

# Kinetics of Nonexchangeable Ammonium Release from Soils

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## ABSTRACT

The rate of nonexchangeable  $\text{NH}_4^+$  release from soils can have a significant effect on N dynamics and environmental quality. Nonexchangeable  $\text{NH}_4^+$  is that N fraction which is fixed in the interlayers of clay minerals. The objective of this study was to determine the kinetics of nonexchangeable  $\text{NH}_4^+$  release from two topsoils from Germany [Giessen Ap (Aqualf) and Hungen Ap (Alfisol)] and from two subsoils, one from Germany [Hungen C (Alfisol)] and one from Kentucky [Shrouts Bt (Hapludalf)]. Calcium-saturated, freeze-dried soils were extracted with H-resin for 0.25 to 384 h. Sodiummethylmercuriothio-salisylate (Thimerosal) was added to the soil/H-resin suspension to inhibit microbiological ammonification. The kinetics of nonexchangeable  $\text{NH}_4^+$  release from the soils were biphasic and were best described by Elovich and heterogeneous diffusion models. The release of nonexchangeable  $\text{NH}_4^+$  as a percentage of total nonexchangeable  $\text{NH}_4^+$  in the soils ranged from 4 to 25% and was lower in subsoils than in topsoils. This was ascribed to the higher levels of indigenous nonexchangeable  $\text{NH}_4^+$  in the subsoils, which is more tightly held than recently fixed nonexchangeable  $\text{NH}_4^+$ .

**F**IXED OR NONEXCHANGEABLE AMMONIUM ( $\text{NH}_4^+$ ) can be an important reservoir of N in soils. Schachtschabel (1961) defined nonexchangeable  $\text{NH}_4^+$  as that fraction that is fixed in the inorganic fraction of the soil components, such as mica, vermiculite, and illite clay minerals, and that is not exchangeable with neutral salt solutions. Nonexchangeable  $\text{NH}_4^+$  can also be defined as that N fraction that is analyzed after potassium hypobromite oxidation, leaching with 0.5 M KCl, and digestion with a mixture of 5 M HF/1 M HCl (Silva and Bremner, 1966). Indigenous or native nonexchangeable  $\text{NH}_4^+$  is that  $\text{NH}_4^+$  that was fixed during the genesis of silicates. The recently or newly fixed nonexchangeable  $\text{NH}_4^+$  is defined as that  $\text{NH}_4^+$  that was fixed after the native nonexchangeable  $\text{NH}_4^+$  and resulted from mineralization of soil organic matter and organic and mineral fertilizers (Schachtschabel, 1961). Indigenous nonexchangeable  $\text{NH}_4^+$  is much less easily released than recently fixed nonexchangeable  $\text{NH}_4^+$ , since the former may be trapped more in the center of the interlayers, while recently fixed  $\text{NH}_4^+$  may be fixed more in the peripheral zone of the interlayers (Scheffer and Schachtschabel, 1984).

The amount of nonexchangeable  $\text{NH}_4^+$  in soils is greatly affected by the clay content and by the types of clay minerals that are present. Vermiculite, mica, and illite, and to some extent smectites (montmorillonite, beidellite), are the clay minerals that have the greatest capacity to fix  $\text{NH}_4^+$ . Said (1973) reported that soils from Sudan, in which montmorillonite was the most abundant clay mineral, contained only small amounts of nonexchange-

able  $\text{NH}_4^+$  ranging between 30 and 60 mg N  $\text{kg}^{-1}$  soil. Scherer and Weimar (1994) applied slurry to different soils and they showed that soils that contained 14% montmorillonite and 13.6% vermiculite in the clay fraction fixed more  $\text{NH}_4^+$  than soils that had 30% montmorillonite and 14% vermiculite in the clay fraction. Beidellite, in contrast to montmorillonite, is a high  $\text{NH}_4^+$  and  $\text{K}^+$  fixing smectite, due to isomorphic substitution in the tetrahedral layer (Niederbudde et al., 1983; Feigenbaum et al., 1994).

Shales and granites can contain indigenous nonexchangeable  $\text{NH}_4^+$ . Stevenson (1959) found that nonexchangeable  $\text{NH}_4^+$  in shales varied from 330 to 420 mg N  $\text{kg}^{-1}$  and ranged from 5 to 27 mg N  $\text{kg}^{-1}$  in granites. Schachtschabel (1961) reported that marsh soils in Northern Germany contained between 150 and 850 mg nonexchangeable  $\text{NH}_4^+$ -N  $\text{kg}^{-1}$  soil. Sparks et al. (1979) found that the Shrouts soils (fine, mixed, mesic Typic Hapludalf) in Kentucky contained in average of 365, 463, 433, 469, and 543 mg N  $\text{kg}^{-1}$  nonexchangeable  $\text{NH}_4^+$  in the Ap, B21t, B22t, C, and Cr horizons, respectively. The high levels of indigenous nonexchangeable  $\text{NH}_4^+$  in these soils were ascribed to the shale parent materials. Baethgen and Alley (1986) found that nonexchangeable  $\text{NH}_4^+$  ranged from 600 to 3000 kg N  $\text{ha}^{-1}$  in the A and B horizons of Virginia soils. In general, nonexchangeable  $\text{NH}_4^+$ , as a percentage of total soil N, increases with increasing soil depth as clay content increases (Sparks et al., 1979; Nette and Resch, 1992).

