Ammonium fixation and release by clay minerals as influenced by potassium

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ABSTRACT

It is postulated that stabilized ammonium fertilizers improve fertilizer-N utilization by crops, leading thus to higher yields with the same fertilizer rate, especially on sandy soils. However, it must be taken into consideration that in clayey soil at least a part of the NH_4^+ ions may be fixed by 2:1 clay minerals, thus delaying the effect of the N fertilizer. Because NH_4^+ and K^+ have similar size and valence properties and therefore compete for the same non-exchangeable sites of 2:1 clay minerals, we investigated the influence of time and K^+ application rate on both fixation and release of NH_4^+. Fixation of NH_4^+ ions was higher when K^+ was applied after NH_4^+, while the influence of the K^+ application rate was less pronounced. Mobilization of non-exchangeable NH_4^+ was retarded when K^+ was applied at the high rate after NH_4^+. At the first harvest yield formation of ryegrass was neither influenced by the amount as well as the application time of K^+, because plant available N was not growth limiting, while yield of the second harvest was significantly higher with the low K^+ application rate after NH_4^+. After the second harvest the blocking effect of K^+ on the release of non-exchangeable NH_4^+ was attenuated and the highest yields of the third cut were reached in the treatments with the high K^+ application rate after NH_4^+. Total dry matter yield was highest when K^+ was applied at the low rate after NH_4^+. Our results show that K^+ governs fixation and release of non-exchangeable NH_4^+, which should be taken into consideration when applying ammonium containing N fertilizers like ammonium sulfate, ammonium sulfate nitrate and ENTEC. Thus K^+ can affect N availability when N is applied as NH_4^+ in both the short and long term.

Keywords: nitrogen; availability; potassium; clay minerals; crop yield

From all plant nutrients N deserves the highest attention. While too low rates may depress the profit, too high rates may result in nitrate leaching (Mengel et al. 2006). According to Peltonen-Sainio and Peltonen (1994) under favourable conditions N application alone in spring may be sufficient to promote plant growth, but may result in insufficient N availability during grain filling. For this reason the splitting of the nitrogen application rate is recommended for an efficient use of fertilizer-N (López-Bellido et al. 2012). Nevertheless in the last years an increasing diffuse nitrate loading of surface water and groundwater has emerged as a major problem in many agricultural areas of the world, resulting in contamination of drinking water resources (Sebilo et al. 2013). An option to minimize nitrate leaching is the use of ammonium-containing N fertilizers. However, in soils ammonium may be converted into mobile nitrate ions within a short period of time. Therefore nitrification inhibitors stabilized N fertilizers, for example, ammonium sulphate nitrate with the nitrification inhibitor 3,4-dimethylpyrazol phosphate (DMPP), were introduced (Di and Cameron 2002, Benckiser et al. 2013). Controlling the microbiological process of nitrification, nitrate losses could be reduced by increasing the assimilated N by plants (Subbarao et al. 2006).

In America and Asia ammonium-based fertilizers have been increasingly used (Prud`homme 2005). However, their recovery efficiency could be influenced by fixation and release of NH_4^+ by 2:1 clay

minerals. In soils with a high ammonium fixation capacity, at least a part of the NH_4^+ supplied as fertilizer may be bound in clay mineral interlayers (Tang et al. 2008). The share of added NH_4^+ fixed depends on the NH_4^+ fixation capacity of the soil (Scherer 1993). Kowalenko (1978) reported that 59% of 152 kg N/ha added as $(NH_4)_2SO_4$ were fixed. In the case of NH_4^+ stabilized fertilizers the process of NH_4^+ fixation may be prolonged and the share of fixed NH_4^+ is assumed to be even higher.

NH_4^+ fixation by clay mineral interlayers also depends on the K^+ status of the soil. If the K^+ concentration of the soil solution is high or increased by K fertilizer application, it can be expected that the interlayer space is also saturated with K^+ (Scherer 1982), resulting in a decreased NH_4^+ fixation. Otherwise K^+ may impede the release of NH_4^+ ions, which may be due to the blocking effect of K^+ ions (Nieder et al. 2011). Therefore, when applying NH_4^+ stabilized fertilizers interactions between NH_4^+ and K^+ ions should be taken into consideration.

