

# **Impacts of iron and steel making facilities on soil quality**

**Chandrakant Chaudhary**  
**Department of Environmental Sciences**  
**Faculty of Science and Engineering**  
**Macquarie University**  
**9<sup>th</sup> October, 2015**

I hereby declare that this thesis has not been previously submitted to any other institution or university for higher degree. Except where otherwise acknowledged, this thesis is comprised entirely of my own work.

A handwritten signature in black ink, appearing to read 'Chandrakant', with a horizontal line underneath.

**Chandrakant Chaudhary**

**October 9, 2015**

## **Acknowledgements**

Firstly, I would like to thank my supervisor Prof. Vladimir Strezov for his continuous guidance and support during the thesis work. His valuable comments and suggestions helped me for improving the quality of my research.

I also like to express my gratitude to Dr. Tao Kan who helped me from the beginning of the research until end in the laboratory analysis and giving thoughtful suggestions. Also, I want to thank Aal-E Ali for helping me in the field visit, sampling and for his valuable suggestions for research.

I also cannot stop thanking my MRes colleagues Nirodha, Niru and Shaun for their constant support and keeping friendly environment during the research period.

# Contents

List of figures .....	v
List of tables.....	vi
Acronyms and abbreviations.....	vii
Abstract.....	ix
Chapter 1: Introduction.....	1
1.1 Aims and Objectives.....	2
1.2 Significance of the study.....	3
1.3 Outline of Study.....	3
Chapter 2: Literature Review.....	4
2.1 Emission from non- ferrous smelters on soil.....	4
2.2 Emission from ferrous smelters on soil.....	10
2.3 Emission from other sources on soil.....	11
Chapter 3: Materials and Methods.....	15
3.1 Study Area.....	15
3.2 Selection of Sampling Sites.....	17
3.3 Sampling Procedure.....	19
3.4 Laboratory Procedure.....	19
3.4.1 Sample Preparation.....	19
3.4.2 Soil Analysis.....	19
Chapter 5: Results.....	24
5.1 Proximate Analysis of soil.....	24
5.1.1 Moisture content.....	24
5.1.2 Volatile matter.....	25
5.1.3 Ash .....	25
5.1.4 Fixed Carbon.....	26
5.2. Acid Extractable elements on soil.....	26
5.2.1 Trace metals mercury, cadmium, and molybdenum concentration.....	26
5.2.2 Trace metal arsenic concentration in the soils.....	29
5.2.3 Heavy metals chromium, copper, lead, nickel, and zinc concentration.....	30

5.2.4 Titanium concentration.....	32
5.2.5 Iron concentration.....	34
5.2.6 Manganese concentration.....	35
5.2.7 Sodium, Potassium, and Magnesium concentration in soils.....	36
5.2.8 Phosphorus, Sulphur and Silicon concentrations in the soils.....	39
5.3 FTIR spectroscopy of Soils.....	41
Chapter 6:	
Discussion.....	44
6.1 Trace metals mercury, cadmium, molybdenum and arsenic distribution.....	44
6.2 Heavy metals chromium, copper, lead, nickel, zinc, titanium, iron and manganese concentrations.....	45
Chapter 7: Conclusion and Recommendations.....	
7.1 Conclusion.....	50
7.2 Recommendations .....	51
References.....	52
Appendices.....	53
Appendix 1- NEPM 2011 Schedule B(1)- Health investigation levels for soil contaminants.....	53

## List of Figures

Figure 3.1	Map of the study area	15
Figure 3.2	Map of sampling sites near the Rooty Hill Steelworks	16
Figure 3.3	Map of sampling sites near the Port Kembla Steelworks	16
Figure 3.4	Map of the sampling site at Macquarie Park	17
Figure 5.1	Trace metal (molybdenum) concentration in the soils near the Rooty Hill Steelworks, Port Kembla and Macquarie Park	29
Figure 5.2	Trace metal Arsenic concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park	30
Figure 5.3	Heavy metals concentration in the soils near the Rooty Hill Steelworks and Macquarie Park	32
Figure 5.4	Heavy metals concentration in the soils near the Port Kembla Steelworks and Macquarie Park	32
Figure 5.5	Titanium concentration in the soils near the Port Kembla Steelworks and Macquarie Park	33
Figure 5.6	Titanium concentration in the soils near the Port Kembla Steelworks and Macquarie Park	34
Figure 5.7	Iron concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park	35
Figure 5.8	Manganese concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park	36
Figure 5.9	Sodium, Potassium and Magnesium concentration in the soils near the Rooty Hill Steelworks and Macquarie Park	38
Figure 5.10	Sodium, Potassium and Magnesium concentration in the soils near the Port Kembla Steelworks and Macquarie Park	38
Figure 5.11	Phosphorus, Sulphur and Silicon concentration in the soils near the Rooty Hill Steelworks and Macquarie Park	40
Figure 5.12	Phosphorus, Sulphur and Silicon concentration in the soils near the Port Kembla Steelworks and Macquarie Park	40
Figure 5.13	FTIR spectra of soils near the Rooty Hill Steelworks	42
Figure 5.14	FTIR spectra of soils near the Port Kembla Steelworks	43
Figure 5.15	FTIR spectra of soil of the Macquarie Park	43

## List of Tables

Table 3.1	List of sampling sites, their coordinates and distances from steel and iron industry	18
Table 5.1	Proximate values of soil near the Rooty Hill Steelworks	24
Table 5.2	Proximate values of soil near the Port Kembla Steelworks and Macquarie Park	25
Table 5.3	Mean, range, standard deviation and NEPM 2011 guideline values for trace metals, heavy metals and other elements in mg/kg	28

## Acronyms and abbreviations

AAS- Atomic Absorption Spectroscopy

Ag –Silver

Al – Aluminium

As- Arsenic

AS-Australian Standard

ASTM- American Society for Testing and Materials

Ba – Barium

Be- Beryllium

Ca- Calcium

Cd-Cadmium

Ce -Cerium

Co- Cobalt

Cr- Chromium

Cs- Cesium

Cu- Copper

CV-AAS-Cold Vapour- Atomic Absorption Spectroscopy

Dy-Dysprosium

Er-Erbium

FC- Fixed Carbon

Fe-Iron

FTIR- Fourier Transform Infrared

Ga- Gallium

Gd-Gadolinium

Ge-Germanium

Hg- Mercury

ICP-AES- Integrated Coupled Plasma- Atomic Emission Spectroscopy

ICP-MS - Integrated Coupled Plasma- Mass Spectroscopy

K- Potassium

Km- Kilometer

La- Lanthanum

Li-Lithium

Mg-Magnesium



Mn- Manganese  
Mo-Molybdenum  
Na-Sodium  
Nb- Niobium  
Nd- Neodymium  
NEPM- National Environment Protection Measure  
Ni-Nickel  
NSW- New South Wales  
Pb- Lead  
P-Phosphorus  
Pr Prasedymium  
QA- Quality Assurance  
QC- Quality Control  
Rb- Rubidium  
S-Sulphur  
Sb – Antimony  
Si- Silicon  
Sm- Samarium  
Sn- Stannum  
Sr- Strontium  
Tb- Terbium  
Th- Thorium  
Ti- Titanium  
Tl-Thallium  
U- Uranium  
USEPA-United States Environmental Protection Agency  
V- Vanadium  
VM- Volatile Matter  
W-Tungsten  
Y -Yttrium  
Yb-Ytterbium  
Zn- Zinc  
Zr- Zirconium

## **Abstract**

The iron and steelworks at Rooty Hill and Port Kembla, NSW, Australia may be emitting heavy and trace metals to the environment. However, their emissions on soil have remained unstudied. This study investigates the trace metals and heavy metals in soils near the two steelworks as compared to the background site at Macquarie Park and also whether the soils from these sites exceed the NEPM 2011 guideline. The proximate, acid extractable elements analysis and Fourier Transform Infrared Spectroscopy (FTIR) were performed for soil analysis. Acid extractable elements analysis for the trace metals and heavy metals showed no considerable difference in trace metals at all sites. However, there was higher concentration of chromium, copper, lead, nickel, zinc, titanium and iron at Port Kembla as compared to Rooty Hill. Rooty Hill had higher concentration of manganese. Furthermore, all the sites had lower concentrations of trace metals and heavy metals with reference to the NEPM guideline 2011, except for molybdenum, titanium and iron which lack guidelines. This study suggests that soils near Port Kembla steelworks have higher heavy metal concentrations as compared to Rooty Hill. Also, the guideline should be established for all heavy metals including molybdenum, titanium and iron due to their high concentrations in soils.

**Key words:** NEPM guideline, heavy metals, trace metals, concentration

## Chapter 1: Introduction

Steel and iron are important metals which have wide use in our modern world. However, there are several environmental problems associated with the production of iron and steel as their processing emits heavy metals to an environment. Rivers and urban environment can be contaminated with heavy metals, like zinc, cadmium, copper and lead, due to historic industrial and mining operations (Hudson-Edwards et al. 2001). Some of the metals which are emitted in the environment near smelters are arsenic, copper, manganese, selenium, zinc and lead (DEC NSW 2005; Standards Australia 2005). The percentage of iron particles in air increases significantly near the iron and steel smelters (Mohiuddin et al. 2014). Not only these, but there are evidences of twice as much as mercury, thrice as much as zinc and copper and six times increase in lead near a road side soil as compared to the background concentrations (Rouillon et al. 2013). Soil contamination near the smelters is a major concern as it is linked with an alternation in soil quality. Freedman et al. (1980) found strong probability that, on increase of soil nickel and copper, it cause retardation on the growth of roots and formation of seedlings on many species of plants. Various smelting and manufacturing activities since the last century have resulted in land contamination around the globe and Australia is no exception from this (Barzi et al. 1996). Some of the areas in Australia which are contaminated with heavy metals due to mining activities are Broken Hill (Lyle et al. 2001), Port Pirie (van Alphen 1999), Wollongong (Martley et al. 2004 a) and Lake Macquarie (Morrison & Gulson 2007). Several studies reveal that contamination with the heavy metals are mainly related to lead, copper and zinc smelters. However, the studies on soil contamination with the iron and steel making industries have not been done in New South Wales and are of concern to study due to heavy metal emission by these industries.

Metals remain in the environment for a long-time as they are not degraded by any physical processes like sunlight, frost and wind. These metals remain in air, water and soil and pass through various biogeochemical cycles such as biotic and abiotic factors. Plants absorb them in the form of minerals from soil and accumulate in their root and shoot system. Different plants accumulate different metals in varied concentrations. Vegetables and cereals constitute about 75% of cadmium in the food chain (Olsson et al. 2005). There is the significant rise of chromium, manganese and lead, in leaf of dandelion (*Taraxacum officinale*) with an increase of metal content in soil (Keane et al. 2001). Furthermore, heavy metals such as zinc, cadmium and lead accumulate significantly in leafy vegetables (*Amaranthus Hybridus* L.) with the heavy metals pollution in soil (Oluwatosin et al. 2010).

There are several health hazards associated with the heavy metals. Human's exposure to the soil heavy metals is mainly through ingestion, inhalation and skin contact (Kasassi et al. 2008). For example, inhalation of iron dust leads to respiratory problems like chronic bronchitis (Xu et al. 1992) and chronic obstructive pulmonary disease (Driscoll et al. 2005). Arsenic has various health effects such as such as cardiovascular, gastrointestinal, dermal, hepatic, and renal effects (Saha et al. 1999). Similarly, copper pollution is associated with Wilson's disease (Randolph & Rotter 1989), and renal damage (van Campen 1991). Zinc toxicity leads to gastrointestinal distress, reduced food consumption, retarded growth, anaemia, poor bone mineralization and arthritis (NRC 1980). Excessive selenium intake and the effects on humans have not been well defined as compared to animals (van Campen 1991). Past studies have revealed that areas with high selenium in the United States do not show any problems (Levander 1986). However, toxicity of selenium in China from 1961 to 1964 showed loss of hair and nail deformities (Yang 1987; Berkow 1992). Manganese toxicity leads to reduced growth, anemia, gastrointestinal lesions and neurological disorders (NRC 1980). Most important to human concern of heavy metals pollution is lead which has impacts on intellectual and neurological functions. The most vulnerable groups of lead pollution are children due to their hand to mouth behaviour and more potentiality of absorption of lead (Koller et al. 2004).

Therefore, to avoid the health hazards and the effects to natural environment i.e., plants and animals, an investigation on the soil quality near steel works is essential. In order to understand the soil quality, this study has the following aims and objectives:

### **1.1. Aims and Objectives**

This study aims to investigate the heavy metals and the trace metals content in the soils near iron and steel smelters in New South Wales. The objectives are:

1. To sample the soils at the vicinities of three areas: Rooty Hill steelworks, Port Kembla integrated iron and steelworks, and Macquarie Park.
2. To test the metals concentrations in the soil samples by performing acid extractable analysis of soil.
3. To perform comparative analysis of the soils from the three sites and validate results with the National Environment Protection Measure (NEPM) guideline 2011 for soil.

## **1.2. Significance of the study**

This research will be able to confirm the amount of heavy metals and trace metals contamination in the study area i.e., near two different smelters: one operated at Rooty Hill as an Electric Arc Furnace and the other at Port Kembla as an integrated iron and steelworks (Blast Furnace-Blast Oxygen Furnace). Comparing the results of the two smelters with the background site (Macquarie Park) with no influence from any industrial activity, it will help in understanding how these smelters are changing the soil quality by adding excess of heavy and trace metals to the soil. The heavy metals and trace metals cause various health hazards to humans and when soil is contaminated they may get exposed to these elements directly due to contact with soil or indirectly through a food chain. Therefore, this study is essential to understand contamination and therefore mitigate the possible contamination by informing about the soil content at the study area.

## **1.3. Outline of Study**

Chapter 1 provides background information on impacts of steel and iron smelters and their effects on soil quality and environment. It also includes aims and objectives of study and presents significance of study.

Chapter 2 highlights the literature review on the soil heavy metals near non-ferrous smelters, ferrous smelters, and other sources that add heavy metals and trace metals to the soils. It also presents the research gap in the field of heavy metals and trace metals content in the soils.

Chapter 3 deals with the materials and methods for soil analysis for this study. It includes methods used for proximate analysis, acid extractable elements analysis, and Fourier Transform Infrared analysis.

Chapter 4 contains the results of the study. Elements such as moisture content, volatile matter, ash content, and fixed carbon are presented. In addition, data related to the trace metals and heavy metals contents are presented. FTIR findings are also illustrated and explained.

Chapter 5 includes the discussion of the heavy and trace metals in the soils by comparing soil content at different sites and with previous studies along with NEPM 2011 guideline.

Chapter 6 includes conclusions of the findings of this study, and recommendations for future research.

## **Chapter 2: Literature Review**

In this chapter, literature review was performed to reveal the emission of heavy metals from the various sources. There are various forms of smelters such as lead, zinc, iron that emit the particulate matter to air which finally get deposited to soil. Others forms of sources are the industrial activities, mining, metallurgical operations and vehicles that emit the heavy metals which come to soil. This literature review will review the methods of soil sampling, analysis and the concentration of the heavy metals on soil near the ferrous, non-ferrous smelters and other sources that add heavy metals to soil.

### **2.1. Emission from non- ferrous smelters on soil**

Cartwright et al. (1976) did their study to know heavy metals contamination near the lead smelter of Australia. The sampling was carried out at 42 sites within an approximately area of 5000 km<sup>2</sup>. At each site, soil was sampled to the depth of 0-5cm and a composite sample was the collection of 10 sub-samples. Atomic absorption spectrophotometry was used for the analysis of some of the metals contents. On analysis, it was revealed that the dispersion of pollutants were as far as 40-65 km depending on directions, but it decreased with the increase in distance from the smelter. Nearer to the smelter, the fall out was consistent with the direction of surface winds. The dispersion of the metals were in a decreasing order for cadmium, lead and zinc. There was no evidence of contamination of copper. Over short distances, soil contamination was as a result of fallout of particulate emissions of variable composition, but beyond about 15km, the heavy metals were dispersed mainly in the form of aerosols.

Henderson et al. (1998) studied the chemical and physical characteristics of heavy metals near the Cu-Zn smelters at Flin flon, Manitoba, Canada. They collected humus and till samples at 23 sites. The till samples were collected from below B horizon, exposed section and from pits up to the depth of 1m. The H horizon of soil with rich organic matter was sampled for the humus whereas in the some areas 5-7 cm of decomposed forest litter and mineralogical soils were sampled. Sequential extraction analyses, scanning electron microscopy and x-ray diffraction analyses were used for the sample analysis. Flame atomic absorption spectrometry (AAS) was used for Cu, Cd, Co, Mn, Fe, Ni, Pb, and Zn. Hg was determined using vapour generation (ICP-MS) whereas As was found using quartz tube AAS after generating hydride. Humus geochemistry revealed the presence of anthropogenic and natural component of heavy metals concentrations. The trace element

geochemistry of humus collected from the lake area of Flin flon contained As, Cd, Cu, Fe, Hg, Pb, and Zn. These elements showed high value near the smelter whereas it continuously decreased in concentration and reached to background value at a distance of 70-104 km. Closer to the smelter the non-labile phases Zn and Hg and their high proportion and concentration indicated that these elements were the smelter derived particles. With an increase in distance from the smelter there was more geochemical elements of bedrock than that of anthropogenic.

Rieuwerts et al. (1999) studied heavy metals concentration in and around the households of secondary lead smelter to know the level of heavy metals contamination. Altogether 61 top soil samples were collected at the depth of 0-5 cm from a 2km<sup>2</sup> grid that surrounded the smelter grounds and surrounding residential areas. A single sample that was collected was the composite of 5 sub-samples within an area of 1 m<sup>2</sup>. The total elemental concentrations were determined with the help of Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). On analysis it was revealed that Pb was main pollutant around residential areas, especially in downwind direction from the smelter. In garden soils, lead was in higher concentration but at the same time there was the elevated level of Zn, Cd, As, and Sb. Household dusts had elevated level of metal concentrations as compared to the urban or residential areas and didn't show any correlation with the metal concentrations in the garden soils.

Sterckeman et al. (2000) studied 12 soil profiles up to the depth of 2 m, to know the vertical distribution of Zn, Pb and Zn near lead and zinc smelters in the north of France. 6 samples were collected from soil developed out of loessic material and other 6 samples were from alluvial soils. Atomic absorption spectrophotometry with electro-thermal atomization and inductively-coupled argon plasma atomic emission spectrophotometry were used for the determination of Fe, Zn, Cd, Pb and Al. On analysis they found that Cd, Pb and Zn were primary pollutants. Contamination was more prominent within 20-30 cm depth of the soils. A minor amount of Cd and Zn were also found at the depth of 2 m. Mobility of the metals were in the increasing order of Cd, Pb and Zn. The depth reached by the metals increased with their concentration in a surface horizon. Moreover, a decrease in pH and an increase in sand content was responsible for the facilitation of movement of the metals. The depth reached by zinc increased with an organic carbon content in the surface horizon. Earthworm galleries were the enhancer of the migration of the metal contents downward.

Fernandez-Turiel et al. (2001) assessed 37 trace elements (Ag, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, La, Li, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Tb, Th, Tl, U, V, W, Y, Yb, Zn and Zr) in surface soil and plants (*Sida rhombifolia*) around a lead smelter in Lastenia, Province of

Tucuman, Argentina. For this, 121 soil samples were sampled to the depth of 0-5cm around a urban area and close to a smelter. Inductively coupled plasma mass spectrometry (ICP-MS) was used for finding trace elements. Analysis revealed that there was the high element concentration of Pb (>5,000 mg/kg), that could had cause serious environmental problems in areas in close proximity to the smelter. Other metal concentrations such as Cd, Ag, Zn,Cu, Sb and Sn were more concentrated within the vicinity of the smelter and they were more prominent within a 400m range. The effects of wind on dispersion for pollutant plumes were observed from sampling of soils and plants.

Huang and Gulson (2001) studied the distribution of selenium concentrations in soils, spermatophytes and bryophytes (mosses) near a Zn- Pb smelter at Cockle Creek, New South Wales. To know this, they collected samples from 25 sites at different directions and distances from the smelter. ICP-MS was used for the determination of selenium. It was found that the selenium was mainly confined within a 3 km range. However, at the distances greater than that was within the range of background value. Furthermore, the concentration of selenium in the soils was double than that of the background value, three times in plants as compared to the plants of background, and twice in the mosses near the smelter as that of background bryophyte. At some points within the 3 km, selenium concentration was high in the soils, thus was not able to define the decreasing trend of selenium concentration in the soils. The concentration of selenium was also above the threshold value as set in the China. Within plants species, the concentration of selenium deposition varied. *P.clandestinum* was seen to absorb more selenium of the four species growing near the smelter. The concentration of the selenium in Eucalyptus and *P.clandestinum* decreased within a 7 km range of transect. The transfer coefficient of selenium between plants and soil were low within a range of 1 km whereas it was reverse for the mosses.

