FACULTY OF ENGINEERING & IT

INVESTIGATION OF INFLUENTIAL FACTORS ON HEAVY METAL CONCENTRATION IN URBAN ROADSIDE SOIL

A thesis submitted in fulfilment of the requirement of the degree of Doctor of Philosophy

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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ABSTRACT

Previous studies have found that there are a variety of factors that influence heavy metal concentrations in roadside soil. The first aim of this study was to investigate heavy metal (Pb, Zn, Cu, Cd, Cr and Ni) distribution patterns in terms of observing the influence by different factors such as soil type, soil depth, rainfall events and distance from traffic, in the roadside soil. In addition, the examination of the influence of these factors on the Pb isotopic ratio ($^{206}Pb/^{207}Pb$) variation in different chemical fractions is conducted also to discriminate between anthropogenic and natural sources.

One hundred and eighty soil samples were collected over more than one year at 1m, 5m and 10m from the road during pre-rainfall and post-rainfall conditions in Miranda Park, Sydney, Australia. This research area was selected for sampling as it is a unique site and allowed for the investigation at the one location of the critical influential factors. Each soil sample was analysed for total heavy metal concentration and chemical fractions were extracted by sequential extraction. The data was statistically analysed using a regionalisation technique to allow discrimination between natural and influential factors variability. Hence, this study statistically investigates the distribution of heavy metals in urban roadside soils (topsoils and subsoils) derived from different geologies at varying perpendicular distance from the road and the concentration changes of heavy metals in those soils pre- and post-rainfall periods.

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I

Chapter 1 INTRODUCTION

1.1 Overview

The rapid global population growth has resulted in an escalation of the volume of vehicle usage. This consequently has led to heavy metal contamination of surrounding areas in the form of road-deposited sediments (RDS) via atmospheric deposition from the vehicular emissions, ending up in the roadside soil. These heavy metals (the term ‘metal’ includes metals and metalloids throughout this study) have been derived from different sources such as: petrol and diesel exhaust, tyre wear, brake, catalyst or catalytic convertors and engine lubricants (Birch and Scollen, 2003, Hjortenkrans et al., 2006, Guney et al., 2010, Loganathan et al., 2013, De Silva et al., 2015, Wichmann and Bahadir, 2015). In the last few decades, numerous new elements have been used for automotive technologies which have eventually been released in the roadside environment resulting from vehicular movement. For example, Guney et al. (2010) described how the platinum group elements (PGE) have been used for catalyst and catalytic convertors to reduce air contamination. Hjortenkrans et al. (2006) reported antimony trisulfide (Sb_2S_3) has been used as a substitute for asbestos in brake pads. These metal emissions have not only accumulated in the roadside environment over time but have also been shown to have a low level of leaching. Several studies (Markus and McBratney, 2001, Snowdon and Birch, 2004, Gunawardena et al., 2013, Werkenthin et al., 2014) focused upon lead contamination in roadside soil have provided reliable evidence that although leaded petrol is no longer used, the roadside soils are still influenced by lead contamination and this scenario is possible to continue in the future. Thus the roadside environment, especially the roadside soil, has been subjected to pressure from heavy metal contamination which will lead to potentially detrimental impacts on not only human wellbeing but also the environmental health (He et al., 2013).

Over the last few years, numerous studies have focussed on heavy metal concentration, spatio-temporal distribution and source apportionment in roadside soil (Akbar et al., 2006, Legret and Pagotto, 2006, Dao et al., 2013, De Silva et al., 2015, Li et al., 2015). However, these studies have mainly concentrated on the influences of anthropogenic activities. In fact, every soil contains two major sources of heavy metal: natural and anthropogenic. The natural amounts of heavy metals are at concentrations called backgrounds. The magnitude of the natural metal concentrations depends on the composition of the soil parent material (De Temmerman et al., 2003, Scazzola et al., 2003, Guo et al., 2012, Karim et al., 2014).

Previous studies have explored the impacts of different factors on heavy metal accumulation distribution patterns and accumulation characteristics along/in the roadside soil. For instance, distance from traffic (Akbar et al., 2006, Chen et al., 2010, Dao et al., 2013, Curran-Cournane et al., 2015), soil type (Turer et al., 2001, Ciazela and Siepak, 2016) and climate (Olajire and Ayodele, 1997, Karim et al., 2014, Zhao and Hazelton, 2016) as the major factors have been mostly addressed.

However, soil type is derived from parent material weathered from '*in-situ*' geologies, and soil type can also determine the metal retention capacity in terms of impacting on different mechanisms, such as physical, chemical and biological processes. According to Wu et al. (2011) and Pagotto et al. (2001), the retention capacity is not only able to influence the metal accumulation in different soil layers, but also is able to have an affect on the composition of soil solution resulting in an impact on metal movement. Therefore, it is also critical to take account of the soil type in the reaction of heavy metal concentration in roadside soils. These previous studies have highlighted many factors influencing the heavy metal concentration of soil. A question, however, that remains unanswered is when are the differences in the field value of concentration due to influencing factors and when are they due to natural variability. Generally, there is field data available and hence techniques applied to discriminating influential factors need to be designed with recognition of this constraint.

1.2 Objectives and Contributions of Study

The main objective of this research is the assessment of the factors which influence heavy metal concentration in different roadside soil types. As will be shown in Chapter 2 (literature review) the influence of soil type has not been considered. Inclusion of soil type as an influential factor is an important component of this study.

To undertake this research the tasks were divided into 4 parts:

a) review of literature to develop a concept model
b) validation of the suitability through the correlation with previous studies
c) validation of the study site enabling an investigation of the influential factors
d) interpretation of collected data through chemical and statistical analysis of data

Tasks for obtaining the objective were

- Determining Pb, Zn, Cu, Cd, Cr and Ni concentrations as well as possible measuring the ^{206}Pb/^{207}Pb ratio.
- Applying chemical sequential extraction procedures (BCR) to extract Pb, Zn, Cu, Cd, Cr and Ni, and comparing the chemical fraction variations with the influential factors.
- Studying, in depth, integrating BCR and Pb isotopic ratio analysis in order to evaluate the anthropogenic and natural variations.

The key objectives of the statistical analyses are:

- Employing a regional frequency approach to extend the data population in order to conduct Student’s t-test for discrimination of influential factors.
- Determining the interrelationship among heavy metals and soil-associated factors through Pearson correlation analysis and multivariate statistical analysis.
- Assessing the heavy metal concentration level through using enrichment factor (EF)

1.3 Expected Contribution

Following this introduction, Chapter 2 provides a comprehensive literature review of past research on heavy metal concentration in roadside soils. The review covered the potential influencing factors which had been studied previously; a conceptual model based on up-to-date studies was created. The review explained the functions of potential influential factors impacting heavy metal concentrations in roadside soils and highlighted the influential factors neglected in historical studies. Additionally, chemical analytical methods, statistical analyses and methods used for heavy metal contamination assessments were also reviewed.

Chapter 3 describes the characteristics of the research site including the site location and history, underlying geology and local vegetation. This study is a field work based research; it is necessary to give the background information for visual understanding of the research site.

Chapter 4 depicts the methodologies and analytical techniques used for this study; it comprises the soil field work strategy, soil chemical analysis and statistical analysis methods for data interpretation.

Chapter 5 describes how an initial transect across the study site was conducted and confirmed the information described in Chapter 3. Chapter 5 relied on soil clay mineral analysis, the results also indicated the heavy metal distribution pattern and provided fundamental information for the design of the final soil sampling approach.

Chapter 6 shows the results obtained from two different chemical methods for extraction of the heavy metals; the heavy metal total concentrations were determined as well as the components of chemical fractions for each heavy metal. Furthermore, In addition to the determination of the Pb concentrations, the Pb isotopic ratios also were determined to discriminate between the anthropogenic and natural sources.

Chapter 7 illustrates three main statistical analyses which were applied for interpretation of the data; the analyses involved a regional frequency approach to extend the pollution data for Student’s t-test, using multivariate analysis and Pearson correlation analysis for determination of inter-relationships among heavy metals and soil-associated factors, and conducting the soil contamination assessment through enrichment factors (EF).

Chapter 8 presents the conclusions of the current research and recommendation for further research, followed by References and Appendices.

II

Chapter 2 LITERATURE REVIEW

2.1 Introduction

The soil is a limited natural resource, but rapid urbanisation with intensive anthropogenic activities has led to a deterioration in the soil quality. Recent studies in roadside soil have shown elevated concentrations of heavy metals which are a result of long-term emissions by vehicular traffic. In addition, soil is able to bind organic or inorganic pollutants via its adsorption mechanisms resulting in accumulation of contaminants. In an urban area, roadside topsoil, which is exposed to the atmosphere, can be contaminated by the traffic emission due to road-deposited sediment (RDS) via atmospheric deposition (Kartal et al., 2006). As a result, roadside soil near heavy traffic flow could be considered as an indicator of heavy metal contamination for an urban environment (Li et al., 2001). In the long term, road dust that comes from the atmospheric deposition by traffic emission and highway runoff may have serious environmental impacts on roadside soil.

Although improved technology such as engine design and new material development (unleaded petrol and brake linings) has led to a reduction in individual vehicle pollution, the amount of vehicle usage has been rapidly increasing in recent decades and new materials which have been substituted for certain pollutants has led to new environmental concerns (Perry and Taylor, 2009). For example, Guney et al. (2010) showed that the new group of metals named platinum group metals (PGM) which have already accumulated in the roadside soil, have been used for catalysts and catalytic convertors and the spread of PGM in the urban environment has already posed a potential risk of contamination for roadside soil since the 1990s (Schäfer and Puchelt, 1998, Whiteley and Murray, 2003, Morcelli et al., 2005).

The occurrence of heavy metals in roadside soil is often manifested as high pollution concentrations or loadings which may eventually result in detrimental impacts on human and ecological health (He et al., 2013). As a consequence, these high levels of heavy metal concentration could contribute to the environmental management and sustainability issues which are not generally encountered in more natural environments.

Several reviews have reported heavy metal contamination of roadside soil and the harmful impacts on the environment from the early 1970s onwards. Earlier reviews (Lagerwerff and Specht, 1970, Ward et al., 1974) explored the basic elements, and mainly focused on Pb pollution which has been related to the use of leaded petrol. Although leaded petrol has been banned for more than ten years (since 2000 in the European Union and 1 January 2002 in Australia) in most Western countries, researchers (Bakirdere and Yaman, 2008, Ayrault et al., 2012) still found that the concentration of Pb was retained at a high level in urban roadside soil due to the long period of usage of leaded fuel and continued to be sourced from the metal parts of the vehicle body (Turer et al., 2001). Furthermore, other elevated elements Fe, Mn, Zn, and Cu in roadside soil have also been studied by many researchers (Bakirdere and Yaman, 2008, Perry and Taylor, 2009, Guney et al., 2010, Davis and Birch, 2011, Olukanni and Adeoye, 2012, Škrbić and Đurišić-Mladenović, 2013).

In addition, researchers (Ball et al., 1991, Peterson and Batley, 1992) believed that vehicle-related heavy metal contamination originates from not only exhaust emission but also abrasion of tyres, brake lining emission and corrosion of vehicle body (Chan and Stachowiak, 2004). Eventually, those pollutants deposit and accumulate on the road surface and roadside topsoil by atmospheric deposition.

As shown by these studies, heavy metal accumulates in roadside soils by a variety of pathways. As a consequence, Hjortenkrans et al. (2006) highlighted that, as traffic emission is one of the major diffuse emission sources, it is important to gain detailed information about the various traffic-related sources, and also to understand how and where the heavy metals are dispersed. Several review papers have been published with regard to the investigation of ‘metal’ distribution and accumulation in the roadside soil in different sites. For example, Wei and Yang (2010) reviewed quite a few heavy metal accumulations from different cities in China; the studies conducted covered a 10 year period. They summarised the results obtained from different studies and used different environmental assessment methods to evaluate the contamination level.

In addition, Werkenthin et al. (2014) reviewed the heavy metal concentrations in soils and soil solution in 64 sites across a number of European roadsides. They focused on how the soil-related factors such as pH, soil organic matter (SOM) and percolation rate influenced the heavy metal distributions. These soil characteristics will vary with soil types which are inherently variable as a result of geology. Hence, there is a need to consider the soil type in relation to heavy metal concentration in roadside soils. The heavy metals have been deposited in the roadside environment through many anthropogenic activities. The recent occurrence of heavy metals in roadside soils has been comprehensively reviewed, and the collected data has been extracted from the studies performed in a number of countries/regions, as shown in Table 2-1.

The sources of heavy metals in the roadside soils are varied and often it is difficult to identify major sources of some pollutants because one single element may originate from multiple sources. However, most of the heavy metals have originated from traffic. Additionally, heavy metals generated from traffic can be divided into two major sub-categories: the most common and recognised source is traffic emission, the other one is from the vehicle bodies including the abrasion of brake linings/pads, tyre wear and wear of metal parts such as car body, clutch, or engine parts. Although in an urban area, traffic is widely recognised as the main source of contamination to the adjacent roadside soil and has been investigated by many studies, other potential sources such as industrial dust, road runoff and residential pollutants were also reported (Dao et al., 2013, Singh et al., 2013, Škrbić and Đurišić-Mladenović, 2013). Moreover, Morcelli et al. (2005) highlighted the PGE (platinum group elements) accumulated in roadside soils showing a similar distribution pattern to other traffic-related heavy metals such as Zn and Cu. Hence, the influential factors which control the heavy metal distribution pattern in roadside soil may also apply to platinum group elements.

The investigation of heavy metals in roadside soil generally includes three major steps. The first step is the field soil sampling investigation which involves the identification of sampling location and field soil texture analysis. This process normally provides a basic understanding of the location features and supplies background information for the soil descriptions. Additionally, the sampling strategies are generally developed in this step; for example, determination of the sampling distance, sampling depth, numbers of samples and sampling duration. The details of soil strategies in some studies are presented in Table 2-2. It can be noted from Table 2-2, that most of the studies illustrated and designed their field sampling methods.

After sample collection, the second step is the chemical analysis of the soil samples. During this step, chemical analyses were developed and utilised for heavy metal detection. The details of the review on chemical analyses are presented in section 2.3. Once the data was obtained from the chemical analysis, the interpretations of data based on statistical analysis such as multivariate analysis and Pearson correlation analysis was normally used for exploring the inter-relationship between different metals.

Table 2-1 Occurrence of some common heavy metal pollutants in roadside topsoil in different countries

Heavy metal	Concentrations (mg/kg, ppm)					
	China[a-1, d-2]	France[b-3. c-4]	Turkey[b-5, d-6]	India[b-7]	Ireland[d-8]	Nigeria[b-9, e-10, e-11]
Pb	35.4, 37.55 (17.11–77.27)	683,94 (20–3784)	45, 191 (21.1–1573)	280.5	39 (14–714)	5.18, 5.57–69.20, 205–730
Zn	92.1, 117.72 (52.17–227)	669,57 (27–1755)	255 (93.4–522)	176.4	94 (22–360)	20.5, 25.87–198.32, 43.5–213
Cu	29.7, 31.71 (21.22–42.52)	173,14 (6.7–201)	27.9, 68.7 (21.4–136)	32.3	25 (10–123)	2.26, 8.94–80.5
Cd	0.215, 0.43 (0.12–2.57)	1.85, 0.3 (0.1–2.7)	527	-	-	0.18–2.70
Cr	61.9, 58.87 (22.67–87.73)	77, 50 (21–80)	-	45.5	-	1.58–347, 20.6–104
Ni	26.7,27.53 (15.51–38.5)	14 (5.9–26)	-	25.5	-	0.68, 0.94–42.73, 10.9–115
As	8.1, 10.18 (6.16–14.89)	-	-	-	-	-
Fe	-	15000 (5800–36400)	-	-	-	403–1528.30, 1737–4455
Mn	-	277 (149–1406)	-	205.8	-	1115.4, 3.72–953.52, 86.2–355
Hg	0.24 (0.08–0.73)	-	-	-	-	-
Al	-	28300 (10800–33400)	-	-	-	-

[a] Average concentration;

[b] Maximum concentration;

[c] Median concentration with minimum and maximum concentration in the brackets;

[d] Average concentration with minimum and maximum concentration in the brackets;

[e] Minimum and maximum concentration;

1.Chen et al. (2010); 2. Wei and Yang (2010); 3.Legret and Pagotto (2006); 4.Pagotto et al. (2001); 5.Bakirdere and Yaman (2008);6.Guney et al. (2010);7.Ramakrishnaiah and Somashekar (2002); 8.Dao et al. (2013); 9.Azeez et al. (2014); 10.Olukanni and Adeoye (2012); 11.Olajire and Ayodele (1997)

Table 2-1
Occurrence of some common heavy metal pollutants in roadside topsoil in different countries (continued)

Heavy metal	Concentrations (mg/kg, ppm)				
	Greece[a-1, e-2]	Australia[a-3, e-4]	UK[a-5, c-6]	USA[d-7, e-8]	HIL[b-9]
Pb	359.4, 4.85–481.51	22–20278, 2910	175(25–1198), 232.7	96.5(14.3–227.8), 13–1910	600
Zn	137.8, 16.77–97.30	200–3000	150(56.7–480), 174.6	74.1(42.3–134.6), 79–1690	14000
Cu	42.7, 9.33–112.44	2–4141	80.4(15.5–240), 87.3	9–2780	40
Cd	0.2, 0.16–1.29	0–14	1.2(0.3–3.8), 1.4	0.8(0.62–1.14), <2–7	40
Cr	193.2, 2.20–31.87	-	-	8–363	200(VI), 240000(III)
Ni	58.2, 2.90–28.78	-	-	16.6(11.4–25.3), 5–154	600
As	62.3, 1.56–1634.46	-	-	<10–220	200
Fe	-	-	-	5600–145000	-
Mn	278.13–1391.63	-	-	158–3670	3000
Hg	0.1, 0.02–0.54	-	-	<0.02–13.1	30
Al	-	-	-	7750–74500	-

[a] Average concentration;

[b] Maximum concentration;

[c] Median concentration with minimum and maximum concentration in the brackets;

[d] Average concentration with minimum and maximum concentration in the brackets;

[e] Minimum and maximum concentration;

1.Christoforidis and Stamatis (2009);2.Papastergios et al. (2004);3.Markus and Mcbratney (1996);4.Al-Chalabi and Hawker (2000); 5.Motto et al. (1970); 6.Akbar et al. (2006);7.Gish and Christensen (1973); 8.Kay et al. (2008); 9. HIL: Health Investigation Limit.NEPC (1999);

Table 2-2 Field sampling strategies applied in recent studies on investigation for roadside soils contamination

Area	Elements	No. of samples	Distance from the road (unit: m)	Sampling depth (unit: cm)	Sampling site changes along the road	Sampling duration	reference
Berlin, Germany	Pb, Cu, Zn, Cr, Cd and Ni	142	2.5,5 and 10	0-30	no changes	11 months	Kluge and Wessolek (2012)
Beijing China	As, Cd, Cr, Cu, Ni, Pb and Zn	80	1,10 and 30	0-20	100 m interval	-	Chen et al. (2010)
Melbourne, Australia	Ag, As, Cd, Co ,Cr, CU, Mo, Mn, Ni, Pb, Pd, Pt, Sb, Se, Sn, Rh, Zn and W	30	2 to 5	0-10	27 sites with different land use	1 month	De Silva et al. (2015)
Kavala, Greece	Pb, Cu, Zn, Ni, Cr and Cd	96	3	around 1	12 sites with different land use	8 months	Christoforidis and Stamatis (2009)
Dublin, Ireland	Pb, Cu and Zn	225	0 to 70 (intervals of 5)	0-10	rectangular grid 70 m (intervals of 5)	1 month	Dao et al. (2013)
Paris, France	Pb, Cu, Zn, Cd, Cr and Ni	29	0.5, 1.8, 2.5, 5, 10	0-2, 2-10, 10-30	width 10 m	1 month	Pagotto et al. (2001)
Nantes, France	Pb, Cu, Zn, Cd and Cr	-	0.5, 5 and 25	0-2, 2-10, 10-30	-	1 year	Legret and Pagotto (2006)
Elazig, Turkey	Pb, Cu and Cd	-	0, 25, 50	0-5	4 sites on both sides of one single road	-	Bakirdere and Yaman (2008)
Dubai, United Arab	Pb, Cu, Zn, Cd and Ni	-	< 5	surface soil	22 sites	-	Aslam et al. (2013)
Bangalore, India	Pb, Cu, Zn, Cd, Cr, Ni and Mn	12	-	0, 2, 5,10,15 and 20	5 sites	2 years	Ramakrishnaiah and Somashekar (2002)
Abeokuta, Nigeria	Pb, Cu, Zn, Cd, Cr, Ni and Mn		0, 50, 100, 150 and 200	0-20, 20-40, 40-60, 60- 80 and 80-100	3 sites	-	Azeez et al. (2014)
São Paulo, Brazil	Pt, Pd and Rh	-	0.4, 1.4, 2.4, 3.4, 4.4 and 5.4	5	rectangular grid 4 sites along 4 m	1 month	Morcelli et al. (2005)
Perth, Australia	Pt, Pd and Rh	-	< 0.5	0-1	4 sites	12 months	Whiteley (2005)
Perth, Australia	Pt, Pd and Rh	-	< 0.5	0-1	11 sites	-	Whiteley and Murray (2003)

The review on statistical methods is presented in section 2.4.

However, no attempt has been made in the literature to provide a comprehensive summary of the up to date techniques used for investigation of the concentration of heavy metals in roadside soil. Therefore, the first aim of this review is to summarise and critically evaluate the existing techniques currently used for investigation of the concentration of heavy metals in roadside soils; this consists of the soil sampling strategy, chemical analysis and statistical analysis. Additionally, the potentially influential factors which could impact the heavy metals distribution and accumulation pattern are systematically summarised. A conceptual model (Figure 2-1) based on current studies was developed during this study to visually illustrate the occurrences of these influential factors.

2.2 Influencing Factors

Heavy metal pollutants in roadside soil have been investigated in many countries; the concentrations of many heavy metals in different studies have been summarised in Table 2-1. It can be noted that reported concentrations of heavy metals in different studies reveal substantial spatial and temporal variations, which are essentially due to a number of influencing factors. Hence, the occurrence of heavy metals in terms of accumulation and distribution in roadside soil is substantially influenced by a range of factors. These influencing factors are able to be interpreted in four-dimensions: along the roadside (x-axis), distance away from the road (y-axis), the soil vertical impact (z-axis) and temporal variation. Previous research into heavy metal concentration adjacent to roads will be presented by using these dimensions as a conceptual model that is illustrated in Figure 2-1.

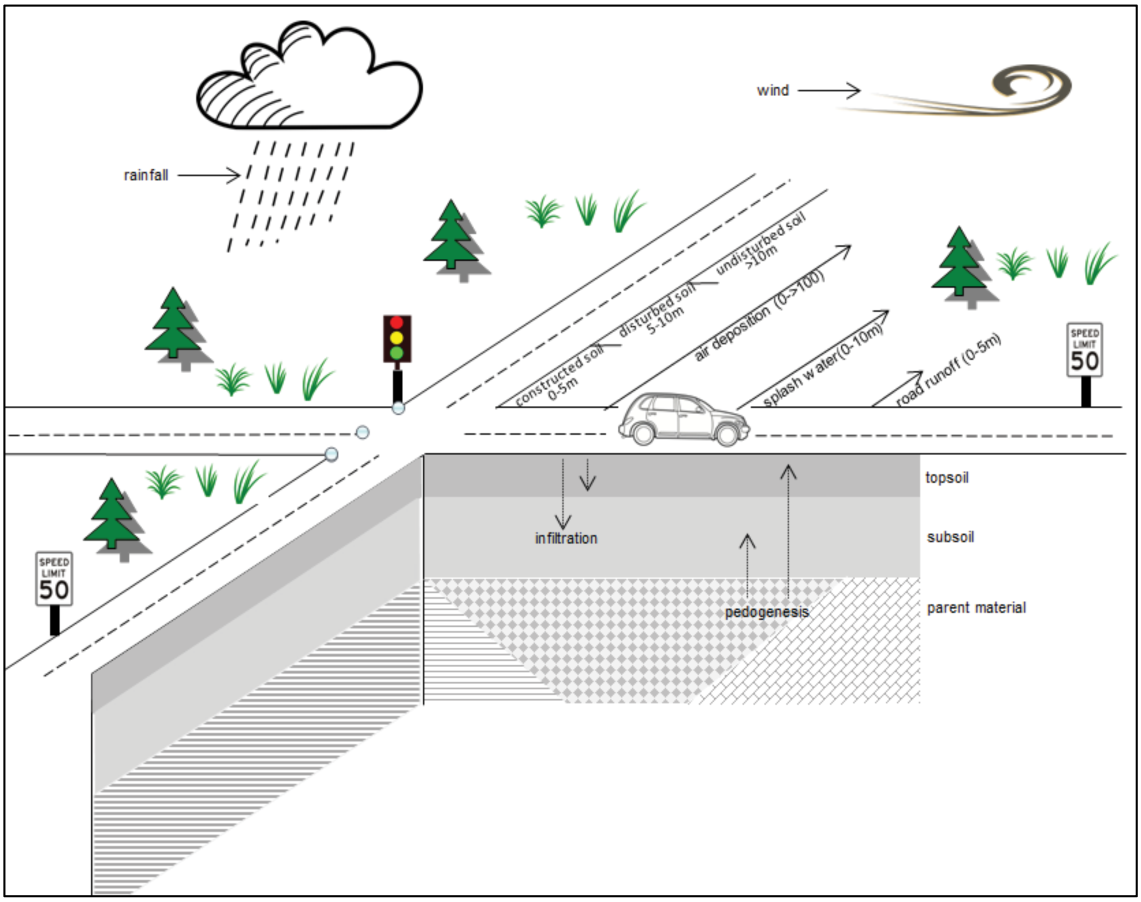

Figure 2-1 The conceptual model designed for heavy metal contamination in roadside soil

2.2.1 Influence of Distance from the Road Edge

Distance from the road edge has generally been considered as a factor in terms of impacting heavy metals distribution patterns in roadside soil, and also distance-associated soil sampling has been widely applied for the soil investigation strategy. It has been reported that the heavy metal concentration decreased exponentially with increase of the distance from the road edge and the distribution pattern parallel to the roadside within a certain distance scope (Legret and Pagotto, 2006, Bakirdere and Yaman, 2008, Davis and Birch, 2011, Wu et al., 2011, Yan et al., 2012, Werkenthin et al., 2014). The distance from the road edge directly controls and restricts the heavy metal transport pathways to the surrounding roadside environment. Legret and Pagotto (2006) highlighted that the particulate or dissolved inorganic pollutants could transfer into the surrounding environment through atmospheric deposition or the infiltration of road runoff and spray water. The distance at which the influence of road traffic on heavy metal concentrations in roadside soils is detectable can, therefore, vary greatly; Grigalavičienė et al. (2005) found Pb is still easily mobile and exceeded maximum limits concentrations at a distance of 40 m from the traffic, whereas Turer and Maynard (2003) argued that the wind-blown induced heavy metal pollutants for roadside soil could reach up to 250 m away from the road. Thus, referring back to the conceptual model (Figure. 2-1), the roadside soil away from the traffic areas can be divided into 3 zones depending on the pathways: heavily influenced (HI, 1-5 m); medium influenced (MI, 5-10 m); rarely influenced (RI, 10-300m). The comparison of heavy metal concentration distribution patterns among these three zones from different studies is presented in Figure 2-2.

Hence, it is essential to understand the heavy metal pathways to the surrounding roadside environment; the pollutants, which are predominantly sourced from the traffic, can transfer into roadside soil via aerial deposition, infiltration of road runoff and splash water (Legret and Pagotto, 2006, Bakirdere and Yaman, 2008, Loganathan et al., 2013). Notably, according to Kocher et al. (2005), it can be argued that infiltration rates in the roadside environment are largely enhanced (13-18 times) by road runoff and splash water especially when observed at a short distance from the road edge. Additionally, they showed that the topographic features of the catchments beside the roads also have potential impacts on the infiltration rates and found that the presence of the slope of the hard shoulder of the road can increase the soil infiltration rates up to 14 times greater at a distance of 1.5-2 m compared to the undisturbed areas. Thus, it can be understood that at a certain distance from the road, the elevated heavy metal concentration may result from multi-pathways. Haygarth and Jones (1992) implied that the decreasing heavy metal concentration with increasing distance from the roadside was possibly because of heavy metals emitted from vehicle exhausts in particular forms which are forced to settle under gravity closer to the road edge. Moreover, it has also been reported by Pagotto et al. (2001) that the soil-related factors such as organic matter (SOM) also decreased with increasing distance from the road edge; this trend may be due to the high accumulation rate of organic matter including debris such as paper and hydrocarbons close to the roadway. In addition, Azeez et al. (2014) also reported that the increasing distance can result in a decrease in the soil organic matter (SOM) and electrical conductivity (EC); they explained the high SOM and EC was potentially caused by anthropogenic factors. The studies presented in this section have shown that distance from the roadside edge is an important factor. Hence this factor has been included in the experimental design outlined in chapter 4.

2.2.2 Influence Along Roadside

The roadway is a part of the entire urban traffic system facilities; a single road may link and cross a wide range of different land use areas. Several studies (Kelly et al., 1996, Pouyat et al., 2007, Li et al., 2013) explored the potential influence of urban land use on the soil contamination; they pointed out that the land use served as an indicator of disturbance in urban soil, as for example, soils in an isolated site with an industrial background are often found associated with exceedingly high heavy metal concentrations. Vehicular transport along road corridors is limited and controlled by the surrounding road conditions which are, for example, traffic lights, road speed limits, deceleration strips and roundabouts. These anthropogenic restrictions are initially designed for providing a safe and orderly traffic condition; hence, these roadside limitations can directly influence vehicular movement behaviour. The consequences of influences from these restrictions are no more than vehicular deceleration or acceleration.

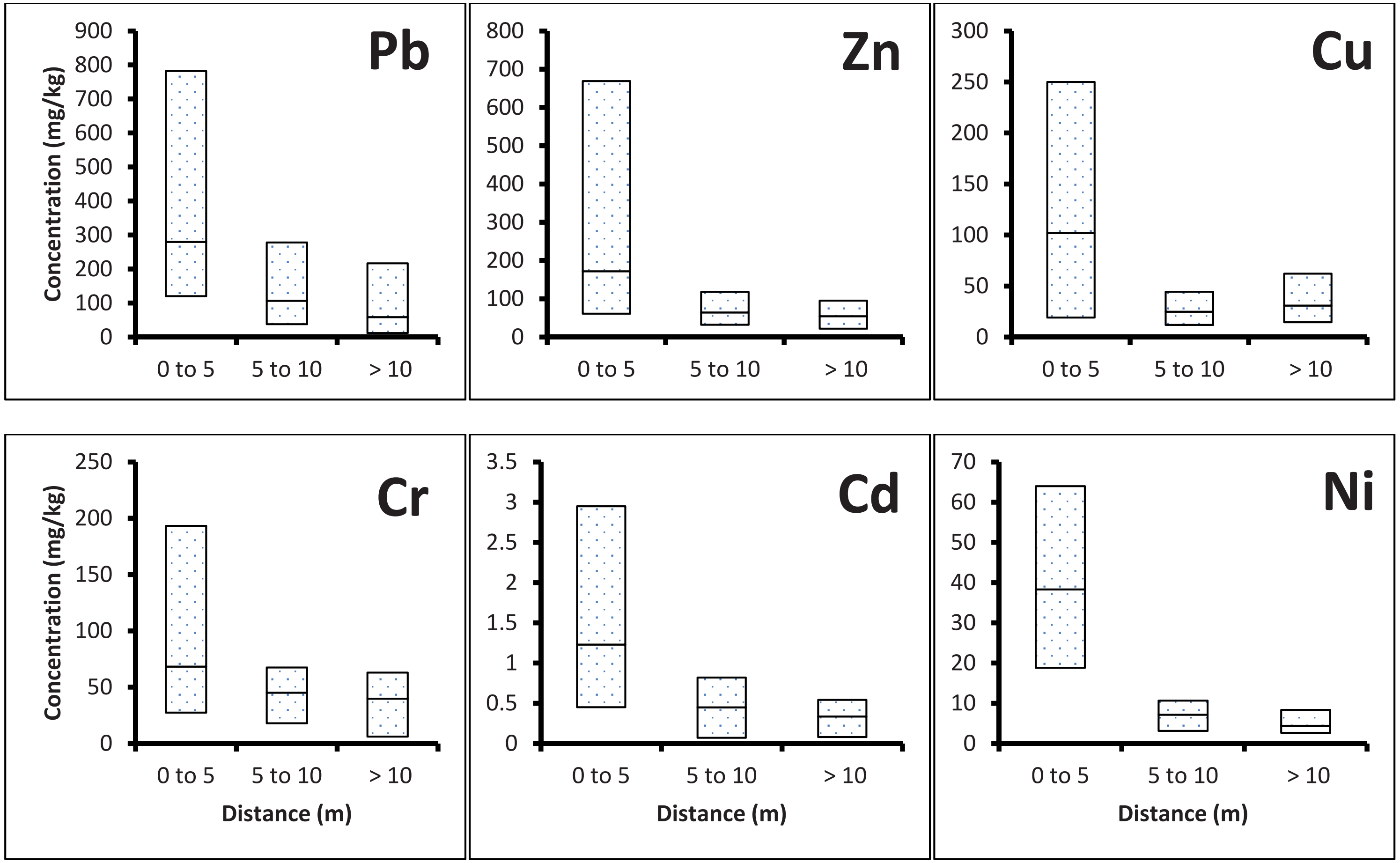

Figure 2-2 Metal concentrations in roadside topsoils as a function of distance to the road edge (mean: middle line, upper line: maximum value and the lower line: minimum value). The data are taken from the studies:1.Pagotto et al. (2001); 2.Christoforidis and Stamatis (2009); 3.(Fakayode and Olu-Owolabi, 2003); 4.Modlingerová et al. (2012); 5.Legret and Pagotto (2006); 6. Olajire and Ayodele (1997); 7.Ndiokwere (1984); 8.Mbah and Anikwe (2010); 9.Bakirdere and Yaman (2008).

For example, road speed limits are applied to indicate the maximum speed (or minimum in some cases) and are generally presented by a traffic sign beside the roadside. Thus, vehicular deceleration or acceleration mostly occurred at the beginning of the area of those speed limits; the occurrence of deceleration is largely related to the function of the brake pads and the force of friction generated between the tyre and the road surface. Thus, the deceleration can lead to intensive abrasion of brake pads and tyres especially during the beginning area of a maximum speed limit. Aslam et al. (2013) observed and compared seven heavy metal contaminations in roadside soil under different numbers of traffic signals with background levels; the highest heavy metal concentration was observed from sites at roundabouts with more than two traffic signals and the lowest heavy metal concentrations was found at sites with no traffic signals. In addition, Whiteley and Murray (2003) explored the presence of PGEs (platinum group elements) in roadside soil; they claimed that the topography along the roadside and the driving style varied along the road exerting influence on PGE accumulation rather than traffic volume. The landscapes and land uses are also able to change the distribution pattern along roadside soil and it is important to understand the function of land use in heavy metal accumulation along the roadside soil. On the other hand, the consequence of vehicular acceleration is mostly considered to be associated with high fuel consumption and high emission. El-Shawarby et al. (2005) simulated vehicle movement by the VT-Micro model (a nonlinear regression model that utilizes a multi-dimensional polynomial model structure) and demonstrated that as the level of aggressiveness for acceleration manoeuvres increases, the fuel-consumption and emission rates per manoeuvre decrease because the vehicle spends less time accelerating. These studies have shown there will be variability along the road. Important factors from the studies for this variation have been suggested, for example, traffic lights, road speed limits, deceleration strips and roundabouts. The experimental design in chapter 4 attempted to ensure the consistency of traffic motion.

2.2.3 Influence of Soil Depth

In addition to the horizontal influence by distance, the importance of soil vertical impact on heavy metal concentration distribution has also been reported in various studies (Turer et al., 2001, Hjortenkrans et al., 2006, Li et al., 2013). The evaluation of heavy metal contamination in roadside soil also relies on the application of a sampling strategy through investigation of heavy metal level gradients in different soil depth. It was well documented that the soil depth-related factor can substantially influence the heavy metal distribution pattern in roadside soil and this commonly stimulated their consideration to design a proper methodology to investigate this roadside soil issue (Kluge and Wessolek, 2012). Interpretation of published literature suggests that the heavy metals mostly accumulated in the topsoil which is generally recognized as from the surface of the soil down to a maximum of 10 cm in depth. In comparison to the topsoil, roadside subsoils (10-30 cm) were found to have less contamination with heavy metals (Amusan et al., 2003, Yang et al., 2007, Batjargal et al., 2010). Hence, the presence of heavy metals in roadside subsoils had been given less emphasis. The heavy metals from anthropogenic sources are introduced in subsoils mainly via leachate. However, a clear vertical heavy metal distribution trend could not be found. One possible reason for higher heavy metal enrichment in topsoils is the physical retardation of particulate bound trace elements (Boivin et al., 2008). A study by Batjargal et al. (2010) had investigated the heavy metal concentrations in subsoil but they found there was no infiltration of heavy metal into subsoil. In fact, compared to the topsoil, the most remarkable feature of subsoil is its lack of organic matter and humus content; it has been shown that the soil absorbability of heavy metal increased by increasing the soil organic matter (SOM); thus SOM is normally recognized as an important scavengers for heavy metal in soils (Turer and Maynard, 2003), especially related with HCl-extracted heavy metals (Bermudez et al., 2010). Additionally, Ramakrishnaiah and Somashekar (2002) investigated the function of soil pH and organic carbon influencing the heavy metal accumulation in different soil depths; they classified the soil depth into 7 vertical zones: 0, 2, 5, 10, 15, 20, 30 cm and found the heavy metals are mainly accumulated in the 0, 2 and 5 cm depth. In addition, they reported that heavy metals except Ni and Cr, have elevated concentrations and presented strong correlation with soil pH and organic carbon. Similar results were also reported by Chen et al. (2005) and Lu et al. (2003) that there was no largely increase for Ni and Cr concentrations in roadside soil due to traffic emission. Moreover, Chen et al. (2010) studied the heavy metal concentrations in roadside soil in Beijing, China. They pointed out that the black carbon (BC) is mainly accumulated and deposited onto the surface layer of roadside soil, which mainly comes from traffic emission. They claimed that the BC is significantly positively correlated with most heavy metals; the correlations were obtained from Pearson's correlation analysis. In addition, Paulette et al. (2006) argued that soil humus content was involved in the reaction in the formation of stable heavy metal compounds; from the coefficients of correlation results obtained in their study, it was shown that humus content had also led to significant impacts on lead and zinc compounds formations. According to Figure 2-3, a comparison of the heavy metal mean concentrations between topsoils and subsoils (data obtained at distances from 0 to 5 m from the road edge) are illustrated. The studies have considered the heavy metal concentrations in topsoils are substantially higher than in the subsoils.

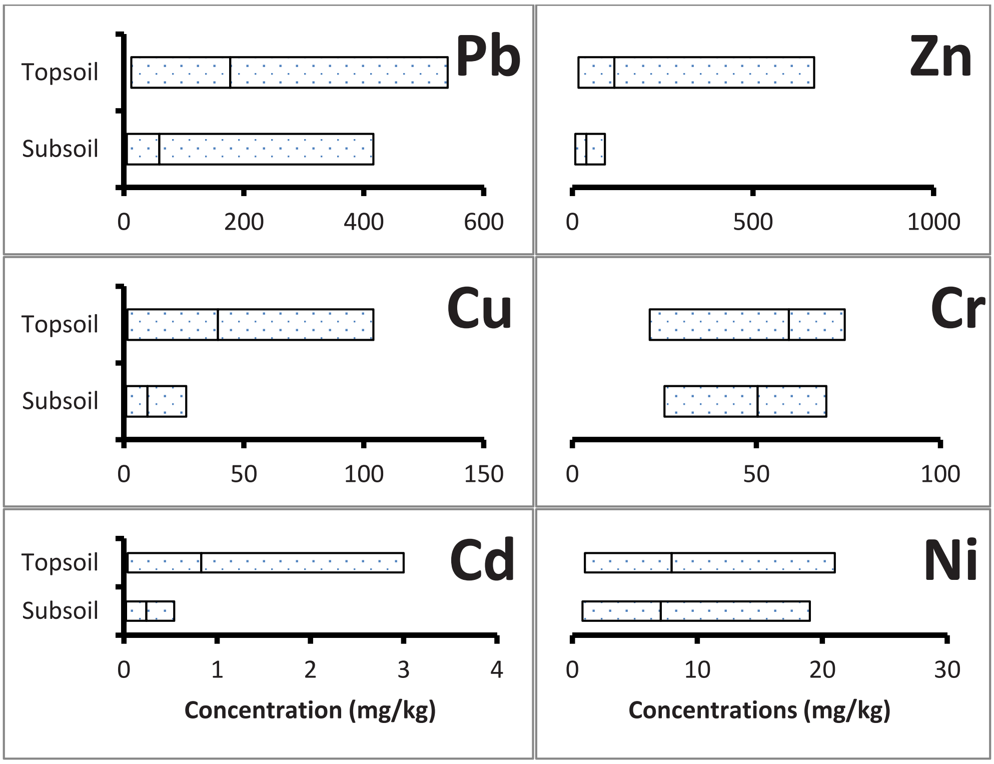

Figure 2-3 Metal concentrations of roadside soils at 0 to 5 m distance as a function of soil depths (mean: middle line, left line: minimum value and right line: maximum value). The data are taken from the studies: 1.Legret and Pagotto (2006); 2.Curran-Cournane et al. (2015); 3.Brümmer (1986); 4,Kluge and Wessolek (2012); 4.David and Williams (1975).

Studies discussed previously have considered total heavy metal concentrations which do not take into account the naturally occurring background concentrations with no human derived inputs. In general, the soil heavy metal concentration is derived from the weathered geology from which the soil is formed. The amount of environmental heavy metals which is bioavailable is usually low because the heavy metals are incorporated into the soil matrix (Reichman, 2014). Although Yesilonis et al. (2008) considered the anthropogenic heavy metal concentrations by subtracting the background concentration from the measured concentrations; they did not relate the background concentration to the geology of the region. However, these is no research which considers the function of inherent geology and resulting soil type impacting on the heavy metal accumulation and distribution in roadside soil. Therefore, this is one of the neglected factors apparent from the review of the literature.