However, no attempts have been made to consolidate the fragmented information on the effects of K^+ on fixation and release of NH_4^+ ions. For this reason the specific objectives of this study were to determine the influence of point of time and amount of K^+ application on the fixation of NH_4^+ stabilized and conventional NH_4^+ containing N fertilizer, as well as on yield and N uptake of ryegrass.

MATERIAL AND METHODS

The subsoil (30–75 cm) from a Luvisol derived from loess with a clay content of 23.9% and expandable illite as the main clay mineral was chosen for the experiment. The initial content of non-exchangeable NH_4^+-N was 115 mg/kg and plant available K 133 mg/kg soil. Fourteen treatments (each with four replications) were established (Table 1). Nitrogen (250 mg/kg soil) was applied as: sodium nitrate ($NaNO_3$), ammonium sulfate (AS), ENTEC 26 (ammonium sulfate nitrate + 3,4-dimethylpyrazol phosphate) and ammonium sulfate nitrate (ASN). K was applied as K_2SO_4 in two application rates (K1 – 250 mg/kg soil, referred to low K; K2 – 500 mg/kg soil, referred to high K). After thoroughly mixing N and K, respectively, into the soil (< 4 mm) the water content was adjusted to 60% of the maximum water holding capacity with deionized water and pre-incubated for 7 days.

Afterwards the soil samples were dried at 40°C in an oven, passed through a 4 mm sieve and N and K incorporated into the soil in reversed order (Table 1). In the following incubation period soil samples were stored again for 7 days after adjusting the maximum water holding capacity of 60%. The temperature during pre-incubation and incubation ranged between 20°C and 25°C. $NaNO_3$ was supplied together with K.

The bottom of the experimental pots were filled with 6 kg soil supplied with 0.4 g P as $Ca(H_2PO_4)_2 \cdot H_2O$ and 0.4 g Mg as 4.06 g $MgSO_4 \cdot 7\ H_2O$ as basal fertilizers, followed by 3 kg pretreated soil (referred as topsoil) according to Table 1.

After planting of ryegrass (*Lolium multiflorum* cv. Adriana) the soil water content was adjusted to 60% of the maximum water holding capacity and controlled daily to replenish water loss with deionized water. Ryegrass was cut three times, dried in an oven at 105°C and dry-matter yield determined. After grinding total N was analyzed using the Dumas combustion method.

After each harvest soil samples were taken from the topsoil with an auger (three cores per pot). The samples from each pot were pooled, air dried and passed through a 1 mm sieve. Non-exchangeable NH_4^+-N was analyzed according to Beuters and

Table 1. Treatments

Treatment	N form	Preincubation		Incubation	
		N	K	N	K
1	$NaNO_3$	–	–	+	K1
2	$NaNO_3$	–	–	+	K2
3	AS	–	K1	+	–
4	AS	–	K2	+	–
5	ENTEC 26	–	K1	+	–
6	ENTEC 26	–	K2	+	–
7	ANS	–	K1	+	–
8	ANS	–	K2	+	–
9	AS	+	–	–	K1
10	AS	+	–	–	K2
11	ENTEC 26	+	–	–	K1
12	ENTEC 26	+	–	–	K2
13	ANS	+	–	–	K1
14	ANS	+	–	–	K2

$NaNO_3$ – sodium nitrate; AS – ammonium sulfate; ENTEC 26 – ammonium sulfate nitrate + 3,4-dimethyl-pyrazol phosphate; ASN – ammonium sulfate nitrate; K1 – 250 mg/kg soil; K2 – 500 mg/kg soil

Scherer (2012). After pretreating the soil sample with KOBr solution and drying at 60°C for 20 h non-exchangeable NH_4^+-N was determined with an elemental analyzer with a thermal conductivity detector. Plant available K^+ was measured after extraction with 0.1 mol/L calcium acetate + 0.1 mol/L calcium lactate + 0.3 mol/L acetic acid with a soil:extract ratio of 1:20 after shaking for 2 h (Schüller 1969).