There are dynamic, equilibrium reactions between nonexchangeable, exchangeable, and solution  $\text{NH}_4^+$ . Fixation and release depends on the level of  $\text{NH}_4^+$  in the soil solution, the type of clay minerals present in the soil, and wetting and drying (Nommik and Vathras, 1982). As levels of solution  $\text{NH}_4^+$  increase, fixation and adsorption of  $\text{NH}_4^+$  on exchange sites of clay minerals and organic matter also can increase. Likewise, with higher levels of nonexchangeable  $\text{NH}_4^+$ , release could occur and exchangeable  $\text{NH}_4^+$  would increase in the soil solution.

Fixation is usually faster than release of  $\text{NH}_4^+$  (Drury and Beauchamp, 1991). Drury et al. (1989) found that 18 to 23% of added  $^{15}\text{NH}_4^+$  was fixed after a 15-d incubation period in soils with high vermiculitic contents. Kowalenko (1978) found that 66% of the  $\text{NH}_4^+$  that was fixed in 1.7 d was released in 86 d. Drury and Beauchamp (1991) showed that  $\approx 10\%$  of  $\text{NH}_4^+$  fixed in 30 d was released in 30 d.

Nonexchangeable  $\text{NH}_4^+$  can be an important source of slow release N for plants and microbes and perhaps could even impact groundwater quality. Investigations by Mengel and Scherer (1981) on western German loess soils and by Li et al. (1990) on Chinese loess soils have shown that considerable amounts of nonexchangeable  $\text{NH}_4^+$  were released during the vegetative growth period of crops, while  $\text{NH}_4^+$  fixation occurred after crop harvest. Nonexchangeable  $\text{NH}_4^+$  was also shown to be important

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**Table 1. Physicochemical characteristics of soils.**

Soil	Clay	Silt	Sand	Organic matter	Carbonates	pH (H <sub>2</sub> O)	CEC	Extractable K <sup>†</sup>
				g kg <sup>-1</sup>				
Giessen Ap	304	590	65	41	— ‡	6.0	28.4	69
Hungen Ap	302	625	54	19	—	6.8	21.4	82
Hungen C	199	621	55	4	121	8.0	12.8	39
Shrouts Bt	582	393	14	11	—	5.6	24.1	121

† Determined using Mehlich-I Extractant.

‡ Not detectable.

to plants growing in paddy rice (*Oryza sativa* L.) soils that contained vermiculite and high-charged smectites (Keerthisinghe et al., 1984; Schnier et al., 1987; Chen et al., 1989).

It has generally been found that aging (residence time) and the source of NH<sub>4</sub><sup>+</sup> affects the availability of nonexchangeable NH<sub>4</sub><sup>+</sup>. Newly fixed NH<sub>4</sub><sup>+</sup>, resulting from fertilizer application, is more available to plants than indigenous nonexchangeable NH<sub>4</sub><sup>+</sup> (Black and Waring, 1972; Kudeyarov, 1981; Mengel and Scherer, 1981; Keerthisinghe et al., 1984). Nommik (1966) found that 37% of newly fixed NH<sub>4</sub><sup>+</sup> could be released on nitrification within a 10-wk incubation period, and Dou and Steffens (1995) showed that 90 to 95% of newly fixed <sup>15</sup>NH<sub>4</sub><sup>+</sup> was released during a 14-wk period when perennial ryegrass (*Lolium perenne* L.) was grown under greenhouse conditions.

A number of investigations have shown that NH<sub>4</sub><sup>+</sup> fixation and release of nonexchangeable NH<sub>4</sub><sup>+</sup> from fertilizer sources within a growing season is important (Sowden, 1976; Kowalenko and Cameron, 1976; Kowalenko and Ross, 1980; Li et al., 1990; Drury et al., 1991; Green et al., 1994). Kowalenko (1978) reported that under field conditions, 66% of newly fixed NH<sub>4</sub><sup>+</sup> was released in the first 86 d, with the remaining fixed NH<sub>4</sub><sup>+</sup> being strongly retained during the next 425 d. The average daily release of nonexchangeable NH<sub>4</sub><sup>+</sup> was 1.70 and 0.65 kg N ha<sup>-1</sup> between 19 June 1974 to 1 Aug. 1974 and between 1 Aug. 1974 to 13 Sept. 1974, respectively (Kowalenko, 1978). Sowden (1976) found that 40 to 50% of added NH<sub>4</sub><sup>+</sup> was fixed and not available to nitrification and leaching. Native nonexchangeable NH<sub>4</sub><sup>+</sup> remained constant for ≈ 100 d, then decreased 20 to 30%.

