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Short communication

Uptake and leaching of sorbed ammonium during early growth of wheat

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Abstract

Purpose Sorption could be a way to concentrate nutrients in diluted waste streams to bring more nutrients back to agriculture. The aim of this work was to model the fate of sorbed NH_4^+ content in liquid waste streams by adding nitrogen (N) sorbed to a sorbent, zeolite, and study its effect on early growth and potential leaching losses.

Methods A pot experiment with two soil types and wheat as test crop was conducted. Mineral N in soil was measured, and a leaching experiment performed. ^{15}N labelled ammonium was sorbed to zeolite. The fertilizer effect was then compared to ammonium fertilizer applied the conventional way, with and without zeolite.

Results Early uptake of sorbed ammonium was reduced by 56% compared to ammonium applied conventionally, and soil uptake compensated only very early. Nitrate concentration in leachates was reduced by 12% in sandy soil when N was applied sorbed to zeolite. However, leaching of water through the profile increased 71% when N was applied sorbed to zeolite, so that there was only a tendency to lower N losses when N was applied sorbed to zeolite.

Conclusion Ammonium-N sorbed to zeolite is less plant available than conventionally applied N but may also be less prone to leaching losses.

Keywords Sorption, Zeolite, Nitrogen leaching, Root: shoot ratio

Introduction

One way to concentrate nutrients in wastewater and waste with high water content, e.g. liquid digestate, would be to sorb it to cheap and abundant sorbents before dewatering (Chin et al. 2018; Guaya et al. 2016; 2017). Cation exchange is the most common, particularly removal of ammonium (Guaya et al. 2016; 2017; Hollister et al. 2012; Mazeikiene and Valentukrvicirne 2016). One widely used sorbent is zeolite. NH_4^+ can easily occupy exchange or sorption sites in zeolite (Eberl 2002). The sorbent loaded with nutrients can then be applied to agricultural soils as fertilizer (Guaya et al. 2018; Kocatürk-Schumacher et al. 2019). Ammonium sorbed to zeolite was shown to be a slow release fertilizer (Faccini et al. 2018; J. Li et al. 2013; Z. Li et al. 2013). Mixing sorbents into ammonium rich residues before application to soil have also been reported to reduce gaseous losses of N (Hill et al. 2016; Redding 2013; Redding et al. 2016), and ammonia/ammonium sorbed to biochar (Taghizadeh-Toosi et al. 2012) and zeolite (Foereid et al. 2019) have been shown to be at least partly plant available. Kocatürk-Schumacher et al. (2019) found that zeolite was better than biochar.

The rhizosphere is the area around the root affected by it. Root induces changes in rhizosphere by exudation of inorganic and organic chemicals that may enhance nutrient sorption (Hinsinger 2001). The root:shoot ratio usually indicates if the plant is most limited by the shoot or root processes, e.g water and nutrient uptake (Fageria and Moreira 2011). Nitrogen (N) supply has strong effect on root development and root:shoot ratio. The general rule is that plants allocate relatively more to roots when nutrients and/or water is limiting, but as also root growth can be reduced if resources are limited, root:shoot ratio is not always predictable (Shangguan et al. 2004).

N applied to agricultural soil is always vulnerable to losses. As well as a loss of fertilizer, losses of N to

