

Effect of residence time on the kinetics of nonexchangeable ammonium release from illite and vermiculite

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Dedicated to Prof. em. Dr. Dr. h.c. *K. Mengel* on the occasion of his 70th birthday

Accepted 20 September 1999

Summary – Zusammenfassung

The fraction of nonexchangeable ammonium (NH_4^+) can play an important role in N cycling of soils as a sink (fixation) or a source (release) of NH_4^+ . Recently fixed nonexchangeable NH_4^+ especially seems to be a significant source for N release. The aim of our study was to determine the effect of residence time on the kinetics of nonexchangeable NH_4^+ release from illite and vermiculite. Calcium-saturated illite and vermiculite, containing NH_4^+ that was "fixed" for one and 60 d, were extracted with a H-resin for 0.25 to 384 h. Both clay minerals "fixed" significantly more NH_4^+ in 60 d than in 1 d, but vermiculite "fixed" more NH_4^+ than illite. The kinetics of nonexchangeable NH_4^+ release from illite and vermiculite were well described by the Elovich equation and by a heterogeneous diffusion model. In vermiculite the percentage of nonexchangeable NH_4^+ release decreased from 84% to 78% when the time of fixation increased from 1 to 60 d. In illite time of residence has not influenced the complete release of newly fixed NH_4^+ .

Key words: ammonium / fixation / clay minerals / nitrogen / kinetics

Einfluss der Bindungsdauer auf die Kinetik der Freisetzung nichtaustauschbaren Ammoniums aus Illit und Vermiculit

Die Fraktion des nichtaustauschbaren Ammoniums (NH_4^+) kann die N-Dynamik eines Bodens durch Fixierung und Freisetzung von NH_4^+ beeinflussen. Es scheint, dass frisch fixiertes nichtaustauschbares NH_4^+ eine bedeutende Quelle für die N-Nachlieferung der Böden ist. Das Ziel unserer Arbeit war es, zu untersuchen, ob die Verweildauer von NH_4^+ in den Zwischenschichten die Kinetik der Freisetzung von nichtaustauschbarem NH_4^+ von Illit und Vermiculit beeinflusst. Dazu fixierten Ca gesättigter Illit und Vermiculit NH_4^+ für einen Tag bzw. 60 Tage. Nach 60 Tagen fixierten die Tonminerale mehr NH_4^+ als nach einem Tag, wobei Vermiculit mehr NH_4^+ fixierte als Illit. Die NH_4^+ -Freisetzung wurde mit einem protonierten Harz in einem Zeitraum von 0,25 Std. bis 384 Std. bestimmt. Die Kinetik der Freisetzung des nichtaustauschbaren NH_4^+ von Illit und Vermiculit konnte gut mit der Elovich-Gleichung und einem heterogenen Diffusionsmodell beschrieben werden. Die Dauer der NH_4^+ -Fixierung beeinflusste die relative Freisetzung von nichtaustauschbarem NH_4^+ . Beim Vermiculit betrug die relative Freisetzung des nichtaustauschbaren NH_4^+ 78% nach 60tägiger Fixierungsdauer und nach einem Tag Fixierung lag die relative Freisetzung bei 84%. Beim Illit wurde die Freisetzung des frisch fixierten nichtaustauschbaren NH_4^+ nicht durch die Dauer der Fixierung beeinflusst.

1 Introduction

It is well established that nonexchangeable ammonium (NH_4^+) can play an important role in the cycling or dynamics of soil N and in the efficiency of applied fertilizer N (Scherer, 1993; Nommik and Vahtras, 1982). Measurements of the N fluxes between different N pools in an Alfisol derived from loess have shown that considerable amounts of N mineralized from the biomass were fixed in the clay minerals and were released under field conditions. Without mineral N application 200 kg nonexchangeable NH_4^+ -N ha^{-1} were released to winter wheat (*Triticum aestivum* L.) from the topsoil layer (0–0.3 m depth), whereas a mineral N application in form of a mixture of NH_4^+ - NO_3 -urea decreased the release of nonexchangeable

NH_4^+ from 200 to 120 kg N ha^{-1} (Nieder et al., 1995). Soon (1998) reported that 150 and 19 kg nonexchangeable NH_4^+ -N ha^{-1} were released during crop growth in 1994 and 1995, respectively. These recently published results and other studies indicate the importance of nonexchangeable NH_4^+ as a slow release N source (Kowalenko, 1978; Kowalenko and Ross, 1980; Mengel and Scherer, 1981; Drury and Beauchamp, 1991).

