

no. 26
technical
report

**Phosphorus management in soils using coal
combustion products**



CRC for Contamination Assessment and Remediation of the Environment

Technical Report no. 26

Phosphorus management in soils using coal combustion products

July 2013



Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report series, no. 26
July 2013

Copyright © CRC CARE Pty Ltd, 2013

This book is copyright. Except as permitted under the Australian *Copyright Act 1968* (Commonwealth) and subsequent amendments, no part of this publication may be reproduced, stored or transmitted in any form or by any means, electronic or otherwise, without the specific written permission of the copyright owner.

ISBN: 978-1-921431-33-3

Enquiries and additional copies:

CRC CARE, P.O. Box 486, Salisbury South, South Australia, Australia 5106
Tel: +61 (0) 8 8302 5038
Fax: +61 (0) 8 8302 3124
www.crccare.com

This report should be cited as:

CRC CARE 2013, *Phosphorus management in soils using coal combustion products*, CRC CARE Technical Report no. 26, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Disclaimer:

This publication is provided for the purpose of disseminating information relating to scientific and technical matters. Participating organisations of CRC CARE do not accept liability for any loss and/or damage, including financial loss, resulting from the reliance upon any information, advice or recommendations contained in this publication. The contents of this publication should not necessarily be taken to represent the views of the participating organisations.

Acknowledgement:

CRC CARE acknowledges the contribution made by Balaji Seshadri, Nanthi S. Bolan and Ravi Naidu of the Centre for Environmental Risk Assessment and Remediation, University of South Australia and CRC CARE, towards the writing and compilation of this report.

Abbreviations

ADL	Adelaide Hills
Al	Aluminium
As	Arsenic
BA	Bottom ash
BRI	Bribie Island
BS	Biosolids
Ca	Calcium
CCPs	Coal combustion products
CCTs	Clean coal technologies
Cu	Copper
FA	Fly ash
FBC	Fluidised bed combustion ash
Fe	Iron
FGD	Flue gas desulfurization
K	Potassium
KPD	Kapunda
K_f	Freundlich distribution coefficient
KUL	Kulpara
Mg	Magnesium
Na	Sodium
P	Phosphorus
P_i	Inorganic phosphorus
PIT	Pittsworth
PM	Poultry manure
P_o	Organic phosphorus
PP	Potassium dihydrogen phosphate
PR	Phosphate rock
PRC	Phosphorus retaining capacity
RAE	Relative agronomic effectiveness
S	Sulfur
Si	Silicon
SSP	Single super phosphate
WAL	Wallaroo
WHC	Water holding capacity
Zn	Zinc

Executive summary

Large quantities of coal combustion products (CCPs) are being generated worldwide annually and dumped in large piles as landfills. These products are residues from the combustion of coal, largely used for electricity generation. The economic availability of coal and the burgeoning demands of the rising population are set to increase the coal-fuelled electricity generation in the future. Australia, being amongst the top nations in using coal for production of electricity, generates enormous quantities of CCPs. There is an increasing concern among the power stations and environmental agencies on the mobility of heavy metals from the CCPs, which may result in contaminating our land resources and water bodies.

Although the coal-fired power generation has evolved a long way towards clean coal processing technologies, resulting in higher energy production and value addition, there has not been any breakthrough in reducing the volume of combustion wastes i.e., the CCPs generated. Consequently, the ash dumps are fast inflating and envisaged for more expansion in the impending years. This is mainly due to the under-utilisation of these waste materials in some countries, where the concerns towards environmental health and public well-being had not been addressed. The possible uses of CCPs in the construction industry as a cement substitute; in agriculture as a liming agent; and in environmental remediation have reaped benefits round the globe. Current utilisation levels of these resources in Australia are low, considering their actual potential in environmental remediation.

Most Australian soils are inherently deficient in phosphorus (P) and many sandy soils are not efficient in the retention of P, thereby results in leaching and (surface) runoff losses. Agricultural application of fertilizer P and wastes including farm effluents, manures and biosolids (BS) have been the most significant contributors of P build-up in soils and consequent accumulation in water bodies causing eutrophication. 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.

Transformation [(im)mobilisation] of P in soil is closely associated with the pH and the concentrations of iron (Fe), aluminium (Al) and calcium (Ca) in the soil. An increase in soil pH generally increases the potential of inorganic P immobilisation in soil *via* P adsorption, especially to acidic and neutral soils. However, Ca concentration also influences adsorption of P. At very high pH and high Ca concentration, inorganic P gets precipitated with Ca and it becomes strongly immobile. However, at low pH, P adsorbs to the surface of Fe and Al oxides. The pH also influences the breakdown of organic P into inorganic P in soil, due to phosphatase activity and the resultant P mineralisation. The CCPs are generally alkaline and are rich in these cations and hence can serve as potential amendments for P management in soil, which will be explained in this report using immobilisation, transformation and bioavailability experiments. Also, this report will serve as an effective guide for the farming communities and a source of information for industries and researchers related to CCPs.

Table of contents

1. Coal combustion products	1
1.1 Production and utilisation	2
1.2 Basic characteristics of the CCPs	3
1.3 Applications of CCPs	3
2. Phosphorus issues in the soil environment	5
3. Phosphorus immobilisation, transformation and reduced leaching in soil	6
3.1 Adsorption of phosphorus in soil	6
3.2 Transformation of applied phosphorus in soil	10
3.3 Reduced leaching of applied phosphorus in soil	13
4. Agronomic response to applied phosphorus in soil	15
5. Possible threats on using coal combustion products	21
6. Conclusions	23
7. References	25

Tables

Table 1	Various types of CCPs, their major constituents and potential uses	4
Table 2	Chemical characteristics of the soils used for the entire study	7
Table 3	Chemical characteristics of the P sources used for the entire study	13
Table 4	Pulse input leaching: Percentage reduction of the amount of P leached (compared to control soil) in the CCPs amended soil.	14
Table 5	Relative agronomic effectiveness of various P treatments	19
Table 6	List of potential hazards and effects on agricultural soil of CCPs application	21

Figures

Figure 1	Total ash production and beneficial usage in Australia	2
Figure 2	Production of CCPs by different technologies and their various applications	4
Figure 3	The effect of CCPs on P sorption as measured by K_f value in ADL soil at four different application rates (0, 15, 30 and 45 % w/w)	7
Figure 4	Effect of CCPs (FA, FBC and FGD) on P adsorption in ADL soil at 15 % application rate	8
Figure 5	The relationship between pH of ADL soil and increase in P sorption as affected by CCPs at three application rates (0, 15 and 30 % w/w)	8
Figure 6	Relationship between % P retention and Ca in solution for seven soils (ADL, KPD, KUL, WAL, BRI, PIT and DRA) at three different (0, 15 and 30 % w/w) application rates of FBC	9
Figure 7	Flow diagram showing sequential extraction of inorganic P	10
Figure 8	Distribution of P fractions in the three soils amended with CCPs	11
Figure 9	Effect of incubation period (63 days) on bioavailable P in CCPs amended a) ADL and b) KPD soils treated with Potassium dihydrogen phosphate, poultry manure and phosphate rock	12
Figure 10	Pulse input leaching - cumulative P for KPD soil treated with PP and PM at 100 mg P kg ⁻¹ soil as affected by CCPs (15 % w/w)	13
Figure 11	Release of phosphate from organic phosphorus compound	15
Figure 12	Set up of Stanford – DeMent bioassay technique	16
Figure 13	Effect of FBC on P uptake in plants for fresh P application and residual P effect.	17
Figure 14	Cumulative P leaching – effect of FBC on P mobility in ADL soil treated with inorganic (PP) and organic (PM) P sources.	17
Figure 15	Effect of FBC on a) sunflower and b) mustard yields, grown on SSP and BS treated soil in the second cropping	19
Figure 16	Relationship between Bioavailable P and total biomass yield as affected by the treatment combinations	20
Figure 17	Schematic representation on the factors of CCPs utilisation	24

1. Coal combustion products

Coal is one of the most inexpensive energy sources for electricity generation, 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 & 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). In Australia, coal's share for electricity generation has ranged between 60 and 80 % since 1960 and the rate of coal consumption is increasing at 5 %, annually (Geoscience Australia 2011). This will apparently result in the production of more coal consumption products (CCPs) and the consequent expansion of landfills. The Ash Development Association of Australia has defined CCPs as follows (ADAA 2009):

Fly Ash (FA) is the non-combustible oxidised elements that exit the combustion chamber in the flue gas and is captured using electrostatic precipitators, filter baghouses, or wet scrubbers. It is typically a pozzolan – a siliceous, or siliceous and aluminous material. Australian FA materials are light to mid-grey in colour, appear as fine powder with particles ranging in size from less than 1 µm to 200 µm and are irregular to spherical in shape.

Bottom Ash (BA) is 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. The BA is typically grey to black in colour and has a porous surface structure.

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 SO₂ released during combustion of the coal to form sulphates. The bed waste product is granular solid material composed of CaSO₄, 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).

Increasing environmental regulations has put enormous pressure on the coal-fired power stations to introduce clean coal technologies (CCTs), which embrace some modifications in the combustion of coal as mentioned above. The products from CCTs are hence value added combustion products, which include FBC and FGD.

1.1 Production and utilisation

With the continual increase in energy demand, large quantities of CCPs are destined to be dumped in landfill sites, and ash ponds, increasing the environmental footprint of electricity generation using coal. The current rate of CCPs production (14.6 million tonnes in Australasia) renders its disposal unviable and may cause detrimental effects on plant, animal, human and environmental health due to the overall toxic effect of the ash materials (Twardowska & Stefaniak 2006).

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 14 million tonnes of CCPs every year, posing threat to the environment due to incessant dumping and under-utilisation of CCPs (Figure 1). Among the CCPs, FA is widely utilised in the construction industry (up to 85%) in Australia since 1960s (ADAA 2009). 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 & 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 & Adriano 1993; Twardowska & Szczepanska 2002). The majority of CCPs produced are dumped in large areas around the power stations called as ash ponds. These ash ponds not only damage the land resources, but also pollute both the ground and surface water resources. The deleterious effects of these products are well studied in most developed nations and they are still being widely used in the developing and under-developed countries.