Statistical analysis. Multivariate analysis (ANOVA) was performed using the SPSS 20 software package (Chicago, USA). Means were compared at significance level of $P = 0.05$ by the Tukey's test. Standard deviation values are depicted in the graphs as bars.

RESULTS

At the first harvest the influence of the kind of N fertilizer as well as the application time and amount of applied K^+ on yield of ryegrass was negligible (Figure 1a). At the second harvest the influence of the N form and amount of K^+ applied was also marginal, when K^+ was applied before N. However, comparing the treatments K^+ after N, yields were significantly higher with K1 (Figure 1b). At the third harvest the influence of the amount of K applied on yield formation was again negligible

when K^+ was applied before N, while when K^+ was applied after N, in contradiction to the second harvest, yield was highest in the treatments with K2 (Figure 1c).

N uptake of the first harvest was on the same level when K^+ was applied at the low K^+ application rate before or after N. When K^+ was applied after N, K2 resulted in a significant decreased N uptake. N uptake was significantly lowest with N as AS (Figure 2a). Independent of the N form N uptake of the second harvest was mostly significantly lower when K^+ was applied before N as compared to K^+ after N. As compared to the first harvest the influence of the amount of applied K^+ on N uptake decreased when K^+ was applied after N (Figure 2b). At the third harvest N uptake was significantly highest when K2 was applied after N. Between these treatments N uptake was significantly highest with AS (Figure 2c).

Before the start of the experiment the soil contained 115 mg non-exchangeable NH_4^+-N/kg (Figure 3a) and was not influenced by the application of $NaNO_3$, but increased after the incorporation of the ammonium containing fertilizers. The increase was lower in the treatments when K^+ was applied before. However, the influence of the different ammonium containing fertilizers as well as the
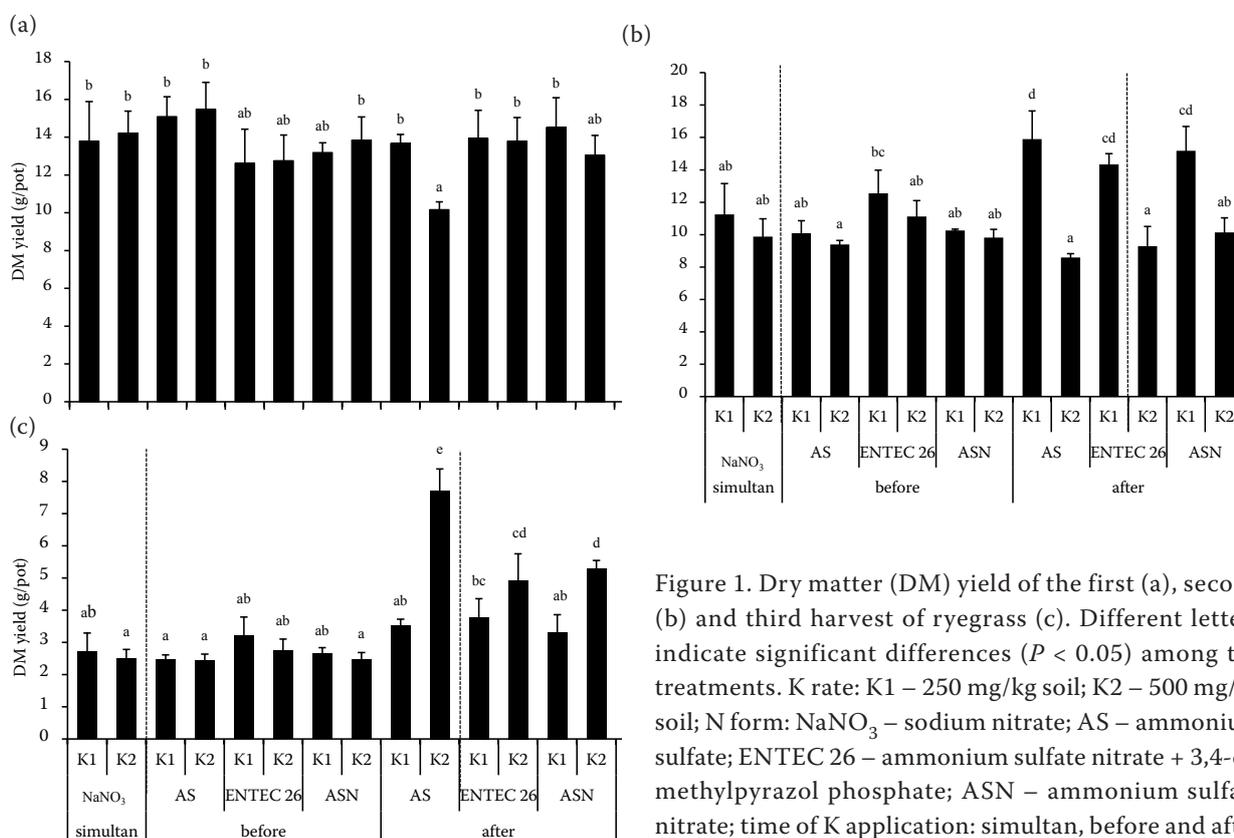

