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**NITROGEN AND PHOSPHORUS DYNAMICS IN  
BAUXITE-PROCESSING RESIDUE SAND – EFFECTS  
OF pH ON AMMONIUM AND PHOSPHORUS  
ADSORPTION AND TRANSFORMATION**

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## SUMMARY

Addition of fertiliser is essential for establishing and maintaining a vegetation cover on Alcoa of Australia (Alcoa) residue sand embankments. Currently, 2.7 t/ha of di-ammonium phosphate (DAP) based inorganic fertiliser are applied as part of residue rehabilitation operations. However, the highly alkaline and saline character, low cation exchange capacity (CEC), presence of phosphorus (P) fixing minerals, and extreme exchangeable sodium (Na) percentage (ESP) of bauxite-processing residue sand (BRS) can severely limit the efficiency of fertiliser use by the growing vegetation, particularly at the time of establishment. Despite the potential existence of key nutrient loss mechanisms in BRS, the impacts of these mechanisms on residue rehabilitation have not been previously investigated.

The major aim of this study was to quantify N and P dynamics in BRS over a range of pH (pH 4, 7, 9 and 11) and cation (Na and Ca) systems. The specific objectives were to (1) to quantify N and P availability and adsorption behaviour in different sources of BRS with different pH treatments and DAP application rates; (2) quantify possible loss mechanisms and transformations (e.g. volatilisation, nitrification, adsorption) affecting N and P availability; and (3) recommend the suitability of the current fertiliser type and rate for residue rehabilitation, and recommend other fertilisers that may be more suitable alternatives.

An incubation study found that approximately 85% of applied N as  $\text{NH}_4^+$ -N was lost as  $\text{NH}_3$  within 24 h after addition to “fresh” BRS (pH > 11), with nearly 95% being lost within 7 days after DAP addition. Although gypsum will reduce the pH of BRS from  $\approx 11$  to 9.5, the heterogeneous distribution of gypsum throughout the residue sand profile means that “fresh” residue sand embankments can be expected to exhibit pH values ranging between  $\approx 9$  to  $\approx 11$ . This provides a mechanism for massive loss of DAP-N through volatilisation. Furthermore, this loss can occur within a very short time period and so little N remains in plant available forms. This may explain the very low to negligible inorganic N concentrations measured in BRS and plant tissue for new (<12 months) and established (>12 months) residue rehabilitation.

Phosphorus sorption was found to decrease with increasing pH (pH 7 to 11), indicating increased availability under highly alkaline conditions. Furthermore, much of the P sorption occurred on Fe and Al oxides and hydrous oxides. Since much of the surface electrical charge and P sorption surfaces are associated with Fe and Al oxides and hydroxides, then factors controlling the precipitation/dissolution (e.g. redox, acidification, etc.) of these surfaces will also affect P

availability. Under current operating conditions, there are no obvious mechanisms which could affect the stability of these oxide surfaces. Although between 25 and 50% of the added P may be present in plant available forms in the short term, information is still required on the long term buffering capacity of BRS in terms of its ability to supply plant available P through desorption (release of sorbed P), the leachability of BRS-P, and the contribution of phosphogypsum to P use by residue rehabilitation.

The incubation study described in this report provides strong evidence that the current use of inorganic  $\text{NH}_4^+$ -N based fertiliser is inappropriate for use in highly alkaline BRS. It is therefore recommended that if the BRS pH cannot be operationally adjusted to near-neutrality, then alternative forms of fertiliser and/or time of application need to be identified. Suitable alternatives include the use of nitrate ( $\text{NO}_3^-$ -N) as the primary inorganic N source. However,  $\text{NO}_3^-$ -N is a highly mobile anion which would not be retained to a large extent by a net negatively charged soil. Since fertiliser is commonly applied during the wet season in Western Australia residue rehabilitation operations, there is an excellent opportunity for loss of  $\text{NO}_3^-$ -N through leaching. This is further exacerbated by the lack of established vegetation with a root structure or capability to take up the applied  $\text{NO}_3^-$ -N before it moves below the rootzone via leaching. Additional studies to understand  $\text{NO}_3^-$  leaching in BRS is required before the role of  $\text{NO}_3^-$ -N-based fertilisers can be properly evaluated.

Organic fertilisers offer an alternative however the BRS (particularly fresh BRS) contains little to no established microbial populations and a period of time is required until the chemical characteristics of BRS are altered to an extent which is suitable to sustain microbial populations. This implies that the addition of organic fertilisers may have little immediate benefit on nutrient availability unless they are already in water-soluble and/or plant available forms (e.g. dissolved organic N can be taken up by plants). The absence of microbial populations may prove to be the limiting factor to the use of organic fertilisers in residue rehabilitation, at least in the short term.

## **INTRODUCTION**

The increasing demand for alumina from fast-growing developing countries such as China and India has driven the increased production of bauxite in recent years. Australia is the largest producer of bauxite in the world, with annual output of approximately 62 million metric dry tons in 2007 (Geosciences Australia 2007). For every tonne of alumina, about two tonnes of highly alkaline and highly saline bauxite-processing residue are produced. In Western Australia, Alcoa of Australia (Alcoa) produces approximately 15 Mt of residue annually from its refineries (Kwinana,

Pinjarra and Wagerup). In contrast to many other bauxite-processing operations, Alcoa separates its residue into two distinct size fractions; <150 microns (termed residue mud) and >150 microns (termed residue sand, BRS). The residue sand fraction represents the primary material for rehabilitating Alcoa's residue storage areas (RSAs).

Rehabilitation of RSAs to produce a self-sustaining vegetation cover is a key guiding principle for Alcoa's continued production of alumina. By 2030, it is expected that Alcoa will need to have rehabilitated >1200 ha of RSA; however, the inherently hostile characteristics of residue sand pose severe limitations for establishing sustainable plant cover systems. The successful rehabilitation of RSAs is highly dependent on reducing residual alkalinity, the use of effective sources of nutrients, and the maintenance of supply of available nutrients for plant growth and development. Although considerable information on rehabilitation of waste rock mine tailings can be found in the literature, studies relevant to highly alkaline BRS are scarce (Wehr *et al.* 2006; Courtney and Timpson 2005a,b; Courtney *et al.* 2009).

Alcoa currently applies 2.7 t/ha of di-ammonium phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>; DAP) fertiliser (plus some trace elements) as part of rehabilitation of the outer residue sand embankments of its RSAs. Limited information on the behaviour of the dominant components of this inorganic fertiliser in highly alkaline BRS is currently available, despite the known effects of pH on ammonium (NH<sub>4</sub><sup>+</sup>) and phosphorus (P) behaviour. The BRS is typically amended with gypsum at a rate of about 225 t/ha over 1.5 m depth (equivalent to 1% on a weight to weight basis) to reduce alkalinity (pH 12 to pH 9.5), and to reduce the exchangeable sodium percentage (ESP) from ≈100% to <20%. Following gypsum incorporation, the pH reduction, change in exchangeable cation composition (NH<sub>4</sub> → Na exchange versus NH<sub>4</sub> → Ca exchange) and the presence of soluble Ca on P precipitation, can markedly affect nitrogen (N) and phosphorus (P) availability. Quantification of N and P dynamics in BRS is critical to establishing the most suitable form of fertiliser, its rate of application, and its timing of application, to optimise nutrient availability during establishment of the plant cover.

This report summarizes the results of NH<sub>4</sub> and P sorption isotherms and incubation experiments investigating the extent of NH<sub>3</sub> volatilization from residue sand as a function of pH, the proportion of N remaining in the residue sand after cessation of volatilisation, and the availability and fractionation of adsorbed P, after 119 days of incubation.

The major aim of this study was to trace DAP fertiliser applied to the BRS and to quantify N and P dynamics in BRS. The specific objectives are:

- To quantify N availability and adsorption behaviour in different sources of BRS with different pH treatments and DAP application rates;
- To quantify P availability and adsorption behaviour in different types of BRS with different pH treatments and DAP application rates;
- To quantify possible loss mechanisms and transformations (e.g. volatilisation, nitrification, adsorption) affecting N and P availability;
- To recommend the suitability of the current fertiliser type and rate for residue rehabilitation, and other fertilisers that may be more-suitable alternatives.

## **MATERIALS AND METHODS**

### *Residue Sand Samples*

Residue sand was sourced from each of Alcoa's three Western Australia Refineries (Kwinana (KW), Pinjarra (PJ) and Wagerup (WG)). All samples were collected fresh from the BRS stockpile, and as such no sample had received previous gypsum or fertiliser addition. The chemical and physical properties are shown in Tables 1, 2 and 3. All three residue sands are characterized by high pH (> 11), high ESP (> 70%) and low nutrient availability. The concentrations of available N were < 3 mg kg<sup>-1</sup>, of available P were 1 to 3 mg kg<sup>-1</sup>, of organic C were 0.05 to 0.13%, and of EDTA extractable Mn were < 0.8 mg kg<sup>-1</sup> and of Cu were < 0.4 mg kg<sup>-1</sup>. However, the BRS did exhibit a high P buffering index (PBI) (> 520) as well as high Fe content (> 200g kg<sup>-1</sup>), indicating potentially high P adsorption potential.

Although gypsum is applied to BRS as part of rehabilitation operations, mixing is heterogeneous and as such, portions of the BRS profile can behave as both non-gypsum amended (fresh) or gypsum amended. Therefore it is important to study nutrient interactions under both Na- and Ca-dominated systems (Table 1). However, the gypsum source used by Alcoa operations is rich in P as it is a by-product of superphosphate manufacture (phosphogypsum). For this reason it could not be used to study P dynamics and a pure source of Ca as either CaCl<sub>2</sub> (for adsorption isotherms) or CaSO<sub>4</sub>·2H<sub>2</sub>O (for incubation study) was used instead.

### *Ammonium and Phosphorus Adsorption Isotherms*

Ammonium (NH<sub>4</sub>) and phosphorus (P) adsorption isotherms were developed by the Western Australia Chemistry Centre. Isotherms were developed at a soil to solution ratio of 1:5 using the standard batch technique, and were undertaken using Na-dominated and Ca-dominated samples of BRS. Fresh BRS was considered to be Na-dominated (Table 2) whereas Ca-dominated BRS was

prepared by successive washing with 1M CaCl<sub>2</sub>, then 0.1M CaCl<sub>2</sub> then 0.01M CaCl<sub>2</sub> at a BRS to solution ratio of 350 g to 2 L. Samples of each BRS were then partially dried by vacuum filtration to remove much of the interstitial CaCl<sub>2</sub> solution. Saturation of the CEC was achieved using CaCl<sub>2</sub> solution rather than CaSO<sub>4</sub>·2H<sub>2</sub>O to remove any competitive effects of SO<sub>4</sub> on P sorption behaviour.

Eight initial solutions containing between 0 and 25 mg NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P were obtained by diluting a di-ammonium phosphate ((NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>) stock solution with Milli-Q deionised water (> 18 MΩ) to achieve final concentrations representing 0, 5, 10, 20, 40, 60, 80, 100% and 200% of the original solution. Adsorption isotherms were performed at a constant temperature of 25 ± 3 °C at pH 7, 9 and 11. The pH of each initial solution was adjusted using quantities of 1M HCl based on previously measured acid neutralisation curves (ANC) (Figure 1).

Isotherms were developed as follows. Approximately 5.5 g of BRS (field-moist and < 2 mm size fraction; equivalent to an oven-dry mass of 5 g) were placed into pre-weighed 50 mL polypropylene centrifuge tubes. The actual mass of residue sand added to each tube was recorded and later converted to an oven-dry weight using measured initial water contents. Twenty-five mL of the initial solutions were added to the centrifuge tube, and the suspension shaken end-over-end for 44 h. After shaking, the pH of the suspension was re-checked and adjusted with 0.01M HCl if required. All samples were then shaken for an additional 4 h, giving a total shaking time of 48 h (previous studies had confirmed that pH stability was achieved within 48 h following adding acid to residue sand). After shaking, all samples were centrifuged at 10,000 rpm for 10 minutes, filtered (Whatman 42), and the filtrate stored frozen prior to analysis for NH<sub>4</sub><sup>+</sup>-N and P (using Flow Injection Analysis (FIA) techniques). The concentration of adsorbed NH<sub>4</sub><sup>+</sup> and P were calculated as:

$$S = ((c_i - c_e) \times v_T \div m_s) \quad [1]$$

where S = adsorbed concentration (mg/kg), c<sub>i</sub> = initial solution concentration (mg/L), c<sub>e</sub> = equilibrium solution concentration (mg/L), v<sub>T</sub> = volume of added solution (L), and m<sub>s</sub> = oven-dry mass of residue sand (kg).

Normally, the concentration of adsorbed ion is calculated using the difference between the amount of ion added initially and that remaining after shaking. However, given the pH-dependence of NH<sub>4</sub><sup>+</sup> behaviour in soil (Cabrera *et al.* 1991), actual measurement of the quantity of NH<sub>4</sub><sup>+</sup> adsorbed by the residue sand was considered a more realistic estimate of adsorbed NH<sub>4</sub>. This cation was removed from the solid phase as follows. After removing the supernatant, each tube was re-weighed to allow the weight of entrained solution to be estimated. The residue sand was then shaken with 25 mL of

2M KCl for 2 h, after which the suspension was centrifuged and the supernatant filtered to obtain a clear solution. This washing step was repeated two more times. The 3 washings were bulked into a 100 mL volumetric flask which was made to volume with 2M KCl. The solution was then analysed for  $\text{NH}_4^+\text{-N}$  as described above. The concentration of adsorbed  $\text{NH}_4$  was calculated as:

$$S_{\text{NH}_4} = ((c_T \times v_T) - (c_e \times v_{\text{ent}})) \div m_s \quad [2]$$

where  $S_{\text{NH}_4}$  = adsorbed  $\text{NH}_4$  concentration (mg/kg),  $c_T$  =  $\text{NH}_4^+\text{-N}$  concentration in bulk wash solution (mg/L),  $c_e$  = equilibrium  $\text{NH}_4^+\text{-N}$  solution concentration (mg/L),  $v_{\text{ent}}$  = volume of entrained solution (L), and  $m_s$  = oven-dry mass of residue sand (kg).

The N and P sorption isotherms were described using the Freundlich equation:

$$S = k c^n \quad [3]$$

where  $c$  = the ion concentration in the leachate (mg/L),  $S$  = the change in ion concentration in the solid phase (mg/kg), and  $k$  and  $n$  are empirical constants related to the sorption index and bonding strength respectively. All fitting was done using the software package Grapher 3 (Golden Software 2000).

#### *Development of a Method for Measuring $\text{NH}_3$ Volatilization*

The sponge-trapping and KCl-extraction method described by Cabrera *et al.* (1994) and He *et al.* (1999) were modified for measuring  $\text{NH}_3$  volatilization. A 500-mL glass bottle with a screw cap lid was used as an incubation container (Figure 2). The glass jars had a 5.3 cm internal diameter. A 2.3 cm diameter hole was cut in the top centre of the plastic lid. Into this hole, a 2 cm length of thick rubber vacuum tubing ( $\approx$  2.5 cm external diameter; 0.6 cm wall thickness) was inserted. Into this tubing, a small sponge was inserted. This small sponge piece was moistened with 200  $\mu\text{L}$  of the sulphuric acid/glycerol trapping solution, with the purpose to allow air exchange while trapping and preventing any external ammonia from entering the system. Circular sponges of 5.5 cm in diameter (Figure 2) were cut from a sheet of  $\sim$ 1cm thick commercial sponge using a metal tool. These were soaked and rinsed in reverse osmosis water and dried prior to use. Preliminary testing of the sponge indicated that the N content within the sponge was negligible irrespective of washing in distilled water, and hence would not act as an additional source of N in the experiment. This circular sponge was evenly moistened with 2 mL of the trapping solution by absorption in a petri

dish for use in the experiment. The trapping solution consisted of 167 mL concentrated sulphuric acid, 60 mL glycerol (6% v/v) and 773 mL distilled water. The amount of acid (in 2 mL of solution for each sponge trap) in this solution was calculated and tested to be sufficient for absorption of  $\text{NH}_3$  volatilized from the BRS in this experiment.

The following experiment was conducted to assess the capacity of the sponge trapping technique in recovery of volatilized  $\text{NH}_3$ . A series of concentrations of  $\text{NH}_4^+$ -N solution (as DAP) were prepared, with each containing 0, 5, 10, 20 and 30 mg N per 3 mL aliquot respectively. A small plastic container with 15 mL of 0.4 M NaOH solution was placed in the base of an empty incubation jar. For each sample, the 3 mL of  $\text{NH}_4^+$ -N solution was added directly to the small container of 0.4 M NaOH, and a sponge moistened evenly with the trapping solution (2 mL) placed in the rim of the jar and immediately sealed. The jars were then incubated for 48 hours prior to removal of the sponge and extraction in 50 mL of 1M KCl solution. From previous preliminary study it was found that all of the ammonia in the recovery checks was volatilized and trapped onto the sponge within 24 hours. A 48 hour incubation time was allowed to ensure that all volatilized ammonia was absorbed onto the sponge. Extraction involved shaking for 2.5 hours at 70 RPM, followed by the removal of the sponge. The 1M KCl extracts were analysed for the content of  $\text{NH}_4^+$ -N on the Flow Injection Analyser (FIA). The above experiment was carried out in duplicates. The results have shown that the sponge-trapping method recovered approximately 100% of  $\text{NH}_4^+$ -N added (Table 6).

#### *Incubation Experiment*

Incubation experiments were conducted using BRS from each of the 3 RSAs (i.e. KW, PJ and WG). Initially, a sub-sample of each BRS was adjusted with 1% calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to mimic field application of gypsum. The pH was then adjusted to either pH 4, 7, 9 or 11 (original) using 2.453 M HCl. The quantity of acid required to achieve the desired pH for each BRS was determined from an acid neutralisation curve (ANC, Figure 1). The actual pH (1:5 BRS to water ratio) measured in each BRS after pH adjustment was 3.81 (KW), 4.19 (PJ) and 4.08 ((WG) for the pH 4 treatment, 7.01 (KW), 7.01 (WG) and 7.10 (PJ) for the pH 7 treatment, and 9.15 (KW), 9.14 (PJ) and 9.14 (WG) for the pH 9 treatment. For the pH 11 treatment, no acid was added and the field pH (Table 1) was considered to approximate pH 11.

Three mL of a solution of di-ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$  (DAP)) were added to each BRS-pH treatment at a rate of either: low (control, without addition of DAP), medium (13.63 mg N of DAP per jar, 100 g BRS), and high (27.26 mg per jar, 100 g BRS). The medium rate corresponded

to the current field DAP application rate of  $2.7 \text{ t ha}^{-1}$ , while the high rate represents double the current rate ( $5.4 \text{ t ha}^{-1}$ ). After DAP addition, the moisture content of each BRS sample was adjusted to 55% WHC using distilled water after taking into account the solution of DAP added.

