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# Subsoil retention of organic and inorganic nitrogen in a Brazilian savanna Oxisol

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**Abstract.** Nitrogen (N) loss by leaching poses great challenges for N availability to crops as well as nitrate pollution of groundwater. Few studies address this issue with respect to the role of the subsoil in the deep and highly weathered savanna soils of the tropics, which exhibit different adsorption and drainage patterns to soils in temperate environments. In an Anionic Acrustox of the Brazilian savanna, the Cerrado, dynamics and budgets of applied N were studied in organic and inorganic soil pools of two maize (*Zea mays* L.) – soybean (*Glycine max* (L.) Merr.) rotations using $^{15}N$ tracing. Labelled ammonium sulphate was applied at $10\,kg\,N\,ha^{-1}$ (with 10 atom% $^{15}N$ excess) to both maize and soybean at the beginning of the cropping season. Amounts and isotopic composition of N were determined in above-ground biomass, soil, adsorbed mineral N, and in soil solution at 0.15, 0.3, 0.8, 1.2 and 2 m depths using suction lysimeters throughout one cropping season. The applied ammonium was rapidly nitrified or immobilized in soil organic matter, and recovery of applied ammonium in soil 2 weeks after application was negligible. Large amounts of nitrate were adsorbed in the subsoil ($150–300\,kg\,NO_3^-$-$N\,ha^{-1}$ per 2 m) matching total N uptake by the crops ($130–400\,kg\,N\,ha^{-1}$). Throughout one cropping season, more applied N (49–77%; determined by $^{15}N$ tracers) was immobilized in soil organic matter than was present as adsorbed nitrate (2–3%). Most of the applied N (71–96% of $^{15}N$ recovery) was found in the subsoil at 0.15–2 m depth. This coincided with an increase with depth of dissolved organic N as a proportion of total dissolved N (39–63%). Hydrophilic organic N was the dominant fraction of dissolved organic N and was, together with nitrate, the most important carrier for applied N. Most of this N (>80%) was leached from the topsoil (0–0.15 m) during the first 30 days after application. Subsoil N retention as both adsorbed inorganic N, and especially soil organic N, was found to be of great importance in determining N losses, soil N depletion and the potential of nitrate contamination of groundwater.

**Keywords:** Cerrado, leaching, organic nitrogen, Oxisol, stable isotope, subsoil, tropics

## INTRODUCTION

Highly weathered soils such as Oxisols are known for their low retention capacity of nutrients and high susceptibility to leaching (Van Wambeke 1992). Applied fertilizer nitrogen (N) is particularly susceptible to leaching losses, since mineralization and nitrification are rapid under tropical conditions (Vitousek & Matson 1988) and nitrate is mobile in most soils. As a consequence, soil fertility can decrease rapidly (Poss & Saragoni 1992) and the leached nitrate constitutes a pollution hazard for groundwaters and aquifers (Bijay-Sing *et al.* 1995; Mayer *et al.* 2000; Bouman *et al.* 2002).

A large proportion of added inorganic N is usually immobilized in soil within a few hours after application as shown by microcosm experiments (Watson *et al.* 2000; Burger & Jackson 2003). The temporal and spatial dynamics of applied N in the field are not known for highly weathered soils in the tropics. Large amounts of subsoil nitrate were reported from various tropical sites and land use systems (Mekonnen *et al.* 1997; Schroth *et al.* 1999); the contribution of applied N to leaching was not assessed in the experiments and no information is available about the forms in which N is transported into the subsoil. Tracer studies, using $Cl^-$ or $Br^-$ or water movement, may not be useful for the quantification of leaching of applied N, as they do not account for specific adsorption of N compounds as well as biological immobilization or mobilization in soil. Inorganic N can be rapidly immobilized in soil solution and leached in organic forms (Seely & Lajitha 1997). Consequently, dissolved organic matter was found to be an important

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Table 1. Physical and chemical characteristics of an Anionic Acrustox in the Brazilian Cerrado.

| Depth (m) | Bulk density ($t\,m^{-3}$) | SOC[a] ($g\,kg^{-1}$) | pH ($H_2O$) | pH (KCl) | $K_s$[b] ($m\,day^{-1}$) | ECEC[c] ($mmol_c\,kg^{-1}$) | BS[d] (%) | Coarse sand ($g\,kg^{-1}$) | Fine sand ($g\,kg^{-1}$) | Silt ($g\,kg^{-1}$) | Clay ($g\,kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maize cropping system | | | | | | | | | | | |
| 0–0.15 | 1.03 | 20.8 | 5.6 | 5.1 | 0.56 | 36.7 | 97 | 127 | 67 | 115 | 692 |
| 0.15–0.3 | 1.10 | 17.4 | 5.0 | 4.6 | nd | 21.3 | 89 | 121 | 64 | 110 | 705 |
| 0.3–0.8 | 0.85 | 10.9 | 5.0 | 4.9 | nd | 14.6 | 73 | 103 | 60 | 107 | 730 |
| 0.8–1.2 | 0.89 | 7.4 | 4.9 | 5.5 | nd | 11.2 | 62 | 101 | 58 | 141 | 700 |
| 1.2–2 | 0.99 | 6.3 | 5.0 | 5.8 | nd | 11.3 | 58 | 100 | 59 | 102 | 738 |
| Soybean cropping system | | | | | | | | | | | |
| 0–0.15 | 0.99 | 21.7 | 5.5 | 4.9 | 1.56 | 35.1 | 96 | 104 | 62 | 116 | 718 |
| 0.15–0.3 | 0.93 | 19.0 | 5.5 | 4.7 | nd | 28.2 | 95 | 104 | 62 | 133 | 702 |
| 0.3–0.8 | 0.87 | 11.7 | 5.4 | 5.0 | nd | 14.9 | 78 | 89 | 53 | 125 | 733 |
| 0.8–1.2 | 0.85 | 8.9 | 5.0 | 4.8 | nd | 11.8 | 68 | 88 | 53 | 130 | 729 |
| 1.2–2 | 0.83 | 6.8 | 4.9 | 6.0 | nd | 11.3 | 69 | 85 | 55 | 139 | 721 |

[a]Soil organic carbon; [b]saturated hydraulic conductivity (U. Schwantag, pers. comm.); [c]effective cation exchange capacity; [d]base saturation. nd = not determined.

carrier for N in South American ecosystems (Van Breemen 2002; Perakis & Hedin 2002). The mobility of this N may then depend partly on the properties of organic N in dissolved organic matter (Qualls *et al.* 1991) and has to be quantified separately.