The release of nonexchangeable NH_4^+ is not the result of a surface chemical process from primary or secondary NH_4^+ bearing clay minerals such as micas, vermiculite or smectites, but a diffusion-controlled release mechanism (Steffens and Sparks, 1997) which is similar to the release of nonexchangeable K^+ from soils and minerals (Martin and Sparks, 1983; Sparks and Huang, 1985). A net release of nonexchangeable NH_4^+ requires low concentrations of NH_4^+ and K^+ in the soil solution (Smith et al., 1994). It

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occurs more in cultivated than in fallow soils (Scherer, 1993) since crops take up large amounts of K^+ and NH_4^+ , which decreases the K^+ and NH_4^+ concentrations in the rhizosphere and enhances the release of nonexchangeable NH_4^+ (Mengel et al., 1990). However, plant species have a different potential for mobilizing nonexchangeable NH_4^+ . Rape (*Brassica napus* L.) depleted the concentration of nonexchangeable NH_4^+ in the root vicinity more than ryegrass (*Lolium perenne* L.) and red clover (*Trifolium pratense* L.), since rape roots released more protons than the roots of ryegrass and red clover which promoted NH_4^+ release (Scherer and Ahrens, 1996).

A major problem in defining and in estimating the bioavailability of nonexchangeable NH_4^+ is that nonexchangeable NH_4^+ is often comprised of two types with different binding energies. One type is defined as the indigenous or native nonexchangeable NH_4^+ and the other is defined as recently or newly fixed nonexchangeable NH_4^+ (Schachtschabel, 1961). The native nonexchangeable NH_4^+ is less readily released than the recently fixed nonexchangeable NH_4^+ (Allison et al., 1951; Black and Waring, 1972; Kowalenko and Cameron, 1978; Kuderyarov, 1981; Niederbudde, 1983; Scheffer and Schachtschabel, 1984). For example, Kowalenko and Ross (1980) reported that the release of nonexchangeable NH_4^+ was relatively slow after an initial rapid release. The initial release was ascribed to recently fixed NH_4^+ and the slow release was attributed to the release of indigenous fixed NH_4^+ .

Steffens and Sparks (1997) studied the kinetics of nonexchangeable NH_4^+ release from different soils using a H-resin extraction method. It was shown that the release of nonexchangeable NH_4^+ from the soils ranged from 4 to 25% of the total nonexchangeable NH_4^+ with the subsoils releasing less nonexchangeable NH_4^+ than the topsoils. This was ascribed to a higher amount of indigenous nonexchangeable NH_4^+ in the subsoils which was less easily released.

It appears that the location of NH_4^+ in the clay interlayer spaces and the time of contact between clay minerals and NH_4^+ (residence time) may influence the quantity and the kinetics of nonexchangeable NH_4^+ release. Accordingly, the objectives of our investigation were to determine the effect of time on NH_4^+ fixation in illite, vermiculite and montmorillonite and to investigate the effect of residence time on the kinetics of nonexchangeable NH_4^+ release from illite and vermiculite.

2 Materials and methods

2.1 Clay preparation and NH_4^+ fixation experiment

Llano Vermiculite (Texas, USA), illite (Silver Hill, Montana, USA) and Wyoming Montmorillonite (Swy-1 from the Source Clays Repository of the Clay Minerals Society at the University of Missouri) were selected for the experiments. Since the particles of Llano vermiculite were rather thick in comparison to those of illite and montmorillonite, a 500 g sample of Llano vermiculite was ground in a mortar to pass a 0.50 mm sieve. Then