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the environment represent a problem (Bechmann and Stålnacke 2019). Nitrate is easily lost by leaching, but losses are not easily predicted from N input (Wang et al. 2019; Xin et al. 2019). Losses depend on soil type more than fertiliser application, sandy soils with few sorption sites are particularly vulnerable (Köhler et al. 2006). Ammonium is usually nitrified to nitrate soon after application to agricultural soil, so ammonium application can also cause nitrate leaching (Sogn et al. 2018). The best way to reduce leaching losses would be to make sure that plants can take up the N before it is lost. Ways to bind N in the soil hard enough to prevent leaching but still allow plant uptake are therefore sought. Sorbed nutrients may be less vulnerable to leaching and other losses. Most research so far has focussed on applying sorbents separately to improve sorption properties in the soil. Addition of sorbents to soil can improve nutrient retention, although results vary and depend on conditions (Nakhli et al. 2017). More recently, there has also been more research on sorbing nutrients before applying nutrient loaded sorbents to soil. Results suggest that sorbed nutrients are leached out slowly (Chin et al. 2018; Eslami et al. 2017; Guaya et al. 2016; 2017; Mazloomi and Jalali 2019). It is likely that applying N sorbed to a sorbent can reduce leaching and therefore increase crop yield in some situations. Malekian et al. (2011) found that zeolite application reduced nitrate leaching and increased plant uptake of N, although it depends on zeolite type. Perrin et al. (1998) found higher yields when nutrients were applied sorbed in a field experiment with maize, most likely because of reduced N leaching. However, lower availability of sorbed N (Foereid et al. 2019) works in the opposite direction. In that study, it was found that N uptake was reduced when N was applied sorbed to zeolite.

Here mineral N transformations during early growth of wheat and leaching during a leaching event are compared when N was applied with and without zeolite and sorbed to zeolite. The aim was to simulate ammonium behaviour when applied after sorbents have been mixed into ammonium rich liquid wastes compared to conventional application of ammonium-N.

Materials and methods

The general setup of the experiment was described by Foereid et al. (2019). Briefly, the treatments were no applied N (0N) and N applied sorbed to zeolite (Nsorb), same amount of N and zeolite applied, but just mixed (N+zeo) and same amount of N, but no zeolite (N). The amounts were 0.2 g N to all pots receiving N fertilizer, and 11.67 g zeolite to all pots receiving zeolite (Nsorb and N+zeo). ^{15}N labelled ammonium sulphate labelled at 5% strength was used in all treatments receiving N. Solutions of 1 g L^{-1} labelled ammonium sulphate were prepared and 16 g L^{-1} zeolite was applied. The sorption is described in Foereid et al. (2019). P and K were applied as recommended (NIBIO 2016), 0.6 g K_2SO_4 and 0.25 g KH_2PO_4 per pot.

Two contrasting soil types, one chernozem and one sandy soil were used in the experiment. The soils are described earlier (Foereid et al. 2019), and the properties are shown in Table 1. Briefly, both soils were collected in May 2016 in Nyíregyháza and Tiszavasvári (30 km from Nyíregyháza), Hungary, and all treatments were done with 3 replicates. Wheat was used as a test crop because it is one of the most commonly grown crops in Europe, and because many experiments use this crop, making comparisons easier. 13 wheat (*Triticum aestivum* var "Bjarne") seeds were sown in 2 L of volume pots, thinned to 10 shortly after germination. Pots were watered to maintain water content between half field capacity and field capacity. The temperature in the greenhouse was kept at or above 20/12 ºC day/night and light was for16 hours a day. Two series of treatment (each 24 pots) were started, to get two harvest times. In one series, 50 g of soil was sampled on day 12 and at harvest, on day 28. The soil was sampled with a 1 cm diameter corer. Soils were frozen (-20°C) for analysis of mineral N. In addition, 3 samples from each soil before growth were collected and frozen for analysis in the same way. In the other series, plants were harvested on day 14. Just before harvest, a leaching experiment was performed. 0.6 L water was applied to the top of each pot, and leachates collected at the bottom. Aboveground plant parts were harvested shortly after addition of water, and pots were covered and put in a cold store (4°C) for 24 hours to finalize leaching without evaporation. Total amount of leachate from each pot was measured, and leachates were frozen (-20°C) until further analysis of mineral N and ^{15}N signature in mineral N. After the leaching experiment, roots were washed out.