It is well established that nonexchangeable NH<sub>4</sub><sup>+</sup> release can play important roles in the dynamic N cycle in soils. However, beyond a study by Scott et al. (1958) on vermiculite, little is known about the kinetics of nonexchangeable NH<sub>4</sub><sup>+</sup> release from soil components and particularly from soils. Accordingly, the objectives of this study were to determine the kinetics of nonexchangeable NH<sub>4</sub><sup>+</sup> from four soils that contained different levels and sources of nonexchangeable NH<sub>4</sub><sup>+</sup>. The mechanism

of this release was assessed using different chemical and physical nonequilibrium models.

## MATERIALS AND METHODS

Two topsoil samples from Germany [Giessen Ap (Aqualf) and Hungen Ap (Alfisol derived from loess)] at 0- to 0.25-m depth and two subsoil samples, a Hungen C (Alfisol derived from loess) at 0.8- to 1.0-m depth from Germany and one from Kentucky [Shrouts Bt (Hapludalf)] at 0.10- to 0.20-m were chosen to examine the effect of clay mineralogy and applied and indigenous NH<sub>4</sub><sup>+</sup> on the kinetics of nonexchangeable NH<sub>4</sub><sup>+</sup> release. We assumed that the two topsoils contained less indigenous nonexchangeable NH<sub>4</sub><sup>+</sup> than the two subsoils. The Giessen Ap soil was selected because in incubation experiments with green manure, this soil exhibited a relatively high capacity to fix NH<sub>4</sub><sup>+</sup> (Steffens et al., 1996). The two soil samples from the Hungen site were chosen because soils derived from loess often contain considerable concentrations of nonexchangeable NH<sub>4</sub><sup>+</sup> (Scherer, 1993). The Shrouts soil contains large quantities of indigenous nonexchangeable NH<sub>4</sub><sup>+</sup> (Sparks et al., 1979).

In preparation for characterization analyses, the soils were air dried and ground to pass a 1-mm sieve. Basic physicochemical and mineralogical characteristics of the soils including particle size, mineralogical analyses of the <2-μm clay fraction, pH, organic matter, cation-exchange capacity (CEC), extractable P and K, and carbonates were determined using standard methods (Klute, 1986; Page, 1982) and are shown in Tables 1 and 2, respectively. The clay fraction of the Shrouts Bt soil was predominately mica while illite and montmorillonite were prevalent minerals in the clay fraction of the German soils (Table 2).

The Giessen soil was in grassland until 1982. During this time, ≈ 100 kg N ha<sup>-1</sup> were applied annually. Since 1983, the Giessen soil was cropped and ≈ 100 to 200 kg N ha<sup>-1</sup> were applied annually in the springtime. The Hungen soil has been cropped extensively. Since 1975, a crop rotation of sugarbeet (*Beta vulgaris* L.)-wheat (*Triticum aestivum* L.)-barley (*Hordeum vulgare* L.) has been used. With beets, 50 to 150 kg N ha<sup>-1</sup> were applied annually, while with wheat and barley, N was applied at a rate of 120 to 180 kg N ha<sup>-1</sup>, three times annually. The form of N applied to the German soils was NH<sub>4</sub>NO<sub>3</sub>. The Shrouts soil has been in grassland with little, if any, N application. The parent material is high in shale.

## Nitrogen Indices

Exchangeable NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and the low molecular weight organic N fraction (N<sub>org</sub>) were extracted with 0.01 M CaCl<sub>2</sub> (Houba et al., 1986). Total nonexchangeable NH<sub>4</sub><sup>+</sup> was analyzed according to Silva and Bremner (1966). One molar HCl was used to extract the peripheral nonexchangeable NH<sub>4</sub><sup>+</sup>, which is defined as the NH<sub>4</sub><sup>+</sup> determined by subtracting exchangeable NH<sub>4</sub><sup>+</sup> from 1 M HCl extractable NH<sub>4</sub><sup>+</sup> (Dressler

**Table 2. Mineralogy of the clay fraction of the soils.**

Soil	Mica	Illite	Montmo-	Vermic-	Kaolinite	Feldspars	Quartz
			rillonite	ulite			
Giessen Ap	—	1†	2	3	4	5	6
Hungen Ap	—	1	2	5	6	4	3
Hungen C	—	1	4	5	6	2	3
Shrouts Bt	1	—	—	3	2	5	4

† 1 = most abundant, 6 = least abundant.

and Mengel, 1985). Total N was analyzed with the Kjeldahl method (Bremner and Mulvaney, 1982). Nitrogen fractions in the 0.01 M CaCl<sub>2</sub> and in 1 M HCl extracts were measured colorimetrically using a continuous flow autoanalyzer (Braan & Lübke Co., Hamburg, Germany).

### Effect of Thimerosal on Ammonification

Thimerosal was used by Ahrens and Thalmann (1970) as a nonspecific inhibitor of microbiological activity in soils. The effects of Thimerosal on inhibition of ammonification during the nonexchangeable NH<sub>4</sub><sup>+</sup> release study were investigated, since ammonification of amino-N could occur during the release study. Ammonification is an oxygen and pH independent microbiological process (Mengel, 1991). In another study, arginine, to equal 80 mg N kg<sup>-1</sup> soil, as a substrate of ammonification was added to the soil/H-resin/Thimerosal suspension of the Giessen Ap and Hungen Ap soils. These soil suspensions and comparable blank samples in duplicate treated with arginine, were equilibrated for 192 and 384 h. The separation of resin from the soil and the analytical determinations carried out are given below.

