Particulate Matter Emissions from Sydney Railway System: Concentration, Heavy Metal Content and Implications for Public Health

By

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I hereby declare that this thesis has not been submitted, either in the same form or a different form, to UTS or any other university for the award of any other degree. To the best of my knowledge and belief, the thesis contains no material that has been previously published or written by another person except where references are made.

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Abstract

Studies have shown that commuters can be exposed to substantial amounts of particulate matter (PM) during commuting time using the railway networks with major implications to public health. According to the Bureau of Transport statistics, Sydney Trains run about 1 million customer journeys per weekday in Sydney commuting people to different destinations. This thesis focuses on the PM assessment in the Sydney railway system at different railway microenvironments including measurements from the train carriages and the platforms at underground and ground levels.

First the thesis focuses on PM_{10} and $PM_{2.5}$ measurements taken from four different microenvironments and two fixed air quality stations during seven weeks of sampling (September to November 2015). Results indicate that average underground PM_{10} and $PM_{2.5}$ concentrations from inside the trains were 2.8 and 2.5 times greater than the ground level measurements. Similarly, PM_{10} and $PM_{2.5}$ concentrations on the underground platforms were 2.7 and 2.5 times greater than at ground level platforms. Average underground PM levels have exceeded the national limits during the sampling period. Correlation analysis showed a strong to moderate association between ambient background and ground level PM (r^2, 0.952 - 0.50) and weak association with the underground concentrations with a maximum r^2 of 0.264. It was also found that Sydney railway can be considered as one of the cleanest systems in comparison with different railway systems globally.

Then the thesis focuses on the metal content in the railway-derived PM. Another sampling campaign was conducted to collect the dust samples needed for the metal analysis. Samples were collected from five railway microenvironments (underground platforms) and also from an urban park for comparison purposes. The USEPA 3050B method was employed to extract the dust samples and to prepare them for metal analysis. Using the

Microwave Plasma - Atomic Emission Spectroscopy (MP-AES), the concentrations of twelve metals were detected. Based on the pollution index (PI), integrated pollution index (IPI) and enrichment factor (EF) analyses, the metals content in the railway PM indicated high levels of pollution from anthropogenic sources mainly attributed to local railway sources. Fe was the most enriched element with an EF value of 61.3, and PI and IPI values of more than 9. After Fe, the EF values for the other metals followed the order of Ni, Cr, Mn, Ba, Zn, Cu. Consistent with previous studies, the current results indicate that high metal content in the railway PM is mainly attributed to local railway sources such as the wear and abrasion processes.

The last part focuses on the potential health risks based on the metal content. Three probabilistic risk assessments approaches have been applied in this chapter: average daily dose method for non-carcinogenic effect, dose effect method for the carcinogenic effect and qualitative risk assessment. Results indicate that no potential risks to cause non-carcinogenic effects from any metal can occur at the measured concentrations except a very low indication from Cr levels. A carcinogenic effect was only performed for Ni and Cr indicating no potential cancer risks based on the measured concentrations. Finally, a qualitative risk assessment was employed to overcome the problem of the scarce information needed for estimating the potential cancer risk for the rest of elements using the ISO31000 method. The results also indicate low to moderate potential carcinogenic risks from Zn, Fe, Mn, Ba and Cu.

Finally, the limitations of this study have been stated with some recommendations for future studies and applications which might help in reducing the PM levels at the railway networks.

Chapter 1. Introduction

Epidemiological studies carried out over the last decades have demonstrated strong relationship between exposure to polluted air and various health and environmental problems. This issue raised the need to establish national and international air quality regulations to reduce, monitor, and improve the air quality. The aim of different regulations is to protect human health, ambient air and our environment from the effect of different air pollutants. Particulate Matter (PM) is one of the six main pollutants that have been regulated by agencies worldwide with an increasing body of evidence of their potential to seriously affect the human health (Alfaro-Moreno et al., 2007; Anderson et al., 2012; Li et al., 2003; Ristovski et al., 2012). PM is a complex mixture of liquid droplets and solid particles suspended in the atmosphere in the form of dust, soot, black smoke, ash and other forms with different chemical composition (US EPA, 2016). Therefore, there is a necessity to establish regulations and monitoring methods to reduce their impact.

The application of global air quality regulations has achieved notable improvement in the surrounding and urban air quality. One of the most significant sources of PM pollution, especially in urban areas, can be derived from the transportation sector. Private cars, buses, trains are all transportation modes that contribute to a specific amount of the total particulate matter in the air. When regulations were firstly introduced, special attention was given to exhaust emissions for different pollutant types. However, non-exhaust emissions were significantly underestimated (Amato et al., 2014; Ketzel et al., 2007; Thorpe and Harrison, 2008), and they have become a more serious issue nowadays.

Railway networks have been considered as a vital mode of public transport in many developed and developing countries where people rely highly on them as a preferred

commuting mode. The application of policies, control regulations, and operational improvement plans have significantly reduced PM emissions from railway networks in addition to the advanced technological applications such as energy efficiency and alternative power solutions (Hyman et al., 2010). However, these improvements have been offset by increasing the length of railway lines in many countries around the world. According to a World Bank study, the length of world's railway lines has been increased immensely by about 40% over the last two decades (World Bank, 2016). Studies conducted around the world have shown that the air quality along the railway systems can sometimes be substantially different from air quality of urban background vicinities, in terms of the size fraction, mass concentrations and chemical composition of PM (Aarnio et al., 2005; Kam et al., 2011a; Salma et al., 2007). Recent studies have shown elevated levels of PM in subways and tunnels (Midander et al., 2012; Seaton et al., 2005; Sohn et al., 2008). Each railway system has shown unique results depending on its own factors that might affect the PM levels such as the fuel used or the power type, braking systems, age of railway tracks, and ventilation systems (Moreno et al., 2014).

Sydney as the capital city of NSW and the most populated city in Australia has a very extensive railway network services. Sydney Trains have made about 276.5 and 33.6 million journeys for Sydney and intercity services, respectively (Bureau of Transport Statistics, 2014). Despite the immense number of journeys run each year, private vehicles are still the dominant mode of transport used by people there. However, new railway networks are showing a rapid expanding trend owing to many reasons. Railway networks are safer, more convenient to travel on, faster and in many cases even cheaper than private vehicles especially after the introduction of toll roads. Depending on railway carriage capacity, this mode of transport is an effective alternative to other commuting modes which can reduce road congestions especially in megacities. One train with 8 carriages

can replace about 15 buses or no less than 250 cars saving large land areas which can be used for new road projects and/or parking spaces (Sydney Trains, 2016).

1.1 Research Rationale

PM pollution can be emitted from various sources; though the first step into improving and monitoring the air quality should be to distinguish the contribution made by each source. People spend most of their day and night hours indoor, however big contribution of their pollution exposure is usually from outdoor activities. In major metropolitan areas, traffic emissions have always been considered as one of the primary source of PM pollution. In the Sydney region, about 19% and 23% of PM_{10} and $PM_{2.5}$ concentrations, respectively, were from road vehicles, according to NSW EPA (2012), Private cars are the most dominant mode of transport in Sydney due to its sprawled urban nature, followed by the train mode of transport (Hay, 2009). Sydney trains run numerous numbers of journeys each year as mentioned previously; and the number of commuters and railway workers susceptible to the impact of railway services is consequently high. Even residents living in the proximity of the railway services or near any other transport environment might be affected (Tonne et al., 2007). PM is heterogeneous combination which have different chemical and physical characteristics that depend on their original sources and other surrounding factors. Accordingly, it may have different impact on human health than particles from urban air. Numerous studies have been done to assess PM levels and chemical composition in worldwide railway networks indicating elevated concentrations and toxic particle composition especially in underground systems (Cheng and Yan, 2011; Kam et al., 2011a; Murruni et al., 2009; Perrino et al., 2015). Passengers spend a relatively short time commuting in subway systems, however, exposures to elevated concentrations of PM with enriched concentration of toxic and carcinogenic chemicals may cause health problems. This finding is of great concern because Sydney railway network is immensely

used by the public as the second common mode of transport after private cars. Until the time of this research there were no previous studies that have reported field concentration data and chemical composition from the railway samples in Sydney railway network. There is an essential need for a comprehensive study to substantially enhance the current knowledge about PM levels and their potential to cause health problems in Sydney railway environments.

1.2 Aims and Objectives

1.2.1 Aims

The main aim of this thesis is to investigate PM levels and characteristics which have the potential to adversely affect susceptible people in Sydney railway environment. Particle mass concentrations and their heavy metal content, as the main chemical component in railway PM, will be analysed. Based on the metal content, risk assessment will also be presented to assess potential health implications.

1.2.2 Objectives

1.   To investigate the concentration levels of PM_{10} and $PM_{2.5}$ from the underground and ground level environments of Sydney railway system, and to compare them with their corresponding urban concentrations.

2.   To investigate the heavy metals content in Sydney railway particles and assess their enrichment levels.

3.   To assess the potential health risks associated with exposure to PM based on their heavy metal concentrations.

1.3 Thesis Layout

This thesis is composed of six chapters, two of them are experimental. Chapter 1 provides a broad introduction to the topic and briefly describes the problem background and the

research rationale. In addition, it explains the main aims and objectives of this thesis. Chapter 2 provides a comprehensive literature review investigating PM's physical and chemical properties, sources, its effect on human health and the environment, previous results, and global regulation and methods applied especially in the railway industry to reduce the particles impact. Chapter 3 illustrates the data collection method, statistical analysis and results of PM_{10} and $PM_{2.5}$ concentrations obtained during the sampling period from September to November 2015 in different railway microenvironments. Chapter 4 shows the metal analysis based on different indices which will help estimating the potential health risks associated with exposure to the railway-derived PM. Chapter 5 provides qualitative and quantitative risk assessments from the metal concentrations for the potential to cause carcinogenic and non-carcinogenic health effects. Chapter 6 provides a summary of the main findings and conclusions driven from this thesis, the main research limitations will be explained along with some recommendations for future research.

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Chapter 2. Literature Review

2.1 Particulate Matter

PM is a complex mixture of liquid droplets and solid particles suspended in the atmosphere, varying in origin, size, chemical composition and solubility. They are classified as primary and secondary particles based on their mechanism of formation. Primary particles are released directly into the atmosphere from their origin, whereas secondary particles are formed in the atmosphere through converting precursor gas emissions into particles (Kelly and Fussell, 2012). PM can also be classified based on their physical or chemical properties.

2.1.1 Physical characteristics of particulate matter

PM exists in the atmosphere in different shapes and sizes making it very difficult to monitor it individually. Therefore, a good criterion has been introduced to be able to classify PM based on its size using the aerodynamic diameter. To measure the equivalent aerodynamic diameter of any particle, the settling velocity of that particle is compared to that of an ideal spherical shape particle with a density of 1 g/cm^3 (US EPA, 2016b). Particle sizes are usually presented by the notation PM_X to refer to the particle diameter (x) measured in micrometres (μm). The most common size fraction used globally for regulations, standards and research are PM_1, $PM_{2.5}$ and PM_{10}. For example, $PM_{2.5}$ encompasses all particles with aerodynamic diameters of 2.5 μm or less. As mentioned before, PM_{10} and smaller fractions sizes are the most recognised particle size fractions because of their adverse health effects. Ultrafine particles (UFP) are particles smaller than 100 nm and their mass can be negligible to some extent; however, due to their dominant particle number concentrations along with their large surface area per mass they are considered biologically the most active size fraction (Oberdörster et al. 2005). Figure 2.1

illustrates the size of PM_{10} and $PM_{2.5}$ in relation to human hair size and beach sand particles as shown in US EPA PM criteria.
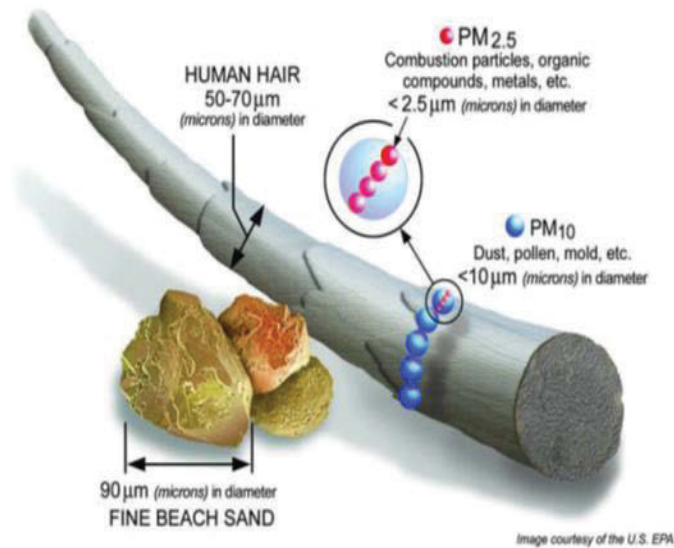
Figure 2.1 PM_{10} and $PM_{2.5}$ particles size relative to human hair and fine beach sand (US EPA, 2004).

PM can have different shapes which have important effects on the diameter measurements and hence its health risk effect (DeCarlo et al., 2004). Studies have shown that the coarse particles from non-exhaust sources are mainly in flake shapes, whereas the fine and ultrafine particles have spherical, semi-spherical, or ellipsoidal shapes (Abbasi et al., 2012; Salma et al., 2009; Sundh and Olofsson, 2011). Particles with diameters of 10 μm or less can be transported for a long distance from their origin before settling, and have more potential to adversely impact human health than larger particles. The dominant particle number concentrations and their large surface areas per mass are the key-points of making the UFP biologically active (Oberdörster et al., 2005).

2.1.2 Chemical characteristics of particulate matter

PM is different not only in its aerodynamic diameter or shape but also in its chemical composition. It is vital to determine the main chemical substances in PM to evaluate their adverse health effects, as they govern their chemical reactivity (Hauck et al., 2004). During particles' transportation in the atmosphere, their chemical characteristics may change by reacting with the surrounding substances forming bigger particles. The chemical composition of PM comes from factors such as the source of the particles, metrological factors and the surrounding ambient air conditions (Hasegawa et al., 2004). In urban areas, PM chemical analysis from air samples worldwide showed the same main compounds but with considerably different magnitudes according to the factors mentioned previously (Harrison and Yin, 2000). The majority of the PM consists of carbonaceous material, such as elemental carbon, semi-volatile organic compounds e.g. polycyclic aromatic hydrocarbons (PAHs), sulphate derived mainly from sulphur dioxide, nitrate predominantly formed from oxidation of NO and NO_2, ammonium from atmospheric ammonia, chloride mainly from sea spray, and metals (Marko, 2005; Putaud et al., 2010). Studies showed that the chemical components of wood combustions particles have a greater proportion of carbonaceous material than particles from railways due to the incomplete combustions processes (Frey et al., 2009; Kim Oanh et al., 1999; Simpson et al., 2005). Conversely, particles from railway networks usually have more trace metals than PAHs due to excessive wear and abrasive operations (Aarnio et al., 2005; Kam et al., 2011). Chemical compounds in PM are crucial in assessing the potential health and environment risks and previous studies have reported significant correlations between PM chemical composition and a wide range of health problems which will be covered in section 2.3.

2.2 Sources of Particulate Matter

PM can be formed in the atmosphere as primary particles emitted directly from the source, or as secondary particles formed in the atmosphere as a result of some chemical reactions (US EPA, 2016b). There are two main sources of PM in the air: natural and anthropogenic. Depending on their origin, the properties of particles can be very different in terms of the physical and chemical characteristics. To monitor and improve the air quality in terms of PM, it is essential to distinguish between these two main sources. PM from natural sources is the main contributor of atmospheric PM including sea spray, volcanoes, bush and forest fires, pollen, in addition to natural gaseous emissions. Despite the large amounts of PM in the atmosphere being mainly from natural sources, its even distribution leads to relatively low background concentrations from these sources (Marko, 2005). The majority of anthropogenic particles are emitted within limited areas, especially urban areas, with high background concentrations of PM. The main anthropogenic sources are biomass fuel burning, mining, on-road and off-road vehicles, and other industrial processes.

NSW, the focus of this study, is the most populated state in Australia with about 32% of its total population according to the 2016 Australian Demographic Statistics (ABS, 2016), and about 75% of the NSW population resides in the Greater Metropolitan Region (GMR). According to the emission inventory study conducted in the GMR, anthropogenic sources contributed to about 73% and 81% of PM_{10} and $PM_{2.5}$, respectively (NSW EPA, 2012). Figure 2.2 illustrates in detail the contribution of different man-made sources. It can be seen that the main contributor activity for both particle sizes is from industrial sources, while the cumulative off-road and on-road vehicle contribution is the third one. Greater air pollution is expected with any population expansion due to the increase in the anthropogenic activities to meet the population needs.

(a) Commercial 2.2%
On-road mobile 3.1%
Off-road mobile 4.0%
Domestic-commercial 9.1%
Industrial 81.5%

(b) On-road mobile 6.5%
Commercial 2.2%
Off-road mobile 10.8%
Domestic-commercial 24.8%
Industrial 55.7%
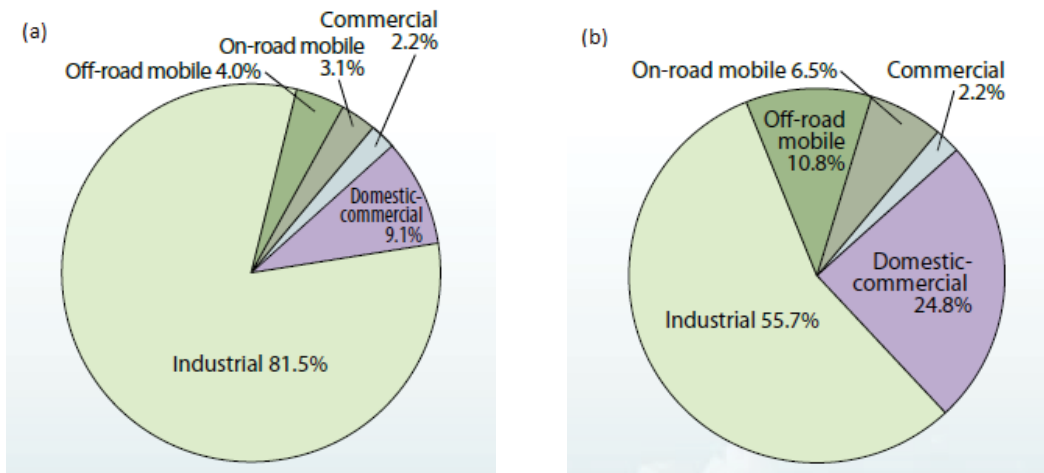
Figure 2.2 The contribution of the main anthropogenic sources of (a) PM_{10}, (b) $PM_{2.5}$ in the GMR- NSW (NSW EPA, 2012).

2.3 Adverse Effects of PM

2.3.1 Effect of PM on human health

The awareness of the public and governments about the impact of atmospheric particles on human health has significantly increased since the London smog pollution episode which occurred during the winter of 1952. The Greater London area had been completely covered with a dense fog for four days from the 5th to 8th of December 1952. The Ministry of Health in the UK reported that the rates of mortality due to respiratory and cardiovascular complications had risen dramatically over that period of time (Figure 2.3) (Ministry of Health, 1954).
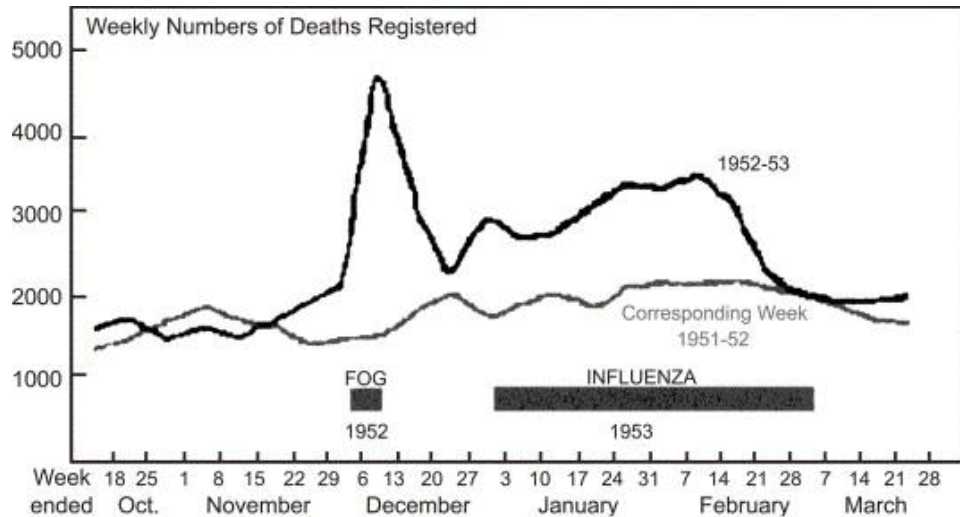
Figure 2.3 Death rates prior to, during and after the London pollution episode in 1952 (Ministry of Health, 1954).

The potential of PM to cause health problems has led to a substantial number of epidemiological studies along with numerous studies to evaluate PM levels from different natural and anthropogenic sources. Studies have shown a wide range of health problems associated with exposure to ambient PM (Brook et al., 2010; Farraj et al., 2015; Stafoggia et al., 2008). Depending on the particles' physical and chemical properties and their levels, a specific range of health problems can eventuate (Cassee et al., 2013). Around 800,000 premature deaths per year are caused by short term ((hours, days) and/or long term (months, years) exposure to PM, ranking it as the 13th leading cause of mortality according to the World Health Organization study (WHO, 2002), though PM health effects are far from being fully understood.

The particle size is an important parameter when estimating the effect of PM on human health. PM_{10} and less are the most important sizes to study, as particles with bigger aerodynamic diameters are usually filtered out by the nose or the upper airway (Anderson et al., 2012). $PM_{2.5}$ can penetrate deeper into the human respiratory system compared to

PM$_{10}$ and this can cause serious and acute health problems (Hoek et al., 2002; Pope III et al., 2002; US EPA, 2015). However, recent studies have shown a strong correlation between high rates of mortality and morbidity and PM$_{10}$ exposure on different age groups. Therefore the impact of PM$_{10}$ should be assessed regularly (Anderson et al., 2012; Lu et al. 2015; Xu et al., 2011). Based on particle number, ultrafine particles should also be monitored due to their potential to pass deeply into the blood stream and lead to thrombosis as a result of their extensive surface area and also due to their enhanced oxidative capacity (Brown et al., 2001; Terzano et al., 2010; Weichenthal, 2012). Until now, international regulations only regulated PM$_{10}$ and PM$_{2.5}$, but there is a push towards the legal regulation of ultrafine particles.

Another important issue to consider when estimating the health effect of PM is its chemical composition. Depending on its source, PM is a complex mixture of chemical substances. Many studies have reported the important role of particle chemistry in determining its effect on human health (Abbasi et al., 2013; Kelly and Fussell, 2012; Valavanidis et al., 2008). For example, elevated metal concentrations in PM can cause an imbalance in the reactive oxygen species (ROS) concentrations affecting the tissue oxygen homeostasis in the human body (Tao et al., 2003). Another study stated that elevated concentration of polycyclic aromatic hydrocarbons (PAHs) has the ability to damage the DNA (Gutiérrez-Castillo et al., 2006; Krzyzanowski et al., 2005). The redox cycling of particles' organic compounds such as PAHs could also increase the formation of superoxide radicals with the chemical formula of (O_2^-) (Carlsten et al., 2010; Xia et al., 2004). However, it is not clear which particle properties are specifically responsible for causing the health problems.

2.3.1.1 Respiratory problems

Breathing air that is contaminated with PM (e.g. dust, vapour) is a very important exposure route that causes diverse respiratory problems. Respiratory problems can occur directly or after a period of time based on the physiochemical properties of particles, susceptible groups, and timeframes of inhalation occurrence, the size of particles and how far they have penetrated inside the body (Freitas et al., 2010). *In vivo* and *in vitro* epidemiological studies have reported a strong positive correlation between exposure to PM and the incidence of asthma, pulmonary functions decline, chronic bronchitis, and increased respiratory-related medical visits (Epton et al., 2008; Kim et al., 2015; Liu et al., 2014; Morgenstern et al., 2007).

2.3.1.2 Cardiovascular problems

Epidemiological studies reported various cardiac problems and morbidity indicators attributed to PM exposure such as ischemic heart disease (blood flow), vascular inflammation, and cardiac arrhythmias (increased or decreased heart pulse rate) (Alfaro-Moreno et al., 2007; Brook et al., 2010; Farraj et al., 2015). Furthermore, studies found an increase in cardiopulmonary mortality rates from PM exposure by 3-13% for both coarse and fine particles (Krewski et al., 2009; Lopez et al., 2006; Peters and Pope III, 2002). Cardiac problems could also develop via other exposure routes. For example, exposure to PM during an injury event can cause blood coagulation resulting in platelet activation which in turn leads to acute cardiac problems.

2.3.1.3 Carcinogenic effects

A substantial increase in lung cancer rates among non-smoking people was first reported by Stocks and Campbell (1955). Since that time, a series of studies have been done to estimate the potential of air pollutants to cause cancer risks especially in urban areas

where people are highly susceptible to elevated concentrations of PM. Special attention has been given to $PM_{2.5}$ as the size of particles allows their geno-toxic chemical substances to penetrate deep into human lungs. A study by Lopez et al. (2006) estimated the global contribution of PM to lung cancer deaths was around 5% from both coarse and fine particles. A recent meta-analysis review study on 18 epidemiological studies on $PM_{2.5}$ and PM_{10} exposure in residential areas reported a 9% increase in lung cancer risk with each 10 µg/m^3 increase in PM exposure (Hamra et al., 2014). Another study showed that individuals who live in big cities with more than 30.39 µg/m^3 $PM_{2.5}$ levels, and particles have elevated levels of PAH and are at an increased risk of death from ovarian cancer with a factor of 1.2 (Hung et al., 2012). Until this time, it has not been clear which particle property is mainly responsible for causing the health problems. Is it the size of particles or the chemical components? Thus, there is no clear consensus about the carcinogenic effects of PM.

2.3.2 Effects of PM on the environment

The effect of PM on the environment is a crucial topic that has been studied extensively worldwide. Atmospheric particles are ubiquitous, and according to their physical and chemical properties they can interact with other natural and/or anthropogenic processes. Consequently, direct and indirect impacts on the environment can occur. This falls beyond the objectives of this research in estimating in detail the environmental problems associated with exposure to PM. However, indirect health effects can arise as a result of these hazards. Hence, a brief explanation about the major environmental problems from ambient PM will be presented.

