The inherent 'safety-net' of an Acrisol: measuring and modelling retarded leaching of mineral nitrogen

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Summary

The inherent features of Acrisols with their increasing clay content with depth are conducive to reducing nutrient losses by nutrient adsorption on the matrix soil surfaces. Ammonium (NH_4^+) and nitrate (NO_3^-) adsorption by a Plinthic Acrisol from Lampung, Indonesia was studied in column experiments. The peak of the H₂¹⁸O breakthrough occurred at 1 pore volume, whereas the median pore volumes for NH₄⁺ and NO₃⁻ ranged from 6.4 to 6.9 and 1.1 to 1.6, respectively. The adsorption coefficients $(K_a \text{ in cm}^3 \text{ g}^1)$ measured were 1.81, 1.51, 1.64 and 1.47 for NH₄⁺ and 0.03, 0.09, 0.10 and 0.17 for NO₃⁻, respectively, in the 0–0.2, 0.2–0.4, 0.4–0.6 and 0.6–0.8 m soil depth layers. The NH₄⁺ and NO₃⁻ adsorption coefficients derived from this study were put in to the Water, Nutrient and Light Capture in Agroforestry Systems (WaNuLCAS) model to evaluate their effect on leaching in the context of several cropping systems in the humid tropics. The resulting simulations indicate that the inherent 'safety-net' (retardation mechanism) of a shallow (0.8–1 m) Plinthic Acrisol can reduce the leaching of mineral N by between 5 and 33% (or up to 2.1 g m⁻²), mainly due to the NH₄⁺ retardation factor, and that the effectiveness in reducing N leaching increases with increasing depth. However, the inherent 'safety-net' is useful only if deep-rooted plants can recover the N subsequently.

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Introduction

Efforts to increase the efficiency of nitrogen use in cropping systems should be based on (i) an understanding of the processes leading to losses, (ii) the factors that slow down or reduce losses, and (iii) the options farmers have to manage these factors. Percolating water leaches mineral N (NH4⁺ and NO₃⁻) from the root zone to the subsoil. Its relative impact depends on rainfall, nutrient adsorption and the rooting depth. The rate and amount of N leached can be derived from the concentration of the mineral N 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 predominate. The charge on clay minerals in tropical soils can be divided into two major types; constant or permanent charge due to isomorphous substitution (cation exchange capacity) and variable charge on oxides and the edge faces of clay minerals (pH-dependent charge) (Sanchez, 1976). Acrisols are dominated by families of kaolonitic (Toncr et al., 1989; Gillman, 1991), oxidic, gibbsitic, ferritic, and mixed mineralogy with significant amounts of iron and aluminium oxides (Sanchez, 1976). They have both

Correspondence: G. Cadisch. E-mail: g.cadisch@ic.ac.uk Received 24 October 2000; revised version accepted 15 October 2001 permanent and variable charges. In soils, clay minerals interact with each other and with organic matter. The charge of organic matter depends on pH as a result of the dissociation of carboxyl (COOH) and phenolic OH groups (Hayes & Swift, 1978). Ammonium in the soil solution is thus exchanged with cations adsorbed on to negatively charged surfaces of clay minerals or humus and therefore NH_4^+ leaching is retarded. By contrast, NO_3^- in the soil solution is repelled from negatively charged clay surfaces.

Nitrate is usually assumed to move freely through most soils, but its adsorption has been observed in soils from Mexico and South America (Kinjo & Pratt, 1971), Georgia (Ogwada & Sparks, 1986) and from the Middle Atlantic region of the United States (Toner et al., 1989). Wong et al. (1987) found that leaching of NO3⁻ in a Nigerian Acrisol could be significantly delayed because of the positive charges present. According to Toner et al. (1989), adsorption of NO3⁺ increased with decreasing pH because of pH-dependent variable charge. Adsorption of NO₃⁻ occurs at positively charged sites on kaolinite, ferric and other oxides that are created by protonation in excess of OH⁻ ions adsorbed (Hingston et al., 1967). In Acrisols the clay content increases with increasing depth, and so the potential for NO₃⁻ adsorption increases. Thus, the presence of positive charges in Acrisols may be of major significance in retarding the leaching of NO₃⁻.