the Llano-vermiculite was placed in a porcelain-zircon-ball-grinder (Fisher Scientific Co.) and ground for four days to increase the particle size. The clay minerals were transferred into beakers and carbonates were removed by treating the clay minerals for two weeks with a Na-acetate buffer solution at pH 4.6 and 298 K. The $< 2 \mu\text{m}$ fraction of the Na-saturated clay minerals was separated by decantation and centrifugation. Then the $< 2 \mu\text{m}$ -fractions of the clay minerals were saturated with 0.5 M CaCl_2 , and washed with distilled water until a negative test for Cl^- was observed with 1 M AgNO_3 . The Ca-saturated clay suspensions were then placed in dialysis tubes and transferred into a double-distilled water bath. The water bath was changed daily until the electrical conductivity of the water was $< 10 \mu\text{S cm}^{-1}$. Then the clay suspensions were freeze-dried. X-ray diffraction analyses confirmed the identity of each of the clay minerals.

Before each clay was exposed to NH_4^+ , indigenous fixed NH_4^+ was analyzed using the method of Silva and Bremner (1966). The effect of residence time (1 d, 60 d) on the fixation of added NH_4^+ was investigated as follows: Eighteen g of the freeze-dried clay minerals, in duplicate, were placed in 250 mL tubes and equilibrated with 180 mL of 0.03 M NH_4Cl solution at 298 K on a reciprocating shaker. The clay suspensions were shaken after 1 d for 1 h each day. After 1 and 60 days of equilibration, 10 mL of 0.5 M CaCl_2 were added to the clay- NH_4Cl suspensions to remove exchangeable NH_4^+ . Afterwards the suspensions were centrifuged and the supernatant was discarded. Equilibration of the clay-suspensions with 180 mL of 0.5 M CaCl_2 was repeated three more times to desorb additional exchangeable NH_4^+ . Then the Ca-saturated clays were washed with distilled water until a negative test for Cl^- was obtained with 1 M AgNO_3 and then freeze-dried. The nonexchangeable NH_4^+ content of the clay minerals was analyzed as before. The kinetics of nonexchangeable NH_4^+ release were investigated using a procedure described by Steffens and Sparks (1997).

2.2 Kinetics of nonexchangeable NH_4^+ release

Duplicate 0.5 g samples of the Ca-saturated freeze-dried clays ($< 2 \mu\text{m}$) which had fixed NH_4^+ for 1 d or 60 d were placed in 50 mL polypropylene tubes and extracted in an equilibration medium of 25 mL distilled water and 1 g of freeze-dried H-saturated resin [Rexyn (0.30–0.82 mm), Fisher Scientific Co., Pittsburgh, PA] at 298 K for 0.25, 0.50, 1, 2, 4, 8, 16, 24, 48, 96, 192 and 384 h on a reciprocating shaker. For each of these extraction periods duplicate blank samples (1 g freeze-dried H-resin and 25 mL distilled water) also were equilibrated. Also the Ca-saturated illite, to which NH_4^+ had not been added, was equilibrated for 0.25, 1, 8, 24, 48 and 192 h. This was done to distinguish the release of indigenous and newly fixed NH_4^+ from the illite, since previous analyses showed that only illite contained indigenous fixed NH_4^+ (Tab. 1). Since Scott et al. (1960) assumed that grinding of clay particles by a resin could increase the release of nonexchangeable NH_4^+ the shaker was operated on a 1 h on, 1 h off sequence for the first 8 d of the equilibration periods to minimize particle abrasion and enhanced release of nonexchangeable NH_4^+ .

After each equilibration time, the resin was separated from the clay suspension on a 0.25 mm sieve, and the resin and sieve were washed five times with distilled water. The separated resin was transferred to a funnel containing a Whatman 22 filter and was leached twice with 40 mL 1 M KCl to exchange the released fixed NH_4^+ . The concentration of NH_4^+ in the leachates was determined colorimetrically by a continuous flow autoanalyzer (Braan & Luebbe Co, Germany).

The clay suspension, which was separated from the resin, was centrifuged for 30 min at 7649 g and 293 K and the supernatant was analyzed for NH_4^+ and NO_3^- concentrations as described above. At each equilibration time the NO_3^- concentrations of the clay suspensions were in the same range as those for the blank samples (resin plus distilled water). This indicated that nitrification of NH_4^+ did not occur in the equilibrium medium.

