ESTIMATION OF DIFFUSE POLLUTION LOADS OF PESTICIDES IN TERSAKAN SUB-BASIN OF YEŞİLIRMAK RIVER

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ABSTRACT

ESTIMATION OF DIFFUSE POLLUTION LOADS OF PESTICIDES IN TERSAKAN SUB-BASIN OF YEŞİLIRMAK RIVER

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Tersakan Creek is one of the highly polluted tributaries of Yeşilırmak River because it receives pollution loads both from discharges of the industrial facilities and run-off water of the agricultural areas in the sub-basin. A monitoring program was implemented to determine the water quality status of the sub-basin in accordance with the EU Water Framework Directive (WFD). The results of the water sample analyses revealed that concentrations of 22 pesticides, out of the detected 57 pesticides, exceeded the pre-defined environmental quality standards (EQSs). Some of the pesticides are discharged by industries; however, mass balance calculations showed that their contribution to the pollution was relatively lower. This implied that main contribution to pesticide load to the Tersakan Creek was attributable to diffuse loads from agricultural lands. This study aimed to estimate the agricultural diffuse pollution loads for pesticides exceeding EQSs in the Tersakan Creek, which is simply calculated through multiplying the sediment yield (estimated by a GIS based model, Dynamic Erosion Model and Monitoring System developed by the General Directorate of Combating Desertification and Erosion) by pesticide soil concentration (estimated by a pesticide fate and transport model PESTRANS). Results from a drainage area of the Tersakan Creek showed that suggested and reported application rates of the pesticides such as Cypermethrin, Alpha-cypermetrhin and Dichlorvos contribute to diffuse pollution loads causing the exceedance of EQSs at the Tersakan Creek. Furthermore, additional calculations were also performed to estimate the required maximum pesticide application rate not to exceed EQSs.

Keywords: Pesticides, Sediment yield, Diffuse pollution load, Tersakan Sub-basin, Yeşilırmak River

ÖZ

YEŞİLIRMAK TERSAKAN ALT-HAVZASI’NDA PESTİSİT YAYILI YÜKLERİNİN BELİRLENMESİ

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Yeşilırmak Nehri'nin su kalitesi oldukça kötü durumdaki kollarından biri olan Tersakan Çayı, hem sanayi tesislerinin deşarjlarının yüklerini hem de alt havzadaki tarım alanlarının yayılı kirlilik yüklerini bünyesinde bulundurmaktadır. Bu bağlamda AB Su Çerçeve Direktifi (SÇD) ile uyumlu olarak Tersakan Çayı’nda su kalite izleme programı uygulanmıştır. Su numunesi analiz sonuçları, tespit edilen 57 pestisitten 22’sinin konsantrasyonunun, Yerüstü Su Kalite Yönetmeliğinde yer alan çevresel kalite standartlarını (ÇKS) aştığını göstermiştir. Pestisitlerin bazıları endüstriler tarafından deşarj edilmektedir; ancak, yapılan kütle dengesi hesaplamaları, noktasal kirliliğin toplam kirliliğe olan katkısını ihmal edilebilir boyutta olduğunu göstermiştir. Bu nedenle Tersakan Çayı’ndaki pestisit kirliliği, tarım alanlarından kaynaklanan yayılı yüklere atfedilmiştir. Bu çalışma, Tersakan Çayı’nda ÇKS'yi en az bir defa aşan pestisitlerin, tarımsal alanlardan kaynaklanan yayılı kaynaklı yüklerini tahmin etmeyi amaçlamıştır. Yayılı kaynaklı yükler, basitçe, Çölleşme ile Erozyonla Mücadele Genel Müdürlüğü tarafından geliştirilen GIS tabanlı bir model olan Dinamik Erozyon Modeli ve İzleme Sistemi ile tahmin edilen sediman yükünün, topraktaki pestisit konsantrasyonunun çarpımıyla belirlenmiştir. Topraktaki pestisit konsantrasyonu ise PESTRANS modeli ile önerilen ve rapor edilen pestisit uygulama miktarlarından toprakta artakalan konsantrasyonlar olarak belirlenmiştir. Sonuç olarak Cypermethrin, Alpha-cypermetrhin ve Dichlorvos gibi pestisitlerin önerilen ve raporlanan uygulama oranlarının, Tersakan Çayı'nda ÇKS değerlerinin aşılmasına neden olan yaygın kirlilik yüklerine katkıda bulunduğunu göstermiştir. Çalışmada, ayrıca, ÇKS'lerin aşılmaması için gerekli maksimum pestisit uygulama miktarları da belirlenmiştir.

Anahtar Kelimeler: Pestisitler, Sediman yükü, Yayılı kirlilik yükleri, Tersakan alt-havzası, Yeşilırmak

To my beloved family.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ACTMO: Agricultural Chemical Transport Model

AGNPS: Agricultural Nonpoint Source Pollution Model

a.s.: active subtance

CDE: General Directorate of Combating Desertification and Erosion

CORINE: Coordination of Information on the Environment

CPM: Cornell Pesticide Model

CREAMS: Chemicals, Runoff, and Erosion from Agricultural Management Systems

D: Discharge

DEM: Digital Elevation Model

DEMIS: Dynamic Erosion Model and Monitoring System

DRIPS: Drainage Spraydrift and Runoff Input of Pesticides in Surface Waters

EC: European Commission

EEA: European Environment Agency

EEA: European Environmtent Agency

EFSA: European Food Safety Agency

EQS: Environmental Quality Standards

EU: European Union

FOCUS DG SANTE: Forum for the Co-ordination of pesticide fate models and their use

FSG: Fuller, Schettler and Giddings

GIS: Geographical Information System

GLEAMS: Groundwater Loading Effects of Agricultural Management Systems

GWLF: Generalized Watershed Loading Functions Model

HSPF: Hydrological Simulation Program – Fortran

LOD: Limit of Detection

MoAF: Ministry of Agriculure and Forestry,

MRL: Maximum residue levels

OIZ: Organized Industrial Zone,

PEC: Predicted environmental concentrations

PELMO: Pesticide Leaching Model

PPP: Plant Protection Products

PRZM: Pesticide Root Zone Model

RAIS: Risk Assessment Information System

RB: Receiving Body

RB2: Receiving Body only flow rate measurement,

RBD: River Basin District

RBMP: River Basin Management Plan

RUSLE: Revised Universal Soil Loss Equation

SCS: Soil Conservation Service

STORM: Storage, Treatment, Overflow Runoff Model

SWAT: Soil and Water Assessment Tool

SWMM: Storm Water Management Model

SWRRBWQ: Simulation for Water Resources in Rural Basins–Water Quality Model

TUBITAK: Scientific and Technological Research Council of Turkey

TURKSTAT: Turkey Statistics Institute

TURKTOB: Turkish Seed Union

UK: United Kingdom

EPA: Environmental Protection Agency

USA: United States of America

USDA: US Department of Agriculture

USLE: Universal Soil Loss Equation

WEPP: Water Erosion Prediction Project

WFD: Water framework directive

WWTP: Wastewater Treatment Plant

LIST OF SYMBOLS

SYMBOLS

n_W: Viscosity of water (cp)

$\mathcal{D}_{BA}$: Gas diffusion coefficient (cm^2/s)

$\mathcal{D}_{BW}$: Diffusion coefficient of pesticide in water (cm^2/s),

μ: Biodegradation rate coefficient (day^{-1})

A: Area

a: Sediment delivery coefficient (-)

AppRate: Pesticide application rate (kg/ha)

C: Cover factor (-)

C_{EQS}: Environmental quality standard concentration (µg/L)

C_{est}: Estimated concentration (µg/L)

C_{obs}: Observed concentration (µg/L)

$C_{T,M}$: Soil pesticide concentration (µg/g)

C_T: Yotal concentration of the pesticide in the soil system ($\mu g/cm^3$)

d= Air layer width (cm)

D_E: Effective dispersion coefficient (cm^2/day)

f_{oc}: Organic carbon fraction (-)

f_p: Fraction of rainfall (-)

K: Soil erodibility factor (tons ha hr ha^{-1} MJ^{-1} mm^{-1})

K_H: Dimentionless Henry’s constant

K_{oc}: Organic Carbon Partititon Coefficient (L/kg)

k_r: Relative permeability (-)

K_s: Saturated hydraulic conductivity (hr^{-1})

L= Mixing zone (cm)

LS: Slope-length factor (-) and Slope-steepness factor (-)

L_z: Soil depth (cm)

M_A: Molecular weight of air (mol/g)

M_B: Molecular weight of chemical (mol/g)

M_r: Molecular weight defined by intermolecular collision (mol/g)

n: van Genuchten parameter (water retention model parameter) (-)

PL: Pesticide load (mg/day)

Q: Flow rate (m^3/s)

q_s: Infiltration rate (cm/day)

$R_{\%}$: Remained pesticide mass on soil (%)

R: Rainfall factor (MJ mm ha^{-1} hr^{-1} $year^{-1}$)

S_d: Sediment delivery ratio (-)

SUMM: Remaining mass in soil ($\mu g/cm^2$)

SY: Sediment Yield (ton/year)

T: Temperature (^oK)

t: Time (day)

t_{adv}: Advective transport time (day)

V_A and V_B: Molar volumes for air and the pesticide in question (cm^3/mol)

V_E: Effective transport velocity of pesticide (cm/day)

z: Depth of soil (cm)

γ: Pore size distribution parameter

θ_a: Volumetric air content (cm^3/cm^3)

θ_{rw}: Residual water content (cm^3/cm^3)

θ_{sw}: Saturated water content (cm^3/cm^3)

θ_w: Volumetric water content (cm^3/cm^3)

ρ_b: soil bulk density (g/cm^3)

ρ_s: Particle density (g/cm^3)

ϕ: Porosity (cm^3/cm^3)

CHAPTER 1

INTRODUCTION

Great benefits of pesticides come forward from the utilization of them in forestry, public health and agriculture. Such as the increase in wheat yields in the UK and corn yields in the USA, agricultural production is improved considerably in many countries by preventing weeds, diseases and insect pests that pull down the amount of harvestable product (Aktar, Sengupta, & Chowdhury, 2009).

Even if the handiness of pesticides involves elevation of the economic potential of agriculture, their harm comes into view as health implications for the people and the environment. For example, some human health effects such as hormone disruption, immunity suppression, reproductive abnormalities, and cancer are known to link with the long term and low-dose of exposure of pesticides. For example, Chlorpyrifos pesticide detected commonly in urban streams has caused fish kills near application areas (Aktar, Sengupta, & Chowdhury, 2009).

Pesticides are disturbing the natural characteristics of receiving water bodies and their ecosystem. The main pathway of pesticides resulting in ecological impacts is that water contaminated by the transport of pesticides. It is said that areas (mainly central and north-western Europe) with the dense agricultural production and high population, take part in having water bodies poor ecological standing (Altmayer, 2017).

Point and non-point or diffuse sources are two main components for tracking the pollution in a receiving water body. Point sources are apparent sources where pollutants are discharged. Pollution from point sources such as industry and wastewater treatment plants (WWTP) is reduced considerably through improved effluent controls. On the other hand, diffuse pollution sources are not easy to identify and control, because their origin is not known precisely (Altmayer, 2017).

It is reported that % 33 of groundwaters, 50 % of surface waters and 90 % of river basins in European Union is affected from diffuse pollution sources as at the same time they represent a major problem worldwide. 50 % to 80 % of all water pollution are originated from agriculture as well as soil erosion of soil containing nutrients (Altmayer, 2017).

When pesticides are observed in water resources due to the percolation and surface run-off, their toxicity becomes alarming. Even if certain characteristics are known, pesticide molecules are comprised of several functional groups; partitioning, mobility and reactivity characteristics make them more difficult to predict and estimate upon reaching a water body than that for less complex compounds. Mathematical models that can estimate the fate and transport of the pesticides are beneficial for determination of the exposure concentrations of them to living creatures (Gönenç & Wolfin, 2005). In this context, this study will focus on estimating diffuse pesticide loads originated from agricultural areas in the Tersakan sub-basin of the Yeşilırmak River Basin of Turkey through load function approach.

For further understanding of position of diffuse pollution notion and, scope and aim of the study, in the following parts ‘EU Water Framework Directive, diffuse pollution source management and approach of Turkey’ are summarized. Implications of existing Turkish legislations regarding control of diffuse pollution of surface waters are also presented. The scope and objectives of the TUBITAK Project (No: 115Y013) called Management of Point and Non-Point Source Pollution in the Yeşilırmak River Basin is presented in which this study takes place as an integral part. Finally, scope and aim of the study is presented.

1.1. EU Water Framework Directive, diffuse pollution source management and approach of Turkey

Established in 2000, the Water Framework Directive (WFD) presents a legal framework to protect, manage, assess, and to improve of the quality of surface waters and groundwater bodies across the EU. River basin districts (RBDs) are the building blocks for the implementation of the WFD (EEA, 2018). These districts cover the area of rain and river drainage areas, upstream and downstream of river, small tributaries that feed the main stream, the reach and also groundwater beneath the river basin (Altmayer, 2017). It was previously mentioned that most of the diffuse pollution arise from agricultural areas. Thus, river basin approach is crucial for assessment of diffuse pollution sources.

Since 2014, Turkey, as candidate country to the EU, is developing river basin management plans (RBMPs) in accordance with the WFD necessities and procedures. The management plans of five RBDs are completed out of 25 RBDs that are delineated in the country (SYGM, 2018). Till 2023, it is planned to complete 25 RBMPs (Sahtiyancı, 2014).

In terms of protecting or reaching the goal of surface waters having good quality, concentrations of 45 hazardous substances (which are called priority substances) are limited by environmental quality standards (EQSs). These EQSs, established by the Environmental Quality Standards Directive 2008/105/EC, shelter most susceptible species (EEA, 2018).

In addition to 45 priority substances, 250 specific pollutants were identified by the Ministry of Forestry and Water Affairs of Turkey (currently Ministry of Agriculture and Forestry of Turkey) according to the risk they create for the surface waters bodies of Turkey (Surface Water Quality Regulation, 30.11.2012/28483). While 117 of them are mainly originated from point pollution sources, 113 of them originated from diffuse pollution sources. These specific pollutants such as endocrine disrupters, heavy metals and pesticides and their respective EQSs are provided in the above mentioned regulation. (Orhon, Şıltu, Güçver, & Karaaslan, 2017).

Since compliance with EQSs specified for hazardous substances in Environmental Quality Standards Directive supports the goal of WFD, also EU legislation on pesticides (Regulation (EC) 1107/2009 and Directive 2009/128/EC), Nitrates Directive (96/676/EEC) and Industrial Emissions Directive (Directive 2010/75/EU) promote the good ecological and chemical status of surface waters through managing the chemical substances such as metals, pesticides, and other industrial chemicals. Regulation on Water Protection against Agricultural Nitrate Pollution (dated 23.07.2016/29779), Control of Plant Protection Products (dated 20.05.2011/27939) Wholesale, Retail Sale and Storage of Plant Protection Products (dated 13.02.2019/30685) and Recommendation, Application and Registration of Plant Protection Products (dated 03.12.2014/29194) promote same goals in Turkey. Directive 2009/128/EC on the sustainable use of pesticides is not directly aiming to protect or improve the quality status of surface waters but it is said that the EU Member States must follow the program to reduce the risks and effects of pesticide use on public health, ecosystem and indirectly protect surface waters (Altmayer, 2017).

According to EEA (2018), supplementary measures and holistic view of RBMPs supports to overcome one of the main pressures on surface water quality, being diffuse pollution from agriculture. If the rate of improvement continues, there will be fewer failing water bodies due to the priority pesticides.

In the Regulation on Determination of Vulnerable Water Bodies and Areas Affecting These Bodies and Improving Water Quality, Tersakan Creek and Lake Ladik are included in the vulnerable river water bodies, nitrate vulnerable areas and vulnerable lake water bodies tables with the codes YEN_044, YEN_045, YEN_046 and YEG_028. According to the regulation, good agricultural practices regarding the control of agriculture originated pollution will be implemented in these areas in 2023. Afforestation, erosion and sediment rehabilitation will be implemented in these areas in order to reduce the pollution load by 50%.

As the Member States of EU, a code of good agriculture practices is put into action in Turkey called “Code of Good Agricultural Practices for the Prevention of Nitrate Pollution in Waters from Agricultural Activities” according to Regulation on the Protection of Waters against Nitrate Pollution from Agricultural Sources. The Code mainly focuses on the prevention of nitrate pollution, but guidelines about land management, prevention of surface over-flow and erosion, leaving buffer strips comprised from natural vegetation between the lots may help the retention of pesticides and prevent the transportation of pesticides to surface waters. For example, according to the modeling study of Zhang and Zhang (2011) building vegetated buffer strips and reducing application rates a certain amount reduced the diffuse load of Chlorpyrifos pesticide more than 94%.

Moreover "Application of Plant Protection Products (PPP)" part in the Code is separated for the prevention of misuse of pesticides that threaten the public health, ecosystem, and yield of the agricultural production. It is stated that, with the application of forecasting and warning systems, the economic threshold value should be determined. As a result of monitoring of the abundance and biology of pests and diseases, and plant phenology; PPPs should be applied when necessary. In this way environment, practitioners and consumers will be protected from negative impacts.

Protection of the surface waters should be a priority however if the water body is already contaminated, source and the magnitude of the pollution must be determined before taking the necessary measures to prevent the transportation of pollution further and rehabilitate the contaminated waters. Measuring diffuse water pollution associated with soil erosion or runoff by applying standard point sampling and chemical analysis is very hard often due to seasonality of the pollution. Thus, a better understanding of the origin and the extent of pressures is required by modeling and monitoring at the same time. Remote sensing, bio-assays, impact-based ecological monitoring, non-stop monitoring during rainfalls may be remarkable monitoring approaches to examine diffuse water pollution (Environment Agency, 2014).

1.2. Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project

The Water Framework Directive requires the implementation of the EQSs for the 45 priority pollutants in the EQS Directive (2013/39/EU), the identification of river basin specific pollutants, and their specific EQSs of the Member States, and the meeting of these EQSs in the waters. For that purpose, in 2016, Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project No: 115Y013 has started with the support of TUBITAK. The main goal of this project is building a management strategy that has a holistic approach of point and diffuse pollution in order to ensure the water bodies in the Yeşilırmak River Basin reach the "good status" target in accordance with the WFD. Within this context, an important basis for the preparation of the Yeşilırmak River Basin Management Plan (RBMP) will be created during the WFD adaptation process and significant technical support will be provided to policy-makers, decision-makers and implementing institutions /organizations, especially to Ministry of Forestry and Water Affairs and General Directorate of Water Management (currently Ministry of Agriculture and Forestry). Main focus areas of the project are as follows:

- Identification of point and non-point pollution sources through water quality monitoring of Yeşilırmak River, coastal waters and, industrial and domestic wastewater treatment plants' discharges

- Evaluation of water quality status of receiving water bodies, industrial and domestic WWTPs' discharges and leachate of solid waste storage facilities in terms of conventional parameters and 250+45 specific and priority pollutants

- Prioritization and identification of causal link of pollutants that observed in receiving water bodies and industrial and domestic WWTPs' discharges

- Identification of micropollutants that originated from domestic WWTPs and studies related to biological treatment of pesticides

- Determination of discharge limits based on EQSs in Tersakan Creek

- Estimation of agricultural diffuse pollution loads and proposing a management strategy for such pollution loads

- Ecotoxicological tests for pollutants in sediment/biota to eliminate lack of data for the determination of specific EQSs in the Yeşilırmak River

This study assesses water quality monitoring results, presents a methodology regarding estimation of diffuse pesticide loads, estimates diffuse pesticide loads in Tersakan Sub-basin and suggests strategies regarding controlling agricultural diffuse pollution. Thus it will make a significant contribution to the project and planned Yeşilırmak River Basin Management Plan in terms of determination of EQS based discharge standards, developing control strategies for diffuse pesticide loads and minimization of diffuse pesticide pollution.

1.3. Objective and Scope of the Study

The thesis also shares the core objective with the previously mentioned Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project as being a part of the project. The primary purpose of the study is the identification of diffuse agricultural pollution sources and estimation of their loads, which may create significant pollution in the Tersakan Creek being one of the main tributaries of the Yeşilırmak River. Moreover, the specific objectives of the study are as follows:

- to assess the results of periodic receiving body and discharge water quality monitoring study conducted at the Tersakan Creek,
- to develop an approach for estimation of diffuse pesticide loads
- to check pesticide application rates recommended or reported by the authorities and propose environmentally suitable application rates,
- to suggest control measurements regarding the potential reductions of diffuse pesticide pollution loads.

In order to achieve these objectives, the overall framework and the scope of the study can be summarized as follows. Firstly, a literature survey was conducted to determine an approach for the estimation of diffuse pesticide loads and to review their applications. Models that are used for estimation of diffuse pesticide loads in the U.S.A. and Europe are presented. Moreover, studies regarding pesticide concentrations observed in agricultural soils and diffuse pesticide load estimation applications are presented in Chapter 2.

Secondly, general information regarding Tersakan Sub-basin and its drainage areas and data requirement for estimation of diffuse pesticide loads are gathered in Chapter 3. Using a geographical information system (GIS) based program; mainstream, borders, drainage areas, provinces, and their counties in Tersakan Sub-basin are delineated. Land use details; agricultural areas gathered from CORINE 2012 Land Cover map and TURKSTAT Crop Production Statistics are presented. According to the spatial information gathered and predetermined water quality sampling points in the monitoring study; discharge and receiving body sampling points, and drainage area pairing is presented.

Moreover, available data for estimation of diffuse pesticide load (such as water quality monitoring data, recommended and reported pesticide application rates for different crops, site-specific rainfall data, soil and hydraulic properties and, physicochemical properties of pesticides), methodology of sediment yield and, pesticide fate and transport modeling studies are also presented in Chapter 3 in detail.

Thirdly, in Chapter 4, assessment of results regarding monitoring water quality of receiving water body, and industrial and domestic WWTP discharge sampling points; out of 250 specific and 45 priority pollutants, pesticides that are detected and that exceed corresponding EQSs; relative contributions of point and diffuse source loads into the Tersakan Creek based on upstream and downstream mass balance considerations; sediment yield results of DEMIS model and soil pesticide concentrations obtained using pesticide fate and transport model (PESTRANS) are presented. Also, pesticide application rates determined corresponding to EQS values as an estimate of maximum possible pesticide application rates for drainage areas; comparison of estimated diffuse pesticide loads, and observed pesticide loads and suggested diffuse source control measures for prominent drainage areas are presented in Chapter 4.

Finally, in Chapter 5, conclusions of the study and recommendations for future studies are presented concerning the establishment of minimalized pesticide application rates and methods of controlling diffuse pesticide loads for specific drainage areas of the Tersakan Creek.

CHAPTER 2

LITERATURE REVIEW

Ecosystems are facing with discharges of various chemicals such as solvents, industrial wastes, and pesticides. Thus, the entry of pollutants, their transport, and transformations, the transfer of the chemicals between the water and sediment, and the impacts on organisms worth to be studied in terms of assessment of the risks and the extent of environmental pollution. Mathematical models that can estimate the fate and transport of the chemical compounds are beneficial for determination of the exposure concentrations of chemicals to living creatures. Also, waste load allocations can be performed by models to fulfill water quality standards (Gönenç & Wolfin, 2005).

In this context, a literature survey on previously reported diffuse pesticide load estimation techniques and other studies regarding modeling fate and transport of pesticides in soils is conducted, and results are presented in the following parts.

2.1. Diffuse load estimation models for pesticides

According to FAO (1997), complexity of drainage water management regarding pesticides are increasing due to the increasing cost, decreasing of producing information, decreasing knowledge base, increasing scientific complexity.

Nature of pesticide fate and transport is quite complex since it is affected both from physical and chemical properties of pesticides and the characteristics of the environment or media they are in. Molecular weight, density, solubility in water, vapor pressure, n-octanol-water partition coefficient (K_{ow}), Henry's Law Constant and dissociation constant in water (pKa or pKb); the air-water partition coefficient (K_{aw}), n-octanol-air partition coefficient (K_{oa}) and UV/visible light absorption properties may point out the likely behavior in the environment. Abiotic degradation, biotic degradation, sorption and bioconcentration of pesticides depend on the conditions of the environment. For example, sunlight intensity, pH, hydroxyl radical concentration, microbial community, components of soil, type of organic carbon present in the soil affects hydrolysis and photolysis, aerobic and anaerobic degradation, bioconcentration, sorption and field dissipation. Persistence, potential transport pathways and bioavailability of the pesticides are explained by all of these factors (EPA, 2010).

FAO (1996) (FAO, 1997) states that rainfall and irrigation cause contamination of surface water by pesticides through surface runoff. Sediment formed through rainfall and irrigation may carry certain pesticides to surface waters. Wind also carries pesticides over very long distances and can contaminate surface waters thousands of miles away. For example, it is found that Arctic mammals take in tropical/ subtropical pesticides.

Many watershed management plans are developed based on a crucial component, pollutant load estimation. A mass balance analysis which is a quantitative estimation of sources and sinks of the related pollutants would determine the connection between an identified water quality problem and the sources of the pollution (US EPA, 2003-a).

There are several types of models that estimate pollutant loads through modeling. They can be sorted into various classes. According to US EPA (1997), these are watershed-scale loading models, field-scale loading models, receiving water models and integrated modeling systems.

Watershed-scale loading models rely on mainly predicting the transport of pollutants from land surface to receiving water bodies. They can be categorized into three main groups: simple methods, mid-range models and detailed models as presented in Figure 2.1. Simple loading rate assessment primarily based on land use type only. Empirical relationships between physiographic characteristics of the watershed and the pollutant transport are typically the basis of these models. They are practiced through a spreadsheet or hand-held calculator. However, they estimate pollution loads roughly and they have a very limited predictive capacity (US EPA, 2003-a). According to US EPA (2003-a), models such as EPA Screening, SLOSS-PHOSPH, and Watershed are few examples in this context.

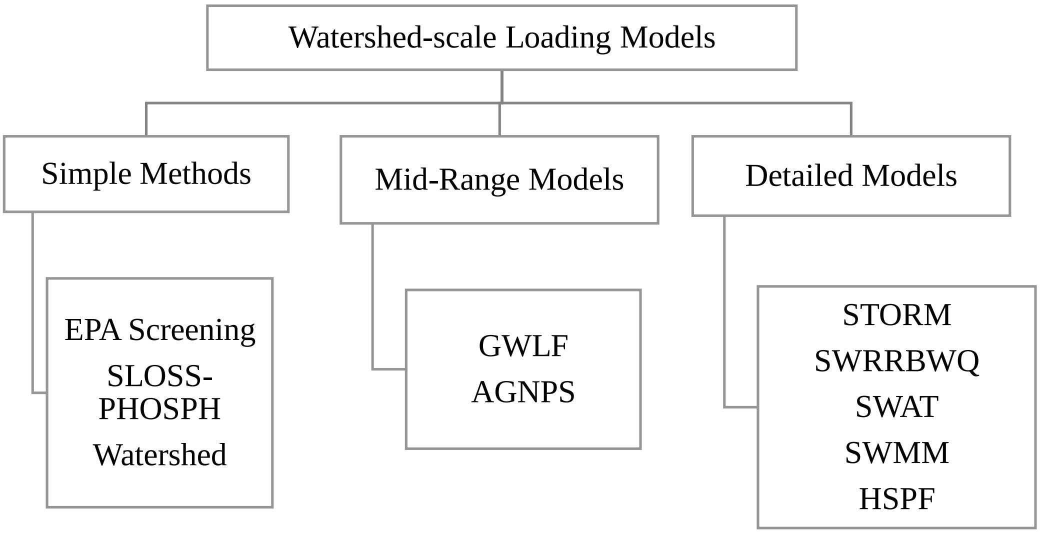

Figure 2.1. Watershed-scale loading models *(US EPA, 1997)*.

Pollutant loads from a point and non-point sources are included within EPA Screening Procedures (McElroy, 1976). This model is based on Universal Soil Loss Equation (USLE), loading functions and simple empirical expressions in terms of transport of pollutants. They are not coded into a computer program, but the loading function concept to estimate pollutant loadings have been adapted to several computer-based models. This model can work on a wide variety of pollutants such as phosphorus, nitrogen, pesticide, salinity and heavy metal loadings (US EPA, 1997).

Two simplified loading algorithms are used in Simplified Pollutant Yield Approach (SLOSS-PHOSPH) for evaluation of soil erosion (USLE), sedimentation and phosphorus transport. Few applications limited the evaluation of non-point pollution to only phosphorus loading. In case of the availability of input data and default parameters, the model can be simulated for other pollutants. Moreover, full-scale GIS capability and trained personnel are required for this approach (US EPA, 1997).

In order to summarize watershed characteristics and predict pollutant loadings, a course of worksheets is used by Watershed loading model. It is developed to estimate phosphorus loadings, but due to its simplicity, various pollutant cases can apply this model with readily obtainable values. Only pollutants associated with soils and sediments can be simulated with this model. The USLE is the basis of the model for rural cropland loads. Eroded sediment is converted to sediment delivered by delivery ratios (US EPA, 1997).

Mid-range watershed models are midway between the empiricism of simple methods and sophistication of detailed models. They are generally used for the identification of lands to apply pollution mitigation measures and compare alternative of management practices. Long term water quality trends and storm-driven loads can be assessed using midrange models. However, their accuracy of estimates is limited due to simplification of assumptions, general exclusion of degradation and transformation processes and most management practices (US EPA, 2003-a). Generalized Watershed Loading Functions (GWLF) Model and Agricultural Nonpoint Source Pollution Model (AGNPS) are two examples of midrange models.

The point and non-point loadings of nitrogen and phosphorus from urban and agricultural watersheds and the efficacy of some land use management practices are assessed by the GWLF model. Total and dissolved nitrogen and phosphorus loadings and rainfall/runoff, erosion (using USLE), and sediment production are the components of the model. The delivery ratio is the basis for the transport of pollutants. Default parameters are one of the advantages of simulation of this model without any necessity of calibration. However, peak fluxes are underestimated, and loadings of pesticides are not simulated in the current version of the GWLF (US EPA, 1997).

The USDA Agricultural Research Service has developed the AGNPS model which predicts pollution loads from agricultural lands and examines the utility of pollution management practices. Surface runoff having nutrient and sediment constituents related to agricultural practices (such as pesticides) are simulated event-based or continuously based on a grid system by this model. Moreover, it simulates cropping systems, fertilizer application rates and the effect of terraced fields. Sediment yield is predicted by the USLE. Connection to Geographical Information Systems (GIS) and digital elevation models (DEM), and thus input parameter developments are enabled due to this grid system (US EPA, 1997).

Identification of pollution problems, estimation of loads and their impact on receiving water bodies, and simulation of infiltration, runoff and instream effects are few features of the detailed models. Event-based or continuous simulations are enabled in order to estimate pollutant loadings for a range of flow conditions in the detailed models. Accurate predictions, high spatial and temporal resolutions, new interfaces are good sides of the detailed models, however, they require a considerable amount of time, expenditure, and data collection (US EPA, 2003-a). Thus mainly they are used for research purposes rather than decision making. Storage, Treatment, Overflow Runoff Model (STORM), Simulation for Water Resources in Rural Basins – Water Quality (SWRRBWQ) model/ Soil and Water Assessment Tool (SWAT), Storm Water Management Model (SWMM) and the Hydrological Simulation Program – Fortran (HSPF) are examples of the detailed loading models (US EPA, 1997).

US Army Corps of Engineers designed the STORM mainly for stormwater runoff from urban areas and evaluation of treatment and control options of combined sewer overflows. Rainfall and runoff assessment, water quality analysis and statistical and sensitivity analysis are the main components of the model. Runoff and erosion are simulated by the SCS (Soil Conservation Service) curve number equation and the USLE respectively. However model works on six prespecified pollutants; pesticides are not included (US EPA, 1997).

USDA adopted the field scale CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) model into the SWRRBWQ model which simulates sediment, nutrient, pesticide, and hydrologic movement in complex and large basins. Surface runoff, sedimentation, irrigation return flow, percolation, evapotranspiration, and other processes such as crop growth are included in this model to evaluate pesticide loadings. Modified SCS curve number method and Hydrogeomorphic USLE (HUSLE) are used for estimation of surface runoff and sediment yield respectively. Soil, land use, daily precipitation, and pesticide application are some of the input data requirements. However, the degradation of nutrients and pesticides during transportation is not considered in this model. Experienced personnel and high amount of data are required for precise simulations. This model is incorporated into the SWAT model (US EPA, 1997).

SWMM cover stormwater pollution, analyze storm events and derive design criteria for structural control of stormwater pollution in continued simulation for various land uses (mainly urban) and complex watersheds. Runoff and sedimentation are simulated using nonlinear reservoir approach and the USLE respectively (US EPA, 1997).

The HSPF model can simulate the quantity and quality of water in terms of pesticides from complex watersheds. Continuous simulations are used to simulate water balance and pesticide generation, transformation and transport. Moreover, the determination and quantification of pollution contributions from the point and diffuse pollution sources and related management techniques can be evaluated. Transfer and reaction processes are comprised of hydrolysis, photolysis, oxidation, biodegradation, volatilization, and sorption (first-order kinetics). The model can simulate sand, silt and clay and an organic chemical and its metabolites. The application of the model requires calibration. Thus it requires an extensive amount of data and highly trained personnel (US EPA, 1997).

Field-scale models consider relatively smaller and homogenous areas than watershed-scale loading models for basin-wise implementation of recommended management practices to reduce non-point pollution loads. The effects of various management scenarios are studied in the context of the movement of water and pollutants within and from a small catchment. According to US EPA (1997), Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS)/Groundwater Loading Effects of Agricultural Management Systems (GLEAMS), Opus and the Water Erosion Prediction Project (WEPP) models are few examples.

CREAMS is a continuous simulation model where separate erosion, hydrology, and chemistry sub-models are used. The SCS curve number and the USLE is used for runoff and erosion component respectively. The model partitions pesticides in runoff between the solution and sediment phases using an isotherm model. This model is replaced by GLEAMS model (US EPA, 1997). Similarly, the movement of pesticides and nutrients and sediment from various combinations of land uses and management is predicted by GLEAMS. Irrigation, drainage, tillage, crop planting date, crop rotation, residue, commercial nitrogen, and phosphorus applications and pesticides on pollutant movement changes are assessed through this model (US EPA, 2003-b).

Opus model performs to achieve similar objectives by take into account management options such as the use of impoundments, grass buffer strips and terracing, and the type and direction of tillage. WEPP model can estimate runoff, erosion, sediment delivery, sediment enrichment and spatial distribution of erosion storm-by-storm, monthly, annual, or average annual basis (US EPA, 1997).

Moreover, it is stated that the ACTMO (Agricultural Chemical Transport Model) CPM (Cornell Pesticide Model) can predict runoff losses of soil and pesticides from field- to watershed-sized areas (Larson, Capel, & Majewski, 1998).

Developed in Belgium, the SEPTWA model estimated the average pesticide loads leaving the catchment by taking into account detailed application information and loss pathways of pesticides into surface waters (Holvoeta et.al. (2007).

European Hydrological System (MIKE SHE) is a computationally comprehensive model simulating hydrology and diffuse pollution of pesticides for small catchments and watersheds. Multi-dimensional flow-governing equations with numerical solution schemes lay behind the core of the model (Holvoeta et.al. (2007).

According to Wang et. al. (2019), 11 watershed models are compared such as the Annualized Agricultural Non-Point Source (AnnAGNPS), HSPF, MIKE SHE, and SWAT. Hydrology, sediment, and chemical components are applicable to watersheds through models AnnAGNPS, HSPF, MIKE SHE, and SWAT. It is concluded that MIKE SHE model is not suitable for large watersheds due to its complexity. HSPF model is considered more fitting for mixed urban and agricultural watersheds. SWAT model is favorable to work on intensively farmed watersheds. It is presented that in another study; SWAT is recognized as the best-fitted model for assessing the effectiveness of best management practices on reducing concentrations of pesticides in surrounding environment in watershed scale.

An overview of the leaching, erosion and hydrological transport and fate models for pesticides are presented by Schulz and Matthies (2007) in their study. ANSWERS, KINEROS, EUROSEM, EROSION 2D and 3D and WEPP are examples of erosion models. Erosion models which are based on USLE, are contemporarily moved to event-oriented approaches of surface erosion and particle load. According to Schulz and Matthies (2007), subsurface flow and attenuation and partitioning of soluble pesticide transport are neglected by these models. Besides surface runoff, these deficits are filled with dynamic hydrological models; merely most of them are not focused to simulate the transport of pesticides exclusively.

Namely, InHM, MOD-HMS, and HydroGeoSphere models are fully coupled, numerical watershed models. These new-generation models solve flow and transport in surface and subsurface hydrologic components simultaneously in one system of non-linear discrete equations (Holvoeta et.al. (2007).

FOCUS DG SANTE stands for FOrum for the Co-ordination of pesticide fate models and their USe and is an initiative of the European Commission to create common ground in assessments of predicted environmental concentrations (PEC) of active substances of plant protection products (PPP) in the framework of the EU Directive 91/414/EEC, which meanwhile has been repealed and replaced by the new Regulation (EU) No 1107/2009 concerning the placing of plant protection products on the market (ESDAC, 2017).

FOCUS has defined 125 realistic worst-case groundwater scenarios (based on nine standard combinations of weather, soil and cropping data with 12 to 16 crops each) and 10 representative EU scenarios (based on different climatic conditions, soil properties and water bodies such as rivers or ditches) for surface water to collectively represent agriculture in the EU, leaching potential and transportation of active substances and metabolites to groundwater and surface waters. Standard scenarios are valuable because they increase the consistency of the regulatory evaluation process by minimizing the subjective influence of the person who performs the calculation. They also make interpretation much easier, and enable the adoption of a consistent scientific process for evaluation of the pollution potential at the EU level. Scenarios have been implemented as sets of input files for MACRO, PEARL, PELMO & PRZM models for groundwater and MACRO, PRZM, and TOXSWA models for surface water. These models do not estimate diffuse loads originated from sediments (ESDAC, 2017).

TOXSWA model is advised to estimate predicted environmental concentrations (PEC) by FOCUS work group. Resuspension, sedimentation and biomass growth is neglected by the model. Outputs of PRZM (runoff and erosion) and MACRO (drainage) are required by this model (Holvoeta et.al. (2007).

Röpke et. al. (2004) developed Drainage Spraydrift and Runoff Input of Pesticides in Surface Waters (DRIPS) model which is a GIS-based decision support system. The model estimates total diffuse source inputs (only runoff, tile drainage and spray drift) in a catchment or watershed representing predicted environmental concentration (PEC_{sw}). These transport pathways of pesticides are executed in independent components of the model modules. They adopted the US SCS curve number method, PELMO (Pesticide Leaching Model) and drift tables presented by Federal Biological Research Center for Agriculture and Forestry (BBA) to estimate the runoff volume, quantity of pesticides that leached through soil and the fraction of a substance that transported by spray drift.