To account for the specific transformation and mobility of applied inorganic fertilizer N, a tracer experiment was conducted using $^{15}N$ to investigate the fate of applied ammonium sulphate in maize and soybean cropping systems in a Brazilian savanna Oxisol. The objectives were to assess (i) the importance of the subsoil for N retention, and (ii) the role of organic N in N-leaching.

## MATERIALS AND METHODS

### *Study site*

The study area is located southeast of Uberlândia in the State of Minas Gerais, 400 km south of Brasília, Brazil (48°8′ W, 19°0′S). The mean annual temperature is 22 °C and annual precipitation 1550 mm. Between 1981 and 1990, on average, 1420 mm rainfall occurred during the rainy season between October and April, and only 130 mm during the dry season between May and September (Rosa *et al.* 1991). During the experimental season 1997/98, rainfall amounted to 210 mm during the period May to September 1997, 569 mm during October to December 1997, and 783 mm during January to April 1998. During crop growth from December 1997 to April 1998, total rainfall was 716 mm. The soils were very fine, isohyperthermic Anionic Acrustox (Soil Survey Staff 1997) developed from fine limnic sediments of the lower Tertiary, which were homogeneously weathered to a depth of several metres. Selected chemical and physical characteristics are described in Table 1. The sites had slopes <1°.

### *Experimental design*

Two maize (*Zea mays* L.) – soybean (*Glycine max* (L.) Merr.) rotations were studied, which are widespread in the Cerrado savanna of Brazil. Three spatially disconnected sites on farmers' fields were selected in either soybean or maize during the study period. The sites were fertilized with an annual average of 70 $kg\,N\,ha^{-1}$ (urea), 100 $kg\,P\,ha^{-1}$ (triple superphosphate) and 160 $kg\,K\,ha^{-1}$ (KCl). The current study was carried out on farmed fields, without any change to the crop rotation and crop management currently practised. The fields cropped to soybean during the experimental period were under no-tillage for the past 1–3 years and the fields cropped to maize were under conventional tillage. Maize was planted in rows 0.8 m apart and spacing within the row of 0.22 m (56 800 plants $ha^{-1}$) on 11 November 1997 and harvested on 1 April 1998. Soybean was sown in rows 0.5 m apart and spacing within the row of 0.07 m (285 000 plants $ha^{-1}$) on 28 November 1997 and harvested on 16 April 1998. At planting, maize received 120 $kg\,N\,ha^{-1}$, 100 $kg\,P\,ha^{-1}$ and 140 $kg\,K\,ha^{-1}$; soybean received 60 $kg\,P\,ha^{-1}$ and 170 $kg\,K\,ha^{-1}$. Ammonium sulphate at 10 $kg\,N\,ha^{-1}$ was applied as a solution with 10 atom% $^{15}N$ excess (containing 1 $kg\,^{15}N\,ha^{-1}$) to an area of $3 \times 3$ m on 30 November 1997. The labelled N was used to trace the fate and transformation of ammonium at the beginning of the rainy season when fertilizers are usually added to crops, or when wetting of soil leads to N mineralization (further called 'applied N').

In March 1997, each of the six sites was equipped with five replicate tensiometers and suction cups at depths of 0.15, 0.3, 0.8, 1.2 and 2 m, respectively. Both tensiometers and suction cups were inserted within and between the plant rows. The cups were made of $Al_2O_3$ (70%) and $SiO_2$ (29%) with an average pore size of 1 μm. Soil solution was collected using a permanent vacuum applied by electric pumps and controlled by a pressure gauge. The vacuum was adjusted weekly according to the soil water suction measured by the tensiometers at the same depth. The soil solutions collected from the five samplers were mixed to give one composite sample. Sampling of soil solution was started in April 1997, and the first 3 months of sampled soil solution were discarded until an equilibrium of nutrient concentration could be assumed between the solution in ceramic cup and the soil solution. The bottles were cleaned with distilled water after each sample collection. Soil solution was sampled 13 times during the experimental period between the end of November 1997 and April 1998.

Soil samples were taken on 17 and 19 December 1997, 26 January, and 1 April 1998 (maize) and 16 April 1998 (soybean) at depths of 0–0.15, 0.15–0.3, 0.3–0.8, 0.8–1.2 and 1.2–2 m using one composite sample from five locations (Purkhauer auger system, 2 cm diameter). The samples were immediately transported to the laboratory, then dried at 40 °C and sieved to <2 mm; mineral N was determined on field-moist samples.

Grain yield and crop residues were harvested separately from a central plot area of 2 × 2 m, dried at 70 °C for 48 hours and weighed. Total N concentrations and isotopic composition were determined by dry combustion after grinding to a fine powder as described below.

### *Chemical analyses*

Soil samples obtained in January 1998 were analysed for: soil organic carbon (SOC) by dry combustion using an automatic CHNS-analyser (Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany) after grinding to a fine powder; effective cation exchange capacity (ECEC) by extraction with 1 M ammonium acetate (Sumner & Miller 1996); base saturation (BS) by calculating the proportion of the charge equivalent of extractable Ca, Mg, K and Na of the ECEC; soil pH in water and 1 M KCl (soil solution ratio 1 : 2.5) with a standard pH electrode (Orion U402-S7, Boston MA); particle-size distribution after removal of Fe oxides with sodium dithionite; and organic matter with $H_2O_2$ at 90 °C, following dispersion with hexametaphosphate. Coarse and fine sand were sieved at 250–2000 and 50–250 µm, respectively. Silt (2–50 µm) and clay (<2 µm) were determined by the pipette method (Gee & Bauder 1986). In December, January and April total N isotope composition in soil and plants was determined using an Elemental Analyzer (Carlo Erba NA 1500, Carlo Erba Reagenti, Rodano, Italy; for Dumas combustion) connected to an isotope mass spectrometer (FINNIGAN MAT delta E; Thermo Finnigan, San Jose CA) via a split interface.

