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Modeling irrigation with nitrate contaminated groundwater

Sulamada nitratla kirlenmiş yeraltısuyu kullanımının modellenmesi

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Abstract

An alternative method to treat the nitrate-contaminated groundwater under the agricultural fields while providing economic benefit is called pump and fertilize. Pump and fertilize, while removing the nitrate in the groundwater, can reduce nitrate and pesticide requirement. However, up to date, there are no studies evaluating the effect of this application under different soil/climate conditions. In order to apply this technology in the field and to determine its effect, a feasibility study needs to be performed. Therefore, we constructed unsaturated zone groundwater models via HYDRUS 1D for one-hectare corn field in prevalent soils and under Eskişehir, Adana, Şanlıurfa, Düzce climates in Turkey. Our results indicated that even groundwater with 50 mg/L nitrate contamination could provide economic benefit to the agriculture especially where climates and soil types are similar to Şanlıurfa. In this climate using pump and fertilize technique saves 97 kg N/year in a 1-hectare farm. The technique was especially effective for fluvisol, vertisol soils as nitrate leaching are very low, and for cambisol soils since very high nitrogen use efficiency was seen for the climates present in Turkey. Our results indicated that in general the pump and treat efficiency is less effective in wet and cold climates, like in Düzce. As a general result of our study, we concluded that dry and warm climates with relatively permeable soils are more promising for the pump and fertilize application.

Keywords: Hypothetical model, Pump & Fertilize, Contaminated groundwater irrigation.

Öz

Tarım alanlarının altında bulunan nitratla kirlenmiş yeraltısuyunu temizlemenin ekonomik yarar amaçlı alternatif bir yolu pompala ve gübrele yöntemidir. Pompala ve gübrele yöntemi hem yeraltısuyunu kirlilikten arındırırken hem de nitrat, pestisit gibi gereksinimleri azaltabilir. Buna ragmen bugüne kadar bu prosesin değişik iklim ve toprak koşullarında ne düzeyde etkili olduğunu dair bir değerlendirme bulunmamaktadır. Bu tekniği arazide uygulayabilmek için öncesinde bir fizibilite çalışması gerekmektedir. Bu nedenle HYDRUS 1D ile doymamış bölgelerde 1 hektar mısır tarlasına karşılık gelecek yeraltısuyu modelleri yaparak Türkiye'de yaygın olan toprak tiplerinin hidrolojik özelliklerini derleyip Eskişehir, Adana, Şanlıurfa ve Düzce benzeri iklimlerde, pompala ve gübrele yöntemi için en çok gelecek vadeden koşulları bulduk. Çalışmamız bu teknolojinin Şanlıurfa benzeri çok daha kuru ve sıcak iklimlerde 50 mg/L nitrat değerinde bile oldukça karlı olduğunu ortaya koydu. Bu teknikle birlikte bu iklimde 1 hektar tarlada 97 kg N/yıl telafi edilebileceği görüldü. Aynı zamanda fluvisol ve vertisol toprak tiplerinde nitrat sızıntısı en düşükken, cambisol tipi topraklarda nitrojen kullanım verimi bütün iklimler için en yüksek düzeyde bulundu. Düzce gibi oldukça nemli ve soğuk iklimler için ise, bu yöntemin düşük azot kullanım verimleri ve yüksek nitrat sızıntıları nedeniyle uygun olmadığı görülmüştür. Sonuç olarak görece kuru iklimler ve geçirgen topraklar pompala ve gübrele yöntemi için uygun bulundu.

Anahtar kelimeler: Hipotetik modelleme, Pompala & Gübrele, Kirli yeraltı suyu ile sulama.

1 Introduction

Agricultural activities cause severe water pollution globally, including but not limited to United States (USA) [1] and in the majority of OECD countries [2]. Nutrients and pesticides are the main pollutants observed due to agricultural activities [1] and among nutrients mostly nitrogen (N) plays an important role. Even though nitrate (NO_3^-) pollution of groundwater may have resulted from improper wastewater treatment [3], sewage leackage [4] or septic waste leackage [5], the increasing rate of applied nitrogen (N) fertilizer is the major reason of the groundwater nitrate contamination [6],[7]. N fertilizer not only cause the groundwater contamination but also its production is energy intensive and has a significant environmental impact, it emits up to 575 megatons of carbon dioxide equivalent every year (~ 1% of total global emission) [8].

The remediation of nitrate-contaminated groundwater, on the other hand, usually focuses on transforming the excess NO_3^- into dinitrogen (N_2), neglecting its agricultural potential. Methods like bioagumentation of denitrifying bacteria or using abiotic methods are present to decontaminate the NO_3^- contaminated water/groundwater, and transform NO_3^- into N_2 [9]-[18]. Removal of NO_3^- through adsorption with granulated activated carbon [19], ion exchange resin IRN-78 [20], biological assimilation by cyanobacteria [21] and macrophytes [22] are other methods that could overcome the NO_3^- pollution in the contaminated groundwaters. Since NO_3^- can be an important N source for plants, this type of treatment discards a significant resource that could be used in an alternate way.

A treatment method which reduces NO_3^- concentration in groundwater by directly using it is the pump and fertilize [23]. It consists of pumping the NO_3^- contaminated groundwater and applying it as an irrigation water for agricultural purposes [23-27]. Combined with the full control fertigation and compensating fertilizer cost by already present NO_3^- in the water, pump and fertilize method has great potentials.

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If drip irrigation systems is used with pump and fertilize for row crops like corn, the waste NO_3^- in empty areas in farm would be reduced. This type of approach is relevant to Turkey since there are many reported areas with NO_3^- contaminated groundwater (Figure 1).

Up to date few studies have focused on pump and fertilize. A field calibrated modeling study reported more than 1-fold compensation of NO_3^- in fertilizer by nitrate in groundwater [24]. One study found no difference between side-dress fertilizer application and irrigating with contaminated water [25], another claimed that both pump and treat and side fertilization cleaned the contaminated groundwater while decreasing the fertilizer requirement [26]. Only one study that applied drip irrigation system stressed the relation of NO_3^- leaching and initial NO_3^- concentration. It showed the connection between the use of NO_3^- contaminated groundwater for irrigation and higher NO_3^- leaching [27]. In addition to these studies, the California Department of Food and Agriculture reported that in the field NO_3^- concentrations could be reduced in the groundwater when contaminated water is applied as a fertilizer without affecting the product yield [23]. The previous studies were strictly site-specific and only focused on one soil and climate type, however, there are many other climates and soils which might be much more suitable for this process.

