

Fixation and defixation of ammonium in soils: a review

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Abstract Fixed NH_4^+ ($\text{NH}_4^+_f$) and fixation and defixation of NH_4^+ in soils have been the subject of a number of investigations with conflicting results. The results vary because of differences in methodology, soil type, mineralogical composition, and agro-climatic conditions. Most investigators have determined $\text{NH}_4^+_f$ using strong oxidizing agents (KOB or KOH) to remove organic N and the remaining $\text{NH}_4^+_f$ does not necessarily reflect the fraction that is truly available to plants. The content of native $\text{NH}_4^+_f$ in different soils is related to parent material, texture, clay content, clay mineral composition, potassium status of the soil and K saturation of the interlayers of 2:1 clay minerals, and moisture conditions. Evaluation of the literature shows that the $\text{NH}_4^+_f$ -N content amounts to 10–90 mg kg^{-1} in coarse-textured soils (e.g., diluvial sand, red sandstone, granite), 60–270 mg kg^{-1} in medium-textured soils (loess, marsh, alluvial sediment, basalt) and 90–460 mg kg^{-1} in fine-textured soils (limestone, clay stone). Variable results on plant availability of $\text{NH}_4^+_f$ are mainly due to the fact that some investigators distinguished between native and recently fixed NH_4^+ while others did not. Recently fixed NH_4^+ is available to plants to a greater degree than the

native $\text{NH}_4^+_f$, and soil microflora play an important role in the defixation process. The temporal changes in the content of recently fixed NH_4^+ suggest that it is actively involved in N dynamics during a crop growth season. The amounts of NH_4^+ defixed during a growing season varied greatly within the groups of silty (20–200 $\text{kg NH}_4^+\text{-N ha}^{-1} 30 \text{ cm}^{-1}$) as well as clayey (40–188 $\text{kg NH}_4^+\text{-N ha}^{-1} 30 \text{ cm}^{-1}$) soils. The pool of recently fixed NH_4^+ may therefore be considered in fertilizer management programs for increasing N use efficiency and reducing N losses from soils.

Keywords Fixed NH_4^+ ($\text{NH}_4^+_f$) · Native $\text{NH}_4^+_f$ · Recently fixed NH_4^+ · N dynamics · $\text{NH}_4^+_f$ availability to plants and microflora

Introduction

Some soils are able to bind ammonium (NH_4^+) and potassium (K^+) in such a manner that these cannot be easily replaced by other cations. McBeth (1917) was the first who observed that NH_4^+ added to soils could not be completely recovered by alkaline distillation or by extraction with 10% hydrochloric acid. McBeth (1917) defined the unrecovered portion of the added NH_4^+ as “fixed NH_4^+ ” (henceafter referred as $\text{NH}_4^+_f$). The fixation of NH_4^+ is defined as “the adsorption or absorption of ammonium ions by the mineral or organic fraction of the soil in a manner that they are relatively unexchangeable by the usual methods of cation exchange” (Osborne 1976a; SSSA 1984). Osborne (1976a) suggested “intercalary NH_4^+ ” and Mengel and Scherer (1981) “non-exchangeable NH_4^+ ” to distinguish between the NH_4^+ recovered from clay minerals by digestion of the soil with 5 N HF:1 N HCl and NH_4^+ which is bound organically or as NH_4 -phosphate (Frye and

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Hutcheson 1981). While earlier investigations concluded that only a very small amount of NH_4^+ is available to microorganisms and plants (Allison et al. 1951, 1953b; Axley and Legg 1960; Lutz 1966), studies in the last three decades suggest that NH_4^+ may be released and used by crops (Kudeyarov 1981; Nommik 1981; Mengel and Scherer 1981, 1986; Nommik and Vahtras 1982; Preston 1982; Scherer 1984, 1987, 1993; Lu et al. 2010).

Ammonium fixation and release can play a crucial role for the efficiency of fertilizer N (Scherer and Mengel 1986; Dou and Steffens 1995; Steffens and Sparks 1999; Juang et al. 2001) as it impacts the indigenous soil N supply towards crop N uptake. Nitrogen contributions from soil including defixation of NH_4^+ in a given year/season can greatly alter recovery efficiency of applied N because there occurs a large fertilizer N substitution of soil N. With current concerns about the environment and the need to produce more food with less fertilizer N input there is an increased focus for quantifying soil borne N supply. The need to boost agricultural production worldwide is stimulating N fertilizer consumption. In Asia and the Americas, ammonium-based N fertilizers are increasingly used (Prud'homme 2005) and their recovery efficiency by the plants, inter alia, could be influenced by fixation and release of NH_4^+ . In soils with high NH_4^+ fixation capacity a part of the NH_4^+ supplied through NH_4^+ -forming or NH_4^+ -containing fertilizers may be bound in clay mineral interlayers. Increasing NH_4^+ fixation can be a way in building up an available N pool in soils to optimize crop recovery and minimize N losses into the environment (Liu et al. 2008) as the NH_4^+ ions after penetration into the clay mineral interlayers are excluded from nitrification (Guo et al. 1983) and are thus protected against leaching. The NH_4^+ pool can thus function as a kind of buffer that could influence N losses from soils and mineral N availability to crops.

Some reviews on the fixation and availability of fixed NH_4^+ have been published in the past (Rodrigues 1954; Nommik 1957; Bremner 1959; Nommik and Vahtras 1982; Scherer 1993). These reviews mainly focused on the chemistry and factors influencing NH_4^+ fixation in soils and gave relatively less attention to the seasonal dynamics and plant availability of NH_4^+ . While the chemistry of NH_4^+ fixation is fairly well understood (Baethgen and Alley 1987; Nommik and Vahtras 1982), there are conflicting reports on the availability of NH_4^+ . This is assumed to be due to differences in methodology, soil type, mineralogical composition, and agro-climatic conditions. It is, therefore, important that the existing information may be integrated with underlying variants for better understanding the role of NH_4^+ fixation and release on N dynamics in the soil–plant system.

The present paper gives an overview of the current knowledge on NH_4^+ and ammonium fixation and defix-

ation, particularly on pool sizes in different soils with particular emphasis on new aspects on availability of recently fixed NH_4^+ to crops and microflora and seasonal changes of NH_4^+ pools under plant cover. The information is important not only for fertilizer management but also on the background of increasing importance of NH_4^+ -based fertilization, namely urea, and an intensive debate on NH_4^+ -based fertilization (cultan fertilization) in plant nutrition (Sommer and Scherer 2009). The paper includes literature of the last few decades, and the soils were grouped according to parent material and texture.

