The inherent ‘safety-net’ of Ultisols: measuring and modelling retarded leaching of mineral nitrogen

D. SUPRAYOGO [a], K. HAIRIAH [a], M. VAN NOORDWIJK [b] & G. CADISCH [c*]

[a]*Soil Science Department, Faculty of Agriculture, Brawijaya University, Malang, Indonesia.*

[b]*ICRAF-S.E Asia, Bogor, Indonesia*

[d]*Department of Biology, Imperial College at Wye, University of London, Wye, Ashford, Kent, TN25 5 AH. UK. (* Author for correspondence: E-mail: g.cadisch@ic.ac.uk).*

Text Pages: 22

No. of Tables: 6

No. of Figures: 4

Received:

Accepted:

Keywords: humid tropics, Ultisols, cation and anion adsorption, nitrogen, leaching, model.

Summary

The inherent features of Ultisols with their increasing clay content with depth are conducive in reducing nutrient losses by nutrient adsorption on the matric soil surfaces. Ammonium (NH_4^+) and nitrate (NO_3^-) adsorption by a Plinthic Kandiudult from Lampung, Indonesia was studied in column experiments. Main water ($H_2^{18}O$) breakthrough occurred at one pore volume whereas respective events for NH_4^+ and NO_3^- ranged from 13 to 20 and 3 to 4 pore volumes respectively. The adsorption coefficients measured were 1.81, 1.51, 1.64 and 1.47 for NH_4^+ and 0.03, 0.09, 0.10 and 0.17 for NO_3^-, respectively, in the 0 – 0.2, 0.2 – 0.4, 0.4 – 0.6, and 0.6 – 0.8 m soil depth layers. Increasing pH and soil organic matter were associated with increased adsorption of NH_4^+ in the upper soil layer, whereas decreasing soil pH and soil organic matter, and increasing clay content increased the adsorption of NO_3^- in deeper zones. The NH_4^+ and NO_3^- adsorption coefficients derived from this study were incorporated into the Water, Nutrient and Light Capture in Agroforestry Systems (WaNuLCAS) model to evaluate their effect on leaching in the context of an agroforestry system in the humid tropics. The resulting simulation by the improved WaNuLCAS model indicated that the internal soil characteristics of the investigated shallow (0.8 to 1 m) Plinthic Kandiudult had the capacity to reduce the leaching of mineral N by between 7.2 to 20.0 % mainly due to the NH_4^+ retardation factor. The inherent 'safety-net' however is only useful if subsequent recovery is possible, e.g. the presence of deep rooted plants and occurrence of a deep subsoil.

Introduction

Efforts to increase nitrogen use efficiency in cropping systems, should be based on understanding of the processes leading to losses, the factors that slow down or reduce losses and the options farmers have to manage these factors. Leaching of mineral N

(NH_4^++NO_3^-) from the root zone to the sub-soil is driven by percolation of water through the soil and its relative impact depends on rainfall, nutrient adsorption and the depth of the rooted layers of soil. The amount of N leached can be derived from the mineral N concentration in the soil solution, the change in soil water content and knowledge of retarded mineral N caused by negative and positive charges in the soil. In most soils negative charges attributable to both inorganic and organic soil constituents predominate. In the lattices of clay minerals, the source of negative charges arises from the substitution of Mg^{2+}, Al^{3+}, Si^{4+} within the octahedral or tetrahedral sheets by isomorphic ions of smaller valency such as Li^+, Mg^{2+}, Fe^{2+}, Al^{3+} (Talibudeen, 1981). The charge of clay minerals occurring in the tropics can be divided into two major groups: those with mainly constant or permanent charge (cation exchange capacity) and those with mainly variable charge (pH-dependent charge) (Sanchez, 1976). Ultisols are mostly dominated by kaolonitic (Toner *et al.*, 1989; Gillman, 1991), halloysitic, oxidic, gibbsitic, ferritic, siliceous, and mixed mineralogy families with a significant amount of iron and aluminium oxides (Sanchez, 1976). These soils have both permanent and variable charges. Variable charge surfaces are found, for example, on aluminium and iron oxides and on the edge surfaces of silicate clays (Gillman, 1991). In soils, clay minerals interact with each other and with organic matter. Organic matter has a high amount of pH-dependence charge (Sanchez, 1976). On soil organic matter the negative charges originate from dissociation of carboxyl (COOH) and phenolic OH groups (Hayes & Swift, 1978). NH_4^+ in soil solution is thus exchanged with cations adsorbed onto negatively charged clay mineral or humus surfaces and therefore, NH_4^+ leaching is retarded. In contrast, NO_3^- in soil solution is repelled from rather than adsorbed onto negatively charged clay surfaces.

Nitrate (NO_3^-) is usually assumed to move freely through most soils. However, NO_3^- adsorption has been observed in Oxisols, Alfisols, and Andepths from Mexico and South America (Kinjo & Pratt, 1971), in Hapludults from Georgia (Ogwada & Sparks, 1986) and in Middle Atlantic soils (Toner *et al*., 1989). In Nigerian Ultisols, Wong *et al*. (1987) found that leaching of NO_3^- can be significantly delayed, due to positive charges present. Adsorption of NO_3^- increased with decreasing pH, indicating pH-dependent variable charge was operative (Toner *et al*., 1989). Adsorption for NO_3^- occurs at the positively charged surfaces of kaolinite, ferric and other oxides that are created by protonation in excess of OH^- ions adsorbed (Hingston *et al*., 1967). In Ultisols the clay content increases with soil depth, hence NO_3^- adsorption potential increases. Thus, the presence of positive charges in Ultisols may be of major significance in retarding NO_3^- leaching.

Cameron & Haynes (1986) emphasised that retardation of NH_4^+ and NO_3^- in the soil effectively protected mineral N against leaching by percolating waters. To provide a better understanding of retardation effects on leaching, additional knowledge about solute mobility and its interaction with the soil is necessary. Therefore, we describe here (1) how pH, soil organic matter and clay content affect the retardation of mineral nitrogen (NH_4^+ and NO_3^-) and (2) to what extend these anion and cation adsorption capacities as inherent of ‘safety-net’ of Ultisols, protect mineral N against leaching by percolating water from different cropping systems in a Plinthic Kandiudult using an improved Water, Nutrient, and Light Capture in Agroforestry Systems (WaNuLCAS) model.

Material and methods

Location of soil samples

Soil samples were taken from the Plinthic Kandiudult profile (Soil-Survey-Staff, 1992), at the BMSF-Project site (4^o 31’ S, 104^o55’ E, experiment 17), Kotabumi, Lampung, Indonesia (Van Der Heide *et al*., 1992). The site has *Peltophorum dasyrrhachis* (PP), *Gliricidia sepium* (GG) and alternate peltophorum /gliricidia (PG) hedgerow cropping systems and maize monoculture (C) treatments. The test crop, maize (*Zea mays L.*) var Arjuna - maize rotation started in the rainy season 1986/87, was grown in mono or hedgerow intercropping until 1997. The maize-maize rotation was planted without N fertiliser application in hedgerow cropping systems. The monoculture treatment plots were split to create four nitrogen treatments: 0, 45, 90 and 135 kg N ha^{-1}. In the crop growing period 1997/1998 and 1998/1999, the crop rotation was changed to maize-groundnut and all plots received urea fertiliser at the rate of 90 kg N ha^{-1}. Each experimental plot was 24 m long with a 4-m-wide alleyway and 0.5 m spacing between trees, and a plot area of 284 m^2.

