PESTRANS: A SOFTWARE DEVELOPED FOR ASSESSING THE FATE AND TRANSPORT OF PESTICIDES IN SOIL ENVIRONMENT

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ABSTRACT

PESTRANS: A SOFTWARE DEVELOPED FOR ASSESSING THE FATE AND TRANSPORT OF PESTICIDES IN SOIL ENVIRONMENT

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Excessive and uncontrolled use of plant protection products in Turkey caused major concerns as many pesticides proved to possess hazardous impact on soil and groundwater systems. The main objective of this thesis is to develop a computer screening model that has capabilities to simulate fate and transport of pesticides in soil. The developed computer model integrated with a graphical user interface, named as PETRANS GUI, enables users to screen pesticides based on mobility, volatility, persistence, and determines their pollution potential. PETRANS GUI model development was based on an earlier FORTRAN source code that was created by Ünlü et al. (1995). Source code algorithms were reconstructed on an up-to-date programming language, python, to facilitate the construction of a new version of PETRANS screening model, which is computationally more robust and efficient than its earlier version. PESTRANS GUI is a 1-D simulation toolkit which utilizes finite-difference method to provide numerical simulations of real case pesticide application scenarios on agricultural soils. Computational speed of PETRSANS GUI, on standard PC, was less than 5.5 seconds CPU time for 10 years real-time pesticide simulation of 1-m soil depth. The model assessed fate and transport behavior of 24 priority pesticides in Turkey and the EU, in terms of mobility, volatility and persistence. Pesticides such as simazine, atrazine and diuron proved to have higher groundwater pollution

potential. Whereas pesticides; heptachlor epoxide and quinoxyfen demonstrated high pollution potential to surface water. It is important to re-regulate or ban the use of these priority pesticides for eliminating their adverse environmental impacts.

Keywords: Pesticide Modeling, Priority Pollutants, Python programming, Graphical User Interface (GUI), Screening Pollutants

ÖZ

PESTRANS: PESTİSİTLERİN TOPRAKTAKİ AKIBETİNİN VE TAŞINIMININ DEĞERLENDİRİLMESİ İÇİN GELİŞTİRİLMİŞ BİR YAZILIM

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Türkiye'de bitki koruma ürünlerinin aşırı miktarda ve kontrolsüz kullanımı, pek çok pestisitin toprak ve yeraltı suyu kirliliğine yol açması sebebiyle en kritik konulardan biri olarak kabul edilmektedir. Bu tezin temel amacı, tarımsal topraklarda uygulanan pestisitin akıbetinin ve davranışınının anlaşılmasını sağlayacak bir bilgisyar tarama modeli geliştirmektir. PESTRANS GUI adı verilen bir bir kullanıcı arayüzü ile engre edilen bu tarama modeli kullanıcının pestisitleri hareketlilik, buharlaşma ve dayanıklılık özelliklerine sınıflamasını ve kirlilik potansiyellerini belirlemesini sağlamaktadır. PESTRANS GUI modeli daha önce Ünlü et al. (1995) tarafından FORTRAN dilinde geliştirlen pestisit taşınım modelinin sayısal çözümlerine dayalı olarak tasarlanıp geliştirilmiş bir modeldir. PESTRANS GUI, gerçek durum pestisit uygulama senaryolarının matematiksel modelinin sayısal çözümlerini sağlamak için Finite-Difference yöntemini kullanan Python Tkinter araç seti üzerine inşa edilmiş tek boyutlu bir simülasyon modelidir. PESTRANS GUI'nin yeni versiyonu eski versiyonuna göre sayısal hesaplama olarak daha hızlı ve verimlidir. PETRSANS GUI'nin , 1 m toprak derinliğinde, 10 yıllık gerçek zamanlı pestisit taşınım simülasyonu için standart bilgisayarlardaki hesaplama hızı CPU zamanı olarak 5,5 saniyeden azdır. Geliştirilen model kullanılarak Türkiye ve AB'de araştırmalarda

öncelikli kimyasallar olarak sınıflandırılan yirmi dört pestisitin akıbeti ve davranışı hareketlilik, buharlaşma ve dayanıklık açısından ayrıntılı incelenmiştir. Simazin, atrazin ve diuron gibi pestisitlerin daha yüksek yeraltı suyu kirliliği potansiyeline sahip olduğu kanıtlanmıştır. Heptaklor epoksit ve kinoksifen gibi pestisitler ise yüzey suyunda yüksek kirlilik potansiyeli sergilemiştir. Bu öncelikli pestisitlerin olumsuz çevresel etkilerini giderecek şekilde kullanımlarının yeniden düzenlenmesi veya yasaklanması önem arz etmektedir.

Anahtar Kelimeler: Pestisit Modelleme, Öncelikli Kimyasal maddeler, Python programlama, Grafiksel Kullanıcı Arayüzü (GUI), Kirleticileri Tarama

To my Parents

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LIST OF ABBREVIATIONS

ABBREVIATIONS

EC: European Commission

EEA: European Environmental Agency

EPA: Environmental Protection Agency, USA

EQS: Environmental Quality Standards

EU: European Union

GLEAMS: Groundwater Loading Effects of Agricultural Management Systems

MAF: Ministry of Agriculture and Forestry in Turkey

MEU: Ministry of Environment and Urbanization in Turkey

PELMO: Pesticide Leaching Model

PPP: Plant Protection Product

PRZM: Pesticide Root Zone Model

RAIS: Risk Assessment Information system

SWAT: Soil and Water Assessment Tool

TU: Tennessee University

TUBITAK: Scientific and Technological Research Council of Turkey

USDA: United States Department of Agriculture

WFD: Water Framework Directive

WTP: Water Treatment Plant

WWTP: Wastewater Treatment Plant

LIST OF SYMBOLS

SYMBOLS

C_T: Total concentration of pesticide in soil

C_s: Pesticide concentration in Solid phase

C_w: Pesticide concentration in aqueous phase

C_g: Pesticide concentration in gaseous phase

ρ_b: Bulk density of soil

f_{oc}: organic carbon fraction in the soil

K_{oc}: Organic Carbon partitioning coefficient

K_H: Dimensionless Henry's constant

θw: Volumetric water content in the soil

θg: Volumetric air content in the soil

q_w: Water flux: Infiltration/Evaporation rate

D^o_g: Bulk air diffusion coefficient

D^o_W: Bulk water diffusion coefficient

d: Air boundary layer thickness

Δz: Depth increment

H: Total depth

L: Pesticide mixing depth in soil

$T_{1/2}$: Half-life

PESTRANS GUI Output Symbols and Abbreviations:

TIME: Time

VAPF: Vapor Flux within Δt time segment

SVAPF: Sum of Vapor flux within Δt

VAPM: Vapor Mass within Δt

SVAPM: Sum of Vapor mass within Δt

DRAINF: Leaching Flux within Δt

SUMDRF: Sum of Leaching Flux within Δt

DRAINM: Leaching Mass within Δt

SUMDRM: Sum of Leaching Mass within Δt

SUMM: Pesticide Mass remaining at time t

PCDECM: Pesticide Degradation Percentage at time t

PCVAPM: Pesticide Volatilization Percentage at time t

PCDRM: Pesticide Leaching Percentage at time t

PCTMR: Pesticide Remaining Percentage at time t

PCTML: Pesticide Loss Percentage at time t

ORMBE: General Mass Balance Error Percentage at time t

DEPTH: Depth

CONC: Pesticide Concentration

TVM: Total Evaporated Pesticide Mass at time t

CHAPTER 1

INTRODUCTION

Plant protection products (PPP), which are well known as pesticides, are chemical pollutants used to protect agricultural plants from pests. Pesticides mostly include herbicides, insecticides and fungicides, which eliminate source of damage to plants. The dependence on pesticides in agricultural production has been a controversial issue worldwide since its early discovery in 1930s. Use of pesticides in agricultural lands improved food productivity from 50 million tons in 1948 to 198 million tons in 1997 (Aktar et al., 2009). Famine decreased significantly after protecting agricultural plants with pesticides. However, it was discovered that many pesticides have pollution potential that would impose risk to disturb the ecological system, human health, as well as the quality of soil and water resources. Pesticides are considered as a direct hazard on farmers. In a study of Indian Institute of Occupational Health in 1992, farmers who spray methomyl in agricultural lands found to suffer from cardio toxic health impact. Other pesticides such as malathion, lindane and DDT caused symptoms including cardiorespiratory, nausea and irritation in case of direct exposure with the chemical (Aktar et al., 2009).

Remaining of pesticides were found in food commodity products by the European Union Monitoring Program established in 1996. Indirect exposure to pesticides-imposed risk on health of consumers as well. Depending on their physical and chemical properties many pesticides tend to indicate high leaching potential to cause contamination of soil and groundwater. According to Vryzas (2018) pesticides' physical and chemical properties determine their mobility, persistence, and bioactivity as well as environmental factors and site conditions. Metabolic and physicochemical processes affect the behavior of pesticides applied on agricultural soils. Transfer of pesticides is normally caused by leaching, volatilization, and water drifting to expand

the contaminated area. Pesticides were categorized from relatively mobile chemicals to low mobility. Diffusion, advection and mass transfer, which is related to adsorption and volatilization, cause pesticides to migrate through soil profile where mobility is considered highest in low organic matter soil textures. Microbial bioactivity increases with high solubility and moderate pH levels. Degradation of pesticides due to microbial activity is a crucial process to break down the persistence of the chemicals.

In order to reach comprehensive understanding of pesticides fate and behavior in the environment, a multi-disciplinary approach must be implemented to conduct a successful environmental assessment. Estevez et al. (2008) studies the relationship between mobility and degradation of pesticides in the environment. Degradation increases for pesticides which bind strongly to soil surface, thus, increasing the retention time for such process. In addition, organic carbon content, moisture content and pH play significant role in the degradation of pesticides. Consideration of physical and chemical interactions between pesticides molecules and environmental components would lead to enhanced environmental assessment then to justified regulations to increase the awareness of the controversial effects of these pollutants. For example, Silva et al. (2019) investigated pesticides remaining in 11 EU countries collecting samples from 317 agricultural soils in 2015. The aim was to prove that some pesticides have strong resistance to biodegradation. Among the tested agricultural soils 80% of the samples contained pesticides remaining. Although some pesticides such as DDTs and epoxiconazole were banned from use long time ago, they were found in high concentrations. This triggers the need to regulate pesticide use and implementation of modeling as a tool to propose action plans for pollution prevention.

1.1 Trends of Pesticide use in the world and Turkey

Insecticides were produced significantly in the 1940s after it was discovered that DDT played noticeable role in fighting malaria and diseases caused by insect transport. Since then, extensive use of pesticides was conducted for decades. However, dependency on these chemical compounds increased until their negative impact on human health was discovered.

Recently, many developed countries tend to reduce their reliance on chemical intervention during agricultural production process. Utilizing organic and biological means indicated fewer risks to human health and provided safer food products. Figure 1.1 shows the evolution of pesticide use in the world, then in the USA, European Union (EU) countries and the least developed countries, respectively. Apparently, EU countries reduced their dependence on pesticides significantly in the past 20 years by issuance of new legislations and regulations which limits the consumption of these chemicals to a certain extent. USA also takes a slightly inclined trend to reduce pesticide applications. However, agricultural sector in the world in general is still in favor of pesticides instead of biological and organic technologies taking into consideration of cost prospective. Least developed countries still consider plant production products as useful gadget to enhance agricultural production and thus economic welfare. These countries continue to have increasing trend of pesticides consumption owing to limited number of restricting environmental laws to regulate pesticide usage.

The total consumption of pesticides worldwide was approximately 2 million tons a year in early 1990s. China has been considered to be the highest contributor to pesticide consumption, then the United States and Argentina follow. The annual consumption of pesticides is expected to increase to 3.5 million tons by 2020 (Sharma, et al., 2019).

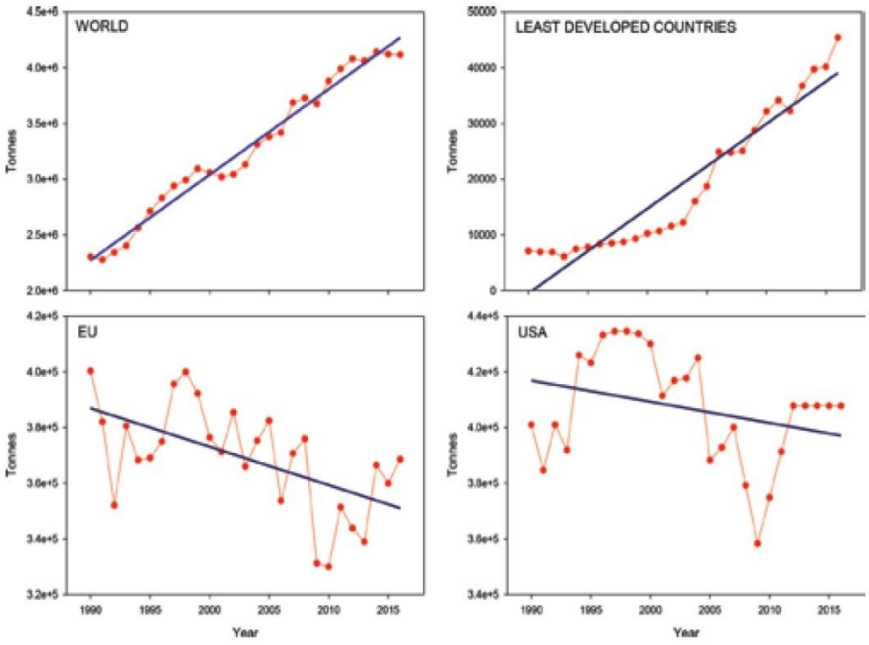


Figure 1.1: Trends of worldwide pesticide use during the last two decades, (Larramendy and Soloneski, 2019)

Since its recognition as a candidate for EU member state in 1999, Turkey has been working to reduce the use of PPPs. Environmental Quality Standards (EQS) were adapted in order to regulate consumption of pesticides during agricultural production. Between 2011 and 2016, Turkey classified 45 chemicals as priority pollutants, which are associated with high potential to disturb ecological system. Those 45 priority pollutants were previously declared within the EU Water Framework Directive (2000/60/EC) (Orhon et al., 2017). Plans for management of River Basins were prepared by Turkey since 2014 as part of the steps of the EU accession. In addition, 250 specific pollutants were recognized by Turkey to minimize risk of pollution imposed on water bodies. Regulations have been implemented by the Ministry of Agriculture and Forestry (MAF) in Turkey to adhere to EQSs. For example, use of agricultural nitrate pollutants was regulated by the Turkish government in 2004 to protect water basins (Akay, 2016). MAF has been conducting several projects within the scope of "Good Agricultural Practices" to minimize dependence on PPPs. It aims to reduce consumption of pesticides in agriculture by 50 % by 2023. Few projects

recommended the increase of the awareness of Turkish farmers to mitigate the dependency on use of chemicals in agricultural production (Gün & Kan, 2009).

Many agricultural areas in Turkey depend on PPP as shown in Figure 1.2 prepared by the Ministry of Environment and Urbanization (MEU) in Turkey in 2017. It was reported by Ministry of Agriculture and Forestry (MAF, 2017) that the use of pesticides increased approximately 8% between 2016 and 2017. Antalya, Manisa and Adana were among the provinces with the highest consumption of pesticides in agricultural activities. Use of pesticides in Turkey was distributed as 44% fungicides, 22.8% insecticides, 23.5% herbicides, 4.9% acaricides, 0.5% rodenticides and 12.4% other PPPs in a survey conducted by Turkish Statistical Institute (TSI, 2017).

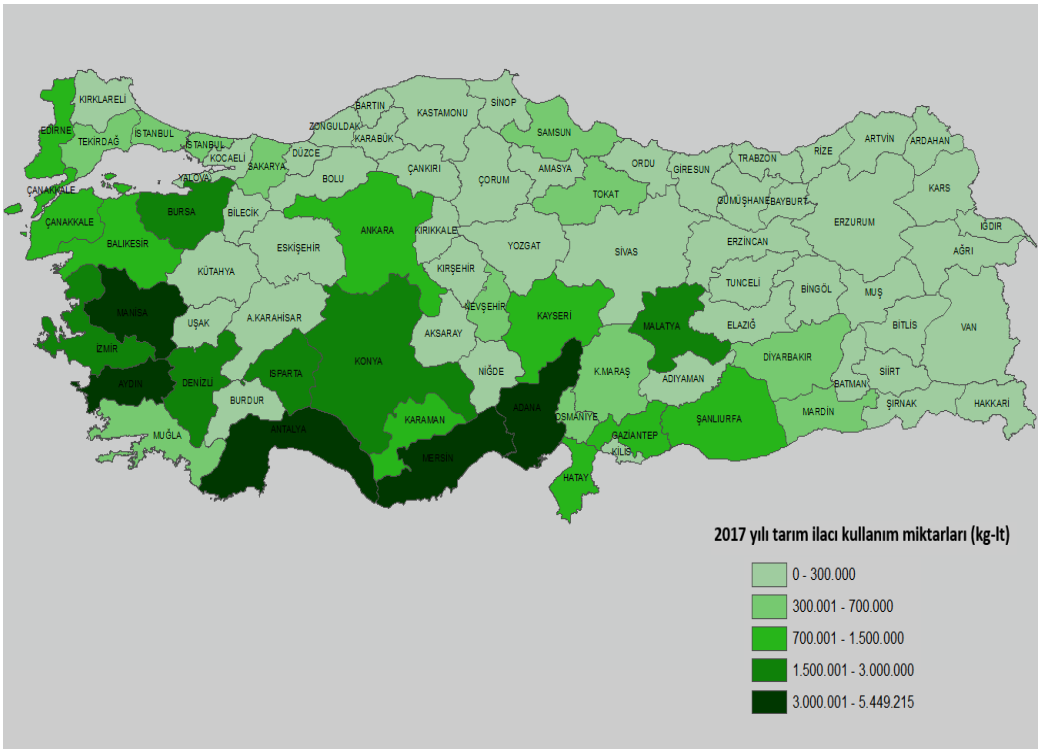


Figure 1.2: Distribution of pesticide use in Turkey in kg/l (MAF, 2017)

Erdoğan et al. (2017) conducted a study to indicate the amount of pesticides consumed in Turkey between the years 2006 and 2015 based on the information gathered from Turkish Statistical Institute for the years investigated. Table 1.1 shows the amount of product consumed in tones per annum. The study shows a decrease in pesticide and

fungicide consumptions. However, dependence on insecticides and herbicides increased between 2006 and 2015 in Turkey. The excessive use of pesticides triggers the need to investigate fate and behavior of these chemicals after applications.

Table 1.1: Pesticide consumption in Turkey between 2006-2015, (Erdogan et al., 2017)

Plant protection product	Consumption (tons), Turkey 2006	Consumption (tons), Turkey 2015
Pesticides	45,376	39,026
Insecticides	7,628	8,177
Herbicides	6,956	7,825
Fungicides	19,900	15,984

1.2 Environmental Fate and Transport of Pesticides

Pesticides undergo several pathways after applications on agricultural soils. Figure 1.3 depicts the processes regarding the pesticide fate and transport in the environment. Many factors control the fate and transport of PPP such as soil texture and other physical, chemical, and biological soil characteristics, site climatic conditions, and physical and chemical properties of the pesticides. For example, plant root uptake of pesticide may differ according to pesticides' water solubility and potential to be absorbed by plant roots.

Transport of pesticide after application may occur owing to drift of air movement or washing out with rain run-off. Pesticides may transport from the application area to surrounding lands by wind drift or rain-wash. Run-off is considered as a significant factor in contamination of surface water. It may cause up to 90% of pesticide to be drifted from the agricultural area of interest. In addition, loss of pesticide may occur owing to air drift. Wind blows up to 25% of the pesticide applied on agricultural lands causing ecological disturbance in the surrounding areas (Ahemad & Khan, 2013).

Magnitudes of drifts or run-off determine amount of pesticide to be drifted away from the applied soil.

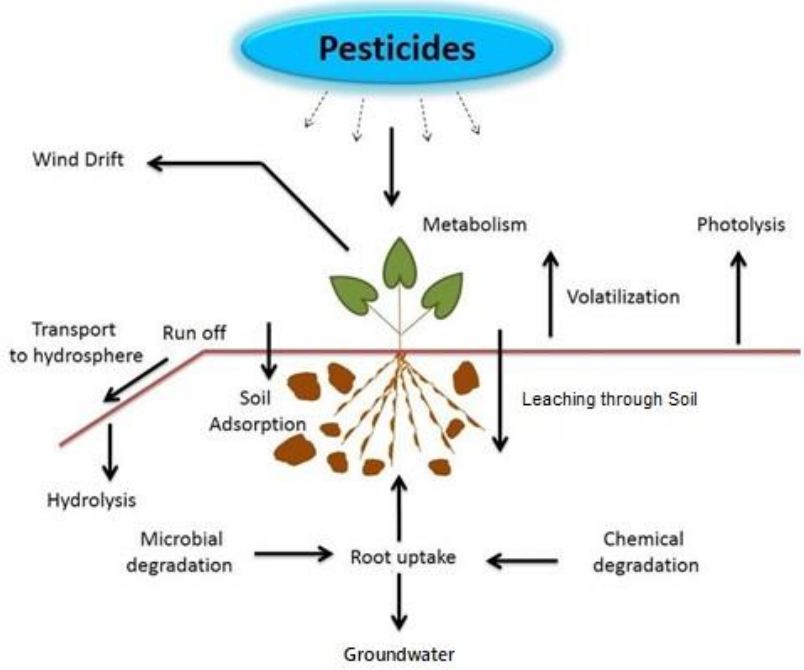


Figure 1.3: Pesticide fate and transport in the environment, adopted from Ahemad & Khan (2013)

The breakdown of pesticides into simpler chemicals is called degradation. Breakdowns are caused by microbial activity, light energy and chemical interactions. Processes require a certain period of time to occur and they depend on physical and chemical properties of both pesticide and soil. Biodegradation is a process carried out by microorganisms to use pesticide as a source of energy. Temperature, water content and pH levels as well as organic matter content in the soil affect microbial activity. Half-life of pesticide is related to biodegradation and a crucial parameter to indicate the persistence of pesticide in the environment. According to Tiryaki (2010), if half-life of a pesticide is more than 100 days, then pesticide is considered to be persistent in soil; when half-life is in the range between 30 to 100 days, pesticides are considered to be moderately persistent; finally, if half-life is below 30 days, they are classified as

degradable. In addition, pesticides undergo rapid chemical transformation caused by redox reactions in soil. As a result, acidic or alkaline soil environments affect the degradation of pesticide by lowering the microbial activity. Photochemical reactions also increase the degradation of pesticides after exposure to certain sunlight intensity. For example, glass filters ultraviolet sunlight and thus, more pesticide degradation takes place in plastic greenhouses (Tiryaki, 2010).

Pesticides may reach groundwater by downward movement through porous media in a phenomenon called leaching. Force of gravity play significant role to increase water movement, thus, vertical mobility of pesticide as well. However, many factors involve in slowing down pesticide movement such as sorption interactions, capillary forces and pesticide volatility. Soil texture acts as a filter to clean infiltration flux from contaminants due to adsorption, but differences in chemical properties of pesticides may increase or decrease their leaching potential. Pesticide application rate and plant uptake are also considered during estimation of pesticide leaching concentrations. The downward movement of water transports pesticides to contaminate unsaturated soil zones and further reach the groundwater. Pesticides physical and chemical properties determine type of interactions with the soil texture. Pesticides' organic carbon partition coefficient (K_{oc}) and adsorption (distribution) coefficient (K_d) are good indicators for their leaching potential through soil zones to contaminate groundwater (Ahemad & Khan, 2013).

Pesticide molecules may interact with surface of soil particles via adsorption-desorption processes, which slow down the movement of pesticide in aqueous phase. Dry soil adsorbs more contaminants than soil with high moisture content owing to higher available surface sites. The K_d value of a pesticide indicates the amount of interactions with the solid surfaces. High K_d values would result in high adsorption to soil particle surfaces. Fine particles adsorb more than coarse soil particles owing to larger surface area available for adsorption. The K_{oc} value is also an important parameter to determine sorption interactions of pesticide molecules with soil organic carbon surfaces. High K_{oc} values of pesticides show greater tendency for binding on organic solid surfaces. Strong binding between solid surfaces and pesticide molecules

would decrease pesticide mobility and contain the contaminant within the application zone (Tiryaki, 2010).

Pesticide may be transferred from solid or liquid phase to gas phase through a process called volatilization. Properties such as vapor pressure and Henry's law constant are in general considered to classify pesticides based upon their volatilities. Volatile pesticides are likely to have high vapor pressure and high Henry's law constant, as the chemical molecules tend to maintain stability in the gaseous phase. Volatilization may be induced by other factors such as temperature, wind velocity and moisture content in the soil. However, water solubility of pesticide is also important in the volatilization process, as more soluble chemicals would have tendencies to volatilize into air depending on their hydrophilicity. Volatilization of applied pesticides is a crucial process in the consideration of persistence. For example, Jury et al. (1984) calculated a dimensionless K_H value to categorize volatility of pesticides based on environmental and soil properties affecting volatilization from soil. $K_H=10^{-5}$ as a dimensionless value is applicable for volatilization of pesticides from soil, which is obtained based on other environmental and soil properties affecting volatilization from soil, such as f_{oc}, K_{oc}, presence or absence of water evaporation from soil. In another words, pesticide with dimensionless $K_H > 2.5x10^{-5}$ were categorized as volatile chemicals. However, chemicals with dimensionless $K_H < 2.5x10^{-5}$ were categories to be less volatile compounds (Jury et al. ,1984).

1.3 Objective and Scope of the Study

This study aims to develop a 1D numerical computer model integrated into a user-friendly Graphical User Interface (GUI) software to simulate fate and transport behavior of pesticides listed as Priority Pollutants in Turkey for the purpose of classifying these pesticides according to their pollution potential. PESTRANS GUI software is built based on the source code of PESTRANS model which was developed by Ünlü et al. (1995). PESTRANS source code was written in the early 1990s on less versatile programming language FORTRAN without a graphical user interface to facilitate the application of the model. With the availability of more up to date programming language such as python and graphical tools, PESTRANS GUI model was constructed to provide a useful pesticide screening tool. Even less experienced users may face no difficulty to run the updated PESTANS GUI Model. Python programming language is considered one of the most useful programming languages nowadays. Thus, PESTRANS GUI model used the FORTRAN source code of Ünlü et al. (1995) and re-developed it on python programming language to produce the numerical code and a Graphical User Interface, which works easily on modern computer machines. Using PESTRANS GUI model, the user is enabled to simulate pesticides fate and transport in agricultural soils easily by entering input parameters to define the soil environmental system.

One of the other major purposes of this study is to develop an updated, reliable database to include pesticide physical and chemical properties and soil characteristics in order to facilitate pesticide fate and transport simulation for the user. In addition, options to enter user-defined values of input parameters are available in case the user acquires all values to define the soil environmental system without the need to the software database. Then, PESTRANS GUI considers all input parameters including pesticide physical and chemical properties, site climatic conditions, soil properties, in addition to application rate and spatial and temporal requirements of simulation to solve the governing differential equation in accordance with the relevant initial and

boundary conditions. The software utilizes Crank Nicholson numerical algorithms to solve the governing equation and provide the model output.

Model output obtained after a simulation run includes percentages of degraded, volatilized, leached and residual pesticide mass applied at the soil surface. In addition, a graphical plot of pesticide concentration versus vertical depth of soil profile is produced in the results window to allow the user to understand the pesticide behavior after application in agricultural lands. Python codes were converted to executable files to help the user to run the graphical user interface on modern computer machines with Windows Platform without the need of installation. Since the software includes databases and simplifies user handling of the input data, users with less expertise in environmental modeling would be able to simulate pesticides' fate and transport in unsaturated zone environmental systems easily without complications to propose recommendations for pesticides safer use in agricultural sector.

CHAPTER 2

LITERATURE REVIEW

The use of PPP increased agricultural productivity and enhanced economic welfare for human beings. However, the fate of these chemicals has been a major concern as some of these chemicals proved to possess a high contamination potential. Disruption of ecological systems and imposing a health risk on human beings triggered the need to investigate the behavior of pesticides in order to regulate their use. Researchers and scientific experts have been studying pesticides for decades by developing computer programs as an effective tool to understand the fate and behavior of these chemicals as well as conducting experimental and laboratory studies. Many researches created powerful modeling tools to identify major loss pathways of pesticides in the environment. However, each modeling software was associated with limitations and disadvantages which motivated other researchers to continue contributing to this field of study (FOCUS, 2014).

In this study, a comprehensive survey has been conducted over the literature to investigate previous scientific work in the field of pesticide fate modeling. It is very important to investigate major researches in the field of pesticide modeling to gain knowledge about the effective tools that have been developed over the past years to understand the challenges of modeling fate and transport of pesticides in the environment. Before the development of computer pesticide fate models, theoretical pesticide fate models were derived to investigate microbial biodegradation in soil (Soulas, 1982). Mathematical models were obtained based on mass balances to generate differential equations. However, consideration of all possible pesticide loss pathways without simplifications or assumptions lead to complicated partial differential equations which needed intensive numerical solution to solve the fate models. Computer models were not used frequently in the early 1980s. Therefore,

simplifications based on assumptions such as steady state dissipation of the pesticide in soil produced ordinary differential equations that can be solved with analytical solutions (Richter et al.,1996). In addition, linear models were derived by the assuming linear sorption and degradation processes for the pesticide in soil which simplified the differential equations to an extent that could be solved without the need to computer iterative numerical solution. According to Richter et al. 1996, analytical and Laplace methods were useful to solve the governing differential equations for simplified pesticide fate models in soil. However, the need to effective iterative numerical solutions for the governing differential equations urged pesticide model developers to use computer models to facilitate the cumbersome iterative numerical solution. Computer models were considered as helpful tools to evaluate pesticide fate in the environment before conducting field experiments. They provide the user with initial assessment of the climatic and variations that would create major impact on the pesticide fate, then they allow the user to run countless number of modeling scenarios to have a better understanding of the pesticide fate and behavior in soil (Calvet, 1995).

Computer models simulating fate and transport of pesticides in soil and groundwater has been developed gradually over the past years taking into relevant complexities. In one of the earliest attempts, Jury et al. (1983) developed a pesticide screening model to assess the fate and behavior of pesticides in soil. Loss pathways of the chemicals in the environment were investigated by constructing a mathematical model based on mass balance formulations. Chemicals tended to partition between air, water and a solid surface in an unsaturated soil layer as well as they degraded due to microbial activity. Some simplified assumptions such as uniformity and homogeneity of soil, linear equilibrium partitioning of the chemical through air, water and solid phases were introduced to construct the mathematical model. The model predicted the loss pathways of Lindane (γ-Hexachlorocyclohexane) and 2, 4-dichlorophenoxy acetic acid and identified the persistence, volatility and mobility of the chemicals. The model provided good predictions when validated to measured data. Thus, Jury et al. (1984) conducted further studies making use of the screening model to categorize pesticides based on persistence, volatility and mobility. Dividing chemicals into categories would

help to understand their behavior in the environment after application. A total of 35 chemicals, including some pesticides, were tested using the screening model to determine loss pathways. As a result, majority of chemicals such pesticides as bromacil, DDT, dieldrin demonstrated strong persistence, while other chemicals such as Benzene, Chloroform and Vinyl chloride showed high loss due to volatilization. After reasonable agreement with measured data, Jury et al. (1984) concluded that the environmental screening model could be used to classify pesticides to understand their behavior in the environment.

The sequence of studies conducted by Jury et al. in the 1980s motivated many researchers to work in the field of pesticide modeling to develop new computer programs to facilitate simulation of pesticide fate and transport. Carsel et al. (1985) evaluated the risk of pesticide leaching to groundwater utilizing Pesticide Root Zone Model (PRZM). PRZM was a one-dimensional computer simulation program developed in the 1980s by the US EPA to assess the behavior of pesticides in unsaturated environment. The model was used to simulate Aldicarb applied in agricultural soils in New York, Florida and Wisconsin. PRZM's simulation improved after calibrating sorption coefficients with measured data. Although the software proved to be a helpful tool to assess the behavior of pesticides in the environment, it showed overestimations in some cases. The first version of PRZM was restricted to few environmental scenarios and default values for pesticides properties, especially, gas diffusion coefficient. Also, PRZM did not consider the variations of water content in the soil during pesticide fate and transport modeling which lead to inaccurate simulations (Boesten, et al., 1997). Thus, the need for a flexible and accurate environmental model to simulate pesticide fate increased with time.

The study of pesticide fate and transport has been the main concern for governments worldwide to protect soil and groundwater environment. For example, the European union (EU) established a list of 45 priority pollutants in 2001 to investigate and assess the fate of these chemicals within the Water Framework Directive. The Framework approach was to prescribe steps to achieve goals and one of these steps was to prioritize certain chemicals for assessment. These pollutants proved to have significant pollution

potential which disrupted the ecological system and in order to protect water bodies and accomplish “good” qualitative status these 45 pollutants were given the priority to be studies thoroughly for their usage to be regulated (WFD, 2001). Certain pesticides were categorized among the 45 priority chemicals owing to their application practices and controversial environmental impact. The list included 24 concerning pesticides to be given priority in the environmental investigations and thus regulations. This thesis was also interested in investigating the fate and transport these priority pesticides to provide a recommendation of their usage. Furthermore, the EU supported projects to develop modeling tools assessing fate and transport the extent of contamination by simulating soil environmental systems to seek solutions for preventing pollution. For example, the EU supported the Forum for Co-ordination of pesticide fate models and their Use (FORUM) project which produced multiple pesticide fate computer models such as MACRO, PEARL and PELMO to understand the fate and behavior of pesticides in unsaturated soil (ESDAC, 2009). These efforts of software development came in parallel with the Water Framework directive which considered approach of pesticide fate simulation very useful to deal with these pollutants.

Computer modeling must reflect the parameters of site to create reliable approximation to the real system (Vanclooster, 2000). Computer programs concerned with pesticide fate and transport lead to creative mitigation opportunities before application of pesticides. Economically, computer simulations are useful for any environmental study to provide a thorough understanding of the problem and the feasible ways to create a solution. Computer modeling has been considered as useful tools to simplify complex real systems of groundwater and unsaturated soil zones (Kumar, 2019). However, the limitations of computer programs still exist to restrict the ability to simulate real life scenarios. Therefore, field and laboratory studies must be conducted to understand pesticide fate and behavior with minimal uncertainty. Screening models provide an estimation of the behavior of pesticides in the environment.

2.1 Field and Laboratory Studies on Environmental Fate of Pesticides

Field and laboratory studies are crucial for pesticide fate and transport modeling. These studies provide measured data to verify simulations of pesticide models and eliminate overestimations. Calibration of model input parameters is an essential step of the environmental modeling process to reduce the uncertainties in the outcome of the model. In addition, physical and chemical properties of pesticides as well as soil properties are usually obtained from field and laboratory studies. Many studies have been conducted in the fields and laboratories to understand the dissipation and partitioning pathways of pesticides in the environment after application.

In this study, field and laboratory studies concerned with environmental modeling of pesticides were investigated to understand the approach used by researchers to reach reliable modeling. For example, Phelps et al (2002) conducted a study to investigate atrazine dissipation after its implementation on agricultural soils. Atrazine is a well-known herbicide, which is used to stop the formation of weeds in such plants as sugarcane and maize. Atrazine has adverse environmental impacts and significant health risks. Therefore, it was categorized as priority pollutant in Turkey and EU. Phelps' study aimed to compare fate of atrazine in laboratory and field using a lysimetric setup. Parameters to be compared were the significant effectiveness on atrazine fate and transport while changing surface soil texture, temperature and organic matter content. Vaporization of atrazine increased with increasing temperatures during laboratory studies. Loss ranged between 19-79% at 50 ^{o}C. In addition, soil texture played a significant role in the determination of atrazine fate during field study even though atrazine had low adsorption potential. A decrease in particle size increased the adsorption of atrazine. While, volatilization increased with increasing particle size in the soil texture especially with a decrease in soil organic matter (OM) content. It is important to understand the behavior of atrazine in real experimental setup to check the compatibility with the environmental model. During the development of PESTRANS GUI, such field studies were helpful to assess sensitivity of some input

parameters during the simulation process. Sensitivity analysis of PESTRANS GUI model's parameters is discussed thoroughly in section 4.2.

Significant numbers of environmental studies have been conducted in Turkey revealed the importance of regulating usage of pesticides. Researchers and environmental experts urged to increase the awareness of the adverse effects of these pollutants and search for safer alternatives that will not cause disruption to the ecological system. For example, Yılıdırım & Ozcan (2007) investigated pesticide remaining in Çanakkale, Turkey. Samples were collected from 14 different sites in a total land of 5,260 hectares and soil depth between 0 – 20 cm. Analysis were conducted on auto system XL GC device to identify pesticides and their remaining through the soil depth. Trifluralin, captan, endosulfan, hexachlorocyclohexane (HCH), cypermethrin, ethion and mancozeb were detected in soil depth of 20 cm. Among these chemicals' priority pesticides were detected as well to prove that some chemicals were persistent, such as endosulfan and captan with concentration of 230 ppb within a few centimeters in depth. Although, HCH was banned in Turkey long time ago, traces of the pesticide were detected around 9 – 49 ppb in 20 cm depth. It was reported in a previous study in Canada that about 4% of the initial amount of HCH still existed after 15 years of the application due to resistance to microbial degradation (Howard, 1991). Considering that the half-life of HCH in soil is approximately 35 days on the average, HCH might still be in use illegally in Canada and Çanakkale during the period of these studies.

Yurtkuran and Saygı (2013) assessed the remaining of pesticides in Karabogaz Lake of Kizilirmak Delta in Turkey. Eight intensively used pesticides were detected for a one-year period. Oxamyl, malathion and etofenprox were detected demonstrating high persistence and a potential risk to disturb the unsaturated zone. In addition, tebufenoziode was detected mostly in the sediments. Yurtkuran and Saygi (2013) collected thirty samples of sediments and water from the delta area between the summers of 2011 and 2012. Limit of Quantification (LOQ) and limit of Detection (LOD) were identified using Gas Chromatography Mass Spectrometry equipment for each sample. Malathion and etofenprox were found to have high persistence in addition to high toxicity levels.

Blumhorst (1996) studied biodegradation of pesticides in soil. Small scale laboratory soil vessels were formed to have more control over degradation factors such as temperature, soil moisture content and soil texture. First order degradation was found to fit the concentration data very well to determine degradation rate constant for future modeling purposes. Half-life of pesticides was calculated easily for atrazine and trifluralin using exponential equations. Such study was crucial to calibrate input parameters for environmental modeling programs to provide reliable simulation outcome. Many pesticide modeling software use the calculated data to simulate the fate of atrazine and trifluralin in different environmental conditions. Such laboratory studies can validate the assumption of considering 1^{st} order degradation rate in many pesticide modeling tools. Another study was performed by Brodsky et al. (1997) to assess environmental fate of six chemicals with different chemical and physical properties in laboratory tests. The experiments intended to study degradation and leaching potential of dichlorophenol, dinitro toluene, trichloroethylphosphate, tetrachloroethene, anthracene and octachorodibenzo-p-dioxin. Half-lives of chemicals such as anthracene, dichlorophenol, dinitro toluene, trichloro ethyl phosphate and octachorodibenzo-p-dioxin were determined as 21.3, 4.1, 7.0, 166.9 and 13,002 days, respectively, based on first-order degradation kinetics.

Hmimou et al. (2014) conducted an experimental field study to monitor the mobility of carbofuran insecticide used in agricultural lands in Mnasra, Morocco. Although carbofuran is not included among priority pesticides but it is one of the most concerning pesticides due to low volatilization and high mobility. The aim of the study was to investigate the effect of irrigation rate on the leaching potential of the pesticide through soil. It was concluded that the amount of irrigation water application plays a significant role in the mobility of pesticide. An increase in the amount of irrigation water increased carbofuran penetration in the soil profile causing leaching. Characteristics of soil properties such as low organic matter and clay content made the unsaturated zone more vulnerable to contamination with carbofuran. High hydraulic conductivity of the field soil also strongly influenced the mobility of the pesticide.

Carbofuran was leached below the root zone due to high mobility despite the low amounts of precipitation and irrigation water applications.

Adverse environmental impact caused by unwise (excessive and uncontrolled) use of pesticides on agricultural soils urged the need for close understanding of fate and transport of pesticides in the environment. For the purpose of understanding the environmental behavior of pesticides in greater details, various computer modeling software were developed since the discovery of pesticides' risks over human health and ecological system. Computer simulation has been considered as a useful tool to understand pesticide behavior in the environment by taking into account pesticides' physical and chemical properties in addition to site characteristics and conditions. The United States Environmental Protection Agency (US EPA) has been working closely with different pesticide exposure models to assess the risk of pesticide application in agricultural lands. For example, in 2014 US EPA collaborated with Pest Management Regulatory Agency (PMRA) of Canada to assess concentration of pesticides in groundwater after leaching from agricultural soils using Pesticide Root Zone Model (PRZM) computer simulation model (US EPA, 2020).

2.2 Available Pesticide Fate Simulation Models and Software

From an economic and environmental perspective, use of computer software is an effective tool to understand fate and behavior of pollutants. Main pesticide loss pathways are degradation, volatilization, plant uptake, run-off and leaching. Functionality of available models is assessed within the scope of this thesis to determine advantages and disadvantages of each model. Garratt et al.,(2002) assessed and compared the performance of commonly used seven one-dimensional pesticide fate models, by simulating aclonifen and ethoprophos fate in unsaturated soil environment. The study aimed to calibrate input parameters and obtain prediction of aclonifen and ethoprophos behavior in soil. The compared models were Pesticide Leaching Model (PELMO), Pesticide Root Zone Model (PRZM), Leaching Estimation And CHemistry Pesticide model (LEACHP), PESTicide Leaching and Accumulation

Model (PESTLA), MACROporous pesticide model (MACRO), Leaching Model (VARLEACH), Pesticide Leaching Model (PLM). All pesticide models mentioned above were listed as a part of the "Forum for the Co-ordination of Pesticide fate models and their USe (FOCUS)" project which was created by the European Commission. Table 2.1 shows the major pesticide fate and transport processes considered in each software. Major differences between the software come from the water flow regime. According to Garrat et al. (2002), PELMO featured by the inclusion of a variety of processes to allow the user to simulate pesticide application considering different system factors. LEACHP, PESTLA, MACRO use Richard's equation to describe water flow. Richard's equation describes the dynamics of the water flow regime and considers variability of hydraulic conductivity of each soil layer. However, PELMO, PRZM, PLM and VARLEACH models the flow regime based on the "field capacity" concept allowing water in excess of field capacity flows down to the layer beneath within unit time step. First-order biodegradation and linear adsorption-desorption are included in all computer programs listed in table 2.1. Only MACRO and PELMO have Freundlich non-linear sorption option in addition. Second-order degradation is also embedded with PELMO package. All models were able to simulate aclonifen behavior in the environmental system to an acceptable extent. However, simulation of ethoprophos remaining deviated from model to model producing different soil concentration profiles. Temperature and soil moisture content were handled differently in each model causing the variation of the simulation outcome of each model. On the other hand, Soil and Water Assessment Tool (SWAT) is a model to simulate non-point pollutants including pesticides to predict environmental impact for a watershed to river basin scale of surface and groundwater systems. SWAT has a comprehensive ArcGIS interface which utilizes Groundwater Loading Effects of Agricultural Management system (GLEAMS) to simulate fate and transport of pesticides in watershed systems. Calibrated input parameters differed from model to model based on the measured data from the site. Model user should be able to identify the most suitable input parameters to obtain simulation close to reality. The use of the same input parameters on different pesticide fate models may not sometimes lead to the same simulation output.

According to Brown et al. (1996), differences in simulation outputs obtained from different models may come from calibration of certain input parameters. Each model should be calibrated individually. Thus, generalization of input parameters for all models would not result in a compatible fit between measure and predicted data.