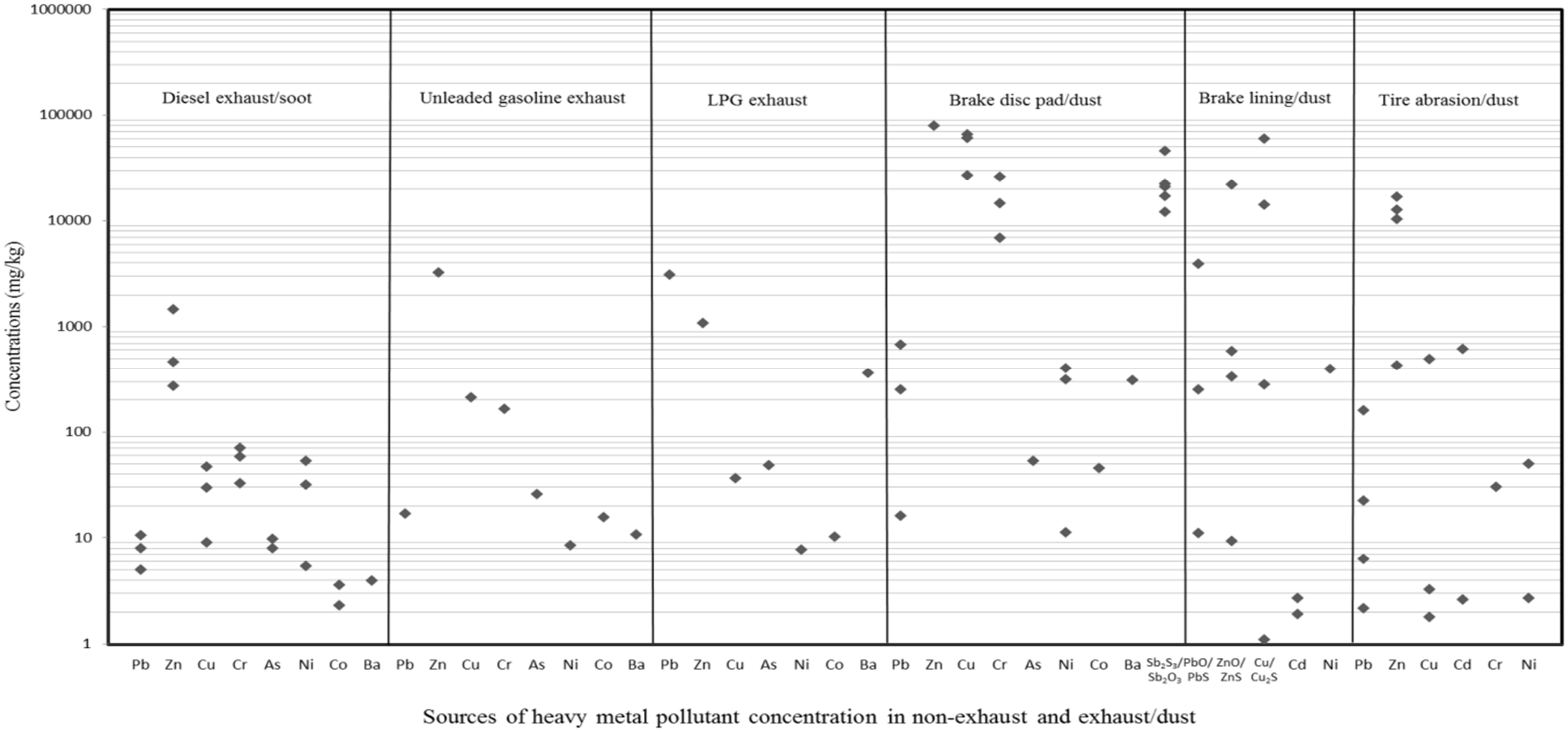

Figure 2-4 Summary of sources of heavy metal pollutant concentration[a] (on the logarithmic Y axis) for roadside soil by a vehicle in non-exhaust and exhaust/dust from other studies[b]

[a] results including both total acid extractable and water extractable form

[b] 1.Kadıoğlu et al. (2010);2.Hildemann et al. (1991);3.Legret and Pagotto (1999);4.von Uexküll et al. (2005); 5, Davis et al. (2001); 6.Ozaki et al. (2004); 7.Shupert et al. (2013); 8.Varrica et al. (2013); 9.Agarwal et al. (2011); 10. Figi et al. (2010); 11. von Uexküll et al. (2005)

2.2.4 Influence of Temporal Variability

In order to develop an appropriate management approach and comprehensive monitoring strategy towards heavy metal concentrations in roadside soil, it is also crucial to take account of the temporal variability. However, unlike many studies focused on the spatial factors impacting on the heavy metal distribution and accumulation in roadside soil, only a limited number of studies have been focused on the influence of the temporal factors. The weather and road conditions are the two major factors which have been widely considered in most studies. In detail, the road condition consists of road age and traffic density. On the other hand, some researchers (Turer et al., 2001, Kluge and Wessolek, 2012) argue on the consequences from different aspects of weather conditions such as the impacts of occasional rainfall and snow events as well as the prevailing wind. The characteristic of heavy metal retention in roadside soil is that it is not laterally mobile; therefore, over a long period of time, the heavy metals have leached through the soil matrix. This can be used to explain that even though using leaded petrol was prohibited in most of the countries for more than 10 years, recently elevated Pb concentrations are still found in many studies (Hu et al., 2014, Zhang et al., 2016).

Regarding the weather conditions, a few studies (Chon et al., 1998, Turer et al., 2001, Kluge and Wessolek, 2012) reported the importance of rainfall impacting the heavy metal concentrations in the roadside. Rainfall events can contribute an intensive surface run-off which normally carries an abundance of heavy metals to the soil matrix. Barrett et al. (1998) who studied the characterization of highway runoff reported that the concentrations of constituents in runoff are related to traffic density, rainfall intensity and other factors. In addition, they highlighted that vehicles not only provide a continuous input of pollutants to the road surface but also could impact on the duration of runoff events. Lee and Touray (1998) studied the heavy metal geochemical behaviours in artificial soils; it was found that if the pH of the runoff from rainfall events is slightly below 7.0, the Cd and Zn going to solution more easily than Pb during the rain water leaching reaction. Additionally, it is noted that the adjacent soils are still impacted by the splashing water even after the rainfall events due to the traffic travelling through the water hazard area along the road.

A systematic investigation had been conducted by De Silva et al. (2015); they explored the correlation between road conditions and heavy metal concentrations in Australia, and the multiple regression analysis indicated the road age and traffic density are strong factors that correlated with heavy metal concentrations. Additionally, Imperato et al. (2003) investigated the variation of heavy metal concentration over 25 years; they also found the typical elements such as Pb, Zn and Cu have significantly increased due to rapidly increasing atmospheric deposition in Italy. Moreover, some studies (Ho and Tai, 1988, Amusan et al., 2003, Fakayode and Olu-Owolabi, 2003, Azeez et al., 2014) concentrated on the function of traffic forms impacting on the heavy metal distribution in roadside soil; they implied that not only the traffic density but also the major component of vehicle forms could be a potential factor impacting on the form of vehicle emission. However, in a study conducted by Bai et al. (2009), they explored the soil heavy metal concentrations around four different roadsides in Yunnan, China. The results from this study demonstrated that the heavy metal concentrations in Dali Roadside soils (open to traffic for more than 20 years; approximate AADT: 15,000) are much higher than Dabao Highway soils (open to traffic for 5 years; approximate AADT: 29,000). It can be noted that compared to the influence of traffic density, the road age in terms of the road transportation period appears to play a more predominant role as a temporal variable than the road traffic density. Additionally, Plesničar and Zupančič (2005) argued that it was not possible to compare the temporal influence on the heavy metal concentrations due to the anthropogenic activities. For example, there was a significant change from 1993 two-lane high-speed road to a four-lane highway in 2004. For example, they found a substantial change in the heavy metal concentrations when a two-lane high-speed road in1993 changed to a four-lane highway in 2004. However, there has not been any major change in the road structure of the research site of this study for at least the past 20 years. It is necessary to ensure the features of research site has not been destroyed for evaluating the temporal influence on the distribution of heavy metal concentration

2.3 Review of Chemical Methods

2.3.1 Introduction

The methodologies conducted in the literature have been discussed in two major parts: soil chemical analysis and statistical analysis of the results. The first is discussed in this section and the statistical analysis will be presented in section 2.4. Accurate determination of potentially toxic trace metals in soils is important for cleaning up contaminated soils and monitoring the land application of metal-bearing non-hazardous materials. Soil digestion is often a necessary procedure before determining metal concentrations in soils. The common digestion methods used in recent studies are shown in Table 2-3; the review on soil chemical analysis also includes the soil chemical sequential extraction analysis and Pb isotopic analysis.

2.3.2 Soil Digestion Methods

Different digestion methods have been used for the purpose of soil chemical analysis including various combinations of concentrated acids such as hydroflouric acid (HF), hydrochloric acid (HCl), nitric acid (HNO3), perchloric acid (HClO4), and sulfuric acid (H2SO4) (Page, 1982). Different digestion equipment was likewise employed such as open beakers heated on hot plates, digestion tubes put in block digestors, and digestion bombs placed in conventional and microwave ovens (Page, 1982). Table 2-3 shows the recent studies which have used different digestion methods to investigate the heavy metal contamination in roadside soils. The aqua regia (3: 1, v/v, HCl to HNO3) digestion procedure (ISO standard 11466 or USEPA Method 3050) is considered adequate for analysing total-recoverable heavy metals in soils of certain regions and so is used to estimate the maximum element availability. The residual elements that are not released by aqua regia digestion generally are bound to silicate minerals and are considered not important for estimating the mobility and behaviour of the elements. The commonly used aqua regia digestion procedure consists of digesting soil samples on a hotplate with a 3: 1 mixture of HCl and HNO3. The nitric acid reacts with concentrated HCl to form aqua regia: $3\ HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$. Simplicity and adaptability as a routine procedure have led to the widespread use of the aqua regia method for the determination of total amounts of Cd, Cr, Cu, Ni, Pb, and Zn in contaminated soils and sediments. The mixture of HF-HNO3-HClO4-H2SO4 was recommended by Baker and Amacher (1982) for the total analysis of Cd, Cu, Ni, and Zn in soils.

A similar digestion method using the reagents of HF-HNO3- HClO4-H2SO4, but modified in certain heating processes, was recommended for the total analysis of Cr in soils by Page (1982). Page (1982) used HCl to replace H_2SO_4 in the digestion mixture of $HF\text{-}HNO_3\text{-}HClO_4\text{-}H_2SO_4$ for the total analysis of Pb in soil samples. Hseu et al. (2002) compared the different digestion methods for the total analysis of heavy metals and explained the dissolution effects of the digestion methods for soils by using inorganic acid mixtures; they highlighted that the method designed by Baker and Amacher (1982) which used the mixture of $HF\text{-}HNO_3\text{-}HClO_4\text{-}H_2SO_4$ had the best performance to evaluate the heavy metals.

Since the 1980s, microwave-assisted aqua regia digestions have become popular and are widely used; this technique provides a rapid, safe and efficient digestion and is not susceptible to losses of volatile metals. Chen and Ma (2001) examined the accuracy and precision of three different aqua regia digestion methods; they found the microwave aqua regia method was comparable in both precision and accuracy with the hotplate aqua regia method for analysing most of the target elements except for the silicate-binding metals, such as Al, Ba and K.

2.3.3 Chemical Sequential Extractions

Sequential extraction involves treatment of a sample of soil with a series of reagents in order to partition the trace element content. The principal advantage claimed for sequential extraction over the use of single extractants is that the phase specificity is improved (Kaplan and Yaman, 2009, Romic, 2012). This occurs because each reagent has a different chemical nature (e.g. a dilute acid, reducing or oxidising agent) and the steps are performed roughly in order of increasing "vigour." Hence, in a typical procedure, the first species to be isolated are those already in the soil solution or sediment pore water, perhaps together with those loosely attached at cation-exchange sites in the matrix. This is generally followed by stepwise attack on the carbonate phase, iron and manganese oxyhydroxides and organic matter. Finally, more refractory soil components, sometimes including the primary silicates, may be dissolved. With the use of additional reagents, the mineralogical phases may be further subdivided: for example, many procedures involve separate attacks on the more labile, amorphous iron oxyhydroxides and the more refractory, crystalline forms.

There are several sequential extraction procedures shown in the literature. However, the Tessier et al. (1979) scheme (Table 2-4) and the BCR scheme (Rauret et al., 1999) (Table 2-5) are the most frequently adopted methods by various researchers. The BCR sequential extraction scheme which was originally developed for the analysis of heavy metals in sediments, has been standardized and reference materials are available; this procedure has been successfully applied to a variety of matrices, including calcareous soils (Alvarez et al., 2006), contaminated soils (Pueyo et al., 2003), roadside soils (Yusuf, 2006), industrially contaminated soils (Van Herreweghe et al., 2003), sewage sludge (Lihareva et al., 2006), sludge amended soil (Rauret et al., 2000), fly ash (Smeda and Zyrnicki, 2002), mining waste (Marguí et al., 2007).

Although these procedures are not fully specific, they may provide comparative information on trace-metal mobility in soils with changing environmental conditions, such as pH or redox potential, and may help to evaluate the relative contribution of mixed pollution sources such as particulate/soluble sources to this mobility. Despite the operational information yielded by the BCR sequential extraction procedure, it has been shown to be more useful than single extractions for obtaining information about trace element dynamics in soils, especially in complex systems, such as in the case of soils with particulate contamination sources. For these reasons, the use of sequential extraction procedures to evaluate the risk in contaminated soils has increased. Sequential extractions, such as the Tessier procedure, have been applied to soils contaminated by various sources, such as irrigation with wastewater, mining activity, automobile emissions or sewage sludge addition (Rauret et al., 2000, Sutherland and Tack, 2002, Lihareva et al., 2006, Žemberyová et al., 2006).

The modified version of the three-step procedure proposed and validated by the BCR (Community Bureau of Reference) (Pueyo et al., 2003, Žemberyová et al., 2006, Pueyo et al., 2008) has an important potential for being accepted as the standard method by laboratories working in the area of trace metal operationally defined fractionation. Therefore, the procedure is a good option for the analysis of contaminated soils and data derived from the application of the procedure has been used in exercises to predict metal mobility in soils. (The detail of the modified three steps sequential extraction procedures are presented in Chapter 4).

Table 2-3 The chemical analysis used for heavy metal analysis in roadside soil in recent studies

Chemical analysis	Elements or Isotope	Reagent or method	Technical equipment[a]	Reference
Total metal extraction	Ag, As, Cd, Cr, Cu, Pb and, Zn	aqua regia, H_2O_2	ICP-MS, AAS	De Silva et al. (2015)
	Pb, Cu, Cd, Cr and Ni	aqua regia, HF	ICP-MS	Chen et al. (2010)
	Zn	aqua regia, HF	ICP-OES	Chen et al. (2010)
	As	aqua regia, $KMnO_4$	HG-AFS	Chen et al. (2010)
	Pb, Zu, Cu, Cr and Fe	aqua regia	AAS	Karim et al. (2014)
	Pb, Zn, Cu, Cr, Ni, Sn and Fe	aqua regia	AAS	Massas et al. (2009)
	Pb, Zn, Cu, Cr, Cd and Ni	aqua regia	AAS	Ciazela and Siepak (2016)
	Pb, Zn, Cu, Cr and Cd	HNO_3, H_2O_2	FAAS	Bakirdere and Yaman (2008)
Chemical sequential extraction	Pb, Zn, Cu and Cd	Tessier four-steps	ICP-AES	Li et al. (2001)
	Pb, Zn, Cu, Cd and As	Modified BCR three-steps	ICP-MS	Pueyo et al. (2008)
	Pb, Zn, Cu, Cd, Cr and Ni	Modified BCR three-steps	FAAS	Žemberyová et al. (2006)
	Pb, Zn and Cu	BCR three-steps	AAS	Yusuf (2006)
Metal isotopic analysis	^{206}Pb, ^{207}Pb	HNO_3, $HClO_4$	ICP-AES	Wong and Li (2004)
	^{206}Pb, ^{207}Pb	aqua regia, HF	ICP-MS	Walraven et al. (2014)
	^{206}Pb, ^{207}Pb and ^{208}Pb	aqua regia, HF	ICP-MS	Mao et al. (2014)

[a] Technical equipment abbreviation: ICP-MS: inductively coupled plasma-mass spectrometry; AAS: atomic absorption spectrometry; ICP-OES: inductively coupled plasma optical emission spectroscopy; HG-AFS: hydride generation-atomic fluorescence spectrometry; ICP-AES: inductively coupled plasma-atomic emission spectrometry; FAAS: flame atomic absorption spectrometry

2.3.4 Heavy Metal Isotope Analysis

There are four naturally occurring Pb stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). Their abundance varies extensively because of different decay pathways from ^{238}U, ^{235}U and ^{232}Th to ^{206}Pb, ^{207}Pb, ^{208}Pb, respectively (Faure, 1977). Different types of ore deposits and anthropogenic sources have their distinct isotopic ratios or signatures (Cheng and Hu, 2010). The Pb isotope ratio did not change in industrial or environmental processing, and retained its characteristic ratio from its source ore (Ault et al., 1970). Pb isotopes are commonly utilised as ratios; with the ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios often used in environmental studies as they can be determined quickly and precisely with ICP-MS and generally exhibit sufficient variability between different sources.

Polluted soils always contain lithologically inherited as well as anthropogenic Pb. If the ratio of anthropogenic Pb versus lithologically inherited Pb is high, the influence of the latter on the Pb isotope composition is negligible. Conversely, if this ratio is small, the presence of lithologically inherited Pb dominates the Pb isotope composition of the total sample. For this reason, knowledge of the lithologically inherited variability and spatial distribution of the Pb content and the Pb isotope composition of soils is indispensable in environmental tracer studies involving Pb. The isotopic characteristics of Pb are dependent upon the original composition and age of the ore bodies. In general, the ^{206}Pb/^{207}Pb ratios of naturally derived Pb are high (>1.20). In comparison, the ^{206}Pb/^{207}Pb ratios of anthropogenic Pb tend to be low, ranging from 0.96 to 1.20 (Sturges and Barrie, 1987). Owing to these inherited differences in Pb isotopic signatures between natural and anthropogenic Pb, the use of Pb isotopic analysis can assist in the identification of Pb sources and, in some cases, may also enable the apportionment of Pb contaminant sources. For example, the Pb isotope ratios can be used to identify the sources and transport pathways of Pb in pollution studies (Hu et al., 2014, Liu et al., 2014, Han et al., 2015). In addition, certain studies have shown that the qualitative analysis based on the Pb isotope ratios have been well performed in many study areas (Zhu et al., 2013, Hu et al., 2014). The Pb isotope ratios were determined for various environmental media including organisms, atmospheric aerosol, soil, urban dust and sediment (Ip et al., 2005, Zhu et al., 2013, Walraven et al., 2014, Félix et al., 2015). At the same time, the Pb isotope ratios of pollution sources were also investigated such as in coal combustion, mining, industrial emissions, vehicle exhaust (Félix et al., 2015, Sen et al., 2016, Zhang et al., 2016). Information on the occurrence, behaviour and fate of the various anthropogenic Pb sources in the environment is considered to be crucial in understanding and abating the lead problem. This includes distinguishing historic from recent pollution, as the former of course cannot be further prevented; identifying the source-related chemical form of environmental Pb, as this may influence its toxicity; and the need to sometimes legally identify the origin of Pb pollution. Lead is the most widely dispersed of all the heavy metal contaminants and, given its known toxicity, represents the most serious of these potential ‘‘time bombs’’. A large pool of potentially labile lead is held in surface soils so it is imperative that we understand the processes which control its mobilisation, in particular in environmentally sensitive situations. A particularly powerful approach to the characterisation of lead in soils and sediments is the combination of sequential extraction and isotope analysis (Bäckström et al., 2004, Wong and Li, 2004, Bacon et al., 2006).

2.4 Reviews on Data Interpretation

Once having obtained the data from the soil chemical analysis, relevant statistical approaches have been utilised in data interpretation. Source apportionment and discrimination of data are the two main processes which are attempted by most studies.

Heavy metals in roadside soils usually have complicated inter-relationships, due to their complicated sources and various pathways.

Table 2-4 Operating conditions required in the Tessier sequential extraction procedure (for 1g sample)

Stage	Fraction	Reagent	Experimental condition
1	Exchangeable	8 ml of 1 mol l^{-1} $MgCl_2$ (pH 7)	1 h at 25°C
2	Assicated with carbonates	8 ml of 1 mol l^{-1} NaOAc (pH 5 with acetic acid)	5 h at 25°C
3	Assocated with Fe-Mn oxides	20 ml of NH2OH·HCl, 0.04 mol l^{-1} in 25% w/v HOAc (pH~2)	6 h at 96°C
4	Associated with organic matter	3 ml of 0.02 mol l^{-1} HNO3/5 ml of 30% m/v H2O2	2 h at 85°C
		+3 ml of 30% m/v H_2O_2	3 h at 85°C
		+5 ml of 3.2 mol l^{-1} NH_4Oac	30 min at 25°C

Table 2-5 The BCR (Community Bureau of Reference, now the Standards, Measurement and Testing Program (SM&T) optimized sequential extraction procedure (Rauret et al., 1999) (for 1g sample)

Stage	Extractant	Fraction	Nominal target phase(s)	Experimental conditions
1	40 ml of 0.11 mol l^{-1} acetic acid solution	Exchangeable, acid-and water soluble	Soil solution, exchangeable cations, carbonates	Room temperature, 16 h, constant shaking
2	40 ml of 0.5 mol l^{-1} hydroxyl amine hydrochloride solution at pH 1.5 (with nitric acid)	Reducible	Iron and manganese oxyhydroxides	Room temperature, 16 h, constant shaking
3	10 ml of 30% w/v H_2O_2	Oxidisable	Organic matter and sulfides	Room temperature, 1 h, occasional agitation +85°C, 1 h
	10 ml of 30% w/v H_2O_2			85°C, 1 h, Reduce the volume to a few ml
	1 M ammonium acetate at pH 2			Room temperature, 16 h, constant shaking
4	Aqua regia	Residual	Non-silicate minerals	ISO 11466 (1995) method adopted

It was also noted from this review that numerous factors control their relative abundance, for example, original contents of heavy metals in rocks and parent materials, various processes of soil formation and anthropogenic factors such as the traffic density and traffic component

Therefore, several studies (Morcelli et al., 2005, Chen et al., 2010, Sun et al., 2010) applied correlation analysis to determine the correlation between different metals; hence the high correlations between soil heavy metals may reflect that these heavy metals had similar levels of pollution and similar pollution sources. Pearson correlation coefficients were the common statistics in the analysis which has been applied in most studies to determine their inter-element relationships. It has been noted that sources of various heavy metals in urban environments are numerous and often difficult to identify. Statistical analyses, such as principal component analysis (PCA), clustering analysis (CA), and multivariate statistical analysis, were popularly used to identify the sources and pathways of heavy metal contamination (Lu et al., 2012, Loganathan et al., 2013, Hussain et al., 2015, Nguyen et al., 2015). The essence of those statistical analyses is converting the variables under investigation into factors or principal components so that correlation among the original variables can be minimised. These methods are easy to use, but usually provide only general information on the sources.

However, there are very few studies which have utilised statistical tools to explore and discriminate the potentially influential factors impacting the heavy metal concentration in roadside soils. In particular, one of the major restrictions for field soil study is the lack of adequate soil samples. Therefore, an approach which could expand the data population in order to provide a more reliable, proper and sufficient data set is imperative. The basis of the regional frequency analysis used was the conversion of space to sample number; Hosking and Wallis (1993) showed how it was possible to extend the length of hydrological records by a suitable combination of adjacent records. The concept of this approach could also be applied for future roadside soil study to extend the data population (refer to Chapter 4).

2.5. Pollutant Enrichment

Most of the heavy metals are toxic to living organisms and even those considered as essential can be toxic if present in excess (Akbar et al., 2006). The heavy metals can impair crucial biochemical processes posing a threat to human well-being, plant growth and animal health. Numerous studies have revealed that such pollutants can play a detrimental role to the roadside plants, animals, and the surrounding human settlements. In order to evaluate the metal contamination level in the soil, Tomlinson et al. (1980) firstly introduced and defined ‘concentration factor’(CF) and ‘pollution load index’(PLI) to assess each heavy metal contamination in soil. PLI describes the quality of a site or an estuary in terms which are easily understood by the non-specialist and which also can be used to compare the pollution loadings of a different location (lands or estuaries).

The degree of pollutant enrichment in roadside soils depends on the relative contribution of the various pollutant sources (Figure 2-4). The sources can be classified into geogenic (natural) and anthropogenic origin. The geogenic pollution is derived from the parent material of soils that have varied pollutant elemental concentration. The anthropogenic sources are roads, industry, and buildings, and other activities in the vicinity of the roads. The contribution of the roads can be assessed by comparing the pollutant concentrations in roadside soils with those in soils away from the roads (the background soils). If the concentrations in roadside soils are higher than those in the background soils, it is assumed that roads are the major contributor to the pollutant enrichment in those roadside soils. Several methods have been used to quantify and assess pollutant enrichment in roadside soils; these methods are similar to those used in contamination evaluation of sediments (Mohammed et al., 2012, Loganathan et al., 2013, Nguyen et al., 2015). Assessment of heavy metal concentrations and soil contamination required pre-anthropogenic knowledge of metal concentrations to act as pristine values. The contribution of the traffic can be assessed by comparing the pollutant concentration in sampling roadside soil with those in soil far away from the roads. If the heavy metal concentrations in roadside soil are greater than those in the background soils, it is assumed that traffic is the major contributor to the pollutant enrichment in the roadside soil. The common methods used in the assessment of heavy metal enrichment in roadside soils are:

- Enrichment factor (EF)
- Geo-accumulation index (I_{geo})
- Pollution index (PI)
- Pollution load index (PLI)

1. Enrichment Factor (EF) is the most popular index of pollutant enrichment index used in literature. EF of a pollutant is based on the standardisation of a measured pollutant against a reference element. A reference element is often characterised by low occurrence variability (e.g., Fe, Al, Ti, Sr and K) (Ogunsola et al., 1994, Massadeh et al., 2004, Liu et al., 2009, Mmolawa et al., 2011). The EF is calculated using the following equation:

$$EF=\frac{(C_x/C_{ref})sample}{(C_x/C_{ref})background}$$

where C_x is the concentration of the examined heavy metal in the sample and the background soil reference, and C_{ref} is the concentration of the reference element in the sample and the background soil. Five contamination categories are recognized on the basis of the EF: these are <2 denotes deficiency to minimal enrichment; 2-5, moderate enrichment; 5-20, significant enrichment; 20-40, very high enrichment; >40, extremely high enrichment (Lu et al., 2009).

2.The geo-accumulation index (I_{geo}) defined by Muller (1969), can also be used to assess heavy metal contamination in roadside soils. The I_{geo} has been modified by Faiz et al. (2009) for RDS pollution assessment. This method assesses the heavy metal contamination in terms of seven (0 to 6) enrichment classes (Table 2-6) ranging from background concentration to very highly polluted, as follows:

$$I_{geo} = \log 2 \left[\frac{C_m}{1.5 \times C_b} \right]$$

where C_m represents the measured heavy metal concentration in roadside soil, C_b is the geochemical background value of the pollutant, which may be attributed to lithogenic variations in different environments.

Table 2-6 The Igeo classes with respect to soil quality

I_{geo} value	I_{geo} class	Designation of soil quality
>5	6	Extremely contaminated
4-5	5	Strongly to extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
0	0	Uncontaminated

3. Pollution index (PI) which is also named contamination factor (CF) (Tomlinson et al., 1980, Mmolawa et al., 2011, Usman et al., 2012, Tian and Zhu, 2014) is defined as:

$$PI = C_m / C_b$$

where C_m is the measured concentration and C_b is the background concentration of heavy metal in roadside soil, where the contamination factor $CF < 1$ refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination. Furthermore,

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the mean value of the PI of a heavy metal which is defined as integrated pollution index (IPI) by Faiz et al. (2009) and the sum of pollution indexes (sum of PIs) for all heavy metals by Duong and Lee (2011) are also used to assess heavy metal pollution.

4. Pollution load index (PLI) was introduced by Tomlinson et al. (1980) and is based on the pollution index (PI) to evaluate the extent of heavy metal pollution.

$$\text{PLI} = \sqrt[n]{(PI_1 \times PI_2 \times PI_3 \times \ldots \times PI_n)}$$

The PLI also provides a simple but comparative means to assess an area heavy metal contamination, where a value of PLI < 1 denotes negligible contamination; PLI = 1 indicates that only baseline levels of pollutants are present and PLI >1 would indicate deterioration of site quality.

A contamination index (P_i) was introduced by Huang (1987) in order to measure the contamination of a given toxic substance in one area and could be expressed by the following functions:

$$P_i = \frac{C_i}{X_a} \; (Ci \le X_a)$$

$$P_i = 1 + \frac{C_i - X_a}{X_b - X_a} \; (X_a < C_i \le X_b)$$

$$P_i = 2 + \frac{C_i - X_b}{X_c - X_b} \; (X_b < C_i \le X_c)$$

$$P_i = 3 + \frac{C_i - X_c}{X_c - X_b} \; (C_i > X_c)$$

where C_i is the observed concentration of the heavy metal; X_a is the no contamination threshold level; X_b is the lowly contaminated threshold level, and X_c is the highly contaminated threshold level based on the toxic substances effects on plant growth (Huang, 1987).The following terminologies are used to describe the contamination index: $P_i \leq 1$ no contamination; $1 < P_i \leq 2$ low contamination; $2 < P_i \leq 3$ moderate contamination; $P_i > 3$ high contamination.

The integrated contamination index (P) could be calculated according to the modified Nemerow index suggested by Huang (1987) and is expressed in the equation:

$$P= \sqrt{\max(P_i) \times (\frac{1}{n}\sum_{i=1}^{n} \overline{P_i}\,)}$$

where n is the heavy metal number; $\overline{P_i}$ is the average contamination index of each heavy metal. For the description of integrated contamination index, the same terminologies are used to describe the assessment: $Pi \leq 1$ no contamination; $1< Pi \leq 2$ low contamination; $2 < Pi \leq 3$ moderate contamination; $Pi > 3$ high contamination.

From the literature reviewed, EF was the most widely used approach to assess the heavy metal contamination for roadside soil, therefore, it has been chosen for this study.

2.6 Summary

From the literature reviewed, a fundamental conceptual model was created based on the spatial and temporal influential factors. This conceptual model illustrated the features of heavy metal distribution and accumulation patterns in roadside soils. Moreover, this model can provide a comprehensive and systematic field sampling strategy to investigate the heavy metal concentration. The four dimension influential factors such as distance from the road, along with the road, the soil depth and temporal factors were critically reviewed in this chapter.

Chemical analysis (refer to section 2.3) including the soil digestion method, chemical extraction and isotopic analysis were reviewed in this chapter. This will provide relative methods and skills to achieve a comprehensive analysis in the study of heavy metal concentrations. The critical review of the available statistical analysis (section 2.4) which has been applied in previous studies was also conducted.

It is evident that there has been no investigation on the impact of the influence of soil type derived from different geology on the heavy metal concentration in roadside soil. In addition, the lack of adequate studies focussing on the function of rainfall events to the roadside soil is apparent. Therefore, it is necessary to fill this gap and explore how these factors potentially affect the heavy metal concentration distribution in roadside soil as well as having an impact on different metals fractions.

Additionally, the application of a regional frequency approach from the field of hydrology to a soil study could become an efficient method to extend the soil data set for discrimination of the potentially influential factors. Although the literature reviewed in this chapter provides background information and useful techniques for the research, also it has identified gaps and limitations in knowledge on this topic which this dissertation can address; it can contribute to knowledge in this field and can indicate directions for further research.

III

Chapter 3 RESEARCH SITE

3.1 Introduction

From the literature reviewed, it can be concluded that there are three main pathways (atmospheric deposition, road runoff and spray by the wind) resulting in enrichment of heavy metals in roadside soils (Werkenthin et al., 2014). However, in this study, roadside runoff is considered to be the principal pathway. From consideration of the literature review, it is hypothesised that the factors influencing the concentration of heavy metals in roadside soil are: distance from the road, soil type, soil depth (topsoil and subsoil) and rainfall. These influential factors were used in the determination of the final site selected.

The study site is located in Miranda a suburb in the Sutherland Shire approximately 24 km south of the Sydney central business district. The terrain is slightly sloping to flat. The mean annual rainfall is approximately 1000mm (refer Chapter 5). The site, Miranda Park, is located between two major roads with similar traffic volumes: The Boulevard (northern side) and The Kingsway (southern side) (refer to Figure 4-1). The annual average daily traffic (AADT) of 30,000 on each road was calculated based on the data from Traffic Authority New South Wales (2005). Although more up to date daily traffic data was sought for this site, none was available.

3.2 Site History

From the examination of aerial photographs from 1930 to 2014 (Figure 3-1) sourced from Sutherland Shire Council, there were no obvious changes to the area under investigation from 1930 to the present. It can be seen that since 1961 the research area in Miranda Park had not been used for any commercial or residential purposes. This stable situation indicates that there is no apparent anthropogenic activity to lead to heavy metal deposition in-situ from other sources and affords this research a site in which the main source of heavy metals is from traffic flow. The only crucial change for the area around the periphery of the Park is that a school, Port Hacking High School, was established in the south-east corner and more residential buildings were also constructed on the north-west side of the park. However, neither the location of the school nor the residences affects the current sampling sites in the research area.

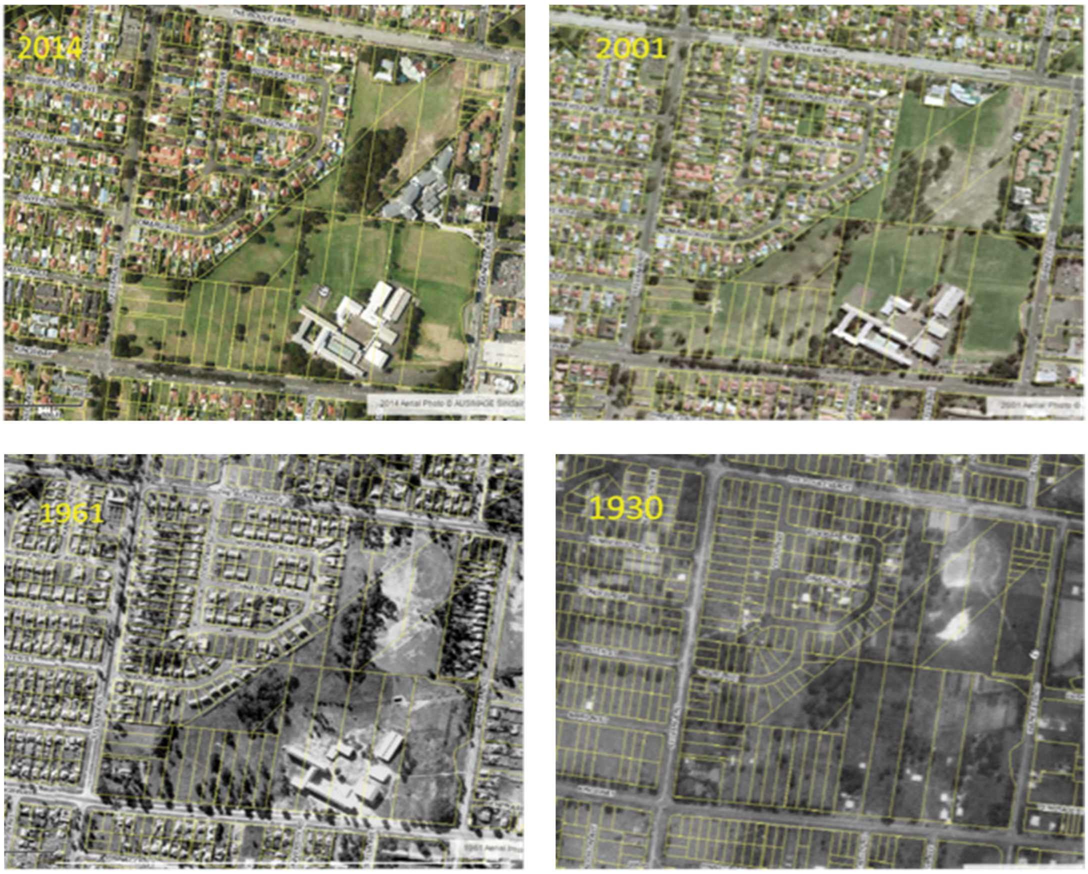

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Figure 3-1 Aerial photographs of the Research Site, Miranda Park from 1930-2014 source: Sutherland Shire Council

3.3 Site Geology and Soil Landscape Mapping

After initially consulting the Sydney 1:100000 geology sheet (Herbert, 1983) and a geology map of the specific area (Branagan, 1993), see Figure 3-2. and the Wollongong-Port Hacking Soil landscape 1:100000 sheet map (Hazelton and Tille, 1990), see Figure 3-3 it was determined that this park has three different geological areas.

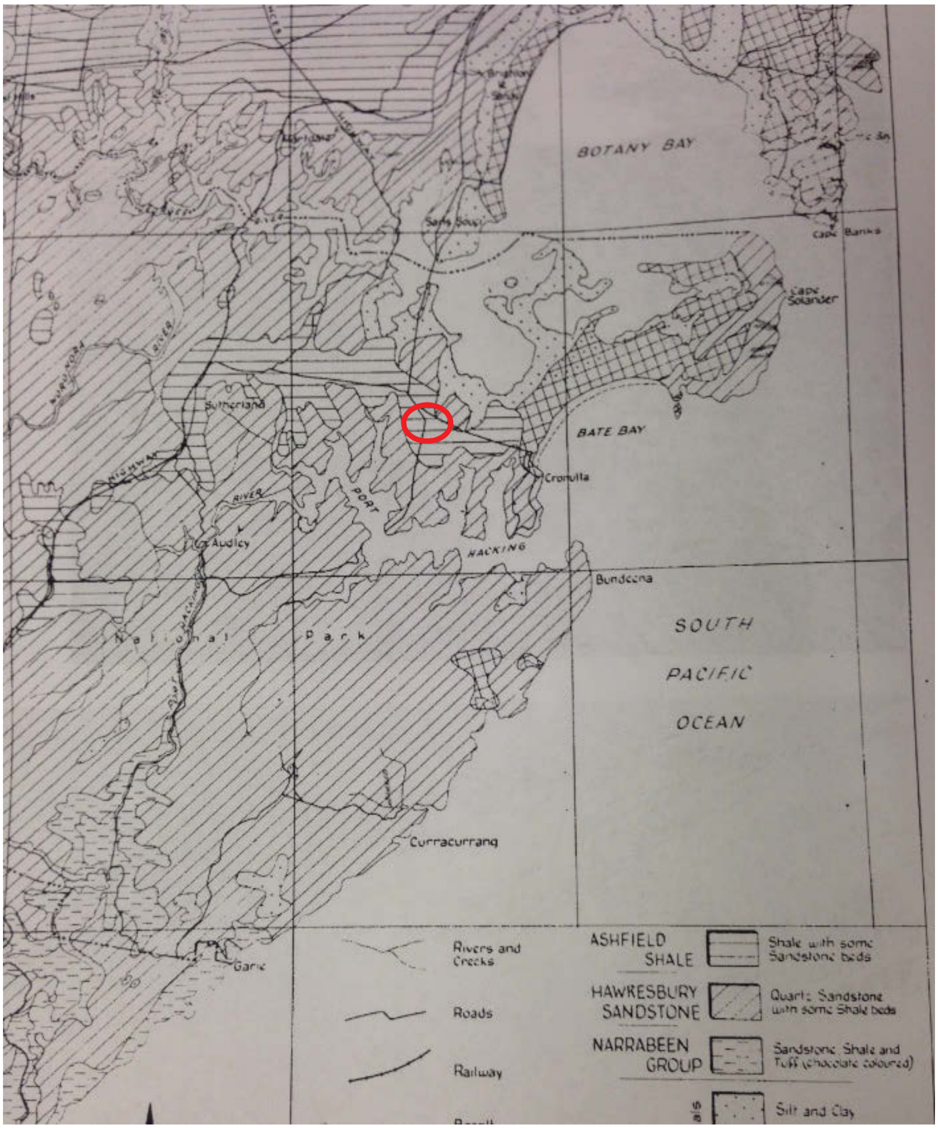

Figure 3-2 Geography and geology of Sutherland shire (Branagan, 1993); Note approxmiation of Miranda Park (red circle)

It is also indicated from the geological map by Stroud (1985) that Miranda Park is underlain on the western ridge by the Wianamatta Group. At this site a remnant cap of Ashfield Shale (laminate and dark grey siltstone) of the Wianamatta Group (Branagan, 1993) overlies Hawkesbury Sandstone, a medium to coarse-grained sandstone with infrequent minor shale and laminate lenses. The Mittagong Formation noted in Wollongong-Port Hacking Soil landscape 1:100000 sheet map (Hazelton and Tille, 1990) was evident in the north-eastern corner of the site (refer Figure 3-3). The Mittagong Formation is generally described as “passage beds” between Ashfield shale and Hawkesbury Sandstone. Mittagong Formation is made up of interbedded shale, laminate and fine to medium- grained quartz sandstone with localised lateritic outcrops (Herbert, 1983).

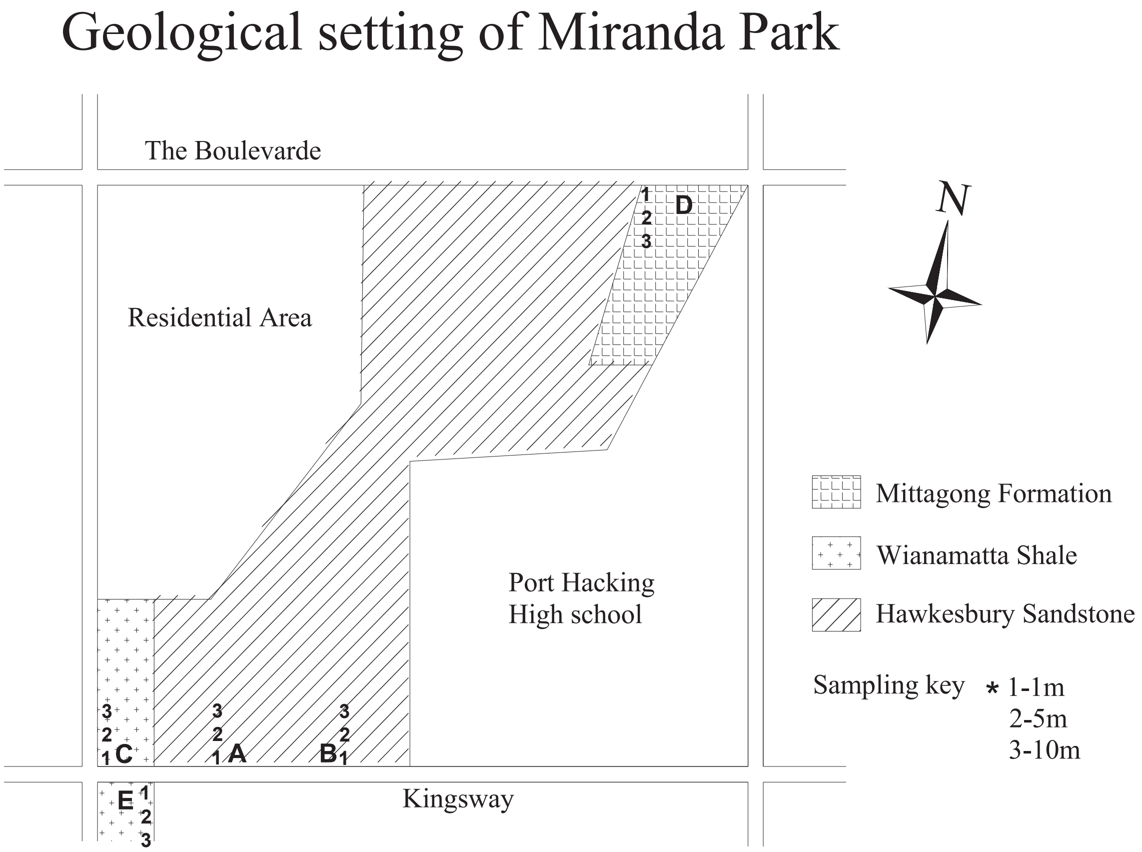

Figure 3-3. The geological setting of the sampling sites and the map is adapted from Wollongong-Port Hacking Soil Landscape 1:100,000 map (Hazelton and Tille, 1990)

3.4 Soil Field Description

According to the Soil Landscapes of the Wollongong-Port Hacking 1:100 000 Map Sheet (Hazelton and Tille, 1990) Miranda Park lies within the Hawkesbury Soil Landscape (Hawkesbury sandstone) and Blacktown Soil Landscapes (Wianamatta Group) with the associated Soil Landscape of Lucas Heights (Mittagong Formation) (refer Figure 3-3). The site was inspected from which it was confirmed from "ground truth" after the initial soil samples were described using colour (Munsell and Color, 2000) (see Appendix A) and texture (Northcote, 1979, McDonald, 2009), that different soils were present. These soils appeared to be similar to those described in the soil landscape derived from Hawkesbury Sandstone, Wianamatta Shale, and Mittagong Formation. The description of soil field texture and colour of the samples from the initial transect is presented in Chapter 5 Table 5-1. The structure of the topsoil showed moderate pedality. However, the structure was not described in detail, because the site was a park and an auger was used to excavate the soil.