Field-moist soil was extracted with 2 M KCl by shaking 10 g of soil with 100 mL of extracting solution for 10 h (Mulvaney 1996). In the soil extracts, nitrate and ammonium concentrations (adsorbed nitrate and adsorbed ammonium) were determined photometrically with a rapid flow analyser (RFA–300, Alpkem Corp., Clackamas OR). Adsorbed ammonium could not be determined in soil extract samples in December 1997 and January 1998 because the KCl used for extraction was contaminated with ammonium by the manufacturer. Nitrate values determined by KCl extraction included dissolved nitrate in addition to the adsorbed nitrate. However, anion exchange capacity is large in acid soils with variable charge (Cahn *et al.* 1992; Qafoku & Sumner 2001) and the majority of the nitrate extracted is adsorbed nitrate.

The isotopic composition of adsorbed ammonium and nitrate was determined after steam distillation (Buresh *et al.* 1982) and freeze-drying of the extracts, using isotope mass spectrometry as described above. Volumes of 60 mL of KCl extracts were distilled for each of the ammonium and ammonium + nitrate assays, separately. Nitrate values were obtained by difference between results of ammonium and ammonium + nitrate. The pH was raised by addition of 1.5 g MgO for the distillation of ammonium. For the distillation of ammonium + nitrate, 2 g Devardas alloy was added to the extracts prior to distillation. The ammonia was trapped in 20 mL of an acid solution containing 0.01 M $H_2SO_4$. The distillation was done in duplicate and the first distillation was used to clean the apparatus to avoid carry-over and was discarded (Mulvanay 1986).

The isotopic signature of dissolved organic N (DON) was determined separately in hydrophilic (DHION) and hydrophobic (DHOON) fractions in the soil solution (Aiken & Leenheer 1993). Soil solution was pumped through a column filled with Amberlite XAD-8 adsorber resin (Rohm and Haas Co., Philadelphia, PA). The adsorbed organic substances were eluted with 0.05 M NaOH, protonated by pumping through a column filled with strongly acid cation exchanger resin (AG-MP 50, BioRad Laboratories, Richmond CA), and freeze-dried. Total N and N isotope composition in soil solution and hydrophobic separates were measured by isotope mass spectrometry of a known volume of freeze-dried solution as described above. DON or soil organic N (SON) was calculated as the difference between dissolved (DIN) or adsorbed inorganic and total N in solution or soil, respectively. The difference between DON and DHOON was taken as DHION. DON and DIN fractions are only shown for the month of December when more than 80% of the leaching of the cropping season occurred. Nitrate concentrations in the soil solution for the entire cropping season were presented by Lilienfein *et al.* (2000a, b).

### *Calculation of applied N leaching*

Water drainage and leaching of the applied N were modelled using a simple water balance, as described in the GAPS model (Riha *et al.* 1994), and $^{15}N$ recovery in the soil solution. Inputs into the model are weather data, vegetation data and soil data. Daily potential evapotranspiration (PET) is calculated using the Priestley–Taylor equation with rainfall, relative humidity, radiation, air temperature, and wind speed at 2 m height from a weather station located close to the experimental sites (rainfall data were not available from 23 December to 7 January due to instrument failure). Plant rooting depth and distribution were calculated using an inverse modelling approach based on soil water contents, combined with experimentally obtained root distribution. Soil water content at field capacity was assigned to each soil layer from measurements of the soil water potential and soil water retention curves. Soil water retention curves were determined in laboratory experiments using pressure plates (Lilienfein *et al.* 1999). Based on the field capacity of each layer and measured water potentials, the water contents at permanent wilting point and at saturation were assigned, as well as the relative saturated conductivity of the layer. After simulations, modelled water contents were compared to measured water contents. Convective transport of applied N in soil was obtained with the determined water fluxes and the $^{15}N$ concentrations of the soil solution, which were then calculated on a daily basis by interpolation using cubic splines.

In a second approach, a simple water balance was computed using rainfall, soil water storage and evapotranspiration. Evapotranspiration was estimated from literature

Table 2. Crop biomass production, grain yield, and $^{15}$N contents[a] in maize and soybean cropping systems in a Brazilian savanna Oxisol.

| | | Yield ($t\,ha^{-1}$ DM) | N concentration ($g\,kg^{-1}$) | Recovery of applied N (% of applied N) | Total N uptake ($kg\,ha^{-1}$) |
|---|---|---|---|---|---|
| Maize | Stems[b] | 8.76ac ± 0.32 | 8.17b ± 0.68 | 10.0a ± 0.16 | 72a ±8.1 |
| | Grain | 4.07b ± 0.22 | 13.24a ± 1.07 | 6.9b ± 0.42 | 54a ±5.9 |
| | Total | 12.83 ± 0.53 | | 16.9 ±0.27 | 126 ± 13.3 |
| Soybean | Stems | 6.42a ± 0.42 | 10.43b ± 0.77 | 3.2b ± 0.42 | 67b ±4.1 |
| | Grain | 4.85a ± 0.95 | 67.88a ± 1.42 | 11.4a ± 2.75 | 327a ±59.3 |
| | Total | 11.27 ± 1.32 | | 14.6 ±3.04 | 393 ± 58.7 |

[a]Means ± standard errors; $n = 3$. [b]Above-ground plant material other than grain. [c]Means within one column followed by the same letter within the same crop are not significantly different at $P < 0.05$.