Immediately following the addition of DAP, a circular sponge was moistened evenly with the ammonia ( $\text{NH}_3$ ) trapping solution and then immediately placed in the rim of the incubation jar. The jar was sealed and randomly arranged in the incubator. All incubation work was conducted at a constant temperature of  $25^\circ\text{C}$ , and the study was undertaken in triplicate ( $n = 3$ ).

The sponges were sampled after the following incubation periods: 4 and 24 hours, and 3, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84, 92, 98, 105, 112 and 119 days, respectively. The trapping sponge was removed from the neck of the jar and placed in a 120 mL Sarstedt container containing 50 mL of 1M KCl solution. A new trapping sponge was quickly placed into the neck of the jar, the lid re-sealed, and the jars placed back into the incubator ( $T = 25^\circ\text{C}$ ). Trapped  $\text{NH}_3$  was extracted by shaking the sponge in 1M KCl for 2.5 hours at 70 RPM. The sponge was then removed and  $\text{NH}_4^+\text{-N}$  in the 1M KCl solution determined by flow injection analysis (Lachat FIA (Quik Chem Method 10-107-06-4-D)). For treatments receiving the low rate of DAP application (ie. distilled water only), and samples with a initial pH value of 4, the incubation study was aborted once  $\text{NH}_4^+\text{-N}$  concentrations became negligible.

The incubation study was terminated after 119 days as  $\text{NH}_3$  volatilization had essentially ceased. At this time, the BRS from each incubation jar was decanted to an individual plastic zip-lock bag and the contents of each bag mixed thoroughly. The samples were then stored at  $4^\circ\text{C}$  prior to analysis (see below). Sub-samples of BRS from each incubation treatment were analysed for pH,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , pH, 0.1 M  $\text{H}_2\text{SO}_4$  extractable P and Colwell available P as follows. The final pH of the 108 incubated BRS samples was measured using a 1:5 soil:water ratio. Inorganic N ( $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$ ) were determined by end-over-end shaking 5 g (oven-dry weight equivalent) of BRS from each incubation treatment with 50 mL of 2M KCl solution for 1 h. After shaking, the samples were filtered through a Whatman 42 paper, and the extracted solution stored at  $-20^\circ\text{C}$  prior to analysis (Lachat FIA (Quik Chem Method 10-107-06-4-D)). For samples where a high  $\text{NH}_4^+\text{-N}$  content was observed in the 1<sup>st</sup> 2M KCl extract, a second extraction was performed following the procedure above on the same BRS soil sample. A 3<sup>rd</sup> 2M KCl extraction was performed on the same BRS sample where the  $\text{NH}_4^+\text{-N}$  results in the 2<sup>nd</sup> extraction exceeded 1 mg/L. This approach ensured that most, if not all, mineral N has been extracted from the BRS.

Analysis for 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P and Colwell available P were undertaken as follows. A subsample of each BRS was oven dried at 40°C for 7 days prior to analysis for 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P and Colwell available P. For 0.1M H<sub>2</sub>SO<sub>4</sub> extractable P, 2 g of dried BRS were extracted with 20 mL of 0.1M H<sub>2</sub>SO<sub>4</sub> (1:10 ratio) by end-over-end shaking for 16 hours. After shaking, the suspensions were centrifuged at 2000RPM for 10 minutes, and filtered (Whatman 42) to obtain a clear solution. The extracts were then analysed for P using the Murphy and Riley method (Rayment and Higginson 1992). For determining Colwell available P, 1g of dried BRS was shaken for 16 h with 30 mL of 0.5M NaHCO<sub>3</sub>. The extracts were centrifuged and filtered (Whatman 42) prior to analysis using the Murphy and Riley procedure.

### *Phosphorus Fractionation*

Phosphorus fractionation provides an important insight into the availability of the nutrient in soil systems. A wide range of fractionation schemes can be found in the literature; however, all schemes involve a range of extracting solutions that sequentially become more aggressive in their removal of soil P. Irrespective of the fractionation scheme employed, all have inherent advantages and disadvantages for a specific soil type. Residue sand exhibits relatively unique chemical characteristics relative to natural soils, and as such selecting the most appropriate technique for measuring P is unclear. During this study the opportunity arose to compare two commonly used P fractionation schemes; that by Hedley *et al.* (1982a) and that by Tiessen and Moir (1993). The scheme proposed by Tiessen and Moir is in fact a modified version of that by Hedley *et al.* (1982a). The scheme by Hedley *et al.* (1982a) was used by Griffith University using BRS incubation samples from the KW RSA only. The scheme by Tiessen and Moir (1993) was used by the Western Australia Chemistry Centre using samples from KW and PJ that had been reacted with 200% DAP stock solution.

The P fractionation schemes described by Hedley *et al.* (1982a, b) and Condron *et al.* (1996) were modified by including an analysis of the residual P (i.e. non-extracted P) using nitric acid (HNO<sub>3</sub>) - perchloric acid (HClO<sub>4</sub>) digestion (Olsen and Sommers 1982). This scheme is shown in Figure 3 and involved the determination of various forms of inorganic (Pi) and organic (Po) soil P by sequential extraction of finely ground (< 150 µm) BRS with 1 M ammonium chloride (NH<sub>4</sub>Cl) (APi), 0.5 M sodium bicarbonate (NaHCO<sub>3</sub>) (pH 8.5) (BPi, BPo), 0.1 M sodium hydroxide (NaOH) (N(I)Pi, N(I)Po), 1 M hydrochloric acid (HCl) (HPi) and 0.1 M NaOH (N(II)Pi, N(II)Po). The concentration of inorganic P in the extracts was determined after the precipitation of organic matter by acidification. Concentrations of organic P fractions from the different extractions were found to be below the analytical detection limit after persulfate oxidation and P analysis. Therefore, organic

P fractions in BRS were regarded as being negligible. The inorganic fractions separated by the above procedure generally correspond to the following soil P pools:

- *NH<sub>4</sub>Cl extractable Pi (AP)* – solution Pi.
- *NaHCO<sub>3</sub> extractable Pi (BP)* – labile Pi, adsorbed on the surface of more crystalline P compounds, sesquioxides or carbonate.
- *First NaOH extractable Pi ((N(I)P)* – moderately labile Pi, associated with amorphous and some crystalline Al, Fe hydrous oxides.
- *HCl extractable Pi (HPi)* – less labile Pi, associated with primary calcium minerals (e.g. apatite). *Second NaOH extractable Pi ((N(II)P)* – moderately stable Pi, which adsorbed into the mineral structure of soil components, or occluded by Fe and Al coatings.
- *Residual P* – non-extracted/ recalcitrant P.

The P fractionation scheme by Tiessen and Moir (1993) is outlined below.

- *Resin-P*: Extraction with anion-exchange resin strip in deionised water. Phosphate stripped from the resin with 0.25 M HCl and the extract analysed for inorganic phosphorus (P<sub>i</sub>). This fraction includes soluble and very weakly adsorbed (exchangeable) forms of P.
- *Bicarbonate-P*: The residue is extracted with 0.5 M NaHCO<sub>3</sub> at pH 8.5. Extracts analysed for inorganic (P<sub>i</sub>) and total (P<sub>t</sub>) phosphorus. This fraction includes phosphates adsorbed to hydrous iron and aluminium oxide surfaces and sparingly soluble calcium phosphates (eg, CaHPO<sub>4</sub>).
- *Hydroxide-P*: The residue from step 2 is extracted with 0.1 M NaOH and analysed for total phosphorus (P<sub>t</sub>) by colorimetry following oxidative digestion of the extract with perchloric acid. This fraction includes forms of phosphate associated with aluminium oxides, organic matter and forms strongly adsorbed to iron oxide surfaces.
- *HCl-P*: The residue from step 3 is extracted with 1 M HCl and analysed for inorganic P (P<sub>i</sub>). This fraction is designed to specifically measure insoluble calcium phosphates.
- *Boiling HCl-P*: The residue from step 4 is boiled with concentrated HCl and analysed for P<sub>t</sub> by ICP-AES. This fraction mainly consists of iron phosphates.
- *Residual-P*: The residue from step 5 is digested with sulphuric acid and K<sub>2</sub>SO<sub>4</sub>/CuSO<sub>4</sub> at 360°C. This procedure recovers the most recalcitrant forms of P, such as those occluded in silicate minerals.

### *Statistical Analysis*

All data ( $\text{NH}_3$  loss, soil  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N contents, total N recovery, Colwell available P, 0.1 M  $\text{H}_2\text{SO}_4$  extractable P, P fractions from sequential fractionation scheme and soil pH etc.) collected from this experiment were subject to the descriptive analysis and the analysis of variance (General linear model) (sand type x pH x DAP rate x replicate) using Statistix version 8 (Analytical Software 1994). In addition, multiple comparison analysis was carried out to examine the effects of different treatments (sand type, pH and DAP rate). The significant differences among the main treatment (either pH, sand type or DAP rate) were separated by LSD ( $P < 0.05$ ). For the parameters,  $\text{NH}_3$  loss%, total N recovery%, Colwell P/total P added% and  $\text{H}_2\text{SO}_4$  extractable P / total P added%, we only used data from the treatments - medium and high DAP rates for statistical analyses since no N or P added as DAP for low DAP rate treatments. For all other parameters, the complete data set was used for statistical analyses. The effect of pH and cation composition on P and  $\text{NH}_4$  sorption parameters were evaluated using analysis of variance (ANOVA) and comparison of means by least significant differences (LSD,  $P < 0.05$ ) procedures (Analytical Software 1994).

## **RESULTS AND DISCUSSION**

### *Ammonium Adsorption Isotherms*

Ammonium sorption isotherms (Figure 4) revealed the following important points:

- For each BRS,  $\text{NH}_4$  sorption (calculated using Eqn [1]) and adsorption (calculated using Eqn [2]) increased with increasing solution  $\text{NH}_4$ . For pH 7, and to a lesser extent pH 9, the increase followed a near-linear relationship.
- At the lower pH (i.e. pH 7), sorbed  $\text{NH}_4$  tended to be higher in the Ca-dominated system than in Na-dominated systems. The opposite trend was observed for adsorbed  $\text{NH}_4$ .
- As pH increased from pH 7 to 9,  $\text{NH}_4$  adsorption decreased dramatically.

The loss of solution  $\text{NH}_4$  under the imposed experimental conditions can occur via two primary mechanisms: cation exchange and volatilisation. Other loss mechanisms such as fixation by zeolite-type minerals, immobilisation by microbes, and/or nitrification were not considered to be important in this study (e.g. Phillips 2002). If cation exchange was largely responsible for loss of soluble  $\text{NH}_4$  then sorbed  $\text{NH}_4$  concentrations may be expected to be higher under Ca- $\text{NH}_4$  rather than Na- $\text{NH}_4$  exchange conditions due to the higher affinity of residue materials for monovalent cations (Wong and Ho 1995). Interestingly, this behaviour is atypical to that commonly observed in soils in which surface charge arises principally from hydrous Fe and/or Al oxides (Kinniburgh *et al.* 1975).

Residue sand contains not only a range of naturally-occurring minerals (e.g. aluminosilicate clays and hydrous Fe and Al oxides), but also a range of synthetic minerals generated during the bauxite refining process (e.g. desilication product (DSP) and tricalcium aluminate (TCA6)). This mineralogical composition has demonstrated a preference for smaller, monovalent cations ( $K^+$  and  $NH_4^+$ ) relative to multivalent ( $Ca^{2+}$  and  $Mg^{2+}$ ) cations (Wong and Ho 1995). Wong and Ho (1995) demonstrated that DSP- $Na^+$  could be released from these zeolite-type minerals via cation exchange mechanisms. These workers showed that monovalent cations (e.g.  $K^+ > Li^+ > NH_4^+$ ) were more efficient than divalent cations ( $Ba^{2+} > Ca^{2+} > Mg^{2+}$ ) in replacing  $Na^+$  from within the aluminosilicate framework of DSP. In fact, complete replacement of  $Na^+$  can be achieved by incremental extraction using 1M KCl without altering the aluminosilicate framework of DSP. This led Wong and Ho (1995) to conclude that cation exchange was the mechanism responsible for the release of  $Na^+$  from DSP. Furthermore,  $Na^+$  exchange in residue sand can be characterised by an initially rapid stage, followed by a very slow release of  $Na^+$ . The rapid stage of release represents  $Na^+$  in easily accessible sites (approximately 20% of Total  $Na^+$ , Wong and Ho 1995), whereas the slower rate of release from within the DSP framework will be dependent on the displacing cation (monovalent versus multivalent) and changes in soil solution chemistry (whereby a reduction in the sodium activity ratio will encourage  $Na^+$  release from the DSP). Although residue sand only contains a relatively small proportion of these synthetic minerals, they appear to combine with other naturally-occurring minerals to produce unique chemical properties that must be fully understood to ensure successful rehabilitation of residue storage areas.

From a cation exchange perspective, a general description of  $NH_4$  adsorption could be as follows. At lower solution  $NH_4$  concentrations,  $NH_4$  appears to be more efficient at displacing Ca than Na from the exchange sites. This suggests that replacement of exchangeable Na by Ca has introduced a cation with a lower affinity for the exchange sites. These sites may be associated with the zeolite-type minerals which exhibit a stronger preference for Na relative to Ca (Wong and Ho 1995). Once these Na-selective sites are occupied with increasing  $NH_4$  adsorption, any additional solution  $NH_4$  will have to compete with resident cations for other exchange sites such as those arising from hydrous Fe and Al oxides. These oxides have a preference for multivalent cations and as such  $NH_4$  adsorption may be expected to decrease in a Ca-system relative to a Na-system. Therefore, the shapes of  $NH_4$  adsorption isotherms in Na- and Ca- dominated systems may in fact reflect the range of exchange present in residue sand and the relative affinity of these sites for  $NH_4$ .

Given that residue sand contains colloids with variable surface charge, then increasing the pH should result in increased  $NH_4$  adsorption. Whilst sorption isotherms suggest this behaviour, the

more realistic adsorption isotherms clearly show  $\text{NH}_4$  adsorption decreasing with increasing pH. This contradictory relationship between  $\text{NH}_4$  adsorption and pH provides strong evidence that mechanisms other than cation exchange are responsible for loss of solution  $\text{NH}_4$  in residue sand.

Extraction of BRS solids after equilibration with  $\text{NH}_4$  solutions clearly show that little  $\text{NH}_4$  resides in the exchange phase, and this behaviour is more pronounced at the higher pH treatments (compare sorbed versus adsorbed  $\text{NH}_4$  concentrations; Figure 4). Ammonia ( $\text{NH}_3$ ) volatilisation is well-known to occur following application of  $\text{NH}_4$  based fertilisers to alkaline soils, following urea application and subsequent hydrolysis, and from animal urine patches (e.g. Cabrera *et al.* 1991, 1994, 2008). Reported  $\text{NH}_3$  losses from urea applied to grasslands range for 5 to 48% of the applied urea (see Cabrera *et al.* 2008). The adsorption isotherms presented in Figure 4 provide strong evidence that loss of added  $\text{NH}_4$  from BRS has primarily occurred via  $\text{NH}_3$  volatilisation with increasing alkaline conditions. This aspect of the study will be investigated in greater detail later in this report.

The cation exchange behaviour may provide additional support for the contention that  $\text{NH}_3$  volatilisation is the primary loss mechanism of  $\text{NH}_4$  in BRS. Sorbed  $\text{NH}_4$  calculated using Eqn [1] suggested greater exchange in Ca- $\text{NH}_4$  system than a Na- $\text{NH}_4$  system, whereas adsorbed  $\text{NH}_4$  confirmed the opposite effect (particularly at lower pH). It is postulated that Ca- $\text{NH}_4$  exchange did in fact limit  $\text{NH}_4$  adsorption (hence removal from solution), resulting in higher solution  $\text{NH}_4$  in the Ca- relative to the Na- treatments. This would encourage greater loss of solution  $\text{NH}_4$  as it would be more susceptible to  $\text{NH}_3$  volatilisation. Therefore, the lower concentrations of exchangeable  $\text{NH}_4$  in Ca-systems may be due to its greater susceptibility to loss via volatilisation under alkaline conditions. This behaviour would be more pronounced at the lower (but still alkaline) pH values (ie. pH 7 to 9) since under strongly alkaline conditions (pH 11) the rate of  $\text{NH}_3$  formation probably exceeds the rate of cation exchange (since  $\text{NH}_3$  already exists in solution) (Stumm and Morgan 1981).

### *Phosphorus Sorption Isotherms*

Phosphorus sorption isotherms for each BRS are presented in Figure 5. Most treatments exhibited a curvilinear shape (*L-curve*, Sposito 1984), although P sorption in Na-system at pH 7 could be better described as *C-curves* (Sposito 1984). The different shape of the P sorption isotherm at pH 7 may be explained by the negligible P concentrations in the equilibrium solutions relative to those at higher pH. The shape of *L-curves* indicates that the surface bonding energy was not constant, but varied as a function of adsorption. This shape of isotherm can be explained by a dominance of high-

affinity sites at low solution P concentrations, with the relative proportions of high to low affinity sites decreasing with increasing P loading. The ability of BRS to sorb large amounts of P (PBI >500 L/kg; Table 1) may be attributed to the presence of significant amounts of (amorphous) hydrous Fe and Al oxides of soils (Table 2). The importance of hydrous Fe and Al oxides on P adsorption has been documented extensively in the literature (Sanyal and De Datta 1991).

The sorption process involves both precipitation and adsorption processes. At low solution concentrations, P sorption has been largely attributed to the presence of high-affinity sites which are immediately accessible to solution P, while at higher concentrations precipitation with solution cations (e.g. Ca, Fe and Al) can effectively remove solution P (Sanyal and De Datta 1991). This aspect of P sorption will be discussed in Section 4.4 on P fractionation.

Phosphorus sorption was found to decrease with increasing pH (Figure 5). For example, at pH 7, P sorption at the highest addition was about 200 to 300 mg/kg, while at pH 11, P sorption was about 120 to 200 mg/kg. A similar effect of pH on P sorption has been reported by Parfitt (1980) on goethite and Barrow (1982) on residue mud. Decreased P sorption with increasing pH may be due to the presence of competing anions (eg. OH and CO<sub>3</sub> for sorption sites (Parfitt 1978), changes in form of P as a function of dissociation constant (pK<sub>a</sub> of H<sub>3</sub>PO<sub>4</sub> is 2 [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>], 7 [HPO<sub>4</sub><sup>2-</sup>], and 12 [PO<sub>4</sub><sup>3-</sup>]; Bowden et al. 1980), and increasing negative surface charge with increasing pH (Bowden *et al.* 1980). Phillips and Chen (2010) found that the zero point of charge of residue sand was approximately 7, and that much of the surface electrical charge arises from colloids with variable charge (e.g. hydrous Fe and Al oxides). This implies at pH >7 much of the surface charge will be negative and can repel anions such as P.