3.5 Site Vegetation

The vegetation on site was used as an indicator of different geologies, because there is a relationship between geological substrate, soil type and vegetation (Benson and Howell, 1990, Tozer, 2003). At the research site well-established trees such as *Eucalyptus crebra* (narrow-leaved ironbarks) (Figure 3-4) are on the western ridge. Narrow-leaved ironbarks grow on shale-derived soil (Benson et al., 1990, Cuneo and Leishman, 2006). *Eucalyptus* species including *Eucalyptus haemastoma* (scribbly gum) and *Eucalyptus punctata* (grey gum) (see Figure 3-5) grow on the sandstone derived soil (Beadle et al., 1982) and are the major vegetation cover in the park, the vegetation of which has not changed very noticeably since 1930. However, vegetation has been cleared from the Mittagong Formation area since 2001.

3.6 Collection of Sampling Sites

In order to have a non-biased survey (Chapman and Atkinson, 2007) a transect that intersected these three geologies was established. In consideration of the previously stated influential factor of soil type derived from specific geologies, Miranda Park was selected as the project site. The analytical results from soil sampled on the initial transect, were consistent with the literature reviewed about concentration of heavy metals in relation to the distance from the road. Thus three sampling locations were selected; these were AB for Hawkesbury Sandstone, CE for Wianamatta Shale and D for Mittagong Formation). : The soil samples were initially measured in the field for pH with fresh Raupach indicator. These sites were then sampled over 18 months after long dry periods and within days of a heavy rain event.

Figure 3-4 Stand of Eucalyptus crebra (narrow-leaved ironbark) in shale derived soil on the western ridge of the study site

Figure 3-5 Stand of *Eucalyptus haemastoma* (scribbly gum) and *Eucalyptus punctata* (grey gum) in sandstone derived soil on the study site

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3.7 Summary

From the research undertaken in this study, it was necessary to consider one or more sites that had variation in influencing heavy metal concentration in roadside soils. As outlined in Chapter 2, the influential factors considered important were:

- Distance from the road;
- Underlying geology and characteristic soil type 'in situ'
- Soil layers (topsoil and subsoil); and
- Rainfall events.

As presented in this chapter, Miranda Park, the selected site was unique having variability in these influential factors and therefore was suitable as the study area for sampling and subsequent chemical and statistical analyses to discriminate between the influential factors.

IV

Chapter 4 METHODOLOGY

4.1 Introduction

The methodology used throughout this research was designed to optimise the utility of the unique selected site. The following program of investigation was established to understand the factors influencing heavy metal concentrations in soils along road corridors. To determine the presence of heavy metals and to establish final sampling sites in Miranda Park, topsoil and subsoil samples were collected and field assessment was undertaken in a non-biased systematic survey along a transect (Chapman and Atkinson, 2007) (refer Figure 4-1).

Figure 4-1 The initial transect conducted for preliminary analysis; the 9 yellow dots indicated the nine sampling locations for the trial test

The initial soil samples were described in the field according to the Australian Soil and Land Survey criteria in McDonald et al., 2009. Field texture (Northcote, 1979, McDonald et al., 2009), soil colour (Munsell and Color, 2000) and field soil pH

(Raupach and Tucker, 1959) were determined both for topsoil and subsoil for each location. From the results obtained the following sites A, B, C, D and E were selected to be sampled for further investigation in the three known different geology sites (refer to Chapter 3 Figureure 3-3).

4.2 Soil Sample Collection

On the initial visit to the site a few samples were collected using a steel pipe as an auger. However, in order to prevent any sampling contamination of the soil, a special stainless steel auger was designed which enabled an easy collection of both topsoil and subsoil (see Figure 4-2 and Figure 4-3).

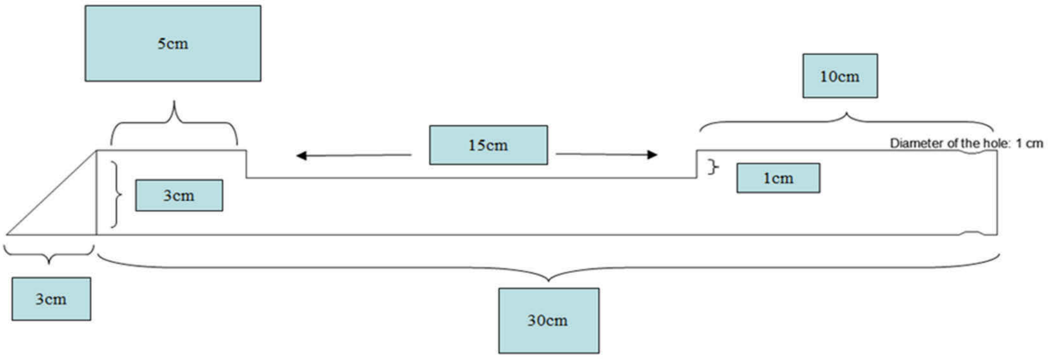


Figure 4-2 The design for the stainless steel auger

Figure 4-3 Stainless steel auger used for collection of samples

Samples were collected at each of the five selected sites using the stainless steel auger. The samples were collected at depths of 0–10 cm (topsoil) and 10–30 cm (subsoil) and as already determined in the literature review at distances of 1, 5, and 10 m from the edge of both major roads (See Figure 4-4). Six soil sample collections were conducted according to rainfall events; three times pre-rainfall collections (after extended periods of no rain) and three times post intensive rainfall events over a period of 18 months from November 2013 to May 2015. During this period a total 180 samples (details shown in Table 4-1) were only collected because of the constraint of the number of rainfall events above 30 mm within 24 hours. All the sample locations were recorded using GPS in order to consistently collect samples at the same location during the whole sampling period.

Table 4-1 details of field soil collection and total soil samples

Locations	Sampling distance	Sampling depth	Sampling times	Sampling	Total samples
A	1m	Top (0-10cm)	1st	Pre-rainfall	
B	5m	Sub (10-30cm)	2nd	Post-rainfall	
C	10m		3rd		
D					
E					
5 ×	3 ×	2 ×	3 ×	2 =	180

After completion of the soil sample collection and on consideration of the available literature reviewed, the following laboratory procedures were undertaken.

4.2.1 Sample Preliminary Preparation

Following each site visit, the soil samples, in labelled plastic bags were transferred into the laboratory. The bags were left open overnight. The next day inclusions such as leaves and stones were removed from all of the field soil samples. All the soils were then air-dried, ground, and passed through a 2-mm sieve in order to obtain a dry particle size fraction smaller than 2 mm.

Soil sampling holes overlaid on the NearMap aerial photograph (dated 30 Sep 2013) with geological map units (adapted from Stroud et al. 1985)

Figure 4-4 Indication of sampling strategy used for Miranda Park. Number 1 to 6 indicated the sample collection locations for Hawkesbury Sandstone. Number 7 to 10 and 14 to 17 indicated the sample collection locations for Wianamatta Shale. Number 11 to 13 are for Mittagong Formation. The heavy metal in sampling locations of 10, 17, 18, 19, 20 and 21 are not chosen for comparison due to the inconsistent distance from the road edge

4.2.2 Analysis of Soil Properties

The characteristics of parent material that will strongly influence the properties of soils are the mineralogical and chemical composition (Gray and Murphy, 1999). From Chapter 3 Figure 3-2 (Branagan, 1993) it was determined that Miranda Park is underlain by Wianamatta Group Shale which overlies Hawkesbury Sandstone and the transition beds of Mittagong Formation in the area of Sites D and F. The pH of the samples in the field was confirmed by the soil pH laboratory test. It is known when examined by X-ray diffraction techniques that the Hawkesbury Sandstone and the Wianamatta Group consists of kaolinite and illite clay (Bowman, 1974). Accordingly, X-ray diffraction (XRD, Siemens D-5000, shown in Figure 4-5) was also used to determine soil sample mineralogy, for the clay mineral types. Soil samples of 5-10 g were sieved before drying in 110 °C oven overnight. Dry soil samples were ground using a mortar and pestle. Each of the ground soil samples was transferred to a particular labelled plastic slide (Figure 4-6). The XRD analysis was used for both top and sub soils at the six locations.

The LECO method of estimating total organic carbon (TOC) uses an instrument known as a LECO carbon analyser to measure TOC values by combusting the organic carbon and measuring the resulting carbon dioxide produced (Jarvie, 1991). The soil total organic carbon (TOC) is the carbon (C) stored in soil organic matter (SOM); SOM is normally measured by loss-on-ignition method (Konen et al., 2002, Barille-Boyer et al., 2003, Hazelton and Murphy 2016) and there is a conversion equation between soil organic carbon (TOC) and loss-on-ignition (Yang et al., 2006, Pribyl, 2010). LECO analysis was applied in order to determine the total organic carbon content in the soils (Schumacher, 2002). Total C and total S were run on dried powders. Organic carbon was measured on acidified samples. The acidification was done using 50 mL of 1 N HCl to 0.5 g of sample on a hot plate at 60 ◦C for 12 hr. Fifty mL of distilled water was then added to stop the reaction. The solution was filtered through a glass fibre filter and the residue rinsed with distilled water to remove all acid. Samples were then dried for at least four hours.

The soil cation exchange capacity (CEC) was determined using the method of Rayment and Lyons (2011). The method 15D3 is described as follows: four grams of sample was weighed into a centrifuge tube and 40 ml 0.1 M Barium chloride/0.1 M Ammonium chloride extracting solution was added. Samples were shaken end-over-end at 25 °C for 2h, centrifuged (2000 rpm) and diluted (1:5) and analysed by ICP–AES. Results are reported as CEC cmol$^+$/kg (Hazelton and Murphy, 2016).

Figure 4-5 X-Ray Diffractometer, Siemens D-5000 used for soil mineralogy analysis

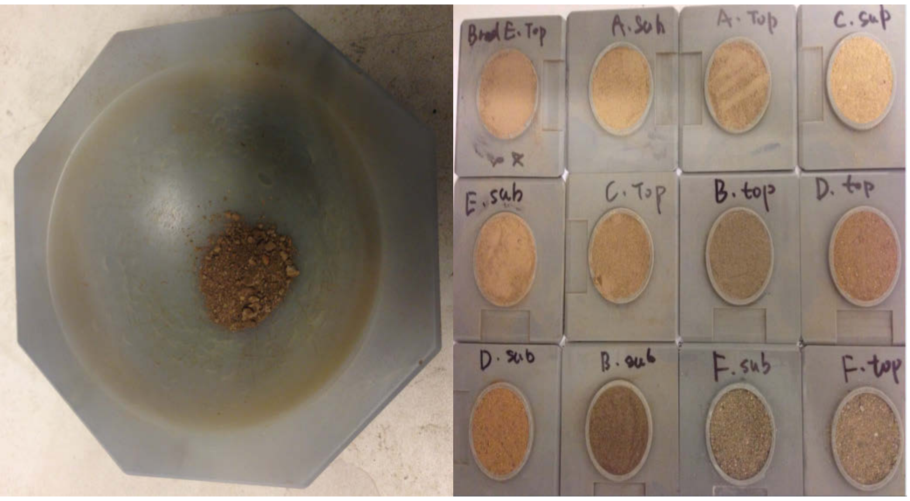


Figure 4-6 soil samples preparation for XRD analysis

4.3 Laboratory Analytical Procedure

In order to investigate the heavy metal behaviour and evaluate their distribution in roadside soil, the following three different chemical analyses from different aspects were carried out and successfully achieved the particular aims. The modified aqua regia digestion method due to its safe and simple procedures was used for soil digestion and detection of the total heavy metal concentration. Three-step chemical extraction procedures were applied to explore the impact of different influential factors on soil chemical fraction variations. Moreover, metal isotopic analysis as a more in-depth method was used to identify the origins of different heavy metals.

4.3.1 Soil Digestion and Total Heavy Metal Concentration Measurement

From the literature reviewed, it was decided to use the modified aqua regia digestion method (Gaudino et al., 2007) for analysis of the soil samples for total heavy metal concentration. Gaudino et al. (2007) critically compared three different digestion methods used to determine elemental mass fraction in soils. They pointed out the modified aqua regia digestion method which is specified in Italian legislation can be conducted under not only hot plate heating but also microwave-oven heating. In addition, compared to the hot plate heating process, the microwave-assisted sample digestion technique has become popular and presently it is widely used due to its safe, rapid and efficient performance (Quevauviller et al., 1993, Smith and Arsenault, 1996, Chen and Ma, 2001). Other alternative techniques were considered; however, there are fewer possibilities of loss of quality using this procedure that can transform the soil from solid phase to liquid phase. The modified aqua regia digestion method (Gaudino et al., 2007) was summarized as follow: Firstly, 1.5 mL H_2O_2, 4.5 mL HCl, and 1.5 mL HNO_3 were mixed and added to the soil. Hydrogen peroxide was used to enhance the destruction of organic matter. After adding the chemical reagent, all the samples were transferred to microwave digestion. Each sample solution was transferred from the beaker to the volumetric polypropylene tube (25 ml) via filter media and the solution was made up to the mark with dilute nitric acid. Thereafter, the soil solution was analysed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) in order to measure the heavy metal concentrations at a distance greater than 5m from the roadside. The concentrations of Pb, Zn, Cu, Cr, Ni, Cd and Fe were measured by ICP-MS.

To ensure the quality of the results, prior to the commencement of the laboratory work all glass that was to be in contact with the samples was cleaned with 10 % nitric acid and rinsed with Milli-Q water. Throughout the entire procedure all the reagents used were analytical grade. In addition, the quality assurance and quality control (QA/QC) procedures were conducted by Certified Reference Material (CRM, DC73309) which is approved by the China National Analysis Centre. CRM was paralleled and analysed with roadside soil samples using identical procedures. Duplicate and blank samples were analysed as part of the methodology to ensure repeatable results.

4.3.2 Chemical Sequential Extraction (BCR)

This study requires not only the determination of the total concentration of the heavy metals but also an estimation of their labile fraction. Dynamic studies are also required to predict changes over time in the fate of the pollutants in an area affected by contamination, and are based on quantifying the changes over time of the parameters that control soil-pollutant interaction. Sequential extractions were first designed for the selective removal of trace elements bound to operationally defined sediment fractions (Tessier et al., 1979, Meguellati et al., 1983, Salomons and Förstner, 2012). Although these procedures are not fully specific, they may provide comparative information on trace-metal mobility in soils with changing environmental conditions, such as pH or redox potential, and may help to evaluate the relative contribution of mixed pollution sources (i.e. particulate/soluble sources) to this mobility. For these reasons, the use of sequential extraction procedures to evaluate the risk in contaminated soils has increased. Sequential extractions, such as the Tessier procedure, have been applied to soils contaminated by various sources, such as irrigation with wastewater, mining activity, automobile emissions or sewage sludge addition (The next laboratory procedure in this study was the use of chemical sequential extraction to examine the temporal dynamics of trace elements in soil. Sequential extraction was applied for all the topsoil samples according to the modified BCR (Community Bureau of Reference) three-step (shown in Figure 4-7) sequential extraction procedure (Pueyo et al., 2008).The modified version of the three-step procedure proposed and validated by the BCR (Ure et al., 1993, Rauret et al., 1999) has an important potential for being accepted as the standard method by laboratories working in the area of trace metal operationally defined fractionation. Moreover, Certified Reference Materials availability (i.e. BCR-601, BCR-701 and BCR-483) offers support to laboratories which use this procedure, in terms of method validation and quality control. Therefore, the procedure is a good option for the analysis of contaminated soils and data derived from the application of the procedure has been used in exercises to predict metal mobility in soils (Sutherland and Tack, 2002, Kaasalainen and Yli-Halla, 2003, Kubova et al., 2004, Larner et al., 2006, Tokalıoğlu and Kartal, 2006).

In the first step, the exchangeable and weak acid soluble fraction can be extracted. In the second step, the reducible fraction can be extracted and the oxidisable fraction can be extracted in the third step. Moreover, the residue from the third step is the residual fraction. Initial statistical analysis (mean, standard error) was conducted by Excel 2010 (Microsoft Inc., Redmond, USA) and SPSS v.22.0 (SPSS Inc. Chicago, USA). Then, to provide more accurate, adequate and reliable evidence to understand the behaviour of metal movement and distribution in roadside soil derived from different geologies, the experimental design selected for this study linked the modified chemical sequential extraction method and the metal isotopic composition analysis of the soils.

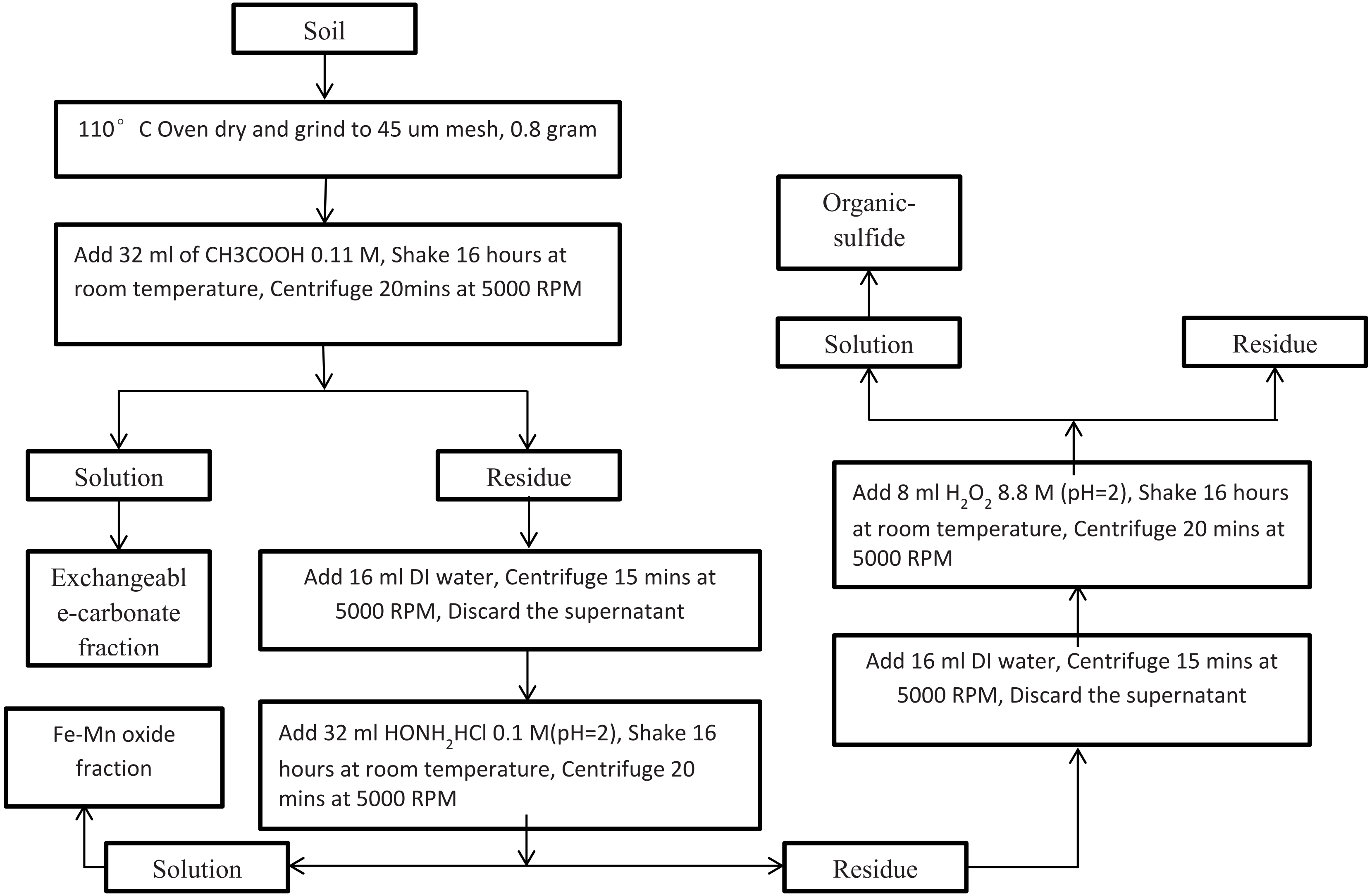
4.2.3 Chemical Sequential Extraction Analysis Combined with Isotope Analysis

The technique of isotopic fingerprinting (Alewell et al., 2008, Cheng and Hu, 2010, Kumar et al., 2013) based on the measurement of the ratios of stable metal isotopes was used to discriminate between the field value of heavy metal concentration due to the influencing factors and natural variability. This technique is considered to be a more in-depth method used to identify the origins of various contaminants (Gulson et al., 1981, Wong et al., 2002, Kumar et al., 2013).

The procedures consisted of two major stages: firstly, the modified three-step sequential extraction procedure (BCR) (Pueyo et al., 2008) for metal fraction was conducted in order to extract different chemical fractions for all the 90 topsoil samples. The extraction procedure divides the metals into four chemical forms: (1) exchangeable and weak acid soluble fraction (extracted by 0.11 mol L^{-1} acetic acid), (2) reducible fraction (extracted by 0.5 mol L^{-1} hydroxylammonium chloride), (3) oxidisable fraction (8.8 mol L^{-1} hydrogen peroxide), and (4) residue (1.0 mol L^{-1} ammonium acetate).

After the BCR treatment, there were a total of 90 (samples) × 4 = 360 fractions. In the second stage, lead isotope analysis was performed after chemical sequential extraction. The diluted extracted samples were purified, and then $^{207}Pb/^{206}Pb$ analyses were carried out for the Pb isotopic ratios analysis. The entire isotope measurement was undertaken by a Man Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) with a low uptake nebulizer. The results obtained from all the laboratory analysis of field data was used to distinguish between natural variability and variability arising from influential factors. This focus can be restated as an aim to ascertain if alternative field data are statistically different.

Figure 4-7 the details of BCR procedure



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4.4 Statistical Analysis of Samples

One approach for discrimination between natural variability and variability arising from influencing factors is to assume the data comes from different statistical populations and to test whether the populations are different. A Student's t-test can be used for this purpose by testing the hypothesis that the means of different sample populations (two or three groups of field samples) are not significantly different. The volume of data available will influence the results of any statistical test. Commonly, it is found that the most robust conclusions are developed when large volumes of data are available. However, when field data is considered, there is a trade-off between the collection of more data and the efficient usage of the collected field data. In this study, rather than collect additional field data, the statistical analysis of the field data was undertaken in a manner to maximise the extraction of information from the available data. In other words, an efficient statistical analysis of the field data was undertaken. Using this efficient statistical analysis approach, the variability arising from the individual influential factors was tested.

The basis of the approach used was the conversion of space to sample number. Hosking and Wallis (1993) showed how it was possible to extend the length of hydrological records by a suitable combination of adjacent records. For this study, the soil field data was combined in a manner whereby only the influential factor differed between the two or three sample populations. The regional frequency approach was applied as follows; if the influential factor being considered was soil type then the data from the soils derived from the three geologies were separated into three sample populations. For example, in order to discriminate the soil type as an influential factor between sampling location AB and CE, for Pb, the concentrations in sampling location AB at distance 1m, 5m and 10m in both topsoil and subsoil after different weather condition were normalised using their local mean. For the sampling location CE, the data were normalised using the mean of this population. This increased the number of samples to 120. Four influential factors were considered in this manner. These factors were: (1) soil type derived from three different geologies; (2) topsoils and subsoils; (3) pre-rainfall period and post-rainfall period; and (4) distance from traffic (1m, 5m and 10m).

4.5 Multivariate Statistical Analysis

Correlation analysis was conducted between metals separately for topsoil and subsoil to determine inter-metal relationship in different layers. Pearson correlation coefficients were used to examine the degree of significance of the above relationships. A significant and positive correlation between metals often shows that the metals are derived from the same sources (Singh et al., 2013).

Principal component analysis (PCA) as a multivariate statistical tool was used to reduce a set of original variables to extract a small number of latent factors called principal components for analysing relationships among the observed variables (Golobočanin et al., 2004). Variables with similar characteristics are grouped into factors and factors with eigen values greater than one are selected as principal components. The analysis provides information on the percentage of variance explained by each of the factors and factor loadings of each of the variables. Before running the statistical software tool, the concentration of each metal was normalized by calculated the average value for each soil type under different soil condition.

The correlation, cluster analyses and PCA were performed using IBM SPSS Statistic version 22.0; other statistical analyses and Figureures were carried out with Origin 9.1.

4.6 Roadside Soil Assessment

Enrichment factor (EF) is the most popular index of heavy metal enrichment used in the literature. The EF is determined by a similar method to that used for the pollution index, with the exception that the measured metal concentrations in roadside soil and background soils are normalized against a reference metal. The EF is calculated using the following equation:

$$EF=\frac{(C_x/C_{ref})sample}{(C_x/C_{ref})background}$$

where C_x is the concentration of the examined heavy metal in the sample and the background soil reference, and C_{ref} is the concentration of the reference element in the sample and the background soil. In this study, a normalised enrichment factor approach was employed for metal concentrations using the background soil values from the site, the soil samples collected at location 5 and 6 from the initial transect were used for background standard, and Fe was used for the reference metal for normalization. Five contamination categories are recognized on the basis of the following: EF value less than 2 denotes deficiency to minimal enrichment; 2-5, moderate enrichment; 5-20, significant enrichment; 20-40, very high enrichment; >40, extremely high enrichment (Lu et al., 2009).

4.7 Summary

The experimental methods have been designed for this study in order to discriminate between the effects of factors which have an influence on the heavy metal concentration distribution and accumulation in roadside soils. Adequate consideration and sufficient field analyses were conducted to determine the soil sample area in order to examine the impact of different geologies on heavy metal concentration in roadside soil. After the soil site selection, the standard field soil sample collection methods were used (McDonald et al., 2009) in order to assess the targeted influential factors:

- Distance from the road;
- Underlying geology and characteristic soil type 'in situ'
- Soil layers (topsoil and subsoil); and
- Rainfall events.

Three different chemical measurements were undertaken for soil analysis including determination of total heavy metal concentration, soil chemical sequential extraction and soil metal isotopic analysis. Due to the consideration of the influence of rainfall, one major restriction of soil sampling was limited to the occurrence of rainfall events. As a consequence, the results generated from those soil chemical measurements did not provide adequate data to conduct statistical analysis in order to assess the relative significance of these influential factors. Therefore, a regional approach, which was firstly introduced by Hosking and Wallis (1993) was implemented for this study; the soil field data was combined in a manner whereby only the influential factor differed between the two or three sample populations. Four influential factors (distance, soil depth, underlying geology and rainfall) were considered in this manner.

V

Chapter 5 ANALYSIS OF SOIL PROPERTIES

5.1 Introduction

Prior to the systematic soil sample collection, the consideration of *in-situ* soil field measurements provided preliminary information to determine the final location of the soil sampling sites. The preliminary soil measurements comprised the soil field physical and chemical properties. Additionally, the heavy metal concentrations were analysed for the soil collected from the initial transect. Moreover, the preliminary analysis also included soil clay type using X-ray Diffraction (XRD) and soil cation exchange capacity (CEC) (results shown in Appendix B).

From the literature review conducted in chapter 2, it has been noted that these soil-associated factors are able to affect the heavy metal accumulation and distribution in roadside soils. For example, Turer and Maynard (2003) argued that soil absorbability of heavy metal increased by increasing the soil organic matter (SOM). Also SOM is normally recognised as an important scavenger for heavy metal in soils especially related with HCl-extracted heavy metals. Hence, it was necessary to take into account and determine the soil-associated factors prior to any further chemical heavy metal measurements.

The results obtained from these analyses built a solid foundation for a better understanding of the heavy metal concentration distribution pattern in the roadside soil. The initial transect decided upon for this study as a conceptual investigation approach, has been used as the standard method for other soil investigations (Chapman and Atkinson, 2007, McDonald et al., 2009). This transect provided the 'baseline' to detect the proximate heavy metal contents as a function of distance from each road. Furthermore, due to the investigation of the influence of geological variations on heavy metal concentrations as one of the main purposes of this study, it is very important confirm the soil types as consistent with the different geologies underlying the research site before setting down the field sampling strategy. Therefore, the results gained from the soil characteristic analyses (such as soil organic carbon and soil clay mineralogy) can not only be used for distinguishing and confirming the potential three geologies noted by Branagan (1993) in chapter 3, but also could supply the data for further multivariate statistical analysis to determine the correlation between soil-associated factors and heavy metal concentrations (refer to Chapter 7).

The analyses and investigations carried out in this chapter are presented below:

- Determine the heavy metal concentrations via the initial transect in order to decide the final sampling distances from the road edge;
- Determine and confirm the underlying geologies;
- Decide the final soil sampling locations based on the various geologies;
- Determine the soil-associated factors (such as clay mineralogy, total organic carbon and cation exchange capacity) for statistical analysis.

5.2 Heavy Metal Concentrations in the Initial Transect

In almost all soil surveys some attempt is made in the early stages to assess the scale at which the soil changes and the information required is often obtained from transects. By recording soil properties at a constant close spacing on such transect methods of analysis, data can be applied to reveal patterns of variation, and hence lead to a rational mapping strategy (Burgess and Webster, 1980). Correlograms, which show on average the relation of soil at one point to that at another, seem especially promising (Webster and Cuanalo, 1975). In order to have a non-biased survey (Chapman and Atkinson, 2007), an initial transect that intersected these different geologies across the whole park was established (Chapter 4 Figure 4-1). A total of 9 soil samples were collected in this transect which linked the two major highways. Then these soil samples were transferred to the laboratory to determine the heavy metal concentrations via aqua regia digestion (for the details of the methods refer to chapter 4.3.1). Then the digested soil sample solutions were analysed via microwave plasma atomic emission spectrometry (MP-AES). The heavy metal concentrations of Pb, Zn and Cu were measured for these 9 soil samples (Figure 5-1).

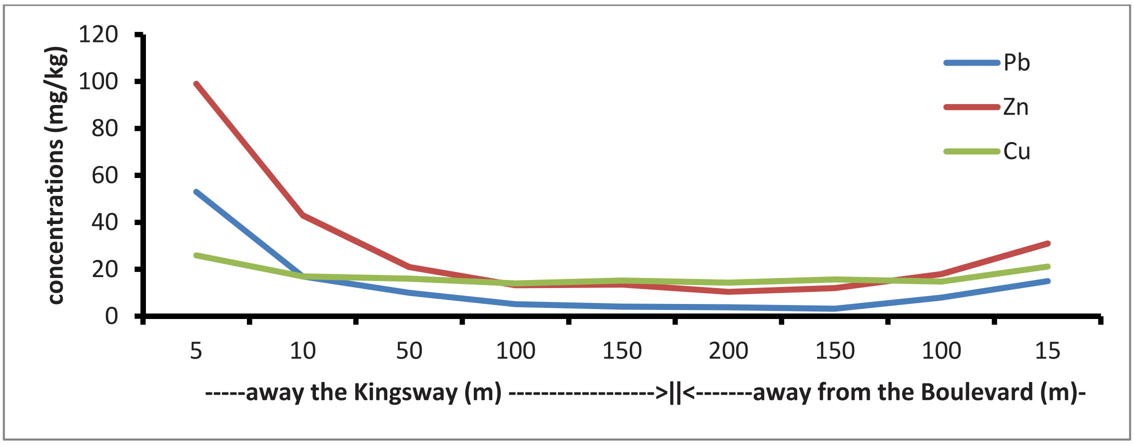

Figure 5-1 the heavy metal concentration of Pb, Zn and Cu in the 9 sample locations from the initial transect. The x-axis shown the distance away from the Kingsway from the left and the distance away from the Boulevard from the right side

The heavy metal distributions on the initial transect showed a decreasing trend with increasing distance from the road. There was an obvious reduction of heavy metal concentration in the distance of 10 m from the road for all the three metals (see Figure 5-1). The magnitude of these metal concentrations is in order: Zn > Pb > Cu. In addition, all the metal concentrations started to reduce to the background levels at 50 m from the road edge.

Therefore, the results obtained from this initial test indicated that the elevation of heavy metal concentrations occurred within 10 m distance from the roadside edge. Meanwhile, the soil field texture analysis was undertaken and is presented in Table 5-1. From the results obtained from field soil texture, it can be noted that the soils at location 1 and 9 are substantially different. The topsoils are silt loam (estimated clay content of approximately 25%) (Northcote, 1979, McDonald et al., 2009, Hazelton and Murphy, 2011). at location 1 and clayey sand (estimated clay content of approximately 5-10%, Northcote 1979, McDonald et al. 1994 and Hazelton and Murphy 2016) at location 9. Additionally, the data from the transect provided a basic understanding of the heavy metal distribution patterns and determined the strategy for further sampling collection.

Table 5-1 field soil texture analysis and colour description

No	topsoil		subsoil	
	colour[a]	texture[b]	colour	texture
1	5YR 3/1	silt loam	5YR 3/3	light clay
2	5YR 3/1	silt loam	5YR 3/3	light clay
3	5YR 2/2	sandy clay loam	5YR 2/2	sandy clay loam
4	5YR 2/1	clayey sand	5YR 2/2	silty clay loam
5	5YR 5/1	silty clay loam	5YR 3/2	sandy clay loam
6	5YR 4/1	loamy sand	5YR 4/2	clay loam
7	5YR 2/3	loam	5YR 2/4	sandy clay loam
8	5YR 3/6	sandy clay loam	5YR 4/3	sandy clay
9	5YR 3/3	clayey sand	5YR 3/4	clayey sand

[a] refer to the colour code by Munsell and Color (2000)
[b] Northcote (1979); McDonald et al. (2009)

5.3 Soil Clay Mineral Analysis

The determination of the type and relative amounts of the minerals present in soil forms an essential component of most soil characterization efforts. The use of X-ray diffraction based on quantitative clay mineral analysis was conducted for the roadside soil samples collected from the initial transect. Soil clay minerals almost invariably occur as mixtures. The signal intensity of individual clay mineral phases in mixtures depends on a number of physical properties, which are not constant among different clay mineral phases (Brown and Brindley, 1980). This consequently leads to the well-known phenomenon that in a mixture of equal parts of, for example, smectite, muscovite and kaolinite the relative 001 peak areas of these minerals are not equal. This evidence together with what is known about the theory of X-ray diffraction (Moore and Reynolds, 1989) clearly indicates that an attempt to accurately quantify clay minerals on the basis of referencing individual 001 peak areas to the sum of peak areas in a diffractogram is bound to fail. From chapter 3, the local tree around location 1 (refer to

Chapter 3 Figure 3-4) is mainly *Eucalyptus crebra* (narrow-leaved ironbark); previous studies pointed out that narrow-leaved ironbarks generally grow on shale-derived soil (Benson and Howell, 1990, Cuneo and Leishman, 2006).

As shown in the previous work of site distribution, Miranda Park is in a conjunction of three different geologies: Wianamatta Shale, Hawkesbury Sandstone and Mittagong Formation (refer chapter 3, Figure 3-2). Therefore, the identification of different geologies was conducted by the X-ray diffraction method in this study. In order to distinguish and identify the geologies in Miranda Park, the first step was to take account of the difference between the two corners along the transect; from the X-ray diffraction results conducted for the location 1 to 9, it was shown that the clay mineralogy is obviously different between location 1 (Figure 5-2) and location 9 (Figure 5-4). The results of XRD had shown the kaolinite is the predominant clay mineral for both location 1 and 9. In addition, illite was found only in location 1 and sanidine was only found in the soil in location 9. This is in agreement with the study conducted by Ghafoori et al. (1993); they argued that kaolinite is the main component clay mineral for Ashfield shales which also contain large amounts of illite. Grim and Loughnan (1962) explained the formation of illite in the Sydney area; they pointed out that the illite is generally found in Ashfield Shales due to river bank erosion. Ashfield Shale is part of the Wiannamatta group of sedimentary rocks in the Sydney Basin (Ghafoori et al., 1993, William and Airey, 1999, Haworth, 2003). Therefore, it can be inferred that the soil around location 1 is derived from the Wianamatta Shale.

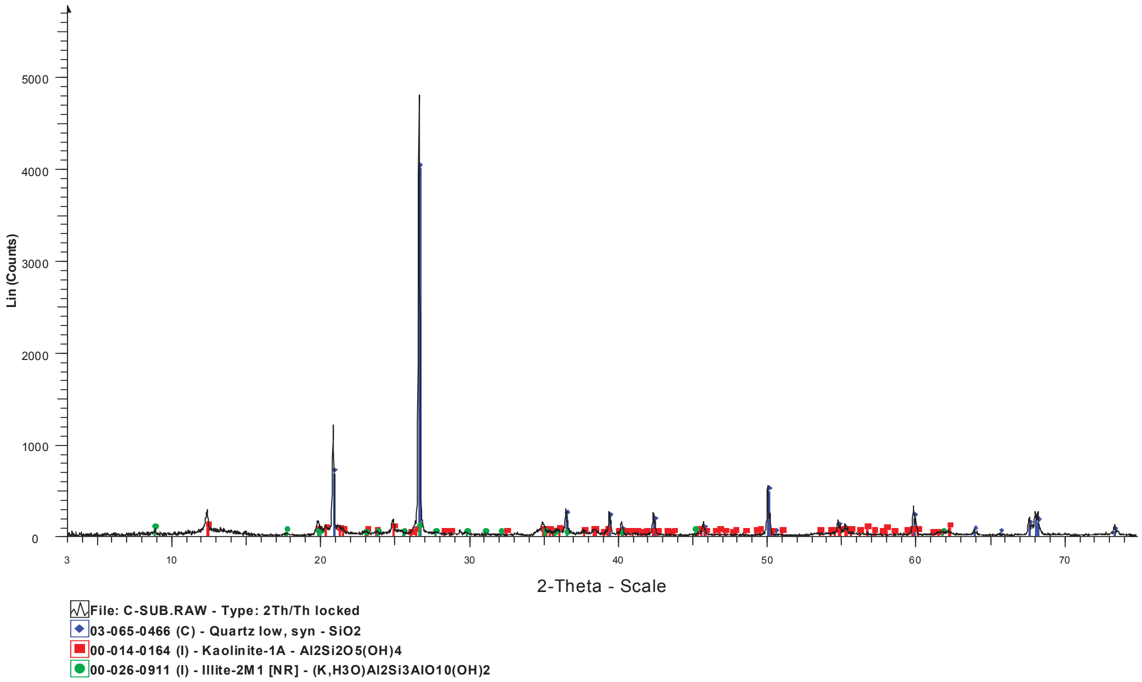

Figure 5-2 the X-ray Diffraction results obtained for the initial transect at location 1

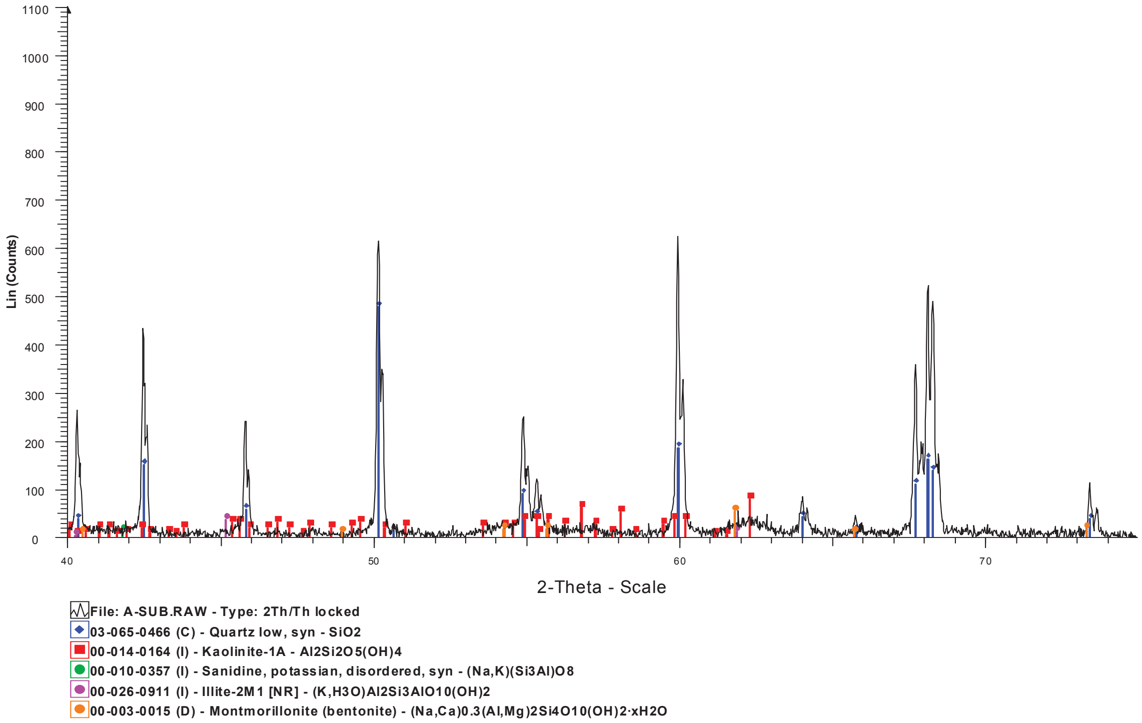

Figure 5-3 the X-ray Diffraction results obtained for the initial transect at location 4, the results shown the clay minerals found in soil collected from location 4

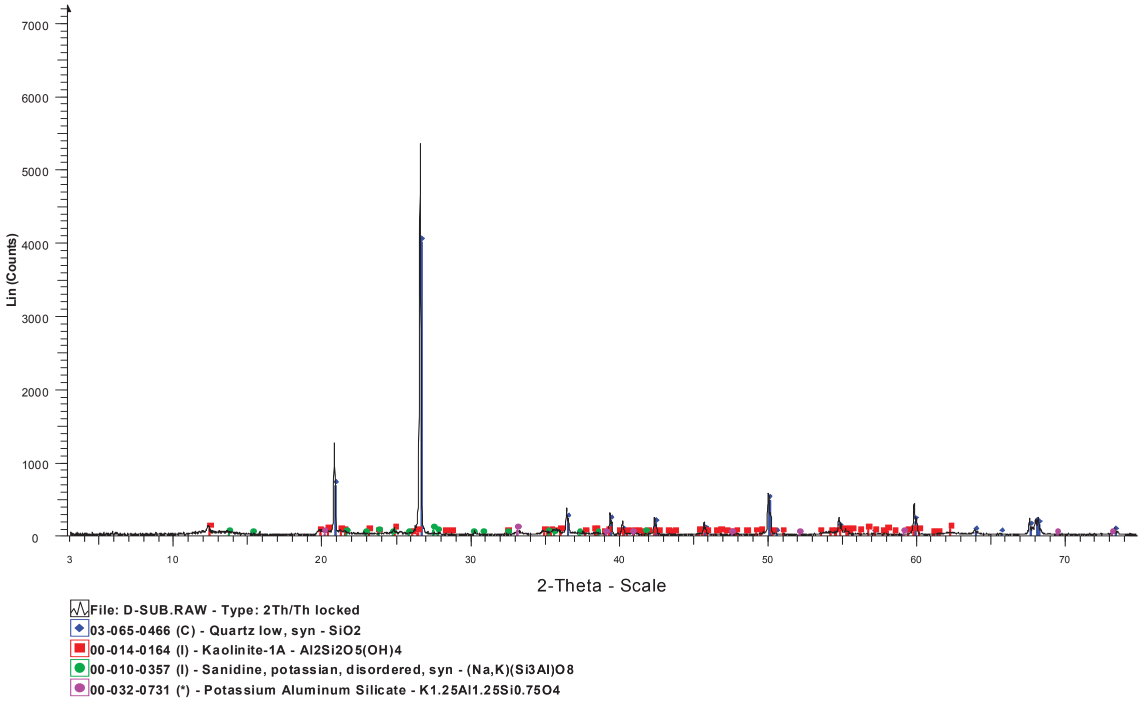

Figure 5-4 the X-ray Diffraction results obtained for the initial transect at location 9

Saynor and Erskine (1993) claimed that Hawkesbury Sandstone consists mainly of quartzose sandstone with interbedded lenticular shale beds. Moreover, Zaid and Al Gahtani (2015) investigated the authigenic clay minerals for Hawkesbury Sandstone in southern Sydney Basin, Australia. They pointed out that the clay minerals identified for Hawkesbury Sandstone are kaolinite, mixed-layer illite/smectite, illite, and chlorite in decreasing order of their abundance. In addition, kaolinite and a mixed-layer of illite/smectite (Avg. 18.35%) dominate over illite and chlorite in their study. The results of Figure 5-3 illustrated the clay mineralogy at location 4 on the initial transects. Montmorillonite is one of the clay minerals found at this location; it belongs to the group of phyllosilicate mineral species and is one of the most important subclasses of smectite. Furthermore, the scanning electron microscope (SEM) results confirmed the results obtained by the XRD.