2.3.2.1 Visibility degradation

Visibility has been defined by EPA as "the greatest distance at which an observer can just see a black object viewed against the horizon sky" (Malm, 1999). Visibility impairment is a critical pollution problem which can adversely affect the atmospheric air. Haze is the most recognised form of visibility degradation which can occur from the substantial presence of PM and certain gases in the atmosphere affecting human activities and health. For example, all forms of traffic (road, railway networks, and aviation) can be adversely affected by visibility impairment which causes traffic accidents, congestions and delays. The degree of visibility reduction by PM depends on particles properties and the surrounding meteorological factors. Particles of nearly the same size as the light wavelength, have the ability to scatter and absorb the light by reducing the light intensity of radiation (Malm, 1999). Therefore, as the particle size increases, more light tends to scatter in the vision direction causing more visibility degradation. Relative humidity (RH) is one of the most important meteorological factors affecting visibility (Jin and Zhou, 2016; Malm and Day, 2001). Particle size increases (coagulation process) under higher RH rates (>70), where water soluble particles bump against each other and stick to form bigger particle sizes causing visibility problems. Figure 2.4 illustrates how PM grow rapidly in the atmosphere and have high RH rates causing visibility impairment.
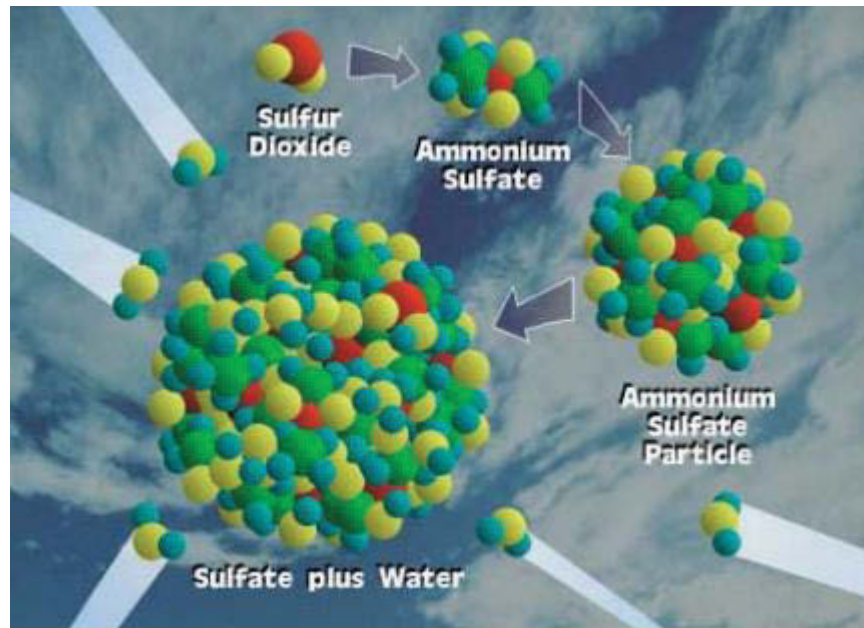
Figure 2.4 Sulphur dioxide gas converts in the atmosphere to ammonium sulphate particles and grows rapidly in high RH atmosphere to reach a size that causes visibility impairment (Malm, 1999).

2.3.2.2 Effects on vegetation

Plants and vegetation are key members of the ecosystem and human lives. They can be significantly affected by the atmospheric PM levels and properties. However, current regulations and threshold levels for PM are firstly driven by the PM effect on human health. Studies have shown that the physiochemical properties of PM have the potential to affect different parts of the plants e.g. leaves, and roots (Grantz et al., 2003; Prajapati, 2012; Prajapati and Tripathi, 2008). The airborne particles can be deposited on different parts of the plants via three methods: dry, wet and occult (Grantz et al., 2003). PM deposition on leaves reduces the amount of reachable light which is usually required for the photosynthesis process leading to vegetation degradation. Another major effect of PM is acid rains due to the deposition of sulphuric acid (H_2SO_4) and ammonium sulphate ($(NH_4)_2SO_4$) from the atmosphere causing visible symptoms of plant injury (Velikova et

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al., 2000). Atmospheric cooling-down and reducing evaporation due to haze may be viewed as the indirect impacts of PM on vegetation. An historical study from India showed the adverse effects of a brown haze on a region over a three month period in 2006. According to Auffhammer et al. (2006), rice harvests would have produced about 11% more without the brown haze in addition to other crops.

2.3.2.3 Effects on global warming

During the last century, a gradual increase in the Earth's overall temperature occurred and was attributed to increased greenhouse gas emissions (GHG). Advanced research conducted by the UN Intergovernmental Panel on Climate Change (IPCC) has shown that particulate matter is another air pollutant which also contributes directly to global warming (Solomon et al., 2007). On one hand, PM is generally considered to be a cooling factor in the atmosphere since it absorbs, scatters, and reflects the sunlight. However a study from China has shown a strong correlation between increasing the smoke particles (black Carbon) and rainfall reduction (Zhao et al., 2006). The reason behind that is the formation of small cloud droplets in the atmosphere which have a tendency to repel each other preventing the big droplets needed for rain to be formed and thus leading to dry hot seasons.

2.4 Standards and Regulations

Due to the significant effects of air pollutant PM on human health and the environment, many governments in different countries have established air pollution regulations and standards with the aim of managing and improving air quality. Since the introduction of these regulations, substantial reductions have been achieved in the amounts of air pollutants. Six air pollutants have been primarily regulated worldwide; these are carbon monoxide, ground-level ozone, particulate matter, nitrogen dioxide, lead, and sulfur

dioxide. PM is usually regulated under two fraction sizes (PM_{10} and $PM_{2.5}$). Standards values are usually set in correspondence to the safe level of exposure by a population based on extensive studies on the consequences of air pollution (WHO, 2006).

In Australia, the first national ambient air quality standards were set in June 1998 by the National Environment Protection Council (NEPC) as part of the National Environment Protection Council Act. Formal reporting against these values commenced on 2002 by the jurisdictions (NEPC, 2015). Prior to the Australian standards, other countries established their own air quality standards. The US Government set its standards based on two types: primary and secondary standards. A primary standard is set for sensitive population (e.g. elderly people, children, and people with specific health problems), and secondary standards set for public welfare protection (US EPA, 2016a). The European Union and the World Health Organization (WHO) have also issued their own air quality standards. Table 2.1 shows worldwide PM standards set by different organisations. It can be seen that there are some differences in the concentrations values between the selected countries due to some political and social factors and also the economic limitations of each country. The commonly used indicator to describe PM in worldwide standards is the PM concentration in $\mu g/m^3$. It is evident that there are some differences in the allowable concentrations values between the countries. These values are different according to some political and social factors in addition to the economic development level for any country (WHO, 2006). The given numbers represent PM concentration levels at which increased mortality responses can occur based on the available epidemiological studies findings. However, there is a need to set PM thresholds which offer complete protection for every individual against the health effects of PM.

Table 2.1 PM standards set by the Australian and other governing bodies.

Country / Organisation	Average Period	PM$_{10}$ ($\mu g/m^3$)	PM$_{2.5}$ ($\mu g/m^3$)	Reference
Australia	24 hr.	50	25	NEPC (2015)
	Annual	25	8	
USA	24 hr. - Primary	150	35	US EPA (2016a)
	24 hr. - Secondary	150	35	
	Annual - Primary	-	12	
	Annual - Secondary	-	15	
EU Union	24 hr.	50	-	European Commission (2015)
	Annual	40	25	
WHO	24 hr.	50	25	WHO (2006)
	Annual	20	10	
China	24 hr.	150	75	MOEP (2012)
	Annual	70	35	
Japan	24 hr.	10	35	MOE (2014)
	Annual	-	15	

2.5 Particulate Matter from Railway Networks

Studies of PM from different transport modes (e.g. private cars and buses) have shown substantial contribution from these sources to the total ambient PM pollution (Chan et al., 2002; Kaur et al., 2007; Yan et al., 2014). In comparison, the number of PM studies in the railway field is very limited despite being one of the most vital modes of transportation, especially in urban areas. Railway transport started more than a century ago. The first railway line was established in the United Kingdom early in the 19th century powered by steam with the first underground line opening in 1863 (Casson, 2009). Thereafter, many countries around the world utilized the railway system as one of the

public transportation modes. Currently, private cars are considered to be the preferable mode of transport; however, the trend of using the railway system is significantly increasing, especially in urban areas.

There is a notable trend by governments around the world to encourage people to use the railway networks rather than on-road cars to prevent traffic congestion in major cities and reduce the health effects on commuters which can be generated from different sources. In general, exhaust emissions of pollutants (e.g. PM, CO, NO_x) from the railway sector are significantly less than private cars, buses, and aviation. According to Chertok et al. (2004), a study between five commuting systems in Sydney showed that train commuters were the least exposed to volatile organic compounds from exhaust emissions. Another study showed that among four public transport modes, the exposure level of different pollutants inside the railway carriages were 1.2 to 9.3 times less than other roadway transport modes including buses (air conditioned and non-air conditioned) and taxis (Chan et al., 2002). In addition to this, railway systems are usually considered as an environmentally friendly mode of transport in comparison to other commuting modes. However, this fact has been offset by increasing the length of global railway lines. Figure 2.5 illustrates the results from a World Bank study showing a substantial increase in the total global length of the world's railway lines (World Bank, 2016). An increase of about 40% occurred over the last 15 years and the main contributors to that trend were from USA (about 25%) followed by China (Figure 2.5a). Since 2009, no data are available in the World Bank study about the total number of Australian railway lines. However between the selected countries illustrated in Figure 2.5b, Australia had the least rail length.
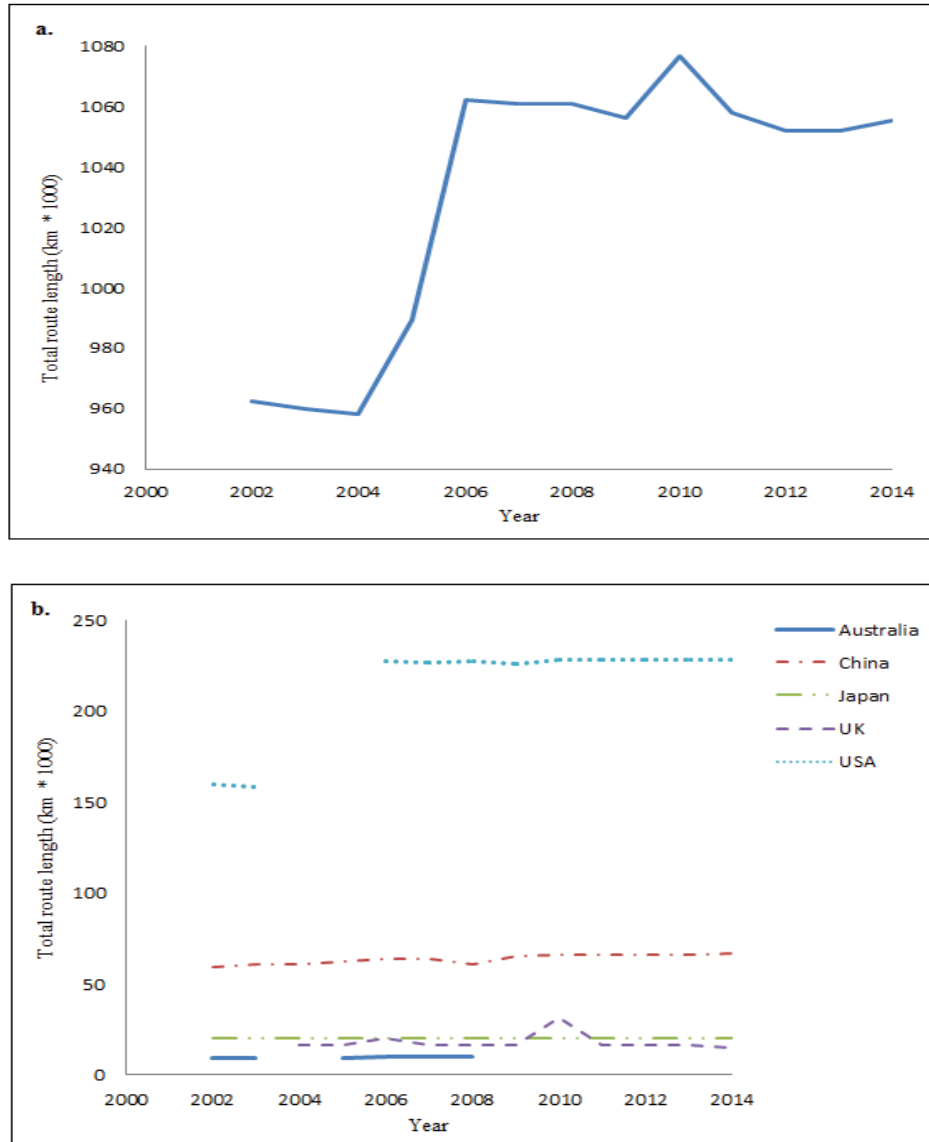
Figure 2.5 Rail Lines Expansion over a fourteen year period given by total route length (km) (a) global trend, (b) in five selected developed and developing countries (World Bank, 2016).

PM in the railway environment is unique in terms of its physiochemical characteristics, sources and concentrations. Even the same railway network has different potential pollution levels depending on their surrounding microenvironment conditions. Duan (1982) in his study defined the microenvironment as "a location with a chunk of air with homogeneous pollutant distribution". In the context of railways, the microenvironment may be part of the platforms, inside the train carriages or near the ticket offices.

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Consequently, the level of pollution from this mode of transport can significantly differ from one system to another. Regression modelling is usually used to identify the key factors affecting PM levels in the railway microenvironments. Variation in PM levels in the railway systems has been mainly associated with the railway infrastructure conditions, system age, ventilation system applied, engine type, meteorological and climatic conditions, and the type of power used (diesel, electricity) (Abbasi et al., 2013; Nieuwenhuijsen et al., 2007; Salma et al., 2009). Some studies show that the exposure levels of PM in the railway system far exceeds PM levels in the ambient background air, and even exceeds the acceptable regulations and standards limits (Guo et al., 2014; Jung et al., 2012). Other studies show different results and report that the railway microenvironments are relatively clean in comparison with the urban background air and other transport modes (Kam et al., 2011a). Therefore, to assess specific railway systems in terms of air pollutants and more precisely PM, data should be obtained directly from the field to adequately evaluate it.

2.5.1 Physiochemical properties of the railway-derived particles

Railway particles have different physiochemical properties and morphology characteristics to ambient particles, these differences have helped researchers to distinguish the main factors and sources contributing to PM formation (Salma et al.. 2009; Stachowiak et al., 2008). Most importantly beside the total PM concentration, the results of epidemiological and toxic studies usually rely on the particles' physical and chemical analysis to estimate the particles risks. According to recent studies in railway microenvironments using scanning electron microscopy to analyse the particles' physical characteristics, PM_{10} is considered to be the dominant particle size with its flaky, jagged edged appearance, while $PM_{2.5}$ has more spherical granular layered shape (Abbasi et al., 2012; Loxham et al., 2013; Salma et al., 2009; Stachowiak et al., 2008).

The chemical composition of PM is a vital factor to consider when estimating health impacts. In general, PM can be formed in a complex mixture of diverse chemical compounds depending on their original sources. US EPA has classified PM according to its chemistry into acids e.g. nitrates and sulphates, organic compounds e.g. PAH, crustal material and metals, soil or dust (US EPA, 2004). In railway systems, it has been well documented that the predominant pollutants of concern in railway particles are metals with the potential to cause carcinogenic risks. These are mainly Fe with lower concentrations of Si, Mn, Ni, Cd and Cu (Chan et al., 2002a; Kam et al., 2011; Kim et al., 2008; Perrino et al., 2015). Heavy metals can be transported for long distances from their source as absorbed substances in PM via air and these pose serious health risks (Shah and Shaheen, 2008). A study conducted on the Switzerland railway system found Fe, Al and Ca contributions to the railway related PM_{10} are 67%, 23% and 10% respectively (Lorenzo et al., 2006). Another study from the Helsinki subway system found elevated concentrations of Fe, Cu, Mn and Ni with much higher measurements at underground levels than the ground levels (Aarnio et al., 2005). According to several epidemiological studies, PM with high concentrations of heavy metals has the ability to induce the formation of reactive oxygen species (ROS) (Cavallo et al., 2008; Jung et al. 2012; Karlsson et al., 2005). ROS cause damage to DNA when an inflammatory response occurs in living cells due to increased oxidative stress (Akhtar et al., 2014). A study conducted by Karlsson et al. (2005) has reported that PM from underground railways can cause four times the oxidative stress than PM found in a very busy urban street; consequently the DNA damage can be increased by up to eight times. To be able to assess the risks imposed by PMs from any source, it is important to assess the chemical compounds of the particles, as well as their total concentrations. In the case of railway studies (electrical systems), special attention should be given to assessing heavy metal concentrations in the particle

samples along with their health hazards. Many studies have proposed health risk assessments to estimate the potential threats from exposure to PM especially particles with high concentrations of heavy metals (Lee et al., 2006; Lin et al., 2015; Liu et al., 2015). Most of the studies have divided the risk assessment into carcinogenic and non-carcinogenic effects. For the carcinogenic effect, the predicted levels should be compared with the thresholds suggested by the Integrated Risk Information System (IRIS) (US EPA, 2016a). However, this approach has been limited by the availability of information approved by IRIS. The non-carcinogenic effect usually utilises the Target Hazard Quotient (THQ) method, the results from this method indicate the risk level associated with a specific pollutant exposure level (Zheng et al., 2010). Therefore, to estimate the health risks due to metals exposure associated with PM in Sydney railway samples, a detailed risk assessment chapter will be provided in Chapter Five.

2.5.2 Particulate matter sources from railway networks

Before the introduction of electric trains, exhaust emissions were the major source of particulate matter from the railway networks due to combustion processes. Thereafter, electric trains made great progress in reducing significant amounts of railway particles. Beside internal sources (non-exhaust particles), outside atmosphere and surrounding operation conditions significantly contribute to the total amounts of PM in railway environments. Underground spaces are vulnerable areas of air pollution not only in the railway systems, but also inside bus and cars tunnels. Many studies reported poor air quality in terms of PM inside the underground environments (Cheng and Yan, 2011; Murruni et al., 2009; Nieuwenhuijsen et al., 2007; Perrino et al., 2015). To be able to control and mitigate them, the main sources of railway particles should be defined and regulated. Wear abrasion is a substantial source of PM that can occur due to trains' wheel movement on tracks and/or the wear on electrical cables due to friction processes. Brake

- wheels abrasion is another important source of railway wear PM which has been recognized in many studies by the existence of inhomogeneous distribution trace elements in the railway particles (Abbasi et al., 2011; Moreno et al., 2015; Olofsson, 2011). A study in a New York City subway has reported that subway transit workers have considerably higher exposure levels to steel wear dust than public commuters (Chillrud et al., 2005). Another study performed in Switzerland concluded that railway track abrasion and traction lines were the main PM sources in railway systems, and that PM concentration decreased by 25% when moving away from the tracks by a distance of 120 m (Gehrig et al., 2007). The latter study has emphasised the need to perform further studies on the Switzerland subway system. Based on the material losses rates from the brakes systems, rails, wheels friction and the overhead lines; PM generated from 7200 km of railway tracks in Switzerland contributed to the amounts of 1912, 550, 124, and 38 tonnes of the total ambient PM, respectively (Burkhardt et al., 2008). The problem of abrasion particles is not only from increasing the total concentration, but most importantly the chemical components of these particles. Subway commuters may be exposed to less PM concentrations than other commuting modes, but the chemical substances such as Fe from the wear and abrasion processes might be more toxic (Bukowiecki et al., 2007; Chillrud et al., 2005). Another source to consider in railway particles is the vaporisation of metal from sparking. The effect of this factor has been mentioned in many studies, however, there has been no specific study done in this field (Abbasi et al., 2013).

Ventilation design in underground railway systems is another factor when considering PM sources. Concentrations and characteristics of PM inside the train carriages and the subway platforms are prominently dependent on the tunnel ventilation system (natural or mechanical), the number of air inlet locations, and the train carriages air-conditioning systems (Moreno et al., 2014; Murruni et al., 2009; Park and Ha, 2008). Some ventilation

systems are more efficient at removing PM than others, which makes for substantial variation in the total concentration of PM inside and outside the train carriages. According to the results performed by Moreno et al. (2014) in the Barcelona subway system, average concentration of PM_{10} for ten platforms had risen from 159 - 178 $\mu g/m^3$ at the same underground line after switching off the tunnel ventilation system. A study conducted in the Seoul subway concluded that the concentration of PM inside the trains was much higher than on the platforms. The reason behind this was because the train carriages had no mechanical ventilation systems (AC system), which could supply fresh air inside the train (Park and Ha, 2008). Another study showed elevated levels of PM concentration inside the subway trains and the platforms due to the use of a passive (natural) ventilation system where the air inlets located at street level were subjected to heavy traffic (Murruni et al., 2009). National and international regulations prompted transport authorities and manufacturers to bring new solutions to reduce road pollutants. However, railway regulations are still behind due to the scarce number of studies done in this field. To improve the railway air quality and to reduce the contribution to the total ambient PM, there is an immense need to regulate this mode of transport so that train authorities will retrofit their applications. Another strategy suggested by Abbasi et al. (2013) to lower non-exhaust particles was to impose national non-exhaust emission tax on railway operators.

2.5.3 Methods for reducing and mitigating particle emissions

The principal approach to reduce railway particles is to control the sources of both exhaust and non-exhaust particles. Like other transport modes, lots of effort has recently been concentrated on different applications to reduce exhaust emissions. Methods such as diesel oxidation catalysts (DOC), continuous regenerative traps (CRT), crank case emission controls (CCEC), engine's fuel composition have been applied as a promising

techniques to reduce diesel engine emissions. According to Tsang et al. (2010), the application of DOC combined with a specific engine's fuel composition has led to a 30% reduction in the PM concentration depending on the engine load. Other studies have indicated that the combination of the DOC technique with CRT was able to remove up to 90% of the total PM (Liu et al., 2012; Shah et al., 2007). Optimisation by using biodiesel fuelled engines has also been considered as one of the most effective solutions to reduce exhaust diesel emissions by reducing total PM concentrations by 30% in comparison to fossil fuel (Leung et al., 2006). Similar results were reported by Demirbas (2007) with some drawbacks in terms of increasing other sorts of air pollutants.

On the other hand, non-exhaust railway emission sources (mainly from wear processes) have received less attention since no regulations have been issued in this field yet. Many subway studies have shown elevated concentrations of PM inside the train carriages and stations despite all the networks having been powered by electricity (Aarnio et al., 2005; Kam et al., 2011a; Park and Ha, 2008). Methods to reduce wear particles and the installation of efficient ventilation systems are the most desirable ways to reduce PM in railway enclosed microenvironments. Depending on the ventilation system used, the effect of the wear particles may differ substantially as some systems are more efficient in removing different particles sizes. This statement can be also be confirmed by reviewing the results from a Paris subway study done by Tokarek and Bernis (2006) in a subway line with only limited number of mechanical ventilators between stations leading to a very high PM concentration. Results indicated that PM concentration was halved from 230 to 135 μg/m^3 by installing 20 filters (electrostatic precipitator). Besides improving the ventilation systems, rolling stock, and the use of friction modifiers to decrease wear particles, different methods have been applied concurrently to achieve optimum reduction rates. Methods include, but are not limited to, platform screen doors (PSDs) which can

reduce PM on the platforms significantly by obstructing air diffusion (Lee et al., 2010; Son et al., 2013); magnetic filters installation on the top of the ventilation openings (Son et al., 2014); and regular washing to slightly inhibit particle re-suspension from the settled PM on the platforms (Johansson and Johansson, 2003). The Sydney trains authority has implemented a set of applications to reduce all sorts of air pollutants in order to comply with the required levels of the regulations. The majority of their trains utilise a regenerative braking system where the traction engines act as electricity power generators when braking. Sydney trains also utilises an efficient ventilation system and the majority of their train carriages run with heating, ventilation and air conditioning (HVAC) systems (Sydney Trains, 2016). However, neither PDSs nor magnetic filters applications are used in the network despite the fact that these can offer efficient solutions to reduce potentially elevated PM concentrations.

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Chapter 3. Particulate Matter Concentrations in the Underground and Ground Levels of the Sydney Railway System

3.1 Introduction

PM is one of the six air pollutants that have been regulated worldwide. Short term and long term exposure to elevated levels of PM is associated with the development of respiratory and cardiovascular disease as well as carcinogenic problems (WHO, 2013). An estimate from the World Health Organisation (WHO) showed that about 800,000 premature deaths per year were caused by short term and long term exposure to $PM_{2.5}$ (WHO, 2002). Epidemiological and toxicity studies have shown that exposure to elevated concentrations of PM can cause serious respiratory problems (Epton et al., 2008; Kim et al., 2015; Liu et al., 2014); cardiovascular problems (Brook et al., 2010; Farraj et al., 2015; Lopez et al., 2006); and increased carcinogenic risks (Gray et al., 2015; Hamra et al., 2014; Lopez et al., 2006). As a result of ever-growing traffic volumes along with the associated health effects, people in megacities and urban areas are more exposed to elevated levels of airborne particles. $PM_{2.5}$ and PM_{10} are globally regulated by different regulatory authorities using the metric unit of mass concentrations in the air ($\mu g/m^3$) with different monitoring methods e.g. tapered element oscillating microbalance (TEOM), manual gravimetric analysis, and light scattering devices.

Sydney as the capital city of NSW with a large population of more than 5 million people has different transport modes to cope with the need of its residents. Due to its geographical nature covering a wide urban area, the major transport mode used in Sydney is the private car followed by buses and trains (Bureau of Transport Statistics, 2015). There have been limited numbers of studies in the field of PM and Sydney transport with a major emphasis on private cars, buses and tunnels (Knibbs et al., 2009; Knibbs and

Morawska, 2011). To our knowledge there has been no detailed study to evaluate Sydney railway microenvironments in terms of PM concentrations. Currently, the patronage of Sydney train is about 328 million customer journeys annually; this number is expected to increase in future to meet the expansion demands of the population in Sydney (Bureau of Transport Statistics, 2015). Therefore, with such a significant number of journeys, it is important to evaluate the particle concentrations in Sydney railways.