Table 2.1: Commonly used pesticide fate computer models

Model	Water Flow	Degradation	Volatilization	Plant Uptake	Sorption	Run-off
PELMO	Field-Capacity	✓	✓	✓	✓	✓
PRZM	Field-Capacity	✓	✓	✓	✓	✓
LEACHP	Richard's equation	✓	✓	✓	✓	
PESTLA	Richard's equation	✓		✓	✓	
MACRO	Richard's equation Macrospores by gravity flow	✓		✓	✓	
VARLEACH	Field-Capacity & immobile water	✓			✓	
PLM	Field-Capacity & immobile water; macrospores fast flow regime	✓			✓	
SWAT	Hydrological transport model	✓	✓		✓	✓

Another comparison was conducted by Jolicoeur (2000) who evaluated the differences between five unsaturated soil zones software designed to study groundwater contamination potential of pesticides. Agricultural soil zones around lake Naivasha, Kenya were chosen to conduct the comparison of five simulation models with three different scenarios. Simulation Models included WAVE (Water and Agrochemical in Soil), SESOIL (Seasonal Soil Compartment Model), PESTAN (Pesticide Analytical), SWAP (Soil Water Atmosphere Plant system) and PRZM-2 (Pesticide Root Zone Model). The aim was to compare the software capabilities to assess leaching potential of pesticides through the unsaturated soil zones. Different scenarios were created by changing number of pesticides load and different infiltration rates. PESTAN is only a

screening model based on simplified differential equation. It had limited capabilities to run different scenarios of different input parameters. SWAP and SESOIL software provided the flexibility to simulate the zone of concern with various parameters. SESOIL provided reliable results and showed suitability to be used to investigate leaching potential of pesticides in unsaturated zones with less costs than SWAP. WAVE also had limited input options and did not run all the scenarios. Finally, PRZM2 was disqualified to simulate the zone of concern owing to incorrect numerical results.

There are many computer programs developed for assessment of the fate and transport of agricultural pesticides. The development and features of the most commonly and frequently used models should be clarified. For example, PELMO is free computer software to simulate leaching of applied pesticides in agricultural soils based on PRZM 1 model of US EPA (FOCUS, 2011). It investigates the concentration of the pesticides in the vadose zone below plant roots. Database regarding degradation and sorption of certain pesticides is integrated within the computer program for the user. Then, leaching potential is approximately calculated according to input parameters by solving transport and transformation equations. The program also takes into consideration of plant uptake, run-off, volatilization and erosional loss pathways. The European Soil Data Centre (ESDAC) adopted PELMO as a reliable software for determination of pesticide leaching potential.

In the late 1980s and early 1990s, Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) was introduced by Leonard et al. (1987) as a mathematical, field scale model based on previous chemical fate model CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems). Main assumptions of GLEAMS were that it assumes field soils to be homogeneous and precipitation is distributed equally as it has combinations between pesticide transport, sedimentation and hydrology. It was developed as a tool to evaluate leaching of chemicals and nutrients in the root zone and below. However, GLEAMS could not be used as a predictor of absolute concentrations of pollutants.

SIMULAT was a developed model in the early 1990s in Braunschweig University, Germany to conduct a one-dimensional quantitative analysis of pesticides' degradation, transformation, transport, and volatilization in unsaturated soils (Aden & Diekkruger, 2000). The model combines convection-dispersion equation and Richard's equation. Macrospores are simulated by preferential flow and infiltration capacity is numerically calculated through Richard's equation. However, the model ignores dispersion and assumes sorption and degradation can be neglected through the microspores. Water then assumed to flow only by gravity as a driving force.

2.3 Case Studies based on leaching evaluation tools

Mobility of pesticides should be assessed thoroughly to classify which pesticides have high mobility and thus high potential to contaminate groundwater. One of the case studies used the mechanistic computer model (MACRO) to determine source of error in model predictions of pesticide leaching (Jarvis et al., 2000). The case study was implemented by allowing three different users to simulate leaching process of bromide and bentazone in sandy soils. Samples of soil were collected three times for 14 months period in Vredepeel, Netherlands. This case study showed the errors of simulation programs when it was used by different users. It was considered of minor differences. However, the output of computer software depended on the user's conceptualization of the environmental systems and consequently selected input parameters. Users of MACRO model faced difficulty to determine degradation rate coefficient during laboratory tests. The interpretation of laboratory results to determine degradation rate coefficient had to be standard so that uncertainty is eliminated. MACRO model did not consider abiotic dissipation of Bentazone such as photolysis. Thus, results of prediction model did not overlap measured data towards the end of experimental period.

Tiktak et al. (1998) developed a software to simulate mobility and fate of pesticide applied on field soil. The model was called Pesticide Transport Assessment model (PESTRAS). PESTRAS was designed as a one-dimensional multi-layer model to

simulate hydrodynamic dispersion, volatilization, plant uptake, transient flow and equilibrium sorption in unsaturated soil. A case study was conducted to evaluate fate and leaching potential of ethoprophos insecticide applied on humic sandy soil in the vicinity of Vredepeel, Netherlands. The pesticide concentration soil profiles obtained as a result of Simulation in the humic sandy soil were not in agreement with measured data due to negligence of sorption kinetics by the model. Mobility and volatility of ethorpophos were overestimated by the model. The study concluded that PESTRAS model should have been evaluated under wider range of soil and pesticide properties as well as site hydrological condition.

In order to investigate atrazine transport and mobility in unsaturated soil, Ladu & Zhang (2011) conducted a case study using computer simulation model called HYDRUS-1D, which simulate water flow and transport of solute in unsaturated soils. The authors validated the model using experimentally measured data. The model takes into account of diffusive, advective-dispersive mass transport coupled with Richard's equation to generate both solute and water flow profile. The main aim of the study was to simulate Atrazine mobility through soil column. Bromide was used as a tracer to determine characteristics of soil column such as longitudinal dispersivity and non-equilibrium adsorption coefficient. Experiment was conducted based on the dual-porosity model with two-site sorption for disturbed and undisturbed soil columns. Atrazine leaching through soil column was simulated successfully with HYDRUS-1D as the concentration profile fitted the measured values to close extent. The study also concluded that leaching of atrazine simulation demonstrated high sensitivity to soil properties such as dispersity and soil homogeneity. During simulations to investigate leaching potential of pesticides through unsaturated soil zone, it is important to be cautious to sensitive simulation parameters that would have a direct impact on the fate and transport processes of pesticide. Variations of certain parameters associated with sorption (organic carbon fraction and organic carbon partitioning coefficient), degradation (Half-life) and volatilization (Henry's law ocnstant) of the pesticide during screening simulation may produce different simulation results. For example, Dubus (2002) performed a sensitivey analyses case study using four different leaching

models (MACRO, PESTLA, PELMO and PRZM) but manipulating input parameters of the simulation such as f_{oc}, K_{oc}, $T_{1/2}$, infiltration rate and soil water content. These four leahcing models are considered reliable models and they are used for registration of pesticides by Eupoean countries. The study colcuded that models demonstrated highest sensitivity with repsect to degradation and soprtion parameters whereas hydrological paramters such as infitration rate and soil water content demonstrated smaller influence in the leaching simulations.

Many pesticide fate and transport computer models have been developed since the 1980s. However, each model featured limitations and drawbacks during simulations such as lack of essential loss pathways of pesticides in the soil, extensive input data requirement, or overestimation of concentrations. In addition, the need of expertise in environmental modeling to use such modeling computer programs complicated the process to the less experienced users who might benefit from easy-to-use reliable screening tool to understand behavior of pesticides in the environment. Thus, PESTRANS GUI was developed to provide an alternative tool for the users who have limited modeling experience to carry out simulations within an interactive user interface, which considers the essential loss pathways and major fate and transport processes of pesticides in unsaturated soils using readily available integrated databases for the required input data. Graphical and numerical presentation of simulation results makes PESTRANS GUI a good candidate among other models to be used as a screening tool for assessing pesticide fate and transport behavior in the environment.

CHAPTER 3

MODEL DEVELOPMENT

3.1 Pesticide Fate and Transport Process

PESTRANS model is developed based on interactive processes that plant protection chemical would undergo in accordance with the conservation of mass principles. Pesticides applied in the surface soils subject to phase partitioning processes based on their physical and chemical properties. PESTRANS focuses on three phases, namely solid, gas and liquid phases, which exit in the soils of unsaturated zone. Solid, gas and liquid phases are mainly the three partitioning phases available for the chemical. Figure 3.1 below shows the chemical and physical processes governing the partitioning of the pesticide.

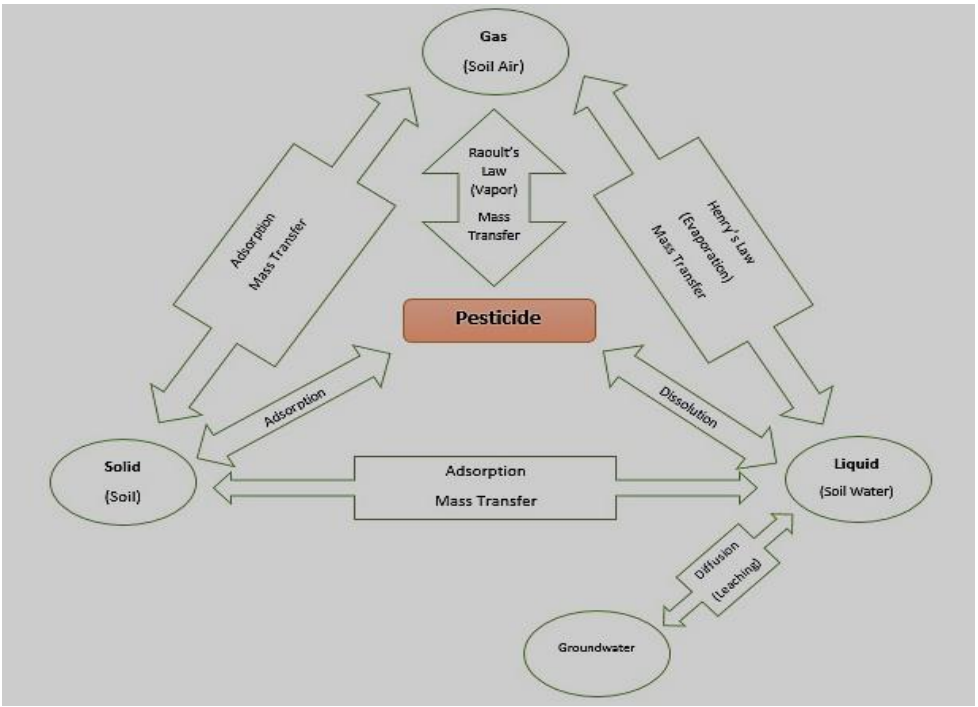


Figure 3.1: Phase partitioning of pesticide and relevant processes in soil (Ünlü et al., 1995)

The phase summed total concentration of pesticide partitioning into solid, liquid and gas phases can be expresses as;

$$C_T = \rho_b * C_s + \theta_w * C_w + \theta_g * C_g \quad (3.1)$$

where C_T: total concentration of pesticide in soil (µg/cm^3), C_s: pesticide concentration in solid phase (µg/g), C_w: pesticide concentration in aqueous phase (µg/cm^3), C_g: pesticide concentration in gaseous phase (µg/cm^3), ρ_b: bulk density of soil (g/cm^3), and θ_w and θ_g: volumetric water and air contents in the soil (cm^3/cm^3), respectively (Ünlü et al., 1995). Assuming linear partitioning between solid-liquid, and gas-liquid phases,

$$C_s = f_{oc} * K_{oc} * C_w \quad (3.2)$$

$$C_g = K_H * C_w \quad (3.3)$$

Eqn. 3.1 takes the form

$$C_T = \left(\rho_b * f_{oc} * K_{oc} + \theta_w + \theta_g * K_H\right) * C_w \quad (3.4)$$

where f_{oc}: organic carbon fraction in the soil, K_{oc}: organic carbon partition coefficient, and K_H: dimensionless Henry's law constant,

Total concentration of the pesticide indicates the sum of pesticide amounts in the three phases of the unsaturated zone soil. Based on the pesticide volatility, it can be partitioned from the aqueous phase (water) into the gaseous phase (air) through volatilization process. Pesticides with high Henry's law constant (K_H) would demonstrate high volatility and more partitioning in air phase of the soil pores. Hydrophilic and hydrophobic properties of the pesticide would also affect the

partitioning of the pesticide between air and water phases. Pesticides with high hydrophobicity would readily tend to volatilize and remain in the air-filled pores.

Pesticide deposits on the solid surfaces of soil particles through adsorption processes. Adsorption process is governed by pesticide soil-water partition coefficient (K_d). Each pesticide demonstrates different potential to adhere to the solid surfaces. Also, organic carbon partition coefficient (K_{oc}) is a considerably important factor in the partitioning of pesticide chemicals on soil solids such that;

$$K_d = K_{oc} * f_{oc} \tag{3.5}$$

$$C_s = K_d * C_w = K_{oc} * f_{oc} * C_w \tag{3.6}$$

Increase in the fraction of organic carbon content in the soil would increase the retention of the pesticides with high hydrophobicity on the solid surfaces of soil.

Leaching is considered one of the major physical processes, which the pesticides undergo after application on the soil surface. It significantly takes place by the combination of the advective and dispersive mass transport processes through aqueous phase. The pesticide mass leached through the soil profile ultimately reaches the underlying groundwater. The transport of the pesticide with the drained water through soil pores to reach the saturated zone is one of the most concerning process as it leads to groundwater pollution. Drainage of water takes place owing to force of gravity in which the infiltrating water penetrates the soil layers downwards. Capillary forces also play significant role in the leaching process. In addition, adsorption-desorption processes taking place between chemical molecules and surface of soil particles significantly change the leaching potential of the pesticide.

Biodegradation is considered in PESTRANS model owing to the significant loss of pesticides due to microbial activity within the soil. Pesticides are presumably following first-order biodegradation degradation process in which pesticide is partly consumed by microorganisms in the soil. PESTRANS considers that the biodegradation occurs at a maximum rate at the surface layer of the soil, where the biological activity is at maximum level, while at deeper soil depths the biodegradation

rate decreases due to gradual decrease in biological activity. These leads to a spatially variable biodegradation rate coefficient of μ described according to the following equations;

$$\mu = \frac{\ln(2)}{T_{\frac{1}{2}}} \qquad 0 < z < W \tag{3.7}$$

$$\mu = \frac{\ln(2)}{T_{\frac{1}{2}}}\, e^{-\gamma(z-W)} \qquad W < z < H \tag{3.8}$$

where $T_{1/2}$ represents half-life of pesticides (days), W is the thickness of surface soils with maximum biological activity (cm), H is the total soil depth of concern (cm), γ soil microorganism distribution coefficient (cm^{-1}).

3.2 Mathematical Model Description

Based on the principle of conservation of mass, the mathematical model is derived assuming linear equilibrium partitioning of pesticide into gas, liquid and solid phases and the major transport processes of advection and hydrodynamic dispersion, as well as first-order biodegradation process. Based on the forgoing considerations, Ünlü et al. (1995) presented the one-dimensional, transient governing model equation of PESTRANS as follows:

$$V_E \frac{\partial C_T}{\partial z} - D_E \frac{\partial^2 C_T}{\partial z^2} + \mu C_T = \frac{\partial C_T}{\partial t} \tag{3.9}$$

where C_T: total concentration of the pesticide in the soil ($\mu g/cm^3$), z: depth (cm), t: time (days), μ: first-order biodegradation rate coefficient ($days^{-1}$), V_E: effective advective transport velocity of pesticide (cm/day), D_E: effective dispersion coefficient (cm^2/day). Based on linear phase partitioning, the forgoing effective advective and dispersive mass transport parameters can be defined as (Ünlü et al., 1995):

$$V_E = \frac{q_w}{\rho_b \, f_{OC} \, K_{OC} + \theta_w + \theta_g \, K_H} \tag{3.10}$$

$$D_E = \frac{\mathcal{D}_g^o \, K_H + \mathcal{D}_w^o}{\rho_b \, f_{OC} \, K_{OC} + \theta_w + \theta_g \, K_H} \tag{3.11}$$

where q_w: water flux (infiltration) rate (cm/day), D^o_g: gaseous pesticide diffusion coefficient in in soil (cm^2/day), D^o_w: dissolved pesticide dispersion coefficient in soil (cm^2/day),

The appropriate initial and upper and lower boundary conditions of Eqn. (3.9) are assumed, respectively, as:

$$C_T(z, 0) = C_0 \qquad when \qquad 0 < z < L \tag{3.12}$$

$$C_T(z, 0) = 0 \qquad when \qquad z > L \tag{3.13}$$

where L is surface layer thickness where pesticide mass applied uniformly at an initial concentration of C_0, the upper boundary conditions at z = 0 as:

$$-H_E C_T = -D_E \frac{\partial C_T}{\partial z} + V_E C_T \tag{3.14}$$

$$H_E = \frac{\mathcal{D}_g{}^o \, K_H}{d(\rho_b \, f_{OC} \, K_{OC} + \theta_w + \theta_g \, K_H)} \tag{3.15}$$

where $D_g{}^o$: diffusion coefficient of gaseous pesticide in bulk air, d: the stagnant atmospheric boundary layer thickness; and finally, the lower Boundary condition at z = L as:

$\frac{\partial C_T}{\partial z} = 0$ is for free drainage regime, and (3.16-a)

$C_T(\infty, t) = 0$ is for semi-infinite soil domain consideration (3.17-b)

As output, PESTRANS model provides concentration distribution with time and depth, as well as fluxes of losses of applied pesticide mass by biodegradation, leaching, and volatilization, and the mass of the pesticide remained in the soil.

3.3 Numerical Solutions of Model Equations

Ünlü et al. (1995) developed an algorithm for the numerical solution of the derived mathematical model using Crank-Nicolson finite-difference method. It is assumed that the soil depth of concern is divided into finite difference layers of Δz in the vertical z coordinate, with Δz being the difference between locations z_i and z_{i-1}. Each location separated by Δz represents a spatial node of discretized model domain such that $\{z_i\}$: i = 1, 2, 3…*n*, where n is the total number of nodes. Also, time domain is divided into finite difference increments of Δt with Δt being the time interval between t_j and t_{j-1} and $\{t_j\}$: j = 0,1,2,3 … Formation of a systematic finite difference grid system as shown in Figure 3.2 facilitates the numerical solution of the governing differential equation to quantitatively analyze pesticide fate and transport.

According to Crank-Nicolson method the mathematical representations of the differential terms are approximated as;

$$\frac{\partial C_T}{\partial t} \alpha \frac{\mathrm{C_i^{j+1}} - \mathrm{C_i^{j}}}{\Delta t} \tag{3.18}$$

$$\frac{\partial C_T}{\partial z} \alpha \frac{1}{2}\left(\frac{\mathrm{C_{i+1}^{j+1}} - \mathrm{C_{i-1}^{j+1}}}{2 * \Delta z} + \frac{\mathrm{C_{i+1}^{j}} - \mathrm{C_{i-1}^{j}}}{2 * \Delta z}\right) \tag{3.19}$$

$$\frac{\partial^2 C_T}{\partial z^2} \alpha \frac{1}{2}\left(\frac{\mathrm{C_{i+1}^{j+1}} - 2\mathrm{C_i^{j+1}} + \mathrm{C_{i-1}^{j+1}}}{(\Delta z)^2} + \frac{\mathrm{C_{i+1}^{j}} - 2\mathrm{C_i^{j}} + \mathrm{C_{i-1}^{j}}}{(\Delta z)^2}\right) \tag{3.20}$$

$$C_T \alpha \frac{1}{2}\left(C_i^{j+1} + C_i^{j}\right) \tag{3.21}$$

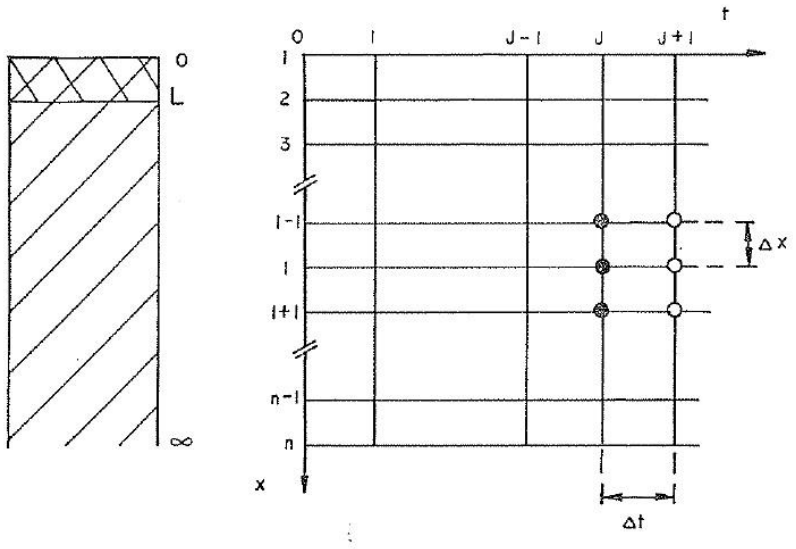


Figure 3.2: Finite difference grid system used for the numerical solution (Ünlü et al., 1995)

Hence, the numerical representation of the main governing equation (Eqn 3.9) derived in the mathematical model description section with implementations of Equations 3.18 through 3.21 is given for i=2, 3, ...n-1 as;

$$\frac{1}{\Delta t}\left(C_i^{j+1} - C_i^j\right) = \frac{D_E}{2\Delta z^2}\left(\mathrm{C}_{\mathrm{i+1}}^{j+1} - 2\mathrm{C}_{\mathrm{i}}^{j+1} + \mathrm{C}_{\mathrm{i-1}}^{j+1} + \mathrm{C}_{\mathrm{i+1}}^{j} - 2\mathrm{C}_{\mathrm{i}}^{j} + \mathrm{C}_{\mathrm{i-1}}^{j}\right) - \frac{V_E}{4(\Delta z)}\left(\mathrm{C}_{\mathrm{i+1}}^{j+1} - \mathrm{C}_{\mathrm{i-1}}^{j+1} + \mathrm{C}_{\mathrm{i+1}}^{j} - \mathrm{C}_{\mathrm{i-1}}^{j}\right) - \frac{\mu}{2}\left(C_i^{j+1} + C_i^j\right) \quad (3.22)$$

Also, the numerical representation of the initial conditions is given as;

$$C_i^j = C_0 \qquad 1 \le i \le 1 + \frac{L}{\Delta z} \quad ; j = 0 \quad (3.23)$$

$$C_i^j = 0 \qquad 1 + \frac{L}{\Delta z} \le i \le n \quad ; j = 0 \quad (3.24)$$

The boundary conditions at z = 0 and z = ∞ are given respectively as;

$$-\frac{D_E}{4(\Delta z)}\left(C_2^{j+1}-C_0^{j+1}+C_2^{j}-C_0^{j}\right)+\frac{V_E}{2}\left(C_1^{j+1}+C_1^{j}\right) \tag{3.25}$$

$$=-\frac{H_E}{2}\left(C_1^{j+1}+C_1^{j}\right)$$

$$C_n^j = C_n^{j+1} = 0 \quad for\ large\ n\ ; \quad j \geq 0 \tag{3.26}$$

Reorganizing the governing numerical equation (Eqn 3.22) accordingly;

$$G = \frac{D_E}{2(\Delta z)^2} \tag{3.27}$$

$$H = \frac{V_E}{4(\Delta z)} \tag{3.28}$$

$$(-G-H)C_{i-1}^{j+1}+\left(\frac{1}{\Delta t}+2G+\frac{\mu}{2}\right)C_i^{j+1}+(-G+H)C_{i+1}^{j+1}$$
$$=(G+H)C_{i-1}^{j}+\left(\frac{1}{\Delta t}-2G-\frac{\mu}{2}\right)C_i^{j}+(G-H)C_{i+1}^{j} \tag{3.29}$$

By substitution of i = 2, 3… *n*-1 and j = 1, 2, 3…. *n* will produce the following algebraic equations to be solved simultaneously where a_i (i=2, 3…n), b_i (i =1, 2, 3…*n*) and c_i (i =1, 2, 3…*n*-1)

$$\begin{vmatrix} b_1 & c_1 & . & . & . & . & 0 \\ a_2 & b_2 & c_2 & . & . & . & 0 \\ 0 & a_3 & b_3 & c_3 & . & . & 0 \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ 0 & . & . & . & a_{n-1} & b_{n-1} & c_{n-1} \\ 0 & . & . & . & . & a_n & b_n \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \\ . \\ . \\ . \\ C_{n-1} \\ C_n \end{vmatrix} = \begin{vmatrix} f_1 \\ f_2 \\ . \\ . \\ . \\ f_{n-1} \\ f_n \end{vmatrix} \tag{3.30}$$

$$b_1 = 1 + \Delta t[\left(1 + \frac{H}{G}\right)\left(4H + \frac{H_E}{\Delta z}\right) + 2G + \frac{\mu}{2}] \quad (3.31)$$

$$C_1 = -2(\Delta t)G \quad (3.32)$$

$$f_1 = 2(\Delta t)GC_2^j + (2 - b_1)C_1^j \quad (3.33)$$

$$a_i = -G - H \quad (3.34)$$

$$b_i = \frac{1}{\Delta t} + 2G + \frac{\mu}{2} \quad (3.35)$$

$$c_i = -G + H \quad (3.36)$$

$$f_i = -a_i C_{i-1}^j + (b_i - 4G - \mu)C_i^j - c_i C_{i+1}^j \quad (3.37)$$

$$a_n = 0 \ ; b_n = 1 \ \ ; f_n = 0 \quad (3.38)$$

The method of numerical solution of the Tridiagonal matrix equation was established by Thomas Algorithm (Press et al, 1989). PESTRANS utilized the described algorithm in python programming language to obtain the numerical solution of the governing equation. Appendix D shows the python source code of PESTRANS GUI software which embeds the algorithm above as well as the iterative solution with respect to discrete increments of time and soil depth.

3.4 Soil and Pesticide Database for the Model Inputs

One of the objectives of this work is to develop reliable database for pesticides' chemical and physical properties as well as soil properties to assess pesticides' fate and transport in unsaturated soils. Database library adopted these properties from reliable references to conduct sound modeling and to obtain trustable results. The database comprehensively includes 24 priority pesticides which were listed among the 45 priority chemicals declared by the EU (EU Council, 2001) by Water Directive Framework of the European Union since these chemicals were associated with potential to cause environmental disturbance. Turkey adopted the list of 45 priority chemicals including the 24 pesticides in 2012 and established list of

priority pollutants via the updated the regulation in 2015 and 2016 (Resmi Gazzette, no: 29797 , Date: 10/8/2016). Among these 45 priority chemicals, 24 pesticides were designated as ”priority pesticides” to be investigated thoroughly and categorized according to their mobility, volatility, and persistence properties. The main aim of this thesis to investigate these 24 pesticides specifically because these pesticides were prioritized by Turkey as they have high potential to cause serious soil and groundwater contamination.

PESTRANS GUI gives the user the option of using database information which was collected from reliable database (RAIS, 2019) or another option is the entry of user's own information regarding the pesticide of concern. U.S Department of Energy (US DOE) sponsored a project of University of Tennessee to create an up-to-date reliable database of physical and chemical properties of various chemicals. The Risk Assessment Information System (RAIS) developed an interactive search engine to tabulate chemical and physical properties of specific chemicals (URL1:RAIS). Organic carbon partitioning coefficient (K_{oc}), Henry's law constant (K_H), in addition to diffusion coefficients in air and water were the main chemical related parameters embedded in the governing equation for PESTRANS modeling. These parameters are crucial for the pesticide fate in the unsaturated soil zone. Half-lives of chemicals also play significant role in degradation of pollutants (Aronson et al., 1998).

Table 3.1 shows chemical properties of 24 pesticides included in priority list by Turkey and the European Union (EU). PESTRANS GUI focuses mainly on the screening of chemicals used in agricultural activities where the chemicals are introduced to the agricultural soils directly. Fate of priority pesticides is a matter of concern since these pollutants proved to have adverse contamination potential. Metal priority pollutants as well as industrial chemicals were excluded from the list of Table 3.1, even though PESTRANS GUI has the capabilities to simulate fate and behavior of most organic chemicals. It was designed to screen fate and transport behavior of pesticides in particular. Values of organic carbon partition coefficient (K_{oc}), Henry's law constant (K_H), half-life as well as diffusion coefficients in air and water ($D_g^{o}{}_{,Water}$) were adopted from Risk Assessment Information System (RAIS, 2019). Tributyltin herbicide has the

highest organic carbon partitioning coefficient. However, Dichlorvos has the lowest K_{oc} among the chemicals listed in Table 3.1. Organic carbon partition coefficient (K_{oc}) shows tendency of chemical to adsorb on the surface of soil particles. Henry's law constant indicates partitioning tendency of chemical between air and aqueous phases. Higher K_H values show high tendency while low values indicate low volatilization tendency of chemicals. Half-life is an indicator for degradation potential of chemicals. Long half-life values indicate high persistence of chemical in the environment. Diffusion coefficients show tendency of chemicals to diffuse through water and air media. Fungicides Hexachlorobenzene and Pentachloro benzene as well as insecticide Trichlorobenzene are well known for high tendency to volatilize immediately after application on agricultural soils. Henry's law constant (K_H) of these chemicals was found to be high in comparison with other pesticides. Half-life of pesticides was reported as range of time based on field and laboratory experiments in which the chemical naturally degraded in agricultural soil (NIH, 2019). Half-life ($T_{1/2}$) is a major indicator of pesticide fate in the environment. Thus, pesticides with high persistence take longer period of time to dissipate showing resistance to biological activities.

Table 3.1: Database for properties of priority pesticides used as input data in PESTRANS (adopted from RAIS & PUBCHEM NIH, 2019)

PRIORITY CHEMICALS	K_{OC} (cm^3/g)	HENRY'S LAW CONSTANT (DIMENSIONLESS)	HALF-LIFE+ (days)	D_g^o (cm^2/day)	D_w^o (cm^2/day)
Aclonifen	7.13E+03	1.22E-06	195.0	5148.21	0.602
Alachlor	3.12E+02	3.40E-07	11.0	1956.15	0.492
Atrazine	2.25E+02	9.65E-08	71.0	2286.62	0.591
Bifenox	3.68E+03	4.42E-06	7.0	1742.14	0.431
Chlorfenvinphos	3.08E+03	1.18E-06	150	3246.41	0.379
Chlorpyrifos	8.15E+03	1.20E-04	30.0	3301.68	0.386
Cybutryne	3.1E+03	1.23E-6	200.0	3400.00	0.430
Cypermethrin	7.28E+03	1.72E-05	30.0	1633.35	0.402
Dichlorvos	3.96E+01	2.35E-05	17.0	2408.55	0.633
Dicofol	5.40E+01	9.89E-06	60.0	3182.36	0.372
Diuron	1.27E+04	2.06E-08	97.7	4334.17	0.506
Endosulfan	1.09E+02	2.66E-03	43.0	1942.66	0.498
Heptachlor epoxide	4.13E+04	6.25E-06	730.0	2073.65	0.540
Hexachloro-benzene	6.20E+03	6.95E-02	1600.0	2503.40	0.678
Hexachlorocyclohexane	1.07E+03	5.74E-04	35.0	1226.88	0.634
Isoproturon	1.95E+06	4.58E-09	24.0	2174.55	0.552
Pentachloro-benzene	3.71E+03	2.87E-02	270.0	2543.03	0.687
Pentachloro-phenol	3.71E+03	1.00E-06	45.0	2550.50	0.692
Quinoxyfen	3.60E+3	3.95E-7	200	4200	0.42
Simazine	1.46E+02	3.85E-08	60.0	2431.24	0.636
Terbutryn	1.47E+02	8.79E-07	21.0	2058.58	0.521
Tributyltin	2.59E+07	1.23E-05	161.0	3469.30	0.405
Trichloro-benzenes	1.32E+03	7.73E-02	65.0	1884.53	0.477
Trifluralin	1.63E+04	4.21E-03	132.0	1905.29	0.482

+Average values were considered for Half-life of chemicals

Consideration of soil texture and other related soil properties are also important to understand chemicals' behaviors in the soil. Partitioning and transport of pollutants can be affected by different soil properties such as organic carbon fraction f_{oc}, dispersivity α and volumetric water content. PESTRANS investigate fate of chemicals in 12 different soil textural classes tabulated with their relevant soil properties in Table 3.2 below.

Chaudhari et al. (2013) correlated the values of bulk density to soil textures. They concluded that bulk density is inversely correlated with the particle size. Smaller particle size such as clay will have more compact packing filling voids. Also, bulk density is found to be affected by other parameters such as mineral content, organic carbon content and electrical conductivity of soil samples. An increase in these parameters lowers the bulk density value of the soil samples.

Tarboton et al (2003) tabulated the values of porosity of each soil texture. Porosity, as a parameter, is crucial in the partitioning of the pesticide in soil. Voids can be filled with water and air which allows the chemical molecules to undergo different chemical and physical processes. Volumetric water content (θ_w) values for different soil texture were reported in a study to investigate distribution of water retention properties in soil (Carsel and Parrish, 1988). Values of volumetric water content for various soil textures were obtained from Soil Conservation Service project to identify hydraulic conductivity and water retention parameters for the van Genuchten model by regression analysis. Volumetric air content of the different soil textures was calculated as the difference between porosity and volumetric water content assuming that empty voids will be more likely to be filled with air. Solute and transport models require the input of dispersivity (α) as a parameter of the advection-dispersion equation. Perfect et al. (2002) experimentally estimated the dispersivity (α) values of 11 soil textures using pedo transfer functions by measuring soil hydraulic properties with solute breakthrough curves. The predictions decreased from 12.8 cm for clay to 0.8 cm for sands. The experiment also found that an increase in water retention parameters would increase dispersivity parameter.

Fraction of organic matter is a key factor in the adsorption process of chemicals on soil particle surface. Nath et al. (2014) reported values of organic carbon content (f_{oc}) for different types of soil textures. Organic carbon content is estimated to be 58% of the total organic matter. It was observed that increasing organic matter and clay content in soil increase water holding capacity. Table 3.2 shows the soil properties of 12 type of soil texture. PESTRANS GUI imports soil parameters such as bulk density, volumetric water and air contents, dispersivity, porosity and organic carbon content from the database for pesticide fate and transport simulations. Values of each property were obtained from experimental studies as shown in the table and average values were considered for properties which were reported as range.

Table 3.2: Generic soil properties database

Soil Texture	Bulk Density, ρ_b (g/cm3)	Volumetric gas content, θ_{air} (cm^3/cm^3)	Volumetric water content, θ_w (cm^3/cm^3)	Dispersivity α (cm)	Porosity φ (cm^3/cm^3)	Organic Carbon fraction, f_{oc}
Clay	1.64	0.259	0.223	12.8	0.482	0.015
Silt	1.45	0.184	0.276	5.2*	0.460	0.013*
Loam	1.45	0.193	0.258	4.6	0.451	0.016
Clay Loam	1.45	0.142	0.268	8.1	0.410	0.014
Loamy Sand	1.54	0.246	0.164	2.6	0.410	0.012*
Silt Loam	1.50	0.157	0.293	5.6	0.485	0.015*
Silty Clay	1.45	0.126	0.234	11	0.492	0.013*
Silty Clay Loam	1.40	0.215	0.262	9.6	0.477	0.014*
Sandy Clay	1.40	0.190	0.190	10.9	0.426	0.011*
Sandy Clay Loam	1.63	0.210	0.210	6.0	0.420	0.015
Sandy Loam	1.50	0.215	0.220	3.4	0.435	0.013
Sand	1.56	0.297	0.098	0.8	0.395	0.007*
Reference	(Chaudhari, 2013)	(Carsel, 1988)	(Carsel, 1988)	(Perfect, 2002)	(Tarboton, 2003)	(Nath, 2014)

*estimated average values

Figure 3.3 below shows soil textural classes based on the percentages of sand, silt and clay fractions composing the soil material. Fine textured soils with higher organic carbon content will have higher surface area available for adsorption of pesticides in the soil profile. These interactions may reduce pesticides' leaching potential to reach groundwater and will reduce the mobility. Coarse textured soils, on the other hand, have less surface area available for adsorption of pesticides and thus exhibit higher pesticide leaching potential to groundwater due to increased mobility. Fine textured soil adsorbs more pesticide and reduces leaching potential to groundwater; however, they contribute to surface water pollution through transport of adsorbed pesticides during soil erosion.

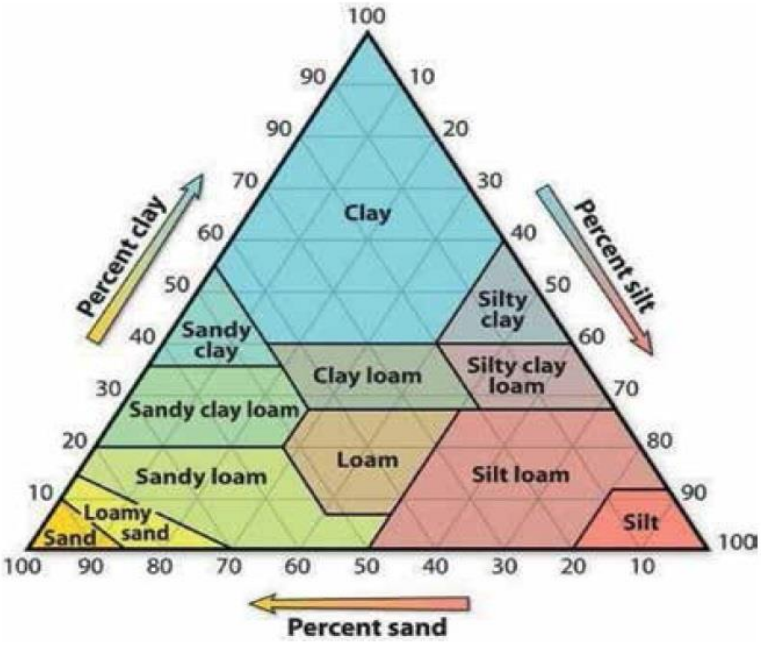


Figure 3.3: Soil Texture Diagram, (adopted from Larramendy & Soloneski, 2019)

3.5 PESTRANS GUI Software Development

The need for a screening tool to investigate pesticide fate and behavior in the environment has been increasing since the discovery of the adverse effects of such chemicals. Many environmental modeling experts have been developing computer programs to simulate the partitioning and dissipation of pesticides in the agricultural soils. However, these computer models had advantages and disadvantages while being used to screen environmental behavior of such chemicals. Computer models such as PELMO, PRZM and MACRO provide simulation with acceptable accuracy, but they require a certain level of expertise in environmental modeling to be used. Therefore, the necessity to develop a user-friendly screening tools that can serve for users who have limited experience in modeling lead to the development of PESTRANS GUI.

One of the main objectives of this thesis is to build a user-interface using an up-to-date programing language Python (Tkinter). The user-interface utilized the source code of the previously created PESTRANS model by (Ünlü et al. 1995) and re-developed the environmental model to create PESTRANS GUI computer model. Source code of PESTRANS was developed in mid-1990s based on FORTRAN programming language to screen fate of pesticides. However, it has been difficult to run FORTRAN PESTRANS code on modern computers by ordinary users. Re-development of PESTRANS model on python programming platform created the PESTRANS GUI software which allows the user to conduct fate and transport screening assessment for pesticides on modern computers. PESTRANS GUI software was converted to an executable computer application to run on Windows Platform without the need of installation. The user downloads the compressed PESTRANS GUI package and extracts the file. Then, the application will be ready for use without installation. It is considered as an advantage for the user to be able to use the software without installations. Most installation processes result in computer errors and prevent the user for using the intended software.

PESTRANS GUI facilitates the pesticide modeling process by providing guidance and instructions for the user to follow. Then, it takes all input parameters into python code

algorithms to solve the environmental model and provide the screening results of pesticides fate and transport. Python source code of PESTRANS GUI is provided in Appendix D where it included the interface codes for the graphical user interface as well as the simulation algorithm used to solve the environmental system.

Database of physical and chemical properties as well as soil properties were created on separate python scripts where the main code imports data from library if the user decides to use the embedded database. Then, the software imports properties from the database of the selected pesticides and soil texture accordingly. The scheme in Figure 3.4 illustrates flow chart of PESTRANS GUI model during pesticide simulation. The user is guided to enter input parameters to define the environmental system then input parameters are processed through the numerical algorithms to solve the system and provide simulation outcome.

PESTRANS GUI is a deterministic model which imports the input parameters from the user interface and uses them in the numerical solution of the governing partial differential equation of the mathematical model for the environmental system. It simulates the fate and transport of a selected, surface applied pesticide in soil of different textures under various site and climatic conditions to determine the fraction of applied pesticide mass fluxes, volatilized, biodegraded, leached to below root-zone or to groundwater, and finaly the fraction remained as rediual mass in the soil. Firstly, PESTRANS GUI has two model engines PESTRANS and PESTGRW. PESTRANS is designed to simulate shallow soil systems. It investigates the pesticide fate for less than 50 cm where the microbial bioactivity is considered to be constant. PESTGRW is used for deeper soil systems to assess the fate and behavior chemicals where microbial bioactivity changes as a function of depth. The user chooses the appropriate engine in accordance with the environmental system of concern. In case the potential of pesticide to leach to groundwater is of concern, PESGRW will be the suitable engine for modeling. Secondly, time and space variables should be defined for PESTRANS GUI to carry out the simulation. Total depth and total simulation time should be entered by the user as well as discrete time and space increments for the iterative numerical solution to be completed. The user should then choose a pesticide the fate

and transport behavior of which is to be assessed to import physical and chemical properties from the database. If the user prefers to simulate another chemical, “other” should be selected on the dropdown menu then physical and chemical properties must be entered manually. Similarly, soil texture is selected from the database otherwise soil properties must be entered manually. The interface is designed to guide the user to enter the required input parameters in accordance with the specific simulation problem of concern to start pesticide fate and transport simulation in soil system. Then, after defining the soil environmental system to be simulated, the Python computer codes simultaneously provide the numerical solution to the governing partial differential equation taking into consideration of initial and boundary conditions and present quantitative analysis of the pesticide fate. In addition, PESTRANS GUI provides the user a graphical representation of the pesticide leaching potential showing concentration versus depth graphs as well as temporal variations of mass fluxes of volatilized , leached and biodegraded pesticide mass, and screening matrix of pesticides loss and remaining. PESTRANS GUI is designed to be an easy-to-use software with minimal programming skills requirement. PETRANS GUI’s user guide is presented in section 3.6 which provides all instructions on how the model can be used to understand fate and transport of pesticides in unsaturated soil environment.