Methods for the determination of NH_4^+

Several methods have been proposed for determining NH_4^+ in soil. Most of the methods involve pretreatment of the samples to remove organic matter and exchangeable NH_4^+ and dissolution/extraction of the residual sample for release of NH_4^+ . Barshad (1951) suggested distilling NH_4^+ -treated soil with NaOH and KOH to remove exchangeable NH_4^+ . This method resulted in an incomplete recovery in some cases probably because of blocking effect of K^+ or interference by soil organic matter. In the method by Mogilevkina (1964), soil organic matter is removed by dry combustion at 400°C during time periods between 24 and 72 h, depending on the organic matter content, prior removal of the fixed NH_4^+ using sulfuric acid (Kjeldahl procedure). Most of the other methods use HF for the extraction of NH_4^+ (Rodrigues 1954; Dhariwal and Stevenson 1958; Bremner 1959). The method proposed by Silva and Bremner (1966) is the most commonly used and involves treating the soil with alkaline KOBBr solution (to remove organic compounds), washing the residue with 0.5 M KCl and shaking with 5 N HF:1 N HCl for 24 h. The 24 h time for HF–HCl treatment could be reduced to 30 min by performing the treatment at 100°C. The NH_4^+ released is determined by steam distillation of the soil–acid mixture after adding KOH. The pretreatment used in this method to remove organic compounds is considered superior to those used in previous methods for estimating fixed ammonium because it effects an almost entire removal of organic soil N without the risk of fixation of NH_4^+ by soil minerals. Zhang and Scherer (1998) suggested replacing the boiling of the mixture of soil and KOBBr on a hot plate with keeping the soil–KOBBr mixture for 10 min either in a water bath at 95°C or heating in a microwave oven (1,150 W) at 50% of full power for 10 min. Marzadori et al. (1994) boiled the soil–KOBBr mixture in a microwave digestion system for 5 min at 90% and 2 min at 80% of the maximum oven energy (600 W). Antisari et al. (1987) used H_2O_2 along with pyrophosphate and NaCl (H_2O_2 –NaCl) for the destruction of organic matter

and the reproducibility of their method was better than that of the Silva and Bremner (1966) method. The method of Paramasivam and Breitenbeck (2000) excludes the alkaline pretreatment that removes labile organic compounds. Cox et al. (1996) suggested the use of sodium tetraphenylboron (NaBPh_4) that facilitates the release of NH_4^+ as NH_4BPh_4 . However, compared with the method of Silva and Bremner (1966), only 71% of NH_4^+ were extracted. Although the method may extract only a part of the NH_4^+ , it may be a better estimate of potentially plant-available NH_4^+ (Cox et al. 1996).

Comparison of some of the methods showed that these give widely different values for a given amount of NH_4^+ . For example, the method of Mogilevkina (1964) could recover only a quarter while the rest was lost during ignition of the soil sample to remove organic matter (Bremner et al. 1967). Similarly, Moyano and Gallardo (1988) also obtained significantly lower values with the method of Mogilevkina (1964) as compared to that of Silva and Bremner (1966). The method of Silva and Bremner (1966) gave higher values than the Dhariwal and Stevenson (1958), Bremner (1959), and Mogilevkina (1964) methods and lower values than the Rodrigues (1954) and Schachtschabel (1960) methods (Silva and Bremner 1966; Osborne 1976a).

Dixit and Mir (1987) compared the methods proposed by Rodrigues (1954), the modified Rodrigues method (Bremner et al. 1967) and those by Dhariwal and Stevenson (1958), Bremner (1959), and Silva and Bremner (1966) on ten soils varying in clay content from 12% to 31%. The highest values were obtained in the method of Rodrigues and the lowest by the method of Bremner. Similar results were reported by Opuwaribo and Odu (1974). Antisari and Sequi (1988) compared results after the application of three methods (Silva and Bremner's method, HF–HCl treatment in a microwave system, and CHN analyzer). The microwave system and CHN analyzer produced similar results and the values were generally 1.5 to 2.7 times higher than those obtained with Silva and Bremner's treatment indicating incomplete recovery by the latter method.

Mechanism of NH_4^+ fixation

Ammonium fixation is greatest in 2:1 type clay minerals such as illite, vermiculite, and montmorillonite. Clay minerals possess negative charges balanced by cations, for example, NH_4^+ or K^+ . The physics of NH_4^+ is closely related to that of K^+ because both ions have similar ionic radii and low hydration energy. The complete concept with all its further aspects has been nicely put down in detail by Nommik (1965). For both NH_4^+ and K^+ , the same mechanism is responsible for fixation and both fit exactly into the ditrigonal holes in the basal oxygen plane of 2:1

clay minerals. The penetration of both cations into the clay mineral interlayers causes the clay layers to collapse to 1 nm, and NH_4^+ and K^+ ions are trapped between silicate sheets and largely withdrawn from exchange reactions (Nommik 1965). Therefore, both cations held in the interlayers of collapsed 2:1 clay minerals are said to be “fixed” and the term “fixed NH_4^+ ” was formerly used. The electrostatic energy between NH_4^+ (or K^+) and the negative charges in the crystal sheets is greater than the hydration energy of ammonium. The NH_4^+ ion readily sheds its hydration water shell and enters the lattice void, where fixation occurs (Kittrick 1966).

Contents of NH_4^+ in soils and influencing factors

Contents of NH_4^+

Contents of NH_4^+ -N in the plough layer of arable soils cover a wide range (Table 1). Parent material has a major influence on the NH_4^+ -N pool in soils developed from different parent materials, which increases in the order sand (diluvial sand and red sandstone) < basalt \approx granite < loess \approx ground moraine < alluvial sediment < limestone < marsh sediment. The high discrepancy in the NH_4^+ -N content of soils that developed from clay stone (Mohammed 1979 vs. Zhang et al. 2007) may be mainly due to different clay mineralogy (note that the clay contents given by Zhang et al. (2007) only represent the fraction <1 μm). In summary, the NH_4^+ -N content amounts to 10–90 mg kg^{-1} in coarse-textured soils (e.g. diluvial sand, red sandstone, granite), 60–270 mg kg^{-1} in medium-textured soils (loess, marsh, alluvial sediment, basalt), and 90–460 mg kg^{-1} in fine-textured soils (limestone, clay stone).