Figure 1. Dry matter (DM) yield of the first (a), second (b) and third harvest of ryegrass (c). Different letters indicate significant differences ($P < 0.05$) among the treatments. K rate: K1 – 250 mg/kg soil; K2 – 500 mg/kg soil; N form: $NaNO_3$ – sodium nitrate; AS – ammonium sulfate; ENTEC 26 – ammonium sulfate nitrate + 3,4-dimethylpyrazol phosphate; ASN – ammonium sulfate nitrate; time of K application: simultan, before and after
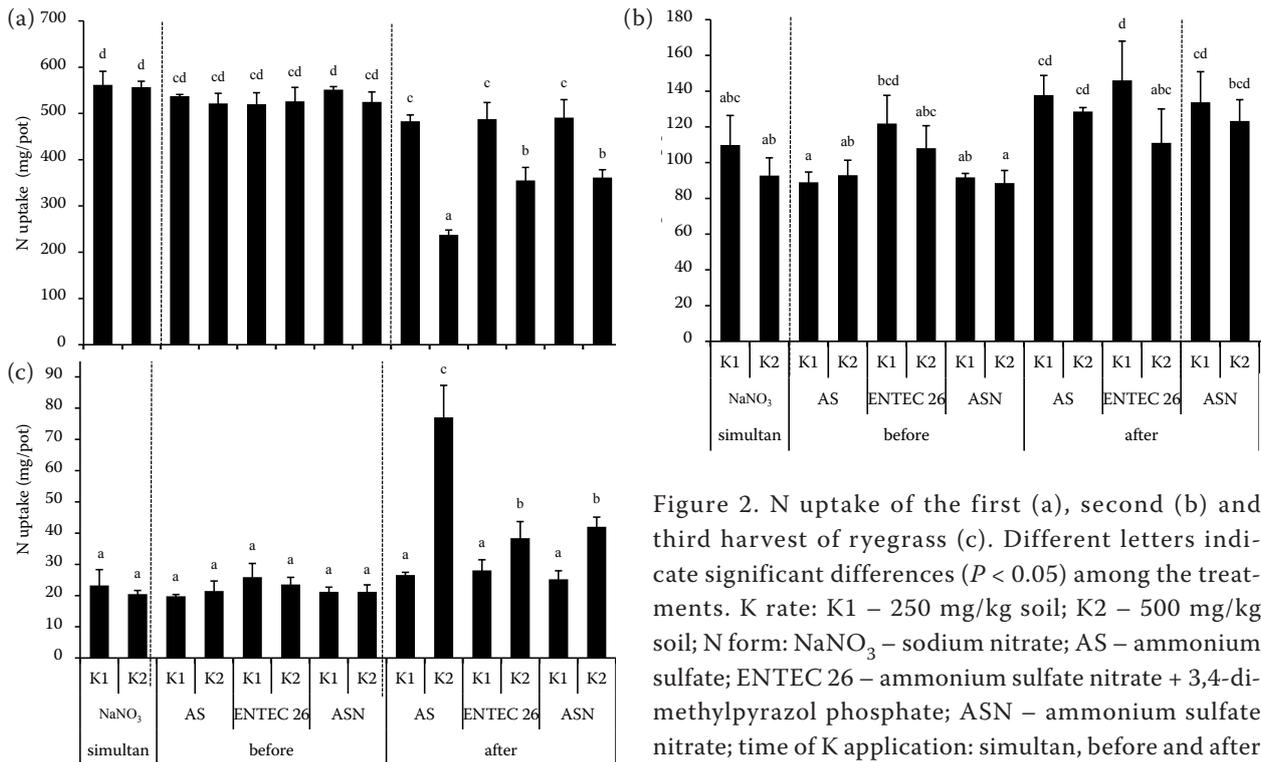
Figure 2. N uptake of the first (a), second (b) and third harvest of ryegrass (c). Different letters indicate significant differences ($P < 0.05$) among the treatments. K rate: K1 – 250 mg/kg soil; K2 – 500 mg/kg soil; N form: NaNO$_3$ – sodium nitrate; AS – ammonium sulfate; ENTEC 26 – ammonium sulfate nitrate + 3,4-dimethylpyrazol phosphate; ASN – ammonium sulfate nitrate; time of K application: simultan, before and after

