agronomy

MDPI

Article

Effects of Cultivation Years on the Distribution of Nitrogen and Base Cations in 0–7 m Soil Profiles of Plastic-Greenhouse Pepper

Haofeng Lv [1], Zhongjun Pang [1], Fei Chen [1], Hongxu Ji [1], Weixuan Wang [1], Weiwei Zhou [1], Jing Dong [2], Junliang Li [1] and Bin Liang [1,*]

[1] College of Resources and Environmental Sciences, Qingdao Agricultural University, Qingdao 266109, China; lvhaofeng@qau.edu.cn (H.L.); pang18553621997@163.com (Z.P.); chenfei19961224@163.com (F.C.); 20212108008@stu.qau.edu.cn (H.J.); amicelogo@126.com (W.W.); qnzhouww@qau.edu.cn (W.Z.); jlli1962@163.com (J.L.)

[2] Shouguang Municipal Agricultural Bureau, Shouguang 262700, China; dongjing316@163.com

* Correspondence: liangbin306@163.com

Abstract: To clarify the migration and accumulation of nitrogen (N), magnesium (Mg), calcium (Ca), and potassium (K) in soil profiles of plastic-greenhouse vegetable fields with cultivation years, soil samples from the 0–7 m soil profiles were collected from 10 pepper greenhouses with 10 and 20 years planting history, and parallel soil samples were taken from adjacent wheat-maize fields as controls. The results showed that: (1) Compared with wheat-maize fields, the total N amount in the 0–7 m soil layers from the greenhouses increased by 6.19 ± 1.16 and 9.11 ± 3.43 t ha^{-1} at 10 and 20 years, respectively, accounting for about 30.4% and 17.5% of the N input. (2) The N amount that entered the environment outside the 0–7 m soil layers were 6.95 t ± 2.76 and 29.10 ± 10.14 t ha^{-1} after 10 and 20 years of continuous planting, accounting for approximately 34.2% and 55.9% of the N input, respectively. (3) The concentration of water-soluble Ca and Mg in the 0–7 m soil layers increased significantly with cultivation years, and correlated positively with mineral N concentration. (4) Moreover, K mainly accumulates in the form of non-exchangeable K in the surface layers (0–50 cm). Our results demonstrated that huge amounts of N migrate to the deep soil with the extension of cultivation years in plastic-greenhouse pepper production systems, accompanied by significant leaching of Ca and Mg, while K mainly accumulates in the surface layers.

Keywords: greenhouse pepper; cultivation years; soil depths; nitrogen balance; base cations leaching

check for updates

Citation: Lv, H.; Pang, Z.; Chen, F.; Ji, H.; Wang, W.; Zhou, W.; Dong, J.; Li, J.; Liang, B. Effects of Cultivation Years on the Distribution of Nitrogen and Base Cations in 0–7 m Soil Profiles of Plastic-Greenhouse Pepper. *Agronomy* **2024**, *14*, 1060. https://doi.org/10.3390/agronomy14051060

Academic Editor: Nazim S. Gruda

Received: 23 April 2024
Revised: 14 May 2024
Accepted: 14 May 2024
Published: 16 May 2024

1. Introduction

Plastic-greenhouse vegetable planting can produce vegetable products in winter, realizing the balanced supply of vegetables throughout the year, which has developed rapidly in recent decades in China. By 2020, the planting area of greenhouse vegetables is approximately 4.1 million hectares [1], which is approximately 26 times that of 1990 [2]. To avoid the high cost of installing warming equipment during winter, the topsoil will be excavated, causing the planting surface to be 0.5–2 m below the ground level during the construction of the greenhouse. The frame structure on the top floor of the greenhouses are covered with plastic film in the south side (sunward side) and in addition to a waterproof felt on winter nights for heat preservation, which provides suitable growing conditions for vegetables [3].

Although this kind of sunken greenhouse can realize low-cost and environmentally friendly production, it also has defects. The fertile topsoil is removed, and the vegetables are directly planted on the barren and compact subsoil. In order to improve soil structure and meet the nutrient requirements of intensive high-yield vegetables, farmers often overuse organic fertilizer and chemical fertilizer. Annual total N input exceeds 2000 kg ha^{-1}, i.e., far exceeding the demands of crops [4,5]. The N use efficiency in vegetable production systems is less than 12% [6], which is significantly lower than that in the USA and Europe (up to

37–68%) [7]. The huge N surplus causes serious pollution to the ecological environment, for example, increasing greenhouse gas (N_2O and NO) emissions and accelerating global warming [8], increasing the hydrological transport of N, and intensifying nitrate pollution of water bodies [9].

Research indicated that nitrate-N concentrations in almost all shallow groundwater in plastic-greenhouse vegetable planting areas in northern China has already exceed the US-EPA threshold of 10 mg NO_3^--N L^{-1} [10]. The concentration of nitrates in groundwater generally decreased between 2009 and 2019 in Weifang, Shandong province, likely because of the reduction of agricultural land area and fertilizer application, and the increase of the depth of the wells [11]. However, the nitrate concentration of groundwater in greenhouse vegetable planting areas is still significantly higher than that in winter wheat planting areas. Nitrogen fertilizer is the main source of nitrate in groundwater [11], and the excessive irrigation is an important driving force causing N entry into groundwater [12,13]. Currently, flood irrigation remains the most common phenomenon in most plastic-greenhouse vegetables planting areas in China [14,15]. The total irrigation rate exceeds 1300 mm/year [16], with the average irrigation amount reaching 60–80 mm per time [17]. Excessive N input combined with flood irrigation have resulted in large N leaching losses. Approximately 450 kg N ha^{-1} $season^{-1}$ was leached to below the 90 cm soil layer in the form of mineral N (67%) and dissolved organic N (33%, DON) in greenhouse tomato production systems, which half of the N application amount is lost by leaching [18].

Previous studies on plastic-greenhouse vegetable N leaching loss mainly focused on 1 m soil layers [19,20]. However, with the increase of cultivation years, the fate of N leached into deep soil is unclear. In addition, from the perspective of charge balance, during the leaching process of NO_3^--N, there must be cations with the same charge leaching together. Soil base cations play an important role in acid buffering. However, in recent years, the concentration of base cations in groundwater is also constantly increasing with nitrate-N [4], causing a large amount of scale formation in the heating process of groundwater. This is also one of the important reasons why people give up drinking groundwater. Where do the basic cations in groundwater come from? Is it related to soil N leaching? These questions deserve further verification.

Pepper is one of the most important vegetables in the world, accounting for about 10% of the vegetables planting area and total yield, and China produces more than half (50.8%) of the worldwide pepper crop [21]. Consequently, the aims of this study were to identify the fate of N in deeper soil layers at different cultivation years of plastic-greenhouse pepper and clarify the relationship between N leaching and base cations leaching in different soil layers.

2. Materials and Methods

2.1. Site Description

The site was in the Shouguang of Shandong province (36.91° N, 118.87° E), which is a famous plastic-greenhouse pepper planting area in China. The mean annual air temperature and precipitation were 12.7 °C and 594 mm (1981–2010), respectively. All sampling points were located in Zhaili village, including six pepper greenhouses with a 7–10 years (10-year) history of planting, four pepper greenhouses with a 20 years (20-year) history, and three wheat-maize fields as controls for comparison (Figure S1).

2.2. Production Management of Plastic Greenhouses and Wheat-Maize Fields

Information on the cultivation history of the plastic-greenhouses, the fertilization and irrigation regimes of pepper were obtained through questionnaire survey with growers. To facilitate the sales of vegetable products, vegetable planting has a variety agglomeration effect in this area. According to our survey, the 10-year and 20-year greenhouses were built in 2009 and 2000 respectively, with the planting surface sinking by 1 m. Since the construction of those plastic-greenhouses, one crop of pepper has been planted every year (transplanted in late August and harvested in early July of the next year).