Reduced P sorption by wastewater-irrigated soils compared to non-irrigated soils has been reported by Holford *et al.* (1997), Nair *et al.* (1998), Falkiner and Polglase (1999), Menzies *et al.* (1999), Sui and Thompson (2000) and Phillips (2002), and has been attributed to a loss of high-affinity and readily-accessible P sorption sites, and from competition with other organic ligands. Whilst loss of high-affinity sites may occur in residue due to inorganic anion competition, and/or change in surface electrostatic potential, the effects of organic acids are uncertain. Indeed, independent studies found that soluble organic carbon increased three-fold as pH increased from 7 to 11 for the three residue sands (Phillips unpublished data). Although Menzies *et al.* (1999) partly attributed reduced P sorption by irrigated soils to competition by organic ligands, they could not identify wastewater or naturally-occurring organic matter as being the major source. Further research is required to identify

the major organic components of piggery wastewater, and the effect of these organic compounds on soil chemical and physical properties, and on nutrient behaviour in irrigated soils.

#### *Freundlich Parameters*

Freundlich parameters obtained by fitting Eqn [3] to  $\text{NH}_4$  and P sorption/adsorption isotherms are provided in Table 4. Since it has been established that  $\text{NH}_4$  exchange calculated using changes in this cation between the initial and equilibrium solution concentrations is erroneous (i.e. sorption), only parameters fitted to adsorption isotherms (i.e. obtained by displacing actual exchangeable  $\text{NH}_4$ ) will be discussed.

The parameter  $k$  provides an indication of the preference of a cation for the exchange sites. Statistically ( $p < 0.05$ ),  $\text{NH}_4$  exchange was more favourable in Ca-dominated residue sand than in Na-dominated residue sand. This suggests that the ability of solution  $\text{NH}_4$  to displace exchangeable Ca was greater than its ability to displace exchangeable Na. This behaviour is not what is commonly observed in soils dominated by hydrous Fe oxides (Kinniburgh *et al.* 1975). The parameter  $n$  provides an indication of the curvature of the isotherm shape (i.e. values approaching unity describe a linear relationship between solution and adsorbed  $\text{NH}_4$ ). Values were significantly greater in the Na-dominated system than in the Ca-dominated system, suggesting that  $\text{NH}_4^+$ -Ca exchange diminished with increasing solution  $\text{NH}_4^+$  concentrations. It is possible that at low solution  $\text{NH}_4^+$  concentrations this cation was largely retained on readily-accessible exchange sites with a high affinity for  $\text{NH}_4^+$ , after which  $\text{NH}_4^+$  exchange occurred on sites with a higher affinity for Ca. Kinniburgh *et al.* (1975) demonstrated that hydrous Fe oxides have a greater preference for multivalent cations such as Ca relative to monovalent cations (e.g. Na and  $\text{NH}_4^+$ ).

Alternately, it could be argued that the resulting isotherms reflect the combined effects of cation exchange, cation selectivity and volatilisation. If the exchange sites were in fact predominantly associated with hydrous Fe and Al oxides, then the preference of this material for Ca relative to Na would result in more  $\text{NH}_4$  remaining in solution in a Ca-system. Here, the  $\text{NH}_4$  would be more susceptible to  $\text{NH}_3$  volatilisation, thereby the quantity of  $\text{NH}_4$  present in solution which could be involved in adsorption reactions.

With the exception of pH 7 Na-treatments, the parameter  $k$  for P sorption was commonly found to be significantly smaller for Na-systems relative to Ca-systems (Table 4). This behaviour was not unexpected as P sorption would be a combination of adsorption onto hydrous Fe and Al oxides and formation of low solubility calcium-phosphate precipitates (Sanyal and de Datta 1991).

### *Incubation Experiments - Availability and dynamics of N in BRS*

Statistical analysis indicated that there were no significant BRS x DAP x pH interactions on the cumulative NH<sub>3</sub> volatilization at various sampling times ( $P > 0.05$ ) (data not shown). The interactions between BRS type and DAP rate treatments on the cumulative NH<sub>3</sub> volatilization were significant at the end of incubation (119 days after incubation) ( $P < 0.05$ ), but not for the short period after incubation (4 hours, 24 hours and 7 days) ( $P > 0.05$ ). However, there were significant DAP x pH and Sand x pH interactions on the cumulative NH<sub>3</sub> volatilization at 4 hours and 24 hours and 119 days after incubation.

The initial pH treatments have significant impacts on the amount and the percentage of NH<sub>3</sub> volatilized (Figures 7, 8 and 9, Table 5). For pH 4 treatments, there was no or negligible NH<sub>3</sub> volatilized over the period of incubation (Figures 7, 8 and 9). The proportion of NH<sub>3</sub> volatilized increased dramatically as the initial pH increased. On average (across the 3 BRS types), about 2.2%, 8.4% and 33.9% of DAP-N was lost from the pH 7, 9 and 11 treatments, respectively, after 4 h of incubation (Figure 9). After 24 hours of incubation, loss of NH<sub>3</sub> through volatilization reached 11.6%, 40.7% and 85.2% of added DAP-N for the pH 7, 9 and 11 treatments, respectively. The corresponding proportions lost after 7 days incubation were 39.5%, 83.1% and 95.2%. At the end of incubation (119 days), on average, 80.0%, 90.1% and 95.7% of added DAP-N had been lost as NH<sub>3</sub> for the pH 7, 9 and 11 treatments, respectively (Figures 7, 8 9). These results indicate that much of the N lost as NH<sub>3</sub> (up to 95.2%) occurred within a short period (24 hours to 7 days), particularly at the higher pH (pH 9 and 11) treatments. Correlation analysis showed that BRS pH at the end of incubation was highly correlated to cumulative NH<sub>3</sub> volatilized during the incubation period (Figure 10).

The proportion and rate of NH<sub>3</sub> volatilization was observed to vary between source of BRS and rate of DAP addition (Figures 7 and 8). Irrespective of pH and BRS source, a higher percentage of the NH<sub>4</sub> applied at the medium rate was lost as NH<sub>3</sub> within the first 24 hours of incubation relative to that lost from the high DAP rate treatments. The opposite trend was observed at the later stages of incubation (Figure 9). At the medium DAP rate, there were no significant differences in total cumulative NH<sub>3</sub> loss over the entire period of incubation among pH 7, 9 and 11 treatments for the Wagerup (WG) BRS (Figure 7a, Table 7). For the other BRS sources (KW and PJ), losses via NH<sub>3</sub> volatilization were more pronounced at pH 11 than at pH 7 and 9 (Figure 4). These results suggest that in the absence of plant uptake, much of the applied DAP can be rapidly lost from all BRS (particularly WG) despite pH reduction through gypsum incorporation.

At the high rate of DAP,  $\text{NH}_3$  volatilization was significantly greater at pH 9 and 11 than at pH 7, irrespective of BRS source (Table 7, Figure 8). This suggests that excessively high rates of DAP-N should be avoided for all BRS sources in order to minimise DAP-N loss via  $\text{NH}_3$  volatilization. The quantity of  $\text{NH}_3$  loss via volatilization for high DAP rate treatments continued for a longer period than the medium rate (Figures 7 and 8). This result was not unexpected given the higher amount of available  $\text{NH}_4$  at the higher DAP rate.

There were no significant pH x DAP x BRS interactions for residual mineral N ( $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ ) and %N recovery (data not shown). In addition, interactions between BRS type and DAP rate, and between BRS source and pH were not significant. However, there were significant DAP x pH interactions across different BRS source. Concentrations of  $\text{NH}_4\text{-N}$  in BRS without addition of DAP were low ( $< 1 \mu\text{g g}^{-1}$  for most cases). Concentrations of  $\text{NH}_4\text{-N}$  in BRS treated with DAP decreased as the initial pH in BRS increased due to the loss N as  $\text{NH}_3$  under the high pH (Table 7, Figure 11). Concentrations of  $\text{NH}_4\text{-N}$  in BRS were highly correlated with BRS pH at the end of incubation (Figure 12). At low initial pH (pH 4), nearly 100% of N added as DAP was recovered in the form of  $\text{NH}_4\text{-N}$  in BRS for both the medium and high DAP rate treatments (Table 7). At an initial pH of 7, up to 15% of DAP-N could still be recovered in the form of  $\text{NH}_4\text{-N}$ , particularly for PJ and KW BRS (Table 7). This was significantly greater than the amount of  $\text{NH}_4\text{-N}$  recovered from BRS at both pH 9 and 11, which ranged from 0 to 4.5% of N added as DAP (Table 7). The source of BRS did not significantly affect the final  $\text{NH}_4\text{-N}$  concentration in BRS, although this concentration did increase as the DAP rate increased (Figure 11).

Concentrations of  $\text{NO}_3\text{-N}$  in BRS across all treatments were low, ranging from 1.3 to  $2.8 \mu\text{g g}^{-1}$  (Table 5). This indicates that nitrifying activity was low in all three sources of BRS. Concentrations of  $\text{NO}_3\text{-N}$  were slightly greater in the pH 7 and 9 treatments than those in the pH 3 and 11 treatment (Figure 11). It is possible that if nitrifying bacteria were present in the BRS, then the optimum range for  $\text{NH}_4 \rightarrow \text{NO}_3$  may be between pH  $>3$  and  $<11$  (Tisdale *et al.* 1993). Correlation analysis showed that  $\text{NO}_3\text{-N}$  concentrations were related to BRS pH at the end of incubation (Figure 12). Differences in the concentration of  $\text{NO}_3\text{-N}$  among BRS sources and DAP rate treatments were small (Figure 11, Table 7). The %N recovery was generally greater in the pH 3 and 11 treatments than in the pH 7 and 9 treatments (Table 7 and Figure 11). This may be attributed to the fact that only negligible N was lost as  $\text{NH}_3\text{-N}$  in the pH 3 treatments, and much of the N lost as  $\text{NH}_3\text{-N}$  at pH 11 occurred over the first few samplings. This would have resulted in less  $\text{NH}_3\text{-N}$  that could not be

recovered compared with the pH 7 and 9 treatments. For WG BRS, the %N recovery was greater than in KW and PJ BRS, while the %N recovery increased as the DAP rate increased (Figure 11).

#### *Incubation Experiments - Phosphorus Availability and Fractionation in BRS*

Phosphorus (P) availability was evaluated by measuring Colwell P and 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P for all 108 BRS samples from the incubation experiment. Concentrations of available P in the original BRS were low (< 3.1 µg g<sup>-1</sup> P) (Table 8). The 0.1 M H<sub>2</sub>SO<sub>4</sub> extraction recovered 33 to 67% of P added as DAP. The initial pH did not significantly affect 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P, suggesting that the acidity of the extracting solution overwhelmed the alkalinity of the samples. More P was extracted by 0.1 M H<sub>2</sub>SO<sub>4</sub> from KW BRS than PJ and WG BRS (Table 6, Figure 10). As expected, concentrations of 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P increased as the DAP rate increased (Table 8 and Figure 13).

Colwell P removed between 22 and 57% of P added as DAP, which was smaller compared with 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P. This finding suggests that care should be taken when selecting appropriate extracting solution for assessing nutrient availability in residue sand. Colwell P was highly correlated with 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P (Figure 14). Concentrations of Colwell P in the higher pH treatments (i.e. pH 7, 9 and 11) were greater than in the pH 4 treatments, while concentrations of Colwell P in the pH 9 treatments were greater than in the pH 7 and 11 treatments (Table 8 and Figure 13). The reason for the variability in P extractability may be related to its dissociation constant (pK<sub>a</sub> of H<sub>3</sub>PO<sub>4</sub> is 2 [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>], 7 [HPO<sub>4</sub><sup>2-</sup>], and 12 [PO<sub>4</sub><sup>3-</sup>]. Maximum adsorption of a particular species of P will occur near its pK<sub>a</sub>, which is pH 7 for HPO<sub>4</sub><sup>2-</sup>, and 12 for PO<sub>4</sub><sup>3-</sup> (Bowden *et al.* 1980).

Colwell P also increased as the DAP rate increased (Figure 13). Concentrations of Colwell P were higher in KW BRS than in PJ and WG BRS (Table 8, Figure 13). On average, approximately 50% of P added as DAP was recovered by Colwell and 0.1 M H<sub>2</sub>SO<sub>4</sub> extraction, and this proportion is considered to be available for the plant use. This may explain the absence of extensive P deficiencies in relatively new residue rehabilitation (Bell *et al.* 2008).

Results from P sequential fractionation using the scheme by Hedley *et al.* (1982a) for KW BRS are shown in Table 9. Negligible P was associated with organic matter, which was not unexpected given the very low organic carbon levels of BRS. The NH<sub>4</sub>Cl extractable P (AP) pool (solution P) was very small, ranging from 0.16 to 2.75 µg g<sup>-1</sup>. Phosphorus associated with this pool represented <1% of total P (Table 9). Concentrations in the AP pool increased with as the initial pH increased,

and with the increasing DAP rate. It is possible that as pH increased, the surface charge became increasingly negative which concomitantly reduced surface positive charge. This relationship between surface charge and pH was considered to be responsible for decreased P sorption observed in the sorption isotherms (Figure 5). A small proportion of BRS P would be expected to balance positive surface charge via electrostatic attraction (Parfitt 1978).

Bicarbonate extractable P (BP) ranged from 3 to 87  $\mu\text{g g}^{-1}$  and represented about 3 to 23% of the total P added. The initial pH did not significantly affect BP pool, while concentrations of BP pool increased as the DAP rate increased (Table 9). The absence of pH effect differed from that observed for available P (Section 4.3.1). Available P (as Colwell P) would include both water-soluble and weakly retained forms of P, whereas BP would contain a much lower proportion of these forms of P due to prior removal by  $\text{NH}_4\text{Cl}$ . Changes in pH would be expected to have a greater impact on these weakly adsorbed forms P, and as such, solubility of weakly-sorbed P would be expected to increase with increasing pH (due to loss of positive surface charge).

The first NaOH extraction step (N(I)P) comprised the largest P fraction in DAP treated BRS (both medium and high rates) (46 to 53% of total P added) (Table 7). The initial pH treatment did not affect the N(I)P pool at the medium DAP rate treatments, while the N(I)P pool in BRS treated with the high rate of DAP was greater for pH 4 and 11 treatments than for the pH 7 and 9 treatments. These results indicate that P applied to BRS reacts primarily with the hydrous Fe and Al oxides components. These findings are consistent with known behaviour of P sorption by natural soils (e.g. Oxisols), and synthetic materials rich in hydrous Fe and Al oxides (e.g. Parfitt 1978; Phillips 2002).

The HCl extractable P (HP) fraction consists of P from less-labile fractions such as P associated with primary calcium-based minerals (e.g. apatite). Approximately 15% of total P in BRS without DAP addition (low DAP treatments) was associated with this fraction; however, in DAP treated BRS, only 2 to 6% of the total P could be recovered in this fraction. This finding is not unexpected since the likelihood of significant quantities of apatite forming in recently deposited BRS is limited due to the lack of a Ca source. For DAP treated BRS, the P associated with the HP fraction generally decreased as the initial pH and DAP rate increased (Table 9). If a small amount of Ca minerals were present in BRS, then saturation of potential reaction sites would be expected as applied P increased. However, if reaction of P with Ca minerals or formation of low solubility Ca-P (e.g. apatite) did occur, it may be after much of the applied P has reacted with readily-available, high affinity sorption sites (e.g. amorphous Fe and Al oxides).

For the N(II)P pool, impacts of the initial pH were not significant (Table 9). The N(II)P pools comprised <10% of total P across all pH and DAP rate treatments and increased with the DAP rate.

The residual P (Res-P) was the major fraction for the original BPS without addition of DAP, consisting of 53 to 56% of total P (Table 7), but only 16 to 26% of total P for the BRS treated with DAP.

Approximately 87 to >100% of P added as DAP was recovered by the sequential P fractionation procedure. The most labile fractions, and therefore the most plant-available, would be associated with the soluble (AP) and bicarbonate (BP) fractions, which represented up to 25% of the added P. Much of the added P was associated with hydrous Fe and Al oxides but the plant availability of this P pool is uncertain. Whether or not desorption of P occurs in response to decreases in the soil solution, or is transformed into less available forms (Sanyal and de Datta 1991) requires further research. If labile P includes that adsorbed by hydrous Fe and Al oxides (i.e. the sum of AP, BP and N(I)P) then this would represent 59 to 64% and 71 to 73% of total P for the medium and high DAP treatments, respectively. Thus, if most of the P added as DAP was still available after the 119 day incubation, then that which was not taken up by the vegetation would be susceptible to leaching. The importance of leaching to loss of essential nutrient in BRS has not yet been investigated.

The proportions of total P extracted by the Tiessen and Moir (1993) fractionation scheme are presented in Figure 6. This scheme is routinely used for Western Australia soils, and has been adapted from that proposed by Hedley *et al.* (1982a). The main difference between the two schemes is the use of an anion exchange resin for removing water-soluble P rather than  $\text{NH}_4\text{Cl}$  and a “boiling with HCl” step to remove P associated with Fe-P minerals. Using the Tiessen and Moir (1993) scheme, it was found that there were no significant differences between BRS source or cation system (Na and Ca) or initial pH (pH 7, 9 or 11). Interestingly, the greatest proportion of total P was extracted from the Fe-P pool ( $\approx 39\%$  of total), closely followed by P retained by Fe and Al oxide surfaces (0.1M NaOH extractable). The remaining P was distributed between the residual (occluded P (18%)), hydrous Fe and Al oxides (FeOH & AlOH (13%)) and soluble (resin (3%)) fractions. There were negligible amounts of P associated with organic matter and insoluble Ca-P.

Generally, the conclusions from both fractionation schemes are similar in that (1) much of the added P is associated with Fe and Al oxides and hydrous oxides present in BRS; (2) negligible amounts of P are associated with organic matter or present as insoluble Ca-P; (3) a small but

important proportion remains in solution which is readily-available for plant uptake; (4) labile forms of P comprise <25% of the total P.

Interestingly,  $\text{HCO}_3^-$  extractable P was found to be significantly ( $p < 0.05$ ) higher in Ca-treated BRS than Na-treated BRS. It is possible that a proportion of added P has reacted with soluble Ca to form sparingly soluble Ca-P, which was subsequently dissolved in 0.5M  $\text{NaHCO}_3$  (pH 8.5).

It should be highlighted that the fractionation schemes were carried out using samples which had undergone short-term reaction with added P. More research is required to understand if labile P is progressively re-distributed into less-available fractions over time, or if the moderate to strongly adsorbed forms of P are slowly released back into the soil solution to provide a P source for plant growth.