To obtain the applicability of the pump and fertilize, experimental and field work is highly time consuming, costly and site-specific. Therefore, hypothetical models to find when this process is promising are essential. This study aims to

assess the conditions in which the pump and fertilize is promising in a hypothetical agricultural area via extracting various parameters from previous studies and open databases. Corn is selected to be farmed due to its high global demand and its high N requirement [28],[29]. Because there is a considerable amount of NO_3^- contaminated groundwater in its several regions, Turkey was selected to be a baseline for this study (see Figure 2 for the hypothetical pump and fertilize setting of this study).

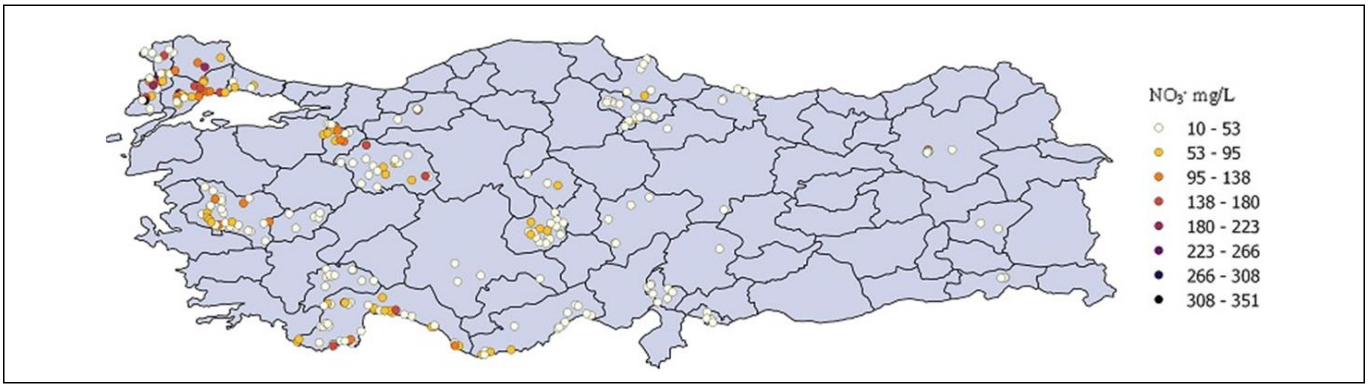

Figure 1. Groundwater nitrate contamination in Turkey (compiled from "Province, Environment, State Reports" of Ministry of Environment and Urbanization for 2016-2017 years, see Appendix A).

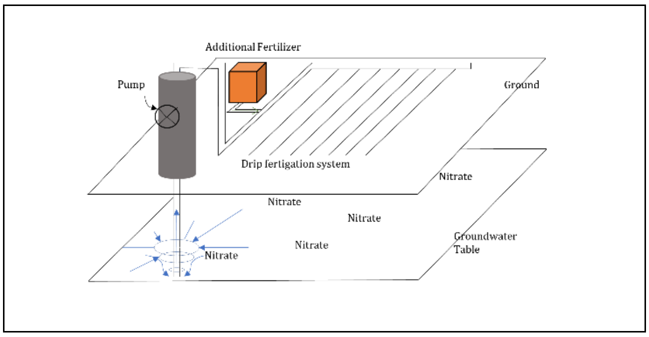

Figure 2. Depiction of hypothetical pump and fertilize system.

2 Material & Methods

Hypothetical unsaturated zone models were constructed from common soils and relevant climates in Turkey for corn production. Criwar 3.0 [30] was used to process climate parameters from Turkish State Meteorological Services' website (see Appendix B) and Rosetta Lite v1.1 was used to process soil texture information (2.1 Soil Parameters). With their output, HYDRUS 1D [31] unsaturated zone models were run, and nitrogen use efficiency (NUE), NO_3^- leaching, denitrification, and NO_3^- removal were calculated for 1 ha hypothetical corn field.

2.1 Soil parameters

Soil types are from Soil Atlas of Europe [32]. Its map indicates that calcisol, cambisol, fluvisol, kastanozem, leptosol, and vertisol are the major types of soil in Turkey. Among these types of soil, leptosol was not considered for agricultural purposes [33], therefore discarded from our study. Remaining soils texture properties were from literature [34]-[37]and presented in Table 1. After that, Rosetta Lite v 1.1, a built-in module in HYDRUS 1D, used these to generate saturated hydraulic conductivity and van Genuchten soil water retention curve parameters from its database through neural network prediction (Equation (1) for the retention function these parameters employed).

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\propto h)^n]^{1-1/n}} \tag{1}$$

"n" is the parameter related to pore-size distribution (>1). θ_s is saturated water content and $\theta_r$is residual water content, h is hydraulic head, and $\propto$ is an empirical constant. The results of this process are present in Table 2. Percentages of clay, silt and sand later were used to find out the soil texture of each type of example soil using texture triangle present in USDA Natural Resource Conservation Service's website [38], and this texture information was later used to have a dispersivity length for each soil.

Table 1. Soil texture data found in literature*[34] **[35]***[36]****[37].

Parameters	Calcisol*	Cambisol **	Fluvisol***	Kastanozem ****	Vertisol ****
Sand %	50	58	3	6.1	11.6
Clay %	30	2	38	44	28.2
Silt %	20	40	59	49.9	60.2

Table 2. Parameters generated via Rosetta v.1.1, saturated hydraulic conductivity (K), porosity(pore), empirical soil-water retention curve constant (n), specific yield and texture.

Parameters	K (m/d)	Pore	n	Specific Yield	Texture
Calcisol	0.0851	0.4018	1.3138	0.3278	Sandy clay loam
Cambisol	0.7114	0.4122	1.4314	0.3854	Sandy loam
Fluvisol	0.1124	0.4966	1.4564	0.3990	Silty clay loam
Kastanozem	0.1404	0.5020	1.3907	0.4009	Silty clay
Vertisol	0.1197	0.4596	1.5547	0.3762	Silty clay loam

Porosity is equal to saturated soil water content (θ_s) [39], and specific yield is calculated from θ_s- θ_r, in which θ_r is residual water content. Since all of our aquifers in this study are unconfined aquifers, specific storage was taken as equal to the specific yield [40]. α, an empirical constant in soil-water retention curve of van Genuchten model [41], in which the generated values were 0.0229, 0.0234, 0.0104, 0.0123, and 0.0068 for calcisol, cambisol, fluvisol, kastanozem, and vertisol, respectively. Dispersivity values were obtaines as the average of a reported dispersivity lengths [42] in the database of soils by textures. The values were 36.2, 11.64, 6.23, 40.9 and 6.23 cm for calcisol, cambisol, fluvisol, kastanozem and vertisol respectively.

