Influence of coal combustion products on the transformation and bioavailability of phosphorus in soils

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TABLE OF CONTENTS

TABLE OF CONTENTS ..... **ii**

LIST OF TABLES ..... **xii**

LIST OF PLATES ..... **xiv**

LIST OF PUBLICATIONS ..... **xv**

ABSTRACT ..... **xvii**

DECLARATION ..... **xx**

ACKNOWLEDGEMENTS ..... **xxi**

Chapter 1 ..... **1**

Introduction **1**

1.1 The menace behind coal-fired power generation 1

1.2 The age-old problem of phosphorus loss in soils 2

1.3 Use of CCPs in phosphorus immobilisation in soils 3

1.4 Objectives of this research 4

1.5 Layout of chapters 4

Chapter 2 ..... **6**

Review of Literature **6**

2.1 Production and global market demand of CCPs 6

2.2 Physical and Chemical properties of CCPs 10

2.2.1 Physical Properties 10

2.2.2 Chemical Properties 10

2.3 Application of CCPs 11

2.3.1 Industrial applications 11

2.3.2 Agricultural applications 14

2.3.3 Environmental applications 25

2.4 Microbial studies on CCPs application 31

2.5 Risks of CCPs in the environment 32

2.6 Conclusions 34

Chapter 3 ..... **36**

Effect of coal combustion products on phosphate adsorption **36**

3.1 Introduction 36
3.2 Objectives 38
3.3 Hypothesis 38
3.4 Experiments 38
3.5 Materials and methods 39
3.5.1 Soils and coal combustion products 39
3.5.2 Characterisation of soil and CCPs samples 39
3.5.3 Soil preparation and incubation with CCPs 40
3.5.4 Sorption experiment 41
3.5.5 Effect of pH on CCPs-induced increase in P retention 42
3.5.6 Statistical analysis 42
3.6 Results and discussion 42
3.6.1 Properties of soils and CCPs 42
3.6.2 Sorption experiment 44
3.6.3 The role of pH in the sorption of P 48
3.6.4 The role of P sorptive components like Al, Fe and Ca in sorption of P 50
3.7 Conclusions 52
Chapter 4 53
Effect of coal combustion products on the transformation of phosphorus from various sources 53
4.1 Introduction 53
4.2 Objectives 55
4.3 Hypothesis 55
4.4 Experiments 56
4.5 Materials and methods 56
4.5.1 Soils and coal combustion products 56
4.5.2 Incubation 57
4.5.3 Characterisation of soils, CCPs and P samples 57
4.5.4 Fractionation experiment 57
4.5.5 Analysis of phosphatase activity 58
4.5.6 Physical characterisation studies on CCPs incubated soil samples 59
4.5.7 Statistical analysis 59
4.6 Results and discussion 59
4.6.1 Properties of soils, CCPs and P sources used 59

4.6.2 Fractionation experiment 61
4.7 Conclusions 72
Chapter 5 73
Effect of coal combustion products on the leaching of phosphorus in soils 73
5.1 Introduction 73
5.2 Objectives 74
5.3 Hypothesis 75
5.4 Experiments 75
5.5 Materials and Methods 75
5.5.1 Characterisation of soils, CCPs and P sources 75
5.5.2 Column leaching experiments 75
5.5.3 Statistical analysis 78
5.6 Results and discussion 78
5.6.1 Properties of soils, CCPs and P sources used 78
5.6.2 Column leaching experiments 78
5.7 Conclusions 85
Chapter 6 87
Plant acquisition of phosphorus from soil enriched with inorganic and organic phosphorus sources as affected by coal combustion products 87
6.1 Introduction 87
6.2 Objectives 89
6.3 Hypothesis 89
6.4 Experiment 90
6.5 Materials and methods 90
6.5.1 Characterisation of soils, CCPs and P sources 90
6.5.2 Sample preparation 90
6.5.3 Plant growth experiment 91
6.5.4 Leachate analyses 93
6.5.5 Plant analysis 93
6.5.6 Soil analysis 93
6.5.7 Statistical analysis 93

6.6 Results and discussion 94
6.6.1 Properties of soils, CCPs and P sources used 94
6.6.2 Leachate P analyses 94
6.6.3 Plant analysis 95
6.7 Conclusions 102
Chapter 7 103
The effect of biosolids on plant availability of applied phosphorus as affected by coal combustion products 103
7.1 Introduction 103
7.2 Objectives 104
7.3 Hypothesis 105
7.4 Experiments 105
7.5 Materials and methods 105
7.5.1 Site Description 105
7.5.2 Experimental Design 106
7.5.3 Plant analysis 106
7.5.4 Soil analysis 107
7.5.5 Analysis of phosphatase activity 107
7.5.6 Statistical analysis 107
7.6 Results and discussion 108
7.6.1 Properties of the materials used 108
7.6.2 Plant analysis 109
7.6.3 Soil analysis 114
7.7 Conclusions 116
Chapter 8 117
Summary and Conclusions 117
8.1 Research concept 117
8.2 Phosphorus adsorption 118
8.3 Phosphorus dynamics 119
8.3.1 Fractionation experiments 119
8.3.2 Microscopic and spectrometric analyses 120
8.4 Phosphorus leaching 120
8.5 Phosphorus bioavailability 121

8.5.1 Glasshouse experiments 121
8.5.2 Field trials 122
8.6 Application of this research 122
8.7 Future research 124
References 126

LIST OF FIGURES

Figure 2.1 Total ash production and beneficial usage in Australia (Adapted from ADAA, 2008)……..7

Figure 2.2 Total CCPs sale and utilisation in Australia (Heidrich, 2003)……8

Figure 2.3 Contribution to total net CO_2 emissions by various sectors in Australia……30

Figure 3.1 The effect of CCPs on P sorption as measured by K_f value in Adelaide hills (ADL) soil at four different application rates (0, 15, 30 and 45 % w/w). 45

Figure 3.2 Sorption of P in Adelaide hills (ADL) soil amended with a. FA; b. FBC and c. FGD at four different application rates (0, 15, 30 and 45 % w/w)……45

Figure 3.3 Sorption of P in Adelaide hills (ADL) soil at a. 15 %; b. 30 % and c. 45 % (w/w) application rates of three different CCPs (FA, FBC and FGD). 46

Figure 3.4 Effect of FBC (0, 15 and 30 % w/w) on P sorption in a. Birbie Islands (BIR), b. Kapunda (KPD) and c. Kulpara (KUL) soils..... 48

Figure 3.5 The relationship between pH of Adelaide hills (ADL) soil and increase in P sorption as affected by CCPs at three application rates (0, 15 and 30 % w/w). Error bars represent the standard deviation between replicates..... 49

Figure 3.6 Relationship between initial soil pH and increase in P retention (delta P retention) resulting from FBC application at 15 % (w/w) rate to seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)]. Error bars represent the standard deviation between replicates.....49

Figure 3.7 Relationship between % P retention and a. Al_{cd}, b Al_{ox}, c. Fe_{cd} and d. Fe_{ox} for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates……..50

Figure 3.8 Relationship between % P retention and a. $(Al + Fe)_{cd}$ and b. $(Al = Fe)_{ox}$ for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates……..51

Figure 3.9 Relationship between % P retention and Ca in solution. for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates..... 51

Figure 4.1 Flow diagram showing sequential extraction of inorganic P..... 58

Figure 4.2 Distribution of P fractions in the three soils (a: Adelaide hills – ADL; b: Kapunda – KPD; c: Virginia – VIR) amended with CCPs, without P treatment. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the Y axis indicates control.... 62

Figure 4.3 Effect of CCPs on P transformation in Adelaide hills (ADL) soil treated with three different P sources a. Potassium dihydrogen phosphate – PP; b. Poultry manure – PM and c. Phosphate rock – PR. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates..... 63

Figure 4.4 Effect of FBC and FGD on $NaHCO_3$-P values of Adelaide hills (ADL) soil treated with a. Potassium dihydrogen phosphate – PP; b. Poultry manure – PM and c. Phosphate rock – PR. FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates..... 63

Figure 4.5 Effect of incubation time on the enzyme activity as influenced by CCPs in poultry manure (PM) treated Adelaide hills (ADL) soil. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates 64

Figure 4.6 Effect of CCPs (in 21 days of incubation) on P fractions in Adelaide hills (ADL) soil treated with various P sources (Potassium dihydrogen phosphate – PP; Poultry manure – PM; and Phosphate rock – PP). PP1, PP2; PM1, PM2; and PR1, PR2 indicate the 100 and 200 mg P kg^{-1} soil treatment rates. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates. 66

Figure 4.7 Effect of CCPs (in 63 days of incubation) on P fractions in Adelaide hills (ADL) soil treated with various P sources (Potassium dihydrogen phosphate – PP; Poultry manure – PM; and Phosphate rock – PP). PP1, PP2; PM1, PM2; and PR1, PR2 indicate the 100 and 200 mg P kg^{-1} soil treatment rates. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates. 67

Figure 4.8 Effect of incubation periods (21, 42 and 63 days) on bioavailable P in CCPs amended Adelaide hills (ADL) soil treated with (a) Potassium dihydrogen phospahte – PP; (b) Poultry manure – PM and (c) Phosphate rock – PR. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates. 68

Figure 4.9 FESEM images of PP treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA and c. FGD..... 69

Figure 4.9 d. EDS peaks for PP treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples)……...69

Figure 4.10 FESEM images of PM treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA and c. FGD..... 70

Figure 4.10 d. EDS peaks for PM treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples) 70

Figure 4.11 FESEM images of PR treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA……..……..70

Figure 4.11 c. EDS peaks for PR treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples) 70

Figure 4.12 a-f. XRD patterns of FA amended Adelaide hills (ADL) soil treated with 3 sources of P (Potassium dihydrogen phospahte – PP; Poultry manure – PM and Phosphate rock – PR). C:Chlorite (ClO_2); E:Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$); H:Hematite ($Fe_2O_3$); Hy:Hydrogarnet ($4CaOAl_2O_3.\ 13H_2O$); Ka:Kaolinite ($Al_2Si_2O_5(OH)_4$); K:Kennedyite ($Fe_2MgTi_3O_{10}$); M:Merwinite ($Ca_3Mg(SiO_4)_2$); Q:Quartz ($SiO_2$); W:Wollastanite ($CaSiO_3$). 71

Figure 5.1 Pulse-input leaching - Cumulative P for Birbie Island (BIR) soil treated with a. PP and b. PM at 100 mg P kg^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates. 80

Figure 5.2 Pulse input leaching - Cumulative P for Kapunda (KPD) soil treated with a. PP and b. PM. at 100 mg P kg^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates. 80

Figure 5.3 Step input leaching – Breakthrough curves for a. Birbie Island (BIR) and b. Kapunda (KPD) soils, treated with PP at 100 mg P L^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates..... 82

Figure 5.4 Relationship between P adsorption measured in batch (represented by Kf values) and column experiments for Birbie Island (BIR) and Kapunda (KPD) soils amended with FBC**.** Error bars represent the standard deviation between replicates..... 82

Figure 5.5 Pulse input leaching – pH in the leachates of Birbie Island (BIR) soil, treated with a. PP and b. PM. Error bars represent the standard deviation between the replicates. 83

Figure 5.6 Pulse input leaching – pH in the leachates of Kapunda (KPD) soil treated with a. PP and b. PM. Error bars represent the standard deviation between the replicates. 84

Figure 5.7 Relationship between PP and PM treatments in Birbie Island (BIR) and Kapunda (KPD) soils as affected by addition of CCPs. Error bars indicate the standard deviation between the replicates. 84

Figure 5.8 Pulse leaching – Concentration of Ca in leachates in PP treated Birbie Island (BIR) soil, as affected by CCPs. 85

Figure 6.1 Release of phosphate from organic phosphorus compound 88

Figure 6.2 Cumulative P leaching – effect of FBC on P mobility in Kapunda (KPD) soil treated with inorganic (PP) and organic (PM) P sources. Error bars represent the standard deviation between the replicates. 95

Figure 6.3 Effects of FBC on biomass yield in PP treatment – fresh P application. Error bars represent the standard deviation between the replicates. 96

Figure 6.4 Effect of FBC on biomass yield in PP treatment – residual P effect. Error bars represent the standard deviation between the replicates. 97

Figure 6.5 Effect of FBC on cumulative (fresh P + residual P) biomass yields in PP treatment. Error bars represent the standard deviation between the replicates…….97

Figure 6.6 Effect of FBC on biomass yield in PM treatment – fresh P application. Error bars represent the standard deviation between the replicates. 98

Figure 6.7 Effect of FBC on biomass yield in PM treatment – residual P effect. Error bars represent the standard deviation between the replicates. 98

Figure 6.8 Effect of FBC on P uptake in plants for fresh P application and residual P effect. Error bars represent the standard deviation between the replicates. 99

Figure 6.9 Effect of FBC on bioavailable P concentrations in the shoots for unleached pots and shoots and leachates for leached pots. Error bars represent the standard deviation between the replicates. 101

Figure 6.10 Relationship between Olsen P in soil and Bioavailable P in plants. Error bars represent the standard deviation between the replicates. 101

Figure 7.1 Effect of various treatment combinations (Nil, SSP alone, BS alone, FBC alone, BS+FBC, SSP+BS, SSP+FBC and SSP+BS+FBC) on the biomass yield of sunflower plants. Error bars represent the standard deviation between the replicates. 109

Figure 7.2 Effect of FBC on the sunflower yields in the second cropping. Relative yield increase = [(Yield for residual – fresh)/Yield of residual] x 100 110

Figure 7.3 Effect of various treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS on the biomass yield of mustard plants. Error bars represent the standard deviation between the replicates……..... 110

Figure 7.4 Comparison between overall dry weights of sunflower and mustard plants as affected by the treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS). Error bars represent the standard deviation between the replicates……..... 111

Figure 7.5 Accumulation of P in the plant biomass as affected by various treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS) in a. Sunflower and b. Mustard plants 113

Figure 7.6 Effect of treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS) on plant available P in a. Sunflower and b. Mustard plants. Error bars represent the standard deviation between the replicates. 114

Figure 7.7 Relationship between Bioavailable P and total biomass yield as affected by the treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS)..... 114

Figure 7.8 Relationship between P accumulation in shoots and phosphatase activity in the Anthroposol as affected by the treatment combinations (Nil, SSP alone, BS alone, FBC alone, SSP+BS, SSP+FBC, BS+FBC, SSP+BS+FBC). Error bars represent the standard deviation of replicates analysed for phosphatase activity. 115

Figure 8.1 Flow diagram describing overall concept of this research..... 118

LIST OF TABLES

Table 2.1 Coal ash production and use (in kilo tonnes) for selected non-OECD countries 7

Table 2.2 Groups of solid components in FA 11

Table 2.3 Various types of CCPs, their major constituents and potential uses. 12

Table 2.4 Effects of Fly ash application in Agricultural crops 16

Table 2.5 List of potential hazard and effects on agricultural soil of CCPs application 18

Table 2.6 Selected references on nutrient and heavy metal concentrations in CCPs . 21

Table 2.7 Potential and observed effects of fly ash amendment on soil properties 25

Table 3.1 The major experiments and the treatments used in this Chapter. 38

Table 3.2 Soil textural characteristics 39

Table 3.3 Chemical characteristics of the soils used for sorption experiment 43

Table 3.4 Basic characteristics of CCPs used 43

Table 3.5 Elemental analysis of CCPs. 44

Table 3.6 Freundlich and Langmuir equations describing the adsorption of P in variable pH soils added with increasing application rates of FBC. 47

Table 4.1 The major experiments and the treatments used in this Chapter. 56

Table 4.2 Sequential extraction steps of Condron *et al.* (1990) and the expected P species in the fractions. 57

Table 4.3 Basic characteristics of soils, CCPs and P sources used 60

Table 4.4 Selected elemental composition of materials used 60

Table 4.5 Composition of P in the P sources 60

Table 4.6 The changes in pH for the incubated samples 61

Table 4.7 Effects of CCPs on the bioavailable P among various P sources 65

Table 5.1 Experiments, treatments and analyses 75

Table 5.2 Leachate collection and pore volume (V_p) 78

Table 5.3 Pulse input leaching: Percentage reduction of the amount of P leached (compared to control soil) in the CCPs amended soils. 81

Table 6.1 Experiments and treatments for plant experiment 90

Table 6.2 Effect of FBC on P concentration in shoots 100

Table 7.1 The major experiments and the treatments used in this Chapter 105

Table 7.2 Selected properties of soil and amendments used 108

Table 7.3 Elemental composition of the materials used 108

Table 7.4 Relative agronomic effectiveness of various P treatments 112

Table 7.5 Effect of the amendments on phosphatase activity 115

LIST OF PLATES

Plate 5.1 Set up of column leaching experiment……..76

Plate 6.1 Set up of Stanford – DeMent bioassay technique..... 92

Plate 7.1 Field description (a) Tilled plots before sowing; (b) Fully grown crops..... 107

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1. **Seshadri, B.,** Bolan, N.S., Naidu, R. and Brodie, K. (2010). The role of coal combustion products in managing the bioavailability of nutrients and heavy metals in soils. *Journal of Soil Science and Plant Nutrition*. **10**: 378-398.
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1. **Seshadri, B.,** Bolan, N.S. and Naidu, R. (2011). Agricultural and environmental applications of combustion products from clean coal techonologies. *Advances in Agronomy* (Submitted).
2. **Seshadri, B.,** Bolan, N.S. and Naidu, R. (2011). Efficacy of coal combustion products on the adsorption of inorganic phosphorus in soils (Potential paper arising from Chapter 3).
3. **Seshadri, B.,** Bolan, N.S. and Naidu, R. (2011). The effectiveness of coal combustion products on the transformation of phosphorus in soils treated with organic and inorganic phosphorus sources (Potential paper arising from Chapter 4).
4. **Seshadri, B.,** Bolan, N.S. and Naidu, R. (2011). Enhancing the bioavailability and plant uptake of phosphorus applied from organic and inorganic sources in soil as affected by fluidised bed combustion ash (Potential paper arising from Chapter 6 and 7).

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1. **Seshadri, B.,** Wickramaratne, C., Bolan, N.S., Brodie, K. and Naidu, R. (2010). Sorption and bioavailability of phosphorus in soils as affected by coal combustion products. *In: 19th World Congress of Soil Science.* 1-7 August, Brisbane, Australia (Poster).
2. **Seshadri, B.,** Wickramaratne, C., Bolan, N.S., Brodie, K. and Naidu, R. (2009). Enhancing phosphorus retention capacity of soils using coal combustion products. *In*:

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ABSTRACT

Coal provides the primary source of energy for many countries including Australia, and large quantities of waste products are produced during the combustion of coal in coal-fired power stations. The most basic residues from the burning of coal in coal-fired power stations are coal combustion products (CCPs) and they include fly ash (FA) and bottom ash (BA) and the emerging products derived from clean coal technologies including fluidised bed boiler (FBC) ash and flue gas desulphurisation (FGD) gypsum. The major applications of the CCPs encompasses a range of industries like construction for cement manufacture and concrete, agriculture as liming agent and nutrient source, and in environmental restoration such as phosphorus (P) immobilisation, mitigation of acid mine drainage and carbon sequestration. The immobilisation of P in soils using CCPs has been a significant area of research over the past decade not only for the potential of CCPs in minimising the loss of P, but also making the P bioavailable for agronomic utilisation.

Most Australian soils are naturally low in P and many sandy soils are not efficient in the retention of P leading to losses due to leaching and surface runoff. Agricultural application of fertilizer P and wastes including farm effluents, manures and biosolids have been the most significant contributors of P build-up in soils and consequent accumulation in water bodies causing eutrophication.

Although a number of studies have examined the effect of CCPs on P adsorption, no comprehensive study has been done evaluating the role of CCPs in the transformation and bioavailability of both inorganic and organic P sources. This study hypothesises that the CCPs enhance the immobilisation of inorganic P and mineralisation of organic P sources, thereby affecting the bioavailability of P to plants. The overall objective of this research work is to examine the effect of CCPs on the immobilisation and mineralisation of P sources, and bioavailability of P in soils. The specific objectives of this thesis include: (i) to study the effect of CCPs on the adsorption of P in soils; (ii) to elucidate the dynamics of P applied from different sources to soils amended with CCPs; (iii) to evaluate the effect of CCPs on P leaching in soils; and (iv) to examine the effect of CCPs on the uptake of applied P. The study was conducted using a range of soils differing in pH, texture and P retaining capacity (PRC); three CCPs (FA, FBC and FGD) of different characteristics and three P sources (potassium dihydrogen phosphate, poultry manure and phosphate rock) with varying P solubility.

The first experiment examined the effect of CCPs on P adsorption in soils using batch sorption studies. The results indicated that P adsorption increased with increasing application rates (0, 15, 30 and 45 % w/w) of CCPs. The effect of CCPs in increasing P

adsorption followed: FBC > FA > FGD. There was an inverse relationship between the CCPs-induced increase in P adsorption and initial soil pH, demonstrating that acidic and neutral soils responded more effectively to the addition of CCPs than alkaline soils. The increases in soil pH and Ca concentration in the soil solution resulting from the application of CCPs, enhanced P retention through adsorption and precipitation reactions.

In the second experiment, the effect of CCPs on the transformation of three sources of P (inorganic soluble P - KH_2PO_4; inorganic insoluble P – phosphate rock; organic P – poultry manure) in soil was examined using sequential fractionation, field emission scanning electron microscopy (FESEM) and an advanced spectroscopy technique such as electron dispersive spectroscopy (EDS). An XRD study was also conducted to observe the chemical mineralogy of soils amended with CCPs. In the case of KH_2PO_4 application, CCPs enhanced immobilisation, which is attributed to a pH-induced increase in P adsorption. In the case of phosphate rock, CCPs decreased dissolution which is attributed to increases in soil pH (less acid to dissolve) and Ca concentration in solution (common ion effect). The CCPs enhanced the mineralisation of poultry manure P, which is attributed to an increase in pH and alkaline phosphatase activity. The data from the FESEM, EDS and XRD analyses corroborated the results from chemical fractionation experiments, supporting the presence of Ca, Fe and Al associated P in CCPs amended soils. The microscopic and spectroscopic studies revealed the presence of inorganic P adsorbed to metal oxides/oxyhydrides. The precipitation of P as Ca-P in the case of inorganic P application and adsorption of P to Al for organic P application was evident from FESEM/EDS data and the presence of potential P sorbents such as wollastonite, ettringite, hydrogarnet, hematite and kennedyite was detected using XRD. As the applied P aged, the adsorbed P transformed largely to bioavailable P, hence demonstrating the value of CCPs for enhancing the supply of P for plant growth.

In the third experiment, the mobility of inorganic and organic P sources (100 mg P kg^{-1} soil), as affected by CCPs application to soils was evaluated using column leaching experiments. The data indicated that P leaching decreased with the application of CCPs to soils. There was a negative relationship between increase in CCP-induced pH and P leaching demonstrating that pH plays a crucial role in P immobilisation, transformation and leaching. The CCPs-induced P leaching was higher in poultry manure applied soils compared to KH_2PO_4 applied soils, because of the mineralisation of the organic P from the poultry manure.

Finally, the effect of CCPs (15 % w/w application rate) on the bioavailability of freshly added (200 mg P kg^{-1} soil) and residual P from inorganic (KH_2PO_4) and organic (poultry manure) sources to plants was examined using glass house and field experiments. The glass house study was conducted using mustard plants involving

Stanford-DeMent bioassay. The plant uptake of P increased with both inorganic and organic P application in the first crop (fresh P application) and plants utilised more P from organic P application than the inorganic P applied soil during the second cropping (residual P effect). The FBC used in this experiment enhanced the immobilisation and bioavailability of P in soils receiving inorganic and organic P, respectively. This is attributed to the adsorption of inorganic P and increases in the mineralisation of organic P sources on FBC application.

The objective of the field experiment was to assess the effectiveness of FBC (25 Mg ha^{-1} soil) alone and its blending with biosolids (BS – 50 Mg ha^{-1} soil) on the uptake of applied P (single super phosphate – SSP) by plants. For the fresh P application (50 kg P ha^{-1} soil), the biomass yield was higher in crops supplied with SSP alone and SSP amended with BS than combinations such as SSP+FBC and SSP+FBC blended with BS. The effects of FBC were apparent in the second crop, where the yields were higher in the presence than absence of FBC. Hence, FBC proved to be effective in increasing the bioavailability of P in soil, through slow release of the applied P, thereby ensuring P uptake by subsequent crops.

In Conclusions, the CCPs generally increased adsorption of P in soils and enhanced the uptake of P by plants. The (im)mobilisation of P was mainly controlled by increases in pH of the soil and Ca concentration in the soil solution. In the case of inorganic P application, the CCPs enhanced immobilisation of P and increased the bioavailability of the immobilised P in subsequent cropping. For organic P application, CCPs facilitated the release of soluble P through mineralisation, mediated by increase in pH and phosphatase activity, thereby increasing their bioavailability.

DECLARATION

I declare that:

This thesis presents work carried out by myself and does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university. To the best of my knowledge it does not contain any materials previously published or written by another person except where due reference is made in the text; and all substantive contributions by others to the work presented, including jointly authored publications, are clearly acknowledged.

Balaji Seshadri

Signed _____ Date _____

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Chapter 1

INTRODUCTION

The growing population round the globe and consequently, the ever increasing energy needs have not only put pressure on the natural resources, but also generated wastes in undesirable quantities. Converting these wastes into resources has been challenging and less cost effective in terms of volume generated, transportation and safe disposal. One such waste is the coal combustion products (CCPs) derived from coal-fired power stations. Beneficial utilisation of these CCPs is likely to provide a solution for sustainable management of this resource and hence this study will examine the potential value of CCPs in enhancing the efficiency of phosphorus (P) nutrient utilisation in soils.

1.1 The menace behind coal-fired power generation

Coal is one of the most inexpensive energy sources of electricity generation for over a century, making it the reliable choice for both developed and developing countries. The global coal usage for primary energy supply has increased sharply (up to one-quarter of the world's share) over the past three decades and predicted to follow the trends through 2030 (Dellantonio and Fitz, 2010). Between 2000 and 2006, the annual coal consumption increased globally at the rate of 4.9 % and the production is envisaged to increase up to 60 % by 2030 (IEA, 2008). All these statistics clearly indicate the extent of potential environmental impact caused by the utilisation of coal, in terms of wastes generated. Although the coal-fired power generation has evolved a long way towards processing of coal, higher energy production and value addition for reducing air pollution, there has not been any breakthrough in reducing the volume of combustion wastes i.e., the CCPs generated.

A wide range of CCPs are generated post combustion, which includes fly ash (FA) and bottom ash (BA). The value added combustion products include fluidised bed combustion (FBC) ash and flue gas desulphurisation (FGD) gypsum, which are produced by combustion of coal coupled with lime, mainly to trap gaseous emission of sulphur. With the continual increase in energy demand, large quantities of CCPs are destined to be dumped in landfill sites and ash ponds in the forthcoming decades increasing the environmental footprint of electricity generation

using coal. The current rate of CCPs production renders its disposal unviable (Twardowska and Stefaniak, 2006) and may cause detrimental effects on plant, animal, human and environmental health due to overall toxic effect of the ash materials.

Australia, being the world's largest coal-exporting country with about 9 % of total coal reserves in the world, has around 30 coal fired power stations. They generate more than 12 million tonnes (Mt) of CCPs every year, posing threat to the environment due to incessant dumping and under utilisation of CCPs. Among the CCPs, FA is widely utilised in the construction industry (up to 85% of the total 10% usage) in Australia since 1960s (ADAA, 2009a). The remaining CCPs are largely dumped in landfills or settling ponds around the power stations, and scantily (less than 10%) used for agricultural and other environmental applications. The unused CCPs are hazardous to terrestrial, aquatic and atmospheric environments due to dispersion of dust, runoff and leaching of heavy metals and nutrients, leading to poor plant establishment and growth in soil, changes in plant elemental composition, reduced water quality levels and therefore, changes in the aquatic biota. (Twardowska and Szczepanska, 2002) Above all, poor management of this resource will result in the overall rise of the movement of potentially toxic elements through the food chain in both terrestrial and aquatic ecosystems (Carlson and Adriano, 1993; Twardowska and Szczepanska, 2002).

1.2 The age-old problem of phosphorus loss in soils

Phosphorus (P) is the second major essential nutrient for plants after nitrogen (N) and a critical component for all living organisms. It occurs naturally in rocks and gets released to the soil during pedogenesis. In soils, P occurs in inorganic (derived from minerals, e.g. apatite) and organic (derived from organisms) forms. There are over 170 phosphate bearing minerals and most of them are chemically reactive (Holford, 1997). Walker and Syers (1976) suggested that pedogenesis can be understood to a considerable extent by determining the amount, forms and distribution of P in soil. The distribution of P also reflects the reactivity of phosphate (anion) ion with cations. Therefore, P loss in soil can be estimated by understanding the soil processes and pathways involved in P transformation.

Plants can acquire P only in the inorganic (P_i) forms such as the orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-}), and the organic (P_o) forms are unavailable to plants, unless mineralised. However, the P_i ions can also adsorb to the surface cations (iron-Fe, aluminium-Al and calcium-Ca) in the soil, which makes it unavailable. Soil pH plays a major role in the adsorption of P. In neutral and alkaline soils, P bind with Ca carbonates in the form of phosphate ions whereas, in

acidic soils they occur as Fe and Al phosphates. The un-adsorbed P ends up in the soil solution and reaches water bodies through surface runoff and leaching. Hence, understanding the bioavailability of soil P to plants and transport in soil is a challenging research question for over 150 years. Although initial research focussed on the acquisition of P in cultivated crops, recently the problems pertaining to excessive dosage through fertiliser applications and hence losses from the soil have been widely studied (Sharpley and Withers, 1994; Haygarth and Jarvis, 1997; Heathwaite *et al.*, 1997; McDowell and Sharpley, 2001; Syers *et al.*, 2008).

Globally, P loss is a major problem not only to agriculture but also to the total environment. Also, the anthropogenic activities like mining and fertiliser applications release more P from terrestrial to aquatic environment resulting in eutrophication. Most soils in Australia are inherently deficient in P and also poor in retaining P which is attributed to low levels of silicate clays and iron and aluminium oxides, which are efficient in the retention and immobilisation of P. Efforts have been made to enhance the P retention capacity of soils by increasing the clay content using red mud and other waste resources (Sumners *et al.*, 1996; Snars *et al.,* 2002) and altering the pH of the soil using liming material. With the increasing pressure on some of these natural resources, alternative amendments are being researched for P immobilisation in soil.

1.3 Use of CCPs in phosphorus immobilisation in soils

Generally, P is transported from soil in particulate and dissolved forms (soluble inorganic P). Although the particulate P loss can be decreased through management practices such as riparian buffers, the soluble inorganic P loss had been an issue in soils having low P retention capacity (McDowell, 2004). An understanding of P retention capacity (PRC) of soils is vital for fertiliser management and safeguarding water quality. High pH and high calcium (Ca), Fe and Al concentration in soil solution are good prerequisites for enhancing the retention of P in soils. Traditionally, lime ($CaCO_3$) has been widely used to overcome soil acidity, thereby enhancing P retention.

It has been shown that CCPs such as FA, BA and other by-products of the contemporary coal-fired power stations such as FBC and FGD have been effective in decreasing soil solution P loss, through the increases in pH of the soil (Stout *et al*., 2000; Callahan *et al*., 2002; McDowell, 2005). Some studies also showed the effectiveness of FA in mitigating particulate and organic P loss (Eg: Stuczynski *et al*., 1998a, 1998b), but the effectiveness was found to be pH and charge dependent (Reichert and Norton, 1994). These

coal ash materials can be an effective replacement for their natural counterparts if used judiciously. Hence, efforts have been made globally on the possible usage of CCPs for increasing P retention in soils that are naturally poor in P retention. This study will not only focus on the immobilisation of P in CCPs amended soil, but also examine the effect of CCPs on the subsequent bioavailability of the immobilised P in soil.

1.4 Objectives of this research

The overall objective of this research is to examine the value of CCPs in minimising the loss of P in soil and enhancing the bioavailability of the retained P. The specific objectives of this research involve:

- The characterisation of soils with variable pH and P retaining capacity
- The characterisation of various types of CCPs (FA, BA, FBC, FGD)
- The sorption of P by soils as influenced by CCPs application
- The transformation of various sources of P in soils as influenced by of CCPs application
- The leaching of various sources of P in the presence of CCPs
- The acquisition of P by plants in CCPs incorporated soils

1.5 Layout of chapters

Chapter 1 (Introduction) provides an initial outline of CCPs production and problems of disposal, P reactivity in soil and the overall P loss issues, application of CCPs to immobilise P in soil, objectives of the research and a concise organisation of the remaining chapters.

Chapter 2 (Review of literature) will cover a review of previous researches on CCPs and their environmental applications with specific focus on P immobilisation and bioavailability in soils.

Chapter 3 (Effect of coal combustion products on phosphate adsorption) describes the change in pH and concentration of P-sorptive cations like Fe, Al and Ca resulting from the application of various sources of CCPs, and their significance in P adsorption using adsorption isotherms and measurement of solution concentration of the above mentioned cations. This

chapter will quantify the role of pH as affected by CCPs application on P adsorption in soils with diverse pH and varying P retention capacity.

Chapter 4 (Effect of coal combustion products on the transformation of phosphorus from various sources) categorizes the forms of P in CCPs amended soils which were pretreated with inorganic and organic P sources. The P sources had varying degree of solubility in the soil. The transformation of P in CCPs amended soils was tested using a sequential extraction procedure, analysis of pH and cations (Ca, Fe and Al) in soil solution and testing of enzyme activity in the soils used.

Chapter 5 (Effect of coal combustion products on the leaching of phosphorus in soils) describes the effect of CCPs in inhibiting the leaching of soil P using column (pulse and step) experiments. The effect of CCPs on the leaching of both freshly added and aged P inputs to soils was examined in order to understand P chemodynamics in relation to CCPs application.

Chapter 6 (Plant acquisition of phosphorus from soil enriched with inorganic and organic phosphorus sources as affected by coal combustion products) synchronizes the results from above experiments and examines the effect of CCPs on the uptake of P both under leaching and non-leaching conditions in a glasshouse study.

Chapter 7 (The effect of biosolids on plant availability of applied phosphorus as affected by coal combustion products) justifies the results obtained from glasshouse experiment as demonstrated by field experiments amended with biosolids and CCPs.

Chapter 8 (Summary and Conclusions) portrays the overall research with a conceptual diagram and summarises the research findings. This chapter will also suggest the avenues of future research and list out the potential applications based on the findings.

Chapter 2

REVIEW OF LITERATURE

2.1 Production and global market demand of CCPs

Coal is known to be the mainstay in the economy of many successful industrial nations like United States, Japan, China, India, Australia and South Africa, because of its place in power generation, with coal power plants contributing over 50 % to the energy needs of some of these countries (IEA, 2008). For example, in the US, where coal is mined in 27 states, over 90 % of the coal used is for generating electricity with coal plants contributing up to 45 % of the country's energy needs (US EIA, 2010).

Global coal consumption is expected to increase at an average rate of 1.7 %/yr until 2020. Share of coal in world primary energy demand will remain stable at about 25 % until 2020. With a current share of 38 %, coal is the largest contributor to power production. In developing countries, coal consumption will increase at a rate of about 3 %/yr until 2020. Much of the global coal consumption growth takes place in China and India (Van der Zwaan, 2004). Ash utilisation as a percentage of total ash generated in different countries amounts to around 85 % in West Germany, 73 % in Denmark, 60 % in France and UK, 50 % in Poland, 32 % in US, 25 % in China and 15 % in India (Sinha and Basu, 1998). But in most other countries, the level of utilisation is very low (Table 2.1). However, in 2001 the coal ash utilisation in Poland steeply increased to 70 %, due to improvements in the quality of ash produced (Barnes and Sear, 2006).

In supplying the power requirements for Australian households, around 12 million tonnes (Mt) of CCPs are produced annually of which about only 1 Mt is utilised primarily in the construction industry. In Australasia, about 85 % of the current "beneficial use" of fly ash (FA) is for partial cement replacement (between 10 and 20 %) to enhance the properties of concrete and other building materials. Today, the cement and concrete industry through their channel members are continuously building up significant market for the beneficial use of certain CCPs, especially FA.

Table 2.1 Coal ash production and use (in kilo tonnes) for selected non-OECD countries

Country	FA	Coarse ash	Total ash	Utilisation	% used
Czech Republic	13,800	4,300	18,100	1,400	8
Hungary	3,880	940	4,820	600	12
Poland	26,300	3,200	29,500	4500	15
Romania	7,000	20,000	27,000	700	3
South Africa	10,000	3,000	13,000	580	4
Former USSR	90,000	35,000	1,25,000	11,500	9

Adapted from Clarke (1994)

The Productivity Commission, Victoria conducted a major survey on the use of CCPs for the calendar period 2008 and the major Conclusionss include (ADAA, 2008):

- Approximately 14.6 Mt of CCPs were produced within Australasia (Australia and New Zealand). On per capita basis this equates to 682 kg per person.

- From 1990 to 2008 utilisation rates have increased from 8.4 % to 47 %. The marked increase from 1994 was the result of ash use for bulk-fill applications and for use in the backfilling of mines in NSW and SA (Figure 2.1).

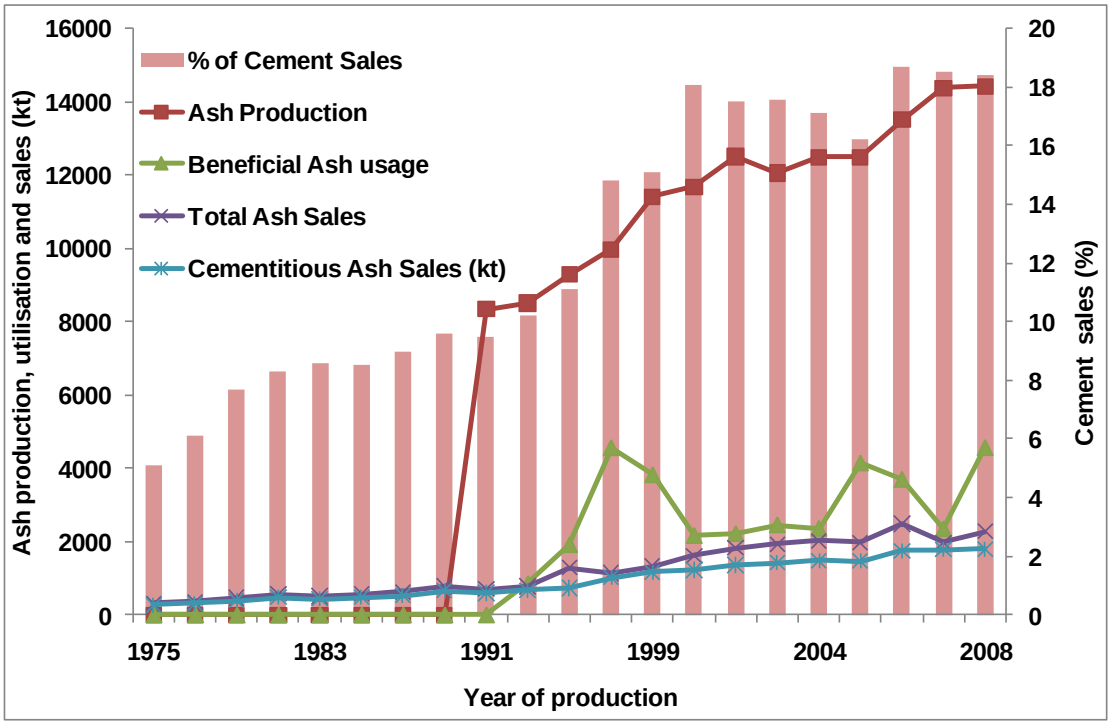


Figure 2.4 Total ash production and beneficial usage in Australia (Adapted from ADAA, 2008)

- Some 6.103 Mt (47 %) of CCPs have been effectively utilised in various value added products or to some beneficial end. On per capita basis this equates to 320 kg per person recycled or reused.

- 1.46 Mt (11 %) was used in high value added applications such as cementitious applications or concrete manufacture. This use resulted in more than 1.1 Mt of CO_2 being abated through reduced clinker manufacture. 0.550 Mt (4 %) was used in non cementitious applications.

- 4.131 Mt (32 %) was used in projects offering some beneficial uses (e.g. onsite mine site remediation, local haul roads, etc). These uses typically generate no economic return, cover only the cost recovery.

- Surplus (6.897 Mt) is typically placed into onsite storage ponds awaiting some future opportunity for economic reuse.

- Revenues of more than $100 million were generated from the reuse of 6.103 Mt of CCPs.

Similar trend in the CCPs utilisation has been noticed for the calendar year 2006 with a total quantity of reuse of 6.165 Mt of CCPs generating over $120 million in revenue (Figure 2.2). Surplus CCPs represent a significant alternative raw material, with characteristics and properties lending themselves to a wide range of potential applications (cement, concrete manufacture, engineering fills and agricultural applications) and when effectively utilised, CCPs can provide significant positive environmental impacts and economic returns (ADAA, 2007).

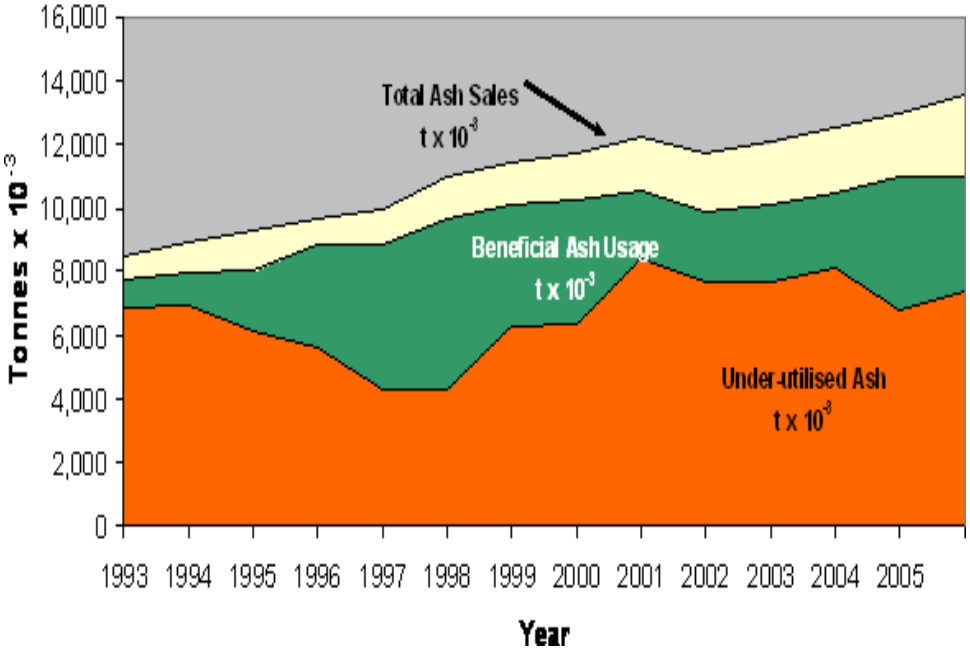


Figure 2.5 Total CCPs sale and utilisation in Australia (Heidrich, 2003)

The Ash Development Association of Australia has defined CCPs as follows (ADAA, 2009c):

Fly Ash (FA) – the non-combustible oxidized elements that exit the combustion chamber in the flue gas and is captured using Electrostatic Precipitators, Filter Baghouses, or wet scrubbers. Fly ash is typically a pozzolan (a siliceous, or siliceous and aluminous material). Australian fly ash material is light to mid-grey in colour, has the appearance of fine powder with particles ranging in size from < 1 μm to 200 μm and is irregular to spherical in shape.

Furnace Bottom Ash (FBA) - agglomerated ash particles formed in pulverized coal furnaces that are too large to be carried in the flue gas stream and impinge on the furnace walls or fall through open grates to an ash hopper at the bottom of the furnace. Bottom ash is typically grey to black in colour, is quite angular, and has a porous surface structure. Bottom ash is used as an aggregate, as feedstock for cement manufacturing or in construction applications along with sand.

Flue-gas-desulphurization (FGD) by-products are the residues of alkaline scrubbing of sulphur oxides from flue gases of coal-fired power stations and they have traditionally been treated as a waste product and land filled. A range of amendments including lime and ammonia are used to trap sulphur oxides, resulting in a range of FGD products. For example, FGD Gypsum is obtained in the desulphurization of flue gases with lime or limestone suspension.

Fluidised Bed Combustion (FBC) by-product is formed when fine coal is burnt in the presence of crushed limestone as a bedding material. The bed is fluidised by injection of air through perforated bed at control rates. The lime reacts with SO_2 released during combustion of the coal to form sulphates. The bed waste product is granular solid material composed of $CaSO_4$, CaO, metal oxides and fly ash. Upon exposure to moisture and atmospheric air, the bed waste first forms hydroxides and then carbonates (Adriano *et al.*, 1980).

The use of coal combustion products (CCPs) as a soil amendment has been an ongoing area of investigation by the Ash Development Association of Australia (ADAA) since the mid 1990s. International research into the use of CCPs for soil amendment has grown markedly over the past few decades. This research has focused on identifying the physical and chemical properties of CCPs and determining the feasibility of using these products in agricultural, horticultural and forest ecosystems.

2.2 Physical and Chemical properties of CCPs

The physical and chemical properties of CCPs depend upon a number of factors, including the type of coal burnt, the boiler conditions, the type and efficiency of the emission controls (Adriano *et al.*, 1980; Basu *et al.,* 2009). Certain characteristics have a propensity to be similar in most ashes. Chemically, CCPs are mainly silico-aluminate glasses, though some mineral materials may be present (ADAA, 2007). In Australia the majority of ash produced is categorised as Class F – being mainly silica and alumina (80-85 %) and less than 10 % CaO. Class F ash is highly pozzolanic and reacts with various cementitious materials. The other type of FA produced in a few countries is the Class C FA. Class C FA generally contains more than 20 % lime (CaO). Hence, they do not require an activator for cementing. Alkali and sulphate (SO_4) contents are generally higher in Class C FA. Furnace bottom ash can comprise 10 to 20 % of the total CCPs produced and range in grain size from fine sand to coarse lumps. They have chemical compositions similar to FA.