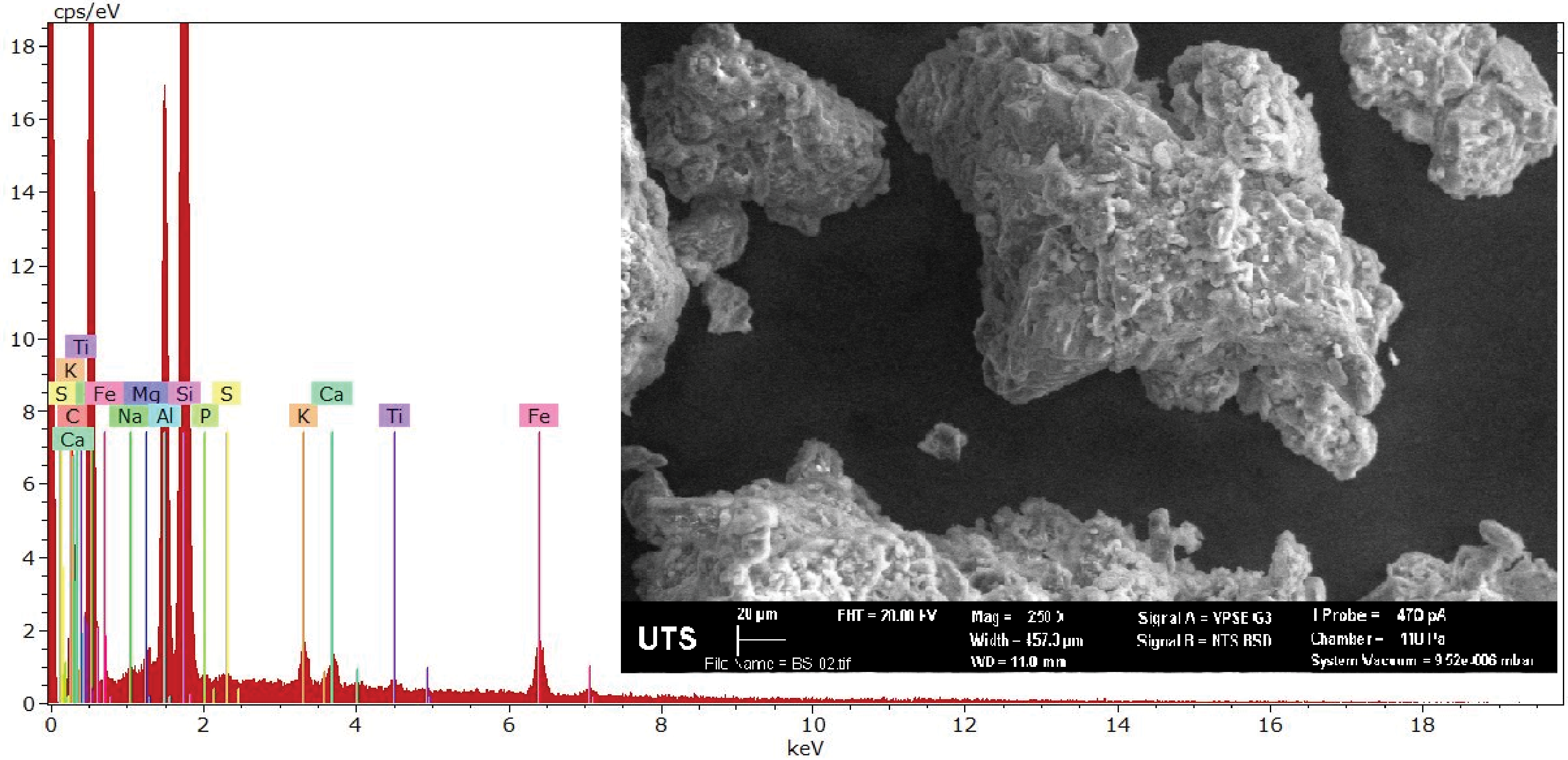

Figure 5-5 the SEM results obtained for the initial transect and the SEM results indicated the elements formed the clay mineral in location 4

From the SEM results presented in Figure 5-5, it can be noted that the elements such as Mg, Na, Ca, Si and Al were detected. Chemically, its formula is $(Na, Ca)_{0.33}(Al, Mg)_{2}(Si4O10)(OH)_{2}\cdot nH2O$ (Greene-Kelly, 1957). Therefore, it can be inferred that the soil around the location 4 is mainly derived from Hawkesbury Sandstone. On the northern side of the park, the XRD result was conducted for location 9 (see Figure 5-4). The XRD indicated the clay mineral does not comprise either illite or Montmorillonite. In addition the soil field colour and texture are also different from the soils at the other locations. Hence, it can be inferred that the soils at location 9 are derived from Mittagong Formation. The Mittagong Formation was at one time described as ‘passage beds’ between the Hawkesbury Sandstone and the overlying Ashfield Shale. It comprises fine-grained quartzose sandstone interbedded with dark grey siltstone and laminate (Herbert, 1983, Rust and Jones, 1987, Chan et al., 2005).

5.4 Determination of Final Sample Location

After considering the results obtained from the XRD and SEM analyses for soil clay detection along the initial transect, the final soil sampling locations were chosen because of the three different underlying geologies. The final soil sample locations were identified in Chapter 4, Figure 4-4, another round of soil field survey for the description of the soil texture and colour at the final sampling locations was undertaken and the results are shown in Table 5-2. The soil of yellow areas is derived from Hawkesbury Sandstone (named A and B), soil in the purple areas are derived from Wianamatta Shale (named C and E), and the soil in the orange area is derived from Mittagong Formation. For each location, the field properties of texture and colour were described for topsoil and subsoil using the standard field texture grade criteria (Northcote, 1978, McDonald et al., 2009) (Hazelton and Murphy, 2016) and the International Munsell Colour Chart (Munsell and Color, 2000).

Table 5-2 Description of soil sampled in the final sampling location after the second round of field work

site	Soil depth	Distance from the road (m)					
		1		5		10	
		Texture[a]	Colour[b]	Texture	Colour	Texture	Colour
A	Topsoil	sandy loam	5YR 3/1	sandy loam	5YR 3/1	sandy loam	5YR 3/1
	Subsoil	light clay	5YR 4/6	light clay	5YR 4/6	light clay	5YR 4/6
B	Topsoil	sandy loam	5YR 3/1	sandy loam	5YR 3/1	sandy loam	5YR 3/1
	Subsoil	light clay	5YR 4/6	light clay	5YR 4/6	light clay	5YR 4/6
C	Topsoil	silt loam	5YR 3/1	silt loam	5YR 3/1	silt loam	5YR 3/1
	Subsoil	light clay	5YR 3/3	light medium clay with silt	5YR 3/3	light to light medium clay	5YR 3/3
D	Topsoil	clay sand to sandy loam	7.5 YR 5/2	sandy loam	7.5 YR 5/2	sandy loam	7.5 YR 5/2
	Subsoil	sandy clay loam	7.5 YR 8/6	sandy clay	7.5 YR 7/6	sandy clay	7.5 YR 8/6
E	Topsoil	light sandy clay loam	5 YR 3/3	light sandy clay loam	5 YR 3/3	light sandy clay loam	5 YR 3/3
	Subsoil	silty clay	5 YR 3/4	silty clay	5 YR 3/4	silty clay	5 YR 3/4

[a] Northcote (1979); McDonald et al. (2009)

[b] refer to the colour code by Munsell and Color (2000)

Soils with the combination of high clay content, high organic matter content and pH 6.5-7.5 and in an aerobic condition have much less risk of contaminants becoming mobile in the environment. The bioavailability of the contaminant is also a factor, as that determines the portion of the total concentration of a contaminant that is mobile (this will be discussed in chapter 6). The forms of heavy metals in soil generally regarded as the bioavailable fraction are those in the soil solution, together with those held on the surface that are easily displaced into the soil solution (Hazelton and Murphy, 2011).

Individual metals respond differently to changes in soil conditions, and the bioavailable fraction is different for each metal (Bernard, 1997). Many properties such as soil pH, clay content, organic matter and cation exchange capacity influence their retention and mobility (Helmke and Naidu, 1996, Hazelton and Murphy, 2011). Chen et al. (2010)

investigated the correlation between heavy metal contamination and soil total organic carbon (TOC) in Beijing, China. They employed a Pearson correlation analysis which indicated that the Cd, Cu, Pb and Zn were significantly positively correlated with TOC. Nevertheless, a survey conducted by Huang et al. (2007) also found the contents of Cd, Hg and TOC in the upper parts of the soil layer increased gradually. However, the strong correlation between TOC and heavy metals did not appear in unpolluted soils reported by Tack et al. (1997), especially with the range of TOC between 0.2 to 0.4. Additionally, McGrath (1996) claimed that extractable Zn instead of total Zn was significantly correlated with organic C in Irish agricultural soils.

Table 5-3 Results of total organic carbon (mean) from LECO analyser for three geologies derived soils at different distance from the road (unit:%)

Geologies	Distance (m)		
	1	5	10
Hawkesbury Sandstone	4.72	3.54	4.96
Wianamatta Shale	4.93	5.79	7.35
Mittagong Formation	6.78	1.78	4.67

The soil total organic carbon (TOC) results measured in this study via LECO analysis for the final locations are presented in Table 5-3. The LECO was conducted for the soil samples at 1m, 5m and 10m away from the roadside for three geologies derived soils. There is no substantial variation for the TOC in the soils derived from Hawkesbury Sandstone and Wianamatta Shale with increasing distance.

Table 5-4 Results of cation exchange capacity (CEC) for three geologies derived both topsoils and subsoils at different distance from the road (unit: cmol$^+$/Kg)

Weather condition	Geologies	Distance					
		Topsoils			Subsoils		
		1	5	10	1	5	10
Pre-rainfall	Hawkesbury Sandstone	16.42	14.33	13.52	15.02	21.92	10.37
	Wianamatta Shale	19.01	17.21	14.00	14.20	16.46	13.10
	Mittagong Formation	19.84	9.57	19.72	14.52	18.31	10.91
Post-rainfall	Hawkesbury Sandstone	16.44	11.77	17.15	16.25	17.72	21.84
	Wianamatta Shale	21.62	23.63	32.85	29.33	13.03	15.04
	Mittagong Formation	21.78	25.83	5.81	14.78	16.51	11.35

The soil organic carbon within Miranda Park is approximately around 5 % at a distance from 1m to 10 m. However, the TOC in the soil derived from Mittagong Formation had no trend pattern, and the minimum value (1.78%) was found at 5m from the road in this soil type. The variation of soil organic matter may be attributed to the soil acidity because research reported by Nabulo et al. (2006) indicated that soil organic matter (SOM) and soil clay content are significantly correlated with soil pH.

Both the Raupach methodology and Laboratory methodology corresponds to 1:5 pH in water ± 0.5pH units of pH. A general interpretation 1:5 of pH measured in soil/water ratio is 5.5-6.0 moderately acid, 6.0-7.0 slightly acid. At these pH values heavy metals would not be markedly mobilized. The pH of the soil fluctuates especially with changes in soil moisture. Climate, particularly rainfall affects the acidity. Parent materials because of differences in their acid neutralizing capability affect the pH. Therefore natural pH varies greatly between soil types.

Cation exchange capacity is the capacity of the soil to hold and exchange cations. It is a major controlling agent of stability of soil structure, nutrient availability, soil pH and the soil reaction to fertilisers and other ameliorates. A low CEC means that the soil has a low resistance to changes in soil chemistry that are caused by land use change. Soils with high amounts of clay, especially smectite-type clays can have high CEC. The soil CEC results for both topsoils and subsoils under different weather conditions were presented in Table 5-4. The soil CEC for Hawkesbury Sandstone ranges from 10.37 to 21.92; Wianamatta Shale ranges from 13.03 to 32.85 and Mittagong Formation ranges from 5.81 to 25.83, respectively. The soil CEC results revealed that other factors such as a rainfall event, soil depth and the distance from the roadway can also influence the soil cation exchange capacity. The most substantial change of soil CEC due to the rainfall was found in the soil derived from Wianamatta Shale.

5.5 Summary

The aim of this research is to evaluate the influence of soil type on the heavy metal accumulation and distribution pattern in roadside soils. In this chapter, the information obtained from the first round of field work provided a fundamental understanding of the soil characteristics in this experimental site (Miranda Park), and the geologies described by Branagan (1993) were confirmed through the preliminary field inspection and XRD/SEM analysis. In detail, the clay mineral and approximately content in soil derived from different geologies were determined. The soil field colour and texture were also determined in the first round of field work. Hence, after careful consideration of the local geology, the final sampling locations were determined based on the locations of these three geologies. Two sites named A and B located in the middle of the Kingsway were decided upon for assessing the heavy metal concentration in Hawkesbury Sandstone derived soils, two sites named C and E for Wianamatta Shale-derived soils and site D for Mittagong formation derived soils, respectively. Then the final soil survey was employed for these five locations (the detailed soil sampling strategy is shown in Chapter 4). Moreover, the main soil properties such as soil total organic carbon (TOC) and soil cation exchange capacity (CEC) were analysed prior to the heavy metal chemical analysis in this chapter. The LECO results showed the soil organic carbon within Miranda Park is approximately around 5 % at a distance from 1m to 10 m. However, the TOC in the soil derived from Mittagong Formation had no trend pattern, and the minimum value (1.78%) was found at 5m from the road in this soil type. The soil CEC for Hawkesbury Sandstone ranges from 10.37 to 21.92; Wianamatta Shale ranges from 13.03 to 32.85 and Mittagong Formation ranges from 5.81 to 25.83, respectively. The soil CEC results revealed that other influential factors such as rainfall event, soil depth and the distance from the road can also impact on the soil cation exchange capacity. The most significant change of soils CEC after the rainfall was found in the soil derived from Wianamatta Shale. In addition, description of the final soil sampling locations including the road information, local annual mean precipitation and the details of local soil properties is presented in Table 5-5

Table 5-5 General description of the final soil sample locations

	Site A,B	Site C,E	Site D
Close Highway name	Kingsway	Kingsway	The Boulevard
AADT(% heavy) 2014	30,148	30,148	28,424
Speed limit (km/h)	60, 40 in school time	60, 40 in school time	60
Road type, Lanes	1+1	1+1	1+1
Annual mean precipitation (mm)	1000	1000	1000
Topsoil field texture and clay content (%)	Sandy loam, 10-20	Silt loam, approx. 25	Sandy clay loam, 20-30
Subsoil field texture and clay content (%)	Light clay, 35-40	Silty clay, 35-40	Sandy clay, 35-40
Range of TOC (unit:%)	3.54-4.96	4.93-7.35	1.78-6.78
Range of ECEC (unit: $cmol^{+}/Kg$)	11.77-21.92	13.10-32.85	9.57-25.83
Soil pH	7.2	6.7	7.2
Geology Herbert (1983)	Hawkesbury Sandstone	Wianamatta Shale	Mittagong Formation
Topography	Slope from 10 m	No slope	No slope
Road inclining	Flat	Flat	Flat

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VI

Chapter 6 CHEMISTRY ANALYSIS

6.1 Introduction[1]

As discussed previously, assessment of the heavy metal content of roadside soils requires the completion of a number of steps. One of these steps is the chemical analysis of the soil samples. In the discussion of the investigation methodology (outlined in Chapter 4 of this dissertation), steps in the chemical analysis of the soils can be categorised as extraction of the metals from the soil, and determination of the metal concentrations. In addition to the determination of the Pb concentrations, the Pb isotopic ratios also were determined. Presented in this chapter are details of the chemical analyses undertaken and the results obtained. Two extraction techniques have been utilised with the first technique being total extraction while the second was sequential extraction. Details of these techniques and the results obtained are presented in Sections 6.2 and 6.3 respectively. In a similar manner, the isotope analysis and the results obtained are presented in Section 6.4.

6.2 Total Heavy Metal Concentrations

The results of the heavy metal concentration in the roadside soil obtained from the six times sampling (three times pre-rainfall sampling and three times post-rainfall sampling) at the five locations are presented in Table 6-1. From the field sampling 180 samples were collected and analysed for heavy metals. Table 6-2 shows the range of

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[1] This chapter is based on a published journal paper by Zhao and Hazelton (2016), Evaluation of accumulation and concentration of heavy metals in different urban roadside soil types in Miranda Park, Sydney. *Journal of Soils and Sediments*, 1-9. (see Appendix C)

concentrations of heavy metals obtained during this study. Also, included in Table 6-2, is the range of concentrations for heavy metals reported in the literature by other researchers at other sites. From the consideration of Table 6-2, the concentrations obtained are consistent within the bounds of the other studies. The heavy metal concentration was found to be as follows: Zn > Pb > Cu > Cr > Ni > Cd. The results of the order of heavy metal magnitude could imply the soil in Miranda Park is contaminated by anthropogenic activities.

Table 6-1 The mean (n=6 for AB and CE; n=3 for D) value of heavy metal concentrations in both top- and subsoil derived from different geologies under different weather condition at different distance from traffic

Soil layer	Weather condition	Site	Distance (m)	Mean value of heavy metal concentration (ug/g)					
				Pb	Zn	Cu	Cr	Ni	Cd
Topsoil	Pre-rainfall	AB	1	103.63	223.41	43.98	38.78	18.93	2.24
			5	47.36	94.53	25.48	21.30	11.53	0.42
			10	21.15	42.36	18.33	13.20	8.22	0.14
		CE	1	159.32	254.12	57.74	52.49	30.76	3.32
			5	56.31	100.32	31.52	26.31	16.55	0.55
			10	16.21	33.64	21.38	16.50	9.96	0.16
		D	1	137.50	264.23	63.85	57.68	32.64	4.33
			5	50.74	113.21	35.35	30.12	19.29	0.47
			10	17.35	51.32	22.55	17.65	11.83	0.17
	Post-rainfall	AB	1	78.87	213.35	38.54	33.62	18.14	2.07
			5	44.14	97.34	22.58	17.28	9.50	0.35
			10	19.24	39.32	16.26	11.87	7.23	0.17
		CE	1	139.09	230.24	51.64	46.87	27.71	3.08
			5	42.32	103.24	26.45	21.84	11.06	0.41
			10	20.34	39.35	18.25	12.76	8.71	0.17
		D	1	135.69	222.36	59.06	52.95	31.63	4.15
			5	55.18	101.42	32.58	26.60	15.29	0.39
			10	24.31	45.62	20.31	14.35	11.55	0.19
Subsoil	Pre-rainfall	AB	1	86.08	164.78	37.15	32.40	16.94	2.02
			5	36.41	66.24	22.61	18.51	8.88	0.35
			10	18.21	27.35	14.58	9.38	6.60	0.15
		CE	1	103.23	138.54	50.29	44.75	28.68	3.00
			5	40.21	55.34	28.47	23.42	13.54	0.44
			10	19.16	24.36	18.98	12.31	9.22	0.17
		D	1	97.35	142.64	55.54	49.44	29.53	4.26
			5	48.61	71.23	31.34	26.68	16.30	0.41
			10	22.74	33.21	19.40	14.67	9.99	0.16
	Post-rainfall	AB	1	94.32	174.33	42.72	37.26	18.66	2.25
			5	47.11	70.31	24.94	18.26	10.54	0.45
			10	20.74	23.32	20.02	14.70	7.79	0.19
		CE	1	124.32	158.64	54.54	47.62	29.77	3.24

	5	44.27	62.31	30.97	25.69	15.47	0.52
	10	24.12	30.74	21.40	17.74	11.52	0.18
D	1	110.34	166.21	58.49	52.24	32.00	4.48
	5	57.41	77.41	35.57	30.57	16.64	0.51
	10	27.15	27.54	22.61	16.29	11.75	0.17

It was found that the rainfall can reduce the metal concentration in the topsoil in all the locations; the changes are more pronounced at a distance of 1m. This result could be due to the sampling location being adjacent to the traffic and subjected to more water splash and spray.

The elevated heavy metal concentration both before and after rainfall could be explained due to the usage of heavy metals in vehicle tyres, abrasion of brake pads and fall-out from the exhaust of vehicle fuel consumption (Turer et al., 2001, De Silva et al., 2015). The rainfall also would change the metal concentrations in subsoils. For the topsoils, the rainfall has contributed to produce the most substantial percentage change in Pb (23.89%), Cu (12.37%), Cr (13.31%) and Cd (7.59%) for Hawkesbury Sandstone-derived soil, Ni (9.92%) for Wianamatta Shale-derived soil and Zn (15.85%) for Mittagong Formation-derived soil. In contrast, for the subsoils, due to the rainfall infiltration carrying the metals down from the upper layer, the metal concentrations increased post-rainfall compared to pre-rainfall. This result agrees with Chen et al. (2010). They explored the heavy metal concentrations in roadside soils in Beijing, and argued that the rainfall runoff from roads and pavements is able to make a small but significant contribution to the roadside soil concentration which could be explained because the rainfall could leach the metal through the soil profile and even into the groundwater. The greatest percentage changes in Cu (14.99%), Cr (15.00%), Ni (10.15%) and Cd (10.15%) are in Hawkesbury Sandstone-derived soil and Pb (20.43%), Zn (15.85%) for Wianamatta Shale-derived soil. Heavy metal concentrations were higher in the topsoils. The relative difference between the topsoils and subsoils was typically most pronounced at the distance of 1m from the traffic and the lowest at the

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distance of 10m from the traffic. For example, in the pre-rainfall period, for the soil derived from Hawkesbury Sandstone, the Pb and Zn concentration in the samples of topsoil for the distance of 1m (103.63µg/g and 223.41 µg/g) is substantially greater than the Zn concentration in the samples of subsoil for the same 1m distance (88.08µg/g and 164.78 µg/g), respectively. Although the concentrations of Pb and Zn have strong differences between topsoils and subsoils especially at a distance of 1m, similar differences for Cu, Cr, Ni and Cd have not been observed.

The concentration of Zn is greater than the concentration of Pb in all the three different soil types. The highest concentration of Pb was in Wianamatta Shale derived soil, 159.32 mg/kg and the highest concentration of Zn, 254.12 mg/kg occurred in Mittagong Formation derived soil, all at a distance of 1 m from the road. The rainfall would change the metal concentration in the subsoil; however, the rainfall reduced the metal concentration in the topsoil in all the locations. This could be explained by the rain leaching the metal deep into the soil profile. For the topsoil, the rainfall has been shown to produce the most significant percentage change in Hawkesbury Sandstone derived soil for Pb (23.89%) and Mittagong Formation derived soil for Zn (15.85%) at a distance of 1 m. In contrast, for the subsoil, due to heavy metal leaching by rainfall from the upper layer, the concentrations of both Pb and Zn increased substantially. The greatest percentage change for Pb is 20.43% and Zn is 19.97% in location C, E (Wianamatta Shale derived soil). The high level of metal concentration may be the result of the higher clay content in the subsoil of Wianamatta Shale which has the greatest clay content (more than 40%); the clay plays a critical role in soil absorption of heavy metals (Hazelton and Murphy, 2016).

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Table 6-2 Heavy metals concentration (µg/g) mean or ranges with standard deviation or ranges in roadside soils in various cities

City	Pb	Zn	Cu	Cr	Ni	Cd	Reference
Sydney, Australia	16.2-159.3	23.3-264.2	16.3-59.1	9.38-52.5	6.6-32.6	0.14-4.48	This study
Melbourne, Australia	16-144	10.4-88.8	4-12	18-29	7-20	0.06-0.59	De Silva et al. (2015)
Sydney, Australia	24-198	71-238	6-225	10-79	27-242	0-0.5	Mohammed et al. (2012)
Beijing, China	35.4 ± 13.5	92.1 ± 18.7	29.7 ± 5.7	61.9 ± 2.3	26.7 ± 2.4	0.2 ± 0.07	Chen et al. (2010)
Shanghai, China	13.7-192	103-1025	23.1-151.7	25.5-233.3	4.95-65.7	0.19-3.66	Shi et al. (2008)
Shenyang, China	1.9-940	25-1140	7.6-430	4.8-207	-	0.01-9.64	Li et al. (2013)
Xushe, China	35.6-53.7	48.9-97.4	20.3-30.4	43.3-70.8	23.3-38.8	0.09-0.15	Wu et al. (2011)
Yibin, China	20.3-223.9	36.2-362.2	19.2-163.3	-	-	-	Guo et al. (2012)
Paris, France	20-3784	27-1755	6.7-201	21-80	5.9-26	0.1-2.7	Pagotto et al. (2001)
Dublin, Ireland	14-714	22-360	10-123	-	-	-	Dao et al. (2013)

6.3 Analysis of Soil by Sequential Extraction Procedures

The Pb, Zn, Cu, Cd, Ni and Cr fractions expressed as amounts and percentages of the sum of individual chemical fraction are presented in Figure 6-1 to Figure 6-6. The distribution of metal varies greatly with the sampling distance and soil types. A decreasing trend in percentage of total metals in the exchangeable, and an increasing trend in the residual fractions was observed with an increasing total metals contents.

6.3.1 BCR for Lead

The percentage of exchangeable fraction (F1) of Pb decreases with an increase in the distance from the road. The percentages of F1 decreased from approximately 40% down to approximately 5%. At a distance of 1 m, there is a clear reduction of exchangeable fraction in all locations in the post-rainfall period. This could explain the reduction of total Pb concentration in all the locations. The exchangeable fraction is an indicator of the metal mobility and accounts for the metal mobility through the soil profile. In contrast, the oxidisable fraction (F3) and residual fraction (F4) predominantly come from the parent material. The lead in the roadside soil is strongly associated with organic matter and Fe-Mn oxide phases (ca. 70%) with small amounts in the residual and carbonate fraction at a distance of 5 m from the traffic. The percentage of exchangeable Pb is very low (ca. 5%) in roadside soil in all these three locations at a distance of 10 m from the roadside. However, there is a significant exception occurring in location A, B at a distance of 5 m from the roadside where the exchangeable Pb percentage increases significantly. From Figure 6-1, the rainfall significantly influenced F1 at a distance of 1 m from the roadside, because at this distance, the roadside soil is critically impacted by the deposition from vehicles onto the road surface as dust in the form of aerosols. Moreover, the rainfall changed the exchangeable fraction especially at a distance of 1m and 5m from the roadside.

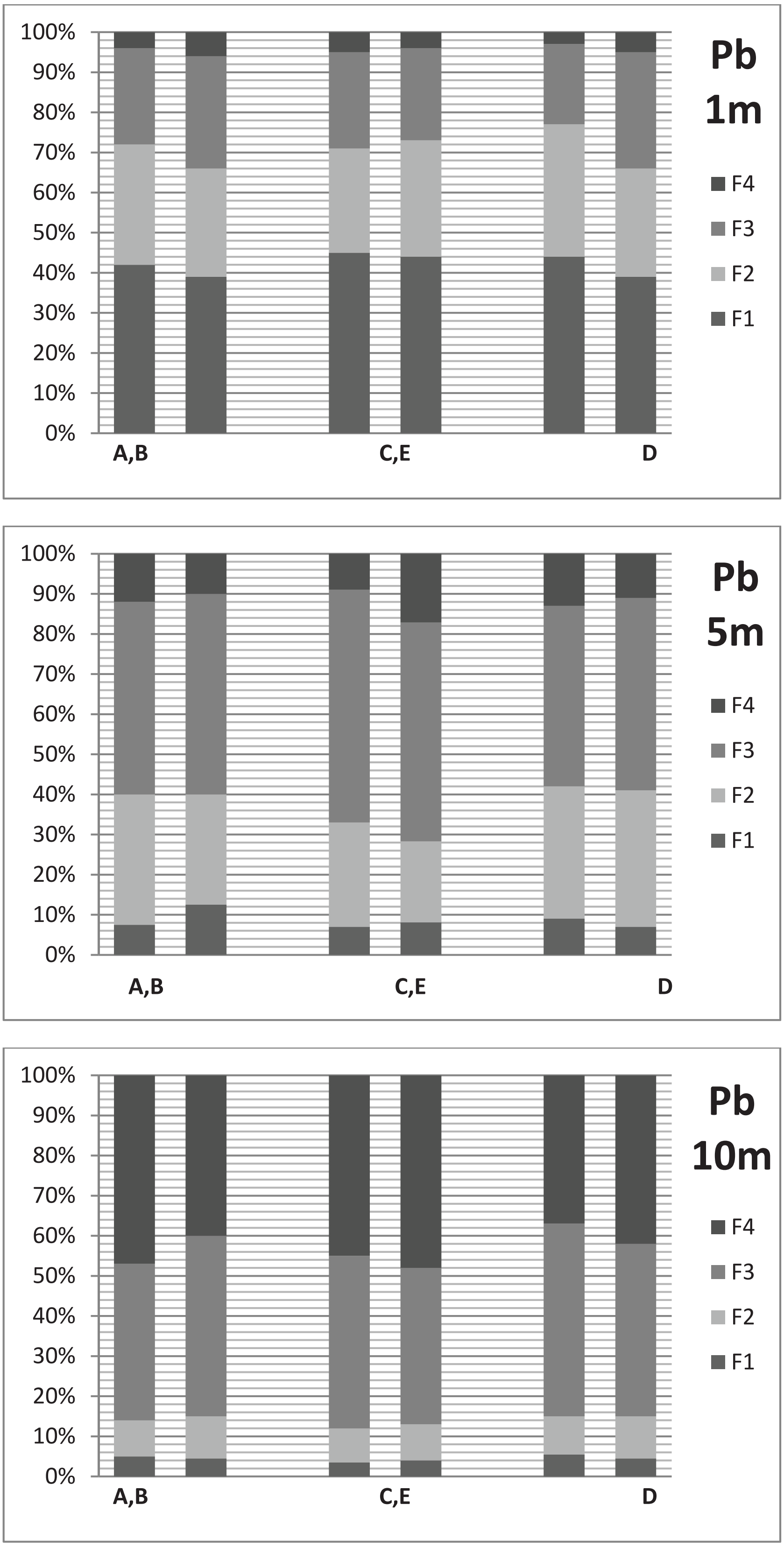

Figure 6-1 The mean lead BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated to organic matter); F4: Residual fraction

6.3.2 BCR for Zinc

In this study, according to Figure 6-2, at a distance of 1m from the roadside, the exchangeable fraction varied from approximately 30% to approximately 52%. In the comparison between different soil types, a significant reduction of F1 was found in location D. Similarly, the most significant reduction of total Zn concentration was also in this soil type. However, at a distance of 5 m from the roadside, the predominant fraction for Zn is the Fe-Mn oxide phase (ca. 40%). The next important fractions are the exchangeable fractions, (ca. 30%). The exchangeable Zn in location D in the post-rainfall period is above 50%, which could be a topic for further study to investigate its bioavailability and ecological implications. At a distance of 10 m, the Zn chemical composition percentage has a similar value to Pb; this implies the metal concentration is mostly contributed from the parent materials and other stable forms. Furthermore, comparing the chemical fraction composition at different distances, the total Zn elevation is mainly due to the increase of exchangeable fraction and it also could be influenced by rainfall.

6.3.3 BCR for Copper

Copper (Cu) has the highest exchangeable fraction averaging 42% for all three soils types at a distance of 1m from the road (Figure 6-3). The exchangeable fraction has a considerable reduction at 5m and 10m away from the road edge for all the three soil types indicating the Cu was significantly influenced by anthropogenic activities such as traffic emission at 1m from the road. This is in line with a previous study (Ma and Rao, 1997) that as the total Cu in the exchangeable fraction increased, Fe-Mn oxide and organic fraction increased the Cu in the residual fraction decreased. Moreover, from Figure 6-3, it can be seen that the rainfall can slightly change the percentage of all four fractions at different distances.

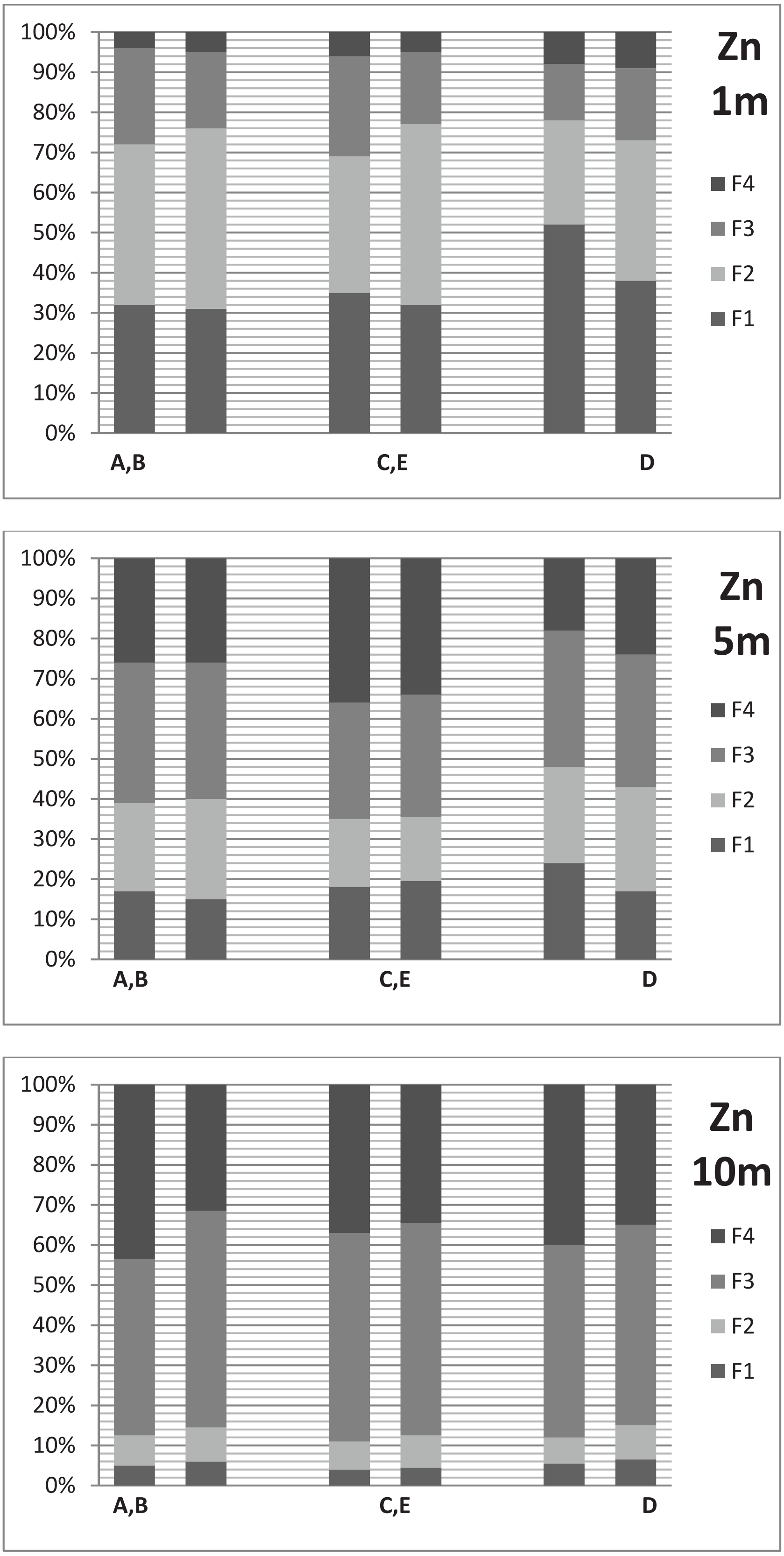

Figure 6-2 The mean zinc BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning is showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated with organic matter); F4: Residual fraction

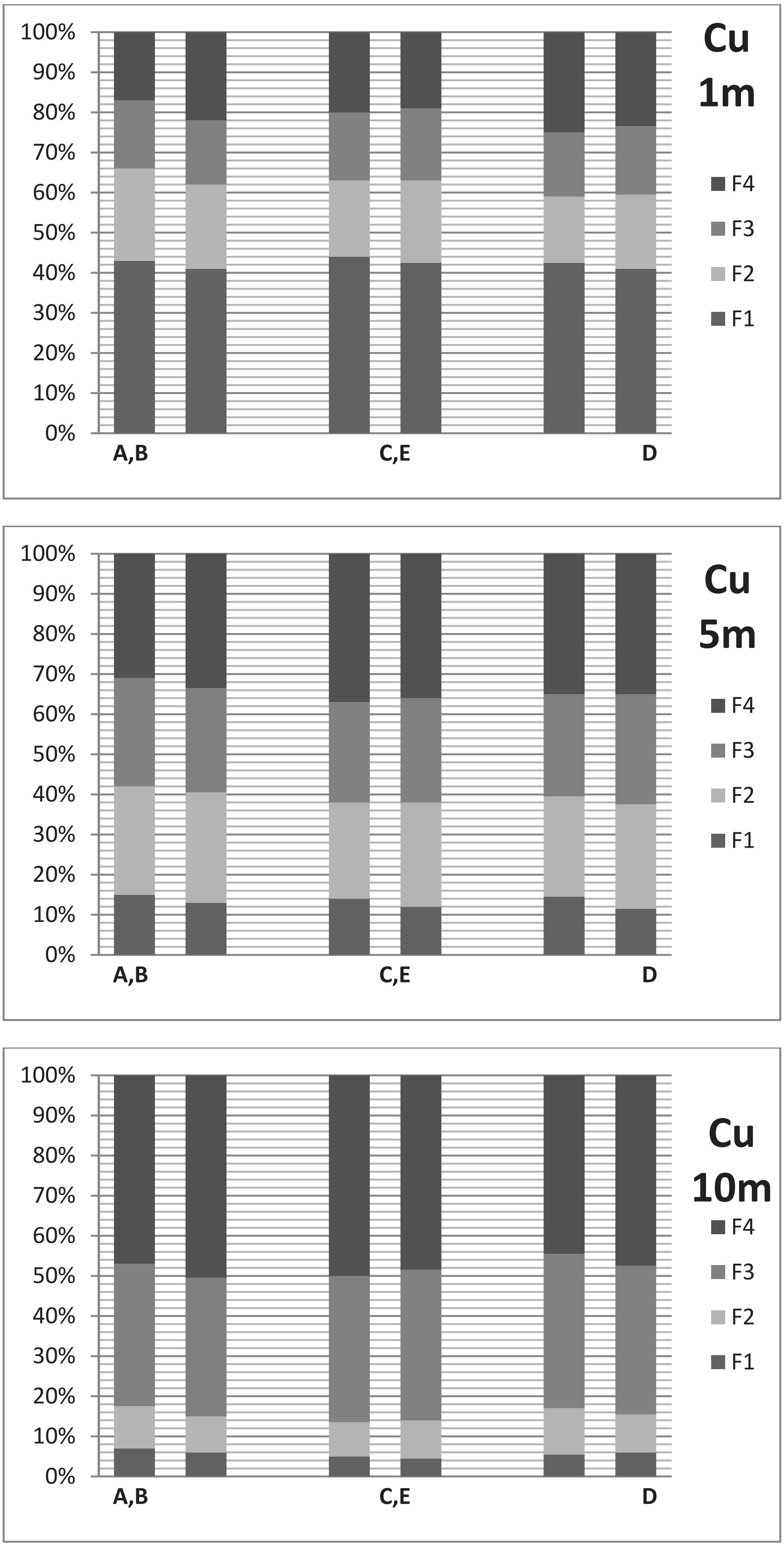

Figure 6-3 The mean copper BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning is showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated with organic matter); F4: Residual fraction

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6.3.4 BCR for Cadmium

The Cd in roadside soils is predominant in the exchangeable fraction at distance 1m from the road which accounted for approximately 80% (see in Figure 6-3). This can be explained due to the low total concentration of Cd (Pueyo et al., 2008, Nguyen et al., 2015). In contrast, the residual fraction is the most dominant fraction for all the soil types from all the parent materials at distance 10m from the road, averages of 70.75% for Hawkesbury Sandstone, 71.25% for Wianamatta Shale and 74% for Mittagong Formation, respectively.