2.2 Climates

According to a study on Köppen-Geiger climate classification in Turkey [43], five prevalent climates in Turkey were chosen; Eskişehir, Adana, Şanlıurfa, Düzce and Rize similar climates. These climates together contain more than 90 % of the corn production in Turkey. Crop evapotranspiration values and irrigation water requirements were calculated for all climates except Eastern Anatolian ones. Those climates were ignored as corn farming is very low in these places. Temperature, precipitation, sunshine duration parameters were from Turkish State Meteorological Services, the average value of 1981-2010, [44]-[48] (Table S-1-5 in Appendix B). Mean and maximum relative humidity and average wind speed values were taken from Meteoblue website simulation archive [49]-[53] (Table S-1-5). Criwar 3.0 employs the Penman-Monteith method to calculate crop irrigation water requirement, therefore, latitude/longitude and altitude were also required, which was entered according to the city centers in this study. Using the provided information Criwar estimates solar flux and water flux and finds reference evapotranspiration for certain period and location. Later, using the crop coefficient, the evapotranspiration of the crop of interest was found. The difference between evapotranspiration and precipitation was estimated as the irrigation requirement. All the mentioned parameters were presented in Table 3.

In this table, "Crop ET mm" values are the calculated plant water demand. In order to meet those requirements, irrigation water was assumed to be added based on Irrigation requirement m^3 on Table 3. However, for E climate (Rize), the required water was very low to expect a reasonable groundwater abstraction and subsequent removal of NO_3^-. As a result, E climate irrigation requirements were excluded from the models.

2.3 HYDRUS 1D models

In reality modeling soil exactly is very difficult due to heterogeneity. Even though the soil is not homogeneous in reality, homogenous soil parametes were assumed to be able to identify the capacity of selected soils. Constant soil parameters were chosen to be able to perform HYDRUS models.

Change of the water content, and thus water flow, in the unsaturated zone were defined by Richards Equation in 1 dimension (equation (2)),

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial z}\left[K\left(\frac{\partial h}{\partial z}+cos\alpha\right)\right]-S \qquad (2)$$

where θ is water content, t is time, z is the spatial dimension (here in vertical direction parallel with gravity), K is hydraulic conductivity, h is the hydraulic head, α is the angle of flow direction to gravity and S is the sink (or source) of water. Since K is also dependent on the head (or water content), the equation is analytically impossible to solve. Thus, numerical methods are used to evaluate water flow in the unsaturated zone. HYDRUS 1D is one of the most used software for this purpose. It models Richard equation in this one-dimensional flow, with finite element method in space and finite difference method in time (Crank-Nicholson scheme in this study).Area of the unsaturated models is 1 cm^2, and cell depth is 0.5 cm. The entire soil column was in 120 cm depth, corresponding to 240 equally sized finite element cells with the same soil hydraulic parameters. The upper boundary of the model was chosen as the atmospheric boundary, in which previously calculated irrigation/precipitation/transpiration values were entered to HYDRUS manually. . The lower boundary of the models was free drainage, indicating a groundwater table deeper than 10 meters, where no capillary fringe related effects are seen. As these were 1D models, lateral boundaries were indicated as no-flow boundaries. Modeling period was divided into two as precipitation only and irrigation/precipitation period. In first 4 months of the year, there was only precipitation, in the following 5 months from May to September, inclusive, irrigation and precipitation are applied from the upper boundary, and at the same time required amount of the fertilizer. Plant root water and solute uptake were also modeled in this period only, as it corresponds to sowing – harvest period of corn. Critical head for no-further evaporative loss from the given cell (hcritA) was calculated as described in HYDRUS 1D Application Help from climate variables. The iteration criteria window, choices related to increasing or decreasing time-step and internal interpolation tables were left in their default values.

Table 3. Monthly evapotranspiration(ET) and irrigation water outputs of Criwar 3.0 for selected cities, A (Eskişehir similar, Csb in Köppen-Geiger classification) [44],[49], B (Adana similar, Csa) [45],[50], C (Şanlıurfa similar, Bsh-Bsk) [46],[51], D (Düzce similar, Cfb) [47],[52] and E (Rize similar, Cfa) [48],[53]. Empty cells in irrigation requirement corresponds to no additional water requirement, i.e. precipitation is sufficient to meet the plant water demand.

Climate	Months	ET_0 mm	Crop Coefficient	Crop ET mm	Irrigation requirement m^3
A	May	143	0.41	58	290
	June	167	0.70	117	920
	July	210	1.06	223	2110
	August	182	1.04	190	1815
	Sep.	142	0.28	42	
B	May	175	0.41	71	430
	June	189	0.70	132	1170
	July	218	1.06	231	2220
	August	196	1.04	205	1980
	Sep.	157	0.28	46	
C	May	210	0.41	86	670
	June	284	0.70	199	1950
	July	317	1.06	336	3350
	August	254	1.04	265	2640
	Sep.	199	0.28	58	
D	May	121	0.41	47	150
	June	141	0.70	96	560
	July	158	1.06	158	1190
	August	127	1.04	127	930
	Sep.	114	0.28	30	120
E	May	96	0.41	37	
	June	117	0.70	78	
	July	112	1.06	112	150
	August	102	1.04	93	
	Sep.	84	0.28	24	

Plant water uptake was selected according to Feddes [54], and the Feddes parameters were from the database of HYDRUS 1D where the values are obtained from Wesseling's work [55].

The solute transport in HYDRUS 1D in our study took into account advection (1st term), dispersion(2nd term) and source/sink terms (3rd term) (equation (3)),

$$\int_{0}^{L} (-v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t})\, \varphi_n dx \qquad (3)$$

For NO$_3^-$ part, our hypothetical contaminated groundwater had 50 mg/L NO$_3^-$. This is the threshold value for groundwater contamination according to European Union's Nitrates Directive in 1991 and Groundwater Directive in 2006. The loss mechanisms are plant-uptake, denitrification, or NO$_3^-$ simply leaches. To the best of our knowledge, currently, there is neither any measured denitrification rate nor any kind of denitrifier bacteria sequenced and identified in Turkey. Thus, denitrification values were obtained from a study done in a corn/wheat agricultural field in another country (India), from corn rotation's denitrification rates in 0-30 cm region with 0.04 d- first-order decay constant, and remaining regions as 30-60 cm with 0.03 d-, 60-120 cm with 0.01 d- denitrification rates [56]. Since denitrifying bacteria are ubiquitous in the environment, it could be easily assumed that denitrification is a valid NO$_3^-$ loss route. Considering that plant NO$_3^-$ uptake is completely passive, 1 ha field's daily requirements were estimated as 12.4, 90, 62, 46.5, 30 kg N in May, June, July, August, and September months, respectively (approx. taken from [29]. In total, ~239 kg of N (or ~1058 kg of NO$_3^-$) is supplied to the 1 ha corn field in one year. These 1-hectare values were scaled down to 1 cm^2 for our models. The fertilizer requirement of corns was always higher than what was supplied by the 50 mg/L NO$_3^-$ containing groundwater, so the remaining amount was added. The exact NO$_3^-$ concentrations in irrigation water for each climate in different months are present in Appendix Table S-6, which was also the top boundary condition of the NO$_3^-$.

