Leaching of nitrogen from calcareous soils in western Iran: a soil leaching column study

Mahboubeh Zarabi · Mohsen Jalali

Abstract Nitrogen (N) leaching has become a matter of worldwide concern. The objectives of this study were: (1) to use soil columns to investigate the leaching of nitrate (NO_3^-), ammonium (NH_4^+), and nitrite (NO_2^-) from calcareous soils that had received an average of 200 kg^{-1} N ha^{-1} $year^{-1}$ for the previous 30 years and (2) to determine the relationship between soil properties and NO_3^-, NH_4^+, and NO_2^- leaching. The soils used in this study ranged in texture from clay to sandy loam. Leaching experiments were conducted under saturation conditions and consisted of the collection of 1,047–2,524 mL of leachate (12 pore volumes (PVs)), which was equivalent to 534–1,286 mm from rainfall or irrigation. Losses of NO_3^- ranged from 62 to 437 kg ha^{-1}, while losses of NH_4^+ and NO_2^- ranged from 2.5 to 19.3 kg ha^{-1} and 0.1 to 10.6 kg ha^{-1}, respectively. Leaching rates differed between soil samples. The initial and secondary rate of NO_3^- leaching was determined using an exponential model, and it ranged from 2.8 to 14.7 mg kg^{-1} PV^{-1} and 0.11 to 0.32 mg kg^{-1} PV^{-1}. Greater leaching rates in the initial period could be due to leaching of NO_3^- in solution, while the secondary leaching might be attributable to the diffusion-controlled transfer of NO_3^- between mobile and immobile liquid phases. Analysis of variance indicated that the effects of soil type on total NO_3^- leaching were highly significant ($p < 0.001$). The results showed that soil NO_3^- concentration was positively correlated with the peak concentration of NO_3^- ($r = 0.86$; $p < 0.01$) and the total NO_3^- leached ($r = 0.93$; $p < 0.01$). In addition, the total NH_4^+ leached was positively correlated with silt ($r = 0.67$; $p < 0.05$), clay ($r = 0.61$; $p < 0.05$), and pH ($r = 0.77$; $p < 0.01$), which suggests that soil parameters might be useful indicators of NO_3^- and NH_4^+ leaching from calcareous soils. Nitrate leaching from soils could threaten groundwater supplies, so possible strategies for minimizing NO_3^- leaching losses may need to be considered.

Keywords Nitrate · Ammonium · Leaching · Groundwater · Contamination

Introduction

Nitrogen (N) is a key nutrient that influences soil fertility and crop production. Nitrogen is required in greater quantities by plants compared with other essential elements derived from the soil. The application of agricultural chemicals has increased the productivity of modern agriculture, but overfertilization with N does not lead to any extra yield of grain (Berenguer et al. 2009). Instead the excess N accumulates in the soil in the form of NO_3^-, and it can become a potential

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source of NO_3^- in groundwater (Hayshi and Hatano 1999). Other researchers (e.g., Hallberg 1989) have reported that the application of fertilizer to irrigated crops is the most extensive human cause of NO_3^- pollution of groundwater systems.

Nitrate is highly mobile in the soil, and it can readily move down into the subsoil and from there into groundwater. In certain soils, NO_3^- movement could be as much as six times greater than NH_4^+.

Nitrate contamination of groundwater and surface water is a global agricultural and environmental issue (Böhlke 2002; Almasri and Kaluarachchi 2004; Beeson and Cook 2004; Wassenaar et al. 2006; Rivett et al. 2007; Roy et al. 2007). Nitrate pollution originating from fertilizers has been reported in groundwater from many parts of the world (Shomar et al. 2008; Angelopoulos et al. 2009). In Europe, NO_3^- concentrations exceeding the World Health Organization (WHO) recommendations (1993) for drinking water (50 mg L^{-1}) were found in groundwater beneath 22% of the cultivated land (Lægreid et al. 1999). Chen et al. (2007) reported that excessive chemical fertilizer application in the Tai Lake region led to an increase of NO_3^- in groundwater, which in turn led to eutrophication of Tai Lake. Song et al. (2009) found large differences in leachate NO_3^- concentrations (ranging from 17 to 457 mg N L^{-1}) and NO_3^- losses (152–347 kg N ha^{-1}) from 1 m of soil profiles in the field, with conventional agronomic practices.

Nitrogen fertilization of agricultural crops is an important economic and environmental issue, especially in high-yielding irrigated Asian areas. The intensification of agriculture has contaminated groundwater with NO_3^- in many parts of Iran. Producers have traditionally applied more N fertilizer than required, which has led to environmental problems in recent years. In some regions of Iran, groundwater is polluted with NO_3^-, often at levels exceeding 50 mg L^{-1} NO_3^-, which is the maximum permissible concentration recommended by the WHO. Jalali (2005) studied the NO_3^- pollution of groundwater in Hamedan and found that 196 of 311 wells (63%) had NO_3^- levels lower than 50 mg L^{-1}, whereas the remaining 115 (37%) exceeded this level. The extent and intensity of agriculture in Hamedan, located in the west of Iran, has led to much higher annual rates of fertilizer application, and this has greatly affected water quality. Farmers in this area tend to apply high amounts of N fertilizer (ranging from 138 to

230 kg N ha^{-1}) to their crops, which include potatoes, corn, tomatoes, and other vegetables (Jalali 2005). This high application rate resulted in a total loading that was much higher than the N demand of vegetables and other crops in fields (Jalali 2005). The contamination was detected in groundwater from wells in most of the potato and vegetable crop production areas, which exhibited NO_3^- concentrations that were significantly elevated above the level that affects humans (13 mg L^{-1}), while some exceeded the WHO limit of 50 mg L^{-1}. Jalali (2008) also studied NO_3^- concentrations in vegetables and soils in Hamedan, western Iran, and concluded that continuous vegetable cropping caused accumulation of NO_3^- in the soil, with a mean N accumulation of 81 mg NO_3^-–N kg^{-1}.

The population is increasing in this region and farm land is limited, so it is important to understand the process of NO_3^- movement in soil and to assess the consequences of new agricultural management practices. Identifying sites and soils that are prone to NO_3^- leaching is necessary to ensure regularly monitoring and appropriate management.

A number of laboratory soil column studies on NO_3^- leaching have been published in recent years (Azevedo et al. 1996; Chinkuyu and Kanwar 1999; Chen et al. 2007), but none report the effects of soil properties on N leaching in calcareous soils. Therefore, the objectives of this study were: (1) to examine leaching of NO_3^-, NH_4^+, and NO_2^- in soil columns and (2) to determine the relationship between soil properties and the amount of NO_3^-, NH_4^+, and NO_2^- leached.

