# MODELING THE EFFECTS OF IRRIGATION BY CONTAMINATED GROUNDWATER

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**MODELING THE EFFECTS OF IRRIGATION BY CONTAMINATED GROUNDWATER**

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**I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.**

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## ABSTRACT

## MODELING THE EFFECTS OF IRRIGATION BY CONTAMINATED GROUNDWATER

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Pump and fertilize, while removing nitrate the groundwater, can also reduce nitrate and pesticide requirement. In this study, we constructed groundwater models via HYDRUS 1D for one-hectare maize field in prevalent soils in Turkey and Eskişehir, Adana, Şanlıurfa, Düzce climates in Turkey, assessed the most likely promising conditions for pump and fertilize, and found that even in 50 mg/L nitrate concentrations, this process is beneficial, especially in Şanlıurfa similar climates (687 TL/year). Nitrogen leaching loss were more in sandy soils. Later, we modeled the atrazine and cypermethrin contaminated water irrigation, with also using leonardite as adsorbent to facilitate controlled desorption of pesticides. We found that using leonardite, one can both effectively immobilize the contaminant or dilute its concentration to its 1/5, 1/10 of applied concentration.

Keywords: groundwater contamination, nitrate, reuse approach, pump and fertilize

## ÖZ

### KİRLİ YERALTISUYU İLE SULAMANIN ETKİLERİNİN MODELLENMESİ

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Pompala ve gübrele yöntemi hem yeraltısuyunu kirlilikten arındırırken hem de tarıma yardımcı olabilecek bir prosestir. Biz bu çalışmada HYDRUS 1D ile 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 iklimlerde 50 mg/L nitrat değerinde bile karlı olduğunu ortaya koydu (687 TL/yıl). Nitrojen sızıntı kaybı ise çoğunlukla kumlu topraklarda daha tehlikeli bulundu. Bundan sonra cypermethrin ve atrazin ile kontamine olmuş suyun sulamada kullanılmasını modelledik, aynı zamanda leonarditi de sorbent olarak bu prosese dahil ettik. Sonuçta sorbentle pestisitleri hem fiilen hapsedebileceğimizi, hem de 5'te, 10'da bir derişimlerine kolayca seyreltebileceğimizi bulduk.

Anahtar sözcükler: yeraltı suyu kirliliği, nitrat, yeniden kullanım, pompala ve gübrele

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# CHAPTER 1

# INTRODUCTION

Agriculture is one of the most significant and influential human activity. It allegedly changed the human lifestyle from hunter-gatherer to cultivator and breeder (Mazoyer & Roudart, 2006), it has the highest water usage around the globe (FAO, 2016), and leading water polluter, such as in USA (FAO, 1996) and in the majority of OECD countries (Parris, 2011). Major pollutants originating from agriculture are nutrients and pesticides (FAO, 1996), and among nutrients mostly nitrogen (N), then phosphorus (P). In addition to these, agriculture was estimated to be responsible for nearly one-third of greenhouse gas emissions, and solely fertilizer production contributes up to 575 megatons (approximately 1%) of carbon dioxide equivalent (Vermeulen, et al., 2012). These facts necessitate new management approach to mitigate problems related to fertilizer production and also remediation of the already polluted areas.

Pump & fertilize (King, et al., 2012) can do both simultaneously. Even though the valorization of the groundwater contamination sounds simple, the literature is very poor in this treatment method, and there only a couple of case studies with 1-year field experiments. This makes the feasibility assessment for the process impossible. Thus, prior to the very laborious and costly experimental studies for the evaluation of pump & fertilize process, a general modeling study to find out under what conditions of climate and in what types of soils this process is more promising, is required.

## 1.1 Agricultural Pollution

In the book written by Merrington and others (2014), pollution by agricultural activities was clearly defined with the United Kingdom focused data. Nitrogen and phosphorus (nutrient) losses, pesticides, soil erosion, gaseous emission, genetically modified organisms, and organic wastes are main categories related to the pollution pathways. However, these pollutants can very well arise from other sources as well (Hallberg, 1987), such as in Warta River, Poland (Górski, t al., 2017) there was a trend of nitrate ($NO_3^-$) concentration with nitrogen fertilizer use, between 1956-1990, but even though fertilizer usage started to increase gradually after 1992, river $NO_3^-$ concentration was in decreasing trend and this fact was attributed to (i)-more rational usage of fertilizer, (ii)-improvements in wastewater treatment. Another example for $NO_3^-$ source of both fertilizer (for coffee production) and sewage from urban areas is from Costa Rica (Reynolds-Vargas, et al., 2006). Still, although not all $NO_3^-$ contamination can be ascribed to agricultural practices, especially excess N applied for agricultural purposes has clear trends with that of groundwater $NO_3^-$ concentration (Hansen, et al., 2017), (Commoner, 1970).

Though fertilizer application is numerous times found to be responsible for increased $NO_3^-$ concentration in aquifers, the effect is not immediate, for example in Geer Basin, Belgium, unsaturated movement of mean vertical $NO_3^-$ velocity found to be approximately -1 m/year (Batlle Aguilar, et al., 2007). This points out the fact that even in shallow aquifers (<10 meters of groundwater table depth) the effect of nitrogen management is observed very slowly, and this means nitrogen inputs from agriculture or another source will be detected in years, in general. As a result, precise agriculture should be a part of the remediation of groundwater $NO_3^-$ contamination.

## 1.2 Basic Requirements of Plants

The followings are the conventional parts of the agriculture: Irrigation, fertilization, pest management, and organic amendments. The last 3 have the special focus on our study.

### 1.2.1 Fertilizer

Crops require nitrogen, phosphorus and potassium. In last decade, synthetic N fixation was stated to be almost in the same magnitude with natural, biological fixation of the N (Ritter, 2008). Phosphate fertilizer is also very crucial, and even a more limiting substance than N especially in terms of eutrophication danger. However, phosphorus leaching is more associated with macro pore/preferential flow than micro pore groundwater flow, because of high adsorption (Yoon, n.d.), and thus, it was not included in our study. The other fertilizer is potassium, which in Turkey's soil's minerals, abundantly adsorbed.

#### *1.2.1.1 Nitrogen Fertilizers*

N containing fertilizer can be direct, such as urea or ammonia, or composite NPK fertilizers, containing each of three major requirements of crops in differing percentages. There are also slow and controlled release fertilizers for more efficient supplying of nutrients to plants, i.e. to lower the N requirement to grow a unit amount of plant. The direction of development is to the exact supply of plant demand in 100 % efficiency and results in no N loss. This means that the fertilizers, like potassium nitrate, will be less and less available to farmers as a meaningful choice;

however, its modeling is still crucial as no matter what type of N is applied to the soil, in the end only $NO_3^-$ has serious accumulative potential in groundwater, and all fertilizers slowly or rapidly transforms into $NO_3^-$ in the soil. As a result, modeling its fate and transport will continue to be significant in the following years, as well.

#### *1.2.1.2 Current Demand / Cost*

Different types of fertilizers have different prices, and even though prices are changing, it is still useful to take a look at the approximate costs of N fertilizers in July, 2018 in Turkey, in the following Table 1 (TMO, 2018).

**Table 1.** Unit costs of two N fertilizer in Turkey, July, 2018 (TMO, 2018)

| Fertilizer cost | Diammonium phosphate (18% N) | Urea (46% N) |
|---|---|---|
| Unit cost (TL/ ton) | 2015 | 1350 |
| Unit N cost (TL/ ton) | 11194 | 2935 |

Synthetic fertilizers are still cheaper than the organic ones, as the latter always includes transportation in huge amounts compared to the synthetic fertilizers, to supply same N in a given time. Nevertheless, fertilizers are still an expensive commodity for an ordinary farmer in Turkey, and without subsidies, fertilizers may cost a significant proportion of the income of field. Because of this fact, people generally don’t expect agricultural $NO_3^-$ pollution in Turkey. Still, $NO_3^-$ leaching is not only related to the excess application of fertilizer but also sudden heavy precipitation and timing of fertilizer applications (Havlin, et al., 2013). The former is expected to be more aggravated due to the global warming and climate change, and the latter, poor management is present in Turkey. Henceforth, $NO_3^-$ leaching and denitrification from farms in Turkey should be carefully considered.

#### *1.2.1.3 Fertigation as Fertilizing Method*

With the help of fertigation, nitrogen loses, especially leaching N can be lowered (Azad, et al. 2018; Singandhupe, et al. 2003). Leaching of N is a serious issue. For instance, in the research of Khanif and his team (1984), maize was able to incorporate only 17.5 % of applied nitrogen by fertilizer, the remaining was speculated to be moved to the deeper parts than maize roots by unexpectedly high rains after fertilization, and also due to the very early application of fertilizer to maize as considerable amount of time passes until it starts to utilize nitrogen in its vicinity. This results in a very long residence of the nutrients in the soil, and make them vulnerable to the other loss mechanisms than plant uptake.

### 1.2.2 Pesticide

Unlike fertilizer, plants don’t actually need pesticides, but in an open field farm, not using pesticides can severely affect the yield. Especially in monoculture, one-kind of crop was sown to the soil repeatedly to the corresponding area and its insect, herb, fungi, and other parasites may very well bloom with this abundance, also considering fragile nature of crops exposed to high amount of nitrate (Merrington, et al., 2014), this is detrimental to the yields.

Stockholm Convention (Stockholm Convention, n.d.) and Europe’s Water Framework Directive includes many pesticides/herbicides. A pesticide may be produced for a certain enzyme of a specific pest, but then, it may also be found that similar harmful effects can be observed in humans as well, such as organophosphorus pesticides (Barlow, et al., 2015) chlorpyrifos and malathion, both are licensed in Turkey (Tarım ve Orman Bakanlığı, n.d.). Atrazine is used in maize weed controls (Cornell CALS, 2018), even if banned under European Union and

Turkey (Food, Agriculture and Husbandry, 2016), it is still used in the USA, where the highest maize production took place in the world. Another example is cypermethrin, a foliar application pesticide for crops, also for maize (Villanueva, 2018), (USEPA, 2011). Alpha and zeta isomers of cypermethrin have licensed products in Turkey (Tarım ve Orman Bakanlığı, n.d.) and cypermethrin was detected in Turkey's water bodies (Güner, 2017). Thus, both atrazine and cypermethrin are relevant considerations while modeling the irrigation of maize field by contaminated groundwater resources.

### 1.2.3 Organic Amendments

Soils without the appropriate amount of organic matter have poor water and nutrient, especially cationic nutrient holding capacity (Radcliffe & Šimůnek, 2010). The major part of the soils in Turkey has less than 2% of organic matter (Sonmez, et al., 2017), and this has an impact on nutrient and also trace metal leach to the groundwater. Many types of organic amendment options exist, including but not limited to sewage sludge, conventional compost and vermicompost, peat, humic acids, lignite, leonardite and even the remnants of the crops harvested previously. Organic amendments, like pesticides, are not directly used by plants, but their indirect impacts are plenty. Biochar amendments, for instance, (Khan, et al., 2018) can mask the cadmium in soil and in this way reduce toxicity. Organic amendments are from either sewage or directly food waste in general. These require heat application (as in biochar production) or more processing to make it suitable as an amendment, like anaerobic stabilization. One of the promising options as a soil amendment without any pretreatment is leonardite, which will further be elaborated under section 1.5.1.

## 1.3 Groundwater Nitrate Pollution in Turkey

In the following map (Figure 1), we have compiled $NO_3^-$ groundwater pollution data around Turkey, from the Province, Environment, State reports of Ministry of Environment & Urbanization for 2017-2018 years, with the analysis data of 2016 and 2017, respectively.


**Figure 1.** Groundwater nitrate concentrations between 2016-2017 period, data compiled from Ministry of Environment & Urbanization Province, Environment, State reports

As seen in Figure 1, there are many places in Turkey, polluted with $NO_3^-$ and/or pesticides in high amounts. From the thesis study of Özgür Çakmak (2007), 14 well's $NO_3^-$ measurements can be seen in Eskişehir, and average values are in between 24 mg/L and 341.7 mg/L $NO_3^-$, and though there are also livestock, slaughterhouse or solid waste storage facilities, the pollution was mostly ascribed to agricultural practices. The last important remark related to this study is, from the measurements between October 2005 and July 2006, groundwater $NO_3^-$ concentrations were either in increasing trend or in steady level. Thus, a considerable

$NO_3^-$ contamination is expected in that area. In a thesis study of Kahraman (2015) in Harran Plain, the concentrations were in the range of 20 – 327 mg/L and the mean was 88 mg/L. There were temporal variations in every 20 wells, yet the mean was always over 50 mg/L, with lowest concentrations seen in August. The study area was entire plain, around 4500 ha, and a considerable amount of contaminated groundwater is expected. In another thesis study done by Yinanç (2013), $NO_3^-$ concentrations were temporally varied very much, with the highest observed pollution seen in July, between 12,5 and 132 mg/L, with a spatial mean of 56.11 mg/L in July for all wells, and the temporal mean value for the highest contaminated well is 68.5 mg/L. In another study in Melendiz Basin, Aksaray (Karadavut, 2007), the concentrations in February were varied in between 9.72 mg/L and 43.19 mg/L $NO_3^-$. For June, these values were in 5.88 and 62.56 mg/L, for September 3.93 mg/L to 18.78 mg/L and for December, they were in 9.60 mg/L and 44.05 mg/L. Higher concentrations in months other than September were explained as precipitation related leaching. A study, done in Kızılırmak Delta shore in Samsun by Özgül (2018) clearly indicated the differences in $NO_3^-$ concentrations before and after irrigation in 48 sampling points. The concentrations were mostly around 10 mg/L before irrigation. However, after irrigation, there was even 177 mg/L, and in general the concentrations are in 30-70 mg/L. In a review of Sünal & Erşahin (2012), there were studies regarding average $NO_3^-$ pollution in Mersin from 205 wells as 16.41 mg/L, values in range of 0.44 and 73.48 mg/L, from anthropogenic sources, in İzmir in which some wells exceed the threshold level 50 mg/L, in Kumluca, Antalya with $NO_3^-$ range of 2.46 – 164.91 mg/L and half of the wells exceeded the threshold value, in Manisa, only one sample value with an exceeding value of 448.3 mg/L, due to the potassium nitrate presence in that region, in Bursa, specifically in summer months wells were reported to contain $NO_3^-$ up to 110-150 mg/L, ascribed to fertilizer application. There was also one study in Eskişehir with temporally variable $NO_3^-$ concentrations exceeding the threshold in 34.2 % of the samples.

As mentioned before, agricultural activities are not the sole factor on $NO_3^-$ pollution, yet a considerable fraction of the reported cases, more than half of them indicated fertilizer application. This illustrates the fact that agricultural $NO_3^-$ pollution in Turkey is apparent and remediation of contaminated groundwater is required.

## 1.4 Proposed Solutions

For groundwater nitrate ($NO_3^-$) pollution, various remediation methods were studied such as bioremediation, algal remediation, adsorption, ion-exchange and chemical reduction by pyrite or nano zero valent iron. Luo and others (2018) studied a membrane biofilm reactor fed by methane to denitrify oxygenated groundwater from 50 mg/L of $NO_3^-$ contamination, biofilm mostly consisted of denitrifying anaerobic methane oxidation bacteria and some heterotrophic denitrifiers. They achieve effluent $NO_3^-$ concentrations of <10 mg/L. Yu and others (2010) used biodegradable snack ware (lignin and cellulose shreds) as a source and measured factors on denitrification efficiency, in which they found out that reduced temperatures have a tremendous effect on the efficiency of the process, with 5 % of and 13 % of observed efficiency in 30 $^0$C, in 5 and 10 $^0$C, respectively. In a study, done by Mohseni-Bandpi & Elliott (1996), rotation biological contactors, an elaborate reactor setup was used with aerobic and anaerobic steps to fully get rid of nitrite and nitrate. Ethanol was the organic source for bacteria and 2.35 mass ratio to $NO_3^-$-N was found to be optimum. In practice, this system requires groundwater to be pumped first, so a pump & treat system is necessary, and there is just no output, ethanol and nitrate were completely consumed and a final destination for the treated water was not considered. Another similar study (Kim, et al., 2002) took into account lower temperatures of groundwater and constructed an on-site system with psychrophilic bacteria (cold-lovers) to treat 13-16.5 mg/L $NO_3^-$ contaminated groundwater for drinking purposes. Starch was used as C source for bacteria in a ratio of 2.5-3.0 C/N, but at the end, TOC was high enough (11.2 mg/L) further require post-treatment for drinking purpose, and again pumping of the groundwater was needed. Feng and others (2012) faced a similar problem of leftover organic content with their walnut shell organic carbon source, while the difference was that their system was predicted to be suitable for permeable reactive barrier application, with > 90% removal rates in 24 hours of retention time. In the study of Zhao and Yang (2002), a bacteria culture was sampled from fertilizer applied soils in cold regions, for also having freeze resistance. They were further trained to have better freeze resistance and denitrification abilities and soil column test were done. C source was glucose with undisclosed amount and $NO_3^-$ was effectively degraded by more than 98 %. This method does not require pump & treat system and once the bacteria was cultured and induced with strengthened denitrifying abilities. One study worked on integration of a microbial fuel cell to a denitrifier bioelectrical reactor to increase efficiency (Zhang, et al. 2014). The $NO_3^-$ concentration was 60 mg/L, carbon source for denitrifiers was ethanol, and vitamin solution was put for fuel cell. With a range of voltage between 500 -700 mV applied, ATP concentration in bioelectrical reactor increased up to 1.5 times of its initial control concentration, and clear acceleration was seen in $NO_3^-$ removal COD concentration also declined from 60 mg/L onwards to 5 in control and 3 in bioelectrical reactor, if rapid removal of $NO_3^-$ is necessary, such as in wastewater effluent treatment, this method has its clear advantages, but groundwater remediation projects are in a distinctively different timescale. An interesting study evaluated the simultaneous degradation of $NO_3^-$ and atrazine, as both are agricultural related contaminants and expected to be found at the same time (Herzberg, et al., 2004). They used very high $NO_3^-$ feed, around 450 – 4600 mg/L, they found efficient use of granulated activated carbon as a place to selectively enhance proliferation of atrazine + $NO_3^-$ degrading bacteria (*Pseudomonas* sp strain ADP), and results in > 90% $NO_3^-$ removal, atrazine removal with these bacteria in granulated activated carbon was markedly enhanced. This system would also require previous abstraction of the groundwater, and possible lower loads of $NO_3^-$ from contaminated groundwater might prove to be problematic.