Obtained results were converted from mmol/cm (HYDRUS 1D default) to kg/ha values for the entire year. Nitrogen use efficiency (NUE %) was calculated as the ratio of plant NO$_3^-$ uptake to applied NO$_3^-$, in percentage. Leached NO$_3^-$ was the total bottom flux of NO$_3^-$ for the entire year, from 1 ha farm. Denitrification was the amount of NO$_3^-$ lost to denitrification bacteria under a 1 ha farm. "Uptake NO$_3^-$" was plant uptake of NO$_3^-$ through its lifetime. Finally, the net NO$_3^-$ removal was the amount of NO$_3^-$ abstracted with groundwater for irrigation before fertilizer addition (50 mg/L NO$_3^-$ concentration multiplied by the amount of water pumped) subtracted by leached NO$_3^-$ (Equation (4)).

$$\mathrm{NO_3^-}\ removal = 50\,\frac{\mathrm{mg}}{\mathrm{L}}\mathrm{NO_3^-} * \text{irrigation water} - \text{leach } \mathrm{NO_3^-} \qquad (4)$$

2.4 Assumptions

- Homogeneous distribution of the monthly rain throughout the entire month,
- Groundwater level is deeper than 10 meters,

- Constant hydrological properties in any direction,
- Different precipitation/ irrigation values for each month added as a top flux,
- Feddes uptake reduction model for plant water stress,
- For N fate and transport part,
- Plants in 1 ha need 239 kg of N through their lifetime,
- No Dry/Wet Deposition of N present,
- No temperature/pH effect and fluctuations on denitrification present,
- Plant NO_3^- uptake is passive,
- Plant is a type of corn which grow for 153 days from May 1 to September 30,
- No N generation from organic matter decomposition,
- No harmful elements such as heavy metals present in groundwater to effect the the environment or the corn growth,
- Pumped groundwater has an initial NO_3^- concentration of 50 mg/L before the addition of fertilizer (after fertilizer additions the resultant concentrations were given in Table S-6).

3 Results

The outputs of the models of 5 prevalent soil types of Turkey and 4 different climates are present in Table 4. The results indicated that fluvisol and vertisol are the type of soils with the lowest leaching which was related to their low hydraulic conductivities and relatively high porosities. Similarly, calcisol and cambisol type of soils had the highest leaching rates.

The leaching results were highly correlated with the climate type. Since each climate has its own characteristics, the detailed explanation of the results were discussed climate-by-climate for the following 4 chapters, in which especially NO_3^- leaching values were stressed. The reason for elaborating leaching is that it returns the NO_3^- contamination back to the groundwater, i.e. reduces groundwater NO_3^- removal.

3.1 Nitrate leaching in climate A

In climate A models, the highest values of leaching were in the order of 0.1 % of applied NO_3^- (~1058 kg) (Figure 3). Other than plant uptake, major losses of different cases were because of denitrification, as there is a fixed value for NO_3^- loss through this pathway and these soils have comparatively low saturated hydraulic conductivities (between 0.0851 and 0.7114 m/d and mostly 0.1 m/d, compared to the 7.12 m/d in sandy soils). Saturated hydraulic conductivities result in low bottom fluxes in all climates, yet the fluxes were also affected by plant uptake.

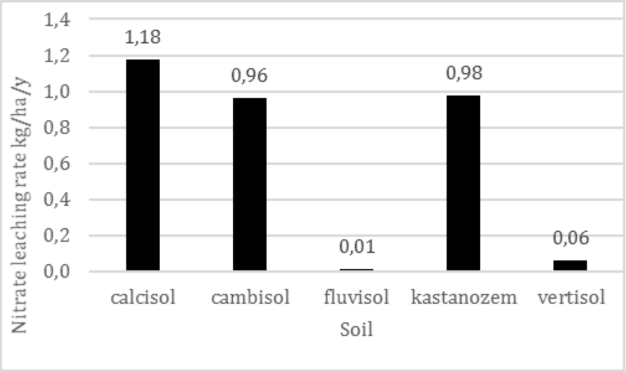

Figure 3. Amount of nitrate leached after the application of 1058 kg of nitrate in A climate models (kg/ha/y).

In terms of leaching, fluvisol and vertisol performed good, though they had high porosity and consequently high denitrification (Table 4). Cambisol (sandy loam) had very high hydraulic conductivity and relatively small porosity, which led to highest nitrogen use efficiency (NUE 48.3 %), and lowest denitrification loss. This is a reasonable number as in three reported cases for corn, for instance, plant uptake accounted for 32.4 %, 45.5 % and 35.7 % of applied N, and in general NO_3^- containing fertilizer resulted in higher plant uptakes, such as 45.5 % above was ammonium nitrate) [57].

Table 4. Nitrogen use efficiency (NUE), Nitrate (NO_3^-) leaching, NO_3^- denitrification, plant NO_3^- uptake and NO_3^- removal from the groundwater beneathfarms for 4 climates and 5 soils in Turkey.

Soil	Climate	NUE %	Leach NO_3^- kg/ha/y	Denit NO_3^- kg/ha/y	Uptake NO_3^- kg/ha/y	NO_3^- removal kg/ha/y
calcisol	A	38.9	1.18	638.4	414.3	255.6
cambisol	A	48.3	0.96	540.4	514.1	255.8
fluvisol	A	37.4	0.01	659.7	397.9	256.7
kastanozem	A	35.7	0.98	671.7	380.5	255.8
vertisol	A	40.9	0.06	622.0	434.9	256.7
calcisol	B	40.3	7.38	619.9	429.3	282.6
cambisol	B	49.7	8.37	521.4	528.9	281.6
fluvisol	B	38.8	1.39	641.9	413.3	288.6
kastanozem	B	37.1	5.61	654.7	394.6	284.4
vertisol	B	42.3	2.43	603.9	450.2	287.6
calcisol	C	48.0	1.11	543.3	511.0	429.4
cambisol	C	57.2	1.06	446.6	609.3	429.4
fluvisol	C	46.2	0.03	565.5	492.1	430.5
kastanozem	C	44.6	0.90	578.5	475.0	429.6
vertisol	C	49.7	0.12	527.6	529.5	430.4
calcisol	D	30.9	25.00	701.0	328.8	122.5
cambisol	D	39.4	28.01	611.3	419.1	119.5
fluvisol	D	29.9	6.28	728.9	318.4	141.2
kastanozem	D	28.0	19.55	735.1	298.2	128.0
vertisol	D	32.9	10.05	693.8	350.3	137.4

3.2 Nitrate leaching in climate B

Total transpiration in A and B were 63.19 and 68.72 cm (Table 3), respectively. This type of climate results in more NUE in B climates, therefore applied irrigation water in B climate is much more (total of 5800 m^3 compared to the 5135 m^3 of A climate (Table 3)). This leads to more pronounced leaching, albeit still very low compared to the applied NO_3^- (Figure 4).