According to Young (2019), three principal components form Pesticide in Water Calculator (PWC), which are field model, water body model, and user interface. Significant components for pesticide transport such as weather patterns, soil properties, field hydrology, crop growth, and pesticide fate are considered by the field model. Hydrological runoff, erosion and pesticide application is simulated by The Pesticide Root Zone Model (PRZM5) which estimates runoff using National Resources Conservation Service (NRCS) curve number (CN) method and erosion using the Modified USLE for Small Watersheds (MUSS). The output data gathered from the field model such as runoff, eroded soil and water and soil phase pesticide mass is used as input data by the water body model. In the end, surface water concentrations of pesticides are produced by the water body component which is Variable Volume Waterbody Model (VVWM). The PWC is capable to estimate diffuse pollution loads specific to location, and precisely as research models, but results represent regulatory risk assessment values estimated using predetermined scenarios.

In conclusion, soil weathering and erosion processes leads the transport of pesticides from land to stream and water bodies since these chemicals may strongly associate with sediment and especially with organic carbon that is part of the soil (Neitsch, Arnold, Kiniry, & Williams, 2009) (FAO, 1996). Erosion and sediment-associated pesticide runoff, and water quality impacts of pesticides are predicted by various methods and tools which also reveal land management practices, site-specific control options and generic approaches for pesticide control (FAO, 1996). Rather simple empirical relationship Universal Soil Loss Equation (USLE) is widely used for the prediction of erosion and sediment yields has been incorporated into many complex most worked on models such as SWAT, CREAMS, AGNPS and EPIC has had remarkable success (FAO, 1996) (Alewell, Borelli, Meusburger, & Panagos, 2019). For example, it is stated that SWAT 2009 model uses modified version of the loading function developed by McElroy et al. (1976) in order to estimate the amount of pesticide transport with sediment to stream (Neitsch, Arnold, Kiniry, & Williams, 2009). These models are highly sophisticated, including many specific processes such as detailed descriptions of infiltration and evapotranspiration, rainfall, erosion, tillage, loading, transport, and management practices. Having the best extent in terms of fate modeling, these models require a considerable amount of data, financial resources, competence and time. Thus, according to best available data that is gathered in a sense simpler PESTRANS pesticide fate and transport model (Ünlü et al., 1995) and pesticide loading functions (McElroy, 1976) are used for diffuse pesticide load estimations. Either enough competence or easiness of gathering required data, PESTRANS and loading functions will give considerable insight regarding concentrations of pesticides remaining in the soil after application and probable diffuse loads. Structure of PESTRANS and loading functions are presented in Chapters 3.5 and 3.6 respectively.

2.2. Studies related to soil pesticide concentrations and diffuse pesticide loads

In this section featured studies regarding pesticide concentrations observed in agricultural soils and diffuse pesticide load estimation approaches are presented. In terms of diffuse pollution of rivers, pathways that pollutants are lost from originated areas should be determined. Holvoeta et.al. (2007) presented an overview regarding pathways of pesticides that end in surface waters and available watershed and in-river water quality models which are used to estimate pesticide levels in surface waters. Pesticides are transported in the water phase and solid phase, sorbed to sediment particles during a runoff event. Soil particles are detached due to the abrasive power of raindrops and surface runoff and thus create soil erosion. Organic carbon content and texture of the soil affects the partitioning of pesticides between these water and soil phases. It is noted that if the silt fraction of soil texture is high, the soil tends to erode more easily. Besides abrasive power of runoff and erodibility of soil; size and shape of the contributing area, the steepness, land use, and buffer zones affect the sediment delivery in the direction of surface waters.

Loss of parent active substances from the aquatic environment through biodegradation and abiotic degradation can be affected by the sorption of pesticides to suspended solids and sediment organic carbon. Several studies indicate that the decay of pesticides is hindered due to adsorption and persistency, however in some cases decay of pesticides is accelerated by sorption due to abiotic degradation pathways. Moreover, high temporal concentrations of pesticides in small rivers and agricultural ditches can be caused by the preferential flow in soil macrospores to the drains. A relatively fast initial release and a subsequent longer and slower release are two phases of the process of desorption of pesticides from sediment particles (Holvoeta et.al. (2007).

According to Holvoeta et.al. (2007), runoff volume is mostly higher than the amount of eroded soil. Thus transport of soluble pesticides is governed predominantly by surface runoff rather than transport with soil erosion. Pesticides with an organic carbon partition coefficient (K_{oc}) higher than 1000 L/kg are transported mainly by soil erosion since they are adsorbed strongly to the soil particles. Application rate and the period of time between application and the first rainfall event and the concentration of pesticide in the topsoil are very important parameters in terms of the determination of the load of pesticides transported to the rivers.

According to Novotny (1999) Elementary carriers of organic toxic compounds are sediments, particularly their fine fractions. For example, suspended sediments readily adsorb pesticides with persistent organochlorine structured ones.

Silva et. al. (2019) analyzed a total of 76 pesticide residues (active substances and metabolites) in 317 European agricultural 0-15/20 cm of topsoil samples gathered during the period April to October. 43 of these pesticide residues (%57) are detected in soil samples using LC-MS/MS and GC-HRMS methods. In most of the soil samples, more than one pesticide residues are quantified. While maximum total soil pesticide concentration was found 2.87 mg/kg, maximum individual soil pesticide concentration was found 2.05 mg/kg. Chlorpyrifos and Fenpropimorph active substances which exceed EQS at least one time in the Tersakan Creek were detected in soil samples of this study. In these samples while Chlorpyrifos has a soil concentration of 0.03 mg/kg median and 0.11 mg/kg maximum; Fenpropimorph has a soil concentration of 0.02 mg/kg median and 0.09 mg/kg maximum. According to Silva et. al. (2019), uppermost 1 cm of the soil surface layer should be focused in future assessments of field monitoring programs and predicted environmental concentration (PEC) calculations, since pesticide residues often accumulate on the soil surface. Also, the representativeness of measured pesticide data results of a single sampling time should be addressed. In future assessments, in order to provide a better indication of background values of currently used pesticides; sampling should be before the first pesticide applications. It is stated that conclusions related to the diversity of agricultural products and pesticide usage in the different EU regions and the occurrence and measured residue concentrations in soil cannot be drawn due to the lack of information on the pesticide application and the change by country/region. Moreover, it is claimed that underestimations of the potential transport of remaining pesticides to the receiving water bodies by water and wind erosion processes can be encountered due to underestimations of soil surface pesticide concentrations.

Markovic et. al. (2010) assessed the residues of pesticides in soil, vegetable and fruits samples collected from July to November of 2006 from an agricultural area of Belgrade, Serbia. Solid-phase microextraction technique and gas chromatography-mass spectrometry are used for analyzing pesticide residues. Chlorpyrifos and Fenitrothion active substances were the only insecticides that were detected in soil samples. Chlorpyrifos active substance is also exceeded the EQS at least once in Tersakan Creek water quality monitoring study. Soil concentrations of Chlorpyrifos were found out to be 26.6 μg/kg, 36.6 μg/kg and 47.4 μg/kg in three different soil samples out of 24 samples, where 1.2 μg/kg is limit of detection (LOD) of Chlorpyrifos. Another active substance Chlorothalonil which is also exceeded the EQS in Tersakan Creek water quality monitoring study were investigated in these soil samples but soil concentrations in all of them were below detection limit (LOD=2.4 μg/kg). Residue levels of Chlorpyrifos and Cypermethrin (also exceeded EQS in Tersakan Creek water quality monitoring study) active substances in vegetable samples were found out to be several times higher than MRLs (Maximum Residue Levels). It is claimed that the reason behind this contamination is the inappropriate use of plant protection products.

Huber et al. (2000) developed a model estimating the loss of 42 pesticides through runoff, spray drift and subsurface drains, which represent non-point source paths. It is stated that bulk of active substances are transported in the water phase since very small fraction of runoff following highly erosive rainfall formed by sediments. SCS curve number method is used for runoff volume. The approach of GLEAMS model is used for transfer of active substances to surface runoff. Pesticide leaching is simulated using PELMO (Pesticide Leaching Model) for different rainfall situations and properties of soils, physicochemical properties of active ingredients, crops and application days. The spatial resolution of the model is enhanced using the market survey among farmers on the application of active ingredients, 1993/1994 CORINE Land Cover data and the community level agricultural census. It is presented that dominant non-point source pathway is surface runoff. Estimated non-point source load are matching a sufficient degree of accordance with the monitoring results gathered from different studies: At 47 of the 64 data points, modeled results are within a range of %10-%1000 of monitored results. Still, it is mentioned that, since each pathway of non-point source pollution is not considered, validation of prediction accuracy is not possible. They also attributed most of the pollution in surface waters to point sources (Bach, Huber, & Frede, 2001). Thus at particular catchments, non-point loads are underestimated. It is stated that generalization of spatial input data in small catchments and complex nature of pesticide loss to surface water are likely to distort model results. Therefore, comparative aspects such as relative impact of regions, field crops or periods of use to the total losses are discussed in terms of results of the model.

In the report of Williams et al. (1999), pesticide concentrations arise in soil and water as a result of usage of total 19 herbicides, fungicides, and insecticides on arable crops at the Rosemaund farm is studied. More than 99% of applied pesticides remained and degraded in soil. By-pass flow to the field drains, overland flow, and seepage were the dominant pathways for pesticide loss from soil to surface waters. According to water quality monitoring results of field drains and stream, pesticide translocation occurred after critical rainfall events (24 hours), and detected high concentrations fall below the LOD within about 12-24 hours. It is stated that even if Chlorpyrifos and Fenpropimorph active substances (which also exceeded EQS according to Tersakan Creek water quality monitoring results) adsorbed strongly to soil (high K_{oc}), they are found in the stream. Thus, hydrological regime in the soil is the prominent factor for transportation of the fine mobile soil particles where pesticides adsorbed to rather than solution; meaning that bulk of the pesticide transport occurs through translocation of fine soil particles. Chlorpyrifos is applied with a rate of 0.72 kg/ha. In the end of 18-38 days of lag (time between application date and rainfall event), 0.012-0.056 g Chlorpyrifos mass is obtained that passes the sampling point. Concentrations of Chlorpyrifos were changing between 0.05 and 4.29 μg/l. Similarly, Fenpropimorph is applied with a rate of 0.75 kg/ha. At the end of 18-20 days of lag, 0.004-0.027 g Fenpropimorph mass has obtained that pass the sampling point. Concentrations of Fenpropimorph were changing between 0.66 and 1.58 μg/l. Small mass loses may seem insignificant, but they reveal the translocation of pesticides in a short amount of time-independent from good agricultural practices. Moreover, SoilFug and a model of Institute of Hydrology (IH) are used for the prediction of concentrations in the stream; while SoilFug overpredicted the concentrations, log of the accuracy ratio of the latter model was mostly between -1 and 1: close to perfect fit.

Dong et. al. (2017) modified the export coefficient model to assess the change in agricultural non-point source pollution loads after cropping pattern alteration. It is stated that modified export coefficient model is suitable where information regarding estimation of diffuse pollution loads is lacking. Export coefficients are gathered from literature search: 25%, 3-5% and 10% of application rate of pesticides, in particular, are lost due to drift and volatilization, soil evaporation and plant evaporation, respectively. Thus export coefficient for pesticides is accepted as 40%.

HSPF model is used by Laroche et al. (1996) to simulate Atrazine active substance transport for a 78 ha watershed and calibrated by water quality monitoring extended from February to November 1993. As previously mentioned, surface runoff, sediment, nutrient, and pesticide transport can be simulated by HSPF. Translocation of pesticides is carried out with degradation, adsorption/desorption, and transport. It is stated that while non-optimized model yielded underestimated Atrazine concentrations, optimized values were much closer to the observation concentrations. In terms of exported loads from watershed, optimized results were overestimated, but still they were very close to observed ones. However, it is stated that slight improvement is observed in results with optimization, thus the model can be used with minimal calibration. They simulated diffuse loads with different application rates and determined lowest application rate was safe for aquatic life, while higher ones reveal aquatic life could be affected since exposure days are longer.

Donoso et al. (1999) simulated nitrate and pesticide diffuse loads originated from dairy and breeding farms in Chile using the model EPIC. Erosion, loss of productivity, nutrients, and pesticides that pollute water can be simulated by 5 possible equations that EPIC has to estimate erosion. While lowest soil loss is predicted by MUSS and highest soil loss is predicted by USLE out of these 5 methodologies. Fate of three PPPs estimated using USLE and MUSS revealed that pesticides are mostly degraded in soil or lost in runoff. Pesticides in sediments were between 0-1.4% of the application rate for USLE. It is stated that losses are compared with maximum allowed emission concentration and it is found that pesticide losses estimated by MUSS and USLE did not exceed the levels is attributed partly to the hydrological deficit in characterization of the area.

Previously mentioned studies are carried out using sophisticated models requiring extensive input data requirement which may be difficult to meet most often. In this study, PESTRANS pesticide fate and transport model is used for estimation of remaining pesticide concentration in the soil after a time of its application and pesticide loading functions is used for diffuse pesticide load estimations which are based on sediment yield (RUSLE) (Ünlü et al., 1995; McElroy, 1976). Many other detailed models use fate models and RUSLE as a basis for pesticide transport to surface waters. It is believed that this methodology will support the assessment of best management techniques for reduction of pollution in Tersakan Sub-basin in a practical way due to deficiency in input data regarding characterization of areas. Detailed content regarding the structure of PESTRANS and loading functions are presented in Chapter 3.5 and 3.6, respectively.

CHAPTER 3

MATERIAL AND METHODS

In this chapter, data requirements and a methodology for estimation of diffuse pesticide load were presented as presented in Figure 3.1. Firstly, details of the study area and water quality monitoring study carried out within the scope of Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project are presented. In terms of details of the study area, after the delineation of Tersakan Sub-basin area; CORINE 2012 Land Cover and TURKSTAT agricultural areas, reported and suggested pesticide application rates, rainfall and soil properties of Tersakan Sub-basin are compiled. Water quality monitoring results revealed the most polluted sampling points and pesticides that exceed EQS in these sampling points. Physicochemical properties of pesticides that exceed EQSs are gathered.

Finally, methodology regarding estimation of diffuse pesticide load of Tersakan Sub-basin and recommended pesticide application rates to comply with EQS is presented using sediment yield model and PESTRANS fate and transport model. The results and their discussion are presented in Chapter 4.

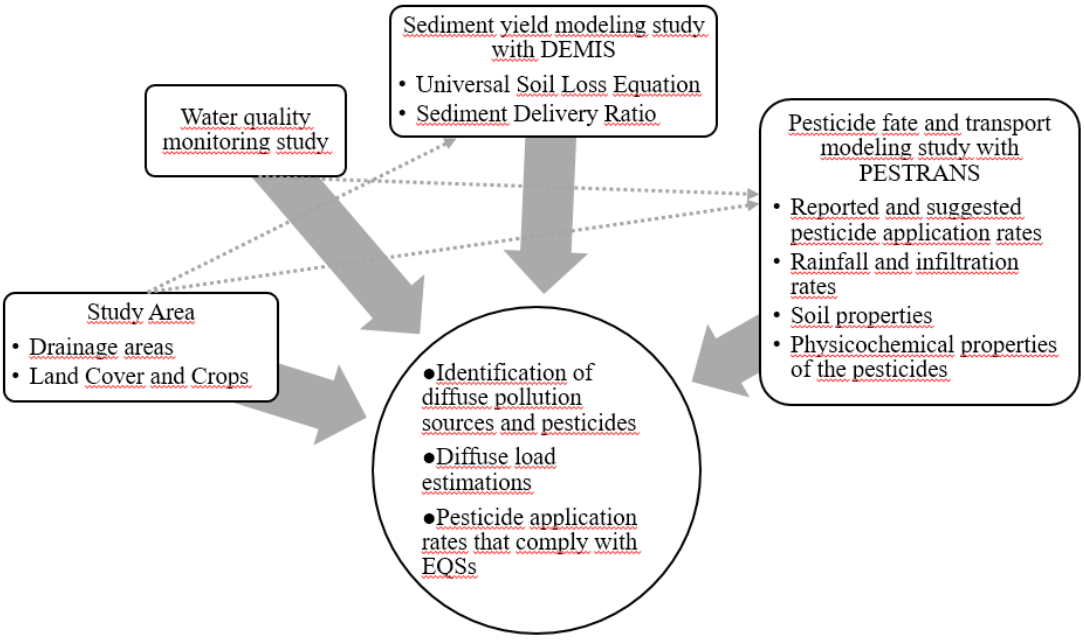

Figure 3.1. Components of identification of diffuse pollution sources and pesticides; diffuse load estimations and pesticide application rates that comply with EQSs

3.1. Description of the study area

Yeşilırmak Basin covers the area that discharges its waters to the Black Sea via Yeşilırmak River in the northern part of Anatolia. Yeşilırmak River, which flows westward from the Köse Mountains where it was born, makes a wide delta through the Çarşamba Plain and flows into the sea through Cape Çatlı. The basin area is approximately 3.87 million hectares which are 5% of Turkey's area. A total of 11 provinces including Amasya, Çorum, Gümüşhane, Tokat, Samsun, Sivas, Yozgat, Giresun, Erzincan, Ordu, and Bayburt are within the borders of Yeşilırmak Basin as presented in Figure 3.2 (TÜBİTAK MAM, 2010).

Figure 3.2. Yeşilırmak River Basin, Tersakan Sub-basin and provinces

Tersakan Creek is one of the important branches of Yeşilırmak River. It originates from Akdağ at an altitude of 1,925 m at the east of the Ladik County of Samsun. It draws an arc opposite to Yeşilırmak, taking the excess water of Lake Ladik, it merges with Yeşilırmak in Amasya. Lake Ladik is located in the east of Ladik County of Samsun within the Tersakan Sub-basin. In 1933, a regular flow of lake water was enabled by building a regulator at the starting point of the Tersakan River. The regulator was renewed in 1986, and Ladik Lake was turned into a reservoir for irrigation purposes (TÜBİTAK MAM, 2010). Şeyhsuyu, Gümüşsuyu, Derinöz, and Salhan brooks are important branches of Tersakan Creek (Amasya KTB, 2018).

Tersakan Basin falls within the boundaries of three provinces, Amasya, Çorum, and Samsun and their 10 counties as presented in Table 3.1.

Table 3.1. *Provinces and their counties fall within the borders of Tersakan Sub-basin*

Amasya	**Çorum**	**Samsun**
Hamamözü	Mecitözü	Havza
Gümüşhacıköy	Merkez	Ladik
Merkez		Kavak
Merzifon		
Suluova		

There are industries in Tersakan Sub-basin, which may be significant pollutant sources. Wastes from different sized livestock barns are used randomly in agricultural areas in Amasya, Suluova County, and its surroundings. The excess portion of these wastes is discharged to the Tersakan Creek (TÜBİTAK MAM, 2010). Moreover, as presented in Table 3.2, Amasya Sugar Factory, Bakraç Dairy Industry, Meray Oil Industry is some of the industries that discharge their treated wastewaters to Tersakan Creek.

Table 3.2. *Industries, Municipal WWTPs and Organized Industrial Zones in Tersakan Sub-basin*

Sampling Station	Name of the Discharge Point
Y-58	Merzifon OIZ (Amasya/Merzifon)
Y-65	Meray Oil Industry (Amasya/Merzifon)
Y-77	ET-BIR Meat Industry (Suluova - Merkez)
Y-78	Kozlu Food (Suluova - Merkez)
Y-79	Bakrac Dairy Industry (Amasya/Merkez)
Y-108	Havza WWTP

Urban land, forestry, atmospheric deposition, and rural dwellings can be significant sources but agriculture is a key source of diffuse pollution. Careful analysis is required for the management of diffuse pollution since by nature it is very complex (EEA, 2018). Thus, as a first step, agricultural areas of Tersakan Sub-basin are delineated for the estimation of diffuse pollution.

A large part, 59% of the Tersakan Sub-basin is composed of agricultural land according to CORINE 2012 Land Use map (MoAF, 2017). As presented in Figure 3.3, Suluova, Gümüşhacıköy and Merzifon counties of province Amasya are comprised of 69%, 54%, and 68% agricultural areas, respectively. Havza County of province Samsun is comprised of 65% agricultural areas. Monitoring results (Chapter 4.1) and the fact that the agricultural land use is dominant in the Tersakan sub-basin reveal the pressure of diffuse pollution by agricultural areas. The remaining areas are mostly forests and semi-natural areas. Additionally, distributions of the areas of other counties are presented Appendix A in detail.

It is reported that Tersakan Creek is mainly used for irrigation purposes. Since almost all of the water is used as irrigation water in the Tersakan Creek, it becomes completely dry especially in dry years (TÜBİTAK MAM, 2010). In the irrigated areas, the water is drained, and the drained water is given to open drainage channels and then back to Tersakan Creek (Amasya ÇDR, 2018). Thus agricultural areas of Tersakan Sub-basin and their management require special attention.

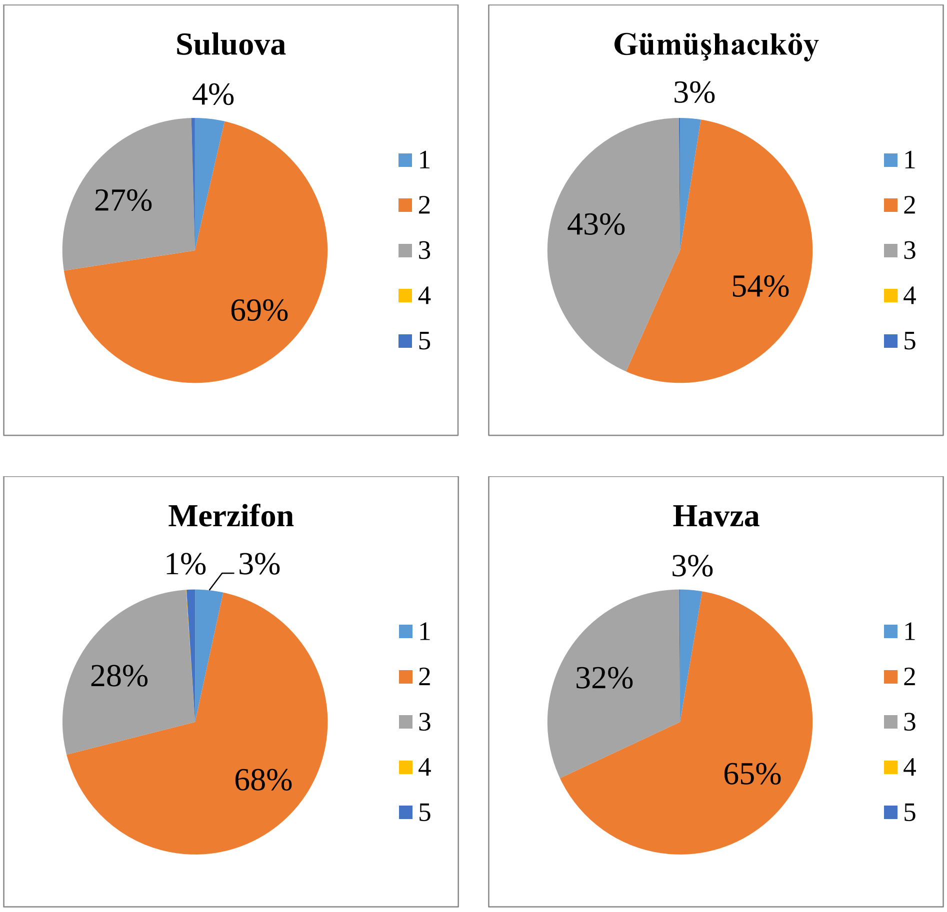

Figure 3.3. Composition of areas of counties Suluova, Gümüşhacıköy and Merzifon in province Amasya and county Havza of province Samsun according to CORINE 2012 Land Use (Here 1 represents Artificial Surfaces; 2, Agricultural Areas; 3, Forests and Seminatural Areas; 4, Wetlands, and 5 represents Water Bodies)

3.2. Delineation of the drainage areas of Tersakan Sub-basin

A drainage area is a land area that precipitation is drained by an outlet, such as creeks, streams, rivers, lakes, and reservoirs. Smaller drainage basins are gathered to form larger drainage basins called watersheds (USGS, 2018). For example, Yeşilırmak Basin comprised of many smaller drainage basins; one of them being Tersakan Sub-basin drains its water through Tersakan Creek to the Yeşilırmak River.

Drainage areas are important since, through runoff and sediment load, they carry the matter on soil such as the nutrients and inorganics as well as pesticides to other drainage areas and receiving water bodies. Therefore, delineation of drainage areas is significant as they are areal units of diffuse transport of pollution.

Borders and drainage areas of Tersakan Sub-basin are demarcated, and the network of Tersakan Creek is shaped using 10m x 10m Digital Elevation Model (DEM) through spatial analyst tools of a Geographic Information System (GIS). Micro drainage areas are merged in order to link with predetermined receiving body sampling points for water quality monitoring study. In the end 16 drainage areas coded with ‘YB’ are determined as presented in Figure 3.4. In the map triangles represent receiving body, and the circles represent discharge sampling points.

Counties within the Tersakan Sub-basin are determined by superimposing both drainage area border map and county map. County information is required for gathering data regarding agricultural products and pesticide application rates. Figure 3.5 and Table 3.3 are formed to clarify the drainage areas, discharge sampling points, paired receiving body sampling points and counties in Tersakan Sub-basin. The drainage area-receiving body sampling point pairing in Table 3.3 is not cumulative. Some of the drainage areas are not represented directly by receiving body sampling points, thus according to flow chart of Tersakan Sub-basin (see Figure 4.1), they are coupled with next receiving body sampling points (the ones in brackets in Table 3.3). Discharge points Y-65 and Y-77 are in the brackets meaning that they are actually in another drainage area, but due to their location relative to the receiving body sampling point that their drainage area linked with, their effects would rather be expected in the receiving body sampling points they are linked in the table. For example, Y-65 discharge sampling point lays within the YB12 drainage area and diffuse pesticide loads of YB12 drainage area may clearly represented by Y-31 receiving body sampling point. However, there is another receiving body sampling point, Y-97, which is between Y-65 and Y-31. Thus Y-65 discharge point is represented by Y-97 due to the proximity.

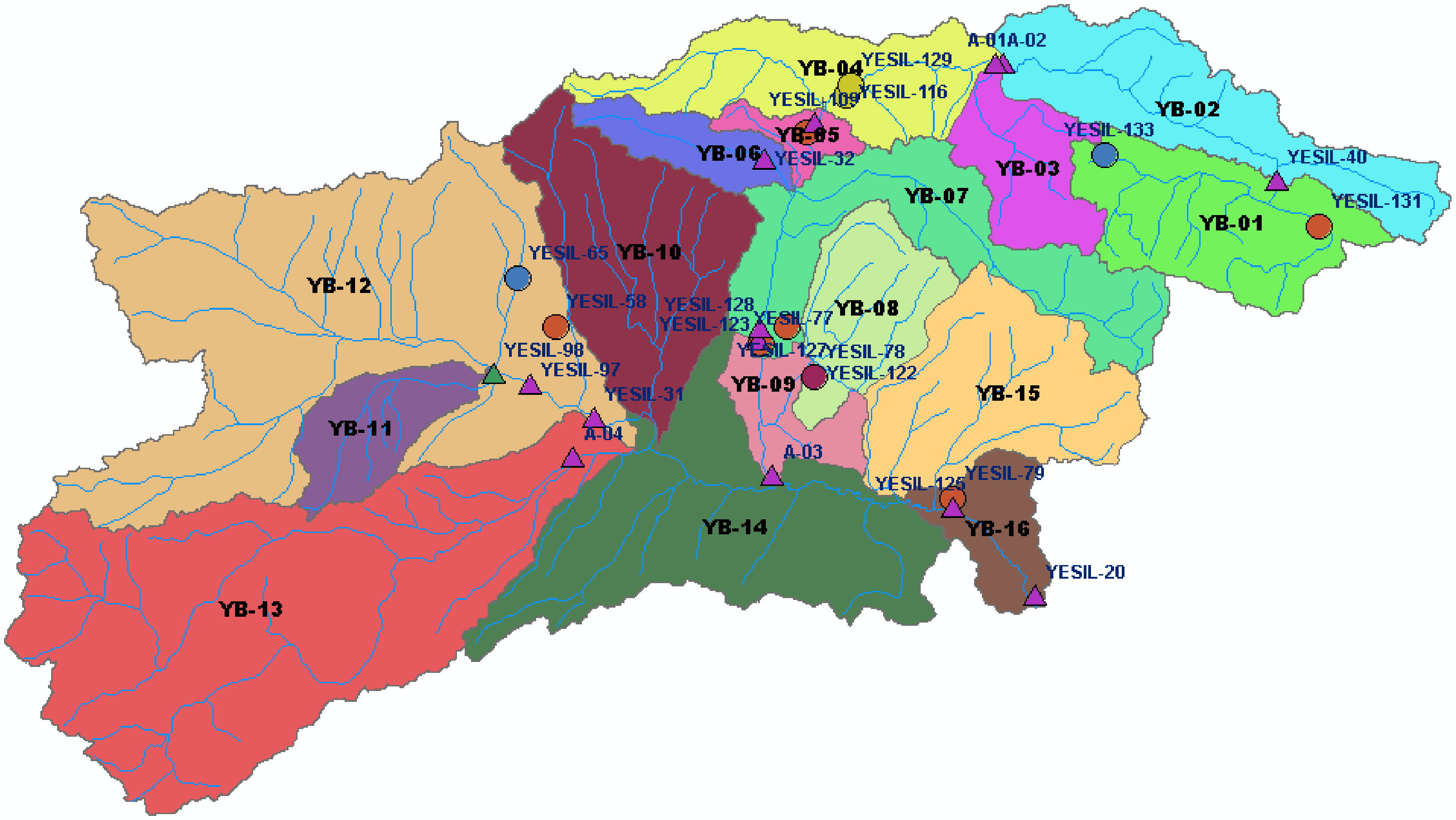

Figure 3.4. Sixteen main drainage areas, receiving body and discharge sampling points forming Tersakan Sub-Basin (triangles are receiving body, circles are discharge sampling points)

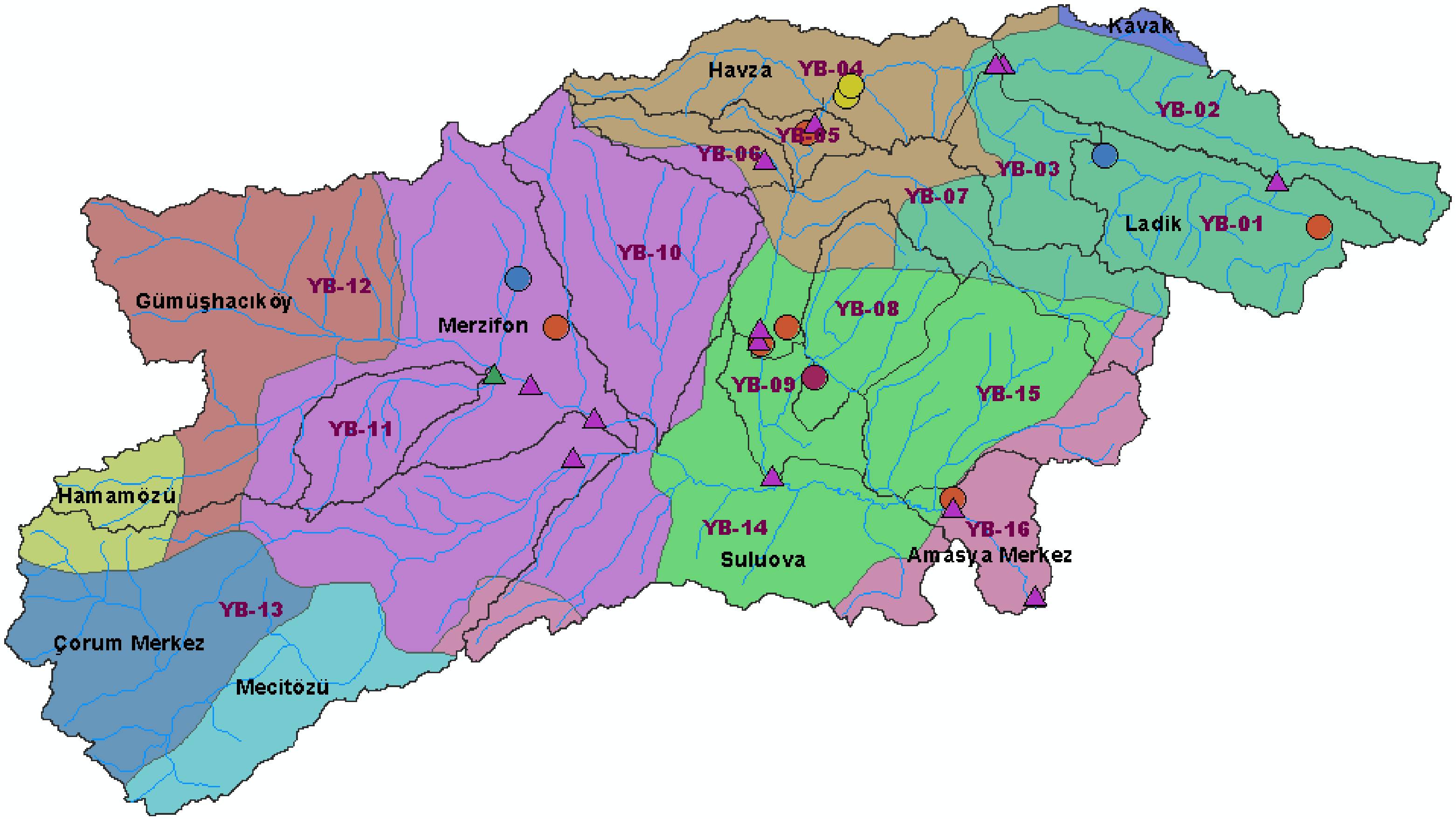

Figure 3.5. Counties and drainage areas forming Tersakan Sub-Basin

Table 3.3. *Drainage areas in the Tersakan Sub-basin, provinces and counties within the sub-basin, discharge sampling points and non-cumulative receiving body sampling points*

Codes of drainage areas	**Discharge sampling points**	**Receiving body sampling points paired with drainage areas**	**Provinces and counties within sub-basin**									
			Çorum		**Amasya**					**Samsun**		
			Mecitözü	**Merkez**	**Hamamözü**	**Gümüşhacıköy**	**Merzifon**	**Suluova**	**Merkez**	**Havza**	**Kavak**	**Ladik**
YB01	Y133, Y131	Y40										1
YB02	-	A01								1	1	1
YB03	-	A02								1		1
YB04	-	Y109								1		1
YB05	Y108	(Y128)								1		
YB06	-	Y32					1			1		
YB07	Y127	Y123					1	1	1	1		1
YB08	Y78	Y122						1		1		1
YB09	(Y77)	A03						1				
YB10	-	(Y125)					1	1		1		
YB11	(Y65)	(Y97)					1					
YB12	Y58	Y31			1	1	1					
YB13	-	A04	1	1	1	1	1		1			
YB14	-	(Y125)					1	1	1			
YB15	-	(Y125)						1	1			
YB16	Y79	Y20						1	1			

1: There is an area from this county in the drainage area.

3.3. Available data for the estimation of agricultural pesticide diffuse load

In this section, details regarding the water quality monitoring study of Tersakan Creek are presented. Moreover, required information and input data for estimation of pesticide diffuse load methodology and PESTRANS fate and transport models such as land cover and crops, pesticide application rates, rainfall and infiltration, soil properties and physicochemical properties of pesticides are gathered.

3.3.1. Water quality monitoring data of Tersakan Creek

A monitoring program was implemented to determine the water quality status of the Yeşilırmak River in accordance with the EU Water Framework Directive (WFD) in the context of Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project which is mentioned in Section 1.2 of Chapter 1. Specific to Tersakan Creek, the monitoring program involved collections of water samples from the creek at 14 points and from the effluents of wastewater treatment plants at 12 points up to 8 times, each representing different periods over 2-years of monitoring as presented in Table 3.4. The first period carried out in August 2016, 2nd period in October 2016, 3rd period in February 2017, 4th period in April 2017, 5th period in June 2017, 6th period in August, 7th period in November 2017 and finally 8th period carried out in January 2018. Furthermore, flow rate measurements are performed in these periods.

Receiving body and discharge sampling points marked as RB and D, respectively as presented in Table 3.4. Only flow rate measurements are carried out for Y-98 receiving body sampling point, thus it is marked as RB2.

Each sample was analyzed by TUBITAK MAM for pesticides that are classified as “specific pollutants” and “priority pollutions” according to the Surface Water Quality Regulation (dated 30.11.2012/28483). Results of the monitoring study are examined in terms of exceedance of environmental quality standards (EQSs) presented in Surface Water Quality Regulation (dated 30.11.2012/28483). Pesticides that will be worked on in terms of estimation of diffuse pollution loads are identified from the examination of the monitoring program.

Pesticides that are detected and exceed EQS are presented in Section 4.1 of Chapter 4. Moreover, a mass balance study is carried out to determine the contribution of point and diffuse sources to the pesticide pollution in Tersakan Creek. During calculations flow rates presented in Table E.25 in Appendix E. The results are discussed in this chapter considering flow pattern of the Tersakan Creek.

Table 3.4. *Sampling points in Tersakan Sub-basin and their availability in predetermined periods*

Code of Sampling Point	Name of the point	Type	Availability of sampling in the periods							
			1	2	3	4	5	6	7	8
Y-20	YEOIN015 (MoAF Operational Station)	RB	+	+	+	+	+	+	+	+
Y-31	Before Merzifon	RB	+	0	0	0	0	+	+	0
Y-32	YEOIN001 (MoAF Operational Station)	RB	+	+	+	+	+	+	+	+
Y-40	Outlet of Lake Ladik	RB	+	+	+	+	+	+	+	+
Y-58	Merzifon OIZ (Amasya/Merzifon)	D			+	+	+	+	+	+
Y-65	Meray Oil Industry (Amasya/Merzifon)	D			+	+	+	+	+	+
Y-77	ET-BIR Meat Industry (Suluova)	D					+	+	+	+
Y-78	Kozlu Food (Suluova - Merkez)	D					+	+	+	+
Y-79	Bakrac Dairy Industry (Amasya/Merkez)	D					+	+	+	+
Y-97	Downstream of Meray Oil Industry	RB						+	+	+
Y-98	Meray Oil Industry – sidebranch	RB2						+	+	
Y-108	Havza WWTP	D						+	+	+
Y-109	Before Havza WWTP discharge	RB						+	+	+
Y-116	Otat Food Industry	D						+	+	+
Y-122	Before Kozlu Food Industry discharge	RB						+	+	+
Y-123	Before ET-BIR Meat Industry discharge	RB						+	+	+
Y-125	Before Bakrac Dairy Industry discharge	RB							+	+
Y-127	Amasya Sugar Factory	D							+	
Y-128	Before Amasya Sugar Factory discharge	RB							+	
Y-129	Aydınoglu Flour Food Industry	D							+	+
Y-131	Doga Food, Agriculture, Livestock	D							+	+
Y-133	Akcansa Cement Industry	D							+	
A-01	Tersakan Receiving Body Station 1	RB								+
A-02	Tersakan Receiving Body Station 2	RB								+
A-03	Tersakan Receiving Body Station 3	RB								+
A-04	Tersakan Receiving Body Station 4	RB								+

+*: Sampling is available, 0: Still water sampling, Empty boxes: No available sampling*

Eighteen of pesticides are sorted out of 22 pesticides, which include metabolites or isomers of main active substances, for estimation of diffuse pollution loads (see Table

4.1). Chosen 18 pesticides that exceed EQSs are used for pest control at present or in the past. In the relevant literature, being out of chosen 18 pesticides, Cyfluthrin and Beta-cyfluthrin has few different physicochemical properties thus, they are separated during estimation of diffuse pollution loads even if they are represented as one in monitoring result as presented in Section 3.3.1.

