# ENVIRONMENTAL IMPACTS OF NITRIFICATION AND NITRATE ADSORPTION IN FERTILIZED ANDISOLS IN THE VALLE CENTRAL OF COSTA RICA

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A major scientific challenge for modern agriculture is control of off-site effects on the water resource. In the Valle Central of Costa Rica, coffee plantations may leach fertilizer-derived NO<sub>3</sub> to groundwaters, as a result of high fertilization rates (annually ~270 kg/ha as N), highly permeable and well structured Andisols, and high rates of annual runoff (>1000 mm). The objective of this study was to examine several aspects of the nitrification and NO<sub>3</sub> adsorption that control NO<sub>3</sub> leaching from these highly productive soils. Monthly collections from four Andisols indicated that soil NO3 varied seasonally, with NO3 accumulating to about 280 kg/ha in the upper meter of soil during the 5-month dry season. Soil NO<sub>3</sub> was reduced during wet season months, even though fertilization was confined to the wet season. During these months, soil NO<sub>3</sub> averaged about 140 kg/ha as N in the upper meter of soil, apparently reduced by wet season leaching, root uptake, and, possibly, dentrification. Field and laboratory incubations at different soil moisture and temperature regimes demonstrated how soil microflora mineralized N and nitrified NH4 at relatively high rates, even at low water potentials, e.g., <-1.5 MPa. During the dry season, field incubations suggested that nitrification rates were about 30 kg/ha per month as N in the upper 20 cm of soil. Relatively large contents of NO<sub>3</sub> can be adsorbed by these allophanous Andisols, especially at low pH (up to about 5 cmol/kg at pH <3). Nitrate adsorption potentially retards leaching of NO<sub>3</sub> to groundwater; however, the effectiveness of adsorption as a protection of groundwater quality is probably limited due to high inputs of fertilizer N

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and to liming management of coffee soils that maintains relatively high soil pH. Additional research into the coffee N cycle and fertilizer efficiency in coffee is needed to ensure high coffee productivity and to protect aquifer water quality in the Valle Central.

Improving the efficiency with which nitrogen (N) fertilizer is used by crop plants is a high priority topic for research. The efficiency of N fertilization in many crop systems is relatively low, and fertilizer N not used by crops or soil microbes may leach as nitrate  $(NO_3^-)$  into groundwater and potentially threaten the quality of the water resource.

In the Valle Central of Costa Rica, goals of high coffee production and high quality groundwater must be met jointly because of demands for both coffee production and groundwater quality. To maintain high coffee productivity, N is applied at high rates that average nationally about 270 kg/ha per year (Sanchez-Salas 1988). Two or three split applications of about 90 kg/ ha each are recommended to maximize yields, recommendations based on many years of doseresponse studies of coffee growth, physiology, and crop health (Carvajal 1984). Fertilizer N, a combination of ammonium sulfate and ammonium nitrate, is applied during the wet season, generally in May or June, August, and October or November. The efficiency with which fertilizer N is used by coffee is apparently relatively low. Sommer (1978) estimated that about 30% of the N applied as fertilizer was absorbed by coffee roots. Aboveground, coffee grows mainly during the wet season, and similarly, root activity is presumed to occur mainly during the wet season and to be concentrated in the upper meter of soil (Carvajal 1984).

A better understanding of the N cycle is important in the Valle Central because intensively managed coffee plantations cover large areas of mid-elevation slopes. Beneath this area, aquifers accumulate water used for drinking by San Jose and many other cities and smaller communities.

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Currently, NO<sub>3</sub> concentrations in groundwaters under coffee-growing areas of the Valle Central are up to 10-fold higher than in groundwaters beneath unfertilized pastures and forests (Reynolds-Vargas and Richter, manuscript submitted). In a 2-year study of 14 springs and wells, concentrations of NO<sub>3</sub>-N averaged 0.37 mg/L under unfertilized pastures and forests, compared with 2.1 to 4.4 mg/L under coffee and urban areas (Reynolds-Vargas and Richter, manuscript submitted).

To better understand soil N dynamics in fertilized coffee ecosystems, seasonal variations of soil  $NO_3^-$  should be better quantified, as should processes that control soil  $NO_3^-$  mobility. Two processes that are not well documented include N mineralization and nitrification as affected by soil moisture in this climate with pronounced wet-dry seasons, and nitrate adsorption in the Andisols that make up the majority of the soils that support coffee in the Valle Central. Both processes are potentially important to  $NO_3^-$  leaching in coffee ecosystems of Costa Rica, and they are also important to the study of soil N in general.