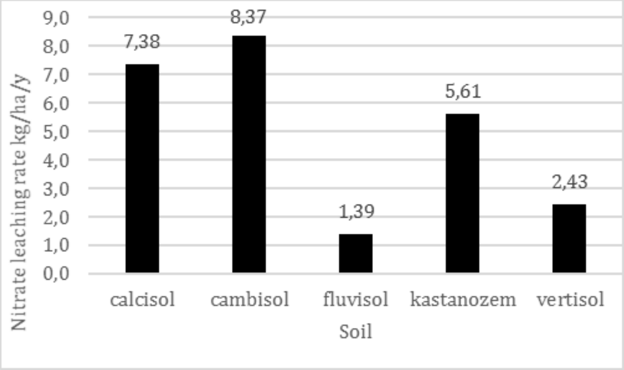

Figure 4. Amount of nitrate leached after the application of 1058 kg of nitrate in B climate models (kg/ha/y).

3.3 Nitrate leaching in climate C

Climate C was the dryest climate in our models, requiring ~8610 m^3 of irrigation water in total, and plant transpiration is 94.91 cm (Table 3), very promising in catching NO_3^- in percolating water, and that was also what predicted by our models (Table 4). Since plants took much more NO_3^- and in general NO_3^- concentrations in applied water was low even though the same amount of fertilizer was applied with much more water. In this climate denitrification was in lowest, in turn resulted in highest NUE.

The N leaching profile was very similar to that of climate A (Figure 5). There were slight differences yet very negligible compared to its benefits in both removing NO_3^- and having more plant uptake.

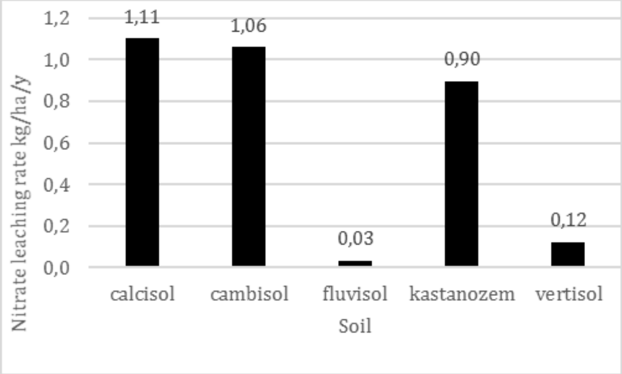

Figure 5. Amount of nitrate leached after the application of 1058 kg of nitrate in C climate models (kg/ha/y).

3.4 Nitrate leaching in Climate D

This was the wettest climate in our models, and required much less irrigation water (2950 m^3) and consequently higher NO_3^- concentration in applied irrigation water (Table 3). This partly resulted in more denitrification (~70 % of applied NO_3^-) and N leaching (in the order of 1-2 % of applied NO_3^-) (Figure 5). The reason for this poor performance is that climate D was also the coldest climate, corresponding to less evaporative demand and lower transpiration (46.15 cm in total), and thus, plants did not catch the NO_3^- in water efficiently (~30% NUE).

This illustrates the fact that pump & fertilize application was less promising in wetter climates both in terms of removal efficiency of NO_3^- and plant uptake. Not only less amount of water was abstracted from groundwater, but also N leaching was more severe (Figure 6).

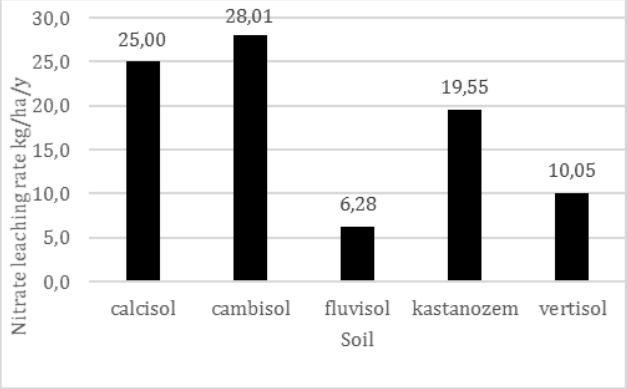

Figure 6. Amount of nitrate leached after the application of 1058 kg of nitrate in D climate models (kg/ha/y)

3.5 Nitrate leaching in zero-denitrification models

From the study we cited for denitrification first order rates [56], very high denitrification values were observed. Yet, oxygen is expected to be present in top 120 cm soil and it inhibits the denitrification; thus, additional models of every soils and climate without any denitrification rate were also conducted. The remaining parameters were same with same soils and climates, respectively. The results of the zero-denitrification models are presented in Table 5.

Since denitrification was modeled as the first-order degradation, removing it did not change the rankings of the previous models in terms of NO_3^- uptake and Leach NO_3^-, as well as rate of NO_3^- removal, i.e. same explanations hold for the more realistic zero-denitrification case. Nevertheless, there were some serious implications in NO_3^- removal rates (kg/ha/y). Again, the leaching rates had the same rankings (Figure 7), but in this case, especially in Düzce similar climates, excluding fluvisol, there was actually no remediation at all (negative values indicates an increase in the NO_3^- budget of this study's hypothetical groundwater). Thus, pump and fertilize process in these conditions could not remove the NO_3- from groundwater.

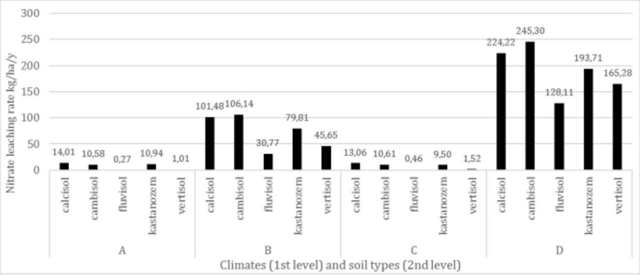

Figure 7. Nitrate leaching (kg/ha/year) values for models with zero-denitrification in all climates and soils.