The soil samples for the retardation experiment were taken from the peltophorum hedgerow intercropping system in February 1999 from 0-0.2 m, 0.2-0.4 m, 0.4-0.6 m and 0.6-0.8 m soil depths. No soil samples were taken below 0.8 m due to the occurrence of a plinthic layer. Undisturbed soil samples, 5 cm diameter and 15 cm long were taken for NH_4^+ and NO_3^- adsorption determination with 4 replications for the treatment of NH_4^+ or NO_3^- solution flow and one sample for water flow (control).

To obtain the fraction of mineral N in NO_3^- form, soil samples were taken after harvesting maize and groundnut at 0-0.05, 0.05-0.2, 0.2- 0.4, 0.4-0.6, 0.6-0.8 and 0.8-1 m depths from 3 types of hedgerow cropping systems from 3 zones in peltophroum and gliricidia hedgerows, 5 zones in alternate peltophorum and gliricidia hedgerow, and from a monoculture cropping system. Each cropping system consisted of 2 blocks ((2 x 3 + 1 x 5 + 1 x 1)x 2 = 24 samples for each depth). All soil samples were taken using a 2 cm diameter soil auger.

Soil analysis

The data set collected for calculating the retardation coefficient included percentage clay, bulk density, saturated volumetric water content, organic matter content and pH; these are ‘easily’ measured soil properties. Soil texture was analysed by the “pipette method" (Klute, 1986) using the TSBF method of soil dispersion (Anderson & Ingram, 1993). The bulk density and saturated volumetric water content were measured by taking undisturbed volumetric soil samples by pressing sharp steel core samplers (5 cm long with a 10 cm inner-diameter) into the soil. The samples were saturated and wet and dry weight were measured. Soil organic C was determined using the Walkley-Black dichromate method (Nelson & Sommers, 1982) and total N content by Kjeldahl (Anderson & Ingram, 1993). The soil pH was measured in a 1:2.5 soil: water mixture. Cation exchange capacity (CEC) was determined as the quantity of cations absorbed from solutions buffered at pH 7 with NH_4OAc (Anderson & Ingram, 1993). Mineral N in soil was measured by extraction of 5 g soil with 20 cm^3 2 M KCl and determination of NH_4^+ and NO_3^- in the extracts by flow injection analysis (Alves *et al.*, 1993).

Ammonium (NH_4^+) and nitrate (NO_3^-) adsorption determination

Adsorption of mineral N ($NH_4^+ + NO_3^-$) was measured using the methods of Wong *et al*. (1990b) in undisturbed soil columns. A stopper or funnel were placed above and below the column respectively. Using a peristaltic pump, a potassium chloride solution (2 mM), containing toluene (to suppress microbial growth), was pumped up through the column. The flow was then reversed with the solution pumped into the top and out from the bottom of the column at the same rate (70 $cm^3 h^{-1}$ to simulate infiltration rate under field conditions). Flow was continued until the column mass was constant indicating saturation. This weight allowed the calculation of the weight of one pore volume (volume of water for replacement). When the soil had come to saturation, 1 cm^3 of potassium nitrate solution (2 mM) containing $H_2{}^{18}O$ with 0.06% atom ^{18}O access was added to the top of the column, followed by an unlabelled nitrate solution (2 mM) containing toluene. The water flow through the soil column was 72 $cm^3 h^{-1}$. Samples were collected every 0.5 hour until 16 hours. On the same soil column, the retardation of NH_4^+ was measured using similar steps as for the NO_3^-. The concentration of ammonium sulphate was 2 mM and samples were collected every hour until 32 hours. Ammonium (NH_4^+) and nitrate (NO_3^-) content in solutes were measured using flow injection analysis (Alves *et al*., 1993). The ^{18}O content of water in the solutes was measured using the direct equilibration method developed by Scrimgeour (1995) and analysed using a C/N analyser, fitted with an gas injection port, coupled to an Europa 20-20 mass-spectrometer.

The NH_4^+ and NO_3^- content data (pooled from four replications) were analyzed by a sigmoidial regression model in Sigmaplot version 4.0 (Norby *et al*., 1990). The sigmoidal model was used to adjust each breakthrough curve. The NH_4^+ and NO_3^-

retardation factors (pore volumes) and their adsorption coefficients were determined from the adjusted curves. The former was taken as the number of pore volumes that was required to give the mid-point NH_4^+ and NO_3^- concentration in the solute (Wong *et al*., 1990a), and the latter was obtained by using Equation 5 below.

The adsorption coefficients of mineral N were correlated with “easily” measured soil properties using Minitab version 12.1 (Minitab, 1998). These measured soil properties were pH, soil organic matter, clay content, and cation exchange capacity. The stepwise linear regression was used for individual soil properties.

Assessing adsorption coefficients and incorporation into WaNuLCAS model

For steady state water flow conditions, Van Genuchten & Dalton (1986, cited by Matos *et al.*, 1999) and De Willigen & Van Noordwijk (1987) presented an equation of the continuity for sorbed solutes through soils:

$$\rho_b \frac{\delta S}{\delta t} + \theta \frac{\delta C}{\delta t} = \theta\, D \frac{\delta^2 C}{\delta^2 x} + q \frac{\delta C}{\delta x} \qquad (1)$$

where S is the sorbed-phase concentration (g g^{-1}), C is the solution-phase concentration (g cm^{-3}), ρ_b is the bulk density of the soil (g cm^{-3}), θ is the volumetric soil water content (cm^3 cm^{-3}), D is the dispertion-diffusion coefficient (cm^2 s^{-1}), q is the volumetric flux density of displacing solution (cm s^{-1}), x is the distance (cm), and t is the time (s).

Matos *et al*. (1999) introduced the retardation factor (*R*, dimensionless) in Eq. 1 by writing *S* as a function of *C* and dividing the whole equation by volumetric water content, then equation 1 can be rewritten as:

$$R\,\frac{\delta C}{\delta t} = D\,\frac{\delta^2 C}{\delta^2 x} + v\,\frac{\delta C}{\delta x} \qquad (2)$$

where v is the average pore-water velocity (cm s^{-1}).

The retardation factor can be defined as the retention capacity for a given element (in this case NH_4^+ and NO_3^-) in the soil solute (Matos *et al*., 1999). The retardation factor, *R*, is the proportion of time spent by a solute molecule (or ion) in solution (Wong *et al*., 1987). That is:

$$R = \frac{1}{1 + K_a\,\frac{\rho_b}{\theta}} \qquad (3)$$

where K_a is the adsorption coefficient: NH_4^+ or NO_3^- adsorbed (µM g^{-1}) / NH_4^+ or NO_3^- in solution (µM cm^{-3}).