In addition to bacteria, cyanobacteria can also be utilized to remove $NO_3^-$ from groundwater, and rather than simple denitrification, $NO_3^-$ will be immobilized into cyanobacterial biomass, and makes this source available to use in other places (Hu, et al., 2000). Many species were tested and found to be efficient, but *Synechococcus* sp strain PCC 7942 was best, with initial 93 mg/L $NO_3^-$ concentration, there was about 3 mg/L $NO_3^-$ reduction in an hour, with also addition of P sources and 180 µmol of photons density per second per square meters. In terms of sustainability, it is a better choice than the previous denitrification cases, as transforming inorganic nitrogen to $N_2$ has does not have any economical input and it should again be converted to fertilizer to be used, which is a very expensive process. Algae were also utilized, as similar to the cyanobacteria, only light energy, and some phosphate input is sufficient to both sequester carbon and nitrogen, instead of organic matter oxidation by denitrifying bacteria. However, in a review done by Tuna-Öztürk & Göncü (2017), especially due to the suitable temperature requirement for algae growth, ex situ treatments by pump & treat methods were found to be necessary, which substantially increases the costs. Macrophytes were also used (Ayyasamy, et al., 2009), among hyacinth, water lettuce and salvinia, hyacinth showed the best removal rate, and up until 300 mg/L $NO_3^-$ concentration its removal rate was proportional with that of $NO_3^-$ concentration, then started to diminish with increased concentration. At best removal rate was 83 % but also dependent on phosphate and sulfate constituents, the duration of the experiment was 10 days. There is no end product defined for corresponding aquatic macrophytes after the treatment of contaminated groundwater.

Another way of remediating contaminated groundwater is adsorption. Granulated activated carbon was used for this process in Mosneag and others' research (2013). Approximately 3.16 L/mg adsorption coefficient for Langmuir isotherm was found, and the entire process only required 30 minutes with groundwater initial $NO_3^-$ concentration as 58.44 mg/L. However, pump & treat system is required to employ this setup for real cases, and there is no defined end route for sorbent. Another study (de Heredia, et al., 2006) utilized ion exchange resin IRN-78, for both removing $NO_3^-$ and also modeling the sorption kinetics of the $NO_3^-$ from both synthetic and real groundwater samples. Nitrate contaminations were 78.1 mg/L and 259 mg/L in real samples. Effects of the other ions on adsorption were also studied. 2.58 adsorption coefficient was found for this resin. It had lower sorption property than the previous activated carbon example, with still requiring pump & treat system.

The remaining options are abiotic reduction methods. Electrolytic reduction is an example (Raghu Prasad, et al., 2005), with generating $N_2$ and $O_2$ at the end of the process, $NO_3^-$ concentration was lowered from 190 mg/L to 36 mg/L with 40 mA current through 7 hours (with 600 mL cells). In another electrolytic reduction study, more selective catalysts were employed (which among Pt, Pd, and Rh, Rh was found to be best), and with use of different voltages, maximum removal was from 40 mg/L to 7.9 mg/L $NO_3^-$. As it both requires pump & treat, additional electricity and also simply destroy $NO_3^-$, it is not a sustainable remediation method. Another example to abiotic reductions are nanoparticles (Mueller, et al., 2012), such as in this research (Liu, et al., 2014) Fe/Pd/Cu composite, for selective denitrification of $NO_3^-$ to $N_2$, with lower amount of $NH_3$ side product. Initial $NO_3^-$ was 100 mg/L concentration. At best, 40.8 % of total N removal was observed, effects of other solutes and pollutants on $NO_3^-$ removal efficiency were also studied, but the produced solution and side products remained from the reducing agents were unknown. So this and similar methods are also not sustainable for effectively removing groundwater $NO_3^-$.

There are many more similar removal studies in the literature. They have different advantages/disadvantages but have one common property: They are mostly trying to destroy $NO_3^-$ and then for farming practices, again fertilizers are applied with conventional methods and another pollution cycle begins. Combined with a precision agriculture perspective, pump and fertilize (P&F) can both remove $NO_3^-$ in the environment and also reduce its leach, with additional economic benefits.

## 1.5 Pump and Fertilize (P&F)

When a remediation is planned for an $NO_3^-$ contaminated groundwater, albeit loosely, pump and fertilize (P&F) is generally suggested. It is very practical to see the contamination as a potential input to the farm and while getting rid of them, also grow plants. Treatment wetlands are good for N removal, algae are even better, and P&F is in fact, no different in the process as plants rapidly consumes $NO_3^-$ and at the same time grow. Even if it was not specified clearly elsewhere, probable limitations are other contaminants found in $NO_3^-$ contaminated groundwater and longevity of the profit from P&F. The following case studies are examples of P&F, however, even considering all of them at once, it is still quite hard to come up to a solution as they are not comprehensive.

Francis & Schepers (1994) made a research on maize production with high $NO_3^-$ containing irrigation water. They did not find any difference between the side-dress application of N and dissolved $NO_3^-$ in irrigation water. But irrigation was only done for a certain, limited period of time and the exact amount of the irrigation, also type of the maize was not reported. However, these are both critical for water use efficiency (Howell, 2001) and N use efficiency (Yolcu & Çetin, 2015).

The other example for a pump & fertilize (P&F) approach in literature is the work of Liang and others (2016). In a field & modeling study for maize field in Inner

Mongolia, as irrigation water in the well had 20 mg/L N, proper arrangement of the water application beside fertilizer input reduced leaching of N from 55% to 26% with conservative irrigation, with a type of flood irrigation. They also did not see any yield reduction.

In addition to these scientific studies, there are also reports of the California Department of Food and Agriculture. This originates from "Addressing Nitrate in California's Drinking Water" study by University of California, Davis Center for Watershed Sciences (2012) with trials of broccoli and lettuce, also requiring high amount of N (Doerge, et al. 1991), similar to the maize irrigated with $NO_3^-$ contaminated groundwater and as a result, N in irrigation water was in the same value as in fertilizer, and it was possible to reduce leaching with this kind of fertigation application while remediating contaminated groundwater.

Only reported drip irrigation system, using contaminated water is the work of Libutti and Monteleone (2017). They had tomato-spinach, zucchini-broccoli and pepper-wheat crop rotations for each year in 3-year-study. They clearly showed that initial $NO_3^-$ in soil and supplied $NO_3^-$ by irrigation were main actors of N leach, and proper management of salinity build-up can ensure both utilization of N from saline water and prevent soil salinization at the same time. Additional fertilizer application also took place in this study.

In the USA, some universities extension/outreach programs suggest farmers to take into account $NO_3^-$ in their irrigation water, yet there is not any regulation on country-wide management of $NO_3^-$ in groundwater through P&F similar way. European Union Nitrate Directive, for instance, does not include this.

### 1.5.1 Leonardite

Leonardite, also known as oxyhumolite, immature coal, oxidized coal, are found directly on the lignite sources, where exposed to more oxidizing environment, i.e. atmosphere, in the coalification process. As a result, oxygen and humic acid ratio of leonardite is much higher (it can contain up to 80 % humic acid (Qian, et al., 2015)) than lignite's are, and this will not only render leonardite as a poor candidate for combustion processes, but also make it more important as a soil conditioner application for agricultural soils (Alagöz, et al., 2014), (Gül, et al., 2015), (Küçükyumuk, et al., 2014), (Nikpeyma, 2008), (Tamer, et al., 2016).

In addition to these, there have been many studies regarding leonardite in Turkey. It was observed that leonardite could be used to drop the pH in alkaline soils (which are prevalent in Turkey) (Yaraş & Daşgan, 2012). In another study, thanks to the chemical constituents of the leonardite it was found that its water holding capacity is higher than bare soil, and plants can be grown with a lower amount of water input without facing a yield reduction (Gökçek & Kütük, 2012). As leonardite can also harbor bacteria colonies, it has been applied with many other ingredients to the plants and highest growth was seen in leonardite cases (Çakmakçı, et al. 2016). In a research investigating the effect of leonardite application on soil aggregate stability, it was found to be especially effective on increasing the stability of 4-8 mm particles (Yılmaz, et al. 2014), as might be seen from other studies (Ouyang, et al., 2013) this can enhance the hydraulic activity of the soil. In another study where different fertilizer and soil amendment were tried on wheat to see whether any kind of treatment will decrease the frequency of wheat illnesses, leonardite was found to be beneficial against some of the illnesses of wheat (Eken, et al., 2014), and actually with different C/N ratios, different leonardites can be chosen for the control of other illnesses as well (Bonanomi, et al. 2007), (McSorley, 2011). In a study done by Kolay and colleagues (2016), besides many other benefits, the leonardite application was also found to decrease the penetration resistance of the soil, and as a consequence, make it easier for plants to advance their roots through soil.

The trend in the studies done in foreign countries is in a different direction. There are many studies on the constituents and characterization of the leonardites (Ayuso, 1996), (Mao & Schmidt-Rohr, 2003), (Pokorná, et al., 1999), (Ritchie, and Perdue, 2003), (Xing, et al. 1999). Leonardites were also used in studies where compost and similar amendments are used as a comparison or as an additive (Madejón, et al., 2001), (Madejón, et al., 2002). One study worked on the methods of humus extraction from leonardite (Gonet, 1996). Especially for metals, there are many adsorption studies (Chen, et al., 1999), (Hanzlík, et al., 2004), (Sanjay, et al., 1999). Organic pollutants were also investigated in terms of their adsorption on leonardite: direct adsorption of PAH (benzo(a)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, fluorene, pyrene) (Zeledón-Toruño, et al., 2007), PAH (chrysene and phenanthrene) adsorption to humic acid extract of leonardite (Wang, et al., 2012), norfloxacin adsorption (Zhang, et al., 2012). Different than the aforementioned studies, there were also researches on the supplementary effect of leonardite on bioremediation (Cervantes, et al., 2011), (Loffredo, et al. 2012).

These facts make leonardite considerable in the scope of our study as well, for the use of contaminated groundwater as an irrigation water source.

## 1.6 Hypothesis

Pump and Fertilize process can be used to both decontaminate groundwater from nitrate/atrazine/cypermethrin and also reduce the required fertilizer/pesticide application in an efficient, sustainable way.

## 1.7 Aim

### 1.7.1 Scope of the Study

5 prevalent agricultural soils in Turkey were selected, and the aquifers beneath them were assumed to have the same texture properties, these were to account for leaching of N. 4 climate properties were selected from Eskişehir, Adana, Şanlıurfa and Düzce as A, B, C and D cases, to find out the significance of precipitation and irrigation water requirement. By comparing the results of these models we aimed to determine under which conditions P&F will be more promising.

### 1.7.2 Procedure

Our study can be mainly divided into 2 as nitrate removal and pesticide adsorption. In the following Materials & Method chapter, the tools, the data, generated and specified values for models, the structure of the models, assumptions and evaluation of the results are presented. Then, initial conditions were defined. A brief description of the HYDRUS 1D (Simunek, et al. 2013), for our models were given. With section titled as "Soil", the data and references related to soils in our nitrate removal models were presented (except sorption models, in which their soil properties were given directly with their results). The following Material & Methods chapters illustrate how the maize farm is modeled in our study, following these specifications, a section was devoted to clearly show in what part of the modeling studies assumptions were made, and their reasons and soundness were briefly discussed.

# CHAPTER 2

# MATERIALS & METHODS

## 2.1 Parameters for Water Transport

Under this section, we illustrated the data and methods we used for modeling water transport.

### 2.1.1 Model Properties

Flow in unsaturated zone is generally characterized to be 1-dimensional and through vertical direction (Testoni, et al., 2017). HYDRUS 1D models Richard equation in this one-dimensional flow with finite element method. The following equation show the relationship of water content change with head difference in unsaturated zone through Richards' equation,

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

in which θ is water content, h is pressure head, K is hydraulic conductivity, t is time, z is coordinate in vertical direction, S is sink/source term, α is the angle of the flow direction to vertical axis (Testoni, et al., 2017).

Area of the unsaturated models were 1 $cm^2$, and cell depth was 0.5 cm. The entire soil column was in 120 cm depth, corresponding to 240 finite element cells. Upper boundary was variable flux boundary, in which previously calculated irrigation/precipitation/transpiration values were entered to HYDRUS manually. Lower boundary of the models was free drainage, indicating at least >10 meters of depth of groundwater table, where no capillary fringe related effects were seen.

Temporal discretization of the model was composed of precipitation period 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 was jointly applied from the upper boundary, and at the same time required amount of the fertilizer. Plant root water and solute uptake also modeled in this period only, as it corresponds to sowing – harvest period of maize. Details for each climate conditions studied in this thesis research were given in chapter 2.1.4.

The process of HYDRUS 1D models were shown in Figure 2.

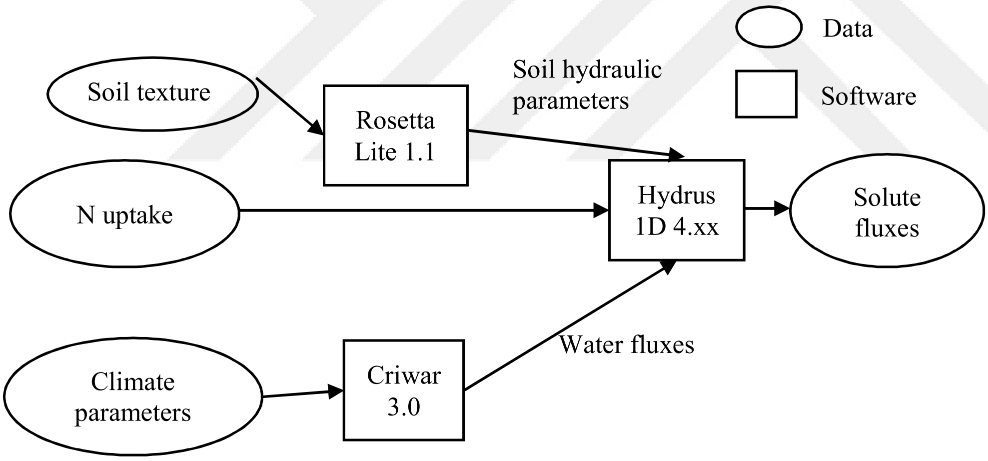


**Figure 2.** Procedure for HYDRUS 1D models

The same procedure in Figure 2 was followed for Pesticide Sorption models, in which sorption equilibrium constants were directly taken from the column sorption studies in literature.

2.1.2 Soil

There are many soil classification systems; such as USDA, Western Europe, and Russian. Nevertheless, for this study, we only needed to find average values for the hydraulic properties of alluvial aquifers, which requires soil texture parameters. These are sand, clay, and silt percentage, which allow us to define soil texture using the following triangle in Figure 3.

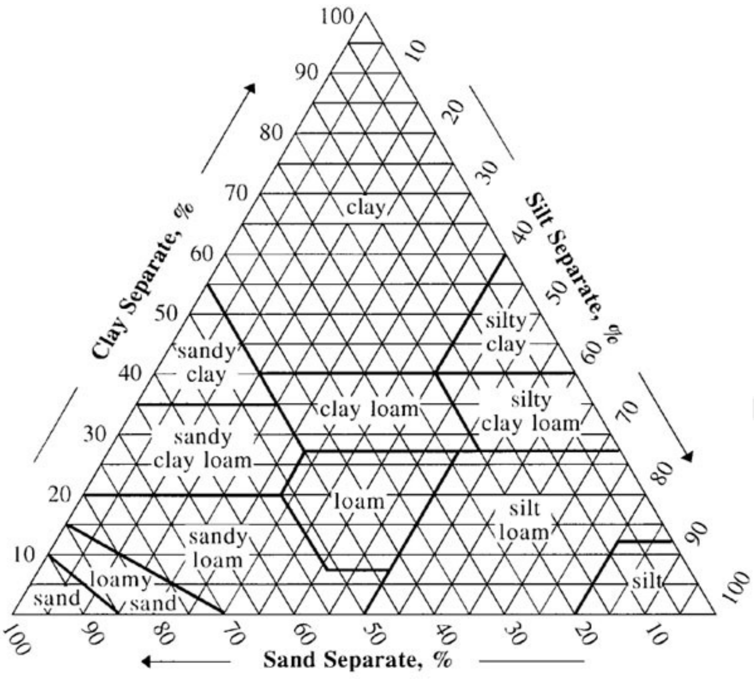


**Figure 3.** Triangle to define the type of the soil texture (taken from NRCS, n.d.)

Newest available source for the major soil types in Turkey is Soil Atlas of the Europe (2015). From this source, the soil types in Turkey are following (Figure 4).