2.2.1 Physical Properties

Fly ash is mainly composed of silt-sized materials having a diameter from 0.01 - 100 µm (Chang *et al.*, 1977). When compared with mineral soils, FA has lower values for bulk density, hydraulic conductivity, and specific gravity. Both crystalline (mullite) and amorphous (glass) phases have been identified by X-ray diffraction in FA (Mattigod *et al.*, 1990).

2.2.2 Chemical Properties

The chemical properties of FA will largely be determined by the metal oxides (Si, Al, Fe, Ca, Mg, Na, K) that are surface adsorbed during particle formation. Most of these elements can substitute into the iron pyrite structure, and coals higher in pyrite therefore producing FA, which contain higher levels of these elements. Selenium is known to be a volatile element and its behavior may be highly dependent upon the burning conditions within the boiler. Similarly, Australian coal ash has low sulphur content.

Fly ash is also composed of silt sized glassy spheres (Fisher *et al.*, 1976), some of the spheres are hollow, termed cenospheres, or spheres filled with smaller spheres termed plerospheres. During the combustion and subsequent cooling process, many different metal oxides can precipitate and concentrate on the surfaces on these spheres. These oxides control the chemical properties of the ash, and tend to vary from ash to ash. The oxides may also affect

the physico-chemical properties of some FAs, especially the pozzalonic (cementitious) reactivity (Stewart *et al.*, 1997). Three groups of solid components have been identified in FA (Terman, 1978; Adriano *et al*., 1980; Table 2.2).

Table 2.2 Groups of solid components in FA (Terman, 1978; Adriano *et al.*, 1980).

Groups	Components	Properties
Group I	Oxides of Si, Al, Fe and Ti	Low water reactivity, possess surface charge
Group II	Metals and metalloids	Adsorption to oxides
Group III	Oxides of Ca, Mg, K, Na, Ba, SO_3, Gypsum	High water reactivity

The above mentioned physical and chemical properties have driven the coal industries and environment researchers to mine the possible applications of CCPs as part of the sustainable utilisation strategies of these mined resources.

2.3 Application of CCPs

The CCPs are used extensively in the agricultural and construction industries. In agriculture, they are used primarily as an amendment to improve the physical and chemical properties of soil, as a source of liming material to ameliorate soil acidity and as a nutrient source to supply calcium and sulphur (Korcak, 1995; Wang *et al.*, 1999; Heidrich, 2003). In the construction industry, they are used mainly as a source of concrete, roofing material and road surface sealing (Chugh *et al.*, 2006). The various types of CCPs and their potential applications are listed in the Table 2.3.

2.3.1 Industrial applications

The CCPs used in cement and concrete manufacture is more commonly referred to as FA. Australian FA is made up of silica and alumina (80-85 %). It is used in other cementitious materials (Portland and slag cements) to manufacture concrete. Although FA *per se* has no cementitious value, it can be used to replace up to 40 % of the volume of milled cement. Not all FA is suitable for use in cement and concrete manufacture due to a number of factors including carbon content, method of capture (bag filter verses electrostatic separation process), onsite CCP classification and storage capacity. In 2004, about 1.48 Mt of FA was used to replace cement in the manufacture of concrete, contributing a net reduction of 1 Mt of CO_2 emissions. Whilst subject to the variables outlined above, industry estimates that by 2007, some 2 Mt of FA

suitable for concrete manufacture will be available annually. With further capital investment, this volume could increase to 4 Mt after 2012.

Table 2.3 Various types of CCPs, their major constituents and potential uses. (Seshadri *et al.*, 2010)

Type	Major constituents	Potential areas of major use
FA	Si, Al, Fe, Ca (CaO, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Cement replacement in concrete/grout, structural fill, waste stabilization, surface mine reclamation, soil stabilization, road based, mineral filler, Si and Ca source
FBA	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Concrete block, road sub-base, snow and ice control, structural fill, waste stabilization, cement manufacture, liming material, Si, Ca and S source
FGD	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, $CaSO_3$, MgO, SiO_2, K_2O, Al_2O_3, Fe_2O_3)	Wallboard, stabilised road base/sub-base, structural fill, surface mine reclamation, underground mine injection, livestock pad, low permeability liner, sludge stabilization
FBC	Si, Al, Fe, Ca, S ($CaSO_4$, CaO, Quartz, gypsum)	Slow release fertiliser, liming material

Australia produces only Class F type ash, being mainly silica and alumina (80-85 %) having less than 10 % CaO. About 85 % of the current use of FA is for partial cement replacement (between 10-20 %) to enhance the properties of concrete and other building materials. The coarse furnace bottom ash (FBA) is used as a sand replacement, aggregate for lightweight blocks, a road-base component, for agricultural drainage mediums and as engineered bulk fill. The pozzolanic property of coal ash means in finely divided form and in the presence of moisture, it could chemically react with calcium hydroxide at ordinary temperatures to form compounds that have cementitious properties.

Supplementary cementitious materials (SCMs or cement extenders) are materials that exhibit inherent or latent cementitious properties. SCMs are added to a concrete mix either to partially replace or supplement the cement, or improve the properties of the resultant concrete. The main types of SCMs are pozzolanic compounds such as FA, ground granulated blast furnace slag, silica fume and natural pozzolans.

2.3.1.1 Cement and construction industry

The Australian cement industry uses 15 manufacturing sites, 10 mines and 74 distribution terminals in Australia, and produces more than 8 Mt of cement per year – enough to construct over 3,600 Sydney Opera Houses. Sales exceed $1 billion annually, $2.5 billion of capital is in place and 1925 people are employed across regional and urban Australia. Australia has three major cement companies:

- Adelaide Brighton Cement Ltd;
- Blue Circle Southern Cement Ltd; and
- Cement Australia Pty Ltd.

These companies supply the vast bulk of the cement used in Australia. Together, they account for all the integrated production of clinker and cement in Australia. Figure 2.1 plotted the growth in FA (cementitious use) sales compared to cement sales over the past 11 years. Although cement sales have grown over the corresponding period, FA sales have increased at a much faster rate, mainly due to the progress in research and revision in Environmental regulations.

The recycling of FA into construction related applications can reap substantial environmental benefits. These include:

- Waste stream reduction and associated reductions in requirements for landfill.
- When used as a cement replacement, FA use contributes to the conservation of resources such as gypsum, limestone and natural gas which would otherwise be used in cement production.
- The use of FA as a cement replacement also leads to reduction in Greenhouse Gas (GHG) emissions from cement production of almost 1 tonne of CO_2 per tonne of cement. Highlighting this point, since 1975 emission of some 16 Mt of GHG has been avoided by the use of FA in concrete (ADAA, 2009a).

Fly ash direct, a company, which promotes the use of FA in USA, has listed the following benefits of using FA to harden concrete:

- Increased strength – FA will continue to react with available lime and alkali in concrete, producing additional cementitious compounds that allow the concrete to continue to gain strength beyond 28 days.
- Reduces drying shrinkage – The reduced water demand allows FA concrete to maintain workability and therefore reduces drying shrinkage.
- Decreased permeability – The packing effect of the FA particles helps to reduce permeability. The chemical reaction between FA and lime forms additional bonds that block bleed channels and fill pore spaces.
- Improved durability - The decrease in free lime and the resulting increase in cementitious compounds, combined with the reduction in permeability enhance concrete durability.

- Resistance to sulphate attack – FA combines with free lime making it unavailable to react with sulphates that can cause expansion problems.
- Reduced heat of hydration – Large masses of concrete typically produce high internal temperatures and thermal cracking. Less heat is generated when FA is used to replace a portion of Portland cement in the mix.
- Mitigates alkali aggregate – FA reacts with available alkalis in the hardened cement matrix making them less likely to react with the aggregate.

Fly ash, as a partial replacement of the sand and cement in concrete, economically enhances performance in regard to workability, shrinkage creep and durability. Production of High Performance Concrete generally involves the use of FA. Several lightweight aggregates for concrete can be produced from ash. In addition to the use of furnace bottom ash in concrete masonry, pellets of FA can be bound by thermal fusion or chemically, using cement or lime. Such materials have many desirable properties.

2.3.1.2 Structural Fill and Road Works

Ash products have a long history of successful use both locally and overseas in structural fills and road works. Most of the pioneering work was done in the United Kingdom by the Central Electricity Generating Board. Structural fills have been successfully completed with conditioned FA, furnace bottom ash and pond ash (a mixture of FA and furnace bottom ash reclaimed from settlement ponds). For example in Australia, at Vales Point Power Station near Newcastle, the capacity of the ash settlement pond has been increased by building above the dam wall with compacted, conditioned FA. This range of applications also includes flowable fills and controlled low strength materials. Fly ash is widely used in the binder component of road base mixtures and in 5 MPa concrete sub base in NSW. At Port Augusta Power Station, roads and cover over coal stockpiles have been constructed successfully using cement bound mixtures of FA and furnace bottom ash. ADAA (2009a) reports that Queensland Transport requires the use of FA in concrete used in roads and bridges as insurance against alkali-silica reaction.

2.3.2 Agricultural applications

The idea of utilising CCPs in agriculture has originally arisen as a result of their role as a nutrient supplement to crops and soils low in Se, Mo, Cu, Zn, or B (Page *et al.*, 1979, Adriano *et*

al., 1980, Aitken *et al.*, 1984). Fly ash, the major CCP has a considerable content of K, Ca, Mg, S and P (Martens *et al.*, 1970; Page *et al.*, 1979; Adriano *et al.*, 1980; Cerevelli *et al.*, 1987; Sikka and Kansal, 1995; Kalra *et al.*, 1997; Singh *et al.*, 1997, Pathan *et al.*, 2002). The addition of FA generally increases plant growth and nutrient uptake (Ciravolo and Adriano, 1979; Aitken *et al.*, 1984; Stout *et al.*, 2003). El Mogazi *et al.* (1988) reported that application rates are typically modified according to soil type and their physical or chemical characteristics (Table 2.4).

The use of CCPs in agriculture not only offers potential chemical (nutrient) and physical (structural) benefits but also environmental benefits through resource reuse instead of landfilling. Much of the literature regarding the beneficial use of CCPs in agricultural applications describes application rates at levels of 5 to 20 %. Application rates are typically modified (Table 2.4) according to soil type and the physical or chemical characteristic being modified (e.g. pH modification, drainage etc).

Much research and development has been carried out in the past three decades on the use of FA in agriculture (Bhumbla *et al.*, 1991; Kumar and Singh, 2003; Stevens and Dunn, 2004), where the potential of FA as liming agent, source of plant nutrients, and soil modifier has been exploited. The uptake or enrichment of various nutrients and toxic trace elements (Table 2.5) in soil after fly-ash amendment has been investigated, and crop produce has been found safe for consumption (Sen *et al.*, 1997).

In Australian soils, FA released Mg at rates comparable with established Mg fertilizers. The Mg in FA was more soluble than that in the established fertilizers. It released significant amounts of Mg over a wide range of pH. It contained both a water-soluble, and a citrate-soluble fraction (Hill and Lamp, 1980; Stehouwer *et al.* 1995). The strong correlation between pH correction and nutrient availability in the soil suggests that in FA, most elements are associated with the mineral phase. One can therefore expect that interaction between the predominantly inorganic FA and organic matter may further enhance its beneficial effect on plant growth in problem soils (Page *et al.*, 1979; Molliner and Street, 1982; Dou *et al.*, 2003). Boron toxicity is the major limiting factor in agricultural use of FA. Boron induced inhibition of microbial respiration can be prevented by the co-application of a readily oxidizable organic substrate (Page *et al.*, 1979).

Table 2.4 Effects of Fly ash application in Agricultural crops
(El-Mogazi *et al,* 1988; Yunusa *et al.,* 2006; Manoharan *et al.,* 2010a and b)

Ash description and power plant location	Soil description	Crops grown	Ash increased plant uptake of	Ash produced toxic levels of	Change in yield due to ash	Comments
Acidic ash derived from bituminous coal; S. Carolina	Acidic sandy loam	Corn, bush bean	Ca, Mg, S	B (to plants)	None	B toxicity and P deficiency were limiting factors for crop growth. Fe and Al in ash may inhibit P availability by forming insoluble complexes
Acidic ash derived from bituminous coal: New York	Acidic fine sandy loam	Several vegetables and millet	As, B, Ca, Cu, Fe, Hg, I, K, Mg, Mo, Ni, Sb, Se	-	Variable	Se uptake was proportional to ash application rate
Three basic ashes derived from bituminous coals: Virginia and W.Virginia One ash was pre-leached	Variable	Corn, alfalfa	Mo	B (to plants, leached ash only)	Decreased (unleached ash)	Plants were much more tolerant to pre-leached ash than to unleached ash
Neutral scrubber sludge derived from subtuminous coal; Minnesota	Acidic loamy sand	Soybeans	B	B (to plants)	Decreased	Crop yields recovered by the third growing season
Basic coal ash; India	None (used aqueous nutrient solutions)	Corn and soybean seedlings	Mn, B, Cu, Zn, K, P, Ca, Mg	-	Decreased	2.5% extract had deleterious effects on seedling development possibly due to B or heavy metals
Basic brown coal ash; Australia	Washed river sand	Ryegrass seedlings	Mg, S, Na	-	Increased	Mg in ash was as available to plants as Mg in some fertilizers. S in ash was not as available as S in sulphate

Adriano *et al.* (1980) recommended mixing alkaline FA with highly carbonaceous acidic material to make compost for soil treatment. Interestingly, with several essential plant nutrients, CCPs are devoid of the much important humus and nitrogen (Menon *et al.*, 1990), which can be supplemented by organic amendments (Adriano *et al.*, 1980).

In 2003, the ADAA commenced a four year research project with the University of Technology Sydney to assess the use of CCPs in various agricultural systems and with various soil types. The goal of this research was to gather additional information demonstrating the economic and agronomic benefits from the application of CCPs in horticultural and agricultural systems (ADAA, 2007).

The agricultural use of FA highly depends on the nature of parent coal used for power generation (Table 2.4). The agricultural use of a FA has often been assessed in relation to its effects on: (1) crop yield and development; (2) uptake and accumulation of nutrient and non-nutrient elements; and (3) toxicity levels of trace elements (El Mogazi *et al*. 1988; Yunusa *et al.,* 2006; Manoharan *et al.*, 2010a and b).

2.3.2.1 Effect on soil structure and quality

Effect of FA on soil quality, which determines the soil health, manifests into soil productivity and has far reaching effect on the soil ecosystem. While the health of soil depends on inorganic and organic matter content, processes like erosion, salinization and chemical contamination have a direct bearing on ground water contamination, land use and management practices (Acton and Gregorich, 1995). Fly ash contains trace and heavy metals, which readily percolate down from conventionally used earthlined lagoons and pollute ground water. The solubility of these elements is less than 10 % (Rohriman, 1971). Natusch and Wallace (1974) observed that 5-30 % of toxic elements, especially Cd, Cu and Pb, are leachable. Radionuclides of uranium (U) and thorium (Th) series were reported in FA (Eisenbud and Petrow, 1964; Tadmore, 1986). Majority of FA are not significantly enriched in radioactive elements or in associated radioactivity compared to common soils or rocks (Zielinski and Finkelman, 1997).

Fly ash has overall beneficial effects on soil physico-chemical and biological properties if applied judiciously. In the presence of Ca–Si minerals with a pozzolanic nature (zeolite formation), along with the moisture of the soil (Fulekar and Dave, 1986; Pratt *et al.*, 2007), FA brings about improvements in various physico-chemical properties such as porosity, water-holding capacity and the available water in the soil (Table 2.5). In particular, FA has higher silt

content than soil, and the infiltration rate of sandy soils or mine spoil is drastically checked because of the increase in silt (Furr *et al.*, 1977), whereas in the clay-rich type of soils, the reverse is the case, with better water movement and workability, apart from decreased plasticity or crack formation after drying.

Table 2.5 List of potential hazard and effects on agricultural soil of CCPs application (Korcak, 1985; Whitehouse *et al.* 2000)

S.No	Potential Hazard	Possible effects on Agricultural soil
1.	Excessive trace metal loadings	Accumulation in food chain
2.	High soluble salt loadings	Reduction in initial plant growth
3.	High Na loadings	Reduction in water infiltration in the soil
4.	Sulphite damage to crops	Reduced rates of crop establishment and growth
5.	Leaching of toxic substances	Contamination of ground and surface water
6.	Imbalance in Ca:Mg ratio (due to the use of Ca-based sorbent during combustion)	Mg and P deficiency

As FA has most of the essential plant nutrients other than nitrogen and humus (Menon *et al.*, 1990; Pathan *et al.*, 2002), applying it to the soil naturally improves its fertility by enriching it with the essential elements, thereby resulting in increased crop yield. The organic amendments co-composted with FA also help in improving the humus and microbial activities of the amended soil or mine spoil, besides adjusting the pH by way of decomposition and N demineralisation (Adriano *et al.*, 1982; Sims *et al*., 1993; Wong, 1995), controlling the availability of metals to the plant by chelation, and releasing nutrients during vegetation (Logan and Traina, 1993).

The surface of FA particles consists of exchangeable sites, to accommodate micronutrients (Fe, Co, Cr, Cu, I, Mn, Se, Zn, and Mo) and macronutrients (Ca, Mg, P, K, Na, S, Cl), so that ash particles becomes a repository of nutrients and a potential nutrient pump (Sahu, 1999). Besides, adsorption, desorption, and exchange being pH dependent, the mineral pump is energized selectively for nutrient transfer to achieve rapid growth of plant in the fly-ash-amended soils. Furthermore, during the ash–water interaction, oxyhydroxide of iron (goethite) is formed and acts as a major scavenger of trace metals. The oxyhydroxide flocculates, either as coating or as discrete grains, and thus immobilises heavy metals, leading to their reduced availability (Leekie *et al.*, 1980).

Fly ash also helps in the retention of the chemical fertilizer applied through inorganic sources in the soil system for longer periods (CFRI, 2000; Seshadri *et al.*, 2010), leading to

prolonged residual effects of FA application. The uptake and accumulation of trace and heavy metals in grain crops depend on several factors such as pH, OC, CEC, micro-organisms, concentration of metals and their form of occurrence, their mobility to the root and transport from root surface to root interior, and their translocation from root to shoot (Ram *et al.*, 2006).

Since FA contains many silt-sized particles its addition at high rates to soils high in sand or clay can change the soil texture (Chang *et al.*, 1977, 1989; Pathan *et al.*, 2002). When ash was added to five soils with sandy textures the bulk density increased, while ash addition to three soils with clayey textures decreased bulk density. This difference could be due to the structural position where the FA resides after incorporation and the changes in pore space.

Ash additions have also been found to increase the water holding capacity of soils. Addition of I0 % ash to fine (0.2-0.5 mm) and coarse (1.4-2.0 mm) sand fractions increased the available water content by 7.2 and 13.5 %, respectively (Campbell *et al.*, 1983). Ash alone was found to have > 40 % available water in 11 of 13 Australian ashes tested (Aitken *et al.*, 1984). Improvements in available water in ash amended soils have also been reported by other researchers (Salter *et al.*, 1971; Chang *et al.*, 1977, 1989; Summers *et al.,* 1998; Pathan *et al.*, 2002). It is unclear whether the increases in water holding capacity also result in increases in plant available water; Chang *et al.* (1989) reported that water in FA amended soils is less available. Other studies have noted a lack of yield response to the increase in water retention. This could be due to other growth limiting effects of the FA, such as B toxicity or high soluble salts. The yields of carrot *(Daucus carota),* beet *(Beta vulgaris),* radish *(Raphanus sativus),* and bean *(Phaseolus vulgaris)* showed no improvement in response to the application of FA to a sandy loam soil, even though the water holding capacity had increased (Salter *et al.*, 1971).

Addition of FA at 70 tonnes per hectare was reported to alter the texture of sandy and clay soils to loamy soils (Fail and Wochok, 1977; Capp, 1978). Soils prone to soil or water erosion can be stabilized through FA amendment. The fine nature of FA is beneficial in increasing water holding capacity of sandy soils and removing compaction in clay soils. These improvements in physical and chemical nature coupled with positive effect on soil microorganisms make the problem soils productive. Thus, the use of FA for reclaiming threatened soils provides an economical way of disposal (Jala and Goyal, 2006).

The ADAA is a joint research sponsor of a four year test program with the University of Western Australia. The research program has already demonstrated substantial improvement in water retention and pasture growth in sandy soils. Some of the findings have highlighted the ability of FA to improve water retention in soils with low moisture holding capacity (i.e. sandy

soils) to over 30 % compared to untreated soils. Furthermore, FA provided increased plant growth without the need for additional fertilizers (ADAA, 2009b).

2.3.2.2 Nutrient source

A number of studies have examined the value of CCPs as a nutrient source (Table 2.6). The major nutrient elements in CCPs include Si, Al, Fe, Ca and S, together with lesser amounts of Na, Mg, B, Sr and K. For example, FBC and FGD ashes have a Ca and Mg contents ranging from 13 % to 39 % and from 0.1 % to 16 %, respectively depending on whether the sorbent is calcite or dolomite. Due to the presence of unspent sorbent, FBC is usually highly alkaline (pH_{water} 10.5-12.5) with significant neutralization potential. It has been reported that the best agricultural use of FBC ash is as a liming source to overcome the problems associated with soil acidity (Terman *et al.*, 1978; Wang *et al*. 1994; Stout *et al.*, 1998; Stout *et al.*, 2000). The S content of FBC and FGD is also relatively high, being mainly in the form of $CaSO_4$ (anhydrite), which also acts as a Ca source in addition to relatively high liming value (Wang *et al*. 1994). Compared with Ca and S, the amounts of N, P and K in CCPs are negligible. The micronutrient content in CCPs is low except for boron (B) that ranges from 36 to 1360 mg kg^{-1} (Table 2.6). Boron is an essential mineral nutrient for all vascular plants. The functions of B are primarily extracellular, which relates to lignification and xylem differentiation. Some of the CCPs such as FBC also contain small amounts of selenium (Se, 0.16 to 5.6 mg kg^{-1}) which is an essential nutrient for animals but not plants. Due to the exposure of these elements to oxidizing conditions during combustion, Fe, Mn, Cu and Zn occur as oxides in FBC.

The presence of S in FBC and FGD ashes as anhydrite ($CaSO_4$) or gypsum ($CaSO_4.2H_2O$) after hydration make these CCPs the major source of S in S-deficient soils. Gypsum, including industrial by-products, such as phosphogypsum, has been successfully used as an S fertilizer to increase the yields of winter wheat, rice and pasture. To date, data on the use of these two CCPs as an S fertilizer is limited, although Terman *et al*. (1978) demonstrated that FBC ash is an effective S source for growing corn and peanuts. Approximately 50 % of S in slaked FBC ash is present as sparingly soluble ettringite, which can act as a slow-release S fertilizer (Wang, 1996). Therefore, slaked FBC ash shows potential to be used as a basal S fertilizer in soils prone to severe leaching, which are common in some high rainfall areas of New Zealand and in soils with low anion retention capacities. For example, results from a field study in the peat soil indicated that ettringite-S in

Table 2.6 Selected references on nutrient and heavy metal concentrations in CCPs

CCPs	Nutrients (g kg^{-1})						Trace elements (mg kg^{-1})						Reference
	P	**S**	**Al**	**Ca**	**Fe**	**B**	**As**	**Cd**	**Cr**	**Hg**	**Pb**	**Se**	
FA	-	-	-	-	-	1.69	7.0	0.1	38	1.3	15	2.9	**McDowell (2005)**
	0.956-1.002	-	110-130	5.3-5.7	82-100	0.003-0.0036	116-129	2.8-3.5	155-169	0.27-0.45	60-63	12-17	**Punshon *et al*. (2002)**
	1.388-1.432	1.26-1.3	75-117	13-14	41-73	0.0199-0.0211	112-125	3.0-5.0	97-155	0.22-0.31	247-263	8.4-11	**Adriano *et al*. (2002)**
	0.4-8	1-15	1-173	1.1-222	10-290	0.01-6.18	2.3-6300	0.7-130	10-1000	0.02-1.0	3.1-5000	0.2-134	**Sharma and Kalra (2006)**
	0.2315	2.738	4.136	8.435	13.51	0.298	-	2.8	26.8	-	2.5	-	**Sajwan *et al*. (2007)**
	3.760	0.948	147	27.4	90.9	0.056	22.3	0.52	69.2	-	49	2.26	**Jankowski *et al*. (2006)**
FBC	-	-	13.0	300	55.0	-	-	<2	50.0	-	85.0	-	**Karapanagioti and Atalay (2001)**
	0.875	62.0	18.0	254	36.0	1.36	6.5	<0.1	<0.1	-	<2.0	<3.0	**Wang *et al*. (1995)**
	0.1	86.4	27.5	244	20.8	0.206	46.7	3.5	17.5	-	28.0	2.3	**Stehouwer *et al*. (1996)**
	0.2	38	0.1	391	5.0	1.328	8.1	0.2	33	-	88.0	3.3	**Wright *et al*. (1998)**
FGD	0.573	85	25.5	146	85	0.356	107	<0.2	51	-	15	-	**Ahn *et al*. (2001)**
	-	67.1	19.6	260	16.5	0.194	118	<0.1	123	-	139	<6.0	**Chen *et al*. (2005)**
	-	-	-	193	51	0.0422	68.9	0.35	13.7	0.036	17.1	29.2	**Punshon *et al*. (2001)**
	0.2	52.1	39.3	175	51.7	0.171	75.0	1.9	36.9	-	16	5.6	**Stehouwer *et al*. (1999)**
	0.2	182	8.0	201	0.1	0.131	6.3	0.7	15.0	-	100	2.3	**Wright *et al*. (1998)**
	-	205.4	3.3	269.1	-	-	1.08	<0.1	9.70	0.658	4.08	0.84	**Wang *et al*. (2008)**

slaked FBC ash was less affected by leaching loss than gypsum and resulted in longer-term pasture yield S responses to FBC ash treatments (Wang, 1996). This was supported by herbage S analysis where, 8 months after application, herbage S contents in the high rates of FBC ash treatments (6616 and 26462 kg ha^{-1}) were significantly higher than the control.

A number of studies have examined the value of CCPs in the immobilisation of P (Cheung and Venkitachalam, 2000; Stout *et al.*, 2000; McDowell, 2004 and 2005). Loss of P through leaching and surface runoff, especially in sandy soils is a major environmental issue in many countries including Australia, resulting in the eutrophication of surface waters. For example, concentrations of P in runoff from agricultural catchments in southern Australia are high and well above national and international limits (Cox *et al.*, 2005). They argue that P loss is a serious problem in most parts of Australia due to its unique soil (sandy texture) and climatic (xeric; i.e., strong seasonal wetting and drying cycles) conditions. Cheung and Venkitachalam (2000) reported that coarse, sandy soil such as those found in Perth, Western Australia, exhibit low attenuation capabilities for P during effluent infiltration.

Various CCP sources including FA, FBC and FGD have shown potential as soil amendments to decrease soil inorganic P solubility. For example, Stout *et al*. (2000) reported that FBC has consistently reduced concentrations of water-soluble P in a number of soils with high concentration of soluble P. They found that amendment with FBC resulted in a shift from readily available resin P and less available NaOH-extractable Fe and Al-bound P fractions to HCl-extractable Ca-bound P, which can be attributed to their neutralizing capacity. However, considering the high treatment rates (22 tonnes h^{-1}) required to significantly reduce readily available P in soils, Codling *et al.* (2002) suggested that FBC may not be suitable for field application to sequester P in high P soils.

The FBC was also been tested in a number of studies to reduce solubility and mobility of P in soils with high P concentration and in P-rich organic wastes (Codling *et al.*, 2002; Dou *et al.*, 2003). In a packed column leaching study involving dairy manure, Elrashidi *et al.* (1999) reported that P in leachate in FBC treated column was reduced by more than 80 % compared with the control treatment containing dairy manure only. In a laboratory incubation and extraction study, Dou *et al.* (2003) found that FBC applied at a rate of 400 g kg^{-1} reduced readily soluble P by 50 to 60 % in P-rich manures including dairy, swine and broiler litter.

Seshadri *et al.* (2009) compared the effect of various sources of CCPs including FA, FBC and FGD ashes on P sorption in a variable charge soil. The increase in P sorption with the addition of CCPs is attributed to an increase in soil pH and an increase

in the concentration of aluminium (Al), Iron (Fe) and Ca in soil solution resulting in the formation of insoluble Al-P, Fe-P and Ca-P (McDowell, 2004). The decrease in P sorption with increasing levels of FGD gypsum is attributed to the decrease in soil pH. Bolan *et al.* (2007) examined P leaching as affected by various liming materials including FBC, which decreased both bioavailable P as measured by Olsen P and leaching of P.

However, McDowell (2004) observed increased P losses in New Zealand pasture soils when soil pH was raised with the application of FBC ash which has been attributed to the solubilisation of organic P due to free CaO in this ash by-product. He consequently concluded that ash could be useful as a supplement or alternative to lime in cropping soils where the pH is commonly maintained at a higher level and may, in these soils, prove beneficial in mitigating P loss (McDowell, 2005). Similarly, although most of CCPs contain insignificant amount of nitrogen, application of CCPs with organic amendments such as biosolids has been shown to increase the mobilisation of N by inducing the mineralisation of organic N (Stuczynski *et al.*, 1998).

Page *et al.* (1979) demonstrated higher yield of several crops in acidic soils by adding up to 8 % (w/w) of unweathered FA, mainly due to increased availability of S to plants. FA applied on acidic strip mine spoils at different locations increased the yield of many crops which was attributed to increased availability of Ca^{2+} and Mg^{2+} in soil and preventing toxic effects of Al^{3+}, Mn^{2+} and other metallic ions by neutralizing the soil acidity (Fail and Wochok, 1977). Fly ash does not seem to be an optimal source of phosphorus as it was found inferior to monocalcium phosphate (Martens, 1970), but some FA are high in phosphorus (Pathan *et al.*, 2002; Seshadri *et al.*, 2010). It however accelerated Ca^{2+} and Mg^{2+} uptake by legumes (Adriano *et al.*, 1978; Page *et al.*, 1979). Use of swine manure with FA increased the availability of Ca and Mg by balancing the ratio between monovalent and bivalent cations (Na^{+} + K^{+}/Ca^{2+} + Mg^{2+}), which otherwise proves detrimental to the soil (Giardini, 1991). Calcium readily replaces Na at clay exchange sites to enhance soil flocculation and stability. An appreciable change in the soil physicochemical properties, rising of pH and increased rice crop yield was obtained by mixed application of FA and paper factory sludge and farmyard manure (Hill and Lamp, 1980; Molliner and Street, 1982).

Although, higher B availability limits the use of FA in crop production (Page *et al.*, 1979; Aitken and Bell, 1985), the problem can be overcome by proper weathering of the FA (Table 2.7), which reduces B availability to below toxic level (Cope, 1962; Hodgson and Townsend, 1973; Townsend and Gillham, 1975). Increased Se accumulation in plant tissues with increased FA application warrants close monitoring and use of appropriate quantity of weathered FA depending upon the end use of the produced biomass (Furr *et al.*, 1977; Straughan *et al.*, 1978).

2.3.2.3 Liming potential

One most beneficial property of certain types of CCPs is their liming potential. The liming potential of FA is derived primarily from CaO, MgO and other alkaline metal oxides that react with water to generate net alkalinity, meaning they will react with and neutralize acidity (protons; H^+). In a study of 23 ashes from across the U.S., Furr *et al.* (1977) found that ash pH ranged from 4.2 to 11.8. Fresh unweathered FA can have pH values higher than 9 but it is rare to find pH values higher than 8.5 for weathered FA.

Many ashes are high in Ca and Mg oxides and have a significant neutralizing capacity. Fly ashes with neutralizing capacities of up to 10 % calcium carbonate equivalent (CCE) have been reported, but CCE values of l to 6 % are more common (Aitken, *et al.*, 1984). Thus, more than 20 tonnes of most FA would be required to replace 1 ton of ground limestone. This indicates that ash would not be effective in raising a low pH, highly buffered system due to the large amount of ash needed, but may be more effective in poorly buffered, coarse textured systems, such as coal refuse. Water soluble Ca content was found to be the best indicator of ash potential to produce alkalinity (Theis and Wirth, 1977). Unweathered FA also contains high levels of soluble salts (Table 2.7). Ash from lignite and sub-bituminous coals tend to have the highest salt levels (Adriano *et al.,* 1980), and the application of 179 Mg ha^{-1} of unweathered FA was found to increase soil salinity from 500 to 600 %, thereby causing significant increases in soluble B, Ca, and Mg (Page *et al.*, 1979). A long term study on the environmental benefits for CCPs utilisation in Australian Agricultural and horticultural systems reveals that when FA is considered as a liming agent in terms of agricultural applications, the levels of cadmium, mercury and lead is well under the permissible limit under Fertiliser Act, 1985 (Heidrich, 2003). Lime in FA readily reacts with acidic components in soil and releases nutrients such as S, B and Mo in the form and amount beneficial to crop plants (Elseewi *et al.*, 1978; Phung *et al.*, 1978). The best liming agent among the CCPs is FBC (CCE ranging from 31-105 %) which is often utilised as a liming source to overcome the problems of associated with soil acidity (Korcak *et al.*, 1980; Stout *et al.*, 1998; Marsh and Grove, 1992; Korcak, 1993; Wang *et al.*, 1994; Stehouwer *et al.*, 1999).

Korcak and Kemper (1993) investigated the long term effects of FBC applied at disposal levels on soil chemical properties. In 1980, FBC was applied as a soil ‘cap’ about 50 mm thick within the rows of an established, young apple orchard at rates up to 112 tonnes ha^{-1}. Eleven years after application, soil profile pH was significantly elevated by the FBC treatment to a depth of 660 mm. They suggested that horticultural utilisation of FBC at relatively high rates of application may be a practical consideration for disposing of FBC. In orchard settings, FBC can be surface applied and remain in place for long periods. Results from their original apple study showed overall good growth and

productivity of the trees.

Table 2.7 Potential and observed effects of fly ash amendment on soil properties (Carlson and Adriano, 1993; Pathan *et al.,* 2002).

Soil property	Typical agricultural soil	Soil amended with weathered ash	Soil amended with unweathered ash
Aeration	High	Higher	Higher
Bulk density	1.3 g cm^{-3} (avg.)	Lower	Lower
Cation Exchange Capacity	Medium	Higher	Higher
Electrical conductivity	Low	Moderate to higher	Higher
Hydraulic conductivity	High	Increased by low rates; decreased by high rates	Increased by low rates; decreased by high rates
Nutrient availability	Balanced supply of nutrients	Deficient in N, P, and potentially Cu, Mn, Zn; potential for food chain concern with Mo and Se	Deficient in N, P, and potentially Cu, Mn, Zn; potential for food chain concern with Mo and Se
Nutrient content	All nutrients present	Very low N, potentially high B; others present	Very low N, often excessive B; others present
Organic matter	High	Lower	lower
pH	6.0 to7.5	> 6.0 to 8.0	> 6.0 to 12.0
Plant available water	High	No effect to large increase	No effect to large increase
Salinity	Low	Moderate	High but decreases with time
Toxic salts	None	May have enough B to toxic to sensitive plants	High B and soluble salts of Ca, K, Mg and Na
Water holding capacity	High	Higher	Higher

The liming potential is not only influenced by CCE value, but also by its particle size. Edwards *et al.* (1985) indicated that FBC from a calcitic sorbent source (ground to pass a 0.15 mm sieve) was more effective in altering soil pH than FBC from a dolomitic source (90 % passing through a 2 mm sieve and 25 % passing through a 0.15 mm sieve). Both FBC sources, however, were adjusted to equal Ca contents. They suggested that the smaller particle size of the calcitic FBC was more reactive than the bigger sized dolomitic FBC. Thus, when comparing FBC's liming effectiveness, FBC's particle size must be considered as well as the nature of the fuel and sorbent source.

2.3.3 Environmental applications

Coal combustion by-products are used as an amendment for coal refuse piles and non-agricultural lands, especially for reclaiming mined areas (Stehouwer and Sutton, 1992). Australia has been quite efficient in controlling the green house gas (GHG) emission GHGs through sustainable use of available resources in all aspects of industrialization. For example, since 1975 some 16Mt of GHG have been replaced

indirectly by the effective use of FA concrete in Australia (ADAA, 2009a). CCPs are used for various environmental application that include,

- Heavy metal immobilisation
- AMD mitigation and mine site reclamation
- Carbon sequestration.

2.3.3.1 Immobilisation of heavy metals

Principally, the amount of trace elements (including heavy metals) in CCPs, excluding B is found within the range actually present in soils (Table 2.6). For example, Korcak and Kemper (1993) observed no phytotoxic effects of micronutrients when FBC ash was used as a liming source even at very high rates. However, the availability of micronutrients to plants depends not only on the amounts applied in FBC ash, but also on the soil properties and the specific crop being grown.

Although the concentrations of B in CCPs (Table 2.6) are higher than that found in most soils, it is not toxic in most agricultural soils, unless supplied in excessive amounts through additional fertilizers. Wang (1996) reported that high rate application of FBC (up to 19, 185 kg ha^{-1}) in a field trial had not induced visual symptom of B toxicity in a white clover and ryegrass dairy pasture in a peat soil. However, Clark *et al.* (1999) reported that a soil mixed with more than 0.5 % FBC resulted in significant dry matter reduction of maize in a pot experiment due to B toxicity. Crews and Dick (1998) observed B toxicity symptoms in plant tissue when red oak is grown in soil applied with FGD at two times or higher the lime requirement rate. Therefore, care should be taken when applying CCPs with high levels of B to sensitive crops such as cherry, peach, lupin, and kidney bean, especially when these crops are growing on sandy soils.

Stout *et al.* (2000) reported that the heavy metal content in CCPs is comparable to that of more traditional agricultural soil amendment products, such as lime and gypsum. In addition, the oxide form of heavy metals in FBC makes them much less available to plants than the organic forms in sewage sludge. However, any increase in the quantity or availability of these metals in soils should be carefully monitored using appropriate soil tests.

The value of CCPs as a viable option in immobilising heavy metals in contaminated soils had been examined in many studies. For example, Ciccu *et al.* (2001) conducted a study using soils from Italian mine site contaminated severely with heavy metals and showed decreased levels of heavy metals in percolating water from FA mixed soil, indicating that FA in such soils can lead to immobilisation of heavy metal ions.

Kumpiene *et al.* (2007) demonstrated reduced leaching of Cu and Pb from

contaminated soil using coal FA and peat as soil amendments. They observed that the amendments reduced the exchangeable metal forms, likely because of the formation of new mineral Cu- and Pb-bearing phases and the enhanced metal sorption due to increased amount of sorptive sites. They also observed reduced metal uptake by plants and reduced soil toxicity to microorganisms. This was attributed to the rise of soil pH and the lowered metal mobility due to FA additions. Stehouwer *et al.* (1995) observed that FBC reduced leachate concentrations of Al, Fe, Mn and Zn that are frequently phytotoxic in acid soils. Decreased solubility and mobility of these metals would also improve surface and drainage water quality.

The remediation measures required to clean up heavy metal contaminated sites is often complex that their implementation becomes economically unsustainable. The value of CCPs as a viable option in immobilising heavy metals in contaminated soils has been examined in many studies. For example, Ciccu *et al.* (2001) conducted a study using soils from Italian mine site contaminated severely with heavy metals and showed decreased levels of heavy metals in percolating water from FA mixed soil, indicating that FA in such soils can lead to immobilisation of heavy metal ion. Recently, numerous studies have demonstrated the successful immobilisation of metals, especially Pb, by P containing materials due to the precipitation of pyromorphite-type minerals (McGowen *et al.*, 2001; Cao *et al.*, 2003, 2004; Chen *et al.*, 2003; Melamed *et al.*, 2003; Brown *et al.*, 2005).

Soil amendment such as Fe oxides, organic matter, alkaline materials can reduce metal mobility and availability in soil by adsorption, complexation, (co)precipitation or a combination thereof, and help to restore soil properties (Basta *et al.*, 2005). Iron oxides (FeO_x) have a high sorptive capacity for metals (Chen *et al.*, 2000; Lombi *et al.*, 2002; Brown *et al.*, 2005).

Fly ash can be used to overcome problems related to acid mine drainage and metal solubility (Misra *et al.*, 1996; Iyer and Scott, 2001; Xenidis *et al.*, 2002). Application of FA increases the surface area available for element adsorption, improve the physical properties of soil (Gorman *et al.*, 2000), neutralize the pH of acidic soils and render most cationic metals less mobile (Ciccu *et al.*, 2003). These authors have demonstrated that relatively small additions of FA can drastically reduce the heavy metal contents of the soil leachates. They attributed this effect to the alkaline nature of the materials used and to the coexistence of constituents potentially capable of adsorbing heavy metals.

Kumpiene *et al.* (2007) demonstrated reduced leaching of Cu and Pb from contaminated soil using coal FA and peat as soil amendments. They observed that the amendments reduced the exchangeable metal forms, likely because of the formation of new mineral Cu- and Pb-bearing phases and the enhanced metal sorption due to increased amount of sorptive sites. They also observed reduced metal uptake by plants

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2.3.3.2 Acid mine drainage (AMD) and Mine site rehabilitation

The use of FA and other CCPs with or without the addition of an organic material may allow revegetation of mine sites without application of a topsoil cap. Addition of a topsoil cap is generally the major expense in reclamation of disturbed lands. Abandoned ash basins have been successfully revegetated with trees without the need for topsoil (Carlson and Adriano 1991).

The common properties of spoils and refuse that restrict plant growth and limit their productivity are acidity, compaction near the surface and course texture. In the case of steep slope terrain these problems are compounded by erosion, runoff and difficulty in operation machinery. Application of CCPs could remedy some of these problems. Many ashes are alkaline in nature and could neutralize acidity. Ashes are also fine in texture and water holding capacity may be improved through the application of ash (Stewart *et al.*, 1997).

Ongoing projects initiated by ADAA are evaluating the co-utilisation of CCPs and organic amendments such as municipal biosolids in disturbed land reclamation. The biosolids provide a N source for plant establishment and growth. As with CCPs, biosolids addition should be accompanied by the maintenance of a suitable pH to keep trace elements in the desired concentration ranges. Application of alkaline CCPs and in particular alkaline FA would decrease particle size, and neutralize acidity if applied in large quantities.

The use of coal FA in reclamation of coal refuse has been the subject of several experiments (Adams *et al.*, 1972; Jastrow *et al.*, 1981), but has not become a widespread practice in the U. S., primarily due to regulatory constraints and the lack of ash sources within many mining districts. The extremely acidic nature of mined lands, resulting from oxidation of Fe and sulfites, often requires basic material additions to bring pH into the range where plants can grow and where trace element availability is controlled. Consequently the use of power plant byproducts, which are generally alkaline, can assist in moderating pH to the desired levels to reduce trace element availability (Haering and Daniels, 1991).

Because of the alkaline nature of many CCPs, a number of studies have examined

their effect on modifying soil chemistry, primarily pH. The basic property of CCPs measured to quantify the effect on soil pH is the calcium carbonate equivalence (CCE) of the materials. The neutralizing effect of pure $CaCO_3$ is 100 % and that of coal combustion by-products usually ranges from 20 to 60 %. Therefore, if a coal combustion by-product has a CCE of 50 %, twice as much coal combustion by-product as $CaCO_3$ is needed to neutralize the same amount of soil acidity. Successful modification of soil pH has been demonstrated with a wide range of coal combustion by-products. Agricultural applications in most situations will probably be based on soil pH modification (Korcak, 1993). It has also been used for the neutralization of acidic mine spoils and restoration of nutrient balance in alkaline wastelands. The quantity of FA required to reclaim such areas depends upon the pH of FA, state of weathering and pH of the land to be reclaimed. FA acts as an alternative to lime for reclaiming the acidic mine spoils (Singh *et al.*, 1982; Haering and Daniels, 1991; Carlson and Adriano, 1993; Stehouwer *et al.*, 1995).

Stehouwer *et al.* (1995) investigated the efficacy of FBC as an amendment for acidic mine spoils and the potential for adverse environmental impacts from salts and trace elements when FBC was applied at high rates needed for mine spoil reclamation. In their eight month column leaching and greenhouse study, they found that FBC (60 % CCE) was effective in neutralizing acid conditions in the mine spoils when added to spoil at 30 to 60 g/kg spoil weight. This solves not only the AMD problem, but also disposal difficulties of FBC. They concluded that FBC is very suitable for mine spoil amendment if the amendment is limited to amounts that will not cause excessively high pH, or, phytotoxic salt concentrations.

2.3.3.3 Carbon Sequestration

The carbon intensity of world energy use during 2000-2030 is expected to decrease by about 25 %, due to the deployment of efficient and clean fossil fuel combustion technologies, CO_2 sequestration and use of more renewable energy source. Indeed, by 2030, 72 % of global coal-based power generation will be using advanced technologies. But, energy-related emissions of CO_2 had almost doubled in the past decade, due to the growth of population and related energy demand in the developing countries (ADAA, 2009b).

Gases in the earth's lower atmosphere that may contribute to global warming include CO_2, SO_2, CH_4, NO_x, CFCs, etc. Carbon dioxide is the major greenhouse gas in Australia's inventory with a share of 73.6 % (404.6 Mt) of the total CO_2 emissions, followed by methane (CH_4) which comprises 19.7 % (108.5 Mt CO_2). The remaining gases make up 6.7 %. These include, nitrous oxide (N_2O), perfluorocarbons (PFC), hydro fluorocarbons (HFC), and sulphur hexafluoride (SF_6). Emission of CO_2 in Australia from

various sources has been charted in Figure 2.3, where stationary energy is the largest contributor (NGGI, 2007).