There have been many studies to evaluate PM concentrations in the railway and subway networks, most of them have shown elevated levels of PM in the underground when compared with ambient measurements and street levels. For example, personal exposure levels of $PM_{2.5}$ for the commuters of London underground rail were up to 8 times higher than three different ground level commuting modes (bicycle, bus, car) (Adams et al., 2001). Another study from Paris showed that PM_{10} and $PM_{2.5}$ concentrations in the central railway station were 5–30 times higher than those measured on streets (Raut et al., 2009). Furthermore, a study from Los Angeles metro system showed that the average concentrations of PM_{10} and $PM_{2.5}$ were about 2 times higher in the underground platforms and the train carriages in comparison to the ground level light rail stations and carriages (Kam et al., 2011). Previous railway studies reported different results in terms of PM concentrations which were justified by major factors that can significantly affect the air quality measurements such as the age of the metro network, the braking system used, the ventilation system and the availability of an air conditioning system, the frequency of the trains' passage, in addition to other operating factors (Aarnio et al., 2005; Abbasi et al., 2011; Moreno et al., 2014; Namgung et al., 2016).

PM concentrations can be measured using different monitoring methods. TEOM is a recommended method to measure PM concentrations; however, it cannot be utilised because of the large area needed for setting up this kind of equipment. Furthermore, the

TEOM sampler needs an external power supply to run it which is not feasible when sampling from inside the train carriages. The second method is the gravimetric filter analysis which also offers very accurate results, but the major drawback of this method is the extensive time interval required. Therefore, a portable light scattering instrument from TSI has been chosen for sampling purposes. The instrument runs by a rechargeable battery making it ideal method to use in different railway environments.

In this chapter, PM concentrations in the Sydney railway system were assessed based on: (1) PM_{10} and $PM_{2.5}$ measurements at both underground and ground platforms, (2) PM_{10} and $PM_{2.5}$ concentrations from inside the train carriages running at both underground and ground levels, (3) a comparison between the railway environments and the ambient measurements, (4) a comparison of PM levels from the Sydney railway system and worldwide railway networks.

3.2 Experimental Methodology

3.2.1 Sampling sites

Stations along the Airport Line T2 were sampled, which links the western suburbs to the Sydney CBD, passing through Sydney Airport including international and domestic terminals (Figure 3.1). About 21 km in length was included in the data collection of PM_{10} and $PM_{2.5}$ running from Revesby Station to Central Station during a 7-week sampling period during September-November 2015. Particles were measured from inside the train carriages and the platforms at ground and underground levels, at the same time the corresponding particles from the nearest fixed air quality monitoring stations were recorded. Further investigations were carried out during a second sampling period (February-March 2016) to better understand the effect of the different platforms levels on the particles concentrations. Town Hall Station was sampled at three different operating levels. Details of the sampled stations are shown in Table 3.1.

The T2 line was chosen due to its diverse operating levels (ground and underground levels). Part of the chosen line operates at the ground level, stopping at four stations connecting Revesby to Wolli Creek Station with a total length of 13.7 km. The other part runs inside the underground tunnel connecting Wolli Creek to Central Station with a total length of 7.3 km. This line was also chosen for sampling due to its high annual number of journeys growth rate of 15.6% and its high annual patronage number of 20.5 million commuters (Bureau of Transport Statistics, 2014). Measurements from Central Station represent the ground level platform data, while the underground measurements were collected from Green Square Station. The distance between these two stations is less than 2.5 km, so it was assumed that there was no significant difference in the ambient sources. Central Station is one of the oldest stations in Sydney opened in 1906, and located at the southern end of the Sydney CBD. It has 25 platforms (15 terminating and 10 through), and all the trains pass through this station are electric commuter trains. According to the Train Statistics 2014 report, Central Station is the busiest station in terms of the number of entries and exits in comparison to 40 other Sydney Train stations; it had the highest number of issued tickets (5.4 million) during 2013 (Bureau of Transport Statistics, 2014). Almost all the intercity train lines pass through Central Station, in addition to some interstate rail services. To compare the particles measurement with the urban background data, two fixed air quality stations located near the T2 line and platforms were chosen to collect data. These stations are operated by the NSW Office of Environment and Heritage (NSW OEH) and the data from them can be accessed through their website, which is usually updated hourly.

The first air quality monitoring station was Rozelle station located at 4.6 km and 5.6 km from Central and Green Square Stations, respectively. The second air quality station considered was Earlwood Station at Beaman Park located at 1-9 km from the sampled

train line (T2). Both stations provided measurements for PM_{10} and $PM_{2.5}$ concentrations which were obtained correspondingly to the sampling date and time (typically at any time from 9 am to 5 pm) via the NSW OEH website.
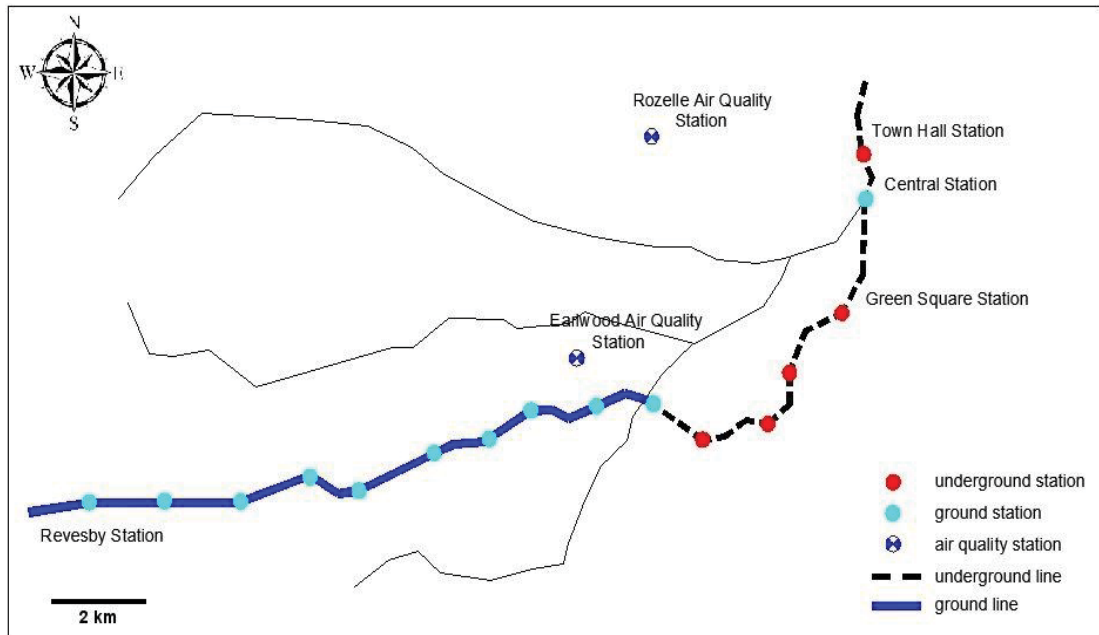
Figure 3.1 Map indicating the sampled line (T2), underground and ground level platforms, and nearby ambient air quality monitoring stations monitored by NSW OEH. The bold section represents the corresponding study area.

Table 3.1 Details of all stations sampled during first and second data collection periods.

Station Name	Structure Type	Number of Platforms	Distance to Central Station (km)
Central	Ground, elevated and Underground	25	0
Green Square	Underground	2	2.50
Town Hall concourse	underground	None	1.18
Town Hall 1	Underground	3	1.18
Town Hall 2	underground (lowest level)	3	1.18

3.2.2 Monitoring instruments and sampling campaigns

A portable light scattering photometer called Dust Track (model 8532) purchased from TSI Inc. (Figure 3.2). USA was used. The photometer runs on a rechargeable lithium ion battery, eliminating the need for an external power supply. Different impaction inlets can be attached to the model, which can measure aerosol size fractions ranging from PM_1 to PM_{10} with a concentration range from 0.001 to 150 $\mu g/m^3$.

PM_{10} and $PM_{2.5}$ inlets were used to continuously measure concentrations of these two size fractions at a logging interval of 2 min. The instrument flow rate was set to 3 L/min by the manufacturer and was calibrated regularly with an external flow meter during the sampling campaign (as recommended by the manufacturer). A clean filter was used every day at the beginning of each sampling day to ensure a zero calibration for the model. The inlet impactors were periodically removed and cleaned, and the impactor plates were re-greased every other day using the oil provided from the manufacturer. In the case of sampling from inside the train, the user calibration was set to the factory calibration setting which is appropriate for most aerosol monitoring microenvironments. When sampling was done on the platforms, an ambient calibration setting was applied.

Figure 3.2 DustTrak II Handheld Aerosol Monitor (8532), a real-time aerosol mass readings device from TSI used for PM_{10} and $PM_{2.5}$ concentration measurements.

The sampling campaign was carried out during September-November 2015 on different working days at any time from 9 am to 5 pm. The data collected from the campaign was divided into four sets of data: (i) PM_{10} inside the train, (ii) PM_{10} on the platforms, (iii) $PM_{2.5}$ inside the train, and (iv) $PM_{2.5}$ on the platforms. Each set of data was subdivided into two groups depending on the measuring level (ground level vs underground level). The device tracked at the breathing level of commuters in compliance with recommendations and practices reported in other studies (Gulliver and Briggs, 2004; Ma et al., 2012; Moore and Figureliozzi, 2011).

To further investigate the effect of the operating levels (ground and underground), a sampling campaign was conducted from 22nd February to 4th March 2016 at the Town Hall Station platforms and the concourse level for 30 min from each level to measure PM_{10} (Table 3.1). The sampling started from the highest underground level (Town Hall concourse) moving down to the first underground level (Town Hall 1) and then to the lowest underground level (Town Hall 2).

Data from two fixed monitoring stations provided by the NSW Office of Environment and Heritage (NSW OEH) to represent the ambient PM concentrations from ambient sources were used. Average data from the two fixed air quality stations (Earlwood and Rozelle) were recorded concurrently as the data collection from 9 am to 5 pm, to compare them with the corresponding railway microenvironment data. These data were usually updated hourly for both PM_{10} and $PM_{2.5}$, and were recorded and stored at the end of each sampling day.

3.2.3 Quality assurance

Comparability studies results between the light scattering measurements method and other methods usually used in the air quality fixed monitoring stations have shown some differences. Therefore, a correction factor was usually determined to obtain the accurate measurements from the scattering methods (Cheng, 2008; Kam et al., 2011; Yanosky et al., 2002). To assess the level of accuracy for the collected data from Sydney railway environments, the dust track was taken to one of the fixed air quality stations (Liverpool Station) usually run by TEOM. The aim was to check and compare the data from both sources collected at the same time. The tests were performed in October 2015, during the first sampling campaign for 5 h (10 am to 3 pm). Regression analysis performed by SPSS showed that the TEOM measurements were within 2% of the dust truck measurements with a regression coefficient R^2 of 0.866 (Figure 3.3). Based on these results, the dust track data was directly used without applying a correction factor. In addition, as mentioned previously calibration and continuous cleaning processes were undertaken in compliance with the manufacturer recommendations to ensure the best measurement accuracy.
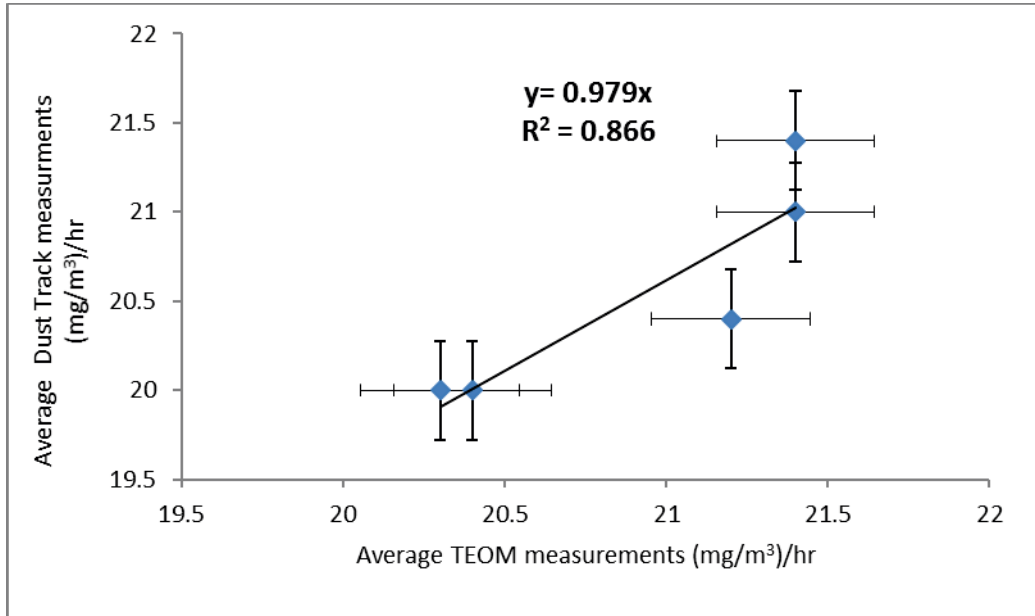
Figure 3.3 Average hourly real time measurements from TEOM and Dust Track performed at Liverpool air quality station.

3.2.4 Data analysis

Mean concentration values of PM were classified under eight different groups based on the railway microenvironments along with two set of values from the fixed monitoring stations to represent the ambient measurements. Differences in PM sources between ground level, underground levels and the urban ambient were determined by correlation analysis performed with SPSS (version 22). Comparison between average PM concentrations and worldwide railway systems was performed based on the ratio between railway and ambient measurements.

3.3 Results and Discussion

3.3.1 Ground and underground level concentrations of PM_{10} and $PM_{2.5}$

Data obtained over seven weeks of sampling are summarised in Table 3.2 representing mean concentration values of PM_{10} and $PM_{2.5}$ from the railway microenvironments. The mean concentration values measured by the TEOM method from two fixed air quality

stations represent the ambient background PM levels. In general, both size fractions were elevated at the railway underground microenvironments in comparison to the ground level results. Measurements of PM_{10} and $PM_{2.5}$ from inside the train carriages showed that the average concentrations at the underground level were higher than the ground level particles by approximately 2.8 and 2.5 times, respectively. Similarly, PM_{10} and $PM_{2.5}$ concentrations on the platforms were 2.7 and 2.5 times higher at the underground level. These findings are consistent with previous studies carried out in different railway and metro networks in the world, showing that underground metro systems are the most polluted environments in terms of PM (Aarnio et al., 2005; Cheng and Yan, 2011; Kam et al., 2011; Perrino et al., 2015; Ye et al., 2010). Underground tunnels are fully enclosed environments with a complete reliance on ventilation systems; hence the surrounding air quality is likely to be dominated by the internal environment.

Table 3.2 PM_{10} and $PM_{2.5}$ concentrations from inside the train and the platforms both at ground and underground levels using DustTrak (model 8532), and urban ambient concentrations measured by the TEOM method.

		Particle Concentrations ($\mu g/m^3$)	
		Ground Level	Underground Level
Train	PM_{10}	18.2 ± 18 (n=125)	50 ± 48 (n=93)
	$PM_{2.5}$	15.4 ± 13 (n=133)	38.1 ± 23.7 (n=93)
Platforms	PM_{10}	20.1 ± 10.4 (n=93)	54.9 ± 20.7 (n=91)
	$PM_{2.5}$	16.7 ± 6.5 (n=93)	40.6 ± 12.0 (n=104)
Urban ambient station	PM_{10}	19.4 ± 6.3	
	$PM_{2.5}$	7.5 ± 2.9	

The elevated concentrations of PM at underground levels have been mainly attributed to non-exhaust particles from local railway sources such as wheel track, brakes, overhead power lines wear and abrasion (Moreno et al., 2015; Namgung et al., 2016; Olofsson, 2011; Querol et al., 2012). To investigate the effect of these sources in the Sydney underground system, results from the second sampling period showed that PM_{10} concentrations in Town Hall Station were noticeably different depending on the measurement level. Figure 3.4 shows that on the lowest platform level with a complete reliance on the mechanical ventilation system of the station, PM_{10} concentrations could reach double the concentrations observed from the concourse level which has a mixed method of ventilation (natural and mechanical). Correlation analysis between three levels of measurements (n = 10) revealed a weak correlation between Town Hall concourse measurements, where no trains are passing, and the two lower level platforms (Town Hall 1 and Town Hall 2) with a correlation factors of 0.39 and 0.37, respectively. At the same time, Town Hall 1 and Town Hall 2 measurements were strongly correlated with each other with a factor of 0.84. Despite the difference between PM_{10} concentrations between the two underground platforms, their strong correlations indicated that they share the same sources of PM which can be mainly attributed to the train operation activities.
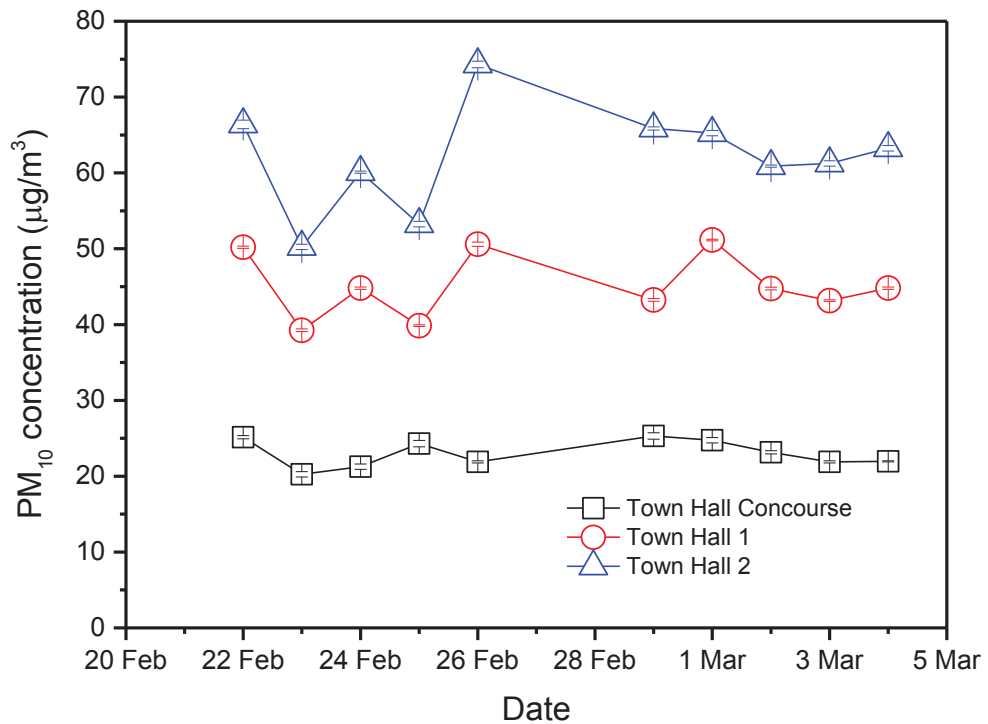
Figure 3.4 PM$_{10}$ measurements using dust truck (model 8532) from three different levels at Town Hall Station, Sydney. Error bars represent the standard deviation based on two measurements of each sample.

Another important observation to consider is the ratio between PM$_{2.5}$ and PM$_{10}$ to assess the fine particles proportion, the results can help future epidemiological studies to estimate the potential health risks associated with exposure to PM. Results showed very slight differences in PM$_{2.5}$/PM$_{10}$ ratio between the platforms and the train carriages. Commuters are exposed to relatively higher levels of PM$_{2.5}$ than PM$_{10}$ when travelling inside the train at both ground and underground levels. At underground levels, PM$_{2.5}$/PM$_{10}$ inside the train was approximately 0.76, while on the platforms it was 0.73. For the ground level, PM$_{2.5}$/PM$_{10}$ ratios from inside the train and from the platforms measurements were 0.85 and 0.81, respectively. The same result was reported by the Los

Angeles Metro study, showing that commuters were exposed to lower levels of fine particles while waiting on the metro platforms by a factor of 6% (Kam et al., 2011). Such studies suggested that lower coarse fraction inside the trains was possibly the result of the air-conditioning systems, which could eliminate more coarse particles from the air than fine fractions (Chan et al., 2002; Kam et al., 2011; Martins et al., 2015).

Higher standard deviation values were observed for PM measurements inside train carriages at both ground and underground levels. This is likely due to the fact that PM concentrations can be significantly affected by the air coming from the platforms when stopping at a station with the doors opening to allow commuters movement. As a result, PM measurements inside the train carriages will be significantly affected by the platforms' air quality and air flow directions.

3.3.2 Comparison between PM concentration from Sydney railway microenvironments and ambient air

Correlation analysis was performed to investigate the influence of PM_{10} and $PM_{2.5}$ in the railway microenvironments by the surrounding sources. The level of impact from ambient sources can be very different depending on the surrounding conditions. A study undertaken in the Prague underground railway system showed a strong association between ambient PM and particles from the underground microenvironments despite the statistically significant differences between the two measurements ($P < 0.001$) (Braniš, 2006). Another study from Taipei Rapid Transit network showed that correlation analysis for both PM_{10} and $PM_{2.5}$ was highly influenced by ambient PM with correlation factors of 0.72 and 0.78, respectively (Cheng et al., 2008). On the other hand, regression analysis for the Los Angeles Metro suggested PM from the subway line (underground) was considerably less influenced by ambient conditions, but strongly correlated with ground level concentrations (Kam et al., 2011). Comparable results from a recent study on the

Barcelona subway system indicated higher concentrations of PM from the underground tunnel by up to 6.7 times compared to outdoor environments with a weak association between the two sources (Martins et al., 2015). At underground levels, particles from ambient sources may penetrate inside the enclosed trains' tunnels and the platforms through air corridors and ventilation openings adding more PM to the local railway sources.

Figure 3.5a-h illustrates the correlation analysis and r^2 values between different railway microenvironments and ambient measurements. PM_{10} and $PM_{2.5}$ data from the platforms were assessed against the data from Rozelle air quality station, whereas data from inside the train carriages running at both ground and underground levels were assessed against concentrations from Earlwood air quality satiation. Australian PM Standards were also shown in Figure 3.5 for both $PM_{2.5}$ (25 µg/m^3) and PM_{10} (50 µg/m^3) to assess the allowable exceeding rates (NEPC, 2015). Each data point represented the average of 1-3 h of sampling, with corresponding ambient measurements.

The results showed a strong positive association between PM_{10}, $PM_{2.5}$ from the ground level platforms and ambient data with r^2 values of 0.843 and 0.952, respectively (Figure 3.5a-b). PM from both levels was well under the allowable national standards. For underground platforms measurements, a weak correlation was observed with r^2 values of 0.072 for PM_{10} and 0.210 for $PM_{2.5}$ (Figure 3.5c-d). PM_{10} and $PM_{2.5}$ at underground levels exceeded the national air quality standards during almost all sampling days. These results indicated that the ground level particles on the platforms were significantly influenced by the ambient sources, while underground PM levels could also be affected by urban sources but to a lesser extent. Results from inside the train measurements showed similar results in terms of association with ambient particles sources (Figure 3.5e-h). At ground levels, r^2 values were 0.50 for PM_{10} and 0.823 for $PM_{2.5}$, indicating a moderate to strong

positive correlation. Unlike the underground measurements which showed weak correlation for PM_{10} ($r^2 = 0.123$) and $PM_{2.5}$ ($r^2 = 0.264$).

Higher concentrations of PM from underground microenvironments along with the moderate to weak correlations coefficients confirmed the presence of additional local railway PM sources. Particles generated from the railway environment accumulated inside the trains and on the platforms over time due to its enclosed conditions leading to elevated levels of PM. To further confirm this, two paired sampled t-tests were carried out to compare the ground and underground levels of $PM_{2.5}$ from inside the train and the PM_{10} from the platforms. The results showed that at a 95% confidence interval, both $PM_{2.5}$ and PM_{10} at the underground level were significantly different from those at the ground level ($P < 0.005$).

Adverse health effects associated with exposure to PM are well documented based on their concentrations and the chemical composition (Anderson et al., 2012; Gray et al., 2015; Liu et al., 2014; Valavanidis et al., 2008). To estimate the potential health risks associated with exposure to elevated concentrations of PM, 24-h monitoring measurements should be presented to comply with the global air quality standards which are normally stated in terms of daily or annual mean concentrations per cubic metre. Underground measurements were above the allowable Australian Standards. However, the potential health risks from these measurements should be further assessed based on continuous daily measurement, in addition to rush hour data.

Table 3.3 Comparison of PM_{10} and $PM_{2.5}$ concentrations ($\mu g/m^3$) measured from Sydney

railway microenvironments and worldwide subway systems.