amount of applied K$^+$ was negligible. Also when K$^+$ was applied after the ammonium containing

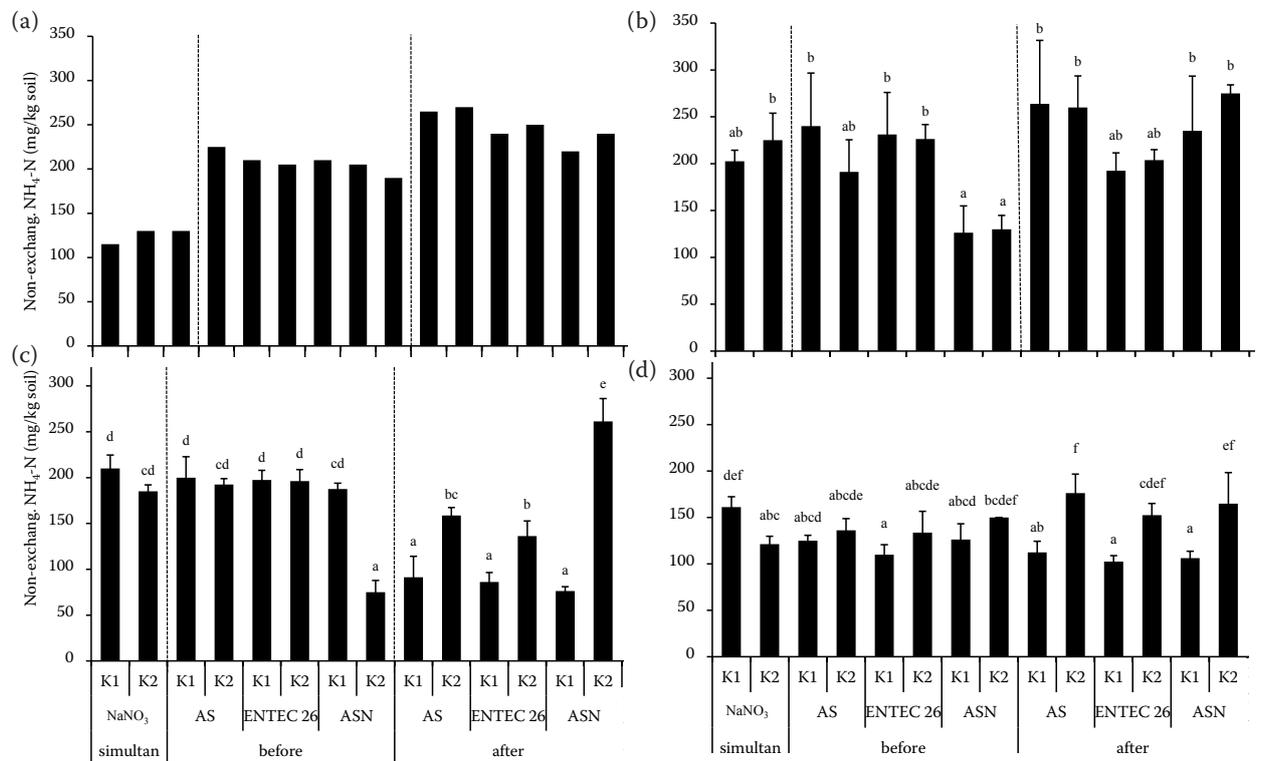fertilizers NH$_4^+$ fixation was not influenced by the K$^+$ application rate. The NH$_4^+$ fixation rate was