The pore volume for the NH_4^+ or NO_3^- peak (V_p) is the number of pore volumes required to move the NH_4^+ or NO_3^- peak through the soil column and is taken as the reciprocal of the retardation factor, *R* (Wild, 1981). Thus,

$$V_p = 1 + K_a \frac{\rho_b}{\theta} \tag{4}$$

and,

$$K_a = \left(V_p - 1\right) \frac{\theta}{\rho_b} \tag{5}$$

The adsorption coefficient of mineral N (K_a) should be considered in simulation of N leaching rate and N movement to roots. Thus to assess the effects of adsorption coefficients on mineral N leaching they were incorporated into the WaNuLCAS model (Van Noordwijk & Lusiana, 1999). In the WaNuLCAS model a single pool of mineral N is simulated, but it covers both forms if a weighed average adsorption constant is used. The potential uptake is inversely proportional to (K_a + volumetric soil water content), while the leaching rate is inversely proportional to (K_a +1). Both potential uptake and leaching are directly propotional to the N-stock, so the sum over NO_3^- and NH_4^+ forms of mineral N can be obtained by adding $Frac_{NO3}$ times the term with Ka for NO_3^- plus (1 - $Frac_{NO3}$) times the K_a for NH_4^+, where $Frac_{NO3}$ is the fraction of mineral N in nitrate form. Therefore, in the WaNuLCAS model, where $NH_4^+ + NO_3^-$ are not explicitly treated separately, the adsorption constant of mineral N (*Ka eff*) is calculated as a weighted average:

$$K_{a-eff} = -X + \frac{\left(K_{a-NO_3} + X\right)\left(K_{a-NH_4} + X\right)}{K_{a-NO_3} + Frac_{NO_3}\left(K_{a-NH_4} - K_{a-NO_3}\right) + X} \tag{6}$$

Where *X* equals 1 for the leaching equation, and soil water content for the plant N uptake equation. $Frac_{NO3}$ is the fraction of mineral N in NO_3^- form.

WaNuLCAS simulation: N-leaching rate with and without mineral N adsorption

The revised (see above) WaNuLCAS model was used to simulate leached N on a daily time step for a year for some of the described cropping systems in Northern Lampung. The simulation scenarios were:

1. With and without NH_4^+ and NO_3^- adsorption coefficients in bare soils, with and without fertiliser-N (90 kg N ha^{-1}).
2. With and without N adsorption coefficients in maize – groundnut rotation monoculture cropping system, with and without fertilizer-N (90 kg N ha^{-1}).
3. With and without N adsorption coefficients, on peltophorum hedgerow intercropping (maize – groundnut) systems, with and without fertilizer-N (90 kg N ha^{-1}).

A site specific file for Lampung was made for 1997/1998 cropping systems from climate data, with the annual total (1 Nov 97 – 31 Oct 98) of 3102 mm (Figure 1) and cropping systems and their management practice (Table 1) according to the model requirements. The results of the simulations were presented as the effectiveness of mineral N adsorption coefficients on reducing leaching of mineral N and N in harvested maize and groundnut compared with that without adsorption coefficients.

Results

Soil properties

The average soil properties showed decreasing pH and organic matter content but increasing clay content with increasing soil depth (Table 2). The pH of the soil was relatively acid (4.6-5.3). The cation exchange capacity varied from 2.42 to 5.05 cmol kg^{-1}. The organic matter content decreased sharply with depth (from 2.04 % to 0.14 %). The soil texture was a sandy clay loam but the clay contents increased from 27.5 % to 38.0 % with depth. The bulk density ranged from 1.38 to 1.55 g cm^{-3} with the topsoil being less dense.

Ammonium (NH_4^+) and nitrate (NO_3^-) adsorption

The $H_2^{18}O$ flow peak appeared at one gravimetric pore volume (Figure 2). There was some enrichment in ^{18}O in the outflow before the peak. The amount of $H_2^{18}O$ gradually deceased after one gravimetric pore volume but the enrichment of $H_2^{18}O$ was still high.

The breakthrough curves for the replacement of potassium by NH_4^+ and the replacement of Cl^- by NO_3^- for different soil depths had sigmoid shapes particularly in the topsoil (Figure 3 + 4). At all soil depths, NH_4^+ concentration in leachates had reached the NH_4^+ concentration in the leaching solution (2 mM) within 32 hours (20 pore volumes) of solute flow. In all soil columns, complete replacement of Cl^- by NO_3^- was reached (2 mM) within 16 hours (10 pore volumes) of solute flow. The delay to the midpoint of the breakthrough curve of NH_4^+(1 mM) ranged from 6.44 to 6.94 pore volumes and gave adsorption coefficients using equation 5.5 from 1.47 to 1.81 (Table 2). The delay of NO_3^- midpoint breakthrough showed an increase with depth in the soil profile and ranged from 1.47 to 1.81 pore volume and thereby resulted in adsorption coefficients from 0.03 to 0.17 (Table 3).

The adsorption coefficient of mineral NH_4^+ was significantly correlated with measured soil properties except with cation exchange capacity. Based on a stepwise analysis, pH gave the best regression coefficient (R^2=0.88) with the adsorption coefficient of mineral NH_4^+. The ranking of the coefficients of determination (R^2) from fitted linear regressions were pH > soil organic matter content > clay content in order of importance (Table 4). The slope of the linear regressions revealed that decreasing clay content, increasing pH and soil organic matter content increased the adsorption coefficient of mineral NH_4^+.

The adsorption coefficient of mineral NO_3^- was also significantly correlated with “easily” measured soil properties except with cation exchange capacity. Based on the stepwise analysis, clay gave the best regression coefficient (R^2=0.88) for the adsorption coefficient of NO_3^-. The coefficient of determination (R^2) ranked clay content > soil organic matter content > pH in order of importance (Table 4). The slope of the linear regressions revealed that a decreasing pH and soil organic content or increasing clay increased the adsorption coefficient of NO_3^-.

The average NO_3^- fraction in soil mineral N was similar at around 30 – 40 % throughout the soil profile except for the 0.2-0.4 m soil depth (Table 5) where it was only 0.24. Variability of NO_3^- fraction increased with soil depth.

WaNuLCAS simulations

The result of WaNuLCAS simulations using soil properties in Table 2 (soil organic matter, total N content, soil particle distribution and bulk density) and incorporating adsorption coefficients and proportions of NH_4^+ and NO_3^- (Table 3 + 5) into the model showed that mineral N leaching in Ultisols was significantly influenced by the inherent retardation mechanism in this Ultisol (adsorption capacities of NH_4^+ and NO_3^-) by up to 20% (Table 6). The adsorption coefficient of NO_3^- had little effect (increasing of 0.4 % – decreasing of 1.0 %) on the mineral N leaching in the tested ecosystem. Thus most of the effect on leaching was due to the adsorption coefficient of NH_4^+ 8.1–18.1%. The application of fertilizer reduced the effectiveness of the adsorption coefficient of NH_4^+ and NO_3^- on leached mineral N in bare soil and monoculture cropping systems, but not in the hedgerow cropping systems. The planting of crops increased the effectiveness of adsorption coefficients in reducing leaching and increasing N in harvested crops but no consistent trend was observed when trees were inserted as hedges in the peltophorum hedgerow intercropping system.