Cameron & Haynes (1986) emphasized that retardation of NH_4^+ and NO_3^- in the soil effectively protected mineral N against leaching. To provide a better understanding of retardation on leaching we must know more about solute mobility and its interaction with the soil. Therefore, we describe here (i) how pH, soil organic matter and clay content affect the retardation of mineral nitrogen (NH_4^+ and NO_3^-) and (ii) to what extent these anion and cation adsorption capacities act as an inherent 'safety-net' to protect mineral N against leaching. We have tested the following specific hypotheses. I That increasing pH, soil organic matter and clay content

will increase the adsorption of NH_4^+ N.

- 2 That decreasing soil pH and soil organic matter and increasing clay content will increase the adsorption of NO₃⁻ N.
- 3 That the adsorbed mineral N will be protected against leaching and the effectiveness of the 'safety-net' (retardation mechanisms) will increase with increasing depth.

The study was carried out on a Plinthic Acrisol under various cropping systems, and the data were modelled using an improved Water, Nutrient and Light Capture in Agroforestry Systems (WaNuLCAS) model (Van Noordwijk & Lusiana, 1998, 1999).

Materials and methods

Location of soil samples

Soil samples were taken from the Plinthic Acrisol profile, at the BMSF-Project site (4°31'S, 104°55'E, experiment 17), Kotabumi, Lampung, Indonesia (Van der Heide et al., 1992). A hedgerow intercropping experiment was established in 1986--87. Two tree species were planted as hedgerows, namely Peltophorum dasyrraclys (peltophorum) and Gliricidia sepium (gliricidia), either alone or as alternating rows of peltophorum and gliricidia; a control plot without hedgerows was also included. The trees were spaced 0.5 m apart in hedgerows 4 m apart, giving 5000 trees per ha. Each plot contained four hedgerows and was 24 m long. Each cropping system consisted of two blocks. Maize (Zea mays L.) var. Ajuna was planted at the beginning of the rainy season (December-March), followed by a second crop of maize (growing season II, March-June), and during the dry season plots were covered by Mucuna pruriens (growing season III), but in 1997-98 and 1998-99 the cropping pattern was changed to maize followed by groundnuts only. All plots received urea fertilizer at the rate of 90 kg N ha⁻¹. The control treatment was divided into four subtreatments of N application: 0, 45, 90 and 135 kg ha⁻¹. Further details are given by Hairiah et al. (1992).

The soil samples for the retardation experiment were taken from the peltophorum hedgerow intercropping system in February 1999 at 0–0.2 m, 0.2–0.4 m, 0.4–0.6 m and 0.6–0.8 m depths. No soil samples were taken below 0.8 m because of a plinthic layer. Undisturbed soil cores, 5 cm diameter and 15 cm long, were taken for NH_4^+ and NO_3^- adsorption measurements with four 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 NO₃ form, soil samples were taken after harvesting maize and groundnuts 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 three types of hedgerow cropping systems from three zones (distance to hedgerow) in peltophorum and gliricidia hedgerows, five zones in alternate peltophorum and gliricidia hedgerows, and from the control cropping system with no hedges. These soil samples were taken using a 2-cm-diameter auger.

Soil analysis

The data collected for calculating the retardation coefficient included percentage clay, bulk density, saturated volumetric water content, organic matter content and pH. Particle size distribution was determined by the pipette method (Klute, 1986) using the Tropical Soil Biology and Fertility (TSBF) method of soil dispersion (Anderson & Ingram, 1993). The bulk density and saturated volumetric water content were measured by taking undisturbed 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 weighed under saturated conditions. Dry weights (oven-dried at 105°C) were also measured. The wet weight data allowed us to calculate the weight of 1 pore volume (volume of water for replacement). Organic C was determined using the Walkley-Black dichromate method (Nclson & Sommers, 1982) and total N content by Kjeldahl digestion (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 displaced by NH4OAc buffered at pH 7 (Anderson & Ingram, 1993). Mineral N in the soil was measured by extraction of 5g soil with 20 cm³ 2 M KCl and determination of NH_4^+ and NO_3^- in the extracts by colorimetric flow injection analysis (Alves et al., 1993).