The kinetics of nonexchangeable NH₄⁺ release from the clay minerals were analyzed using Elovich equation, parabolic diffusion, power function, zero-order, first-order, and heterogeneous diffusion models (Sparks, 1989; Sparks and Huang, 1995; Steffens and Sparks, 1997) and are given below.

Elovich equation $Y = a + blnt$ [1]

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

Power function $\ln Y = \ln a + blnt$ [3]

Zero-order $(Y - Y_0) = a - bt$ [4]

First-order $\ln(Y - Y_0) = a - bt$ [5]

where Y denotes the released NH₄⁺ at 384 h, t = time (h), Y₁ = released NH₄⁺ at time t, and a and b are constants.

The heterogeneous diffusion model is presented in equation [6] and [7]:

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

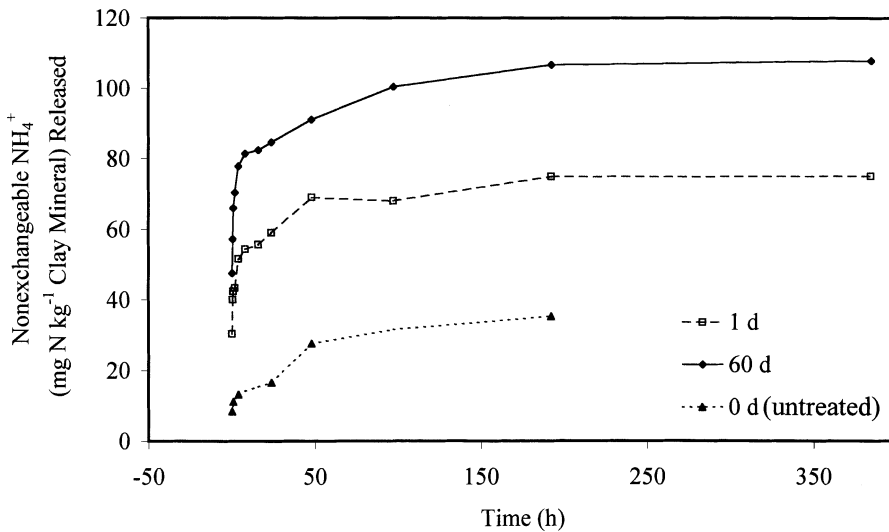
Table 1: Effect of residence time on the quantity of nonexchangeable NH₄⁺ in different clay minerals.

Tabelle 1: Einfluss der Fixierungsdauer auf das nichtaustauschbare NH₄⁺ bei verschiedenen Tonmineralen.

Clay Mineral	Residence Time (d)		
	0	1	60
	mg NH ₄ ⁺ -N kg ⁻¹ clay		
Illite	297	337 ^{a†}	362 ^c
Vermiculite	0	810 ^b	913 ^d
Montmorillonite	0	8 ^e	9 ^e

† Different letters between the treatments indicate significant differences at the 0.05 probability level.

Illite



Vermiculite

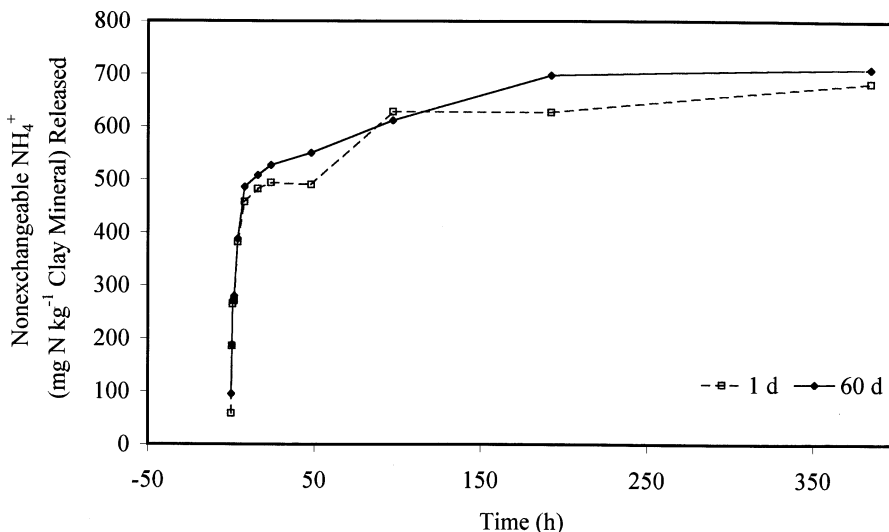


Figure 1: Effect of time of NH₄⁺ fixation (1 d or 60 d) on the cumulative nonexchangeable NH₄⁺ release from clay minerals.