Discussion

Ammonium (NH_4^+) and nitrate (NO_3^-) adsorption

The shape of the NH_4^+ breakthrough curve was more gradual (less steep slope) than that of NO_3^-, indicating that the mobility of the NH_4^+ was lower than NO_3^- in this Plinthic Kandiudult. The data revealed that the adsorption coefficient of NH_4^+ differed slightly between the different soil depths (Figure 3 and Table 3). This was likely due to the interactions between soil pH, clay content and soil organic content with soil depths with soil pH apparently having the strongest effect. Soil clay and organic matter content have a predominantly negative charge and are able to attract and hold positively charged cations such as NH_4^+ by the process of cation exchange (Cameron & Haynes, 1986). The result of the regression of clay content with adsorption coefficient of NH_4^+ suggested only a moderate influence of clay on NH_4^+ retardation possibly because of interactions with other factors (pH and soil organic content) and their effects on the adsorption coefficient of NH_4^+ in the complex system of soils. A decreasing soil pH strongly decreased NH_4^+ adsorption. It is thought that under acidic conditions the positively charged sites including iron and aluminum oxides and hydroxides in lattices of clay increase, hence restricting NH_4^+ ion entry to the soil surface (Mortland & Wolcott, 1965). A second factor may be the relatively higher replacing power of the H^+ ion competing for the exchange sites (Nommik & Vahtras, 1982). Thus the results also indicated that the negatively charged sites are pH dependent.

Nitrate (NO_3^-) retardation increased with soil depth (Figure 4 and Table 3). This increase corresponded to an increasing clay content and decreasing soil pH and soil organic matter content. In Ultisols, the source of positive charges are the broken edges of kaolinites and variable charges of Fe and Al oxide/hydroxide colloids (Uehara & Gillman, 1981). The positive charge on Fe and Al oxide/hydroxide colloids increases as the pH is lowered (Kinjo *et al.*, 1971). The presence of organic matter due to negative charges originating from the dissociation of carboxyl (COOH) and phenolic OH groups, tends to decrease adsorption of NO_3^- (Black & Waring, 1976). Our measurement confirm that on a Plinthic Kandiudult the clay content was the predominant factor affecting the adsorption coefficient of mineral NO_3^-.

The peak concentration for $H_2^{18}O$ occurred at 1.0 pore volume. Thus, the water in these undisturbed soil cores moved largely following a piston flow model. However, same early breakhthrough indicated that some of the H_2^{18} O moved by fast flow (macropores). This fast flow could have reduce the effectiveness of adsorption of mineral N during the experiments. Suprayogo *et al.* (2000) found more by pass flow occurring in the field than in laboratory soil columns. Therefore, although the current laboratory experiment does not give directly an indication of flow patterns in the field, the determined adsorption coefficient are valid as little macropore were present in the soil column because the mineral N is mainly present within micropores of aggregates (Nortcliff & Thornes, 1989).

The exchange of K^+/NH_4^+ or Cl^-/NO_3^- in the experiment may be more complex in the field where a range of soil solution cations or anions are available competing for the exchange sites. Also, when a pulse of NH_4^+ or NO_3^- will move through the soil it will change the electrolyte concentration and pH and hence the charge will not be constant (Wong *et al*., 1987). Immobilization may cause further delay (Wong *et al*., 1987) however, this was avoided in the current experiment by use of a microbial inhibitor. Despite these limitations the incorporation of retardation factors as inputs in models such as the agroforestry model WaNuLCAS can greatly enhance the accuracy to test the potential effect of different management strategies to reduce N leaching.

The adsorption coefficients of mineral NO_3^- for this Plintic Kandiudult from Lampung were slightly lower than the adsorption coefficient of Nigerian-Ultisols. Wong *et al.* (1987) in a Nigerian-Ultisols found positive adsorption coefficients of 0.07, 0.11, 0.28 in 0-32 cm, 32- 67 cm and 67-130 cm soil depth respectively while our measurement suggested that the value of the adsorption coefficient of mineral $NO_3^-$was 0.03, 0.09, 0.1 and 0.17 in 0 - 0.2 m, 0.2 – 0.4 m, 0.4 – 0.6 m, and 0.6 – 0.8 m soil depths respectively. There was no information on the adsorption coefficients of mineral NH_4^+ in the Nigerian example, thus we were not able to compare it with our results.

The inherent soil characteristic of Ultisols based on the WaNuLCAS simulation had the capacity to reduce leaching of mineral N by 7.2 to 20.0 % (Table 6). The effectiveness of the retardation functions increased when crops and trees were present. These results suggested that the effect on mineral N uptake by crops and trees reduces the amount of mineral N in the soil solution, and hence the saturation charge on the matrix soil surface will be reduced. Therefore, the capacity of the soil to adsorb mineral N will be increased. Increased mineral N in solution from fertiliser increased the saturation charge processes and thus the effectiveness of adsorption coefficient was decreased. However in the peltophorum hedgerow intercropping system addition of fertiliser did not decrease the effectiveness of the adsorption coefficient due to the large N uptake by the non-fixing peltophorum trees. Increasing the effectiveness of the retardation functions when crops and trees were present were also caused by the increased depletion of soil water stocks in the rooting zone due to crop or tree water uptake. Incoming water from the subsequent rain event will then fill the larger empty pores, and hence lead to a lower concentration of mineral nitrogen in the solute. Lower concentrations of mineral nitrogen in the soil solute system will decrease the possibility of saturation charge on the matric soil surface, and hence the inherent ‘safety-net’ of the soil will increase. Increasing the depletion of soil water stocks by plants will increase the retention of incoming water from rain events, and hence will be reducing the amount of water drainage and thus potentially reduce leaching of mineral nitrogen.

Ammonium adsorption coefficients had by far the largest effect on reducing leaching in the tested agroforestry cropping systems. The effectiveness of nitrate retardation mechanisms in reducing leaching in this Plinthic Kandiudult situated in the humid tropics was apparently low partly due the shallowness of the investigated soil. However, anion adsorption capacities may have a much higher effectiveness in deep Oxisols with less intensive rainfall. Mekonnen *et al.* (1997) found large accumulations of nitrate under maize monoculture systems in a Kandiudalthic Eutrudox in Wetern Kenya. The increased subsoil depth in such an Eutrodox compared to the Kandiudult will greatly increase the ‘safety-net’ opportunities particularly in association with deep root trees.

Conclusions

The hypotheses that increasing pH and soil organic matter will increase the adsorption of NH_4^+, and decreasing soil pH and soil organic matter, and increasing clay content will increase the adsorption of NO_3^- were confirmed. The hypothised increases in the adsorption of NH_4^+ due to increased clay content in this soil, was not proven in this experiment due to interactions with other factors such as pH and soil organic matter. The relationship between soil pH, soil organic matter and clay content, as “easily” measurable soil properties, with adsorption coefficient of mineral N developed from this study gave reasonable predictions, but more examples are needed to test these models.