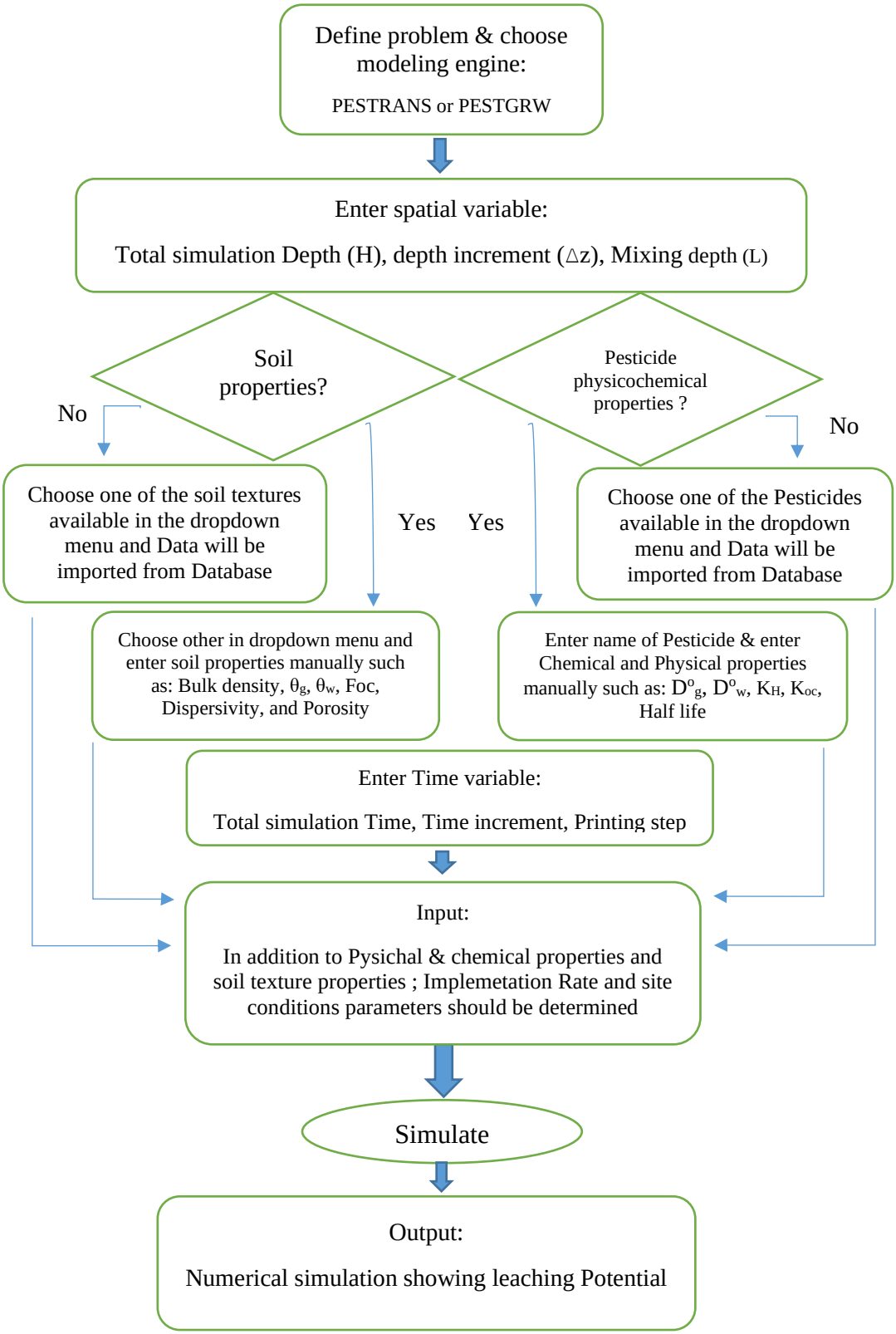


Figure 3.4: PESTRANS GUI Scheme

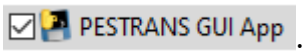
3.6 PETRANS GUI User Guide

The fate and transport behavior of pesticides in agricultural soils are one of the most interesting topics in enviornemtnal modeling. When pesticide contamination problem occurs in soil, the need to investigate and increase to understand its fate and behavior, PESTRANS GUI model can be useful tool to screen the fate and transport and categorize them according to their moblility, volatility and persistence potential. The User Guide of PETRANS GUI model is presented in the form of steps, to ease its use to the users. In order to use PETRANS GUI model, the user should follow these steps:

1. Download the compressed PETRANS GUI package from the following link: URL2: PESTRANS GUI Model

   The compressed folder is 38 MB in size and it contains the whole package of PETRANS GUI model including the database.

2. Extract compressed package: PESTRANS GUI model comes in the form of compressed folder to reduce the size of the package. Note that: PESTRANS GUI model will not run, if the compressed folder is not extracted.

3. Double-click on PESTRANS GUI App icon 

; One of the advantages of this software is that it does not require the users to run any installations on their personal computers since it is in the form of execuatble file.
4. The user interface will take few seconds to appear as on the monitor and it will be ready to run simulations to screen polluants in unsatuarted soil environment. Figure 3.5 present PESTRANS GUI model interface with explanations of input parameters.

Illustrated Screenshot of PETRANS GUI is given in Figure 3.5. The interface is designed to facilitate pesticide fate and transport modeling by guiding the user to input certain modeling parameters in order to run the software. Input parameters are organized in rows and blocks as can be seen in Figure 3.5. Help buttons were designed

to provide the user with guidance and recommendations to facilitate pesticide modeling process. It was intended to keep the design of PESTRANS GUI interface as simple and effective as possible to allow users to interact with PESTRANS GUI easily without high level of experitise in software usage. The user must provide all parameter values with star (*) to start screening of pesticides in unsaturated soil systems At the top of the interface, the user chooses the engine of modeling based on two types of soil regimes. PESTRANS engine is assigned for pesticide modeling in shallow soil profile and PESTGRW engine is used for deeper soil profiles. In addition, the user must choose modeling graph with three different options; pesticide concentration versus soil depth, Vapor flux versus time, or plotting percentages of loss pathways such as degrdation and volatilization over time. Then, parameters in illustrative blocks should be define accordingly. Block 1 in red shows the user to define spatial and temporal parameters where the user define the depth of soil as well as simulation time. The help button provides the user with recommendation for the choice discrete depth and time increment for convergence of numerical solution. Block 2 is assgined for boundary conditions and application rate. Blocks 3 and 5 show the input parameters for soil and pesticide properties. The user is free to import data from the embedded database or input the parameters manually. All parameteres should be provided in accordance with the assigned units for unit consistency and accurate numerical calculations. Defining biological activity parameter of depth and distribution coefficient is only assigned while using PESTGRW to model pesticides in deep soil profiles. In addition evaporation/infitration rate must be provided by the user since it is essential to the modeling mathematical algorithm. After providing all parameters in star (*), the user will be able to run the software and graphical Figures will popup after simluation to explain pesticide partionationing and loss pathways. It was intended to create the interface as one layer. Therefore, the output of numerical modeling will apprear in output area as shown in block 7.

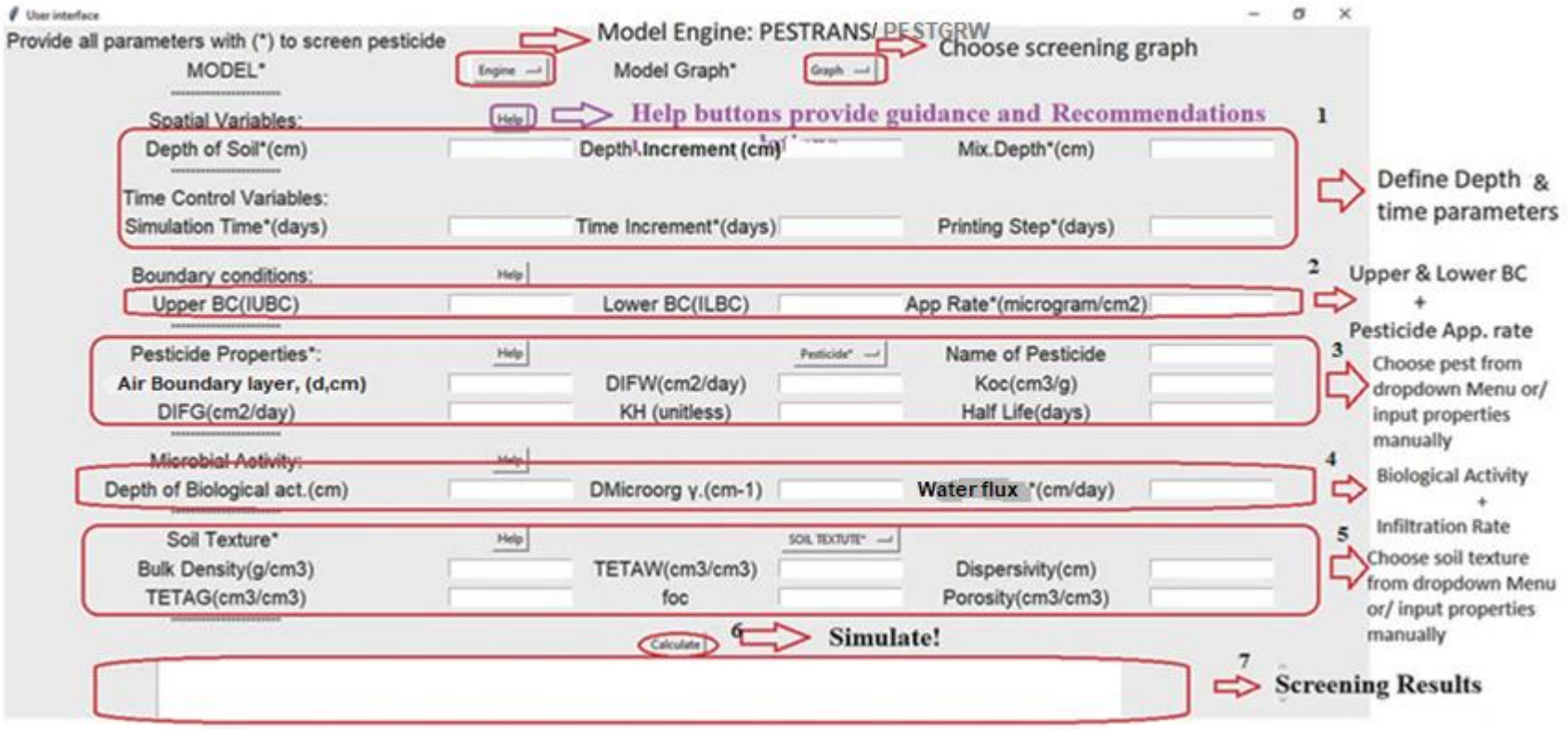
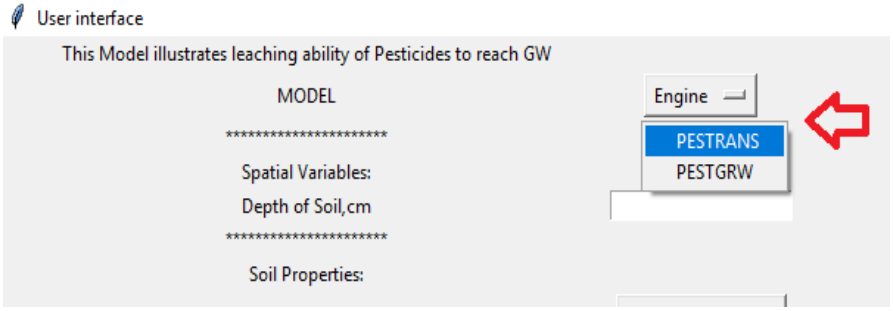


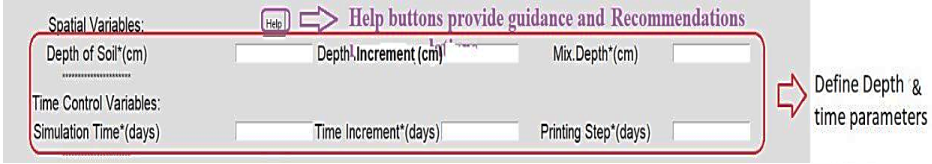
Figure 3.5: PESTRANS Graphical User Interface User Guide

The user can start simulation of pesticides on PESTRANS GUI model by defining all the required input paramters to define the unsatuatered soil system of concern. The user is free to choose any preferred values for the input parameters as shwn in the block of Figure 3.5. In addition, Help buttons are placed adjecent to each input parameters to guide the user through out the simulation. Note that units of each parameter are indicated beside each box and the user should stick to the units illustrated for unit consistancy and correct arethmatic calculations. Users will follow the sequence of steps as in Figure 3.5 to define the unsaturated soil system.

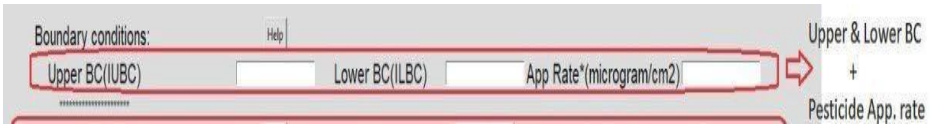
1. Select a model engine from dropdown menu to define the unsaturated soil regime; use PESTRANS engine to simulate shallow soil profiles for assessing impacts of near surface processes, such as pesticide remaining available for surface run-off and PESTGRW to simulate deeper soil profiles for assessing impacts of pesticide leaching to groundwater.



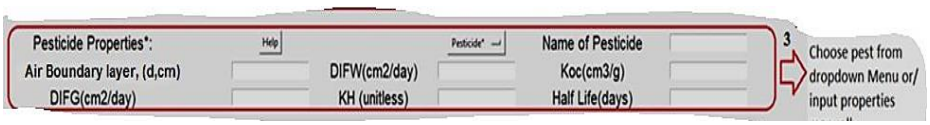
2. Define spatial and temporal discritization parameters, "Δz" and "Δt" for numerical simulations. First, enter simulation depth (H), depth increment (Δz) and mixing depth (L) in cm. Help buttons provide recommendation and guidance for the users on the choice of increments for the sake of convergence of the iterative numerical solution. Also, simulation time parameters should be determined in days. Printing step determines the output production time in the simulation.



3. Choose boundary indices to define the upper and lower boundary conditions ; for lower boundary condition condition index 3 was assigned to indicate free-drainage regime whereas index 1 to indicate semi-infinite lower boundary condition. On the other hand, index 3 was assigned for constant pesticide application flux at the upper boundary conition and index 1 was assigned to indicate constant concetration. Boundary condition indices are untilless and the user have only two options (1 or 3). In this row also, pestcide application rate should be entered in ($\mu g/cm^2$) units.

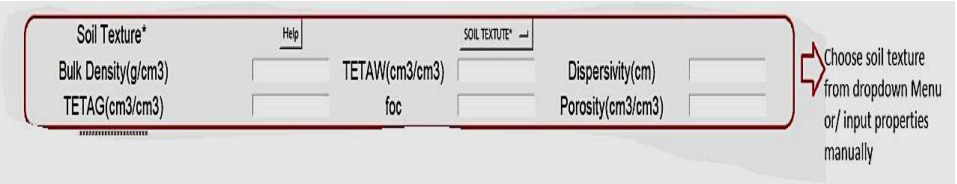


4. Pesticide choice should be determined by one of two ways; whether the user chooses one the pesticides listed in the dropdown menu to import physical and chemical properties accordingly from database or "other" should be selected from the dropdown menu for manual input of physical and chemical properties. Parameters of pesticide chemical properties are gaseous and dissolved pesticide diffusion coefficient in in soil in (cm^2/day) (noted as DIFG & DIFW since the coding syntax does not show superscripts or subscript), dimensionless Henry's law (K_H), organic carbon partitioning coefficient (K_{oc}) in (cm^3/g) and Half-life of the pesticides in soil in days as a unit. In addition, Atmospheric boundary layer thickness (d, (cm)). If the user chooses to input pesticide properties manually, the user should also name the pesticide in the designated box.

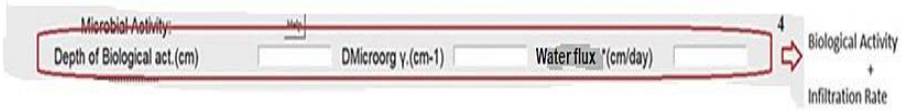


5. Similarly, soil texture can be chosen from the dropdown menu to import parameters from database or the user can choose "other" to enter the properties manually. Soil properties are soil bulk density in (g/cm^3), Volumetric gas and water content (noted in the interface as TETAG & TETAW), organic carbon

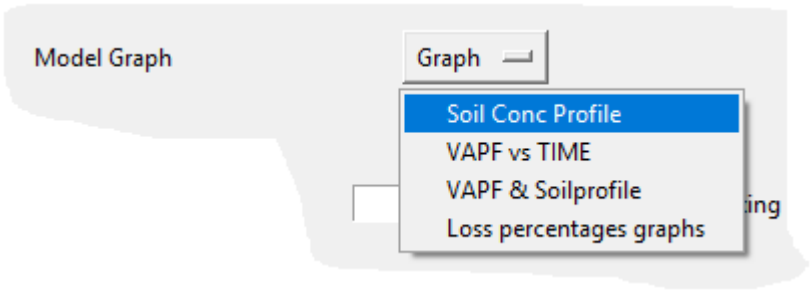
fraction (f_{oc}), dispersivity (cm) and soil porosity. There are 12 different soil textures included in the database and they are presented in Table 3.2.



6. Microbial bioactivity conditions are must parameters when PESTGRW engine is seleced for investigating pesticide leaching potential in deep soil. Otherwise, they are optional in the case of PESTRANS engine's simulations during pesticides modeling in shallow soil depth. Evaporation/infiltration rate should be defined in (cm/day). For evaporation rate, negative sign (-) should be entered with the value. No need to put (+) sign for infiltration rates. infiltration rate q_w should always be assigned a value as it is an important parameters in the numerical calculations.



7. After defining all parameters with (*), the user should select the graphical output of interest. There are different options of graphical presentations; pesticide soil concentration profile, vapor flux versus time, or both of them side-by-side and finally loss percentages graphs. Soil concentration profile will plot the concentration of pesticide through previously determined depth. Vapor flux versus time graph will plot vapot flux of pesticide from soil to the atmosphere at each printing time step determined by the user. Loss percetages graphs will plot loss percetage of pesticide due to degrdation, volatilzation, also resideue over time for each printing tiime step. Graphs are considered an advantage of PESTRANS GUI to facilitate the interpretetion of pesticide modeling results.



Although PESTRANS GUI does not provide unit conversion calculator, it guides the user to enter input parameters in specified units. So, the user will be able to follow the calculations in accordance with the given units. PESTRANS GUI intended to avoid unit conversion features to facilitate the interaction between the user and the software. Infiltration rate represents the summation of rainfall and irrigation rate to show water flow in the vertical orientation. Minimizing the errors in compiling computer codes required skipping less needed features to make the software more user-friendly.

Figure 3.6 shows a screenshot of a sample pesticide selected from dropdown menu for pesticide modeling in unsaturated soil. The values of the parameters were entered according to application scenario of aclonifen and the previous steps were followed to run the software. The reuslts and outcome of the pesticide modeling will apprear in numerical and graphical representations as a result of numerical iterative finite-difference algorithm solution according to the input values deteremined by the user.

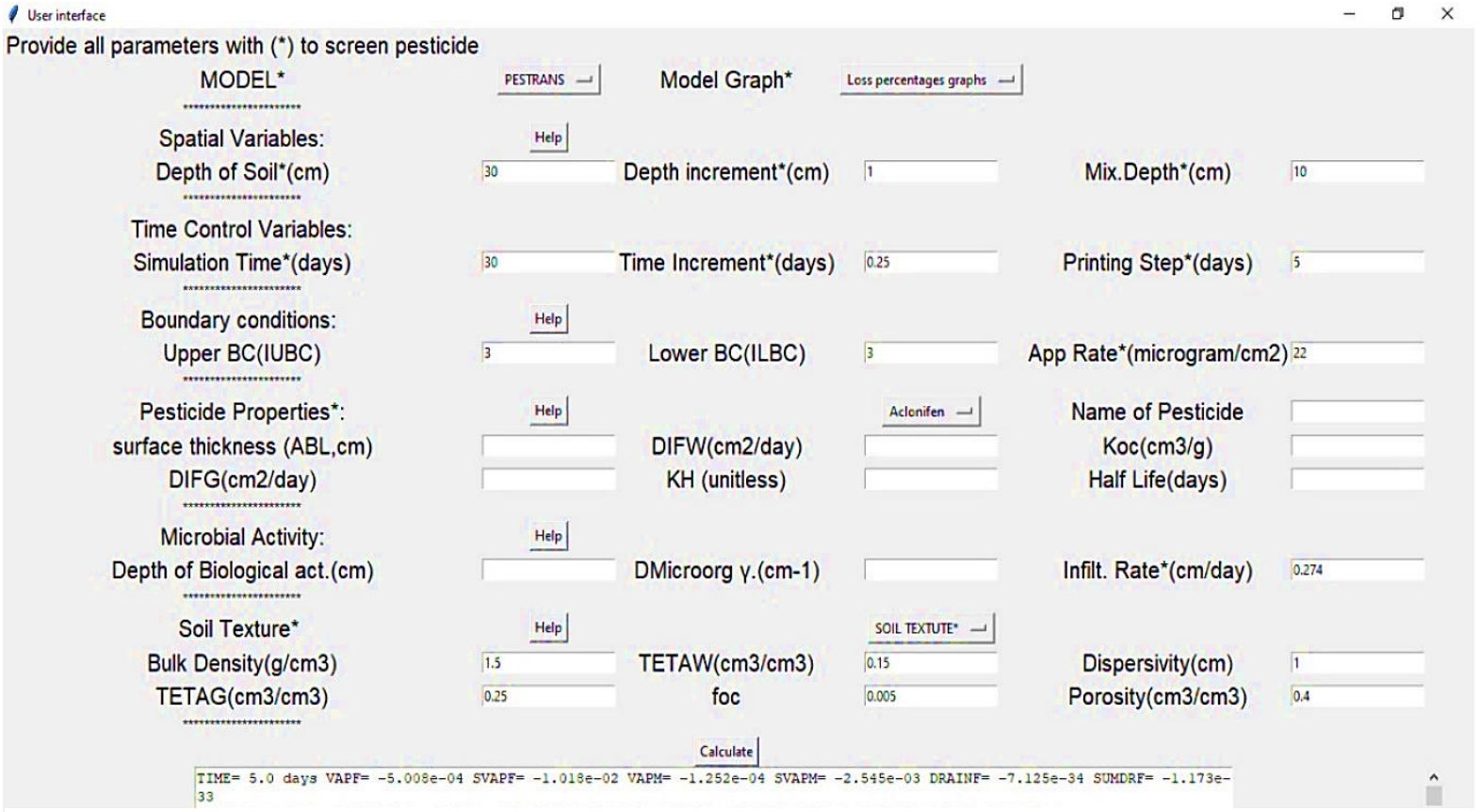


Figure 3.6: Screenshot of sample pesticide simulation

PESTRANS GUI modeling output:

After setting PESTRANS GUI with all the required parameters for pesticide modeing as mentioned before, PESTRANS GUI will run mathematical algorithms to iteratively calcualte pesticide concentration through soil depth with respect to printing time period. Appendix C shows a sample of PESTRANS GUI numerical output and Figure 3.7 shows the graphical plots of pesticide modeling including concetration profile versus depth, vapor flux versus time profile, degradtion and volitioation percentages lost in soil through simulation time and the percertages of pesticides loss and remaining veruss time profile. Legend in Figure 3.7 represent each printing time step as the software produces results at each printing time determined piori to simulation by the user.Numerical output of pesticide fate modeling provides loss percetages of the pesticide due to volatilization, degrdation and leaching as well as pesticide concentration at each depth increament. PESTRANS GUI was designed to provide pesticide loss pathways in clear and simple representations so that it helps the user understandt the fate and behaviour of pesticide in unsature soil after application.

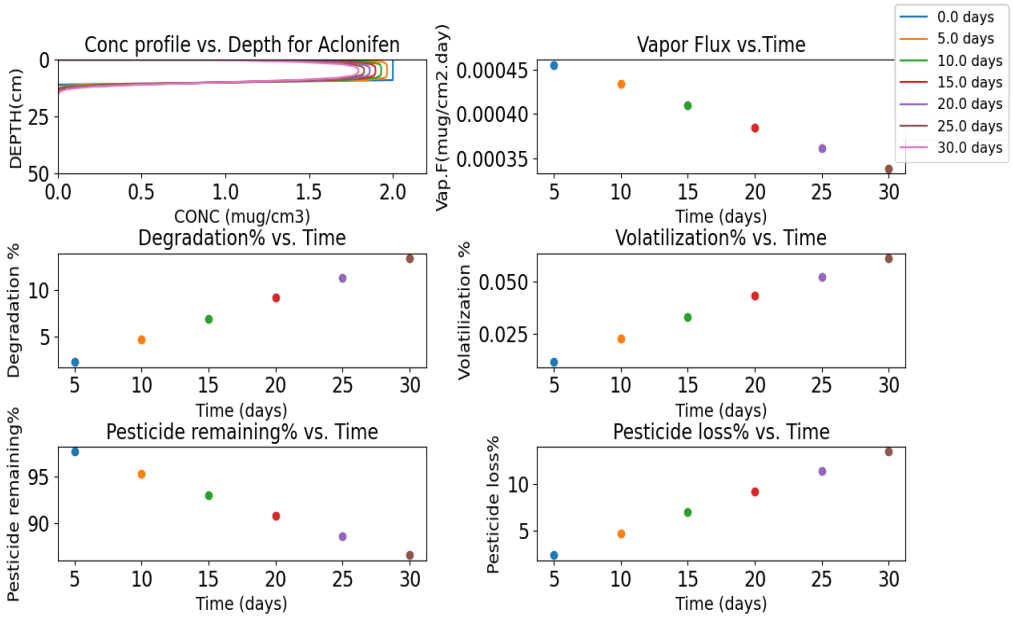


Figure 3.7: Graphs of sample simulation output

3.7 Capabilities and Limitations of the Model

The PESTRANS GUI model is a computer graphical user interface for simulating-e the fate and transport of pesticides in the soil environment. It was designed over python platform (Tkinter) as a 1-D simulation tool to screen pesticide fate and behavior in unsaturated soil zones. Therefore, it enables the user to have a better understanding of pesticides' behavior in the soil environment and classify them according to their volatility, persistence and mobility as well as groundwater pollution potential.

Capabilities and advantages of PETRANS GUI make the software a useful alternative to other pesticides screening tools. PESTRANS GUI has the privilege of simplicity to define soil environmental system in which the fate and transport behavior of pesticide is evaluated. From installation to simulation, PETRANS GUI was designed to facilitate its use for the user unlike the other pesticide screening models which require high expertise in environmental modeling for the user to able to start the simulation on personal computers. PETRANS GUI does not require any installation procedure. It comes in the form of package folder with one executable file which runs in all computers with Windows platform. Double-clicking on the executable file of PETRANS GUI model will started the program immediately without any troubles. All installation steps were shortened for the user to double-clicking only once to start the program. PESTRANS GUI model is capable of producing simulation results in terms of mass balance percentages which show the amount of degraded, volatilized, leached and remained pesticide mass in the soil after application. In addition, the software generates graphical representation of pesticide concentration distribution through soil depth and time distribution of volatilization fluxes over the soil surface. Graphs of pesticide concentration verses depth for selected time periods provide a better visualization of pesticide penetration through the soil which helps the user to have a better understanding of pesticide behavior. PESTRANS GUI currently offers only the "save" option only for graphical output of pesticide modeling. However, numerical output of pesticide modeling in soil, that will appear on the interface output results

section, can be easily copied to any text file, for example Notepad, then saved. The software was designed this way to avoid debugging and code compiling problems.

PESTRANS GUI software has Database in its library for 24 pesticides considered as priority chemicals by Turkey and EU countries. The database helps the user to import chemical and physical properties. It allows the user to simulate any chemical by giving the options to input parameters manually. Properties of different soil types can be both entered manually or imported from database to provide the user with flexibility to prepare the input files. Soil database of PESTRANS GUI has 12 different soil textures and the relevant physical and hydraulic soil properties which were compiled from reliable up-to-date sources reported in the literature.

PESTRANS GUI model has two separate modeling engines PESTRAN and PESTGRW assigned for shallow and deep soil simulations. It provides the user with more flexibility during simulations and better approaches to real site conditions as deep soil conditions may differ than shallow soil especially regarding the extent of transport processes and biodegradation activity.

Every pesticide screening model has limitations including PETRANS GUI model. The software was designed as a 1-D simulation tool in homogeneous and isotropic soils with uniform and constant boundary conditions, which limits the capabilities to investigate pesticide leaching and make it unsuitable for soil cracks and heterogeneity. Also, plant uptake is not considered as it conservatively causes overestimation of pesticide loss in soil. This helps considering worst case scenario during environmental risk assessment. The software provides good approximation to pesticide fate modeling in unsaturated soil, which makes it good tool to be used in environmental risk assessment. However, PESTRANS GUI was developed based on assumptions such as linear adsorption, first-order degradation rate and linear phase partitioning which may be appropriate for some pesticide simulations. Thus, deviations may occur from these assumptions. Assumption of linear isotherms of the partitioning phenomena of pesticides may lead different results depending upon the temperature of the soil environment. Pesticide adsorption may not follow linear isotherm in low temperatures

between 10-20 ^{0}C but it fits well for environmental systems between 20-40 ^{0}C (Rani & Sud, 2015). PESTRANS GUI does not included time-dependent and equilibrium adsorption-desorption reversibility in this version. However, kinetic sorption model is intended to be included in future versions.

PESTRANS GUI is designed to do simulation assuming that soil profile is clean in order to classify pesticides potential to contaminate the soil environment. Therefore, previously accumulated pesticides are not considered because it focuses only on the pesticide chosen for simulation to classify the applied pesticides.

Table 3.3 shows the developed model PESTRANS GUI compared to few popular computer models used to simulate pesticide fate and transport in unsaturated soil in terms of embedded loss pathways. PESTRANS GUI does not included plant-uptake or run-off drifting, yet, it includes degradation, volatilization, adsorption as major loss pathways to assess pesticide transport and partitioning in soil environment. It is intended to include more loss pathways such as photochemical dissipation and plant uptake as well as drifting and erosion to enable the user to investigate thoroughly surface water and groundwater contamination potential in future versions of the model. In addition, new features such as temperature dependency, alternative adoption isotherms and layering in soil profile will be added. However, the main intention for development of the current version was to provide users with less expertise in software programming, such as environmental modeling students who are interested in pesticide modeling in unsaturated soil, with an interface to facilitate their interaction with the software during input and output stages of pesticide modeling.

PESTRANS GUI does not require installation process as it was designed as an executable package ready for use. In addition, it provides output of pesticide modeling relatively fast owing to fast convergence of numerical solution. Simulation using PESTRANS GUI for real time simulation of 10 years and 1-m depth will take less than 5.5 seconds for the numerical and graphical simulation to appear on the monitor. The numerical output takes less time that the graphical output owing to python capability of conducting fast numerical iterative calculations. On the other hand, PRZM's

execuation time is less than a minute for surfacewater run-off and erosion simulation scenario on standard PC and the computing time for PELMO was 5-10 minutes to simulate standard Tier 1 risk assessment simulation with 9 senarios (ESDAC,2009). The computing time for any two models cannot be compared because each model includes different calculation processes owing to different loss pathways within the algorithms. However, these computational times are given to illustrate the computational capabilities for few models under certain pesticide application scenarios.

Table 3.3: PESTRANS GUI model compared to available pesticide modeling computer models

Model	Water Flow	Degradation	Volatilization	Plant Uptake	Adsorption	Run-off
PELMO	Field-Capacity	✓	✓	✓	✓	✓
PRZM	Field-Capacity	✓	✓	✓	✓	✓
LEACHP	Richard's equation	✓	✓	✓	✓	
PESTLA	Richard's equation	✓		✓	✓	
MACRO	Richard's equation Macrospores by gravity flow	✓		✓	✓	
VARLEACH	Field-Capacity & immobile water	✓			✓	
PLM	Field-Capacity & immobile water; macrospores fast flow regime	✓			✓	
PESTRANS GUI	Field-Capacity	✓	✓		✓	

CHAPTER 4

MODEL APPLICATIONS

4.1 Model Verification

Oscillations resulting from the inherent numerical dispersion in the numerical solutions of the advective-dispersive equation may cause errors. To hold this error under acceptable value, choice of the size of time and space increments Δt and Δz, respectively should be reasonable. Huyakorn and Pinder (1983) suggested that the dimensionless Peclet number ($Pe = \Delta z V_E/D_E$) < 2 and dimensionless Courant number ($Cr = \Delta t V_E/\Delta z$) < 1 in order to minimize the error of numerical dispersion during iterative solutions. In this regard, for PESTRANS GUI, Δt = 0.25 day and Δz = 1.0 cm are the recommended values for the convergence of the numerical solution. These Pe and Cr number values provided accurate numerical solutions upon comparison of numerical solutions with the corresponding analytical solutions.

Validation of PESTRANS GUI model is very important step by comparing model simulation output with measured values. Jury et al. (1980) conducted a laboratory study in order to measure triallate concentrations with soil depth and volatilization from soil surface. The experiment of Jury et al. (1980) was conducted using a soil column (with dimensions of 10 cm depth and 30 cm^2 surface area) filled with of San Joaquin sandy loam soil for a duration of 30 days at constant temperature 25 ^oC. Air flow was applied at a rate of 1 liter/min to the chamber to produce steady wind speed across the soil surface of 1 km/hr. Porous ceramic tubes were used at the bottom of the chamber to wet the soil column and above the soil 100% relative humidity was maintained. To capture triallate at the exit stream, polyurethane plugs were used then analyses were conducted in accordance with cross-referenced method.

The values of input parameters of PETRANS GUI for soil and chemical properties are shown in Table 4.1. Values were adopted from (Ünlü et al, 1995) which used Jury's experimentally measured data to validate the original PESTRAN original model. Half-life of triallate in soil was updated according to (NIH, 2020) as 77 days. Water infiltration rate was held to be 0.0 cm/day while the application rate of triallate was 134 μg/cm^2. PETRANS GUI was run to simulate concentration profile through soil depth using the input data presented in Figure 4.1 and the results were plotted against measured data of triallate as presented in Figure 4.2. Output simulation of PESTRANS GUI provided good fit with measured concentration values report in Jury et al (1980). RMSE was calculated between measured and simulated data to be 0.1021.

Table 4.1: Values of Parameters for triallate simulation through soil profile, Ünlü et al. (1995)

Parameter	Symbol	Value	units
Porosity	ϕ	0.5	cm^3/cm^3
Bulk density	ρ_b	1.34	g/cm^3
Volumetric water content	θ_w	0.28	cm^3/cm^3
Volumetric air content	θ_g	0.22	cm^3/cm^3
Organic carbon fraction	f_{oc}	0.00124	-
Bulk air diffusion coefficient	D_g^o	3888.8	cm^2/day
Bulk water diffusion coefficient	D_w^o	0.4493	cm^2/day
Atmospheric boundary layer thickness	d	0.5	cm
Pesticide mixing depth in soil	L	10	cm
Pesticide application rate	M	134	$\mu g/cm^2$
Water flux	q_w	0	cm/day
Dispersivity	α	0	cm
Organic carbon partitioning coefficient	k_{oc}	2588.7	cm^3/g
Henry's law constant	K_H	9.46×10^{-4}	-
Half-life*	$T_{1/2}$	77	days

*Half-life was adopted from (NIH, 2020)

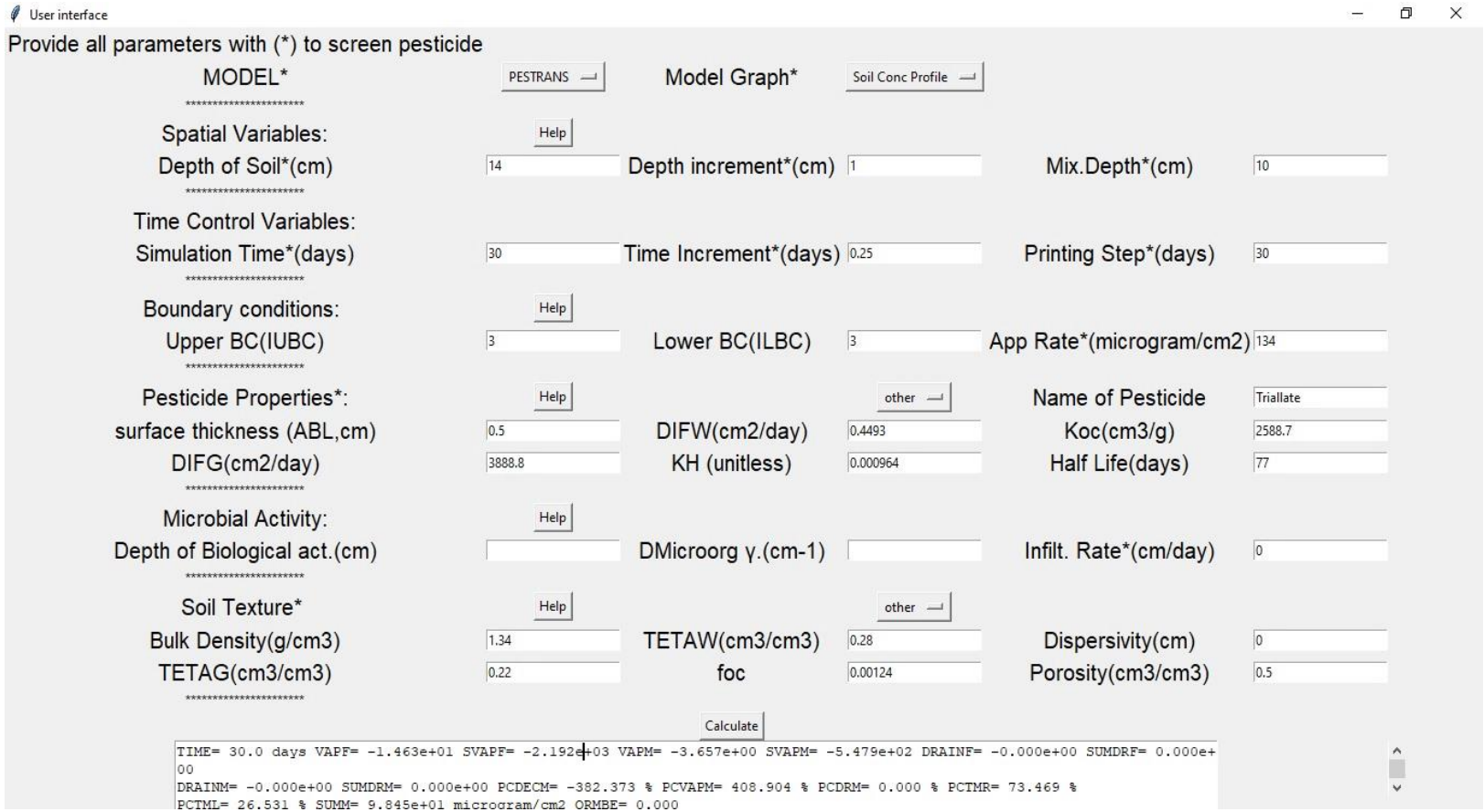


Figure 4.1: Screenshot of PESTRANS GUI Triallate simulation for verification

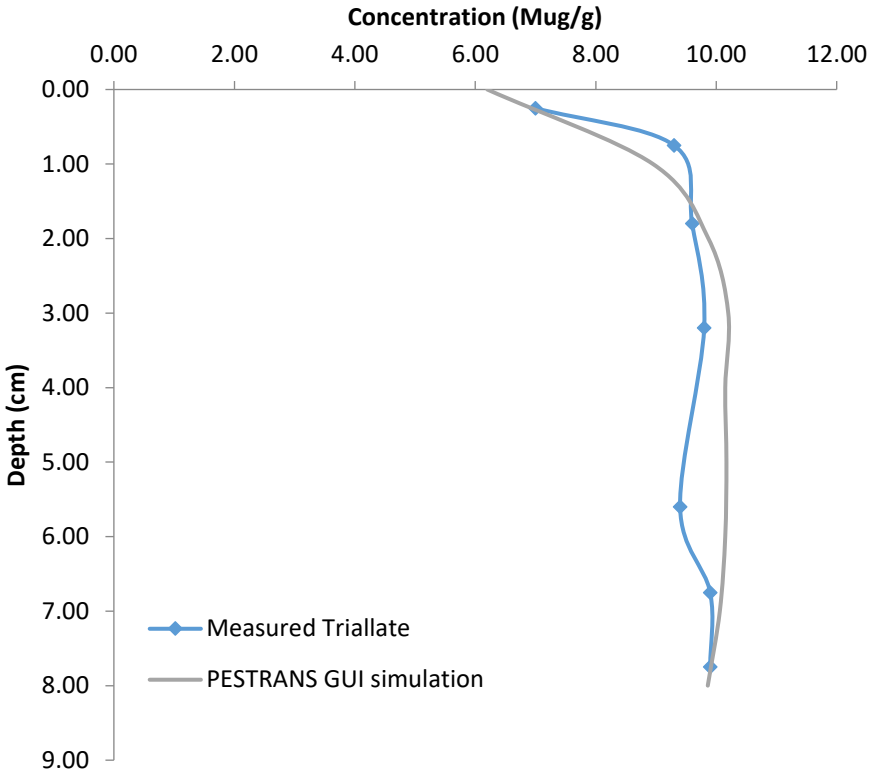


Figure 4.2: Comparison between measured and simulated soil profiles of Triallate

In addition, experimental data of Jury et al. (1980) for vapor flux graph versus time was used to validate simulated vapor flux by PESTRANS GUI. Figure 4.3 shows the graph of vapor flux versus time between measured and simulated data. RMSE was calculated to be 0.09624 which indicate good fit between measured and simulated data of PETRANS GUI model. The good fit between measured data of triallate adopted from Jury et.al, (1980) and simulated data of PESTRANS GUI validated the main assumptions of PETRANS GUI model. For example, linear partitioning of pesticide between air and aqueous phase according to Henry's law was proven to be valid in such experiments. In addition, the assumption of linear adsorption of pesticide's molecules on soil particle surface was possible. Such validation and verification

comparisons increase the confidence to use PESTRANS GUI as a useful tool to screen fate and behavior of pesticides in unsaturated soil zone.

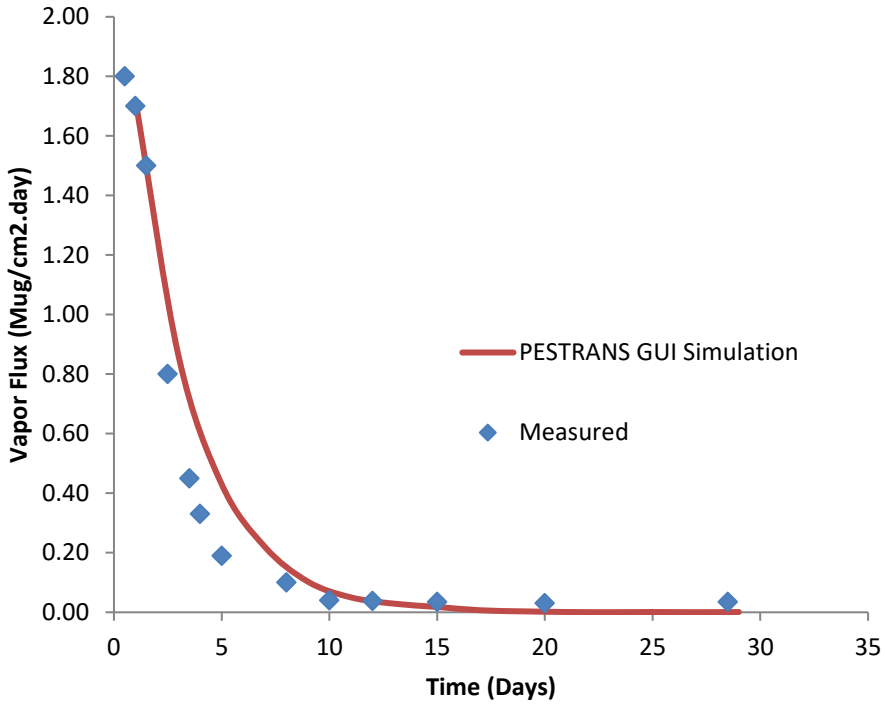


Figure 4.3: Comparison between measured and simulated vapor fluxes of Triallate

4.2 PESTRANS Demonstration Runs and Sensitivity Analysis

The accuracy of PESTRANS GUI Model output is directly affected by the choice of input parameter values. Thus, a sensitivity analysis was conducted to determine the most sensitive input parameters of PESTRANS GUI model so that the user pay attention to decide which input parameter values require the most accurate numerical values. PESTRANS GUI allows the user to choose any input values that the user believes closer to real-life scenario to facilitate simulation process. Thus, the user mainly is responsible for the simulation outcome by choosing the suitable values for input parameters.

In order to illustrate the sensitivity of certain input parameters of PESTRANS GUI model, simulations of chlorpyrifos and simazine were performed using high and low pollution potential scenarios with respect to soil and environmental conditions as adopted from Ünlü et al. (1995) as shown in Table 4.2. Both chlorpyrifos and simazine were selected due to their different properties of mobility, volatility and leaching. As seen in Table 3.1 of the physical and chemical properties, chlorpyrifos has high adsorption property (high K_{oc}), whereas simazine demonstrated low adsorption potential (low K_{oc}) which indicate difference in mobility through soil environment. Henry's law constant indicated difference in volatility potential. In another word, K_H of chlorpyrifos was low but K_H of simazine was extremely lower. Also, half-life of chlorpyrifos was lower than simazine demonstrating difference in persistence in soil. Thus, these two chemicals were chosen to perform sensitivity analysis of PETRANS GUI model due to their vast difference in mobility, volatility and persistence. Table 4.2 shows the soil parameters for the simulation runs. High pollution potential scenario was chosen as it represents the worst-case scenario for the pesticide to leach through soil or volatilize to the atmosphere.