6.3.5 BCR for Nickel

The Ni chemical sequential fractions were presented in Figure 6-4; the pattern of nickel chemical fractions was similar to Cu (Ma and Rao, 1997), the predominant fraction is exchangeable fraction at 1m distance; the highest percentage of exchangeable fraction was found in soils derived from Mittagong Formation because of the high total Ni concentrations (see Table 6-1) at this location. The Fe-Mn oxides associated fraction had no substantial variation at the three distances; the percentage of this fraction is 12.01% for 1m, 11.03% for 5m and 10.85% for 10m, respectively. At a distance of 10m, the residual fraction was the most predominant fraction for Ni. This result was similar for Zn, Cu and Cd at 10m.

6.3.6 BCR for Chromium

It is evident from Figure 6-6 that rainfall could substantially reduce the exchangeable Cr fraction especially at distance 1m from the road. This could be explained by part of the soluble chromium was either washed out with rain water or became bound in the organic and sparingly soluble fractions (Milacic and Stupar, 1995).

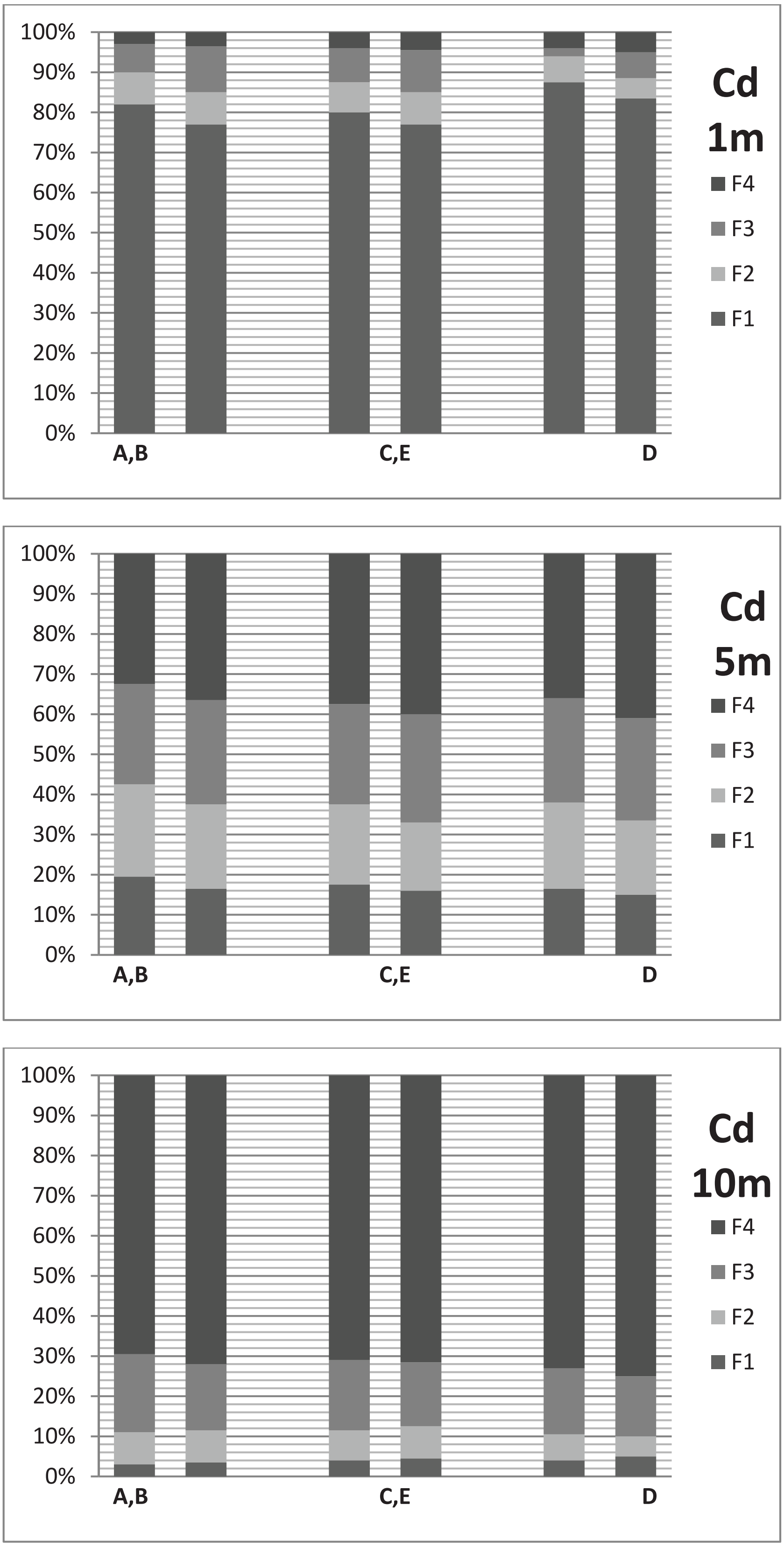

Figure 6-4 The mean cadmium BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning is showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated with organic matter); F4: Residual fraction

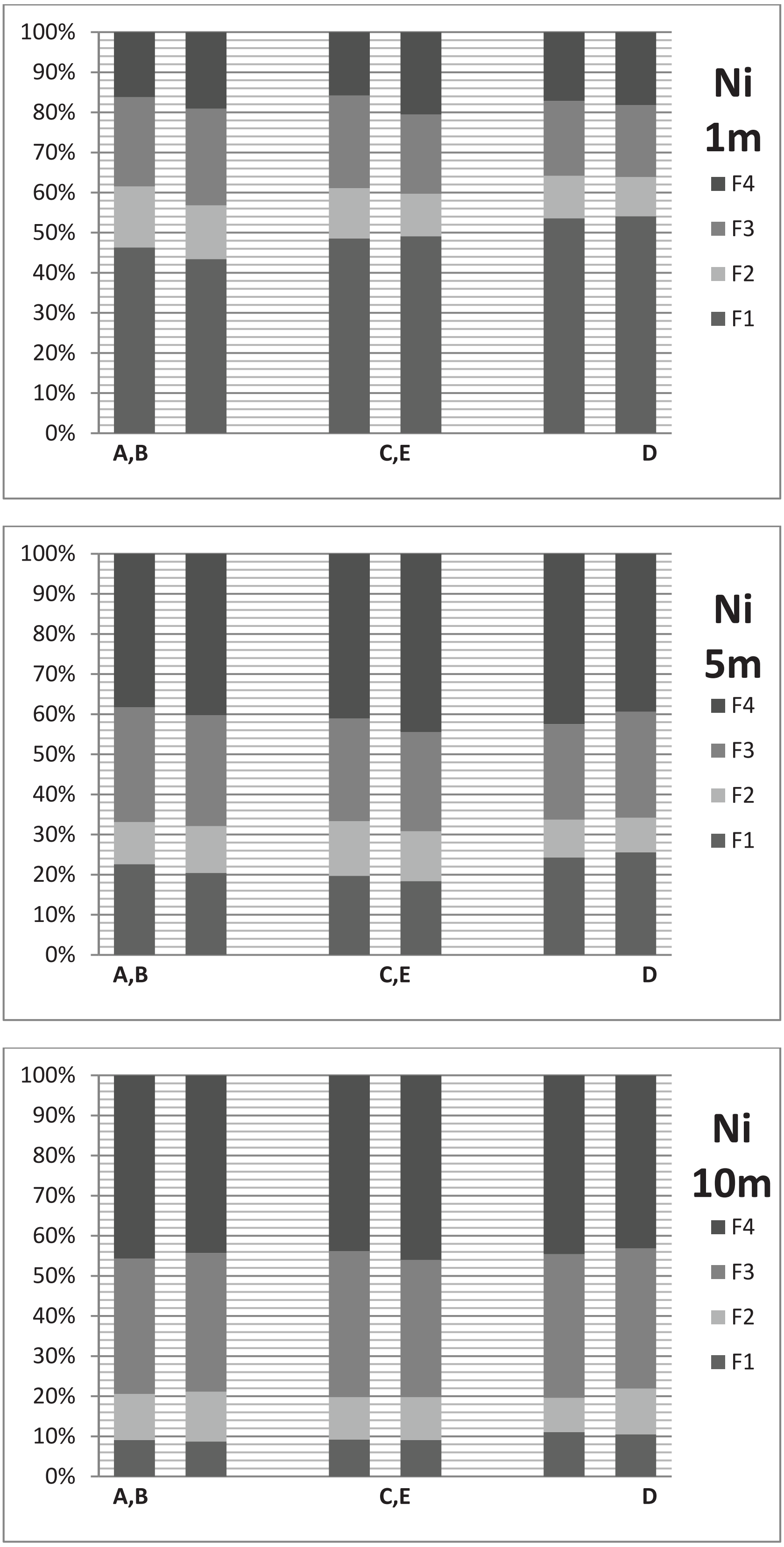

Figure 6-5 The mean nickel BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning is showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated with organic matter); F4: Residual fraction

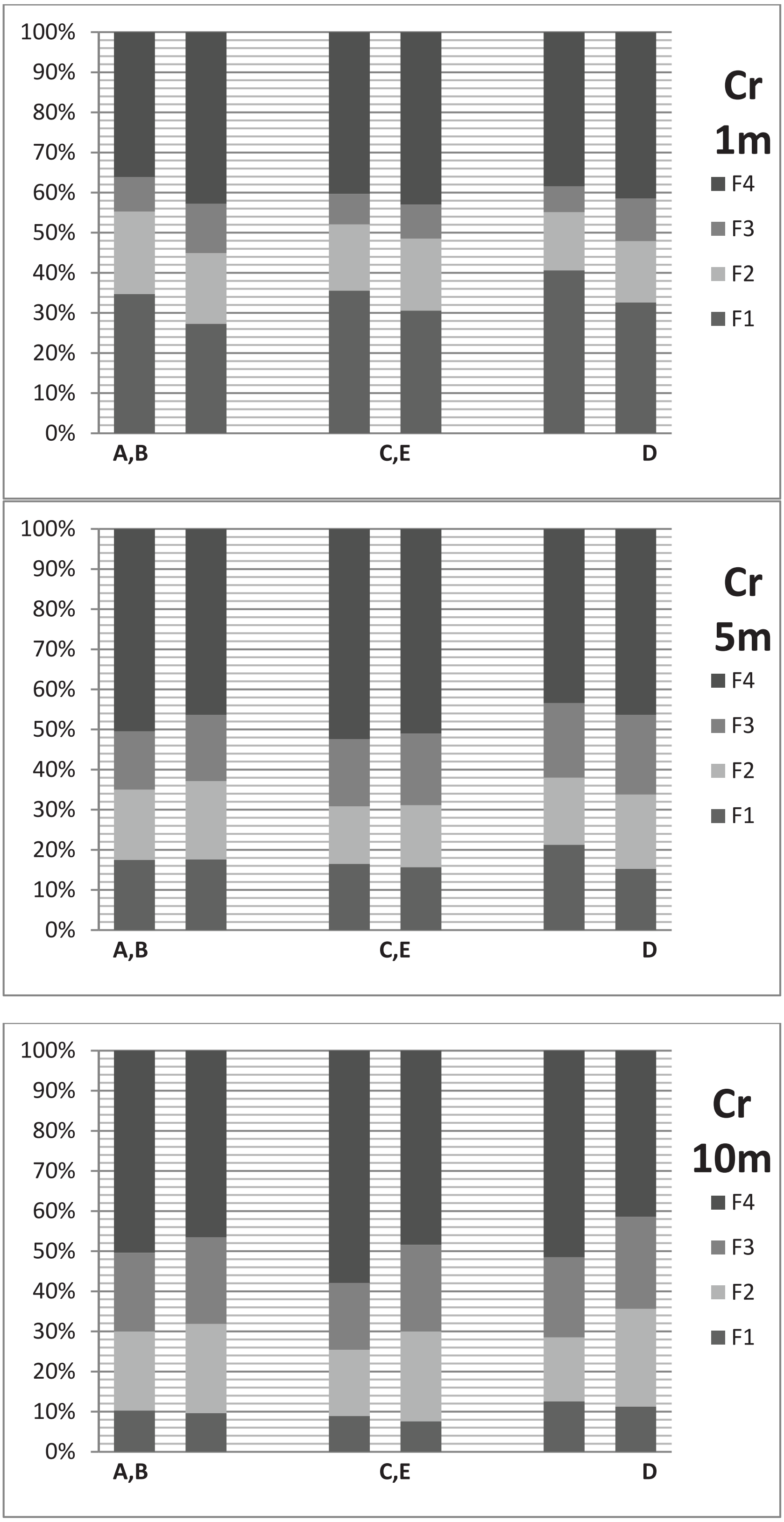

Figure 6-6 The mean chromium BCR results of three times pre-rainfall sampling and three times post-rainfall sampling in three different locations at distance 1, 5 and 10 meters are shown. The mean chemical partitioning is showed in percentage. The left columns indicate the pre-rainfall results and the right columns indicate the post-rainfall results. F1: Exchangeable and weak acid soluble fraction (soluble and carbonate fraction); F2: Reducible fraction (associated with Fe-Mn oxides); F3: Oxidisable fraction (associated with organic matter); F4: Residual fraction

6.4 Heavy Metal Isotopic Analysis

Knowledge of the cause and source of Pb pollution is important to abate it by taking source-related actions. Pb isotope analysis is a potentially powerful tool to identify anthropogenic Pb and its sources in the environment. Spatial information about the variation in anthropogenic Pb content and anthropogenic Pb sources in roadside soil has only had a very limited study in Australia. Pb isotope compositions were determined for the total 90 topsoil samples collected in this project. The specific aim of this novel analysis is to determine the anthropogenic Pb sources in the different chemical fractions instead of merely combined with 'total' concentration.

The experimental design selected for this study linked the modified chemical sequential extraction method and metal isotopic composition analysis for roadside soils at variable distances from the roadside and has provided more accurate, adequate and reliable evidence to understand the behaviour of metal movement and distribution in roadside soil derived from different geologies. The procedures consisted of two major stages: firstly, the modified three-step sequential extraction procedure (BCR) (Pueyo et al., 2008) for metal fraction was conducted in order to extract different chemical fractions for the total 90 topsoil samples. The extraction procedure defines the metals into four chemical forms: (1) exchangeable and weak acid soluble fraction (extracted by 0.11 mol L^{-1} acetic acid, F1), (2) reducible fraction (extracted by 0.5 mol L^{-1} hydroxylammonium chloride, F2), (3) oxidisable fraction (8.8 mol L^{-1} hydrogen peroxide, F3), and (4) residue (1.0 mol L^{-1} ammonium acetate, F4). After the BCR treatment, there was a total 90 (samples) × 4 = 360 fractions. In the second stage, lead isotope analysis was performed after chemical sequential extraction. The diluted extracted samples were purified, and then $^{207}Pb/^{206}Pb$ analyses were carried out for the Pb isotopic ratios analysis. The entire isotope measurement was undertaken by a Man Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) with a low uptake nebulizer.

The detailed Pb isotopic ratios ($^{206}Pb/^{207}Pb$) in each fraction are provided in Table 6-3. Descriptive analysis was carried out with Excel 2010 (Microsoft Inc., Redmond, USA). Statistical tests were also used to assess the difference between natural variability in the data and variability in the data resulting from different influencing factors: soil type, rainfall impact and distance. The lead isotopic ratios were analysed in a similar matter with various fractions. Interpretation of the results obtained from these fractions highlight the anthropogenic sources of the metal concentrations. The results obtained in this study were compared with other studies in Table 6-4; it can be seen the results of $^{206}Pb/^{207}Pb$ ratios of this study are in a similar range to other studies. Figure 6-7 indicates the $^{206}Pb/^{207}Pb$ ratio trend in the four fractions; it shows the ratio increasing from F1 to F4. The $^{206}Pb/^{207}Pb$ ratios of Pb in the residual fraction were always higher than those in the non-residual fraction. This result is similar to that found in the study by Wong and Li (2004). The increasing $^{206}Pb/^{207}Pb$ ratio from readily mobile fraction to immobile fraction could therefore indicate an increased proportion of lithogenic Pb in this fraction.

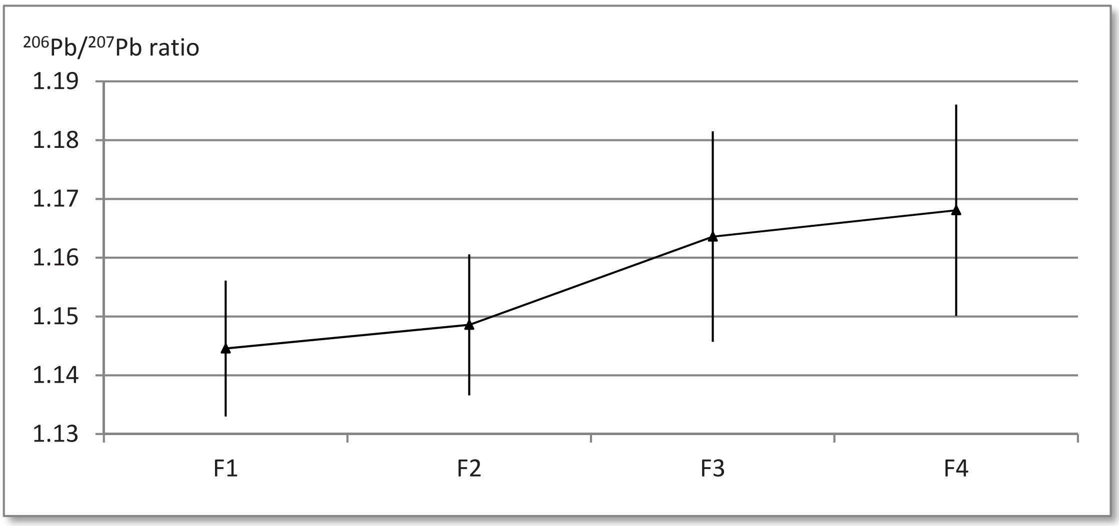

Figure 6-7 The mean value of $^{206}Pb/^{207}Pb$ ratios in the four chemical fractionations with standard deviation; F1: exchangeable and weak acid soluble fraction; F2: reducible fraction; F3: oxidisable fraction; F4: residue

From Table 6-3, it also can be found that the ^{206}Pb/^{207}Pb ratios in the first three fractions (exchangeable and weak acid soluble fraction, reducible fraction and oxidisable fraction) are increasing with increased distance from the road. Bacon et al. (2006) and Farmer et al. (2005) pointed out that low ^{206}Pb/^{207}Pb ratios are generally associated with lead added to petrol, therefore, it could be expected that the soils at 1m are more impacted by an anthropogenic source. Moreover, when comparing the ratio between pre-rainfall and post-rainfall for these three fractions, the ratio could elevate in the post-rainfall period. However, the residual fraction is an exception; the ratio does not change with distance and rainfall event, because F4 is the residual phase and is considered the most immobile fraction.

Table 6-3 The mean (n=6 for AB and CE; n=3 for D) ^{206}Pb/^{207}Pb ratios in four chemical fractions in 90 topsoil samples derived from three geologies under different weather condition at different distance

Weather condition	Site	Distance(m)	^{206}Pb/^{207}Pb ratios			
			F1	F2	F3	F4
Pre-rainfall	AB	1	1.125	1.127	1.137	1.142
		5	1.129	1.132	1.138	1.145
		10	1.138	1.142	1.143	1.143
	CE	1	1.138	1.140	1.163	1.175
		5	1.142	1.146	1.164	1.175
		10	1.144	1.148	1.171	1.175
	D	1	1.153	1.158	1.181	1.185
		5	1.155	1.161	1.182	1.184
		10	1.157	1.162	1.182	1.184
Post-rainfall	AB	1	1.131	1.134	1.138	1.142
		5	1.133	1.138	1.142	1.144
		10	1.141	1.143	1.144	1.143
	CE	1	1.141	1.143	1.167	1.175
		5	1.145	1.151	1.169	1.176
		10	1.146	1.153	1.170	1.178
	D	1	1.159	1.163	1.183	1.185
		5	1.162	1.165	1.185	1.185
		10	1.165	1.167	1.184	1.184

F1: exchangeable and weak acid soluble fraction; F2: reducible fraction; F3: oxidisable fraction; F4: residual fraction.

It can imply that the soil type could have an influence on the composition of anthropogenic Pb and lithogenic Pb in different chemical fractions. Each chemical fraction is related to its original soil characteristic, because the exchangeable and weak acid soluble fraction is associated with the soil carbonate content, the reducible fraction is associated with Fe-Mn oxides, the oxidisable fraction is associated with organic matter and the residual fraction is associated with the lattice of minerals (Mossop and Davidson, 2003, Tokalioğlu et al., 2003, Žemberyová et al., 2006).

Table 6-4 Comparison[1] of $^{206}Pb/^{207}Pb$ ratios in soil reported with other studies

location	Depth (cm)	$^{206}Pb/^{207}Pb$ ratio	Reference
Sydney, Australia	0-30	1.125-1.185	This study
Powys, UK	0-100	1.054-1.189	Dawson et al. (2009)
Marque`ze and Puy de la Vache, France	0- >210	1.176-1.240	Semlali et al. (2001)
Multi cities, Europe	0-20	1.116-1.202	Reimann et al. (2012)

[1] The Pb isotopic ratios reported here for Miranda park relate to fractionation results, and to other studies which relate to entire the soil profile

6.5 Summary

There is a range of concentrations for heavy metals reported in the literature by other researchers at other sites. From the consideration of Table 6-2, the concentrations obtained are consistent within the bounds of the other studies. Also, the results of $^{206}Pb/^{207}Pb$ ratios obtained in this study compared with other studies (Table 6-4) were in a similar range.

It was found that the concentrations of both Pb and Zn showed a clear negative correlation with distance and soil depth in all the soil types as determined in many other previous studies. However, there are differences in the results between the soil types. The heavy metal concentrations at the same distance in different soil types are different, particularly at the distance of 1m. Also, the rainfall events do influence the heavy metal deposition differently in both topsoil and subsoil of the three soil types. The results of BCR indicate the Pb and Zn input by traffic are mainly as the exchangeable fraction in the topsoil because the percentage of exchangeable fraction also decreases with increase in distance. The rainfall could importantly decrease the percentage of exchangeable fraction (F1) in topsoil and that could explain the total metal concentration reduction after rainfall. The F1 of both Pb and Zn have a similar percentage at a distance of 10m in this study. The concentrations of Pb and Zn have regressed to the background level at 10m. The concentration of exchangeable fraction tends to be very low at a distance of 10m from the BCR results for all the soil types. The rainfall would carry the metals into a deeper layer; as a result, the total heavy metal concentration decreased in the topsoil and increased in the subsoil due to the rainfall event. However, different soil types have different ability to reflect this variation. Therefore, there is a relationship between heavy metal concentrations, the influence of rainfall events on heavy metals deposition and movement and soil types. The exchangeable fraction shows a very considerable reduction at 5m and 10m away from the road edge for all the three soil types indicating the Cu was mainly influenced by anthropogenic activities such as traffic emission at 1m from the road. The Cd in roadside soils is predominant in the exchangeable fraction at distance 1m from the road which accounted for approximately 80% of all the Cd. The pattern of nickel chemical fractions was similar to Cu and the highest percentage of exchangeable fraction was found in soils derived from Mittagong Formation because of the high total Ni concentrations at this location. The rainfall could substantially reduce the exchangeable Cr fraction especially at distance 1m from the road

It has been suggested that the mobility and bioavailability of metals decrease approximately in the order of the extraction sequence, from readily available to unavailable, because the strength of extraction reagents used increases in this order (Li et al., 2001). Considering the first 2 extraction steps, the exchangeable and carbonate/specific adsorbed phases, the relative mobility and bioavailability of the heavy metals in roadside soils decrease in the following order: F1> F2> F3> F4.

Heavy metal concentrations and Pb (^{206}Pb/^{207}Pb) isotopic ratios were investigated in the roadside soil in Miranda Park, Sydney. Ninety topsoils (0-10cm) samples and 90 subsoils (10-30cm) samples were collected at 1m, 5m and 10m during three pre-rainfall periods and three post-rainfall periods. All of the 180 soil samples were measured for heavy metal concentrations. It was found that the heavy metal concentration magnitudes followed the order: Zn > Pb > Cu > Cr > Ni > Cd. The Pb isotopic measurement combined with sequential extraction procedure was conducted for the 90 topsoil samples. The $^{206}Pb/^{207}Pb$ ratios substantially increase with increased distance from the road with the exception of the residual fraction. The increasing $^{206}Pb/^{207}Pb$ ratio from the readily mobile fraction to immobile fraction could therefore indicate an increased proportion of lithogenic Pb in this fraction. Independent sample Student’s t-test was applied to the data and treated by the regionalisation approach for both heavy metal concentration and $^{206}Pb/^{207}Pb$ ratio. The details of the statistical analyses are discussed in Chapter 7.

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Chapter 7 STATISTICAL ANALYSIS

7.1 Introduction

As discussed earlier sections, the focus of this component of this research is the statistical analysis of field and chemical data. Three main statistical analyses were applied for interpretation of the data obtained from chapter 5 and chapter 6; the analyses involved the attempt of regional frequency approach to extend the heavy metal concentration data for Student's t-test[2], using multivariate analysis and Pearson correlation analysis for determination of inter-relationship among heavy metals and soil-associated factors, and conducting the soil contamination assessment through enrichment factors (EF).

7.2 Statistical Analysis Based on Regional Approach

One of foci of this study is the analysis of field data to distinguish between natural variability and variability arising from influential factors. This focus can be restated as a desire to ascertain if alternative field data are statistically different. One approach for this discrimination is to assume the data come from different statistical populations and to test whether the populations are different. A Student's t-test can be used for this purpose by testing the hypothesis. A t-test is any statistical hypothesis test in which the test statistic follows a Student's t-distribution under the null hypothesis. It can be used to determine if two sets of data are significantly different from each other.ie the means of different sample populations (two or three groups of field samples) are equal.

The volume of data available often will influence the results of any statistical tests. Commonly, it is found that the most robust conclusions are developed when large volumes of data are available. However, when field data is considered, there is a trade-off between a collection of more data and the efficient usage of the collected field data. In this study, due to the difficult of collection of field data (see Chapter 4), the statistical

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[2] A journal paper based on the results was under review (see Appendix D)

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analysis of the field data was undertaken in a manner to maximise the extraction of information from the available data. In other words, an efficient statistical analysis of the field data was undertaken. Using this efficient statistical analysis approach, the variability arising from the individual influential factors was tested. The basis of the approach used was the conversion of space to sample number. Hosking and Wallis (1993) showed how it was possible to extend the length of hydrological records by a suitable combination of adjacent records. For this study, the soil field data was combined in a manner whereby only the influential factor differed between the two or three sample populations. For example, there are three sample population for soil types (derived from Hawkesbury Sandstone, Winamatta Shale and Mittagong Formation) and distance from the roadside (1m, 5m and 10m); two sample population for the influential factors of soil depth (topsoil and subsoil) and weather condition (pre-rainfall period and post-rainfall period). The regional frequency approach was applied as follows, if the influential factor being considered was soil type then the data from the soils derived from the three geologies were separated into three sample populations. For example, in order to discriminate the soil type as an influential factor between sampling location AB and CE. For Pb, The concentrations in sampling location AB at distance 1m, 5m and 10m in both topsoil and subsoil after different weather condition were normalised using their local mean. For the sampling location CE, the data were normalised using the mean of this population. This increased the number of samples to 120. Four influential factors were considered in this manner. These factors were: (1) soil type derived from three different geologies; (2) topsoils and subsoils; (3) pre-rainfall period and post-rainfall period; and (4) distance from traffic (1m, 5m and 10m).

7.2.1 Heavy Metal Total Concentrations

In order to assess the influencing factor of soil type on heavy metal concentrations, the mean value of the soil type at AB at a distance of 1m, 5m and 10m is normalised around 1. Similarly the mean values of soil types of CE and D at a distance of 1m, 5m and 10m are normalised by the mean value from AB. Therefore, there are 18 values for AB and CE centred around 1, and 9 values for D. Therefore, 45 values are analysed for both pre-rainfall and post-rainfall i.e. there are 90 values analysed for the topsoil. From the Student's t-test, between different populations, 36 variables of heavy metals in AB and CE showed in Table 7-1 give a better understanding of variability in the data. From Table 7-1, it can be seen that the six heavy metal concentrations at AB, CE and D are statistically different. The final results show that the soil type influences the heavy metal concentration in roadside soil.

Table 7-1 2-tailed P-values from independent samples student's t-test for equality of means

Factor	Comparison	Heavy metal					
		Pb	Zn	Cu	Cr	Ni	Cd
Soil types	AB-CE	<0.05	0.391	<0.05	<0.05	<0.05	<0.05
	AB-D	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	CE-D	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Distance	1m-5m	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	1m-10m	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	5m-10m	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Rainfall	pre-post	<0.05	0.077	0.429	0.346	0.961	<0.05
Soil depth	top-sub	0.079	<0.05	0.744	0.542	0.967	0.071

Regionalization of field data results from the capability to discriminate between variation from influential factors and natural variability. For example, when the field data was organised into regions, where the only distance from the road was the variable as shown in Table 7-1 all the six metal concentrations at 1m, 5m and 10m were statistically different. This result shows the methodology is capable of confirming results previously reported by Dao et al. (2013) and Akbar et al. (2006). Other influential factors considered in this matter, for example, all the heavy metal concentrations were found statistically different among these three soil types, but the only exception was found for the Zn concentration between the soil derived from Hawkesbury Sandstone and Winamatta Shale (P-value = 0.391). In addition, t-test showed the rainfall can significantly impact on Pb and Cd concentrations, this could be explained by that the rainfall events can contribute an intensive surface run-off which normally carries an abundance of heavy metals to the soil matrix (Chon et al., 1998, Kluge and Wessolek, 2012); However, for one influential factor, namely soil depth, the concentration of only one metal (Zn, 2-tail P value <0.05) was found to be statistically different. The difference between Zn levels in the topsoil and subsoil emphasised that Zn is the current major heavy metal pollutant from atmospheric deposition of traffic emission since prohibited using leaded petrol. Thus, it can be interpreted that the primary factors influencing metal concentration in roadside soils are soil types, distance and rainfall. Soil depth is a secondary influence.

7.2.2 $^{206}Pb/^{207}Pb$ ratio in Chemical Fractions

Table 7-2 2-tailed P-values from independent samples student's t-test for equality of means for Pb isotopic ratio

Factors	comparison	^{206}Pb/^{207}Pb ratios			
		F1	F2	F3	F4
Distance	1m-5m	<0.05	<0.05	<0.05	0.067
	1m-10m	<0.05	<0.05	<0.05	0.124
	5m-10m	<0.05	<0.05	<0.05	0.165
soil type	AB-CE	<0.05	<0.05	<0.05	<0.05
	AB-D	<0.05	<0.05	<0.05	<0.05
	CE-D	<0.05	<0.05	<0.05	<0.05
Rainfall	pre-post	<0.05	<0.05	<0.05	0.061

The results from the Student's t-test (Table 7-2) for ^{206}Pb/^{207}Pb ratios in this fraction on distance and rainfall are different from the results obtained in the other three (F1, F2 and F3) fractions. In this fraction, 2-tailed P values upon the factor of distance are 0.067, 0.124 and 0.165 for 1m-5m, 1m-10m and 5m-10m, respectively. Moreover, the value is

0.061 for comparison with the $^{206}Pb/^{207}Pb$ ratio between pre-rainfall and post-rainfall periods in this fraction. The 2-tail P values above 0.05 inferred the mean value $^{206}Pb/^{207}Pb$ ratios for these comparisons are not statistically significantly different. Hence these results from the Student's t-test can imply that the $^{206}Pb/^{207}Pb$ ratio in the residual fraction is not significantly influenced by two influential factors: distance and rainfall. It can be explained that the residual fraction usually represents metals incorporated in the lattice of minerals and most likely reflects the geological characteristics of the soils (Stone and Marsalek, 1996, Li et al., 2001, Bacon et al., 2006).The statistical analysis results shown in Table 7-2 indicate the soil type is an important influential factor for the $^{206}Pb/^{207}Pb$ ratio in the entire four fractions. The $^{206}Pb/^{207}Pb$ ratio in each fraction at different locations is statistically significantly different. It can imply that the soil type could have an influence on the composition of anthropogenic Pb and lithogenic Pb in different chemical fractions. Each chemical fraction is related to its original soil characteristic, because the exchangeable and weak acid soluble fraction is associated with the soil carbonate content, the reducible fraction is associated with Fe-Mn oxides, the oxidisable fraction is associated with organic matter and the residual fraction is associated with the lattice of minerals (Mossop and Davidson, 2003, Tokalioğlu et al., 2003, Žemberyová et al., 2006).

7.3 Interpretation of Interrelationships

7.3.1 Pearson Correlation Analysis

Pearson Correlation is a measure of the linear dependence (correlation) between two variables X and Y. It has been widely applied in environmental studies. It provides an effective way to reveal the relationships between two variables and thus has been helpful for understanding the chemical components (Li et al., 2013). Heavy metals in roadside soils usually have very complicated relationships among them. The high correlations between heavy metals in soils may reflect that the accumulated concentrations of these heavy metals come from similar pollution sources.

Table 7-3 Pearson correlation analysis for heavy metals and soil-associated factors

	Pb	Zn	Cu	Cr	Cd	Ni	SOM	CEC
Pb	1							
Zn	.761**	1						
Cu	.783**	.556**	1					
Cr	.029	.034	.019	1				
Cd	.661**	.450**	.668**	.026	1			
Ni	.044*	.036	.008	.127*	.041	1		
SOC	.027	.061	.084	.086	.254*	.122	1	
CEC	-.002	-.051	.089	.095	.015	.014	.518**	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

The Pearson correlation analysis was conducted for the original contents of Pb, Zn, Cu, Cr, Cd and Ni as well as soil-associated factors (SOC and CEC). The results of the Pearson correlation coefficients and their significance levels ($P < 0.01$) are shown in Table 7-3, the concentration of Pb showed a high significant positive relationship with Zn (0.761), Cu (0.783) and Cd (0.661). Additionally, the Pearson correlation analysis indicated the soil CEC and soil organic carbon also have a significant positive relationship (0.518, $P < 0.01$), because a higher CEC usually indicates more clay and organic matter is present in the soil (Hazelton and Murphy, 2016). However, the concentration of Ni showed weak correlations with Cd ($P < 0.05$).

7.3.2 Multivariate Analysis

The contents of heavy metals in soils are a result of geological and anthropogenic inputs (Hooda, 2010), Cluster analysis and principal component analysis (PCA) were performed on not only the contents of the 6 heavy metals but also the soil-associated factors for example, soil organic carbon (SOC) and cation exchange capacity (CEC) determined in roadside soils and this further verified the results obtained through Pearson correlation analysis.

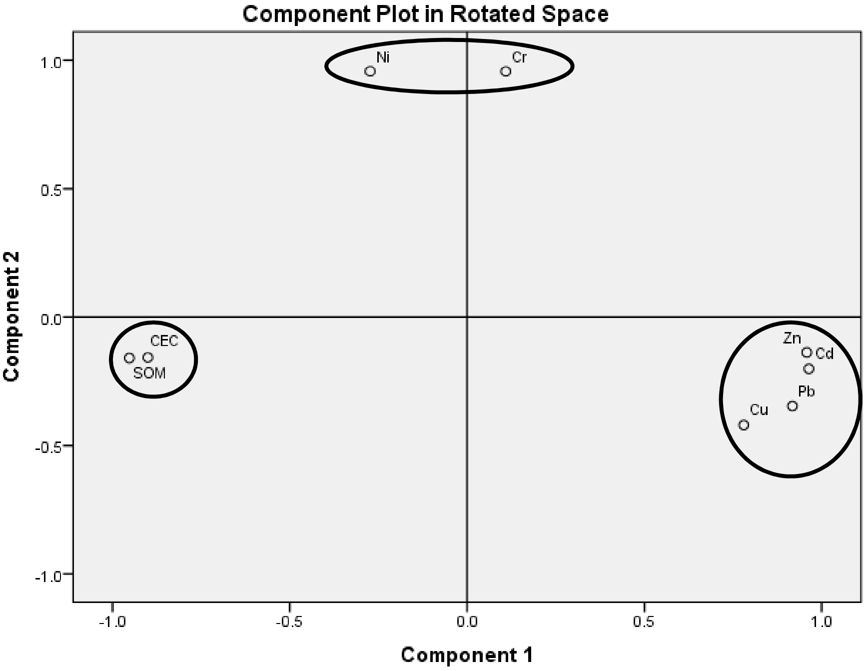

Figure 7-1 Scatter pots obtained from principal component analysis

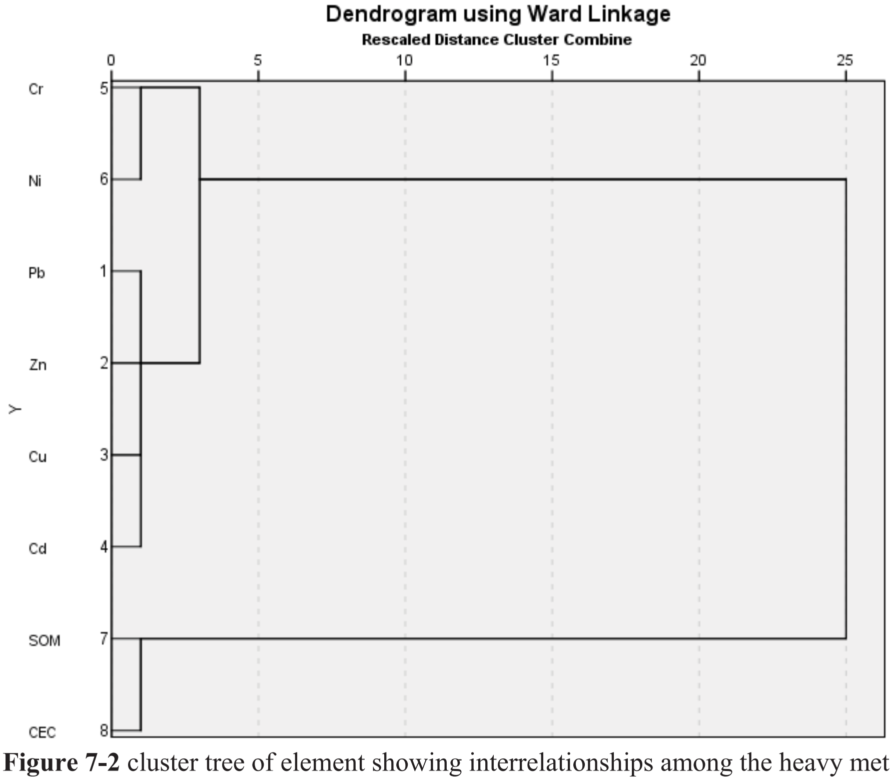

Figure 7-2 cluster tree of element showing interrelationships among the heavy metals and soil-associated factors

The result from PCA was presented in Figure 7-1 and the results of cluster analysis was presented (Figure 7-2) as a hierarchical dendrogram and heavy metals in the same group are expected to be from a common anthropogenic or natural source (Khan and Kathi, 2014) .Three distinct groups can consistently be identified in Figure 7-1 and Figure 7-2, the first group consisted of Cr and Ni; the second group consisted Pb, Zn, Cu and Cd; the third group consisted of SOC and CEC. Mooi and Sarstedt (2010) claimed that for the cluster analysis, a lower distance criterion interpreted a closer association. Clustering of the heavy metals occurred at a high distance criterion (Lee et al., 2006), possibly due to environmental heterogeneity (Zhang et al., 2015). As a whole, the grouping of heavy metals based on cluster analysis was consistent with results from Pearson correlation analysis. Many previously published studies have also pointed out that Pb, Zn, Cu and Cd are indicator heavy metals in contaminated soils along roadside soils (Chen et al., 2010, Mmolawa et al., 2011, Werkenthin et al., 2014) Thus, it was speculated that Pb, Zn, Cu and Cd were derived from a similar anthropogenic source.

7.4 Assessment of Heavy Metal Contamination

The heavy metal contamination assessment was conducted by Enrichment Factor (EF), which as the most popular index of pollutant enrichment index reviewed in the literature. EF is based on the standardisation of a measured pollutant against a reference element. A reference element is often characterised by low occurrence variability (for example Fe, Al, Ti, Sr and K) (Ogunsola et al., 1994, Massadeh et al., 2004, Liu et al., 2009, Mmolawa et al., 2011).The EF is calculated using the following equation:

$$\mathrm{EF}=\frac{(C_x/C_{ref})sample}{(C_x/C_{ref})background}$$

where C_x is the concentration of the examined heavy metal in the sample and the background soil reference, And C_{ref} is the concentration of the reference element in the soil sample and the background soil. The validity of such an enrichment factor will differ with values used for the reference material, therefore most studies have used metal concentration in the Earth's crust as reference for interpreting the results (Liaghati et al., 2004) and Fe was selected as the reference element in this study because it mainly originated from soil lithogenic sources (Lu et al., 2009). The examined soil heavy metal values of C_x (Pb, Zn, Cu, Cd, Ni and Cr) were used from the data obtained in Chapter 6 (see Table 6-1), and the examined Fe concentrations were presented in Table 7-4. Loring (1991) argued that there were many restrictions for utilising EF, for example, concentrations for crustal abundances are not appropriate because they may not represent regional background and normalising with the meal concentration of the regional background will not reflect the real situation (Fang and Hong, 1999). Hence, as mentioned in Chapter 4, the soil samples collected at location 5 and 6 from the initial transect were analysed as the background standards for this study; the concentrations of Pb, Zn, Cu, Cd, Ni, Cr and Fe were also determined by ICP-MS, the mean values of these metals are 3.95, 11.95, 14.75, 0.12, 8.21, 9.83 and 5929.19 mg/kg, respectively.