Based on the WaNuLCAS simulation, the internal soil characteristics of Ultisols had the capacity to reduce the leaching of mineral N by 7.2 to 20 % mainly due to the ammonium retardation. Comparison on leaching of mineral N with and without adsorption occurrence in different systems (combination of cropping systems and application of fertiliser treatments) suggested that the inherent ‘safety-net’ of Ultisols is only useful if subsequent recovery is possible.

Acknowledgements

Support for the experiments presented in this paper was provided by (1) the Department for International Development of the United Kingdom (R6523, Forestry Research Program) and EU funded (TS3*CT94-0261) via the Biological Management of Soil Fertility (BMSF) Project in N. Lampung. However, the Department for International Development of the UK can accept no responsibility for any information provided or views expressed. The authors wish to thank Betha Lusiana for technical help with the WaNuLCAS model, Pratiknyo, and all BMSF field assistants for their technical assistance. We also thank PTPN VII Bungamayang for field experiment facilities.

References

Alves, J.R., Boddey, R.M. & Urquiaga, S. S. 1993. A. rapid and sensetive flow injection tecnique for the analysis of ammonium in soil extracts. *Communnication Soil Science Plant Analysis*, **24**, 277-284.

Anderson, J.M. & Ingram, J.S.I. 1993. *Tropical Soil Biology and Fertility: A handbook of Methods.* CAB International, Wallingford, UK.

Black, A.S. & Waring, S.A. 1976. Nitrate leaching and adsorption in a Krasnozem from Redland Bay, Queensland. *Australia Journal of Soil Research,* **14**, 181-188.

Cameron, K.C. & Haynes, R.J. 1986. Retention and movement of nitrogen in soils. In: *Mineral-Nitrogen in The Plant-Soil System* (ed. R.J. Haynes), pp. 167-241. Academic Press Inc., New York.

De Willigen, P. & Van Noordwijk, M. 1987. *Roots, Plant Production and Nutrient Use Efficiency*. PhD. Thesis, Wageningen Agricultural University, The Netherlands.

Gillman, G.P. 1991. The chemical properties of acid soils with emphasis on soils of the humid tropics. In: *Plant-Soil Interactions at Low pH* (eds R.J. Wright, V.C. Baligar & R.P. Murrmann), pp. 3-14. Kluwer Academic Publishers, Dordrecht.

Hayes, M.H.B. & Swift, R.S. 1978. The chemistry of soil organic colloids. In: *The Chemistry of Soil Constituents* (eds D. J. Greenland & M. H. B. Hayes), pp. 179-320. Wiley, New York.

Haynes, R.J. 1986. The decomposition process: mineralization, immobilization, humus formation, and degradation. In*: Mineral Nitrogen in The Plant-Soil System* (ed R.J. Haynes), pp. 52-109. Academic Press Inc., New York.

Hingston, F.J., Atkinson, R.J., Posner, A.M. & Quirk, J.P. 1967. Specific adsorption of anions. *Nature*, **215**, 1459-1461.

Kinjo, T. & Pratt, P.F. 1971. Nitrate adsorption. I: in some acid soils of Mexico and South America. *Soil Science Society of America Proceedings,* **35**, 722-725.

Kinjo, T. Pratt, P.F., & Page, A. L. 1971. Nitrate adsorption. III: Desorption movement and distribution in Andepts. *Soil Science Society of America,* **35**, 728-732.

Klute, A. 1986. *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods.* America Society of Agronomy, Madison, Wisconsin.

Matos, A.T., Costa, L.M., Fontes, M.P.F. & Martinez, M.A. 1999. Retardation factor and the dispersion-diffusion coefficients of Zn, Cd, Cu, Pb in soils from Vicosa-MG, Brazil. *Transactions of the ASAE,* **42**, 903-910.

Mekonnen K., Buresh R.J. & Jama, B. 1997. Root and inorganic nitrogen distribution in sesbania fallow, natural fallow and maize fields. *Plant and Soil,* **188,** 319-327.

Minitab, I. 1998. *MINITAB, Release 12.1 For Windows*. Minitab Statistical Software, Pennsylvania, USA.

Mortland, M.M. & Wolcott, A.R. 1965. Sorption of inorganic nitrogen compounds by soil materials. In: *Soil Nitrogen* (eds W. V. Bartholomew & F. E. Clark), pp. 150-197. America Society of Agronomy, Madison, Wisconsin.

Nelson, D.W. & Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties, Second Edition* (eds A.L. Page, R.H. Miller & D.R. Keeney), pp. 539-580. American society of Agronomy Inc., Soil Science Society of America Inc., Madison, Wisconsin, USA.

Nommik, H. & Vahtras, K. 1982. Retention and fixation of ammonium and ammonia in soils. In: *Nitrogen in Agricultural Soils* (ed F.J. Stevenson), pp. 123-126. American Society of Agronomy, Madison, Wsconsin.

Norby, J., Rubenstein, S., Tuerke, T., Farmer, C.S. & Bennington, J. 1990. *Sigma Plot : Scientific Graph System*. Jandel Scientific, Corte Madera.

Nortcliff, S. & Thornes, J.B. 1989. Variations in soil nutrient in relation to soil moisture status in a tropical forested ecosystem. In: *Mineral Nutrients in Tropical Forest and Savanna Ecosystems* (ed J. Proctor). Special Publication No 9 of the British Ecological Society. Blackwell Science, Oxford.

Ogwada, R.A. & Sparks, D.L. 1986. Kinetics of ion exchange on clay minerals and soil: I evaluation of methods. *Soil Science Society of America Journal*, **50**, 1158-1162.

Sanchez, P.A. 1976. *Properties and Management of Soils in the Tropics*. John Wiley, New York.

Scrimgeour, C.M. 1995. Measurement of plant and soil water isotope composition by direct equilibration methods. *Journal of Hydrology,* **172**, 261-274.

Soil-Survey-Staff 1992. Key to Soil Taxonomy. Pocahontas Press, Inc., Blackburg, Virginia.

Suprayogo, D., Hairiah, K., Van Noordwijk, M. & Cadisch, G. 2000. Evidence of macropore flow in hedgerow intercropping systems and implications for drainage, runoff and leaching. *Pant and Soil, submitted.*

Talibudeen, O. 1981. Cation exchange in soils. In: *The Chemistry of Soil Processes* (eds D.J. Greenland & M.H.B. Hayes), pp. 115-177. Wiley, New York.

Toner, C.V., Sparks, D.L. & Carski, T.H. 1989. Anion exchange chemistry of Middle Atlantic soils: charge properties and nitrate retention kinetics. *Soil Science Society America Journal,* **53**, 1061-1067.

Uehara, G. & Gillman, G. P. 1981. *Mineralogy, Chemistry and Physics of Tropical Soils with Variable Charge Clays*. Westview Press, Boulder, Colorado, USA.