Materials and methods

Experimental soils

Eleven soil samples were collected from the surface (0–30 cm) horizon of agricultural soils in Hamedan province, western Iran. The soils represented typical soils continuously cultivated for winter wheat (*Triticum aestivum* L.), potatoes (*Solanum tubersum*), garlic (*Allium sativum*), vegetables, pasture, and gardens. The soils were collected from fields with a history of 30 years continuous fertilization with 138 to 230 N kg^{-1} ha^{-1} $year^{-1}$ (mean=200 kg^{-1} N ha^{-1} $year^{-1}$). Soils were air-dried and passed through a 2-mm mesh sieve to remove stones before analysis. Soil pH,

organic matter, texture, electrical conductivity, and equivalent calcium carbonate were determined according to the methods of Rowell (1994). Mineral N (NO_3^-, NH_4^+, and NO_2^-) was extracted from soils using 1 M KCl in a 1:10 solution ratio, with shaking for 1 h. Concentrations of NO_3^-, NH_4^+, and NO_2^- were determined colorimetrically (Mulvaney 1996). Nitrate can be expressed as either NO_3^- (nitrate) or NO_3^-–N (nitrate–nitrogen). Maximum acceptable nitrate levels according to the U.S. Environmental Protection Agency (USEPA) are 10 mg L^{-1} NO_3^-–N or 50 mg L^{-1} NO_3^-.

Soil column leaching experiment

The leaching of native N was investigated using leaching columns, which consisted of Pyrex tubes that were 30 cm in length with an internal diameter of 5 cm. Soils of different textures were added to the columns to a height of 20 cm, with uniform tapping by a wooden rod to achieve a uniform bulk density of 1.2–1.7 gcm^{-3}, which was dependent on field bulk densities. A gap of 10 cm remained above the soil in the columns. The soil was retained by a Whatman no. 42 filter paper, which was supported by a nylon mesh base. The soil was covered with a filter paper after packing to avoid dispersion of the surface soil. Columns were saturated with distilled water for 24 h, and the native N of soils was leached with distilled water. Distilled water was used to represent the relatively low salinity precipitation received from rainfall or snowmelt in arid and semi-arid regions (Rowell 1994; Al-Webel et al. 2002). The leaching trial resulted in the collection of 1,047–2,524 mL of leachate (12 pore volumes (PVs)), which was equivalent to 534–1,286 mm of rainfall or irrigation. The annual rainfall was assumed to equal 300 mm. The PV of soil columns was the volume of water-filled pores in the column, and it was calculated as 138–210 mL, based on the bulk density (1.23–1.73 gcm^{-3}) and particle density (2.65 gcm^{-3}) of the soil in the column (Rowell 1994). The PV enables comparisons of leaching studies. Leaching experiments were conducted under saturation conditions, with two replicates at room temperature (22–26°C). The leaching process was stopped after 7 PV with soil sample 4, due to blockage of the column. The solution level was maintained at approximately 5± 1 cm above the soil surface in the columns. Leachates

from each leaching stage were collected at the following intervals: 1/8 PV until 1.5 PV; 2/8 PV until 7 PV; 4/8 PV until 10 PV; and every PV until 12 PV. Leachates were analyzed for pH, electrical conductivity (EC), NO_3^-, NO_2^-, and NH_4^+. Concentrations of NO_3^- NO_2^-, and NH_4^+ were determined colorimetrically (Mulvaney 1996). The concentration change of solute in the leachate was determined using a breakthrough curve (BTC), and the observed concentration data were presented in a standard graphical form.

Cumulative leaching

To evaluate the cumulative leaching of N forms, two nonlinear regression mathematical models were used. The equations are as follows:

$$Y = a\left(1 - e^{-bx}\right) + c\left(1 - e^{-dx}\right), \quad (1)$$

where Y is the cumulative NO_3^- or NO_2^- leached (mg kg^{-1}); parameters a and c are initially ($a_{NO_3^-}$), ($a_{NO_2^-}$), and secondarily ($c_{NO_3^-}$), ($c_{NO_2^-}$), values for NO_3^- or NO_2^- leached (mg kg^{-1}), respectively; parameters b and d are initially ($b_{NO_3^-}$), ($b_{NO_2^-}$), and secondarily ($d_{NO_3^-}$), ($d_{NO_2^-}$), values for the NO_3^- or NO_2^- leaching rate constant (mg kg^{-1} PV^{-1}), respectively.

$$Y = a\left(1 - e^{-bx}\right) \quad (2)$$

Y is the cumulative NH_4^+ leached (mg kg^{-1}), parameter a is the leached NH_4^+ as mg kg^{-1} ($a_{NH_4^+}$), and parameter b is the NH_4^+ leaching rate constant as mg kg^{-1} PV^{-1} ($b_{NH_4^+}$). The parameters of the models were obtained by fitting experimental data to the models using the nonlinear procedure with Sigmaplot statistical software package version 10.0.

Result and discussion

Soil characteristics

The chemical and physical properties of the soils studied are given in Table 1. The soils used in this study ranged in texture from clay to sandy loam. The NO_3^- level extracted by KCl ranged from 18 to 180 g kg^{-1}, indicating that application of N fertilizers over the past 30 years has increased the amount of NO_3^- stored in the soil. The NH_4^+ level ranged from 2.7 to

Table 1 Selected physical and chemical characteristics of the studied soils

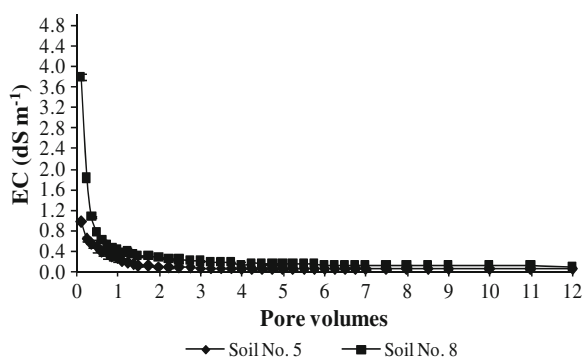| Soil no.	Land use	Clay (g kg^{-1})	Silt	Sand	Texture	CEC (cmol$_c$ kg^{-1})	pH	EC (dS m^{-1})	CCE[a] (g kg^{-1})	OM	NO$_3^-$ (mg kg^{-1})	NH$_4^+$
1	Pasture	68	214	718	SL	22.8	7.2	0.147	7	6.4	21	2.9
2	Vegetable	108	194	698	SL	17.6	7.1	0.140	134	13.0	88	11.4
3	Garden	28	254	718	LS	15.7	7.4	0.140	69	39.0	63	5.1
4	Pasture	48	274	678	SL	20.9	7.1	0.130	70	114.0	21	2.7
5	Pasture	28	274	698	SL	14.3	7.0	0.163	28	353.0	20	3.8
6	Garden	88	414	498	SL	21.2	7.2	0.127	67	35.0	60	4.3
7	Wheat	208	354	438	L	25.0	7.5	0.134	249	9.5	18	4.0
8	Wheat	288	274	438	L	22.8	7.4	0.205	119	15.3	180	7.1
9	Potato	308	368	324	CL	28.0	7.5	0.179	190	9.9	38	5.1
10	Garlic	248	428	324	L	27.1	7.4	0.130	244	6.6	18	4.2
11	Garlic	488	308	204	C	31.4	7.4	0.116	249	6.7	49	15.9