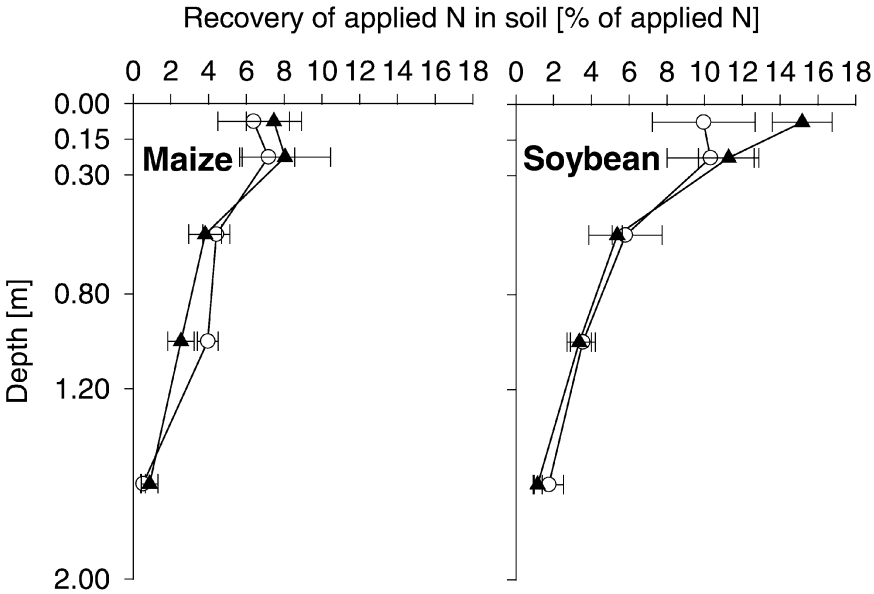

Figure 1. Recovery of applied N in total soil to 2 m depth of maize and soybean cropping systems in a Brazilian savanna Oxisol at the beginning (○, December 1997) and the end (▲, April 1998) of the cropping season (means and standard errors; $n = 3$).

values of the amount of water transpired per unit biomass production: $300\,L\,kg^{-1}$ for maize (Mason *et al.* 1982) and $480\,L\,kg^{-1}$ for soybean (Geisler 1980). Soil water storage was measured as soil water potential and converted to soil water content using water retention curves (Lilienfein *et al.* 1999). Total leaching ($L$) was computed as:

$$L = (S_{t_1} - S_{t_0}) + R - PET \qquad (1)$$

where $S$ is the soil water storage at the beginning ($t_0$) and the end ($t_1$) of the experiment, $R$ is rainfall, and $PET$ the potential evapotranspiration.

Calculations of $^{15}$N fluxes and budgets were done on the basis of $^{15}$N in excess of natural abundance (atom% $^{15}$N excess). The natural $^{15}$N abundance was determined for soil (0.3666–0.3678 atom% $^{15}$N), soil solution (0.3625–0.3681 atom% $^{15}$N), and plants (0.3671–0.3687 atom% $^{15}$N) before the isotope was applied and subtracted from total amounts of $^{15}$N measured in the samples.

### *Statistical analyses*

The data were compared by analysis of variance using a completely randomized design (ANOVA of Statistica 5.1; StatSoft, Hamburg, Germany). In case of significant effects or interactions, multiple comparisons of means were computed with the least significant difference (LSD) test at $P < 0.05$ if not indicated otherwise. For comparisons of N forms, comparisons were calculated using the non-parametric $t$-test.

## RESULTS

### *Biomass production and N uptake*

In the maize crop, more total N and applied N (from the $^{15}$N-labelled N) were taken up into stems and leaves than grain, whereas it was the reverse for soybean (Table 2). This was largely an effect of much greater N concentrations in soybean grain than leaves, not of greater grain mass. More N was found in the above-ground biomass of soybean ($393\,kg\,N\,ha^{-1}$) than of maize ($126\,kg\,N\,ha^{-1}$).

### *Nitrogen dynamics in the soil*

Most of the applied N (>85%) was found in the first 1.2 m of the soil, but less than 25% near the soil surface (0–0.15 m) (Figure 1). The depth distribution of the total recovery of