Table 4.2: Input parameters for leaching sensitivity analysis tests adopted from Ünlü et al. 1995

Parameter	Symbol	High Pollution Potential scenario	Low Pollution Potential scenario	Units
Porosity	ϕ	0.4	0.5	cm^3/cm^3
Bulk density	ρ_b	1.5	1.2	g/cm^3
Volumetric water content	θ_w	0.15	0.35	cm^3/cm^3
Volumetric air content	θ_g	0.25	0.15	cm^3/cm^3
Organic carbon fraction	f_{oc}	0.005	0.025	-
Bulk air diffusion coefficient	D_g^o	Table 3.1	Table 3.1	cm^2/day
Bulk water diffusion coefficient	D_w^o	Table 3.1	Table 3.1	cm^2/day
Air boundary layer thickness	d	0.5	0.5	cm
Pesticide mixing depth	L	10	10	cm
Water Flux	q_w	0.5	0.0	cm/day
Dispersivity	α	0.01	12	cm
Microbial activity depth	W	50	100	cm
Microorganisms distribution constant	γ	0.03	0.03	cm^{-1}
Total soil depth	H	30	30	cm
Simulation time	t	30	30	days

Pesticide modeling runs were conducted with PETRANS GUI model for both chlorpyrifos and simazine for total depth of H=50 cm and simulation time was 30 days at different water infiltration/evaporation rates. The soil concentration profiles of chlorpyrifos and simazine are shown in Figures 4.4 and 4.6, respectively. Whereas, vapor flux versus time graphs at different water evaporation rates are presented in Figure 4.5 and 4.7, respectively. In PETRANS GUI model, infiltration or evaporation rate can be adjusted through parameter namely water flux (q_w). Sensitivity analysis was conducted using different q_w values for chlorpyrifos and simazine to demonstrate its impact on the pesticide concentration distribution in the soil environment. Chlorpyrifos concentration profile did not demonstrate strong change while changing values of infiltration rate (q_w) between 0 and 0.5 cm/day as well as evaporation rate q_w=-0.25 cm/day indicating strong immobility of the chlorpyrifos pesticide in soil as shown in Figure 4.4. However, soil concentration profile of simazine was very sensitive to water flux q_w (if positive infiltration rate while if negative evaporation rate) between 0, 0.5 and evaporation rate of -0.25 cm/day as indicated in Figure 4.6.

As a rule of thumb, volatilization rate increase with increasing water evaporation rate. For example, the application of induced evaporation rate to contaminated soil will cause forced volatilization of the pesticides to the atmosphere. Figures 4.5 and 4.7 show the vapor flux of chlorpyrifos and simazine at different evaporation rates, respectively. PESTRANS GUI considers amount of pesticide loss due to volatilization as negative mass flux since it is lost from the soil profile.

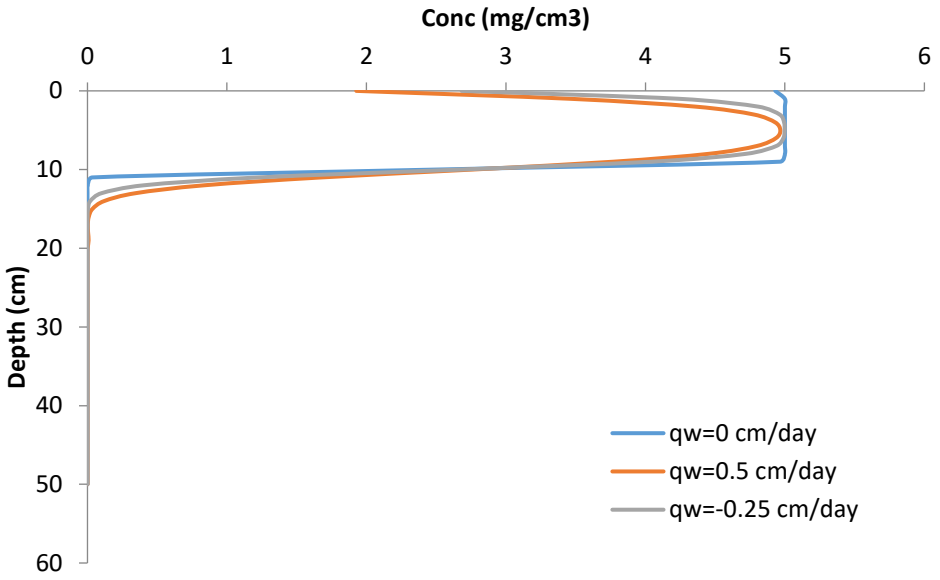


Figure 4.4: Soil concentration profile of chlorpyrifos after 30 days simulation

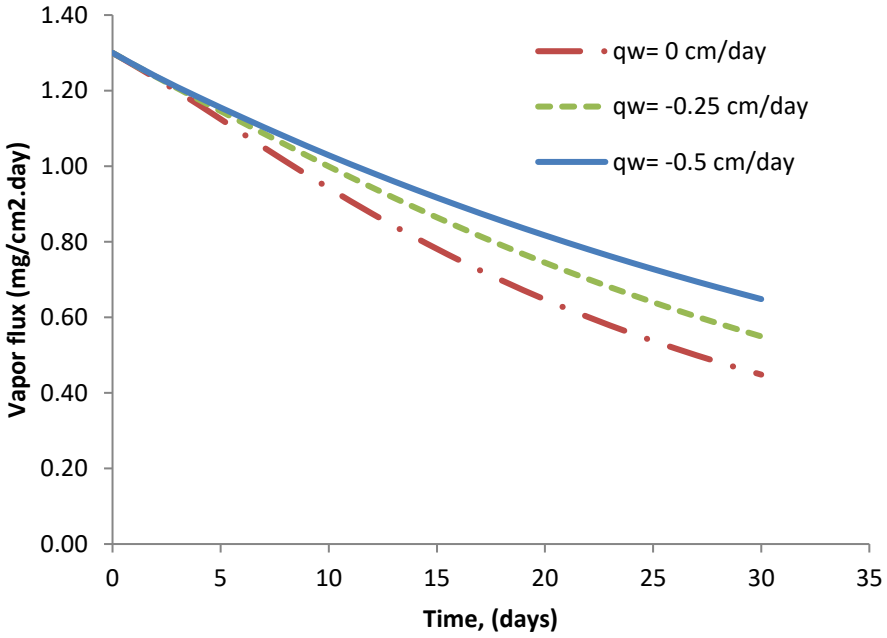


Figure 4.5: Vapor Flux versus Time of chlorpyrifos after 30 days simulation

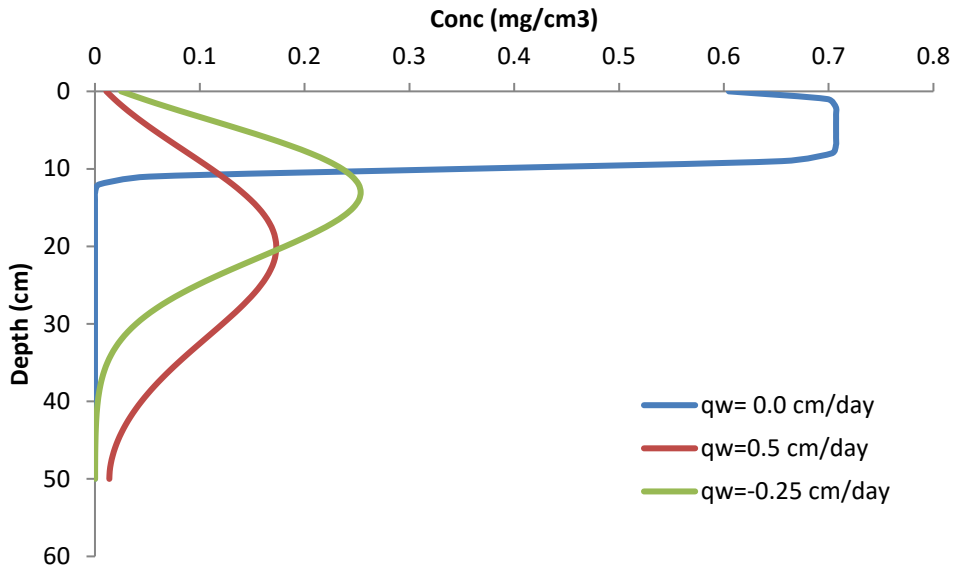


Figure 4.6:Soil concentration profile of simazine after 30 days simulation

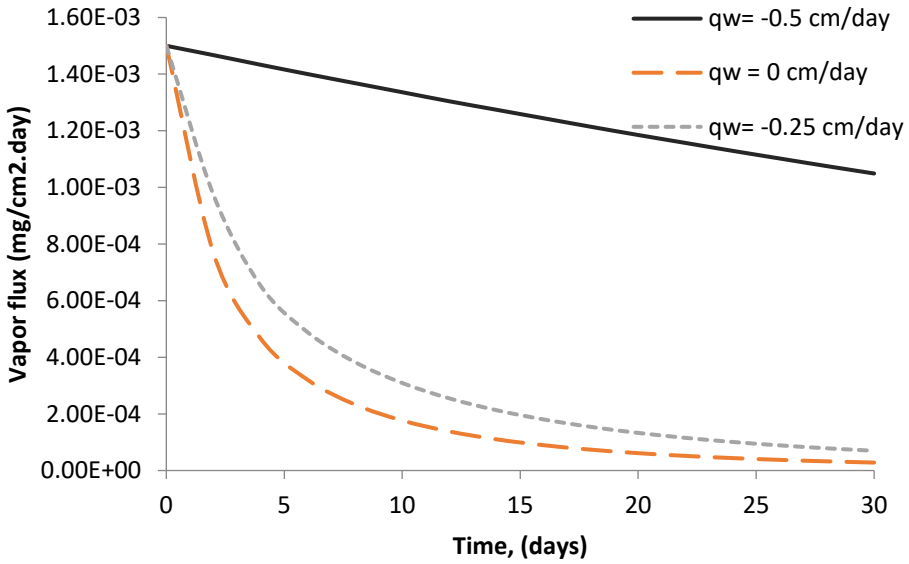


Figure 4.7: Vapor Flux versus Time of simazine after 30 days simulation

Tables 4.3, 4.4 and 4.5 present the effect of organic carbon fraction (f_{oc}) and mixing depth (L) on pesticide modeling in soil. Simulation runs were conducted for chlorpyrifos and simazine to investigate loss pathways due to volatilization and leaching as well as remaining of pesticide in the soil at the end of the simulation time. Increasing organic carbon fraction (f_{oc}) will reduce the mobility (leaching or volatilization) of pesticides especially pesticides with high K_{oc}, for example, Chlorpyrifos. As seen in Table 4.3, percentage of volatilization of chlorpyrifos and simazine deceased with an increase in organic carbon fraction (f_{oc}). In addition, an increase in mixing depth, which is the thickness of the soil layer where pesticide is applied homogeneously at the surface, leads to a decrease in percentage due to volatilization. Table 4.4 shows the effect of manipulating f_{oc} and L causing leaching of chlorpyrifos and simazine. Since chlorpyrifos has low mobility (high K_{oc}), manipulation of the parameters did not demonstrate any change. However, simazine leaching percentage was different owing to change in f_{oc} and L. When f_{oc} is increased, less mobility was demonstrated by simazine in soil and vice versa. Increasing the thickness of the mixing layer increased the leaching percentage yet reduced volatilization percentage. Table 4.5 demonstrates the change in chlorpyrifos and simazine remaining percentages when manipulating f_{oc} and L. Remaining percentage of chlorpyrifos did not show significance while changing f_{oc} and L owing to the low mobility of the pesticide. On the other hand, remaining percentage of simazine increased with an increase in f_{oc} and L because simazine has high mobility. The three tables 4.3, 4.4 and 4.5 gave a comprehensive assessment of the sensitivity of f_{oc} and L in modeling pesticides with different properties such as chlorpyrifos and simazine. Volatilization, leaching and remaining percentages demonstrated how organic carbon fraction and mixing depth are crucial parameters in pesticide modeling to investigate loss pathways in soil environment.

Table 4.3: Percentage of pesticide volatized after 30 days simulation with application rate of M=1 kg/ha and water evaporation rate q_w = 0.0 cm /day

Chlorpyrifos		Simazine	
f_{oc} = 0.0125	f_{oc} = 0.025	f_{oc} = 0.0125	f_{oc} = 0.025
L= 1.0 cm			
6.992	3.502	0.083	0.048
L= 10.0 cm			
1.398	0.700	0.018	0.010

Table 4.4: Percentage of Pesticide leached after 30 days simulation with application rate of M=1 kg/ha and water infiltration rate q_w = 0.5 cm /day

Chlorpyrifos		Simazine	
f_{oc} = 0.0125	f_{oc} = 0.025	f_{oc} = 0.0125	f_{oc} = 0.025
L = 1.0 cm			
0.000	0.000	0.008	0.000
L = 10.0 cm			
0.000	0.000	0.233	0.002

Table 4.5: Percentage of Pesticide remaining after 30 days simulation with application rate of M=1 kg/ha and infiltration rate q_w = 0.0 cm /day

Chlorpyrifos		Simazine	
foc = 0.0125	foc = 0.025	foc = 0.0125	foc = 0.025
L = 1.0 cm			
49.849	49.925	57.051	62.723
L = 10.0 cm			
49.969	49.985	67.748	69.052

Table 4.6 demonstrates the change in volatilization percentages in chlorpyrifos and simazine while changing air boundary layer thickness (d). This layer thickness is very crucial to the transport of pollutant between gas and aqueous phases. An increase in the film thickness reduced the percentage of volatilized chlorpyrifos and simazine. The transport of molecules between the two phases become more difficult with thicker films. Since chlorpyrifos is more volatile than simazine, it demonstrated significant decrease in volatilization percentage. Simazine also demonstrated a decrease in volatilization percentage but to lower extent due to low volatility potential (low K_H). In addition, an increase of soil mixing depth (L) from 1 cm to 10 cm reduced the percentage of volatilized chlorpyrifos and simazine.

Table 4.6: Percentage of pesticide volatized after 30 days simulation with application rate of M=1 kg/ha and water evaporation rate q_w = -0.5 cm /day.

Chlorpyrifos		Simazine	
d=0.05 cm	d=0.5 cm	d=0.05 cm	d=0.5 cm
L= 1.0 cm			
61.543	11.322	0.164	0.016
L= 10.0 cm			
24.390	2.439	0.065	0.007

Sensitivity analysis was made also to see the impact of water content in soil (θ_w) on pesticide concentration distribution in soil and volatilization mass fluxes in the presence/absence of water evaporation flux. Tables 4.7 and 4.8 show the percentage of volatilization loss and pesticide remaining in soil profile, respectively, for modeling of chlorpyrifos and simazine for 30 days. Simazine has lower volatility potential and higher mobility than chlorpyrifos. An increase in soil water content from 0.15 to 0.45 at the absence of infiltration did not change the percentage of volatized in chlorpyrifos and fluctuated in simazine since it possesses low volatility. The percentage of pesticide remained within the unsaturated soil zone decreased with water evaporation rate of -0.5 cm/day in simazine more than chlorpyrifos owing to mobility difference between the two pesticides.

Table 4.7: Pesticide volatilzation percentage (%) after simulation for 30 days at different soil volumetriv water content and evaporation rates.

Chlorpyrifos			Simazine		
θ_w=0.15	θ_w=0.30	θ_w=0.45	θ_w=0.15	θ_w=0.30	θ_w=0.45
q_w= 0.0 cm/day					
13.990	13.952	13.891	0.189	0.133	0.069
q_w= -0.5 cm/day					
11.322	13.226	13.769	0.016	0.022	0.025

Table 4.8: Pesticide remaining percentage (%) after simulation for 30 days at different soil volumetric water content and evaporation rates.

Chlorpyrifos			Simazine		
θ_w=0.15	θ_w=0.30	θ_w=0.45	θ_w=0.15	θ_w=0.30	θ_w=0.45
q_w= 0.0 cm/day					
49.827	49.589	48.839	67.759	50.488	33.372
q_w= -0.5 cm/day					
38.476	45.461	47.920	32.082	46.632	52.226

In Table 4.9, sensitivity analysis was performed to assess the impact of soil dispersivity on leaching percentage of chlorpyrifos and simazine. Chlorpyrifos did not demonstrate any leaching percentage owing to low mobility (high K_{oc}). However, simazine leaching percentage increased with increasing dispersivity due to high mobility. Physical and chemical properties of pesticides play a significant role in the transport and partitioning in the soil. Thus, some modeling parameters can generate huge difference in some pesticides while their manipulation would not show the same significance in other pesticides as seen in chlorpyrifos and simazine situation.

Table 4.9: Pesticide leaching percentage (%) after simulation for 30 days at different soil volumetric water content conditions (L=10.0 cm and q_w=0.5 cm/day).

Chlorpyrifos			Simazine		
θ_w=0.15	θ_w=0.30	θ_w=0.45	θ_w=0.15	θ_w=0.30	θ_w=0.45
α= 1.0 cm					
0.000	0.000	0.000	11.682	4.933	2.377
α= 10.0 cm					
0.007	0.000	0.000	15.481	16.103	15.209

4.3 Simulation Runs for Classification of Priority Pesticides According to Their Fate and Transport Behavior in Soil

Based on the simulations made with the developed pesticide fate and transport model, PESTRANS GUI, priority pesticides that are widely used in Turkey are classified according to their pollution potential. For this purpose, pesticides have been subjected to volatility, mobility, persistence and leaching tests under standard soil and environmental conditions. Pesticides, which exhibit similar behavior as a result of the tests, are classified in the same category.

The following scenario was established for classification tests:

1. The pesticide is uniformly applied with constant application rate of M ($\mu g/cm^2$) over soil with depth L cm from the surface.
2. Volatilization rate of pesticide from soil surface occurs by passing through a stagnant air layer of thickness d.
3. Advective transport of pesticide is under steady state flow conditions, ($q_w = \pm q_w$ or 0)
4. Properties of soil below the pesticide application depth is uniformly distributed.

For simulation runs conducted with PESTRANS GUI to classify pesticides based on their volatility, mobility and persistence, parameter values given in Table 4.2 describing the standard soil and environmental conditions and physico-chemical properties of pesticides given in Table 3.1 are used. For simulation runs with PESTRGW GUI to classify pesticides based on their potential to leach to groundwater, parameter values given in Table 4.14 describing soil and environmental properties and physico-chemical properties of pesticides were imported from the embedded data base given in table 3.1.

4.3.1 Volatility classification:

Volatility of pesticide in the soil occurs via diffusion through the stagnant layer of air that separates the soil and atmosphere. The degree to which this stagnant air layer affects volatilization losses has been used as a criterion in classifying pesticides according to their volatility properties. The presence or absence of water evaporation from the soil significantly affects the vapor losses of some pesticides. Therefore, this situation has been taken into account in volatility classification.

In the absence of water evaporation, the highest pesticide volatility rate from the soil surface will be controlled by the rate of pesticide volatilization from the stagnant air layer on the surface, J_{v1} or the rate of transport of the pesticide in the soil to the soil surface by diffusion-dispersion J_{v2}. Therefore, the stagnant air layer on the surface will only limit the pesticide volatilization if $J_{v1} << J_{v2}$. For $t > 0$, J_{v1} reaches the highest value if the concentration gradient between the soil surface and the atmosphere is the maximum, that is $C_g(0,t) = K_H C_0 / (\rho_b K_d + \theta_w + K_H \theta_g)$, while J_{v2} reaches its maximum level if the concentration gradient in the soil towards the soil surface is the maximum, that is $C_T(0,t) = 0$ and D_E is the maximum. In case of presence of water evaporation, the pesticide volatilization rate will vary depending on the rate at which the pesticide is transported to the soil surface with the advective upward water flow. Therefore, as the amount of the pesticide in the liquid phase increases (the solubility in water and its adsorption in water decreases), the pesticide volatilization rate will increase.

Volatility potential of pesticides are indicated by Henry's law constant, K_H. According to Jury et al.(19984), at steady state water evaporation flux pesticides with K_H values less than 2.5×10^{-5} have less tendency to volatilize and more likely to be partitioned into the surface of solid soil particles. Whereas pesticides with K_H values higher than 2.5×10^{-5} possess high potential to volatilize into gaseous phase. Pesticides with high volatilization potential were included in Category I, low volatilization in Category III and medium volatilization in Category II. The list of pesticides belonging to these categories is given in Table 4.10. Vapor diffusion plays an important role in the

transport of Category I pesticides, and liquid diffusion-dispersion plays an important role in the transport of Category III pesticides. Category II pesticides exhibit a behavior between Category I and Category III; In other words, vapor diffusion plays an important role in low soil water amounts, whereas liquid diffusion-dispersion plays an important role in high soil water amounts. This causes the pesticides in each category to exhibit different transport properties. Then, PESTRANS GUI is used to model pesticide volatility in each category to check on volatility potential and the impact of infiltration/evaporation rates on pesticide fate and transport in unsaturated soil environment.

Table 4.10: Pesticides Volatility Categories

Category I Pesticides (High volatility) $K_H > 2.5x10^{-5}$	Category II Pesticides (Moderate volatility) $K_H = 2.5x10^{-5}$	Category III Pesticides (Low volatility) $K_H < 2.5x10^{-5}$
Chlorpyrifos	Dichlorvos	Aclonifen
Endosulfan		Alachlor
Hexachlorobenzene		Atrazine
Hexachlorocyclohexane		Bifenox
Pentachloro benzene		Chlorfenvinfos
Tributyltin		Cybutryne
Trichloro-benzenes		Cypermethrin
Trifluralin		Dicofol
		Diuron
		Heptachlor epoxide
		Isoproturon
		Pentachloro-phenol
		Quinoxyfen
		Simazine
		Terbutryn

Graphical results of pesticide fate modeling are shown in Figures 4.8 to 4.13 for the three different volatility categories using the developed software PESTRANS GUI. Endosulfan, dichlorvos and atrazine were selected for to be shown for volatility tests owing to their high mobility (low K_{oc}). Pesticide with high volatility in category I such as endosulfan (dimensionless K_H =2.66x10^{-3}), from category II dichlorvos (dimensionless K_H =2.35x10^{-5}) and from less volatile category atrazine (dimensionless K_H =9.65x10^{-8}) were simulated using PESTRANS GUI according to the modeling parameters in Tables 4.2 and 3.1 mentioned previously. Manipulating evaporation/infiltration rates demonstrated a change in soil profile as well as vapor flux profile. Increasing water evaporation rate increased the vapor flux of each pesticide. In general , vapor flux deceased over time. Endosulfan demonstrated relatively small change in soil concentration profile when comparing simulations with profile without evaporation/infiltration rates. While dichlorvos and atrazine showed more significant change when manipulating evaporation/infiltration rates. Although Atrazine has low volatility potential, increasing evaporation rate increased its vapor flux which is considered as induced volatilization. When looking at the concentration profile of pesticide in soil depth, it is seen that pesticides with high evaporation (Category I) stay closer to the soil surface than pesticides with low evaporation (Category III). In addition, pesticides' sorption and degradation properties such as K_{oc} and $T_{1/2}$ have a direct impact on the deceasing trend of pesticide decrease over time whether in soil concentration profile or vapor flux over time profile.

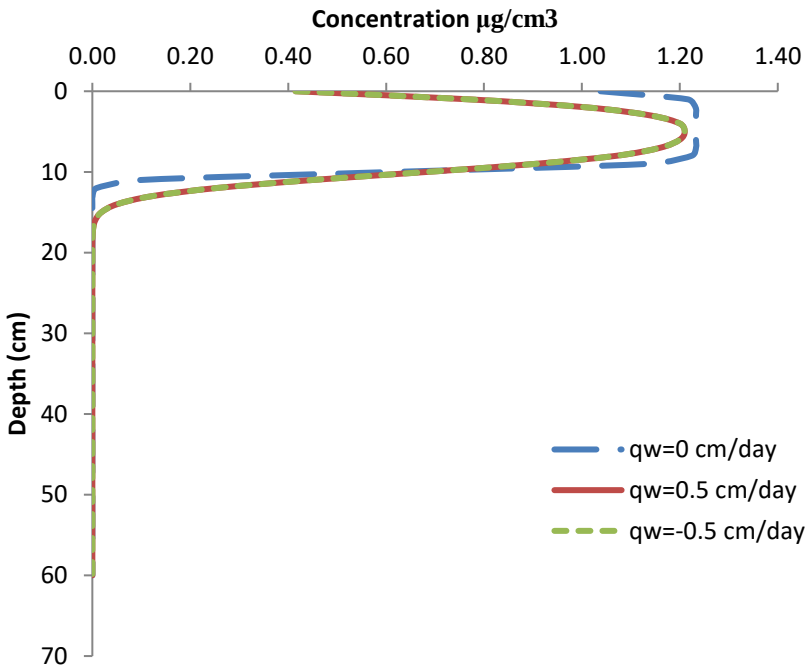


Figure 4.8: Endosulfan soil profile after 30 days modeling

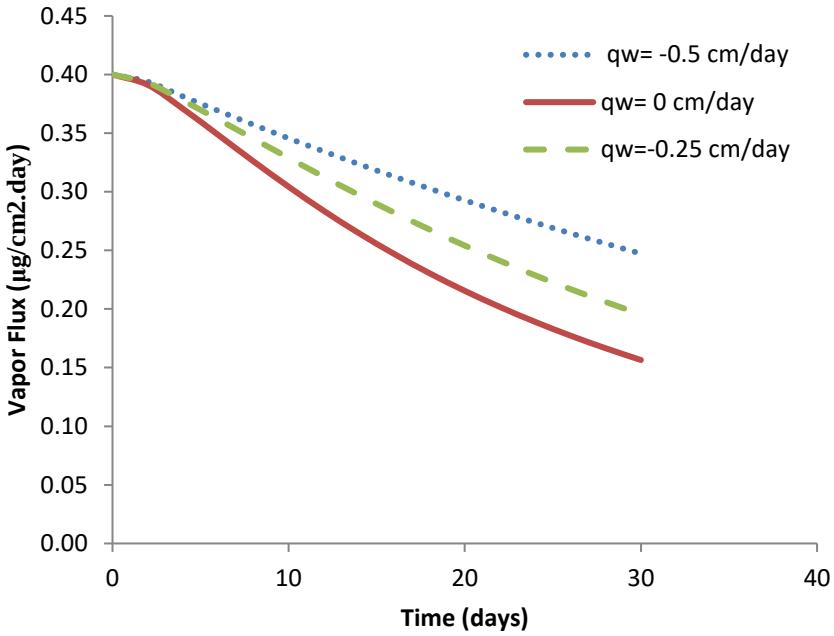


Figure 4.9: Endosulfan vapor flux versus time profile

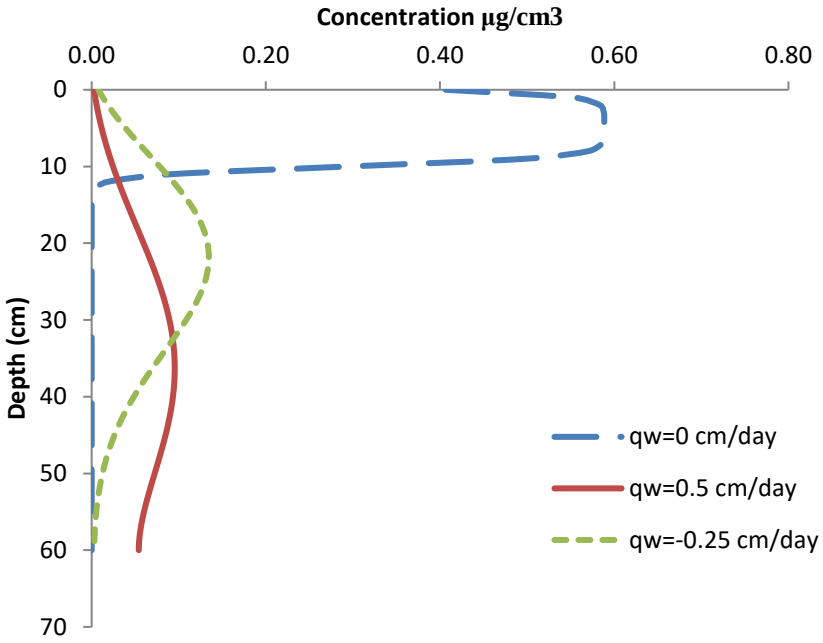


Figure 4.10: Dichlorvos soil profile after 30 days modeling

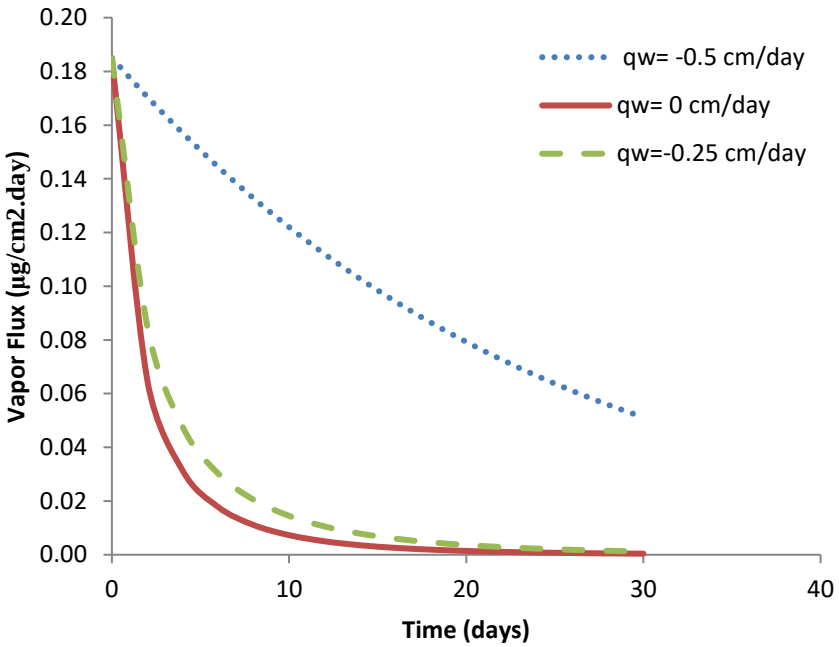


Figure 4.11: Dichlorvos vapor flux versus time profile

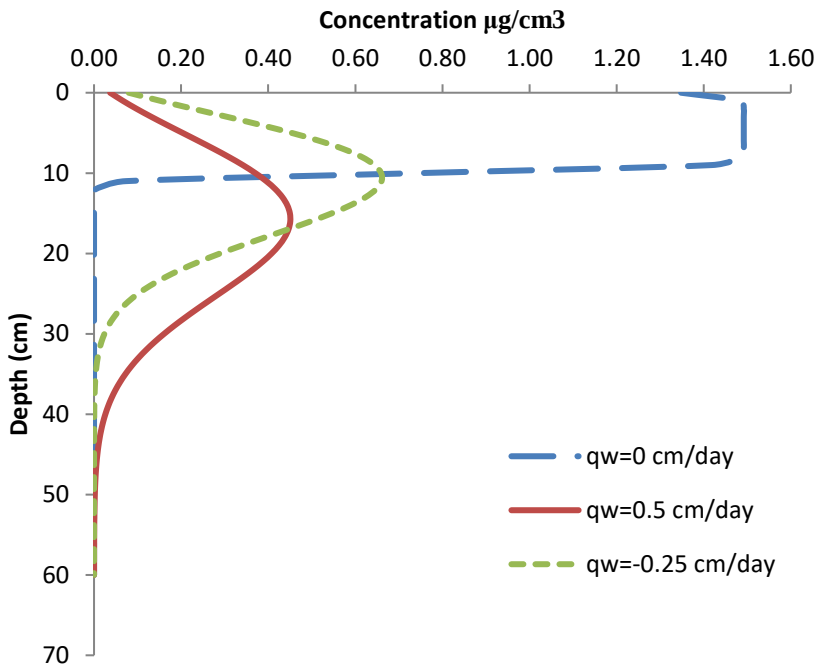


Figure 4.12: Atrazine soil profile after 30 days modeling

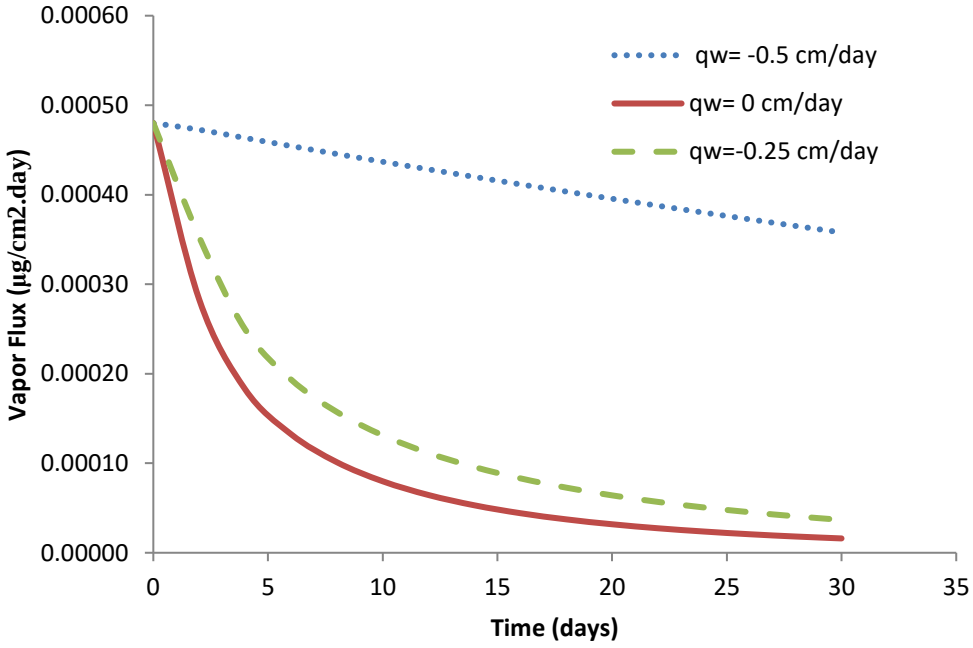


Figure 4.13: Atrazine vapor flux versus time profile

4.3.2 Mobility classifications

The mobility of pesticides dissolved in water is an important feature that determines the depth of transport in the soil through advection or diffusion-dispersion. For this reason, pesticides have been classified by subjecting them to advective, diffusive and dispersive mobility tests.

In this classification, three parameters were taken into account; namely the "advective time"; which is the time required for the pesticide to reach certain depth under certain water flow rates, and "dispersive time" as well as "diffusive time" which are the times required for the pesticide to spread over certain area by diffusion or dispersion process under certain water flow rates.

Advective time t_{advec} is the time required to transport the pesticide by distance l when water flux (infiltration rate) is q_w.

$$t_{advec} = \frac{l}{V_E} = \frac{l\left(\rho_b f_{oc} K_{oc} + \theta_w + \theta_g K_H\right)}{q_w} \qquad (4.1)$$

As it can be seen from this equation, the advective transport time of pesticides with high adsorption (for example $K_d > 4x10^{-3}$ m^3/kg) will be very high, so the advective mobility will be very low. The effect of θ_w, and $\theta_g K_H$ factors on advective transport of pesticides with high K_d value will be insignificant. Advective time is a very useful indicator for determining the relative mobility of the pesticide and the depth of the peak concentration of pesticides in the soil.

Dispersive time t_{dis} is the time needed for the pesticide to spread over an area of l^2 at an infiltration rate of q_w;

$$t_{dis} = \frac{l^2}{D_E} = \frac{l^2 \phi^2 \left(\rho_b f_{oc} K_{oc} + \theta_w + \theta_g K_g\right)}{D_g^o \theta_g^{\frac{10}{3}} K_H + \alpha_z \left(\frac{q_w}{\theta_w}\right) \phi^2 + D_w^o \theta_w^{\frac{10}{3}}} \qquad (4.2)$$

Increasing dispersivity decreases dispersive time. In general, pesticides with high advective time would have high dispersive time as well.

Diffusive time (t_{dif}) is the time for the pesticide molecules to spread through gas and liquid phases over an area l^2 when there is no water flux; i.e., infiltration rate q_w=0.

$$t_{dif} = \frac{l^2}{D_E} = \frac{l^2 \phi^2 (\rho_b f_{oc} K_{oc} + \theta_w + \theta_g K_H)}{D_g^o \theta_g^{10/3} K_H} \qquad (4.3)$$

Diffusive time is relatively short for pesticides with high volatility (K_H) and low adsorption (K_{oc}). Among the pesticides, those with low t_{dis} and t_{dif} values tend to spread deeper in the soil since their dispersive and diffusive action will be high. Unlike advective time, dispersive and diffusive times are significantly dependent on the volumetric air (θ_g) and water (θ_w) contents in the soil.

Equations 4.1 through 4.3 show that advective, dispersive and diffusive times of pesticides varies depending on soil characteristics, as well as physico-chemical properties of pesticides. Using these equations Table 4.11 was generated to classify the 24 pesticides included in priority pollutants list of Turkey. For classification, physical and chemical properties of these pesticides were obtained from PESTRANS GUI database given in Table 3.1, and soil properties are from Table 4.2 Infiltration rate was assumed to be q_w=1 cm/day and mixing depth L=10 cm. As seen from Table 4.11 for mobility classification based on advective time t_{advec}, 5 different mobility classes between 1 and 5 were defined following McCall et. al (1980). The lowest advective mobility class is defined as $t_{advec} > 250$ days for Class 1, $101 < t_{advec} \leq 250$ days for Class 2, $31 < t_{advec} \leq 100$ days for Class 3, $11 < t_{advec} \leq 30$ days for Class 4, and finally the highest advective mobility class is defined as $t_{advec} < 10$ days for Class 5. Similarly, classes 1-3 were used for t_{dis} and t_{dif}. Class 1 ($t_d > 100$ days) represents low, Class 2 ($20 < t_d < 100$ days) medium and Class 3 ($t_d < 20$ days) high dispersive-diffusive mobility (Jury et al., 1984).

The results of the mobility classification show that the K_{oc} value is an important factor for pesticides transported primarily by the water phase (high water solubility) and such pesticides can be classified only on the basis of advective time. However, in the mobility classification of pesticides that are transported significantly by gas phase

(high K_H value) and do not undergo adsorption much (low K_{oc} value), the advective and diffusive times should be considered together. Because such pesticides may not be very mobile advectively, but because of their diffusive mobility, they can easily penetrate deeper by vapor diffusion. As can be seen from Table 4.11, it is understood that almost all pesticides have very low diffusive mobility. On the other hand, they are diverse in terms of advective and dispersive mobility. Among the 24 priority pesticides, there are pesticides which demonstrated high advective mobility such as dichlorvos and dicofol which were included in class 4. Then, atrazine, alachlor, endosulfan and Terbutryn were classified in class 3 with less advective mobility. The rest of priority pesticides demonstrated low advective as well as dispersive and diffusive mobilities. Majority of prioirty pesticides demonstrated low diffusive moblility except tributyltin which was categorized to have high diffusive and dispersive mobility owing to high adsoprtion potetial (high K_{oc}). On the other hand, three pesticides showed higher dispersive mobility than the ther prioirty pesticides. Dichlorvos and dicofol had higher dispersive mobility and were categoized in Category II because of their low volatility (low K_H) and high mobility (low K_{oc}). As can be seen in Table 4.11, majority of the priority pesticides tend to resist advective mobility and likely tend to remain in soil after their application.

Table 4.11: Classification of priority pesticides according to advective, dispersive and diffusive mobilities

Priority Pesticide	t_{advec} (days)	Category	t_{dis} (days)	Category	t_{dif} (days)	Category
Aclonifen	2142.5	1	7312.4	1	4.76E+08	1
Alachlor	97.1	3	332.9	1	2.04E+08	1
Atrazine	71.0	3	242.4	1	4.49E+08	1
Bifenox	1107.5	1	3806.8	1	2.01E+08	1
Chlopyrifos	927.5	1	3195.0	1	3.38E+08	1
Chlorfenvinfos	2448.5	1	8423.8	1	8.62E+06	1
Cybutryne	933.5	1	3220.9	1	3.11E+08	1
Cypermethrin	2187.5	1	7527.7	1	1.09E+08	1
Dichlorvos	15.4	4	52.4	2	3.79E+05	1
Dicofol	19.7	4	67.9	2	8.73E+05	1
Diuron	3813.5	1	13067.5	1	5.95E+10	1
Endosulfan	36.2	3	122.5	1	9.77E+03	1
Heptachlor epoxide	12393.5	1	42407.2	1	1.33E+09	1
Hexachlorobenzene	3033.6	1	7245.2	1	2.43E+04	1
Hexachlorocyclohexane	324.5	1	1104.2	1	6.42E+05	1
Isoproturon	585003.5	1	2000792.9	1	8.19E+13	1
Pentachlorobenzene	7653.5	1	22096.5	1	1.46E+05	1
Pentachlorophenol	1116.5	1	3796.6	1	6.10E+08	1
Quinoxyfen	1083.5	1	3726.0	1	9.11E+08	1
Simazine	115.1	2	392.3	1	1.71E+09	1
Terbutryn	47.6	3	163.0	1	3.67E+07	1
Tributyltin	264.7	1	2.0	3	2.02E+00	3
Trichlorobenzene	402.3	1	1016.0	1	3.85E+03	1
Trifluralin	4920.5	1	16551.0	1	8.55E+05	1

4.3.3 Persistence classification

The loss of any pesticide from the soil occurs through biodegradation and/or volatilization. The biological or chemical degradation rate of organic pollutants depends significantly on soil properties and environmental parameters such as water content, temperature, organic carbon content and soil pH. In the absence of detailed information about these factors, the biodegradation potential of pesticides can be defined with first order reaction coefficient μ or half-life $T_{1/2}$ parameters. This parameter represents the degradation in all phases and it is calculated by the following equation (4.4) as the ratio of the amount of pesticide remaining in the soil at the end of time *t* , *M(t),* to the amount of pesticide initially applied to the soil M (0):

$$\mu = \frac{\ln\left(\frac{M(t)}{M(0)}\right)}{t} = \frac{\ln(2.0)}{T_{1/2}} \qquad (4.4)$$

For the pesticides with high volatilization potential, volatilization losses can be important in determining the residual pesticide mass. Since the persistence of pesticides is an important indicator in terms of their functional efficiency and pollution potential, effective or dynamic half-life $T_{1/2}^{E}$ calculation, which also takes into account volatilization losses, is the proper approach. Similar to Equation 4.4, the effective half-life can be calculated using the following equation:

$$T_{1/2}^{E} = \frac{\ln(2.0)}{M(t)/M(0)} \qquad (4.5)$$

Here, M (t)/M (0) represent the ratio of the amount of pesticide remaining in the soil after volatilization and biodegradation to the amount of pesticide initially applied to the soil. Using PESTRANS GUI, shallow (L=1 cm) and deep (L=10 cm) pesticide application with water evaporation (q_w = -0.5 cm/day) and without water evaporation (q_w= 0.0 cm / day) conditions. Percentage of pesticide remaining mass was considered after volatilization and biodegradation amounts were subtracted from the amount of pesticide initially applied to the soil as a result of 30 days simulation. Then,

$T_{1/2}^{E}$was caluctated based on equation 4.5. The results in Table 4.12 show that priority pesticides exhibit quite different properties. In order to present these differences in a more systematic and understandable way, pesticides have been divided into the persistence classes given in Table 4.13.

Table 4.12: Percent pesticides remaining and effective pesticide half-lives after 30-day simulations as affected by water evaporation rate (E= 0.0 , 0.5 cm/day) and pesticide application depth (L=1 cm and L=10 cm).