Table 1 Chemical and physical characteristics of the soils used measured by Eurofins standard methods (Foereid et al. 2019)

Physical and chemical properties	Sandy soil	Chernozem
Dry matter (%)	99.4	96.9
pH	7.0	6.4
Conductivity (mS/m)	2.5	5.4
Loss on ignition (%)	1.2	5.7
Elements for plant growth	Sandy soil	Chernozem
Total carbon (%)	0.22	1.9
Nitrogen (%)	0.04	0.21
Phosphorous (%)	0.023	0.071
Potassium (%)	0.067	0.31
Calcium (%)	0.092	0.36
Magnesium (%)	0.12	0.36
Iron (%)	1.00	2.3
Aluminium (%)	0.67	1.7
Boron (mg/kg)	< 5	6.9
Manganese (mg/kg)	170	490
Sodium (mg/kg)	< 50	
Sulphur (mg/kg)	49	210
Available nutrients	Sandy soil	Chernozem
Ammonium-N (%)	0.000755	0.00187
Nitrate-N (%)	0.000294	0.00317
Phosphorous (%)	0.0047	0.010
Potassium (%)	0.010	0.036
Calcium (%)	0.11	0.31
Magnesium (%)	0.0079	0.033
Sodium (%)	<0.005	<0.0051

Harvested plant shoots and roots were dried at 70°C and weighed. Weights were used to calculate root: shoot ratio. Dry plant and soil samples were grinded to < 2 mm and analysed for total N and C and ^{15}N signature. Total N and C in plant samples were measured on CHN analyzer (Elementar Vario EL with TCD decetor). Mineral N (nitrate and ammonium) in frozen soil samples was measured by KCl extraction with subsequent measurement on Tecator Flow injection analysis (Ogner et al. 2000). Leachates were filtered and ammonium concentration was measured on the same instrument (Ogner et al. 2000). ^{15}N signature was measured in UCDavies Stable Isotope Laboratory. Isotope ratio in plant and soil samples were measured directly on grinded samples.

Minitab v18 program was used for statistical analysis with 5% significance level. One and two-way ANOVAs were used to compare treatments. The treatment with no N was excluded from these analyses when the aim was to compare different ways of applying N. Individual treatments were also compared using t-test when appropriate.

Results and discussion

Plant growth (Fig. 1) and N uptake (Fig. 2) were not significantly different between treatments the first 28 days, but there was a tendency that N uptake from fertilizer was lower when N was applied sorbed to zeolite. A study with biochar indicates that whilst biochar can increase crop yield when applied with fertiliser, it can reduce it when applied without fertiliser (Oladele et al. 2019), suggesting that some N may be made unavailable by strong sorption to biochar. Previous studies without plants (Chin et al. 2018; Guaya et al. 2016; 2017) suggest that nutrients are released slower when applied sorbed to a sorbent. In the 0N treatment, N uptake from soil compensated from lower N uptake from fertilizer only in the very beginning (Fig. 2). N uptake from soil compensated more in the chernozem than the sandy soil. Less soil uptake from sandy soil has also been found by others (Sogn et al. 2018). On day 28, uptake from soil was reduced in the 0N treatment compared to the treatments receiving N fertiliser. This indicates that plants were not able to compensate for lack of N fertiliser by increased uptake from soil. This seems to indicate that N starved plants quickly lag behind fertilized plants, and that also limits uptake from soil.