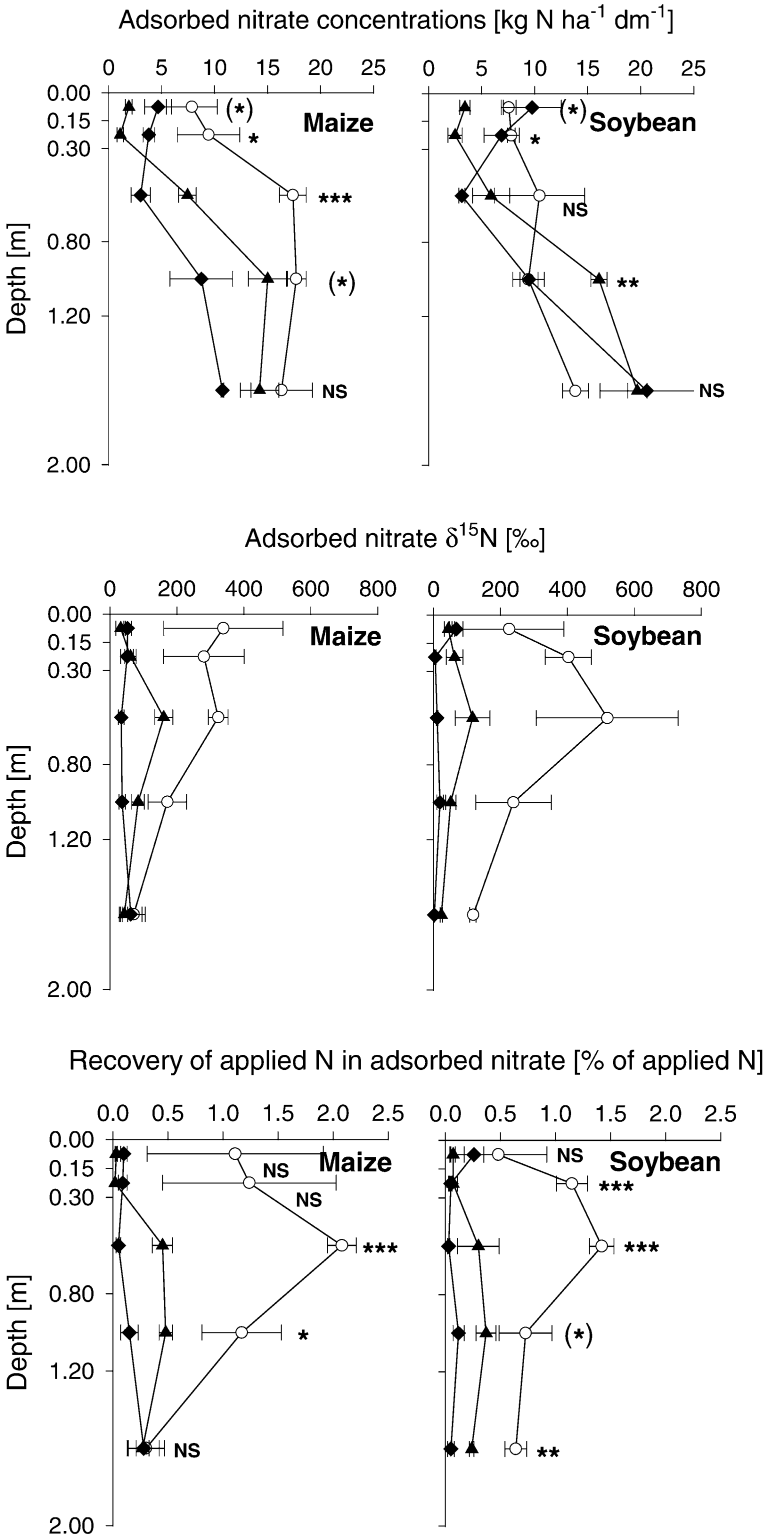

Figure 2. Total adsorbed nitrate (KCl extract), $^{15}$N enrichment and recovery of applied N in adsorbed nitrate of maize and soybean cropping systems in a Brazilian savanna Oxisol at different times in the cropping season: ○, December 1997; ▲, January 1998; ◆, April 1998. Significant effects of time at $P<0.1$, 0.05, 0.01, 0.001 as well as non-significant effects are shown as (*), *, **, ***, and NS, respectively (means and standard errors; $n = 3$).

Table 3. Recovery[a] of applied N in plant and soil (% of applied N) in maize and soybean cropping systems in a Brazilian savanna Oxisol at crop harvest.

| | Biomass | Topsoil | Subsoil | Total soil | Leaching | Total recovery |
|---|---|---|---|---|---|---|
| | | (0–0.15 m) | (0.15–2 m) | (0–2 m) | | |
| Maize cropping system | | | | | | |
| Ammonium[b] | – | 0.01c[c] | 0.18b | 0.19b | nd[d] | – |
| Nitrate[b] | – | 0.14b | 3.11b | 3.26b | nd | – |
| Organic N | – | 11.04a | 37.70a | 48.74a | nd | – |
| Total | 16.94B | 11.19B | 40.76A | 51.95 | 0.51 | 69.41 |
| Soybean cropping system | | | | | | |
| Ammonium[b] | – | 0.01b | 0.04b | 0.04c | nd | – |
| Nitrate[b] | – | 0.39b | 1.07b | 1.47b | nd | – |
| Organic N | – | 22.35a | 54.64a | 76.99a | nd | – |
| Total | 14.57B | 22.75B | 55.74A | 78.50 | 0.09 | 93.16 |

[a]Means; $n = 3$; [b]Adsorbed and soluble ammonium and nitrate; [c]Means within one column for the same crop followed by the same small letter, and means within one row followed by the same capital letter are not significantly different at $P < 0.05$; [d]nd = not determined.

applied N in soil did not change significantly throughout the cropping season, and remained constant from December 1997 (1 month after the application) to April 1998, except for the increase in recovery of applied N at 0.15 m soil depth under soybean.

The depth distribution of recovery of applied N in adsorbed nitrate differed from that in soil. The highest $\delta^{15}N$ and recovery of applied N in adsorbed nitrate was found at a depth of 0.3–0.8 m, and not in the topsoil (Figure 2). Concentrations of adsorbed nitrate even increased with depth and were greatest below 1.2 m. Recovery of applied N in nitrate was dominant (>75%) compared to that in ammonium at all depths, and adsorbed nitrate constituted more than 95% of adsorbed mineral N (ammonium + nitrate) throughout the soil profile (Figure 2; ammonium and ammonium-$^{15}N$ data not shown). Therefore, very low amounts of applied N were found in the form of ammonium at the end of the cropping season (Table 3). The amounts of applied N in adsorbed nitrate and total adsorbed inorganic N decreased significantly ($P < 0.001$) in both cropping systems throughout the cropping season, and in April 1998 applied N in the form of nitrate only amounted to 12% of the values found in December 1997.

### *Nitrogen dynamics in the soil solution*

The $^{15}N$ enrichment ($\delta^{15}N$ values) in the soil solution at 0.15 and 0.3 m depths and losses of applied N increased rapidly after application of N (Figures 3 & 4). The isotope signatures increased at greater depth to a lesser extent but were still significantly ($P < 0.05$) greater than before fertilization. Leaching of total N followed the same pattern as the leaching of applied N (Figure 4) and was greatest in December during the most intense rainfall and decreased to very small values towards the end of the cropping season. Leaching of both total N and applied N (Figure 4) was greater at 0.3 than 2 m depth.