Determination of ammonium (NH_4^+) and nitrate (NO_3) adsorption

Adsorption of mineral N (NH₄⁺ and NO₃⁻) was measured using the methods of Wong *et al.* (1990 a,b) on undisturbed soil columns. A stopper was placed above each column and a funnel below it. Using a peristaltic pump, potassium chloride solution (2mM), 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 cm³ hour⁻¹ to simulate infiltration rate under field conditions). Flow was continued until the column mass was constant at which time 1 cm³ of potassium nitrate solution (2 mM) containing H₂¹⁸O with 0.06 atom%¹⁸O excess was added to the top of the column, followed by an unlabelled nitrate solution (2 mM) containing toluene. The water flow through the column was 72 cm^3 hour⁻¹. Samples were collected every 0.5 hours for 16 hours. On the same soil column, the retardation of NH₄⁺ was measured using similar steps as for NO₃⁻. The concentration of ammonium sulphate was 2 mM, and samples were collected every hour for 32 hours. Ammonium and nitrate concentrations in solution were measured using colorimetric flow injection analysis (Alves *et al.*, 1993). The ¹⁸O content of water in the effluent was measured using the direct equilibration method developed by Scrimgeour (1995) and analysed by fitting a gas injection port after the reduction column of an automated C–N analyser coupled to a Europa 20-20 mass spectrometer (PDZ, Crewe, UK).

For steady-state flow, Van Genuchten & Dalton (1986) presented a continuity equation for the transport of sorbed solutes in soil:

$$\rho_{\rm b}\frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta \ D \frac{\partial^2 C}{\partial x^2} + q \frac{\partial C}{\partial x},\tag{1}$$

where S is the concentration of the sorbed phase (g g⁻¹), C that of the solution phase (g cm⁻³), ρ_b is the bulk density of the soil (g cm⁻³), θ is the volumetric soil water content, D is the dispersion coefficient (cm² 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 Equation (1) by defining *S* as a function of *C*, i.e. $S = K_{\rm H}C$, where $K_{\rm a}$ (cm³ g⁻¹) is the adsorption coefficient, i.e. NH₄⁺ or NO₃⁻ adsorbed (µmol g⁻¹) divided by NH₄⁺ or NO₃⁻ in solution (µmol cm⁻³). By dividing the whole equation by volumetric water content Equation (1) can be rewritten as

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

where v is the mean pore-water velocity (cm s⁻¹) and

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$$R = \frac{\theta + K_{\rm w} \, \rho_{\rm b}}{\theta}.$$
 (3)

A retarded solute will move at velocity v/R through the soil. Since the number of pore volumes (V_p) required for half the mass ($C_1/C_0 = 0.5$, e.g. concentration in effluent at time t/concentration of input solution = 0.5) of the retarded NH₄⁺ or NO₃⁻ to appear at the bottom of the column is inversely proportional to its mean velocity (under steady-state conditions), R can be calculated from the ratio of pore volumes for solute to pore volumes for water (= 1, see Figure 1). Thus under steady-state flow V_p will be equal to the retardation factor R, and

$$K_{a} = (V_{p} - 1) \frac{\theta}{\rho_{b}}.$$
 (4)

The breakthrough curves of NH_4^+ and NO_3^- (pooled from four replications) were analysed by a sigmoidal regression model, and the retardation factors and their adsorption coefficients determined by Equation (4). The adsorption coefficients of NH_4^+ and NO_3^- were correlated with easily measured soil properties, i.e. pH, soil organic matter, clay content and cation exchange capacity, and individual soil properties tested using linear regression.