According to EFSA (2018), Beta-cypermethrin is applied to oilseed rape, wheat, and maize between application rates of 20 g/ha and 35 g/ha. Nevertheless it is a prohibited active substance since 2010 (MoAF, 2018). Also having four cis- and four trans- in total eight isomers, Cypermethrin is a chiral molecule. Beta-cypermethrin is a reaction mixture of two enantiomeric forms; Alpha- and Theta-Cypermethrin (University of Hertfordshire, 2017). Theta-Cypermethrin is not a major active substance in Plant Protection Products (PPP). Thus, Beta-Cypermethrin and Theta-Cypermethrin are not included in estimation of diffuse pollution loads.

3.3.2. Land cover and agricultural crops in Tersakan Sub-basin

Determination of the distribution of agricultural areas over Tersakan Sub-basin is important in terms of estimation of diffuse pesticide loads. One of the main components of diffuse load estimation, namely sediment yield is based on area and spatial information. Thus in this section, areal information regarding agricultural activities is gathered.

3.3.2.1. CORINE 2012 Land Cover

In 1985, the European Union initiated the CORINE program. It means 'Coordination of Information on the Environment' and is an inventory of land cover in 44 classes, and presented as a cartographic product, at a scale of 1:100,000 (EEA, 2017). Information on land cover provides a reference source for various studies as estimation of diffuse pollution to determine and implement environmental policy and can be used with other data (on climate, inclines, soil, etc.) to make complex assessments (e.g.

mapping erosion risks) (EEA, 2017). A total of 44 land cover classes are gathered under the 5 main groups as they are previously mentioned in Section 3.1. They are artificial surfaces, agricultural areas, forests and semi-natural areas, wetlands, and water bodies.

Determination of CORINE 2012 Land Cover of Tersakan Sub-basin is important in terms of the spatial utility of the cartographic product. Classes will guide the locations of agricultural areas with different agricultural products. This way, application rates and areas of pesticides specific for drainage areas are determined as described in Section 3.5 in detail.

In order to determine CORINE 2012 Land Cover of Tersakan Sub-basin; CORINE 2012 Land Cover, drainage area borders map and county borders map of Tersakan Sub-basin are overlaid in a GIS-based program. It is found that Tersakan Sub-basin land cover is comprised of 23 subclasses; 7 of them are related to agricultural areas. In Section 3.3.5, Table 3.14 and Figure 3.8, CORINE 2012 Land Cover map and classes are presented, and relevant issues are discussed in greater detail. Since pastures are separated from agricultural areas during estimation of erosion by Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry), they are not included in determination of pesticide application areas presented in Chapter 3.5. About 24% of the total area of Tersakan Sub-basin is classed as 212 (permanently irrigated arable land) and 21% is classed as 211 (non-irrigated arable land). The third-largest area is covered with forests and seminatural areas in total 38%. All regions in terms of counties and the agricultural regions of drainage areas are presented in Appendix B in detail.

3.3.2.2. TURKSTAT Crop Production Statistics

Pesticides are suggested specific to the crop and the problem encountered. Thus information on the areas sown in terms of crops and counties in years 2015, 2016 and 2017 for each county are gathered from TURKSTAT (2017). Three-year averages of these areas in terms of percentages presented in Table 3.5, Table 3.6, and Table 3.7

for Amasya, Samsun, and Çorum, respectively. In terms of crop and county, arithmetic averages of three years are used. Merzifon county of Amasya is presented as an example in Appendix C. Wheat, sunflower and barley are the crops that cover the most of the agricultural lands as presented in Table C.9 of Appendix C. As presented in Table 3.5, Table 3.6, and Table 3.7 cereal and the other crop products cover the largest agricultural lands in the counties. Second largest coverage is generally fallow lands. Coverage of fruits, beverage and spice crops, and vegetables are changing from county to country between 0.26 and 5.98 %. Then crop-based areas are used in weighted average calculation for determination of specific application rates for pesticides that exceed EQS for each drainage area since application rates are quite variable. Specific application rates of pesticides for drainage areas are significant inputs for PESTRANS pesticide fate and transport model as presented in Section 3.5 (Ünlü et al., 1995).

Table 3.5. *Percentages of areas of crop groups in counties of Amasya*

Land cover/Counties	Gümüşhacıköy	Hamamözü	Merkez	Merzifon	Suluova
Fruits, beverage and spice crops (%)	1.98	4.10	3.59	1.59	3.69
Fallow lands (%)	8.07	23.89	21.85	13.71	2.14
Vegetables (%)	5.98	1.85	5.48	3.74	4.63
Cereal and other crop products (%)	83.97	70.16	69.08	80.95	89.55

Table 3.6. *Percentages of areas of crop groups in counties of Samsun*

Land cover/Counties	Havza	Kavak	Ladik
Fruits, beverage and spice crops (%)	0.26	1.28	0.66
Fallow lands (%)	1.38	23.95	19.07
Vegetables (%)	0.44	1.19	1.39
Cereal and other crop products (%)	97.92	73.57	78.88

Table 3.7. *Percentages of areas of crop groups in counties of Çorum*

Land cover/Counties	Mecitözü	Merkez
Fruits, beverage and spice crops (%)	1.12	1.88
Fallow lands (%)	26.23	34.90
Vegetables (%)	0.79	2.53
Cereal and other crop products (%)	71.86	60.70

‘TURKSTAT areas sown’ is a detailed database in terms of crops which CORINE 2012 Land Cover lacks. On the other hand, TURKSTAT data lacks spatial information of the crop areas. Since areal information is required to determine specific application rates of pesticides for each drainage area, these two databases are linked as presented in Section 3.5. Specific application rates and application areas of pesticides are required for PESTRANS fate and transport model and estimation of diffuse pesticide loads, respectively.

3.3.3. Recommended and reported pesticide use

In the PESTRANS model, which is used to determine the amount of pesticides remaining in the soil after application as presented in Section 3.5, the application rate of pesticides is one of the critical inputs required.

Reported data on agricultural pesticide use in Amasya, Samsun and Çorum provinces for the year 2018 is obtained from the Ministry of Agriculture and Forestry, after the determination of the provinces and their counties within the boundaries of the Tersakan Sub-basin. Usage data of pesticides that exceed the EQSs are sorted from the whole data. Out of the counties of Samsun within the borders of Tersakan Sub-Basin, only the data belonging to Kavak County was obtained. Data on pesticide use in Çorum Province was sparce/incomplete only total pesticide usage data for total agricultural products cultivated in Merkez and Mecitözü counties is obtained. Overall, there were insufficient data on pesticide application rate (pesticide usage per area; kg/ha or $\mu g/cm^2$) to run PESTRANS model, total amount of pesticide usage data is eliminated. As indicated in Table 3.8, lack of data on pesticide use has been overcame by assuming application rates and active substances for specific crops are the same as reported for other counties.

In Table 3.9 and Table 3.10, active substances exceeding the EQS are gathered from the reported pesticide usage data obtained from the Ministry of Agriculture and Forestry for Samsun province and the counties in Amasya. Application amount per hectare is estimated from the percentage (content), dosage and the number of repetitions of the licensed plant protection product (PPP) which is reported in the data of the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry.

Table 3.8. *Content of reported pesticide usage data and elimination of usage data deficiencies*

Provinces	Amasya					Samsun	Çorum
Counties	Gümüşhacıköy	Hamamözü	Merzifon	Suluova	Merkez	Havza, Ladik, Kavak	Mecitözü, Merkez
Aclonifen	X	X	X	X	X	Δ	Δ
Chlorfenapyr	O	O	O	O	O	O	O
Chlorothalonil	X	Δ	X	X	X	X	Δ
Chlorpyrifos (Chlorpyrifos-ethyl)	X	Δ	X	X	X	X	Δ
Chlorsulfuron	Δ	Δ	Δ	Δ	Δ	X	Δ
Beta-Cyfluthrin/ Cyfluthrin	Δ	Δ	Δ	Δ	Δ	X	Δ
Cypermethrin	Δ	Δ	X	X	X	X	Δ
Alpha-cypermethrin	Δ	Δ	Δ	Δ	Δ	X	Δ
Zeta-cypermethrin	Δ	Δ	Δ	Δ	Δ	X	Δ
Cyromazine	O	O	O	O	O	O	O
Dichlorvos	O	O	O	O	O	O	O
Diflubenzuron	Δ	Δ	Δ	X	X	X	Δ
Ethalfluralin	O	O	O	O	O	O	O
Fenpropimorf	Δ	Δ	Δ	Δ	Δ	X	Δ
Fenthion	O	O	O	O	O	O	O
Nicosulfuron	Δ	Δ	Δ	Δ	Δ	X	Δ
Prothiofos	O	O	O	O	O	O	O

X: This pesticide is used in this county. In the estimation of diffuse pesticide load, the highest values of application rate reported by the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry) and the recommended in the PPP Database were used.

O: This pesticide has exceeded its EQS in the water quality measurements of Tersakan Creek but there is no data about its use. Thus, the current or past recommended use will be used in the calculation of the diffuse pesticide load.

Δ: There is data on the use of this pesticide in other districts within the borders of Tersakan Sub-Basin. The values in other districts will be used in estimating the diffuse pesticide load.

Reported application rates are compared with the maximum recommended amount for that product and that active substance in the PPP Database (Ministry of Agriculture and Forestry, 2017). Since there is no data belonging to the counties of Samsun (Havza and Ladik) within the boundaries of the Tersakan Sub-Basin except Kavak (which is a very small area), application rates are gathered for the whole province. Alpha-cypermethrin, Beta-cyfluhthrin, Chlorpyrifos, Chlorpyrifos-ethyl, Cypermethrin, Diflubenzuron, Nicosulfuron, and Zeta-cypermethrin have been used above the recommended values for at least one crop. Application areas that are estimated for Amasya from total application amount and dosages are quite variable compared to agricultural crop areas reported in TURKSTAT (2017).

Table 3.9. *Reported and recommended application rates of pesticides that exceed EQSs in Tersakan Creek at Samsun province*

	Crop	Reported application rate (kg a.s./ha)	Recommended application rate (kg a.s. /ha)
Alpha-cypermethrin	Apple	0.24	0.02
	Corn	0.04	0.12
Beta-cyfluthrin	Tobacco	0.027	0.018
Chlorothalonil	Vegetables	0.006	0.75-1.5**
Chlorpyrifos-ethyl	Hazelnut	0.002- 0.006- 0.2- 1.2*	0.6
	Corn	0.05- 0.375- 0.75- 0.864*	2.592
	Vegetables	0.05- 0.375- 20*	1
	Vegetables	1.703	0.343-0.851**
Chlorsulfuron	Wheat	0.008	0.008
Cypermethrin	Apple	0.6	0.05
	Hazelnut	0.0006-0.12*	0.06
	Corn	0.002-0.075*	0.225
	Vegetables	0.001-0.08-1*	0.04-0.1**
Diflubenzuron	Apple	0.4	0.1
Fenpropimorph	Cereals	0.25	0.3-0.313**
Nicosulfuron	Corn	0.05-0.06*	0.06
Zeta-cypermethrin	Hazelnut	0.0002-0.03*	0.02

**Application rates in the same district or in different counties*

*** Recommended application rates vary in this range depending on the type of cereal or vegetable.*

Table 3.10. Application rates, application areas and crop areas of pesticides that exceed EQSs in Tersakan Creek at the counties of Amasya province

County	Crop	Reported application rate (kg a.s.* /ha)	Recommended application rate (kg a.s. /ha)	Reported application area** (ha)	Crop area stated in TURKSTAT (ha)
Aclonifen					
Merkez	Chickpea	0.75	0.75	32	581
	Sunflower	1.2	1.95	333.33	1351
Gümüşhacıköy	Sunflower	1.2	1.95	33.33	751
	Chickpea	0.75	0.75	7	107
Hamamözü	Chickpea	0.75	0.75	1	50
Merzifon	Chickpea	0.75	0.75	34	300
	Sunflower	1.2	1.95	50	8083
Suluova	Chickpea	0.75	0.75	16	162
	Sunflower	1.2	1.95	66.665	644
Chlorothalonil					
Gümüşhacıköy	Tomato	1.125	1.5	50	26
Merzifon	Tomato	1.125	1.5	100	71
Suluova	Tomato	1.125	1.5	100	30.9
Merkez	Vegetables	0.5	1	110	82-1497***
Chlorpyrifos-ethyl					
Gümüşhacıköy	Vegetables	0.5	1	5	34-1142***
Merzifon	Vegetables	0.5	1	25	0.6-1749***
Suluova	Vegetables	0.5	1	100	0.5-1246***
Cypermethrin					
Merkez	Cherry	0.3	0.2	300	1263
	Pear	0.2	0.1	5.625	25
	Grape	0.2	0.05	22.5	216
Merzifon	Cherry	0.3	0.2	12	99
	Grape	0.2	0.05	9.375	94
Suluova	Cherry	0.3	0.2	20	378.9
	Pear	0.2	0.1	1.0375	15.3
Diflubenzuron					
Merkez	Quince	0.384	0.12	3.4	2.4
Suluova	Quince	0.384	0.12	1.6	2

** is kg active substance/ha; ** is where values are obtained from the equivalence of total usage (kg) / application rate (kg a.s./ha) where components are reported by the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry); *** Areas of vegetables at the counties change between these ranges.*

Banned pesticides (MoAF, 2018) that are exceeding EQSs were also found in the Tersakan Creek receiving body samples collected for the monitoring study. Application rates of these pesticides were obtained from other documents (EFSA, 2018; Yücer, 2008; Adana Provincial Directorate of Agriculture and Forestry, 2019) and are given in Table 3.11. Regarding some agricultural crop groups (such as cereals, fruits, and vegetables), there is no particular information (either the applied pesticide or the application rates) in the abovementioned sources. Thus, active substance information on agricultural crop basis was collected from the website of TURKTOB (2019).

Table 3.11. *Application rates of banned pesticides*

Pesticide	Agricultural product	Application rate (kg/ha)	Pesticide	Agricultural product	Application rate (kg/ha)
Bifenox	Cereals*	0.75	Ethalfluralin	Potato*	18
Chlorfenapyr	Eggpplant **	0.126		Chickpea*	1
	Pepper**	0.216		Cereals*	1.68
	Strawberry**	0.126		Corn*	1.25
	Grape**	0.216		Cucumber*	1.68
	Apple**	0.108		Bean*	1.68
	Cucumber**	0.144		Peas	1
	Watermelon **	0.035	Fenthion	Fruits**	0.7875
	Corn***	0.2		Grape**	0.7875
Dichlorvos	Fruits **	1.1		Peas**	1.05
	Vegetables**	1.1		Watermelon	0.7875
	Grape**	1.1		Melon	0.63
Prothiofos	Apple**	0.5		Cereals	0.91875

* (EFSA, 2018).

** (Yücer, 2008).

*** (Adana Provincial Directorate of Agriculture and Forestry, 2019).

3.3.4. Rainfall and infiltration rate in Tersakan Sub-basin

In the PESTRANS model, which is used to determine the amount of pesticides remaining in the soil after application, the annual average net infiltration rate is required as an important input. The infiltration rate is ultimately needed for the estimation of average values of volumetric soil water and air contents as presented in Section 3.3.5.

Rainfall data are obtained from the General Directorate of Combating Desertification and Erosion, Ministry of Agriculture and Forestry (2018)., The data are collected from Merzifon meteorology station in the sub-basin and two other meteorology stations closest to the Tersakan Sub-basin (see Table 3.12). A regression method proposed by the General Directorate of Combating Desertification and Erosion was used to determine the rainfall-altitude relationship.

Table 3.12. *Annual average rainfall data of stations near or in Tersakan Sub-Basin*

Station Name	Altitude (m)	Rainfall amount (mm)
Merzifon	759	436.1
Amasya	412	448.5
Turhal	500	442.5

The rainfall map of Tersakan sub-basin is obtained in GIS using the resulting rainfall-altitude regression equation, and the map is presented in Figure 3.6. The raster rainfall map for each drainage area is clipped with the polygon boundaries of the drainage areas. Then the average annual rainfall values are determined for each drainage area through the GIS-based program. Infiltration rates for each drainage area are calculated using Equation (1).

$$q_s = P \times f_p \times 2{,}74 \times 10^{-4} \tag{1}$$

where q_s is the net annual average infiltration rate (cm/day), depending on the annual average amount of rainfall; P is the annual average rainfall (mm/year); f_p is the fraction of precipitation that contributes to the net infiltration rate; and 2.74×10^{-4} is a factor for unit conversion. According to Avon and Durbin (1994), if the average rainfall is between 380 mm and 510 mm, which is the case for each drainage area in Tersakan Sub-basin, f_p is taken as 15% of the annual average amount of rainfall in arid and semi-arid climatic regions.

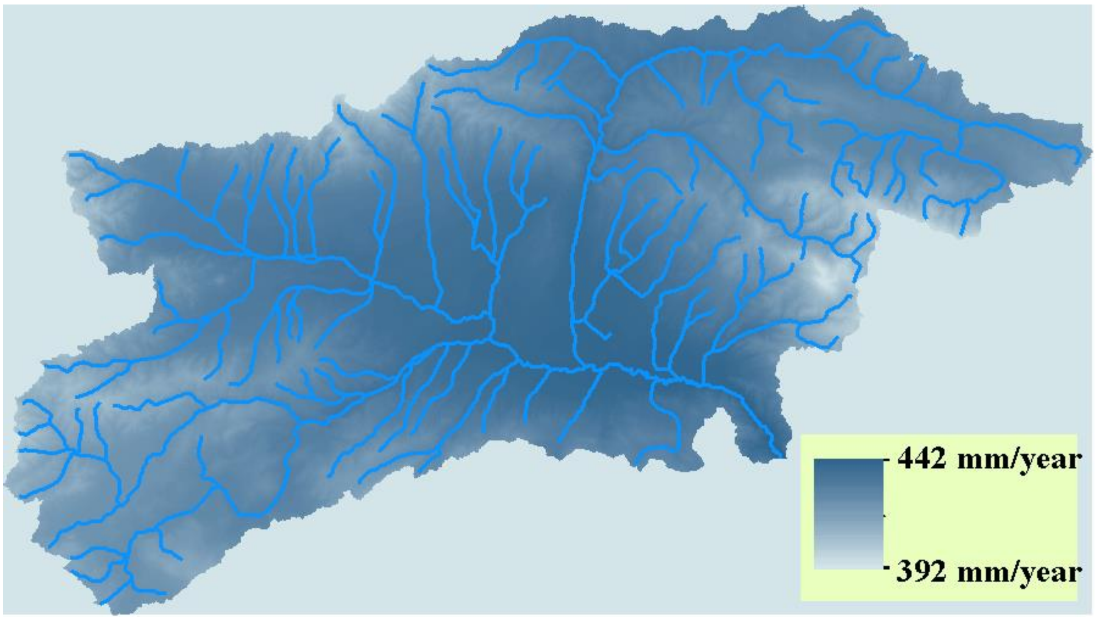

Figure 3.6. Rainfall map of Tersakan Sub-basin

Table 3.13. *Average rainfall in drainage areas of Tersakan Sub-basin and corresponding infiltration rates*

Drainage Area	*Average rainfall (mm/year)*	*Infiltration rate (qs) (cm/day)*	Drainage Area	*Average rainfall (mm/year)*	*Infiltration rate (qs) (cm/day)*
YB-01	425	0.017461	YB-09	445	0.018298
YB-02	431	0.017696	YB-10	436	0.017897
YB-03	429	0.017625	YB-11	434	0.017836
YB-04	434	0.01783	YB-12	431	0.017704
YB-05	436	0.017896	YB-13	427	0.017531
YB-06	428	0.017571	YB-14	439	0.018035
YB-07	429	0.017618	YB-15	428	0.017586
YB-08	436	0.017935	YB-16	441	0.018112

3.3.5. Distribution of soil properties in Tersakan Sub-basin

Properties of soil in the study area were obtained from the General Directorate of Combating Desertification and Erosion of Ministry of Agriculture and Forestry (2018). Raw data, in the form of a GIS-based map, contains silt, clay, sand and organic matter content of soils measured at 365 sampling points. Soil texture classes for each sampling point are determined by entering silt, clay and sand contents to Soil Water Characteristics program (ARS US, 2018). As indicated in Figure 3.7, the textures of soils in the Tersakan Sub-basin are mostly comprised of clay, clay loam, loam, and sandy clay loam.

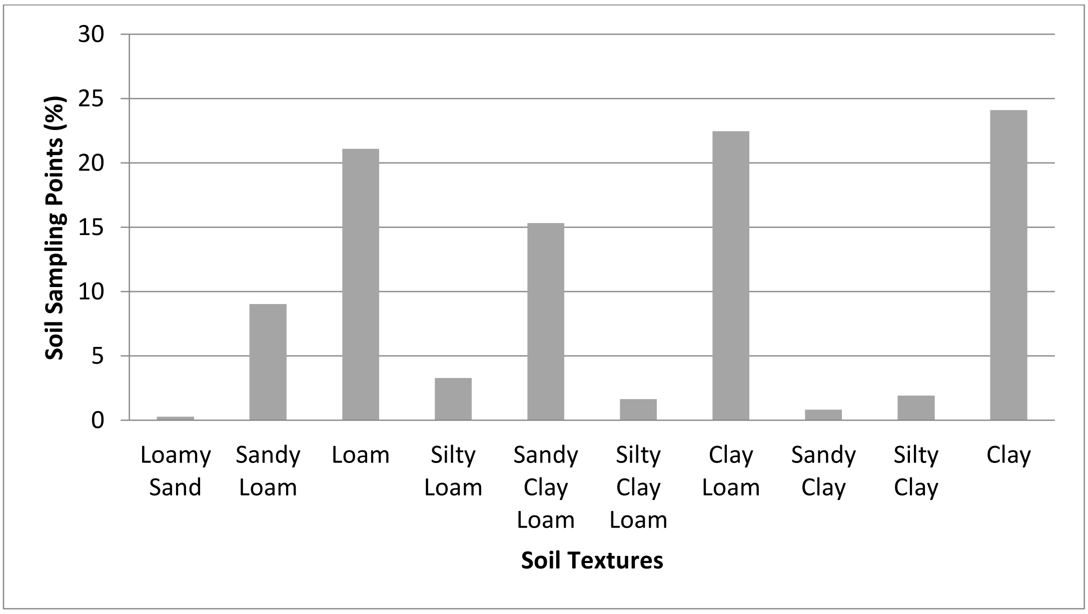

Figure 3.7. Soil texture of Tersakan Sub-basin

Soil sampling points, which are not in the agricultural areas of CORINE 2012 Land Cover map, are eliminated by overlapping CORINE 2012 Land Cover, drainage areas and soil texture map using a GIS-based program. The resulting map of soil texture classes and CORINE 2012 Land Cover of Tersakan Sub-basin is shown in Figure 3.8. Classes of CORINE 2012 Land Cover map shown in the legend of this map are presented in Table 3.14. A soil texture is assigned for each drainage area, based on the dominating textural class that falls into the borders of the drainage area. Soil textures of each drainage area are presented in Table 3.16.

Table 3.14 *Names, codes, and colors of CORINE Land Cover Classes*

CORINE Land Cover	**Code and Color**	**CORINE Land Cover**	**Code and Color**
1) Artificial surfaces		2.4 Heterogeneous agricultural areas	
1.1.1 Continuous urban fabric	🟥 111	2.4.2 Complex cultivation patterns	🟨 242
1.1.2 Discontinuous urban fabric	🟥 112	2.4.3 Land principally occupied by agriculture, with significant areas of natural vegetation	🟧 243
1.2.1 Industrial or commercial units	🟪 121	3) Forest and semi-natural areas	
1.2.2 Road and rail networks and associated land	🟥 122	3.1.1 Broad-leaved forest	🟩 311
1.2.4 Airports	🟪 124	3.1.2 Coniferous forest	🟩 312
1.3.1 Mineral extraction sites	🟪 131	3.1.3 Mixed forests	🟩 313
1.3.3 Construction sites	🟪 133	3.2.1 Natural grassland	🟩 321
1.4.2 Sport and leisure facilities	⬜ 142	3.2.4 Transitional woodland/shrub	🟩 324
2) Agricultural areas		3.3.2 Bare rock	⬜ 332
2.1 Arable land		3.3.3 Sparsely vegetated areas	🟩 323
2.1.1 Non-irrigated arable land	🟨 211	3.3.4 Burnt areas	⬛ 334
2.1.2 Permanently irrigated arable land	🟨 212	4) Wetlands	
2.1.3 Rice fields	🟥 213	4.1.1 Inland marshes	🟦 411
2.2 Permanent crops		5) Water bodies	
2.2.1 Vineyards	🟧 221	5.1.2 Water bodies	🟦 512
2.2.2 Fruit trees and berry plantations	🟧 222		
2.3 Pastures			
2.3.1 Pastures	🟨 231		

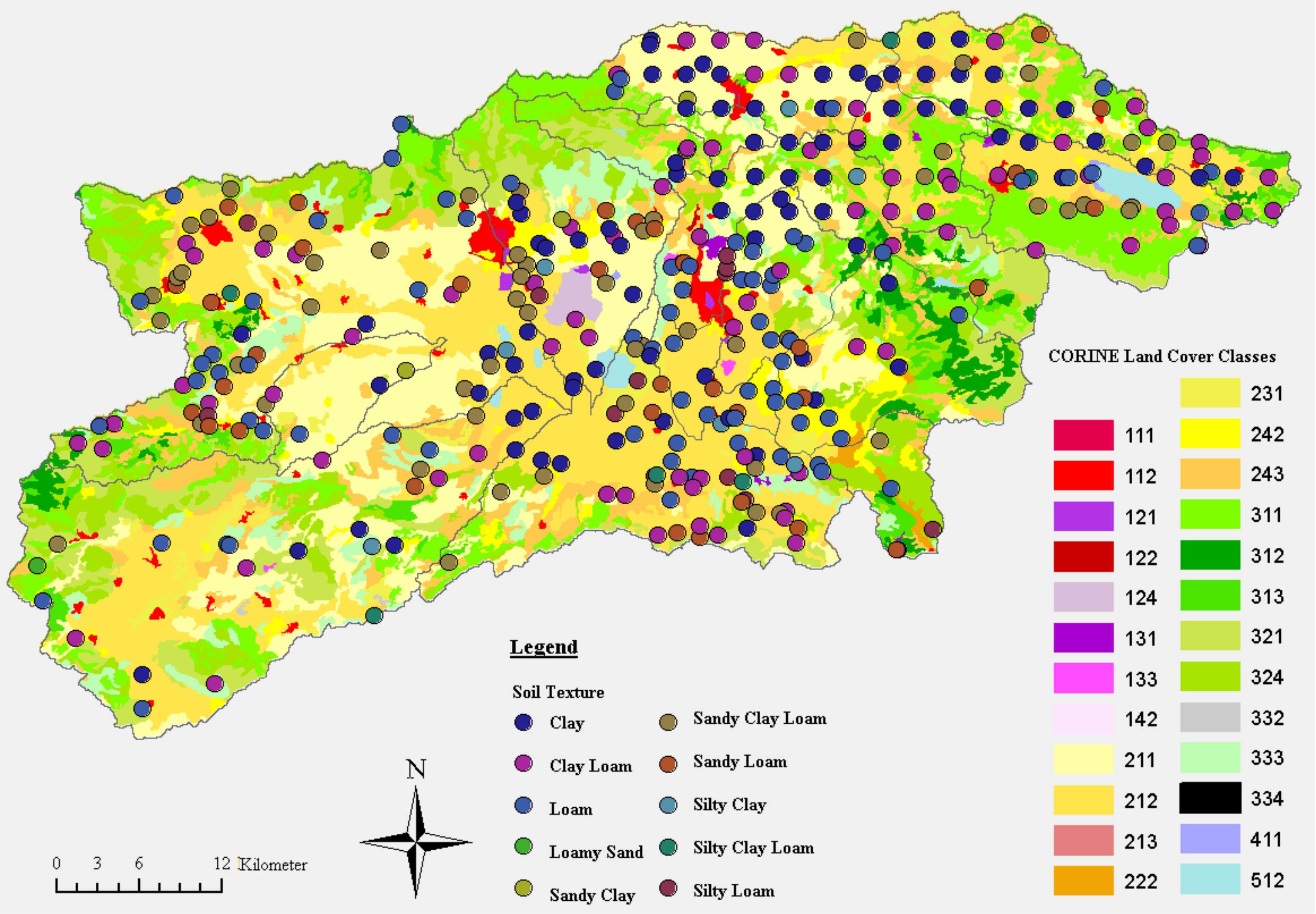

Figure 3.8. Soil texture classes and CORINE 2012 Land Cover of Tersakan Sub-basin (CORINE 2012 Land Cover Classes are in Table 3.14)

Soil texture and annual average infiltration rate are used for the estimation of average volumetric water and air contents in soil profile. For this purpose, the following unit gradient approach as proposed and formulated by Ünlü et al. (1992) was used:

$$q_s = K_s \times k_r \qquad (2\text{-a})$$

$$k_r = \left[\frac{\theta_w - \theta_{rw}}{\phi - \theta_{rw}}\right]^{\gamma} \qquad (2\text{-b})$$

where, q_s is the net infiltration rate (cm/day), K_s is the saturated hydraulic conductivity (cm/day) and k_r (dimensionless) is the relative permeability described by the Brooks-Corey model (Brooks & Corey, 1964); θ_w is volumetric water content, (cm^3/cm^3); θ_{rw} is residual water content (cm^3/cm^3); ϕ is porosity (cm^3/cm^3) taken being equal to saturated water content θ_{sw} (cm^3/cm^3); and γ is a pore size distribution parameter. Owing to the availability of a large database on statistical distributions of van Genuchten soil-moisture retention model parameters (Carsel & Parish, 1988), Ünlü et al. (1992) related the pore size distribution parameter γ to the van Genuchten parameter n following Lenhard et al. (1989) as:

$$\gamma = 3 + \left((n-1) \times \left(1 - 0.5^{\left(\frac{n}{n-1}\right)}\right)\right)^{-1} \qquad (3)$$

Using equation (2) where Brooks-Corey exponent (γ) is related to van Genuchten parameter (n) via equation (3), water content is calculated using as (Ünlü et al., 1992):

$$\theta_w = \theta_{rw} + (\phi - \theta_{rw}) \times \left(\frac{q_s}{K_s}\right)^{1/\gamma} \qquad (4)$$

Air content θ_a(cm^3/cm^3) and soil bulk density (ρ_b) (g/cm^3) is calculated using the following equations 5-a and 5-b:

$$\theta_a = \phi - \theta_w \qquad (5\text{-a})$$

$$\rho_b = \rho_s \times (1 - \phi) \qquad (5\text{-b})$$

where ρ_s is particle density, which is assumed to be 2.65 g/cm^3 (Ünlü et al., 1992).

Values of soil parameters for soil textural classes taken from Carsel and Parish (1988) and presented in Table 3.15 are used for estimations of bulk density, water, and air contents. The results are presented in Table 3.16.

Table 3.15. *Saturated and residual water contents, hydraulic conductivity and water retention model parameter of soil textures by Carsel and Parish (1988)*

Parameters/Soil Textures	Loam	Sandy Clay Loam	Clay Loam	Clay
Saturated water content (Θ_{ds}) = Porosity(Φ)	0.43	0.39	0.41	0.38
Residual water content (Θ_{rs})	0.078	0.1	0.095	0.068
Hydraulic conductivity (K_s) (1/hr)	1.04	1.31	0.26	0.2
Water retention model parameter (n)(-)	1.56	1.48	1.31	1.09

A representative value of soil organic carbon fractions, f_{oc}, for each textural class is estimated from the measured values of organic matter content, assuming organic carbon is 58% of organic matter (Soil Quality , 2018). Figure 3.9 presents the distribution of calculated values of organic carbon fractions in agricultural areas of Tersakan Sub-basin. As presented in the figure, organic carbon fractions mostly change between 1% and 2%. The average value of organic carbon fractions of dominant soil textural classes is assigned for each drainage area (Table 3.16).

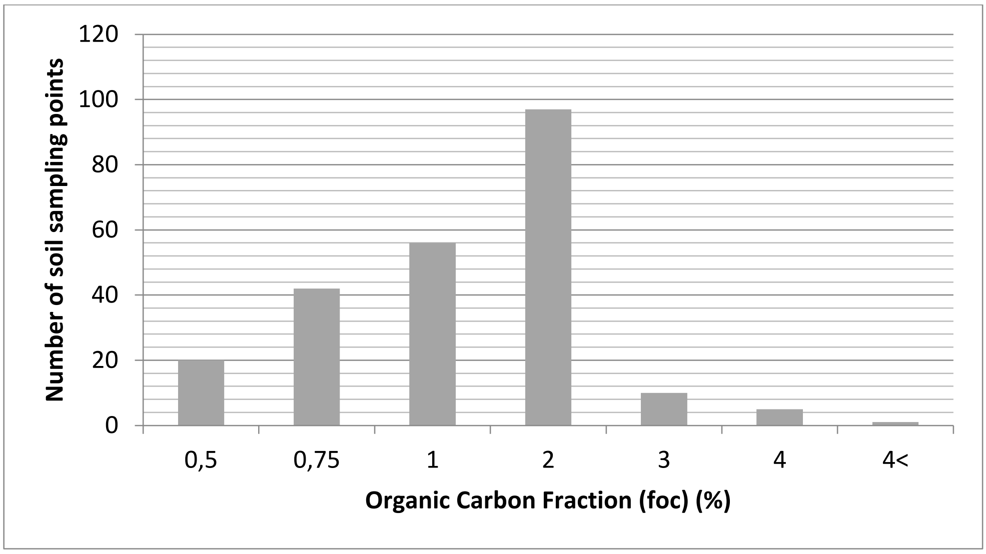

Figure 3.9. Organic carbon fractions in agricultural areas of Tersakan Sub-basin

Table 3.16. *Soil texture, bulk density, volumetric water and air content, and organic carbon or assigned for each drainage area*

Drainage area	Soil texture	Bulk density (ρ_b) (g/cm^3)	Volumetric water content (θ_w) (cm3/cm3)	Volumetric air content (θ_a) (cm3/cm3)	Organic carbon fraction (f_{oc}) (-)
YB-01	Clay Loam	1.5635	0.268	0.142	0.01513
YB-02	Clay	1.643	0.318	0.062	0.01586
YB-03	Clay Loam	1.5635	0.268	0.142	0.01461
YB-04	Clay	1.643	0.318	0.062	0.01158
YB-05	Clay	1.643	0.318	0.062	0.01587
YB-06	Clay Loam	1.5635	0.268	0.142	0.00233
YB-07	Clay	1.643	0.318	0.062	0.01261
YB-08	Loam	1.5105	0.206	0.224	0.00706
YB-09	Loam	1.5105	0.207	0.223	0.00828
YB-10	Clay	1.643	0.318	0.062	0.00782
YB-11	Loam	1.5105	0.206	0.224	0.01692
YB-12	Sandy Clay Loam	1.6165	0.21	0.18	0.00961
YB-13	Clay	1.643	0.318	0.062	0.00891
YB-14	Loam	1.5105	0.207	0.223	0.00742
YB-15	Loam	1.5105	0.206	0.224	0.00873
YB-16	Loam	1.5105	0.207	0.223	0.01167

Later dispersivity values are obtained from Perfect et al. (2002) based on the knowledge of soil textural class in the drainage areas as presented in Table 3.17.

Table 3.17. *Dispersivities assigned to each drainage area*

Soil Texture	Dispersivity (cm)
Loam	4.6
Sandy Clay Loam	6.0
Clay Loam	8.1
Clay	12.8

3.3.6. Physicochemical properties of pesticides that exceed EQSs

In the PESTRANS model, which is summarized in Section 3.5 of this chapter, the physicochemical properties of active substances are required. Physicochemical properties of pesticides that exceed EQSs are gathered in Table 3.18. Although water quality measurement of Cyfluthrin and Beta-Cyfluthrin active substances are presented as a single substance, they are considered as individual substances in PESTRANS simulations due to the differences in their physicochemical properties.

Water and air diffusion coefficients of Aclonifen, Chlorfenapyr, and Prothiofos are estimated using Fuller, Schettler ve Giddings (FSG) method, which is recommended by Tucker and Nelken (1981) due to its ease of use, availability of input data and accuracy of results for a general chemical population. The results are presented in Table 3.18. The required molar volume in the model was calculated by dividing the molecular weight of the active substance by its density (Ware, 1999).

The FSG method uses the following equation (6) to estimate the diffusion coefficient in the air:

$$\mathcal{D}_{BA} = \frac{10^{-3} \times T^{1.75} \times \sqrt{M_r}}{P \times \left(V_A^{1/3} + V_B^{1/3}\right)^2} \qquad (6)$$

where $\mathcal{D}_{BA}$ is gas diffusion coefficient in the air (cm^2/s); T is temperature (^{o}K); P is pressure (atm); V_A and V_B are the molar volumes for air and the pesticide in question (cm^3/mol), respectively; M_r is molecular weight defined by intermolecular collision (mol/g) which is estimated through equation (7) requiring M_A molecular weight of air is equal to 28.97 g/mol and M_B is molecular weight of pesticides.

$$M_r = \frac{M_A + M_B}{M_A \times M_B} \qquad (7)$$

The Hayduk and Laudie method for estimating the diffusion coefficient of organic compounds in water (equation 8) is recommended by Tucker and Nelken (1981) since it is easier to compute and it has been validated by a more recent database. This method uses the following equation:

$$\mathcal{D}_{BW} = \frac{13{,}26 \times 10^{-5}}{n_W^{1.14} \times V'^{0.589}_B} \qquad (8)$$

where $\mathcal{D}_{BW}$ is the diffusion coefficient of pesticide in water (cm^2/s), n_W is the viscosity of water (centipoises; cP) (taken as 1.002 cP at temperature 20^{o}C), and V_B is molar volume of pesticide.