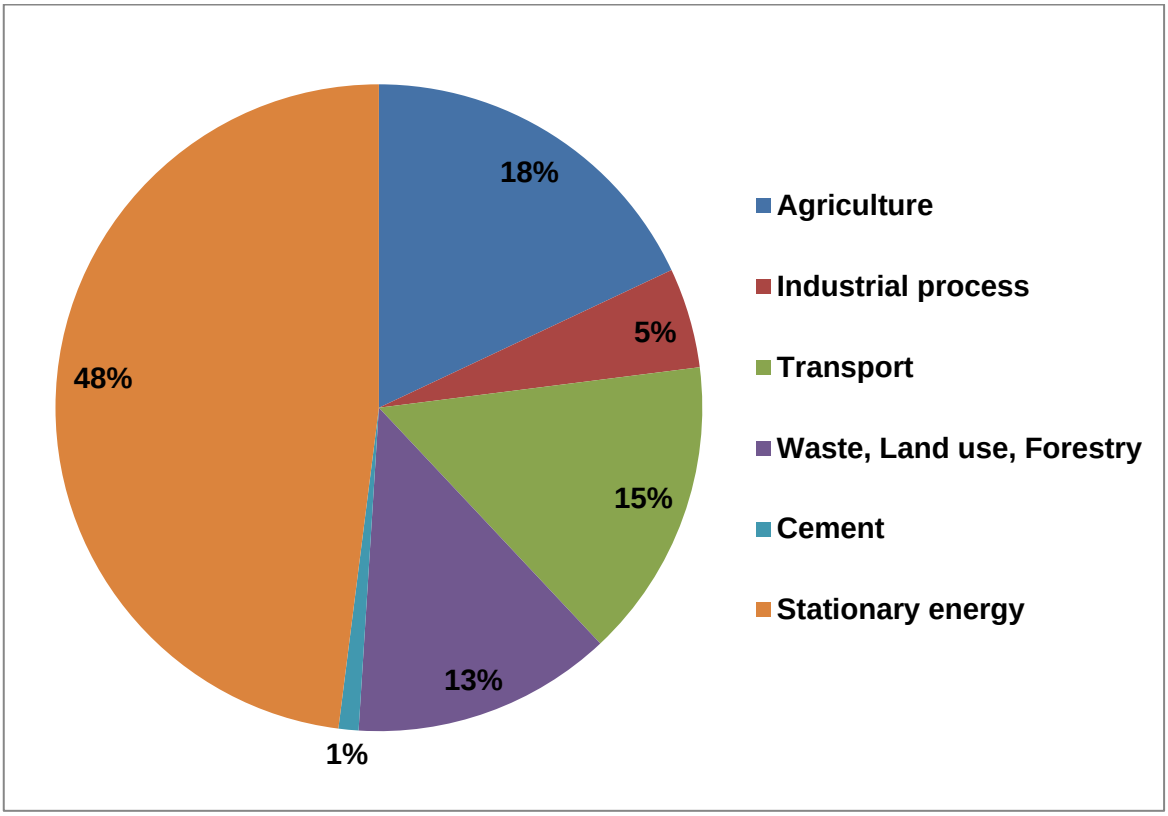


Figure 2.6 Contribution to total net CO_2 emissions by various sectors in Australia.

A potential approach to mitigate rising CO_2 concentrations currently of interest and one that is designed to complement the development of energy efficient technologies is the enhanced storage or sequestration of C in terrestrial ecosystems (e.g. Paustian *et al.*, 1998; Reichle *et al.*, 1999). One aspect of the terrestrial sequestration approach envisions the use of soil and vegetation functioning as long-term storage pools for atmosphere-derived C. To accomplish this, increased sequestration of C can be conceptually achieved by enhancing the atural biological processes that assimilate CO_2 (i.e. increased productivity of lands) and then allocating the assimilated C to plant tissues and/or pools of soil organic matter (SOM) resistant to microbial decomposition. Although a key objective in C management research is to enhance the natural capacity of plants and soils to sequester C, the functionality of C storage in terrestrial ecosystems as a whole is a poorly understood process. Many facets of terrestrial C sequestration have been explored, including the use of forest ecosystems, grasslands (Fisher *et al.*, 1994; Richter *et al.*, 1994; Post and Kwon, 2000; Conant *et al.*, 2001) and agricultural applications.

Scientists from Tennessee Valley Authority (TVA), USA are working on carbon sequestration using CCPs as a sequestering medium for CO_2 with subsequent conversion of CO_2 into algal biomass for production of methane and other carbon-containing

products.

The ADAA (2009b) focuses on increasing user awareness of the benefits arising through the effective utilisation of this valuable mineral by-product, which if realised, has benefits for industry, the environment and the community as a whole. Highlighting this aspect of the environment, since 1975 about 16 Mt of GHG has been replaced indirectly by the effective use of FA concrete.

Majority of Australian agricultural soils are hard setting due to their poor aggregation or structure and extremely low organic carbon (Chittleborough, 1992; Oades, 1993). Application of CCPs including FA is likely to increase carbon sequestration by promoting formation of humus and physically protecting existing organic carbon from decomposition (Amonette *et al.*, 2003; Palumbo *et al.*, 2004). Alkalinity of FA and its Fe oxides contents stabilise tyrosinase enzymes that catalyse oxidative polymerization reactions of humification (Humus formation), for which Class F FA is particularly effective (Amonette *et al.*, 2003; 2004). The preponderance of nanometre-sized pores, such as plerospheres, physically protects any organic matter that is sorbed onto mineral surfaces from microbial decomposition of humus that librates carbon dioxide (Palumbo *et al.*, 2004).

2.4 Microbial studies on CCPs application

Very little is known regarding the effects of FA amendment on soil biological properties (Schutter and Fuhrmann, 2001). Few studies have been conducted on the size, activity and nature of the microbial community on ash disposal sites. All of the factors discussed above (viz. high pH, salinity, toxicities of B and other elements, poor physical conditions) can limit colonization of microorganisms as well as plants in the ash (Carlson and Adriano, 1993). Even so, by far the most limiting factors for microbial activity are often a lack of substrate C as an energy source for heterotrophic microorganisms and the lack of an adequate N supply (Klubek *et al.*, 1992).

Several short-term laboratory incubation studies found that addition of unweathered FA to sandy soils severely inhibited microbial respiration, enzyme activity and soil nitrogen cycling processes such as nitrification and N mineralisation (Wong and Wong, 1986; Cerevelli *et al*., 1987; Pitchel, 1990; Pitchel and Hayes, 1990; Garau *et al.*, 1991). Fly ash composted with wheat straw and 2 % rock phosphate (w/w) for 90 days enhanced chemical and microbiological properties of the compost up to 60 %, and did not exert any detrimental effect on either C:N ratio or microbial population (Gaind and Gaur, 2003). Increased microbial activity was reported for ash-amended soils containing sewage sludge (Pitchel, 1990; Pitchel and Hayes, 1990). Moreover, the microorganisms invariably

adapt to the stressed conditions and show a gradual increase in respiration after an initial lag period. Presence of organic matter has an additive effect as it reduces the concentration of toxic metals through sorption, lowers the C/N ratio and provides organic compounds, which promote microbial proliferation and diversity (Wong and Wong, 1986; Pitchel and Hayes, 1990).

Available data indicate that microbial incidence and diversity generally increases as ash weathers and nutrients accumulate (Rippon and Wood, 1975). The supply of simple organic compounds and N are crucial for sustaining rich microbial population at ash-amended sites (Klubek *et al.*, 1992). Alkaline coal FA and lime were tested for their effectiveness in pathogen removal from biosolids (Wong *et al.*, 2001) and it was observed that mixture of 10 % ash–biosolids and 8.5 % lime on dry weight basis had acceptable levels of Salmonella and total coliforms. Application of FA at 40 t ha^{-1} in conjunction with phosphate solubilizer, *Pseudomonas striata* improved the bean yield and P uptake by grain and FA did not exert any detrimental effect on the population of *P. striata* in soil (Gaind and Gaur, 2002). Amendment of Class F FA to soil at a rate of 0.5 Mt ha^{-1} did not show any detrimental effect on soil microbial communities. Analysis of community fatty acids indicated elevated populations of fungi, including arbuscular mycorrhizal fungi and Gram-negative bacteria (Schutter and Fuhrmann, 2001). Fly ash–sludge mixtures containing 10 % ash had positive effect on soil microorganisms in terms of enzyme activity, N and P cycling and reduction in the availability of heavy metals (Lai *et al.*, 1999). Fly ash and its different combinations with soil were tested for use as a carrier for diazotrophs (*Azotobacter chroococcum, Azospirillum brasilense*) and phosphobacteria (*Bacillus circulans, P. striata*) (Gaind and Gaur, 2003) which showed their maximum viability in FA alone or soil:FA (1:1) combination.

Adriano *et al.* (1978) reported that at higher levels of FA, some heavy metals might become more active and hinder microbial activity. These metals form complexes, which undergo transformation, influenced by various factors like pH, moisture, cation exchange and microbial activity (Milovsky and Kononov, 1992).

2.5 Risks of CCPs in the environment

Extensive Environmental and Health impacts studies have been carried out only on FA. FA contains trace and heavy metals, which readily percolate down from conventionally used earth-lined ash lagoons and pollute ground water. Effect of FA on ground water is a function of physical and chemical characteristics of ash and hydrogeologic and climatic conditions of the disposal site (Theis *et al.*, 1978; Kopsick and Angino, 1981; Goetz, 1983). Weathered FA deposits cause more ground water contamination because of the presence of higher levels of soluble salts. In unweathered

ash, although there is generally a higher release of soluble salts initially, it declines rapidly with time (Jones and Lewis, 1960; Kopsick and Angino, 1981; Theis *et al*., 1989; Hjelmar, 1990; Mattigod *et al.*, 1990).

Fly ash, particularly when it has been dry collected and handled, contains moderate to high levels of soluble salts, primarily sulphates and borates. Dissolution of these salts into soil solution can generate high levels of salts which can suppress plant growth or actually kill salt-sensitive seedlings and/or established vegetation. This behaviour is referred to as phytotoxicity, and generally decreases drastically once the ash-bound salts are leached away by rainfall. The soluble salt content of an ash or an ash-treated soil is measured by an assessment of the electrical conductance (EC) of a water extract. Under strongly acidic conditions (< pH 5.0), ash bound heavy metals such as Al, Mn, Zn and Cu can also come into solution and become phytotoxic (Daniels, 2002).

FA particles are small enough to escape emission control devices and easily get suspended in the air. Repeated exposure to FA can cause irritation in eyes, skin, nose, throat and respiratory tract and result in As poisoning (Davison *et al.*, 1974; Natusch and Wallace, 1974; Carlson and Adriano, 1993; Belkin *et al.*, 1999; Finkelman *et al.*, 2000).

Fine ash particles formed during coal combustion in power stations, if not collected in the air pollution control devices are emitted into the atmosphere. The fine ash particles can remain airborne for long periods and can result in deleterious health effects when inhaled and deposited in the lungs (Buhre *et al*., 2005).

Harrison and Jianxin (2000) conducted epidemiological studies on FA particulate matter exposure and consistently demonstrated adverse effects on human health, the mechanism of effect was unclear. Depending on their toxicity, chemical properties and concentration in the air, FA particles may pose an inhalation hazard to exposed workers. When FA particles are inhaled and deposited in the lung they can impose health risks by leaching genotoxic compounds, and through the alteration of immunological mechanisms. Studies have indicated that exposure to high concentrations of fine particulate matter may not be the sole contributor to these adverse effects, but that particle toxicology could also play an important role (Harrison and Jianxin, 2000). The emissions of fine ash particles and trace (toxic) elements from coal combustion are closely associated because of the relative enrichment in trace elements of these fine particles (Lighty *et al.*, 2000). Although the fine particles are enriched in trace elements, their composition is not determined by these elements. Coal composition is shown to be an important parameter affecting the amount and composition of the submicron ash particles (Buhre *et al.*, 2005).

Toxic heavy metals from FA are likely to be leached under acidic conditions. These metals can be easily taken up by humans through drinking water supplies, causing severe health problems:

- Lead - brain, kidney, and nervous system damage
- Cadmium - high blood pressure, liver damage, cancer
- Mercury - deterioration of the nervous system
- Arsenic – carcinogenic

Arsenic is classified as Class A human Carcinogen (US EPA), and is at the top of the most Hazardous substances list (ATSDR, 1997). Viriyavejakul and Watanasak (2003) evaluated carcinogenic risks of As present in FA and observed that As levels are within the acceptable limits. They also related the potential human health risk with the distance from the contaminated site and concluded health risk decreased with the distance away from the site.

In vitro studies show that coal FA - independent of type of coal combustion, origin or precipitation – exerts cytotoxicity in a number of conventional tests using either animal lung cells, human red blood cells or cell lines such as hamster ovary cells (Borm, 1997). Dogra *et al.* (1995) demonstrated that FA burden of lungs results in an impairment of the local immune response of the lungs without an associated effect on the systemic immunity. They have shown that Phagocytosis and adherence of Alveolar macrophages, as well as the appearance of antibody forming cells in lymph nodes were moderately but significantly affected by *in vivo* exposure to both FA and silica (Dogra *et al.,* 1995).

In general, FA is less toxic than crystalline silica (when used as positive control) but significantly more toxic than negative controls (TiO_2, latex beads, methacrylate-polymers). McDonald (2001) observed strong association between silicosis and lung cancer in silica-exposed cohorts, demanding a careful evaluation of the health effects of FA containing considerable amount of silica.

2.6 Conclusions

The abundance of research in utilising CCPs for construction, agricultural and environmental applications has increased the usage of these products among a range of industries including agriculture. Most governments in developed and developing countries encourage farmers to utilise these resources and some agencies also provide them free of cost to farmers. With increasing interests in agriculture, the CCPs as a liming agent, nutrient source, and immobiliser of some nutrients and heavy metals are the most explored research areas. However, immobilisation of applied P has been an area to be investigated, given the high pH and presence of P-sorptive elements such as Ca, Al and Fe in the CCPs. Hence, this doctoral study will probe the following aspects of CCPs:

- The effect of CCPs on P adsorption in soils and optimal application rates of CCPs for P adsorption.

- The effect of CCPs on P transformation in soils, applied with organic and inorganic P sources and the mechanisms of P transformation based on the P sources.
- The effect of CCPs on P leaching in soils under organic and inorganic P treatments.
- The effect of CCPs on the bioavailability of P to plants under glass house and field conditions.

Chapter 3

EFFECT OF COAL COMBUSTION PRODUCTS ON PHOSPHATE ADSORPTION

3.1 Introduction

Coal combustion products (CCPs) are generated in large quantities as a result of coal-fired power generation worldwide and dumped in and/or around the power stations. The volume being generated is so enormous that the ash ponds and dump sites, which accumulate these CCPs, are fast expanding. Coal still remains to be the less expensive fuel and available in abundance atleast for the next 50 years. International Energy Agency - IEA (2010) reports that coal fuels 41 % of global electricity and has also predicted to increase up to 44 % by 2030. This means more CCPs will be produced in the impending years. Australia, being the largest coal exporter, uses coal for 77 % of its electricity generation (IEA, 2010). In Australia, the 30 coal fired power stations generate more than 12 Mt of CCPs every year, posing threat to the environment due to incessant dumping and under utilisation of CCPs (ADAA, 2009b). The current rate of CCPs production renders its disposal unviable and may cause detrimental effects on the environment owing to the overall toxic effect of the ash materials.

Over the years, the CCPs are being used extensively in the construction industry, agriculture and towards environmental restoration. Agricultural applications focussed mainly on improving the soil structural attributes (Fulekar and Dave, 1986; Acton and Gregorich, 1995; Sahu, 1999), liming value (Terman *et al.*, 1978; Wang *et al*. 1994; Stout *et al.*, 1996), phosphorus (im)mobilisation capacity (Cheung and Venkitachalam, 2000; Stout *et al.*, 2003; McDowell, 2004 and 2005) of the soil. With the above-mentioned characteristics related to agricultural uses, CCPs can also be used for reclaiming degraded soils, thereby providing an economical way of disposal. This chapter will focus on the effect of CCPs on phosphorus adsorption in soil.

Phosphorus (P) has been the most limiting nutrient in most agricultural soils throughout the world. Australian soils are generally poor in retaining P and also inherently low in P. Loss of P from soils through run off and leaching poses environmental degradation not only to the land resources but also to surface water (eutrophication) and ground water (Pierzynski *et al.*, 2005). Generally, P is transported from soil in particulate form and dissolved form (soluble inorganic P). Although the particulate P loss can be

decreased through management practices such as riparian buffers, the soluble inorganic P loss had been an issue in soils having low P retention capacity (Mc Dowell *et al*. 2004). An understanding of P retention capacity (PRC) of soils is vital for fertiliser management (Hedley and McLaughlin, 2005) and safeguarding water quality (Sharpley *et al.*, 1994). Optimal pH and high concentration of P sorptive components such as calcium (Ca), iron (Fe) and aluminium (Al) in soil solution are good prerequisites for enhancing the retention of P in soils (Stout *et al.*, 1998; McDowell, 2004). Generally, at alkaline pH, Ca forms precipitates with P and in acidic conditions, P adsorbs to hydrated Al and Fe oxides. Traditionally, lime ($CaCO_3$) has been widely used to overcome soil acidity by increasing the soil pH (Anderson *et al.*, 1995; Sumner and Yamadu, 2002). Several studies have investigated that liming can also enhance P adsorption in soils through addition of Ca^+ to the soil solution (Barrow, 1984; Bolan *et al*., 1988; Curtin and Smillie, 1995; Murphy and Stevens, 2010).

Recent studies have shown that some of the CCPs are effective in decreasing soil solution P loss (Stout *et al*., 2000; Callahan *et al*., 2002; McDowell, 2005) because of their high alkalinity and liming value. Some studies have also shown the effectiveness of fly ash (FA) in mitigating particulate P loss through erosion or organic P loss through mineralisation (Stuczynski *et al*., 1998a, 1998b). The mechanisms by which the CCPs minimise P loss mainly constitute their neutralising capacity in acidic soils and precipitation of P with Ca in alkaline soils. Various reasons have been attributed to the beneficial effects of CCPs in reducing the loss of P through leaching and erosion (Reichert and Norton, 1994; Stout *et al*., 2000; Callahan *et al*., 2002; Pathan *et al.*, 2002; McDowell, 2005), which include: (i) increase in soil pH resulting from the addition of alkaline CCPs; (ii) increases in surface area, anion exchange capacity (AEC) and water holding capacity (WHC); (iii) increases in Ca, Fe and Al concentration; and (iv) increase in soil strength through slaking and soil dispersion. These CCPs can be an effective replacement for their natural counterparts if used judiciously. Hence, efforts have been taken globally on the possible usage of CCPs for increasing P retention in soils that are naturally poor in P retention.

Development of strategies to minimise the loss of P from soils requires a detailed understanding of P interactions and factors of immobilisation. There has been no comprehensive study comparing the effect of various CCPs on P adsorption and their influencing chemical characteristics such as pH, PRC and concentration of P-sorptive components such as Fe, Al and Ca. Therefore, the objective of this study is to examine the effect of CCPs on P adsorption in soils.

3.2 Objectives

The overall objective of this study is to compare the effect of various CCPs on P adsorption in soils with varying pH and P retention capacities. The specific objectives include,

- To evaluate the effect of CCPs on the retention of P in soil
- To examine the effect of soil pH on CCPs-induced increase in P retention
- To observe the role of cations such as Fe, Al and Ca on P adsorption in CCPs amended soil.

3.3 Hypothesis

Application of CCPs increases P adsorption in soils which is attributed to increases in soil pH and concentrations of Ca, Fe and Al in the soil solution.

3.4 Experiments

The major experiments conducted to test the hypotheses and the treatments used in these experiments are listed in Table 3.1. The soils used for the entire study were collected from South Australia (4 soils) – Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL) and Wallaro (WAL); Queensland (2 soils) – Birbie island (BIR) and Pittsworth (PIT); and New South Wales (1 soil) – Drake (DRA). The soils selected were varying in pH and P retaining capacity. The CCPs used were fly ash (FA), fluidised bed combustion ash (FBC) and flue gas desulphurisation gypsum (FGD).

Table 3.1 The major experiments and the treatments used in this Chapter.

No.	Title	Treatments
1	Effect of CCPs and their different application rates on P adsorption	One soil (ADL) and three CCPs (FA, FBC and FGD) at 0, 15, 30 and 45 % application rates.
2	Effect of FBC on P adsorption in soils with varying pH.	Three soils (BIR, KUL and KPD) and one CCP (FBC) at 0, 15 and 30 % application rates.
3	The role of pH in sorption of P in FBC amended soils	Seven soils (ADL, KPD, KUL, WAL, BIR, DRA and PIT) and one CCP (FBC) at 0 and 30 % application rates.
4.	The role of P sorptive components like Al, Fe and Ca in P sorption in FBC amended soils	Seven soils (ADL, KPD, KUL, WAL, BIR, DRA and PIT) and one CCP (FBC) at 0 and 30 % application rates.

3.5 Materials and methods

3.5.1 Soils and coal combustion products

All the soils were collected from surface (0–5 cm), air-dried and passed through a 2 mm sieve. The CCPs used for the experiment were FA from Port Augusta Power station, South Australia; FBC from Redbank Power limited, Queensland; and FGD from Illinois, the United States.

3.5.2 Characterisation of soil and CCPs samples

The soil samples were analysed for pH, electrical conductivity (EC), soil texture and total heavy metals. The soil pH and EC were determined by end-over-end equilibration of soil with water at a ratio of 1:5 for an hour and measured the solution with a pH/conductivity meter. The soil texture was established using a micropipette method (Miller and Miller, 1987) and shown in Table 3.2. For the total metal analysis, the soils were digested using aqua-regia (3:1 – HNO_3:HCl) and the concentration of metals in the extract was determined by ICP-MS (McDowell, 2005). The P retention capacity (PRC) of the soils was determined using the Phosphate retention test (Saunders, 1965), where 5 g of soils were shaken with 25 mL P retention solution (as KH_2PO_4) (1000 mg P L^{-1}) for 16 hours at 25°C. The soil-solution mixture was centrifuged to clarify and 1 mL of clear aliquots was mixed with 19 mL nitric-vanadomolybdate acid reagent. After 30 minutes, absorbance was read at 466 nm using an Agilent 8453 UV-visible spectroscopy system (Germany). The percentage P retention was determined using Eq. 3.1.

$$\boldsymbol{P\ retention}\ (\%) = \frac{(Ci - Ce)}{Ci} \times \mathbf{100} \qquad \textbf{(3.1)}$$

where, where C_e is the equilibrium P concentration in the solution (mg L^{-1}), C_i is the initial P concentration in the solution (mg L^{-1})

Table 3.2 Soil textural characteristics

Soil	Sand	Silt	Clay	Soil type
ADL	33.6±1.08	49.3±0.47	17.1±0.18	Loam
BIR	94.1±1.73	2.92±0.06	3.13±0.09	Sand
DRA	39.1±0.65	47.6±1.56	13.1±0.79	Loam
KPD	53.2±0.45	29.2±0.19	15.5±0.11	Sandy loam
KUL	52.1±0.44	26.3±0.17	21.5±0.15	Sandy clay loam
PIT	4.83±0.14	47.8±1.29	47.2±0.64	Silty clay
WAL	75.3±1.37	13.9±0.21	10.7±0.04	Sandy loam

The CCPs were analysed for pH, EC and elemental composition following the above mentioned methods. The $CaCO_3$ equivalence (CCE) was determined using the

method described by Rayment and Higginson (1992). The CCPs (5 g each) and a reference sample (0.5 g $CaCO_3$ powder) were added into a 250 mL extracting bottle and 100 mL of 1 M HCl was added while swirling continuously. The bottles were covered in a manner which allowed release of any CO_2 present and occasionally swirled for 1 hour at 25°C. The bottles were allowed to stand overnight with secured covering and then mechanically shaken for two hours. The suspension was allowed to settle and filtered immediately. The filtrate was taken in a 100 mL Erlenmeyer flask and 25 mL deionised water was added. Two drops of phenolphthalein indicator was added and the coloured solution was titrated with 0.5 M NaOH. The CCE (%) was calculated based on the following equation (Eq. 3.2).

$$\% \ CCE = \frac{M*(a-b)*50}{S} \qquad (3.2)$$

where,

a = mL standard 0.5 M NaOH used for blank
b = mL standard 0.5 M NaOH used for sample
S = weight (mg) of CCPs and $CaCO_3$ powder
M = molarity of standard NaOH (usually 0.5 M)
50 = equivalent weight of $CaCO_3$

The Olsen P (Olsen *et al.*, 1954) was measured for all CCPs and soil samples. The samples (1 g each) were weighed into a 25 mL centrifuge tube and 20 mL extracting solution (0.5 M $NaHCO_3$ at pH 8.5) was added, stoppered and mechanically shaken in an end-over-end shaker for 30 minutes at 25°C. The solution was immediately filtered using Whatman no. 42 (tested P free) and the filtered clear solution (2 mL) was taken in a 10 mL volumetric flask. A drop of *p*-nitrophenol indicator was added and the solution was acidified carefully using 2.5 M H_2SO_4. After lowering the pH, the solution was diluted to 8 mL with deionised water, mixed and 1.6 mL colour reagent (ammonium molybdate-antimonyl tartarate-H_2SO_4-ascorbic acid) was added. Finally, the volume was made up to 10 mL with deionised water and mixed well. After 30 minutes, absorbance was measured at 882 nm in an Agilent 8453 UV-visible spectroscopy system (Germany) and the Olsen P concentrations were calculated by preparing a calibration curve against the standard values used.

3.5.3 Soil preparation and incubation with CCPs

The soils were air dried and sieved to < 2 mm size and incubated with 0, 15 and 30 % (w/w) of CCPs in a plastic bag for 21 days at 80 % of the total water holding capacity (WHC). After 21 days incubation the samples were air dried and stored in an airtight bottle until further analyses.

The pH and electrical conductivity of the incubated samples were monitored at regular intervals (7, 14 and 21 days). All the incubated samples were analysed for Fe and

Al using ammonium oxalate solution for amorphous (Fe_{ox} and Al_{ox}) fractions (McKeague and Day, 1966) and dithionite-citrate solution for crystalline (Fe_{cd} and Al_{cd}) fractions (USDA, 1972). For the Fe_{ox} and Al_{ox}, 1 g of <0.15 mm soil sample was weighed in a 50 mL centrifuge tube and 40 mL of acid ammonium oxalate solution (pH=3.0) was added and stoppered the tube tightly. The tubes were shaken in an end-over-end shaker for 4 hours in the dark. The tubes were then centrifuged at 4000 rpm for 20 minutes and the clear supernatant was transferred to glass containers and stored in dark before analysis. For the Fe_{cd} and Al_{cd}, 1 g of <0.15 mm soil sample was weighed in a 50 mL centrifuge tube and 50 mL of sodium citrate solution was added along with 0.8 g of dithionate. The tubes were stoppered and shaken in an end-over-end shaker for 16 hours. The tubes were then centrifuged at 4000 rpm for 20 minutes and the clear supernatant was transferred to glass containers and stored before analysis. The Ca concentration in the solution was determined by extracting Ca with deionised water (1:2 sample to water ratio) in a 50 mL centrifuge tube (Seoane and LeirÓs, 2001). All the extracts were analysed using ICP-MS.

3.5.4 Sorption experiment

The effect of CCPs on P sorption was studied using batch sorption experiments and fitted to isotherm equations (Eq. 3.4 and 3.5). Two different P sorption experiments were carried out, (1) to study the effects of the three CCPs (FA, FBC and FGD) on P adsorption in ADL soil at four different application rates (0, 15, 30 and 45 % w/w) and (2) to study the effect of FBC (0, 15 and 30 % w/w) induced pH increase on P adsorption in three different soils (Table 3.1).

For the P sorption measurement, 1 g of CCPs amended soil sample was weighed into 50 mL centrifuge tubes and then mixed with 20 mL of water containing graded concentrations of P (0, 5, 10, 20, 50, 150, 500 mg P L^{-1}) as KH_2PO_4 (McDowell, 2004). Then the tubes were equilibrated for 16 hours using a end over end shaker at the room temp (25°C ± 2). The tubes were then centrifuged for 20 minutes (4000 rpm) and 1mL aliquots of the supernatant solution were transferred to 50 mL centrifuge tubes. The phosphate concentrations of the solutions were measured using the phosphomolybdate method (Murphy and Riley, 1962). The amount of P sorbed was calculated from the difference between added and equilibrium concentrations (Eq. 3.3).

$$\boldsymbol{S = (C_i - C_e)V/W} \quad \textbf{(3.3)}$$

where *S* is the adsorbed P amount per unit weight of solid (mg kg^{-1}), C_e is the equilibrium P concentration in the solution (mg L^{-1}), C_i is the initial P concentration in the solution (mg L^{-1}), V is the volume of the solution (L) and W is the weight of the air-dried soil (g).

The sorption data were fitted to the two most common equilibrium isotherms [Langmuir (Eq. 3.4) and Freundlich (Eq. 3.5)].

$$S = X_m bC/(1 + bC) \quad \textbf{(3.4)}$$

$$S = K_f C^n \quad \textbf{(3.5)}$$

where, S is amount of P sorbed (mg kg^{-1}), C is equilibrium P concentration (mg L^{-1}), b is constant related to the binding strength, X_m is the maximum adsorption amount determined by the specific surface area, K_f and n are constants. K_f (L kg^{-1}) is the Freundlich distribution coefficient which describes the equilibrium partitioning of P between solid and liquid phases, and thus can be used as an index of P mobility in the soil, and n is an empirical constant related to the intensity of the adsorption.

3.5.5 Effect of pH on CCPs-induced increase in P retention

To study the effect of initial soil pH on CCPs-induced increase in P retention, seven different soils (Table 3.1) with varying pHs were used. The pH and the location of soils are provided in Table 3.3a. The soils were incubated with 0, 15 and 30 % (w/w) FBC for 21 days and the pH and P retention were determined as mentioned in Section 3.5.2.

3.5.6 Statistical analysis

All statistical analyses were carried out using Microsoft excel 2010 software package. The effect of CCPs on the sorption of P in soils was examined by correlation analysis. General curve fitting software was used to obtain the sorption isotherms for the soils and their components. Sorption isotherm data were fitted to the Freundlich and Langmuir sorption models.

3.6 Results and discussion

3.6.1 Properties of soils and CCPs

The pHs of the soils used ranged from 3.4 to 9.1 with KPD showing neutral pH (7.1) and PRC ranged from about 4.6 % to 23.4 %. The elemental analysis results are listed in Table 3.3. The KPD soil showed the highest total P concentration among the soils and KPD and KUL showed high concentrations of Ca. Total Fe and Al concentrations were high for all the soils except BIR, which also had low Ca concentration and total P was below detectable limits. The Olsen P values for the soils ranged from 3.82 mg kg^{-1} to 9.6 mg kg^{-1}.

Table 3.3 Chemical characteristics of the soils used for sorption experiment

Samples, Soil type and Location	pH	Olsen P (mg kg^{-1})	PRC (%)	Total elemental concentration (mg kg^{-1})			
				P	Ca	Fe	Al
ADL Kurosol SA	5.65 ±0.29	3.82 ±0.09	23.4	34.12 ±3.621	52.02 ±4.163	16364 ±45.013	19474 ±49.12
BIR Podosol Qld	3.42 ±0.24	N.D	4.62	N.D.	169.8 ±6.142	502.64 ±11.543	456.44 ±10.423
DRA Tenosol NSW	5.17 ±0.28	2.43 ±0.06	19.6	26.32 ±3.174	47.82 ±3.921	16019 ±41.233	10418 ±42.196
KPD Calcarosol SA	7.14 ±0.42	9.60 ±0.34	7.43	348.4 ±9.892	5996 ±29.62	18170 ±35.672	25865 ±51.294
KUL Calcarosol SA	9.12 ±0.57	8.32 ±0.31	11.5	74.26 ±1.812	6566 ±33.22	16099 ±75.816	24911 ±49.345
PIT Vertosol QLD	6.46 ±0.39	2.96 ±0.08	21.6	31.24 ±3.296	45.18 ±3.785	16942 ±47.823	19827 ±52.363
WAL Calcarosol SA	7.76 ±0.45	7.71 ±0.27	22.7	396.2 ±9.973	6723 ±36.14	16421 ±71.861	22948 ±38.722

N.D. – not detected (Detection limit – 0.09 mg kg^{-1}); PRC – Phosphorus retention capacity

In the case of CCPs, the pHs were high (>10) for all CCPs and FBC had the highest pH (12.7). The FBC (23.25 %) had highest CCE value, followed by FA (16.75 %). The Olsen P was extremely high for FA (260.4 mg kg^{-1}), whereas FBC and FGD had very low Olsen P values (Table 3.4). Pathan *et al.* (2002) observed 92.5 mg kg^{-1} extractable P concentration from a weathered fly ash in a Western Australia power station.

Table 3.4 Basic characteristics of CCPs used

CCPs	pH	EC (µS cm^{-1})	Olsen P (mg kg^{-1})	CCE (%)
FA	10.2±0.17	1.34±0.08	260.4±8.234	16.75
FBC	12.7±0.12	9.70±0.17	11.52±1.623	23.25
FGD	10.1±0.07	2.33±0.11	2.252±0.936	11.25

The total P concentration was highest for FA (1522 mg kg^{-1}), followed by FGD (623.85 mg kg^{-1}) and FBC (154.35 mg kg^{-1}). Aitken *et al.* (1984) observed 1010 mg kg^{-1} total P concentration in FA collected from Port Augusta Power station, which is close to the observed value of the FA used in this experiment. Contrastingly, FGD had the highest total Ca concentration at 220,800 mg kg^{-1} (Table 3.5), which is attributed to the liming of coal before combustion. Killingley *et al.* (2000) studied FAs from various power stations in Australia and found total P concentrations ranging from 648 to 7360 mg kg^{-1} and total Ca concentration reached up to 27,400 mg kg^{-1}. The high sulphur (S) contents in FBC and

FGD are a result of limestone scrubbing in the coal combustion units (Ritchey *et al.*, 1995) to meet the emission standards set by the local environment authorities globally.

Table 3.5 Elemental analysis of CCPs.

CCPs	Total elemental concentration (mg kg^{-1})				
	P	Ca	Fe	Al	S
FA	1522 ±18.38	18035.1 ±51.6232	121300 ±185.971	25170 ±50.217	N.D.
FBC	154.3 ±3.751	49675.2 ±76.3761	157600 ±173.952	34015 ±57.285	5905.53 ±32.8831
FGD	623.8 ±12.38	220800 ±196.581	2530.23 ±23.3334	1164.1 ±14.142	156250 ±172.536

N.D. – not detected (Detection limit – 0.01 mg kg^{-1})

3.6.2 Sorption experiment

The effect of CCPs on P adsorption was measured using batch sorption isotherms. Overall, the addition of CCPs increased the sorption of P as measured by the K_f value and the sorption of P increased with increasing levels of amendments (Figure 3.1). Initially, the ADL soil was used to study the effects of the three CCPs (FA, FBC and FGD) at varying application rates. The results showed that FBC was the most effective amendment in sorbing P followed by FA. For both FA and FBC additions, the P sorption increased with increasing application rates. The ADL soil amended with FGD showed the least response, although there was over 50 % increase in P sorption at 15 % application rate (Figure 3.1).

3.6.2.1 The sorption of P in ADL soil at different application rates of CCPs

The K_f values for the CCPs amended soils are higher compared to the control soil (Table 3.6). The FBC amended soils have the highest sorption of P, followed by FA and FGD (Figures 3.2 a, b and c). This can be attributed to pH and CCE values (Table 3.3). The P sorption was highest at the maximum application rates of the CCPs, except for FGD (Figure 3.1 and 3.3 c), which may be attributed to a decrease in pH.

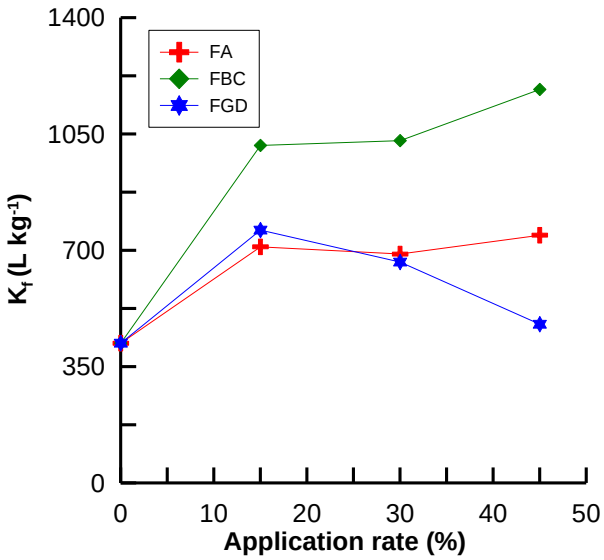


Figure 3.1 The effect of CCPs on P sorption as measured by K_f value in Adelaide hills (ADL) soil at four different application rates (0, 15, 30 and 45 % w/w).

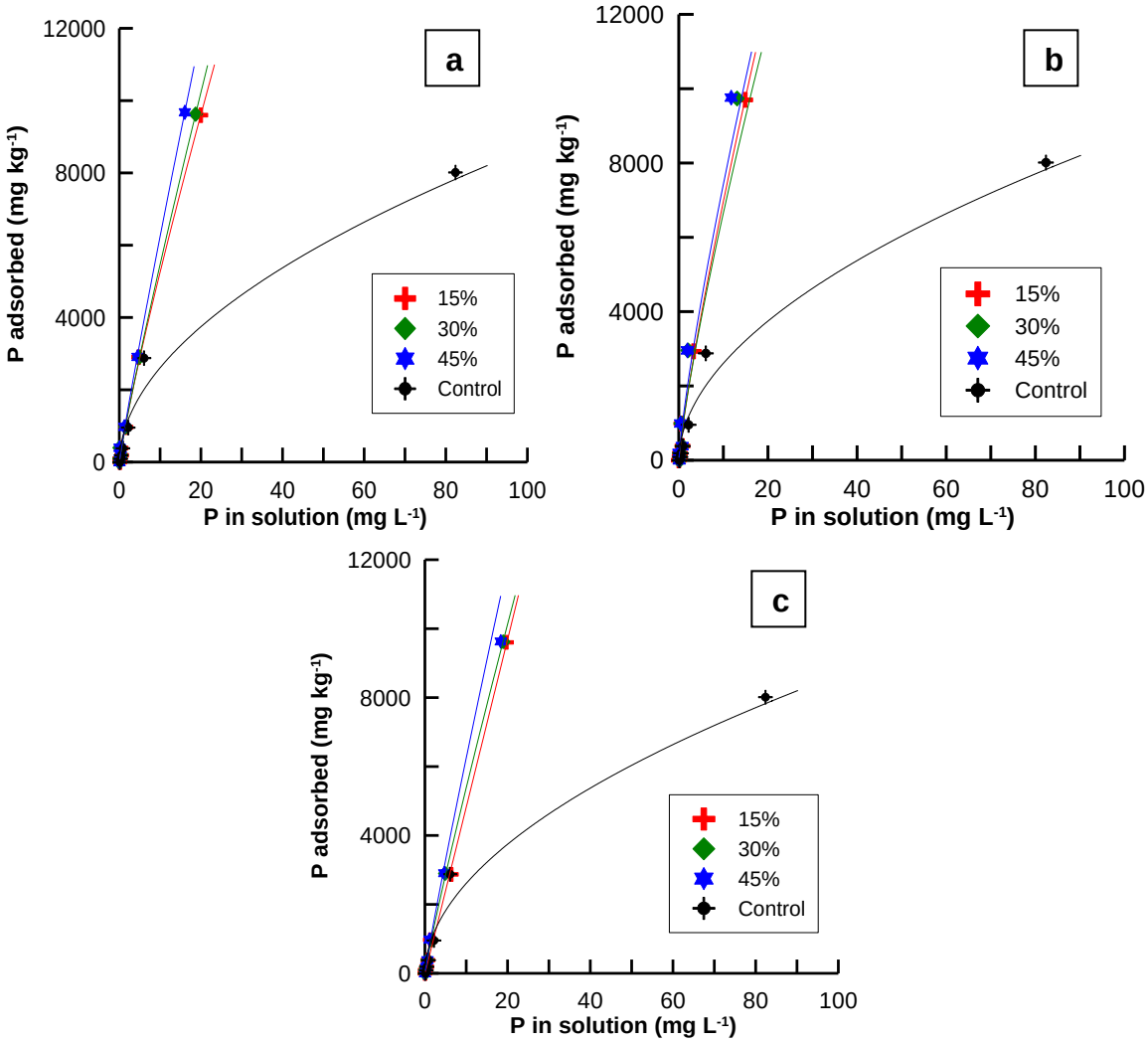


Figure 3.2 Sorption of P in Adelaide hills (ADL) soil amended with a. FA; b. FBC and c. FGD at four different application rates (0, 15, 30 and 45 % w/w).

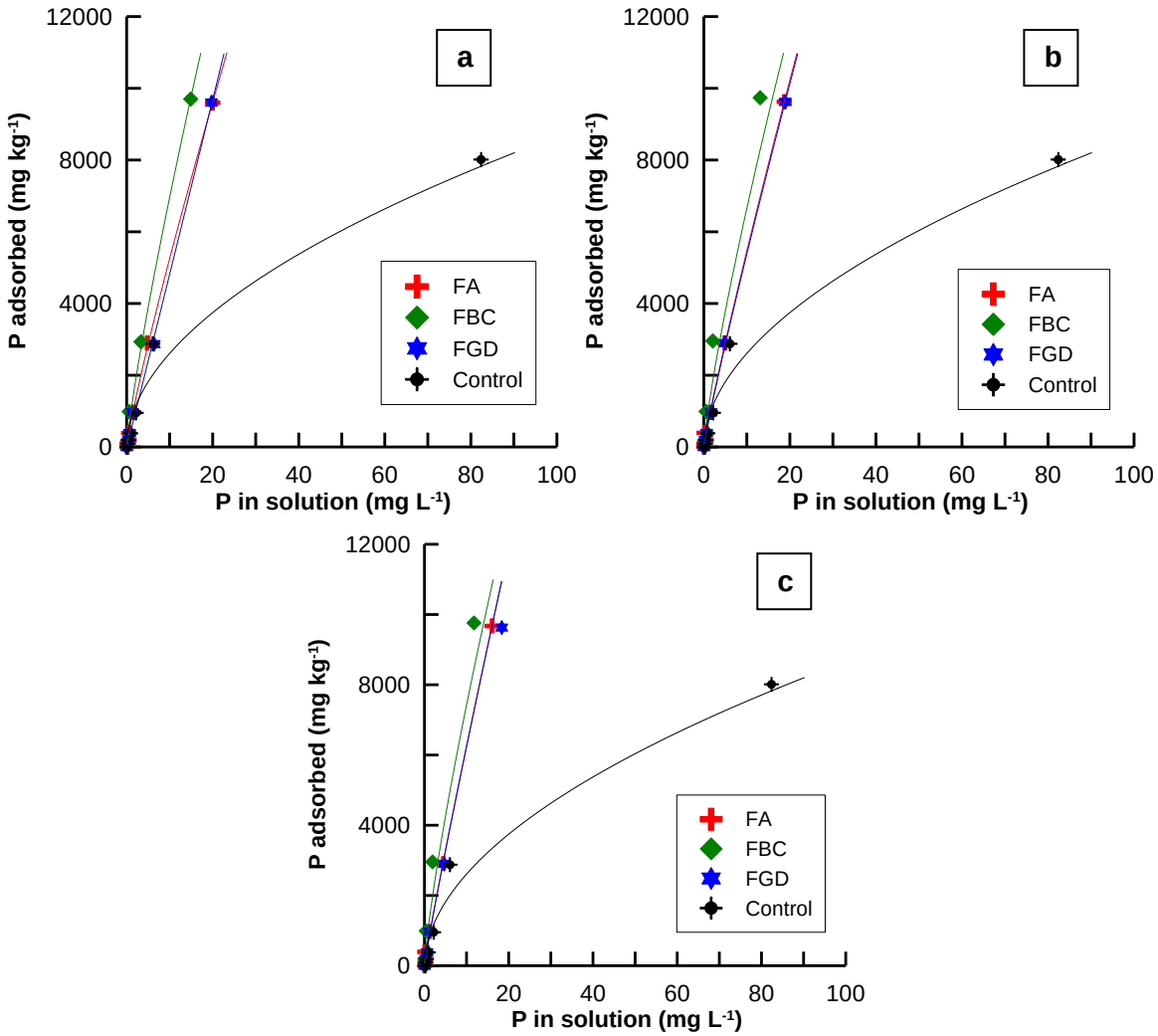


Figure 3.3 Sorption of P in Adelaide hills (ADL) soil at a. 15 %; b. 30 % and c. 45 % (w/w) application rates of three different CCPs (FA, FBC and FGD).

3.6.2.2 Sorption isotherms

The sorption isotherms are explained using the three soils (BIR, KPD and KUL) with variable pHs, amended with 0, 15 and 30 % of FBC (Figure 3.4 a, b and c). The reason for using soils with variable pHs is because the difference in initial pHs of the soil showed distinct changes in P sorption on the application of CCPs to the soil (Table 3.6), which will be discussed in detail in Section 3.6.3. The results indicated that the addition of FBC affected P sorption in all the three soils. The difference in K_f values between the soils at various application rates of CCPs was more pronounced in BIR soil, followed by KPD and KUL which can be attributed to the initial pH of the soils and the change in pH after the application of FBC (Table 3.6). The sorption isotherms fitted better to the Freundlich equation than to the Langmuir equation, based on the R^2 values (Zhou and Li, 2001) which ranged from 0.991 to 0.999 for Freundlich equation and 0.979 to 0.991 for Langmuir equation (Table 3.6).

Table 3.6 Freundlich and Langmuir equations describing the adsorption of P in variable pH soils added with increasing application rates of FBC.

Soil samples	Application rates	Freundlich equation			Langmuir equation		
		K_f	n	R^2	X_m	b	R^2
BIR **pH – 3.4 ΔpH – 3.04**	**0 % FBC**	649.07	0.737	0.991	5913.12	0.133	0.979
	15 % FBC	935.65	0.625	0.999	6104.71	0.123	0.983
	30 % FBC	1476.7	0.507	0.991	7863.21	0.164	0.981
KPD **pH – 7.2 ΔpH – 1.7**	**0 % FBC**	881.34	0.627	0.998	2606.32	0.166	0.987
	15 % FBC	1175.3	0.552	0.992	2986.41	0.172	0.984
	30 % FBC	1381.6	0.514	0.992	3100.50	0.179	0.991
KUL **pH – 9.1 ΔpH – 0.43**	**0 % FBC**	777.67	0.686	0.998	3128.48	0.128	0.985
	15 % FBC	927.16	0.675	0.998	3463.82	0.156	0.981
	30 % FBC	1092.1	0.644	0.995	3891.16	0.161	0.986

pH – initial soil pH; **ΔpH** – difference between initial soil pH and pH of amended soil

Several studies reported that Freundlich equation is effective in describing P sorption for soils (Barrow 1978; Barrow 2000; Cheung and Venkitachalam, 2000). It is an empirical equation and corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases. Rushton *et al.* (2005) stated that advantage of Freundlich isotherm is that it assumes unlimited sorption sites which correlated better with a heterogeneous soil medium having different chemical/physical properties. Cheung and Venkitachalam (2000) argued that although K_f and X_m (Langmuir sorption maximum) showed good correlation, they do not reflect same characteristics because X_m represents the saturation level of sorbed P at high solution concentrations.