Table 5. Nitrogen use efficiency (NUE), Nitrate (NO_3^-) leaching, plant NO_3^- uptake and NO_3^- removal in zero NO_3^- denitrification models from the groundwater beneath farms for 4 climates and 5 soils in Turkey.

Soil	Climate	NUE %	Leach NO_3^- kg/ha/y	Uptake NO_3^- kg/ha/y	NO_3^- removal kg/ha/y
calcisol	A	67.7	14.01	720.3	242.7
cambisol	A	76.0	10.58	809.4	246.2
fluvisol	A	66.6	0.27	709.3	256.5
kastanozem	A	64.1	10.94	682.9	245.8
vertisol	A	69.8	1.01	742.6	255.7
calcisol	B	68.9	101.48	733.4	188.5
cambisol	B	77.0	106.14	820.2	183.9
fluvisol	B	67.9	30.77	723.2	259.2
kastanozem	B	65.4	79.81	696.4	210.2
vertisol	B	71.0	45.65	755.5	244.4
calcisol	C	74.7	13.06	795.0	417.4
cambisol	C	81.4	10.61	866.6	419.9
fluvisol	C	73.4	0.46	781.4	430.0
kastanozem	C	71.7	9.50	762.8	421.0
vertisol	C	75.9	1.52	808.3	429.0
calcisol	D	56.6	224.22	602.8	-76.7
cambisol	D	66.2	245.30	704.9	-97.8
fluvisol	D	56.7	128.11	603.3	19.4
kastanozem	D	52.9	193.71	563.1	-46.2
vertisol	D	60.0	165.28	638.8	-17.8

With these high-denitrification and zero-denitrification models, one can see the two margins of the denitrification effect. In the case of higher denitrification, nutrient losses were higher, and NUE values were lower, but leaching was insignificant. This fact allows high NO_3^- leaching soils still be suitable for the pump and fertilize. On the other hand, when there is negligible denitrification the utilization of the fertilizer NO_3^- and leaching are much higher. This renders high leaching soils unsuitable for the pump and fertilize application. Moreover, for A and C climates, high leaching soils are calcisol, cambisol, and kastanozem; for B and D climates they are cambisol, calcisol, and kastanozem respectively (Figure 7). Overall results clearly indicate that the climate determines which soil is more vulnerable in terms of NO_3^- leaching.

4 Discussion

NO_3^- in the irrigation water can be utilized by crops same as fertilizer NO_3^- [58], and also 1 g of NO_3^- in water can correspond to more than 1 gram of NO_3^- in conventional fertilizer in some cases [23]. However, the studies were specific to their location[24]-[26], which renders impossible to comment on the promise it has in other areas. Moreover, their focus was on increasing the corn or other plants yield, rather than decreasing the amount of the NO_3^- present in the groundwater. This study provides a general understanding of the potential of the pump and fertilize in Turkey, as well as its ability to remove the NO_3^- in groundwater under different soils and climates. Excluding the Black Sea and Eastern Anatolian regions, many parts of Turkey are promising for pump and fertilize, and as seen in Figure 1, there is a significant number of regions where the groundwater has NO_3^- concentration more than 50 mg/L. One risk is that NO_3^- fertigation both reduces the air in the soil pores and supply dissolved NO_3^- continuously, two requirements for denitrification [57]. However, another requirement is organic matter, and it is quite low in the soils of Turkey, especially after the exclusion of Black Sea region[59]. Additionally, dissolved oxygen existence limits denitrification as bacteria utilizes oxygen preferentially over NO_3^-. For these reasons, pump and fertilize process will likely to result in high NUE values in Turkey, while decontaminating the groundwater.

NUE values in this study (29-57% with denitrification and 52-81% in zero-denitrification models) are reasonable as there are reported cases for corn in literature with similar percentages (32.4-45.5%, [57]; 9.2-57.8% [60]; 43-57 %[61], up to 76.97 % [62]). The comparison of NUE in different soils, of course, changes according to leaching and denitrification. In a research related to corn and fertilizer application in Canada [63], four different textures as clay, loam and 2 different sandy soils, were studied, NUEs were inversely proportional with hydraulic conductivity, indicating a more dominant effect of leaching. Loam had comparatively low NUE even though it had similar hydraulic conductivity with clay, yet its porosity was low and organic matter content was significantly higher than others, possible extra loss by denitrification. In another study [64], sandy clay loam soil had lower denitrification compared to clay dominated imperfectly drained soil, indicating possible oxygen deficient points, also clay soil had twice as much of organic carbon as sandy clay loam had. In short, with lower denitrification values, NUE was higher in less leaching soils, and in higher denitrification values, denitrification also becomes a decisive factor on NUE.

Denitrification values, on the other hand, might be inflated in our models with denitrification. Turkey generally has low organic carbon-containing soils, <2%, and the lower the organic content of the soil, the lower the denitrification[65],[66], since organic matter is the major electron donating source for denitrification process. Thus, models of zero- denitrification condition were also considered (Figure 7). In zero-denitrification models, the rate of leaching was in the same order with that of other models with denitrification. After the pump and fertilize some part of the NO_3^- was also left in the soil profile, which would be expected to leach in winter periods. In other words, when zero-denitrification is the case, the order of the pump and fertilize efficiency/suitability will switch to cambisol > vertisol > calcisol ~fluvisol > kastanozem, which correlates to the magnitude of their NUE values for all climates. In this case, the weight of NUE on deciding the feasibility will strongly depend on the predicted application rate of nitrate-laden groundwater as irrigation water.

As all these parameters related to each other, the real case for denitrification will surely change the leached amount of NO_3^-, that's why there are both high and zero-denitrification models in this study to be able to predict both scenario's impact. Even though drip fertigation system usually lowers the NO_3^- leaching [67],[68], the real world examples are expected to have higher NO_3^- leaching values. If leaching NO_3^- in these soils is larger that would improve the significance and the feasibility of pump and fertilize (Figure 7).

There are water flow related and solute transport related assumptions in our study. Among water flow, there is "homogeneous distribution of monthly rain to the entire month". Our models have 5 stress periods for each month, from May to September. Working with daily precipitation values instead of monthly averaging the total monthly precipitation would result in high computational load and also the daily data were not available. The realistic case, in which rain is intermittent, more plant stress will be observed due to temporary too dry and too wet conditions, which will reduce NUEs and increase other loses. Those type of isses could be adjusted through drip irrigation systems [69]. However, especially in dry climates, the precipitation is considerably low in the growing period of corn (Table S-3), in other words, this assumption is less critical in dry climates. Modeling with daily climatic data would lead to the enlargement of the difference between dry and wet climates, and still favor the pump and fertilize in dryer climates.