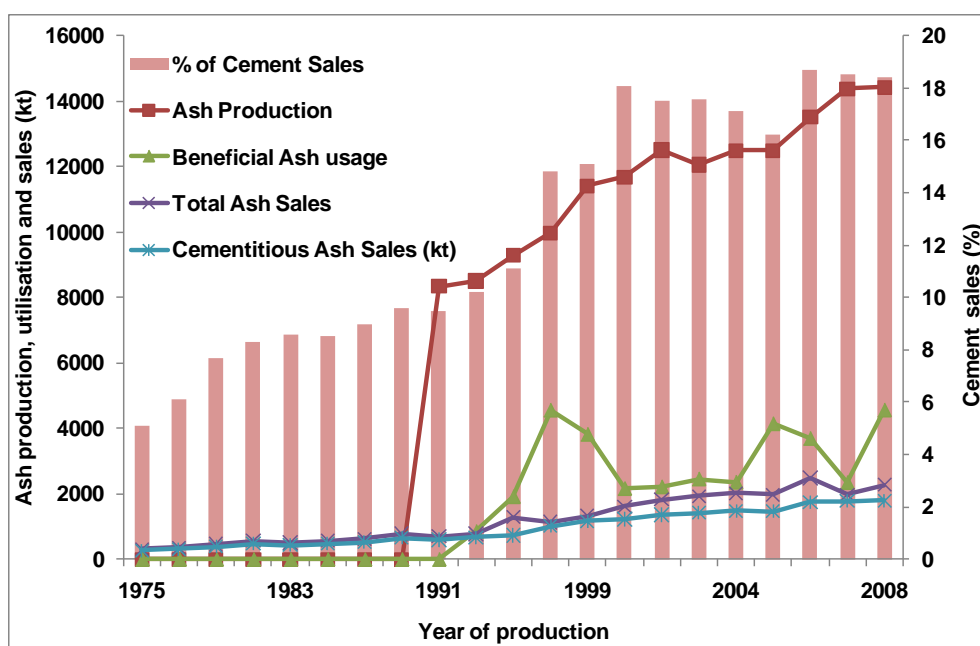


Figure 1 Total ash production and beneficial usage in Australia (Adapted from ADAA 2008)

1.2 Basic characteristics of the CCPs

The physical and chemical properties of CCPs depend upon a number of factors, including the type of coal burnt, the boiler conditions and 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 CCPs. Chemically, CCPs are mainly silico-aluminate glasses, though some mineral materials may be present (ADAA 2007). In Australia, the majority of FA produced is categorised as Class F – being mainly silica and alumina (80-85 %) and less than 10 % CaO. Class F FA 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 sulfate (SO₄) contents are generally higher in Class C FA. Furnace bottom ash (BA) 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.

Physically, CCPs (especially FA) are mainly composed of silt-sized materials having a diameter ranging from 0.01 to 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).

The chemical properties of CCPs will largely be determined by the metal oxides (Si, Al, Fe, Ca, Mg, Na, and 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 CCPs 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. During the combustion and subsequent cooling processes, many different metal oxides can precipitate and concentrate on the surfaces on these spheres. These oxides control the chemical properties of CCPs, and tend to vary based on the combustion processes. The oxides may also affect the physico-chemical properties of some CCPs, especially the pozzalonic (cementitious) reactivity (Stewart *et al* 1997).

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

1.3 Applications of CCPs

The CCPs are used extensively in the agricultural and construction industries. International research into the use of CCPs as a soil amendment has grown markedly over the past few decades, focusing mainly on the feasibility of using these products in agriculture and some environmental applications (see Adriano *et al* 1980; El-Mogazi *et al* 1988; Yunusa *et al* 2006; Basu *et al* 2009). 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 1.

Table 1 Various types of CCPs, their major constituents and potential uses.

Types of CCPs	Major constituents	Potential areas of major use
FA	Si, Al, Fe, Ca (CaO, MgO, SiO ₂ , K ₂ O, Al ₂ O ₃ , Fe ₂ O ₃)	Cement replacement in concrete/grout, structural fill, waste stabilization, surface mine reclamation, soil stabilization, road based, mineral filler, Si and Ca source
FBC	Si, Al, Fe, Ca, S (CaSO ₄ , CaO, Quartz, gypsum)	Slow release fertiliser, liming material
FGD	Si, Al, Fe, Ca, S (CaSO ₄ , CaO, CaSO ₃ , MgO, SiO ₂ , K ₂ O, Al ₂ O ₃ , Fe ₂ O ₃)	Wallboard, stabilised road base/sub-base, structural fill, surface mine reclamation, underground mine injection, livestock pad, low permeability liner, sludge stabilization

This report will discuss the current and potential benefits of CCPs in the soil environment (Figure 2), focusing on phosphorus retention and bioavailability in soils.

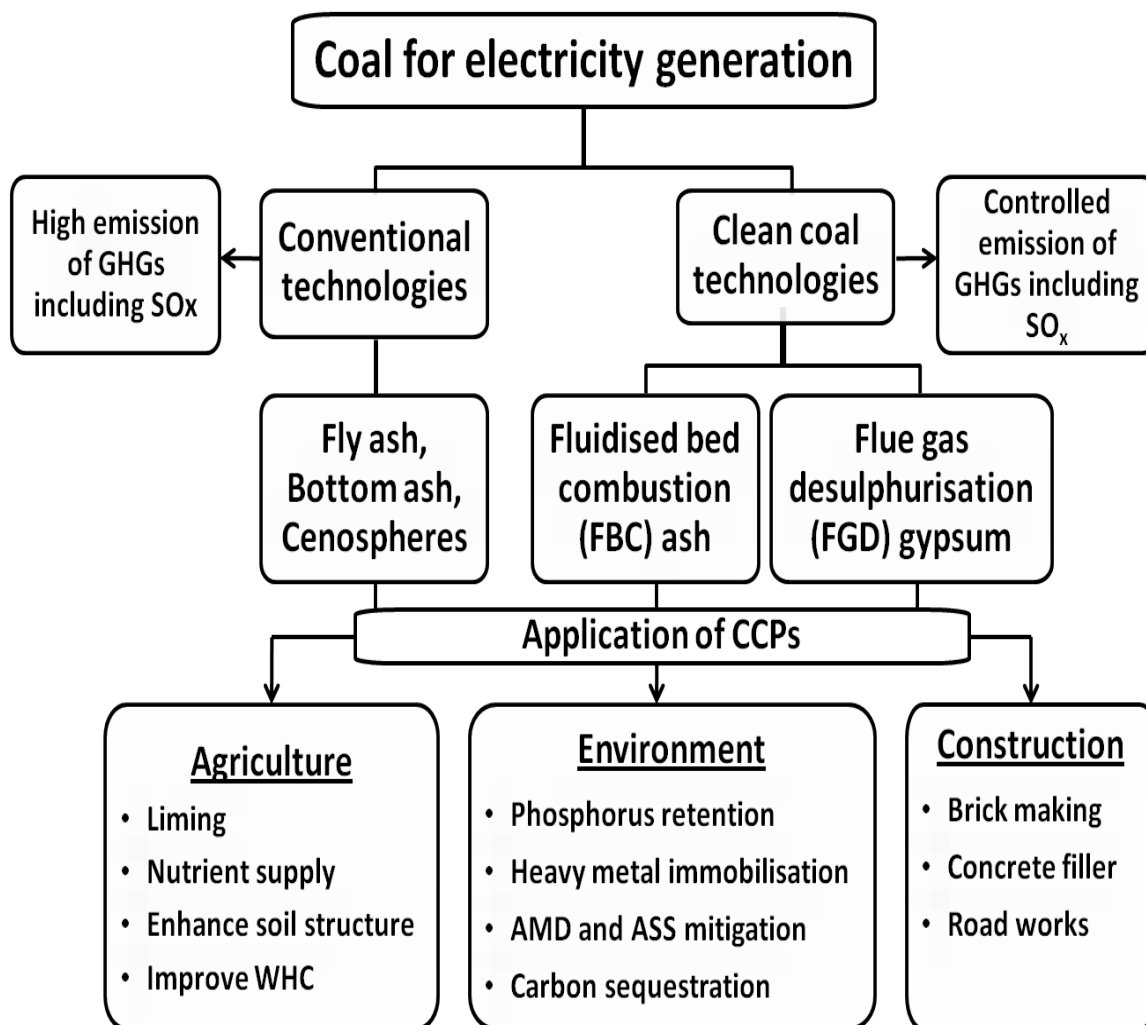


Figure 2 Production of CCPs by different technologies and their various applications

2. Phosphorus issues in the soil environment

Phosphorus (P) is the second major essential nutrient for plants 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, for example apatite) and organic (derived from organisms) forms. There are over 170 phosphate bearing minerals and most of them are chemically reactive (Holford 1997). Plants can acquire P only in the inorganic (P_i) forms such as the orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-}); with the organic (P_o) forms unavailable to plants, unless mineralised. However, the P_i ions which are negatively charged interact with positively charged iron (Fe), aluminium (Al), and calcium (Ca) ions to form relatively insoluble substances (Stout *et al* 2000; McDowell 2005).

Soil pH plays a major role in the adsorption of P. 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 & Schwab 1993; Grubb *et al* 2000). The un-adsorbed P ends up in the soil solution and reaches water bodies through surface runoff and leaching. Although initial research focussed on the acquisition of P in cultivated crops, currently the problems pertaining to excessive dosage through fertiliser applications and hence losses from the soil have been widely studied (Sharpley & Withers 1994; Haygarth & Jarvis 1997; Heathwaite *et al* 1997; McDowell & 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 many sandy soils are also poor in retaining P which is attributed to low levels of silicate clays, and iron and aluminium oxides, which are also 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 (Summers *et al* 1996; Snars *et al* 2002) and altering the pH of the soil using liming material. With the increasing pressure on lime, alternative amendments are being researched for P immobilisation in soil.

3. Phosphorus immobilisation, transformation and reduced leaching in soil

3.1 Adsorption of phosphorus in soil

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 P_i). Although the particulate P loss can be decreased through management practices such as riparian buffers, the soluble P_i 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 (Hedley & McLaughlin 2005) and safeguarding water quality (Sharpley *et al* 1994). Optimal pH and high concentration of P sorptive components such as Ca, Fe and Al in soil solution are prerequisites for enhancing the retention of P in soils (Stout *et al* 1998; McDowell 2004). Traditionally, lime ($CaCO_3$) has been widely used to overcome soil acidity by increasing the soil pH (Anderson *et al* 1995; Sumner & 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 & Smillie 1995; Murphy & 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 FA in mitigating particulate P loss through erosion or organic P loss through mineralisation (Stuczynski *et al* 1998a, 1998b). Various reasons have been attributed to the beneficial effects of CCPs in reducing the loss of P through leaching and erosion (Reichert & Norton 1994; Stout *et al* 2000; Callahan *et al* 2002; Pathan *et al* 2002; McDowell 2005), which include:

- increase in soil pH resulting from the addition of alkaline CCPs
- increases in surface area, anion exchange capacity (AEC) and water holding capacity (WHC)
- increases in Ca, Fe and Al concentration, and
- increase in soil strength through prevention of slaking and soil dispersion.

The above mentioned factors facilitate P interactions in soil and will help minimise the loss of P from soils. Some selected chemical characteristics of the soils from the Adelaide hills (ADL), Kapunda (KPD) and Bribie Island (BRI) used in the entire study are listed in Table 4. The pHs of the soils used ranged from 3.4 to 7.1 with KPD showing neutral pH (7.1) and PRC ranged from about 4.6 % to 23.4 %. The KPD soil showed the highest concentration of P and Ca whereas the BRI soil had the least (Table 2). Total Fe and Al concentrations were high for all the soils except BRI, which also had low Ca concentration and total P was below detectable limits. The Olsen P values for ADL and KPD soils were 3.82 and 9.6 $mg\ kg^{-1}$ respectively (Table 2).