WaNuLCAS simulation: N leaching with and without mineral N adsorption

The WaNuLCAS model (Van Noordwijk & Lusiana, 1998, 1999) simulates a four-layer by four-horizontal zone segment of an agroforestry or other mixed-plant species system and predicts interactions between the tree, soil and crop components on the basis of light, water, nitrogen and phosphorus capture. Competition for below-ground resources is based on the root distribution over the 16 cells, as well as on current



gure 1 The $H_2^{18}O$ flow in soil column from c peltophorum hedgerow intercropping stem (0–0.2 m soil depth). Vertical bars ow standard errors based on four replicates.

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Activity		Date	Mineral N uptake by plant /g m ⁻²		
Ι.	First pruning	1 December 97	1.08		
2.	Maize planting	14 December 97			
3.	First N application (30 kg N ha ⁻¹)	21 December 97			
4.	Second N application (60 kg N ha ⁻¹)	10 January 98			
5.	Maize harvesting	11 March 98	4.76		
6.	Second pruning	22 March 98	2.17		
7.	Groundnut planting	27 March 98			
8.	Groundnut harvesting	29 June 98	2.62		

Table 1 Timetable of management practices in a *Peltophorum dasyrrachys* hedgerow intercropping system used in the WaNuLCAS simulations, and simulated mineral N uptake by plants

demand. For both the tree and the crop a potential growth, applicable to local climate, is used as input, and daily reduction factors are calculated where actual uptake could not meet the 'demand'. The dynamics of water and nutrients in the four vertical columns of soil are connected via the tree roots, as well as through lateral flows of water (if a slope value other than zero is chosen) on the surface (runoff-runon) or through the soil. Both vertical and horizontal flows of water have consequences for nutrient transport. In this paper we focus on the aspects of nutrient transport using a model parameterization for hedgerow-maize intercropping described above.

The adsorption coefficient of mineral N (K_a) must be considered in simulation of N leaching and N movement to roots. To assess their effects on mineral N leaching adsorption coefficients were incorporated into the WaNuLCAS model (Van Noordwijk & Lusiana, 1998, 1999). In this model a single pool of mineral N is simulated, but it covers both forms if a weighted average adsorption constant (K_{a-eff}) is used. The potential N uptake (PotUpt) by plants is inversely proportional to ($K_a + \theta$), while the leaching rate is inversely proportional to ($K_a + \theta_{saturation}$). Both potential uptake and leaching are directly proportional to the soil mineral N pool (StockN). Thus,

$$PotUpt = a \frac{StockN_{NO_3}}{K_{aNO_3} + \theta} + a \frac{StockN_{NH_4}}{K_{aNH_4} + \theta} = a \frac{StockN_{tot}}{K_{a-eff} + \theta},$$
 (5)

where $StockN_{NO_3}$ is mineral N in NO_3^- form, $StockN_{NH_4}$ is mineral N in NH_4^+ form and $StockN_{tot}$ is total mineral N in the soil, and *a* is the relative value from other factors (i.e. the water flow factor).

Therefore, solving Equation (5) for K_{a-eff} yields

$$K_{\text{a-cli}} = -\theta + \frac{(K_{\text{a}NO_3} + \theta)(K_{\text{a}NH_4} + \theta)}{K_{\text{a}NO_3} + F_{NO_3}(K_{\text{a}NH_4} - K_{\text{a}NO_3}) + \theta}, \quad (6)$$

where θ equals $\theta_{\text{saturation}}$ for the leaching equation. The quantity FNO₃ is the fraction of mineral N in NO₃⁻ form.

The WaNuLCAS model (version 2.05) was then used to simulate leached N on a daily time step for a year for some of the cropping systems at our study site. The simulation scenarios were as follows.