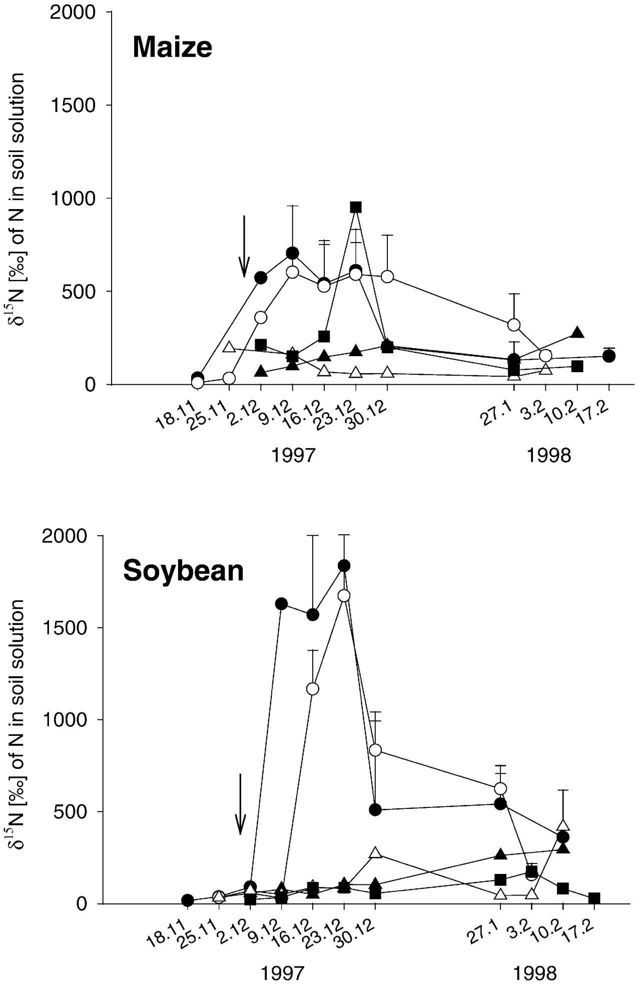

Figure 3. Dynamics of $^{15}N$ enrichment in total dissolved N in soil solution at depths: ●, 0.15 m; ○, 0.3 m; ▲, 0.8 m; △, 1.2 m; and ■, 2 m in maize and soybean cropping systems in a Brazilian savanna Oxisol (means, standard errors shown only for 0.15 m and 0.3 m; $n = 3$). The vertical arrows indicate time of fertilizer application.

During the period of most intense leaching in December 1997, dissolved hydrophilic organic N had similar $\delta^{15}N$ values as nitrate in the soil solution, and the isotope enrichment was greater at 0.8 m depth and above than in the subsoil below 0.8 m depth (Figure 5). In contrast, the $\delta^{15}N$ values in the dissolved hydrophobic organic N and ammonium did not change with depth. Most of the N in soil solution was found in nitrate (30–80%), followed by DHION (20–50%), DHOON (3–20%), and ammonium (0–4%). Therefore, the greatest concentration of the applied

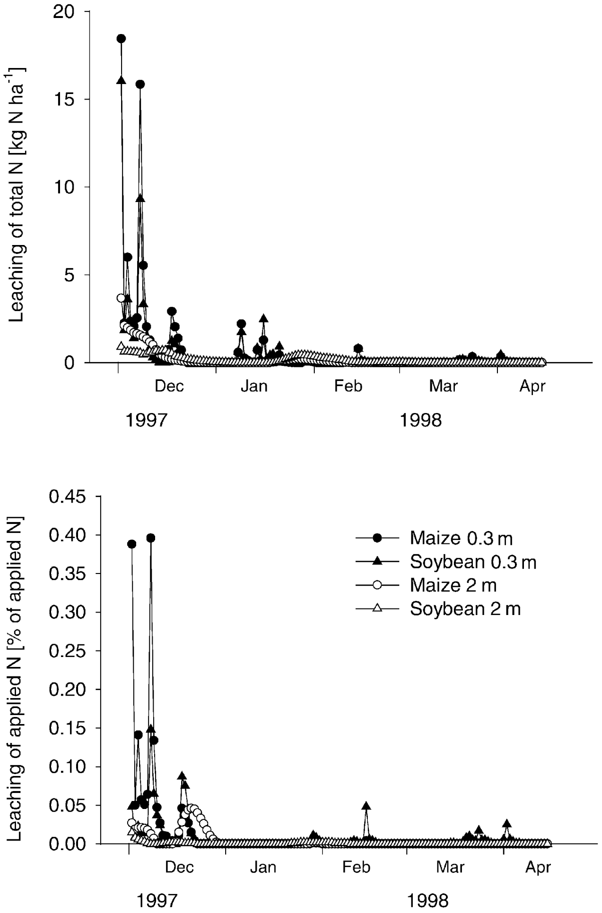

**Figure 4.** Dynamics of applied N in soil solution at depths of 0.3 m and 2 m in maize and soybean cropping systems in a Brazilian savanna Oxisol; water transport from tipping bucket model.

N in the soil solution was found in nitrate in the first 0.3 m. However, concentrations of applied N in DHION proportionally increased with depth and were greater than those in nitrate at 2 m depth.

### *Recovery of applied N in the agricultural system*

Total recovery of the applied N in plant and soil amounted to 70–93% (Table 3). Only 17% and 15% of the applied N were taken up by maize and soybean, respectively (Table 3). In the soil, most of the applied N was found in organic form (Table 3). Less than 4% of the applied N was present as adsorbed mineral N. Although the enrichment of $^{15}N$ ($\delta^{15}N$ values) was greatest near the soil surface, more of the applied N accumulated in the subsoil (41–56%; 0.15–2 m) than the topsoil (11–23%; 0–0.15 m) (Figure 1).

Soil water balances indicated similar drainage under both maize and soybean (Table 4), and modelled soil water contents agreed well with measured values (Figure 6). Soil water drainage at 2 m was about 54–65% of rainfall during the same period. The leaching losses of N at 2 m depth were significant with 19–26 kg N ha$^{-1}$ throughout the cropping season (Table 4). The leaching losses of applied N at 2 m depth, however, were found to be small compared with plant uptake and soil storage (Table 3). Most of the applied N (>80%) was leached within the first 4 weeks after the N application.