Table 2 Chemical characteristics of the soils used for the entire study

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 ±3.62	52.02 ±4.16	16364 ±45.01	19474 ±49.12
KPD, Calcarosol, SA	7.14 ±0.42	9.60 ±0.34	7.43	348.4 ±9.89	5996 ±29.62	18170 ±35.67	25865 ±51.29
BRI, Podosol, Qld	3.42 ±0.24	N.D.	4.62	N.D.	169.8 ±6.142	502.64 ±11.54	456.44 ±10.42

N.D. – Not determined (detection limit of 0.01 mg kg⁻¹); PRC-Phosphorus retention capacity.

The ADL soil was used to study the effects of the three CCPs (FA, FBC and FGD) on P adsorption in the soil. The batch sorption isotherms showed that 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). 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. The results demonstrated the high effectiveness of FBC in sorbing P, followed by FA (Figure 4). 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).

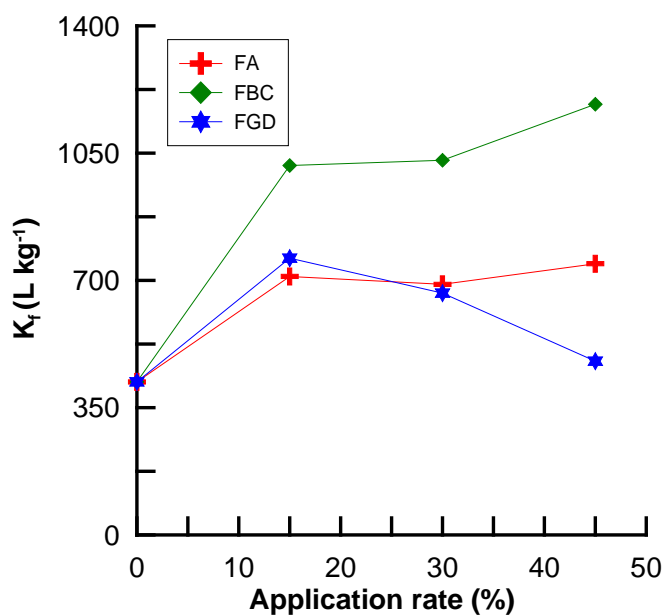


Figure 3 The effect of CCPs on P sorption as measured by K_f value in ADL soil at four different application rates (0, 15, 30 and 45 % w/w).

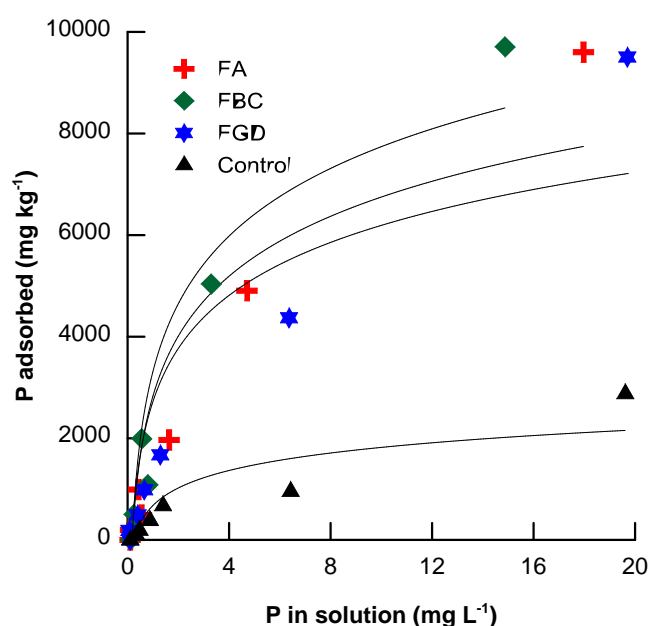


Figure 4 Effect of CCPs (FA, FBC and FGD) on P adsorption in ADL soil at 15 % application rate.

The increase in P sorption (as measured by K_f value) with the addition of CCPs to ADL soil is attributed to an increase in soil pH (Figure 5). The pH increased with the increasing CCPs application rate and the greatest pH increases were seen for 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 with FGD application. 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.

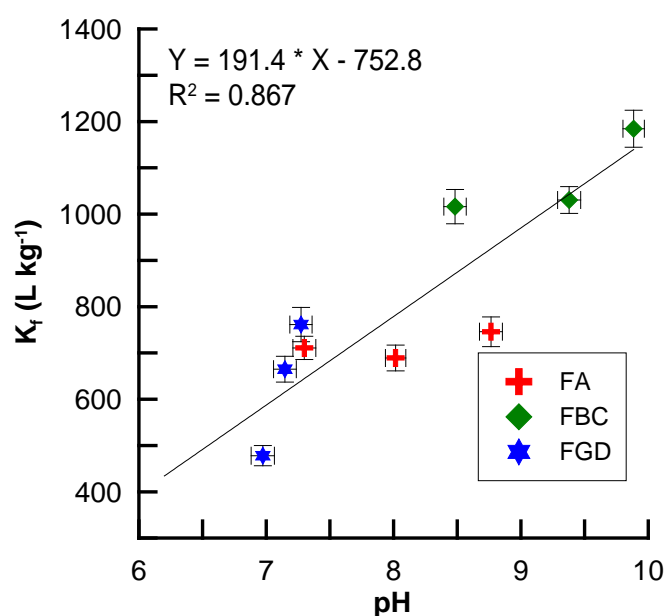


Figure 5 The relationship between pH of ADL soil and increase in P sorption as affected by CCPs at three application rates (0, 15 and 30 % w/w). Error bars represent the standard deviation between replicates.

Apart from pH, Ca in solution also played an important role in the adsorption of P as evident from the relationship between Ca in solution and the percentage P retention

showed an R^2 value of 0.5137 (Figure 6), which is comparatively higher than that of extractable Fe (0.1267) and Al (0.1265). 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 CaSO₄) and Fe (especially citrate-dithionate extractable Fe) 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 crystalline Fe compounds.

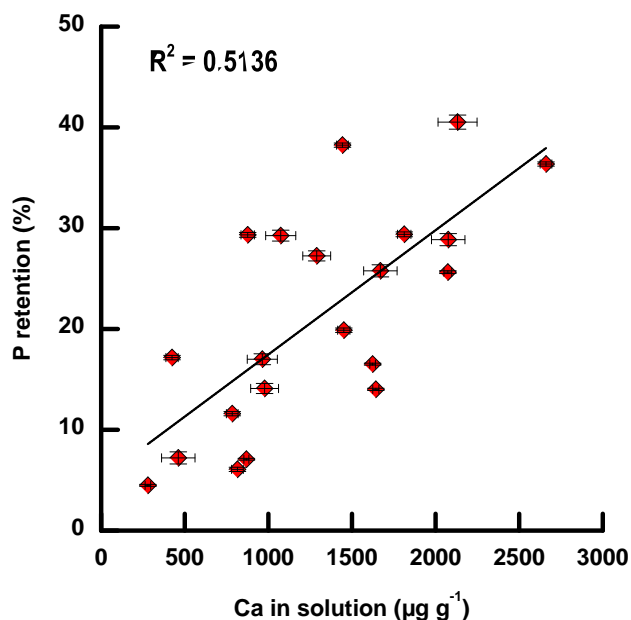


Figure 6 Relationship between % P retention and Ca in solution for seven soils (ADL, KPD, KUL, WAL, BRI, PIT and DRA) at three different (0, 15 and 30 % w/w) application rates of FBC. Error bars represent the standard deviation between replicates.

3.2 Transformation of applied phosphorus in soil

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). 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). With the proven ability of CCPs in P sorption, the role of the CCPs in the transformation of applied P (inorganic and organic P) was explored using two soils (ADL and KPD) 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). In this study, the effect of CCPs on P transformation was examined using chemical fractionation analyses.

The soils were treated with inorganic and organic P sources and then incubated with CCPs. The incubated soils were chemically fractionated for understanding the amount of each form of P present using the fractionation scheme as followed by McDowell (2005). For this fractionation procedure, incubated soil samples (1 g each) were extracted sequentially by shaking with deionised water, NaHCO₃ (0.5 M), NaOH-I (0.1 M), H₂SO₄ (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 HNO₃:HCl – 3:1). Details of the sequential extraction along with the fractions removed sequentially are showed in Figure 7.

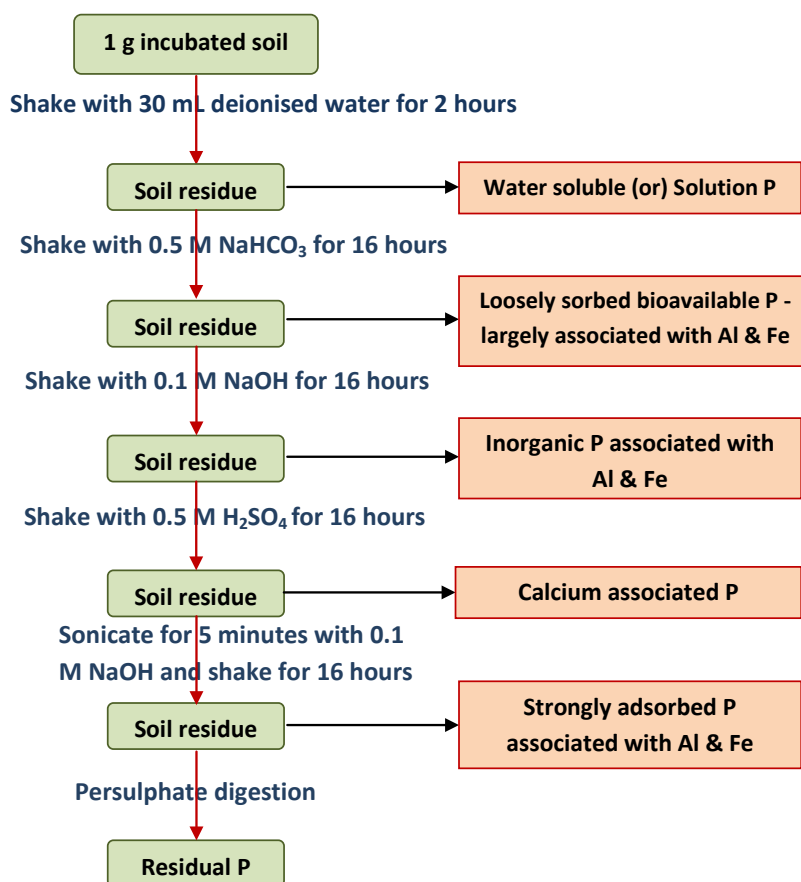


Figure 7 Flow diagram showing sequential extraction of inorganic P

The application of CCPs showed major changes in P concentration and distribution of different P fractions. Initially, the highly responsive P fractions to CCPs application were $\text{NaHCO}_3\text{-P}$ and NaOH-I-P for FA and FBC application and in the case of FGD application, $\text{H}_2\text{SO}_4\text{-P}$ dominated the P extraction. The increase in P extraction in NaOH-I-P and $\text{H}_2\text{SO}_4\text{-P}$ fractions confirms increased P adsorption and is attributed to the increase in soil pH and also due to the liming effect of these CCPs (McDowell 2004).