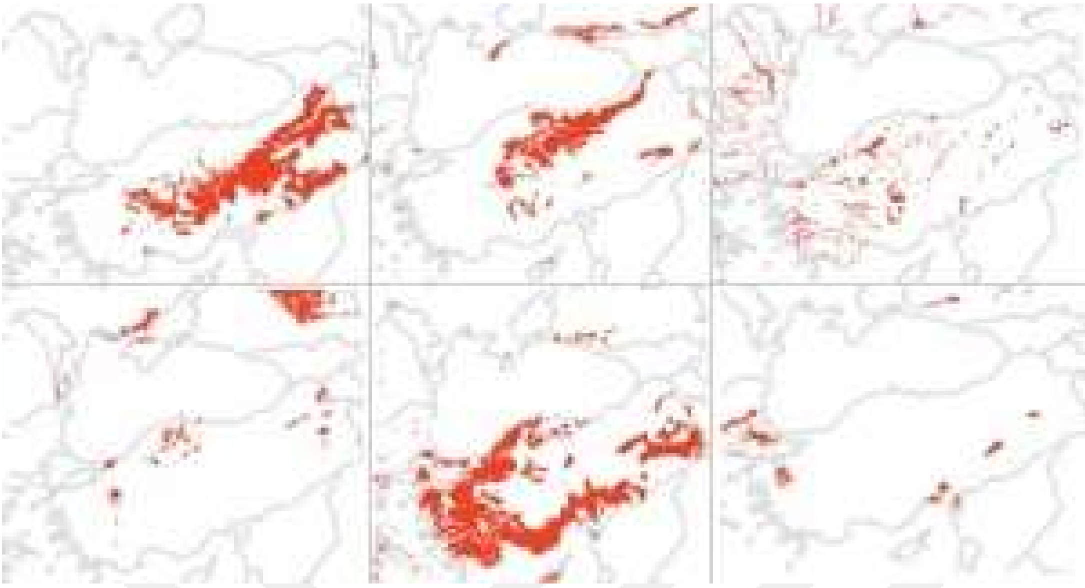

**Figure 4.** Major soil types in Turkey, from left top to right bottom, Calcisol, Cambisol, Fluvisol, Kastanozem, Leptosol, Vertisol (reproduced from Soil Atlas of the Europe, 2005)

By FAO (2001), leptosol type soils are defined as unattractive in agricultural perspective since it does not hold water sufficiently for crop production, therefore it was left out in this study. For the remaining type of soils, hydrogeological parameters were generated from Rosetta Lite v1.1, a built-in model in HYDRUS 1D, for groundwater modeling, using an array of references to get soil texture parameters. From these resources, the following parameters were collected (Table 2).

**Table 2.** Data from the references for textures of following soils

| 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 |

**(Fricke, 2016)*
***(Soil Survey Staff, 1999)*
****(KU LEUVEN, n.d.)*
*****(Ovens & Collins, 2008)*

Hydrologic parameters generated from texture information by Rosetta Lite v1.1 were given below in Table 3.

**Table 3.** Hydrological parameters generated via Rosetta Lite v1.1

| | Calcisol | Cambisol | Fluvisol | Kastanozem | Vertisol |
|---|---|---|---|---|---|
| Saturated $K_h$ cm/d | 8.51 | 71.14 | 11.24 | 14.04 | 11.97 |
| Porosity | 0.4018 | 0.4122 | 0.4966 | 0.5020 | 0.4596 |
| Texture | Sandy clay loam | Sandy loam | Silty clay loam | Silty clay | Silty clay loam |

Besides, we also modeled common soil textures in order to give more clear picture of the effect of changing hydrogeological parameters, such as; specific yield, hydraulic conductivity on N fate and transport Table 4. These values were generated through HYDRUS software.

**Table 4.** Soil hydraulic parameters of the common textures in our study

| Texture | Porosity | Hydr. Conductivity (cm/d) |
|---|---|---|
| clay | 0,38 | 4,80 |
| clay loam | 0,41 | 6,24 |
| loam | 0,43 | 24,96 |
| loamy sand | 0,41 | 350,20 |
| sand | 0,43 | 712,80 |
| sandy clay | 0,38 | 2,88 |
| sandy clay loam | 0,39 | 31,44 |
| sandy loam | 0,41 | 106,10 |
| silty clay loam | 0,43 | 1,68 |
| silt loam | 0,45 | 10,80 |

### 2.1.3 Precipitation, Evapotranspiration, Irrigation

Precipitation values were taken from State Meteorological Service's website, from 1981-2010 interval seasonal average values for each city, and for models in our study, they were directly entered as recharges to the farm (Table 5-9). We assumed that the farm field will be flat, and with the combination of rain and irrigation, water flux did not exceed the basic infiltration rate of the soil, so they will become recharge to groundwater in 100%, i.e. no surface runoff. See “Justification for No-Runoff” part in Assumptions (Chapter 2.5) section for additional information.

Using values from MGM and Meteoblue, reference evapotranspiration ($ET_0$), crop evapotranspiration (ET) and irrigation water requirements were calculated by CRIWAR 3.0 software (Bos, et al. 2008) with Penman-Monteith method (Table 10-14), and then $ET_0$, crop ET, and irrigation water values were further used as input for our groundwater models. Eskişehir (for its nitrate contaminated groundwater), Adana and Şanlıurfa (major maize producing cities in Turkey) were chosen to get climatic parameters. Temperature, precipitation and sunshine values were taken from MGM (n.d.), humidity (Rhmean, Rhmax) and mean windspeed from the simulation database of Meteoblue (Meteoblue, n.d.)

**Table 5.** Input for the CRIWAR 3.0, Eskişehir climate data, 2017

| Month | min T(°C)* | max T(°C)* | Rain (mm)* | Sunshine (hours)* | Rhmean (%)** | Rhmax (%)** | 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 |

Above values correspond to Eskişehir, the climate A. Same procedure was followed for Adana (B), Şanlıurfa (C), Düzce (D) and Rize (E) cities.

**Table 6.** Input for the CRIWAR 3.0, Adana climate data, 2017

| Month | min T(°C)* | max T(°C)* | Rain (mm)* | Sunshine (hours)* | Rhmean (%)** | Rhmax (%)** | Mean Windspeed (m/s)** |
|---|---|---|---|---|---|---|---|
| Jan | 5.5 | 15.1 | 105.1 | 4.4 | 65 | 90 | 2.78 |
| Feb | 5.9 | 16.1 | 85.1 | 5.1 | 60 | 80 | 2.78 |
| Mar | 8.5 | 19.5 | 60.4 | 5.5 | 64 | 90 | 2.78 |
| Apr | 12.3 | 23.8 | 50.3 | 6.5 | 60 | 90 | 2.78 |
| May | 16.2 | 28.2 | 42.8 | 8.5 | 60 | 80 | 3.06 |
| Jun | 20.4 | 31.7 | 19.3 | 10.2 | 70 | 78 | 3.47 |
| Jul | 23.9 | 33.7 | 9.4 | 10.2 | 60 | 80 | 3.33 |
| Aug | 24.2 | 34.6 | 7.0 | 9.6 | 70 | 76 | 3.61 |
| Sep | 21.0 | 33.2 | 15.1 | 8.3 | 64 | 80 | 2.78 |
| Oct | 16.4 | 29.2 | 47.9 | 7.1 | 44 | 78 | 2.50 |
| Nov | 10.7 | 22.0 | 82.6 | 5.3 | 60 | 92 | 2.50 |
| Dec | 7.0 | 16.8 | 120.7 | 4.2 | 60 | 95 | 2.36 |

**Table 7.** Input for the CRIWAR 3.0, Şanlıurfa climate data, 2017

| Month | min T(°C)* | max T(°C)* | Rain (mm)* | Sunshine (hours)* | Rhmean (%)** | Rhmax (%)** | Mean Windspeed (m/s)** |
|---|---|---|---|---|---|---|---|
| Jan | 2.5 | 10.3 | 76.7 | 4.0 | 70 | 85 | 3.33 |
| Feb | 3.0 | 11.8 | 70.3 | 4.9 | 55 | 68 | 3.06 |
| Mar | 6.4 | 16.7 | 63.9 | 6.2 | 60 | 85 | 3.33 |
| Apr | 10.9 | 22.6 | 40.9 | 7.6 | 55 | 85 | 3.19 |
| May | 16.0 | 29.0 | 26.2 | 9.8 | 45 | 70 | 3.47 |
| Jun | 21.3 | 35.1 | 4.2 | 11.9 | 35 | 45 | 4.17 |
| Jul | 24.9 | 39.0 | 0.9 | 12.0 | 25 | 39 | 3.75 |
| Aug | 24.4 | 38.5 | 1.2 | 11.1 | 40 | 45 | 3.06 |
| Sep | 20.4 | 34.1 | 4.1 | 9.6 | 30 | 50 | 2.78 |
| Oct | 15.1 | 27.0 | 27.7 | 7.5 | 45 | 80 | 3.33 |
| Nov | 8.4 | 18.2 | 50.2 | 5.5 | 55 | 80 | 2.92 |
| Dec | 4.3 | 12.1 | 67.5 | 3.9 | 55 | 80 | 2.78 |

After the information from Table 5-9, the following Table 10-14 for Eskişehir, Adana and Şanlıurfa were generated by Criwar software. Irrigation water was allocated so as to meet the evaporative demand of the farm together with precipitation. Only September month did not have irrigation for first three climates as precipitation was sufficient to meet evaporative demand.

**Table 8.** Input for the CRIWAR 3.0, Düzce climate data, 2017

| Month | min T(°C)* | max T(°C)* | Rain (mm)* | Sunshine (hours)* | Rhmean (%)** | Rhmax (%)** | Mean Windspeed (m/s)** |
|---|---|---|---|---|---|---|---|
| Jan | 0.50 | 8.20 | 85.90 | 1.90 | 85 | 100 | 5.3 |
| Feb | 0.80 | 9.90 | 73.00 | 2.70 | 75 | 100 | 3.3 |
| Mar | 3.10 | 13.40 | 70.80 | 3.50 | 75 | 100 | 2.5 |
| Apr | 7.10 | 18.70 | 58.70 | 4.80 | 70 | 95 | 2.5 |
| May | 10.90 | 23.20 | 53.90 | 6.70 | 75 | 100 | 2.2 |
| Jun | 14.50 | 26.90 | 58.00 | 8.00 | 70 | 95 | 2.1 |
| Jul | 16.90 | 28.80 | 47.50 | 8.20 | 70 | 100 | 2.5 |
| Aug | 17.10 | 29.10 | 43.60 | 7.80 | 85 | 95 | 2.2 |
| Sep | 13.30 | 25.80 | 48.80 | 6.20 | 60 | 80 | 2.2 |
| Oct | 9.80 | 20.60 | 87.90 | 4.10 | 65 | 100 | 2.6 |
| Nov | 4.90 | 15.00 | 85.30 | 2.70 | 70 | 95 | 2.8 |
| Dec | 2.40 | 10.10 | 95.60 | 1.80 | 75 | 100 | 4.2 |

**Table 9.** Input for the CRIWAR 3.0, Rize climate data, 2017

| Month | min T(°C)* | max T(°C)* | Rain (mm)* | Sunshine (hours)* | Rhmean (%)** | Rhmax (%)** | 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 |

The following tables are results generated through Criwar software for HYDRUS 1D models and calculation of yearly groundwater abstraction and P&F N compensation.

**Table 10.** Irrigation water requirements of a maize field under A climate

| Eskişehir | $ET_0$ mm/ha/d | Crop Coef. $K_c$ | ET mm/ha/d | Irrigation Requirement $m^3$/ha |
|---|---|---|---|---|
| January | 1.1 | | | |
| February | 1.3 | | | |
| March | 2.1 | | | |
| April | 3.4 | | | |
| May | 4.6 | 0.41 | 1.9 | 290 |
| June | 5.6 | 0.70 | 3.9 | 920 |
| July | 6.8 | 1.06 | 7.2 | 2110 |
| August | 5.9 | 1.04 | 6.1 | 1815 |
| September | 4.8 | 0.28 | 1.4 | |
| October | 3.1 | | | |
| November | 1.7 | | | |
| December | 1.1 | | | |

**Table 11.** Irrigation water requirements of a maize field under B climate

| Adana | $ET_0$ mm/ha/d | Crop Coef. $K_c$ | ET mm/ha/d | Irrigation Requirement $m^3$/ha |
|---|---|---|---|---|
| January | 1.9 | | | |
| February | 2.5 | | | |
| March | 3.1 | | | |
| April | 4.3 | | | |
| May | 5.7 | 0.41 | 2.3 | 430 |
| June | 6.3 | 0.70 | 4.4 | 1170 |
| July | 7 | 1.06 | 7.5 | 2220 |
| August | 6.3 | 1.04 | 6.6 | 1980 |
| September | 5.2 | 0.28 | 1.5 | |
| October | 4.5 | | | |
| November | 2.6 | | | |
| December | 1.9 | | | |

**Table 12.** Irrigation water requirements of a maize field under C climate

| Şanlıurfa | $ET_0$ mm/ha/d | Crop Coef. $K_c$ | ET mm/ha/d | Irrigation Requirement $m^3$/ha |
|---|---|---|---|---|
| January | 1.5 | | | |
| February | 2.3 | | | |
| March | 3.1 | | | |
| April | 4.6 | | | |
| May | 6.8 | 0.41 | 2.8 | 670 |
| June | 9.5 | 0.70 | 6.6 | 1950 |
| July | 10.2 | 1.06 | 10.8 | 3350 |
| August | 8.2 | 1.04 | 8.6 | 2640 |
| September | 6.6 | 0.28 | 2.0 | |
| October | 4.7 | | | |
| November | 2.6 | | | |
| December | 1.8 | | | |

**Table 13.** Irrigation water requirements of a maize field under D climate

| Düzce | $ET_0$ mm/ha /d | Crop Coef. $K_c$ | ET mm/ha/d | Irrigation Requirement $m^3$/ha |
|---|---|---|---|---|
| January | 1.0 | | | |
| February | 1.5 | | | |
| March | 1.9 | | | |
| April | 3.0 | | | |
| May | 3.9 | 0.41 | 1.5 | 150 |
| June | 4.7 | 0.70 | 3.2 | 560 |
| July | 5.1 | 1.06 | 5.1 | 1190 |
| August | 4.1 | 1.04 | 4.1 | 930 |
| September | 3.8 | 0.28 | 0.1 | 120 |
| October | 2.6 | | | |
| November | 1.7 | | | |
| December | 1.4 | | | |

**Table 14.** Irrigation water requirements of a maize field under E climate

| Rize | $ET_0$ mm/ha /d | Crop Coef. $K_c$ | ET mm/ha/d | Irrigation Requirement $m^3$/ha |
|---|---|---|---|---|
| January | 1.5 | | | |
| February | 1.9 | | | |
| March | 1.9 | | | |
| April | 2.8 | | | |
| May | 3.1 | 0.41 | 0.12 | |
| June | 3.9 | 0.70 | 0.26 | |
| July | 3.6 | 1.06 | 0.36 | 150 |
| August | 3.3 | 1.04 | 0.3 | |
| September | 2.8 | 0.28 | 0.08 | |
| October | 2.5 | | | |
| November | 1.9 | | | |
| December | 1.8 | | | |

As seen, in climate E condition the requirement of water other than precipitation for agriculture is very low even compared to D climate, therefore it was not considered as an option for P&F application.

### 2.1.4 Crop Modeling

To model crop transpiration grass was taken as reference compound at first. Then, the crops state is divided into 4 periods as *initial*, *develop*, *mid* and *late*. The difference of crop and grass is introduced to the equation through crop coefficient:

$$ET = K_C * ET_0 \qquad \text{(Rushton, 2003)}$$

$K_c$ is the experimental constant *crop coefficient*, specific for each type of plant and its developmental period, $ET_0$ is reference evapotranspiration. Even though evapotranspiration is affected by many factors, in general, for plants it changes with a following trend as in Figure 5.