### Kinetics of Nonexchangeable Ammonium Release

Before performing the kinetic studies, each of the soils was Ca-saturated with 0.01 M CaCl<sub>2</sub> to remove exchangeable NH<sub>4</sub><sup>+</sup>. The soils were washed with distilled water until a negative test for Cl<sup>-</sup> was obtained with 1 M AgNO<sub>3</sub> and then freeze-dried. Duplicate 2-g samples of Ca-saturated freeze-dried soil [<60 mesh (<0.25 mm)] were added to 100 mL polypropylene flasks with 2 g of freeze-dried H-saturated resin [Rexyn, 20–50 mesh (0.30–0.82 mm), Fisher Scientific Co., Pittsburgh, PA] and 50 mL of a 158.1-μM Thimerosal solution (Sodiummethylmercurithio-salicylate, C<sub>6</sub>H<sub>5</sub>HgNaO<sub>2</sub>S). The active group of the Rexyn-resin was R-SO<sub>3</sub><sup>-</sup>, and the CEC was 5200 cmol kg<sup>-1</sup>. The H-saturated resin was prepared in a column by leaching the resin with 2 M HCl and washing out the salts with distilled water until no Cl<sup>-</sup> was detected by 1 M AgNO<sub>3</sub>. Then the H-resin was freeze-dried. Preliminary experiments showed that freeze-drying only slightly altered the CEC of the resin.

Nommik and Vathras (1982) have noted that freezing of soils at 258 to 256 K resulted in a small increase in NH<sub>4</sub><sup>+</sup> fixation. Accordingly, we studied the effect of freeze-drying on nonexchangeable NH<sub>4</sub><sup>+</sup> release. No release occurred from three of the soils and an insignificant quantity of NH<sub>4</sub><sup>+</sup> release occurred from the Giessen Ap soil.

The soil/resin/Thimerosal solution suspensions were equilibrated in duplicate at 298 K for 0.25, 0.50, 1, 2, 4, 8, 16, 24, 48, 96, 192, and 384 h on a reciprocating shaker with a speed of 56 oscillations min<sup>-1</sup>. The 384-h equilibration period was a sufficient time to permit nonexchangeable NH<sub>4</sub><sup>+</sup> release to approach a steady state. For each equilibration time, duplicate blank samples (2 g of freeze-dried H-resin plus 50 mL of 158.1-μM Thimerosal solution) were also equilibrated.

To minimize weathering and abrading of the soil particles,

the shaker was operated on a 1 h on, 1 h off schedule for the first 8 d of equilibration. After 8 d of equilibration, the samples were shaken 1 h d<sup>-1</sup>. This equilibration procedure was also used by Martin and Sparks (1983), who determined the kinetics of nonexchangeable K<sup>+</sup> release from soils and their findings indicated that particle abrasion and mineral alterations were not significant during the K<sup>+</sup> release process.

After equilibration, the resin was separated from the soil suspension on a 0.25-mm sieve, and the resin was washed three times with deionized water. Then the resin was transferred to a funnel, which contained Whatman 22 filterpaper, and it was leached with 80 mL 1 M KCl to desorb the released nonexchangeable NH<sub>4</sub><sup>+</sup>. The leachate was made up to a volume of 100 mL and the NH<sub>4</sub><sup>+</sup> concentrations were measured colorimetrically using a continuous flow autoanalyzer (Braan & Luebbe Co.).

The soil suspension was centrifuged for 20 min at 7649 × g and 293 K. The pH of the supernatant was analyzed and the concentrations of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were measured as before. The concentrations of NH<sub>4</sub><sup>+</sup> in the supernatant of the soil/H-resin suspension were low indicating that there was no inhibition of nonexchangeable NH<sub>4</sub><sup>+</sup> release due to excessive levels of NH<sub>4</sub><sup>+</sup> in the solution phase. The average concentrations during the time in which nonexchangeable NH<sub>4</sub><sup>+</sup> release was studied were 2.2, 3.3, 1.5, and 1.3 μmol NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> for the Giessen Ap, Hungen Ap, Hungen C, and Shrouts Bt soils, respectively. Such low concentrations are comparable with those found for soil/H-resin suspensions used in previous studies of nonexchangeable K<sup>+</sup> release (Martin and Sparks, 1983).

### Kinetic Models

A number of kinetic models were applied to nonexchangeable NH<sub>4</sub><sup>+</sup> release data including the Elovich equation, parabolic diffusion law, power function, zero-order, first-order, and a heterogeneous diffusion model (Sparks, 1989, 1995) and are given below:

$$\text{Elovich equation} \quad Y = a + b \ln t \quad [1]$$

$$\text{Parabolic diffusion law} \quad Y = a + bt^{1/2} \quad [2]$$

$$\text{Power function} \quad \ln Y = \ln a + b \ln t \quad [3]$$

$$\text{Zero-order} \quad (Y - Y_t) = a - bt \quad [4]$$

$$\text{First-order} \quad \ln(Y - Y_t) = a - bt \quad [5]$$

where  $Y$  denotes the released nonexchangeable NH<sub>4</sub><sup>+</sup> at 384 h,  $t$  = time (h),  $Y_t$  = released nonexchangeable NH<sub>4</sub><sup>+</sup> at time  $t$ , and  $a$  and  $b$  are constants. The heterogeneous diffusion model is presented in Eq. [6] and [7] in the next section.

