High nitrate accumulation in vadose zone after land use change from cropland to orchards

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Abstract

More evidence indicates that the nitrate stored in the deep soil profile has an important role in regulating the global nitrogen (N) cycle. This study assessed the effects of land use changes from crop land to intensive orchards (LUCO) on the N surplus, nitrate accumulation in deep soil, and groundwater quality in the kiwifruit belt of the northern slope region of the Qinling Mountains, China. LUCO resulted in comparatively high N surplus in orchards (282 vs 1206 kg ha^{-1} yr^{-1}, respectively). The average nitrate accumulation within the 0–10 m profiles of orchards was 7113 kg N ha^{-1}, which was equal to approximate the total N surplus of 6 years of the orchards. The total nitrate stock within 0–10 m soil profiles of the kiwifruit belt was 266.5 Gg N, which was 3.5 times higher than the total annual N input. The nitrate concentrations of 97% of groundwater samples exceeded the WHO standard. The LUAO resulted in large nitrate storage in the vadose zone and caused serious contamination of groundwater. Our study highlights that nitrate accumulation at vadose zone of intensive land use system is one of main fates of surplus N, and also hotspot of nitrate accumulation.

Keywords

Land use change, kiwifruit orchard, nitrogen input, nitrate accumulation, groundwater quality

Synopsis

Nitrate accumulation at vadose zone of intensive land use system is one of main fates of surplus N, and should be included in nitrogen budgets to close N cycle..

1 Introduction

Studies on nitrogen (N) cycling in terrestrial ecosystems have generally focused on the upper 1-m soil profile, which is biologically active and important for root growth.[1] However, recent studies at catchment and national scales have showed that there are substantial nitrate storages in the unsaturated zone above the groundwater table (vadose zone), which has an important role in regulating the global N cycle.[2,3] The vadose zone is an important storage location for nitrate before it leaches into groundwater.[2] Therefore, nitrate accumulation in the deep vadose zone has received increasing attention in recent years.[4] The thickness of the vadose zone varies in different regions of the world, between very shallow (<1 m) and very deep (>100 m) thicknesses. The thickness of the vadose zone controls the time required for nitrate to enter the aquifer.[5] Nitrate may leach into groundwater in a short time at a shallow vadose zone. In comparison, it takes decades even longer for nitrate to enter groundwater through a thick vadose zone.[6] Therefore, the 'time lag' is defined as the time between management changes and change in water quality.[7,8] This is the reason why the quality of groundwater in many regions of the world has still not improved despite many interventions for reducing N loading.[9,10]

Methods to quantify nitrate storage in the vadose zone include numerical modelling and borehole drilling. Compared with modelling method, direct measurements of nitrate in deep soil are difficult, tedious, and very expensive, but it can reflect the true status and variation of the nutrient content.[11-14] Ascott et al.[3] estimated the global nitrate storage in the vadose zone using a model as 605–1814 Tg.

Wang et al.[6] simulated nitrate transport and calculated its lag time in variable thicknesses of vadose zone using a catchment-scale model. With the borehole drilling method, Jankowski et al.[15] reported large quantities of nitrate stored in 8-m deep soil profiles after land use change from single-cropping of soybean to double-cropped soybean–maize farmland in intensifying Amazon agriculture in Brazil. A study conducted in the Chinese Loess Plateau characterised the mineral N content and accumulation in deep soils (50–200 m) with borehole drilling, and found that significant nitrate accumulation was observed in the upper 30-m soil profile at agricultural sites.[16]

The spatial variation and distribution of nitrate in deep soil is affected by topography, soil properties, and various agricultural management practices, such as land-use type, fertilisation, and irrigation.[4,17-19] Various N fertilisation rates have been used in different planting patterns, resulting in significant variations in nitrate accumulation in soils. Scanlon et al.[20] indicated that the inventories of nitrate in deep soil profiles of croplands are much higher than those under natural ecosystems. A literature study of soil nitrate accumulation in semi-humid croplands of China showed that the nitrate accumulations in 0–4 m soil profiles of vegetable fields and orchard fields, which received more N fertiliser, were higher than those in wheat or maize fields. In addition, comparably higher amounts of nitrate accumulation were found in the vadose zone deeper than 4 m.[21] The land-use pattern was the most important controlling factor explaining the variation of nitrate accumulation in deep horizons in red soil regions of subtropical China.[19] The distribution and amount of nitrate in different soil layers of a profile is also related to the soil properties. Intrinsic soil properties, such as soil texture, control the variations in nitrate concentrations in different soil layers by affecting the solute transport process.[22] For example, Su et al.[23] indicated that the nitrate leaching from soil layers was significantly correlated to the clay + silt content. However, the comprehensive study of N surplus under highly intensive agricultural system at the reginal scale on nitrogen use efficiency, spatial variation of nitrate accumulation in soil profiles, and groundwater quality is not well understand due to the laborious cost and sampling challenge.

The northern slope region of the Qinling Mountains is a typical region in which major changes of land use patterns have occurred since 1990. A large area of arable lands has been converted to kiwifruit orchards. This region has become the largest kiwifruit production belt in the world, accounting for near 30% of the global total kiwifruit cultivation area.[24,25] Similar to the case for other horticultural crops, excessive N fertilisation and irrigation are very common in kiwifruit orchards in this region.[13] Therefore, it is critical to understand the effect of changes from cropland to kiwifruit orchard on nitrate accumulation and potential risks to the local aquifer. One of our studies conducted in a small catchment of this region found that inefficient N use in this region led to a high N surplus and an enormous nitrate reservoir with an accumulation of 3288 kg N ha^{-1} in the 0–4 m soil profile. Furthermore, a high average nitrate content (50 mg N kg^{-1}) was observed at the depth of 4 m, indicating that nitrate leached into deeper soil.[26] Therefore, we hypothesise that land use change from cropland to orchards (LUCO) would increase nitrate accumulation in the deeper vadose zone. In addition, variations in soil texture and thickness of the vadose zone resulted in spatial variations of nitrate accumulation in soil and nitrate concentration in groundwater of this region.

In this study, we quantified (1) how N inputs and surpluses changed in response to land conversion from arable cropland to kiwifruit orchards; (2) whether nitrate accumulation and leaching to deeper soil increased with land use change; and (3) the impacts of land use change on groundwater quality.

2 Materials and methods

2.1 Study region

The study region includes Meixian and Zhouzhi Counties (1047 km^2; 34°3′23.6″–34°18′24.74″ N, 107°37′25.52″–108°26′8.26″ E), Shaanxi, China (Fig. 1). This site is a typical intensive agricultural area in the northern slope region of the Qinling Mountains. The Weihe River crosses through this region along the northern boundary of the study area. The region has a typical warm-temperate, sub-humid continental monsoon climate with an average annual temperature of 13.2 ℃ and average precipitation of 620 mm. A total of 60–80% of the annual precipitation occurs between July and September. The elevation of this region, which increase from northeast to southwest, ranges from 387 m to 974 m (Fig. 2a). The thickness of the vadose zone ranges from 0 to 100 m (Fig. 2b). The dominant soil textures in this region include loam, sandy clay loam, and loamy sand (USDA Soil Taxonomy) (Fig. 2c). In 1985, the total area of wheat–maize fields, the dominant land-use type, was 81.8 kha, accounting for 78.2% of the total study area (Fig. 1a). Since 1990, land use pattern change from cereal cropland to kiwifruit orchards has occurred. Currently, kiwifruit orchards are the dominant land-use type, accounting for 54.3% of the entire region (Fig. 1b). The density of kiwifruit orchards is between 1660 and 2220 vines ha^{-1}. Vines are trained on a T-bar trellis system. The average area of farmers' kiwifruit orchards is approximate 0.15 ha. The orchards are flood irrigated. Irrigation frequency depends on the precipitation rate and frequency each year. The orchards are usually irrigated 3 - 4 time annually, with an irrigation depth between 100 and 150 mm each time.[13,26]

2.2 Study method

To evaluate the N inputs and surpluses in orchards and croplands, 430 kiwifruit orchards and 18 wheat–maize fields were surveyed in 2018 and 2019. The survey details for each field included the area, application rates of synthetic fertiliser and manure, kiwifruit yield, biomass of vine pruning, grain and straw yields of wheat and maize.