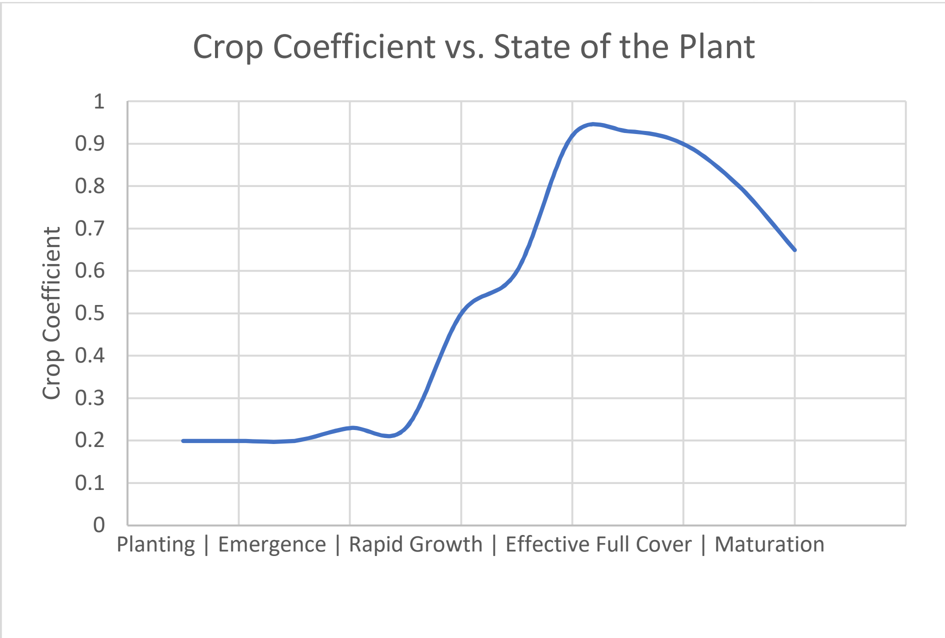


**Figure 5.** Crop coefficient through the life of the plant (Wright, 1982 (simplified))

We chose maize to study in our groundwater models. After the calculation of $ET_c$ with Criwar 3.0, (Table 10-13), corresponding evapotranspiration values were entered manually to HYDRUS and the root depth was 1 m, as maize has approximately this maximum root length.

## 2.2 Parameters for Reactive Transport Modeling

Under this section, all the data and methods to conduct reactive transport modeling of nitrate were explained. Essentially, there are 60 models each with combinations of climate and soil types.

### 2.2.1 Advection & Dispersion & Source & Sinks

Longitudinal dispersivity values were taken from (Vanderborght & Vereecken, n.d.). Horizontal transverse dispersivity was set to be % 33 of longitudinal, and vertical transverse dispersivity was set to be % 5 of longitudinal following the suggestions of Iowa Administrative Code (Lovanh, et al., 2000).

These values are for first 100 or at most 125 cm of soil, not reported to be representative of entire soil column. But, for our case it is assumed to be same through 120-cm-depth column. As a result, 36.2 cm used for calcisol, 11.64 for cambisol, 6.23 for fluvisol and vertisol and 40.9 for kastanozem. For remaining models composed of soil textures, following dispersivity values were used from the same database Table 15.

**Table 15.** Dispersivity values used in modeling of the following soil textures

| Soil Texture | Dispersivity (cm) |
|---|---|
| clay | 13.1 |
| clay loam | 62.96 |
| loam | 8.15 |
| loamy sand | 10.49 |
| sand | 17.27 |
| sandy clay | 15.9 |
| sandy clay loam | 36.2 |
| sandy loam | 11.64 |
| silty clay loam | 6.23 |
| silty loam | 3.88 |

2.2.2 Fertilizer & Plant Uptake

From the report (Doerge, et al. 1991), cited from a 1986 report of "How a corn plant develops", there is a graph for nitrogen flux for 11200 lbs. grain /acre as following in Figure 6.

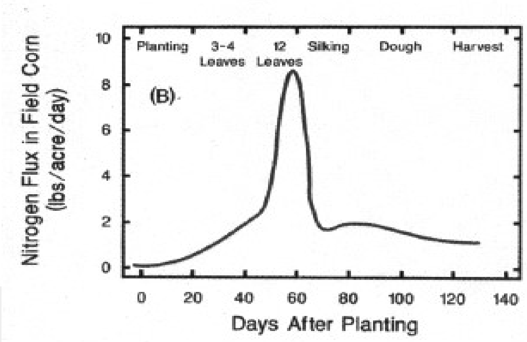


**Figure 6.** Total areal nitrogen uptake rate of maize field for 10000 kg grains/ha density.

11200 lbs. grains /acre correspond to 10000 kg grains / ha. Maize is assumed to have these properties throughout entire model. Maize's root is maximum in 1-meter length, as seen in Criwar 3.0 software we employed for irrigation water requirement. Still, different hybrids have different N use efficiencies (Goodroad & Jellum, 1988). They may also have different N uptake rates (Li, et al., 2017). From Figure 9, we interpreted 1 ha of maize's N requirement in kg as 0.4 kg N, 3 kg N, 2 kg N, 1.5 kg N and 1 kg N for May, June, July, August and September, respectively. For instance, in May, in 1 da area, 4 grams of nitrogen would be required each day, which corresponds to 17.72 g $NO_3^-$ from yield coefficient of 4.43. The model area was 1 $cm^2$ and related values of irrigation and N requirement scaled down accordingly. These values were conveyed through water flow to the soil column.

Plant solute uptake was modeled to be completely passive for $NO_3^-$, as it is usually modeled as a non-sorbing chemical species, ion exchange of plant root and soil mineral/organic matters are not possible under this assumption (Benbi, et al., 1991), (Dash Ch, et al., 2016), (Mahbod, et al., 2015).

### 2.2.3 Denitrification

For soil column's first 0-30 cm, 0.04 $day^{-1}$ denitrification was set, for the remaining 30-60, 60-90, 90-120 denitrification were 0.03, 0.01 and 0.01 $day^{-1}$, respectively. For our hypothetical models, same values with that of (Dash Ch, et al., 2016) was used for denitrification, which again, modeled agricultural soils.

### 2.2.4 Reduced Sulfur Species

It is assumed that no pyrite and related reduced species are also absent. Stable contact with $O_2$, $NO_3^-$ or similar species transform sulfide ($S^{2-}$) to sulfate ($SO_4^{2-}$).

### 2.2.5 Pump & Fertilize with Leonardite

This is direct application of leonardite to soil as an amendment. In sorption models done in HYDRUS 1D, when it is thought that soil is not able to sorb the pesticide efficiently, a leonardite cover between 2-10 cm were modeled on top of the 100 cm soil + leonardite column (Figure 7). Immobilizer completely adsorbs contaminant, simply acts as a filter. In diluter at right, leonardite solely retards contaminant's movement. As a result, with subsequent application of non-contaminated (fresh) water later, the flux concentration of the contaminant decreases.

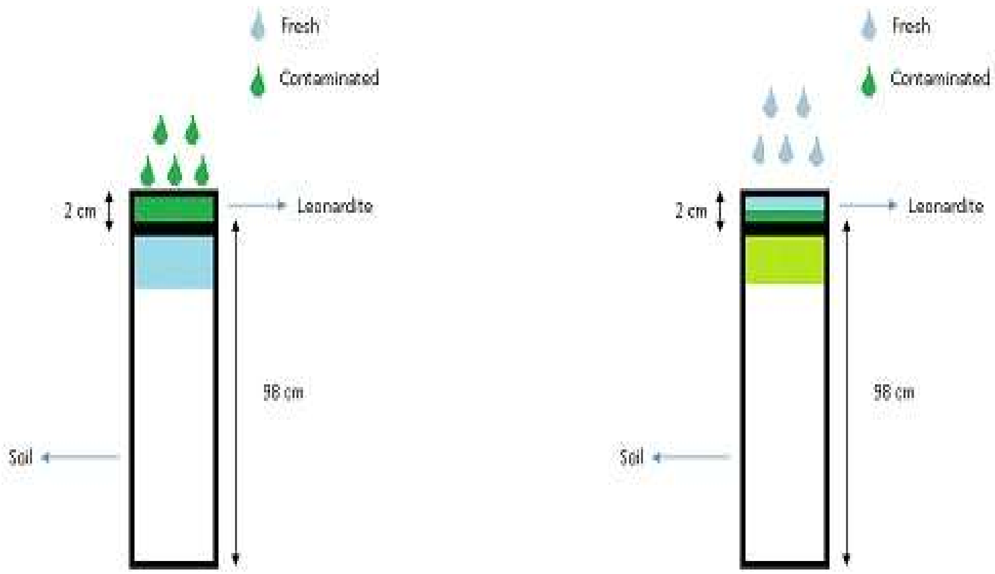


**Figure 7.** Leonardite as an immobilizer (left) and contaminant diluter (right)

## 2.3 Assumptions

For the water flow part of the model;

- Justification of No-Runoff Condition

The following numbers from Food and Agricultural Organization were used to assess whether there is an apparent possibility for runoff in our farm models. According to them, maximum infiltration rate is smaller than 30 mm/h in sand, between 20 and 30 in sandy loam, 10 and 20 in loam, 5 and 10 in clay loam and 1 and 5 between clay (FAO, n.d.).

We have considered that, if water input in an hour does not exceed the maximum infiltration rates, runoff is unlikely. For all of the cities, July was the month with higher total water input, which is the sum of precipitation and irrigation water. And their corresponding flow rate for each climate in this study were 0.3, 0.31, 0.45 and 0.22 for A, B, C and D climates, respectively.

Assuming average distribution of rain and irrigation, even if the farm soil was clay, there was not any indication for runoff. Even if entire month's rain suddenly precipitates in an hour for C case, it would not cause runoff under these conditions. 10 $m^3$ of rain in one hour, on 10000 $m^2$ area corresponds to 1 mm, and this would not increase that hours input to more than 1.5 mm/h.

-Soil Erosion

Soil erosion might affect crops and nutrient loss, but management can alleviate it, as can be seen from the following, universal soil loss equation.

Soil loss = Rainfall * erodibility * slope length* slope steepness* management * support practice

Besides, 0 soil loss, as examples can be seen from the data in USDA Agricultural Research Service website (USDA ARS, 2016), is not impossible for row crops, such as maize fields. Thus, for simplification, soil erosion effect was assumed to be absent in our study.

-Homogeneous and isotropic medium

This is a common assumption in groundwater models, briefly, it means constant hydrological properties in any location. Field conditions will never be in this ideal state. However, what we want to assess here is among 15 aquifer materials studied, which one(s) are more amenable to commence more detailed study, including field works.

-Flow was 1-dimensional and vertical

For deep aquifers, where water table is situated below 10 meters of depth, the flow can be simplified as 1-dimensional and vertical (Testoni, et al., 2017).

For N fate and transport part;

-No Dry/Wet Deposition

Dry deposition is a considerable input of nitrogen to the soil such as in Hůnová et al., (2017). Yet, in general, they are comparable to the wet deposition levels, such as in Güven & Tuncel (1997) 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 (Demir, et al., 2017), just minor contributions. Thus, the presence or absence of dry deposition flux would not change the results considerably and ignored.

-No temperature/ pH effect and fluctuations

Higher temperature may result in more denitrification than in the colder groundwater, but in field conditions, it was stated that (Peoples, et al., 1995), 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.

-Plant is a maize which grows for 153 days from May 1 to September 30

There are even hybrids grow in 120 days, yet as explained, while getting data from (Doerge, et al. 1991), 153 days were the most suitable approach. There is also a period, September where there is not actually an irrigation water requirement, so the N was applied in August to compensate both months, and this lets us also decide the factor of leaching in different models, otherwise invisible as we only put so much as necessary, there were not any leaching for the first 3 months of irrigation practice.

-Plant $NO_3^-$ uptake is passive

Plant solute uptake was modeled to be passive for $NO_3^-$, as it is usually modeled as a non-sorbing chemical species, ion exchange of plant root and soil mineral/organic matters are not possible under this assumption (Benbi, et al., 1991), (Dash Ch, et al., 2016), (Mahbod, et al., 2015).

-No N generation from organic matter decomposition, excrements of insects/animals etc.

This is a crucial parameter in case heavy application of manure/biosolids/compost or other organic-rich materials take place. However, they would also change the hydraulic properties of the corresponding soils with different degrees and this would negatively impact the comparison efficiency between different aquifers in our model. That’s why we assumed that no organic matter addition/decomposition in the field. Turkey’s soils are in majority contains less than 2% of organic matter so N supply of its own decomposition is in fact, negligible.

# CHAPTER 3

# NITRATE MODELS

Here in 15 different types of soil textures, there were some variations in the trends of model N related results in different climates, that's why, each climate A, B, C and D were investigated separately in this section.

## 3.1 Climate A

From the Köppen-Geiger climate classification (Öztürk, et al., 2017), west borders of the Inner Anatolian region and middle lower part of the Black Sea region were also in same climate classification. Summary of the results of "A" models are given in the following Table 16.

**Table 16.** Summary of climate A model results

| Soil | $NO_3$ leach | N leach | Denitrification | NUE | Plant Uptake | Sum $NO_3$ removal |
|---|---|---|---|---|---|---|
| | kg/ha/y | kg/ha/y | kg/ha/y | % | kg/ha/y | kg/ha/y |
| calcisol | 1.175 | 0.265 | 144.1 | 38.9 | 93.5 | 255.6 |
| cambisol | 0.963 | 0.217 | 122.0 | 48.3 | 116.1 | 255.8 |
| fluvisol | 0.015 | 0.003 | 148.9 | 37.4 | 89.8 | 256.7 |
| kastanozem | 0.977 | 0.221 | 151.6 | 35.7 | 85.9 | 255.8 |
| vertisol | 0.063 | 0.014 | 140.4 | 40.9 | 98.2 | 256.7 |
| clay | 0.359 | 0.081 | 150.2 | 36.8 | 88.3 | 256.4 |
| clay loam | 1.735 | 0.392 | 148.1 | 37.1 | 89.1 | 255.0 |
| loam | 0.319 | 0.072 | 133.2 | 43.8 | 105.2 | 256.4 |
| loamy sand | 62.980 | 14.217 | 101.2 | 51.4 | 123.5 | 193.8 |
| sand | 279.453 | 63.082 | 99.5 | 32.0 | 77.0 | -22.7 |
| sandy clay | 78.523 | 17.725 | 172.5 | 19.2 | 46.1 | 178.2 |
| sandy clay loam | 1.914 | 0.432 | 132.4 | 43.8 | 105.3 | 254.8 |
| sandy loam | 3.138 | 0.708 | 109.8 | 53.3 | 128.0 | 253.6 |
| silt loam | 0.006 | 0.001 | 144.3 | 39.3 | 94.5 | 256.7 |

$NO_3^-$ leaching was elaborated under section 3.1.1. Denitrification loss was directly related to the residence time of the water. This originates from the fact that we have fixed denitrification rates for the entire soil column. Still, less residence of the $NO_3^-$ in soil column may result in less time for bacteria to utilize this as an oxidant source. Nitrogen use efficiency (NUE) is relatively high in loam texture soils, as the loam word itself even means "fertile soil", this was expected. Dominantly silt, clay or sand characterized soils gave lower NUE, and the actual soils in Turkey also show comparatively lower NUE values, i.e. only ~30 % of applied N was utilized by plants. These are reasonable numbers, as in three reported cases for maize, 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) (Peoples, et al., 1995). From the study of Reddy and Reddy (2005), it is also clear that the higher N application was done to the field, the less NUE will be observed, and their applications of N to maize fields were 50, 100 and 200 kg N/ha, compared to the 239 kg N/ha in our study. This number may appear large, however, suggested N fertilizer application to fields by Ministry of

Agriculture and Forestry for Inner Anatolian Region is higher than 1600 kg N/ha with soils <2 % organic matter content (Tarım ve Orman Bakanlığı, 2015). Among soils in Turkey, cambisol was the best choice for high NUE, followed by vertisol and in terms of leaching, fluvisol was the least leaching soil.

### 3.1.1 Nitrate Leaching

As seen from Figure 9, sand dominated textures were more prone to N leaching.

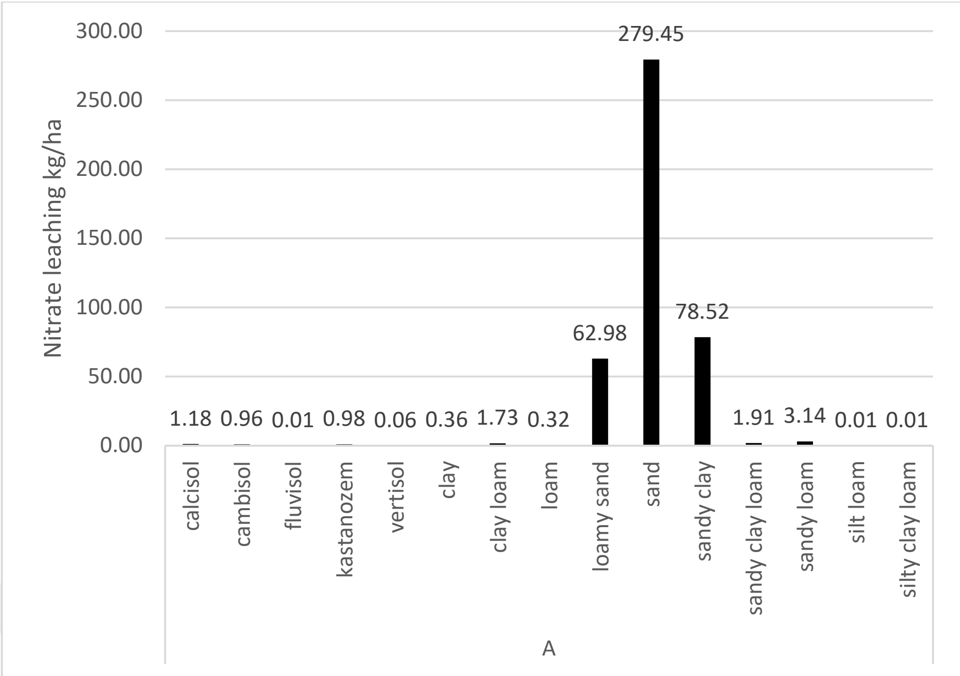


**Figure 8.** Nitrate leaching from the bottom of the 120 soil columns in A climate

Loamy sand, for instance, was the best choice while considering high NUE and with a slight difference 2nd least denitrification took place, yet the leaching was quite severe that its overall aquifer $NO_3^-$ removal property was impaired (Figure 8). Soils in Turkey generally had better results in leaching, and overall nearer to the least leaching soil types with fluvisol and vertisol. Comparing with their hydraulic conductivities, cambisol's is almost 7 times higher than other soils and this results in an expectation of more leaching, yet it actually led much better plant N uptake so its ~71 cm/d hydraulic conductivity is not a severely high value, even 106 cm/d value of sandy loam is not excessively bad in this sense, compared to the 712 cm/d of sand. Still, it should be kept in mind that these results are for A climate, as will be seen later that other climates have slightly different results, as well.