## RESULTS AND DISCUSSION

The quantity of nonexchangeable NH<sub>4</sub><sup>+</sup> in the four soil horizons ranged from 122 mg N kg<sup>-1</sup> in the Hungen Ap and C horizons to 518 mg N kg<sup>-1</sup> in the Shrouts Bt horizon (Table 3). The quantity of nonexchangeable

Table 3. Nitrogen chemistry of four soils.

Soil	NO <sub>3</sub> <sup>-</sup>	Exchangeable NH <sub>4</sub> <sup>+</sup>	N <sub>organic</sub>	1 M HCl	Nonexchangeable NH <sub>4</sub> <sup>+</sup>	Total N	Total N as
				extractable NH <sub>4</sub> <sup>+</sup>			nonexchangeable NH <sub>4</sub> <sup>+</sup> -N
mg N kg <sup>-1</sup>							
Giessen Ap	16.8	1.9	15.7	12.8	243.4	2780	8.8
Hungen Ap	2.2	0.3	7.6	6.8	122.1	1170	10.4
Hungen C	0.3	0.2	1.4	3.9	121.7	360	33.8
Shrouts Bt	0.6	1.1	5.4	3.2	518.3	1000	51.8

**Table 4.** Effect of thimerosal addition on the release of  $\text{NH}_4^+$  in treatments with and without arginine application.

Time h	Giessen Ap		Hungen A	
	- Arginine	+ Arginine	- Arginine	+ Arginine
	mg $\text{NH}_4^+$ -N $\text{kg}^{-1}$			
192	46.1	45.0 <sup>ns</sup> †	24.6	26.6 <sup>ns</sup>
384	50.9	52.9 <sup>ns</sup>	31.1	31.1

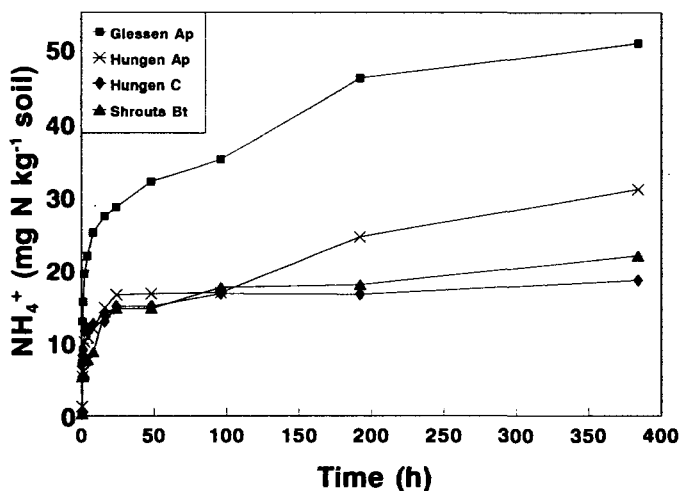
† ns = differences were not statistically significant.

$\text{NH}_4^+$  in the Shrouts Bt and Giessen Ap soils was higher than in the Hungen Ap and C soils (Table 3). This can be related to the higher clay contents in these soils that were dominated by mica, illite, and vermiculite and to the indigenous  $\text{NH}_4^+$  derived from the shale parent material in the Shrouts Bt soil (Tables 1 and 2). The observed nonexchangeable  $\text{NH}_4^+$  levels in the soils are in the range reported by others (Sparks et al., 1979; Scherer, 1993). The percentage of the total N as nonexchangeable  $\text{NH}_4^+$ -N was much higher (Table 3) in the subsoil horizons (Hungen C, 33.8%; Shrouts Bt, 51.8%) than in the topsoil horizons (Giessen Ap, 8.8%; Hungen Ap, 10.4%). This is consistent with findings of others (Sparks et al., 1979; Nette and Resch, 1992).

Although the Shrouts Bt soil contained the highest amount of nonexchangeable  $\text{NH}_4^+$ , 1 M HCl extractable  $\text{NH}_4^+$  was low compared with the other soils. The amount of 1 M HCl extractable  $\text{NH}_4^+$  in the topsoils (Giessen Ap and Hungen Ap) was higher than in the subsoils (Hungen C and Shrouts Bt; Table 3).

The highest amount of exchangeable  $\text{NH}_4^+$  was found in the soils that contained the highest quantity of nonexchangeable  $\text{NH}_4^+$  (Table 3). This finding is consistent with the strong correlation often observed between nonexchangeable  $\text{NH}_4^+$  and exchangeable  $\text{NH}_4^+$  (Sparks et al., 1979).

Since the topsoil samples contained more organic matter than the subsoil samples, the concentrations of  $\text{CaCl}_2$  extractable  $\text{NO}_3^-$  and  $\text{N}_{\text{org}}$  were higher in the Giessen Ap and Hungen Ap soils than in the Hungen C and Shrouts Bt soils (Table 3).