Abbildung 1: Einfluss der Fixierungszeit (1 Tag und 60 Tage) auf die kumulative Freisetzung von nichtaustauschbarem NH₄⁺ von Tonmineralen.

Table 2: Effect of residence time on nonexchangeable NH_4^+ release and the percentage of nonexchangeable NH_4^+ and recently fixed NH_4^+ released to an H-resin at an apparent equilibrium.

Tabelle 2: Einfluss der Fixierungsdauer auf die mittels protoniertem Harz gefundene Freisetzung an nichtaustauschbarem NH_4^+ sowie auf die Freisetzung an frisch fixiertem NH_4^+ bei scheinbarem Gleichgewicht.

Clay Mineral	Residence Time (d)	Nonexchangeable NH_4^+ Released at an Apparent Equilibrium (mg NH_4^+ -N kg^{-1} clay)	Nonexchangeable NH_4^+ -N Released ^f (%)	Recently Fixed NH_4^+ -N Released (%)
Illite	0	35.4 [†]	12	–
Illite	1	75.3 [‡]	22.3	99.8 [#]
Illite	60	107.9 [‡]	29.8	111.5
Vermiculite	1	684.0 [‡]	84	84
Vermiculite	60	710.0 [‡]	78	78

[†] Represents indigenous nonexchangeable NH_4^+ release from illite at an apparent equilibrium of 192 h.

[‡] Represents nonexchangeable NH_4^+ release from clay minerals reacted with added NH_4^+ for 1 and 60 d (See Fig. 1a and b) at an apparent equilibrium of 384 h.

^f Percentage of total nonexchangeable NH_4^+ , at different residence times, released at apparent equilibrium.

[#] [(Nonexchangeable NH_4^+ -N released at 384 h – Indigenous nonexchangeable NH_4^+ -N released)/(Recently fixed NH_4^+ -N)] X 100.

where Z = the reciprocal of the rate of NH_4^+ release, t = time (h), $\rho = \ln(\tau_m/\tau_i)$; τ_i = smallest τ and τ_m largest τ ; $\tau = r^2/D$, where r = maximum length of the diffusion path, D = diffusion coefficient; q_∞ = quantity of NH_4^+ released at 384 h, q = NH_4^+ released at a certain time (t).

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

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

3 Results and discussion

Illite contained a significant quantity (297 mg NH_4^+ -N kg^{-1}) of indigenous nonexchangeable NH_4^+ whereas only traces of indigenous nonexchangeable NH_4^+ were found in vermiculite and montmorillonite (Tab. 1). As residence time (contact time between clay minerals and added NH_4^+) increased from 1 to 60 d, the quantity of nonexchangeable NH_4^+ increased in illite and vermiculite. Vermiculite fixed significantly more NH_4^+ than illite after residence times of 1 and 60 d (Tab. 1). Dyal and Hendricks (1952) found that vermiculites have the greatest capacity to fix NH_4^+ , whereas illite may or may not fix NH_4^+ , depending on the degree of weathering. Sparks et al. (1979) also found a strong correlation between the mica and vermiculite content of a Kentucky soil and the quantity of nonexchangeable NH_4^+ .

In contrast to illite and vermiculite, Wyoming montmorillonite fixed little added NH_4^+ and residence time had no effect on the quantity of nonexchangeable NH_4^+ (Tab. 1). These results are not surprising since montmorillonite typically does not fix notable quantities of NH_4^+ (Dyal and Hendricks, 1952; Said, 1973).