Location	Measurement environment	PM_{10}		$PM_{2.5}$		Reference
		Mean	S D	Mean	S D	
Naples,	in train/ground level	37	7	13	3	Carteni et al. (2015)
Italy	in train/underground level	87.1	29	29	9	
Italy	on platform/ground level	16	9	10	4	
	on platform/underground level	195	42	52.3	8	
Prague, Czech	on platform/underground level	214.8	50	93.9	24	Cusack et al. (2015)
Rome,	in train/underground level	158	14	-	-	Perrino et al. (2015)
Italy	on platform/underground level	59	6	-	-	
Los Angeles, USA	in train/ground level	16	7	14	5	Kam et al. (2011)
	in train/underground level	31	11	24	7	
	on platform/ground level	38	4	29	11	
	on platform/underground level	78	17	57	11	
Taipei, Taiwan	in train/underground level	42.7	12	32.7	8	Cheng and Yan (2011)
	on platform/ground level	44	33	33	23	
	on platform/underground level	50	28	35	18	
Seoul, Korea	in train/ground level	141.5	13	121.7	16	Park and Ha (2008)
	in train/underground level	145.3	13	116.6	13	
	on platform/ground level	123	7	115.6	9	
	on platform/underground level	129.3	21	105.4	14	
Beijing, China	in train/ground level	108	56	36.9	18.7	Li et al. (2007)
	in train/underground level	324.8	125.5	112.6	42.7	
Sydney, Australia	in train/ground level	18.2	18	15.4	13	Current study
	in train/underground level	50	49	38.1	23	
	on platform/ground level	20.1	10	16.7	7	
	on platform/underground level	54.9	21	40.6	12	
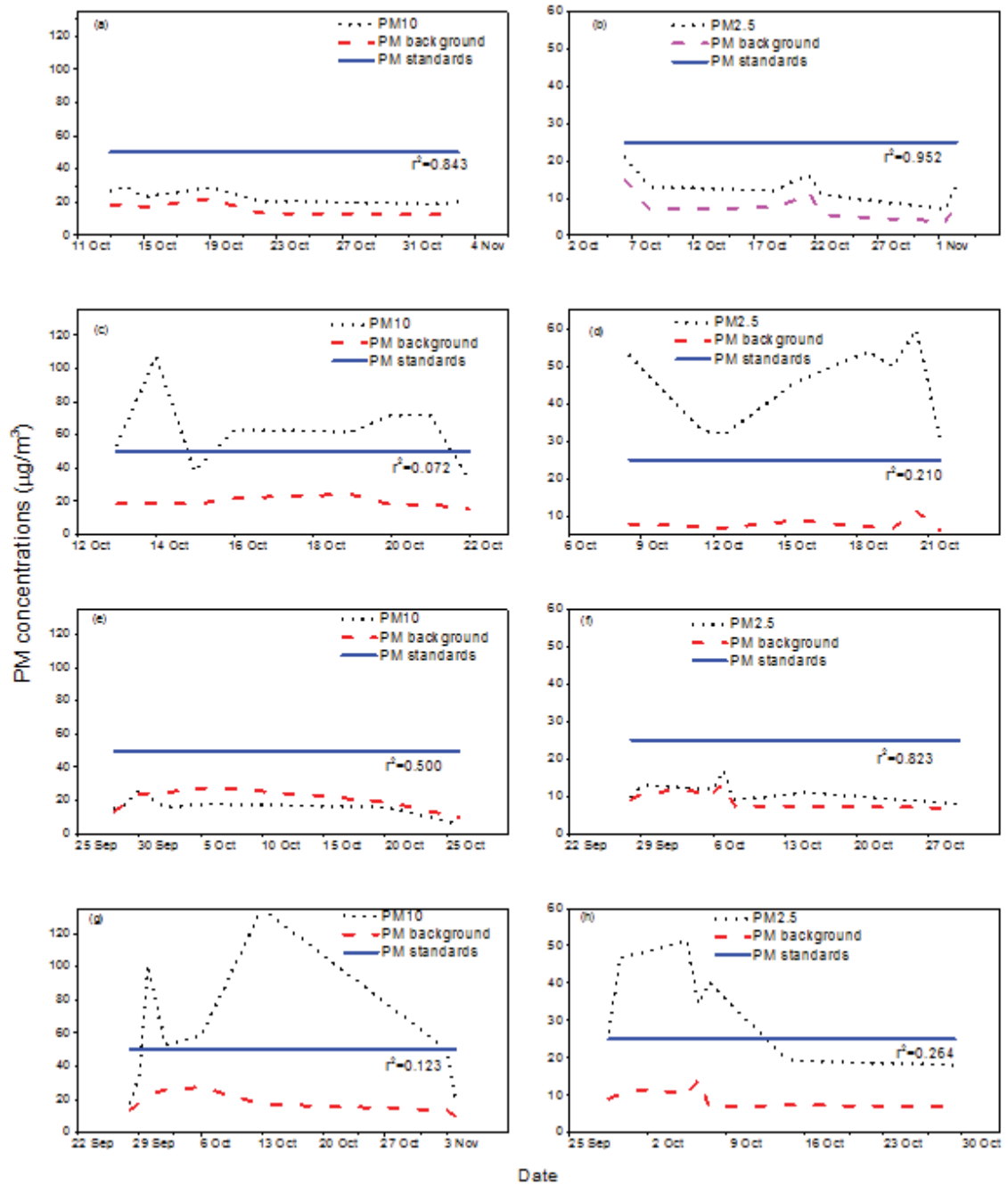
Figure 3.5 Sydney railway PM$_{10}$ and PM$_{2.5}$ concentrations and their corresponding ambient measurements (PM background) values from Sydney Park, along with the Australian PM Standard values (a-b) ground level platform measurements, (c-d) underground platforms measurements, (c-d) underground platforms measurements, (e-f) inside the train carriages running at ground levels, (g-h) inside the train carriages running at underground levels.

3.3.3 Comparison of PM from Sydney train with global railway systems

Since the first operation of electrical powered trains introduced in Sydney railway system, continuous improvements have been applied to ensure reliable and environmentally friendly practices for this transport mode. To assess the level of PM exposure in Sydney railway, the mean values of PM_{10} and $PM_{2.5}$ from Sydney and worldwide railway systems were summarised (Table 3.4). Some of these systems are relatively new systems which have only been operating for the last two decades; some of them are equipped with the latest clean operation technologies to ensure the lowest pollution levels. It is worth noting that all systems included in Table 3.4 were electrically powered systems and the main PM was assumed to be from non-exhaust sources. Current results show that PM_{10} and $PM_{2.5}$ at ground and underground levels are within, or less than, the range of other railway systems (Figure 3.6). Sydney railway PM levels were very close to the Los Angles system or may be better especially if considering that all data from the study were only collected during weekday rush hours. Ground and underground concentrations from inside the trains were better in the Los Angeles and Taipei systems suggesting that their air conditioning systems technology could be more efficient to remove the particles. However, PM concentrations from the platforms of the Sydney system were less than in other systems suggesting that the ventilation system design and technology could be more efficient in Sydney. The effect of the ventilation systems can be clearly noticed from the Seoul study by the exceptional elevated levels of PM in all microenvironments due to the lack of mechanical ventilation systems (Park and Ha, 2008). Wind velocity is another factor which might affect the outdoor particles levels. Studies found a strong negative correlation between wind velocity and PM concentrations (Braniš, 2009; Jones, 2010). The mean value of wind speed at the time of sampling as obtained from the Australian Bureau of Meteorology was relatively high (about 23 km/h in Sydney CBD and Sydney

Airport areas). With this magnitude of wind velocity suggesting better air dispersion and less PM concentrations.

The Sydney railway system has a relatively low level of PM pollution compared with other railway systems based on the ratio between the railway and the ambient background mean concentrations. Results show that the rate of PM_{10} and $PM_{2.5}$ between different railway microenvironments and urban ambient range between 0.9 and 5.4 in comparison to 0.52 and 2.8 for the Los Angeles railway system (Kam et al., 2011); 5-30 for the Paris underground railway station (Raut et al., 2009); and 4-14 for the Naples (Italy) Metro system (Cartenì et al., 2015). The notable differences can be mainly attributed to differences in the monitoring methods (e.g. dust track, TEOM), rail system age and condition, geographic level of measurements (e.g. tunnel depth), ventilation and brakes systems, surrounding meteorological conditions and other factors which might significantly affect PM concentrations. Studies have also shown remarkable improvements in the levels of PM after the installation of the platforms screen doors (PSDs) which act as a physical barrier to isolate the air quality on the platforms (Kim et al., 2012; Ma et al., 2012; Martins et al., 2015). For comparability purposes, no system with this technology was included in Table 3.3.
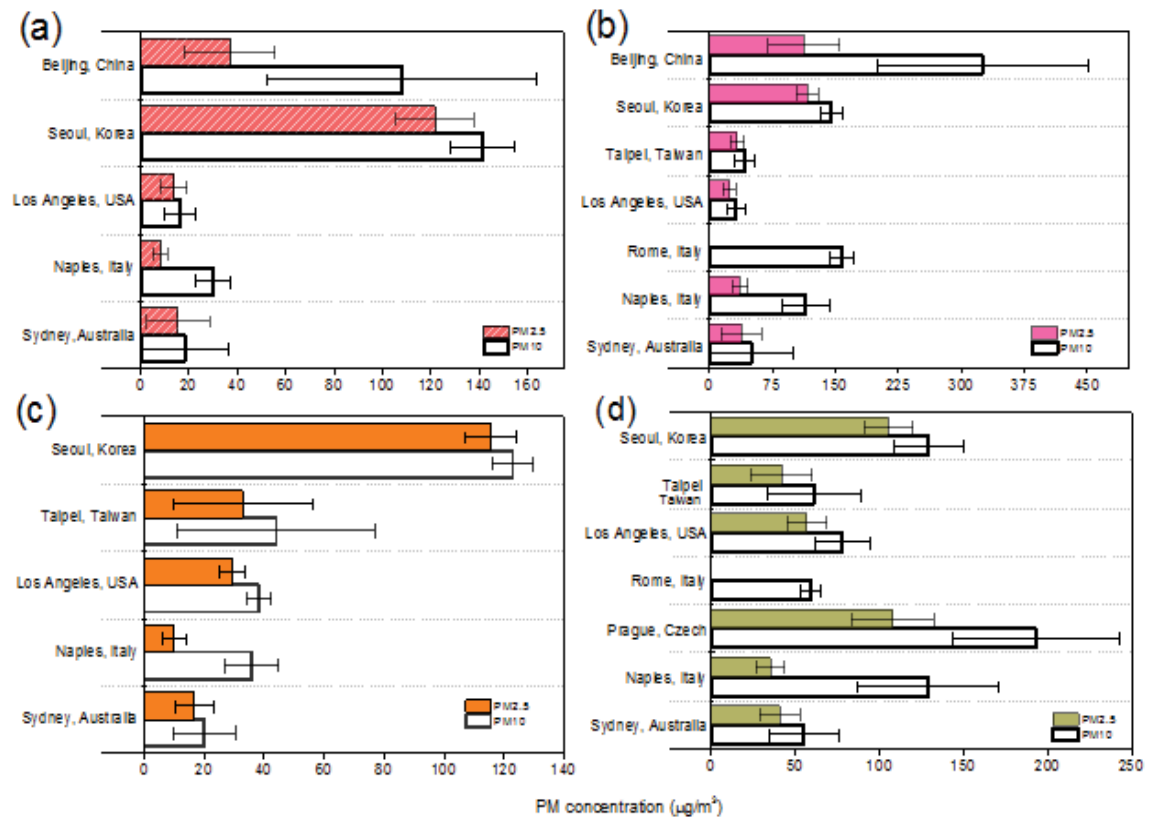
Figure 3.6 PM concentrations from Sydney and different railway systems (a) PM from inside the train at the ground level, (b) PM from inside the train at the underground level, (c) PM from the ground level platform, (d) PM from the underground level platform.

3.4 Summary

An intensive PM sampling campaign was conducted at ground and underground railway microenvironments in Sydney Trains, to assess the level of PM pollution and potential sources. Data were collected from inside the train carriages and from platforms from the busiest lines operated by Sydney Trains. Overall, commuters can be exposed to higher levels of PM when commuting at underground levels by a factor of 2.8 for PM_{10} and 2.5 for $PM_{2.5}$. Commuters were exposed to relatively higher levels of $PM_{2.5}$ than PM_{10} when riding inside the train carriages. Correlation analysis showed that ambient sources can strongly affect the railway PM at ground levels with r^2 of up to 0.952, unlike the weak effect on all underground PM ($r^2 < 0.264$). This finding is consistent with results from

other studies in signifying the role of local railway PM sources such as wear and abrasion operations at the underground environments. $PM_{2.5}/PM_{10}$ ratio was lower when measured from the platforms at both levels suggesting that the air conditioning system inside the train carriages was efficient in removing more PM_{10} than $PM_{2.5}$. In addition, air dispersion at the platforms can also help to reduce the levels of PM. All ground level PM concentrations were less than the national air quality standards, while underground PM levels exceeded the standards during almost all sampling days. Exceeding the national limits indicated the potential to cause different health problems. As all measurements represented mean PM concentrations collected during rush hours only, then unless 24 h monitoring data becomes available with details about their chemical composition, the potential health risks associated with exposure to PM cannot be fully considered. Finally, based on the mean concentration ratio between the railway and the ambient background measurements, the Sydney railway system is relatively clean in comparison with railway systems in other major cities.

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Chapter 4. Heavy Metal Analysis in PM samples from Sydney Railway

4.1 Heavy Metals in the Railway-Derived Particles

The amount of heavy metal emissions has increased considerably since the last century due to the industrial revolution. Beside the natural sources of heavy metals, their presence in urban environments is mainly due to anthropogenic sources such as traffic, and industrial and commercial enterprises. Exposures to airborne heavy metals are known to cause a wide range of adverse health issues for humans. Heavy metal pollutants are non-degradable, thus elevated concentrations of these pollutants may cause serious health problems and adversely impact the environment. Human can be exposed to heavy metals through inhalation and ingestion pathways which can cause moderate to serious health problems because of their bio-accumulation inside the human body (Kampa and Castanas, 2008). Determination of the sources of these substances is a very important issue in relation to epidemiological and toxicological studies.

Among different air pollutants from the electrified railway networks, heavy metals were found to be the most abundant substances in suspended air and dust samples (e.g. Fe, Ni, Mn, Pb, and Cu) (Kam et al., 2011a; Perrino et al., 2015). Therefore, this chapter will cover the heavy metal analysis taken from dust samples in Sydney railway microenvironments to assess the intensity of specific metal contamination.

4.2 Sampling Methodology

For heavy metals analysis, dust sample collection was undertaken over 14 consecutive days excluding the weekends from the 1st to 19th March 2016. A total number of 7 dust samples were collected (five samples from very busy platforms and two from Sydney Park to represent the urban dust samples). Three underground platforms were utilised to

collect the required amounts of dust, these were: Green Square (G.S), Mascot and Town Hall (T.H) stations. The first and the last stations were also utilised in the particles concentrations data collection which was analysed in the last chapter (G.S and T.H stations). Green Square station samples were collected from both sides of the platform (G.S$_1$ and G.S$_2$). Samples from Town Hall Station were also collected from two different levels to investigate the differences in the metal concentration based on the platform depth, where T.H$_1$ represents data from the lowest platform level.

For comparability purposes, urban ambient dust samples were collected from Sydney Park located at 2-4.5 km from the three sampled platforms (Figure 4.1). Samples from all the above-mentioned places represent urban environments based on their locations near Sydney CBD suburbs. However, different contamination levels can be noticed depending on the surrounding air pollutants metals sources.

Also, three pollution indices have been determined: pollution index (PI), integrated pollution index (IPI), and enrichment factor (EF). These indices have been extensively used in many studies to indicate the level of contamination by heavy metals from different sources and industries (Abrahim and Parker, 2008; Chen et al., 2007; Kamani et al., 2015; Saeedi et al., 2012). In addition to the method efficiency to indicate the pollution levels, this method was applied because it only needs two parameters to determine based on its equation which will be covered in section 4.7.1. The method eliminates the need for elements concentration references by analysing surrounding local dust from unaffected areas by anthropogenic activities along with measurements for the same element from the area of study.

Dust samples were collected using a new plastic brush and dustpan from an area of 2.5 × 2 m^2 at a distance of 40 cm away from the platform-train edge (Figure 4.2). A random

amount of about 300 g dust was collected each sampling time, stored in a new sealed plastic bag, properly labelled, and then sent to the UTS laboratory to undergo chemical analysis. Samples were collected from three different areas along the platforms to investigate all possible variation in the subway dust spatial distribution due to the train direction movement. The collected samples will then have analysed by the scanning electron microscope (SEM). SEM analysis uses a focused beam of high energy electrons to generate a variety of signals that could be used for different purposes. The signals can be used to examine the particles external morphology and structure, particles number-size, and for the chemical composition analysis. SEM was employed in this study to estimate the particle number-size distributions in the collected dust samples. The main aim was to determine the main particles' size in the collected dust samples.

To avoid any contamination of dust samples from external metals sources, no metal tools were used during sampling. This method of sampling has been successfully applied in many studies to investigate the level of metals contamination in urban dust and soil samples (Charlesworth et al., 2003; Kamani et al., 2015; Saeedi et al., 2012). However, the major drawback of this method is that the collected dust samples are a mixture of many fractions which need further processing to get the smallest fraction size of particles via sieving. Before the spectrometry analysis, dust samples need to undergo a digestion process to convert them from a solid to an aqueous solution.
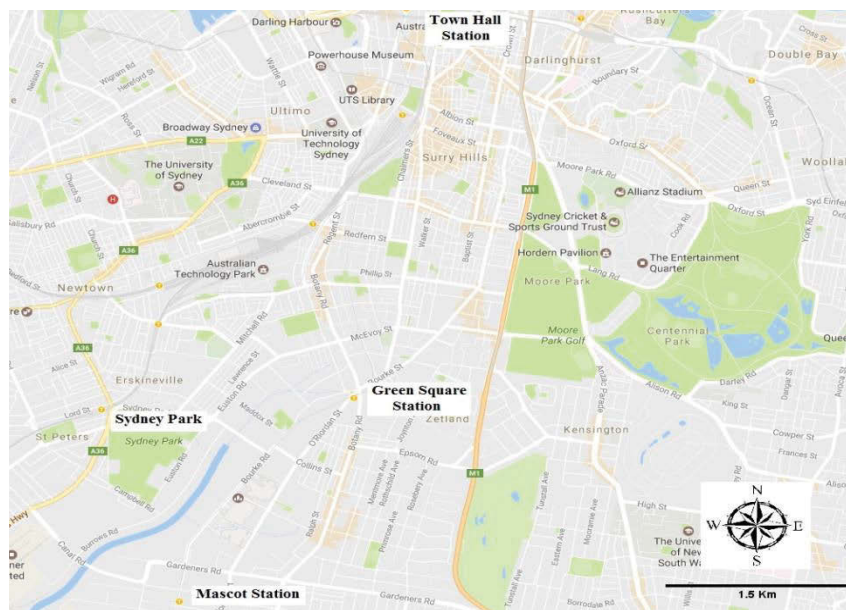
Figure 4.1 Map of dust sampling locations in Sydney from three different underground railway platforms (G.S, Mas, and T.H stations) and one urban ambient background location from Sydney Park.
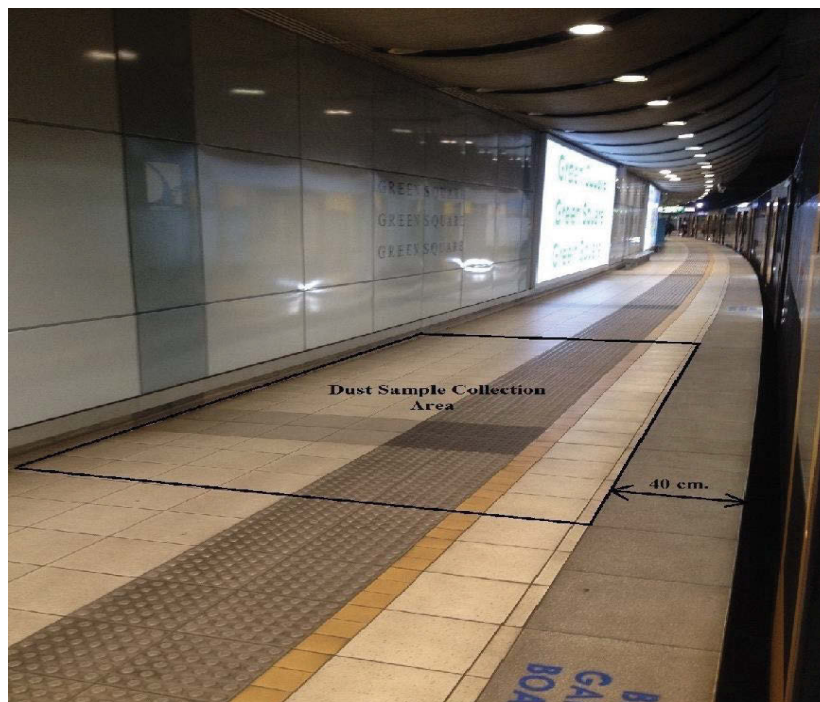
Figure 4.2 Dust samples collection area from Green Square Station, Sydney representing one of three areas sampled from different distances along the platform (left end, middle end and right end).

4.2.1 Scanning Electron Microscopy (SEM) Analysis

Dust samples were analysed by the SEM to generate high resolution images to give an overview about the particle size. The produced images showed that that particles diameter in the Sydney underground platforms dust are predominantly finer than 10 μm (Figure 4.3). Therefore, the chemical analysis of PM using the dust samples should give a good indication about the metals components of PM_{10} and $PM_{2.5}$ in the railway air environments.
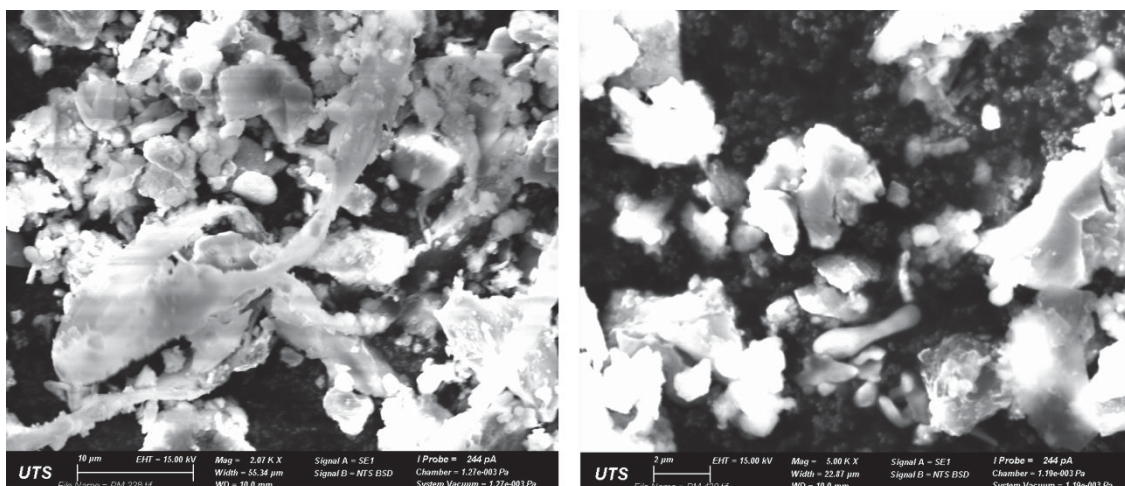
Figure 4.3 Overview of the particles size distribution in the platforms dust samples with two different scales: (10 µm scale on the left and 2 µm scale on the right). The image indicates that the dust samples mainly contains particle with a diameter ≤ 10 µm.

4.2.2 Digestion Method

For metal analysis, the dust samples need to be prepared as an aqueous solution before the chemical analysis. Different extraction methods can be applied. However, to select the proper method of extraction some crucial factors should be considered. Firstly, the time and cost of the analytical instrumentation device should be considered. In addition, the chemical substances need to be analysed (e.g. organic, metals, ions) (Welna et al., 2011). Following recommendations from previous studies in this field based on the recovery analyses, the best extraction method to be used for metal extraction from PM is by strong acid solution according to the USEPA 3050B Method. In this study, nitric acid (HNO_3) combined with hydrochloric acid (HCl) was used to break the metal bonds from the existing organic substances (Charlesworth et al., 2003; Kamani et al., 2015; Lin et al., 2015).

The dust samples were left for 24 h at the laboratory room temperature before sieving via the 75 µm sieve. For each sample, only 1 g of the dry sieved dust was used for digestion

purposes based on the requirements of the USEPA 3050B Method. Then after repeated additions of HNO$_3$ and HCl acids with heating, the final solution was diluted to 100 ml volume with distilled water. The procedure of each dust sample extraction based on the USEPA 3050B Method is shown in Figure 4.4, and all the details about the extraction procedure can be viewed on the US EPA website (US EPA, 1996).

At this stage, the samples were ready to undergo chemical analysis using the Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) available at the university environmental laboratory. Due to continuous cleaning of the platforms, only small amounts of dust were able to be collected. Accordingly, samples analysed were representing only one size fraction of less than 75 μm.
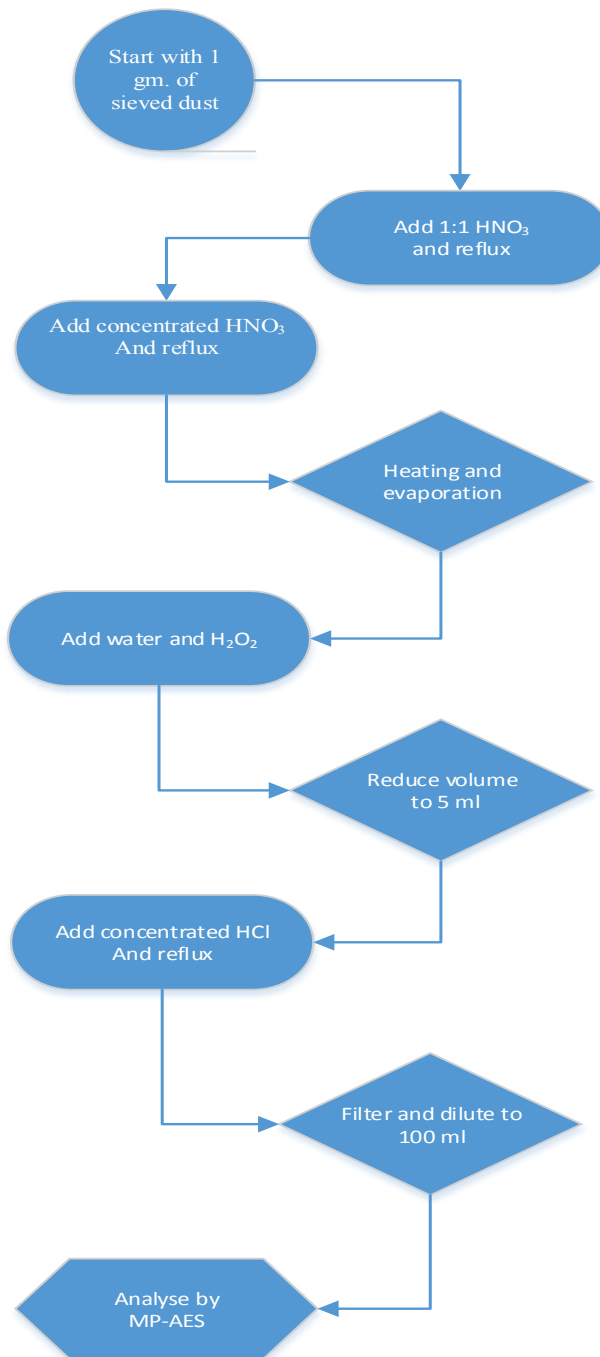
Figure 4.4 Digestion procedure based on the USEPA 3050B Method for heavy metal analysis by MP-AES.

4.2.3 MP-AES Analysis

After the digestion process, all samples were ready for heavy metal concentration analysis by MP-AES. The MP-AES is a modern spectrometry technique which offers accurate analysis results reaching very small detection limits. It takes less than one hour for each sample results to appear on the attached desktop (Figure 4.5). After digestion, the concentration of 16 metals was analysed, and the selection of these metals was based on the most elevated metals concentrations from other railway studies (Kam et al., 2011a; Perrino et al., 2015; Salma et al., 2009, Abbasi et al., 2012). The amount of Magnesium (Mg), Cadmium (Cd), Molybdenum (Mo), and Potassium (K) was under the detection limit for the MP-AES in all samples. It should be noticed that the detection limits in MP-AES method varies for different elements. Therefore, their concentration measurements have been excluded in this study. For each sample, the concentrations of Iron (Fe), Calcium (Ca), Zinc (Zn), Copper (Cu), Aluminium (Al), Lead (Pb), Cobalt (Co), Nickel (Ni), Manganese (Mn), Chromium (Cr), Barium (Ba), and Sodium (Na) was measured. The metal concentration results will be utilised in Chapter Five to estimate their potential risks.

Figure 4.5 Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) setup.