Martley et al. (2004b) studied metals partitioning in soil profile in the vicinity of the industrial complex of Port Kembla. For this they collected soil samples from six different horizons and at distances of 70 m, 1km and 22 km respectively from the complex. Soil samples were collected from depths of 0–5, 5–10, 10–20, 20–30, 30–40 and 40–50 cm. Inductively coupled plasma mass spectrometry (ICP-MS) and ICP atomic emission spectrometry (ICP-AES) were used for analysis of Cd, Cr, Cu, Pb and Zn. Analysis of the samples revealed that uncontaminated soil profile at the distance of 22 km from the complex had the metals bound to less mobile fractions (crystalline Fe oxides, sulfides and organic matter) except for Pb, which was preferentially bound to hydrous Fe–Mn oxides. The metals partitioning were relatively constant except for Zn. In the contaminated undisturbed soil profile located at 1km form the complex, the proportion of mobile metals decreased with depth. Also, the metal partitioning was same as that of the uncontaminated soil



profile. Cr was found in sulfides and organic matter fractions, whereas, Cu was preferentially bound to hydrous Fe–Mn oxides, crystalline Fe oxides, sulphides and organic matter at the surface. In the contaminated disturbed soil profile located at 70 m from point source, the large proportion of metals were found in the labile forms to the depth of 40-50 cm. The extent of mobility of the metals in soil core was seen to be in a decreasing order of Cd, Zn, Cu, Pb, Cr.

Martley et al. (2004a) studied metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW. Altogether 25 top soil samples within the range of 24 km were collected for analysis from two different depths: 0-5 cm and 5-20 cm. Three samples from few distances apart were mixed to make a single sample. The samples were collected using dormer soil steel auger. The concentrations of arsenic, chromium, copper, lead and zinc were analyzed by Inductively Coupled Plasma -Mass Spectroscopy and inductively coupled plasma - Atomic Emission Spectroscopy for high concentrations of metals. Analysis of the samples revealed that As, and Cu concentrations were higher than the background values within the 4 km range of Port Kembla industrial complex. There was also higher concentration of Pb at two sites and zinc at six sites up to the 23 km range of Port Kembla. There was no significant difference in metal concentration at 0-5 cm depth and 5-20 cm depth except for Pb and Zn. The metals concentration were mostly limited within a 1-4 km range.

Kachenko et al. (2006) studied heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. For this sampling were carried out on four sites: Boolaroo, Port Kembla, Cowra and the Sydney Basin of New South Wales, a mix of commercial and residential vegetable growing areas. Altogether 113 soil samples and a total of 138 plant samples were collected from 46 sites from the four regions. The samples were collected from the transect of  $5 \times 5$  m laid randomly at two different depths of 0-30 cm and 60-90 cm. Vista Varian inductively coupled plasma atomic emission spectrometer (ICP-AES) and a graphite furnace atomic absorption spectrometer (Vista Varian Spectra 220Z) were used for metals analysis. The extent of metal contamination in the soils sampled was greatest in the vicinity of smelters, such as in Boolaroo and Port Kembla. Soil metal concentrations decreased with depth inferring contamination due to anthropogenic activities. Cd, Pb and Zn contamination were greatest in vegetables from Boolaroo, whereas Cu concentrations were greatest in vegetables sampled from Port Kembla. At Boolaroo, nearly all the samples exceeded the Australian Food Standards maximum level (ML) (0.01 mg kg<sup>-1</sup> fresh weight) of Cd and Pb in vegetables. Over 63% of samples exceeded international food standard guidelines set by the Commission of the European Communities and the Codex

Alimentarius Commission. All the vegetables sampled from Cowra, had Cd and Pb levels below the Australian and international food standards guideline values.

Yu et al. (2006) studied heavy metal contents in the soils and vegetables of four villages located between 14 and 160 km from the mines and metal smelters in the Baiyin region, China. Eight vegetables species were selected for study. At each sampling site, vegetables and the soils of 0-20 cm depth were collected. Metals concentrations were found using Agilent 7500i inductively coupled plasma mass spectrometer (ICP-MS). It was seen that Cd, Cu and As concentrations exceeded the allowable for Chinese agricultural soil in Shuichuan. In terms of concentrations of the heavy metals, leafy vegetables were more contaminated than non-leafy vegetables. Chinese cabbage was most severely contaminated. Contamination of the soil was due to mining, smelting activities, and the agricultural management (use of agrochemicals). Three of the sites had higher toxicity levels for three metals (Cd and Cu) whereas Pb in all the four sites as recommended for daily dietary intake.

Chopin et al. (2007) studied to know the distribution and mobility of trace elements in soils and vegetation near the copper smelter and mines. Altogether 313 soil samples were taken from three different locations and the samples were taken at an interval of 3 km up to a distance of around 15-20 km from the mine and smelter. The soils were sampled from two depths: 0-20 cm, and 20-40 cm. Perkin Elmer Optima 3000 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was used to find the 22 elements such as (Ag, Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Sr, Ti, V and Zn). The mobility of the elements was defined within the range of 2-3 km. However, their distribution in soils were poorly correlated with the parent material, prevailing wind direction, and soil physical and chemical characteristics. Higher the total concentrations of the trace elements in the soils and vegetation, lower was the mobility, whereas the mobility was high in lower concentrations.

Douay et al. (2007) did their study to know the long term effects on soil contamination and the quality of crops grown after the closure of Metaleurop Nord, a zinc smelter in France. For this they examined the 26 urban top soils, 17 dust and 38 vegetable samples. From the playground, urban top soils were taken from 0-2 cm depth whereas in the kitchen garden, samples were drilled from 0-25 cm. ICP- MS and ICP- OES were used for the analysis of metals as per the concentration of the metals. It was revealed that the agriculture and urban top soils were strongly contaminated by Cd, Pb, and Zn. The kitchen garden top soils were more contaminated as compared to the agricultural soils and were having great variability in the metal concentrations. Most of the agricultural crops

for foodstuffs were not within the European legislation. For the feedstuffs, most of the samples did not exceed the Cd, and Pb legislation limits, which indicated the potentiality of feedstuffs as an agriculture produce. Also, a high proportion of the vegetables in the kitchen gardens didn't conform to the European foodstuff legislation.

Chary et al. (2008) assessed the risk of heavy metals by consuming food grown on sewage soils near Musi River, India. Soil sampling was carried out within a stretch of 8km of the river and 2km on the both sides of the river. At 12 sites samples, a stainless steel auger with a diameter of 8cm was used to collect soil samples from a depth of 0-20 cm. The samples were analyzed using Varian Ultra Mass 700 ICP-MS. Result showed that there was high levels of Zn, Cr, and Cu. These metals were associated with labile fractions, making them more mobile and plant available. On screening venous blood and urine of humans, it was revealed that there were high amounts of Pb, Zn, Cr. Hazard quotients were also very high for Zn followed by Cr and Pb with reference to leafy vegetables such as spinach and amaranthus.

Wang et al. (2008) did their study on heavy metal pollution of soils and vegetables in the midstream and downstream of the Xiangjiang River, Hunan Province, China. The province had the industrial activities with Pb/Zn smelters. Altogether 219 soil samples were collected from 0-20 cm depth and a total of 48 vegetable samples were collected from mainstream and downstream of the river. The edible parts of the plants were collected for the examination. Presence of arsenic on the samples was found using hydrogen generation-atomic fluorescence spectrometer (HG-AFS), Cd by using graphite furnace atomic absorption spectrophotometer, and Cu, Cr, Pb, Ni, and Zn contents were determined with an atomic absorption spectrophotometer. It was seen that there was high accumulation of heavy metals such as As, Cd, Cu, Ni, Pb and Zn in agriculture soils. Also, there was a significant high level of As, Cd, Cu, Pb and Zn in vegetable soils as compared to the paddy soil. The pollution characteristics of multi-metals in soils were mainly due to Cd. For As, Cd, Ni and Pb, vegetable samples exceeded the maximum levels of contaminants in foods (GB2762-2005). Hence, there was a risk for human health in the mainstream and downstream of the province.

Li et al. (2009) examined the accumulation, chemical speciation and vertical distribution of Cu, Zn, Pb and Cd in soils of the Tiexi Industrial district of Shenyang in the Northeastern China. The industrial district comprised 5800 industrial enterprises with metallurgy, chemistry, pharmacy, textile, electronics, automobiles, aviation, building materials, and machine manufacturing. They collected samples near 20 different enterprises and at a depth of 0-20 cm. To know the vertical distribution of metals near the metal smeltery, from two soil profile, samples were collected from

depths of 0-20 cm, 40-60 cm and 80-100 cm. The result showed that soil metals were above the national threshold limit. Particularly for those old enterprises related to metals treating and chemical industry, the concentrations of the metals were several times higher than that of the threshold limit. The concentration on the top soil was in the decreasing order of Cd, Cu, Zn, Pb. The metals were mainly existing in residual form of Fe and Mn-oxide bound, and organic bound forms, while the percentages of carbonate-bound and exchangeable forms were smaller. The study indicated that the long term industrial activities were behind the high level of heavy metals pollution of soil.

Douay et al. (2013) investigated the heavy metals on urban soils, dust and vegetables near the lead smelter in France to know the potential health risk to the population living nearby. For this they sampled the soils to a depth of 0-25 cm and plants within a plot from 91 sampling sites which contained 57 agricultural fields and 34 kitchen gardens. Inductively coupled plasma atomic emission spectrometry (ICPOES, Vista Pro, Varian, and France) was used to determine zinc and other high concentrations Cd and Pb. The low concentrations Cd and Pb were determined using inductively coupled plasma mass spectrometry (ICPMS, Série X2, Thermo, France).

All the soil samples besides one exceeded the normal regional agricultural reference values of Cd and Pb. 45% of the vegetables samples were higher than the European foodstuff limits and one dust sample in the playground was above the French limit set up for lead. There was fluctuation of Cd, Pb levels depending on the use on the ground (kitchen garden, lawn, and courtyard) and its location. Also, there was lack of simple correlation between the smelter and Pb concentration to distance which concluded that human activities led to local urban contamination.

## **2.2. Emission from ferrous smelters on soil**

Schulin et al. (2007) did their study on heavy metal contamination of soil near the iron smelter in Bulgaria. For this they analyzed the sequence of soil profile along the 2km north-south transect at an increasing distance from the smelter and passing through the two soil types: Chromic Luvisols and Alluvial Fluvisols. Soil samples were collected at 10 and 4 different locations from Chromic Luvisols and Alluvial Fluvisols respectively and at depths of 0–20, 40–50, 60–70, and 100–110 cm 135–145 cm. X-ray fluorescence was used for analyzing total concentrations of Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Mo, Ni, P, Pb, S, Sb, Si, Ti, V, Zn and Zr. On analysis it was revealed that agricultural soils near the smelter of Kremikovtzi village was due to pollution from dusts emitted by the iron smelter. As, Pb, and Zn were the main pollutants. The concentration of metals at different depths were different in two different forms of soils: chromic luvisols and alluvial fluvisols while it was not too much different within each unit. The main contribution of metals was of geogenic origin

rather than the anthropogenic source. So, pedological factors was a key role player for the heavy metals contribution to the soils.

Yuan et al. (2013) did their study on heavy metals (Ni, Cr, V, As, Cu, Pb, Cd, Zn and Hg) in top soils of a closed steel smelter at the former Capital Iron and Steel Factory, Beijing, China. The plant area included the blast furnace and smelting, pyrogenation, steel casting and steel-rolling. Altogether, 400 soil samples were collected from the top layer 0-20 cm. Analysis of soil Cr, Fe, Ni, V, Pb, Cu, and Zn were done using X-ray fluorescence spectrometry (RS-1818, HORNGJAAN). Graphite atomic absorption spectrophotometer (AA6810 SONGPU) was used to analyze Cd. An atomic fluorescence spectrophotometer (XGY-1011A) was used for the analysis of Hg and As. It was revealed that Ni, Cr, Va and As were close to the background values. The soil concentration of Cu, Pb, Cd, Zn and Hg were higher than the background values especially Hg. Multivariate geostatistical analysis suggested that Cu, Pb, Cd and Zn had similar properties and the presence were mainly from steel smelting activities. The Hg contamination was more weakly related to the steel smelting activities, partially due to other anthropogenic activities.

### **2.3. Emission from other sources on soil**

Peters et al. (1999) did their study to know the selenium in the sediments, pore water and benthic fauna of Lake Macquarie, an estuary at the east coast of Australia. For this they collected the samples of sediments below the sea bed grass to a depth of 3 cm, sediment core for pore water analysis and benthic animals. In the metals analysis atomic absorption spectrophotometry was used. Sediments were seen as the significant source of selenium in the lake's food web. Analysis of the surface sediments revealed that there were higher selenium content near the industrial sources: a smelter and a power station. Near the power station it was 12 times more selenium as compared to the sediment cores. Even there was 69 times more selenium in some areas as compared to the background concentration. Selenium concentration in three benthic feeding species (*Mugil cephalus*, *Platycephalus fuscus*, *Acanthopagrus australis*) were co-related with surface sediment selenium concentration. The data suggested that benthic food webs were the important sources of selenium to the fishes of Lake Macquarie.

Snowdon et al. (2004) studied the nature and distribution of copper, lead, and zinc in soils of a highly urbanized sub-catchment of Sydney. Altogether 374 top soil samples were collected from a depth of 0-2.5 cm. Analysis for the heavy metals in the samples was done using Perkin Elmer Inductively Coupled Mass spectrometer (ICP-MS). Analysis showed that the heavy metals were

resulted as an atmospheric deposition from the industries inside and beyond the catchment. Concentrations of the metals were mainly near the dwellings, oldest buildings, nearby major roads and converged railway lines. The data sources revealed that the contribution of metals were from roads, railway lines, and older lead painted houses. Total soil chemistry indicated that the 34, 33 and 56% of the samples were above the Australian and New Zealand Environment and Conservation Council (ANZECC) and National Health and Medical Research Council (NH&MRC) guidelines for Cu, Pb, and Zn respectively.

Xing et al. (2004) studied the soil profiles of different climatic zones and agro-ecosystems in China to know some of the trace elements in surface soil layer around the power, industrial and metallurgical smelters. For this, 28 soil profiles were collected from different climate zones and agro-ecosystems that were far from the industrial activities. To know the sources of these trace metals, 12 major coal mines coals were analyzed. Double-focusing type of ICP-MS was used for the determination of Ag, Ta, Ru, and Ir. Analysis revealed that the pollution was not limited to the soils in the vicinity of power, metallurgic, metalworking, and machine making industries but the pollution was found extensively on land besides cities and industrial regions.

Roach et al. (2005) did their study on assessment of metals in the sediments of the Lake Macquarie, NSW. They sampled the sediments at 23 sites in which 3 surface sediments were collected from an area of 50–100 m<sup>2</sup>. Inductively coupled plasma mass spectrometry was used for the determination of cadmium, chromium, copper, aluminium, iron, nickel, lead, lithium, zinc and silver. For the determination of mercury, arsenic and selenium, atomic fluorescence spectrometry was used. The result showed that the cadmium, lead, mercury, selenium, silver, and zinc were enriched throughout the lake surface sediments. Near the power stations in the north of the lake had high content of selenium. On comparing the metals concentration with sediment quality guidelines (SQGs) it showed the concentration had the likelihood of effect on sediment associated biota. History of sediment quality data revealed that there was a reduction in surface metal concentrations throughout the lake over 15 years.

Zhang et al. (2009) did their study on surface soil samples in Fuyang county of China to know the contribution of human activities on the increase of heavy metals concentration on soil. They sampled 286 soils from different location based on their uniformity of distribution and soil types in the study area. The total Cu, Pb, Cd and Ni were analyzed using inductively coupled plasma mass spectrometry (ICP-MS), whereas Zn was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES). Study revealed that Cu, Zn, Pb, Cd were added by the external

sources whereas Ni was mainly controlled by natural factors. Cu, Zn and Pb were polluting 15.76% of the area whereas 46.14% of the area was having Cd pollution. Spatial analysis revealed that the limestone mining activities, paper mills, cement factory and metallurgic activities were the main sources for the concentration of Cu, Zn, Pb and Cd in soil, whereas, soil Ni was determined by the presence of parent material.

Zhuang et al. (2009) assessed the heavy metals (Cu, Zn, Pb and Cd) in soils and food crops in four villages around the Dabaoshan mine, South China. Four sampling sites up to a distance of 18 km were selected near the vicinities of the mine. At each random sampling site, soil was collected from 0-20 cm depth and the plant was collected at the same site. Metals on the soils and the plants were analyzed using flame atomic adsorption spectrophotometer (AAS, GBC932AA), whereas the concentrations of Pb and Cd were found by using graphite furnace atomic absorption spectrophotometer (GFAAs, GBC932AA). They found that the paddy and the garden soils exceeded the maximum permissible concentrations for Chinese agricultural soil. Rice tended to accumulate higher concentration of Cd and Pb in grain parts. The concentrations of Cd, Pb and Zn in vegetables were exceeding the maximum permissible concentration in China. Taro accumulated the higher concentration of Zn and Pb. Bioaccumulation was in a decreasing order of Cd, Zn, Cu, and Pb and also bioaccumulation was higher for leafy and non-leafy vegetables. The daily intake of Cd, and Pb of rice and vegetables exceeded the maximum Food and Agricultural Organization/World Health Organization (FAO/WHO). Thus consumption of rice and food crops growing near the mine were posing risk to human health.

Cai et al. (2010) studied heavy metals concentration on agricultural soils and vegetables in Dongguan city, Guangdong, China, which was experiencing rapid industrialization and urbanization. A total of 118 surface soil samples were collected from a depth of 0-20 cm and a total of 43 vegetable samples were collected for analysis. The edible parts of the foliage of vegetables were sampled. Hg was analyzed with cold atomic absorption spectrometer, As content by DDCAg spectrophotometry, and Ni, Cu, Cr, Pb, Cd and Zn were analyzed using atomic absorption spectrometer. Analysis of the samples revealed higher accumulation of heavy metals such as Cu, Zn, Ni, Pb, Cd, and Hg in agricultural soils. The contents of Pb and Hg were comparatively higher than the other heavy metals contents and also exceeded the background level. The Cu, Ni, Cd, and Hg exceeded the China Environmental Quality Standard for soils. The sources of Cu, Zn, Ni, Cr and As were predominantly derived from parent materials. The presence of Pb, Hg and Cd metals were from anthropogenic activities. In vegetables, the bio-concentration factors (BCF) of heavy metals were in the decreasing order of Cd, Zn, Cu, As, Ni, Hg, Cr and Pb respectively.

Gjoka et al. (2011) studied soil samples of Albania (Tirana) to establish background and reference values of total heavy metals. They collected thirty eight soil samples from the genetic horizons of the major soil types. Such obtained soil samples were analyzed for their physiochemical properties by the use of standard methods. Atomic absorption spectrometer was used for the analysis of the total contents of Cd, Cr, Ni, Pb, Zn, and Cu. It was found that the highest metal contents were in two soils developed in limestone. Metal contents of the soil were controlled by soil properties, including pH, Calcium Carbonate ( $\text{CaCO}_3$ ), clay, organic matter, cation exchange capacity, and Fe oxides. The depth distribution of metals showed a tendency for accumulation of Cd, and Pb in the surface horizons of three soils, thus suggesting the inputs of the metals were from the anthropogenic sources. The background value was naturally higher and the total metal contents of some of the soils were above the background level and thus indicating metal pollution.

From the literatures it is obvious that the soils around the various types of smelters, mines and industrial plants have higher concentration of heavy metals. Vegetables, plants and benthic fauna showed the presence of heavy metals in these soils. Heavy metals have also transferred to the sediments of water bodies. So far, fewer studies have been done on the soil heavy metals due to the emission of ferrous smelters whereas a wide range of studies are performed on pollution near the lead and zinc smelters. In Australia, there are a number of studies done on soil heavy metals but most of them are confined to lead smelters. In Port Kembla industrial complex, the heavy metals on soil due to copper smelter has been studied, however, the study has not been conducted to know the heavy metals deposition in soil due to iron and steelworks. The study near Rooty Hill steelworks has also been not done and hence, this could be a research of study.



## Chapter 3: Materials and Methods

### 3.1. Study Area

Soil samplings were carried out in three different locations in New South Wales: near Rooty Hill Steelworks (Electric Arc Furnace), near Port Kembla integrated iron and steelworks (Blast Furnace and Blast Oxygen Furnace) and Macquarie Park (Figure 3.1-3.4). Rooty Hill sampling sites are close to the Rooty Hill Steelworks (Electric Arc Furnace). The area has moderate traffic condition and maximum industrial influence. Similarly, sampling sites near Port Kembla integrated iron and steelworks have moderate vehicles movement and strong influence of industrial activities. The sampling site near Macquarie Park in the Macquarie Sports ground is surrounded by residential area and is close to a highway and commercial buildings. It has insignificant influence of industrial activities.

