used for the curves are averages of the data collected over the 14-dry day period. The distribution patterns are similar to those published in earlier studies (e.g. Deletic and Orr, 2005; Egodawatta, 2007). These graphs were then used to calculate the d_{10} and d_{50} particle sizes, for which 10% and 50% of all particles are smaller, respectively. The values of d_{10} and d_{50} are presented in Table 4.6.

Figure 4.7 shows that particle size distributions are different at both sampling positions for all primary study sites. Across the sites, the d_{50} and d_{10} values in RDS at sampling position A were found to be approximately 20 to 50% higher than their values at sampling position B. Variability between sampling sites were found to exist for these parameters. As displayed in Table 4.6, the smallest d_{10} and d_{50} (average over 14 dry days) were found at the SR site, whilst the largest values were at the RSC site. The d_{10} and d_{50} at the RB and RI sites fall in between the smallest and largest values. This difference in d_{10} and d_{50} across the sites may be linked to the site specific attributes, as discussed in section 4.4.1, with an influence of degree of disturbance on RDS due to the traffic load, as noted by Mahbub et al. (2010).

The median diameters, $d_{50,}$ of RDS reported here fall within published ranges in the literature noted as anything between 150 to 4000 µm (Sartor and Boyd, 1972; Pitt, 1979; Butler and Clark, 1995, Ball et al., 1998; Deletic and Orr, 2005). Based on the results, it can be speculated that sediment at the SR and RI sites may likely be more available during runoff events compared to the slightly coarser particles at the RB and RSC sites. This finding may have site specific implications for the pollution potential of road drainage in the study area.

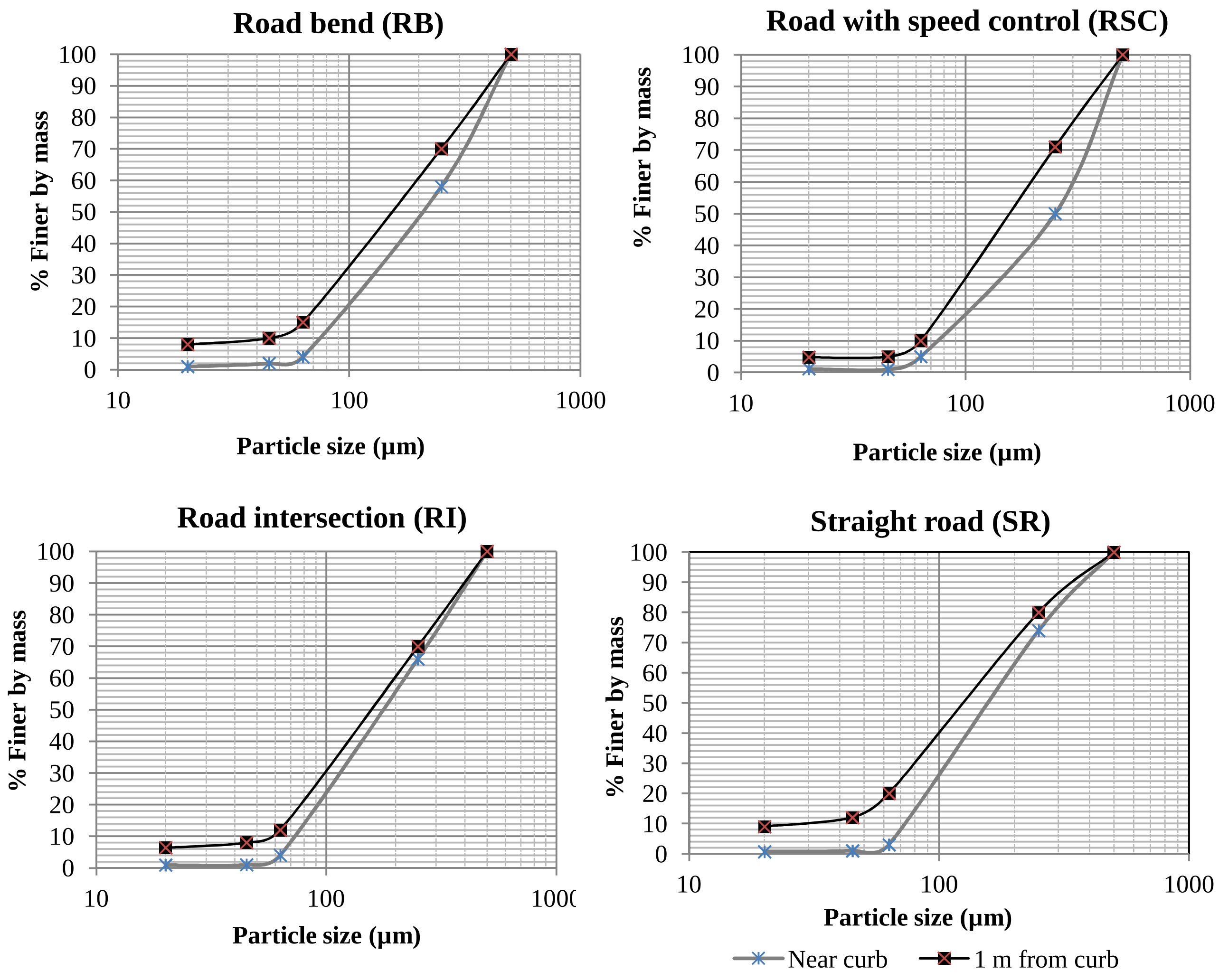


Figure 4.7: Particle size distributions (average over 14 antecedent dry days) for both sampling positions at the primary study sites.

Table 4.6: Values of d_{10} and d_{50} for both sampling positions (A: near curb & B: 1 m from curb)

Particle diameter (µm)	Sampling position	Study sites			
		Road bend (RB)	Road with speed control (RSC)	Road intersection (RI)	Straight road (SR)
d_{10}	A	75	78	75	72
	B	45	65	60	28
d_{50}	A	225	255	185	160
	B	170	170	155	120

4.4.5 Heavy Metals Build-up

In this section the relationship between heavy metal concentrations in RDS and antecedent dry days for both sampling positions is discussed. Out of six metals, Cd, Cu, Pb and Zn were considered for this investigation, primarily based on their accumulation index, AI > 1.5, (see Table 4.1), as discussed earlier in section 4.2. Initially, metal concentrations (irrespective of sediment size fraction) were averaged over all the primary study sites. These data are presented in Figure 4.8, where trend lines using the power law function (found most suitable for best fit of heavy metal concentration data), are also shown. Note that the concentration scales are different for each metal in Figure 4.8. The R^2 values, ranging from 0.002 to 0.655, vary according to individual metals and sampling positions. It should also be noted that except for Cu at sampling position B, the statistical strength of the relationships are in general weak to moderate ($R^2 < 0.5$).

Based on the metal build-up results from Figure 4.8, both increasing and decreasing trends with increasing ADD were found. In general, at sampling position B, all the metal concentrations showed an increasing trend with increasing ADD, which is consistent with current thinking in literature of a positive linear, or non linear, pollutant build-up with ADD. In contrast, at sampling position A, all metal concentrations were found to decrease with increasing ADD (although the Cd concentration did not vary significantly over the ADD). The decreasing trend of heavy metal concentration with increasing ADD is surprising and differs from current thinking. A similar downward trend of pollutant constituents is also reported by Li and Barrett (2008) at College Station site in Texas, USA. They further noted that although this relationship is unexpected, it should not be overlooked.

An increasing trend with increasing ADD for all metals, further from the curb towards middle of the road could be explained by a continuous input of smaller particles from traffic, while near curb sides RDS may likely altered its chemical composition through volatilization, biodegradation and chemical decay process and reduce pollutants attached to the road deposited sediments, as speculated by Li and Barrett (2008). Moreover, as discussed earlier in section 4.4.4, this difference in metal concentration may be linked to the particle size distribution of RDS, for which the mass of finer size fractions (< 63 µm) increased with increased ADD at sampling position B, whilst reverse scenarios was found at sampling position A. Therefore, the point is being re-affirmed from the results of this study that pollutant build-up varies with transverse sampling positions.

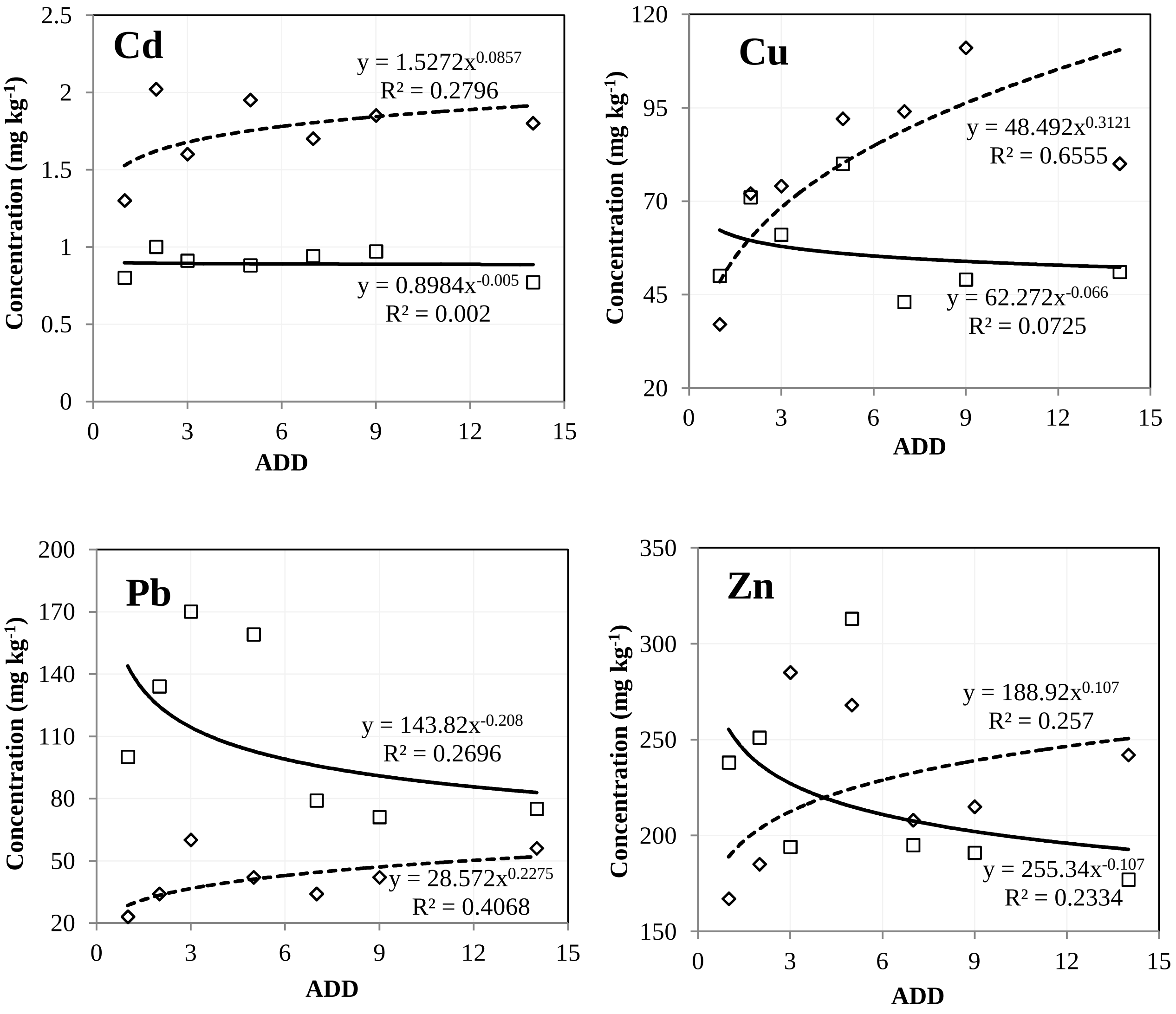


Figure 4.8: Relationship between heavy metal concentrations and ADD (squares and diamonds represent data for near the curb [A] and 1 m from the curb [B] sampling positions, respectively).

Furthermore, considering the data in a different way, metal concentrations in RDS are now averaged over sampling positions for each individual primary site and are studied to gain supplementary insight into these relationships. Figure 4.9 shows RDS metal build-up over dry days in the same format as Figure 4.8 for all four primary study sites.

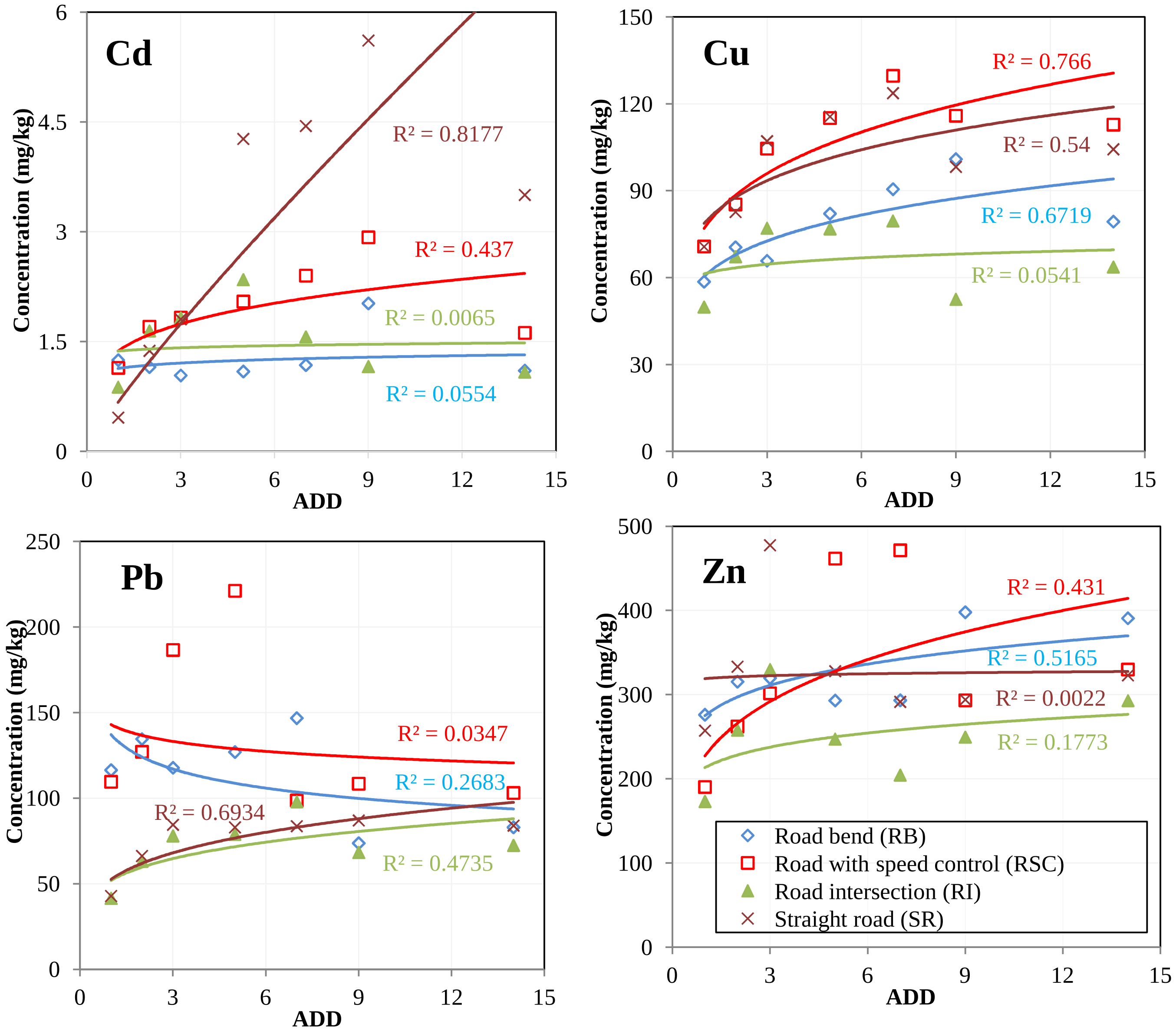


Figure 4.9: Heavy metal concentration in road deposited sediment over the antecedent dry days at the primary study sites (average over sampling positions and different size fractions).

As seen in Figure 4.9, based on the statistical strength (R^2), the pollutant build-up relationships varied between study sites. However the strength of the relationships (R^2) were found to be improved in Figure 4.9 compared to the values in Figure 4.8. Aprat from Pb (at the RB and RSC sites), all other metals show an increasing trend with increasing ADD for all the sites. The build-up pattern was generally more consistent for Cu (except at the RI site) and Zn (except at the SR site), while they were rather inconsistent for Cd between the sites. For example, Cd build-up patterns at the RB and RI sites were not significantly different over the ADD based on the trend lines, while in contrast Cd at the SR site showed a high rate of build-up over the entire build-up period. The nature of the diverse data found for Cd at the above site may not likely be well described by the trend lines using the power law function. However, the build-up pattern of Cd at the RSC site can still be replicated reasonably using this function, as seen in the figure.

In contrast to other metals, Pb concentrations showed both positive and negative relationship with the ADD. While Pb concentrations at the RI and SR sites were found to increase with increasing ADD, they were found to decrease with increasing ADD at the RB and RSC sites, which is inconsistent with current understanding of the pollutant build-up pattern. However, this may not be surprising, as discussed earlier. The primary source of the Pb at the RB and RSC sites is likely to be the road paint (double yellow lines) rather than traffic, from which a continuous input of metals may better explain the pollutant build-up at the other sites (see Table 3.1 for detailed site description).

Moreover, as discussed earlier, road lay-out, sediment particle sizes, presence of road paints and traffic movement pattern can influence site specific heavy metals emission (see Tables 4.1, 4.2), which may also explain the variability of heavy metal build-up over ADD between sites.

4.5 Conclusions

This chapter reveals that dry road deposited sediment (RDS) contains significant amounts of heavy metals compared to their background levels. A spatial variability of heavy metal concentrations were found on the studied road network according to site-specific attributes rather than due to traffic volume alone. A road bend, bus stops, a road with speed control measures, a road intersection and a straight road were all found as pollutant hot-spot sites. RDS and RDS associated heavy metal build-up patterns were found to be site-specific. Hence, local build-up parameters were derived and compared with default values in commonly used commercial urban drainage software, suggesting that the default values are (significantly) inappropriate for a road network, such as Riccarton Campus. Furthermore, the analysis of the relationship between heavy metal build-up and antecedent dry days revealed that RDS sampling position was an important factor. Although the pattern of pollutant build-up was common, a transverse distribution of sediment build-up was also observed.

Chapter – 5 Analyses of Heavy Metals in Dry Weather Derived Sediment

5.1 Introduction

In contrast to the previous chapter which concerned the analysis of information from a intensive data collection exercise, this chapter is concerned with the analysis of heavy metals in dry road deposited sediment (RDS) collected from the primary study sites at approximately monthly intervals over a year. The data from the short duration exercise (April 2010), as discussed in Chapter 4, also features part of the second month of the longer exercise (March 2010 to February 2011). The data set and all the analysis are based on the primary study sites, namely, the road bend (RB), road with speed control (RSC), road intersection (RI) and straight road section (SR). The data is analysed with the aim of quantifying heavy metals Cd, Cr, Cu, Ni, Pb and Zn in RDS and exploring the influence of sampling position and different sediment size fractions on heavy metal concentrations. The temporal (monthly) and seasonal variations of heavy metals in RDS are analysed and presented. Furthermore, evaluation of heavy metal contamination is also discussed.

5.2 Grain Size and Sampling Position Specific Heavy Metals in RDS

Table 5.1 presents the grain size specific heavy metal concentrations in RDS for both sampling positions (A: near the curb and B: 1 m from the curb) determined by averaging metal concentrations over the 4 primary study sites. The local background values of the metals from Riccarton Campus are also shown. The accumulation index, which is the ratio of the mean to the local background mean, is also presented in the table. The ranges, mean and median for heavy metal concentrations in all size fractions of RDS at both the sampling positions were found within the ranges of values reported by previous studies for residential catchments in the UK, such as Deletic and Orr (2005) and Robertson and Taylor (2007), and in other parts of the world (e.g. Kim et al., 1998; Sutherland, 2003).

Table 5.1: Descriptive statistics of grain size specific metal concentrations (average over sites) in mg kg-1 for both sampling positions (A: near curb & B: 1 m from curb) as measured between March, 2010 and February 2011 (n = 120).

Metals	Sampling position	Size fraction (µm)	Range	Median	Mean ± Standard deviation	Background mean[1]	Accumulation index[2]
Cd	A	500-250	0.16 –1.6	0.80	0.77 ± 0.38	1	0.77
		250-63	0.13 – 2.2	1.24	1.20 ± 0.47		1.20
		<63	0.56 – 4.1	2.16	2.06 ± 0.65		2.06
	B	500-250	0.20 – 2.0	0.80	0.82 ± 0.38		0.82
		250-63	0.15 – 3.1	1.25	1.32 ± 0.46		1.32
		<63	0.71– 16.7	2.30	2.76 ± 2.14		2.76
Cr	A	500-250	2 – 25	8	10 ± 6	8	1.25
		250-63	2 – 73	14	14 ± 8		1.75
		<63	6 – 47	23	23 ± 9		2.87
	B	500-250	1 – 20	5	8 ± 5		1.00
		250-63	2 – 32	11	12 ± 6		1.25
		<63	0 – 54	20	19 ± 9		2.37
Cu	A	500-250	10 – 82	35	38 ± 14	44	0.86
		250-63	16 – 154	72	75 ± 30		1.70
		<63	52 – 289	196	183 ± 53		4.16
	B	500-250	14 – 89	41	45 ± 17		1.02
		250-63	28 – 185	87	94 ± 34		2.14
		<63	44 – 330	189	193 ± 56		4.39
Ni	A	500-250	1 – 24	8	9 ± 5	20	0.40
		250-63	2 – 37	14	15 ± 7		0.75
		<63	9 – 64	26	28 ± 13		1.40
	B	500-250	2 – 20	7	8 ± 5		0.40
		250-63	2 – 35	11	14 ± 7		0.70
		<63	0 – 54	22	24 ± 13		1.20
Pb	A	500-250	12 – 275	69	93 ± 65	28	3.32
		250-63	13 – 669	102	132 ± 105		4.71
		<63	26 – 345	142	147 ± 60		5.25
	B	500-250	4 – 90	24	32 ± 20		1.14
		250-63	10 – 180	53	58 ± 32		2.07
		<63	14 – 215	111	113 ± 37		4.04
Zn	A	500-250	63 – 224	115	122 ± 38	107	1.14
		250-63	79 – 400	218	225 ± 82		2.10
		<63	190 – 907	523	501 ± 133		4.68
	B	500-250	38 – 220	107	110 ± 41		1.03
		250-63	86 – 487	210	220 ± 82		2.06
		<63	89 – 893	499	483 ± 134		4.51

[1] The background concentrations were measured in RDS from roads which carry no traffic

[2] Ratio of the mean to the local background mean

As seen in Table 5.1, the mean concentrations increased as sediment size fraction decreased for both sampling positions suggesting lower size fractions have greater attachment of heavy metals. In general, the mean and median heavy metal concentrations for the < 63 µm size fraction were approximately 2 to 5 times larger compared to the mean and median values for 250-63 µm and 500-250 µm size fractions, respectively, for both sampling positions. A significant difference for heavy metal concentrations always exists between the sediment size fractions (Kruskall-Wallis test; $p \leq 0.05$).

Based on the sampling positions, it has been found that Cd and Cu showed higher concentrations in RDS at sampling position B than sampling position A, while Cr, Ni, Pb and Zn displayed the opposite trend (Table 5.1). The differences between sampling positions varied between the heavy metals with Ni and Zn showing the smallest differences, and Cu and Pb showing the largest. Furthermore, Table 5.1 reveals an average 16% increase of Cd and Cu concentrations, and an average 25% and 50% decrease of Cr and Pb concentrations, respectively, between sampling positions A and B, while in contrast, Ni and Zn exhibit little or no differences between the two transverse sampling positions (particularly for both 250-63 µm and 500-250 µm size fractions).

The accumulation indices for most of the metals (except Pb near the curb) in the 500-250 µm size fraction were near 1.0, suggesting that the larger RDS are unlikely to be contaminated by heavy metals from road traffic activity. In contrast, all heavy metals except Ni showed elevated concentrations compared to background concentrations for 250-63 µm and < 63 µm size fractions, indicating that there are indeed some local anthropogenic inputs (e.g. from the road-traffic environment) on top of atmospheric deposition. For the latter two size fractions, in general, at sampling position A, the order of accumulation coefficient is found as Pb > Zn > Cu > Cr > Cd, and at sampling position B, the order of increase is found as Zn > Cu > Pb > Cd > Cr.

As discussed earlier in section 4.2, these heavy metals are somewhat related to road traffic and are found at elevated levels in urban road traffic environments. However, an unusually high level of Pb in the study area is surprising because a major source of Pb was phased out more than a decade ago as it had been added to fuel as an anti-knocking additive. Additionally, any residual effect from the previous use of Pb is unlikely as road sediment is characterized by short residence times with recent accumulation on road surfaces (Harrison et al., 1985; Allott et al., 1990; Xiangdong et al., 2001). The only other likely source of Pb in RDS near curb sides is from particles of degrading road paint of the double yellow lines (see Table 4.2). The input of Pb from yellow road paint was first reported by Deletic and Orr (2005). However, elevated concentrations of Pb in particularly at sampling position B (especially for the size fraction < 63 µm), suggests that other traffic related inputs, such as wheel bearings, oil drips, vehicle exhaust, may still deliver Pb to the road traffic environment, as reported by Napier et al. (2008) and Ewen et al. (2009).

The reason behind higher concentrations for Zn, Cu and Cd at sampling position B than sampling position A may be linked with vehicular emission, as it was observed that usually vehicles passed directly over position B, and hence any deposition of particulates, from e.g. tyres and brakes, containing heavy metals would most likely occur at this position (Deletic and Orr, 2005). Moreover, prevalence of transverse gradient of heavy metal concentrations in road dust was found to exist, as reported by Johnston and Harrison (1984) and Deletic and Orr (2005), suggests that the rate of redistribution (by vehicle induced turbulence or natural processes, such as wind) is always less than the rate of deposition.

5.3 Variability of Heavy Metals across the Study Sites

Following on section 5.2, this section describes the variability of heavy metals across the primary study sites. Figures 5.1 to 5.6 display box plots of Cd, Cr, Cu, Ni, Pb and Zn concentrations, respectively, at each site for different grain sizes and for both sampling positions. The influence of grain size and sampling position on metal emissions was discussed in the previous section, which are also evident from the figures plotted here. However, in this section site specific variability of heavy metal concentration is primarily discussed, which was absent in Table 5.1. As seen in Figures 5.1 to 5.6, heavy metal concentration is found to vary between sites. In general, the metal concentrations are found to increase with decreasing particle size fractions except Pb. However, with a few exceptions, the mean concentrations for most of the metals in the largest size fraction of RDS (500-250 µm) are not significantly different to their local background concentrations. The variation of each heavy metal is discussed briefly below.

Cadmium (Cd)

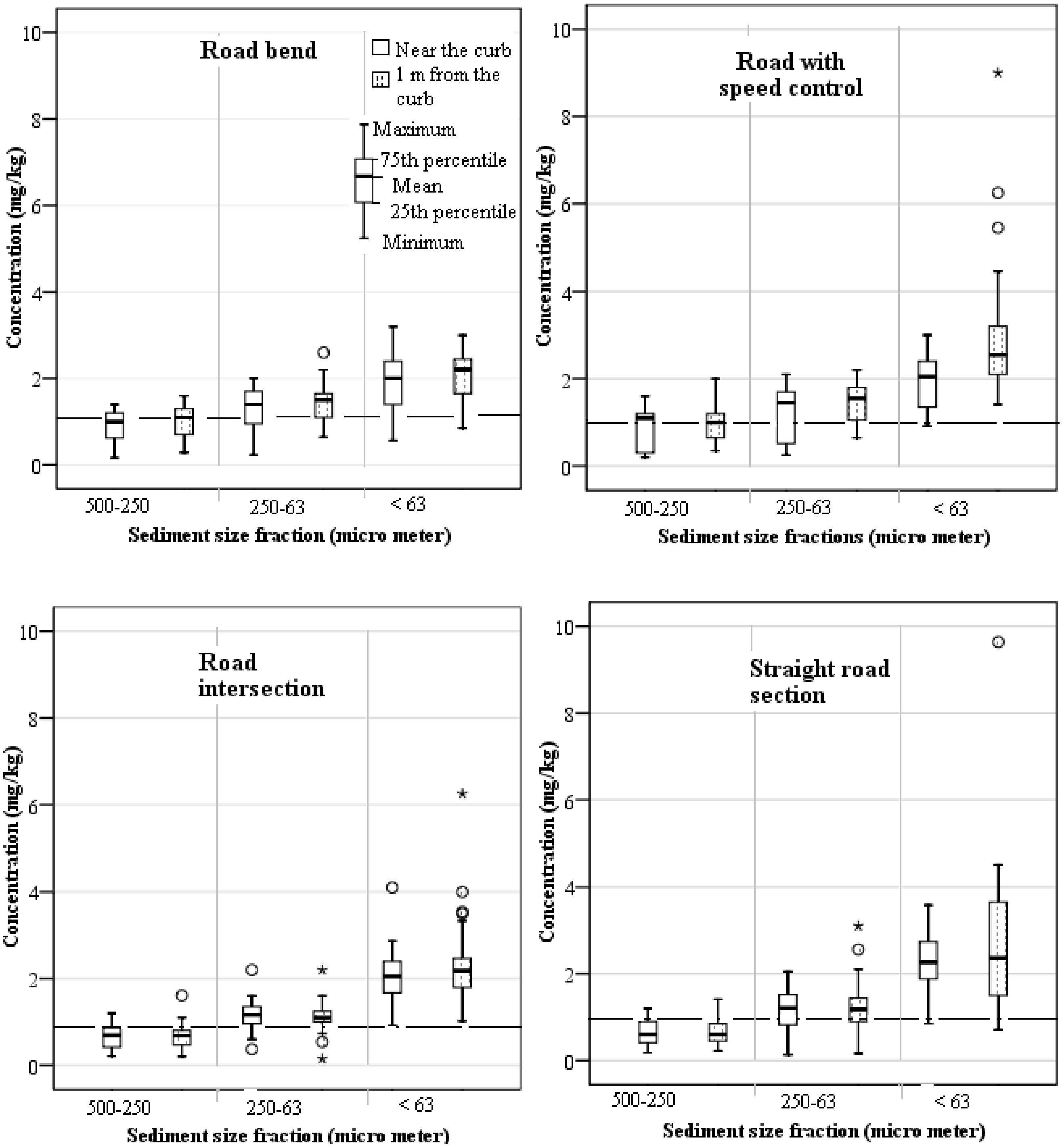


Figure 5.1: Box plots of grain size and site specific Cadmium (Cd) in RDS for both sampling positions (dashed line represents local background value).

Chromium (Cr)

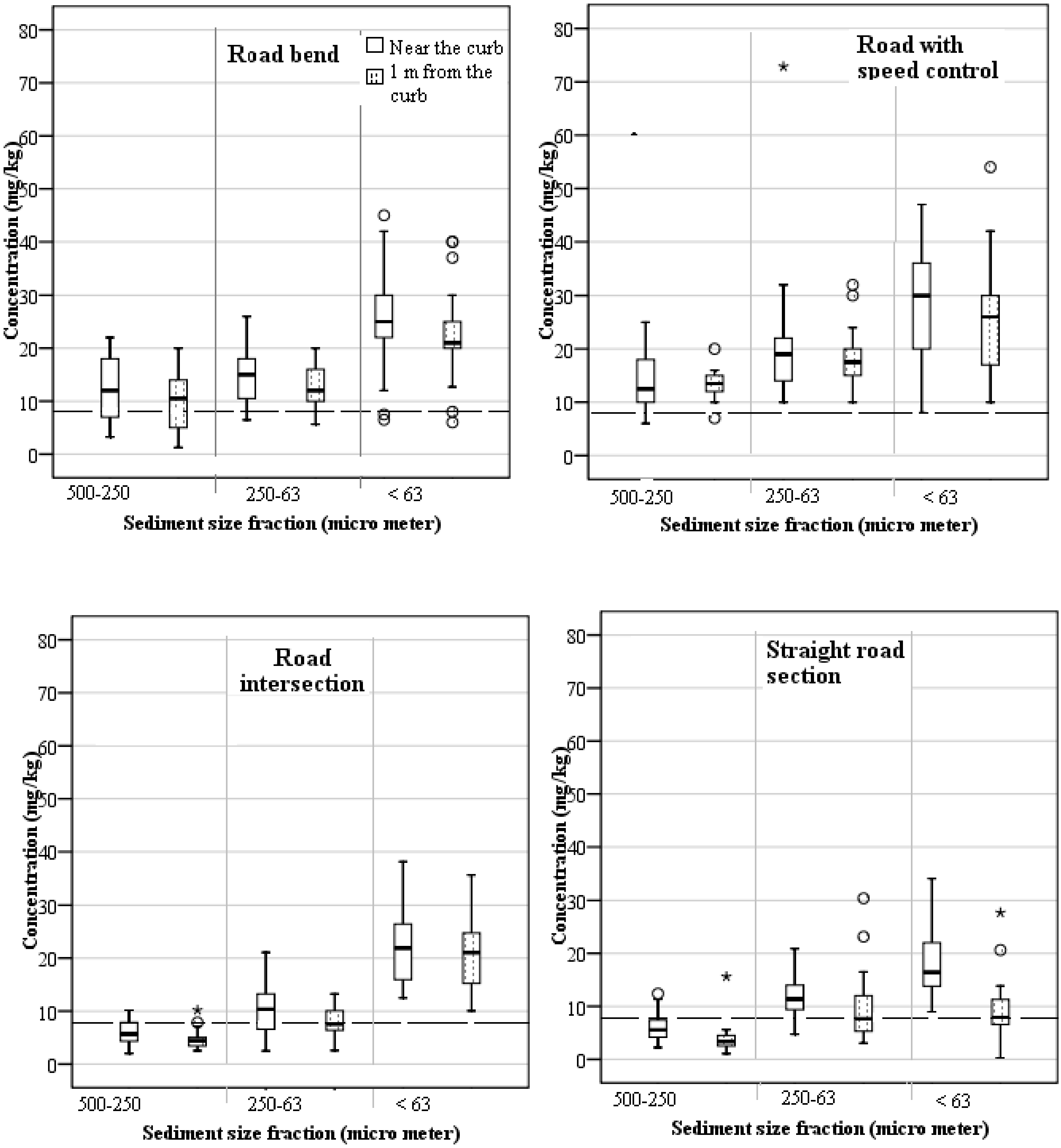


Figure 5.2: Box plots of grain size and site specific Chromium (Cr) concentration in RDS for both sampling positions (dashed line represents local background value).

Copper (Cu)

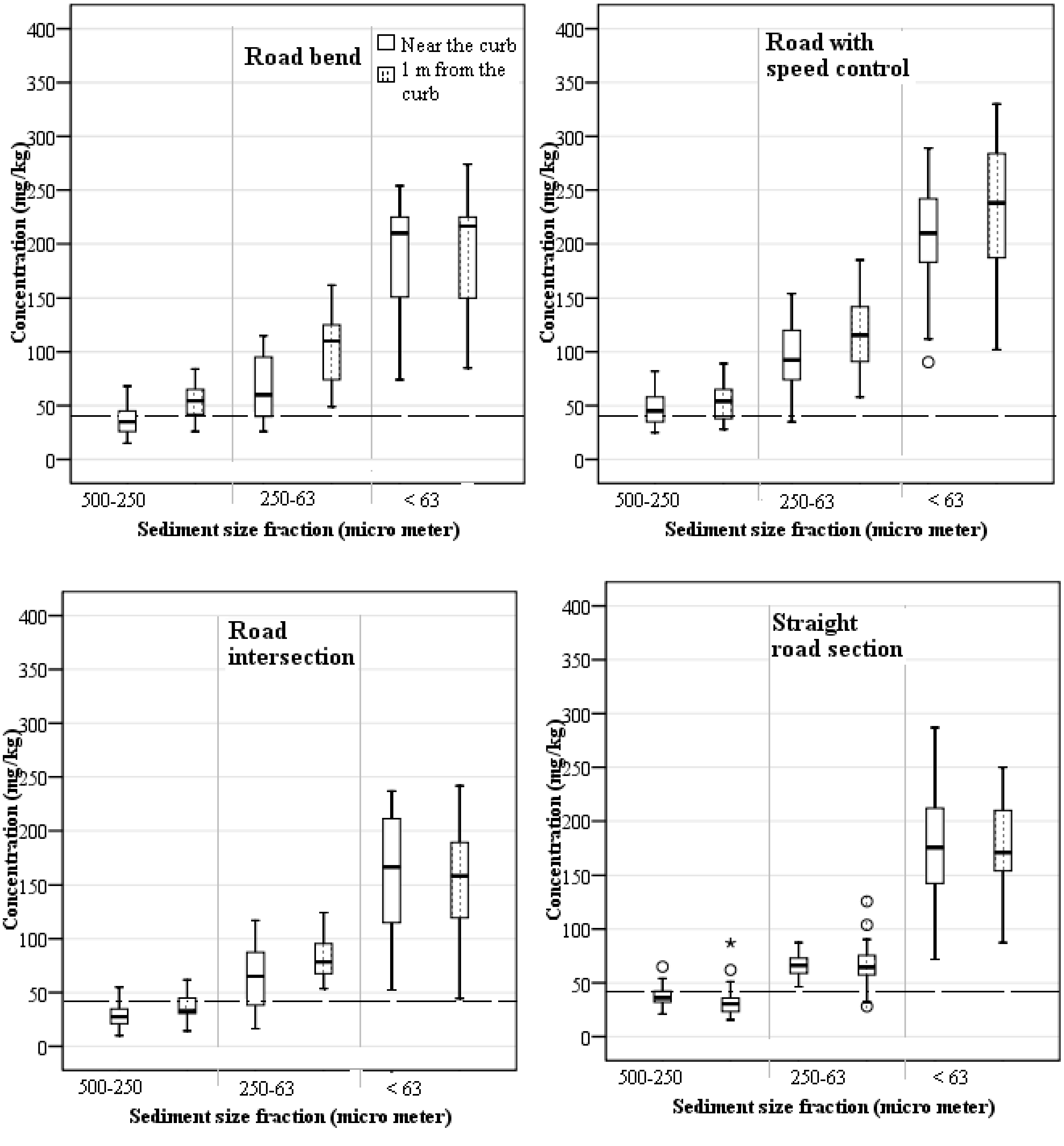


Figure 5.3: Box plots of grain size and site specific Copper (Cu) concentration in RDS for both sampling positions (dashed line represents local background value).

Nickel (Ni)

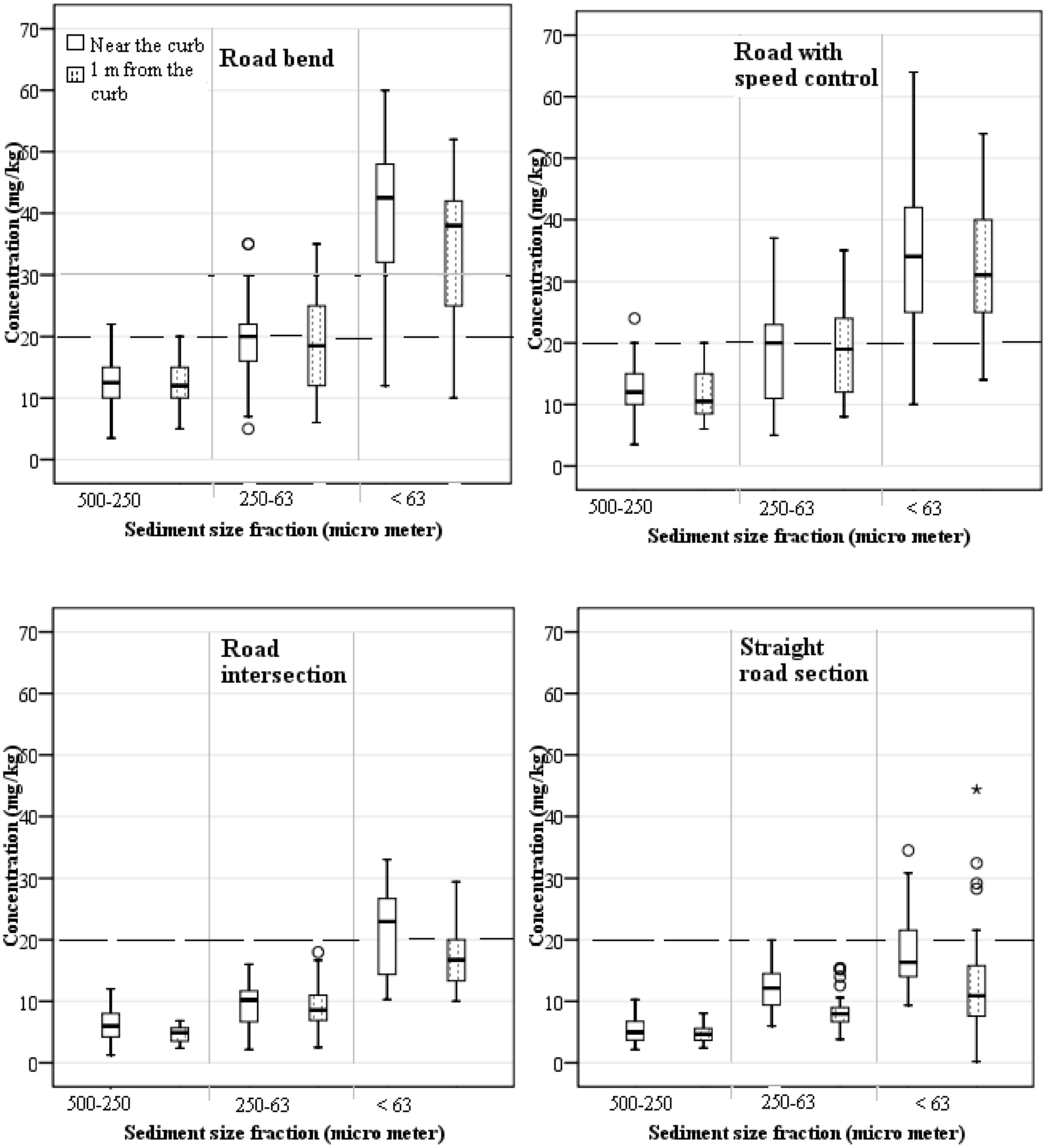


Figure 5.4: Box plots of grain size and site specific Nickel (Ni) concentration in RDS for both sampling positions (dashed line represents local background value).