## 3.2 Climate B

B is a typical Mediterranean climate example in Turkey and prevalent in the coastal cities of Mediterranean and Aegean seas. Its model results are given in Table 17.

**Table 17.** Summary of climate B model results

| Soil | $NO_3$ leach | N leach | Denitrification | NUE | Plant Uptake | Sum $NO_3$ removal |
|---|---|---|---|---|---|---|
| | kg/ha/y | kg/ha/y | kg/ha/y | % | kg/ha/y | kg/ha/y |
| calcisol | 7.380 | 1.666 | 139.9 | 40.3 | 96.9 | 282.6 |
| cambisol | 8.372 | 1.890 | 117.7 | 49.7 | 119.4 | 281.6 |
| fluvisol | 1.390 | 0.314 | 144.9 | 38.8 | 93.3 | 288.6 |
| kastanozem | 5.611 | 1.267 | 147.8 | 37.1 | 89.1 | 284.4 |
| vertisol | 2.431 | 0.549 | 136.3 | 42.3 | 101.6 | 287.6 |
| clay | 4.778 | 1.079 | 145.5 | 38.3 | 92.1 | 285.2 |
| clay loam | 8.213 | 1.854 | 144.1 | 38.4 | 92.4 | 281.8 |
| loam | 5.544 | 1.251 | 128.9 | 45.2 | 108.6 | 284.5 |
| loamy sand | 154.349 | 34.842 | 86.9 | 49.1 | 117.9 | 135.7 |
| sand | 321.991 | 72.684 | 95.1 | 30.2 | 72.5 | -32.0 |
| sandy clay | 106.634 | 24.071 | 167.8 | 19.1 | 45.9 | 183.4 |
| sandy clay loam | 9.629 | 2.174 | 128.0 | 45.2 | 108.6 | 280.4 |
| sandy loam | 13.526 | 3.053 | 105.2 | 54.7 | 131.4 | 276.5 |
| silt loam | 1.708 | 0.386 | 140.2 | 40.8 | 98.0 | 288.3 |

### 3.2.1 Nitrate Leaching

The general trend was very similar to that of climate A, like sand dominated soils have much higher N leaching and high silt containing textures have the least leaching (Figure 9). However, leaching was more pronounced for every models, and this difference is even more apparent in textures other than sands, where in climate A example there were many soils with leaching values in scale of grams, but here the lowest value, which belongs to fluvisol, is 1.39 kg of N leaching.

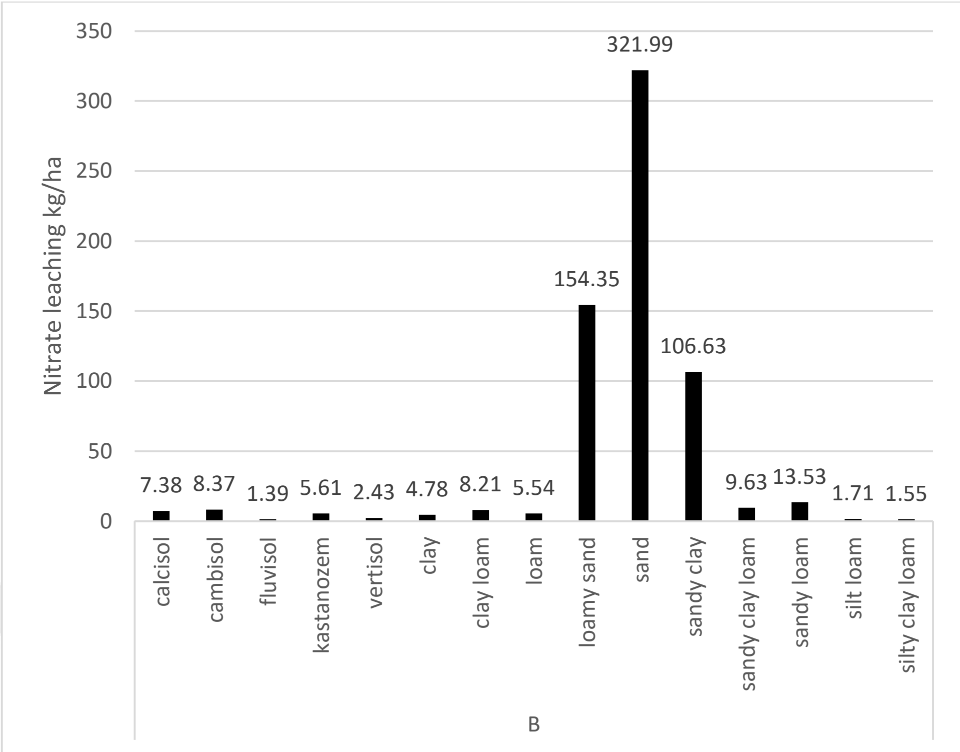


**Figure 9.** Nitrate leaching from the bottom of the 120 soil columns in B climate

Applied $NO_3^-$ concentrations were always higher in A climate than B, results in more denitrification, but at the same time less leaching. 5135 and 5800 $m^3$ was 1 ha equivalent irrigation water application for A and B climates, respectively, and since the aim was conveying same amount of N requirement in a given time, the result was different $NO_3^-$ concentration in irrigation water.

## 3.3 Climate C

In C climates, total transpiration was 1.5 times higher than that of A and B, and this also means that crops had the opportunity to uptake more $NO_3^-$, up to 10 % increase in NUE, and considerable decrease in denitrification and leaching, as well.

**Table 18.** Summary of climate C model results

| Soil | $NO_3$ leach | N leach | Denitrification | NUE | Plant Uptake | Sum $NO_3$ removal |
|---|---|---|---|---|---|---|
| | kg/ha/y | kg/ha/y | kg/ha/y | % | kg/ha/y | kg/ha/y |
| calcisol | 1.105 | 0.249 | 122.6 | 48.0 | 115.3 | 429.4 |
| cambisol | 1.059 | 0.239 | 100.8 | 57.2 | 137.5 | 429.4 |
| fluvisol | 0.033 | 0.007 | 127.6 | 46.2 | 111.1 | 430.5 |
| kastanozem | 0.897 | 0.202 | 130.6 | 44.6 | 107.2 | 429.6 |
| vertisol | 0.123 | 0.028 | 119.1 | 49.7 | 119.5 | 430.4 |
| clay | 0.842 | 0.190 | 129.1 | 45.5 | 109.3 | 429.7 |
| clay loam | 1.451 | 0.328 | 126.7 | 46.2 | 110.9 | 429.0 |
| loam | 0.405 | 0.091 | 112.0 | 52.6 | 126.5 | 430.1 |
| loamy sand | 89.075 | 20.107 | 97.3 | 51.1 | 122.8 | 341.4 |
| sand | 414.786 | 93.631 | 83.2 | 26.3 | 63.1 | 15.7 |
| sandy clay | 162.676 | 36.721 | 151.8 | 20.1 | 48.4 | 267.8 |
| sandy clay loam | 1.840 | 0.415 | 111.1 | 52.8 | 127.0 | 428.7 |
| sandy loam | 3.396 | 0.767 | 89.5 | 61.9 | 148.7 | 427.1 |
| silt loam | 0.017 | 0.004 | 123.1 | 48.1 | 115.7 | 430.5 |

### 3.3.1 Nitrate Leaching

Trend was similar to that of A climate, yet silty clay loam was exceptional (Figure 10).

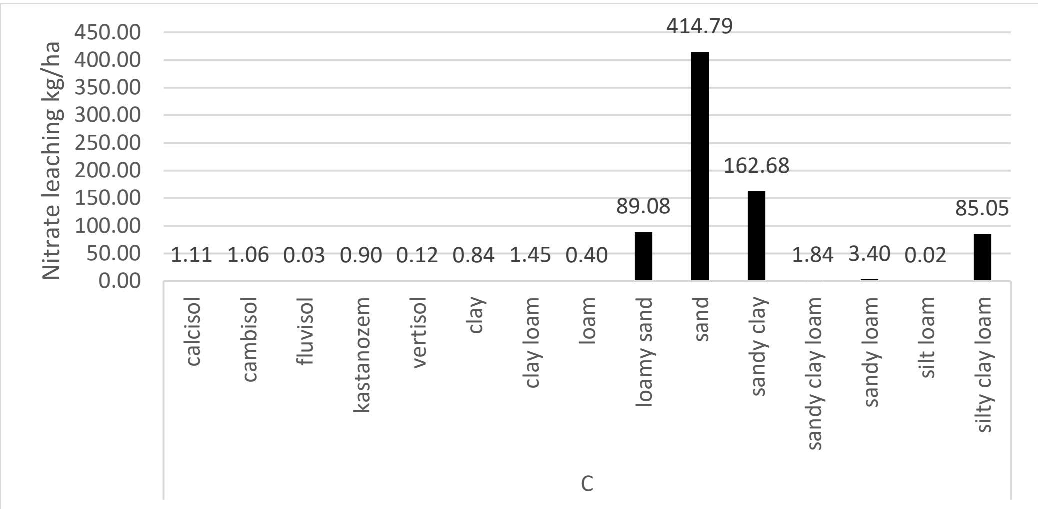


**Figure 10.** Nitrate leaching from the bottom of the 120 soil columns in C climate

The reason of high leaching of $NO_3^-$ is its very low hydraulic conductivity. Comparatively too much water application caused excessive pressure increase in the root zone, and plant was unable to uptake water in this time interval (~200-250 days in Figure 11) due to the water stress. From the database suggested by HYDRUS software and used in this study for maize (Wesseling, 1991), in order for plants to uptake water pressure is needed to be below -15 cm. Consequently, there was only denitrification (highest among C climates) and leaching in that period.

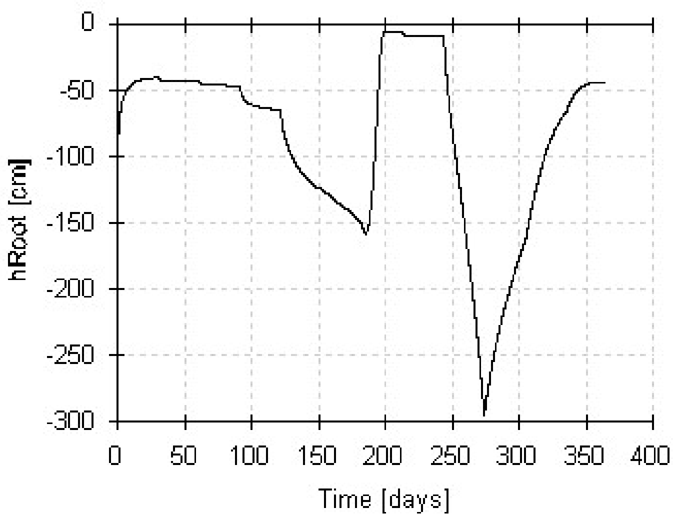


**Figure 11.** Root zone pressure head versus time graph of silty clay loam in C climate

This result also indicates that marginal soil types, such as sand with very high hydraulic conductivity and silt clay loam with very low hydraulic conductivity, are unsuitable for not only groundwater nitrate removal studies, but also overall agricultural purposes. Sand's and similar high water leaching soils had another kind of plant water stress problem. In C climate September month did not have irrigation water. However, after the cessation of the water application, the following root zone pressure head reduction were observed.

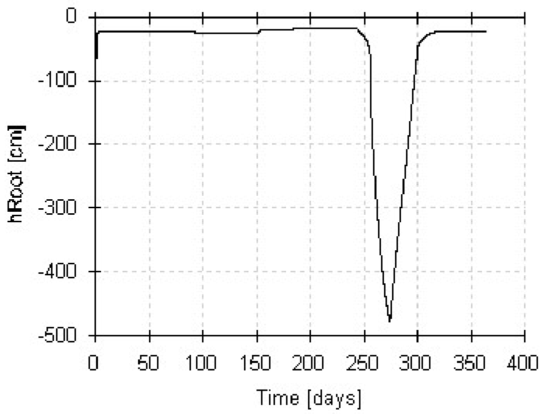


**Figure 12.** Root zone pressure head versus time graph of sand in C climate

In regions similar to 250-300 days of the Figure 12, sand in C climate, transpiration becomes suboptimal, decreasing with each decreasing pressure till reaching wilting point, where plant will be unable to uptake any water at all. For our models this corresponds to below -325 pressure head value. Mostly sand containing textures high N leaching partly originates from this phenomenon, partly from their already high hydraulic conductivity.

Overall higher $NO_3^-$ removal from the hypothesized 50 mg/L $NO_3^-$ contaminated aquifer beneath the farm in C climate simply a result of 1.5 times high water abstraction. In fact, volume of groundwater abstraction has the most significant impact on both $NO_3^-$ removal and P&F fertilizer cost compensation.

## 3.4 Climate D

Approximately half of the Black Sea region in Turkey has similar climate with D. It is the wettest climate in our study, as a result requiring less amount of additional water. Also since the temperature of this climate is also coldest.

**Table 19.** Summary of climate D model results

| Soil | $NO_3$ leach | N leach | Denitrification | NUE | Plant Uptake | Sum $NO_3$ removal |
|---|---|---|---|---|---|---|
| | kg/ha/y | kg/ha/y | kg/ha/y | % | kg/ha/y | kg/ha/y |
| calcisol | 24.999 | 5.643 | 158.2 | 30.9 | 74.2 | 122.5 |
| cambisol | 28.008 | 6.322 | 138.0 | 39.4 | 94.6 | 119.5 |
| fluvisol | 6.277 | 1.417 | 164.5 | 29.9 | 71.9 | 141.2 |
| kastanozem | 19.546 | 4.412 | 165.9 | 28.0 | 67.3 | 128.0 |
| vertisol | 10.054 | 2.270 | 156.6 | 32.9 | 79.1 | 137.4 |
| clay | 14.025 | 3.166 | 163.8 | 29.6 | 71.1 | 133.5 |
| clay loam | 28.629 | 6.463 | 161.7 | 29.0 | 69.7 | 118.9 |
| loam | 19.234 | 4.342 | 148.5 | 35.7 | 85.7 | 128.3 |
| loamy sand | 87.215 | 19.687 | 108.8 | 46.5 | 111.7 | 60.3 |
| sand | 297.364 | 67.125 | 105.7 | 28.1 | 67.4 | -149.9 |
| sandy clay | 25.911 | 5.849 | 169.9 | 25.9 | 62.2 | 121.6 |
| sandy clay loam | 33.957 | 7.665 | 146.5 | 35.2 | 84.5 | 113.5 |
| sandy loam | 42.622 | 9.621 | 123.3 | 44.4 | 106.8 | 104.9 |
| silt loam | 7.349 | 1.659 | 159.9 | 31.8 | 76.4 | 140.2 |

From aforementioned reasons, D climate have lower transpirations in their crops and consequently lower N uptakes. This may both correspond to the grain yield reduction and protein content reduction. Loamy sand and sandy loam textures still have considerable NUE values, (46.5 % and 44.4 %) yet the prevalent soils in Turkey did not exceed 30.9 % of NUE, indicating loss of more than 2/3 of the applied fertilizer to the environment. $NO_3^-$ removal values are also much lower than other examples, again expected from the less amount of water necessity for crops.

### 3.4.1 Nitrate Leaching

In general, high concentrations of $NO_3^-$ imparted leaching in all but sandy soils. As explained, the leaching of $NO_3^-$ from sand dominated textures comes from rapid movement of water, yet in D climate there was actually less amount of water demand and water application, so lower leaching of water. This diminished the magnitude of the $NO_3^-$ leach (Figure 13).