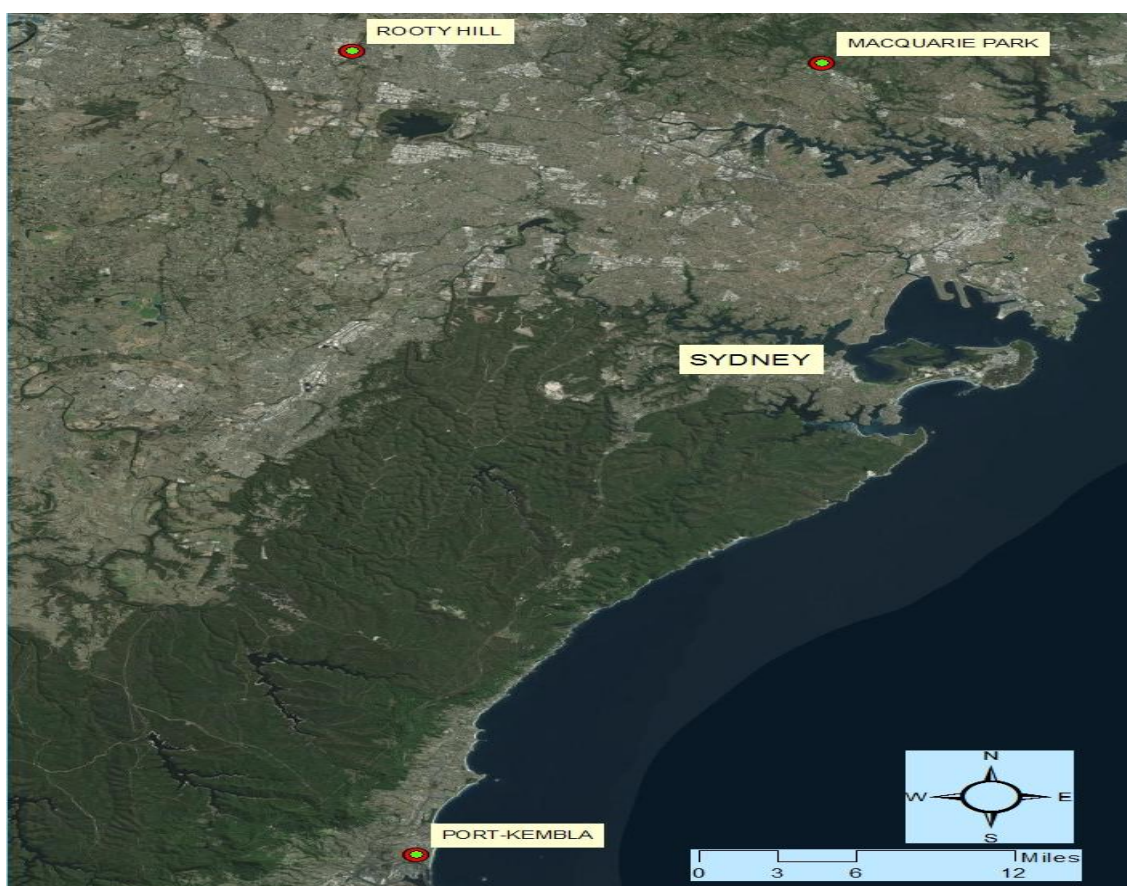


Figure 3.1 Map of the study area

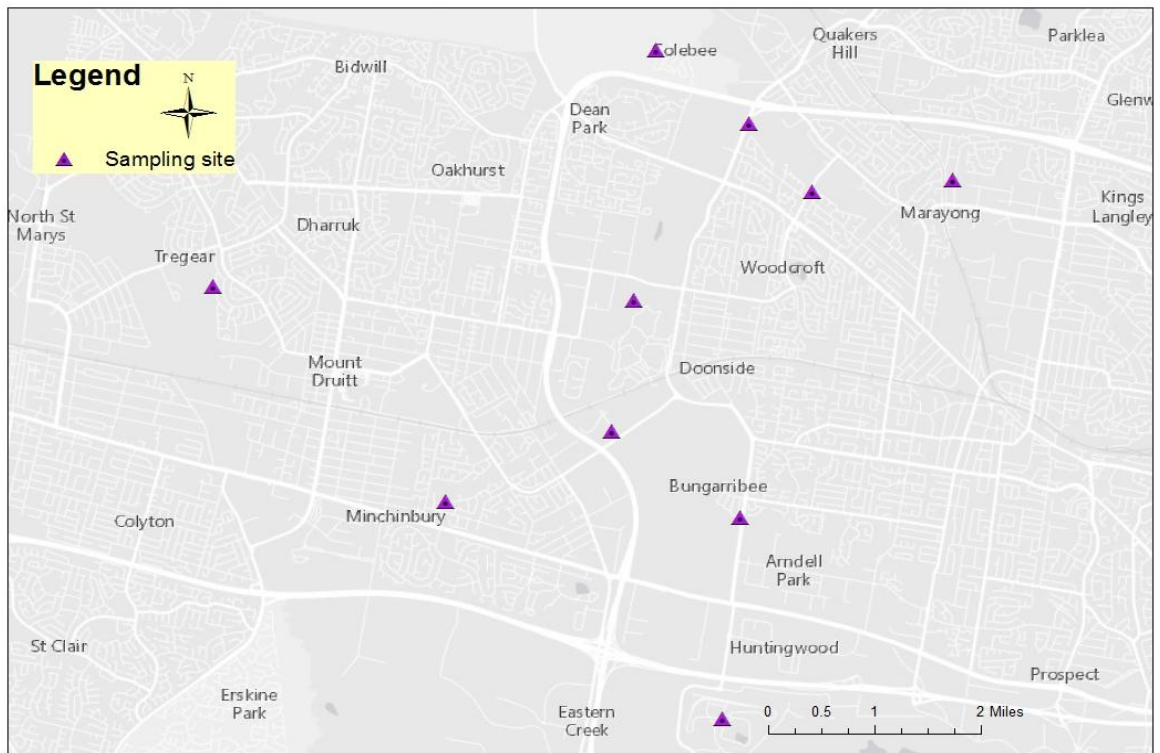


Figure 3.2 Map of sampling sites near the Rooty Hill Steelworks

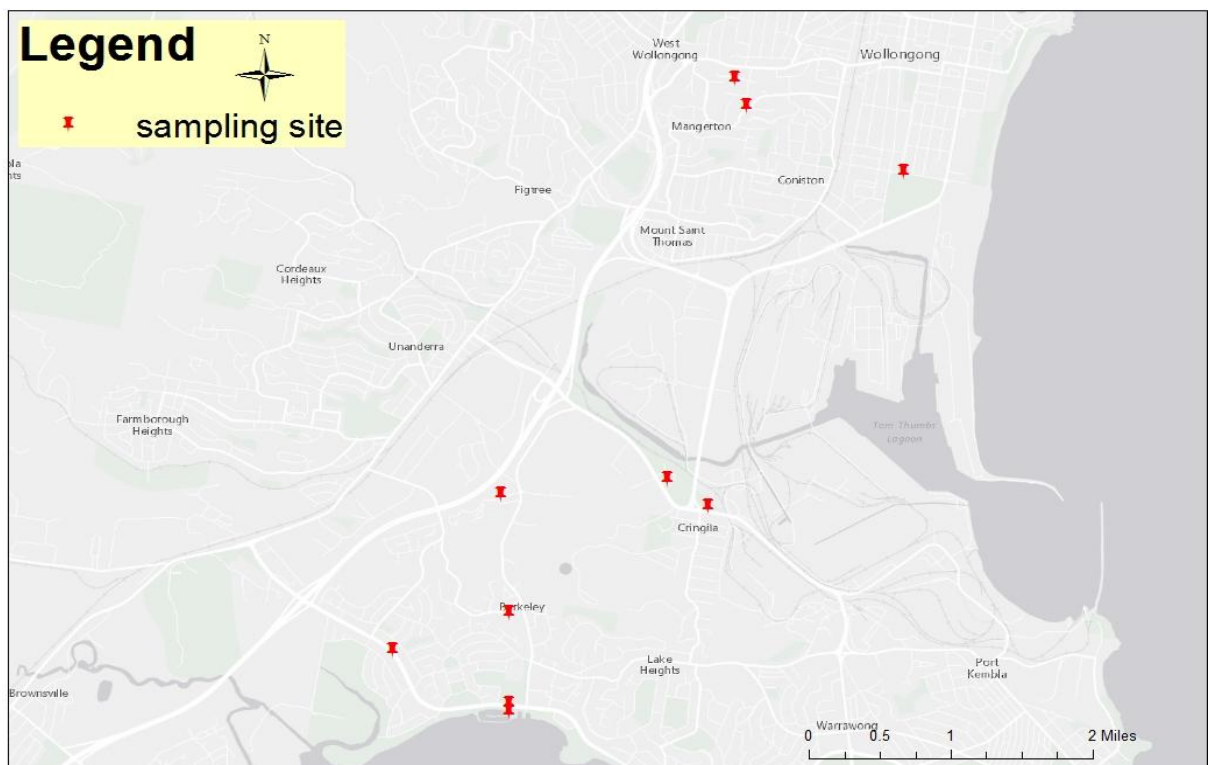


Figure 3.3 Map of sampling sites near the Port Kembla steelworks

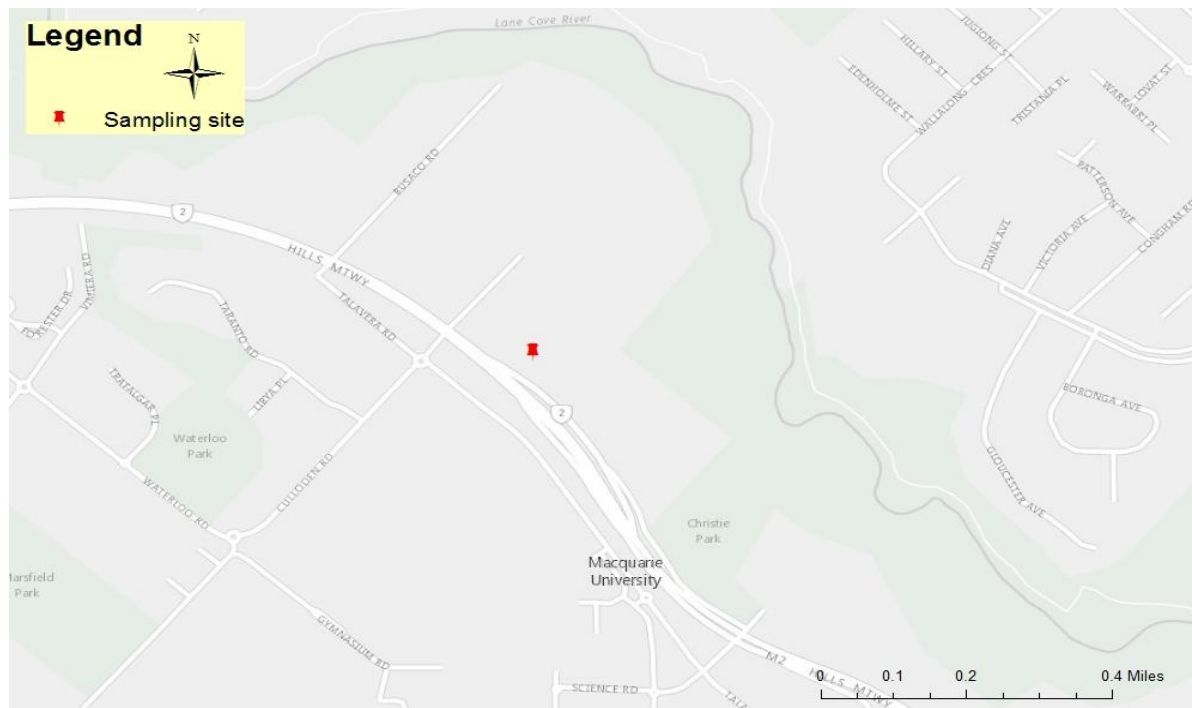


Figure 3.4 Map of the sampling site at Macquarie Park

### 3.2. Selection of Sampling Sites

Ten different sampling sites were selected using a Google map around each steel industry i.e., 10 sites near Rooty Hill steelworks, and 10 other sites near Port Kembla integrated iron and steelworks. All the sites were within a range of 6 km. Mostly parks and reserves were selected for sampling near Rooty Hill Steelworks and Port Kembla Steelworks, whereas only one site was selected at the Macquarie Park Sports ground. The distances of each of the sites from the Steelworks were measured (Table 3.1).

**Table 3.1.** List of sampling sites, their coordinates and distances from steel and iron industry

Sampling Areas	Locations	Coordinates	Distance from steel industry (kilometer)
<b>Rooty Hill Steelworks</b>	1. Whalan Reserve	33° 45' 18" S 150° 48' 3" E	4.39
	2. May Cowpse Reserve	33° 46' 49" S 150° 49' 57" E	1.59
	3. Nurrangingly Reserve	33° 45' 24" S 150° 51' 29" E	2.17
	4. Colebee Nature Reserve	33° 43' 38.9" S 150° 51' 40.5" E	4.58
	5. Harvey Park	33° 44' 38" S 150° 52' 56" E	3.9
	6. Faulkland Crescent Reserve	33° 44' 33" S 150° 54' 5" E	5.81
	7. Melrose Park	33° 44' 09" S 150° 52' 25" E	3.99
	8. Blacktown International Sportspark	33° 46' 19" S 150° 51' 18" E	1.24
	9. Bungaribee Creek Reserve	33° 46' 56" S 150° 52' 22" E	2.89
	10. Sydney Motorsport Park	33° 48' 21" S 150° 52' 12" E	6
<b>Port Kembla Steelworks</b>	1. Brownlee Park	34° 25' 46" S 150° 52' 38" E	4.06
	2. Margerton Park	34° 25' 37" S 150° 52' 34" E	3.43
	3. J.J Kelly Park	34° 26' 7" S 150° 53' 36" E	2.75
	4. Bph Centenary park	34° 26' 7" S 150° 53' 36" E	1
	5. John Crehan Park	34° 27' 46" S 150° 52' 9" E	1.17
	6. Nan Tien Temple	34° 27' 51" S 150° 51' 8" E	3.04
	7. Semaphore Road	34° 28' 29" S 150° 51' 11" E	2.89
	8. Winnima way	34° 29' 1" S 150° 51' 11" E	3.5
	9. Kelly Street	34° 28' 59" S 150° 51' 11" E	3.8
	10. Macedonia Park	34° 28' 41" S 150° 50' 28" E	4.98
<b>Macquarie Park</b>	Macquarie Park Sports ground	33° 46' 2" S 151° 6' 54" E	Not applicable

### **3.3. Sampling Procedure**

Soil samples were collected from 0-10 cm depth with a dormer steel soil sampler, which was comparable to the soil sampling procedure used by Ullrich et al. (1999). From each sampling sites, three samples within few meters apart were collected in a plastic zip bag to get a composite soil sample. After sampling on each site, the sampler was cleaned with the help of MiliQ water and paper towel in order to avoid contamination. The co-ordinates for the sampling sites were also noted down (Table 3.1). After that all the collected samples were brought in a laboratory and kept inside a freezer at a temperature of 0 °C.

### **3.4. Laboratory Procedure**

Laboratory procedure involved sample preparation and analysis of samples.

#### **3.4.1 Sample Preparation**

Sample preparation involved the use of equipment such as grinder, vacuum oven, dessicator, weighing machine, sieve, plastic bottles, aluminum tray, gloves, dryer and thermometer. Ethanol was used for cleaning purposes.

In order to prepare the soil samples, following steps were involved:

- At first the soil samples were left for an hour at a normal room temperature
- Unnecessary particles and grits were removed with hands
- Approximately 250 gram of soil was weighed from each of the samples
- They were kept in a vacuum oven for drying for 3 hours at a temperature of 70°C.
- Dried samples were kept in a dessicator and their weights were noted
- Each dried samples were grinded again and sieved to 0.18 mm mesh
- The 0.18 mm sieved samples were kept inside the plastic bottles for further analysis

#### **3.4.2 Soil Analysis**

Three types of soil analysis were performed to each samples from all sites (Table 3.1). They were: Proximate Analysis, Fourier Transform Infrared (FTIR) Analysis and Acid extractable elements analysis. Proximate analysis, and Fourier Transform Infrared (FTIR) analysis were performed at laboratory in Macquarie University, whereas Acid extractable elements analysis was performed in National Measurement Institute at North Ryde, New South Wales, Australia.

### ***Proximate Analysis***

Proximate analysis is used for the solid fuel testing and is applicable for soil. With this analysis soil moisture content, volatile matter, ash and fixed carbon were found in all the soil samples testing (Parikh, et. al. 2005) using American Society for Testing and Materials (ASTM) test protocol D1102 (ASTM, D1102-841995).

### **Moisture content**

The moisture content was the total moisture loss when the soil samples were kept inside the vacuum oven and later on the cylindrical furnace at a temperature of 105 °C in a Nitrogen environment (Donahue et al. 2009). The moisture content was determined using the formula

$$M = \frac{m_2 - m_3}{m_2 - m_1} * 100$$

(Standards Australia International, 2000)

Where,

M= moisture in vacuum oven dried sample, in weight percent

m<sub>2</sub>= mass of sample along with crucible and lid, before heating, in grams

m<sub>3</sub>= mass of sample along with crucible and lid, after heating, in grams

m<sub>1</sub>= mass of sample crucible and lid, in grams

Determination of moisture content involved the following steps for each of the samples

- An empty crucible with its lid was cleaned and dried with ethanol and was weighed
- Approximately 1 gram of prepared soil sample was added and weighed again
- In another clean and dried crucible, the same sample was weighed as the above process
- Then the cylindrical furnace was heated to 105 °C and nitrogen gas was allowed to pass at the rate of 1.2 litre per minute
- The samples were then placed inside the furnace for 3 hours
- After 3 hours, samples were removed and allowed to cool for few minutes before placing inside the desiccators
- Then weighing was done
- The difference in the loss of weight was noted down which gave the moisture content in the samples

### Ash content

Ash was the residue left after the loss of moisture, volatile matter and the fixed carbon when the soil samples were heated in the cylindrical furnace for 3 hours to a temperature of 575<sup>0</sup>C in air (Donahue et al. 2009). The ash content was determined using the formula

$$A = \frac{m_2 - m_3}{m_2 - m_1} * 100$$

(Standards Australia International, 2000)

Where,

A= ash in vacuum oven dried sample, in weight percent

m<sub>2</sub>= mass of sample along with crucible and lid, before heating, in grams

m<sub>3</sub>= mass of sample along with crucible and lid, after heating, in grams

m<sub>1</sub>= mass of sample crucible and lid, in grams

The determination of the ash content in the soil samples involved the following steps:

- An empty crucible was cleaned and dried with ethanol and weighed
- Approximately 1 gram of prepared soil sample was added and weighed again
- In another clean and dried crucible, the same sample was weighed as the above process
- Then the cylindrical furnace was heated to 575<sup>0</sup>C and air was allowed to pass at the rate of 1.2 litre per minute.
- The samples were then placed inside the furnace for 3 hours
- After 3 hours, samples were removed and allowed to cool for few minutes before placing inside the desiccators
- Then weighing was done
- The difference in the loss of weight was noted down and the ash content was calculated using the above formula

### Volatile Matter

The volatile matter on soils was the volatile matters formed on heating the soil samples at a temperature of 902<sup>0</sup> C in the nitrogen environment for 7 minutes in a cylindrical furnace (Donahue et al. 2009).

$$VM = \frac{m_2 - m_3}{m_2 - m_1} * 100 - M$$

(Standards Australia International, 2000)

Where,

VM= volatile matter in vacuum oven dried sample, in weight percent

m2= mass of sample along with crucible and lid, before heating, in grams

m3= mass of sample along with crucible and lid, after heating, in grams

m1= mass of sample crucible and lid, in grams

M = moisture in vacuum oven dried sample, in weight percent

Determination of volatile matter involved the following steps:

- An empty crucible was cleaned and dried with ethanol and was weighed.
- Approximately 1 gram of prepared soil sample was added and weighed again.
- In another clean and dried crucible, the same sample was weighed as the above process.
- Cylindrical furnace was heated to 902<sup>0</sup> C in the nitrogen environment at a flow of 1.2 l/min
- Then the samples were placed inside the furnace for 7 minutes.
- After 7 minutes, samples were taken out and allowed to cool for few minutes before placing inside the desiccators.
- Then weighing was done.
- The difference in the loss of weight was noted down and the volatile matter was calculated using the above formula.

### Fixed Carbon

Fixed carbon was the remains that was left after the loss of moisture, volatile matter and deducting ash from the soil sample after heating to a temperature of 575<sup>0</sup>C in air inside the cylindrical furnace (Donahue et al. 2009).

The fixed carbon content was determined by difference with the following equation:

$$FC = 100 - \text{Moisture} - \text{VM} - \text{Ash} \text{ (LECO, 2015)}$$

Where FC is fixed carbon expressed in weight percent, VM is volatile matter expressed in weight percent.



### ***Determination of Acid Extractable elements in soils***

The reference method Australian Standard (AS) 4479; United States Environmental Protection Agency (USEPA 2013) 3050; 200.8; 200.7, 6010, 6020 were used for finding the elements in soils. For the determination of Arsenic(As), Cadmium(Cd), Chromium(Cr), Copper(Cu), Iron(Fe), Mercury (Hg), Manganese (Mn), Molybdenum(Mo), Nickel(Ni), Lead(Pb), Titanium(Ti), Zinc(Zn), Magnesium(Mg), Potassium( K), Phosphorus(P), Sulphur(S), Silicon(Si), and Sodium(Na), two grams of each of the soil samples were digested with  $\text{HNO}_3$  /  $\text{HCl}$  at 100 °C for two hours. Then appropriate dilution was done to all the samples. After dilution, Integrated Coupled Plasma-Mass Spectroscopy (ICP-MS) and Integrated Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES) were used for the determination of metals present in the samples. Any matrix interferences were corrected using matrix spike samples. For the determination of mercury lower than 0.1 mg/kg Cold Vapour- Atomic Absorption Spectroscopy (CV-AAS) technique was used. This technique was also used for the determination of sulphur. The three equipments that were used for the determination of the elements were ICP-AES (Varian 730-ES), ICP-MS (Perkin Elmer Elan Dynamic Reaction Cell II), and CV-AAS (Cetac QuickTrace M-7500 Mercury Analyser). Quality Assurance/ Quality Control (QA/ QC) protocols were used (as for example number of duplicates, spikes, matrix spikes, blanks per batch). For every batch of 20 samples or less, there were at least one blank, one duplicate, one blank spike, one sample spike and one laboratory control sample (Evans 2011).