Higher K_f values indicate higher retention of P in soils (Barrow, 2000). Generally, higher the sorption intensity parameter (n), a relatively large change in sorbed P can be observed when the solution concentration deviates from unity and hence ‘n’ measures the extent of impact on P sorption when a solution concentration changes from unity (Cheung and Venkitachalam, 2000). The Freundlich distribution coefficient (K_f) is positively related to P sorption capacity of soils. The ‘n’ values for P adsorption decreased with increasing CCP application rates, but the differences were less than that of the K_f values (Table 3.6).

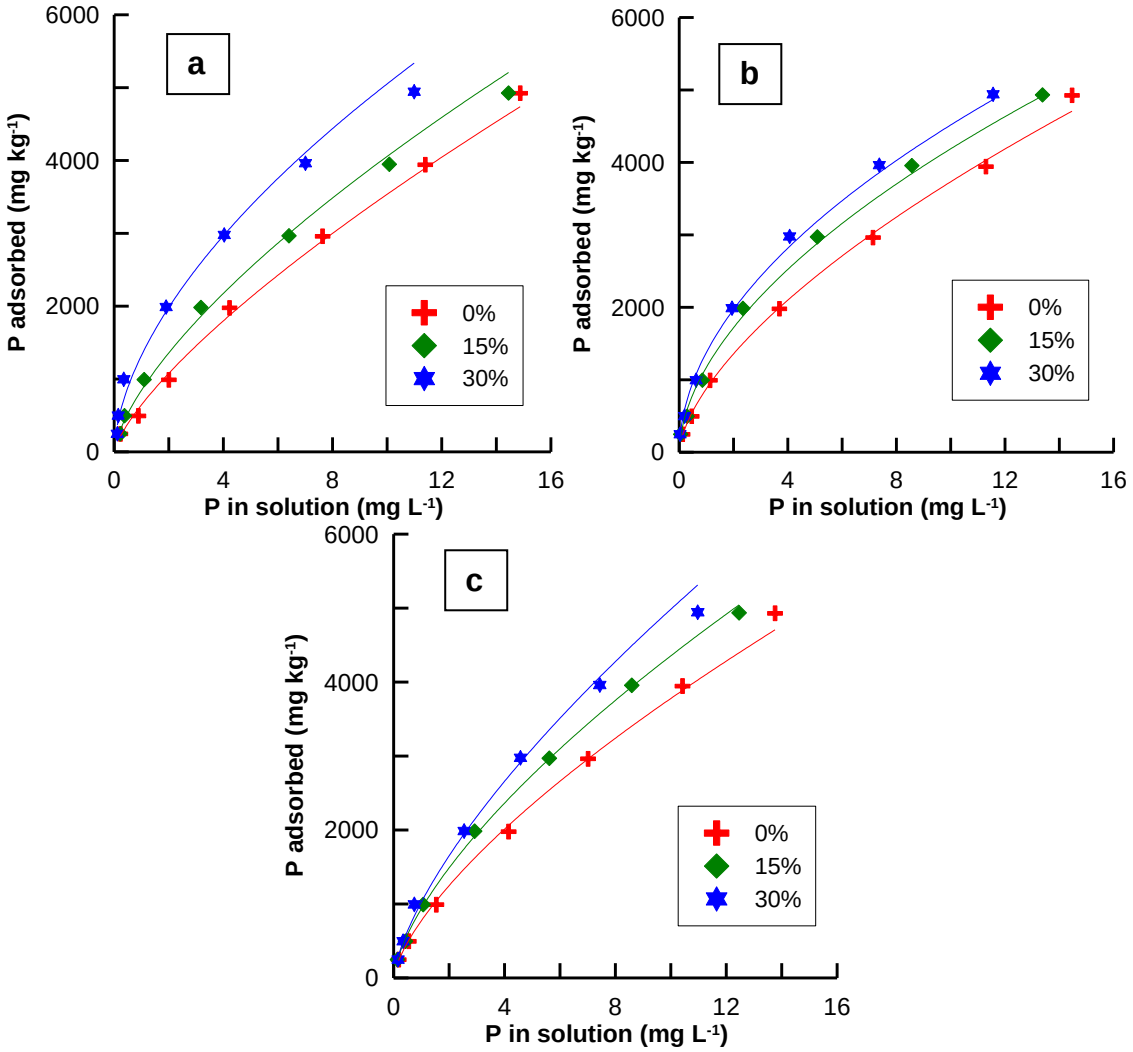


Figure 3.4 Effect of FBC (0, 15 and 30 % w/w) on P sorption in a. Birbie Islands (BIR), b. Kapunda (KPD) and c. Kulpara (KUL) soils.

3.6.3 The role of pH in the sorption of P

The increase in P sorption (as measure by K_f value) with the addition of CCPs to ADL soil is attributed to an increase in soil pH (Figure 3.5). The pH increased with the increasing CCPs application rate and the greatest pH increases were seen in FBC and FA. The decline in P sorption after an initial increase at 15 % application rate of FGD is attributed to the decrease in soil pH. Barrow (1969) argued that while the adsorption of anions such as sulphate and molybdate has often been shown to decrease with an increase in pH, the opposite effect has been noticed in the case of adsorption of P. Hence pH is an important factor in anion adsorption, especially sorption of P. For this reason, seven different soils with varying pHs were chosen to study the role of pH as affected by FBC application in the retention of P. The soils were measured for the pH changes and PRC. The changes in PRC were expressed as delta P retention and were determined by calculating the difference between the P retention values of amended soils and control soils.

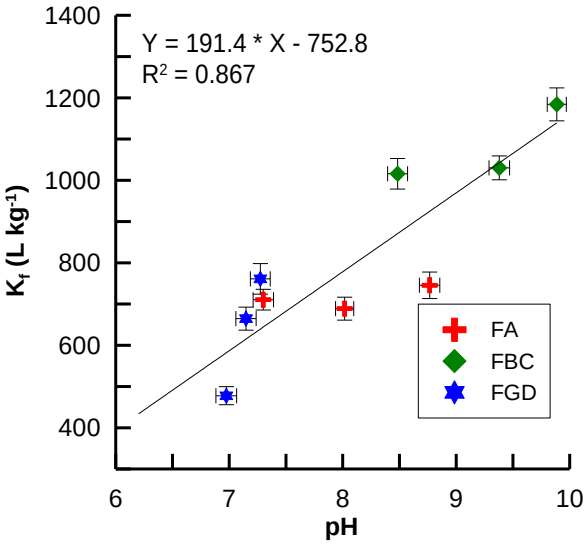


Figure 3.5 The relationship between pH of Adelaide hills (ADL) soil and increase in P sorption as affected by CCPs at three application rates (0, 15 and 30 % w/w). Error bars represent the standard deviation between replicates.

A comparison between delta P retention and initial soil pH showed the decrease in delta P with an increase in initial soil pH (Fig 3.6). This indicates that the effect of CCPs in increasing P sorption was less pronounced in soils with high initial pH. The delta pH values also influenced changes in the P adsorption (Table 3.5). The acidic soil (BIR) with a delta pH of 3.04 showed higher increase in P sorption at the highest application rate of FBC compared to an alkaline soil (KUL) with a delta pH of 0.43. Curtin *et al.* (1992) saturated a soil with Ca and observed that an increase in pH increased the retention of P, which they attributed to the precipitation of Ca phosphates. Chen *et al.* (2007) compared the P sorption capacities of 15 different FA (with different pHs) and concluded that highest P sorption occurred at alkaline pH.

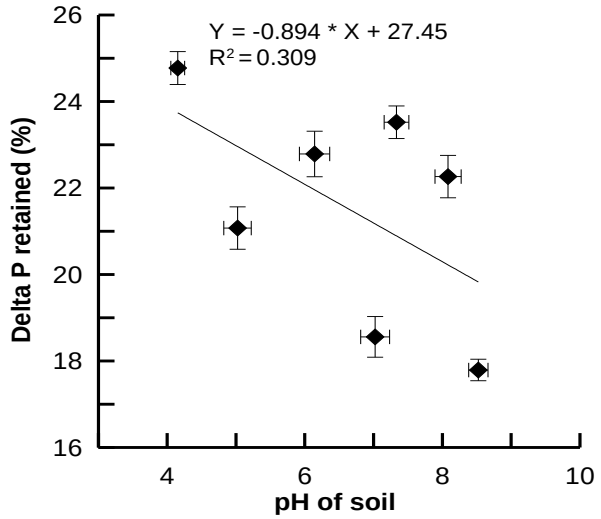


Figure 3.6 Relationship between initial soil pH and increase in P retention (delta P retention) resulting from FBC application at 15 % (w/w) rate to seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)]. Error bars represent the standard deviation between replicates.

3.6.4 The role of P sorptive components like Al, Fe and Ca in sorption of P

The influence of Al, Fe and Ca in soil solution on P sorption was evaluated by relating various fractions of these cations with % P retention at varying rates of FBC application to seven different soils. Deleted: Both crystalline and amorphous fractions of Al and Fe showed poor correlation (Fig 3.7 a, b, c and d), in which the greatest relation with % P retention was for Al_{ox} (R^2 = 0.4435). When the values of both Al and Fe were combined, the correlation between $(Al+Fe)_{ox}$ and % P retention slightly increased (R^2 = 0.4914) and was the highest among the extractable Fe and Al values (Fig 3.8 a and b). Sakadevan and Bavor (1998) related P sorption with Al_{ox}, Fe_{ox} and also combination of both Al_{ox} and Fe_{ox} for soils treated with blast furnace slag and observed that the $(Al+Fe)_{ox}$ played significant role in P sorption. A significant relation between the extractable Fe fractions and % P retention was not found. Also, the regression between $(Al+Fe)_{cd}$ and % P retention was also very low. Stout *et al.* (1998) found that the increase in the concentration of aluminium (Al), iron (Fe) and Ca in soil solution resulting from the application of CCPs decreased P loss in soils, which was due to the formation of insoluble Al-P, Fe-P and Ca-P (McDowell, 2005).

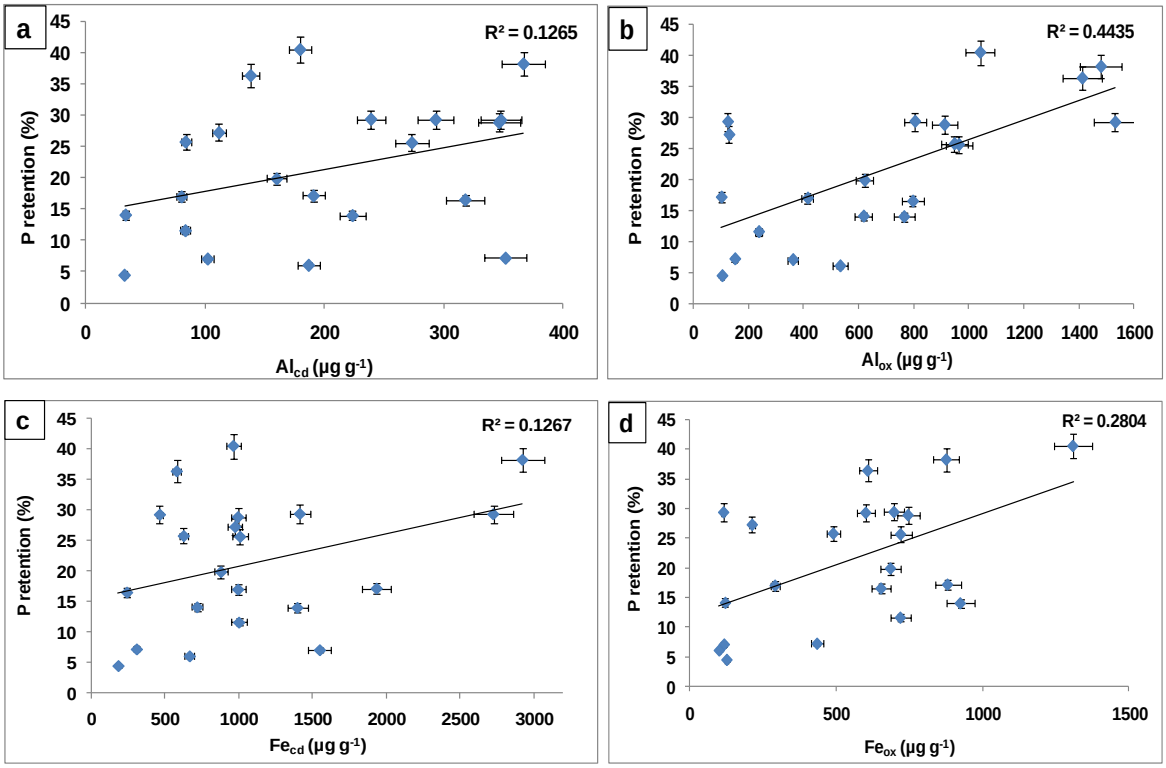


Figure 3.7 Relationship between % P retention and a. Al_{cd}, b Al_{ox}, c. Fe_{cd} and d. Fe_{ox} for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates.

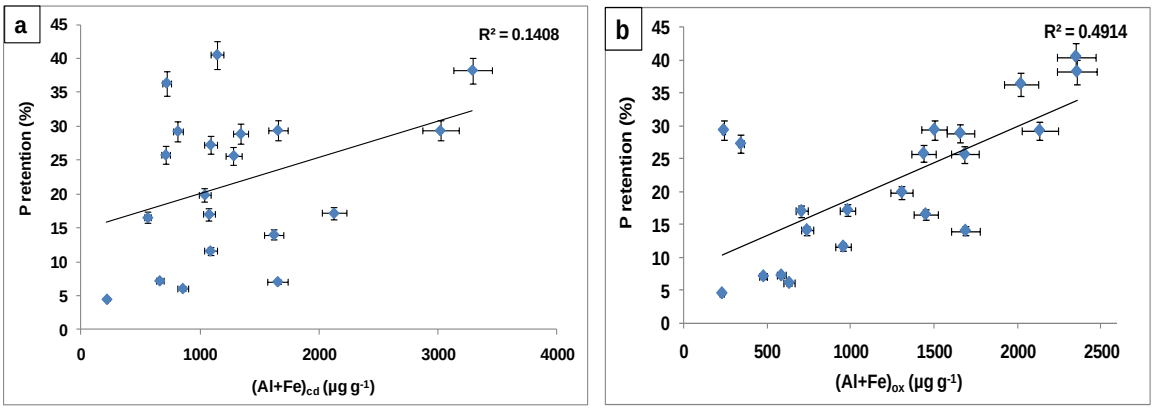


Figure 3.8 Relationship between % P retention and a. (Al + Fe)$_{cd}$ and b. (Al = Fe)$_{ox}$ for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates.

However, among the three cations, Ca in solution was best associated (R^2 = 0.5137) with % P retention (Figure 3.9). This suggests that Ca in solution may be the influencing factor for P retention, which can also be justified by the increase in pH on the addition of CCPs (McDowell, 2005). Chen *et al.* (2007) analysed 15 different FA for P sorption maxima and found that P immobilisation was governed by Ca (especially CaO and $CaSO_4$) and Fe (especially Fe_{cd}) ingredients. They also proposed that P immobilisation by FA may be due to the formation of Ca-P precipitate and sorption through ligand exchange with Fe related compounds.

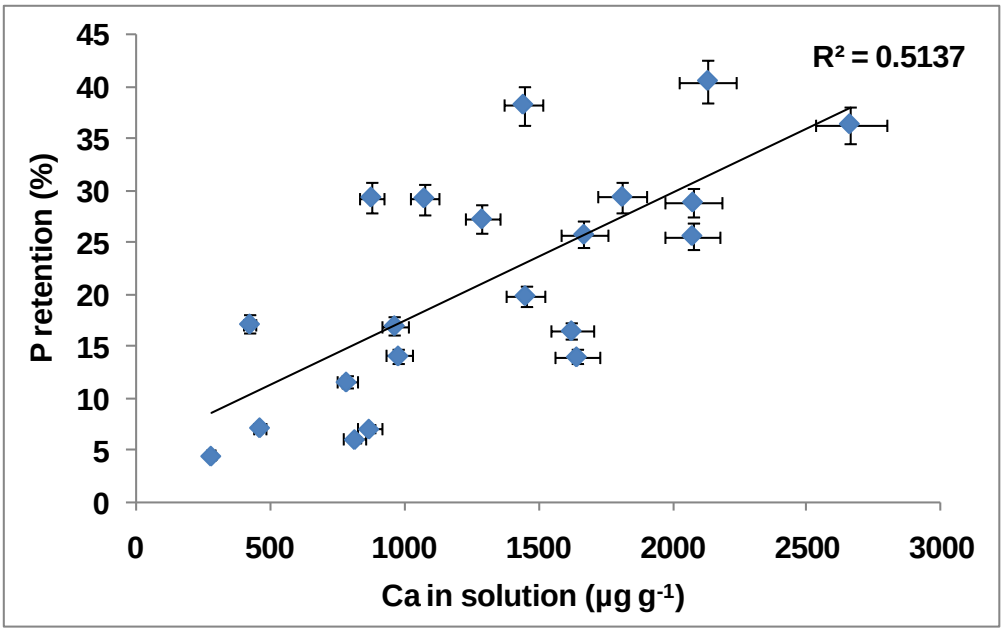


Figure 3.9 Relationship between % P retention and Ca in solution. for seven soils [Adelaide hills (ADL), Kapunda (KPD), Kulpara (KUL), Wallaro (WAL), Birbie Island (BIR), Pittsworth (PIT) and Drake (DRA)] at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates.

3.7 Conclusions

- The CCPs proved to increase the sorption of P in soils when applied at optimal rates.
- The sorption results indicate that CCPs are effective in enhancing the P retention capacity of soils by decreasing the soil solution P.
- Among the CCPs, FBC was very effective in increasing P sorption, followed by FA and FGD.
- At the highest application rate, FBC showed maximum sorption amongst the three CCPs.
- The pH played a major role in P sorption in all the soil samples. The addition of CCPs showed positive results in acidic and neutral soils in terms of increase in P adsorption whereas, alkaline soils showed least response on the effect of CCPs.
- The Ca concentration in the soil solution as supplied by the CCPs has also been a major factor for P adsorption compared to Al and Fe in the solution.

Chapter 4

EFFECT OF COAL COMBUSTION PRODUCTS ON THE TRANSFORMATION OF PHOSPHORUS FROM VARIOUS SOURCES

4.1 Introduction

Generally, phosphorus (P) exists in organic and inorganic forms in soil, which are important sources of P for plant growth and microbial uptake. The organic P (Po) forms mostly exist in humus and other organic materials, associated with carbon and carbon related compounds in the soil (Condron *et al.*, 2005). The inorganic (Pi) forms are the plant available forms and principally labile, unless they are associated to metals with limited solubility. The chemically reactive nature of P plays a significant role in its interaction with cations (mainly iron [Fe], aluminium [Al] and calcium [Ca]) and its distribution characteristics in soil. The reactivity and mobility of P is highly influenced by pH (Chapter 3) of the soil and the maximum P availability occurs at soil pH levels from 6.5 to 7.5. Lindsay (1979), through the thermodynamic models of mineral solubility, predicted that dissolved P would be controlled at equilibrium by Fe- and Al-phosphates in acidic soils and by Ca-phosphates in neutral and alkaline soils. Hence, the metal phosphates such as strengite ($FePO_4$) and variscite ($AlPO_4$) are stable at lower pH range (<6.5) and the chemistry of Fe and Al are increasingly influenced by the formation of oxides and hydroxides at higher pHs (>6.5). Under these conditions, P bonding slowly shifts towards calcium and precipitation occurs at pH above 8.5 forming apatites and hydroxyapatites (Lindsay *et al.*, 1989; Gray and Schwab, 1993; Grubb *et al.*, 2000), which is undesirable in an agronomic point of view (Rajan *et al.*, 1996; McDowell, 2004). These phosphates are the most stable forms of Pi and are neither soluble nor bioavailable.

The foremost objective in the management of P pertaining to natural and agricultural soils is to reduce the loss of P from soil through immobilisation using appropriate soil amendments, which contains P sorptive components such as Fe, Al and Ca. Traditionally, lime and gypsum (Murphy and Stevens, 2010) are being used for P immobilisation in soils, but owing to their expensiveness and depletion risks, other options such as the use of some industrial wastes and by products are being explored. However, liming can also increase available P because of the P sparing effect (Bolan *et al.*, 2003a). Several

researchers have studied the effects of coal combustion products (CCPs) on P immobilisation in soil (Gray and Schwab, 1993; Stout *et al*., 1999; Dou *et al.*, 2003; McDowell, 2004). Most researches were focussed towards the agronomic and environmental benefits of the CCPs such as increasing the soil pH and reducing P in the surface run off and subsurface drainage, sustaining bioavailability of P (i.e. Olsen P concentrations), and deducing optimal application rates (Stout *et al*., 1988; Norton *et al.*, 1993; Stout and Priddy, 1996; McDowell, 2004). Stout *et al.* (1999) observed that fluidised bed combustion ash (FBC) and flue gas desulphurisation (FGD) gypsum reduced water soluble P up to 60 % and 50 % respectively, when applied at the rate of 3 tonnes ha^{-1}. In agricultural soils, freshly applied P will get adsorbed onto the surface of soil minerals and then slowly diffused to the strongly bound forms (Barrow, 1979). The application of P in the form of natural inorganic (e.g. phosphate rock) or organic (e.g. manure) sources also influence the extent of P losses. There are limited studies on the direct effects of CCPs on manure applied P in soils that showed potential effects on P immobilisation and utilisation (Dao, 1999; Elrashidi *et al*., 1999; Dou *et al.*, 2003). Lai *et al.* (1999) amended a sandy soil with fly ash (FA)-sludge mixture and observed increased phosphatase activity and higher P mineralisation rates with increasing FA application rates. Although P in organic wastes is present in both inorganic and organic forms that display a complex continuum of solubilities, several researchers have suggested that the water-extractable inorganic P provides a simple indicator of the potential release of dissolved P into agricultural runoff (Dou *et al.*, 2000; Sharpley and Moyer, 2000; Vadas *et al.*, 2005). This relationship between the measured water extractable P and the runoff P is probably the strongest where the wastes are broadcast at the land surface (Kleinman and Sharpley, 2003).

The CCPs have the potential to transform P in soils through (im)mobilisation (either immobilisation or mobilisation) of P compounds. Distribution of P forms and speciation of P in soils is generally studied using chemical fractionation (sequential extraction using water, alkaline and acidic reagents) methods, supported by advanced microscopic and X-ray enabled spectroscopic studies (Beauchemin *et al.*, 2003; Pratt *et al.*, 2007; Seiter *et al.*, 2008; Eveborn *et al.*, 2009). Seiter *et al.* (2008) also indicated that the traditional sequential extraction procedures may not identify all P species in some animal manures. Sharpley and Moyer (2000) have indicated that in manures, P is present in both organic and inorganic fractions, mostly dominated by the inorganic form (84 % of total P). Hence, the P transformation in various P applied soils can be understood by sequentially extracting the inorganic P fractions and then substantiated with the physical characterisation methods like scanning electron microscopy (SEM), and advanced spectroscopy techniques such as electron dispersive spectroscopy (EDS) and X ray diffraction (XRD). One best example for the need of physical methods is the observation of Pierzynski *et al.* (1990) on P-rich particles in heavily fertilised soils using energy

dispersive X-ray analyses, demonstrating that P was largely associated with Al in amorphous solid phases even for neutral to slightly alkaline soil samples. This underlines the importance of direct identification of soil P species, where soil chemical properties can give the trends of P transformation. Pratt *et al.* (2007) argued that elemental analyses alone may not provide accurate information on the occurrence of P associated oxides/oxyhydroxides.

With the proven ability of CCPs in P sorption as evidenced from Chapter 3, the role of the CCPs in the transformation of applied P (inorganic and organic P) will be explored in this Chapter. This study involving three soils treated with three different P sources (potassium dihydrogen phosphate-PP, poultry manure-PM and phosphate rock-PR) and incubated with three different CCPs (FA, FBC and FGD) is expected to demonstrate dynamic P transformation characteristics. The major factors in the (im)mobilisation of P will be pH and the solution concentration of P sorptive components such as Al, Fe and Ca. The effect of CCPs on P transformation will be examined using chemical fractionation analyses and the results will be corroborated with the help of X-ray, spectroscopic and electron microscopic studies.

4.2 Objectives

The overall objective of this research is to understand the effect of CCPs on the transformation of P in soils treated with various P sources. The specific objectives are,

- To examine the effect of CCPs on the mobilisation of phosphorus in soil applied with various P sources.
- To categorise and quantify the various forms of P in CCPs incubated soils.
- To validate the chemical analyses results using SEM-EDS and XRD analyses by studying the surface chemistry of P transformations in CCPs incubated soils.

4.3 Hypothesis

The effect of CCPs on the (im)mobilisation of P depends on the P source and soil type and the consequent pH of the soil after CCP treatment (Chapter 3). The transformation of P into various forms may vary between the P sources and is postulated as follows,

- In the case of soluble inorganic P source, namely potassium dihydrogen phosphate, CCPs addition enhances immobilisation, which is attributed to a pH-induced increase in P adsorption.

- In the case of insoluble inorganic P sources such a phosphate rock (PR), CCPs addition decreases dissolution which is attributed to increases in soil pH (less acid to dissolve) and calcium concentration in solution (common ion effect).
- In the case of organic P sources such as poultry manure (PM), CCPs enhances the mineralisation of P which is attributed to an increase in pH and enzyme activity.

4.4 Experiments

The major experiments conducted to test the hypotheses and the treatments used in these experiments are listed in Table 4.1.

Table 4.1 The major experiments and the treatments used in this Chapter.

No.	Title	Treatments
1	Fractionation experiment	Three soils (Adelaide hills, Kapunda and Virginia), three P sources (PP, PM and PR) and three CCPs (FA, FBC, FGD)
2	Enzymatic analysis	Three soils (Adelaide hills, Kapunda and Virginia), one P source (PM) and three CCPs (FA, FBC, FGD)
3	Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS)	One soil (Adelaide hills), two P sources (PP and PM) and two CCPs (FA and FGD)
4.	X-ray diffraction (XRD) study	One soil (Adelaide hills), two P sources (PP and PM) and two CCPs (FA and FGD)

4.5 Materials and methods

4.5.1 Soils and coal combustion products

The soils for the fractionation experiment were collected from three different locations around Adelaide, Australia – Adelaide hills (ADL), Kapunda (KPD) and Virginia (VIR). All the soils were collected from surface (0 – 5 cm depth), air-dried and passed through a 2 mm sieve. The textural characteristics of the soils were already discussed in Chapter 3 (Table 3.2). The CCPs used for the experiment were fly ash (FA) from Port Augusta Power station, South Australia; fluidised bed boiler ash (FBC) from Redbank Power limited, Queensland, and flue gas desulphurisation gypsum (FGD) from Illinois, the United States. The P sources used for the experiment were laboratory grade potassium dihydrogen phosphate (PP), commercial poultry manure (PM) and phosphate rock (PR) from Nutri-Tech Solution, Queensland.

4.5.2 Incubation

The soils (500 g each) were initially treated with the three P sources at the rates of 0, 100 and 200 mg P kg^{-1} soil. The soils were incubated in plastic bags for 21 days at 80 % of the total water holding capacity (WHC). Soils incubated without P treatment served as control. After 21 days of incubation, all the P treated soils were incubated with CCPs at the rates of 0, 15 and 30 % (w/w). The CCPs treated samples were incubated separately for 21, 42 and 63 days at 80 % of the total WHC.

4.5.3 Characterisation of soils, CCPs and P samples

The soils, CCPs and P sources were characterised for pH, chemical composition, Olsen P, phosphorus retention capacity (PRC) and calcium carbonate equivalence (CCE) using the methodologies mentioned in Section 3.5.2.

4.5.4 Fractionation experiment

The incubated soil samples were air-dried immediately after the incubation period and analysed for P fractions using the fractionation scheme slightly modified from Condron *et al.* (1990) as followed by McDowell (2005). The incubated samples (1 g each) were also analysed for pH, electrical conductivity (EC) and Ca concentration in solution before the fractionation experiment. For this fractionation procedure, incubated soil samples (1 g each) were extracted sequentially by shaking with deionised water, $NaHCO_3$ (0.5 M), NaOH-I (0.1 M), H_2SO_4 (0.5 M) and ultra-sonication with NaOH-II (0.1 M). The remaining P was extracted by digesting the samples with *aqua regia* (concentrated HNO_3:HCl – 3:1). Details of the sequential extraction along with the fractions removed sequentially are showed in Table 4.2 and Figure 4.1.

Table 4.2 Sequential extraction steps of Condron *et al.* (1990) and the expected P species in the fractions.

Extractant	Shake time	Analysed	Expected P species
Deionised H_2O	2 h	P_i (H_2O-P)	Water soluble P or soil solution P
0.5 M $NaHCO_3$	16 h	P_i ($NaHCO_3$-P)	Loosely sorbed bioavailable P largely associated with Al and Fe.
0.1 M NaOH	16 h	P_i (NaOH-I-P)	Inorganic and organic P associated with Al, Fe and humic substances
0.5 M H_2SO_4	16 h	P_i (H_2SO_4-P)	Strongly bound Ca associated P
0.1 M NaOH	16 h	P_i (NaOH-II-P)	Recalcitrant/occluded inorganic and organic P
Aqua regia	Digest	TP	Residual P

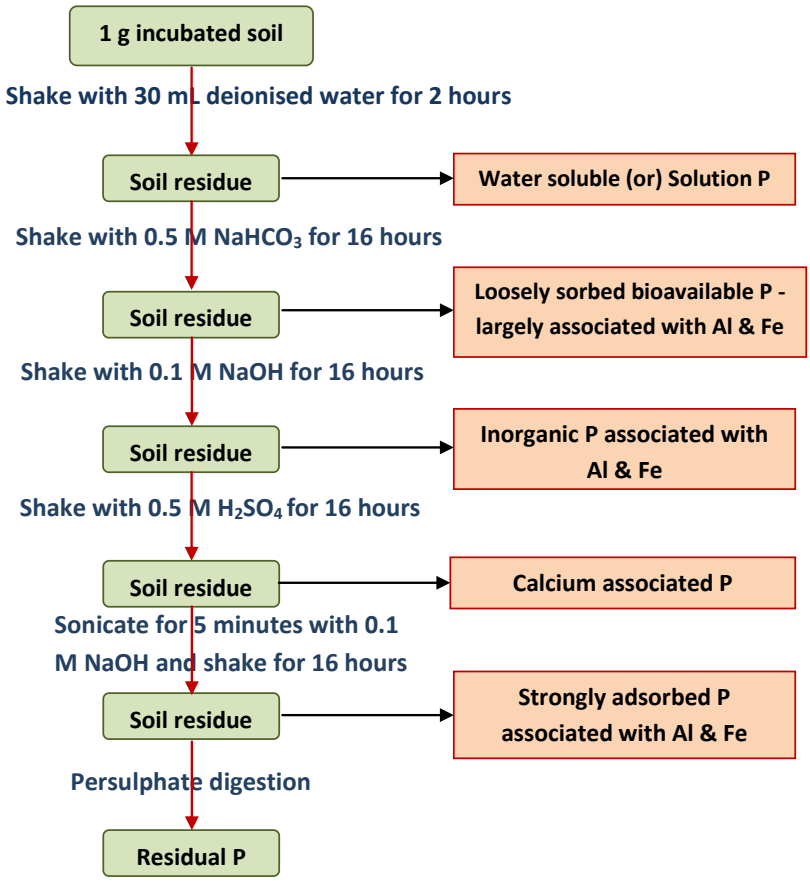
The extracted Pi fractions were analysed for their P concentration using the colorimetric method of Murphy and Riley (1962), using Agilent 8453 UV-visible spectroscopy system

(Germany) at 882 nm and the Total P (TP) was determined by analysing the acid-digested samples using ICP-OES

4.5.4.1 Bioavailable P

The bioavailable P in the fraction scheme can be defined as the P present in non adsorbed forms, which is soluble in water and sodium bicarbonate solution. It is a measure of P with agronomical significance, which is readily taken up by plants. The bioavailable P from the P fractions was calculated by adding the P concentration of H_2O-P and $NaHCO_3$-P fractions.

Figure 4.1 Flow diagram showing sequential extraction of inorganic P



4.5.5 Analysis of phosphatase activity

The phosphatase activity of the soil samples was determined by measuring the release of para-nitrophenol from para-nitrophenyl phosphate (PNP). The CCPs incubated soils were exposed to a modified universal buffer (MUB) at pH 11 for the assay of alkaline phosphatase activity, as described by Tabatabai and Bremner (1969) and 1 mL PNP

(0.025 M) was added to 1 g soil samples, followed by the addition of 0.2 mL toluene. The mixture was incubation at 37 °C for 90 minutes and centrifuged at 4000 rpm for 5 min. The p-nitrophenol formed was determined by spectrophotometer (Agilent 8453 UV-visible spectroscopy (Germany) system) at 440 nm.

4.5.6 Physical characterisation studies on CCPs incubated soil samples

The surface morphology of the incubated soil samples and the distribution of P with the cations (Fe, Al and Ca) were studied by Field emission scanning electron microscopy – FESEM (JSM6700F, JEOL USA Inc.). The elemental distribution was analysed using an energy dispersive spectrometric (EDS) analysis. All the samples were coated with platinum before doing FESEM analysis. The magnification ranged from 1000 to 2000 X with 10 µm resolution for all the samples. The electron beam diameter during EDS acquisition was approximately 3 µm and the acquisition time was 100 seconds. The instrument detects sample X-ray energy values from the EDS spectrum and compares with known characteristic X-ray energy values to determine the presence and concentration of an element in the sample. The mineralogy of the above samples was determined with powder X-ray diffraction (XRD, Shimadzu XRD-6000). The XRD analysis was performed using an aluminium holder and the scanning range was between 10 and 70 degrees.

4.5.7 Statistical analysis

The calculations and standard deviation were carried out using Microsoft excel 2010 software package for the properties of soils, P sources and CCPs. The difference between the treatments and incubation periods were also determined by the standard deviation values of the replicates.

4.6 Results and discussion

4.6.1 Properties of soils, CCPs and P sources used

The properties of the VIR soil and P sources used in this study are given in Tables 4.3 and 4.4. The properties of other soils (ADL and KPD) and CCPs were already mentioned in Chapter 3 (Tables 3.3 to 3.5). The soil pH ranged from acidic (ADL-5.6) to near neutral (KPD-7.1 and VIR-7.3). The phosphate retention capacities (PRC) of the soils were ADL-23.89 %; KPD-5.05 % and VIR-2.73 %. The elemental analysis results for the materials used are listed in Table 4.4. The soil collected from the Virginia agricultural farm,

South Australia (VIR) had the highest Olsen P (88.3 mg kg^{-1}) among the three soils used in this research.

The three CCPs had high pH (>10) values, with FBC measuring the highest pH (12.7). The calcium carbonate equivalence (CCE) value was the highest in FBC (23.25 %), followed by FA (16.75 %) and FGD (11.25 %). The Olsen P was very high for FA (260.44 mg kg^{-1}), whereas FBC and FGD had very low Olsen P values (Table 3.4). The Al and Fe contents are highest in the FBC and FA. The FBC also had a high Ca content (49.68 %) followed by FGD (22.08 %), because of scrubbing coal with lime as a part of clean coal technologies and consequently these products exhibit high Ca and S concentrations (Wang *et al.*, 1994). The S contents for FBC and FGD used in this study were 5.91 % and 15.63 % respectively (Table 3.5).

Table 4.3 Basic characteristics of soils, CCPs and P sources used

Materials	Sources	pH	Olsen P (mg kg^{-1})	PRC (%)
Soil	VIR	7.33±0.41	88.31±4.126	2.73
P sources	PM	5.12±0.23	-	-
	PR	6.81±0.36	-	-

Table 4.4 Selected elemental composition of materials used

Materials	Total elemental concentration (mg kg^{-1})				
	P	Al	Fe	Ca	S
VIR soil	74.2312 ±7.81322	24911 ±49.342	16099 ±75.872	6566.1 ±33.252	-
P sources					
PP	227600 ±199.321	-	-	-	-
PM	147800 ±171.672	43510 ±21.386	24890 ±19.254	50500 ±22.635	45820 ±21.521
PR	108700 ±139.071	74310 ±26.739	59900 ±23.828	85620 ±39.562	141.12 ±1.0234

The inorganic P (KH_2PO_4) source is the most soluble among the three P sources used. The P content in PM is 14.78 % and PR is 10.87 % (Table 4.4). The PR was high in Ca (8.56 %) and relatively rich in Al (7.43 %) and Fe (5.99 %). The water soluble P and the Olsen P are the highest for PP and lowest for PR (Table 4.5).

Table 4.5 Composition of P in the P sources

P compound	Total P (%)	Water soluble P		Olsen P	
		(% w/w)	(% total P)	(% w/w)	(% total P)
PP	22.76	18.7	82.24	21.2	93.49
PM	14.78	2.35	15.89	5.73	38.76
PR	10.87	2.16	19.87	3.71	34.13

4.6.2 Fractionation experiment

The application of CCPs showed major changes in P concentration and distribution of different P fractions. Initially, the highly responsive fractions to CCPs application were $NaHCO_3$–P and NaOH-I-P for FA and FBC application; for FGD application, H_2SO_4–P dominated the P extraction. The increase in P extraction in NaOH-I-P and H_2SO_4–P fractions confirms increased P adsorption (Chapter 3) and is attributed to the increase in soil pH (Table 4.6) and also due to the liming effect of these CCPs (McDowell, 2004). At higher incubation periods, the P from NaOH-I-P fraction slowly transformed to H_2SO_4–P fraction, resulting in strongly bound P. The $NaHCO_3$–P fraction (corresponds to major portion of the bioavailable P) and soil solution P (water-extractable P) in FA applied soils increased with increasing application rates, which is because of the high Olsen P value of the FA material (Table 3.4). NaOH-P-II and residual-P fractions were relatively low in P concentrations. However, these fractions did not show significant changes in the redistribution of P with the addition of CCPs.

Table 4.6 The changes in pH for the incubated samples

Treatments		No CCPs	FA		FBC		FGD	
			15 %	30 %	15 %	30 %	15 %	30 %
No P		6.23	6.76	7.04	7.02	7.86	6.02	5.98
PP	100 mg kg^{-1}	5.97	6.03	6.86	6.82	7.01	5.86	5.82
	200 mg kg^{-1}	5.99	6.04	6.92	7.09	7.46	5.86	5.85
PM	100 mg kg^{-1}	5.92	6.12	6.97	7.11	7.49	5.89	5.97
	200 mg kg^{-1}	5.89	6.11	6.98	7.09	7.43	5.86	5.97
PR	100 mg kg^{-1}	5.91	6.08	6.81	6.76	7.06	5.99	5.94
	200 mg kg^{-1}	5.94	5.97	6.42	6.12	6.97	5.89	5.86

4.6.2.1 Effect of CCPs on native P distribution in three soils

The soils with varying P retaining capacities (ADL - 23.89 %; KPD - 5.05 % and VIR - 2.73 %) exhibited almost similar P distribution patterns, except for ADL which had lower soluble and loosely bound P (NaOH-I-P), which maybe attributed to the differences in pH among the soils (Table 4.6). The CCPs transformed P from loosely bound Fe and Al (NaOH-I-P) to tightly bound Ca-associated P and Fe and Al-associated P (NaOH-II-P) in ADL (Figure 4.2 a), whereas KPD and VIR showed greater extraction of NaOH-I-P fractions (Figures 4.2 b and 4.2 c). Stout *et al.* (1999) observed similar shift for FBC and FGD treated soils and indicated that the high pH change and the Ca addition has induced the displacement of Fe and Al to the solution and hence more P bound to the NaOH-I-P fraction. The addition of P-rich FA to all the three soils showed increased concentration of P in the solution form and had relatively equal distribution of P in all fractions. In the case

of FBC, the water soluble P (H_2O-P) decreased as the application rate increased. The addition of FGD also decreased water soluble P in all soils with the greatest effect on the water soluble P occurring at 15 % application rate. Beyond this rate, i.e., at 30% application rate, the effect on the reduction of soil solution P decreased, agreeing with P adsorption results in Chapter 3. The $NaHCO_3$-P fractions were largely unaffected by FBC and FGD addition in all the three soils. (Figures 4.2 a, b and c).

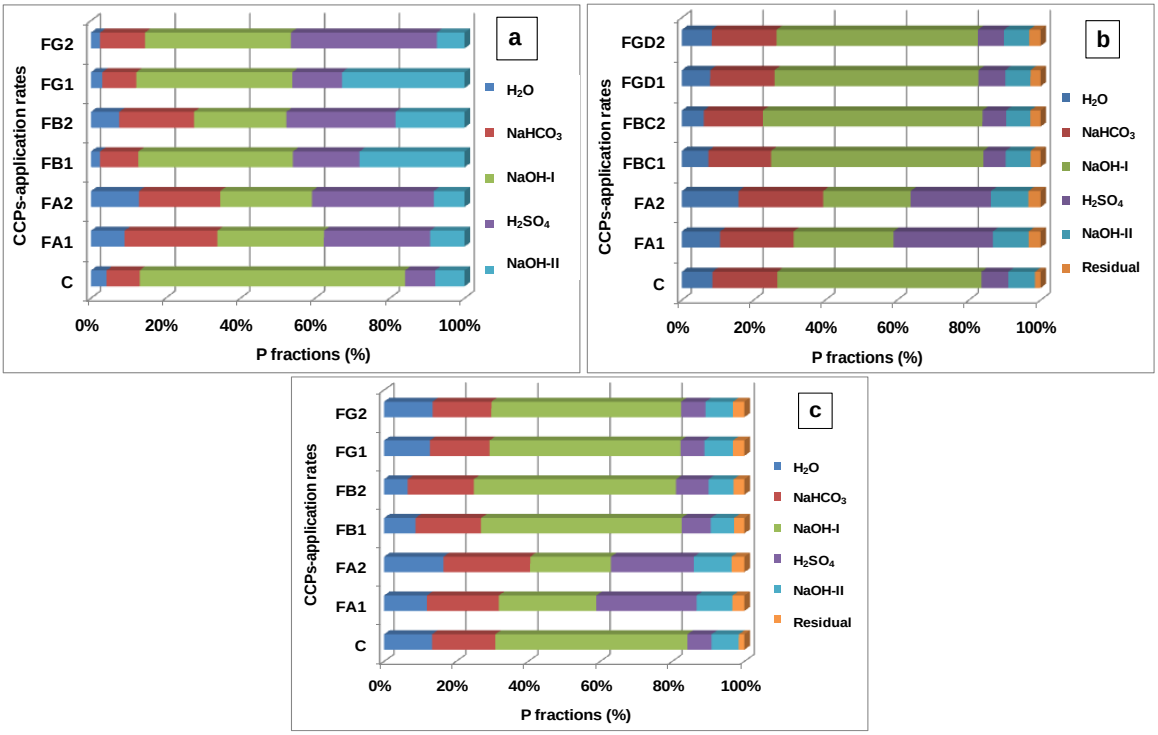


Figure 4.2 Distribution of P fractions in the three soils (a: Adelaide hills – ADL; b: Kapunda – KPD; c: Virginia – VIR) amended with CCPs, without P treatment. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the Y axis indicates control.

4.6.2.2 Effect of CCPs on applied P transformation in ADL soil

The application of P to the ADL soil showed major shifts in the P distribution for each treatment and application rates of P and CCPs (Figures 4.3 a, b and c). The CCPs (except FA) reduced the water soluble P and bicarbonate P from the inorganic P (KH_2PO_4) application and increased the P associated with Fe and Al (Figures 4.3 a and 4.8 d). In the case of FGD, the concentration of NaOH-I fraction decreased, which may be due to the lower pH values of FGD amended soils (Table 4.6).

Organic P (PM) applied soils showed low adsorption and hence relatively lower concentration of P in bound fractions. Increases in $NaHCO_3$–P (Figure 4.4) and other bound fractions (NaOH-I-P, H_2SO_4-P and NaOH-II-P) were observed for FA and FBC amendments and FGD showed minimal impact on the distribution of P fractions (Figures 4.3 a, b and c). Interestingly, Dou *et al.* (2003) while examining the effect of CCPs on P

mobilisation from swine manure and broiler litter, observed that FBC and FGD are effective in reducing readily soluble P, but FA proved to be ineffective in immobilising P from manures.

