Sorption and bioavailability of phosphorus in soils as affected by coal combustion products

Balaji Seshadri[A, C], Chaturangi Wickremaratne[B], Nanthi S. Bolan[C], Ken Brodie[D], Ravi Naidu[A, C]

[A]Cooperative Research Centre – Contamination Assessment and Remediation of Environment (CRC-CARE), Mawson Lakes, SA 5095, Australia, Email Balaji.Seshadri@postgrads.unisa.edu.au
[B]Australian National University, Canberra, Australia
[C]Centre for Environmental Remediation and Risk Assessment, University of South Australia, Mawson Lakes campus, SA 5095, Australia
[D]Flinders Power, Port Augusta Power Stations, Port Augusta, SA, Australia

Abstract

The retention and transformation of phosphorus (P) in soils, to which coal combustion products (CCPs) had been applied, were evaluated using sorption and fractionation experiments. Fly ash (FA), fluidised bed boiler ash (FB) and flue gas desulphurisation gypsum (FG) were applied (0%, 15% and 30%) to three different soils – loam (from Adelaide hills), silty loam (from Kapunda) and loamy sand (from Virginia agricultural land) and incubated for 21 days at 25ºC. The soils were pre-treated with P from three different sources (potassium dihydrogen phosphate, poultry manure and rock phosphate) at the rate of 100 mg P/kg soil and 200 mg P/kg soil. In all soils, pH and P sorption increased with increasing application rates of FA and FB application. In the case of FG, both pH and P sorption decreased at the highest level of application. The fractionation of P in CCPs amended soils showed high concentration of P in Ca-associated P (H_2SO_4-P) followed by bioavailable P ($NaHCO_3$-P). Soil solution P (H_2O-P) decreased with increasing application rates of CCPs except for FG amended soils. The NaOH-P was relatively less responsive to CCPs application.

Key Words

P retention capacity, coal-fired power stations, eutrophication, run off, leaching, environmental degradation

Introduction

Phosphorus (P) has been the most limiting nutrient in most agricultural soils throughout the world. Australian soils are inherently deficient in P and are also poor in retaining 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. 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 and safeguarding water quality. High pH and high calcium (Ca) 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 coal combustion products (CCPs) such as fly ash (FA), bottom ash and other by-products of the coal-fired power stations such as fluidised bed boiler ash (FB) and flue gas desulphurisation gypsum (FG) have been effective in decreasing soil solution P loss (Callahan *et al.* 2002; McDowell 2005; Stout *et al.* 2000). Some studies also showed the effectiveness of FA in mitigating particulate or 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 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 forms. Hence, the objective of this study was to examine the effect of CCPs on the retention and transformation of P in soils treated with various P sources.

Methods

Soils and coal combustion products:

The soils for the fractionation experiment were collected from three different locations around Adelaide, Australia – Adelaide hills loam (natural soil), Kapunda silty loam (natural soil) and Virginia loamy sand (Agricultural soil). All the soils were collected from surface (0-5cm), air-dried and sieved <2 mm depth. The

CCPs used for the experiment were fly ash (FA) from Port Augusta Power station, South Australia; fluidised bed boiler ash (FB) from Redbank Power limited, Queensland, and flue gas desulphurisation gypsum (FG) from Illinois, the United States. The P sources used for the experiment were potassium dihydrogen phosphate (PP), poultry manure (PM) and phosphate rock (PR). The basic characteristics of the materials used are given in Table 1.

Table 1. Basic characteristics of soils and CCPs used.

Materials	Sources	pH	EC (µS/cm)	Olsen P (mg/kg)	$CaCO_3$ equivalence
Soils	Adelaide hills – Loamy	5.6	30.04	3.82	-
	Kapunda – Silty loam	7.1	49.5	9.60	-
	Virginia – Loamy sand	7.3	364	88.31	-
CCPs	FB – Redbank Power, QLD	12.7	9.70	11.52	23.25%
	FG – United States	10.1	2.332	2.25	11.25%
	FA – Port Augusta	10.2	1.34	260.44	16.75%

Incubation

The soils (500 g each) were initially treated with the three P sources at the rates of 100 mg/kg soil and 200 mg/kg soil. The soils were incubated in a plastic bag 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 0%, 15% and 30% (w/w) of CCPs. The CCPs treated samples were again incubated for 21 days at 80% of the total WHC.