### ***Fourier Transform Infrared (FTIR) Analysis***

Fourier Transform Infrared (FTIR) NICOLET 6700 was used to know the vibrational spectra of soils in the range of 4000 to  $400\text{cm}^{-1}$ . A pinch of soil sample was kept in the FTIR sampler holder after cleaning with ethanol and drying. OMNIC 7.4 software was used in the computer for the Fourier transformation. The final infrared spectrum for each of the samples were saved for the further manipulation.

## Chapter 5: Results

### 5.1 Proximate Analysis of soil

Proximate analysis was performed for the determination of moisture content, volatile matter, ash content, and fixed carbon of soils near the Rooty Hill Steelworks, Port Kembla Steelworks and at Macquarie Park.

#### 5.1.1 Moisture content

The moisture content varied from 15.6% to 23.82% in the soil samples near the Rooty Hill steelworks (Table 5.1). At the nearest distance 1.24 km from the Rooty Hill steelworks, the Blacktown International Sports Park had the moisture content of 18.33% whereas at the furthest distance of 6 km, the Sydney Motorsport Park, had moisture content of 21.1%. In the sites near the steelworks at Port Kembla, soil moisture varied from 19.88% to 32.08% (Table 5.2). The nearest soil sampled at BHP Centenary Park at a 1 km distance had soil moisture of 24.05% and the soil sampled at Macedonia Park at a distance of 4.98 km had 32.08%. In the Macquarie Park, soil sample had the moisture content of 25.19%.

Table 5.1 Proximate values of soil near the Rooty Hill Steelworks

Locations	Distance from steelworks(km)	Final results (weight %)			
		Moisture	Volatile	Ash	Fixed carbon
Blacktown International Sports park	1.24	18.33	5.38	76.28	0
May Cowpse Reserve	1.59	16.09	6.26	77.65	0
Nurrangingly Reserve	2.17	22.35	5.35	71.17	1.13
Bungaribee Creek Reserve	2.89	23.82	6.96	69.22	0
Harvey Park	3.9	15.92	5.30	78.78	0
Melrose Park	3.99	15.60	7.18	77.21	0
Whalan	4.39	19.15	6.75	74.10	0
Colebee Nature Reserve	4.58	16.08	3.47	80.29	0.16
Faukland Crescent	5.81	15.27	8.36	74.55	1.82
Sydney Motorsport Park	6	21.10	4.90	73.99	0

### 5.1.2 Volatile matter

The volatile matter varied from 3.47% to 8.36% in the soils from Rooty Hill Steelworks (Table 5.1). The lowest was at a distance of 4.58 km in the Colebee Nature Reserve and the highest percentage of volatile matter was at a distance of 5.81 km in the Faulkland Crescent Reserve. At the nearest distance of 1.24 km (Blacktown International Sports Park) from the Steelworks, the volatile matter was 5.38% whereas in the furthest Sydney Motorsport Park (6 km), the volatile matter was 4.9%. Similarly, in the soil samples near the Port Kembla Steelworks, volatile matter varied from 5.87% to 11.92% (Table 5.2). The lowest was at a distance of 1 km at the BHP Centenary Park, whereas the highest was at a distance of 2.75 km at the JJ Kelly Park. The furthest Macedonia Park at a distance of 4.98 km from the steelworks had 7.48% of volatile matter. Also the soil in the Macquarie Park had 6.57 % of volatile matter.

Table 5.2 Proximate values of soil near the Port Kembla Steelworks and Macquarie Park

Locations	Distance from steelworks (km)	Final results (weight %)			
		Moisture	Volatile	Ash	Fixed carbon
BPH Centenary Park	1	24.05	5.87	69.42	0.66
John Crehan Park	1.17	20.15	7.32	72.46	0.07
Semaphore Road	2.89	29.79	6.85	63.31	0.06
Nan Tien Temple	3.04	29.35	7.18	63.47	0
Margeton Park	3.43	24.00	11.30	64.70	0
Winnima way	3.5	19.88	6.83	73.29	0
JJ Kelly Park	2.75	22.77	11.92	53.46	11.85
Kelly Street	3.8	22.75	9.04	66.95	1.26
Brownlee Park	4.06	22.61	7.65	69.11	0.63
Macedonia Park	4.98	32.08	7.48	59.94	0.50
Macquarie Park	Not Applicable	25.19	6.57	67.89	0.34

### 5.1.3 Ash

In the soil samples near the Rooty Hill Steelworks, the ash content ranged from 69.22% to 80.29% (Table 5.1). The lowest value of 69.22% was at a distance of 2.89 km at Bungaribee Creek Reserve whereas the highest 80.29% was at a distance of 4.58 km at the Colebee Nature Reserve. Near the Port Kembla steelworks the ash content varied from 53.46% to 72.46% (Table 5.2). The JJKelly Park at a distance of 2.75 km had lowest ash content whereas the highest was at the Winnima way

at a distance of 3.5 km from the Steelworks. Similarly, the site in the Macquarie Park had ash content of 67.89%.

#### **5.1.4 Fixed Carbon**

In the soil samples near the Rooty Hill Steelworks, the carbon content ranged from 1.82% to 0% (Table 5.1). The highest was at the Faulkland Crescent at a distance of 5.81 km from the steelworks with 1.82%, whereas the 7 sampled areas had 0% of fixed carbon. The sites at Blacktown International Sports Park, May Cowpse Reserve, Bungaribee Creek Reserve, Harvey Park, Melrose Park, Whalan Reserve, and Sydney Motorsport Park had soils with no fixed carbon. The Nurrangingly Reserve (2.17km), Colebee Nature Reserve (4.58km), and Faulkland Crescent Reserve had 1.13%, 0.16%, and 1.82% of fixed carbon, respectively. Similarly, near the soils of Port Kembla Steelworks, the carbon content varied from 0% to 1.26% (Table 5.2). The 0% were in the Nan Tien Temple area (3.04 km), Margeton Park (3.43km), and Winnima way (3.5 km). The nearest BHP Centenary Park at a distance of 1 km from the Port Kembla Steelworks had fixed carbon of 0.66% in the soil whereas the furthest Macedonian park at a distance of 4.98 km had 0.5%. The site near the Kelly road (3.8 km) had the highest carbon content. Also, the soil of the Macquarie Park had the fixed carbon of 0.34%.

#### **5.2 Acid Extractable elements on soil**

It involved the determination of trace elements: mercury, cadmium, molybdenum, and arsenic; and heavy metals: chromium, copper, lead, zinc, titanium, iron and manganese in soils. Others elements, such as sodium, potassium, magnesium were also determined. Non-metals, such as sulphur, phosphorus, and silicon were also examined in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and the Macquarie Park.

##### **5.2.1 Trace metals mercury, cadmium, and molybdenum concentration**

In the soils near the Rooty Hill Steelworks, and the Port Kembla Steelworks, cadmium and mercury were < 0.5 mg/kg and <0.2 mg/kg respectively whereas the Macquarie Park had 0.21 mg/kg of mercury.

The molybdenum varied between less than 0.5 mg/kg to 0.83 mg/kg in the Rooty Hill sites (Table 5.3). The Colebee Nature Reserve, which was at a distance of 4.58 km from the Rooty Hill Steelworks, had the lowest value of 0.5 mg/kg, whereas the Faulkland Crescent at a distance of 5.81 km had the highest value of 0.83 mg/kg. The Blacktown International Sports Park at the nearest

distance of 1.24 km from the steelworks had molybdenum at 0.69 mg/kg, whereas the furthest Sydney Motorsport Park at a distance of 6 km had 0.73mg/kg of molybdenum (Figure 5.1).

Similarly, the molybdenum in the soils ranged from 0.5 mg/kg to 1.7 mg/kg in the sites of Port Kembla (Table 5.3). This lowest 0.5 mg/kg of molybdenum was near the Semaphore Road at 2.89 km whereas the highest 1.7 mg/kg was at Margeton Park at a distance of 3.43km. The nearest BHP Centenary Park (1km) from the Port Kembla steelworks and the furthest Macedonia Park (4.98 km) had equal 1.1 mg/kg of molybdenum concentration ( Figure 5.1). Some of the Port Kembla sites had higher concentration of molybdenum compared to the sites near the Rooty Hill Steelworks and Macquarie Park (0.93 mg/kg).

The soil values of trace metals in all the three sites were far below the guideline of mercury and cadmium which are 100 mg/kg and 400 mg/kg respectively for recreational soil, as per National Environment Protection Measure (NEPM) 2011 guideline (Table 5.3) (Schedule B1 2011).

Table 5.3 Mean, range, standard deviation and NEPM 2011 guideline values for trace metals, heavy metals and other elements in mg/kg

NEPM 2011	Rooty Hill			Port Kembla			Elements
	Standard Deviation	range	mean	Standard Deviation	range	mean	
400							Hg
100							Cd
	0.09	<0.5-0.83	0.954333	0.39	0.5-1.7	0.949	Mo
300	2.06	3.6-9.5	34.33	1.50	1.9-7.3	4.2	As
240	23.33	24-100	108.43	37.091	49-170	89.3	Cr
20000	31.20	13-120	2062.59	23.435	47-110	74.9	Cu
600	15.71	15-71	92.55	20.62	16-72	39.5	Pb
800	13.71	9.8-55	117.17	16.41	25-75	40.7	Ni
700	28.60	20-120	170.19	32.55235	75-190	110.9	Zn
	12.55	30-69	714.6333	762.95	37-2680	700.7	Ti
	11573.42	14000-49700	39914.44	13212.96	22100-61300	39930	Fe
9000	388.81	210-1300	1589.5	451.98	350-1950	805	Mn
	124.72	60-430	222.3333	85.95	110-350	231	Na
	424.51	850-2340	1322.333	373.61	670-1790	1231	K
	716.22	550-2950	4317.667	2667.772	1390-10600	4339	Mg
	130.31	170-590	821.6667	112.37	580-980	695	P
	61.49	150-390	389.3333	114.91	240-610	394	S
	185.28	1360-2060	1879	242.64	1570-2320	2001	Si

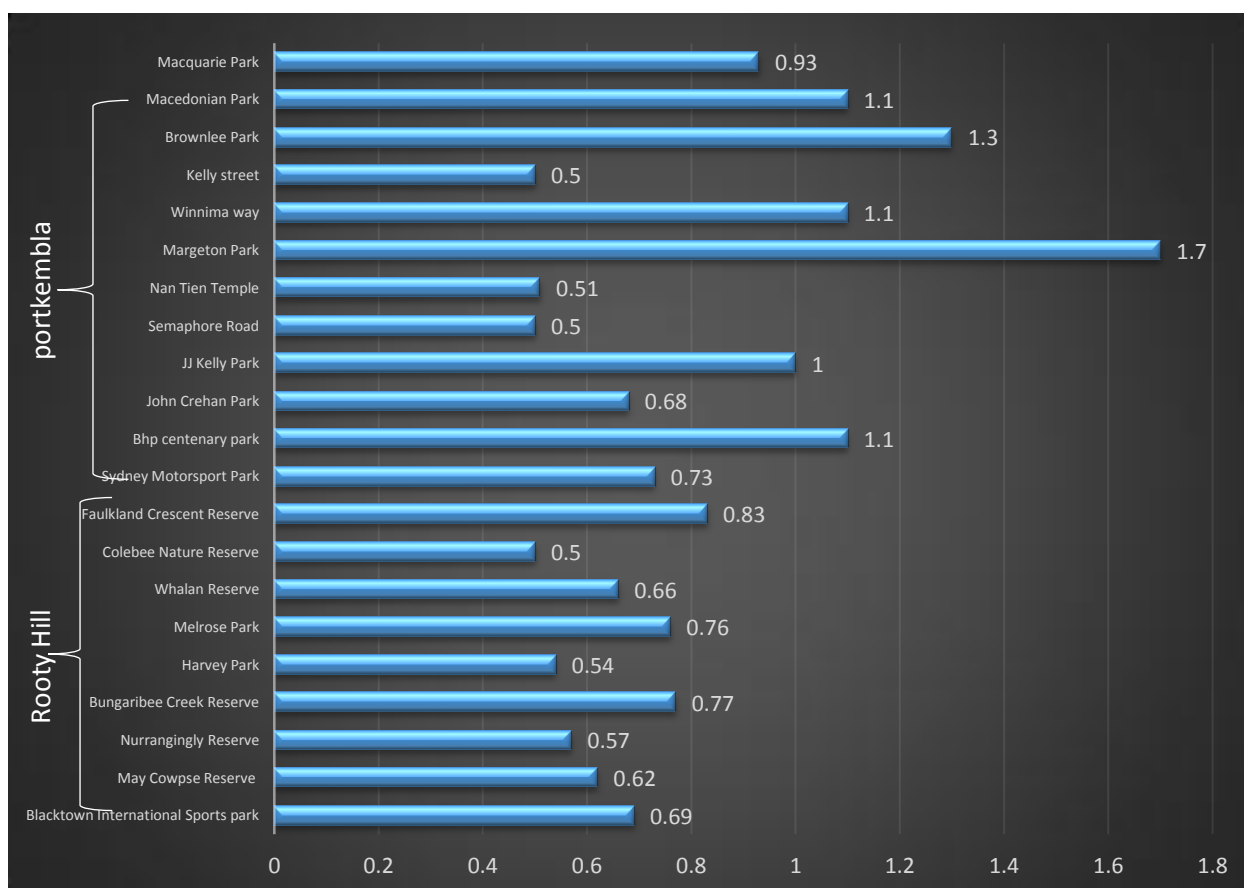


Figure 5.1 Trace metal (molybdenum) concentration in the soils near the Rooty Hill Steelworks, Port Kembla and Macquarie Park

### 5.2.2 Trace metal arsenic concentration in the soils

Arsenic concentration varied from 3.6 mg/kg to 9.5 mg/kg in the soils near the Rooty Hill Steelworks (Table 5.3). The lowest was at the Colebee Nature Reserve at 4.58 km from the Steelworks, whereas the highest was at the Melrose Park (3.99 km) and Faulkland Crescent Reserve (5.81 km). The nearest Blacktown International Sports Park (1.24 km) had 5mg/kg of arsenic whereas the furthest Sydney Motorsport Park (6 km) had a concentration of 6.3mg/kg (Figure 5.2)

Similarly, near the soils of Port Kembla Steelworks, the concentration of arsenic ranged from 1.9 mg/kg to 7.3 mg/kg (Table 5.3). The lowest concentration was near the Kelly Street (3.8 km) and the highest was at the Margeton Park (3.43 km). The nearest BHP Centenary Park (1 km) from the Port Kembla Steelworks had a concentration of 4.1 mg/kg and the furthest Macedonia Park (4.98 km) had 4.4 mg/kg of arsenic( Figure 5.2). In some of the sites in the Rooty Hill, arsenic was high as compared to the Port Kembla Steelworks sites. Likewise, arsenic was comparatively lower near both of the steelworks sites, as compared to the site of the Macquarie Park, where the concentration was 10 mg/kg. Also, all the three locations: Rooty Hill, Port Kembla and Macquarie Park had

arsenic concentration far below the NEPM 2011 guideline which is 300 mg/kg in soil for recreational purpose (Table 5.3)

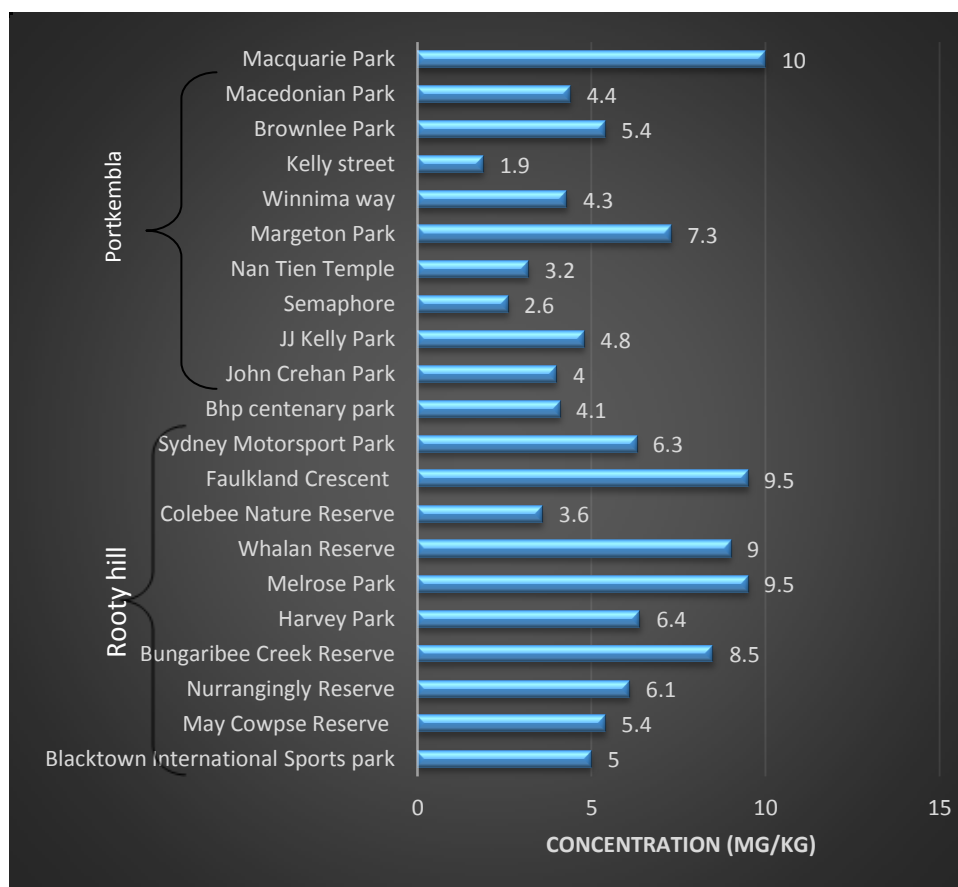


Figure 5.2 Trace metal Arsenic concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park

### 5.2.3 Heavy metals chromium, copper, lead, nickel, and zinc concentration

In the 10 sites near the Rooty Hill steelworks, the concentration of chromium ranged from 24 mg/kg to 100 mg/kg (Table 5.3). The Colebee Nature Reserve at a distance of 4.58 km from the Rooty Hill Steelworks had the lowest concentration whereas the Blacktown International Sports Park and Sydney Motorsport Park at the distances of 1.24 km and 6 km respectively had the highest concentration of chromium (Figure 5.3). Blacktown International Sports Park was closest to the Steelworks whereas the Sydney Motorsport Park was the furthest site.

The lowest copper concentration was 13 mg/kg in the Colebee Nature Reserve (4.58 km) whereas it was highest with a value of 120 mg/kg at the Nurrangingly Reserve (2.17 km). In the nearest



distance of 1.24 km at the Blacktown International Sports, the concentration of copper was 19 mg/kg whereas at the furthest distance at the Sydney Motorsport Park it was 22 mg/kg (Figure 5.3). Lead ranged from 15 mg/kg to 71 mg/kg (Table 5.3). The lowest lead was reported in Colebee Nature Reserve and the highest was in Nurrangingly Reserve. At the nearest distance, lead concentration was 23 mg/kg whereas at the furthest it was 25 mg/kg (Figure 5.3).

Likewise, Nickel concentration varied from 9.8 mg/kg to 55 mg/kg (Table 5.3). The lowest value was at the Colebee Nature Reserve and the highest was recorded at Sydney Motorsport Park. At the nearest to the Steelworks at the Blacktown International Sports Park, the concentration was 47 mg/kg whereas at the furthest the concentration was the highest (Figure 5.3).

In the case of zinc, it ranged from 20 mg/kg in Colebee Reserve to 120 mg/kg at Nurrangingly Reserve (Table 5.3). The nearest Blacktown International Sports had 48 mg/kg of zinc whereas the furthest Sydney Motorsport Park had 44 mg/kg (Figure 5.3).

All the heavy metals, chromium, cadmium, lead, nickel, and zinc, were the lowest in the Colebee Nature Reserve whereas the Nurrangingly Nature Reserve showed the highest for the copper, lead and zinc. The concentrations of zinc in all the 10 sites near the Rooty Hill Steelworks were the lowest as compared to the Macquarie Park (170 mg/kg). Two of the sites showed higher chromium, each one of them having higher copper and lead, and two sites showed lower nickel concentrations.

Near the Port Kembla Steelworks, the chromium concentration ranged from 49 mg/kg to 170 mg/kg, copper 47 mg/kg to 110 mg/kg, lead 16 mg/kg to 72 mg/kg, nickel 25 mg/kg to 75 mg/kg (Figure 5.4). At the nearest distance of 1 km, the concentration of chromium was 52 mg/kg, copper 110 mg/kg, lead 72 mg/kg, nickel 25 mg/kg, and zinc 190 mg/kg. At the furthest distance at 4.98 km from the Steelworks, chromium was 91 mg/kg, copper 51 mg/kg, lead 57 mg/kg, nickel 23 mg/kg, and zinc 170 mg/kg (Figure 5.4). As compared to the Macquarie Park soil, three of the sites out of 10, had higher concentration of chromium, 9 sites had higher copper, 3 sites had higher lead, all the 10 sites had higher nickel, and only one site had higher zinc.