**Fig. 1.** Cumulative nonexchangeable  $\text{NH}_4^+$  release vs. time for the four soils.

**Table 5.** Nonexchangeable  $\text{NH}_4^+$  released at an apparent steady state and the percentage of total nonexchangeable  $\text{NH}_4^+$  released by H-resin in the kinetic studies.

Soil	Nonexchangeable $\text{NH}_4^+$ released†	Total nonexchangeable $\text{NH}_4^+$ released‡
	mg $\text{NH}_4^+$ -N $\text{kg}^{-1}$	%
Giessen Ap	50.9	21
Hungen Ap	31.1 a§	25
Hungen C	18.6 b	15
Shrouts Bt	22.0 c	4

† Represents the quantity of nonexchangeable  $\text{NH}_4^+$  released at 384 h.

‡ (Total nonexchangeable  $\text{NH}_4^+$  [as determined from Silva and Bremner (1966) extraction procedure])/H-resin released nonexchangeable  $\text{NH}_4^+$   $\times$  100.

§ Means not followed by the same letter are significantly different at the 0.05 level of probability.

### Effect of Thimerosal on Microbiological Ammonification

Addition of arginine to the soil/H-resin/Thimerosal-solution suspension did not result in a statistically significant increase in  $\text{NH}_4^+$  released from the two topsoils, Giessen Ap and Hungen Ap, compared with the treatments without arginine addition (Table 4). These findings confirm that Thimerosal added to the soil/H-resin suspension inhibited microbiological ammonification during the nonexchangeable  $\text{NH}_4^+$  release studies.

### Kinetics of Nonexchangeable Ammonium Release

The kinetics of nonexchangeable  $\text{NH}_4^+$  release from the soils are shown in Fig. 1. The release was initially rapid followed by a slower reaction. The rapid release continued for  $\approx 24$  h. There was a slower, continued release of nonexchangeable  $\text{NH}_4^+$  after 24 h in the Giessen Ap and Hungen Ap soils. This biphasic release is characteristic of a diffusion-controlled process that has been observed for ions similar to  $\text{NH}_4^+$  like  $\text{K}^+$  (Martin and Sparks, 1983; Feigenbaum et al., 1981).

The two topsoils released more nonexchangeable  $\text{NH}_4^+$  than the two subsoils at the end of the kinetic studies. Smith et al. (1994) investigated the release of nonexchangeable  $\text{NH}_4^+$  from soils during a 7-d period, and they also found that subsoils released less nonexchangeable  $\text{NH}_4^+$  than topsoils. This may be related to nonexchangeable  $\text{NH}_4^+$  in subsoils being more tightly held in micas and other less weathered soil minerals and to indigenous  $\text{NH}_4^+$  sources from parent materials (Stevenson, 1959).

The percentage of total nonexchangeable  $\text{NH}_4^+$  released in the kinetic studies was also much higher in the topsoils than in the subsoils (Table 5). This latter finding is particularly striking for the Shrouts Bt soil (Table 5). This soil contained the highest quantity of nonexchangeable  $\text{NH}_4^+$  (Table 3), yet only 4% of the total nonexchangeable  $\text{NH}_4^+$  was released by H-resin in the release studies (Table 5). This low release is ascribed to the indigenous  $\text{NH}_4^+$  in the Shrouts Bt soil, which is slowly and difficultly released (Black and Waring, 1972; Mengel and Scherer, 1981). The lower percentage release in the subsoils could also be ascribed to the high amount of mica and illite in the clay fraction (Table 2). Other studies on  $\text{K}^+$ , which behaves very similarly to  $\text{NH}_4^+$