Figure 3. Contents of non-exchangeable NH$_4^+$-N after soil incubation (a) and after the first (b), second (c) and third harvest (d) of ryegrass. Different letters indicate significant differences ($P < 0.05$) among the treatments. K rate: K1 – 250 mg/kg soil; K2 – 500 mg/kg soil; N form: NaNO$_3$ – sodium nitrate; AS – ammonium sulfate; ENTEC 26 – ammonium sulfate nitrate + 3,4-dimethylpyrazol phosphate; ASN – ammonium sulfate nitrate; time of K application: simultan, before and after

highest in the case of $(NH_4)_2SO_4$. Between the start of the experiment and the first harvest the content of non-exchangeable NH_4^+-N increased in both $NaNO_3$ treatments, while in most of the other treatments non-exchangeable NH_4^+-N was mobilized. Until the first harvest mobilization was highest when ASN was applied before K^+ (Figure 3b). After the first harvest until to the second harvest the influence of time and amount of K^+ application on NH_4^+ mobilization was negligible, when K^+ was applied before N, except in the treatment when K^+ was applied after ASN at the high rate. In the treatments when K^+ was applied after N, mobilization of non-exchangeable NH_4^+-N was significantly lower at the high K^+ application rate (Figure 3c). After the second harvest the influence of the K^+ application rate on the content of non-exchangeable NH_4^+-N was negligible when K^+ was applied before N. However, the high K^+ application rate after NH_4^+ resulted in a significantly higher content of non-exchangeable NH_4^+-N as compared to the treatments with the low K^+ application rate (Figure 3d).

After treating the soil with N and K independent of the time of K^+ application the content of plant available K^+ was always higher with the high K^+ application rate. In the concomitant N fertilizer treatment the content of plant available K^+ was higher when K^+ was applied after NH_4^+ (Figure 4a). After the first harvest the content of plant available K^+ was significantly highest in the treatments with the high K^+ application rate after NH_4^+ (Figure 4b) while after the second (Figure 4c) and third harvest (Figure 4d) the content of plant available K^+ was significantly higher with the high K^+ application rate independent of the time of K^+ application.