#### *Incubation Experiments – Changes in pH of BRS*

Generally, after the 119-day incubation period, the pH of BRS tended to be slightly less than that at the start of the incubation experiment, particularly for samples receiving DAP addition. This may be partly due to dissolution of DAP with subsequent P hydrolysis (i.e. changing species from  $\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-}$ ) and the production of protons ( $\text{H}^+$ ) (Figure 12). Although small changes in pH were observed over the incubation period, these changes were not considered to be large enough to affect the interpretation of the data in terms of effect of pH on N and P dynamics in BRS.

## **CONCLUSIONS AND RECOMMENDATIONS**

Work presented in this report provide strong evidence the pH plays a very important role in controlling the fate of applied N (as  $\text{NH}_4$ ) and P in bauxite-processing residue sand. At near-neutral pH (i.e. pH 7), cation exchange can remove significant amounts of added  $\text{NH}_4$  which can be subsequently released back into solution for plant uptake. The importance of cation exchange however diminishes with increasing pH (pH >7) due to loss via  $\text{NH}_3$  volatilization. The incubation study found that approximately 85% of applied N as  $\text{NH}_4$  was lost as  $\text{NH}_3$  within 24 h after addition to “fresh” BRS (pH > 11), with nearly 95% being lost within 7 days after DAP addition. Although gypsum is incorporated to reduce the pH of BRS from  $\approx 11$  to 9.5, this does not occur uniformly throughout BRS under operational conditions. Consequently, “fresh” residue sand embankments can be expected to exhibit pH values ranging between  $\approx 9$  to  $\approx 11$ , so the opportunity exists for massive loss of DAP-N through volatilisation. Furthermore, this loss can occur within a very short time period and so little N remains in plant available forms. This may explain the very low to

negligible inorganic N concentrations measured in BRS and plant tissue for new (<3 months) and established (>12 months) residue rehabilitation.

Phosphorus sorption was found to decrease with increasing pH (pH 7 to 11), indicating increased availability and leachability under highly alkaline conditions. Furthermore, much of the P sorption occurred on Fe and Al oxides and hydrous oxides. Since much of the surface electrical charge and P sorption surfaces are associated with Fe and Al oxides and hydroxides, then factors controlling the precipitation/dissolution (e.g. redox, acidification, etc.) of these surfaces will also affect P availability. Under current operating conditions, there are no obvious mechanisms which could affect the stability of these oxide surfaces. Although between 25 and 50% of the added P may be in plant available forms in the short term, information is still required on the long term buffering capacity of BRS in terms of its ability to supply plant available P through desorption (release) of sorbed P.

Findings from this study and others (e.g. Bell *et al.* 2008) provide strong evidence that the current use of inorganic  $\text{NH}_4$  based fertiliser is inappropriate for use in highly alkaline BRS. It is therefore recommended that if the BRS pH cannot be operationally adjusted to near-neutrality, then alternative forms of fertiliser and/or time of application need to be identified. Suitable alternatives include the use of nitrate ( $\text{NO}_3$ ) as the primary inorganic N source. However,  $\text{NO}_3$  is a highly mobile anion which would not be retained to a large extent by a net negatively charged soil. Since fertiliser is commonly applied during the wet season in Western Australia residue rehabilitation operations, there is an excellent opportunity for loss of  $\text{NO}_3$  through leaching. This is further exacerbated by the lack of established vegetation with a root structure or capability to take up the applied  $\text{NO}_3$  before it moves below the rootzone via leaching.

Organic fertilisers offer an alternative however the BRS (particularly fresh BRS) contains little to no established microbial populations and a period of time is required until the chemical characteristics of BRS are altered to an extent which is suitable to sustain microbial populations. This implies that the addition of organic fertilisers may have little immediate benefit on nutrient availability unless they are already in water-soluble and/or plant available forms (e.g. dissolved organic N can be taken up by plants). The absence of microbial populations may prove to be the limiting factor to the use of organic fertilisers in residue rehabilitation, at least in the short term.

From an operational perspective, managing the BRS embankments to achieve the appropriate physical, chemical and microbial conditions for optimising rehabilitation performance warrants

attention. The application of successive plant systems (e.g. grass then shrubs), and/or extended “fallow” periods to allow excessive alkalinity and salinity to be removed from the upper 1m of the BRS embankment profile through leaching are two low-cost options that are achievable within the current operational residue rehabilitation program. These options in conjunction with the addition of gypsum, organic matter (biosolids, biochar etc.) and other amendments (e.g. flyash) need detailed investigation as part of overall residue rehabilitation fertiliser management.

## ACKNOWLEDGEMENTS

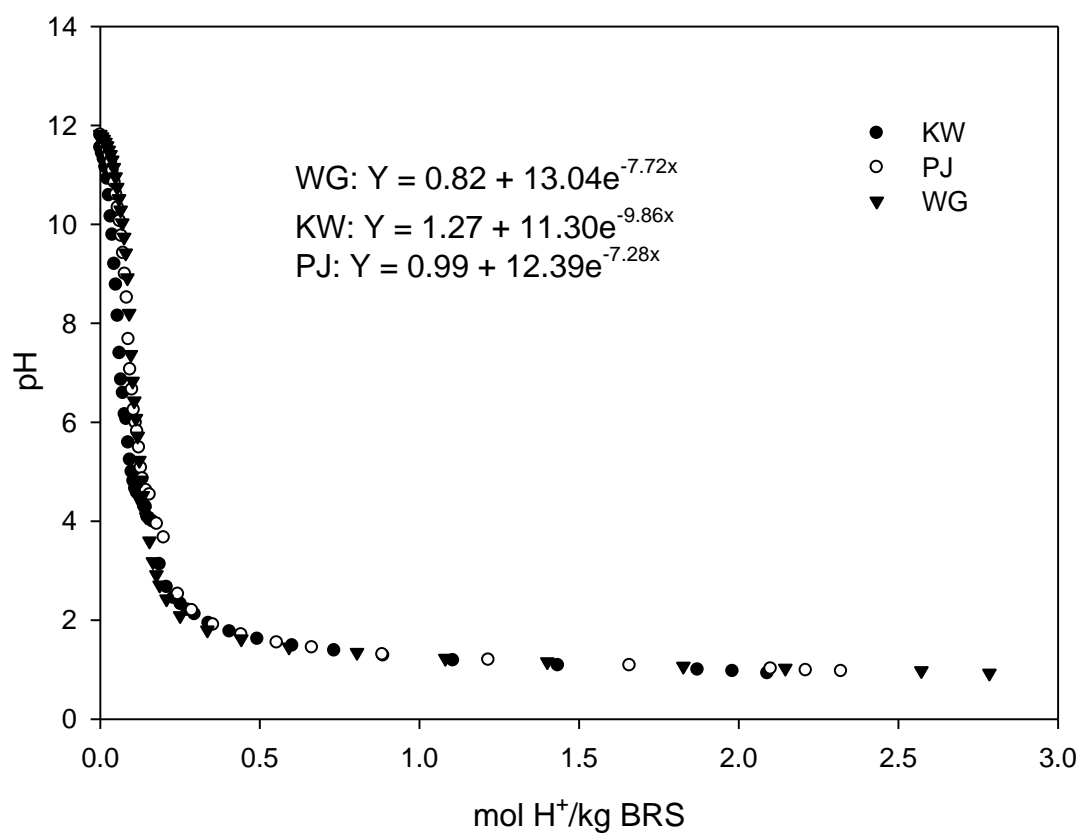
Funding for this project was provided by Alcoa of Australia (WAO-Residue). Ms Marijke Heenan and Dr Lily Wei are gratefully acknowledged for their assistance in the experiment and chemical analysis.

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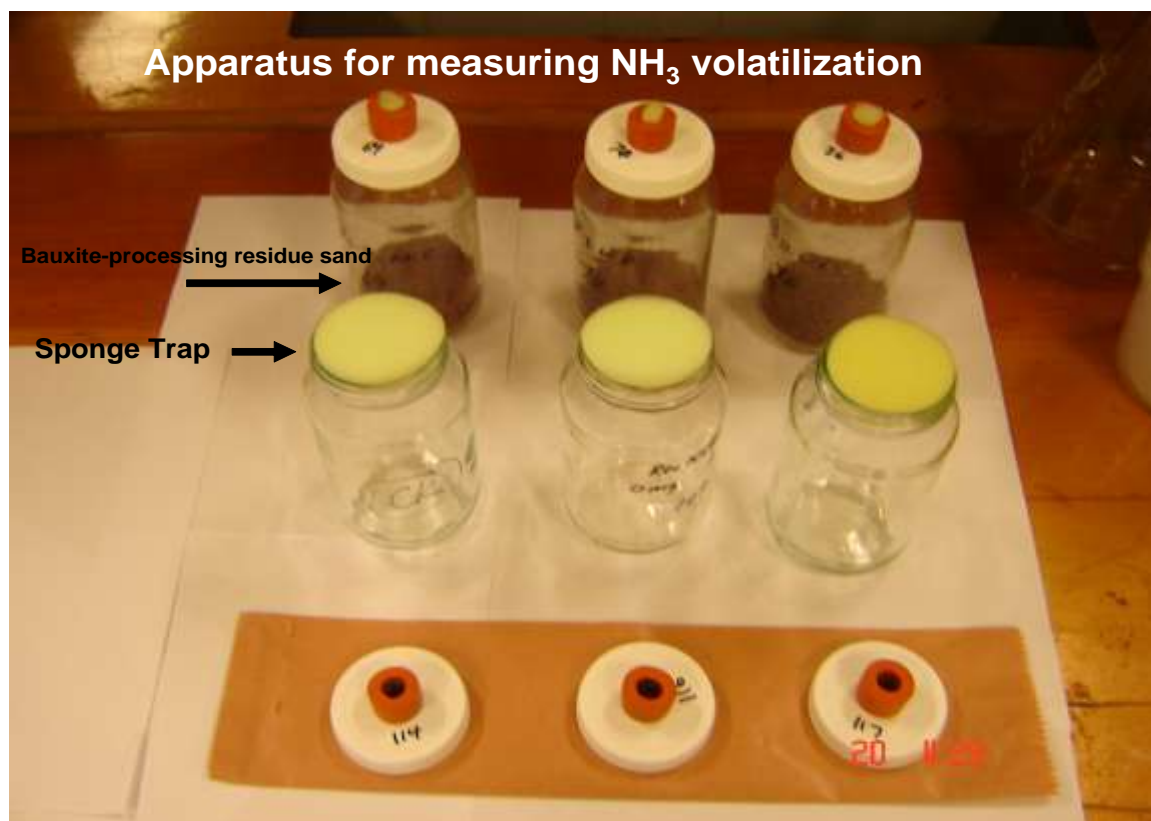
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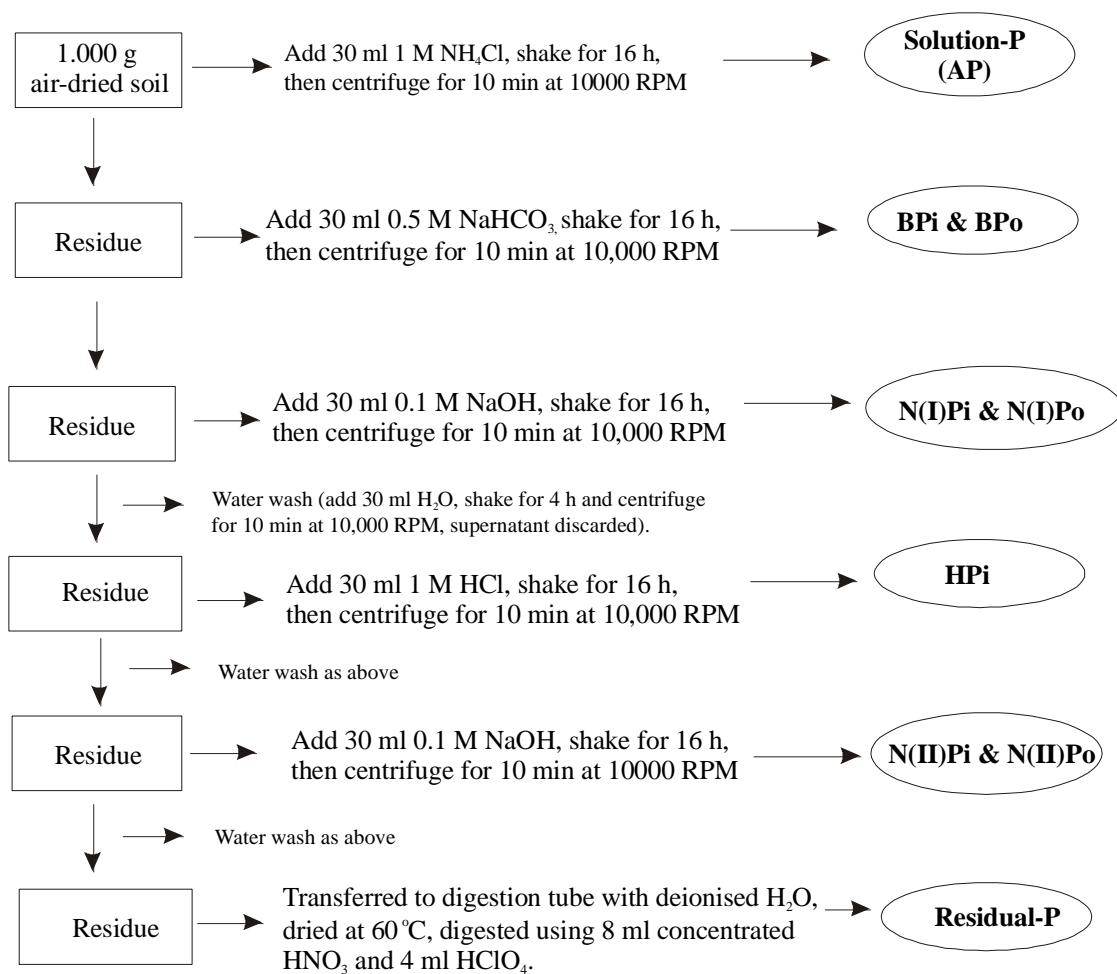
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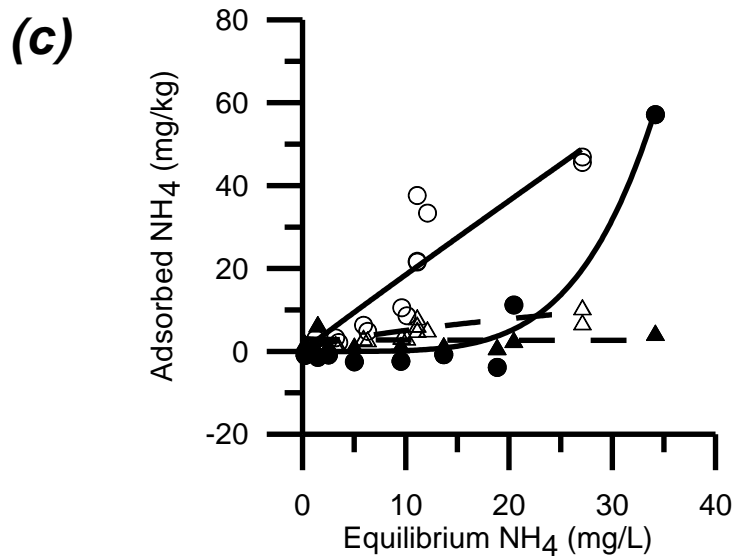
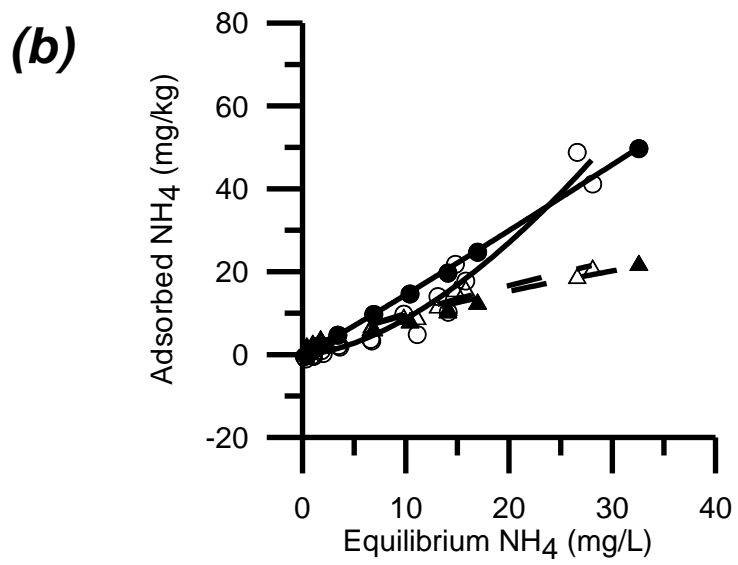
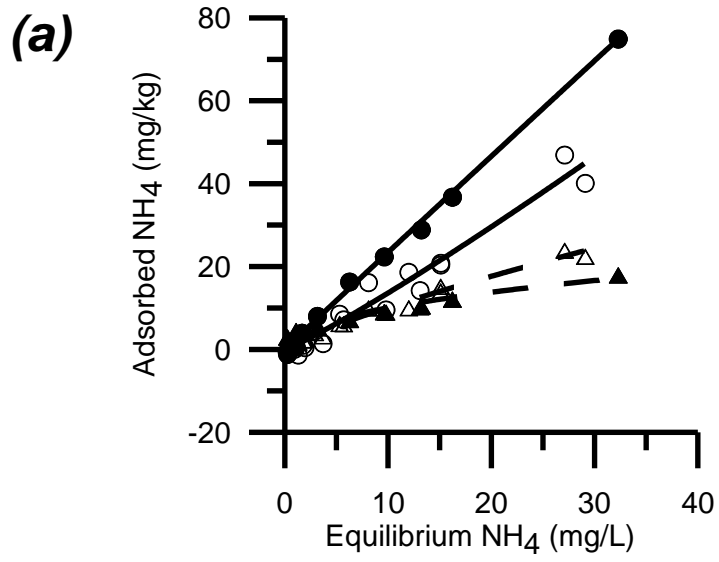
**Figure 1.** Acid neutralization curves (ANCs) for BRS from Alcoa's three Western Australia refineries (KW, Kwinana; PJ, Pinjarra; WG, Wagerup)