To understand the spatial variation of nitrate accumulation at the regional scale, 57 mature kiwifruit orchards (orchard ages: 16±5 yrs.) in the study region were selected to collect soil samples (down to a depth of 5 m in 20 cm intervals) in fall of 2018, after harvesting the fruits. In addition, the soil profiles from 11 wheat–maize fields were also collected within 0–2 m from the surface (in 20 cm intervals) for comparison with those from the kiwifruit orchards (Fig. 1b). The boreholes were drilled from two sites in each cereal field and then mixed to form one composite sample of each depth. For the orchard, only one borehole was drilled in the middle of the two kiwi-vines rows of the orchards due to the laborious work. Considering the high rates of water permeability and nitrate leaching in the sandstone layers, the sampling depth was extended only to the depth at which the sandstone (>2 mm) layer appeared. The sandstone layer distribution was mapped based on the data of boreholes drilling (Fig. 2d). To estimate the status of nitrate accumulation in deeper soil depths (>5 m) further, another 12 soil profiles (down to 10 m from the surface in 20 cm intervals) were collected from kiwifruit orchards in the Yujiahe catchment (a small catchment in the study region) (Fig. 1b). To evaluate the impact of land use change on local groundwater quality, 31 shallow wells were sampled during the soil sampling (Fig. 1b and S1). The groundwater samples were filtered through 0.45 μm filters and stored in 4℃ until further analysis. The physical-chemical parameters of groundwater samples were presented in Table S1.

2.3 Sample analysis

Soil samples were extracted with 1 M KCl (soil:solution, 1:10) and shaken for 1 h, followed by filtration. The nitrate-N concentrations of the KCl extract and groundwater samples were determined by a continuous-flow N analyser (Bran and Luebbe AA3, Norderstedt, Germany). The water content of the soil samples was determined by oven-drying at 105 ℃. The values of pH, dissolved oxygen (DO) and electrical conductivity (EC) of groundwater samples were determined by a handled multi-parameters probe (YSI, USA).

2.4 Calculation method

The N surplus per unit area of soil in the two systems studied was calculated using the following equation:[13,27]

N surplus (kg N ha^{-1}) = inputs (inorganic fertiliser + manure + seeds + deposition + irrigation) – outputs (nitrogen removed by straw and grain or by fruits and pruning). (1)

The inputs of N from synthetic inorganic fertilisers and manure were calculated based on the N content and the application rate of each fertiliser. The annual input from atmospheric N deposition was 46.4 kg ha^{-1}, as determined by Liang et al.[28]. There was no N input from irrigation in the wheat–maize rotations because there was no irrigation. The N input to the kiwifruit orchards from irrigation in this region was 41 kg N ha^{-1}, as calculated by Lu et al.[13] based on the N concentration of the groundwater and the annual irrigation rates in the orchards. The annual N input to the cereal fields from the seeds was 4.4 kg N ha^{-1}, which was calculated by multiplying the N content of the seeds by the sowing rate. The N input from other surface vegetation in the orchards was not considered because farmers usually kept the surface clean to prevent other plants from competing for nutrients with kiwifruit vines, so the biomass of the vegetation was very low.

The outputs of N in the kiwifruit orchards consisted mainly of N removed by the fruit harvest, vine pruning in winter, and N stored in kiwifruit vines. The amount of N removed by kiwifruit harvest was calculated based on the N concentrations of dried kiwifruits, their water content, and the kiwifruit yields. The annual N stored in mature kiwifruit vines in this region was estimated as 37.1 kg N ha^{-1}, a value obtained from

Wang and Tong[29]. The N removed by pruned vines was calculated using the N concentration (dry weight) of the kiwifruit vines, the total branch weight, and the water content of pruned vines. The outputs of N by the wheat and maize harvest were calculated based on the N concentrations of the grains and straw and their biomasses. The N concentrations of kiwifruit, pruned vine, grain, and straw were obtained from Lu et al.[13]. The N losses from the residual straws of wheat and maize and the fallen leaves from the kiwifruit vines were not considered because the N was returned to the system.

The nitrogen use efficiency (NUE) was calculated according to the following equation:

$$NUE = N_{output\ by\ harvest} / N_{input} \ , \qquad (2)$$

The nitrate accumulation (kg N ha^{-1}) in soil was calculated using Eq. 3 :[30]

$$\text{Nitrate accumulation} = BD \times d \times Con_i / 10 \ , \qquad (3)$$

where *BD* is the soil bulk density (g cm^{-3}) of the different cropping systems, *d* is the soil sampling depth (cm), and *Con* is the nitrate content in the soil (mg N kg^{-1}) of crop *i*. The average *BD* values in the orchards and fields for soil depths of 0–20, 20–40, and 40–60 cm were 1.28, 1.37, and 1.38 g cm^{-3} and 1.37, 1.45, and 1.47 g cm^{-3}, respectively.[26] The *BD*s of the deep soil layers below 60 cm were considered to be the same as those of a depth of 40–60 cm because of small variations in deeper layers.[31]

The total N input in the entire kiwifruit belt of the study region was calculated using the following equation:

$$\text{Total N input} = N_{rate} \times S \ , \qquad (4)$$

where N_{rate} is the average input rate of N (kg N ha^{-1}) in the kiwifruit orchards, and S is the total area of kiwifruit orchard in the study region.

The total N surplus in the entire kiwifruit belt was calculated using the same method used for the total N input calculation.

The total soil nitrate storage in the entire kiwifruit belt above the sandstone layer and within 0–5 m was calculated as follows:

$$\text{Total nitrate storage}_{(0-5\ m)} = \sum_{i=1}^{n} N_{accumulationi} \times S_i \quad (5)$$
,

where $N_{accumulation}$ is the average of soil nitrate accumulation above the sandstone layer and within 0–5 m (kg N ha^{-1}) of cell i, S_i is the area of cultivated kiwifruit of cell i, and n is the total number of cells in the entire kiwifruit production area.

The total nitrate storage in the entire kiwifruit production area within 0–10 m was calculated as follows:

$$\text{Total nitrate storage}_{(0-10\ m)} = Total\ nitrate\ storage_{(0\text{-}5\ m)} + N_{accumulation} \times S \quad (6)$$

where $N_{accumulation}$ is the average value of soil nitrate accumulation within the 5–10 m soil profile (kg N ha^{-1}) and S is the total area of kiwifruit orchards distributed in areas with vadose zone thicknesses greater than 10 m.