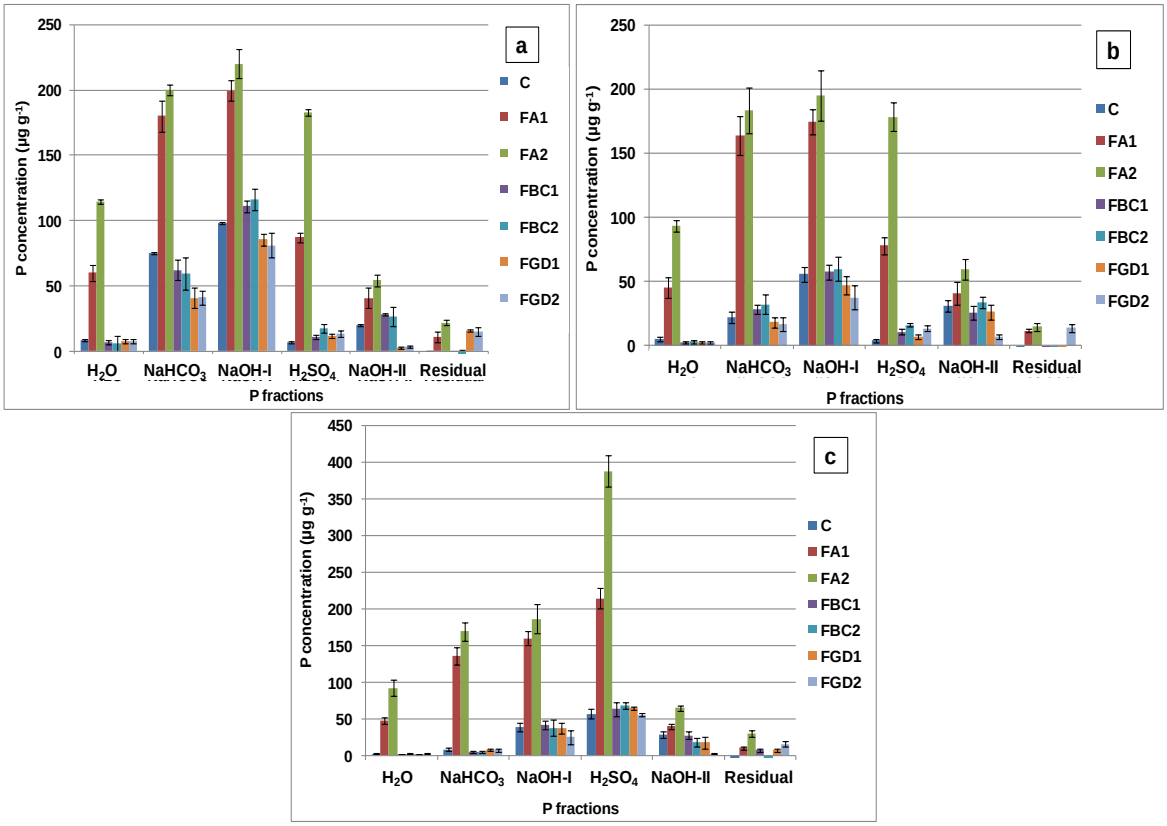


Figure 4.3 Effect of CCPs on P transformation in Adelaide hills (ADL) soil treated with three different P sources a. Potassium dihydrogen phosphate – PP; b. Poultry manure – PM and c. Phosphate rock – PR. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

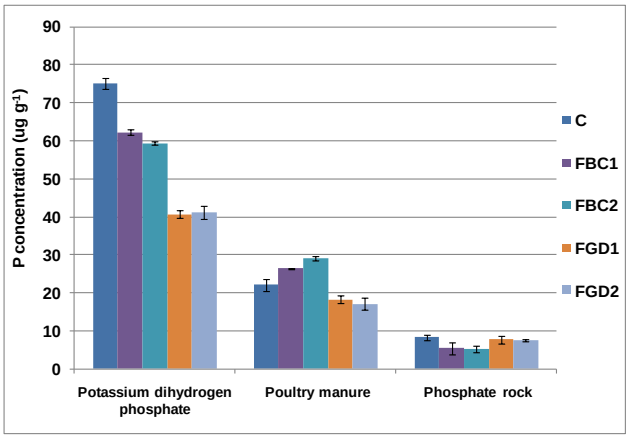


Figure 4.4 Effect of FBC and FGD on $NaHCO_3$-P values of Adelaide hills (ADL) soil treated with a. Potassium dihydrogen phosphate – PP; b. Poultry manure – PM and c. Phosphate rock – PR. FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

The CCP-induced increase in soluble P (H_2O-P and $NaHCO_3$-P) in PM amended soil (Figure 4.3 b) can be attributed to: (i) chemical hydrolysis of organic P resulting from the increases in pH and (ii) enzymatic mineralisation of organic P (Trasar-Cepada and Carballas, 1991). The production of enzymes can be mediated by soil microbial activities. However, at high application rates of CCPs, the soil microbial process may be adversely affected due to high salt contents in the CCPs (Wong and Lai, 1996) and also the influence of abiotic (extracellular) components such as clay minerals and soil aqueous phase (Dick, 1994). The effect of pH on mineralisation in PM applied soil is evident from the effect of CCPs on phosphatase activity (Figure 4.5). This is attributed to the improved soil texture as influenced by CCPs and the consequent reduction in binding of the enzyme to soil particles (Lai *et al.*, 1999). The phosphatase activity of PM applied soil increased (FBC>FA>FGD) with the increasing application rates of CCPs, but the effectiveness decreased with aging. Lai *et al.* (1999) observed initial increase in phosphatase activity for FA and sludge amended soil samples. But after 30 days, they found decreased phosphatase activity, which they attributed to substrate depletion or accumulation of toxic substances. In this experiment, the decline may be due to the increase in pH. Trasar-Cepeda and Carballas (1991) observed that increase in pH reduced acid phosphatase activity when an acid soil was limed and also showed that mineralisation of P increased at pH above 6.5. Higher the incubation period also means increase in pH (Table 4.6) of the CCPs incubated soil. Hence, the phosphatase activity declined with the increase in incubation period.

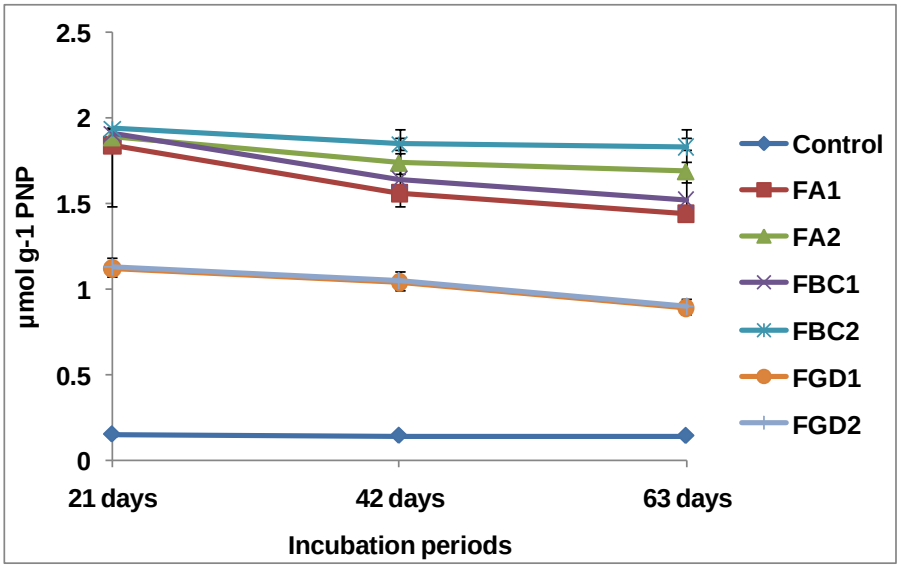


Figure 4.5 Effect of incubation time on the enzyme activity as influenced by CCPs in poultry manure (PM) treated Adelaide hills (ADL) soil. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

Therefore the addition of CCPs to soils has increased the bioavailable P for inorganic P application through adsorption and for organic P application through

mineralisation (Table 4.7). The increase in bioavailable P was characterised by decreases in water soluble P for both PP and PR applications. In PM applied soils, both water soluble P and bicarbonate extractable P increased due to the mineralising effect of CCPs. The increase in bioavailable P was highest for FA amended soils. On PP treatment, FA increased the bioavailable P from 95.56 to 309 mg kg^{-1}. For PM, the bioavailable P increased from 46.58 to 265.3 mg kg^{-1} and in the case of PR, the FA induced increase in bioavailable P was the highest from 12.08 to 229.59 mg kg^{-1}. This may be attributed to the high level of Olsen P present in FA (Table 3.4). Pathan *et al.* (2002) also observed high Olsen P concentration (92.5 mg kg^{-1}) in a Western Australian FA, while studying the effect of FA on adsorption of nutrients including P in a sandy soil.

Table 4.7 Effects of CCPs on the bioavailable P among various P sources

P forms and CCPs		Water extractable P (mg kg^{-1} soil)			Bicarbonate extractable P (mg kg^{-1} soil)			Bioavailable P (mg kg^{-1} soil)		
		PP	**PM**	**PR**	**PP**	**PM**	**PR**	**PP**	**PM**	**PR**
FA	**0%**	18.82	6.85	5.14	76.74	39.73	6.940	95.56	46.58	12.08
	15%	75.50	54.5	57.6	177.4	164.1	135.9	252.9	218.7	193.5
	30%	114.5	87.4	72.6	194.5	177.8	156.9	309.2	265.3	229.5
FBC	**0%**	14.82	6.85	5.14	72.74	39.73	6.940	87.56	46.58	12.08
	15%	12.16	4.31	4.81	76.11	43.21	12.02	88.27	47.52	16.83
	30%	10.56	4.21	4.49	79.11	45.70	20.95	89.67	49.91	25.44
FGD	**0%**	18.82	6.85	5.14	76.86	39.73	6.940	95.68	46.58	12.08
	15%	15.72	3.02	3.45	70.06	33.40	5.150	85.78	36.41	8.613
	30%	17.42	4.62	4.47	72.60	24.77	5.960	90.03	29.38	10.43

In the case of insoluble (PR) P application, the P was largely associated with Ca followed by Fe- and Al-P associated fractions. All the CCPs were found to be effective in increasing the Ca-P (Figure 4.3 c). This is largely because of high pH resulting in less acid to dissolve the PR and increase in Ca concentration in solution influenced by a common ion effect. Bolan and Hedley (1990) observed that dissolution of PR increases with decreasing pH and also suggested an equation (Eq. 4.1) showing the possible mechanism behind PR dissolution, based on Khawawneh and Doll (1978).

$$Ca_{10}(PO_4)6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \qquad \textbf{(Eq 4.1)}$$

Contrastingly, when CCPs are applied to soil containing PR, the increase in pH reduces the P dissolution, resulting in the reduction of soil solution P or mobile P.

4.6.2.3 Effect of incubation periods on P transformation in CCPs amended soil

As the incubation period increased, major shifts from NaOH-I fraction to $NaHCO_3$ and H_2SO_4 fractions were observed in all soils and for all P sources (Figures 4.6 and 4.7).

This shift to bicarbonate associated P and the consequent increases in bioavailable P is illustrated in Figure 4.8. While in PP and PR, the majority of Fe- and Al- associated P was shifted to Ca-associated P, in PM treated soil, majority of NaOH-I-P fraction moved towards loosely bound $NaHCO_3$-P fractions. While in PP and PR, the majority of Fe- and Al-associated P was shifted to Ca-associated P, in PM treated soil, majority of NaOH-I-P fraction moved towards loosely bound $NaHCO_3$-P fractions.

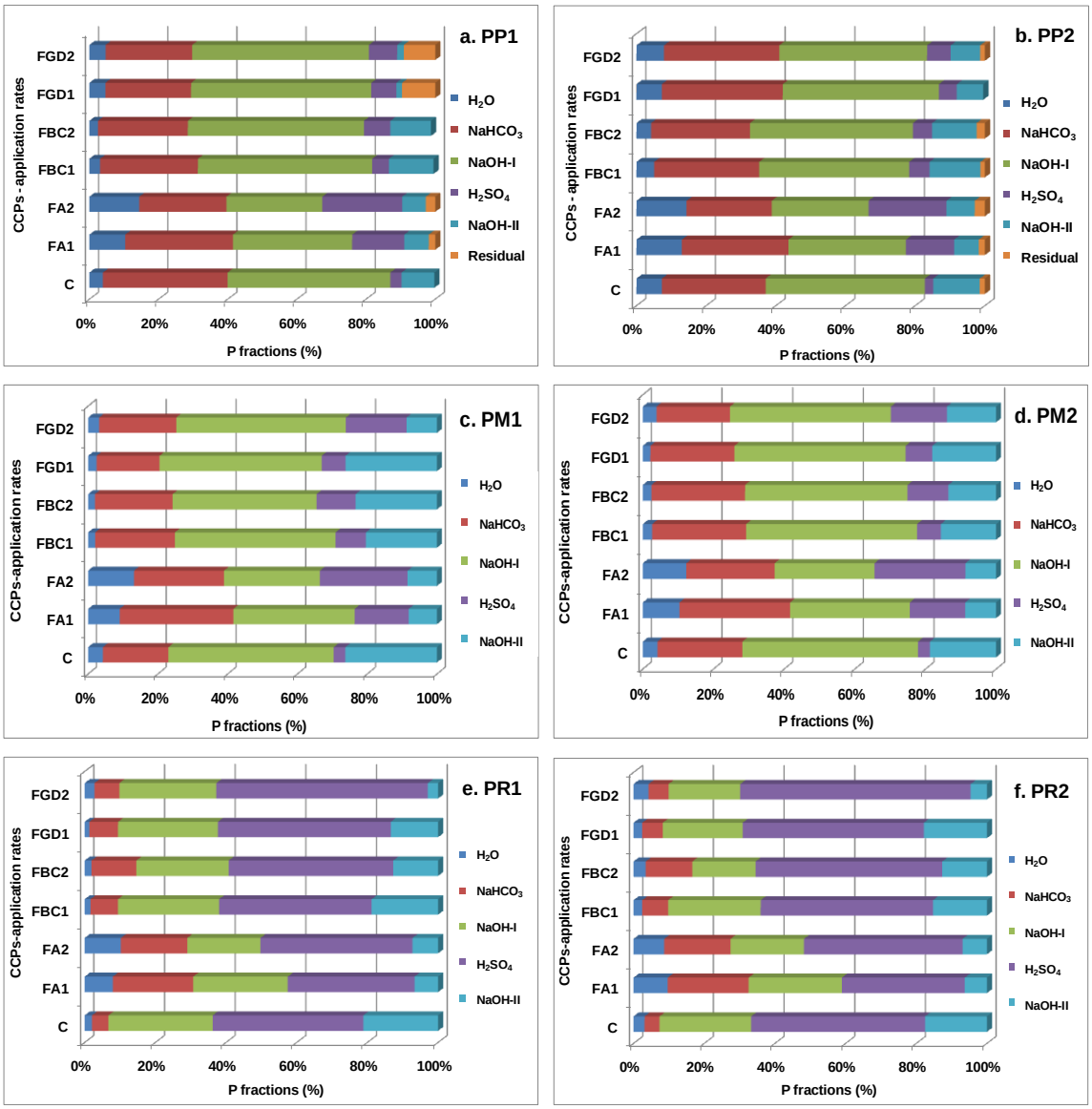


Figure 4.6 Effect of CCPs (in 21 days of incubation) on P fractions in Adelaide hills (ADL) soil treated with various P sources (Potassium dihydrogen phosphate – PP; Poultry manure – PM; and Phosphate rock – PP). PP1, PP2; PM1, PM2; and PR1, PR2 indicate the 100 and 200 mg P kg^{-1} soil treatment rates. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

Hernandez *et al.* (2005) studied the sorption of P from three different P sources (Triple super phosphate (TSP), bone material and PR) applied at 40 mg kg^{-1} each, for seven

different incubation periods and observed the increase in P sorption. The other tightly bound P such as NaOH-II-P and residual P were least responsive to incubation periods, although residual P increased on CCPs application. McDowell (2005) observed increase in residual P concentration with FA treatment in some grassland soils.

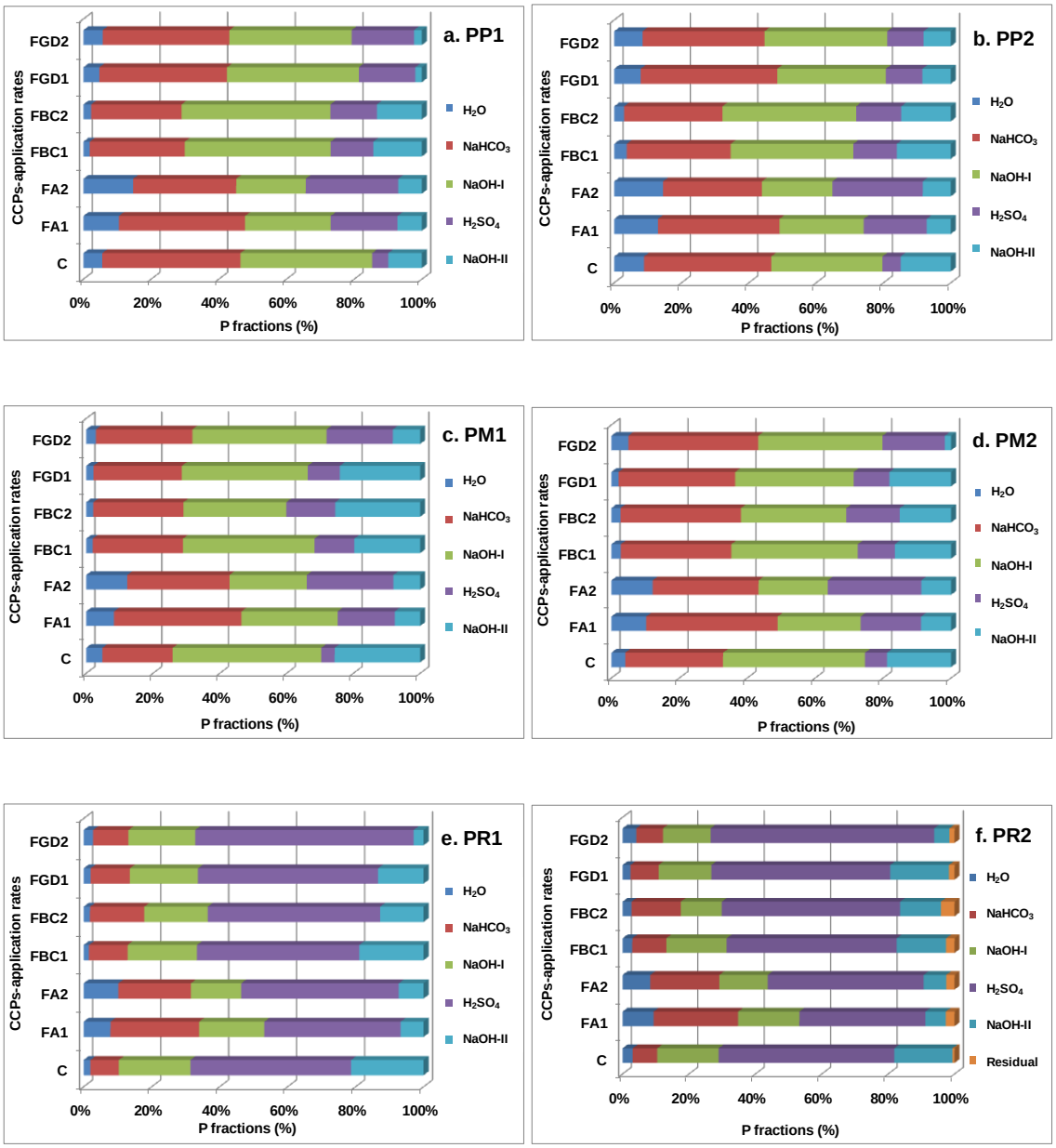


Figure 4.7 Effect of CCPs (in 63 days of incubation) on P fractions in Adelaide hills (ADL) soil treated with various P sources (Potassium dihydrogen phosphate – PP; Poultry manure – PM; and Phosphate rock – PP). PP1, PP2; PM1, PM2; and PR1, PR2 indicate the 100 and 200 mg P kg^{-1} soil treatment rates. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

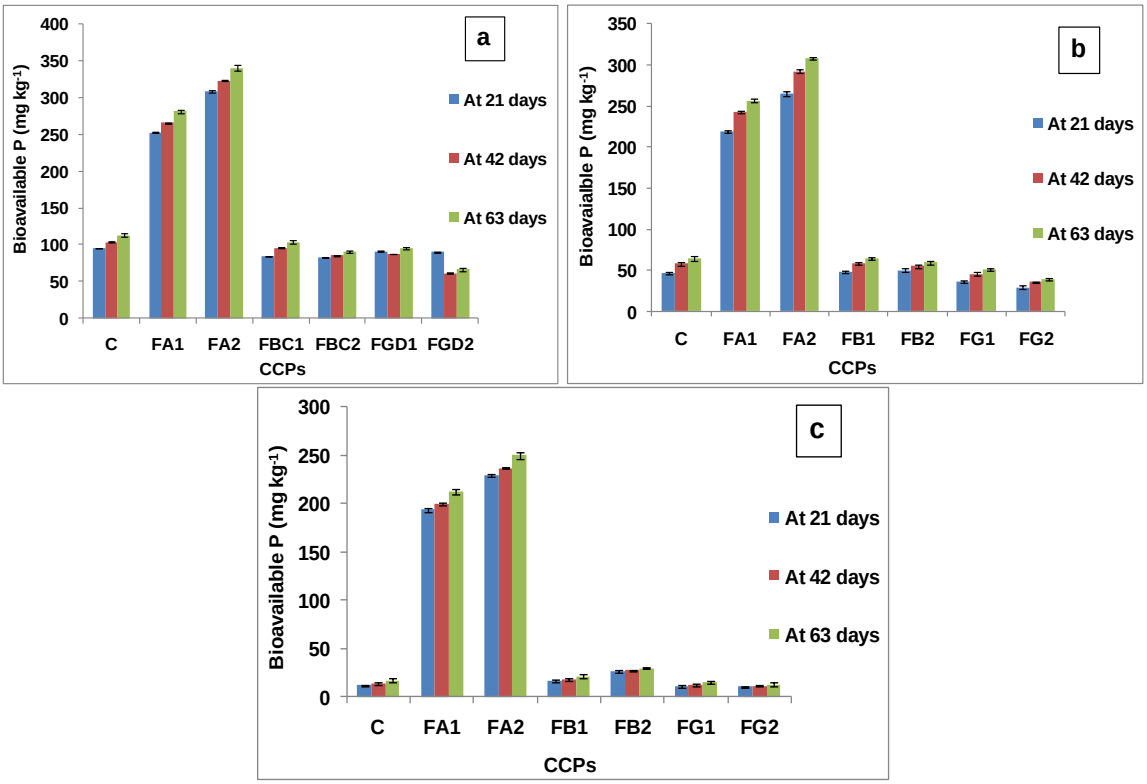


Figure 4.8 Effect of incubation periods (21, 42 and 63 days) on bioavailable P in CCPs amended Adelaide hills (ADL) soil treated with (a) Potassium dihydrogen phospahte – PP; (b) Poultry manure – PM and (c) Phosphate rock – PR. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

4.6.2.4 Advanced microscopic and spectroscopic studies

The physical characterisation studies comprising of XRD, SEM and EDS suggested all the incubated samples were rich in Al, but the Fe contents were low (Figures 4.9, 4.10 and 4.11). The FESEM/EDS data showed amorphous oxide and crystalline minerals in FA and FGD amended samples, respectively (Figures 4.9 b and c). The amorphous minerals are non-crystalline and can be present either in the form of oxides or oxyhydrides as affected by soil incubation. Pratt *et al.* (2007) reasoned this phenomenon to the alteration of oxides and silicates to hydrous oxides present in the fresh slag used by them. Most CCPs are generally rich in silicates and total Al, Fe and Mg are present as oxides (Page *et al.* 1979; El-Mogazi *et al.* 1988; Peng *et al.* 2004). The presence of these oxides/oxyhydrides signifies the P adsorbing capacity of the materials used (Olila and Reddy, 1997). The Ca concentration was relatively low in FA amended samples compared to FGD samples and is evident from the crystalline structures formed in FGD amended samples (Figure 4.9 d, 4.10 d and 4.11 c). DeBusk *et al.* (1997) and Pratt *et al.* (2007) identified the Ca in the porous matrix of the materials used as calcium silicates (eg: Wollastonite), which are capable of forming Ca/S/O (mostly gypsum) and Ca/P/O

precipitates. However, DeBusk *et al.* (1997) failed to observe the presence of these crystalline minerals in the fresh slag porous matrix through SEM/EDS. The pH and the solution composition of Ca and P play an important role on the formation of various Ca-P forms such amorphous calcium phosphates (ACPs), octacalcium phosphate (OCP), dicalcium phosphate (DCP), dicalcium phosphate dihydrate (DCPD), tricalcium phosphate (TCP) and hydroxyapatite (HAP). The precipitation of Ca requires high total Ca^{2+} concentration and high pH (Lindsay, 1979; House, 1999; Valsami-Jones, 2001; Ádám *et al.*, 2005). The pH values of the CCPs used were fairly high (FA-10.2 and FGD-10.1) which was in the range of values that support the formation of Ca-P precipitates.

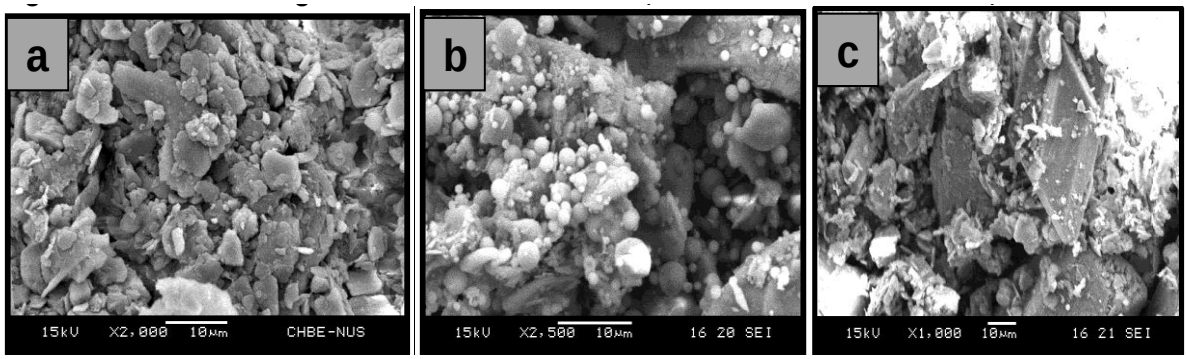
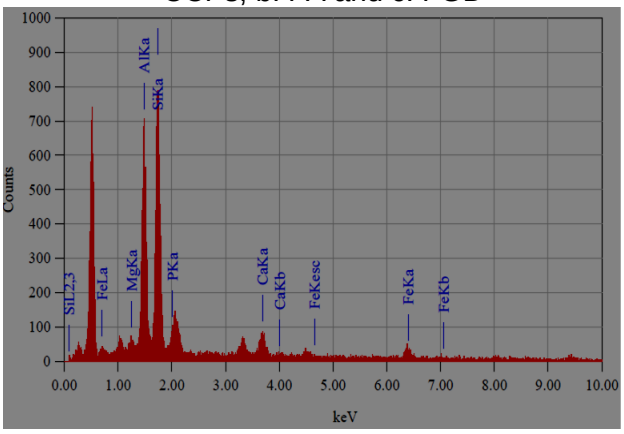


Figure 4.9 FESEM images of PP treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA and c. FGD



Treatment	Fe	Al	Ca	P
Soil + KH_2PO_4 + 0 CCPs	11.28	25.16	0.26	-
Soil + KH_2PO_4 + FA	7.57	32.78	6.11	1.46
Soil + KH_2PO_4 + FGD	6.74	27.88	29.08	0.26

Figure 4.9 d. EDS peaks for PP treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples)

The XRD data expressing the mineralogy of the CCPs incubated soil matrix reveals the presence of quartz, silicates of Ca, oxides of Ca, Al, Fe, titanium (Ti) and magnesium (Mg) (Figures 4.12 a-f). Quartz was predominant in all the samples analysed. The Al based minerals identified were ettringite and hydrogarnet. Hematite and kennedyite were the Fe based minerals present in the incubated samples. Calcium was present as wollastonite and calcium sulphate ($CaSO_4.2H_2O$-Gypsum), especially in FGD amended samples (Figures 4.12 c and e). Several studies indicated gypsum as a P sorbent (e.g. Delgado *et al.*, 2002; Bryant, 2005). However, in this study, gypsum may not be an effective P sorbent because of low pH values in FGD amended samples (Table 4.5). Hence, Ca present as wollastonite mineral can be relatively an effective P sorbent in the

current study. Other potential P sorbents identified in this research were ettringite, hydrogarnet, hematite and kennedyite.

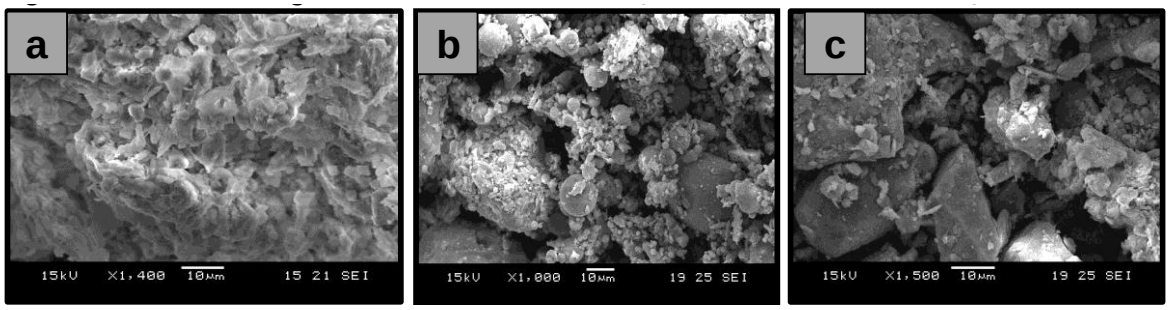
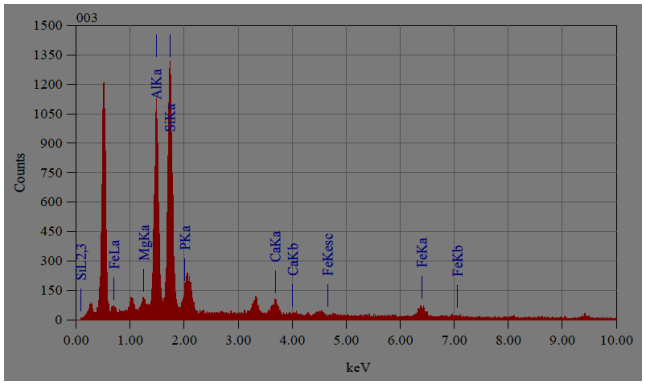


Figure 4.10 FESEM images of PM treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA and c. FGD



Treatment	Fe	Al	Ca	P
Soil + PM + 0 CCPs	10.05	26.56	0.12	2.47
Soil + PM + FA	5.19	32.25	5.41	1.46
Soil + PM + FGD	6.85	26.12	16.24	0.26

Figure 4.10 d. EDS peaks for PM treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples)

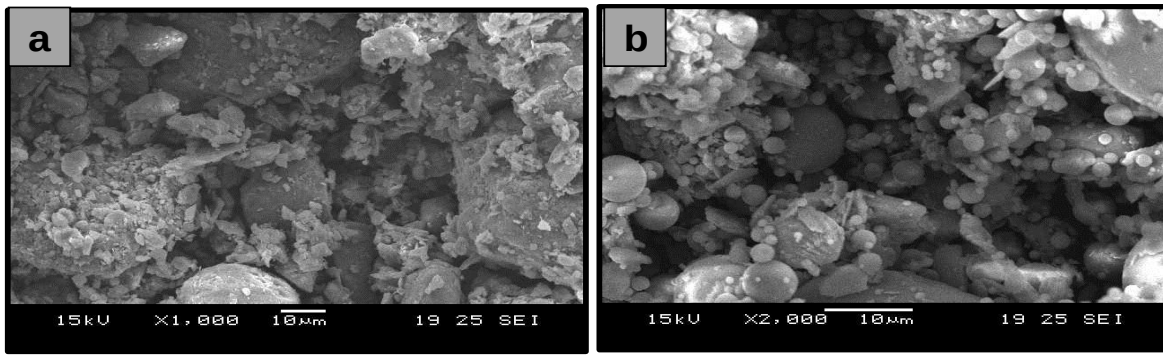
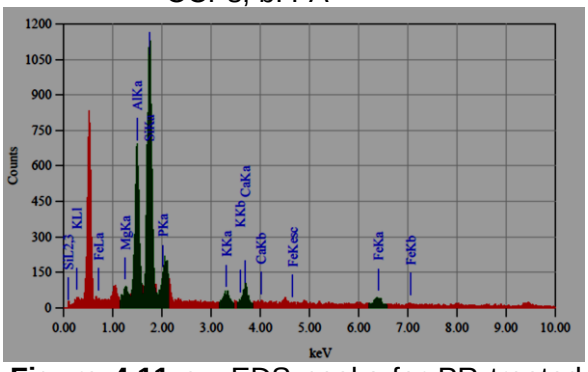


Figure 4.11 FESEM images of PR treated Adelaide hills (ADL) soil, incubated with a. 0 CCPs; b. FA



Treatment	Fe	Al	Ca	P
Soil + PR + 0 CCPs	6.66	36.04	0.6	1.61
Soil + PR + FA	6.75	35.76	2.31	2.06

Figure 4.11 c. EDS peaks for PR treated Adelaide hills (ADL) soil incubated with FA (Values in the table indicate % content of the elements present in the samples)

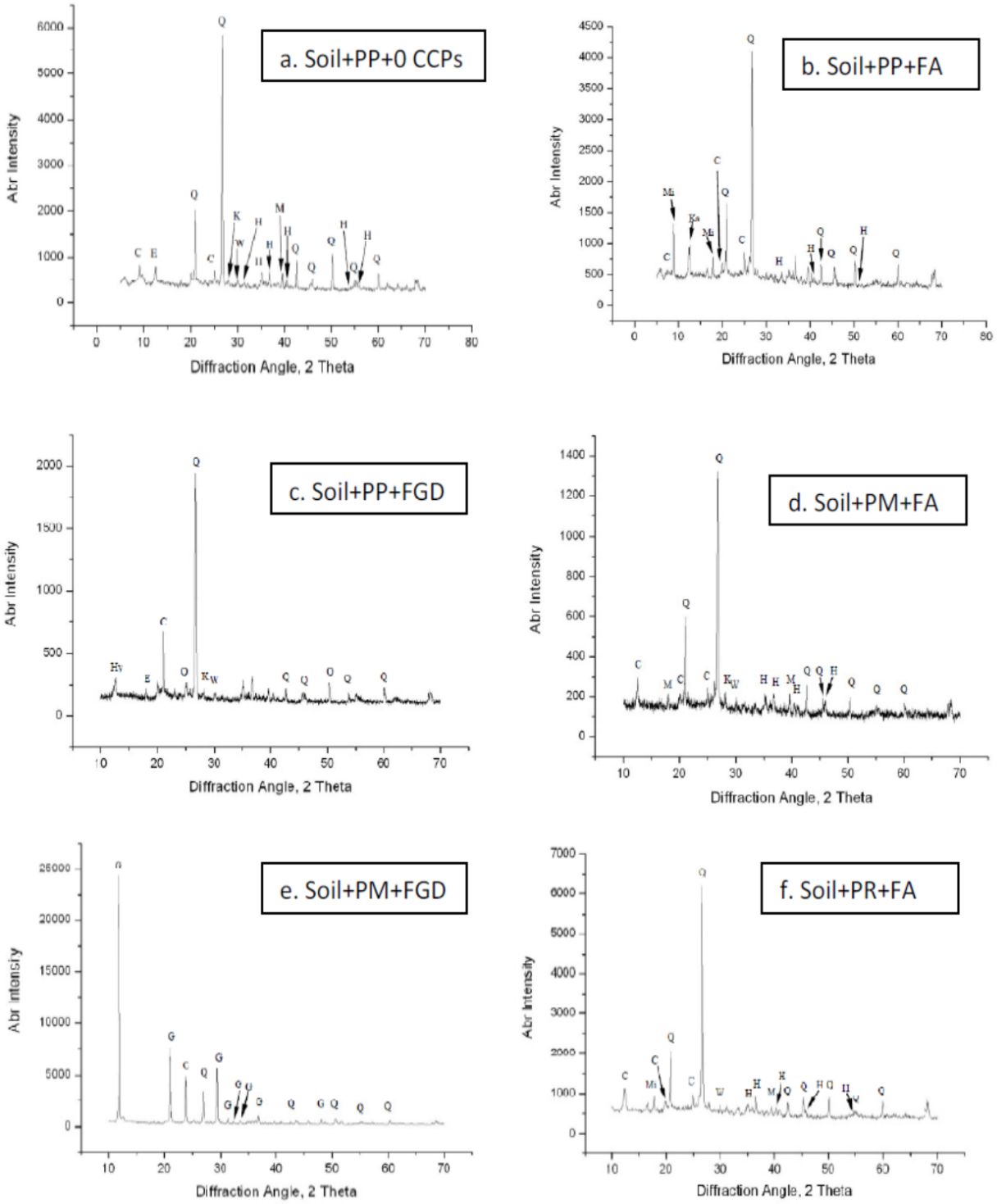


Figure 4.12 **a-f**. XRD patterns of FA amended Adelaide hills (ADL) soil treated with 3 sources of P (Potassium dihydrogen phospahte – PP; Poultry manure – PM and Phosphate rock – PR). C:Chlorite (ClO_2); E:Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$); H:Hematite ($Fe_2O_3$); Hy:Hydrogarnet ($4CaOAl_2O_3.\ 13H_2O$); Ka:Kaolinite ($Al_2Si_2O_5(OH)_4$); K:Kennedyite ($Fe_2MgTi_3O_{10}$); M:Merwinite ($Ca_3Mg(SiO_4)_2$); Q:Quartz ($SiO_2$); W:Wollastanite ($CaSiO_3$).

4.7 Conclusions

- In the case of soluble inorganic P (KH_2PO_4) source, CCPs enhanced immobilisation, which is attributed to a pH-induced increase in P adsorption.
- In the case of insoluble P source (RP), CCPs decreased dissolution which is attributed to an increase in soil pH (less acid to dissolve) and Ca concentration in solution (common ion effect).
- For organic P (PM) application, CCPs enhanced the mineralisation of P which is attributed to an increase in pH and enzyme activity.
- The CCPs influenced transformation of P from one form to other, mainly through (im)mobilisation and the effect varied between P sources.
- The ADL soil with acidic pH exhibited more loosely bound P compared to the soils with higher pH values, which is attributed to the increase in soil pH by the CCPs. In the case of soils with pH values higher than 7, further increases in pH results in the formation of Ca-P precipitates.
- The FESEM/EDS and XRD studies supported the presence of P sorptive oxides/oxyhydrides of Fe, Al and Ca, which play an important role in P immobilisation.
- The role of CCPs in leaching characteristics of P need to be quantified to validate the observations on soluble P in the fractionation experiments (Chapter 5). Plant uptake of P using a glass house experiment with similar combination of amendments will give a better idea on the bioavailable P fraction (Chapter 6).

Chapter 5

EFFECT OF COAL COMBUSTION PRODUCTS ON THE LEACHING OF PHOSPHORUS IN SOILS

5.1 Introduction

High concentration of phosphorus (P) in soils due to agricultural P (organic and inorganic fertilisers) application poses serious risks on the soil environment and water bodies. The excess P in the soil is prone to movement through the soil profile in the form of either runoff or leaching. This is because of the lack of sufficient sorptive mineral (immobile) components in soil like Al, Fe and Ca, which can easily bind with the P in solution (McDowell, 2005). Surface runoff to water bodies has been the most dominant pathway of P loss (Carpentar *et al.* 1998; USEPA, 1996; Stout *et al.* 2000). Although subsurface application of P can considerably reduce the risk of P transport as runoff, this practice enhances the risk of subsurface horizontal and vertical movement of P. There were several studies on subsurface transport of P covering various aspects such as landscape variations (Sharpley and Withers, 1994), soil textural effects (Sims *et al.*, 1998; Djodjic *et al.*, 2004) and redistribution of P in the soil profile (Kleinman *et al.*, 2003). In sandy soils, the limitations in P-retaining soil constituents such as clay content, organic matter and oxides of Fe and Al contribute to immediate P leaching on the application of water-soluble P fertilisers (Elliott *et al.*, 2002; Chen *et al.*, 2006).

Soil's adsorption capacity and redistribution of both cations and anions are significant factors that affect P leaching. The extent of P adsorption is chiefly controlled by the pH (Chapter 3), especially in variable-charge surface and by the amount of P sorbing cations such as Ca, Fe and Al in the soil solution (Stout *et al.*, 1998). Generally, an increase in the pH increases the net negative charge on the variable-charge surface, resulting in the decrease of non-specific anion adsorption (Barrow, 1985). Liming of soil not only increases the pH but also the Ca in solution, which can exhibit an opposite effect compared to pH, thereby increasing the P sorption as a result of precipitation as calcium phosphate (Bolan *et al.*, 1988; Elrashidi *et al.* 1999). Chen *et al.* (2007) showed that low pH value with high calcium concentration and vice versa are not beneficial for P immobilisation. Bolan *et al.* (1988) and Naidu *et al.* (1990) also observed that liming

increased ionic strength of the solution, which consequently increased P adsorption when the pH is above the point of net zero charge (PZC).

As an alternative to liming, coal combustion products (CCPs) such as fly ash (FA), fluidised bed combustion ash (FBC) and flue gas desulphurisation (FGD) gypsum are being used for P retention in soil, thereby reducing the P transport to water bodies (Stout *et al.*, 1998; Pathan *et al.*, 2002; McDowell, 2005). The CCPs are generally alkaline with pH ranging from 8 to 11, which can increase the pH of the soil considerably thereby enhancing the possibility of precipitation of P with Ca (Chapter 3). CCPs, being rich in Al, Fe and Ca, can bind P to these cations based on the pH. For example, in alkaline soils, the addition of CCPs trigger precipitation of Ca-P compounds, whereas in acidic soils, oxides of Fe and Al present in the CCPs may adsorb P in their hydrated forms, resulting in the formation of iron and aluminium phosphates (McDowell, 2004).

The adsorption and the redistribution of P in CCPs amended soils had been clearly discussed in Chapters 3 and 4. The vertical transport of P in soils is not only dependent on the adsorbing capacity, but also on the amount of desorbed P. The crucial factor in desorption of P is the extent of saturation (Hooda *et al.*, 2000). Bolan *et al*. (1988) also showed that the effect of liming on P adsorption varied between the batch and column experiments, mainly due to the continuous removal of Ca in the soil solution. The results from the fractionation experiment (Chapter 4) showed increases in the solution P for both inorganic and organic P applications. The effect of CCPs on the amount of recoverable solution P from P treated soils will be validated using column leaching experiments in this study. Hence, this chapter will consider the effect of CCPs on P leaching in low P retaining soils, focussing on the effects of pH and concentrations of Ca in solution on P leaching.

5.2 Objectives

The overall objective of this study is to examine the effect of CCPs on P leaching in low P retaining soils. The specific objectives are:

- To evaluate CCPs affected P leaching in soils using pulse-input and step-input experiments.
- To compare the effect of CCPs on P leaching between different soils treated with different P sources.
- To determine the factors that affect P leaching such as pH and the concentration of Ca in the leachates.

5.3 Hypothesis

The application of CCPs decreases leaching of P from soils, which is attributed to increase in P sorption as a result of increases in soil pH and concentration of calcium in soil solution.

5.4 Experiments

The major experiments conducted to test the hypotheses and the treatments used in these experiments involving Kapunda (KPD) and Birbie Island (BIR) soils are listed in Table 5.1.

Table 5.1 Experiments, treatments and analyses

No.	Title	Treatments	Analyses
1	Pulse leaching	Two soils (KPD and BIR), two P sources (KH_2PO_4 and poultry manure), and two CCPs (FA and FBC)	Inorganic P, pH and Ca concentration in leachates
2	Step leaching	Two soils (KPD and BIR), one P source (KH_2PO_4), and two CCPs (FA and FBC)	Inorganic P, pH and Ca concentration in leachates

5.5 Materials and methods

5.5.1 Characterisation of soils, CCPs and P sources

The leaching experiments were performed using a sandy loam soil collected from South Australia (Kapunda - KPD) and a sandy soil collected from Queensland (Podosol - BIR). The soil's textural characteristics were determined using a micropipette method (Miller and Miller, 1987) and was already shown in Table 3.2 (Chapter 3). The CCPs used were fly ash (FA) from Port Augusta power station, South Australia and fludised bed combustion ash (FBC) from Redbank power station, Queensland. The P sources applied to the soils were inorganic P (KH_2PO_4 - PP) and organic P (poultry manure - PM).

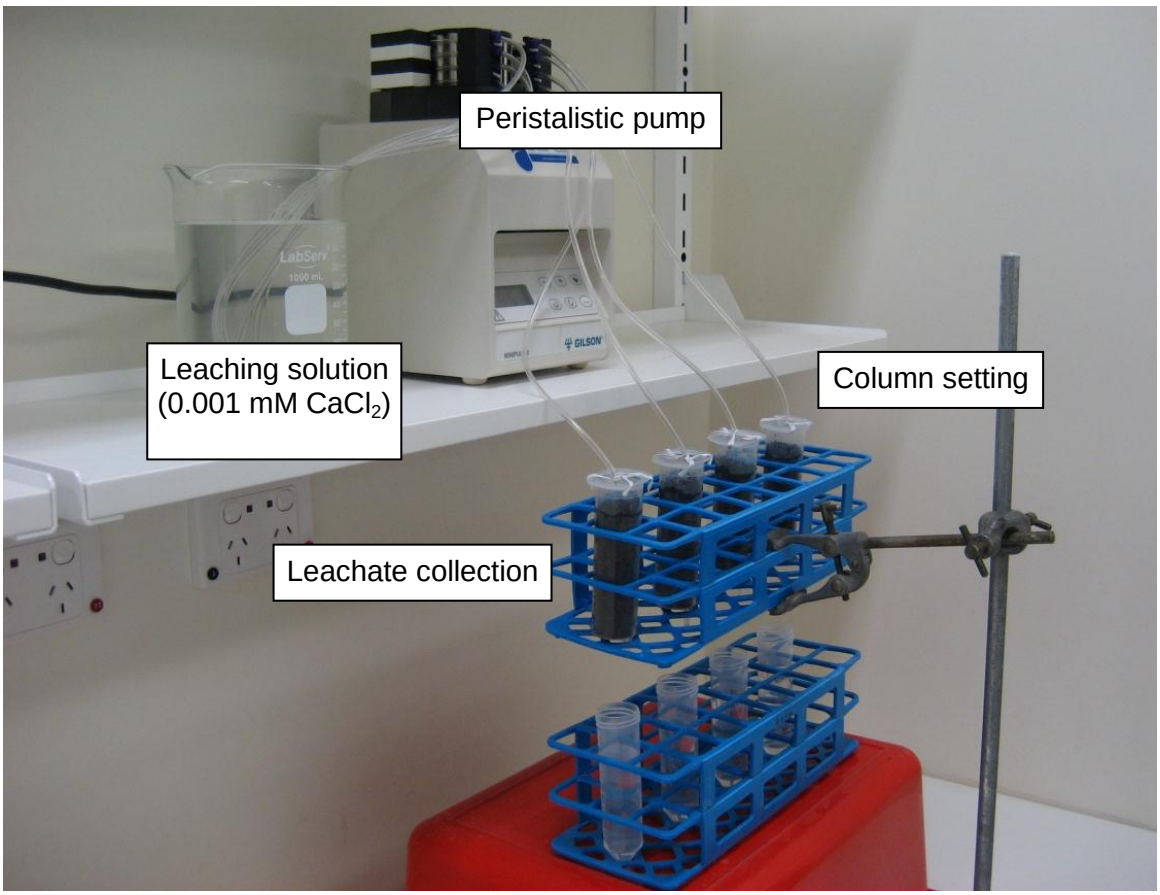
The soils used differed in their pH values (KPD-7.1 and BIR-3.4) and also P retention capacities (KPD-7.41 % and BIR-1.63 %). The CCPs – FA and FBC used in this experiment has proven abilities on their effect on P adsorption in soils (Chapter 3). The characterisation of the materials used was previously explained in Section 3.4.2.