Table 3.18. *Physicochemical properties of the pesticides (*These active substances are separated, ** These are calculated.)*

	Half-life (day)	**Air diffusion coefficient (cm^2/day)**	**Water diffusion coefficient (cm^2/day)**	**Henry's constant (-)**	**Organic carbon partition coefficient (L/kg)**	**Sources**
Aclonifen	195	5148.214**	0.60203	1.22E-06	7126	EC(2018).
Bifenox	17.7	1742.142	0.43133	6.54E-08	7143	EFSA (2018).
Chlorfenapyr	1370	4238.027**	0.48739	2.79E-06	11959.5	EC(2012), FAO(2018).
Chlorothalonil	70	2382.797	0.63272	8.18E-05	1041	EC(2006), RAIS (2018).
Chlorpyrifos (Chlorpyrifos-ethyl)	74	3301.675	0.38577	1.20E-04	8151.31	EC(2006), RAIS (2018).
Chlorsulfuron	232	3257.292	0.38059	1.41E-14	36.3	EFSA (2018), RAIS (2018).
Cyfluthrin*	98.5	2862.469	0.33446	1.31E-06	123930	EU(2018), RAIS (2018).
Beta-Cyfluthrin*	45	2862.469	0.33446	3.27E-06	180.29	RAIS (2018).
Cypermethrin	60	1633.354	0.40205	1.72E-05	79750	RAIS (2018), RED (2018).
Alpha-Cypermethrin	42.6	1633.354	0.40205	2.14E-05	288735	(University of Hertfordshire, 2017).
Zeta-Cypermethrin	60	1633.354	0.40205	9.32E-07	121786	(University of Hertfordshire, 2017).
Cyromazine	56	5430.803	0.63455	2.31E-12	409	RAIS (2018), EFSA (2018).
Dichlorvos	0.42	2408.551	0.63333	1.06E-05	53.96	EFSA (2018).
Diflubenzuron	6.7	3578.622	0.41813	1.88E-07	4609	EFSA (2018), RAIS (2018).
Ethalfluralin	45	1909.255	0.48268	0.005233	6364	RAIS (2018), (University of Hertfordshire, 2017).
Fenpropimorph	19.6	3635.016	0.42472	1.12E-04	2772	EFSA (2018), RAIS (2018).
Fenthion	34	3850.886	0.44995	5.97E-05	1500	NPIC(2018), RAIS (2018).
Nicosulfuron	16.4	2972.501	0.34731	6.07E-15	20.7	EFSA (2018), RAIS (2018).
Prothiofos	45	4285.026**	0.49050	1.23E-03	24158	PAN (2018).

3.4. Sediment yield modeling study with DEMIS

The diffuse load function and approach of McElroy (1976) to estimate pesticide pollution depends on a function of sediment yield. The quantity of soil material that is eroded and transported into watercourse is stated as sediment loading (sediment yield). Mechanisms of gross erosion and sediment delivery are the basis of the sediment loading function. In order to determine the on-site surface erosion, McElroy (1976) used The Universal Soil Loss Equation (USLE), since the equation is suitable to diverse land uses and climatic conditions, predicts erosion rates by storm event, season and annual averages, and has nationwide collection of data for the factors.

In 2011, the Ministry of Forestry and Water Affairs Department of Data Processing and Directorate of Combating Desertification and Erosion started the project called Development of Sediment Model and Erosion Risk Maps of Watersheds in Turkey. Due to the high data load required to be used within the scope of the project, geographical information system (GIS) based Dynamic Erosion Model, and Monitoring System (DEMIS) software was developed. In the DEMIS, USLE/ Revised USLE (RUSLE) methodology is used to estimate water erosion and prepare erosion maps for 25 watersheds. Moreover, sediment delivery rates of each micro-basin that form watersheds are calculated to estimate and assess sediment loads which are reaching river systems and are observed at the stations (ÇEM, 2018; Erpul, 2011).

GIS, remote sensing (RS) and geo-statistics (spatial statistical methods) were used to determine DEMIS model parameters and evaluate erosion risk with the following databases: topographic maps, digital elevation model (DEM), forest (stand data) maps, soil maps, land use data (CORINE 2012 Land Cover map), watershed and river data, watershed dam data, river sediment data and Turkey rainfall energy and intensity data (Erpul, 2011).

According to McElroy (1976), Erpul (2011), ÇEM (2018), sediment yield function is mainly as follows:

$$SY = A \times (R \times K \times L \times S \times C \times P) \times S_d \qquad (9)$$

Where SY is sediment loading from surface erosion (tons/year), A is the area of the agricultural lands in the drainage basin (ha), inside the brackets is USLE equation (which produces a resultant in unit of tons ha^{-1} year^{-1}) and S_d is sediment delivery ratio (dimensionless). USLE equation is comprised of 6 main parameters, which are explained as follows:

R: Rainfall factor (MJ mm ha^{-1} hr^{-1} year^{-1})

The rainfall factor represents the erosion potential of average annual rainfall. This factor is estimated within the TUBITAK project (no: ÇAYDAĞ 107Y155) called Determination of the Rainfall Energy and Intensity using Long-term Meteorological Data for Water Erosion Studies in Turkey. R factor is mapped within GIS environment (geospatial methods and spatial distributions) by Inverse Distance Weighting method using long-term (2005-2014) average R values obtained on the basis of 329 precipitation stations (Erpul, et al., 2016).

K: Soil erodibility factor (tons ha hr ha^{-1} MJ^{-1} mm^{-1})

K factor represents susceptibility of soils to erosion. It is obtained using three different mathematical equations due to variations in content of 115.000 soil profile data (in 22.000 soil profile) such as organic matter, soil structure, and permeability classes, and clay, silt, and sand content of soils (ÇEM, 2018).

L: Slope-length factor (-) and S: Slope-steepness factor (-)

LS factor is obtained separately for 25 watersheds using DEM and fill, flow direction and accumulation and raster calculator in GIS environment (ÇEM, 2018).

C: Cover factor (-)

Cover factor represents the management of the lands and vegetation cover to investigate the effect of land cover on erosion. C factor map is obtained by assigning C factors to forest (stand data) maps and CORINE 2012 Land Cover classes (ÇEM, 2018).

P: Erosion practice factor (-)

Erosion practice factor represents the water and soil protection management measures. The digital data of soil protection methods cannot be obtained thus P value is taken as 1 in the map of P factor (ÇEM, 2018).

Sediment delivery ratio, S_d, in equation (9) is estimated for each drainage area in the Tersakan Sub-basin by using the following equation developed by the USDA (Erpul, 2011; USDA, 1972), given as the power function of the drainage area (A, km^2):

$$S_d = a \times A^{-0.11} \tag{10}$$

where the coefficient 'a' is specifically equal to 0.5151 for Tersakan Sub-basin. The sediment delivery ratio is inversely proportional to the size of the agricultural areas.

Total soil loss, sediment yield, and sediment delivery ratio are estimated through the count of pixels and their representative area that has same average erosion class. The methodology for obtaining the model and results are explained in detail in Erpul, (2011), ÇEM, (2018) and (Şahin, et al., 2019) . The results of sediment yield estimation are presented in Section 4.2 of Chapter 4.

3.5. Pesticide fate and transport modeling study with PESTRANS

Regarding the diffuse loading function and approach of McElroy (1976), it is necessary to know the sediment load as well as the residual pesticide concentration in the soil after application to a crop. Pesticide fate and transport model, PESTRANS, developed by Ünlü et al. (1995) was used to estimate the residual concentration of pesticide in soil. PESTRANS takes into account of the basic fate and transport processes such as diffusion, dispersion, leaching, evaporation, biodegradation, and adsorption that pesticides will undergo in soil (Figure 3.10).

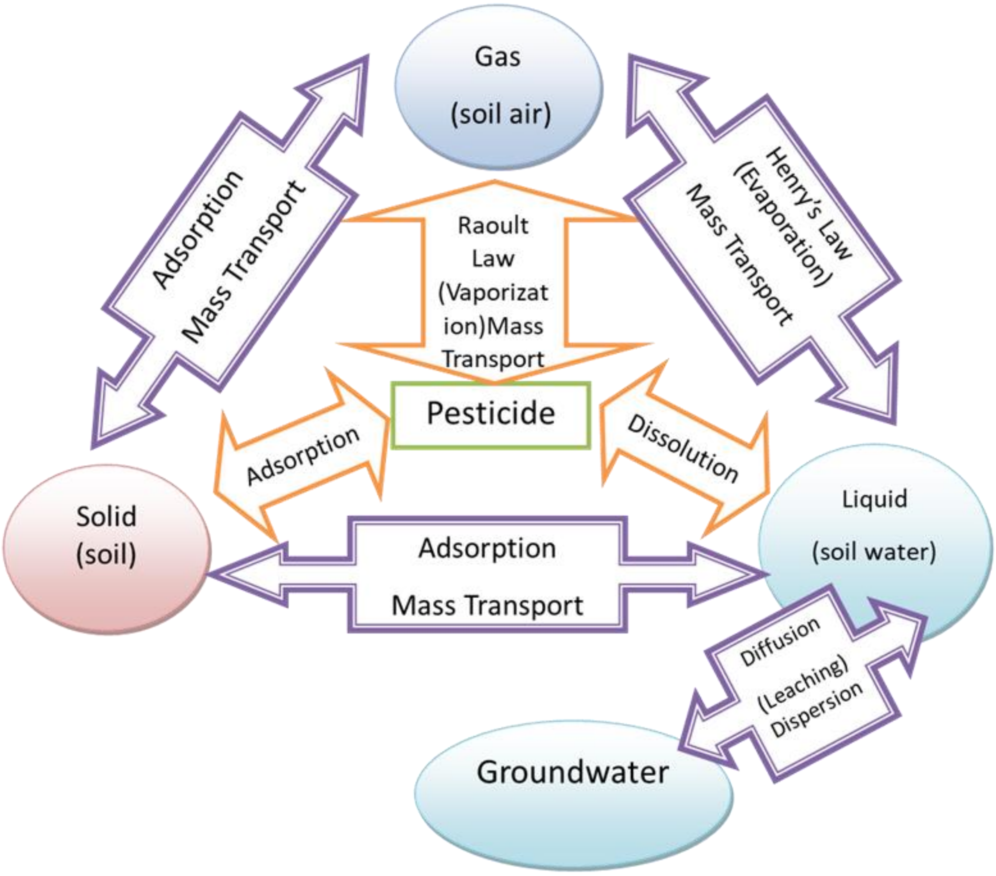

Figure 3.10. Processes that pesticides undergo during transport in the soil according to Ünlü et.al *(1995)*

Pesticide application rate, soil properties, and physicochemical properties of pesticides are the main inputs of the PESTRANS model (Table 3.19). Infiltration rate, soil properties, physicochemical properties of pesticides are required inputs of the PESTRANS model and presented previously in sections 3.3.4, 3.3.5 and 3.3.6, respectively.

Table 3.19 *Required inputs of PESTRANS model*

Soil Properties	Pesticide Properties
Bulk density (ρ_b) (g/cm^3)	Half-life ($t_{1/2}$) (day)
Volumetric air content (θ_a) (cm^3/cm^3)	Diffusion coefficient in air ($\mathcal{D}_{BA}$) (cm^2/s)
Volumetric water content (θ_w) (cm^3/cm^3)	Diffusion coefficient in water ($\mathcal{D}_{BW}$) (cm^2/s)
Dispersivity (cm)	Henry's constant (K_H) (-)
Organic carbon fraction (f_{oc}) (-)	Organic carbon partition coefficient (K_{oc}) (L/kg)
Porosity (Φ) (cm^3/cm^3)	Pesticide application rate (µg/cm^2)
Infiltration rate (cm/day)	

Details of mathematical model formulation, numerical solution of equations, the developed code and the detailed information about model inputs and model outputs of PESTRANS are presented in the final report of TÜBİTAK project (No: KTÇAG-124) called "Development of Mathematical and Computer Model to Evaluate Contamination Potential of Groundwater Resources by Pesticides" (Ünlü et al., 1995) and related paper by Ünlü et. al. (1997). In the following part mathematical model, simulation duration, and specific application rates of pesticides in each drainage area are summarized.

3.5.1. Mathematical model

The mathematical model is formulated based on the assumption of linear, equilibrium partitioning of pesticides into solid, liquid, and gas phases and the principle of mass conservation. The movement of pesticide in the soil is assumed to occur due to liquid and vapor diffusion, hydrodynamic dispersion, and advective mass transport, subject to adsorption and first-order biodegradation under one-dimensional steady-state flow conditions. Under these assumptions, the 1-D model equation of PESTRANS is given as

$$\frac{\partial C_T}{\partial t} - D_E \frac{\partial^2 C_T}{\partial z^2} + V_E \frac{\partial C_T}{\partial z} + \mu C_T = 0 \tag{11}$$

where C_T is the phased summed total concentration of the pesticide in the soil (µg/cm^3 soil); t, time (day); z, depth of soil (cm); µ, the biodegradation rate coefficient (day^{-1}); and, D_E and V_E are the effective dispersion coefficient (cm^2/day); and the effective transport velocity of pesticide (cm/day), respectively, which are parametrically described as:

$$V_E = \frac{q_S}{\rho_b\, f_{OC}\ K_{OC} + \theta_S + \theta_g\, K_H} \tag{12}$$

$$D_E = \frac{\mathcal{D}_{BA}\, K_H + \mathcal{D}_{BW}}{\rho_b\, f_{OC}\ K_{OC} + \theta_S + \theta_g\, K_H} \tag{13}$$

where q_s is infiltration rate (cm/day); ρ_b bulk density of soil (g/cm$_3$); f_{oc} is the organic carbon fraction of soil; K_{oc}, organic carbon partition coefficient (cm^3/g); θ_w, volumetric water content of soil (cm^3/cm^3); θ_g is the volumetric air content of soil (cm^3/cm^3); K_H is the dimensionless Henry's law constant; $\mathcal{D}_{BA}$ is the diffusion coefficient of pesticide in the air (cm^2/day) in soil; $\mathcal{D}_{BW}$ is the diffusion coefficient of pesticide in water (cm^2/day) (Ünlü et al., 1995).

The initial, upper, and lower boundary conditions of the model are selected as follows:

The initial conditions were assumed that the applied pesticide mass was initially distributed uniformly at the surface soil to a depth of L = 5 cm at a concentration of C_o:

$$C_T(z, 0) = C_0 \qquad if\ \ 0 < z < L$$

$$C_T(z, 0) = 0 \qquad if \qquad z > L$$

Upper boundary conditions where it is assumed that pesticide is diffused into the atmosphere along d=5 cm stagnant air layer:

$$z = 0 \qquad -D_E \frac{\partial C_T}{\partial z} + V_E\, C_T = -H_E C_T$$

where $$H_E = \frac{\mathcal{D}_{BA}{}^{o}\, K_H}{d(\rho_b\, f_{OC}\, K_{OC} + \theta_S + \theta_g\, K_H)}$$

Lower boundary conditions (free drainage conditions) (L_z = 20 cm):

$$z = L_z \qquad \frac{\partial C}{\partial z} = 0$$

Using the above described mathematical model PETRANS simulates the mass fraction of applied pesticide that is lost from the soil by volatilization, biodegradation, and leaching as well as the mass remaining in the soil. Based on the residual pesticide mass in soil (SUMM), pesticide concentration in 20 cm deep soil profile was calculated) as

$$Soil\,pesticide\,concentration\,(C_{T,M})\,\left({}^{\mu g}/_{g}\right) = \frac{SUMM\,\left({}^{\mu g}/_{cm^2}\right)}{L_z(cm) \times\, \rho_b\left({}^{g}/_{cm^3}\right)} \tag{14}$$

where SUMM is remaining pesticide mass in the soil; L_z is the soil thickness of 0-20 cm representing the topsoil where surface erosion takes place and makes the most important contribution to the formation of sediment load and subsequent pesticide load; and ρ_b is soil bulk density.

3.5.2. Simulation time

The duration of the simulation was determined as 30 days, since pesticide leaching and surface run-off are affected by weather conditions, besides the physicochemical properties of pesticides and soil properties. Transportation of a considerable amount of pesticides from agricultural land occurs overtime period between application and the first rainfall event depending on the rainfall intensity (Gönenç & Wolfin, 2005). Thus, 30 days is considered to be a reasonably conservative time for the simulation period. Moreover, this duration determined based on considering both the advective transport time (equation 15) and half-life of the pesticides (Table 3.18).

$$t_{adv}\ (day) = \frac{L_z(cm) \times \theta_w \left({cm^3}/{cm^3} \right)}{qs\left({cm}/{day} \right)} \tag{15}$$

Advective transport time was taken as the time required for the pesticides to be transported from the soil surface to a depth of L_z = 20 cm under a certain infiltration rate. Since the transport of pesticides by sediment to surface waters is mostly contributed by topsoil, 20 cm soil depth is plausible for estimations and important in terms of advective transport time. Advective transport time, which changes between 226.3 and 362.8 days according to volumetric soil content and infiltration rate of soils linked with each drainage area as presented in Table 3.16, is much longer than 30 days. Accordingly, to be conservative, pesticide half-life and 30 days are compared; if the pesticide half-life was less than 30 days, the simulation time was taken as half-life of the pesticide as presented in Table 3.20.

Table 3.20. *Simulation times of pesticides in PESTRANS model*

Pesticide	Simulation Time (day)	Pesticide	Simulation Time (day)	Pesticide	Simulation time (day)
Aclonifen	30	Beta-Cyfluthrin	30	Ethalfluralin	30
Bifenox	17.7	Cypermethrin	30	Fenpropimorph	19.6
Chlorfenapyr	30	Alpha-cypermethrin	30	Fenthion	30
Chlorothalonil	30	Zeta-cypermethrin	30	Nicosulfuron	16.4
(Chlorpyrifos) Chlorpyrifos-ethyl	30	Cyromazine	30	Prothiofos	30
Chlorsulfuron	30	Dichlorvos	0.42		
Cyfluthrin	30	Diflubenzuron	6.7		

3.5.3. A specific application rate of pesticides in each drainage area

In the PESTRANS model, the pesticide application rate (kg/ha) is used in each drainage area as input data. The required data were obtained from the PPP Database, the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry); and other sources (EFSA, 2018; Yücer, 2008; Adana Provincial Directorate of Agriculture and Forestry, 2019) which are compiled in Table 3.9, Table 3.10 and Table 3.11.

Available data shows that different doses of pesticides are recommended for different problems with respect to various agricultural products. In order to determine the active substance application rate specific to each drainage area, the maximum application rates out of recommended application rates and reported application rates for each agricultural product in the counties have been determined. An example of the comparison between recommended and reported application rates for Merzifon county of Amasya province is presented in Table C.9 in the Appendix C. For instance, according to Table C.9 in Appendix C, reported application rate of Alpha-Cypermethrin for apple is higher than the maximum recommended application rate, thus, as a conservative approach, reported application rate is used for diffuse pesticide load estimations. There is no reported pesticide use for poppy, walnut, and some other crops; thus it is assumed that there is no pesticide use for these crops. However, for banned pesticides (see Table 3.11), since there isn't any reported use, but they are detected in water quality monitoring results, they are assumed to be applied for related crops. Tables similar to Table C.9 were produced for all counties, yet since they are too long, summarized versions of them were presented previously in Table 3.9, Table 3.10 and Table 3.11.

Since more than one county can be located in the same drainage area, the county boundary map, the drainage area map, and the CORINE 2012 Land Cover map are overlaid in the GIS-based program (see Figure 3.5) to identify agricultural areas in each drainage area. Results are presented in Appendix B. As an example, results for the drainage area YB06 are presented in Figure 3.11 and Table 3.21. As presented in Figure 3.11, YB06 drainage area and its CORINE 2012 agricultural areas are split by Havza and Merzifon county borders. Thus, it is seen that most of the agricultural areas in YB06 drainage area are within Havza county.

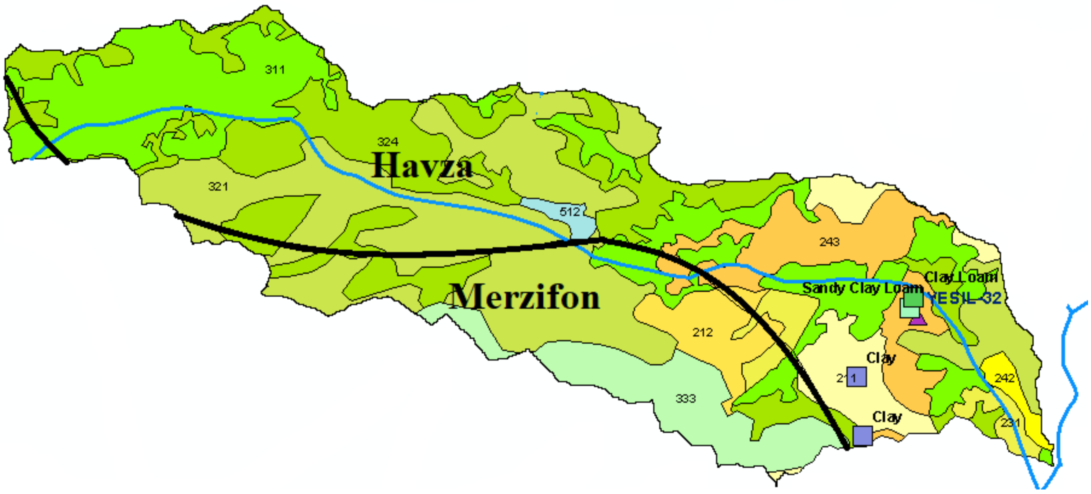

Figure 3.11. CORINE 2012 Land Cover map and county borders of YB06 drainage area

Table 3.21. *CORINE 2012 Land cover agricultural areas of drainage area YB-06*

Class Code	**Class Name**	**Havza**	**Merzifon**
211	Non-irrigated arable land (ha)	220,1	12,7
212	Permanently irrigated land (ha)	19,2	138,7
242	Complex cultivation (ha)	38,0	None
243	Land principally occupied by agriculture, with significant areas of natural vegetation (ha)	346,6	18,3

CORINE 2012 agricultural area classes do not provide precise information about agricultural crops; thus the agricultural land codes were paired with the crop areas reported in TURKSTAT (see Table C.9 in Appendix C) according to land cover class explanations of CORINE 2012 (MoAF, 2017). These CORINE land cover class explanations include the most probable agricultural products. For example, it is indicated that 211: Non-irrigated arable land class is comprised of regular annual crops, such as cereals, oil, leguminous, and root crops; semi-permanent crops as strawberries; tobacco; weeds, etc.

Since the amount of pesticides that are transported depends largely on the application area, the size of the application areas of the pesticides should be determined. For this purpose, after pairing the TURKSTAT products with the CORINE classes, the percentages of crops within the paired class are obtained. Areas of the CORINE classes were multiplied with these percentages of TURKSTAT crop areas with respect to paired CORINE classes. For example, crops matched with 211 and 24 classes in YB06 drainage area and their estimated areas in CORINE map are given in Table 3.22 and Table 3.23. The point is, it is assumed that crops of counties stated in TURKSTAT are represented in CORINE 2012 agricultural areas according to CORINE Land Cover class specifications.

Table 3.22. *TURKSTAT crops matched with CORINE 2012 211 class and their percentages in 211 class*

Crops	**Average areas (da) (TURKSTAT)**	**Percentage of crops in terms of area**	**CORINE areas (ha)**
Wheat	20176,2	49,20%	6,2
Sunflower	8082,9	19,71%	2,5
Barley	4758,3	11,60%	1,5
Sugar beet	2220,4	5,41%	0,7
Corn	557,8	1,36%	0,2
Chickpea	300,0	0,73%	0,1
Potato	109,9	0,27%	0,03

Using CORINE 2012 Land Cover agricultural areas and the arithmetic average of TURKSTAT 2015-2016-2017 years crop areas, weighted average of application rates thus, specific application amounts for each drainage area were obtained.

Table 3.23. *Percentages of TURKSTAT crops in total area and matching of crops with CORINE class 2012/24*

Crops	**Average areas (da) (TURKSTAT)**	**Percentage of crops in terms of area**	**CORINE areas (ha)**
Walnut	184,9	%24,30	4,45
Apple (Amasya)	120,8	%15,88	2,91
Apple (Other)	100,7	%13,23	2,42
Cherry	99,2	%13,03	2,39
Apple (Starking)	87,6	%11,52	2,12
Seeded grape	54	%7,10	1,3
Apple (Golden)	42,4	%5,57	1,02
Wine grape	40,03	%5,26	0,96
Apple (Granny Smith)	11,03	%1,45	0,27
Peach	6,1	%0,80	0,15
Quince	5,3	%0,70	0,13
Pear	5,1	%0,67	0,12
Sour cherry	3,7	%0,49	0,09
Total (da)	760,9	%100	

For example, active substance Aclonifen, an herbicide, has been proposed in different dosages to sunflower and chickpea crops according to the data obtained from the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry) and in the PPP Database (Section 3.3.3). Table 3.24 presents the maximum rates of Aclonifen active substance that can be applied to the crops in Havza and Merzifon counties. The weighted average of the application rate of Aclonifen for YB06 drainage area was found by multiplying the areas and application amount and then by dividing it to the total area. Thus, the application rates required to run the PESTRANS model are obtained as presented in Table 4.6.

Table 3.24. *Application rates of Aclonifen in YB06 drainage area*

Crops	Code	CORINE area (ha)	Maximum application rate (kg/ha)	The weighted average (kg/ha)
		Havza County		1,88
Sunflower	211	35,25	1,95	
Chickpea	211	2,39	1,2	
		Merzifon County		
Sunflower	211	2,59	1,95	
Chickpea	211	0,1	1,2	

3.6. Estimation of diffuse pesticide loads

According to McElroy (1976), diffuse pollution load reaches surface waters by total erosion mechanics and transportation of sediments. The following equation of McElroy (1976) was used in the calculation of the diffuse pesticide load in Tersakan Sub-basin:

$$\begin{aligned} &Pesticide\ Load\ (PL)\left({}^{mg}/_{day}\right) \\ &\quad = Soil\ Pesticide\ Concentration\ (C_{T,M})\left({}^{mg}/_{kg}\right) \\ &\quad \times Sediment\ Yield\ (SY)\left({}^{ton}/_{year}\right) \\ &\quad \times \frac{Pesticide\ application\ area\ (ha)}{Total\ agricultural\ area\ (ha)} \times 2.74 \end{aligned} \tag{16}$$

Here, the coefficient of 2.74 is required for unit conversion. This equation requires data on sediment load and pesticide concentration in soil. The previous sections describe in detail how sediment loads (Section 3.4) and soil pesticide concentrations (Section 3.5) are determined. Since sediment yields represent whole agricultural lands, they are proportioned according to the estimated pesticide application areas by dividing the pesticide application area to total agricultural area as presented in equation (16) in and Section 3.5.3

The pesticide concentrations that diffuse pesticide loads can create in the Tersakan Creek (C_{est}) are calculated as

$$Estimated\ Concentration\ (C_{est})\ \left({}^{\mu g}/_{L}\right) = \frac{Pesticide\ Load\ (PL)\ \left({}^{mg}/_{day}\right)}{Flow\ rate\ (Q)\ \left({}^{m^3}/_{s}\right)\ \times 86400} \tag{17}$$

where pesticide load is estimated previously in equation (16); flow rates gathered from water quality monitoring study are presented in Table E.25 in Appendix E; 86400 is required for unit conversion. Estimated pesticide concentrations are obtained *using corresponding flow rate measurement* at the period when particular EQS exceeding concentration of a pesticide is observed in water quality measurements. For example, in order to obtain the estimated concentration of Aclonifen developed from diffuse loads of YB01 drainage area, flow rate when Aclonifen active substance exceeds EQS in Y-40 receiving body sampling point at 2nd period is used. Previously it was presented that Y-40 receiving body sampling point is paired with YB01 drainage area (see Table 3.3). Another point worth mentioning is that in order to estimate potential concentrations of Aclonifen developed from other drainage areas, an *average of 8-period flow rate measurements* belongs to paired receiving body sampling point is used since Aclonifen doesn't exceed in other receiving body water quality measurements. The same approach is applied to all concentration (C_{est}) estimations and, Table E.25 in Appendix E is prepared accordingly. Furthermore, Y-31 and Y-97 receiving body sampling points are missing few flow rate measurements due to stagnant water and insufficient flow. Thus average of obtained flow rate measurements are used for drainage areas paired with these sampling points. This flow rate adjustment is performed to make estimated and observed concentration comparisons plausible.

Estimated concentration (C_{est}) is compared to water quality monitoring results to assess the relevance of the estimation of diffuse pesticide loads. These comparisons and their interpretation are presented in Section 4.4 of Chapter 4.

3.7. Recommended pesticide application rates to comply with EQSs

Pesticide application rates satisfy the environmental quality standard (EQS) were calculated in order to determine the maximum quantities that can be applied in agricultural crops of the drainage areas and to interpret the reported and recommended values mentioned in Section 3.3.3.

Firstly, pesticide loads may occur on the threshold are estimated using EQS concentrations and the flow rates presented in Appendix E as

$$\begin{aligned} &Pesticide\ Load\ (PL)\left({}^{mg}/_{day}\right) \\ &= EQS\ (C_{EQS})\left({}^{\mu g}/_{L}\right) \times Flow\ rate\ (Q)\left({}^{m^3}/_{s}\right) \times 86400 \end{aligned} \tag{18}$$

where the value, 86400 is for unit conversion. Secondly, corresponding soil pesticide concentrations, $C_{T,M}$, are estimated using pesticide loads, sediment yields of total agricultural area (see Section 3.4) and pesticide application areas (see Section 3.5.3) as:

$$\begin{aligned} &Soil\ Pesticide\ Concentration\ (C_{T,M})\left({}^{mg}/_{kg}\right) \\ &= \frac{Pesticide\ Load\ (PL)\left({}^{mg}/_{day}\right)}{Sediment\ Yield\ (SY)\left({}^{ton}/_{year}\right) \times \frac{Pesticide\ application\ area\ (ha)}{Total\ agricultural\ area\ (ha)} \times 2.74} \end{aligned} \tag{19}$$

where 2.74 is for unit conversion.

In order to make the transition from soil pesticide concentration to the application rate of pesticide which ultimately satisfy the EQS, it is necessary to know the residual pesticide mass in 20 cm depth soil, SUMM, and the percentage of the residual pesticide mass in the soil, $R_{\%}$, both of which are obtained from the PESTRANS model. SUMM was calculated from:

$$SUMM\left({}^{\mu g}/_{cm^2}\right) = Soil\ pesticide\ concentration\left(C_{T,M}\right)\left({}^{\mu g}/_{g}\right) \times L_z(cm) \times \rho_b\left({}^{g}/_{cm^3}\right) \tag{20}$$

where L_z is topsoil depth (20 cm) and ρ_b is soil bulk density. And finally, the application rate of pesticides corresponding to the EQS for each drainage area (AppRate (kg/ha)) is calculated as:

$$AppRate\left({}^{kg}/_{ha}\right) = \frac{SUMM\left({}^{\mu g}/_{cm^2}\right)}{R_{\%} \times 10} \tag{21}$$

where the value 10 is for unit conversion; the values for percentage of the residual pesticide mass in the soil ($R_{\%}$) are estimated by PESTRANS simulations (see Chapter 4, Table 4.8) The overall results are presented and discussed in Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, results of water quality monitoring, sediment yield modeling study, pesticide fate, and transport modeling study, estimation diffuse pesticide loads and diffuse source control measures are presented and discussed. It is determined from water quality monitoring studies that 22 pesticides out of 57 are exceeding EQS in receiving body and discharge samples. After the identification of the pesticides that exceed EQS, their diffuse loads are estimated using the results of sediment yield and pesticide fate and transport modeling study. The upstream and downstream relationships between the receiving environment, discharge points and diffuse loads are taken into consideration, and estimated diffuse pesticide loads are compared with the receiving body and discharge sampling point loads. As a result of these comparisons, it is seen that pesticide pollution caused mainly by a diffuse load is limited to the certain drainage areas of the Tersakan Sub-basin. Although the diffuse pollution load estimation methodology revealed the diffuse pollution potential of the pesticides in the drainage areas, difficulties are encountered for some pesticides due to the high uncertainities in areal extent of pesticide application.

The drainage areas with remarkable pesticide contamination due to both point and diffuse sources are marked red in Figure 4.1, representing the main flow chart of Tersakan Sub-basin. These drainage areas starting from the upstream part of the Tersakan Creek are YB01, YB06, YB11 + YB12, and YB16. They are not related to each other topologically. Therefore, in Section 4.5, local diffuse source control measures are proposed for these areas. Moreover, in Figure 4.1, red boxes and green boxes represent discharge and receiving body sampling points, respectively. The names of the sampling points were presented earlier in Table 3.4. Boxes that cover the sampling points and the main flow line represent the drainage areas. Their layout can be followed from the map presented in Figure 3.4; in other words, Figure 4.1 is simplified and schematized representation of Figure 3.3. In the following sections these drainage areas and their pollution loads will be examined in detail.

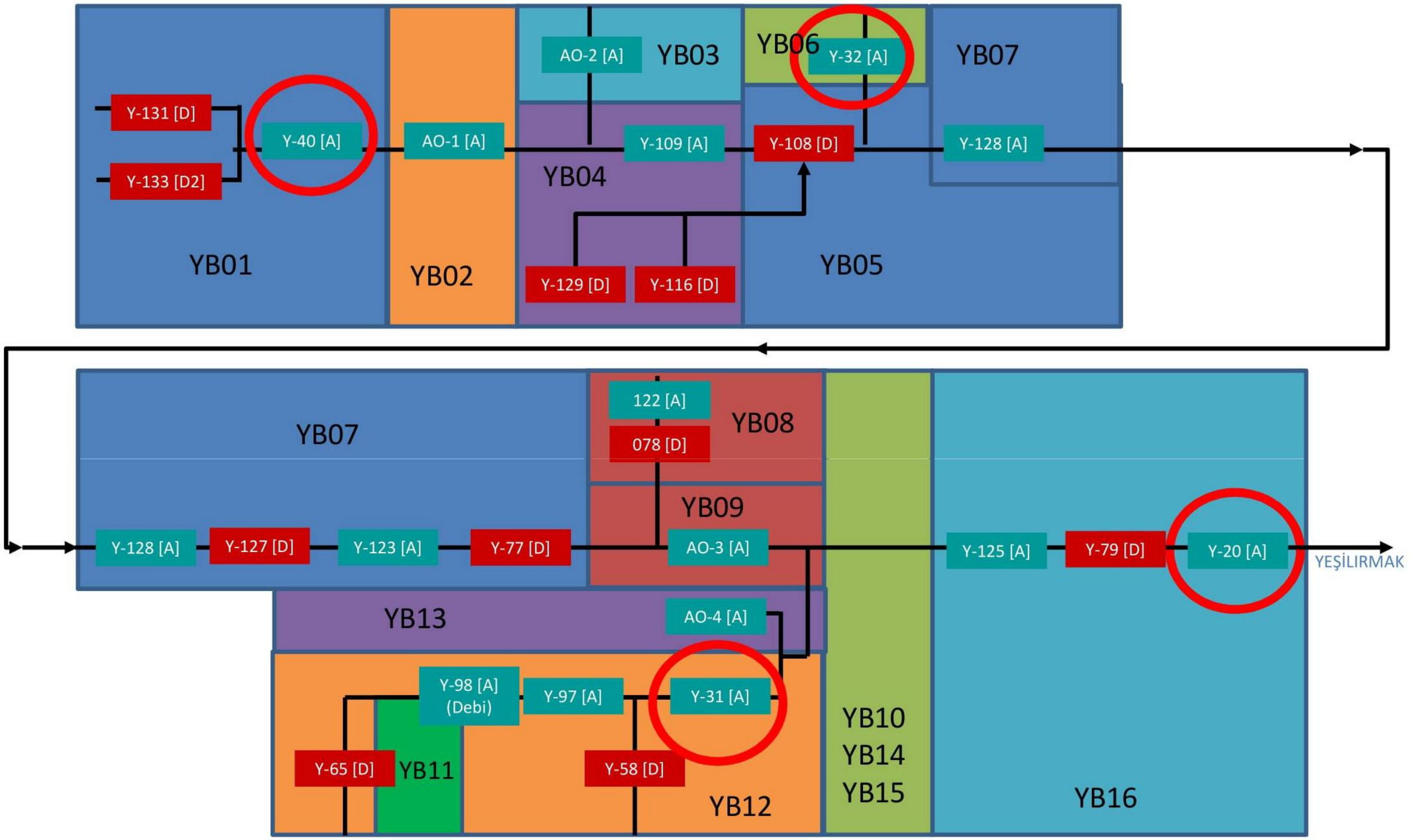

Figure 4.1. Flow chart of Tersakan Sub-basin containing receiving body and discharge sampling points and prominent drainage areas

4.1. Implications of Water Quality Monitoring Data

Determination of the water quality status of the Tersakan Creek is carried out through the results of the implemented monitoring program in the context of Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin Project presented in Section 3.3.1 of Chapter 3. Receiving body and discharge water sample analyses revealed that concentrations of 22 pesticides, out of the detected 57 pesticides, exceeded the pre-defined EQSs. Remaining 35 pesticides, concentrations of which are between LOD and EQSs, are presented in Table 4.1. The detected active substances were measured at least 1 to 12 times as indicated in the brackets, concentrations between LOD and EQS. Twenty pesticides that exceed EQS were monitored in receiving body sampling points are given in Table 4.2. The other two active substances, o, p'-DDT and p, p'-DDE, which are the metabolites of the prohibited active substance DDT, exceeded the EQS only in discharged wastewater sampling points.

Table 4.1. Pesticides that their concentration exceeds EQS or are just detected in Tersakan Creek water quality monitoring study

Pesticides that exceed EQS (EQS<C)		**Pesticides that just detected (LOD<C<EQS)**		
Aclonifen	Cyromazine	4,4'-DDD	Fosetyl-Al (2)	Pendimethalin
Bifenox	Dichlorvos	Azoxystrobin	Imazalil (2)	Pirimicarb (2)
Chlorfenapyr	Diflubenzuron	Captan (3)	Imidacloprid (12)	p,p'-DDT (2)
Chlorothalonil	Ethalfluralin	Carbaryl	Isoproturon (3)	Procymidone (2)
Chlorpyrifos-ethyl	Fenpropimorph	Carbendazim (5)	Lenacil (3)	Propamocarb HCl
Chlorsulfuron	Fenthion	Clopyralid	Mesotrione	Pyrimethanil (2)
Beta-cyfluthrin (Cyfluthrin)	Nicosulfuron	Clothianidin	Metalaxyl	Tebuconazole (3)
Cypermethrin	o,p'-DDT	DDT	Metamitron	Thiacloprid (2)
Alpha-cypermethrin	p,p'-DDE	Epoxiconazole (9)	Methidation	Thiamethoxam (4)
Beta-cypermethrin	Prothiofos	Ethofumesate (2)	Metolachlor	Trifloxystrobin
Teta-cypermethrin		Fluroxypyr (3)	Monocrotophos	Trinexapac-ethyl (2)
Zeta-cypermethrin		Flutriafol	Myclobutanil	

Numbers in parentheses indicate how many times they have been detected.

As presented in Table 4.2, Dichlorvos and Alpha-Cypermethrin active substances exceed EQS 6 times in total. Cypermethrin and its isomers, Beta-Cyfluthrin (Cyfluthrin) and Dichlorvos, have exceeded their EQS values at least 45 and a maximum of 2813 folds. Alpha-Cypermethrin (see Figure 4.2), Dichlorvos (see Figure 4.3), Theta-Cypermethrin, and Prothiofos (see Figure 4.4) pesticides were detected for two periods at the same receiving body sampling point. Other pesticides were observed at a single period at different points. In the 7th period, pesticide concentrations didn't exceed EQS; therefore, it is not included in Table 4.2.