2.5 Statistical analysis

The significance of differences in fertiliser inputs, mineral N concentrations, and N accumulation within the soil between the two cropping systems and the mineral N concentrations and accumulation in the soil at different locations were evaluated by analysis of variance using SAS 9.0, followed by the least significant difference test for comparing the mean values at the 1% and 5% levels.

3 Results and Discussion

3.1 N inputs and NUE in the kiwifruit orchards and wheat–maize fields

The mean annual N input in the kiwifruit orchards was 1332 kg N ha^{-1}, which was 2.7 times higher than that in the wheat–maize fields. The mean N application rate in the orchards from chemical fertiliser (961 kg N ha^{-1} yr^{-1}) was significantly higher than that of manure (281 kg N ha^{-1} yr^{-1}) (Fig. 3). The N fertiliser rates in the kiwifruit orchards were evaluated by the recommendation rates established by Lu et al.[32] Only 7.0% of the orchards surveyed received a rational input of chemical N fertiliser (375–500 kg N ha^{-1} yr^{-1}), whereas more than 82.8% of the orchards received an excessive input of N fertiliser (>500 kg N ha^{-1}) (Fig. S2). Only 9.5% of the total annual N input to kiwifruit orchards was used for growing fruits and vines, leading to a high N surplus of 1206 kg N ha^{-1}, which was significantly higher than that of wheat–maize fields (282 kg N ha^{-1}) (Fig. 3). It is consistent with other studies. For example, Bai et al.[33] found that the mean annual N surplus in newly built solar greenhouse vegetable production in the Loess Plateau was 1354 kg N ha^{-1}. The N inputs and outputs of the wheat–maize fields (n = 18) and kiwifruit orchards (n = 430) were plotted as suggested by the EU Nitrogen Expert Panel[34] (Fig. S3). More than 41% of the investigated wheat–maize fields had an NUE within the desirable range (50% to 90%). In contrast, the excessive N application led to low NUE in the orchards, with more than 92% having values below 20%.

3.2 Nitrate-N accumulation in orchards and fields

The nitrate contents in soils of the kiwifruit orchards (ranging from 35.8 to 75.8 mg N kg^{-1}) were significantly higher than those in cropland soils (ranging from 4.3 to 9.3 mg N kg^{-1}) (Fig. 4). The nitrate contents in the 0–5 m soil profiles of the orchards increased rapidly with soil depth. The peak of nitrate content in soil profiles (75.8 mg N kg^{-1}) was found in the 4.8–5.0 m layer; and the content was still as high as 45.2 mg N kg^{-1} at the depth of 10 m, indicating that nitrate was leached into deeper soils. The average nitrate accumulation values in the soil profiles of 0–1, 0–2, 0–5, and 0–10 m in the orchards were 594, 1230, 3674, and 7113 kg N ha^{-1}, which were significantly higher than the values in the same layers in the cropland ($p < 0.05$). It confirmed our first hypothesis, i.e., the LUCO resulted in high nitrate accumulation in the deeper soil profiles. Liu et al.[14] showed that the mean nitrate accumulation in 0–6 m soil profile in 25-year-old apple orchards in the Loess Plateau was 7250 kg N ha^{-1}. Compared to the studies at other regions,[15,21,35] nitrate accumulated in soil profiles of orchards in the Loess Plateau was very high. The main reason is that over-application of N is very common in our study region.[12,21]

The nitrate accumulation in the 1–2 m soil profiles of wheat–maize field was lower than 0-1 m. In contrast, for orchards, a high and increasing mass of nitrate was found at depths below 1 m. The different nitrate accumulation pattern in soil profiles of the two systems (cereal cropland and orchards) could be explained by the different irrigation rates. There was no irrigation for the cropland. However, a high flood irrigation rate, with an annual amount of 450 mm, was applied in the kiwifruit orchards.[26] Therefore, the excessive irrigation in the orchards increased nitrate leaching to deeper soils. In comparison with apple and peach trees in the study region, kiwifruit vines have a relatively shallow root system, with more than 90% of the root system at a soil depth of 0–60 cm.[36,37] It means that nitrate accumulated below 1 m will not be easily taken up by kiwifruit root. The depth of nitrate leaching in kiwi orchards was deeper than that in dryland apple orchards in the northern region of the Chinese Loess Plateau.[14] This difference is mainly attributable to the high precipitation and irrigation in the kiwifruit orchards in the study region. The intensive precipitation and irrigation increased nitrate leaching in kiwifruit orchards.[38,39]

Denitrification is generally considered to be the main process eliminating nitrate in the deep vadose zone. It usually depends on the availability of soil organic carbon and the oxygen concentration.[1,40-43] The denitrification in deep soil profiles at humid subtropical and tropical regions is strong due to high precipitation and high temperature.[44,45] Compared with the studies at subtropical and tropical regions,[15,35] weak denitrification was another reason for the high levels of nitrate stored in the vadose zone in our study region.

3.3 Total nitrate stock and spatial variation in the kiwifruit belt

The total annual N input to the kiwifruit belt was estimated as 75.7 Gg N, and the output by harvest and vine pruning was only 7.3 Gg N, leading to a large N surplus (68.3 Gg N) in the soil profiles. The total nitrate stocks within 0–1, 0–5, and 0–10 m were 30.5, 156.5, and 266.5 Gg N, which were 0.4, 2.1, and 3.5 times higher than the total annual N input, respectively. Substantial nitrate storage in the vadose zone has also been documented in other regions of the world.[3,19]

The nitrate accumulations above the sandstone layers within 0–5 m soil profiles in different zones of the kiwifruit belt ranged from 249 to 11415 kg N ha^{-1}. Nitrate accumulation within the 0–1 m soil profile ranged from 75 to 2492 kg N ha^{-1} and was significantly lower than the values within the 0–5 m soil profile, indicating that nitrate accumulated mainly at depths greater than 1 m (Fig. 5a). The spatial pattern of nitrate accumulation across this region showed a decrease from west to east. Lower nitrate accumulation was found in zones near the rivers. The nitrate accumulation in zones with a thick vadose zone were higher than those where the vadose zone was thin (Fig. 5b; Fig. 2b).

Our results showed a significant negative correlation between soil nitrate accumulation and the percentage of sand within the 0–1 m soil profile (Fig. S4). Soils with a high percentage of clay and silt retain more nitrate than soils without much clay and silt. Soil texture also affects the water percolation. Soils with high amounts of sand usually have high water percolation rates, which increase nitrate leaching when precipitation or irrigation occurs.[46-48] Donner et al.[49] found that the nitrate leaching rate in soils with a higher sand content was significantly higher than that in soils with a high percentage of clay. Kurunc et al.[22] revealed a positive relationship between the nitrate concentration of groundwater and the amount of sand in soil at the catchment scale. In our study region, the depth of sandstone layers was related to the thickness of the vadose zone (Fig. 2d). The depth that nitrate can accumulate increases with increasing thickness of the vadose zone. Thus, high nitrate leaching rates occurred in areas with a thin vadose zone and soils having a higher percentage of sand.