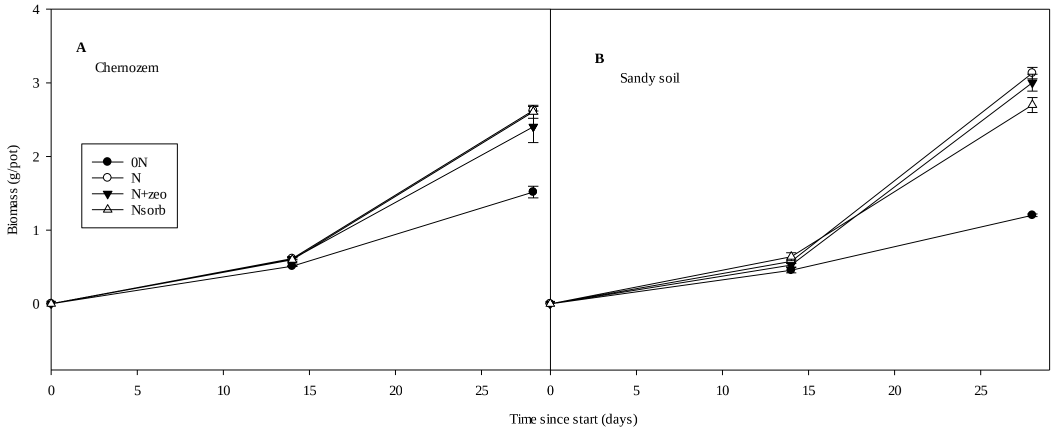

Fig.1 Biomass as a function of time since start for chernozem (A) and sandy soil (B). Error bars are standard error (N=3)

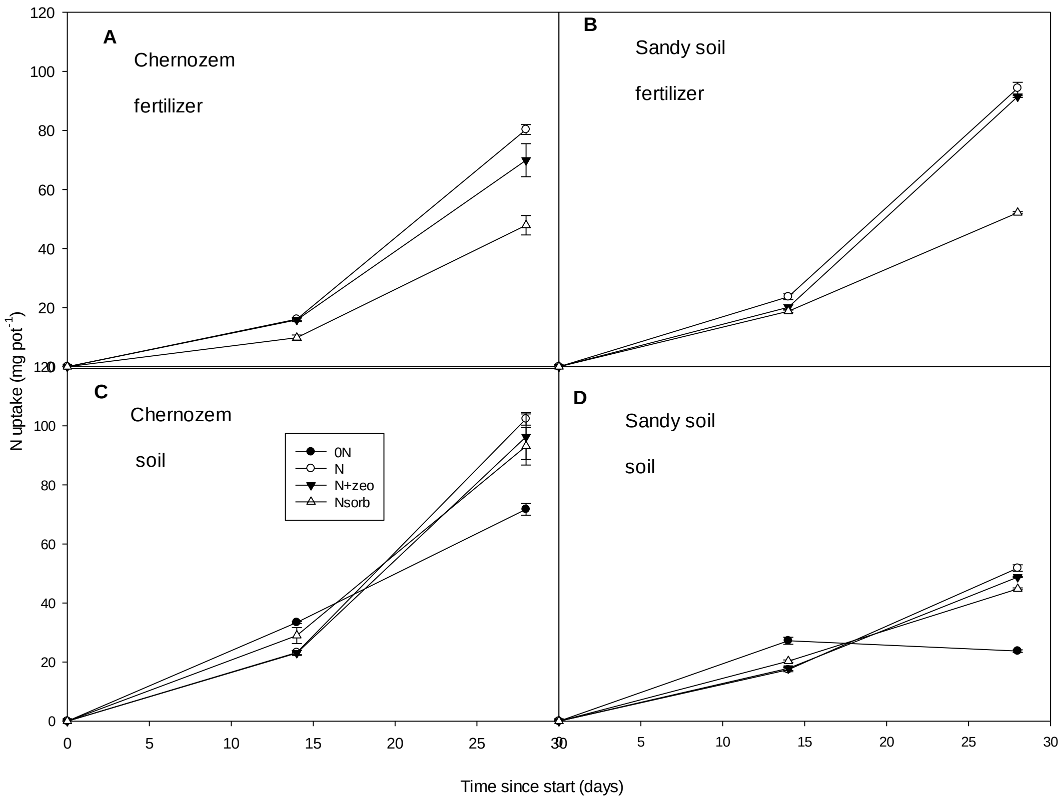

Fig. 2 N uptake from fertilizer (A-B) and soil (C-D) calculated from ^{15}N signature for sandy soil (right) and chernozem (left). 0N: no Nitrogen; N: N fertilizer; N+zeo: N fertilizer with zeolite without sorption; Nsorb: N sorbed to zeolite. Error bars are standard error (N=3)