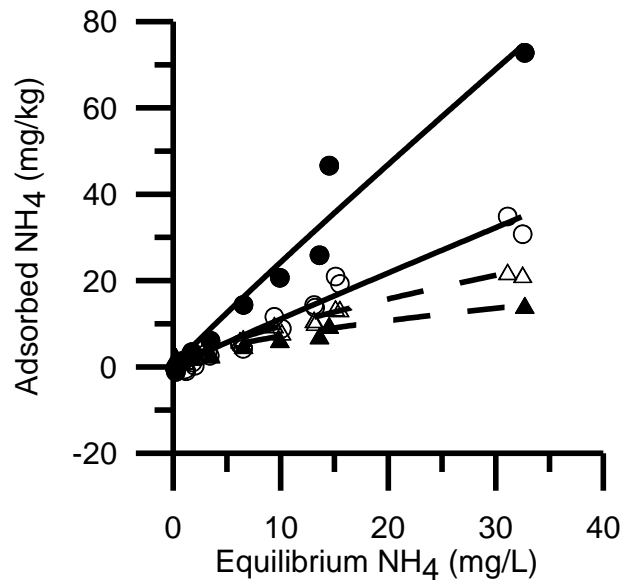
**Figure 2.** Apparatus (Sponge trapping system) for measuring  $\text{NH}_3$  volatilization from BRS



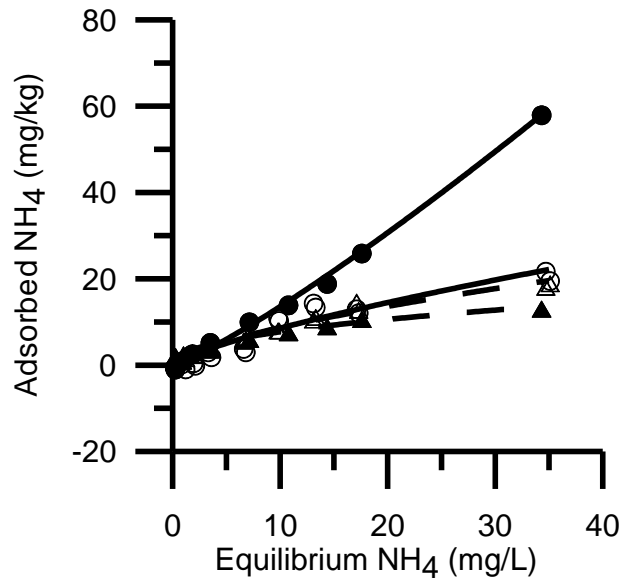
**Figure 3.** Flow chart of phosphorus sequential fractionation scheme



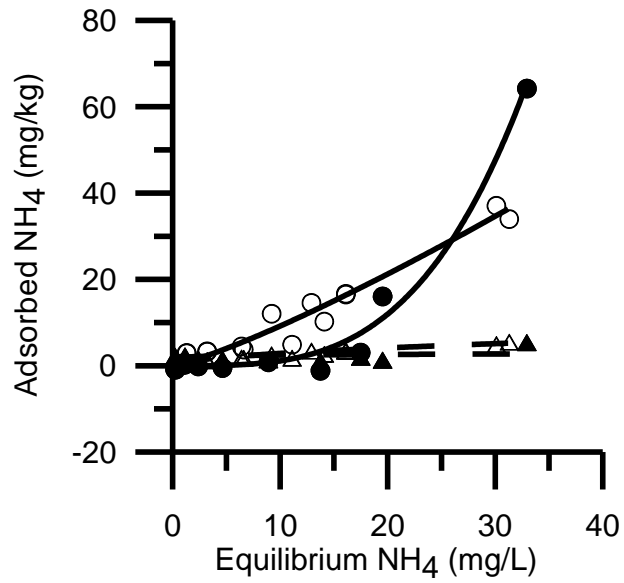
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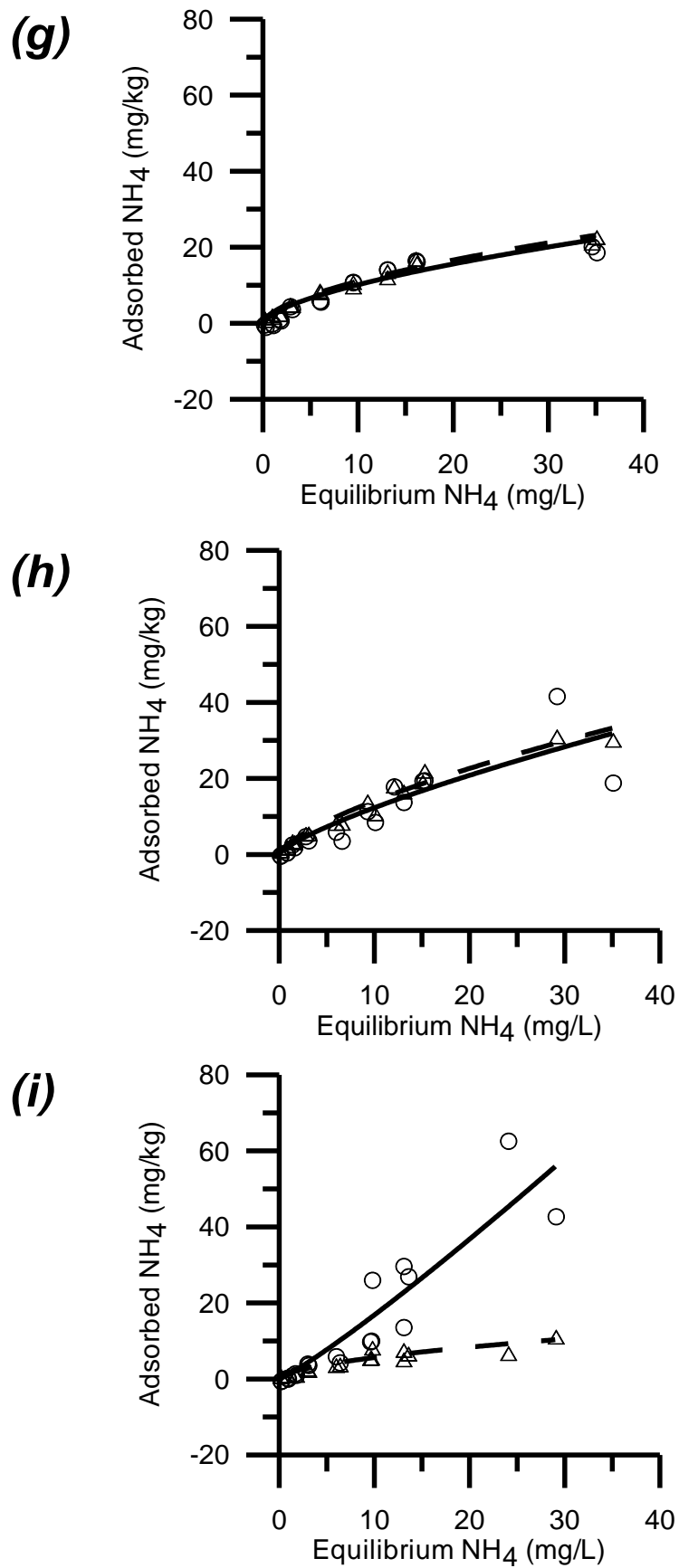


(e)

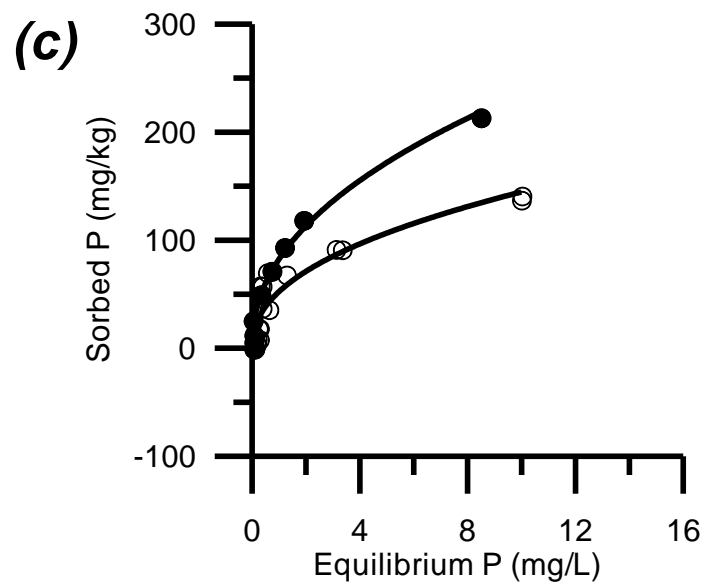
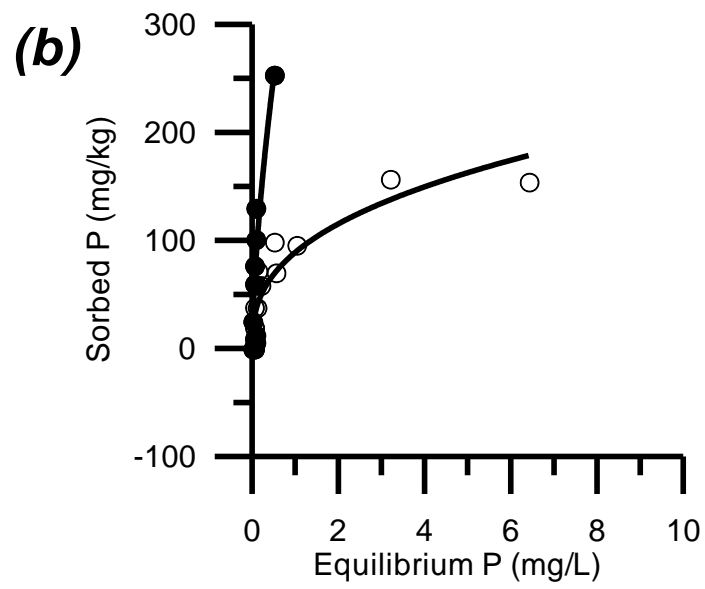
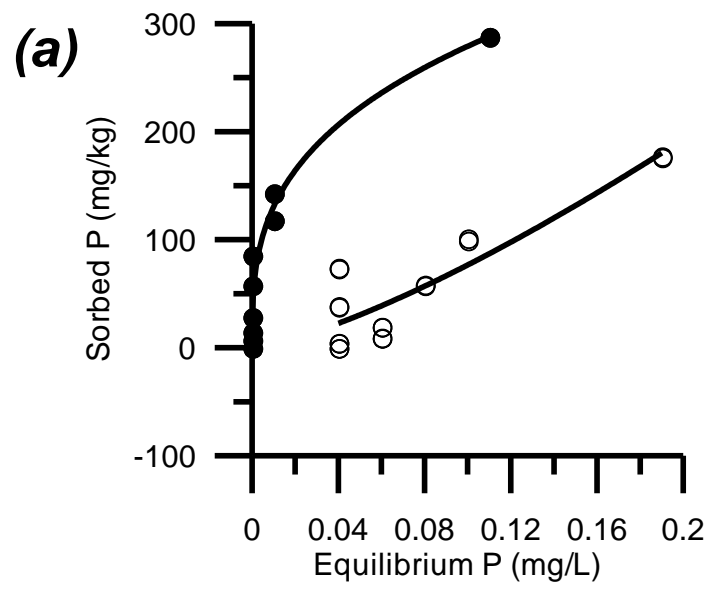


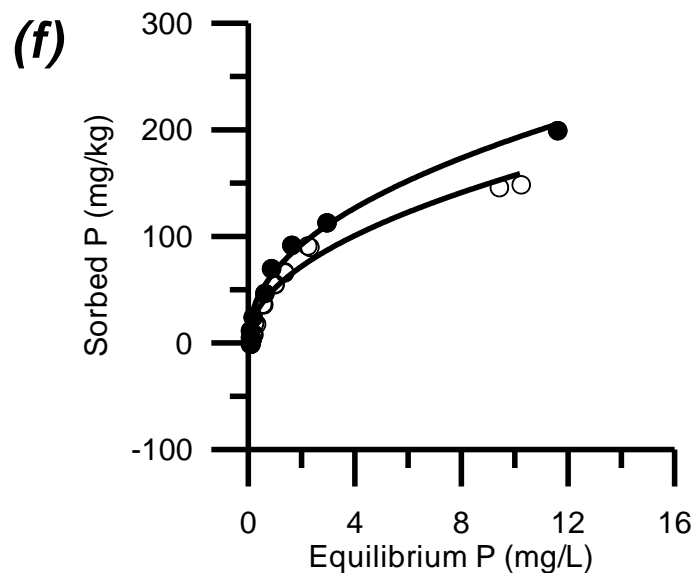
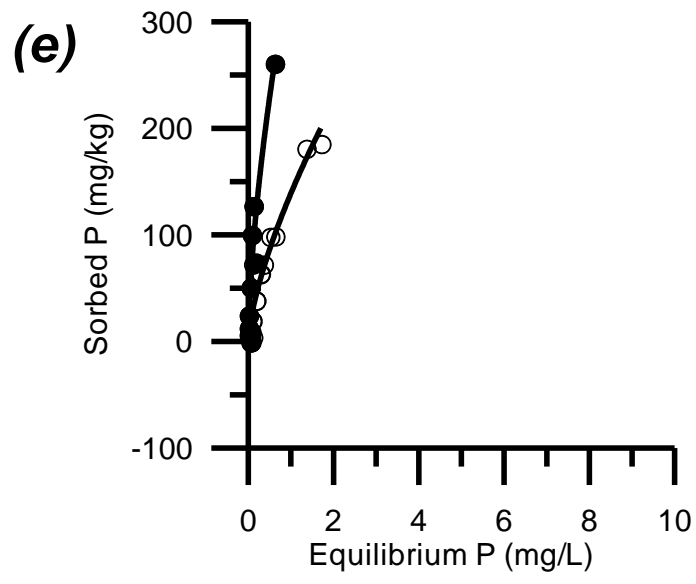
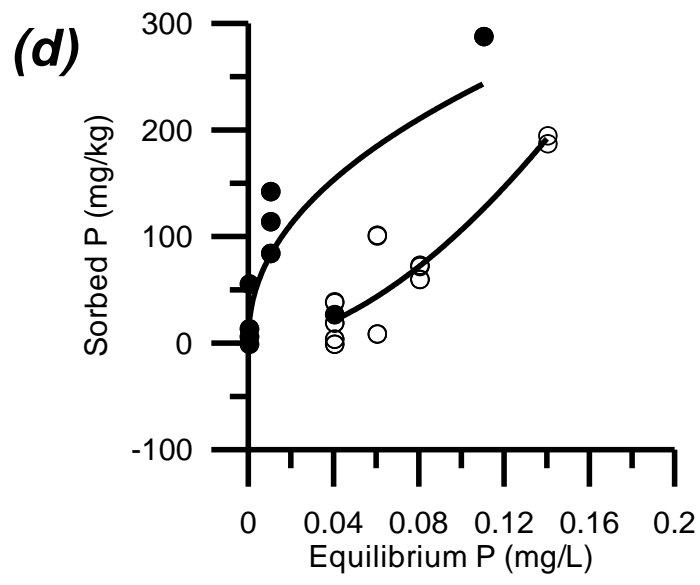
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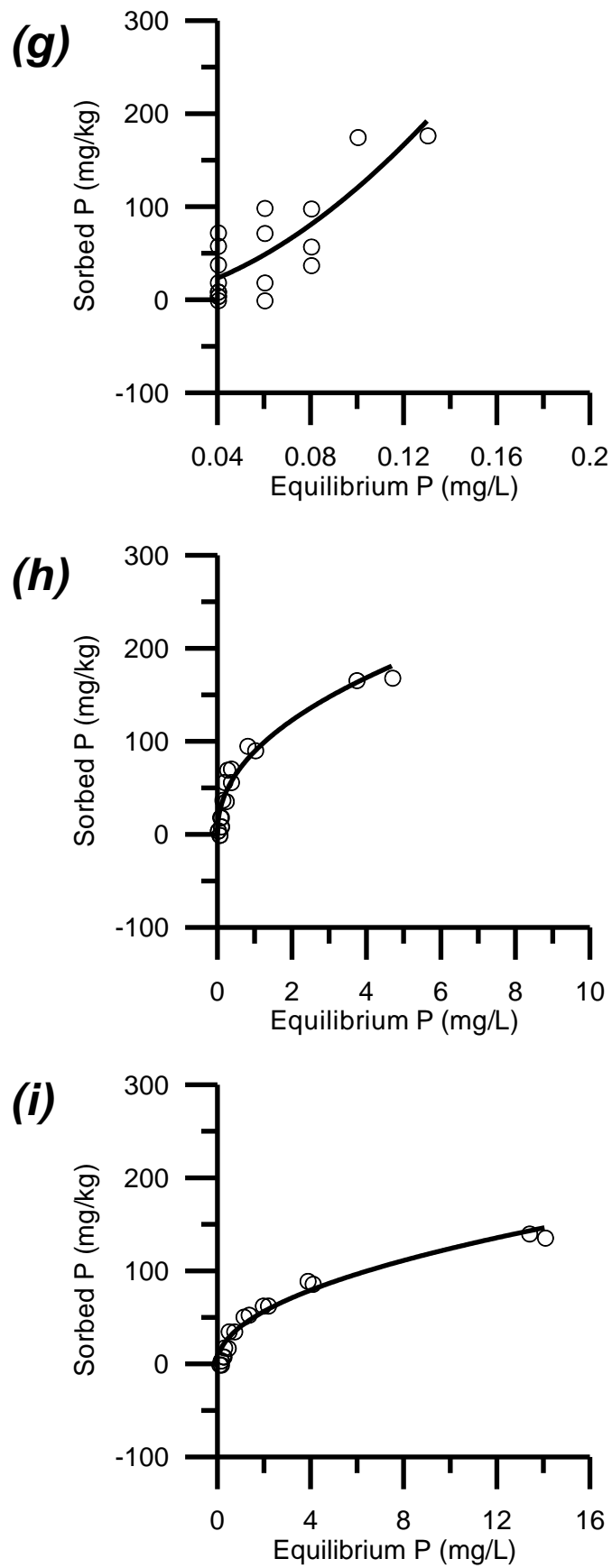