Table 4.2 Distribution of occurrence and multiplier of EQSs of pesticides that exceed EQS in the Tersakan River at least once

Pesticides/Period	1	2	3	4	5	6	8	Multiplier
Aclonifen (Herbicide)		1						7
Bifenox (Herbicide)						3		9-20
Chlorfenapyr (Insecticide)				2				1-2
Chlorothalonil (Fungicide)				1				2
Chlorpyrifos (Insecticide)			1					1
Chlorsulfuron (Herbicide)		3						1-4
Cyfluthrin (Beta-Cyfluthrin) (Insecticide)				1				316
Cypermethrin (Insecticide)				4				1082-2750
Alfa-Cypermethrin	1	1		4				94-2813
Beta-Cypermethrin	1	1						153-1150
Teta-Cypermethrin				1				1607
Zeta-Cypermethrin	1			1				576-1675
Cyromazine (Insecticide)	a		1, a					1
Dichlorvos (Insecticide)	3	2					1	45-712
Diflubenzuron (Insecticide)		1			a			19
Ethalfluralin (Herbicide)		1, a		1				1-11
Fenpropimorph (Fungicide)				1				7
Fenthion (Insecticide)		1						4
Nicosulfuron (Herbicide)						1		2
Prothiofos (Insecticide)	a	1						2

a: Pesticide exceeding EQS at least once is also detected between LOD and EQS.

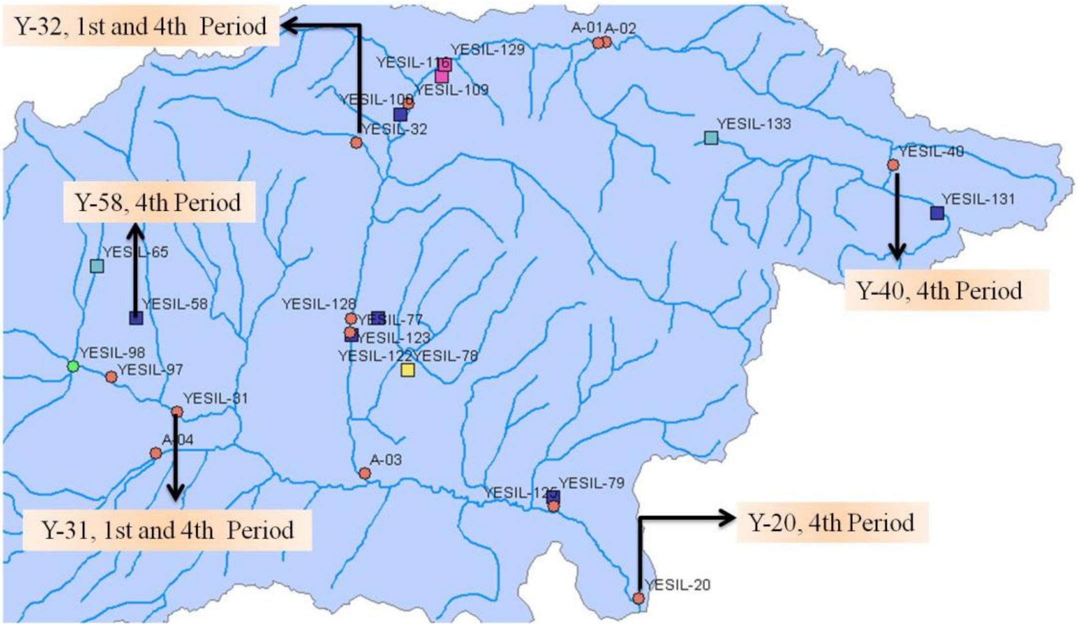

Figure 4.2 The points and periods in which Alpha-Cypermethrin exceeds the EQS (orange circles in the figure indicate the receiving medium and the squares indicate the points where the discharge samples are taken.)

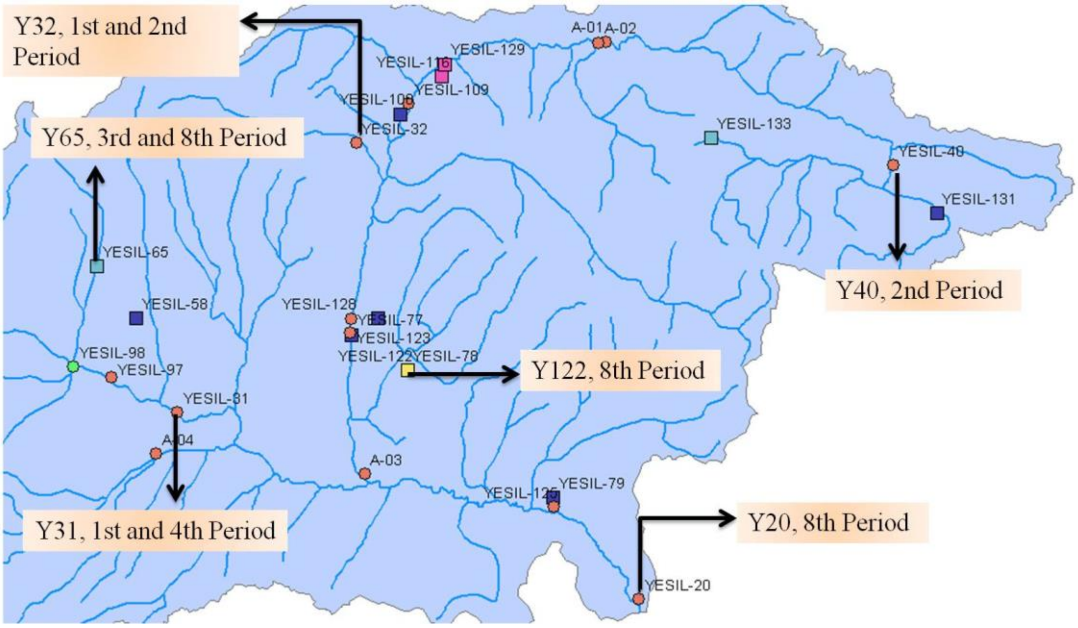

Figure 4.3. Points and periods in which Dichlorvos exceeds EQS (orange circles in the figure indicate the receiving medium and the squares indicate the points where the discharge samples are taken.)

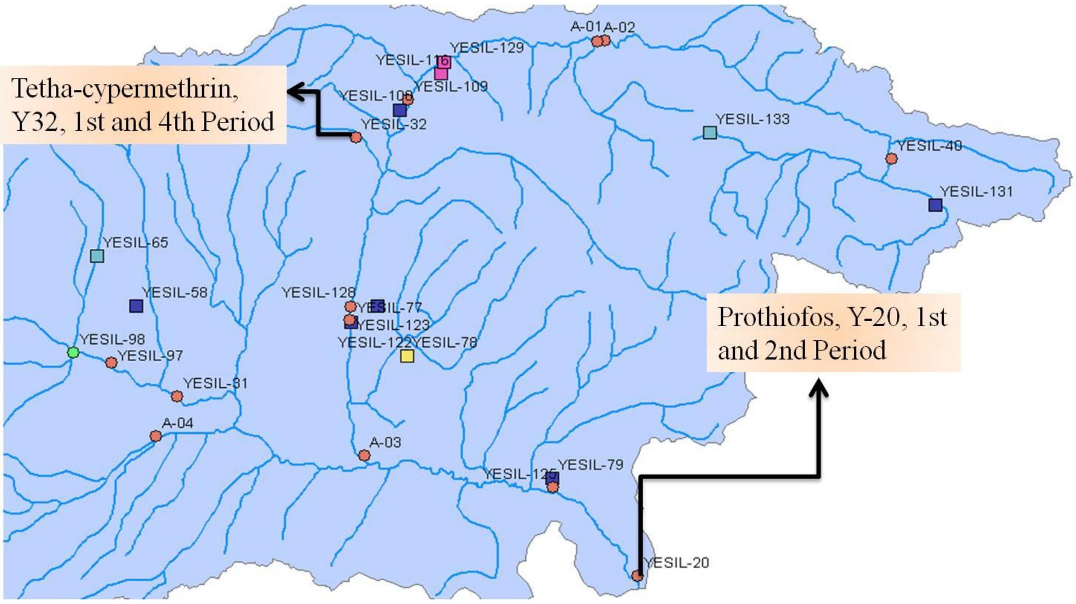

Figure 4.4 Sampling points where Theta-cypermethrin exceeds EQS and Prothiofos has been detected in the 1^{st} period and exceeded the 2^{nd} period has exceeded the EQS. (orange circles in the figure indicate the receiving medium and the squares indicate the points where the discharge samples are taken.)

Pesticides exceeding EQS in WWTP discharge samples are given in Table 4.3. o, p'-DDT and p, p'-DDE, as well as some of the active substances that exceed EQS in the receiving body, has found to be exceeding EQS also in WWTP discharges. Alpha-cypermethrin exceeds the EQS concentration at Y-58 discharge point 1478 folds (see Figure 4.2).

Table 4.3. *Distribution of occurrence and multiplier of EQSs of pesticides that exceed EQS in the WWTP discharge samples in the Tersakan Sub-Basin*

Pesticides/Period	1	2	3	4	5	6	8	Multiplier
Chlorfenapyr				1				4
Alpha-Cypermethrin				1				1478
Dichlorvos			1				2	29-68
Ethalfluralin				1				22
Fenpropimorph				1				6
o,p'-DDT							1	1
p,p'-DDE							1	1

In terms of pesticide pollution, Y-40, Y-32, Y-31 and Y-20 receiving sampling points are standing out, thus their periodic monitoring results are compared with monthly rainfall amounts presented by Turkish State Meteorological Service (2019-a). It is noted that in these sampling points during October (2nd period) and April (4th period) two or more EQS exceeding pesticide concentrations are detected. These months are also most rainy months for Amasya and Samsun provinces. Thus, these concentrations may be due to the rainfall (intensity) which is higher than the infiltration capacity of the soil (Critchley, Siegert, & Chapman, 1991). In other months such as August (1st period), wild irrigation may lead to EQS exceeding concentrations.

Discharge points Y-131 and Y-133 precede Y-40 receiving body sampling point (the outlet of Lake Ladik). There is no exceedance of pesticides in these discharge points. However, in Y-40 receiving body samples, Aclonifen, Bifenox, Chlorothalonil, Chlorsulfuron, Dichlorvos, Ethalfluralin, Cypermethrin, and Alpha-Cypermethrin pesticides were found to exceed EQS. In these conditions, the pollution at Y-40 is considered to be originating mainly from diffuse sources.

At the Y-32 receiving body sampling point, where no discharge point was specified before, Bifenox, Chlorfenapyr, Chlorsulfuron, Dichlorvos, Diflubenzuron, Ethalfluralin, Fenpropimorph, Nicosulfuron, Cypermethrin, Alpha-Cypermethrin, Beta-Cypermethrin, Cypermethrin active substances exceeded EQS at least once. In these conditions, the pollution detected at Y-32 was evaluated as diffuse-origin.

In order to determine if loads of Chlorfenapyr, Dichlorvos, Alpha-cypermethrin, Fenpropimorph, and Ethalfluralin active substances are attributable to diffuse sources or point sources, a mass balance approach is considered using concentration of samples, flow rate (see Table E.25 in Appendix E) and flow chart of the stations (see Figure 4.1) as presented in Table 4.4. Here gray boxes represent EQS exceeding concentrations. Due to lack of Y-31 receiving body flow rate data (could not be obtained due to insufficient flow) and the start of sampling from Y-97 discharge point is from the 6th period, the highest flow rate measured during the other monitoring periods of the same points are used during mass balance calculations. These are the 8th period of Yeşil-97 and the 1st period of Yeşil-31. According to guidance documents of US EPA (2019) and OECD (2019), concentrations below the LOD were taken as half of the LOD during load calculations.

As presented in Table 4.4 (based on the flow chart in Figure 4.5) mass balance of Chlorfenapyr, Dichlorvos (3rd period), Alpha-Cypermethrin, and Fenpropimorph active substances which exceed EQS in WWTP discharges shows that the load in the following receiving body point is higher than the discharge load. Alpha-cypermetrin monitoring results at 4th period show that it exceeds EQS both in discharge and receiving body sampling point, it can be said that Y-58 discharge point contributes to the pollution in the receiving body approximately 6% (considering average flow rates). There is approximately 9 km distance between Y-65 and Y-97 points, and approximately 8 km between Y-58 and Y-31 points. Considering the factors such as dilution, degradation, evaporation, and adsorption to which active substances are exposed to during the transport in the Creek, it has been evaluated that the contribution of point sources to the pollution in the receiving body is not high and the pollution is largely diffuse-origin.

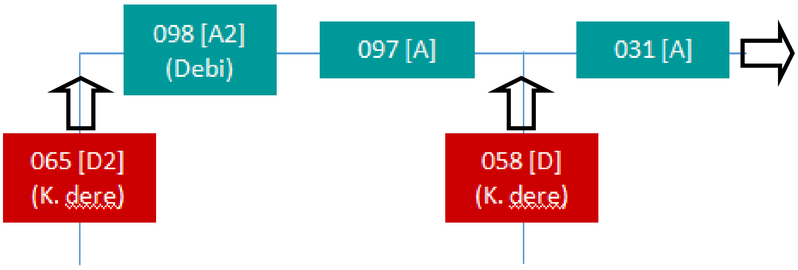

Figure 4.5. Flow chart of Y-97 and Y-31 receiving body; and Y-65 and Y-58 discharge points

The discharge loads of Dichlorvos (8th period Y-65) and Ethalfluralin appear to be higher than the subsequent receiving body loads in the flow chart (see Figure 4.5 and Table 4.4). Under such conditions, it was evaluated that the point discharges of the active substances Dichlorvos and Ethalfluralin were diluted, degraded, evaporated, and adsorbed or *contributed to the total load*.

Table 4.4. *Mass balance of pesticides which exceed EQS in WWTP Discharges*

		Previous RB Point	**Discharge exceeding EQS**	**Following RB Point**
Chlorfenapyr		**Y-97**	**Y-58**	**Y-31**
	Flow rate (m^3/s)	0.1052	0.0035	0.1166
	Conc. (µg/L)	0.0025*	0.025	0.0025*
	Load (mg/day)	22.7318	7.7964	25.1762
Dichlorvos (3rd period)		**None****	**Y-65**	**Y-97**
	Flow rate (m^3/s)	0	8.75E-05	0.1052
	Conc. (µg/L)	0	0.033451	0.00025*
	Load (mg/day)	0	0.2529	2.2732
Dichlorvos (8th period)		**None****	**Y-65**	**Y-97**
	Flow rate (m^3/s)	0	0.0056	0.1052
	Conc. (µg/L)	0	0.040918	0.00025*
	Load (mg/day)	0	19.6404	2.2732
Alpha-Cypermethrin		**Y-97**	**Y-58**	**Y-31**
	Flow rate (m^3/s)	0.1052	0.0035	0.1166
	Conc. (µg/L)	0.0025*	0.1183	0.086546
	Load (mg/day)	22.7318	35.4779	871.559
Fenpropimorph		**Y-97**	**Y-58**	**Y-31**
	Flow rate (m^3/s)	0.1052	0.0035	0.1166
	Conc. (µg/L)	0.05*	0.6207	0.05*
	Load (mg/day)	454.6368	186.1975	503.5235
Ethalfluralin		**Y-97**	**Y-58**	**Y-31**
	Flow rate (m^3/s)	0.10524	0.0035	0.1166
	Conc. (µg/L)	0.025*	6.557092	0.025*
	Load (mg/day)	227.3184	1967.128	251.7618

*RB: Receiving Body, Conc.: Concentration, *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2), ** There is no sampling point before the discharge for comparison.*

Fosetyl-Al and Epoxiconazole active substances are detected in Y-58 and Y-31 sampling points in different periods. It is reported that reflection of seasonal and weather-related variations in pesticide concentrations, and pesticide risk can be failed by grab sampling monitoring since single samples taken at a specific time (EC, 2018). Thus, monitoring of these sampling points and pesticides should be continued in future studies.

Results showed that the contribution by the discharges of point sources to the overall pollution load was a relatively minor issue. Therefore, an estimation of diffuse pesticide loads is required. Mass balance assessments are performed by taking into consideration water quality monitoring and diffuse load estimation results in Section 4.4.

4.2. Sediment yield of the drainage areas

Estimation of diffuse pesticide loads partly depends on the sediment yield of the drainage areas. The methodology of sediment yield estimation suing the DEMIS model is presented in Section 3.4 of Chapter 3. DEMIS model provides as the major output total soil loss by water erosion, sediment delivery ratio and sediment yield for each drainage area in Tersakan Sub-basin. Sediment yield map of Tersakan Sub-basin and the results are presented in Figure 4.6 and Table 4.5. In the figure sediment yield is highest in the dark areas. These areas have rather high altitude and steep slope.

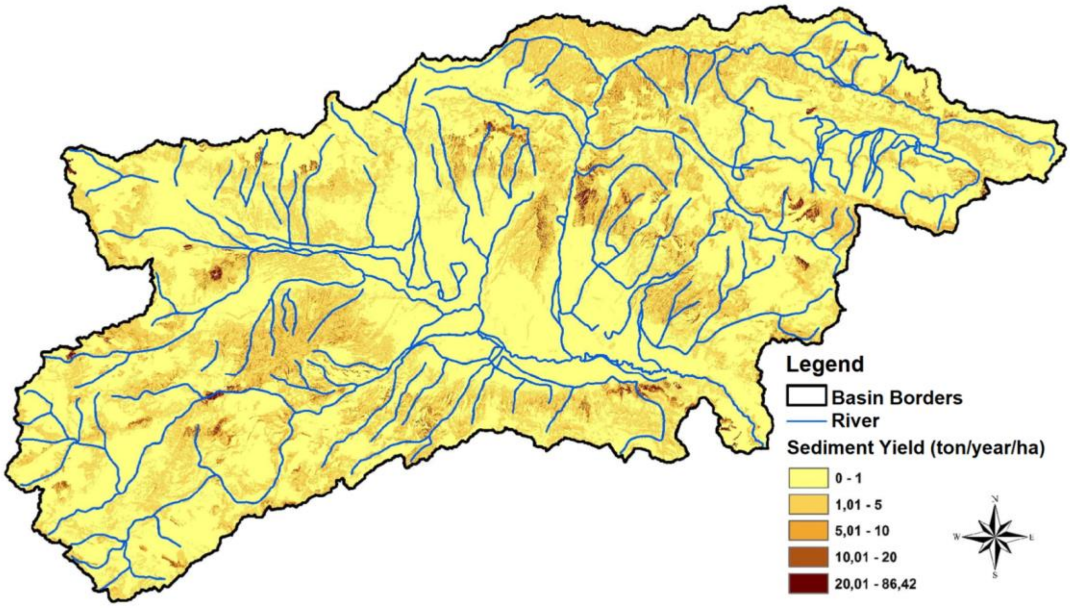

Figure 4.6. Sediment yield map of Tersakan Sub-basin

As seen from Table 4.5 sediment delivery ratio is changing between 0.259 and 0.337, while the sediment yield of agricultural areas is changing between 4,332.2 tons/year and 53,626.1 tons/year. Moreover, the sediment delivery ratio is increasing as size of the area is decreasing depending on the area according to the equation (10). Drainage areas of YB04, YB08, YB09, YB10, YB11, YB12 and YB14 are mostly comprised of agricultural land. Contribution of agricultural areas to total sediment yield changes between 53% and 94%. Thus, their sediment yield is mostly originated from agricultural areas.

Even if, YB02, YB03, YB05, YB13 and YB15 drainage areas mostly covered with forests, pastures, and artificial areas, their sediment yield is mostly originated from agricultural areas; 53 to 74% of total sediment yield is contributed by agricultural land, while only the 39 to 49% of total area is agricultural land. This situation shows that soil particles in these areas are more prone to slope, detachment, and transport by rainfall and runoff.

Table 4.5. *Sediment delivery ratio, agricultural and total areas, total erosion and, sediment yield of 16 drainage area of Tersakan Sub-basin*

Code of Drainage Area	Erosion in total drainage area				Erosion in agricultural areas of drainages		
	Total area (km^2)	Sediment Delivery Ratio (S_d) (-)	Total Soil Loss (tons/year)	Sediment Yield (tons/year)	Agricultural areas (km^2)	Total Soil Loss (tons/year)	Sediment Yield (tons/year)
YB-01	143.27	0.298	62,155.6	26,014.4	53.33	37,098.8	12,867
YB-02	158.68	0.295	88,912.3	33,388.4	77.95	77,265.5	24,681.4
YB-03	73.26	0.321	30,709.6	13,299.2	33.52	24,322	8,716
YB-04	132.67	0.301	127,913.0	42,436.2	102.24	122,945.9	38,974.8
YB-05	23.01	0.365	20,311.8	8,264.8	10.53	15,532.3	5,869.1
YB-06	45.09	0.339	21,342.0	9,094.1	6.38	6,922.3	2,461.6
YB-07	169.11	0.293	178,397.1	58,385.2	67.38	78,183.2	24,633.7
YB-08	90.63	0.314	71,692.9	25,747.7	57.50	54,196.3	18,555
YB-09	47.50	0.337	10,655.2	6,330	43.18	7,213.1	4,978.4
YB-10	188.74	0.289	99,819.3	37,656.5	100.44	44,754	16,988.5
YB-11	66.42	0.325	68,375.2	23,967.8	60.83	64,786.8	22,605.4
YB-12	521.11	0.259	275,171.8	95,605.1	295.20	163,250.5	53,815
YB-13	509.94	0.259	302,935.3	101,469.3	250.68	173,368.6	53,626.1
YB-14	266.94	0.279	164,474.9	57,398.1	180.06	103820.7	36,171.7
YB-15	166.96	0.293	107,775.7	39,166.8	65.11	80,074.6	25,092
YB-16	55.38	0.331	27,259.9	11,663	15.33	11,748.2	4,332.2

Sediment yield originated from YB01, YB06, YB07, and YB16 drainage agricultural areas changes between 27% and 49 % of total sediment yield. Contribution of forests, pastures and artificial areas to the total sediment yield cannot be ignored; still agricultural areas are important sediment sources for these drainage areas. Since values are estimated using count of pixels and average soil loss class, direct multiplication doesn’t express the results of total soil loss, sediment yield, and sediment delivery ratio.

Sediment yields originating from agricultural areas were subsequently used for estimation of diffuse pollution loads of pesticides based on the methodology described in Section 3.6 of Chapter 3. In Section 4.4, their results are discussed.

4.3. Pesticide fate and transport modeling study

Pesticide fate and modeling study is carried through using PESTRANS model as presented in Section 3.5 for each drainage area. Previously input requirements of PESTRANS mentioned in Table 3.19 are fulfilled as presented in Section 3.3; such as physicochemical properties presented in Table 3.18 and specific pesticide application rates for drainage areas presented in Table 4.6 are used for the modeling.

Pesticide fate and modeling results of the drainage areas show mostly similar results as they are assigned with the same soil texture. Results of YB06 drainage area is presented in Table 4.7 and other drainage areas in Appendix D. As seen in Table 4.7, SUMM, PCDECM, PCVAPM, PCDRM, PCTMR, PCTML are important outputs of PESTRANS model which stand for remained pesticide mass on soil, degraded pesticide mass, evaporated pesticide mass, leached pesticide mass, remained pesticide mass on soil ($R_{\%}$), pesticide mass lost from the soil (%), respectively. SUMM and PCTMR represent remaining mass and remaining percent mass of pesticide after application of pesticides with a rate presented in Table 4.6 to soil. Following the application, pesticides undergo degradation, evaporation, and leaching to the deeper part of soil from 20 cm depth. Thus, active substances are lost from the top 20 cm soil medium due to these processes.

YB01, YB03, and YB06 drainage areas are assigned with clay loam soil as presented in Section 3.5, thus their results are quite identical. However due to low organic carbon fraction of YB06 soil, and also due to having low organic carbon partition coefficient (K_{oc}<500) Chlorsulfuron, Beta-cyfluthrin, Cyromazine, and Nicosulfuron active substances tend to leach to the deeper part of soil more. In Chapter 2.2, it was mentioned that Holvoeta et al. (2007) states pesticides with organic carbon partition coefficient (K_{oc}) smaller than 1000 L/kg are transported mainly by water since they are not adsorbed strongly to the soil particles. Moreover, these pesticides seem to not evaporate due to having rather low Henry's constant.

Table 4.6. *Pesticide application rates of each drainage area to be used in PESTRANS model*

	Pesticide application rates (AppRate) (kg/ha)															
Pesticides / Drainage Areas	**YB01**	**YB02**	**YB03**	**YB04**	**YB05**	**YB06**	**YB07**	**YB08**	**YB09**	**YB10**	**YB11**	**YB12**	**YB13**	**YB14**	**YB15**	**YB16**
Aclonifen	1.874	1.937	1.927	1.875	1.874	1.876	1.882	1.849	1.709	1.906	1.907	1.893	1.875	1.850	1.711	1.906
Bifenox	0.750	0.750	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Chlorfenapyr	0.123	0.137	0.140	0.148	0.177	0.118	0.140	0.171	0.135	0.140	0.162	0.159	0.162	0.140	0.210	0.184
Chlorothalonil	1.484	1.411	1.446	1.490	1.480	1.054	1.083	1.016	1.013	1.032	1.035	1.027	1.105	1.028	1.096	1.019
Chlorpyrifos-ethyl	1.340	1.212	1.180	1.389	1.694	0.984	1.221	1.212	1.019	1.081	1.191	1.031	1.027	1.024	1.453	1.023
Chlorsulfuron	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075
Cyfluthrin	0.029	0.029	0.029	na*	0.029	0.027	0.027	0.027	0.036	0.027	0.0268	0.0290	0.027	0.027	na*	na*
Beta-Cyfluthrin	0.027	0.027	0.027	0.029	0.027	0.029	0.032	0.036	na*	0.027	0.027	0.026	0.029	0.030	0.039	0.027
Cypermethrin	0.392	0.149	0.140	0.215	0.174	0.377	0.252	0.290	0.331	0.396	0.308	0.247	0.164	0.338	0.205	0.313
Alpha-Cypermethrin	0.233	0.220	0.220	0.195	0.146	0.233	0.203	0.160	0.220	0.225	0.185	0.203	0.229	0.225	0.200	0.205
Zeta-Cypermethrin	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.400	na*	na*	na*	na*	na*	na*	0.040	na*
Cyromazine	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Dichlorvos	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Diflubenzuron	0.400	0.400	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Ethalfluralin	1.709	1.704	1.700	1.709	1.709	1.708	1.702	1.665	1.633	1.725	1.732	1.717	1.735	1.700	1.636	1.725
Fenpropimorph	0.312	0.312	0.312	0.312	0.312	0.312	0.312	0.311	0.311	0.310	0.310	0.310	0.310	0.310	0.311	0.310
Fenthion	0.846	0.883	0.886	0.902	0.916	0.845	0.881	0.894	0.816	0.873	0.910	0.907	0.857	0.830	0.836	0.797
Nicosulfuron	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Prothiofos	0.50	0.50	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Half-life and simulation times of pesticides presented in Table 3.18 and Table 3.20 play a significant role in terms of pesticide mass remained in the soil. For example, half-life and simulation time of Bifenox is 17.7 days, thus nearly 50% of application remains in the soil. The half-life of Chlorfenapyr is 1370 days and its simulation time is 30 days, thus, nearly all applied mass remains in the soil. The percentage of the residual pesticide mass in the soil for these drainage areas are presented in Table 4.8. If pesticides with same simulation duration (30 days) are compared for YB01 and YB03 drainage areas, pesticides that remain most in the soil from less to more can be listed as; Fenthion, Ethalfluralin, Prothiofos, Alpha-cypermethrin, Beta-cyfluthrin, Cyromazine, Chlorothalonil, Cypermethrin, Zeta-cypermethrin, Chlorpyrifos-ethyl, Cyfluthrin, Aclonifen, Chlorsulfuron and Chlorfenapyr, respectively. This order is mainly dominated by half-life of the pesticides. In YB06 drainage area, Chlorpyrifos-ethyl, Chlorothalonil, and Beta-Cyfluthrin alter this order by having a rather lower percentage of the residual pesticide mass in the soil due to low organic carbon fraction of soil. In Table 4.10, Appendix F Table F.27, and Table 4.11 estimated remaining soil concentrations ($C_{T,M}$) using equation (14) for these drainage areas are presented, respectively.

YB02, YB04, YB05, YB07, YB10 and YB13 drainage areas are assigned with clay soil, thus their results are similar. On the other hand, since organic carbon fractions of YB10 and YB13 are rather low, as in the previous case higher mass of Chlorsulfuron, Beta-cyfluthrin and Nicosulfuron active substances are observed below 20 cm soil depth. Similarly, these pesticides seem to not evaporate due to having rather low Henry's constant. Having a rather low infiltration and low organic carbon partition coefficient, only Beta-cyfluthrin application in YB10 drainage area is leaching and also evaporating. Likewise, pesticide mass remained in soil is affected by half-life and simulation times of pesticides presented in Table 3.18 and Table 3.20. For example, half-life and simulation time of Diflubenzuron is 6,7 days, thus nearly 50% of application remains in the soil. The half-life of Aclonifen is 195 days and its simulation time is 30 days, thus, nearly 90% of applied mass remains in the soil. In

Table F.26, Table F.28, Table F.29, Table F.30, Table F.33 and Table F.35 of Appendix F remaining soil concentrations ($C_{T,M}$) estimated using equation (14) are presented.

Table 4.7. *Pesticide fate and modeling results of drainage area YB06*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB06	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil ($R_{\%}$) (%)	Pesticide mass loss (%)
Aclonifen	1.68	10.11	0.27	0	89.63	10.37
Bifenox	0.37	50.10	0.002	0	49.90	50.10
Chlorfenapyr	0.12	1.51	0.31	0	98.18	1.82
Chlorothalonil	0.58	22.06	22.68	0	55.27	44.74
(Chlorpyrifos) Chlorpyrifos-ethyl	0.70	23.29	8.38	0	68.32	31.68
Chlorsulfuron	0.07	9.22	0	0.371	90.41	9.59
Cyfluthrin	0.02	19.03	0.01	0	80.96	19.04
Beta-Cyfluthrin	0.02	35.51	6.50	0.023	57.97	42.04
Cypermethrin	0.27	29.28	0.10	0	70.63	29.37
Alpha-cypermethrin	0.14	38.62	0.03	0	61.35	38.65
Zeta-cypermethrin	0.03	29.29	0.003	0	70.71	29.29
Cyromazine	0.10	31.05	0	0.001	68.95	31.05
Dichlorvos	0.47	56.46	0.72	0	42.81	57.19
Diflubenzuron	0.20	50.26	0.01	0	49.73	50.27
Ethalfluralin	0.85	31.47	19.02	0	49.51	50.49
Fenpropimorph	0.13	46.35	11.23	0	42.42	57.58
Fenthion	0.36	40.39	17.33	0	42.27	57.73
Nicosulfuron	0.03	50.32	0	0.042	49.64	50.36
Prothiofos	0.28	33.68	11.27	0	55.05	44.95

YB08, YB09, YB11, YB14, YB15, and YB16 drainage areas are assigned with loam soil and YB12 is the only drainage area that is assigned with sandy clay loam soil thus their results are parallel with each other. Organic carbon fractions of YB08 and YB14 drainage areas are rather low. Thus Chlorsulfuron and Nicosulfuron active substances are leaching further from 20 cm soil depth more. As the infiltration rate and organic carbon fraction increase, the evaporation of active substances is decreasing as in the previous cases. Half-life and simulation time of active substances presented in Table 3.18 and Table 3.20 influence remained mass of active substances after application. For example, half-life and simulation time of Dichlorvos is 0.42 days; thus nearly 44% of application remains in the soil. The half-life of Chlorpyrifos-ethyl is 74 days and its simulation time is 30 days. Thus, more than 70% of applied mass remains in the soil. In Table F.31, Table F.34, Table F.36, Table F.37 of Appendix F and Table 4.11 estimated remaining soil concentrations ($C_{T,M}$) using equation (14) are presented.

Percent remaining mass of the pesticides that simulated for 30 days presented in Table 4.8. were compared for YB01, YB03, and YB06 drainage areas. Pesticides are aligned quite similar to other drainage areas too. Similarly, the half-life of the pesticides is the prevalent reason for the percent remaining masses. Nevertheless, rather low organic fraction of soil in YB04, YB10 and YB13 drainage areas causes Chlorothalonil and Beta-Cyfluthrin active substances to have lower percentage of the residual pesticide mass in the soil. Likewise, the YB11 drainage area has rather high organic carbon fractioned loam soil. Thus Beta-Cyfluthrin alters the order by having higher percentage of the residual pesticide mass in the soil.

Estimated remaining soil concentrations ($C_{T,M}$) results are used for the estimation of diffuse pollution loads of which results are presented in Section 4.4. Moreover, deduced precautions regarding pesticides for control of diffuse pesticide pollution out of this section are presented in Section 4.5.

Table 4.8. Percentage of the residual pesticide mass in the soil

	The percentage of the residual pesticide mass in the soil ($R_{\%}$) (%)															
	YB01	**YB02**	**YB03**	**YB04**	**YB05**	**YB06**	**YB07**	**YB08**	**YB09**	**YB10**	**YB11**	**YB12**	**YB13**	**YB14**	**YB15**	**YB16**
Aclonifen	89.84	89.85	89.84	89.84	89.85	89.63	89.84	89.79	89.81	89.81	89.85	89.82	89.82	89.80	89.81	89.83
Bifenox	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90	49.90
Chlorfenapyr	98.44	98.45	98.44	98.43	98.45	98.18	98.44	98.38	98.40	98.40	98.45	98.42	98.41	98.39	98.40	98.43
Chlorothalonil	69.18	69.44	69.03	68.03	69.44	55.27	68.45	65.37	66.30	65.77	65.37	67.27	66.60	65.67	66.62	68.05
Chlorpyrifos-ethyl	73.83	73.97	73.77	73.47	73.97	68.32	73.62	72.22	72.61	72.67	73.93	73.09	72.96	72.35	72.74	73.33
Chlorsulfuron	91.35	91.35	91.35	91.30	91.35	90.41	91.32	91.22	91.26	91.16	91.35	91.28	91.23	91.23	91.28	91.32
Cyfluthrin	80.97	80.97	80.97	80.97	80.97	80.96	80.97	80.97	80.97	80.97	80.97	80.97	80.97	80.97	80.97	80.97
Beta-Cyfluthrin	61.58	61.71	61.54	61.34	61.72	57.97	61.45	60.24	60.56	60.78	61.65	60.96	60.97	60.35	60.66	61.15
Cypermethrin	70.70	70.70	70.70	70.70	70.70	70.63	70.70	70.68	70.69	70.69	70.68	70.69	70.69	70.68	70.69	70.69
Alpha-cypermethrin	61.37	61.37	61.37	61.37	61.37	61.35	61.37	61.37	61.37	61.37	61.37	61.37	61.37	61.37	61.37	61.37
Zeta-cypermethrin	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71	70.71
Cyromazine	68.98	68.98	68.98	68.98	68.98	68.95	68.98	68.97	68.97	68.97	68.97	68.97	68.97	68.97	68.97	68.97
Dichlorvos	43.14	43.16	43.14	43.12	43.16	42.81	43.13	43.00	43.03	43.07	43.15	43.07	43.09	43.01	43.04	43.09
Diflubenzuron	49.74	49.74	49.74	49.74	49.74	49.73	49.74	49.74	49.74	49.74	49.74	49.74	49.74	49.74	49.74	49.74
Ethalfluralin	55.58	55.52	55.52	54.95	55.51	49.51	55.13	53.49	53.97	53.99	55.50	54.64	54.38	53.66	54.14	54.82
Fenpropimorph	47.76	47.90	47.70	47.36	47.90	42.42	47.52	46.18	46.54	46.52	47.88	46.99	46.83	46.30	46.18	47.25
Fenthion	51.08	51.27	50.99	50.41	51.27	42.27	50.66	48.69	49.27	49.02	51.30	49.90	49.53	48.88	49.46	50.35
Nicosulfuron	49.76	49.76	49.76	49.75	49.76	49.64	49.75	49.72	49.73	49.73	49.75	49.74	49.74	49.73	49.74	49.74
Prothiofos	58.70	58.93	58.62	58.17	58.94	55.05	58.37	56.94	57.25	57.26	58.89	57.71	57.55	57.04	57.36	58.00

4.4. Pesticide loads and recommended pesticide application rates to comply with EQSs

As previously mentioned YB01, YB06, YB11 + YB12, and YB16 drainage areas are prominent due to both point and diffuse pesticide pollution. Both concentrations determined with water quality monitoring and probable concentrations created by diffuse pesticide loads (estimated by equation (17)) of Cypermethrin, Alpha-Cypermethrin, and Dichlorvos active substances are exceeding EQS. Estimated probable concentrations for these four drainage areas change between 0,01% and 9716% of the receiving body water quality monitoring results. In this section, these drainage areas are discussed in detail, while the results of the other drainage areas are presented in Appendix F are not discussed since no pesticide is exceeding EQS in the receiving body and discharge sampling points linked with these drainage areas. For example, YB10, YB14 and YB15 drainage areas have not exact receiving body sampling points that match to the outlet.

YB11 and YB12 drainage areas are collected together since YB11 drainage area isn't represented by a particular receiving body sampling point. Moreover, the nearest receiving body sampling point to the YB11 drainage area in the flow chart (see Figure 4.1) also represents a large part of YB12. Thus they are estimated together through serving them by YB11+YB12. The following discussions pertain to prominent drainage areas of YB01, YB06, YB11 + YB12, and YB16.

4.4.1. YB01 drainage area

Point and diffuse loads originating from the YB01 drainage area are compared with the receiving body (RB) sample measurements taken from the Y-40 point according to their upstream and downstream relationship. In other words, discharge water quality monitoring results in YB01 drainage area, receiving body monitoring results, and estimated diffuse pesticide loads are assessed. As presented in Table 4.9, the point loads from Y-131 and Y-133 discharge points reach Y-40 receiving body sampling point. Red-colored values represent EQS exceeding concentrations (C_{est}) that are estimated using diffuse load estimations (see equation (16) and (17)). Yellow boxes represent receiving body water quality monitoring results (C_{obs}) that exceed EQS. The loads for the undetected and non-exceeding EQS points are calculated using concentrations that are half of the LOD specified in the water quality measurements (LOD/2)). According to the periodic measurements of discharge points and receiving body measurements (besides Cypermethrin, Alpha-Cypermethrin, and Dichlorvos), there is no load of pesticides that their concentrations are exceeding the EQS at these points. Observed receiving body concentrations (C_{obs}) of the active substances, Aclonifen, Bifenox, Chlorothalonil, Chlorsulfuron, Cypermethrin, Alpha-Cypermethrin, Dichlorvos, and Ethalfluralin exceeded EQS at Y-40 point as presented in Table 4.6. The comparison between estimated diffuse loads and receiving body water quality monitoring loads show that monitored loads are changing between one to three orders of magnitudes of estimated diffuse loads. Also, the effect of point sources is negligible compared to receiving body water quality.