Root: shoot ratio after 14 days of growth is shown in Fig. 3. There was no significant effect of treatment or soil type, but there was a significant interaction between them. This indicates that the effect of the treatment depends on soil type. High root:shoot ratio usually indicates nutrient and/or water limitation (Ericsson 1995; Hilbert 1990; Shangguan et al. 2004; Ågren and Franklin 2003). This tendency was seen in the chernozem, whilst the opposite tendency was seen in sandy soil (Fig. 3). Investment in roots would pay off in the chernozem even when no fertilizer was applied, but not in the sandy soil because the chernozem contains more mineral N (Table 1) and more N mineralisation potential (Fig. 4). Different responses to nitrate and ammonium as N source have been reported (Drew 1975; Lima et al. 2010). It is possible that this could explain the results as nitrate concentrations were always higher in the chernozem than the sandy soil.

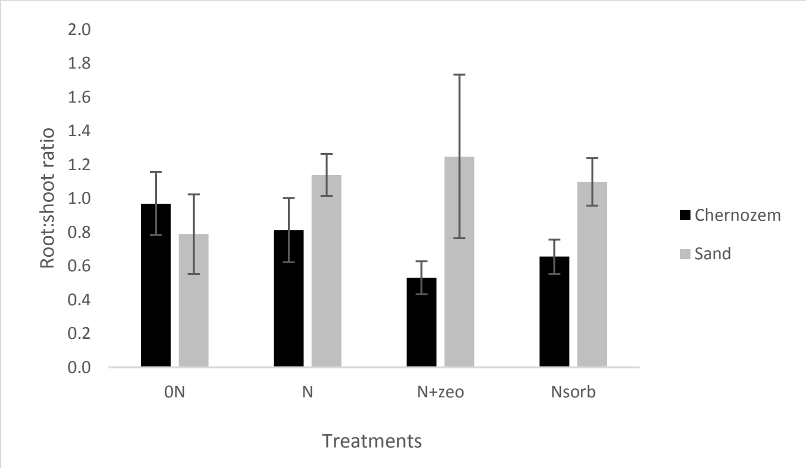

Fig. 3 Root to shoot ratio on weight basis after 14 days of growth. Error bars are standard error (N=3). 0N: no N; N: N fertilizer; N+zeo: N fertilizer with zeolite without sorption; Nsorb: N sorbed to zeolite. Error bars are standard error (N=3)

Extractable mineral N was higher on day 12 than at the start, before fertilizer application, in all treatments that received fertilizer. Then concentration of both nitrate and ammonium decreased towards the end on day 28 (Fig. 4). There were less differences between treatments in nitrate than ammonium concentration, but also nitrate concentration increased after fertilizer application, indicating that significant nitrification was happening in all treatments. Caspersen and Ganot (2018) concluded that nitrification was the main mechanism of N release from biochar soaked in urine. There is little indication that this was the mechanism here, but lower nitrate concentration in leachates in the Nsorb treatment may indicate reduced nitrification in this treatment. Barbarick and Pirola (1984) showed that ammonium is bound within the pores of zeolite that are too small for microbes to enter, and this can explain less nitrification in the treatment where N was applied sorbed to zeolite. The applied N was used by plants much faster in the sandy soil than in the chernozem. The faster utilization of applied N could be forced by the lower N content of sand than of chernozem (Table 1).