At the regional scale, the contents of NH_4^+ -N also vary considerably. For example, the content of NH_4^+ -N of different soils in Austria ranged between 45 and 190 mg kg^{-1} (Schiller and Wallicord 1964), of Spanish soils between 180 and 490 mg kg^{-1} (Moyano and Gallardo 1988), of soils in Turkey between 60 and 230 mg kg^{-1} (Elmaci et al. 2002), of soils in Queensland (Australia) between 6 and 107 mg kg^{-1} (Osborne 1976b), of soils of the former USSR between 40 and 490 mg kg^{-1} (Skonde et al. 1974), of soils in China between 35 and 573 mg kg^{-1} (Qi-Xiao et al. 1995), of soils in Nigeria between 8 and 98 mg kg^{-1} (Opuwaribo and Odu 1974), and of soils in southern Ontario (Canada) between 57 and 367 mg kg^{-1} non-exchangeable NH_4 -N (Doram and Evans 1983). The content in soils in Kentucky (USA) was as high as 365 mg kg^{-1} (Sparks et al. 1979). Investigations on top soils from Antarctic also showed that NH_4^+ -N occurs in amounts (0 to 322 mg kg^{-1}) similar to elsewhere in the world (Greenfield 1991).

Table 1 Contents of fixed NH_4^+ in soils derived from different parent materials (Source: Nieder and Benbi 2008, extended)

Authors	Country	Reference soil group (FAO 1998)	Parent material	Clay (%)	Method	NH_4^+ -N content (mg N kg^{-1})	NH_4^+ -N content (kg N ha^{-1} 30 cm^{-1}) ^a
Upland soils							
Nommik (1967)	Sweden	Dystric Podzol	Diluvial sand	<5	Bremner (1959)	10–17	45–77
Fleige and Meyer (1975)	Germany	Dystric Podzol		<2	Silva and Bremner (1966)	80	360
Scherer and Mengel (1979)		Dystric Cambisol	Red sandstone	17	Modified Silva and Bremner (1966) ^b	12.5	50
Zhang et al. (2007)	China	Chromic Cambisol	Granite	13 ^d	Silva and Bremner (1966)	86	387
Scherer and Mengel (1979)	Germany	Different soil groups	Basalt	17–38		60–80	270–360
Mengel et al. (1990)		Eutric Vertisol		24		100	450
Sahrawat (1995)	India	Eutric Vertisol		51	Silva and Bremner (1966)	134	603
Hinman (1964)	Canada	Different soil groups	Loess	12–35	Bremner (1959)	130–300	580–1,350
Scheffer and Meyer (1970)	Germany	Haplic Luvisol		10	Silva and Bremner (1966)	170	760
Meyer and Scheffer (1970)				15		100	450
Fleige and Meyer (1975)		Phaeozem		?		140	650
Scherer and Mengel (1979)		Haplic Luvisols		12–18	Modified Silva and Bremner (1966) ^b	120–160	540–720
Beese (1986)		Haplic Luvisol		13		100	450
Nieder et al. (1996)		Haplic Luvisol		19	Silva and Bremner (1966)	115–170	520–760
Lu et al. (2010)	China	Chernozem		26		172	774
Fleige and Meyer (1975)	Germany	Vertic Cambisol	Ground moraine	30		170–220	765–1,000
Soon (1998)	Canada	Dystric Luvisol	Ground moraine	31		85–144	383–648
Zhang et al. (2007)	China	Chromic Cambisol	Quaternary red clay	16 ^d		173	779
Fleige and Meyer (1975)	Germany	Rendzic Leptosol	Limestone	?		340	1,530
		Vertic Cambisol		?		460	2,070
Nannipieri et al. (1999)	Italy	Chromic Vertisol		46	Modified Silva and Bremner (1966) ^c	84–135	378–608
		Vertic Cambisol		50		190–209	855–940
Mohammed (1979)	Libya	Different soil groups	Clay stone	38–46		90–100	415–450
Fleige and Meyer (1975)	Germany	Eutric Fluvisol	Alluvial sediment	20	Silva and Bremner (1966)	260	1,170
Scherer and Mengel (1979)		Arenic/Eutric Fluvisols		10–40	Modified Silva and Bremner (1966) ^b	70–270	315–1,215
Gorlach and Grywnowicz (1988)	Poland	Eutric Fluvisol		17	Silva and Bremner (1966)	122	549
Nannipieri et al. (1999)	Italy	Chromic Cambisol		16	Modified Silva and Bremner (1966) ^c	175–184	787–828
Sahrawat (1995)	India	Chromic Luvisol		19	Silva and Bremner (1966)	93	420
		Eutric Vertisol		55		77	346
Schachtschabel (1961)	Germany	Eutric Fluvisols	Marsh sediment	20–70	Schachtschabel (1960)	150–850	675–3,825
Mengel et al. (1990)		Eutric Fluvisol		41	Modified Silva and Bremner (1966) ^b	195	880

Paddy soils	China	Hydragric Anthrosol	Slate and shale	27 ^d	Silva and Bremner (1966)	373	1,678
Zhang et al. (2007)			Purple sandstone	20 ^d		314	1,413
			Quaternary red clay	28 ^d		229	1,030
			Limestone	32 ^d		241	1,085
			Alluvial sediment	24 ^d		342	1,539
			Lake deposit	24 ^d		413	1,858
			Granite	19 ^d		135	608

^aThe N mass was calculated on a basis of a 30-cm plough layer and a mean bulk density of 1.5 g cm⁻³. In some cases, the plough layer was thicker or shallower than 30 cm

^bModified according to Scherer and Mengel (1979)

^cModified according to Marzadori et al. (1994)

^dFraction <1 μm

The percentage of total N present as NH₄⁺_f-N in main soil groups of Israel ranged between 1.8% and 78.6%, with most of the values falling between 2% and 25%. Highest values were obtained for the deepest horizons (Feigin and Yaalon 1974), where it ranged from 14% to 78% in British Caribbean soils (Rodrigues 1954), 3% to 44% in southern Ontario soils (Doram and Evans 1983), 16% to 59% in Vertisols and 13% to 31% in Cambisols in India (Sahrawat 1995), 21% in Italian Fluvisols (Benedetti et al. 1996), and up to 85% in subsoils in the USA (Smith et al. 1994).

In a soil profile, the NH₄⁺_f-N content as percent of the total N (inorganic plus organic) generally increases with soil depth (Black and Waring 1972; Doram and Evans 1983; Smith et al. 1994; Sahrawat 1995; Zhang et al. 2003) due to decreasing soil organic matter content. Fixation of NH₄⁺ in soil organic matter is negligible (Kowalenko and Cameron 1976). Contents of NH₄⁺_f-N in 24 soils from Queensland (Australia) averaged 4% of total N in surface soil and 6.4% for subsoils (Black and Waring 1972). The magnitude of increase with depth was much higher in soils from southwestern Saskatchewan where it ranged from 7% of the total N in the surface soil to 58% in 120 cm depth (Hinman 1964). In Spanish soils, it ranged from 21% to 33% in the surface layers and 30% to 83% in subsoils with illite as the dominant clay mineral (Moyano and Gallardo 1988).