- 1 With and without NH_4^+ and NO_3^- adsorption coefficients in bare soils; with and without fertilizer N (90 kg N ha⁻¹).
- 2 With and without N adsorption coefficients in maizegroundnut rotation monoculture cropping system; with and without fertilizer N (90 kg N ha⁻¹).
- 3 With and without N adsorption coefficients in 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 the 1997-98 cropping systems (Table 1) from climate data, with the annual total rainfall (1 November 1997-31 October 1998) of 3102 mm, soil data (Table 2) and cropping systems and their management practice (Table 1), according to the model requirements.

Table 2 Properties of soil used for NH_4^+ and NO_3^- retardation experiments (mean values based on four replicates)

			Organic content/%		Soil particles /%				
Soil depth /m.	pH(H ₂ O)	CEC /cmol _e kg ⁻¹		Total N /%	Sand	Silt	Clay	$ ho_{ m b}$ /g cm ⁻³	θ_s /cm ³ cm ⁻²
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

CEC, cation exchange capacity; $\rho_{\rm b}$, bulk density; $\theta_{\rm s}$, saturated volumetric water content.

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Table 3 Ammonium (NH_4^{-1}) and nitrate (NO_3^{-1}) breakthrough pore volumes and measured adsorption coefficients

	Delay /p	ore volumes (V _p)	Adsorption coefficient $(K_a) / \text{cm}^3 \text{g}^{-1}$		
Soil depth/m	NH4 '	NO ₃ -	NH4 [†]	NO ₃	
0.0-0.2	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	

The results of the simulations were presented as the effectiveness of mineral N adsorption coefficients on reducing leaching of mineral N compared with that without adsorption coefficients. The effectiveness of the inherent 'safety-net' was calculated as a percentage using

$$Effectiveness = \frac{(LeachedN_{without_Ka} - LeachedN_{with_Ka}) \times 100}{LeachedN_{without_Ka}}, (7)$$

where LeachedN_{without_Ka} is the mineral N leached without an adsorption mechanism and LeachedN_{with_Ka} is the mineral N leached with effects of adsorption factors.

The WaNuLCAS model was also used to explore the effect of increasing soil depth (0.8–7 m) on the leaching of mineral N with and without N adsorption coefficients. This was done specifically for the system peltophorum hedgerow with intercropped maize and groundnut to which fertilizer N (90 kg N ha^{-1}) was added. Adsorption coefficients and other properties of the deeper soil and nitrate fraction were assumed to be the same as those of the soil between 0.6 and 0.8 m.

Results

Soil properties

Table 2 lists the average values of the soil properties we measured. The soil was acid (pH 4.6-5.3), the more so with increasing depth. The cation exchange capacity varied from

2.42 to $5.05 \text{ cmol}_{e} \text{ kg}^{-1}$. The organic matter content decreased markedly with depth (from 2.04% to 0.14%). The soil texture was a sandy clay loam but the clay content increased from 27.5% to 38.0% with increasing depth. The bulk density ranged from 1.38 to 1.55 g cm⁻³, the topsoil being least dense.

Adsorption of ammonium (NH_4^+) and nitrate (NO_3^-)

The peak flow of $H_2^{18}O$ appeared at 1 pore volume (Figure 1). There was some enrichment in ¹⁸O in the outflow before the peak. The amount of $H_2^{18}O$ gradually decreased after 1 pore volume, but the enrichment of $H_2^{18}O$ was still large.

The breakthrough curves for the replacement of potassium by NH_4^+ for the upper soil layers had sigmoid shapes (Figure 2). At all depths, the concentration of NH_4^+ in the leachates reached that in the leaching solution (2mM) within 32 hours (20 pore volumes) of solute flow. In all columns, complete replacement of CI^- by NO_3^- was reached (2mM) within 16 hours (10 pore volumes) of solute flow (Figure 3). The delay to the midpoint of the breakthrough curve of NH_4^+ ($C_t/C_0 = 0.5$, e.g. 1 mM) ranged from 6.44 to 6.94 pore volumes and gave adsorption coefficients using Equation (4) of from 1.47 to 1.81 (Table 3). The delay of midpoint in the breakthrough of NO_3^- increased with depth and ranged from 1.10 to 1.62 pore volumes, 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 soil pH (Table 4). The order of importance of the coefficients of determination (R^2) from fitted linear regressions were pH > soil organic matter content > clay content. The slope of the linear regressions revealed that an increasing pH and soil organic matter content increased the adsorption coefficient of mineral NH_4^+ . The adsorption coefficient of mineral NO_3^- was significantly correlated with easily measured properties such as clay and organic matter. 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^- .