Fractionation experiment

The incubated soil samples were air-dried immediately after the incubation period and analysed for P fractions using Mc Dowell's fractionation methodology (Mc Dowell 2005), pH and EC. For this fractionation procedure, incubated soil samples (1 g each) were extracted sequentially by shaking with the following solutions: i. 30 mL of deionised water for 2 hours, ii. 0.5 M $NaHCO_3$ for 16 hours, iii. 0.1 M NaOH-I for 16 hours, iv. 0.5 M H_2SO_4 for 16 hours and v. 0.1 NaOH-II – Sonicated for 5 minutes and shaken for 16 hours. The remaining P was extracted by digesting the samples with *aqua regia* (concentrated HNO_3:HCl – 3:1). The P from the extracted samples were analysed using the colorimetric method of Murphy and Riley (1962).

Sorption experiment

For P sorption measurement, 1g of CCPs incubated soil was weighed into 50 ml centrifuge tubes and then mixed with 20 mL of P solution containing graded concentrations of P (0, 5, 10, 20, 50, 150, 500 mg P/L) as KH_2PO_4 (McDowell and Condron 2004). Then the tubes were shaken for 16 hours using a shaker at the room temp (25^0C $\pm$ 2). The tubes were centrifuged for 20 minutes (4000 rpm) and filtered. The phosphate concentration of the filtered solutions was measured using the phosphomolybdate method (Murphy and Riley 1962). The amount of P sorbed was calculated from the difference between added and equilibrium concentrations.

The Freundlich equation (1) was used to fit the adsorption data and to estimate the sorption parameters.

$$\mathbf{S = K_f C^n} \qquad (1)$$

Where, S= Amount Adsorbed (mg/kg); C= Equilibrium Concentration (mg/L); n and K_f are constants.

Results

Fractionation experiment

The application of CCPs showed significant changes in P concentration and distribution of different P fractions. The highly responsive fractions to CCPs application were $NaHCO_3$–P and H_2SO_4–P, where P concentration increased with increasing application rates of all the amendments (Figure 1). This is attributed to the increase in soil pH due to the liming effect of these CCPs, except FG (McDowell 2004). The $NaHCO_3$–P and H_2SO_4–P fractions were the major portions of the extracted P. Soil solution P (water-extractable P) in FA applied soils increased with increasing application rates of FA but showed decreasing trends on application of FB and FG. NaOH-P-I and NaOH-P-II fractions were relatively low in P concentrations; however, these fractions showed similar trends as other fractions on CCPs application. In all the fractions, FA application showed the highest P concentrations followed by FB and FG.