In Table 4.10, components of the estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration are presented. In the first column, pesticide application rates specific to YB01 drainage area which are used in the fate and transport model PESTRANS are presented. In the second column, pesticide concentrations remained in the soil, which is estimated using equation (14) are shown. In the third column, the percent remaining mass of the applied pesticides in the soil are presented. %R also obtained from PESTRANS model. In the fourth column, estimated diffuse pesticide loads are presented which is calculated using equation (16). In the fifth column, potential concentrations in the receiving body estimated using equation (17) is presented. In the sixth and seventh column EQSs and corresponding pesticide application rates are presented. They are calculated using as presented in Section 3.5.3 in detail. In the last column, receiving body monitoring results is presented.

In Table 4.10, it is seen that the concentrations (both C_{est} and C_{obs}) of Cypermethrin, Alpha-Cypermethrin, and Dichlorvos wherein the table are bold, exceed the EQS. The loads observed in the receiving body are several times (6 to 171) higher than the amounts of the estimated diffuse loads that create these C_{est} concentrations. The estimated concentration C_{est} of Aclonifen, Bifenox, Chlorothalonil, Chlorsulfuron and Ethalfluralin (to account for the impact of estimated diffuse loads) does not exceed EQS, as presented in Table 4.10. However, their observed concentrations exceed EQS, as indicated with gray boxes. C_{est} are one to three order of magnitude are lower than C_{obs}.

One of the reasons behind the inconsistency between C_{obs} and C_{est} is attributable to the uncertainties in the pesticide application areas (which were estimated in section 3.5). Moreover, this may also indicate that pesticides are applied more than suggested application rates. Additionally, Y-40 receiving body sampling point (outlet of Lake Ladik) also may not represent one-time application of pesticides but the accumulation of these agricultural practices.

Nevertheless, the measurements in the receiving body reveal the levels of diffuse pesticide pollution in Tersakan Creek. The assessment highlights that the application rates of Cypermethrin, Alpha-cypermethrin, and Dichlorvos must be reduced to AppRate EQS values. Cypermethrin and Alpha-cypermethrin application rates that correspond to EQS are zero, and Dichlorvos application rate is reduced to 0.87 kg/ha, as presented in Table 4.7. Cypermethrin and Alpha-cypermethrin use must be restricted, or alternative pesticides should be used. Aclonifen, Bifenox, Chlorothalonil, Chlorsulfuron, and Ethalfluralin use must be controlled and good agricultural practices must be implemented in this area. Suggested control measures for diffuse pesticide pollution in the light of these results are presented in Section 4.5.

Table 4.9. *Point and diffuse pollution loading comparison for YB01 drainage area*

		Drainage area	Discharge	Discharge	RB
		YB-01	Y-131	Y-133	Y-40
Aclonifen	Flow rate (m3/s)	2.629208	0.000389	0.000521	2.629208
	Conc. (µg/L)	0.00059	0.0025*	0.0025*	0.844498
	Load (mg/day)	133.9302	0.084	0.1125	191839.2
Bifenox	Flow rate (m3/s)	0.47	0.000389	0.000521	0.47
	Conc. (µg/L)	0.002469	0.0025*	0.0025*	0.236201
	Load (mg/day)	100.2806	0.084	0.1125	9591.65
Chlorothalonil	Flow rate (m3/s)	0.0836	0.000389	0.000521	0.0836
	Conc. (µg/L)	0.001919	0.005*	0.005*	0.621058
	Load (mg/day)	13.8585	0.168	0.225	4485.927
Chlorsulfuron	Flow rate (m3/s)	2.629208	0.000389	0.000521	2.629208
	Conc. (µg/L)	7.51E-05	0.01*	0.01**	0.073103
	Load (mg/day)	17.06863	0.336	0.45	16606.34
Cypermethrin	Flow rate (m3/s)	0.0836	0.000389	0.000521	0.0836
	Conc. (µg/L)	**0.017002**	0.0025*	0.0025*	0.106028
	Load (mg/day)	122.808	0.084	0.1125	765.8445
Alpha-Cypermethrin	Flow rate (m3/s)	0.0836	0.000389	0.000521	0.0836
	Conc. (µg/L)	**0.004658**	0.0025*	0.0025*	0.106028
	Load (mg/day)	33.6457	0.084	0.1125	765.8445
Dichlorvos	Flow rate (m3/s)	2.629208	0.000389	0.000521	2.629208
	Conc. (µg/L)	**0.000762**	0.00025*	0.00025*	0.130546
	Load (mg/day)	173.1596	0.0084	0.01125	29655.29
Ethalfluralin	Flow rate (m3/s)	0.0836	0.000389	0.000521	0.0836
	Conc. (µg/L)	0.040819	0.0025*	0.0025*	3.279348
	Load (mg/day)	294.8346	0.084	0.1125	23686.86

*RB: Receiving Body, Conc.: Concentration, *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2)*

Table 4.10 *Components of estimation of diffuse pesticide loads and its results in the YB01 drainage area*

	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.874	0.538	89.8	133.930	5.90E-04	0.12	381.27	**0.844498**
Bifenox	0.750	0.120	49.9	100.281	2.47E-03	0.012	3.64	**0.236201**
Chlorfenapyr	0.123	0.039	98.4	31.658	2.77E-04	0.007	3.11	0.0025*
Chlorothalonil	1.484	0.328	69.2	13.858	1.92E-03	0.3	231.91	**0.621058**
Chlorpyrifos (Chlorpyrifos-ethyl)	1.340	0.316	73.8	102.028	8.91E-04	0.03	45.10	0.005*
Chlorsulfuron	0.008	0.022	91.4	17.069	7.51E-05	0.02	19.96	**0.073103**
Cyfluthrin	0.029	0.008	81.0	6.740	5.89E-05	0.001	0.49	0.005*
Beta-Cyfluthrin	0.027	0.005	61.6	0.018	1.58E-07	0.001	171.02	0.005*
Cypermethrin	0.392	0.089	70.7	122.808	**1.70E-02**	0.00008	0.00	**0.106028**
Alpha-Cypermethrin	0.233	0.046	61.4	33.646	**4.66E-03**	0.00008	0.00	**0.106028**
Zeta-Cypermethrin	0.040	0.009	70.7	1.973	1.72E-05	0.00008	0.19	0.0025*
Cyromazine	0.150	0.033	69.0	3.202	2.80E-05	0.2	1073.15	0.025*
Dichlorvos	1.100	0.152	43.1	173.160	**7.62E-04**	0.0006	0.87	**0.130546**
Diflubenzuron	0.400	0.064	49.7	44.155	3.86E-04	0.13	134.86	0.025*
Ethalfluralin	1.709	0.304	55.6	294.835	4.08E-02	0.3	12.56	**3.279348**
Fenpropimorph	0.312	0.048	47.8	39.892	3.48E-04	0.1	89.43	0.05*
Fenthion	0.846	0.138	51.1	286.541	2.50E-03	0.05	16.89	0.025*
Nicosulfuron	0.060	0.010	49.8	0.395	3.45E-06	0.05	869.15	0.01*
Prothiofos	0.500	0.094	58.7	65.123	5.69E-04	0.1	87.90	0.025*

AppRate is the pesticide application rate used in PESTRANS model; $C_{T,M}$*, is Pesticide Concentration Remained in the Soil;* $R_{\%}$ *is Percent Remaining Pesticide Mass; PL is Diffuse Pesticide Load; AppRate EQS is Application Rate Corresponding to EQS; Cobs is Observed Concentration; *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2).*

4.4.2. YB06 drainage area

The diffuse pesticide loads from the YB-06 drainage area were compared with the receiving body loads taken from the Y-32 receiving body sampling point according to their upstream and downstream relationship. No discharge point was reported before this receiving body monitoring station. Therefore, it is determined that pollution is due to diffuse pollution from intensive farming.

Concentrations of Bifenox, Chlorfenapyr, Chlorsulfuron, Cypermethrin, Alpha-Cypermethrin, Zeta-Cypermethrin, Dichlorvos, Diflubenzuron Ethalfluralin, Fenpropimorph, Fenthion and Nicosulfuron active substances have exceeded the EQS *at least once* in the observations (C_{obs}) as presented in gray boxes in Table 4.11. This study showed that calculated concentrations created by the diffuse loads (C_{est}) are exceeded the EQS only for Cypermethrin, Alpha-Cypermethrin and Dichlorvos active subtances which are indicated in bold. Loads of the pesticides that their observed concentration is exceeding EQS in receiving body are still much higher than estimated diffuse pollution loads. The reason behind the inconsistency between observed and estimated loads, in the meantime between C_{obs} and C_{est}, is mainly due to the uncertainties of pesticide application areas which were estimated in section 3.5. This may also indicate that these pesticides are applied more than suggested application rates. Nevertheless, the observed concentrations reveal the levels of diffuse pesticide pollution in Tersakan Creek.

The assessment highlights that the application rates of Cypermethrin, Alpha-cypermethrin, and Dichlorvos must be reduced to AppRate EQS values. According to estimations in Section 3.7, Cypermethrin application rate should be zero. Alpha-cypermethrin application rates that correspond to EQS should be reduced from 0.233 kg/ha to 0.01 g/ha. Dichlorvos application rate should be reduced from 1,1 kg/ha to 0.09 and 0.012 kg/ha, as presented in Table 4.11. As a result, application rates of Cypermethrin, Alpha-cypermethrin and Dichlorvos must be reduced and their use must be restricted or alternative pesticides should be used. Use of Bifenox, Chlorfenapyr, Chlorsulfuron, Zeta-Cypermethrin, Diflubenzuron, Ethalfluralin, Fenpropimorph, Fenthion and Nicosulfuron must be controlled and good agricultural practices must be implemented in this area as presented in Section 4.5.

Table 4.11 *Components of estimation of diffuse pesticide loads and its results in YB06 drainage area*

	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.876	0.538	89.6	229.251	0.003871	0.12	58.16	0.0025*
Bifenox	0.750	0.120	49.9	170.437	0.002283	0.012	3.94	**0.225**
Chlorfenapyr	0.118	0.037	98.2	55.670	0.001938	0.007	0.43	**0.011019**
Chlorothalonil	1.054	0.186	55.3	256.296	0.004327	0.3	73.07	0.005*
Chlorpyrifos (Chlorpyrifos-ethyl)	1.018	0.222	68.3	493.344	0.00833	0.03	3.67	0.005*
Chlorsulfuron	0.008	0.002	90.4	3.094	4.67E-05	0.02	3.49	0.027447
Cyfluthrin	0.029	0.008	81.0	0.041	6.94E-07	0.001	41.77	0.005*
Beta-Cyfluthrin	0.027	0.005	58.0	7.958	0.000134	0.001	0.20	0.005*
Cypermethrin	0.377	0.085	70.6	215.806	**0.00751**	0.00008	0.00	**0.22**
Alpha-cypermethrin (1st period)	0.233	0.046	61.4	58.215	**0.000628**	0.00008	0.03	**0.225**
Alpha-cypermethrin (4th period)	0.233	0.046	61.4	58.215	**0.002026**	0.00008	0.01	**0.102219**
Zeta-cypermethrin	0.040	0.009	70.7	3.156	3.4E-05	0.00008	0.09	**0.134**
Cyromazine	0.150	0.033	68.9	8.591	0.000317	0.2	94.62	0.10216*
Dichlorvos (1st period)	1.100	0.151	42.8	501.360	**0.005406**	0.0006	0.12	**0.151497**
Dichlorvos (8th period)	1.100	0.151	42.8	501.360	**0.007563**	0.0006	0.09	**0.427066**
Diflubenzuron	0.400	0.064	49.7	76.527	0.001154	0.13	45.04	**2.432362**
Ethalfluralin	1.708	0.270	49.5	463.797	0.006996	0.3	73.26	**0.420978**
Fenpropimorph	0.312	0.042	42.4	59.931	0.002085	0.1	14.87	**0.731264**
Fenthion	0.845	0.114	42.3	406.754	0.006136	0.05	6.89	**0.208139**
Nicosulfuron	0.060	0.010	49.6	0.662	8.86E-06	0.05	338.52	**0.080794**
Prothiofos	0,500	0,088	55,0	105,764	0,001786	0,1	27,99	0,025*

AppRate is pesticide application rate used in PESTRANS model; $C_{T,M}$*, is Pesticide Concentration Remained in the Soil;* $R_{\%}$ *is Percent Remaining Pesticide Mass; PL is Diffuse Pesticide Load; AppRate EQS is Application Rate Corresponding to EQS; Cobs is Observed Concentration.; *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2).*

4.4.3. YB11+YB12 drainage areas

Estimated diffuse pesticide loads of YB11 and YB12 drainage areas were compared with the Y-97 and Y-31 receiving body sampling points according to their upstream and downstream relationships. YB11 and YB12 drainage areas are approached together since there is no particular receiving body monitoring point that represents YB11. Moreover, closest receiving body monitoring point to YB11 drainage area, Y-97, also represents a large part of YB12 drainage area. There are two point sources reported in these drainage areas: they are Y-65 and Y-58 discharge sampling points.

In Table 4.12, the mass balances of pesticides that exceed EQS are assessed as mentioned in their upstream and downstream relationship for YB11+YB12 drainage areas. In order to compare Y-97 receiving body monitoring results, a sub-total is calculated by including pesticide loads of Y-65 discharge sampling point and estimated diffuse pesticide loads of YB11 and YB12 drainage areas. Bold values represent the loads that their corresponding concentrations exceed EQS. Y-65 discharges only Dichlorvos active substance to Tersakan Creek with concentrations exceeding EQS represented in gray boxes. Estimated diffuse pesticide loads imply that these drainage areas are a potential significant pressure for the water quality of the Tersakan Creek due to large agricultural areas. However, pesticide concentrations don’t exceed EQS in the downstream Y-97 receiving body sampling point. If it is assumed that point sampling from receiving bodies represent the water quality status accurately for that moment, it can be deduced that discharges from Y-65 and potential diffuse pesticide loads are diluted and degraded along the transport. In order to protect the water quality status of this part of the Tersakan Creek, wastewater treatment conditions of Y-65 discharge point should be inspected.

Additionally, in Table 4.12, another receiving body sampling point Y-31, subsequent to Y-97, and other discharge point Y-58 in YB12 drainage area is presented. Y-58 discharges Chlorfenapyr, Cypermethrin, Alpha-Cypermethrin, Ethalfluralin, and Fenpropimorph active substances to Tersakan Creek with concentrations exceeding

EQS which are represented in gray boxes. Chlorpyrifos-ethyl, Chlorsulfuron, Cyfluthrin (Beta-Cyfluthrin), Cypermethrin, Alpha-Cypermethrin, and Dichlorvos exceeds EQS at least once in Y-31 receiving body sampling point. Other than Dichlorvos and Ethalfluralin, it can be deduced that pollution is mainly diffuse sources. Detailed mass balance of discharge points and receiving body sampling points are carried out in Section 4.1. Still, wastewater treatment units of Y-58 should be investigated to prevent the pesticide pollution in this part of the Tersakan Creek.

In Table 4.13, estimated pesticide concentrations are higher than the observed concentrations which are exceeding EQSs for active substances such as Chlorpyrifos-ethyl, Cypermethrin, Alpha-cypermethrin, Dichlorvos and Cyromazine (zero to two order of magnitudes) but remain below the observed concentrations for active substances Chlorsulfuron, Cyfluthrin, Beta-cyfluthrin and Alpha-cypermethrin (one to three order of magnitudes). Inconsistency between observed loads and estimated diffuse loads is most likely due to the uncertainties of pesticide application area in YB-12 which were estimated in Chapter 3.5 and also missing flowrate measurements due to stagnant water or insufficient flow. Furthermore, Chlorsulfuron, Cyfluthrin, and Alpha-cypermethrin active substances may be used more than suggested application rates. These estimations reveal the diffuse pesticide pollution potential of YB-12. Another point is that between the distance of two points Y-97 and Y-31, there must be intensive farming. Thus, diffuse pesticide pollution control measures are suggested for these areas in Section 4.4.

Recommended pesticide application rates to comply with EQSs study revealed that the application rates of Chlorpyrifos-ethyl, Chlorsulfuron, Cyfluthrin (Beta-Cyfluthrin), Cypermethrin, Alpha-Cypermethrin, and Dichlorvos must be reduced to AppRate EQS values as presented in Table 4.13. C_{est} of Cyromazine exceeds EQS. Besides, AppRate EQS of Cyromazine is higher than recommended application rate previously introduced in Table 3.11. Therefore, Cyromazine shouldn’t be used. Moreover, the application rates of Chlorpyrifos-ethyl, Chlorsulfuron, Cyfluthrin (Beta-Cyfluthrin), Cypermethrin, Alpha-Cypermethrin, and Dichlorvos must be reduced, their use must be restricted or alternative pesticides should be applied. Moreover, good agricultural practices must be performed between Y-97 and Y-31 points.

Table 4.12. Loads of pesticides that exceed EQS and their mass balance for YB11+YB12 drainage areas

	Discharge	DA	DA		RB	Discharge		RB
Load (mg/day)	Y-65	YB11	YB12	Sub-Total	Y-97	Y-58	Total	Y-31
Chlorfenapyr	0.6	184.0	**296.9**	481.4	4.45	7.8	489.2	17.5
Chlorothalonil	1.1	1,934.8	**12,056**	13,992	8.9	1.7	13,994	35
Chlorpyrifos-ethyl	1.1	208.3	**12,482**	12,692	8.9	1.7	12,693	128.5
Chlorsulfuron	2.3	58.7	67.7	128.6	17.8	3.3	131.9	235.0
Cyfluthrin	1.1	266.9	**326.3**	594.3	8.9	1.7	596.0	2208.6
Beta-Cyfluthrin	1.1	0.1	**2.7**	3.9	8.9	1.7	5.6	2208.6
Cypermethrin	0.6	2399.6	**576.5**	2,977	4.5	35.5	3012.1	605.3
Alpha-Cypermethrin (2nd period)	0.6	100.2	**137.7**	238.5	4.5	0.8	239.3	52.4
Alpha-Cypermethrin (4th period)	0.6	100.2	**137.7**	238.5	4.5	35.5	273.9	605.3
Dichlorvos (1st period)	0.1	1,792.6	**8,354.6**	10,147	0.45	0.082	10,147	2547.6
Dichlorvos (3rd period)	0.3	1,792.6	**8,354.6**	10,147	0.45	0.082	10,148	1.8
Dichlorvos (8th period)	26.5	1,792.6	**8,354.6**	10174	0.45	0.082	10,174	1.8
Ethalfluralin	0.6	10,841.8	**12,448**	23,290	4.5	1967.1	25,257	17.5
Fenpropimorph	11.3	1,572.6	**1,722**	3,306	89	186.2	3,492.3	349.7

*DA: Drainage area, RB: Receiving Body; *Loads represented for Y-65, Y-97, Y-58 and Y-31 sampling points in non-grey boxes are calculated using half of LOD (LOD/2) since there is no detection (<LOD).*

Table 4.13. *Components of estimation of diffuse pesticide loads and its results in YB12 drainage area*

	App Rate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	App Rate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.893	0.554	89.8	5294.6	**0.7571**	0.12	0.316	0.0025*
Bifenox	0.750	0.116	49.9	4418.2	**0.6317**	0.012	0.014	0.0025*
Chlorfenapyr	0.159	0.048	98.4	296.9	**0.0425**	0.007	0.026	0.0025*
Chlorothalonil	1.027	0.214	67.3	12056.4	**1.7239**	0.3	0.179	0.005*
Chlorpyrifos (Chlorpyrifos-ethyl)	1.031	0.233	73.1	12482.2	**3.2254**	0.03	0.010	**0.033196**
Chlorsulfuron	0.008	0.002	91.3	67.7	0.0097	0.02	0.016	**0.033602**
Cyfluthrin	0.029	0.007	81.0	326.3	**0.0467**	0.001	0.001	**0.315797**
Beta-Cyfluthrin	0.026	0.005	61.0	2.7	0.0004	0.001	0.067	**0.315797**
Cypermethrin	0.247	0.054	70.7	576.5	**0.0824**	0.00008	0.000	**0.086546**
Alpha-Cypermethrin (2nd period)	0.203	0.039	61.4	137.7	**0.0197**	0.00008	0.001	**0.007498**
Alpha-Cypermethrin (4th period)	0.203	0.039	61.4	137.7	**0.0197**	0.00008	0.001	**0.086546**
Cyromazine	0.150	0.032	69.0	113.2	**0.0162**	0.0006	1.855	**0.025**
Dichlorvos	1.100	0.147	43.1	8354.6	**0.8258**	0.13	0.001	**0.251798**
Diflubenzuron	0.400	0.062	49.7	154.8	0.0221	0.3	2.349	0.025*
Ethalfluralin	1.717	0.290	54.6	12447.6	**1.7798**	0.1	0.289	0.0025*
Fenpropimorph	0.310	0.045	47.0	1722.2	**0.2462**	0.05	0.126	0.05*
Fenthion	0.907	0.140	49.9	6213.2	**0.8884**	0.05	0.051	0.025*
Nicosulfuron	0.060	0.009	49.7	10.1	0.0014	0.1	2.083	0.01*
Prothiofos	0.500	0.089	57.7	220.9	0.0316	0.1	1.583	0.025*

AppRate is pesticide application rate used in PESTRANS model; $C_{T,M}$*, is Pesticide Soil Concentration;* $R_{\%}$ *is Percent Remaining Pesticide Mass; PL is Diffuse Pesticide Load; AppRate EQS is Application Rate Corresponding to EQS; Cobs is Observed Concentration.; *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2).*

4.4.4. YB16 drainage area

YB16 drainage area is downstream of Tersakan Sub-basin and the diffuse pesticide loads from this area were compared with the Y-20 receiving body sampling point monitoring results which is the last receiving body sampling point in the Creek before connection to Yeşilırmak River. There is another receiving body sampling point Y-

125 in YB16 drainage area which is at the upstream of YB16 and one point source which is Y-79, as previously presented in Figure 4.1.

According to the periodic measurements, there are no pesticides that their concentrations are exceeding the EQS at Y-125 and Y-97 points. Thus their loads were estimated using half of the LOD values (LOD/2). Results are presented in Table 4.14. Since Y-125 receiving body sampling point is at the upstream of the last drainage area, loads from subsequent drainage areas which have not water quality measurement points may be negligible. Still downstream of these drainage areas must be included future water quality monitoring studies.

Y-20 point is one of the most polluted points of the Tersakan Creek as presented in Table 4.14. The concentrations of Bifenox, Chlorfenapyr, Cypermethrin, Alpha-Cypermetrin, Zeta-Cypermethrin, Cyromazine, Dichlorvos and Prothiofos in the receiving body exceeded EQS at least once (C_{obs}) as presented in bold and gray boxes. It can be deduced that there is intensive farming between points Y-125 and Y-20. Concentrations created by the diffuse load estimation (C_{est}) exceeded the EQS only for Cypermethrin, Alpha-Cypermethrin and Dichlorvos. Pesticide loads observed in Y-20 is mostly much higher than the estimated diffuse pesticide loads.

According to the mass balance calculation in Table 4.14, Zeta-Cypermethrin exceeded EQS once, but the diffuse load estimation was not performed. Because according to the data obtained from the Ministry of Agriculture and Forestry, Zeta-Cypermethrin is applied only to hazelnuts, and hazelnuts are not produced according to TURKSTAT crop data of Suluova and Merkez counties of Amasya whose area lay within this drainage area. Thus, Zeta-cypermethrin is most likely used for other crops, and these applications are not reported by the ministry.

Uncertainities of pesticide application areas and application rates which were gathered in Section 3.3.3 and 3.5 cause inconsistency between C_{obs} and C_{est} as shown in Table 4.12. Moreover, these results may reveal the excessive use of these pesticides.

Nevertheless, the observed concentrations reveal the levels of pesticide pollution in the downstream of Tersakan Creek.

Table 4.14. *Loads of pesticides that exceed EQS and their mass balance for YB16 drainage area*

	RB	Discharge	DA		RB
Load (mg/day)	Y-125	Y-79	YB16	Total	Y-20
Aclonifen	134.352	0.5124	131.2	266.1	436.0
Bifenox	134.352	0.5124	86.5	221.4	**24825.0**
Chlorfenapyr	134.352	0.5124	500.4	635.3	**1920.0**
Cypermethrin	134.352	0.5124	**700.8**	835.7	**29518.0**
Alpha-Cypermethrin (4th period)	134.352	0.5124	**104.1**	239.0	**20654.2**
Zeta-Cypermethrin (1st period)	134.352	0.5124	0	134.9	435.99
Zeta-Cypermethrin (4th period)	134.352	0.5124	0	134.9	**11330.24**
Cyromazine (3rd period)	1343.52	5.124	3.9	1352.5	**18154.69**
Cyromazine (4th period)	1343.52	5.124	3.9	1352.5	4359.9
Dichlorvos (1st period)	13.435	0.05124	**1850.9**	1864.4	**20136.26**
Dichlorvos (8th period)	13.4352	0.05124	**1850.9**	1864.4	**1662.993**
Prothiofos	1343.52	5.124	237.45	1586.1	**1026414**

*DA: Drainage area, RB: Receiving Body; *Loads represented for Y-125, Y-79 and Y-20 sampling points in non-grey boxes are calculated using half of LOD (LOD/2) since there is no detection (<LOD).*

In Table 4.15, components for estimating diffuse pesticide loads and results of the estimation in YB16 drainage area are presented. As previously stated, Cypermethrin, Alpha-cypermethrin and Dichlorvos active substances are exceeding EQS in estimated concentrations (C_{est}) as they are already exceeding EQS in observed concentrations. Their estimated concentrations are zero to three order of magnitudes are lower than observed concentrations. Accordingly, the results put forward application rates corresponding to EQSs for these pesticides as presented in Table 4.15. Application rates of Cypermethrin, Alpha-Cypermetrin and Dichlorvos should be reduced to 0.01 to 0.10 kg/ha. Other pesticides that C_{obs} exceed EQS (Bifenox, Chlorfenapyr, Cyromazine and Ethalfluralin) but their estimated concentrations do not exceed EQSs. Their estimated concentrations are zero to four order of magnitudes are lower than observed concentrations. These pesticides should be used within the limits of suggested application rates or alternative pesticides should be used. Good agricultural practices should have been performed in this part of Tersakan Creek.

As previously mentioned in Chapter 2.2, Huber et al. (2000) stated that their modeled diffuse load results are within a range of 10%-1000% of the monitored results. Moreover, it is mentioned that still, validation of prediction accuracy is not possible, because of not considering each pathway of diffuse loads. Thus, diffuse loads are underestimated at particular catchments due to the generalization of spatial input data and complex nature of pesticide loss in their study. In this study, diffuse load results of EQS exceeding pesticides for YB01, YB06, YB11+YB12 and YB16 drainage areas change between 0.07% and 16%, 0.01% and 17.6%, 0.13% and 9716%, 0.02% and 111.3% of the monitoring results, respectively. Since agricultural areas are the largest in YB11+YB12 drainage areas, results are more variational. Therefore, the generalization of land cover and the exclusion of other pathways of diffuse pollution reveal a similar range of change in the order of magnitude.

In the report of Williams et al. (1999) which is mentioned in Chapter 2.2 in detail, Chlorpyrifos was applied with a rate of 0.72 kg/ha. At the end of 18-38 days (time between the application date and rainfall event) Chlorpyrifos was detected in sampling points between 0.05 and 4.29 μg/l. As an example, in YB01 drainage area, it is assumed that 1.34 kg/ha Chlorpyrifos is applied and at the end of 30 days, probable concentration (C_{est}) is rather underestimated as 8.91E-04 μg/l. Moreover, according to Williams et. al. (1999) Fenpropimorph was applied with a rate of 0.75 kg/ha. At the end of 18-20 days Fenpropimorph was detected in sampling points between 0.66 and 1.58 μg/l. In YB01 drainage area, it is assumed that 0.312 kg/ha Fenpropimorph is applied, and at the end, probable concentration is rather underestimated as 3.48E-04 μg/l. Similar comparisons are obtained with YB06, YB11+YB12 and YB16 drainage areas. According to Williams et al. (1999), water quality monitoring results of field drains and stream, pesticide translocation occurred after critical rainfall events (24 hours) through runoff. Moreover, detected high concentrations fall below the LOD within about 12-24 hours. Thus, in critical rainfall events, higher concentrations are expected. In our study, the transport of diffuse pesticide load to the surface waters is formed with the transport of sediment in a year. Therefore, estimating lower concentrations in receiving body due to the longer duration and form of the transport is highly expected.

Table 4.15. *Components of estimation of diffuse pesticide loads and its results in YB16 drainage area*

	App Rate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	App Rate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.849	0.567	89.8	131.189	0.000752	0.12	304.20	0.0025*
Bifenox	0.750	0.124	49.9	86.519	0.000387	0.012	23.28	**0.11094**
Chlorfenapyr	0.171	0.060	98.4	500.400	0.002034	0.007	0.63	**0.00781**
Chlorothalonil	1.016	0.229	68.1	474.980	0.002724	0.3	112.21	0.005*
Chlorpyrifos (Chlorpyrifos-ethyl)	1.212	0.248	73.3	527.976	0.003027	0.03	10.14	0.005*
Chlorsulfuron	0.008	0.002	91.3	1.283	7.36E-06	0.02	20.39	0.01*
Beta-Cyfluthrin	0.036	0.005	61.2	4.769	2.73E-05	0.001	0.99	0.005*
Cypermethrin	0.290	0.073	70.7	700.807	**0.002849**	0.00008	0.01	**0.12**
Alpha-Cypermethrin	0.160	0.042	61.4	104.115	**0.000423**	0.00008	0.04	**0.08397**
Cyromazine	0.150	0.034	69.0	3.876	4.45E-05	0.2	674.30	**0.20849**
Dichlorvos (1st period)	1.100	0.157	43.1	1850.935	**0.006904**	0.0006	0.10	**0.07511**
Dichlorvos (8th period)	1.100	0.157	43.1	1850.935	**0.029713**	0.0006	0.02	**0.0267**
Diflubenzuron	0.400	0.066	49.7	165.065	0.000946	0.13	54.93	0.025*
Ethalfluralin	1.665	0.313	54.8	249.642	0.001431	0.3	361.53	0.0025*
Fenpropimorph	0.311	0.048	47.2	33.863	0.000194	0.1	159.69	0.05*
Fenthion	0.894	0.133	50.4	1387.346	0.007955	0.05	5.01	0.025*
Nicosulfuron	0.060	0.010	49.7	0.301	1.72E-06	0.05	1740.99	0.01*
Prothiofos	0.500	0.096	58.0	237.472	0.000963	0.1	51.94	**4.1608**

AppRate is pesticide application rate used in PESTRANS model; $C_{T,M}$*, is Pesticide Soil Concentration;* $R_{\%}$ *is Percent Remaining Pesticide Mass; PL is Diffuse Pesticide Load; AppRate EQS is Application Rate Corresponding to EQS; Cobs is Observed Concentration.; *Since there is no detection (<LOD), these values are taken as half of LOD (LOD/2).*

Consequently, in this section mass balances of four drainage areas YB01, YB06, YB11+YB12 and YB16 is assessed using discharge and receiving body water quality monitoring results, and estimated diffuse pesticide loads by taking into consideration upstream and downstream relationships. These four drainage areas have key importance in terms of diffuse pesticide loads according to the results of water quality measurements. Aclonifen, Bifenox, Chlorfenapyr, Chlorothalonil, Chlorpyrifos (Chlorpyrifos-ethyl), Chlorsulfuron, Cyfluthrin (Beta-cyfluthrin), Cypermethrin, Alpha-cypermethrin, Zeta-cypermethrin, Cyromazine, Dichlorvos, Diflubenzuron, Ethalfluralin, Fenpropimorph, Fenthion, Nicosulfuron and Prothiofos active substances are exceeding at least one time in the receiving body sampling points. Mass balances revealed that pollution is mostly diffuse sourced. Diffuse pesticide load estimations indicated the pollution potential of agricultural areas in these drainage areas. Estimated diffuse load results are within a range of 0.01% -9716 % of the monitored results. Mostly actual loads are higher than estimated diffuse loads. Moreover, only estimated potential concentrations due to diffuse loads of Cypermethrin, Alpha-cypermethrin and Dichlorvos active substances exceed the EQSs. One of the reasons behind the inconsistency between actual and estimated loads is attributed to the uncertainties in the pesticide application areas and application rates. Results may indicate that pesticides are applied more than suggested application rates. Thus in this section, pesticide application rates that comply with EQSs are also presented. The assessment highlights that the application rates of Cypermethrin, Alpha-cypermethrin, and Dichlorvos must be reduced to AppRate EQS values. Also, the use of other EQS exceeding pesticides should be controlled and alternative pesticides should be used. Good agricultural practices must be implemented in these four drainage areas. Suggested control measures for diffuse pesticide pollution in the light of these results are presented in Section 4.5.

4.5. Proposal of diffuse source control measures for Tersakan Creek

Good agricultural practices such as reduction in pesticide application rates and building vegetated waterways to maintain good water quality status and prevent diffuse pesticide loads in the Tersakan Creek are presented in this section. As previously mentioned, the irrigation water used is drained back to the Tersakan Creek via open channels (Amasya ÇDR, 2018) can be important locations to apply these prevention methods and help improving the water quality of Tersakan Creek. In this manner, YB01, YB06, YB11+YB12 and YB16 drainage areas are hot points for the control of diffuse pesticide pollution in Tersakan Sub-basin.

In order to control the transport of diffuse pesticide load to the receiving water bodies, methods with the following basic principles should be implemented in these four drainage areas: minimizing the use of existing pollutants (resource reduction), delaying the transport and/or distribution of pesticides by reducing the amount of water transported or by intercepting the pollutant and reducing/removing contaminants by chemical or biological processes before or after reaching the water source (US EPA, 2003-b). In terms of reducing diffuse pesticide pollution in critical drainage areas, assistance should be requested from authorized people and institutions in any circumstance that raise a question mark in minds. Farmers and PPP sector members should be subjected to detailed training for effective and efficient use of the pesticides. Primarily, information regarding past pest problems, pesticide use, agricultural product and size of agricultural area should be collected (US EPA, 2003-b).

According to US EPA (2003-b), Integrated Pest Management (IPM) strategies should be followed. For example, pesticides should be applied efficiently at times when transport by runoff are least likely that if an economic benefit will be gained. Weather forecast and agricultural projection reports of the Turkish State Meteorological Service should be followed (2019). According to FAO (2019), it is suggested that if rain is imminent (definite rain is less than 1.6 kilometers away, or there is more than a 75% chance) or foliage is dripping wet, pesticides should not be sprayed.

The physical characteristics of the site should be evaluated for the presence of wells, proximity to surface water, slope, tillage practices and potential loss of pesticide by leaching and surface runoff (US EPA, 2003-b). In terms of erosion and sediment control, there are many recommended methods to prevent soil from detaching and transporting by rainfall. Moreover, persistence, toxicity, runoff and leaching potential of pesticides should be considered while making a selection from registered pesticides which are presented in the following paragraphs.

Spills of pesticides should be prevented while preparing the mixture and transferring it to the spray equipment such as through using solid pad and pesticides should be applied only in the recommended amounts presented in Table 3.9, Table 3.10 and also PPP Database of Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry) (2017). Pesticides in Table 3.11 shouldn't be used since they are banned by the Ministry. Also, the study revealed that the pesticide application rates of Cypermethrin and Alpha-cypermethrin should be reduced between 75% and 99% comply with EQSs. Chlorsulfuron, Beta-Cyfluthrin, Cyromazine and Nicosulfuron active substances tend to leach further from 20 cm depth of soil. Moreover, Chlorfenapyr, Chlorsulfuron, Aclonifen and Cyfluthrin active substances remain in the soil more than 80% at the end of 30 days. Users must not exceed the recommended application rates. The equipment must be checked and readjusted during each application period. According to U.S. EPA (2003-b), conservation methods applied and were evaluated beneficial in terms of their effect on surface water quality regarding pesticides are presented in Table 4.16. Thus, few literature examples for the application of these conservation methods are presented.

In the study of Shulz & Peall (2001), the effect of artificial wetlands on diffuse pollution loads was examined. Accordingly, under no rainfall conditions 15%; under rainy conditions 78% of the total suspended solids was intercepted. Chlorpyrifos and Endosulfan pesticides were not detected at the outlet, while azinphos-methyl pesticide load was intercepted at 77% and 93%. In another part, higher concentrations of Azinphos-methyl, Chlorpyrifos and Prothiofos pesticides were detected at the entrance. However, no organic phosphorus pesticides were detected in the suspended sample sampling analyzes. Thus, it has been evaluated that artificial wetlands are effective in reducing the diffuse pollution load.

As previously mentioned, according to Zhang and Zhang's modeling study (2011), the formation of vegetated buffer zones and the reduction of application amounts reduced the load of Chlorpyrifos active substance more than 94%.

According to Baker et al. (2000), the vegetated buffer strips effectively reduce the diffuse loads of pesticides adsorbed in the soil, since they are effective in reducing sediment transport. Conservative soil tillage method is one of these applications that reduces sediment transport and surface water flow. Since the soil tillage method provides erosion control, it is one of the best management practices to control the loss of strongly adsorbed pesticides such as Trifluralin and Chlorpyrifos to surface waters. Baker et al. (2000) published a number of studies in his publication:

In order to evaluate the effect of the vegetated buffer strips, a study was carried out in a field with Trifluralin pesticide and loamy sand with 0.5% organic material, canine tooth and shiny pseudocarcus grass. In no rainfall conditions and where area vegetated was 4 times of that area was used pesticide, surface water flow with sediment load decreased by 73%, Trifluralin pesticide decreased by 53% through adsorption. In rainy conditions, surface water flow with sediment load decreased by 44%, Trifluralin pesticide decreased by 57% through adsorption (Baker, Mickelson, Arora, & Misra, 2000).

In another study performed with Atrazine pesticide, which was less susceptible to adsorption than the active substance Trifluralin and the planted strips, the field was grazed with bromine, clot and reed ball. Areas of buffer zones were prepared as 1 in 10 and 1 in 5 of pesticide application areas. In the 1:10 ratio where the protective tillage method was used, atrazine pesticide decreased by 28.3% and sediment load decreased by 72.2%. In the 1:5 ratio scale area, atrazine pesticide decreased by 51.3% and sediment load by 75.7%. In conditions were no tillage is applied, Atrazine decreased by 35% in the 1:10 ratio and decreased by 59% in the 1:5 ratio (Baker, Mickelson, Arora, & Misra, 2000).

Table 4.16. Conservation practices (USDA, 2017)

Conservation practices	Explanations
Channel vegetation	Planting suitable vegetation in channels to regulate surface water flow to a non-erosive velocity.
Conservation cover	Establishment and maintenance of permanent vegetation cover.
Constructed wetland	An artificial ecosystem with hydrophilic vegetation for water treatment.
Contour buffer strips	Permanent and herbaceous vegetation is formed around the hill slope and contour into strips that alternated down the slope.
Critical area planting	Formation of permanent vegetation in areas with high erosion rates or in areas with physical, chemical or biological conditions that prevent the formation of vegetation.
Hedgerow planting	Establishment of dense vegetation in a linear design
Micro and sprinkler irrigation systems	A watering system that frequently delivers small amounts of water to or below the surface of the soil: drip, low-flow, or miniature spray irrigation via emitters or equipment located along the water distribution line.
Mulching	Application of plant residues or suitable materials produced in other places to the field surface.
Prescribed grazing	Managing plant harvesting with grazing.
Wetland restoration	Returning and functioning of wetlands approaching to the first conditions.
Agrichemical Handling Facility	A facility with an impervious surface to provide an environmentally safe area for the handling of on-farm agrichemicals.
Alley cropping	Trees or shrubs are planted in series or in series of single or multiple rows of agronomic, horticultural plants or grasses produced in side streets between rows of woody plants.