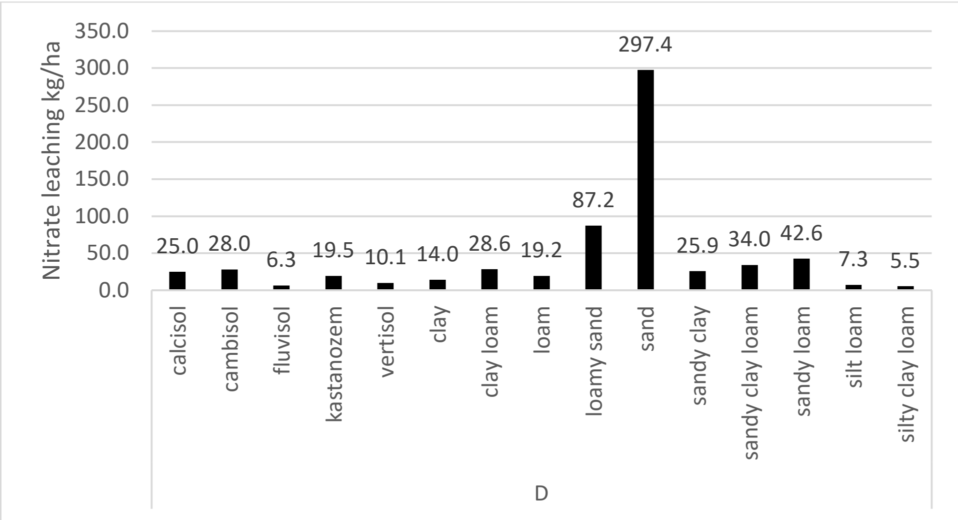


**Figure 13.** Nitrate leaching from the bottom of the 120 soil columns in D climate

## 3.5 Summary of All Nitrate Models

Different climates have different $NO_3^-$ leach, denitrification and plant uptake values. These differences also arisen from different plant water stresses occurring in different climates. Excluding sand dominated textures, C climate is much more suitable for P&F process than any other models. Loam soils are better for plants and leaching is generally much less severe in low hydraulic conductivity values, such as in silt loam, fluvisol, vertisol.

# CHAPTER 4

## ATRAZINE AND CYPERMETHRIN MODELS

In HYDRUS 1D atrazine/cypermethrin models, the water fluxes for C climate modeled in our study were used. And in May, June, July, August irrigation water was also added to the flux. Then as a solute boundary condition, for the irrigation period 1 mmol of solute was assumed to enter with 1 milliliter of infiltrating water. For pesticides, it is a very huge value but we will compare the models and percentages of the leaching pesticide in the following models, and all the models have either linear or Langmuir/Freundlich sorption, thus the concentration of the pesticide does not have any effect on the graphs.

**Table 20.** Soil texture and sorption properties of referenced atrazine sorption studies

| | Clay | Silt | Sand | OC | CEC cmol/kg | logKf-1/n | Ref |
|---|---|---|---|---|---|---|---|
| Haplic Calcisol | 24 | 66 | 10 | 1.8 | | 2.42-0.9 | Roulier, et al. 2006 |
| Eutric Cambisol | 10.4 | 19 | 70.6 | 3.66 om | 7.9 | 3.9-0.93 | Boivin, et al. 2005 |
| Dystric Cambisol | 17.7 | 45.2 | 37.1 | 6.03 om | 13.5 | 6.3-0.93 | Boivin, et al. 2005 |
| Kastanozem ( db) | 46 | 47 | 7 | 4.7 | | 15 kd | db |
| Vertisol | 42 | 26 | 32 | 10.9 | 26.6 | 0.89 kd | Prado, et al. 2014 |
| Fluvisol (db) | 38 | 54 | 9 | 5.2 | | 8 kd | db |

“db” is from the study of Ahmad & Rahman (2009) with adsorption studies of atrazine and imazethapyr in 101 different soils in New Zealand (Table 20). Relatively similar texture and OC values were selected for Kastanozem and Fluvisol named soils here from that reference. In other words, these soils in sorption models are not same with the ones nitrogen models were done, nevertheless, they are very similar. The height of the column was 100 cm, and free drainage boundary was assumed for bottom end, recommended by the software producers in cases with at least ~10m depth of groundwater table.

Top boundary condition was variable flux, in which for C climate models, irrigation and precipitation values were summed for each day and this much of water entered to the soil (Table 21). Lower boundary conditions were in free drainage, emphasizing deeper groundwater table, not similar to the 1 m depth of $NO_3^-$ models.

**Table 21.** Yearly water flux to the top to the soil column (irrigation period is highlighted)

| Month # | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flux(mm/day) | 24.7 | 22.6 | 20.6 | 13.1 | 30.0 | 66.4 | 108 | 85.5 | 1.36 | 9.23 | 16.7 | 22.5 |

In the following sections, we always gave 20-year-long graphs, except one with 60 years, so yearly flux differences are difficult to perceive. 1-year is actually the same with that of Figure 14.

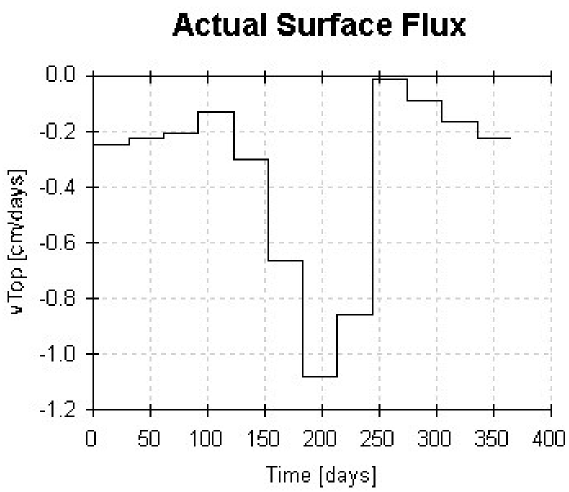


**Figure 14.** FLU_C actual surface flux within a year, - values means percolation

Distinctively higher values in magnitude in Figure 18 corresponds irrigation periods, shaded in Table 54. Remaining water fluxes merely come from precipitation. In short, this is the water flux seen on top of 100 cm soil column through a year.

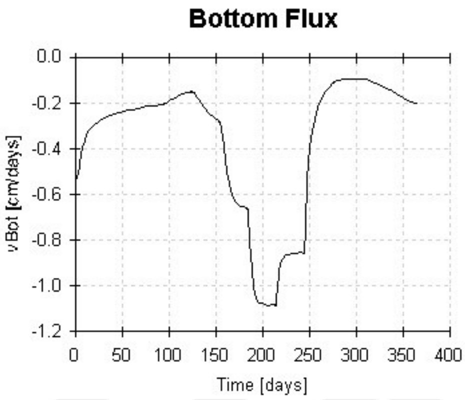


**Figure 15.** FLU_C bottom water flux through 1 year, negative values indicates fluxes out of 100 cm soil column to the deeper regions.

For a given top water flux as in Figure 14, the bottom flux as in Figure 15 was seen from the 100 cm depth of the soil column. It resembles very much to the top flux. With these water fluxes, top solute fluxes is in the following Figure 16.

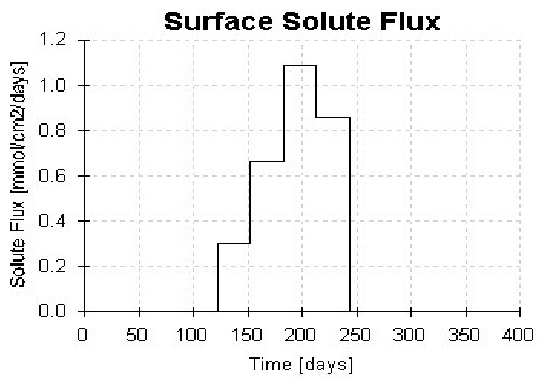


**Figure 16.** FLU_C surface solute flux for 1 year

Here in Figure 16, it is apparent that solute flux is very similar to the irrigation water. Indeed, the solute is applied only with irrigation and with fixed, 1 mmol/cm$^3$ of concentration. The area of soil column is 1 cm$^2$, so when surface water flux is slightly higher than 1.0 cm/day, solute flux is also slightly higher than 1 mmol/day.

The top solute fluxes seen in the remaining figures are very compressed in shape, such as in Figure 19, as they try to show 7300 days in a similar size graph, but they are almost exactly same with Figure 18 surface solute flux, only some little differences related to runoff.

## 4.1 Atrazine sorption models

As seen from Figure 17, atrazine has apolar structures, such as ethyl and isopropyl groups on its left and right sides, but also many nitrogen-carbon bonds and carbon-chloride bonds, which are polar, along with a 6 $\pi$-electrons delocalized through the s-triazine ring in the center. This impacts its solubility characteristics, and make it difficult to predict in under what conditions it will be adsorbed more. Therefore, we only compiled the studies in the literature directly made sorption studies of atrazine to specific soils, and modeled them only.

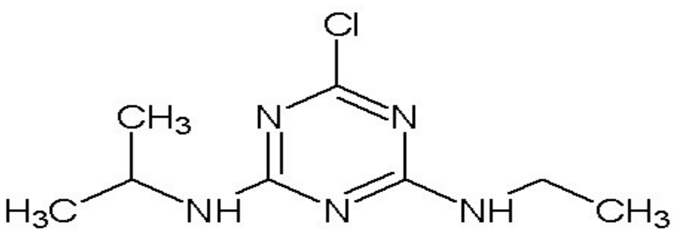


**Figure 17.** Atrazine chemical structure

FLU_C

Total atrazine application to the soil column was in 123 days, the changes of solute flux relates the irrigation water application with a peak in July (1.08 cm). Then up to approximately 5 years, no appreciable leaching of atrazine was expected from the 100 cm depth bottom of soil column (Figure 18). Afterwards, very widened leaching was seen. With other models, this lengthening of the flux and height of its peak should be compared to assess overall expected leaching of pesticides.

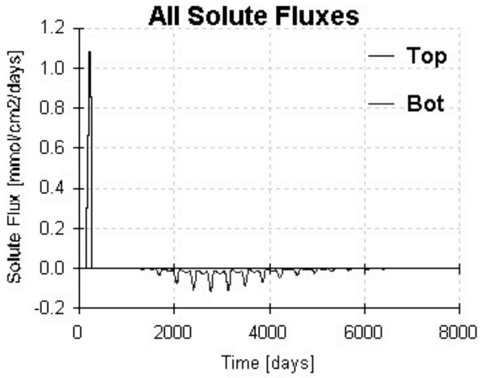


**Figure 18.** Fluvisol similar soil, atrazine contaminated water application for 1 year, bottom flux for 20 years on bottom

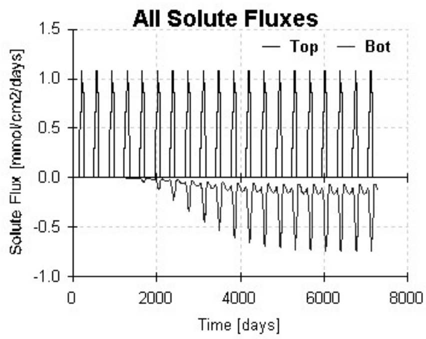


**Figure 19.** Fluvisol similar soil, atrazine contaminated water application for 20 years on top, bottom flux for 20 years on bottom on bottom

In Figure 19, after around 5000 days the bottom solute flux reached a steady state, which means entry of contaminants exceeded the sorption capacity of the soil, and simply they bypass 100 cm column, even if for each contaminant there is a substantial lag phase of almost 2000 days.

CAL_C

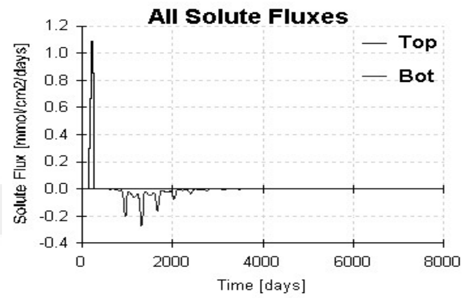


**Figure 20.** Calcisol similar soil, atrazine contaminated water application for 1 year on top, bottom flux for 20 years on bottom on bottom

The maximum bottom flux in Figure 20 was one fifth of the flux entry.

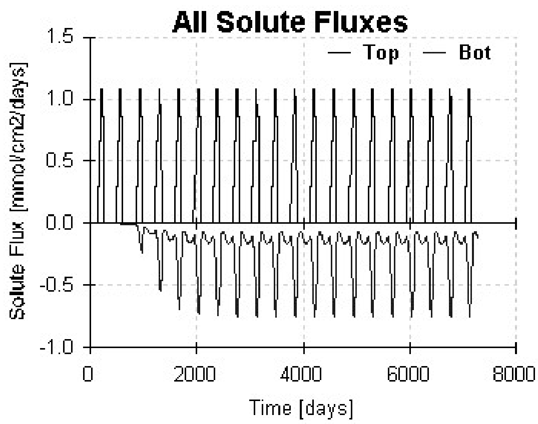


**Figure 21.** Calcisol similar soil, atrazine contaminated water application for 20 years on top, bottom flux for 20 years on bottom on bottom

Again, repeated applications will start to be ineffective as a contaminant retarder, after around 2000 days later, in this case (Figure 21).

CAM_C1 – Eutric Cambisol

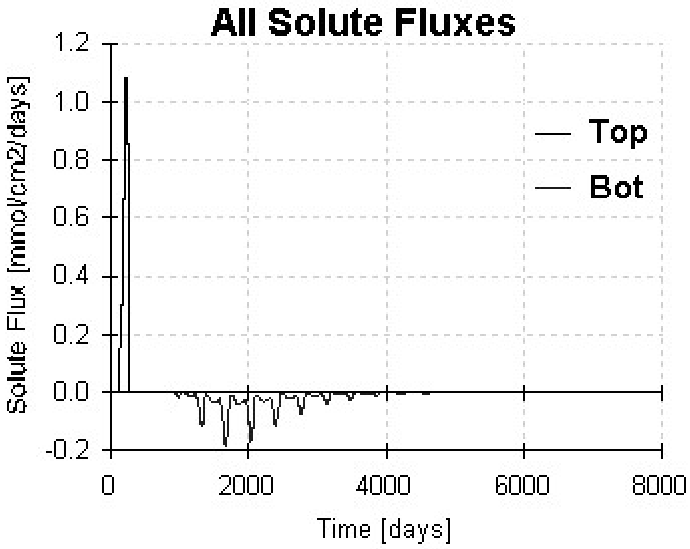


**Figure 22.** Eutric cambisol similar soil, atrazine contaminated water application for 1 year on top, bottom flux for 20 years on bottom on bottom

The performance of eutric cambisol (Figure 22) is better than calcisol in Şanlıurfa climate conditions. It simply distributed the contaminant flux into four major cycles while never exceeding one fifth of the entry flux. It can be meaningful, for instance, in cases where for the first ~900 days one will not plant the crops requiring atrazine for effective agriculture. And since after 900 days of irrigation water it will start to be available for the target herbs and weeds, then for following 4 years the stored atrazine in the soil can be used. It is known that strongly sorbed herbicides' efficacy will be reduced (Kookana, et al., 2011).

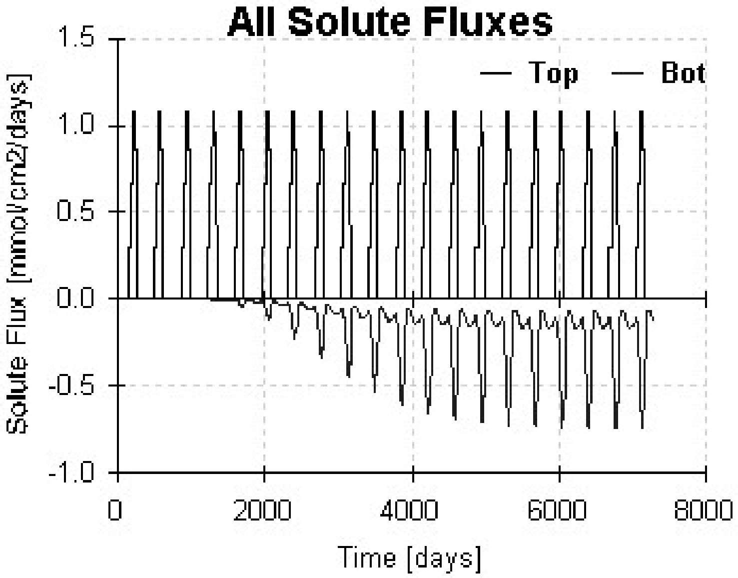


**Figure 23.** Eutric cambisol similar soil, atrazine contaminated water application for 20 years, bottom flux for 20 years on bottom

As Eutric Cambisol soil here adsorbs herbicide better, only after 5000 days onward that bottom flux was stabilized at its maximum output rate (Figure 23).

CAM_C 2 Dystric Cambisol

Compared to the Eutric Cambisol example, dystric cambisol is even better at sorption, and this results in more distributed efflux of contaminant and longer lag times up until first appearance of pesticide at the bottom of the soil. In this case there were 6 considerable output times from the bottom with its maximum not more than one tenth of the entry solute flux. Essentially its sorption constant was not seeming to be higher than eutric cambisol soil, but combining with hydrologic and other properties, it is better in atrazine retardation (Figure 24).