SL sandy loam, *LS* loam sandy, *L* loam, *CL* clay loam, *C* clay

[a] CaCO$_3$ equivalent

15.9 g kg^{-1}. The NO$_2^-$ concentration was below the instrument detection limit.
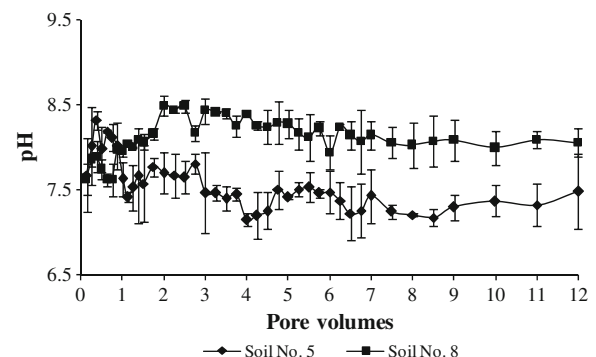
Electrical conductivity and pH

Breakthrough curves (BTCs) (plots of concentration as a function of PV) of EC for two soils are presented in Fig. 1. Other soils shared the same trends. The EC of leachates ranged from 0.72 to 3.82 dS m^{-1} at the beginning of the experiment. These values were in the usual EC range for irrigation water (0–3.0 dS m^{-1}), according to the Food and Agriculture Organization of the United Nations (Ayers and Westcot 1985). However, the leachate EC values showed a marked

reduction at the end of the experiment from 0.05 to 0.26 dS m^{-1}. A similar trend was observed by Civeira and Lavado (2008) and Santibáñez et al. (2007). The drop in EC suggests that an initial high level of soluble salts was reduced by the leaching process (Civeira and Lavado 2008). The highest EC value during the initial leaching was found in soils 2 and 8, whereas the lowest value was found in soil 3.

Breakthrough pH curves for the two soils are presented in Fig. 2. The pH of the leachates ranged from 7.4 to 8 at the beginning of the experiment, and no variation was observed over time. These results can be attributed to the high calcium carbonate content of the soils (Table 1). The presence of calcium carbonate

Fig. 1 Electrical conductivity of the two native soils leached with distilled water. Other soils had similar trends. *Bars* indicate standard error of the means ($n=2$)
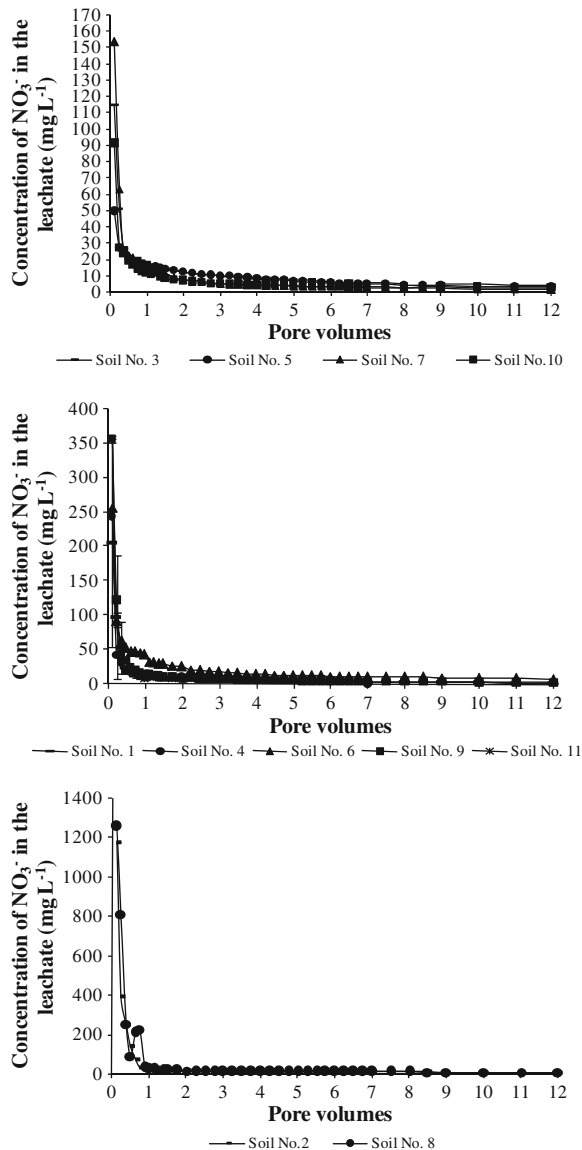

Fig. 2 pH of the two native soils leached with distilled water. Other soils had similar trends. *Bars* indicate standard error of the means ($n=2$)

buffered the soil system and inhibited further pH decreases. A similar trend was reported by Qian and Cai (2007) and Santibáñez et al. (2007).

Nitrate leaching from soils

Breakthrough curves were used to identify processes that affected N leaching (Fig. 3). The BTCs were characterized by a peak concentration of NO_3^- in the

Fig. 3 Breakthrough curves for NO_3^- from the native soils leached with distilled water. *Bars* indicate standard error of the means (*n*=2)

0.125 PV leachates, followed by a sharp decline and extensive tailing in subsequent leachate fractions. The highest peak concentration of NO_3^- was found in soil 8 (1,257 mg L^{-1}), while the lowest was found in soil 5 (49 mg L^{-1}) (Table 2). The NO_3^- concentration in leachates from all soils (except soil 5) was greater than the drinking water limit of 50 mg L^{-1} after 0.125 PV, but declined to 8 to 40 mg L^{-1} after 1 PV. The results of leaching for these calcareous soils indicated that there was a high risk of NO_3^- movement into groundwater at concentrations exceeding the groundwater quality standard. Behera et al. (2003) also studied the dynamics of water flow and fertilizer solute leaching in lateritic soils and reported an initial NO_3^- concentration in the soil profile that exceeded the permissible limit for potable water.

Jiao et al. (2004) reported that the NO_3^-–N concentration in leachate from intact soil cores exceeded the Canadian drinking water limit of 10 mg L^{-1} after the first leaching trial, but declined to 3,08 mg L^{-1} by the third leaching trial.

The differences in NO_3^- movement and concentration in the leachate were probably attributable to the soil properties and soil NO_3^-.

The rapid decrease in EC and NO_3^- concentration might be related to preferential (non-uniform) flow or bypass flow. Thus, the concentrations in the leachate were strongly not in equilibrium with the soil, and

Table 2 Peak concentration of NO_3^-, NH_4^+, and NO_2^- leached from soils column

Soil no.	Peak concentration		
	NO_3^- (mg L^{-1})	NH_4^+	NO_2^-
1	206	3.70	27.35
2	1,173	8.27	23.92
3	114	2.07	59.28
4	244	1.90	41.89
5	49	3.90	0.01
6	256	3.40	7.35
7	149	1.50	1.58
8	1,257	2.40	16.04
9	356	1.10	7.54
10	91	2.50	1.62
11	356	10.40	0.84

non-equilibrium transport was probably the most important processes during NO_3^- transport in soil columns. Hendrickx and Flury (2001) defined preferential flow as all phenomena where water and solutes move along certain pathways, while bypassing a fraction of the porous matrix.