Lead (Pb)

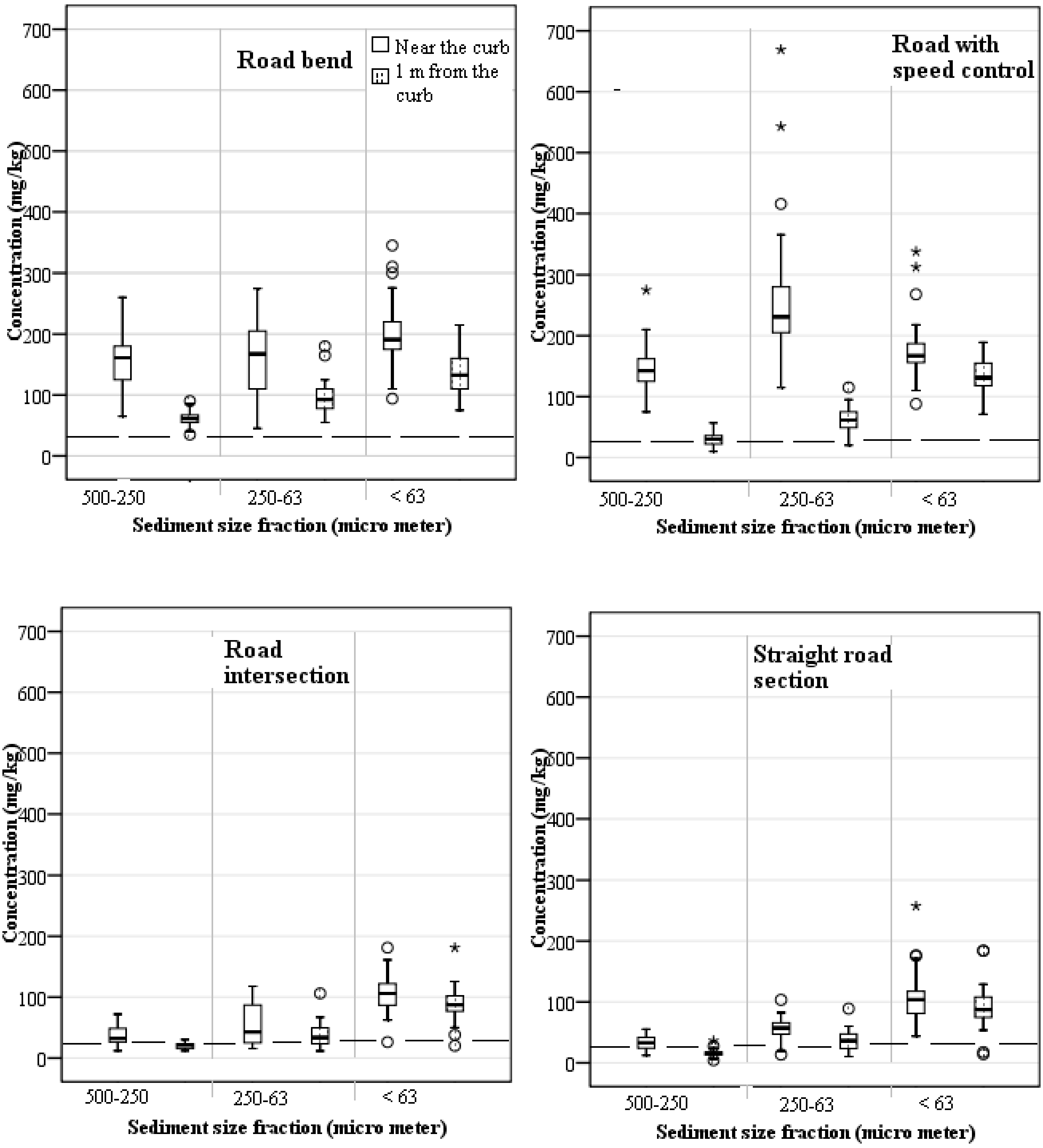


Figure 5.5: Box plots of grain size and site specific Lead (Pb) concentration in RDS for both sampling positions (dashed line represents local background value).

Zinc (Zn)

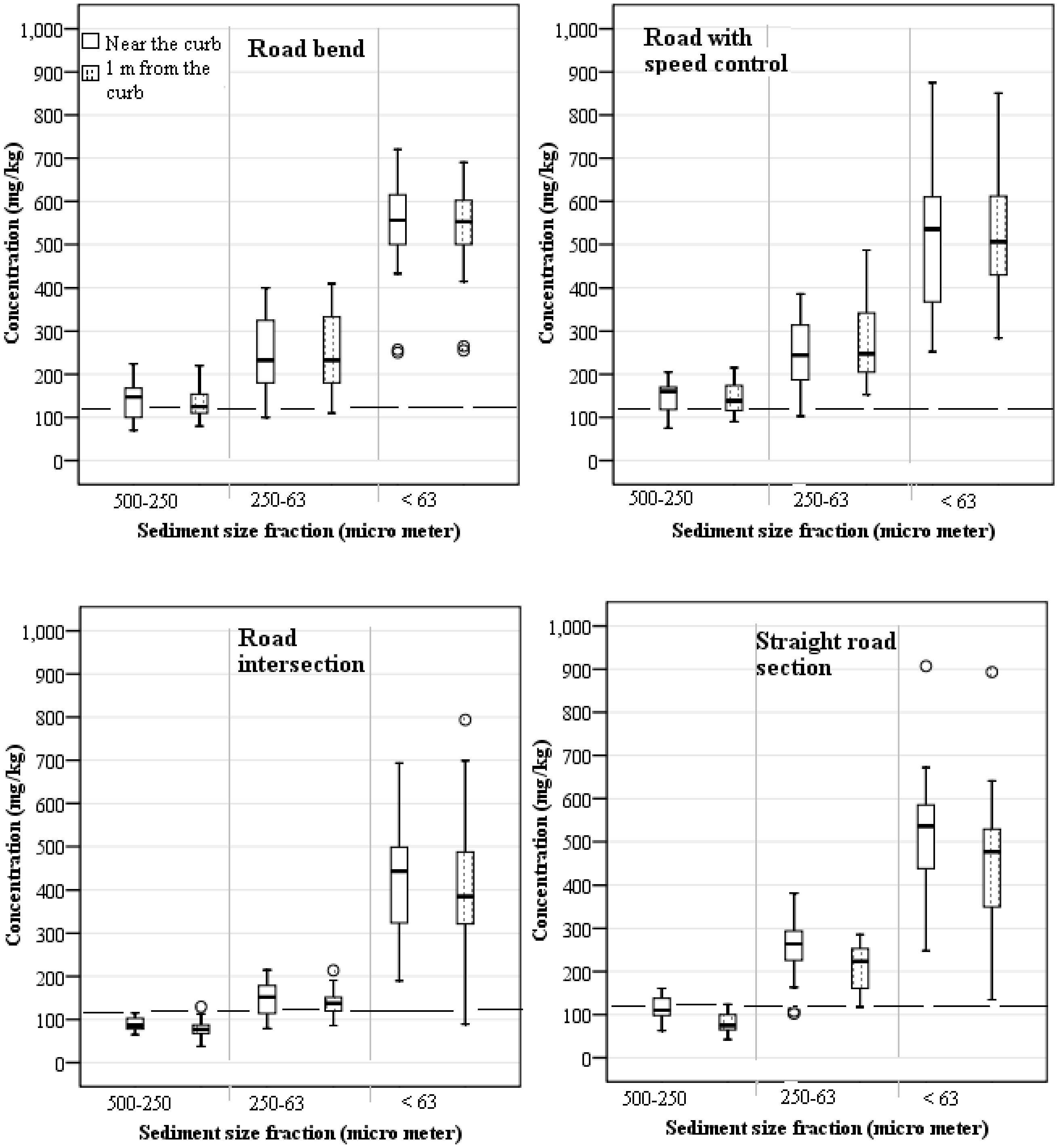


Figure 5.6: Box plots of grain size and site specific Zinc (Zn) concentration in RDS for both sampling positions (dashed line represents local background value).

As seen in Figure 5.1, generally the highest mean Cd concentrations were at the RSC site, while they were lowest at the RI site. Except the SR site, the mean concentrations were found very similar (particularly for the < 63 µm size fraction) at sampling position A between the sites, while at sampling position B they varied between the sites. The mean Cd concentrations were similar between the RSC and SR sites (≈2.8 mg kg-1), and between the RB and RI sites (≈2. mg kg-1).

The variation of Cr across the sites was found in the order of the RSC > RB > RI > SR sites, as seen in Figure 5.2. For the sediment size fraction 250-63 µm, the highest mean Cr of 18 mg kg-1 (A) was at the RSC site, while the lowest was 7 mg kg-1 (B) at the RI site. Similarly for the smallest sediment size fraction (< 63 µm), the highest mean concentration of 28 mg kg-1 (A) was at the RSC site and the lowest concentration of 8 mg kg-1 (B) was at the SR site.

The Cu concentrations were found to vary widely between sites. As seen in Figure 5.3, generally Cu concentration was higher at the RSC site compared to the RI and SR sites in particular. However, Cu concentration at the RB site was only a little below that at the RSC site. For the sediment size fraction 250-63 µm, the highest mean Cu concentration of 120 mg kg-1 (B) was at the RSC site followed by 105 (B), 83 (B) and 67 (A) mg kg-1 at the RB, RI and SR sites, respectively. Similarly, for the smallest sediment size (< 63 µm), the highest Cu concentration of 234 mg kg-1 (B) was also at the RSC site, while the lowest concentration of 161 mg kg-1 (A) was at the RI site, as seen in Figure 5.3.

A site specific variability of Ni concentration revealed that the highest concentration was for the RB site and the lowest was for the SR site, see Figure 5.4. Based on the mean value, the concentration of Ni at the RSC site was a little smaller compared to the RB site. Similarly, the RI site showed a little higher value than in the SR site. For the sediment size fraction of 250-63 µm, the highest mean of 20 mg kg-1 (A) was at the RB and RSC sites, while the lowest was 8 mg kg-1 (B) at the RI and SR sites. Similarly, for the < 63 µm size fraction, the highest mean Ni concentration was approximately 43 mg kg-1 (A) at the RB site compared to the lowest concentration of approximately 11 mg kg-1 (B) at the SR site.

The variation of Pb concentrations between the sampling sites and between the sampling positions is rather inconsistent, as seen in Figure 5.5, compared to the variations found for other metals. Generally, Pb concentration was found higher in RDS collected from the sampling position A than B across the sites. Based on sites, except the RSC site, all others showed increased concentration with decreased sediment sizes. For the RSC site, the highest mean concentration of 261 mg kg-1 was in the 250-63 µm size fraction compared to the value of 177 mg kg-1 in the < 63 µm size fraction. In contrast, the highest mean Pb concentrations were 156, 52 and 33 mg kg-1 in the sediment size fraction 250- 63 µm at the RB, SR and RI sites, respectively, while these were 180, 110 and 105 mg kg-1 in the sediment size fraction < 63 µm at the RB, RI and SR sites, respectively. Subsequently, a relatively high Pb concentration (particularly, in the < 63 µm sediment size fraction) at sampling position B was also evident across the sites showing concentrations range from 90 to 134 mg kg-1 across the sites.

The Zn concentration across the sampling sites did not display much variation, as seen in Figure 5.6. Moreover, Zn concentrations were found very similar at both sampling positions at each site. Briefly, for both 250-63 µm and < 63 µm sediment size fractions, the highest Zn concentrations were found at the RB and RSC sites, while the lowest concentrations were at the RI site. The concentrations at the SR site were either marginally higher or lower compared to their values at the RSC site.

Based on the discussion above, it has been revealed that RDS at the RSC site is more contaminated for most of the metals followed by the RB site. Similarly, RDS at the RI and SR sites have similar compositions with generally lower metal concentration compared to the aforementioned sites. As mentioned elsewhere, traffic volume for the SR site (650 VPH) is significantly higher than the RB (200 VPH) and RSC (250 VPH) sites, however, the higher metal concentration is not found in accordance with the traffic volume. This corroborates the idea that site-specific attributes (road lay-out, traffic movement patterns, road condition, and presence of road paints) are important influences in addition to the traffic volume.

5.4 Monthly Distribution of Heavy Metals

5.4.1 Temporal Variation of Heavy Metals in RDS

Recognizing the importance of the temporal variability of heavy metals to urban diffuse pollution from roads (Robertson and Taylor, 2007), this study carried out monthly metal analyses at the primary study sites. In the literature a few previous studies had focused on the spatial variability of heavy metals on road surfaces (Linton et al., 1980; Harrison et al., 1985; Deletic and Orr, 2005), while a number of studies also existed on the city scale (Robertson et al., 2003; Charlesworth et al., 2003; Carraz et al., 2006). However, only limited information was available on the monthly metal distribution pattern (Robertson and Taylor, 2007), while some seasonal variability of RDS heavy metals had been published (e.g. Hamilton et al., 1984; Fergusson and Kim, 1991). Figure 5.7 shows the monthly mean metal distribution (averaged over sampling positions and all 3 size fractions) at the primary study sites. A greater variability was apparent between the study sites for Cr, Ni and Pb compared to Cd, Cu and Zn. Additionally, metal concentrations throughout the year tended to be higher at the RB and RSC sites than at the RI and SR sites. Overall higher metal concentrations were found during summer months than in spring and autumn, and the lowest were found in late winter/early spring, as seen in Figure 5.7. A similar observation was reported by Robertson and Taylor (2007) from their study in Manchester, UK.

In general for most of the sites, the highest metal concentrations were found to occur in July (except Cd in June at the SR site and Pb in April at the RSC site) and the lowest concentrations were in March. The peak concentration of the metals varied between the sites. Considering the overall trend, the high metal concentrations, for example, in July may be due to relatively long dry spells after rain events, while low concentrations, for example, in March may likely be linked to frequent rainfall for the study area (see the climate data in Appendix A). A similar suggestion was made by Robertson and Taylor (2007) in their study in Manchester, UK. Furthermore, Hamilton (1984) and Fergusson and Kim (1991) noted that weather patterns had a significant influence on RDS metal compositions stating that metal concentrations fell after heavy rain, while warmer and drier periods promoted pollutant accumulation.

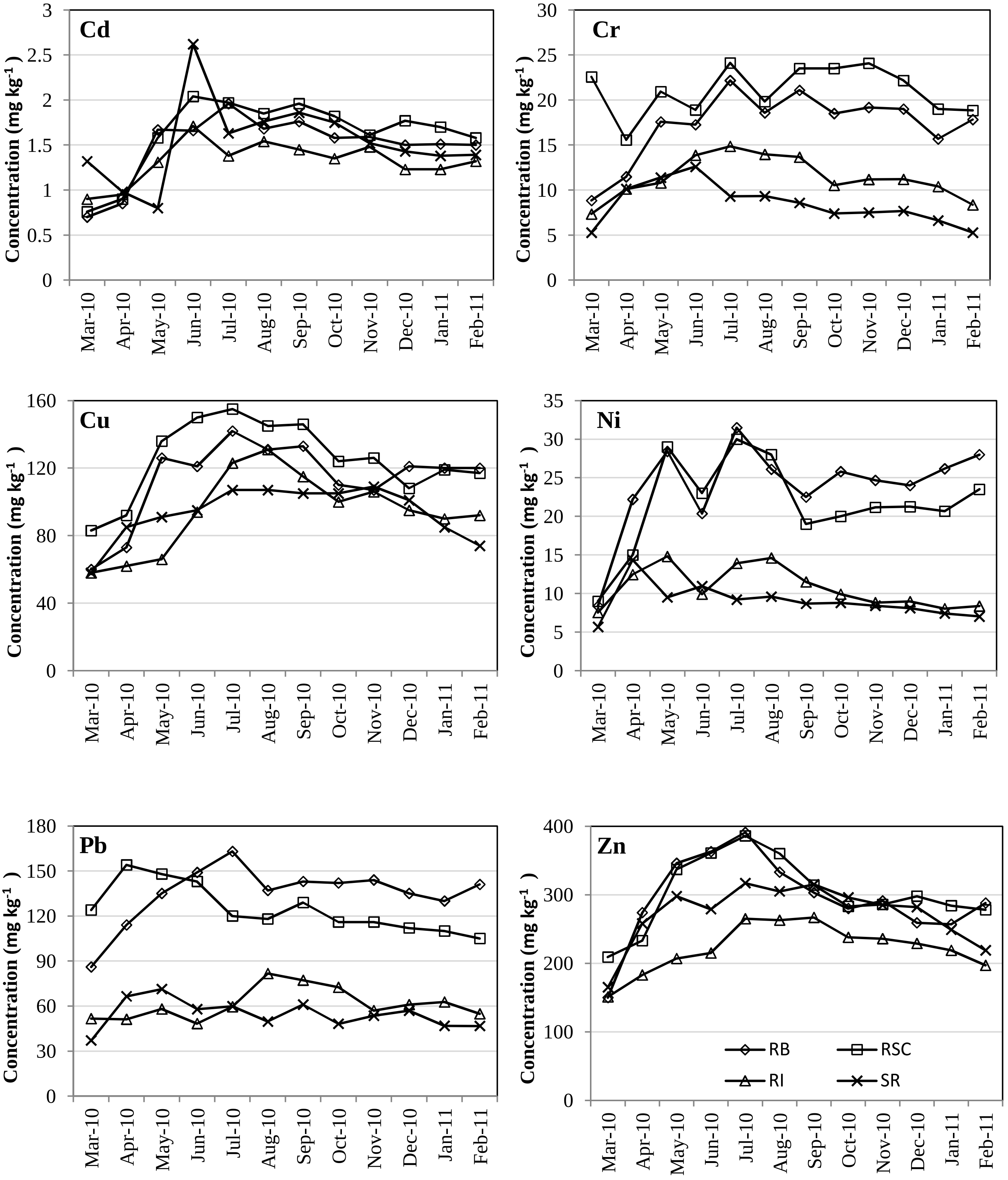


Figure 5.7: Monthly mean metal concentrations for different sampling sites (RB: road bend; RSC: road with speed controls; RI: road intersection and SR: straight road section).

The only significant anomaly in the data is that Ni, in particular at the RB and RSC sites, showed an increasing trend during winter months. This may indicate that Ni is being released from the corrosion products of road infrastructures (crash barriers, lamp post, road signs etc.) and vehicles during the winter, as suggested by Göbel et al. (2007).

5.4.2 Grain Size Specific Monthly Mean Metal Variation

Figure 5.8 illustrates monthly mean metal concentrations (now averaged over primary sites) in different sediment size fractions for both sampling positions (A and B). The temporal variability of monthly mean metal concentrations in all 3 size fractions is consistent with each other. The highest concentrations occur in the summer, while the lowest concentrations are in late winter for most of the metals, with the exception of Ni which shows an increasing trend in the winter months.

As seen in Figure 5.8, the distributions of monthly mean concentrations for any metal are similar for all size fractions. As expected however, metal concentrations increase with decreased sediment particle size fraction for both sampling positions, with the exception of Pb, for which the largest values are found in the 250-63 µm size fraction. The concentration differences between the sediment size fractions varied between the metals with Cu, Ni and Zn showing the largest differences and Cd, Cr and Pb showing the smallest.

Considering the sampling positions, higher concentrations of Cd, Cr and Cu are found in RDS at B than A, while Ni and Pb show the reverse picture. Zn concentration only exhibits a small difference.

The mean monthly metal concentrations in 250-63 µm and < 63 µm size fractions of RDS from the present study fall within the range of values reported in previous studies (Ellis and Revitt, 1982; Bris et al., 1999; Robertson and Taylor, 2007). However the monthly mean metal concentrations in the 500-250 µm (except Pb) size fraction fall well below the reported values from the above mentioned studies, some of which documented high metal concentrations associated with coarse grain-sizes.

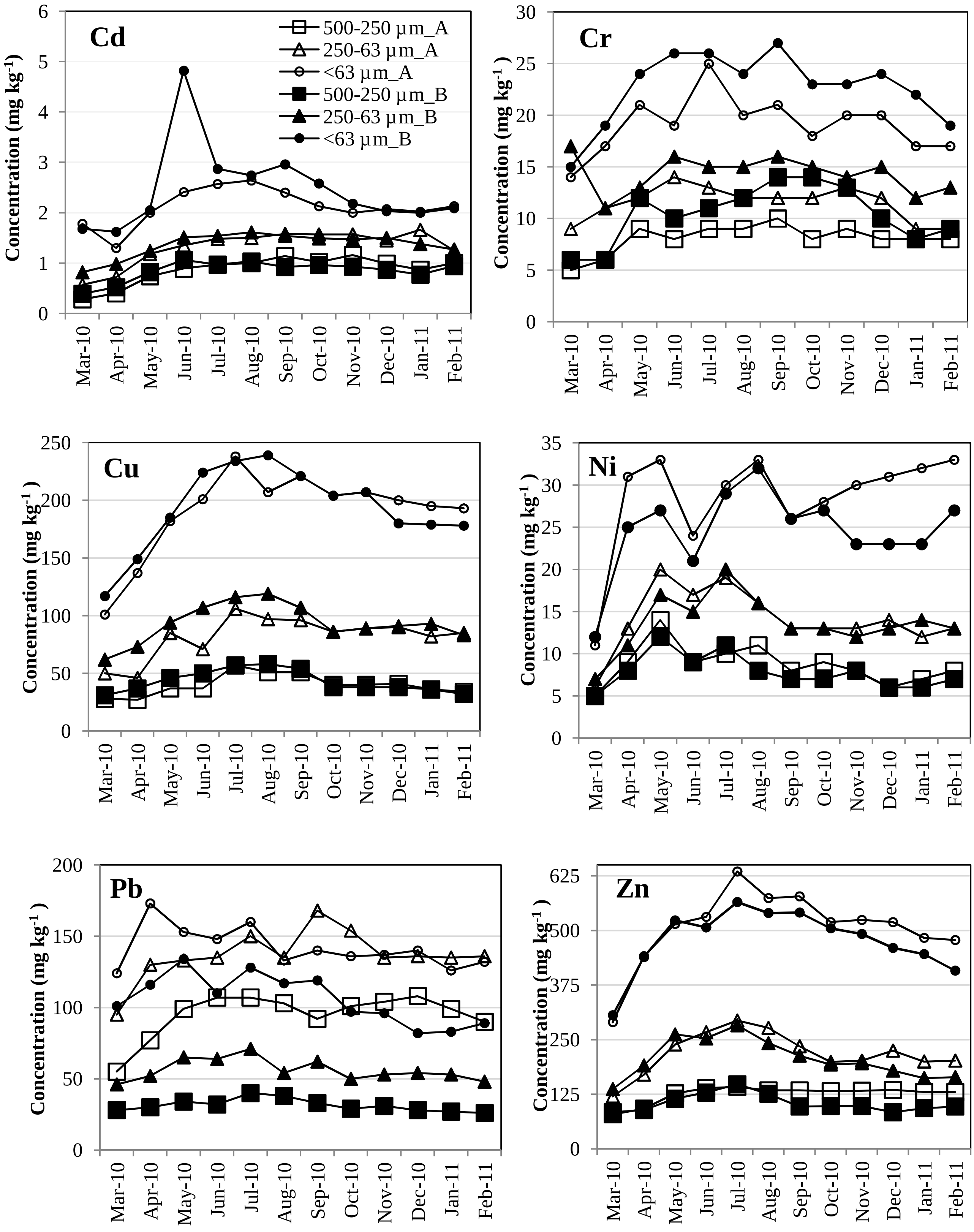


Figure 5.8: Grain size specific monthly mean metal concentrations (average for all four sites) in mg/kg (A: near curb and B: 1 m from the curb sampling positions).

Based on the data presented in Figures 5.7 and 5.8, it is likely that any significant rainfall events during summer and autumn (preceded by prolonged periods of dry weather which allow pollutants to build-up) are likely to generate considerable metal loads from road surfaces that potentially pose a threat to nearby waters in the study area. Moreover, significant differences in monthly mean metal concentrations suggest that the potential control measures at study sites should not only be limited to summer and autumn runoff events.

5.5 Correlation Analysis of RDS Heavy metals

To assess the influence of traffic–related sources (tyres, brakes, corrosion, exhaust fumes and pavement wear), correlations between the metal concentrations (averaged over all sites) were analysed for both sampling positions using the entire metal data set derived from the RDS collected over a year at all the primary study sites. Firstly, correlation was tested between heavy metal concentrations for RDS (irrespective of sediment size fractions) for both sampling position, as seen in Table 5.2, showing Spearman's rank correlation coefficients, r, (these being used because the experimental data did not follow a Gaussian distribution). The correlation coefficient, r, ranges from 0.324 to 0.675, indicating poor to moderate strength of the relationships between metals. Although the r values are not very high from this study, they are still in the ranges of values reported by previous published work elsewhere (e.g. Deletic and Orr, 2005).

Table 5.2: Spearman rank correlation coefficient among metal concentrations in RDS

	Cd	Cr	Cu	Ni	Pb	Zn
Position A: near curb (120 samples)						
Cd	1.000					
Cr		1.000				
Cu		0.544^{**}	1.000			
Ni				1.000		
Pb				0.585^{**}	1.000	
Zn	0.617^{**}			0.528^{**}	0.534^{**}	1.000
Position B: 1 m from curb (120 samples)						
Cd	1.000					
Cr		1.000				
Cu	0.423^{**}	0.481^{**}	1.000			
Ni		0.455^{**}	0.324^{*}	1.000		
Pb		0.657^{**}			1.000	
Zn	0.429^{**}	0.615^{**}	0.639^{**}	0.675^{**}		1.000

*Significant to 0.05%; **Significant to 0.01%; blanks indicate no significant correlation.

As seen in Table 5.2, concentrations of certain metals did correlate well with each other, and there were more statistically significant correlations between metals in RDS at sampling position B (9) than sampling position A (4). The most plausible explanation is that metals accumulating on the road surface farther from the curb may all be of the same origin (road-traffic), while the sources of the metals along the curb are more diverse (e.g. traffic – passed through very close to the curb side, redistribution of road sediment – from middle to edge of the road, nearby sources - foot path, surrounding land etc.).

Furthermore, correlation analyses were carried out for both sampling positions but now separating samples into different particle size fractions, as presented in Tables 5.3 and 5.4. It was found that the strength of the correlations was improved by separating metal concentration into separate size fractions of RDS. It was also found to increase with decreasing particle size fraction (Tables 5.3 and 5.4). For example, all metals in the < 63 µm fraction size correlate with each other with $r \geq 0.50$ for both sampling positions, while for the largest fraction size (500-250 µm) only Pb and Ni showed good correlation ($r \geq 0.50$) in particular for RDS collected at sampling position A. With the exception of a few weak correlation coefficients, generally correlations were good between metal concentrations in the 250-63 µm size fraction of RDS at both sampling positions.

Moreover, a greater number of statistically significant correlations between metal concentrations were found taking size fractions into account (see Tables 5.3 and 5.4) than were apparent in integrated samples (see Table 5.2). For example, at sampling position A, Pb was only found to correlate with Ni (Table 5.2), however, separating RDS into different sediment sizes, Pb (particularly in the 250-63 and < 63 µm size fractions) was correlated with all other metals (Table 5.3). Similarly, at sampling position B, Ni showed correlation with Zn only (Table 5.2) compared to Ni (in 250-63 and < 63 µm size fractions of RDS), for which significant correlations existed with all other metals (Table 5.4).

Table 5.3: Spearman rank correlation coefficient between metal concentrations in different RDS size fractions from near curb sampling

	Cd (500-250)	Cd (250-63)	Cd (<63)	Cr (500-250)	Cr (250-63)	Cr (<63)	Cu (500-250)	Cu (250-63)	Cu (< 63)	Ni (500-250)	Ni (250-63)	Ni (<63)	Pb (500-250)	Pb (250-63)	Pb (< 63)	Zn (500-250)	Zn (250-63)	Zn (< 63)
Cd in 500-250 µm	1.000																	
Cd in 250-63 µm	0.555**	1.000																
Cd in < 63 µm	0.535**	0.837**	1.000															
Cr in 500-250 µm		0.368	0.422	1.000														
Cr in 250-63 µm		0.277**	0.358**	0.518**	1.000													
Cr in < 63 µm	0.255**	0.451**	**0.564****	0.467**	0.690**	1.000												
Cu in 500-250 µm	0.452**	**0.580****	**0.671****	0.318**	0.375**	**0.572****	1.000											
Cu in 250-63 µm	0.421	**0.573****	**0.596****	0.333	0.461**	**0.631****	0.699**	1.000										
Cu in < 63 µm	0.413**	**0.528****	**0.598****	0.325**	0.497**	**0.561****	0.589**	0.780**	1.000									
Ni in 500-250 µm		0.199*	0.337**	0.478	0.257**	0.423**	0.201*	0.212*	0.212*	1.000								
Ni in 250-63 µm	0.263**	0.448**	**0.519****	**0.537****	0.446**	**0.607****	0.422**	0.342**	0.355**	0.672**	1.000							
Ni in < 63 µm		0.279**	0.390**	**0.563****	**0.507****	**0.606****	0.280**	0.285**	0.283**	0.728**	0.831**	1.000						
Pb in 500-250 µm			0.226*	0.358**	0.340*	**0.502****	0.229*		0.209*	**0.544****	**0.576****	**0.691****	1.000					
Pb in 250-63 µm		0.255**	0.397**	0.409**	0.603**	**0.743****	**0.506****	**0.536****	**0.532****	0.437**	0.495**	**0.592****	0.620**	1.000				
Pb in < 63 µm		0.306**	0.478**	0.477**	0.474**	**0.667****	0.368**	0.381**	0.464**	**0.595****	**0.577****	**0.686****	0.689**	0.795**	1.000			
Zn in 500-250 µm	0.349**	0.426**	**0.503****	0.245*	0.213*	0.366**	0.479**	0.414**	**0.594****	0.356**	0.444**	0.296**	0.203*	0.306**	0.418**	1.000		
Zn in 250-63 µm	0.406**	0.446**	**0.520****	0.320**	0.405**	0.474**	**0.542****	0.420**	**0.608****	0.244**	**0.586****	0.347**	0.254**	0.392**	0.420**	0.686**	1.000	
Zn in < 63 µm	0.318**	**0.523****	**0.590****	**0.549****	**0.550****	**0.688****	**0.513****	**0.537****	**0.595****	0.432**	**0.650****	0.481**	0.375**	**0.599****	**0.598****	0.571**	0.744**	1.000

**. Significant to 0.01%; *. Significant to 0.05%
Correlation coefficients ≥ 0.500 between metals are in bold.

Table 5.4: Spearman rank correlation coefficient between metal concentrations for different RDS size fractions from 1 m from the curb sampling.

	Cd (500-250)	Cd (250-63)	Cd (<63)	Cr (500-250)	Cr (250-63)	Cr (<63)	Cu (500-250)	Cu (250-63)	Cu (< 63)	Ni (500-250)	Ni (250-63)	Ni (<63)	Pb (500-250)	Pb (250-63)	Pb (< 63)	Zn (500-250)	Zn (250-63)	Zn (< 63)
Cd in 500-250 µm	1.000																	
Cd in 250-63 µm	0.572**	1.000																
Cd in < 63 µm	0.483**	0.738**	1.000															
Cr in 500-250 µm		0.313**	0.425**	1.000														
Cr in 250-63 µm	0.296**	0.442**	0.483**	0.425**	1.000													
Cr in < 63 µm		0.435**	**0.518****	0.597**	0.754**	1.000												
Cu in 500-250 µm	**0.553****	**0.576****	**0.694****	0.343**	**0.512****	**0.559****	1.000											
Cu in 250-63 µm	0.347**	**0.544****	**0.649****	**0.550****	**0.519****	**0.735****	0.704**	1.000										
Cu in < 63 µm	0.354**	0.437**	**0.529****	0.423**	**0.528****	**0.697****	0.562**	0.771**	1.000									
Ni in 500-250 µm		0.241	0.401**	**0.612****	0.445**	**0.643****	0.411*	**0.592****	**0.620****	1.000								
Ni in 250-63 µm	0.183*	0.452**	**0.531****	**0.568****	0.482**	**0.651****	**0.557****	**0.668****	**0.637****	0.785**	1.000							
Ni in < 63 µm		0.379**	**0.533****	**0.592****	**0.598****	**0.672****	**0.545****	**0.566****	**0.624****	0.724**	0.805**	1.000						
Pb in 500-250 µm	0.197	0.245	0.359**	0.365*	0.420**	**0.549****	0.341**	0.436**	**0.542****	0.482**	0.494**	**0.600****	1.000					
Pb in 250-63 µm		0.186*	0.311**	0.312**	0.473**	**0.520****	0.228*	0.387**	**0.574****	**0.519****	**0.546****	**0.599****	0.516**	1.000				
Pb in < 63 µm		0.202*	0.349**	0.398**	0.379**	**0.552****	0.235**	0.444**	**0.655****	**0.581****	**0.524****	**0.596****	0.552**	0.796**	1.000			
Zn in 500-250 µm	0.264**	0.391**	0.486**	0.367**	0.355**	0.427**	0.492**	**0.502****	**0.514****	0.469**	**0.505****	**0.516****	0.352**	0.411**	0.346**	1.000		
Zn in 250-63 µm	0.340**	0.366**	0.463**	0.225*	**0.506****	0.489**	**0.591****	0.490**	**0.548****	0.415**	**0.550****	**0.605****	0.396**	0.463**	0.360**	0.697**	1.000	
Zn in < 63 µm	0.357**	0.488**	**0.598****	0.493**	**0.654****	**0.704****	**0.662****	**0.665****	**0.668****	**0.612****	**0.735****	**0.774****	**0.518****	**0.507****	**0.523****	0.538**	0.661**	1.000

**. Significant to 0.01%; *. Significant to 0.05%;
Correlation coefficients ≥ 0.500 between metals are in bold.

5.6 Heavy Metal Pollution Assessment

With increasing urbanisation, the impact of heavy metal pollution on the nearby water environment becomes a more serious issue, and so has received much attention in environmental research studies. To control or regulate the pollution, countries usually specify up limits on levels of heavy metals in the environment that should not be exceeded. Monitoring trace metals has seen an upsurge of interest as a way to study environmental consequences derived from road traffic (Kadi, 2009). As a result, a variety of pollution indices for sediment associated heavy metals have been proposed to quantify the level of pollution and associated impacts on aquatic life (Yu et al., 2003; Huang et al., 2009). This section discusses the potential heavy metal pollution derived from the road traffic environment at the primary study sites using the entire data set for all the primary sites over a year.

5.6.1 Environmental Significance

For metals having an accumulation index > 1, the highest mean (and maximum) concentration obtained from all size fractions and both sampling positions (taken from Table 5.1) were compared with several trigger concentrations (used to monitor hazard assessment relating to soil quality), see Table 5.5. Note that the three sets of trigger values shown in Table 5.5 are rather inconsistent, but the soil guideline value (SGV) is used here because it is relevant to UK locations whereas the other trigger values apply to Canada. These indices, however, have previously been used to evaluate road sediment quality for environmental pollution assessment (e.g. Heal et al., 2006). The metals were arranged under two groups consistent with the format described in ICRCL (1983) based on their hazard potential. Briefly, the highest mean concentrations (averaged over the primary sites) were associated with the size fraction <63 µm at sampling position B for Cd and Cu, but at position A for Cr, Pb and Zn. These highest mean concentrations for Zn, Cu and Cd were found to exceed their respective values in the SGV, but those for Cr and Pb did not. Similar comments are also true for the maximum concentrations except for Pb (where the maximum concentration was found for the 250-63 µm size fraction). None of the mean or maximum concentrations of metals for the largest size fraction 500-250 µm were found to exceed any of the guideline values.

Table 5.5: Comparison of observed metal concentrations with published guide line values (A: near curb & B: 1m from the curb)

Group 1: Contaminants which may pose hazard to health

Contaminant		Metal concentration		Trigger concentrations (mg kg^{-1})		
		Size fraction 250-63µm	Size fraction < 63µm	SGV[a]	SQG[b]	SQGEH[c]
Cd (B)	Mean	1.30	**3**	3*	-	-
	Max.	3.10	17	15**	-	-
Cr (A)	Mean	14	23	600*	250*	64*
	Max.	73	47	1000**	750**	64**
Pb (A)	Mean	132	**147**	500*	500*	140*
	Max.	669	345	2000**	375**	70**

Group 2: Phytotoxic contaminants not normally hazardous to health

Contaminant		Metal concentration		Trigger concentrations (mg kg^{-1})		
		Size fraction 250-63µm	Size fraction < 63µm	SGV[a]	SQG[b]	SQGEH[c]
Cu (B)	Mean	**94**	**193**	130	100-150	63
	Max.	185	330			
Zn (A)	Mean	225	**501**	300	500-600	200-600
	Max.	400	907			

Mean concentrations exceeding trigger values are shown in bold

[a] Soil Guideline values (SGV) (Inter-Departmental Committee on the Redevelopment of Contaminated Land, ICRCL, 1983); [b] Sediment Quality Guidelines (SQG) & [c] Sediment Quality Guidelines for Environmental Health (SQGEH) (CCME, 2007)

* Open space, park, Playing ground & ** any places where plants grow

Referring to Tables 5.1 and 5.5, it is interesting to see that the mean concentrations for metals in road deposited sediment (RDS) at sampling position A are generally lower than the trigger concentrations; however they are higher than the trigger values for RDS at sampling position B. Therefore, an assessment of hazard associated with metals in dry sediment might be misleading if only sampling near the curb side is taken. Furthermore, concentrations may be even higher further than position B towards the centre of the road, due to the effect of transverse gradient as reported by Johnston and Harrison (1984) and Deletic and Orr (2005), which was not studied here, so the figures presented here may be conservative also. However, considering the values outlined in Table 5.5, it is clear that RDS contaminated by heavy metals may have environmental consequences for all users of the campus roads as well as for nearby farm land (Kalavrouziotis et al., 2007; Vissikirsky et al., 2008) and watercourses (Hjortenkrans et al., 2006; Zhu et al., 2008).

5.6.2 RDS Heavy metal Contamination

In order to achieve a general overview of heavy metal contamination levels across the primary study sites on the road network used for this study, the degree of contamination (CD) and potential ecological risk index (PERI) were calculated. As discussed in Chapter 3, both of these indices indicate overall contamination caused by the six heavy metals studied (Cd, Cr, Cu, Ni, Pb and Zn) incorporated in a single index value. To estimate these indices, the metal concentrations of Cd, Cr, Cu, Ni, Pb and Zn in RDS (averaged over sampling positions) from the entire data set for all the primary sites were used.