Van Der Heide, J., Setijono, S., Syekhfani, M.S., Flach, E.N., Hairiah, K., Ismunandar, S., Sitompul, S.M. & Van Noordwijk, M. 1992. Can low external input cropping systems on acid upland soils in the humid tropics be sustainable ?: Backgrounds of the UNIBRAW/IB Nitrogen management project in Bunga Mayang (Sungai Selatan, Kota bumi, N. Lampung, S. Sumatra, Indonesia). *Agrivita,* **15,** 1-9.

Van Noordwijk, M. & Lusiana, B. 1999. *WaNuLCAS 2.0.: Backgrounds of a Models of Water, Nutrient and Light Capture in Agroforetsry Systems.* International Centre for Research in Agroforestry (ICRAF), ICRAF-S.E. Asia, Bogor.

Wild, A. 1981. Mass flow and diffusion. In: *The Chemistry of Soil Processes* (eds D.J. Greenland & M.H.B. Hayes), pp. 37-80. Wiley, New York.

Wong, M.T.F., Hughes, R. & Rowell, D.L. 1990a. Retarded leaching of nitrate in acid soils from the tropics: measurement of the effective anion exchange capacity. *Journal of Soil Science,* **41**, 655-663.

Wong, M.T.F., Hughes, R. & Rowell, D.L. 1990b. The retention of nitrate in acid soils from the tropics. *Soil Use and Management,* **6**, 72-74.

Wong, M.T.F., Wild, A. & Juo, A.S.R. 1987. Retarded leaching of nitrate measured in monolith lysimeters in south-east Nigeria. *Journal of Soil Science,* **38**, 511-518.

Table 1 Time-table of management practices in a hedgerow intercropping system used in the WaNuLCAS simulations

Activity	1997/98
1. First pruning	01-12-97
2. Maize planting	14-12-97
3. First N application (30 kg N ha^{-1})	21-12-97
4. Second pruning	05-01-98
5. Second N application (60 kg N ha^{-1})	10-01-98
6. Maize harvesting	11-03-98
7. Third pruning	22-03-98
8. Groundnut planting	27-03-98
9. Groundnut harvesting	29-06-98

Table 2 Properties of soil used for NH_4^+ and NO_3^- retardation experiments (n=4)

Soil depth (m)	**PH (H_2O)**	**CEC (cmol(+) kg^{-1})**	**Organic Content (%)**	**Total N (%)**	**Soil particles (%)**			**ρ_b (g cm^{-3})**	**θ_s (cm^3 cm^{-3})**
					Sand	**Silt**	**Clay**		
0.0-0.2	5.3	5.05	2.04	0.13	58.7	13.8	27.5	1.38	0.42
0.2-0.4	4.6	2.42	0.83	0.09	54.1	13.7	32.2	1.52	0.42
0.4-0.6	4.7	2.83	0.43	0.05	51.5	12.7	35.8	1.52	0.43
0.6-0.8	4.6	4.65	0.14	0.03	48.2	13.8	38.0	1.55	0.42

Note: CEC = Cation Exchange Capacity, ρ_b = Bulk density, θ_s = saturated volumetric water content.

Table 3 Ammonium (NH_4^+) and nitrate (NO_3^-) breakthrough pore volumes and adsorption coefficients measured in a Plinthic Kandiudult

Soil depth (m)	**Delay (pore volumes, Vp)**		**Adsorption coefficient (Ka)**	
	NH_4^+	**NO_3^-**	**NH_4^+**	**NO_3^-**
00-0.2	6.94	1.10	1.81	0.03
0.2-0.4	6.44	1.33	1.51	0.09
0.4-0.6	6.86	1.36	1.64	0.10
0.6-0.8	6.48	1.62	1.47	0.17

Table 4 Linear relationship coefficients between NH_4^+ and NO_3^- adsorption coefficients (Ka NH_4^+ and Ka NO_3^-) with pH, soil organic matter (SOM), clay content and cation exchange capacity (CEC) of a Plinthic Kandiudult

Parameters	NH_4^+			NO_3^-		
	constant	slope	R^2	constant	Slope	R^2
PH	-0.44	+0.43	0.88	+0.76	-0.14	0.66
SOM (%)	+1.47	+0.16	0.72	+0.15	-0.06	0.85
Clay(%)	+2.47	-0.03	0.60	-0.30	+0.01	0.89
CEC (cmol(+) kg^{-1})	+1.43	+0.05	0.16	+0.11	-0.003	0.04

Table 5 Fraction of NO_3^- in soil mineral N at different soil depths in a Plinthic Kandiudult (n = 24 for each soil depth)

Soil depth (m)	Fraction of soil mineral NO_3^-		
	mean	SEM	CV(%)
0-0.05	0.40	0.020	46
0.05-0.2	0.36	0.018	44
0.2-0.4	0.24	0.012	43
0.4-0.6	0.31	0.026	75
0.6-0.8	0.36	0.028	71
0.8-1.0	0.36	0.028	73

SEM = standard error of mean, CV = coefficient variation

Table 6 The effectiveness of adsorption coefficients of NH_4^+ and NO_3^- (Table 3) on leaching of mineral N compared with that without adsorption occurrence (set 100%) in different cropping systems (combination of cropping systems and application of fertiliser treatments) on a Plinthic Kandiudult in the humid tropics over one year

Cropping System	Change in mineral N leaching, g m^{-2} (%)			
	$-R_{amm}-R_{nit}$	$-R_{amm}+R_{nit}$	$+R_{amm}-R_{nit}$	$+R_{amm}+R_{nit}$
-F-C-H	20.0 (0)	19.8 (0.7↓)	17.7 (11.4↓)	17.4 (13.0↓)
+F-C-H	29.0 (0)	28.8 (0.5↓)	26.6 (8.1↓)	26.3 (9.2↓)
-F+C-H	15.3 (0)	15.2 (1.0↓)	12.6 (18.1↓)	12.4 (20.0↓)
+F+C-H	23.9 (0)	23.8 (0.6↓)	21.4 (10.6↓)	21.0 (12.0↓)
-F+C+H	11.6 (0)	11.7 (0.4↑)	10.5 (9.8↓)	10.8 (7.2↓)
+F+C+H	18.6 (0)	18.6 (0.1↑)	16.5 (11.6↓)	16.7 (10.7↓)

- = without, + = with, R_{amm} and R_{nit} = coefficient adsorption of NH_4^+ and NO_3^-, F = fertilizer N (30 kgN + 60 kg N ha^{-1} topdressing), C = maize- groundnut rotation, H = peltophorum hedge, ↑ = increase ,↓ = decrease.