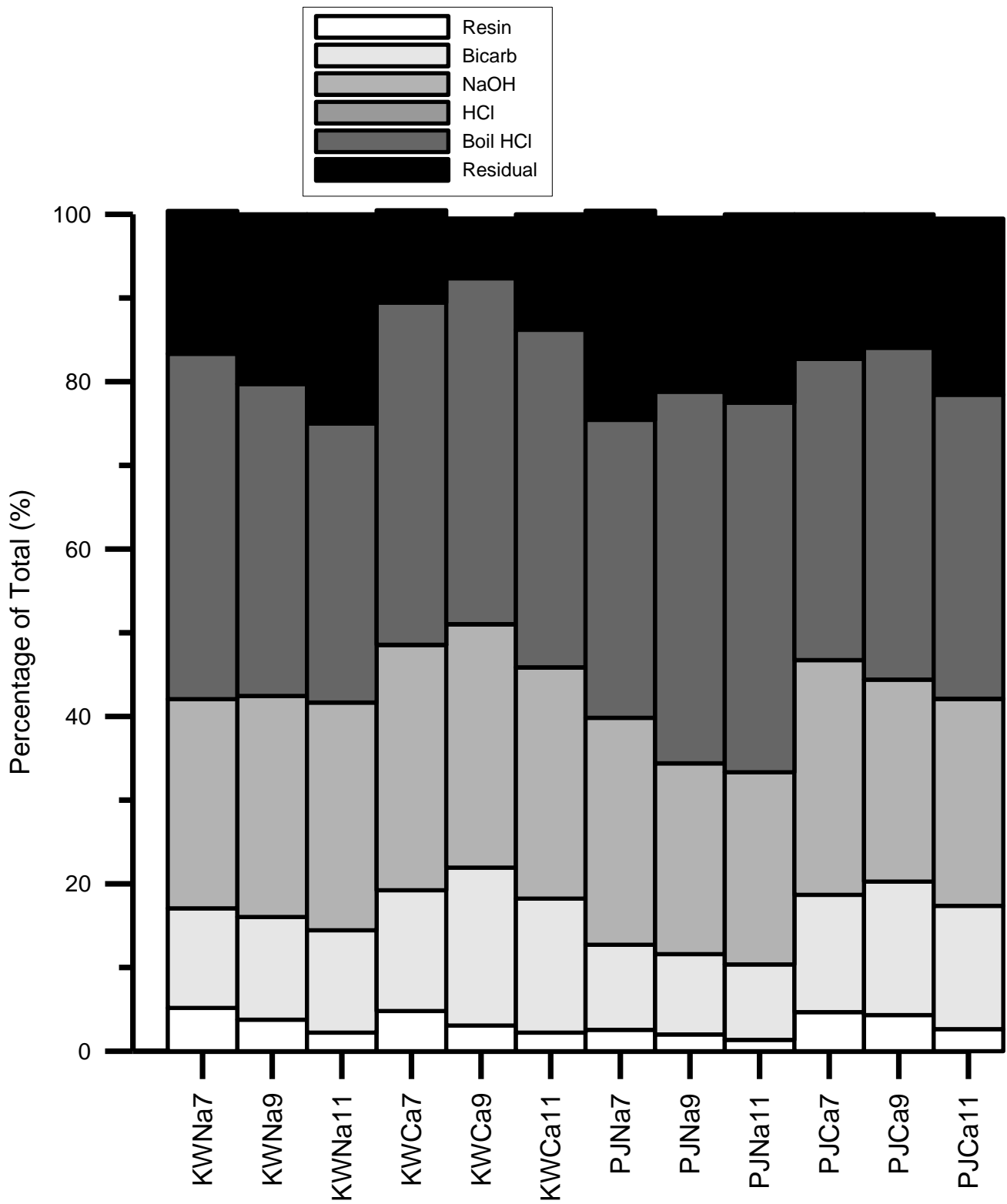
**Figure 4.** Ammonium adsorption isotherms for (a) KW pH 7, (b) KW pH 9, (c) KW pH 11, (d) PJ pH 7, (e) PJ pH 9, (f) PJ pH 11, (g) WG pH 7, (h) WG pH 9 and (i) WG pH 11. ● Sorbed – Ca; ○ Sorbed – Na; ▲ Adsorbed – Ca; △ Adsorbed – Na. Solid and dashed lines are fitted using Eqn [3]



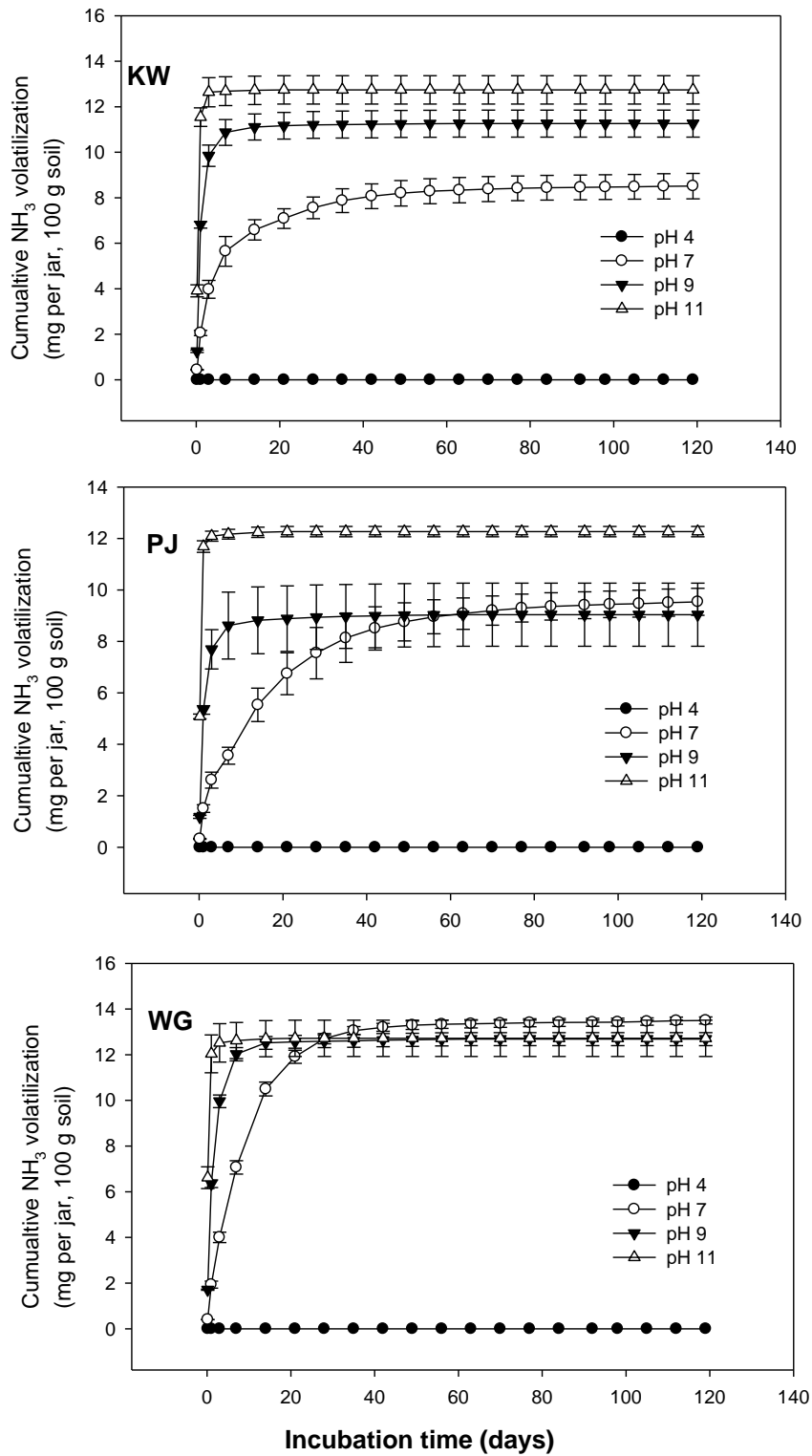




**Figure 5.** Phosphorus adsorption isotherms for (a) KW pH 7, (b) KW pH 9, (c) KW pH 11, (d) PJ pH 7, (e) PJ pH 9, (f) PJ pH 11, (g) WG pH 7, (h) WG pH 9 and (i) WG pH 11. ● Sorbed – Ca; ○ Sorbed – Na; ▲ Adsorbed – Ca; △ Adsorbed – Na. Solid and dashed lines are fitted using Eqn [3]

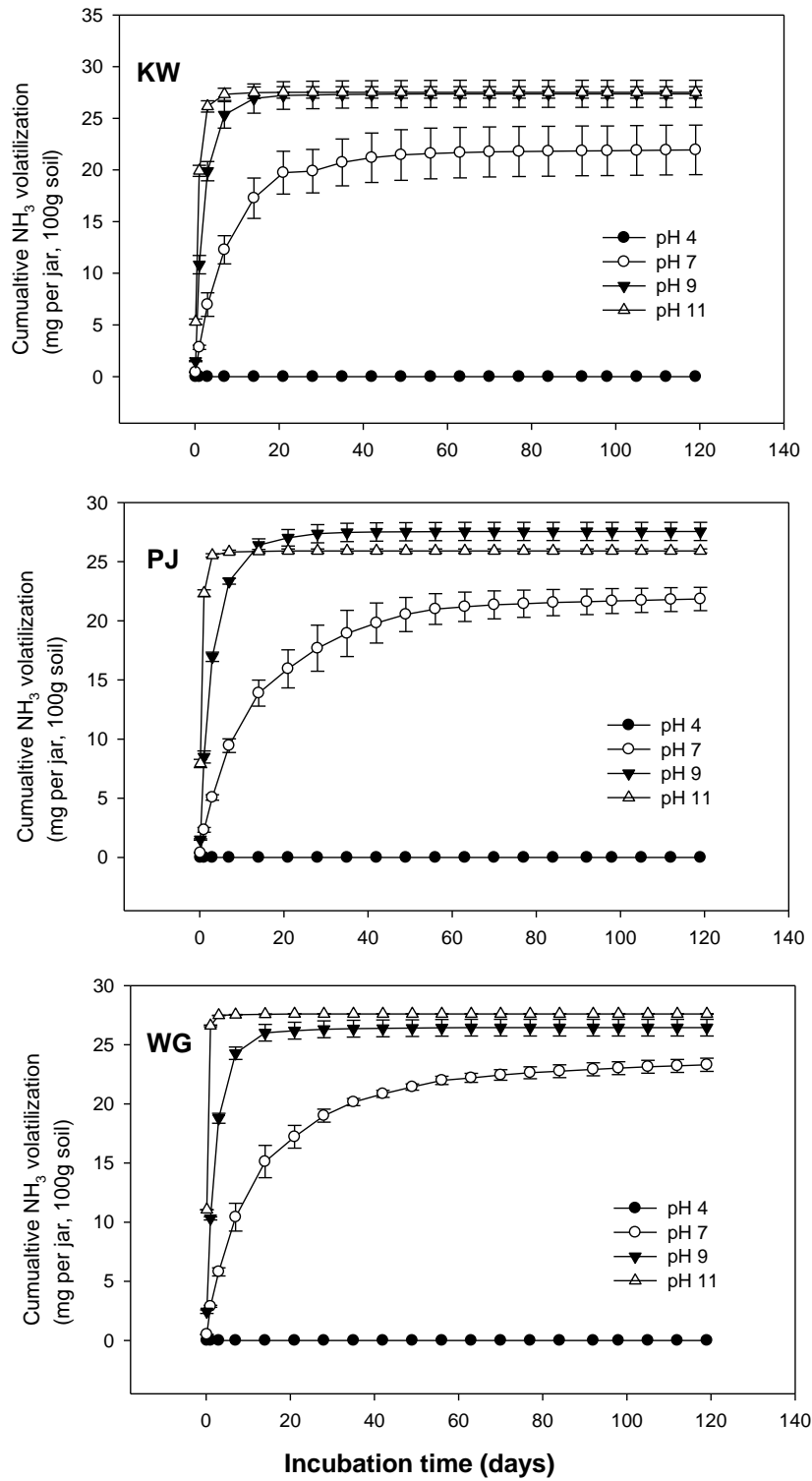


**Figure 6.** P fractionation of the KW and PJ residue sand samples as a function of pH (7, 9 and 11) and cation (Ca and Na) system. Values expressed as a percentage of Total P extracted

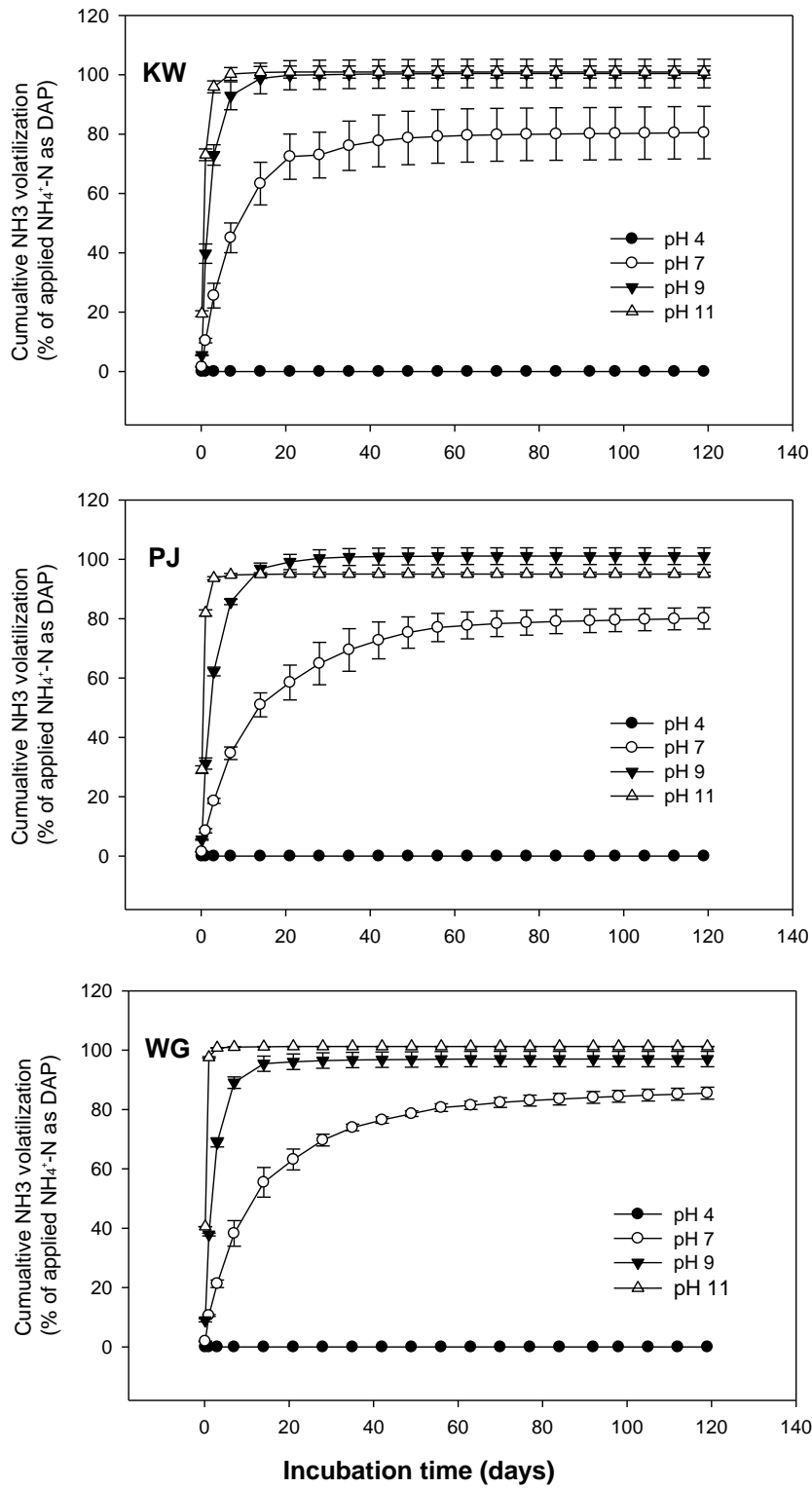


**Figure 7a.** The amount of cumulative NH<sub>3</sub> volatilization in the BRS from three refineries of Alcoa in Western Australia (KW, Kwinana; PJ, Pinjarra; WG, Wagerup) at the medium DAP rate