Another assumption the study considers is homogeneous and isotropic soil media. Field conditions will never be in this ideal state. Indeed, even the soil in one m^2 area has quite distinct features from each other [70]. However, the study assessed among 5 soils studied, which one(s) are more amenable to commence more detailed study, including field works. A fairly reasonable and extremely common assumption of 1-D vertical flow in the unsaturated zone makes the model area unimportant, i.e. 1 ha will still give the same result from what is taken from 1 cm^2 and then extrapolated to 1 ha later. Another important issue is that the aim of the study is finding the performance of each soil type under the pump and fertilize. In other words, there is no 1 hectare of homogeneous calcisol, cambisol, fluvisol, kastanozem or vertisol in Şanlıurfa city for instance. Nevertheless, the majority of the agricultural soils in Turkey composed of these types (Harmonized World Soil Database [71]). According to the results Şanlıurfa similar climate is the most promising climate for the pump and fertilize and fluvisol (lowest leaching), cambisol (highest NUE), and vertisol (good leaching and NUE values) soils are expected to perform better under this condition. When the field's soil has similar properties to these soils under Şanlıurfa similar climate, the process will be beneficial.

The last water flow related assumption is that corn behaves under water-stressed conditions as defined in Feddes uptake reduction model. There is a database related to corn [54] for Feddes parameters, that's why it was chosen to model different cases of climate/soil to assess semi-quantitatively the models more promising for pump and fertilize.

The explanations for NO_3^- related assumptions are following. Firstly, plants in 1 ha are assumed to need 239 kg of N through its lifetime. From the report of Nitrogen Management Guide [29], approximately this amount of N was required from the N flux of field corn graph. Different types, hybrids of corn might have slightly different requirements of N, and even different NUE [72], but this will not alter our results, as the crop is the same for all models. This is also the optimum N fertilizer rate in a contemporary study with drip fertigation system and corn field [73]. Thus, we can assume that it is still valid. This 239 kg corresponds to 1058 kg NO_3^-, the NO_3^- application in our models.

Besides, no dry/wet deposition of NO_3^-, assumed to take place. Dry deposition is a considerable input of nitrogen to the soil in some cases [74]. Also, they are comparable to the wet deposition levels, such as in [75] ratio of the dry and wet deposition flux of NO_3^- and NH_4^+ in Ankara were 0.8 and 0.9, respectively. In Turkey, comprehensive data are absent and known numbers are low [76]. Thus, the presence of dry deposition flux would not change the results considerably and neglected.

Temperature/pH effect and fluctuations on denitrification were ignored. Higher temperature may result in more denitrification than in the colder groundwater, but in field conditions, it was stated that [57], compared to the dissolved oxygen, organic matter and NO_3^- concentration the effects of the changes in T and pH is not worth considering, as in general similar conditions of T and pH should be arranged for many crops.

The plant is a type of corn which grows for 153 days from May 1 to September 30, there are actually, hybrids which grow in 120 days, yet as explained, while getting data from [29], 153 days was the most suitable approach. Plant NO_3^- uptake is considered completely passive. Since it is usually modeled as a non-sorbing chemical species, ion exchange of plant root and soil mineral/organic matters, and consequently active uptake, are not possible [56],[77],[78]. No N generation from organic matter decomposition is considered. This is a crucial parameter in case heavy application of manure/biosolids/compost or other organic-rich materials take place. However, Turkey's soils are in majority contains less than 2% of organic matter, and N supply of its own decomposition is low. Last, no harmful elements to the environment or livings, such as heavy metals, are assumed to be present in groundwater. There are, many pre-treatment options to solve this problem for VOC [79], for heavy metals [80]. There might be problems coming from other ions in the groundwater, rendering them inappropriate for irrigation purposes, such as high sodium ion content. This might limit the feasible choices for the pump and fertilize. Yet for instance in the case of Şanlıurfa city, from the Kahraman's thesis done in 2015 [81], most of the NO_3^- contaminated water in the Harran Basin aquifer was found to be suitable for irrigation. This supports the potential of this study's most feasible place for the pump and fertilize: the Şanlıurfa climate.

5 Conclusion

Current literature is lacking modeling studies about pump-and-fertilize applications, albeit there are many studies on NO3- leaching under corn agriculture. Not only agricultural management practices but also groundwater remediation topics are very complex in their nature. Therefore, in order to select the most promising and significant case for pump and fertilize, there should first be a hypothetical study in which the effects of the main variables were found out. With this study, we were able to assess the promising soil and climates in Turkey for pump and fertilize application under significant denitrification, around 60 % of applied NO3- (Table 4) and under zero-denitrification (Table 5). Moreover, when denitrification is negligible, major loss NO3- is leaching and we also compared the soils and climates of Turkey in that situation, as well (Figure 6). This study illustrates the impacts of different soil and climate types in Turkey on pump and fertilize treatment. According to the results, high irrigation water requiring regions with soils having low leaching property, fluvisol, vertisol are promising areas for pump and fertilize application, cambisol may also be considered if the nitrogen use efficiency weighs more. Table 6 shows how much fertilizer was reclaimed in each type of climate of our study for 1 hectare of a cornfield in 1 year.

Table 6. Nitrogen (N) Fertilizer benefit under different climates in 1 ha farm in 1 year.

Climates	A	B	C	D
N fertilizer benefit (kg/ha/y)	58	65.4	97.2	33.3

The important point to be reminded is that these values (Table 6) are for 50 mg/L contamination. Having 100 mg/L NO_3^- in Şanlıurfa similar model, for instance would make the fertilizer benefit 194.4 kg N/ha/year, ~80% of what we used in this study, and more than almost equal to what is suggested as solid fertilizer in the guide of the Ministry of Agriculture and Forestry [82]. Thus, field studies are suggested especially for Şanlıurfa region to make use of the NO_3^- in groundwater and progressively mitigate the NO_3^- pollution, while reducing the fertilizer expenditure. In conclusion, pump and fertilize can be a very promising choice for not only diminishing the required N fertilizer but also remediate the NO_3^- contaminated groundwater at the same time. It also lowers the carbon footprint of the agricultural activity as the N fertilizer production emits significant greenhouse gases [8].

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Appendix A

Groundwater nitrate concentration map was drawn with the available data in the website of Ministry of Environment & Urbanization related to “Province, Environment and State Reports” for 2017 year [83] (when 2017 is not available, 2016).

Only the groundwater nitrate concentrations more than 10 mg/L were considered.