The high NO_3^- concentration in the leachate could also be related to anion exclusion. Jury et al. (1991) defined anion exclusion as the process of high mobility of anions due to repulsion between anions and the negatively charged mineral surface. This process influences chemical transport through the soil because it enables anions to move faster than neutral ions moving with water.

Figure 4 shows the cumulative amounts of NO_3^- leached from two soils. The cumulative NO_3^- leaching BTC showed an initial rapid phase followed by a slow phase of NO_3^- leaching. The rapid leaching continued for 0.375–0.500 PV. There was a slower continued leaching of NO_3^- after 0.500 PV.

Table 3 shows the total amount of NO_3^- leached after up to 12 PV. Between 17.9 and 158.2 mg NO_3^- kg^{-1} (average, 56.8 mg kg^{-1}) were leached during the 12 PV leaching period (equivalent to 534–1,286 mm of water), which accounted for between 61.4% and 160.8% of NO_3^-. The total amount of NO_3^- leached in soils 2, 5, 6, 7, 9 and 10 was higher than the initial NO_3^- extracted by KCl. This may be attributed to the low ability of KCl in extracting NO_3^- from soil compared with distilled water and nitrogen mineralization in the soil.

The results indicate that soils irrigated with good quality water can lose large amounts of NO_3^- in field conditions, which ranged from 62 to 437 kg ha^{-1} (on a column surface area basis) after 12 PV leaching. Nitrate leaching loss mainly occurred with 1 PV of leaching (on average 92 mm of water), which accounted for between 20.7% and 98.4% of total NO_3^- leached.

The highest amount of leached NO_3^- was found in soil 8 (437 kg ha^{-1}), while the lowest was found in soil 1 (62 kg ha^{-1}). Soil 8 came from a wheat field, where excessive amounts of N fertilizer may have been applied. This could have resulted in low N fertilizer efficiency because a large fraction of the applied N may have remained unutilized in the soil where it posed a potential risk for NO_3^- leaching.

A long-term field study in England (over 140 years) reported leaching losses of NO_3^- up to 442 kg ha^{-1} $year^{-1}$ from silty clay loam soils (Johnston et al. 1989). Coarse-textured soils are particularly susceptible to leaching, and nearly 60% of the applied N fertilizer can be lost by leaching of these soils (Gaines and Gaines 1994). Rapid N leaching losses may be expected from soils with high permeability, high porosity, and a rapid infiltration rate.

Figure 4 shows plots of the cumulative NO_3^- leaching data vs. the predicted leaching data for the two soils, using Eq. 1. The fit between the equation and the experimental data is indicated by the coefficient of determination and standard deviation, as shown in Table 4. Equation 1 provided a satisfactory prediction of the cumulative NO_3^- because the r^2 values were high while the SE values were low.

The rate of leaching for the initial and secondary periods of leaching ranged from 2.8 to 14.7 mg kg^{-1} PV^{-1} and from 0.11 to 0.32 mg kg^{-1} PV^{-1}, respectively. Greater leaching rates during the initial period could be due to the leaching of NO_3^- in solution. Leaching in the secondary period could be due to diffusion-controlled transfer of NO_3^- between mobile and immobile liquid phases in the soil (van Genuchten and Wierenga 1976; Nielsen et al. 1986).

Nitrate moves readily through the soil by diffusion and with the mass flow of water (Vitousek et al. 2002; Herrmann et al. 2005). Thus, there is the potential for a significant portion of the applied N fertilizer and

Fig. 4 Cumulative leaching of NO_3^- from two studied soils. Other soils had similar trends. (*filled circle*) measured, and (*line*) simulated using Eq. 1
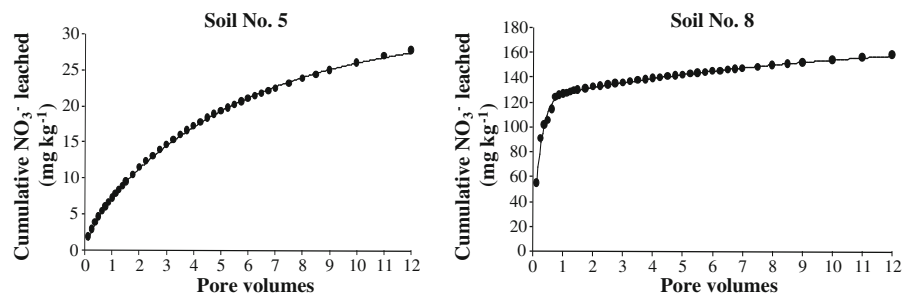
Table 3 Cumulative amount of NO_3^- leached from columns of native soils

Soil no.	1/8 of first PV (12 mm)			2/8 of first PV (24 mm)			4/8 of first PV (46 mm)			1 PV (92 mm)			3 PV (276 mm)			7 PV (644 mm)			12 PV (1,104 mm)		
	(mg kg⁻¹)	(kg ha⁻¹)[a]	NO_3^- leached (%)[b]	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NO_3^- leached (%)
1	5.1	17.8	24.5	7.6	26.3	36.1	9.5	32.9	45.3	10.8	37.4	51.5	13.4	46.4	63.8	16.3	56.3	77.5	17.9	61.9	85.2
2	48.0	137.0	54.8	64.2	182.5	73.0	80.3	228.1	91.3	86.6	245.8	98.4	97.4	276.7	110.7	110.5	313.7	125.5	121.4	344.8	137.9
3	5.1	14.0	8.2	7.5	20.2	11.9	9.6	29.9	15.2	13.0	35.2	20.7	21.7	58.5	34.4	32.0	86.4	50.8	38.7	104.5	61.4
4	7.2	23.4	34.0	8.3	27.4	39.8	9.8	32.2	46.8	11.6	37.9	55.1	16.2	53.1	77.0	20.0	65.6	95.3	–[c]	–	–
5	2.0	5.6	9.6	3.0	8.6	14.9	4.7	13.7	23.6	7.3	21.2	36.5	14.7	42.5	73.3	22.4	65.4	112.7	27.8	80.6	138.4
6	12.5	32.6	20.9	16.9	44.1	28.3	22.6	58.8	37.7	31.6	82.1	52.6	50.3	130.9	83.9	70.3	182.8	117.2	87.4	227.4	145.7
7	6.8	18.6	38.0	9.5	25.9	52.8	11.7	31.8	64.9	14.6	39.8	81.3	20.0	54.4	111.1	25.0	67.7	138.3	28.0	75.9	155.1
8	55.3	152.7	30.7	90.9	251.0	50.5	105.8	292.0	58.8	127.0	350.6	70.6	136.2	375.9	75.7	147.5	407.1	81.9	158.2	436.6	87.9
9	17.0	44.6	44.8	22.9	59.9	60.2	26.6	69.7	69.9	30.1	79.2	79.6	37.6	98.4	98.8	44.7	117.1	117.6	48.9	128.3	128.9
10	5.0	12.2	27.5	6.4	15.8	35.6	8.7	21.5	48.6	11.7	28.7	64.8	18.1	44.5	100.6	24.0	59.0	133.2	29.0	71.2	160.8
11	17.3	45.4	35.4	21.9	57.3	44.7	24.7	64.7	50.4	27.3	71.5	55.7	33.6	88.0	68.6	41.5	108.7	84.7	47.3	123.9	96.5