4.2.4 Quality Assurance and Calibration

The accuracy of the analysis was obtained by diverse ways to ensure the best representative results from the collected dust samples following recommendations from previous studies (Mummullage et al., 2014; Zhao et al., 2015). As mentioned before, all samples were collected from three different areas during each sampling day to account for the variance in dust accumulation in the trains and along airway directions. Then, duplicate samples analyses were regularly performed during the experiments which showed that all the concentrations results obtained were within 10% of each other for the same extracted sample. As part of the calibration process, internal standards and quality control blanks for the twelve metals were used. Each element was calibrated using four points linearity curves; all the correlation coefficients yielded for the twelve metals were more than 0.996 (Appendix A-1).

4.3 Results and Discussion

Tables 4.1 and 4.2 show the results of mean concentration values for all the above listed metals analysed by MP-AES, measured in ppm (mg/l) and then converted to (mg/g.). Figure 4.6(a-b) shows the weight contribution of each metal from the platforms and the ambient measurements. The most significant differences between the two environments are the abundance of Fe in the subway platforms samples, and Ca in the ambient background samples. The mean concentration results from all five railway platforms followed the decreasing order of Fe, Cr, Ca, Al, Na, Ba, Mn, Zn, Cu, Ni, Co and Pb. Fe shared a dominant level with a mean concentration value of 73.51 mg/g, which is almost 7.5% of the total dust weight (Figure 4.6a). In comparison to the ambient measurements, commuters on Sydney underground platforms are exposed to substantially higher levels of some of these metals.

Fe concentration was almost 20 times greater than the ambient results suggesting that the railway environment has additional local sources of Fe which need to be carefully considered when estimating the potential health implications that might result from personal exposure. The substantial presence of Fe has also been reported in worldwide subway studies suggesting the wear and abrasion processes as the main sources of Fe and most other metal components (Kam et al., 2011a; Ma et al., 2012; Martins et al., 2016; Moreno et al., 2015). Concentrations results of Ni, Mn, Cr, and Ba were consistent with observations from other subway studies. These metals were 2 to 10 times greater than corresponding ambient measurements measured from Sydney Park.

To consider the effect of the platforms depth from the ground level on the pollution levels, correlation analysis for two different level platforms ($T.H_1$ and $T.H_2$) located within the same station is presented. The results showed a strong positive correlation between the two measurements ($P < 0.01$), indicating a minimal effect of the platforms depth. The strong correlation also indicates that if platforms are at underground levels, the main source of the metals is from local railway processes. Commuters are expected to be exposed to the same metal concentration in these microenvironments. Potential sources of these metals will be discussed in more detail in the following sections.

Table 4.1 Mean metal concentration in five samples taken from three platforms subway stations.

Element	Platform measurements (mg/g)					Average
	G.S$_1$	T.H$_1$	Mascot	G.S$_2$	T.H$_2$	(mg/g)
Fe	74.08	74.32	78.8	68.2	72.16	73.51 ± 3.84
Ca	3.40	4.10	3.00	2.50	3.32	3.26 ± 0.59
Zn	0.50	0.26	0.56	0.44	0.60	0.47 ± 0.13
Cu	0.48	0.38	0.36	0.40	0.30	0.38 ± 0.07
Al	0.88	1.26	0.64	0.96	0.56	0.86 ± 0.28
Pb	0.12	0.22	0.36	0.10	0.10	0.18 ± 0.11
Co	0.18	0.22	0.04	0.26	0.30	0.20 ± 0.10
Ni	0.14	0.26	0.42	0.16	0.30	0.26 ± 0.11
Mn	0.50	0.72	0.68	0.54	0.64	0.62 ± 0.09
Cr	6.08	5.78	8.60	6.12	6.76	6.67 ± 1.14
Ba	0.54	0.64	0.96	0.62	0.56	0.66 ± 0.17
Na	0.56	0.62	0.60	1.04	1.16	0.80 ± 0.28

Table 4.2 Mean heavy metal concentration in two samples taken from Sydney Park to represent the ambient measurements.

Element	Ambient measurements (mg/g)		Average (mg/g)
	B.G$_1$	B.G$_2$	
Fe	3.20	4.30	3.75 ± 0.78
Ca	10.46	8.30	9.38 ± 1.53
Zn	0.26	0.42	0.34 ± 0.11
Cu	0.28	0.34	0.31 ± 0.04
Al	2.30	3.08	2.69 ± 0.55
Pb	0.62	0.54	0.58 ± 0.06
Co	0.28	0.40	0.34 ± 0.08
Ni	0.02	0.04	0.03 ± 0.01
Mn	0.14	0.20	0.17 ± 0.04
Cr	1.08	0.88	0.98 ± 0.14
Ba	0.24	0.34	0.29 ± 0.07
Na	3.06	3.44	3.25 ± 0.27
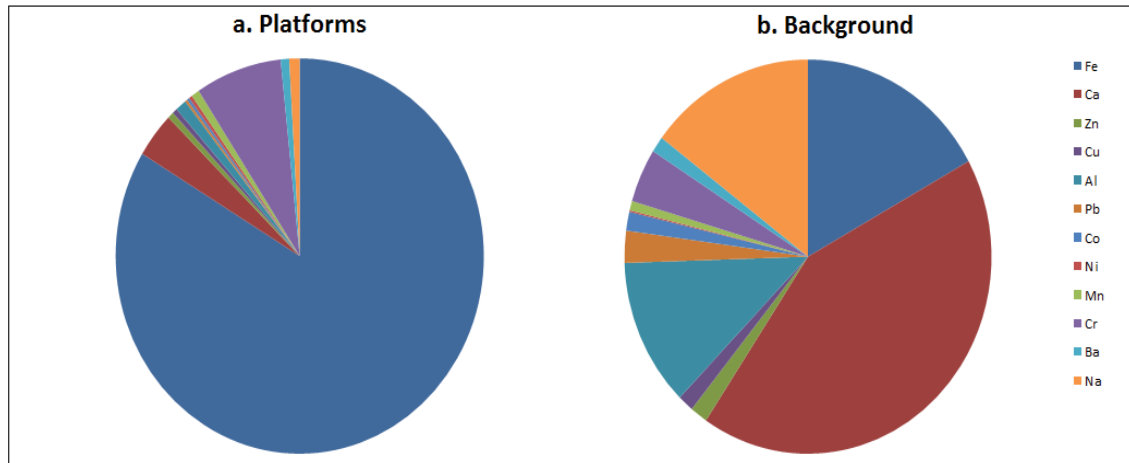
Figure 4.6 Metal concentration contributions from (a) subway platforms and (b) ambient (background) dust samples.

4.3.1 Pollution Index (PI) and Integrated Pollution Index (IPI)

To consider the level of contamination by heavy metals which can occur in the Sydney railway system, PI values for the twelve metals have been determined. PI values can simply be found by calculating the ratio of the railway concentrations divided by the ambient concentrations measurements as shown in equation (4.1).

$$PI = \frac{C_{railway}}{C_{background}}$$ equation (4.1)

where $C_{railway}$ represents the mean concentration value from the subway measurements for a specific metal (mg/g), while $C_{background}$ represents the corresponding value of that metal from the ambient measurements (Sydney Park) measured also in (mg/g). These values have then been interpreted according to the Hakanson (1980) categorisation method to consider PI impact as follows:

- PI < 1   low level of pollution.

- $1 \leq PI < 3$ moderate level of pollution.

- $3 \leq PI < 6$ considerable level of pollution.

- PI ≥ 6 very high level of pollution.

Figure 4.7 shows the obtained values of the PI using mean concentrations values from Tables 4.1 and 4.2. Based on the suggested categorisation for PI values, three out of twelve metals indicated very high contamination levels; these were Fe, Ni, and Cr with PI values of 19.6, 8.53 and 6.8 respectively. Mn was within the considerable range with a PI value of 3.6, whereas Ba, Cu and Zn were considered as moderate with PI values of 2.3, 1.2 and 1.4, respectively. The rest of the measured metals indicated no contamination from the subway sources since their PI values were all < 1.
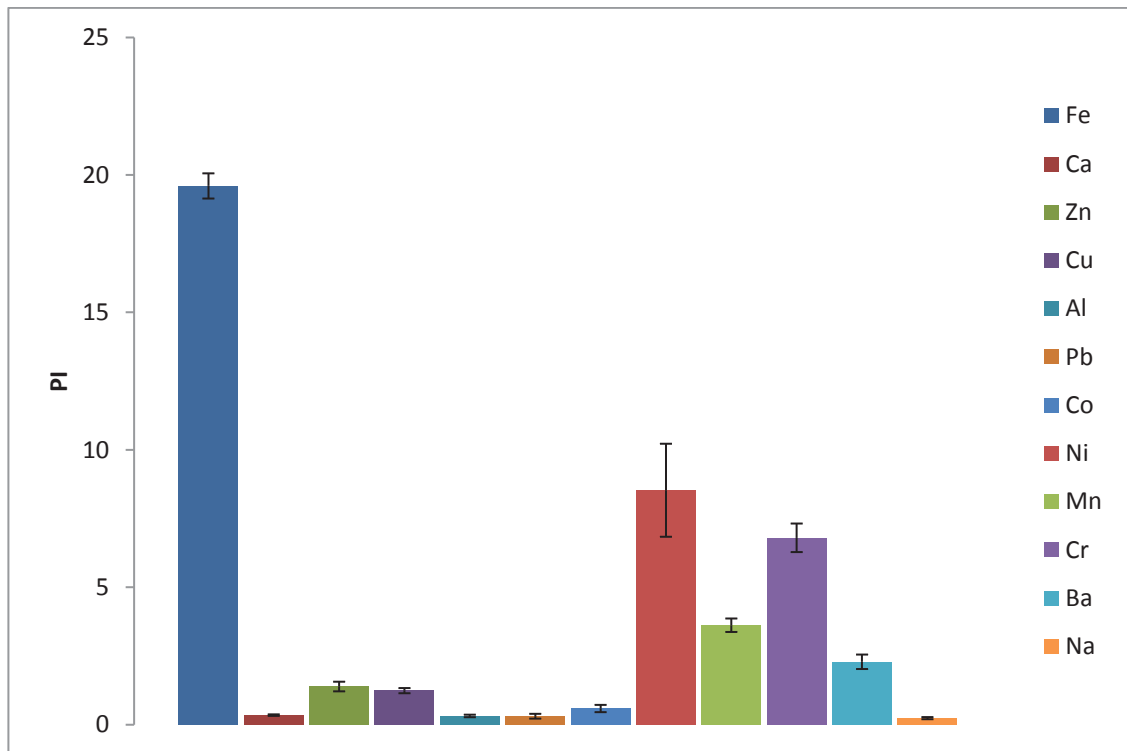
Figure 4.7 Pollution Index (PI) values for twelve heavy metals measured by using the mean concentration values of the subway and the ambient dust samples.

Consistent with other studies, the PI values from the Sydney railway system indicated moderate to very high pollution levels. The results indicate a significant role of local

subway sources in reaching high PI values (Cui et al., 2016; Kam et al., 2011a; Moreno et al., 2017; Nieuwenhuijsen et al., 2007).

Possible sources of the elevated metals might be generated by the friction processes between the train wheels and trucks, where both of these parts manufactured from stainless steel mix with other metals to enhance the mixture manufacturing and serviceability properties. The brakes system also contributes to considerable amounts of metals due to using them in the manufacturing process of the brakes. Furthermore, the mechanical wearing of the railway system parts can also generate substantial amounts of the subway dust. According to Abbasi et al. (2012); Fe, Mn, Cr, and Ni are among the primary elements which have been used in manufacturing the train wheels, brakes pads, and the rails/tracks. Another source of Fe suggested by Qiao et al. (2015) can be from the interaction between the catenaries providing the electricity power to the trains and the pantographs located on the top roof of the trains' carriages. Therefore, friction and abrasion particles will be formed primarily from these metals. Ba is usually used as a filler element in manufacturing the brakes pads. According to recent a Korean study, the amounts of brake friction particles depend on the pad composition, brake forces and brakes disks temperature, where the loss in the brakes operation can release about 35% of the total pads' mass (Namgung et al., 2016).

IPI is another index used widely in many studies to indicate the level of pollution in different environments. According to Faiz et al. (2009), IPI can be defined as the mean value of PI measured for each element; this index can be calculated using equation (4.2):

$$\text{IPI}_e = \frac{\sum_n PI_e}{n} \qquad \text{equation (4.2)}$$

where PI_e represents the pollution index for element (e) measured from any environment, while (*n*) is the number of environments measured. In this study, five platforms were considered in the IPI calculation *(n =5)*. The results were interpreted using the following categorisation:

- Low level of contamination at $(IPI \leq 1)$.

- Middle level of contamination at $(1 < IPI \leq 2)$.

- High level of contamination at $(IPI > 2)$.

IPI values are shown in Table 4.3 indicating a high level of contamination from Fe, Ni and Cr with an IPI value of up to 9.8 along the platforms, Mn and Ba were under the range of middle contamination. The rest of the elements had IPI values of less than one, implying low contamination levels.

Table 4.3 Integrated pollution index (IPI) of heavy metals in the railway particles of five underground platforms (n=5).

Element	PI					IPI
	$G.S_1$	$T.H_1$	Mascot	$G.S_2$	$T.H_2$	
Fe	9.9	9.9	10.5	9.1	9.6	9.8
Ca	0.2	0.2	0.2	0.1	0.2	0.2
Zn	0.7	0.4	0.8	0.7	0.9	0.7
Cu	0.8	0.6	0.6	0.7	0.5	0.6
Al	0.2	0.2	0.1	0.2	0.1	0.2
Pb	0.1	0.2	0.3	0.1	0.1	0.2
Co	0.3	0.3	0.1	0.4	0.4	0.3
Ni	2.3	4.3	7.0	2.7	5.0	4.3
Mn	1.5	2.1	2.0	1.6	1.9	1.8
Cr	3.1	2.9	4.4	3.1	3.5	3.4
Ba	0.9	1.1	1.7	1.1	1.0	1.1
Na	0.1	0.1	0.1	0.2	0.2	0.1

4.3.2 Enrichment Factor (EF)

A very common approach which has been used in previous environmental studies is the enrichment factor (EF). It is an efficient tool and widely used indicator to speculate and differentiate between the sources of metals in a specific environment based on choosing the appropriate normalisation element. The EF can be directly determined by applying equation (4.3):

$$EF_e = \frac{(Ce/Cr)sample}{(Ce/Cr)background} \qquad \text{equation (4.3)}$$

where EF_e represents the enrichment factor for metal (e), $(C_e)_{sample}$ and $(C_r)_{sample}$ are the mean concentrations values of specific (e) element and the reference element in the subway dust sample, respectively. While $(C_e)_{background}$ and $(C_r)_{background}$ are the mean concentration values of the same specific element and the same reference element measured from the ambient dust samples.

Reference or normalisation element as named in some studies is usually used for geochemical data to compensate for the mineralogy effect and to ensure that the elemental concentration in the sample is entirely influenced by crustal sources (Sakan et al., 2011). Accordingly, the appropriate reference element should be the weakest and/or negatively correlated with other elements. Previous studies suggested that the appropriate reference element can be chosen based on results from correlation coefficient analysis (Abrahim and Parker, 2008; Saeedi et al., 2012). Therefore, to choose the right reference element for this study, the matrix presented in Table (4.4) shows Pearson's correlation coefficients for all the presented metals taken from the platforms and ambient samples from Sydney Park. Negative correlation was found between Al and seven other elements and there was a moderate to weak positive correlation between Al and the rest of the elements. It can be inferred from these correlation coefficients that Al might be generated from crustal

sources rather than subway sources. Furthermore, Al has been widely used before as a reference element for enrichment factor measurements and it is believed to be derived from crustal materials (Chen et al., 2007; Kam et al., 2011a; Kamani et al., 2015; Karbassi et al., 2008). Accordingly, Al was chosen as the reference element in this study. The results were then interpreted using the EF categorisation suggested by Birth (2003) as follows:

- EF < 3 (minor enrichment), suggesting no or marginal contamination.
- 3 ≤ EF < 5 (moderate enrichment), suggesting moderate contamination.
- 5 ≤ EF < 10 (moderately severe enrichment), suggesting moderately severe contamination.
- 10 ≤ EF < 25 (severe enrichment), suggesting severe contamination.
- 25 ≤ EF < 50 (very severe enrichment), suggesting very severe or high contamination at dangerous levels.
- and EF ≥ 50 (extremely severe enrichment), suggesting extreme severe contamination.

Enrichment factor values of all heavy metals are shown in Table 4.5 following the deceasing order of Fe, Ni, Cr, Mn, Ba, Zn, Cu, Co, Ca, Al, Pb and Na. The results indicated that Fe was the most enriched element with a factor value of 61.31 (extremely severe), followed by Ni (EF = 26.7) indicating severe anthropogenic origins and then Cr (EF = 21.3). While EFs for Co, Ca, Al, Pb and Na were around 1 indicating crustal origins. Examining the mean concentrations values from Tables 4.1 and 4.2, it can be observed that Co, Cu and Zn mass from the railway were less or about the same as those for the ambient measurements. However, normalised EF of 1.8–4.3 indicated moderate to minor enrichment for those elements. The main source of Zn in the railway

microenvironments is attributed to using it as a coating layer for the steel tracks to prevent excessive corrosion or it could be from street level vehicles (Chen et al., 2009; Kam et al., 2011a). However, there is no evidence of using Zn in coating the rail tracks used in the Sydney railway system due to the lack of manufacturing data.

High EF value of more than 3 indicates that these elements have been subjected to subway sources (e.g. rail and brake friction and abrasion) confirming previous findings presented in this chapter. They are local and have no effect on the vicinity of the ambient background site. However, it can affect the surrounding railway microenvironments. These results are consistent with findings from other subway studies indicating that the same metals are always the most enriched elements in the subway microenvironments, although in different order (Kam et al., 2011a; Qiao et al., 2015; Salma et al., 2009).

Table 4.4 Pearson's correlation coefficients for mean concentration values of twelve metals tested from the Sydney subway dust samples and ambient sources.

	Fe	Ca	Zn	Cu	Al	Pb	Co	Ni	Mn	Cr	Ba	Na
Fe	1.00											
Ca	0.35	1.00										
Zn	0.15	-0.39	1.00									
Cu	-0.05	0.36	-0.28	1.00								
Al	-0.22	0.41	-.981**	0.45	1.00							
Pb	0.86	-0.02	-0.03	-0.16	-0.07	1.00						
Co	-0.84	0.21	-0.15	-0.21	0.17	-.882*	1.00					
Ni	0.72	-0.19	0.32	-0.68	-0.47	0.80	-0.56	1.00				
Mn	0.51	0.12	-0.29	-0.67	0.10	0.64	-0.21	0.77	1.00			
Cr	0.68	-0.41	0.61	-0.39	-0.69	0.75	-0.74	0.85	0.34	1.00		
Ba	0.71	-0.36	0.17	-0.24	-0.27	.935*	-0.86	0.81	0.50	0.88	1.00	
Na	-0.72	-0.58	0.35	-0.60	-0.37	-0.61	0.74	-0.10	-0.13	-0.14	-0.38	1.00

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

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

Table 4.5 Enrichment factors from Sydney subway dust samples measured by using Al as the   reference element.

Element	EF	Category
Fe	61.3	extremely severe
Ca	1.1	minor
Zn	4.3	moderate
Cu	3.9	moderate
Al	1.0	no enrichment
Pb	1.0	no enrichment
Co	1.8	minor
Ni	26.7	very severe
Mn	11.3	severe
Cr	21.3	severe
Ba	7.2	moderate severe
Na	0.8	no enrichment

4.4 Summary

In this chapter, underground dust samples were collected and analysed by employing the MP-AES method. Samples were collected from five railway microenvironments (underground platforms) and from an urban park. A total number of seven samples were analysed and the following conclusions have been derived from this chapter:

- By comparing the metal concentrations of samples taken from two different levels in the same station, strong correlation coefficients were found between the two measurements indicating insignificant effect of the platform depth.

- Based on the PI values; Fe, Ni and Cr were substantially higher than the ambient values. IPI values indicated a high potential to cause environmental contamination based on levels of the twelve metals.

- EF analysis showed that seven metals were enriched in the range of extremely severe to moderate, suggesting the principal contribution of anthropogenic sources.

- Based on the current analysis results in addition to previous railway studies, the main sources of PM in the rail microenvironment are localised from steel, brakes abrasion and wear processes.

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Chapter 5. Human Health Risk Assessment

5.1 Background

Following the rapid economic development in many developed and developing countries, health problems associated with exposure to heavy metals in the air have become a big concern due to their toxicity (Charlesworth et al., 2003; Loredo et al., 2003; Qiao et al., 2015; Saeedi et al., 2012). Some metals (e.g. Mn, Na, K, Fe and Ca) exist naturally inside human bodies and are considered as essential elements in order to form part of the blood cells, bones, immune system and teeth. However, the presence of any metal in excessive amounts may cause different health problems (Cui et al., 2016; Goorzadi et al., 2009; Martins et al., 2016; Moreno et al., 2017). Other metals which are not essential for human bodies (e.g. Pb, Cd and As) might cause serious health problems even at very low exposure levels or during short term exposure (Karbassi et al., 2008; Namgung et al., 2016; Sakan et al., 2011). The cancer risk from heavy metals may occur as a consequence of short term exposure to elevated amounts of a carcinogenic element or from chronic exposure to low doses of these elements (Li et al., 2007; Pope III et al., 2002).

Heavy metals are detected at extensive amounts in the railway systems which have been explained in Chapter 4. Commuters and workers at the railway systems may be exposed to elevated heavy metals released in the air through inhalation, dermal skin contact and food and drinks consumption (ingestion) (Kurt-Karakus, 2012; Pereira et al., 2007; Wei and Yang, 2010). The existence of any enriched metals in these environments indicates the potential to cause different health problems. Heavy metals are highly non-degradable, at the same time these elements can accumulate in any environment over time causing serious health and environmental problems (Wei and Yang, 2010). Therefore, there is a necessity to conduct a risk assessment of contaminants such as heavy metals in the

polluted environments as this will help the decision makers to better control the release of these pollutants from different sources.

"Health risk assessment can be defined as a systematic process for generating a probability distribution or similar quantification that describes uncertainty about the magnitude, timing, or nature of possible health and environmental consequences associated with possible exposure to specified substances, processes, or actions" (Covello and Merkhoher, 2013). Health risk assessment models have been used to determine the potential adverse health effects to human health that can result from chemicals at any dose. The US EPA model will be employed in this study to assess the potential of heavy metal levels to induce health risks.

Three probabilistic risk assessments approaches have been applied in this chapter: average daily dose method for non-carcinogenic effect, dose effect method for the carcinogenic effect and qualitative risk assessment. By applying the US EPA method, the dose amounts in addition to the exposure period will be considered as essential risk factors. By combining the results from these three assessments, a clear overview about the potential health risks at the Sydney railway vicinities from heavy metals in PM samples can be determined.

5.2 Quantitative Risk Assessment

5.2.1 Average daily dose methodology

Several methods have been applied to estimate the potential health risks caused by exposure to heavy metals. The probabilistic health risk assessment by average daily dose method introduced by the US EPA (2001) was used to estimate two major health effects: carcinogenic and non-carcinogenic risks. Four steps should be applied to conduct a health risk assessment: hazard identification, dose-response assessment, exposure assessment

and finally risk characterisation (US EPA, 2001). Figure 5.1 represents the risk assessment procedure applied in this study.
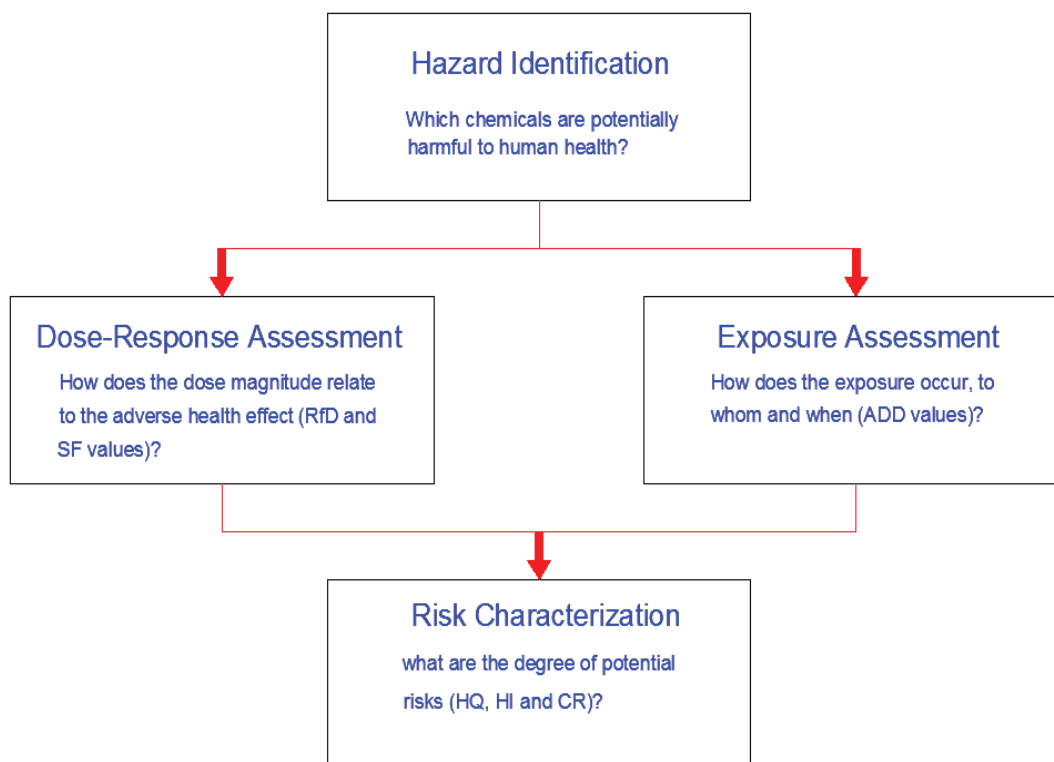
Figure 5.1 Average daily dose risk assessment procedure.

The purpose of hazard identification is to identify which element can impose an adverse effect on the human body. Based on the enrichment factor, any element in the chemical analysis section with EF > 3 (moderate – extremely severe enrichment) is considered as a health hazard. Seven elements (Fe, Zn, Cu, Ni, Mn, Cr, Ba) examined from the PM samples of Sydney trains/platforms were enriched. Therefore, these elements will be assessed to examine their potential risks. The next step is to determine the potential toxicity for each element.