Table 4 Linear regression parameters between NH₄⁺ and NO₃⁻ adsorption coefficients ($K_{\mu NH4}$ and K_{nNO3}) with pH, soil organic matter (SOM), clay content and cation exchange capacity (CEC)

	NH4'			NO ₃ .		
Parameter and range	Constant	Slope		Constant	Slope	R ²
pH ranges: 4.6–5.3	-0.44	+ 0.43	0.82*	+ 0.76	-0.14	0.49
SOM ranges: 0.14-2.04 /%	+ 1.47	+ 0.16	0.59	+0.15	-0.06	0.78*
Clay ranges: 27.5-38.0 /%	+ 2.47	-0.03	0.40	-0.30	+ 0.01	0.84*
CEC ranges: 2.42–5.05 /cmol _c kg ⁻¹	+1.43	+ 0.05	0.04	+ 0.11	-0.003	0.02

P < 0.10.



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Figure 2 The breakthrough curves (y) of NH₄⁺ (2mM) for four depths (0–0.8m), where x is the number of pore volumes. Vertical bars are standard errors.

Figure 3 The breakthrough curves (y) of NO₃ (2mM) for four depths (0-0.8m), where x is the number of pore volumes. Vertical bars are standard errors.



Figure 4 Trend of soil water content (0-0.8 m) from 1 November 1997 to 31 October 1998 where (---) is the monoculture system and (\dots) the peltophorum hedgerow intercropping system in the 90 kg N ha⁻¹ treatment.

Table 5 Fraction of NO_3^{-1} in soil mineral N at different soil depths (24 replicates for each soil depth)

	Fraction of soil mineral NO3			
Soil depth /m	Mean	SE		
0-0.05	0.40	0.020		
0.05-0.2	0.36	0.018		
0.2-0.4	0.24	0.012		
0.4-0.6	0.31	0.026		
0.6-0.8	0.36	0.028		
0.8-1.0	0.36	0.028		

SE, standard error of mean.

The average NO_3^- fraction in mineral N was similar at around 30-40% throughout the soil profile except for the 0.2-0.4 m depth (Table 5) where it was only 24%. Variation of the 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^- (Tables 3 and 5) into the model showed that leaching was significantly influenced by the inherent retardation mechanism in this soil (adsorption capacities of NH_4^+ and NO_3^-) by up to 33% (Table 6). The adsorption coefficient of NO₃⁻ had little effect on simulated leaching (decreasing leaching by less than 2%) in the ecosystem we tested. Thus most of the effect on leaching was due to the adsorption coefficient of NH4⁺ (5-32% reduction in leaching). The application of fertilizer made the adsorption coefficients less effective in reducing leaching of mineral N in all systems. Planting crops increased the effectiveness of adsorption coefficients in reducing leaching. However, the inclusion of N2-fixing groundnuts (50% fixation) slightly increased the amount of N leached when compared with bare soil in the treatment without N fertilizer. This was due to the recycling of fixed N in plant residues. Inserting trees into the system substantially decreased the amount of N leached, particularly on plots to which N fertilizer was added when compared with those with bare soil or single crops. Peltophorum hedgerows also had a stronger effect on depleting the water content in the soil than the monoculture

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 fertilizer treatments) on a Plinthic Acrisol in the humid tropics over one year