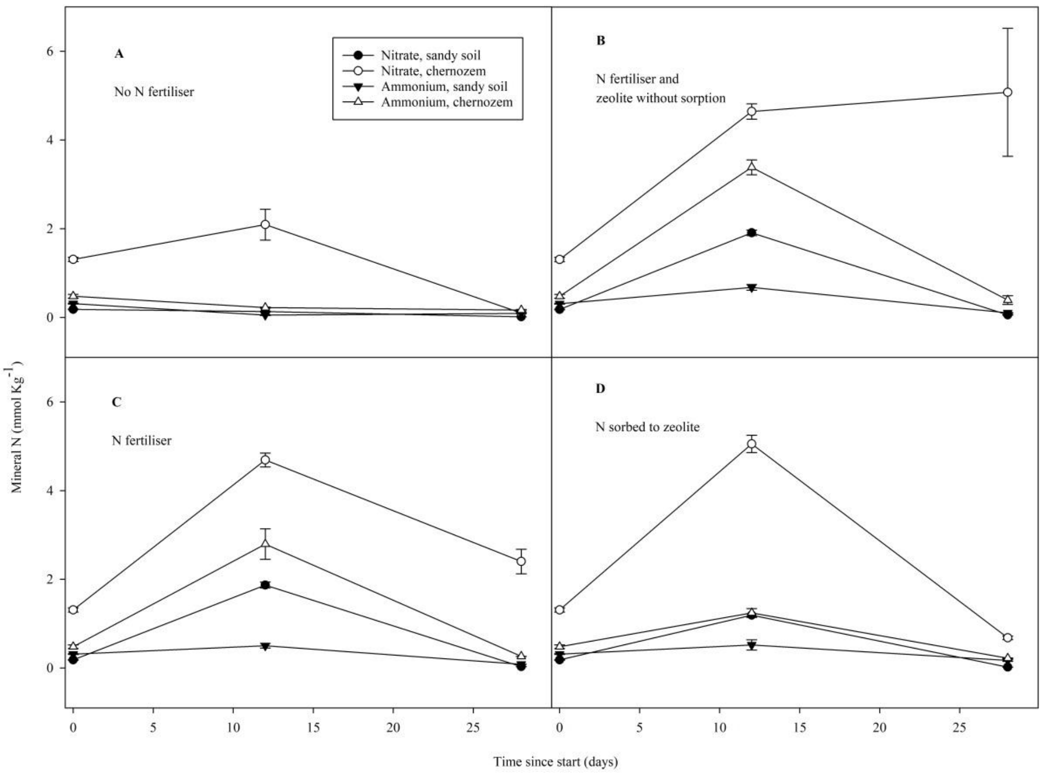

Fig. 4 Nitrate and ammonium concentration in each soil as function of time after sowing for each treatment (A-D). Error bars are standard error (N=3)

Nitrate concentration in leachates was significantly lower when N was applied sorbed to zeolite than in the other treatment receiving N in the sandy soil. However surprisingly, there were also some differences in the amount of water leached (Fig. 5), so there was only a tendency to lower total losses of ammonium and nitrate per pot when N was applied sorbed to zeolite (Fig. 6). Whilst it is known that zeolite additions can change water relations (Nakhli et al. 2017), it is harder to explain how N sorbed to the zeolite could affect it differently from zeolite and N applied separately. However, root growth pattern may change (Chin et al. 2018) to grow more into the zeolite, and this may lead water to more efficient flow paths.