5.5.2 Column leaching experiments

The soils were treated with the two P sources (PP and PM – for pulse experiment only) and incubated with the CCPs (FA and FBC) for 21 days at 60 % water holding

capacity (WHC). The specific treatments and methodology for the incubation of the soils will be detailed in the following sections (5.5.2.1 and 5.5.2.2). Two types of column experiments were employed based on the P application – step input and pulse input. In step input, a known concentration of P was continuously leached through the soil column and the leachates collected as volume-defined aliquots called pore volume. In a pulse input experiment, a known concentration P is applied along with the soil and incubated, where deionised water (with 0.001mM $CaCl_2$ solution) replaces the P solution for leaching. The experiments were conducted in triplicates. The design and arrangement of the experimental set up involving the columns and peristaltic pump are shown in Plate 5.1.

Plate 5.1 Set up of column leaching experiment



5.5.2.1 Pulse leaching

The soils (40 g each) were thoroughly mixed with two different P sources (PP and PM), applied at two levels of P: 0 and 100 mg P kg^{-1} soil and then incubated for 21 days with two different CCPs (FA and FBC) at the rates of 0 and 15 % of the P treated soils. The P from PP is readily soluble and from PM is sparingly soluble. The methodology for incubation was already explained in Section 4.5.2.

The pulse leaching was undertaken using 60 mL syringe columns (3 cm in diameter and 7.5 cm in height). The incubated soils were added in small increments (to curtail particle size aggregation) to the syringe columns and packed at a bulk density of 1.18 g cm^{-3}. The base of the syringe was sealed using a nylon mesh with an effective pore diameter of 60 µm to minimize the dead-end volume. The columns were leached with 0.001 mM $CaCl_2$ solution at a flow rate of 1.2 mL min^{-1} for KPD soil and 0.74 mL min^{-1} for BIR soil using a peristaltic pump. The reason for the difference in flow rates is the texture of the soils used, where BIR is more sandy compared to KPD and hence allows the solution to leach faster. Before leaching with the $CaCl_2$ solution, the columns were allowed to saturate with deionised water from the bottom in order to minimise the air bubble traps. The leachates were collected at definite pore volumes (V_p), calculated based on the volume, bulk density and porosity. The V_p and the total number of V_p collected for various amendments are listed in Table-5.3. The fractions of Vp collected are as follows,

- ✓ First 3 pore volumes (V_P-1,2,3) – 1 aliquot = 0.25 Vp (4 aliquots per V_p).
- ✓ Next 2 pore volumes (V_P-4,5) – 1 aliquot = 0.5 Vp (2 aliquots per V_p).
- ✓ Remaining pore volumes (V_P-6,7,8,…..) – 1 aliquot = 1 Vp (1 aliquot per V_p).

The leachates collected were analysed for inorganic P using phosphomolybdate method (Murphy and Riley, 1962). The pH was analysed using a pH/conductivity meter and the concentration of Ca, Al and Fe in the leachates were analysed using ICP-OES. The cumulative amount of P leached (mg P kg^{-1} soil) was calculated by adding the P concentrations of subsequent V_p as expressed in Eq. 5.1,

$$\textbf{Cumulative P leached} = V_1xC_1,\ V_1xC_1+V_2xC_2,\ V_2xC_2+V_3xC_3,\ V_3xC_3+V_4xC_4,\ldots..,\ V_yxC_y+V_zx_{Cz} \quad \textbf{(5.1)}$$

where,

V is the volume leached in each aliquot
C is the concentration of leached P (mg L^{-1}) from each aliquot
y and z denotes respective volume and concentrations in the final two aliquots of leached P

5.5.2.2 Step leaching

The CCPs incubated soils (40 g) with similar column characteristics mentioned in section 5.2.2.1 were leached with 100 mg P L^{-1} KH_2PO_4 solution. The leachates were analysed similar to those in section 5.2.2.1.

Table 5.2 Leachate collection and pore volume (V_p) for soils without CCPs

Amended soil	No. of Vp	Vp (mL)	Total volume leached (mL)
Pulse leaching			
BIR+PP	16	18.80	300.8
BIR+PM	28	18.80	526.4
KPD+PP	22	17.74	390.2
KPD+PM	31	17.74	549.9
Step leaching			
BIR+PP	24	18.80	451.2
KPD+PP	27	17.74	478.9

5.5.3 Statistical analysis

Statistical analysis was performed for the elemental analyses data and the chemical properties of soils, CCPs and P sources using Microsoft excel 2010 package. The mean and standard deviation of the mean were analysed for all the replicates. The relationships between the data were evaluated using a simple regression analysis.

5.6 Results and discussion

5.6.1 Properties of soils, CCPs and P sources used

The properties of the soils, CCPs and P sources used in this study were already given in Tables - 3.3 and 3.4 in Chapter 3 and Table 4.4 in Chapter 4. The pH of the soils ranged from acidic for BIR (3.4) to near neutral for KPD (7.1). The PRC of the soils were BIR-1.63 % and KPD-7.41 %. The BIR soil had very low native total P (0.1 %) and the Olsen P was below detection limits.

The two CCPs used had high pH (>10) and the pH of FBC was 12.7. The calcium carbonate equivalence (CCE) value was also higher for FBC (23.25 %) compared to FA (16.75 %). The Olsen P was very high for FA (260.44 mg kg^{-1}). Pathan *et al.* (2002) also observed high extractable P (92.5 mg kg^{-1}) concentration in a FA collected from Western Australia. The Ca content was higher in FBC (49.68 %) compared to FA (18.04 %), which is attributed to the addition of lime before burning in the furnace.

5.6.2 Column leaching experiments

In all the leaching experiments, FA showed highest leaching of P followed by the control and FBC. This is attributed to the high P content (1.52 %), with an Olsen P concentration of 260.44 mg kg^{-1} present in FA. Pathan *et al.* (2002) also observed high extractable (Olsen) P concentration (92.5 mg kg^{-1}) in a Western Australia FA. In this research, the leaching of P from FA (amended separately with BIR and KPD) was also measured in the absence of P treatment. In order to account for P leaching from FA, the

difference between the leachate P from FA with P and FA without P was calculated and plotted in Figures - 5.4 to 5.6. The highest cumulative leachate P concentration for FA amended soil was 13.82 mg kg^{-1} at V_p-31, which accounts to 15.15 % of P leaching from the applied P in FA (15 % of FA application adds 91.2 mg P to the 40 g soil). Also, FBC confirmed the highest adsorption (Chapter 3) as evident from the minimal leaching of P for FBC amended samples. In the case of pulse leaching, the P leaching in PP treated soils was more pronounced compared to the PM treat soils, where the leaching increased gradually (Figures - 5.1 to 5.4).

5.6.2.1 Pulse input leaching

For the podosol (BIR), the P leaching was high compared to KPD soil (Figures 5.1 and 5.2) and the numbers of pore volume aliquots collected ranged from 16 to 31 (BIR+PP-16; BIR+PM-28; KPD+PP-22; KPD+PM-31). The differences in the pore volume collected between the soils can be attributed to the texture of the soils used (Table 5.2). In the case of the P treatments, the leaching was continued to more number of pore volumes for PM treated soils considering the slow solubilisation of the manure compared to PP. The P in the leachates appeared earlier in PP treated soil compared to PM treated soil and FA showed the highest P leaching, which can be linked to the slow release characteristics of the manure P (Trasar-Cepada and Carballas, 1991; Toor and Bahl, 1997). McDowell (2004) associated increased P retention to the increase in free lime (CaO) content at high pH.

In the case of BIR soil, the total amount of P leached for PP treatment was 96.47 mg kg^{-1}, 92.43 mg kg^{-1} and 84.86 mg kg^{-1} for control (with no CCP addition), FA and FBC respectively (Figure 5.1 a). The results illustrated 4.18 % decrease in P leaching induced by FA and 12.03 % on FBC addition. Whereas for PM treated soil (Figure 5.1 b), the total amount of P leached increased as a result of CCP addition with 22.09 % increase on FA (86.07 mg kg^{-1}) addition and 16.01 % for FBC (79.84 mg kg^{-1}), compared to control (PM amended) soil (67.06 mg kg^{-1}). The increase in P on CCP addition can be associated the increase in pH induced mineralisation of the manure P (Chapter 4). Several researchers observed increased mineralisation of organic P on the application of lime to acid soils. (Trasar-Cepada and Carballas, 1991; Condron *et al.,* 1993; Haynes and Naidu, 1998; Bolan *et al.*, 1999; Fernandes and Coutinho, 1999).

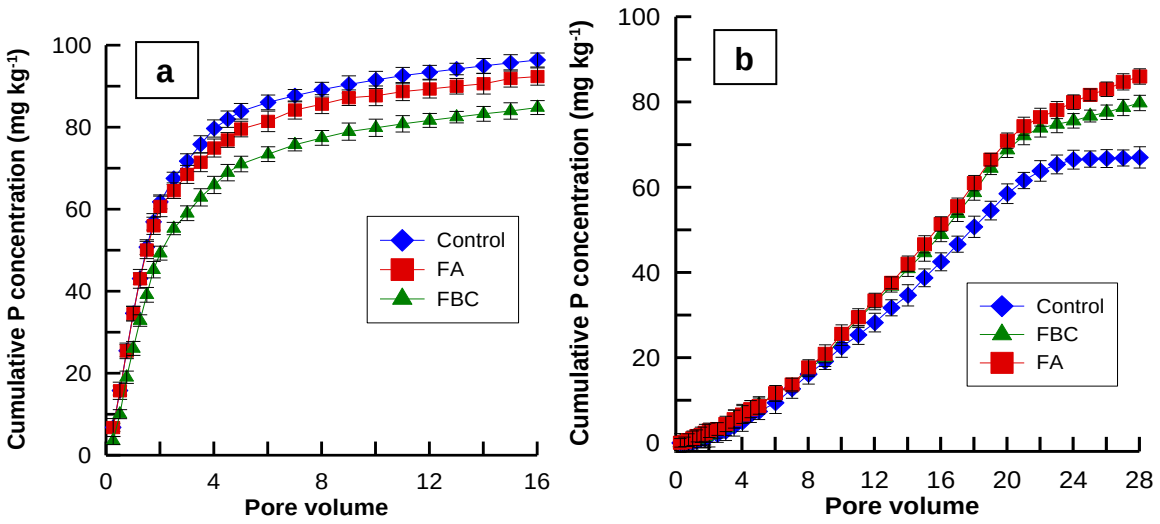


Figure 5.1 Pulse-input leaching - Cumulative P for Birbie Island (BIR) soil treated with a. PP and b. PM at 100 mg P kg^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates.

In the case of KPD soil, the P leaching was relatively lower compared to BIR soil. Although the P leaching in KPD soil was lower than BIR soil, the cumulative leaching curves showed similar trends as of BIR soil except for the differences in reduced leaching between FA and FBC (Figures 5.2 a and b). For PP treatment, the cumulatively leached P from control, FA and FBC was 91.88, 87.75 and 84.99 mg kg^{-1} respectively, accounting for FA-4.49 % and FBC-7.5 % reductions (Table 5.3). In BIR soil, FBC reduced higher (12.01 %) amount of leachate P compared to PP treated KPD soil, because of greater P adsorption in KPD soil (Chapter 3). Bolan *et al.* (1988) positively related increasing ionic strength to increased P adsorption.

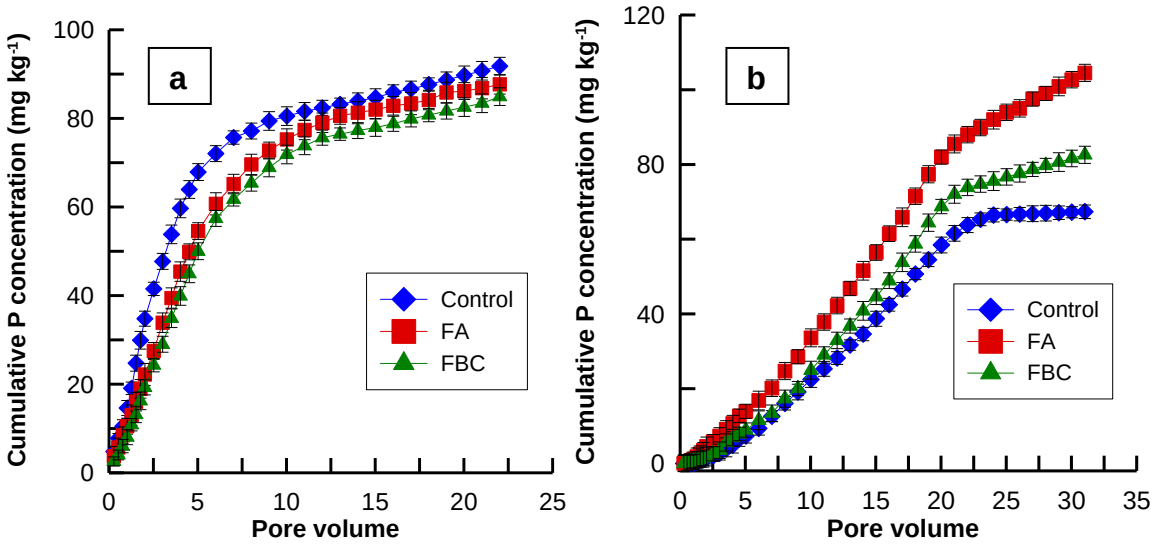


Figure 5.2 Pulse input leaching - Cumulative P for Kapunda (KPD) soil treated with a. PP and b. PM. at 100 mg P kg^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates.

In the case of PM treatment to KPD soil, both the CCPs increased the P in leachates by 35.53 % (FA) and 18.44 % (FBC). The increase in leachate P for FA amendment may be attributed to the increase in the soil solution P because of manure addition (Figure 5.2 b). Urvashi *et al.* (2007) utilised farm manure to examine their effects on mobilising P in FA and found up to 50 times increase in soluble P.

Table 5.3 Pulse input leaching: Percentage reduction of the amount of P leached (compared to control soil) in the CCPs amended soils.

Soils and P treatments	CCPs	P added (mg/kg)	P leached (mg/kg)	% of P leached*	CCP-induced change (%)**
BIR-PP	Control	100	96.46	96.46	-
	FA	100	92.43	92.43	- 4.18
	FBC	100	84.87	84.87	- 12.01
BIR-PM	Control	100	67.06	67.6	-
	FA	100	86.07	86.07	+ 21.46
	FBC	100	79.84	79.84	+ 15.33
KPD-PP	Control	100	91.88	91.88	-
	FA	100	87.75	87.75	- 4.49
	FBC	100	84.99	84.99	- 7.49
KPD-PM	Control	100	67.45	67.45	-
	FA	100	104.6	104.6	+ 35.52
	FBC	100	82.69	82.69	+ 18.43

* % of P leached = (Cumulative leached/Added) x 100

** CCP-induced % change in P leaching = (Cumulative leached for control - Cumulative leached for FA or FBC/Cumulative leached for control) x 100; "+" indicates increase over control treatment; "-" indicates decrease over control.

5.6.2.2 Step input leaching

The breakthrough curves (BTCs) for the P treated soils, which were amended with two different CCPs are shown in Figures 5.3 a and b. Consistent with the P sorption results obtained in Chapter 3, P appeared earlier in BIR than KPD owing to the difference in their PRCs. The CCPs showed similar effects as exhibited in pulse leaching as the order of P in leachates followed Control > FA > FBC trend for both the soils treated with PP. Of all the soils, P appeared in the BIR soils faster than KPD. The results indicate that CCPs reduced the leaching of P in both the soils. Among the CCP amendments, FBC was more effective in reducing the leachate P followed by FA.

The amount of P adsorbed in these step leaching experiments was estimated using the breakthrough curves and compared with batch sorption experiment as mentioned in Chapter 3. However, the data indicated that the P sorption in column experiment was higher than that of batch sorption (Figure 5.4). This could be associated with the K_f values, which are used for batch sorption experiments measured at 1 mg L^{-1},

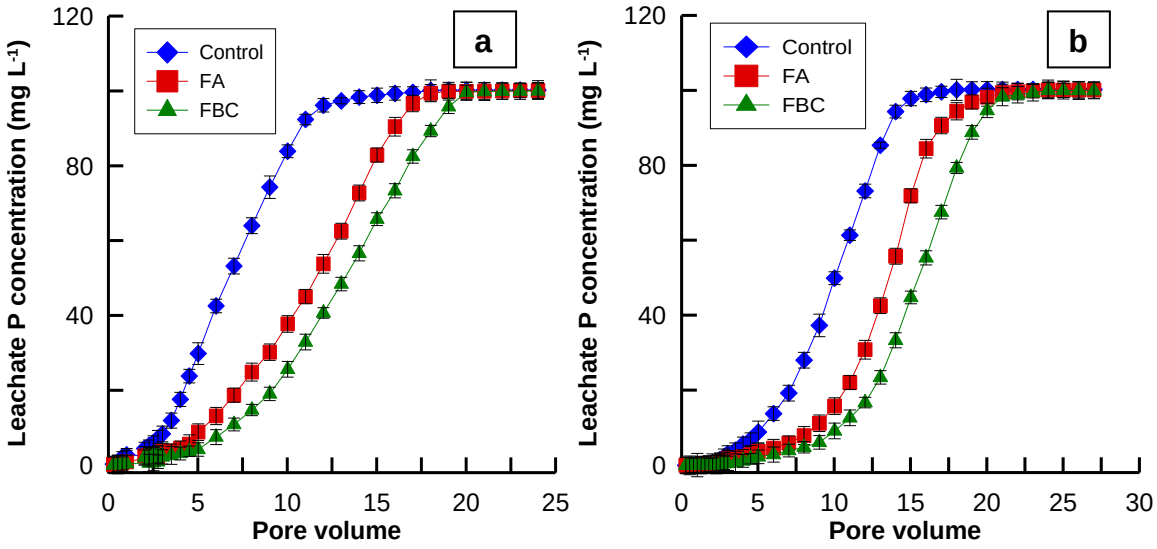


Figure 5.3 Step input leaching – Breakthrough curves for a. Birbie Island (BIR) and b. Kapunda (KPD) soils, treated with PP at 100 mg P L^{-1} soil as affected by CCPs (15 % w/w). *FA values in the figures are derived from difference between FA with P and FA without P. Error bars represent the standard deviation between replicates.

compared to the input concentration of 100 mg L^{-1} in column sorption experiment. The sorption of P has been shown to increase with increasing concentration of the equilibrium solution (Figures 3.2 to 3.4, Chapter 3). Leaching studies by Bolan *et al.* (1988) and Wang *et al.* (2009) illustrated higher adsorption in batch experiments compared to column experiments, which has been related either to a greater contact of solute soil due to vigorous shaking or to a difference in the ionic strength between the two systems.

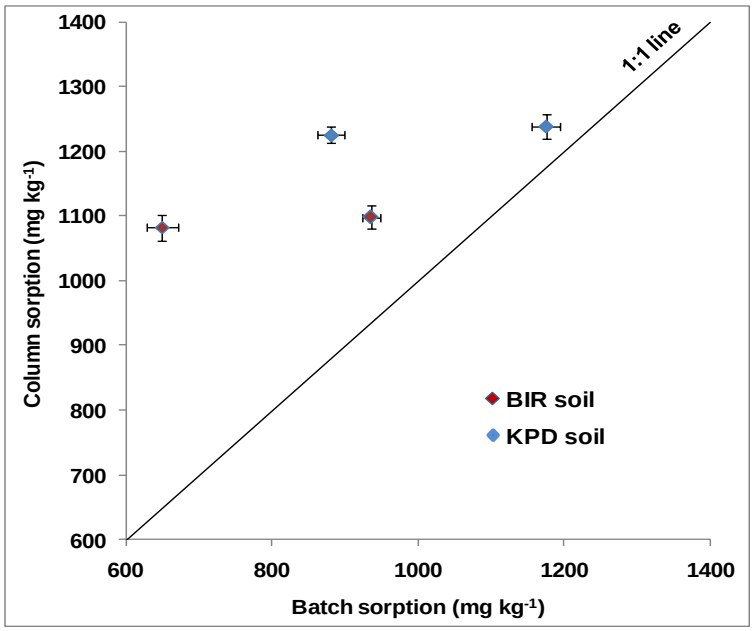


Figure 5.4 Relationship between P adsorption measured in batch (represented by Kf values) and column experiments for Birbie Island (BIR) and Kapunda (KPD) soils amended with FBC**.** Error bars represent the standard deviation between replicates.

Also, column experiments can provide a closer estimation of physical and chemical processes occurring in the field conditions whereas in a batch technique, measuring K_f does not necessarily reproduce the conditions that take place in the environment. For example, in a soil column, water passes through at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a batch experiment.

5.6.2.3 Effect of pH on P leaching

The pH of the leachates were analysed and plotted against their cumulative P concentration. The treatment effects on pH varied based on the type of soil, P sources and CCPs. Of all the treatments, leachate pH increased consistently for FBC amended samples. In the case of BIR, pH in the leachates of FA amended samples increased for both PP and PM treatments, whereas control samples showed decreasing trends in the leachate pH (Figures 5.5 a and b).

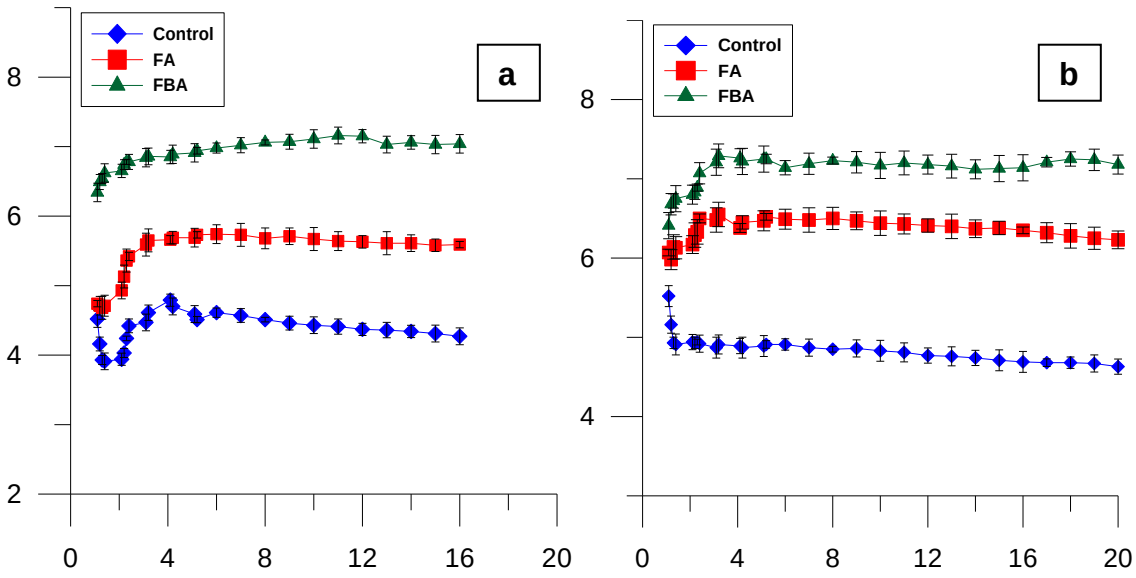


Figure 5.5 Pulse input leaching – pH in the leachates of Birbie Island (BIR) soil, treated with a. PP and b. PM. Error bars represent the standard deviation between the replicates.

For the KPD soil, the P sorption was higher compared to BIR (Chapter 3). The addition of CCPs in PP treated KPD soil showed similar trends as PP treated BIR soil. However, for PM treated KPD soil, the pH in the leachates of FA and FBC showed steady increase, along with increasing P concentrations in the leachates, indicating the mobilisation of manure P (Figures 5.6 a and b). Dou *et al.* (2003) observed that pH and Ca are the main factors influencing P solubility and its reduction in CCPs amended soils. Furthermore, Chen *et al.* (2007) proved that limitations in either pH or Ca concentration i.e., high pH and low Ca concentration or low Ca concentration and high pH in the leachates can negatively affect P immobilisation.

The effect of pH on P leaching was determined by relating the pH of the soil and the cumulatively leached P concentration and the R^2 values were PP-0.7714 and PM-0.3242. In the case of PP treatment, the pH of the soil was negatively correlated with cumulatively leached P and for PM treatment, there was a positive correlation between pH and cumulatively leached P (Figure 5.7). This can be attributed to the increase in the solubility of P, as affected by the CCPs induced pH increase. Moreover, the high increase in the leachate P for FA amended samples is due to the mobilisation of the intact native P content present in FA. The low R^2 value for PM treatment can be attributed to the mobilisation of P from FA, despite lower pH compared to FBC amended samples (Urvashi *et al.*, 2007).

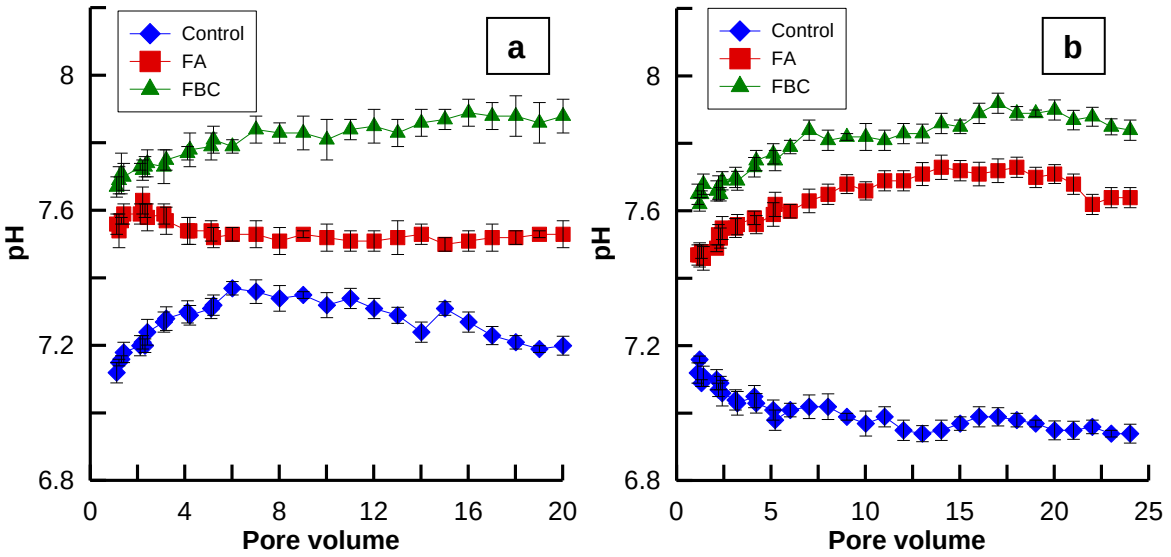


Figure 5.6 Pulse input leaching – pH in the leachates of Kapunda (KPD) soil treated with a. PP and b. PM. Error bars represent the standard deviation between the replicates.

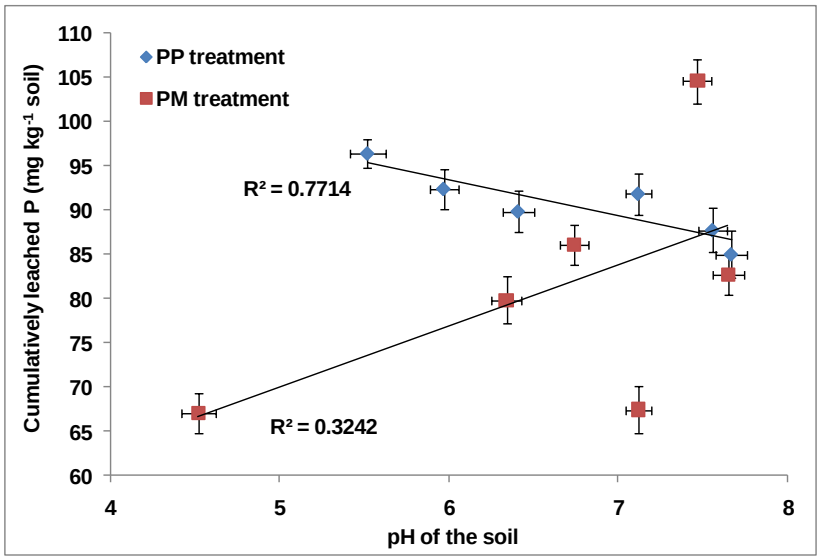


Figure 5.7 Relationship between PP and PM treatments in Birbie Island (BIR) and Kapunda (KPD) soils as affected by addition of CCPs. Error bars indicate the standard deviation between the replicates.

5.6.2.4 Effect of leachate Ca concentration on P leaching

The Ca concentration in the leachates was highest for FA amended samples, followed by FBC (Figure 5.8). For BIR soil, FA and FBC amendment increased pH thereby increasing Ca in soil solution (Mc Dowell, 2004) and consequently reduction in P loss. However, the high P content in FA is also a contributing factor for high loss of P in the early stages of leaching (Pathan *et al.*, 2002). The increasing pH and the relatively high Ca concentration in leachates influenced the decrease in P leaching for FBC amended samples. Dou *et al.* (2002) observed increases in pH and Ca when high rates (200 and 400 g kg^{-1}) of FBC were applied to dairy manure which had a low initial pH (6.01). Hence, Ca concentration in solution along with pH is an important factor in reducing P loss to the environment.

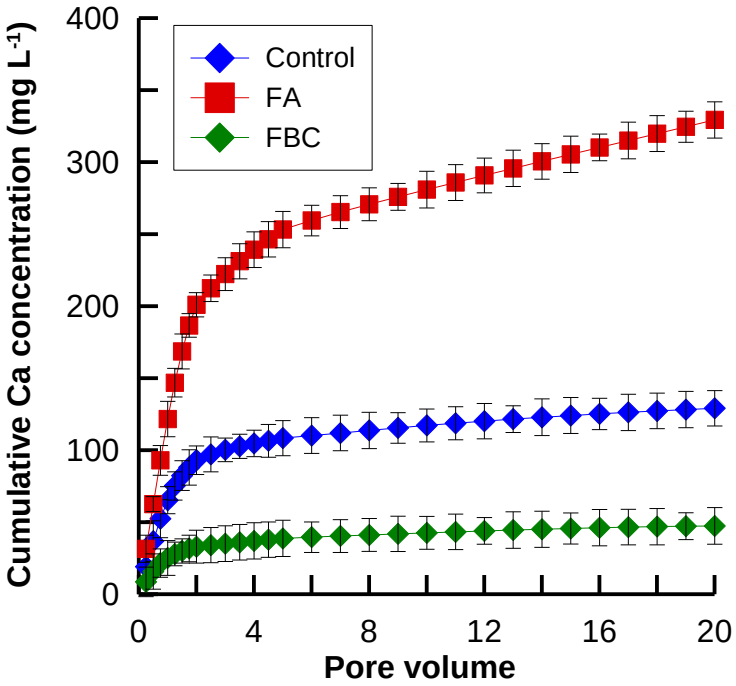


Figure 5.8 Pulse leaching – Concentration of Ca in leachates in PP treated Birbie Island (BIR) soil, as affected by CCPs.

5.7 Conclusions

- Among the soils, P leaching was lower in KPD compared with BIR, reflecting their difference in P retaining capacities.
- Among the CCPs, FBC was effective in the reduction of P leaching, followed by FA. This is attributed to increases in pH and Ca concentration in the leachates.
- While the CCPs enhanced the immobilisation of inorganic P addition (KH_2PO_4), they induced the mineralisation of organic P addition (poultry manure addition).

- Mineralisation of organic P by the addition of CCPs resulted in the mobilisation of P and hence the increase in P leaching for PM treated soils.
- The crucial factor in P immobilisation and transformation by CCPs has been pH. However, high pH triggered P leaching for FA application due to high native P.
- More information on the P in solution and their mobilisation is required to understand the plant uptake of solution P, which will be discussed in Chapter 6 using glasshouse experiments.

Chapter 6

PLANT ACQUISITION OF PHOSPHORUS FROM SOIL ENRICHED WITH INORGANIC AND ORGANIC PHOSPHORUS SOURCES AS AFFECTED BY COAL COMBUSTION PRODUCTS

6.1 Introduction

Agricultural application of nutrients, especially phosphorus (P) has evolved through the last five decades in terms of P sources, application rates, timing of application and additional amendments for enhanced utilisation of P. Being an essential nutrient for plant growth, adequate supply of P is necessary to optimise plant growth, especially in the early stages of development (Grant *et al.*, 2001). The management of P has both economic and environmental implications (Sharpley, 1999). The P applied from inorganic (Pi) sources such as single superphosphate (SSP) and diammonium phosphate (DAP), and organic (Po) sources such as poultry manure (PM) and biosolids have different pathways for P release and also the rate of P release differs significantly between P sources (Headley and McLaughlin, 2005; Turner *et al.*, 2003; Hansen *et al.*, 2004; Bolan *et al.*, 2010). The pH of the soil plays an important role in the (im)mobilisation and bioavailability of P in soils. The inorganic P sources releases phosphate ions which are negatively charged and interact with positively charged iron (Fe), aluminium (Al), and calcium (Ca) ions to form relatively insoluble substances (Stout *et al.* 2000; McDowell, 2005). When this occurs, the P is considered fixed or immobilised or occluded. In the case of organic P sources, the P gets mineralised slowly and consequently the rate of supply of plant available phosphorus is slow compared to Pi application (Shand and Smith, 1997; Kwabiah *et al.*, 2003).

The solubility of the various Pi compounds directly affects the availability of P for plant growth. The solubility is influenced by the soil pH. The maximum P availability occurs at soil pH levels from 6.5 to 7.5 (Lindsay, 1979). But Ullrich-Eberius *et al.* (1984) and Furihata *et al.* (1992) have identified that the P uptake by higher plants was the highest between pH 5.0 and 6.0. When pH is less than 6, plant available P becomes increasingly immobilised with iron and aluminium. When pH values exceed 7.5, P is increasingly made unavailable by fixation in calcium phosphates (Lindsay *et al.*, 1989;

Gray and Schwab, 1993; Grubb *et al.*, 2000). The pH also influences the mineralisation of Po (Chapter 5). An increase in pH increases the phosphatase activity, thereby increasing the mineralisation of organic P (Chapter 5; Lai *et al.*, 1999).

Plants assimilate P only in their orthophosphate forms (HPO_4^- and HPO_4^{2-}), but most soils contain organic and mineral forms of P which are not readily available to plants. When P fertiliser is applied in agricultural systems, only around 20 % becomes immediately available to the crops and the remaining is either immobile or unavailable to the plants because of adsorption, precipitation or conversion to the organic forms (Holford, 1997; Syers *et al.*, 2008). Hence, during successive crops, the P pool needs to replenish for the new crops to grow economically (Smith, 2002; McDowell *et al.*, 2004). This prompted the use of slow release fertilisers including reactive rock phosphates and organic fertilisers. The Po from organic fertilisers can be converted to orthophosphates in the presence of phosphatase enzymes (Figure 6.1), which helps in the mineralisation process (Haygrath and Harvis, 1997; Hayes *et al.*, 2000; Fuentes *et al.*, 2006). Although the mineralisation of Po yields significant P source for plants (Parfitt *et al.*, 2005), an adequate level of P in solution is the prerequisite for plant uptake, especially at the early growth stage of the crops. This is because of high reactivity of phosphate ions to readily bond with soil particles. Hence, there is a need for specific amendments which could mineralise organic P forms and immobilise the orthophosphate P forms.

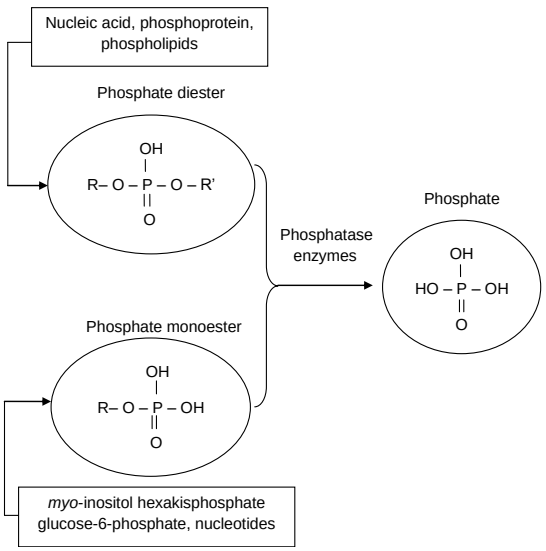


Figure 6.1 Release of phosphate from organic phosphorus compound (Adapted from *Fuentes et al.*, 2006).

Apart from external P applications, there have been a range of amendments such as fly ash (FA), biosolid, red mud and composts have been effectively used for enhancing P utilisation in agricultural crops (Stout *et al.*, 2000; Punshon *et al.*, 2002; Zou *et al.*, 2003; McDowell, 2005). These amendments are not only cost effective, but also a menace to the environment if not utilised. The combustion products from the coal-fired power plants

are effective in P immobilisation and transformation including mineralisation (Sharpley *et al.*, 1998; Stout *et al.,* 1999, Pathan *et al.,* 2002; Mc Dowell, 2005). The increase in soil pH is one of the most significant characteristics of these CCPs for P transformation. The results from the previous Chapters (4, 5 and 6) showed that pH played a significant role in the (im)mobilisation and transformation of P. An increase in pH increased the immobilisation of inorganic P and mineralisation of organic P.

From the results obtained in the previous experiments, FBC emerged as the best amendment in terms of adsorption and transformation of P and hence this plant experiment will aim to examine the effect of FBC on improving the bioavailability of P applied as organic and inorganic amendments. In the previous chapter (6), FBC proved to be effective in reducing the leaching loss of applied P and hence this chapter will cover the overall effect of FBC on plant uptake of the bioavailable P, by considering the leaching characteristics as well. Based on the *a priori* data on adsorption, redistribution and leaching of P in soils, the plant experiment was conducted and hypothesised for the increased bioavailability of P form CCPs incubated soils.

6.2 Objectives

The overall objective is to study the effect of FBC on uptake of P from P treated soil, evaluated using European mustard (*Brassica hirta*) in glasshouse experiments. The specific objectives are,

- To examine the effect of FBC on P concentrations in leachates collected from the drainage of the soil, in the presence of mustard plants.
- To determine the influence of FBC on fresh and residual P in soil by observing the biomass of plants and analysing the P concentration in plants.
- To evaluate the changes in bioavailable P from organic and inorganic P sources applied to FBC incubated soil.

6.3 Hypothesis

- Application of FBC increases adsorption of P in soils and thereby reduces P losses from soils, which is attributed to increases in soil pH and concentration of Ca, Fe and Al in solution (Chapter 3).
- The application of FBC can enhance the uptake of residual P by plants, which is attributed to the transformation of P into available forms.

6.4 Experiment

The major experiments conducted to test the hypotheses and the treatments used in these experiments are listed in Table 6.1.

Table 6.1 Experiments and treatments for plant experiment

Title	Treatments	Measurements/Analysis
Glass house experiment Fresh P application	Soil: Kapunda (KPD). CCPs: FBC (0 and 15% application rates) P sources: PP and PM P levels: 0 and 200 mg/kg	1.Dry weight of roots and shoots 2. P concentration in shoots and roots
Glass house experiment Residual P effects	Soil: Kapunda (KPD). CCPs: FBC (0 and 15% application rates) P sources: PP and PM P levels: 0 and 200 mg/kg	1. Dry weight of roots and shoots 2. P concentration in shoots and roots
Leaching experiment	Soil: Kapunda (KPD). CCPs: FBC (0 and 15% application rates) P sources: PP and PM P levels: 0 and 200 mg/kg	1.Total P concentration in leachates 2.Total P concentration in pore water

6.5 Materials and methods

6.5.1 Characterisation of soils, CCPs and P sources

The plant growth experiments were performed using a sandy loam collected from Kapunda (KPD), South Australia (Table 3.1, Chapter 3). The CCPs used was fludised bed combustion ash (FBC) from Redbank power station, Queensland. The P sources applied to the soil were inorganic P (KH_2PO_4 - PP) and organic P (poultry manure - PM). The objective for using two different P sources was to deduce the effects of FBC on inorganic and organic P applications for effective plant growth. The characterisation of the materials used was previously explained in Section 3.4.2 (Chapter 3) and the properties of the materials used were also shown in Tables 3.3, 3.4 and 4.4 (Chapters 3 and 4).

6.5.2 Sample preparation

The KPD soil was first treated with two P sources (PP and PM) at the rates of 0 and 200 mg P kg^{-1} soil. The soils were incubated in plastic bags for 7 days at 80 % of the total water holding capacity (WHC). Soils incubated without P treatment served as control. After 7 days of incubation, all the P treated soils were incubated with FBC at the rates of 0 and 15 % (w/w). The CCPs treated samples were incubated for 21 more days at 80 % of the total WHC in a glass house.

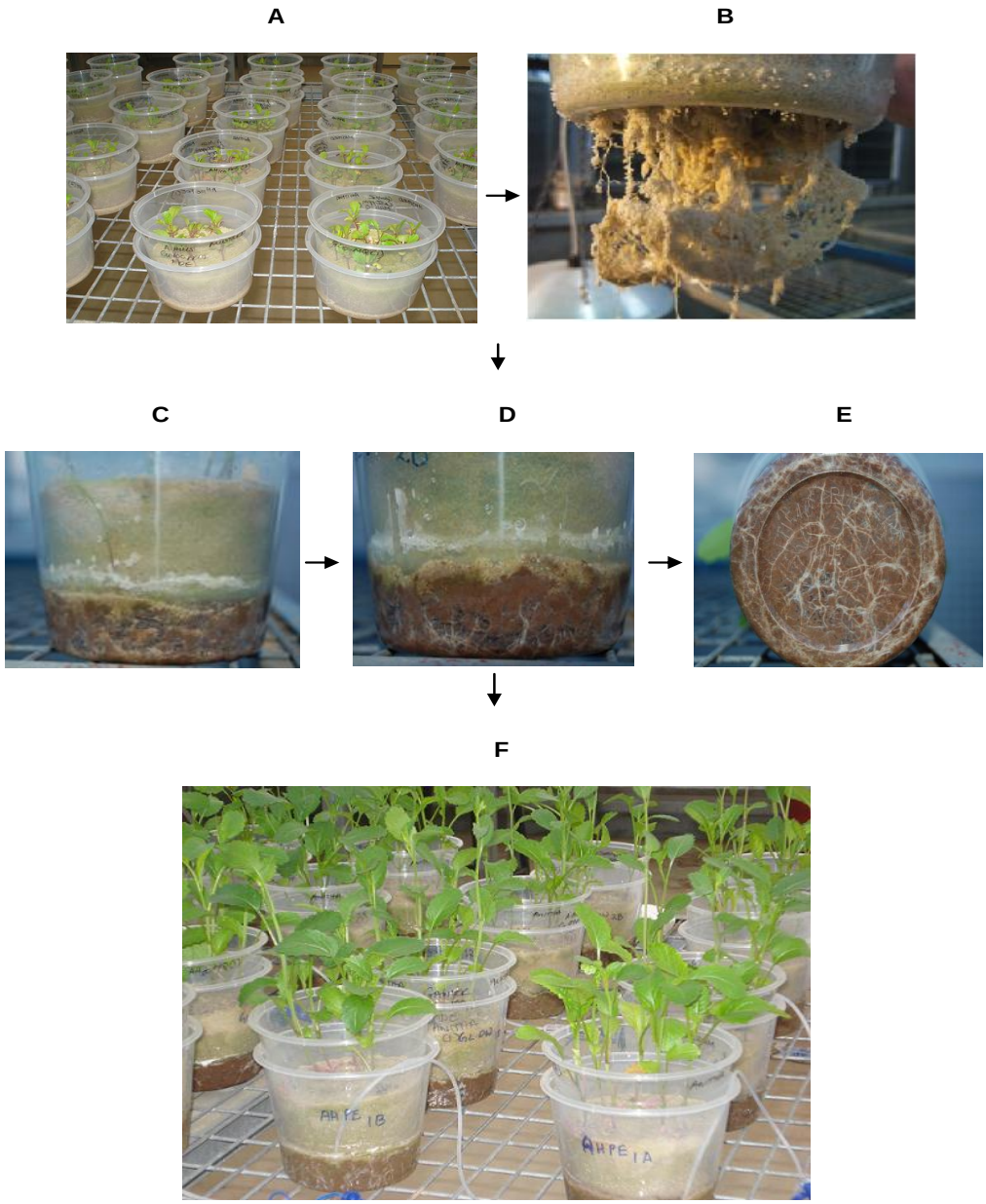
6.5.3 Plant growth experiment

The method devised by Stanford and Dement, originally developed to measure plant available phosphorus in soil (Stanford and DeMent, 1957) was used for the plant growth experiment in this chapter. This method permits the measurement of nutrient absorption by plants during relatively short periods of root-soil contact. In the usual pot-type plant assay, the seed is germinated in the soil material to be tested and permitted to grow for a specified period of time. Such a technique imposes limitations such as, (i) possible secondary effects of soil treatment on seed germination and seedling growth, prior to the time which the metal may affect the plant, (ii) undue length of time for chemical or microbial activities to occur in the soil resulting in masking of the effects of the original treatment, (iii) the usual problems of obtaining uniform seedling stands for suitable controls. The advantages of Stanford-Dement bioassay are (i) short term effects on higher plants where dry matter production is not the parameter of concern, (ii) simple and economical to use and allows for adequate replication without much work and (iii) only small quantities of soil are needed. The procedure used for the current experiment includes the following steps.