Pesticide	L=1 cm				L=10 cm			
	q_w=0.0 cm/day		q_w=-0.5 cm/day		q_w=0.0 cm/day		q_w=-0.5 cm/day	
	Remaining mass (%)	$T^{E}_{1/2}$ days	Remaing mass (%)	$T^{E}_{1/2}$ days	Remaing mass (%)	$T^{E}_{1/2}$ days	Remaing mass (%)	$T^{E}_{1/2}$ days
Aclonifen	89.78	67.8	64.01	19.3	89.86	68.4	83.22	41.3
Alachlor	14.80	8.1	7.13	7.5	15.04	8.2	10.27	7.7
Atrazine	72.19	24.9	37.33	11.1	74.12	26.8	49.94	13.8
Bifenox	30.86	10.0	22.01	8.9	30.88	10.0	28.60	9.7
Chlopyrifos	49.78	13.8	36.65	10.9	49.96	13.9	46.64	13.0
Chlorfenvinfos	86.90	52.9	50.52	14.0	87.02	53.4	75.59	28.4
Cybutryne	89.95	68.9	52.38	14.6	90.09	69.9	78.30	31.9
Cypermethrin	50.00	13.9	48.31	13.4	50.00	13.9	49.60	13.8
Dichlorvos	25.73	9.3	22.01	8.9	28.66	9.7	20.47	8.7
Dicofol	70.67	23.6	56.92	16.1	70.70	23.7	67.42	21.3
Diuron	76.68	29.7	49.00	13.6	79.99	34.6	54.21	15.1
Endosulfan	58.11	16.5	41.92	11.9	60.94	17.7	56.45	15.9
Heptachlor epoxide	97.11	239.9	74.82	27.5	97.18	245.4	91.73	83.8
Hexachlorobenzene	37.03	11.0	35.77	10.8	75.07	27.8	72.74	25.4
Hexachlorocyclohexane	52.13	14.5	25.76	9.3	54.58	15.3	42.46	12.0
Isoproturon	39.96	11.5	24.38	9.2	41.62	11.9	28.07	9.6
Pentachlorobenzene	40.52	11.7	36.90	11.0	75.07	27.8	70.61	23.6
Pentachlorophenol	62.01	18.2	28.58	9.7	62.80	18.6	45.37	12.7
Quinoxyfen	89.98	69.2	54.32	15.2	90.10	70.0	79.36	33.6
Simazine	67.14	21.1	39.27	11.4	69.99	23.1	47.09	13.1
Terbutryn	36.72	11.0	16.86	8.3	37.06	11.0	26.83	9.5
Tributyltin	87.88	57.2	87.88	57.2	87.88	57.2	87.88	57.2
Trichlorobenzene	14.55	8.1	15.47	8.2	40.55	11.7	37.32	11.1
Trifluralin	82.89	40.5	72.28	25.0	84.91	45.9	82.39	39.4

In the persistence classification, $T_{1/2}^{E}$ values calculated by taking L = 10 cm and q_w = 0 cm day conditions in Table 4.12 were taken as basis. Priority pesticides

were categorized into 5 classes (Ünlü et al., (1995)). Highly persistent pesticides with ($T_{1/2}^{E}$ > 100 days) were included in Class 1. Persistent pesticides with (31 <$T_{1/2}^{E}$ ≤ 100 days) were categorized in Class 2. Pesticides with low persistence (16 <$T_{1/2}^{E}$ ≤ 30 days) are in Class . Non-persistent pesticides (6 <$T_{1/2}^{E}$ ≤ 15 days) are in Class 4. Finally, Class 5 was assigned for highly degradable pesticides. Each category is illustrated in Table 4.13 and priority pesticides were divided according to each effective half-life ($T_{1/2}^{E}$) value. It can be seen from Table 4.13 that none of the priority pesticides fell under Class 5. In another words, none of the 24 priority pesticides is considered highly degradable within few days. In the contrast heptachlor epoxide demonstrated high persistence which came in accordance with its resistance to biodegradation as well as low volatility. Majority of priority pesticides fell under low persistence and non-persistent Classes 3 and 4.

Table 4.13: Classes of pesticide persistance

Class 1: highly persistent ($T_{1/2}^{E}$ > 100 days)		
Heptachlor epoxide		
Class 2: persistent (31 <$T_{1/2}^{E}$ ≤ 100 days)		
Aclonifen	Chlorfenvinfos	Cybutryne
Diuron	Quinoxyfen	Tributyltin
Trifluralin		
Class 3: low persistence (16 <$T_{1/2}^{E}$ ≤ 30 days)		
Atrazine	Dicofol	Endosulfan
Hexachlorobenzene	Pentachloro benzene	Pentachlorophenol
Simazine		
Class 4: non-persistent (6 <$T_{1/2}^{E}$ ≤ 15 days)		
Alachlor	Bifenox	Chlorpyrifos
Cypermethrin	Dichlorvos	Hexachlorocyclohexane
Isoproturon	Terbutryn	Trichlorobenzene
Class 5: highly non-persistent ($T_{1/2}^{E}$ ≤ 5 days)		
-		

4.3.4 Groundwater pollution potential classification

The volatility, mobility, and persistence classifications obtained as a result of standard simulation scenarios provided important information on the extent to which pesticides can be affected by each of the major loss pathways, such as volatilization, biodegradation and leaching. In order to determine the combined effects of these lost pathways, simulations were carried out to evaluate the leaching of pesticides from the overlying soil profile and thus the potential for groundwater pollution. The simulations have been made by using the most common application amounts of pesticides, taking into account of soil properties that can represent the two scenarios, high pollution potential and low pollution potential. Scenarios with high and low pollution potential have been created in order to evaluate the pollution potential of pesticides by comparing them with each other under conditions where soil and environmental factors affect the groundwater pollution positively or negatively. Table 4.14 gives the values of environmental and soil parameters representing scenarios with high and low pollution potential.

In the high pollution potential scenario, soil property values representing sandy soils, such as low organic carbon fraction (f_{oc} = 0.005) and volumetric water content (θ_w=0.15), high water infiltration rate (q_w=0.274 cm/day =100 cm/year) and low soil depth (*W=50 cm*) for maximum biological activity were assumed. On the other hand, in low pollution potential scenario, soil property values representing clayey soil, such as high organic carbon fraction (f_{oc} = 0.025) and volumetric water content (θ_w=0.35), low infiltration rate (q_w=0.137 cm/day =50 cm/year) and high soil depth (W=100 cm) for maximum biological activity were assumed.

Table 4.14: Parameters values for leaching tests(adopted from Ünlü et al., 1995)

Parameter	Symbol	High Contamination Potential	Low Contamination Potential	Units
Porosity	Φ	0.4	0.5	cm^3/cm^3
Bulk density	ρ_b	1.5	1.2	g/cm^3
Volumetric water content	θ_w	0.15	0.35	cm^3/cm^3
Volumetric air content	θ_g	0.25	0.15	cm^3/cm^3
Organic carbon fraction	f_{oc}	0.005	0.025	-
Bulk air diffusion coefficient	D^o_g	Table 3.1	Table 3.1	cm^2/day
Bulk water diffusion coefficient	D^o_w	Table 3.1	Table 3.1	cm^2/day
Atmospheric boundary layer thickness	d	0.5	0.5	cm
Pesticide mixing depth in soil	L	10	10	cm
water flux	q_w	0.274	0.137	cm/day
Dispersivity	α	1.0	1.0	cm
Microbial Activity Depth	W	50	100	cm
Microorganisms Distribution Constant	γ	0.03	0.03	cm^{-1}
Total Depth	H	300	300	cm

PESTRANS GUI assumes the rate of biodegradation is directly proportional to the level of microbial activity in the soil profile and the level of microbial activity decreases exponentially after certain depth (z=W). This approach has been adopted to represent the biodegradation process more realistically (Jury et al. 1987). When soil depth 0 < z < W, the first-order biodegradation rate coefficient will be at maximum as shown in equation (4.6) and it will decrease exponentially after depth W following equation (4.7).

$$\mu = \frac{\ln(2)}{T_{\frac{1}{2}}} \qquad 0 < z < W \tag{4.6}$$

$$\mu = \frac{\ln(2)}{T_{\frac{1}{2}}}\, e^{-\gamma(z-W)} \qquad W < z < H \tag{4.7}$$

Simulations were assumed to follow free drainage lower boundary condition regime at z = H;

$$\frac{\partial C}{\partial z} = 0 \qquad (4.8)$$

Simulation time was considered to be the advective time for pesticides transport to reach depth of =H=300 cm.

Under the scenarios of high and low pollution potential, after pesticides applied to the soil, the amount of pesticides remaining in the soil, leached into groundwater, lost by biodegradation and volatilization and the advective transport times to reach the groundwater are given in Table 4.15 and Table 4.16, respectively. The results in these tables reveal to what extent pesticides applied to the soil are affected by the basic loss pathways such as leaching (mobility), vaporization and biodegradation processes, and which pesticides are highly likely to be seen in groundwater. For example, under high pollution potential scenario, simazine and atrazine demonstrated leaching potential to groundwater due to high mobility. Diuron also demonstrated leaching potential due to high advective time (t_{advec},years). These pesticides are easily washed in soil to spread the contamination. On the other hand, pesticides such as bifenox and tributyltin completely lost owing to degradation because the advective time for simulation was very long relatively to short half-lives. Pesticides such as hexachlorobenzene, pentachlorbenzene and trichlorobenze demonstrated high volatility percentages owing to being very volatile fungicides. Under low pollution potential scenario all the 24 prioity pesticides did not demonstrate leaching potential to reach groundwater since pesticides' losses were distributed between biodegrdation volatilization. Considereing advective time (t_{advec},years) as the time for simulation gave sufficient retnetion time for biodegrdation process. However, pesticide such as endosulfan demonstrated high resistance to degradation but major loss pathway was volatilization. In addition, trifluralin's major loss pathway was due to volatilization in both high and low pollution potential scenarios.

Table 4.15: The percent amount of pesticides remaining in H=3 m deep soil profile, leached into groundwater, lost by biodegradation and volatilization, and the advective transport times (t_{advec}) to reach the groundwater under high pollution potential scenario.

Priority Pesticide	Application rate (μg/cm²)*	Mass retained % (PCTMR)	Leached mass % (PCDRM)	Degraded mass % (PCDECM)	Volatilized mass % (PCVAPM)	Remained mass (μg/cm²) (SUMM)	t_{advec} (Years)
Aclonifen	17.0	0.00	0.00	99.74	0.26	1.002E-11	160.9
Alachlor	45.0	0.00	0.00	99.97	0.03	6.065E-10	7.5
Atrazine	28.0	0.20	1.51	98.27	0.02	5.680E-02	5.5
Bifenox	7.5	0.00	0.00	100.00	0.00	5.518E-43	83.2
Chlopyrifos	6.0	0.00	0.00	95.57	4.43	5.941E-34	69.7
Chlorfenvinfos	34.0	0.00	0.00	99.79	0.21	2.416E-16	183.8
Cybutryne	10.0	0.00	0.00	99.74	0.25	6.256E-07	70.2
Cypermethrin	37.0	0.00	0.00	99.96	0.04	1.107E-101	164.2
Dichlorvos	11.0	0.25	0.11	96.57	3.07	2.747E-02	1.3
Dicofol	10.0	0.07	0.00	99.50	0.43	7.099E-02	1.7
Diuron	33.0	0.00	10.22	89.77	0.01	1.451E-318	286.2
Endosulfan	15.0	0.00	0.00	15.94	84.06	3.554E-07	2.9
Heptachlor epoxide	22.0	0.00	0.03	99.16	0.81	4.460E-22	929.6
Hexachlorobenzene	50.0	0.02	_	_	_	9.562E-03	227.7
Hexachlorocyclohexane	110.0	0.00	0.00	68.01	31.99	4.256E-32	139.9
Isoproturon	17.0	0.00	0.10	99.90	0.00	1.094e-318	43871.1
Pentachlorobenzene	10.0	0.00	_	_	_	4.788E-18	574.2
Pentachlorophenol	15.0	0.00	0.00	99.83	0.17	6.259E-33	83.9
Quinoxyfen	6.0	0.00	0.00	99.91	0.10	7.286E-08	81.4
Simazine	22.0	0.00	2.56	97.43	0.01	1.276E-07	8.8
Terbutryn	22.0	0.00	0.00	99.91	0.09	2.812E-08	3.8
Tributyltin	4.5	0.00	0.00	100.00	0.00	1.064E-09	14.1
Trichlorobenzene	10.0	0.00	_	_	_	2.296E-05	30.4
Trifluralin	20.0	0.00	0.00	0.00	100.00	3.585E-22	369.2

Table 4.16: The percent amount of pesticides remaining in H=3 m deep soil profile, leached into groundwater, lost by biodegradation and volatilization, and the advective transport times (t_{advec}) to reach the groundwater under low pollution potential scenario.

Priority Pesticide	Application rate (μg/cm²)*	Mass retained % (PCTMR)	Leached mass % (PCDRM)*+	Degraded mass % (PCDECM)	Volatilized mass % (PCVAPM)	Remained mass (μg/cm²) (SUMM)	t_{advec} (Years)
Aclonifen	17.0	0.00	0.000	99.85	0.15	5.497E-74	1285.4
Alachlor	45.0	0.00	0.00	99.98	0.02	7.059E-69	58.3
Atrazine	28.0	0.00	0.00	99.97	0.03	3.664E-18	42.6
Bifenox	7.5	0.00	0.00	100.00	0.00	5.989E-320	664.4
Chlopyrifos	6.0	0.02	0.00	98.59	1.39	1.281E-03	556.4
Chlorfenvinfos	34.0	0.00	0.00	99.86	0.14	7.612E-50	1469.0
Cybutryne	10.0	0.00	0.00	99.81	0.19	1.349E-30	560.0
Cypermethrin	37.0	0.00	0.00	99.99	0.01	2.208E-319	1312.4
Dichlorvos	11.0	0.00	0.00	97.12	2.88	1.388E-18	9.2
Dicofol	10.0	0.00	0.00	99.86	0.14	2.081E-21	11.8
Diuron	33.0	0.00	0.00	99.98	0.02	1.778E-104	2287.9
Endosulfan	15.0	0.00	0.00	69.03	30.97	3.911E-55	21.7
Heptachlor epoxide	22.0	0.00	0.00	99.35	0.65	2.035E-39	7435.4
Hexachlorobenzene	50.0	0.00	_	_	_	4.192E-07	1118.1
Hexachlorocyclohexane	110.0	0.07	0.00	81.12	18.82	4.660E-66	194.7
Isoproturon	17.0	0.00	0.00	100.00	0.00	1.996E-170	350967.0
Pentachlorobenzene	10.0	0.00	_	_	_	7.639E-32	4591.7
Pentachlorophenol	15.0	0.00	0.00	99.87	0.13	1.005E-36	669.8
Quinoxyfen	6.0	0.00	0.00	99.93	0.07	9.415E-51	650.0
Simazine	22.0	0.00	0.00	99.99	0.01	8.363E-30	69.1
Terbutryn	22.0	0.00	0.00	99.95	0.05	1.639E-60	28.6
Tributyltin	4.5	0.00	0.00	100.00	0.00	4.594E-73	111.3
Trichlorobenzene	10.0	0.00	_	_	_	1.437E-33	241.4
Trifluralin	20.0	0.00	0.00	39.56	60.44	8.072E-115	2952.0

Classification of pesticides according to groundwater pollution potential is based on residual and washed mass amounts under high pollution potential conditions (Table 4.15) and is presented in Table 4.17. Those with less than 1% residual and leached mass percentages in the low pollution potential to groundwater category, those with residual and leached mass amounts percentage between 1-15% are in medium pollution potential to groundwater category and more than 15% are classified as pesticides with high pollution potential to groundwater. The results in Table 4.17 show that three out of the 24 priority pesticides which are diuron, simazine and atrazine possess medium potential to reach groundwater. The rest of priority pesticide have low pollution potential to groundwater. However, all these pesticides were regulated or banned owing to their toxicity and environmental impact. One point to mention is that pesticides that are washed significantly into the groundwater show significant differences in terms of the time they reach the groundwater. While some pesticides reach groundwater within a few years, for some pesticides this period may take up to decades.

Table 4.17: Groundwater pollution potential classification

Low pollution potential to groundwater			
Aclonifen	Cypermethrin	Hexachlorocyclohexane	Terbutryn
Alachlor	Dichlorvos	Isoproturon	Tributyltin
Bifenox	Dicofol	Pentachlorobenzene	Trichlorobenzene
Chlopyrifos	Endosulfan	Pentachlorophenol	Trifluralin
Chlorfenvinfos	Heptachlor epoxide	Quinoxyfen	Hexachlorobenzene
		Cybutryne	
Medium pollution potential to groundwater			
Diuron		Simazine	Atrazine
High pollution potential to groundwater			
-			

CHAPTER 5

DISCUSSIONS OF RESULTS

In this thesis, the developed computer model PETRANS GUI was used to simulate the fate and transport of the 24 pesticides classified as priority chemicals by Turkey in 2015 and prior to that by the EU in 2001. PESTRANS GUI model screened the 24 priority pesticides to investigate their behavior in the agricultural soils and classify their pollution potential according to volatility, mobility, persistence and leaching to groundwater. The developed PESTRANS GUI software was supported by updated databases which included physical and chemical properties of priority pesticides (Table 3.1) as well as soil properties (Table 3.2) for simulation purposes. The results of pesticides classifications are presented in section 4.3. Investigating the potential of pesticides with respect to their volatility, mobility and persistence assist the user of PESTRANS GUI model to hold a comprehensive understanding of pesticides fate and behavior in unsaturated soil environment. Results of simulation runs conducted under predefined soil and environmental conditions demonstrated the major loss pathways of pesticides in accordance with their physical and chemical properties.

Volatilization was considered as one significant loss pathway especially for the volatile pesticides. Volatilization classification was necessary to differentiate between pesticides with high volatility and with non-volatile chemicals. Table 4.10 shows categorizations of the 24 priority pesticides based on tendency to volatilize. Volatile chemicals were classified to fall under category I since their dimensionless Henry's law constant ($K_H > 2.5X10^{-5}$) with high volatility according to Jury et al. (1984). Among the 24 priority pesticides 8 chemicals demonstrated high volatility property and they fit under category I. Hexachlorobenzene, Pentachloro benzene and Trichlorobenzene had the highest volatility potential, which was in agreement with their physical nature as volatile compounds with dimensionless K_H close to critical point for volatility. Dichlorvos fell under the second category since K_H was close to

$2.5x10^{-5}$ to be considered as a pesticide with moderate volatility potential. Category III was assigned for pesticides with less volatility potential ($K_H < 2.5x10^{-5}$). Among the 24 pesticides 15 pesticides fell under the less volatile compounds category. However, category III was assigned for wide range of chemicals including non-volatility pesticides. For example, isoproturon, simazine and atrazine demonstrated low tendency to volatilization. Appendix B shows the simulation of the 24 priority pesticides for 30 days according to high and low pollution potential scenarios illustrated in Table 4.14 with the same application rate in order to compare loss percentages due to volatilization. Vapor flux versus time and volatilization percentage versus time plots illustrated volatilization as a significant loss pathway for volatile pesticides such as hexachlorocyclohexane (HCH). On the other hand, pesticides included in category III demonstrated less volatility potential. Thus, loss due to volatilization was considered insignificant such as alachlor and Terbutryn. In addition, manipulation of water evaporation/infiltration rate during pesticide modeling in soil was also investigated to see the impact of this parameter on the volatilization of priority pesticides. Figures 4.9, 4.11 and 4.13 show the vapor flux over time profile of pesticides from each volatility category and the impact of evaporation/infiltration rate. As can be seen in these figures evaporation/infiltration rate play significant role in volatilization rate. An increase in water evaporation rate will cause increase in volatility of the pesticide. This can be referred as induced volatilization. Water evaporation/infiltration rate (q_w) was considered one of the pesticide modeling parameters that shape the pesticide concentration profiles in soil.

Priority pesticides were classified to have low mobility during mobility classifications in terms of advective time (t_{advec}), dispersive time (t_{dis}) and diffusive time (t_{diff}). Majority of priority pesticides, 17 out of the 24, demonstrated low mobility owing to the high adsorption potential (high K_{oc}). On the other hand, pesticides such as dichlorvos and dicofol were categorized as pesticides with high advective mobility as shown in Table 4.11. Endosulfan, alachlor, atrazine and terbutryn had moderate advective mobility. However, the rest of the 17 priority pesticides were classified in Class 1 to have low advective mobility mainly due to high solid adsorption potential

(high K_{oc}). Table 4.11 presents the mobility categorization for the 24 priority pesticides and the calculations of advective time (t_{advec}), dispersive time (t_{dis}) and diffusive time (t_{diff}) in agreement with the physical and chemical properties of the pesticides. Soil concentration profiles of mobile pesticides are more flattened depth wise than pesticides with low mobility. Screening graphs of simulations with high and low pollution potential scenarios as shown in appendix B, present the flattened curves of mobile pesticides such as dichlorvos and simazine. High pollution potential scenario assumes low organic carbon content (f_{oc} = 0.005) for the soil. High organic carbon content may withhold penetration of pesticides with high adsorption potential (high K_{oc}).

As a result of the persistence classification, which was carried out by considering remaining percentage of pesticides after volatilization and biodegradation. Table 4.12 shows calculation of the effective half-life of priority pesticides $T_{1/2}^{E}$. Persistence classifications shown in Table 4.13 present the categories of priority pesticides. Heptachlor epoxide demonstrated highest persistence among the 24 priority pesticides and was categorized in class 1 with high persistence property with $T_{1/2}^{E}$> 100 days. Seven priority pesticides such as chlorfenvinphos and cybutryne were considered persistence with (31 <$T_{1/2}^{E}$ ≤ 100 days). The rest of priority pesticides were categorized to have low persistence. However, none of the pesticides fell under highly degradable category with ($T_{1/2}^{E}$<5 days) indicating that majority of the priority pesticides demonstrated resistance to biodegradation. Persistence tests were consistent with the half-lives of the pesticides listed in Table 3.1. Depth of pesticide application significantly affects the persistence of the pesticides and thus can be a serious criterion to be considered in reducing the pollution potential. Priority pesticides such as Trichlorobenzene, Hexachlorobenzene and Pentachloro benzene demonstrated low persistence potential because their loss due to volatilization was far more than loss due biological degradation. Persistence classification does not exclusively categorize pesticides based on biodegradability, but it also includes volatilization as a significant mass attenuation pathway. Summary of pesticides classifications based on their

mobility, volatility and persistence is given in Table 5.1. Categories were rearranged for the sake of simplicity to increase with increasing magnitude. For example, lowest volatility will be 1 and highest volatility will be 3 and similarly with mobility and persistence but with categories up to 5.

Table 5.1: Mobility, volatility and persistence clasess of 24 priority pesticides

Pesticide included in Priority list	Mobility**	Volatility*	Persistance***
Heptachlor epoxide	1	1	5
Quinoxyfen	1	1	4
Tributyltin	1	3	4
Trifluralin	1	3	4
Aclonifen	1	1	4
Chlorfenvinfos	1	1	4
Cybutryne	1	1	4
Diuron	1	1	4
Pentachlorophenol	1	1	3
Endosulfan	3	3	3
Hexachlorobenzene	1	3	3
Pentachlorobenzene	1	3	3
Dicofol	4	1	3
Atrazine	3	1	3
Simazine	2	1	3
Chlopyrifos	1	3	2
Hexachlorocyclohexane	1	3	2
Trichlorobenzene	1	3	2
Dichlorvos	4	2	2
Alachlor	3	1	2
Terbutryn	3	1	2
Bifenox	1	1	2
Cypermethrin	1	1	2
Isoproturon	1	1	2
* Volatility: Class 1: lowest volatility; class 3: highest volatility ** Mobility: Class 1: lowest mobility; class 5 highest mobility *** Persistence: Class 1: lowest persistence; class 5: highest persistence			

Figures 5.1 and 5.2 show 3D visualization of mobility, volatility, and persistence categories to illustrate pesticides' fate and behavior in unsaturated soil. Clearly, the insecticide Heptachlor epoxide demonstrated high persistence with low volatility and low mobility. Thus, it can be considered as risk to contaminate surface waters because it can be drifted with the run-off to spread the contamination. Similarly, Diuron and Aclonifen may have the same behavior but with less resistance to biological degradation. Even through isoproturon, cypermethrin and bifenox demonstrated low volatility and low mobility yet proved to have low persistence and more potential to biodegrade. Therefore, these pesticides are still approved for regulated use in Turkey and the EU. Appendix A illustrates pesticides usage status of priority pesticides in Turkey and EU countries, as well as screening classification of the developed model PETRANS GUI. Simulations conducted by PETRANS GUI over priority pesticides were compatible with the general findings of these chemicals conducted by Turkey and EU countries. Although some pesticides demonstrated low persistence such as Dichlorvos and Terbutryn, they were banned due to high toxicity and high mobility.As a matter of fact, pesticides with high mobility are very much of concern due to high potential for spreading and enlarging the size of polluted area.

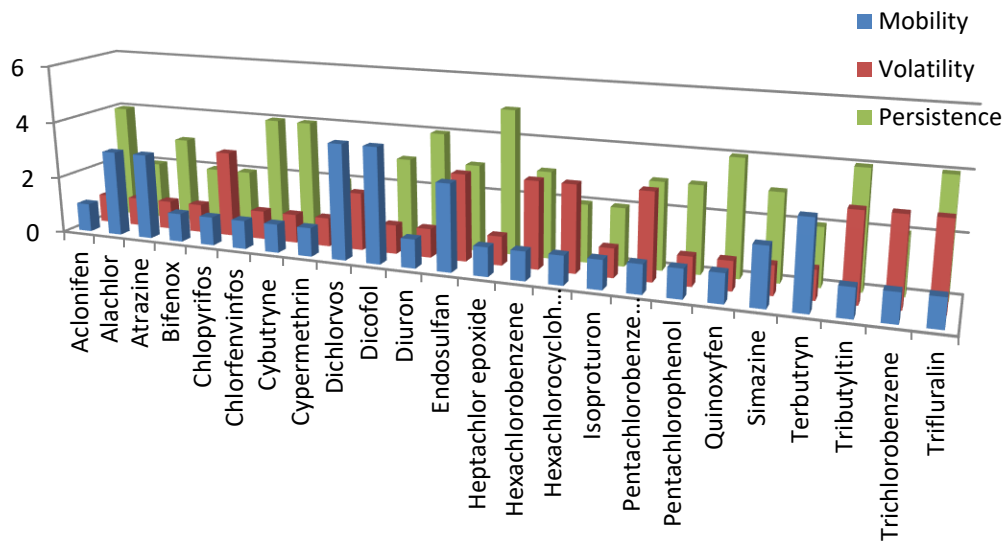


Figure 5.1: Over all screening for priority pesticides based on their mobility, volatility and persistence.

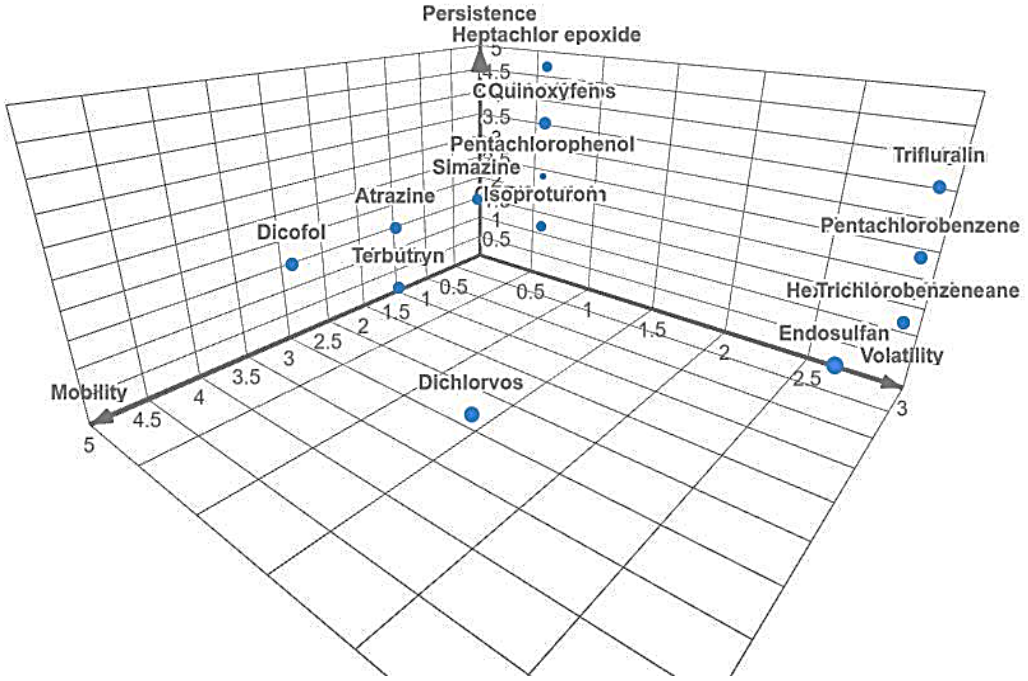


Figure 5.2: 3-D view of over all screening for priority pesticides based on their mobility, volatility and persistence.

Pesticides with high persistence and low mobility are likely to cause serious surface water pollution through sedimentation and runoff rather than groundwater pollution, especially if applied to shallow soil depths (L<5 cm). The list of such pesticides is given in Table 5.2 which is concluded easily by observing Figure 5.2. When Table 4.17 and Table 5.2 are compared, it is seen that pesticides such as heptachlor epoxide, chlorfenvinfos, cybutryne, quinoxyfen and trifluralin are classified as pesticides with low groundwater pollution potential in Table 4.17 and they are included as pesticides with surface water pollution potential in Table 5.2. This overlap in the tables proves that the behavior of the aforementioned pesticides has been correctly and consistently evaluated. On the other hand, pesticides in Table 5.2 such as diuron, endosulfan and dicofol are also classified as low and moderate pollution pesticides in Table 4.17. This situation may seem contradictory at first sight; However, the fact that the mass amounts of these pesticides washed from the soil as well as the residual mass amounts in the soil are much higher than the other pesticides in Table 5.2 lead to this result. In other words, biodegradation and evaporation losses are very low compared to washing losses, A significant amount of the pesticide still remains in the soil that can be transported to surface waters by sedimentation or runoff.

Table 5.2: List of pesticide with high pollution potential to surface water

Heptachlor epoxide	Dicofol	Quinoxyfen
Chlorfenvinfos	Diuron	Tributyltin
Cybutryne	Endosulfan	Trifluralin

The evaluations made in this thesis reveal that the behavior of pesticides in terms of pollution potential is significantly influenced by the parameters determining the physical and chemical properties of the pesticides as well as the soil and environmental parameters. Therefore, the accuracy and reliability of the data used are required in terms of the accuracy and reliability of the results. The developed database for PESTRANS GUI model should be considered as an important step in obtaining

accurate and reliable data on pesticides considered as priority pesticides in Turkey. With the database embedded within the software, it will be possible to provide the information required to evaluate the pollution potential of pesticides collectively. As new data are obtained as a result of experimental studies, physico-chemical parameter values can be updated for pesticides in Table 3.1. As up-to-date and highly accurate information is obtained, in other words by improving and updating the database of PESTRANS GUI, it will be possible to review and re-evaluate the results obtained in this study.

The results obtained from experimental studies to be conducted under field conditions will undoubtedly be the most valid way to evaluate the pollution potential of pesticides accurately and reliably. However, given the large number of pesticides and the amount of time and costs to be spent on such experiments, the benefit of the developed model and simulation studies in assessing the pollution potential of pesticides will be substantial. The classifications made as a result of this study can be taken as an initial guide in regulating the use of pesticides by the experts.

CHAPTER 6

CONCLUSIONS AND FUTURE RECOMMENDATIONS

Analysis of pesticide fate and transport behavior in soil, and subsequent assessment of pesticides' pollution potential based on their fate and transport behavior require a screening tool that is capable of simulating the fate and transport behavior of pesticides in unsaturated soil. In this thesis, a graphical user interface PESTRANS GUI was developed to enable users with less expertise in software programming, such as pesticide manegers, decision makers and environmental modeling students, to simulate real-life pesticide application scenario to screen the behavior of pesticides in unsaturated soils. PESTRANS is capable of providing the users with the output of total mass (as well as percent mass) volatilized, degraded, leached and remained in the soil profile relative to the pesticide mass applied at the soil surface at time zero. In addition, it is capable of simulating the fate and transport behavior of pesticides and any other organic chemicals in the soil profile under site-specific climatic and soil conditions which can be very useful for site specific risk assessment purposes. The model was verified and compared with measured pesticide data showing a good match between measured and simulated data. The software includes database of physical and chemical properties of 24 chemicals that were categorized as priority pollutants in Turkey and the EU. It also includes database for 12 different soil texture properties to facilitate the interaction between the user and the computer model.

The code of the software was written on python Tkinter toolkit owing to python fast development speed. Python includes numerous frameworks and libraries such as NumPy, Matplotlib and SciPy which allow the developer to create the intended graphical user interface (GUI) for the users to facilitate the simulation input and output stages. Python computational speed may not be the fastest among other programming languages. For example, Python NumPy's computational CPU time is 0.1 seconds

using pairwise distance function which is greater than Fortran's computational CPU time of 0.08 seconds showing Fortran to have higher computational speed than Python. However, Fortran does not include gadgets to support the creation of GUI for developers. To illustrate, the computational speed of PETRSANS GUI and the time required to produce simulation output was less than 5.5 seconds CPU time for 10 years real-time pesticide simulation in 1 m soil depth with single printing time-step on a standard PC. In PESTRANS GUI, CPU time will increase when increasing simulation time step because it is designed to provide an output every time step determined by the user. Advantages, such as easy maintenance, graphical visualization and fast computational convergence made python a good candidate for PESTRANS GUI software development to enable the user simulate pesticide fate and transport in unsaturated systems using Finite Difference Crank Nicholson Numerical solutions. PESTRANS GUI was created to carry out pesticide modeling in the most recent Windows^{TM} platforms with more features to enable the user to conduct screening analysis effectively.

In this thesis, PESTRANS GUI pesticide modeling helped to assess the loss pathways of priority pesticides in unsaturated soil to categorize pesticides based on their volatility, mobility and persistence potential. As a result, priority pesticides proved to have potential to pollute groundwater as well as surface waters. Pesticide with high persistence and low mobility such as heptachlor epoxide and Quinoxyfen possess high potential to contaminate surface waters by run-off drifting. Whereas pesticides with high mobility such as simazine, atrazine and diuron proved to have higher groundwater pollution potential than the majority of the 24 priority pesticides as a result of pesticide modeling in unsaturated soils. For groundwater pollution potential, the worst case soil type is related to sandy soil textures because sandy soils have high hydraulic conductivity increasing the leaching potential and low organic carbon content decreasing the adsorption rate; overall enhancing the mobility of pesticides. On the other hand, clayey soils are suitable soil types for reducing the pesticide leaching rates and groundwater pollution potential.

The use of pesticides with low pollution potential can be promoted among pesticides that are similar in purpose and effectiveness but are in different classes in terms of pollution potential; or regulations to reduce pollution in application rates may be suggested. Similarly, the pollution potential of pesticides whose pollution potential is not evaluated in this study, but their use is becoming increasingly common in the future, can be assessed directly by using PESTRANS GUI model or by comparing the behavior of a classified pesticide with similar physical and chemical properties.

It is intended to increase the capabilities of PESTRANS GUI in the future to produce a more powerful tool for pesticide modeling. As illustrated in section 3.7, PESTRANS GUI has limitations during pesticide modeling in unsaturated soil. However, this version of PESTRANS GUI is considered as version 1 and future versions can have more capabilities and flexibility in terms of including other soil and environmental factors such as temperature and pH. These parameters are expected to have an impact in persistence and volatilization fate of pesticides. However, PETRANS GUI model currently assumes standards conditions such as neutrality of pH and room temperature because majority of environmental scenarios occur at standard conditions. In addition, adsorption isotherms such as Freundlich and Langmuir isotherms can be integrated in the source codes for the user to have flexibility to model different soil conditions.Source code can be developed further to include other loss pathways such as photochemical dissipation and plant uptake to improve mathematical model and provide a more detailed fate assessment. Pesticide modeling over multiple soil layers and heterogeneity of soil texture can also be added as well.

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APPENDICES

A. Pesticides included in Priority list

Table 8.1: Status of priority pesticides

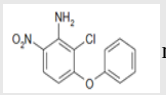
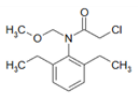
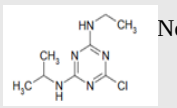
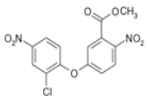
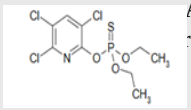
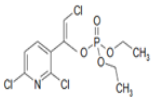
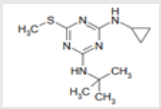
Priority Pesticide	Usage	Chemical Structure	Classification by EU	Status in Turkey	PESTRANS GUI Screening conclusion
Aclonifen	Herbicide		Approved for regulated use; Not Acutely hazardous	Approved for use with recommended Application Rate	Mobility: Low Volatility: Low Persistence: High
Alachlor	Herbicide		Not approved for use; Moderately hazardous	Banned in 2010	Mobility: Medium Volatility: Low Persistence: Medium
Atrazine	Herbicide		Not approved for use; Slightly hazardous	Banned in 2011	Mobility: Medium Volatility: Low Persistence: Medium
Bifenox	Herbicide		Approved for egulated use; Not Acutely hazardous	Approved for use with recommended app. Rate 3.64 kg/ha; EQS	Mobility: Low Volatility: Low Persistence: Medium
Chlorpyrifos	Insecticide		Approved for egulated use; Moderately hazardous	Planned to be banned end of 2021	Mobility: Low Volatility: High Persistence: Medium
Chlorfenvinfos	Insecticide		ot Approved for use; Highly Hazardous	Recommended application rate 45.10 kg/ha ; EQS	Mobility: Low Volatility: Low Persistence: High
Cybutryne	Herbicide		Prohibited	Priority Pollutant under assessment	Mobility: Low Volatility: Low Persistence: High

Table 8.1: Status of priority pesticides (Continued)

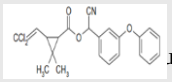
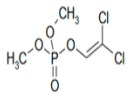
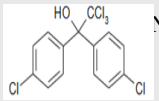
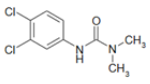
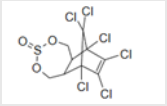
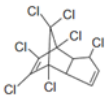
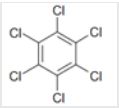
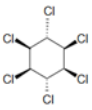
Priority Pesticide	Usage	Chemical Structure	Classification by EU	Status in Turkey	PESTRANS GUI Screening conclusion
Cypermethrin	Herbicide		Approved for use; Moderately hazardous	Still in use	Mobility: Low Volatility: Low Persistence: Low
Dichlorvos	Insecticide		Not Approved for use; Highly Hazardous	Banned in 2011	Mobility: High Volatility: Medium Persistence: Low
Dicofol	Acaricide		Not approved; Moderately hazardous	Banned in 2011	Mobility: High Volatility: Low Persistence: Medium
Diuron	Herbicide		Approved for use; Slightly hazardous	Classified as priority Pollutant but still no regulation	Mobility: Low Volatility: Low Persistence: High
Endosulfan	Insecticide		Not approved; Moderately hazardous	Banned in 2010	Mobility: Medium Volatility: High Persistence: Medium
Heptachlor epoxide	Insecticide		Banned; Acute toxicity	Classified as priority Pollutant; under assessment	Mobility: Low Volatility: Low Persistence: High
Hexachlorobenzene	Fungicide		Not approved for use; extremely hazardous	Classified as priority Pollutant	Mobility: Low Volatility: High Persistence: Medium
Hexachlorocyclohexane	Insecticide		Not approved; Moderately hazardous	Classified as priority Pollutant	Mobility: Low Volatility: High Persistence: Medium

Table 8.1: Status of priority pesticides (Continued)

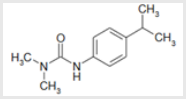
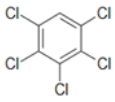
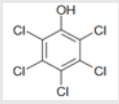
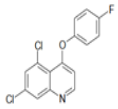
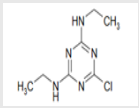
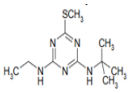
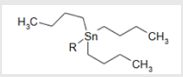
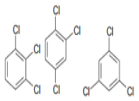
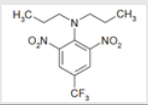
Priority Pesticide	Usage	Chemical Structure	Classification by EU	Status in Turkey	PESTRANS GUI Screening conclusion
Isoproturon	Herbicide		Approved for regulated use; Moderately hazardous	Classified as priority Pollutant but still no regulation	Mobility: Low Volatility: Low Persistence: Low
Pentachloro benzene	Fungicide		Banned	Classified as priority Pollutant	Mobility: Low Volatility: High Persistence: Medium
Pentachlorophenol	Insecticide		Not approved; Highly Hazardous	Classified as priority Pollutant but still no regulation	Mobility: Low Volatility: Low Persistence: Medium
Quinoxyfen	Fungicide		Approved for regulated use; less hazardous	Under assessment, planned to be Banned after 2020	Mobility: Low Volatility: Low Persistence: High
Simazine	Herbicide		Not approved for use; causes aquatic hazard	Banned in 2010	Mobility: Medium Volatility: Low Persistence: Medium
Terbutryn	Herbicide		Not approved for use; Slightly hazardous	Banned in 2011	Mobility: High Volatility: Low Persistence: Low

Table 8.1: Status of priority pesticides (Continued)

Priority Pesticide	Usage	Chemical Structure	Classification by EU	Status in Turkey	PESTRANS GUI Screening conclusion
Tributyltin	Biocide		Not Approved; High toxicity	Priority Pollutant under assessment	Mobility: Low Volatility: High Persistence: High
Trichlorobenzene	Insecticide		Very toxic	Classified as priority Pollutant but with regulated use	Mobility: Low Volatility: High Persistence: Medium
Trifluralin	Herbicide		No approved; less hazardous	Banned in 2013	Mobility: Low Volatility: High Persistence: High

B. Pesticides Screening graphs using PESTRANS GUI

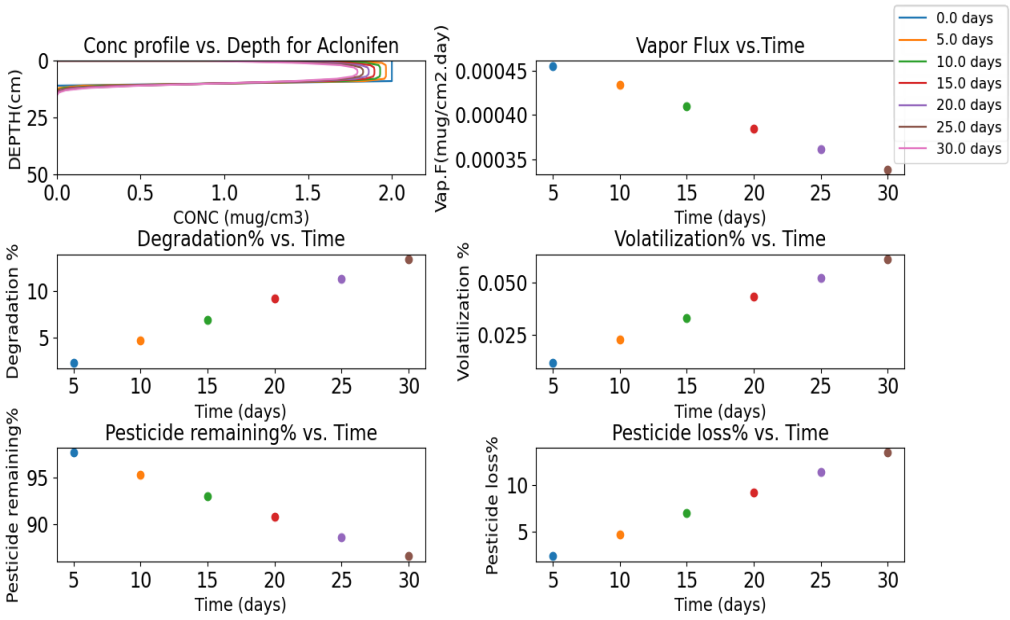


Figure 8.1:Aclonifen PESTRANS GUI fate Screening graphs with High pollution potential scenario

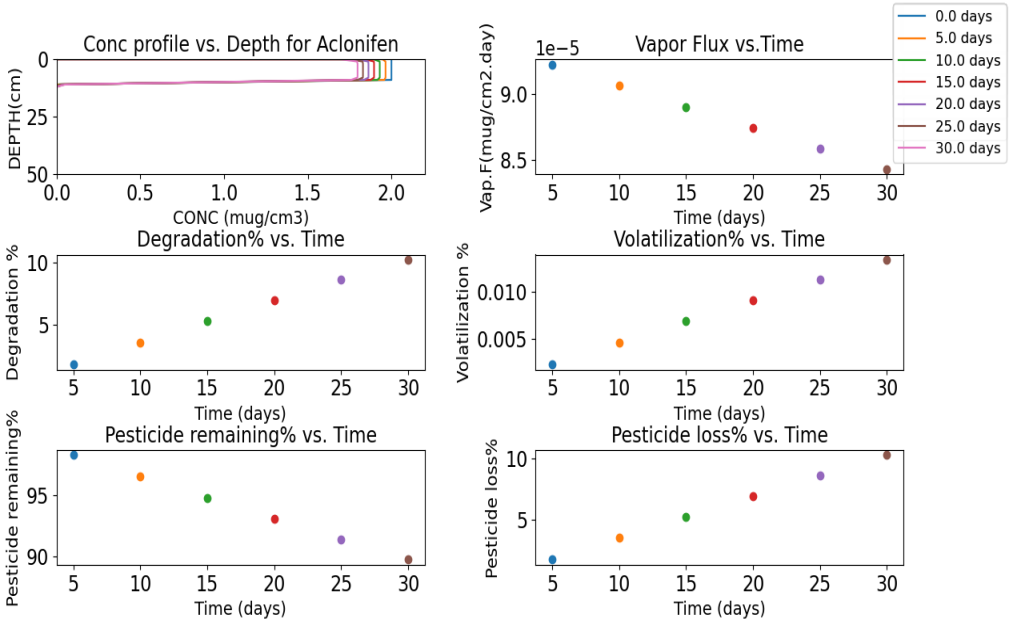


Figure 8.2: Aclonifen PESTRANS GUI fate Screening graphs with Low pollution potential scenario