Appendix B

The meteorological data for Eskişehir, Adana, Şanlıurfa, Düzce and Rize were given below. These were used to generate crop irrigation water requirement and crop evapotranspiration values through the Penman-Monteith equation via Criwar software. The equation requires temperature, precipitation, relative humidity, wind speed, elevation and sunshine hours to calculate reference evapotranspiration value. Table S-6 illustrates the NO_3^- concentrations of irrigation water for each climate in all months. September values for A, B and C climates are quite high as there was not irrigation. Additionally, Rize climate (E) was excluded from the study owing to the very low water demand of the corn in that region, which renders the pump and fertilize virtually out of choice. The following Table S-7 indicates the water entered from the top boundary to the system. The NO_3^- fertilizer comes together with this applied water, too. The concentrations in Table S-6 arranged so as to have in total approximately 240 kg of N applied to the system (around 1070 kg NO_3^-).

Table S-1. Monthly temperature (T), precipitation, sunshine, relative humidity and mean windspeed values for Eskişehir.

Month	min T°C	max T°C	Rain mm	Sunshine hours	Rh mean %	Rh max %	Mean Windspeed m/s
Jan	0	3.8	40.1	2.6	80	100	12
Feb	0	6.2	32.8	3.8	78	85	5
Mar	0	11.3	35.1	5.3	78	85	4.2
Apr	4.2	17.2	38.6	6.4	65	80	3.3
May	8.5	22	44.6	8.5	70	85	4.2
Jun	11.8	25.9	33.1	10.2	65	95	3.3
Jul	14.2	29	12.8	11.2	58	80	4.2
Aug	14.1	29.3	8.7	10.7	70	80	4.2
Sep	10.2	25.4	15.8	8.7	55	78	3.3
Oct	5.8	19.4	28.2	6.2	60	90	3.3
Nov	1.9	12.7	30.2	4.3	65	85	2.8
Dec	0	6.1	46	2.3	75	95	4.2

Table S-2. Monthly temperature (T), precipitation, sunshine, relative humidity and mean windspeed values for Adana.

Month	min T°C	max T°C	Rain mm	Sunshine hours	Rh mean %	Rh max %	Mean Windspeed m/s
Jan	5.5	15.1	105.1	4.4	65	90	2.7
Feb	5.9	16.1	85.1	5.1	60	80	2.7
Mar	8.5	19.5	60.4	5.5	64	90	2.7
Apr	12.3	23.8	50.3	6.5	60	90	2.7
May	16.2	28.2	42.8	8.5	60	80	3.0
Jun	20.4	31.7	19.3	10.2	70	78	3.4
Jul	23.9	33.7	9.4	10.2	60	80	3.3
Aug	24.2	34.6	7.0	9.6	70	76	3.6
Sep	21.0	33.2	15.1	8.3	64	80	2.7
Oct	16.4	29.2	47.9	7.1	44	78	2.5
Nov	10.7	22.0	82.6	5.3	60	92	2.5
Dec	7.0	16.8	120.7	4.2	60	95	2.3

Table S-3. Monthly temperature (T), precipitation, sunshine, relative humidity and mean windspeed values for Şanlıurfa.

Month	min T°C	max T°C	Rain mm	Sunshine hours	Rh mean %	Rh max %	Mean Windspeed m/s
Jan	2.5	10.3	76.7	4.0	70	85	3.3
Feb	3.0	11.8	70.3	4.9	55	68	3.0
Mar	6.4	16.7	63.9	6.2	60	85	3.3
Apr	10.9	22.6	40.9	7.6	55	85	3.1
May	16.0	29.0	26.2	9.8	45	70	3.4
Jun	21.3	35.1	4.2	11.9	35	45	4.1
Jul	24.9	39.0	0.9	12.0	25	39	3.7
Aug	24.4	38.5	1.2	11.1	40	45	3.0
Sep	20.4	34.1	4.1	9.6	30	50	2.7
Oct	15.1	27.0	27.7	7.5	45	80	3.3
Nov	8.4	18.2	50.2	5.5	55	80	2.9
Dec	4.3	12.1	67.5	3.9	55	80	2.7

Table S-4. Monthly temperature (T), precipitation, sunshine, relative humidity and mean windspeed values for Düzce.

Month	min T°C	max T°C	Rain mm	Sunshine hours	Rh mean %	Rh max %	Mean Windspeed m/s
Jan	0.5	8.2	85.9	1.9	85	100	5.3
Feb	0.8	9.9	73.0	2.7	75	100	3.3
Mar	3.1	13.4	70.8	3.5	75	100	2.5
Apr	7.1	18.7	58.7	4.8	70	95	2.5
May	10.9	23.2	53.9	6.7	75	100	2.2
Jun	14.5	26.9	58.0	8.0	70	95	2.1
Jul	16.9	28.8	47.5	8.2	70	100	2.5
Aug	17.1	29.1	43.6	7.8	85	95	2.2
Sep	13.3	25.8	48.8	6.2	60	80	2.2
Oct	9.8	20.6	87.9	4.1	65	100	2.6
Nov	4.9	15.0	85.3	2.7	70	95	2.8
Dec	2.4	10.1	95.6	1.8	75	100	4.2

Table S-5. Monthly temperature (T), precipitation, sunshine, relative humidity and mean windspeed values for Rize.

Month	min T°C	max T°C	Rain mm	Sunshine hours	Rh mean %	Rh max %	Mean Windspeed m/s
Jan	3.6	10.6	207.2	2	65	91	3.1
Feb	3.3	10.5	182.5	2.9	60	95	3.1
Mar	4.8	12	152.7	3.5	65	85	1.7
Apr	8.4	15.6	88	4.5	61	95	1.9
May	12.5	19.5	100.4	5.7	75	100	1.4
Jun	16.7	24	138.7	6.6	75	100	1.5
Jul	19.9	26.5	150.7	5.2	83	100	1.5
Aug	20.4	27.2	179.2	5.2	85	100	1.5
Sep	17	24.5	245.4	5.1	75	100	1.5
Oct	13.2	20.6	320.5	3.9	59	100	2.1
Nov	8.4	16.2	256.3	2.8	60	100	2.5
Dec	5.3	12.7	247	1.9	55	95	2.8

Table S-6. Nitrate concentrations in irrigation water for each climate for different months.

Nitrate (mg/L)	A	B	C	D
May	79.0	64.0	58.9	80.2
June	342.5	292.5	200.2	351.0
July	122.4	118.7	81.8	164.5
August	108.5	100.5	77.7	151.2
September	970.1	880.1	3241.5	219.7

Table S-7. Combined irrigation and precipitation water entered to the soil column.

Water (m^3)	A	B	C	D
May	695	858	932	685
June	1164	1363	2058.4	1136
July	2244	2314	3359	1670
August	1898	2050	2652	1362
September	137	151	42.4	605