3.4 Nitrate concentrations in groundwater of the kiwifruit belt

The nitrate concentrations of groundwater in this region ranged from 46.2 to 210.0 mg L^{-1}, with a mean value of 120.1 mg L^{-1}. More than 97% of the groundwater samples had a nitrate concentration exceeding the permissible standard for drinking water established by the WHO (50 mg L^{-1})[50] (Fig. 5c). There was a significant negative correlation between the groundwater nitrate concentration and the thickness of the vadose zone. High groundwater nitrate concentrations occurred in areas with thin vadose zones (Fig. S5). The high dissolved oxygen (DO) concentrations of the groundwater ranged from 3.5 to 8.3 mg L^{-1} (Table S1), and were much higher than the appropriate limit (<2 mg L^{-1}) for the denitrification,[51,52] indicating that the denitrification processes in the groundwater of the study region is very weak.

The groundwater nitrate concentrations in most areas of the study region in the year 2001 were below 50 mg L^{-1}.[53] However, in 2018, with more than 97% of groundwater having concentrations exceeded 50 mg L^{-1} in this region (Fig. 5c), indicating the severe nitrate contamination of groundwater. This result confirmed our second hypothesis, i.e., the conversion from croplands to orchards significantly polluted the groundwater quality of the kiwifruit belt.

3.5 Environmental Implications

Our study highlights that there are huge nitrate storages in vadose zone of the intensive horticultural crop production system. If the root zone of kiwifruit vines is defined as being within the 0–1 m soil depth, we estimate that more than 89% (236.0 Gg N) of nitrate in 0-10 m vadose zone has been leached out of rooting zone, which is

3 times of the total annual N input to the kiwifruit belt. It not only wastes nutrient resources and farmers' money, but also results in a series of environmental problems. Therefore, measures to reduce the soil nitrate accumulation and its losses are required. Optimizing the N application rate to meet crop demand is a practical method for the intensive agricultural system. In comparison with the case of the farmers' conventional fertilisation (900 kg N ha^{-1}), our 3-year field experiments in this region showed that no reductions of yield or quality of kiwifruit occurred when the N fertilisation rate was reduced by 25% (675 kg N ha^{-1}) in 2012–2014 and by 45% (495 kg N ha^{-1}) in 2014–2015.[54] In addition, adopting fertigation is another effective way to decrease nitrate leaching.[55,56] Finally, educating farmers, writing legislation controlling N fertilisation, and strengthening the dissemination of scientific nutrient management strategies are also possible ways to reduce N loss and nitrate accumulation in vadose zone.

The nitrate in vadose zone may serve as an important temporary or permanent N pool.[4] The nitrate in the vadose zone may be moved upward to rooting zone as the movement of water from the deep soil profile, and acts as sources for crop uptake. However, few studies have explored the potential contribution of nitrate in the vadose zone to crop nutrition. Due to the complex to directly determine N loss in N_2 and N_2O forms from nitrification and denitrification, the difference method (the indirect method) is usually used to estimate N loss in N_2 and N_2O forms from these two processes.[18,57] Obviously, if the nitrate stock in the vadose zone is neglected, it will overestimate N_2 and N_2O losses from nitrification and denitrification. Therefore, the nitrate accumulation in the vadose zone should be included in nitrogen budgets at the different scales to close N cycle and improve agricultural managements.

The nitrate stocked in the deep soil could not be removed easily by denitrification because of the limited carbon source for microorganisms.[43] Therefore, the large storage of nitrate in the vadose zone could migrate largely to the groundwater and eventually pollute the groundwater. Growing evidence suggests that legacy nitrate continues to impair the groundwater quality due to the lag time for nitrate transfer from the vadose zone to groundwater.[6,9] The lag time is strongly controlled by the thickness of the vadose zone and soil properties. It takes decades for nitrate to move down and reach the groundwater in some areas with a thick vadose zone.[6] Thus, in areas with a thick vadose zone, such as the central part of the Loess Plateau (>100 m),[58] there may not be a problem of groundwater nitrate contamination for many years.[59] However, our study region is located at the south of the Loess Plateau; and most areas (70.4%) have relatively shallow vadose zones (<20 m). A significant negative correlation between groundwater nitrate concentration and thickness of vadose zone was confirmed (Fig. S5). Therefore, this region with a high nitrate accumulation in the vadose may face high risks of groundwater polluted by nitrate in the near future. Nitrate storage in the vadose zone has significant implication for environmental policy.[3] If the time lags of nitrate to aquifer is not considered, nitrate control policy may appear not to be working.

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Acknowledgements

The authors thank the National Key R&D Program of China (No. 2017YFD0200106), the National Natural Science Foundation of China (No. 41671295), Defra and Ministry of Agriculture China under the Sustainable Agriculture Innovation Network (SAIN), and the 111 Project (No. B12007) for financial support of this study. Jingbo Gao received the funds from the China Scholarship Council for a 1-year study at British Geological Survey, Keyworth, Nottingham NG12 5GG, UK.

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Supplementary material

Table S1. Physical-chemical parameters of groundwater samples of the study region

Well ID	Groundwater table depth (m）	pH	Dissolved oxygen concentration (DO) (mg/L)	EC (us/cm)	NO_3^- (mg/L)
1	5.0	7.43	7.04	710	124.27
2	8.4	6.87	8.31	790	128.78
3	7.0	7.05	7.50	540	127.87
4	20.2	8.14	7.71	860	134.83
5	22.0	7.69	7.95	880	85.28
6	15.7	7.25	7.35	990	128.62
7	9.8	7.57	7.68	960	125.81
8	9.6	7.1	7.05	1100	129.65
9	20.2	7.41	7.38	700	99.17
10	10.9	7.72	7.15	1200	132.08
11	8.0	7.63	6.47	990	140.16
12	8.3	7.64	7.59	1050	129.79
13	13.8	7.28	7.81	610	85.36
14	18.0	7.93	6.78	570	114.35
15	11.8	7.63	5.85	2150	141.01
16	5.6	7.46	8.33	1230	131.79
17	4.0	7.76	3.52	1240	131.62
18	14.0	7.71	7.88	690	85.4
19	6.5	7.46	6.45	800	67.11
20	7.8	7.87	7.36	1010	131.32
21	7.2	7.51	7.16	1230	127.57
22	9.0	7.60	4.92	1050	123.23
23	10.3	7.70	5.81	1170	136.76
24	15.9	7.33	6.3	1412	100.05
25	16.9	7.42	6.58	1169	97.05
26	17.3	7.5	6.50	1074	98.01
27	17.8	7.66	5.52	788	84.63
28	8.7	7.55	4.91	1014	130.74
29	23.1	7.65	6.43	724	46.16
30	7.4	7.11	7.33	2050	195.81
31	7.8	7.20	7.28	2100	210.00