Table 7-4 the mean concentration of Fe the soils sample (unit: mg/kg)

distance	Topsoil			Subsoil		
	A-B	C-E	D	A-B	C-E	D
1	6230	5536	5147	5321	5102	5028
5	6120	5514	5014	5213	5368	5248
10	6240	5596	5310	5323	5321	5698

The Five contamination categories are recognised on the basis of the EF: these are <2 denotes deficiency to minimal enrichment; 2-5, moderate enrichment; 5-20, significant enrichment; 20-40, very high enrichment; >40, extremely high enrichment (Loska et al., 2003). The results of the EF in soil derived from three geologies were illustrated in Figure 7-3, Figure 7-4 and Figure 7-5. It can be noted that each type of heavy metal had different enrichments in different soil types; also there were different enrichments among different heavy metals. The EF of Pb, Zn, Cu, Cr, Cd and Ni is in the range of

4.7-29.5, 2.1-20.5, 1.1-3.3, 1.0-4.4, 1.1-21.7 and 0.8-2.7 for the soils derived from Hawkesbury Sandstone (see Figure 7-3). Refer to the categories, the results of EF shown the Pb, Zn and Cd are between significantly and extremely high enriched, the highest EF value were also occurred at distance of 1m from the roadside. Hence it can be inferred that the soils had mostly enriched at a shorter distance from the roadside. Additionally, the EF indicated the Cu, Cr and Ni had minimal to moderate enrichment in Hawkesbury Sandstone derived soils.

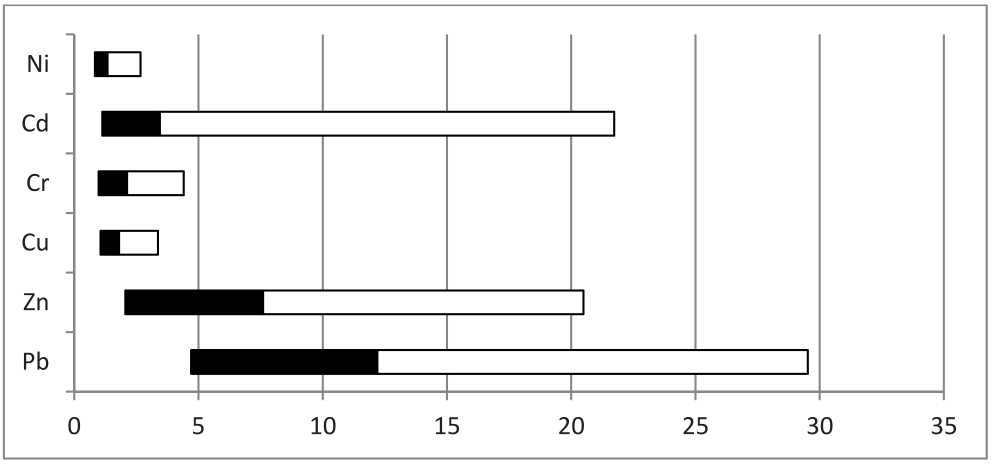

Figure 7-3 the enrichment factor in soils derived from Hawkesbury Sandstone; the line separating the dark and light shaded area inside the box represents the median; the boxes mark the minimum and maximum values

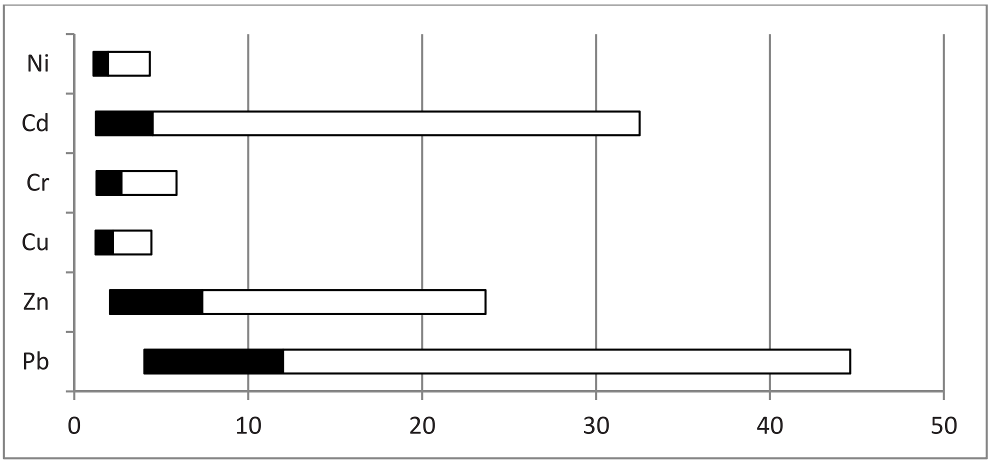

Figure 7-4 the enrichment factor in soils derived from Winamatta Shale; the line separating the dark and light shaded area inside the box represents the median; the boxes mark the minimum and maximum values

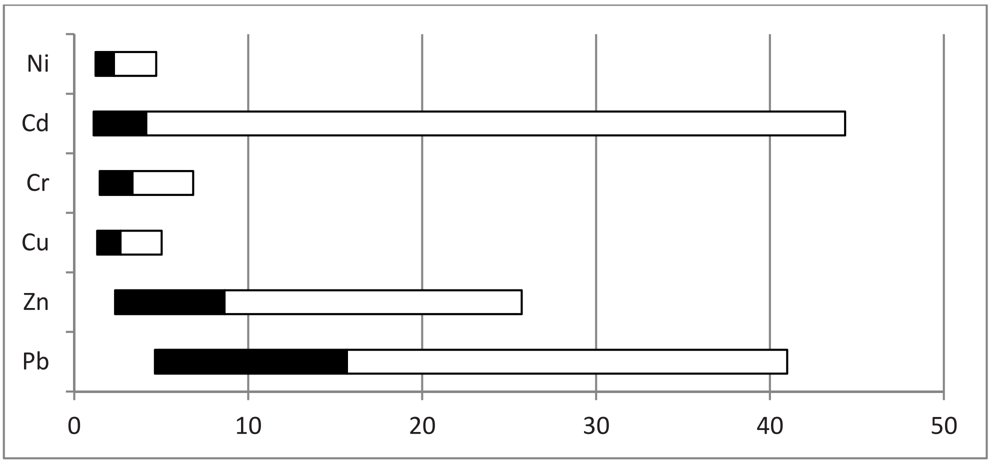

Figure 7-5 the enrichment factor in soils derived from Mittagong Formation; the line separating the dark and light shaded area inside the box represents the median; the boxes mark the minimum and maximum values

Compare to the EF in Hawkesbury Sandstone and from Mittagong Formation derived soils, the highest enrichment was found in Winamatta Shale derived soil (see Figure 7-4), and the Cu, Cr and Ni also had minimal to moderate enrichment. Moreover, the most enriched Cd was found in the soil derived from Mittagong Formation (Figure 7-5), the range is from 1.1 to 44.3.

The enrichment factors indicated the soils in different sampling locations had different enrichments from the anthropogenic sources which mainly attributed to the traffic in this study. The difference also reflected the soil type is an important factor that is influencing the heavy metal distribution in roadside soils. According to the categories, the results of EF also implied that Cu, Cr and Ni had minimal to moderate enrichment at three (1, 5 and 10m) distances in all three geologies, The enrichment factor of Pb, Zn and Cd varied significantly reported in this study indicating that these three heavy metals are significantly controlled by the anthropogenic activities.

7.5 Summary

Statistical tools were applied for interpretation of soil data; the analyses involved the regional approach based t-test for discrimination of influential factors of heavy metal concentrations, multivariate statistical analysis and Pearson correlation analysis for interpreting the interrelationships among heavy metals and soil-associated factors, and also the use of enrichment factors to assess heavy metal contaminations.

Student's t-test was applied to the data and treated by the regionalisation approach for both heavy metal concentration and $^{206}Pb/^{207}Pb$ ratio. Influential factors such as soil type, distance from the road, rainfall and soil layers (topsoils and subsoils) were statistically analysed for heavy metal concentration. Three factors such as soil type, distance from the road, rainfall also carried out for $^{206}Pb/^{207}Pb$ ratios in different chemical fractions. The results indicated that the primary factors influencing heavy metal concentration are soil type, distance from the road and rainfall. Soil depth is a secondary influence. On the other hand, results from Student's t-test can imply the $^{206}Pb/^{207}Pb$ ratio in the residual fraction is not significantly influenced by two influential factors: distance from the road and rainfall. This result can be explained because the residual fraction usually represents metals incorporated in the lattice of minerals and most likely reflects the geological characteristics of the soils. Analysis of field data using the regionalisation approach has enabled more rigorous statistically interpretation. Thus, it can be concluded that using the regionalisation approach outlined in this study enabled discrimination between changing influential factors and natural variability from field data (refer section 7-2).

The results of the Pearson correlation coefficients indicated the concentration of Pb showed a high significant positive relationship with Zn (0.761), Cu (0.783) and Cd (0.661). Additionally, the Pearson correlation analysis indicated the soil CEC and soil organic carbon also have a significant positive relationship (0.518, $P < 0.01$). However, the concentration of Ni showed weak correlations with Cd ($P < 0.05$). The results obtained from PCA and cluster analysis confirmed and verified the results of Pearson correlation analysis. Three distinct groups can consistently be identified from PCA and cluster analysis, the first group consisted of Cr and Ni; the second group consisted Pb, Zn, Cu and Cd; the third group consisted of SOC and CEC. It was speculated that Pb, Zn, Cu and Cd were derived from a similar anthropogenic source (refer to section 7-3). The enrichment factors indicated the soils in different sampling locations had different enrichments from the anthropogenic sources which mainly attributed to the traffic in this study. The difference also reflected the soil type is an important factor that is influencing the heavy metal distribution in roadside soils. According to the categories, the results of EF also implied that Cu, Cr and Ni had minimal to moderate enrichment at three (1, 5 and 10m) distances in all three geologies, The enrichment factor of Pb, Zn and Cd varied significantly reported in this study indicating that these three heavy metals are significantly controlled by the anthropogenic activities (refer to section 7-4).

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VIII

Chapter 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusion

As outlined in Chapter 2 roadside soils have been shown to have elevated concentrations of heavy metals that are a result of long term emissions by vehicular traffic. Investigation of heavy metal concentration was the focus of this research. The following summarised conclusions were developed as outcomes of this research:

- A systematic literature review critically evaluated past studies from which a comprehensive concept model highlighting influential factors was developed.
- From consideration of the conceptual model the influential factors selected for this research were a variation in soil type due to the underlying geology, a variation in soil depth, perpendicular distance from the road and rainfall.
- Miranda Park was selected for sampling because it was a unique site which allowed investigation at the one location of the critical influential factors stated in the previous point.
- A soil sampling strategy was developed to provide the samples to assess the variability arising from the influential factors.
- Chemical analysis of all the soil samples was undertaken for total heavy metal concentrations and the chemical fractions via BCR procedures; and was also conducted for Pb isotope measurement. Soil organic carbon and cation exchange capacity were also measured.
- During the research, 180 soil samples were collected from Miranda Park. However,

the numbers of unique samples considering all four factors were inadequate for reliable statistical interpretation therefore a regional approach was adopted.

- When the samples were categorised using regionalisation for different influential factors, there were statistical differences between categories.
- Hence four influential factors have been found to influence heavy metal concentration of roadside soil.

8.2 Conceptual Model

From the literature reviewed, a fundamental conceptual model was created based on the spatial and temporal influential factors. This conceptual model illustrated the features of heavy metal distribution and accumulation patterns in roadside soils. Moreover, this model can provide a comprehensive and systematic field sampling strategy to investigate the heavy metal concentration. It is evident that there has been no investigation on the impact of the influence of soil type derived from different geology on the heavy metal concentration in roadside soil. In addition, the lack of adequate studies focussing on the function of rainfall events to the roadside soil is apparent. Therefore, it is necessary to fill this gap and explore how these factors potentially affect the heavy metal concentration distribution in roadside soil as well as having an impact on different metals fractions (refer Chapter 2).

8.3 Validation of the Suitability of the Data

There is a range of concentrations for heavy metals reported in the literature by other researchers at other sites. From the consideration of Table 6-2, the heavy metal concentrations obtained during this study are consistent with the bounds of other studies. The heavy metal concentration was found to be as follows: Zn > Pb > Cu > Cr > Ni > Cd. Also which is similar to other studies, the results of ^{206}Pb/^{207}Pb ratios obtained in this study compared with other studies (Table 6-4) were in a similar range (refer Chapter 6).

8.4 Validation of the Study Site

Miranda Park, the selected site, had variability in these influential factors and therefore was suitable as the study area for sampling and subsequent chemical and statistical analyses to discriminate between the influential factors (refer Chapter 3).

8.5 Interpretation of Data

It was found that the heavy metal concentration magnitudes followed the order: Zn > Pb > Cu > Cr > Ni > Cd. The distribution of heavy metals varies greatly among the sampling distance and soil types. The influence of distance from the road can substantially impact on the exchangeable fraction. A decreasing trend in the percentage of total metals in the exchangeable fraction, and an increasing trend in the residual fractions was observed with an increasing total metal content.

Student's t-test was applied to the data and treated by the regionalisation approach for both heavy metal concentration and ^{206}Pb/^{207}Pb ratio. The results indicated that the primary factors influencing heavy metal concentration are soil type, distance from the road and rainfall. Soil depth is a secondary influence. On the other hand, results from Student's t-test can imply the ^{206}Pb/^{207}Pb ratio in the residual fraction is not significantly influenced by two influential factors: distance from the road and rainfall. Analysis of field data using the regionalisation approach has enabled more rigorous statistically interpretation. Thus, it can be concluded that using the regionalisation approach outlined in this study enabled discrimination between changing influential factors and natural variability from field data (refer Chapter 7).

8.6 Recommendations and Future Works

The constraints identified earlier in this research highlight areas where further work could be undertaken. The following aspects were beyond the scope of this research:

1. Other climatic factors such as wind and snow could also be considered in a future study.
2. The factors investigated in this study need to apply to other elements such as trace elements, platinum group elements (PGEs) and polycyclic aromatic hydrocarbons (PAHs)
3. The positioning of traffic lights and other traffic management devices need to be considered.

REFERENCES

AGARWAL, A. K., GUPTA, T. & KOTHARI, A. 2011. Particulate emissions from biodiesel vs diesel fuelled compression ignition engine. *Renewable and Sustainable Energy Reviews,* 15**,** 3278-3300.

AKBAR, K. F., HALE, W. H., HEADLEY, A. D. & ATHAR, M. 2006. Heavy metal contamination of roadside soils of Northern England. *Soil Water Res,* 1**,** 158-163.

AL-CHALABI, A. S. & HAWKER, D. 2000. Distribution of vehicular lead in roadside soils of major roads of Brisbane, Australia. *Water, Air, and Soil Pollution,* 118**,** 299-310.

ALEWELL, C., MEUSBURGER, K., BRODBECK, M. & BÄNNINGER, D. 2008. Methods to describe and predict soil erosion in mountain regions. *Landscape and Urban Planning,* 88**,** 46-53.

ALVAREZ, J. M., LOPEZ-VALDIVIA, L. M., NOVILLO, J., OBRADOR, A. & RICO, M. I. 2006. Comparison of EDTA and sequential extraction tests for phytoavailability prediction of manganese and zinc in agricultural alkaline soils. *Geoderma,* 132**,** 450-463.

AMUSAN, A., BADA, S. & SALAMI, A. 2003. Effect of traffic density on heavy metal content of soil and vegetation along roadsides in Osun state, Nigeria. *West African Journal of Applied Ecology,* 4.

ASLAM, J., KHAN, S. A. & KHAN, S. H. 2013. Heavy metals contamination in roadside soil near different traffic signals in Dubai, United Arab Emirates. *Journal of Saudi Chemical Society,* 17**,** 315-319.

AULT, W. U., SENECHAL, R. G. & ERLEBACH, W. E. 1970. Isotopic composition as a natural tracer of lead in the environment. *Environmental Science & Technology,* 4**,** 305-313.

AYRAULT, S., ROY-BARMAN, M., LE CLOAREC, M.-F., PRIADI, C. R., BONTÉ, P. & GÖPEL, C. 2012. Lead contamination of the Seine River, France: Geochemical implications of a historical perspective. *Chemosphere,* 87**,** 902-910.

AZEEZ, J. O., MESELE, S. A., SARUMI, B. O., OGUNDELE, J. A., UPONI, A. O. & HASSAN, A. O. 2014. Soil metal pollution as a function of traffic density and distance from road in emerging cities: a case study of Abeokuta, southwestern Nigeria. *Archives of Agronomy and Soil Science,* 60**,** 275-295.

BÄCKSTRÖM, M., KARLSSON, S. & ALLARD, B. 2004. Metal leachability and anthropogenic signal in roadside soils estimated from sequential extraction and stable lead isotopes. *Environmental Monitoring and Assessment,* 90**,** 135-160.

BACON, J. R., FARMER, J. G., DUNN, S. M., GRAHAM, M. C. & VINOGRADOFF, S. I. 2006. Sequential extraction combined with isotope analysis as a tool for the investigation of lead mobilisation in soils: Application to organic-rich soils in an upland catchment in Scotland. *Environmental pollution,* 141**,** 469-481.

BAI, J., CUI, B., WANG, Q., GAO, H. & DING, Q. 2009. Assessment of heavy metal contamination of roadside soils in Southwest China. *Stochastic Environmental Research and Risk Assessment,* 23**,** 341-347.

BAKER, D. E. & AMACHER, M. C. 1982. Nickel, copper, zinc, and cadmium. *Methods of soil analysis. Part 2. Chemical and microbiological properties***,** 323-336.

BAKIRDERE, S. & YAMAN, M. 2008. Determination of lead, cadmium and copper in roadside soil and plants in Elazig, Turkey. *Environmental Monitoring and Assessment,* 136**,** 401-410.

BALL, D., HAMILTON, R. & HARRISON, R. 1991. The influence of highway-related pollutants on environmental quality. *Studies in Environmental Science,* 44**,** 1-47.

BARILLE-BOYER, A.-L., BARILLE, L., MASSE, H., RAZET, D. & HERAL, M. 2003. Correction for particulate organic matter as estimated by loss on ignition in estuarine ecosystems. *Estuarine, Coastal and Shelf Science,* 58**,** 147-153.

BARRETT, M. E., JR, L. B. I., JR, J. F. M. & CHARBENEAU, R. J. 1998. Characterization of highway runoff in Austin, Texas, area. *Journal of Environmental Engineering,* 124**,** 131-137.

BATJARGAL, T., OTGONJARGAL, E., BAEK, K. & YANG, J.-S. 2010. Assessment of metals contamination of soils in Ulaanbaatar, Mongolia. *Journal of Hazardous Materials,* 184**,** 872-876.

BEADLE, N. C. W., EVANS, O. D., CAROLIN, R. C. & TINDALE, M. D. 1982. *Flora of the Sydney region*, Wellington, Reed.

BENSON, D. & HOWELL, J. Sydney's vegetation 1788–1988: utilization, degradation and rehabilitation. Proceedings of the Ecological Society of Australia, 1990. 115-27.

BENSON, D., THOMAS, J. & BURKITT, J. 1990. The natural vegetation of Bents Basin State Recreation Area. *New South Wales. Cunninghamia,* 2**,** 223-62.

BERMUDEZ, G. M., MORENO, M., INVERNIZZI, R., PLÁ, R. & PIGNATA, M. L. 2010. Heavy metal pollution in topsoils near a cement plant: the role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations. *Chemosphere,* 78**,** 375-381.

BERNARD, A. 1997. Effects of heavy metals in the environment on human health. *Les Colloques de l'INRA***,** 21-34.

BIRCH, G. & SCOLLEN, A. 2003. Heavy metals in road dust, gully pots and parkland soils in a highly urbanised sub-catchment of Port Jackson, Australia. *Soil Research,* 41, 1329-1342.

BOIVIN, P., SAADE, M., PFEIFFER, H., HAMMECKER, C. & DEGOUMOIS, Y. 2008. DEPURATION OF HIGHWAY RUNOFF WATER INTO GRASS-COVERED EMBANKMENTS. *Environmental technology,* 29, 709-720.

BOWMAN, H. 1974. *Geology of the Wollongong, Kiama, and Robertson 1: 50,000 sheets*, Department of Mines, Geological Survey of New South Wales.

BRANAGAN, D. Marks on sandstone surfaces-Sydney Region, Australia: Cultural origins and meanings? Journal and Proceedings of the Royal Society of New South Wales, 1993. Australasian Medical Publishing Company, 125.

BROWN, G. T. & BRINDLEY, G. 1980. X-ray diffraction procedures for clay mineral identification. *Crystal structures of clay minerals and their X-ray identification,* 5, 305-359.

BRÜMMER, G. 1986. *Heavy metal species, mobility and availability in soils*, Springer.

BURGESS, T. & WEBSTER, R. 1980. Optimal interpolation and isar1thmic mapping of soil properties. *Journal of Soil Science,* 31, 315-331.

CHAN, D. & STACHOWIAK, G. 2004. Review of automotive brake friction materials. *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering,* 218, 953-966.

CHAN, K. F., KOTZE, G. P. & STONE, P. C. Geotechnical modelling of station caverns for the Epping to Chatswood rail line project. AGS-AUCTA Mini-symposium: Geotechnical Aspects of Tunnelling for Infrastructure Projects. Sydney, 2005.

CHAPMAN, G. & ATKINSON, G. 2007. Soil survey and mapping. In 'Soils: Their properties and management'.(Eds P Charman, B Murphy) pp. 106–132. Oxford University Press: Melbourne.

CHEN, M. & MA, L. Q. 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil science society of America Journal,* 65, 491-499.

CHEN, T.-B., ZHENG, Y.-M., LEI, M., HUANG, Z.-C., WU, H.-T., CHEN, H., FAN, K.-K., YU, K., WU, X. & TIAN, Q.-Z. 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere,* 60, 542-551.

CHEN, X., XIA, X., ZHAO, Y. & ZHANG, P. 2010. Heavy metal concentrations in roadside soils and correlation with urban traffic in Beijing, China. *Journal of Hazardous Materials,* 181, 640-646.

CHENG, H. & HU, Y. 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environmental pollution,* 158, 1134-1146.

CHON, H.-T., AHN, J.-S. & JUNG, M. C. 1998. Seasonal variations and chemical forms of heavy metals in soils and dusts from the satellite cities of Seoul, Korea. *Environmental Geochemistry and Health,* 20**,** 77-86.

CHRISTOFORIDIS, A. & 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.

CIAZELA, J. & SIEPAK, M. 2016. Environmental factors affecting soil metals near outlet roads in Poznań, Poland: impact of grain size, soil depth, and wind dispersal. *Environmental Monitoring and Assessment,* 188**,** 1-12.

CUNEO, P. & LEISHMAN, M. R. 2006. African Olive (Olea europaea subsp. cuspidata) as an environmental weed in eastern Australia: a review. *Cunninghamia,* 9**,** 545-577.

CURRAN-COURNANE, F., LEAR, G., SCHWENDENMANN, L. & KHIN, J. 2015. Heavy metal soil pollution is influenced by the location of green spaces within urban settings. *Soil Research,* 53**,** 306-315.

DAO, L., MORRISON, L., ZHANG, H. & ZHANG, C. 2013. Influences of traffic on Pb, Cu and Zn concentrations in roadside soils of an urban park in Dublin, Ireland. *Environmental Geochemistry and Health,* 36**,** 1-11.

DAVID, D. & WILLIAMS, C. 1975. Heavy metal contents of soils and plants adjacent to the Hume Highway near Marulan, New South Wales. *Animal Production Science,* 15**,** 414-418.

DAVIS, A. P., SHOKOUHIAN, M. & NI, S. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere,* 44**,** 997-1009.

DAVIS, B. S. & BIRCH, G. F. 2011. Spatial distribution of bulk atmospheric deposition of heavy metals in metropolitan Sydney, Australia. *Water, Air, & Soil Pollution,* 214**,** 147-162.

DAWSON, J. J., TETZLAFF, D., CAREY, A.-M., RAAB, A., SOULSBY, C., KILLHAM, K. & MEHARG, A. A. 2009. Characterizing Pb mobilization from upland soils to streams using 206Pb/207Pb isotopic ratios. *Environmental Science & Technology,* 44**,** 243-249.

DE SILVA, S., BALL, A. S., HUYNH, T. & REICHMAN, S. M. 2015. Metal accumulation in roadside soil in Melbourne, Australia: Effect of road age, traffic density and vehicular speed. *Environmental pollution,* 208**,** 102-109.

DE TEMMERMAN, L., VANONGEVAL, L., BOON, W., HOENIG, M. & GEYPENS, M. 2003. Heavy metal content of arable soils in Northern Belgium. *Water, Air, and Soil Pollution,* 148**,** 61-76.

DUONG, T. T. & 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.

EL-SHAWARBY, I., AHN, K. & RAKHA, H. 2005. Comparative field evaluation of vehicle cruise speed and acceleration level impacts on hot stabilized emissions. *Transportation Research Part D: Transport and Environment,* 10**,** 13-30.

FAIZ, Y., TUFAIL, M., JAVED, M. T. & CHAUDHRY, M. 2009. Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad Expressway, Pakistan. *Microchemical Journal,* 92**,** 186-192.

FAKAYODE, S. O. & OLU-OWOLABI, B. 2003. Heavy metal contamination of roadside topsoil in Osogbo, Nigeria: Its relationship to traffic density and proximity to highways. *Environmental Geology,* 44**,** 150-157.

FANG, T.-H. & HONG, E. 1999. Mechanisms influencing the spatial distribution of trace metals in surficial sediments off the south-western Taiwan. *Marine pollution bulletin,* 38**,** 1026-1037.

FARMER, J. G., GRAHAM, M. C., BACON, J. R., DUNN, S. M., VINOGRADOFF, S. I. & MACKENZIE, A. B. 2005. Isotopic characterisation of the historical lead deposition record at Glensaugh, an organic-rich, upland catchment in rural N.E. Scotland. *Science of the total environment,* 346**,** 121-137.

FAURE, G. 1977. Principles of isotope geology.

FÉLIX, O. I., CSAVINA, J., FIELD, J., RINE, K. P., SÁEZ, A. E. & BETTERTON, E. A. 2015. Use of lead isotopes to identify sources of metal and metalloid contaminants in atmospheric aerosol from mining operations. *Chemosphere,* 122**,** 219-226.

FIGI, R., NAGEL, O., TUCHSCHMID, M., LIENEMANN, P., GFELLER, U. & BUKOWIECKI, N. 2010. Quantitative analysis of heavy metals in automotive brake linings: A comparison between wet-chemistry based analysis and in-situ screening with a handheld X-ray fluorescence spectrometer. *Analytica chimica acta,* 676**,** 46-52.

GAUDINO, S., GALAS, C., BELLI, M., BARBIZZI, S., DE ZORZI, P., JAĆIMOVIĆ, R., JERAN, Z., PATI, A. & SANSONE, U. 2007. The role of different soil sample digestion methods on trace elements analysis: a comparison of ICP-MS and INAA measurement results. *Accreditation and quality assurance,* 12**,** 84-93.

GHAFOORI, M., MASTROPASQUA, M., CARTER, J. & AIREY, D. 1993. Engineering properties of ashfield shale, Australia. *Bulletin of the International Association of Engineering Geology-Bulletin de l'Association Internationale de Géologie de l'Ingénieur,* 48**,** 43-58.

GISH, C. D. & CHRISTENSEN, R. E. 1973. Cadmium, nickel, lead, and zinc in earthworms from roadside soil. *Environmental Science & Technology,* 7**,** 1060-1062.

GOLOBOČANIN, D. D., ŠKRBIĆ, B. D. & MILJEVIĆ, N. R. 2004. Principal component analysis for soil contamination with PAHs. *Chemometrics and Intelligent Laboratory Systems,* 72**,** 219-223.

GRAY, J. & MURPHY, B. 1999. Parent Material and Soils. *A Guide to the Influence of Parent Material on Soil Distribution in Eastern Australia. NSW Department of Land and Water Conservation Technical Report*.

GREENE-KELLY, R. 1957. The montmorillonite minerals (smectites). *The differential thermal investigation of clays,* 2**,** 140-161.

GRIGALAVIČIENĖ, I., RUTKOVIENĖ, V. & MAROZAS, V. 2005. The accumulation of heavy metals Pb, Cu and Cd at roadside forest soil. *Polish Journal of Environmental Studies,* 14**,** 109-115.

GRIM, R. & LOUGHNAN, F. 1962. Clay minerals in sediments from Sydney Harbour, Australia. *Journal of Sedimentary Research,* 32**,** 240-248.

GULSON, B. L., TILLER, K. G., MIZON, K. J. & MERRY, R. H. 1981. Use of lead isotopes in soils to identify the source of lead contamination near Adelaide, South Australia. *Environmental Science & Technology,* 15**,** 691-696.

GUNAWARDENA, J., EGODAWATTA, P., AYOKO, G. A. & GOONETILLEKE, A. 2013. Atmospheric deposition as a source of heavy metals in urban stormwater. *Atmospheric Environment,* 68**,** 235-242.

GUNEY, M., ONAY, T. T. & COPTY, N. K. 2010. Impact of overland traffic on heavy metal levels in highway dust and soils of Istanbul, Turkey. *Environmental Monitoring and Assessment,* 164**,** 101-110.

GUO, G., WU, F., XIE, F. & ZHANG, R. 2012. Spatial distribution and pollution assessment of heavy metals in urban soils from southwest China. *Journal of Environmental Sciences,* 24**,** 410-418.

HAN, L., GAO, B., WEI, X., GAO, L., XU, D. & SUN, K. 2015. The characteristic of Pb isotopic compositions in different chemical fractions in sediments from Three Gorges Reservoir, China. *Environmental pollution,* 206**,** 627-635.

HAWORTH, R. 2003. The shaping of Sydney by its urban geology. *Quaternary International,* 103**,** 41-55.

HAYGARTH, P. & JONES, K. 1992. Atmospheric deposition of metals to agricultural surfaces.

HAZELTON, P. & MURPHY, B. 2011. *Understanding soils in urban environments*, Csiro publishing.

HAZELTON, P. & TILLE, P. 1990. Soil Landscapes of the Wollongong-Port Hacking 1: 100 000 Sheet Map, Soil Conservation Service of NSW, Sydney.

HAZELTON, P. A. & MURPHY, B. W. 2016. *Interpreting soil test results: what do all the numbers mean?*, CSIRO publishing.

HE, B., YUN, Z., SHI, J. & JIANG, G. 2013. Research progress of heavy metal pollution in China: Sources, analytical methods, status, and toxicity. *Chinese Science Bulletin,* 58**,** 134-140.

HELMKE, P. A. & NAIDU, R. 1996. Fate of contaminants in the soil environment: metal contaminants. *Contaminants and the soil environment in the Australasia-Pacific region.* Springer.

HERBERT, C. 1983. Sydney 1: 100 000 Geological Sheet 9130. Geological Survey of New South Wales, Sydney.

HILDEMANN, L. M., MARKOWSKI, G. R. & CASS, G. R. 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environmental Science & Technology,* 25**,** 744-759.

HJORTENKRANS, D., BERGBÄCK, B. & HÄGGERUD, A. 2006. New metal emission patterns in road traffic environments. *Environmental Monitoring and Assessment,* 117**,** 85-98.

HO, Y. & TAI, K. 1988. Elevated levels of lead and other metals in roadside soil and grass and their use to monitor aerial metal depositions in Hong Kong. *Environmental pollution,* 49**,** 37-51.

HOODA, P. 2010. *Trace elements in soils*, John Wiley & Sons.

HOSKING, J. & WALLIS, J. 1993. Some statistics useful in regional frequency analysis. *Water resources research,* 29**,** 271-281.

HSEU, Z.-Y., CHEN, Z.-S., TSAI, C.-C., TSUI, C.-C., CHENG, S.-F., LIU, C.-L. & LIN, H.-T. 2002. Digestion methods for total heavy metals in sediments and soils. *Water, Air, and Soil Pollution,* 141**,** 189-205.

HU, X., SUN, Y., DING, Z., ZHANG, Y., WU, J., LIAN, H. & WANG, T. 2014. Lead contamination and transfer in urban environmental compartments analyzed by lead levels and isotopic compositions. *Environmental pollution,* 187**,** 42-48.

HUANG, R. 1987. Environmental peodology. Higher Education Press, Beijing (in Chinese).

HUANG, S., LIAO, Q., HUA, M., WU, X., BI, K., YAN, C., CHEN, B. & ZHANG, X. 2007. Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. *Chemosphere,* 67**,** 2148-2155.

HUSSAIN, R., KHATTAK, S. A., SHAH, M. T. & ALI, L. 2015. Multistatistical approaches for environmental geochemical assessment of pollutants in soils of Gadoon Amazai Industrial Estate, Pakistan. *Journal of Soils and Sediments,* 15**,** 1119-1129.

IMPERATO, M., ADAMO, P., NAIMO, D., ARIENZO, M., STANZIONE, D. & VIOLANTE, P. 2003. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental pollution,* 124**,** 247-256.

IP, C., LI, X., ZHANG, G., WONG, C. & ZHANG, W. 2005. Heavy metal and Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South China. *Environmental pollution,* 138**,** 494-504.

JARVIE, D. M. 1991. Total organic carbon (TOC) analysis: Chapter 11: Geochemical methods and exploration.

KAASALAINEN, M. & YLI-HALLA, M. 2003. Use of sequential extraction to assess metal partitioning in soils. *Environmental pollution,* 126**,** 225-233.

KADıOĞLU, Y. K., ÜSTÜNDAĞ, Z., SOLAK, A. O. & KARABıYıKOĞLU, G. 2010. Sources of Environmental Pollution in Ankara (Turkey): Geochemistry and Traffic Effects—PEDXRF Applications. *Spectroscopy Letters,* 43**,** 247-257.

KAPLAN, O. & YAMAN, M. 2009. Selective and sequential extraction of lead in soil samples and plant parts taken from a serpentine and copper mining area. *Atomic Spectroscopy,* 30**,** 1-9.

KARIM, Z., QURESHI, B. A., MUMTAZ, M. & QURESHI, S. 2014. Heavy metal content in urban soils as an indicator of anthropogenic and natural influences on landscape of Karachi—a multivariate spatio-temporal analysis. *Ecological Indicators,* 42**,** 20-31.

KARTAL, Ş., AYDıN, Z. & TOKALıOĞLU, Ş. 2006. Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials,* 132**,** 80-89.

KAY, R. T., ARNOLD, T. L., CANNON, W. F. & GRAHAM, D. 2008. Concentrations of polycyclic aromatic hydrocarbons and inorganic constituents in ambient surface soils, Chicago, Illinois: 2001–2002. *Soil & Sediment Contamination,* 17**,** 221-236.

KELLY, J., THORNTON, I. & SIMPSON, P. 1996. Urban geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. *Applied Geochemistry,* 11**,** 363-370.

KHAN, A. & KATHI, S. 2014. Evaluation of heavy metal and total petroleum hydrocarbon contamination of roadside surface soil. *International Journal of Environmental Science and Technology,* 11**,** 2259-2270.

KLUGE, B. & WESSOLEK, G. 2012. Heavy metal pattern and solute concentration in soils along the oldest highway of the world–the AVUS Autobahn. *Environmental Monitoring and Assessment,* 184**,** 6469-6481.

KOCHER, B., WESSOLEK, G. & STOFFREGEN, H. 2005. Water and heavy metal transport in roadside soils. *PEDOSPHERE,* 15**,** 746-753.

KONEN, M. E., JACOBS, P. M., BURRAS, C. L., TALAGA, B. J. & MASON, J. A. 2002. Equations for predicting soil organic carbon using loss-on-ignition for north central US soils. *Soil science society of America Journal,* 66**,** 1878-1881.

KUBOVA, J., STREŠKO, V., BUJDOŠ, M., MATÚŠ, P. & MEDVED, J. 2004. Fractionation of various elements in CRMs and in polluted soils. *Analytical and bioanalytical chemistry,* 379**,** 108-114.

KUMAR, M., FURUMAI, H., KURISU, F. & KASUGA, I. 2013. Tracing source and distribution of heavy metals in road dust, soil and soakaway sediment through speciation and isotopic fingerprinting. *Geoderma,* 211**,** 8-17.

LAGERWERFF, J. V. & SPECHT, A. 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc. *Environmental Science & Technology,* 4**,** 583-586.

LARNER, B. L., SEEN, A. J. & TOWNSEND, A. T. 2006. Comparative study of optimised BCR sequential extraction scheme and acid leaching of elements in the certified reference material NIST 2711. *Analytica chimica acta,* 556**,** 444-449.

LEE, C. S.-L., LI, X., SHI, W., CHEUNG, S. C.-N. & THORNTON, I. 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. *Science of the total environment,* 356**,** 45-61.

LEE, P.-K. & TOURAY, J.-C. 1998. Characteristics of a polluted artificial soil located along a motorway and effects of acidification on the leaching behavior of heavy metals (Pb, Zn, Cd). *Water research,* 32**,** 3425-3435.

LEGRET, M. & PAGOTTO, C. 1999. Evaluation of pollutant loadings in the runoff waters from a major rural highway. *Science of the total environment,* 235**,** 143-150.

LEGRET, M. & PAGOTTO, C. 2006. Heavy metal deposition and soil pollution along two major rural highways. *Environmental technology,* 27**,** 247-254.

LI, J., PU, L., LIAO, Q., ZHU, M., DAI, X., XU, Y., ZHANG, L., HUA, M. & JIN, Y. 2015. How anthropogenic activities affect soil heavy metal concentration on a broad scale: a geochemistry survey in Yangtze River Delta, Eastern China. *Environmental Earth Sciences,* 73**,** 1823-1835.

LI, X., LIU, L., WANG, Y., LUO, G., CHEN, X., YANG, X., HALL, M. H., GUO, R., WANG, H. & CUI, J. 2013. Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. *Geoderma,* 192**,** 50-58.

LI, X., POON, C.-S. & LIU, P. S. 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry,* 16**,** 1361-1368.

LIAGHATI, T., PREDA, M. & COX, M. 2004. Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. *Environment International,* 29**,** 935-948.

LIHAREVA, N., PETROV, O. & TZVETANOVA, Y. 2006. Application of the BCR sequential extraction procedure to studying the partitioning of metals in sewage sludge and sediments. *Bulgarian chemical communications,* 38**,** 131-139.

LIU, E., YAN, T., BIRCH, G. & ZHU, Y. 2014. Pollution and health risk of potentially toxic metals in urban road dust in Nanjing, a mega-city of China. *Science of the total environment,* 476**,** 522-531.

LIU, H., CHEN, L.-P., AI, Y.-W., YANG, X., YU, Y.-H., ZUO, Y.-B. & FU, G.-Y. 2009. Heavy metal contamination in soil alongside mountain railway in Sichuan, China. *Environmental Monitoring and Assessment,* 152**,** 25-33.

LOGANATHAN, P., VIGNESWARAN, S. & KANDASAMY, J. 2013. Road-Deposited Sediment Pollutants: A Critical Review of their Characteristics, Source Apportionment, and Management. *Critical Reviews in Environmental Science and Technology,* 43**,** 1315-1348.

LORING, D. 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science: Journal du Conseil,* 48**,** 101-115.

LOSKA, K., WIECHULA, D., BARSKA, B., CEBULA, E. & CHOJNECKA, A. 2003. Assessment of arsenic enrichment of cultivated soils in Southern Poland. *Polish Journal of Environmental Studies,* 12**,** 187-192.

LU, A., WANG, J., QIN, X., WANG, K., HAN, P. & ZHANG, S. 2012. Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Science of the total environment,* 425**,** 66-74.

LU, X., WANG, L., LEI, K., HUANG, J. & 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.

LU, Y., GONG, Z., ZHANG, G. & BURGHARDT, W. 2003. Concentrations and chemical speciations of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. *Geoderma,* 115**,** 101-111.

MA, L. Q. & RAO, G. N. 1997. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *Journal of Environmental Quality,* 26**,** 259-264.

MAO, L., BAILEY, E. H., CHESTER, J., DEAN, J., ANDER, E. L., CHENERY, S. R. & YOUNG, S. D. 2014. Lability of Pb in soil: effects of soil properties and contaminant source. *Environmental Chemistry,* 11**,** 690-701.

MARGUÍ, E., QUERALT, I., CARVALHO, M. & HIDALGO, M. 2007. Assessment of metal availability to vegetation (Betula pendula) in Pb-Zn ore concentrate residues with different features. *Environmental pollution,* 145**,** 179-184.

MARKUS, J. & MCBRATNEY, A. B. 2001. A review of the contamination of soil with lead: II. Spatial distribution and risk assessment of soil lead. *Environment International,* 27**,** 399-411.

MARKUS, J. A. & MCBRATNEY, A. B. 1996. An urban soil study: heavy metals in Glebe, Australia. *Soil Research,* 34**,** 453-465.

MASSADEH, A., TAHAT, M., JARADAT, Q. & AL-MOMANI, I. 2004. Lead and cadmium contamination in roadside soils in Irbid City, Jordan: A case study. *Soil & Sediment Contamination,* 13**,** 347-359.

MASSAS, I., EHALIOTIS, C., GERONTIDIS, S. & SARRIS, E. 2009. Elevated heavy metal concentrations in top soils of an Aegean island town (Greece): total and available forms, origin and distribution. *Environmental Monitoring and Assessment,* 151**,** 105-116.

MBAH, C. & ANIKWE, M. 2010. Variation in heavy metal contents on roadside soils along a major express way in South east Nigeria. *New York Science Journal,* 3**,** 106-110.

MCDONALD 2009. *Australian Soil and Land Survey Field Handbook,* Melbourne, Inkata Press.

MCDONALD, R. C., ISBELL, R., SPEIGHT, J. G., WALKER, J. & HOPKINS, M. 2009. *Australian soil and land survey: field handbook*, CSIRO publishing.

MCGRATH, D. 1996. Application of single and sequential extraction procedures to polluted and unpolluted soils. *Science of the total environment,* 178**,** 37-44.

MEGUELLATI, N., ROBBE, D., MARCHANDISE, P. & ASTRUC, M. A new chemical extraction procedure in the fractionation of heavy metals in sediments-interpretation. Proceedings of the International Conference Heavy Metals in the Environment. CEP, Edinburgh, 1983. 1090-1093.

MILACIC, R. & STUPAR, J. 1995. Fractionation and oxidation of chromium in tannery waste- and sewage sludge-amended soils. *Environmental Science & Technology,* 29**,** 506-514.

MMOLAWA, K., LIKUKU, A. & GABOUTLOELOE, G. 2011. Assessment of heavy metal pollution in soils along major roadside areas in Botswana. *African Journal of Environmental Science and Technology,* 5**,** 186-196.

MODLINGEROVÁ, V., SZÁKOVÁ, J., SYSALOVÁ, J. & TLUSTOŠ, P. 2012. The effect of intensive traffic on soil and vegetation risk element contents as affected by the distance from a highway. *Plant Soil Environ,* 58**,** 379-384.

MOHAMMED, T., LOGANATHAN, P., KINSELA, A., VIGNESWARAN, S. & KANDASAMY, J. 2012. Enrichment, inter-relationship, and fractionation of heavy metals in road-deposited sediments of Sydney, Australia. *Soil Research,* 50**,** 229-238.

MOOI, E. & SARSTEDT, M. 2010. *Cluster analysis*, Springer.

MOORE, D. M. & REYNOLDS, R. C. 1989. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford university press Oxford.

MORCELLI, C. P. R., FIGUEIREDO, A. M. G., SARKIS, J., ENZWEILER, J., KAKAZU, M. & SIGOLO, J. 2005. PGEs and other traffic-related elements in roadside soils from Sao Paulo, Brazil. *Science of the total environment,* 345**,** 81-91.