Yaalon and Feigin (1970) found that illite contains approximately 600 mg N kg⁻¹ illite, whereas montmorillonite contains small and kaolinite clays only negligible amounts. In mixed soil clays, the NH₄⁺_f-N level is determined by the quantity of illite (Feigin and Yaalon 1974) and illite plus vermiculite (Sparks et al. 1979; Doram and Evans 1983), respectively. In contrast to the above results, Bajwa (1985) in a comparative study on fixation of NH₄⁺ and K⁺ in wetland rice soils found that in five soil clays, montmorillonitic clay fixed the maximum of the added NH₄⁺ (98%) followed by vermiculite (88%) and least (34%) in clay containing hydrous mica, chlorite, and halloysite. On the other hand, montmorillonite, contrary to the other clay minerals, had no capacity for fixing K⁺. The overall capacity for fixation of monovalent cations (K⁺ plus NH₄⁺) may therefore be greater for vermiculite compared to montmorillonite.

Influencing factors

The content of NH₄⁺_f and the capacity of soils to fix NH₄⁺ is related to parent material (Table 1), texture (Baethgen and Alley 1987), clay content (Opuwaribo and Odu 1974; Sowden et al. 1978; Moyano and Gallardo 1988; Juang 1990), clay mineral composition (Feigin and Yaalon 1974; Sparks et al. 1979; Doram and Evans 1983; Niederbudde 1983), the K concentration in soil solution, the degree of K saturation of the exchange complex of the soil colloids and

K saturation of the interlayers of 2:1 clay minerals (Hinman 1966; Doram and Evans 1983), and soil moisture conditions (Black and Waring 1972). Allison et al. (1953a) showed that vermiculite and illite have the greatest capacity to fix NH_4^+ , while montmorillonite fixed less NH_4^+ and held it less tenaciously. Said (1973) reported that soils from Sudan with montmorillonite as the dominant clay mineral contained only small amounts of NH_4^+ -N ranging between 30 and 60 kg N kg^{-1} soil. As compared to montmorillonite, beidelite is a high fixing smectite, due to the isomorphic substitution in the tetrahedral layer (Feigenbaum et al. 1994). Kaolinites, belonging to the 1:1 type of clay minerals, are not able to bind NH_4^+ ions in their interlayers because hydrogen bonds which join the interlayers allow only very little dilatation of the narrow interlayer space (Mela Mela 1962).

In addition to clay minerals, the silt fraction has also been reported to bind NH_4^+ -N in a non-exchangeable form. For example, in loess soils of central Europe, about only 65% of the NH_4^+ -N is interlayer ammonium (Niederbudde and Friedrich 1984), while the rest is found in the silt fraction. The content of NH_4^+ -N in the clay and silt ranged from 255 to 430 mg N kg^{-1} and from 72 to 166 mg N kg^{-1} , respectively (Jensen et al. 1989). In a Canadian soil with 37% clay, Kowalenko and Ross (1980) found similar amounts of NH_4^+ -N for the clay and the silt fraction. In different primary minerals, the content of NH_4^+ -N has been reported to vary between nil in quartz to 266 mg kg^{-1} in biotite (Wlotzka 1961).

Some studies have demonstrated that the NH_4^+ fixation capacity strongly depended on the degree of K saturation of the interlayers of the 2:1 clay minerals. If the K content of a soil is high, it can be expected that the interlayer space will also be saturated with potassium (Scherer 1982) and to a smaller extend with NH_4^+ ions (Petersburgsky and Smirnov 1966). As a result of competition for fixation sites, the presence of NH_4^+ or K^+ may alter both fixation and release of these cations. In several studies, addition of K^+ prior to NH_4^+ depressed NH_4^+ fixation (Stanford and Pierre 1947; Nommik and Vahtras 1982), and addition of NH_4^+ prior to or at the same time as K^+ reduced K^+ fixation (Aquaye and MacLean 1966; Bartlett and Simpson 1967). Contrarily, Drury et al. (1989) found that K^+ pre-addition did not block subsequent NH_4^+ fixation and the presence of K^+ induced greater NH_4^+ fixation (Chen et al. 1989). This is in agreement with the study by Bajwa (1985) in that the sequence in which NH_4^+ and K^+ were applied did not appear to affect the relative amounts that were fixed.

Application of NH_4^+ -containing fertilizers may result in fixation of the added NH_4^+ . However, the amount fixed is not directly proportional to the amount of fertilizer N added (Liang and MacKenzie 1994). Fixation is usually fast and occurs within the first few hours after fertilizer application.

The fixation rate is controlled mainly by ion diffusion and declines with time until the equilibrium point is approached (Nommik 1965). In experiments under laboratory conditions, Kowalenko and Cameron (1976) found that 50% of added NH_4^+ was fixed within a short period of time, while in a field experiment, Kowalenko (1978) found that 59% of 152 kg N ha^{-1} added as $(\text{NH}_4)_2\text{SO}_4$ was fixed within a few minutes after addition. In some soils of eastern Canada, more than 40% of the added NH_4^+ was fixed in less than 2 h and further fixation was negligible (Sowden et al. 1978). According to Chantigny et al. (2004), the highest fixation of NH_4^+ by clay minerals occurred within the first day and was greater in the clay soil (34% of applied $^{15}\text{NH}_4\text{-N}$) than in the sandy soil (11%). In studies with ^{15}N -labeled NH_4^+ 18% to 23% of the applied $^{15}\text{NH}_4^+$ was fixed after a 15-day incubation in soils with high contents of vermiculite (Drury et al. 1989).

The amount of added NH_4^+ fixed depends on the NH_4^+ -fixing capacity of the soil. The estimation of the NH_4^+ fixation capacity of a soil involves treatment of the soil with excessive amounts of concentrated NH_4^+ solution in order to achieve complete saturation of the fixing minerals with NH_4^+ (Nommik and Vahtras 1982) before estimation of the fixed NH_4^+ by one of the methods described above. In a Gleysol with high NH_4^+ -fixing capacity, Fischer et al. (1981) found that 47% of added ^{15}N were fixed, whereas in a Histosol with very low NH_4^+ fixation capacity, only 7% of the added NH_4^+ entered the interlayers of the clay minerals. Rider et al. (2005) focusing on the occurrence of NH_4^+ fixation on a decomposed granitic substrate showed that the fixation capacities of these sandy saprolites are significant. At field loading rates equivalent to less than 300 kg $\text{NH}_4^+\text{-N ha}^{-1}$ 36% to 42% of the added N became unavailable to plants due to interlayer collapse and fixation. Ammonium fixation did not vary significantly in relation to substrate weathering class in these samples.