Conventional flood irrigation was used in the investigated greenhouses and every irrigation interval of 7–20 d, mainly related to the plants growth period and season. The annual irrigation amount was about 1035 mm, with 45–50 mm for each irrigation. The N inputs from organic fertilizer, synthetic fertilizer, and irrigation water were 1106 $\pm$ 51, 940 $\pm$ 109, and 210 kg ha^{-1} yr^{-1} for the six sampled 10-year plastic greenhouses, and 800 $\pm$ 126, 1655 $\pm$ 242, and 150 kg ha^{-1} yr^{-1} for the four sampled 20-year plastic greenhouses, on average (Table S1). Chicken manure, solid compound fertilizer (diammonium phosphate), and water-soluble fertilizer were the commonly fertilizer types. Chicken manure and solid compound fertilizer were used as basal fertilization, and the water-soluble fertilizer was used as topdressing.

Winter wheat and summer maize rotation has been used in the investigated wheat maize fields. The annual irrigation amount was about 500 mm, with 100 mm for each irrigation. Irrigation was mainly carried out during the growth of winter wheat, whereas maize mainly depends on summer rainfall in this area. The average annual application rate of chemical N fertilizer in wheat-maize rotation system was about 450 kg N ha^{-1} for the three sampled wheat-maize fields, and no organic fertilizer was applied (Table S1). In addition, approximately 65 kg N ha^{-1} was brought in by irrigation water every year. Moreover, there was no significant difference in total N input, crop yield, and N uptake between sampled greenhouses and fields and the surrounding greenhouses and fields according to the interviews with the farmers (Table S2).

2.3. Soil Sampling and Analysis

Soil samples were collected from November to December 2020. Soil profiles at a depth of 0–7 m were obtained using an excavator in the selected plastic greenhouses. Due to the ground of the wheat-maize fields is 1 m higher than that of the pepper greenhouses, soil profiles of 0–8 m were excavated on the wheat-maize fields, and the 1–8 m profiles were selected to correspond to the 0–7 m profiles of the pepper greenhouse. The 7 m soil samples were collected from 14 soil layers (50 cm for each layer) with approximately 500 g of uniformly mixed soil per layer. Moreover, the soil samples of 0–25 and 25–50 cm were obtained by soil auger. Undisturbed soil samples were collected using a cutting ring with a volume of 100 cm^3 at the middle position of each layer. These samples were subsequently dried at 105 °C for 24 h and the soil bulk density was obtained after weighing (Table S3).

After air drying, the soil samples were sieved through a 1mm sieve. Subsamples of 10 g were extracted by shaking with 100 mL 0.5 mol L^{-1} K_2SO_4 for 30 min and mineral N concentration were measured using an autoanalyzer (AA3, Nordstadt Hamburg, Germany). The soluble total N (STN) was measured using dual-wavelength ultraviolet spectrophotometry after alkaline persulfate oxidation of the above soil extract [22]. The difference between STN and mineral N is the soluble organic N (SON). The soil total N (TN) was determined using the Kjeldahl method. Subsamples of 10 g were weighed and extracted with 50 mL water oscillate for 10 min and soil water-soluble K, Ca, and Mg were determined using inductively coupled plasma atomic emission spectroscopy (Optima 3300 DV, Perkin Elmer, Waltham, MA, USA). Subsamples of 10 g were extracted with 100 mL 1.0 mol L^{-1} NH_4OAC oscillate for 30 min, and soil exchangeable K concentration was measured using a flame photometer. Subsamples of 10 g were extracted by heating with 100 mL 1.0 mol L^{-1} HNO_3 for 10 min, and soil non-exchangeable K concentration was measured using a flame photometer [23]. The soil pH were measured in 1:5 soil:water solutions using a pH meter.

2.4. Statistical Analysis

Statistical analyses were carried out using SAS version 8.0 (SAS Institute Inc., Cary, NC, USA). Two factor analysis of variance is used to determine the significance and interaction effects between treatments. One-way analysis of variance with a least significant difference test (LSD, $p < 0.05$) was conducted to determined the differences of soil water soluble K, exchangeable K, non-exchangeable K between planting years. The relationships between mineral N and water-soluble K, Ca, and Mg concentrations in the 0–7 m soil layers were assessed using Pearson's correlation coefficient analysis.

3. Results

3.1. Effects of Cultivation Years and Soil Depth on Different Forms of N

Cultivation years significantly affected the concentration of soil mineral N, soluble organic N (SON), soluble total N (STN) and total N (TN, Table 1).

Table 1. NOVA F-values of the effects of planting years and soil depths on the concentration of soil mineral N, soluble organic N (SON), soluble total N (STN), total N (TN), water soluble K, Ca, and Mg.

Factors	Mineral N	SON	STN	TN	Water Soluble K	Water Soluble Ca	Water Soluble Mg
				ANOVA, F value			
Years (Y)	63.61 ***	3.40 *	76.67 ***	6.26 **	2.47 ns	32.43 ***	30.81 ***
Depths (D)	1.55 ns	0.46 ns	1.79 *	41.61 ***	12.98 ***	3.00 ***	7.06 ***
Y*D	1.03 ns	0.73 ns	1.08 ns	3.20 ***	9.26 ***	0.48 ns	0.96 ns

***: $p < 0.001$; **: $0.001 < p < 0.01$; *: $0.01 < p < 0.05$; ns: not significant.

The concentration of soil mineral N, STN and TN increased significantly with cultivation years (Figure 1a,c,d). The average soil mineral N concentration ranged from 11–97 mg kg^{-1} in all soil samples (Figure 1a). After 20 years of continuous planting of pepper in plastic greenhouses, the cumulative amount of mineral N in 0–7 m soil profile was up to 7.39 t ha^{-1}, which were 1.76 and 3.70 times of that in 10-year greenhouses and wheat-maize fields, respectively (Figure 2). Compared with mineral N, cultivation years has less influence on SON (Table 1, Figure 1b). The average STN concentration ranged from 31–103 mg kg^{-1} in all soil samples (Figure 1c). The amount of STN in 0–7 m soil profile for 20-year greenhouses was 9.60 t ha^{-1} which significantly higher than that in 10-year greenhouses (6.35 t ha^{-1}) and wheat-maize fields (4.47 t ha^{-1}, Figure 2). In addition, the average soil TN concentration ranged from 120–1065 mg kg^{-1} in all soil samples (Figure 1d). The amount of TN in 0–7 m soil profiles were 36.16, 42.35 and 45.28 t ha^{-1} for wheat-maize fields, 10-year and 20-year greenhouses (Figure 2). In addition, soil depths significantly affected the concentration of soil TN and STN (Table 1). In general, the highest concentrations of TN were detected in 0–50 cm soil layer, with gradually declining with soil depths (Figure 1d). However, soil depths have no significant effect on mineral N and SON concentrations (Table 1).