[a] Based on column surface area

[b] Percentage of native NO_3^- in soils

[c] Leaching process after 7 PV stopped

Table 4 Parameters, R^2 and SE of various nonlinear models used to describe cumulative NO_3^-, NH_4^+, and NO_2^- leached from soils column

| Soils no. | NO_3^- | | | | | | NH_4^+ | | | | NO_2^- | | | | | |
| | Exponential rise to maximum; double, 4 parameter; $Y = a(1 - e^{-bx}) + c(1 - e^{-dx})$ | | | | | | Exponential rise to maximum; single, 2 parameter; $Y = a(1 - e^{-bx})$ | | | | Exponential rise to maximum; double, 4 parameter; $Y = a(1 - e^{-bx}) + c(1 - e^{-dx})$ | | | | | |
	a (mg kg^{-1})	b (mg kg^{-1} per PV)	c (mg kg^{-1})	d (mg kg^{-1} per PV)	R^2	SE	a (mg kg^{-1})	b (mg kg^{-1} per PV)	R^2	SE	a (mg kg^{-1})	b (mg kg^{-1} per PV)	c (mg kg^{-1} per PV)	d (mg kg^{-1} per PV)	R^2	SE
1	9.2	5.9	9.6	0.19	0.99	0.04	1.32	0.14	0.99	0.04	–	–	–	–	–	–
2	80.2	6.6	49.7	0.14	0.99	0.67	1.36	0.30	0.97	0.24	1.12	4.73	1.08	4.70	0.99	0.014
3	7.7	5.9	36.0	0.16	0.99	0.23	4.35	0.09	0.99	0.05	–	–	–	–	–	–
4	7.8	14.7	13.5	0.32	0.99	0.10	0.87	0.28	0.99	0.03	–	–	–	–	–	–
5	3.2	2.8	27.5	0.18	0.99	0.16	1.63	0.46	0.98	0.11	0.02	0.88	0.02	0.88	0.97	0.004
6	23.1	3.3	78.4	0.14	0.99	0.99	4.76	0.09	0.99	0.06	0.40	4.80	0.42	4.84	0.99	0.048
7	11.1	5.5	17.4	0.23	0.99	0.31	17.82	0.03	0.99	0.05	0.32	0.78	0.33	0.78	0.97	0.053
8	122.7	4.6	47.8	0.11	0.99	1.76	11.37	0.04	0.99	0.12	–	–	–	–	–	–
9	25.2	7.8	25.0	0.22	0.99	0.34	–[a]	–	–	–	0.20	8.94	1.19	1.88	0.99	0.013
10	10.0	2.8	22.5	0.14	0.99	0.43	10.10	0.05	0.99	0.11	–	–	–	–	–	–
11	23.0	9.7	28.5	0.15	0.99	0.22	3.42	0.12	0.93	0.29	–	–	–	–	–	–

R^2 coefficient of determination, SE standard error of the estimate

[a] Equation did not fit to the data

naturally mineralized N to be leached from the root zone (Gulliam et al. 1985).

Ammonium leaching from soils

The results of NH_4^+ leaching for two soils are shown as a BTC in Fig. 5. The peak concentration of NH_4^+ in the leachate was observed at 0.125 PV, with the exception of soils 5 and 10, and it gradually decreased in subsequent leachate fractions. Ammonium concentration in soils 5 and 10 increased during 0.750 PV. The highest peak concentration of NH_4^+ was found in soil 11 (10.4 mg L^{-1}), while the lowest was found in soil 9 (1.1 mg L^{-1}). The concentration of NH_4^+ in leachates from soils 1 and 3 were lower than the detection limit after 7 and 11 PV, respectively, while in the other soils it decreased to between 0.2 and 1 mg L^{-1} at the end of the leaching experiment. The observed differences in NH_4^+ movement and concentration in the leachates may be related to levels of exchangeable and fixed NH_4^+ under nitrification conditions.

Exhaustion of oxygen occurs within several hours under conditions of soil flooding, which results in a variety of soil changes (Gliński and Stępniewski 1985; McKenney et al. 2001). In particular, the redox potential of the soil decreases, with a drop in Eh value to below +300 mV caused by the reduction of soil and successive activation of redox couples, other than the O_2/H_2O system, e.g., $NO_3^- - N/NO_2^- - N$ (Gliński and Stępniewski 1985). Under favorable conditions (minimal Eh value and available organic matter), NO_3^- (V) enters a path of dissimilative reduction, where the final product is the NH_4^+ ions, and its
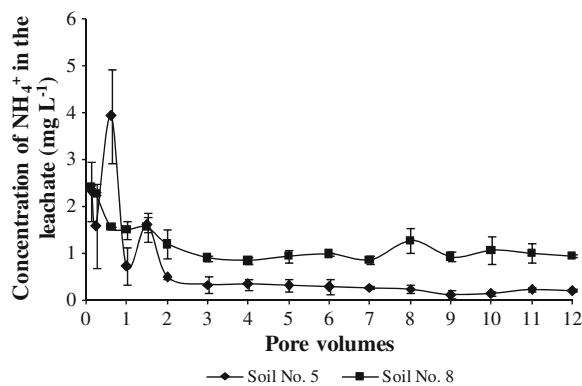
Fig. 5 Breakthrough curves for NH_4^+ from two studied native soils leached with distilled water. Other soils had similar trends. *Bars* indicate standard error of the means ($n=2$)

concentration gradually increases in the soil profile, especially in the lower horizons.

Furthermore, denitrification occurs when O_2 is depleted by denitrifying microorganisms. The concentration of NO_3^- (or nitrite) in the soil is another important regulator, and a third main controlling mechanism is the amount of available organic carbon (Tiedje 1988). Dissimilatory NO_3^- reduction to NH_4^+ is an anaerobic microbial pathway in the N cycle that transforms NO_3^- first to NO_2, and then to NH_4^+.