3.1 Kinetics of nonexchangeable NH_4^+ release

The kinetics of nonexchangeable NH_4^+ release from illite and vermiculite which had been treated with NH_4^+ for 1 and 60 d are shown in Fig. 1. In the first hours the release of

NH_4^+ was very rapidly followed by a much slower release of nonexchangeable NH_4^+ . This biphasic NH_4^+ release from the clay minerals was also observed in soils and probably indicates a diffusion-controlled exchange process (Steffens and Sparks, 1997). Vermiculite released significantly more NH_4^+ than illite, reflective of the higher quantity of nonexchangeable NH_4^+ present in vermiculite (Tab. 1).

The clay minerals which had fixed NH_4^+ for 60 d released more NH_4^+ than the clay minerals which had fixed NH_4^+ for 1 d only (Fig. 1). The quantity of nonexchangeable NH_4^+ release increased as residence time increased which correlates to the overall quantity of nonexchangeable NH_4^+ present in the clay minerals at 1 and 60 d. Only 12% of the indigenous nonexchangeable NH_4^+ in illite was released after an apparent equilibrium was reached in 192 hours. As residence time increased, the percentage of nonexchangeable NH_4^+ released from illite increased while in vermiculite it decreased (Tab. 2). A much larger percentage of nonexchangeable NH_4^+ was released from vermiculite at both residence times (84% and 78% at 1 and 60 d, respectively) than from illite (22.3% and 29.8% at 1 and 60 d, respectively). This is reflective of the small amount of indigenous nonexchangeable NH_4^+ released from illite. Indigenous nonexchangeable NH_4^+ is much less easily released than recently “fixed” nonexchangeable NH_4^+ , since the former may be trapped more in the center of the clay interlayers, while recently fixed NH_4^+ may be fixed more in the peripheral zone of the interlayers (Scheffer and Schachtschabel, 1989; Steffens and Sparks, 1997). In contrast to vermiculite recently fixed nonexchangeable NH_4^+ was released completely in illite after 1 and 60 d of residence time. In addition, after 60 d of residence time in illite 11.5% more nonexchangeable NH_4^+ was released than the recently fixed nonexchangeable NH_4^+ (Tab. 2). We assume that the interlayers of illite were expanded during the 60 d of fixation and that this could have effected the release of the indigenous nonexchangeable NH_4^+ .

3.2 Application of different kinetic models for describing nonexchangeable NH_4^+ release

We employed different kinetic models (Sparks, 1989) to describe the kinetics of nonexchangeable NH_4^+ release from the clay minerals. Relatively high coefficients of determination (r^2) can indicate the goodness of fit between the experimental release data and the model-predicted data. Low r^2 -values for measured release data vs. model-predicted data were calculated using the first-order and power function kinetic models. However, r^2 values using the Elovich equation, parabolic diffusion, and heterogeneous diffusion models were above 0.95.

Fits of the experimental nonexchangeable NH_4^+ release data vs. the model-predicted values estimated by the Elovich equation are shown in Fig. 2. The values of r^2

were between 0.9741 and 0.9775 for illite and 0.9606 and 0.9763 for vermiculite (Fig. 2). The Elovich model also described well nonexchangeable NH_4^+ release from soils (Steffens and Sparks, 1997).

The excellent conformity of the experimental data to the Elovich model would suggest that nonexchangeable NH_4^+ release from the clay minerals is a heterogeneous diffusion process (Aharoni et al., 1991). Steffens and Sparks (1997) applied a heterogeneous diffusion model described by Aharoni and Sparks (1991) to experimental data representing nonexchangeable NH_4^+ release from soils.

Plots showing application of the experimental nonexchangeable NH_4^+ release data from clay minerals to the heterogeneous diffusion model of Aharoni and Sparks (1991) are shown in Fig. 3. The r^2 values for illite were 0.9740 and 0.9775 and for vermiculite were 0.9763 and