MOSSOP, K. F. & DAVIDSON, C. M. 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Analytica chimica acta,* 478**,** 111-118.

MOTTO, H. L., DAINES, R. H., CHILKO, D. M. & MOTTO, C. K. 1970. Lead in soils and plants: its relation to traffic volume and proximity to highways. *Environmental Science & Technology,* 4**,** 231-237.

MULLER, G. 1969. Index of geoaccumulation in sediments of the Rhine River. *Geojournal,* 2**,** 108-118.

MUNSELL, A. H. & COLOR, M. 2000. *Munsell soil color charts*, Munsell Color.

NABULO, G., ORYEM-ORIGA, H. & DIAMOND, M. 2006. Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda. *Environmental Research,* 101**,** 42-52.

NDIOKWERE, C. L. 1984. A study of heavy metal pollution from motor vehicle emissions and its effect on roadside soil, vegetation and crops in Nigeria. *Environmental Pollution Series B, Chemical and Physical,* 7**,** 35-42.

NEPC 1999. National Environment Protection Council,National Environment Protection (Assessment of Site Contamination) Measure – Schedule B(1) Guideline on Investigation Levels for Soil and Groundwater.

NGUYEN, T. C., LOGANATHAN, P., NGUYEN, T. V., PHAM, T. T., KANDASAMY, J., WU, M., NAIDU, R. & VIGNESWARAN, S. 2015. Trace elements in road-deposited and waterbed sediments in Kogarah Bay, Sydney: enrichment, sources and fractionation. *Soil Research,* 53**,** 401-411.

NORTHCOTE, K. 1978. Soils and land use. *Atlas of Australian Resources,* 1.

NORTHCOTE, K. 1979. H.(1979).'A Factual Key for the Recognition of Australian Soils.'. *Adelaide: Rellim Technical Publications*.

NSW, R. A. T. A. O. 2005. Traffic volume data for Sydney region. Roads and Traffic Authority of NSW.

OGUNSOLA, O., OLUWOLE, A., ASUBIOJO, O., OLANIYI, H., AKEREDOLU, F., AKANLE, O., SPYROU, N., WARD, N. & RUCK, W. 1994. Traffic pollution: preliminary elemental characterisation of roadside dust in Lagos, Nigeria. *Science of the total environment,* 146**,** 175-184.

OLAJIRE, A. & AYODELE, E. 1997a. Contamination of roadside soil and grass with heavy metals. *Environment International,* 23**,** 91-101.

OLUKANNI, D. O. & ADEOYE, D. O. 2012. Heavy Metal Concentrations in Road Side Soils from Selected Locations in the Lagos Metropolis, Nigeria. *International Journal of Engineering and Technology,* 2**,** 1743-1752.

OZAKI, H., WATANABE, I. & KUNO, K. 2004. Investigation of the heavy metal sources in relation to automobiles. *Water, Air, and Soil Pollution,* 157**,** 209-223.

PAGE, A. L. 1982. *Methods of soil analysis. Part 2. Chemical and microbiological properties*, American Society of Agronomy, Soil Science Society of America.

PAGOTTO, C., REMY, N., LEGRET, M. & LE CLOIREC, P. 2001. Heavy metal pollution of road dust and roadside soil near a major rural highway. *Environmental technology,* 22**,** 307-319.

PAPASTERGIOS, G., GEORGAKOPOULOS, A., FERNANDEZ-TURIEL, J., GIMENO, D., FILIPPIDIS, A., KASSOLI-FOURNARAKI, A. & GRIGORIADOU, A. 2004. Heavy metals and toxic trace elements contents in soils of selected areas of the Kavala prefecture, Northern Greece.

PAULETTE, L., OROIAN, I. & CHIPER, C. 2006. THE INFLUENCE OF SOIL INDICES UPON HEAVY METAL ACCUMULATION. *Bulletin of University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca. Agriculture,* 62.

PERRY, C. & TAYLOR, K. 2009. *Environmental sedimentology*, Wiley. com.

PETERSON, S. & BATLEY, G. E. 1992. *Road runoff and its impact on the aquatic environment: A review*, CSIRO, Centre for Advanced Analytical Chemistry.

PLESNIČAR, A. & ZUPANČIČ, N. 2005. Heavy metal contamination of roadside soil along Ljubljana–Obrežje highway Onesnaženje tal s težkimi kovinami vzdolž avtoceste Ljubljana–Obrežje. *RMZ-Materials and Geoenvironment,* 52**,** 403-418.

POUYAT, R. V., YESILONIS, I., RUSSELL-ANELLI, J. & NEERCHAL, N. 2007. Soil chemical and physical properties that differentiate urban land-use and cover types. *Soil science society of America Journal,* 71**,** 1010-1019.

PRIBYL, D. W. 2010. A critical review of the conventional SOC to SOM conversion factor. *Geoderma,* 156**,** 75-83.

PUEYO, M., MATEU, J., RIGOL, A., VIDAL, M., LÓPEZ-SÁNCHEZ, J. F. & RAURET, G. 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environmental pollution,* 152**,** 330-341.

PUEYO, M., SASTRE, J., HERNANDEZ, E., VIDAL, M., LOPEZ-SANCHEZ, J. & RAURET, G. 2003. Prediction of trace element mobility in contaminated soils by sequential extraction. *Journal of Environmental Quality,* 32**,** 2054-2066.

QUEVAUVILLER, P., IMBERT, J.-L. & OLLÉ, M. 1993. Evaluation of the use of microwave oven systems for the digestion of environmental samples. *Microchimica Acta,* 112**,** 147-154.

RAMAKRISHNAIAH, H. & SOMASHEKAR, R. 2002. Heavy metal contamination in roadside soil and their mobility in relations to pH and organic carbon. *Soil and sediment contamination,* 11**,** 643-654.

RAUPACH, M. & TUCKER, B. 1959. The field determination of soil reaction. *Journal of the Australian Institute of Agricultural Science,* 25**,** 129-133.

RAURET, G., LÓPEZ-SÁNCHEZ, J.-F., SAHUQUILLO, A., BARAHONA, E., LACHICA, M., URE, A. M., DAVIDSON, C., GOMEZ, A., LÜCK, D. & BACON, J. 2000. Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *Journal of Environmental Monitoring,* 2**,** 228-233.

RAURET, G., LOPEZ-SANCHEZ, J., SAHUQUILLO, A., RUBIO, R., DAVIDSON, C., URE, A. & QUEVAUVILLER, P. 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring,* 1**,** 57-61.

RAYMENT, G. E. & LYONS, D. J. 2011. *Soil chemical methods: Australasia*, CSIRO publishing.

REICHMAN, S. Using geochemical indices to establish background concentration ranges in Australian sediments. Securing Australia's soils-for profitable industries and healthy landscapes, 2014. Australian Society of Soil Science Incorporated, 1-4.

REIMANN, C., FLEM, B., FABIAN, K., BIRKE, M., LADENBERGER, A., NÉGREL, P., DEMETRIADES, A., HOOGEWERFF, J. & TEAM, T. G. P. 2012. Lead and lead isotopes in agricultural soils of Europe–The continental perspective. *Applied Geochemistry,* 27**,** 532-542.

ROMIC, M. 2012. Bioavailability of trace metals in terrestrial environment: Methodological issues. *European Chemical Bulletin,* 1**,** 489-493.

RUST, B. R. & JONES, B. G. 1987. The Hawkesbury Sandstone south of Sydney, Australia: Triassic analogue for the deposit of a large, braided river. *Journal of Sedimentary Research,* 57.

SALOMONS, W. & FÖRSTNER, U. 2012. *Metals in the Hydrocycle*, Springer Science & Business Media.

SAYNOR, M. & ERSKINE, W. D. 1993. Characteristics and implications of high-level slackwater deposits in the Fairlight Gorge, Nepean River, Australia. *Marine and Freshwater Research,* 44**,** 735-747.

SCAZZOLA, R., AVEZZÙ, S., BIANCOTTO, R., CHIAMENTI, E., CHIOZZOTTO, E., GEROTTO, M., PALONTA, M. & ROITER, S. 2003. Assessment of heavy metal background values in the soils of inland coastal areas of Venice, Italy. *Annali di chimica,* 93**,** 465-470.

SCHÄFER, J. & PUCHELT, H. 1998. Platinum-Group-Metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. *Journal of Geochemical Exploration,* 64**,** 307-314.

SCHUMACHER, B. A. 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments.

SEMLALI, R. M., VAN OORT, F., DENAIX, L. & LOUBET, M. 2001. Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. *Environmental Science & Technology,* 35**,** 4180-4188.

SEN, I. S., BIZIMIS, M., TRIPATHI, S. N. & PAUL, D. 2016. Lead isotopic fingerprinting of aerosols to characterize the sources of atmospheric lead in an industrial city of India. *Atmospheric Environment,* 129**,** 27-33.

SHI, G., CHEN, Z., XU, S., ZHANG, J., WANG, L., BI, C. & TENG, J. 2008. Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environmental pollution,* 156**,** 251-260.

SHUPERT, L. A., EBBS, S. D., LAWRENCE, J., GIBSON, D. J. & FILIP, P. 2013. Dissolution of copper and iron from automotive brake pad wear debris enhances growth and accumulation by the invasive macrophyte< i> Salvinia molesta</i> Mitchell. *Chemosphere,* 92**,** 45-51.

SINGH, P., THOMAS, T., KUMAR, S. & UPADHYAY, S. 2013. Study on the Accumulation of Pb and Ni Content in Soil near the National Highways in Allahabad. *An Asian Journal of Soil Science,* 8**,** 439-444.

ŠKRBIĆ, B. & ĐURIŠIĆ-MLADENOVIĆ, N. 2013. Distribution of heavy elements in urban and rural surface soils: the Novi Sad city and the surrounding settlements, Serbia. *Environmental Monitoring and Assessment,* 185**,** 457-471.

SMEDA, A. & ZYRNICKI, W. 2002. Application of sequential extraction and the ICP-AES method for study of the partitioning of metals in fly ashes. *Microchemical Journal,* 72**,** 9-16.

SMITH, F. E. & ARSENAULT, E. A. 1996. Microwave-assisted sample preparation in analytical chemistry. *Talanta,* 43**,** 1207-1268.

SNOWDON, R. & BIRCH, G. 2004. The nature and distribution of copper, lead, and zinc in soils of a highly urbanised sub-catchment (Iron Cove) of Port Jackson, Sydney. *Soil Research,* 42**,** 329-338.

STONE, M. & MARSALEK, J. 1996. Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. *Water, Air, and Soil Pollution,* 87**,** 149-169.

STROUD 1985. *Wollongong - Port Hacking 1:100 000 Geological Sheet 9029-9129.*

STURGES, W. & BARRIE, L. 1987. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions. *Nature,* 329**,** 144-146.

SUN, Y., ZHOU, Q., XIE, X. & LIU, R. 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *Journal of Hazardous Materials,* 174**,** 455-462.

SUTHERLAND, R. A. & TACK, F. M. 2002. Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. *Analytica chimica acta,* 454**,** 249-257.

TACK, F., VERLOO, M., VANMECHELEN, L. & VAN RANST, E. 1997. Baseline concentration levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium). *Science of the total environment,* 201**,** 113-123.

TESSIER, A., CAMPBELL, P. G. & BISSON, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry,* 51**,** 844-851.

TIAN, F. & ZHU, S. G. 2014. Assessment on the Environment Risk of Heavy Metals in the Soil of Anhui Province (China) by Pollution Index Method. *Advanced Materials Research,* 864**,** 793-796.

TOKALıOĞLU, Ş. & KARTAL, Ş. 2006. Multivariate analysis of the data and speciation of heavy metals in street dust samples from the Organized Industrial District in Kayseri (Turkey). *Atmospheric Environment,* 40**,** 2797-2805.

TOKALIOĞLU, Ş., KARTAL, Ş. & BİROL, G. 2003. Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. *Turkish Journal of Chemistry,* 27**,** 333-346.

TOMLINSON, D., WILSON, J., HARRIS, C. & JEFFREY, D. 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen,* 33**,** 566-575.

TOZER, M. 2003. The native vegetation of the Cumberland Plain, western Sydney: systematic classification and field identification of communities. *Cunninghamia,* 8**,** 1-75.

TURER, D., MAYNARD, J. B. & SANSALONE, J. J. 2001. Heavy metal contamination in soils of urban highways comparison between runoff and soil concentrations at Cincinnati, Ohio. *Water, Air, and Soil Pollution,* 132**,** 293-314.

TURER, D. G. & MAYNARD, B. J. 2003. Heavy metal contamination in highway soils. Comparison of Corpus Christi, Texas and Cincinnati, Ohio shows organic matter is key to mobility. *Clean Technologies and Environmental Policy,* 4**,** 235-245.

URE, A., QUEVAUVILLER, P., MUNTAU, H. & GRIEPINK, B. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International journal of environmental analytical chemistry,* 51**,** 135-151.

USMAN, A. R., LEE, S. S., AWAD, Y. M., LIM, K. J., YANG, J. E. & OK, Y. S. 2012. Soil pollution assessment and identification of hyperaccumulating plants in chromated copper arsenate (CCA) contaminated sites, Korea. *Chemosphere,* 87**,** 872-878.

VAN HERREWEGHE, S., SWENNEN, R., VANDECASTEELE, C. & CAPPUYNS, V. 2003. Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. *Environmental pollution,* 122**,** 323-342.

VARRICA, D., BARDELLI, F., DONGARRA, G. & TAMBURO, E. 2013. Speciation of Sb in airborne particulate matter, vehicle brake linings, and brake pad wear residues. *Atmospheric Environment,* 64**,** 18-24.

VON UEXKÜLL, O., SKERFVING, S., DOYLE, R. & BRAUNGART, M. 2005. Antimony in brake pads-a carcinogenic component? *Journal of Cleaner Production,* 13**,** 19-31.

WALES, R. A. T. A. N. S. 2005. Traffic volume data for Sydney region 2005.

WALRAVEN, N., VAN OS, B. J. H., KLAVER, G. T., MIDDELBURG, J. J. & DAVIES, G. R. 2014. The lead (Pb) isotope signature, behaviour and fate of traffic-related lead pollution in roadside soils in The Netherlands. *Science of the total environment,* 472**,** 888-900.

WARD, N., BROOKS, R. & REEVES, R. 1974. Effect of lead from motor-vehicle exhausts on trees along a major thoroughfare in Palmerston North, New Zealand. *Environmental Pollution (1970),* 6**,** 149-158.

WEBSTER, R. & CUANALO, H. 1975. Soil transect correlograms of North Oxfordshire and their interpretation. *Journal of Soil Science,* 26**,** 176-194.

WEI, B. & 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.

WERKENTHIN, M., KLUGE, B. & WESSOLEK, G. 2014a. Metals in European roadside soils and soil solution–A review. *Environmental pollution,* 189**,** 98-110.

WHITELEY, J. & MURRAY, F. 2003. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *Science of the total environment,* 317**,** 121-135.

WHITELEY, J. D. 2005. Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. *Water, Air, and Soil Pollution,* 160**,** 77-93.

WICHMANN, H. & BAHADIR, M. 2015. Increase of Platinum Group Element Concentrations in Soils and Airborne Dust During the Period of Vehicular Exhaust Catalysts Introduction. *Platinum Metals in the Environment.* Springer.

WILLIAM, E. & AIREY, D. A review of the engineering properties of the Wianamatta group shales. Proceedings 8th Australia New Zealand Conference on Geomechanics: Consolidating Knowledge, 1999. Australian Geomechanics Society, 641.

WONG, C. S. C. & LI, X. D. 2004. Pb contamination and isotopic composition of urban soils in Hong Kong. *Science of the total environment,* 319**,** 185-195.

WONG, S., LI, X., ZHANG, G., QI, S. & MIN, Y. 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environmental pollution,* 119**,** 33-44.

WU, S., ZHOU, S. & LI, X. 2011. Determining the anthropogenic contribution of heavy metal accumulations around a typical industrial town: Xushe, China. *Journal of Geochemical Exploration,* 110**,** 92-97.

YAN, X., ZHANG, F., ZENG, C., ZHANG, M., DEVKOTA, L. P. & YAO, T. 2012. Relationship between heavy metal concentrations in soils and grasses of roadside farmland in Nepal. *International journal of environmental research and public health,* 9**,** 3209-3226.

YANG, T., LIU, Q., CHAN, L. & CAO, G. 2007. Magnetic investigation of heavy metals contamination in urban topsoils around the East Lake, Wuhan, China. *Geophysical Journal International,* 171**,** 603-612.

YANG, Y., CAMPBELL, C., CLARK, L., CAMERON, C. & PATERSON, E. 2006. Microbial indicators of heavy metal contamination in urban and rural soils. *Chemosphere,* 63**,** 1942-1952.

YESILONIS, I., POUYAT, R. & NEERCHAL, N. 2008. Spatial distribution of metals in soils in Baltimore, Maryland: role of native parent material, proximity to major roads, housing age and screening guidelines. *Environmental pollution,* 156**,** 723-731.

YUSUF, K. 2006. Evaluation of the three-stage BCR (European Community Bureau of Reference) sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in roadside soils. *Pakistan Journal of Scientific and Industrial Research,* 49**,** 181.

ZAID, S. M. & AL GAHTANI, F. 2015. Provenance, diagenesis, tectonic setting, and geochemistry of Hawkesbury Sandstone (Middle Triassic), southern Sydney Basin, Australia. *Turkish Journal of Earth Sciences,* 24**,** 72-98.

ŽEMBERYOVÁ, M., BARTEKOVA, J. & HAGAROVA, I. 2006. The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins. *Talanta,* 70**,** 973-978.

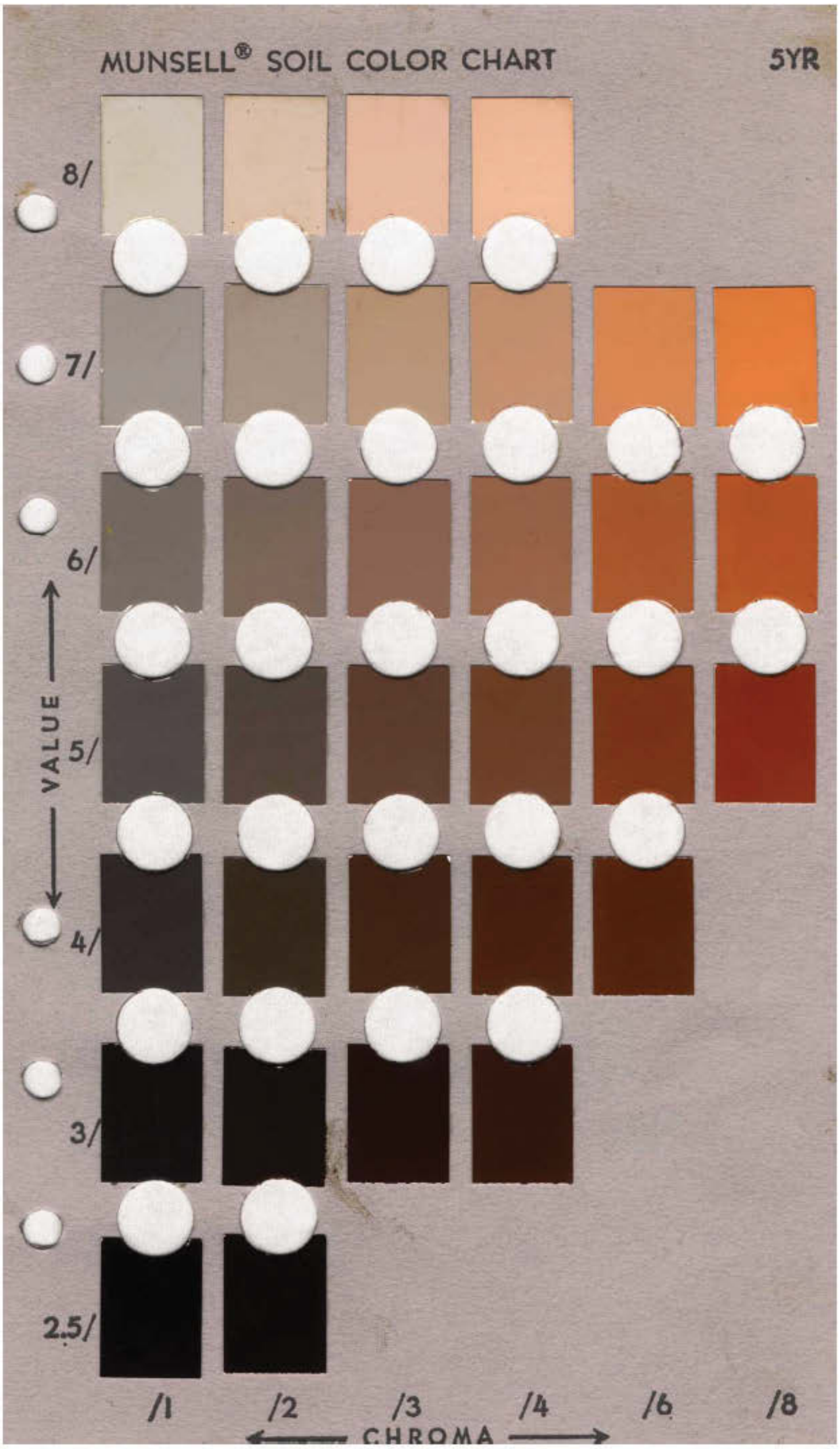
ZHANG, H., WANG, Z., ZHANG, Y., DING, M. & LI, L. 2015. Identification of traffic-related metals and the effects of different environments on their enrichment in roadside soils along the Qinghai–Tibet highway. *Science of the total environment,* 521**,** 160-172.

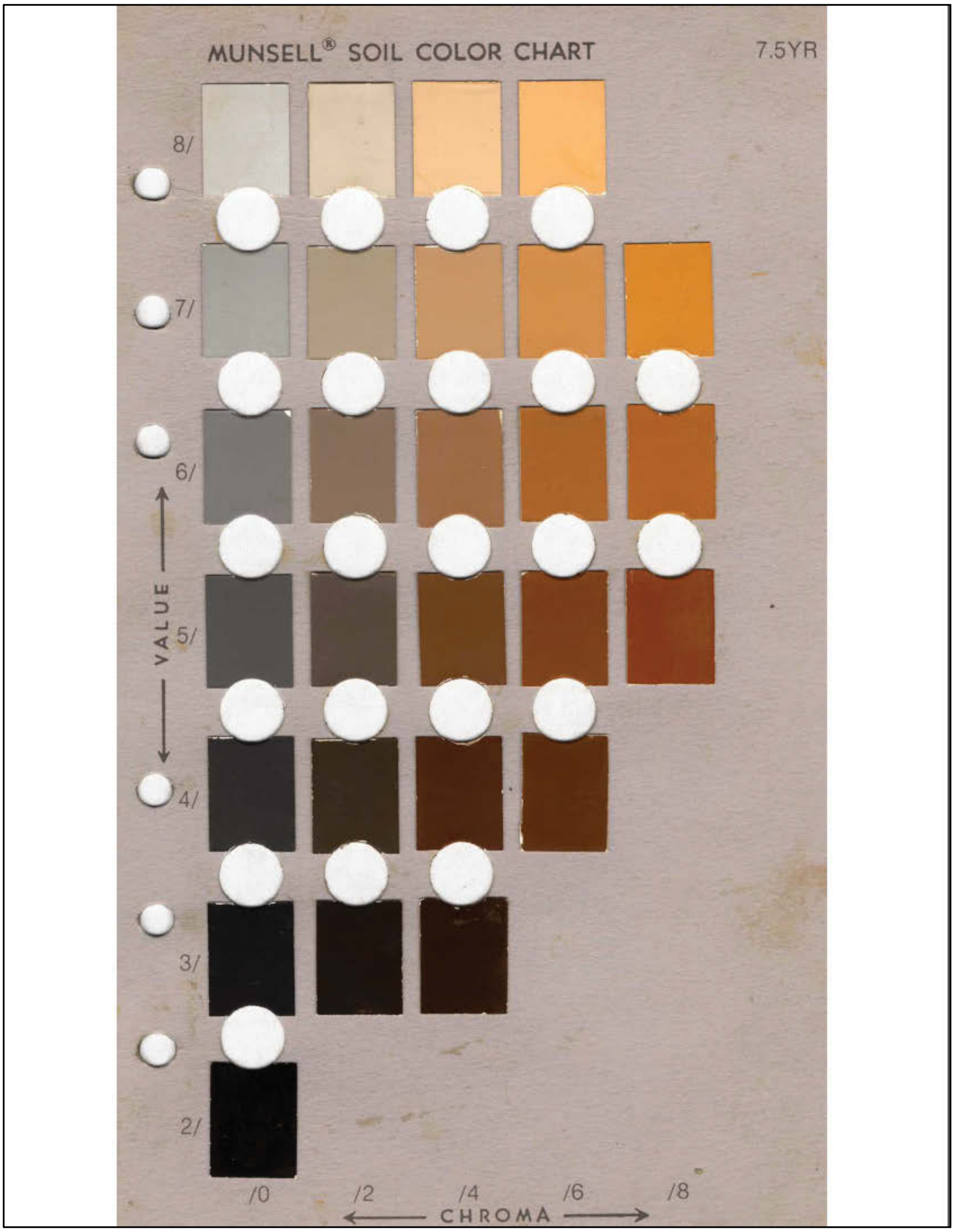
ZHANG, R., GUAN, M., SHU, Y., SHEN, L., CHEN, X., ZHANG, F. & LI, T. 2016. Historical record of lead accumulation and source in the tidal flat of Haizhou Bay, Yellow Sea: Insights from lead isotopes. *Marine pollution bulletin,* 106**,** 383-387.

ZHAO, Z. & HAZELTON, P. 2016. Evaluation of accumulation and concentration of heavy metals in different urban roadside soil types in Miranda Park, Sydney. *Journal of Soils and Sediments***,** 1-9.

ZHU, Z., SUN, G., BI, X., LI, Z. & YU, G. 2013. Identification of trace metal pollution in urban dust from kindergartens using magnetic, geochemical and lead isotopic analyses. *Atmospheric Environment,* 77**,** 9-15.

Appendix A

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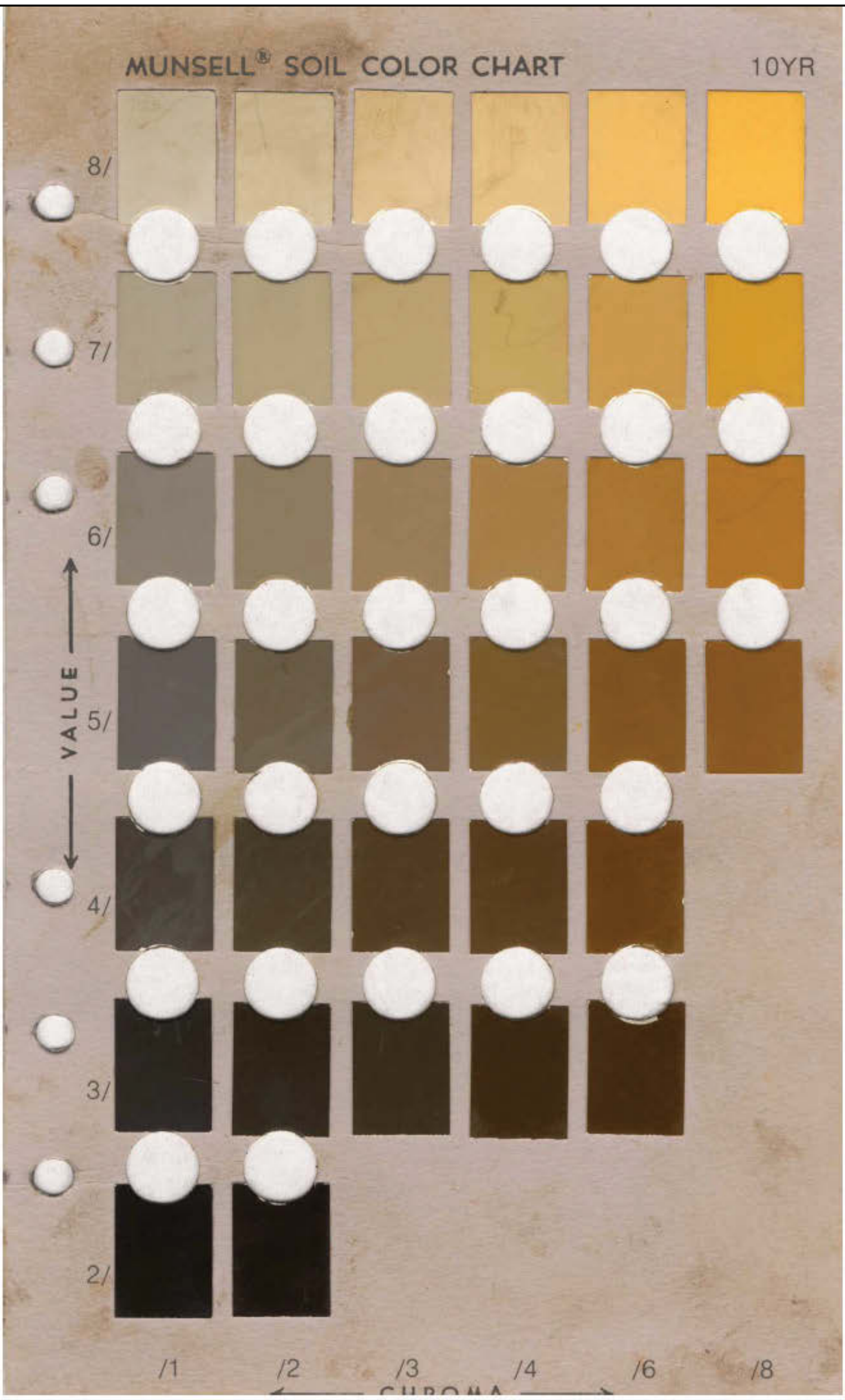
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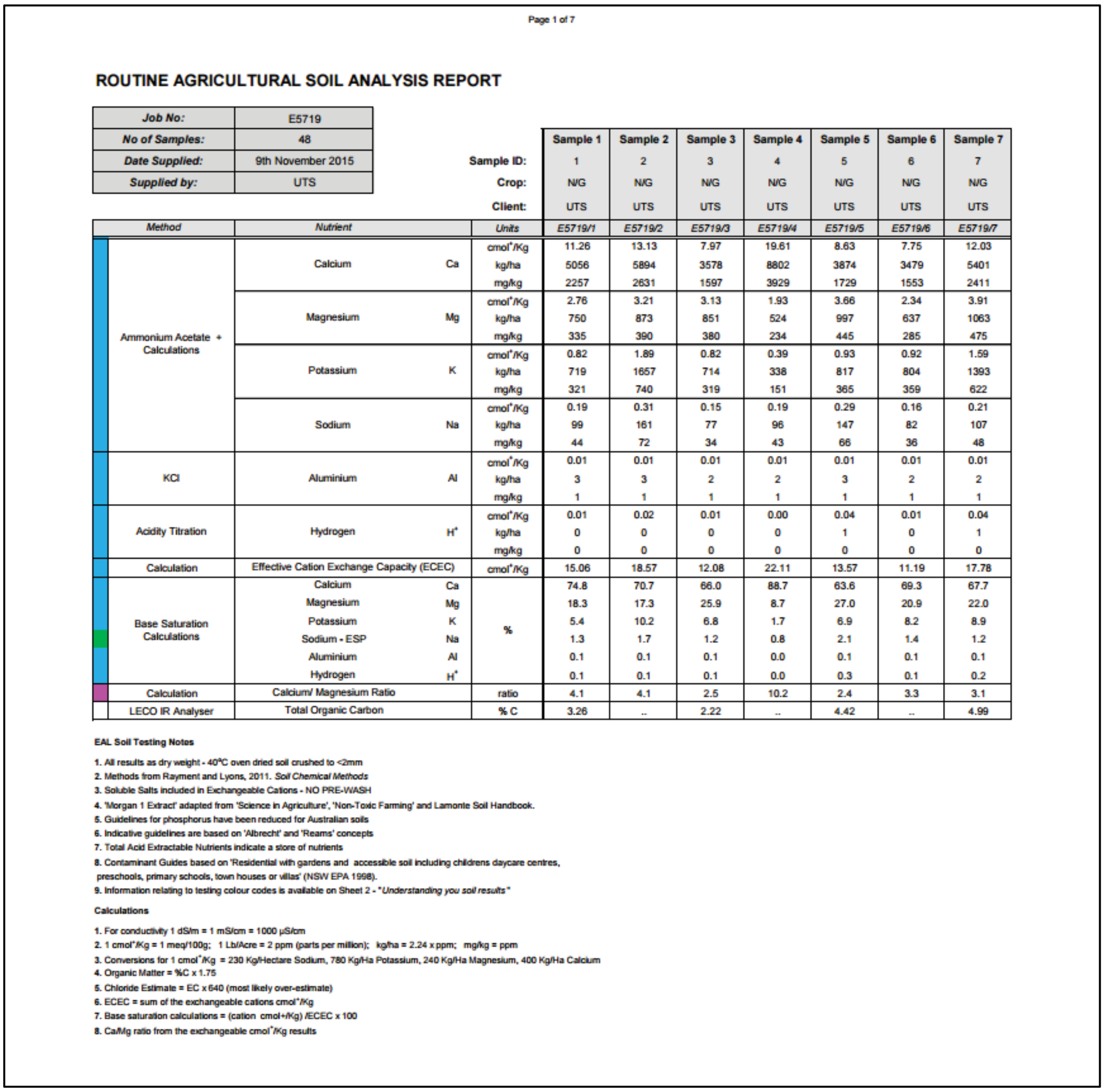
Appendix B
Soil Organic Carbon and Cation Exchange Capacity



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

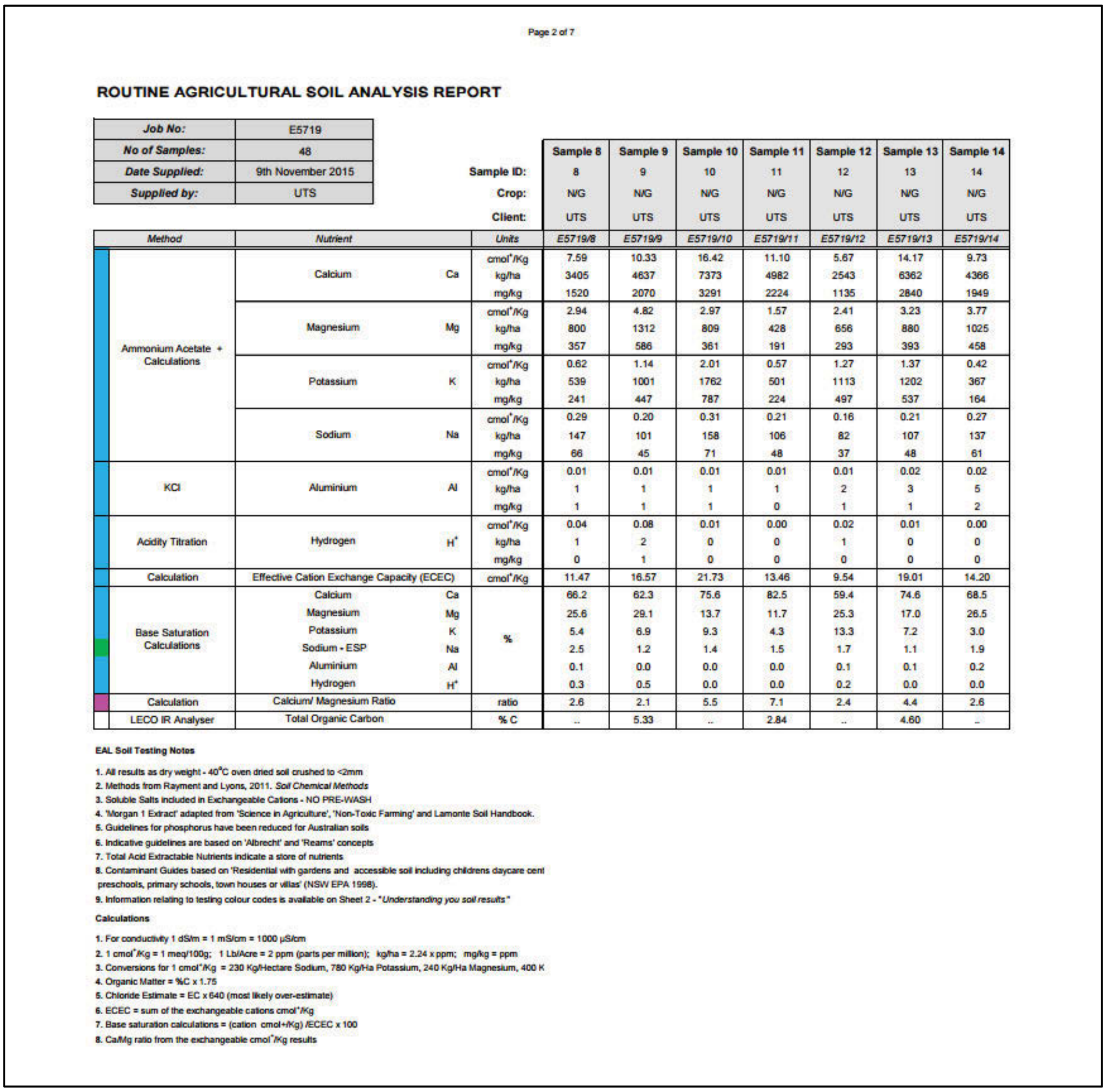
					Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
				Sample ID:	1	2	3	4	5	6	7
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/1*	*E5719/2*	*E5719/3*	*E5719/4*	*E5719/5*	*E5719/6*	*E5719/7*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	11.26	13.13	7.97	19.61	8.63	7.75	12.03
🟦				kg/ha	5056	5894	3578	8802	3874	3479	5401
🟦				mg/kg	2257	2631	1597	3929	1729	1553	2411
🟦		Magnesium	Mg	cmol$^+$/Kg	2.76	3.21	3.13	1.93	3.66	2.34	3.91
🟦				kg/ha	750	873	851	524	997	637	1063
🟦				mg/kg	335	390	380	234	445	285	475
🟦		Potassium	K	cmol$^+$/Kg	0.82	1.89	0.82	0.39	0.93	0.92	1.59
🟦				kg/ha	719	1657	714	338	817	804	1393
🟦				mg/kg	321	740	319	151	365	359	622
🟦		Sodium	Na	cmol$^+$/Kg	0.19	0.31	0.15	0.19	0.29	0.16	0.21
🟦				kg/ha	99	161	77	96	147	82	107
🟦				mg/kg	44	72	34	43	66	36	48
🟦	KCl	Aluminium	Al	cmol$^+$/Kg	0.01	0.01	0.01	0.01	0.01	0.01	0.01
🟦				kg/ha	3	3	2	2	3	2	2
🟦				mg/kg	1	1	1	1	1	1	1
🟦	Acidity Titration	Hydrogen	H$^+$	cmol$^+$/Kg	0.01	0.02	0.01	0.00	0.04	0.01	0.04
🟦				kg/ha	0	0	0	0	1	0	1
🟦				mg/kg	0	0	0	0	0	0	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	15.06	18.57	12.08	22.11	13.57	11.19	17.78
🟦	Base Saturation Calculations	Calcium	Ca	%	74.8	70.7	66.0	88.7	63.6	69.3	67.7
🟦		Magnesium	Mg		18.3	17.3	25.9	8.7	27.0	20.9	22.0
🟦		Potassium	K		5.4	10.2	6.8	1.7	6.9	8.2	8.9
🟩		Sodium - ESP	Na		1.3	1.7	1.2	0.8	2.1	1.4	1.2
🟦		Aluminium	Al		0.1	0.1	0.1	0.0	0.1	0.1	0.1
🟦		Hydrogen	H$^+$		0.1	0.1	0.1	0.0	0.3	0.1	0.2
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	4.1	4.1	2.5	10.2	2.4	3.3	3.1
	LECO IR Analyser	Total Organic Carbon		% C	3.26	..	2.22	..	4.42	..	4.99

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
6. Indicative guidelines are based on 'Albrecht' and 'Reams' concepts
7. Total Acid Extractable Nutrients indicate a store of nutrients
8. Contaminant Guides based on 'Residential with gardens and accessible soil including childrens daycare centres, preschools, primary schools, town houses or villas' (NSW EPA 1998).
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol$^+$/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol$^+$/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 Kg/Ha Calcium
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol$^+$/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

					Sample 8	**Sample 9**	**Sample 10**	**Sample 11**	**Sample 12**	**Sample 13**	**Sample 14**
				Sample ID:	8	9	10	11	12	13	14
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/8*	*E5719/9*	*E5719/10*	*E5719/11*	*E5719/12*	*E5719/13*	*E5719/14*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	7.59	10.33	16.42	11.10	5.67	14.17	9.73
				kg/ha	3405	4637	7373	4982	2543	6362	4366
				mg/kg	1520	2070	3291	2224	1135	2840	1949
		Magnesium	Mg	cmol$^+$/Kg	2.94	4.82	2.97	1.57	2.41	3.23	3.77
				kg/ha	800	1312	809	428	656	880	1025
				mg/kg	357	586	361	191	293	393	458
		Potassium	K	cmol$^+$/Kg	0.62	1.14	2.01	0.57	1.27	1.37	0.42
				kg/ha	539	1001	1762	501	1113	1202	367
				mg/kg	241	447	787	224	497	537	164
		Sodium	Na	cmol$^+$/Kg	0.29	0.20	0.31	0.21	0.16	0.21	0.27
				kg/ha	147	101	158	106	82	107	137
				mg/kg	66	45	71	48	37	48	61
🟦	KCl	Aluminium	Al	cmol$^+$/Kg	0.01	0.01	0.01	0.01	0.01	0.02	0.02
				kg/ha	1	1	1	1	2	3	5
				mg/kg	1	1	1	0	1	1	2
🟦	Acidity Titration	Hydrogen	H$^+$	cmol$^+$/Kg	0.04	0.08	0.01	0.00	0.02	0.01	0.00
				kg/ha	1	2	0	0	1	0	0
				mg/kg	0	1	0	0	0	0	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	11.47	16.57	21.73	13.46	9.54	19.01	14.20
🟦	Base Saturation Calculations	Calcium	Ca	%	66.2	62.3	75.6	82.5	59.4	74.6	68.5
🟦		Magnesium	Mg		25.6	29.1	13.7	11.7	25.3	17.0	26.5
🟦		Potassium	K		5.4	6.9	9.3	4.3	13.3	7.2	3.0
🟩		Sodium - ESP	Na		2.5	1.2	1.4	1.5	1.7	1.1	1.9
🟦		Aluminium	Al		0.1	0.0	0.0	0.0	0.1	0.1	0.2
🟦		Hydrogen	H$^+$		0.3	0.5	0.0	0.0	0.2	0.0	0.0
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	2.6	2.1	5.5	7.1	2.4	4.4	2.6
☐	LECO IR Analyser	Total Organic Carbon		% C	..	5.33	..	2.84	..	4.60	..