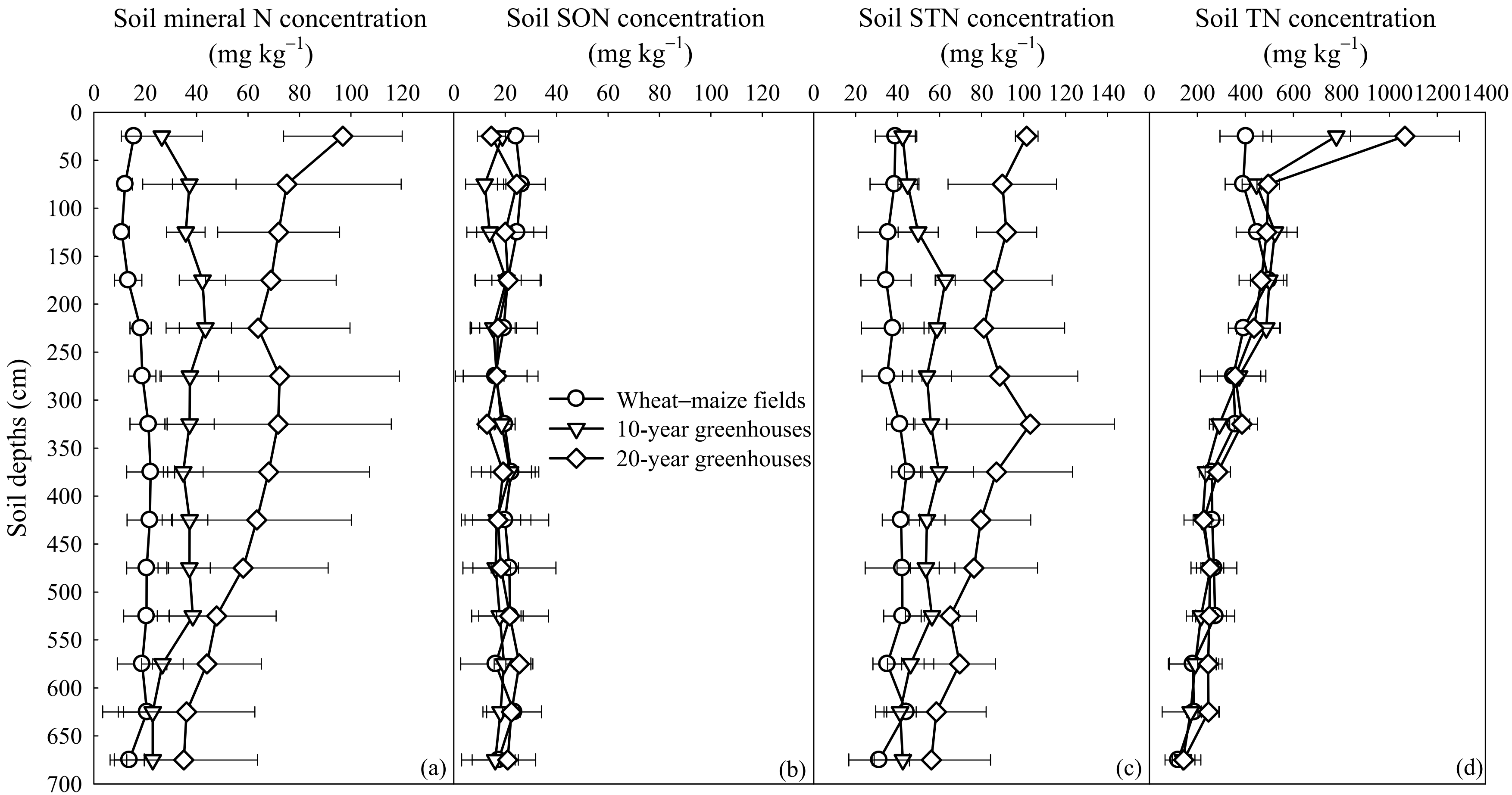

Figure 1. Concentrations of soil mineral N (**a**), soluble organic N (SON, (**b**)), soluble total N (STN, (**c**)), and total N (TN, (**d**)) at different soil depths for wheat–maize fields (n = 3), 10-year-old (n = 6) and 20-year-old (n = 4) pepper greenhouses. Soil STN concentration = Soil mineral N concentration + Soil SON concentration. Data are shown as the mean ± SD.

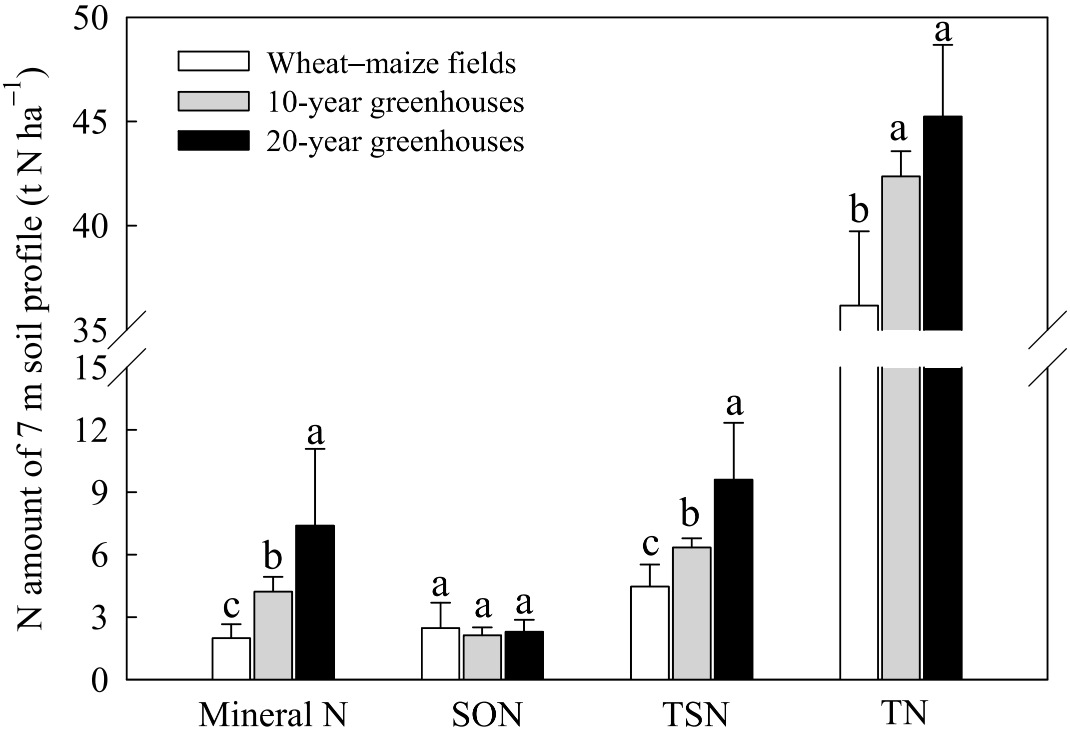

Figure 2. The amount of soil mineral N, soluble organic N (SON), soluble total N (STN) and total N (TN) across 1–8 m soil profiles for wheat–maize fields (n = 3) and 0–7 m soil profiles for 10-year (n = 6) and 20-year (n = 4) old pepper greenhouses. Different lowercase letters indicate significant differences ($p < 0.05$) among cultivation years. Data are shown as the mean ± SD.

3.2. N Balance of Plastic-Greenhouse Pepper Planting System for 10 and 20 Years

In the sampling plastic-greenhouses, the average cumulative N input during 10 years and 20 years planting period were 20.35 ± 4.53 and 52.09 ± 11.75 t ha^{-1} respectively, and the average cumulative N uptake by plants were 7.21 ± 1.36 and 13.88 ± 0.97 t ha^{-1} respectively (Table 2). After 10 years of continuous planting, the soil TN and STN average amount were 42.35 ± 1.16 and 6.35 ± 0.44 t ha^{-1} respectively, increasing by 17.1% and 42.1% compared with the basic amount. For 20-year plastic-greenhouses, the average amount of TN and STN in 0–7 m soil profiles were 45.28 ± 3.43 and 9.60 ± 2.73 t ha^{-1} respectively, increasing by 25.2% and 114.8% compared with the basic amount (Table 2). According to the calculation of N balance, on average 6.95 ± 2.76 and 29.10 ± 10.14 t N ha^{-1} entering the environment beyond the 0–7 m soil profiles during 10 years and 20 years pepper planting period, respectively. Moreover, the amount of soil non-soluble N in 0–7 m soil profiles increased by 4.31 ± 1.12 and 3.99 ± 0.90 t ha^{-1} respectively in 10-year and 20-year plastic-greenhouses (Table 2).

Table 2. The cumulative N input, N uptake, the basic and detection amount of soil total N (TN) and soluble total N (STN) across 0–7 m soil, the amount of N removed out 0–7 m soil and the increased amount of non-soluble N across 0–7 m soil in 10 years and 20 years pepper greenhouses.