	Mineral N leaching /g m ⁻² (% change)					
Cropping system	$-K_{aNH_4}-K_{aNO_5}$	$-K_{aNH_4} + K_{aNO_3}$	+ $K_{\text{BNH}_4} - K_{\text{BNO}_1}$	+ K_{aNH_4} + K_{aNO_4}		
- F - C - H	3.7 (0)	3.7 (0.31)	3.4 (7.8])	3.4 (8.41)		
+ F - C - H	11.8 (0)	11.8 (0.1])	11.3 (4.71)	11.3 (5.01)		
– F+C – H	4.6 (0)	4.6 (1.51)	3.2 (31.61)	3.1 (33.11)		
+F+C-H	10.7 (0)	10.6 (0.81)	8.7 (18.91)	8.6 (19.91)		
- F+C+H	2.8 (0)	2.8 (1.41)	2.1 (27.5])	2.1 (27.81)		
+ F + C + H	8.3 (0)	8.2 (0.61)	6.9 (16.81)	6.8 (17.41)		

- = without, + = with K_{aNH_4} and K_{aNO_5} = coefficient of adsorption of NH₄⁺ and NO₃⁻; F = fertilizer N (30 kg N + 60 kg N ha⁻¹ top dressing); C = maize-groundnut rotation; H = peltophorum hedge; $\downarrow = \%$ decrease.



Figure 5 The effect of available rooting depth on mineral N leaching with and without adsorption coefficients (K_a) of NH₄⁺ and NO₃⁻ and their effectiveness in reducing leaching.

(Figure 4), as well as providing recyclable N in the prunings (Table 1). The effectiveness of the inherent retardation mechanism in this Acrisol increased exponentially with increasing depth (Figure 5). With increasing rooting depth, plants improved the effectiveness of adsorption coefficients in reducing N leaching.

Discussion

Anumonium (NH_4^+) and nitrate $(NO_3^-)_i$ adsorption

The shape of the NH4⁺ breakthrough curve is more gradual (less steep) than that of NO3⁻, indicating that the mobility of NH_4^+ was less than that of NO_3^- in this soil. The data show that the adsorption coefficient of NH4⁺ varies somewhat with depth (Figure 2 and Table 3), This is probably due to the interactions between pH, clay and organic matter content varying with depth. Clay and organic matter content have a predominantly negative charge and can attract and hold positively charged cations such as NH4⁺ by cation exchange. In this study clay content has no significant effect on the adsorption coefficient of NH4⁺ possibly because of interactions with other factors (pH and soil organic content) or because of the narrow range of clay contents. However, a decreasing pH strongly decreased NH_4^+ adsorption. We think that under acidic conditions the positively charged sites increase (including those on iron and aluminium oxides and hydroxides in lattices of clay), hence restricting NH4⁺ entry to the soil surface (Mortland & Wolcott, 1965). A second factor may be the stronger replacing power of the H⁺ ion competing

for the exchange sites (Nommik & Vahtras, 1982). Thus the results also indicate that the negatively charged sites depend on pH.

Nitrate retardation increases with depth (Figure 3 and Table 3). This increase corresponds to an increasing clay content and decreasing pH and organic matter content. In Acrisols the source of positive charges are the broken edges of kaolinites and variable charges of Fe and Al oxide or hydroxide colloids (Uehara & Gillman, 1981). The positive charge on Fe and Al oxide or hydroxide colloids increases as the soil becomes more acid (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 NO₃⁷ (Black & Waring, 1976). Our measurements confirm that for this soil the clay content is the predominant factor affecting the adsorption coefficient of NO₃⁻.

The peak concentration for $H_2^{18}O$ occurred at 1 pore volume. Thus, it seems that the water in these undisturbed cores moved largely by piston flow. However, some early breakthrough indicated that some of the $H_2^{18}O$ moved by bypass flow through macropores. This fast flow could have reduced the effectiveness of adsorption of mineral N during the experiments. Suprayogo (2000) found more bypass flow occurred in the field than in laboratory columns. Therefore, our laboratory experiment does not indicate directly the flow patterns in the field. However, the determined adsorption coefficients are valid as there were few macropores in the soil column. Furthermore, under field conditions mineral N derived from mineralization of organic matter is present mainly within the micropores of aggregates and hence subject to adsorption (Nortcliff & Thornes, 1989).