As compared to the Port Kembla sites, there were highest record of chromium and copper near Rooty Hill sites whereas Port Kembla sites had the highest lead, nickel and zinc. However, all the three locations had lower concentration of chromium, copper, lead, nickel, and zinc as compared to the NEPM 2011 guideline which says chromium 240 mg/kg, copper 20000 mg/kg, lead 600 mg/kg, nickel 800 mg/kg, and zinc 700 mg/kg in soils for recreational purpose (Table 5.3).

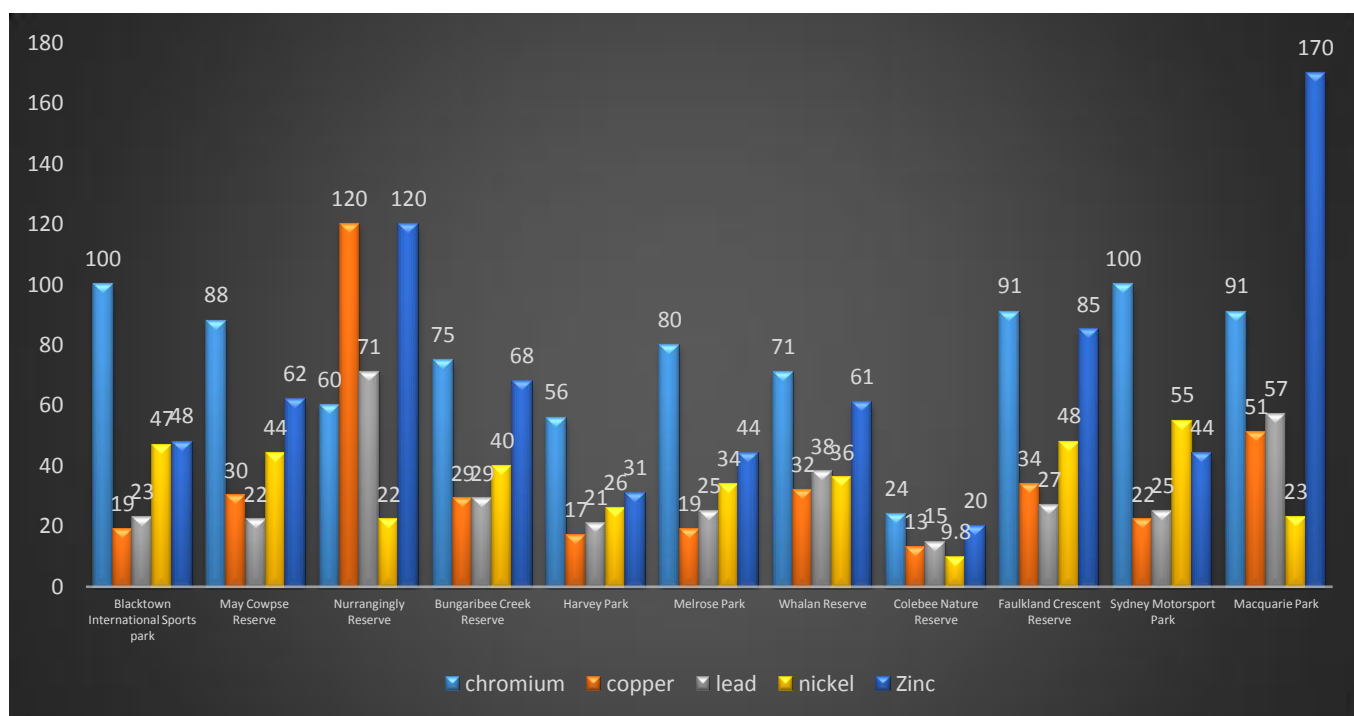


Figure 5.3 Heavy metals concentration in the soils near the Rooty Hill Steelworks and Macquarie Park

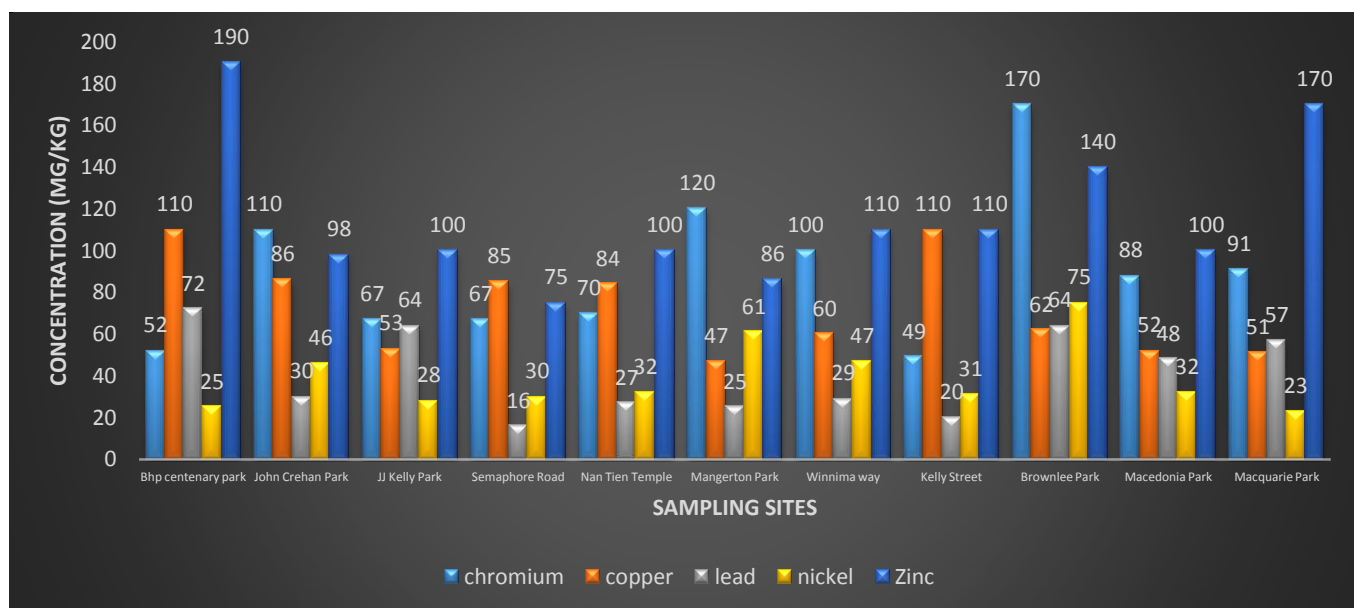


Figure 5.4 Heavy metals concentration in the soils near the Port Kembla Steelworks and Macquarie Park

#### 5.2.4 Titanium concentration

The concentration of titanium near the Rooty Hill sites varied from 30 mg/kg to 69 mg/kg (Table 5.3). The highest was at the Whalan Reserve (4.39 km) whereas the lowest was at the Harvey Park

(3.9 km). The nearest site (1.24 km) had a concentration of 39 mg/kg, whereas the furthest site at 6 km was 57 mg/kg (Figure 5.5)

Similarly, at the Port Kembla sites, the titanium varied from 37 mg/kg to 2680 mg/kg (Table 5.3). The lowest was at the Margeton Park (3.43 km), whereas the highest was near the Kelly road (3.8 km). The nearest site (1km) from the Steelworks had a concentration of 140 mg/kg whereas the furthest site (4.98 km) had a concentration of 420 mg/kg (Figure 5.6).

All the 9 sites, except for 1 site of Port Kembla, had a higher concentration of titanium as compared to the Rooty Hill sites, however as compared to the Macquarie Park site with a concentration of 24 mg/kg, all sites at the Rooty Hill and Port Kembla had higher concentrations of titanium.

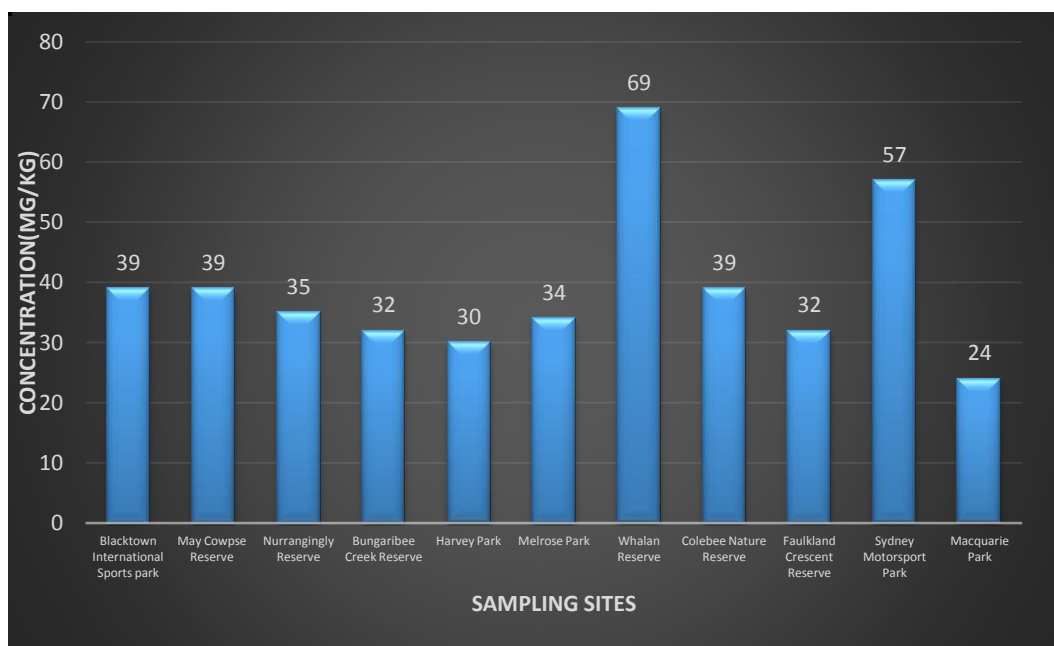


Figure 5.5 Titanium concentration in the soils near the Port Kembla Steelworks and Macquarie Park

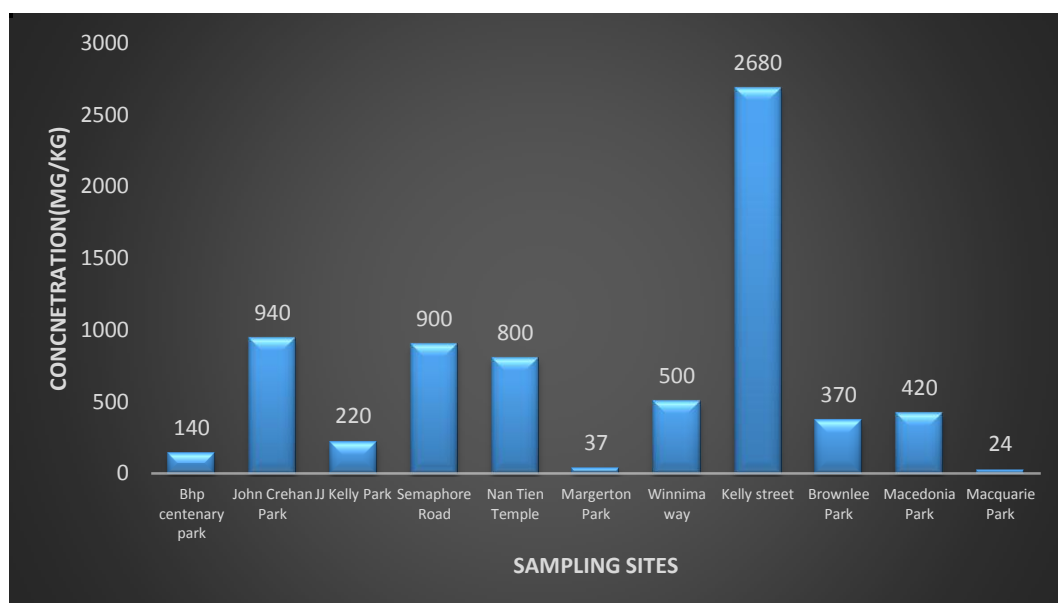


Figure 5.6 Titanium concentration in the soils near the Port Kembla Steelworks and Macquarie Park

### 5.2.5 Iron concentration

Iron concentration near the Rooty Hill sites varied from 14000 mg/kg to 49700 mg/kg (Table 5.3). The lowest was at the Nurrangingly Reserve (2.17 km) and the highest was at the Melrose Park (3.99 km). At the nearest from the Steelworks, the concentration was 25000 mg/kg, whereas at the furthest it was 27600 mg/kg (Figure 5.7).

Similarly, near the Port Kembla Steelworks, the concentration ranged from 22100 mg/kg to 61300 mg/kg in soils (Table 5.3). The lowest was at a distance of 4.98 km which was also the furthest sampling site whereas the highest was near the Kelly Street (3.8 km) (Figure 5.7). Three sites near the Port Kembla Steelworks had higher concentration of iron as compared to all the sites of Rooty Hill. Eight sites out of the 10 sites for Rooty Hill and Port Kembla had higher concentration of iron as compared to the Macquarie Park.

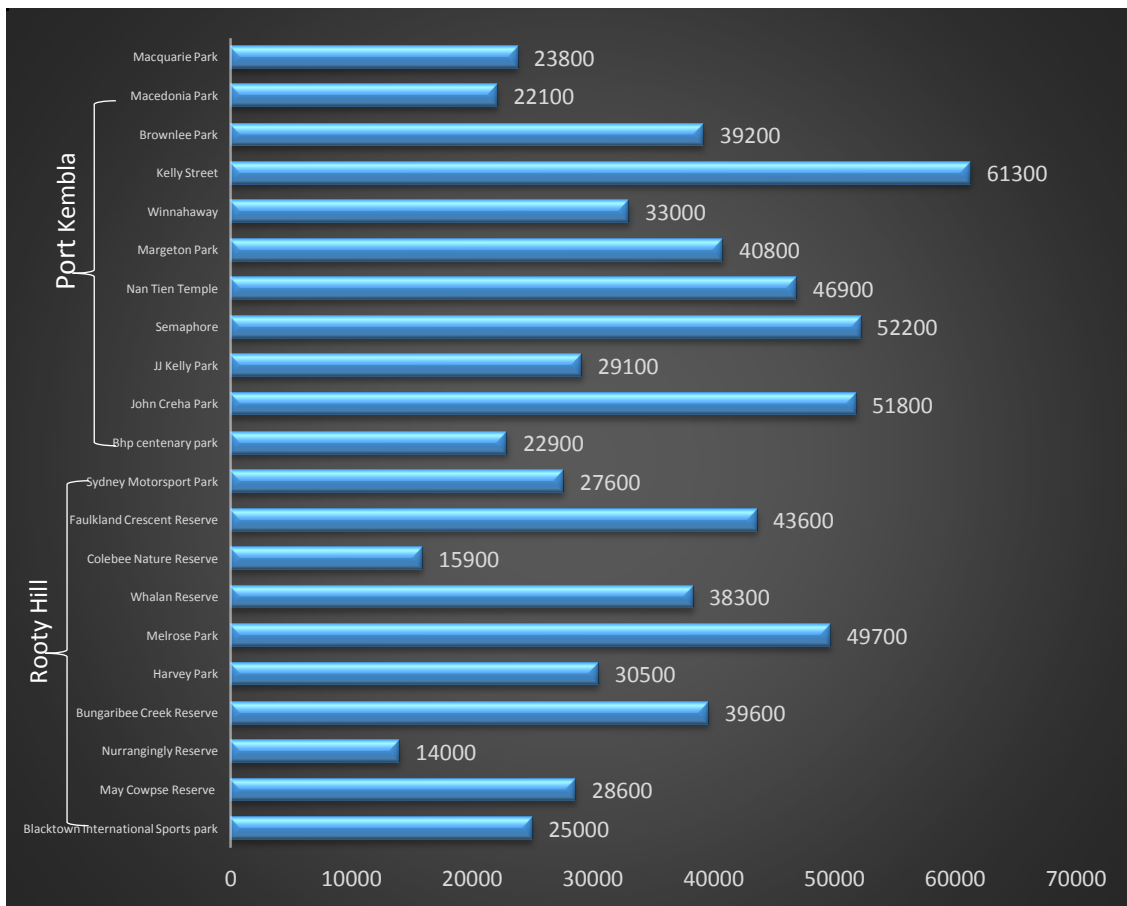


Figure 5.7 Iron concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park

### 5.2.6 Manganese concentration

The manganese concentration near the Rooty Hill Steelworks ranged from 210 mg/kg to 1300 mg/kg in soils (Table 5.3). The lowest was at the Harvey Park (3.9 km) whereas the highest at the Sydney Motorsport Park (6 km). The nearest site from the Steelworks at 1.24 km had concentration of 560 mg/kg (Figure 5.8).

Likewise, near the Port Kembla Steelworks, the concentration of manganese varied from 350 mg/kg to 1950 mg/kg (Table 5.3). The lowest was at the JJ Kelly Park (2.75 km from the Steelworks), whereas the highest was at the Macedonia Park (4.98 km) which was also the furthest site. Closer to the Steelworks, at a distance of 1 km, the concentration was 820 mg/kg (Figure 5.8).

One of the sites near the Port Kembla Steelworks had the highest concentration of manganese as compared to all the sites of the Rooty Hill, however most of the sites at the Rooty Hill had higher concentration than the sites at Port Kembla.

At Port Kembla, all the sites had higher concentration of manganese as compared to the site of Macquarie Park which had concentration of 220 mg/kg whereas at the Rooty Hill, except 1 site, all the 9 sites had higher concentration. All the sites of Rooty Hill, Port Kembla and Macquarie Park had lower concentration of manganese as compared to the NEPM 2011 guideline which is 9000 mg/kg in soil for recreational purpose (Table 5.3).

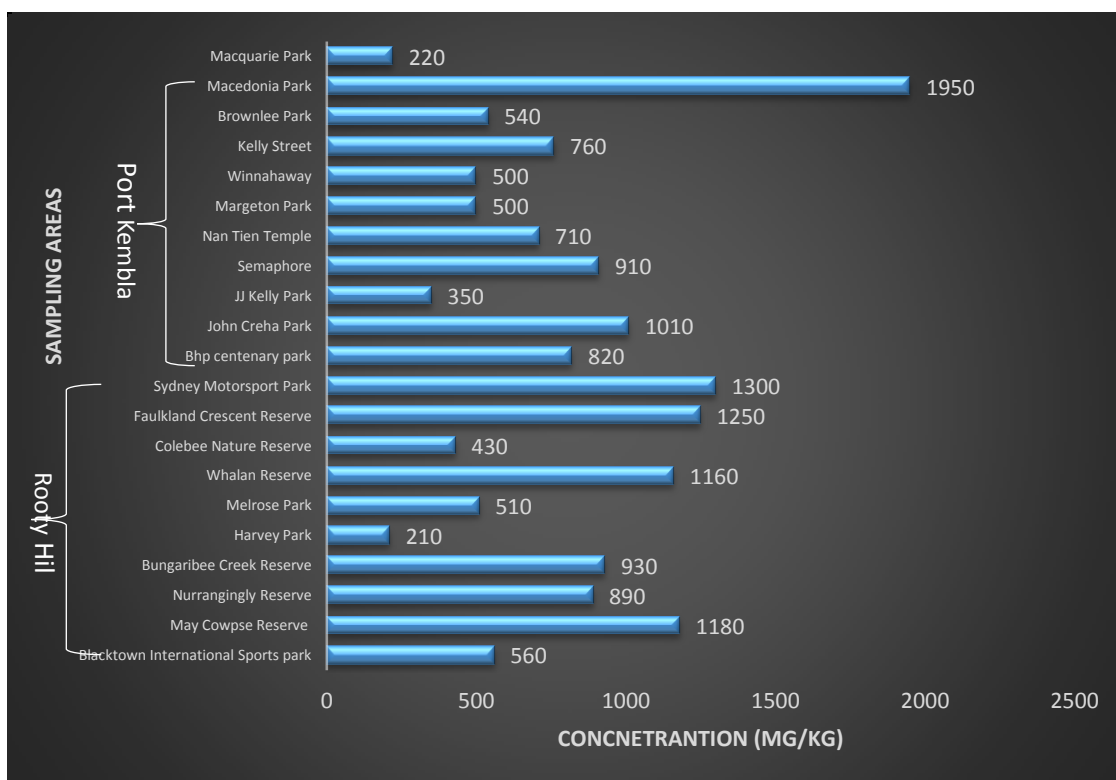


Figure 5.8 Manganese concentration in the soils near the Rooty Hill Steelworks, Port Kembla Steelworks and Macquarie Park

### 5.2.7 Sodium, Potassium, and Magnesium concentration in soils

At the various sites near the Rooty Hill Steelworks, sodium ranged from 60 mg/kg to 430 mg/kg, potassium from 850 mg/kg to 2340 mg/kg, and magnesium from 550 mg/kg to 2950 mg/kg (Table 5.3). Sodium was the lowest at Nurrangingly Reserve and Colebee Nature Reserve at the distances of 2.17 km and 4.58 km, respectively, whereas it was highest at the May Cowpse Reserve at a distance of 1.59 km from the Steelworks. Likewise, Colebee Nature Reserve (4.58 km) had the lowest concentration of potassium, whereas the Faulkland Crescent Reserve (5.81km) had the highest concentration of potassium. Magnesium was the lowest at Colebee Nature Reserve (4.58km) and the highest at the Whalan Reserve (4.39 km). The sodium, potassium and magnesium concentrations nearest to the Steelworks were 270 mg/kg, 1160 mg/kg, and 1900 mg/kg whereas the furthest sites had 290 mg/kg, 1220 mg/kg and 1810 mg/kg, respectively (Figure 5.9) The

concentrations in the various sites near the Rooty Hill Steelworks were in the order of sodium<potassium< magnesium.