The soils with varying P retaining capacities (ADL 23.89 % and KPD 5.05 %) exhibited distinct P distribution patterns. The ADL soil had lower soluble and loosely bound P (NaOH-I-P), which may be attributed to the differences in pH and the concentration of Fe, Al and Ca among the soils (Table 4). 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 8a), whereas KPD showed greater extraction of NaOH-I-P fractions (Figure 8b). Stout *et al* (1998) 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.

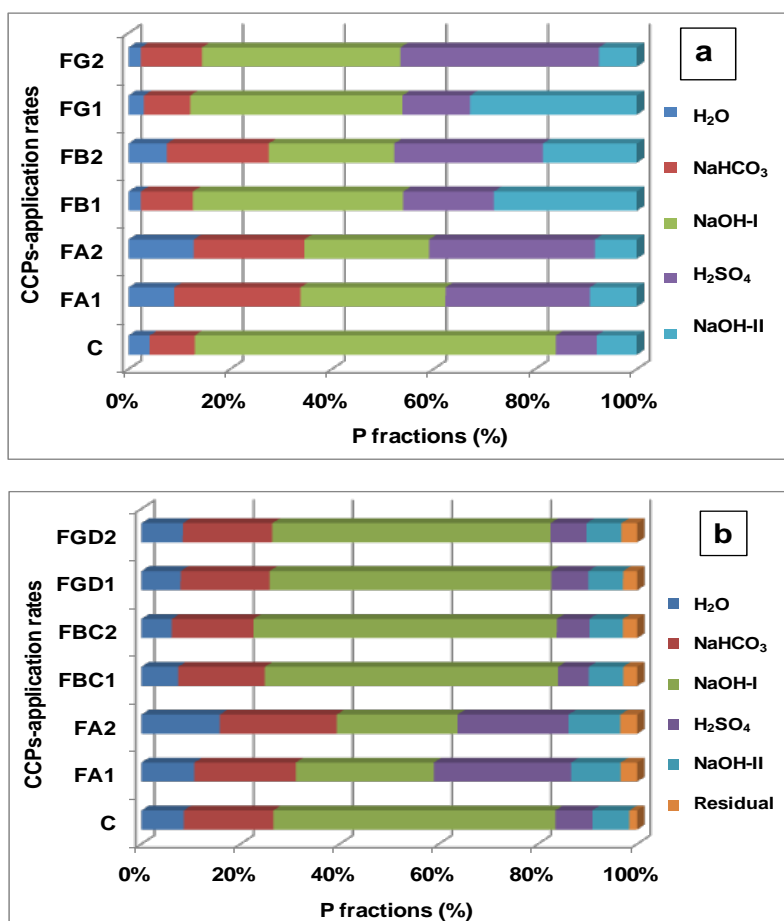


Figure 8 Distribution of P fractions in the two soils a) ADL and b) KPD amended with CCPs. FA1, FA2; FBC1, FBC2; and FGD1, FGD2 indicate 15 and 30 % (w/w) application rates of CCPs, respectively. C in the Y axis indicates control.

In the case of FBC, the water soluble P ($\text{H}_2\text{O-P}$) 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, for example at 30% application rate, the effect on the reduction of soil solution P

decreased, agreeing with P adsorption results (Figure 3). After 63 days of incubation, the P from NaOH-I-P fraction mobilised to $\text{NaHCO}_3\text{-P}$ (Figure 9a and 9b). The $\text{NaHCO}_3\text{-P}$ fraction (corresponds to major portion of the bioavailable P).

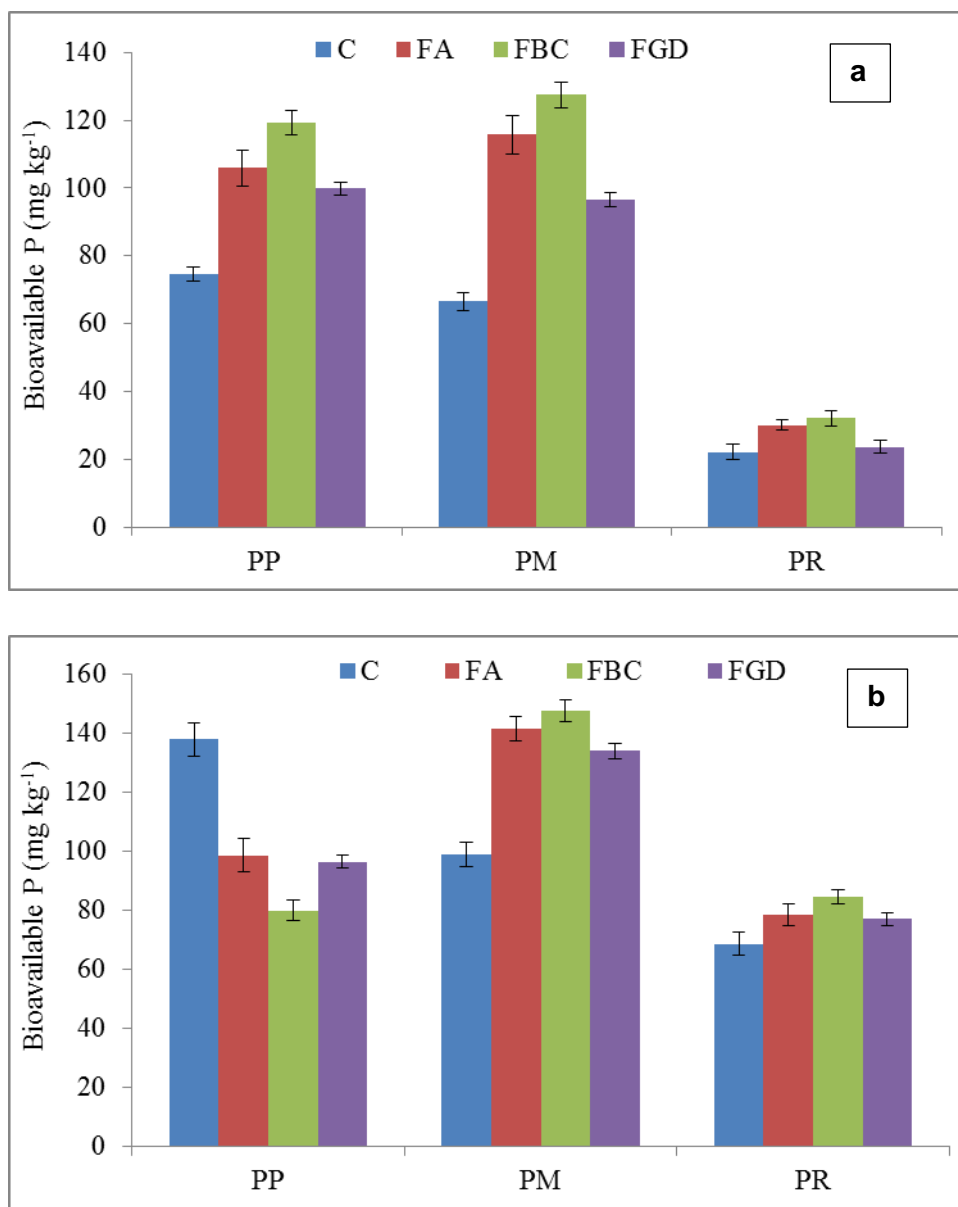


Figure 9 Effect of incubation period (63 days) on bioavailable P in CCPs amended a) ADL and b) KPD soils treated with Potassium dihydrogen phosphite – PP; Poultry manure – PM and Phosphate rock – PR. FA, FBC and FGD indicate 15 % (w/w) application rate of CCPs amended. C in the legend indicates control with no CCPs application. Error bars represent the standard deviation between replicates.

The increase in bioavailable P after long periods (63 days) of CCPs incubation in soils is an encouraging aspect in terms of agronomic importance. Hence, CCPs (especially, FBC) was tried in a leaching study and also a specially designed plant growth experiment to explore their potential in soil management of P and agricultural applications.

3.3 Reduced leaching of applied phosphorus in soil

The leaching of P was studied on ADL soil using two different P sources – potassium dihydrogen phosphate (PP) and poultry manure (PM). The characteristics of the P sources are listed in Table 3. For PP treatment, the leached P from control, FA and FBC were 91.88, 87.75 and 84.99 mg kg⁻¹ respectively, accounting for FA-4.49 % and FBC-7.5 % reductions (Table 4). This reflects the P adsorption values of the CCPs used (Figures 4 and 10a). In the case of PM treatment to ADL soil, both the CCPs increased the P in leachates by 35.53 % (FA) and 18.44 % (FBC). The increase in leachate P for the amendments may be attributed to the increase in the soil solution P because of manure addition (Figure 10 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 3 Chemical characteristics of the soils used for the entire study

P sources	Total elemental concentration (mg kg ⁻¹)				
	P	Al	Fe	Ca	S
Potassium dihydrogen phosphate (PP)	227600 ±199.32	-	-	-	-
Poultry manure (PM)	147800 ±171.67	43510 ±21.38	24890 ±19.25	50500 ±22.63	45820 ±21.52
Phosphate rock (PR)	108700 ±139.07	74310 ±26.73	59900 ±23.82	85620 ±39.56	141.12 ±1.023

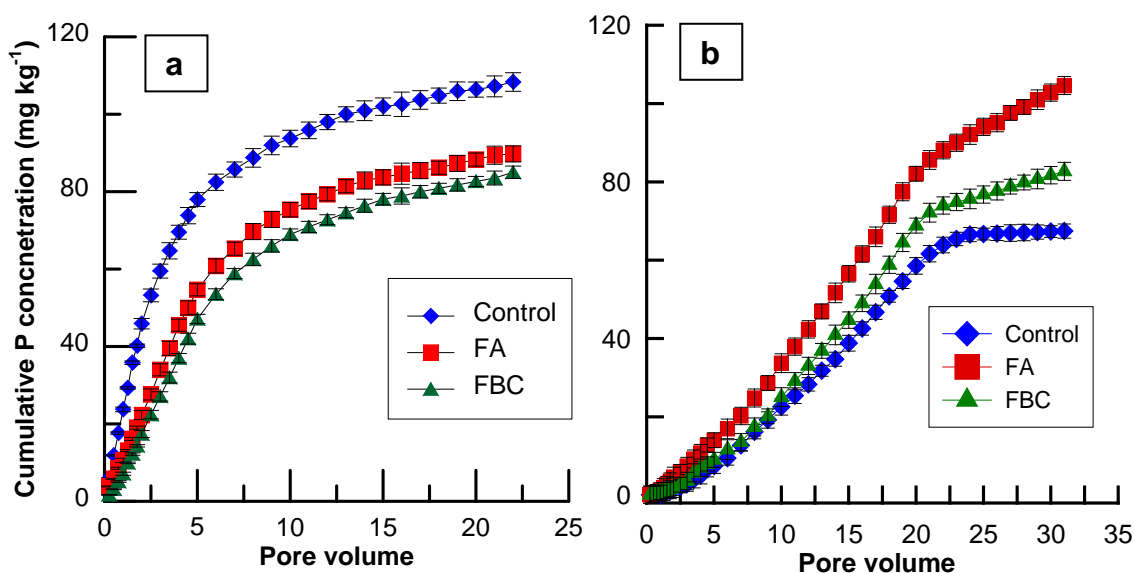


Figure 10 Pulse input leaching - Cumulative P for ADL soil treated with a) PP and b) PM at 100 mg P kg⁻¹ soil as affected by CCPs (15 % w/w). Error bars represent the standard deviation between the replicates.