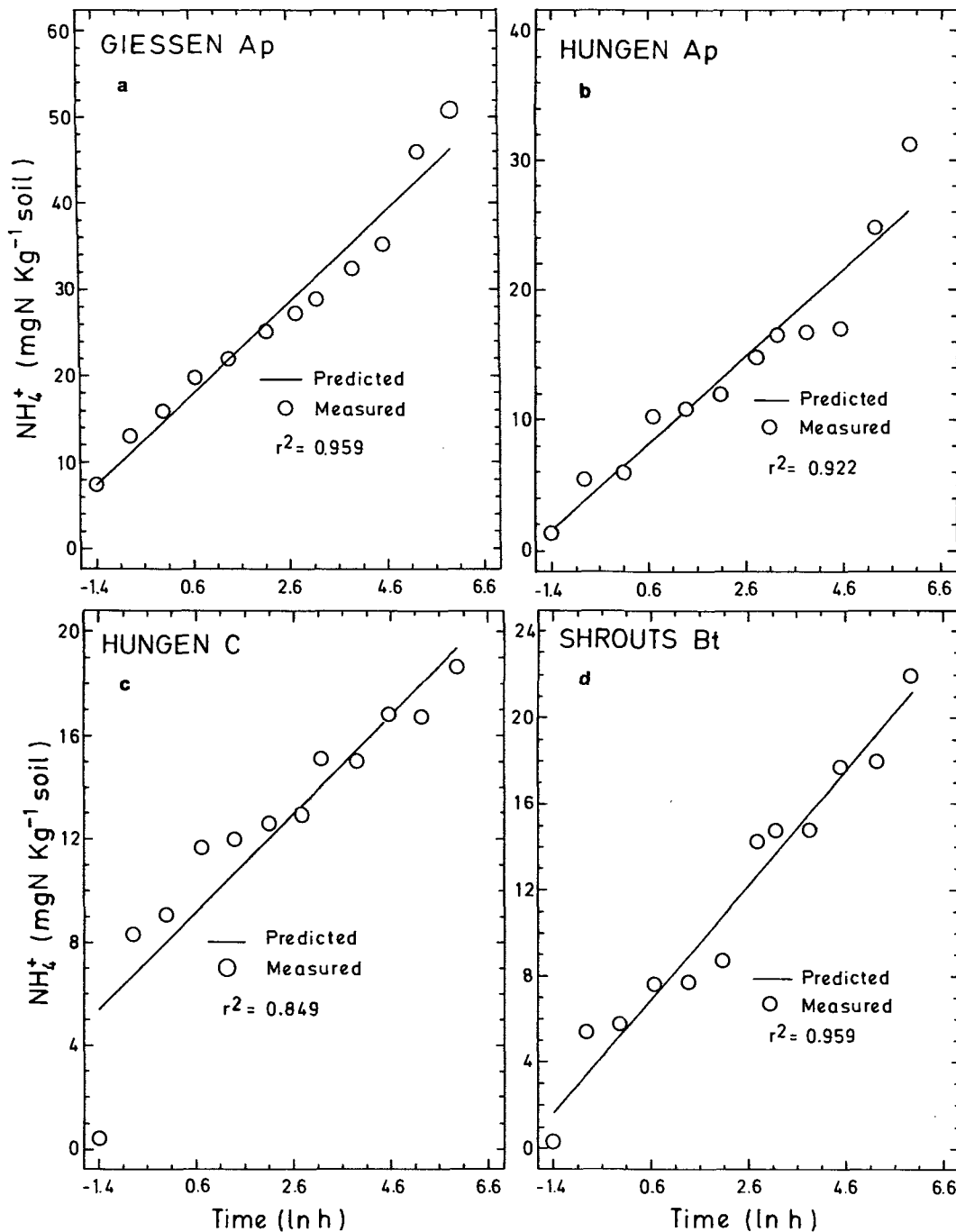


Fig. 2. Application of nonexchangeable  $\text{NH}_4^+$  release data to the Elovich equation, (a) Giessen Ap, (b) Hungen Ap, (c) Hungen C, and (d) Shrouts Bt.

(Sparks and Huang, 1985), have shown that release from mica and illite was much slower than from biotite and vermiculite (Rausell-Colom et al., 1965).

#### Application of Data to Kinetic Models

Different kinetic models were employed to describe nonexchangeable  $\text{NH}_4^+$  release from the four soils. The goodness of conformity between experimental data and the model-predicted values is expressed by the coefficient of determination. A relatively high  $r^2$  value for the relationship between measured and predicted  $\text{NH}_4^+$  re-

lease data indicates that the model can be successfully employed to describe the kinetics of nonexchangeable  $\text{NH}_4^+$  release from the soils. However, note that a high  $r^2$  value for a particular kinetic model does not necessarily mean that this model is the best (Sparks, 1989). Moreover, a model cannot be used to definitively describe nonexchangeable  $\text{NH}_4^+$  release.

Plots of the measured nonexchangeable  $\text{NH}_4^+$  release data vs. the predicted release data employing the Elovich model are shown in Fig. 2a through 2d. The  $r^2$  values of this model were 0.959, 0.922, 0.822, and 0.959 for

**Table 6. Coefficients of determination ( $r^2$ ) and standard errors of the estimate (SE) for nonexchangeable  $\text{NH}_4\text{-N}$  release using several kinetic models.**

Model	Giessen Ap		Hungen Ap		Hungen C		Shrouts Bt		$x\ddagger$	
	$r^2$	SE	$r^2$	SE	$r^2$	SE	$r^2$	SE	$r^2$	SE
Elovich	0.959	2.744	0.922	2.422	0.849	2.001	0.959	1.366	0.922	2.133
Parabolic diffusion	0.819	8.433	0.890	9.259	0.561	18.297	0.786	14.154	0.764	12.536
Power function	0.935	0.147	0.811	0.385	0.447	0.838	0.627	0.746	0.705	0.529
First-order	0.930	0.168	0.823	0.184	0.627	0.451	0.695	0.332	0.769	0.284
Zero-order	0.721	7.144	0.752	4.330	0.372	4.078	0.572	4.403	0.604	4.989

† Represents arithmetic mean of  $r^2$  and SE values for a particular kinetic model.

the Giessen Ap, Hungen Ap, Hungen C, and Shrouts Bt soils, respectively. The parabolic diffusion, power function, first-order, and zero-order models did not describe nonexchangeable  $\text{NH}_4^+$  from the soils nearly as well as the Elovich model (Table 6).