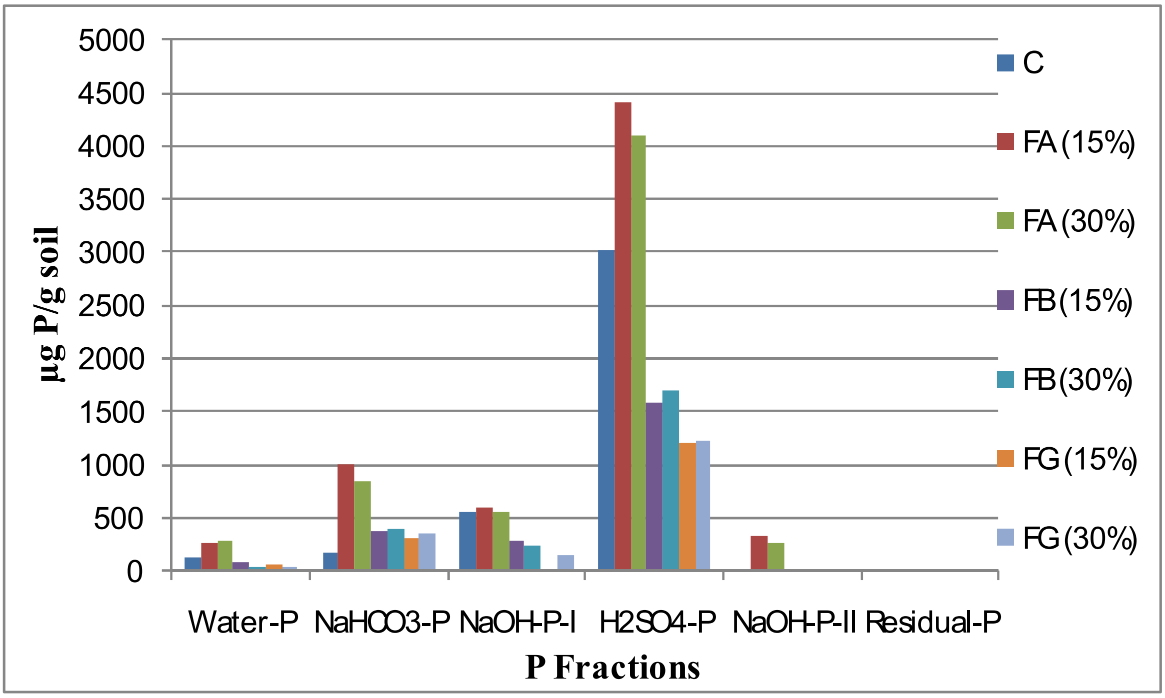

Figure 1. P fractions in CCPs amended soils.

Sorption experiment

Addition of CCPs increased the sorption of P as measured by the K_f value and except for FG the sorption of P increased with increasing levels of amendments (Figure 2 a and b). In the case of FG, the sorption of P decreased at the highest application rate.