DISCUSSION

Frequently claimed advantages for the use of N fertilizers stabilized with nitrification inhibitors are yield increases (Wozniak et al. 1997). However, according to Pasda et al. (2001) the yield-increasing effect of DMPP, having a duration time between 6
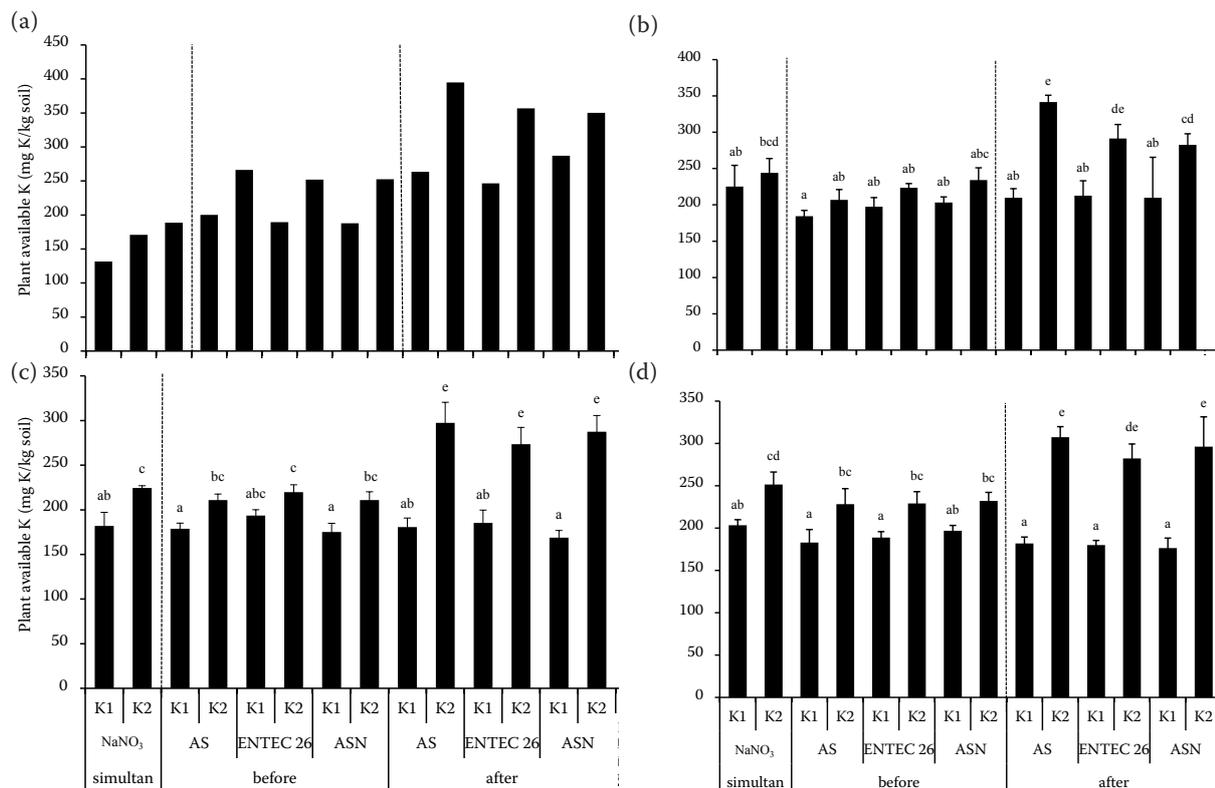

Figure 4. Plant available K after soil incubation (a) and after the first (b), second (c) and third harvest (d) of ryegrass. Different letters indicate significant differences (*P* < 0.05) among the treatments. K rate: K1 – 250 mg/kg soil; K2 – 500 mg/kg soil; N form: $NaNO_3$ – sodium nitrate; AS – ammonium sulfate; ENTEC 26 – ammonium sulfate nitrate + 3,4-dimethylpyrazol phosphate; ASN – ammonium sulfate nitrate; time of K application: simultan, before and after

to 8 weeks (Villar and Guillaumes 2010), is stronger the lighter the soil. When applying ammonium stabilized N fertilizers to heavy soils it must be recognized that at least a part of the NH_4^+ ions may be fixed by clay minerals, decreasing the momentary N availability for plants. Using a soil with a high fixation capacity we found that almost all of the ammonium applied with AS was fixed by clay minerals during the incubation of the soil, when N was applied before K^+. As compared with AS, fixation of NH_4^+ was lowest with ASN, while ENTEC 26 was ranging in between. Because Pasda et al. (2001) found that at 20°C, nitrification of ASN was completed within 7 to 21 days, as compared to 40 days with DMPP, we assume that the lowest fixation in our experiment was caused by a partial nitrification of non-stabilized ammonium of ASN during the incubation period of the soil.