Soil moisture exerts strong control over N mineralization and nitrification (Stanford and Epstein 1974), especially in seasonal wet-dry climates in the tropics (Birch 1964; Greenland 1958; Wetselaar 1962; Sanchez 1976; Fassbender and Bornemisza 1987). Many of these studies in the tropics have reported that during the dry season, soil microbial activity becomes extremely low as a result of low water potential, and early in the wet season, the rewet soil explodes with microbial activity and nutrient mineralization. Soil moisture control over mineralization and nitrification is not well studied in the Andisols of the Valle Central that are managed for coffee. Such dynamics may have a strong influence on the leaching patterns and plant availability of  $NO_3^-$ .

Following nitrification, NO<sub>3</sub><sup>-</sup> cannot simply be assumed to be leached from Andisols, because such soils are potentially able to adsorb anions such as NO<sub>3</sub><sup>-</sup> (Kinjo et al. 1971). Adsorption may even retard NO<sub>3</sub><sup>-</sup> leaching (Singh and Kanehiro 1969). However, electrostatic forces that adsorb NO<sub>3</sub><sup>-</sup> are typically weak, and adsorption is a function of a complex of interrelated soil properties. Allophanous clays give Andisols their variable and potentially positive charge, but NO<sub>3</sub><sup>-</sup> adsorption is also affected by soil pH

(Uehara and Gillman 1981), organic matter (Black and Waring 1979), cation exchange capacity, competing anions (Parfitt 1978), and the soil's point of zero charge (Uehara and Gillman 1981).

Our overall research objectives were to investigate nitrification and  $NO_3^-$  adsorption as processes in fertilized coffee ecosystems that help control  $NO_3^-$  leaching. Specific research objectives were to: (i) estimate monthly  $NO_3^-$  contents in the upper meter of fertilized Andisols; (ii) evaluate effects of soil moisture on rates of mineralization and nitrification; (iii) determine relationships between  $NO_3^-$  adsorption and other soil properties; and (iv) evaluate the potential for  $NO_3^-$  adsorption to limit leaching of  $NO_3^-$  from soil profiles.

### **METHODS**

Study site

The Valle Central, in the Costa Rican central highlands, ranges in elevation from about 800 to 1600 m and is surrounded by volcanoes with elevations up to 3400 m. Soil properties vary with elevation, but at less than about 1600 m in the coffee growing regions of the valley, soils are dominated by Udands, Andisols with a udic moisture regime. The Udands were formerly classified as Dystrandepts (Perez et al. 1978, 1979) before the addition of Andisols to Soil Taxonomy as the eleventh soil order. These Udands are typically deep and highly porous, with low bulk density, high organic matter, and high allophane concentrations. Some properties of soils in the four most intensively studied plantations are described in Table 1.

Average annual rainfall ranges from about 2000 mm at 900 m elevation to 3000 mm at 2300 m elevation and is concentrated from May through November. Annual temperature in the coffee growing area of the Valle Central averages about 20°C. Annual evapotranspiration totals about 1000 to 1500 mm, and annual runoff (surface runoff plus leaching) ranges between 1000 and 2000 mm. When supporting coffee, soils typically receive a combination of ammonium sulfate and ammonium nitrate in three split applications during the wet season, generally in May or June, August, and October or November.

Field studies of soil nitrate contents

Three fertilized plantations (CICAFE, Rojas, and Tibas) were selected for intensive study of

 ${\bf TABLE~1}$  Chemical and physical properties of Udand soils of four coffee plantations in the Valle Central of Costa Rica