	Cumulative N Input ($t N ha^{-1}$)	Cumulative N Uptake ($t N ha^{-1}$)	The Basic Amount of TN † ($t N ha^{-1}$)	The Basic Amount of STN † ($t N ha^{-1}$)	The Detection Amount of TN ($t N ha^{-1}$)	The Detection Amount of STN ($t N ha^{-1}$)	The Amount of N Removed out 0–7 m Soil ‡ ($t N ha^{-1}$)	The Increased Amount of Soil Non-Soluble N in 0–7 m Soil § ($t N ha^{-1}$)
10 years greenhouses								
1	26.40	8.25	36.16	4.47	42.72	6.81	11.60	4.22
2	19.08	7.50	36.16	4.47	42.32	5.88	5.42	4.76
3	21.47	8.25	36.16	4.47	41.48	6.56	7.91	3.23
4	24.24	8.25	36.16	4.47	44.27	6.76	7.88	5.83
5 ¶	15.90	5.25	36.16	4.47	42.45	5.78	4.37	4.98
6 ¶	15.03	5.78	36.16	4.47	40.89	6.34	4.53	2.86
Mean	20.35	7.21	36.16	4.47	42.35	6.35	6.95	4.31
SD	4.53	1.36	3.57	1.05	1.16	0.44	2.76	1.12
20 years greenhouses								
1	59.04	14.25	36.16	4.47	44.48	9.11	36.47	3.68
2	47.04	13.50	36.16	4.47	42.61	8.02	27.09	2.90
3	38.12	15.00	36.16	4.47	43.72	7.69	15.56	4.35
4	64.14	12.75	36.16	4.47	50.29	13.59	37.27	5.01
Mean	52.09	13.88	36.16	4.47	45.28	9.60	29.10	3.99
SD	11.75	0.97	3.57	1.05	3.43	2.73	10.14	0.90

† The amount of TN or STN in 1–8 m soil layer of wheat−maize fields was used as the TN or STN basic content in 0–7 m soil layer in greenhouses due to the planting surface sinks 1 m. ‡ The amount of N removed out 0–7 m soil = Cumulative N input + The basic amount of TN − Cumulative N uptake − The detection amount of TN. § The increased amount of soil non-soluble N in 0–7 m soil = (The detection amount of TN − The basic amount of TN) − (The detection amount of STN − The basic amount of STN). ¶ These two pepper greenhouses have only 7 years planting history.

3.3. Accumulation and Distribution of K, Ca, Mg in Soil Profiles

Cultivation years significantly affected the concentration of water-soluble Ca and Mg, but the effect on soil water-soluble K concentration was not significant (Table 1). The average concentrations of water-soluble K, Ca and Mg ranged from 6–63, 86–196 and 11–41 mg kg^{-1} in all soil samples, respectively (Figure 3). The concentration of soil water-soluble Ca and Mg increased significantly with cultivation years in 0–7 m soil profiles (Figure 3b,c), however, the significant impact of cultivation years on soil water-soluble K concentration only occurs in the surface soil (Figure 3a). In addition, soil depths significantly affected the concentration of soil water-soluble K, Ca and Mg (Table 1). There was little difference in water-soluble K, Ca and Mg concentrations in the whole soil profiles of wheat-maize fields. But the concentrations of water-soluble K, Ca and Mg in topsoil were higher than that in bottom soil for plastic greenhouses (Figure 3). For example, the highest concentration of water-soluble K was found at 0–50 cm soil layer, with concentration sharply declining thereafter (Figure 3a).

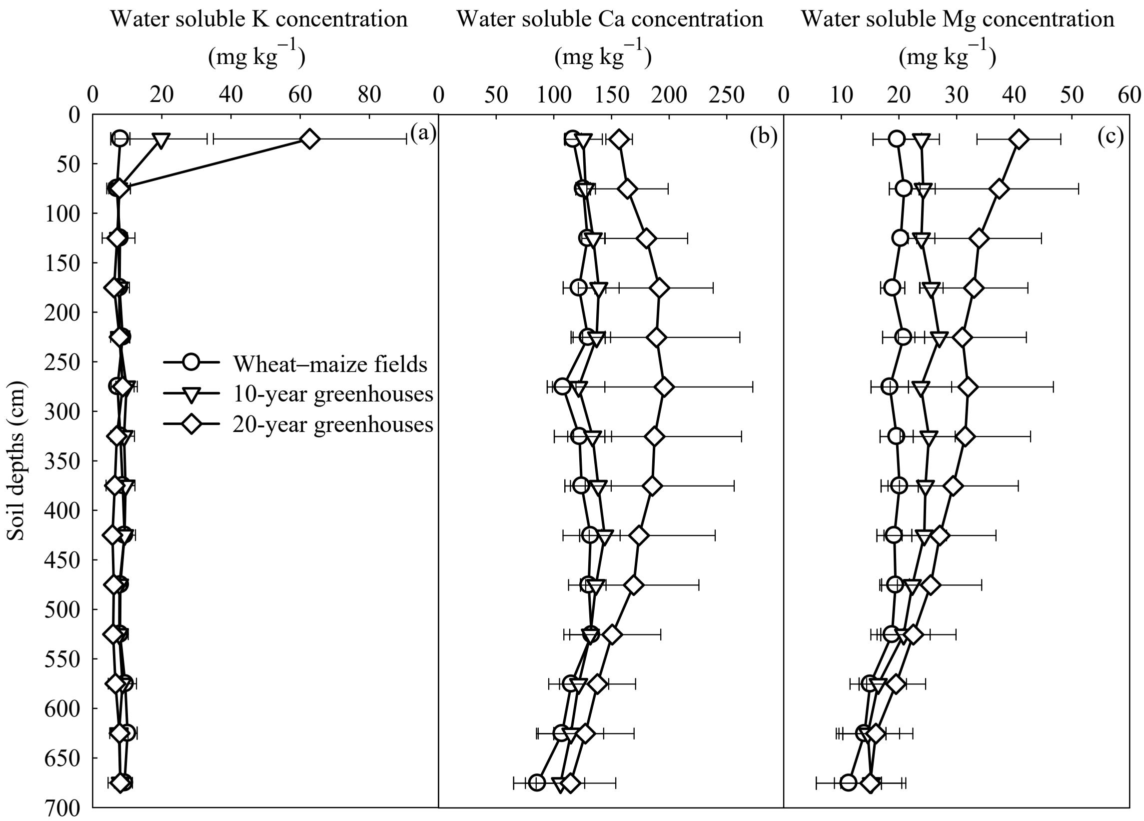

Figure 3. Concentrations of soil water–soluble potassium (K, (**a**)), calcium (Ca, (**b**)), and magnesium (Mg, (**c**)) at different soil depths for wheat–maize fields (n = 3), 10-year-old (n = 6) and 20-year-old (n = 4) pepper greenhouses. Data are shown as mean ± SD.

Through further analysis, we found that K mainly exists as non-exchangeable K in the 0–50 cm soil layer, accounting for 85.4% and 76.8% of the net accumulation of K for 10-year and 20-year greenhouses, respectively, but there is no significant difference between the 10-year and 20-year greenhouses (Figure 4c). Besides, the amount of soil available K (including water soluble K and exchangeable K) significantly increases with cultivation years both 0–25 cm and 25–50 cm soil layers (Figure 4a,b). The accumulated amounts of water-soluble K and exchangeable K at the 0–50 cm soil layers in the 20-year greenhouses were 1026 and 2258 kg ha^{-1}, respectively, an increase of 58.3% and 42.6% compared to the 10-year greenhouses.