According to Allison et al. (1953a), soil moisture can reduce NH_4^+ fixation as clay minerals are expanded under wet conditions. However, in dry soils, the interlayer space is reduced and NH_4^+ fixation also increases. According to Osborne (1976b), NH_4^+ fixation was reduced by 25% in a clay soil moistened to 60% of the maximum water holding capacity as compared with the dry soil. Also, Gouveia and Eudoxie (2007) found a lower NH_4^+ fixation in wet soils. However, investigations in flooded rice soils yielded contradictory results. Some authors (Keerthisinghe et al. 1984; Chen et al. 1987a) observed that NH_4^+ fixation in paddy soils was significantly increased as a consequence of flooding, while others (Williams et al. 1968; Chen et al. 1987b) stated that NH_4^+ fixation was less pronounced under flooded compared to non-flooded conditions. Schneiders and Scherer (1996) observed an increasing concentration of NH_4^+ -N after flooding, which was closely

related to the declining redox potential (E_h). Therefore, E_h may have an important effect on the fate of NH_4^+ in paddy soils (Zhang and Scherer 1999). At a low E_h , the octahedral Fe^{3+} in the clay minerals is assumed to be reduced, resulting in a higher negative charge of the unit cell and therefore a higher Coulombic attraction between the interlayer cations and the silicate layers (Stucki et al. 1984). This increasing NH_4^+ fixation can be an option for building an available N pool in paddy soils to minimize N losses into the environment (Liu et al. 2008). A further prerequisite for the pronounced NH_4^+ fixation in flooded soils is the microbial reduction of Fe^{3+} , followed by the dissolution of Fe oxides coated on the surface of clay minerals at a low E_h , promoting the diffusion of NH_4^+ ions into the interlayers of the clay minerals (Scherer and Zhang 1999). Because of the reversible oxidation and reduction of Fe oxides in paddy soils, this mechanism may be of special importance for fixation of NH_4^+ (Zhang and Scherer 2000; Scherer and Zhang 2002). Figure 1 shows the relationship between the contents of NH_4^+ -N and clay-bound Fe^{2+} in paddy soils and clay minerals.

Availability of fixed NH_4^+ to plants and microflora

Fixation and release of NH_4^+ -N is dependent upon chemical equilibria between the amounts of NH_4^+ , exchangeable NH_4^+ and NH_4^+ in soil solution (Nommik and Vahtras 1982),



where $\text{NH}_4^+_s$ denotes ammonium in the soil solution and $\text{NH}_4^+_e$ and $\text{NH}_4^+_f$ are exchangeable and fixed ions,

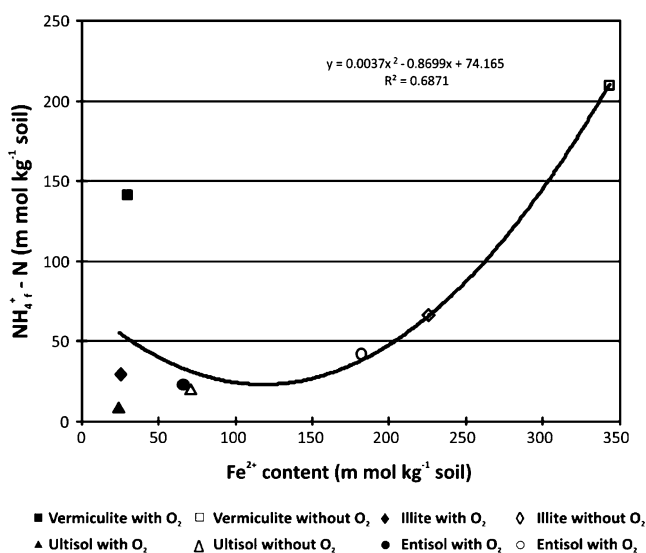


Fig. 1 Relationship between NH_4^+ -N and Fe^{2+} in soils and clay minerals (source: Scherer and Zhang 2002)

respectively. However, results from several studies indicate that there is no equilibrium between exchangeable and fixed NH_4^+ . Because NH_4^+ and K^+ compete for the same binding sites, Nommik (1957) suggested that the sum of NH_4^+ and K^+ rather than NH_4^+ alone should be introduced into the equilibrium equation. Steffens and Sparks (1997) described the kinetics of NH_4^+ -N release from soil using the Elovich model. This model is empirical, and the process is assumed to be diffusion controlled. With decreasing NH_4^+ concentration in soil solution, NH_4^+ ions diffuse from clay mineral interlayers. Therefore, factors such as fertilizer N application, plant cover, soil organic matter, microflora, clay content, and clay mineral composition that affect concentration of NH_4^+ in soil solution may promote either release or fixation of NH_4^+ . Because of methodological limitations (such as proper separation of recently fixed NH_4^+ from native $\text{NH}_4^+_f$) and the involvement of several factors and processes influencing soil N dynamics, it is still difficult to describe the dynamics of fixed NH_4^+ especially under field conditions.

Plant availability

Investigations focusing on the availability of NH_4^+ -N for crops have been reported with conflicting results. While early investigations of Legg and Allison (1959) and Black and Waring (1972) found that this N fraction plays a minor role for the N nutrition of plants, Norman and Gilmour (1987) estimated that the amounts of fertilizer-derived NH_4^+ -N available to ryegrass ranged from 35% to 72%. As percentage of total NH_4^+ -N, the release of this fraction ranged from 4% to 25% in different soils (Osborne 1976b; Smith et al. 1994; Steffens and Sparks 1997). According to Smith et al. (1994), only 8% of NH_4^+ -N were released on average from the surface layers of a number of US soils. In a Luvisol derived from loess, up to 250 kg NH_4^+ -N ha⁻¹ were released during a growing season of annual crops (oats and winter wheat; Van Praag et al. 1980). According to Baethgen and Alley (1987), NH_4^+ -N contributed significantly to N taken up by wheat grown in the greenhouse.

Various plant species influence the $\text{NH}_4^+_f$ pool through different mechanisms. Plants can take up soluble or exchangeable NH_4^+ in the vicinity of NH_4^+ -fixing clays and thus promote diffusion of ions out of the interlayers. Plant roots can also affect the $\text{NH}_4^+_f$ pool indirectly by releasing exudates that promote the activity of the soil microflora and microbial N uptake (Marschner 1995). The magnitude of NH_4^+ -N release strongly depends on the length of crop growth period and plant density (Saha and Mukhopadhyay 1986).