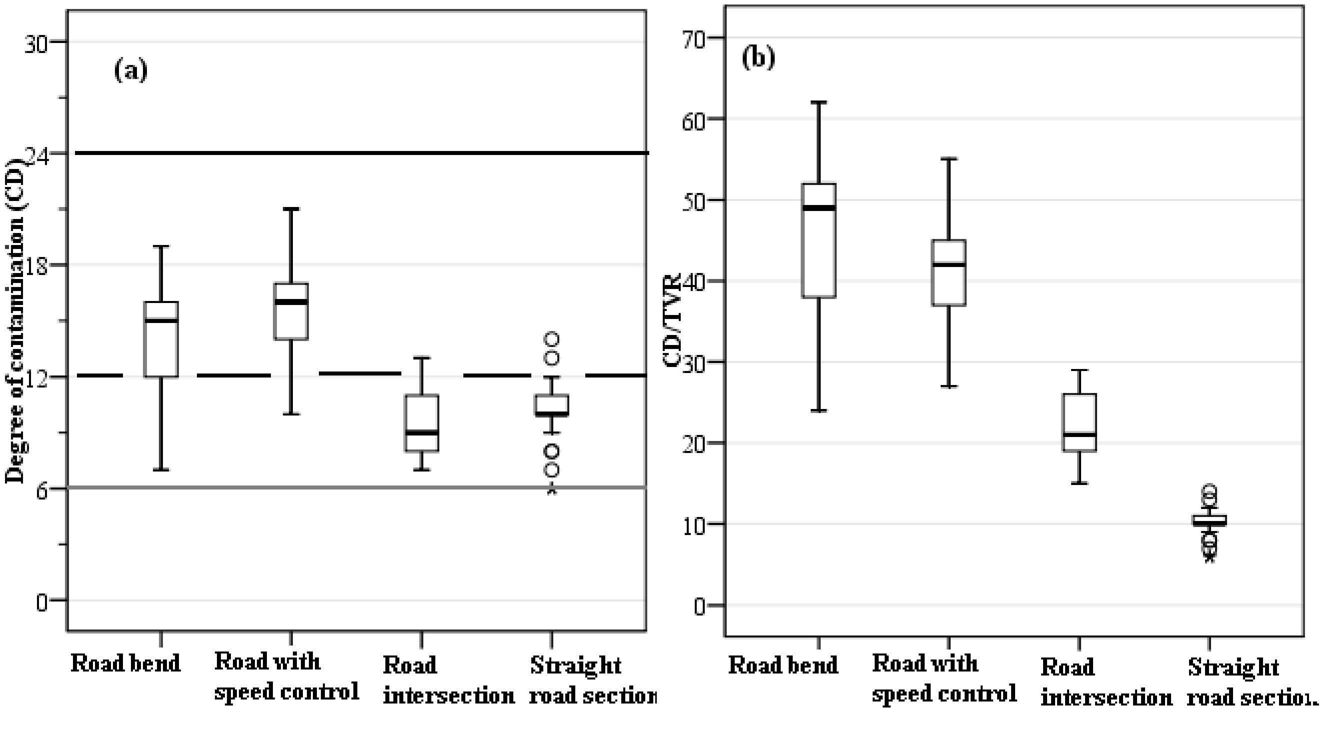


Figure 5.9: (a) Box plots showing the degree of contamination (CD) caused by heavy metals in RDS [Grey, dotted and solid lines represent upper limits of low, moderate and considerable degree of contamination, respectively]; **(b)** Normalised CD index with respect to traffic volume ratio (TVR) [TVR = traffic volume at individual site/maximum traffic volume across the primary sites].

Figures 5.9 (a) and 5.10 (a) show the box plots of CD and PERI, respectively across the primary study sites for the road network in the study area. Figures 5.9 (b) and 5.10 (b) illustrate box plots of the normalised CD and PERI with respect to traffic volume for the above indices. This was done to reveal the influence of site-specific attributes on metal emission patterns and so CD and PERI irrespective of traffic load. The values of CD and PERI for this study are found to be generally consistent with previous studies of RDS elsewhere (e.g. Zhu et al., 2008; Shi et al., 2010; Duong and Lee, 2011). However, the maximum values of CD and PERI here are occasionally exceeded in the aforementioned studies. Moreover, although the mathematical formulation to estimate the indices is similar between studies, there are differences between the number of heavy metals used, the sources of background values for heavy metals and RDS sampling techniques etc.

The site specific similarities and dissimilarities for CD and PERI for the present study are now discussed. As seen in Figure 5.9 (a), the ranges of CD for all the primary sites fall between moderate to considerable degree of contamination ($6 \leq CD \leq 24$). Considering the mean value for each site, $CD \geq 12$, suggesting considerable degree of contamination, was found for the RSC (CD =16) and RB (CD =15) sites. In contrast, the mean CD values for the RI and SR sites were approximately 8 and 10, respectively, indicating these sites are only moderately contaminated. The variability between the sites is certainly linked to the site-specific heavy metal emission pattern, which was found and discussed in section 5.3 (see Figures 5.1 to 5.6). Briefly, the RB and RSC sites are contaminated mainly with Pb followed by Cr, Zn and Cu. The site specific variability is even clearer from Figure 5.9 (b), showing the CD normalised with respect to traffic volume, CD/TVR, for which the normalised index is significantly higher at the RB, RSC and RI sites compared to the SR site. As mentioned earlier, traffic passing the above sites, except the SR site, experiences frequent ‘stop and start’ activities, which likely enhance metal emissions compared to the SR site with steady flow (Napier et al., 2008; Zhu et al., 2008; Ewen et al., 2009; Duong and Lee, 2011). This again corroborated the fact that site specific attributes are important influences on metal emission patterns in addition to traffic volume.

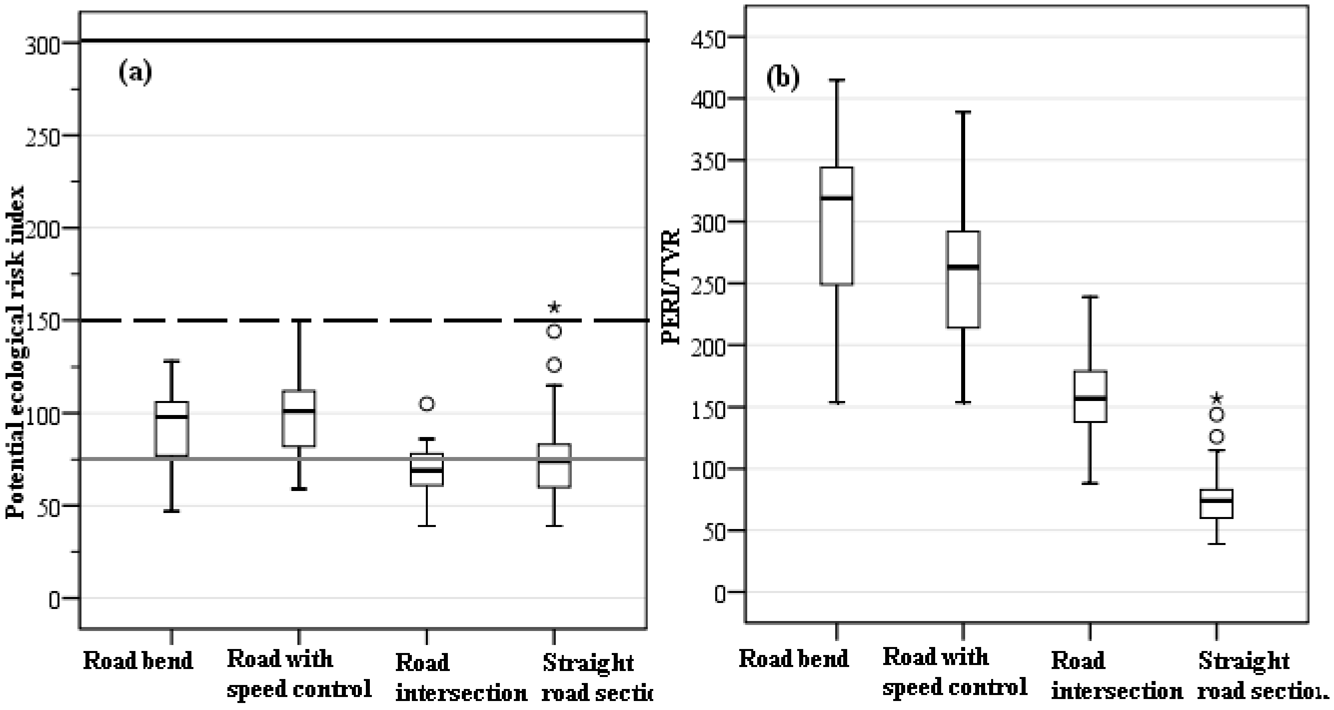


Figure 5.10: Box plots display the potential ecological risk index (PERI) value caused by heavy metals in RDS [Grey, dotted and solid lines represent upper limits of low, moderate and considerable level of ecological risk, respectively]; **(b)** Normalised PERI index with respect to traffic volume ratio (TVR) [TVR = traffic volume at individual site/maximum traffic volume across the primary sites].

Similarly, Figure 5.10 illustrates the potential ecological risk (PERI) caused by heavy metals at different primary sites in the study area. PERI values show a large spatial variability, ranging from approximately 35 to 165 across the sites. The assessment of ecological risk for metals in RDS for all sites (Figure 5.10 a) reveals that the RB and RSC (based on mean values, PERI ≈ 100) sites consist of heavy metal emissions that may have moderate levels of ecological impact (PERI ≥ 75), if transported to nearby water courses. As mentioned earlier, both these sites are primarily contaminated by Pb and Cu (toxic factor, Pb = Cu = 5) along with an influence from Cd (toxic factor = 30) and Zn (toxic factor = 1). Similarly, the mean PERI for the RI site indicates a low level of ecological risk (PERI < 75), while at the SR site it is on the border between low and moderate levels of ecological risk. Furthermore, at this site, a few extreme values of PERI are found (see outliers in Figure 5.10 a) to fall between the moderate and considerable levels of ecological risk, being primarily dominated by the highly toxic Cd (toxic factor =30), as seen in Figure 5.1. The variability between sampling sites is even clearer for PERI normalised with respect to traffic volume, PERI/TVR, as shown in Figure 5.10 (b). The pattern of normalised PERI is consistent with the pattern of normalised CD across the primary study sites, as seen in Figure 5.9 (b).

5.7 Conclusions

This chapter noted that the distribution of heavy metal concentrations in road deposited sediment (RDS) varied with the sediment size fractions and the transverse sampling position. The concentrations for all the metals except Pb decreased with increasing sediment particle size fractions. A transverse distribution of metal concentrations in RDS was observed with higher concentrations of Cd, Cu and Zn in RDS collected at 1 m from the curb, and higher concentrations of Cr, Ni and Pb near the curb. Temporal variability of heavy metal concentrations revealed July as the most polluted month, and March as the least polluted. Correlation analyses revealed a stronger correlation between heavy metals (in particular in the smallest sediment size fraction) at 1 m from the curb than near the curb, indicating different sources for the metals at the two sampling positions. Based on the pollution indices at the primary study sites, the road with speed control site (RSC) is found to be the most contaminated followed by the road bend (RB), straight road (SR), and road intersection (RI) sites. Site specific attributes were found to be drivers of the difference in heavy metal concentrations and so also of the pollution levels: primarily road lay-out with traffic movement patterns, along with influences from road surface condition and presence of road paint rather than due to traffic volume alone.

Chapter – 6 Analysis of Wet-weather Derived Sediments

6.1 Introduction

In the context of urban road water quality related research, two important aspects, namely pollutant build-up during dry days and wash-off during wet weather, need to be understood in depth. As noted by several researchers, pollutant wash-off is a complex process varying with rainfall duration, rainfall intensity, runoff volume and catchment surface characteristics (e.g. Vaize and Chiew, 2002; Brezonik and Stadelmann, 2002). Based on published research (Irish et al., 1995; Sansalone et al., 1996; Crabtree et al., 2006; Westerlund et al., 2003), it has been identified that road runoff caused by rainfall and snow precipitation on roads are often found to contain significant quantities of heavy metals in both dissolved and particulate bound forms along with other pollutants, e.g. oil and grease, nutrients, suspended, colloidal and volatile fractions of particulates, hydrocarbons. Road surfaces, therefore, serve as a temporary sink for pollutants that are washed off during wet weather events to the surrounding water environment. Chapters 4 and 5 discussed an in-depth investigation of dry road sediment and, in sequence, this chapter investigates wet weather issues using samples collected at the four primary study sites introduced earlier in section 4.4, namely a road bend (RB), a road with speed control (RSC), a road intersection (RI) and a straight road section (SR). Briefly, this chapter presents pollutant wash-off during rainfall events, characterising rainfall induced runoff and snow precipitate samples for dissolved and particulate heavy metals. In addition, particle size distribution (PSD), seasonal variability and contamination associated with runoff and snow samples are discussed. The samples were collected for 12 different rainfall-runoff and 5 different snow events from the four primary study sites mentioned above. It is important to note that fresh snow samples rather than snow-melt induced runoff samples during snow precipitation were collected from the sites.

6.2 Analysis of Wash-off Sediment

This section presents results of runoff sediment load from rainfall events, some mathematical modelling to derive local wash-off parameters and information on particle size distributions of runoff sediment. The 12 rain events sampled had rainfall duration ranging from 1 to 11 hours, rainfall intensity ranging from 1.3 to 14 mm/h and occurred between May 2010 and April 2011, as presented in Table 6.1. Details of sample collection, preservation and testing were discussed in section 3.3.2.

6.2.1 Event Mass Load

Table 6.1: Event mass load of road sediment transported in runoff events generated from different sampling sites in Riccarton Campus road network, Edinburgh

Rainfall runoff event	Intensity (mm/h)	Duration (h)	ADD	Sediment load (g)				Average sediment load (g)	Average sediment load (g/m^2)
				RB	RSC	RI	SR		
26/5/ 2010	11.35	1.7	2	251	841	442	610	536	18
01/7/ 2010	1.31	6.25	20	530	1547	876	1243	1049	35
04/7/2010	14.5	1.83	2	338	1026	487	710	640	21
14/7/2010	6.81	10.87	3	297	687	375	430	447	15
01/8/2010	10.96	1.23	10	765	1850	1050	1246	1228	41
12/8/2010	4.05	1.06	2	205	478	280	408	343	11
21/8/2010	10.18	1.42	1	142	352	187	253	233	8
07/9/2010	3.65	2.88	13	841	2320	1260	1742	1541	51
11/9/2010	7.64	2.23	1	110	269	167	188	183	6
20/11/2010	2.7	8.75	7.5	670	870	702	778	755	25
12/3/2011	6.52	5.75	2.5	330	574	363	420	422	14
23/4/2011	9.85	1.55	6	465	695	428	487	519	17

ADD: Antecedent dry days; RB: Road bend; RSC: road with speed control; RI: road intersection; SR: straight road section

Table 6.1 displays event mass loads of sediment collected at the sites for all the rainfall events monitored along average rainfall intensity and event duration. It should be noted that the mass loads are total loads collected from the entire duration of the rainfall event. As mentioned earlier in section 3.2.2, due to limitations of the field set-up no more than 4 *l* of runoff was collected for each event from each site. Hence the wash-off loads presented here may be biased against finer suspended sediment size fractions for the larger rain fall events. However, due to the relatively coarse nature of the RDS in the study area, it can be speculated that most of the sediment mass was captured even though in cases where the collection bucket overflowed some fine sediment was probably lost. As seen in Table 6.1 there is a consistent trend in the data with the highest load of sediment being found at the RSC followed by SR, RI and RB sites. It is likely that local site specific attributes, such as road texture, road surface condition and slope of the road are responsible for this trend. For example, the road surface condition was poor at the RSC site, which is possibly the reason for significantly higher loads during wash-off events compared to the relatively smooth road surface at the RB and SR sites. However, the relatively high load at the SR site was also likely to have been influenced by the input of surrounding soil (observed during rainfall events) [as the sampling position at this site was at a lower elevation than nearby grass strip, foot paths and car park].

Comparing rainfall variables, there is no single variable found to be correlated with observed wash-off loads, as seen in Table 6.1. This may not be surprising, as sediment transport is a complex hydrodynamic process (beyond the scope for this study), and it is also well understood that rainfall intensity and duration are not enough to explain the relationship between wash-off loads and rainfall variables (e.g. Deletic et al., 1997, 2000; Bouteligier et al., 2002; Shaw et al., 2006). However, it can be seen that generally a high intensity, short duration rainfall event generated more wash-off sediment than a less intense, longer duration rainfall event (Table 6.1). In both cases, of course, the number of antecedent dry days affects the mass of sediment available on the road surfaces, as discussed in Chapter 4. As would be expected for a small study area, wash-off patterns could be very similar at all sampling sites.

The wash-off loads for this study (110 to 2320 g) were of the same order of magnitude as those reported by Kim and Sansalone (2008). It should be noted however that Kim and Sansalone (2008) captured entire runoff events and found wash-off loads in the range 544 to 10592 g. Although this study only collected a limited volume of runoff (4 *l*), the differences in the loads can also be affected by the other factors, such as road drainage pathways, rainfall patterns, road maintenance etc.

Table 6.1 also shows the average wash-off load for the four primary study sites for each rainfall - runoff event, which was used to derive the average wash-off load per unit area (final column). The average wash-off load per unit area was calculated using total sediment load collected into the buckets after each runoff event divided by a drainage area of 10 m × 3 m. These average wash-off loads per unit area data were used in two ways. Firstly, comparing results with the RDS build-up pattern data discussed in Chapter 4 (Figure 4.1), it can be confirmed that only part of the sediment was transported during rainfall events, and in particular, the finer fractions (see PSDs in Figure 6.4). The percentage of wash-off load per unit area was estimated as the ratio of predicted built-up load using the parameterised local build-up models as discussed in Table 4.3, for the different ADD between the runoff events. For example, on 01 July 2010 (low intensity, large duration rainfall preceded by 20 dry days) the wash-off loads were 34%, 21%, 12% and 38% of the available loads per unit area, while on 01 August 2010 (high intensity, short duration rainfall preceded by 10 dry days) they were 37%, 27%, 24% and 60% for the RB, RSC, RI and SR sites, respectively. A similar range of values was also reported by Egodawatta (2007) in their study in Queensland, Australia. The second use of the wash-off load per unit area data is described in the next section.

6.2.2 Mathematical Replication of RDS Wash-off

Pollutant wash-off from road surfaces is more complex than build-up and is influenced by a wide range of hydrologic, flow hydraulic and sediment transport variables (Deletic et al., 2000; Shaw et al., 2006). Amongst different rainfall variables, it is believed that wash-off is primarily linked to rainfall intensity, rainfall duration and runoff volume, as noted by Egodawatta et al. (2007). A few other studies have looked into the relative degree of influence exerted by the above three rainfall variables on wash-off loads (e.g. Chui, 1997; Mackay, 1999). They found that these variables are highly correlated with each other and did not exhibit any marked influence between them. In contrast, Egodawatta et al. (2007) found that rainfall intensity and rainfall duration were more dominant variables than runoff volume for replicating sediment wash-off in their study in Queensland, Australia.

Based on the above discussion, this study’s wash-off data was plotted against rainfall intensity, rainfall duration and dry days between rainfall events, as seen in Figure 6.1 for the study sites. Note that only 5 of the 12 rain events monitored were used to generate these plots, for which it is believed that the entire runoff volume was collected in the bucket at the field experimental set-up at each site (see Table 3.2 and Figure 3.5).

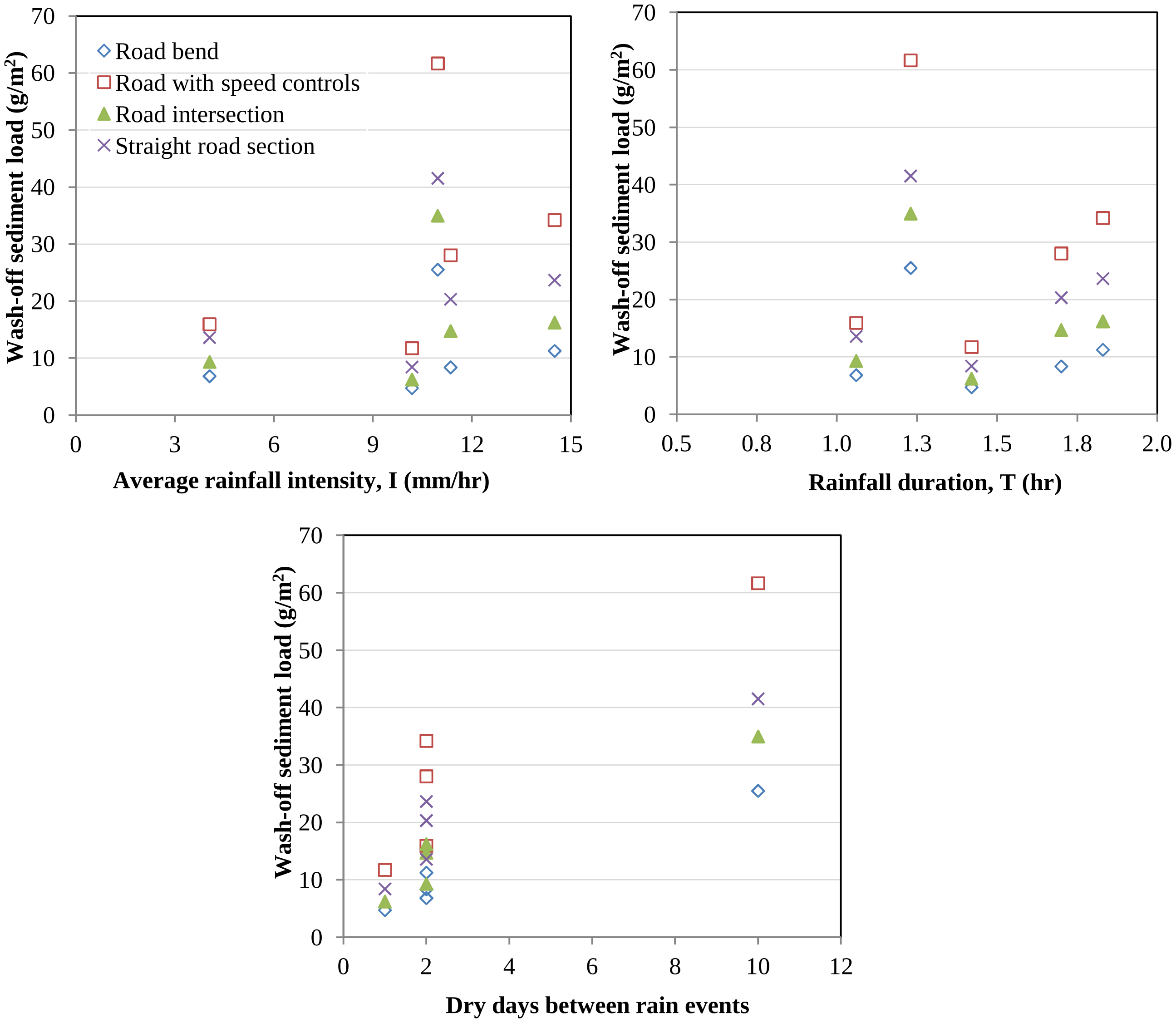


Figure 6.1: Variation of wash-off load across the sites with rainfall intensity, rainfall duration and dry days for rain events.

As seen in Figure 6.1, due to the highly scattered data, it is very difficult to identify any relationships between the sediment wash-off load and the rainfall variables (in particular rainfall intensity and rainfall duration). Although in general, a positive trend can be seen between wash-off loads and the aforementioned rainfall variables. This reflects the complexity of interrelating wash-off behaviour with single rainfall variables. On the contrary, plotting the wash-off data against dry days between the rainfall events shows a better correlation than for the rainfall variables. This finding suggests that there is an influence of the initial sediment availability on road surfaces on wash-off load prior to rainfall events.

An analysis of the combined effect of all three variables on wash-off loads was carried out using multiple linear regressions (MLR) revealed a stronger influence of dry days between the rain events than rainfall intensity and duration. Note that the use of a limited number of data for MLR may not be statistically appropriate and so its outcome may be dubious. However, it is clear that although the number of dry days between rain events was not found to be a direct input variable in any previously published pollutant wash-off formulae, this parameter indeed is of importance for the wash-off load (Gupta and Saul, 1996). Nevertheless, in order to compare the results with published work, it was decided to use rainfall intensity and duration (for the same 5 rainfall events were used in Figure 6.1) as input parameters for modelling sediment wash-off loads. However, antecedent dry days between rainfall events was used to predict the initial sediment load prior to wash-off events in Equation 6.1, as seen below.

A wide variety of models have been proposed to replicate pollutant wash-off, each with varying levels of complexity and accuracy. Although the models are different in their formulation, they have the same target variable of total suspended solids (TSS) because it is believed that TSS can be used as a surrogate for other water quality pollutants, such as nutrients, heavy metals and hydrocarbons adsorbed to suspended solids (Sartor et al., 1974; Akan and Houghtalen, 2003; Herngren et al., 2005). Among several mathematical formulations that are available for wash-off in the literature (e.g. Hossain et al., 2000), an exponential function was selected. The selection was based on two different reasons. Firstly, only a few rainfall-runoff variables, namely rainfall intensity and duration, were available for this study. Secondly to keep the mathematical formulation of pollutant wash-off simple, so as to be consistent with other studies and stormwater quality models, such as, SWMM and MOUSE. Moreover, using the exponential function has the added advantage of comparing the calibration parameters derived for this study with published values in the literature and with default values used in the SWMM and MOUSE models.

The usual form of the exponential representation is as follows:

$$W = C_i \left(1 - e^{-NIT}\right) \qquad \text{(Equation 6.1)}$$

where, W is the wash-off sediment load (mass per unit area), C_i is the initial sediment load (mass per unit area) predicted from Equation 4.2 derived in Chapter 4, N is the wash-off exponent, I is the average rainfall intensity (mm/h) and T is the duration of the storm. In predicting C_i, the antecedent dry days shown in Table 6.1 were used, while k values were from Table 4.2.

As seen in Equation 6.1, the only calibration parameter is the wash-off exponent N, which can be estimated by modifying the equation as shown below. The modified equation transforms into a linear form, the slope of which gives the wash-off exponent N, as seen in Figure 6.2.

$$\frac{Wt}{Ct} = 1 - e^{-NIT}$$

$$\ln(\frac{Ct - Wt}{Ct}) = -NIT$$

$$-\frac{1}{\mathrm{T}}\ln(\frac{Ct - Wt}{Ct}) = NI$$

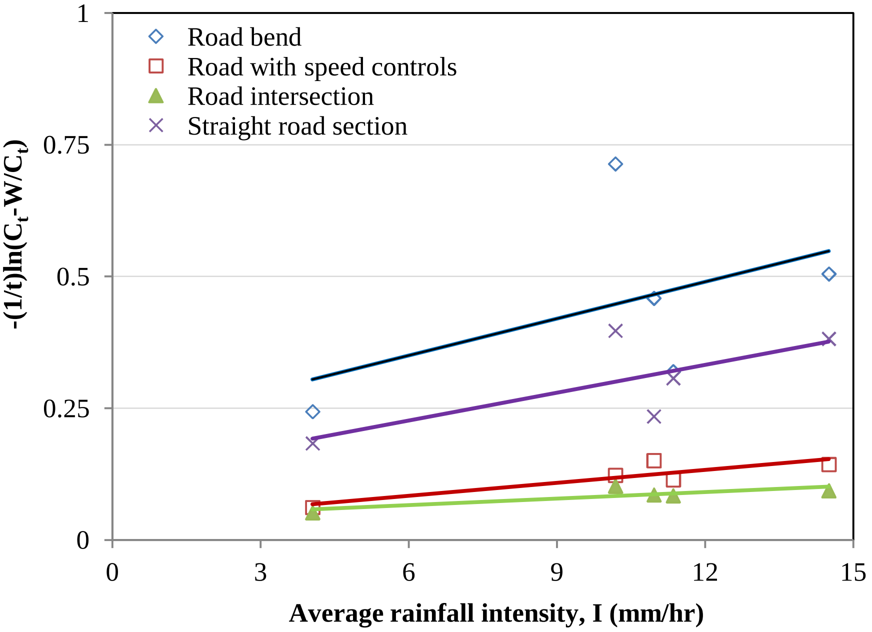


Figure 6.2: Road deposited *sediment wash-off* parameters estimation using **exponential function.**

The wash-off exponent, N derived from Figure 6.2 is tabulated in Table 6.2 for all the four primary study sites. The wash-off exponent reported by Egodawatta et al. (2007) and Hossain et al. (2010) from their studies in Queensland, Australia is also shown in the table for comparison. As seen in Table 6.2, the wash-off exponent estimated for this study ranges from 0.0041 to 0.0233 across the sampling sites. The wash-off exponents at the RB and SR sites are an order of magnitude higher than their values at the RI and RSC sites. The significant differences between sites may be linked with the RDS size distributions across the sites, as discussed in section 4.4.4 (see Table 4.5), for which the RB and SR sites contain the smaller d_{10} and d_{50} values than the RSC and RI sites. Furthermore from the table, it is seen that there is a significant variability for wash-off exponents between the studies. This is particularly true when comparing the present study with the values reported by Egodawatta et al. (2007); however, they are in better agreement with Hossain et al. (2010). Considering the wash-off exponents presented in Table 6.2, it is seen that the default value of 0.2 in the MOUSE and SWMM5 models is much higher when compared to the values found for this study at specific site and to the values reported by others. The difference between wash-off exponents in published studies and the models suggests that the wash-off process is more complex than previously assumed (Millar, 1999; Egodawatta, 2007). Consequently, based on the results presented in Table 6.2, it is clear that the wash-off exponent is site specific and proper calibration is necessary to get better replication of the wash-off loads at particular sites. A similar suggestion was also reported by Alley (1981), Huber and Dickinson (1988), Gupta and Saul (1996), Millar (1999) and Egodawatta et al. (2007).

Table 6.2: Comparison of wash-off exponent, N (mm^{-1}) estimated from field monitoring data with other published values

Site	N	Default value		Hossain et al. (2010)	Egodawatta et al. (2007)
		MOUSE	SWMM5		
Road bend (RB)	0.0233	0.2	0.2	0.011 – 0.028	0.00056-0.00080
Road with speed controls (RSC)	0.0082				
Road intersection (RI)	0.0041				
Straight road (SR)	0.0176				

6.2.3 Validation of Pollutant Wash-off Equation

In order to check the accuracy of the pollutant wash-off equation derived from the 5 rainfall events, as discussed in the previous section, the site specific exponents (Table

6.2) were now used in Equation 6.1 to calculate the simulated wash-off load values for the remaining 7 rainfall events. Simulated values were compared with observed values for all the primary study sites as shown in Figure 6.3.

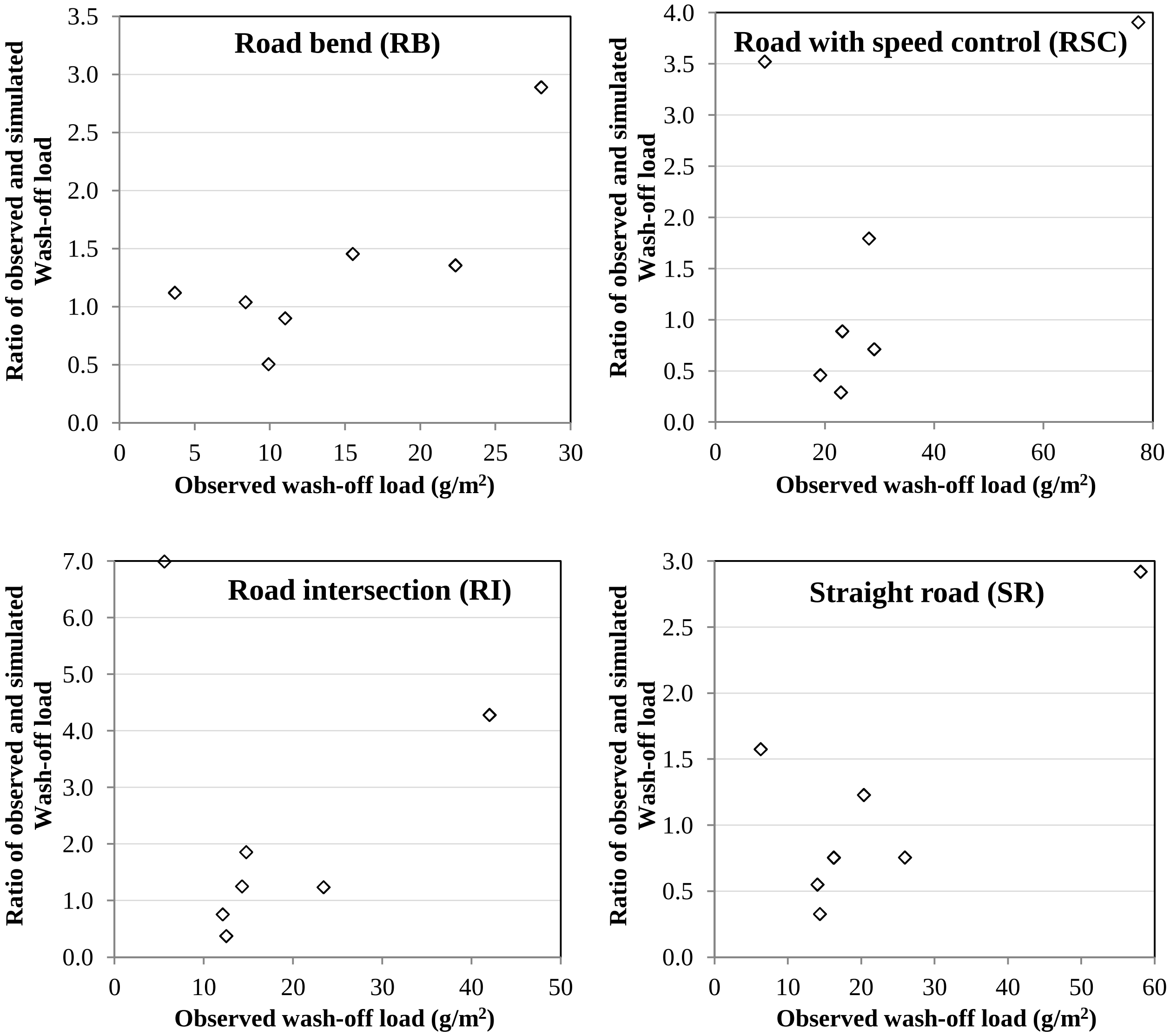


Figure 6.3: Comparison of simulated and observed wash-off load using exponential function at primary study sites.

As seen in the figure, the overall performance of the wash-off equations is not very impressive and for all sites, the ratios of observed to simulated wash-off loads are widely scattered. In general, the model is under predicts the wash-off loads for some of the rainfall events for which ratios of observed to simulated wash-off loads are greater than 1.5. This may likely be from the measurement error, unwanted inclusion of sediment from surrounding land apart from road runoff.

Considering the sites, the results are a little better at the RB and SR sites than at the other two sites. For the former sites, the ratios of observed and simulated wash-off loads for 6 and 5 out of 7 rain events, respectively (Figure 6.3), fluctuate within the ratio of 0.5 to 1.5, which suggests that the performance of the wash-off equations are reasonable although not satisfactory. In contrast, the performance of the equations is rather poor for the RSC and RI sites, for which predictions for only 3 out of 7 rain events showed satisfactory agreement with the observed data.

6.2.4 Particle Size Distribution of Runoff Sediment

Figure 6.4 displays the particle size distributions (PSDs) for runoff sediment (averaged over the sampling sites) for four selected storm events. The selection was based on identifying low intensity, large duration rainfall events and vice versa. It was also found that PSDs for the other 8 rainfall events fell within the range covered by the selected events. The PSDs were found to be consistent with previous research elsewhere (e.g. Egodawatta, 2007; Kim and Sansalone, 2008; Jartun et al., 2008).

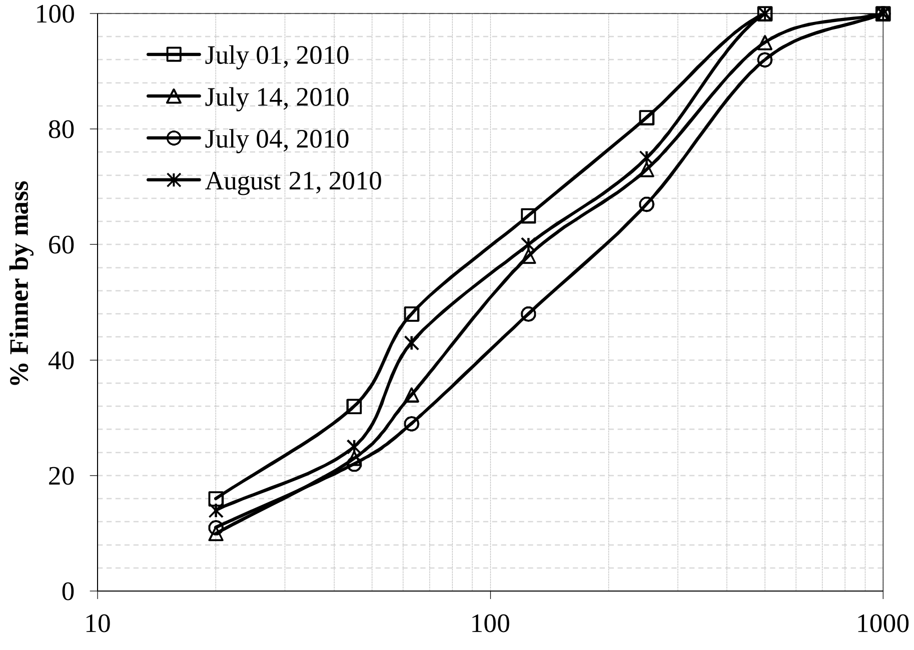


Figure 6.4: Particle size distributions for runoff sediment of selected storm events

As seen in Figure 6.4, a wide particle size range, from very fine to medium coarse sediment was entrained and transported during the monitored runoff events. Variability between event PSDs was also found. For example, the load of sediment finer than 63 µm ranged from 24% to 44% (by mass) between the events shown in Figure 6.4. The data also reveal that a high intensity, short duration rainfall event (July 04 2010) was more able to transport coarse sediment compared to a low intensity, long duration rainfall event (July 01, 2010). It is not clear, however, how intensity and duration combine to enable the transport of coarser sediment. For example, the PSD for the second largest intensity event (21 August 2010) is closer to the PSD for the lowest intensity event than to the PSD for the highest intensity event. The number of antecedent dry days (ADD) between rainfall events probably plays a role (as seen in Figure 6.1 for sediment wash-off load) also, particularly since Chapter 4 highlighted a re-distribution of particles over ADD. Furthermore from analysing all the rain events, it was apparent that none of the sites were likely to derive a significant sediment load in size fraction greater than 500 µm.

Table 6.3: Values of d_{10} and d_{50} for rainfall-runoff PSDs

Rainfall – runoff event	Average rain intensity (mm/h)	Rainfall duration (h)	Dry days between rain events	d_{10} (µm)	d_{50} (µm)
July 01, 2010	1.31	6.25	20	15	68
July 04, 2010	14.5	1.83	2	26	140
July 14, 2010	6.81	10.87	3	23	96
August 21, 2010	10.18	1.42	1	20	80
Mean	*8.20*	*5.10*	*6.25*	*21*	*96*

The characteristics of the PSDs for the selected events are summarised in Table 6.3. The mean d_{50} for all four events was 96 µm (medium to fine sand) with a range of 68 to 140 µm. Similarly the mean d_{10} was 21 µm with a range of 15 to 26 µm. The range of d_{50} and d_{10} for this study compare well with the range reported by Jartun et al. (2008) in their study in Norway. However, the mean d_{50} and d_{10} values found here are lower than in the aforementioned study. Compared to the values reported for RDS (dry sediment) in Chapter 4 (see Table 4.6), the mean d_{50} and d_{10} values for runoff sediment were significantly lower. As mentioned earlier, only some of the road sediment available on the road surfaces (from previous RDS build-up between rainfall events) was transported by the rain events. Since this was dominated by the smaller particles, the smaller values of d_{50} and d_{10} for runoff sediment are expected.

6.3 Total Heavy Metal Concentrations in Runoff

To start with, mean total heavy metal concentrations (averaged over the 12 rainfall events monitored at all four primary sampling sites) measured for the unfiltered runoff samples (as defined in section 3.4.1) are presented in Table 6.4. This was done to compare the results with published heavy metal concentrations elsewhere. Heavy metal concentration data on road runoff studies are well documented in published literature from different parts of the world. Despite some intrinsic variability between studies (e.g. traffic volume, road drainage and maintenance, climate, condition of road surfaces), a few of these were identified with the aim of capturing a global representation, and are collated for compared with the outcomes of the present study, as seen in Table 6.4. Note that all of the data shown are for total metal concentrations (irrespective of different phases).