Property	Depth cm	CICAFE unfertilized	CICAFE fertilized	Rojas	Tibas
Organic matter (%)	0-20	6.2	5.9	12.2	5.5
	40-60	2.8	2.4	3.4	2.8
	80-100	1.3	1.3	1.0	1.2
pH in CaCl <sub>2</sub>	0-20	4.6	4.7	4.4	5.0
	40-60	5.8	4.8	5.2	5.6
	80-100	5.2	5.2	5.7	6.1
pH in NaF	0-20	10.3	10.2	10.7	10.0
	40-60	10.3	10.2	9.8	9.4
	80-100	10.2	10.0	8.8	8.9
Bulk density (g/cm³)	0-20	0.77	0.75	0.71	0.88
v (e)	40-60	0.67	0.77	0.96	0.90
	80-100	0.60	0.76	1.22	1.27
Field capacity water (%) <sup>a</sup>	0-20	47	54	60	39
,	40-60	55	57	55	41
	80-100	64	65	46	36
-1.5 MPa water (%) <sup>a</sup>	0-20	27	28	24	18
	40-60	29	32	25	20
	80-100	34	34	26	16

<sup>&</sup>lt;sup>a</sup> Soil water on mass basis.

monthly variations in soil  $NO_3^-$  contents and of mineralization and nitrification rates (Fig. 1). Annual fertilization to these plots averaged

about 270 kg/ha as N. In each plantation, a 1000-m<sup>2</sup> plot was installed that contained about 700 coffee plants. An unfertilized plot at CI-

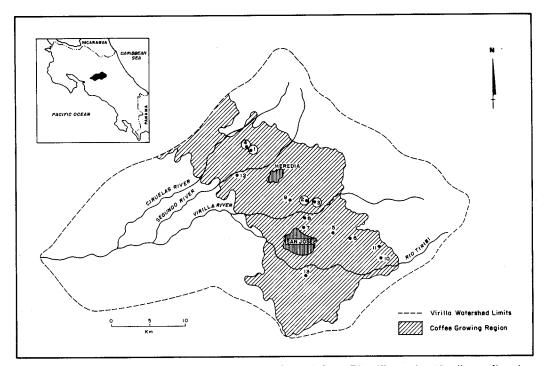


Fig. 1. Map of the Virilla subcatchment of the Valle Central, Costa Rica, illustrating 13 soil-sampling sites, including the four intensively studied coffee plantations (numbered 1 to 4).

CAFE was also selected with about one-third the area of the other plots, because plantation managers would not authorize a larger area to remain unfertilized. The unfertilized plot was last fertilized in May 1989 with 90 kg/ha as N. Details of fertilizer histories of these plots are reported in Reynolds (1991).

To estimate soil NO<sub>3</sub><sup>-</sup> contents, plots were subdivided into six subplots with equal areas. Soil samples were collected monthly from August 1988 to May 1990 as composites from each subplot. A 2.2-cm-diameter punch tube sampled soil from 0 to 20-cm, 40 to 60-cm, and 80 to 100-cm layers. During several dry months, soil physical conditions limited sampling at the CICAFE plots. Bulk density was estimated with soil cores from each of the six subplots.

Soils were returned to the laboratory within 5 hours after sampling. The soils were passed through a 6-mm screen, and water content was gravimetrically determined on subsamples dried at 105°C. Nitrate was extracted by shaking duplicate 4-g field-moist samples with 40 ml of 1 M KCl for 1 hour. Suspensions were centrifuged for 5 min at 3500 rpm and filtered through prewashed Whatman 42 filters. Extracts were refrigerated, prior to analysis, by automated azodye colorimetry for nitrate and by phenate colorimetry for ammonium (Reynolds 1991).

## Field and laboratory incubations

Monthly collections of soil indicate that soil NO<sub>3</sub><sup>-</sup> accumulated during dry seasons. This opened the question of the source of the dryseason soil NO<sub>3</sub><sup>-</sup>. To investigate the relationship of soil moisture to the rates of mineralization and nitrification, incubations with different moisture contents were conducted in the field and laboratory.

Field incubations were conducted for 30 days during the dry season, from mid-January through mid-February. In each plantation, 24 paired cores (8 cm dia, 12 cm deep) were taken beneath coffee plants. Cores were paired on either side of coffee plants, about 40 cm from the plant stem. One core of each pair was sieved and extracted to determine NH<sup>‡</sup> and NO<sup>3</sup><sub>3</sub> at the beginning of the incubation. The second core of each pair was carefully placed into a thin plastic bag and replaced into the core hole. These latter samples remained in the field for 30 days, at which time they were collected for analysis of

mineral N. Gravimetric water content was estimated by drying subsamples at 105°C.