The second step is to determine the dose-response relationship in order to estimate the likelihood of an adverse effect happening within a specific exposure dose. The U.S. EPA's method to assess the risks from systematic toxicity is different from assessing the

carcinogenic risks. Therefore, two toxicity indices will be determined: the reference dose (RfD) and the slope factor (US EPA, 1989; 2001). RfD is usually used as a toxicity index for non-carcinogenic risks, while SF is used as a carcinogenic index. RfD is defined as the ratio between the no-observable adverse health effect and the uncertainty factor usually measured by a milligram per kg of mass weight per day (mg /kg-day) (Chen et al., 2009). SF is defined as the slope of the intake – response curve measured by a milligram per kg of mass weight per day (mg / kg-day) (US EPA, 1989). The values of RfD and SF for this study have been extracted directly from the US EPA documents and from previous studies.

The third step in the quantitative risk assessment will be the exposure assessment. The main purpose of this step is for exposure quantifications via different discharge routes. Three ADD values will be determined as milligrams of the element concentration per kilogram of mass weight per day (mg/kg-day): Average daily exposure dose through ingestion (ADD$_{ing}$), average daily exposure dose through dermal contact (ADD$_{der}$) and average daily exposure dose through inhalation (ADD$_{inh}$) can be calculated using equations 5.1-5.3; respectively (US EPA,1989; 2001).

$$\text{ADD}_{ing} = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}} \qquad \text{equation (5.1)}$$

$$\text{ADD}_{der} = \frac{C \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}} \qquad \text{equation (5.2)}$$

$$\text{ADD}_{inh} = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}} \qquad \text{equation (5.3)}$$

The definitions and values of the parameter in equations 5.1-5.3 are tabulated in Table 5.1.

The risk assessment will be applied to two different population groups (adults and children). Children are more susceptible to the adverse effects of exposure to heavy metals. Therefore to calculate the ADD values, the US EPA has set different parameters values from adults (e.g. exposure duration, body weight and inhalation rate).

The last step in the quantitative risk assessment will be the risk characterisation to estimate potential risks from heavy metals in PM samples. Risk characterisation will be divided into non-carcinogenic risks which will be determined by using the hazard quotient (HQ) and Hazard index (HI), while for carcinogenic risks the cancer risk index (CR) will be used. These indices will be discussed in detail in the following sections:

Table 5.1 Parameter values recommended for ADD equations for two population groups (adults and children).

Parameter	Definition	Value	Reference
C	Average concentration of metals in APM (mg/kg)	depends on the chosen metal	this study
IngR	Ingestion rate (mg/day)	30 (adults) or 60 (children)	US EPA
EV	Events frequency (events/day)	1	US EPA
EF	Exposure frequency (days/year)	180	US EPA
ED	Exposure duration (years)	24 (adults) or 6 (children)	US EPA
CF	Conversion factor to (mg/kg)	10^{-6}	US EPA
BW	Body weight (kg)	70 (adults) or 15 (children)	US EPA
AT	Averaging time (days)	(Non-carcinogens) $AT = ED * 365$	US EPA
		(Carcinogens) $AT = 70 \, year * 365$	US EPA
SA	Skin surface area (cm^2)	5700 (adults), 2800 (children)	US EPA
AF	Adherence factor of soil to skin ($mg/cm^2/event$)	0.07 (adults), 0.2 (children)	US EPA
ABS	Dermal absorption fraction	0.001	US EPA
InhR	Inhalation rate (m^3/day)	7.63 (adults), 20 (children)	US EPA
PEF	Particle emission factor (m^3/kg)	$1.36 * 10^9$	US EPA

*All references for the values in Table 5.1 have been taken from US EPA (1989; 2001) and the IRIS page (US EPA, 2015).

5.2.1.1 Non-carcinogenic risk index

For non-carcinogenic risks the hazard quotient (HQ) is used to determine the risk assessment of each element. HQ is the ratio between the estimated doses of a chemical to its reference dose (RfD). RfD defined by IRIS as the amount of element a person can to

exposed to during a period of time without causing a significant health impact (US EPA, 2015). A probable non-carcinogenic risk occurrence from specific metals can occur when its HQ value is more than one, indicating that ADD value has exceeded the RfD value for that element as set by US EPA (equation 5.4) (US EPA, 1989; 2001). This approach can estimate the risks posed from one element, while in most polluted areas the potential health risk should be considered from all the surrounding contaminates. Therefore, the hazard index (HI) has been introduced to represent the sum of all HQ values for the considered elements via specific exposure pathways which can be calculated using equation 5.5 (US EPA, 1989; 2001). This approach assumes that simultaneous exposures to more than one chemical can cause health problems (Zheng et al., 2007). Following recommendation by the US EPA, if HI value was more than one (HI > 1) then a non-carcinogenic effect from heavy metals in Sydney railway environments may occur. The greater value of HI means the more probability for a risk to occur.

$$HQ = \frac{ADD}{RfD}$$ equation (5.4)

where ADD represents the average daily exposure level value for any heavy metal from a specific exposure pathway (mg/kg/day), and RfD represents the corresponding reference value.

$$HI = \sum_1^n (HQ)$$ equation (5.5)

where n = 7, representing the number of examined metals (enriched metals) included in the risk assessment study.

Table 2 illustrates the corresponding reference dose values (RfD) to be used in equation 4 for each exposure pathway which has been extracted from different US EPA documents

and past research papers (Crawford et al. 2004; Lee et al. 2006; Liu et al. 2015; US EPA 2001).

5.2.1.2 Carcinogenic risk index

Carcinogenic risk is the probability of an individual developing a specific type of cancer from exposure to one or more element which has the potential to cause carcinogenic hazards. The quantitative approach of risk assessment based on the dose-response method will be applied to estimate the potential cancer risks from exposure to some heavy metal found in the railway PM samples. The carcinogenic risk index named "cancer risk (CR)" developed by the US EPA will be applied in this study. To estimate the potential of some elements to develop cancer cells; CR is dimensionless and can be directly calculated from equation 5.6 (US EPA 1989, 2001).

$$CR = ADD \text{ X } SF \qquad\qquad\qquad \text{equation (5.6)}$$

where CR represents the cancer risk, ADD is the average daily exposure dose from the specific exposure pathway measured in (mg/kg-day), and SF is the slope factor measured in (mg/kg-day).

According to the US EPA characterisation, if the CR value for an element is in the range between 10^{-4} to 10^{-6}, then the level of exposure can be considered as acceptable and its carcinogenic effect is negligible (US EPA, 1989; 2001). The safe values indicate that for regulatory purposes, one case of cancer in a population of 10^4 to 10^6 developed by exposure to an element should be within the acceptable limits. The major drawback for this method is despite many metals being classified as carcinogenic elements by the US

EPA, their SF values are yet to be determined. Therefore, in this study only two carcinogenic elements (Cr and Ni) were assessed against their potential carcinogenic effect. Ni is classified as a "Group 1" carcinogenic element, lung and nasal cancer in humans and animals were attributed to exposure to Ni and Ni compounds from various sources (US EPA, 2016). Human exposure to Nickel is strongly associated with adverse health effects such as skin allergies, and lung and respiratory tract cancer risks with an emphasis on generating reactive oxygen species (Das et al., 2008; Latvala et al., 2016). Hence, Ni as an enriched metal at the Sydney railway vicinities will be assessed to consider its potential to cause a carcinogenic risk. Chromium has also been identified as a toxic element "Group D" carcinogenic element that can pose different carcinogenic risks to humans (US EPA, 2016). Stomach cancer and lung cancer are the most recognised problems caused by elevated exposure to Chromium (Beyersmann and Hartwig, 2008; Smith and Steinmaus, 2009; US EPA, 2016). However, not all compounds containing Cr(VI) are carcinogenic (Zheng et al., 2007).

Table 5.2 illustrates the SF values which were used in equation 5.6, the values have been extracted from different US EPA documents and previous research papers (Chang et al., 2009; Liu et al., 2015; US EPA, 2016). For CR calculations, $ADD_{carcinogenic}$ can be determined using equation 5.1-5.3 with different average exposure times (AT) as recommended in Table 5.1.

Table 5.2 Recommended values of RfD for seven elements through three exposure pathways (ingestion, dermal contact and inhalation).

Element	RfD$_{ing}$	RfD$_{der}$	RfD$_{inh}$	SF$_{inh}$
Fe	3.00E-01	3.00E-01	3.00E-01	
Zn	3.00E-01	6.00E-02	3.01E-01	
Cu	4.00E-02	4.02E-02	1.20E-02	
Ni	2.00E-02	2.06E-02	5.40E-03	8.40E-01
Mn	4.60E-02	1.43E-05	1.84E-03	
Cr	3.00E-03	2.86E-05	6.00E-05	4.20E+01
Ba	7.00E-02	7.00E-02	7.00E-02	

5.2.2 Results and discussion

5.2.2.1 Average daily exposure doses

The results of calculating the ADD values based on seven enriched elements' concentrations from PM samples of Sydney underground platforms are shown in Tables 5.3 and 5.4. For the purpose of exposure assessment, ADD value for each element was determined to represent the non-carcinogenic and the carcinogenic doses via three exposure pathways (ingestion, dermal contact and inhalation). ADD values have decreased in the order of Fe > Cr > Ba > Mn > Zn > Cu > Ni for children and adults via all discharge pathways for carcinogenic and non-carcinogenic assessments. ADD value for Fe in all cases was significantly higher than the other metals, while ADD values for

Ni were the smallest, within the other elements, ADD level (Figure 5.2). A risk assessment study of urban PM from Changsha city in China, showed that ADD values were the highest from Fe and the lowest from Ni with the same exposure pathways trend (Liu et al., 2015). Other studies for heavy metals from street dust showed that ingestion is the main exposure pathway which can cause health risks followed by dermal contact and inhalation pathways, respectively (Ferreira-Baptista and De Miguel, 2005; Zheng et al., 2010).

Table 5.3 Average daily dose values for adults from seven heavy metals via three exposure pathways for non-carcinogenic and carcinogenic risk assessments.

		Fe	Zn	Cu	Ni	Mn	Cr	Ba
	Concentration (mg/kg)	73510	470	380	260	620	6670	660
Non-carcinogenic (mg/kg-day)	ADD_{ing}	1.55E-02	9.93E-05	8.03E-05	5.50E-05	1.31E-04	1.41E-03	1.39E-04
	ADD_{der}	2.07E-04	1.32E-06	1.07E-06	7.31E-07	1.74E-06	1.87E-05	1.86E-06
	ADD_{inh}	2.91E-06	1.86E-08	1.50E-08	1.03E-08	2.45E-08	2.64E-07	2.61E-08
Carcinogenic (mg/kg-day)	ADD_{ing}	5.33E-03	3.41E-05	2.75E-05	1.88E-05	4.49E-05	4.83E-04	4.78E-05
	ADD_{der}	7.08E-05	4.53E-07	3.66E-07	2.51E-07	5.98E-07	6.43E-06	6.36E-07
	ADD_{inh}	9.96E-07	6.37E-09	5.15E-09	3.52E-09	8.40E-09	9.04E-08	8.94E-09

Table 5.4 Average daily dose values for children from seven heavy metals via three exposure pathways for non-carcinogenic and carcinogenic risk assessments.

|		Fe	Zn	Cu	Ni	Mn	Cr	Ba
Concentration (mg/kg)		73510	470	380	260	620	6670	660
Non-carcinogenic (mg/kg-day)	ADD_{ing}	3.63E-02	2.32E-04	1.87E-04	1.28E-04	3.06E-04	3.29E-03	3.25E-04
	ADD_{der}	3.38E-04	2.16E-06	1.75E-06	1.20E-06	2.85E-06	3.07E-05	3.04E-06
	ADD_{inh}	8.89E-06	5.68E-08	4.59E-08	3.14E-08	7.49E-08	8.06E-07	7.98E-08
Carcinogenic (mg/kg-day)	ADD_{ing}	5.33E-03	3.41E-05	2.75E-05	1.88E-05	4.49E-05	4.83E-04	4.78E-05
	ADD_{der}	7.08E-05	4.53E-07	3.66E-07	2.51E-07	5.98E-07	6.43E-06	6.36E-07
	ADD_{inh}	3.05E-06	1.95E-08	1.95E-08	1.08E-08	2.57E-08	2.76E-07	2.74E-08
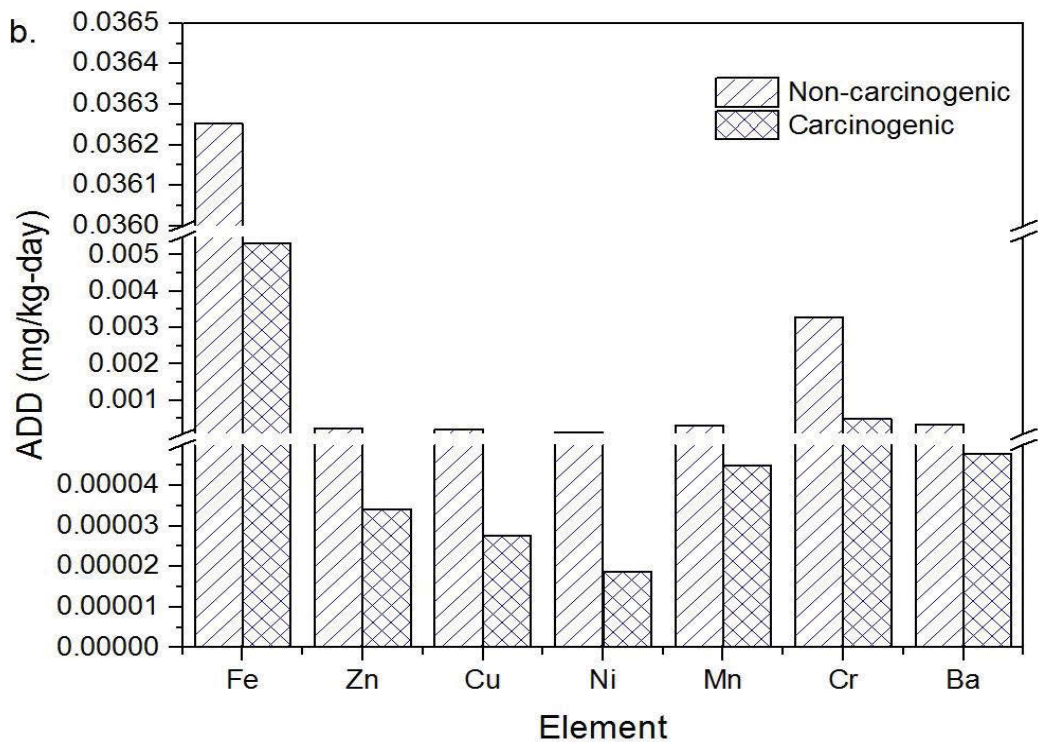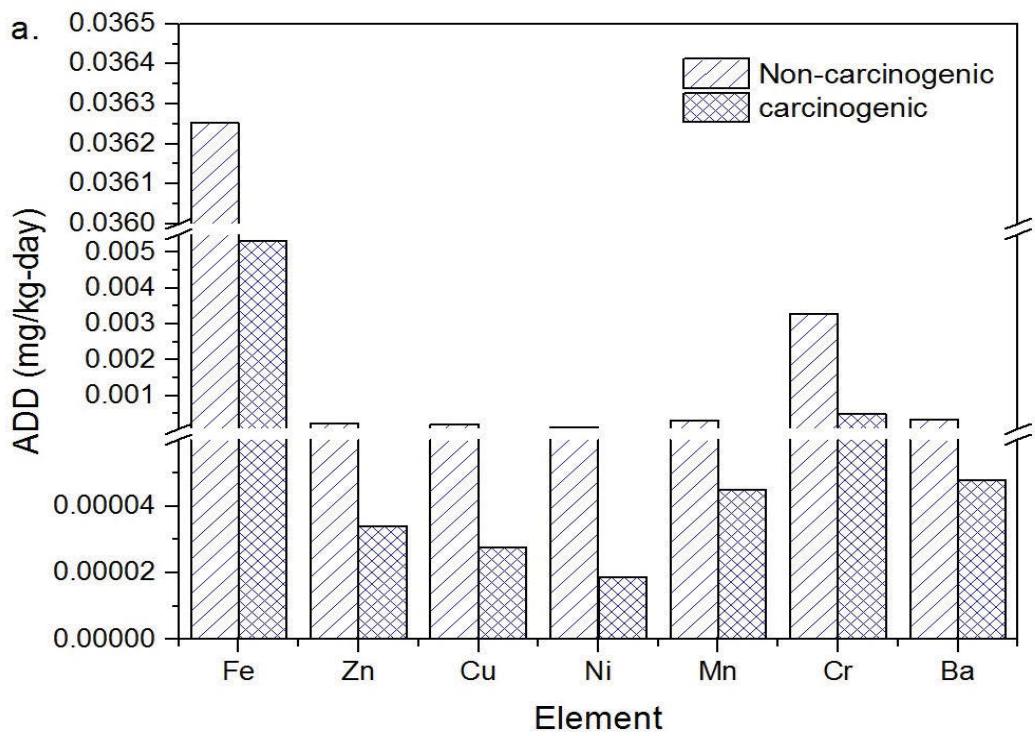
Figure 5.2 ADD via ingestion for carcinogenic and non-carcinogenic risk exposure for (a) adults and (b) children. ADD for Fe were significantly the highest in both populations.

*5.2.2.2 Hazard quotient (HQ) and hazard index (HI) assessments*

HQ values for adults and children are illustrated in Figure 5.3. The results of HQ through all exposure pathways show no indication for non-carcinogenic risks to occur in both children and adults for all elements except Cr. The non-carcinogenic risk of Cr via ingestion is just above one for children, indicating insignificant potential to cause health risks. Exposure via dermal contact showed the same results with a HQ value of 1.07 for Cr. The inhalation pathway results showed that all HQ values were almost zero indicating no potential to cause any non-carcinogenic risks by any element. Despite the fact that ADD values were much higher for Fe than Cr; the HQ values indicate that only Cr has the potential to cause non-carcinogenic risks. For the exposure pathways, the HQ values decreased in the order of dermal contact > ingestion > inhalation.

The potential of non-carcinogenic risks was higher in children in all three exposure pathways, indicating that children were more susceptible to develop health problems from exposure to heavy metals in the subway environments of Sydney. Studies suggested that the inadvertent finger and hand sucking habits in children and Pica behaviour (an eating disorder) have been considered as the most important metal exposure pathways in children (Ljung et al., 2006; Zhao et al., 2014).

HI values for adults and children from each exposure pathway are presented in Table 5.5. In adults, there is no indication of any non-carcinogenic risks in the platform environments for all three exposure pathways since all HI values were considerably less than one. However, the total combined HI value from three pathways was 1.31, indicating a small possibility for non-carcinogenic health risks to occur. The biggest contributor for the combined HI value in adults was from the dermal contact (~ 60%). Similar results were obtained in non-carcinogenic risks studies through the same three exposure

pathways indicating that the inhalation pathway is the least contributor to the total HI values in comparison to ingestion and dermal contact pathways (Ferreira-Baptista and De Miguel, 2005; Hu et al., 2012; Zheng et al., 2010).

The HI values for children through ingestion and dermal contact were almost double the values for adults. However, HI values indicate a very small probability to pose non-carcinogenic risks through the ingestion and dermal contact pathways. No evidence of any non-carcinogenic health risks can occur in children through inhalation since the HI value was almost zero. Nevertheless, the combined HI values for all exposure pathways in children was 2.53 indicating that non-carcinogenic health risks for children can occur from exposure to heavy metals at these concentrations levels.
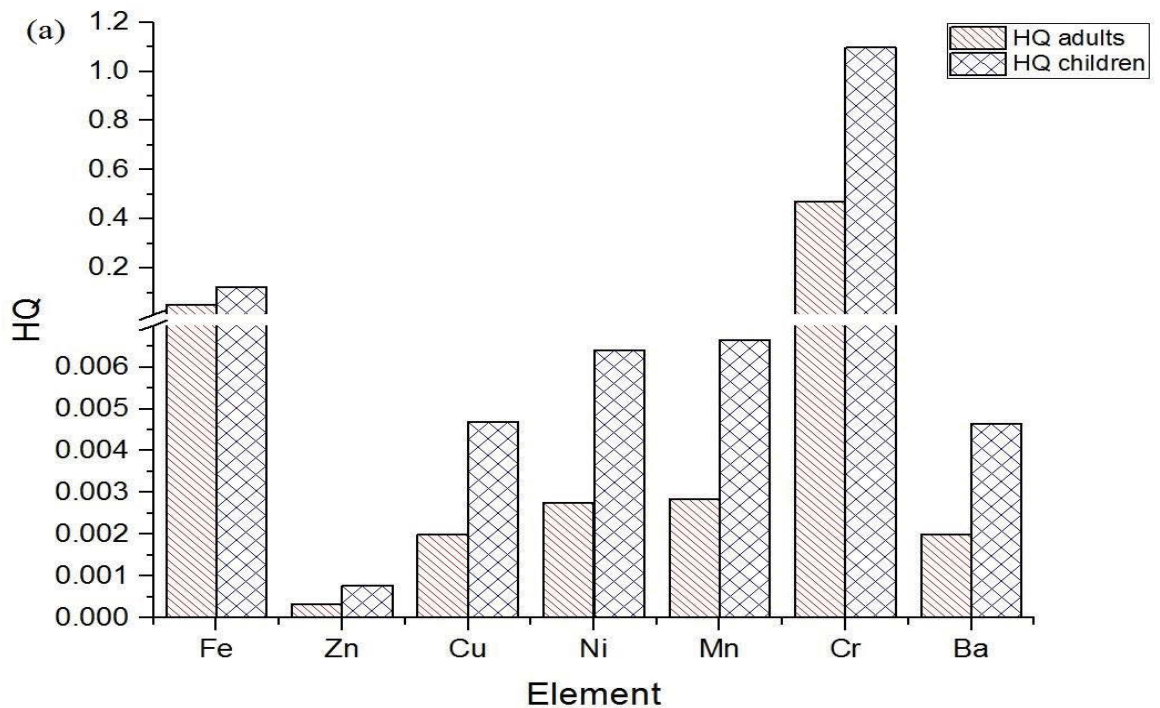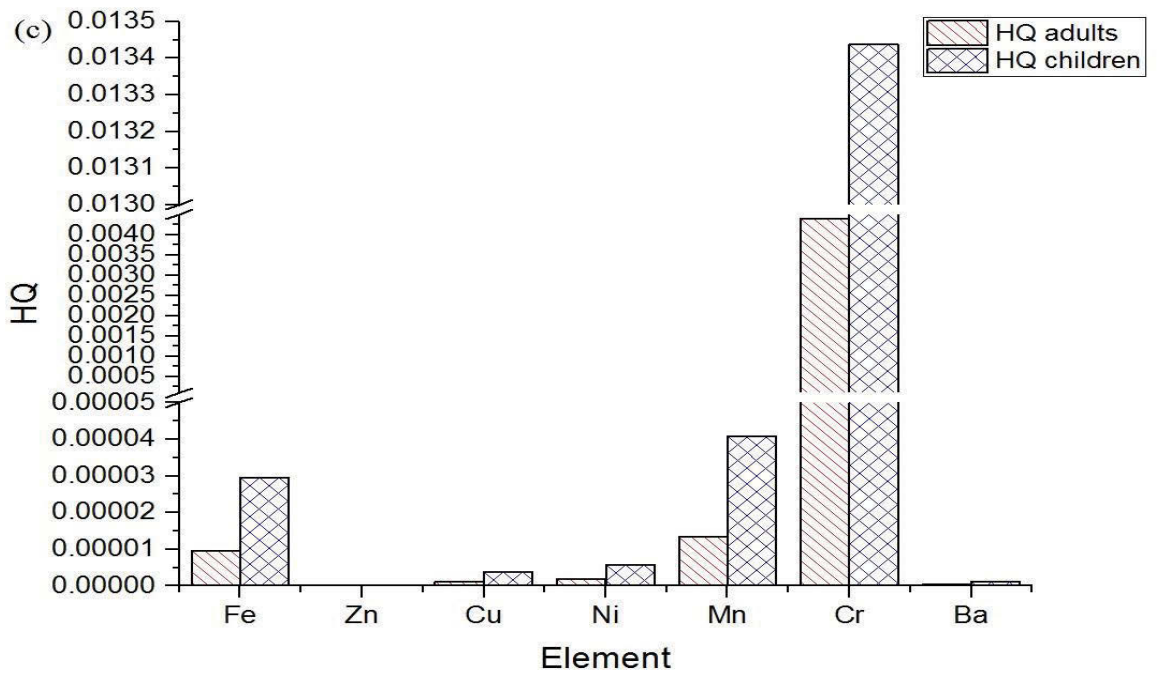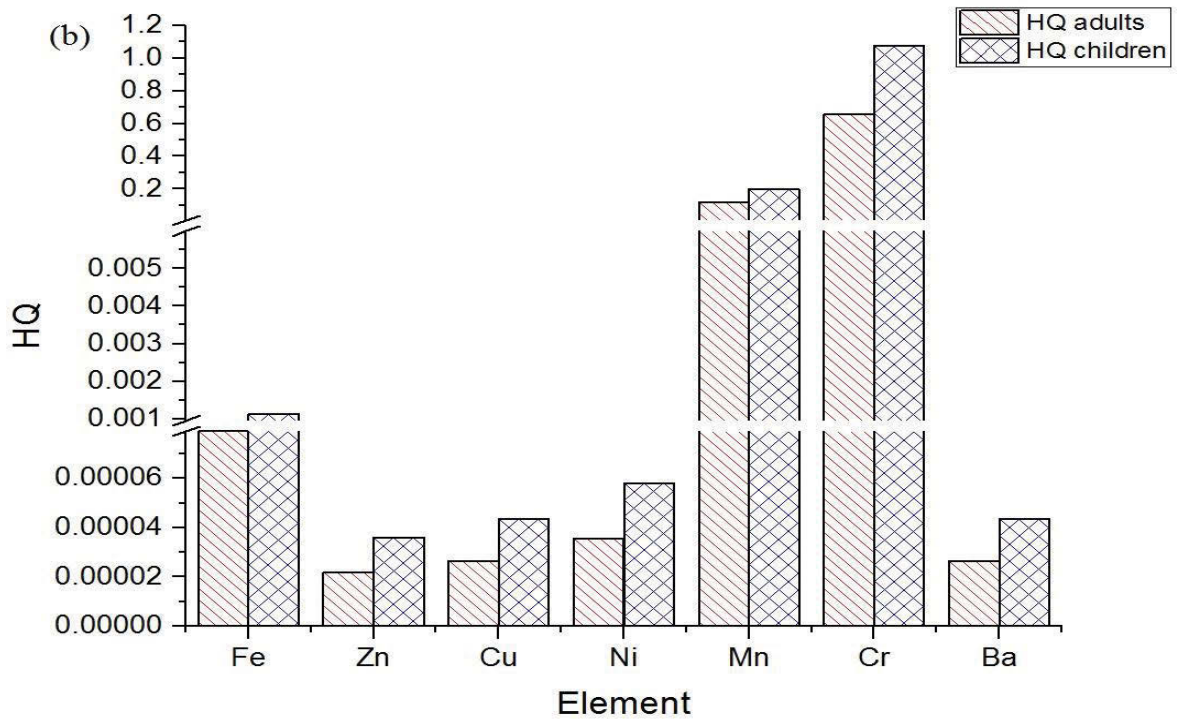
Figure 5.3 HQ values for seven metals via three exposure pathways for adults and children. (a) HQ via ingestion. (b) HQ via dermal contact. (c) HQ via inhalation.