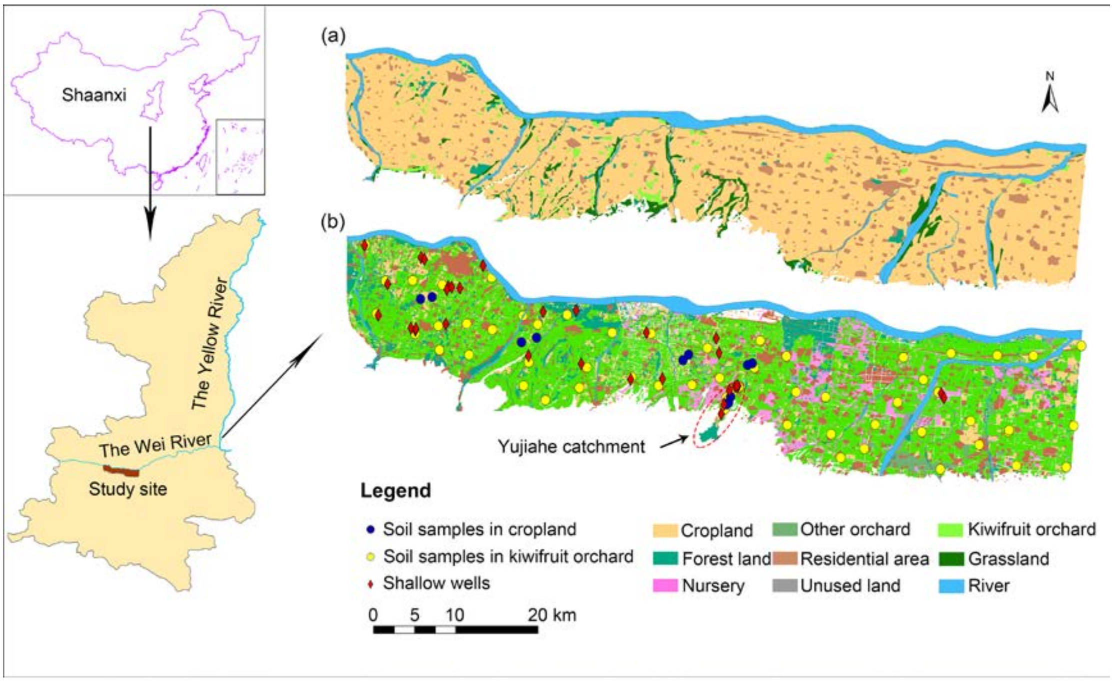

Figure 1. The location and land use status in 1985 (a) and 2018 (b), and sampling sites in the study region.

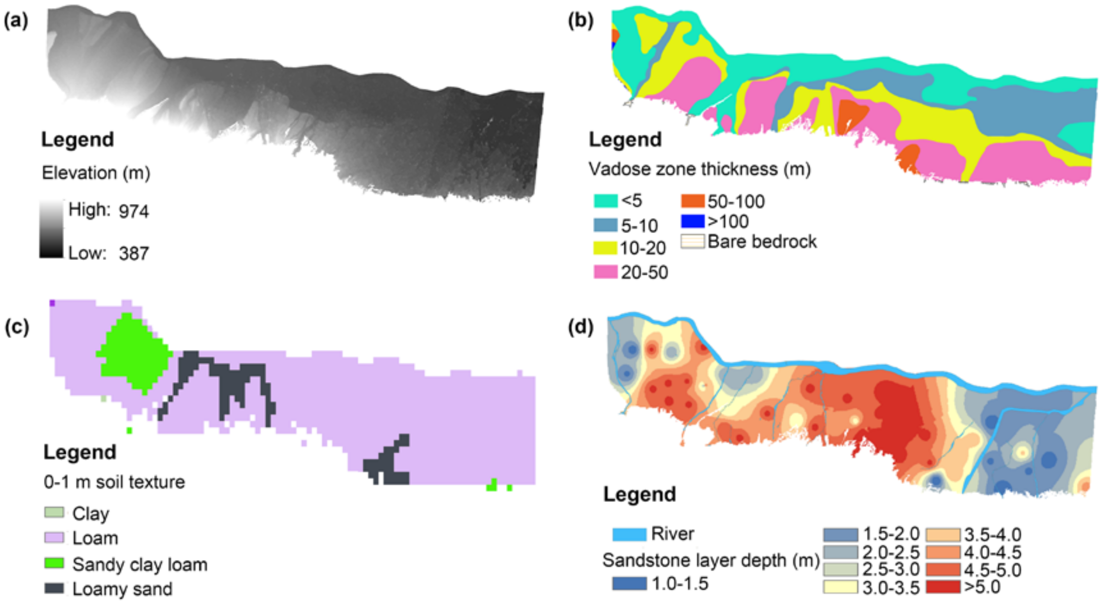

Figure 2. The digital elevation model (DEM) (a), vadose zone thickness (b), USDA soil texture classification (c) and sandstone layers distribution depth (d) of the study region.

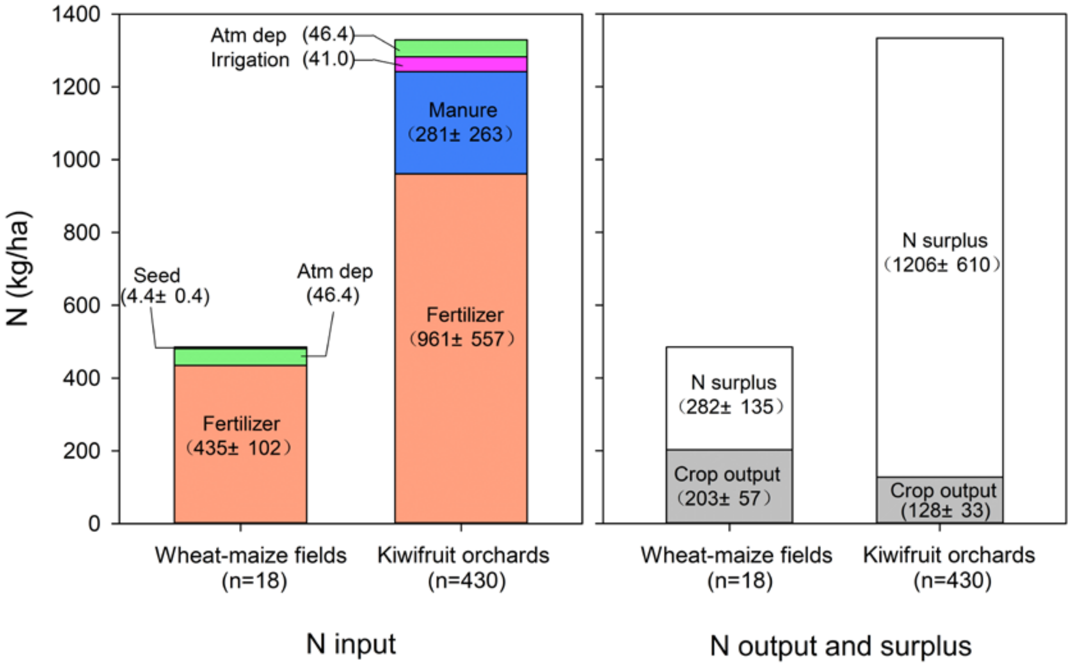

Figure 3. Annual N balance in kiwifruit orchards and wheat–maize fields (kg ha^{-1} yr^{-1}).

Note: Crop output from kiwifruit orchard referred to the removal of N by fruit harvest, pruning in winter and stored in kiwifruit vine. Crop output from wheat–maize fields referred to removal of N by aboveground harvest (grain and straw) of wheat and maize.