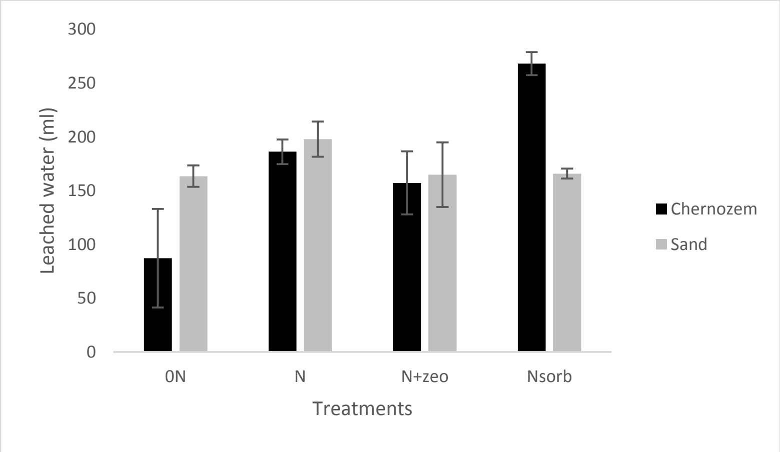

Fig. 5 Amount of leached water (out of 600 mL applied) after 24 hours. 0N: no Nitrogen; N: N fertilizer; N+zeo: N fertilizer with zeolite without sorption; Nsorb:N sorbed to zeolite. Error bars are standard error (N=3)

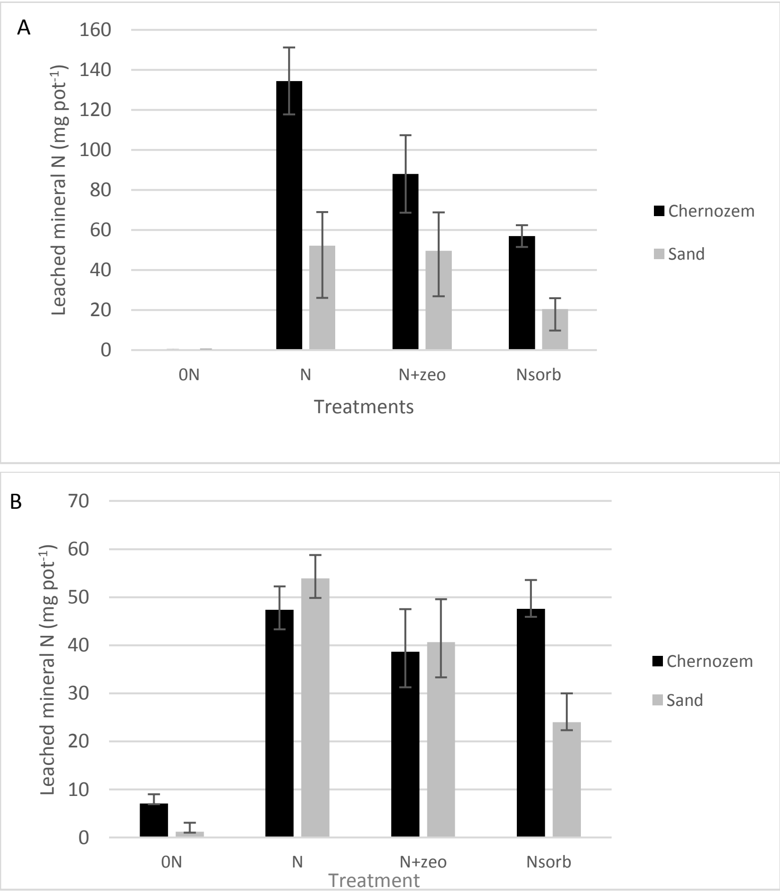

Fig. 6 Mineral N (A – ammonium, B – nitrate) leached after 24 hours. 0N: no Nitrogen; N: N fertilizer; N+zeo: N fertilizer with zeolite without sorption; Nsorb: N sorbed to zeolite. Error bars are standard error (N=3)

Conclusion

Using zeolite as a sorbent for ammonium can make it less available to plants. This should be taken into account when determining the dose of fertiliser based on sorption from liquids, but as the nutrients in the liquid would otherwise be wasted, using sorbents can still be recommended. Our results suggest that it is important to have ample N available to wheat early in growth to build up a root system to take up N efficiently later. Ammonium sorbed to zeolite also seems to be less prone to leaching losses, although the results here are somewhat inconclusive. Further studies are recommended to assess if N sorbed to sorbents is less available for leaching, and to assess the effects on both plant uptake and leaching over more than one growing season. Our results also indicate that these studies should be done under realistic conditions, as the presence of plants may have changed water flow pattern.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study

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