Most of the differences in NH_4^+ -N release can probably be attributed to both the variable pool sizes of “native fixed NH_4^+ ” and “recently fixed NH_4^+ ” and the lack of methods

available to separate these fractions adequately. The recently fixed NH_4^+ is mainly derived from mineral N fertilizers (Chen et al. 1989; Smith et al. 1994), but it may also originate from mineralization of soil organic matter (Nieder et al. 1995b). Dou and Steffens (1995) found that 90% to 95% of recently fixed $^{15}\text{NH}_4^+$ was released during a 14-week period in the soil planted with perennial ryegrass (*Lolium perenne* L.) under greenhouse conditions. Under field conditions, 66% of the recently fixed $\text{NH}_4^+\text{-N}$ was released in the first 86 days after fixation and the remaining was strongly fixed over the next 426 days (Kowalenko 1978). Apparently, recently fixed NH_4^+ resulting from fertilizer application is more available to plants than native $\text{NH}_4^+_f$, which is more tightly held (Black and Waring 1972; Kudeyarov 1981; Mengel and Scherer 1981; Keerthisinghe et al. 1984). Probably native $\text{NH}_4^+_f\text{-N}$ is trapped in the center of the interlayers to a higher degree, while recently fixed NH_4^+ ions are largely retained in the peripheral zone of the interlayers (Nommik and Vahtras 1982). Differences in clay mineralogy and K saturation of the minerals also influence the release of $\text{NH}_4^+_f\text{-N}$. Mengel et al. (1990) found that only soils containing vermiculite and low contents of exchangeable K^+ released significantly higher amounts of $\text{NH}_4^+_f$ as compared to soils with no vermiculite and high percentage of K^+ saturation of the clay minerals. In a pot experiment of Scherer (1985) with ryegrass, where NH_4^+ was added before and after the application of K^+ , respectively or simultaneously, the content of $\text{NH}_4^+_f$ was the highest, when NH_4^+ was applied before K and lowest when K was applied first (Table 2).

Scherer (1987) further reported that in field plots heavily dressed with K^+ , no release of $\text{NH}_4^+_f\text{-N}$ was found, whereas in plots with low K^+ application, considerable amounts of NH_4^+ were released. In analogy to these findings, adsorption/desorption experiments (isotherm studies in soils containing vermiculite and illite) in a binary ($\text{Ca}^{2+}/\text{NH}_4^+$) and a ternary ($\text{Ca}^{2+}/\text{K}^+/\text{NH}_4^+$) cation system (Lumbanraja and Evangelou 1994) revealed that NH_4^+ desorption decreased in the presence of solution K^+ (ternary) relative to that in the absence of K^+ (binary). Fixation of K^+ in the presence of solution NH_4^+ was suppressed as compared to

that in the absence of NH_4^+ . Contrarily, NH_4^+ fixation was enhanced in the presence of solution K^+ relative to that in the absence of K^+ . Thus, contrary to common belief, the two ions do not behave as true analogs with respect to fixation reactions.

The mechanisms regulating the release and subsequent plant uptake are still not completely understood. According to Mengel et al. (1990) and Scherer and Ahrens (1994; 1996), plant roots deplete the NH_4^+ concentration of the soil solution in the rhizosphere and, therefore, promote the release of $\text{NH}_4^+_f$ (Fig. 2).

Further, the relative amounts of NH_4^+ and K^+ in soil solution govern the rate of release of NH_4^+ from interlayer positions (Welch and Scott 1960). Under field conditions, continuous uptake of NH_4^+ and K^+ ions by roots may reduce concentrations of both ions and therefore, diminish the blocking effect of K^+ on the release of NH_4^+ .

Availability to microflora

Early work concerning the influence of the soil microflora on the mobilization of $\text{NH}_4^+_f$ suggested only a minor role for the microflora (Allison et al. 1953b). While only between 13% and 28% of the $\text{NH}_4^+_f$ was oxidized, up to almost 80% of the exchangeable NH_4^+ was nitrified (Bower 1950). However, according to later studies heterotrophic microorganisms can rapidly assimilate NH_4^+ from the non-exchangeable pool (Nommik and Vahtras 1982; Drury and Beauchamp 1991) and therefore favor the release of NH_4^+ ions from the clay minerals (Jensen et al. 1989). In incubation experiments involving ^{15}N -labeled $\text{NH}_4^+_f$, the addition of an easily available C substrate favored the mobilization of this N fraction by heterotrophic microorganisms

Table 2 Influence of the application time of K^+ on the content of $\text{NH}_4^+_f\text{-N}$ and exchangeable K^+ (source: Scherer 1985)

Treatment	Mean \pm SD (mg kg^{-1} soil)	
	$\text{NH}_4^+_f\text{-N}$	Exchangeable K^+
K^+ before NH_4^+	231 \pm 3.7	142 \pm 4.6
K^+ and NH_4^+ simultaneously	246 \pm 4.7	204 \pm 2.4
K^+ following NH_4^+	252 \pm 4.0	214 \pm 4.5
LSD 5%	5	8

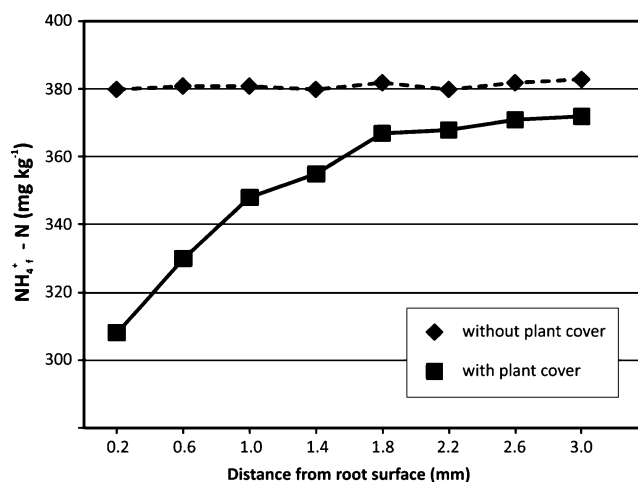


Fig. 2 Depletion profile of $\text{NH}_4^+_f\text{-N}$ in the rhizosphere of oilseed rape in a soil with high amount of expandable clay minerals (57% clay and 17% of smectites and vermiculite in the clay fraction; source: Scherer and Ahrens 1996)

(Breitenbeck and Paramasivam 1995), so that between 64% and 96% of non-exchangeable $^{15}\text{NH}_4^+$ was released. Different plant species produce root exudates with different quantity and quality which can differently affect activity and composition of the soil microflora (Nannipieri et al. 1999). Moreover, the release of NH_4^+ can be promoted by nitrification which causes changes in NH_4^+ equilibria (Green et al. 1994). Fumigation to inhibit soil biological activity as well as the application of a nitrification inhibitor (nitrapyrin) hampered the release of NH_4^+ (Aulakh and Rennie 1984). According to Tang et al. (2008), the stimulated assimilation of ammonium after glucose addition creates a steep concentration gradient between the NH_4^+ concentration of the soil solution and the NH_4^+ and thus promoting the release of NH_4^+ from the clay mineral interlayers. The results also show that K added simultaneously with the carbon source impeded the release of NH_4^+ ions, which may be due to the blocking effect of K^+ ions.