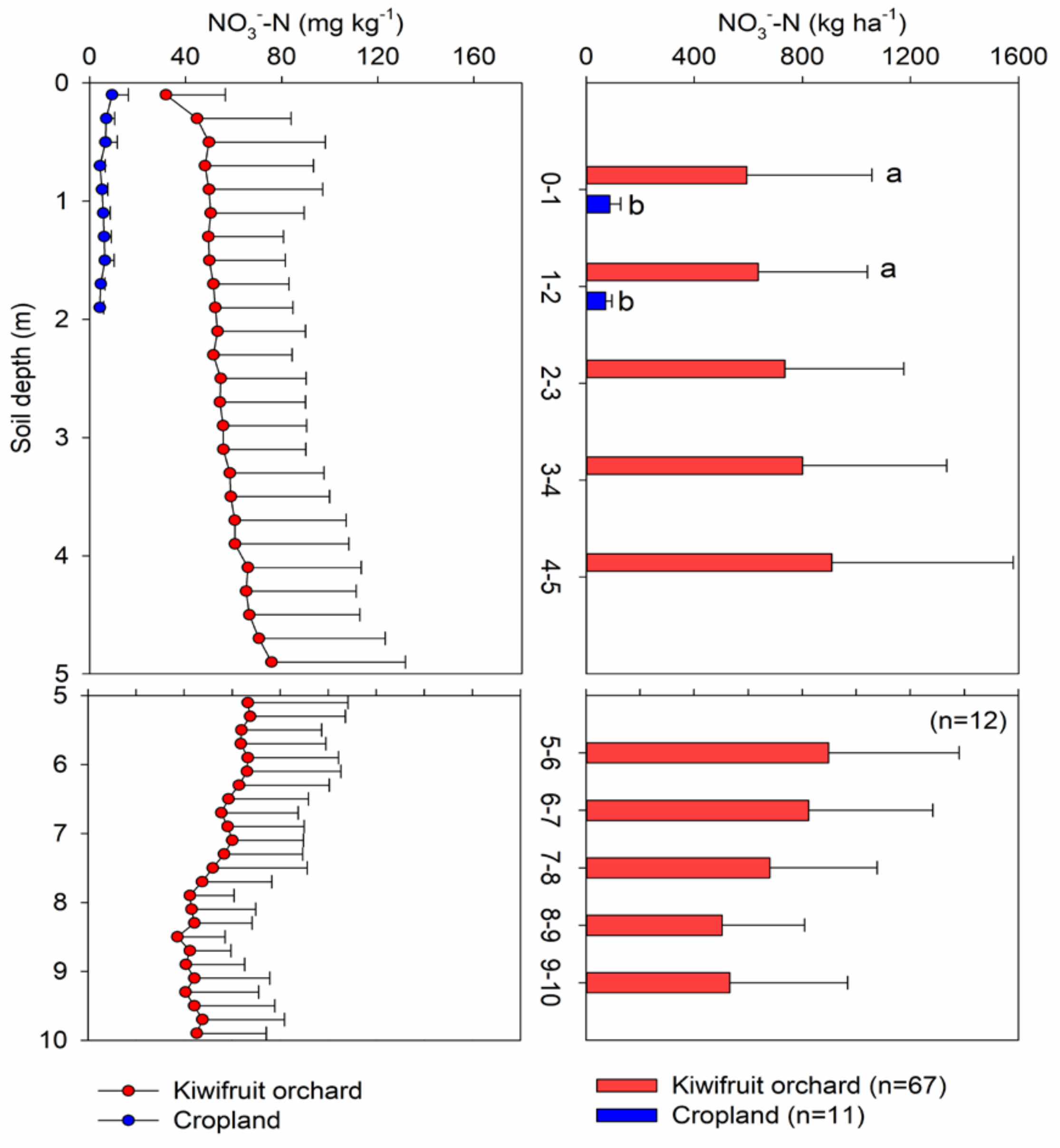

Figure 4. Nitrate-N (a) content and (b) accumulation in soil at a depth of 0–2 m (n=11) in wheat–maize fields and 0–5m (n=67) and 0–10 m (n=12) in kiwifruit orchards. Note: the numbers indicate the numbers of samples. Different lowercase letters in (b) indicate a significant difference of nitrate accumulation in the same soil depth between orchards and fields by analysis of variance and least significant difference test at $p < 0.05$. Error bars indicate the standard errors of nitrate content and accumulation.

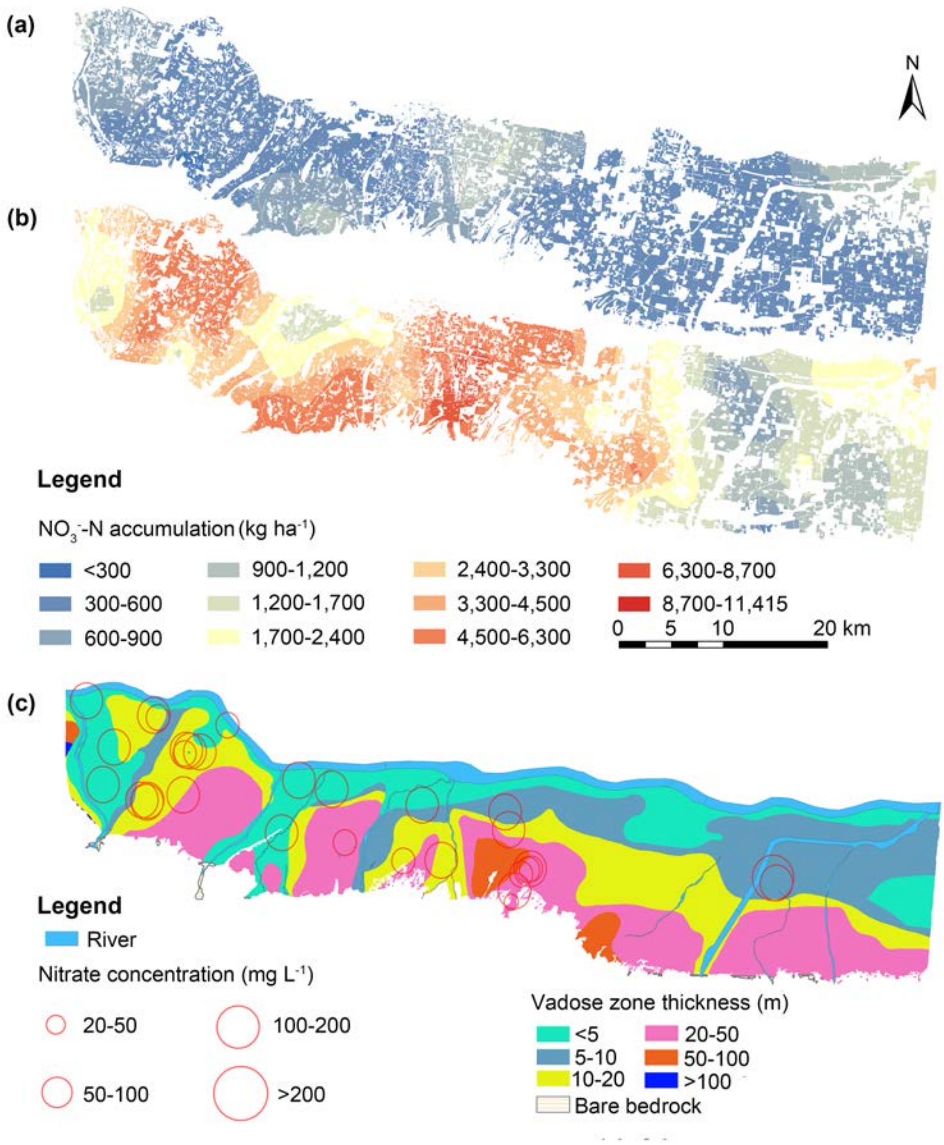

Figure 5. Spatial variation of nitrate accumulation above the sandstone layers within 0–1 m (a) and 0–5 m (b) soil profile in the entire kiwifruit belt.