At the Port Kembla Steelworks sites, the concentration of sodium, potassium and magnesium ranged from 110 mg/kg to 350 mg/kg, 670 mg/kg to 1790 mg/kg, and 1390 mg/kg to 10600 mg/kg respectively (Table 5.3). The lowest sodium, potassium and magnesium concentrations were measured in Margeton Park (3.43 km) and BHP Centenary Park (1 km), Nan Tien Temple site (3.04 km), and Margeton Park (3.43 km), respectively. The highest concentrations of sodium were at the John Crehan Park (1.17 km), whereas potassium and magnesium were both the highest near Kelly Street (3.8 km) (Figure 5.10). In these sites of the Steelworks, the concentrations in the soils were sodium<potassium< magnesium.

In the Rooty Hill sites, sodium and potassium concentrations were recorded higher than the concentrations at the Port Kembla sites, whereas the magnesium concentration was lower than the Port Kembla site.

As compared to the Macquarie Park site having 110 mg/kg of sodium concentration, one site of the Rooty Hill had the same concentration and the others six sites exceeded this background concentration. Seven sites at Rooty Hill exceeded the background potassium concentration measured at the Macquarie Park 1130 mg/kg in soil, whereas eight sites exceeded the magnesium concentration of 860 mg/kg at the Macquarie Park. Similarly, at the Port Kembla, eight sites exceeded the sodium, two sites had same concentration of sodium, seven sites exceeded for potassium, and all the ten sites exceeded the background magnesium concentrations measured at the Macquarie Park site.

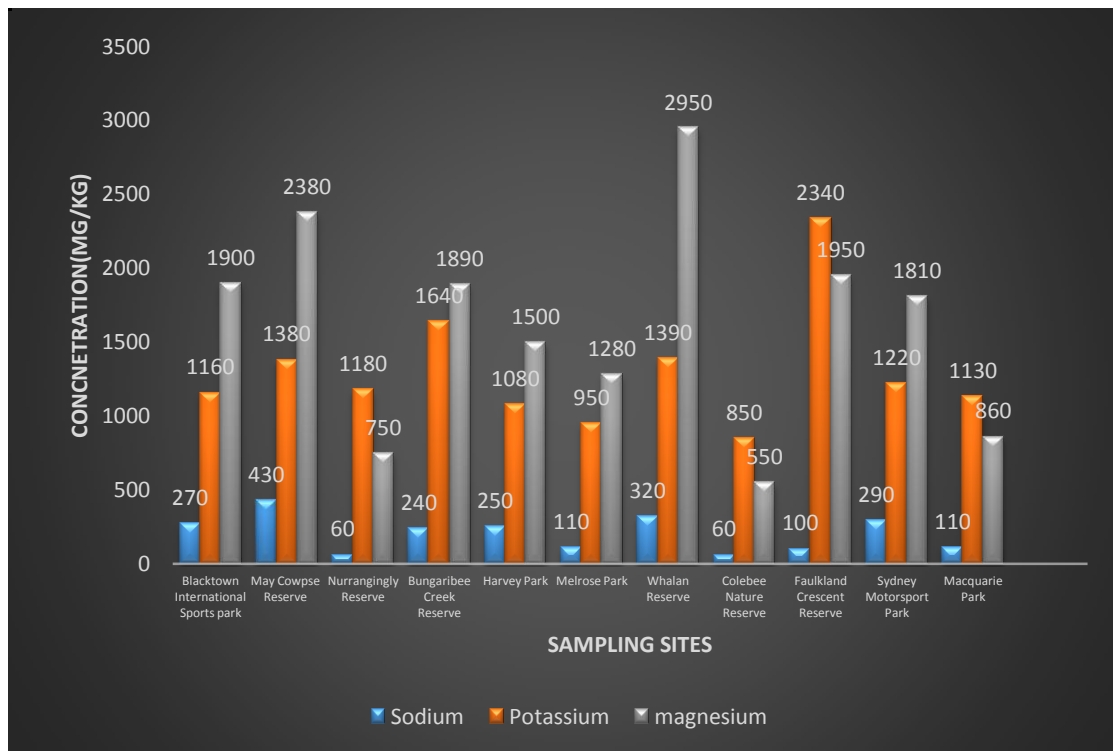


Figure 5.9 Sodium, Potassium and Magnesium concentration in the soils near the Rooty Hill Steelworks and Macquarie Park

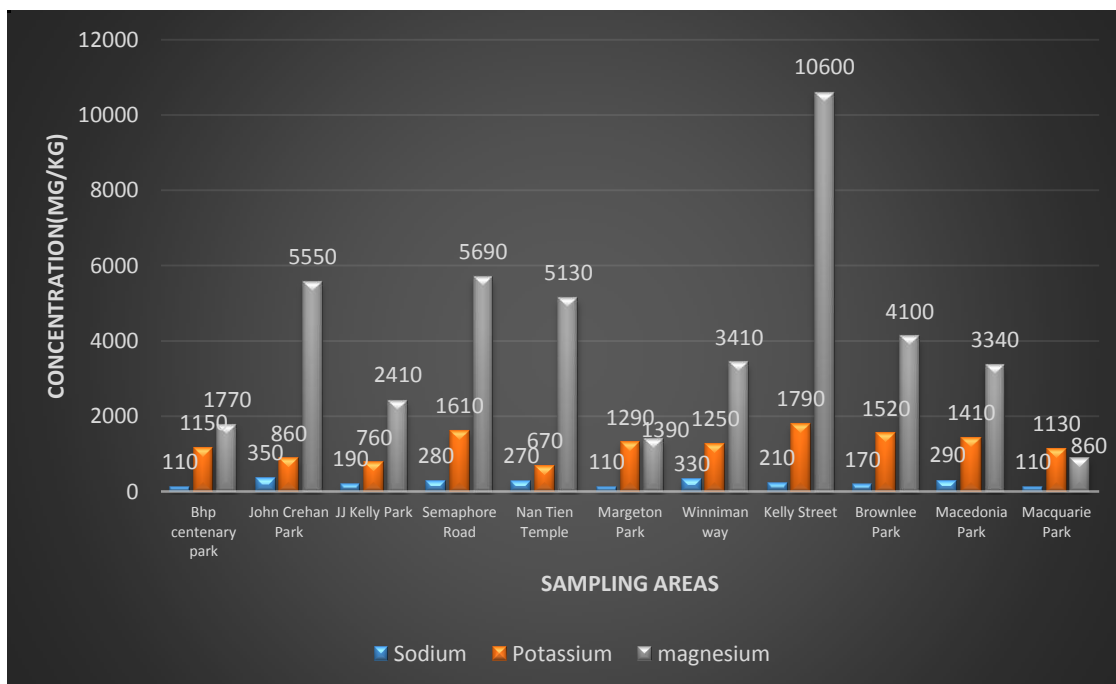


Figure 5.10 Sodium, Potassium and Magnesium concentration in the soils near the Port Kembla Steelworks and Macquarie Park



### ***5.2.8 Phosphorus, Sulphur and Silicon concentrations in the soils***

The phosphorus, sulphur, and silicon concentrations near the Rooty Hill Steelworks varied from 170 mg/kg to 590 mg/kg, 150 mg/kg to 390 mg/kg, and 1360 mg/kg to 2060 mg/kg respectively (Table 5.3). The lowest concentration of phosphorus, sulphur and silicon were at Harvey Park (3.9 km), Colebee Nature Reserve (4.58 km), and May Cowpse Reserve (1.59 km) respectively. The highest phosphorus was at Nurrangingly Reserve (2.17 km), whereas the Bungaribee Creek Reserve (2.89 km) had the highest concentration for sulphur and silicon (Figure 5.11). The concentration in most of the soils were sulphur< phosphorus< silicon.

Similarly, at the Port Kembla Steelworks sites, the phosphorus, sulphur, and silicon concentrations were 580 mg/kg to 980 mg/kg, 240 mg/kg to 610 mg/kg, and 1570 mg/kg to 2320 mg/kg, respectively (Table 5.3). The lowest phosphorus was at BHP Centenary Park (1km) and Margeton Park (3.43 km). Phosphorus and silicon were lowest at John Crehan Park (1.17 km), and Brownlee Park (4.06 km) respectively. The highest concentration of phosphorus, sulphur, and silicon were at Brownlee Park, Macedonia Park (4.98 km), and John Crehan Park respectively. The nearest site had phosphorus, sulphur and silicon concentration of 580 mg/kg, 530 mg/kg, and 2220 mg/kg, whereas the furthest site had a concentration of 710 mg/kg, 610 mg/kg, and 1760 mg/kg respectively (Figure 5.12). The concentration in the soils was sulphur<phosphorus< silicon.

The highest recorded phosphorus, sulphur and silicon were near the Port Kembla Steelworks soils as compared to the Rooty Hill. As compared to the Macquarie Park site, where sodium concentration was 1700 mg/kg, both the Rooty Hill sites and the Port Kembla sites had lower concentration of sodium. At one site at Rooty Hill and five sites at Port Kembla had higher phosphorus as compared to the Macquarie Park site (360 mg/kg), whereas one of the sites at Port Kembla had same concentration as the Macquarie Park site. Silicon at the six sites of Rooty Hill was above the Macquarie Park site concentration (1690 mg/kg), whereas one site was same as the Macquarie Park site. At the Port Kembla, nine sites had higher concentrations of silicon than the Macquarie Park site.

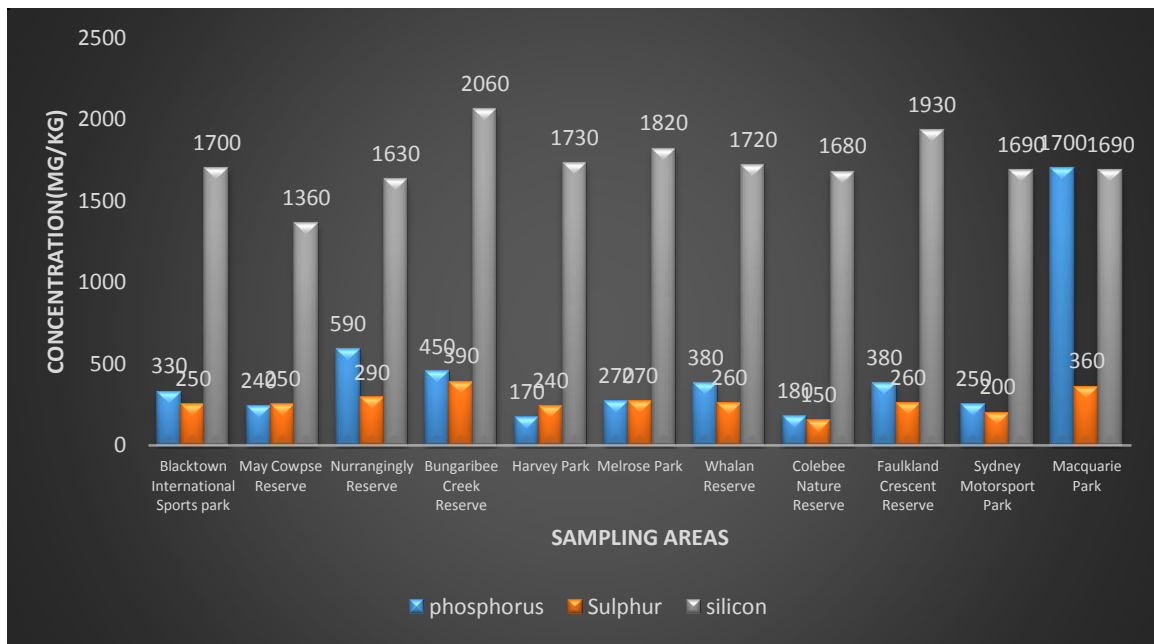


Figure 5.11 Phosphorus, Sulphur and Silicon concentration in the soils near the Rooty Hill Steelworks and Macquarie Park

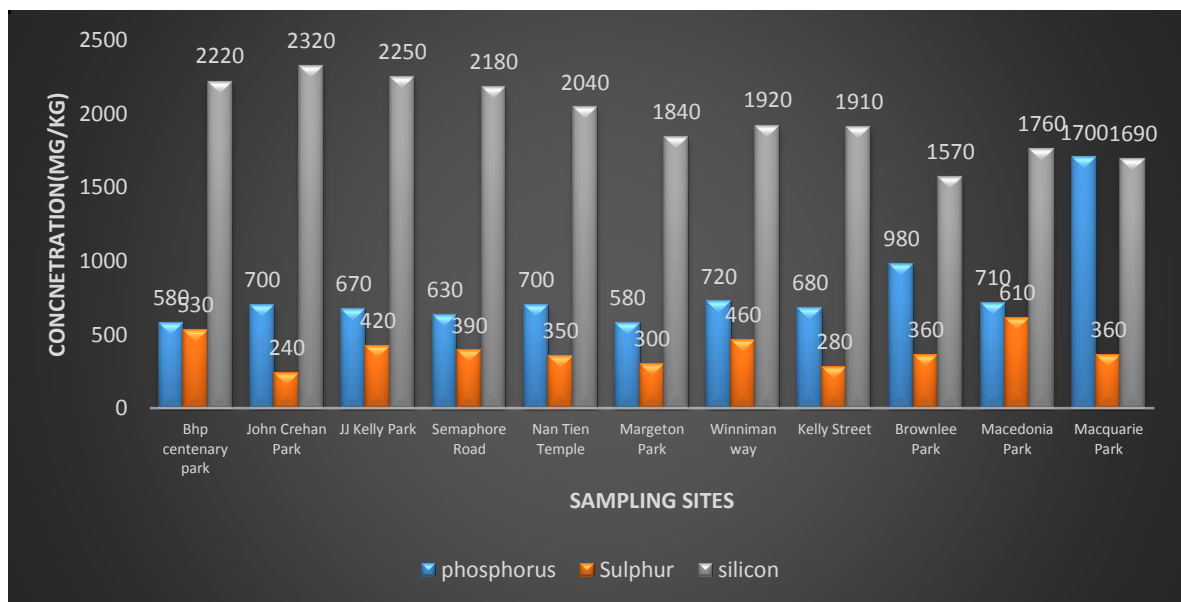


Figure 5.12 Phosphorus, Sulphur and Silicon concentration in the soils near the Port Kembla Steelworks and Macquarie Park

### 5.3 FTIR spectroscopy of Soils

Figure 5.13 presents the FTIR spectra of the soils collected near the Rooty Hill Steelworks. All the soils except the Nurrangingly Reserve site at a distance of 2.17 km, had the broad band spectrum at  $3620\text{ cm}^{-1}$ . It means the soils in the nine sites had the mineral matter associated with the aluminosilicate clay materials kaolinite (Strezov et al. 2010). The other vibrations were in the range of  $910\text{ cm}^{-1}$  and  $532\text{ cm}^{-1}$  in all the soils which represented the presence of anthophyllite (Strezov et al. 2010). Also, all the soils had the spectra band at the range of  $468.9\text{ cm}^{-1}$  which represented the vibration of Si–O structure, Si–O–Me structure in the soils, where Me represents metal, most likely iron. These bands also represented the presence of haematite (Nayak et al. 2007).

All the soils near the Port Kembla Steelworks showed the band spectrum at  $3620\text{ cm}^{-1}$  except one site (Figure 5.14). This spectrum also represented the vibration from the mineral matter associated with the aluminosilicate clay materials kaolinite (Strezov et al. 2010). Other vibrations were at the range of  $910\text{ cm}^{-1}$  and  $532\text{ cm}^{-1}$ , which represented the presence of anthophyllite (Strezov et al. 2010) and the vibrations were also present at the range of  $468.9\text{ cm}^{-1}$  which represented the presence of Si–O structure, Si–O–Me structure in soils (Nayak et al. 2007). In the Macquarie Park soil, there was additional spectrum of  $3696.8\text{ cm}^{-1}$ , which represented the presence of Me–O–H structure in soil, where Me is most likely aluminium (Figure 5.15). This also represented the presence of kaolinite (Nayak et al. 2007).