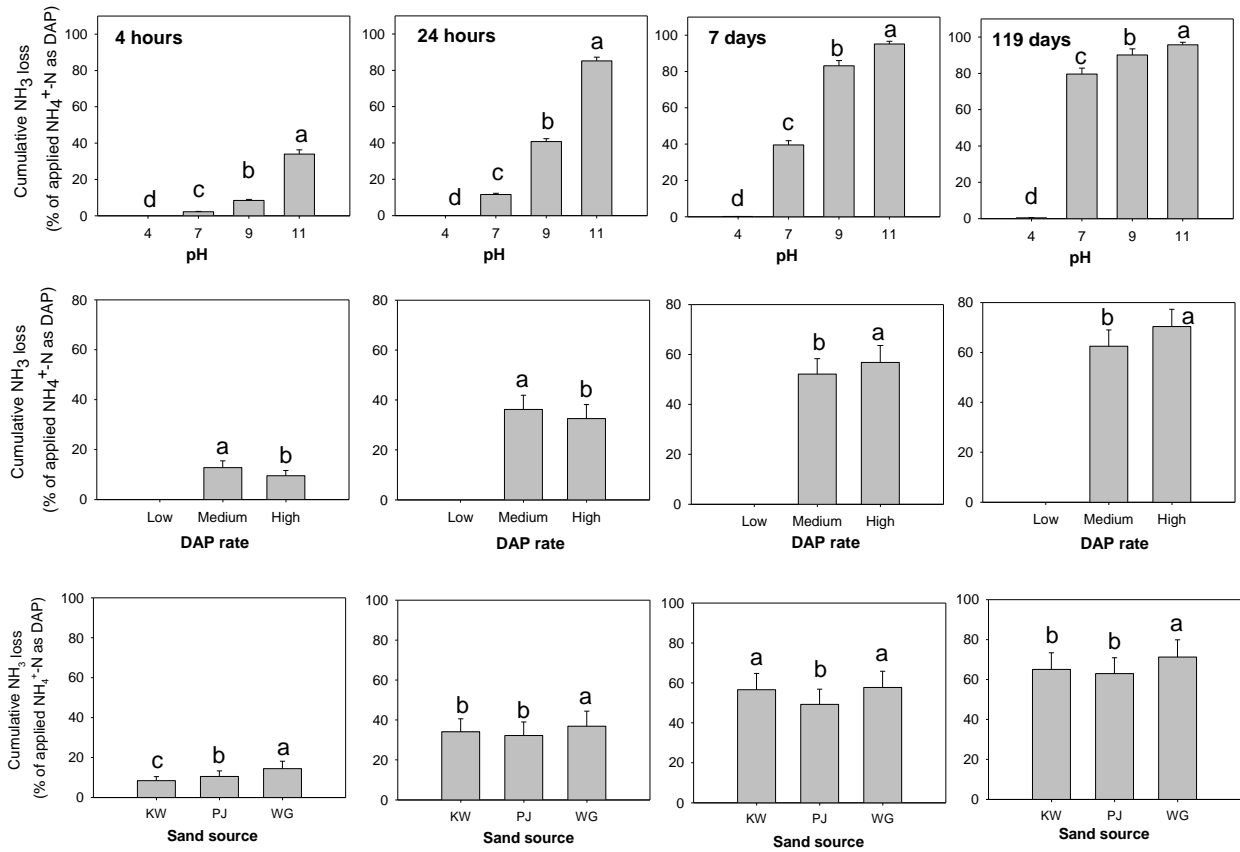




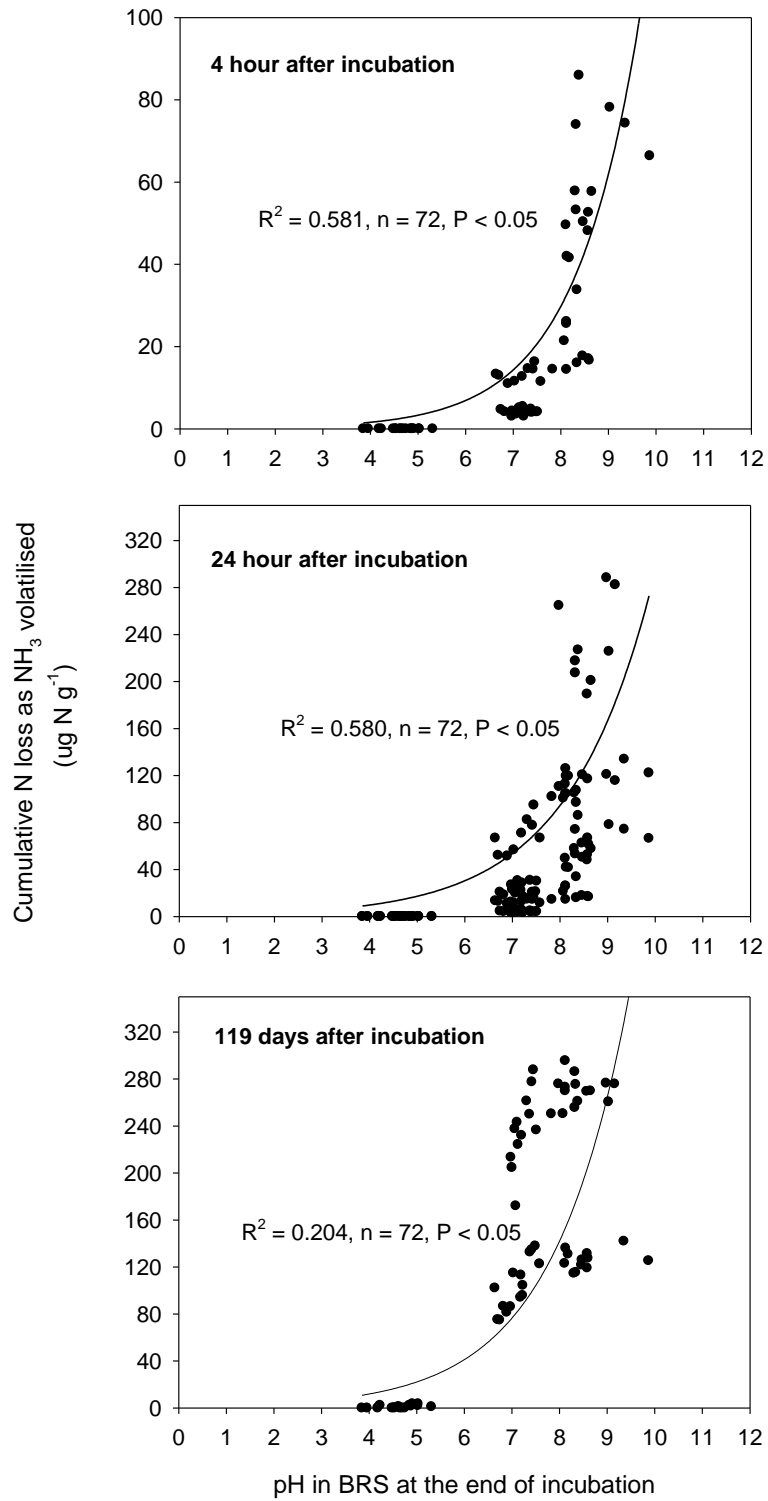
**Figure 8a.** The amount of cumulative NH<sub>3</sub> volatilization in the BRS from three refineries of Alcoa in Western Australia (KW, Kwinana; PJ, Pinjarra; WG, Wagerup) at the high DAP rate



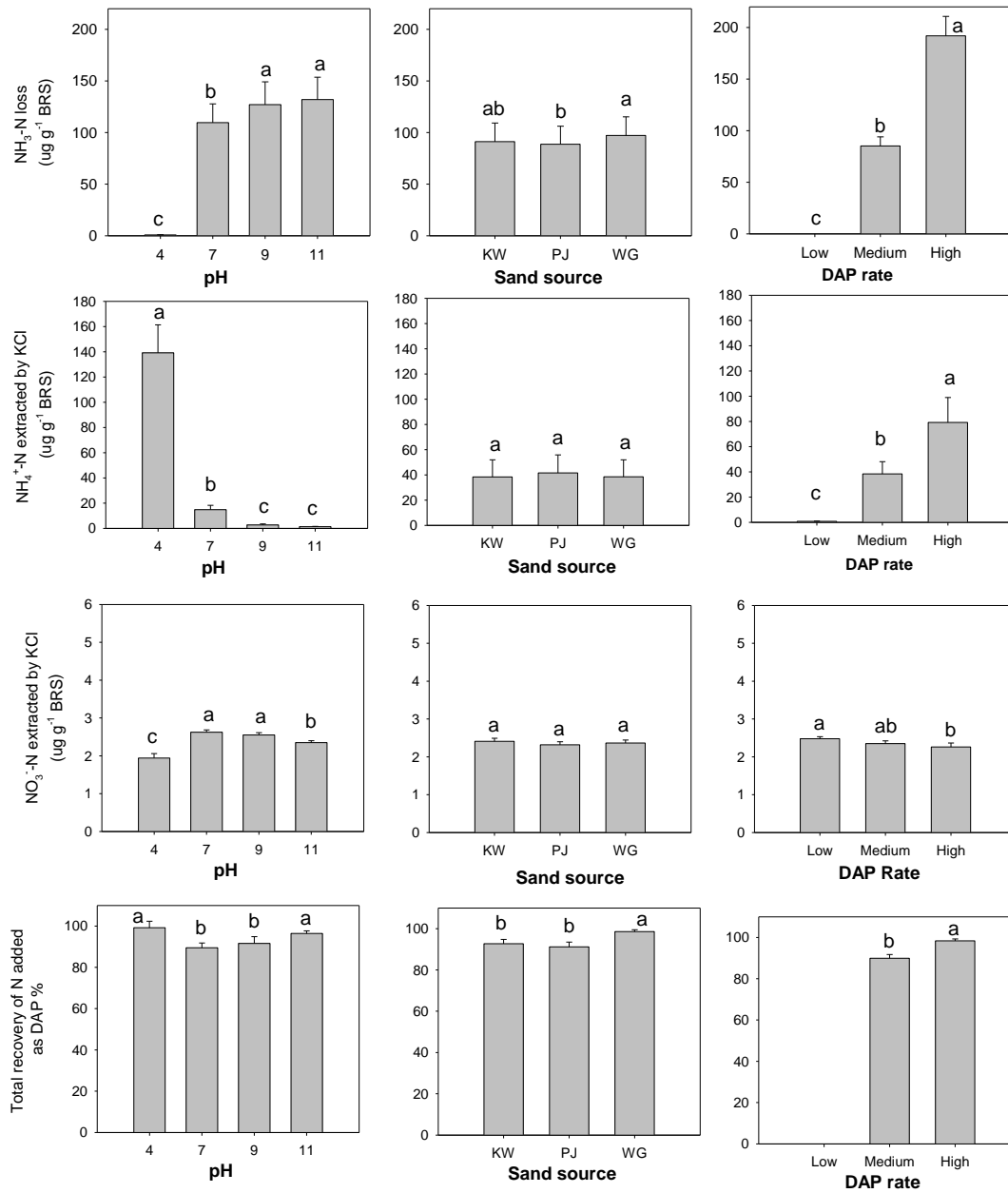
**Figure 8b.** The percentage of cumulative NH<sub>3</sub> volatilization in the BRS from three refineries of Alcoa in Western Australia (KW, Kwinana; PJ, Pinjarra; WG, Wagerup) at the high DAP rate



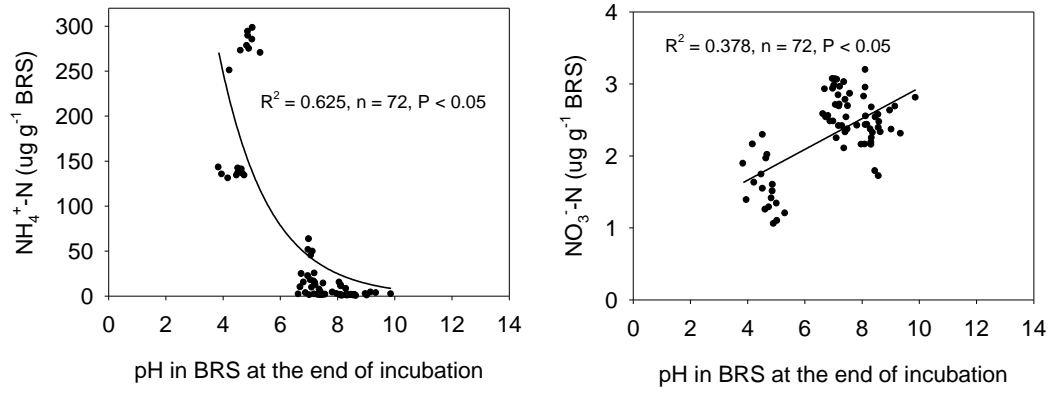
**Figure 9.** Effects of initial pH, sand source and DAP rate treatments on the cumulative NH<sub>3</sub> volatilization loss from the bauxite-processing residue sand (BRS) 4 hours, 24 hours, 7 days and 119 days (at the end) after incubation (KW, Kwinana; PJ, Pinjarra; WG, Wagerup)



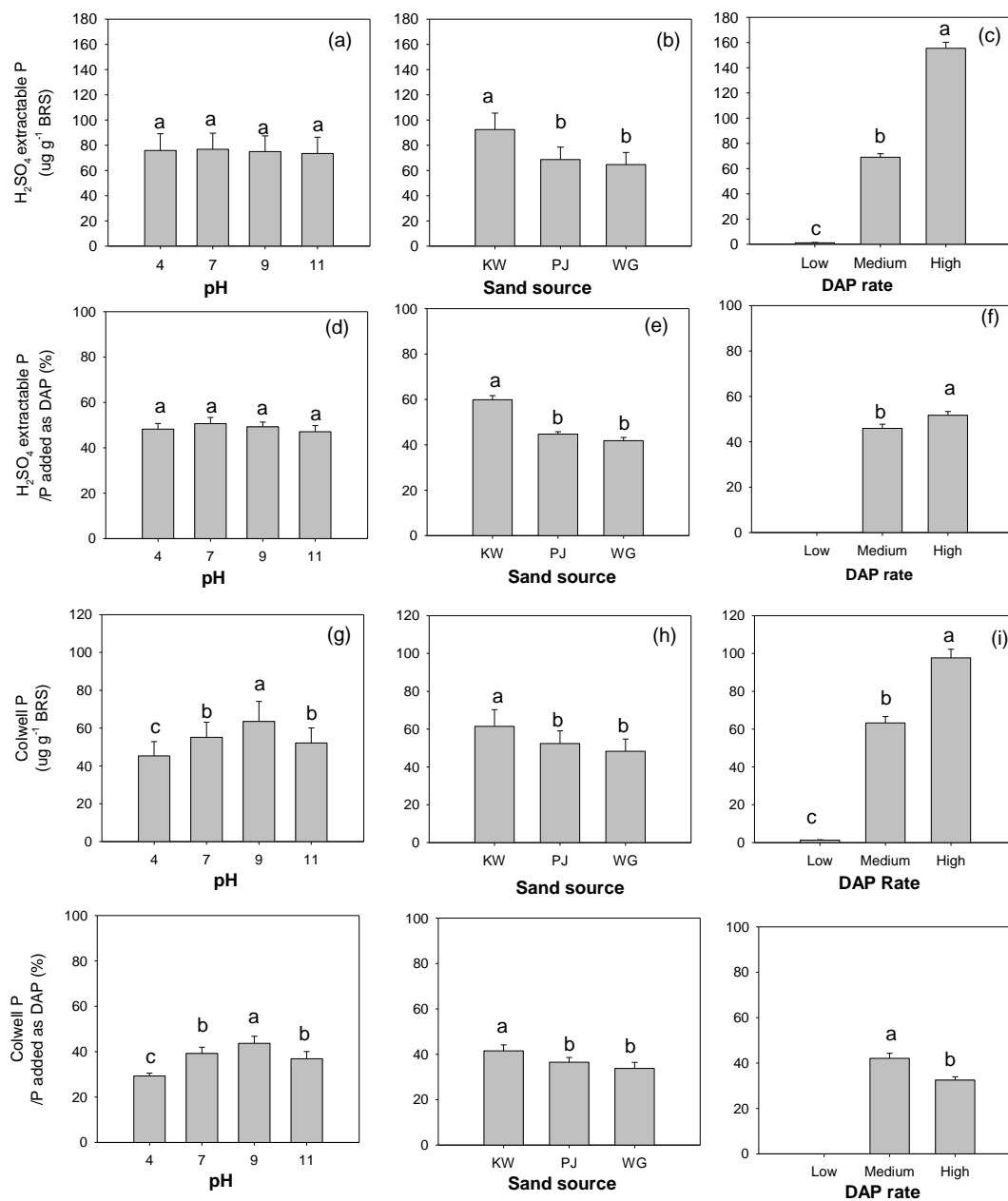
**Figure 10.** Relationships between the cumulative N loss as  $\text{NH}_3$  and the pH in BRS measured at the end of incubation



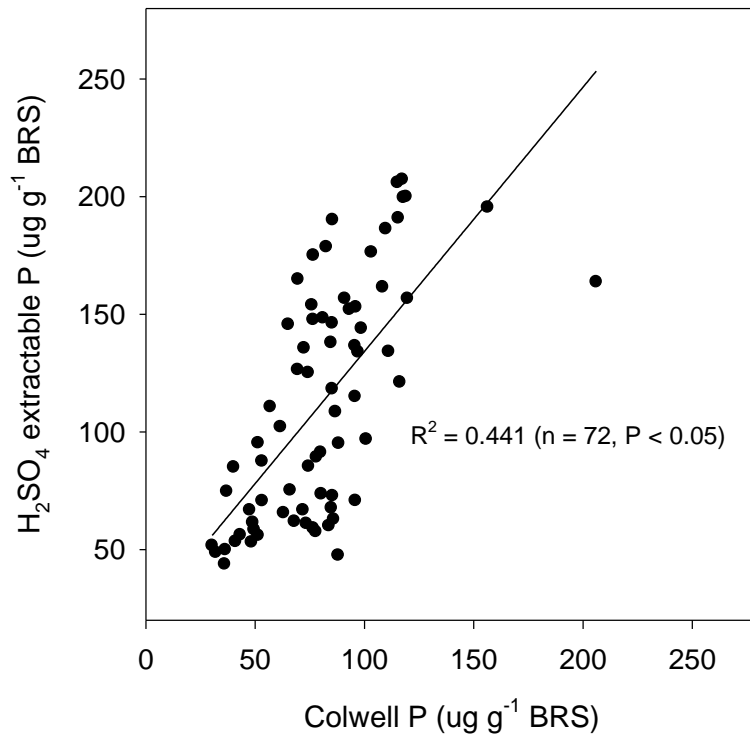
**Figure 11.** Effects of initial pH, sand source and DAP rate treatments on the NH<sub>3</sub>-N loss, residual mineral N and the N recovery in the bauxite-processing residue sand (BRS) (KW, Kwinana; PJ, Pinjarra; WG, Wagerup)



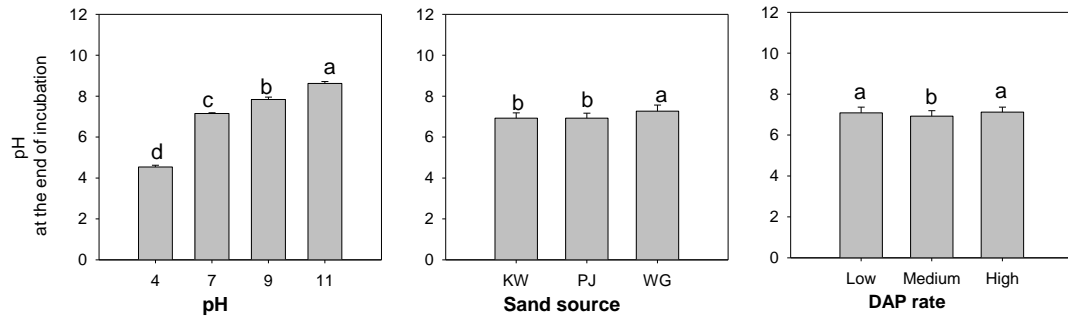
**Figure 12.** Relationships between concentrations of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  and pH in BRS at the end of incubation



**Figure 13.** Effects of initial pH, sand source and DAP rate treatments on H<sub>2</sub>SO<sub>4</sub> extractable P and Colwell P in the bauxite-processing residue sand (BRS) at the end of incubation (KW, Kwinana; PJ, Pinjarra; WG, Wagerup)



**Figure 14.** Relationship between Colwell P and 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P in BRS



**Figure 15.** Effects of initial pH, sand source and DAP rate treatments on the final pH in the bauxite-processing residue sand (BRS) at the end of incubation

**Table 1.** Chemical properties of bauxite-processing residue sand (BRS) from three refineries of Alcoa in Western Australia. All analyses were undertaken using standard procedures provided in Rayment and Higginson (1992)

Source <sup>a</sup>	pH	Organic C (%)	Total N (%)	C:N ratio	Total P (mg kg <sup>-1</sup> )	Total Fe (g kg <sup>-1</sup> )	Total Al (g kg <sup>-1</sup> )	Available NH <sub>4</sub> <sup>+</sup> -N (mg kg <sup>-1</sup> )	Available NO <sub>3</sub> <sup>-</sup> -N (mg kg <sup>-1</sup> )	Available K (mg kg <sup>-1</sup> )	Available S (mg kg <sup>-1</sup> )	PBI <sup>b</sup>
KW	11.6	0.13	0.03	4.2	26.25	44.7	243.7	1	1	11.7	14.12	565
PJ	11.8	0.07	0.01	7.2	24.59	45.1	251.2	1	2	13.2	32.31	551
WG	11.8	0.05	0.02	2.3	28.08	39.3	183.8	1	1	6.9	22.31	521

<sup>a</sup>KW, Kwinana; PJ, Pinjarra; WG, Wagerup

<sup>b</sup>Phosphorus buffering index

**Table 2.** Exchangeable cations in bauxite-processing residue sand (BRS) from three refineries of Alcoa in Western Australia. All analyses were undertaken using standard procedures provided in Rayment and Higginson (1992)

Source <sup>a</sup>	Exchangeable <sup>b</sup> (meq 100 g <sup>-1</sup> )						EDTA extractable (mg kg <sup>-1</sup> )				Oxalate extractable (mg kg <sup>-1</sup> )		ESP (%) <sup>c</sup>
	Ca	Mg	Na	K	Al	Fe	Cu	Zn	Mn	Fe	Fe	Al	
KW	3.29	0.12	8.42	0.02	0.02	0.56	0.27	0.03	0.77	78.8	4690	90.1	71
PJ	2.92	0.06	12.84	0.02	0.02	0.46	0.37	0.13	0.78	84.3	7740	96.8	81
WG	1.25	0.01	9.90	0.02	0.02	0.13	0.24	0.01	0.63	67.2	4370	121.7	88

<sup>a</sup>KW, Kwinana; PJ, Pinjarra; WG, Wagerup

<sup>b</sup> Exchangeable cation concentrations include water-soluble and 0.1M BaCl<sub>2</sub>-extractable forms. Typical cation exchange capacities of each BRS is about 4.5 cmol/kg, of which 90% can be attributed to variable surface charge (Phillips and Chen 2010)

<sup>c</sup>ESP, exchangeable sodium percentage

**Table 3.** Physical properties of bauxite-processing residue sand (BRS) from three refineries of Alcoa in Western Australia. All analyses were undertaken using standard procedures provided in Rayment and Higginson (1992)

Source <sup>a</sup>	Moisture (%)	Water holding capacity (%)	Particle size distribution (µm, %)				
			200-2000	20-200	2-20	< 2	20-2000
KW	9.4	27.1	64.9	28.3	1.9	4.9	93.2
PJ	10.5	24.3	67.1	23.3	1.9	7.7	90.4
WG	6.6	26.8	69.1	24.1	1.0	5.8	93.2

<sup>a</sup>KW, Kwinana; PJ, Pinjarra; WG, Wagerup.