Results from field experiments during the cereal growing season (Nieder et al. 1995a, b, 1996) suggest that the dynamic microflora, due to its influence on the equilibria between the amounts of different N fractions, may exert a great influence on the dynamics of NH_4^+ . The minima of mineral N contents (due to plant and microbial N uptake) and correspondingly, of NH_4^+ contents, occurred during phases of increasing microbial biomass under a C-supplying plant cover, proving that the heterotrophic microflora, as a consequence of the increased microbial N uptake, favor the release of NH_4^+ (Fig. 3).

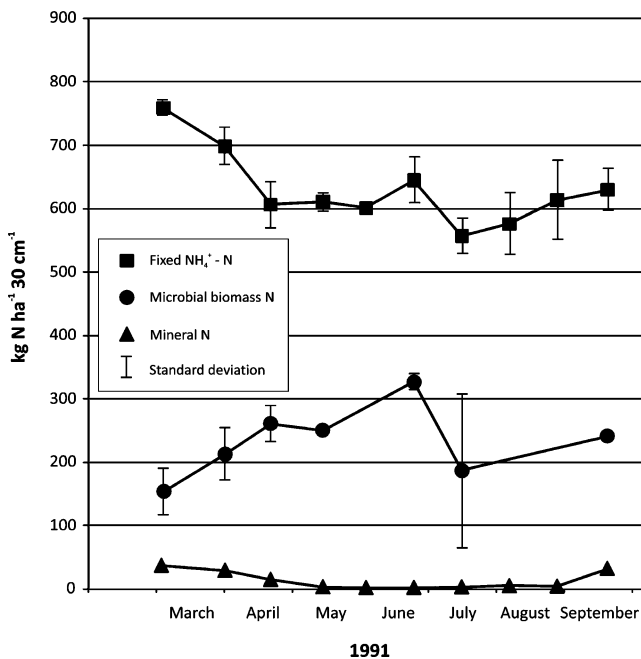


Fig. 3 Dynamics of NH_4^+ -N, microbial biomass N, and mineral N (NH_4^+ -N plus NO_3^- -N) in a Luvisol A_p horizon under winter wheat (source: compiled from Nieder et al. 1995a)

Seasonal dynamics of NH_4^+

The pattern of seasonal changes in the contents of NH_4^+ in arable soils is well-known (Kowalenko and Cameron 1976; Sowden 1976; Kowalenko and Ross 1980; Li et al. 1990a, b; Drury and Beauchamp 1991; Green et al. 1994). Mengel and Scherer (1981), investigating the dynamics of this N fraction in a Fluvisol during the growing season, found that the content of NH_4^+ declined in the top 60 cm from February to May (Fig. 4).

In the deeper soil layer (60–90 cm depth), depletion was observed from May to July, which was in accordance with the root growth of spring oats. At the end of the growing season, the clay mineral interlayers were refilled and almost the same content was attained as in spring. Li et al. (1990a, b) have shown a significant decrease of NH_4^+ in upper soil layers in March and in deeper soil layers during April. In field experiments on loess soils, Nieder et al. (1996) observed a significant correlation between the time course of NH_4^+ and mineral N in soil solution. The refixation of NH_4^+ in autumn may be mainly due to increased mineralization after the harvest of annual crops. Table 3 reflects this pattern (ranges of NH_4^+ fixation in spring, NH_4^+ release in summer and NH_4^+ refixation in autumn) with results (according to pool size or ^{15}N method, respectively) drawn from different studies, grouped according to upland (silty and clayey) and paddy soils.

In most of studies presented in Table 3, the NH_4^+ -N fixation in spring, occurring probably as a consequence of (mineral) fertilizer application at the beginning of the growth period, was not determined. The amounts of NH_4^+ -N released in summer vary greatly within the groups of silty ($20\text{--}200 \text{ kg NH}_4^+\text{-N ha}^{-1} 30 \text{ cm}^{-1}$) as well as clayey ($40\text{--}188 \text{ kg NH}_4^+\text{-N ha}^{-1} 30 \text{ cm}^{-1}$) soils. Studies in which

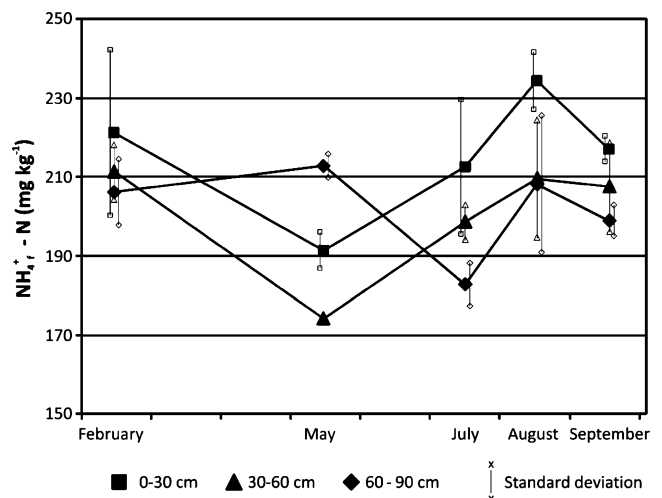


Fig. 4 Release of NH_4^+ -N in a Fluvisol during the growing season of spring oats (source: Mengel and Scherer 1981)

Table 3 Fixation, release and refixation of $\text{NH}_4^+\text{-N}$ in the 30 cm A_p horizon of arable loess soils during the growth period of annual crops as estimated by the temporal variation in pool size and the ^{15}N method