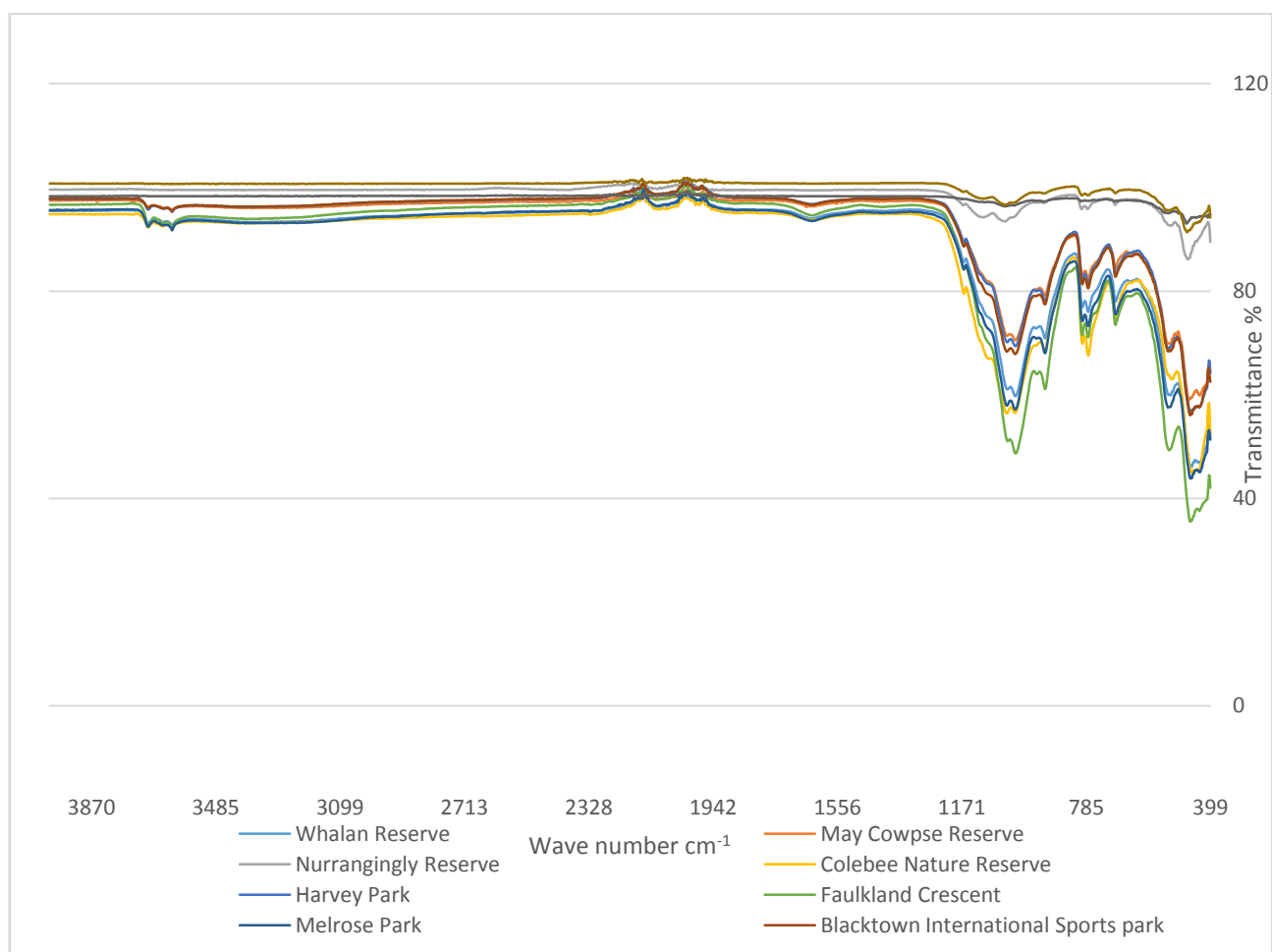


Figure 5.13 FTIR spectra of soils near the Rooty Hill Steelworks

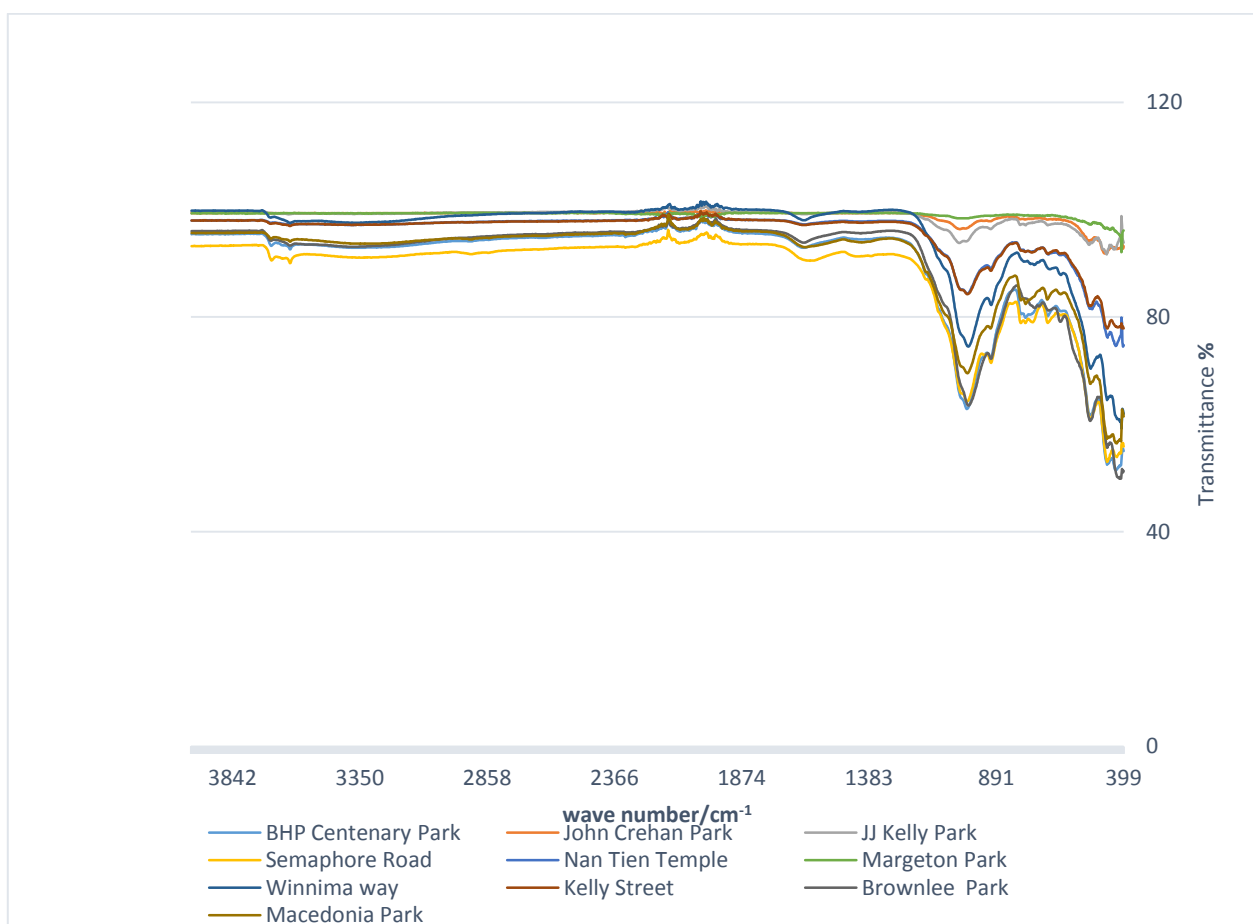


Figure 5.14: FTIR spectra of soil near the Port Kembla Steelworks

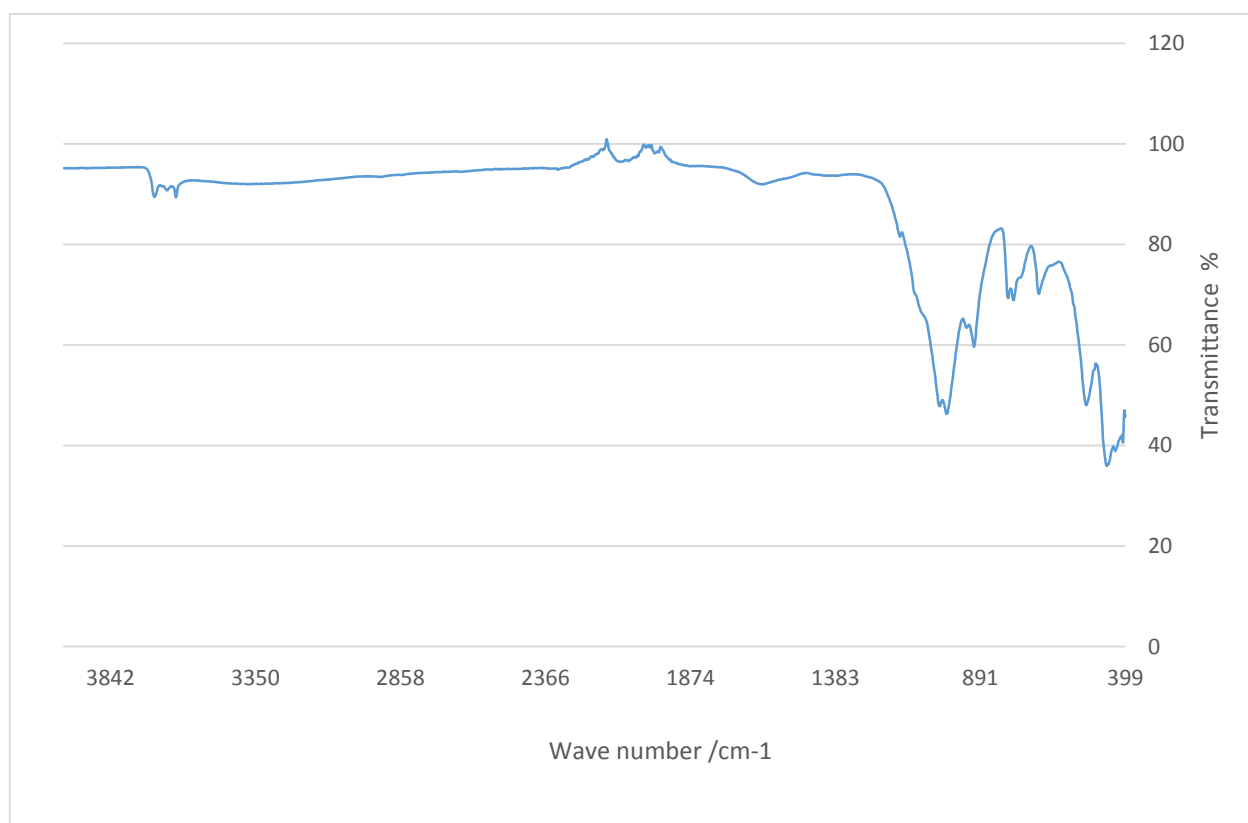


Figure 5.15 FTIR spectra of soil of the Macquarie Park

## **Chapter 6: Discussion**

This chapter discusses the results of the study of trace metals and heavy metals on soils near the three locations: Rooty Hill Steelworks, Port Kembla Steelworks and the Macquarie Park. Comparative analysis of the soils in the three locations is performed and compared with the previous studies. The concentrations of soil heavy metals and trace metals are validated with the NEPM 2011 guideline.

### **6.1 Trace metals mercury, cadmium, molybdenum and arsenic distribution**

The mercury concentration at both steelworks locations, Rooty Hill and Port Kembla had less than 0.2 mg/kg, whereas the Macquarie Park site had 0.21 mg/kg. In the previous studies in the urban soils of Lithgow, Australia, the mercury concentration was as high as 14.9 mg/kg (Rouillon et al. 2013). Ji et al. (2012) reported 0.57-11.25 mg/kg range of mercury in the top soil (0-30 cm) near the retired paint and ink factory, and when comparing the value of mercury in soils near the steelworks and at Macquarie Park, all had low concentrations. Also, these values were below the acceptable limit (12 mg/kg) of mercury in soils as per the estimated level of human intake of mercury and potential accumulation of mercury from soil by specific pathways (Bashor and Turri 1986). The concentrations of mercury in soil at all three locations were below the NEPM 2011 guideline for mercury in soil (100mg/kg) for recreational purpose (Appendix 1). This indicates that the mercury pollution from the two industrial steelworks sites are low which also infers that these two industries are adding low mercury or negligible amount in the surrounding soil.

Cadmium in the soil at all the three locations was below 0.5 mg/kg. This cadmium value was below the historical value of 2.8 mg/kg in the soils from urban grassland, such as farm land, recreational land, industrial land, and roadsides at the Wollongong City area (Beavington 1973). Also, the cadmium values in the soils were below the top soil mean cadmium concentration value of 1.22 mg/kg at Port Kembla, and 5.54 mg/kg at Boolaro (Kachenko et al. 2006). It was also below the mean cadmium in the top soil (0-30 cm) chromic luvisols (0.5 mg/kg) and alluvial fluvisol (2.1 mg/kg) near the iron smelter in Kremikovtzi (Bulgaria) (Schulin et al. 2007). Comparing to the cadmium mean range of <0.1-4.3 mg/kg at the lake Illawara sediments (Ellis and Kanamori 1977), 7 mg/kg Cd in the soil (0-5 cm) near the industrial area in Bucharest (Velea et al. 2009), the cadmium in the soils at the three locations were low. Also, the cadmium values for soil were far below the NEPM 2011 guideline (400 mg/kg) (Appendix 1).

Molybdenum in the soil ranged from < 0.5 mg/kg to 0.83 mg/kg near the Rooty Hill steelworks and 0.5 mg/kg to 1.7 mg/kg around the Port Kembla steelworks (Table 5.3). The mean molybdenum concentrations for these two locations were 0.68 mg/kg and 0.95 mg/kg respectively (Table 5.3). At the Macquarie Park it was 0.93 mg/kg. These values were far below the molybdenum found in the top chromic luvisols (0-20 cm) and alluvial fluvisol (0-20cm) soils near the iron smelters in Kremikovtzi (Bulgaria) with mean values of 4.6 mg/kg and 5.6 mg/kg respectively (Schulin et al. 2007). Also, the molybdenum were below the range of <1 to 3 mg/kg near the railway junction of Ława Główna, Poland (Malawska and Wiołkomirski 2001), and near the industrial area of Chennai, India with mean 7.8 mg/kg and ranging from 2.3 to 15.6 mg/kg (Krishna and Govil 2008). Comparatively, the Rooty Hill sites had lower mean molybdenum value than the Port Kembla Steelworks and Macquarie Park.

Arsenic concentration in the soil near the Rooty Hill Steelworks and the Port Kembla Steelworks were in the range of 3.6 mg/kg to 9.5 mg/kg, and 1.9 mg/kg to 7.3 mg/kg respectively (Table 5.3). The mean values of arsenic for these two locations were 6.93 mg/kg and 4.2 mg/kg respectively (Table 5.3). At the Macquarie Park it was 10mg/kg. Martley et al. (2004a) reported 4.1 mg/kg of arsenic at the soil depth of 0-5 cm and 4.7 mg/kg in the soil depth of 5-20 cm at Port Kembla. Other studies at Port Kembla top soil arsenic was found to be 62.5 mg/kg (Kachenko et al. 2006), 0.93 mg/kg arsenic in the soil near the industrial area of Chennai, India (Krishna and Govil 2008), 107.2 mg/kg near the secondary lead smelter at Ontario, Canada at the depth of soil of 0-5cm (Temple et al. 1977). In this work arsenic was found to have higher value at the background site Macquarie Park than the soil near the two steelworks. Also, the arsenic values in the two steelworks locations are far below the NEPM guideline 2011 (300mg/kg) for recreational purpose (Appendix 1).

## **6.2 Heavy metals chromium, copper, lead, nickel, zinc, titanium, iron and manganese concentrations**

Chromium near the Rooty Hill Steelworks and Port Kembla ranged from 24 mg/kg to 100 mg/kg and 49 mg/kg to 170 mg/kg respectively (Table 5.3). The mean value of the Rooty Hill soil (74.5 mg/kg) and Port Kembla (89.3 mg/kg) were higher than the chromium concentration of 12 mg/kg and 14 mg/kg at depths of 0-5cm and 5-20cm respectively, measured previously by Martley et al. (2004a), chromium in a range of 5-81 mg/kg in the soil near the railway junction at Ława Główna, Poland measured by Malawska and Wiołkomirski (2001), and 50 mg/kg near the industrial area in Chennai, India (Krishna and Govil 2008). The concentration in the soil near the retired paint and

ink factory at Zhejiang Province, China was in the range of 20.6-85.4 mg/kg (Ji et al. 2012). As compared to the Macquarie Park site having the value of 91 mg/kg chromium, these two steelworks location had lower mean chromium; however, they had higher range. Thus the steelworks are not only the contributors of chromium in the soils in the examined sites. As compared to the NEPM guideline 2011 with the chromium value of 240 mg/kg in soil for recreational purpose (Appendix 1), the soils of all the locations were below these guidelines.

Copper near the Rooty Hill steelworks and the Port Kembla steelworks ranged from 13 mg/kg to 120 mg/kg and 47 mg/kg to 110 mg/kg respectively (Table 5.3). The mean values at these two locations for copper were 33.5 mg/kg and 74.9 mg/kg respectively. Kachenko et al. (2006) reported mean value of 338 mg/kg of copper in the top soil at Port Kembla, mean value of 58 mg/kg in a recreational land (Beavington, 1973). Also the copper in the soil near the retired paint and ink factory was reported in the range of 22.3-108.6 mg/kg (Ji et al. 2012), 350 mg/kg in the soil at 0-5cm depth near industrial area in Bucharest (Velea et al. 2009), 6-115 mg/kg in the soil near the railway junction Ława Główna, Poland (Malawska and Wiołkomirski 2001), a range of 22.4–372.0 mg/kg with mean value of 154.4 mg/kg near industrial area in Chennai, India (Krishna and Govil 2008) and mean value of 38 mg/kg and a range of 23-75 mg/kg in the lake Illawara sediments (Ellis and Kanamori 1977). Comparing to the soil copper of 40.1 mg/kg and 61.8 mg/kg on chromic luvisols and alluvial fluvisol at 0-20 cm depth respectively near the iron smelter at Kremikovtzi (Bulgaria) (Schulin et al. 2007), Rooty hill had lower copper concentrations, whereas Port Kembla had higher copper in the soil. The mean values at the two steelworks locations were below 76 mg/kg for 0-5 cm soil and 113 mg/kg for 5-20 cm soil at Port Kembla measured previously (Martley et al. 2004a). This may be due to the sampling location in the current work which was near the iron and steelworks and not near the copper smelter. Also the mean value of copper at Rooty Hill site was lower whereas higher at Port Kembla than the Macquarie Park (51mg/kg); however, having the higher range values for concentration. This indicates that the copper smelter at Port Kembla may be the contributor of copper in that locality. As compared to the NEPM guideline 2011, with a concentration of 20000 mg/kg of copper (Appendix 1), the soil concentrations at all the three locations were very low.

Lead at the two different locations varied from 15 mg/kg to 71 mg/kg, and 16 mg/kg to 72 mg/kg near the Rooty Hill steelworks and Port Kembla steelworks respectively. The mean values of lead for these two locations were 29.6 mg/kg and 39.5 mg/kg respectively, whereas the Macquarie Park had the value of 57 mg/kg. At both steelworks locations, the lead concentration range was higher than the Macquarie Park, whereas mean value was lower. The mean value at Rooty Hill steelworks



and Port Kembla steelworks were lower than the top soil concentration of 430.2 mg/kg of lead (Kachenko et al. 2006), higher than that of Wollongong City of 1.6 mg/kg lead for 5-15 cm deep soil in a recreational land (Beavington, 1973). The soil at the Rooty Hill was almost the same as that of 29mg/kg (0-5cm) and 30mg/kg (5-20cm) near Port Kembla Industrial complex (Martley et al. 2004a); however, it was higher near the Port Kembla steelworks in this study. The lead concentrations were found to be 3106 (165-42850) mg/kg in the soil (0-5cm ) near the secondary lead smelter Ontario, Canada, 22-506 mg/kg near the railway junction Iława Główna, Poland (Malawska and Wiołkomirski 2001), 1.5 to 140.2 mg/kg, with mean content of 41.81 mg/ kg near the industrial area, Chennai, India (Krishna and Govil 2008), 15 mg/kg (11-26 mg/kg) in the sediments of lake Illawara (Ellis and Kanamori 1977). Compared to the NEPM 2011 guideline value of 600 mg/kg (Appendix 1), the soil lead at all the three locations were within the guideline.

Nickel varied from 9.8 mg/kg to 55 mg/kg near the Rooty Hill steelworks whereas it ranged from 25 mg/kg to 75 mg/kg near the Port Kembla steelworks (Table 5.3). The mean values for these two locations for the nickel were 36.1 mg/kg and 40.7 mg/kg respectively, whereas for the Macquarie Park it was 23 mg/kg (Table 5.3). The soil nickel at these two steelworks sites and the Macquarie Park were lower as compared to the soil near the iron smelter at Kremikovtzi (Bulgaria) having chromic luvisols as 108 mg/kg and alluvial fluvisols as 111 mg/kg at the depth of 0-20 cm (Schulin et al. 2007). Nickel concentration varied from 11.8 to 78.8 mg/kg with the mean value of 48.9 mg/kg in the soil near the industrial area, Chennai, India (Krishna and Govil 2008) and 23.6-66.2 mg/kg in the top soils (0-30cm) near the retired ink and paint factory at Zhejiang Province, China (Ji et al. 2012). Since, nickel concentration in the current work was higher at the two steelworks locations when compared to the Macquarie Park, hence the steelworks may be contributing nickel in the soils. Comparatively, Port Kembla steelworks has higher nickel concentrations than Rooty Hill. Comparing the different sites of the steelworks, and the Macquarie Park with the NEPM 2011 guideline for soil (800 mg/kg)( Appendix 1), all the soil nickel concentrations were comparatively low.

Zinc in the soils at the Rooty Hill and Port Kembla steelworks varied in the range from 20 mg/kg to 120 mg/kg and 75 mg/kg to 190 mg/kg (Table 5.3). The mean concentration of zinc at these two locations were 58.3 mg/kg and 110.9 mg/kg respectively (Table 5.3). At the Macquarie Park, the zinc concentration was 170 mg/kg. Zinc ranged from 45- 1244 mg/kg in the soils near the railway junction at Iława Główna, Poland (Malawska and Wiołkomirski 2001), mean value of 128.2 mg/kg and a range from 63.5 to 213.6 mg/kg in the soil near the industrial area at Chennai, India (Krishna and Govil 2008), mean 44 mg/kg and a range from 18-83mg/kg in the sediments of lake Illawara

(Ellis and Kanamori 1977). Martley et al. (2004a) reported 63 mg/kg (0-5 cm soil) and 47 mg/kg (5-20 cm soil) in the soils at Port Kembla. The mean zinc at Rooty Hill and Port Kembla were lower than the 471 mg/kg measured previously in the soils at Port Kembla (Kachenko et al. 2006), whereas higher than 23.4 mg/kg measured at a recreational land in the city of Wollongong (Beavington, 1973). Since, the soil at the Macquarie Park had the concentration of 170 mg/kg which was above the mean values for Rooty Hill and Port Kembla, and below the maximum range at Port Kembla 190 mg/kg, it cannot be inferred that the addition of zinc in the soil is only due to steelworks. Comparing with the NEPM guideline 2011 for soil zinc for recreational purpose as 700 mg/kg (Appendix 1), all the soils at Rooty Hill, Port Kembla steelworks and Macquarie Park were below this range.

Titanium in the soil at Rooty Hill ranged from 30 mg/kg to 69 mg/kg, whereas at Port Kembla, it ranged from 37 mg/kg to 2680 mg/kg (Table 5.3). The mean values at these two sites were 40.6 mg/kg and 700.7 mg/kg (Table 5.3). The Macquarie Park had titanium of 24 mg/kg. Comparing these two steelworks locations with Macquarie Park, both steelworks locations had higher titanium concentrations. Hence it can be said that steelworks activities are adding more titanium to the soil. Port Kembla had higher titanium than that of Rooty Hill and that of the chromic luvisols (4.4 mg/kg) and alluvial fluvisols (4.3 mg/kg) near the iron smelter at Kremikovtzi (Bulgaria) at the depth of 0-20 cm (Schulin et al. 2007).

Iron contents in the soils near the Rooty Hill steelworks varied from 14000 mg/kg to 49700 mg/kg, and near Port Kembla steelworks ranged from 22100 mg/kg to 61300 mg/kg. The mean iron concentration at these two locations were 31280 mg/kg and 39930 mg/kg respectively. At the Macquarie Park, the iron concentration was 23800 mg/kg. Malawska and Wiołkomirski (2001) reported 530-50600 mg/kg iron in the soil near the railway junction at Ława Główna, Poland. Both Port Kembla and Rooty Hill locations had higher concentration as compared to chromic luvisols (0-20 cm) and alluvial luvisols (0-20 cm) near the iron smelter at Kremikovtzi (Bulgaria) where iron concentrations were 46.6 mg/kg and 48.8 mg/kg respectively (Schulin et al. 2007). When compared to the soil near the Rooty Hill site, Port Kembla soil had more iron which may be due to larger deposition of iron particles.

Manganese in the soil ranged from 210 mg/kg to 1300 mg/kg in the soil near the Rooty Hill steelworks, and 350 to 1950 mg/kg near the Port Kembla steelworks (Table 5.3). The mean manganese concentrations in these two locations were 842 mg/kg and 805 mg/kg respectively (Table 5.3). The manganese at the Macquarie Park was 220 mg/kg. Comparing with the 200 mg/kg

manganese within a 6.3 kilometer range at Sudbury, Ontario, Canada (Freedman and Hutchinson 1980), the concentrations of manganese in the current work were at all the three locations. The mean manganese concentration at Rooty Hill was higher but the range of manganese was higher at the Port Kembla steelworks. When compared to the Macquarie Park, both sites had higher concentrations. Thus, it can be concluded that steelworks are contributing manganese in the soils near the Rooty Hill and Port Kembla steelworks. On comparing with the guideline of NEPM 2011, with manganese value of 9000 mg/kg of soil (Appendix 1), all the soils near the three locations had lower concentrations.