- Two plastic containers of two different sizes (small containers - 250 mL and the larger ones - 700 mL) were used for germination of the mustard seeds. The small container was completely cut at the bottom and placed into the larger one. The inner container was filled with 300 g of sand.
- Approximately, 16 seeds of mustard were sown directly below the surface and the plants were thinned to 10 plants per pot after germination. Macro (P excluded) and micro nutrients were supplied and the plants were watered regularly to field capacity for 2 weeks during germination period. The moisture was maintained to field capacity after thinning as well.
- After 4 weeks of plant growth, the inner container containing the sand and the roots were transferred to another intact pot containing 200 g of incubated soils and moisture content of the soil were maintained at 80% field capacity with deionised water.
- Two sets of soil pots were prepared – one for leaching and the other was not allowed to leach. The soil pots for leaching were cut at the bottom and a cotton mesh was placed for each pot before adding soil to avoid any soil loss. These pots were leached with 100 mL of deionised water and the leachates were collected during the experiment at 3 intervals (1, 2 and 3 weeks).

- Plants were harvested after 3 weeks of growth in the soil media and were dried to a constant weight at 70°C. Dry weight was recorded and the dried plant samples were ground to a fine powder for P analysis.
- Seeds from the same source of *Brassica hirta* were re-sown in the harvested pots and similar procedure was followed as for the first crop.

Plate 6.1 Set up of Stanford – DeMent bioassay technique



A: Plastic containers nested in another container with bottoms removed; **B:** Dense root mat facilitating easy transfer; **C:** Transferring plants to treated soil; **D:** Roots entering the treated soil; **E:** Fully established root-soil contact; **F:** Transferred plants.

6.5.4 Leachate analyses

Leachates were collected using the plastic containers at 7, 14 and 21 days after the transfer of pots to the treated soil. Prior to leaching, the moisture content of the soil was maintained at 80 % of WHC and 100 mL of deionised water was added for leaching. The leachates were collected from the bottom container and pH was measured immediately. After pH measurement, the samples were stored at 4° C for the analysis of total P using ICP-OES (Agilent).

6.5.5 Plant analysis

After harvesting plants, the roots and shoots were separated, washed with Milli-Q water and the dry weight was recorded. The samples were then dried to constant weight at 70°C by using a forced-air oven and ground to a fine powder for P analysis. The ground plant material (0.4 g) was weighed directly into 75 mL digestion tube, 5 mL of concentrated nitric acid was added and left to cold digest in a fume cupboard overnight. After keeping the samples overnight, the tubes were heated using a temperature controlled digestion block (AI Scientific Block Digestion System AIM 500) programmed to slowly increase the temperature to 140°C until, approximately 1 mL of digest remained in the tube. The tubes were brought to room temperature prior to dilution with Milli-Q water. The samples were mixed thoroughly and filtered with a syringe filter directly into plastic containers. The digested plant extracts (along with blanks) were analyzed for P by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent).

6.5.6 Soil analysis

The incubated soil samples were analysed for pH, EC, Olsen extractable P and phosphorus retention capacity (PRC) before commencing the experiment as mentioned in Section 3.4.

6.5.7 Statistical analysis

For statistical analysis of data, Excel 2010 package was used. The differences in the replicates were determined using standard deviation for the chemical properties of materials used and also the experimental results. Relationships between Olsen P and bioavailable P was evaluated by means of simple linear regression analysis. The difference between the P concentration in first and second crop was studied using Student t test and the significant level was $p>0.05$.

6.6 Results and discussion

6.6.1 Properties of soils, CCPs and P sources used

The properties of the materials used were already shown in Tables 3.3, 3.4 and 4.4 (Chapters 3 and 4). The KPD soil has low Olsen P and P retention capacity (PRC) and the pH is 7.1. The pH of FBC is high (12.7) and the calcium carbonate equivalence (CCE) is 23.25 %. The CCE of FBC used by Stout *et al.* (2000) and Dou *et al.* (2003) was 12.1 and 13.0% respectively. The poultry manure used in this study contained high Olsen P concentration (643.22 mg P kg^{-1} PM).

The elemental composition of the materials were analysed using ICP-OES after acid digestion and KPD soil contained 25.87% of Al and 18.17% of Fe. The Al and Fe contents in FBC were 34.02 and 15.76 % respectively, with high Ca content (49.68 %). The Ca content in FBCs used by Stout *et al.* (2000) and Dou *et al.* (2003) were 8.7 and 16.1 % respectively. The P contents in P sources were 14.78 % for PM and 22.76 % for PP.

6.6.2 Leachate P analyses

6.6.2.1 Mobile P

The vertical mobility of P was clearly influenced by the addition of CCPs and their influence on P adsorption (Chapter 3) and transformation characteristics (Chapter 4). In the first crop, P in the leachates decreased significantly after FBC application in PP treated soil but increased in PM treated soil. Addition of FBC to PP treated soil reduced the P in leachate from 3.99 to 2.58 % of the applied P, which constitutes around 64 % reduction in leachate P concentration. Stout *et al.* (1999) applied 1 % of FBC (CCE-31 %) to a loamy soil with similar pH (7.2) to the soil used in this study and observed around 60 % of decrease in the concentration of water-soluble P. They attributed this reduction in soluble P to the neutralising capacity of FBC, resulting in the transformation of P to calcium phosphates. Contrastingly, the effect of FBC on PM treated soil resulted in a slight increase of P in leachate from 2.78 to 3.06 % of the applied P (Figure 6.2). Overall, the effect of FBC on PP was attributed to the immobilisation of inorganic P (Chapter 3) and in the case of PM, the increase in leachate P concentration was related to the mineralisation of organic P and increase in phosphatase activity (Chapter 4; Trasar-Cepada and Carballas, 1991; Lai *et al.*, 1999).

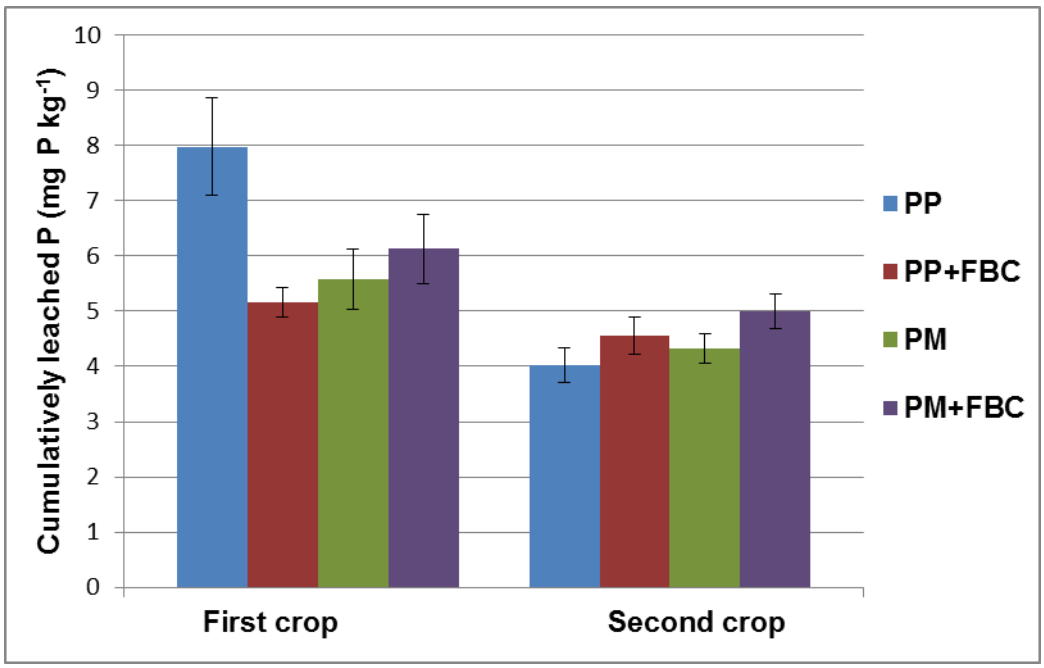


Figure 6.2 Cumulative P leaching – effect of FBC on P mobility in Kapunda (KPD) soil treated with inorganic (PP) and organic (PM) P sources. Error bars represent the standard deviation between the replicates.

In the case of second crop, the remaining or the residual P was generally mobilised by FBC addition, which resulted in up to 12 % (from PP) and 14 % (from PM) increases in the leachate P concentration for the FBC treated samples (FBC+) compared to the non-treated (FBC-) ones. A higher P concentration in the leachates was observed for PM treated soils, compared to PP treatment (Figure 6.2). This is attributed to the mineralisation of organic P and the slow release characteristics of PM (Trasar-Cepada and Carballas, 1991; Toor and Bahl, 1997). Interestingly, some poultry manure used by Moore *et al.* (2000) and Dou *et al.* (2003) contained water soluble P, which was reduced using amendments such as alum and FBC. Also, Urvashi *et al.* (2007) utilised farm manure to examine their effects on mobilising P in FA and found up to 50 times increase in soluble P. Bhattacharya and Chattopadhyay (2002) used cow dung and earthworm compost to increase the P availability in FA.

6.6.3 Plant analysis

6.6.3.1 Plant biomass

The plant biomass reflected the yield of plants for the two different (inorganic and organic) P applications and subsequent effects of FBC (Figures 6.3 to 6.7). The fresh P applied as PP increased yield in both leached and unleached pots, but the influence of FBC on the yield was negligible. In unleached, PP gave higher yield without FBC application, whereas in leached, the yield showed similar results both in the presence and absence of FBC. This is because of the immobilisation of inorganic P, resulting in reduced

bioavailable P (Chapter 3). McDowell (2005) observed increases in tightly bound P on FA application to grassland soils. The difference in the effect of FBC on yields between leached and unleached treatments may be attributed to the difference in the amount of bioavailable P. There was no significant effect of CCPs in no P treatment (Figure 6.3).

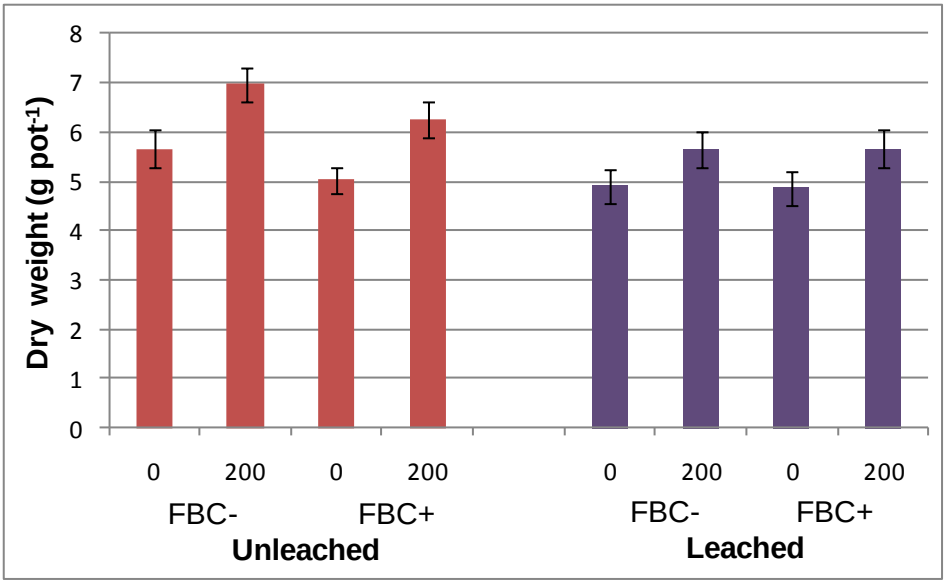


Figure 6.3 Effects of FBC on biomass yield in PP treatment – fresh P application. Error bars represent the standard deviation between the replicates.

Yield data from the second crop showed similar trends to the freshly applied PP only for unleached pots. For the leached pots, the PP gave higher yield in the presence than absence of FBC application (Figure 6.4). This is attributed to the mobilisation of the tightly bound P or the residual P, which resulted in the increase in bioavailable P when P was subjected to leaching. Yang *et al.* (2007) used various amendments to study their effect on the reduction of leaching loss of P applied a KH_2PO_4 and observed that the release of loosely adsorbed or water soluble P was a fast reaction, whereas tightly bound P were more slowly and steadily released. However, Stout *et al.* (2000) studied the effectiveness of CCPs in controlling P export from high P soils and observed negligible effect on the yield of canola plants as measured by their dry matter yield, although there was reduction in P loss through runoff.

In the case of unleached pots, the combined yield showed less influence of FBC compared to control, whereas there was an increase in cumulative yield on the addition of FBC in leached treatment. (Figure 6.5). There were no significant differences in the plant yields between the leached and unleached experiments.

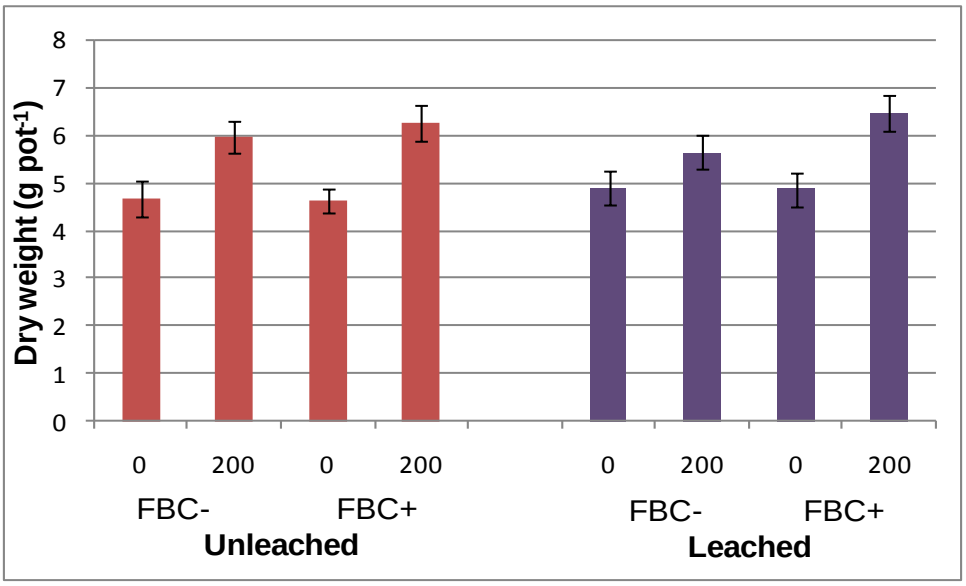


Figure 6.4 Effect of FBC on biomass yield in PP treatment – residual P effect. Error bars represent the standard deviation between the replicates.

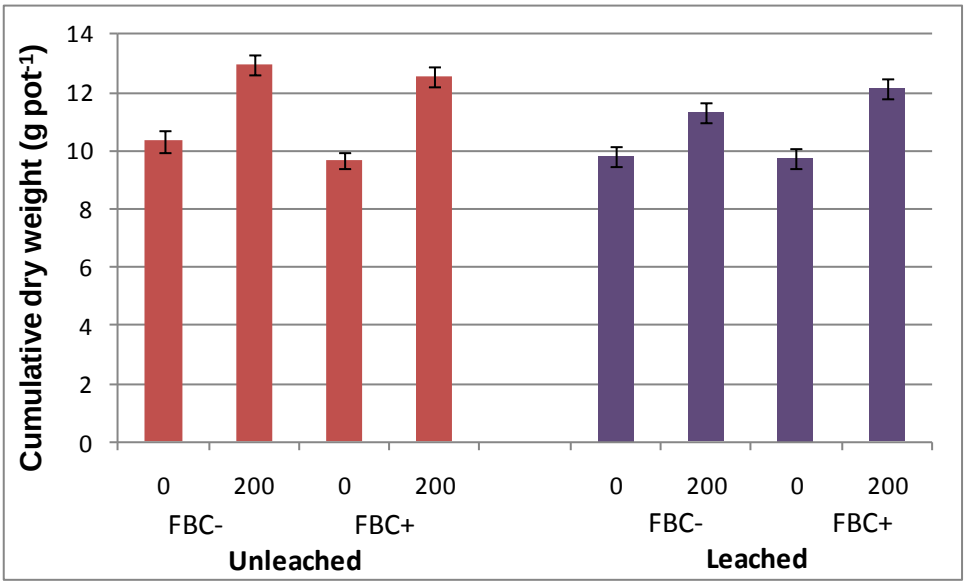


Figure 6.5 Effect of FBC on cumulative (fresh P + residual P) biomass yields in PP treatment.Error bars represent the standard deviation between the replicates.

The organic P applied as PM showed contrasting results on the yield compared to PP treatment. There was less difference between unleached and leached treatments in the absence of FBC (FBC-) for fresh PM, compared to fresh PP application, except for an increase in the yield observed for FBC+ samples in unleached. The effect of FBC was minimal in leached samples, with no significant increase in the biomass (Figure 6.6). The overall biomass data for the first crop suggests that the yield was less in PM treatment compared to PP treatment (Figures 6.3 and 6.6).

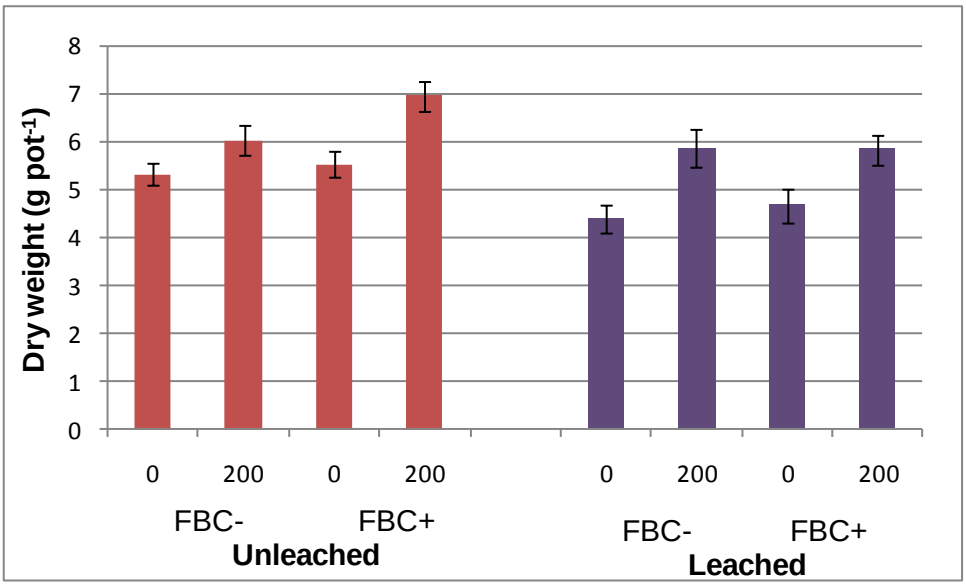


Figure 6.6 Effect of FBC on biomass yield in PM treatment – fresh P application. Error bars represent the standard deviation between the replicates.

In contrast with PP, the yield from the remaining P (residual effect) of PM treatment was more than the first crop, especially in the unleached (Figure 6.7). The increase in yield due to PM application in the second crop is attributed to slow release characteristics of PM and also the mineralisation effects of FBC (Chapter 4; Trasar-Cepada and Carballas, 1991).

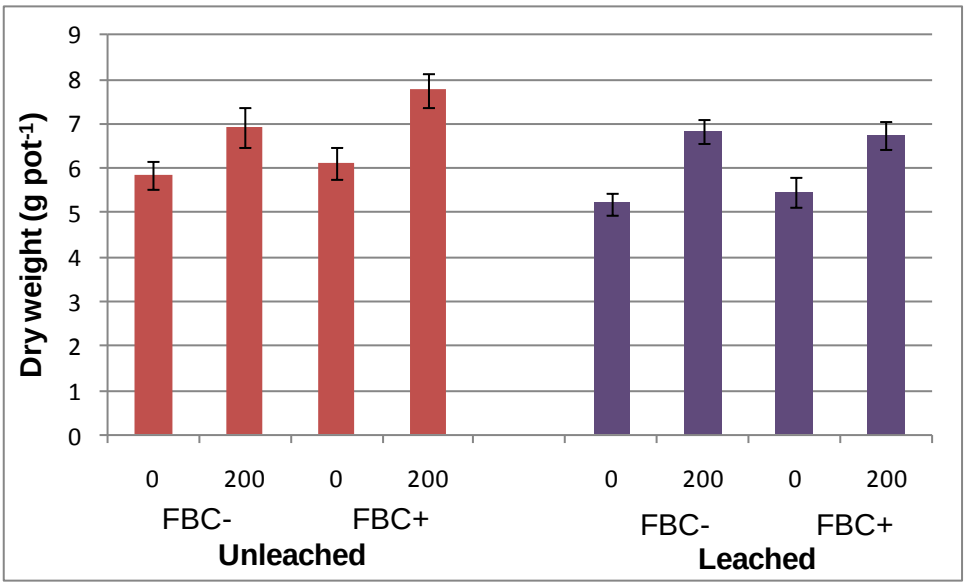


Figure 6.7 Effect of FBC on biomass yield in PM treatment – residual P effect. Error bars represent the standard deviation between the replicates.

Therefore, in terms of dry matter yield, amendment of FBC to freshly applied PP soil resulted in around 10.05 % decrease in plant biomass for unleached treatment and no significant change in leached treatment. The residual P was mobilised by FBC, which increased the plant biomass by 4.78 % for unleached treatment and by 12.57 % in leached pots. The effect of FBC in PM treatment was large compared to PP application. For unleached samples, there was a 3.09 % increase in plant biomass and for leached

samples, there was 6.81 % increase in plant growth between first and second crops as a result of FBC application.

6.6.3.2 Effect of FBC on P uptake in plants

The effect of FBC on mobilising P from PP and PM were clearly evident in the dry matter yield of the plants. The FBC enhances the P uptake from PP and PM, especially under leaching conditions. For PP treatment, P concentration in the shoot biomass of unleached plants was lower with FBC application than without FBC. In leached pots, the P concentration in the biomass was higher on the application of FBC (Table 6.2). The P concentration in the second crop gradually decreased for all the treatments. In the case of PM treatment, the effects were opposite (Figure 6.8). The P from the remaining P in soil was taken up more compared to the first crop, owing to the slow release and mineralisation of the organic P (Section 6.6.3.1).

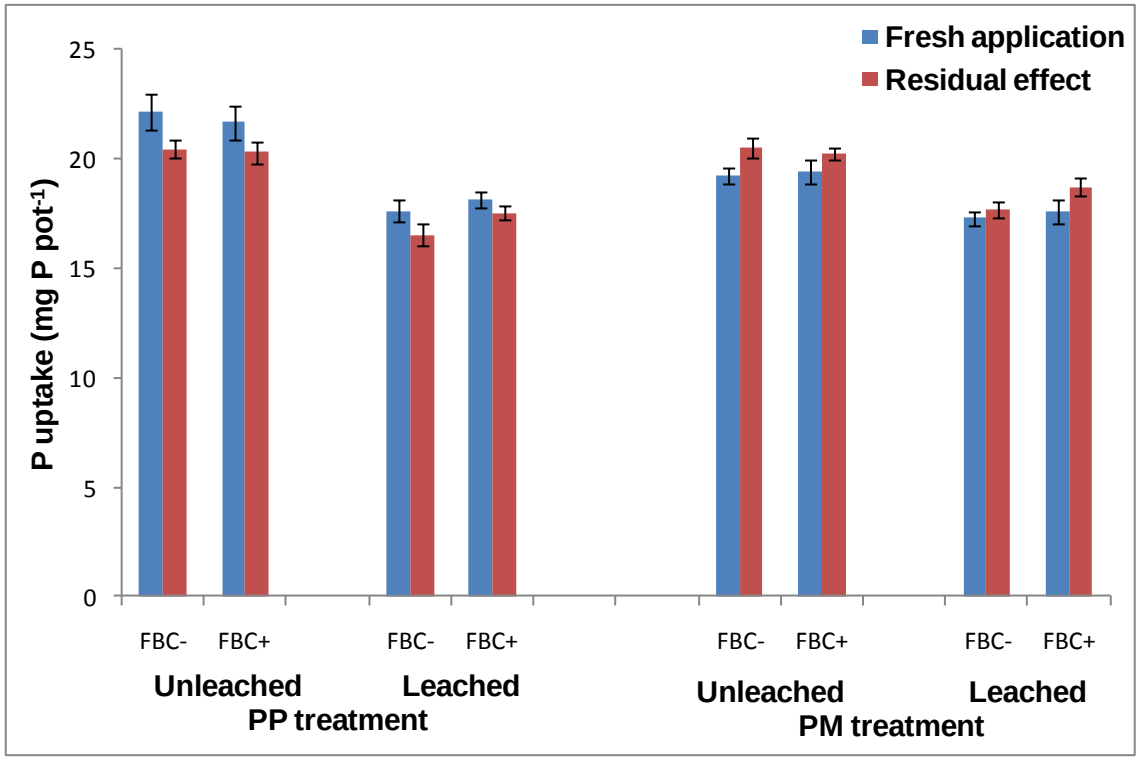


Figure 6.8 Effect of FBC on P uptake in plants for fresh P application and residual P effect. Error bars represent the standard deviation between the replicates.

Therefore, the influence of FBC on the uptake of P from PP and PM followed the trends of plant biomass. The uptake of P was calculated using the following formula (Eq. 6.1),

$$Uptake\ of\ P = Total\ P\ concentration\ in\ shoots\ x\ Plant\ biomass \qquad (6.1)$$

Table 6.2 Effect of FBC on P concentration in shoots

P source	FBC treatment	First crop	Second crop
		mg P plot^{-1}	
PP unleached	FBC-	2975±3.061	2987±4.582
	FBC+	2986±8.734	2973±3.069
PP leached	FBC-	2943±3.061	2927±4.732
	FBC+	2991±7.518	2993±3.614
PM unleached	FBC-	2984±3.063	2978±2.657
	FBC+	2974±6.037	2974±4.513
PM leached	FBC-	2937±5.865	2941±5.131
	FBC+	2948±5.512	2949±4.365

In the case of PP treatment, the FBC increased the P uptake for both fresh P and residual P treatments only in leached samples. For unleached samples, the decrease in P uptake for both fresh and residual P treatments was not significant. For the leached PM treated soils, the P uptake increased in the presence of FBC in both fresh and residual P treatments, but the increase (5.12 %) was significant only for the residual P effect. Dou *et al.* (2003) observed that CCPs induced transformation of manure phosphorus has little influence on the availability of P to crops, but strongly influences the reduction of potential P loss in the environment. Stout *et al.* (2003) examined the effect of FGD on plant uptake of P in high P soils (high rates of fertiliser and manure application) and found minimal decrease in plant production after three growth cycles and harvest with 20 % increase in cumulative plant P uptake.

6.6.3.3 Effect of FBC on bioavailable P concentrations

The bioavailable P was obtained by adding the total P concentration in the plant tissues and total P concentration in the leachates (Eq.2).

$$\boldsymbol{Bioavailable\ P} = \boldsymbol{Total\ P\ concentration\ in\ plant\ tissues} + \boldsymbol{Total\ P\ concentration\ in\ leachates} \quad \textbf{(6.2).}$$

The results on the overall bioavailable P including both fresh P application and the residual P effect suggest that FBC increased the P significantly in solution only for unleached PM treated pots (Figure 6.9). The organic (PM) treated soil showed higher bioavailable P values compared to PP treatments, although it was not significant in leached treatments. The FBC increased the bioavailable P for unleached PM treatment with 11.97 % increase in the cumulative bioavailable P concentration, but for all other treatments, the changes in cumulative bioavailable P was negligible.

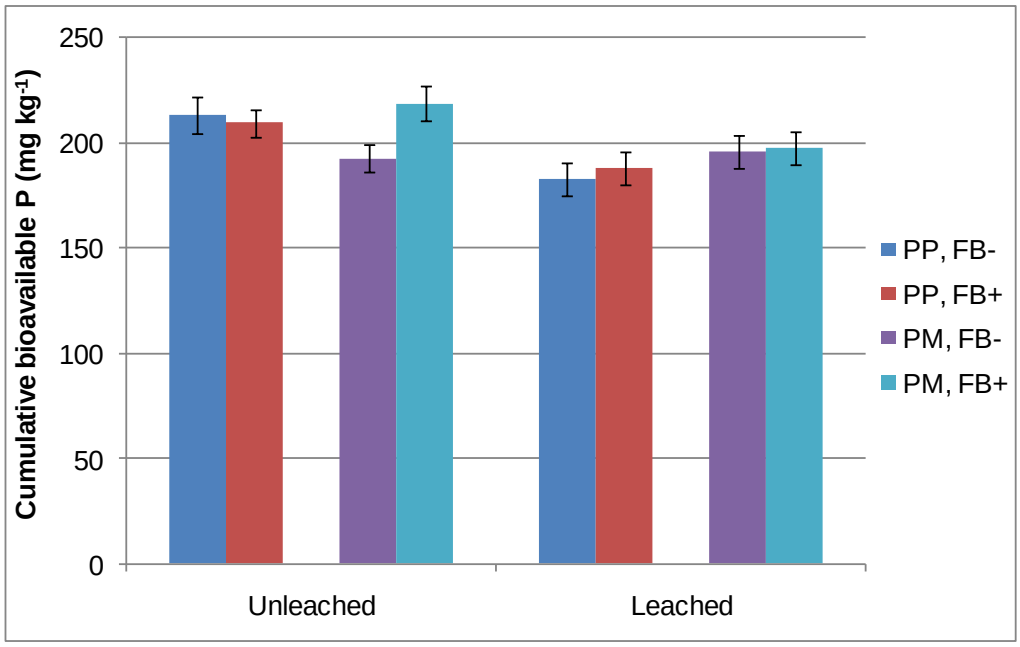


Figure 6.9 Effect of FBC on bioavailable P concentrations in the shoots for unleached pots and shoots and leachates for leached pots. Error bars represent the standard deviation between the replicates.

A 1:1 line graph between Olsen P values and the bioavailable P suggests that bioavailable P values derived from this experiment was higher than the Olsen P measured separately from the soils before plant growth (Figure 6.10). Also, the regression between Olsen P and the bioavailable P values suggests the close relationship between these values, with PM treated soils showing lower correlation compared to PM treated soils.

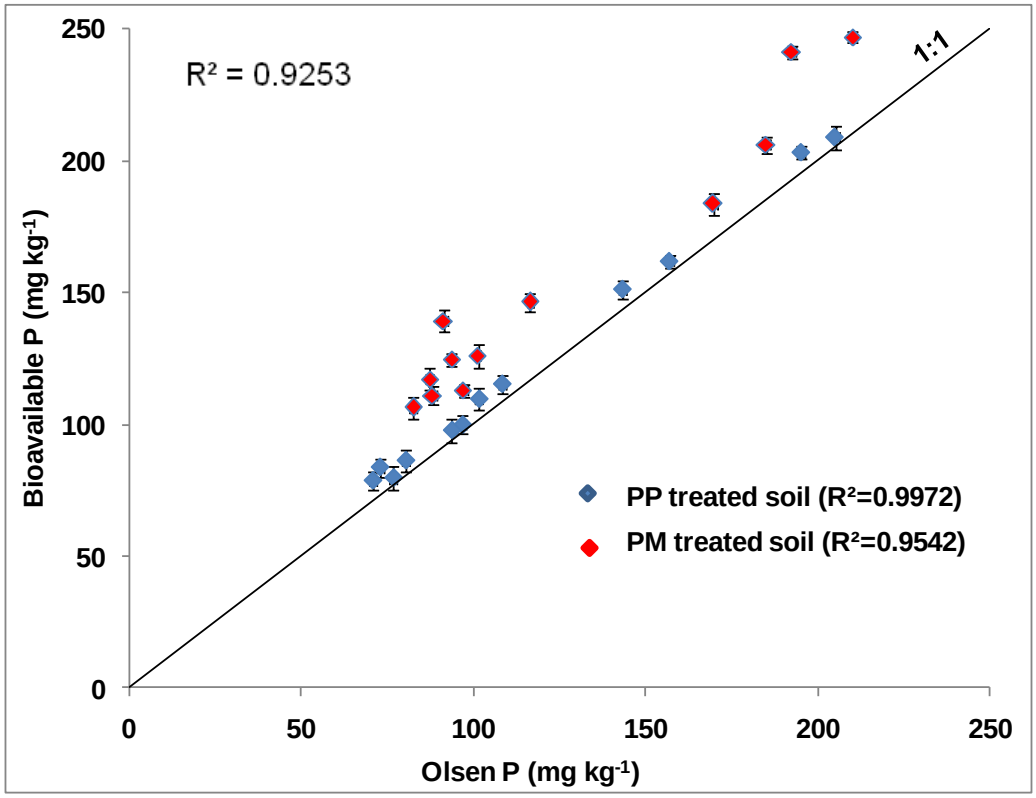


Figure 6.10 Relationship between Olsen P in soil and Bioavailable P in plants. Error bars represent the standard deviation between the replicates.

6.7 Conclusions

- Plant uptake of P increased with both inorganic and organic P application and the yield of the mustard plants reflected the uptake of P
- The effect of FBC on the yield of the mustard plants are as follows,
    - In the case of fresh PP application, FBC decreased the yield which is attributed to the immobilisation of fresh P
    - For residual PP, the yield increased because of the mobilisation of the adsorbed P
    - Fresh application of PM showed low yield compared to PP, but addition of FBC ensured increases in the yield
    - The influence of FBC on PM treated soil was greatest in the second crop, as there was an increase in the yield, which is related to FBC induced mineralisation.
- The effect of FBC on P uptake by plants validated the results from the previous chapters, which explained the FBC-induced immobilisation of inorganic P sources and FBC-induce mineralisation of organic P sources.
- Although FBC was effective in transforming both inorganic and organic P forms, the response to organic P treatment was more pronounced.

Chapter 7

THE EFFECT OF BIOSOLIDS ON PLANT AVAILABILITY OF APPLIED PHOSPHORUS AS AFFECTED BY COAL COMBUSTION PRODUCTS

7.1 Introduction

The incessant rise in global population and the consequent increase in the demands for food production have put enormous pressure on land and water resources. As a result, soils are turning out to be the direct calamity of the anthropological activities such as food production and waste disposal. Firstly, the intensive use of agricultural inputs for maximising crop yields has not only provided nutrients to the growing crops, but also added undesirable nutrients and heavy metals into the soil. On the other hand, disposal from the industrial activities and the release of toxic contaminants to the environment also degraded several productive land resources resulting in the non-availability of lands for agricultural activities. Over decades of agricultural and environmental research, a need for selecting ideal agricultural amendments in the form of wastes and byproducts has been stressed and optimal usage of those products has been advocated to farmers. Remediation of contaminated landfill sites using several organic and inorganic wastes is also a current area of huge interests (Dick *et al.,* 2000; Basta, 2000; Basta *et al.*, 2001; Brown *et al.*, 2004; McLaughlin *et al.*, 2007; Park *et al.*, 2011).

The use of coal combustion products (CCPs) on improving the bioavailability of P has been increasingly explored by many researchers (Bhattacharya and Chattopadhyay, 2002; Pathan *et al.,* 2003; Urvashi *et al.,* 2007). The CCPs such as fly ash (FA), fluidised bed combustion ash (FBC) and flue gas desulphurisation gypsum (FGD) have proven capabilities on the overall transformation of P in soils (Chapter 4; Stout *et al.*, 2000; McDowell 2005). Moreover, the immobilisation of inorganic P and mineralisation of organic P have been the most significant characteristic of these CCPs in relation to the utilisation of P by plants (Chapter 6). Pathan *et al.* (2003) observed increase in bioavailable P from 18.5 to 43 mg kg^{-1} soil in FA amended soil under laboratory conditions. Most of the studies pertaining to plant P availability from soils amended with CCPs were conducted at laboratory scale and a very few researches were conducted at the field level. Ram *et al.* (2007) used lignite FA for long term field trials on an

experimental agricultural plot and observed increased available P (Olsen P) content from 4.5 to 5.6 mg kg^{-1} soil and a consequent increase in the yield of maize crops.

Results in Chapter 6 have demonstrated that the addition of CCPs enhanced the mobilisation of organic P source (i.e. poultry manure) which has been attributed to the increase in alkaline phosphatase activity. There have been increasing interests in the co-composting of organic wastes such as biosolids (BS) with CCPs, thereby reducing the bioavailability of heavy metals in BS (Wong and Su, 1997; Asokan *et al.,* 2005; Punshon *et al.,* 2002; McLaughlin *et al.*, 2007). These co-composted products are used to reduce heavy metal phytotoxicity in contaminated sites, thereby facilitating revegetation (Theodoratos *et al.*, 2000; Haynes *et al.*, 2009). It is important to examine the effect of these co-composts on the bioavailability of nutrients including P. Pritchard *et al.* (2008) reported that land application of lime-amended BS has increased the nutrient value (including P) from BS. Also, BS-amended soils with the addition of alum or iron sulphate have prevented loss of P from soil (Peters and Basta, 1996; Huang *et al.* 2007). Some of the CCPs, especially FBC has liming value similar to conventional liming materials such as lime and dolomite (Wang *et al.,* 2006) and also possess some properties similar to alum in terms of P immobilisation (Dou *et al.,* 2003). Hence, CCPs can be investigated for facilitating P availability in soils amended with organic or/and inorganic amendments.

The complexity of soil and high degree of spatial and temporal variation as one moves from small to large experimental scales forces the scientific community to validate the results obtained from laboratory studies using field trials. In this chapter, the effect of BS on the bioavailability of P from single super phosphate (SSP) in FBC amended soil will be reported using the field performance of Indian mustard and sunflower grown on an Anthroposol (Urban Landfill) in South Australia.

7.2 Objectives

The overall objective of this study is to examine the effect of biosolids on the bioavailability of P as affected by FBC addition under field conditions. The specific objectives of the study include:

- To compare the influence of FBC on the growth of two different plant species with varying P accumulation characteristics under field conditions.
- To evaluate the role of FBC in mobilising P from various amendments (organic and inorganic) applied in the soil.
- To monitor the FBC induced phosphatase activity in soil and the resultant dynamics in P uptake.

7.3 Hypothesis

- Application of FBC increases adsorption of freshly applied inorganic P and mobilisation of organic P in soils, mainly due to the increase in pH (Chapters 3 and 4)
- The adsorbed P (aged P) can be mobilised using FBC, which can enhance the uptake of P in plants by increasing the bioavailable P.
- The addition of FBC mobilises both organic and inorganic P in BS for plant uptake, through increase in pH-induced phosphatase activity.

7.4 Experiments

The major experiments conducted to test the hypotheses and the treatments used in these experiments are listed in Table 7.1.

Table 7.1 The major experiments and the treatments used in this Chapter

Title	Treatments	Treatment Combinations
Field experiment **Fresh P application**	Soil: Anthroposol **Amendments:** P source: SSP (0, 0.05 Mg P ha^{-1}) Organic source: BS (0 and 50 Mg ha^{-1}) CCPs: FBC (0 and 25 Mg ha^{-1}) **Plant species:** Sunflower (*Helianthus annuus)* Indian Mustard (*Brassica juncea*)	1. Nil, SSP alone, BS alone, FBC alone 2. SSP+BS, SSP+FBC, BS+FBC 3. SSP+BS+FBC
Field experiment **Residual P effect**	Soil: Anthroposol **Amendments:** Second cropping on the previously amended soil. **Plant species:** Sunflower (*Helianthus annuus)* Indian Mustard (*Brassica juncea*)	1. Nil, SSP alone, BS alone, FBC alone 2. SSP+BS, SSP+FBC, BS+FBC 3. SSP+BS+FBC

7.5 Materials and methods

7.5.1 Site Description

The experimental site (17 hectares) is located in Saint Kilda, South Australia, approximately 23 km NNE from Adelaide CBD. The landfill site is owned and operated by Salisbury City Council. The municipal landfill began operation in the 1950's and received general municipal waste, including green waste, up to 1990. Subsequently, the landfill was capped with a clay liner, which is classified as a Technosol (IUSS, 2007) or as Anthroposol in the Australian classification system (Isbell, 1996).

7.5.2 Experimental Design

A field experiment was conducted at the Municipal Landfill site at Saint Kilda, South Australia to examine the effect of FBC on the bioavailability of applied inorganic P (SSP) as affected by BS addition. A 10 m x 3 m plot was cleared off a week before the commencement of the experiment to prepare the land for the experiment. The soil at this site is classified as an Anthroposol. The cleared area was equally divided into two blocks and further segregated into eight 1 m^2 plots with definite spacing between each plots. Each plot was treated with the treatment combinations discussed below. One plot from each block was not treated with any of the above products listed in Table 7.1 and served as control. Application rates were: BS - 0 and 50 Mg ha^{-1}, SSP - 0 and 0.05 Mg ha^{-1} and FBC - 0 and 100 Mg ha^{-1}. Amendments were mixed to the top 20 cm of the soil. After 3 weeks, 4 g of sunflower (*Helianthus annuus* "Yellow Impress", Yates Australia) and 0.3 g of Indian mustard (*Brassica juncea* 'Varuna', Department of Primary Industries, Horsham Victoria) seeds were added in four rows per plot (Plate 7.1). They are fast growing plants with different P accumulating capacities (Sharma *et al*. 2007). In total, 16 experimental plots existed with eight per plant species (treatment combinations: control, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS).

The plots were irrigated alternative days with the water from the Salisbury Council. Weeding was necessary twice and an insecticide named Confidor from Yates (Australia) was applied approximately three weeks after germination. The plants were fully grown by three months time since sowing and the entire plants were harvested, washed with Milli-Q water and dried to a constant weight at 70°C. Dry weight was recorded for each row within the plots and the dried plant samples were ground to a fine powder for P analysis. The plots were mowed immediately after the harvest and fresh seeds were sowed again as previously mentioned. The plants were again harvested after three months and the dry matter yields were recorded.

7.5.3 Plant analysis

The ground plant material (0.4 g) was weighed directly into 75 mL digestion tube, 5 mL of concentrated nitric acid was added and left to cold digest in a fume cupboard overnight. After keeping the samples overnight, the tubes were heated using a temperature controlled digestion block (AI Scientific Block Digestion System AIM 500) programmed to slowly increase the temperature to 140 $^{\circ}C$ until, approximately 1 mL of digest remained in the tube. The tubes were brought to room temperature prior to dilution with Milli-Q water. The samples were mixed thoroughly and filtered with a syringe filter directly into plastic containers. The digested plant extracts (along with blanks) were

analysed for P by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent).

Plate 7.1 Field description (a) Tilled plots before sowing; (b) Fully grown crops



7.5.4 Soil analysis

The soil was sampled at three different spots from each plot for uniform assessment and were analysed for pH, EC, $NaHCO_3$ extractable (Olsen) P, and phosphorus retention capacity (PRC) as mentioned in Section 3.4. Soil sampling was carried out after three weeks of amendment addition and just before seed sowing.

7.5.5 Analysis of phosphatase activity

The soil samples were collected from each plot as mentioned in Section 7.5.4 after the first cropping. Enzyme activity is done using field moist soils. The collected soils were air dried and the phosphatase activity of the soil samples was determined by measuring the release of para-nitrophenol from para-nitrophenyl phosphate (PNP). Bandick and Dick (1999) reported that the enzyme assays using air-dried soils can effectively distinguish between different field management practices, regardless of reduction in enzyme activities due to drying. The soils were exposed to a modified universal buffer (MUB) at pH 11 for the assay of alkaline phosphatase activity, as described by Tabatabai and Bremner (1969) and 1 mL PNP (0.025 M) was added to 1 g soil samples, followed by the addition of 0.2 mL toluene. The mixture was incubated at 37 °C for 90 minutes and centrifuged at 4000 rpm for 5 min. The p-nitrophenol formed was determined by spectrophotometer (Agilent 8453 UV-visible spectroscopy (Germany) system) at 440 nm.

7.5.6 Statistical analysis

For statistical analysis of data, the four sowing rows within the plots were used as replications. Microsoft Excel 2010 package was used for finding out the mean and standard deviation of yield parameters and soil chemical properties. Relationships

between different data were evaluated by means of simple linear regression analysis. The acceptance limit was set to 95 % significance level.

7.6 Results and discussion

7.6.1 Properties of the materials used

The soil characteristics were studied at two depths (0-20 and 20-40 cm) and the pH varied from 8.6 to 8.7 (Table 7.2.1). The electrical conductivity (EC) values also increased from 313 to 426 µS cm^{-1} as the depth increased. The Olsen P value was higher (19.42 mg kg^{-1}) in the 0-20 cm zone compared to 20-40 cm region which was 13.21 mg kg^{-1}. The P retention capacity (PRC) decreased with increasing depth. The contents of P, Al, Fe and Ca were 0.35, 25.87, 18.17 and 6 % respectively (Table 7.3). In the case of amendments, FBC had a high pH of 12.7 and the pH of BS was 6.64. The Olsen P values for FBC and BS were 11.52 and 21.67 mg kg^{-1} respectively. The calcium carbonate equivalence (CCE) for FBC was 23.25 %. Wang *et al.* (2006) reported CCE values ranging from 29.1 to 40 % in some of the FBC materials analysed. Both FBC (0.15 %) and BS (0.78 %) had low P contents. The Al and Fe contents for FBC were 34.02 and 15.76 % respectively, and BS was relatively low in Al (4.35 %) and Fe (2.49 %).

Table 7.2 Selected properties of soil and amendments used

Materials	Sources	pH	EC (µS cm^{-1})	Olsen P (mg kg^{-1})	CCE (%)	PRC (%)
Soil Anthroposol	0-20 cm	8.61±0.31	313±7.11	19.42±0.021	NA	7.41
	20-40 cm	8.70±0.24	426±9.53	13.21±0.024	NA	9.63
Soil amendments & P treatment	FBC	12.7±0.21	9.70±0.02	11.52±0.031	23.25	NA
	BS	6.62±0.14	17.8±0.03	21.67±0.041	NA	NA
	SSP	5.15±0.23	6.12±0.02	-	NA	NA

NA – Not applicable

Table 7.3 Elemental composition of the materials used

Materials	P (%)	Al (%)	Fe (%)	Ca (%)
Soil	0.35	25.87	18.17	6.00
BS	0.78	4.351	2.493	5.05
SSP	9.47	0.152	1.277	21.4

The P treatment, namely SSP had a low pH (5.1) and EC (6.12 µS cm^{-1}) values (Table 7.3). The P content was 9.47 % with high Ca content (21.4 %). The total P and Ca contents for BS were 0.78 and 5.05 % respectively The Ca content in FBC was 49.68 %

as it was a lime based by-product of coal fired power station. Wang *et al.* (1995) also observed high Ca contents in the FBC and SSP used by them.