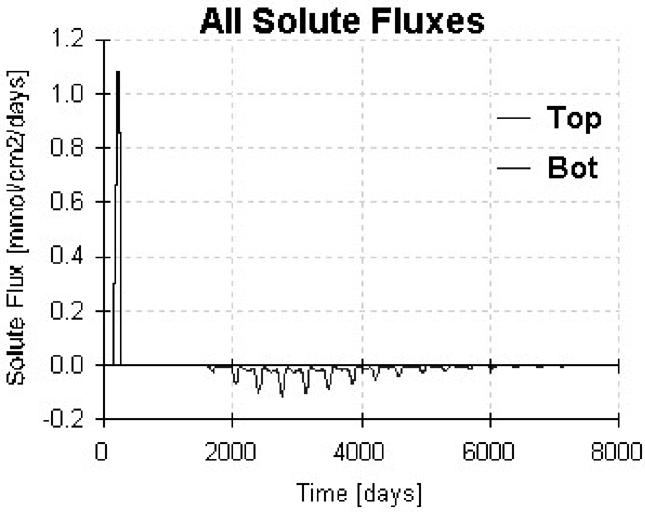


**Figure 24.** Dystric cambisol similar soil, atrazine contaminated water application for 1 year, bottom flux for 20 years on bottom

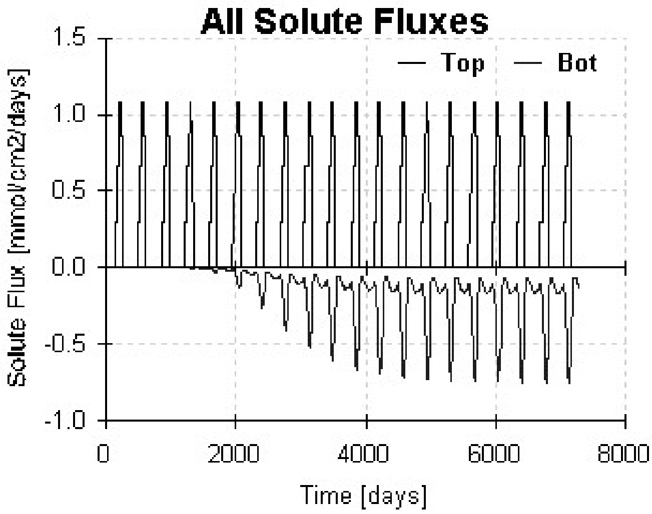


**Figure 25.** Dystric cambisol similar soil, atrazine contaminated water application for 20 years on top, bottom flux for 20 years on bottom on bottom

Most probably due to its lower sorption, it reaches its maximum bottom flux earlier than eutric cambisol (Figure 25). With this, we can state that for continuous applications, higher sorption constants are better.

KAS_C

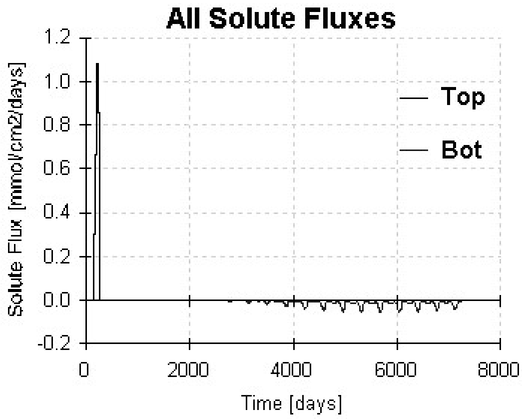


**Figure 26.** Kastanozem similar soil, atrazine contaminated water application for 1 year, bottom flux for 20 years on bottom

Kastanozem example was taken from the database, and have very high sorption constant and this results in extreme retardation, as seen in Figure 26, this application is better for complete immobilization of atrazine.

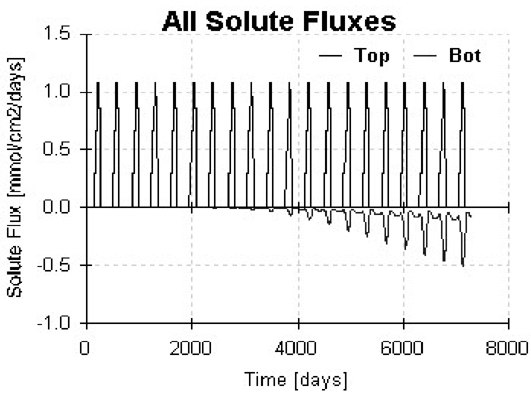


**Figure 27.** Kastanozem similar soil, atrazine contaminated water application for 20 years, bottom flux for 20 years on bottom

From Figure 27, even after continuous 20 years of atrazine contaminated groundwater, it had yet to reached its maximum bottom flux.

VER_C

Vertisol has very little sorption capacity, and just at the second year of application (Figure 28) bottom flux already reached its maximum efflux.

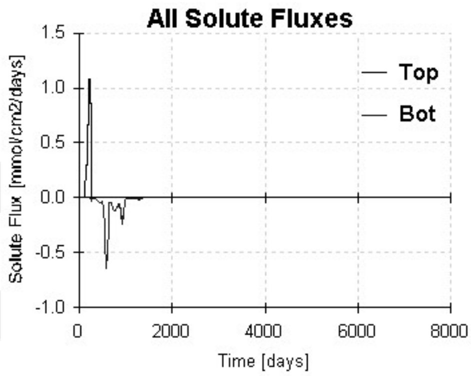


**Figure 28.** Vertisol similar soil, atrazine application for 1 year, bottom flux for 20 years

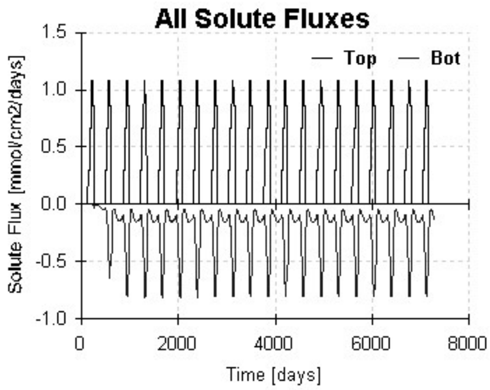


**Figure 29.** Vertisol similar soil, atrazine contaminated water application for 20 years, bottom flux for 20 years on bottom

As seen from both graphs (Figure 28 and 29), atrazine sorption is the lowest in vertisol compared to the others. It is difficult to ascribe the reason for its lowest sorption, even though having a considerable amount of organic carbon (10.9 %) and clay content (42 %). From the database of Ahmad & Rahman (2009), not a significant correlation was found for atrazine sorption and clay content and organic carbon, even though they are influential in many reported studies. Again for atrazine, another study could not find a relation of clay content or organic matter for the sorption behavior (Djurovic, et al., 2009). Atrazine has many polar bonds in it, and still an organic molecule with delocalized pi bonds, similar to benzene groups; and thus, its sorption was expected to be affected by many different factors, from ionic strength, types of the clay mineral and functional groups of the organic matter. Therefore, site specific adsorption values of atrazine are very significant, such as in kastanozem types of soil, the sorption was predicted to be very high, and it might be even higher, or even lower than vertisol example here. For our very low sorbing soil, vertisol, we studied the amendments of leonardite by normalizing $K_{oc}$ value to its organic carbon content to mitigate the leaching risk from vertisol.

*Leonardite atrazine sorption*

Leonardite was assumed to be ineffective on hydrology of the soil, it was assumed as 40% organic corban containing material, and the sorption of atrazine was directly calculated from calculated $K_{oc}$ values in (Ahmad & Rahman, 2009) database. It is safer to state that we don't directly suggest the use of 40 % C containing leonardite for following cases, but a similar inert material with same sorption capacity calculated here for leonardite (Kd = 61.54 L/kg).

For VER_C condition, 2 cm leonardite

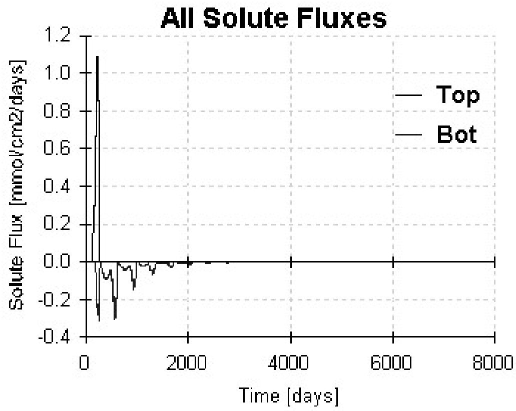


**Figure 30.** Atrazine sorption to 2cm leonardite, with same hydrological properties of vertisol, 1-year atrazine contaminated water application on top, bottom flux for 20 years on bottom

As seen, only 2 cm of 40% organic carbon containing leonardite (calculated $K_d$ value of 61.54) retard the atrazine movement much more than 100 cm vertisol soil in simulated C climate conditions (Figure 30). The next step for leonardite is combining this 2 cm with 98 cm of vertisol and considering overall 100 cm column.

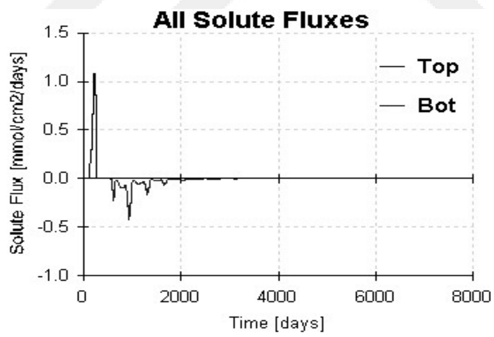


**Figure 31.** Atrazine sorption to 2cm leonardite, then accompanying 98 cm of vertisol, 1-year atrazine contaminated water application on top, bottom flux for 20 years on bottom

This profile was very similar (Figure 31) to the leonardite above, acted as a determining factor. Only there is a lag of approximately 500 days, and that comes from vertisol adsorptive behavior mostly, as its peak was also at that point. With a 2 cm of leonardite cover the leaching was broadened up to 2000 days' region, from almost complete leaching till 1000 days, in 100 cm vertisol model.

The 20 year of continuous application of atrazine would result in the following solute fluxes (Figure 32).

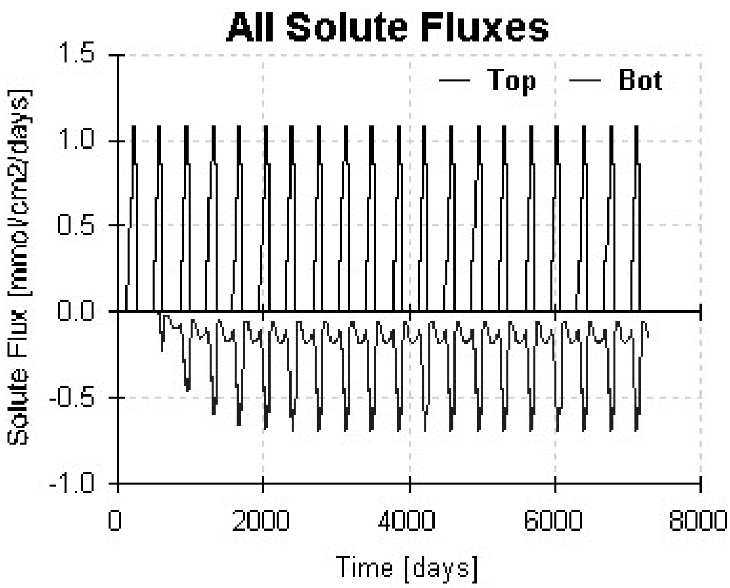


**Figure 32.** Atrazine sorption to 2cm leonardite, then accompanying 98 cm of vertisol, 20 year of atrazine contaminated water application bottom flux for 20 years on bottom

Another interpretation of the impact of both leonardite and atrazine applications is comparison of the cumulative bottom fluxes of these soils for 20 years, yet there were imperceptible differences between the models.

There are two remaining questions, how many years can this application be fruitful and how much centimeters of sorbents required for 20 years?

Along with 2 cm leonardite, 4, 6 and 8 cm sorbent stratification was added in vertisol simulations.

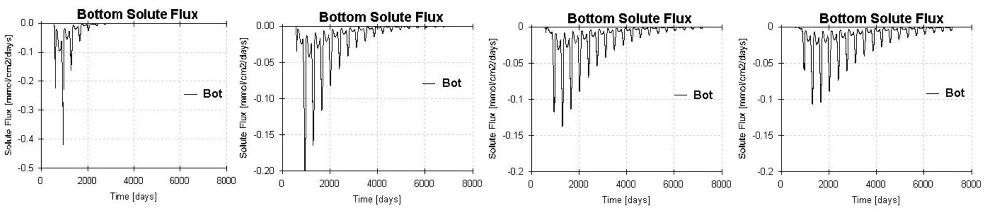


**Figure 33.** Bottom atrazine fluxes of vertisol column with 2,4,6 and 8 cm of top sorbent cover from left to right, 1-year atrazine entry

From Figure 33, it is clear that increasing the height of the added leonardite both widens the general efflux of the atrazine and also makes a slight lag for the appearance of atrazine in leachate. Being careful about the scale of the leftmost 2 cm leonardite, it is also apparent that the relation between the heights of leonardite column and highest peak of the atrazine bottom flux is very linear, with 2-fold increase in leonardite cause 2-fold decrease in highest peak's height in atrazine. The effect of continuous application of atrazine contaminated water for irrigation on different leonardite heights is in the following Figure 34.

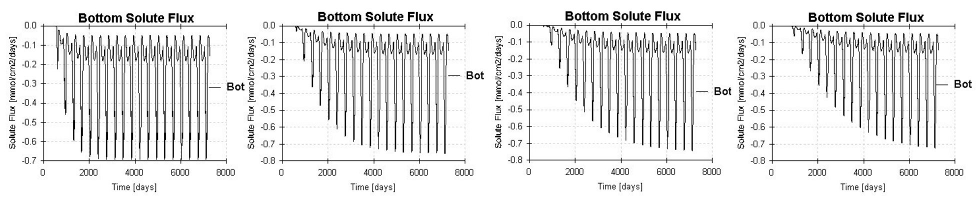


**Figure 34.** Bottom atrazine fluxes of vertisol column with 2,4,6 and 8 cm of top sorbent cover from left to right, 20-year atrazine entry

For instance, in 8 cm leonardite including soil, after almost 20 years we started to see the flux irrespective of leonardite length, overall approximately 12.5 % reduction in the peak atrazine flux was seen, from 0.8 mmol/cm$^2$ in bare vertisol to 0.7 mmol/cm$^2$ in leonardite covered ones, in a day. Thus, mere addition of leonardite slightly reduces the maximum flux, and amount of the added leonardite retards more atrazine, which makes reaching to the maximum flux becomes slower, from about 6 years in 2 cm, to 20 years in 8 cm. All these mean that considering the concentration of our contaminated irrigation water, the length of the leonardite cover can be arranged in a way that allows however many years of application while also maintaining a maximum contaminant flux in a desired level. Of course, even if leonardite is just a one-time application, increasing the height of it in each drip irrigation place will multiple the cost at the same time, especially for large scale projects/farms.

The last remaining topic is yearly application of contaminated water. One may not bound to apply a contaminated irrigation water for all 20 years. Fewer years or intermittent applications may also prove to be successful. For that, the most feasible leonardite cover in this study, 2 cm is chosen to assess 5, 10 and 15 years of atrazine application.

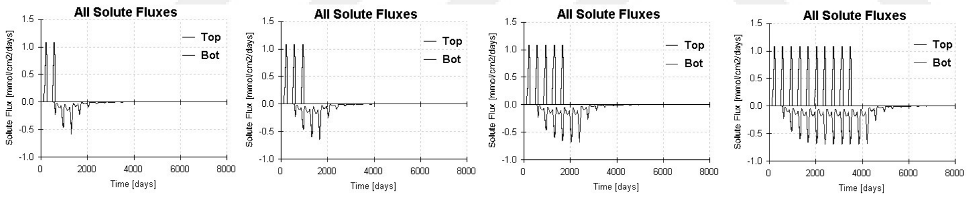


**Figure 35.** From left to right 2,3,5 and 10 years of atrazine contaminated water application to 2 cm leonardite 98 cm vertisol soil

After 3 years of application, atrazine sorbed by leonardite mostly removed (Figure 35). In general, after stopping the application of atrazine contaminated water, 2000 days were required to virtually desorb all sorbed atrazine. Up to 5 years, maximum flux of the atrazine was proportional to the application year, -0.4 onwards from 1 year to almost -0.7 for 5 years, and -0.7 in 10 years.

As a result, with 2 cm leonardite layer, after 2 years of application and 3 years of uncontaminated irrigation water, the peak bottom flux of atrazine will be cut in nearly half and the desorption will be distributed to 3 years, albeit heterogeneously, impacted by heterogeneous application of atrazine (Figure 36).

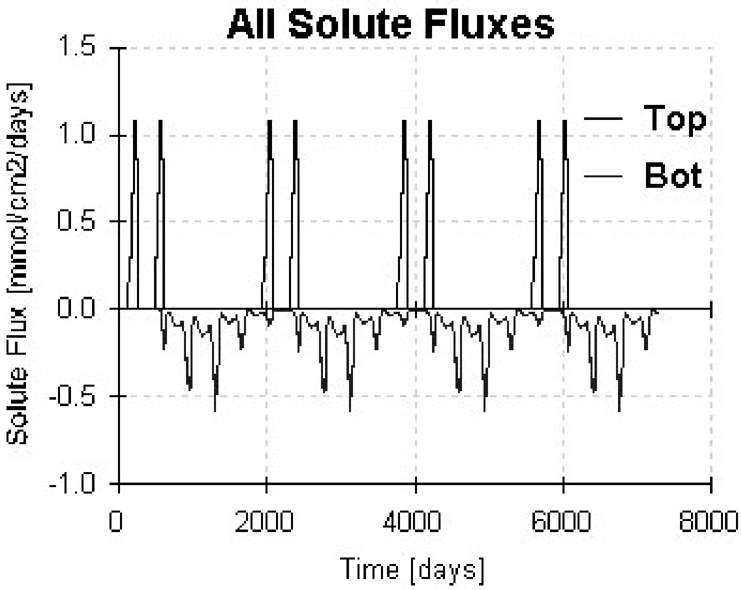


**Figure 36.** Example application of atrazine with 2 years contaminated irrigation and 3 years uncontaminated irrigation on 2 cm leonardite 98 cm vertisol

## 4.2 Cypermethrin sorption models

Cypermethrin has many apolar groups (Figure 37), like diphenyl ether structure, cyclopropane and some other carbon-carbon bonds. It has also some polar parts such as carbon-chlorides, ester and nitrile, yet altogether the structure is quite hydrophobic, with a reported water solubility of 4 µg/L in 20 ºC (National Center for Biotechnology Information, n.d.). As a result, its movement in groundwater, and sorption more affected by soil organic matter, compared to the sorption of atrazine.