Aharoni et al. (1991) and Aharoni and Sparks (1991) have noted that a conformity of experimental data to the Elovich equation indicated by a relatively high  $r^2$  value during an entire experiment could suggest a heterogeneous diffusion process. Heterogeneous diffusion can be mathematically expressed as (Aharoni et al., 1991; Aharoni and Sparks, 1991)

$$Z = (dq/dt)^{-1} = \rho t/q_\infty [1 - (4t/\pi\tau_m)^{1/2} - 8/\pi^2 \exp(-\pi^2 t/4\tau_i)]^{-1} \quad [6]$$

where  $Z$  = the reciprocal of the rate of nonexchangeable  $\text{NH}_4^+$  release;  $t$  = time;  $\rho = \ln(\tau_m/\tau_i)$ ;  $\tau_i$  = smallest  $\tau$  and  $\tau_m$  largest  $\tau$ ;  $\tau = r^2/D$ , where  $r$  = maximum length of the diffusion path;  $D$  = the diffusion coefficient;  $q_\infty$  = the quantity of  $\text{NH}_4^+$  released at 384 h;  $q$  =  $\text{NH}_4^+$  released at a certain  $t$ .

In heterogeneous diffusion, a  $Z(t)$  plot is mainly linear because the negative terms in Eq. [6] are negligible. Hence, Eq. [6] reduces to

$$d(q/q_\infty)/d\ln t = 1/\rho \quad [7]$$

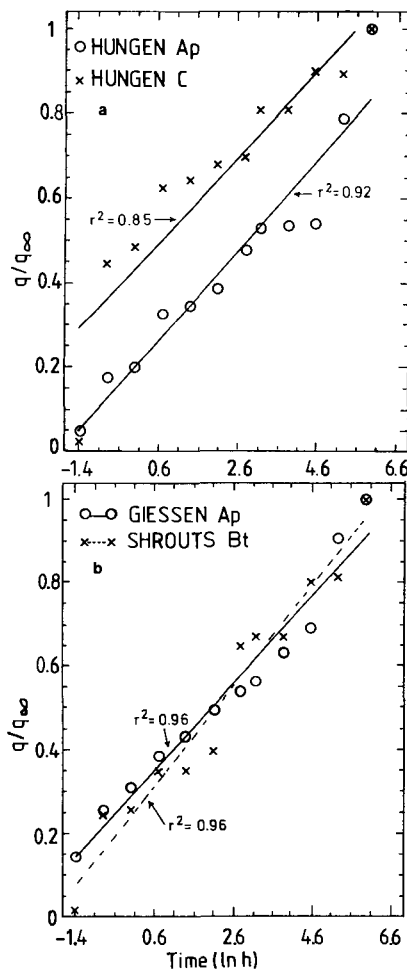
Aharoni and Sparks (1991) predicted that a slope  $<0.24$  for the relationship  $d(q/q_\infty)$  vs.  $\ln t$  would be expected for a heterogeneous diffusion.

Figure 3 shows plots of  $q/q_\infty$  vs.  $\ln t$ , which is quite linear ( $r^2$  values ranged from 0.85–0.96 for the four soils) across the entire reaction period for all soils. The slopes of these plots were 0.11, 0.11, 0.10, and 0.12 for the Giessen Ap, Hungen Ap, Hungen C, and Shrouts Bt horizons, respectively, suggesting heterogeneous diffusion (Aharoni et al., 1991).

The  $r^2$  values for the different kinetic models were lower in the Hungen C soil than in the other soils. The reason for this result may be that the relatively high concentration of carbonates of the Hungen C soil (Table 1) influenced the nonexchangeable  $\text{NH}_4^+$  release by neutralization of the added H-resin. Ammonia losses were unlikely since the pH of the H-resin suspension was below 6.9 in the soil/H-resin suspension of the Hungen C soil during the release study. The pH of the soil/H-resin suspensions of the Hungen C soil was below 5 after 0.5 h of the  $\text{NH}_4^+$  release study. Such low pH values were measured in the rhizosphere of plant roots (Schaller and Fischer, 1985).

## CONCLUSION

The kinetics of nonexchangeable  $\text{NH}_4^+$  release from the four soils were initially rapid followed by a much slower release rate. Total  $\text{NH}_4^+$  release was much less from the subsoils than the topsoils. This was attributed to nonexchangeable  $\text{NH}_4^+$  in the subsoils being more tightly retained due to the prevalence of micas and illite and to the presence of indigenous nonexchangeable  $\text{NH}_4^+$ . Among several kinetic models that were applied to the nonexchangeable  $\text{NH}_4^+$  release data, the Elovich model best described the observed data. Conformity to



**Fig. 3. Nonexchangeable  $\text{NH}_4^+$  release data applied to a heterogeneous diffusion model for (a) Hungen Ap and Hungen C soils and (b) Giessen Ap and Shrouts Bt, where  $q$  is the quantity of nonexchangeable  $\text{NH}_4^+$  released at time  $t$ , and  $q_\infty$  is the quantity released at 384 h.**

this model suggested a heterogeneous diffusion process. Data from this study indicate that nonexchangeable NH<sub>4</sub><sup>+</sup> could be an important source of slow release N for plants and microbes and could affect water quality.

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