7.6.2 Plant analysis

7.6.2.1 Effect of the amendments on plant biomass

The overall yield as measured by the dry weights (kg) of the sunflower plants varied according to the amendments added to the landfill soil (Figure 7.1). The plants grown from the fresh application of the amendments reflected the P solubility of the amendments (SSP>BS>FBC). The yields for SSP alone and SSP+BS applied soil plots were highest, which were 3.29 and 3.36 kg m^{-2} respectively. This can be attributed to the supply of P through SSP and BS addition (Table 7.2). The plots which received FBC and no amendments exhibited lowest biomass yields. Further, in all FBC co-amended plots, the biomass yields decreased compared to SSP alone and SSP+BS. The immobilising property of FBC and the resultant reduction in the bioavailable P from SSP and BS are the reasons for the declining yields (Chapter 3; Stout *et al.*, 2000).

In the second cropping, the plots treated with SSP alone and SSP+BS exhibited lower yields compared to the fresh effects of amendment application (Figure 7.1). This may be because of the P utilised in the first crop and the resultant high biomass yields. The application of FBC to the SSP and SSP+BS treated plots demonstrated an increase in the yields compared to the previous cropping (Figure 7.2). This may be attributed to the mobilisation of the previously immobilised P carried from the remanent of the first harvest (Chapter 6).

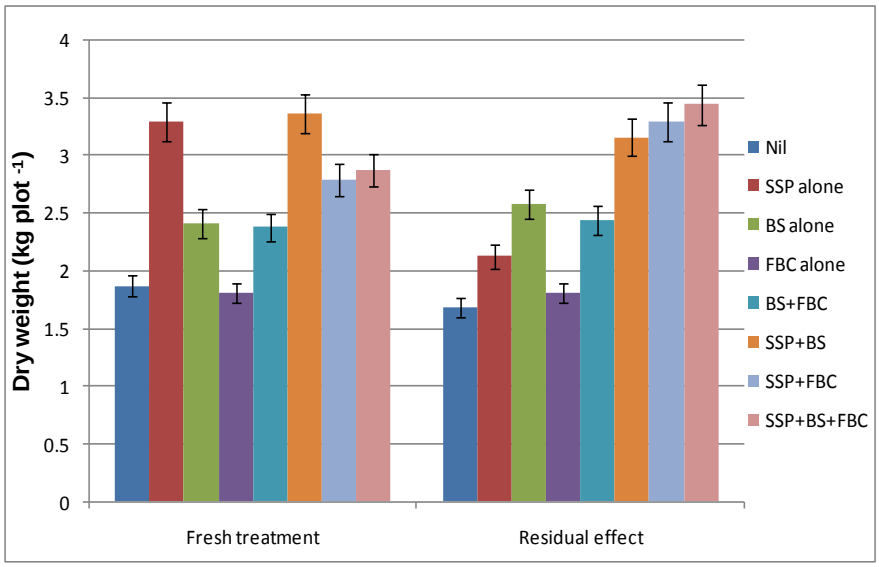


Figure 7.1 Effect of various treatment combinations (Nil, SSP alone, BS alone, FBC alone, BS+FBC, SSP+BS, SSP+FBC and SSP+BS+FBC) on the biomass yield of sunflower plants. Error bars represent the standard deviation between the replicates.

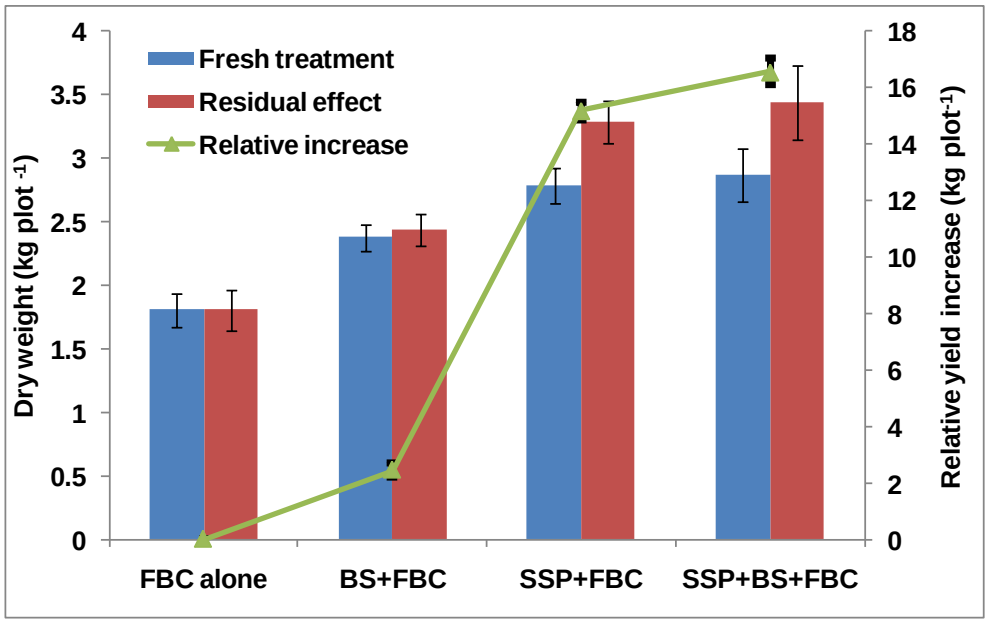


Figure 7.2 Effect of FBC on the sunflower yields in the second cropping. Relative yield increase = [(Yield for residual – fresh)/Yield of residual] x 100

The mustard plants showed similar trends in yield as sunflower plants with respect to various treatment effects (Figure 7.3), but the biomass yields measured as dry weights (kg) were lower compared to the sunflower plants. For example in the SSP+BS treated plot, the highest yield in the first cropping for mustard plants was 3.28 kg , which was found to be lower than their counterparts (3.36 kg) for the same treatment. This may be attributed to the differences in P accumulation between these two plants (Sharma *et al.*, 2007).

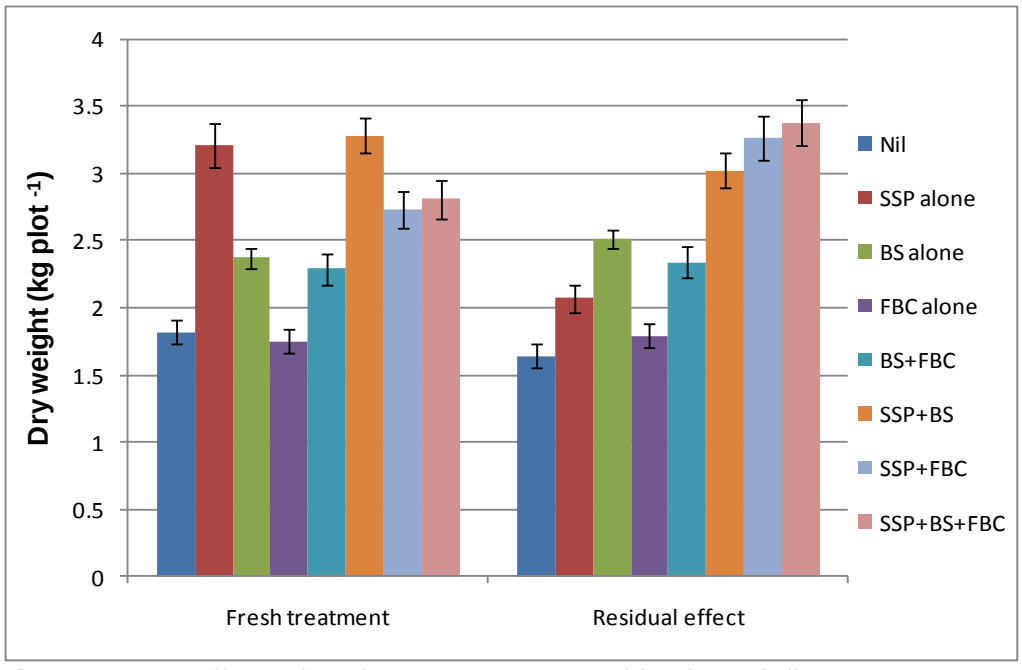


Figure 7.3 Effect of various treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS on the biomass yield of mustard plants. Error bars represent the standard deviation between the replicates.

A comparison between the overall dry weights (kg) of sunflower and mustard plants revealed slightly higher biomass in sunflower than mustard plants and the average difference in plant yields amongst the two plants between the treatments was 2.52 % (Figure 7.4). This minor distinction between sunflower and mustard plant species may be attributed to the difference in the extent of root growth between the plant species. Mertens *et al.* (2005) argued that the depth of rooting zone not only determines the accumulation of elements and the harvestable biomass, but also the uptake of nutrients. This was subsequently proved by Sharma *et al.* (2007) when they observed extensive root growth in sunflower plants grown on high P soils. However, Lamb *et al.* (2010) observed small cup-shaped root zone for sunflower plants grown on an identical soil with similar treatments in the same landfill site, which reduced the vertical expansion of roots. Gahoonia and Nielsen (1998) evidenced the role of root hairs in the uptake of P from soil using isotopic studies.

The effect of FBC on P-induced yield was also examined using the relative agronomic effectiveness (RAE), which expresses the agronomic potential of the farm inputs to produce a yield response (Chien *et al.,* 1990; Bolan *et al.,* 1990). The RAE was calculated using Eq. 7.1.

$$RAE = \frac{(yield\ for\ specific\ treatment - yield\ for\ nil)}{(yield\ for\ SSP\ alone - yield\ for\ nil)} x\ 100 \qquad (7.1)$$

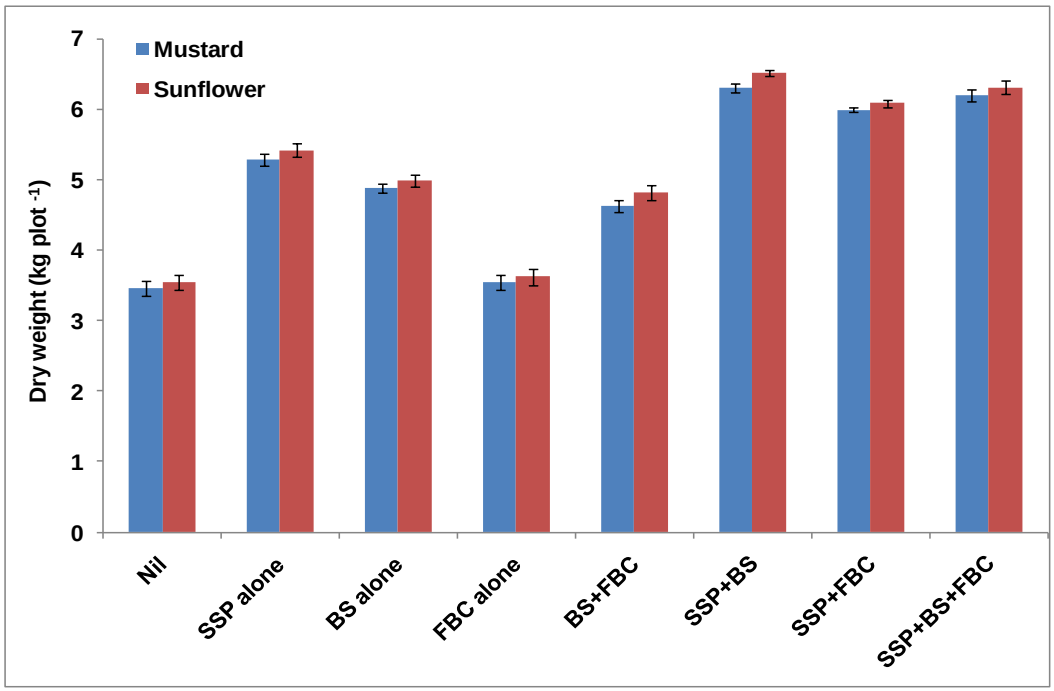


Figure 7.4 Comparison between overall dry weights of sunflower and mustard plants as affected by the treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS). Error bars represent the standard deviation between the replicates.

In the case of fresh application, the RAE was highest for the SSP+BS treatment for both sunflower (104.92 %) and mustard (105.04 %) (Table 7.4). Less than 100 % RAE indicates poor agronomic efficiency compared to the control and RAE higher than 100 % signifies the agronomic potential of the amendment. Application of FBC has reduced the RAE in all the other treatments in both the plant species and the RAE for FBC alone was negative, indicating that FBC application to low P agricultural soils in the absence of any P source is undesirable in an agronomic point of view. In the case of residual application, the RAE increased for all the treatments for the second crop, with SSP+BS+FBC combination showing the highest agronomic potential for both sunflower (391.11 %) and mustard (404.65 %) plants. The agronomic effectiveness of the treatments for the residual effect was in the following order: SSP+BS+FBC > SSP+FBC > SSP+BS > BS alone > BS+ FBC > FBC alone.

Table 7.4 Relative agronomic effectiveness of various P treatments

Treatments	Relative agronomic effectiveness (RAE %)			
	Sunflower		Mustard	
	Fresh application	Residual effect	Fresh application	Residual effect
SSP alone	100.0	100.0	100.0	100.0
FBC alone	-4.236	28.89	-5.044	34.88
BS alone	38.03	200.6	39.57	202.3
BS+FBC	35.91	168.8	33.81	162.7
SSP+BS	104.9	328.8	105.4	320.9
SSP + FBC	64.78	357.7	65.47	376.7
SSP+BS+FBC	70.42	391.1	71.22	404.6

7.6.2.2 Accumulation of P in the plant biomass

The plant accumulation of P was determined from the concentration of P in the biomass yield of sunflower and mustard plants (Figures 7.5 a and b) and was calculated using Eq. 7.2.

$$\boldsymbol{P\ accumulation}\left(\boldsymbol{g\ plot^{-1}}\right) = \boldsymbol{P\ concentration}\left(\boldsymbol{g\ kg^{-1}\ DM}\right) \times \boldsymbol{Biomass}\left(\boldsymbol{kg\ plot^{-1}}\right) \textbf{(7.2)}$$

The sunflower plants accumulated higher P contents (11.89 to 22.41 g P plot^{-1}) compared to mustard plants (7.81 to 15.32 g P plot^{-1}). This is because of the superior P accumulating characteristic of sunflower plants. Sharma *et al.* (2007) observed P accumulation in four different plants (sunflower, Indian mustard, canola and rape oilseed) and established that sunflower has the highest P accumulating capacity (P concentration - 6 to 10 g kg^{-1} biomass), followed by Indian mustard with a P concentration of 4.6 g kg^{-1} biomass. Increases in P concentration of plants (both sunflower and mustard) grown in FBC amended soils in the second cropping were observed, which indicated higher accumulation of P. The maximum increase in P accumulation was detected in plots amended with SSP+BS+FBC, followed by SSP+FBC compared to all other treatments

(Figures 7.5 a and b). Ram *et al.* (2007) amended lignite FA to groundnut crops and observed in increase in P concentration from 5.0 to 5.8 g P kg^{-1} biomass.

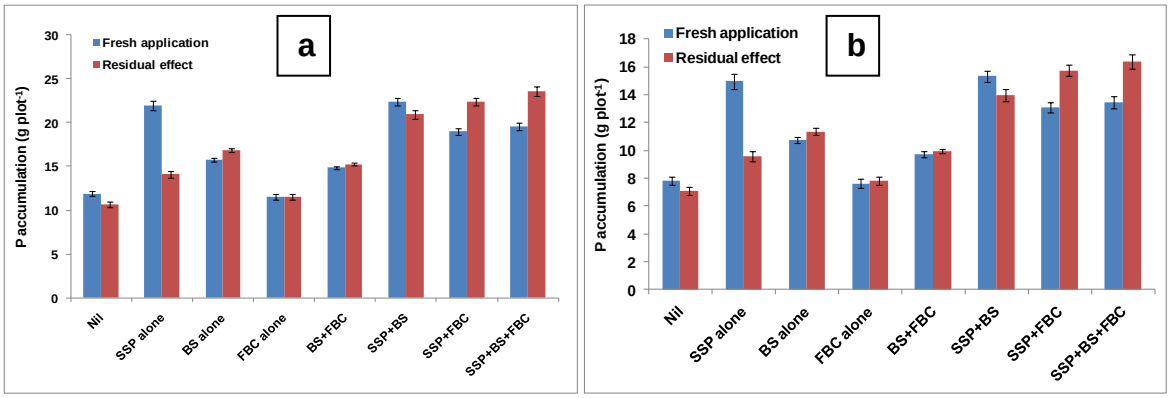


Figure 7.5 Accumulation of P in the plant biomass as affected by various treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS) in a. Sunflower and b. Mustard plants

7.6.2.3 Effect of amendments on Bioavailable P in soil

The bioavailable P was obtained by adding the total P uptake in the plant tissues for both fresh application and second crop as in Eq. 7.3.

$$\boldsymbol{Bioavailable\ P = Total\ P\ accumulation\ in\ plant\ tissues\ (Fresh\ application + Residual\ effect)} \quad \textbf{(7.3)}$$

The results on the bioavailable P for both fresh P application and the residual effect suggest that SSP+BS+FBC combination had the highest bioavailable P, followed by SSP+BS and SSP+FBC. In sunflower plants, the SSP+BS+FBC combination yielded 44.09 g $plot^{-1}$ of bioavailable P and in mustard plants, the bioavailable P for the same combination was 29.84 g $plot^{-1}$. The addition of FBC to SSP+BS did not show significant increases in bioavailable P with just 1.72 % in sunflower and 1.92 % in mustard plants (Figure 7.6 a and b). In both the plants, FBC increased the bioavailable P in FBC+BS treated plot. Several researchers reported slow release of P from BS and the resultant residual P effect in subsequent crops (Hue, 1988; Frossard *et al.*, 1996; Sui *et al.*, 1999).

A regression analysis between Bioavailable P and total biomass yield of all treatments for sunflower and mustard plants showed high correlation of R^2=0.989 and 0.9893 respectively (Figure 7.7). Shujie and Yunfa (2011) observed R^2=0.827 while comparing P concentration of the plants and relative P absorption efficiency (a measure of the capacity of plant roots to acquire P) in soybeans amended with KH_2PO_4.

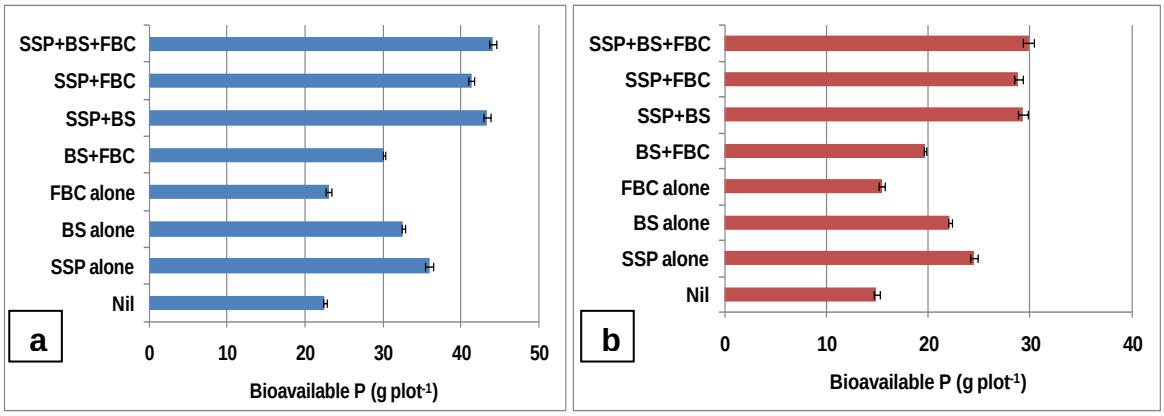


Figure 7.6 Effect of treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS) on plant available P in a. Sunflower and b. Mustard plants. Error bars represent the standard deviation between the replicates.

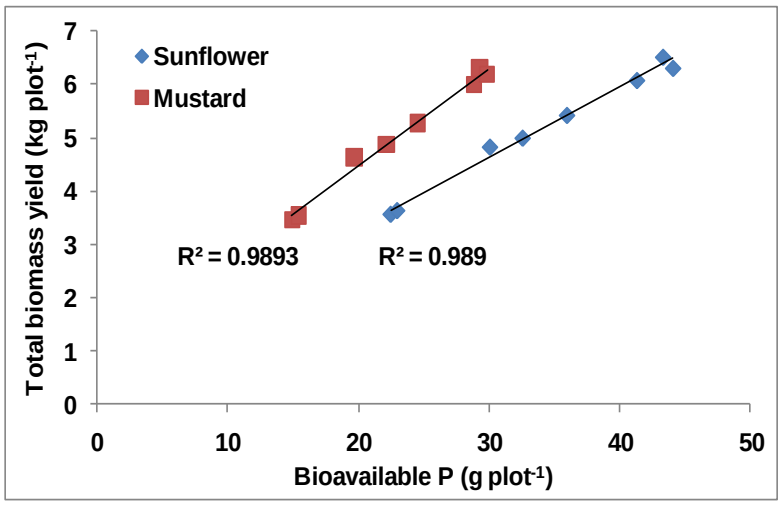


Figure 7.7 Relationship between Bioavailable P and total biomass yield as affected by the treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS).

7.6.3 Soil analysis

7.6.3.1 Effect of FBC on phosphatase activity

The phosphatase activity of the soils analysed during the second cropping revealed the effect of FBC on increasing mineralisation of P. Table 7.5 summarises the phosphatase activity induced by FBC on various amendments during the second cropping period. The order of phosphatase activity between the treatments for both the plants is as follows: SSP+BS+FBC > BS+FBC > SSP+FBC > FBC alone > SSP+BS > BS alone > SSP alone > Nil. The addition of FBC to SSP increased the phosphatase activity from 0.94 to 1.89 µmol g^{-1} PNP, which was 50.26 %. Similarly, FBC enhanced the phosphatase activity of BS application by 23.56 %.

Table 7.5 Effect of the amendments on phosphatase activity

S.No	Treatments	Phosphatase activity (µmol g^{-1} PNP)	
		Sunflower	Mustard
1	Nil	0.73±0.01	0.73±0.01
2	SSP alone	0.94±0.01	0.87±0.05
3	BS alone	1.46±0.04	1.41±0.02
4	FBC alone	1.52±0.04	1.47±0.04
5	BS+FBC	1.91±0.07	1.83±0.06
6	SSP+BS	1.48±0.03	1.41±0.03
7	SSP+FBC	1.89±0.05	1.85±0.05
8	SSP+BS+FBC	1.98±0.06	1.92±0.06

A regression analysis between the phosphatase activity and P accumulation in plants showed R^2 values of 0.4787 and 0.4717 for sunflower and mustard, respectively (Figure 7.8). Yu *et al.* (2006) related phosphatase activity with basic soil properties and soil P fractions. The correlation between natural phosphatase activity and plant available P resulted in an R^2 value of 0.688.

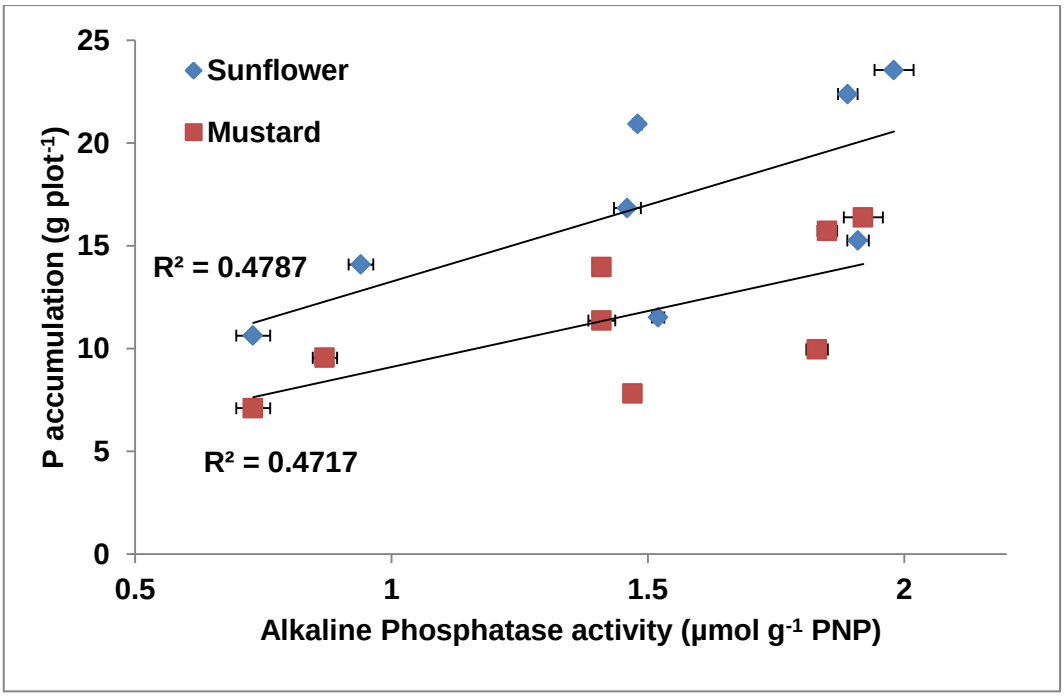


Figure 7.8 Relationship between P accumulation in shoots and phosphatase activity in the Anthroposol as affected by the treatment combinations (Nil, SSP alone, BS alone, FBC alone, SSP+BS, SSP+FBC, BS+FBC, SSP+BS+FBC). Error bars represent the standard deviation of replicates analysed for phosphatase activity.

7.7 Conclusions

- The effect of FBC on the biomass yields of both sunflower and mustard plants are as follows;
    - In the case of fresh P application, FBC decreased the biomass yield and an in increase in the bioavailable P in the second crop facilitated higher plant yield.
    - The addition of biosolid to the P treated soil resulted in the decrease of biomass yield in the residual P effect. However, addition of FBC to the combination of P and biosolid resulted in the highest yield for the second crop.
- Sunflower plants showed slightly higher biomass compared to mustard plants, which is attributed to higher P accumulation capacity by sunflower plants.
- The concentration of P in the plant tissues increased in the second crop, influenced by the effect of FBC on the P treatment and biosolid amendment. The P concentration was highest for the combination of all the three inputs.
- The bioavailable P increased in the second crop for both the plant species due to the mobilisation of the adsorbed P from first cropping. There was a positive correlation between uptake of P by plants and dry matter yield.
- The application of FBC increased the phosphatase activity in soils, thereby increasing the available P and consequently P uptake.

Chapter 8

SUMMARY AND CONCLUSIONS

This chapter summarises the major research findings obtained from various experiments evaluating the effects of coal combustion products (CCPs) on phosphorus (P) adsorption, re-distribution and bioavailability. A range of CCPs (fly ash, fluidised bed combustion ash, flue gas desulphurisation gypsum) derived from the coal-fired power stations were characterised and tested for their P-fixing abilities in a number soils which varied in pH and P adsorption. Further, effects of CCPs on re-distribution, mobility and bioavailability of organic and inorganic P sources in soils were also examined and discussed. Application of this research and future research priorities will be conferred in this chapter.

8.1 Research concept

A flow diagram describing the overall concept of this research is presented in Figure 8.1. The overall effect of the application of CCPs to soils was an increase in adsorption of P, which varied according to the nature of the soils and CCPs used. The most significant factors for the CCP-induced increase in P adsorption were pH and Ca as the adsorption P increased with an increase in pH and Ca with the application of CCPs. The CCPs also played a dual role for P applied from two different sources – immobilisation of inorganic P (P_i) and mineralisation of organic P (P_o). The mobility of P in general decreased with the application of CCPs and the bioavailability of P by and large increased through successive crops. Hence, this research will help in devising strategies for sustainable production in the agronomic perspective and ensure the overall environmental protection.

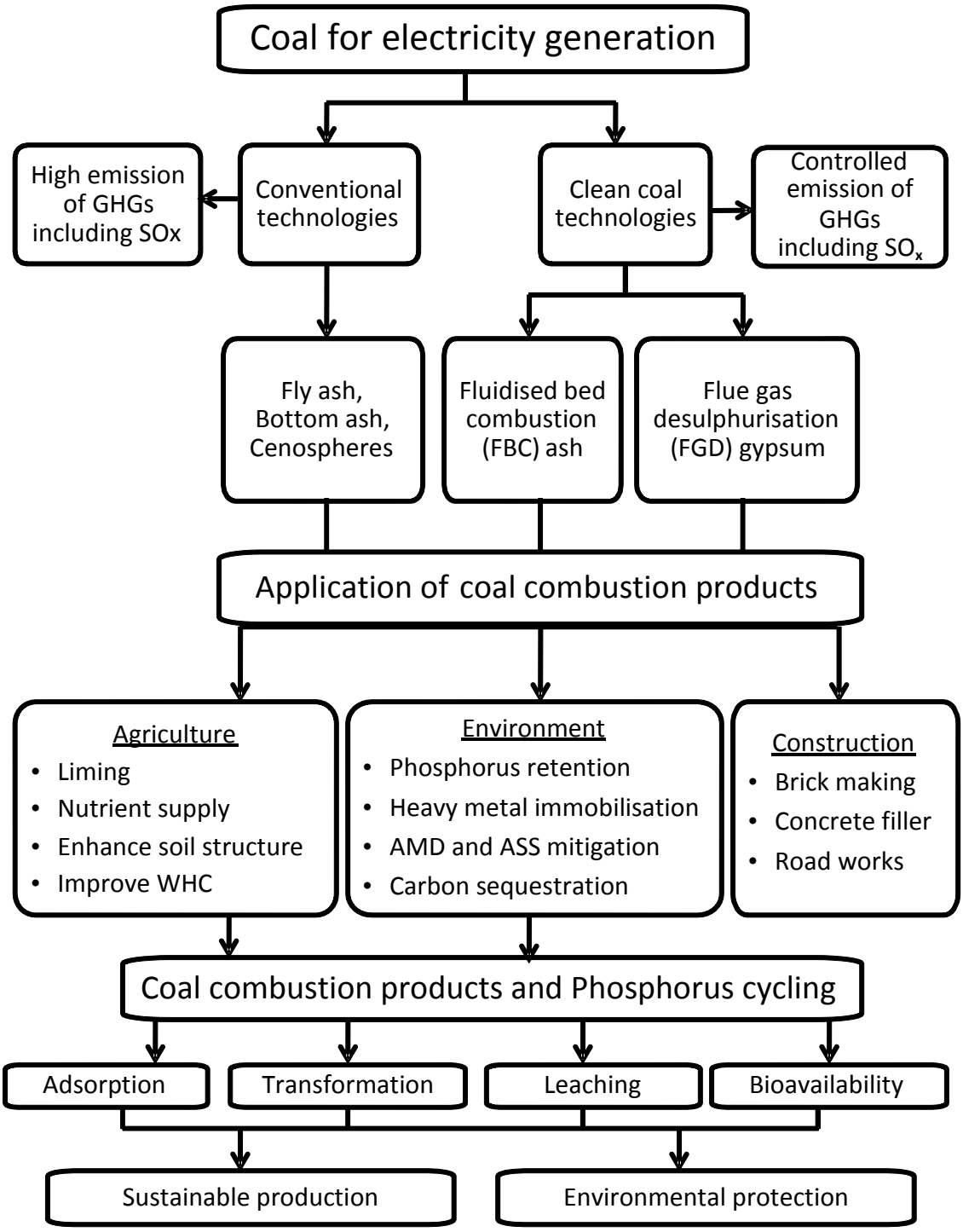


Figure 8.1 Flow diagram describing overall concept of this research

8.2 Phosphorus adsorption

The P sorption results indicate that CCPs are effective in enhancing the P retention capacity of soils mainly by increasing soil pH. Among the CCPs, FBC was most effective in increasing P sorption, followed by FA and FGD. At the highest application rate, FBC showed maximum sorption amongst the three CCPs. The pH played a major role in

P sorption in all the soil samples. There was an inverse relationship between the CCPs-induced increase in P adsorption and initial soil pH. Acidic and near-neutral soils demonstrated higher adsorption on CCPs addition, while alkaline soils showed least response to P adsorption on the application of CCPs. The increase in the concentrations of calcium (Ca), iron (Fe) and aluminium (Al) in soil solution resulting from CCPs application also influenced P adsorption. Depending on the pH of the soil, CCPs enhanced the adsorption of P by forming Ca, Fe or Al phosphate compounds. Also, low P retaining soils (e.g. Kapunda-KPD) responded more effectively to the application of CCPs in terms of P adsorption compared to a high P retaining soil from Adelaide hills (ADL). However, some of these CCPs may contain heavy metals that are toxic to plants and animals. The toxicity of these heavy metals is addressed using appropriate leaching and bioavailability experiments.

8.3 Phosphorus dynamics

8.3.1 Fractionation experiments

The P adsorption capacity of CCPs was not sufficient for understanding the sustainable use of applied P and hence the transformation and dynamics of applied P were studied using a sequential fractionation analysis. The fractionation experiments involving three different P sources and three CCPs demonstrated that the mechanisms pertaining to CCPs-induced transformation of P varied between P sources. For soluble inorganic P (PP-KH_2PO_4) application, CCPs enhanced immobilisation of P, which is attributed to a pH-induced increase in P adsorption to Al and Fe oxides and precipitation as Ca phosphates. In the case of insoluble P source (PR-phosphate rock), CCPs decreased dissolution of P which is attributed to increases in soil pH (less acid to dissolve) and Ca concentration in solution (common ion effect). In the case of organic P (PM-poultry manure), CCPs enhanced the mineralisation of P which is attributed to an increase in pH and enzyme activity. The increase in pH increased the phosphatase activity, thereby mineralising complex organic P into simpler inorganic P forms.

The rate and extent of transformation and redistribution of P varied amongst P sources and soils. Although the three soils (ADL-Adelaide hills, KPD-Kapunda and VIR-Virginia) used in this research showed similar trends in the redistribution patterns of P on the application of CCPs, the ADL soil accumulated lesser soluble and loosely bound P (NaOH-I-P) compared to KPD and VIR soils, which is attributed to the displacement of Fe and Al from soil to the solution by addition of Ca. The difference in P transformation between ADL and the other two soils was because of the lower initial pH (acidic) of the ADL soil, compared to KPD and VIR. The percentage distribution of $NaHCO_3$

(bioavailable) fraction remained consistent for all the three soils. The Ca associated P was highest in the KPD soil indicating highest CCP-induced P sorption among the three soils.

As the incubation time increased, the CCPs mobilised loosely sorbed P (NaOH-I) to bioavailable P fractions, hence demonstrating the value of CCPs for efficient plant growth. However, there are concerns of mobility of P which is evaluated through leaching experiments before conducting the plant growth experiments.

8.3.2 Microscopic and spectrometric analyses

The microscopic studies using field emission scanning electron microscopy (FESEM) and spectrometric analyses including energy dispersive spectroscopy (EDS) were conducted to study the surface characteristics of the CCPs incubated soil. A good understanding of the P rich regions was obtained from the SEM images supported by EDS data. The FESEM-EDS data demonstrated the abundance of Al associated P in all incubated soils for PP and PM treatments and Fe associated P was relatively less. Both Al and Fe associated P represents loosely adsorbed P, which can be readily mobilised to the soluble forms. Overall, the FESEM images identified the mechanisms of P interaction in CCPs incubated soils as (1) adsorption onto metal oxides/oxyhydroxides, mainly Al and (2) precipitation as Ca phosphates. The mineralogy of the CCPs incubated soil samples was acquired using X-ray diffraction studies which showed the presence of potential P sorbents such as wollastonite, ettringite, hydrogarnet, hematite and kennedyite.

8.4 Phosphorus leaching

The effects of CCPs on the extent of P mobility from soils treated with organic (poultry manure - PM) and inorganic P (potassium dihydrogen phosphate - PP) sources were studied using pulse and step-input column leaching experiments. For pulse input, CCPs decreased P leaching in PP treated column and increased P leaching in PM treated soils. In the case of step input, the P in the effluent appeared earlier in BIR soil compared to KPD soil and FA showed the highest P leaching. In the absence of CCPs application, P leaching was lower in sandy loam from Kapunda, South Australia (KPD) compared to the podosol from Queensland (BIR), reflecting their P retaining capacities. The BIR soil was selected for its low P retaining capacity in order to examine the effect of CCPs-enhanced P adsorption on leaching. Among the CCPs, FBC was most effective in reducing P leaching, followed by FA. In the case of FA, the high native FA-borne P resulted in high concentration of P in the leachates. However, the interference of the native P was corrected by calculating difference between the leaching data of FA with P and FA without P. As shown in the previous experiment, while FBC enhanced the immobilisation of inorganic P addition (KH_2PO_4), it induced the mineralisation of organic P addition (poultry

manure). Although leaching was less with organic P than inorganic P (in the absence of CCPs), the CCPs induced decrease in leaching was more for inorganic P. There was a negative relationship between increase in CCP-induced pH and P leaching for PP treated soil, indicating that pH plays a crucial role in P immobilisation, transformation and leaching. Although the leaching study also complemented the results from P adsorption by proving that pH and Ca concentration in solution controlled the extent of P leaching, the P adsorption was more in column experiment compared to the batch adsorption studies. A clear understanding on the adsorption of P by soil amended with CCPs and utilisation of P by plants grown on the CCPs amended soils is represented using plant growth experiments.

8.5 Phosphorus bioavailability

The effect of CCPs application on the bioavailability of fresh and residual P was examined using plant growth experiments, involving a glasshouse study on mustard plants and field trials using mustard and sunflower plants grown in CCPs amended soil. For the glass house experiment, the KPD soil was treated with PP and PM and incubated with FBC. The field experiment involved single super phosphate (SSP) as P treatment, amendments such as biosolids (BS), FBC and the combination of SSP+FBC, SSP+BS and SSP+FBC+BS.

8.5.1 Glasshouse experiments

The plant uptake of P increased with both inorganic and organic P application in the first crop and plants utilised more P on organic P application than the inorganic P applied soil during the second cropping. This is because of the increases in the mineralisation of organic P and immobilisation of inorganic P sources on FBC application. The P in the leachates decreased for PP application and increased in PM treatment which again related to the immobilisation and mineralisation effects of FBC addition. The FBC enhanced the P uptake from PP, especially under leaching conditions and from PM under both leaching and non-leaching conditions. There was a positive correlation between uptake of P by plants and the available P (measured as Olsen P) in soil, but plant uptake values were more than the Olsen P values. The effect of FBC on P uptake by plants validated the results from the P adsorption, P transformation and P leaching, which explained the FBC induced immobilisation of inorganic P and the mobilisation of organic P. Hence, FBC was effective in transforming both the inorganic and organic P forms (1) by immobilising inorganic P and later mobilising the bound P into available P for the second crop; (2) by mineralising organic P into available P forms favourable for P uptake. Further more, the Stanford-DeMent bioassay proved to be a useful technique to study the effect of

CCPs on phytoavailability of P in soils. The heavy metals in the CCPs amended soil and in the plants grown were below the permissible limits as per the ANZAAC guidelines.

8.5.2 Field trials

The field experiment conducted in a landfill site, examined the effect of FBC on P treated as SSP, BS and varying combinations of SSP, BS and FBC, which demonstrated the variation in the yield of plants. The addition of FBC to BS and SSP amended soil treatments decreased the biomass yields of both sunflower and mustard plants. In the first crop, yield was higher in SSP alone and SSP+BS compared to the plots amended with FBC. The residual effect in the second crop showed the beneficial outcome of the FBC addition as the biomass yields of both sunflower and mustard plants increased for BS and SSP treated plots. This ensured the increase in bioavailability of P when FBC is applied. Sunflower plants showed higher biomass compared to mustard plants, which is attributed to higher P accumulation capacity of sunflower plants. The bioavailable P increased in the second crop for both the plants due to the mobilisation of the adsorbed P from first cropping. There was a positive correlation between bioavailable P and total biomass yield of plants. Moreover, an increase in phosphatase activity in FBC amended soils ensured the increase in available P especially for the second crop with a consequent increase in yield.

8.6 Application of this research

The use of coal for electricity in Australia has been increasing over the past few decades and predicted to rise through the next 20 years (IEA, 2008). This means the amount of waste generated as CCPs will also accumulate (ADAA, 2008), rendering pollution of the land and water resources. Although, there have been numerous efforts to utilise these CCPs effectively in construction, agriculture and environmental restoration, these CCPs are largely under-utilised and also had less specific values in terms of targeted applications. They are predominantly used as filling materials in construction industry (ADAA, 2009a) and as a liming material for agriculture (Adriano *et al*., 1980; Sajwan *et al.,* 1995). Several studies targeted the unique characteristics of CCPs such as the liming value (Stehouwer *et al.,* 1999; Mc Dowell, 2004), acid neutralising capacity (Shang and Wang, 2005; Wang *et al.,* 2006) and P immobilising capacity (Stout *et al.,* 1999; Callahan *et al.,* 2002; Mc Dowell, 2005). By using these CCPs, we can considerably reduce the use of natural materials like lime and gypsum, thereby easing the environmental pressure caused by mining and related activities.

Phosphorus is an essential macro nutrient for plant growth, which plays a significant role in the initial (seed germination and root growth) and the final (flowering and

fruit production) stages of plant growth. The deficiency of P in the soil can cause stunted growth in plants characterised by early degeneration of leaves. Excess P may cause micronutrient deficiencies, especially iron or zinc and causes eutrophication in water bodies (Bennett, 1993; Bolan *et al.*, 2003b). Hence, the management of applied P in soils is very important for soil health, growth of plants and also the state of the water bodies. The application of CCPs to soils fertilised with P will not only immobilise the applied P, but also make the bound P available after an aging effect on the P application (Chapters 4 and 6). The CCPs-induced residual effect of increased P availability involves desorption in the case of inorganic P application and mineralisation for organic P application. Also, the CCPs can increase the water holding capacity of the soil. These two features make CCPs a viable option as an agricultural amendment for the P adsorption and utilisation in poor P retaining sandy soils. Apart from the ability to adsorb and transform P, some CCPs, especially FA has high native P concentration (Chapter 3; Pathan *et al.,* 2002). Therefore, they can be utilised as a P source as well, but needs more research on the application needs and issues pertaining to heavy metal accumulation.

Historical applications of P in excess amounts in many agricultural systems have resulted in undesirable build up of soil P. This kind of P enrichment has been more prominent in soils receiving animal wastes (Mullins *et al.,* 2005). The CCPs can also be used in agricultural catchments to adsorb the P from the agricultural effluents as employed by Cox *et al.* (2005) using gypsum in sub-catchments of Adelaide hills in South Australia. The P adsorption capacity of these by-products can be utilised for waste water treatments including domestic (i.e. sewage), farm (e.g. piggery effluent) and industrial (e.g. fertiliser) wastes, where they can act as a sink for P. The P adsorption capacity of the CCPs will therefore help in limiting the P loss to surface and subsurface waters, thereby controlling eutrophication.

The current study clearly shows the effectiveness of CCPs (FBC) in the initial immobilisation of organic and inorganic P sources and subsequent increase in mobilisation and mineralisation as the applied P ages, which is a significant agronomic pre-requisite in terms of P availability and uptake. CCPs application also enhanced the microbial activity of the soil especially in organic P applied soils as indicated by an increase in phosphatase activity. The outcome of this research leads to greater understanding of the potential benefits CCPs in the immobilisation of applied inorganic P, thereby reducing its leaching losses and increasing bioavailability for subsequent crops. In the case of organic P application CCPs enhance mineralisation thereby increasing the bioavailable P for the crop uptake. There have been invariable concerns over the utilisation of these by-products in agricultural applications owing to their environmental risks resulting from heavy metals, but more research of this kind can help address the anomalies and implications on the usage of CCPs. In spite of all apprehensions, the

power stations worldwide encourage farmers to apply CCPs based on their research on optimal application rates. The farmers in some countries are even encouraged by the Government agencies to utilise them based on the recommendations from the researchers. Moreover, power stations in most countries allow the farmers to use the CCPs free of cost.

8.7 Future research

Phosphorus is considered as a significant major nutrient in soil and their reactivity with soil components control their mobility in soil. Any mismanagement of P usage can be detrimental to plant growth and can cause serious concerns to water quality (both surface and underground). Since soil is the major pool for P, use of amendments such as CCPs and biosolids can serve as both source and (im)mobilising agents for P transformation in soil. With the results obtained from the existing research, new avenues of exploration can refine the existing limitations of CCPs' usage. Some of the potential areas of further studies include,

- Although the study focused on the effect of CCPs on P transformation in soil, their role in the dynamics of other nutrients such as nitrogen, carbon, sulphur and potassium cannot be ruled out. The add-up or draining of these major nutrients can significantly affect the soil ecosystem and consequently plant life.
- The chemical aspects of P transformation in CCPs amended soil such as the ionic strength and stability, relationship with other anions such as sulphate and carbonate, possible bonding with cations other than Ca, Fe and Al using synchrotron techniques needed to be carried out to understand comprehensively the overall P dynamics.
- There is a possibility of accumulation of heavy metals in the case of long term CCPs application although the current research proved to keep the heavy metals under permissible limits. Hence, a long term study involving a range of soils and a range of plant species need to be conducted to improve the validity of using CCPs.
- In the lines of field trials, more novel combinations of CCPs and compatible amendments (like earthworm compost and swine manure) are needed to enhance the current efficiency levels of the CCPs. The accrual of heavy metals should again be carefully monitored.
- Another important area to be explored is the effect of CCPs on P uptake in plants and their influence on plant physiological processes such as senescence and chlorophyll production in the tissues and rhizosphere related metabolic pathways.
- Studies on the influence of CCPs on microbial processes such as microbial immobilisation and bioavailability should also be carried out.

- For addressing the P related issues in water bodies, novel materials with CCPs should be designed to adsorb P in a more sustainable way and hence ensuring the longer durability of the adsorbents. Trials with CCPs-based nano-materials can prove to be more economic and sustainable.

The sustained efforts of the research community and the continual support from the related industries and Government institutions can provide effective solution to the community by

- ✓ minimising the utilisation of natural resources
- ✓ consuming the so-called wastes generated due to industrial growth and growing population
- ✓ cleaning the environment to sustain life on this planet.

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