Table 6.4: Comparison of mean heavy metals concentration (µg/l) and TSS (mg/l) in road runoff with previous published results

Sources	n[1]	Cd	Cr	Cu	Ni	Pb	Zn	TSS
Crabtree et al. (2008)	340	0.60	7	91	10	37	353	244
Gan et al. (2008)	11	1.60	40	140	23	118	1760	416
Crabtree et al. (2006)	11	0.50	6	41	5	23	140	115
Preciado and Li (2006)	5	-	-	62	-	45	364	197
Backstrom et al. ((2003)	10	0.05	-	13	-	7	89	-
Kayhanian et al. (2002)	32	0.20	2.4	13	4	5	73	148
This study[2]	**12**	**1.20 ±0.30**	**56 ±18**	**176 ±44**	**27 ±7**	**136 ±51**	**1364 ±196**	**243 ±164**

[1] Number of monitored storm events; [2] mean ± standard deviation

As seen in Table 6.4, the mean TSS concentration of 243 mg/l from the present study was very similar to the 244 mg/l reported by Crabtree et al. (2008) in their study in the UK, a little higher than the 197 mg/l found by Preciado and Li (2006), significantly greater than the 115 and the 148 mg/l reported by Crabtree et al. (2006) and Kayhanian et al. (2002) and significantly lower than the 416 mg/l found by Gan et al. (2008).

For metals in the current study, Zn showed the highest mean concentration of 1364 µg/l followed by Cu (176 µg/l), Pb (136 µg/l), Cr (56 µgl), Ni (27 µg/l) and Cd (1.20 µg/l). The metal concentrations in this study are found significantly higher than the previously reported values with the exception of Zn and Cd reported by Gan et al. (2008), as seen in Table 6.4. This difference in metal concentrations is not surprising because of the significant variability between the site and climatic conditions under consideration. However, it is also important to note that the total mean concentrations for Cd, Ni and Pb in this study were lower than their lowest detection limits (LODs) (see Table 3.4). Furthermore, Cd concentration was an order of magnitude lower than its LOD, while mean total Ni and Pb concentrations were only marginally lower than their LODs. Analysing raw data for unfiltered runoff samples, it has been identified that the 30 out of 48 data for Cd (4 data for the 4 primary study sites for each runoff events) were below LOD, while for Ni and Pb they were 21 and 12 out of 48 lower than their LODs. Therefore, mean concentrations of these three heavy metals for total runoff samples (unfiltered) must be used with caution.

6.3.1 Descriptive Statistics of Site-specific Heavy Metals

Now summary statistics of heavy metal concentrations for both dissolved and particulate phases are presented for all four primary study sites, see Table 6.5. Standard values for dissolved and particle bound heavy metal concentrations associated with the protection of aquatic species are also shown in the table. Note that at present in the UK only environmental quality standards (EQS) for dissolved metals are available from the Environmental Agency (EA, 2003), and no such standard is adopted for particle bound heavy metals; hence sediment quality guidelines (SQG) suggested by the Canadian Council of Ministers of the Environment (CCME, 2007), and Flemish SQG (de Deckere et al., 2011) are used for this study. Note that there are some differences between the Canadian and Flemish standards (Table 6.5). The recent study by Zgheib et al. (2011) also used these guidelines to evaluate their results on stormwater quality in Paris, France.

In general, the mean dissolved concentrations for Cu and Zn at all sites exceeds recommended values, while other metal concentrations fall significantly below their respective EQS values. In contrast, the mean concentrations of all the particle bound heavy metals for most of the sites were found to be significantly higher than the recommended guideline values for the protection of aquatic life, as seen in Table 6.5. Overall, comparing metal concentrations in the present study to respective standard values, it can be noted that levels of Cd, Cr and Zn are unlikely to pose any acute danger, while Cu and Pb levels may have a fatal effect on sensitive aquatic species for short and long term exposure, as was also found by Clements et al. (2000).

Table 6.5: Summary statistics of heavy metal concentrations in road runoff (a total of 12 rainfall monitored) at the sampling sites along with standard guideline values

Metal	Dissolved concentration (µg/l)				EQS^1 (µg/l)	Particle bound concentration (mg Kg^{-1})				SQG^2 (mg/kg)	SQG^3 (mg/kg)
	RB	RSC	RI	SR		RB	RSC	RI	SR		
Cd	0.098 ± 0.06	0.120 ±0.091	0.124 ±0.092	0.099 ±0.07	5	0.90 ±0.21	1.11 ±0.28	1.00 ±0.23	1.13 ±0.27	0.60	1
Cr	7.500 ±2.541	8.758 ±3.282	8.172 ±2.250	10.33 ±4.91	20	57.67 ±13.93	65.58 ±18.89	59.79 ±20.07	74.33 ±22.71	37.3	62
Cu	17.174 ±5.812	19.834 ±6.356	21.255 ±8.854	22.25 ±7.52	5	110.67 ±21.98	145.79 ±27.76	137.29 ±29.32	142.63 ±31.26	35.7	20
Ni	1.654 ±0.590	2.187 ±0.792	1.984 ±0.672	1.82 ±0.63	30	28.75 ±5.28	34.29 ±8.11	31.79 ±6.24	36.92 ±6.43	-	16
Pb	0.576 ±0.593	1.248 ±1.220	0.718 ±0.801	0.92 ±1.06	25	61.50 ±10.98	95.42 ±27.67	52.87 ±16.07	66.83 ±16.73	35	40
Zn	41.425 ±8.652	55.084 ±8.792	56.504 ±13.92	73.08 ±17.05	40	193.42 ±23.38	206.62 ±27.17	204.17 ±25.66	214.79 ±30.38	123	147

Metal concentration is presented as: mean ±standard deviation
Site ID: RB = Road bend, RSC = Road with speed control measures, RI = Road intersection, SR = Straight road
1 EQS = Environmental Quality Standard (Annual average value) in the UK (EA, 2003)
2 SQG = Sediment Quality Guidelines for the protection of aquatic life (CCME, 2007)
3 SQG = Final Flemish Sediment Quality Guidelines (de Deckere et al., 2011)

The mean concentration of dissolved Cu ranges from 17 to 22 µg/l, which is approximately 3.5 to 4.0 times higher than the recommended EQS values. Similarly Zn concentrations (ranges from 41 - 73 µg/l) are 1.0 to 1.8 times greater than the EQS values. Conversely, dissolved concentrations of Cr are 1/3 to ½ of the EQS value, while concentrations of Cd, Ni and Pb are an order of magnitude lower than their respective EQS values. Concentration ranges for particle bound metals are found as 0.90 to 1.13, 58 to 74, 111 to 143, 61 to 67 and 193 to 214 mg kg^{-1} for Cd, Cr, Cu, Pb and Zn, respectively, across the sampling sites, which are approximately 1.5 to 2.0, 1.6 to 2.0, 3.0 to 4.0, 1.8 to 2.7, and 1.6 to 1.7, respectively, times greater than the Canadian standard values for protecting aquatic species (Table 6.5).

Apart from Pb, other metal concentrations did not exhibit any statistically significant difference between the sampling sites ($p > 0.05$ from the Kruskall - Wallis test). However, as seen in Table 6.5, the SR site contains the largest concentrations for most of the metals in both phases with the exception of dissolved and particulate Pb, dissolved Cd and Ni, and particulate Cu, for which greater concentrations were found at RSC site. The concentrations of metals at the RI site are marginally lower than the concentrations found at the RSC site, with the exception of Pb in both phases for which concentrations are significantly smaller, while dissolved Cd, Cu and Zn show marginally greater concentrations than those at the RSC site. The metal concentrations in both phases at the RB site display the lowest values for all the metals, but they are not significantly different to their values from the other three sites (with the exception of dissolved Zn).

The greater concentrations at the SR site are probably due to the high traffic volume there. In addition, there is a greater availability of finer RDS at this site compared to the other sites (believed to be more chemically active for heavy metals), as seen in Chapter 4 (Table 4.5). However, considering the traffic volumes of 200, 250 and 285 VPH at the RB, RSC and RI sites, respectively, which were approximately one third to one half of the SR site (650 VPH), heavy metal concentrations are not always found to vary in accordance with increasing traffic volume, rather a few metals were present at even higher concentrations at lower traffic volume sites (for example, RSC), as noted earlier. The higher metal concentrations at lower traffic sites suggest that site specific attributes (road lay-out, road condition, traffic movement patterns, and presence of road paints) are important influences on metal emission patterns in the road traffic environment.

6.3.2 Influence of Particle Sizes on Particle-bound Metal Concentrations

The distributions of metals on different particle sizes of road runoff sediment are of particular importance for urban diffuse pollution mitigation. The distributions of heavy metal concentrations (from 12 runoff events) for each of two particle size fractions for all four primary study sites are presented as box plots in Figure 6.5. Note that concentration scales vary between the metals presented. The concentrations vary significantly in magnitude between metals and are found in the order of Zn, Cu, Pb, Cr, Ni and Cd for the present study. This pattern is generally consistent with previous studies elsewhere (e.g. Drapper et al., 2000; Hallberg et al., 2007; Crabtree et al., 2008).

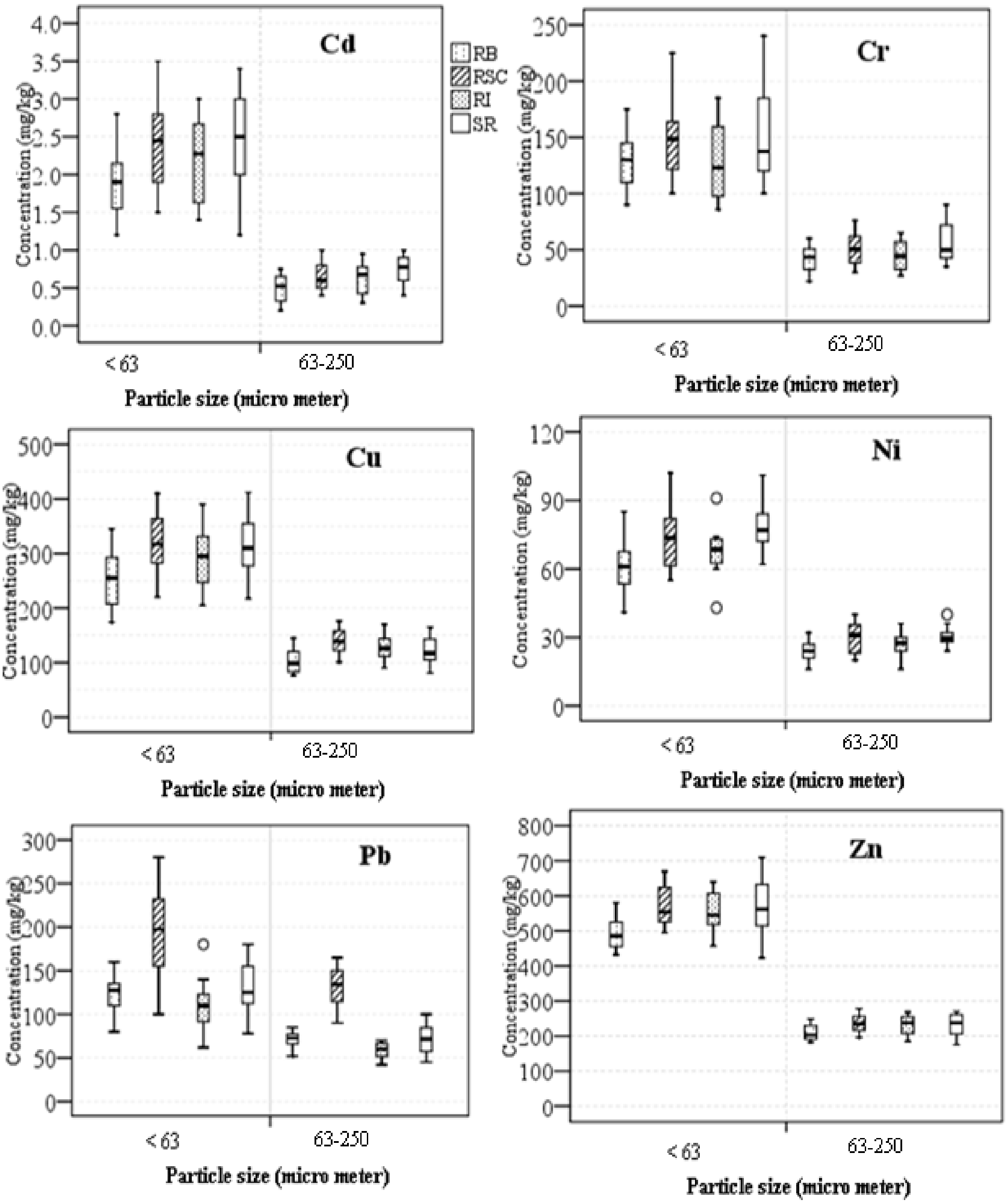


Figure 6.5: Box plot of size specific heavy metal concentrations in road runoff across the sites [RB: Road bend; RSC: Road with speed control measure; RI: Road intersection and SR: Straight road]

As seen in Figure 6.5, usually the highest mean concentration for all metals was associated with the finer size fraction (<63µm) for all four sites. It can be seen that the variation of all the metals between all the sampling sites was similar with the exception of Pb at the RSC site. The Kruskal-Wallis tests showed that there is always a significant difference (p <0.05) between the mean concentrations measured in the two size fractions. In general, the <63 µm size fraction contained 2 to 4 times larger concentrations of Cd, Cr, Cu and Zn than the 250-63 µm size fraction for all four sites, indicating the metals' affinities to the finer fraction.

For the smaller size fraction (<63 µm), the highest mean concentrations of Cr, Cu and Pb were found at the RSC site, while Cd, Ni and Zn were highest at the SR site. The mean metal concentrations of Cd, Cu, Ni and Zn at the RI site were close to the values at the RSC and SR sites, while at the RB they were found to be lower than their respective values at the RSC and SR sites. Mean Cr and Pb concentrations were more variable across the sampling sites.

For the larger size fraction (250-63 µm) the mean concentrations for all metals except Pb showed only a very small variation across the RSC, RI and SR sites. However, all the metal concentrations were marginally lower at the RB site than at the other three sites. In the case of Pb, an unusually high level was found at the RSC site for both size fractions compared to all other sites.

6.4 Seasonal Variability of Runoff Quality

Table 6.6 shows the seasonal variability of metal concentrations in runoff water averaged over all four primary study sites. For comparison, published studies are available in the literature. In particular, seasonal influence has been found to be studied extensively in Sweden (e.g. Backstrom et al., 2003; Westerlund and Viklander, 2006; Hallberg et al., 2007). However, a few other studies are also available from the USA (Glenn and Sansalone, 2002; Lee et al., 2004), UK (Crabtree et al., 2006) and Germany (Helmreich et al., 2010).

To start with, TSS concentrations were found to be highest in summer and lowest in autumn and winter. Note that the standard deviations of TSS concentrations are relatively high which indicates that the TSS data were spread out over large ranges. The high TSS during summer months is probably associated with the number of dry days between rainfall events which allows sediment build-up on road surfaces, as found for dry sediment in Chapter 4. The TSS concentration for this study in winter, smaller than the expected values reported elsewhere (e.g. Westerlund et al., 2003), did not reflect a significant influence of using de-icing salt and road grits, which are typically greater than 500 µm in size. The possible explanation for this could be linked to the low intensity rain (2.7 mm/hr) of the single monitored winter rainfall event, which was unlikely to transport these particles during this runoff event. However, the seasonal TSS profile for this study was found to be consistent with other published studies by Brezonik and Stadelmann (2002) from the USA and Preciado and Li (2006) from Canada.

Table 6.6: Seasonal variability of storm events and heavy metal concentrations (averaged over sampling sites) in road runoff

	Summer (SUMM)	Autumn (AUT)	Winter (WINT)*	Spring (SPR)
n	16	20	4	8
ADD (day)	2-20	0.2-13	7.5	2.5-6
PRE (mm)	8-74	4-17.5	24	15-38
DUR (hr)	1.7-10.87	1.06-2.88	8.75	1.55-5.75
INT (mm/hr)	1.3-11.35	3.65-10.96	2.7	6.52-9.85
TSS (mg/l)	302 ± 240	203 ± 100	209 ± 112	242 ± 107

Metal	*Dissolved concentration (µg/l)*				*Particle bound concentration (mg kg^{-1})*			
	SUMM	AUT	WINT	SPR	SUMM	AUT	WINT	SPR
Cd	1.00	0.09	0.26	0.16	1.0	1.11	1.16	0.94
	±1.00	±0.07	±0.03	±0.05	±0.27	±0.33	±0.19	±0.16
Cr	6.31	8.30	15.00	11.25	70.88	68.50	49.37	43.62
	±2.18	±2.13	±3.83	±2.82	±20.09	±22.13	±7.74	±7.73
Cu	20.81	15.15	29.00	26.75	141.44	130.73	126.25	110.63
	±5.50	±5.77	±2.58	±5.36	±30.03	±36.44	±8.54	±16.13
Ni	1.57	1.70	2.90	2.59	32.18	34.75	32.50	24.62
	±0.56	±0.57	±0.26	±0.25	±7.06	±8.23	±2.89	±4.40
Pb	1.00	0.14	2.32	1.65	79.84	60.25	66.25	55.75
	±0.98	±0.15	±0.55	±0.61	±27.36	±23.03	±14.36	±11.98
Zn	59.75	50.85	67.75	57.87	218.94	197.75	192.50	182.87
	±21.31	±12.57	±17.84	±10.88	±30.05	±24.25	±19.36	±18.07

* Only a single rain event was sampled during winter; n – Total number of runoff samples collected and analysed; ADD- Antecedent dry days; PRE-Precipitation depth; DUR-Duration of rainfall; INT- Average rainfall intensity; TSS - Total suspended solids

TSS and metal concentrations are presented as: mean ±standard deviation of all events occurring in each period

Considering heavy metal concentrations, all metals except Cd showed higher concentrations in the dissolved fraction during the winter followed by the spring, summer and autumn. For example, dissolved Ni, Pb and Cr were 1.85, 2.32 and 2.40 times higher during the winter compared to their respective summer concentrations (Table 6.6). In contrast dissolved Cd was 4 times higher in the summer than in the winter, which shows disparity with other previous studies elsewhere (Westerlund et al., 2003; Hallberg et al., 2007). Both dissolved Cu and Zn showed only a slight increase during the winter.

On the other hand, the particulate Cr, Cu, Pb and Zn exhibited elevated concentrations in the summer. For example, concentrations of approximately 219, 141 and 80 mg kg^{-1} in the summer compared to approximately 192, 126 and 66 mg kg^{-1} in the winter for Zn, Cu and Pb, respectively (Table 6.6). In contrast, the highest concentrations of Cd and Ni occurred in autumn and winter, respectively. Statistically significant differences ($p<$ 0.05 the Kruskal-Wallis test) were found for both metal partitions between seasons for all metals except Zn and Cu.

Comparing the variability of seasonal metal concentrations with published studies elsewhere, the seasonal pattern of metal concentration is basically consistent with that reported by Lee et al. (2004), Crabtree et al. (2006) and Hallberg et al. (2007). However, a marked variation, particularly for the winter metal concentrations, is found in Swedish (Westerlaund et al., 2003) and German studies (Helmreich et al., 2010). This variation is not unexpected and is possibly linked to the nature of the winter weather in Sweden and Germany. It appears that the winter weather often stays as long as 4-6 months in Sweden, which requires extensive use of road grit and road salt for road surfaces, and in addition, studded tyres are used on cars (e.g. Westerlund and Viklander, 2006). Hence, increased corrosion of vehicles and road furniture (due to the longer wet exposure to a hostile environment) along with greater degradation of road surfaces may increase the metal concentrations during the winter in Sweden, compared to shorter spans of snow and ice in regions like the UK. A similar suggestion was reported by Helmreich et al. (2010) in their study in Germany.

6.5 Correlation Analyses

6.5.1 Heavy metal Concentrations and TSS

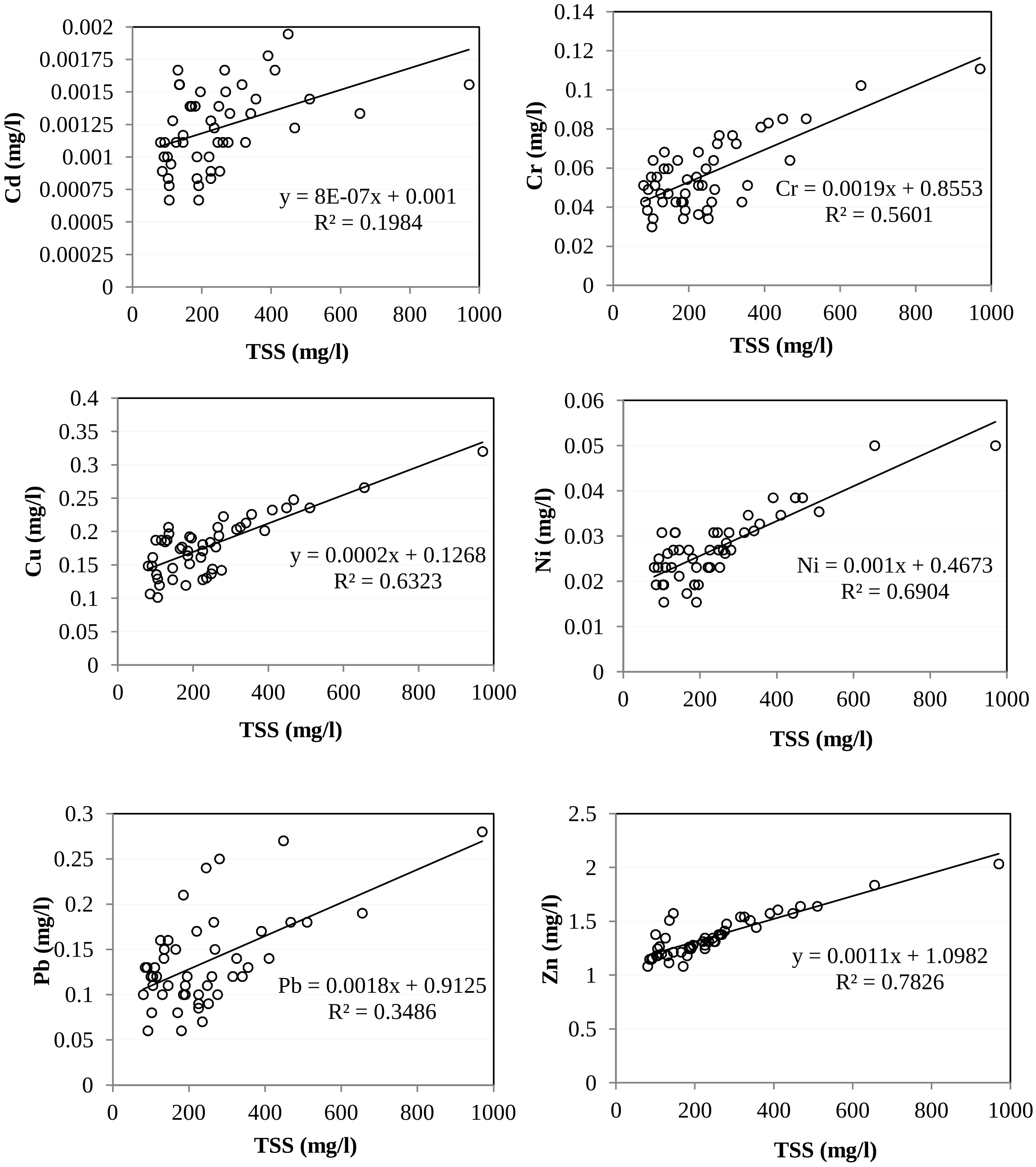


Figure 6.6: Correlation between metal and TSS measured on runoff samples.

It is very common practice in road runoff studies to explore the relationship between metal concentrations and TSS with the aim of quantifying metal load by measuring

TSS. In this regard, a linear correlation between the mean metal concentrations and TSS, measured from the total runoff sample (as discussed in beginning of section 6.3), was explored (combining data from all four sampling sites), as seen in Figure 6.6. The results from a regression analysis for each metal are presented in the figure, showing the intercept and slope. The coefficients range from 0.20 to 0.78, suggesting weak to strong relationships between metal concentrations and TSS. While Zn, Ni, Cu and Cr showed moderate strength ($R^2 > 0.50$), Cd and Pb indicated little or no relationship with TSS.

The strength of relationship found for this study is significantly below what would be expected from the literature. In general, most of the earlier studies on road runoff elsewhere reported a very strong relationship ($R^2 > 0.90$) between metal concentrations and TSS (e.g. Sansalone and Buchberger, 1997; Drapper et al., 2000; Shinya et al., 2000; Hallberg et al., 2007). Although the findings from the present study differ (based on the strength of the correlation) with aforementioned studies, they are not unique, as they are in accordance with a few other previous studies. For example, Han et al. (2006) reported some weak to moderate relationships in their study in the USA. In even greater contrast to much published work, Crabtree et al. (2008) found none of the analysed metals correlated well with TSS considering 340 runoff events at 30 different sites in the UK. Based on the discussion above, it is clear that using TSS as a sole surrogate parameter in the modelling of road runoff pollutants may not always generate a satisfactory result for all stormwater pollutants, unless other issues e.g. the dynamics of metals' affinity to attach to sediment is well understood. However, in the context of this study, all metals except Cd and Pb can be modelled reasonably well with TSS.

6.5.2 Correlations between Metal Concentrations and Storm Variables

To evaluate the influence of rainfall variables on the road runoff metal concentrations, a correlation analysis was carried out. The explanatory variables considered for rainfall were precipitation depth (mm), rainfall duration (h), average rain intensity (mm/h) and days since last rain event. Initially, a correlation analysis was performed between total heavy metal concentrations found in unfiltered runoff samples (without separating into dissolved and particulate phases) and storm variables, however, not many statistically significant correlations were found. Therefore, separate correlations for dissolved and particle phases (for different size fractions) with explanatory variables were performed for heavy metal concentrations data (averaged over all four primary study sites), as presented in Table 6.7. For the present study, the data did not display Gaussian distributions for most of the parameters; hence the non-parametric Spearmen rank-order correlation was used. Only statistically significant correlations at a 95% confidence limit between heavy metal concentrations and explanatory variables are presented in Table 6.7.

As seen in the table, the correlation coefficient ranges from 0.195 to 0.805, indicating weak to strong statistical strength between metal concentrations and rainfall variables. This finding is consistent with other published studies, for which similar variability and ranges were also found for concentrations between pollutants in road runoff and rainfall variables (e.g. Brezonik and Stadelmann, 2002; Kayhnian et al., 2002).

Table 6.7: Spearmen rank-order correlation coefficients between runoff pollutants and storm variables (only statistically significant correlations are shown here)

Dissolved metals (n=48)

	PRE	DUR	INT	ADD
Cd				
Cr				
Cu	0.406	0.707	-0.384	
Ni		0.328	-0.386	
Pb	0.372	0.805	-0.534	0.374
Zn	0.396	0.434		

Particle bound metals for size fractions 250-63 µm (n=48)

	PRE	DUR	INT	ADD
Cd			0.195	0.414
Cr				0.389
Cu			0.345	0.367
Ni				0.387
Pb			0.425	
Zn		0.309	0.359	0.548

Particle bound metals for size fractions <63 µm (n=48)

	PRE	DUR	INT	ADD
Cd			0.223	0.424
Cr				0.407
Cu			0.421	0.594
Ni				0.417
Pb	0.389		0.328	0.347
Zn			0.485	0.697

PRE=precipitation (mm); DUR=duration (h);
INT=average intensity (mm/h); ADD= antecedent dry days since last event

Furthermore from Table 6.7, the dissolved fraction of all metals except Cd and Cr were correlated with rainfall duration. The strongest relationships were for Pb (r = 0.805) and

Cu (r = 0.707). Cu, Pb and Zn were correlated with depth of precipitation. All metals except Zn were negatively correlated with rainfall intensity. Only Pb showed a relationship with the number of antecedent dry days. Dissolved Cd and Cr did not display any significant correlation with any of the explanatory variables. Overall rainfall duration was found to be the primary factor with some influence from precipitation depth and intensity for most of the dissolved metal concentrations. Similar suggestions were found from previous research. For example, Sansalone et al. (1996) found that less intense rain with longer duration was capable of generating runoff containing higher dissolved metal concentrations than shorter, more intense events.

For particle bound metal concentrations, depth of precipitation and rainfall duration have almost no correlation with metal concentrations for both particle size fractions, as seen in Table 6.7. The strength of correlation with rainfall intensity and the number of dry days between rainfall events is found to be higher for the finer size fraction (< 63 μm) than the larger size fraction (250-63 μm), although none of the correlations are strong. All metals except Pb in the 250-63 μm size fraction were correlated with the number of dry days, signifying the idea of a particulate metal build-up on roads, as discussed in Chapter 4. The strongest relationships were for Zn (r = 0.697) and Cu (r = 0.594) for the size fraction below 63 μm. 4 out of 6 metals were correlated with rainfall intensity for both size fractions, which possibly suggests that intense rainfall is capable of dislodging sediments deposited on road surfaces over the dry period, which are then washed-off in the runoff (Irish et al., 1995; Sansalone et al., 1998; Shaw et al., 2006). These results highlight the different processes involved in generating metal pollution in the dissolved and particulate phases of runoff for a rainfall event.

6.5.3 Correlations between Metal Concentrations

Next, correlations between metal concentrations were assessed to explore any inter-relationships that could help to describe several metal distributions from one other metal, thus removing the need to monitor all the pollutants. Table 6.8 shows the correlation coefficients between the metal concentrations. It shows that dissolved Cu shows a relatively good association ($r \geq 0.6$) with all other metals except Cr (r = 0.418). The results suggest that dissolved Cu can be used as a surrogate parameter for other dissolved metals, thus minimising time and cost in monitoring road runoff water quality pollutants.

All particulate bound metals exhibit statistically significant relationships with each other with the exception of Pb and Cd in the 250-63 µm size fraction. The correlation coefficients range from 0.315 to 0.702 for the 250-63 µm size fraction. Relatively strong correlations (r ≈ 0.7) were obtained for Cr with Cd and Ni, and for Cd with Ni (r =0.697), while moderate relationships (r ≈ 0.6) were found for Cu with Zn and Ni (Table 6.8).

Table 6.8: Spearmen rank-order correlation coefficients between runoff mean metal concentrations (only statistically significant correlations are shown here)

Dissolved metals (n=48)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.692	0.652	0.834	0.466	
Cr	0.692		0.418	0.609		
Cu	0.652	0.418		0.639	0.702	0.601
Ni	0.834	0.609	0.639		0.528	0.323
Pb	0.466		0.702	0.528		0.398
Zn			0.601	0.323	0.398	
Particle bound metals for size fractions 250-63 µm (n=48)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.702	0.544	0.697		0.586
Cr	0.702		0.530	0.700	0.315	0.513
Cu	0.544	0.530		0.586	0.540	0.603
Ni	0.697	0.700	0.586		0.341	0.442
Pb		0.315	0.540	0.341		0.372
Zn	0.586	0.513	0.603	0.442	0.372	
Particle bound metals for size fractions <63 µm (n=48)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.557	0.673	0.794	0.358	0.501
Cr	0.557		0.675	0.705	0.527	0.487
Cu	0.673	0.675		0.707	0.557	0.722
Ni	0.794	0.705	0.707		0.386	0.459
Pb	0.358	0.527	0.557	0.386		0.496
Zn	0.501	0.487	0.722	0.459	0.496	

Although similar patterns of correlation were found for the size fraction below 63 µm compared to 250-63 µm size fraction, the strength of correlations for the finer fraction were found to be a little higher. The correlation coefficients range from 0.358 to 0.794 for size fraction below 63 µm. The stronger relationships were for Ni with Cd (r = 0.794) and Cr (r = 0.705) followed by Cu with Zn (r = 0.722) and Ni (r = 0.707). Cu shows good association with Cd, Cr, Ni and Zn, in which cases correlation coefficients were above 0.60. Similar correlations between the particulate phase of many metals can be found elsewhere (Mosley and Peake, 2001; Hallberg et al., 2007; Helmreich et al., 2010). Furthermore to note that, based on the strength of relationship between particulate metals (Table 6.8), it can be suggested that similar to dissolved metals particulate Cu can be used as a surrogate parameter for other particulate metals (particularly for the sediment size < 63 µm).

The association of heavy metals with runoff sediment suggests that the implementation of infiltration trenches or retention basins, capable to retain finer sediment, could be a viable source/site control option for the study area, so mitigating the potential pollution exerted by runoff water on nearby receiving waters.

6.6 Pollution Assessment for Runoff Sediment

To better judge the potential environmental contamination, the degree of contamination (CD) and potential ecological risk (PERI) were calculated for the runoff sediment (irrespective of sediment size fractions), as shown in Figures 6.7 and 6.8.

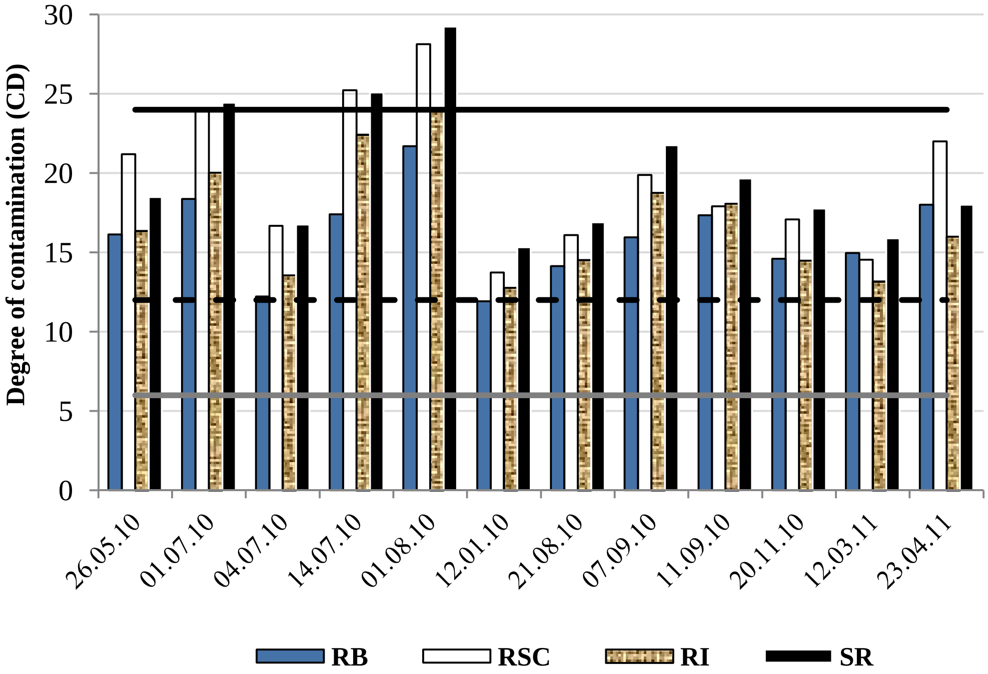


Figure 6.7: Bar chart of degree of contamination (CD) for metals in runoff sediment. (Grey, dotted and solid lines represent upper limits of low, moderate and considerable degree of contamination, respectively) [RB-Road bend, RSC-Road with speed control, RI-Road intersection, SR-Straight road]

From the CD values, it appears that sediment associated with runoff events falls within the considerable to high degree of contamination bands for all monitored events and sampling sites. The RSC and SR sites for 3 out of 12 monitored rain events had CD ≥ 24 (suggesting high degree of contamination) and were the most contaminated sites. However, none of the monitored rain events at the RB and RI sites displayed CD ≥ 24. Furthermore, all 3 rainfall events with CD ≥ 24 occurred between the summer and early autumn. The highest CD of 29 was at the SR site followed by 28, 24 and 22 at the RSC, RI and RB sites, respectively, all for the 1 August 2010 rain event. This 1 August 2010 rain event was a high intensity (10.96 mm/hr), short duration (1.23 h) event following a relatively long dry period (10 days), which may likely have transported more fine sediment and associated pollutants. Similarly, in two other rain events on 14 July 2010 and 1 July 2010, the CD values were 25 and 24 at the SR and RSC sites, respectively. The degrees of contamination for other rain events monitored during late autumn, winter and spring, were lower than 24, suggesting low to moderate degrees of contamination.

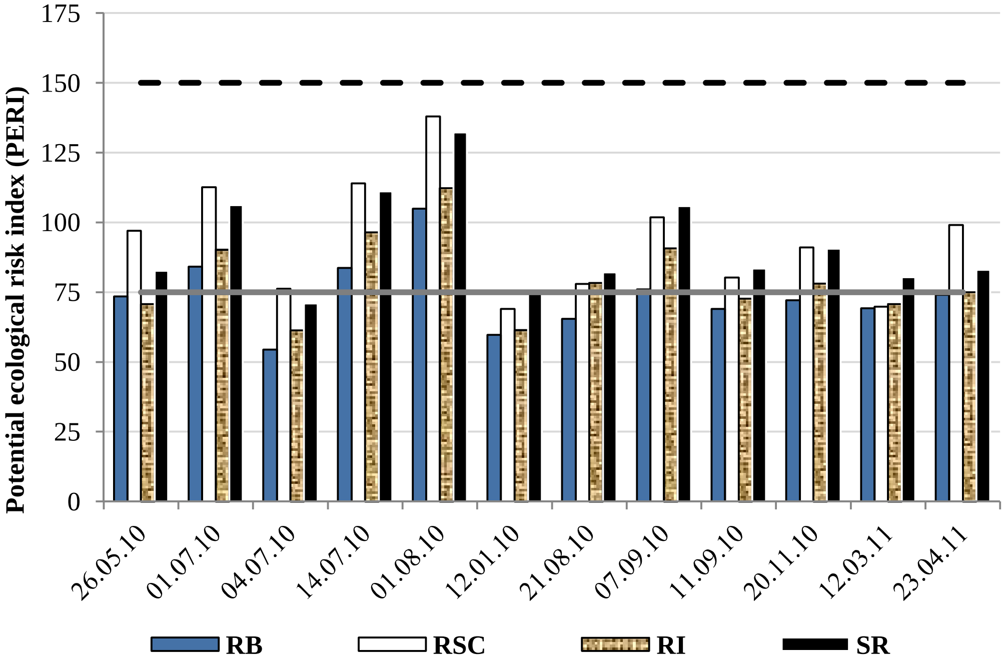


Figure 6.8: Bar chart of potential ecological risk index (PERI) for metals in runoff sediment. (Grey and dotted lines represent upper limits of low and moderate level of ecological risk, respectively) [RB-Road bend, RSC-Road with speed control, RI-Road intersection, SR-Straight road section]

The potential ecological risk index, PERI, gives individual weights for the metals depending upon their toxic effect on healthy aquatic life, as proposed by Hakanson (1980). As seen in Figure 6.8 and as expected, PERI shows peaks for similar rain events as seen for CD. Based on the results, it has been found that in general the runoff water posed low to moderate levels of ecological risk. However, 1 July, 14 July, 1 August and 7 September 2010 rain events, where all the sampling sites showed PERI ≥ 75, suggest an occasional significantly higher moderate level of risk from the runoff sediment that may in turn have a significant effect on sensitive aquatic species (Clements et al., 2000). The SR sampling site was most contaminated with a PERI ≥ 75 for 10 out of 12 monitored rain events, followed by the RSC site with 9 events exceeding PERI ≥ 75, the RI site with 6 events, and the RB site with 4 rain events. However, considering the magnitudes of PERI from all 12 rain events, on average, the highest values are at the RSC, while the lowest are at the RB. The SR site has PERI values very close to the RSC site, while at the RI site they are marginally higher than the RB site.

6.7 Analysis of Snow Samples

Snow is another type of wet weather by which pollutants could be transported to the drainage system. This was studied at a limited scale to get an initial impression of pollutant wash-off during snow events. Note that fresh snow samples were collected rather than runoff induced by snow-melt on roads. Details of sample collection, preservation and testing methods were discussed earlier in Chapter 3. This section presents particle size distributions, dissolved metal and particle bound metal concentrations. Finally, pollution assessment for heavy metals in snow samples is also presented and discussed.

6.7.1 Particle Size Distribution

Figure 6.9 displays snow derived sediment size distributions from 5 monitored events sampled at the four primary study sites. As seen in the figure, the particle size distributions for all the snow events monitored were very similar, with few significant differences between them. The mean d_{50} was found as 38 µm (with a range of 35 - 42 µm), indicating very fine sediment in comparison to that observed in dry sediment (d_{50} =

120 – 255 µm) and in runoff sediment (d_{50} = 68 – 140 µm). The difference between the rainfall and snowfall events may be linked to the kinetic energy required to transport the available sediment, for which the snow-melt runoff (although not sampled here) likely had the lowest.