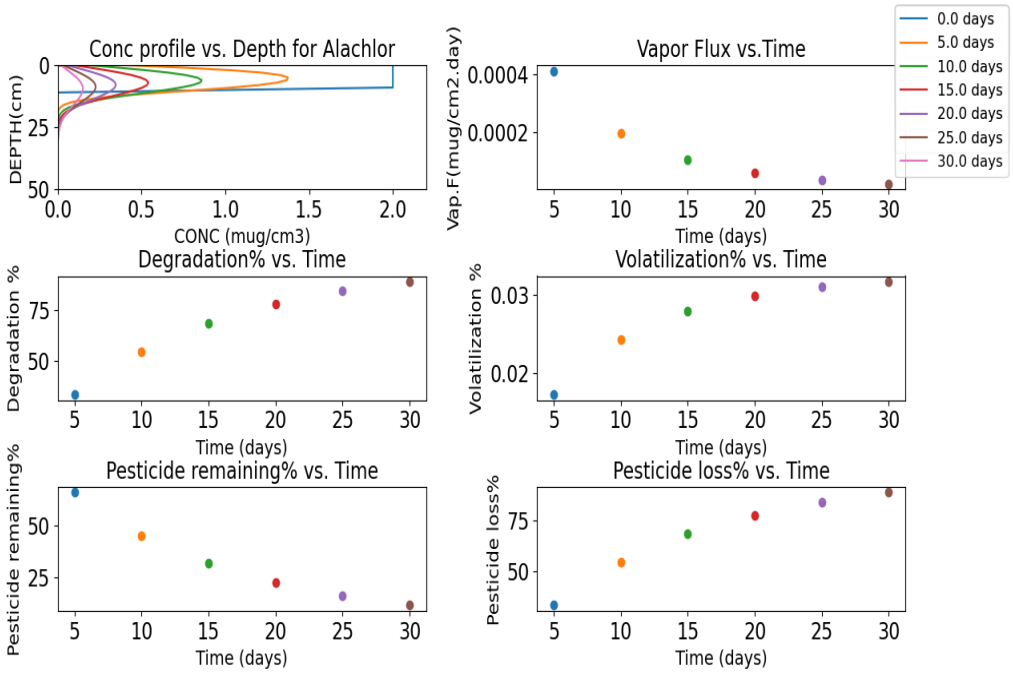


Figure 8.3: Alachlor PESTRANS GUI fate Screening graphs with High pollution potential scenario

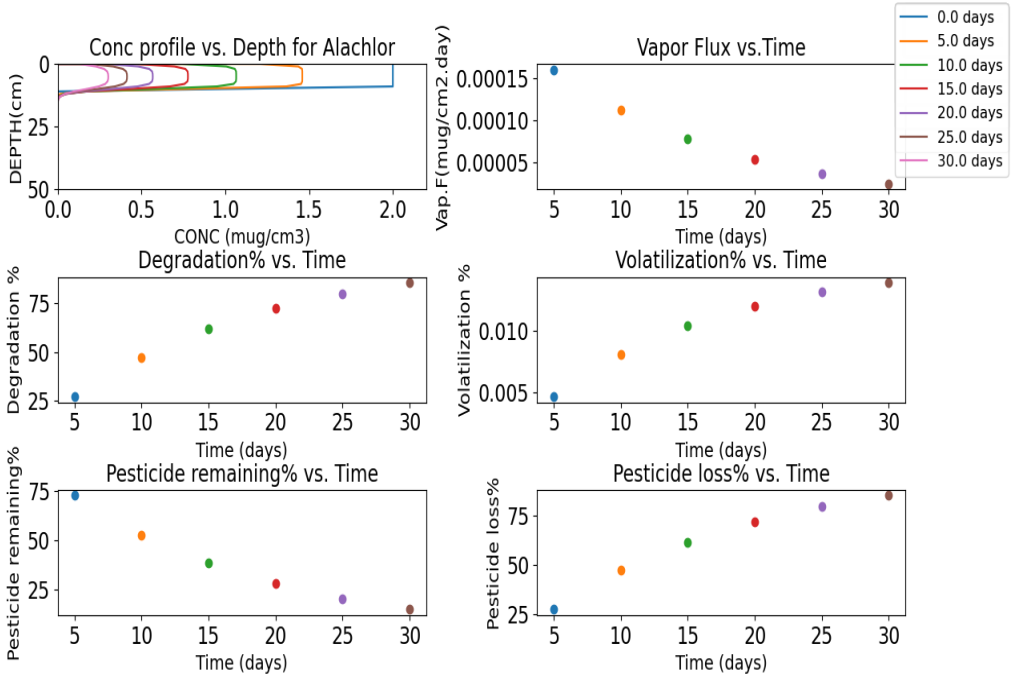


Figure 8.4: Alachlor PESTRANS GUI fate Screening graphs with Low pollution potential scenario

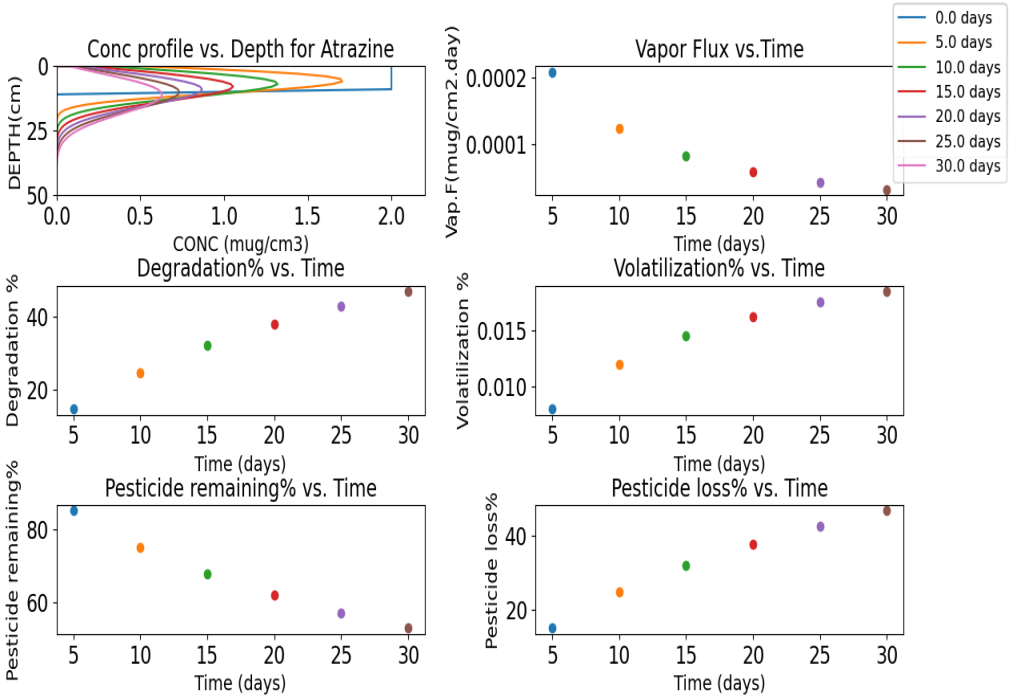


Figure 8.5: Atrazine PESTRANS GUI fate Screening graphs with High pollution potential scenario

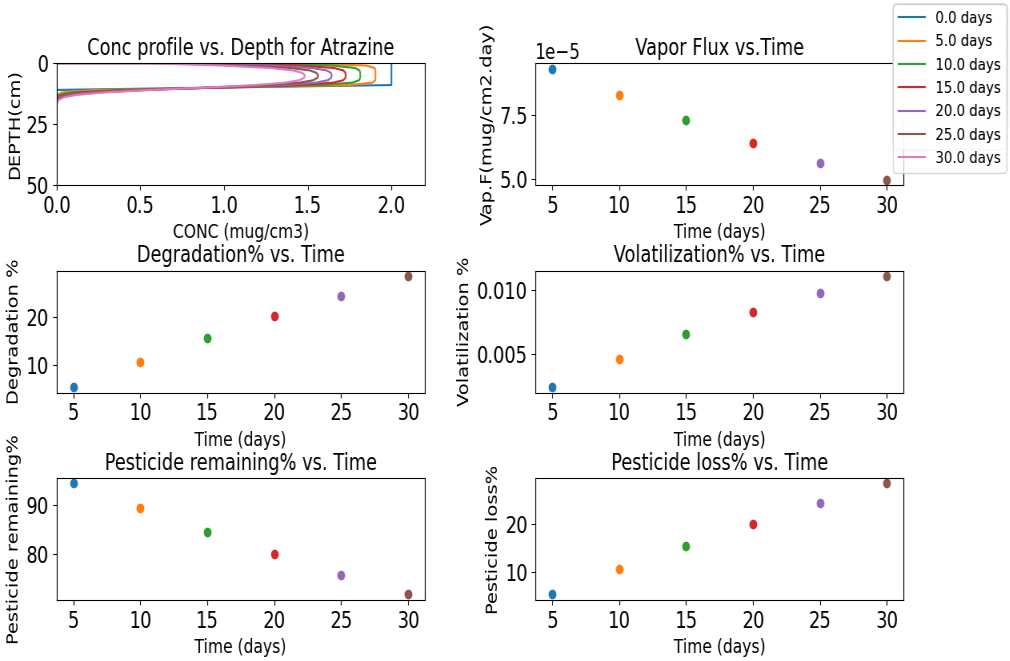


Figure 8.6: Atrazine PESTRANS GUI fate Screening graphs with Low pollution potential scenario

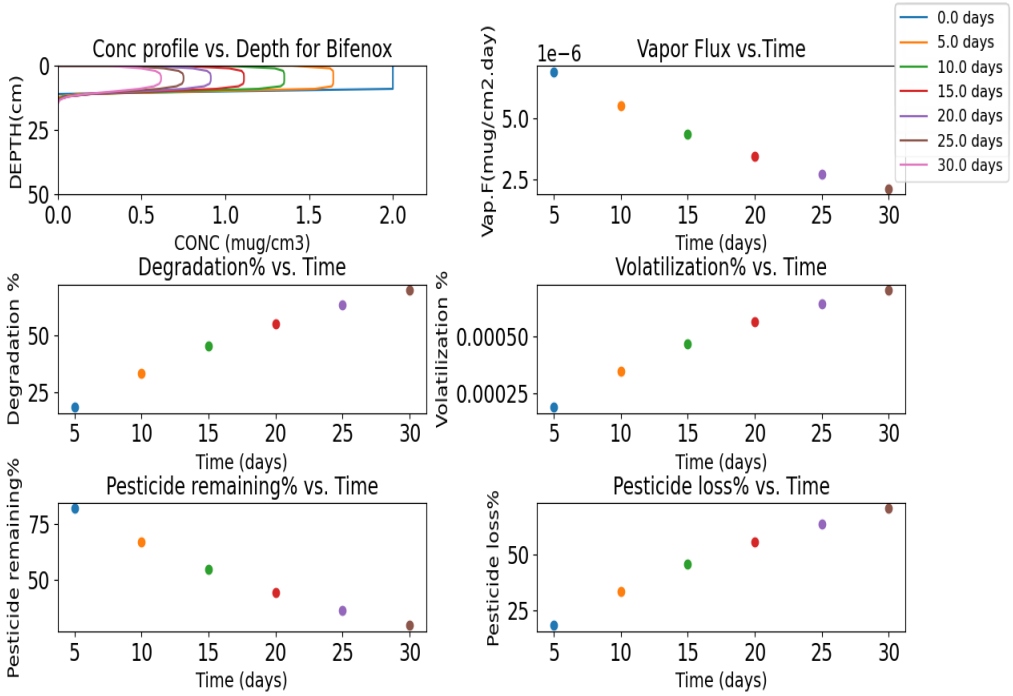


Figure 8.7: Bifenox PESTRANS GUI fate Screening graphs with High pollution potential scenario

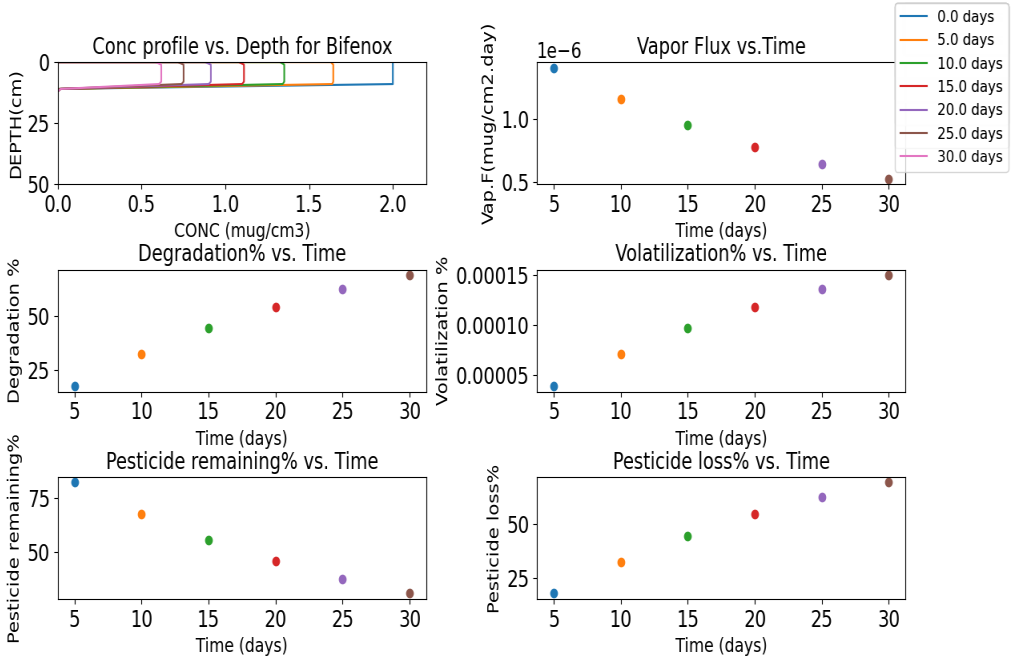


Figure 8.8: Bifenox PESTRANS GUI fate Screening graphs with Low pollution potential scenario

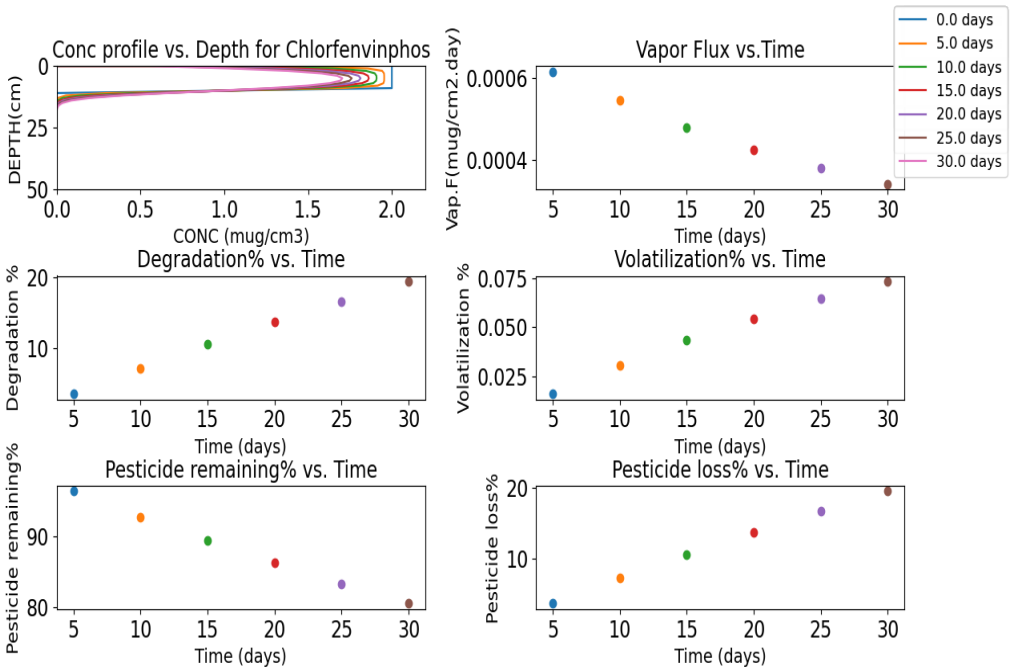


Figure 8.9: Chlorfenvinphos PESTRANS GUI fate Screening graphs with High pollution potential scenario

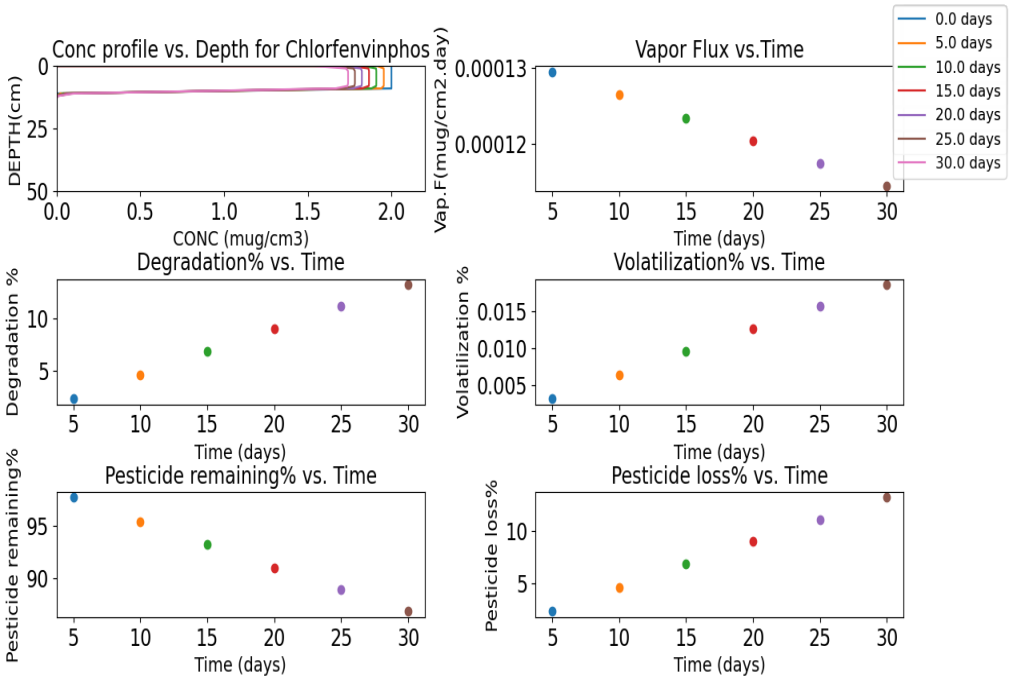


Figure 8.10: Chlorfenvinphos PESTRANS GUI fate Screening graphs with Low pollution potential scenario

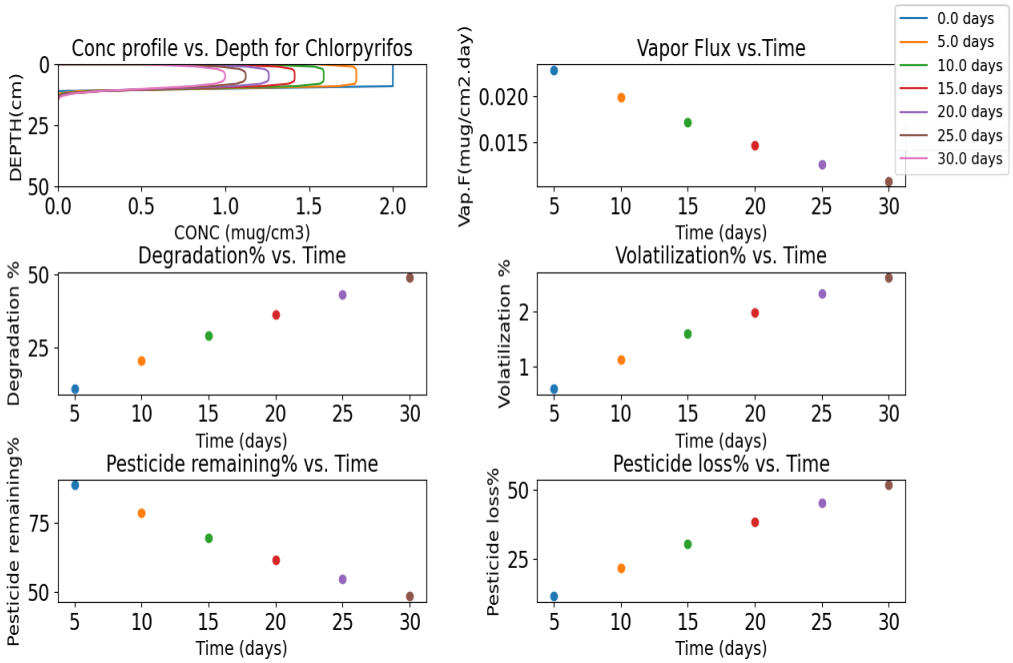


Figure 8.11: Chlorpyrifos PESTRANS GUI fate Screening graphs with High pollution potential scenario

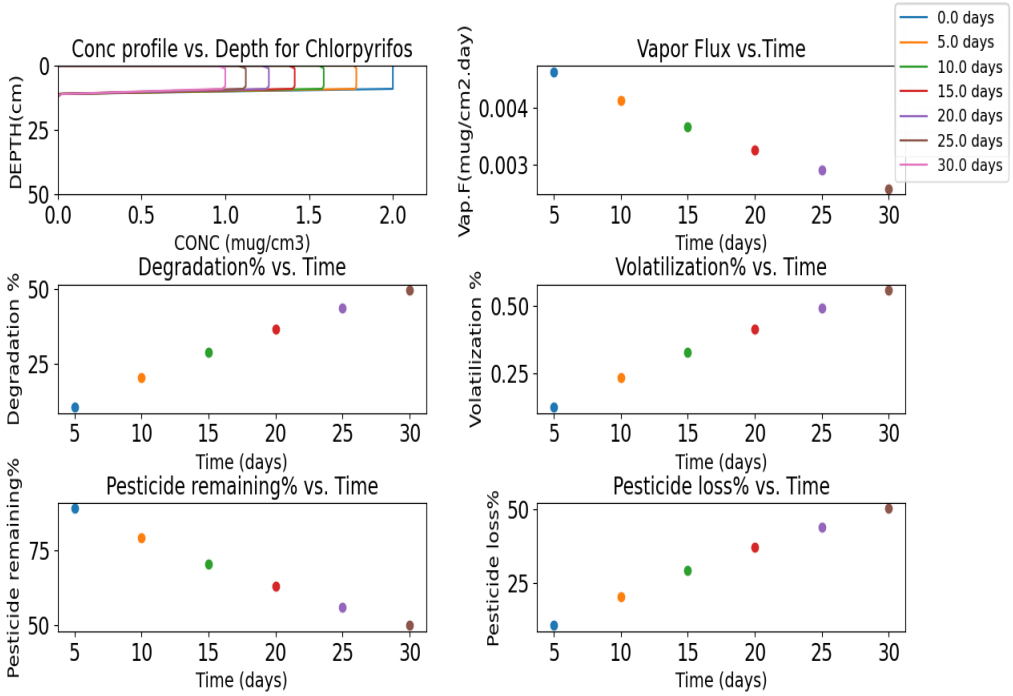


Figure 8.12: Chlorpyrifos PESTRANS GUI fate Screening graphs with Low pollution potential scenario

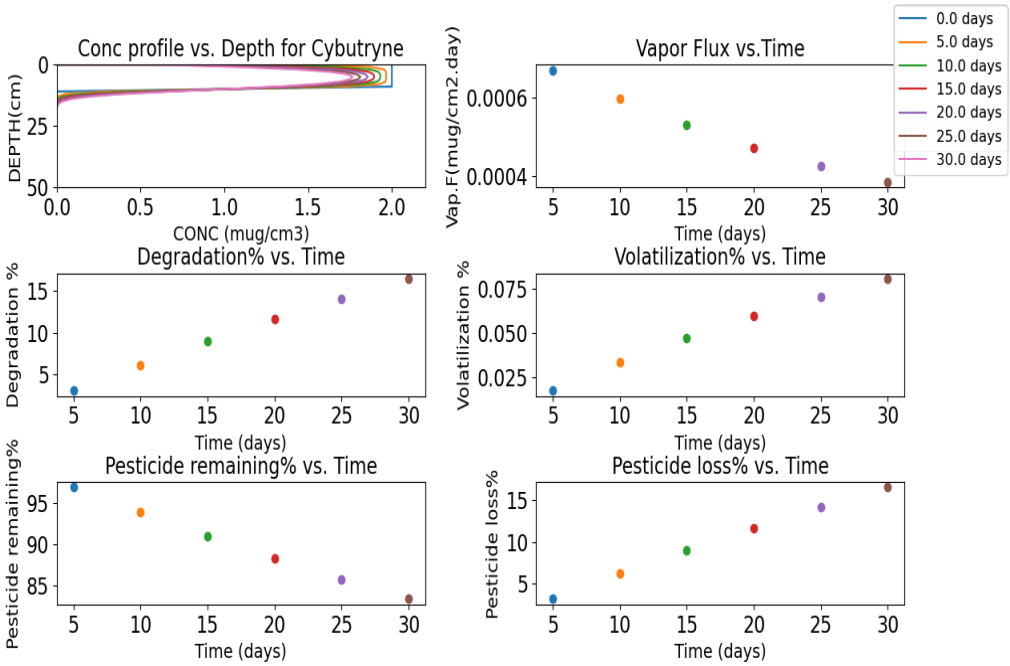


Figure 8.13: Cybutryne PESTRANS GUI fate Screening graphs with High pollution potential scenario

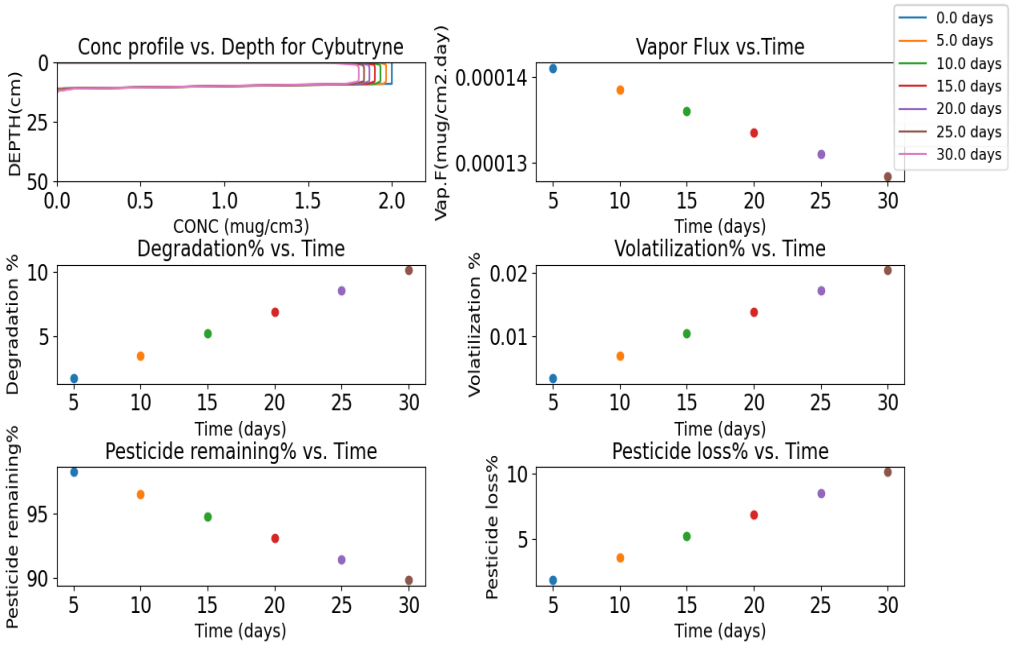


Figure 8.14: Cybutryne PESTRANS GUI fate Screening graphs with Low pollution potential scenario

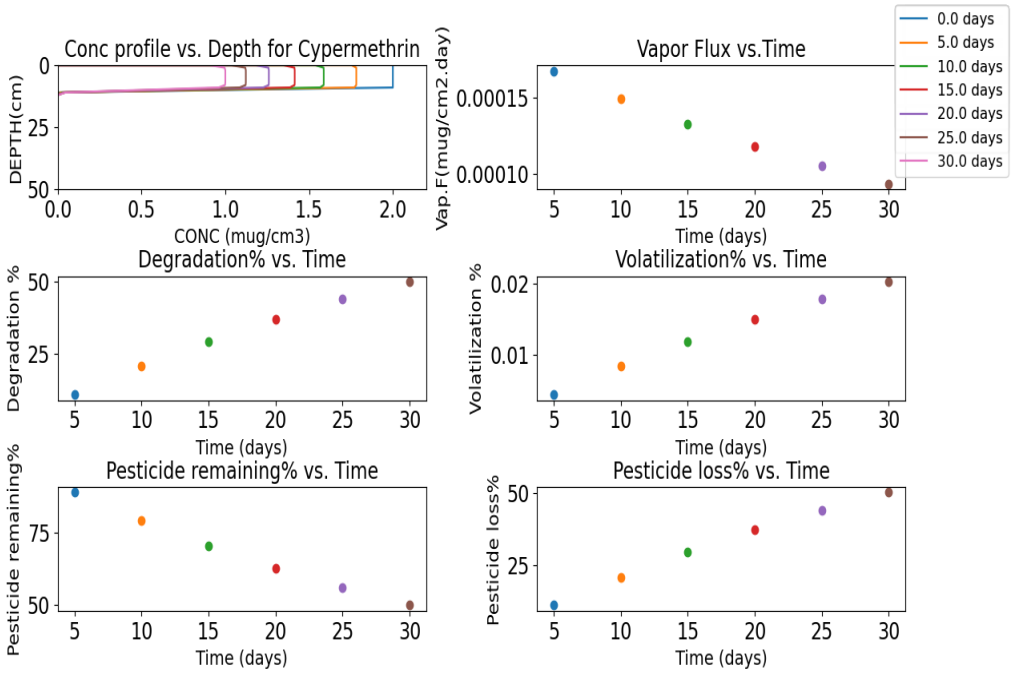


Figure 8.15: Cypermethrin PESTRANS GUI fate Screening graphs with High pollution potential scenario

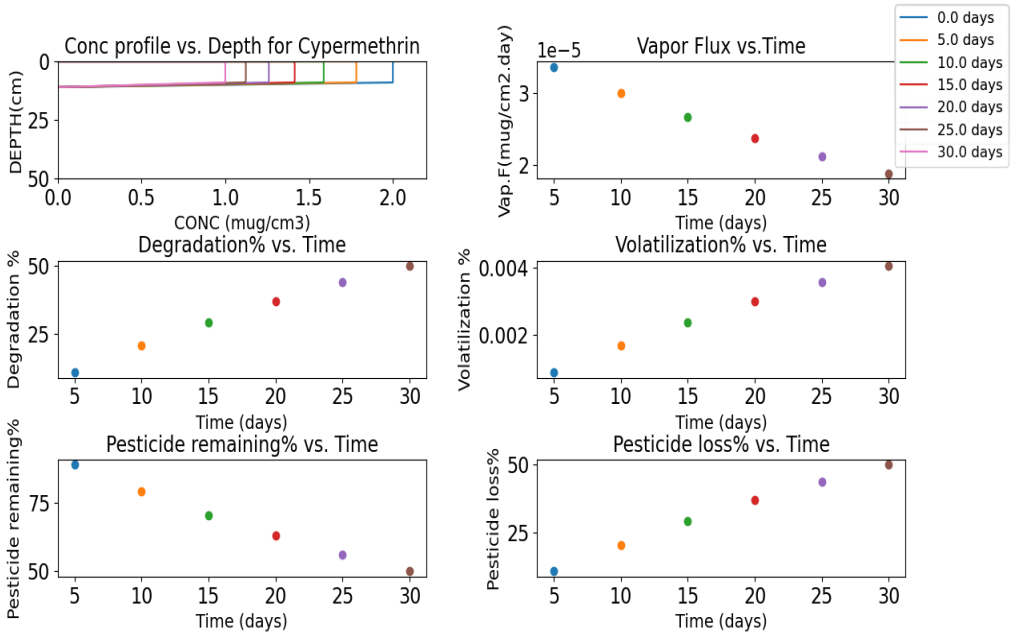


Figure 8.16: Cypermethrin PESTRANS GUI fate Screening graphs with Low pollution potential scenario

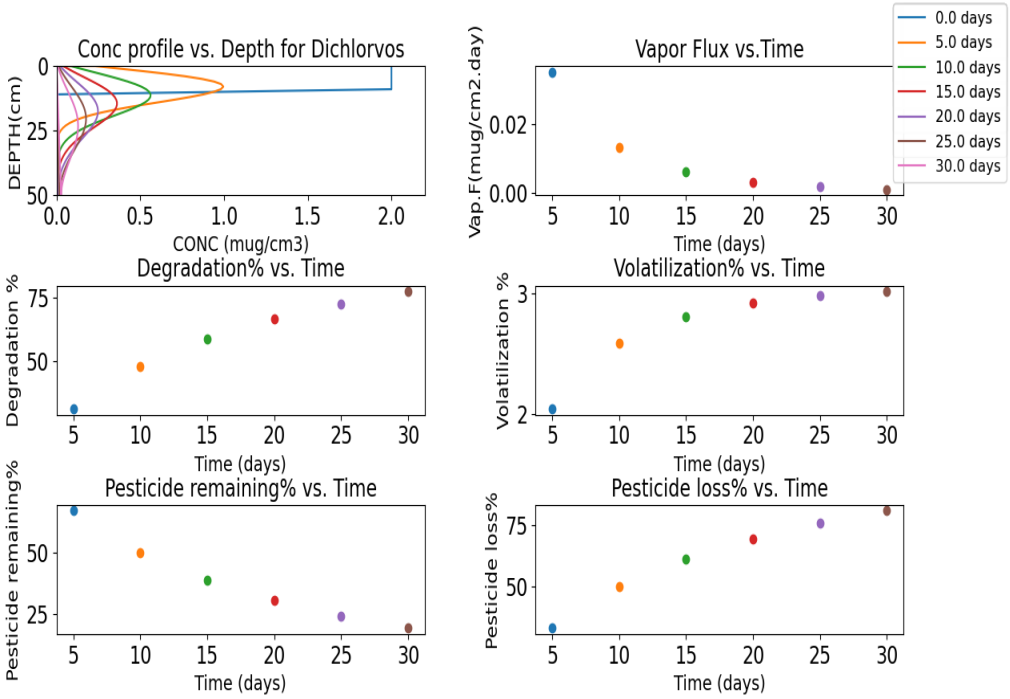


Figure 8.17: Dichlorvos PESTRANS GUI fate Screening graphs with High pollution potential scenario

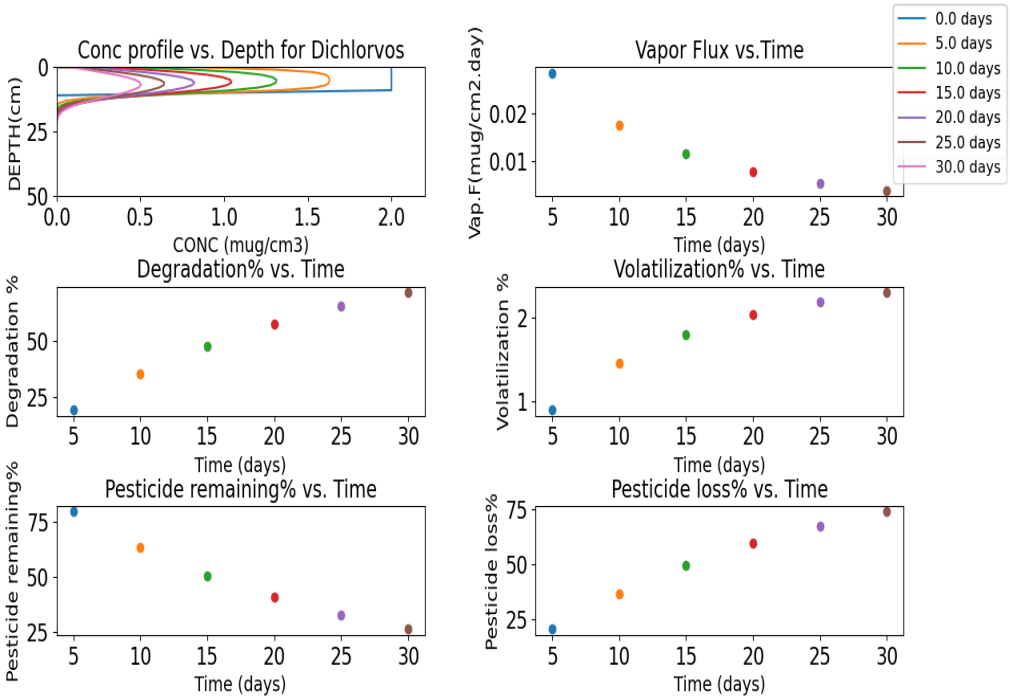


Figure 8.18: Dichlorvos PESTRANS GUI fate Screening graphs with Low pollution potential scenario

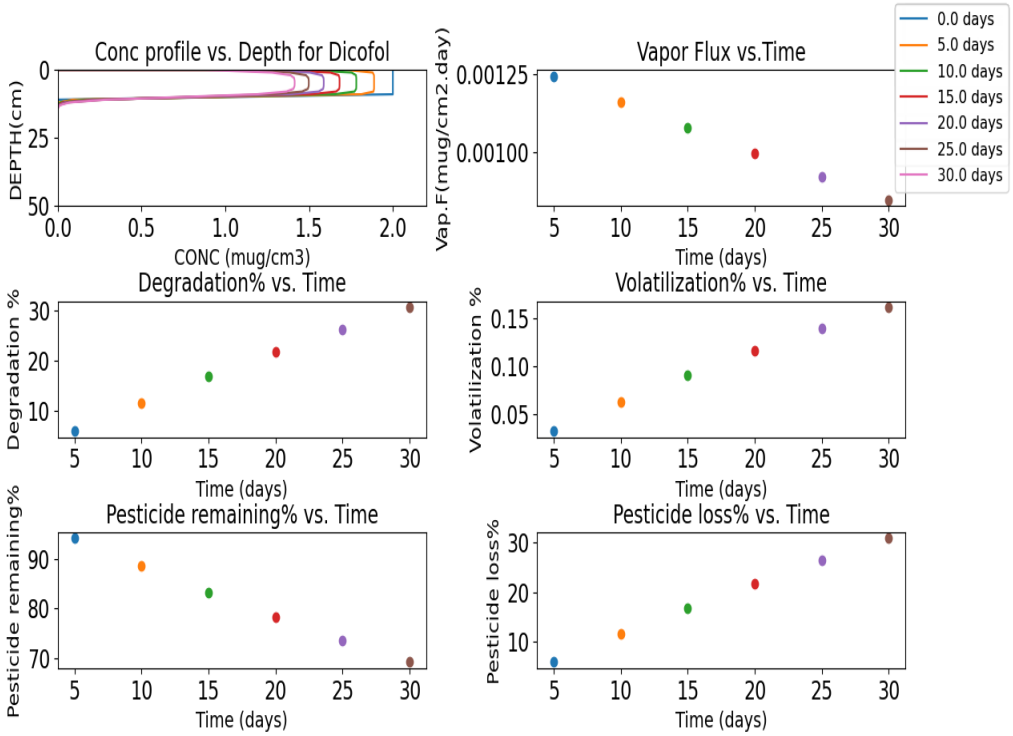


Figure 8.19: Dicofol PESTRANS GUI fate Screening graphs with High pollution potential scenario

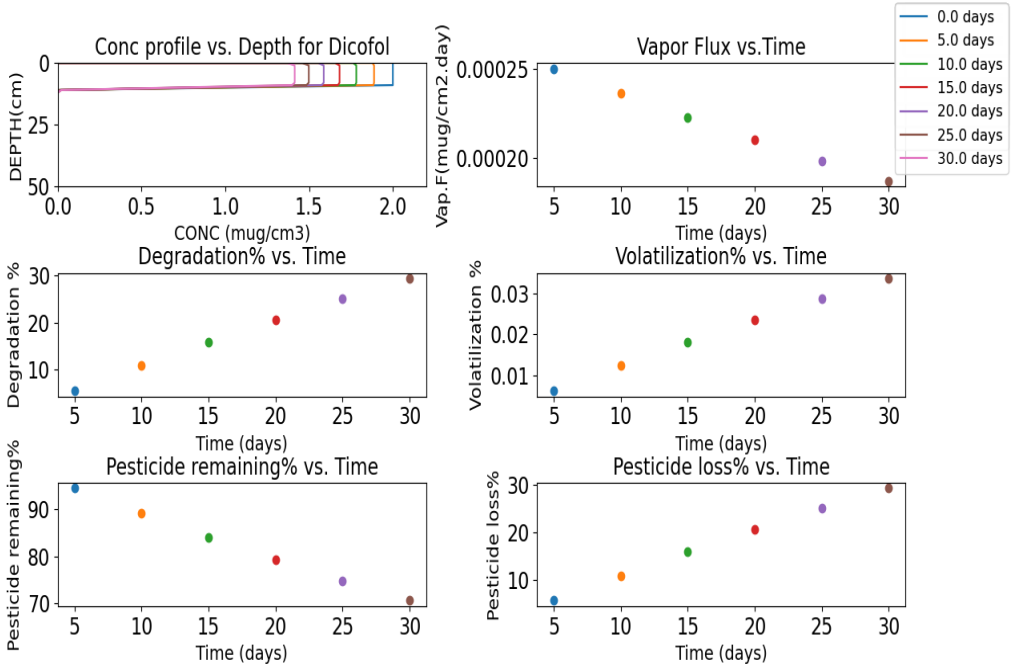


Figure 8.20: Dicofol PESTRANS GUI fate Screening graphs with Low pollution potential scenario

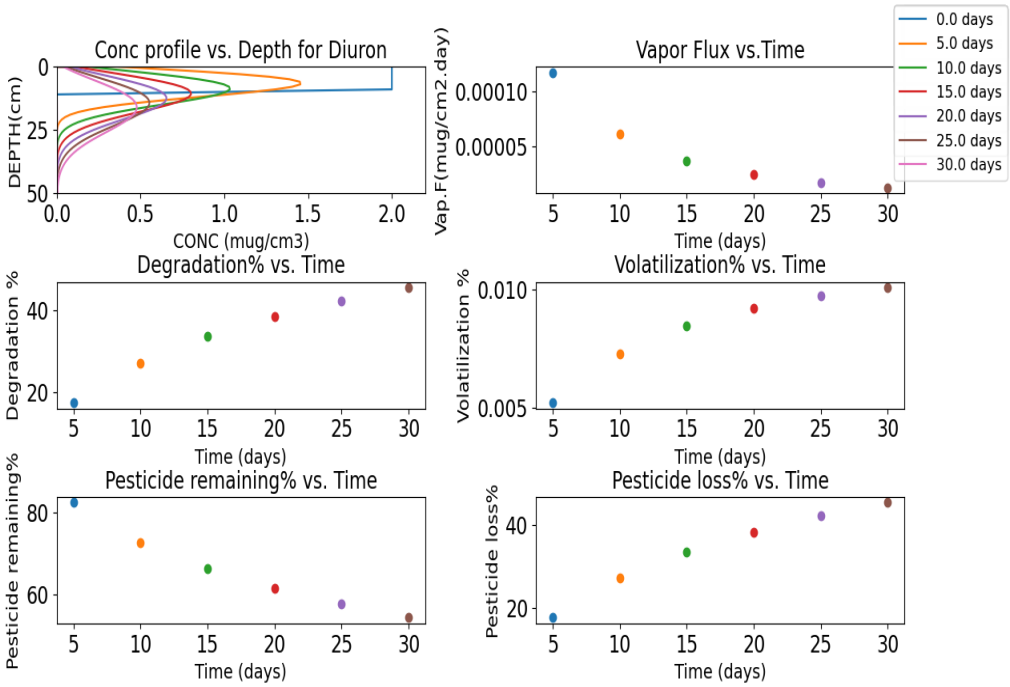


Figure 8.21: Diuron PESTRANS GUI fate Screening graphs with High pollution potential scenario