As a result of competition for fixation sites (Beauchamp 1982) applying K^+ before NH_4^+ containing N fertilizers resulted in a decreased NH_4^+ fixation, with a mean decrease of about 20%. This is in accordance with the results of Bartlett and Simpson (1967) showing that K^+ pre-addition depressed NH_4^+ fixation by occupying interlayer positions of 2:1 clay minerals. As expected after applying $NaNO_3$ the increase of non-exchangeable NH_4^+-N was negligible. However, after the first harvest a steep increase of this N fraction was observed, assuming that the NH_4^+ ions are derived from mineralization of soil organic matter (Tang et al. 2008).

As expected independent of the time of K^+ application the content of plant available K^+ was higher with the high K^+ application rate. However, the time of K^+ application was of prime importance resulting in higher contents of plant available K^+ when K^+ was applied after NH_4^+, because as a result of competition for the same fixation sites less interlayer space was available for K^+ (Scherer 1982).

Steffens and Sparks (1997) described the kinetics of mobilization of non-exchangeable NH_4^+-N from clay minerals by the Elovich model. Whether non-exchangeable NH_4^+-N can be released depends on the concentration gradient of NH_4^+ in the interlayers and soil solution (Tang et al. 2008). However, Nommik (1957) suggested that also K^+ should be introduced into the equilibrium equation. Therefore the influence of K^+ becomes of practical importance (Axley and Legg 1960, Škarpa and Hlušek 2012). When the content of plant available K^+ is high as in our treatments K^+ after NH_4^+, it may be assumed that also the edge positions of

the clay minerals are occupied by K^+, hindering the diffusion of NH_4^+ ions out of the interlayers. Indeed after the second and third harvest, the content of non-exchangeable NH_4^+-N was higher in the treatments with the high K^+ application rate after NH_4^+.

At the first harvest the influence of the amount as well as the application time of K^+ on yield formation was negligible, because plant available N was not growth limiting. However, yield of the second harvest was significantly highest with the low K^+ application rate after NH_4^+. We assume that in the mean K^+ ions, mainly located at the edge position of the clay mineral interlayers, were mobilized and the blocking effect of K^+ diminished, favouring the release of non-exchangeable NH_4^+-N. With the high K^+ application rate the release of non-exchangeable NH_4^+-N was still blocked and N uptake was significantly lower, confirming that K^+ governs the release of non-exchangeable NH_4^+-N (Welch and Scott 1960) and therefore yield formation. After the second harvest the blocking effect of K^+ on the release of non-exchangeable NH_4^+-N seems to be overcome and highest yields of the third harvest were now reached in the treatments with the high K^+ application rate after NH_4^+.

Calculating total yield (sum of three harvests) there is evidence that the K^+ application rate has no impact on the availability of non-exchangeable NH_4^+-N when K^+ is applied before ammonium containing fertilizers. However, when K^+ was applied after ammonium containing fertilizers total yield was significantly higher with K1. Although continuous uptake of K^+ ions reduced the K^+ concentration and diminished the blocking effect on the release of NH_4^+ (Nieder et al. 2011) the K^+ concentration in the treatments with K2 was still too high to overcome the blocking effect. Therefore the statement of Pasda et al. (2001) that N fertilizers combined with DMPP may improve yields of agricultural crops and vegetables must be observed in more details.

Besides yield formation total N uptake was significantly lower with the high K^+ application rate after ammonium-containing fertilizers. The depression of N uptake at the first harvest could not be compensated by the higher N uptake of the third harvest. The mean total N uptake was lower by about 25%. Therefore from a practical point of view N fertilizers with a high share of ammonium should not be applied before potassium to soils with an appreciable fixation capacity (Axley and Legg 1960).

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