Another study was carried out to reduce the diffuse load of Chlorpyrifos pesticide with silty loam soil vegetated with canine grass. The ratio of pesticide application area to grazed area was 2:1 and 1:1. Chlorpyrifos load was reduced between 64% and 100% (Baker, Mickelson, Arora, & Misra, 2000).

The methods and studies applied to reduce the diffuse pesticide loads indicate that the 2023 targets for 50% reduction of pollution in Tersakan Sub-basin mentioned in Chapter 1.1 can be achieved. In order to reduce the diffuse loads of general population of pesticides used in Tersakan Creek and protect the good status of water quality, methods in Table 4.16 and particularly application of licenced pesticides, application of pesticides in suggested amounts, reduction in pesticide usage, artificial wetlands, vegetated buffer strips and conservative soil tillage is suggested for the drainage areas

YB01, YB06, YB11+YB12, YB16. Their locations are presented in Figure 3.4 and Figure 3.5.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

According to US EPA (2003-b) in terms of preventing diffuse pollution by pesticides; properties of the soil and site should be evaluated, such as proximity to surface water, slope, leaching and loss of pesticide by transportation. Moreover, information about pesticide use, agricultural product, size of agricultural area should be gathered. Thus this study mainly aimed to estimate diffuse loads of pesticides by gathering this information to be able to identify the sources and reasons of pesticide pollution in the Tersakan Creek. Estimation is completed using loading functions presented by McElroy (1976), which lie at the bottom of most diffuse load estimation models, mainly requires the erosion (the USLE) and soil pesticide concentration information about the sub-basin.

Four receiving body water quality sampling points draw the attention regarding concentrations exceeding the EQS in the monitoring results: Y-40, Y-32, Y-31 and Y-20. These sampling points were paired with YB01, YB06, YB12, and YB16 drainage areas since it has been evaluated that the contribution of point sources to the pollution in the receiving body is a minor issue and the pollution is largely diffuse-origin. In other drainage areas, there are agricultural areas according to the CORINE Land Cover map. However, they are not prioritized, since there is no exceedance of EQS in receiving body sampling points paired with these areas or there are no predetermined receiving body sampling points downstream at these drainage areas. YB01 drainage area is located in the upstream while YB16 drainage area is located in the downstream of the Tersakan Creek. Drainage area of YB06 lies next to the mainstream and YB11+YB12 drainage areas are in the another branch of Tersakan sub-basin. Drainage areas of YB11+YB12, YB01, YB16, and YB06 cover, 22.1 %, 5.4%, 2.1 % and 1.7% area of the Tersakan sub-basin, respectively. Thus, diffuse pesticide pollution is not sub-basin wide but local; pollution is originated from 1/3 of the Tersakan sub-basin. In the four drainage areas, good agricultural practices such as application of licenced pesticides, use of pesticides in suggested amounts, reduction in pesticide usage (between 75% and 99% for Cypermethrin and Alpha-cypermethrin to satisfy EQSs), conservative soil tillage, artificial wetlands, vegetated buffer zones should be applied to reduce unconscious excessive application of the pesticides and the transport of the diffuse pesticide loads in the future.

Chlorfenapyr, Alpha-cypermethrin, Dichlorvos, Ethalfluralin, Fenpropimorph and metabolites of DDT are detected in EQS exceeding concentrations in discharge samples. Water quality monitoring results of 4th period (April 2017) reveal that both Merzifon OIZ and preceding Y-31 receiving body have EQS exceeding concentrations of Alpha-cypermethrin. In this case, 6% of the pollution thus may be result of the point source. However, due to grab sampling, deficiencies in flow rate measurements and wastewater discharge to dry river bed, presence and significance of pesticides in discharges and receiving body of Tersakan Creek can be inadequately represented. Thus, industries must inquire about the pesticides that is applied and the residue concentrations on crops that they process, also they must review their waste water treatment systems.

It is reported in the provincial environmental status report of Amasya that in the irrigated agricultural lands, the water is drained, and the drained water is given to open drainage channels and then back to the Tersakan Creek (Amasya ÇDR, 2018). According to US EPA (2003-b), in order to control the transmission of diffuse source pollutants to the receiving water bodies, delaying the discharge of the pollutant in the drainage water by reducing the amount of water transported and by precipitating the pollutant or by converting active substances chemically or biologically, before or after reaching the reveiving water source are the main elements of management for diffuse pollution. Vegetated channels, waterways and riversides, contour buffer strips (terracing), and drip and sprinkler irrigation systems are several methods suggested for the protection of the surface water from various diffuse pollution loads. For example, studies show that vegetated buffer zones are reducing the load of pesticides by more than 90% (Zhang & Zhang, 2011). These diffuse load control measures can be tested in future studies for the effectiveness in Tersakan sub-basin by changing erosion practice factor (P) in USLE equation that DEMIS model is using or by using more advanced models such as SWAT or HSPF.

Estimated concentrations (C_{est}) of Cypermethrin, Alpha-Cypermethrin, and Dichlorvos active substances in each drainage area exceeded the EQS. The application amounts of Cypermethrin, Alpha-Cypermethrin and Dichlorvos should be reduced to the application rates corresponding to the EQS, from 0,290-0,392 kg/ha to 0-0.01 kg/ha, 0.160-0.233 kg/ha to 0-0.04 kg/ha and 1.1 kg/ha to 0.001-0.87 kg/ha, respectively. Chlorsulfuron, Beta-cyfluthrin, Cyromazine, and Nicosulfuron pesticides tend to leach deeper layers of soil. Furthermore, more than 80% of Chlorsulfuron, Aclonifen, Cyfluthrin and Chlorpyrifos-ethyl active substances tend to remain in soil. Thus, users must not exceed recommended application rates and follow good agricultural practices. According to US EPA (2003-b), in terms of preventing diffuse pollution by pesticides, minimization of the use of existing pollutants by resource reduction and conscious applications (applying pesticides only with recommended amount, method and timing, and preventing spills while preparing and transferring the mixture into the spray equipment) are one of the management practices followed. Moreover, it was reported during the sampling of Tersakan Creek that there were empty pesticide containers at some points in the riverside. These containers should be disposed according to the best available hazardous waste management techniques, all active substances mentioned above should be applied with care, and assistance should be sought from authorized personnel and institutions.

Although the concentrations of some pesticides, such as Aclonifen, Bifenox, and Chlorsulfuron, exceed the EQS in the receiving body samples, the estimated concentration (C_{est}) that is generated by the diffuse loads calculated using reported application amounts remained below the EQS. The uncertainties in the size and location of agricultural areas, flow rates or the reported pesticide use, may have led to estimated diffuse pollution loads to be lower than it actually is. For example, there is inconsistency between application areas of pesticides in Amasya and the agricultural regions reported by TURKSTAT (2017). Moreover, active substances Chlorfenapyr, Dichlorvos, Ethalfluralin, Fenthion, Prothiofos, which exceed EQS at least one time are entirely prohibited in years 2011, 2011, 2012, 2011 and 2012 respectively, but they are observed in receiving body and discharge samples. Moreover, according to the data obtained from the Ministry of Forestry and Water Affairs (currently Ministry of Agriculture and Forestry) Zeta-Cypermethrin is applied to hazelnuts. However, hazelnuts are not produced according to TURKSTAT crop data of Suluova and Merkez counties of Amasya whose area lie within the related drainage area where Zeta-cypermethrin exceeds EQS. Thus, Zeta-cypermethrin is most likely used for other crops, and these applications are not reported by the authorities.

It is seen that pesticides that their observed and estimated concentrations exceed EQS at the same time are Cypetmethrin, Alpha-cypermethrin and Dichlorvos for YB01, YB06, YB16 drainage areas, and are Chlorpyrifos-ethyl, Cyfluthrin, Cypermethrin, Alpha-cypermethrin, Cyromazine and Dichlorvos. For YB01, YB06, YB16 drainage areas, estimated concentrations are lower than observed concentrations zero to three orders of magnitude. For YB12 drainage area, except Cyfluthrin, estimated concentrations are higher than observed concentrations zero to two order of magnitudes. Furthermore, for pesticides such as Aclonifen estimated concentrations can be lower than observed concentrations zero to four orders of magnitude even if their observed concentrations are exceeding EQSs. This situation may indicate water quality monitoring sampling deficiencies (stagnant water and insufficient flow), uncertainties in pesticide application areas (generalization of spatial data or larger applications areas may exist), and uncertainties in the pesticide application rates (applying more than suggested rates, or unreported applications) complex nature of pesticide fate and transport (such as degradation of active substances during transport over distances).

Application of Chlorpyrifos-methyl active substance is reported by the Ministry of Agriculture and Forestry as 1.7025 kg a.s./ha. It is suggested in Plant Protection Products Database as 0.85125 kg a.s./ha (Ministry of Agriculture and Forestry, 2017). Reported application rate is higher than suggested value. However, Chlorpyrifos-methyl is not included in 45 priority and 250 specific pollutants in Surface Water Quality Regulation (30.11.2012/28483). Thus, Chlorpyrifos-methyl should be included in future water quality monitoring programs.

In conclusion, immediate measures should be taken to reduce pollution in four drainage areas YB01, YB06, YB11+YB12 and YB16 for 22 pesticides that exceed EQSs and other 35 that is detected. Pesticide usage and pesticide application areas should be determined accurately in order to perform good agricultural measures succesfully. Locations of drainage channels of excess agricultural water should be determined. The loading function method is the basis of common diffuse pesticide load estimation models. Results revealed that this method has produced reasonable estimations of the diffuse pollution potential of pesticides, even if there are inconsistencies due to lack of knowledge of pesticide application areas and pesticide usage. According to the verbal information exchange with Directorate General for State Hydraulic Works (DSİ), sediment yield estimated by DEMIS model gives accurate results with on-site measurements at DSI stations. As watershed scale models requiring significant amount of data provide accurate and reasonable results if all input data requirement is satisfied, more reliable estimation of diffuse pesticide loads can also be obtained with loading functions coupled with DEMIS and PESTRANS models, and with accurate input data.

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APPENDICES

A. Percentages of areas that are comprised of main classes of CORINE 2012 Land Cover in terms of counties

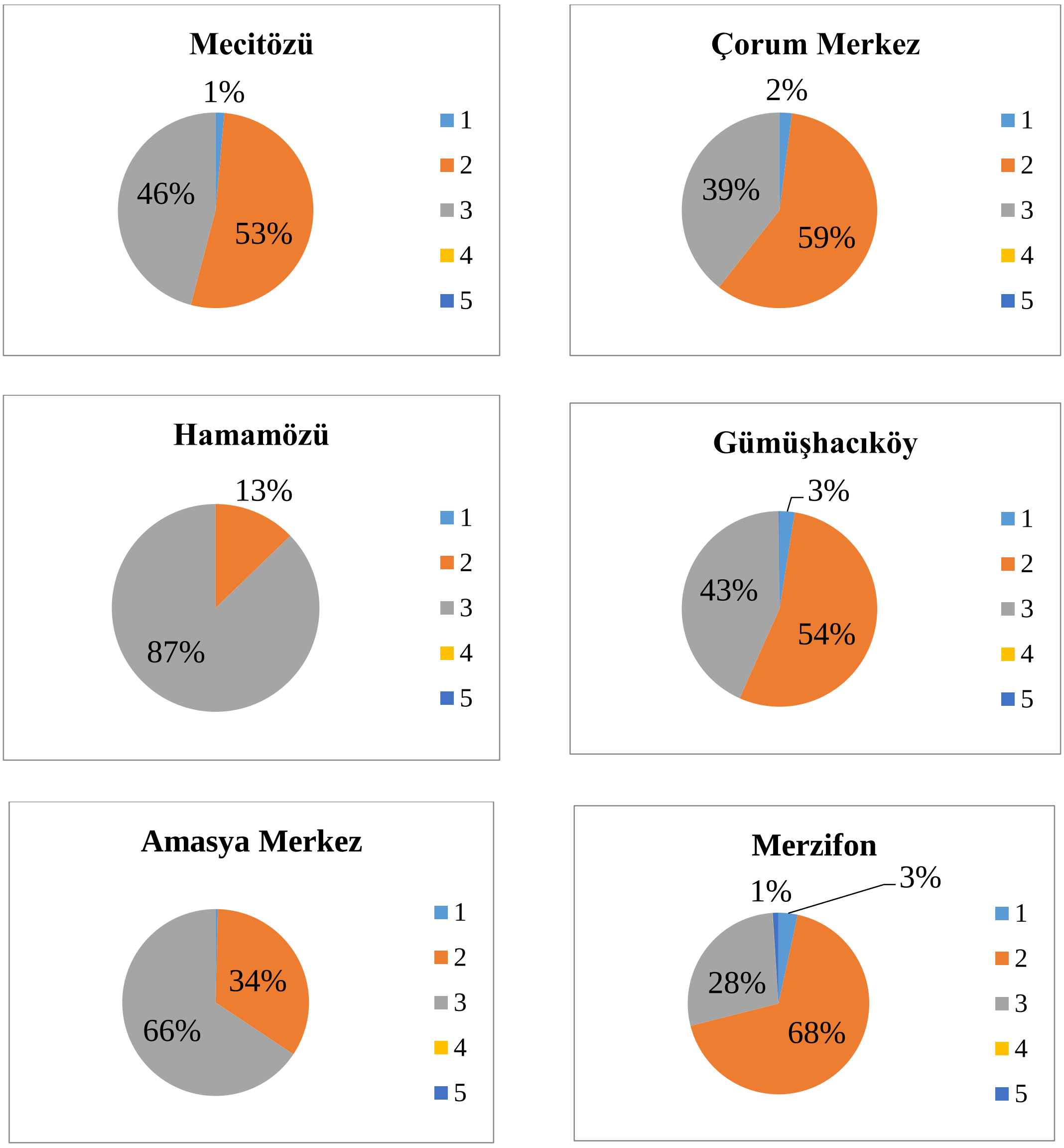

Figure A.0.1. Percentages of areas that are comprised of main classes of CORINE 2012 Land Cover in terms of counties

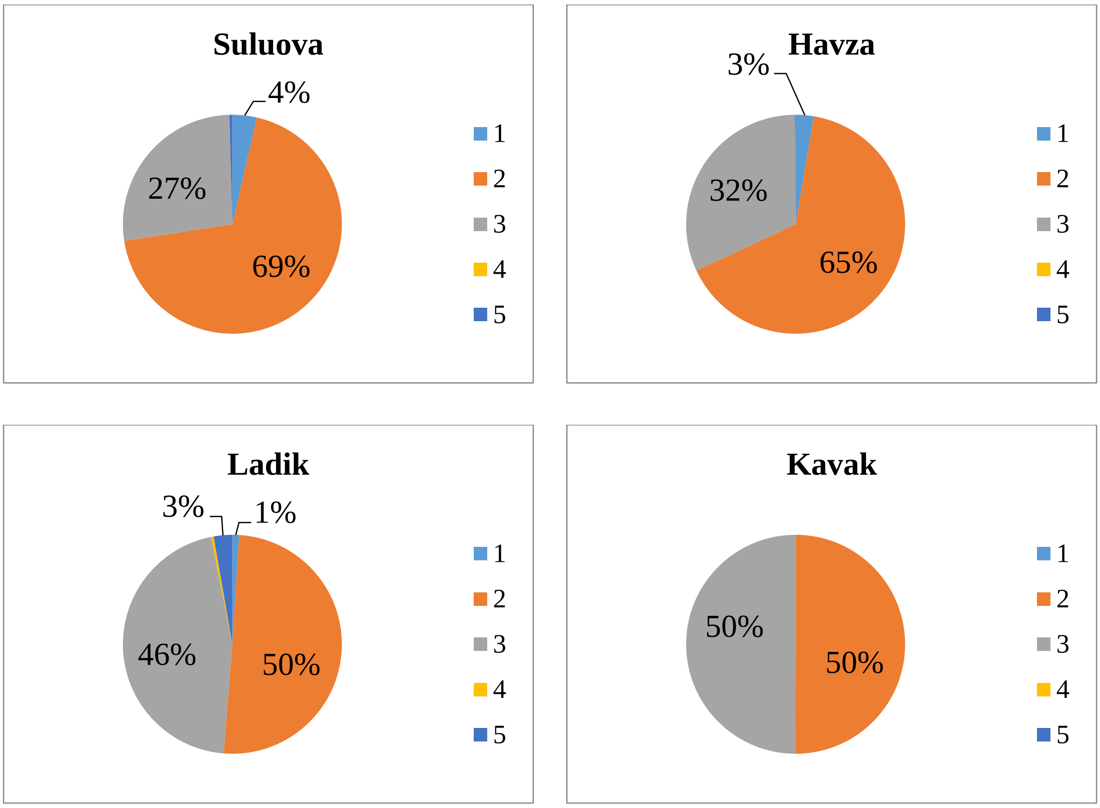

Figure A.1. Percentages of areas that are comprised of main classes of CORINE 2012 Land Cover in terms of counties (Here 1 represents Artificial Surfaces; 2, Agricultural Areas; 3, Forests and Seminatural Areas; 4, Wetlands, and 5 represents Water Bodies) (Continued)

B. CORINE Land Cover 2012 agricultural areas of drainage areas in terms of counties

Table B.1. CORINE Land Cover 2012 agricultural areas of YB01, YB02 and YB03 drainage areas in terms of counties

Drainage Areas	**YB01**	**YB02**			**YB03**	
Counties/CORINE Land Cover Classes	Ladik	Havza	Kavak	Ladik	Havza	Ladik
211 (ha)	201.2	-	5.7	2006.4	170.0	661.5
212 (ha)	3917.2	146.7	276.7	4050.5	238.2	1686.5
231 (ha)	210.4	319.9	47.1	548.1	3.0	50.6
242 (ha)	138.1	-	5.2	356.1	-	72.5
243 (ha)	1493.9	0.1	324.3	1647.2	-	911.4

Names of the CORINE Land Cover Classes are presented in Table *3.14*

Table B.2. CORINE Land Cover 2012 agricultural areas of YB04, YB05 and YB06 drainage areas in terms of counties

Drainage Areas	**YB04**		**YB05**	**YB06**	
Counties/CORINE Land Cover Classes	Havza	Ladik	Havza	Havza	Merzifon
211 (ha)	7522.5	230.6	1063.4	220.1	12.7
212 (ha)	1269.6	99.0	-	19.2	138.7
231 (ha)	37.4	-	33.3	86.9	25.5
242 (ha)	489.0	-	12.8	38.0	-
243 (ha)	834.3	51.5	92.2	346.6	18.3

Names of the CORINE Land Cover Classes are presented in Table *3.14*

Table B.3. CORINE Land Cover 2012 agricultural areas of YB07 drainage area in terms of counties

Drainage Areas	**YB07**				
Counties/CORINE Land Cover Classes	Amasya Merkez	Havza	Ladik	Merzifon	Suluova
211 (ha)	-	1910.2	989.3	30.6	692.0
212 (ha)	-	386.3	555.7	-	844.8
231 (ha)	-	118.2	67.6	20.3	9.3
242 (ha)	-	81.3	-	-	10.6
243 (ha)	52.5	814.3	820.2	185.2	366.9

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

Table B.4. CORINE Land Cover 2012 agricultural areas of YB08,, YB09 and YB10 drainage areas in terms of counties

Drainage Areas	**YB08**			**YB09**	**YB10**		
Counties/CORINE Land Cover Classes	Havza	Ladik	Suluova	Suluova	Havza	Merzifon	Suluova
211 (ha)	1385.1	157.2	1616.5	214.0	-	4698.6	185.3
212 (ha)	-	-	2334.9	3462.0	-	3046.1	-
231 (ha)	3.3	-	-	179.5	-	334.7	-
242 (ha)	33.2	-	250.1	643.2	-	1655.0	-
243 (ha)	-	5.8	301.4	-	-	636.7	-

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

Table B.5. CORINE Land Cover 2012 agricultural areas of YB11 and YB12 drainage areas in terms of counties

Drainage Areas	**YB11**	**YB12**		
Counties/CORINE Land Cover Classes	Merzifon	Gümüşhacıköy	Hamamözü	Merzifon
211 (ha)	4913.4	-	-	8211.4
212 (ha)	922.7	3677.4	-	7620.7
231 (ha)	228.6	281.7	-	71.0
242 (ha)	114.2	1413.1	98.7	345.1
243 (ha)	182.2	1459.4	650.0	619.0

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

Table B.6. CORINE Land Cover 2012 agricultural areas of YB13 drainage area in terms of counties

Drainage Areas	**YB13**					
Counties/CORINE Land Cover Classes	Amasya Merkez	Çorum Merkez	Gümüşhacıköy	Hamamözü	Mecitözü	Merzifon
211 (ha)	285.4	1477.0	-	5.0	1899.0	4338.6
212 (ha)	-	6251.5	-	-	2781.2	2677.9
231 (ha)	5.2	693.0	-	0.2	194.0	489.3
242 (ha)	-	1452.0	-	65.2	267.4	309.3
243 (ha)	171.8	1059.3	635.4	24.5	129.6	2931.2

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

Table B.7. CORINE Land Cover 2012 agricultural areas of YB14 drainage area in terms of counties

Drainage Areas	**YB14**		
Counties/CORINE Land Cover Classes	Amasya Merkez	Merzifon	Suluova
211 (ha)	702.1	773.2	699.0
212 (ha)	813.5	2923.9	8618.9
222 (ha)	-	115.9	1361.1
231 (ha)	296.4	430.3	335.9
242 (ha)	289.4	1392.6	1343.2

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

Table B.8. CORINE Land Cover 2012 agricultural areas of YB15 drainage areas in terms of counties

Drainage Areas	**YB15**			**YB16**	
Counties/CORINE Land Cover Classes	Amasya Merkez	Ladik	Suluova	Amasya Merkez	Suluova
211 (ha)	149.1	-	2361.5	138.6	-
212 (ha)	-	-	713.8	82.6	202.6
222 (ha)	9.2	-	206.4	495.9	162.6
231 (ha)	-	-	334.3	1.7	-
242 (ha)	120.7	-	2474.4	356.5	2.7
243 (ha)	387.5	29.1	750.0	393.4	-

Names of the CORINE Land Cover Classes corresponding to the codes are presented in Table *3.14*

C. Agricultural products of Amasya Merzifon and their 2015-2016-2017 year average of areas, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate

Table C.9. Agricultural products and their 2015-2016-2017 year average of areas in Amasya Merzifon, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate

Agricultural products	Three year average of areas (ha)	Paired CORINE 2012 Land Cover Class	Pesticide	Reported application rate (kg a.s. /ha)	Recommended application rate (kg a.s. /ha)
Wheat	201762.3	211	Chlorsulfuron	0.0075	0.0075
Wheat	201762.3	211	Fenpropimorph	0.25	0.3125
Wheat	201762.3	211	Ethalfluralin	-	1.68
Wheat	201762.3	211	Fenthion	-	0.91875
Wheat	201762.3	211	Cyfluthrin	-	0.025
Wheat	201762.3	211	Bifenox	-	0.75
Sunflower seed	80828.7	211	Aclonifen	1.2	1.95
Barley	47582.7	211	Fenpropimorph	0.25	0.3
Barley	47582.7	211	Ethalfluralin	-	1.68
Barley	47582.7	211	Fenthion	-	0.91875
Barley	47582.7	211	Cyfluthrin	-	0.025
Barley	47582.7	211	Bifenox	-	0.75
Sugar Beet	25246.67	211	Cyfluthrin	-	0.0125
Onion	15026.7	212	Chlorpyrifos-ethyl	0.5	1
Onion	15026.7	212	Dichlorvos	-	1.1
Onion	15026.7	212	Chlorothalonil	0.006	1

Table C.9. Agricultural products and their 2015-2016-2017 year average of areas in Amasya Merzifon, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate, continued

Agricultural products	Three year average of areas (ha)	Paired CORINE 2012 Land Cover Class	Pesticide	Reported application rate (kg a.s. /ha)	Recommended application rate (kg a.s. /ha)
Vetch	1148.3	211	-	-	-
Corn	964.1	211	Alpha-cypermethrin	0.04	0.12
Corn	964.1	211	Chlorpyrifos-ethyl	0.864	2.592
Corn	964.1	211	Cypermethrin	0.075	0.225
Corn	964.1	211	Nicosulfuron	0.06	0.06
Corn	964.1	211	Ethalfluralin	-	1.25
Corn	964.1	211	Fenthion	-	0.91875
Corn	964.1	211	Cyfluthrin	-	0.1125
Corn	964.1	211	Chlorfenapyr	-	0.2
Poppy seeds	506.17	211	-	-	-
Poppy	506.17	211	-	-	-
Chickpea	300	211	Aclonifen	0.75	0.75
Walnut	184.93	222	-	-	-
Apple	362.57	222	Alpha-cypermethrin	**0.24**	0.02
Apple	362.57	222	Cypermethrin	**0.6**	0.05
Apple	362.57	222	Diflubenzuron	**0.4**	0.1
Apple	362.57	222	Chlorfenapyr	-	0.108
Apple	362.57	222	Dichlorvos	-	1.1
Apple	362.57	222	Fenthion	-	0.7875
Apple	362.57	222	Prothiofos	-	0.5
Safflower seed	118.33	211	-	-	-
Potato	109.9	211	Chlorpyrifos-ethyl	0.5	1
Potato	109.9	211	Chlorothalonil	0.006	1.26
Potato	109.9	211	Cypermethrin	**0.1**	0.04
Potato	109.9	211	Ethalfluralin	-	18
Potato	109.9	211	Cyfluthrin	-	0.025
Potato	109.9	211	Dichlorvos	-	1.1
Cherry	99.17	222	Cypermethrin	**0.3**	0.2
Cherry	99.17	222	Fenthion	-	0.7875
Cherry	99.17	222	Dichlorvos	-	1.1
Clover	87.5	211	-	-	-
Tomato	70.83	212	Chlorothalonil	1.125	1.5

Table C.9. Agricultural products and their 2015-2016-2017 year average of areas in Amasya Merzifon, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate, continued

Agricultural products	Three year average of areas (ha)	Paired CORINE 2012 Land Cover Class	Pesticide	Reported application rate (kg a.s. /ha)	Recommended application rate (kg a.s. /ha)
Tomato	70.83	212	Chlorpyrifos-ethyl	0.5	1
Tomato	70.83	212	Chlorpyrifos-methyl	**1.7025**	0.85125
Tomato	70.83	212	Cypermethrin	**0.1**	0.075
Tomato	70.83	212	Cyromazine	-	0.15
Tomato	70.83	212	Dichlorvos	-	1.1
Tomato	70.83	212	Cyfluthrin	-	0.025
Green beans	58.5	212	Cypermethrin	**0.1**	0.08
Green beans	58.5	212	Cyromazine	-	0.15
Green beans	58.5	212	Ethalfluralin	-	1.68
Grape	94.03	221	Cypermethrin	**0.2**	0.05
Grape	94.03	221	Chlorfenapyr	-	0.216
Grape	94.03	221	Dichlorvos	-	1.1
Grape	94.03	221	Fenthion	-	0.7875
Triticale	53	211	Ethalfluralin	-	1.68
Triticale	53	211	Fenthion	-	0.91875
Triticale	53	211	Cyfluthrin	-	0.025
Green pepper	43.23	212	Chlorpyrifos-ethyl	0.5	1
Green pepper	43.23	212	Chlorpyrifos-methyl	**1.7025**	0.85125
Green pepper	43.23	212	Cypermethrin	0.1	0.1
Green pepper	43.23	212	Chlorfenapyr	-	0.216
Green pepper	43.23	212	Dichlorvos	-	1.1
Dried beans	38.33	211	Cypermethrin	0.1	0.08
Dried beans	38.33	211	Cyromazine	-	0.15
Dried beans	38.33	211	Ethalfluralin	-	1.68
Oat	75.97	211	Ethalfluralin	-	1.68
Oat	75.97	211	Fenthion	-	0.91875
Oat	75.97	211	Cyfluthrin	-	0.025
Cucumber	30.63	212	Chlorpyrifos-ethyl	0.5	1
Cucumber	30.63	212	Chlorothalonil	0.006	1.5
Cucumber	30.63	212	Cypermethrin	**0.1**	0.075
Cucumber	30.63	212	Chlorfenapyr	-	0.144
Cucumber	30.63	212	Ethalfluralin	-	1.68

Table C.9. Agricultural products and their 2015-2016-2017 year average of areas in Amasya Merzifon, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate, continued

Agricultural products	Three year average of areas (ha)	Paired CORINE 2012 Land Cover Class	Pesticide	Reported application rate (kg a.s. /ha)	Recommended application rate (kg a.s. /ha)
Cucumber	30.63	212	Dichlorvos	-	1.1
Spinach	23.83	212	-	-	-
Fenugreek	21.33	211	-	-	-
Winter Squash	18.5	212	-	-	-
Leek	17.33	212	-	-	-
Tobacco	11.8	211	Beta-cyfluthrin	**0.027**	0.018
Garlic	6.33	212	-	-	-
Watermelon	6.23	212	Chlorpyrifos-methyl	**1.7025**	0.85125
Watermelon	6.23	212	Fenthion	-	0.7875
Watermelon	6.23	212	Chlorfenapyr	-	0.175
Watermelon	6.23	212	Dichlorvos	-	1.1
Peach	6.1	222	Dichlorvos	-	1.1
Peach	6.1	222	Fenthion	-	0.7875
Lettuce	7.7	212	Chlorpyrifos-ethyl	0.5	1
Lettuce	7.7	212	Dichlorvos	-	1.1
Quince	5.33	222	Diflubenzuron	**0.384**	0.12
Quince	5.33	222	Dichlorvos	-	1.1
Quince	5.33	222	Fenthion	-	0.7875
Pear	5.07	222	Cypermethrin	**0.2**	0.1
Pear	5.07	222	Dichlorvos	-	1.1
Pear	5.07	222	Fenthion	-	0.7875
Trefoil	4.5	211	-	-	-
Parsley	3.7	212	-	-	-
Sour Cherry	3.7	222	Fenthion	-	0.7875
Green lentil	3.5	211	-	-	-
Scallion	3.47	212	Chlorpyrifos-ethyl	0.5	1
Scallion	3.47	212	Dichlorvos	-	1.1
Scallion	3.47	212	Chlorothalonil	0.006	1
Strawberry	2.93	211	Chlorfenapyr	-	0.126
Strawberry	2.93	211	Dichlorvos	-	1.1
White Cabbage	2.67	212	Chlorpyrifos-methyl	0.3405	0.3405
White Cabbage	2.67	212	Chlorpyrifos-ethyl	0.5	1

Table C.9. Agricultural products and their 2015-2016-2017 year average of areas in Amasya Merzifon, paired CORINE 2012 Land Cover Classes with agricultural products, reported pesticide application and corresponding recommended application rate, continued

Agricultural products	Three year average of areas (ha)	Paired CORINE 2012 Land Cover Class	Pesticide	Reported application rate (kg a.s. /ha)	Recommended application rate (kg a.s. /ha)
White Cabbage	2.67	212	Chlorpyrifos-methyl	**1.7025**	0.3405
White Cabbage	2.67	212	Dichlorvos	-	1.1
Broad Bean	2.43	212	Cypermethrin	0.1	0.1
Melon	2.17	212	Chlorothalonil	0.006	0.9375
Melon	2.17	212	Chlorpyrifos-methyl	**1.7025**	0.85125
Melon	2.17	212	Fenthion	-	0.63
Melon	2.17	212	Dichlorvos	-	1.1
Green pea	2.07	212	Cypermethrin	0.1	0.1
Green pea	2.07	212	Ethalfluralin	-	1
Green pea	2.07	212	Fenthion	-	1.05
Green pea	2.07	212	Dichlorvos	-	1.1
Eggplant	1.57	212	Chlorothalonil	0.006	0.864
Eggplant	1.57	212	Chlorpyrifos-ethyl	0.5	1
Eggplant	1.57	212	Cypermethrin	**0.1**	0.075
Eggplant	1.57	212	Chlorfenapyr	-	0.126
Eggplant	1.57	212	Dichlorvos	-	1.1
Shell beans	1.43	211	-	-	-
Marrow	1.03	212	-	-	-
Okra	0.57	212	-	-	-
Cress	0.47	212	-	-	-

D. PESTRANS fate and transport modeling results of the drainage areas

Table D.10. *PESTRANS fate and transport modeling results of YB01 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB01	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.68	10.11	0.04	0	89.84	10.16
Bifenox	0.37	50.10	0.00	0	49.90	50.10
Chlorfenapyr	0.12	1.51	0.05	0	98.44	1.56
Chlorothalonil	1.03	24.83	5.99	0	69.18	30.83
(Chlorpyrifos) Chlorpyrifos-ethyl	0.99	24.26	1.92	0	73.83	26.17
Chlorsulfuron	0.07	8.63	0.00	0.014	91.35	8.65
Cyfluthrin	0.02	19.03	0.00	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.63	1.79	0	61.58	38.42
Cypermethrin	0.28	29.29	0.02	0	70.70	29.30
Alpha-cypermethrin	0.14	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.00	0	70.71	29.29
Cyromazine	0.10	31.02	0.00	0	68.98	31.02
Dichlorvos	0.47	56.63	0.22	0	43.14	56.86
Diflubenzuron	0.20	50.26	0.00	0	49.74	50.26
Ethalfluralin	0.95	33.73	10.69	0	55.58	44.42
Fenpropimorph	0.15	49.35	2.90	0	47.76	52.25
Fenthion	0.43	44.48	4.44	0	51.08	48.92
Nicosulfuron	0.03	50.24	0.00	0.002	49.76	50.24
Prothiofos	0.29	35.69	5.60	0	58.70	41.30

Table D.11. *PESTRANS fate and transport modeling results of YB02 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB02	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.74	10.11	0.04	0	89.85	10.15
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.14	1.51	0.05	0	98.45	1.55
Chlorothalonil	0.98	24.87	5.69	0	69.44	30.56
(Chlorpyrifos) Chlorpyrifos-ethyl	0.90	24.27	1.76	0	73.97	26.03
Chlorsulfuron	0.01	8.62	0	0.032	91.35	8.65
Cyfluthrin	0.02	19.03	0.00	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.66	1.63	0	61.71	38.29
Cypermethrin	0.11	29.29	0.01	0	70.70	29.30
Alpha-cypermethrin	0.14	38.62	0.00	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0	0	70.71	29.29
Cyromazine	0.10	31.02	0	0	68.98	31.02
Dichlorvos	0.47	56.64	0.20	0	43.16	56.84
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.95	33.76	10.73	0	55.52	44.48
Fenpropimorph	0.15	49.41	2.69	0	47.90	52.10
Fenthion	0.45	44.56	4.17	0	51.27	48.73
Nicosulfuron	0.03	50.24	0	0.004	49.76	50.24
Prothiofos	0.29	35.77	5.30	0	58.93	41.07

Table D.12. *PESTRANS fate and transport modeling results of YB03 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB03	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.73	10.11	0.04	0	89.84	10.16
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.14	1.51	0.05	0	98.44	1.56
Chlorothalonil	1.00	24.81	6.17	0	69.03	30.97
(Chlorpyrifos) Chlorpyrifos-ethyl	0.87	24.25	1.98	0	73.77	26.23
Chlorsulfuron	0.01	8.63	0	0.016	91.35	8.65
Cyfluthrin	0.02	19.03	0.00	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.62	1.85	0	61.54	38.46
Cypermethrin	0.10	29.29	0.02	0	70.70	29.30
Alpha-cypermethrin	0.13	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.00	0	70.71	29.29
Cyromazine	0.10	31.02	0	0	68.98	31.02
Dichlorvos	0.47	56.63	0.23	0	43.14	56.86
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.94	33.70	10.78	0	55.52	44.48
Fenpropimorph	0.15	49.32	2.98	0	47.70	52.30
Fenthion	0.45	44.45	4.56	0	50.99	49.01
Nicosulfuron	0.03	50.24	0	0.002	49.76	50.24
Prothiofos	0.29	35.66	5.72	0	58.62	41.38

Table D.13. PESTRANS fate and transport modeling results of YB04 drainage area

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB04	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.69	10.11	0.05	0	89.84	10.17
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.15	1.51	0.06	0	98.43	1.57
Chlorothalonil	1.01	24.62	7.35	0	68.03	31.97
(Chlorpyrifos) Chlorpyrifos-ethyl	1.02	24.19	2.33	0	73.47	26.53
Chlorsulfuron	0.01	8.63	0	0.075	91.30	8.70
Cyfluthrin	0.02	19.03	0.001	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.56	2.10	0	61.34	38.66
Cypermethrin	0.15	29.29	0.02	0	70.70	29.31
Alpha-cypermethrin	0.12	38.62	0.006	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.98	31.03
Dichlorvos	0.47	56.62	0.26	0	43.12	56.88
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.94	33.46	11.60	0	54.95	45.06
Fenpropimorph	0.15	49.14	3.50	0	47.36	52.64
Fenthion	0.45	44.19	5.40	0	50.41	49.60
Nicosulfuron	0.03	50.24	0	0.01	49.75	50.25
Prothiofos	0.29	35.46	6.37	0	58.17	41.83

Table D.14. *PESTRANS fate and transport modeling results of YB05 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB05	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.77	10.11	0.04	0	89.85	10.15
Bifenox	0.37	50.10	49.90	0	49.90	50.10
Chlorfenapyr	0.17	1.51	0.05	0	98.45	1.55
Chlorothalonil	1.03	24.87	5.69	0	69.44	30.56
(Chlorpyrifos) Chlorpyrifos-ethyl	1.25	24.27	1.76	0	73.97	26.03
Chlorsulfuron	0.01	8.62	0	0.034	91.35	8.65
Cyfluthrin	0.02	19.03	0.001	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.66	1.62	0	61.72	38.29
Cypermethrin	0.12	29.29	0.01	0	70.70	29.30
Alpha-cypermethrin	0.09	38.62	0.004	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0	0	70.71	29.29
Cyromazine	0.10	31.02	0	0	68.98	31.02
Dichlorvos	0.47	56.64	0.2	0	43.16	56.84
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.95	33.75	10.74	0	55.51	44.49
Fenpropimorph	0.15	49.41	2.69	0	47.90	52.10
Fenthion	0.47	44.56	4.17	0	51.27	48.73
Nicosulfuron	0.03	50.24	0	0.004	49.76	50.24
Prothiofos	0.29	35.77	5.30	0	58.94	41.07