Figure 6 shows the cumulative levels of NH_4^+ leached for two soils. Cumulative NH_4^+ leached from calcareous soils ranged from 0.85 to 7.40 mg kg^{-1} (mean, 3.1 mg kg^{-1}) (Table 5). The highest and lowest amounts leached were in soil 9 (19.3 kg ha^{-1}) and soil 4 (2.5 kg ha^{-1}), respectively. All of the soil NH_4^+ was leached from soil 7 and soil 9 within 10 PV. The results show that soil irrigated with good quality water can lose a large proportion of NH_4^+, between 2.5 and 19.3 kg ha^{-1}, within 12 PV.

The total amounts of NH_4^+ leached from soils 7 and 9 were in excess of the initial exchangeable NH_4^+ (approximately 118% and 144%, respectively), which indicates the release of NH_4^+ from nonexchangeable sites (Table 5). Mendoza et al. (2006) reported that cumulative NH_4^+ leaching from moderately alkaline and calcareous soils was 5.1 mg $column^{-1}$. Yu et al. (2007) reported cumulative NH_4^+ losses of 1.2, and 0.9 mg $column^{-1}$ from silty loam and heavy clay soils, respectively. Xiong et al. (2010) reported that cumulative NH_4^+ amounts leached from variable and permanent charge paddy soils during the drained season were 229.8 and 30.3 mg $column^{-1}$, respectively, while during the flooded season the levels were 298.2 and 59.8 mg $column^{-1}$, respectively.

The NH_4^+ concentration in soils was less than the NO_3^- concentration. This clearly indicates a lower leaching rate of NH_4^+ compared with NO_3^-. The peak NO_3^- concentration was about 100 times higher than the peak concentration of NH_4^+. However, the total leached NH_4^+ was less than the total leached NO_3^-. Electrostatic forces hold the cation, NH_4^+, to negatively charged clay particle surfaces and functional groups of soil organic matter. This binding is sufficient to limit NH_4^+ loss by leaching (Amberger 1993). Zhou et al. (2006) reported that the total NO_3^- and NH_4^+ leached from soil columns in a drip fertigation system were 1.9 and 1.1 mg $column^{-1}$, respectively. From an
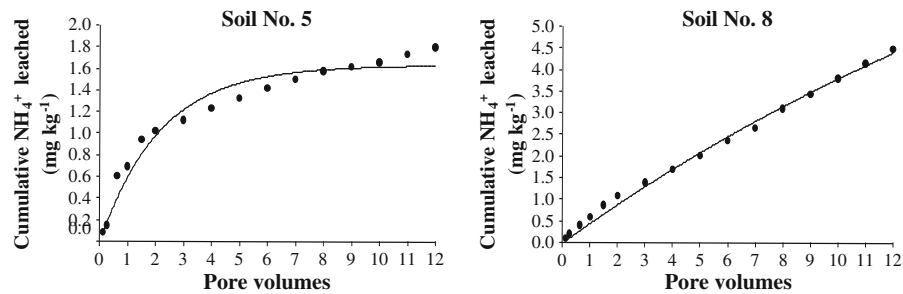
Fig. 6 Cumulative leaching of NH_4^+ from two studied soils. Other soils had similar trends. (*Filled circle*) measured and (*lines*) simulated using Eq. 2

agricultural viewpoint, maintaining N in the form of NH_4^+ has the advantage of extending the time N remains in the rooting zone, which provides more time for plant absorption (Slangen and Kerkhoff 1984). Ammonium leaching depends on cation exchange, the fixing capacity of the soil, and the concentration of other cations in solution.

Most of the inorganic N is in the form of NO_3^- in managed agricultural systems (Harmsen and Van Schreven 1955) and usually nitrification is very rapid in these systems (Huber and Watson 1974; Sahrawat 1980). However, poor quality groundwaters are a common feature of arid and semi-arid regions. When combined irrigation and rainfall exceeds the crop water requirement, excess soil water drains downward and soluble salts are carried with it, including NH_4^+. Soils containing $CaCO_3$ can solubilize and supply Ca^{2+} to replace NH_4^+ ions. However, the extremely low solubility (0.0131 g L^{-1}) (Qadir et al. 1996) of this native Ca^{2+} source means it makes an insignificant contribution to the replacement of NH_4^+. In the field, the release of CO_2 in the root zone results from root and microbial respiration, and CO_2 dissolution in water produces H_2CO_3, which in turn increases the dissolved $CaCO_3$. Hydrogen ions released in the root zone also lower the soil pH and can dissolve further $CaCO_3$. Thus, the dissolution of calcite can be enhanced when the CO_2 concentration in the soil air is higher than that in the atmosphere. Increased Ca^{2+} concentrations would lead to increasingly rapid leaching of NH_4^+ and other cations with more realistic field flow rates and CO_2 concentrations (Kolahchi and Jalali 2007).

Figure 6 shows plots of the cumulative NH_4^+ leaching data vs. the predicted leaching data for two soils, using Eq. 2. The fit between the equation and

experimental data is indicated by the coefficient of determination and standard deviation, as shown in Table 4. With the exception of soil 9, Eq. 2 satisfactorily described the cumulative leaching of NH_4^+ because the r^2 values were high while the SE values were low.

The value of *a* ranged from 0.87 to 17.82 mg kg^{-1}, whereas the value of *b* ranged from 0.03 to 0.46 mg kg^{-1} PV^{-1}. Parameter *b* was less than 1 in all soils, indicating that NH_4^+ leaching rates decreased with PV. The difference between *b* values indicated that the NH_4^+ leaching rate was different for different soils. The high leaching rate for soil 5 could be due to its low CEC.

Nitrite leaching from soils

Figure 7 shows the results of NO_2^- leaching for two soils. The results indicate that considerable amounts of NO_2^- were leached from soils. A possible explanation is that NO_3^- may be reduced to NO_2^- during water saturation. The highest peak concentration of NO_2^- was found in soil 3 (59.28 mg L^{-1}), whereas the lowest was found in soil 5 (0.01 mg L^{-1}) (Table 2). The NO_2^- concentration at 0.125 PV exceeded the maximum concentration allowable by the Drinking Water Directive (USEPA 1986), i.e., a NO_2^- level of 3 mg L^{-1}, with the exception of soils 5, 7, 10, and 11. The concentration of NO_2^- in soils 1, 2, 4, 5, 6, and 11 was lower than the detection limit after 1 PV, whereas it was detectable in soils 7, 8, 9, and 10 up to 5 PV. The concentration of NO_2^- in soil 3 gradually decreased to 0.7 mg L^{-1} at the end of the leaching experiment. This can be explained by the relatively large content of organic matter in soil 3. The amount leached varied from 0.1 to 10.6 kg ha^{-1} when