## DISCUSSION

### *Subsoil nitrate accumulation*

The large accumulation of adsorbed nitrate in the subsoil at the beginning of this experiment indicated intensive leaching from the topsoil over the previous cropping seasons. The quantity of adsorbed nitrate may have been even greater below 2 m, since adsorbed nitrate concentrations increased towards 2 m. The total amount of adsorbed nitrate in the soil profile to a depth of 2 m throughout the cropping season (150–300 kg $NO_3^-$-N ha$^{-1}$) was of the same order of magnitude as the total N uptake by the plants (130–400 kg N ha$^{-1}$) and therefore constitutes an important pool of available soil N. Since the early studies by Wild (1972) from Nigeria, similar large accumulations of adsorbed nitrate in subsoils have been reported over the past years from Brazil (Cahn *et al.* 1992; Schroth *et al.* 1999), Kenya (Warren & Kihanda 2001), and Australia (Rasiah & Armour 2001). Nitrification is very rapid in tropical ecosystems (Vitousek & Matson 1988) and ammonium from applied fertilizers or from mineralization of organic N is rapidly transformed into nitrate. Therefore ammonium did not play a significant role in leaching and most likely not in plant uptake either. Variable charge clay minerals may have created a significant anion exchange capacity, similar to other acid tropical soils (Cahn *et al.* 1992; Eick *et al.* 2000; Qafoku *et al.* 2000; Qafoku & Sumner 2001). The dominance of variable charge at depth was suggested by higher pH values in KCl than in water (Table 1), which coincides with results from the literature cited above. Nitrate leaching is typically retarded in acid subsoils such as Brazilian Oxisols (Dynia 2000), which can serve as a temporary sink for leached N as seen in our study.

### *Subsoil recovery of applied N*

Large amounts of percolating N from applied N rapidly reached a depth between 0.3 and 0.8 m, but were retained between 0.8 and 1.2 m during the rest of the cropping season. The results indicate, however, that adsorbed nitrate was a minor component of total N recovered from the acid subsoils. A far greater proportion of the applied N was found as soil organic N (Table 3). Subsoil organic N has received little attention, because concentrations are commonly small and comparable to the detection limits of dry combustion. Only isotope labelling experiments such as those we used here are able to detect added soil organic N at the levels found in our study.

### *Leaching and retention of dissolved organic N*

Few results are available that show losses of organic N by leaching. Schroth *et al.* (2000) found up to 60% of total N in organic form in the soil solution of a central Amazonian Oxisol under fallow. Our results indicate a DON proportion of total dissolved N ranging from 39% in the topsoil to 63% in the subsoil (Figure 5). No information is available about the retention of organic N in subsoils of Oxisols. The high

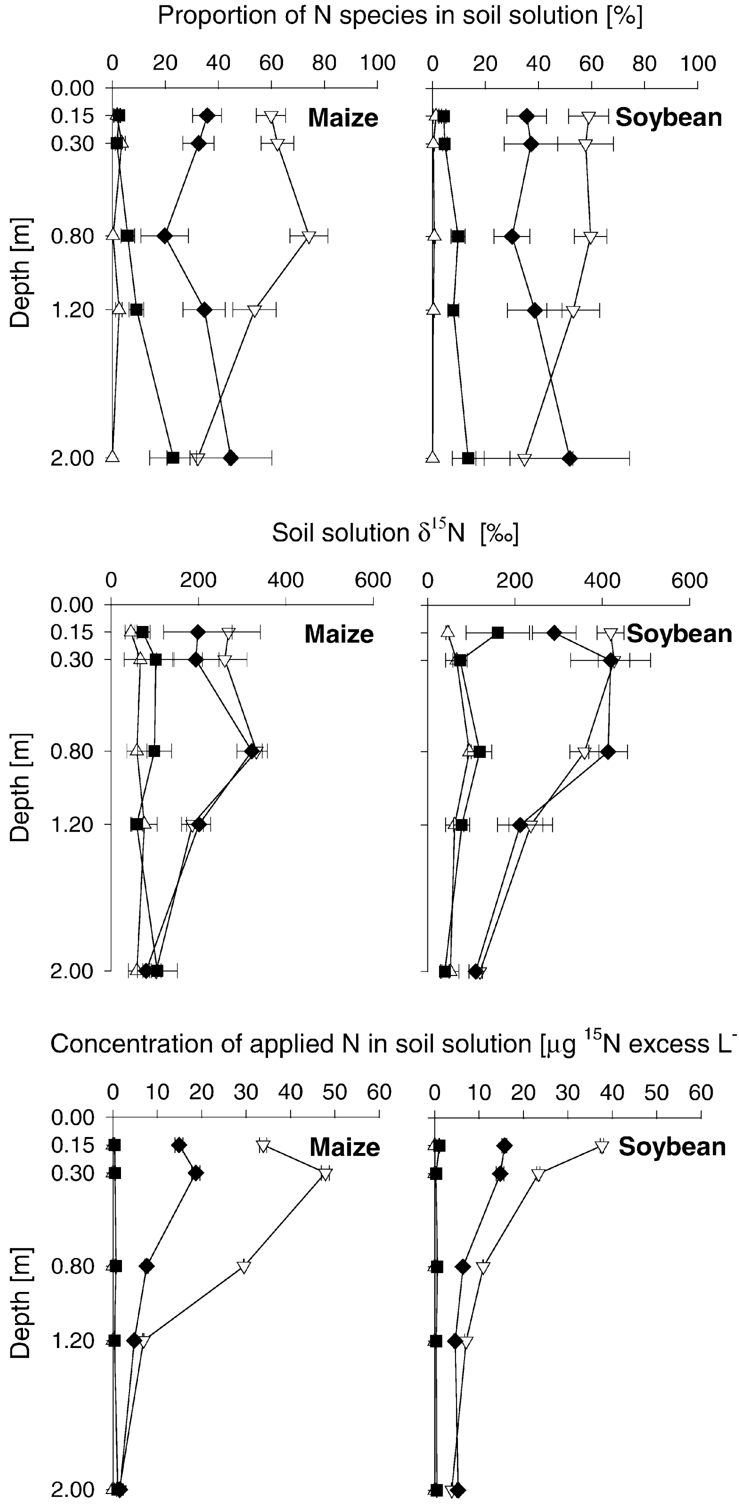

Figure 5. Proportion of N species in soil solution, $^{15}$N enrichment and proportion of concentration of applied N in dissolved nitrate (▽) and ammonium (△), dissolved hydrophilic (◆) and hydrophobic organic N (■) in the soil solution of maize and soybean cropping systems in a Brazilian savanna Oxisol; average values during the period of most intense leaching in December 1997 (means and standard errors; $n = 5$ to $n = 12$).