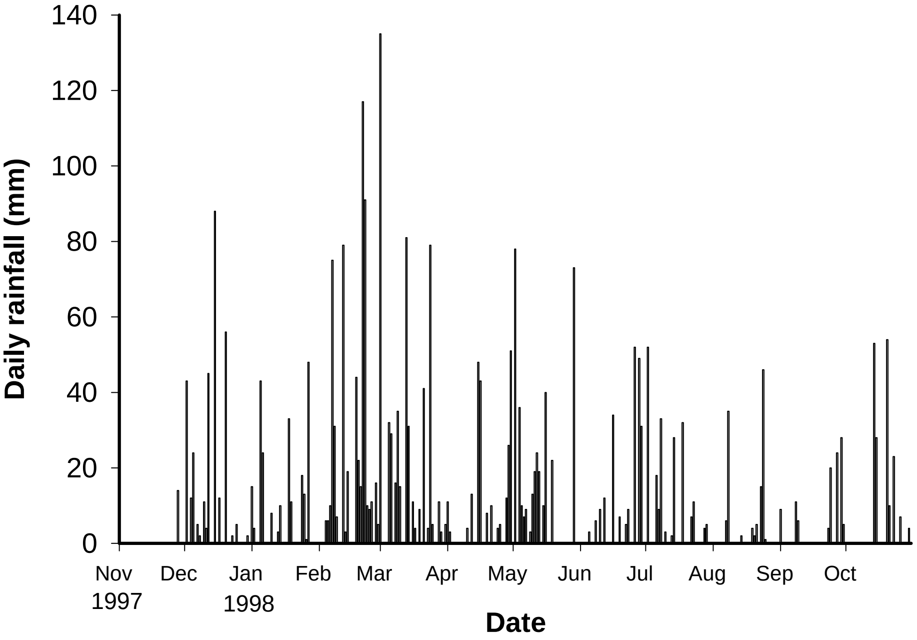
Figures:

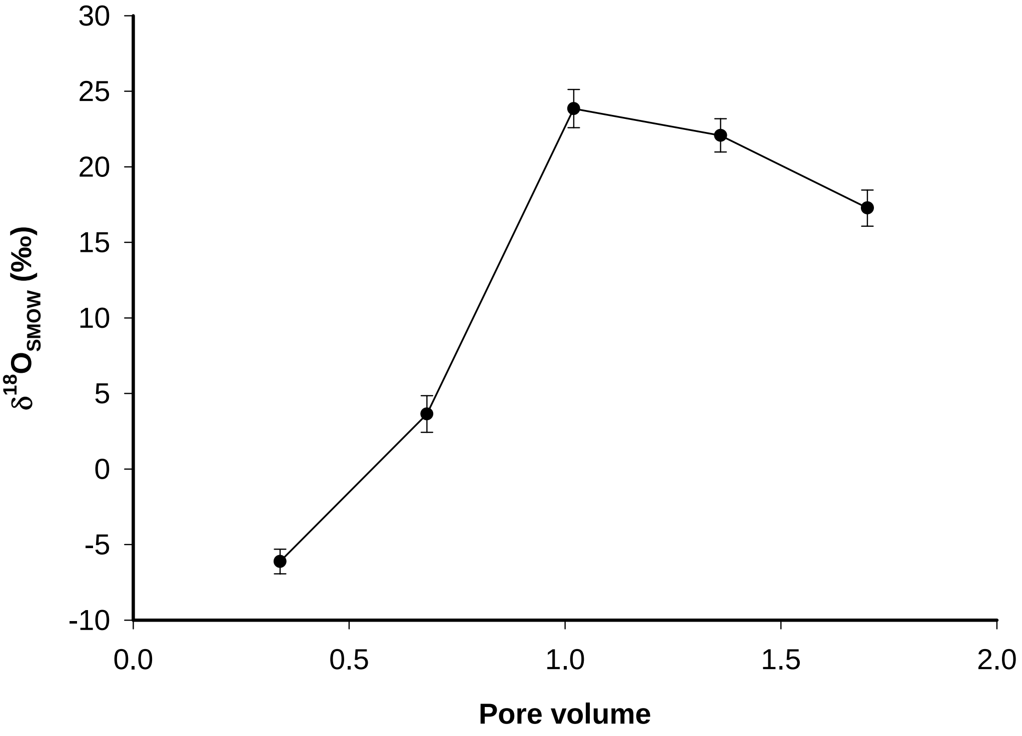
Figure1 Rainfall at BMSF station from 01 November 1997 to 31 October 1998. Annual total (Nov 1997-Oct 1998) was 3102 mm.

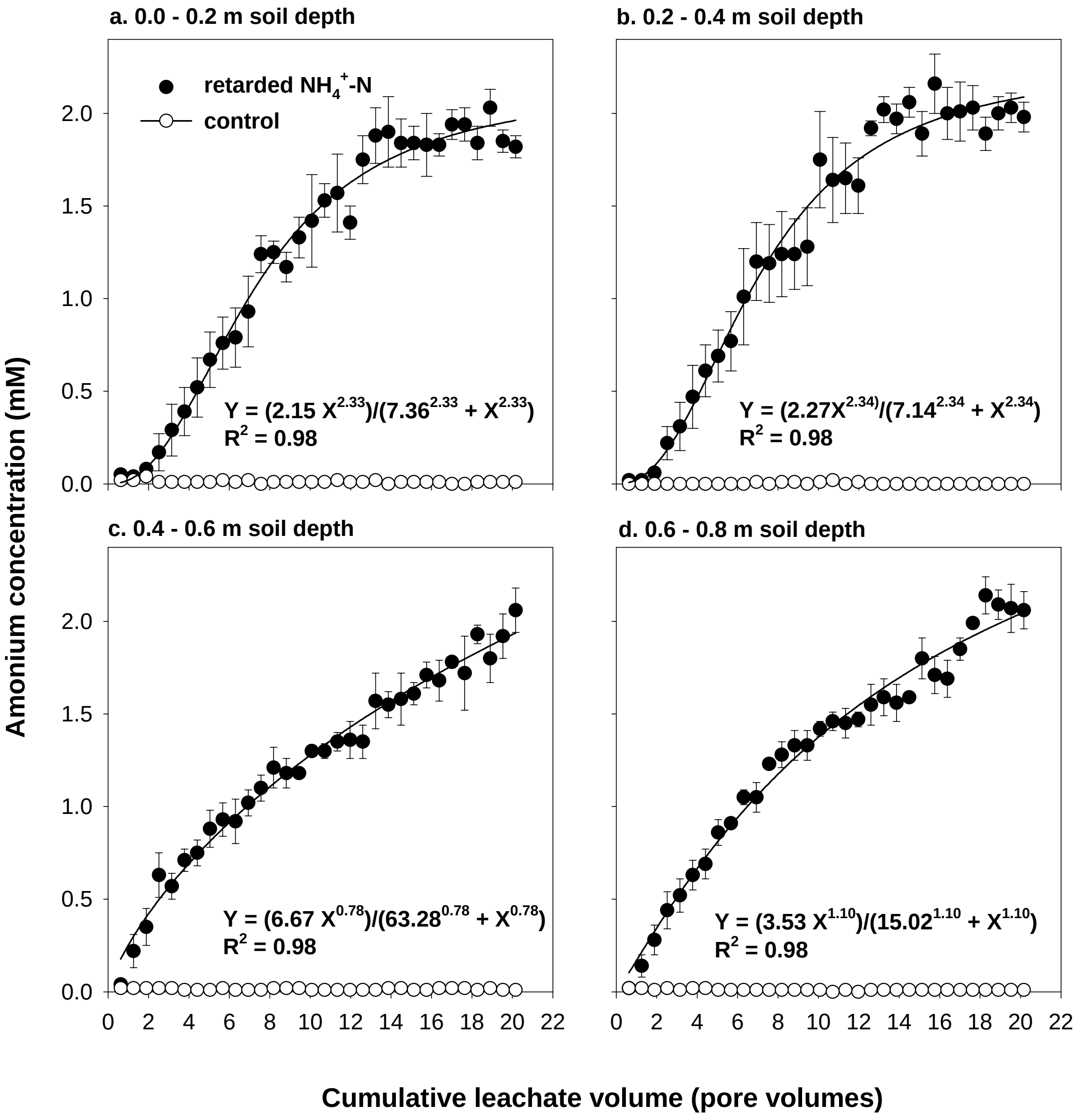
Figure 2 The $H_2{}^{18}O$ flow in soil column from peltophorum hedgerow intercropping system (0-20 cm soil depth) (n=4).