Laboratory incubations were conducted to evaluate effects of a wide range of soil moisture contents on rates of mineralization and nitrification. Near the end of the dry season, in late March 1991, composite samples were collected for laboratory incubations from the 0 to 20-cm soil layer of each of the four plantations. Water content, NH<sub>4</sub>, and NO<sub>3</sub> were estimated at the beginning of the incubation. Water was added to field-moist 5-g samples to bring samples to one of four water contents to ensure that water potential spanned from <-1.5 MPa to about field capacity. Moisture content at -1.5 MPa was determined on a pressure plate, whereas field capacity was estimated from the moisture content that soils reached by the middle of the wet season. The monthly soil collections over two wet seasons substantiate these estimates of field capacity. Wet season water content was taken as an accurate estimate of field capacity because soils are very well drained as a result of structural development, and once soil moisture capacity is recharged during the mid-wet season, the near-daily rainfall helps ensure that soil moisture is relatively constant throughout the remainder of the wet season. Plant-available water capacity was estimated as the difference in water contents between -1.5 MPa and field capacity.

All laboratory incubations were conducted at 34.9°C in triplicate for 21 days. Soils from two plantations, however, the fertilized and unfertilized CICAFE plantations, were incubated at four moisture contents and four temperatures to evaluate interactive effects of water and temperature on soil N mineralization and nitrification.

Nitrate adsorption in Andisols of the Valle Central

In addition to the four coffee plantations intensively studied, nine additional plantations within the Valle Central were selected for studies of soil NO<sub>3</sub> adsorption. Soils in all plantations were classified as Dystrandepts by Perez et al. (1978, 1979) and are now classified as Udands. At each site, composite samples were made of 0 to 40-cm and 60 to 100-cm soil layers, composites that were collected from six individual cores using a 2.2-cm-diameter punch tube. Samples were stored in polyethylene bags for transport to the laboratory within several hours.

Sieved, field moist soils from the 13 coffee plantations were used for tests of NO<sub>3</sub> adsorption. Duplicate samples of 4.0 g were mixed in a centrifuge tube with 40 ml of 0.1 M KNO<sub>3</sub> that had been adjusted with HNO<sub>3</sub> to one of three pHs, 5.6, 3.8, and 2.1, before adding soils. Supensions were agitated gently for 30 min and centrifuged for 10 min at 3500 rpm. Supernatants were discarded, and this KNO<sub>3</sub> equilibration procedure was repeated four times. In the fourth equilibration, soil was allowed to remain in contact with the KNO<sub>3</sub> for 15 h. The final centrifugate was carefully and thoroughly removed and measured for pH.

Adsorbed plus interstitial NO<sub>3</sub> were then determined by extracting the 4-g samples of soil with 40 ml of 1 M KCl. The KCl suspensions were shaken for 60 min, centrifuged for 5 min at 3500 rpm, and filtered with prewashed Whatman 42 paper. Since a significant amount of NO<sub>3</sub> can be in the KNO<sub>3</sub> solution entrapped in the soil pores after the final KNO<sub>3</sub> equilibration, the volume of liquid retained by the soil was determined gravimetrically and its NO<sub>3</sub> content subtracted from the amount of  $NO_3^-$  extracted with 1 M KCl. The assumption that  $NO_3^-$  in interstitial solution was 0.1 M is robust and not likely to pose a problem with estimations of adsorption. To estimate adsorbed NO3, interstitial NO3 was subtracted from the total NO3 extracted by KCl.

A variety of physical and chemical properties were estimated in air-dried samples that had been passed through a 6-mm screen. Soil pH was measured in water, 0.01 M CaCl<sub>2</sub>, 1 M KCl, and 1 M NaF. Soil pH in NaF that is >9.4 has been taken to indicate high allophane activity (Fassbender and Bornemisza 1987). In addition, effective cation exchange capacity (ECEC) was estimated by the sum of exchangeable base cations plus KCl exchangeable acidity; total CEC was estimated from the sum of exchangeable base cations plus acidity determined with BaCl<sub>2</sub>-TEA buffered at pH 8.2 (Thomas 1982). Base saturation was estimated using both ECEC and total CEC determinations. Organic carbon was estimated with a Walkley-Black wet combustion method.