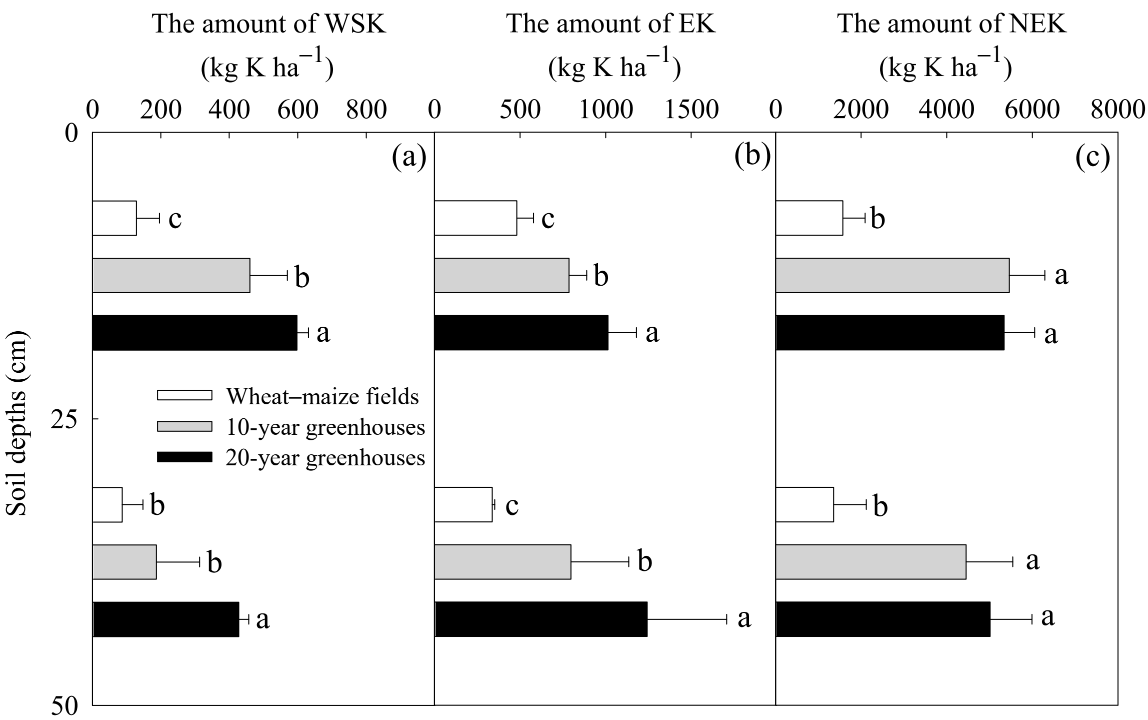

Figure 4. The amount of soil water soluble K (WSK, (**a**)), exchangeable K (EK, (**b**)), non–exchangeable K (NEK, (**c**)) across 0–50 cm soil depths for wheat–maize fields (n = 3), 10 years (n = 7) and 20 years (n = 4) pepper greenhouses. Different lowercase letters indicate significant differences ($p < 0.05$) among cultivation years at the same soil depth. Data are shown as the mean ± SD.

Moreover, there were significant positive correlation ($p < 0.001$) between soil mineral N and water–soluble Ca and Mg concentration in 0–7 m soil profiles (Figure 5b,c). However, significant positive correlation ($p < 0.001$) between soil mineral N and water–soluble K concentration was only found in 0–50 cm soil layers (Figure 5a).

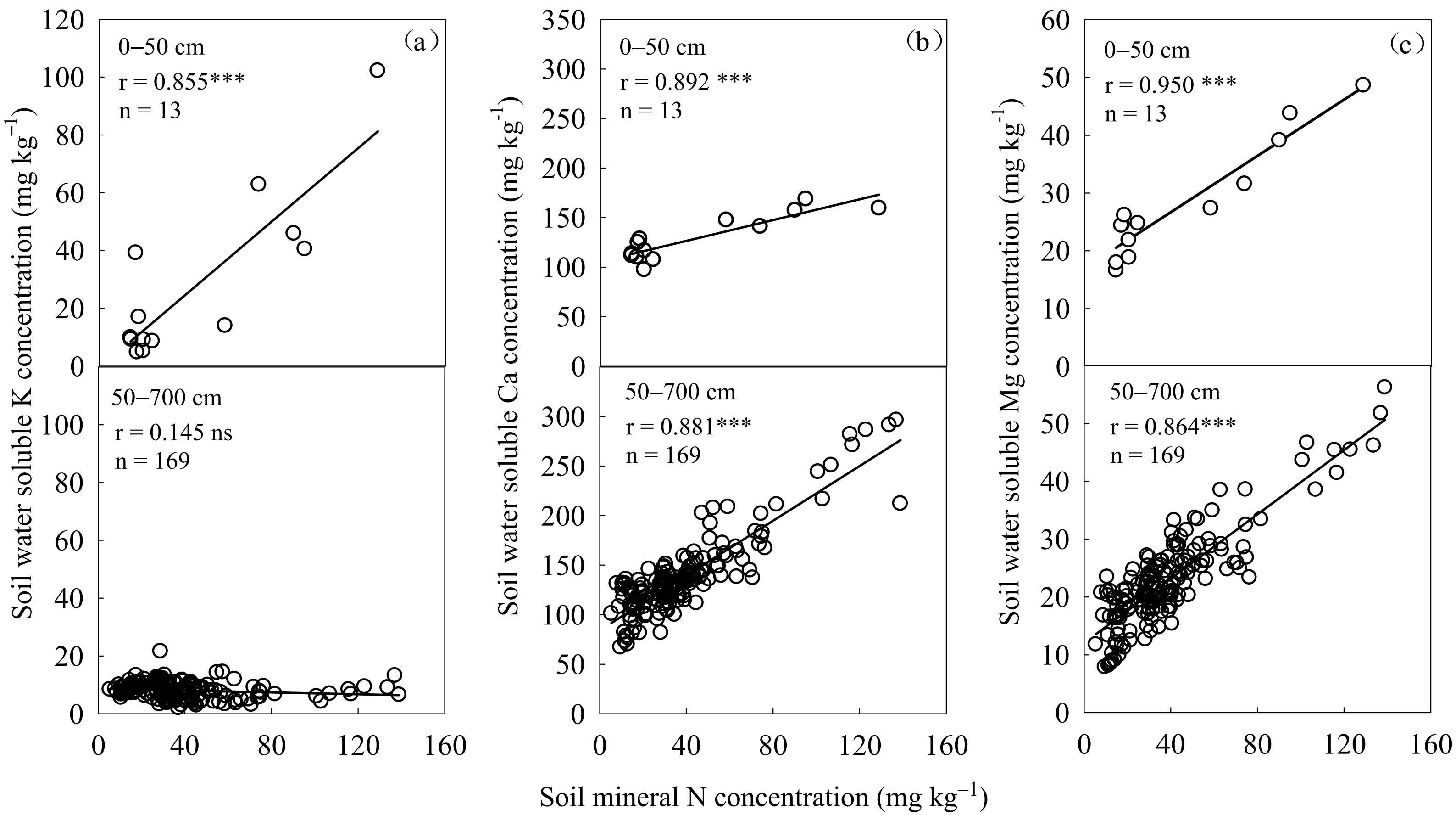

Figure 5. Correlation of the soil mineral N concentration with the soil water soluble potassium (K, (**a**)), calcium (Ca, (**b**)), and magnesium (Mg, (**c**)) concentrations at 0–50 cm and 50–700 cm depths. ***: $p < 0.001$; ns indicates no significant correlation.

4. Discussion

4.1. Analysis of N Balance in Plastic-Greenhouse Pepper Planting System

In this study, the average recovery rates of N were 35.4% and 26.6% for 10-year and 20-year greenhouses, respectively (Table 2). The recovery rates of N in this study correspond to reports by Wang et al., who reported the N recovery rates of plastic-greenhouse pepper ranges from 25.5% to 35.9% through the investigation of 160 farmer fields in China [24]. The average N recovery rate of pepper in 20-year greenhouses was significantly lower than that in 10-year greenhouses. On the one hand, the average annual N input in 20-year greenhouses was 15.4% higher than that in 10-year greenhouses (Table S1), following further decreases in application amount of N fertilizer owing to improvements in fertilization techniques and agronomic managements in recent years [25]. On the other hand, the pepper yield in 20-year greenhouses was 13.1% lower than that in 10-year greenhouses (Table S1), which may be related to the continuous cropping obstacle and soil quality degradation caused by long-term single planting and excessive input of water and fertilizer in 20-year greenhouses [26,27].