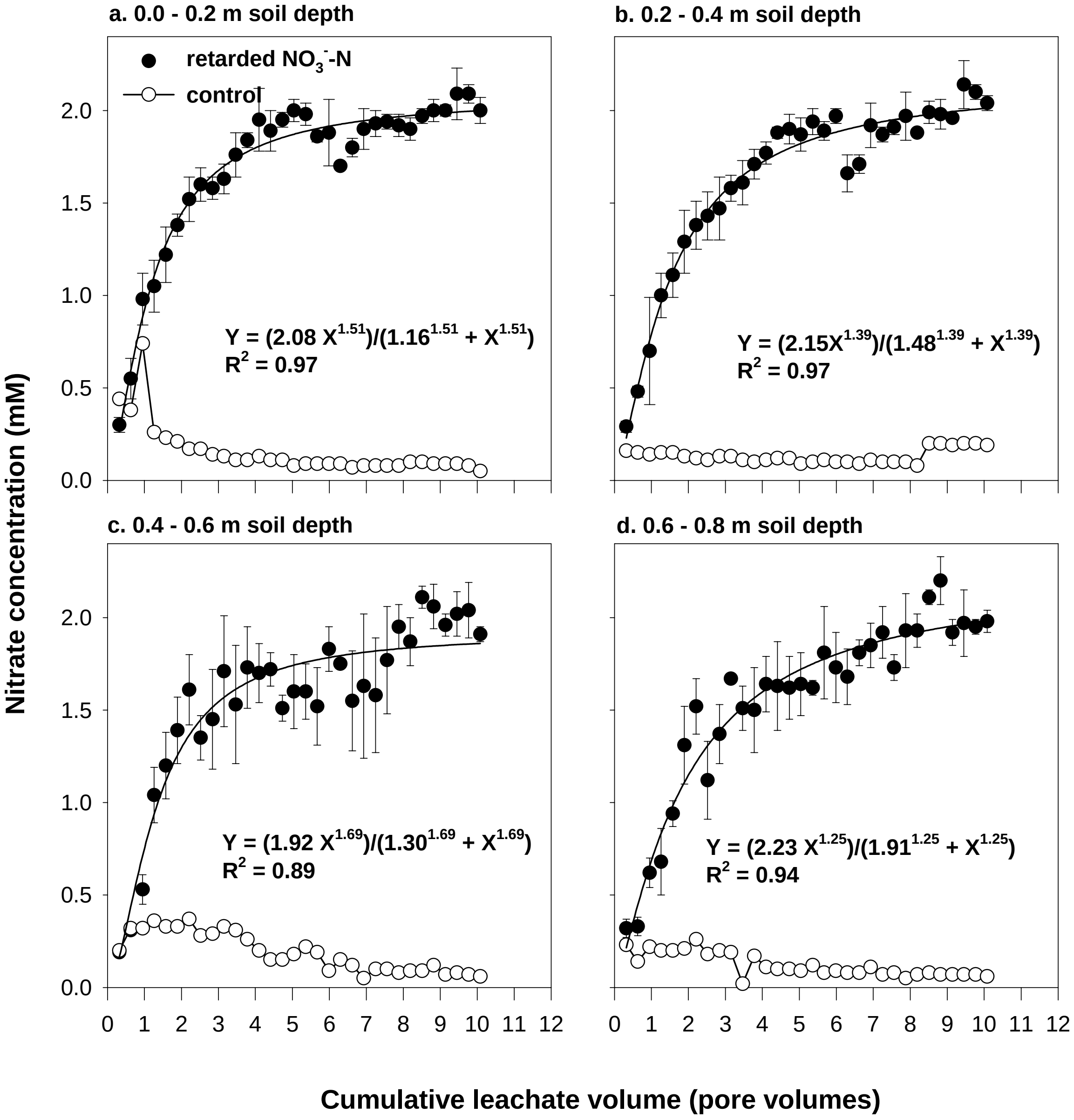
Figure 3 The breakthrough curves of NH_4^+ (2 mM) for different soil depths (0-0.8 m) in a Plinthic Kandiudult.

Figure 4 The breakthrough curves of NO_3^- (2mM) for different soil depths (0 – 0.8 m) in a Plinthic Kandiudult.


140
120
100
80
60
40
20
0
Daily rainfall (mm)
Nov 1997
Dec
Jan 1998
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Date


30
25
20
15
10
5
0
-5
-10
0.0
0.5
1.0
1.5
2.0
δ18OSMOW (‰)
Pore volume


a. 0.0 - 0.2 m soil depth
b. 0.2 - 0.4 m soil depth
c. 0.4 - 0.6 m soil depth
d. 0.6 - 0.8 m soil depth
● retarded NH_4^+-N
○ control
$Y = (2.15\ X^{2.33})/(7.36^{2.33} + X^{2.33})$
$R^2 = 0.98$
$Y = (2.27X^{2.34)}/(7.14^{2.34} + X^{2.34})$
$R^2 = 0.98$
$Y = (6.67\ X^{0.78})/(63.28^{0.78} + X^{0.78})$
$R^2 = 0.98$
$Y = (3.53\ X^{1.10})/(15.02^{1.10} + X^{1.10})$
$R^2 = 0.98$
Amonium concentration (mM)
0.0
0.5
1.0
1.5
2.0
0
2
4
6
8
10
12
14
16
18
20
22
Cumulative leachate volume (pore volumes)


a. 0.0 - 0.2 m soil depth
b. 0.2 - 0.4 m soil depth
c. 0.4 - 0.6 m soil depth
d. 0.6 - 0.8 m soil depth
retarded NO_3^--N
control
$Y = (2.08\ X^{1.51})/(1.16^{1.51} + X^{1.51})$
$R^2 = 0.97$
$Y = (2.15X^{1.39})/(1.48^{1.39} + X^{1.39})$
$R^2 = 0.97$
$Y = (1.92\ X^{1.69})/(1.30^{1.69} + X^{1.69})$
$R^2 = 0.89$
$Y = (2.23\ X^{1.25})/(1.91^{1.25} + X^{1.25})$
$R^2 = 0.94$
Nitrate concentration (mM)
0.0
0.5
1.0
1.5
2.0
0 1 2 3 4 5 6 7 8 9 10 11 12
Cumulative leachate volume (pore volumes)