Table 5.5 HI values for Fe, Zn, Cu, Ni, Mn, Cr, Ba via three different exposure pathways for adults and children.

	HI_{adults}	$HI_{children}$
Ingestion	5.32E-01	1.24E+00
Dermal contact	7.78E-01	1.27E+00
Inhalation	4.42E-03	1.35E-02
Combined	1.31E+00	2.53E+00

5.2.2.3 Cancer risk (CR) assessment

Carcinogenic risk assessment using CR for two metals is presented in Table 5.6. The slope factors values through dermal contact or ingestion pathways for the examined metals have not been determined by any regulatory agency. Therefore, CR values for children and adults were only determined via inhalation based on the $ADD_{carcinogenic}$ values from Tables 5.3 and 5.4. Due to the lack of information about the SF values for many metals, only the Ni and Cr cancer risks were determined in this study. The CR value for Ni in adults and children indicates a negligible potential cancer risk (about 3 cancer patients among 1000 million people occur), since it was significantly under the acceptable limits set by the US EPA (10^{-4} - 10^{-6}). The CR value in adults for Cr was less than the acceptable limits. However, for children the CR value was within the acceptable regulatory limits for children indicating a very low potential to pose carcinogenic problems. Combined CR values for Ni and Cr were also considered to be within the acceptable limits for adults and children with no potential to cause any carcinogenic risks. In general, metal concentrations in PM from the Sydney platforms were within the

threshold (10^{-6}-10^{-4}), and there is no concern at these levels of Ni and Cr for commuters or workers to develop carcinogenic problems from long-term or short term exposure. However, there is a need to include all other enriched elements to build better estimation about the potential carcinogenic risks in the Sydney railway system.

Table 5.6 Cancer Risk (CR) values via inhalation exposure pathway in adults and children based on Ni and Cr concentrations from Sydney railway platforms.

Element	SF	CR_{adults}	$CR_{children}$
Ni	8.40E-01	2.96E-09	9.05E-09
Cr	4.20E+01	3.80E-06	1.16E-05
Combined	-	3.80E-06	1.16E-05

5.3 Qualitative Risk Assessment

To overcome the limitations from the quantitative risk assessment due to the scarce and limited information about some chemical values like the cancer slope factor, a qualitative risk assessment will be applied in this part to assess the risks from the rest of the enriched elements (Zn, Fe, Mn, Ba, Cu) which have no SF values. The qualitative risk assessment is a simple method to manage potential risks using a relative or descriptive scale to measure the probability of risk to occur. The method is very similar to the quantitative risk assessment procedure. However, the main differences are in the hazard identification and risk characterisation methods. To better observe the potential carcinogenic risks in

the Sydney railway, the hazard assessment will be considered by a qualitative description rather than dose-response assessment. While for risk characterisation, a risk justification is used rather than the risk indices ratios.

Qualitative carcinogenic risk assessment was performed based on the ISO 31000 methodology. The ISO 31000 approach for risk assessment concerns about risk source separately and to achieve that three steps should be applied to produce efficient risk assessment: risk identification, risk analysis and risk evaluation (Card et al., 2014; Purdy, 2010).

5.3.1 Risk identification

Seven elements were found to be enriched in this study; two of them were assessed against their potential carcinogenic effect using the CR method. The other five elements (Zn, Fe, Mn, Ba, Cu) carcinogenic effects were qualitatively assessed. The assessment was conducted for three different populations based on their commuting time; these groups are named as follows:

- Group one: refers to people spending many hours weekly in a railway environment working or commuting (e.g. railway workers), so $G1 \geq 20$ h/week.

- Group two: refers to people spending less hours weekly in a railway environment working or commuting (e.g. journeys to and from work), so $20 > G2 > 2$ h/week.

- Group three: refers to people spending limited hours weekly in a railway environment working or commuting (e.g. tourists), so $G3 < 2$ h/week.

From the available literature, the adverse health effect from exposure to any of the five metals was identified separately with the aim of identifying the severity of risk in each group.

➢ Zinc (Zn)

Different health problems have been associated with exposure to excess zinc (> 2.3 g in the adult body) such as gastrointestinal and respiratory problems (Chasapis et al., 2012; Plum et al., 2010). Prostate cancer risks can be developed by excess exposure to zinc but generally this element has not been considered as a toxic metal nor causative agent for other carcinogenic problems (Leitzmann et al., 2003; Plum et al., 2010). The US EPA has stated in its toxicity review for Zn that the available information was inadequate to estimate the association between cancer and zinc exposure (US EPA, 2016).

➢ Iron (Fe)

Iron is an essential element in the human body at certain levels. Recommended dietary allowances for Iron set by the Food and Nutrition Board (FNB) is up to 18 mg/day (Institute of Medicine, 2002). However, elevated intakes of iron can cause chronic and acute health problems such as mortality, cardiovascular diseases and liver failure (Coates et al., 2016; Zacharski et al., 2008). The carcinogenic effect of Iron is still unclear. However, previous epidemiological studies have shown a positive correlation between iron and colon cancer (Cho et al., 2013; Muthunayagam et al., 2009).

➢ Manganese (Mn)

Human bodies need Mn at certain levels as an essential antioxidant cofactor. the Australian National Health and Medical Research Council recommendation for Mn is up to 5.5 mg/day depends on the age and gender (NHMRC, 2006). Mn is also well-known as a toxic element at excessive exposure levels over time (Trumbo et al., 2001). Elevated exposure to Mn through ingestion or inhalation can directly affect the nervous system causing neurologic and psychiatric disorders such as Parkinsons disease and violent behaviour (Dobson et al., 2004; McMillan, 1998). However, Mn has not been classified

as a carcinogenic substance to humans based on studies from the WHO and US EPA (Slob et al., 1996; US EPA, 2016).

➢ Barium (Ba)

Barium has been classified as a highly toxic element for human in case of long term and acute exposure mainly affecting the respiratory system (Ananda et al., 2013; Bhoelan et al., 2014). Barium is a well-known metal for affecting the potassium infusion in the blood leading to difficulty in breathing and respiratory problems (Ananda et al., 2013). For the carcinogenic risk assessment, until the time of this study the US EPA has considered Br as a non- carcinogenic substance for humans (US EPA, 2016).

➢ Copper (Cu)

Copper is an essential element for human health and like other elements excess exposure to Cu can cause different health problems. There is a lack of information about the effect of Cu but some recent studies stated an adverse effect on the liver function and a probability to initiate neurodegeneration diseases (Araya et al., 2007; Uriu-Adams and Keen, 2005). No statically significant results of excessive exposure to Cu causing carcinogenic problems were observed in the US EPA studies on mice and no risk assessment on humans was available until the time of this study (US EPA, 2016).

5.3.2 Risk analysis

After identifying the risks that could occur from exposure to five elements, risk analysis will be the second step in the qualitative risk assessment. This step provides an input to help the decision-makers to determine whether the risk requires any action or not depending on the likelihood of occurrence and the severity of risk. Figure 5.4 illustrates the likelihood- consequence matrix designed for the purpose of this study.

	Consequence				
Likelihood	**Insignificant**	**Minor**	**Moderate**	**Major**	**Severe**
Almost certain	Moderate	High	High	Extreme	Extreme
Likely	Moderate	Moderate	High	High	Extreme
Possible	Low	Moderate	Moderate	High	Extreme
Unlikely	Low	Moderate	Moderate	Moderate	High
Rare	Low	Low	Moderate	Moderate	High

Figure 5.4 Risk analysis matrix based on the ISO31000 method.

5.3.3 Risk evaluation

Risk evaluation is the last step in the qualitative risk assessment which involves the characterisation of the risk level based on pre-developed criteria. Risk evaluation cannot reduce the effect of a risk if it happened, it only works as a guide for regulatory and decision makers to reduce the likelihood of a risk to occur (Covello and Merkhoher, 2013). Risk evaluation has been derived by considering the risk identification of each element in each group with the likelihood-consequence analysis using Figure 5.4. The group classification and the element enrichment factor used to consider the likelihood of occurrence have been considered based on the US EPA and the literature recommendations for an element to develop carcinogenic health issues. For example, Mn risk likelihood is considered to be unlikely to occur for group one if we consider long term exposure (G1 ≥ 20 h/week) is a minor consequence effect following the US EPA and other studies recommendations. However, the likelihood of Mn risk for group two

and three is classified as rare if we consider the short term exposure of less than 20 h, and its exposure consequence is considered as minor following the US EPA and other studies' recommendations.

The results have been illustrated in Table 5.7 with three risk evaluations for each element based on each population group. The potential carcinogenic risks from five metals ranged from low to moderate. Only Zn showed a moderate potential risk to occur in group two, the rest of the elements and all the results from group three showed a low potential for cancer risks.

A limited number of studies have examined the carcinogenic effect from metals in the railway systems. However, these studies indicated a negligible carcinogenic risk from a number of enriched elements. While the results of group one indicated a moderate potential risks for all elements except Cu. Results from the Chapter 4 showed that the Fe enrichment factor was approximately triple the value of Cu. However, these two elements share the same potential to cause a cancer risk in the Sydney railway environments if we consider the consequence effect from these elements in addition to the likelihood of occurrence. The results from this assessment cannot be generalised due to the lack of accumulative risk assessment for all potential carcinogenic contaminants. However, it gives an indication about the potential of some elements to develop a cancer risk.

Table 5.7 Carcinogenic risk evaluation for five metals based on three population groups.

	Group One	Group Two	Group three
Zn	Moderate	Moderate	Low
Fe	Moderate	Low	Low
Mn	Moderate	Low	Low
Ba	Moderate	Low	Low
Cu	Low	Low	Low

5.4 Conclusions and Recommendations

The carcinogenic and non-carcinogenic risk assessment of seven metals (Fe, Zn, Cu, Ni, Mn, Cr, and Ba) found in enriched levels in the Sydney railway systems have been studied. A non-carcinogenic risk assessment was investigated by calculating the HQ and HI values based on the metals concentrations results from Chapter Four. The results indicated that children are more susceptible to develop non-carcinogenic health problems mainly due to finger sucking and pica behaviour. HQ values indicated no potential risk from any metal except for Cr with a HQ value of just above one. However the cumulative risk for adults and children using HI indicates minor non-carcinogenic risk potential. Carcinogenic risk is determined by two different methods to overcome the problem of undefined SF values. Using the CR method, Ni and Cu cancer risk assessments were within the acceptable limits set by the US EPA for children and adults. For the rest of the metals, a qualitative risk assessment was applied based on the ISO31000 method. The results also indicate low to moderate potential carcinogenic risks from Zn, Fe, Mn, Ba

and Cu. To better understand the potential health risks in the Sydney railway, there is a need for more comprehensive studies, including the risks from organic contaminants such as polycyclic aromatic hydrocarbons. The combined adverse effects of organic and inorganic contaminants will provide a more comprehensive estimate for contamination-related health risks.

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Chapter 6. Conclusions, Limitations and Recommendations for Future Work

Due to the limited knowledge of PM pollution from railway systems, it is necessary to conduct research to assess PM levels and their effect in the railway environments of Sydney. PM has the potential to cause substantial adverse effects on human health. This thesis focuses on PM exposure assessment for commuters and workers in the Sydney railway system. The airport line (T2) was selected to represent unique microenvironments of the railway system (underground and ground level particles). The main aim of the study was to assess the particle concentrations, metal composition in PM, and their potential health risks based on field data collection and laboratory chemical analysis.

6.1 Summary on PM Concentrations

Chapter 3 focused on the mass concentrations of PM_{10} and $PM_{2.5}$ based on the dust track real time measurements on the underground and ground levels, data were collected from the platforms and the train carriages. Results indicated that average underground PM_{10} and $PM_{2.5}$ concentrations from inside the trains were 2.8 and 2.5 times greater than the ground levels measurements. Similarly, PM_{10} and $PM_{2.5}$ concentrations on the underground platforms were 2.7 and 2.5 times greater than ground level platforms. Unlike ground level concentrations, average underground PM levels have exceeded the national limits for both PM_{10} and $PM_{2.5}$ over the study period. However, these measurements represent the rush hour concentrations only, which may be significantly decreased by monitoring PM over 24 h. Correlation analysis showed a moderate to strong association between ambient background and ground level PM (r^2, 0.50 - 0.952,) and weak association with the underground concentrations with a maximum r^2 value of 0.264. This finding suggests that underground PM concentrations are less influenced by the ambient

than the ground level particles. The main sources of PM at underground levels are likely from local railway operation processes.

6.2 Summary on Metal Composition in PM

Chapter 4 focused on the metal composition of PM collected from the underground platforms. After the dust samples extraction and preparations processes, metal composition was considered by the Microwave Plasma-Atomic Emission Spectroscopy (MP-AES). Results were obtained based on the different pollution indices (PI, IPI, and EF). Fe was the most abundant element based on all three indices. PI and IPI results indicated high potential to cause environmental contaminations from the particle metals components. EF values for Fe, Ni, and Cr indicated that the metals' sources are mainly from the local railway operation processes such as the wear and abrasion of the steel tracks and brakes pads. However, Mn, Ba, Zn and Cu sources are a combination from crustal origin and the railway. The rest of the elements are mainly derived from crustal origins.

6.3 Summary on Risk Assessment

Two risk assessments are presented in Chapter Five (quantitative and qualitative risk assessments). However, the results were derived based on the potential health effects as follows:

6.3.1 Non-carcinogenic risks

Results were shown based on the HQ and HI method developed by the US EPA. In general, HQ results indicated that children are more susceptible to develop non-carcinogenic health problems than adults. Based on the HQ analysis of seven metals, there is no indication for potential risks at the examined levels from any metal except in Cr (HQ > 1). However the cumulative risk index (HI) indicated a minor potential to cause

non-carcinogenic health problems in adults and children. Fe was the most enriched element, however in the risk assessment results Cr was the main contributor to cause potential health problems. These results indicate that the health risks associated with any metals are dependent on their concentration levels as well as their potential to cause health problems.

6.3.2 Carcinogenic risks

The carcinogenic risk assessment for the enriched element was considered based on two methods. The US EPA quantitative method applied on two metals (Ni and Cr) using the CR index. Results indicated that CR values for the two metals were within or less than the allowable limits. For the rest of the elements (Zn, Fe, Mn, Ba, Cu), a qualitative risk assessment has been applied to consider the cancer risk factor. The examinations were based on three population groups: group one with the highest commuting time followed by group two and then group three with the least commuting time. Results indicated that people who usually use the underground railways could be susceptible to develop a cancer risk from Zn, Fe, Mn and Ba but not from Cu where the cancer risk is classified as low.

6.4 Limitations of the Current Study

- PM was collected from four different railway microenvironments in the Sydney railway system. All data were collected during rush commuting hours (9am – 5pm) on seven consequent weeks from the same line (T2 line). Due to the limited resources availability, concurrent sampling at all four microenvironments was not possible. Only one dust track model was available for the study, and only one person was able to collect the data due to the sampling approval conditions from Sydney Trains authorities. Therefore, temporal or seasonal variations during the sampling period

could affect the particles levels at each microenvironment. However, all data was collected during one season with insignificant temperature changes.

- For the chemical analysis and risk assessment results, PM samples were analysed for their metals components only due to the given time frame of this study. Following recommendations from other subway PM studies, the most abundant and enriched element in the subway particles were metals components (Aarnio et al. 2005; Grass et al. 2010; Seaton et al. 2005). Therefore, in this study twelve metals have been investigated. For more comprehensive understanding about the potential health risks, the inclusion of organic contaminants (e.g. PAHs) would be beneficial to support the health risk assessment results.

- For the metals analysis, dust samples were used to represent the particles size of 75μm and less. No fractionation was done to get PM_{10} and $PM_{2.5}$ samples due to the limited resources availability (sieve size) and also due to the limited amounts of dust which can be collected on each sampling day.

- Metals components were measured by using dust samples. The results would be more accurate if the samples were collected by using air-impactors. However, using air impactor is a time consuming method. Due to the limited time frame for this study, dust samples method were used for the metal composition analysis.

6.5 Recommendations for Future Research

To build a better understanding about PM levels and their health effects, a comprehensive study about how and what particles' properties are the most significant is required. Considering these factors are very important to guide future practices in reducing the particles effect. Perhaps results of this study representing data from the worst-case scenario (e.g. peak-hours sampling, busiest line) can help. However for future studies, these results can be more useful if data are collected concurrently for 24 h over one year

of sampling from more railway stations to investigate the temporal and seasonal variations impact. This would be a valuable extension for the current research, and comparisons with the national air quality standards would be more accurate.

For the risk assessment results, future studies should include all hazardous chemicals in one study. The potential health impact should be based on cumulative risk assessment indications from all chemicals (e.g. metals, PAHs).

For regulatory advancement, results from the current study indicated that PM in the underground microenvironments was mainly from local railway sources based on the enrichment factors values. The main attributers were the ventilation system on the platforms and the air conditioning efficiency inside the train carriages. High standard deviation values inside the train carriages were attributed to the significant effect of the platforms air quality. Therefore, new implementations to improve these issues should take place in future planning to enhance the airflow and the air quality in the railway systems.

6.6 References

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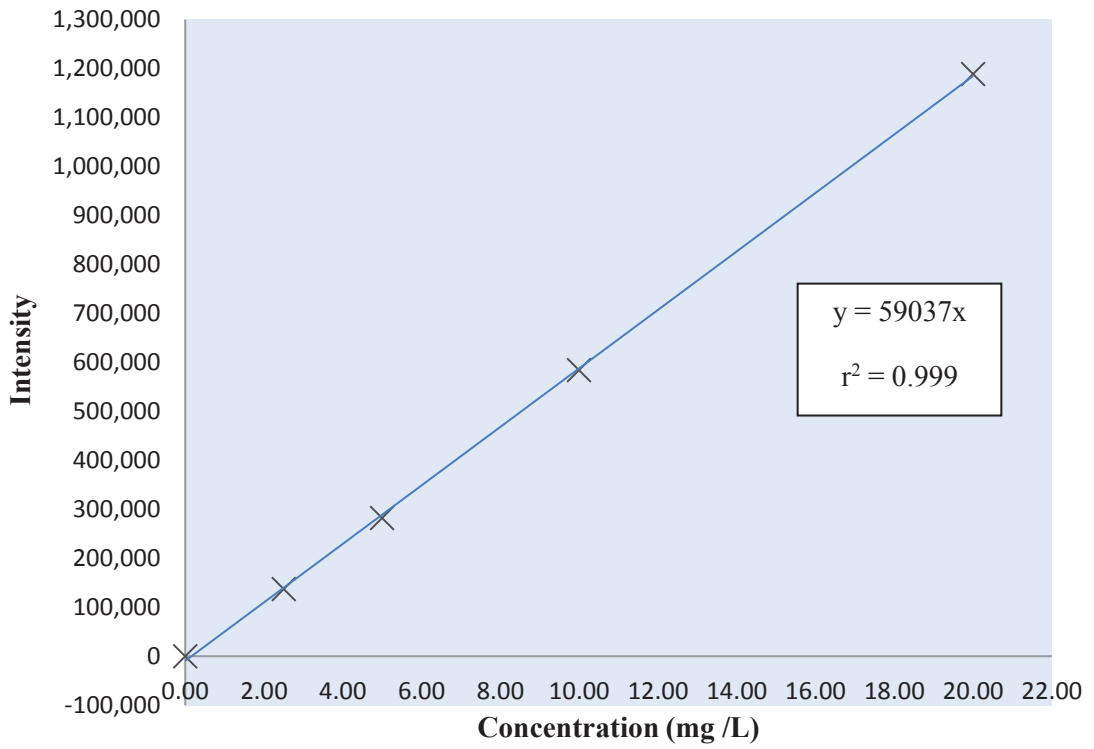
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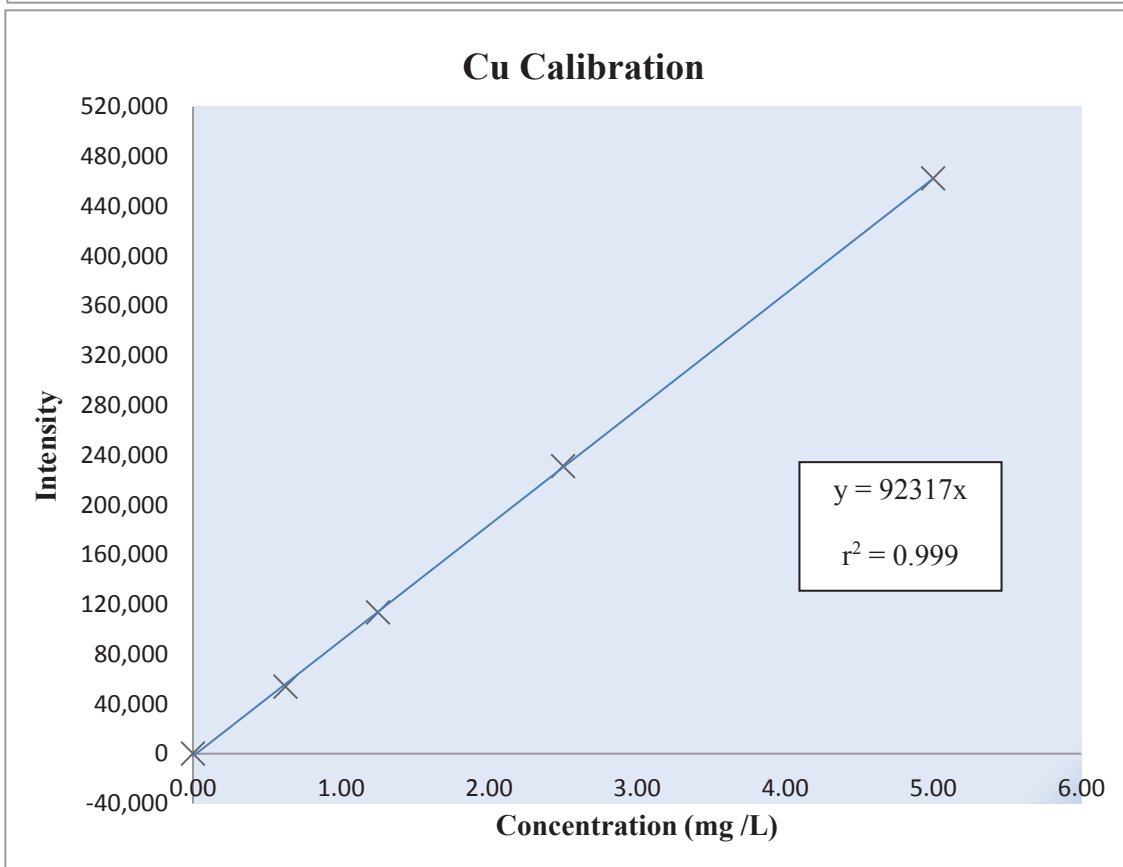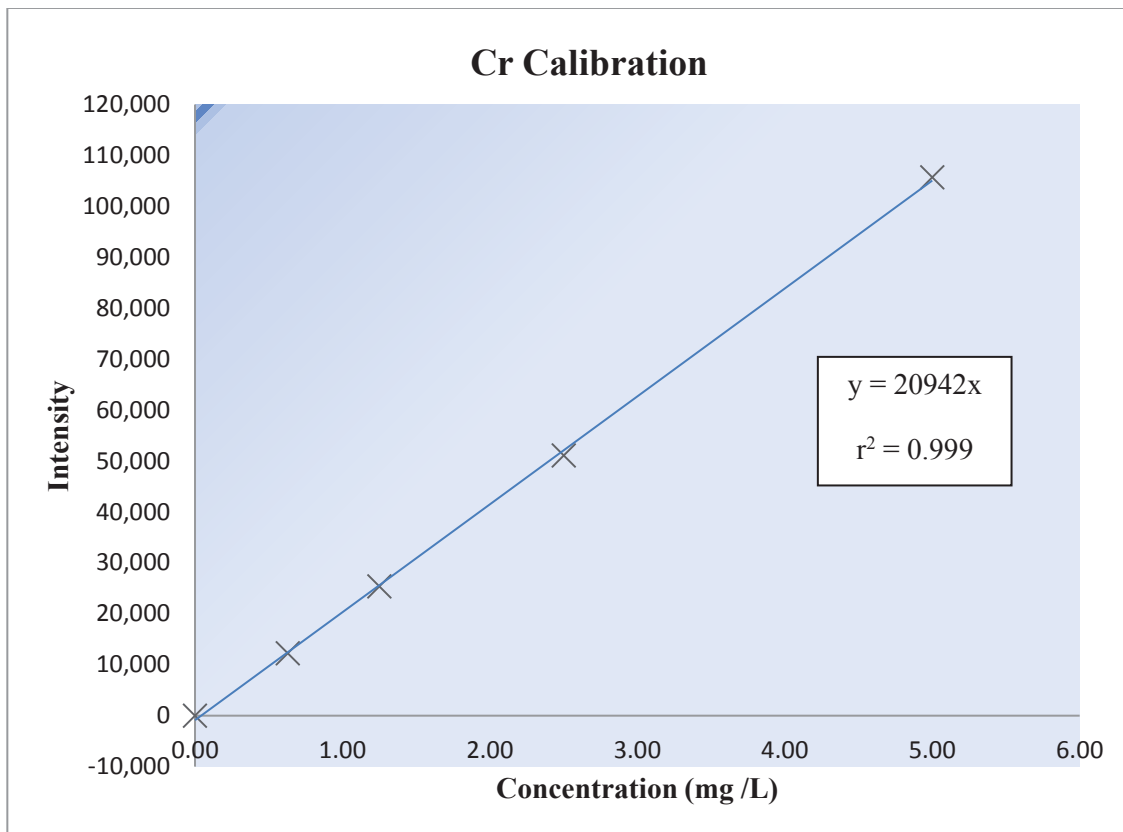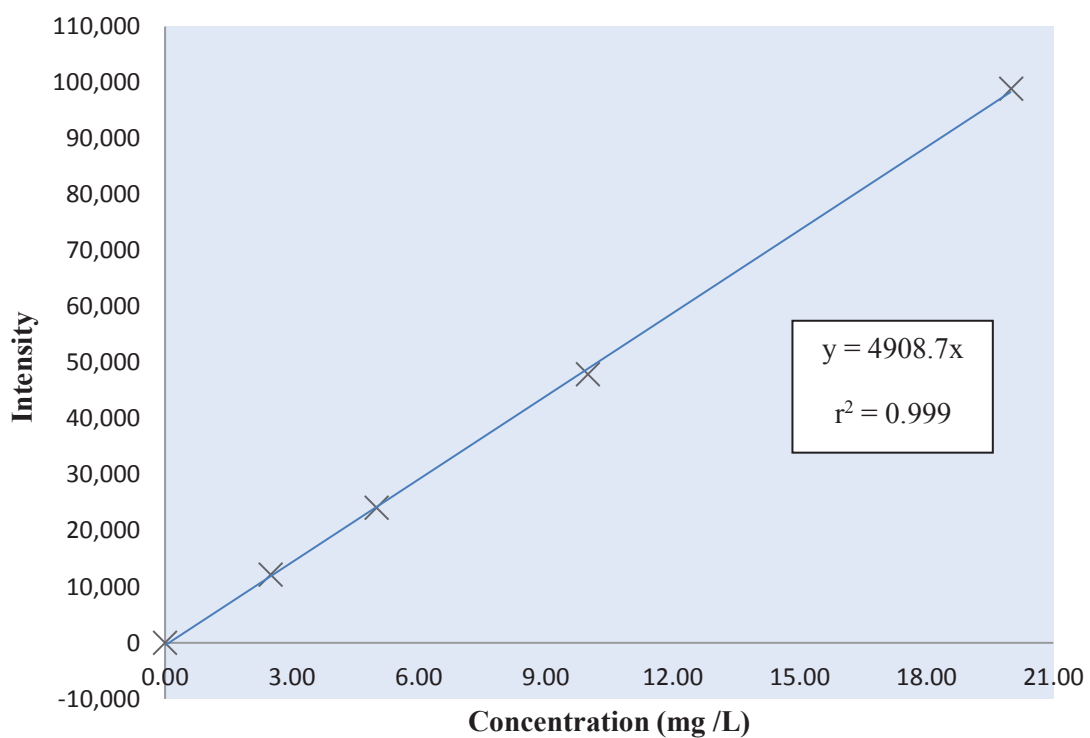
Appendix A-1