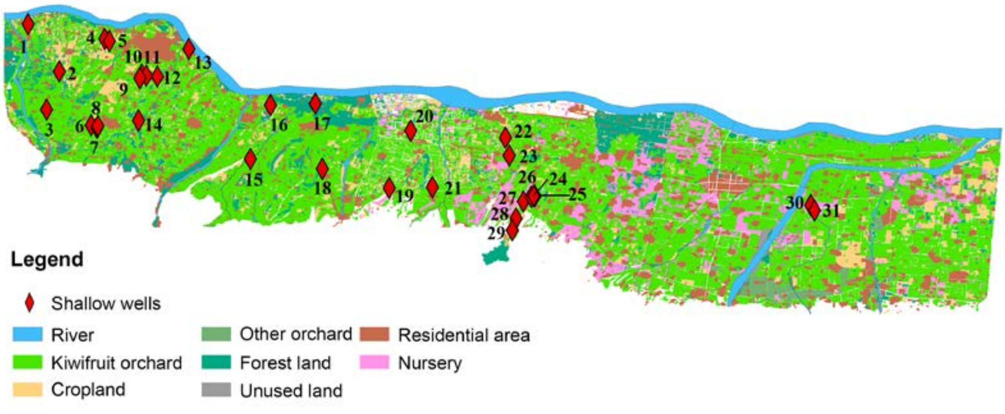

Figure S1. The sampling sites of shallow wells in the study region.

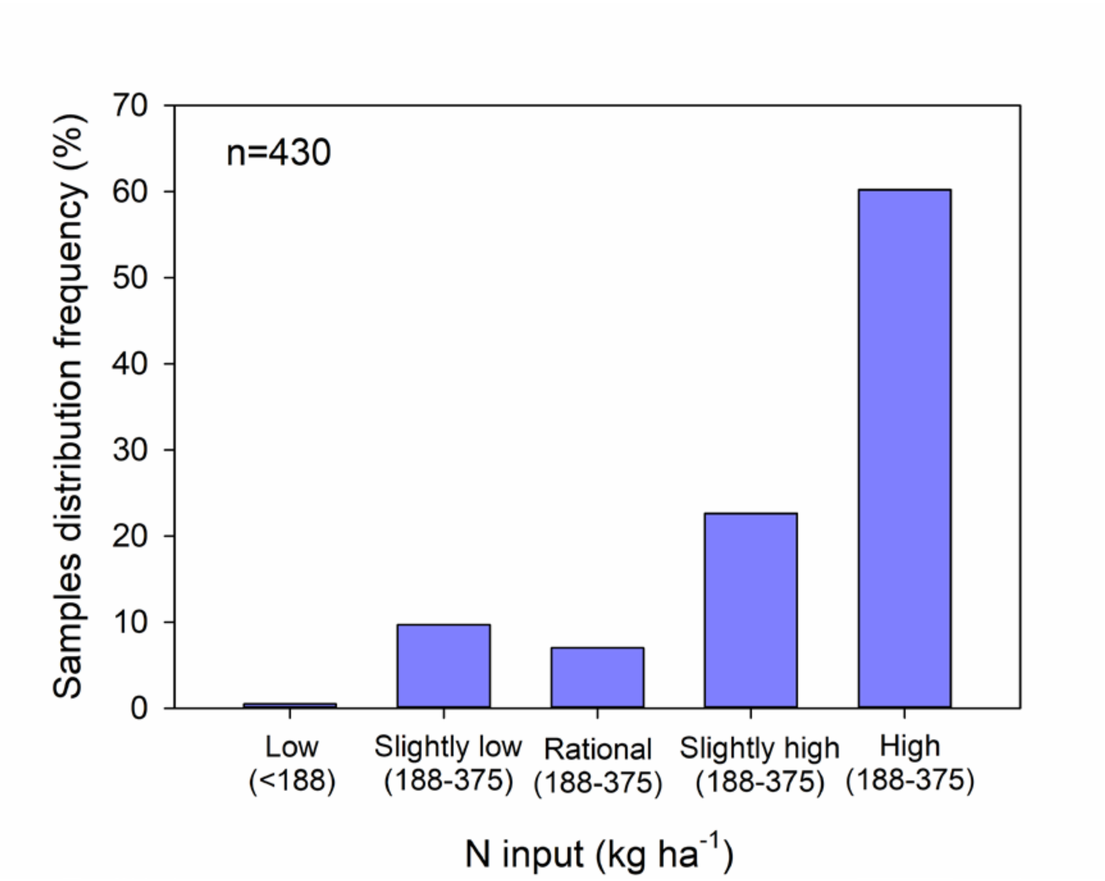

Figure S2. Status of chemical N fertiliser rates in kiwifruit orchards in the study region. Note: The classification standard is from Lu et al.[32], summarized based on a combination of a survey of 242 kiwifruit orchards and literatures in this region.

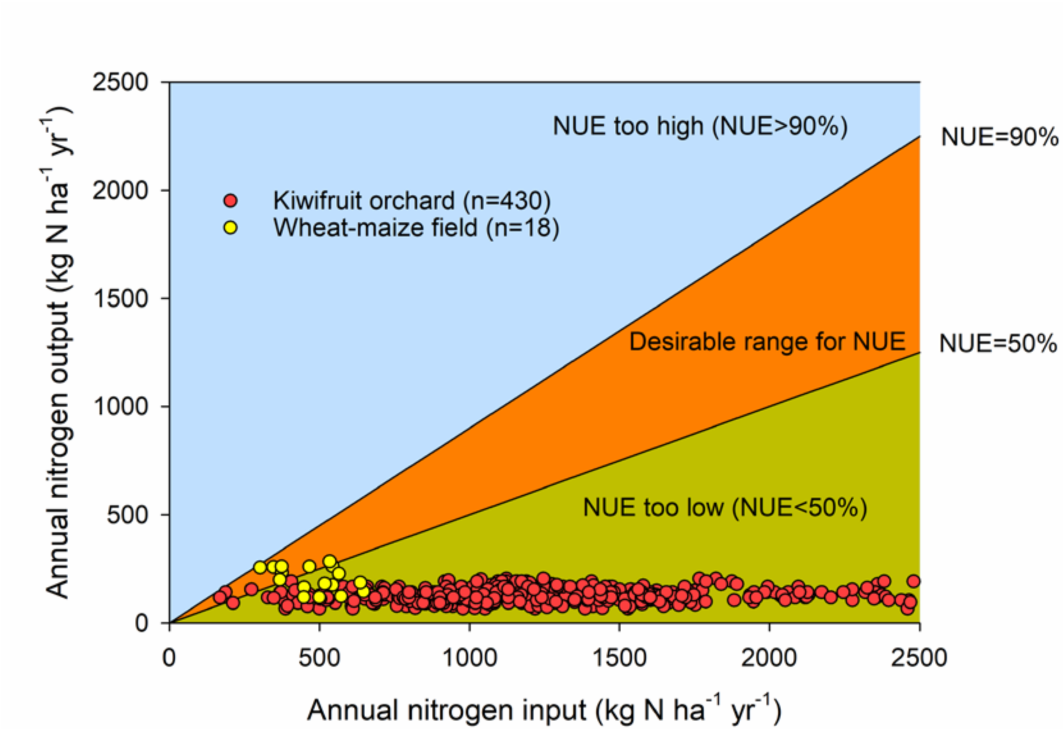

Figure S3. Comparison of Nitrogen use efficiency (NUE) in the kiwifruit orchards and wheat–maize fields. The ranges for NUE are divided according to the EU Nitrogen Expert Panel[34].