Compared to wheat-maize fields, the total N (TN) of the 0–7 m soil profiles in 10-year and 20-year greenhouses increased by 6.19 and 9.12 t ha^{-1} on average, respectively, accounting for 30.4% and 17.5% of the total N input (Table 2). Reports on N accumulation in soil profiles also be found in intensive orchards in northwest China, and average amount of nitrate accumulation within the 0–10 m soil layers was 7.11 t N ha^{-1} [28]. The huge residual N in soil profile poses a serious threat to the ecological environment, especially the water environment. Some studies show that even if N fertilizer utilization rate reaches 100%, it would take decades to meet target N loads in surface water due to residual N in soil [29,30]. Moreover, if the flood irrigation method is not changed, the residual N in the soil profile will be gradually leached to the groundwater even if N fertilizer management is optimized. In brief, soil residual N can serve as long-term sources of nitrate to surface water and groundwater, thus reductions in N fertilizer use may have little effect on short-term changes in water N pollution. Therefore, to completely solve the problem of non-point source pollution caused by N, it is necessary to reduce the amount of water and N input, while reducing the N storage in the soil layers to mitigate its hysteretic effect on environmental pollution.

According to the calculation of N balance, approximately 34.2% (6.95 t ha^{-1}) and 55.9% (29.10 t ha^{-1}) of total N input entering the environment beyond the 0–7 m soil profiles for 10-year and 20-year greenhouses (Table 2), respectively, including N leached to below 7 m soil profile and gaseous N (N_2O, NO, N_2 and NH_3) loss. Although this study did not accurately detect the loss of gaseous N in the sampled pepper greenhouse, it can be estimated by referring to the results under similar experiment conditions. The greenhouse cucumber experiment conducted in Shouguang showed that the annual emissions of N_2O and NO were 60.5 and 1.4 kg N ha^{-1}, respectively, under the condition of 2252 kg N application per year [31]. Schlesinger et al. obtained a N_2O:(N_2O + N_2) ratio of 0.37 based on a meta-analysis of the N losses from soil denitrification in agricultural systems. Thus, it can be calculated that the N_2 emission was about 103 kg N ha^{-1} yr^{-1} when the N_2O emission was 60.5 kg N ha^{-1} yr^{-1} [32]. In addition, the amount of NH_3 volatilization from the soil surface were approximately 30 kg N ha^{-1} yr^{-1} in greenhouse pepper in Shouguang [33]. To sum up, the possible gaseous N loss in pepper greenhouses in this study was approximately 195 kg N ha^{-1} yr^{-1}, and accumulatively 1.76 and 3.90 t N ha^{-1} entered the atmosphere for 10-year and 20-year greenhouses, respectively, accounting for approximately 8.6% and 7.5% of the total N input, respectively. As a result, the N leached to below 7 m soil profile were approximately 5.19 and 25.2 t N ha^{-1} for 10-year and 20-year greenhouses, respectively, accounting for approximately 25.5% and 48.4% of the total N input, respectively. The N leached to the soil below 7 m will continue to migrate to the groundwater, eventually causing nitrate contamination of the groundwater in the vegetable planting area. Kou et al. also confirmed that more than 90% of the N in the groundwater in the Weifang area (including Shouguang) comes from manure, soil residual N, and chemical N fertilizer [11].

4.2. The Leaching of N, K, Ca, Mg and Soil Acidification

The consensus is that the application of chemical N fertilizer in agricultural ecosystems can lead to soil acidification, which is particularly serious in greenhouse vegetable fields with higher application rates of N fertilizer [34,35]. The results of our study also showed that the soil pH value of the 0–50 cm soil layer in the 20-year greenhouses significantly decreased by 0.29 units on average, compared with that in the wheat-maize fields (Figure S2). There is an opinion that the main source of hydrogen ions (H^+) in calcareous soil is the transformation of N forms (nitrification process) in soil, with excess leaching of nitrification products (NO_3^--N) [36–38].

Soils also have a buffering capacity to neutralize excess H^+. For example, basic cations, such as potassium ion (K^+), calcium ion (Ca^{2+}), and magnesium ion (Mg^{2+}), are critically important to buffer against N-induced soil acidification at the early stage [39,40]. Soil acidification is strongly buffered by carbonate in calcareous soils in our study area (pH > 7.5) [41,42]. During the acidification process, exchangeable base cations held on clay and organic matter surfaces will exchange with H^+ and enter the soil solution, thereby neutralizing the increase in soil acidity [43]. Meanwhile, the risk of base cations entering the soil solution being leached significantly increases. The leaching amount of Ca^{2+} and Mg^{2+} at 90 cm depth were average 600 and 340 kg ha^{-1} $year^{-1}$, respectively, under the conventional flooding irrigation and over-fertilization in plastic-greenhouse vegetable production systems in North China [12,44]. And the concentrations of total base cations correlated strongly with NO_3^- concentrations in leachates [36]. Our study also confirms the viewpoint by analyzing the correlation between residual nutrients in soil profiles. There were significant positive correlations ($p < 0.001$) between soil mineral N and water-soluble Ca and Mg concentration in 0–7 m soil profiles, while significant positive correlation ($p < 0.001$) between soil mineral N concentration and water-soluble K concentration was only found in surface soil (Figure 5). In other words, the Ca and Mg in surface soil leached to the deep soil together with NO_3^--N, while K did not. This might be because K^+ more easily enters the crystal lattice of clay minerals where it is fixed compared with Ca^{2+} and Mg^{2+} [45]. In addition, high-yield fruit vegetables (e.g., tomato, pepper, cucumber, etc.) removal a large amount of basic cations from soil by plants uptake and harvest but pay no attention to return [4]. As discussed above, the soil exchangeable base cations are gradually exhausted by leaching and plants uptake with the extension of cultivation years, and it will hamper the acid-buffering capacity of soils and accelerate soil acidification [46].

5. Conclusions

Our research showed that with the extension of plastic-greenhouse pepper cultivation years, huge amounts of N migrate to the deep soil layers and environment, accompanied by significant leaching of Ca and Mg. For achieving sustainable production of plastic-greenhouse vegetables and environmental protection, we suggest that it is necessary to reduce the amount of water and N input by optimizing current irrigation and fertilization methods, while reducing the N storage in the deep soil by employing suitable measures, such as denitrification technology. On the other hand, attention should be paid to the return of Ca and Mg to the soil during intensive plastic-greenhouse vegetables production to avoid rapid soil acidification.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14051060/s1, Figure S1: Satellite picture of sampling points. The yellow square, triangle and circle in the picture represents the wheat-maize fields, 10-year and 20-year old pepper greenhouses, respectively; Figure S2: The soil pH of different depths for wheat-maize fields (n = 3), 10-year (n = 6) and 20-year (n = 4) old pepper greenhouses. Given are mean values ± SE; Table S1: The amount of N input, crops yield and N uptake of sampling wheat (W)-maize (M) fields and pepper greenhouses; Table S2: The amount of N input, crops yield and N uptake of wheat (W)-maize (M) fields and pepper greenhouses according to the interview of individual farmers around the sampling point; Table S3: Soil bulk density at different depths of wheat-maize fields, 10-year and 20-year old pepper greenhouses; Table S4: Nitrogen (N) requirement of per 100 kg grain or yield for wheat, maize and greenhouse pepper in northern China from references [47–50].