It is also apparent from Figure 6.9 that approximately 70% of the sediment had sizes below 63 µm. Dust particles in the atmosphere during snow precipitation may likely contribute to high percentage of fine particles along with particulate matter derived from the road traffic environment. Dust particles, derived from atmospheric deposition and from the car exhaust, often called particulate matter, PM_{10} for which $d_{50} \leq 10$ µm, are more prone to be re-suspended due to wind and vehicular turbulence from the road surface. The proportion of this PM_{10} in atmosphere may likely be trapped and deposited on the road surfaces during snow and so be available on the road surfaces. However, in the case of the dry sediment, it is very likely that some of the PM_{10} sediment is lost prior to collection due to the turbulence induced by wind and traffic movement.

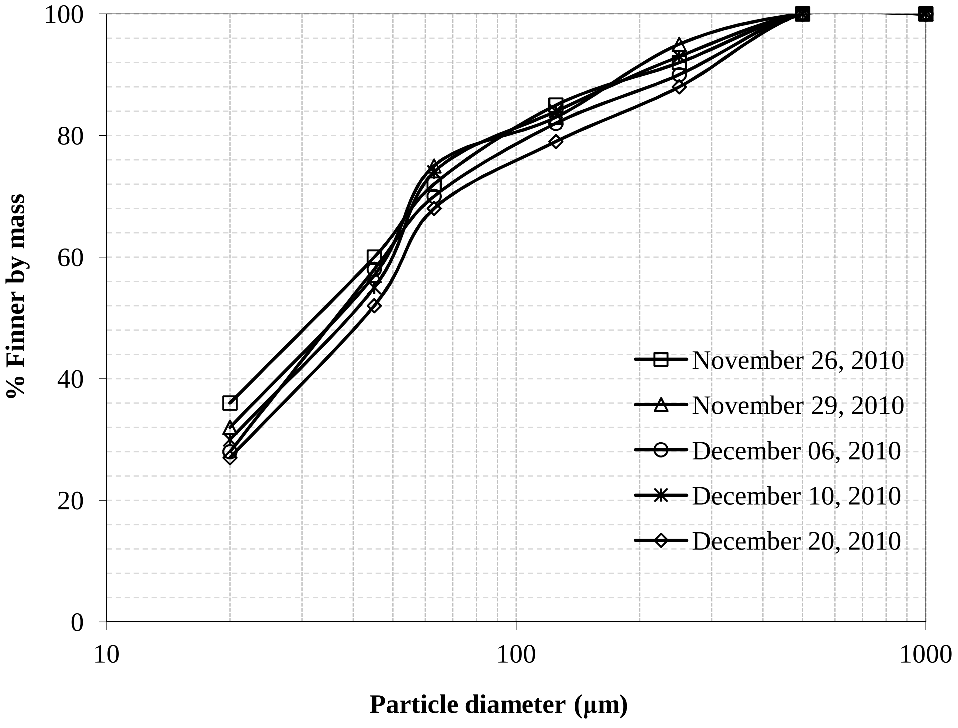


Figure 6.9: Particle size distribution curve for snow derived sediment from road surfaces (average over all sites)

Considering the event mass loads from the snow samples, mass load ranged from 20 g to 400 g for all 5 snow events across the sites (from 2 kg of snow collected from each site), which is significantly below the range of 50 g to 6370 g, reported by Westerlund et al. (2003) in their study in Sweden. As discussed earlier in section 6.4, this difference may be explained the nature and extent of the winter in the two different climate regions. Based on the Swedish study by Westerlund and Viklander (2006), it is apparent that winter weather often lasts for as long as 4-6 months in Sweden, thus requiring extensive use of road grit and road salt for road surfaces, and studded tyres on cars. Therefore, any snowpack will remain for several months in Sweden and is likely to trap more particulates, whereas the snowpack in the UK is normally only present for a few days - week.

6.7.2 Descriptive Statistics of Heavy metal Concentrations in Snow

Summary statistics of both dissolved and particle bound heavy metal concentrations (irrespective of particle size fractions and averaged over all sites) are presented in Table 6.9. Standard values for dissolved and particle bound heavy metal concentrations to maintain water quality for the protection of aquatic species, are also shown in the table. Details regarding the standard values were discussed earlier in section 6.3.1.

Table 6.9: Descriptive statistics of heavy metal concentrations (averaged over the sites and sediment size fractions) in snow samples

Metal	Dissolved metals (µg/l)		EQS[1]	Particulate metals (mg kg^{-1})		Flemish SQG[2]
	Range	Mean ± SD	(µg/l)	Range	Mean ± SD	(mg kg^{-1})
Cd	0.01 – 0.07	0.04 ± 0.02	5	1 – 2	1.3 ± 0.30	1
Cr	7 – 22	13 ± 3.7	20	15 – 28	21 ± 4	62
Cu	4 – 20	11 ± 4	5	59 – 125	87 ± 19	20
Ni	0.4 – 2.2	1.3 ± 0.4	30	13 – 27	21 ± 3	16
Pb	0.06 – 0.75	0.22 ± 0.2	25	61 – 138	88 ± 22	40
Zn	12 – 24	17 ± 4	40	185 – 292	233 ± 34	147

[1] EQS = Environmental Quality Standard (Annual average value) in the UK (EA, 2003)
[2] SQG = Final Flemish Sediment Quality Guidelines (de Deckere et al., 2011)

As seen in Table 5.9, all the dissolved metals except Cu were significantly below their EQS values, while all the particulate metals except Cr were found to exceed the Flemish

SQG for protecting fresh water ecosystems. It is important to note that all the dissolved metal concentrations were lower than their LODs; therefore these results should be used with caution.

The mean concentrations reported here are lower than in Swedish and German studies (e.g. Westerlaund and Viklander, 2006; Hallberg et al., 2007; Helmreich et al., 2010). As stated earlier, differences in climatic conditions (longer and colder winter in Sweden compared to the UK), and hence snow management measures required for roads (road salt and road grit, studded tyres for cars) may likely explain this variability. Moreover, snow subjected to prolonged exposure to road salt (NaCl) is found to behave differently than fresh snow, as found in Novotny et al. (1999), Glenn and Sansalone (2002), Reinsdotter and Viklander (2007). These authors also noted that the presence of road salt during snow-melt significantly influences the heavy metal concentrations, and their partition between dissolved and sediment phases.

6.7.3 Site and Grain size Specific Heavy Metal Concentrations

Grain size specific heavy metal concentrations in snow samples for each site are presented in Table 6.10.

Table 6.10: Site and size specific metal concentrations (mg kg^{-1}) in snow sediment

Metal	Particle size 250-63 μm				Particle size < 63 μm			
	RB	RSC	RI	SR	RB	RSC	RI	SR
Cd	1.3 ± 0.4	1.2 ± 0.3	1.3 ± 0.3	1.5 ± 0.3	1.4 ± 0.5	1.3 ± 0.6	1.5 ± 0.7	1.7 ± 0.9
Cr	19 ± 11	22 ± 13	24 ± 10	19 ± 13	79 ± 23	109 ± 33	59 ± 18	95 ± 41
Cu	72 ± 29	82 ± 22	87 ± 20	106 ± 21	184 ± 54	234 ± 64	178 ± 41	212 ± 59
Ni	21 ± 4	21 ± 5	18 ± 3	23 ± 4	37 ± 13	33 ± 8	20 ± 5	34 ± 10
Pb	64 ± 31	118 ± 61	46 ± 16	57 ± 17	109 ± 33	112 ± 37	87 ± 23	110 ± 40
Zn	167 ± 40	209 ± 47	199 ± 38	219 ± 42	418 ± 101	521 ± 108	415 ± 110	487 ± 105

Sampling sites: RB – Road bend; RSC – Road with speed control; RI – Road intersection; SR – Straight road section

As seen in Table 6.10, snow sediment size fraction < 63 μm contains up to 5 times higher metal concentrations than the 250-63 μm size fraction across the sampling sites (except Pb at the RSC site and for Cd at all sites). The distribution of heavy metals in different sediment size fractions is consistent with the results found for dry and runoff sediment. For each sediment size fraction, there were no statistically significant differences between the site-specific metal concentrations ($p > 0.05$; Kruskal-Wallis test).

Considering sites, for the < 63 µm size fraction, the highest concentrations for most of the metals were found at the RSC site followed by the SR, RB and RI sites. In contrast, for the sediment size fraction 250- 63 µm, the highest concentrations for all the metals, except Pb and Cr, were found at the SR site. The highest Cr and Pb concentrations were found at the RSC and RI sites. It was further noted that although Cr concentrations were similar at all sites, Pb concentrations were approximately 2 to 3 times higher at the RSC site than elsewhere. The weathering of road paints (particularly yellow lines) at this site may likely cause this difference, as commented on earlier.

6.7.4 Correlations between Heavy Metal Concentrations

Correlation analysis between heavy metal concentrations in snow samples were carried out averaging data over all 4 sites and all 5 snow events, as seen in Table 6.11. For dissolved metals, correlation coefficients range from 0.223 to 0.681 suggesting strength of correlation is weak to moderate. In general, it can be seen that dissolved Cu shows a relatively good association ($r \geq 0.5$) with all metals (see Table 6.8). The results suggest that dissolved Cu can be used as a surrogate parameter for other dissolved metals, as also found for runoff samples.

For particulate bound metals, only Ni exhibited statistically significant relationships with other metals in the 250-63 µm size fraction. In contrast, Cr showed the lowest number (2 out of 5) of statistically significant correlations, only for Cr with Cd and Cr with Ni. Cd, Cu and Zn, all display 4 out of 5 possible correlation coefficients with other metals, while for Pb the number of statistically significant relations was 3 in the 250-63 µm size fraction (Table 6.11). The correlation coefficients range from 0.139 to 0.591 indicating poor to moderate association between metals in the 250-63 µm size fraction. Only the correlation coefficient between Cd and Cu was found above 0.50, while relationships for other metals ($0.1 < r < 0.5$) were found as very poor to weak.

Table 6.11: Spearmen rank-order correlation coefficients between heavy metal concentrations in snow (only statistically significant correlations are shown here)

Dissolved metals (n=20)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.263	0.580	0.346	0.418	0.468
Cr	0.263		0.681	0.485	0.507	0.590
Cu	0.580	0.681		0.524	0.578	0.659
Ni	0.346	0.485	0.524		0.461	0.540
Pb	0.418	0.507	0.578	0.461		0.223
Zn	0.468	0.590	0.659	0.540	0.223	
Particle bound metals for size fractions 250-63 µm (n=20)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.318	0.591	0.395		0.327
Cr	0.318			0.149		
Cu	0.591			0.463	0.420	0.478
Ni	0.395	0.149	0.463		0.139	0.427
Pb			0.420	0.139		0.403
Zn	0.327		0.478	0.427	0.403	
Particle bound metals for size fractions <63 µm (n=20)						
	Cd	Cr	Cu	Ni	Pb	Zn
Cd		0.457	0.672	0.441	0.387	0.587
Cr	0.457		0.702	0.356	0.495	0.664
Cu	0.672	0.702		0.634	0.618	0.763
Ni	0.441	0.356	0.634		0.319	0.602
Pb	0.387	0.495	0.618	0.319		0.662
Zn	0.587	0.664	0.763	0.602	0.662	

In contrast, for the size fraction below 63 µm, all the metals showed correlations with others, as seen in Table 6.11. Moreover, the strength of correlations between metals was found to be higher. The correlation coefficients range from 0.319 to 0.763 for size fraction below 63 µm. The stronger relationships were for Cu with Zn (r = 0.763) and Cr (r = 0.702) followed by moderate relationships for Cu with Cd (r = 0.672) and Cr with Zn (r = 0.664). Briefly, Cu was found to show good association with other metals in snow sediment, with correlation coefficients above 0.60. Similar correlations between the many metals in the finer sediment size fractions of snow sediment can be found in Hallberg et al. (2007) and Helmreich et al. (2010).

6.8 Pollution Assessment of Snow Sediment

The degree of contamination (CD) and potential ecological risk index (PERI) were calculated for snow sediment (irrespective of sediment size fraction) to assess the contamination at the primary study sites. Figures 6.10 and 6.11 demonstrate the CD and PERI results (averaged over all 5 snow events), respectively, for snow samples.

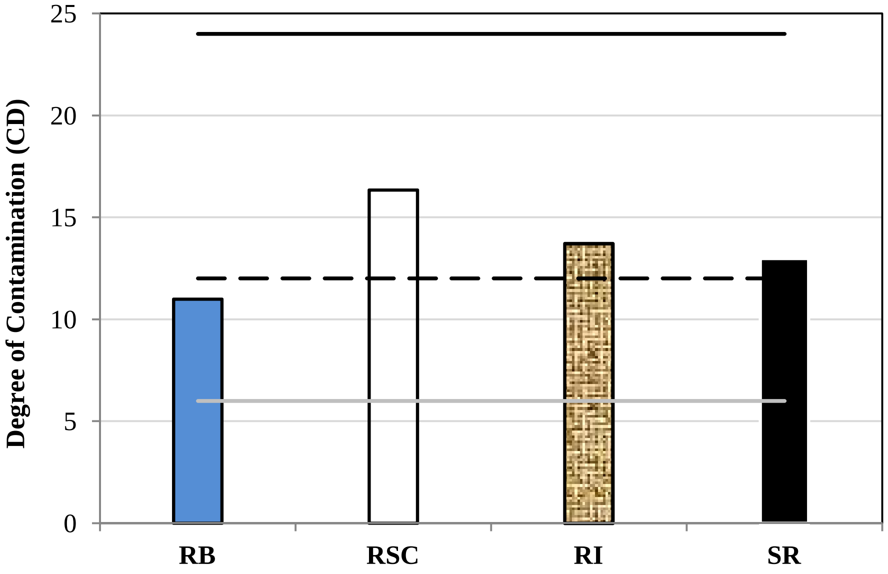


Figure 6.10: Bar chart of degree of contamination (CD) for metals in snow sediment. (Grey, dotted and solid lines represent upper limits of low, moderate and considerable degree of contamination, respectively) [RB-Road bends, RSC-Road with speed control, RI-Road intersection, SR-Straight road]

As seen Figure 6.10, snow sediment at all the sites except the RB site showed considerable level of contamination (CD ≥ 12). The highest degree of contamination was at the RSC site (CD = 16) followed by the RI (CD = 14) and the SR (CD = 13) sites. The higher CD at the RSC site was dominated by considerable contamination with Pb and Zn and moderate contamination of Cr and Cu in the snow sediment. As stated earlier, degradation of road paint (Pb) along with speed control measures (Zn, Cr, Cu) may explain the abundance of these metals in snow sediment at this site compared to the other sites.

The potential ecological risk index, PERI, which uses individual weights for the metals depending upon their toxic effect on healthy aquatic life, as suggested by Hakanson (1980), was estimated with necessary modification for snow sediment. As seen in Figure 6.11 the results are consistent with the CD results, with the largest PERI being at the RSC and the smallest at the RB.

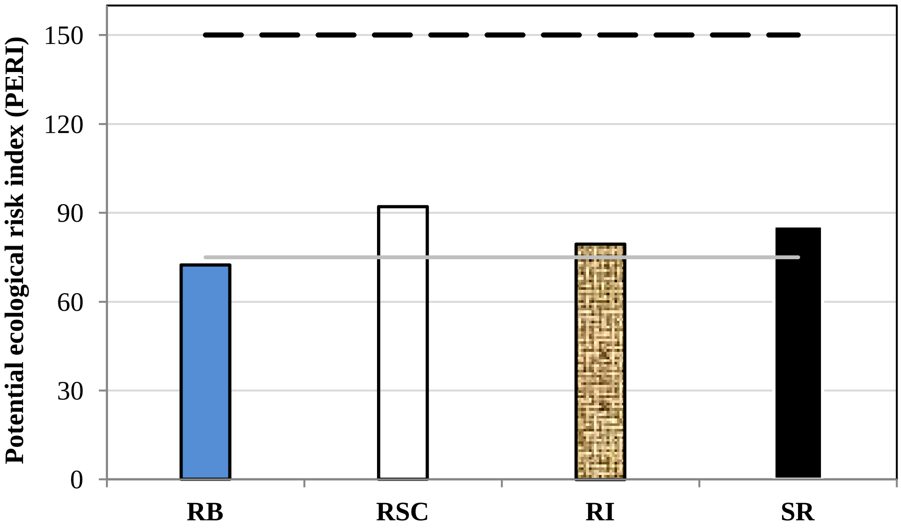


Figure 6.11: Bar chart of potential ecological risk index (PERI) for metals in snow sediment. (Grey and dotted lines represent upper limits of low and moderate level of ecological risk, respectively) [RB-Road bends, RSC-Road with speed control, RI-Road intersection, SR-Straight road]

The PERI ranges from 72 to 92, suggesting low to moderate levels of ecological risk from the snow sediment at the study sites. The PERI values are not markedly varied between the sites. Based on the values of PERI at sites, it is seen that snow sediment in general posed marginally higher than a low level of ecological risk similar to runoff se diment discussed earlier in section 6.6, if being transported during snow-melt runoff or runoff from rain-in snow events (not monitored for the present study) to the nearby watercourse in the study area. However, a more extensive investigation is needed to increase the certainty of this conclusion. Indeed collection of runoff induced by snow-melt (not sampled) rather than snow samples might be useful for pollution assessment.

6.9 Conclusions

It has been revealed that only part of the initially available sediment was transported during rainfall events, in particular, the finer fractions. The pollutant wash-off was found to be a site-specific issue: a local wash-off parameter was derived and compared with a default value commonly used in commercial urban drainage models, suggesting that the default value is (significantly) inappropriate for the studied road network. The metal concentrations in runoff, especially for the particulate phase, were significantly higher at all the sampling sites than guideline values. A significant seasonal difference for the dissolved and particulate concentrations in runoff samples for most of the metals was observed between winter and summer rainfall events. An assessment of the contamination associated with the runoff sediment indicates a low level of ecological risk for most of the runoff events monitored during winter and spring, while a few summer rain events may likely pose a moderate (significantly higher) risk across the sampling sites.

Heavy metal concentrations in snow samples exhibited similar patterns to runoff samples. An assessment of the contamination revealed that snow sediment posed a marginally greater than low level of ecological risk for most of the monitoring sites, if being transported during runoff induced by snow-melt.

Considering wash-off events (runoff and snow), the strongest correlations between particulate metals were found to be associated with the smaller size fractions compared to larger size fractions. Based on the strength of the correlations, it appears that Cu can be used as a surrogate parameter for other metals in both dissolved and particulate phases (in particular for the sediment size fraction ≤ 63 µm) for wash-off events.

Chapter 7 – Comparative Assessment of Dry, Runoff and Snow Sediment

7.1 Introduction

This chapter summarises the key results from Chapters 4, 5 and 6 with the aim of discussing the comparative assessment of dry and wet weather (runoff and snow) sediment monitored at the four primary study sites during March 2010 to February 2011. The quantification of heavy metals in dry, runoff and snow sediment from roads could provide more insight for an improved understanding of how best to tackle diffuse pollution using sustainable urban drainage systems for roads. Heavy metal concentrations and their distribution in different size fractions of the different categories of road sediment (dry, runoff and snow) at the four sites are compared and discussed. Note that the monitored runoff and snow sediment did not contain the largest sediment size fraction (500-250 µm), hence to keep the comparison consistent between the categories of the sediments, only 250-63 µm and < 63 µm size fractions are used here. Following on, an assessment of pollution caused by heavy metals in the different categories of road sediment is presented. A summary of the key findings should be helpful for getting an overview of sediment quality derived from the road-traffic environment.

7.2 Particle Size Distributions

Table 7.1: Summary statistics of d_{50} from the particle size distributions for road sediment

Sediment type	n[1]	Minimum (µm)	Maximum (µm)	Mean ± standard deviation (µm)
Dry road sediment	120	85	250	165 ± 42
Runoff sediment	48	68	140	96 ± 31
Snow sediment	20	35	42	38 ± 3

[1] Number of samples

Table 7.1 describes the range and mean d_{50} from the particle size distribution analyses for dry, runoff and snow road sediments. As seen in the table, the d_{50} lies between 85 –

250 µm, 68 – 140 µm and 35 – 42 µm, respectively for the dry, runoff and snow sediment sampled from the road surfaces (averaged over all events and all the primary study sites), as also discussed in detail elsewhere in Chapters 4 (Table 4.5) and 6 (Table 6.3 and Figure 6.9). Similarly, the order of mean median diameter, d_{50} was found as 165 µm, 96 µm and 38 µm, respectively.

The median diameter of dry road deposited sediment values reported here fall within published ranges in the literature noted as anything between 150 to 4000 µm (Sartor and Boyd, 1972; Pitt, 1979; Butler and Clark, 1995, Ball et al., 1998; Deletic and Orr, 2005). However, mean d_{50} values for runoff and snow sediments were significantly smaller compared to the dry sediment, suggesting that coarser particles, although available on the roads may not be transported to the drainage system by runoff from rainfall or snow-melt runoff at the study sites. This may also be due to the nature of rainfall at the study sites (usually low intensity). Similarly it can be speculated that the kinetic energy generated by runoff from the snow-melt event (although not studied) is usually much lower than that from the low intensity rainfall, and hence very unlikely to transport coarser particles. This finding indicates that only a fraction of initially available sediment on road, built-up between rain events (in particular), was being washed-off, for which smaller sediment size fractions were the key contributors, as evident in Table 7.1.

7.3 Descriptive Statistics of Heavy Metals in Road Sediment

The descriptive statistics of heavy metal concentrations (averaged over all sites and sampling events) in dry, runoff and snow derived sediment on road surfaces are presented in Table 7.2. The background concentrations of the metals from Riccarton Campus are also shown along with the regional background values for Scotland (Appleton, 1995). The local background values for all the metals except Pb are found very similar to the regional background values. The lower background value for Pb is possibly Pb is phased-out of petrol nearly two decades or more in the UK. The mean concentrations for all the heavy metals except Ni show elevated concentrations compared to their local background values (Table 7.2) in dry, runoff and snow derived sediments, suggesting that the road sediments are highly contaminated by heavy metals related to the road-traffic inputs in addition to atmospheric deposition.

The mean concentrations reported here for heavy metals in dry and runoff sediment are consistent with previous studies in the UK (Charlesworth et al., 2003; Deletic and Orr, 2005; Crabtree et al., 2006; Robertson and Taylor, 2007; Crabtree et al., 2008; Pal et al., 2011), and other parts of the world (Ball et al., 1998; Kim et al., 1998; Drapper et al., 2000; Brezonik and Stadelmann, 2002; Sutherland, 2003; Han et al., 2006; Gan et al., 2008). The metal concentrations in snow sediments for this study were lower than previously reported values in Swedish and German studies (Westerlund et al., 2003; Hallberg et al., 2007; Helmreich et al., 2010). The difference may be linked to a relatively longer winter spell with persistent snow coverage in Swedish studies compared to a rather short span of snow and quick melting in the Edinburgh study.

Table 7.2: Descriptive statistics of heavy metal concentrations (mg kg^{-1}) in road sediments (averaged over sites)

Metal	Dry sediment (n =120)		Runoff sediment (n = 48)		Snow sediment (n = 20)		Local background mean [a] (n = 4)	Regional background mean [b]
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD		
Cd	0-4.00	1.00 ±0.80	0.60-1.75	1.00 ± 0.26	0.90-2.00	1.32 ±0.3	1	1.4
Cr	4-76	17 ± 11	35-120	64 ± 20	15-28	21 ± 4	8	n.a.
Cu	20-220	67 ± 41	79-206	134 ± 30	59-125	87 ± 19	44	46
Ni	3-33	12 ± 6	20-50	33 ± 7	13-27	21 ± 3	20	n.a.
Pb	6-621	92 ± 101	30-140	69 ± 24	61-138	88 ±22	28	115
Zn	99-460	212 ± 88	165-280	205 ± 27	185-292	233 ± 34	107	120

n - Number of samples analysed

SD – Standard deviation

[a] Metal concentrations were measured in RDS from road sites which carry no traffic

[b] Appleton, 1995

The distribution of the highest mean concentration of individual metals was found as follows: 1.32 and 233 mg kg^{-1} for Cd and Zn, respectively (in snow sediment); 64, 134 and 33 mg kg^{-1} for Cr, Cu and Ni, respectively (in runoff sediment); 92 mg kg^{-1} for Pb (in dry sediment). On average, Cr and Cu concentrations in the runoff sediment were significantly higher compared to their concentrations in dry and snow derived sediments, while Cd, Ni and Pb exhibited little variation, and Zn showed even less variation among the three categories of sediment. These findings suggest that rainfall runoff derived sediment carry the highest load by mass for most of the metals, followed by the snow and dry sediment.

7.4 Site and Size Specific Heavy metal Concentrations

The distribution of mean heavy metal concentrations in the different particle sizes of road sediments are of particular importance for best management practice regarding road drainage. The influence and importance of the particle size distribution on sediment associated metal concentrations have been extensively studied and are well documented in the published literature (e.g. Robertson and Taylor, 2007; Sansalone et al., 2010). The distributions of heavy metal concentrations for each of the two particle size fractions (250-63 µm and < 63 µm) of road sediment for the four primary study sites are presented in Table 7.3. Only heavy metals found at levels 150% higher than their respective local background values (based on Table 7.2), which is indicative of an anthropogenic input (traffic) in addition to atmospheric deposition, are presented here.

As seen in Table 7.3, on average, the highest concentrations for most of the metals (across the sampling sites for both particle size fractions) were found in the order of runoff sediment > snow sediment > dry sediment. In general, sediment size < 63 µm usually contains approximately 2 to 4 times higher concentrations than the size fraction 250-63 µm for most of the metals across the sampling sites. For example, particle size < 63 µm contains the highest mean concentrations for Zn and Cu with the value of 572 and 320 mg kg^{-1}, respectively, compared to their concentrations of 237 and 140 mg kg^{-1}, respectively, in the size fraction 250-63 µm (for the runoff sediment at the RSC site). Similarly for Cr, the highest mean of 153 mg/kg in the < 63 µm size fraction compared to 56 mg/kg in the 250-63 µm size fraction (in the runoff sediment at the SR site). In contrast, the highest mean concentration of 250 mg kg^{-1} for Pb was in the 250-63 µm size fraction (in the dry sediment at the RSC site) compared to 195 mg/kg in the < 63 µm size fraction (in the runoff sediment at the RSC site). This is consistent with the vast majority of previously published work (e.g. Ball et al., 1998; Kim et al., 1998; Drapper et al., 2000; Sutherland, 2003; Deletic and Orr, 2005; Han et al., 2006; Robertson and Taylor, 2007; Crabtree et al., 2008).

Based on the sampling sites, a greater number of the highest mean concentrations for metals in different sediment categories for both sediment size fractions were found at the RSC site than at the SR site (Table 7.3). The RB and RI sites rarely contain the highest metal concentrations (only Cr and Zn in the < 63 µm of dry sediment, and only

Cr in the 250-63 µm of snow sediment). The concentrations for most of the metals in both runoff and snow derived sediments (for both particle sizes) were found to be similar at the RB and SR sites, while their concentrations in the dry sediment showed significant differences between the sites (in particular, all metals except Cr in the <63 µm size fraction were found approximately doubled at the SR site, while Cr in the 250-63 µm size fraction was tripled at the RB site). At the RI site all the metals (except Pb) for larger size fraction (250-63 µm) were marginally higher than their values at the RB site, while for finer size fractions (< 63 µm) concentrations were found relatively close to their values at the SR site (except Zn).

Table 7.3: Site and grain size specific mean metal concentrations (mg kg^{-1}) in road sediment

Site (Traffic volume)	Category	Particle size fraction 250-63 µm				Particle size fraction < 63 µm			
		Cr	Cu	Pb	Zn	Cr	Cu	Pb	Zn
Road bend, RB (200 VPH)	Dry Sediment	11	35	90	128	58	94	135	522
	Runoff sediment	42	103	71	202	130	254	125	494
	Snow sediment	19	72	64	167	79	184	109	418
Road with speed controls, RSC (250 VPH)	Dry Sediment	23	34	250	134	26	102	157	426
	Runoff sediment	51	140	132	237	149	320	195	572
	Snow sediment	22	82	118	209	109	234	112	521
Road intersection, RI (285 VPH)	Dry Sediment	7	45	34	121	21	114	115	287
	Runoff sediment	45	127	59	242	126	292	111	555
	Snow sediment	24	87	46	199	59	178	87	415
Straight road, SR (650 VPH)	Dry Sediment	12	65	49	217	21	142	137	518
	Runoff sediment	56	120	71	247	135	312	120	571
	Snow sediment	19	106	57	219	95	212	110	487

Furthermore, although the traffic volumes at the RB, RSC and RI sites are about one third to one half that for the SR site (Table 7.3), the higher metal concentrations were not found in accordance with the higher traffic volume. The variations across the sites appear to be primarily due to site- specific attributes, such as road lay-out, road surface condition and presence of road paint rather than due to traffic volume alone. Taking Pb as an example, significantly higher Pb concentrations at the RB and RSC sites in dry road sediment were found compared to other sites. Since, the previous use of Pb in fuel was phased out more than a decade ago, the only other likely source of Pb may be linked to the road paint particles at these sites (such as double yellow lines), as presented in Table 4.2 and discussed in Chapter 4. The similar idea was also reported by Deletic and Orr (2005). In contrast, elevated concentrations of Pb in particular for the size fractions <63 μm at the other sites, suggests that other traffic related inputs, such as wheel bearings, car paints etc are likely sources of Pb in the road-traffic environment (Napier et al., 2008; Ewen et al, 2009). Similarly, the other heavy metals studied here are also found to be linked with road-traffic emissions in the literature. Briefly, Zn and Ni is primarily linked with tyre wear; while Cd, Cr and Cu are linked with brake wear and exhaust emissions (Charlesworth et al., 2003; Ward et al., 2004; Zanders, 2005). To relate these sources to the present study it can be noted that as traffic passed through all the above sites (except the straight road section), it experienced frequent acceleration and deceleration, which increase metal concentrations, as suggested by Ewen et al. (2009) for traffic undergoing 'stop-start' activities. This is true for the RB and RSC sites in particular (almost all traffic was observed to undergo braking during the sampling period) compared to the RI site (controlled braking) and the SR site (steady speed), as discussed in section 4.2.

7.5 Metal Contamination

7.5.1 Road Sediment Quality Assessment

Heavy metal concentrations (combined from all sites and size fractions) in dry, runoff and snow derived sediments (taken from Table 7.2) were compared with several trigger concentrations (used for hazard assessment relating to sediment quality), see Table 7.4. Note that the two sets of trigger values from The Netherlands and Canada shown in Table 7.4 are rather inconsistent, but are used here, in the absence of such for the UK, for gaining an initial impression of sediment quality for the study sites. Another point to be noted is that all these guideline values were derived for fluvial sediment with the aim of protecting fresh water ecosystems, as stated earlier. However, in the absence of particular guidelines for road sediment, these alternatives can be used to gain an impression of how hazardous the road sediment could be in relation to ecological aspects, as evident from previous use in literature (e.g. Heal et al., 2006; Shi et al., 2010). The mean suspended sediment associated metal concentrations from rural rivers in the UK are also shown alongside. Although the three sets of guidelines give rather inconsistent metal concentration values, a few similarities are found in the order of metal concentrations. For example, for both triggers, the highest concentration is for Zn followed by Cr, while the lowest is for Cd, and Pb and Cu in the Dutch guideline are found in reverse order in the Canadian guideline. The UK rural river sediment quality values are consistent with the highest and lowest being for Zn and Cd, respectively. The order for the other metals is Pb, Cu and Cr.

Table 7.4: Comparison of mean heavy metal concentrations with published guide line values

Metal	Dry sediment (n =120)	Runoff sediment (n = 48)	Snow sediment (n = 20)	Dutch sediment quality guideline[*]	Canadian sediment quality guideline[**]	UK rural river sediment quality[***]
Cd	**1.00**	**1.00**	***1.32***	1	0.60	3.98
Cr	17	***64***	21	62	37.3	41.81
Cu	***67***	***134***	***87***	20	35.7	48.88
Ni	12	**33**	**21**	16	n.a.	67.54
Pb	***92***	***69***	***88***	40	35	440.50
Zn	***212***	***205***	***233***	147	123	682.91

Data measured in mg kg^{-1}; Data in bold indicate metal concentrations exceed or equal to at least one of the two guidelines, while bold and italic indicate concentrations exceed both guidelines, as shown in the table

[*] (de Deckere et al., 2011)

[**] Sediment Quality Guidelines for the protection of aquatic life (CCME, 2007)

[***] Neal and Robson (2000)

As seen in Table 7.4, except for Cr and Ni, all metal concentrations in dry, runoff and snow derived sediments exceed or equal their guideline values in the Dutch and Canadian standards. Considering the exceptions, Cr in runoff sediment and Ni in both runoff and snow sediment were higher than their values in both guidelines. Cr in runoff and Cu in all different categories of road sediments from this study were well above their typical values in UK rural river sediment, while the other metal concentrations were found to be significantly lower in the road sediment than in the river sediment. Taking the different categories of road sediments into account, all the metals in runoff sediment were found to exceed the guideline values, indicating runoff as the dominant medium of pollutant transport from roads in the study area followed by the snow precipitation (except Cr) and the dry weather derived sediment (except Cr and Ni).

7.5.2 Pollution Indices for Heavy Metals

Transforming heavy metal concentration levels into a single index value is often preferred to derive better understanding and to inform decision making tools in environmental pollution research. In this regard, the degree of contamination (CD) and potential ecological risk (PERI) indices were estimated and are presented in Table 7.5. It may be debatable to use these indices, as they were primarily designed for the assessment of aquatic toxicity of natural sediment. However, due to the robustness of the indices, they have previously been used (with necessary modification) to assess metal contamination for road sediment (e.g. Yu et al., 2003; Huang et al., 2009; Shi et al., 2010).

Table 7.5 demonstrates the CD and PERI indices for three different categories of road sediments at the primary study sites. The last two columns contain these indices for integrated samples (defined as sediment irrespective of fractions), were derived by integrating the individual size fractions data (the metal concentrations were weighted by size fraction before calculation of integrated CD and PERI in the 250-63 µm and < 63 µm size fractions), which are shown in columns 3 – 6. As the methods used here to calculate CD and PERI, proposed by Hakanson (1980), were for undisturbed sediment overlooking different size fractions. Estimating these indices for different size fractions is open to question. However, the intention here is to inform readers regarding the influence of the sediment size fractions on overall pollution levels.

Based on the integrated samples (penultimate column in Table 7.5), the degree of contamination caused by metals in road sediments falls between 8 and 20, indicates low to moderate degree of contamination. CD $\geq$ 12, suggesting a considerable degree of contamination, was found at the RSC site for all three categories of road sediments. For the other 3 sites 1 of the 3 sediment categories fell below the same contamination level. The CD for the snow derived sediment at the RB site and for the dry sediment at the SR site are only marginally below 12, while only the dry sediment at the RI site was below moderate contamination level.

Similarly, PERI (last column in Table 7.5) which indicates a metal toxicity for aquatic species, ranges from 72 to 100, indicating low to moderate levels of ecological risk across the sites, and was found to be generally consistent with the pattern of CD. PERI ≥ 75, suggesting a moderate level of ecological risk, was found for all sediment categories for all the sites with the only exception being at the RB site for snow sediment. However, even this exception was only marginally below the moderate ecological risk level mark.

Comparing the different road sediment for the pollution indices, the runoff sediment was found to be the most contaminated followed by dry and snow sediment.

Table 7.5: Pollution indices (Degree of contamination, CD and Potential ecological risk index, PERI) for the heavy metals associated with road sediment

Site	Category	Sediment size fractions 250-63 µm		Sediment size fractions < 63 µm		Integrated sediment [a]	
		CD	PERI	CD	PERI	CD	PERI
Road bend (RB)	Dry Sediment	8	78	23	178	14	95
	Runoff sediment	14	68	36	160	16	75
	Snow sediment	10	70	25	116	11	72
Road with speed controls (RSC)	Dry Sediment	15	84	17	241	16	100
	Runoff sediment	19	81	44	204	20	94
	Snow sediment	13	79	31	129	16	92
Road intersection (RI)	Dry Sediment	5	66	15	92	8	75
	Runoff sediment	15	64	38	173	17	80
	Snow sediment	11	69	21	105	14	79
Straight road (SR)	Dry Sediment	9	86	18	124	10	80
	Runoff sediment	17	73	43	196	20	92
	Snow sediment	11	80	29	131	13	86

[a] Irrespective of sediment fraction sizes

In contrast to the integrated sediment (irrespective of size fractions), both the CD and PERI in the sediment size fraction < 63 µm (usually considered as the most chemically active) were values 1.5 to 3 times greater, raising the pollution level to the next hierarchy of ecological risk (columns 5 and 6 in Table 7.5). For example, at all sampling sites except the RI, CD ≥ 24, suggesting a high level of contamination for both runoff and snow sediment. Conversely, CD associated with the larger sediment size fraction (250-63 µm), displays a similar level of contamination as seen in the integrated sediment samples, but with a different magnitude. Taking the sediment size into account on potential ecological risk index, the size fraction < 63 µm, PERI ≥ 150, suggesting considerable ecological risk needing immediate attention, was found at all the sites for the runoff sediment. A similar level of ecological risk was also found at the RB and RSC sites for the dry road sediment, while none of the snow sediment at the sites showed such a high risk. The low ecological risk for snow sediment was because of the lower concentration of the most toxic metals Cd (toxic factor = 30) and Pb (toxic factor = 5) compared to other two sediment categories. Furthermore, PERI associated with larger sediment size fraction (250-63 µm), displays a low to moderate level of ecological risk as found for the integrated sediment, but with a different magnitude.

It is therefore clear that pollution indices based on integrated sediment (irrespective of size fractions) may underestimate the level of ecological risk. However, as the local background values of metals were derived for integrated RDS (not separating into different sediment size fractions) and these values were used for different sediment size fractions, the probable higher pollution indices for the finer sediment particles could be biased. Therefore these pollution indices derived for finer sediment fractions need to be used with caution. In future work related to this, local background values for metals in different size fractions could be used to derive the pollution indices, which may eliminate the present limitations.

7.6 Conclusions

This chapter identified that only a fraction of sediment built-up during dry days was washed-off during rainfall and snow events, for which smaller sediment size fractions were the key contributors. The road sediment contained significant amounts of heavy metals and their concentrations varied with sediment type in the order of runoff > snow > dry, and between the sampling sites as RSC > RB > SR > RI, irrespective of traffic volume. The contamination assessment suggested that road sediment may likely pose a moderate to considerable level of ecological risk to the nearby water environment: among which runoff from the rainfall event was the most dominant medium of pollution followed by the dry and snow sediment.

Chapter 8 - Conclusions and Recommendations

8.1 Introduction

This research study used an easy to replicate experimental methodology with the aim of characterising the heavy metal contamination of road deposited sediment. The investigation focused on the hypothesis that traffic movement patterns, which are conditioned by road lay-out, have a significant influence on heavy metal emission patterns and associated pollution. The intrinsic variability of the pollutant build-up and wash-off processes, and the unsuitability of applying data and information that are available in the literature to local conditions, warranted the study of these processes as part of the research study. A total of 12 different sampling sites were initially selected on the Riccarton Campus road network at Heriot Watt University in Edinburgh to represent a range of typical road lay-outs. The sites comprised straight sections of road, roundabouts, a road bend, a road with speed control measures (speed bumps), a road intersection, bus stops and a car park. Based on the study objectives, 4 of the sampling sites were selected for long term monitoring (over a year). These four primary sites were a road bend (RB), a section of road with speed control measures (RSC), a road intersection (RI) and a straight road section (SR).

The pollutant build-up at these primary study sites was studied in-depth by analysing road deposited sediment (RDS) and RDS associated heavy metals at two transverse sampling positions (near the curb and 1 m from the curb). Several wash-off events comprising 12 different rainfall events covering a year, and 5 snow precipitation events during winter were also monitored at the primary sites. The pollutant wash-off was studied by analysing sediment load derived from rainfall-runoff events only, as for snow events only fresh snow rather than snow-melt runoff was sampled.

The data was used to derive calibrated parameters for the mathematical replication of the pollutant build-up and wash-off for the four primary study sites. These mathematical models were validated using independent data and the parameters were compared with default values used in commercial urban drainage models.

Subsequently, grain size and site specific heavy metal, temporal and seasonal variability, and relationships between heavy metals were studied and discussed. Furthermore contamination levels associated with heavy metals in the road sediment were assessed in relation to potential ecological risk for nearby receiving waters. Based on the results obtained the following conclusions can be drawn, which are presented below in a few sub sections.