#### RESULTS AND DISCUSSION

Monthly variation in soil nitrate

Soil nitrate concentrations were often very high, due in large part to the high rate of N

fertilization. However, soil nitrate was typically highest during the dry season and lowest during the wet season, a somewhat unexpected pattern since fertilizers are applied during wet season months. Depending on the plantation, nitrate contents in the 0 to 20-cm layers averaged two-to four-fold greater in the dry season than in the wet season (Table 2). Nitrate that was deeper in the soil profile (>40 cm) also appeared to differ between dry and wet seasons, but not nearly as much as that in more surficial layers. In periodic samples tested for NH<sub>4</sub>, it was found that NO<sub>3</sub> was overwhelmingly the dominant form of mineral N.

In the upper 1 m of soil during the wet season,  $NO_3$ -N averaged 138 kg/ha in the three fertilized plantations, whereas during dry season months, soil  $NO_3$ -N averaged 279 kg/ha (Table 2). In the unfertilized soils, wet and dry season contents averaged 54 and 83 kg/ha, respectively.

Correlations between monthly soil NO<sub>3</sub> and soil moisture (which ranged from field capacity to less than -1.5 MPa) were strongly negative in the upper 20 cm of soil. Simple Pearson correlation coefficients were -0.81 in the unfertilized plantation and were also negative in the fertilized plots: -0.69 at CICAFE, -0.45 at Rojas, and -0.40 at Tibas. All correlations but Tibas were significant at the 0.05 probability level. Correlations in Tibas soil had a probability of about 0.07.

Since fertilizer N is applied during wet season months, the relatively low contents of soil nitrate in the wet season were of considerable interest. The seasonal pattern of soil NO3 in wet and dry months (Fig. 2) was associated with the seasonality of N removals. The potential for plant uptake, leaching loss, and possibly denitrification to remove soil NO3 are greatest during the wet season. In contrast, plant uptake (Carvajal 1984), leaching (Reynolds 1991), and possibly denitrification are diminished due to low soil water during the dry season. Beyond leaching of fertilizer into the profile in the late wet season and early dry season, there are two possible explanations for dry season increases in surface soil NO<sub>3</sub>: (i) continued mineralization and nitrification despite low soil water potential that is occasionally <-1.5 MPa in surficial layers and (ii) a movement of soil NO3 upward from moist subsoils into the dry surface soil. We evaluated the first of these possibilities with incubations in the field and laboratory.

TABLE 2 Soil moisture and soil nitrate contents during wet and dry season months (CV in parentheses)

		Wet seaso	on months	Dry sease	on months
Plantation	Depth cm	Soil water % by mass	Nitrate-N kg/ha	Soil water % by mass	Nitrate-N kg/ha
Unfertilized CICAFE	0-20	46 (1)	13 (17)	31 (25)	45 (38)
	40-60	54(2)	8 (46)	45 nsª	6 ns
	80-100	63 (2)	12 (96)	57 nsª	2 ns
	0-100		54		83
Fertilized CICAFE	0-20	49 (5)	29 (73)	34 (23)	116 (60)
	4060	55 (3)	17 (86)	45 (5)	30 (103)
	80-100	62 (3)	12 (46)	51 (8)	12 (39)
	0-100		96		252
Rojas	0-20	54 (10)	63 (48)	32 (24)	113 (37)
	40-60	49 (11)	26 (62)	35 (15)	35 (66)
	80-100	44 (3)	18 (37)	38 (30)	20 (1)
	0-100		174		270
Tibas	0-20	37 (6)	45 (63)	21 (25)	84 (40)
	40-60	38 (7)	25 (56)	24 (19)	34 (78)
	80-100	34 (3)	21 (37)	30 (6)	49 (119)
	0-100		149	` ′	267
All fertilized sites	0 - 100		138		279

<sup>&</sup>lt;sup>a</sup> Insufficient sample for CV estimate.

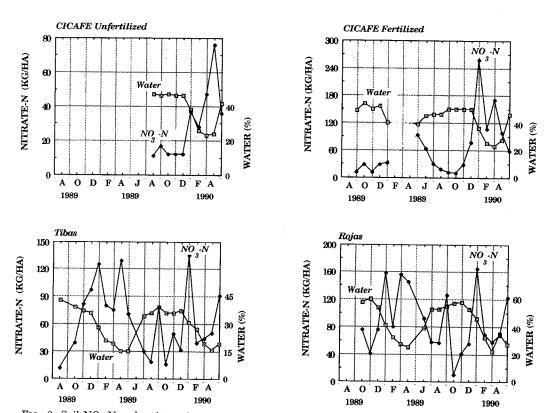


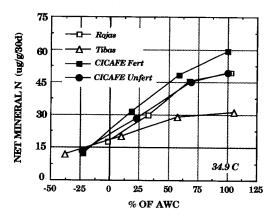
Fig. 2. Soil  $NO_3$ -N and moisture in upper 20-cm layer in monthly collections from four coffee plantations in the Valle Central.