Table 4 Pulse input leaching: Percentage reduction of the amount of P leached (compared to control soil) in the CCPs amended soil.

Soils and P treatments	CCPs	P added (mg/kg)	P leached (mg/kg)	% of P leached*	CCP-induced change (%)**
Soil+PP	Control	100	91.88	91.88	-
	FA	100	87.75	87.75	- 4.49
	FBC	100	84.99	84.99	- 7.49
Soil+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.

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 ADL) 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 before plotting Figures 10a and 10b.

4. Agronomic response to applied phosphorus in soil

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 solubility of the various P_i compounds directly affects the availability of P for plant growth. The solubility is influenced by the soil pH. The pH also influences the mineralisation of P_o . An increase in pH increases the alkaline phosphatase activity, thereby increasing the mineralisation of organic P (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 be replenished for continued supply to crops (Smith 2002; McDowell 2004). This prompted the use of slow release fertilisers including reactive rock phosphates and organic fertilisers. The P_o from organic fertilisers can be converted to orthophosphates in the presence of phosphatase enzymes (Figure 11), which helps in the mineralisation process (Haygrath & Jarvis 1997; Hayes *et al* 2000; Fuentes *et al* 2006). Although the mineralisation of P_o 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.

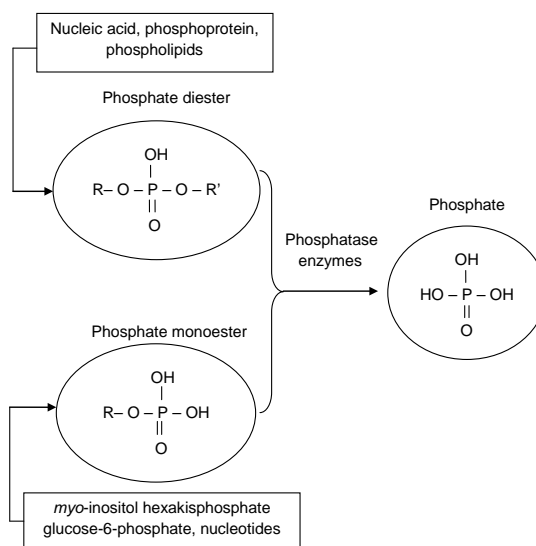


Figure 11 Release of phosphate from organic phosphorus compound

The methodology used for studying the effect of CCPs on plant growth was based on the experiment conducted by Stanford and Dement (1957), which involved the growth of plant initially in a sand medium (Figure 12).

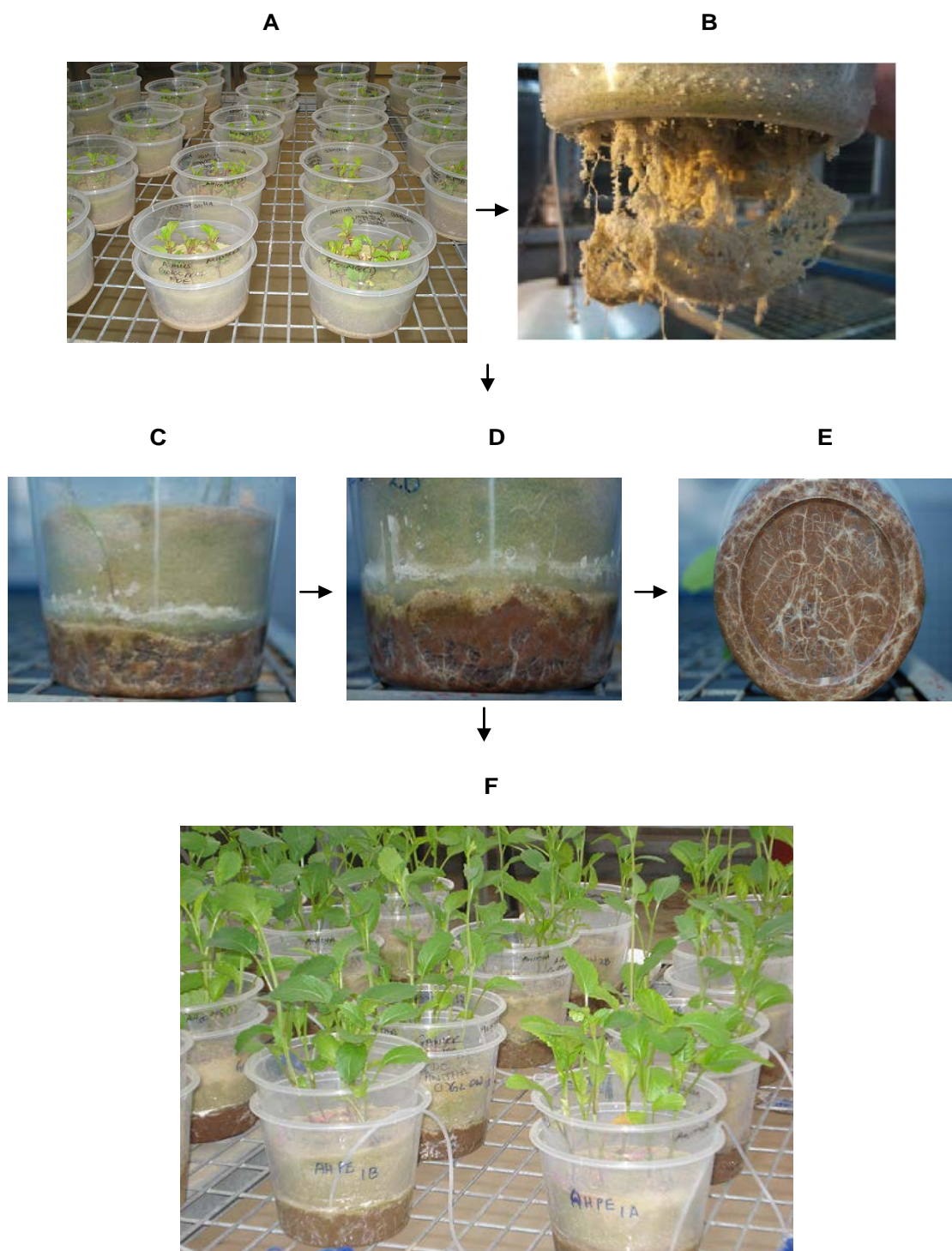


Figure 12 Set up of Stanford – DeMent bioassay technique

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.

On the application of FBC, 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 FBC-induced increases in the mineralisation of P_o and immobilisation of P_i sources (Figure 13).

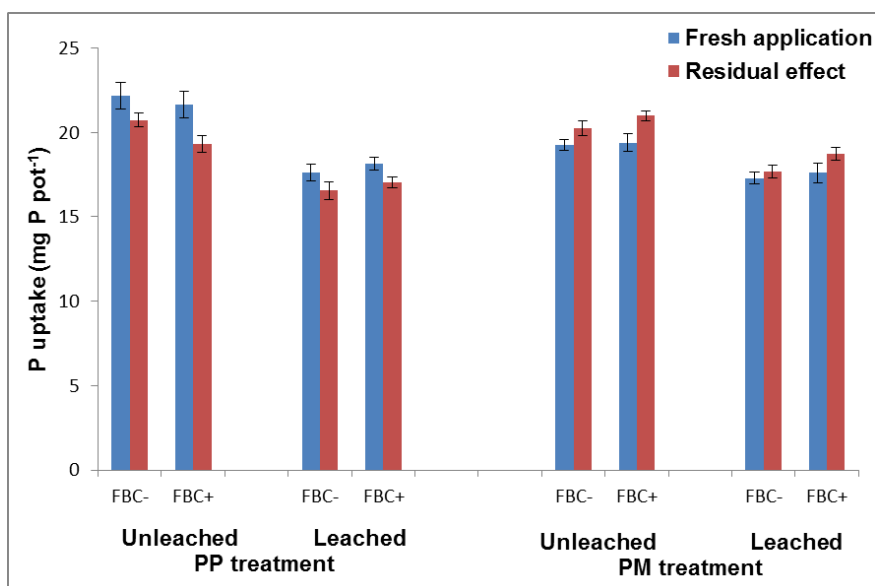


Figure 13 Effect of FBC on P uptake in plants for fresh P application and residual P effect. Error bars represent the standard deviation between the replicates.

In the presence of FBC application, the P in the leachates decreased for PP application and increased in PM treatment which is 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 (Figure 14).

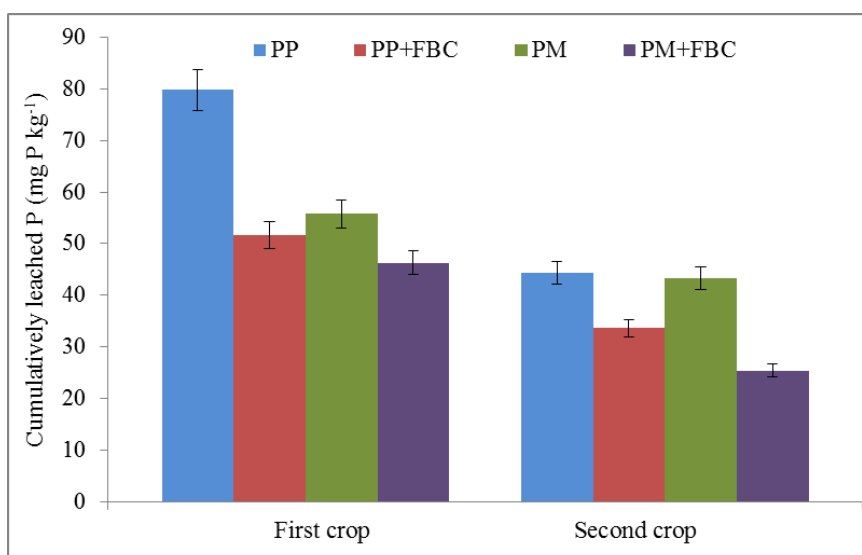


Figure 14 Cumulative P leaching – effect of FBC on P mobility in ADL soil treated with inorganic (PP) and organic (PM) P sources. Error bars represent the standard deviation between the replicates.