8.2 Major Conclusions

- Road sediment on Riccarton Campus is highly contaminated by heavy metals compared to their local background values, signifying an anthropogenic input most likely from the road-traffic environment. The RB, RSC, RI and SR sites were all found as pollutant hot-spot sites.
- The variations across the sites appear to be primarily due to site-specific attributes, such as road lay-out, road surface condition and presence of road paint rather than due to traffic volume alone. Moreover, as traffic passed through all the above sites (except the straight road section), it experienced acceleration and deceleration whilst undergoing ‘stop-start’ activities conditioned by road lay-out, which more likely influenced metal emission patterns than traffic volume.
- The build-up of road deposited sediment over antecedent dry days is highly site-specific and varies with position across the road. These are also true of the relationship between heavy metal build-up and the number of antecedent dry days.
- The pollutant wash-off is site-specific and only part of the initially available sediment is transported during rainfall events, in particular, the finer fractions. There is also an influence from the type of rainfall and the number of dry days between rainfall events.
- Comparing site-specific build-up and wash-off parameters with default values in commonly used commercial urban drainage models suggests that the default values are (significantly) inappropriate for road networks, such as Riccarton Campus.
- Heavy metal concentrations decrease with increasing sediment particle size fractions, which is consistent with current knowledge of trace metal distributions in sediment.
- The concentrations of most of the heavy metals are significantly higher in runoff sediment followed by the snow and the dry sediment for all the sampling sites.

- Stronger correlations between heavy metals are associated with the lower fraction sizes (≤ 63 µm) than with the larger fraction sizes (> 63 µm). Based on the strength of the correlations between metals, it appears that Cu can be used as a surrogate parameter for other metals in both dissolved and particulate phases (in particular for the sediment size fraction ≤ 63 µm).
- The contamination assessment reveals that runoff is the largest potential contributor of pollution followed by snow and dry sediment. The pollution risk levels vary from low to moderate, however they could reach considerable levels for a few rainfall events during summer and autumn months.

8.3 Themed Conclusions

This section outlines classified conclusions that can be drawn from the results presented in Chapters 4 to 7.

8.3.1 Dry Road Sediment

- RDS on the Riccarton Campus road network is highly contaminated with heavy metals, with larger concentrations compared to their local background values, suggesting an anthropogenic input (most likely from traffic) in addition to atmospheric deposition.
- Spatial variations of heavy metal emission patterns were found across the 12 monitoring sites on the road network. Based on the average values of pollution indices, RB, RSC, RI, SR and bus stops were found as the pollutant hot-spot sites.
- RDS and RDS associated heavy metal build-up on roads were primarily site-specific. The variability is primarily governed by road lay-out with influences from traffic movement patterns, road surface condition, presence of road paints and surrounding land use.
- For the relationship between heavy metal build-up and the number of antecedent dry days (ADD), it was revealed that RDS sampling position had the major influence on this. Although the pattern of pollutant build-up was common, a transverse distribution of sediment build-up was also observed. Heavy metals analysed from RDS collected at 1 m from the curb showed a generally increasing trend with increasing ADD as expected, however, near the curb the trends were found to be decreasing with increasing

ADD, which is surprising and contrary to current understanding derived from previous published work.

- Generally, RDS collected at 1 m from the curb contained a larger percentage of smaller particles than RDS collected near the curb. Likewise, there was a greater percentage of larger particles in RDS near the curb than in RDS at 1 m from the curb. A similar distribution of metal concentrations was also observed with higher concentrations of Cd, Cu and Zn in RDS collected at 1 m from the curb, and higher concentrations of Cr, Ni and Pb in RDS near the curb.
- The concentrations for all metals except Pb were found to decrease with increasing RDS particle size fractions, which is consistent with current knowledge of trace metal distributions in road sediment. Overall, particles in the < 63 µm size fraction made a dominant contribution to metal loading in RDS.
- Correlation analyses revealed a stronger correlation between heavy metals (in particular in the smallest sediment size fraction) at 1 m from the curb than near the curb, indicating different sources for the metals at the two sampling positions.
- Furthermore, from a detailed study of the four primary study sites, using the CD and PERI, the degree of contamination and potential ecological risk index, respectively, revealed that the RSC is the most contaminated site followed by the RB, SR and RI sites. As mentioned earlier, site specific attributes were found to be drivers of the difference in heavy metal concentrations in the RDS and so it was the case for the pollution levels: primarily road lay-out with traffic movement patterns, along with influences from road surface condition and road paint rather than traffic volume alone.

8.3.2 Wet Weather Samples

8.3.2.1 Runoff Samples

- Only the mean concentrations of dissolved Cu and Zn, among the 6 heavy metals studied, were found to exceed environmental quality standards, while all the particulate metals displayed significantly higher concentrations than recommended for most of the sampling sites.
- Particles in the < 63 µm size fraction made a dominant contribution to the particulate metal concentrations of runoff sediments at all sampling sites.

- Significant seasonal variations of most of the heavy metal concentrations were found. Mean concentrations for most of the dissolved metals were higher in winter and spring than in autumn and summer, while reverse patterns were found for most of the particle bound metals.
- In general, correlations between metal concentrations and storm variables were weak to moderate. Rainfall duration was found as a primary driving variable for most of the dissolved metal concentrations, while the number of antecedent dry days was key followed by rainfall intensity, for most of the particle bound metals.
- The strongest correlations between metals were found to be associated with the smaller size fractions (< 63 µm) compared to larger size fractions (250-63 µm). However, the relationships between heavy metals and total suspended solids (TSS) were not very strong.
- An assessment of the contamination indicated that runoff sediment posed a moderate to considerable degree contamination (based on the CD), for which the associated ecological risk (based on the PERI) indicated low to moderate ecological risks. However a few storm events during the summer and autumn were found to display a considerable level of contamination, and a moderate ecological risk, for most of the sampling sites, when a high intensity rainfall followed a long dry spell.

8.3.2.2 Snow Samples

- For all sampling sites, only the mean concentration of dissolved Cu, out of 6 heavy metals studied, was found to exceed environmental quality standards, while all the particulate metals except Cr displayed higher concentrations than recommended.
- The concentrations for most of the metals (except Pb) in the <63 µm size fraction were found to be up to 5 times as high as in the 250-63 µm size fraction.
- The strongest correlations between metals were found to be associated with the smaller size fractions (< 63 µm) compared to larger size fractions (250-63 µm).
- An assessment of the contamination revealed that snow sediment posed a marginally greater than low level of ecological risk for most of the monitoring sites on the studied road network, if being transported in runoff induced by snow-melt.

8.3.3 Comparative Assessment of Dry, Runoff and Snow Sediment

- The median diameter of the dry road sediment was approximately 2 to 4 times larger than that of the runoff and snow sediment, respectively, suggesting that only a fraction of the initially available sediment was washed-off during rainfall-runoff events.
- The smaller sediment size fraction (<63 µm) for the 3 different road sediment types contain up to 5 times greater concentrations for all the heavy metals (except Pb), compared to the larger sediment size fraction (250-63 µm).
- The pollutant concentrations for most of the metals are significantly higher in runoff sediment followed by the snow and dry sediment for all the sampling sites. Similarly, the heavy metal contamination assessment indicated that there is a low to moderate level of ecological risk associated with the road sediment; among which runoff from the rainfall event is the most dominant medium of pollution followed by the dry and snow sediment.
- The pollution level could potentially reach a considerable level of ecological risk (the highest risk being associated for the < 63 µm size fraction of the runoff and dry road sediment), if the influence of sediment particle sizes is considered.

8.4 Implications of the Research

The identification of pollutant ‘hot spot’ sites on a suburban road network, quantified by heavy metal concentrations and associated pollution levels in different categories of road sediment derived by dry and wet weather, has a direct application on the selection of site/source control measures outlined in the ‘SUDS for Roads’ manual (Pittner and Allerton, 2009). The derived local build-up and wash-off models, although site-specific at this stage, may be used to establish a quick estimate of the pollutant build-up and wash-off loads with reasonable confidence for a given rainfall intensity, rainfall duration and antecedent dry days in other parts of Scotland and the UK. This should be possible given the reasonably uniform climate condition across the British Isle, although further studies may be required to fully establish this. A transverse gradient of RDS and RDS heavy metals was found to have a significant influence on the pollutant build-up process: hence the design of future monitoring of RDS needs to be specified in light of this. Additionally, the interpretation of already published data may need to be modified unless the transverse location of the sampling position was clearly specified. In terms of monitoring heavy metals in wash-off from roads, the measurement of Cu alone can be taken, as a surrogate parameter of other heavy metals, to gain a reasonable understanding of other pollutants and thus to avoid time and cost involved in monitoring a full list of pollutants, if not necessary.

8.5 Recommendations for Further Research

The outcomes of this research have contributed to the current knowledge base on urban diffuse pollution from the road-traffic environment. Apart from the main findings, several areas are identified, where further research studies are recommended, as summarised below.

- The understanding gained of the influence of site-specific attributes on heavy metal emission patterns is limited to a suburban road network with low traffic density and a combination of rural and urban land uses. Further investigations on roads with high traffic volumes, such as main roads and motorways, and with specialised land uses, such as industrial or commercial activities, would be a useful extension to this work, which would enable it to fit into urban diffuse pollution studies in a more holistic way.
- Although pollutant build-up was investigated in detail, pollutant wash-off for the largest rainfall events was limited to only a part of the runoff volume. Hence, future research should focus on capturing the entire runoff volume. Furthermore, monitoring the composition of runoff during rainfall events could be useful.
- A total of 5 snow events were monitored and sampling was limited to the collection of fresh snow. Collection of snow-melt and rain-in-snow induced runoff samples instead of fresh snow could be a better way to compare and contrast the characteristics of pollutants in snow derived sediment with those in rainfall induced runoff and in dry sediment.
- The assessment of metal contamination was based on simplified methods and, therefore, the pollution levels reported may be rather conservative. For example, the bio-availability of metals (not studied), might be a useful issue to include in further research to gain a proper understanding of the actual impact of road runoff on the water quality of receiving waters. Other additional information might include the type of aquatic species present, the variability of bed sediment quality in receiving waters before and after storm events and the influence of surrounding soils.

- An investigation of the use of treatment trains of SUDS, at the sites that have been identified as hot-spot areas, would be a valuable extension of this research, which could provide a valid platform to translate the knowledge gained from this study into practical measures.
- As the transverse gradient of road sediment has revealed that the chemically active finer sediment (< 250 µm) generally deposited away from the curb edge, the conventional street sweeping technique should be modified to also target to remove sediment deposited away from the curb rather than along the edges.
- While the design of a typical road lay-out in suburban roads with more bends, more speed bumps, more intersections etc to restrict vehicle speed is believed to be safer for pedestrians, they are potentially environmental pollution hot-spot sites, as evident from this study. Therefore future road design in suburban area needs to assess the trade-off between road designs for safety vs. road design to minimise environmental pollution.

Appendix A – Study Area

Site Description

Edinburgh, a city in the southeast of Scotland, lies on the east coast of Scotland's central belt, alongside the Firth of Forth, as seen in Figure A1. Heriot Watt University's Riccarton Campus (latitude: 55.91^{0} and longitude: -3.31^{0}) is located southwest of Edinburgh city (Figure A2) and has been developed during the last 40 years with good ecological and environmental perspectives.

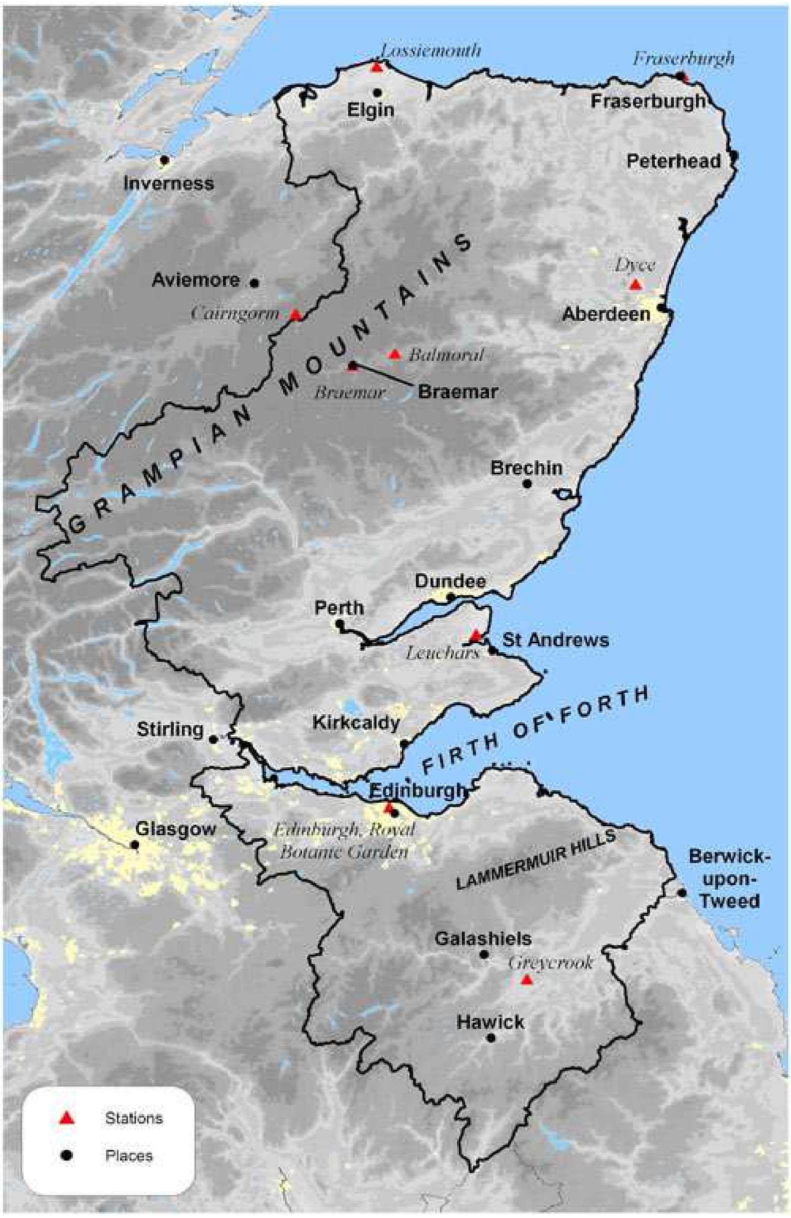


Figure A1: Map showing Edinburgh City (adapted from http://www.metoffice.gov.uk).

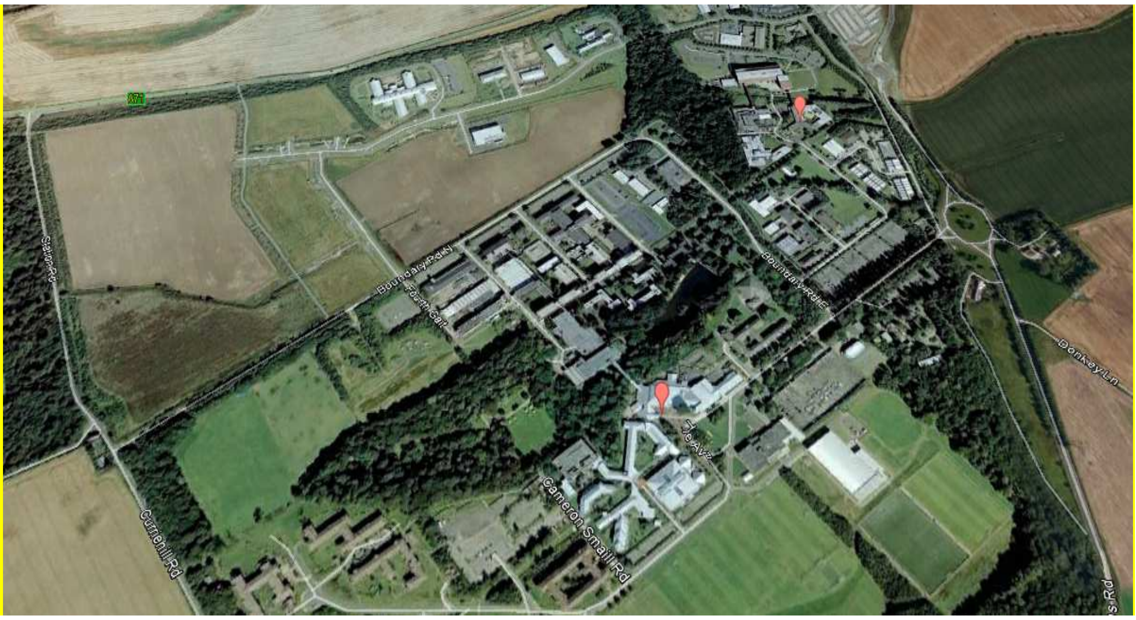


Figure A2: 3D view of Heriot Watt University Riccarton Campus in Edinburgh City (adapted from google earth map)

Figure A3: Sampling sites on Campus road network.

Site Photos

Site 1: Roundabout at Gait 4 on Boundary Road North

Site 2: Straight road section on link road between Boundary Road North and Research Avenue North Road

Site 3: Road bend on Research Avenue North Road

Site 4: Straight road section on Research Avenue North Road

Site 5: Bus stop on Research Avenue North Road

Site 6: Road with Speed control measures on Research Avenue North road

Site 7: Straight road section on Research Avenue North Road

Site 8: Road intersection on Research Avenue North Road

Site 9: Straight road section on Riccarton Avenue Road

Site 10: Roundabout on Riccarton Avenue Road

Site 11: Bus stop on Riccarton Avenue Road

Site 12: Car park A (alongside Riccarton Avenue Road)

Edinburgh Climate

Edinburgh City has a temperate maritime climate (moderate summer and mild winter), the annual average temperature range is about 0.9 – 12.2 ^{0}C and the annual average precipitation is about 668 mm distributed fairly evenly throughout the year. The variation of mean daily maximum and minimum temperatures month by month, together with the highest and lowest temperatures recorded, is shown in Figure A4 for Edinburgh RBG (Royal Botanic Garden). The wettest months tend to be in autumn and early winter, whereas late winter and spring is normally the driest part of the year. The course of mean monthly rainfall for 1971-2000 for Edinburgh RBG site is shown in Figure A5. Over most of the area, snowfall is normally confined to the months from November to April with average number of days with snow falling is about 20 per winter. The depth of snow fall recorded at Edinburgh RBG site for 25 November to 12 December 2010 is shown in Figure A6.

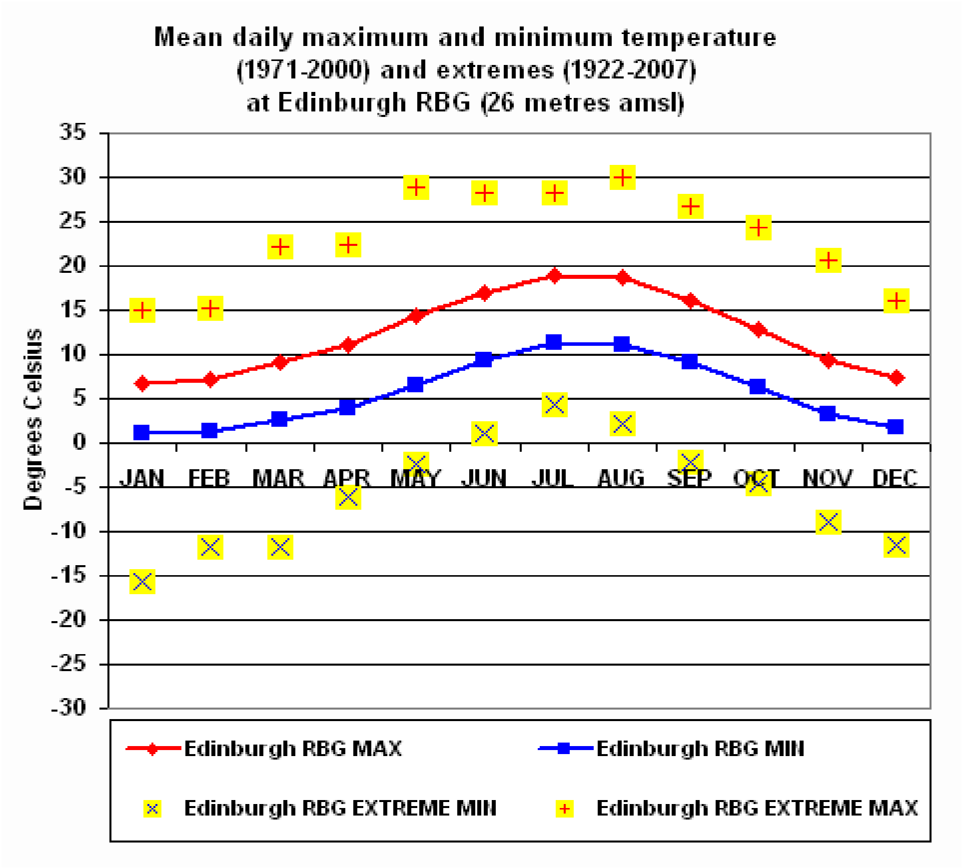


Figure A4: Variation of mean daily temperature averaged over 1971 to 2000 at Edinburgh RBG (adapted from http://www.metoffice.gov.uk).

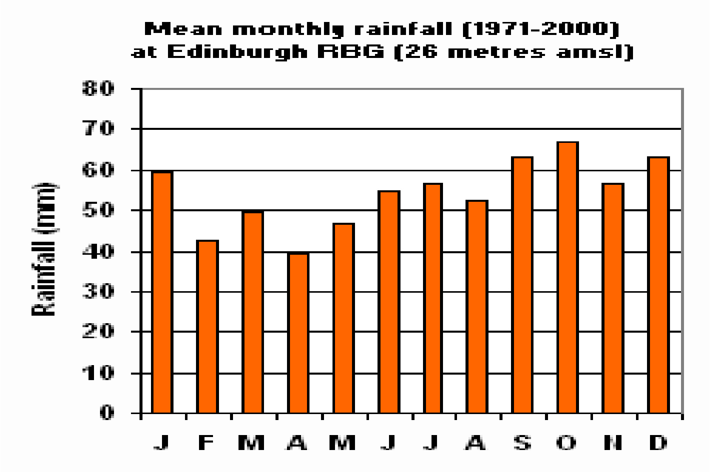


Figure A5: Mean monthly rainfall averaged over 1971 to 2000 at Edinburgh RBG (adapted from http://www.metoffice.gov.uk).

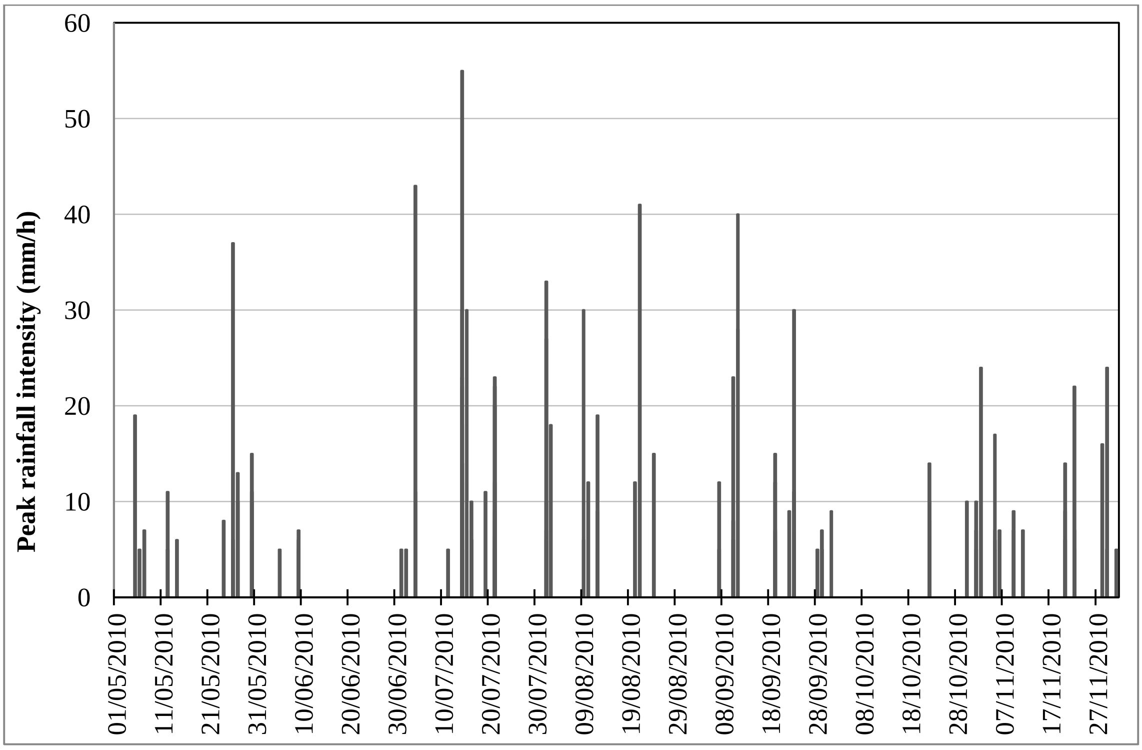


Figure A6: Rainfall intensity recorded at local rain-gauge (a tipping bucket type) setup near to Riccarton Campus of Heriot Watt University in Edinburgh for a period of May to December 2010 (Bars filled with red colour are some the monitored events during the study period).

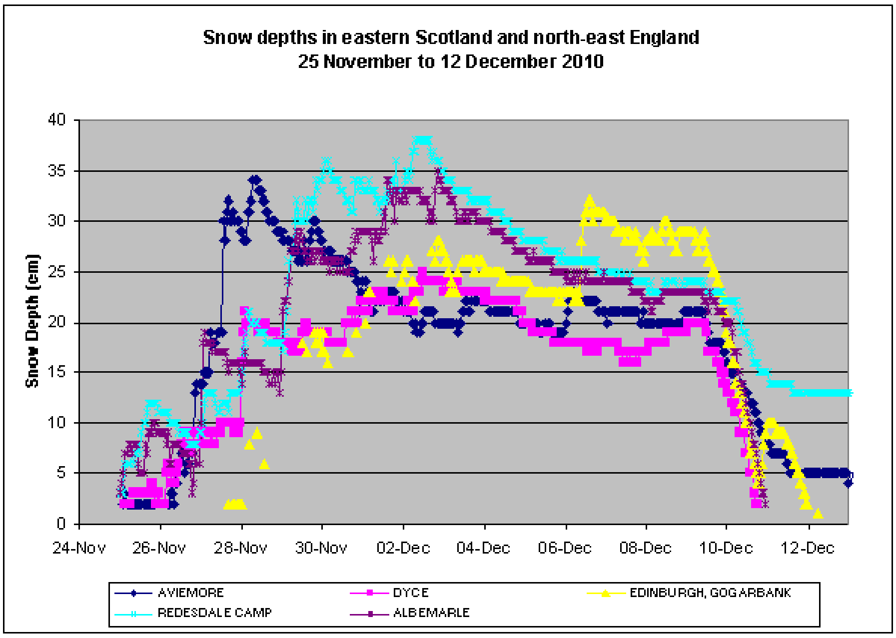


Figure A7: Snow depths measured at different sampling sites in eastern Scotland and north-east England during November and December 2010 (adapted from http://www.metoffice.gov.uk).

Appendix B – Laboratory Testing

Laboratory Testing Equipments Photos

Figure B1: Electric water bath to heat sediment samples followed by acid digestion.

Figure B2: Perkin Elmer Atomic Absorption Spectrometer 200 Analyst.

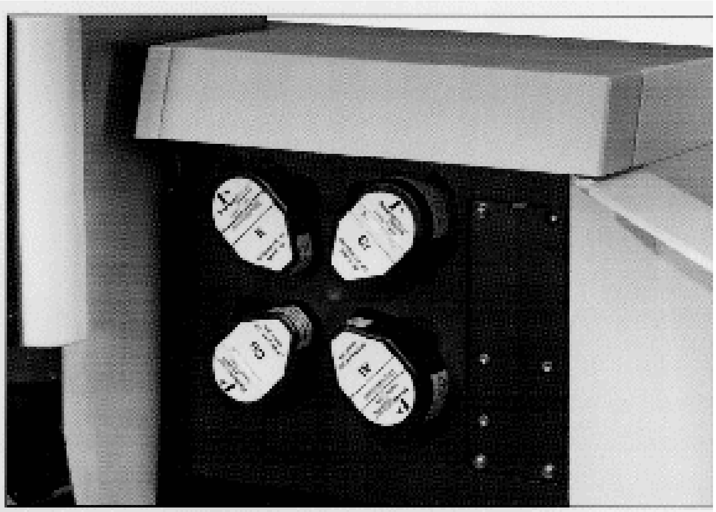


Figure B3: Hollow cathode lamp (HCL) arrangement on Perkin Elmer 200 AAS analyst (adapted from Perkin Elmer 200 AAS manual).

A photograph of four unit lamp mount on Perkin Elmer 200 AAS is shown in Figure B3. A single lamp can be made to generate characteristic radiation for up to two or three elements without interference problems.

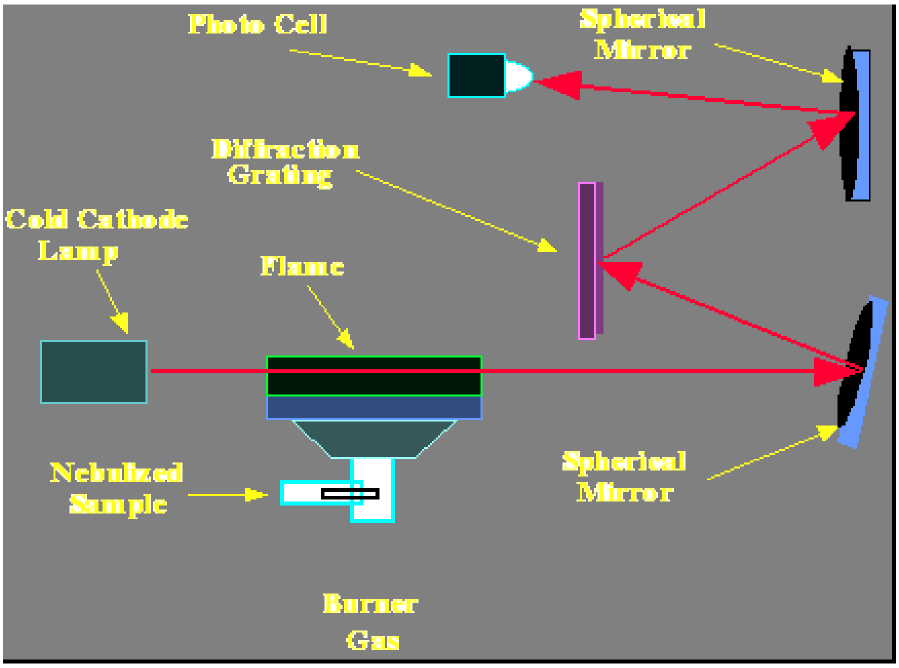


Figure B4: The basic system of a Flame Atomic Absorption Spectrometer (adapted from Perkin Elmer 200 AAS manual)

A diagram of a Flame Atomic Absorption Spectrometer (FAAS) is shown in Figure B4. The light source is a cold hollow cathode lamp that produces the light that would be naturally emitted by the element to be measured at a high temperature. Depending on the metals to be analysed, a large range of such lamps are available. Consequently, each of the lights contains specifically those wavelengths that the element in the flame will selectively absorb. The light passes through the flame, which is usually rectangular in shape for allowing an adequate path length of flame for the light to be absorbed, and then into the optical system of the spectrometer, as seen in Figure B4.

The flame is fed with a combustible gas, customarily air/acetylene, nitrous oxide/acetylene or air/propane or butane. The sample, dissolved in a suitable solvent, is nebulised and fed into the gas stream at the base of the burner. The light, having passed through the flame, can be focused directly onto a photo-cell or onto a diffraction grating by means of a spherical mirror. The diffraction grating can be made movable, and so it can be set to monitor a particular wavelength that is characteristic of the element being measured, or it can be scanned to produce a complete absorption spectrum of the sample. After leaving the grating, light of a selected wavelength, or range of wavelengths, is focused onto the photocell. The position of the diffraction grating determines the wavelength of the light that is to be monitored. More details of the basic system of a flame atomic absorption spectrometry can be found in Perkin Elmer 200 AAS manual.

Analytical Test Results

On 10 occasions blanks (distilled water) were tested for metals by using calibration solutions prepared from the standard stock solutions. The results obtained are presented in Table B1.

Table B1: Test results of blank (distilled water) at laboratory using calibration solutions for metals

Metal (µg/l)	1	2	3	4	5	6	7	8	9	10	Average	Standard deviation
Cd	0.15	0.11	0.11	0.12	0.098	0.099	0.095	0.013	0.101	0.12	**0.1**	0.0
Cr	8.4	8.98	8.14	7.95	8.68	9.32	8.67	9.54	8.23	8.95	**8.7**	0.5
Cu	1.21	1.42	1.32	1.28	1.2	1.18	1.3	1.4	1.34	1.35	**1.3**	0.1
Ni	0.75	0.72	0.7	0.65	0.71	0.64	0.72	0.7	0.7	0.71	**0.7**	0.0
Pb	1.01	1.15	0.98	0.87	1.21	1.07	0.95	1.31	1.21	1.25	**1.1**	0.1
Zn	12.5	12	11.78	13.02	12	11.18	12.87	12.68	12.95	11.24	**12.2**	0.6

Table B2 presents test results of certified reference material MESS-3 using metal calibration solutions for quality control and quality assurance purposes.

Table B2: Test results of certified reference material MESS – 3 at laboratory using calibration solutions for metals

Metal (mg/l)	MESS-3(1)	MESS-3(2)	MESS-3(3)	Average	Standard deviation	Certified values (mg/l)	% Recovery of reference value
Cd	0.24	0.235	0.241	**0.24**	0.00	**0.24**	100
Cr	109	103.4	107	**106.5**	2.84	**105**	101
Cu	31.54	35.42	35.2	**34.0**	2.18	**33.9**	99.5
Ni	51.05	44.5	48.12	**47.9**	3.28	**46.9**	102
Pb	22.01	21.34	22.1	**21.8**	0.42	**21.1**	103
Zn	157.5	168.4	149.2	**158.4**	9.63	**159**	99.6

Table B3 illustrates the results obtained for the heavy metal concentration in RDS carried out for 12 initial RDS samples by using three different metal extractants, such as strong HNO_3, aqua-regia (HCl-HNO_3 in 3:1 by volume) and a mix of HCl-HNO_3-$HClO_4$ (2:1:2 by volume). As seen in Table B3, there is no marked variation between metal concentrations for the three different metal extractants.

Table B3: Descriptive statistics of the mean heavy metal concentration (mg/kg) in the road sediment for different strength extractions

Metal	Conc. HNO_3	Aqua-regia (HCl-HNO_3)	HCl-HNO_3-$HClO_4$
Cd	1.31 ± 0.51	0.92 ± 0.37	1.02 ± 0.29
Cr	15 ± 7	18 ± 5	19 ± 8
Cu	99 ± 32	87 ± 30	93 ± 41
Ni	17 ± 8	19 ± 10	14 ± 7
Pb	114 ± 101	89 ± 77	93 ± 81
Zn	280 ± 82	267 ± 69	270 ± 58

Values are in mean ± standard deviation (the number of samples analysed were 10)

Appendix – C (Supporting Results)

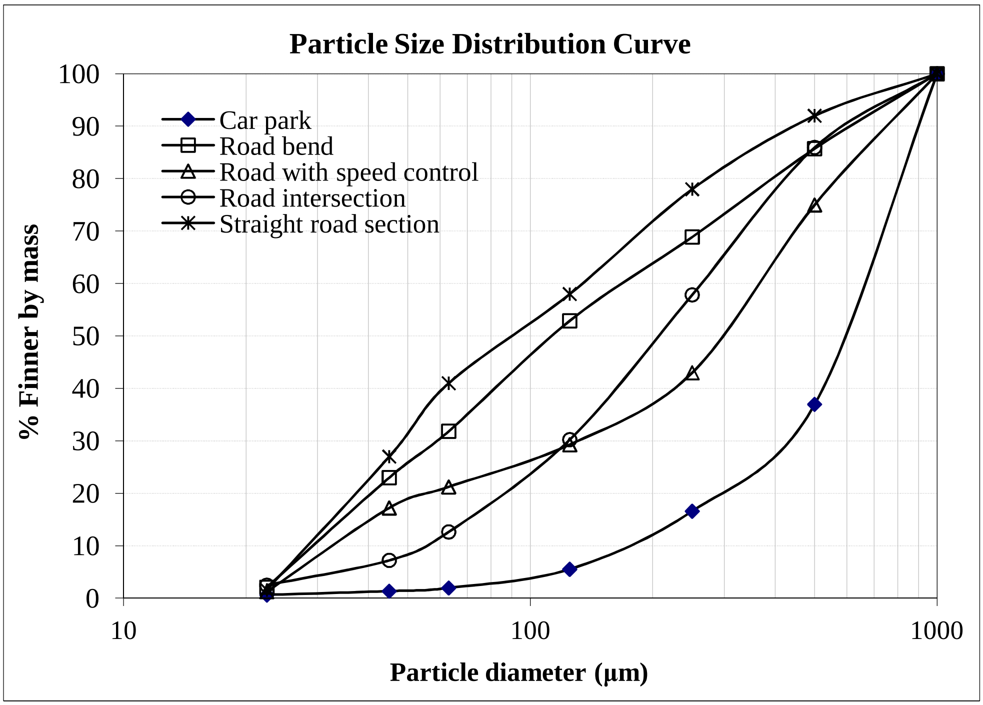


Figure C1: Particle size distribution curve for initial sampling of dry road sediment (RDS) at several sites along the studied road network.