Mineralization and nitrification at low soil water potential

Mineralization and nitrification rates were relatively high during the dry season incubations conducted in the field. In all four soils, nearly all N mineralized was nitrified. Rates of mineralization for the three fertilized soils averaged between 39.9 and 54.3  $\mu$ g of N per g over the 30day incubation. The unfertilized CICAFE soil mineralized soil N at 25.8  $\mu$ g/g in the 30 days. These rates were substantial, especially considering that these incubations were conducted in the middle of the dry season at low soil moisture. For example, mineralization and nitrification rates in surficial horizons of Oxisols and Ultisols (0 to 10 cm) collected during the rainy season in the Rio Negro basin of Venezuela averaged between 3.5 and 23.2 µg/g per 30 days (Montagnini and Buschbacher 1989). In more fertile forest soils in an Atlantic lowland forest in Costa Rica, mineralization and nitrification were estimated to range from approximately 15 to 65  $\mu g/g$  per 30 days in field incubations under relatively moist conditions (Vitousek and Denslow 1986).

During the field incubations in the coffee plantations, soil water contents were close to -1.5 MPa in the unfertilized and fertilized CI-CAFE soils and were somewhat higher than -1.5 MPa in the soils from the Rojas and Tibas plantations. Water contents of Rojas and Tibas soils averaged about 39 and 42%, respectively, of the water that could be held between -1.5 MPa and field capacity in these two soils (Table 3). The much lower water potentials of soil from the fertilized CICAFE soil may explain its lower rate of mineralization and nitrification compared with soils from Rojas and Tibas.

Laboratory incubations were also conducted to determine how mineralization and nitrifica-



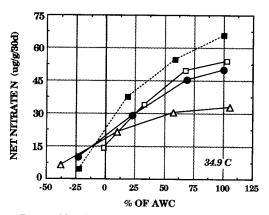


FIG. 3. Nitrification of surficial 20-cm soil from four coffee plantations as a function of soil moisture (34.9°C).

tion were controlled by soil water content. At -1.5 MPa moisture potential, mineralization and nitrification rates were about one-half to one-third rates observed at field capacity (Fig. 3). Nitrification oxidized nearly all of the N that was mineralized at all moisture contents. Al-

TABLE 3

Ammonium and nitrate accumulation during 30-day in situ incubations during the mid-dry season (coefficients of variation (%) in parentheses)

Plantation	Soil moisture		A	>7" . >Y	N
	% by mass	% of AWC <sup>a</sup>	Ammonium-N	Nitrate-N	N mineralization
				μg/g	
Unfertilized CICAFE	26.5	-3	7.5	18.3	25.8 (49)
Fertilized CICAFE	26.5	-6	2.7	37.5	39.9 (175)
Rojas	37.5	39	-3.0	57.3	54.3 (119)
Tibas	28.5	42	3.0	48.0	51.0 (87)

0

though the four soils mineralized and nitrified at different rates when they had a relatively high water potential, at a soil water potential of about -1.5 MPa, all soils mineralized and nitrified at similar rates (between 15 and 22.5  $\mu g/g$ per 30 days as N, Fig. 3). At water potentials below -1.5 MPa, both mineralization and nitrification proceeded although at much reduced rates.