Table 5 Cumulative amount of NH_4^+ leached from columns of native soils

Soil no.	1/8 of first PV (12 mm)			1 PV (92 mm)			3 PV (276 mm)			7 PV (644 mm)			12 PV (1,104 mm)		
	(mg kg⁻¹)[a]	(kg ha⁻¹)[a]	NH_4^+ leached (%)[b]	(mg kg⁻¹)	(kg ha⁻¹)	NH_4^+ leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NH_4^+ leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NH_4^+ leached (%)	(mg kg⁻¹)	(kg ha⁻¹)	NH_4^+ leached (%)
1	0.09	0.32	3.2	0.18	0.6	6.3	0.42	1.5	14.8	0.9	2.9	29.3	–[c]	–	–
2	0.34	0.96	3.0	0.61	1.8	5.4	0.74	2.1	6.5	1.0	2.9	9.0	1.7	4.6	14.1
3	0.09	0.25	1.8	0.22	0.6	4.3	0.28	0.8	5.5	1.4	3.7	26.9	2.2	5.9	43.5
4	0.05	0.18	1.9	0.18	0.6	6.7	0.52	1.7	19.4	0.8	2.5	28.3	–[d]	–	–
5	0.09	0.26	2.4	0.69	2.0	18.3	1.12	3.3	29.6	1.5	4.4	39.5	1.8	5.2	47.1
6	0.17	0.44	3.9	0.41	1.1	9.5	1.14	2.9	29.5	2.5	6.4	56.9	3.3	8.6	76.9
7	0.07	0.19	1.7	0.47	1.3	11.6	1.40	3.8	34.6	3.0	8.1	74.6	4.3	12.9	118.1
8	0.11	0.29	1.5	0.60	1.7	8.5	1.40	3.8	19.6	2.7	7.3	37.4	4.5	12.3	62.9
9	0.05	0.14	1.0	0.48	1.3	9.5	1.60	4.1	30.5	3.7	9.6	71.4	7.4	19.3	143.8
10	0.06	0.15	1.5	0.67	1.6	15.9	1.40	3.5	34.3	2.8	6.9	66.8	4.6	11.3	109.7
11	0.51	1.32	3.2	0.76	2.0	4.8	1.12	3.0	7.1	1.8	4.7	11.1	3.0	7.8	18.8

[a] Based on column surface area

[b] Percentage of native NH_4^+ in soils

[c] Not detected in leachate

[d] Leaching process after 7 PV stopped
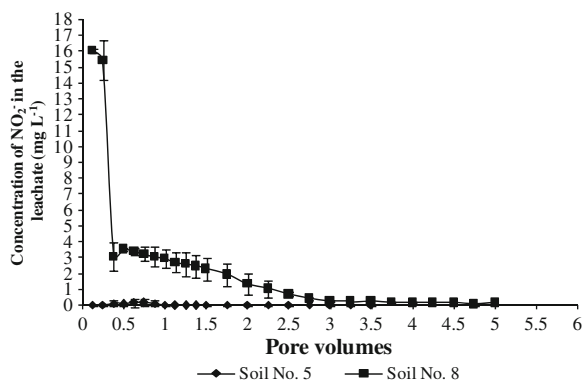
Fig. 7 Breakthrough curves for NO_2^- from two studied native soils leached with distilled water. Other soils had similar trends. *Bars* indicate standard error of the means ($n=2$)

12 PV had passed through the column (Table 6). High mobility is the characteristic of NO_2^- in soil, and it tended to move downward as the wetting front moved through the profile.

The cumulative amounts of NO_2^- leached for two soils are shown in Fig. 8. Cumulative NO_2^- leached from calcareous soils was in the range of 0.04 to 3.94 mg kg^{-1} (mean, 1.45 mg kg^{-1}) (Table 6).

Figure 8 shows plots of the cumulative NO_2^- leaching data vs. the predicted leaching data for two soils, using Eq. 1. Equation 1 satisfactorily described the cumulative leaching of NO_2^- for soils 2, 5, 6, 7, and 9 (Table 4). The NO_2^- leaching BTC has two distinct sections: (1) the initial section and (2) the later section. The value of b ranged from 0.78 to 8.94 mg kg^{-1}

Table 6 Amount of NO_2^- leached from columns of native soils

Soil no.	NO_2^- leached	
	(mg kg^{-1})	(kg ha^{-1})[a]
1	0.82	2.8
2	2.18	6.2
3	3.94	10.6
4	1.69	5.6
5	0.04	0.1
6	0.76	2.0
7	0.60	1.6
8	3.30	9.1
9	1.37	3.6
10	1.11	2.7
11	0.18	0.5

[a] Based on column surface area

PV^{-1}, while d ranged from 0.78 to 4.84 mg kg^{-1} PV^{-1}. The difference between b and d values indicate that NO_2^- leaching rates differed between different soils. Nitrite leaching was initially rapid but decreased in subsequent leachate fractions.

Relationships between soil properties and N leaching

The influence of soil properties on N leaching was tested by calculating simple correlation coefficients and the results are shown in Table 7. Soil NO_3^- concentration correlated with peak concentration of NO_3^- ($r=0.86$; $p<0.01$) and total NO_3^- amount leached ($r=0.93$; $p<0.01$). Jiao et al. (2004) found that the NO_3^- load in leachates was positively related to soil NO_3^- concentration in both intact soil cores and disturbed small soil columns, which indicated that soil NO_3^- levels may be indicators of NO_3^- leaching from top soils down to subsurface soils.

Total leached NH_4^+ was negatively correlated with sand ($r=0.75$; $p<0.01$). Clay soils contain more available sites compared with sandy soils, which enhances the retention of more NH_4^+. Ammonium ions present in exchangeable sites will be exchanged for ions such as Ca^{2+}, Mg^{2+}, and Na^+ in poor quality waters, so leached NH_4^+ will exceed the amount evaluated in this study. Total NO_2^- in leachates was positively correlated with soil NO_3^- ($r=0.64$; $p<0.05$). Total leached NH_4^+ was positively correlated with clay ($r=0.61$; $p<0.05$). These results suggest that soil particle distribution might influence NH_4^+ leaching. There was no significant correlation between soil particle distribution and leached NO_3^- or NO_2^-. Parameter $a_{NH_4^+}$ was positively correlated with pH ($r=0.80$; $p<0.05$) and CCE ($r=0.62$; $p<0.05$), while parameter $b_{NH_4^+}$ was negatively correlated with pH ($r=-0.84$; $p<0.05$).

Table 8 shows that a multiple regression approach yielded better results. Multiple regression identified significant correlations between pH, EC, and silt and total leached NH_4^+, which explained 95% of the variability in total leached NH_4^+. There was also a significant correlation between sand and organic matter and total leached NO_2^-, which explained 78% of the variability in total leached NO_2^-. There was a significant correlation between the soil pH and the organic matter and $b_{NH_4^+}$ ($r=0.92$; $p<0.01$).