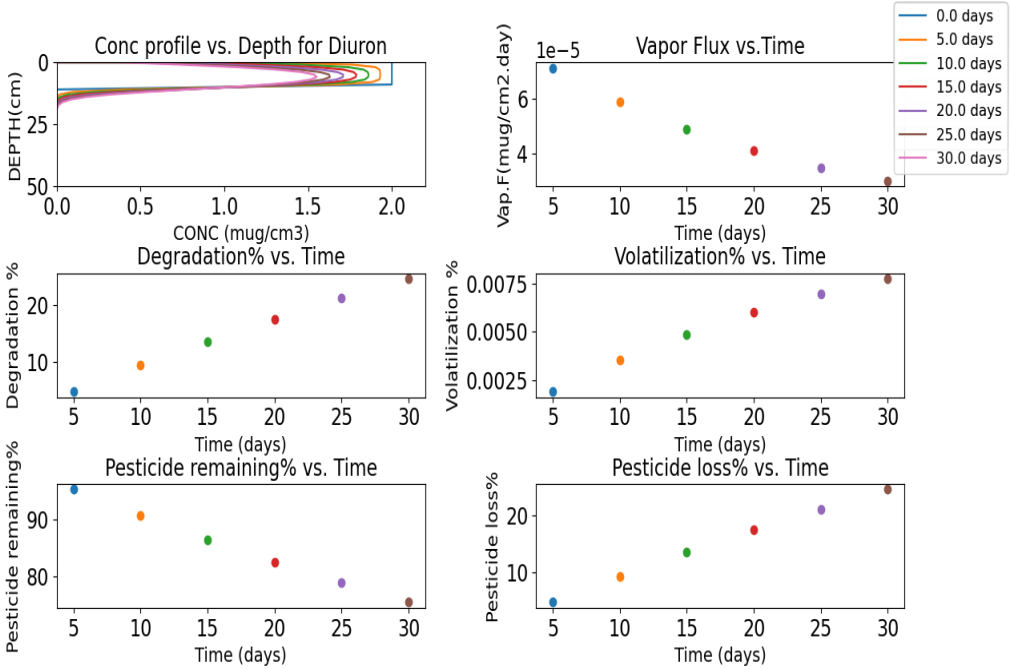


Figure 8.22: Diuron PESTRANS GUI fate Screening graphs with Low pollution potential scenario

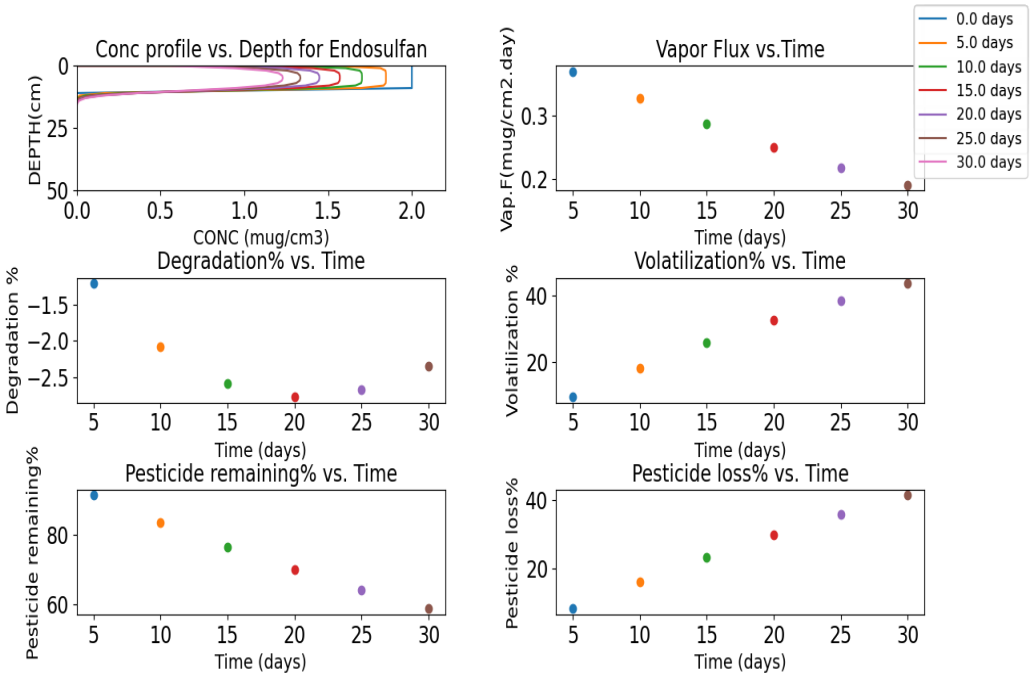


Figure 8.23: Endosulfan PESTRANS GUI fate Screening graphs with High pollution potential scenario

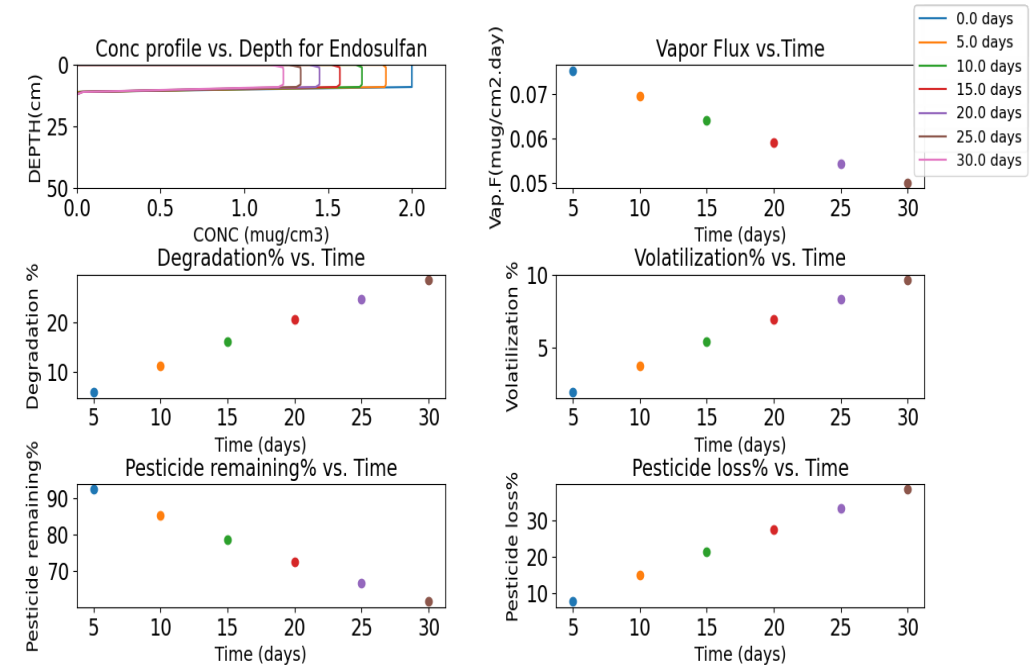


Figure 8.24: Endosulfan PESTRANS GUI fate Screening graphs with Low pollution potential scenario

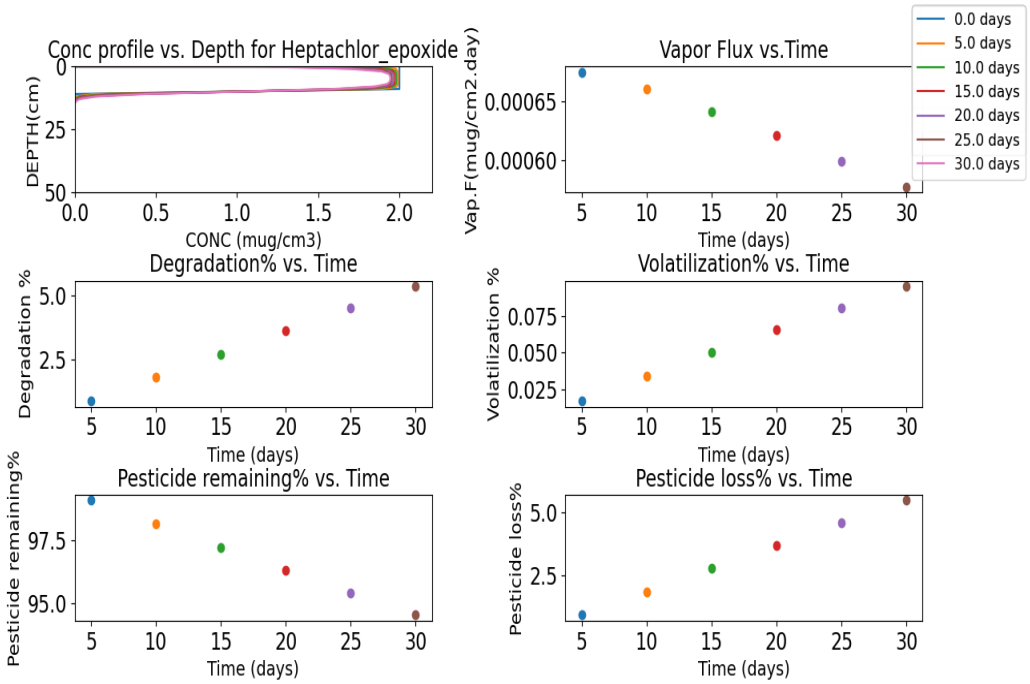


Figure 8.25: Heptachlor epoxide PESTRANS GUI fate Screening graphs with High pollution potential scenario

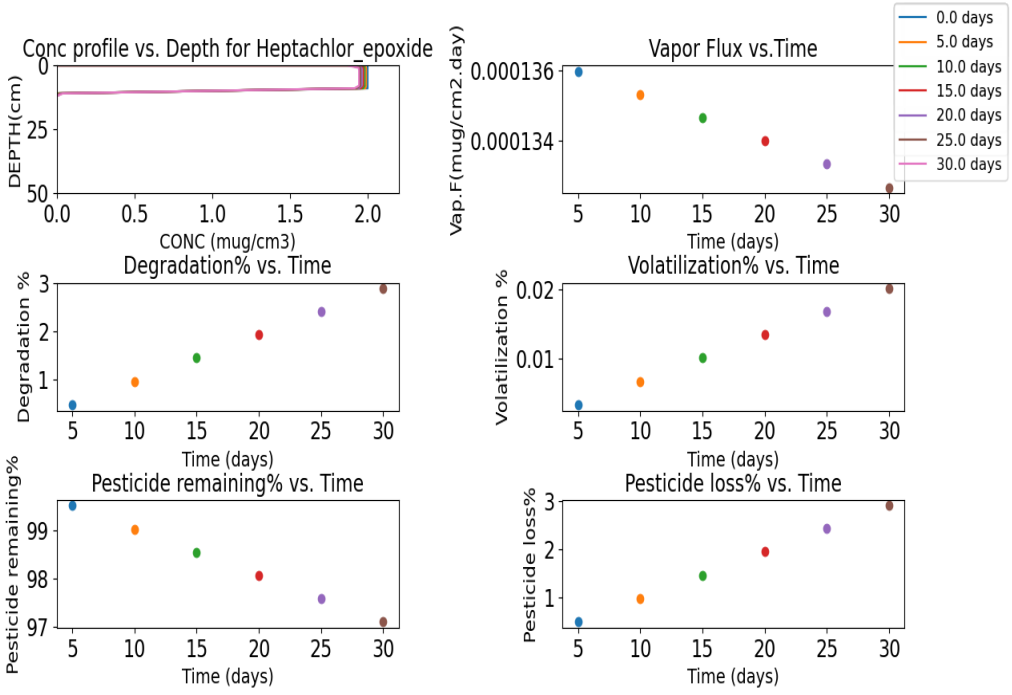


Figure 8.26: Heptachlor Epoxide PESTRANS GUI fate Screening graphs with Low pollution potential scenario

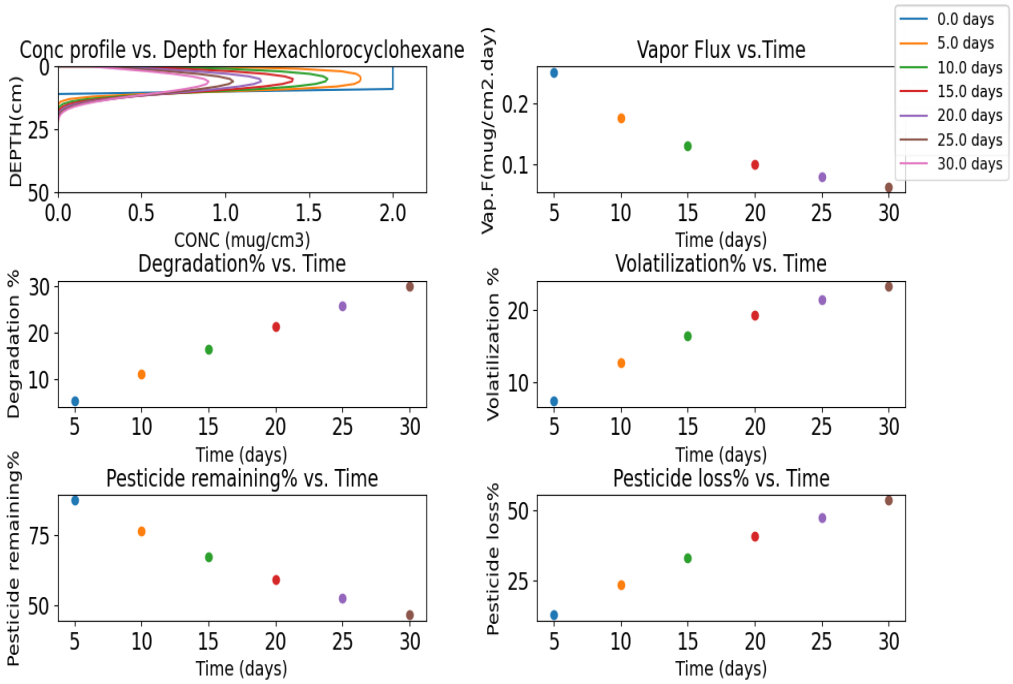


Figure 8.27: Hexachlorocyclohexane PESTRANS GUI fate Screening graphs with High pollution potential scenario

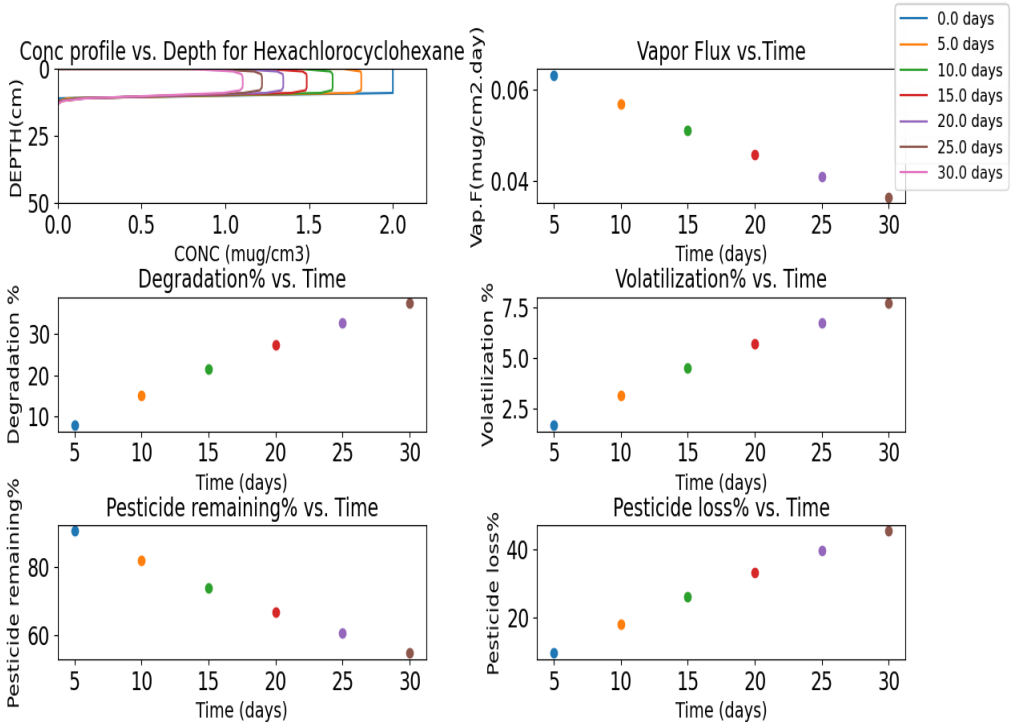


Figure 8.28: Hexachlorocyclohexane PESTRANS GUI fate Screening graphs with Low pollution potential scenario

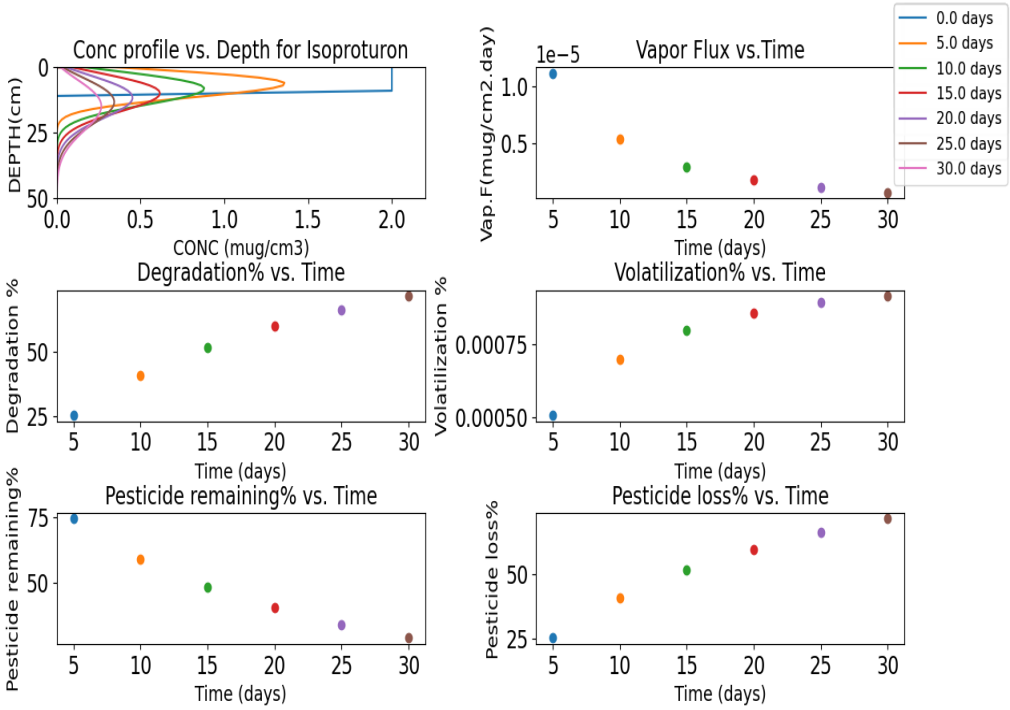


Figure 8.29: Isoproturon PESTRANS GUI fate Screening graphs with High pollution potential scenario

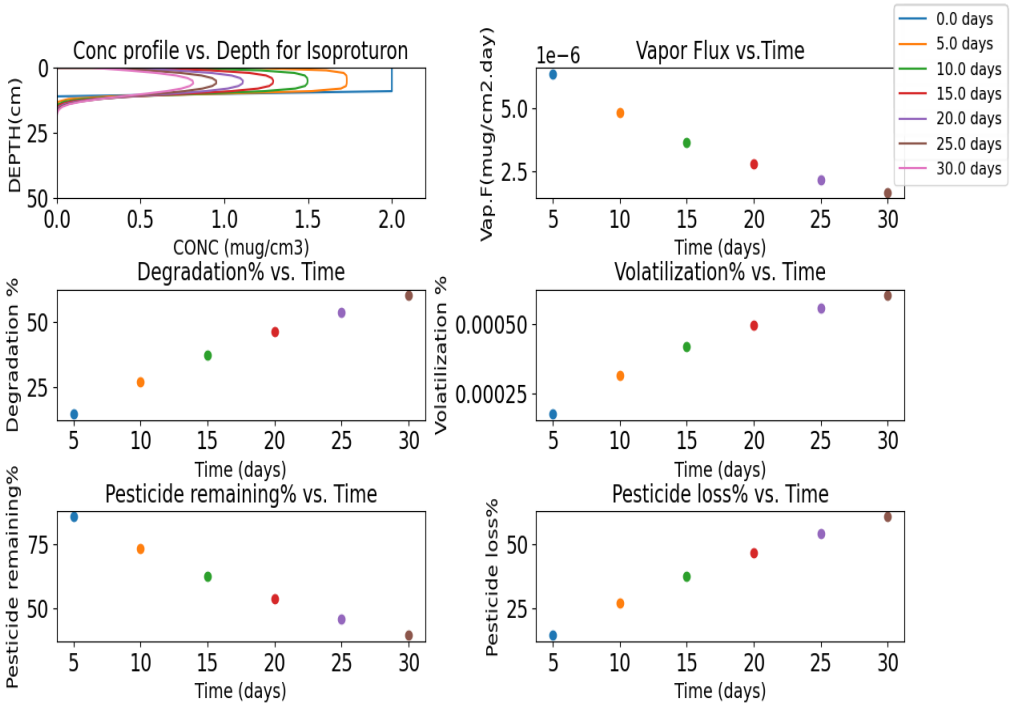


Figure 8.30: Isoproturon PESTRANS GUI fate Screening graphs with Low pollution potential scenario

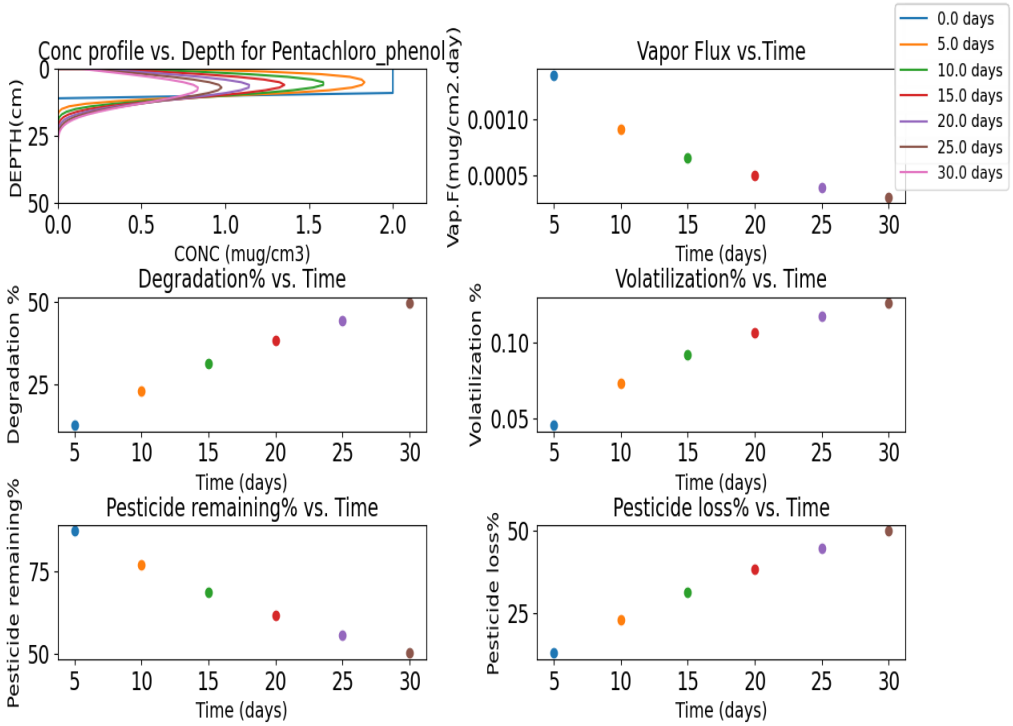


Figure 8.31: Pentachlorophenol PESTRANS GUI fate Screening graphs with High pollution potential scenario

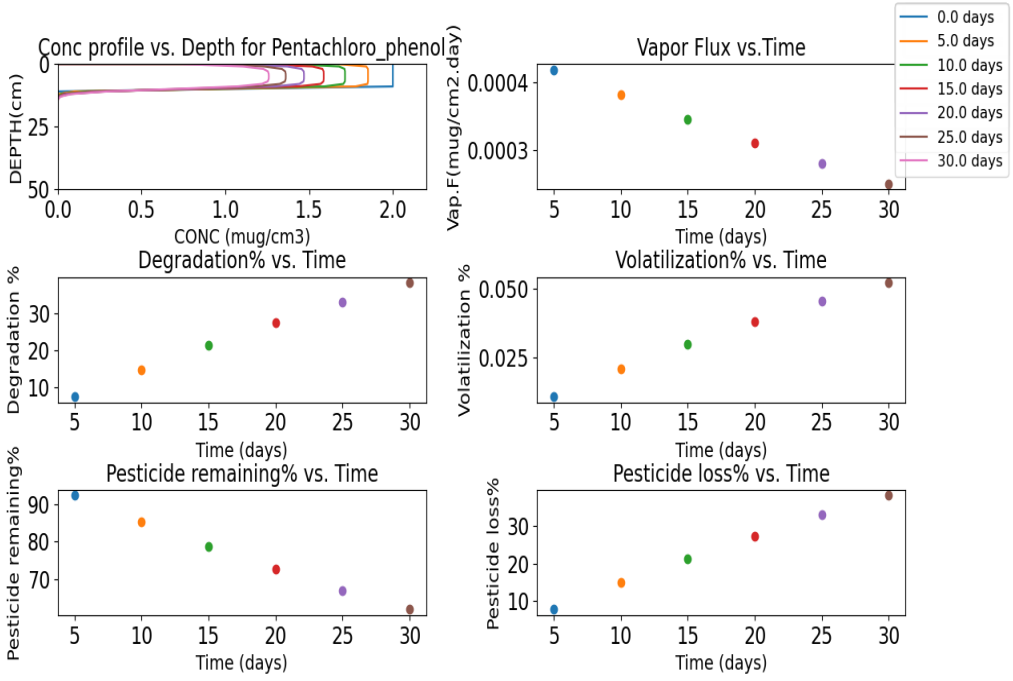


Figure 8.32: Pentachlorophenol PESTRANS GUI fate Screening graphs with Low pollution potential scenario

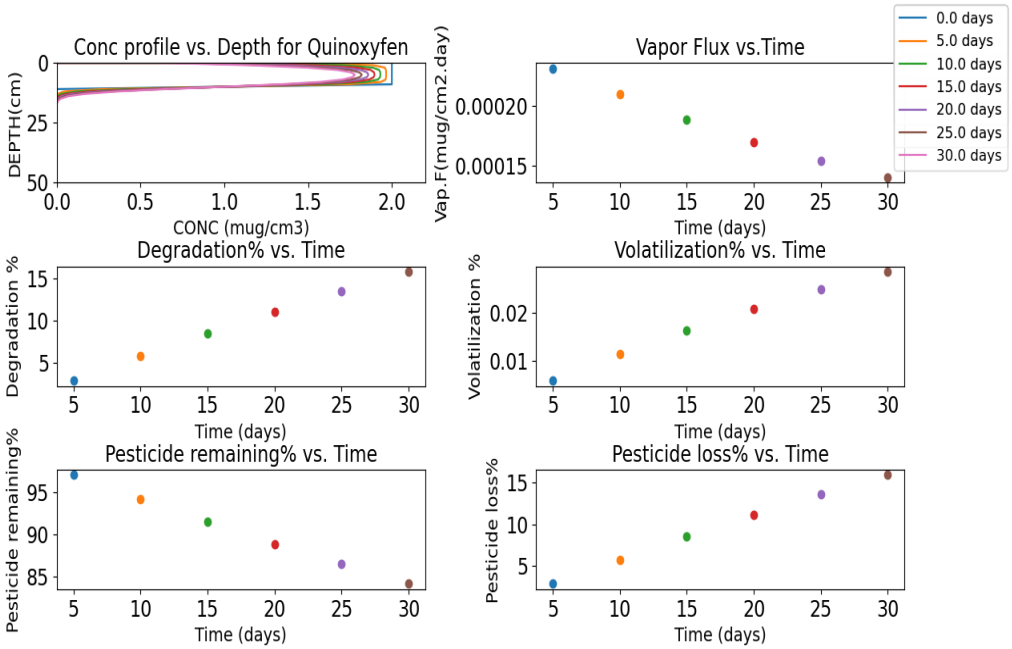


Figure 8.33: Quinoxyfen PESTRANS GUI fate Screening graphs with High pollution potential scenario

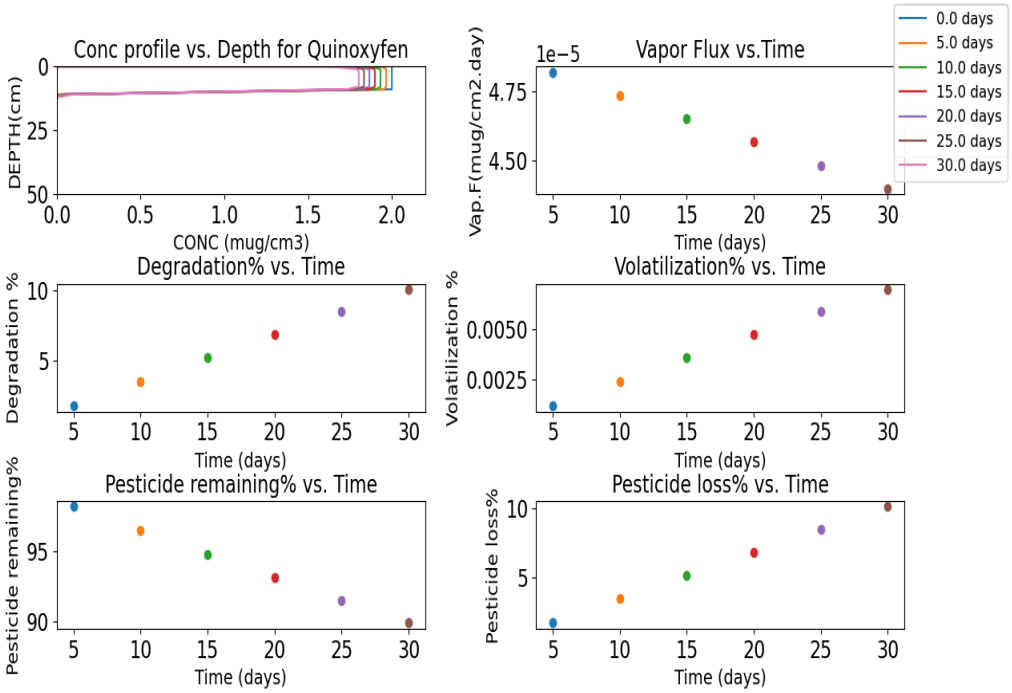


Figure 8.34: Quinoxyfen PESTRANS GUI fate Screening graphs with Low pollution potential scenario

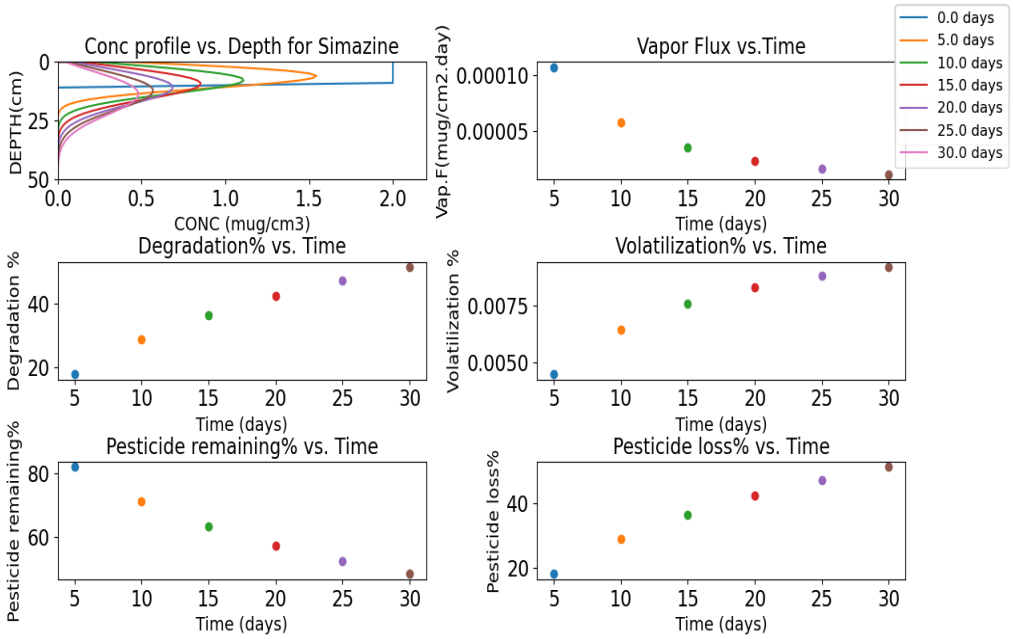


Figure 8.35: Simazine PESTRANS GUI fate Screening graphs with High pollution potential scenario

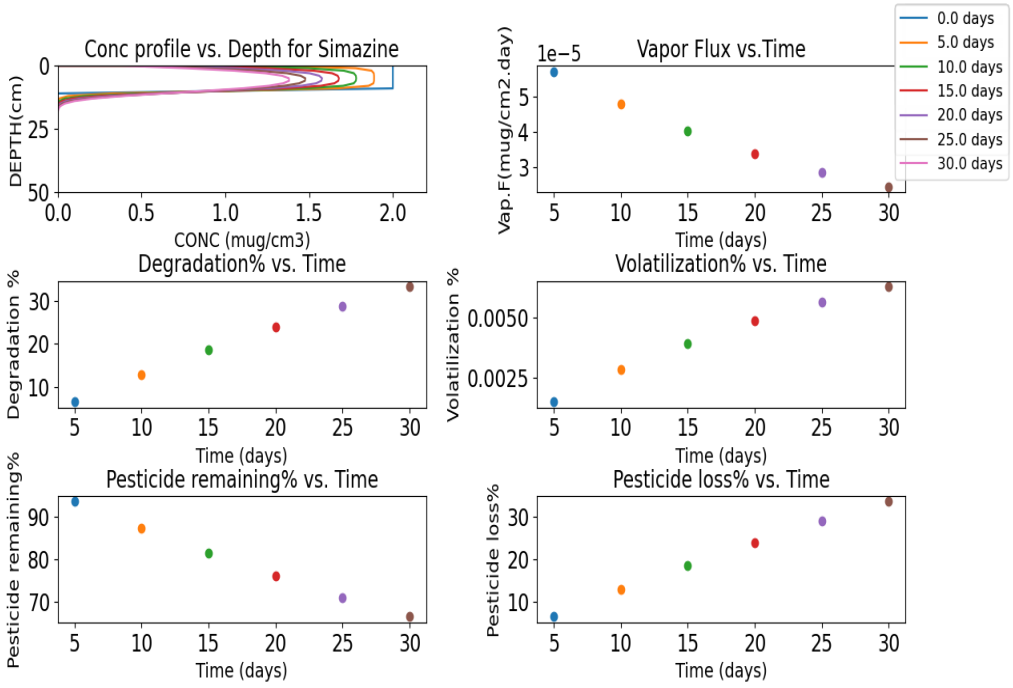


Figure 8.36: Simazine PESTRANS GUI fate Screening graphs with Low pollution potential scenario

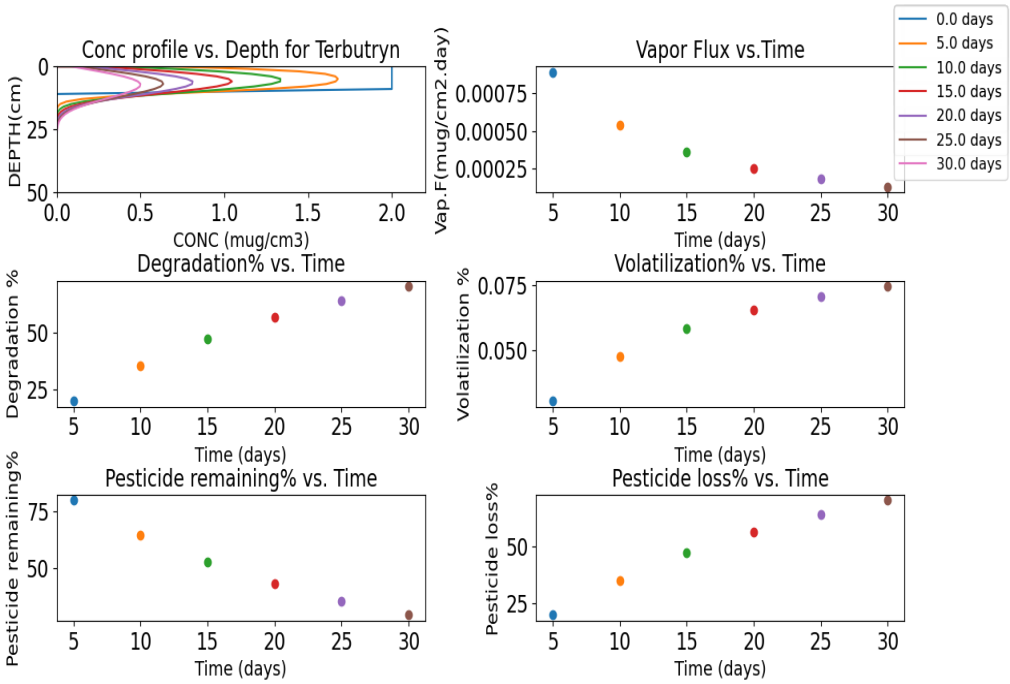


Figure 8.37: Terbutryn PESTRANS GUI fate Screening graphs with High pollution potential scenario

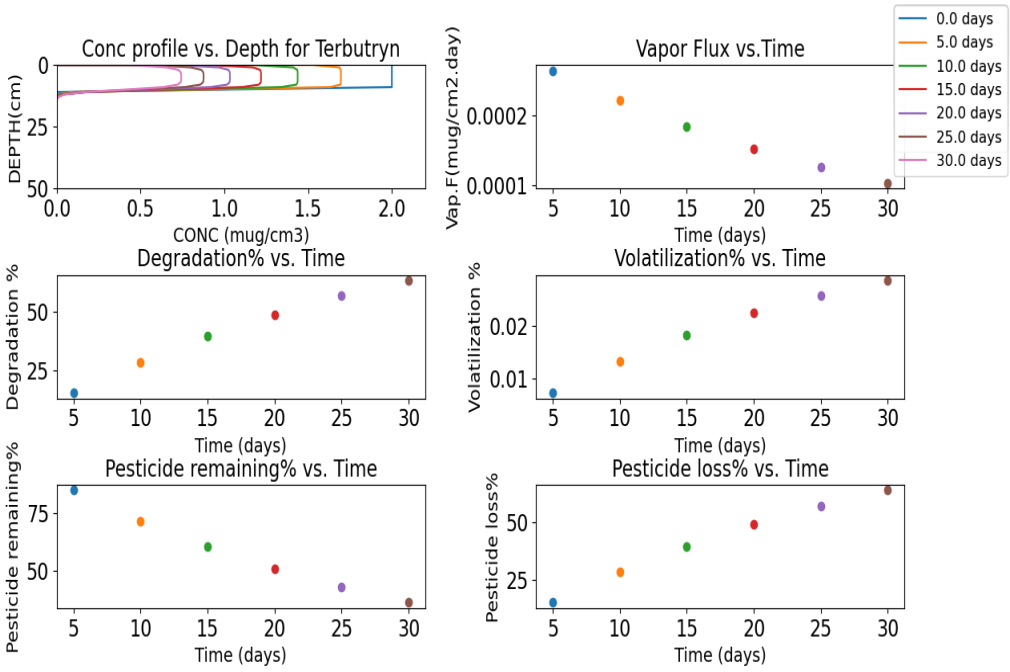


Figure 8.38: Terbutryn PESTRANS GUI fate Screening graphs with Low pollution potential scenario

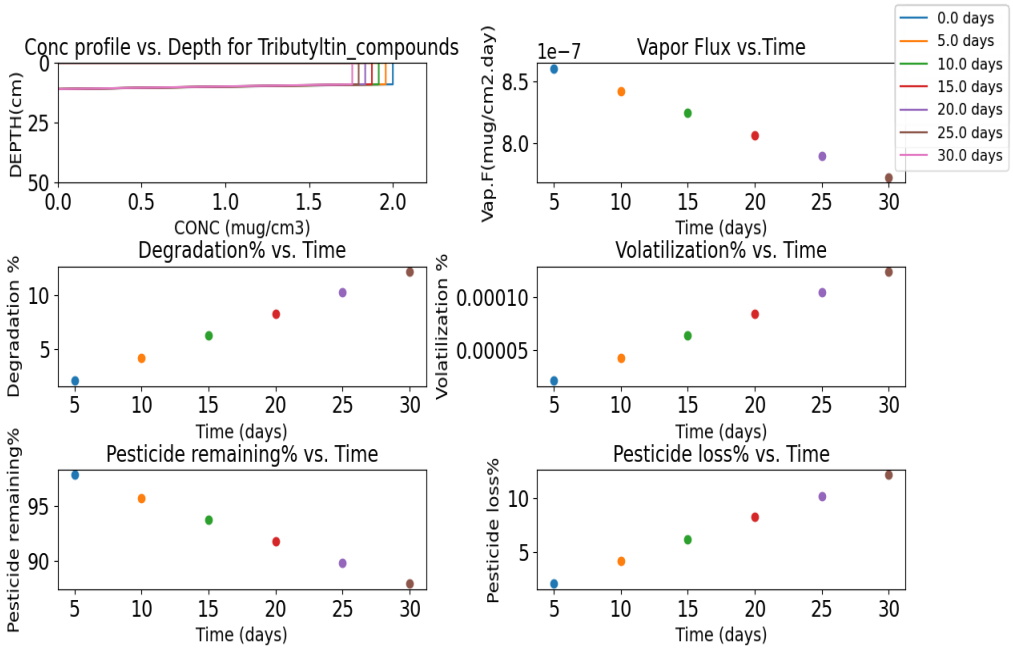


Figure 8.39: Tributyltin PESTRANS GUI fate Screening graphs with High pollution potential scenario

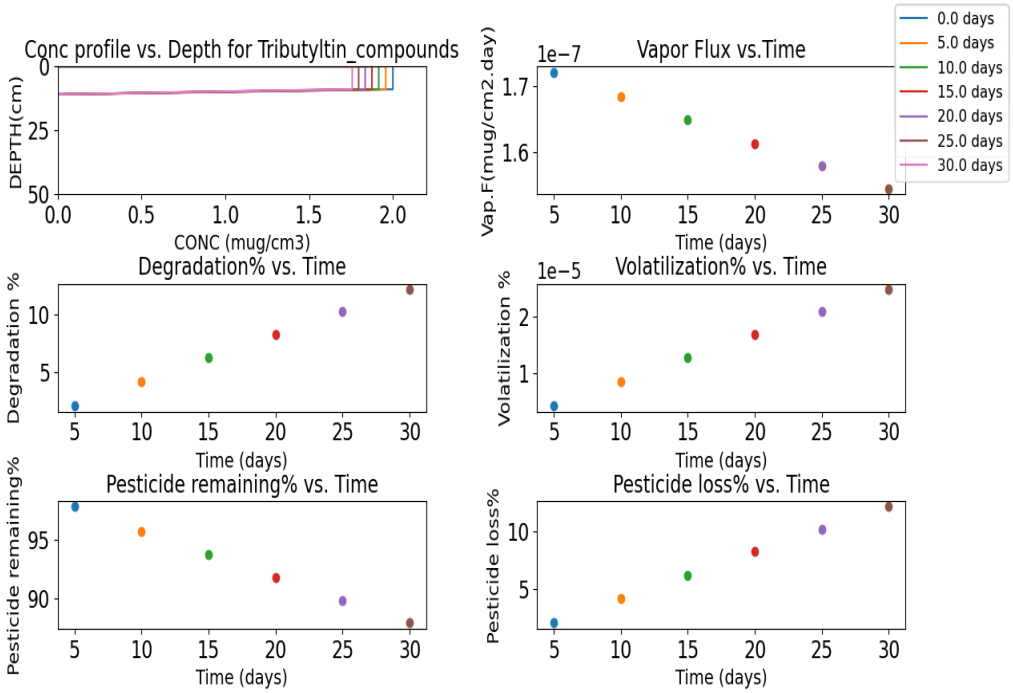


Figure 8.40: Tributyltin PESTRANS GUI fate Screening graphs with Low pollution potential scenario