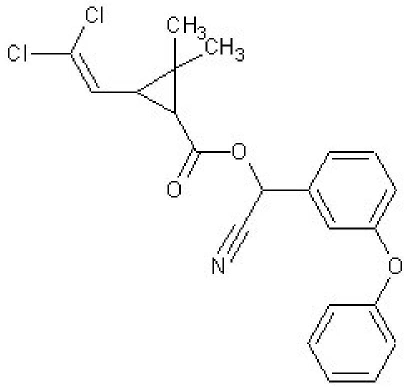


**Figure 37.** Cypermethrin molecular structure

Literature is, especially compared to the atrazine, very poor in terms of sorption behavior of cypermethrin species in soil. Only the following research with two soils (Table 22) were found regarding cypermethrin sorption in soil.

**Table 22.** Properties of the two soils modeled in cypermethrin adsorption experiments

| Soil Texture | Clay % | Silt % | Sand % | $K_f$ | 1/n | OC % |
|---|---|---|---|---|---|---|
| Sandy loam | 7 | 22.8 | 70.2 | 9.12 | 1.07 | 0.33 |
| Silt loam | 18.5 | 56.9 | 24.6 | 22.9 | 1 | 1.25 |

Data for cypermethrin sorption was taken from a study (Singh & Singh, 2004) which investigated two different Indian soil with given properties. Sandy loam soil for cypermethrin sorption study is loosely similar to the cambisol properties in our groundwater models, so its results were interpreted as CAM_C, and eutric cambisol of atrazine models. Silt loam is more similar to the haplic calcisol of atrazine sorption models and outputs named as CAL_C.

CAL_C

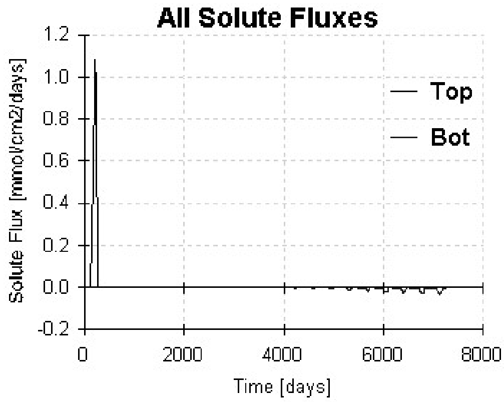


**Figure 38.** Cypermethrin leach after 1-year application of cypermethrin contaminated water to calcisol similar soil

Calcisol similar soil in this example, effectively immobilized cypermethrin, as seen in Figure 38. Unlike atrazine, as cypermethrin's sorption is very high to the organic matter, and at the same it is not advised to apply with drip irrigation system, since it was used as foliar application, the complete immobilization should be sought.

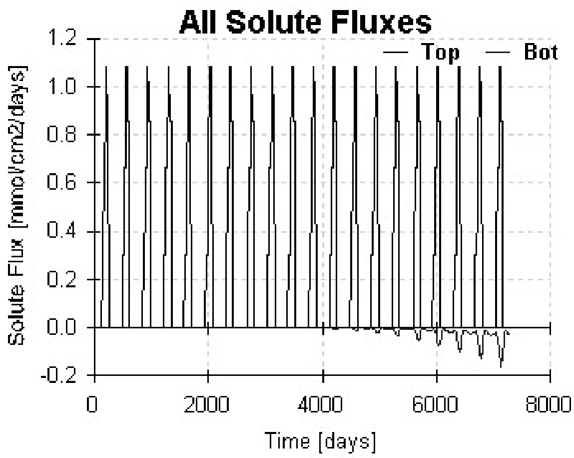


**Figure 39.** Cypermethrin leach after 20-year application of cypermethrin contaminated water to calcisol similar soil

Even with 20 years of continuous cypermethrin application (Figure 39), bottom flux was seen very small compared to the cypermethrin entry in cambisol. Yet, what should ben remarked is that there is a considerable amount of mass of cypermethrin in soil after 20 years of application and it was expected to leach for a very long time as more than 11 years were required to see cypermethrin at the bottom. In order to see the shape of this widened desorption, 60 years of modeling was done, with only 20 years of pesticide contaminated irrigation water application.

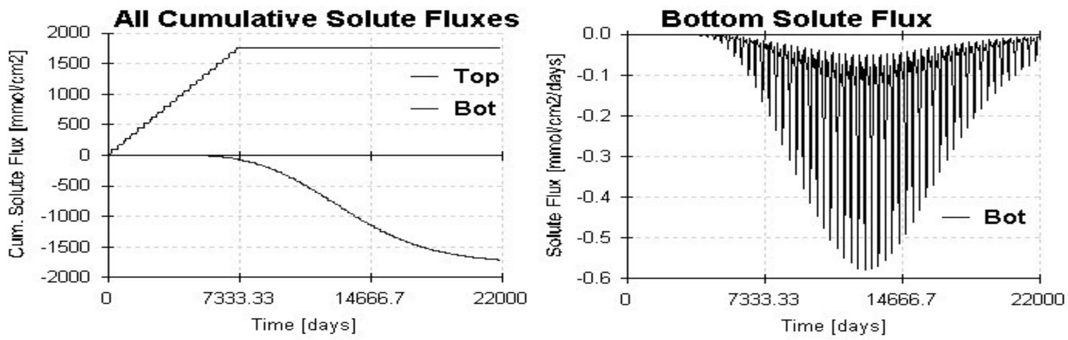


**Figure 40.** 60 years of desorption model of Calcisol, after 20 years of cypermethrin application

The lag time for desorption is nearly 20 years (Figure 40), and due to the high sorption capacity of corresponding soil, almost a Gaussian dispersion curve seen in the bottom flux of cypermethrin. The maximum efflux is almost half of the influx.

CAM_C

Cambisol type soil's sorption was not as effective as calcisol (Figure 41 and 42), most probably due to the organic carbon percentages, with calcisol (1.25 %) has nearly 4 times of organic carbon that cambisol contains (0.33 %).

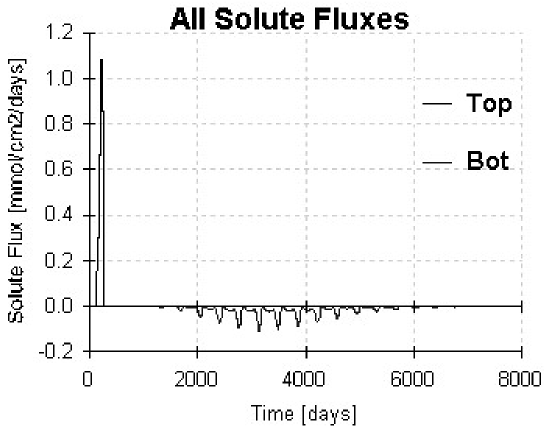


**Figure 41.** Cypermethrin leach after 1-year application of cypermethrin contaminated water to cambisol similar soil

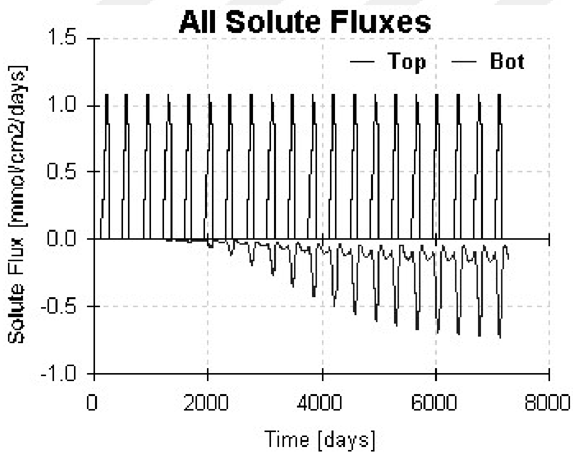


**Figure 42.** Cypermethrin leach after 1-year application of cypermethrin contaminated water to cambisol similar soil

Thus, it was not recommended to use cypermethrin contaminated groundwater on soils similar to this much of sorption, as it will not be able retard cypermethrin completely, even though there is still a considerable lag time of 2000 days exist.

# CHAPTER 5

# DISCUSSION

## 5.1 Assumptions

Many other parameters, such as, organic matter decomposition to form plant-available N, soil heterogeneities and plant solute stress were also not modeled. The principal aim of this study was a comparison between these 15 different soil types and under 4 different climates to see which ones are more likely to have high NUE, cause lower amount of N leach and faster N removal from aquifer. Addition of more components to these model would overshadow the differences. Another assumption to be considered is *No harmful elements in groundwater.* There are, many pre-treatment options to solve this problem for VOC (Richardson & Kern, 1998), for heavy metals (Salahdin, et al. 2016). So this will not render P&F out of option.

## 5.2 Cost Savings

In our models, benefit was only dependent on how much water were abstracted from the ground. As in Table 23;

**Table 23.** Cost savings in different climates by redeemed N mass from aquifer

| Climates | A | B | C | D |
|---|---|---|---|---|
| Pumped N mass (g) | 57957 | 65463 | 97176 | 33296 |
| Value (TL) | 410 | 463 | 687 | 235 |

value was calculated as the average of diammonium phosphate and urea costs mentioned earlier, which is equivalent to 7.07 TL/kg N. From unofficial discussions of farmers about the money can be earnt with 1 ha farm, it is in the orders of 20000 TL to 30000 TL for entire year. It is certainly profitable if drip fertigation system is considered.

In short, the more groundwater requirement, the more profit, and same for more contamination. This results in elimination of Black Sea or similar rainy regions for P&F process. For the other regions of Turkey, contamination level and longevity, required water, leaching N should be considered together to reach a conclusion.

## 5.3 Model Stability

Peclet number is a dimensionless number used to see here whether our groundwater models are advection dominated. It is calculated as in the following equation:

$$Pe = \frac{v\Delta x}{D} = \frac{\Delta x}{\lambda}$$

where, $\lambda$ is dispersivity and $\Delta x$ is length of the cell dimension in models. In all of the models run in this study, Peclet number was below 1, and Courant number also never exceeded 1, from the constraint of HYDRUS software itself, and there was not any mass balance error for solutes above 0.01 %.

# CHAPTER 6

# CONCLUSION

Pump & fertilize (P&F) research in literature is poor, even if it seems quite simple. 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 P&F, there should first be a hypothetical study in which the effects of the main variables, such as soil and climate properties, were found out. This is the aim of this thesis. We took one kind of crop (maize), homogeneous-isotropic aquifer and investigated the changes in the outcome in different climate and soils prevalent in Turkey. Meteorological data were available in website of Turkish State Meteorological Service and Meteoblue, textures of soils were found from the literature. Software Criwar 3.0 and Rosetta Lite v1.1 were used to generate parameters required for modeling water transport. Additionally, possible other ingredients in contaminated groundwater, atrazine and cypermethrin in our study, were also modeled with HYDRUS 1D to check their leaching to deeper regions.

From our exploratory modeling study, with hypothetical values generated by academic software, especially C (Şanlıurfa similar) climate conditions were found to be very promising to realize P&F method in terms of $NO_3^-$ contamination for the reclaiming of groundwater. As a threshold value, we chose 50 mg/L of $NO_3^-$ to model, yet, there are many reported cases, in Şanlıurfa as well, that even exceeds 300 mg/L $NO_3^-$, which makes P&F even more attractive. And for leaching, silt loam, fluvisol and vertisol were found to be more satisfactory. From the sorption studies of atrazine and cypermethrin, we found out that instead of fixed limits for pesticides/herbicides, determination should be done specifically for each site. In the case of high leaching potential from a certain soil, amendments can be applied to increase the efficacy of sorption, and consequently retardation of the pesticide. Differences of sorptive power of the soils should be taken into account as it may act as a slow releasing pesticide source even though the pesticide just applied directly. From our HYDRUS 1D models, fluvisol and dystric cambisol example soils reduced the concentration of atrazine in the top flux to 1/10 of it in bottom flux, calcisol and eutric cambisol diluted it to 1/5, and kastanozem similar soil reduced it to 1/20 of its applied concentration and only started to leach after more than 2000 days. Additionally, in the case of an unwanted species, effective immobilization can be achieved with very strong sorbents, like leonardites. For cypermethrin, calcisol example effectively immobilized 1 year of cypermethrin application, and after 20 years of continuous application it only leached between 20$^{th}$ and 60$^{th}$ years, with 1 half of applied concentration at its maximum.

However, hypothetical studies have their own limitations. Precipitation and irrigation were assumed to be averaged entirely for each stress period. This assumption certainly underestimates N leaching. Aquifer was homogeneous and isotropic. For a small scale calculation this assumption will most probably yield incorrect results, yet in a regional setting effective soil hydraulic parameters might be averaged to some values. Erosion was neglected, and even if there are cases where it is virtually negligible, in most open settings they are present, still, its effect can be diminished by management.

N fate in groundwater, also in unsaturated soil is quite complex. For the assessment of the real cases as to decide whether or not to apply P&F, entire soil profile, hydraulic properties, cationic/anionic exchange capacities, reducing mineral ingredients; such as sulfur or manganese minerals, prevalent bacteria in the corresponding environment; *Nitrospira spp.* (Daims & Wagner, 2018), ANAMMOX (Smith, et al., 2015), and entire source/sink documentation for N in that region is critical. In addition to all these significant parameters, though, the real N uptake rate of major produced plants should be determined. To the best of our knowledge, there is no such disseminated knowledge around the world, except the source we used in this study, about maize, for instance, yet since then many different hybrids and species of maize were developed. It is apparent that there will be both agronomic and environmental value on this information. In conclusion, to feed the growing population of the world, while moving through more sustainable agricultural options, in the transition period P&F can be a very promising choice for not only diminishing the required N to be fixed from atmosphere, but also remove $NO_3^-$ from contaminated groundwater at the same time.

One drawback of P&F is that, high $NO_3^-$ concentrated irrigation water can only be applied with micro-irrigation methods. Among the most produced global crops, wheat and rice are out of option, only row crops, like maize, are suitable; and another concern is leafy vegetables with a harmful nitrate accumulation potential on leaves, causing health problems, even colorectal due to the generation of *N*-nitroso compounds in body (DellaValle, et al., 2014). Second, precise agriculture is even more critical, as slightly incorrect convey of fertilizer containing water will result in excessive weed formation, and consequently reduce the efficiency of entire process. Third, $NO_3^-$ is the most leaching susceptible form of the N fertilizer, ensuring efficient uptake of it by plants is difficult, especially with soils vulnerable to N leach, such as high sand containing textures.

Moreover, continuous monitoring of N concentration in groundwater is necessary to get maximum profit and minimum loss/leaching. With these prerequisites, high irrigation water requiring regions with aquifers having low leaching, like silty clay loam, are promising for P&F. One of the main risk is possibility of co-contaminants, but pre-treatment options are present, such as leonardite cover. The other one is climate change, in which it might disrupt the farm by sudden flooding or extended droughts, and not only trigger more N leach but also can damage crops directly. Even though there are possible risks on profiting P&F in a long term, the system can be adjusted for many things as well. Other crops can be planted than maize, or double cropping in a year might be done if situation allows. If $NO_3^-$ leaching is more severe than expected, trees can be planted, especially the ones with uncompetitive root structure, i.e. less shallow roots and more deep roots (Schroth & Sinclair, 2003). If climate variables are extremely problematic and even damaging, a greenhouse closure may be a solution. In short, P&F is a very versatile and sustainable option.

Another thing to be kept in mind is that for remediation methods, such as permeable reactive barrier of zero valent iron, denitrifying bacteria or adsorptive media, there will always be additional cost to destroy the potential fertilizer and at the same time there will not be any compensation for both their side products and environmental burden of manufacture of nitrate.

With this study, we pointed out the fact that climate, and consequently, irrigation water requirement is crucial while calculating the feasibility of P&F, as the more increasing irrigation water requirement, the more beneficial process becomes (687 TL/year in C climates). And we indicated the places/conditions in Turkey where P&F is promising. We also found that other contaminants in nitrate containing groundwater can be handled by sorbents, such as leonardite, to both reclaim groundwater as an irrigation/fertilizer source as well as valor other ingredients. All in all, this system was found to be promising for people who already considers drip-fertigation system for their farms, which are composed of row crops and situated in climates, where irrigation water requirement is comparatively higher.

However, many kinds of studies are necessary to actualize P&F application on $NO_3^-$ contaminated groundwater. First of all, daily nutrient uptake of crops sown in Turkey should be precisely modeled. Secondly, reactive transport model for Nitrogen species should be established and generalized, right now individual researches make many different reactive transport models under different platforms. Thirdly, a comparatively easier part, leaching of $NO_3^-$ in different homogeneous soils, and also undisturbed soil columns should be studied. Lastly, precise application of the fertilizer to increase N use efficiency and reduce N losses should be researched and developed.

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