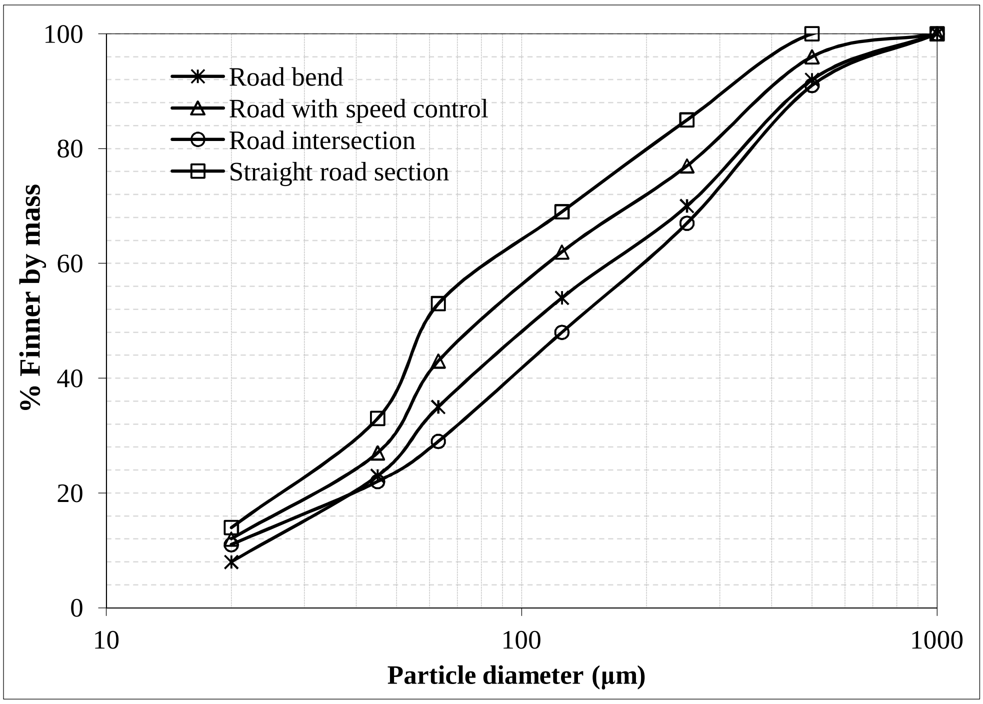
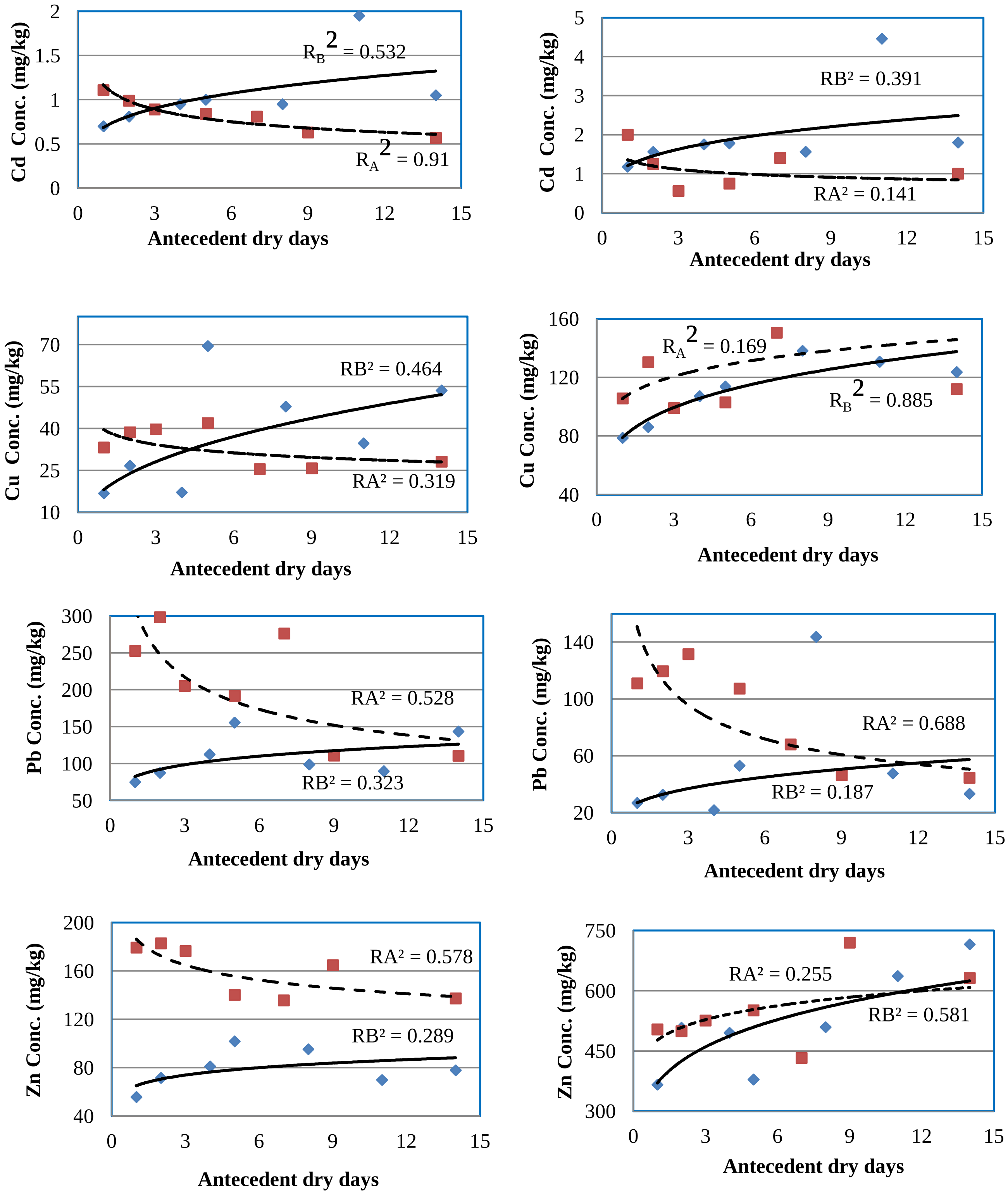


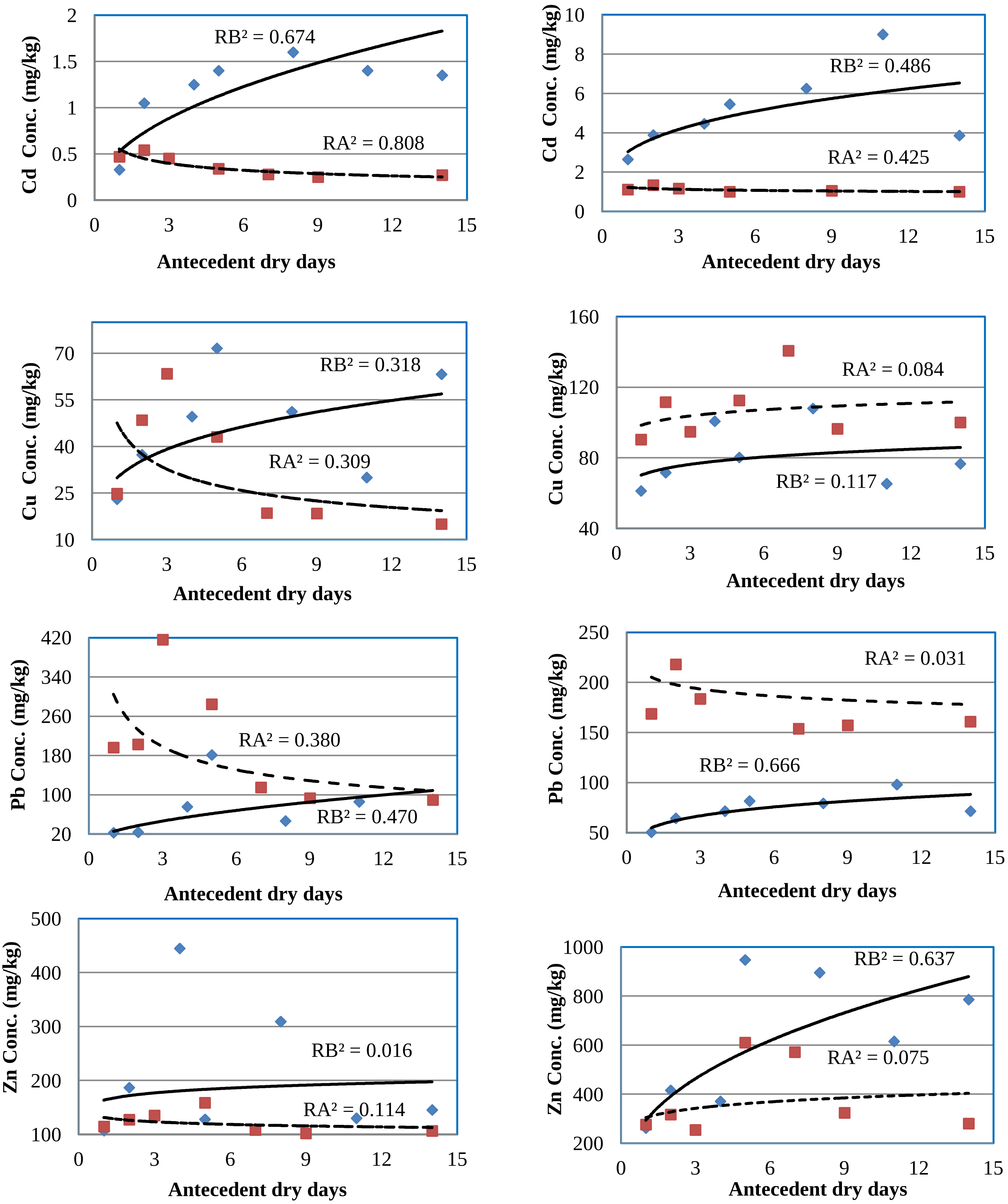
Figure C2: Particle size distribution curve for wash-off sediment at the primary study sites for 01 July 2010 rain events.

Influence of PSDs on Heavy metals Build-up at Primary Study Sites



Sediment fraction sizes: 250-63 µm ***Sediment fraction sizes: < 63 µm***

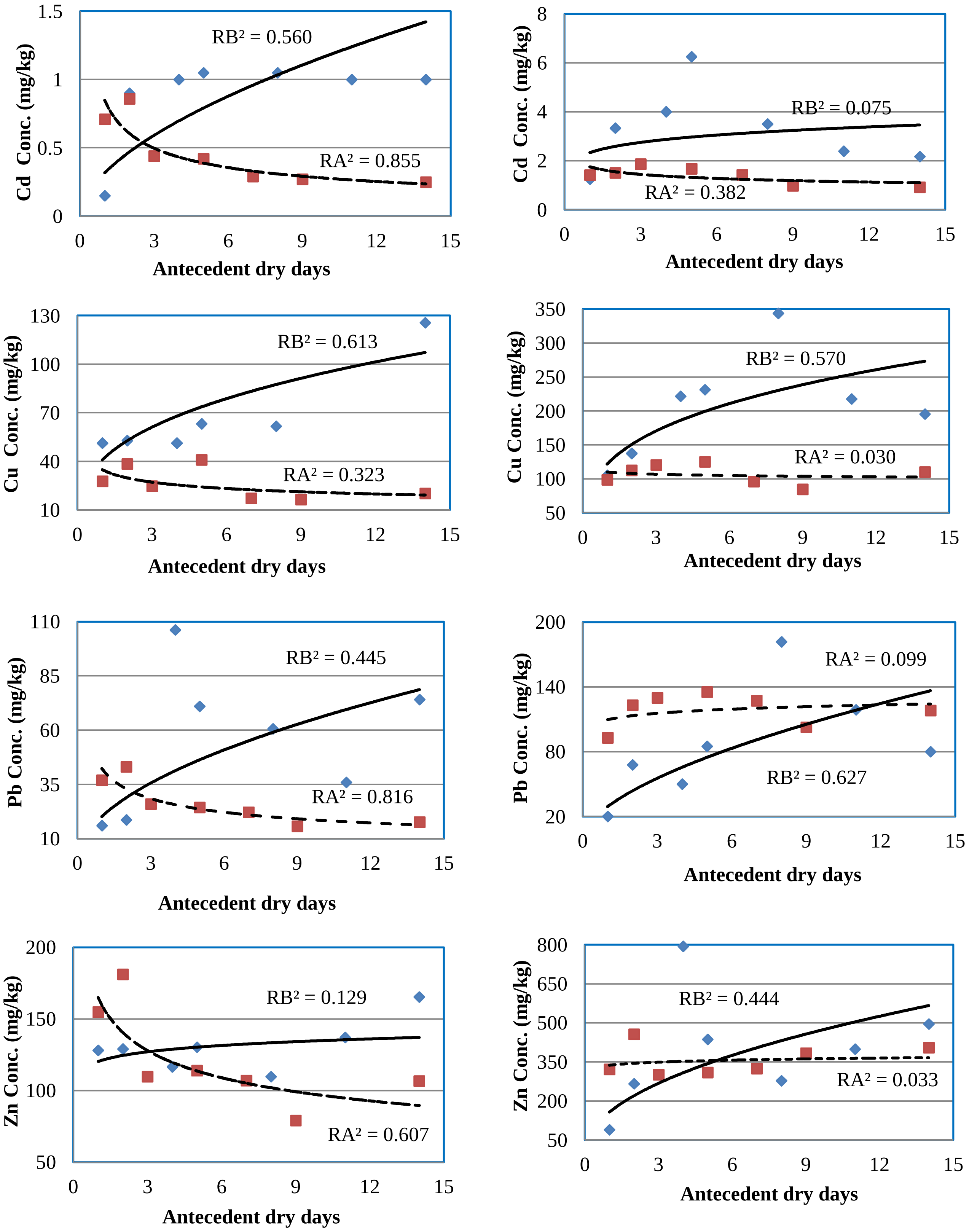
Figure C3: Heavy metal concentrations in RDS over the antecedent dry days at the **road bend** site (squares and diamonds represent data from the near curb and 1m from the curb, respectively).



Sediment fraction sizes: 250-63 µm

Sediment fraction sizes: < 63 µm

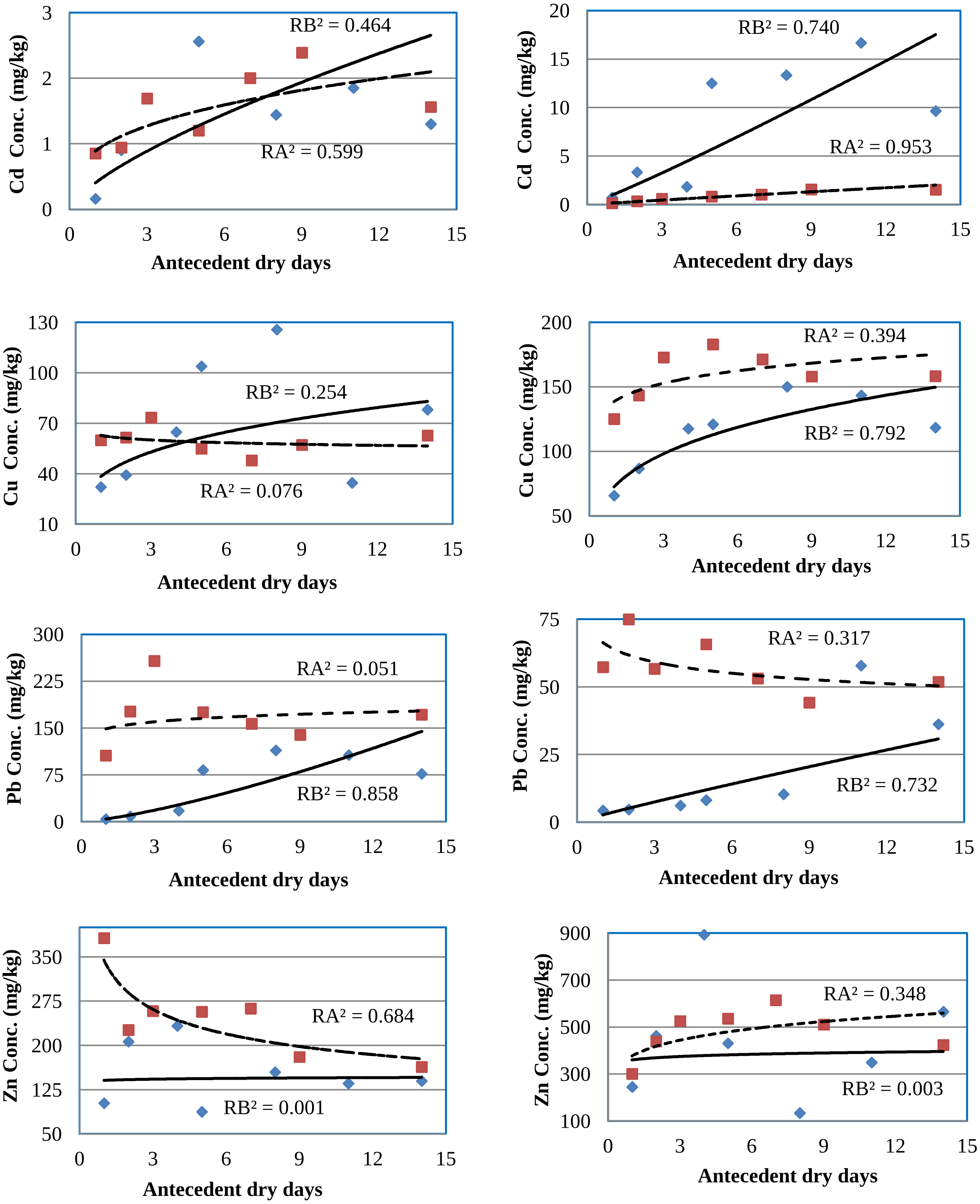
Figure C4: Heavy metal concentrations in road deposited sediment over the antecedent dry days at the **road with speed control** site (squares and diamonds represent data from the near curb and 1m from the curb, respectively).



<u>Sediment fraction sizes: 250-63 µm</u>

<u>Sediment fraction sizes: < 63 µm</u>

Figure C5: Heavy metal concentrations in road deposited sediment over the antecedent dry days at the **road intersection** site (squares and diamonds represent data from the near curb and 1m from the curb, respectively).



Sediment fraction sizes: 250-63 µm ***Sediment fraction sizes: < 63 µm***

Figure C6: Heavy metal concentrations in road deposited sediment over the antecedent dry days at the **straight road section** site (squares and diamonds represent data from the near curb and 1m from the curb, respectively).

Table C1: Steps showing calculation of pollution indices (CD: degree of contamination; PERI: potential ecological risk index) for heavy metals in dry, snow and runoff derived road sediment at four primary study sites as a function of sediment size fractions

RDS	**c_f**		250-63 µm				**CD**		<63 µm					**CD**			Integrated				**CD**
	Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn	
RB	0.76	1.34	0.79	0.7	3.21	1.19	**7.99**	0.78	7.32	3.38	1.65	4.82	4.87	**22.82**	0.76	2.99	1.16	0.96	3.64	2.21	**11.72**
RSC	0.49	2.84	0.76	0.45	8.95	1.25	**14.74**	1.24	3.22	2.31	1.13	5.61	3.98	**17.49**	0.74	2.96	1.27	0.67	7.85	2.15	**15.64**
RI	0.51	0.94	1.01	0.52	1.19	1.13	**5.30**	1.52	2.62	2.59	1	4.11	2.69	**14.53**	0.85	1.51	1.54	0.69	2.19	1.66	**8.44**
SR	1.29	1.46	1.48	0.62	1.75	2.03	**8.63**	1.37	2.6	3.23	1.46	4.89	4.84	**18.39**	1.31	1.73	1.88	0.82	2.49	2.69	**10.92**
	E_f						**PERI**							**PERI**							**PERI**
RB	22.8	2.68	3.95	3.5	16.05	1.19	**50.17**	23.4	14.64	16.9	8.25	24.1	4.87	**92.16**	22.8	5.98	5.8	4.8	18.2	2.21	**59.79**
RSC	14.7	5.68	3.8	2.25	44.75	1.25	**72.43**	37.2	6.44	11.55	5.65	28.05	3.98	**92.87**	22.2	5.92	6.35	3.35	39.3	2.15	**79.22**
RI	15.3	1.88	5.05	2.6	5.95	1.13	**31.91**	45.6	5.24	12.95	5	20.55	2.69	**92.03**	25.5	3.02	7.7	3.45	11	1.66	**52.28**
SR	38.7	2.92	7.4	3.1	8.75	2.03	**62.9**	41.1	5.2	16.15	7.3	24.45	4.84	**99.04**	39.3	3.46	9.4	4.1	12.5	2.69	**71.4**

Snow	**c_f**		250-63 µm				**CD**		<63 µm					**CD**			Integrated				**CD**
	Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn	
RB	1.3	2.37	1.64	1.07	2.29	1.56	**10.23**	1.42	9.87	4.18	1.85	3.89	3.91	**25.12**	1.3	2.37	1.64	1.07	2.64	1.96	**10.98**
RSC	1.2	2.75	1.86	1.07	4.21	1.95	**13.04**	1.35	13.62	5.32	1.67	4.2	4.87	**31.03**	1.28	2.75	2.35	1.35	5.26	3.35	**16.34**
RI	1.3	3	1.98	0.89	1.64	1.86	**10.67**	1.51	7.37	4.04	1	3.11	3.88	**20.91**	1.3	3	2.04	1.02	3.21	3.15	**13.72**
SR	1.5	2.37	2.41	1.13	2.04	2.05	**11.5**	1.7	11.87	4.82	1.7	3.93	4.55	**28.57**	1.5	2.25	2.41	1.2	3.11	2.51	**12.98**
	E_f						**PERI**							**PERI**							**PERI**
RB	39	4.74	8.2	5.35	11.45	1.56	**70.3**	42.6	19.74	20.9	9.25	19.45	3.91	**115.85**	39	4.74	8.2	5.35	13.2	1.96	**72.45**
RSC	36	5.5	9.3	5.35	21.05	1.95	**79.15**	40.5	27.24	26.6	8.35	21	4.87	**128.56**	38.4	5.5	11.8	6.75	26.3	3.35	**92.05**
RI	39	6	9.9	4.45	8.2	1.86	**69.41**	45.3	14.74	20.2	5	15.55	3.88	**104.67**	39	6	10.2	5.1	16.1	3.15	**79.5**
SR	45	4.74	12.05	5.65	10.2	2.05	**79.69**	51	23.74	24.1	8.5	19.65	4.55	**131.54**	45	4.5	12.1	6	15.6	2.51	**85.61**

Table C1 continued

Runoff	c_f		250-63 µm				CD		<63 µm					CD			Integrated				CD
	Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn		Cd	Cr	Cu	Ni	Pb	Zn	
RB	0.498	5.25	2.34	1.2	2.54	1.96	**13.788**	1.9	16.25	5.77	3.07	4.43	4.62	**36.04**	0.9	7.21	2.52	1.438	2.2	1.808	**16.06**
RSC	0.64	6.37	3.18	1.49	4.71	2.21	**18.6**	2.4	18.63	7.27	3.7	6.96	5.34	**44.3**	1.11	8.198	3.31	1.715	3.4	1.931	**19.67**
RI	0.62	5.62	2.89	1.34	2.1	2.17	**14.74**	2.2	16.12	6.64	3.4	3.96	5.19	**37.51**	1	7.474	3.12	1.59	1.89	1.908	**16.98**
SR	0.75	7	2.77	1.47	2.55	2.15	**16.69**	2.45	19.12	7.09	3.95	4.71	5.34	**42.66**	1.13	9.292	3.24	1.846	2.46	2.007	**19.98**
	E_f						**PERI**							**PERI**							**PERI**
RB	14.94	10.5	11.7	6	12.7	1.96	**57.8**	57	32.5	28.85	15.35	22.15	4.62	**160.47**	26.9	14.42	12.6	7.188	11	1.808	**73.85**
RSC	19.2	12.74	15.9	7.45	23.55	2.21	**81.05**	72	37.26	36.35	18.5	34.8	5.34	**204.25**	33.4	16.4	16.6	8.573	17	1.931	**93.84**
RI	18.6	11.24	14.45	6.7	10.5	2.17	**63.66**	66	32.24	33.2	17	19.8	5.19	**173.43**	30	14.95	15.6	7.948	9.44	1.908	**79.84**
SR	22.5	14	13.85	7.35	12.75	2.15	**72.6**	73.5	38.24	35.45	19.75	23.55	5.34	**195.83**	34	18.58	16.2	9.229	12.3	2.007	**92.32**

C_f is contamination index for an individual metal; E_f is ecological risk index for an individual metal; Integrated-weighted average of different sediment size fractions; RB: road bend site; RSC: road with speed controls site; RI: road intersection site; SR: straight road section site

Table C2: Dissolved heavy metal concentrations (µg/l) in snow samples monitored at the primary study sites

	RB						**RSC**						**RI**						**SR**					
Date	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
26.115.10	0.07	12	15	1.4	0.14	18	0.07	14	17	2.2	0.65	22	0.03	12	12	1.6	0.21	15	0.06	17	18	1.5	0.24	24
29.11.10	0.03	10	12	0.8	0.08	15	0.05	16	15	1.6	0.45	16	0.01	9	10	1.1	0.15	12	0.04	13	15	1.2	0.18	17
06.12.10	0.03	15	7	0.6	0.06	14	0.03	12	9	1.2	0.25	19	0.04	7	8	0.9	0.08	10	0.02	11	10	1.0	0.15	14
10.12.10	0.02	9	5	1.2	0.10	16	0.06	10	7	0.9	0.32	17	0.02	11	4	1.2	0.10	12	0.02	10	12	1.2	0.10	18
20.12.10	0.08	12	9	2	0.12	21	0.05	20	15	1.8	0.75	15	0.05	14	9	1.8	0.15	16	0.03	22	20	1.6	0.18	26

RB: road bend site; RSC: road with speed controls site; RI: road intersection site; SR: straight road section site

Table C3: Dissolved heavy metal concentrations (µg/l) in runoff samples monitored at the primary study sites

	RB						**RSC**						**RI**						**SR**					
Date	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
26.05.10	0.04	4	15	1.4	0.12	48	0.0	6	17	2.2	0.26	62	0.04	7	12	1.6	0.09	45	0.05	8	18	1.5	0.18	74
01.07.10	0.12	8	24	1.25	1.11	30	0.2	5	22	3.26	2.8	45	0.15	6	26	2.26	1.85	65	0.1	4	32	1.52	2.6	85
04.07.10	0.08	8	17	1	0.12	34	0.1	10	19	1.2	0.3	49	0.07	8	15	1.3	0.14	60	0.06	10	20	1.4	0.15	64
14.07.10	0.034	3	23	1.2	1.2	56	0.0	5	18	1.3	2.5	47	0.012	4	28	1.5	1.2	75	0.007	5	27	1.3	1.4	117
01.08.10	0.08	6	11	1.1	0.12	36	0.1	7	16	1.5	0.75	55	0.057	7	13	1.8	0.15	46	0.063	8	15	1.6	0.18	66
12.08.10	0.025	6	8	1	0.08	30	0.0	8	10	1.2	0.12	42	0.028	7	9	1	0.04	35	0.03	6	9	1	0.07	58
21.08.10	0.045	7	10	1.5	0.1	38	0.1	6	12	1.6	0.15	48	0.048	8	12	1.5	0.08	52	0.055	8	14	1.4	0.1	64
07.09.10	0.1	8	14	1.8	0.08	42	0.1	10	17	2.3	0.11	57	0.15	8	20	1.7	0.07	35	0.16	10	18	1.6	0.09	54
11.09.10	0.18	10	18	2.2	0.13	55	0.2	12	22	2.6	0.18	62	0.23	10	25	2.86	0.1	68	0.18	14	30	2.75	0.1	74
20.11.10	0.25	12	26	2.6	1.6	45	0.3	16	32	3.2	2.8	70	0.28	12	28	3	2.2	75	0.22	20	30	2.8	2.7	87
12.03.11	0.12	8	22	2.3	1	39	0.2	9	28	2.8	2.5	64	0.22	10	35	2.4	1.2	62	0.16	15	26	2.6	2.2	72
23.04.11	0.1	10	18	2.4	1.2	44	0.2	11	25	3.0	2.4	60	0.2	11	32	2.8	1.4	60	0.11	16	28	2.4	1.3	62

RB: road bend site; RSC: road with speed controls site; RI: road intersection site; SR: straight road section site

Appendix – D (Abstracts of the Published Papers)

Journal Papers

Cent. Eur. J. Chem. • 9(2) • 2011 • 314-319
DOI: 10.2478/s11532-011-0005-y

Central European Journal of **Chemistry**

Assessment of heavy metals emission from traffic on road surfaces

Sudip K. Pal*; Steve Wallis and Scott Arthur

* School of the Built-Environment, Heriot-Watt University, Edinburgh, UK, EH14 4AS
Email:skp7@hw.ac.uk, Tel: +44(0) 131 451 4434; Fax: +44(0)131 451 4617

Abstract: This study aims to analyse RDS heavy metal concentrations on road deposited sediment (RDS) using Riccarton Campus of Heriot-Watt University, Edinburgh, Scotland as a study site. RDS samples were collected at two transverse positions from different sites over a 4 month period in order to describe the influence of traffic on heavy metal emissions. The heavy metal concentrations of the RDS were determined by strong nitric acid digestion and atomic absorption spectrometry. The mean concentrations for Zn, Cu, Cd, Cr, Ni, Pb and Fe were found to be 213, 57, 1, 16, 15, 118, and 13497 mg kg^{-1} from samples near to the curb and 211, 79, 2, 15, 9, 35, and 14276 mg kg^{-1} from samples 1 m from the curb respectively. Furthermore for both positions the highest concentrations for all metals were associated with the finer fraction (<63µm) and stronger correlations between the metals were found further from the curb than near the curb, indicating that metals accumulating on the road surface further from the curb may likely be from the same source (traffic), while the sources of metals near the curb are more diverse.

Keywords: *Edinburgh***;** *Heavy metals; atomic absorption spectrometry; road deposited sediment; particle size.*

Int. J. Environmental Engineering (Article in press)

Emission patterns of traffic-related metals and associated contamination in road deposited sediment

Sudip Pal[*], Steve Wallis, Scott Arthur

[*] School of the Built-Environment, Heriot-Watt University, Edinburgh, UK, EH14 4AS
Email:skp7@hw.ac.uk, Tel: +44(0) 131 451 4434; Fax: +44(0)131 451 4617

Abstract: Road deposited sediment (RDS) is regarded as a sinks for metal pollutants derived from road-traffic that may pose a danger for the nearby water environment. The reported study aims to analyse RDS build-up and associated metal emission patterns using Riccarton Campus of Heriot Watt University, Edinburgh, Scotland as a study site. The RDS samples were collected from four different sites over a 4 month period to characterize the influence of road lay-out on metal emissions. The metal concentrations associated with the RDS were determined by strong nitric acid digestion and atomic absorption spectrometry. The outcomes of the investigation show highly site-specific variability of the RDS build-up primarily linked to road lay-out, and that road surface conditions and surrounding land use influenced the results. Similarly, irrespective of traffic volume, site attributes were found to be the drivers for the observed differences in metal concentration. Furthermore, a significant proportion of pollutants were found to be associated with finer particles (size <63 µm) and that RDS exhibited moderate to strong levels of pollution for Zn, Cu and Pb.

***Keywords**: Atomic absorption spectrometry; Contamination assessment; Heavy metal; Road-layout; Road deposited sediment*

Water Environment Research (under review)

Heavy metals in road sediment and associated contamination: a comparative assessment of the dry, runoff and snow derived sediment on road surfaces

Sudip K Pal*; Steve G. Wallis and Scott Arthur

* School of the Built-Environment, Heriot Watt University, Riccarton, Edinburgh, EH14 4AS
Email:skp7@hw.ac.uk, Tel: +44(0) 131 451 4434; Fax: +44(0)131 451 4617

Abstract: The quantification of heavy metals in dry, wet weather and snow derived sediment from roads has the potential to allow improved understanding diffuse heavy metal pollution within the context of sustainable urban drainage systems for roads. With that aim, the reported study determined heavy metal concentrations in road sediment and associated pollution levels at four road different sites as part of a 12 month field study. The results reveal that road sediment contain significant amounts of heavy metals and their concentrations vary with sediment type (wet weather, snow and dry sediments) and between sampling sites according to the site specific attributes irrespective of traffic volume. Contamination assessment suggests that road sediment may likely pose a moderate to considerable level of ecological risk to the nearby water environment.

Keywords: *Heavy metals; road lay-out; road sediment; contamination; Edinburgh*

Environmental Monitoring and Assessment (under review)

Assessing heavy metals and associated contamination in road runoff

Sudip K Pal[*]; Steve G. Wallis and Scott Arthur

[*] School of the Built-Environment, Heriot Watt University, Riccarton, Edinburgh, EH14 4AS
Email:skp7@hw.ac.uk, Tel: +44(0) 131 451 4434; Fax: +44(0)131 451 4617

Abstract: The quality of road runoff at different road lay-outs on Riccarton Campus road network at Heriot Watt University in Edinburgh was studied for a year. Twelve storm events were sampled and analysed for Cd, Cr, Cu, Ni, Pb and Zn, both in dissolved and particulate form. The heavy metal concentrations were determined by nitric acid digestion and atomic absorption spectroscopy. Seasonal variability of metal concentrations was studied, and correlation analysis between metal concentrations and storm variables was also carried out. In addition the contamination levels of the heavy metals in runoff samples were evaluated. The outcomes of this study show that runoff samples contain significantly higher metal concentrations at all the sampling sites than guideline values. A significant seasonal difference in metal concentrations was observed for most of the metals. Correlation analyses revealed that rainfall duration is significant for most of the dissolved metals, while the number of antecedent dry days is a primary variable for particulate metals. An assessment of the contamination associated with the runoff sediment indicates a low level of ecological risk for most of the runoff events monitored during winter and spring, while a few summer rain events may likely pose a moderate to considerable risk across the sampling sites.

Keywords: *Road runoff; Heavy metals; seasonal influence; contamination; Edinburgh*

12th International Conference on Urban Drainage, Porto Alegre/Brazil, 11-16 September 2011

On the relationship between pollutant build-up on roads and antecedent dry days

S. Pal[1]*, S. G. Wallis[1]& S. Arthur[1]

[1]School of the Built Environment, Heriot-Watt University, Edinburgh, EH14 4AS, UK
Corresponding author, e-mail skp7@hw.ac.uk

ABSTRACT

Heavy metal build-up patterns on roads were investigated using the Riccarton Campus of Heriot-Watt University as a study site. As well as observing the influence of the number of antecedent dry days on heavy metal concentrations on road deposited sediment, for the first time this study also considered the variability of pollutant build-up with sampling position across the road. Total metal concentrations for Zn, Cu, Cd and Pb from road sediments were determined by atomic absorption spectrometry using strong nitric acid digestion. The outcomes of this study revealed that mean Cu and Cd concentrations were much higher at 1 m from the curb than near the curb, Pb showed an inverse picture, while Zn concentrations were similar for both sampling positions. Heavy metal build-up over dry spells showed both increasing and decreasing trends. Decreasing trend was found for all metals near the curb which was unexpected and is contrary to current understanding of pollutant build-up while an increasing trend was found for metals at 1 m away from the curb. This inferred that pollutants deposited away from the curb may have the same origin (traffic) with continuous input, while near the curb the sources are diverse. Correlation between metals for both positions also supported this fact. The results indicate that when deriving a relationship between pollutant build-up and antecedent dry days, it would be important to include the effect of transverse location.

KEYWORDS: Heavy metals; antecedent dry days; atomic absorption spectrometry; road deposited sediments; Edinburgh

EMISSION PATTERNS OF TRAFFIC-RELATED METALS ON ROADS

SUDIP K PAL[*], STEVE WALLIS, SCOTT ARTHUR

School of the Built-Environment, Heriot-Watt University
Riccarton, Edinburgh, EH14 4AS, Scotland.
[*] E-mail: skp7@hw.ac.uk

ABSTRACT

Road deposited sediments (RDS) are regarded as sinks for metal pollutants derived from road-traffic that may pose a danger for the environment. This study aims to analyse RDS metal concentrations using Riccarton Campus of Heriot-Watt University, Edinburgh, Scotland as a study site. RDS samples were collected from different sites over a 4 month period to characterize the influence of road layout on metal emissions. The metal concentrations of the RDS were determined by strong nitric acid digestion and atomic absorption spectrometry. The outcomes of the investigation show highly site-specific rates of build-up, and metal emissions that primarily varied with road lay-out with also an influence from road surface conditions and surrounding land use. Further analysis revealed that a significant proportion of pollutants was associated with the finer particles (size <63 μm). A contamination assessment indicated that RDS from the study site exhibit moderate to strong levels of pollution for Zn, Cu and Pb.

Keywords: Heavy metal; Road-layout; Atomic absorption spectrometry; Road deposited sediment; Contamination assessment.

Spatial variation of heavy metal pollution on an urban road network

Sudip K. Pal*; Steve G. Wallis and Scott Arthur

School of the Built-Environment, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS
**Corresponding author's e-mail: skp7@hw.ac.uk*

ABSTRACT

This study investigated the spatial variability of heavy metal emission patterns and associated measures of contamination on Riccarton Campus, Heriot-Watt University, Edinburgh, Scotland. Road deposited sediments were collected from 12-different sites representing typical road lay-outs over a 10 month period. The heavy metal concentrations of the road sediments were determined by strong nitric acid digestion and atomic absorption spectrometry. The contamination levels of the heavy metals in the road deposited sediments were assessed by the accumulation index, the degree of contamination and the ecological risk index. The outcomes of the investigation showed highly site-specific heavy metal emissions that primarily varied with road lay-out, with also influences from road surface condition, surrounding land use and traffic volume. The degree of contamination and the associated ecological risk index revealed that bus stops, a road bend, a road with speed control measures and a road intersection site were the pollutant hot-spot areas among all the sites that may likely pose moderate to considerable levels of pollution to the nearby water environment.

Keywords: Heavy metal; road deposited sediments; atomic absorption spectrometry; metal contamination; Edinburgh.

Assessment of Heavy Metals Emission on Road Surfaces

S.K. Pal[1], S.G. Wallis[2], S. Arthur[3]

[1]School of the Built-Environment, Heriot-Watt University, Edinburgh, UK,
skp7@hw.ac.uk
[2]School of the Built-Environment, Heriot-Watt University, Edinburgh, UK,
s.g.wallis@hw.ac.uk
[3]School of the Built-Environment, Heriot-Watt University, Edinburgh, UK,
s.arthur@hw.ac.uk

Abstract

Road deposited sediments (RDS) are regarded as sinks for metal pollutants derived from road-traffic that may find their way into nearby soils, plants, human beings or are washed-off by rain events to receiving streams posing danger for the environment. This study aimed to analyse RDS metal concentrations using Riccarton Campus of Heriot-Watt University, Edinburgh, Scotland as a study site. RDS samples were collected at two positions from different sites over a 4 month period to characterize the influence of traffic. The metal concentrations of the RDS were determined by strong nitric acid digestion and atomic absorption spectrometry. The mean concentrations were found to be 213.22, 57.36, 0.80, 15.75, 15.19, 118.20, 13497 mg kg-1 respectively from samples near to the curb and 210.93, 78.81, 1.80, 15.31, 8.70, 34.57, 14276 mg kg-1 respectively from samples 1 m from the curb for Zn, Cu, Cd, Cr, Ni, Pb and Fe, respectively. Furthermore for both positions the highest concentrations for all metals were associated with the finer fraction (<63 µm) and significant correlations between the metals were found further from the curb than near the curb, indicating that metals accumulating on the road surface further from the curb may all be of the same origin (traffic), while the sources of metals in the gutter are far more diverse.

Keywords: Heavy metals, atomic absorption spectrometry, road deposited sediment, particle size.

References

Ahyerre, M., Chebbo, G., Tassin, B. and Gaume, E. (1998) Storm water quality modelling, an ambitious objective? Water Science and Technology 37(1), 205-213.

Akan, A.O. and Haughtalen, R.J. (2003) Urban Hydrology, Hydraulics and Stormwater Quality – Engineering Applications and Computer Modelling. New Jersey: John Willey and Sons.

Akhter, M.S. and Madany, I.M. (1993) Heavy metal in street and house dust in Bahrain. Water, Air and Soil Pollution 66, 111-119.

Allott, R.W., Hewitt, C.N. and Kelly, M.R. (1990) The environmental half-lives and mean residence times of contaminants in dust for an urban environment: Barrow-in-Furness. Science of the Total Environment 93, 403-410.

Al-Khashman, O. (2007) Determination of metal accumulation in deposited street dusts in Amman, Jordan. Environmental Geochemistry and Health 29(1), 1-10.

Andral, M.C., Roger, S., Montrejaud-Vignoles, M. and Herremans, L. (1999) Particle size distribution and hydrodynamic characteristics of solid matter carried by runoff from motorways. Water Environment Research 71, 398–407.

APHA (1998) Standard methods for the examination of water and waste water-Technical report, 20th Edition. American Public Health Association, Washington DC, USA.

Appleton, J.D. (1995) Review of natural contamination in Great Britain. *Report No. PECD7/1/734*, 1995, Department of the Environment, London, UK.

Aryala, R. K., Furumai, H., Nakajima, F., and Boller, M. (2005) Dynamic behaviour of suspended pollutants and particle size distribution in highway runoff. Water Research 39(20), 5126-5134.

ASTM (2002) Standard Practice for Classification of Soils for Engineering Purposes, D2487-06. ASTM International, West Conshohocken: Pennsylvania.

Backstrom, M., Nilson, U., Hakanson, K., Allard, B. and Karlsson, S. (2003) Speciation of Heavy metals in road runoff and roadside total deposition. Water Air and Soil Pollution 147, 343-366.

Ball, D., Hamilton, R., and Harrison, R. (1991) The Influence of Highway-Related Pollutants on Environmental Quality: In Hamilton, R. and Harrison, R. (Eds.) *Highway Pollution, Elsevier Science,* New York, 1-47.

Ball, J.E.; Hogan, P.M.; Batley, G.E.; and Brockbank, C.I. (1994) Assessing the quantity and quality of stormwater runoff from road surfaces: In Water Down Under 94: Surface Hydrology and Water Resources Papers. Barton, ACT: Institution of Engineers, Australia, 299-304.

Ball, J.E., Jenks, R. and Aubourg, D. (1998) An assessment of the availability of pollutant concentrations on road surfaces. Science of the Total Environment 209, 243-254.

Banerjee, A.D.K. (2003) Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environmental Pollution 123, 95-105.

Bannerman, R.T., Owens, D.W., Dodds, R.B. and Hornewer, N.J. (1993) Sources of pollutants in Wisconsin stormwater. Water Science and Technology 28(3-5), 241-259.

Barrett, M. E., Zuber, R. D., Collins, E. R., Malina, J. F. Jr., Charbeneau, R. J., and Ward, G. H. (1993) A review and evaluation of the literature pertaining to the quality and control of pollution from highway runoff and construction. Report CRWR 239, Centre for Research in Water Resources, University of Texas at Austin.

Barrett, M.E., Malina, J.F., Charbeneau, R.J., and Ward, G.H. (1995) Characterization of Highway Runoff in the Austin, Texas Area. Report CRWR 263, Centre for Research in Water Resources, University of Texas at Austin.

Barrett, M., Irish, L., Malina, J., and Charbeneau, R. (1998) Characterisation of highway runoff in Austin, Texas area. Journal of Environmental Engineering 124, 131-137.

Beasley, G. and Kneale, P.E. (2004) Assessment of heavy metal and PAH contamination of urban streambed sediments on macroinvertebrates. Water Air Soil Pollution: Focus 4, 563-578.