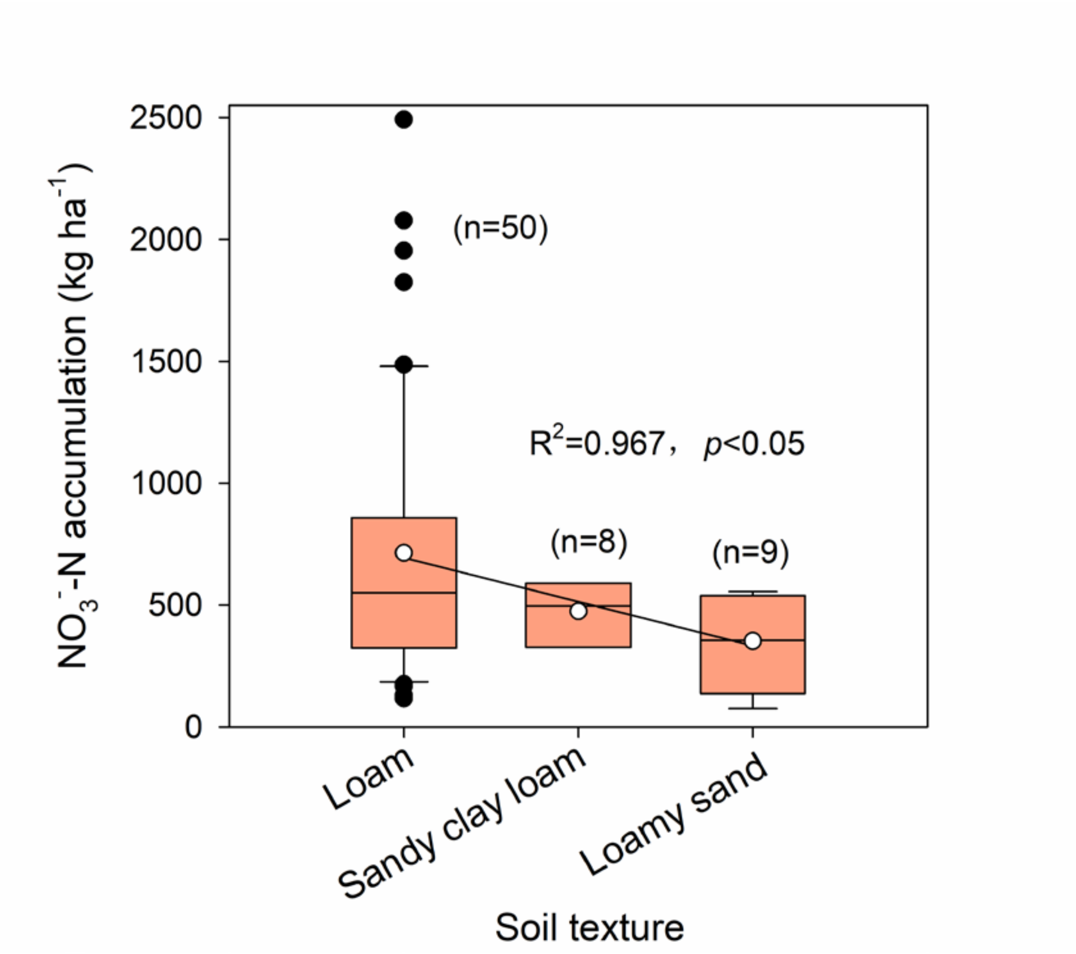

Figure S4. Box-whisker plot of NO_3^--N accumulation in 0–1 m from the soil surface with different soil texture. Note: The number shows the numbers of samples. The circle indicates the mean. The straight line indicates the correlation between soil texture and soil NO_3^--N accumulation.

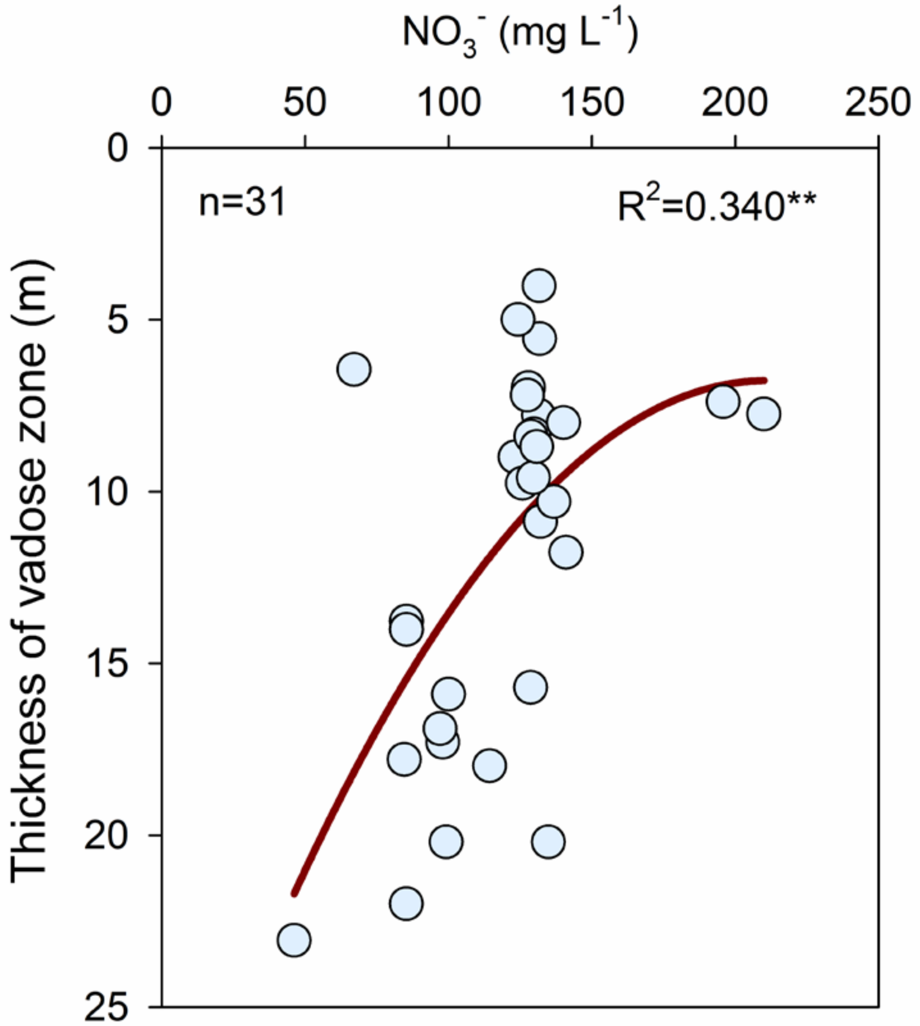

Figure S5. The correlation between the thickness of vadose zone and the groundwater nitrate concentrations.