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, and
- (2) by mineralising organic P into available P forms favourable for P uptake.

The field experiment conducted in a landfill site using sunflower and mustard plants, examined the effect of FBC on P treated as single super phosphate (SSP), biosolids (BS) and varying combinations of SSP, BS and FBC. In the first crop, yield was higher in SSP alone compared to the plots amended with FBC and BS (Figure 15a and 15b).

The residual effect in the second crop showed the beneficial outcome of the FBC addition as the biomass yields of the plants increased for BS and SSP treated plots (Figure 15a and 15b). This ensured the long-term increase in the bioavailability of P when FBC is applied. 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 (Figure 16). The agronomic effectiveness of the treatments for the residual effect was in the following order: SSP+FBC > BS+FBC > BS alone > SSP alone (Table 5), indicating the role of FBC in mobilising P from SSP and BS. The relative agronomic effectiveness (RAE) was calculated using the following equation (Eqn.1).

$$RAE = \frac{(\text{yield for specific treatment} - \text{yield for nil})}{(\text{yield for SSP alone} - \text{yield for nil})} \times 100 \quad 1$$

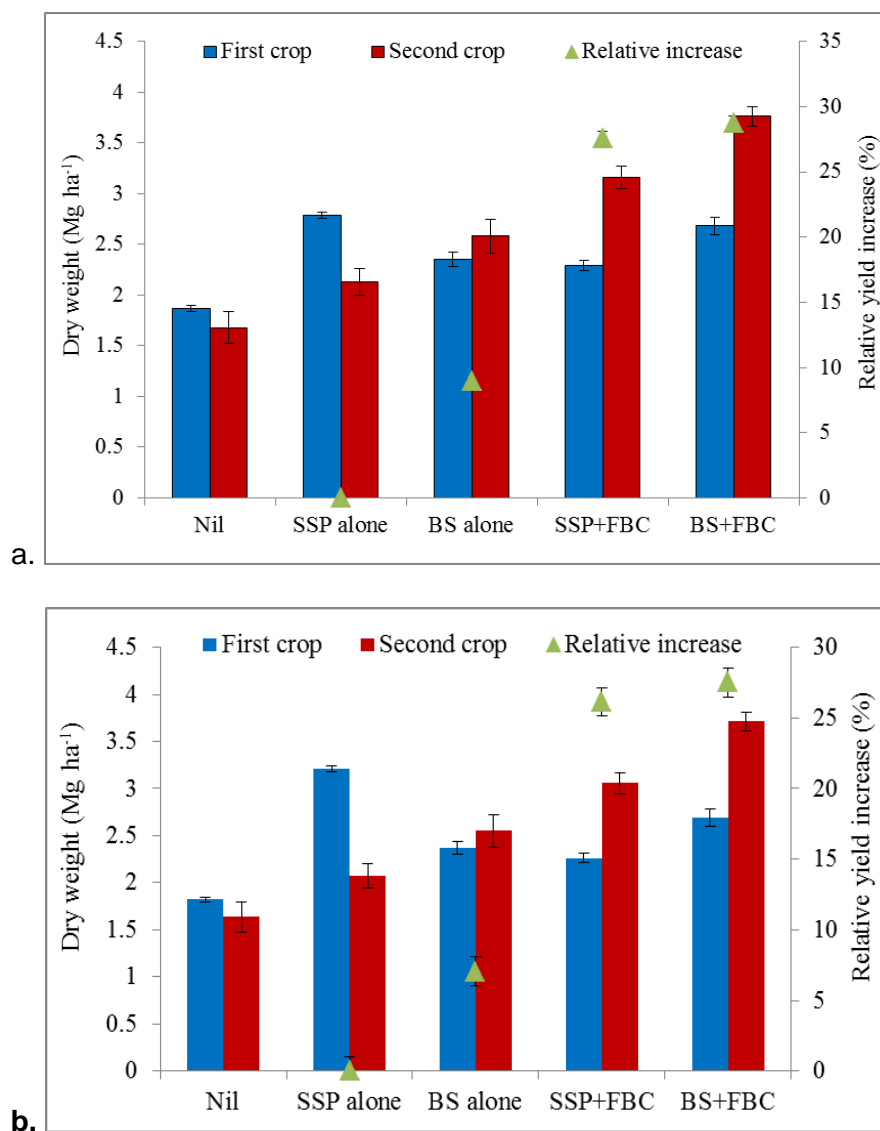


Figure 15 Effect of FBC on (a) sunflower and (b) mustard yields, grown on SSP and BS treated soil in the second cropping.

Relative yield increase = [(Yield for residual – fresh)/Yield of residual] x 100.

Error bars represent the standard deviation between the replicates.

Table 5 Relative agronomic effectiveness of various P treatments

Crops	Relative agronomic effectiveness (RAE %)			
	Sunflower		Mustard	
Treatments	Fresh application	Residual effect	Fresh application	Residual effect
SSP alone	100.0	100.0	100.0	100.0
BS alone	35.91	168.8	33.81	162.7
BS+FBC	38.03	200.6	39.57	202.3
SSP+FBC	64.78	357.7	65.47	376.7

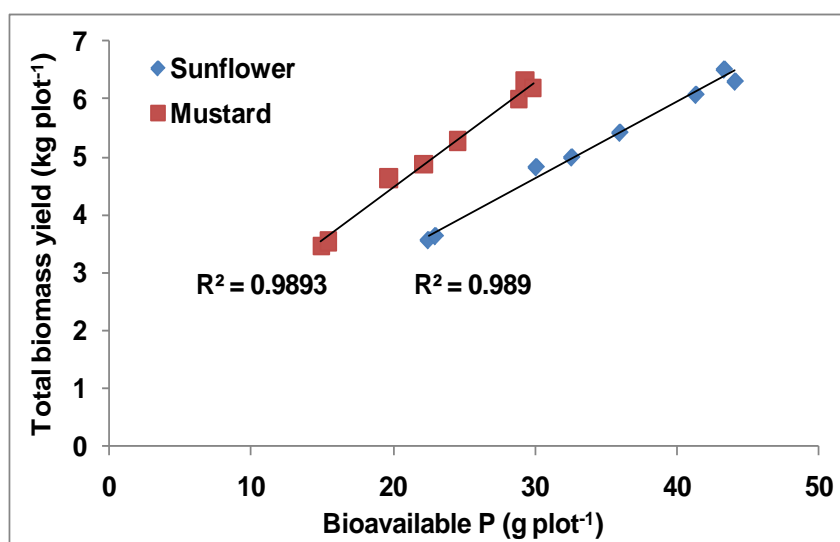


Figure 16 Relationship between Bioavailable P and total biomass yield as affected by the treatment combinations (Nil, SSP, BS, FBC, SSP+BS, SSP+FBC, FBC+BS and SSP+FBC+BS).

5. Possible threats on using coal combustion products

Extensive Environmental and Health impact studies have been carried out on CCPs, especially on FA. The trace elements and heavy metals present in most CCPs readily percolate down from conventionally used earth-lined ash lagoons and pollute ground water. Effect of CCPs on ground water is a function of physical and chemical characteristics of the ash materials and also hydrogeologic and climatic conditions of the disposal site (Theis *et al* 1978; Kopsick & Angino 1981; Goetz 1983). Weathered FA deposits cause more ground water contamination because of the presence of higher levels of soluble salts (Jones & Lewis 1960; Kopsick & Angino 1981; Theis *et al* 1978; Hjelm 1990; Mattigod *et al* 1990). Fly ash, particularly when it has been collected dry 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 CCPs-bound salts are leached away by rainfall. The soluble salt content in CCPs or CCP-treated soil is measured by an assessment of the electrical conductivity (EC) over a water extract. Under strongly acidic conditions (< pH 5.0), CCPs bound heavy metals such as Al, Mn, Zn and Cu can also come into solution and become phytotoxic (Daniels 2002). Table 6 lists out other hazardous effects of CCPs application in soil.

Table 6 List of potential hazards 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

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

Harrison and Yin (2000) conducted epidemiological studies on FA particulate matter exposure and consistently demonstrated adverse effects on human health. 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). 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.

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 in 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, most CCPs are less toxic than crystalline silica (when used as positive control) but significantly more toxic than negative controls (TiO₂, 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. Above all, the usage of CCPs at moderate levels (up to 15 %) of application proved to be non-hazardous to the soil environment. However, more studies are needed to know the fate of CCPs application in the long term perspective.

6. Conclusions

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), potentially 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 in terms of targeted applications, they have less specific values. The CCPs are predominantly used as filling materials in construction industry (ADAA 2009) 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; McDowell 2004), acid neutralising capacity (Shang & Wang 2005; Wang *et al* 2006) and P immobilising capacity (Stout *et al* 1999; Callahan *et al* 2002; McDowell 2005) for sustainable utilization of this resource. By using these CCPs in degraded soils, 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* 2003). 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. 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 (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 (Figure 18). 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 (including Australia) allow the farmers to use the CCPs free of cost.