Site/country	Reference soil group (FAO 1998)	Parent material	Soil texture	Clay (%)	Crop	Soil depth (cm)	N application rate/kind of N fertilizer	$\text{NH}_4^+\text{-N}$ fixation in spring	$\text{NH}_4^+\text{-N}$ release in summer	$\text{NH}_4^+\text{-N}$ refixation in autumn	Experimental period	Authors
Upland soils												
Silty soils												
?/Belgium	Haplic Luvisol	Loess	Silty loam	?	Oats	0–30	100/ ^{15}N /(NH_4) ₂ SO ₄	n.d.	>100	n.d.	Vegetation period ^a	Van Praag et al. (1980) ^{b,d}
Tula/Russia	Podzoluvisol	?	?	?	WB	0–30	?	100	180	65	Vegetation period	Kudeyarov (1981) ^c
Göttingen/Germany	Loess	Loess		14	Fallow		Nil	20	20	0	1 year	Mba-Chibogu et al. (1975) ^e
Einbeck/Germany				11	SB		80/K ¹⁵ NO ₃	n.d.	115	25	April–July	Fleige et al. (1971) ^c
Heegheim/Germany				12	WW		?/Ammonium fertilizer	100	150	50	February–September	Mengel and Scherer (1981) ^c
Burggrafenrode/Germany				12	SB		?/Slurry	70	120	40	March–November	(1981) ^c
Kassel/Germany				?	WW		?	0	55	44	March–August	Scherer (1986) ^c
				?	WB		?	40	36	40	March–August	
Neuenkirchen/Germany				19	WW		Nil	n.d.	200	70	March–September	Nieder et al. (1996) ^e
				20	WW		213/Ammonium nitrate urea	n.d.	110	90		
	Haplic Phaeozem			20	WW		207/Ammonium nitrate urea	n.d.	120	80		
Clayey soils												
Leeheim/Germany	Eutric Fluvisol	Alluvial sediment	Clay loam	33	WW	0–30	?/Ammonium fertilizer	100	150	50	February–September	Mengel and Scherer (1981) ^c
Carpì/Italy	Fluvisol	Alluvial sediment		34	Sugar beets	0–40	Nil	n.d.	182	151		Marzadori et al. (1994) ^c
Cadriano/Italy				31		0–40	Nil	n.d.	188	161		
NW Alberta/Canada	“Gray Luvisol”	?		31	SB	0–30	80/Urea	n.d.	40–50	40–50	May–September	Soon (1998) ^{c,d}
Paddy soils												
Malgaya/Philippines	Hydragric Anthrosol	?	Clay loam	?	Rice	0–20	¹⁵ NH ₄ Cl<120	n.d.	80–100	n.d.	Vegetation period ^a	Keerthisinghe et al. (1984) ^{a,b}
Guadelupe/Philippines		?	Clay	?				n.d.	20–25	n.d.		
Santa Rita/Philippines		?		?				n.d.	40–50	n.d.		
Kuban/Russia	Alluvial sediment	Alluvial sediment	Silty loam	?		0–30	Nil	120	220	130		Kudeyarov (1981) ^c

n.d. not determined, SB spring barley, WW winter wheat, WB winter barley

^a Only two samplings before and after the vegetation period

^b ¹⁵N method

^c pool size method

^d Different field experiments

subsoils (>30 cm) were included indicate even higher amounts of NH_4^+ -N release. For example, estimates were up to 250 kg NH_4^+ -N release to a soil depth of 70 cm in Belgium (Van Praag et al. 1980) and up to 350 kg NH_4^+ -N release to a soil depth of 75 cm in Germany (Mengel and Scherer 1981).

Although the total amounts of NH_4^+ (“native” plus “recently fixed”) are probably much higher in the clayey soils (clay contents >30%) compared to the silty soils (10–20% clay), the amounts of NH_4^+ which are available in a growth period of annual crops seem to be in a similar order of magnitude (Table 3). This indicates a wider ratio of “native” to “recently fixed” NH_4^+ in the clayey soils. The low values of NH_4^+ release presented in Table 3 can partly be attributed to the fact that the experimental plot was kept fallow (study by Mba-Chibogu et al. 1975) or that the experimental soil had a history of only moderate N fertilization (not more than 60 kg N ha⁻¹ year⁻¹ for 25 years prior to the initiation of the study) with a low yield level (study by Soon 1998). In contrast, soils with a high level of long-term N fertilizer application and a high yield level show a high temporal variation in the interlayer NH_4^+ concentration, especially on control plots with limited contents of mineral N (see plot with nil N application in the study by Nieder et al. 1996). Most field observations show that the amounts of NH_4^+ -N refixed in autumn are commonly smaller compared to the amounts of NH_4^+ -N which are fixed in spring minus the amounts of NH_4^+ released in summer. It is thus obvious that for replenishment of the plant-available NH_4^+ pool to levels that occur at the beginning of the growth periods, the preceding winter periods would additionally be required.

Fixation is usually faster than release of NH_4^+ (Drury and Beauchamp 1991). Kowalenko and Cameron (1976) observed that more than one half of the added NH_4^+ -N was fixed within 1.7 days, whereas the average daily release of NH_4^+ was 1.7 and 0.65 kg N ha⁻¹ between 19 June to 1 August 1974 and between 1 August to 13 September 1974, respectively (Kowalenko 1978). From the foregoing, it appears that while the native NH_4^+ has no significance in the soil N dynamics (Mengel and Scherer 1981; Smith et al. 1994), the temporal changes in the content of recently fixed NH_4^+ show that this fraction is actively involved in the N dynamics during the crop growth period. Added NH_4^+ is quickly fixed by the clay minerals and later released slowly during the crop growth season due to increased crop demand with concomitant decrease in NH_4^+ concentration in soil solution. Supply of C-containing root exudates by the plant enhances the activity of heterotrophic microorganisms which may promote the release of fixed NH_4^+ .

The phenomenon of temporary fixation and release of added fertilizer NH_4^+ may contribute to retarding nitrification and thus to reducing N losses from the soil–plant system via NO_3^- leaching and denitrification (N_2 , N_2O). In

the winter-humid temperate climate, it is generally observed that contents of NH_4^+ reach their maximum during the winter period, when nitrate leaching occurs frequently. The extent of nitrate leaching may then partly depend on the NH_4^+ fixation capacity of the soil. For example, the losses of added fertilizer N ($^{15}\text{NH}_4^+$) were more than double in a Histosol with extremely low NH_4^+ -fixing capacity as compared to that from a clay containing Gleysol with high fixing capacity (Fischer et al. 1981). Similarly, NH_4^+ -N fixation by clay minerals may also contribute to reducing NH_3 volatilization losses (Dou and Steffens 1995). It may, therefore, be argued that clay fixation of NH_4^+ can provide a temporary sink for fertilizer N that subsequently acts as a source of N for plant uptake. Information on soil NH_4^+ -N fixation capacity and its plant availability is necessary for developing efficient N fertilizer management programs.

Although the knowledge on the magnitude and the dynamics of NH_4^+ has increased during the last few decades, there are still conflicting reports about the importance of NH_4^+ for plants and microflora. This may be due to the fact that up to now, it is not possible to distinguish properly between native fixed (non-available) and recently fixed (plant-available) NH_4^+ . As a consequence, the pool of plant-available NH_4^+ has hardly been integrated into models to describe the N dynamics of soils. Further research on methodological aspects is, therefore, required for both proper separation of recently fixed NH_4^+ from native fixed NH_4^+ and modeling the kinetics of plant-available NH_4^+ . This would be a basis for integrating the pool of recently fixed NH_4^+ in fertilizer management programs.

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