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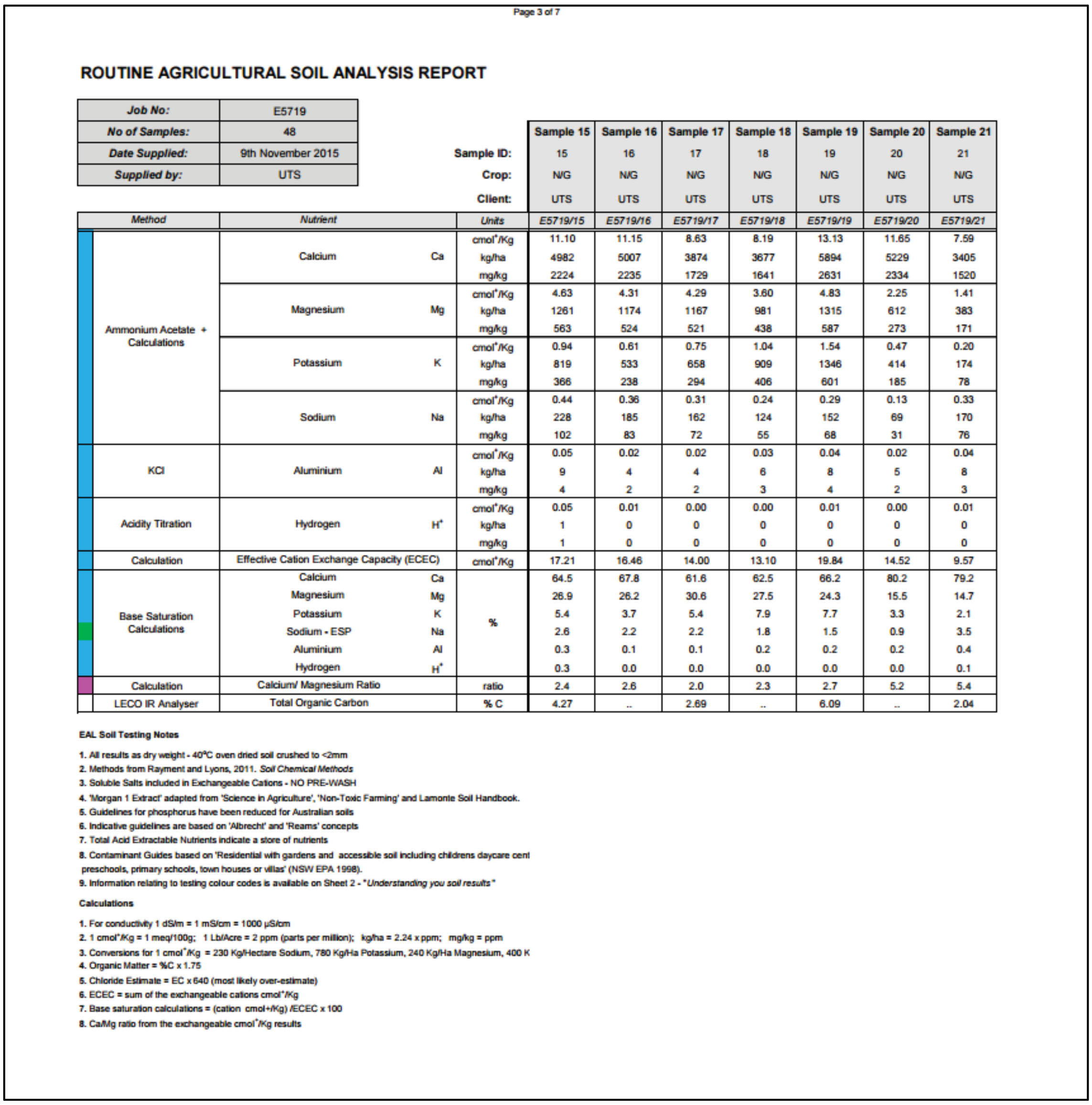
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

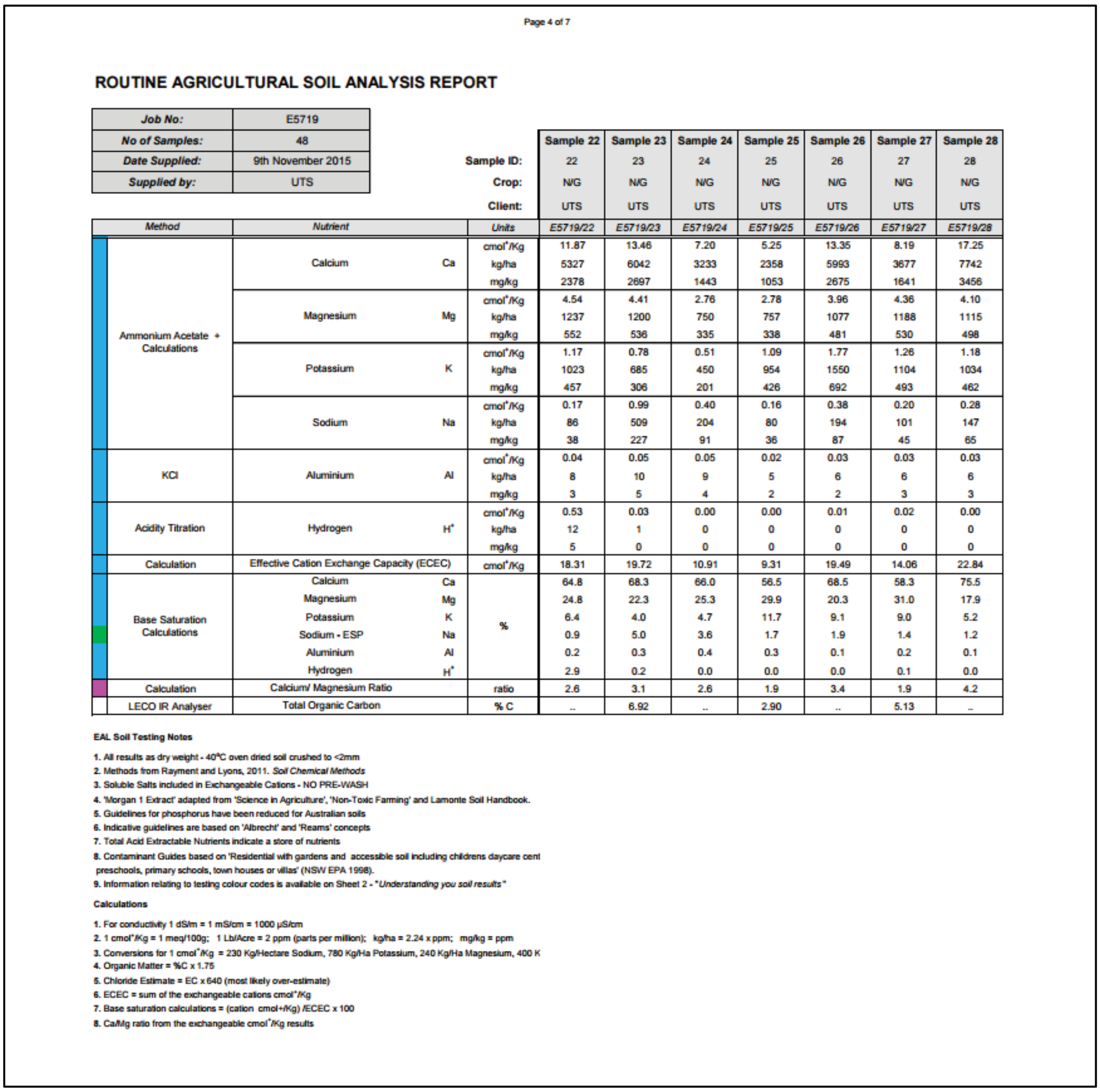
					Sample 15	**Sample 16**	**Sample 17**	**Sample 18**	**Sample 19**	**Sample 20**	**Sample 21**
				Sample ID:	15	16	17	18	19	20	21
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/15*	*E5719/16*	*E5719/17*	*E5719/18*	*E5719/19*	*E5719/20*	*E5719/21*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	11.10	11.15	8.63	8.19	13.13	11.65	7.59
				kg/ha	4982	5007	3874	3677	5894	5229	3405
				mg/kg	2224	2235	1729	1641	2631	2334	1520
		Magnesium	Mg	cmol$^+$/Kg	4.63	4.31	4.29	3.60	4.83	2.25	1.41
				kg/ha	1261	1174	1167	981	1315	612	383
				mg/kg	563	524	521	438	587	273	171
		Potassium	K	cmol$^+$/Kg	0.94	0.61	0.75	1.04	1.54	0.47	0.20
				kg/ha	819	533	658	909	1346	414	174
				mg/kg	366	238	294	406	601	185	78
		Sodium	Na	cmol$^+$/Kg	0.44	0.36	0.31	0.24	0.29	0.13	0.33
				kg/ha	228	185	162	124	152	69	170
				mg/kg	102	83	72	55	68	31	76
🟦	KCl	Aluminium	Al	cmol$^+$/Kg	0.05	0.02	0.02	0.03	0.04	0.02	0.04
				kg/ha	9	4	4	6	8	5	8
				mg/kg	4	2	2	3	4	2	3
🟦	Acidity Titration	Hydrogen	H$^+$	cmol$^+$/Kg	0.05	0.01	0.00	0.00	0.01	0.00	0.01
				kg/ha	1	0	0	0	0	0	0
				mg/kg	1	0	0	0	0	0	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	17.21	16.46	14.00	13.10	19.84	14.52	9.57
🟦	Base Saturation Calculations	Calcium	Ca	%	64.5	67.8	61.6	62.5	66.2	80.2	79.2
🟦		Magnesium	Mg		26.9	26.2	30.6	27.5	24.3	15.5	14.7
🟦		Potassium	K		5.4	3.7	5.4	7.9	7.7	3.3	2.1
🟩		Sodium - ESP	Na		2.6	2.2	2.2	1.8	1.5	0.9	3.5
🟦		Aluminium	Al		0.3	0.1	0.1	0.2	0.2	0.2	0.4
🟦		Hydrogen	H$^+$		0.3	0.0	0.0	0.0	0.0	0.0	0.1
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	2.4	2.6	2.0	2.3	2.7	5.2	5.4
	LECO IR Analyser	Total Organic Carbon		% C	4.27	..	2.69	..	6.09	..	2.04

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
6. Indicative guidelines are based on 'Albrecht' and 'Reams' concepts
7. Total Acid Extractable Nutrients indicate a store of nutrients
8. Contaminant Guides based on 'Residential with gardens and accessible soil including childrens daycare cent preschools, primary schools, town houses or villas' (NSW EPA 1998).
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol$^+$/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol$^+$/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 K
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol$^+$/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

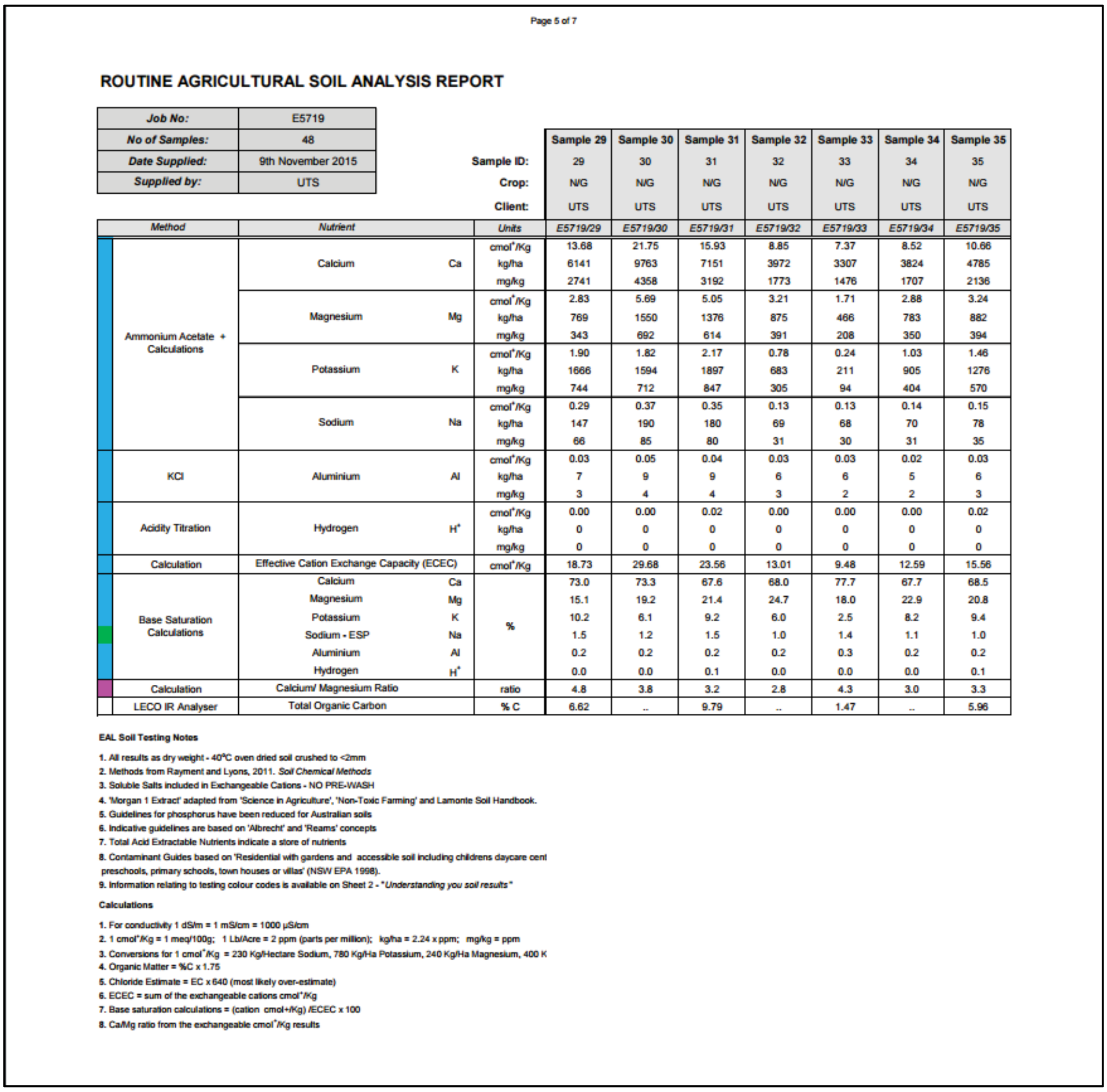
				Sample 22	**Sample 23**	**Sample 24**	**Sample 25**	**Sample 26**	**Sample 27**	**Sample 28**
			Sample ID:	22	23	24	25	26	27	28
			Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
			Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
Method	*Nutrient*		*Units*	*E5719/22*	*E5719/23*	*E5719/24*	*E5719/25*	*E5719/26*	*E5719/27*	*E5719/28*
Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	11.87	13.46	7.20	5.25	13.35	8.19	17.25
			kg/ha	5327	6042	3233	2358	5993	3677	7742
			mg/kg	2378	2697	1443	1053	2675	1641	3456
	Magnesium	Mg	cmol$^+$/Kg	4.54	4.41	2.76	2.78	3.96	4.36	4.10
			kg/ha	1237	1200	750	757	1077	1188	1115
			mg/kg	552	536	335	338	481	530	498
	Potassium	K	cmol$^+$/Kg	1.17	0.78	0.51	1.09	1.77	1.26	1.18
			kg/ha	1023	685	450	954	1550	1104	1034
			mg/kg	457	306	201	426	692	493	462
	Sodium	Na	cmol$^+$/Kg	0.17	0.99	0.40	0.16	0.38	0.20	0.28
			kg/ha	86	509	204	80	194	101	147
			mg/kg	38	227	91	36	87	45	65
KCl	Aluminium	Al	cmol$^+$/Kg	0.04	0.05	0.05	0.02	0.03	0.03	0.03
			kg/ha	8	10	9	5	6	6	6
			mg/kg	3	5	4	2	2	3	3
Acidity Titration	Hydrogen	H$^+$	cmol$^+$/Kg	0.53	0.03	0.00	0.00	0.01	0.02	0.00
			kg/ha	12	1	0	0	0	0	0
			mg/kg	5	0	0	0	0	0	0
Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	18.31	19.72	10.91	9.31	19.49	14.06	22.84
Base Saturation Calculations	Calcium	Ca	%	64.8	68.3	66.0	56.5	68.5	58.3	75.5
	Magnesium	Mg		24.8	22.3	25.3	29.9	20.3	31.0	17.9
	Potassium	K		6.4	4.0	4.7	11.7	9.1	9.0	5.2
	Sodium - ESP	Na		0.9	5.0	3.6	1.7	1.9	1.4	1.2
	Aluminium	Al		0.2	0.3	0.4	0.3	0.1	0.2	0.1
	Hydrogen	H$^+$		2.9	0.2	0.0	0.0	0.0	0.1	0.0
Calculation	Calcium/ Magnesium Ratio		ratio	2.6	3.1	2.6	1.9	3.4	1.9	4.2
LECO IR Analyser	Total Organic Carbon		% C	..	6.92	..	2.90	..	5.13	..

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
6. Indicative guidelines are based on 'Albrecht' and 'Reams' concepts
7. Total Acid Extractable Nutrients indicate a store of nutrients
8. Contaminant Guides based on 'Residential with gardens and accessible soil including childrens daycare cent preschools, primary schools, town houses or villas' (NSW EPA 1998).
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol$^+$/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol$^+$/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 K
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol$^+$/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

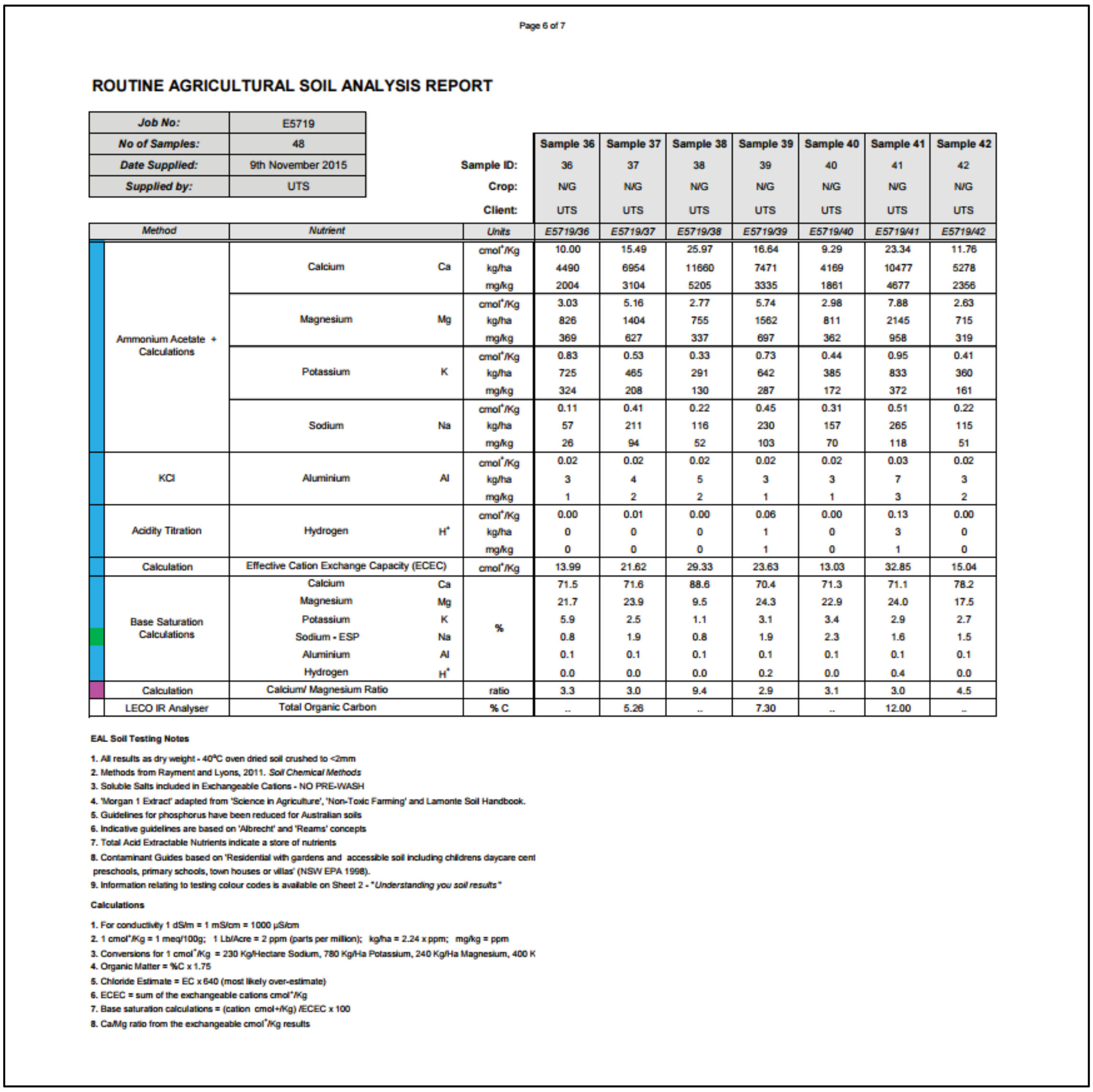
					Sample 29	Sample 30	Sample 31	Sample 32	Sample 33	Sample 34	Sample 35
				Sample ID:	29	30	31	32	33	34	35
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/29*	*E5719/30*	*E5719/31*	*E5719/32*	*E5719/33*	*E5719/34*	*E5719/35*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	13.68	21.75	15.93	8.85	7.37	8.52	10.66
				kg/ha	6141	9763	7151	3972	3307	3824	4785
				mg/kg	2741	4358	3192	1773	1476	1707	2136
		Magnesium	Mg	cmol$^+$/Kg	2.83	5.69	5.05	3.21	1.71	2.88	3.24
				kg/ha	769	1550	1376	875	466	783	882
				mg/kg	343	692	614	391	208	350	394
		Potassium	K	cmol$^+$/Kg	1.90	1.82	2.17	0.78	0.24	1.03	1.46
				kg/ha	1666	1594	1897	683	211	905	1276
				mg/kg	744	712	847	305	94	404	570
		Sodium	Na	cmol$^+$/Kg	0.29	0.37	0.35	0.13	0.13	0.14	0.15
				kg/ha	147	190	180	69	68	70	78
				mg/kg	66	85	80	31	30	31	35
🟦	KCl	Aluminium	Al	cmol$^+$/Kg	0.03	0.05	0.04	0.03	0.03	0.02	0.03
				kg/ha	7	9	9	6	6	5	6
				mg/kg	3	4	4	3	2	2	3
🟦	Acidity Titration	Hydrogen	H^+	cmol$^+$/Kg	0.00	0.00	0.02	0.00	0.00	0.00	0.02
				kg/ha	0	0	0	0	0	0	0
				mg/kg	0	0	0	0	0	0	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	18.73	29.68	23.56	13.01	9.48	12.59	15.56
🟦	Base Saturation Calculations	Calcium	Ca	%	73.0	73.3	67.6	68.0	77.7	67.7	68.5
🟦		Magnesium	Mg		15.1	19.2	21.4	24.7	18.0	22.9	20.8
🟦		Potassium	K		10.2	6.1	9.2	6.0	2.5	8.2	9.4
🟩		Sodium - ESP	Na		1.5	1.2	1.5	1.0	1.4	1.1	1.0
🟦		Aluminium	Al		0.2	0.2	0.2	0.2	0.3	0.2	0.2
🟦		Hydrogen	H^+		0.0	0.0	0.1	0.0	0.0	0.0	0.1
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	4.8	3.8	3.2	2.8	4.3	3.0	3.3
	LECO IR Analyser	Total Organic Carbon		% C	6.62	..	9.79	..	1.47	..	5.96

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
6. Indicative guidelines are based on 'Albrecht' and 'Reams' concepts
7. Total Acid Extractable Nutrients indicate a store of nutrients
8. Contaminant Guides based on 'Residential with gardens and accessible soil including childrens daycare cent preschools, primary schools, town houses or villas' (NSW EPA 1998).
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol$^+$/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol$^+$/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 K
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol$^+$/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results



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ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

					Sample 36	**Sample 37**	**Sample 38**	**Sample 39**	**Sample 40**	**Sample 41**	**Sample 42**
				Sample ID:	36	37	38	39	40	41	42
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/36*	*E5719/37*	*E5719/38*	*E5719/39*	*E5719/40*	*E5719/41*	*E5719/42*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol⁺/Kg	10.00	15.49	25.97	16.64	9.29	23.34	11.76
				kg/ha	4490	6954	11660	7471	4169	10477	5278
				mg/kg	2004	3104	5205	3335	1861	4677	2356
		Magnesium	Mg	cmol⁺/Kg	3.03	5.16	2.77	5.74	2.98	7.88	2.63
				kg/ha	826	1404	755	1562	811	2145	715
				mg/kg	369	627	337	697	362	958	319
		Potassium	K	cmol⁺/Kg	0.83	0.53	0.33	0.73	0.44	0.95	0.41
				kg/ha	725	465	291	642	385	833	360
				mg/kg	324	208	130	287	172	372	161
		Sodium	Na	cmol⁺/Kg	0.11	0.41	0.22	0.45	0.31	0.51	0.22
				kg/ha	57	211	116	230	157	265	115
				mg/kg	26	94	52	103	70	118	51
🟦	KCl	Aluminium	Al	cmol⁺/Kg	0.02	0.02	0.02	0.02	0.02	0.03	0.02
				kg/ha	3	4	5	3	3	7	3
				mg/kg	1	2	2	1	1	3	2
🟦	Acidity Titration	Hydrogen	H⁺	cmol⁺/Kg	0.00	0.01	0.00	0.06	0.00	0.13	0.00
				kg/ha	0	0	0	1	0	3	0
				mg/kg	0	0	0	1	0	1	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol⁺/Kg	13.99	21.62	29.33	23.63	13.03	32.85	15.04
🟦	Base Saturation Calculations	Calcium	Ca	%	71.5	71.6	88.6	70.4	71.3	71.1	78.2
🟦		Magnesium	Mg		21.7	23.9	9.5	24.3	22.9	24.0	17.5
🟦		Potassium	K		5.9	2.5	1.1	3.1	3.4	2.9	2.7
🟩		Sodium - ESP	Na		0.8	1.9	0.8	1.9	2.3	1.6	1.5
🟦		Aluminium	Al		0.1	0.1	0.1	0.1	0.1	0.1	0.1
🟦		Hydrogen	H⁺		0.0	0.0	0.0	0.2	0.0	0.4	0.0
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	3.3	3.0	9.4	2.9	3.1	3.0	4.5
	LECO IR Analyser	Total Organic Carbon		% C	..	5.26	..	7.30	..	12.00	..

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
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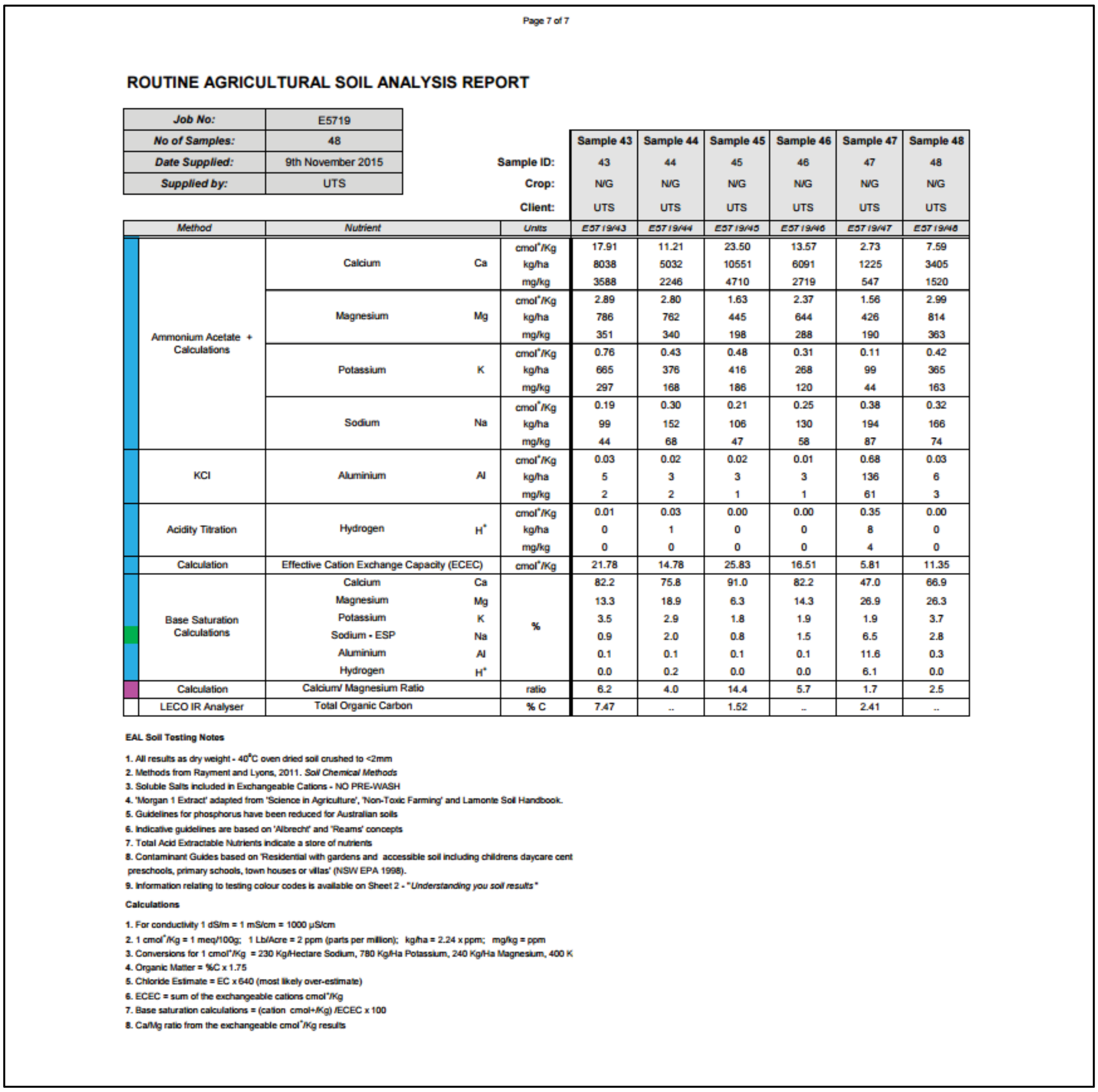
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol⁺/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol⁺/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 K
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol⁺/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol⁺/Kg results



ROUTINE AGRICULTURAL SOIL ANALYSIS REPORT

Job No:	E5719
No of Samples:	48
Date Supplied:	9th November 2015
Supplied by:	UTS

					Sample 43	**Sample 44**	**Sample 45**	**Sample 46**	**Sample 47**	**Sample 48**
				Sample ID:	43	44	45	46	47	48
				Crop:	N/G	N/G	N/G	N/G	N/G	N/G
				Client:	UTS	UTS	UTS	UTS	UTS	UTS
	Method	*Nutrient*		*Units*	*E5719/43*	*E5719/44*	*E5719/45*	*E5719/46*	*E5719/47*	*E5719/48*
🟦	Ammonium Acetate + Calculations	Calcium	Ca	cmol$^+$/Kg	17.91	11.21	23.50	13.57	2.73	7.59
🟦				kg/ha	8038	5032	10551	6091	1225	3405
🟦				mg/kg	3588	2246	4710	2719	547	1520
🟦		Magnesium	Mg	cmol$^+$/Kg	2.89	2.80	1.63	2.37	1.56	2.99
🟦				kg/ha	786	762	445	644	426	814
🟦				mg/kg	351	340	198	288	190	363
🟦		Potassium	K	cmol$^+$/Kg	0.76	0.43	0.48	0.31	0.11	0.42
🟦				kg/ha	665	376	416	268	99	365
🟦				mg/kg	297	168	186	120	44	163
🟦		Sodium	Na	cmol$^+$/Kg	0.19	0.30	0.21	0.25	0.38	0.32
🟦				kg/ha	99	152	106	130	194	166
🟦				mg/kg	44	68	47	58	87	74
🟦	KCl	Aluminium	Al	cmol$^+$/Kg	0.03	0.02	0.02	0.01	0.68	0.03
🟦				kg/ha	5	3	3	3	136	6
🟦				mg/kg	2	2	1	1	61	3
🟦	Acidity Titration	Hydrogen	H^+	cmol$^+$/Kg	0.01	0.03	0.00	0.00	0.35	0.00
🟦				kg/ha	0	1	0	0	8	0
🟦				mg/kg	0	0	0	0	4	0
🟦	Calculation	Effective Cation Exchange Capacity (ECEC)		cmol$^+$/Kg	21.78	14.78	25.83	16.51	5.81	11.35
🟦	Base Saturation Calculations	Calcium	Ca	%	82.2	75.8	91.0	82.2	47.0	66.9
🟦		Magnesium	Mg		13.3	18.9	6.3	14.3	26.9	26.3
🟦		Potassium	K		3.5	2.9	1.8	1.9	1.9	3.7
🟩		Sodium - ESP	Na		0.9	2.0	0.8	1.5	6.5	2.8
🟦		Aluminium	Al		0.1	0.1	0.1	0.1	11.6	0.3
🟦		Hydrogen	H^+		0.0	0.2	0.0	0.0	6.1	0.0
🟪	Calculation	Calcium/ Magnesium Ratio		ratio	6.2	4.0	14.4	5.7	1.7	2.5
	LECO IR Analyser	Total Organic Carbon		% C	7.47	..	1.52	..	2.41	..

EAL Soil Testing Notes

1. All results as dry weight - 40°C oven dried soil crushed to <2mm
2. Methods from Rayment and Lyons, 2011. *Soil Chemical Methods*
3. Soluble Salts included in Exchangeable Cations - NO PRE-WASH
4. 'Morgan 1 Extract' adapted from 'Science in Agriculture', 'Non-Toxic Farming' and Lamonte Soil Handbook.
5. Guidelines for phosphorus have been reduced for Australian soils
6. Indicative guidelines are based on 'Albrecht' and 'Reams' concepts
7. Total Acid Extractable Nutrients indicate a store of nutrients
8. Contaminant Guides based on 'Residential with gardens and accessible soil including childrens daycare cent preschools, primary schools, town houses or villas' (NSW EPA 1998).
9. Information relating to testing colour codes is available on Sheet 2 - "*Understanding you soil results*"

Calculations

1. For conductivity 1 dS/m = 1 mS/cm = 1000 µS/cm
2. 1 cmol$^+$/Kg = 1 meq/100g; 1 Lb/Acre = 2 ppm (parts per million); kg/ha = 2.24 x ppm; mg/kg = ppm
3. Conversions for 1 cmol$^+$/Kg = 230 Kg/Hectare Sodium, 780 Kg/Ha Potassium, 240 Kg/Ha Magnesium, 400 K
4. Organic Matter = %C x 1.75
5. Chloride Estimate = EC x 640 (most likely over-estimate)
6. ECEC = sum of the exchangeable cations cmol$^+$/Kg
7. Base saturation calculations = (cation cmol+/Kg) /ECEC x 100
8. Ca/Mg ratio from the exchangeable cmol$^+$/Kg results

Appendix C
Journal Article One

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URBAN SOILS AND SEDIMENTS

Evaluation of accumulation and concentration of heavy metals in different urban roadside soil types in Miranda Park, Sydney

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Abstract
Purpose The overall objectives of this study were to examine the relationship between the concentrations of heavy metals such as Pb, Zn, Cu, and Cd in roadside soil derived from three different geological parent materials, Hawkesbury Sandstone, Wianamatta Shale, and Mittagong Formation and also to examine the influence of rainfall events on heavy metal concentrations in both the topsoil and the subsoil in all three soil types. In this paper, the focus is on lead and zinc.
Materials and methods The results obtained from the samples taken from an initial transect were used to select the location of the study sites. Soil samples were collected using a stainless steel auger at distances of 1, 5, and 10 m from the edge of two major roads of similar traffic volumes bordering a suburban park. At each of five study sites, samples were collected at depths of 0–10 and 10–30 cm, three times pre-rainfall (after extended periods of no rain) and three times post-rainfall (after intensive rainfall periods). The modified aqua regia digestion method was applied for heavy metal concentrations measurement. To determine the temporal dynamics of trace elements in the soils, sequential extractions were applied to all the topsoil samples according to the modified three-step sequential extraction procedure.
Results and discussion The corresponding concentrations of Pb and Zn were different for the soil derived from Hawkesbury Sandstone and Wianamatta Shale and also Mittagong Formation. The highest concentration of Pb was in the soil from Wianamatta Shale, 159.32 mg/kg and the highest concentration of Zn was in the soil from the Mittagong Formation, 254.12 mg/kg, all at a distance of 1 m from the roadside. From the sequential chemical extraction results, the rainfall substantially influenced the exchangeable fraction (F1) of Pb at a distance from the road of 1 m. A significant reduction of F1 was found for the soil derived from Mittagong Formation which also had the most significant reduction of total Zn concentration.
Conclusions The interpretation of the results showed that there was a clear correlation between the concentration of Pb and Zn with the distance from the roadside and depth in all soil types. However, the results also showed that there are variable concentrations between the soil types. The heavy metal concentrations at the same distance for the three soil types are different. The rainfall events do influence the heavy metal concentration differently in both topsoil and subsoil of the three soil types at the same distance from the roadside.

Keywords Heavy metals · Rainfall events · Soil type · Urban park

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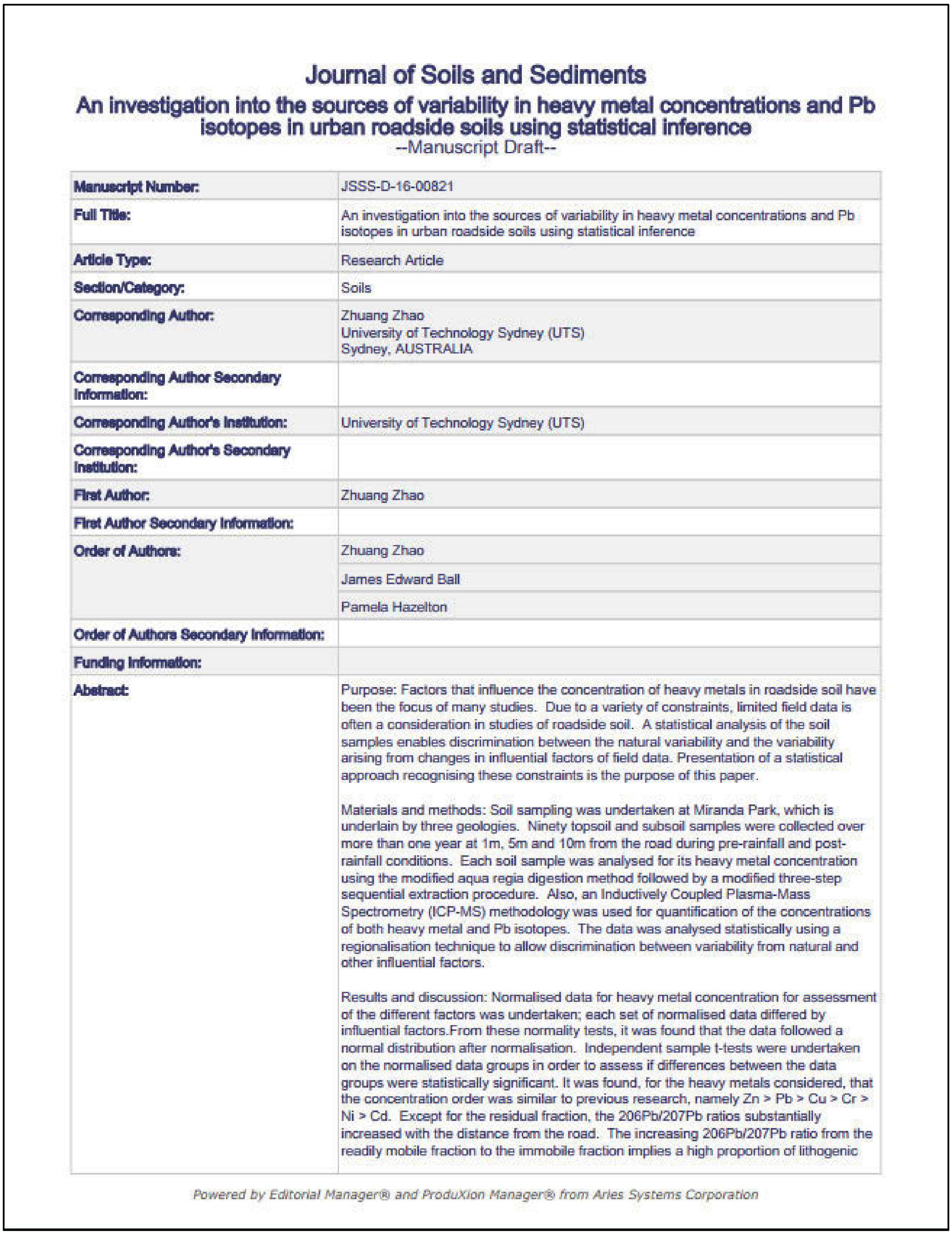
Appendix D
Journal Article Two



Journal of Soils and Sediments
An investigation into the sources of variability in heavy metal concentrations and Pb isotopes in urban roadside soils using statistical inference
--Manuscript Draft--

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Abstract:	Purpose: Factors that influence the concentration of heavy metals in roadside soil have been the focus of many studies. Due to a variety of constraints, limited field data is often a consideration in studies of roadside soil. A statistical analysis of the soil samples enables discrimination between the natural variability and the variability arising from changes in influential factors of field data. Presentation of a statistical approach recognising these constraints is the purpose of this paper. Materials and methods: Soil sampling was undertaken at Miranda Park, which is underlain by three geologies. Ninety topsoil and subsoil samples were collected over more than one year at 1m, 5m and 10m from the road during pre-rainfall and post-rainfall conditions. Each soil sample was analysed for its heavy metal concentration using the modified aqua regia digestion method followed by a modified three-step sequential extraction procedure. Also, an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) methodology was used for quantification of the concentrations of both heavy metal and Pb isotopes. The data was analysed statistically using a regionalisation technique to allow discrimination between variability from natural and other influential factors. Results and discussion: Normalised data for heavy metal concentration for assessment of the different factors was undertaken; each set of normalised data differed by influential factors.From these normality tests, it was found that the data followed a normal distribution after normalisation. Independent sample t-tests were undertaken on the normalised data groups in order to assess if differences between the data groups were statistically significant. It was found, for the heavy metals considered, that the concentration order was similar to previous research, namely Zn > Pb > Cu > Cr > Ni > Cd. Except for the residual fraction, the 206Pb/207Pb ratios substantially increased with the distance from the road. The increasing 206Pb/207Pb ratio from the readily mobile fraction to the immobile fraction implies a high proportion of lithogenic

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