Laboratory incubations were also conducted with CICAFE soils at four water contents and four temperatures from 18.3 to 43.2°C, to evaluate response of soil N to soil water as a function of temperature. Mineralization and nitrification differed in their response to the soil moisturetemperature combinations tested (Fig. 4). In both soils, increasing temperature from 18.3 to 43.2°C increased rates of N mineralization at all moisture contents. In contrast, increasing temperature from 18.3 to 34.9°C increased nitrification, but nitrification was greatly inhibited at 43.2°C in both fertilized and unfertilized soil (Fig. 4). These soils do not often reach such high temperatures (Reynold-Vargas, unpublished data), and perhaps the most significant result of these temperature response data is that under relatively lower temperature treatments. For example, even at 18.3°C, nitrification averaged about 15  $\mu$ g/g per 30 days at -1.5 MPa (Fig. 4). In 20-cm soil depth, this rate is numerically equivalent to 30 kg/ha per month, a relatively high rate considering the low water potential and temperature. Since rates of mineralization and nitrification appeared to be relatively high despite low water potential, the accumulation of soil NO<sub>3</sub> during the dry season is attributed at

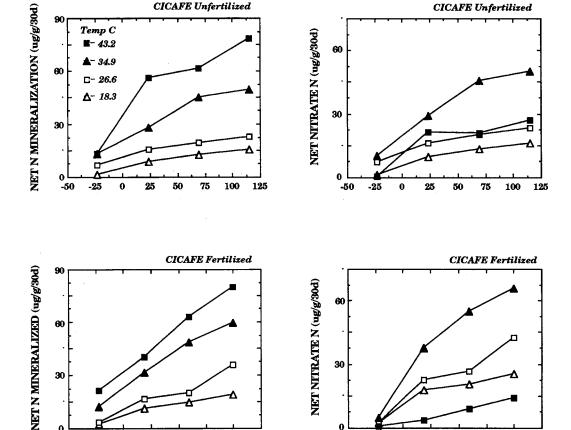


FIG. 4. Mineralization and nitrification of surficial 20-cm soil from fertilized and unfertilized CICAFE soils as a function of soil moisture and temperature.

50

% OF AWC

100

125

0

-50

-25

25

% OF AWC

50

75

100

125

TABLE 4

Comparison of nitrate adsorption properties of surface soils (0–40 cm) and subsoils (60–100 cm) with associations between the two soil depths tested with simple correlation coefficient	oroperties of surface	soils (0–40 cm	) and subsoils (60–100 correlation coefficieni	100 cm) with ent	associations betwee	ı the two soil dept.	hs tested with simple
Dronarty	Thit	Sur	Surface soils	8	Subsoils	Correlation	
roperty	OIIII	Mean	Range	Mean	Range	coefficient	Significance
Adsorption at pH 2.1	cmol/kg	2.61	1.35-4.99	3.06	1.18-5.12	0.77	*
Adsorption at pH 3.8	cmol/kg	0.28	-0.53 - 1.85	0.38	-0.24 - 1.11	0.78	**
Adsorption at pH 5.6	m cmol/kg	0.38	-0.48 - 1.80	0.27	-0.41 - 1.43	0.80	*
Final pH (initial pH 2.1)	Hd	2.5	2.3-2.7	2.3	2.2-2.7	0.40	
Final pH (initial pH 3.8)	Hď	4.9	4.0-5.8	5.1	4.8-5.4	0.75	**
Final pH (initial pH 5.6)	Hd	5.3	4.3-6.3	5.3	4.4-5.8	-0.11	
pH in water	Hď	5.8	4.4-6.6	6.4	5.9-6.9	0.55	*
pH in CaCl <sub>2</sub>	Hd	5.1	4.1-5.8	5.6	5.2 - 6.0	0.65	*
pH in NaF	Hd	10.5	9.5-11.2	8.6	8.9-10.8	0.55	*
ECEC	cmol/kg	8.54	4.10 - 15.4	99.6	4.58 - 17.2	0.56	*
Base saturation	%	87	45-99	96	69–66	0.53	(0.06)
Organic matter	%	7.2	4.3-13.2	3.0	1.3-4.6	-0.21	
C/N	mass ratio	14	11–16	14	10-17	0.3	
Water at $-1.5~\mathrm{MPa}$	% by mass	27	22-41	25	15-32	-0.24	

least partly to continued mineralization and nitrification during a season in which mineral N removals are greatly reduced.

Nitrate adsorption in Andisols of the Valle Central

The rate at which soil NO<sub>3</sub> is leached is affected by adsorption reactions, and many of the Valle Central Andisols can potentially adsorb considerable concentrations of NO<sub>3</sub>. Adsorption varied greatly among soils, but in all soils adsorption was highest at low pH (Table 4). At the lowest pH used for adsorption, 2.1, adsorption of NO<sub>3</sub> ranged from 1.2 to 5.1 cmol/kg.