Thus, the trace metals and heavy metals in soil collected in this work were compared with the soils near iron smelter, copper and other forms of smelters as well as industrial areas, near railway and with the NEPM 2011 guideline. The trace metals in soil were below the NEPM guideline. High titanium and iron concentrations were detected in the soils, which may be potentially a concern to environment but these metals have not yet been incorporated in the NEPM guideline.

## Chapter 7: Conclusion and Recommendations

### 7.1 Conclusion

Soils within 6 kilometers range from two different industrial locations, Rooty Hill steelworks and Port Kembla steelworks, and one background site at Macquarie Park were collected in this study and analyzed for trace metals and heavy metals. Trace metals, such as mercury, cadmium, molybdenum and arsenic, were in lower concentrations than the Australian NEPM 2011 guidelines at all the steelworks and the Macquarie Park background site, thus steelworks were not adding these elements in the surrounding soil, or if they were adding, they were in negligible amount. However, the NEPM 2011 guideline does not include concentration for molybdenum.

For the heavy metals, Port Kembla had higher concentration of chromium, copper, lead, nickel, zinc, titanium, and iron, whereas lower concentrations for manganese, when compared to Rooty Hill steelworks. Chromium, copper, lead and zinc did not show considerable difference in concentrations between the two steelworks; however, copper, lead and zinc were higher at the Macquarie Park background site compared to the locations in the vicinities of the two steelworks. The heavy metals, such as chromium, copper, lead, nickel, and zinc in all of the soil samples at the different sites did not exceed the NEPM 2011 guideline, however, there was no guideline for the limit in concentrations for titanium and iron in NEPM guideline 2011. Since, titanium and iron were present in considerable amount in the soils near the two steelworks locations hence these heavy metals required guidelines to be established. Thus, it can be suggested that the soils had trace metals and heavy metals in the vicinities of the steelworks, yet they are not contaminated to the extent such that human activities could be prohibited.

Trace metals such as mercury, cadmium and molybdenum were in the concentrations of <0.2 mg/kg, <0.5 mg/kg, and <1 mg/kg respectively at Rooty Hill and Port Kembla steelworks sites. Arsenic concentration was 6.93 mg/kg and 4.2 mg/kg at the two steelworks locations, which were lower than the Macquarie Park background (10 mg/kg). Chromium was higher at Port Kembla (89.3 mg/kg) than that of Rooty Hill (74.5 mg/kg), indicating that steelworks was adding more chromium at Port Kembla. Considering the Macquarie Park background site had chromium concentration of 91 mg/kg, it can be concluded that the addition of chromium was not attributed totally to the steelworks. Copper was higher at the Port Kembla (74.9 mg/kg) than the Rooty Hill (33.5 mg/kg), whereas Macquarie Park background (51 mg/kg) had higher than Rooty Hill. Thus

copper addition to soil was not entirely due to the steelworks, but the Port Kembla copper smelter may be responsible for the higher copper concentrations in this site. Lead was also higher at the Port Kembla (39.5 mg/kg) compared to Rooty Hill; however, it was higher at the Macquarie Park background (57 mg/kg) than the two steelworks locations. Thus, it cannot be concluded that the lead in the soil near the steelworks is entirely contributed by the steelworks. Nickel was higher in the soil at the Port Kembla (40.7 mg/kg) than Rooty Hill (36.1 mg/kg) and Macquarie Park (23 mg/kg). Zinc was nearly twice the concentration at Port Kembla (110.9mg/kg) than Rooty Hill (58.3mg/kg), however, the zinc concentration was higher at the Macquarie Park (170mg/kg) than that of the two steelworks. Titanium was nearly eighteen times higher in concentration at Port Kembla (700.7 mg/kg) than Rooty Hill (40.6 mg/kg) and twenty nine times higher than the Macquarie Park background (24 mg/kg). Iron concentration was also higher in Port Kembla (39930 mg/kg) as compared to Rooty Hill (31280 mg/kg) and Macquarie Park (23800 mg/kg). Manganese was higher at Rooty Hill (842 mg/kg) than that of Port Kembla (805 mg/kg) and Macquarie Park (220 mg/kg).

## **7.2 Recommendations**

The surroundings of Port Kembla steelworks had higher concentration of heavy metals, such as chromium, copper, lead, zinc, nickel, titanium, and iron, as compared to the Rooty Hill steelworks. When compared to the Macquarie Park, both steelworks sites had higher concentration of heavy metals in nearby soils. Since the trace metals and heavy metals are linked with health hazards to humans, and also various effects on plants, proper mitigation measures should be applied in order to lessen the emission of heavy metals and trace metals from the steelworks.

The heavy metals such as titanium and iron were detected in considerable amounts in soil; however, there is no guideline for their concentrations on soil as per the NEPM 2011, hence there is need of guidelines for these two metals. Also, for the trace metal molybdenum, there is a need of guideline in NEPM, as it was present in the soil.

The research further recommends for the investigation of other forms of trace and heavy metals within a wider range surrounding the steelworks as the study was limited to a range of 6 km. In addition to that, surrounding rivers and their catchments needs to be investigated to know the metals pollutants on aquatic bodies.

## References

- ASTM D1102-84 (1995). Standard Method for Ash in Wood. *American Society of Testing Materials*, Philadelphia 4 Pp.10
- Barzi, F. Naidu, R. & McLaughlin, M. J. (1996). Contaminants and the Australian soil environment. *Contaminants and the soil environment in the Australasia-Pacific region*, Springer Netherlands Pp. 451-484
- Bashor, B. S. & Turri, P. A. (1986). A method for determining an allowable concentration of mercury in soil. *Archives of environmental contamination and toxicology*, 15(4) Pp. 435-438
- Beavington, F. (1973). Contamination of soil with zinc, copper, lead, and cadmium in the Wollongong city area. *Soil Research*, 11(1) Pp. 27-31
- Berkow, R. (ed.) (1992). Element deficiency and toxicity in 'The Merck Manual of Diagnosis and Therapy'. *Merck Research Laboratory*, Division of Merck & Co., Inc., Rahway NJ. Pp. 975-981, 2685-2697
- Cai, L. Huang, L. Zhou, Y. Xu, Z. Peng, X. Yao, L. A. & Peng, P. A. (2010). Heavy metal concentrations of agricultural soils and vegetables from Dongguan, Guangdong. *Journal of Geographical Sciences*, 20(1) Pp. 121-134
- Cartwright, B. Merry, R. H. & Tiller, K. G. (1976). Heavy metal contamination of soils around a lead smelter at Port Pirie, South Australia. *Soil Research*, 15(1) Pp. 69-81
- Chary, N. S. Kamala, C. T. & Raj, D. S. (2008). Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. *Ecotoxicology and environmental safety*, 69(3) Pp. 513-524
- Chopin, E. I. B. & Alloway, B. J. (2007). Distribution and mobility of trace elements in soils and vegetation around the mining and smelting areas of Tharsis, Riotinto and Huelva, Iberian Pyrite Belt, SW Spain. *Water, Air, and Soil Pollution*, 182 (1-4) Pp. 245-261
- DEC NSW (2005). Information for the Assessment of Former Gasworks Sites, Sydney. *Department of Environment and Conservation*, New South Wales. Available from <http://www.environment.nsw.gov.au/resources/clm/gasworks05237.pdf>
- Donahue, C.J. & Rais E.A. (2009). Proximate analysis of coal. *Journal of Chemical Education*, 86 (2) Pp. 222
- Douay, F. Roussel, H. Fourier, H. Heyman, C. & Chateau, G. (2007). Investigation of heavy metal concentrations on urban soils, dust and vegetables nearby a former smelter site in Mortagne du Nord, Northern France. *Journal of Soils and Sediments* 7(3) Pp. 143-146
- Douay, F. Pelfrène, A. Planque, J. Fourier, H. Richard, A. Roussel, H. & Girondelot, B. (2013). Assessment of potential health risk for inhabitants living near a former lead smelter. Part 1: metal concentrations in soils, agricultural crops, and homegrown vegetables. *Environmental monitoring and assessment*, 185(5) Pp. 3665-3680

- Driscoll, T. Nelson, D. I. Steenland, K. Leigh, J. Concha-Barrientos, M. Fingerhut, M. & Prüss-Üstün, A. (2005). The global burden of disease due to occupational carcinogens. *American journal of industrial medicine*, 48(6) Pp. 419-431
- Ellis, J. & Kanamori, S. (1977). Water pollution studies on Lake Illawarra. III. Distribution of heavy metals in sediments. *Marine and Freshwater Research*, 28(4) Pp. 485-496
- Evans, A. (2011). Method Description Summary. *National Measurement Institute*, North Ryde, NSW, Australia
- Fernandez-Turiel, J. L. Aceñolaza, P. Medina, M. E. Llorens, J. F. & Sardi, F. (2001). Assessment of a smelter impact area using surface soils and plants. *Environmental Geochemistry and Health*, 23(1) Pp. 65-78
- Freedman, B. & Hutchinson, T. C. (1980). Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel-copper smelter at Sudbury, Ontario, Canada. *Canadian Journal of Botany*, 58(1) Pp. 108-132
- Gjoka, F. Felix-Henningsen, P. Wegener, H. R. Salillari, I. & Beqiraj, A. (2011). Heavy metals in soils from Tirana (Albania). *Environmental monitoring and assessment*, 172(1-4) Pp. 517-527
- Henderson, P. J. McMartin, I. Hall, G. E. Percival, J. B. & Walker, D. A. (1998). The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba, Canada. *Environmental Geology*, 34(1) Pp. 39-58
- Huang, Y. J. & Gulson, B. L. (2002). Selenium in soils, spermatophytes and bryophytes around a Zn–Pb smelter, New South Wales, Australia. *Science of the total environment*, 293(1), Pp. 129-141
- Hudson-Edwards, K. A. Macklin, M. G. Miller, J. R. & Lechler, P. J. (2001). Sources, distribution and storage of heavy metals in the Río Pilcomayo, Bolivia. *Journal of Geochemical Exploration*, 72(3) Pp. 229-250
- Ji, W. Yang, T. Ma, S. & Ni, W. (2012). Heavy Metal Pollution of Soils in the Site of a Retired Paint and Ink Factory. *Energy Procedia*, 16 Pp. 21-26
- Kachenko, A. G. & Singh, B. (2006). Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water, Air, and Soil Pollution*. 169(1-4) Pp. 101-123
- Kasassi, A, Rakimbei, P, Karagiannidis, A, Zabaniotou, A, Tsiouvaras, K, Nastis, A & Tzafeiopoulou, K. (2008). Soil contamination by heavy metals: Measurements from a closed unlined landfill. *Bioresource Technology*, 99 Pp. 8578–8584
- Keane, B. Collier, M. H. Shann, J. R. & Rogstad, S. H. (2001). Metal content of dandelion (*Taraxacum officinale*) leaves in relation to soil contamination and airborne particulate matter. *Science of the Total Environment*, 281(1) Pp. 63-78
- Koller, K. Brown, T. Spurgeon, A. & Levy, L. (2004). Recent developments in low-level lead exposure and intellectual impairment in children. *Environmental health perspectives*, Pp.987-994
- Krishna, A. K. & Govil, P. K. (2008). Assessment of heavy metal contamination in soils around Manali industrial area, Chennai, Southern India. *Environmental Geology*, 54(7) Pp. 1465-1472

- LECO (2015). Moisture, Volatile Matter, Ash, and Fixed Carbon Determination in Coal. *LECO Corporation*, Saint Joseph, Michigan USA
- Levander, O. A. (1986). Selenium, in *Trace Elements in Human and Animal Nutrition*, Eds W Mertz 5th edition, Academic Press, Orlando, FL 2 Pp. 209-279
- Li, F. Fan, Z. Xiao, P. Oh, K. Ma, X. & Hou, W. (2009). Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China. *Environmental geology*, 57(8) Pp. 1815-1823
- Lyle, D. Balding, B. Burke, H. & Begg, S. (2001). Lead management program in Broken Hill, NSW. *Public Health Bulletin*, 12 Pp.165–167
- Malawska, M. & Wiołkomirski, B. (2001). An analysis of soil and plant (*Taraxacum officinale*) contamination with heavy metals and polycyclic aromatic hydrocarbons (PAHs) in the area of the railway junction Iława Główna, Poland .*Water, Air, and Soil Pollution*, 127(1-4) Pp. 339-349
- Martley, E. Gulson, B. L. & Pfeifer, H. R. (2004a). Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW, Australia. *Science of the Total Environment*, 325(1) Pp. 113-127
- Martley, E. Gulson, B. Louie, H. Wu, M. & Di, P. (2004b). Metal partitioning in soil profiles in the vicinity of an industrial complex, New South Wales, Australia. *Geochemistry: Exploration, Environment, Analysis*, 4(2) Pp. 171-179
- Mohiuddin, K. Strezov, V. Nelson, P.F. Stelcer, E. & Evans, T. (2014). Mass and elemental distributions of atmospheric particles nearby blast furnace and electric arc furnace operated industrial areas in Australia. *Science of the Total Environment*, 487 Pp. 323–334
- Morrison, A.L. & Gulson, B.L. (2007). Preliminary findings of chemistry and bio accessibility in base metal smelter slags. *Science of the Total Environment*, 382 Pp.30–42
- Nayak, P. S. & Singh, B. K. (2007). Instrumental characterization of clay by XRF, XRD and FTIR. *Bulletin of Materials Science*, 30(3), Pp.235-238
- NRC (1980). Mineral Nutrition of Domestic, Animals National Academy of Science. *National Research Council*, Washington, D.C.
- Olsson, I. M. Eriksson, J. Öborn, I., Skerfving, S. & Oskarsson, A. (2005). Cadmium in food production systems: a health risk for sensitive population groups. *AMBIO: A Journal of the Human Environment*, 34(4), Pp 344-351
- Oluwatosin, G.A. Adeoyolanu, O.D. Ojo, A.O. Are, K.S. Dauda, T.O. & Aduramigba-modupe, V.O. (2010). Heavy Metal Uptake and Accumulation by Edible Leafy Vegetable (*Amaranthus Hybridus* L.) grown on Urban Valley Bottom Soils in Southwestern Nigeria. *Soil and Sediment Contamination*, 19 Pp. 1–20
- Parikh, J. Channiwala, S. A. & Ghosal, G. K. (2005). A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel*, 84(5) Pp. 487-494



- Peters, G. M. Maher, W. A. Krikowa, F. Roach, A. C. Jeswani, H. K. Barford, J. P. & Reible, D. D. (1999). Selenium in sediments, pore waters and benthic infauna of Lake Macquarie, New South Wales, Australia. *Marine environmental research*, 47(5) Pp. 491-508
- Randolph, L.M. & Rotter J.I. (1989). Hereditary disorder of the gut and liver. *Textbook of Internal Medicine*, Eds WM Kelley, JB Lippincot Company, Philadelphia, PA, Pp. 630-649
- Rieuwerts, J. S. Farago, M. Cikrt, M. & Bencko, V. (1999). Heavy metal concentrations in and around households near a secondary lead smelter. *Environmental Monitoring and Assessment*, 58(3), Pp. 317-335
- Roach, A. C. (2005). Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalization models and sediment quality guidelines. *Marine Environmental Research*, 59(5) Pp. 453-472
- Rouillon, M. Gore, D. B. & Taylor, M. P. (2013). The nature and distribution of Cu, Zn, Hg, and Pb in urban soils of a regional city: Lithgow, Australia. *Applied Geochemistry*, 36 Pp. 83-91
- Saha, J. C. Dikshit, A. K. Bandyopadhyay, M. & Saha, K. C. (1999). A review of arsenic poisoning and its effects on human health. *Critical reviews in environmental science and technology*, 29(3), Pp. 281-313
- Schedule B1 (2011). Guideline on investigation levels for soil and groundwater. *National Environment Protection (Assessment of Site Contamination) Measure*, Available from: <http://www.scew.gov.au>
- Schulin, R. Curchod, F. Mondeshka, M. Daskalova, A. & Keller, A. (2007). Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria). *Geoderma*, 140(1) Pp. 52-61
- Snowdon, R. & Birch, G. F. (2004). The nature and distribution of copper, lead, and zinc in soils of a highly urbanized sub-catchment (Iron Cove) of Port Jackson, Sydney. *Soil Research*, 42(3) Pp. 329-338
- Standards Australia (2005). Guide to the Investigation and Sampling of Sites with Potentially Contaminated Soil – Part 1: Non-Volatile and Semi-Volatile Compounds. *Australian Standard AS 4482.1-2005*, pp. 1–69
- Standards Australia International (2000). Coal and coke – Analysis and testing Part 3: Proximate analysis of higher rank coal AS 1038.3-2000. *Australian Standard*
- Sterckeman, T. Douay, F. Proix, N. & Fourrier, H. (2000). Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. *Environmental Pollution*, 107(3) Pp. 377-389
- Strezov, V. Evans, T. J. Ziolkowski, A. & Nelson, P. F. (2009). Mode of Occurrence and Thermal Stability of Mercury in Coal. *Energy & Fuels*, 24(1), Pp. 53-57
- Temple, P. J. Linzon, S. N. & Chai, B. L. (1977). Contamination of vegetation and soil by arsenic emissions from secondary lead smelters. *Environmental Pollution*, 12(4) Pp. 311-320

- Ullrich, S. M. Ramsey, M. H. & Helios-Rybicka, E. (1999). Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland. *Applied Geochemistry*, 14(2) Pp. 187-196.
- Van Alphen, M. (1999). Atmospheric heavy metal deposition plumes adjacent to a primary lead–zinc smelter. *Science of the Total Environment*, 236 Pp. 119–134
- Van Campen, D.R. (1991). Trace elements in human nutrition. *Micronutrients in Agriculture* 2<sup>nd</sup> edition, eds JJ Mortvedt et al. SSSA Book Series 4, Soil Science Society of America, Madison, WI Pp. 663-701
- Velea, T. Gherghe, L. Predica, V. & Krebs, R. (2009). Heavy metal contamination in the vicinity of an industrial area near Bucharest. *Environmental Science and Pollution Research*, 16(1), 27-32
- Wang, L. Guo, Z. Xiao, X. Chen, T. Liao, X. Song, J. & Wu, B. (2008). Heavy metal pollution of soils and vegetables in the midstream and downstream of the Xiangjiang River, Hunan Province. *Journal of Geographical Sciences*, 18(3) Pp. 353-362
- Xing, G. Zhu, J. Xiong, Z. & Yamasaki, S. I. (2004). Ag, Ta, Ru, and Ir enrichment in surface soil: Evidence for land pollution of heavy metal from atmospheric deposition. *Global biogeochemical cycles*, 18(1)
- Xu, X. Christiani, D.C. Dockery, D.W. & Wang, L. (1992). Exposure Response relationships between occupational exposures and chronic respiratory illness: a community-based study. *American Journal of Respiratory and Critical Care Medicine*, 146 Pp. 413-418
- Yang, G. (1987). Research on selenium-related problems in human health in China. *Selenium in Biology and Medicine*, ed G Combs et al., van Nostrand Reinhold Co., New York, NY, Pp. 8-32
- Yu, L. I. Wang, Y. B. Xin, G. O. U. Su, Y. B. & Gang, W. A. N. G. (2006). Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China. *Journal of Environmental Sciences*, 18(6) Pp.1124-1134
- Yuan, G. L. Sun, T. H. Han, P. & Li, J. (2013). Environmental geochemical mapping and multivariate geostatistical analysis of heavy metals in top soils of a closed steel smelter: Capital Iron & Steel Factory, Beijing, China. *Journal of Geochemical Exploration*, 130 Pp.15-21
- Zhang, X. Y. Lin, F. F. Wong, M. T. Feng, X. L. & Wang, K. (2009). Identification of soil heavy metal sources from anthropogenic activities and pollution assessment of Fuyang County, China. *Environmental Monitoring and Assessment*, 154(1-4), Pp. 439-449
- Zhuang, P. McBride, M. B. Xia, H. Li, N. & Li, Z. (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Science of the Total Environment*, 407(5) Pp.1551-1561

## Appendices

### Appendix 1

#### NEPM 2011 Schedule B(1)- Health Investigation levels for soil contaminants

	Health-based investigation levels(mg/kg)			
Metals and inorganics	Residential A	Residential B	Recreational C	Commercial/Industrial D
Arsenic	100	500	300	3000
beryllium	70	100	100	500
Boron	5000	40000	20000	300000
Cadmium	20	140	100	800
Chromium(VI)	100	500	240	3000
Cobalt	100	600	300	4000
Copper	7000	30000	20000	250000
lead	300	1200	600	1500
manganese	3000	8000	9000	40000
Methyl mercury	7	30	10	200
Mercury(inorganic)	200	600	400	4000
Nickel	400	900	800	4000
Selenium	200	1500	700	10000
Zinc	8000	60000	30000	400000

HIL C- Includes developed open space such as parks, playgrounds, playing fields(e.g., ovals), secondary schools and footpaths. This does not include undeveloped public open space which should be subject to a site-specific assessment, where appropriate.