Beckwith, P.R., Warren, R.S., Harrop, D.O. (1984) The behavior of sediment associated heavy metals within an urban surface runoff drainage system: In Proceeding of International Conference on Environmental Contamination, Edinburgh, UK, 785-790.

Blumberg, M.S. and Bell, J.M. (1984) Effect of various hydrological parameters on the quality of stormwater runoff from a West Lafayette, Indiana Urban Watershed. NTIS PB 84-207380, Environmental Protection Agency, USA.

Borrego, C., Tchepel, O., Costa, A.M., Martins, H., Ferreira, J. and Miranda, A.I. (2006) Traffic – related particulate air pollution exposure in urban areas. Atmospheric Environment 40, 7205-7214.

Boxall, A. and Maltby, L. (1997) The effects of motorway runoff on freshwater ecosystems: toxicant confirmation. Architectural Environmental Contamination Toxicology 33, 9-16.

Bouteligier, R., Vaes, G. And berlamount, J. (2002) Sensitivity of urban drainage wash-off models: compatibility analysis of Hydroworks QM and Mouse Trap using CDF relationships. Journal of Hydroinformatics 04, 235-243.

Brezonik, P.L. and Stadelmann, T.H. (2002) Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. Water Research 36, 1743-1757.

Brinkmann, W.L.F. (1985) Urban storm water pollutants: sources and loadings. Geojournal 11(3), 277-283.

Bris, F.J., Garnaud, S., Apperry, N., Gonzalez, A. Mouchel, J.M., Chebbo, G., et al. (1999) A street deposit sampling method for metal and hydrocarbon contamination assessment. Science of the Total Environment 235, 211-220.

Brown, J.N. and Peake, B.M. (2006) Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Science of the Total Environment 359, 145-155.

Butler, D., and Clark P. (1995) Sediment management in urban drainage catchments. *Report No. 134*, Construction Industry Research and Information Association (CIRIA), London, UK

Caltrans (2003) Guidance Manual: Stormwater Monitoring Protocols. Report No. CTSW-RT-03-105, California Department of Transportation, California, USA

Carraz, F., Taylor, K.G., Stainsby, S. and Robertson, D.J. (2006) Contaminated urban road deposited sediment (RDS), Greater Manchester, UK: A spatial assessment of potential surface water impacts. North West Geography 6, 10-19.

CCME (2007) Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment (CCME), Toronto, Ontario, Canada

Charbeneau, R.J. and Barret, M.E. (1998) Evaluation methods for estimating stormwater pollutant loads. Water Environment Research 70(7), 1295-1302.

Charlesworth, S. and Lee, J.A. (1999) The transport of particulate-associated heavy metals from source to deposit in the urban environment, Coventry, UK. Science of the Total Environment 235(1-3), 351-353.

Charlesworth S., Everett, M., McCarthy, R., Ordonez, A. and De Miguel, M. (2003) A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. Environment International 29, 563-573.

Chiew, F.H.S. and MacMahon, T.A. (1999) Modelling runoff and diffuse pollution loads in urban areas. Water Science and Technology 39(12), 241-248.

Christoforidis, A. and Stamatis, N. (2009) Heavy metal contamination in street dust and roadside soil along the major national road in Kavala’s region, Greece. Geoderma 151, 257-263.

CIRIA (1994) Control of Pollution from Highway Drainage Discharges. *Report 142*, Construction Industry Research and Information Association (CIRIA), London, UK

Clements, W.H., Carlisle, D.M., Lazorchak, J.M. and Johnon, P.H. (2000) Heavy metals structure benthic communities in Colorado mountain streams. Ecological Applications 10(2), 626-638.

Corder, G.W. and Foreman, D.I. (2009) Nonparametric statistics for non-statisticians: A step-by-step approach. Jhon Wiley & Sons, Inc.: New Jersey, USA

Crabtree, B., Moy, F., Whitehead, M. And Roe, A. (2006) Monitoring pollutants in highway runoff. Water and Environment 20, 287-294.

Crabtree, B., Dempsey, P., Johnson, I and Whitehead, M. (2008) The development of a risk-based approach to managing the ecological impact of pollutants in highway runoff. Water Science and Technology 57(10), 1595-1600.

Crabtree, B., Dempsey, P., Johnson, I. and Whitehead, M. (2009) The development of an ecological approach to manage the pollution risk from highway runoff. Water Science and Technology 59(3), 549-555.

Datry, T., Malard, F., Vitry, L., Hervant, F. and Gibert, J. (2003) Solute dynamics in bed sediments of a stormwater infiltration basin. Journal of Hydrology 273(1-4), 217-233.

Davis, B. and Birch, G. (2010) Comparison of heavy metal loads in stormwater runoff from major and minor urban roads using pollutant yield rating curves. Environmental Pollution 158, 2541-2545.

D'Arcy, B. J., Ellis, J. B., Ferrier, R., Jenkins, A., and Dils, R. (2000) Diffuse pollution impacts: the environmental and economic impacts of diffuse pollution in the UK. CIWEM Publication, London, UK

Dean, C.M., Sansalone, J.J, Cartledge, F.K. and Pardue, J.H. (2005) Influence of Hydrology on rainfall-runoff metal element speciation. Journal of Environmental Engineering 131(4), 632-642.

Deletic, A., Maksimovic, C. and Ivetic, M. (1997) Modelling of storm wash-off suspended solids from impervious surfaces. Journal of Hydraulic Research 35(1), 99-118.

Delectic, A., Maksimovic, C., Loughreit. F. and Butler, D. (1998) Modelling the management of street surface sediment in urban runoff: In *International Conference NOVATECH 98*, Lyon, France.

Deletic, A., Ashley, R. and Rest, D. (2000) Modelling input of fine granular sediment into drainage systems via gully-pots. Water Research 34(15), 3836–3844.

Deletic, A. and Orr, D.W. (2005) Pollution buildup on road surfaces. Journal of Environmental Engineering 131, 49-59.

de Deckere, E., De Cooman, W., Leloup, V. Meire, P., Schmitt, C., Peter, C., Ohe, v.d (2011) Development of sediment quality guidelines for freshwater ecosystems. Journal of Soils Sediments 11, 504-517.

De Minguel, E., Llamas, J.F., Chacón, E., Berg, T., Larssen, S., Røyset, O. and Vadset, M. (1997) Origin and patterns of distribution of trace elements in street dust: unleaded petrol and urban lead. Atmospheric Environment 31(17), 2733-2740.

DMRB-UK (1998) Design manual for roads and bridges: Water quality and drainage. *Technical Report, 11 (3), part 10*. Highway Agency, London, UK

Drapper, D., Tomlinson, R. and Williams, P. (2000) Pollutant concentration in road runoff: Southeast Queensland case study. Journal of Environmental Engineering 126(4), 313-320.

Dong, A., Simsiman, G.V. and Chesters, G. (1983) Particle-size distribution and phosphorus levels in soil, sediment, and urban dust and dirt sample from the Meonomonee River Watershed, Wisconsin, U.S.A. Water Research 17(5), 569-577.

Driscoll, E. D., Shelley, P. E., Strecker, E. W. (1990) Pollutant loadings and impacts from highway stormwater runoff, Vol. III: analytical investigation and research report, *Report No. FHWA-RD-88-008*, Feral Highway Administration, Office of Research and Development: Washington, D.C.

Droppo, I.G., Irvine, K.N. and Jaskot, C. (2002) Flocculation of cohesive sediments in the urban continuum: implications for stormwater management. Environmental Science and Technology 23, 27-41.

Duncan, H.P. (1995) A review of urban stormwater processes. *Report No 95/9,* Cooperative Research Centre for Catchment Hydrology, Australia

Duong, T.T.T. and Lee, B-K. (2011) Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. Journal of Environmental Management 92, 554-562.

EA (2003) Appendix 8: Standard for selected metals in Hydro-geological risk assessment for landfills. Environmental Agency (EA) for England and Welsh, Bristol, UK

Egodawatta, P. (2007) Translation of small-plot scale pollutant build-up and wash-off measurements to urban catchment scale. PhD thesis, Queensland University of technology, Queensland, Australia

Egodawatta, P., Thomas, E.C. and Goonetilleke, S.A. (2007) Mathematical interpretation of pollutant wash-off from urban road surfaces using simulated rainfall. Water Research 41(13), 3025-3031.

Ellis, J.B. and Revitt, D.M. (1982) Incidence of heavy metals in street surface sediment: solubility and grain size studies. Water Air Soil Pollution 17, 87-100.

Ellis, J.B. (1985) Urban Runoff Quality and Control: In Advance in Water Engineering. Elsevier Applied Science: London, 234-240.

Ellis, J.B. (1986) Pollutional aspect of urban runoff: In Urban Runoff Pollution Vol. G10: NATO ASI Series.

Ellis, J.B., Revitt, D.O., Harrop, A. and Beckwitha, P.R. (1987) The contribution of highway surfaces to urban stromwater sediments and metal loadings. Urban Pollution Research Centre, Middlesex University, UK

Ellis, J.B. and Hvitved-Jacobsen, T. (1996) Urban drainage impacts on receiving waters. Journal of Hydraulic Research 34(6), 771-783.

Ellis, J.B. (2000) Infiltration systems: A sustainable source-control option for urban stormwater quality management. Journal of the Chartered Institution of Water Engineering 14(1), 27-34.

Ewen, C., Maria, A., Anagnostopoulou, and Ward, N.I. (2009) Monitoring of heavy metal levels in roadside dusts of Thessaloniki, Greece in relation to motor vehicle traffic density and flow. Environmental Monitoring and Assessment 157, 483-498.

FHA (2000) Is Highway Runoff a Serious Problem? Office of Infrastructure R&D, Federal Highway Administration (FHA), Washington DC, USA

Fergusson, J.E. and Ryan, D.E. (1984) The elemental composition of street dust from large and small urban areas related to city type, source and particle size. Science of the Total Environment 34, 101-116.

Fergusson, J.E. and Kim, N.D. (1991) Trace elements in street and house dust: Sources and speciation. Science of the Total Environment 100, 125-150.

Folkeson, L. (1994) Environmental effects of highway runoff water: a literature review. *VTI Report No. 391A.* Swedish National Road and Transport Research Institute, Sweden

Furumai, H., Hijioka, Y. and Nakajima, F. (2001) Modelling and field survey on washoff behaviour of suspended particles from roofs and roads. Urban Drainage Modelling-Proceedings of the Specialty Symposium of the World Water and Environmental Resources Congress, Orlando, Florida, USA, 225-237.

Gan, H., Zhuo, M., Li, D. and Zhou, Y. (2008) Quality characterization and impact assessment of highway runoff in urban and rural area of Guangzhou, China. Environmental Monitoring and Assessment 140, 147-159.

Gasperi, J., Garnaud, S., Rocher, V. and Moilleron, R. (2009) priority pollutants in surface waters and settleable particles within a densely urbanised area: case study of Paris (France). Science of the Total Environment 407(8), 2900-2908.

Gibson, M.J., and Farmer, J.G. (1984) Chemical portioning of trace metal contaminants in urban street dirt. Science of the Total Environment 33, 49-57.

Glenn, D.W. and Sansalone, J.J. (2002) Accretion and partitioning of heavy metals associated with snow exposed to urban traffic and winter storm maintenance activities. Journal of Environmental Engineering 128, 167-185.

Göbel, P., Dierkes, C., and Coldewey, W.G. (2007) Storm water runoff concentration matrix for urban areas. Contaminant Hydrology 91, 26-42.

Goonetilleke, A., Thomas, E., Ginn, S. and Gilbert, D. (2005) Understanding the role of land use in urban stromwater quality management. Journal of Environmental Management 74(1), 31-42.

Goonetilleke, A., Egodawatta, P., and Kitchen, B. (2009) Evaluation of pollutant build-up and wash-off from selected land uses at the Port of Brisbane, Australia. Marine Pollution Bulletin 58, 213-221.

Granato, G.E., Dionne, S.G., Tana, C.K. and King, T.L. (2003) National Highway Runoff Water-Quality Data and Methodology Synthesis, Volume-I:Technical Issues for Monitoring Highway Runoff and Urban Stormwater. *Publication No. FHWA-EP-03-054,* Department of Transportation, Washington DC, USA

Gray, S.R. and Becker, N.S.C. (2002) Contaminant flows in urban residential water system. Urban Water Journal 4(4), 331-346.

Gray, L. (2004) Changes in water quality and macroinvertebrate communities resulting from urban stormflows in the Provo River, Utah, USA. Hydrobiologia 518, 33-46.

Greb, S.R. and Bannerman, R.T. (1997) Influence of particle size on wet pond effectiveness. Water Environment Research 69(6), 1134-1138.

Gromaire-Mertz, M.C., Garnaud, S., Gonzalez, A. and Chebbo, G. (1999) Characterization of Urban Runoff Pollution in Paris. Water Science and Technology 39(2), 1-8.

Grottker, M. (1987) Runoff quality from a street with medium traffic loading. Science of the Total Environment 59, 457-466.

Gupta, K and Saul, A.J. (1996) Specific relationship for the first flush load in combined sewer flows. Water Research 30(5), 1244-1252.

Hallberg, M., Renman, G. and Lundbom, T. (2007) Seasonal variations of ten metals in highway runoff and their partition between dissolved and particulate matter. Water Air Soil Pollution 181, 183-191.

Hamilton, R.S., Revitt, D.M. and Warren, R.S. (1984) Levels and physic-chemical association of Cd, Cu, Pb and Zn in road sediments. Science of the Total Environment 33, 59-74.

Han, Y., Lau, S.L., Kayhanian, M. and Stenstrom, M.K. (2006) Characteristics of highway stormwater runoff. Water Environment Research 78(2), 2377-2388.

Hakanson, L. (1980) An ecological risk index for aquatic pollution control- A sediment control approach. Water Research 14, 975-1000.

Harrison, R.M. (1979) Toxic metals in street and household dusts. Science of the Total Environment 11, 89-97.

Harrison, R.M. and Wilson, S.J. (1985) The chemical composition of highway drainage waters I. Major ions and selected trace metals. Science of the Total Environment 43, 63-77.

Harrison, R.M., Johnston, W., Ralph, J., and Wisen, S. (1985) The budget of Pb, Cu and Cd for a major highway. Science of the Total Environment 46, 137-145.

Heal, K.V., Hepburn, D.A. and Lunn, R.J. (2006) Sediment management in sustainable urban drainage system ponds. Water Science and Technology 53(10), 219-227.

Heal, K.V., Bray, R., Willingale, S.A.J., Briers, M., Napier, F., Jefferies, C. and Fogg, P. (2009) Medium-term performance and maintenance of SUDS: a case-study of Hopwood park motorway service area, UK. Water Science and Technology 59(12), 2485-2494.

Heaney, J.P. and Huber, W.C. (1984) Nationwide assessment of urban runoff impact on receiving water quality. Water Research Bulletin 20 (1), 35-42.

Hedley, G. and Lockley, J. (1975) Quality of water discharged from urban motorway water. Pollution Control 74, 659-674.

Helmreich, B., Hilliges, R., Schriewer, A. and Horn, H. (2010) Runoff pollutants of a highly trafficked urban road – correlation analysis and seasonal influences. Chemosphere 80, 991-997.

Herngren, L., Goonetilleke, S.A. and Ayoko, G.A. (2005) Understanding heavy metals and suspended solids relationship in urban stormwater using simulated rainfall. Journal of Environmental Management 76, 149-158.

Herngren, L., Goonetilleke, A. and Ayoko, G.A. (2006) Analysis of heavy metals in road-deposited sediments. Analytica Chemica Acta 571 (2), 270-278.

Hewitt, C. H., and Rashed, M. B. (1992) Removal rates of selected pollutants in the runoff waters from a major rural highway. Water Research 26, 311-319.

Hjortenkrans, D., Bergback, B.O. and Haggerud, A. (2006) New metal emission patterns in road traffic environment. Environmental Monitoring and Assessment 117, 85-98.

Hoenig, M. (2001) Preparation steps in environmental trace element analysis- Facts and traps. Talanta 54, 1021-1038.

Hoffman, E.J., Mills, G.L., Latimer, J.S. and Quinn, J.G. (1984) Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. Environmental Science and Technology 18(8), 580-587.

Hossain, I., Imteaz, M., Gato-Trinidad, S. and Shanableh, A. (2010) Development of a catchment water quality model for continuous simulation of pollutants build-up and wash-off. International Journal of Civil and Environmental Engineering 2(4), 210-217.

Hricko, J., Sefara, J., Kruzliak, P., Martinovic, M., Pospisil, M., Tkacova, H., Grand, T. and Szalaiova, V. (1993) Bratislava- life environment for abiotic components, Final report, Manuscript, Geo-complex, pp. 311

Huang, X., Hu, J., Li, C., Deng, J., Long, J. and Qin, F. (2009) Heavy-metal pollution and potential ecological risk assessment of sediments from Baihua Lake, Guizhou, P.R. China. International Journal of Environmental Health Research 19(6), 405-419.

ICRL (1983) Report on the redevelopment of contaminated sites in the UK. *ICRL Paper 59/83*, Inter-Departmental Committee on the Redevelopment of the Contaminated Land (ICRL), Department of Environment, London, UK

Irish, L. B., Lesso, W. G., Barrett, M. E., Malina, J. F. Jr., Charbeneau, R. J., and Ward, G. H. (1995) An evaluation of the factors affecting the quality of highway runoff in the Austin, Texas Area. *Technical Report CRWR 264*, Centre for Research in Water Resources, The University of Texas at Austin.

Irish, L. B., Barrett, M. E., Malina, J. F. Jr., and Charbeneau, R. J. (1998) Use of regression models for analyzing highway stormwater loads. Journal of Environmental Engineering 124, 987-993.

Jartun, M., Ottensen, R.T., Steinnes, E. and Volden, T. (2008) Runoff of particle bound pollutants from urban impervious surfaces studied by analysis of sediments from stormwater traps. Science of the Total Environment 396, 147-163.

Johnston, W. and Harrison, R. (1984) Deposition of metallic and organic pollutants alongside the M6 motorway. Science of the Total Environment 33, 119-128.

Kadi, M.W. (2009) Soil pollution hazardous to environment: A case study on the chemical composition and correlation to automobile traffic of the roadside soil of Jeddah city, Saudi Arabia. Journal of Hazardous Materials 168, 1280-1283.

Kalavrouziotis, I.K., Carter, J., Varnavas, S.P., Mehra, A. and Drakatos, P.A. (2007) Towards an understanding of the effect of road pollution on adjacent food crops: Zea mays as an example. International Journal of Environment and Pollution 30(3-4), 576-592.

Karlsson, K., Viklander, M., Scholes, L., Revitt, M. (2010) Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks. Journal of Hazardous Materials 178(1-3), 612-618.

Kayhanian, M., Singh, A., Suverkropp, C. and Borroum, S. (2002) The impact of annual average daily traffic on highway runoff pollutant concentrations. Road Ecology Centre, University of California, Davis, USA

Kayhanian, M., Singh, A., Suverkropp, C. & Borroum, S. (2003) Impact of annual average daily traffic on highway runoff pollutant concentrations. Journal of Environmental Engineering, 129(11), 975-990.

Kayhanian, M., Suverkropp, C., Ruby, A., Tsay, K. (2007) Characterization and prediction of highway runoff constituent event mean concentration. Journal of Environmental Management 85, 279-295.

Kayhanian, M., Stransky, C., Bay, S., Lau, S.-L. and Stenstrom, M.K. (2008) Toxicity of urban highway runoff with respect to storm duration. Science of the Total Environment 389, 386-406.

Kaur, S., Nieuwenhuijsen, M.J. and Colvile, R.N. (2007) Fine particulate matter and carbon monoxide exposure concentrations in urban street transportation microenvironments. Atmospheric Environment 41, 4781-4810.

Kennedy, P., Gadd, J., Moncrieff, I. (2002) Emission factors for contaminants released by motor vehicles in New Zealand. Ministry of Transport and Infrastructure, Auckland, New Zealand

Kerri, K.D., Howell, R.B., and Racin, J.A. (1985) Forecasting pollutant loads from highway runoff. Transportation Research Record, Vol. 1017, 39-46.

Kim, K.W., Myung, J.H., Ahn, J.S. and Chon, H.T. (1998) Heavy metal contamination in dusts and stream sediments in the Taejon Area, Korea. Geochemical Exploration 64, 409-419.

Kim, L-H., Kayhanian, M., and Stenstrom, M. K. (2004) Event mean concentration and loading of litter from highways during storms. Science of the Total Environment 330, 101-113.

Kim, L-H., Zoh, K.-D., Jeong, S.-M., Kayhanian, M., Stenstrom, M. K. (2006) Estimating Pollutant mass accumulation on highway during dry periods. Journal of Environmental Engineering 132, 985-993.

Kim, L-H., Ko, S-O., Jeong, S., and Yoon, J. (2007) Characteristics of washed-off pollutants and dynamic EMCs in parking lots and bridges during a storm. Science of the Total Environment 376, 178-184.

Kim, J. and Sansalone, J.J. (2008) Event-based size distributions of particulate matter transported during urban rainfall-runoff events. Water Research 42, 2756-2768.

Krčmová, K., Robertson, D., Cvečková, V., Rapant, S. (2009) Road-deposited sediment, soil and precipitation (RDS) in Bratislava, Slovakia: compositional and spatial assessment. Journal of Soils Sediments 9, 304-316.

Latimer, J., Hoffman, E., Hoffman, G., Fasching, J., and Quinn, J. (1990) Sources of petroleum hydrocarbons in urban runoff. Water Air Soil Pollution 52, 1-21.

Lau, Y.L., Marsalek, J. and Rochfort, Q. (2000) Use of a biofilter for treatment of heavy metals in highway runoff. Water Quality Research Journal of Canada 35(3), 563-580.

Lau, S. L. and Stenstorm, M. K. (2002) Metals and PAHs adsorbed to street particles. Water Research 39(17), 4083-4092.

Lau, S-L., Han, Y., Kang, J-H., Kayhanian, M. and Stenstrom, M.K. (2009) Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons. Water Environment Research 81, 308-318.

Laxen, D. and Harrison, R. (1977) The highway as a source of water pollution: An appraisal with the heavy metal lead. Water Research 11, 1-11.

Lee, J.H., Bang, K.W., Ketchum, L.H., Choe, J.S. and Yu, M.J. (2002) First flush analysis of urban storm runoff. Science of the Total Environment 293, 163-175.

Lee, H., Lau, S.L., Kayhanian, M. and Stenstrom, M.K. (2004) Seasonal first flush phenomenon of urban stormwater discharges. Water Research 38, 4153-4163.

Legret, M. and Pagotto, C. (1999). Evaluation of pollutant loadings in the runoff waters from a major rural highway. *The Science of the Total Environment*, Vol. 235, pp. 143-150.

Li, M.-H. and Barrett, M. E. (2008) Relationship between antecedent dry period and highway pollutant: conceptual models of build-up and removal processes. Water Environment Research 80(8), 740-747.

Li, M.-H., Barrett, M. E., Rammohan, P., Olivera, F., and Landphair, H. C. (2008) Documenting stormwater quality on Texas Highways and adjacent vegetated roadsides. Journal of Environmental Engineering 134, 48-59.

Linton, R.W., Natusch, D.F.S., Solomon, R.L. and Evans, C.A. (1980) Physicochemical characterisation of lead in urban dusts: A microanalytical approach to lead tracing. Environmental Science and Technology 4, 159-164.

Liu, A., Egodawatta, P., kjolby, M.J. and Goonetilleke, A. (2010) Development of pollutant build-up parameters for MIKE URBAN for Southeast Queensland, Australia: In International MIKE by DHI conference, Copenhagen, Denmark

Lu, X., Wang, L., Lei, K., Huang, J. and Zhai, Y. (2009) Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China, Journal of Hazardous Materials 161, 1058-1062.

Mackay, S. (1999) Sediment, nutrient and heavy metals characteristics of urban stormwater runoff. *Report No 139*, Urban Water Research Association of Australia

Mahbub, P., Goonetilleke, A., Ayoko, G.A., Egodawatta, P. And Yigitcanlar, T. (2010) Analysis of build-up of heavy metals and volatile organics on urban roads in Gold Coast, Australia: In the Proceedings of the NOVATECH 2010 - 7th International

Conference on Sustainable Techniques and Strategies for urban Water Management from 28 June to 1 July 2010 in Lyon, France.

Maltby, L., Boxall, A., Forrow, D., Calow, P., and C.I., B. (1995) The effects of motorway runoff on fresh water ecosystems: identifying major toxicants. Environmental Toxicology Chemistry 14(6), 1093-1101.

Manno, E., Varrica, D. and Dongarra, G. (2006) Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily. Atmospheric Environment 40, 5929-5941.

Marcovecchio, J. and Ferrer, L. (2005) Distribution and geochemical partitioning of heavy metals in Sediments of the Bahía Blanca Estuary, Argentina. Journal of Coastal Research 21 (4), 826 – 834.

Marsalek, J., Rochfort, B., Brownlee, B., Mayer, T., and Servos, M. (1999) An exploratory study of urban runoff toxicity. Water Science and Technology 39, 33-39.

Massoudieh, A., Abrishamchi, A. and Kayhanian, M. (2008) Modeling first flush and treatment simulation for a detention basin. Science of the Total Environment 398(1-3), 107-121.

McKenzie, D.J., and Irwin, G.A. (1983) Water-quality assessment of stormwater runoff from a heavily used urban highway bridge in Miami, Florida. *Water Resources Investigation Report 83-4153*, U.S. Geological Survey, Tallahassee, FL.

MIKE URBAN (2008) MIKE URBAN user’s manual. MIKE by DHI, Copenhagen, Denmark

Millar, R.G. (1999) Analytical determination of pollutant wash-off parameters. Journal of Environmental Engineering 125(10), 989-992.

Miller, L.E. (2005) Evaluation of sources of metals in stormwater runoff. University of Toledo, Ohio College of Engineering, USA

Moe, R.D., Bullin, J.A. And Polasek, J. C. (1978) Characteristics of Highway runoff in Texas. *Report No. FHWA-RD-78-197*, Federal Highway Administration, Office of Research and Development: Washington DC, USA

Mosley, L.M. and Peake, B.M. (2001) Partitioning of metals (Fe, Pb, Cu, Zn) in urban runoff from the Kaikorai Valley, Dunedin, New Zealand. New Zealand Journal of Marine Freshwater Research 35, 615-624.

Mungur, A., Schuttes, R., Revitt, D., and House, M. (1995) An assessment of metal removal from highway runoff by a natural wetland. Water Science and Technology 32, 169-175.

Murakami, M., Nakajima, F. and Furumai, H. (2004) Modelling of runoff behaviour of particle-bound polycyclic aromatic hydrocarbons (PAHs) from roads and roofs. Water Research 38, 4475–4483.

Namdeo, A.K., Colls, J.J. and Baker, C.J. (1999) Dispersion and re-suspension of fine and coarse particulates in an urban street Canyon. Science of the Total Environment 235(1-3), 3-13.

Napier, F., Brian, D.A. & Jefferies, C. (2008) A review of vehicle related metals and polycyclic aromatic hydrocarbons in the UK environment. Desalination 226, 143-150.

Napier, F., Jefferies, C., Heal, K.V., Fogg, P., Arcy, B.J.D. and Clarke, R. (2009) Evidence of traffic-related pollutant control in soil-based sustainable urban drainage systems (SUDS). Water Science and Technology 60(1), 221-230.

Neal, C. and Robson, A.J. (2000) A summary of river water quality data collected within the land-ocean interaction study: core data for eastern UK rovers draining to the North Sea. Science of the total Environment 251/252, 585-665.

Ngabe, B., Bidleman, T.F. and Scott, G.I. (2000) Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. Science of the Total Environment 255(1-3), 1-9.

Norrstrom, A. and Jacks, G. (1998) Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. Science of the Total Environment 218, 161-174.

Novotny, V., Sung, H.M., Bannerman, R. and Baum, K. (1985) Estimating nonpoint pollution from small urban watersheds. Journal of Water Pollution Control Federation 57, 744-748.

Novotny, V., Smith, D., Kuemmel, D. Mastriano, J. and Bartosova, A. (1999) Urban and highway snowmelt minimising the impact on receiving waters. Final Report to Water Environment Research Foundation.

Olli, R. (2003) Road salt as a pollutant in Helsinki urban streams, Southern Finland: In Proceedings of 1st International Conference on urban Drainage and Highway Runoff in Cold Climate in Riksgransen, Sweden.

Opher, T. and Friedler, E. (2010) Factors affecting highway runoff quality. Urban Water Journal 7(3), 155-172.

Ordonez, A., Loredo, J., De Minguel, E., and Charlesworth, S. (2003) Distribution of heavy metals in street dust and soils of an industrial city in northern Spain. Archives of Environmental Contamination and Toxicology 44, 160-170.

Pagotto, C.; Legret, M.; Cloirec, P.L. (2000). Portioning and First Flush of Metals in Urban Roadway Storm Water. *Journal of Environmental Engineering, Vol. 123(2)*: 134-143.

Patel, J.A. and Atkins (2005) Briefing: Review of CIRIA *Report 142* on highway pollutants. Proceedings of the Institution of Civil Engineers, Transport 158 (TR3), 137-138.

Paterson, E., Sanka, M. and Clark, L. (1996) Urban soil as pollutant sinks-A case study from Aberdeen, Scotland. Applied Geochemistry 11, 129-131.

Pihl, K.A. and Raaberg, J. (2000) Examination of pollution in soil and water along roads caused by traffic and road pavement:. In 24th International Baltic Road Conference, Riga.

Pitt, R.E. (1979) Demonstration of nonpoint abatement through improved street cleaning practices. *Report No. EPA-600/2-79/161*, Municipal Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, USA

Pitt, R.E., Field, R., Lalor, M. and Brown, M. (1995) Urban stromwater toxic pollutants: assessment, sources, and treatability. Water Environment Research 67(3), 260-275.

Pitt, R. E., Bannerman, R., Clark, S. and Williamson, D. (2004) Sources of pollutants in urban areas (Part-2): Recent sheet-flow monitoring: In James, W., Irvine, K.N., McBean, E.A. and Pitt, R.E. (Eds.), Monograph 13, 485-506.

Pittner, C. and Allerton, G. (2009) *SUDS for Roads*. SUDS Working Party, Edinburgh, UK [Accessed from scots.sharepoint.apptix.net/suds/General Publications/Suds for Roads (Published Aug 2009).pdf]

Preciado, H.F. and Li, L.Y. (2006) Evaluation of metal loadings and bioavailability in air, water and soil along two highways of British Columbia, Canada. Water Air Soil Pollution 172, 81-108.

Ramlan, M.N. and Badri, M.A. (1989) Heavy metals in tropical city street dust and roadside soils: a case of Kuala Lumpur, Malaysia. Environmental Technology Letters 6, 145-148.

Reinsdotter, K. and Viklander, M. (2007) Road salt influence on pollutant releases from melting urban snow. Water Quality Journal of Canada 42(3), 153-161.

Rob, B., Gerard, R., Rene, D., and Lood, V. (1999) Characterisation and treatment of runoff from highways in the Netherlands paved with impervious and pervious asphalt. Water Environment Research 71, 183-190.

Robertson, D.J., Taylor, K.G. and Hoon, S.R. (2003) Geochemical and mineral magnetic characterisation of urban sediment particulates, Manchester, UK. Applied Geochemistry 18, 269–282.

Robertson D.J. and Taylor, K.G. (2007) Temporal variability of metal contamination in urban road-deposited sediment in Manchester, UK: Implications for urban pollution monitoring. Water Air Soil Pollution 186, 209-220.

Roger, S., Montrejaud-Vignoles, M., Andral, M.C., Herremans, L. and Fortune, J.P. (1998) Mineral, physical and chemical analysis of the solid matter carried by motorway runoff water. Water Research 32(4), 1119-1125.

Rosner, L.A. (1982) Quality of urban runoff. Urban Stormwater Hydrology, American Geophysical Union, Washington DC, 161-188.

Rossman, L.A. (2004) SWMM 5: Stormwater Management Model user's manual. US Environmental Protection Agency, Washington DC, USA

Sansalone, J.J., Buchberger, S.G. and Al-abed, S.R. (1996) Fractionation of heavy metals in pavement runoff. Science of the Total Environment 189-190, 371-378.

Sansalone, J.J. and Buchberger, S.G. (1997) Characterization of solid and metal element distributions in urban highway stormwater. Water Science and Technology 36(8-9), 155-160.

Sansalone, J.J., Koran, J.M., Smithson, J.A., and Bucherger, S. G. (1998) Physical characteristics of urban roadway solids transported during rain. Journal of Environmental Engineering 124(5), 427-440.

Sansalone, J.J., Ying, G. and Lin, H. (2010) Distribution of metals for particulate matter transported in sources area rainfall-runoff. Journal of Environmental Engineering 136(2), 172-184.

Sartor, J.D. and Boyd, G.B. (1972) Water pollution aspects of street surface contaminants. *Report No. EPA-R2-72-081*, US Environmental Protection Agency: Washington, DC, USA

Sartor, J.D., Boyd, G.B. and Agardy, F.J. (1974) Water pollution aspects of street surface contaminants. Journal of the Water Pollution Control Federation 46(3), 458-465.

Schwar, M.J.R., Moorcroft, J.S., Laxen, D.P.H., Thomson, M., and Armorgie, C. (1988) Base line metal-in-dust concentration in Greater London. Science of the Total Environment 68, 25-43.

Sezgin, N., Ozcan, H.C., Demir, G., Nemioghu, S. and Bayat, C. (2003) Determination of heavy metal concentrations in street dusts in Istanbul E-5 highway. Environmental International 29, 979-985.

Shaheen, D.G. (1975) Contributions of urban roadways usage to water pollution. *Report No. EPA-600/2-75/004*, Municipal Pollution Control Division, Office of Research and Development, US Environmental Protection Agency: Washington DC, USA

Shaw, S.B., Walter, M.T. and Steenhuis, T.S. (2006) A physical model of particulate wash-off from rough impervious surfaces. Journal of Hydrology 327, 618-626.

Shi, G., Chen, Z., Bi, C., Li, Y., Teng, J., Wang, L., Xu, S. (2010) Comprehensive assessment of toxic metals in urban and suburban street deposited sediments (SDSs) in the biggest metropolitan area of China. Environmental Pollution 158, 694-703.

Shinya, M., Tsuchinaga, T., Kitano, M., Tamada, Y. and Ishikawa, M. (2000) Characterization of heavy metals and policyclic aromatic hydrocarbons in urban highway runoff. Water Sci. and Technology 42(7-8), 201-208.

Smolders, E. and Degryse, F. (2002) Fate and effect of zinc from tire debries in soil. Environmental Science and Technology 36(17), 3706-3710.

SNIFFER (2008) Source control pollution in sustainable drainage. Final report of project UEUW 01, Sotland Northern Ireland Forum for Environmental Research (SNIFFER), Edinburgh, Scotland

Soonthornnonda, P. and Christensen, E.R. (2008) A load model based on antecedent dry periods for pollutants in Stormwater. Water Environment Research 80(2), 162-171.

Stenstrom, M.K. and Kayhnian, M. (2005) First flush phenomena. Report CTSW-RT-05-73-02.6. California Department of Transportation, Sacramento, California, USA

Stone, M. and Marsalek, J. (1996) Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. Water Air Soil Pollution 87, 149-169.

Sutherland, R. C. and Jelen, S. L. (1996) Sophisticated stormwater quality modelling is worth the effort: In Advances in Modelling the Management of Stormwater Impacts, James, W. (Ed.), CHI: Guelph, Canada, 1-4.

Sutherland, R.A. and Tolosa, C.A. (2000) Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. Environmental Pollution 110, 483-495.

Sutherland, R.A., Tack, F.M.G., Tolosa, C.A. and Verloo, M.G. (2001) Metal extraction from road sediment using different strength reagents: Impact on anthropogenic contaminant signals. Environmental Monitoring and Assessment 71, 221-2001.

Sutherland, R.A. (2003) Lead in grain size fractions of road-deposited sediment. Environmental Pollution 121, 229-237.

Turner, A. and Simmonds, L. (2006) Elemental concentrations and metal bio-accessibility in UK household dust. Science of the Total Environment 371, 74-81.

USEPA (1986) Acid digestion of sediments, sludges, and soils - Section A, Part I, Chapter Three – Metallic analytes: In Method 3050. SW-846, Test methods for evaluating solid waste, USEPA: Washington, DC.

USEPA (1993) Natural wetlands and urban stormwater potential impacts and management. US Environmental Protection Agency, Washington, USA

USEPA (1995) Sediment and runoff erosion control for roads and highways. *EPA-841/F-95-008d*, Environmental Protection Agency (USEPA): Washington DC.

Van Metre, P.C., Mahler, B.J. and Furlong, E.T. (2000) Urban sprawl leaves its PAH signature. Environmental Science and Technology 34(19), 4064-4070.

Van Metre, P.C. and Mahler, B.J. (2003) The contribution of particles washed from rooftops to contaminant loadings to urban streams. Chemosphere 52(10), 1727-1741.

Vaze, J. and Chiew, F.H.S. (2002) Experimental study on pollutant accumulation on an urban road surface. Urban Water 4, 379-389.

Viklander, M. (1998) Particle size distribution and metal content in street sediments. Journal of Environmental Engineering 124, 761-766.

Vissikirsky, V.A., Stepashko, V.S., Kalavrouziotis, I.K. and Varnavas, S. P. (2008) The road pollution impact on Zea mays: Inductive modelling and qualitative assessment. Water Air Soil Pollution 195, 301-310.

Ward, N.I., Dudding A. and Lyndon, M. (2004) Platinum emissions and levels in motorway dust samples: Influence of traffic characteristics. Science of the Total Environment 334-335, 457-463.

Warren, N., Allan, I.J., Carter, J.E., House, W.A. and Parker, A. (2003) Pesticides and other micro-organic contaminants in freshwater Sedimentary environments – A review. Applied Geochemistry 18(2), 159-194.

Wei, B. and Yang, L. (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemical Journal 94, 99-107.

Westerlund, C., Viklander, M. and Backstrom, M. (2003) Seasonal variations in road runoff quality in Lulea, Sweden. Water Science and Technology 48, 93-101.

Westerlund, C. and Viklander, M. (2006) Particles and associated metals in road runoff during snowmelt and rainfall. Science of the Total Environment 362, 143-156.

Wilber, W.G. and Hunter, J.V. (1979) The impact of urbanisation on the distribution of heavy metals in bottom sediments of the Saddle River. Water Resources Bulletin 15(3), 790-800.

Wilson, C., Clarke, R., D’Arcy, B. J., Heal, K. V., and Wright, P.W. (2005) Persistent pollutants urban rivers sediment survey: implications for pollution control. Water Science and Technology 51(3-4), 217-224.

Wiseman, C.L.S. and Zereini, F. (2009) Airborne particulate matter, platinum group elements and human health: A review of recent evidence. Science of the Total Environment 407, 2493-2500.

WRc (2002) Long term monitoring of pollution from highway runoff: Final report. *Technical report no. uc 6037*, Water Research Council (WRc), London, UK

Wu, J. S., Allan, D. J., and Saunders, W. L. (1998) Characterization and pollutant loading estimation for highway runoff. Journal of Environmental Engineering 124 (8), 584-592.

Xiangdong, L., Chi-sun, P. and Pui Sum, L. (2001) Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied Geochemistry 16 (11-12), 1361-1368.

Yi Y., Hall, K. and Oldham, C. (2001) A preliminary model for predicting heavy metal contaminant loading from an urban catchment. Science of the Total Environment 266, 299-307.

Yongming, H., Peixuan, D., Junji, C. and Posmentier, E.S. (2006) Multivariate analysis of heavy metal concentration in urban dust of Xi'an, Central China. Science of the Total Environment 355, 176-186.

Yu, Y.J., Huang, H., Wang, X.D., Liu, D. and Wang, L.S. (2003) Sediment heavy metal pollution in the Huaihe River. Research in Environmental Science 16(6), 26-28 [in Chinese]

Zanders, J.M. (2005) Road sediment: Characterization and implications for the performance of vegetated strips for treating road runoff. Science of the Total Environment 339, 41-47.

Zgheib, S., Moilleron, R., Saad, M. and Chebbo, G. (2011) Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stromwater catchments? Water Research 45, 913-925.

Zhou, W., Beck, B.F. and Green, T.S. (2003) Evaluation of a peat filtration systems for treating highway runoff in a karts setting. Environmental Geology 44, 187-202.

Zhu, W., Bian, B. and Li, L. (2008) Heavy metal contamination of road-deposited sediments in a medium size city of China. Environmental Monitoring and Assessment 147, 171-181.

Zoppou, C. (2001) Review of urban storm water models. Environmental Modelling Software 16, 195-231.