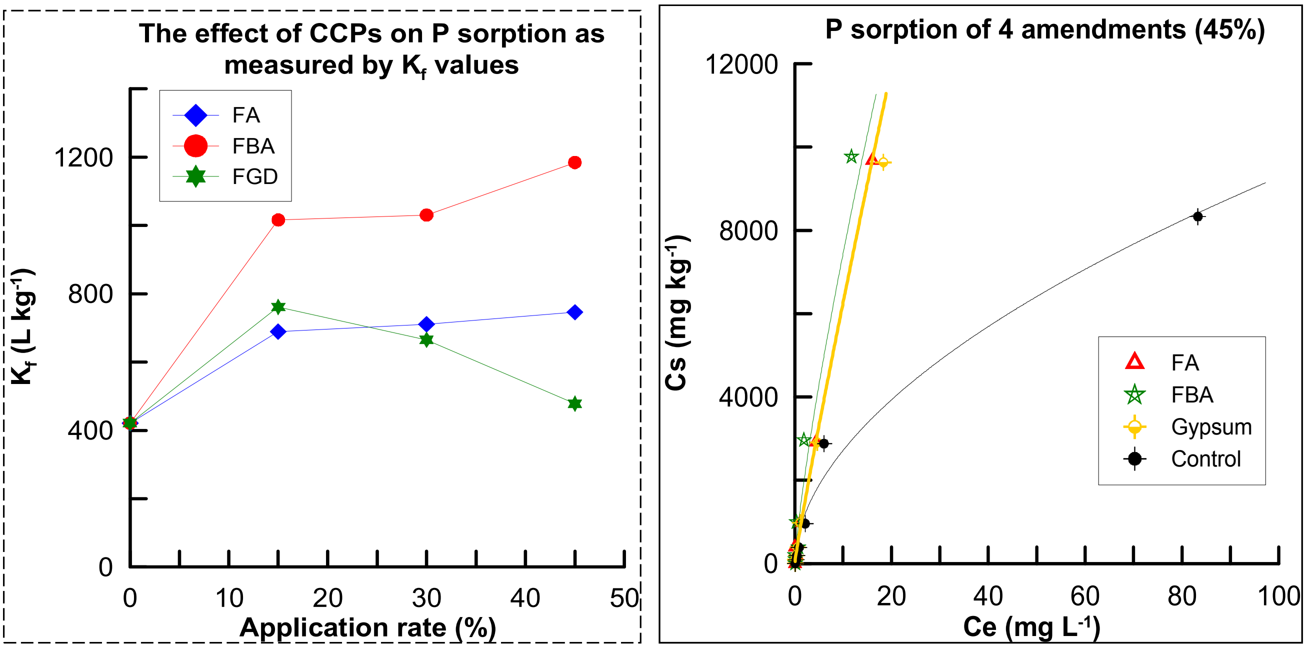

Figure 2a. The effect of CCPs on P sorption as measured by K_f value and b. P sorption of 4 amendments at maximum application rate.

The increase in P sorption with the addition of CCPs is attributed to an increase in soil pH (Figure. 3) 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.

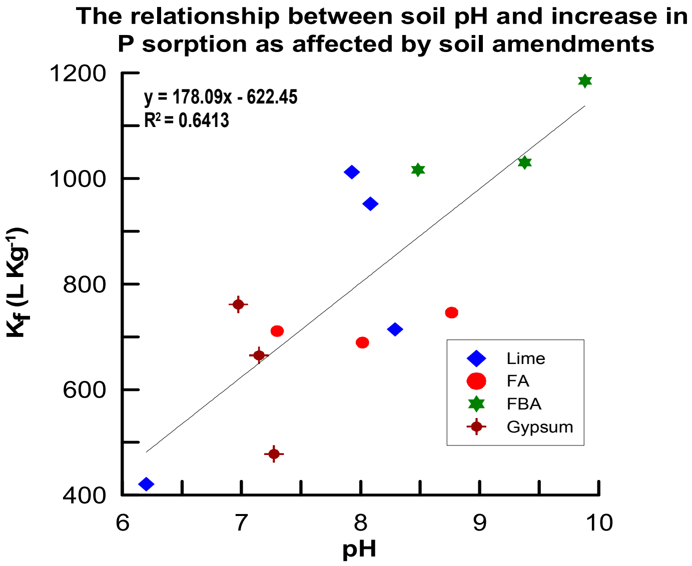

Figure 3. The relationship between soil pH and increase in P sorption as affected by soil amendments.

Conclusion

The results indicate that CCPs proved to increase the sorption and bioavailability 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. However, some of these CCPs may contain heavy metals that are toxic to plants and animals. The toxicity of these heavy metals needs to be addressed using appropriate chemical and biological agents.

References

Callahan MP, Kleinman PJA, Sharpley AN, Stout WL (2002) Assessing the efficacy of alternative phosphorus sorning soil amendments. *Soil Science* **167**, 539-547.

McDowell RW (2004) The effectiveness of industrial by-products to stop phosphorus loss from a Pallic soil. *Australian Journal of Soil Research* **42**, 755-761.

McDowell RW and Condron LM (2004) Estimating phosphorus loss from New Zealand pastoral soils. *New Zealand Journal of Agricultural Research* **47**, 137-145.

McDowell RW (2005) The effectiveness of coal-fly ash to decrease phosphorus loss from grassland soils. *Australian Journal of Soil Research* **43**, 853-860.

Murphy J and Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **27**, 31-36.

Reichert JM and Norton LD (1994) Fluidised bed bottom-ash effects on infiltration and erosion of swelling soils. *Soil Science Society of America Journal* **58**, 1483-1488.

Stout WL, Sharpley AN, Landa J (2000) Effectiveness of coal combustion by-products in controlling phosphorus export from soils. *Journal of Environmental Quality* **20**, 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* **163**, 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* **163**, 960-969.