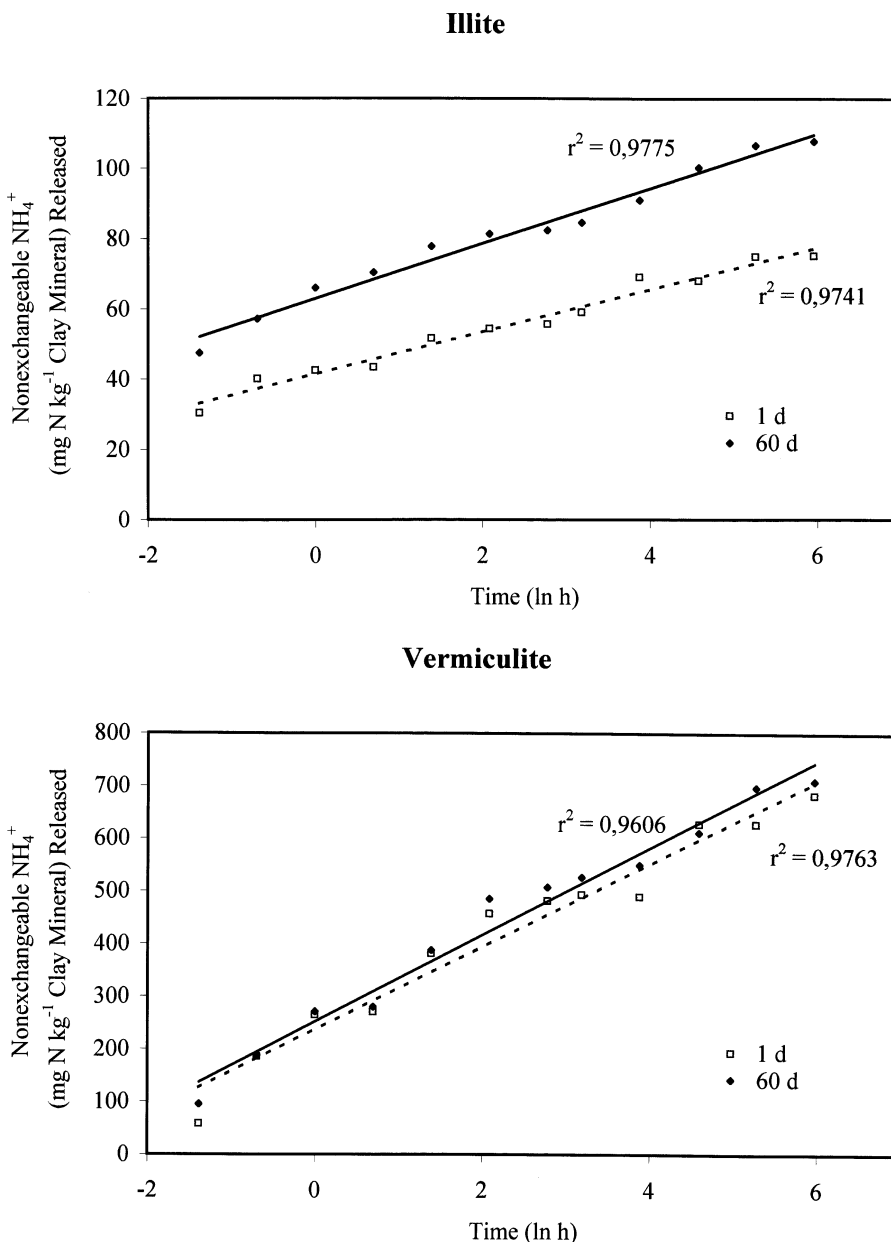


Figure 2: Application of nonexchangeable NH_4^+ release data to the Elovich equation. **Abbildung 2:** Beziehung zwischen der kumulativen Freisetzung des nichtaustauschbaren NH_4^+ und der Zeit mit Hilfe der Elovich-Gleichung.