Author Contributions: Conceptualization, B.L.; methodology, B.L.; validation, Z.P. and W.Z.; formal analysis, H.L.; investigation, F.C. and J.D.; resources, Z.P., H.J. and W.W.; data curation, H.L. and F.C.; writing—original draft preparation, H.L.; writing—review and editing, B.L., W.Z. and J.L.; visualization, H.L.; supervision, J.D.; project administration, B.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Key Research and Development Program of Shandong Province, grant number 2021CXGC010801; the National Key Research and Development Program of China, grant number 2017YFD0201507 and the Shandong Provincial Natural Science Foundation, grant number ZR2021QC132.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: The authors are very grateful to Shan Lin of China Agricultural University for his constructive comments on the writing of the paper.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Zhou, J.; Xia, X.J.; Hu, Z.J.; Fan, P.X.; Shi, K.; Zhou, Y.H.; Yu, J.Q. Progress in Protected Vegetable Production and Research during China's 13th Five-Year Plan. *China Veg.* **2021**, *10*, 20–34. (In Chinese)
2. Guo, S.R.; Sun, J.; Su, S.; Lu, X.M.; Tian, J.; Wang, J.W. Analysis of general situation, characteristics, existing problems and devel opment trend of protected horticulture in China. *China Veg.* **2012**, *18*, 1–14.
3. Gao, L.H.; Qu, M.; Ren, H.Z.; Chen, Q.Y.; Zhang, Z.X. Structure, function, application, and ecological benefit of a single-slope, energy-efficient solar greenhouse in China. *Hort Technol.* **2010**, *20*, 626–631. [CrossRef]
4. Song, H.; Guo, J.H.; Ren, T.; Chen, Q.; Li, B.G.; Wang, J.G. Increase of soil pH in a solar greenhouse vegetable production system. *Soil Sci. Soc. Am. J.* **2012**, *76*, 2074–2082. [CrossRef]
5. Qasim, W.; Xia, L.L.; Shan, L.; Wan, L.; Zhao, Y.M.; Butterbach-Bahl, K. Global greenhouse vegetable production systems are hotspots of soil N_2O emissions and nitrogen leaching: A meta-analysis. *Environ. Pollut.* **2021**, *272*, 116372. [CrossRef] [PubMed]
6. Li, B.; Bi, Z.; Xiong, Z. Dynamic responses of nitrous oxide emission and nitrogen use efficiency to nitrogen and biochar amend ment in an intensified vegetable field in southeastern China. *GCB Bioenergy* **2017**, *9*, 400–413. [CrossRef]
7. Zotarelli, L.; Dukes, M.D.; Scholberg, J.M.S.; Carpena, R.M.; Icerman, J. Tomato nitrogen accumulation and fertilizer use efficiency on a sandy soil, as affected by nitrogen rate and irrigation scheduling. *Agric. Water Manag.* **2009**, *96*, 1247–1258. [CrossRef]
8. Qu, Z.; Wang, J.; Almoy, T.; Bakken, L. Excessive use of nitrogen in Chinese agriculture results in high $N_2O/(N_2O+N_2)$ product ratio of denitrification, primarily due to acidification of the soils. *Glob. Chang. Biol.* **2014**, *20*, 1685–1698. [CrossRef] [PubMed]
9. Fan, Z.B.; Lin, S.; Zhang, X.M.; Jiang, Z.M.; Yang, K.C.; Jian, D.D.; Chen, Y.Z.; Li, J.L.; Chen, Q.; Wang, J.G. Conventional flooding irrigation causes an overuse of nitrogen fertilizer and low nitrogen use efficiency in intensively used solar greenhouse vegetable production. *Agric. Water Manag.* **2014**, *144*, 11–19. [CrossRef]
10. Ju, X.T.; Kou, C.L.; Zhang, F.S.; Christie, P. Nitrogen balance and groundwater nitrate contamination: Comparison among three intensive cropping systems on the North China Plain. *Environ. Pollut.* **2006**, *143*, 117–125. [CrossRef]
11. Kou, X.Y.; Ding, J.J.; Li, Y.Z.; Li, Q.Z.; Ma, L.L.; Xu, C.Y.; Zheng, Q.; Zhuang, S. Tracing nitrate sources in the groundwater of an intensive agricultural region. *Agric. Water Manag.* **2021**, *250*, 106826. [CrossRef]
12. Li, Y.; Li, J.Q.; Gao, L.H.; Tian, Y.Q. Irrigation has more influence than fertilization on leaching water quality and the potential environmental risk in excessively fertilized vegetable soils. *PLoS ONE* **2018**, *13*, e0204570. [CrossRef] [PubMed]
13. Lv, H.F.; Zhou, W.W.; Dong, J.; He, S.P.; Chen, F.; Bi, M.H.; Wang, Q.Y.; Li, J.L.; Liang, B. Irrigation amount dominates soil mineral nitrogen leaching in plastic shed vegetable production systems. *Agric. Ecosyst. Environ.* **2021**, *317*, 107474. [CrossRef]
14. Sun, Y.; Hu, K.L.; Fan, Z.B.; Wei, Y.P.; Lin, S.; Wang, J.G. Simulating the fate of nitrogen and optimizing water and nitrogen management of greenhouse tomato in North China using the EU-Rotate_N model. *Agric. Water Manag.* **2013**, *128*, 72–84. [CrossRef]
15. Min, J.; Zhang, H.L.; Shi, W.M. Optimizing nitrogen input to reduce nitrate leaching loss in greenhouse vegetable production. *Agric. Water Manag.* **2012**, *111*, 53–59. [CrossRef]
16. Min, J.; Shi, W.M.; Xing, G.X.; Zhang, H.L.; Zhu, Z.L. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems. *Nutr. Cycl. Agroecosyst.* **2011**, *91*, 31–39. [CrossRef]