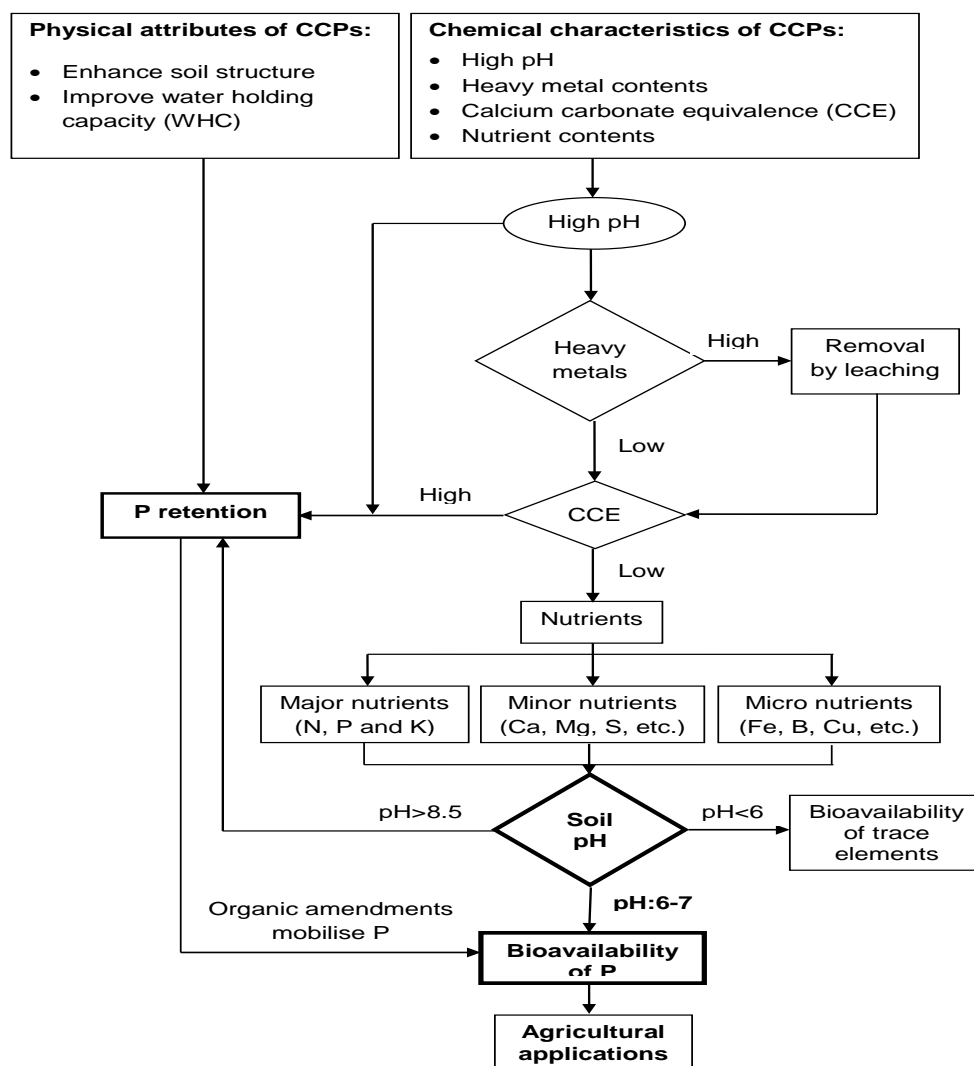


Figure 18 Schematic representation on the factors of CCPs utilisation

7. References

- ADAA 2007, *Coal combustions products – Assessment criteria for use in agricultural applications*, Reference Data Sheet No. 8, Ash Development Association of Australia.
- ADAA 2008, *Annual Membership Survey Results*, Ash Development Association of Australia.
- ADAA 2009, *Australian Amendment of Australian soils by fly ash additions*, Fly ash Technical Note No.9, Ash Development Association of Australia.
- Adriano, D, Page, AL, Elseewi, AA, Chang, AC & Straughan, I 1980, 'Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review', *Journal of Environmental Quality*, vol. 9, pp. 333-344.
- Anderson, DL, Tuovinen, OH, Faber, A & Ostrokowski, I 1995, 'Use of soil amendments to reduce soluble phosphorus in dairy soils', *Ecological Engineering*, vol. 5, pp. 229-246.
- Barrow, NJ 1969, 'Comparison of the sorption of molybdate, sulphate and phosphate by soils', *Soil Science*, vol. 109, pp. 282-289.
- Barrow, NJ 1984, 'Modelling the effects of pH on phosphate sorption by soils', *Journal of Soil Science*, vol. 35, pp. 283-297.
- Basu, M, Pande, M, Bhadoria, PBS & Mahapatra, SC 2009, 'Potential fly-ash utilisation in agriculture: A global review', *Progress in Natural Science*, vol. 19, pp. 1173-1186.
- Beauchemin, S, Hesterberg, D, Chou, J, Beauchemin, M, Simard, RR & Sayers, DE 2003, 'Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation', *Journal of Environmental Quality*, vol. 32, pp. 1809-1819.
- Belkin, HE, Finkelman, RB & Zhang, BS 1999, 'Arsenic poisoning caused by residential coal combustion', in *Pan-Asia-Pacific Conference on Fluoride and Arsenic Research*, Shenyang.
- Bennett, WF 1993, *Nutrient Deficiencies and Toxicities in Crop Plants*, APS Press, St. Paul, Minnesota.
- Bolan, NS, Syers, JK & Tillman, RW 1988, 'Effect of pH on the adsorption of phosphate and potassium in batch and in column experiments', *Australian Journal of Soil Research*, vol. 26, pp. 165-170.
- Bolan, NS, Adriano, D & Curtin, D 2003, 'Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability', *Advances in Agronomy*, vol. 78, pp. 215-272.
- Borm, PJA 1997, 'Toxicity and occupational health hazards of coal fly ash (CFA). A review of data and comparison to coal mine dust', *Annals of Occupational Hygiene*, vol. 41, pp. 659-676.
- Callahan, MP, Kleinman, PJA, Sharpley, AN & Stout, WL 2002, 'Assessing the efficacy of alternative phosphorus sorning soil amendments', *Soil Science*, vol. 167, pp. 539-547.
- Carlson, CL & Adriano, DC 1993, 'Environmental impacts of coal combustion residues', *Journal of Environmental Quality*, vol. 22, pp. 227-247.

- Chen, J, Kong, H, Wu, W, Chen, D, Zhang, X & Sun, Z 2007, 'Phosphate immobilization from aqueous solution by fly ashes in relation to their composition', *Journal of Hazardous Materials*, vol. B139, pp. 293-300.
- Chang, AC, Lund, LJ, Page, AL & Wameke, JE 1977, 'Physical Properties of fly ash-amended soils', *Journal of Environmental Quality*, vol. 6, pp. 267-270.
- Chugh, Y, Patwardhan, A, Munish, S & Botha, F 2006, 'Development of construction materials using sulfite-rich scrubber sludge and fly ash', *Fuel*, vol. 85, pp. 2323-2329.
- Cox, JW, Varcoe, J, Chittleborough, DJ & van Leeuwen, J 2005, 'Using gypsum to reduce phosphorus in runoff from subcatchments in South Australia', *Journal of Environmental Quality*, vol. 34, pp. 2118-2128.
- Curtin, D & Smillie, GW 1995, 'Effect of incubation and pH on soil solution and exchangeable cation ratios', *Soil Science Society of America Journal*, vol. 59, pp. 1006-1011.
- Daniels, LW, Stewart, B, Haering, K & Zipper, C 2002, 'The Potential for Beneficial Reuse of Coal Fly Ash in Southwest Virginia Mining Environments', *Virginia Cooperative Extension*, pp. 460-134.
- Davison, R, Natusch, D & Wallace, J 1974, 'Trace elements in fly ash: Dependence of concentration on particle size', *Environmental Science and Technology*, vol. 8, pp. 1107-1113.
- Dellantonio, A & Fitz, WJ 2010, 'Disposal of coal combustion residues in terrestrial systems: Contamination and risk management', *Journal of Environmental Quality*, vol. 39, pp. 761-775.
- Dogra, S, Khanna, AK & Kaw, JL 1995, 'Alterations in the pulmonary and systemic immune response in rats exposed to coal fly ash', *Immunopharmacology*, vol. 29, pp. 103-109.
- El-Mogazi, D, Lisk, DJ & Weinstein, LH 1988, 'A review of Physical, Chemical and Biological Properties of Fly ash and Effects on Agricultural Ecosystems', *Science of the Total Environment*, vol. 74, pp. 1-37.
- Eveborn, D, Gustafsson, JP, Hesterberg, D & Hillier, S 2009, 'XANES speciation of P in environmental samples: An assessment of filter media for on-site wastewater treatment', *Environmental Science and Technology*, vol. 43, pp. 6515-6521.
- Finkelman, RB, Belkin, HE, Zhang, BS & Centeno, JA 2000, 'Arsenic poisoning caused by residential coal combustion', in *Proceedings of the 31st International Geological Congress*. Guizhou Province, China.
- Fuentes, B, Bolan, NS, Naidu, R & Mora, ML 2006, 'Phosphorus in organic waste-soil systems', *Journal of Soil Science and Plant Nutrition*, vol. 6, pp. 64-83.
- Furihata, T, Suzuki, M & Sakurai, H 1992, 'Kinetic Characterization of two phosphate uptake systems with different affinities in suspension-cultured *Catharanthus roseus* protoplasts', *Plant Cell and Physiology*, vol. 33, pp. 151-1157.
- Geoscience Australia 2011, 'Chapter 5: Coal', *Australian Energy Resource Assessment*, viewed August 2011, https://www.ga.gov.au/image_cache/GA16878.pdf
- Goetz, L 1983, 'Radiochemical techniques applied to laboratory studies of water leaching of heavy metals from coal fly ash', *Water Science and Technology*, vol. 15, pp. 25-47.
- Grant, CA, Grant, DNF, Tomasiewicz, DJ & Sheppard, SC 2001, 'The importance of early season phosphorus nutrition', *Canadian Journal of Plant Science*, vol. 81, pp. 211-224.

Gray, CA & Schwab, AP 1993, 'Phosphorus-fixing ability of high pH, high calcium, coal-combustion, waste materials', *Water, Air and Soil Pollution*, vol. 69, pp. 309-320.

Grubb, DG, Guimaraes, MS & Valencia, R 2000, 'Phosphate immobilization using an acidic type F fly ash', *Journal of Hazardous Materials*, vol. 76, pp. 217-236.

Harrison, RM & Yin, J 2000, 'Particulate matter in the atmosphere: which particle properties are important for its effects on health?', *Science of the Total Environment*, vol. 249, pp. 85-101.

Hayes, JE, Richardson, AE & Simpson, RJ 2000, 'Components of organic phosphorus in soil extracts that are hydrolysed by phytase and acid phosphatase', *Biology and Fertility of Soils*, vol. 32, pp. 279-286.

Haygarth, PM & Jarvis, SC 1997, 'Surface runoff of soil derived phosphorus from grazed grassland lysimeters', *Water Research*, vol. 31, pp. 140-148.

Healthwaite, AL, Griffiths, P, Haygarth, PM & Jarvis, SC 1997, 'Phosphorus loss from grassland soils: Implications of land management for the quality of receiving waters. Freshwater Contamination', in *Proceedings of Rabat Symposium S4*, pp. 177-186.

Hedley, ML & McLaughlin, ML 2005, 'Reactions of phosphate fertilizers and by-products in soil', in *Phosphorus: Agriculture and the Environment*, Sims, JT & Sharpley, AN (eds.), Agricultural Monograph No. 46, ASA-CSSA-SSSA, Madison, Wisconsin, USA.

Heidrich, C 2003, 'Ash Utilisation - a perspective on coal use in Australia', presented at 12th International Conference on Coal Science, Cairns, Australia.

Hjelmar, O 1990, 'Leachate from land disposal of coal fly ash', *Waste Management Research*, vol. 8, pp. 429-449.

Holford, ICR 1997, 'Soil phosphorus: its measurement, and its uptake by plants', *Australian Journal of Soil Research*, vol. 35, pp. 227-239.

IEA 2008, *World energy outlook*, International Energy Agency, Paris.

Jones, LH & Lewis, AV 1960, 'Weathering of fly ash', *Nature*, vol. 185, pp. 404-405.

Kopsick, DA & Angino, EE 1981, 'Effect of leachate solutions from fly and bottom ash on groundwater quality', *Journal of Hydrology*, vol. 54, pp. 341-356.