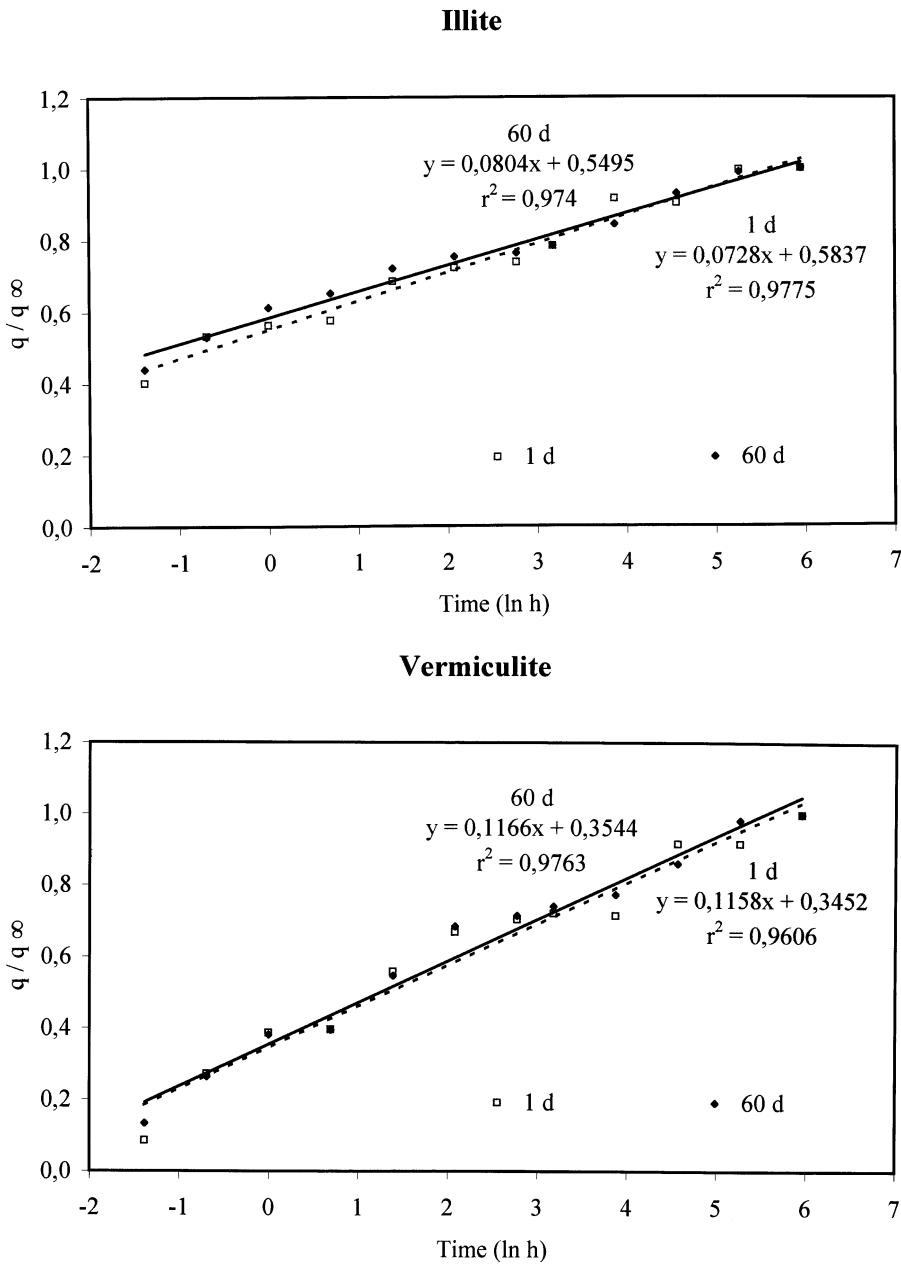


Figure 3: Nonexchangeable NH₄⁺ release data applied to a heterogeneous diffusion model where q is the quantity of nonexchangeable NH₄⁺ released at time t, and q_∞ is the quantity of NH₄⁺ released at 384 h. **Abbildung 3:** Beziehung zwischen der kumulativen Freisetzung des nichtaustauschbaren NH₄⁺ mit dem Heterogen-Diffusions-Modell; q = zur Zeit t freigesetztes nichtaustauschbares NH₄⁺, q_∞ = nach 384 Std. freigesetztes nichtaustauschbares NH₄⁺.

0.9606 for residence times of 1 and 60 d. These high r² values would suggest that the data are described well by a heterogeneous diffusion model.

Conclusions

The kinetics of nonexchangeable NH₄⁺ release from illite and vermiculite were biphasic. As residence time increased (1 vs. 60 d of NH₄⁺ fixation) the percentage of newly fixed nonexchangeable NH₄⁺ release decreased only slightly in vermiculite. These data show that the time of NH₄⁺ residence in the interlayers of clay minerals especially of those like vermiculite, could effect the bioavailability of applied NH₄⁺ fertilizers and reduce N losses to the environment.

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