**Table 4.** Phosphorus and ammonium sorption parameters [ $n$  and  $k$  (L/mg)] for residue sand from KW, PJ and WG obtained using the Freundlich equation ( $S = kc^n$ ). For each parameter and nutrient, values denoted by the same letter are not significantly different from each other ( $P < 0.05$ )

RSA	Cation	Sorbed/Adsorbed	pH	$k$	$n$	$r^2$
			<u>NH<sub>4</sub></u>			
KW	Ca	Sorbed	7	2.396	0.991	0.997
KW	Ca	Adsorbed	7	3.499	0.458	0.963
KW	Na	Sorbed	7	1.038	1.118	0.957
KW	Na	Adsorbed	7	1.587	0.804	0.976
KW	Ca	Sorbed	9	1.286	1.051	0.999
KW	Ca	Adsorbed	9	1.962	0.685	0.966
KW	Na	Sorbed	9	0.199	1.640	0.956
KW	Na	Adsorbed	9	1.750	0.753	0.971
KW	Ca	Sorbed	11	≈0	4.653	0.966
KW	Ca	Adsorbed	11	2.957	-0.032	0.007
KW	Na	Sorbed	11	1.961	0.975	0.853
KW	Na	Adsorbed	11	1.176	0.634	0.848
PJ	Ca	Sorbed	7	2.716	0.951	0.955
PJ	Ca	Adsorbed	7	1.851	0.586	0.938
PJ	Na	Sorbed	7	1.192	0.970	0.964
PJ	Na	Adsorbed	7	1.728	0.738	0.988
PJ	Ca	Sorbed	9	0.900	1.178	0.997
PJ	Ca	Adsorbed	9	2.702	0.456	0.977
PJ	Na	Sorbed	9	1.500	0.758	0.918
PJ	Na	Adsorbed	9	1.958	0.648	0.979
PJ	Ca	Sorbed	11	≈0	3.403	0.982
PJ	Ca	Adsorbed	11	1.971	0.094	0.050
PJ	Na	Sorbed	11	0.574	1.205	0.956
PJ	Na	Adsorbed	11	0.846	0.529	0.924
WG	Ca	Sorbed	7	nd	nd	nd
WG	Ca	Adsorbed	7	nd	nd	nd
WG	Na	Sorbed	7	2.425	0.621	0.918
WG	Na	Adsorbed	7	2.821	0.592	0.976
WG	Ca	Sorbed	9	nd	nd	nd
WG	Ca	Adsorbed	9	nd	nd	nd
WG	Na	Sorbed	9	2.146	0.758	0.775
WG	Na	Adsorbed	9	2.898	0.686	0.970
WG	Ca	Sorbed	11	nd	nd	nd
WG	Ca	Adsorbed	11	nd	nd	nd
WG	Na	Sorbed	11	1.261	1.126	0.842
WG	Na	Adsorbed	11	1.528	0.567	0.879
			<u>P</u>			
KW	Ca	Sorbed	7	596.081	0.330	0.822
KW	Na	Sorbed	7	1649.846	1.333	0.791
KW	Ca	Sorbed	9	392.587	0.642	0.742
KW	Na	Sorbed	9	88.958	0.375	0.836
KW	Ca	Sorbed	11	82.582	0.455	0.976

KW	Na	Sorbed	11	52.431	0.441	0.870
PJ	Ca	Sorbed	7	666.272	0.457	0.615
PJ	Na	Sorbed	7	6072.027	1.757	0.810
PJ	Ca	Sorbed	9	355.001	0.632	0.871
PJ	Na	Sorbed	9	139.074	0.685	0.927
PJ	Ca	Sorbed	11	67.416	0.454	0.983
PJ	Na	Sorbed	11	51.345	0.486	0.952
WG	Ca	Sorbed	7	nd	nd	nd
WG	Na	Sorbed	7	7412.720	1.790	0.658
WG	Ca	Sorbed	9	nd	nd	nd
WG	Na	Sorbed	9	89.29	0.458	0.931
WG	Ca	Sorbed	11	nd	nd	nd
WG	Na	Sorbed	11	40.221	0.4889	0.956

**Table 5.** Phosphorus fractionation of BRS from the KW and PJ RSAs using scheme by Tiessen and Moir (1993)<sup>1</sup>.

RSA	Treatment	pH	Resin-P	Bicarbonate-P <sup>2</sup>			Hydroxide-P	HCl-P	Boiling HCl-P	Residual -P	Total
				P <sub>i</sub>	P <sub>t</sub>	P <sub>o</sub>	P <sub>t</sub>	P <sub>i</sub>	P <sub>t</sub>	P <sub>t</sub>	
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Kwinana	Ca	7	10	28	30	2	61	<1	85	23	208
Kwinana	Ca	9	6	38	37	<1	57	<1	81	14	196
Kwinana	Ca	11	4	27	29	2	50	<1	73	25	181
Kwinana	Na	7	13	28	30	1	63	<1	104	43	252
Kwinana	Na	9	8	23	26	3	56	<1	79	43	212
Kwinana	Na	11	4	20	22	1	49	<1	60	45	180
Pinjarra	Ca	7	10	30	30	<1	60	<1	77	37	214
Pinjarra	Ca	9	10	35	37	1	56	<1	92	37	232
Pinjarra	Ca	11	5	27	28	1	47	<1	69	40	190
Pinjarra	Na	7	6	24	24	<1	64	<1	84	59	236
Pinjarra	Na	9	5	22	24	2	57	<1	111	52	250
Pinjarra	Na	11	3	20	20	<1	51	<1	98	50	222

<sup>1</sup> Samples had received 200% STOCK solution as part of DAP adsorption isotherm experiments

<sup>2</sup> P<sub>i</sub> = inorganic P; P<sub>o</sub> = organic P; P<sub>t</sub> = total P

**Table 6.** Recovery of added  $\text{NH}_4^+$ -N as  $\text{NH}_3$  by the sponge trapping and KCl-extraction method<sup>a</sup>.

$\text{NH}_4^+$ -N added (mg)	$\text{NH}_4^+$ -N recovered (mg)	Recovery (%)
0	0	N/A
4.83	4.91 (0.03)	101.6 (0.6)
9.83	9.86 (0.07)	100.3 (0.6)
20.0	20.07 (0.09)	100.3 (0.8)
30.0	30.45 (0.07)	101.5 (0.2)

<sup>a</sup>Data in the bracket are standard errors ( $n = 4$ )

**Table 7.** Effects of the initial pH, sand source and DAP rate treatments on NH<sub>3</sub>-N loss, residual N and N recovery in the bauxite-processing residue sand (BRS) from three refineries of Alcoa in Western Australia<sup>a</sup>

Source <sup>b</sup>	pH	DAP <sup>c</sup> rate	NH <sub>3</sub> -N <sup>d</sup> (µg g <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> -N <sup>e</sup> (µg g <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N <sup>e</sup> (µg g <sup>-1</sup> )	N recovery <sup>f</sup> (%)
KW	4	L	0e	2.8d	2.6ab	n/a
		M	0e	138.1b	1.9c	98.7a
		H	1.4e	273.5a	1.3d	99.3a
	7	L	0e	0.8d	2.6ab	n/a
		M	85.1d	18.5c	2.6ab	75.4d
		H	219.4b	21.9c	2.8a	88.3bc
	9	L	0	0.1d	2.6ab	n/a
		M	112.6c	1.7d	2.6ab	83.8cd
		H	273.7a	1.8d	2.5ab	101.0a
11	L	0e	0.3d	2.4c	n/a	
	M	127.4c	0.8d	2.5ab	94.0ab	
	H	275.1a	0.4d	2.4c	100.9a	
PJ	4	L	0e	0.5e	2.6abcd	n/a
		M	0e	132.7b	1.7fg	96.4ab
		H	2.5e	293.6a	1.4g	100.5a
	7	L	0e	1.4e	2.4bcde	n/a
		M	95.4d	16.2d	2.9a	81.3c
		H	218.4b	44.0c	2.8ab	96.0ab
	9	L	0e	1.3e	2.5abcd	n/a
		M	90.4d	4.6de	2.8ab	69.0d
		H	275.4a	1.3e	2.4bcde	101.0a
11	L	0e	0.7e	2.0ef	n/a	
	M	122.7c	1.3e	2.1def	90.5b	
	H	259.0a	0.8e	2.3de	95.2ab	
WG	4	L	0e	0.7d	2.8a	n/a
		M	0e	139.4b	1.8cd	101.0a
		H	2.6e	270.1a	1.3d	99.2ab
	7	L	0e	0.5d	2.4abc	n/a
		M	135.0d	2.1d	2.4abc	100.3ab
		H	233.1c	27.8c	2.7a	95.6bc
	9	L	0e	0.2d	2.5ab	n/a
		M	126.8d	0.9d	2.2bc	93.4c
		H	264.5b	12.5cd	2.8a	101.7a
11	L	0e	0.3d	2.4abc	n/a	
	M	127.2d	4.3d	2.5ab	95.4bc	
	H	275.9a	2.7d	2.5ab	102.2	

<sup>a</sup>ANOVA results showed there was no significant Sand x pH x DAP rate interactions and multiple comparisons were then carried out within each BRS. Means within a column of each BRS by the same letter are not different at the 5% level of significance;

<sup>b</sup>KW, Kwinana; PJ, Pinjarra; WG, Wagerup;

<sup>c</sup>L, M and H indicate 0, 13.63 and 27.26 mg N (as DAP) per jar (100 g BRS);

<sup>d</sup>NH<sub>3</sub>-N represents the NH<sub>3</sub>-N volatilization loss during the 119 day incubation;

<sup>e</sup>NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N are residual mineral N recovered by 3 consecutive KCl extraction from BRS after the incubation;

<sup>f</sup>N recovery % = (the sum of NH<sub>3</sub>-N + NH<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N in the M and H DAP rate treatment) – (the sum of NH<sub>3</sub>-N + NH<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N in the L DAP rate treatment)/N added as DAP x 100%.

**Table 8.** Effects of initial pH, sand sources and DAP rate treatments on H<sub>2</sub>SO<sub>4</sub> extractable P, Colwell P and pH in the bauxite-processing residue sand (BRS) from three refineries of Alcoa in Western Australia at the end of the incubation<sup>a</sup>

Source <sup>b</sup>	pH	DAP <sup>c</sup> rate	H <sub>2</sub> SO <sub>4</sub> -P (µg g <sup>-1</sup> ) <sup>d</sup>	H <sub>2</sub> SO <sub>4</sub> -P (%) <sup>d</sup>	Colwell P (µg g <sup>-1</sup> ) <sup>e</sup>	Colwell P (%) <sup>e</sup>	pH at completion
KW	4	L	3.1c	n/a	0f	n/a	4.38g
		M	82.5b	54.8ab	43.1e	28.9c	4.11g
		H	195.8a	65.1a	105.3bc	35.0bc	4.92f
	7	L	2.6c	n/a	1.1f	n/a	6.99e
		M	100.4b	66.7a	65.4de	43.5ab	6.91e
		H	194.5a	64.6ab	112.8b	37.5bc	7.32d
	9	L	2.3c	n/a	0f	n/a	7.94c
		M	83.0b	55.2ab	74.2d	49.3a	7.13de
		H	181.9a	60.5ab	157.4a	52.3a	8.09c
11	L	1.8c	n/a	2.8f	n/a	8.59a	
	M	76.1b	50.6b	82.0cd	54.5a	8.21bc	
	H	184.6a	61.4ab	92.7bcd	30.8c	8.51ab	
PJ	4	L	1.0c	n/a	2.4d	n/a	4.61g
		M	58.7b	39.0b	47.2c	31.3bc	4.47g
		H	146.9a	48.8a	81.4b	27.1c	4.92f
	7	L	1.0c	n/a	1.5d	n/a	7.05de
		M	63.6b	42.3ab	75.4b	50.1a	7.14d
		H	131.9a	43.8ab	80.7b	26.8c	7.01de
	9	L	1.0c	n/a	1.0d	0	8.20bb
		M	66.4b	44.1	55.8c	37.1b	6.87e
		H	142.9a	47.5ab	99.0a	32.9bc	7.39c
11	L	0.6c	n/a	2.1d	n/a	8.40ab	
	M	65.8b	43.7ab	78.3b	52.1a	8.39ab	
	H	143.9a	47.8ab	104.0a	34.6b	8.58a	
WG	4	L	0c	n/a	1.5f	n/a	4.09g
		M	51.3b	34.1bc	34.4e	22.9de	4.62fg
		H	142.6a	47.4a	92.1ab	30.6c	4.72f
	7	L	0c	n/a	1.5	n/a	7.33e
		M	62.6b	41.6ab	75.1c	50.0b	7.43e
		H	134.2a	44.6a	82.8bc	27.5cd	7.14e
	9	L	0cc	n/a	0	n/a	8.30cd
		M	68.2b	45.3a	86.6b	57.6a	8.54bcd
		H	128.8a	42.8a	97.7a	32.5c	8.10d
11	L	0c	n/a	0.9f	n/a	9.01ab	
	M	50.0b	33.2c	41.2e	27.4cd	9.17a	
	H	137.6a	45.7a	65.4d	21.7e	8.71abc	

<sup>a</sup>Means within a column of each sand by the same letter are not different at the 5% level of significance;

<sup>b</sup>KW, Kwinana; PJ, Pinjarra; WG, Wagerup;

<sup>c</sup>L, M and H indicate 0, 13.63 and 27.26 mg N (as DAP) per jar (100 g BRS);

<sup>d</sup>H<sub>2</sub>SO<sub>4</sub>-P, 0.1 M H<sub>2</sub>SO<sub>4</sub> extractable P; H<sub>2</sub>SO<sub>4</sub>-P (%), H<sub>2</sub>SO<sub>4</sub>-P /P added as DAP x 100%;

<sup>e</sup>Colwell P, 0.5M NaHCO<sub>3</sub> extractable P; Colwell P (%), Colwell P /P added as DAP x 100%.

**Table 9.** Effects of initial pH and DAP rate treatments on P fractions and recovery in the bauxite-processing residue sand (BRS) collected from Kwinana<sup>a</sup>

pH	DAP <sup>b</sup> rate	AP ( $\mu\text{g g}^{-1}$ )	BP ( $\mu\text{g g}^{-1}$ )	N(I)P ( $\mu\text{g g}^{-1}$ )	HP ( $\mu\text{g g}^{-1}$ )	N(II)P ( $\mu\text{g g}^{-1}$ )	Res-P ( $\mu\text{g g}^{-1}$ )	Total P ( $\mu\text{g g}^{-1}$ )	P recovery <sup>c</sup> (% of P added as DAP)
4	L	0.24cd (0.3)	3.0d (3.5)	18.1f (20.3)	12.7bcd (14.3)	5.6e (6.3)	49.1c (55.3)	88.8f	n/a
	M	0.16d (0.1)	30.3c (12.2)	115.2d (46.2)	16.4a (6.6)	22.3c (8.9)	65.2a (26.1)	249.6c	106.9a
	H	0.46cd (0.1)	73.1b (19.5)	199.2a (53.2)	10.6cde (2.8)	30.5b (8.1)	60.3ab (16.1)	374.2a	94.9b
7	L	0.45cd (0.5)	4.2d (4.4)	19.2ef (20.1)	13.4abc (14.1)	6.0e (6.3)	51.8bc (54.5)	95.1ef	n/a
	M	0.52cd (0.2)	34.1c (14.3)	113.1d (47.4)	12.9abcd (5.4)	19.4cd (8.1)	58.8abc (24.6)	238.8cd	95.6b
	H	1.68b (0.4)	87.1a (22.9)	188.0b (49.5)	9.5def (2.5)	30.9b (8.1)	62.5ab (16.5)	379.7a	94.6b
9	L	0.36cd (0.4)	3.8d (3.8)	22.1e (22.4)	14.8ab (14.9)	5.8e (5.9)	52.2bc (52.6)	99.2ef	n/a
	M	0.46cd (0.2)	34.8c (14.5)	116.9d (48.5)	10.3cde (4.2)	19.7cd (8.16)	58.8abc (24.4)	241.0cd	94.2b
	H	2.44a (0.7)	81.4ab (22.5)	175.5c (48.6)	8.4ef (2.3)	28.8b (8.0)	64.3a (17.8)	360.9b	87.0c
11	L	0.73cd (0.7)	4.9d (4.7)	22.2e (21.8)	14.3ab (13.7)	6.1e (5.8)	55.6abc (53.3)	104.2e	n/a
	M	0.86c (0.4)	35.6c (15.2)	113.9d (48.6)	6.3f (2.7)	17.8d (7.6)	60.0abc (25.6)	234.5d	86.6c
	H	2.75a (0.7)	75.9b (20.0)	190.6b (50.2)	9.7def (2.5)	34.4a (9.1)	66.6a (17.5)	380.0a	91.7bc

<sup>a</sup>Means within a column by the same letter are not different at the 5% level of significance; data in the brackets are percentage of the fraction over the total P (sum of all P fractions).

<sup>b</sup>L, M and H indicate 0, 13.63 and 27.26 mg N (as DAP) per jar (100 g BRS);

<sup>c</sup>P recovery% = (total P in the M and H DAP treatments – total P in the L DAP rate treatment) /P added as DAP x100%.