proportion of DON in the subsoil solution indicates that a large proportion of the organic N in the subsoil was derived from leaching of DON. Immobilization of DIN may also have played a role, as microbial transformation was reported in acid subsoils of Oxisols found in northeastern Brazil (Verchot *et al.* 1999). Perakis & Hedin (2002) reported that most of the soluble N exported in streams from unpolluted watersheds in Chile was in organic form, which again

Table 4. Cumulative water drainage, leaching of total dissolved N and of fertilizer N at 0.15 m and 2 m depth during the cropping season of maize and soybean in a Brazilian savanna Oxisol.

| | Maize | | Soybean | |
|---|---|---|---|---|
| | 0.15 m | 2 m | 0.15 m | 2 m |
| Drainage calculated with equation 1 (mm)[a] | nd[b] | 388 ± 24 | nd | 466 ± 108 |
| Drainage modelled using daily soil water changes (mm) | 439 | 414 | 425 | 411 |
| Leaching of total dissolved N (kg ha$^{-1}$) | 78 | 26 | 57 | 19 |

[a] Means ± standard errors; $n = 3$.
[b] not determined.

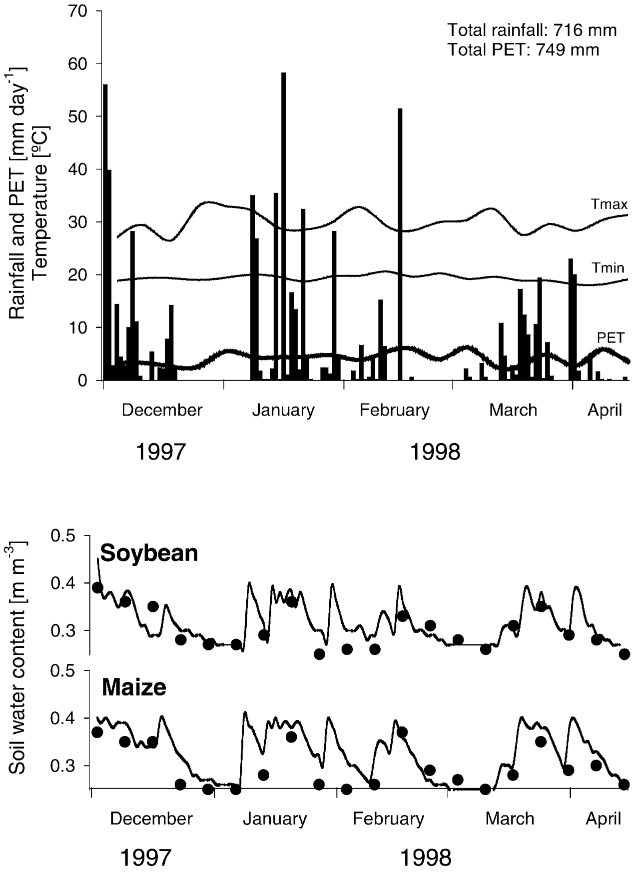

Figure 6. Measured and modelled soil water contents at 0.15 m depth in maize and soybean cropping systems in a Brazilian savanna Oxisol (means; $n = 3$) in comparison to daily rainfall, potential evapotranspiration (PET), and mean weekly maximum (Tmax) and minimum (Tmin) temperature.

indicates that in some circumstances large proportions of dissolved N can actually leach as DON.

DON appeared to be less mobile in acid subsoils than dissolved nitrate, since more organic than inorganic N, derived from the applied N, was retained in the subsoil, even though more nitrate was found in the soil solution than organic N derived from applied N (Figure 5). However, the proportion of DON in the soil solution increased from the topsoil to the subsoil. Therefore, immobilization processes must have occurred in the subsoil in order to explain a higher retention of organic N with a concurrent increase in the mobile DON.

According to our results, most of the DON that was leached into the subsoil was hydrophilic. Dissolved hydrophilic organic matter mainly consists of carbohydrates and is more mobile in soil than dissolved hydrophobic organic matter (Kaiser & Guggenberger 2000). Both fractions are strongly bound to oxides (Kaiser & Guggenberger 2000), and adsorption of the hydrophilic fraction may increase in acid subsoils. Acid subsoils, such as in the Oxisols studied, may therefore retain or retard not only dissolved nitrate, but also DON, and act as a temporary sink for leached N. Whether the SON in the subsoil is later leached as DON or nitrate cannot be resolved from the data obtained in this experiment. The proportion of nitrate in total leached N appeared to decrease with increasing depth as the adsorption of nitrate increased. This may indicate a greater importance of DON than nitrate losses of N from the agroecosystem.

The significant proportion of N leached and temporarily retained in the subsoil is potentially an important source of crop N uptake. The efficient depletion of this subsoil resource by crops, however, appeared to be limited given the large amounts of adsorbed nitrate found in the subsoil. Similar conclusions were drawn from maize cropping systems in Kenya by Mekonnen *et al.* (1997), who found increasing amounts of adsorbed nitrate in acid subsoils to a depth of 4 m. It is unclear whether any of the organic N retained in the subsoil is immediately available to crops, but this should be considered in future research.

## CONCLUSIONS

In the acid savanna soil under high precipitation intensities, retention of applied N was not only a function of adsorption and immobilization in the topsoil, but also of retention in the subsoil. In addition to nitrate adsorption in the acid subsoil, even more importantly the dynamics of organic N controlled total N losses. Applied ammonium was rapidly nitrified and immobilized in organic N and transported as DON through the soil profile. As a consequence, in the subsoil a greater proportion of the applied N was recovered in SON than in adsorbed inorganic N. The quality of DON is a relevant factor for transport and adsorption in the subsoil but is still poorly understood. Subsoil N dynamics play an important role in the N cycles in Oxisols: inorganic–organic N fluxes and transformations, as well as adsorption of DON, need to be investigated in future studies. Apart from the loss of N and consequent lower efficiency of fertilizer N use, N leaching should increasingly be perceived as a potential hazard to groundwater and drinking water resources in both temperate and tropical regions.

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