Overall, the N leaching results showed that leaching of N-rich soils resulted in huge NO_3^- losses over

Fig. 8 Cumulative leaching of NO_2^- from two studied soils. Other soils had similar trends. (*Filled circle*) measured and (*lines*) simulated using Eq. 1
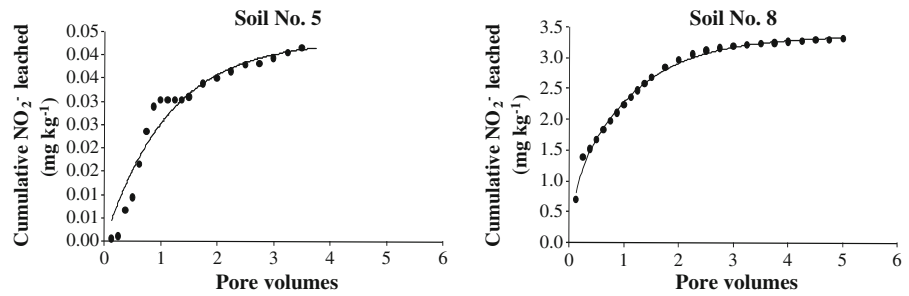
the course of 12 PV of leaching. Approximately 118% (average of all soils) of the extractable soil NO_3^- present was leached.

Nitrate losses via soil water drainage depend on the NO_3^- content of the soil profile, the volume of leaching water, and the efficiency of leaching water exploring the pore volume (Magesan et al. 1996). Poor irrigation management is known to aggravate the polluting effects of fertilizers. Timing and method of both irrigation and fertilizer application are key factors that determine the leaching of chemical fertilizers during irrigated agriculture (Clothier and Green 1994). The amount of water applied in this study (534–1,286 mm) was approximately 1.8 to 4.3 times the average rainfall received in the study area. Therefore, less NO_3^- will be leached on an annual basis. Significant leaching of NH_4^+ from soils raises a further concern in addition to the potential loss of a valuable nutrient. If the leached NH_4^+ subsequently emerges in a stream or other water course, it could have serious consequences for aquatic life. It is more harmful when the water pH is relatively high because this condition increases the proportion of NH_4^+ present as free NH_3 (Qiang et al. 2004).

Intensive agricultural crop production in Iran is largely dependent on the application of N fertilizers. The average N fertilizer application in Iran currently exceeds 200 kg N h^{-1}. Nitrogen fertilizer application typically exceeds 300 kg N ha^{-1} in high yielding crop regions of Iran (Jalali 2005). Agricultural systems in the study area received high amounts of inorganic N fertilizer in the form of NH_4^+, NO_3^-, or a combination of the two, which is expected to result in the accumulation of N in the soil profile.

The fertilizer application level for arable crops in the study area was higher (138–230 kg N ha^{-1} $year^{-1}$) compared with the crop removal of N (29.4–154 kg N ha^{-1} $year^{-1}$).

Table 7 Simple correlation coefficient (r) between soil properties, leaching, and model parameters ($n=11$)

Parameters	r
PC^a of NO_3^- = 7.51 Soil NO_3^- −6.72	0.86[**]
TL^b NO_3^- = 0.88 Soil NO_3^- + 10.31	0.93[**]
TL NH_4^+ = −0.008 Sand + 7.32	−0.75[**]
TL NO_2^- = 0.017 Soil NO_3^- + 0.59	0.64[*]
TL NH_4^+ = 0.008 Clay + 17.32	0.61[*]
aNO_3^- = 0.73 Soil NO_3^- − 8.73	0.94[**]
aNH_4^{+c} = 25.36 pH − 178.54	0.80[*]
aNH_4^+ = 0.41 CCE + 0.43	0.62[*]
bNH_4^{+c} = −0.67 pH + 5.03	−0.84[*]
aNO_2^{-d} = 0.013 Soil NO_3^- − 0.16	0.89[*]
dNO_2^{-d} = 0.06 Soil NO_3^- − 0.23	0.93[*]

[*] $p<0.05$; [**] $p<0.01$, correlation significance

[a] Peak concentration

[b] Total leached in 12 pore volumes

[c] a and b parameters of Eq. 2 used for cumulative NH_4^+ leached, respectively

[d] a, and d parameters of Eq. 1 used for cumulative NO_2^- leached, respectively

Table 8 Multiple correlation coefficient (r) between soil properties, leaching, and model parameters ($n=11$)

Parameters	r
$PC^a NO_2^-$ (mg L^{-1})=−23.88+0.09 Sand −0.09 OM	0.78[*]
$TL^b NH_4^+$ (mg kg^{-1})=−45.53+5.4 pH+0.01 Silt (g kg^{-1})+32.8 EC (dSm^{-1})	0.95[**]
bNH_4^{+c} (mg kg^{-1})=3.28−0.43 pH+0.0006 OM	0.92[**]

[*] $p<0.05$; [**] $p<0.01$, correlation significance

[a] Peak concentration

[b] Total leached in 12 pore volumes

[c] b parameters of Eq. 2 used for cumulative NH_4^+ leached

Farmers rarely take into account the N derived from soil organic matter, organic N application, and N in irrigation water when making decisions about N fertilizer applications, which often results in overfertilization with excess N being lost to the environment (Dinnes et al. 2002). Jalali (2008) reported that the total amount of N (N chemical fertilizer, N organic fertilizer, and N in irrigation water) supplied by the farmers to vegetable fields ranged from 375 to 965 kg ha^{-1} year^{-1}. Nitrate leaching may also occur when the amount of water applied to irrigated soils in arid and semi-arid region exceeds evapotranspiration (Jalali and Rowell 2003). Application of large amounts of N fertilizer and inadequate management of N fertilization coupled with low irrigation efficiency are mainly responsible for the NO_3^- concentrations in groundwater in the study area (Jalali 2005).

In a field situation, it is possible that actively growing plants would be capable of removing a substantial proportion of the N that was leached in this experiment, although perhaps not all. Minimizing the release of NO_3^- from cropped fields to the environment can only be achieved by increased fertilizer efficiency. Agronomic practices such as cultivation, cropping, and irrigation water management may decrease the mean NO_3^- and NH_4^+ concentration in water draining from the soil zone.

Conclusions

A similar pattern of N leaching was found in study soils, i.e., an initial rapid leaching followed by a slow, continuous leaching. The results of the present study indicated that 61.9–436.6, 2.5–19.3, and 0.1–10.6 kg ha^{-1} of NO_3^-, NH_4^+, and NO_2^-, respectively, were leached from these calcareous soils. Ammonium and NO_2^- leaching from the profile was only detected in small quantities, whereas NO_3^- was the predominant form of N that was transferred by vertical water movement. Leaching of mineral N under field conditions will differ from repacked soil columns. Losses are generally expected to be higher under field conditions because of the increased nitrification rates of organic N in soil under unsaturated conditions. Excessive use of readily available chemical fertilizers on agricultural land in the study area was the main source of

groundwater contamination. Lack of vegetation and precipitation can accelerate the risk of N leaching and groundwater pollution. Poor quality groundwater is a common feature of arid and semi-arid regions. Excess soil water drains downward when the combined irrigation and rainfall exceeds the crop water requirement, which carries with it soluble salts including NO_3^-, NH_4^+, and NO_2^-. Regression of the leaching parameters of study soils on soil properties showed that soil NO_3^-, silt, and clay were the most important soil properties that influenced mineral N leaching from soils.

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