Table D.15. PESTRANS fate and transport modeling results of YB07 drainage area

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB07	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.69	10.11	0.05	0	89.84	10.16
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.14	1.51	0.06	0	98.44	1.56
Chlorothalonil	0.74	24.69	6.86	0	68.45	31.55
(Chlorpyrifos) Chlorpyrifos-ethyl	0.90	24.22	2.16	0	73.62	26.38
Chlorsulfuron	0.01	8.62	0	0.058	91.32	8.68
Cyfluthrin	0.02	19.03	0.002	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.59	1.97	0	61.45	38.55
Cypermethrin	0.11	29.29	0.02	0	70.70	29.30
Alpha-cypermethrin	0.12	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.02	0	0	68.98	31.02
Dichlorvos	0.47	56.63	0.24	0	43.13	56.87
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.94	33.54	11.33	0	55.13	44.87
Fenpropimorph	0.15	49.22	3.26	0	47.52	52.48
Fenthion	0.45	44.30	5.04	0	50.66	49.34
Nicosulfuron	0.03	50.24	0	0.008	49.75	50.25
Prothiofos	0.29	35.55	6.08	0	58.37	41.63

Table D.16. *PESTRANS fate and transport modeling results of YB08 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB08	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.66	10.11	0.09	0	89.79	10.21
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.17	1.51	0.11	0	98.38	1.62
Chlorothalonil	0.66	24.12	10.52	0	65.37	34.64
(Chlorpyrifos) Chlorpyrifos-ethyl	0.88	24.02	3.76	0	72.22	27.78
Chlorsulfuron	0.01	8.72	0	0.061	91.22	8.78
Cyfluthrin	0.02	19.03	0.003	0	80.97	19.04
Beta-Cyfluthrin	0.02	36.26	3.49	0	60.24	39.76
Cypermethrin	0.21	29.29	0.03	0	70.68	29.32
Alpha-cypermethrin	0.10	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.28	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.56	0.44	0	43.00	57.00
Diflubenzuron	0.20	50.26	0.003	0	49.74	50.26
Ethalfluralin	0.89	32.86	13.65	0	53.49	46.51
Fenpropimorph	0.14	48.51	5.31	0	46.18	53.82
Fenthion	0.44	43.40	7.91	0	48.69	51.31
Nicosulfuron	0.03	50.27	0	0.007	49.72	50.28
Prothiofos	0.28	34.86	8.21	0	56.94	43.06

Table D.17. PESTRANS fate and transport modeling results of YB09 drainage area

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB09	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.54	10.11	0.08	0	89.81	10.19
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.13	1.51	0.09	0	98.40	1.60
Chlorothalonil	0.67	24.30	9.41	0	66.30	33.71
(Chlorpyrifos) Chlorpyrifos-ethyl	0.74	24.08	3.31	0	72.61	27.39
Chlorpyrifos-methyl	0.83	49.41	1.95	0	48.64	51.36
Chlorsulfuron	0.01	8.70	0	0.044	91.26	8.74
Cyfluthrin	0.03	19.03	0.003	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.36	3.08	0	60.56	39.44
Cypermethrin	0.23	29.29	0.03	0	70.69	29.31
Alpha-cypermethrin	0.13	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.58	0.39	0	43.03	56.97
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.88	33.04	12.99	0	53.97	46.04
Fenpropimorph	0.14	48.72	4.74	0	46.54	53.46
Fenthion	0.40	43.67	7.07	0	49.27	50.73
Nicosulfuron	0.03	50.27	0	0.005	49.73	50.27
Prothiofos	0.29	35.03	7.72	0	57.25	42.75

Table D.18. *PESTRANS fate and transport modeling results of YB10 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB10	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.71	10.11	0.08	0	89.81	10.19
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.14	1.51	0.09	0	98.40	1.60
Chlorothalonil	0.68	24.20	10.04	0	65.77	34.23
(Chlorpyrifos) Chlorpyrifos-ethyl	0.79	24.06	3.27	0	72.67	27.33
Chlorpyrifos-methyl	0.83	49.48	1.70	0	48.82	51.18
Chlorsulfuron	0.01	8.68	0	0.16	91.16	8.84
Cyfluthrin	0.02	19.03	0.003	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.39	2.83	0.001	60.78	39.22
Cypermethrin	0.28	29.29	0.03	0	70.69	29.31
Alpha-cypermethrin	0.14	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.59	0.34	0	43.07	56.93
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.93	33.06	12.95	0	53.99	46.01
Fenpropimorph	0.14	48.70	4.78	0	46.52	53.48
Fenthion	0.43	43.59	7.40	0	49.02	50.98
Nicosulfuron	0.03	50.25	0	0.021	49.73	50.27
Prothiofos	0.29	35.03	7.71	0	57.26	42.75

Table D.19. *PESTRANS fate and transport modeling results of YB11 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB11	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.71	10.12	0.04	0	89.85	10.15
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.16	1.51	0.05	0	98.45	1.55
Chlorothalonil	0.66	24.12	10.52	0	65.37	34.64
(Chlorpyrifos) Chlorpyrifos-ethyl	0.88	24.28	1.79	0	73.93	26.07
Chlorpyrifos-methyl	0.81	49.32	2.24	0	48.44	51.56
Chlorsulfuron	0.01	8.65	0	0.003	91.35	8.65
Cyfluthrin	0.02	19.03	0.001	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.66	1.69	0	61.65	38.35
Cypermethrin	0.21	29.29	0.03	0	70.68	29.32
Alpha-cypermethrin	0.11	38.62	0.004	0	61.37	38.63
Zeta-cypermethrin	0.28	29.29	0	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.64	0.22	0	43.15	56.85
Diflubenzuron	0.20	50.26	0.001	0	49.74	50.26
Ethalfluralin	0.96	33.74	10.75	0	55.50	44.50
Fenpropimorph	0.15	49.42	2.71	0	47.88	52.12
Fenthion	0.47	44.59	4.11	0	51.30	48.70
Nicosulfuron	0.03	50.25	0	0	49.75	50.25
Prothiofos	0.29	35.77	5.34	0	58.89	41.11

Table D.20. *PESTRANS fate and transport modeling results of YB12 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB12	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.79	10.11	0.06	0	89.82	10.18
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.16	1.51	0.08	0	98.42	1.58
Chlorothalonil	0.69	24.48	8.25	0	67.27	32.73
(Chlorpyrifos) Chlorpyrifos-ethyl	0.75	24.14	2.77	0	73.09	26.91
Chlorpyrifos-methyl	0.83	49.48	1.73	0	48.80	51.21
Chlorsulfuron	0.01	8.67	0	0.05	91.28	8.72
Cyfluthrin	0.02	19.03	0.002	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.46	2.58	0	60.96	39.04
Cypermethrin	0.17	29.29	0.02	0	70.69	29.31
Alpha-cypermethrin	0.12	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.60	0.33	0	43.07	56.93
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.94	33.30	12.07	0	54.64	45.36
Fenpropimorph	0.15	48.95	4.06	0	46.99	53.01
Fenthion	0.45	43.96	6.15	0	49.90	50.11
Nicosulfuron	0.03	50.26	0	0.007	49.74	50.26
Prothiofos	0.29	35.26	7.03	0	57.71	42.29

Table D.21. *PESTRANS fate and transport modeling results of YB13 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB13	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.72	10.11	0.07	0	89.82	10.18
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.16	1.51	0.08	0	98.41	1.59
Chlorothalonil	0.74	24.35	9.05	0	66.60	33.40
(Chlorpyrifos) Chlorpyrifos-ethyl	0.75	24.11	2.93	0	72.96	27.04
Chlorpyrifos-methyl	0.83	49.48	1.70	0	48.82	51.18
Chlorsulfuron	0.01	8.65	0	0.119	91.23	8.77
Cyfluthrin	0.02	19.03	0.002	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.45	2.58	0	60.97	39.03
Cypermethrin	0.12	29.29	0.02	0	70.69	29.31
Alpha-cypermethrin	0.14	0.00	38.62	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.60	0.31	0	43.09	56.91
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.94	33.20	12.42	0	54.38	45.62
Fenpropimoph	0.15	48.86	4.31	0	46.83	53.18
Fenthion	0.42	43.81	6.66	0	49.53	50.47
Nicosulfuron	0.03	50.25	0	0.015	49.74	50.26
Prothiofos	0.29	35.18	7.27	0	57.55	42.45

Table D.22. *PESTRANS fate and transport modeling results of YB14 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB14	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.66	10.11	0.09	0	89.80	10.20
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.14	1.51	0.10	0	98.39	1.61
Chlorothalonil	0.68	24.18	10.16	0	65.67	34.33
(Chlorpyrifos) Chlorpyrifos-ethyl	0.74	24.04	3.61	0	72.35	27.65
Chlorpyrifos-methyl	0.83	49.35	2.15	0	48.50	51.50
Chlorsulfuron	0.01	8.71	0	0.054	91.23	8.77
Cyfluthrin	0.02	19.03	0.003	0	80.97	19.04
Beta-Cyfluthrin	0.02	36.29	3.36	0	60.35	39.65
Cypermethrin	0.24	29.29	0	0	70.68	29.32
Alpha-cypermethrin	0.14	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.57	0.42	0	43.01	56.99
Diflubenzuron	0.20	50.26	0.003	0	49.74	50.26
Ethalfluralin	0.91	32.93	13.41	0	53.66	46.34
Fenpropimorph	0.14	48.58	5.12	0	46.30	53.71
Fenthion	0.41	43.49	7.64	0	48.88	51.12
Nicosulfuron	0.03	50.27	0	0.006	49.73	50.27
Prothiofos	0.29	34.91	8.05	0	57.04	42.97

Table D.23. *PESTRANS fate and transport modeling results of YB15 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB15	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.54	10.11	0.08	0	89.81	10.19
Bifenox	0.37	50.10	0.001	0	49.90	50.10
Chlorfenapyr	0.21	1.51	0.09	0	98.40	1.60
Chlorothalonil	0.73	24.36	9.02	0	66.62	33.38
(Chlorpyrifos) Chlorpyrifos-ethyl	1.06	24.10	3.16	0	72.74	27.26
Chlorpyrifos-methyl	0.83	49.44	1.87	0	48.70	51.30
Chlorsulfuron	0.01	8.69	0	0.032	91.28	8.72
Cyfluthrin	0.02	19.03	0.002	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.38	2.96	0	60.66	39.34
Cypermethrin	0.14	29.29	0.03	0	70.69	29.31
Alpha-cypermethrin	0.12	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.59	0.37	0	43.04	56.96
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.89	33.10	12.76	0	54.14	45.87
Fenpropimorph	0.14	48.51	5.31	0	46.18	53.82
Fenthion	0.41	43.76	6.78	0	49.46	50.54
Nicosulfuron	0.03	50.26	0	0.004	49.74	50.27
Prothiofos	0.29	35.09	7.55	0	57.36	42.64

Table D.24. *PESTRANS fate and transport modeling results of YB16 drainage area*

	SUMM	PCDECM	PCVAPM	PCDRM	PCTMR	PCTML
YB16	Remained pesticide mass on soil (kg/ha)	Degraded pesticide mass (%)	Evaporated pesticide mass (%)	Leached pesticide mass (%)	Remained pesticide mass on soil (%)	Pesticide mass loss (%)
Aclonifen	1.71	10.11	0.06	0	89.83	10.17
Bifenox	0.37	50.10	0	0	49.90	50.10
Chlorfenapyr	0.18	1.51	0.07	0	98.43	1.57
Chlorothalonil	0.69	24.64	7.31	0	68.05	31.95
(Chlorpyrifos) Chlorpyrifos-ethyl	0.75	24.19	2.48	0	73.33	26.67
Chlorpyrifos-methyl	0.83	49.45	1.83	0	48.72	51.28
Chlorsulfuron	0.01	8.66	0	0.015	91.32	8.68
Cyfluthrin	0.02	19.03	0.002	0	80.97	19.03
Beta-Cyfluthrin	0.02	36.52	2.33	0	61.15	38.85
Cypermethrin	0.22	29.29	0.02	0	70.69	29.31
Alpha-cypermethrin	0.13	38.62	0.01	0	61.37	38.63
Zeta-cypermethrin	0.03	29.29	0.001	0	70.71	29.29
Cyromazine	0.10	31.03	0	0	68.97	31.03
Dichlorvos	0.47	56.61	0.30	0	43.09	56.91
Diflubenzuron	0.20	50.26	0.002	0	49.74	50.26
Ethalfluralin	0.95	33.40	11.78	0	54.82	45.18
Fenpropimorph	0.15	49.10	3.65	0	47.25	52.75
Fenthion	0.40	44.17	5.48	0	50.35	49.65
Nicosulfuron	0.03	50.26	0	0.002	49.74	50.26
Prothiofos	0.29	50.26	6.59	0	58.00	42.00

E. Flow rates used for estimation of pesticide loads

Table E.25. Flow rates used for estimation of pesticide loads

	Flow rate (Q) (m^3/s)															
Drainage areas; RB sampling poins / Pesticides	**YB01**	**YB02**	**YB03**	**YB04**	**YB05**	**YB06**	**YB07**	**YB08**	**YB09**	**YB10**	**YB11**	**YB12**	**YB13**	**YB14**	**YB15**	**YB16**
	Y-40	**A-01**	**A-02**	**Y-109**	**(Y-128)**	**Y-32**	**Y-123**	**(A-03)**	**A-03**	**(Y-125)**	**(Y-97)**	**Y-31**	**A-04**	**(Y-125)**	**(Y-125)**	**Y-20**
Aclonifen	2.629	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Bifenox	0.470	1.309	0.823	1.276	0.069	0.864	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.590
Chlorfenapyr	1.325	1.309	0.823	1.276	0.069	0.333	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.847
Chlorothalonil	0.084	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Chlorpyrifos-ethyl	1.325	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.045	0.035	0.622	0.622	2.018
Chlorsulfuron	2.629	1.309	0.823	1.276	0.069	0.767	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Cyfluthrin	1.325	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Beta-Cyfluthrin	1.325	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Cypermethrin	0.084	1.309	0.823	1.276	0.069	0.333	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.847
Alpha-cypermethrin (1st period)	0.084	1.309	0.823	1.276	0.069	1.073	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.847
Alpha-cypermethrin (2nd and 4th period)	-	-	-	-	-	-	-	-	-	-	-	0.081	-	-	-	-
Alpha-cypermethrin (8th period)	-	-	-	-	-	0.333	-	-	-	-	-	-	-	-	-	-
Zeta-cypermethrin	1.325	1.309	0.823	1.276	0.069	1.073	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.847
Cyromazine	1.325	1.309	0.823	1.276	0.069	0.314	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	1.008
Dichlorvos (1st period)	2.629	1.309	0.823	1.276	0.069	1.073	0.567	0.677	0.677	0.622	0.021	0.117	0.035	0.622	0.622	3.103
Dichlorvos (8th period)	-	-	-	-	-	0.767	-	-	-	-	-	-	-	-	-	0.721
Diflubenzuron	1.325	1.309	0.823	1.276	0.069	0.767	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Ethalfluralin	0.084	1.309	0.823	1.276	0.069	0.767	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Fenpropimorph	1.325	1.309	0.823	1.276	0.069	0.333	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Fenthion	1.325	1.309	0.823	1.276	0.069	0.767	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Nicosulfuron	1.325	1.309	0.823	1.276	0.069	0.864	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.018
Prothiofos	1.325	1.309	0.823	1.276	0.069	0.685	0.567	0.677	0.677	0.622	0.021	0.081	0.035	0.622	0.622	2.855

F. Diffuse pesticide load estimation results, comparison of observed concentrations with estimated probable concentrations and application rates corresponding EQSs

Table F.26. *Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB02 drainage area*

YB02	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.94	0.5295	89.8	1175.6	0.01039	0.12	22.37	0.0025
Bifenox	0.75	0.1139	49.9	1525.1	**0.01348**	0.012	0.67	0.0025
Chlorfenapyr	0.14	0.0411	98.4	256.8	0.00227	0.007	0.42	0.0025
Chlorothalonil	1.41	0.2981	69.4	795.5	0.00703	0.3	60.18	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.21	0.2728	74.0	3360.2	0.02970	0.03	1.22	0.005
Chlorsulfuron	0.0075	0.0021	91.4	26.1	0.00023	0.02	0.65	0.01
Cyfluthrin	0.029	0.0071	81.0	120.2	**0.00106**	0.001	0.03	0.005
Beta-Cyfluthrin	0.027	0.0051	61.7	0.0	0.00000	0.001	135.02	0.005
Cypermethrin	0.15	0.0320	70.7	1523.3	**0.01346**	0.00008	0.00	0.0025
Alpha-cypermethrin	0.22	0.0411	61.4	191.4	**0.00169**	0.00008	0.01	0.0025
Zeta-cypermethrin	0.0399	0.0086	70.7	59.3	**0.00052**	0.00008	0.01	0.0025
Cyromazine	0.15	0.0315	69.0	1059.8	0.00937	0.2	3.20	0.025
Dichlorvos	1.1	0.1445	43.2	6019.2	**0.05320**	0.0006	0.01	0.00025
Diflubenzuron	0.4	0.0606	49.7	235.2	0.00208	0.13	25.02	0.025
Ethalfluralin	1.704	0.2879	55.5	14028.5	0.12400	0.3	4.12	0.0025
Fenpropimorph	0.312	0.0454	47.9	608.3	0.00538	0.1	5.80	0.05
Fenthion	0.883	0.1378	51.3	2790.8	0.02467	0.05	1.79	0.025
Nicosulfuron	0.06	0.0091	49.8	7.0	0.00006	0.05	48.31	0.01
Prothiofos	0.5	0.0897	58.9	266.7	0.00236	0.1	21.21	0.025

Table F.27. *Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB03 drainage area*

YB03	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.927	0.554	89.8	250287.2	0.0052	0.12	44.5	0.0025
Bifenox	0.75	0.120	49.9	9700.5	0.0063	0.012	1.4	0.0025
Chlorfenapyr	0.140	0.044	98.4	7244.5	0.0011	0.007	0.9	0.0025
Chlorothalonil	1.446	0.319	69.0	86352.4	0.0050	0.3	86.6	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.180	0.278	73.8	21326.2	0.0154	0.03	2.3	0.005
Chlorsulfuron	0.0075	0.002	91.3	189.9	0.0001	0.02	1.4	0.01
Cyfluthrin	0.029	0.008	81.0	495.5	0.0005	0.001	0.1	0.005
Beta-Cyfluthrin	0.027	0.005	61.5	605206.7	0.0000	0.001	136.3	0.005
Cypermethrin	0.140	0.032	70.7	634.5	**0.0067**	0.00008	0.002	0.0025
Alpha-cypermethrin	0.220	0.043	61.4	10506.9	**0.0008**	0.00008	0.02	0.0025
Zeta-cypermethrin	0.0399	0.009	70.7	1462.3	**0.0002**	0.00008	0.01	0.0025
Cyromazine	0.15	0.033	69.0	891.6	0.0052	0.2	5.8	0.025
Dichlorvos	1.1	0.152	43.1	3374.7	**0.0290**	0.0006	0.02	0.00025
Diflubenzuron	0.4	0.064	49.7	18710.7	0.0009	0.13	56.6	0.025
Ethalfluralin	1.700	0.302	55.5	5996.2	0.0646	0.3	7.9	0.0025
Fenpropimorph	0.312	0.048	47.7	3853.0	0.0025	0.1	12.5	0.05
Fenthion	0.886	0.144	51.0	8072.5	0.0110	0.05	4.0	0.025
Nicosulfuron	0.06	0.010	49.8	13638.2	0.0000	0.05	105.7	0.01
Prothiofos	0.5	0.094	58.6	27563.9	0.0014	0.1	36.9	0.025

Table F.28. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB04 drainage area

YB04	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.875	0.513	89.8	5834.9	0.0529	0.12	4.25	0.0025
Bifenox	0.75	0.114	49.9	4440.7	0.0403	0.012	0.22	0.0025
Chlorfenapyr	0.148	0.044	98.4	311.9	0.0028	0.007	0.37	0.0025
Chlorothalonil	1.490	0.308	68.0	1111.1	0.0101	0.3	44.32	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.389	0.311	73.5	2640.2	0.0239	0.03	1.74	0.005
Chlorsulfuron	0.0075	0.002	91.3	75.5	0.0007	0.02	0.22	0.01
Cypermethrin	0.215	0.046	70.7	837.1	**0.0076**	0.00008	0.01	0.0025
Alpha-cypermethrin	0.195	0.036	61.4	187.2	**0.0017**	0.00008	0.002	0.0025
Zeta-cypermethrin	0.0399	0.009	70.7	9.6	**0.0001**	0.00008	0.01	0.0025
Cyromazine	0.15	0.031	69.0	269.3	0.0024	0.2	0.04	0.025
Dichlorvos	1.1	0.144	43.1	2332.0	**0.0212**	0.0006	12.29	0.00025
Diflubenzuron	0.4	0.061	49.7	194.0	0.0018	0.13	0.03	0.025
Ethalfluralin	1.709	0.286	54.9	13892.7	0.1260	0.3	29.55	0.0025
Fenpropimorph	0.312	0.045	47.4	1752.2	0.0159	0.1	4.07	0.05
Fenthion	0.902	0.138	50.4	6256.7	**0.0568**	0.05	1.96	0.025
Nicosulfuron	0.06	0.009	49.8	17.6	0.0002	0.05	0.80	0.01
Prothiofos	0.5	0.088	58.2	283.5	0.0026	0.1	18.78	0.025

Table F.29. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB05 drainage area

YB05	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.874	0.540	89.8	1498.6	**0.251**	0.12	0.943	0.0025
Bifenox	0.75	0.114	49.9	1065.1	**0.178**	0.012	0.050	0.0025
Chlorfenapyr	0.177	0.053	98.4	40.6	0.007	0.007	0.183	0.0025
Chlorothalonil	1.480	0.313	69.4	120.1	0.020	0.3	22.073	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.694	0.381	74.0	408.7	**0.068**	0.03	0.742	0.005
Chlorsulfuron	0.0075	0.002	91.4	18.1	0.003	0.02	0.049	0.01
Cyfluthrin	0.029	0.007	81.0	71.3	**0.012**	0.001	0.002	0.01
Beta-Cyfluthrin	0.027	0.005	61.7	0.2	0.000	0.001	0.837	0.005
Cypermethrin	0.174	0.037	70.7	66.8	**0.011**	0.00008	0.001	0.005
Alpha-cypermethrin	0.146	0.027	61.4	16.1	**0.003**	0.00008	0.004	0.0025
Zeta-cypermethrin	0.0399	0.009	70.7	0.3	0.000	0.00008	0.055	0.0025
Cyromazine	0.15	0.031	69.0	28.3	0.005	0.2	6.320	0.0025
Dichlorvos	1.1	0.144	43.2	203.5	**0.034**	0.0006	0.019	0.00025
Diflubenzuron	0.4	0.061	49.7	7.8	0.001	0.13	39.977	0.025
Ethalfluralin	1.709	0.289	55.5	3087.5	**0.517**	0.3	0.991	0.0025
Fenpropimorph	0.312	0.045	47.9	425.1	0.071	0.1	0.438	0.05
Fenthion	0.916	0.143	51.3	1383.8	**0.232**	0.05	0.197	0.025
Nicosulfuron	0.06	0.009	49.8	4.2	0.001	0.05	4.265	0.01
Prothiofos	0.5	0.090	58.9	11.5	0.002	0.1	25.953	0.025

Table F.30. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB07 drainage area

YB07	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.882	0.515	89.8	2400.0	0.0490	0.12	4.608	0.0025
Bifenox	0.75	0.114	49.9	2572.9	**0.0525**	0.012	0.171	0.0025
Chlorfenapyr	0.140	0.042	98.4	365.7	**0.0075**	0.007	0.132	0.0025
Chlorothalonil	1.083	0.226	68.4	2450.3	0.0500	0.3	6.493	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.221	0.273	73.6	4719.0	**0.0964**	0.03	0.380	0.005
Chlorsulfuron	0.0075	0.002	91.3	43.3	0.0009	0.02	0.170	0.01
Cyfluthrin	0.027	0.007	81.0	0.3	0.0000	0.001	4.436	0.005
Beta-Cyfluthrin	0.032	0.006	61.4	162.5	**0.0033**	0.001	0.010	0.005
Cypermethrin	0.252	0.033	70.7	746.6	**0.0152**	0.00008	0.001	0.0025
Alpha-cypermethrin	0.203	0.038	61.4	282.7	**0.0058**	0.00008	0.003	0.0025
Zeta-cypermethrin	0.0399	0.009	70.7	26.8	**0.0005**	0.00008	0.006	0.0025
Cyromazine	0.15	0.031	69.0	263.5	0.0054	0.2	5.576	0.025
Dichlorvos	1.1	0.144	43.1	4000.9	**0.0817**	0.0006	0.008	0.00025
Diflubenzuron	0.400	0.061	49.7	313.3	0.0064	0.13	8.124	0.025
Ethalfluralin	1.702	0.286	55.1	9582.3	0.1957	0.3	2.610	0.0025
Fenpropimorph	0.312	0.045	47.5	1017.9	0.0208	0.1	1.498	0.05
Fenthion	0.881	0.136	50.7	4736.3	**0.0967**	0.05	0.456	0.025
Nicosulfuron	0.06	0.009	49.8	20.8	0.0004	0.05	7.059	0.01
Prothiofos	0.5	0.089	58.4	458.8	0.0094	0.1	5.337	0.025

Table F.31. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB08 drainage area

YB08	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.849	0.549	89.8	1494.8	0.0256	0.12	8.681	0.0025
Bifenox	0.75	0.124	49.9	2030.6	**0.0347**	0.012	0.259	0.0025
Chlorfenapyr	0.171	0.056	98.4	272.1	0.0047	0.007	0.257	0.0025
Chlorothalonil	1.016	0.220	65.4	4354.4	0.0744	0.3	4.093	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.212	0.290	72.2	6678.6	**0.1142**	0.03	0.319	0.005
Chlorsulfuron	0.0075	0.002	91.2	33.7	0.0006	0.02	0.260	0.01
Cyfluthrin	0.027	0.007	81.0	0.2	0.0000	0.001	7.627	0.005
Beta-Cyfluthrin	0.036	0.007	60.2	160.9	**0.0028**	0.001	0.013	0.005
Cypermethrin	0.290	0.068	70.7	546.9	**0.0094**	0.00008	0.002	0.0025
Alpha-cypermethrin	0.160	0.032	61.4	148.8	**0.0025**	0.00008	0.005	0.0025
Zeta-cypermethrin	0.400	0.094	70.7	1.1	0.0000	0.00008	1.627	0.0025
Cyromazine	0.15	0.034	69.0	41.3	0.0007	0.2	42.436	0.025
Dichlorvos	1.1	0.157	43.0	3925.6	**0.0671**	0.0006	0.010	0.00025
Diflubenzuron	0.4	0.066	49.7	100.4	0.0017	0.13	30.306	0.025
Ethalfluralin	1.665	0.295	53.5	6105.4	0.1044	0.3	4.784	0.0025
Fenpropimorph	0.311	0.048	46.2	780.3	0.0133	0.1	2.334	0.05
Fenthion	0.894	0.144	48.7	3473.4	**0.0594**	0.05	0.753	0.025
Nicosulfuron	0.06	0.010	49.7	30.4	0.0005	0.05	5.780	0.01
Prothiofos	0.5	0.094	56.9	142.7	0.0024	0.1	20.498	0.025

Table F.32. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB09 drainage area

YB09	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.709	0.508	89.8	11.41	0.0002	0.12	1051.540	0.0025
Bifenox	0.75	0.124	49.9	49.00	0.0008	0.012	10.746	0.0025
Chlorfenapyr	0.135	0.044	98.4	38.76	0.0007	0.007	1.422	0.0025
Chlorothalonil	1.013	0.222	66.3	2319.32	0.0397	0.3	7.667	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.019	0.245	72.6	2598.44	**0.0444**	0.03	0.688	0.005
Chlorsulfuron	0.0075	0.002	91.3	0.80	0.0000	0.02	11.034	0.01
Cyfluthrin	0.036	0.010	81.0	8.70	0.0001	0.001	0.243	0.005
Cypermethrin	0.331	0.077	70.7	163.55	**0.0028**	0.00008	0.009	0.0025
Alpha-cypermethrin	0.220	0.045	61.4	33.30	**0.0006**	0.00008	0.031	0.0025
Cyromazine	0.15	0.034	69.0	15.84	0.0003	0.2	110.818	0.025
Dichlorvos	1.1	0.157	43.0	1963.88	**0.0336**	0.0006	0.020	0.00025
Diflubenzuron	0.400	0.066	49.7	41.09	0.0007	0.13	73.996	0.025
Ethalfluralin	1.633	0.292	54.0	214.93	0.0037	0.3	133.349	0.0025
Fenpropimorph	0.311	0.048	46.5	18.95	0.0003	0.1	96.006	0.05
Fenthion	0.816	0.133	49.3	323.01	0.0055	0.05	7.392	0.025
Nicosulfuron	0.06	0.010	49.7	1.25	0.0000	0.05	140.719	0.01
Prothiofos	0.5	0.095	57.3	58.76	0.0010	0.1	49.783	0.025

Table F.33. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB10 drainage area

YB10	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.906	0.521	89.8	2453.84	0.0457	0.12	5.010	0.0025
Bifenox	0.75	0.114	49.9	1643.32	**0.0306**	0.012	0.294	0.0025
Chlorfenapyr	0.140	0.042	98.4	316.26	0.0059	0.007	0.166	0.0025
Chlorothalonil	1.032	0.207	65.8	2615.56	0.0487	0.3	6.364	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.081	0.239	72.7	3288.45	**0.0612**	0.03	0.530	0.005
Chlorpyrifos-methyl	1.7025	0.253	48.8	247.38	0.0046	0.03	11.095	0
Chlorsulfuron	0.0075	0.002	91.2	24.37	0.0005	0.02	0.331	0.01
Cyfluthrin	0.027	0.007	81.0	0.04	0.0000	0.001	33.098	0.005
Beta-Cyfluthrin	0.027	0.005	60.8	87.92	**0.0016**	0.001	0.017	0.005
Cypermethrin	0.396	0.085	70.7	872.64	**0.0162**	0.00008	0.002	0.0025
Alpha-cypermethrin	0.225	0.042	61.4	242.39	**0.0045**	0.00008	0.004	0.0025
Cyromazine	0.15	0.031	69.0	32.54	0.0006	0.2	49.559	0.025
Dichlorvos	1.1	0.144	43.1	3046.33	**0.0567**	0.0006	0.012	0.00025
Diflubenzuron	0.400	0.061	49.7	310.81	0.0058	0.13	8.989	0.025
Ethalfluralin	1.725	0.283	54.0	4539.64	0.0845	0.3	6.126	0.0025
Fenpropimorph	0.310	0.044	46.5	633.53	0.0118	0.1	2.631	0.05
Fenthion	0.873	0.130	49.0	3039.77	**0.0566**	0.05	0.772	0.025
Nicosulfuron	0.06	0.009	49.7	6.35	0.0001	0.05	25.411	0.01
Prothiofos	0.5	0.087	57.3	440.89	0.0082	0.1	6.095	0.025

Table F.34. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB11 drainage area

YB11	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.907	0.567	89.8	6098.78	**3.4266**	0.12	0.0668	0.0025
Bifenox	0.75	0.124	49.9	3963.82	**2.2271**	0.012	0.0040	0.0025
Chlorfenapyr	0.162	0.053	98.4	183.96	**0.1034**	0.007	0.0110	0.0025
Chlorothalonil	1.035	0.220	65.4	1934.79	**1.0871**	0.3	0.2803	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.191	0.291	73.9	208.27	**0.1170**	0.03	0.3053	0.005
Chlorsulfuron	0.0075	0.002	91.4	58.71	**0.0330**	0.02	0.0045	0.01
Cyfluthrin	0.027	0.007	81.0	266.89	**0.1500**	0.001	0.0002	0.005
Beta-Cyfluthrin	0.027	0.006	61.7	0.08	0.0000	0.001	0.5760	0.005
Cypermethrin	0.308	0.068	70.7	2399.56	**1.3482**	0.00008	0.0000	0.0025
Alpha-cypermethrin	0.185	0.037	61.4	100.24	**0.0563**	0.00008	0.0003	0.0025
Cyromazine	0.15	0.034	69.0	25.51	0.0143	0.2	2.0941	0.025
Dichlorvos	1.1	0.157	43.1	1792.56	**1.0071**	0.0006	0.0007	0.00025
Diflubenzuron	0.400	0.066	49.7	96.12	0.0540	0.13	0.9630	0.025
Ethalfluralin	1.732	0.318	55.5	10841.8	**6.0914**	0.3	0.0853	0.0025
Fenpropimorph	0.310	0.049	47.9	1572.61	**0.8836**	0.1	0.0351	0.05
Fenthion	0.910	0.155	51.3	5522.98	**3.1031**	0.05	0.0147	0.025
Nicosulfuron	0.06	0.010	49.8	12.22	0.0069	0.05	0.4368	0.01
Prothiofos	0.5	0.097	58.9	140.14	0.0787	0.1	0.6349	0.025

Table F.35. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB13 drainage area

YB13	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.875	0.513	89.8	4964.1	**1.6244**	0.12	0.13852	0.0025
Bifenox	0.750	0.114	49.9	3686.1	**1.2062**	0.012	0.00746	0.0025
Chlorfenapyr	0.162	0.048	98.4	1315.2	**0.4304**	0.007	0.00263	0.0025
Chlorothalonil	1.105	0.224	66.6	12810.6	**4.1920**	0.3	0.07910	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.027	0.228	73.0	1.4	0.0005	0.03	68.56918	0.005
Chlorsulfuron	0.008	0.002	91.2	53.1	0.0174	0.02	0.00863	0.01
Cyfluthrin	0.027	0.007	81.0	0.7	0.0002	0.001	0.11146	0.005
Beta-Cyfluthrin	0.029	0.005	61.0	247.4	**0.0809**	0.001	0.00035	0.005
Cypermethrin	0.164	0.036	70.7	2217.4	**0.7256**	0.00008	0.00002	0.0025
Alpha-cypermethrin	0.229	0.043	61.4	504.4	**0.1651**	0.00008	0.00011	0.0025
Cyromazine	0.150	0.031	69.0	383.1	0.1254	0.2	0.23941	0.025
Dichlorvos	1.100	0.144	43.1	12840.8	**4.2019**	0.0006	0.00016	0.00025
Diflubenzuron	0.400	0.060	49.7	662.8	**0.2169**	0.13	0.23958	0.025
Ethalfluralin	1.735	0.287	54.4	12579.7	**4.1164**	0.3	0.12648	0.0025
Fenpropimorph	0.310	0.044	46.8	1448.2	**0.4739**	0.1	0.06539	0.05
Fenthion	0.857	0.129	49.5	8287.3	**2.7118**	0.05	0.01580	0.025
Nicosulfuron	0.060	0.009	49.7	9.6	0.0031	0.05	0.95981	0.01
Prothiofos	0.500	0.088	57.6	939.7	**0.3075**	0.1	0.16258	0.025

Table F.36. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB14 drainage area

YB14	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.850	0.550	89.8	654.22	0.0122	0.12	18.24	0.0025
Bifenox	0.75	0.124	49.9	975.54	**0.0182**	0.012	0.50	0.0025
Chlorfenapyr	0.140	0.045	98.4	593.17	**0.0110**	0.007	0.09	0.0025
Chlorothalonil	1.028	0.224	65.7	13706.70	0.2551	0.3	1.21	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.024	0.245	72.4	15980.20	**0.2974**	0.03	0.10	0.005
Chlorpyrifos-methyl	1.7025	0.273	48.5	1056.79	0.0197	0.03	2.60	0
Chlorsulfuron	0.0075	0.002	91.2	14.38	0.0003	0.02	0.56	0.01
Cyfluthrin	0.027	0.007	81.0	0.01	0.0000	0.001	155.68	0.005
Beta-Cyfluthrin	0.030	0.006	60.3	75.73	**0.0014**	0.001	0.02	0.005
Cypermethrin	0.338	0.079	70.7	1880.88	**0.0350**	0.00008	0.00	0.0025
Alpha-cypermethrin	0.225	0.046	61.4	419.82	**0.0078**	0.00008	0.00	0.0025
Cyromazine	0.15	0.034	69.0	139.84	0.0026	0.2	11.52	0.025
Dichlorvos	1.1	0.157	43.0	13147.54	**0.2446**	0.0006	0.00	0.00025
Diflubenzuron	0.400	0.066	49.7	216.23	0.0040	0.13	12.91	0.025
Ethalfluralin	1.700	0.302	53.7	3549.26	0.0660	0.3	7.72	0.0025
Fenpropimorph	0.310	0.048	46.3	376.65	0.0070	0.1	4.43	0.05
Fenthion	0.830	0.134	48.9	3821.69	**0.0711**	0.05	0.58	0.025
Nicosulfuron	0.06	0.010	49.7	11.27	0.0002	0.05	14.30	0.01
Prothiofos	0.5	0.094	57.0	759.25	0.0141	0.1	3.54	0.025

Table F.37. Components of estimation of diffuse pesticide loads and resulting diffuse pesticide load and concentration in YB15 drainage area

YB15	AppRate (kg/ha)	$C_{T,M}$ (mg/kg)	$R_{\%}$	PL (mg/day)	C_{est} (µg/L)	EQS (µg/L)	AppRate EQS (kg/ha)	Cobs (µg/L)
Aclonifen	1.711	0.509	89.8	468.26	0.0087	0.12	23.569	0.0025
Bifenox	0.75	0.124	49.9	1979.63	**0.0368**	0.012	0.244	0.0025
Chlorfenapyr	0.210	0.068	98.4	2809.10	**0.0523**	0.007	0.028	0.0025
Chlorothalonil	1.096	0.242	66.6	2223.79	0.0414	0.3	7.945	0.005
Chlorpyrifos (Chlorpyrifos-ethyl)	1.453	0.350	72.7	5708.46	**0.1062**	0.03	0.410	0.005
Chlorsulfuron	0.0075	0.002	91.3	31.77	0.0006	0.02	0.254	0.01
Beta-Cyfluthrin	0.039	0.008	60.7	203.26	**0.0038**	0.001	0.010	0.005
Cypermethrin	0.205	0.048	70.7	2081.22	**0.0387**	0.00008	0.000	0.0025
Alpha-cypermethrin	0.200	0.041	61.4	602.32	**0.0112**	0.00008	0.001	0.0025
Zeta-cypermethrin	0.0399	0.009	70.7	0.01	0.0000	0.00008	25.660	0.0025
Cyromazine	0.15	0.034	69.0	48.60	0.0009	0.2	33.187	0.025
Dichlorvos	1.1	0.157	43.0	7562.79	**0.1407**	0.0006	0.005	0.00025
Diflubenzuron	0.400	0.066	49.7	45.31	0.0008	0.13	61.665	0.025
Ethalfluralin	1.636	0.293	54.1	6631.36	0.1234	0.3	3.979	0.0025
Fenpropimorph	0.311	0.048	46.2	761.52	0.0142	0.1	2.198	0.05
Fenthion	0.836	0.137	49.5	7910.09	**0.1472**	0.05	0.284	0.025
Nicosulfuron	0.06	0.010	49.7	47.39	0.0009	0.05	3.402	0.01
Prothiofos	0.5	0.095	57.4	935.52	0.0174	0.1	2.872	0.025