17. Ren, T.; Christie, P.; Wang, J.G.; Chen, Q.; Zhang, F.S. Root zone soil nitrogen management to maintain high tomato yields and minimum nitrogen losses to the environment. *Sci. Hortic.* **2010**, *125*, 25–33. [CrossRef]
18. Lv, H.F.; Lin, S.; Wang, Y.F.; Lian, X.J.; Zhao, Y.M.; Li, Y.J.; Du, J.Y.; Wang, Z.X.; Wang, J.G.; Butterbach-Bahl, K. Drip fertigation significantly reduces nitrogen leaching in solar greenhouse vegetable production system. *Environ. Pollut.* **2019**, *245*, 694–701. [CrossRef]
19. Hong, E.M.; Choi, J.Y.; Nam, W.H.; Kang, M.S.; Jang, J.R. Monitoring nutrient accumulation and leaching in plastic greenhouse cultivation. *Agric. Water Manag.* **2014**, *146*, 11–23. [CrossRef]
20. Xu, Y.H.; Liu, X.H.; Jing, Y.P.; Luo, J.; Guo, D.J.; Ma, Y. Dissolved N and C leaching losses mitigated by optimized fertilization management in intensive greenhouse system: Insights from DOM characteristics via EEM-PARAFAC. *J. Soils Sediments* **2023**, *23*, 657–671. [CrossRef]
21. Food and Agriculture Organization of the United Nations. FAOSTAT Database-Resources. Food and Agriculture Organization of the United Nations. In *FAO Statistical Yearbook*; World Food and Agriculture: Rome, Italy, 2013.
22. Norman, R.J.; Edberg, J.C.; Stucki, J.W. Determination of nitrate in soil extracts by dual-wavelength ultraviolet spectrophotometry. *Soil Sci. Soc. Am. J.* **1985**, *49*, 1182–1185. [CrossRef]
23. Bao, S.D. *Soil and Agricultural Chemistry Analysis*, 3rd ed.; China Agricultural Press: Beijing, China, 2000; pp. 106–109. (In Chinese)
24. Wang, X.Z.; Liu, B.; Wu, G.; Sun, Y.X.; Guo, X.S.; Jin, Z.H.; Xu, W.N.; Zhao, Y.Z.; Zhang, F.S.; Zhou, C.Q.; et al. Environmental costs and mitigation potential in plastic-greenhouse pepper production system in China: A life cycle assessment. *Agric. Syst.* **2018**, *167*, 186–194. [CrossRef]
25. Zhang, C.; Ju, X.T.; Powlson, D.; Oenema, O.; Smith, P. Nitrogen surplus benchmarks for controlling N pollution in the main cropping systems of China. *Environ. Sci. Technol.* **2019**, *53*, 6678–6687. [CrossRef] [PubMed]
26. Ruan, W.B.; Ren, T.; Che, Q.; Zhu, X.; Wang, J.G. Effects of conventional and reduced N inputs on nematode communities and plant yield under intensive vegetable production. *Appl. Soil Ecol.* **2013**, *66*, 48–55. [CrossRef]
27. Tian, Y.Q.; Wang, J.G.; Gao, L.H. Research progress on vegetable soil microbial obstacles in protected cropping systems. *China Veg.* **2013**, *20*, 1–9. (In Chinese)
28. Gao, J.B.; Wang, S.M.; Li, Z.Q.; Wang, L.; Chen, Z.J.; Zhou, J.B. High nitrate accumulation in vadose zone after land use change from cropland to orchards. *Environ. Sci. Technol.* **2021**, *55*, 5782–5790. [CrossRef] [PubMed]
29. Van Meter, K.J.; Van Cappellen, P.; Basu, N.B. Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico. *Science* **2018**, *360*, 427–430. [CrossRef] [PubMed]
30. Vero, S.E.; Basu, N.B.; Van Meter, K.; Richards, K.G.; Mellander, P.E.; Healy, M.G.; Fenton, O. Review: The environmental status and implications of the nitrate time lag in Europe and North America. *Hydrogeol. J.* **2018**, *26*, 7–22. [CrossRef]
31. Yao, Z.S.; Yan, G.X.; Wang, R.; Zheng, X.H.; Liu, C.Y.; Butterbach-Bahl, K. Drip irrigation or reduced N-fertilizer rate can mitigate the high annual N_2O+NO fluxes from Chinese intensive greenhouse vegetable systems. *Atmos. Environ.* **2019**, *212*, 183–193. [CrossRef]
32. Schlesinger, W.H. On the fate of anthropogenic nitrogen. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 203–208. [CrossRef]
33. Zhu, J.H.; Li, X.L.; Christie, P.; Li, J.L. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (*Capsicum frutescens* L.) cropping systems. *Agric. Ecosyst. Environ.* **2005**, *111*, 70–80. [CrossRef]
34. Guo, J.H.; Liu, Z.J.; Zhang, Y.; Shen, J.L.; Han, W.X.; Zhang, W.F.; Christie, P.; Goulding, K.W.T.; Vitousek, P.M.; Zhang, F.S. Significant acidification in major Chinese croplands. *Science* **2010**, *327*, 1008–1010. [CrossRef] [PubMed]
35. Lv, H.F.; Zhao, Y.M.; Wang, Y.F.; Wan, L.; Wang, J.G.; Butterbach-Bahl, K.; Lin, S. Conventional flooding irrigation and over fertilization drives soil pH decrease not only in the top- but also in subsoil layers in solar greenhouse vegetable production systems. *Geoderma* **2020**, *363*, 114156. [CrossRef]
36. Dong, Y.; Yang, J.L.; Zhao, X.R.; Yang, S.H.; Zhang, G.L. Contribution of different proton sources to the acidification of red soil with maize cropping in subtropical China. *Geoderma* **2021**, *392*, 114995. [CrossRef]
37. Lu, X.K.; Vitousek, P.M.; Mao, Q.G.; Gilliam, F.S.; Luo, Y.Q.; Zhou, G.Y.; Zou, X.M.; Bai, E.; Scanlon, T.M.; Hou, E.Q.; et al. Plant acclimation to long-term high nitrogen deposition in an N rich tropical forest. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 5187–5192. [CrossRef]
38. Zhu, Q.C.; Liu, X.J.; Hao, T.X.; Zeng, M.F.; Shen, J.B.; Zhang, F.S.; De Vries, W. Modeling soil acidification in typical Chinese cropping systems. *Sci. Total Environ.* **2018**, *613–614*, 1339–1348. [CrossRef] [PubMed]
39. Tian, D.S.; Niu, S.L. A global analysis of soil acidification caused by nitrogen addition. *Environ. Res. Lett.* **2015**, *10*, 024019. [CrossRef]
40. Alves, L.A.; Denardin, L.G.D.; Martins, A.P.; Anghinoni, I.; Carvalho, P.C.D.; Tiecher, T. Soil acidification and P, K, Ca and Mg budget as affected by sheep grazing and crop rotation in a long-term integrated crop-livestock system in southern Brazil. *Geoderma* **2019**, *351*, 197–208. [CrossRef]
41. Yang, Y.H.; Ji, C.J.; Ma, W.H.; Wang, S.F.; Wang, S.P.; Han, W.X.; Mohammat, A.; Robinson, D.; Smith, P. Significant soil acidification across northern China's grasslands during 1980s–2000s. *Glob. Chang. Biol.* **2012**, *18*, 2292–2300. [CrossRef]
42. Slessarev, E.W.; Lin, Y.; Bingham, N.L.; Johnson, J.E.; Dai, Y.; Schimel, J.P.; Chadwick, O.A. Water balance creates a threshold in soil pH at the global scale. *Nature* **2016**, *540*, 567–569. [CrossRef]
43. Yang, J.L.; Zhang, G.L.; Huang, L.M.; Brookes, P.C. Estimating soil acidification rate at watershed scale based on the stoichiometric relations between silicon and base cations. *Chem. Geol.* **2013**, *337*, 30–37. [CrossRef]

44. Zhou, W.W.; Lv, H.F.; Chen, F.; Wang, Q.Y.; Li, J.L.; Chen, Q.; Liang, B. Optimizing nitrogen management reduces mineral nitrogen leaching loss mainly by decreasing water leakage in vegetable fields under plastic-shed greenhouse. *Environ. Pollut.* **2022**, *308*, 119616. [CrossRef] [PubMed]
45. Chen, S.; Yan, Z.J.; Chen, Q. Estimating the potential to reduce potassium surplus in intensive vegetable fields of China. *Nutr. Cycl. Agroecosyst.* **2017**, *107*, 265–277. [CrossRef]
46. Berthrong, S.T.; Jobbagy, E.G.; Jackson, R.B. A global meta-analysis of soil exchangeable base cations, pH, carbon, and nitrogen with afforestation. *Ecol. Appl.* **2009**, *19*, 2228–2241. [CrossRef]
47. Che, S.G.; Yuan, L.; Li, Y.T.; Lin, Z.A.; Shen, B.; Hu, S.W.; Zhao, B.Q. N uptake and yield response of wheat in main wheat production regions of China. *J. Plant Nutr. Fertil.* **2016**, *22*, 287–295. (In Chinese)
48. Cheng, Y.; Liu, P.; Liu, Y.W.; Pang, S.S.; Dong, S.T.; Zhang, J.W.; Zhao, B.; Ren, B.C. Regulation of grain yield and nutrient absorption of modern summer maize varieties in the Yellow-Huaihe-Haihe Rivers region. *Acta Agron. Sin.* **2019**, *45*, 1699–1714. (In Chinese)
49. Yu, H.Y.; Li, T.X.; Zhang, X.Z. Nutrient budget and soil nutrient status in greenhouse system. *Sci. Agric. Sin.* **2010**, *43*, 514–522. (In Chinese) [CrossRef]
50. Liu, B.; Wang, X.Z.; Guan, X.L.; Wu, G.; Sun, Y.X.; Liu, L.; Ge, C.W.; Chen, X.P. Nutrients absorption and distribution rule of pepper grown at autumn-winter season under mulched drop-irrigation system in greenhouse. *China Veg.* **2017**, *5*, 50–57. (In Chinese)