Korcak, RF 1985, 'Effect of coal combustion waste used as lime substitutes on nutrition of apples on three soils', *Plant and Soil*, vol. 85, pp. 437-441.

Korcak, RF 1995, 'Utilization of coal combustion by-products in agriculture and horticulture', in *Agricultural Utilization of Urban and Industrial By-Products*, American Society of Agronomy: Crop Science Society of America: Soil Science Society of America, Madison, USA.

Lai, KM, Ye, DY & Wong, JWC 1999, 'Enzyme activities in a sandy soil amended with sewage sludge and coal fly ash', *Water, Air and Soil Pollution*, vol. 113, pp. 261-272.

Lighty, JS, Veranth, JM & Sarofim, AF 2000, 'Combustion aerosols: factors governing their size and composition and implications to human health', *Journal of Air and Waste Management Association*, vol. 50, pp. 1565-618.

Lindsay, WL 1979, *Chemical equilibria in soils*, John Wiley and Sons, New York.

Lindsay, WL, Vlek, PLG & Chien, SH 1989, 'Phosphate minerals', in *Minerals in soil environment*, 2nd edition, Dixon, JB & Weed, SB (eds), Soil Science Society of America, Madison, U.S.A.

- Mattigod, SV, Rai, D, Early, LE & Ainsworth, CC 1990, 'Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements', *Journal of Environmental Quality*, vol. 19, pp. 188-201.
- McDonald, AD, McDonald, JC, Rando, RJ, Hughes, JM & Cohort, WH 2001, 'Mortality Study of North American Industrial Sand Workers. I. Mortality from Lung Cancer, Silicosis and Other Causes', *Annals of Occupational Hygiene*, vol. 45, pp. 193-199.
- McDowell, RW & Shapley, AN 2001, 'Phosphorus losses in subsurface flow before and after manure application to intensively farmed land', *Science of the Total Environment*, vol. 278, pp. 113-125.
- McDowell, RW 2004, 'The effectiveness of industrial by-products to stop phosphorus loss from a Pallic soil', *Australian Journal of Soil Research*, vol. 42, pp. 755-761
- McDowell, RW 2005, 'The effectiveness of coal-fly ash to decrease phosphorus loss from grassland soils', *Australian Journal of Soil Research*, vol. 43, pp. 853-860.
- Mullins, G, Joern, BC & Moore, PA 2005, 'By-product phosphorus: Sources, characteristics, and management', in *Phosphorus: Agriculture and the Environment*, Sims, JT & Sharpley, AN (eds.), American Society of Agronomy: Crop Science Society of America: Soil Science Society of America, Madison, WI, USA.
- Murphy, PNC & Stevens, RJ 2010, 'Lime and gypsum as source measures to decrease phosphorus loss from soils to water', *Water Air Soil Pollution*, vol. 212, pp. 101-111.
- Natusch, DFS & Wallace, JR 1974, 'Urban aerosol toxicity: The influence of particle size', *Science*, vol. 186, pp. 695-699.
- Parfitt, RL, Yeates, GW, Ross, DJ, Mackay, AD & Budding, PJ 2005, 'Relationships between soil biota, nitrogen and phosphorus availability, and pasture growth under organic and conventional management', *Applied Soil Ecology*, vol. 28, pp. 1-13.
- Pathan, SM, Aylmore, LAG & Colmer, TD 2002, 'Reduced leaching of nitrate, ammonium and phosphorus in a sandy soil by fly ash amendment', *Australian Journal of Soil Research*, vol. 40, pp. 1201-1211.
- Pierzynski, GM, McDowell, RW & Sims, JT 2005, 'Chemistry, cycling, and potential movement of inorganic phosphorus in soils', in *Phosphorus: Agriculture and the Environment*, Sims, JT & Sharpley, AN (eds.), American Society of Agronomy: Crop Science Society of America: Soil Science Society of America, Madison, WI, USA.
- Pratt, C, Shilton, A, Pratt, S, Haverkamp, RG & Bolan, NS 2007, 'Phosphorus removal mechanisms in active slag filters treating waste stabilization pond effluent', *Environmental Science and Technology*, vol. 41, pp. 3296-3301.
- Reichert, JM & Norton, LD 1994, 'Fluidised bed bottom-ash effects on infiltration and erosion of swelling soils', *Soil Science Society of America Journal*, vol. 58, pp. 1483-1488.
- Sajwan, KS, Ornes, WH & Youngblood, T 1995, 'The effect of fly ash/sewage sludge mixtures and application rates on biomass production', *Journal of Environmental Science and Health*, vol. 30, pp. 1327-1337.
- Seiter, JM, Staats-Borda, KE, Ginder-Vogel, M & Sparks, DL 2008, 'XANES spectroscopic analysis of phosphorus speciation in alum-amended poultry litter', *Journal of Environmental Quality*, vol. 37, pp. 477-485.
- Shang, JQ & Wang, HL 2005, 'Coal fly ash as contaminant barrier for reactive mine tailings', *Proceedings of World of Coal Ash Conference*, Lexington, KY.
- Sharpley, A 1999, 'Agricultural phosphorus, water quality, and poultry production: are they compatible?', *Poultry Science*, vol. 78, pp. 660-673.

- Sharpley, AN & Moyer, B 2000, 'Phosphorus forms in manure and compost and their release during simulated rainfall', *Journal of Environmental Quality*, vol. 29, pp. 508-514.
- Sharpley, AN & Withers, PJA 1994, 'The environmentally-sound management of agricultural phosphorus', *Fertiliser Research*, vol. 39, pp. 133-146.
- Sharpley, AN, Chapra, SC, Wedepohl, R, Sims, JT, Daniel, TC & Reddy, KR 1994, 'Managing agricultural phosphorus for protection of surface waters: Issues and options', *Journal of Environmental Quality*, vol. 23, pp. 437-451.
- Smith, F.W. (2002). The phosphate uptake mechanism. *Plant and Soil*. 245: 105-114.
- Snars, K, Gilkes, R & Hughes, J 2002, 'Effect of bauxite residue (red mud) on the availability of phosphorus in very sandy soils' *17th World Congress of Soil Science*, Thailand.
- Stanford, G & Dement, JD 1957, 'A method for measuring short-term nutrient absorption by plants: I. Phosphorus¹', *Soil Science Society of America Journal*, vol. 21, pp. 612-617.
- Stehouwer, RC, Dick, WA & Sutton, P 1999, 'Acidic soil amendment with a magnesium-containing fluidized bed combustion by-product', *Agronomy Journal*, vol. 91, pp. 24-32.
- Stewart, BR, Daniels, WL & Jackson, ML 1997, 'Evaluation of leachate quality for codisposed coal fly ash and coal refuse', *Journal of Environmental Quality*, vol. 26, pp. 1417-1424.
- Stout, WL, Sharpley, AN & Pionke, HB 1998, 'Reducing soil phosphorus solubility with coal combustion by-products', *Journal of Environmental Quality*, vol. 27, pp. 111-118.
- Stout, WL, Sharpley, AN, Gburek, WJ & Pionke, HB 1999, 'Reducing phosphorus export from croplands with FBC fly ash and FGD gypsum', *Fuel*, vol. 78, pp. 175-178.
- Stout, WL, Sharpley, AN & Landa, J 2000, 'Effectiveness of coal combustion by-products in controlling phosphorus export from soils', *Journal of Environmental Quality*, vol. 20, pp. 1239-1244.
- Stuczynski, TI, McCarthy, GW & Wright, RJ 1998a, 'Impact of coal combustion amendments on soil quality: I. Mobilization of soil organic nitrogen', *Soil Science*, vol. 163, pp. 952-959.
- Stuczynski, TI, McCarthy, GW, Wright, RJ & Reeves, JB 1998b, 'Impact of coal combustion amendments on soil quality: II. Mobilization of soil organic carbon', *Soil Science*, vol. 163, pp. 960-969.
- Summers, R, Smirk, D & Karafilis, D 1996, 'Phosphorus Retention and Leachate From Sandy Soil Amended with Bauxite Residue (Red Mud)', *Australian Journal of Soil Research*, vol. 34, pp. 555-567.
- Sumner, ME & Yamadu, T 2002, 'Farming with acidity', *Communications in Soil Science and Plant Analysis*, vol. 33, pp. 2467-2496.
- Syers, JK, Johnston, AE, Curtin, D 2008, 'Efficiency of soil and fertilizer phosphorus: Reconciling changing concepts of soil phosphorus behaviour with agronomic information', *FAO Fertilizer and Plant Nutrition Bulletin* 18, Rome, Italy.
- Theis, TL, Westrick, JD, Hsu, CL & Marley, JJ 1978, 'Field investigation of trace metals in groundwater from fly ash disposal', *Journal of Water Pollution Control Federation*, vol. 50, pp. 2457-2469.

Twardowska, I & Stefaniak, S 2006, 'Coal and coal combustion products: Prospects for future and environmental issues', in *Coal combustion byproducts and environmental issues*, Sajwan, KS, Twardowska, I, Punshon, T & Alva, AK (eds.), Springer Publishers, New York, USA.

Twardowska, I & Szczepanska, J 2002, 'Solid waste: terminological and long-term environmental risk assessment problems exemplified in a power plant fly ash study', *Science of Total Environment*, vol. 285, pp. 29-51.

Ullrich-Eberius, C, Novacky, A & van Bel, A 1984, 'Phosphate uptake in *Lemna gibba* G1: energetics and kinetics', *Planta*, vol. 161, pp. 46–52.

Urvashi, M, Masto, RE, Selvi, VA, Ram, LC & Srivastava, NK 2007, 'An international study: effect of farm yard manure on the release of P from fly ash', *Remediation*, pp. 70-81.

Wang, HL, Hedley, MJ, Bolan, NS & Horne, DJ 1999, 'The influence of surface incorporated lime and gypsiferous by-products on surface and subsurface soil acidity. I. Soil solution chemistry', *Australian Journal of Soil Research*, vol. 37, pp. 165-180.

Wang, H, Bolan, NS, Hedley, MJ & Horne, DJ 2006, 'Potential uses of fluidized bed boiler ash (FBA) as a liming material, soil conditioner and sulfur fertilizer', in *Coal combustion byproducts and environmental issues*, Sajwan, KS, Twardowska, I, Punshon, T & Alva, AK (eds.), Springer Publishers, New York, USA.

Whitehouse, LJ, Wang, H & Tomer, MD 2000, 'Guidelines for the utilisation of sewage effluent on land. Part II: issues for design and management', New Zealand land Treatment Collective and Forest Research, Rotorua, New Zealand.

Yunusa, IAM, Eamus, D, DeSilva, DL, Murray, BR, Burchett, MD, Skilbeck, GC & Heidrich, C 2006, 'Fly-ash: an exploitable resource for management of Australian agricultural soils', *Fuel*, vol. 85, pp. 2337-2344.