Surface soils and subsoils adsorbed similar concentrations of NO<sub>3</sub> (Table 4), and, in fact, adsorption in surficial layers was strongly correlated with adsorption in subsoils (Table 4). For example, the Andisols of CICAFE, used previously for mineralization studies, adsorbed considerable NO<sub>3</sub> in both surface and subsoils, with adsorption in pH 2.1 solutions ranging from 3.5 to 4.8 cmol/kg. In contrast, other profiles adsorbed relatively little NO<sub>3</sub> in both surface or subsoil layers. The soils of the Tibas plantation, for example, adsorbed about 1.5 cmol/kg of NO<sub>3</sub> at pH 2.1 in both surface and subsoil layers.

A correlation matrix demonstrated how strongly nitrate adsorption was associated with soil acidity (Table 5). Soil pH (whether in water or 0.01 M CaCl<sub>2</sub>), ECEC, and base saturation were each negatively correlated with nitrate adsorption (Table 5). Similarly, KCl-exchangeable acidity and delta pH (the difference in pH in 1 M KCl and in water) were positively correlated

with NO<sub>3</sub> adsorption. We conceive of the NO<sub>3</sub> adsorption reaction being an electrostatic, nonspecific anion exchange in which the protonation of the soil surface exerts strong control over adsorption (Hingston et al., 1967).

Given the importance of soil pH to NO<sub>3</sub> adsorption, the standard liming practices in coffee management not only elevate soil pH but also diminish potential adsorption in NO3 in these variable charge soils. The pH in 0.01 M CaCl<sub>2</sub> of the 13 surface soils averaged 5.1, and subsoil pH averaged 5.6, relatively high values for a CaCl<sub>2</sub> pH (Table 4). Moreover, the regular fertilizer inputs of more strongly adsorbing anions than NO<sub>3</sub>, including PO<sub>4</sub>, SO<sub>4</sub>, and even BO<sub>4</sub>, also tend to promote NO<sub>3</sub> desorption and leaching (Parfitt 1978). Thus, in the field, although only 0.1 cmol/kg of adsorption sites may account for 140 kg/ha of NO<sub>3</sub>-N per ha in a meter of soil, liming and fertilization practices probably limit NO<sub>3</sub> adsorption and promote NO<sub>3</sub> mobilitv.

#### CONCLUSION

A more technical understanding of the N dynamics of soils that support coffee in the Valle Central is clearly important to maintain high coffee production and to protect the quality of groundwater that is used for drinking. Field and laboratory incubations demonstrated that mineralization and nitrification are quite active even at low water potentials (<1.5 MPa), and at relatively low temperatures (<20°C), and that  $NO_3^-$  can accumulate in the soil profile during the dry season. The Andisols' ability to retard

TABLE 5

Correlation matrix among soil properties in surface soil (0–40 cm in upper rows) and subsoils (60–100 cm in lower rows)

Property	pH in CaCl <sub>2</sub>	pH in NaF	ECEC	Base saturation	Delta pH	Organic matter
Adsorption at pH 2.1	-0.68**	0.42 (0.14)	-0.71**	-0.58*	0.52 (0.07)	0.14
• •	-0.52(0.07)	0.74**	-0.48(0.10)	-0.61*	0.71**	0.72**
pH in CaCl <sub>2</sub>		-0.40	0.75**	0.90**	-0.65*	-0.56*
-		-0.51(0.08)	0.54 (0.06)	0.59*	-0.52(0.07)	-0.71**
pH in NaF			-0.72**	-0.32	0.52(0.07)	0.71**
•			-0.78**	-0.80**	0.81**	0.74**
ECEC				0.65**	-0.51(0.07)	-0.26
				0.81**	-0.76**	-0.78**
Base saturation					-0.72**	-0.58*
					-0.66**	-0.72
Delta pH						0.71**
*						0.74**

NO<sub>3</sub> leaching by electrostatic adsorption appears limited due to high rates of liming and fertilization. Nonetheless, fundamental processes and fluxes of the coffee N cycle have yet to be estimated, denitrification is not yet explored in much detail, and the hydrogeologic dynamics of NO<sub>3</sub> leaching need to be more fully quantified. The important goals of coffee production and groundwater protection strongly argue for continued research to gather this biogeochemical information.

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