The exchange of K^+ and NH_4^+ or CI^- and NO_3^- in the experiment may be less complex than in the field where a wider range of cations or anions are available to compete for the exchange sites. Also in the field, when a pulse of NH_4^+ or NO_3^- moves through the soil it will change the electrolyte concentration and pH and hence the charge will not be constant (Wong *et al.*, 1987). Immobilization of N may cause further delay in leaching (Wong *et al.*, 1987), but we prevented this in our experiment by using a microbial inhibitor. Despite these limitations, the incorporation of retardation factors as inputs in models such as WaNuLCAS can greatly enhance the accuracy of tests of the potential effect of various management strategies designed to reduce N leaching.

The adsorption coefficients of NO_3^- determined for this soil were smaller than those given by Wong *et al.* (1987) for a Nigerian Acrisol, in which adsorption coefficients for $NO_3^$ were 0.07, 0.11 and 0.28 cm³ g⁻¹ for soil depths of 0–32 cm, 32–67 cm and 67–130 cm, respectively. Our measurements suggest that the values of the adsorption coefficients of NO_3^- are 0.03, 0.09, 0.10 and 0.17 cm³ g⁻¹ for 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 NH_4^+ in the Nigerian example, so we could not compare it with our results.

The effectiveness of retardation mechanisms in reducing leaching

The inherent 'safety-net' of this soil based on the WaNuLCAS simulation could reduce leaching of mineral N by 5-33% (Table 6). Crops and trees increased the effectiveness of the retardation functions. Uptake of mineral N by them (Table 1) reduces the amount of mineral N in the soil solution and hence the amount potentially susceptible to leaching. They also increase the effectiveness of the retardation by drying the soil (Figure 4). Water from any subsequent rain will fill the larger empty pores, and so dilute the mineral nitrogen in the solute. Weaker concentrations of mineral N will decrease the chances of saturation of the charge on the matric surface, and hence the inherent 'safety-net' of the soil will increase. The greater is the depletion of soil water by plants the greater is the retention of any further rainwater, thus restricting through drainage and the leaching of mineral N. Leaching of fertilizer N was reduced most in hedgerow intercropping systems because of the demands of the trees and crops rather than an increased effectiveness of the adsorption coefficients. The simulated leaching for the monocrop and tree based system (with the retardation actors activated) agreed well with actual measured values of 5.5 and 2.0 g m⁻¹ (Suprayogo, 2000).

Animonium adsorption coefficients were by far the most effective in reducing leaching in the systems we tested. The effectiveness of nitrate retardation in reducing leaching was ipparently small, partly due to the shallowness of the soil. However, anion adsorption capacities may be much more effectve (Figure 5) in deep Lixisols with less rainfall. Mekonnen \pm tal. (1997) found large accumulations of nitrate under naize monoculture in a deeper Lixisol in Western Kenya. The greater subsoil depth of such Lixisols will markedly herease the 'safety-net' factor, particularly where deep-rootng trees are planted.

Conclusions

he hypotheses 'that increasing pH and soil organic matter ill increase the adsorption of NH_4^+ , and decreasing soil pH nd soil organic matter, and increasing clay content will icrease the adsorption of NO_3^- , are confirmed. An increase i the adsorption of NH_4^+ due to increased clay content was but demonstrated in our experiment because of interactions ith other factors such as pH, soil organic matter and possibly is narrow range of clay contents of the samples.

Based on the WaNuLCAS simulation, the internal soil charteristics of the Acrisol we studied could reduce the leaching 'mineral N by 5–33% (or up to 2.1 g m⁻²), mainly as a result the ammonium retardation. This effect could be greater in eper soils. Our comparison of the leaching of mineral N with d without adsorption in several tropical agro-ecosystems ggests that the inherent 'safety-net' is useful only when N n be recovered subsequently.

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