C. PESTRANS GUI Output of Aclonifen Simulation

```
*********************************************
*                    PESTRANS                 *
*                                             *
* SOLUTION OF CONVECTION DISPERSION EQUATION *
*       FOR TOTAL CONCENTRATION          *
*    USING THE CRANK NICHOLSON METHOD     *
*                                             *
*     THIRD TYPE IUBC    HOMOGENEOUS SYSTEM *
*                                             *
*********************************************
```

TITLE : Aclonifen

SIZE= 31 DMIX= 10.0 cm IUBC= 3

DELZ= 1.0 cm DELT= 0.25 days TMAX= 30.0 days

HALFT= 195.00000 days APPLPM= 22.0 microgram/cm2 DBD= 1.50000 g/cm3

TETAG= 0.25000 cm3/cm3 TETAS 0.15000 cm3/cm3 DIFGO= 5148.20000 cm2/day

DIFSO= 0.60000 cm2/day ALFA= 1.00000 cm QS= 0.27400 cm/day

PHI= 0.40000 HK= 0.000001 FOC= 0.005000 KOC= 7126.0

ABL= 0.5 cm PRSTEP= 30.0 days ILBC= 3

PE= 0.149 CR= 0.001

CINIT= 2.200e+00 microgram/cm3 MU= 3.555e-03 DIFG= 3.167e+02 DIFS= 1.833e+00

VEFF= 5.112e-03 DEFF= 3.422e-02 HEFF= 2.344e-04

TIME= 30.0 days VAPF= -3.731e-04 SVAPF= -5.384e-02 VAPM= -9.328e-05 SVAPM= -1.346e-02 DRAINF= -2.114e-19 SUMDRF= -1.434e-18

DRAINM= -5.286e-20 SUMDRM= -3.584e-19 PCDECM= 13.423 % PCVAPM= 0.061 % PCDRM= 0.000 % PCTMR= 86.516 %

PCTML= 13.484 % SUMM= 1.903e+01 microgram/cm2 ORMBE= -0.000

NODE	DEPTH (cm)	CONC (microgram/cm3)
1	0.0	9.632e-01
2	1.0	1.589e+00
3	2.0	1.862e+00
4	3.0	1.950e+00

5	4.0	1.972e+00
6	5.0	1.975e+00
7	6.0	1.970e+00
8	7.0	1.941e+00
9	8.0	1.838e+00
10	9.0	1.562e+00
11	10.0	1.067e+00
12	11.0	5.408e-01
13	12.0	2.055e-01
14	13.0	6.088e-02
15	14.0	1.460e-02
16	15.0	2.922e-03
17	16.0	5.002e-04
18	17.0	7.465e-05
19	18.0	9.863e-06
20	19.0	1.168e-06
21	20.0	1.253e-07
22	21.0	1.228e-08
23	22.0	1.108e-09
24	23.0	9.252e-11
25	24.0	7.193e-12
26	25.0	5.232e-13
27	26.0	3.574e-14
28	27.0	2.302e-15
29	28.0	1.403e-16
30	29.0	8.127e-18
31	30.0	8.296e-19

TIME	VFLUX	TVM
0	0.000e+00	0.000e+00
30.0	3.731e-04	1.346e-02

D. Computer (Python) source code for PESTRANS GUI

```
import tkinter as tk
from functools import partial
from tkinter import *
import matplotlib.pyplot as plt
from tkinter import messagebox


def call_result(label_result, TITLE1, SIZE2):

    TITLE = (TITLE1.get())
    SIZE = (SIZE2.get())
    result = main()

    label_result.config(text="Result is %d" % result)

    return


root = tk.Tk()
root.geometry('1500x700')
root.title('User interface')

MODEL = tk.StringVar()
MODEL.set("Engine") # default value
MODELBox = OptionMenu(root, MODEL, "PESTRANS", "PESTGRW")

GRAPHER = tk.StringVar()
GRAPHER.set("Graph") # default value
GRAPHERBox = OptionMenu(root, GRAPHER, "Soil Conc Profile", "VAPF vs TIME", "VAPF &
Soilprofile", "Loss percentages graphs")

TITLE = tk.StringVar()
TITLE.set("Pesticide") # default value
TITLEBox = OptionMenu(root, TITLE,
"Aclonifen","Alachlor","Atrazine","Bifenox","Chlorpyrifos","Chlorfenvinphos","Cybutry
ne","Cypermethrin","Dichlorvos","Dicofol","Diuron","Endosulfan","Heptachlor_epoxide",
"Hexachloro_benzene","Hexachlorocyclohexane","Isoproturon","Pentachloro_benzene","Pen
tachloro_phenol","Quinoxyfen","Simazine","Terbutryn","Tributyltin_compounds","Trichlo
ro_benzenes","Trifluralin","other")

TITLE1Box = tk.Entry()


LENGTHBox = tk.Entry()
DELZBox = tk.Entry()
DMIXBox= tk.Entry()

TEXTURE = tk.StringVar()
TEXTURE.set("SOIL TEXTUTE") # default value
TEXTUREBox = OptionMenu(root, TEXTURE,"Clay","Clay_loam","Loam","Loamy_sand",
"Silt","Silt_loam","Silty_clay","Silty_clay_loam","Sand","Sandy_clay","Sandy_clay_loa
m","Sandy_loam","other")

TMAXBox = tk.Entry()
DELTBox = tk.Entry()
PRSTEPBox = tk.Entry()

IUBCBox = tk.Entry()
ILBCBox = tk.Entry()
APPLPMBox = tk.Entry()

ABLBox = tk.Entry()
DIFGBox = tk.Entry()
DIFSBox = tk.Entry()
```

```
KHBox = tk.Entry()
KOCBox = tk.Entry()
HALFTBox = tk.Entry()

DBAZBox = tk.Entry()
GAMABox = tk.Entry()
QSBox =tk.Entry()

DBDBox = tk.Entry()
TETAGBox = tk.Entry()
TETASBox = tk.Entry()
FOCBox = tk.Entry()
ALPHABox = tk.Entry()
PHIBox = tk.Entry()



labelNum = tk.Label(root, text="This Model screens environmental fate of Pesticides")

labelNum0 = tk.Label(root, text="MODEL*")
labelNum0101 = tk.Label(root, text="Model Graph")
labelNum0001 = tk.Label(root, text="Name of Pesticide")
labelNum000 = tk.Label(root, text="**********************")

def Hint1():
    messagebox.showinfo("Hint", "PESTRANS recommends the choice of space Increment
DelZ= 1.0 cm and Time Increment DelT= 0.25 days as best fit for the convergence of
numerical solution")


labelNum0000 = tk.Label(root, text="Spatial Variables:")
HintBox1 = Button(text="Hint", command=Hint1)
labelNum1 = tk.Label(root, text="Depth of Soil*,cm")
labelNum2 = tk.Label(root, text="Increment (Del Z*,cm)")
labelNum3 = tk.Label(root, text="Mixing Depth (DMIX*,cm)")
labelNum4 = tk.Label(root, text="**********************")

def Hint4():
    messagebox.showinfo("Guidance", "Soil Properties: Choose Type of soil texture
from dropdown menu to import properties from Database or choose other to input soil
properties manually")


labelNum6 = tk.Label(root, text="Soil Texture* ")
HintBox4 = Button(text="Guidance", command=Hint4)
labelNum7 = tk.Label(root, text="Bulk Density,g/cm3")
labelNum8 = tk.Label(root, text="Volumetric gas fraction (TETAG,cm3/cm3)")
labelNum9 = tk.Label(root, text="Volumetric water fraction (TETAS,cm3/cm3)")
labelNum10 = tk.Label(root, text="Organic Carbon Fraction (Foc)")
labelNum11 = tk.Label(root, text="Dispersivity (Alpha)")
labelNum1111 = tk.Label(root, text="Porosity (Phi)")
labelNum12 = tk.Label(root, text="**********************")

def Hint3():
    messagebox.showinfo("Instruction", "Choose Pesticide to import physicochemical
properties from Database or Choose Pesticide as other from dropdown menu then name
your Pesticide for manual inputs*")


HintBox3 = Button(text="Guidance", command=Hint3)
labelNum1333 = tk.Label(root, text="Pesticide Properties:")
labelNum13 = tk.Label(root, text="Application Rate* (APPLPM,microgram/cm2)")
labelNum14 = tk.Label(root, text="Diffusion in gas (DIFG,cm2/day)")
labelNum15 = tk.Label(root, text="Diffusion in water (DIFS,cm2/day)")
labelNum16 = tk.Label(root, text="Henry's constant (KH)")
labelNum17 = tk.Label(root, text="Organic Carbon Partitioning Cofficient (Koc)")
labelNum18 = tk.Label(root, text="Half Life,days")
labelNum19 = tk.Label(root, text="**********************")
```

```
labelNum200 = tk.Label(root, text="Time Control Variables:")
labelNum21 = tk.Label(root, text="Simulation Time* (TMAX,days)")
labelNum22 = tk.Label(root, text="Time Increment*(DELT,days)")
labelNum23 = tk.Label(root, text="Printing Step* (PRSTEP,days)")
labelNum24 = tk.Label(root, text="**********************")

def Hint2():
    messagebox.showinfo("Explanation", "Two types of Boundary codition indices 1 or
3: Choose IUBC= 3 for constant flux or 1 for constant concentration at the upper
Boundary condition; Also choose ILBC = 3 for Free drainage condition or ILBC = 1 for
Semi-infinite condition for lower boundary condition")

labelNum20 = tk.Label(root, text="Boundary conditions: ")
HintBox2 = Button(text="Explanation", command=Hint2)
labelNum25 = tk.Label(root, text="Upper Boundary condition Index* (IUBC)")
labelNum26 = tk.Label(root, text="Lower Boundary condition Index* (ILBC)")
labelNum99 = tk.Label(root, text="Air constant surface thickness (ABL,cm)")
labelNum27 = tk.Label(root, text="**********************")

def Hint5():
    messagebox.showinfo("Explanation", "For PESTRANS model engine is used for short
depth simulations. Thus, microbial bioactivity is assumed to be constant and
calculated from Halflife of Chemical. On the other hand, PESTGRW model engine is used
for deeper simulations. So, PESTGRW recommends DBAZ= 50 cm and for High Pollution
Potential scenario or DBAZ=100 cm for low Pollution scenario; recommended value of
distribution of Microorganisms coefficient, GAMA is  0.03 cm-1")

labelNum28 = tk.Label(root, text="Microbial Activity:")
HintBox5 = Button(text="Explanation", command=Hint5)
labelNum29 = tk.Label(root, text="Depth of Biological activity (DBAZ, cm)")
labelNum30 = tk.Label(root, text="Distribution of Microorganisms (GAMA,cm-1)")
labelNum32 = tk.Label(root, text="Infiltration Rate*(QS,cm/day)")
labelNum31 = tk.Label(root, text="**********************")

list1=Text(root,height=10,width=120)
list1.grid(row=30,column=1,rowspan=5000,columnspan=500)

sb1=Scrollbar(root)
sb1.grid(row=31,column=510,rowspan=200)

list1.configure(yscrollcommand=sb1.set)
sb1.configure(command=list1.yview)

list1.bind('results',call_result)

labelNum.grid(row=1, column=1)

labelNum0.grid(row=2, column=1)
labelNum0101.grid(row=2, column=3)
labelNum0001.grid(row=13, column=5)
labelNum000.grid(row=3, column=1)

labelNum0000.grid(row=4, column=1)
HintBox1.grid(row=4, column=2)
labelNum1.grid(row=5, column=1)
labelNum2.grid(row=5, column=3)
labelNum3.grid(row=5, column=5)
labelNum4.grid(row=6, column=1)

##labelNum5.grid(row=21, column=1)
labelNum6.grid(row=22, column=1)
HintBox4.grid(row=22, column=2)
labelNum7.grid(row=23, column=1)
labelNum8.grid(row=24, column=1)
labelNum9.grid(row=23, column=3)
labelNum10.grid(row=24, column=3)
labelNum11.grid(row=23, column=5)
labelNum1111.grid(row=24, column=5)
labelNum12.grid(row=25, column=1)
```

```
labelNum1333.grid(row=13, column=1)
labelNum99.grid(row=14, column=1)
labelNum14.grid(row=15, column=1)
labelNum15.grid(row=14, column=3)
labelNum16.grid(row=15, column=3)
labelNum17.grid(row=14, column=5)
labelNum18.grid(row=15, column=5)
labelNum19.grid(row=16, column=1)

labelNum200.grid(row=7, column=1)
labelNum21.grid(row=8, column=1)
labelNum22.grid(row=8, column=3)
labelNum23.grid(row=8, column=5)
labelNum24.grid(row=9, column=1)

labelNum20.grid(row=10, column=1)
HintBox2.grid(row=10, column=2)
labelNum25.grid(row=11, column=1)
labelNum26.grid(row=11, column=3)
labelNum13.grid(row=11, column=5)
labelNum27.grid(row=12, column=1)

HintBox3.grid(row=13, column=2)
labelNum28.grid(row=17, column=1)
HintBox5.grid(row=17, column=2)
labelNum29.grid(row=18, column=1)
labelNum30.grid(row=18, column=3)
labelNum32.grid(row=18, column=5)
labelNum31.grid(row=19, column=1)

MODELBox.grid(row=2,column=2)
GRAPHERBox.grid(row=2,column=4)
TITLEBox.grid(row=13,column=4)
TITLE1Box.grid(row=13,column=6)

LENGTHBox.grid(row=5,column=2)
DELZBox.grid(row=5,column=4)
DMIXBox.grid(row=5,column=6)

HintBox4.grid(row=22,column=2)
TEXTUREBox.grid(row=22,column=4)

DBDBox.grid(row=23,column=2)
TETAGBox.grid(row=24,column=2)
TETASBox.grid(row=23,column=4)
PHIBox.grid(row=24,column=6)
FOCBox.grid(row=24,column=4)
ALPHABox.grid(row=23,column=6)

ABLBox.grid(row=14,column=2)
DIFGBox.grid(row=15,column=2)
DIFSBox.grid(row=14,column=4)
KHBox.grid(row=15,column=4)
KOCBox.grid(row=14,column=6)
HALFTBox.grid(row=15,column=6)

TMAXBox.grid(row=8,column=2)
DELTBox.grid(row=8,column=4)
PRSTEPBox.grid(row=8,column=6)

IUBCBox.grid(row=11,column=2)
ILBCBox.grid(row=11,column=4)
APPLPMBox.grid(row=11,column=6)

DBAZBox.grid(row=18,column=2)
GAMABox.grid(row=18,column=4)
QSBox.grid(row=18,column=6)
```

```
def main():

      global MODEL
      global TEXTURE
      global PESTRANS
      global PESTGRW

      global TITLE
      global SIZE
      global DMIX
      global IUBC
      global ILBC

      global DELZ
      global DELT
      global TMAX
      global HALFT
      global APPLPM
      global PRSTEP
      global DBD
      global TETAG
      global TETAS
      global DIFGO
      global DIFSO
      global ALFA
      global QS
      global PHI
      global HK
      global FOC
      global KOC
      global ABL
      global DBAZ
      global GAMA



      MODEL1 = (MODEL.get())

      GRAPHER1 = (GRAPHER.get())

      TITLE1 = (TITLE.get())

      TEXTURE1 = (TEXTURE.get())

      if TEXTURE1=="Clay":
          from Clay import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Clay_loam":
          from Clay_loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Loam":
          from Loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Loamy_sand":
          from Loamy_sand import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Silt":
          from Silt import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Silt_loam":
          from Silt_loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Silty_clay":
          from Silty_clay import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Silty_clay_loam":
          from Silty_clay_loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Sand":
          from Sand import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Sandy_clay":
          from Sandy_clay import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Sandy_clay_loam":
          from Sandy_clay_loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
      elif TEXTURE1=="Sandy_loam":
          from Sandy_loam import DBD,TETAG,TETAS,ALFA,PHI,FOC
```

```
      else:
          DBD=float(DBDBox.get())
          TETAG=float(TETAGBox.get())
          TETAS=float(TETASBox.get())
          PHI=float(PHIBox.get())
          FOC=float(FOCBox.get())
          ALFA=float(ALPHABox.get())


      if TITLE1=="Bifenox":
            from Bifenox import
IUBC,ILBC,APPLPM,HALFT,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA
      elif TITLE1=="Aclonifen":
            from Aclonifen import
IUBC,ILBC,APPLPM,HALFT,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA
      elif TITLE1=="Alachlor":
            from Alachlor import
IUBC,ILBC,APPLPM,HALFT,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA
      elif TITLE1=="Atrazine":
            from Atrazine import
IUBC,ILBC,APPLPM,HALFT,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA
      elif TITLE1=="Chlorfenvinphos":
            from Chlorfenvinphos import
IUBC,ILBC,APPLPM,HALFT,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA
      elif TITLE1=="Chlorpyrifos":
            from Chlorpyrifos import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Cybutryne":
            from Cybutryne import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Cypermethrin":
            from Cypermethrin import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Dichlorvos":
            from Dichlorvos import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Dicofol":
            from Dicofol import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Diuron":
            from Diuron import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Endosulfan":
            from Endosulfan import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Heptachlor_epoxide":
            from Heptachlor_epoxide import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Hexachloro_benzene":
            from Hexachloro_benzene import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Hexachlorocyclohexane":
            from Hexachlorocyclohexane import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Isoproturon":
            from Isoproturon import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Pentachloro_benzene":
            from Pentachloro_benzene import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Pentachloro_phenol":
            from Pentachloro_phenol import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Quinoxyfen":
            from Quinoxyfen import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Simazine":
            from Simazine import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
```

```
      elif TITLE1=="Terbutryn":
            from Terbutryn import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Tributyltin_compounds":
            from Tributyltin_compounds import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Trichloro_benzenes":
            from Trichloro_benzenes import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT
      elif TITLE1=="Trifluralin":
            from Trifluralin import
IUBC,ILBC,APPLPM,DIFGO,DIFSO,QS,HK,KOC,ABL,DBAZ,GAMA,HALFT

      else:
          TITLE1 = (TITLE1Box.get())
          DIFGO=float(DIFGBox.get())
          DIFSO=float(DIFSBox.get())
          HK=float(KHBox.get())
          KOC=float(KOCBox.get())
          HALFT=float(HALFTBox.get())

          IUBC=int(IUBCBox.get())
          ILBC=int(ILBCBox.get())
          ABL=float(ABLBox.get())

      if MODEL1== "PESTGRW" :
          DBAZ=float(DBAZBox.get())
          GAMA=float(GAMABox.get())

      QS=float(QSBox.get())
      APPLPM=float(APPLPMBox.get())
      IUBC=int(IUBCBox.get())
      ILBC=int(ILBCBox.get())

      LENGTH=int(LENGTHBox.get())
      DELZ=float(DELZBox.get())
      DMIX=float(DMIXBox.get())

      TMAX=float(TMAXBox.get())
      DELT=float(DELTBox.get())
      PRSTEP=float(PRSTEPBox.get())

      SIZE=int ((LENGTH/DELZ)+1)
      CINIT=APPLPM/DMIX
      RUNS=int(TMAX/PRSTEP)+1
      Tinterval=int(PRSTEP/DELT)+1

      TIME=0.0
      PC=0
      DUMBOU=SIZE-1

      CT=[0]*(SIZE+1000)
      VFLUX=[0]*(SIZE+1000)
      TVPZDM=[0]*(SIZE+1000)
      DEPTH=[0]*(SIZE+3)
      COLD=[0]*(SIZE+3)

      A=[1]*(SIZE+3)
      C=[0]*(SIZE+3)
      B=[1]*(SIZE+3)
      F=[1]*(SIZE+3)
      BETA=[1]*(SIZE+3)
      GAMMA=[0]*(SIZE+3)
      CNEW=[0]*(SIZE+3)
      MU=[0]*(SIZE+3)

      list1.insert(END,' \n')
      list1.insert(END,' ******************************************\n')
      if MODEL1== "PESTRANS" :
```

```
        list1.insert(END,' *                    PESTRANS                 *\n')
    elif MODEL1== "PESTGRW" :
        list1.insert(END,' *                    PESTGRW                 *\n')

    list1.insert(END,' *                                                *\n')
    list1.insert(END,' * SOLUTION OF CONVECTION DISPERSION EQUATION *\n')
    list1.insert(END,' *         FOR TOTAL CONCENTRATION            *\n')
    list1.insert(END,' *     USING THE CRANK NICHOLSON METHOD       *\n')
    list1.insert(END,' *                                                *\n')



    if (IUBC == 1):
          list1.insert(END,' *      FIRST TYPE IUBC    HOMOGENEOUS SYSTEM *\n')
    else:
          list1.insert(END,' *      THIRD TYPE IUBC    HOMOGENEOUS SYSTEM *\n')
          list1.insert(END,' *                                             *\n')
          list1.insert(END,' ***********************************************\n')
          list1.insert(END,' \n')
          list1.insert(END,' \n')

    list1.insert(END,"TITLE : " + TITLE1)
    list1.insert(END,' \n')
    list1.insert(END,("SIZE=" , SIZE) + ("DMIX=" , DMIX,"cm") + ("IUBC=" , IUBC))
    list1.insert(END,' \n')
    list1.insert(END,("DELZ=" , DELZ,"cm") + ("DELT=", DELT,"days") + ("TMAX=" ,
TMAX,"days"))
    list1.insert(END,' \n')
    list1.insert(END,("HALFT=" , "{0:.5f}".format(HALFT),"days") + ("APPLPM=" ,
APPLPM,"microgram/cm2") + ("DBD=" , "{0:.5f}".format(DBD),"g/cm3"))
    list1.insert(END,' \n')
    list1.insert(END,("TETAG=" , "{0:.5f}".format(TETAG),"cm3/cm3") + ("TETAS" ,
"{0:.5f}".format(TETAS),"cm3/cm3") + ("DIFGO=" , "{0:.5f}".format(DIFGO),"cm2/day"))
    list1.insert(END,' \n')
    list1.insert(END,("DIFSO=" , "{0:.5f}".format(DIFSO),"cm2/day") + ("ALFA=" ,
"{0:.5f}".format(ALFA),"cm") + ("QS=" , "{0:.5f}".format(QS),"cm/day"))
    list1.insert(END,' \n')
    list1.insert(END,("PHI=" , "{0:.5f}".format(PHI)) + ("HK=" ,
"{0:.6f}".format(HK)) + ("FOC=" , "{0:.6f}".format(FOC)) + ("KOC=" , KOC))
    list1.insert(END,' \n')
    list1.insert(END,("ABL=" , ABL,"cm") + ("PRSTEP=", PRSTEP,"days") + ("ILBC=",
ILBC))
    list1.insert(END,' \n')
    list1.insert(END,' \n')

    #
    # CALCULATION OF VARIOUS PARAMETERS
    #

    for  I in range(1,SIZE+1):
          DEPTH[I]=(I-1)*DELZ


    if MODEL1== "PESTRANS" :
        if (HALFT >= 1.0E+05):
          MU=1.0E-20
        else:
          MU=0.69315/HALFT
    elif MODEL1== "PESTGRW" :
        IDBAZ=int(DBAZ/DELZ)+1

        import math

        for i in range(0,SIZE+1):
            if (i<=IDBAZ):
                MU[i]=0.69315/HALFT
            else:
                MU[i]=(0.69315/HALFT)*math.exp(-GAMA*(DEPTH[i]-DBAZ))
```

```
      import math

      DIFG=DIFGO*(TETAG**(10.0/3.0))/(PHI**2)
      DIFS=(ALFA*abs(QS/TETAS))+(DIFSO*(TETAS**(10.0/3.0))/(PHI**2))
      VEFF=QS/((DBD*FOC*KOC)+TETAS+(TETAG*HK))
      DEFF=((HK*DIFG)+DIFS)/((DBD*FOC*KOC)+TETAS+(TETAG*HK))
      HEFF=(HK*DIFGO)/(ABL*((DBD*FOC*KOC)+TETAS+(TETAG*HK)))
      RL=(DBD*FOC*KOC)+TETAS+(TETAG*HK)

      #
      # Pe ve Cr sayilarinin hesaplanmasi
      #

      PE=abs((VEFF*DELZ)/DEFF)
      CR=abs((VEFF*DELT)/DELZ)
      list1.insert(END, ("PE=",format("%.3f" % round(PE,4))) + ("CR=",format("%.3f" %
round(CR,4))))
      list1.insert(END,' \n')
      list1.insert(END,' \n')

      if (PE >= 2 or CR >= 1):
            list1.insert(END,("PE=",PE)+("CR=",CR))
            list1.insert(END,' \n')
            list1.insert(END,' \n')

      if MODEL1== "PESTRANS" :
          list1.insert(END,("CINIT=",format(CINIT,
".3e"),"microgram/cm3")+("MU=",format(MU, ".3e"))+("DIFG=",format(DIFG,
".3e"))+("DIFS=",format(DIFS, ".3e")))
          list1.insert(END,' \n')
          list1.insert(END,("VEFF=",format(VEFF, ".3e"))+("DEFF=",format(DEFF,
".3e"))+("HEFF=",format(HEFF, ".3e")))
          list1.insert(END,' \n')
          list1.insert(END,' \n')
      elif MODEL1== "PESTGRW" :
          list1.insert(END,("CINIT=",format(CINIT,
".3e"),"microgram/cm3")+("DIFG=",format(DIFG, ".3e"))+("DIFS=",format(DIFS, ".3e")))
          list1.insert(END,("VEFF=",format(VEFF, ".3e"))+("DEFF=",format(DEFF,
".3e"))+("HEFF=",format(HEFF, ".3e")))
          list1.insert(END,' \n')
          list1.insert(END,' \n')

      G=DEFF/(2.*DELZ*DELZ)
      H=VEFF/(4.*DELZ)
      NINC=int(DMIX/DELZ)+1

      #
      # DEFINE INITIAL AND BOUNDARY CONDITIONS
      #

##      list1.insert(END,("CINIT=",CINIT,"microgram/cm3"))
      list1.insert(END,' \n')
      list1.insert(END,' \n')

      for  I in range(0,SIZE+1):
             if (I < NINC):
                   COLD[I]=CINIT
             elif (I == NINC):
                   COLD[I]=CINIT*0.5
             elif (I > NINC):
                   COLD[I]=0.0


      ORMB=0.0
      VAPF=0.0
      VAPM=0.0
      DRAINF=0.0
      DRAINM=0.0
```

```
      SVAPF=0.0
      SUMDRF=0.0
      SVAPM=0.0
      SUMDRM=0.0
      SMASS=0.0
      CT[0]=0.0
      VFLUX[0]=0.0
      TVPZDM[0]=0.0

      SMASSI=CINIT*DMIX
      #
      CIN=CINIT

      if (IUBC== 1):
            COLD[0]=CIN
      else:
            COLD[0]=CIN



list1.insert(END,("TIME=",TIME,"days")+("VAPF=",format(VAPF,".3e"))+("SVAPF=",format(
SVAPF,".3e"))+("VAPM=",format(VAPM,".3e")))
      list1.insert(END,' \n')

list1.insert(END,("SVAPM=",format(SVAPM,".3e"))+("DRAINF=",format(DRAINF,".3e"))+("SU
MDRF=",format(SUMDRF,".3e")))
      list1.insert(END,' \n')

list1.insert(END,("DRAINM=",format(DRAINM,".3e"))+("SUMDRM=",format(SUMDRM,".3e"))+("
SMASSI=",format(SMASSI,".3e")))
      list1.insert(END,' \n')
      list1.insert(END,' \n')

      list1.insert(END,("NODE")+("  DEPTH (cm)")+("  CONC (microgram/cm3)\n"))

      for I in range (1,SIZE+1):
            list1.insert(END,('',I)+(' ',DEPTH[I])+('    ',format(COLD[I],".3e")))
            list1.insert(END,' \n')

      list1.insert(END,' \n')
      list1.insert(END,' \n')
      CLIMIT=CINIT+(0.1*CINIT)

      if GRAPHER1 == "Soil Conc Profile":
          graph1=plt.figure()
          graph1 = plt.plot(COLD,DEPTH, label=str(TIME)+" days")
          plt.title('Concentration profile vs Depth for '+str(TITLE1))
          plt.xlabel("CONC (microgram/cm3)")
          plt.tick_params(top=True)
          plt.tick_params(labeltop=True)
          plt.ylabel("DEPTH(cm)")
          CLIMIT=CINIT+(0.1*CINIT)
          plt.xlim(0,CLIMIT)
          plt.ylim(LENGTH,0)

      elif GRAPHER1 == "VAPF vs TIME":
          fig = plt.figure(100)
##          plt.scatter(label=str(QS)+" cm/day")

      elif GRAPHER1 == "VAPF & Soilprofile":
          fig, ax = plt.subplots(2,1)
          graph1= ax[0].plot(COLD, DEPTH,label=str(TIME)+" days")
          ax[0].set(ylabel='DEPTH(cm)', xlabel='CONC (mug/cm3)',title='Concentration
profile vs Depth for '+str(TITLE1))
          ax[0].set_xlim(0,CLIMIT)
          ax[0].set_ylim(LENGTH,0)
          fig.tight_layout(pad=3.0)
          ax[1].set(xlabel='Time (days)', ylabel='Vap.Flux (mug/cm2.day)',title='Time
vs. Vapor Flux')
```

```
      elif GRAPHER1 == "Loss percentages graphs":
          fig, ax = plt.subplots(3,2)
          graph1= ax[0,0].plot(COLD,DEPTH,label=str(TIME)+" days")
          ax[0,0].set(ylabel='DEPTH(cm)', xlabel='CONC
(mug/cm3)',title='Concentration profile vs Depth for '+str(TITLE1))
          ax[0,0].set_xlim(0,CLIMIT)
          ax[0,0].set_ylim(LENGTH,0)
          fig.tight_layout(pad=1.0)
          ax[0,1].set(xlabel='Time (days)', ylabel='Vap.Flux
(mug/cm2.day)',title='Time vs. Vapor Flux')
          ax[1,0].set(xlabel='Time (days)', ylabel='Degradation %',title='Time vs.
PCDECM')
          ax[1,1].set(xlabel='Time (days)', ylabel='Vaporatization %',title='Time vs.
PCVAPM')
          ax[2,0].set(xlabel='Time (days)', ylabel='Pesticide remaining
%',title='Time vs. PCDRM')
          ax[2,1].set(xlabel='Time (days)', ylabel='Pesticide loss %',title='Time vs.
PCTML')


      A[0]=0.0
      C[SIZE]=0.0
      SUMM=0.0

      for i in range(1,RUNS):

          PC=PC+1

          for i in range(1,Tinterval):

              TIME=TIME+DELT
              PRTIME=PC*PRSTEP

              if MODEL1== "PESTRANS" :
                  if (IUBC == 1):
                        B[0]=1.0
                        C[0]=0.0
                        F[0]=CIN
                  else:
                      if QS>= 0:

B[0]=1.0+(DELT*((1.0+(H/G))*((4.0*H)+(HEFF/DELZ))+(2.*G)+(MU/2.0)))
                          C[0]=-2.0*DELT*G
                          AFF=1.0-
(DELT*((1.+(H/G))*((4.*H)+(HEFF/DELZ))+(2.*G)+(MU/2.)))
                          F[0]=(2.0*DELT*G*COLD[1])+(AFF*COLD[0])
                      elif QS<0:
                          B[0]=1.+(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU/2.)))
                          C[0]=-2.*DELT*G
                          AFF=1.-(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU/2.)))
                          F[0]=(2.*DELT*G*COLD[1])+(AFF*COLD[0])


                  # evaporation case


                  #      B[0]=1.+(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU/2.)))
                  #      C[0]=-2.*DELT*G
                  #      AFF=1.-(DELT*((1.-(H/G))*((HEFF/DELZ)-4.*H)+(2.*G)+(MU/2.)))
                  #      F[0]=(2.*DELT*G*COLD(2))+(AFF*COLD(1))

                  #
                  for  i in range (1,DUMBOU+1):
                      if QS>= 0:
                          A[i]=-G-H
```

```
                        B[i]=(2.0*G)+(1.0/DELT)+(MU/2.0)
                        C[i]=-G+H
                        F[i]=((G+H)*COLD[i-1])+(((1.0/DELT)-(2.0*G)-
(MU/2.0))*COLD[i])+((G-H)*COLD[i+1])
                    elif QS<0:
                        A[i]=-G+H
                        B[i]=2.*G+(1./DELT)+(MU/2.)
                        C[i]=-G-H
                        F[i]=((G-H)*COLD[i-1])+(((1./DELT)-(2.*G)-
(MU/2.))*COLD[i])+((G+H)*COLD[i+1])


                #
                # evaporation case
                #
                #       A(I)=-G+H
                #       B(I)=2.*G+(1./DELT)+(MU/2.)
                #       C(I)=-G-H
                #       F(I)=(G-H)*COLD(I-1)+((1./DELT)-(2.*G)-
(MU/2.))*COLD(I)+(G+H)*
                #     &  COLD(I+1)

                #

                if (ILBC == 1):
                       A[SIZE]=0.0
                       B[SIZE]=1.0
                       F[SIZE]=0.0
                else:
                      A[SIZE]=-1.0
                      B[SIZE]=(1./(2.*G*DELT))+1.+(MU/(4.*G))
                      F[SIZE]=(COLD[SIZE-1])+((1.0/(2.0*G*DELT))-1.0-
(MU/(4.0*G)))*COLD[SIZE]

      ##      ** call TRIDA subroutine**

                BETA[0]=B[0]
                GAMMA[0]=F[0]/B[0]
                for I in range (1,SIZE+1):
                      BETA[I]=B[I]-(A[I]*C[I-1]/BETA[I-1])
                      GAMMA[I]=(F[I]-(A[I]*GAMMA[I-1]))/BETA[I]

                CNEW[SIZE]=GAMMA[SIZE]

                for I in range(SIZE-1,0,-1):
                      CNEW[I]=GAMMA[I]-(C[I]*CNEW[I+1]/BETA[I])

            elif MODEL1== "PESTGRW" :
                if (IUBC == 1):
                    B[0]=1.0
                    C[0]=0.0
                    F[0]=CIN
                else:
                    if QS>= 0:

B[0]=1.0+(DELT*((1.0+(H/G))*((4.0*H)+(HEFF/DELZ))+(2.0*G)+(MU[0]/2.0)))
                        C[0]=-2.0*DELT*G
                        AFF=1.0-
(DELT*((1.+(H/G))*((4.0*H)+(HEFF/DELZ))+(2.*G)+(MU[0]/2.0)))
                        F[0]=(2.0*DELT*G*COLD[1])+(AFF*COLD[0])
                    elif QS<0:
                        B[0]=1.+(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU[0]/2.)))
                        C[0]=-2.*DELT*G
                        AFF=1.-(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU[0]/2.)))
                        F[0]=(2.*DELT*G*COLD[1])+(AFF*COLD[0])
```

```
                  # evaporation case

                  #      B[0]=1.+(DELT*((1.-(H/G))*((HEFF/DELZ)-
4.*H)+(2.*G)+(MU/2.)))
                  #      C[0]=-2.*DELT*G
                  #      AFF=1.-(DELT*((1.-(H/G))*((HEFF/DELZ)-4.*H)+(2.*G)+(MU/2.)))
                  #      F[0]=(2.*DELT*G*COLD(2))+(AFF*COLD(1))

                  #


                  for  i in range (1,DUMBOU+1):
                      if QS>=0:
                          A[i]=-G-H
                          B[i]=2*G+(1/DELT)+(MU[i]/2)
                          C[i]=-G+H
                          F[i]=(G+H)*COLD[i-1]+((1.0/DELT)-(2.0*G)-
(MU[i]/2.))*COLD[i]+(G-H)*COLD[i+1]
                      elif QS<0:
                          A[i]=-G+H
                          B[i]=2.*G+(1./DELT)+(MU[i]/2.)
                          C[i]=-G-H
                          F[i]=(G-H)*COLD(i-1)+((1./DELT)-(2.*G)-
(MU[i]/2.))*COLD[i]+(G+H)*COLD[i+1]
                  #    &



                  # evaporation case
                  #
                  #      A(I)=-G+H
                  #      B(I)=2.*G+(1./DELT)+(MU/2.)
                  #      C(I)=-G-H
                  #      F(I)=(G-H)*COLD(I-1)+((1./DELT)-(2.*G)-
(MU/2.))*COLD(I)+(G+H)*
                  #    &  COLD(I+1)

                  #


                  if (ILBC == 1):
                      A[SIZE]=0.0
                      B[SIZE]=1.0
                      F[SIZE]=0.0

                  else:
                      A[SIZE]=-1.0
                      B[SIZE]=(1./(2.*G*DELT))+1.+(MU[SIZE-1]/(4.*G))
                      F[SIZE]=COLD[SIZE-1]+((1./(2.*G*DELT))-1.-(MU[SIZE-
1]/(4.*G)))*COLD[SIZE]


       ##      ** call TRIDA subroutine**

    ##                GAMA=0.03
                  BETA[0]=B[0]
                  GAMMA[0]=F[0]/B[0]
                  for I in range (1,SIZE+1):
                        BETA[I]=B[I]-(A[I]*C[I-1]/BETA[I-1])
                        GAMMA[I]=(F[I]-(A[I]*GAMMA[I-1]))/BETA[I]

                  CNEW[SIZE]=GAMMA[SIZE]

                  for I in range(SIZE-1,0,-1):
                        CNEW[I]=GAMMA[I]-(C[I]*CNEW[I+1]/BETA[I])
```

```
                VAPF=-0.5*HEFF*(CNEW[2]+COLD[2])
                SVAPF=SVAPF+VAPF
                DRAINF=-0.5*QS*(CNEW[SIZE]+COLD[SIZE])
                SUMDRF=SUMDRF+DRAINF

                SUMM=0.0
                for I in range(2,SIZE+1):
                      SUMM=SUMM+(0.5*DELZ*(CNEW[I-1]+CNEW[I]))

                import math

                VAPM=VAPF*DELT
                SVAPM=SVAPM+VAPM
                DRAINM=DRAINF*DELT
                SUMDRM=SUMDRM+DRAINM
                SMASS=SUMM+abs(SVAPM+SUMDRM)
                PCDECM=100.0*(SMASSI-SMASS)/SMASSI
                PCVAPM=100.0*abs(SVAPM/SMASSI)
                PCDRM=100.0*abs(SUMDRM/SMASSI)
                PCTMR=100.0*(SUMM/SMASSI)
                PCTML=PCDECM+PCVAPM+PCDRM
                ORMBE=100.0-(PCTMR+PCTML)
##                TEFFH=(-0.693*TMAX)/(math.log(SUMM/SMASSI))

                for I in range(0,SIZE+1):
                      COLD[I]=CNEW[I]

                if MODEL1== "PESTGRW" :
                    CLIQ=CNEW[SIZE]/RL


                if (TIME>=PRTIME):

list1.insert(END,("TIME=",TIME,"days")+("VAPF=",format(VAPF,".3e"))+("SVAPF=",format(
SVAPF,".3e"))+("VAPM=",format(VAPM,".3e"))+("SVAPM=",format(SVAPM,".3e"))+("DRAINF=",
format(DRAINF,".3e"))+("SUMDRF=",format(SUMDRF,".3e")))
                      list1.insert(END,' \n')

list1.insert(END,("DRAINM=",format(DRAINM,".3e"))+("SUMDRM=",format(SUMDRM,".3e"))+("
PCDECM=","{0:.3f}".format(PCDECM),"%")+("PCVAPM=","{0:.3f}".format(PCVAPM),"%")+("PCD
RM=","{0:.3f}".format(PCDRM),"%")+("PCTMR=","{0:.3f}".format(PCTMR),"%"))
                      list1.insert(END,' \n')

list1.insert(END,("PCTML=","{0:.3f}".format(PCTML),"%")+("SUMM=",format(SUMM,".3e"),"
microgram/cm2")+("ORMBE=","{0:.3f}".format(ORMBE)))
                      list1.insert(END,' \n')
                      list1.insert(END,' \n')

                      TIME1=TIME
                      PCVAPM1=PCVAPM

##                      print("NODE","DEPTH","CONC")
                      list1.insert(END,(" NODE")+(" DEPTH(cm)")+("  CONC
(microgram/cm3) \n"))

                      for I in range (1,SIZE+1):
##                            print(I,DEPTH[I],format(CNEW[I],".3e"))
                            list1.insert(END,("",I)+(" ",DEPTH[I])+("
",format(CNEW[I],".3e")))
                            list1.insert(END,' \n')


                      list1.insert(END,' \n')
                      list1.insert(END,' \n')
                      VAPF1=-VAPF

                      if GRAPHER1 == "Soil Conc Profile":
                          graph1=plt.plot(CNEW,DEPTH, label=str(TIME)+" days")
```

```
                        plt.legend()

                    elif GRAPHER1 == "VAPF vs TIME":
                        plt.scatter(TIME, VAPF1, color='green')
                        plt.xlabel='Time (days)'
                        plt.ylabel='Vap.Flux (mug/cm2.day)'
                        plt.title='Time vs. Vapor Flux'
##                        fig.legend()

                    elif GRAPHER1 == "VAPF & Soilprofile":
                        graph1 = ax[0].plot(CNEW,DEPTH,label=str(TIME)+" days")
                        graph2 = ax[1].scatter(TIME, VAPF1)
                        fig.legend()

                    elif GRAPHER1 == "Loss percentages graphs":
                        graph1 = ax[0,0].plot(CNEW,DEPTH,label=str(TIME)+" days")
                        graph2 = ax[0,1].scatter(TIME, VAPF1)
                        graph2 = ax[1,0].scatter(TIME, PCDECM)
                        graph2 = ax[1,1].scatter(TIME, PCVAPM)
                        graph2 = ax[2,0].scatter(TIME, PCTMR)
                        graph2 = ax[2,1].scatter(TIME, PCTML)
                        fig.legend()


                    VAPF=-VAPF1

            CT[PC-1]=TIME
            VFLUX[PC-1]=abs(VAPF)
            TVPZDM[PC-1]=abs(SVAPM)


            if (TIME>=TMAX):
                list1.insert(END,("  TIME")+("     VFLUX")+("          TVM \n"))

list1.insert(END,('',CT[120])+('',format(VFLUX[120],".3e"))+('',format(TVPZDM[120],".
3e")))
                list1.insert(END,' \n')


list1.insert(END,('',CT[0])+('',format(VFLUX[0],".3e"))+('',format(TVPZDM[0],".3e")))
                list1.insert(END,' \n')
                list1.insert(END,' \n')
                list1.insert(END,' \n')
                list1.insert(END,' \n')

                if (PCTMR<=1.0):
                    list1.insert(END,' This Pesticide has low Pollution Potential')
                elif (PCTMR>=1.0) and (PCTMR<=15.0):
                    list1.insert(END,' This Pesticide has Medium Pollution
Potential')
                elif (PCTMR>=15.0):
                    list1.insert(END,' This Pesticide has High Pollution
Potential')


                list1.insert(END,' \n')
                list1.insert(END,' \n')
                list1.insert(END,' \n')
                list1.insert(END,' \n')


                list1.insert(END,' \n')
                plt.show()

        if MODEL1== "PESTRANS" :
##              print('TEFFH=',format(TEFFH,".3e"))
##              list1.insert(END,('TEFFH=',format(TEFFH,".3e")))
            list1.insert(END,' \n')
            list1.insert(END,' \n')
```

```
          elif MODEL1== "PESTGRW" :
##               print('CLIQ=',format(CLIQ,".3e"))
##               list1.insert(END,('CLIQ=',format(CLIQ,".3e")))
              list1.insert(END,' \n')
              list1.insert(END,' \n')


but = Button(text="Calculate", command=main)

but.grid(row=26,column=3)

root.mainloop()
```