Al Calibration

y = 12746x

$r^2 = 0.999$

Intensity vs. Concentration (mg /L)

Ba Calibration

y = 55427x

$r^2 = 0.999$

Intensity vs. Concentration (mg /L)

Ca Calibration

y = 59037x
r² = 0.999

Co Calibration

y = 7082.6x
r² = 0.999

Cr Calibration

$y = 20942x$

$r^2 = 0.999$

Cu Calibration

$y = 92317x$

$r^2 = 0.999$

Fe Calibration

y = 4908.7x

$r^2 = 0.999$

Mn Calibration

y = 23033x

$r^2 = 0.996$

Na Calibration

y = 167813x

r² = 0.992

$$y = 167813x$$
$$r^2 = 0.992$$

Intensity

Concentration (mg /L)

Ni Calibration

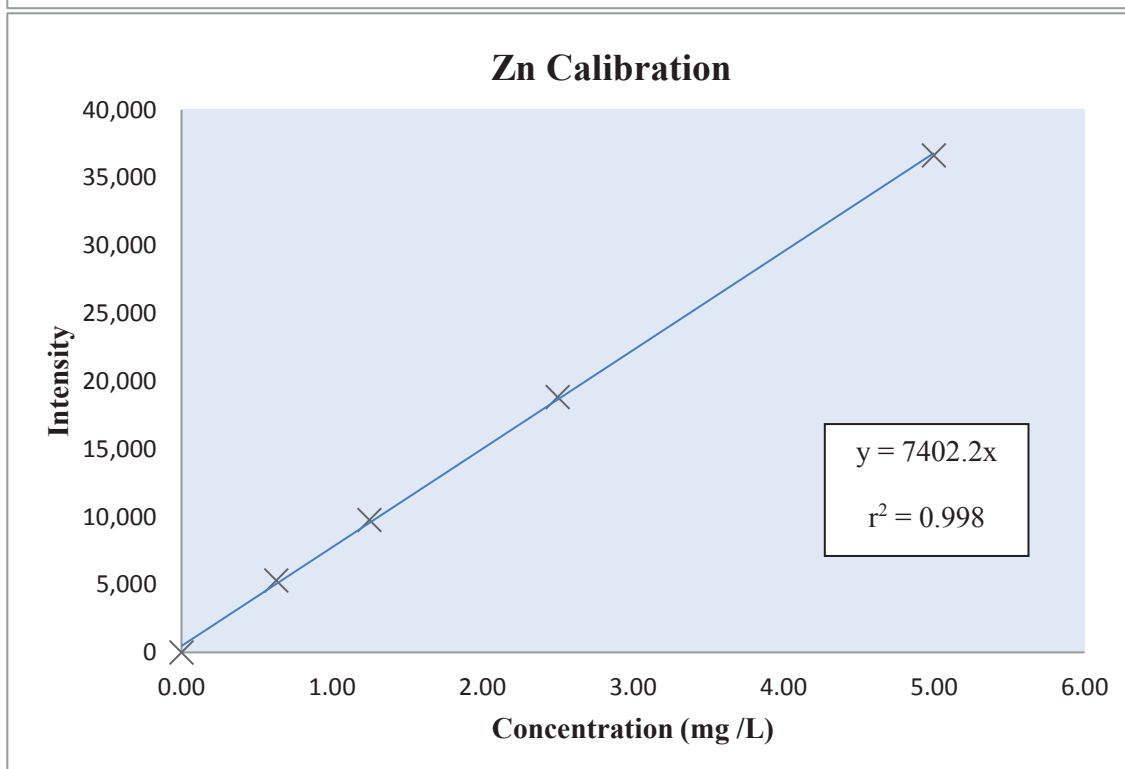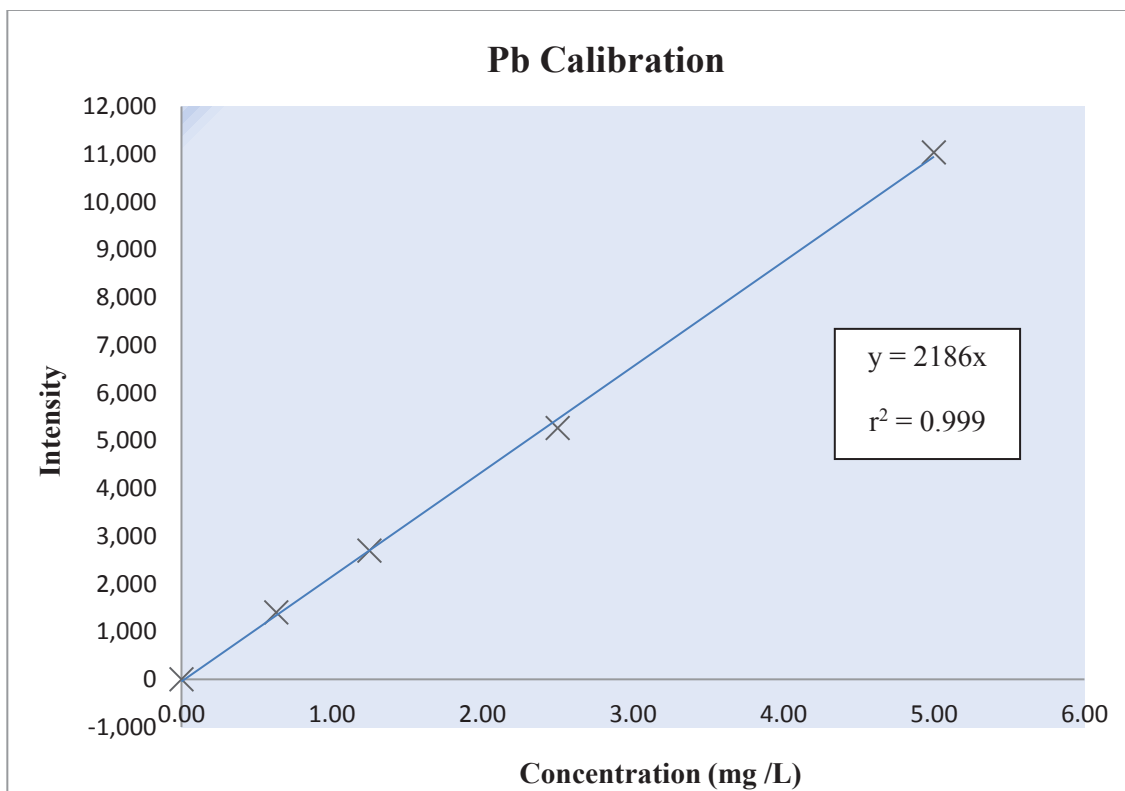$$y = 13603x$$
$$r^2 = 0.999$$

Intensity

Concentration (mg /L)
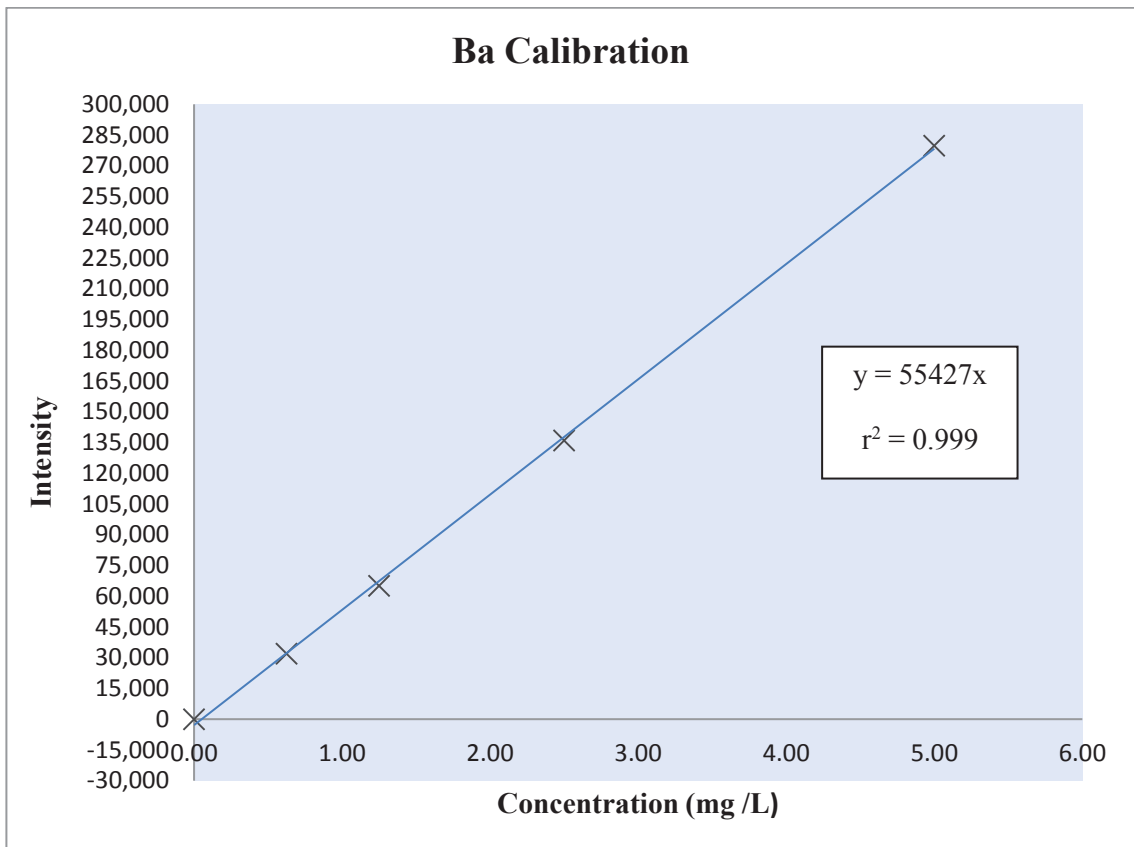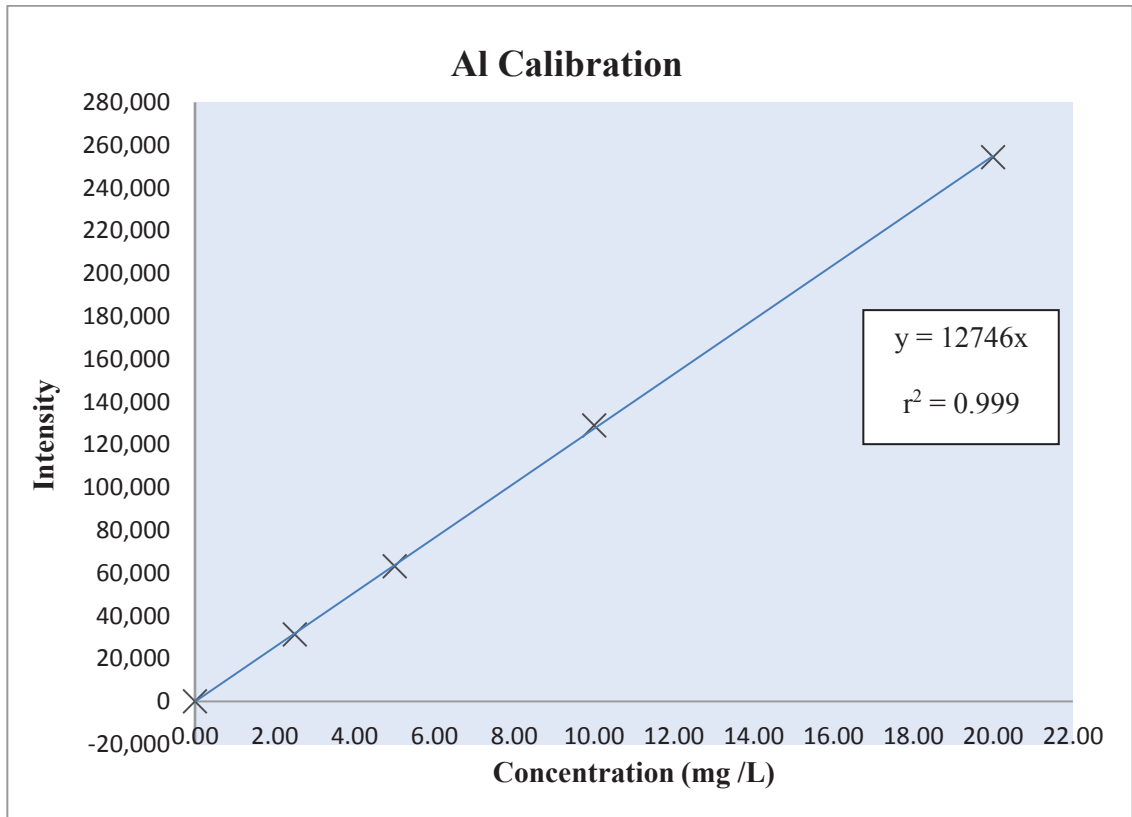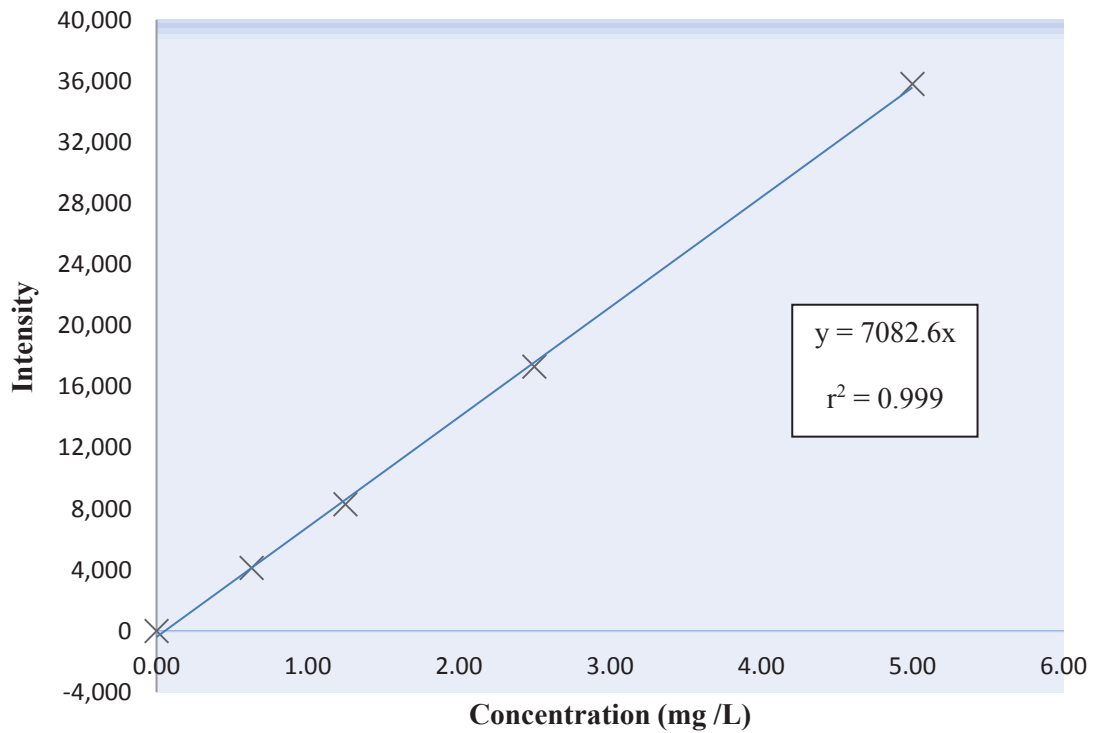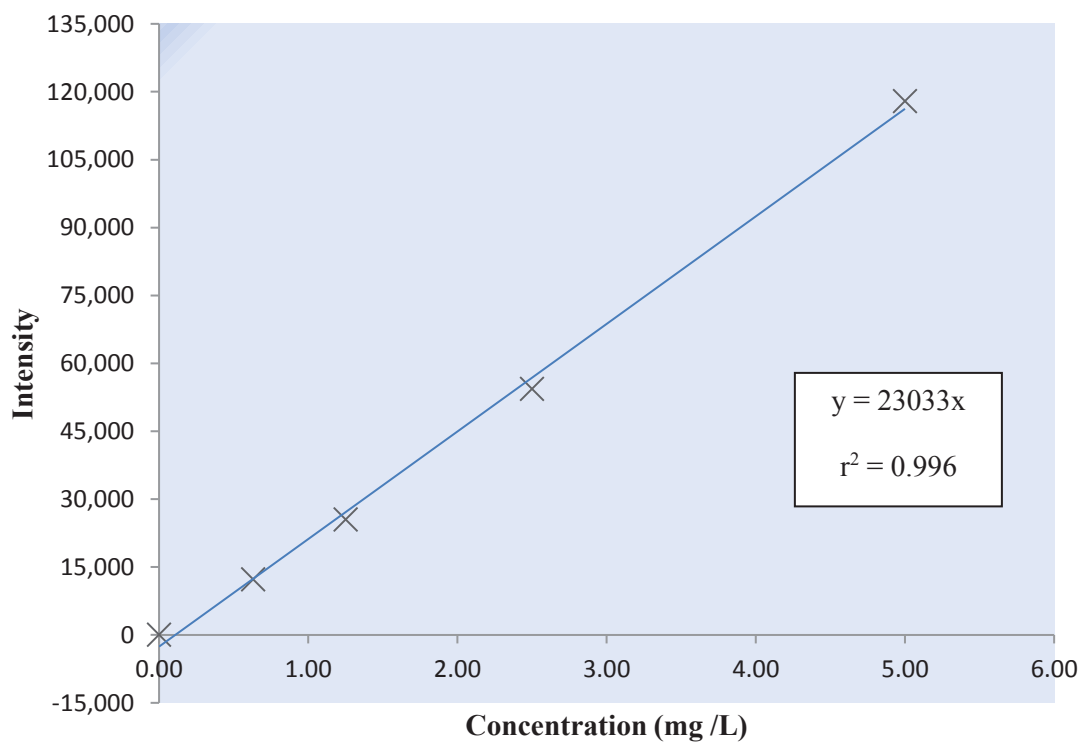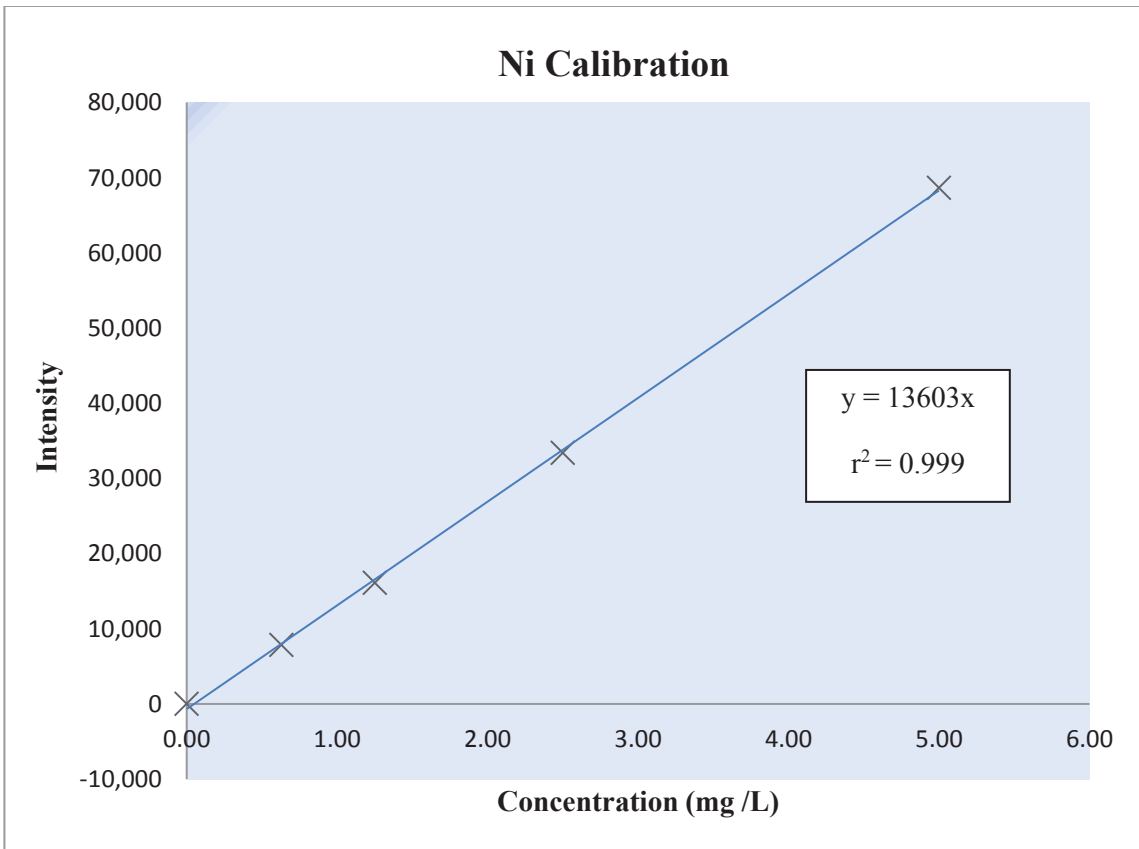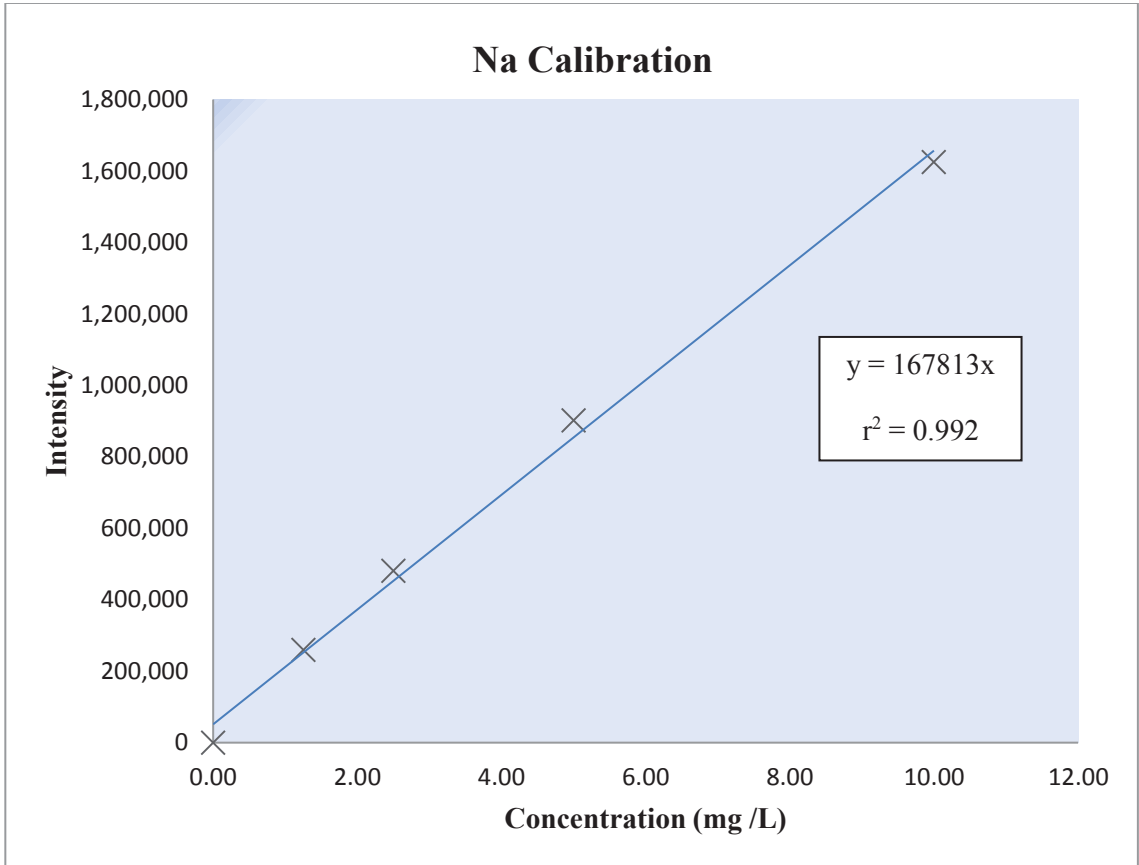
Figure A.1 Calibration graphs for each element with its maximum wavelength measured by MP-AES: Al (396.152 nm), Ba (455.403 nm), Ca (393.366 nm), Co (340.512 nm), Cr (425.433 nm), Cu (324.754 nm), Fe (371.993 nm), Mn (403.076 nm), Na (588.995 nm), Ni (352.454 nm), Pb (405.781 nm), Zn (213.857 nm).